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GY. HARDY, K. LEMPERT, F. MÁRTA,
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B. LENGYEL et GY. DEÁK

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UNTERSUCHUNG DER ZUSAMMENSETZUNG VON EINHEIMISCHEN UND AUSLÄNDISCHEN ÄTHERISCHEN ÖLEN, VI

KUMARANDERIVATE IM ÄTHERISCHEN ÖL DER DILLPFLANZE

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In der qualitativen und quantitativen Analyse des durch Wasserdampfdestillation gewonnenen und raffinierten ätherischen Öles der Dillpflanze wurden zwei Komponenten gefunden, die nicht als bis jetzt bekannte Bestandteile der Dillöle oder anderer ätherischen Öle identifiziert werden konnten. Die in größerer Menge (in Prozent-Größenordnung) erhaltene unbekannte Komponente wurde aufgrund von spektrometrischen, in erster Linie von protonenresonanz-spektrometrischen Strukturuntersuchungen sowie von spektrometrischen Strukturuntersuchungen der chemischen Umwandlungsprodukte als 3,7-Dimethyl-4,5,6,9-tetrahydrokumaran identifiziert. Die andere in Spuren (in Hundertstelprozent-Größenordnung) gefundene unbekannte Komponente wurde mit hoher Wahrscheinlichkeit als 3,6-Dimethylkumaran identifiziert, das mit der obengenannten Verbindung strukturverwandt ist. Innerhalb des gegebenen Größenordnungsbereiches weisen die Anteile dieser neu erkannten Komponenten in den ätherischen Ölen der Dillpflanzen, abhängend vom Reifegrad und von der Methode der Aufbereitung der Pflanze, bedeutende Schwankungen auf.

Anhand der ausführlichen Untersuchung der verschiedenen einheimischen und ausländischen ätherischen Öle wurde in den vergangenen Jahren eine auf wirksame Trennung und spektrometrische Identifikation von Komponenten gegründete, kombinierte Analysenmethode für ätherische Öle entwickelt [1]. Die entwickelte kombinierte Methode ließ sich für die Analyse des »entmentholisierten« Minzöles [1] sowie des Pfefferminzöles [2], des Lavandelöles [3], des Lavandinöles [4], des Muskateller Salbeiöles [4] und des Dillöles [5] einsetzen. Als Ergebnis der Untersuchungen wurden die Bestandteile der ätherischen Öle bis zu einem Anteil von über 95% (in einigen Fällen über 99%) identifiziert und es wurden verschiedene, nach Literaturangaben erwartete, aber auch nicht erwartete, jedoch von anderen ätherischen Ölen her bekannte Komponenten gefunden, sowie in einigen Fällen die Abwesenheit einiger erwarteter Komponenten eindeutig bewiesen.

Im verhältnismäßig einfach zusammengesetzten ätherischen Öl der einheimischen Dillpflanze *(Anethum graveolens)* wurden 14 Komponenten in bedeutenden Mengen ($> 0{,}01\%$) gefunden, die mit zwei Ausnahmen als bekannte Bestandteile ätherischer Öle identifiziert wurden [5]. Die Tabelle I gibt die mittels Gaschromatographie bestimmten Anteile der *identifizierten Komponenten* in der Reihenfolge ihrer gaschromatographischen Retentionen an. In dieser Arbeit wird über Isolation und Strukturanalyse der bisher unbekannten Bestandteile des ätherischen Öles berichtet.

Tabelle I

Zusammensetzung des Dillöles

Laufzahl	Komponente	Menge, Gew.%
1	α-Thujen	0,3
2	α-Pinen	0,8
3	β-Myrcen	0,7
4	α-Phellandren	29,0
5	Limonen	25,0
6	β-Phellandren	4,2
7	*p*-Cymol	1,3
8	1-Methyl-4-isopropenylbenzol	0,0X
9	Unbekannte Komponente	2,9
10	Dihydrocarvon	0,3
11	Isodihydrocarvon	0,2
12	Unbekannte Komponente	0,0X
13	Carvotanaceton	0,0X
14	Carvon	35,2

Anreicherung und Strukturanalyse der Komponenten

Zur Trennung und zur Reinigung bedeutender Mengen der unbekannten Komponenten wurden Halbmikro-Rektifikation und präparative Gaschromatographie angewandt, die Reinheit der Komponenten wurde durch analytische Gaschromatographie kontrolliert.

Die *Halbmikro-Rektifikation* wurde in einer Glaskolonne mit Drehband durchgeführt, die die linearen Abmessungen von 500 mm × 6 mm hatte und eine mit 2 000 U/min rotierende, 5,5 mm breite Stahlband-Einlage besaß. Die Apparatur hatte eine Trennfähigkeit von 30 theoretischen Trennstufen, der Betriebsinhalt betrug 0,1 cm³, der Druckverlust 0,2 Torr [6]. Die Rektifikation wurde bei einer Einwaage von 20 cm³ Dillöl bei 200 Torr durchgeführt. Zur weiteren Konzentrierung wurden die an den unbekannten Komponenten reicheren Fraktionen angewandt.

Die Reinigung der Hauptkomponenten der Konzentrate erfolgte durch *wiederholte gaschromatographische Präparation* mit einem Gerät des Typs Pye Unicam 105 und einer Kolonne mit den Abmessungen 7 m × 5 mm, wobei Carbowax 20 M auf Celite als stationäre Phase verwendet wurde. Die Temperatur der Kolonne betrug 120 °C bzw. 160 °C, als Trägergas diente Argon mit einer Geschwindigkeit von 12 dm³/St. Die Dosierungen schwankten zwischen 1 cm³ und 50 mm³. Als Ergebnis der Präparation wurden wenige Kubikzentimeter von der 9. und wenige Kubikmillimeter von der 12. Komponente erhalten.

Die Reinheit der Komponenten wurde mit einem Gaschromatographen Chrom III mittels einer mit Carbowax—1000 benetzten *Kapillarkolonne* (50 m × 0,25 mm) bestimmt. Die Temperatur betrug bei den analytischen Untersuchungen 130 °C, die Geschwindigkeit des als Trägergas verwendeten Argons 3 cm³/min. Die Reinheit der für die Strukturuntersuchung vorbereiteten Proben erreichte über 99%.

Für die *Strukturuntersuchung* der unbekannten Komponenten wurden Massenspektrometrie mit niedrigem Auflösungsvermögen, Infrarotspektrometrie sowie Protonenresonanzspektrometrie mit mittlerem und hohem Auflösungsvermögen eingesetzt.

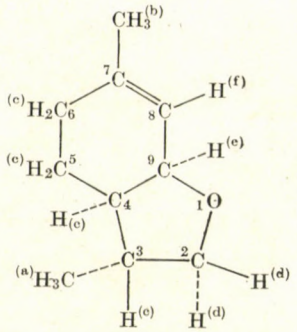
Die Massenspektren der analysierten Proben wurden mit dem für die chemische Untersuchung umgestalteten Massenspektrometer ZEME Typ 1305 aufgenommen [7]. Die Beschleunigungsspannung betrug 50 V, die Aufnahmegeschwindigkeit zwei Masseneinheiten pro Minute, das Auflösungsvermögen $m/\Delta m = 300$.

Die *Infrarotspektren* der Komponenten und ihrer Umwandlungsprodukte wurden mit einem Gerät der Fa Carl Zeiss Jena, Typ UR—20 im Wellenzahlbereich 4000—400 cm^{-1} aufgenommen. Die Schichtdicken betrugen 0,003 cm bei der unmittelbaren Untersuchung der reinen Stoffe bzw. 0,01 cm bei der Untersuchung ihrer Lösungen in Tetrachlorkohlenstoff.

Die *Protonenresonanzspektren* der reinen Stoffe wurden bei 60 MHz mit dem Gerät Varian Typ T—60 bzw. bei 100 MHz mit dem Gerät des Typs XL—100 aufgenommen. Als Lösungsmittel dienten Tetrachlorkohlenstoff bzw. Deuterobenzol. Das untersuchte Verschiebungsintervall (δ) lag zwischen 0 und 8 ppm.

Identifikation des 3,7-Dimethyl-4,5,6,9-tetrahydrokumarans

Die in verhältnismäßig hoher Konzentration vorhandene, unbekannte Komponente erwies sich aufgrund der Strukturanalyse als eine bisher nicht nur im Dillöl, sondern auch in anderen ätherischen Ölen noch nicht nachgewiesene Kumaran-Verbindung, als *3,7-Dimethyl-4,5,6,9-tetrahydrokumaran* (I), mit wahrscheinlich folgender Struktur:



I

Das Massenspektrum mit niedrigem Auflösungsvermögen dieser Komponente ist in Abb. 1 wiedergegeben. Nach den spektrometrischen Daten ist einerseits festzustellen, daß diese Komponente das Molekulargewicht 152 ($M^+ = 152$) hat, andererseits ist es anzunehmen, daß ein mit einer Methylgruppe substituierter aromatischer oder leicht aromatisierbarer sechsgliedriger ungesättigter Ring vorliegt. Die Elementaranalyse der Probe bestätigte die Summenformel $C_{10}H_{16}O$.

Die Hauptmerkmale des in Abb. 2 gezeigten Infrarotspektrums sind die für Äther mit Ringstruktur charakteristische Bandenreihe im Wellenzahlbereich 900—1200 cm^{-1} und das Fehlen der für die $-O-H$ und $>C=O$ Bindungen charakteristischen Valenzschwingungsbanden, die auf ein sich im Ring befindendes Sauerstoffatom hinweisen. Zwischen den Wellenzahlen 1480 cm^{-1} und 1610 cm^{-1} liegen keine Absorptionsbanden, so daß mit dem Vorhandensein eines aromatischen Kohlenwasserstoffringes nicht zu rechnen ist. Die Valenzschwingungsbanden der Bindung $-C=C-$ bei 1675 cm^{-1} und der Bindung $=C-H$ bei 3020 cm^{-1} beweisen jedoch das Vorhandensein einer Doppelbindung. Die hohe Wellenzahl macht ferner wahrscheinlich, daß es

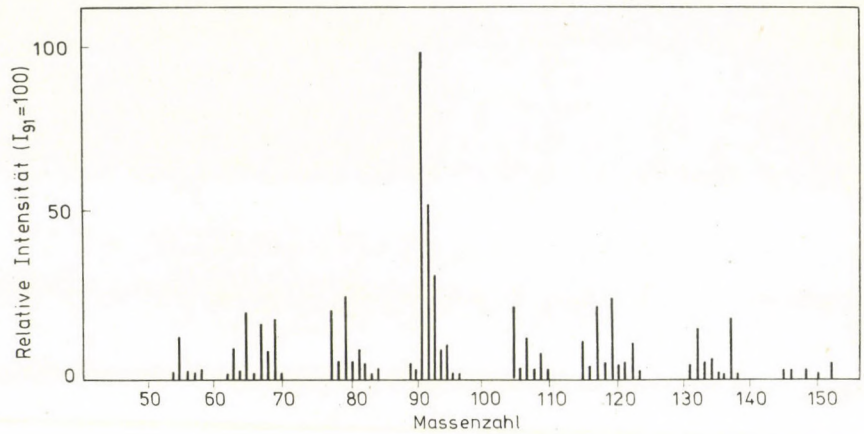


Abb. 1. Massenspektrum des 3,7-Dimethyl-4,5,6,9-tetrahydrokumarans **(I)**

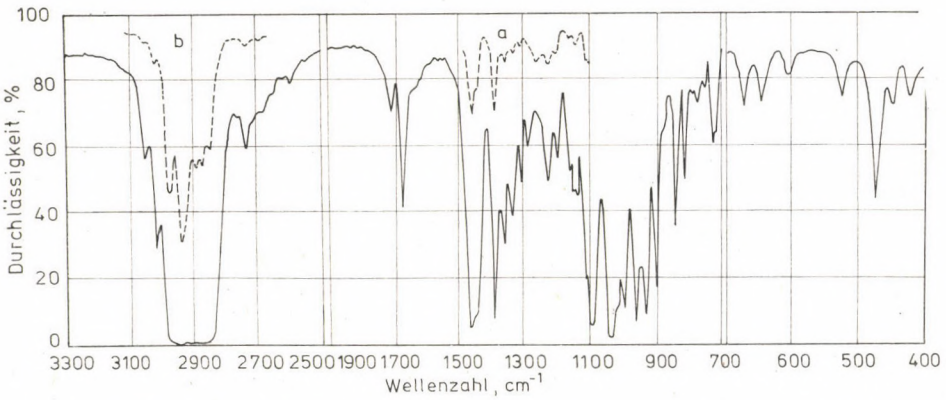
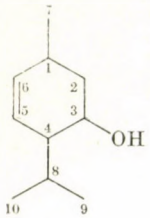


Abb. 2. Infrarotspektrum des 3,7-Dimethyl-4,5,6,9-tetrahydrokumarans **(I)**. (a) Konzentration: 150 g/dm³ in CCl_4; (b) Konzentration: 17 g/dm³ in CCl_4

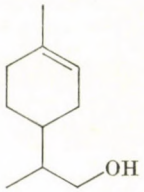
sich um eine neben einer Verzweigung im Ring stehende Doppelbindung handelt. Die zwei Ringe und die Doppelbindung sind mit der Summenformel der Komponente im Einklang.

Die Struktur des ringförmigen Äthers, die Kopplung an den Cyclohexenring und die Lage der Methylgruppen und der Doppelbindung wurden durch eine Umwandlung der Komponente in Alkohole und deren Identifikation untersucht, wobei davon ausgegangen wurde, daß die Infrarotspektren der beim reduktiven Abbau zu erwartenden Terpenalkohole fast ohne Ausnahme bekannt sind [8]. (Durch Kochen der Probe mit Bromwasserstoff in essigsäuriger Lösung [9] wurde übrigens *p*-Cymol (II) erhalten, was in Übereinstimmung mit dem vermuteten Kohlenstoffskelett steht.)

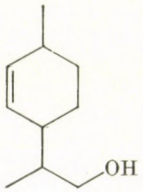
Für den *reduktiven Abbau* wurde Lithium-Aluminium-Hydrid als Katalisator [10] in Gegenwart von Aluminiumchlorid in wasserfreiem Dimethyläther als geeignet gefunden. Das Reaktionsprodukt bestand aus vier wichtigeren (über 1%) Komponenten, deren Strukturen nach gaschromatographischer Präparation aus ihren Infrarotspektren ermittelt wurden. Die Umwandlungsprodukte waren: 5(6)-*p*-Menthen-3-ol (**III**), 1(2)-*p*-Menthen-9-ol (**IV**), 2(3)-*p*-Menthen-9-ol (**V**) und 3(4)-*p*-Menthen-9-ol (**VI**).



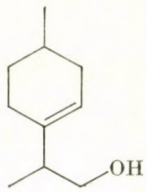
III



IV



V



VI

Durch die chemische Umwandlung wurden die Struktur des ringförmigen Äthers, die Art der Kopplung der Ringe und die Anzahl und Lage der Methylgruppen geklärt, die Isomerisation der Doppelbindung während der Reduktion schließt aber alle Schlußfolgerungen auf die Lage der Doppelbindung aus.

Die angenommene Struktur wurde durch die Aufnahme des Protonenresonanzspektrums bei 60 MHz gestützt und durch die Protonenentkopplung während der Aufnahme bei 100 MHz eindeutig bestätigt, es wurden sogar dadurch Annahmen von weiteren strukturellen Einzelheiten ermöglicht.

In Abb. 3 ist das Protonenresonanzspektrum bei 100 MHz wiedergegeben. Das Dublett bei 1,0 ppm stammt von Methylprotonen (a) neben einer Methingruppe, die mit der Doppelbindung und dem Sauerstoffatom nicht benachbart sind, das Singulett bei 1,7 ppm von einer Doppelbindung nahe liegenden Methylprotonen (b). Die Gruppe der Resonanzsignale zwischen 1,3 und 2,1 ppm entspricht sechs Protonen, die in den Ringen (c) entfernt von der Doppelbindung und dem Sauerstoffatom vorliegen. Den Kohlenstoffatomen neben dem Sauerstoffatom können drei verschiedene Protonensignale zugeordnet werden, zwei doppelte Dublette um 3,2 und 3,9 ppm stammen von zwei nicht gleichwertigen, aber ähnliche Lagen einnehmenden Protonen (d) und ein Multiplett bei 4,2 ppm von einem weiteren Proton (e). Das Multiplett bei 5,4 ppm weist auf ein einziges Proton (f) neben einer Doppelbindung hin, das mit vielen benachbarten Protonen in Kopplung steht. Die aus dem Protonenresonanzspektrum abgeleiteten Einzelheiten sowie andere Beobachtungen können ohne Widerspruch nur mit der Struktur des 3,7-Dimethyl-4,5,6,9-tetrahydrokumarans in Einklang gebracht werden.

Die Einzelheiten des Spektrums, die auf die Doppelbindung und die das Sauerstoffatom umgebenden Protonen zurückzuführen sind, weisen auf die gegenseitige Kopplung dieser Protonen hin. Durch die einzelweise Entkopplung der Protonen (b), (f) und (e) werden die Reihenfolge ihrer Lage sowie die Lage der Doppelbindung und des Sauerstoffatoms klar. Die Spektren sind mit der *Cis*-Anellation der Protonen (c) und (e) an den Kohlenstoffatomen C-4 und C-9 im Einklang, für die wahrscheinliche räumliche Anordnung der Methylgruppe am Kohlenstoffatom C-3 geben aber die Spektren keine ausreichende Information.

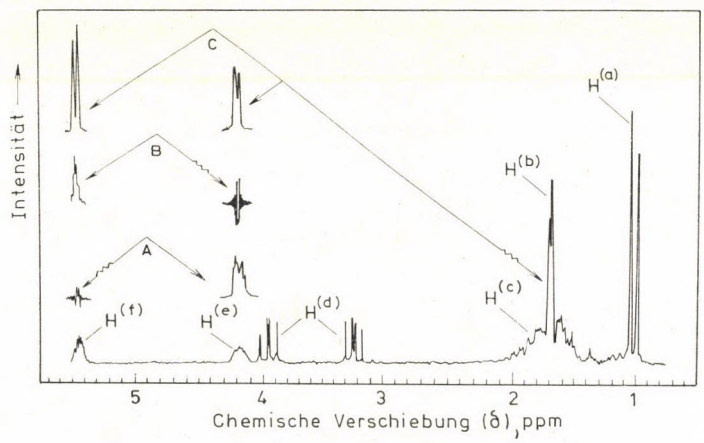
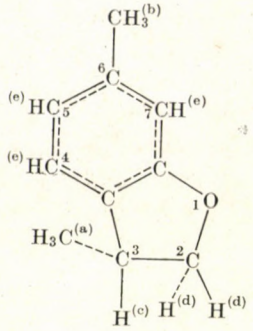


Abb. 3. Kernresonanzspektrum des 3,7-Dimethyl-4,5,6,9-tetrahydrokumarans (**I**) bei 100 MHz. A: Entkopplung des Olefinprotons (H^f); B: Entkopplung des sich neben dem Sauerstoffatom befindlichen Methinprotons (H^e); C: Entkopplung des sich neben der Olefinbindung befindlichen Methylprotons (H^b)

Es wurden einige *physikalische Konstanten* des 3,7-Dimethyl-4,5,6,9-tetrahydrokumarans bestimmt: $d_4^{20} = 0{,}9622 \pm 0{,}0001$ gcm^{-1}, $n_D^{20} = 1{,}4794 \pm \pm 0{,}0002$, $Kp_{9torr} = 51{,}2 \pm 0{,}5$ °C, $Kp_{80torr} = 96{,}6 \pm 0{,}5$ °C, $Kp_{736torr} = 163{,}3 \pm 0{,}5$ °C. Die Dichte wurde mit einem 1-cm^3-Pyknometer, der Brechungsindex mit einem Abbe-Zeiss-Refraktometer und der Siedepunkt nach der Mikromethode von Smith-Menzies bestimmt [11].

Identifikation des 3,6-Dimethylkumarans

Die in Spuren gewonnene andere Dillölkomponente ist mit hoher Wahrscheinlichkeit *3,6-Dimethylkumaran* (**VII**), das in ätherischen Ölen bisher ebenfalls nicht gefunden wurde:



VII

Das in Abb. 4 wiedergegebene Protonenresonanzspektrum bei 60 MHz der in sehr kleiner Menge isolierten Komponente weist mit dem Spektrum des 3,7-Dimethyl-4,5,6,9-tetrahydrokumarans viele Ähnlichkeit auf. Statt der Resonanzsignale der sich neben und an den Doppelbindungen befindenden

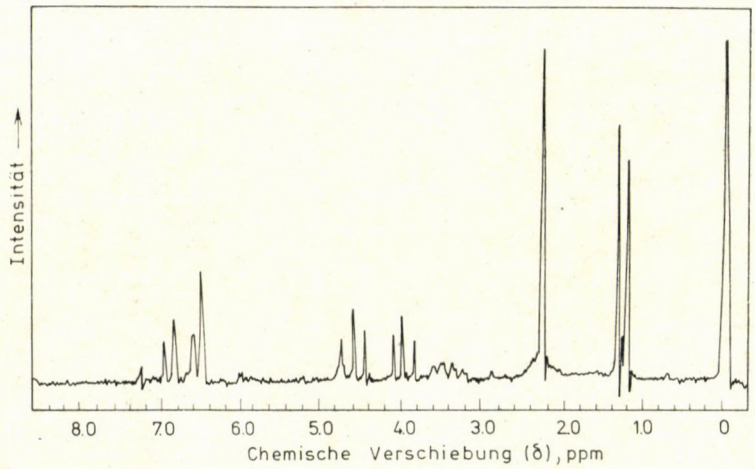


Abb. 4. Kernresonanzspektrum des 3,6-Dimethylkumarans

Protonen erscheinen hier die Signale der an den Aromatenring gebundenen Protonen (c) bei 6,5—7,0 ppm. Die Verschiebung der Signale entspricht Protonen, die in *meta*- (6,9—7,0 ppm), *para*- (6,6—6,7 ppm) und *ortho*-Lage (6,55 ppm) zu dem an den Sauerstoff gebundenen Kohlenstoffatom stehen. Unverändert sind im Spektrum die durch die sich in der Nähe des Sauerstoffatoms befindlichen, eine ähnliche Lage einnehmenden, jedoch nicht äquivalenten Protonen (d) verursachten, doppelten Dublette zwischen 3,8 und 4,8 ppm sowie die Resonanzsignale der isolierten (b) und der neben der Methingruppe liegenden Methylprotonen (a) bei 2,3 und 1,3 ppm, deren Verschiebungen eindeutig auf den benachbarten aromatischen Ring hinweisen. Schließlich

ist das Multiplett um 3,5 ppm dem Proton (c) der mit dem aromatischen Ring verbundenen Methingruppe zuzuschreiben. Die Einzelheiten des Spektrums sind nur mit der angenommenen Struktur im Einklang.

Anteile der Kumaranderivate im Dillöl

Um die pflanzenphysiologische Bedeutung der identifizierten Komponenten nachzuweisen, wurde die Zusammensetzung, in erster Linie der *Anteil an 3,7-Dimethyl-4,5,6,9-tetrahydrokumaran* in den Dillölen, die von Dillpflanzen verschiedenen Reifegrades auf nahezu gleiche Weise gewonnen wurden, untersucht. Die wichtigsten Analyseergebnisse sind in Tabelle II zusammenge-

Tabelle II

Änderung des Anteiles des 3,7-Dimethyl-4,5,6,9,-tetrahydrokumarans im Dillöl in Abhängigkeit vom Reifegrad

Zeitpunkt der Ernte	Komponentenanteil, Gew.%			
	1.–6. Monoterpene	9. Dimethyltetra-hydrokumaran	12. Dimethylkumaran	14. Carvon
10.—20. Juli	65—70	15 —18	0,0X	13—17
1.—10. August	50—55	5 —10	0,0X	35—40
20.—31. August	50—60	1 — 4	0,X	35—45
Anfang September	50—60	0,2— 1	0,X	40—45

stellt. In der Tabelle sind auch der Gehalt an Monoterpenen und der Gehalt an Carvon angegeben. Aus den Daten ist ersichtlich, daß die relative Menge des Dimethyltetrahydrokumarans im ätherischen Öl wesentlich vom Zeitpunkt der Ernte abhängt, der *Anteil an Dimethylkumaran* sich aber ebenfalls bedeutend verändert. Das im Verlaufe der Untersuchungen gefundene Dimethyltetrahydrokumaran und Dimethylkumaran wurden bisher im Dillöl, ja überhaupt in ätherischen Ölen nicht nachgewiesen. Obwohl die Möglichkeit, daß das 3,6-Dimethylkumaran während der Herstellung des Dillöles entsteht, nicht auszuschließen ist, weist die hohe und sich mit dem Reifegrad verändernde Konzentration des 3,7-Dimethyl-4,5,6,9-tetrahydrokumarans darauf hin, daß diese Verbindung eine bestimmte physiologische Rolle spielt.

*

Die Verfasser danken an dieser Stelle Herrn Dr. Rezső Kolta (KHV) für die Dillölmuster, Frau Zsuzsa Régensperger (MÁKFI) für die gaschromatographischen Untersuchungen, Frau Ilona Schultheisz (MÁKFI) für die Bestimmung von physikalischen Konstanten, Herrn Zoltán Décsy (MÁKFI) für die PMR-Spektren bei 60 MHz und Herrn Dr. Lajos Radics (KKKI) für die Spektren bei 100 MHz sowie deren Deutung.

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STUDIES OF SOME CHROMIUM(III) COMPLEXES OF SCHIFF BASES AND CALCULATION OF EXTRA BAND ENERGIES IN OCTAHEDRAL COMPLEXES INVOLVING WEAK LIGAND FIELDS

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The spectral and magnetic properties of the chromium(III) complexes of N-2,5-dihydroxyacetophenacylideneanthranilic acid (H_3 DAPA) and N-2,5-dihydroxyacetophenacylidene-*p*-dimethylaminoaniline (H_2 DAPDA) have been studied and the ligand field parameters evaluated. The spectra of $[Cr(C_{15}H_{11}O_4N)Cl(H_2O)_2]$, $[Cr(C_{15}H_{11}O_4N)Br(H_2O)_2]$, $[Cr(C_{16}H_{17}N_2O_2)_2Cl\ H_2O]$ and $[Cr(C_{16}H_{17}O_2N_2)_2\ Br\ H_2O]$ complexes involving weak ligand field have been interpreted by calculating the extra band energy of the second and third spin-allowed transitions.

Experimental

The tridentate Schiff base N-2,5-dihydroxyacetophenacylideneanthranilic acid was prepared by the method of OZHA and KAUL [1] and its 75% ethanol solution was used throughout. The bidentate N-2,5-dihydroxyacetophenacylidene-*p*-dimethylaminoaniline ligand was prepared by the method of PANWAR and SINGTE [2] and its ethanolic solution was used for chelation [3, 4].

Isolation of complexes

(a) Diaqua chloro(N-2,5-dihydroxyacetophenacylideneanthranilic acid) chromium(III).

A 75% ethanolic solution of H_3 DAPA was added to a 50% ethanolic solution of chromium(III) chloride in a stoichiometric ratio and the mixture refluxed on a water bath for 2.5 hrs; after cooling, the precipitate was filtered and washed successively with water, ethanol and ether, and subsequently dried. The greyish-green coloured chelate compound decomposes between 300—350 °C.

$[Cr(C_{15}H_{11}O_4N)Cl(H_2O)_2]$. Calcd. C 45.85; N 3.56; Cl 9.03; Cr 13.25. Found C 45.62; N 3.41; Cl 8.88; Cr 13.00%.

(b) Diaqua monobromo (N-2,5-dihydroxyacetophenacylideneanthranilic acid) chromium(III).

Procedure (a) was repeated resulting in the isolation of the $[Cr\ (C_{15}H_{11}O_4N)\ Br\ (H_2O)_2]$ complex. $[Cr\ (C_{15}H_{11}O_4N)\ Br\ (H_2O)_2]$. Calcd. C 41.18; N 3.28; Br 18.30; Cr 11.89; Found C 41.00; N 2.18; Br 18.00; Cr 11.62%.

(c) Aqua chlorobis(N-2,5-dihydroxyacetophenacylidene-*p*-dimethylaminoaniline) chromium(III).

The above procedure was employed and a dark brown precipitate of $[Cr\ (C_{16}H_{17}O_2N_2)_2\ Cl\ (H_2O)]$ was obtained; the chelate does not melt or decompose up to 350 °C.

$[Cr\ (C_{16}H_{17}O_2N_2)_2\ Cl\ (H_2O)]$. Calcd. C 59.60; N 8.69; Cl 5.51; Cr 8.26. Found C 59.40; N 8.52; Cl 5.38; Cr 8.15%.

(d) Aqua bromobis(N-2,5-dihydroxyacetophenacylidene-*p*-dimethylaminoaniline) chromium(III).

Procedure (a) was repeated with the difference that the separation of this complex required refrigeration of the reaction mixture for two days.

$[Cr\ (C_{16}H_{17}O_2N_2)_2\ Br\ (H_2O)]$. Calcd. C 55.81; N 8.14; Br 11.12; Cr 7.55. Found C 55.68; N 7.98; Br 10.95; Cr 7.32%.

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Results and discussion

Chromium(III) forms 1 : 2 complexes with N-2,5-dihydroxyacetophenacylidene-*p*-dimethylaminoaniline, whereas it forms 1 : 1 complexes with N-2,5-dihydroxyacetophenacylideneanthranilic acid. The composition of the complexes was confirmed by elemental analysis and by the measuerement of their molar conductances. The molar conductance in DMF of all the complexes is of the order of 50—65 mol^{-1} Ohm^{-1} cm^2 which may be attributed to solvation [5, 6]. Molecular weights of the complexes were determined in a semimicro ebulliometer (GALLENKAMP) using a thermistor as sensor [7]. Molecular weights determined experimentally are in agreement with the values calculated for the proposed formulas of the compounds, showing their monomeric character.

Magnetic and electronic spectral studies

The magnetic moments (3.74, 3.70, 3.58 and 3.71 B.M.) for the present complexes, *viz.* $[Cr(C_{15}H_{11}O_4N)\ Cl(H_2O)_2]$ $[Cr\ (C_{15}H_{11}O_4N)\ Br\ (H_2O)_2]$, $[Cr(C_{16}H_{17}O_2N_2)_2\ Cl\ (H_2O)]$ and $Cr\ (C_{16}H_{17}O_2N_2)_2\ Br\ (H_2O)]$ indicate an octahedral symmetry [8, 9].

In octahedral chromium(III) complexes, (d^3), the spin-allowed transitions have been given the assignments $^4A_{2g}(F) \rightarrow {}^4T_{2g}(t_{2g}^2 e_g)$, $^4T_{1g}(t_{2g}^2 e_g)$ and $^4T_{1g}(t_{2g} e_g^2)$ in the order of increasing energy. Besides this, the lowest energy spin-forbidden transition, $^4A_{2g}\ F — {}^2E_g$, has also been observed in the region [10] 12,500 — 14,000 cm^{-1}. The spin-forbidden transition in complex (a) has been observed at 13,000 cm^{-1}, in (b) at 13,280 cm^{-1}, in (c) at 13,100 cm^{-1} and in (d) at 13,230 cm^{-1}.

Three bands have been observed in the spectra of complexes, which are specifically due to spin-allowed γ_1, γ_2 and γ_3 transitions (Table I); the splitting energy 10 D_q [11] can be directly derived from the first spin-allowed band (γ_1). The energies of γ_2 and γ_3 transitions have been evaluated from the standard equations [12], which include configuration interactions.

The value of the Racah interelectronic repulsion parameter B has been determined by three different methods, *viz.* by fitting (i) the second band (γ_2), (ii) the third band (γ_3) and (iii) the sum of the second and third bands in the equations used by TEOTIA *et al.* [12]. The experimental and calculated values of γ_2 and γ_3 energies are listed in Table I together with the deviations in these transitions, $\delta\gamma_{2,3} = (\gamma_{calcd} — \gamma_{exptl})$. It is worthwhile to mention that the different values of B and β depend noticeably on the method adopted for their calculation. It is evident from Table I that the deviation

Table I

Electronic spectral data and calculated values (cm^{-1}) of the spin-allowed band in octahedral chromium(III) complexes

Compound	Observed and calculated transition energies of octahedral chromium(III) complexes $^4A_{2g}(F)$					δ_γ(%)	B	β	Ligand field stabilization energy, LFSE (kcal/mol)
	^2E_g	$^4T_{2g}(F)_{\gamma 1}$	$^4T_{1g}(F)_{\gamma 2}$	$^4T_{1g}(P)_{\gamma 3}$	$\oplus\delta_\gamma(cm^{-1})$				
$[Cr(C_{15}H_{11}O_4N)Cl(H_2O)_2]$ (a)	13,000	17,750	25,000	38,280	Experimental				60.8
		$10D_q$	Fitted	39,200	Calcd.(I) + 920	2.34	730	0.795	
		$10D_q$	23,980	Fitted	Calcd.(II) —1020	4.25	600	0.668	
		$10D_q$	24,530	38,750	Calcd.(III) ± 470	1.54	668	0.727	
$[Cr(C_{15}H_{11}O_4N)Br(H_2O)_2]$ (b)	13,280	17,400	24,900	37,600	Experimental				59.7
		$10D_q$	Fitted	38,756	Calcd.(I) ±1156	2.98	764	0.832	
		$10D_q$	23,640	Fitted	Calcd.(II) —1260	5.33	600	0.653	
		$10D_q$	24,335	38,165	Calcd.(III) ± 565	1.90	686	0.747	
$[Cr(C_{16}H_{17}N_2O_2)_2\,Cl\cdot H_2O]$ (c)	13,100	17,000	24,600	38,000	Experimental				58.3
		$10D_q$	Fitted	38,267	Calcd.(I) + 267	0.70	795	0.866	
		$10D_q$	24,217	Fitted	Calcd.(II) — 383	1.58	738	0.804	
		$10D_q$	24,473	38,127	Calcd.(III) ± 127	0.43	773	0.842	
$[Cr(C_{16}H_{17}N_2O_2)_2\,Br\cdot H_2O]$ (d)	13,230	16,620	23,510	36,330	Experimental				57.0
		$10D_q$	Fitted	36,800	Calcd.(I) + 470	1.27	697	0.759	
		$10D_q$	23,030	Fitted	Calcd.(II) — 480	2.08	633	0.689	
		$10D_q$	23,280	36,560	Calcd.(III) ± 230	0.81	665	0.724	

$\oplus\ \delta\gamma = (\gamma_{calcd} - \gamma_{exptl})$

β = B in complex/918; $LFSE = \dfrac{12D_q}{350}$

$\delta\gamma_{2,3}$ of the calculated transition energy is of the order of a few per cent and is always the smallest for the third method and the largest for the second method. Therefore, $\delta\gamma_3$ and $\delta\gamma_2$ obtained by fitting γ_2 and γ_3 transitions in the first and second methods, respectively, are always related as $\delta\gamma_2 > \delta\gamma_3$, whereas if the sum of the second and third bands is fitted in method III, then $\delta\gamma_2$ and $\delta\gamma_3$ are correlated by $|\delta\gamma_2| = |\delta\gamma_3|$. Hence it is very interesting to note that in the approximation of the ligand field theory of three parameters, "the energies of both the second and third bands are reproduced well".

Infrared studies

In the IR spectra of chromium(III) complexes with N-2,5-dihydroxyacetophenacylideneanthranilic acid and N-2,5-dihydroxyacetophenacylidene-*p*-dimethylaminoaniline, the stretching frequencies of azomethine ($CH_3C = = N—$) and phenolic OH groups are lowered, showing thereby complex formation through these groups. This view is further supported by the appearance of bands corresponding to M—N and M—O bonds. In the complexes of the former ligand binding of the carboxy group with the metal is also confirmed, while in those of the latter ligand, metal to halogen bonds are also formed as revealed by the appearance of bands at 350 and 375 cm^{-1}.

*

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LIGAND SUBSTITUTION AND COMPLEX STRUCTURE, XIV

THE PROTON-RESONANCE SPECTRUM OF THE BIS-(N-METHYLSALICYLALDIMINATO)NICKEL(II) COMPLEX

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A study was made on the temperature dependence of the PMR spectrum of the bis-(N-methylsalicylaldiminato)nickel(II) complex, and its bispyridine adduct. Conclusions were drawn with regard to the species present in solution.

The PMR spectra of compounds of the type bis-(N-alkylsalicylaldiminato)-nickel(II) were reported earlier [1], with a detailed account of the PMR spectrum of the *n*-hexyl derivative. It was found that the spectral structures of these compounds are practically the same as those of the ligand and of the diamagnetic Zn(II) complex. The effects of variations in concentration and temperature could be observed primarily in the signals of the α-methylene and CH=N protons. It was assumed that at higher temperature there is a possibility for the formation of a paramagnetic, tetrahedral molecular species.

As it is already described [2,3], the methyl derivative exhibits different behaviour in every respect compared to the other members of the series; this refers to the PMR spectrum too. In the present paper we report the PMR spectrum of the first member of the series (in the following: $Ni[SAMA]_2$).

Experimental

The complex was prepared in the usual manner by the reaction of bis-(salicylaldehydato)nickel(II) · $2H_2O$ and methylamine in chloroform solution; the product was purified by recrystallization from acetone. The zinc complex was isolated as described by CHARLES [4].

PMR spectra were recorded in CS_2, C_2Cl_4 and $CDCl_3$ solutions with TMS as internal standard, using a JEOL C—60 HL 60 MHz instrument.*

Results

The spectra of the complex $Ni[SAMA]_2$ and of the diamagnetic zinc complex, regarded as reference curve, are presented in Fig. 1. It can be seen that the spectrum is completely different from that of the zinc complex and from those of the *n*-alkyl derivatives in general [1]. In $CDCl_3$ solution δ CH=

* The authors wish to thank Mr. Gy. DOMBI for recording the spectra.

$=N=$ 8.01 ppm in the spectrum of the free Schiff's base [5]. In the zinc complex δ CH=N is shifted to 8.33 ppm. The sharp band proves that coupling with the aromatic protons can be neglected. For the nickel(II) complex the extent of spin–spin splitting cannot be established, the lines are appreciably broadened because of the decrease of the relaxation time and also because of the presence of paramagnetic species. The latter may play a very important role, for even in an indifferent solvent (in contrast with the other members of

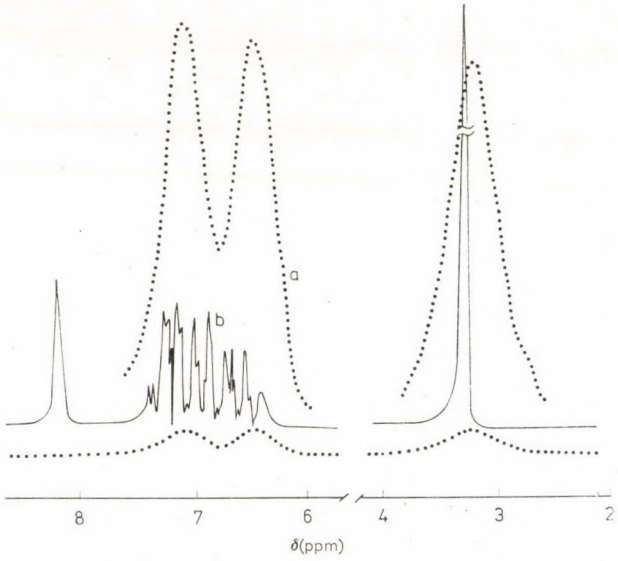


Fig. 1. PMR spectra of (a) $Ni[SAMA]_2$ in CS_2, and (b) the diamagnetic $Zn_2[SAMA]_4$ in $CDCl_3$

the homologous series) $Ni[SAMA]_2$ is present in a paramagnetic associated form to an extent of ca. 30% [6, 7]. It must be noted that the PMR spectrum differs from solvent to solvent.

Figure 2 depicts the temperature dependences of the shifts of different proton signals. While the aromatic proton signal appears in practically the same place, the other two signals shift in a very characteristic manner. This is particularly the case for the methyl signal, which exhibits a jump at ca. 80°. It is assumed that the first section is the range of breakdown of the associates, while the second indicates the formation of a new, paramagnetic species, probably a tetrahedral molecular species. This assumption is strongly suggested by the fact that, with the elevation of the temperature, the equilibrium in solution for the compounds of the type bis(N-iso-alkyl-salicylaldiminato)-nickel(II) is shifted towards the tetrahedral form [8].

In the concentration interval 1.7×10^{-2}—5.5×10^{-2} mole $\cdot$ dm^{-3} in C_2Cl_4 solution, the δ values are practically unchanged. However, this in no

way means that dilution should not lead to changes primarily in the $N-CH_3$ and $CH=N$ signals as a result of the breakdown of the associates. Unfortunately, the solubility conditions and the sensitivity of the instrument do not permit an investigation in a concentration interval so wide that the breakdown or formation of the associates would be expected to show up.

In coordinating solvents adducts are formed; for example, in pyridine a six-coordinated bis-pyridine adduct is formed, and this can be isolated too [9, 10]. Its spectrum is typical of paramagnetic nickel(II) compounds.

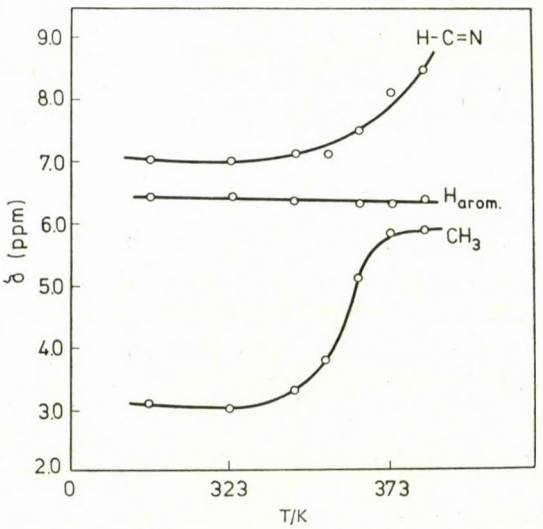


Fig. 2. Temperature dependence of the chemical shift in a C_2Cl_4 solution of $Ni[SAMA]_2$

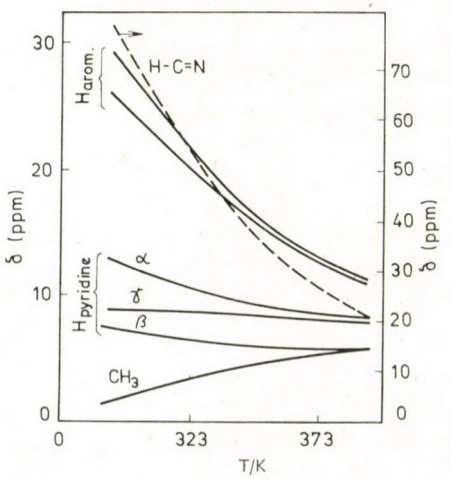


Fig. 3. Temperature dependence of the chemical shift in a C_2Cl_4 solution of $Ni[SAMA]_2 \cdot py_2$.

At room temperature the CH=N proton signal lies at around 73 ppm, the aromatic proton signal at 20—30 ppm, the pyridine proton signal at 6—13 ppm, and the methyl proton signal at 2—3 ppm. On the elevation of the temperature, the spectrum undergoes a considerable transformation (Fig. 3). The azomethyne proton signal shifts from 73 ppm to ca. 20 ppm. The signals of the pyridine α, β and γ protons can also be found; the α-proton signal shifts to the greatest extent. The γ-proton signal scarcely varies with temperature.

It is assumed that the observed change can be interpreted by a very complicated equilibrium system containing at least four different species.

$$Ni[SAMA]_2 \cdot py_2 \rightleftharpoons Ni[SAMA]_2 \cdot py + py$$

$$Ni[SAMA]_2 \cdot py \rightleftharpoons Ni\ [SAMA]_2 + py$$

It is obvious that as the temperature rises the equilibria shift in the direction of the upper arrows, *i.e.* decomposition occurs. This corresponds to the fact that, in addition to the normal paramagnetic bis and monopyridine adducts, the presence of diamagnetic square planar molecules and paramagnetic associates cannot be excluded either. Further, however, above a certain temperature (80°) the possibility exists for strongly paramagnetic tetrahedral molecules to be formed too.

In order to decide the extents to which the above species are present in the system at various temperatures, additional detailed investigations should be carried out.

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MECHANISTIC STUDY OF THE ISOMERIZATION OF *n*-BUTENE ON ACID CATALYSTS, III

ENERGY SCHEME OF THE TRANSFORMATIONS

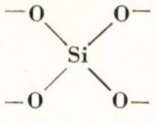
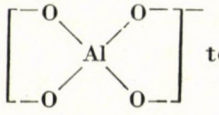
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Received May 24, 1976

On derivatives representing the three basic types of the active sites of zeolite catalysts, on H-, Mg- and Ni-clinoptilolites, the initial rates of the conversions, starting from all three *n*-butene isomers, have been determined at different pressures and temperatures, and have been evaluated on the basis of kinetic relationships deduced earlier. From the temperature dependence of the parameters, characteristic of the single reactions, the energy scheme of conversion has been determined. This supported on the one hand the energy scheme of catalytic conversions, presumed earlier on theoretical basis, and was used on the other hand to obtain more precise information on the mechanism of the isomerization reactions with the aid of this new kinetic method. It has been shown that *n*-butene isomerization proceeds on H-clinoptilolite through a common surface intermediate while in the cases of Mg- and Ni-clinoptilolites through several surface intermediates, which are not in equilibrium with one another. On Ni-clinoptilolite, the rate-determining surface triangle reaction proceeds through isomers in adsorption equilibrium. Therefore, different reaction mechanisms must be taken into account on the basic forms of active sites.

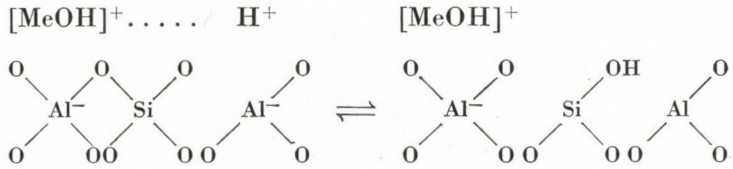
In the previous communications of the series [1, 2], the general problems of the kinetics of catalytic conversion, proceeding between the three components, have been discussed. In the present paper, experimental results obtained on the H-, Mg- (alkali earth metal) and Ni- (transition metal) derivatives of clinoptilolite will be evaluated on the basis of the kinetic relationships deduced. The object is to obtain thereby information, whether the mechanism of isomerization is identical on the derivatives, or not. If only their different acidity were to play a role, the reaction mechanism would then be the same for all the three basic forms of the active species with different parameter values, whereas if the reaction mechanism itself is different, the efficiency of the centers cannot be correlated with acidity alone.

The most widely used heterogeneous catalysts of acid character are the zeolites. In their crystal lattice, the  tetrahedrons are substituted in a larger or smaller number by  tetrahedrons with aluminium

center, and the negative excess charge thus produced is compensated by some cation [3a]. Depending on the nature of the charge compensating cation, different forms of zeolites, *i.e.* different types of the catalytically active formations can be produced. If this is a proton, which is as a matter of course dissociable, Brönsted acid sites are formed. Accordingly, the H-form of zeolites comprises this basic type of catalytically active formation.

Forms neutralized with monovalent alkali metal ions are practically inactive.

Contrary to this, bivalent alkali earth metal (and trivalent earth metal) forms are active, which is also decisively attributed to the formation of acid sites (*e.g.* in [4]), involving the dissociation of the hydrate water in the strong electrostatic field of the multivalent cation, to produce a form characteristic of Brönsted acid species:



However, from the catalytical point of view, this is not equivalent to a simple Brönsted center, since it is affected by the multivalent cation. This latter effect will be particularly conspicuous, if the acid OH group formed by the dissociation of the hydrate water cannot be detected in spite of a considerable catalytic activity.

The picture of the active center is further modified, if a bivalent transition metal ion is attached to the negatively charged site of the zeolite lattice: here already the interaction with the outermost electrons of the incorporated metal ion may play a role in the course of catalytic transformation.

All this results in that the catalyst—substrate interaction changes in the course of a given conversion, which may lead to a change of the intermediate product, and thus to the change of the reaction path.

n-Butene isomerization proved to be an advantageous test reaction for the investigation of the efficiency of acid catalysts. In addition to the determination of the activity, *i.e.* the determination of the reaction rate under certain conditions, it makes possible also the determination of a qualitative characteristic, selectivity, since any of the isomers transforms simultaneously into the other two isomers.

With the exception of a few publications (*e.g.* [5]), conclusions on the kind of the active sites were drawn directly from the phenomenological activation energy and from selectivity, and sometimes even their mode of action was interpreted on this basis [6—10].

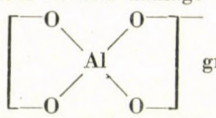
It can be seen from the relationships deduced in communications I and II of our present series of papers that the rate constants characteristic of the single steps cannot be determined directly from experimental data measured or from empirical rate constants, as has been published in [11, 12].

1. Experimental

(a) Selection of the catalyst

For the study of various ion exchanges, clinoptilolite was chosen among the zeolites for our experiments, because:

a) it has a relatively high stability because of its high silicon content (Si : Al ratio being 5 : 1), which is reflected also (1) in its thermal stability (the lattice structure of its de-cationized form collapses only at about 700 °C, (2) in its "chemical" stability, which means that depending on the extent of NH_4^+ ion exchange, after the complete thermal removal of ammonia, it can be transformed even to 90% to the H-form without a damage to its structure, and water adsorbed below 100 °C on the H-form does neither damage the active sites [13, 14];

b) owing similarly to its high silicon content, the  groups are arranged at a greater distance from one another, whereby it has a stronger acid character, so that its interaction with relatively weakly basic hydrocarbons, *e.g.* with olefins, is stronger, and its catalytic activity more pronounced [15];

c) contrary to other molecular sieves, in its alkali earth metal derivatives the acid hydroxyl groups mentioned above, which would modify the catalytic action of the hydrated bivalent cation, are not formed at all [16]. The Mg-derivative was chosen because this has the highest thermal stability.

(b) Preparation of the catalysts

The Hungarian rock used for our investigations contained besides 60% clinoptilolite also feldspar, quartz, tridymite [17], but these proved to be completely inert both catalytically and from the aspect of adsorption or ion exchange. This can be seen by comparing in Table I the values of $H_2O + NH_3$ content, NH_4^+ ion exchange capacity and of the catalytic activity in 1-butene isomerization (last column) of the H-clinoptilolite of practically 100% purity (prepared from the pure mineral occurring in Horseshoe Dam, Arizona, USA) and of the Hungarian clinoptilolite-containing rock; the ratio of the transformation rates of 1-butene into *cis*- and *trans*-2-butenes, *i.e.* the selectivity of isomerization, is the same for the two samples, indicating the identity of their active sites.

From the 0.5—1 mm sieve fraction of the rock, K-clinoptilolite has been prepared by ion-exchange; in the active positions this was already free of alkali earth metal cations.

The NH_4-form has been obtained from K-clinoptilolite by 90% ion exchange, which was kept in the reactor at 450 °C and 10^{-3} Torr for 1 hour, and gave by the desorption of ammonia the H-form.

In the Mg-form, obtained from K-clinoptilolite by ion exchange, 75% of the exchangeable cation positions were occupied by Mg^{2+} ions. Before the experiments, the sample was treated at 450 °C and 10^{-3} Torr for 1 hour in the reactor.

The transition metal derivative, the Ni-derivative, was obtained from the K-form by 25% ion exchange. This was activated before the experiments by a treatment at 200 °C and 10^{-3} Torr for 1 hour in the reactor.

The catalytic action of potassium remaining in active positions is rather subordinate. At the temperature of isomerization experiments with the H-, Mg- and Ni-forms, the activity of the K-form is undetectable, and if the isomerization rates determined on it at 200—300 °C are extrapolated to the temperature of 70—160 °C of the kinetic series measurements, values lower by 9—6 orders of magnitude than those measured on the active derivatives are obtained.

Table I

Comparative test of USA clinoptilolite and Hungarian clinoptilolite

	Hung. clinoptilolite (A)	USA clinoptilolite (B)	(A)/(B)
Loss on ignition of the NH_4^+-form (NH_3 + + H_2O) weight/%	10.33	18.0	0.57
NH_4^+-ion exchange capacity meq./g	1.4	2.28 (2.4)*	0.61
1-butene isomerization rate (H-form, 200°C, 100 Torr, mole $g_{cat}^{-1}\ s^{-1}$)			
into *cis*-2-butene, r_{12}	$3.5 \cdot 10^{-6}$	$6.2 \cdot 10^{-6}$	0.57
into *trans*-2-butene, r_{13}	$5.6 \cdot 10^{-6}$	$10.2 \cdot 10^{-6}$	0.55
selectivity, r_{12}/r_{13}	0.62	0.61	1.0
specific surface, m^2/g			
by Kr adsorption	60	90	0.67
with Hg-porosimeter	15.2	17.7	0.86

*Theoretical value for 100% clinoptilolite, calculated with BERGER's empirical formula [16]

2. Results

The conditions of the experiments, carried out in a closed circulation system, have been given in section 4 *(b)* of our preceding paper [2]. As described there, the parameters of the relationship between the initial partial pressure of the i-th isomer, p_i° and the initial rate of its transformation into j isomer, r_{ij}°,

$$\frac{1}{r_{ij}^\circ} = m_{ij}\frac{1}{p_i^\circ} + b_{ij} = m_{ij}\left(\frac{1}{p_i^\circ} + b_i\right) \tag{1}$$

can be determined on a given catalyst at a given temperature. Let us remind that expression (1) is the linearized form of the general rate equation

$$r_{ij}^\circ = \frac{a_{ij}p_i^\circ}{1 + b_i p_i^\circ}\,; \qquad a_{ij} = 1/m_{ij} \tag{2}$$

of which it has been shown in [2] that it is valid for various, highly different transformation schemes.

Obviously, the parameters determined on the basis of Eqs (1) and (2) can be interpreted only in accordance with kinetic consideration expounded in [2], if the rate values measured are not affected by mass transfer within the catalyst particles. It has been shown that the diffusion mass transfer to 0.1 μm clinoptilolite crystals, embedded in rock particles of 0.5—1 mm grain size, is not rate determining. On the other hand, in accordance with the measured diffusion constant of about 10^{-13} $cm^2\ s^{-1}$ [18], diffusion mass transfer within the crystallite, *i.e.* in the pore system of clinoptilolite, is so slow that

Table IIa

Parameters obtained on H-clinoptilolite by the plotting of experimental data according to Eq. (1) (b_{ij}: in 10^5 mole^{-1} g_{cat} s; m_{ij}: in 10^7 mole^{-1} g_{cat} s Torr; b_i: in 10^{-2} Torr^{-1})

	100°C		130°C		160°C	
b_{12}	0.75		0.40		0.22	
m_{12}	0.75		0.53		0.42	
$b_{12}/m_{12} = b_1$	1.00		0.76		0.52	
b_{13}	0.48		0.22		0.10	
m_{13}	0.50		0.29		0.19	
$b_{13}/m_{13} = b_1$	0.96		0.76		0.53	
b_{23}	0.55		0.25		0.15	
m_{23}	0.40		0.25		0.19	
$b_{23}/m_{23} = b_2$	1.38		1.00		0.79	
b_{21}	2.40		1.20		0.50	
m_{21}	1.85		1.20		0.75	
$b_{21}/m_{21} = b_2$	1.30		1.00		0.67	
b_{31}	2.70		1.20		0.68	
m_{31}	4.20		2.00		1.00	
$b_{31}/m_{31} = b_3$	0.64		0.60		0.68	
b_{32}	0.85		0.50		0.36	
m_{32}	1.50		0.84		0.50	
$b_{32}/m_{32} = b_3$	0.57		0.60		0.72	
m_{21}/m_{12} $(= K_{12})$	2.5	(4.22)	2.3	(3.74)	1.8	(2.97)
m_{32}/m_{23} $(= K_{23}$	3.8	(2.10)	3.4	(1.91)	2.6	(1.78)
m_{13}/m_{31} $(= K_{31})$	0.12	(0.113)	0.14	(0.151)	0.19	(0.188)
$II\ m_{ji}/m_{ij} = 1$		1.1		1.1		0.9

the conversion proceeding at the external surface of the clinoptilolite crystallites is the only detectable transformation.

On a given catalyst, starting from a given isomer, at a given temperature and pressure, the initial rate of conversion into the two other isomers has been obtained in the following way: at 3—5 subsequent values of $t\ m_C/m_F$ (where t is the time of experiment, m_C the mass of the catalyst and m_F the mass of *n*-butene in the closed circulation system), the composition of the *n*-butene mixture in the gas phase has been determined up to a conversion of maximum 10—15%, and the initial section of the conversion curve in question, which can be considered as linear, has been plotted with these values. The slopes of these curves gave the rate values sought.

Performing the above measurements at 4—5 different pressures, the

Table IIb

Kinetic constants calculated from data in Table IIa (k_{-i}: in 10^{-5} mole g_{cat}^{-1} s^{-1}: k_i: in 10^{-7} mole g_{cat}^{-1} s^{-1} $Torr^{-1}$: k^*_{-1}: desorption probability)

	100°C	130°C	160°C
$1/b_{12} = k_{-2}$	1.33	2.50	4.5
$1/b_{13} = k_{-3}$	2.10	4.55	10.0
$1/b_{23} = k_{-3}$	1.82	4.00	6.7
$1/b_{21} = k_{-1}$	0.42	0.83	2.00
$1/b_{31} = k_{-1}$	0.37	0.83	1.47
$1/b_{32} = k_{-2}$	1.18	2.00	2.80
$\bar{k}_{-1}$ (k^*_{-1})	0.39 (0.11)	0.87 (0.12)	1.66 (0.13)
$\bar{k}_{-2}$ (k^*_{-2})	1.26 (0.35)	2.18 (0.30)	3.47 (0.26)
$\bar{k}_{-3}$ (k^*_{-3})	1.95 (0.54)	4.27 (0.58)	8.13 (0.61)
$1/(m_{12}k^*_{-2}) = k_1$	3.8	6.3	9.2
$1/(m_{13}k^*_{-3}) = k_1$	3.7	6.0	8.6
$1/(m_{23}k^*_{-3}) = k_2$	4.6	6.9	8.6
$1/(m_{21}k^*_{-1}) = k_2$	4.9	7.0	10.3
$1/(m_{31}k^*_{-1}) = k_3$	2.15	4.2	7.7
$1/(m_{32}k^*_{-2}) = k_3$	1.90	4.0	7.7

Values of the energy steps in kcal/mole

$E_1^{\pm} = 4.6 \pm 0.2$ $\quad E^{\pm}_{-1} = 7.8 \pm 0.3$

$E_2^{\pm} = 3.9 \pm 0.2$ $\quad E^{\pm}_{-2} = 5.6 \pm 0.4$

$E_3^{\pm} = 7.0 \pm 0.2$ $\quad E^{\pm}_{-3} = 7.6 \pm 0.3$

pairs of values $p_i^\circ - r_{ij}^\circ$ and $p_i^\circ - r_{ik}^\circ$ belonging together have been plotted according to (1). Each of these diagrams represented thus about 15—20 values ($t\, m_C/m_F$)—conversion measured directly.

Owing to the well-known fact that the accuracy of kinetic measurements is strongly limited, the drawing of the lines according to (1) in the diagrams cannot be done unambiguously (see Fig. 2 in [2]), therefore, in the selection of the most probable m_{ij} and b_{ij} values the following requirements were also taken into consideration:

a) in the transformation of an isomer into the other two isomers, the criterion $b_{ij}/m_{ij} = b_{ik}/m_{ik} = b_i$ must be fulfilled, what can be easily seen from (1).

b) b_{ij} and m_{ij} values determined at various temperatures must lie in Arrhenius' plotting along each of a straight line; it can be shown namely that even if their expressions contain from case to case several exponential members (see Tables III and IV in [2]), the Boltzmann factors are such that only a negligibly small error is committed by replacing them with a single exponential expression.

Table III

Parameters obtained on Mg-clinoptilolite by the plotting of experimental data according to Eq. (1) (b_{ij}: in 10^5 mole^{-1} g_{cat} s; m_{ij}: in 10^7 mole^{-1} g_{cat} s Torr; b_i: 10^{-2} Torr^{-1})

	100°C	130°C	160°C
b_{12}	3.0	0.95	0.35
m_{12}	1.8	1.9	1.9
$b_{12}/m_{12} = b_1$	1.66	0.50	0.185
b_{13}	3.0	0.95	0.30
m_{13}	1.8	1.9	1.6
$b_{13}/m_{13} = b_1$	1.66	0.50	0.19
b_{23}	4.2	1.66	0.8
m_{23}	4.6	2.2	1.2
$b_{23}/m_{23} = b_2$	0.91	0.75	0.67
b_{21}	10.0	3.7	1.70
m_{21}	11	5.25	2.9
$b_{21}/m_{21} = b_2$	0.91	0.71	0.59
b_{31}	19	7.0	2.80
m_{31}	42	13.5	5.2
$b_{31}/m_{31} = b_3$	0.45	0.52	0.54
b_{32}	11	4.2	1.85
m_{32}	22	8.1	3.55
$b_{32}/m_{32} = b_3$	0.50	0.52	0.52
m_{21}/m_{12} $(= K_{12})$	6.1 (4.22)	2.8 (3.47)	1.5 (2.97)
m_{32}/m_{23} $(= K_{23})$	4.8 (2.10)	3.7 (1.91)	3.0 (1.78)
m_{13}/m_{31} $(= K_{31})$	0.043 (0.113)	0.14 (0.151)	0.31 (0.188)
IIm_{ji}/m_{ij} $(= 1)$	1.3	1.4	1.4

The parameters of the straight lines, meeting as far as possible the requirements of (a) and (b) and complying also with experimental data according to (1), are summarized for H-clinoptilolite in Table IIa, for Mg-clinoptilolite in Table III, and for Ni-clinoptilolite in Table IV (in which 1 ≡ 1-butene, 2 ≡ *cis*-2-butene, 3 ≡ *trans*-2-butene). It has been checked as control, how close the ratios m_{ji}/m_{ij}, obtained from the forward and backward *initial* conversion rates, are lying to the K_{ij} thermodynamical *equilibrium* constants, determined experimentally (see below the m_{ij} and b_i values of the above tables); it results namely from the kinetic realtionships deduced that in principle $m_{ji}/m_{ij} = a_{ij}/a_{ji} = K_{ij}$ [2].

Table IV

Parameters obtained on Ni-clinoptilolite by the plotting of experimental data according to Eq. (1) (b_{ij}: in 10^5 mole^{-1} g_{cat} s; m_{ij}: in 10^7 mole^{-1} g_{cat} s Torr; B_i in 10^{-2} Torr^{-1})

	70°C		100°C		130°C	
$b_{12} = 1/k_{12}$	2.58		0.78		0.24	
m_{12}	1.21		1.10		1.09	
$b_{12}/m_{12} = b_1 = K_1$	2.13		0.71		0.22	
$b_{13} = 1/k_{13}$	2.40		0.62		0.16	
m_{13}	1.12		0.90		0.73	
$b_{13}/m_{13} = b_1 = K_1$	2.15		0.68		0.22	
$b_{23} = 1/k_{23}$	1.00		0.50		0.24	
m_{23}	2.65		1.90		1.30	
$b_{23}/m_{23} = b_2 = K_2$	0.38		0.26		0.185	
$b_{21} = 1/k_{21}$	4.4		2.10		1.10	
m_{21}	11.6		8.1		5.9	
$b_{21}/m_{21} = b_2 = K_2$	0.38		0.26		0.19	
$b_{31} = 1/k_{31}$	33		7.4		1.8	
m_{31}	19		10.4		6.0	
$b_{31}/m_{31} = b_3 = K_3$	1.75		0.71		0.30	
$b_{32} = 1/k_{32}$	11		2.6		0.80	
m_{32}	6.2		3.7		2.7	
$b_{32}/m_{32} = b_3 = K_3$	1.8		0.70		0.30	
m_{21}/m_{12} (= K_{12})	9.6	(5.28)	7.4	(4.22)	5.4	(3.47)
m_{32}/m_{23} (= K_{23})	2.3	(2.32)	1.95	(2.10)	2.2	(1.91)
m_{13}/m_{31} (= K_{31})	0.059	(0.082)	0.087	(0.113)	0.12	(0.151)

Values of the energy steps in kcal/mole

$E_1 = -10.0 \pm 0.2$ $\quad E_2 = -3.2 \pm 0.2$ $\quad E_3 = -7.9 \pm 0.2$

$E_{12}^{\pm} = 10.0 \pm 0.1$ $\quad E_{23}^{\pm} = 6.5 \pm 0.1$ $\quad E_{31}^{\pm} = 13.0 \pm 0.1$

$E_{13}^{\pm} = 12.3 \pm 0.1$ $\quad E_{21}^{\pm} = 6.2 \pm 0.1$ $\quad E_{32}^{\pm} = 11.9 \pm 0.1$

3. Discussion

It can be seen from data in the tables that the condition $b_{ij} = b_{kj}$ is fulfilled, within the limits of error, in the case of H-clinoptilolite, while in the cases of Mg- and Ni-clinoptilolites not. As has been shown in [2], this means that the conversion of the three isomers into one another proceeds on H-clinoptilolite through one or more surface intermediate products, which are in

equilibrium with one another, while such common surface intermediate products or an equilibrium mixture of surface intermediate products do not come into consideration on Mg- and Ni-clinoptilolites. (That case of transformation through two intermediate products according to scheme IV in [2], in which the surface reaction is the rate-determining step, can always be excluded, because this would request the formation in equilibrium ratio of one of the isomer pairs.)

The evaluation of the results of isothermal measurements does not furnish further informations. However, when the temperature dependence of the values determined is investigated, a possibility is offered for a deeper knowledge of the processes proceeding on the different catalysts, if we succeed to show that the conversion can be characterized with one of the basic schemes shown in [2]. Indeed, if the temperature dependence of m_{ij} $(= 1/a_{ij})$ and of the constants obtained on the basis of some expression of b_i (see Tables III and IV in [2]) make in principle possible to follow the energy changes accompanying the single steps, the picture obtained from kinetic investigations can be considered as realistic, or at least as unambiguous.

(a) n-Butene isomerization on H-clinoptilolite

Those of the schemes discussed in [2], which illustrate conversions through 2 or 3 surface intermediate products in equilibrium [schemes III-(1), IV, III], can be described by rate expressions, in which the equilibrium constants of the surface conversions cannot be separated. Thus, they can be taken as identical with the conversion proceeding through 1 common surface intermediate product (scheme V, see in Fig. 1). According to the scheme, the 3 adsorption and the 3 desorption constants can be determined on the basis of experimental parameters 6 m_{ij} $(= 6\ a_{ij}^{-1})$ and 3 b_i, *i.e.* from 9 independent equations (Table IIb).

Owing to the overdetermination of the system of equations, 2 values are obtained for each of the adsorption constants. As testified by Table IIb, these values determined from independent conversions agree well with one another, indicating that the conversion or the formation of the various isomers takes place on identical active centers.

From the Arrhenius plots of the rate constants, the activation energies of the corresponding steps have been determined (see at the bottom of Table IIb). Energy changes accompanying the successive steps have been plotted on an energy scheme (Fig. 1a).

For starting, that energy level has been considered as 0, in which 1-butene in gaseous phase is present. On its adsorption, the activation energy of adsorption was added to this, and the activation energy of the desorption into 1-butene was subtracted from the energy value of the activated adsorption

complex, and thus, the energy level of the adsorbed species has been obtained. Adding to this the activation energy of the desorption into the *cis*-isomer, the energy level of the activated adsorption complex of the *cis*-isomer has been obtained; subtracting from it its activation energy of adsorption, the energy level of the gaseous phase *cis*-2-butane was obtained which agreed very satis-

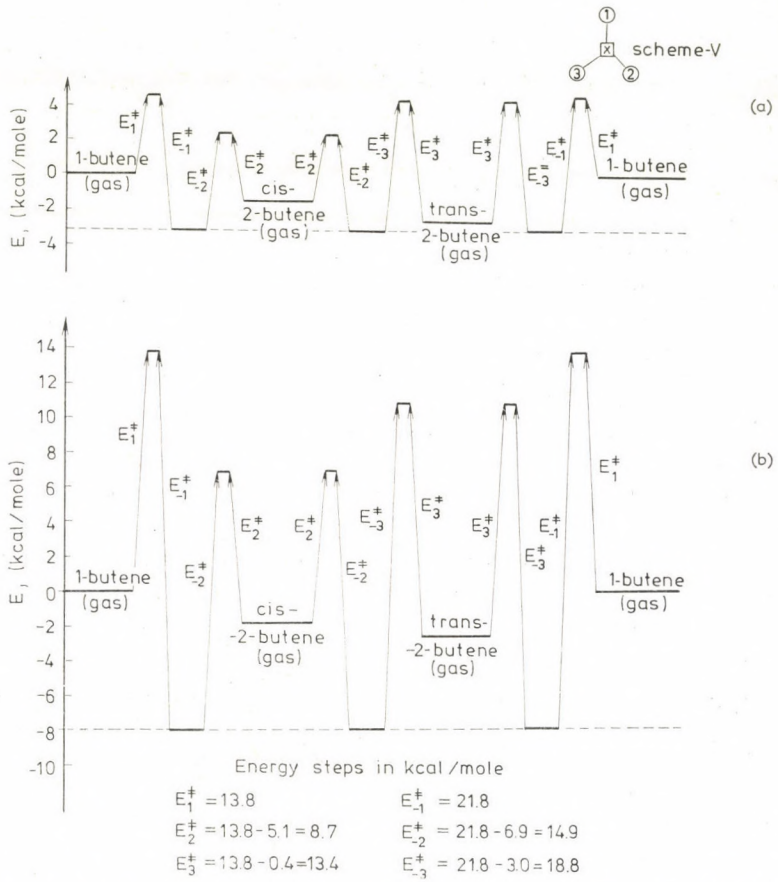


Fig. 1. Energy scheme of *n*-butene isomerization (a) on H-clinoptilolite, (b) on sulfonic acid ion-exchange resin

factorily, with a difference of only 200 cal/mole, with the value calculated from the thermodynamical equilibrium compositions between 1-butene and *cis*-2-butene.

The construction of the energy scheme was continued in this way for the conversions *cis*-2-butene → *trans*-2-butene and, closing the 3-component reaction cycle, for the conversion *trans*-2-butene → 1-butene. Plotting in succession the energy changes accompanying the single steps, finally the

starting energy level of 1-butene has been obtained again with an accuracy of about 50 cal/mole.

In summary, a consistent energy scheme has been obtained, as the energy change of overall conversions is in agreement with the thermodynamical values, the energy level of the system is the same at the beginning and end of the isomerization cycle, and the energy barriers of activation are higher than the energy levels of the intermediate product or of the single gaseous phase isomers, which is consistent with our general kinetic knowledge.

It can be seen from the energy scheme shown in Fig. 1 that the surface intermediate products of the single overall conversions have the same energy level. The findings that the active centers are identical in the conversion of the single isomers (see in **3** (*a*), p. 27 paragraph 2), and the energy levels of the complexes consisting of the active centers and the intermediate products adsorbed on them are identical, indicates the formation of a common surface intermediate, which makes the isothermal kinetic picture more accurate.

In our earlier investigations [19], the energy scheme of isomerization plotted on the basis of results obtained on sulfonic acid ion-exchange resin (Fig. 1b) is similar to that on H-clinoptilolite. The differences can be attributed to the stronger acidity of the sulfonic acid ion-exchange resin. In both cases, *sec*-butyl carbonium ion is the very similar common intermediate.

We attempted the identification of this common surface intermediate by IR spectroscopy.

The film, compressed from NH_4-clinoptilolite to a thickness of $\sim$0.05 mm, was arranged perpendicularly to the radial direction in the evacuable cell. The cell was pumped off at 400°C and 10^{-5} Torr for 60 minutes, and on the H-form formed in this way the isomers of *n*-butene were adsorbed at 100—150°C and 10—50 Torr for 1—60 minutes. During this, the intensity of the absorption band of the acidic OH group decreased at most for 2 minutes to about 85—50% of the original value, depending on conditions. As a result of repeated evacuations up to 10 s, the intensity of the band in question increased to a more or less extent. The original intensity was attained only if the previous adsorption of butene did not last longer than 5 minutes; the longer has been the adsorption period, the lower was the increase in intensity of this band, *i.e.* the regeneration of the acidic OH groups.

However, butene reversibly adsorbed on the acidic OH groups, *i.e.* the assumed common intermediate, could not be investigated, because the cell had to be pumped off, to eliminate the disturbing effect of gaseous phase and physically adsorbed butene. Under such conditions highly differing from those of the isomerization reaction only *n*-butene oligomers, bound strongly in the pores, could be detected.

(b) n-Butene isomerization on Mg-clinoptilolite

Of the schemes discussed in [2], those came into consideration, for which the criterion $b_{ij} = b_{kj}$ is not fulfilled. Of the schemes presented, only III (which is given also here in Fig. 2) can come into consideration for kinetic analysis when the surface triangle reaction is rate determining and the adsorption equilibria are established, because this scheme makes it only possible to calculate from the experimental 6 m_{ij} and 3 b_i parameters the 6 rate constants and the 3 adsorption equilibrium constants. In the case of the other schemes, there are namely more than 9 unknown constants.

From (1) and (2) $b_{ij} = b_i m_{ij} = b_i/a_{ij}$, and we have from [2] $a_{ij}/b_i = k_{ij}$ (the rate constant of the $i \rightarrow j$ surface conversion), hence $b_{ij} = 1/k_{ij}$, and, similarly according to [2], $b_i = K_i$ (the adsorption equilibrium constant of component i).

From the temperature dependence of the constants in question, changes in energy accompanying the assumed steps have been calculated, and the results have been plotted in an energy diagram similar to that in Fig. 2. However, this energy scheme showed an irrealistic pattern. Though the difference between the energy level at the beginning and the end of the conversion cycle was only 200 cal/mole, however, for the change in energy of the conversion of the single isomer pairs into one another about fourfold of the thermodynamical value has been obtained, and the energy level of the activated complex of surface conversions was the same as or somewhat lower than that of gaseous phase 1-butene, which seems also inconsistent.

Most certainly, this false picture is due to the fact that the transformation scheme regarded could be computed, however, it is not realistic. Conversion proceeds according to some other, more complicated scheme through several intermediate products, which are not in equilibrium with one another.

(From the temperature dependence of the single a_{ij} and b_i parameters no conclusions can be drawn at all on the temperature dependence of the constants involved (see [2]). We ascertained by trial calculations that *e.g.* b_i, the sum of the "partial adsorption equilibrium coefficients" of the component i may increase or decrease with temperature, while the adsorption of i is accompanied by a decrease in energy.)

Therefore, in this way alone, no conclusions can be drawn on the reaction mechanism.

Kinetic parameters obtained on Mg-clinoptilolite (see Table III) indicate a few characteristics of the conversion taking place, which could not be observed in the case of the other two catalysts. Thus:

a) starting from 1-butene, the ratio of the formation of *cis*- and *trans*-2-butenes is 1, independently of the temperature ($m_{12} = m_{13}$; this identical formation has been observed in each conversion);

b) starting from *cis*-2-butene, the ratio of formation of *trans*-2-butene and of 1-butene is 2.4 ($m_{21}/m_{23} = 2.4$), independently of the temperature.

Hence, the conversion of 1-butene into the other two isomers differs anyway from the *cis* $\rightleftarrows$ *trans* conversion. This, however, is indicative of a mirror-symmetric scheme (see in [2]), in which there is no equilibrium between the surface intermediate products (consistent with the observation that $b_{ij} \neq b_{kj}$).

(c) n-Butene isomerization on Ni-clinoptilolite

Results obtained, similarly as in conjunction with Mg-clinoptilolite, have been evaluated for the conversion scheme shown in Fig. 2, on the basis of expressions valid in the case of sorption equilibria (see Table IV in [2]). The adsorption equilibrium constants K_i and the rate constants k_{ij} of surface conversion have been determined (see Table IV). Changes in energy, (E_i), accompanying adsorption, and the activation energies of the surface conversions ($E_{ij}^{\neq}$) are given at the bottom of the table.

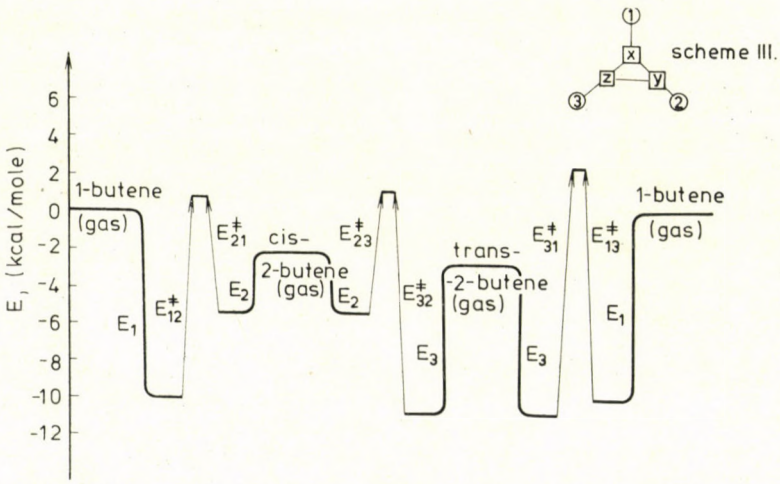


Fig. 2. Energy scheme of *n*-butene isomerization on Ni-clinoptilolite

In the construction of the energy scheme (Fig. 2), that state has been considered as of 0 energy level, in which gaseous phase 1-butene is present. Subtracting from this the heat of adsorption of 1-butene, the energy level of adsorbed 1-butene is obtained; from this, under consideration of the energy barrier of the surface conversion 1 butene $\rightleftarrows$ *cis*-2-butene, the energy level of adsorbed *cis*-2-butene is obtained. Adding to this the heat of adsorption of *cis*-2-butene, the state is reached, in which *cis*-2-butene gas has been formed. Changes in energy accompanying the *cis*-2-butene $\rightarrow$ *trans*-2-butene and, finally, closing

the isomerization cycle, the *trans*-2-butene → 1-butene conversions, are plotted according to the steps of the reaction scheme.

Now, a consistent energy scheme is obtained, insofar that the energy differences between the single gaseous phase isomers differ only by 200—300 cal/mole from the thermodynamical values, the energy level of the system is the same at the beginning and at the end of the isomerization cycle, and the energy barrier of the surface conversions is higher than the energy level of the gaseous phase isomers being in adsorption equilibrium (though this latter is not of necessity a criterion of the rate-determining step).

Thus, on Ni-clinoptilolite isomerization presumably proceeds as follows: at established sorption equilibria, rate-determining surface reactions proceed between the 3 adsorbed isomers, the isomers are different also in the adsorbed state (probably in the form of π-complexes), their surface concentrations differ considerably at identical temperature and pressure, and consequently, the relative rate constants ($k_{ij}/\Sigma k_{ij}$) of the conversions proceeding between them are completely different from those with which the overall conversions can be phenomenologically characterized ($a_{ij}/\Sigma a_{ij}$; $a_{ij} = 1/m_{ij}$).

4. Conclusions

The results of our investigations seem to verify the reason for the existence of the energy scheme, assumed earlier for catalytic conversions [3b]. On the basis of the reaction schemes a new possibility is offered for the elucidation of the reaction mechanism; for the proving of the mechanism by kinetic methods, in addition to isothermal investigations, a new method based on the investigation of temperature dependence has been introduced. On the other hand, the knowledge of the development of energy levels is a new information, relevant to catalytic conversion proper, to the single species of catalytic conversion, as it is based on reaction rate data alone, and not on characteristics, determined independently of the reaction.

While the active sites of H-clinoptilolite and of SO_3H-resin are Brönsted acid centers, and the difference between their strength does not produce qualitative differences in the mechanism, the active sites of Mg-clinoptilolite and Ni-clinoptilolite are qualitatively different, and this changes the route of conversion (as has been seen in the case of the latter the probable route can be given more exactly on the basis of the kinetic measurements). The differences in the catalytic efficiency of the 3 basic types of zeolite catalysts investigated are therefore not simply of quantitative nature, and presumably, in the case of the Mg- and Ni-derivatives, the mechanism is not acid catalysis, as generally thought.

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ADSORPTION OF GAS MIXTURES ON HETEROGENEOUS SOLID SURFACES, II

MULTILAYER ADSORPTION

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The multilayer adsorption of binary gas mixtures on heterogeneous solid surfaces is discussed using the generalized integral equation with a GONZALEZ—HOLLAND isotherm for local adsorption. The overall multilayer adsorption isotherms of binary gas mixtures for Gaussian and exponential energy distributions are considered. These isotherms have been obtained using the monolayer adsorption isotherms discussed in the first part of this series.

In our previous paper [1] the localized monolayer adsorption of gas mixtures on patchwise heterogeneous solid surfaces was discussed. In Ref. [1] the double integral for the adsorption isotherm of binary gas mixtures has been considered in terms of the Jovanic equation [2] and a two-dimensional Gaussian energy distribution. Here, we shall extend this treatment [1, 3—5] to multilayer adsorption of binary gas mixtures on heterogeneous surfaces.

The most important papers concerning the multilayer adsorption of gas mixtures are discussed in Ref. [6]. It follows from this discussion that multilayer adsorption on heterogeneous surfaces was not yet considered.

Multilayer adsorption of gas mixtures on homogeneous surfaces

Recently, GONZALEZ and HOLLAND [7] derived an equation for bilayer adsorption of gas mixtures on homogeneous surfaces:

$$\Theta^{M}_{(1,2,\ldots,n)} = \left(1 + \sum_{i=1}^{n} a_{2i} p_i\right) \cdot \frac{\sum_{i=1}^{n} a_{1i} p_i}{\left(1 + \sum_{i=1}^{n} a_{1i} p_i\right)} \tag{1}$$

where $\Theta^{M}_{1,2,\ldots,n)}$ is the multilayer adsorption isotherm of the n-component mixture on a homogeneous surface; p_i is the partial pressure of the i-th gas; a_{1i} and a_{2i} are the equilibrium constants of the i-th gas for the first and second layers, respectively; n is the number of components in the gas mixture. Constants a_{1i} and a_{2i} ($i = 1, 2, \ldots, n$) can be evaluated from the adsorption isotherms of pure gases.

It follows from Ref. [8] that multilayer adsorption of gas mixtures on homogeneous surfaces may also be described by:

$$\Theta^{M}_{(1,2,\ldots,n)} = \exp\left(\sum_{i=1}^{n} a_{2i} p_i\right)\left[1 - \exp\left(-\sum_{i=1}^{n} a_{1i} p_i\right)\right] \tag{2}$$

Equation (2) results from the Jovanovic adsorption model [1, 2]. For small partial pressures p_i, Eq. (2) reduces to Eq. (1).

In further considerations we shall use the following vectorial notation

$$\begin{aligned} \mathbf{a}_1 &= (a_{11}, a_{12}, \ldots, a_{1n}) \\ \mathbf{a}_2 &= (a_{21}, a_{22}, \ldots, a_{2n}) \\ \mathbf{p} &= (p_1, p_2, \ldots, p_n) \\ \boldsymbol{\varepsilon} &= (\varepsilon_1, \varepsilon_2, \ldots, \varepsilon_n) \\ \mathbf{n} &= (1, 2, \ldots, n) \end{aligned} \tag{3}$$

Then, Eqs (1) and (2) may be rewritten in the following forms:

$$\Theta^{M}_{\mathbf{n}}(\mathbf{p},\boldsymbol{\varepsilon}) = (1 + \mathbf{a}_2\mathbf{p})\frac{\mathbf{a}_1\mathbf{p}}{1 + \mathbf{a}_1\mathbf{p}} \tag{4}$$

$$\Theta^{M}_{\mathbf{n}}(\mathbf{p}\boldsymbol{\varepsilon}) = \exp(\mathbf{a}_2\mathbf{p})\,[1 - \exp(-\mathbf{a}_1\mathbf{p})] \tag{5}$$

In the above equations ε_i is the adsorption energy of the i-th gas; however, constant a_{1i} is defined as:

$$a_{1i} = \frac{1}{K_{1i}} \exp\left(\frac{\varepsilon_i}{RT}\right) \quad \text{for} \quad i = 1, 2, \ldots, n \tag{6}$$

where K_{1i} is the pre-exponential factor of the Henry constant, connected with the molecular partition functions for a molecule of the i-th gas in the bulk and adsorbed phases, respectively [9].

General multilayer adsorption isotherm on heterogeneous surfaces

Multilayer adsorption isotherms (4) and (5) are the products of a monolayer adsorption isotherm $\Theta_{\mathbf{n}}$ and a certain function $g_{\mathbf{n}}(\mathbf{p})$ describing the formation of the mixed multilayer:

$$\Theta^{M}_{\mathbf{n}}(\mathbf{p}, \boldsymbol{\varepsilon})\, g_{\mathbf{n}}(\mathbf{p})\, \Theta_{\mathbf{n}}(\mathbf{p},\boldsymbol{\varepsilon}) \tag{7}$$

Using n-dimensional energy distribution [4], we obtain the following generalized integral equation for the multilayer adsorption isotherm of an n-component gas mixture:

$$\vartheta_{\mathbf{n}}^{M}(\mathbf{p}) = g_{\mathbf{n}}(\mathbf{p}) \int_{\Delta_{\mathbf{n}}} \Theta_{\mathbf{n}}(\mathbf{p}, \boldsymbol{\varepsilon})\, \chi_{\mathbf{n}}(\boldsymbol{\varepsilon})\, d\boldsymbol{\varepsilon} = g_{\mathbf{n}}(\mathbf{p})\, \vartheta_{\mathbf{n}}(\mathbf{p}) \tag{8}$$

where $\Delta_{\mathbf{n}}$ is an n-dimensional integration range and $d\boldsymbol{\varepsilon} = d\varepsilon_1 d\varepsilon_2 \ldots d\varepsilon_n$; $\vartheta_{\mathbf{n}}$ is the overall monolayer adsorption isotherm on a heterogeneous surface.

On applying Eqs (4) and (5) as the local adsorption isotherms in Eq. (8) we obtain:

$$\vartheta_{\mathbf{n}}^{M}(\mathbf{p}) = (1 + \mathbf{a}_2\mathbf{p})\, \vartheta_{\mathbf{n}}(\mathbf{p}) \tag{9}$$

$$\vartheta_{\mathbf{n}}^{M}(\mathbf{p}) = \exp(\mathbf{a}_2\mathbf{p})\, \vartheta_{\mathbf{n}}(\mathbf{p}) \tag{10}$$

From Eqs (9) and (10) the multilayer adsorption isotherms can be obtained if the monolayer adsorption isotherms $\vartheta_{\mathbf{n}}$ are known.

Analytical equations for multilayer adsorption isotherms of binary gas mixtures on heterogeneous surfaces

It follows from Refs. [1, 5] that the analytical solutions of Eq. (8) are possible for a Jovanovic adsorption isotherm [2] and for certain energy distribution functions satisfying the following condition:

$$\chi_{12}(\varepsilon_1, \varepsilon_2) = \chi_1(\varepsilon_1)\, \chi_2(\varepsilon_2) \tag{11}$$

The monolayer adsorption isotherms ϑ_{12}, obtained from the integral equation using the energy distributions satisfying condition (11) and a Jovanovic local isotherm [2], may be presented in the following general form:

$$\vartheta_{12}(p_1, p_2) = \vartheta_1(p_1) + \vartheta_2(p_2) - \vartheta_1(p_1)\, \vartheta_2(p_2) \tag{12}$$

where

$$\vartheta_i(p_i) = 1 - \int_{\Delta_i} \exp\left[-\frac{p_i}{K_{1i}} \exp\left(\frac{\varepsilon_i}{RT}\right)\right] \chi_i(\varepsilon_i)\, d\varepsilon_i \quad \text{for} \quad i = 1, 2 \tag{13}$$

Then, the multilayer adsorption isotherm (10) is given by:

$$\vartheta_{12}^{M} = \exp(a_{21}p_1 + a_{22}p_2)(\vartheta_1 + \vartheta_2 - \vartheta_1\vartheta_2) \tag{14}$$

Equation (12) has also been derived by Roginskii [10] on the basis of the control band approach.

In Ref. [11] MISRA has shown that only two normalized energy distributions exist for which Eq. (13) is exactly solved, *viz.* the exponential and the uniform distribution. For the exponential distribution [1]

$$\chi_{12}(\varepsilon_1, \varepsilon_2) = \frac{c_1 c_2}{(RT)^2} \exp\left[\frac{-c_1(\varepsilon_1 - \varepsilon_{1m}) - c_2(\varepsilon_2 - \varepsilon_{2m})}{RT}\right] \text{ for } \varepsilon_i \geq \varepsilon_{im} \quad (15)$$

Equations (12)—(14) give

$$\vartheta_{12}^M = \exp(a_{21}p_1 + a_{22}p_2) \cdot (K_1^F p_1^{c_1} + K_2^F p_2^{c_2} - K_1^F K_2^F p_1^{c_1} p_2^{c_2}) \quad (16)$$

where K_i^F and c_i $(i = 1, 2)$ are the Freundlich constants for pure gases.

Recently, RUDNITSKY and ALEXEYEV [12] discussed pure-gas adsorption isotherms on heterogeneous surfaces, considering the following exponential distribution:

$$\chi_i(\varepsilon_i) = \frac{c_i^*}{RT} \exp\left[\frac{c_i^*(\varepsilon_i - \varepsilon_{im})}{RT}\right] \quad \text{for} \quad \varepsilon_i \leq \varepsilon_{im} \quad (17)$$

where ε_{im} is the maximum adsorption energy for this distribution. TEMKIN [13] has found that to exponential distribution (17) and a Langmuir adsorption isotherm, there corresponds the negative power isotherm

$$\vartheta_i(p_i) = \alpha_i + \beta_i (p_i)^{-c_i^*} \quad (18)$$

where α_i, β_i and c_i^* are constants.

Now, we consider this problem for a Jovanovic local isotherm [2]. First, pure-gas adsorption isotherm (13) will be found. For $\Delta_i = (-\infty, \varepsilon_{im})$ [integral (13) calculated in the $(-\infty, 0)$ interval can be neglected], Eq. (13) can be rewritten as:

$$\vartheta_i = 1 - \frac{c_i^*}{RT} \int_{-\infty}^{\varepsilon_{im}} \exp\left[-\frac{p_i}{K_{1i}} \exp\left(\frac{\varepsilon_i}{RT}\right)\right] \exp\left[\frac{c_i^*(\varepsilon_i - \varepsilon_{im})}{RT}\right] d\varepsilon_i \quad (19)$$

Introducing the notations

$$q_i = \varepsilon_i - \varepsilon_{im} \quad \text{and} \quad K_{1i}^* = K_{1i} \exp\left(\frac{-\varepsilon_{im}}{RT}\right) \quad (20)$$

from Eq. (19) we have

$$\vartheta_i = 1 - \frac{c_i^*}{RT} \int_{-\infty}^{0} \exp\left[-\frac{p_i}{K_{1i}^*} \exp\left(\frac{q_i}{RT}\right)\right] \exp\left(\frac{c_i^* q_i}{RT}\right) dq_i \quad (21)$$

Integral (21) is equal to [14]:

$$\vartheta_i(p_i) = 1 - c_i^* \left(\frac{p_i}{K_{1i}^*}\right)^{-c_i^*} \Gamma\left(c_i^*; \frac{p_i}{K_{1i}^*}\right) \tag{22}$$

where

$$\Gamma(\nu; y) = \sum_{j=0}^{\infty} \frac{(-1)^j \cdot y^{\nu+j}}{j!\,(\nu + j)} \tag{23}$$

Upon inserting Eqs (22) and (23) into Eq. (14), we obtain:

$$\vartheta_{12}^M = \exp(a_{21}p_1 + a_{22}p_2)\,[A_1(c_1^*; p_1) + A_2(c_2^*; p_2) - A_1(c_1^*; p_1)A_2(c_2^*; p_2)] \tag{24}$$

where

$$A_i(c_i^*; p_i) = c_i^* \sum_{j=1}^{\infty} \frac{(-1)^{j+1} \left(\frac{p_i}{K_{1i}^*}\right)^j}{j!\,(c_i^* + j)} \tag{25}$$

Combination of distribution (15) with the two-dimensional distribution χ_{12} obtained from Eq. (17) leads to

$$\chi_{12}(\varepsilon_1, \varepsilon_2) = \begin{cases} \dfrac{c_1^* c_2^* s^*}{(RT)^2} \exp\left[\dfrac{c_1^*(\varepsilon_1 - \varepsilon_{1m}) + c_2^*(\varepsilon_2 - \varepsilon_{2m})}{RT}\right] & \varepsilon_i \leqq \varepsilon_{im} \\ \dfrac{c_1 c_2 s}{(RT)^2} \exp\left[\dfrac{-c_1(\varepsilon_1 - \varepsilon_{1m}) - c_2(\varepsilon_2 - \varepsilon_{2m})}{RT}\right] & \varepsilon_i > \varepsilon_{im} \end{cases} \tag{26}$$

which, for $c_i = c_i^*$, gives a symmetric distribution with a maximum:

$$\chi_{12}(\varepsilon_1, \varepsilon_2) = \frac{c_1 c_2}{2(RT)^2} \exp\left[\frac{-c_1|\varepsilon_1 - \varepsilon_{1m}| - c_2|\varepsilon_2 - \varepsilon_{2m}|}{RT}\right] \tag{27}$$

In Eq. (26) the constants s^* and s are defined by the following equations:

$$s^* = c_1 c_2/(c_1^* c_2^* + c_1 c_2) \quad \text{and} \quad s = c_1^* c_2^*/(c_1^* c_2^* + c_1 c_2) \tag{28}$$

which satisfy the conditions:

$$s^* + s = 1 \quad \text{and} \quad 0 < s^*, s < 1 \tag{29}$$

Equations (28) and (29) define the constants s^* and s normalizing function (26) to unity.

The one-dimensional energy distribution

$$\chi_i(\varepsilon_i) = \begin{cases} [s_i^* c_i^*/(RT)] \exp[c_i^*(\varepsilon_i - \varepsilon_{im})/(RT)] & \varepsilon_i \leq \varepsilon_{im} \\ [s_i c_i/(RT)] \exp[-c_i(\varepsilon_i - \varepsilon_{im})/(RT)] & \varepsilon_i > \varepsilon_{im} \end{cases} \tag{30}$$

generating distribution (26), is the simple sum of the two exponential functions: the first of them increases from zero to $s_i^* c_i^*/(RT)$, however, the second function decreases from $s_i c_i/(RT)$ to zero. In Eq. (30) the constants s_i^* and s_i are defined similarly by the constants s^* and s:

$$s_i^* = c_i/(c_i^* + c_i) \quad \text{and} \quad s_i = c_i^*/(c_i^* + c_i) \tag{31}$$

Thus, pure-gas adsorption isotherm (13) is given by:

$$\vartheta_i = s_i^* A_i(c_i^*; p_i) + s_i K_i^F (p_i)^{c_i} \tag{32}$$

In Eq. (32) the expression $(s_i^* A_i)$ corresponds to the increasing function (30), however, $[s_i K_i^F (p_i)^{c_i}]$ corresponds to the decreasing function (30). The multilayer adsorption isotherm of binary gas mixtures may be derived by means of Eq. (10) and distribution function (26):

$$\begin{aligned} \vartheta_{12}^M = \exp(a_{21}p_1 + a_{22}p_2) \{ & s^*(A_1 + A_2 - A_1 A_2) + \\ & + s[K_1^F (p_1)^{c_1} + K_2^F (p_2)^{c_2} - K_1^F K_2^F (p_1)^{c_1} (p_2)^{c_2}] \} \end{aligned} \tag{33}$$

Replacing in Eq. (33) parameter c_i^* by c_i, we obtain the multilayer adsorption isotherm corresponding to symmetric distribution (27). For this distribution the parameters s^* and s are equal to 1/2.

Nonanalytical multilayer adsorption isotherms of binary gas mixtures on heterogeneous surfaces

The adsorption isotherms numerically investigated by us [1] were based on the Jovanovic equation and a Gaussian energy distribution. According to Ref. [1] and Eq. (10), the multilayer adsorption isotherm ϑ_{12}^M corresponding to a Gaussian distribution may be represented by:

$$\begin{aligned} \vartheta_{12}^M = \exp(a_{21}p_1 + a_{22}p_2) \{ & 1 - (2\pi\gamma_1\gamma_2 \sqrt{1 - \varrho^2})^{-1} \cdot \\ & \iint_{A12} \exp(-a_{11}p_2 - a_{12}p_2) \exp\left[\frac{(\varepsilon_1^*)^2 - 2\varrho\varepsilon_1^*\varepsilon_2^* + (\varepsilon_2^*)^2}{-2(1 - \varrho^2)} \right] d\varepsilon_1 d\varepsilon_2 \} \end{aligned} \tag{34}$$

where

$$\varepsilon_i^* = (\varepsilon_i - \bar{\varepsilon}_i)/\gamma_i; \quad i = 1, 2 \tag{35}$$

In the above $\bar{\varepsilon}_1$ and $\bar{\varepsilon}_2$ are the mean values of ε_1 and ε_2, respectively; γ_1 and γ_2 are the variances of the Gaussian distribution; ϱ is the correlation coefficient. Equation (35) for $\varrho = 0$ assumes a considerably simpler form:

$$\vartheta_{12}^M = \exp(a_{21}p_1 + a_{22}p_2)\left\{1 - (2\pi\gamma_1\gamma_2)^{-1} \cdot \iint_{\Delta 12} \exp(-a_{11}p_1 - a_{12}p_2) \exp\left[\frac{(\varepsilon_1^*)^2 + (\varepsilon_2^*)^2}{-2}\right] d\varepsilon_1 d\varepsilon_2\right\} \tag{36}$$

All parameters of Eqs (34) and (36), excluding parameter ϱ, can be evaluated from the pure-gas adsorption isotherms.

Results and discussion

For illustrative purposes the adsorption of a propane–propylene mixture on Nuxit-AL at 293 K is discussed. This adsorption system was investigated experimentally by SZEPESY and ILLÉS [15, 16]. However, in the first part of this paper [1] the theoretical monolayer adsorption isotherm has been compared with the experimental one. The theoretical adsorption isotherm was calculated using the double integral with the Jovanovic mixed-gas adsorption isotherm (local isotherm) and a two-dimensional Gaussian distribution (see Eq. (19) in Ref. [1]). The best agreement between the theoretical and the experimental adsorption isotherms has been observed for correlation coefficient ϱ equal to zero.

Now, we have calculated the multilayer adsorption isotherms according to Eq. (36) using the parameters K_{1i}, $\bar{\varepsilon}_i$ and γ_i reported in Table III of Ref. [1]. Similarly to GONZALEZ and HOLLAND [7], we assume the following relation between parameters a_{1i} and a_{2i}:

$$a_{2i}/a_{1i} = \eta \quad \text{for } i = 1, 2, \ldots \tag{37}$$

In the numerical calculations of the multilayer adsorption isotherm (36), η was treated as a best-fit parameter. Figure 1 shows the theoretical adsorption isotherms (36) calculated for different values of η: 0.001, 0.004, 0.014 (long dashes) and 0.01 (solid line). These isotherms have been compared with the experimental data (circles), and with the monolayer isotherm (short dashes) discussed in Ref. [1]. It follows from the comparison that Eq. (36) gives a good agreement with the experimental data for $\eta = 0.01$. Evidently the

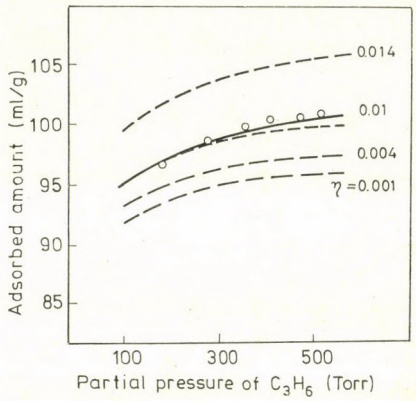


Fig. 1. Adsorption of a propane–propylene mixture on Nuxit-AL at 293 K. Solid line and long dashes denote theoretical multilayer adsorption isotherms (36) calculated for different values of η, short dashes represent the theoretical monolayer isotherm, and circles refer to the experimental points

multilayer adsorption isotherm (36) calculated for $\eta = 0.01$ (solid line in Fig. 1) gives a better agreement with the experimental results than the monolayer isotherm (shorthy dashed line in Fig. 1).

Figures 2 and 3 show model calculations for the adsorption of a propane–propylene mixture on Nuxit-AL at 293 K. In Fig. 2 the functions g_{12},

$$g_{12}(p_1,p_2) = \exp\,(a_{21}p_1 + a_{22}p_2) \tag{38}$$

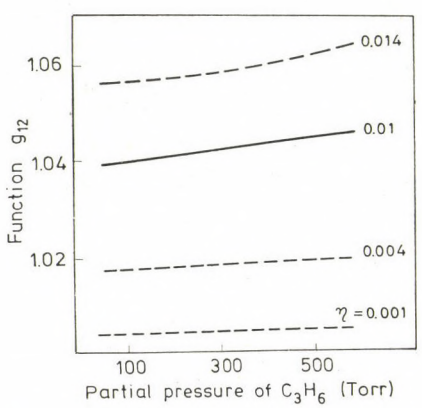


Fig. 2. Functions g_{12} calculated for the adsorption of a propane–propylene mixture on Nuxit-AL at 293 K according to Eq. (38) for different values of η. Solid line denotes the best-fit function g_{12}

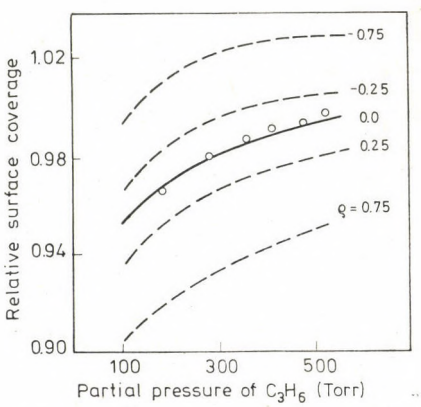


Fig. 3. Theoretical multilayer adsorption isotherms (34) calculated for different values of ϱ (solid and dashed lines) in comparison with the experimental points (circles). In numerical calculations the parameter $\eta = 0.01$ was used. Solid line denotes the best-fit adsorption isotherm

characterizing the formation of the second layer are presented. These functions have been calculated for different values of η: 0.01 (solid line), 0.001, 0.004 and 0.014 (dashed lines). In Fig. 3 the theoretical adsorption isotherms (34) calculated for different values of ϱ are compared with the experimental data (circles).

It follows from the model calculations that it is primarily the parameters ϱ and η that influence the adsorption isotherm of binary gas mixtures. Parameter ϱ takes into account the influence of the first component on the adsorption of the second component. On the other hand parameter η characterizes the formation of the mixed multilayer.

The last point is connected with the formation of multilayer in the case of hydrocarbon adsorption on Nuxit-AL. It can be concluded that, in the case of the experimental data studied, multilayer effects play a considerably smaller part in comparison with monolayer adsorption.

In this paper we did not discuss Eqs (16), (24) and (33); these may be useful for the description of the adsorption of binary gas mixtures, when:

1. both components of the gas mixture show a very similar behaviour on the adsorbent surface, *i.e.* the molecular sizes and the adsorption energies are approximately equal;

2. the adsorption of both components is characterized by exponential energy distributions.

Unfortunately, the lack of suitable experimental data for mixed-gas adsorption makes the testing of Eqs (16), (24) and (33) impossible.

*

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SOME QUESTIONS OF THE ADSORPTION OF THIOUREA ON A NOBLE METAL ELECTRODE

GY. HORÁNYI and E. M. RIZMAYER

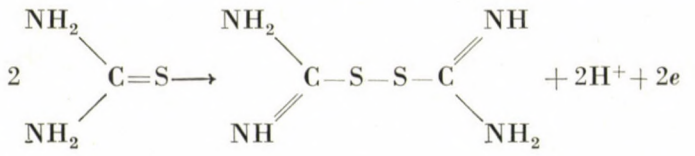
(Central Research Institute for Chemistry, Hungarian Academy of Sciences, Budapest)

Received August 25, 1976

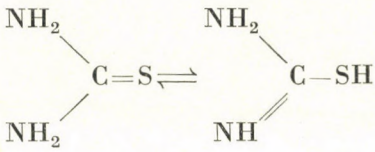
The adsorption of thiourea was investigated with a tracer technique. It was found that on a gold electrode the study of the adsorption may be disturbed by both the oxidation of thiourea and the dissolution of gold. At low potentials, where these interfering effects can be decreased to a minimum, the adsorption proves to be reversible.

The adsorption of thiourea on a gold electrode was studied by WROBLOWA and GREEN with a tracer technique at the beginning of the 1960's [1]. The experimental data obtained in terms of the concentration and potential dependences of the adsorption were interpreted by the assumption of molecular adsorption, and the adsorption of thiourea was regarded as a model well reflecting the adsorption properties of organic compounds. More recently, KAZARINOV and ANDREEV have come to a different conclusion, on the basis of their investigations of the adsorption of thiourea labelled with ^{35}S and ^{14}C on platinum and gold electrodes in a broad potential interval [2—4]. As a result of the high degree of irreversibility of the adsorption, and of the differences in the results obtained with thiourea labelled with ^{35}S and with ^{14}C, they concluded that strong chemisorption is involved, and that, depending on the potential, this may also be followed by cleavage of the molecule. Other authors have also supported the occurrence of chemisorption [5]. In the light of the new experimental results, it appears to be fairly well proved that the simple molecular adsorption model cannot be suitable for the description of the adsorption properties of thiourea; certain doubts also arise with regard to the correctness of the conclusions drawn from the measurements in the broad potential interval.

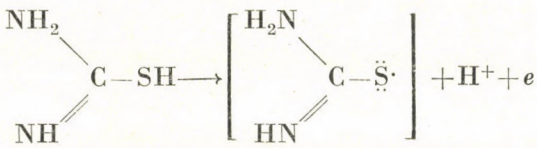
Firstly, it must be borne in mind that on noble metal electrodes thiourea is comparatively readily oxidized. The literature [6, 7] reveals that formamidine disulfide is formed in accordance with the following overall equation:



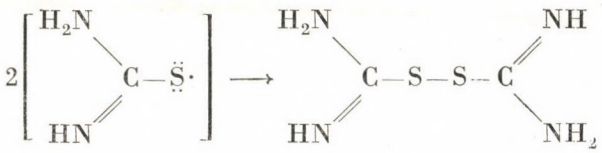
The oxidation reaction presumably takes place *via* the following steps:



(1)



(2)



(3)

Step 2 is probably rate-determining. It has emerged from a study of the thiourea — formamidine disulfide system [8] that in solutions of various concentrations the redox potentials on a platinum electrode, which are well reproducible and rapidly established, can be given by the relation

$$E = E^0 + \frac{RT}{2F} \, In \frac{[\mathrm{RSSR}]}{[\mathrm{RSH}]^2}$$

where [RSSR] is the concentration of formamidine disulfide, and [RSH] is that of thiourea, that is an ordinary redox system is involved. The value of E^0 is at around 420 mV. The results of measurements relating to the oxidation of thiourea were in agreement with this. The question next arises as to whether the results obtained at potentials where thiourea also undergoes oxidation reflect the adsorption of thiourea. The answer is presumably negative, for two reasons. (i) As a consequence of the oxidation, formamidine disulfide too is present, and it is not possible to decide whether the adsorbed molecule is thiourea or its oxidation product. (ii) The intermediate of the oxidation reaction may also be adsorbed. As the above scheme shows, this is a radical, and can presumably interact strongly with the metal surface. The adsorbed radical may undergo further decomposition and transformation, thereby complicating the picture even more.

In the present paper a study is made with regard to the potential interval in which one may speak of the adsorption of thiourea, and whether it is really necessary to reckon with the irreversibility of the adsorption at all potentials.

Experimental

Adsorption was studied with the aid of the tracer technique reported in detail previously [9].

The reactivity of thiourea was examined by carrying out polarization measurements with a potentiostatic method on bright platinum and gold electrodes in a 1 *M* $HClO_4$ background solution. The customary three-electrode system was used for this purpose. The auxiliary electrode was platinized platinum. A hydrogen electrode immersed in the background solution was used as reference electrode. In the following, all potentials are given against this electrode.

Results

In accordance with the results in the literature already referred to, on both bright gold and bright platinum electrodes the oxidation of thiourea occurs at potentials more positive than 500 mV. One section of the polarization curve for a platinum electrode and a given thiourea concentration is to be seen in Fig. 1. If the electrode is maintained for a definite time (20—30 min)

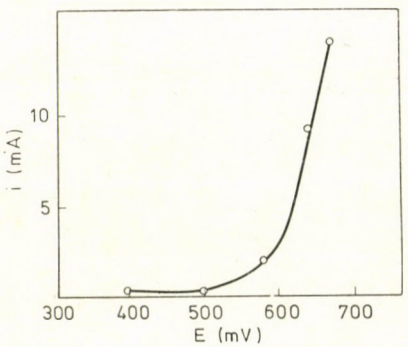


Fig. 1. Polarization curve of thiourea in 1 *M* $HClO_4$ background solution; $c = 2 \times 10^{-2}$ mol dm^{-3}

at a potential of 600 mV and the polarization curve is again recorded, the appearance of a cathodic branch can be observed; this is illustrated in Fig. 2.

In agreement with what was said in the introduction, the appearance of the cathodic branch can be attributed to reduction of the formamidine disulfide formed upon oxidation. The magnitude of the current to be observed at a given potential in the cathodic branch depends on the magnitude of the charge introduced during the anodic polarization, *i.e.* on the concentration of formamidine disulfide formed. If the polarizing circuit is interrupted, then, depending on the thiourea and formamidine disulfide concentrations, the rest potential is established, which is presumably an equilibrium potential. However, this latter is not certain, for the thiourea — formamidine disulfide transition is accompanied by other reactions. This is indicated by the fact that at a given polarization potential the magnitude of the current varies

in time, and an ageing process occurs; this is presumably connected with the adsorption of a strongly chemisorbing product formed in some side reaction.

In the case of a gold electrode, the suspicion also arose that, besides the oxidation of the thiourea, dissolution of the electrode must be considered too. The corrosion of the electrode was concluded from the decrease in weight

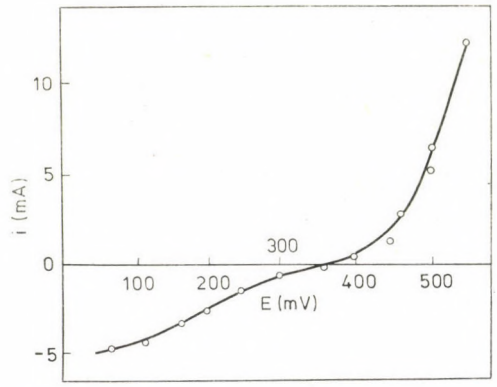


Fig. 2. Polarization curve of thiourea after the potential of the electrode has been kept at 600 mV for 25 min

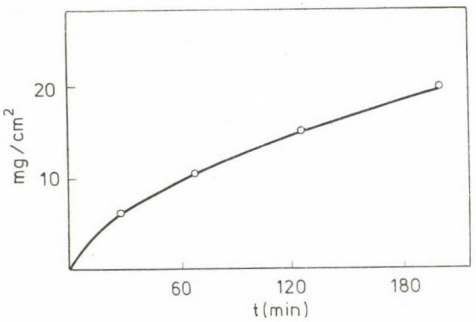


Fig. 3. Increase in weight loss of gold electrode as a function of time at 600 mV

occurring after polarization for a definite time. Figure 3 shows the decrease in weight of a 1 cm^2 gold electrode at 600 mV as a function of time. Curves of similar type were also obtained at 500 mV. The experimental results clearly demonstrate, therefore, that at potentials more positive than 500 mV the gold electrode dissolves at an appreciable rate in the presence of thiourea, and thus neither the oxidation nor the adsorption of thiourea can be studied satisfactorily at these potentials. In the event of a platinum electrode under similar experimental conditions, no such decrease in weight of the electrode could be observed.

The tracer technique was used to study the adsorption of thiourea on a gold electrode, care being taken that the potential be as far as possible from those values at which polarization measurements indicate that oxidation processes and dissolution of the electrode must also be reckoned with.

Accordingly, for the sake of safety, the electrode was not polarized at a potential more positive than +100 mV. Figure 4 shows the change in the ad-

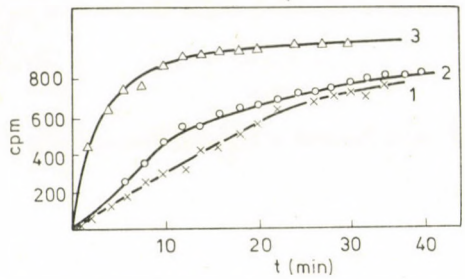


Fig. 4. Change in adsorption of thiourea on a gold electrode as a function of time. (1) 10^{-6} mol dm^{-3}; (2) 3×10^{-6} mol dm^{-3}; (3) 10^{-5} mol dm^{-3} (200 cpm $\sim$ 10^{-10} mol cm^{-2})

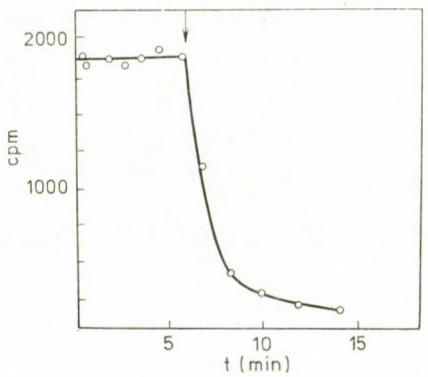


Fig. 5. Exchange of labelled adsorbed thiourea with unlabelled thiourea at 0 mV. (The latter was added to the system at the time indicated by the arrow.)

sorption as a function of time, at various thiourea concentrations. At a given concentration, the extent of adsorption does not depend on the potential in the interval 150—100 mV. It was surprising, however, that labelled thiourea adsorbed at 0 mV and at potentials more negative than this undergoes exchange if inactive thiourea is added to the solution. This is shown in Fig. 5.

On the basis of this experiment, therefore, the conclusion must be drawn that at these potentials the adsorption of thiourea cannot be regarded as irreversible.

To summarize our observations, it may be said that the adsorption of thiourea can be studied in only a narrow potential interval, partly because of

oxidation, and partly (in the case of a gold electrode) because of dissolution of the electrode. Since the molecules adsorbed on a gold electrode at potentials around 0 mV were found to be mobile, it may be presumed that the irreversibility frequently observed in the adsorption is connected with the adsorption of substances formed in reactions occurring at higher potentials.

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SPECTRAL AND MAGNETIC STUDIES OF THE COMPLEXES OF INDAZOLE AND 5-NITROINDAZOLE WITH COBALT(II) AND NICKEL(II)

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Several new complexes of the general formula ML_2X_2 and ML_4X_2 [M = Co(II) or Ni(II); L = indazole or 5-nitroindazole, X = Cl^-, Br^-, NO_3^-, $1/2\ SO_4^{2-}$, SCN^-] have been prepared. All these complexes have been characterized by elemental analysis, infrared spectra, magnetic moment and electronic spectral measurements. Two different types of complexes have been observed. The indazole complexes are monomeric and the ligand is bidentate, coordinated through both the pyridine and the pyrrole nitrogen; the 5-nitroindazole complexes are polymeric with the ligand mono-coordinated through the pyrrole nitrogen. On the basis of magnetic moments, electronic and infrared spectral measurements, an octahedral geometry is proposed for all compounds.

Introduction

Except for reports on the complexes of cobalt [1] and copper [2], there has been no interest in the coordination chemistry of indazole. Recently we reported on a few complexes of indazoles [3—5], from which it became evident that the indazoles have an extensive coordination chemistry. In the case of 5-aminoindazole, most of the complexes were found to be polymeric with anion bridging and unidentate ligand coordination occurring through the pyridine rather than the pyrrole nitrogen. It was, therefore, assumed that if the basicity of the pyridine nitrogen could be reduced by introducing an electron-withdrawing group into the benzene ring, *viz.* NO_2, in place of the NH_2 group of 5-aminoindazole or by using the unsubstituted indazole itself, one might observe preferential coordination through the pyrrole nitrogen and it might be possible to prepare different types of new complexes. With this end in view, complexes of 5-nitroindazole and indazole with Co(II) and Ni(II) were prepared and studied, the results being reported here.

Experimental

Indazole and 5-nitroindazole (Koch-Light, m. p. 146 °C and 205 °C, respectively) were recrystallized from methanol. All the metal salts (BDH, AR quality), dimethyl-sulfoxide (BDH reagent grade) and nitromethane (Eastman Kodak reagent grade) were used as such.

Preparation of the complexes

An alcoholic or aqueous solution of the metal hexahydrate and ligand were mixed in the required ratio. In all cases a solid appeared after mixing or on stirring and slight heating. The complexes were isolated after washing and drying in vacuum at room temperature. The indazole complexes are soluble, and were recrystallized from ethanol while the 5-nitroindazole complexes are insoluble in the usual organic solvents and could not be recrystallized. All the complexes are quite stable at room temperature.

Analysis and physical measurements

Molar conductances were determined on a Systronix 321 bridge and magnetic susceptibilities were measured on a Gouy balance. The IR spectra were recorded on a Perkin—Elmer 521 spectrophotometer in KBr discs (4000—650 cm^{-1}) or in nujol mull (650—250 cm^{-1}). Diffuse reflectance spectra were recorded on a Carl Zeiss VSU—2P spectrophotometer with MgO as a reflectance standard. The visible absorption spectra were recorded in methanol on a DK 2A spectrophotometer. The elemental analyses were performed by microanalytical techniques. Halogens and sulfur were determined gravimetrically and the metals were estimated by complexometric titrations [6].

Results and discussion

The analytical results of all complexes (Table I) are in good agreement with the suggested stoichiometries. The molar conductances in nitromethane are indicative of the nonionic nature of these complexes. Though the molar conductance in DMSO of some of the complexes is in the range characteristic of 1 : 1 electrolytes, this fact is attributed [5] to partial substitution of the anions by the solvent molecule. The insolubility of the 5-nitroindazole complexes in the usual organic solvents and their high melting point or decomposition temperatures suggest that they are polymeric. The indazole complexes are, however, soluble in the usual organic solvents and are monomeric in nature.

Nature of bonding from IR spectra

(i) Indazole complexes

As indazole is associated in the solid phase, the spectrum of indazole in CCl_4 is to be compared with those of its complexes (Table II). These spectra are very similar except for a marked decrease in the NH stretching frequency, suggesting coordination through the pyrrole nitrogen atom. The C=N stretching frequency at 1507 cm^{-1} in indazole remains practically unchanged after complexation. However, as the complexes are monomeric and the anions unidentate, in order to account for the octahedral geometry substantiated by electronic spectral and magnetic studies, bidentate coordination of the ligand also involving the pyridine nitrogen is proposed in these complexes, excepting the case of $Ni(Inz)_4Cl_2$, where the ligand is unidentate, being coordinated through the pyrrole nitrogen.

Table I

Analytical data and physical properties of indazole and 5-nitroindazole complexes

Complex	Colour	M.p.(°C)	%M Calcd. (Obsd.)	%N Calcd. (Obsd.)	%C Calcd. (Obsd.)	%H Calcd. (Obsd.)	% Anion Calcd. (Obsd.)
1. $Co(Inz)_2Cl_2$	Pink	288	16.10 (16.16)	15.30 (15.29)	45.88 (45.87)	2.73 (2.73)	19.39 (19.36)
2. $Co(Inz)_2Br_2$	Pink	217	12.95 (12.96)	12.33 (12.34)	36.92 (36.89)	2.64 (2.63)	35.16 (35.14)
3. $Co(Inz)_2(SCN)_2$	Brownish pink	226	14.36 (14.38)	20.48 (20.47)	46.71 (46.71)	2.93 (2.92)	15.60 (15.68)
4. $Ni(Inz)_2Cl_2$	Light green	290°(d)	16.04 (16.06)	15.31 (15.28)	45.90 (45.00)	2.70 (2.70)	19.40 (19.36)
5. $Ni(Inz)_4Cl_2$	Blue	320°(d)	9.75 10.80	18.61 18.90	55.81 56.11	4.00 4.20	11.80 11.38
6. $Co(5\text{-}NInz)_2Cl_2$	Brownish yellow	310°(d)	12.15 12.14	18.66 18.65	37.15 37.15	2.21 2.22	15.70 15.69
7. $Co(5\text{-}NInz)_2Br_2$	Pink	310°(d)	10.80 (10.77)	15.40 (14.40)	30.81 (30.78)	1.83 (1.90)	29.34 (29.31)
8. $Ni(5\text{-}NInz)_2Cl_2$	Light yellow	300°(d)	12.87 (12.89)	18.42 (18.45)	36.84 (36.85)	2.19 (2.20)	15.57 (15.49)
9. $Ni(5\text{-}NInz)_2Br_2$	Light yellow	300°(d)	10.77 (10.78)	15.41 (15.42)	30.82 (30.82)	1.48 (1.80)	29.36 (29.29)
10. $Ni(5\text{-}NInz)_2(NO_3)_2$	Green	300°(d)	11.53 (11.47)	20.01 (22.12)	33.01 (33.32)	1.96 (1.99)	— —
11. $Ni(5\text{-}NInz)_2SO_4$	Greenish yellow	300°(d)	12.20 (12.23)	17.47 (17.42)	34.93 (34.98)	2.08 (2.10)	6.65 (6.64)
12. $Ni(5\text{-}NInz)_2(SCN)_2$	Light yellow	240°(d)	11.71 (11.90)	22.36 (22.36)	38.32 (38.31)	2.00 (2.01)	12.79 (12.69)

d=decomposition

Table II

Infrared spectra (cm^{-1}) of indazole and 5-nitroindazole complexes

Complex	N–H	C=N	M–N
Inz	3450 (s)	1507 (s)	
$Co(Inz)_2Cl_2$	3413 (s)	1503 (s)	
$Co(Inz)_2Br_2$	3390 (s)	1502 (s)	544 (s), 544 (m)
$Co(Inz)_2(SCN)_2$	3415 (s)	1495 (s)	507 (s), 488 (s)
$Ni(Inz)_2Cl_2$	3264 (s)	1500 (s)	522 (s)
$Ni(Inz)_4Cl_2$	3220 (s)	1560 (m)	520 (s), 540 (s)
5-NInz	3450 (m)	1499 (s)	
$Co(5\text{-}NInz)_2Cl_2$	3368 (s)	1498 (s)	480 (s)
$Co(5\text{-}NInz)_2Br_2$	3366 (s)	1493 (s)	488 (s)
$Ni(5\text{-}NInz)_2Cl_2$	3390 (s)	1500 (s)	483 (s)
$Ni(5\text{-}NInz)_2Br_2$	3368 (s)	1494 (s)	484 (s)
$Ni(5\text{-}NInz)_2(NO_3)_2$	3360 (s, b)	1494 (s)	
$Ni(5\text{-}NInz)_2SO_4$	3280 (s, b)	1500 (m)	
$Ni(5\text{-}NInz)_2(SCN)_2$	3350 (m)	1493 (s)	
	3334 (m, b)		

s = strong; m = medium; b = broad

In $Co(Inz)_2(SCN)_2$ the IR bands of NCS^- occur at 2100 cm^{-1} (C=N); 962 cm^{-1} (C—S stretch), showing that the thiocyanate groups are bonded through nitrogen to the metal ion [8, 10]. The presence of only one band in the 2100—2180 cm^{-1} region suggests unidentate terminal NCS^- coordination.

(ii) 5-Nitroindazole complexes

As 5-nitroindazole is also associated in the solid phase, its spectrum in CCl_4 is compared with that of its complexes (Table II). In this case too, there is not much change except for a marked decrease in the N–H stretching frequency. As there is no evidence of the lowering of the N–H frequency due to intramolecular hydrogen bonding as was noted in the case of the copper complex of indazole [5], the 5-aminoindazole complexes of Co(II) and Ni(II) [4], it is clear that coordination must be through the pyrrole nitrogen.

The nitrate ion in $Ni(5\text{-}NInz)_2(NO_3)_2$ exhibits very strong bands at 1530 cm^{-1} (NO_2 asymmetric stretch) and 1290 cm^{-1} (NO_2 symmetric stretch) and strong bands at 1050 cm^{-1} (NO stretch) and 818 cm^{-1} (out-of-plane deformation), suggesting coordination to the metal ion [9]. It must be mentioned here that some of these bands might overlap with those of the nitro group in the ligand. From the stoichiometry, the polymeric nature of the complex,

Table III

Molar conductances, magnetic moments and electronic spectra of indazole and 5-nitroindazole complexes

Complex	Molar conductance of a 0.001 *M* solution (Ohm^{-1} cm^2 mol^{-1}) DMSO	Nitromethane	Magnetic moment μ_{eff} (BM)	Electronic spectral bands (cm^{-1})
$Co(Inz)_2Cl_2$	30.2	26.2	5.21	22,220; 19,230; 8000
$Co(Inz)_2Br_2$	68.4	25.7		20,620; 19,050; 8000
$Co(Inz)_2(SCN)_2$	54.7	38.0		20,620; 19,230; 7874
$Ni(Inz)_2Cl_2$	37.6	—		25,000; 13,510; 8696
$Ni(Inz)_4Cl_2$	79.8	—	3.20	25,640; 13,510
$Co(5\text{-}NInz)_2Cl_2$	27.4	—	5.06	19,610; 16,390
$Co(5\text{-}NInz)_2Br_2$	36.4	—	5.19	18,870; 15,620
$Ni(5\text{-}NInz)_2Cl_2$	32.5	—	3.18	24,690; 14,490
$Ni(5\text{-}NInz)_2Br_2$	35.0	—	3.19	24,390; 13,890
$Ni(5\text{-}NInz)_2(NO_3)_2$	43.3	—	3.25	25,000; 14,390
$Ni(5\text{-}NInz)_2(SO_4)$	10.6	—	2.85	24,690; 13,700; 10,640
$Ni(5\text{-}NInz)_2(SCN)_2$	45.6	—	2.99	23,960; 14,710; 10,640

— = insoluble

and the fact that nickel ion is in an octahedral environment, it is clear that nitrate ion must be coordinated as a bidentate ligand, or what seems to be more probable, as a bridging bidentate ligand.

The thiocyanate ion in dithiocyanatobis(5-nitroindazole)nickel(II) shows two very strong C=N absorption bands at 2095 and 2030 cm^{-1} (ν_3), characteristic of NCS^- bridges [7, 10]. Sulfate bands at 1170, 1090, 1052 cm^{-1} (ν_3) and 990 cm^{-1} (ν_1) have been observed in the spectrum of sulfatobis(5-nitroindazole)nickel(II) [11]. This is due to the splitting of ν_3 into three bands because of the lowering of the symmetry of the sulfate group T_d to C_2v. It is therefore suggested that sulfate is also a bidentate ligand, as has been shown by BARRACLOUGH and TOBE [12].

Structure from reflectance spectra and magnetic measurements

In all the nickel complexes (Table III) the observed bands are assigned to the following transitions expected for an octahedral geometry: 8696—10,640 cm^{-1} ($^3T_{2g}(F) \leftarrow {}^3A_{2g}(F)$); 13,510—14,710 cm^{-1} ($^3T_{1g}(F) \leftarrow {}^3A_{2g}(F)$ and 23,960—25,640 cm^{-1} ($^3T_{1g}(P) \leftarrow {}^3A_{2g}(F)$). The μ_{eff} values between 3.25—2.85 BM is also consistent with an octahedral geometry. In $Ni(Inz)_4Cl_2$ there are

two additional bands at 15,870 and 20,830 cm,$^{-1}$, which may be due to spin-forbidden transitions. This complex is stable only up to 100°C but if it is kept at a temperature of 140°C, in about four hours, the blue form is converted to a light green modification of the composition $Ni(Inz)_2Cl_2$, which is similar to the 1 : 2 nickel complex described earlier.

In the case of cobalt complexes, the observed electronic spectra suggest an octahedral geometry. The absorption bands have been assigned to the following transitions in O_h symmetry; 22,220—15,620 cm^{-1} ($^4T_{2g}(P) \leftarrow {}^4T_{1g}(F)$); 19,610—18,770 cm^{-1} ($^4A_{2g}(F) \leftarrow {}^4T_{1g}(F)$) and 8000—7874 cm^{-1}($^4T_{2g}(F) \leftarrow \leftarrow {}^4T_{1g}(F)$). The absorption due to ($^4T_{2g}(F) \leftarrow {}^4T_{1g}(F)$) transitions could, however, not be observed in the reflectance spectrum of the insoluble 5-nitroindazolecobalt(II) complexes as it falls out of the range of the instrument. The μ_{eff} values between 5.21—5.06 BM are also in agreement with an octahedral geometry.

Far-infrared spectra

The new bands appearing in the region of 450—544 cm^{-1} have been tentatively assigned to M–N absorptions as was also done in the case of copper(II) complexes of indazoles [5].

*

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THE REACTIVITY OF THE CARBONYL GROUP IN FLAVONOID COMPOUNDS, III

BASICITY OF 2'-HYDROXY- AND 2'-BENZYLOXYCHALCONES

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Changes in the UV spectra of 2'-hydroxy- and 2'-benzyloxychalcones depending on substitution, as well as the calculation of basicity constants by the use of the H_0 acidity function are described. The values of basicity constants are given in Tables III and IV.

Chalcones, having a 1,3-diphenylpropane skeleton, belong to the family of flavonoid compounds. However, the chemical and physical properties of chalcones are different from those of the flavone and flavanone derivatives examined by us earlier, owing to the absence of the heterocyclic ring [1, 2, 3].

The basicity of some substituted *trans* chalcones [4] and chalcone analogues [5, 6] have been determined earlier, while the non-substituted chalcone (benzalacetophenone) was initially used as a Hammett indicator in the determination of the acidity function H_0 [7, 8, 9]. In spite of this, widely different values have been reported in the literature regarding the basicity of non-substituted chalcone (—5.73 [9]; —5.68 [10]; —5.17 [11]; —5.00 [4]; —4.86 [6]). This has been explained by the fact that chalcones do not behave as ideal Hammett bases.

Therefore, in the present work the applicability of the acidity function H_0 was examined for the determination of the basicity of the carbonyl groups of 2'-hydroxychalcones and 2'-benzyloxychalcones as a function of the substitution. Since the protonated ionic form exhibited light absorption properties significantly different from those of the neutral molecular form, the spectrophotometric technique proved suitable for the determination of the relative basicities of these compounds.

Experimental

The compounds examined were prepared according to literature procedures [12]. The UV spectra were recorded with a UNICAM SP 800 spectrophotometer in $5 \cdot 10^{-5}$ molar solutions. Tables I and II show spectral data of the molecular and ionic forms in ethanolic solutions, while in Tables III and IV the same data are given for aqueous sulfuric acid solutions, together with the negative logarithm values of the calculated basicity constants (pK_{BH^+}).

The aqueous sulfuric acid solutions used in the determination of the basicity constants were prepared as described earlier [1] and the acidity function H_0 was checked by the use

of indicator bases [7, 8, 9]. In the knowledge of H_0, the following correlation was applied for calculating the basicity of chalcones depending on substitution [4—9, 13]:

$$pK_{BH^+} = H_0 + log \frac{C_{BH^+}}{C_B}$$

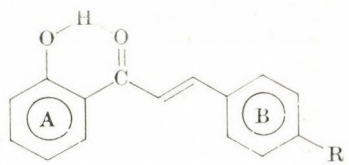
where pK_{BH^+} is the negative logarithm of the equilibrium constant of the protonated form (conjugated acid), H_0 is the Hammett acidity value of the aqueous sulfuric acid solution of known concentration, and C_{BH^+}/C_B is the concentration ratio of the protonated form and the free base at a given H_0 value, determined spectrophotometrically on the basis of the molar extinction values measured in acid solutions of various concentrations.

Results and discussion

It can be seen from the data listed in Tables I and II that C-4 substitution in ring B causes — depending on the electron-donating or electron-withdrawing character of the substituents — shifts to a different extent in the spectra of 2'-hydroxy- and 2'-benzyloxychalcone, but the characteristic shape of the spectrum is retained (Figs 1 and 2). The same substituent causes a larger shift in the 2'-hydroxy series than in the 2'-benzyloxy series, owing to the presence of the "resonance chelate" in 2'-hydroxychalcone. However, the occurrence of the shift, of mainly bathochromic character, in both series confirms the participation in conjugation of the non-bonding electrons of the C-4 substituents and coplanarity. Thus, in both series, the bands can be regarded as intramolecular *para* "charge transfer" bands [14—16].

Table I

Spectral data of C-4 substituted 2'-hydroxychalcones in ethanol



R	Band I	(log ε)	Δ nm	Band II	(log ε)	Δ nm
H	317.5	(4.35)	—	222	(4.09)	—
OH	374	(4.42)	56.5	243	(4.09)	21
OCH_3	368	(4.41)	50.5	243	(4.06)	21
CH_3	336	(4.48)	18.5	230	(4.15)	8
$N(CH_3)_2$	435	(4.47)	117.5	275	(4.05)	53
Cl	319	(4.45)	1.5	225	(4.13)	3
Br	322	(4.39)	4.5	225	(4.03)	3
NO_2	320	(4.49)	1.5	—	—	—

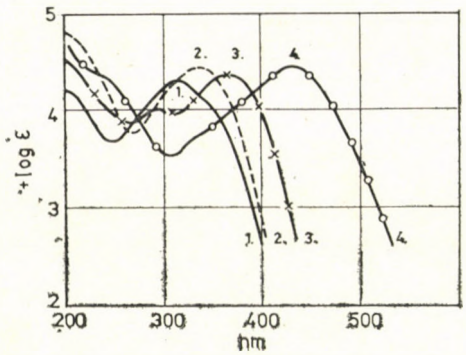


Fig. 1. Spectra of some 2'-hydroxychalcones substituted at C-4 in ring B, recorded in ethanol (1) = H; (2) = CH_3; (3) = OCH_3; (4) = $N(CH_3)_2$

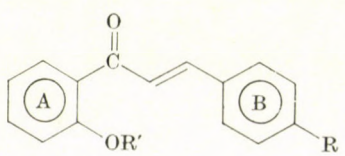
Shift in the spectra of 2'-hydroxy- and 2'-benzyloxychalcones depending on substitution were interpreted and graphically represented in a way similar to the Hammett correlations [17—19]:

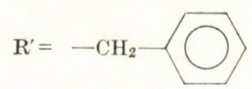
$$1/\lambda_{max}^{H} - 1/\lambda_{max}^{R} = \varrho\sigma,$$

where σ is the Hammett substituent constant, and ϱ is the reaction constant.

Table II

Spectral data of C-4 substituted 2'-benzyloxychalcones in ethanol





R	Band I	(log ε)	Δ nm	Band II	(log ε)	Δ nm
H	307	(4.26)	—	217	(4.20)	—
OH	345	(4.35)	+ 38	237	(4.08)	+ 20
OCH_3	337	(4.38)	+ 30	237	(4.08)	+ 20
CH_3	318	(4.38)	+ 11	230	(4.18)	+ 13
$N(CH_3)_2$	409	(4.54)	+ 102	325	(4.10)	+ 108
F	309	(4.33)	+ 2	217	(4.39)	0
Cl	312	(4.37)	+ 5	217	(4.36)	0
Br	313	(4.35)	+ 6	218	(4.30)	+ 1
CN	301	(4.44)	— 6	220	(4.31)	+ 3
COOH	313	(4.65)	+ 6	225	(4.08)	+ 8
NO_2	316	(4.50)	+ 9	—	—	—

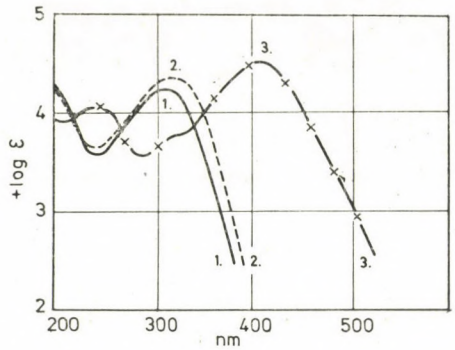
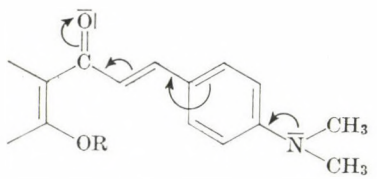
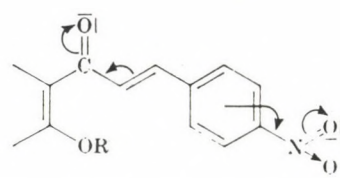


Fig. 2. Spectra of some 2'-benzyloxychalcones substituted at C-4 in ring B, recorded in ethanol (1) = H; (2) = CH_3; (3) = $N(CH_3)_2$

In both series, a sharp break is observed in the plot when changing from substituent constants with positive sign to those with negative sign (Figs 3 and 4).

A fundamental requirement for the linear free energy relationship (LFER) is to have the same reaction mechanism for all substitution effects [20]. The sharp break observed by the use of substituents with different effects ($-M$ and $+M$) may be due to a change in the mechanism of excitation of the conjugated system of chalcones caused by the electron displacement of opposite direction as represented by the following formula:



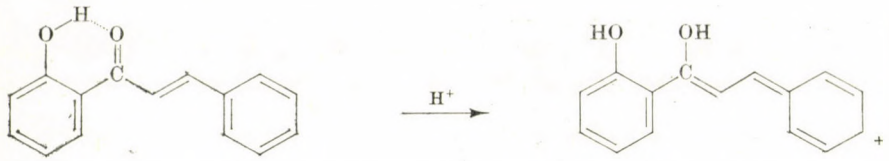


The same sharp break was observed when examining the substitution effect as a function of any of the substituent constants (σ, σ^+ σ^*, σ^R, etc.) in spite of the fact that in some literature data [21—23] a linear relationship was established for compounds with similar substitution pattern (aromatic ketones).

The electron-donating and electron-withdrawing nature of the substituents also appears in the basicity of the carbonyl groups of chalcones related to their proton-binding ability.

The spectra of the chalcones recorded in acid solution are characterized by a strong bathochromic shift and an increase in the intensity of the new band [Figs 5, 6 and 7]. The magnitude of the bathochromic shift is more than

100 nm for most of the compounds (Tables III and IV), which can be explained by the expanded state of the protonated molecule and the presence of a long conjugation chain:



The curves recorded in aqueous sulfuric acid solutions of different concentrations intersect at the isobestic point, which also proves the equilibrium system for the molecular (B) and ionic (BH^+) forms.

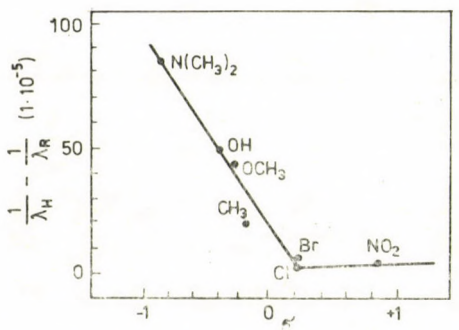


Fig. 3. Relationship between the wavelength shift and the Hammett σ constant in the 2'-hydroxychalcone series

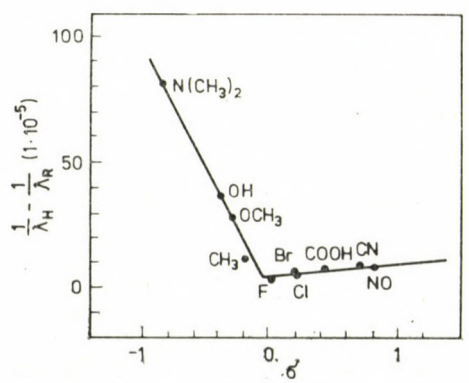


Fig. 4. Relationship between the wavelength shift and the Hammett σ constant in the 2'-benzyloxychalcone series

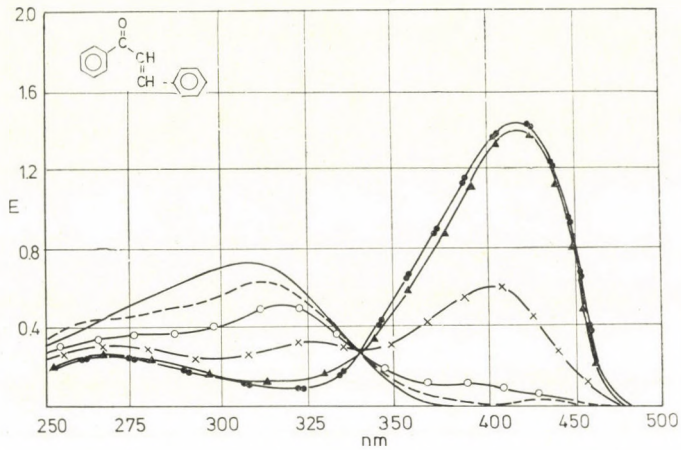


Fig. 5. Spectral changes of chalcone (benzalacetophenone) as a function of sulfuric acid concentration
(—— 50% ethanol–water; — — —21.27% H_2SO_4; — ○ — 56.4% H_2SO_4; — × — 60.27% H_2SO_4; — ▲ —80.90% H_2SO_4; — • • — 93.13% H_2SO_4)

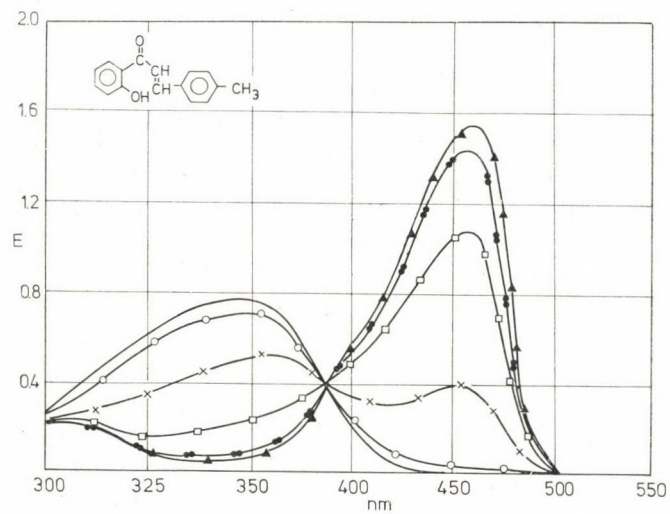


Fig. 6. Spectral changes of 2'-hydroxy-4-methylchalcone as a function of sulfuric acid concentration (—— 50% ethanol–water; —○— 49.58% H_2SO_4; —×— 55.15% H_2SO_4; —□— 60.27%; —• •— 71.41% H_2SO_4; —▲— 91.39% H_2SO_4)

If the logarithm of C_{BH^+}/C, calculated from the intensity values at the maximum of the ionic, protonated form and at wavelengths in its vicinity, is plotted as a function of H_0, straight lines having the same slope are obtained for the chalcones examined (Fig. 8), and the slope is nearly unity [7—9, 14]. This is evidence to show that *ortho*-substituted 2'-hydroxy- and 2'-benzyloxy-

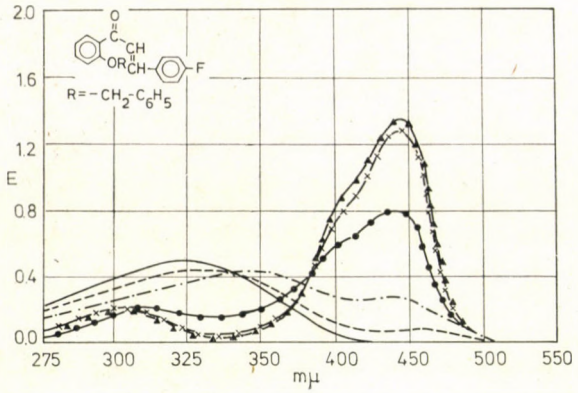


Fig. 7. Spectral changes of 2'-benzyloxy-4-fluorochalcone as a function of sulfuric acid concentration, (—— 0.1*N* sulfuric acid in ethanol; - - - 53.00% H_2SO_4; —·— 60.22% H_2SO_4; —●— 70.41% H_2SO_4; —×— 86.54% H_2SO_4; —▲— 93.26% H_2SO_4)

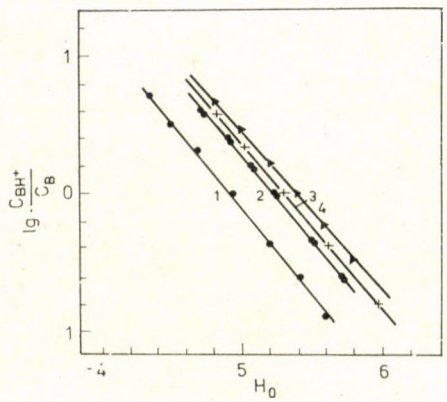


Fig. 8. Logarithm of C_{BH^+}/C_B as a function of H_0. (1) chalcone; (2) 2'-hydroxychalcone; (3) 2'-benzyloxychalcone; (4) 2'-benzyloxy-4-bromochalcone

chalcones as well as the non-substituted chalcones, behave as ideal Hammett bases in aqueous sulfuric acid solutions, thus their basicity can exactly be determined in the knowledge of H_0.

Tables III and IV list the basicity values determined in this way. The value $pK_{BH}{}^+ = -4.92$ obtained for non-substituted chalcone is in good agreement with the value determined by Soviet authors [6] ($pK_{BH+} = -4.86$). The basicities of 2'-hydroxy-and 2'-benzyloxychalcone are about 0.3 $pK_{BH}{}^+$ units lower than that of non-substituted chalcone (—5.22 and —5.28, respectively), since *ortho* substitution gives rise to steric hindrance in solvation.

The differences in $pK_{BH}{}^+$ values clearly reflect the electron-donating or electron-withdrawing tendency of the C-4 substituents, which produce different degrees of electron density at the carbonyl group acting along the

Table III

Spectral data of the molecular (B) and ionic (BH^+) forms of 2'-hydroxychalcones and the basicity data calculated

4-R	(B)*	(ε) λ_{max}	(BH^+)**	(ε) λ_{max}	pK_{BH^+}
OH	375	(22500)	468	(42000)	— 4.66 ± 0.04
OCH_3	372	(21300)	475	(43950)	— 4.58 ± 0.07
CH_3	348	(25300)	461	(57300)	— 4.85 ± 0.02
$N(CH_3)_2$	310	(17600)	383	(24800)	— 5.64 ± 0.05
Cl	326	(22400)	436	(39200)	— 5.40 ± 0.03
Br	335	(20400)	449	(38000)	— 5.40 ± 0.03
NO_2	320	(28000)	392	(42000)	— 5.80 ± 0.05

* 1.985% sulfuric acid
** 91% sulfuric acid. At higher concentrations of sulfuric acid, the curves do not pass through the isobestic point

conjugated aromatic system. Protonation of the carbonyl group will thus depend on the substitution, and will take place at different concentrations of sulfuric acid. The higher the electron density at the carbonyl group, the lower concentration of sulfuric acid is required for the appearance of the ionic form, and thus the compound is more basic.

Table IV

Spectral data of the molecular (B) and ionic (BH^+) forms of 2'-benzyloxychalcones and the basicity data calculated

R	(B)*	(ε) λ_{max}	(BH^+)**	(ε) λ_{max}	pK_{BH^+}
H	312	(16500)	440	(33200)	— 5.28 ± 0.02
OH	385	(12000)	485	(32000)	— 4.25. ± .0.02
OCH_3	370	(12000)	470	(32000)	— 4.46 ± 0.02
$N(CH_3)_2$***	300	(12000)	385	(20000)	— 5.55 ± 0.02
F	325	(8500)	445	(26000)	— 5.51 ± 0.02
Cl	330	(10000)	450	(24000)	— 5.45 ± 0.02
Br	350	(9500)	455	(24000)	— 5.30 ± 0.02
COOH	320	(10000)	390	(18000)	— 5.75 ± 0.03
NO_2	335	(8000)	395	(17500)	— 6.85 ± 0.05

* 1.985% sulfuric acid
** 96.5% sulfuric acid
*** $pK_{N(CH_3)_2} = +2.60$

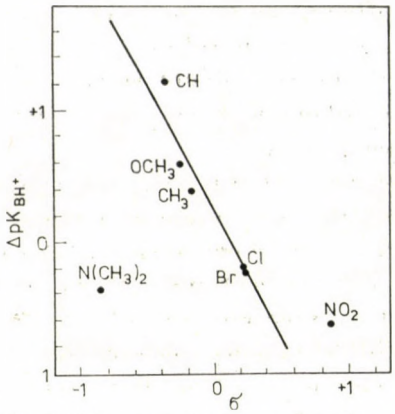


Fig. 9. Dependence of the basicity constants as a function of the Hammett σ constants in the 2'-hydroxychalcone series

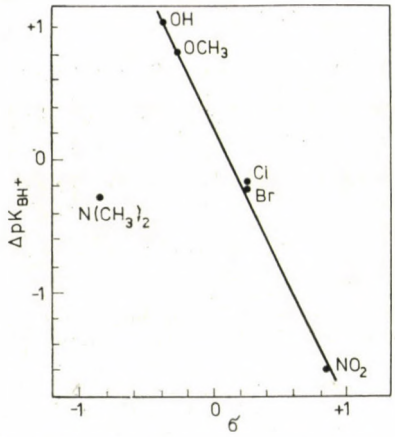


Fig. 10. Variation of the basicity constants as a function of the Hammett σ constants in the 2'-benzyloxychalcone series

Similarly to the wavelength shift caused by substitution, the Hammett relationship was also applied to the change in basicity constants [20—23]:

$$\log \frac{K}{K_0} = \varrho\sigma ,$$

where K and K_0 are the equilibrium constants of the substituted and non-substituted compounds, respectively, σ is the Hammett substituent constant, and ϱ is the reaction constant; its value is calculated from the slope of the straight line.

It can well be seen in Figs 9 and 10 that the effect of the dimethylamino group having the most positive mesomeric effect does not show up

in the basicity of the carbonyl group in either of the series, since, — as indicated by the spectra recorded in sulfuric acid — this group becomes completely protonated even in very dilute sulfuric acid solution (pK_{BH}^{+} $N(CH_3)_2 = +2.6$), thus its non-bonding electrons become ineffective in respect of the basicity of the carbonyl group.

A deviation was also observed with the nitro group having the most positive σ value (exhibiting the most negative mesomeric effect) in the 2'-hydroxychalcone series (Fig. 9), since here a partial ring closure process takes place at 50—70% sulfuric acid concentration. Owing to this, the absorption of the chalcone band having a high intensity changes in time (it decreases), and this results in changes in the basicity constant, too.

Linear relationship was obtained in both series when difference of basicity constants was represented as a function of the Hammett substituent constants, σ.

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THE CONFIGURATION OF CAPSANTHIN EPOXIDES

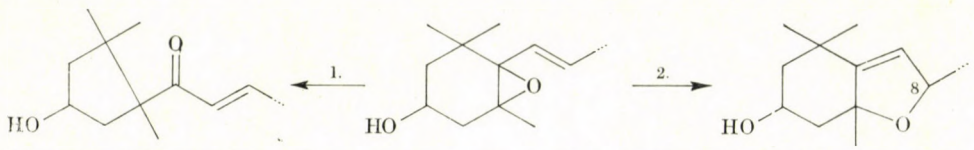
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It has been shown that 'capsanthin epoxide' can be separated by chromatography into two isomers, namely capsanthin epoxide A and capsanthin epoxide B. ^{1}H-NMR, ORD and CD studies indicated that capsanthin epoxide A has a violaxanthin A type end group (3*S*, 5*S*, 6*R*), whereas capsanthin epoxide B has a violaxanthin type end group (3*S*, 5*R*, 6*S*).

It had been previously observed [1, 2, 3] that treatment of xanthophylls, containing zeaxanthin type end groups (**I**), with monoperphthalic acid and subsequent hydrolysis resulted in diastereomeric 5,6-epoxy derivatives with 3*S*, 5*R*, 6*S* and 3*S*, 5*S*, 6*R* absolute configuration. We have now turned our respect to the stereochemistry of the 5,6-epoxy derivatives of capsanthin (**II**), which is the main pigment in red paprika. In spite of the fact that 5,6-epoxycapsanthin was prepared by KARRER's school [4] as early as 1945, and its occurrence in nature was reported by CURL [5] in 1962, the diastereomeric forms of the compound have not been prepared and analyzed yet. The presence of capsanthin epoxide in red paprika is of particular interest because it might indicate capsanthin epoxide as the intermediate [6] which is converted into capsorubin (**VII**) *via* epoxide (pinacol) rearrangement [7] (see Scheme I).



Scheme I. 1. Epoxide (pinacol) rearrangement (in nature). 2. Epoxide-furanoid rearrangement (under acid condition)

Epoxidation of capsanthin diacetate by monoperphthalic acid gave a mixture of 5,6-epoxides, which were separated on a calcium carbonate column with benzene–petroleum ether. The product of epoxidation consisted of ca. 60% capsanthin epoxide A (**III**), ca. 20% capsanthin epoxide B (**IV**) and ca. 20% capsanthin (**II**). Capsanthin epoxide B (m.p. 185°C) was found on the chromatogram below capsanthin epoxide A (m.p. 178°C) but above capsanthin.

The MS spectra of **III** and **IV** showed the same molecular ion [*m/e*: 600 (19%, 11%)] and the same fragments indicating [8, 9, 10] a 3-hydroxy-5,6-epoxycyclohexyl end group (violaxanthin type) [*m/e*: 221 (59%, 50%); *M*—180 (1%, 2%)], and a 3-hydroxycyclopentyl end group (capsorubin type) [*m/e*: 109 (100%, 100%); *M*—127 (3%, 2%)]. Other fragments characteristic of carotenoids [*M*—80 (2%, 2%), etc.] also appear in the MS spectra.

The light absorption properties of capsanthin epoxide A and capsanthin epoxide B are identical [λ_{max} (ε_{max}) in benzene: 508 (80,800) 479 (99,800)

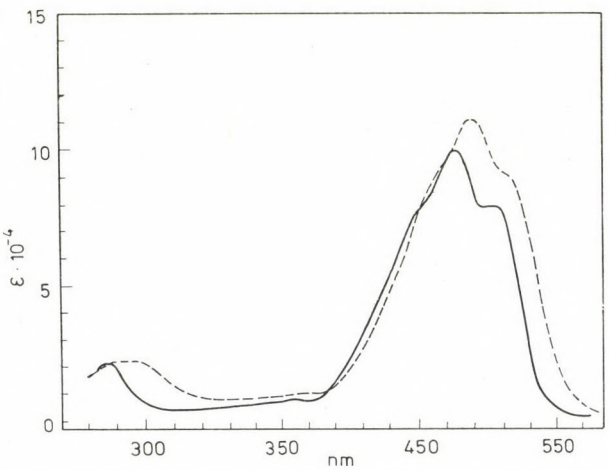


Fig. 1. Molecular extinction curves of capsanthin - - - - -, capsanthin epoxide A and B ——— (in benzene)

and 454 (88.300) nm; ν_{max} ($CHCl_3$): 3610, 1660, 1580 and 1550 cm^{-1}] (Fig. 1), and they correspond to the 3,3'-dihydroxy-5,6-epoxy-5,6-dihydro-β,K-carotene structures [3].

The above conclusions concerning the structure were confirmed by the ^{1}H-NMR spectra; bands attributable to the ring methyls are shown in Table I. The slight shielding differences of the methyl protons between **III** and **IV** agree with those described for the ring methyls of violaxanthin A (3*S*, 5*S*, 6*R*) and violaxanthin (3*S*, 5*R*, 6*S*) [1]. This suggests that capsanthin epoxide A (**III**) has a violaxanthin A (**V**) type end group, whereas capsanthin epoxide B (**IV**) has a violaxanthin (**VI**) type end group.

The ORD curves of capsanthin epoxide A (Fig. 2) and capsanthin epoxide B (Fig. 3) are of about the same magnitude but opposite in sign, showing the structures of the two substances to be nearly enantiomeric. As is known, the 3-hydroxyl group has practically no influence on the Cotton effects [1]. All these facts are in good agreement with the proposed structures being enantiomeric only in the configuration of the 5,6-epoxy group. The shapes of the

Table I

		Chemical shifts (δ) in ppm of ring methyls (in $CDCl_3$)		
		C_1-Me's		C_5-Me's
[a]Violaxanthin		0.95 (s,6H)	1.12 (s,6H)	1.16 (s,6H)
[a]Violaxanthin A		1.00 (s,6H)	1.14 (s,6H)	1.17 (s,6H)
[b]Capsorubin		0.84 (s,6H)	1.20 (s,6H)	1.37 (s,6H)
[b]Capsanthin epoxide A	Capsorubin type end group	0.85	1.21	1.38
	Violaxanthin A type end group	1.02	1.16	1.18
[b]Capsanthin epoxide B	Capsorubin type end group	0.85	1.21	1.38
	Violaxanthin type end group	0.98	1.15	1.19

^{1}H-NMR spectra marked with [a] were determined at 100 MHz [1], and those marked with [b] at 60 MHz (see Experimental)

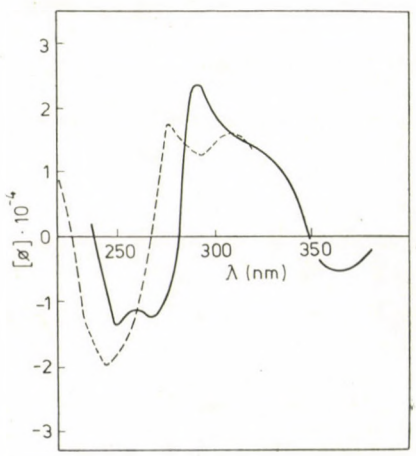


Fig. 2. ORD curves for capsanthin epoxide A (3*S*, 5*S*, 6*R*, 3'*S*, 5'*R*), experimental (———) (in methanol) and calculated for 1/2 violaxanthin A + 1/2 capsorubin (- - - -) (in dioxan)

experimental ORD curves of capsanthin epoxide A and capsanthin epoxide B showed fairly good agreement with those calculated on the basis of the additivity hypothesis [1, 3] for 1/2 violaxanthin A + 1/2 capsorubin, and for 1/2 violaxanthin + 1/2 capsorubin, respectively. Capsanthin epoxide A may therefore be assigned 3*S*, 5*S*, 6*R*, 3'*S*, 5'*R* configuration, and capsanthin epoxide B 3*S*, 5*R*, 6*S*, 3'*S*, 5'*R* configuration.

The conclusions drawn from the ORD spectra are supported also by the CD spectra. As can be seen in Fig. 4, the CD curves of capsanthin epoxide

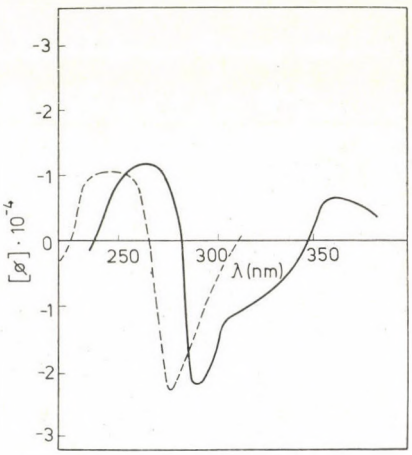
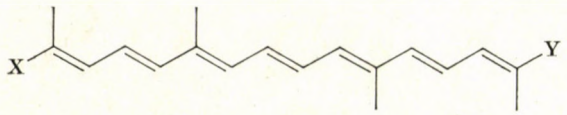
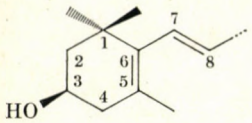


Fig. 3. ORD curves for capsanthin epoxide B (3*S*, 5*R*, 6*S*, 3'*S*, 5'*R*), experimental (——— (in methanol) and calculated for 1/2 violaxanthin + 1/2 capsorubin (- - - - -) (in dioxan)

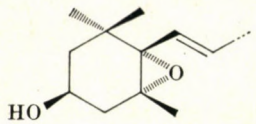
A and B are opposite in sign showing the enantiomeric configuration of the epoxy groups, which are mainly responsible for the sign of the Cotton effects.

Recently it has been reported [11] that mild acid treatment of 3-hydroxy-5,6-epoxyxanthophylls having violaxanthin type end groups (3*S*, 5*R*, 6*S*) results in a pair of stereoisomeric furanoid oxides, and that of 3-hydroxy-5,6-epoxyxanthophylls having semisynthetic violaxanthin A type end groups (3*S*, 5*S*, 6*R*) results in a different pair of stereoisomeric furanoid oxides. Since each end group gives only two furanoid oxides, differing at C-8 (see Scheme I), the absolute configuration is preserved at C-5 during the epoxide–furanoid rearrangement. So it was expected that capsanthin epoxide A (**III**) with the violaxanthin A type end group and capsanthin epoxide B (**IV**) with the violaxanthin type end group also furnish similar pairs of furanoid oxides (**VIII**). The present experiments have proved this assumption: capsanthin epoxide A underwent epoxide–furanoid rearrangement giving capsochrome A and capsochrome A', whereas under similar conditions capsanthin epoxide B resulted in capsochrome B and capsochrome B'. All these substance have the

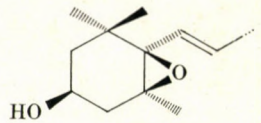




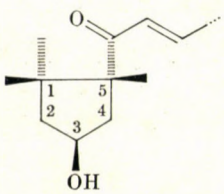
a (3*R*)*



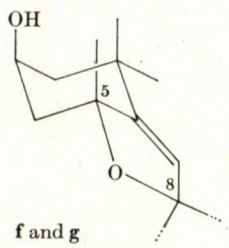
b (3*S*, 5*R*, 6*S*)



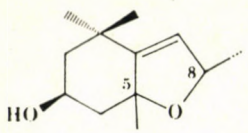
c (3*S*, 5*S*, 6*R*)



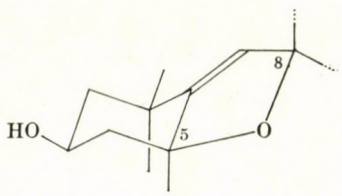
d (3*S*, 5*R*)



f and **g**



e



h and **i**

I X = Y = **a**

II X = **a**, Y = **d**

III X = **c**, Y = **d**

IV X = **b**, Y = **d**

V X = Y = **c**

VI X = Y = **b**

VII X = Y = **d**

VIII X = **e**, Y = **d**

IX X = Y = **e**

same electronic spectra [λ_{max} (C_6H_6) : 485, 460 and 440 nm] (Fig. 5) and show hypophasic behaviour on partition tests between petroleum ether and 90% methanol but have different adsorption affinities. In the order of decreasing adsorption affinities the relative positions of the stereoisomeric capsochromes on a calcium carbonate column are as follows: A, B, A' and B'. Owing to the small amount of capsochromes, no attempt at crystallization could as yet be made. On the analogy of the configuration of auroxanthins (**IX**) [11] we

* The change of designation at C-3 from *R* to *S* in the end groups of *b*, *c* and *d* results from the Sequence Rule and does not involve inversion of configuration

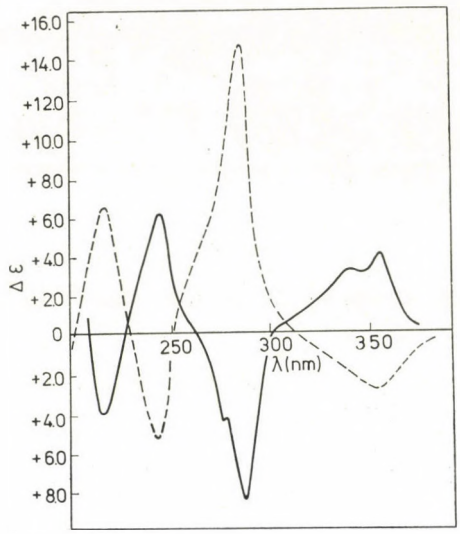


Fig. 4. CD curves for capsanthin epoxide A (3*S*, 5*S*, 6*R*, 3'*S*, 5'*R*) in methanol (— — —) and capsanthin epoxide B (3*S*, 5*R*, 6*S*, 3'*S*, 5'*R*) in dioxan(———)

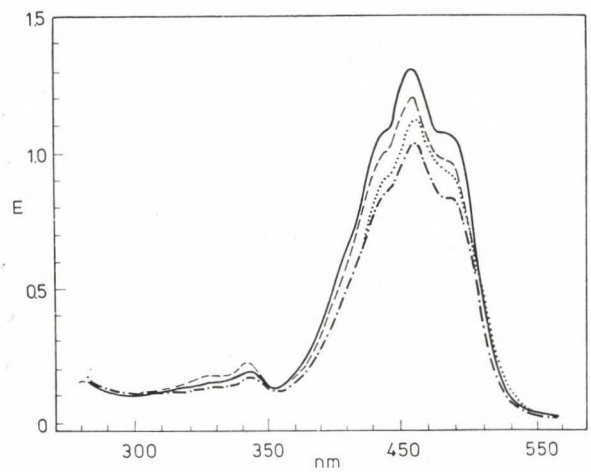


Fig. 5. Ultraviolet and visible light absorption spectra of capsochrome A (———), capsochrome A' (- - - -), capsochrome B (. . . . .) and capsochrome B' (-.-.-.-.) (in benzene)

propose configuration **f** and **g** for capsochrome A and A' (differing at C-8) and configuration **h** and **i** for capsochrome B and B' (differing at C-8). The hydroxyl groups of **f** and **g** are *axial*, while that of **h** and **i** are *equatorial*.

Considering that analysis of a great number of paprika samples in our laboratory during the past 30 years failed to identify capsanthin epoxide (even in traces), we conclude that capsanthin epoxide is not present among the carotenoids occurring in red paprika.

Experimental

The routine procedures and methods used here were the same as those described before [12]. Capsanthin diacetate [m.p. 140 °C; λ_{max} (C_6H_6) 517, 486 nm] was prepared from natural capsanthin (ex *Capsicum annuum rubrum*).

^{1}H-NMR spectra were determined in deuteriochloroform with a Perkin—Elmer R—12 (60 MHz) spectrometer. The mass spectra were recorded by an AEI MS—902 type mass spectrometer. Samples were introduced by use of a direct insertion probe. An ion accelerating potential of 8 kV, ionizing electron voltage of 70 V, trap current of 100 μA and an ion source temperature of 180 °C were used. The abundances of ions given in parentheses, refer to the intensity of the line relative to that of the base peak, the intensity of the latter being represented as 100%. ORD spectra were measured by an Opton (Zeiss) REPM 12 spectropolorimeter; c = 0.1 mg/ml in methanol, cell length 5 mm, t = 30 °C. The CD spectra were determined on a Jobin—Yvonne Dicrograph Model III; c = 0.1 mg/ml, in methanol or dioxan, cell length 1 mm, t = 20 °C. The light absorption spectra were run on a Perkin—Elmer Model 402 and a Zeiss (Jena) UR 10 spectrophotometer.

Preparation of capsanthin epoxide A and B

To a solution of 310 mg capsanthin diacetate in 110 ml absolute ether there was added an ethereal solution of monoperphthalic acid (4 ml, containing 0.45 mg oxygen/ml) and the mixture was kept at room temperature in darkness for 46 hrs. After 20 hrs epoxidation, further 3 ml of monoperphthalic acid solution was added to the reaction mixture. The epoxidation was followed by paper chromatography; Whatman SG 81, solvent petroleum ether containing 5% ethanol. The ethereal solution was transferred to a separatory funnel, washed first with aqueous 10% sodium hydrogen carbonate solution then with water, and finally dried (Na_2SO_4). The ethereal solution was evaporated to 150 ml and then hydrolyzed with 15 ml of a 30% KOH solution in methanol for 20 hrs. After completion of saponification the solution was washed alkali-free with water, dried (Na_2SO_4) and evaporated under reduced pressure. The residue was dissolved in benzene (600 ml) and chromatographed on calcium carbonate from benzene.

	λ_{max} in benzene	
20 red and yellow (mixture of unidentified pigments)		
(1) 40 brick-red (capsanthin epoxide A)	508	479
(2) 20 red (capsanthin epoxide B)	508	479
5 pale red (unidentified)		
(3) 20 red (capsanthin)	516	486
10 pale yellow (unidentified)		

The zones were eluted with a mixture of benzene and methanol, transferred to benzene in separatory funnels, washed with water, dried (Na_2SO_4), evaporated to dryness in vacuum, and the residues were crystallized.

Zone 1 (capsanthin epoxide A) was dissolved in 3 ml of benzene, then 15 ml of petroleum ether was carefully added, and the mixture was allowed to stand at —15 °C overnight. The pigment crystallized in glittering yellow needles, which were grouped in star-like formations; 13 mg, m.p. 178 °C.

Zone 2 (capsanthin epoxide B) was crystallized in a similar manner as Zone 1. It gave 40 mg of glittering yellow leaflets, m.p. 185 °C.

It is noticed that, in their diacetate forms, capsanthin epoxide A and B can be separated on calcium carbonate with a mixture of benzene and petroleum ether (2 : 3) as well, and the diacetate of capsanthin epoxide A shows the greater adsorption affinity.

Acid-catalysed rearrangement of capsanthin epoxide A; preparation of capsochrome A and A

To 3 mg capsanthin epoxide A in 10 ml ether 4 drops of HCl–acetic acid solution (1 : 10) were added and the mixture was kept in scattered daylight for 20 min [6]. The solution was thoroughly washed first with aqueous sodium hydrogen carbonate solution (10%) and then with water, dried (Na_2SO_4) and evaporated under reduced pressure. Chromatography of the residue on calcium carbonate with benzene as eluant gave the following chromatogram.

		λ_{max} in benzene		
8	reddish ochre (mixture of unidentified pigments)			
(11) 20	brick-red (capsochrome A)	485	460	440
(12) 20	reddish ochre (capsochrome A')	485	460	440
4	pale yellow			
40	reddish ochre	(504	472	450)*
3	pale red			
3	pale red			

* Unsharp

After the usual procedures, the pigments were identified in solution by λ_{max}, partition tests, mixed chromatography, etc.

Acid-catalysed rearrangement of capsanthin epoxide B; preparation of capsochrome B and B'

Three mg of capsanthin epoxide B when treated with acid as described for capsanthin epoxide A gave the following chromatogram.

		λ_{max} in benzene		
15	brick-red (mixture of unidentified pigments)			
(21) 20	red (capsochrome B)	485	460	440
(22) 10	reddish ochre (capsochrome B')	485	460	440
10	pale pink	—	—	—
15	pale yellow			
3	pale red	510	474	450

After the usual procedures, the products were analyzed in solution by λ_{max}, partition tests, mixed chromatography, etc.

According to the mixed chromatograms ($CaCO_3$, benzene) the order of decreasing adsorption affinities of capsochromes was: capsochrome A, —B, —A' and —B'.

*

We would like to express our thanks to Miss M. HÁM and Miss E. NYERS for their skilful assistance.

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Acta Chimica Academiae Scientiarum Hungaricae, Tomus 94 (1), pp. 75—77 (1977)

THE OXIDATIVE REARRANGEMENT OF CHALCONES THALLIUM(III) NITRATE, VII*

THE SYNTHESIS OF ODORATIN AND 7-HYDROXY-2',4',5',6-TETRAMETHOXY-ISOFLAVONE

Zs. KARDOS-BALOGH, L. FARKAS and A. WOLFNER

(Research Group for Alkaloid Chemistry of the Hungarian Academy of Sciences, and Institute of Organic Chemistry, Technical University, Budapest)

Received June 17, 1976

The synthesis of 3',7-dihydroxy-4',6-dimethoxyisoflavone (odoratin **1**) and 7-hydroxy-2',4',5',6-tetramethoxyisoflavone (**2**), two natural isoflavones from tropical woods, has been accomplished by oxidative rearrangement of the corresponding chalcones by $Tl(NO_3)_2$ as the key step.

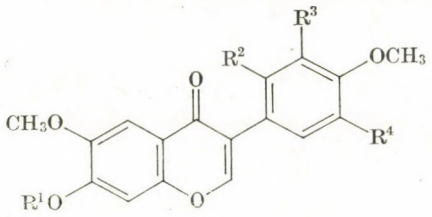
In 1974 HAYASHI and THOMSON [2] isolated several new isoflavones from the heartwood of the tropical tree *Dipteryx odorata*. We have already reported the unambiguous synthesis of one of them: 3'-hydroxyretusin 8-methyl ether [3]. To another constituent, named odoratin, the structure 3',7-dihydroxy-4',6-dimethoxyisoflavone (**1**) has been assigned on spectroscopic evidence. This was confirmed by methylation that gave 3',4',6,7-tetramethoxyisoflavone, a known compound, which is also a natural product [4].

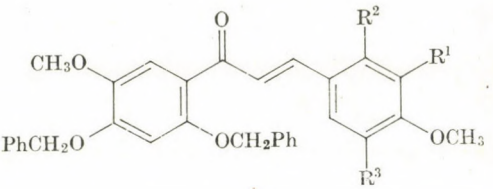
GALINA and GOTTLIEB reported the isolation of four new isoflavones from the heartwood of *Pterodon apparicioi*, a tree indigenous to South America [5]. One of them was identified, based on spectroscopic evidence, with 3',7-dihydroxy-4',6-dimethoxyisoflavone, *i.e.* odoratin, which had been described by HAYASHI and THOMSON [2]. The physical data published by the two laboratories for the new compound were also nearly identical. In the same publication the isolation and spectroscopic identification of 7-hydroxy-2',4',5',6-tetramethoxyisoflavone (**2**) was also described.

The synthesis of odoratin (**1**) and 7-hydroxy-2',4',5',6-tetramethoxyisoflavone (**2**) has now been accomplished by means of the oxidative rearrangement of the appropriately substituted chalcones by thallium(III) nitrate [6]. In order to avoid side reactions, 2,4-dibenzyloxy-5-methoxyacetophenone [7] has been selected as starting material for both syntheses. Condensation of this acetophenone in alkali with benzylvanillin and asaraldehyde afforded 4,5'-dimethoxy-2',3,4'-tribenzyloxy (**3**) and 2',4'-dibenzyloxy-2,4,5,5'-tetramethoxychalcone (**4**), respectively. Reaction of **3** and **4** with thallium(III) nitrate in methanol under the usual conditions followed by removal of the benzyl groups by catalytic hydrogenation and finally cyclization by treatment with acid yielded directly **1** and **2**, respectively.

* For Part VI, see Ref. [1].

Synthetic odoratin (**1**) and 7-hydroxy-2',4'5',6-tetramethoxyisoflavone (**2**), as well as the corresponding acetates (**5** and **6**) had the same melting points and infrared spectra as reported for the natural products. No m.p. depression was observed when mixing the natural and synthetic hydroxyisoflavones.





	R^1	R^2	R^3	R^4
1	H	H	OH	H
2	H	OCH_3	H	OCH_3
5	$COCH_3$	H	$OCOCH_3$	H
6	$COCH_3$	OCH_3	H	OCH_3

	R^1	R^2	R^3
3	OCH_2Ph	H	H
4	H	OCH_3	OCH_3

Experimental

4,5'-Dimethoxy-2',3,4'-tribenzyloxychalcone (3)

2,4-Dibenzyloxy-5-methoxyacetophenone [7] (0.60 g) and benzylisovanillin (0.65 g) were suspended in methanol (100 ml). After the addition of a solution of potassium hydroxide (15 g) in water (15 ml) the mixture was stirred at room temperature for one day. The precipitate was filtered off, dried and recrystallized from acetic acid (20 ml) to give the product as a yellow powder (0.8 g; 91%), m.p. 173—175 °C, which was found pure by TLC (silicagel plates; solvent: benzene—ethyl acetate 2 : 1). A sample was recrystallized for analysis from ethanol; small yellow needles, m.p. 174—175 °C.

$C_{38}H_{35}O_6$ (585.7). Calcd. C 77.93; H 5.69. Found C 77.65; H 5.94%.

3',7-Dihydroxy-4',6-dimethoxyisoflavone; odoratin (1)

To a solution of **3** (0.33 g) in a mixture of abs. methanol and chloroform (1 : 1, 50 ml) thallium trinitrate (0.5 g) was added. After stirring for 90 min the solution was neutralized with sodium methoxide, filtered, and evaporated in vacuum at room temperature. Water (20 ml) was added to the residue and the mixture extracted with chloroform (2×20 ml). The combined extracts were dried over magnesium sulfate, filtered and evaporated. The residue, a pale yellow oil, was dissolved in acetone (25 ml) and hydrogenated over palladium-on-charcoal catalyst when 28.8 ml hydrogen was absorbed (calcd. 36 ml). After removing the catalyst by filtration, the solution was evaporated, the residue taken up in methanol (18 ml) and the solution boiled for 10 min in the presence of two drops of hydrochloric acid. The cold solution deposited the product as off-white crystals (0.047 g), m.p. 204—205 °C. Recrystallization from methanol gave colorless prisms, m.p. 214.5—215 °C, (lit. m.p. 210—211 °C [2], 213—215 °C [5]). No depression of m.p. was observed in admixture with a natural sample.

IR: ν_{max} (KBr): 3400 br, 1620, 1580, 1513, 1280, 1140, 1020 cm^{-1} (lit. [4, 5] data: 3400 br, 1625, 1585, 1510; 3515, 3160, 1620, 1570, 1512, 1280, 1140, and 1020 cm^{-1}).

3',7-Diacetoxy-4',6-dimethoxyisoflavone; odoratin diacetate (5)

1 (10 mg) was acetylated by the usual method with acetic anhydride–sodium acetate to yield, after recrystallization, small colorless needles, m.p. 185—186 °C (from ethanol) (lit. [2, 5] m.p. 185—187 °C).

2',4'-Dibenzyloxy-2,4,5,5'-tetramethoxychalcone (4)

2,4-Dibenzyloxy-5-methoxyacetophenone [7] (0.6 g) was condensed with asaraldehyde (0.5 g) as described for **3** to give the crude chalcone (0.7 g; 78%) as a yellow powder. Successive recrystallizations from acetic acid and ethanol gave yellow prisms, m.p. 151—152 °C.

$C_{33}H_{32}O_7$ (540.5). Calcd. C 73.31; H 5.97. Found C 73.09; H 5.93%.

7-Hydroxy-2',4',5',6-tetramethoxyisoflavone (2)

To a solution of **4** (0.3 g) in abs. methanol and chloroform (1 : 1, 20 ml) thallium trinitrate (0.4 g) was added and the mixture stirred for 30 min. Work-up as described for **1** gave pale green crystals (0.49 g, m.p. 194—195 °C). After two recrystallizations from ethanol and one from acetone the m.p. rose to 205—206 °C (lit. m.p. 205—207 °C [5]). No depression of m.p. was found in admixture with a sample of the natural product.

IR: ν_{max} (KBr): 3160, 1625, 1580, 1512, 1470, 1275 cm^{-1} (lit. [5]: 3150, 1628, 1580, 1515, 1280 cm^{-1}).

7-Acetoxy-2',4',5',6-tetramethoxyisoflavone (6)

Crude **2** (30 mg) was acetylated with acetic anhydride–sodium acetate in the usual way. The product (32 mg; m.p. 161—153° C) was recrystallized twice from ethanol–chloroform to give small colorless needles, m.p. 167—169 °C (lit. [5] m.p. 166—168 °C).

*

The authors are indebted to Professor R. H. THOMSON (Aberdeen, Scotland) for a sample of natural odoratin and to Professor O. R. GOTTLIEB (Rio de Janeiro, Brasil) for natural 7-hydroxy-2',4',5',6-tetramethoxyisoflavone.

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RECENSIONES

A. HULANICKI (editor): *Plenary Lectures Presented at the Fourth Polish Conference on Analytical Chemistry*

Butterworths, London 1975, 690 pages.

This book is a joint edition published by the Analytical Chemistry Division of IUPAC, the Commission on Analytical Chemistry of the Polish Acedemy of Sciences, and the Polish Chemical Society; it contains the text of the plenary lectures presented at the Analytical Conference in Warsaw, August 26—31, 1974.

These plenary lectures are in accord with the profile of research carried out in Poland, and at the same time, they embrace the most important actual problems in analytical chemistry. Prominent specialists in the various fields of analytical chemistry acquaint the reader with recent results of chemical analysis in preventing damage to the environment, a problem of great current interest; the most up-to-date instrumental methods of analytical chemistry, and recent progress in the evaluation and interpretation of analytical data are discussed.

K. DOERFFEL (GDR), in his paper entitled "Methodische Konsequenzen des 3σ-Kriteriums", summarizes the quantitative assessing of the systematic limits of spectroscopic methods and demonstrates, with the help of examples, the possibilities of improvement and of enhancement of selectivity.

The paper by C. LITEANU and I. RICA (Romania) similarly deals with theoretical problems of chemical analysis in a rigorous discussion of the limits of detection and determination.

A detailed survey of the problems encountered in the elementary analysis of organometallic compounds is given in a paper by N. E. GELMAN (USSR).

In his paper entitled "Activation Analysis in Clinical and Biological Research" J. M. A. LANIHAN (Scotland) describes the application of activation analysis in the exploration of the past, environmental protection, and therapeutics; results of recent research are discussed.

G. TÖLG (GFR) presents a detailed report on the fields of application of high-performance micro-analytical techniques, modern methods of fusion, separation, enrichment, also describing the pertinent apparatus.

Enrichment techniques applicable in the determination of elements present in trace quantities in geological samples, the analysis of lunar samples, and a comparison of methods are given in the paper by Yu. A. ZOLOTOV and I. A. BLUM.

Two papers deal with the analytical problems of environmental pollution. A. LIBERTI (Italy) describes modern methods for the determination of the most important pollutants in air, sulfur, nitrogen oxides, carbon monoxide, hydrocarbons, ozone, etc. According to the fundamental principle and technique, the author discerns three groups: primary, secondary, and tertiary generative methods; direct optical methods belong in the last group. K. H. MANCY (USA) deals with current problems of water pollution, with the planning of its control, and with the processing, evaluation, and presentation of the pertinent data.

Further chapters severally contain reports on recent results in the domain of electroanalytical methods. W. SIMON *et al.* (Switzerland) deal with ion-selective electrodes; E. PUNGOR *et al.* (Hungary) discuss results achieved in voltammetry. J. ZYKA (Czechoslovakia) describes applications of redox titrations.

Finally, a paper by J. MINCZEWSKI (Poland) summarizes the new scientific results achieved by Polish scientists between 1944 and 1974. During these thirty years, in nearly every branch of analytical chemistry some important contribution by Polish researchers has furthered the progress of this discipline.

The nice and careful presentation of the book praise the efforts of Prof. A. HULANICKI. Considering that in each of the fourteen lectures some highly interesting problem

is dealt with by a most competent author, this book is recommended as an instructive reading for practising analytical chemists as well as for those who want information on the present state of analytical chemistry.

J. INCZÉDY

Mechanisms of Hydrocarbon Reactions — A Symposium. 5—7 June, 1973, Siófok, Hungary

Edited by F. MÁRTA and D. KALLÓ, Akadémiai Kiadó, Budapest 1975, 812 pages.

This impressive volume contains the proceedings of the Symposium organized jointly by the Institute of Isotopes of the Hungarian Academy of Sciences and the Hungarian Chemical Society. 57 papers and 4 plenary lectures were presented at the Symposium, their common feature being that each of them dealt with one or another aspect of hydrocarbon reactions. This concept is justified by the enormous importance of natural hydrocarbons, not only as fuels, but also as chemical raw materials, any so-called energy crisis affecting only their economy but not their indispensability. From theoretical aspects, hydrocarbons may not offer such a dramatic variety of reactions as other classes of organic compounds, but just because of their simplicity they may be excellent model substances to demonstrate the effects of more subtle variations in molecular structure.

The volume has been divided into two main parts: I. Heterogeneous catalytic reactions and II. Homogeneous reactions.

The first contribution of Part One is the plenary lecture of one of the Great Old Men in catalysis: B. A. KAZANSKII ("On the mechanism of hydrocarbon conversions in the presence of some heterogeneous catalysts"). Unfortunately, this paper giving an excellent summary of nearly 25 years of work of a long and successful scientific career, had to be the last one written by the famous scientist himself and could be delivered only as a posthumous lecture, followed by the obituary of the author presented by one of his closest co-workers: A. F. PLATÉ.

The rest of Part One has been subdivided into four chapters: The first of them (Catalysis by metals) is the most voluminous containing Plenary Lecture 2 by G. C. BOND ("An extension of the active centre concept in hydrocarbon reactions ion metal catalysts") and 13 contributed papers, underlining the theoretical and practical importance of metal catalysis in hydrocarbon chemistry. The separation of "Catalysis by metal oxides" (7 contributed papers) and "Catalysis on insulators" (4 papers) is not quite justified since these "insulators" are aluminium oxide species which also belong to "metal oxides" even if their electrical conductivity may be different from those (molybdenum, tin, bismuth, etc.) oxides treated in Chapter 2. On the other hand, one can fully agree with the collection of the 9 papers dealing with "Catalysis by zeolites" into a separate chapter, emphasizing by doing so the extreme and continuously increasing importance of zeolites as catalysts.

The topics discussed in Part Two dealing with homogeneous reactions are somewhat more diverse. This part is headed by a chapter entitled "Catalysis by Coordination Compounds" representing a bridge from Part One to catalytic reactions. The six paper of this chapter could give only sketchy outlines of the increasing importance of complex catalysis — although it is true that one of its main fields, polymerization, was excluded from the topics of the Symposium. The next chapter (Pyrolysis) contains 6 papers from 5 countries. The importance of the topic in the chapter on Radiolysis has been underlined by including here another plenary lecture by P. AUSLOOS ("Pulse radiolysis of alkanes in the gas phase, ion–molecule reactions and neutralization mechanism of hydrocarbon ions") in addition to the 7 contributed papers. The last chapter incorporates 5 papers on oxidation reactions. The volume is concluded by a fourth plenary lecture of general interest by M. J. GOLDSTEIN and co-workers ("The Linear Analysis of Labeling Experiments — LALE") being the only representative of pure theoretical chemistry in the meeting.

The material included into the volume bears a real international character: Hungarian authors presented only 15 papers (of these two with co-authors from abroad) representing adequately Hungarian science in all of the topics mentioned. The other 42 papers came from 11 different countries. A hot and spontaneous discussion followed most of the papers. In addition to the high scientific standard incorporated into the contribution, the value of the book is highly increased by including all discussion remarks giving almost 15% of the volume. I think that the publication of the proceedings has been a useful contribution for

almost everybody devoted to homogeneous or heterogeneous reactions of hydrocarbons; in spite of the somewhat delayed publication the volume is often quoted in international literature.

The external appearance of the volume is nice and worthy of the valuable contents.

Z. PAÁL

Recent Developments in the Chemistry of Natural Carbon Compounds, Vol. 7

Akadémiai Kiadó, Budapest 1976, 256 pages.

The present volume of this well established series contains five contributions from experts in the respective fields. The selection of the topics is very fortunate, it covers a rather wide range of interest from structural work on phenolics to biomedical aspects of peptide chemistry.

The first paper by the late T. R. SESHADRI (30 pp.) is a historic review of "*Naturally occurring anhydro-colour bases*", a special class of natural dyes containing a quinonemethide moiety. The first sections deal with classical investigations by PERKIN, WILLSTÄTTER, ROBINSON, ROBERTSON, and others. One feels some nostalgia for those times when structural work was really chemistry and not, as now, more or less applied spectroscopy. Of course, the unravelling of the structure of santalin pigments which have been investigated by the author himself, would not have been possible by classical means.

The spectroscopic approach is, in turn, the leading theme in K. VENKATARAMAN's account ("*Recent work on some natural phenolic pigments*", 22 pp.) on structural work carried out in the author's laboratory on flavones and xanthones, mainly prenylated ones. Though structural elucidation by modern methods is an exacting task and the results may be of high interest, I am afraid that, for the general reader, such reports crammed with spectroscopic data are rather uninspiring.

The short (22 pp.) but excellent contribution on "*Structure and chemical topography of the active site of aspartate aminotransferase*" by E. S. SEVERIN and N. N. GULYAEV is the most enjoyable piece of the volume. It illustrates the utility of carefully chosen substrate analogues and/or inhibitors in the elucidation of the stereochemistry of enzyme action. The experiments provided a novel and more satisfactory explanation for the fact (discovered by ARIGONI) that saturation of the aldimine bond in the apoenzyme and the apoenzyme–substrate complex takes a different stereochemical course.

In the fourth paper K. WEINGES and B. STEMMLE review recent advances (1969—1974) of "*Asymmetric syntheses of α-amino acids*" (24 pp.). Though not too many of the numerous approaches presented have much practical value, the progress in this field has been rapid, the theoretical implications are important, and there is a hope for the advent of a more or less general method. The best though rather restricted procedure is just the one elaborated by the authors themselves, namely asymmetric Strecker synthesis coupled with second order transformation.

The authors' recommendation, however, to revive the adjective "dissymmetric", which has caused so much confusion in the past, is both out of place in this review and, I hope, also not welcome by chemists. The authors fell into their own trap and denoted the asymmetric compound 21 (p. 96) as dissymmetric. Also why to put *R*, *S* symbols into square brackets, when everyone puts them into round ones?

The most ambitious review in this volume is the one by K. MEDZIHRADSZKY: "*Synthesis and biological activity of adrenocorticotropic and melanotropic hormones*" (131 pp.).

It covers the synthesis, biological testing methods and structure–activity correlations of the title hormones, its fragments and analogues. The treatment is concise and critical. First of all, the part about structure–activity relationships is a highly stimulating reading not only for those directly involved in the field, but for everyone interested in bio-organic chemistry.

The number of ACTH and MSH analogues is awesome and almost every factor contributing to biological activity, such as receptor site specificity, immunological properties, rate of metabolism, etc. can be exemplified by them.

The author himself is an active worker in this line and the modesty by which he presented his own results is remarkable.

M. NÓGRÁDI

Wolfgang PFLEIDERER (editor): *Chemistry and Biology of Pteridines*

Walter de Gruyter, Berlin 1976, 949 pages.

This book contains seventy-one lectures presented at the 5th International Symposium on Pteridines, Konstanz, April 14—18, 1975. These symposia are arranged every five or six years, bringing together specialists who study the various aspects of pteridines. According to the organizing body, the interdisciplinary character of these meetings is of fundamental importance in fostering development in this domain of scientific work. The book, actually the proceedings of the Symposium, contains, besides the complete text and figures of the lectures, the ensuing discussions, as well as references to the literature: a very useful feature.

The majority of the papers acquaint the reader with the results of biological and enzymological research. Likewise, only a part of the chemical work dealt with organic syntheses and structure elucidation. Owing to the biological importance of pterins (2-amino--3H-pteridin-4-ones), several authors report on the reduction of these compounds and on the oxidation of the reduced (quinoidal, 7,8-dihydro-, and 5,6,7,8-tetrahydro-) forms.

A comprehensive review of the electrochemistry of pteridines is given by H. LUND. Proton resonance studies have been made to elucidate stereochemical problems of tetrahydropteridines, and to determine the sites of covalent hydratation and protonation.

Of the organic chemical synthetic work, two comprehensive lectures deserve special mention. A. ALBERT reviewed the important moments of the discovery and application of pteridines. No doubt, the verification, in 1946, of the structure of folic acid gave a great impetus to pertinent chemical, pharmacological, and biological research. In contrast to most pathogenic bacteria, mammals do not synthesize folic acid. The first results helped to explain the action of sulfonamides: the latter compounds displace *p*-aminobenzoic acid in the synthesis of folic acid, thus the action of the dihydrofolic acid synthetase enzyme is inhibited. Further progress was due to sequential blocking achieved by the combined use of Trimethoprim and sulfonamide, which inhibit the synthesis of the tetrahydrofolate co-enzyme at two consecutive stages (Trimethoprim blocks dehydrofolate reductase). A new, promising field of research is offered by biopterin which carries the 1',2'-dihydroxypropyl side chain in position 6; the tetrahydro variant of this compound performs important *in vivo* hydroxylations with molecular oxygen (phenylalanine → tyrosine; catecholamines from the latter; hydroxylation of tryptophan).

In another lecture, E. C. TAYLOR reported on his work on the synthesis of pteridines. Condensation of α-aminonitriles with α-oximinocarbonyl compounds yields pyrazine-1-oxide. The advantage of this novel approach consists in its flexibility and the unequivocal synthesis exclusively of 6-substituted, or of 7-substituted pteridines. Pyrazine-1-oxide, as well as pteridin-8-oxide derived therefrom, allows a number of transformations at position 7. An anomalous transformation can also be achieved: with a mixture of trifluoroacetic acid and trifluoroacetic anhydride a trifluoroacetic group can be introduced at position 6.

The paper by H. C. S. WOOD is also of special interest, describing the inhibition, at a new phase, of the fully explained course of the biosynthesis of dihydrofolic acid. In a preceding phase, 6-hydroxymethylpterin is converted into pyrophosphate by the use of adenosine triphosphate; pyrophosphotinase is the enzyme of the process. From among a number of groups of compounds, 7,8-dihydro-7,7-disubstituted pteridines proved effective for blocking this enzyme.

A comprehensive review on 7-azapteridines was presented by D. J. BROWN. One of the important trends in this field is the modification of the side chain of folic acid, partly by varying the distance between the pteridine and the benzene rings, and partly by replacing the N^{10} atom originating from *p*-aminobenzoic acid, *e.g.* by S (H. G. MAUTNER, R. L. KISLIUK, M. G. NAIR).

J. A. MONTGOMERY describes an improved synthesis of methotrexate, a drug for the treatment of leukaemia, differing from folic acid by containing an imino (amino) group instead of the 4-oxo group and substituted with a N^{10} methyl group.

In conclusion it can be stated that this book is useful primarily for those who are active workers in the field of pteridine chemistry.

K. HARSÁNYI

T. Braun and E. Bujdosó (Eds): *Nuclear Methods in Physical Chemistry* (Proceedings of the 8th Radiochemical Conference)

Akadémiai Kiadó, (Publishing House of the Hungarian Academy of Sciences),

Budapest 1976, 601 pages.

The radiochemical conferences organized biennally in Czechoslovakia have already gained a remarkable reputation since they summarize the most up-to-date achievements in the field in general and at the same time cover special topics of temporary interest. The proceedings of the 8th conference prove these statements. This volume contains the full text of the lectures held at Mariánské Lázne (April 27—May 2, 1975) which already appeared in the Journal of Radioanalytical Chemistry.

The preface (written by the chairman and the general secretary of the conference) is followed by the opening address delivered by the representative of the Czechoslovak Atomic Energy Commission and a general review referring to the main trends in the developments of nuclear power engineering in the Czechoslovak Socialist Republic.

Five plenary lectures were held by invited speakers who rendered possible to get an insight into the recent developments achieved at leading radiochemical laboratories.

The text of the 53 individual lectures is presented in the following eight groups according to the sections of the conference: Ion Exchange, Trace Radiochemistry, Stable Isotopes — Isotopic Exchange, Liquid–Liquid Distribution, Radiation Chemistry, Catalysis — Diffusion, Labelled Compounds, Other Applications and Techniques. At the end of the volume one gets information regarding the twenty years existence of the Department of Nuclear Chemistry of the Technical University of Prague.

The general get-up of the compilation is excellent. The perspicuous figures and tables as well as the conscientious printing contribute to its prospective success. The setting up of every single paper is systematically constructed praising the fatiguing work of the editors and that of the authors.

There is little to be added to the concluding sentence of the preface of the proceedings: it can be taken as granted that the written text of the conference is a contribution to the progress of science and the Publishing House of the Hungarian Academy of Sciences shares the merits of the organizing committee.

T. Lengyel

G. H. Wagnière: *Introduction to Elementary Molecular Orbital Theory and to Semiempirical Methods*

Springer-Verlag, Berlin—Heidelberg—New York 1976, 109 pages.

The increasing importance of quantum chemistry results in appearing of more and more textbooks on the topic. This booklet is a valuable piece of the vast selection. Intended for graduate students the hierarchy of approximations is outlined in an inductive manner. Simple Hückel, PPP as well as the more advanced all-valence electron methods (EHT, CNDO) are treated. Special topics as optical activity, selection rules for electrocyclic and cycloaddition reactions, periodic structures are handled, too. The language is strictly mathematical but qualitative chemical aspects are enlightened with special care. Thirty-three illustrative figures make the book as didactic as possible. It is a pity that comparative tables, concerning the reliability of the different methods, are completely missing. According to the absence of the numbering of the mathematical equations referring to them is rather complicated. Despite these minor objections this book yields a useful tool in understanding elementary molecular orbital theory.

G. Náray-Szabó

Topics in Current Chemistry, Vol. 61

Volume 61 of the series "Topics in Current Chemistry, Fortschritte der chemischen Forschung" (Springer Verlag, Berlin—Heidelberg—New York) was published in 1976 entitled: "Physical and Chemical Application of Dyestuffs" (187 pages).

The authors of the four independent chapters have reported several novel applications of substances which are known as dyestuffs, together with some of their properties not investigated so far.

Chapter One has the title "Organic Dyes in Laser Technology" by Fritz Peter SCHÄFER (Max-Planck-Institut für Biophysikalische Chemie).

A passive Q-switching using organic dyes was achieved as early as 1964. The application of dyestuffs in laser technology has become more and more important since then. A further physical possibility is expected in the field of dyestuff–light interaction in the spectral ranges of visible light, near ultraviolet and infrared. From the chemical point of view, the almost inexhaustible varieties of dye syntheses and their low prices make their application attractive.

Nonlinear light absorption of dyestuffs permits their use in laser technology in the fields of passive Q-switching pulse shaping, measurement of intensity of high-energy ultrashort pulses, optical isolation between amplification levels of solid lasers and pulse width measurements of ultrashort pulses by means of the two-photon-fluorescence method.

Lasers with dyestuffs utilize the fluorescence of dyes. Their nonlinear polarizability is used for the output frequency tripling in high intensity lasers.

In this respect, every organic compound containing a conjugated double bond system is regarded as 'dyestuff' in a wider sense.

This chapter occupies the first 30 pages of the volume. This short summary, sufficient for those familiar with the topic, contains 70 references giving adequate further information for those who are interested in the details of the subject.

Chapter Two is entitled "Reaction of Excited Dye Molecules at Electrodes" by Heinz GERISCHER and Frantz WILLIG (Fritz—Haber-Institut der Max-Planck-Gesellschaft).

In solutions of dye molecules excited by light, redox reactions occur at electrodes behaving as an electron acceptor or electron donor.

The probability of the reaction is the function of the lifetime of the excited state as well as of the coupling intensity, and of the structures of dye molecules and the electrodes.

In photochemical redox reactions, primary electron transfer is often compensated by electron transfer between the reaction products. In the case of heterogeneous electron transfer effected by electrodes, the above-mentioned undesirable secondary process can be prevented, provided that the electric field is appropriate. The reactions of dyestuff-sensitized silver halides, zinc oxide and other photographic materials have been studied in this way.

The chapter occupying the pages of the volume between 31 and 84 deals with the redox properties of excited molecules, redox processes in semiconductor and organic insulator electrodes, adding 108 references to the written text.

The author of Chapter Three ("Application of Semiconductor Properties of Dyes; Possibilities and Problems") is Hans MEIER (Staatliches Forschungsinstitut für Geochemie). The electronic conductivity of organic dyes was first studied in the early 1950's for the elucidation of the mechanism of spectral sensitization processes. Some organic dyes as well as other compounds (such as charge transfer complexes) have proved to be semiconductors of great importance. Nevertheless, the possibility of their industrial application has been a subject of dispute up to now.

The chapter describes the mechanisms of dark- and photoconductivity, the clarified correlations between the structure of organic compounds and their electric properties, the role of the latter characteristics in industrial processes (lightfastness, spectral sensitization, catalytic processes, electrocatalysis in fuel cells) and finally, the possibilities of application based on the electric properties of dyestuffs (rectifying, microwave generation, thermoelectric devices, gas detectors, electric energy storage, pressure indication, organic supraconductors, photoresistors, Vidicon television pickup tubes, reprography, etc.). The chapter is presented between pages 85 and 131 and contains 176 references.

Chapter Four is "Organic Dyestuffs as Catalysts for Fuel Cells" by Horst JAHNKE, Manfred SCHÖNBORN and Georg ZIMMERMANN (Robert Bosch GmbH, Research Centre).

Dyes with an N_4-chelate structure are very active electrocatalysts. The first such effect recognized was the oxidation acceleration effect of phthalocyanins (similar to that of haemoglobin); later, other useful N_4-chelates have also been found. In this chapter 24

compounds are described; of these, CoTAA (dihydrodibenzotetraazaannulene) catalyzes anodic oxidation, whereas the other 23 are catalysts in cathodic processes.

This chapter is found between pages 133 and 181, with 59 references to assist further studies.

The volume covers the literature up to 1975 inclusive, and it is a source of useful information not only for those interested in details described in the chapters, but also to scientists working in borderline fields. Appreciation of the details requires, however, a profound knowledge of the special fields.

I. RUSZNÁK

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РЕЗЮМЕ

Исследование отечественных и иностранных летучих масел, VI

Производные кумарана в летучем масле укропа

К. БЕЛАФИ-РЕТИ и Э. КЕРЕНИ

При исследовании качественного и количественного состава летучего масла, полученного при перегонке с паром и последующем рафинировании укропа, были найдены два компонента, которые до сих пор не были обнаружены в укропном масле и в других летучих маслах. Одним из этих неизвестных компонентов, присутствующим в больших количествах (порядка процента) — на основе спектрометрических, в первую очередь ЯМР исследований, а также спектрометрических структурных исследований, проведенных с продуктами химических превращений — оказался 3,7-диметил-4,5,6,9-тетрагидрокумаран. В микроколичествах (порядка сотой процента) был обнаружен другой, родственный по строению компонент — 3,6-диметилкумаран. Отношение этих двух компонентов друг к другу, в пределах данного интервала, сильно зависит от зрелости и метода обработки растений.

Исследование некоторых комплексов хрома(III) с основаниями Шиффа; расчет энергий экстрасвязей в октаэдрических комплексах с лигандами слабого поля

П. СИНГ, В. СИНГ, Г. П. ПОХАРЯЛ и Р. П. МАХЕШ

Были исследованы спектральные и магнитные свойства комплексов хрома(III) с N-2,5-дигидроксиацетофенацилиденантраниловой кислотой (H_3DAPA) и N-2,5-дигидроксиацетофенацилиден-п-диметиламиноанилином (H_2DAPDA), а также рассчитаны параметры лигандного поля этих комплексов. Спектры комплексов $[Cr(C_{15}H_{11}O_4N)Cl(H_2O)_2]$, $[Cr(C_{15}H_{11}O_4N)Br(H_2O)_2]$, $[Cr(C_{16}H_{17}N_2O_2)_2Cl(H_2O)]$ и $[Cr(C_{16}H_{17}O_2N_2)_2Br(H_2O)]$, с лигандами слабого поля были интерпретированы, рассчитывая энергии экстрасвязей второго и третьего спин-разрешаемых переходов.

Лигандное замещение и строение комплекса, XIV

Спектры ПМР комплекса бис(N-метилсалицилидениминато)никеля(II)

Й. ЧАСАР и Т. САБО

Спектры ПМР комплекса бис(N-метилсалицилалдиминато)никеля(II) и его бис-пиридино производного были исследованы в зависимости от температуры. Исходя из полученных результатов, были сделаны заключения относительно строения молекул, присутствующих в растворе.

Исследование механизма изомеризации н-бутена на кислых катализаторах, III

Энергетическая схема превращений

Д. КАЛЛО, Э. ДЕТРЕКЁИ и Г. ШАЙ

Были определены начальные скорости превращений всех трех изомеров н-бутена на трех основных типах активных форм цеолитных катализаторов, а именно на H-, Mg- и Ni-клиноптилолитах при различных давлениях и различных температурах. Эти данные подвергались обработке согласно кинетическим зависимостям, выведенным ранее. На основе температууной зависимости параметров, характерных для отдельных реакций, была составлена энергетическая схема превращений. Т. о., с одной стороны экспериментально была подтверждена энергетическая схема каталитических превращений, выведенная ранее теоретически, а с другой стороны, с помощью этого нового кинетического метода уточнялся механизм реакций изомеризации. Оказалось, что изомеризация н-бутена на H-клиноптилолитах протекает через образование общего поверхностного промежуточного продукта, а в случае Mg- и Ni-клиноптилолитов образуется несколько поверхностных промежуточных продуктов, не равновесных друг с другом. На Ni-клиноптилолите поверхностная трехугольная реакция, лимитирующая скорость процесса, протекает между изомерами, находящимися в адсорбционном равновесии. Т. о., на основных формах активных модификаций процесс протекает по различным механизмам.

Адсорбция газовых смесей на твердых гетерогенных поверхностях, II

Многослойная адсорбция

М. ЯРОНИЕЦ, Й. ТОТ и В. РУДЗИНСКИ

Многослойная адсобция из бинарных газовых смесей на гетерогенных твердых поверхностях обсуждается на основе обобщенного интегрального уравнения Гонзалеса и Холланда для изотермы местной адсорбции. Обсуждаются суммарные изотермы многослойной адсорбции из бинарных газовых смесей для гауссовского и экспоненциального распределения энергии. Эти изотермы были получены, используя изотермы однослойной адсорбции, которые обсуждаются в первой части этой серии сообщений.

Некоторые вопросы адсорбции тиокарбамида на электродах благородных металлов

ДЬ. ХОРАНИ и Э. РИЗМАЙЕР

Адсорбция тиокарбамида была исследована с помощью радиоактивной техники. Было установлено, что измерению адсорбции на золотом электроде мешают как окисление тиокарбамида, так и растворение золота. При низких потенциалах, где эти влияния могут быть минимализированы, адсорбция представляет собой обратимый процесс.

Спектральное и магнитное исследования комплексов индазола и 5-нитроиндазола с Co(II) и Ni(II)

С. А. А. ЗАИДИ, А. С. ФАРУКИ и Н. СИНГАЛ

Были приготовлены некоторые новые комплексы с общей формулой $M[L]_2X_2$ или $M_1L]_2X_4$ (где M = Co(II) или Ni(II), L = индазол или 5-нитроиндазол, а X = Cl^-, Br^-, NO^-, 1/2 SO_4, SCN^-). Все эти комплексы были охарактеризованы данными элементарного анализа, их ИК и электронными спектрами, а также данными измерений магнитных моментов. Было найдено два различных типа комплексов. Комплексы индазола являются мономерными и бидентатный лиганд координируется как через пиридильный, так и через пиррольный азот, а комплексы 5-нитроиндазола являются полимерными и лиганд монокоординирован через пиррольный азот. Исходя из электронных и ИК спектров, а также измерений магнитных моментов, было заключено, что все эти соединения обладают октаэдрической геометрией.

Исследование реакционной способности карбонильной группы флавоноидов, III

Основность 2'-гидрокси- и 2'-бензилоксихалконов

Е. Р. ДАВИД, Г. Й. САБО, М. РАКОШИ и ДЬ. ЛИТКЕИ

Описывается определение постоянных основности 2'-гидрокси- и 2'-бензилоксихалконов, исходя из изменений в УФ спектрах, вызванных различными заместителями, а также используя кислые функции H_0. Величины этих постоянных основности собраны в таблицах III и IV.

О конфигурации капсантинэпоксидов

М. БАРАНЯИ, Й. КАЙТАР, ДЬ. БУЙТАШ и Й. САБОЛЬЧ

С помощью хроматографии «капсантинэпоксид» удалось разделить на два диастереомера: капсантинэпоксид А и капсантинэпоксид В. На основе исследований H^1—ЯМР, ДОВ и ЦД капсантинэпоксид А содержит конечную группу типа виолаксантин А (3*S*, 5*S*, 6*R*), а капсантинэпоксид В — виолаксантин В (3*S*, 6*R*, 6*S*).

Окислительная перегруппировка халконов нитратом таллия(III), VII

Синтез одоратина и 7-гидрокси-2', 4', 5', 6-тетраметоксиизофлавона

Ж. КАРДОШ-БАЛОГ, Л. ФАРКАШ и А. ВОЛЬФНЕР

Синтез 3',7-дигидрокси-4',6-диметоксиизофлавона (одоратин *1*) и 7-гидрокси-2',4',5', 6-тетраметоксиизофлавона (*2*) — двух производных изофлавонов из тропической древесины — был осуществлен окислительной перегруппировкой соответствующих халконов с помощью $Tl(NO_3)_3$, которая является ключевой ступенью всего синтеза.

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SENSITIZED FLUORESCENCE OF NAPHTHACENE BY 3,4-BENZPYRENE AND ITS ANALYTICAL APPLICATION

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Received June 1, 1976

Under the effect of UV light, 3,4-benzpyrene on Whatman paper emits a fluorescence spectrum consisting of a broad band. At 77 K the band structure splits into three sub-bands. Solid-state 3,4-benzpyrene sensitizes the fluorescence of naphthacene; this phenomenon can readily be interpreted by the delayed triplet-triplet mechanism. Its application for the quantitative determination of naphthacene is described.

Introduction

In recent years, spectrofluorometric analysis and quantitative determination of 3,4-benzpyrene (BP) has become an increasingly important problem in relation to cancer research. This compound has strong carcinogenic properties. Its presence has been identified among air-polluting substances [1—5], in cigarette smokes [6, 7], in exhaust gases of automobiles [8], in petroleum products [9, 10] and in smoked food products [11]. Several analytical procedures for its separation and identification are known [12—15]. Fluorescence properties of 3,4-BP have been investigated in solution [16, 17], in the crystalline state [18, 19] and as a solid solution frozen in paraffinic hydrocarbons [20]. The 3,4-BP sensitizes the emission of other polycyclic aromatic compounds fluorescing weakly or not at all, if incident light corresponding to the absorption band of 3,4-BP is used [21]. As a result of energy transfer, the fluorescence of 3,4-BP substantially decreases, while the characteristic emission of naphthacene becomes dominant. The phenomenon of sensitized luminescence has not yet been studied in this system. The fluorescence intensity of 3,4-BP changes proportionally to the naphthacene content, and hence the phenomenon can be utilized for analytical purposes. The fluorescence properties of 3,4-BP on Whatman paper at room temperature and at 77 K was studied. The sensitized fluorescence of naphthacene was investigated a procedure for the quantitative determination of naphthacene was developed.

Experimental

Measurements were made on a Hitachi MPF—SA spectrofluorimeter equipped with corrected accessory. At 77 K measurements the phosphorescence attachment of the instrument was used. The substances studied were products of FERAK and REANAL. Preliminary

tests indicated that their purity was satisfactory, so that no further purification was performed. A 5.10^{-3} *M* solution in benzene was prepared from 3,4-BP, and Whatman paper strips were immersed into the solution. About 15 minutes after the evaporation of the benzene, the fluorescence spectrum of 3,4-BP was measured with 365 nm exciting light. The exciting slit was set to 8 nm, the emission slit to 2 nm. Varying quantities of naphthacene were then added to the solution of 3,4-BP in benzene, and the sensitized fluorescence of naphthacene was measured at the same slit conditions, on Whatman paper strips immersed in the solution. The naphthacene amounts varied between 10^{-9} and 3.10^{-4} *M*, and fluorescence intensities were measured at one maximum each (at 465 nm, for 3,4-BP and at 498 nm for napthacene).

Results and discussion

3,4-BP emits a fluorescence spectrum consisting of one broad band (Fig. 1). The spectrum covers the whole visible range, with a maximum at 456 nm. The characteristic of the spectrum reveals that it is the result of the coalescence of a multi-band structure. When cooled down to 77 K, the bands separate, and a three-maxima structure is formed, with peaks at 439, 466 and 500 nm, respectively. The intensity decreases from band to band in the direction towards the longer wavelength, by a factor of about 1/3.

With 3,4-BP, containing naphthacene, the characteristic bands of both substances are present in the emission spectrum as a result of sensitized fluorescence (Fig. 2). Increasing amounts of naphthacene lead to a gradual decrease in the intensity of 3,4-BP fluorescence. At a defined naphthacene concentration, this fluorescence completely disappears, and only the luminescence of naphthacene is observable. The bands at 423 and 456 nm in the short wave range of the fluorescence spectrum belong to the luminescence of 3,4-BP, while the maxima at 498, 533 and 570 nm originate from the fluorescence

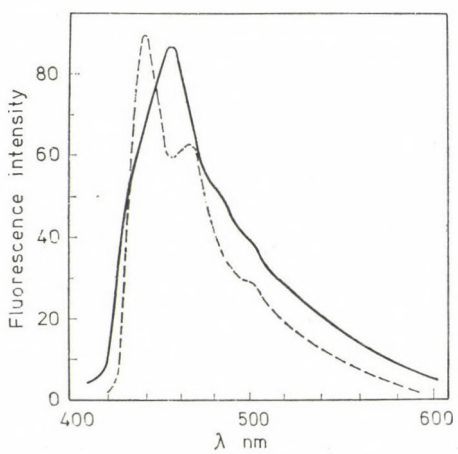


Fig. 1. Fluorescence spectrum of the 3,4-benzpyrene on Whatman paper: ——— at room temperature; — — — at 77 K.

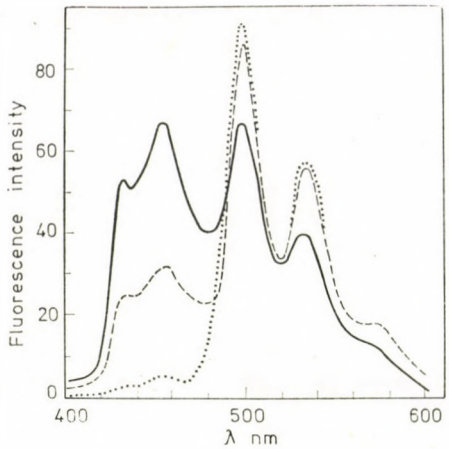


Fig. 2. The fluorescence intensity change of the 3,4-benzpyrene-naphthacene system for different naphthacene concentrations on Whatman paper. Conc. of naphthacene: ..... 10^{-5}- — — — — 10^{-6}; ——— 3.10^{-7}; Ml^{-1}.

of naphthacene. The phenomenon of sensitized fluorescence can readily be interpreted by the triplet-triplet mechanism of delayed fluorescence [22]:

$$^3D + {}^3D \longrightarrow {}^1D^* + {}^1D$$

$$\downarrow$$

$$^1D + h\nu'$$

(1) delayed 3,4-benzpyrene emission

$$^3D + {}^3A \longrightarrow {}^1A^* + {}^1D$$

$$\downarrow$$

$$^1A + h\nu''$$

(2) delayed naphthacene emission

where *D* is the symbol for the donor, *A* the symbol for the acceptor, 1 and 3 for the singlet and triplet, resp., and asterisk for the excited singlet energy. It may be seen from process (1) that if the concentration of donor triplets is high, the delayed fluorescence of 3,4-BP can be detected. At a sufficiently high donor concentration, deactivation takes place by the interaction of the mixed triplets, resulting the sensitized fluorescence emission of naphthacene (process (2)). When the concentration of naphthacene reaches a value that is lower by only about one order of magnitude than the 3,4-BP concentration, process (1) will successively decrease, *i.e.* the fluorescence emission of the donor will disappear. At a further increase of the ratio of naphthacene to 3,4-BP, the donor triplets will not be able to support the process (2), and

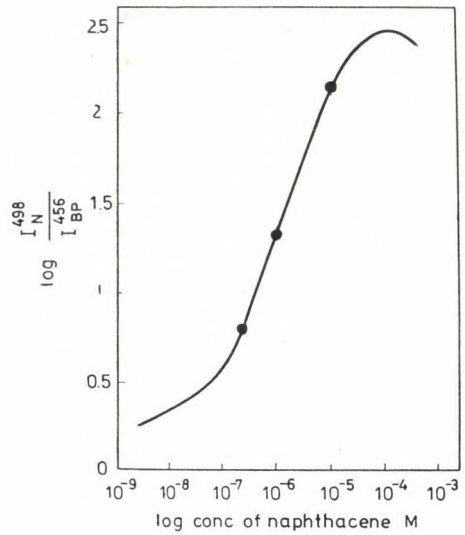


Fig. 3. Intensity ratio of the fluorescence of 3,4-benzpyrene containing naphthacene vs. naphthacene concentration. I_N^{498} = naphthacene intensity at 498 nm. I_{BP}^{456} = 3,4-benzpyrene intensity at 456 nm.

hence the fluorescence emission of the system will begin to decrease. This situation is shown in the upper part of Fig. 3, where the ratio of the fluorescence intensities of naphthacene and 3,4-BP are plotted against naphthacene concentration. In the linear part of the curve, the concentration ratio of donor to acceptor is $D \gg A$, while in the upper section of the curve, $D \approx A$. At low naphthacene concentrations, the deviation from linearity is probably due to the effect of other trace impurities. The total concentration range of the curve is suitable for analytical purposes. Using a calibration curve as low as $3 \cdot 10^{-9}$ M naphthacene could be determined. In the linear range, the relative error between parallel measurements is about 1 per cent; in the lower and upper sections of the curve it reaches values of 8 to 10 per cent. At 77 K, however, the fluorescence intensity of the 3,4-benzpyrene-naphthacene system increases by a factor of about 8, so that at this temperature, the sensitivity of naphthacene determination will be increased by almost one order of magnitude.

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PROPERTIES OF ALCOHOL–AMINE MIXTURES, XIV

THE AVERAGE DEGREE OF ASSOCIATION

F. RATKOVICS and T. SALAMON

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Received June 6, 1976

The density at 20 °C and the dynamic viscosity in the temperature range from 20 th 40 °C were measured in mixtures of 1-butanol with mono-, di- and tri-(n-butyl)--amine.

The activation enthalpy of viscous flow and the average degree of association were calculated from the viscosity data as a function of the composition. Earlier information on the association of alcohol–amine mixtures has been completed by conclusions from these measurements. The enthalpy of formation of the OH...N bond is larger then those of the O—H...O and N—H...N bonds. Qualitative conclusions are possible regarding the formation of mixed alcohol-amine species of various structures.

In studies on the association conditions of alcohol-amine mixtures it has been shown that if primary, secondary or tertiary amines are mixed with alcohols, mixed associated species (containing both alcohol and amine) are obtained [1—4]. In order to determine the degree of association, we have applied our method, based on the activation enthalpy of viscous flow, to alcohol–amine mixtures [6]. In this paper, we report the results of experiments performed on the 1-butanol–*n*-butylamine, 1-butanol–di(*n*-butylamine) and 1-butanol–tri(*n*-butyl)amine mixtures.

The viscosities of mictures were determined with a Höppler viscosimeter. The densities were measured with a DMA 02C digital densimeter. Pure 1-butanol was used as reference substance.

The viscosity measurements were performed in the temperature range of 20—40 °C. The results are listed in Tables I, II, III.

Table I

Density (ϱ) and dynamic viscosity (η) of the 1-butanol–n-butylamine mixture as a function of the amine mole fraction (x_{am})

x_{am}	ϱ (g/cm³)	Dynamic viscosity η (cP)				
	20 °C	20 °C	25 °C	30 °C	35 °C	40 °C
0.000	0.8100	2.94	2.45	2.28	1.92	1.73
0.140	0.8044	2.39	2.06	1.75	1.53	1.36
0.305	0.7962	1.87	1.59	1.35	1.20	1.11
0.516	0.7828	1.23	1.10	0.98	0.88	0.78
0.684	0.7697	0.88	0.81	0.74	0.66	0.61
0.931	0.7498	0.60	0.54	0.50	0.47	0.45
1.000	0.7439	0.53	0.50	0.47	0.43	0.41

Table II

Density (ϱ) and dynamic viscosity (η) of the 1-*butanol–di(n-butyl)amine mixture as a function of the amine mole fraction (x_{am})*

x_{am}	ϱ (g/cm³)	Dynamic viscosity η (cP)				
	20 °C	20 °C	25 °C	30 °C	35 °C	40 °C
0.000	0.8100	2.95	2.45	2.28	1.92	1.73
0.091	0.8079	2.70	2.43	2.11	1.91	1.70
0.272	0.7971	2.32	1.93	1.72	1.53	1.42
0.440	0.7901	1.74	1.51	1.36	1.32	1.09
0.510	0.7865	1.56	1.39	1.24	1.11	1.02
0.702	0.7758	1.19	1.06	0.96	0.87	0.82
0.919	0.7648	0.94	0.84	0.78	0.73	0.68
1.000	0.7609	0.85	0.79	0.73	0.68	0.64

Table III

Density (ϱ) and dynamic viscosity (η) of the 1-*butanol–tri(n-butyl)amine mixture as a function of the amine mole fraction (x_{am})*

x_{am}	ϱ, g/cm³	Dynamic viscosity η, cP				
	20 °C	20 °C	25 °C	30 °C	35 °C	40 °C
0.000	0.8100	2.95	2.45	2.28	1.92	1.73
0.102	0.8056	2.60	2.30	2.02	1.80	1.55
0.311	0.7968	2.08	1.91	1.70	1.48	1.41
0.488	0.7904	1.78	1.67	1.49	1.30	1.16
0.661	0.7856	1.58	1.49	1.31	1.16	1.08
0.880	0.7802	1.44	1.33	1.18	1.08	1.02
1.000	0.7772	1.35	1.23	1.12	1.01	0.94

Discussion

From viscosity *vs.* temperature data, the activation enthalpy of viscous flow has been determined in the three mixtures as a function of the composition, in the temperature range of 20—40 °C.

In the calculation process we assumed that, within a relatively narrow temperature range, the temperature dependence of the activation enthalpy of viscous flow may be neglected. By the method of least squares, we have determined the equations of the best η *vs.* $\frac{1}{T}$ straight lines connecting points of the same mole fraction. The errors of the activation enthalpies have been calculated [7] from the scatter of the data (σ).

Table IV

Average enthalpy of activation (H_v) of viscous flow, and average degree of association (α) for the 1-butanol–n-butylamine mixture as a function of the amine mole fraction, in the temperature range of 20—40 °C

x_{am}	H_v (kcal/mol)	α
0.000	4764 ± 395	4.03 ± 0.37
0.140	5179 ± 158	4.45 ± 0.15
0.305	4822 ± 415	4.11 ± 0.40
0.516	4117 ± 87	3.44 ± 0.08
0.684	3403 ± 123	2.76 ± 0.12
0.931	2601 ± 267	2.00 ± 0.25
1.000	2411 ± 153	1.83 ± 0.14

Table V

Average enthalpy of activation (H_v) of viscous flow, and average degree of association (α) for the 1-butanol–tri(n-butyl)amine mixture as a function of the amine mole fraction, in the temperature range of 20—40 °C

x_{am}	H_v (kcal/mol)	α
0.000	4764 ± 395	4.03 ± 0.37
0.102	4644 ± 178	3.40 ± 0.11
0.311	3752 ± 334	2.10 ± 0.21
0.488	4011 ± 373	1.92 ± 0.20
0.661	3670 ± 325	1.51 ± 0.15
0.880	3264 ± 231	1.13 ± 0.09
1.000	3346 ± 100	1.07 ± 0.04

From the known activation enthalpies of viscous flow, using a previously elaborated method [6], we have calculated the average degree of association (α) as a function of the composition.

The results are summarized in Tables IV, V and VI (Fig. 1).

As far as the accuracy of the results is concerned, the errors of the activation enthalpies are slightly greater than those in pure alcohols and in alcohol–hydrocarbon mixtures. This is due to some variation of the activation enthalpy of viscous flow in alcohol–amine mixtures even in the relatively narrow temperature range examined.

Table VI

Average enthalpy of activation (H_v) of viscous flow, and average degree of association (α) for the 1-butanol–di(n-butyl)amine mixture as a function of the amine mole fraction, in the temperature range of 20—40 °C

x_{am}	H_v (kcal/mol)	
0.000	4764 ± 395	4.03 ± 0.37
0.091	4234 ± 143	3.35 ± 0.13
0.272	4096 ± 238	2.86 ± 0.19
0.440	4174 ± 127	2.65 ± 0.09
0.510	3906 ± 111	2.36 ± 0.08
0.700	3428 ± 215	1.85 ± 0.13
0.920	2866 ± 193	1.35 ± 0.11
1.000	2795 ± 42	1.26 ± 0.02

Properties of the butanol–tri(n-butyl) amine mixture

In accordance with our former results, the properties of the system can be interpreted in the following way.

Pure 1-butanol contains mainly multimers with cyclic structures. In addition to these, linear associated species are also present in significant amounts. The concentration of monomer molecules does not surpass 1 mol % (7). Upon the addition of triamine to butanol, this will form mixed associated species of type A_iB, with the linear associated alcohol species. (A denotes an alcohol while B an amine molecule.)

The determination of the composition of mixed associated species containing both alcohol and amine molecules is considerably facilitated by the fact that tertiary amines can form only such associated species with alcohols which contain a single amine molecule. (The unshared electron pair on the nitrogen atom of the tertiary amine forms a hydrogen bond with the hydroxy hydrogen of the alcohol molecule.) As the concentration of monomeric alcohol is very low the examined mixtures studied [10], the linear alcohol multimers should also be involved in mixed association, through their terminal hydroxy groups. The highly exothermic differential heat of mixing [10] observed at low amine concentrations can be explained by the formation of N . . .H—O hydrogen bonds in the mixed associated species.

As according to viscosity data, the average degree of association of the mixture is lower than that of pure butanol, the simultaneous association equilibrium between associated species of different types (cyclic and linear

alcohol, and linear mixed associated species) presumably changes as follows.

In the alcohol–triamine mixture, the association equilibrium between linear alcohol multimers is shifted by the formation of mixed associated species toward the disintegration of the alcohol chains. Thus the formation of mixed associated species containing fewer alcohol molecules seems likely at low amine concentrations. Also the previously considered possibility that the enthalpies of formation of the OH . . .O and OH . .N hydrogen bonds may be nearly the same, can be excluded. The decrease in the degree of association, observed simultaneously with the exothermic heat of mixing, can be interpreted only if the hydrogen bonds between mixed associated species are stronger than those formed between associated alcohol species.

According to denductivity data obtained at low amine concentrations, in the *n*-butanol–tri(*n*-butyl)amine mixture, the average number of alcohol molecules in A_iB type mixed associated species is $n \sim 9$, which seems to contradict the facts mentioned in the former paragraph. However, as already shown [9], conductivity data permit conclusions only on the average degree of association of electrolytically dissociating mixed associated species. As this is mainly characteristic mixed associated species containing several alcohol molecules, the dissociation constant decreases with *i*, *i.e.* the number of alcohol molecules bound in the mixed associated species. Therefore, it seems very likely that the average degree of association of A_iB species is significantly lower than that expected from conductivity measurements, and the triamine is primarily present in mixed associated species containing alcohol molecules. This is in line with the very low specific conductivity of the mixture (1 μS/cm). Consequently, very few dissociated particles are present in the system.

In parallel with the rapidly decreasing average degree of association observed at higher triamine concentrations, the heat of mixing decreases rapidly too [10], although the effect remains exothermic. This can be explained by the following considerations. Upon dilution with the triamine, the cleavage of cyclic alcohol multimers starts at amine mole fractions $0.1 < x_{am} < 0.4$, resulting in the formation of linear multimers. In our opinion, this process is similar to that taking place in alcohol–alkan mixtures (7). Besides the decrease of the number of cyclic associated species, the disintegration of linear associated alcohol species and the formation of mixed associated species is continued. The average degree of association of the mixture is $\alpha \sim 2$ in the neighbourhood of equimolar composition, which indicates that a significant part of triamine molecules is already in monomeric form.

In the mixtures with excess amine, mixed associated species continue to form at the expense of the associated species of alcohol. This is supported by the fact that the differential heat of mixing remains exothermic, whereas the degree of association, although more slowly, continues to decrease with increasing amine concentration.

At an amine mole fraction of $x_{am} \approx 0.85$, the sign of the mixing heat is reversed. In the mixtures containing little alcohol an endothermic effect can be observed. Considering our former conclusions, this can only be explained by assuming that a little alcohol added to pure triamine will break the hydrogen bonds, between the alcohol molecules, which shifts the equilibrium toward monomeric alcohol molecules. This explains the endothermic heat of mixing and the average degree of association of about 1. However, we have also to explain why the total amount of monomers formed upon cleavage of the associated alcohol species does not form AB associated species with the triamine molecules. This however, implies an exothermic mixing heat in contrast with experience, since we have supposed that the N . . .HO bonds have a larger enthalpy of formation than the O . . .HO bonds. Furthermore, the above observations concerning the degree of association also do not support the formation of such mixed species as, in this particular range, there is practically no association ($\alpha \sim 1$). We have to refine our physical model in order to achieve an explanation.

First of all, let us accept the conclusion drawn from experimental results that only few AB associated species may be present in the system. In this case, it is correct to assume that if the equilibrium constant is small, the free enthalpy change for the formation of AB mixed associated species cannot be a high negative value. As the enthalpy of formation of the N . . .HO bond is negative, this is only possible, if the formation of AB species involves considerable negative change in entropy.

The negative entropy of formation is related in the first place to the decrease in the number of independent kinetic elements available in the system, as well as to the decrease in the rotational and vibrational degrees of freedom of the monomer molecules upon association. The enthalpy and entropy changes partly compensate one another, which may explain the small equilibrium constant. It should be mentioned that if an alcohol molecule is hydrogen-bonded to a tertiary amine, the degrees of freedom decrease more strongly than for bonding with primary or secondary amines: the three alkyl groups of the tertiary amine fix the alcohol molecule linked to the central nitrogen atom. It is obvious that the equilibrium constant of mixed association is much lower for tertiary, than for primary or secondary amines.

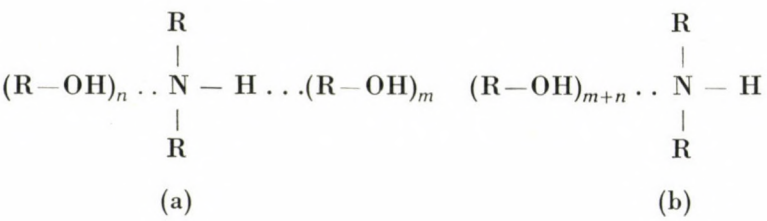
Properties of the 1-butanol–di(n-butyl) amine mixture

We have completed the results of our former studies concerning association in the 1-butanol–di(*n*-butyl)amine system. The following has been established.

The heat of mixing is exothermic in the whole range of concentrations and is considerably higher than that for the tri(*n*-butyl)amine–butanol system

(5). Initially the average degree of association varies with the composition similarly as in the triamine–alcohol system. In mixtures containing more than 10 mol % amine it is higher and decreases almost linearly with the mole fraction of amine. According to conductivity data, the average degree of association of dissociable mixed alcohol–amine species is higher in the $0.0 < x_{am} < 0.5$ range than in the tri(*n*-butyl)amine–butanol mixture.

These experimental results may be explained in the following way. Di(*n*-butyl)amine is inclined to self-association, however, as already mentioned [11], the molecules form mainly linear species. The average degree of association of the pure amine is relatively low. From the activation enthalpy of viscous flow (neglecting the temperature dependence) $\alpha = 1.26$ has been obtained for the average degree of association. This does not differ significantly from the value of $\alpha = 1.1$ [11] determined from dielectric properties on the basis of Kirkwood's g factor. As the structure of mixed alcohol-amine associated species, we may assume that they also form multimers. According to the strongly exothermic heat of mixing observed in addition to the decrease of the average degree of association, we can suppose that the mixed species are mostly of the A_iB (and not of the A_iB_j) type, *i.e.* they contain only a single amine molecule. (In this way, the decrease in the degree of association can be explained also for exothermic mixing heats, if, according to the above, we take into account that the enthalpy of formation of the N . . .HO hydrogen bond is larger than those of the O . . .H . . .O or N . .H—N bonds.) In spite of this, we cannot determine which of the following two possible structures of the A_iB mixed associated species is more likely.



(a) (b)

On the basis of electric conductivity it has been found that the number of alcohol molecules in dissociable mixed species is larger than that in the case of tri(*n*-butyl)amine. This can probably be explained by the simultaneous presence of (a) and (b) structures. It is obvious that the average degree of association of the mixture is greater in the diamine–alcohol than in the triamine–alcohol system.

In accordance with the higher degree of association, the equilibrium constant for the formation of mixed species should be larger in diamine–alcohol than in triamine–alcohol mixtures. In line with the greater heat of mixing

this is due to the smaller entropy effect accompanying association. The smaller entropy change can be explained by the following: the formation of mixed associated species via the cleavage of short diamine polymers, decreases the entropy of the system but slightly, because neither the number of independent elements, nor the degree of freedom of diamine molecules changes considerably.

At the same time, as mentioned before the formation of mixed associated species from monomeric diamine molecules may involve a smaller decrease in entropy than in the case of tertiary amines.

Properties of the 1-butanol–n-butyl-amine mixture

The properties of the 1-butanol–*n*-butylamine mixture have already been discussed (1, 2, 3, 4, 5, 8). As a result of former experiments, the following has been established on the basis of mixing heats, vapour–liquid equilibrium, dielectric properties and conductivity data.

1. The system is characterized by the formation of A_iB_j type associated species.

2. In mixtures containing little amine, mostly A_iB type mixed associated species are formed. Their average degree of association is probably higher than that of pure alcohols. The maximum of the conductivity and of the dielectric loss factor [3] observed at an amine mole fraction of 0.15 is due to some electrolytic dissociation of these mixed associated species.

3. The formation of AB species can be supposed in the neighbourhood of equimolar composition.

4. Relative to the number of amine molecules, the number of alcohol molecules in the mixed associated species continues to decrease in systems containing little alcohol. Formation of AB_j mixed associated species is also possible.

5. In the whole range of compositions alcohol monomers are present in quantities less than 2 mol %.

Now let us investigate, whether the average degree of association calculated from viscosity data is in accord with our statements.

It can be seen in Fig. 1 that upon the addition of amine the average degree of association of the *n*-butanol–*n*-butylamine mixture first increases then at an amine mole fraction of 0.15 it reaches a maximum. The maximum is at the same composition where maxima are observed in the dielectric loss factor and the conductivity [3]. In accordance with our former statements and considering the exothermic mixing heat, A_iB mixed species should be formed in this range. Their electrolytic dissociation results in a high specific conductivity of the mixture.

Considering the endothermic mixing heats obtained in *n*-butylamine–hydrocarbon mixtures [12], the exothermic mixing heats observed in the

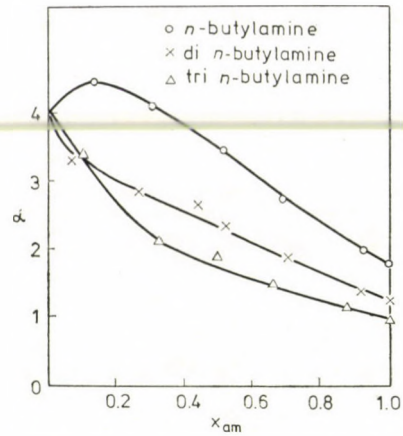


Fig. 1. Average degree of association in mono-, di- and tri(*n*-butyl)amine–l-butanol mixtures as a function of composition in the temperature range of 20—40 °C

present mixture can only be explained by assuming that the enthalpy of O . . .N bond formation is larger than that of OH . . .O bonding even in primary amines. The decrease in the average degree of association of the mixture inside the composition range shows that upon increasing the butylamine concentration, more OH . . .O bonds in alcohol multimers are broken than OH . . .N bonds formed in mixed associated species.

The excess mixing entropy shows a well-defined minimum in the vicinity of equimolar composition [1], indicating that the number of independent elements available the system is the smallest in this range. However, the maximum of the average degree of association is not in this range. So we have to assume that beside undecomposed multimers and A_iB mixed associated species, present also AB complexes are formed in larger amounts. In addition to this, according to conductivity data [8, 13], we have to take into consideration the formation of A_iB_j mixed species, too.

The minimum in the excess molar polarization *vs.* composition diagram [3] is also indicative of the formation of AB associated species.

At amine contents above the equimolar composition, the slope of the h^E/X_{am}(1-am) *vs.* X_{am} curve decreases. This shows that when more amine is added, the differential mixing heat decreases. Since in this range the average degree of association of the mixture shows a monotonous decrease up to pure *n*-butylamine, we have to assume that, according to former experience, although AB_j mixed species may form, owing to the presence of undecomposed alcohol multimers, the mixed associated species can contain but a small number of amine.

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LONE PAIR ELECTRON CONTRIBUTIONS TO THE NATURE OF FORCE FIELD ELLIPSES AND SPECTROSCOPIC CONSTANTS OF DIHALIDES OF GROUP IV A ELEMENTS AND NO_2

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The contribution of lone pair electrons to the molecular constants and force field ellipses of some dihalides of Group IV A elements and NO_2 has been investigated by adopting the formalism of Green's function and partitioning techniques. Essentially, the lone pair is considered in place of atom Z of the XY_2Z type structure assumed for these molecules. The evaluated force constants, symmetrized mean square amplitudes, Coriolis coupling coefficients and potential energy distribution matrices and the generated force field ellipses are also reported for a comparative study and discussion.

1. Introduction

In most recent discussions of molecular geometry [1], the presence of lone pair electrons on the central atom is shown to cause distortions from the structures of highest symmetry, thereby being responsible for the perturbations in the molecular force fields. Attempts have been made previously [2–5] to determine the force fields of systems with lone pairs by adopting the molecular geometries obtainable from electron diffraction or microwave techniques. RAMASWAMY *et al.* [6] have utilized the TORKINGTON kinematic method [7] to calculate the potential energy constants of SF_4. With isotopic frequency data available, however, the GREEN'S function formalism of DEWAMES *et al.* [8] is the most appropriate method to evaluate a unique set of molecular constants. This formalism, employing the partitioning technique has been successfully used by us earlier to obtain modified DEWAMES formulae which take into account the contributions of lone pair electrons. An account of the modified formulae is given in our recent papers on the ozone [9] and tin dichloride [10] molecules and on the coordinated water of titanium complexes [11]. The purpose of the present paper is to examine such lone pair electron contributions to the molecular force field ellipses and other constants (using the above modified formulae) of NO_2 and the following dihalides of Group IV A elements:

$CCl_2^{35,37}$, $SiCl_2^{35,37}$, $GeCl_2^{35,37}$, $SnCl_2^{35,37}$, $PbCl_2^{35,37}$

$^{12,13}CF_2$, $^{28,30}SiF_2$, $^{72,74}GeF_2$ and $^{119,120}SnF_2$

Table I

Molecular parameters used and mixing parameters calculated for the lone pair dihalides and NO_2

No.	Molecule	ω_1 (cm^{-1})	ω_2 (cm^{-1})	ω_3 (cm^{-1})	Y-X-Y Angle, bond length[a] and r	Ref.	Mixing parameters		
							Assumed		Calculated
							ω_1^i (cm^{-1})	ω_2^i (cm^{-1})	c
1	$^{12}CCl_2^{35}$	745.7	490	719.5	112°,		743.7	475.97	Complex
	$^{12}CCl_2^{37}$	743.7	490	716.7	1.7	[19]	742.0	477.06	± 4.627
					0.772		740.0	478.35	± 2.262
							738.0	479.65	± 1.6002
							730.0	484.9	± 1.3712
							726.0	487.58	Complex
2	$^{13}CCl_2^{35}$	723.2	490	698.5	112°,		721.2	475.88	Complex
	$^{13}CCl_2^{37}$	721.2	490	695.5	1.7	[19]	720.0	476.67	± 10.983
					0.772		718.0	479.99	± 2.546
							716.0	479.33	± 1.855
							714.0	480.68	± 1.371
							706.0	486.12	Complex
3	$SiCl_2^{35}$	512.7	248	502	90°,		510.3	240.47	Complex
	$SiCl_2^{37}$	510.3	248	498.7	2.01	[19]	509.0	241.08	Complex
					1.17		507.0	242.03	± 2.174
							505.0	242.99	± 1.290
							503.0	243.95	± 0.86
							501.0	244.93	± 0.544
							499.0	245.91	± 0.185
							498.0	246.40	Complex

4	$GeCl_2^{35}$	399.7	162	374.5	111°,		396.6	156.58	Complex
	$GeCl_2^{37}$	396.6	162	371.5	2.08	[19]	394	157.61	± 2.592
					1.22		390	159.23	± 0.547
							389	159,64	± 0.218
							388.8	159.72	± 0.093
							388.7	159.49	Complex
5	$PbCl_2^{35}$	322.3	100	299.3	96°,		319.5	96.088	Complex
	$PbCl_2^{37}$	319.5	100	295.5	2.46	[19]	316	97.153	Complex
					1.58		315	97.461	± 1.558
							314	97.771	± 0.589
							312	98.40	Complex
6	$^{12}CF_2$	1222	668	1102	105.14°		1191	661.74	± 1.707,531
	$^{13}CF_2$	1191	668	1073	1.3,	[20]			
					0.772				
7	$^{28}SiF_2$	855	345	872	101.13°		843.1	346.166	± 1.759,597
					1.595,	[21]			
	$^{29}SiF_2$	843.1	345	855.1	1.17	[25]			
8	$^{74}GeF_2$	692	263	663	94.2°,	[22]	686.5	266.29	Complex
	$^{72}GeF_2$	686.5	263	656.8	1.732,		692.0	264.17	Complex
					1.22		694.0	263.41	± 1.357,072
							695.0	263.03	± 6.022,07
							700.0	261.0	Complex

Table I (cont.)

No.	Molecule	ω_1 (cm^{-1})	ω_2 (cm^{-1})	ω_3 (cm^{-1})	Y-X-Y Angle, bond lenght[a] and r	Ref.	Mixing prameters		
							Assumed		Calculated
							ω_1^1 (cm^{-1})	ω_2^1 (cm^{-1})	c
9	$^{120}SnF_2$	592.7	197	570.9	94°, 1.91,	[23]	519.4	196.72	± 1.382,833
	$^{124}SnF_2$	519.4	—	569.5	1.4				
10	$^{14}NO_2$	1356.91	754.07	1665.5	134° 2.206,	[24]	1343.55	741.162	± 0.776,660
	$^{15}NO_2$	1343.55	743.76	1628.56	0.74				

[a] Bond length refers to the XY distance (Å)
[b] r is the distance of the lone pair of electrons from the central atom X (Å)

2. Method of calculations

The method consists of estimating the mixing parameter 'c' from the known isotopic frequencies and other data, using the appropriate sum and product rules of the isotope substituted molecules; such mixing parameter data are then utilized to evaluate the molecular constants with the help of the modified formulae reported [11]. For the Y-substituted molecules, the sum and product rules may be found elsewhere [10], while those for X-substitutes are given below:

$$\omega_1^{i2}\,\omega_2^{i2} = \frac{\sigma}{\alpha^2\epsilon + \sigma}\,\omega_1^2\,\omega_2^2 \tag{1}$$

$$\omega_1^{i2} + \omega_2^{i2} = \frac{(\sigma c^2 + \alpha^2\epsilon)\,\omega_1^2}{c^2(\alpha^2\epsilon + \sigma)} + \frac{(\sigma c^2 + \alpha^2\epsilon c^2)\,\omega_2^2}{c^2(\alpha^2\epsilon + \sigma)} \tag{2}$$

where ω's are the vibration frequencies, the superscript 'i' referring to isotopes and

$$\epsilon = \frac{m_x^i - m_x}{m_x}\,; \quad \sigma = \frac{m_x\epsilon}{d_1^2} + 1; \quad C^2 = 1 + c^2$$

$$d_1^2 = m_x + 2m_y + m_e, \quad \alpha = \frac{\sqrt{2m_y}\,m_x^i}{(m_x + m_e)\,d_5}$$

$$\text{and } d_5 = \sqrt{\frac{(m_x + 2m_y + m_e)\,m_x}{(m_x + m_e)}} \text{ with } m_x, m_y, m_e$$

being the masses of atoms X and Y, and of the lone pair respectively.

3. Results and discussion

3.1. *Selection of Mixing Parameters*

Using relations (1) and (2) and those given in Ref. [10], the mixing parameters have been estimated and are reported in Table I. Surprisingly, for all dichlorides and GeF_2, the use of experimentally reported ω_1^i values yields complex values for the mixing parameters. Consequently, a number of possible ω_1^i values are assumed around the experimental value in each case. For dichlorides, these turn out to be less than the experimental values, excepting the case of GeF_2. Thus for each of these molecules, the mixing parameters form a range of finite values with complex limits, the shortest possible range being found for $PbCl_2$. These sets of parameter values and the corresponding ω_1^i values estimated are listed in Table I. From the Table I it may be noted that the mixing parameter decreases in absolute value following the decrease in the values assumed for ω_1^i. Drastic drops in the magnitudes of the mixing parameter upon a slight change in any of the ω_1^i values have been found for

$^{13}CCl_2$ and $GeCl_2$. Hence empirical relations for the mixing parameter values, such as those given by MOHAN *et al.* [12], should be tested with caution when isotopic frequency data are available. Since usually experimental frequencies are assigned with the help of rough estimates following the TELLER-REDLICH rule, the present study indicates, in such assignments, the necessity of a combined approach of utilizing both the TELLER-REDLICH rule and certain criteria of realness of the mixing parameter values.

The selection of an appropriate c value in the absence of a unique ω_1^i value for a given set of isotopically substituted molecules is a difficult, but perhaps not impossible task when one applies the following criteria (1). The experimental assignment of ω_1^i may be uncertain to the extent of a few angstroms. Hence, starting from such an assigned value, a gradual variation on either side of it would give rise to mixing parameter values which are not imaginary (complex). Among such c's, the smaller values may be preferred. Although this criterion reduces the arbitrariness involved in selecting the exact c value, it is still not definite as to which one of the smaller c values is to be chosen. Hence follows the second criterion: (2). Each c value estimated with the corresponding ω_1^i value assumed, may then be utilized to calculate the symmetry force constants and other related constants of the non-isotopic molecule. The latter data are available from the literature for a number of XY_2 molecules, estimated by different methods such as GVFF, VFF, etc., which roughly estimate the *probable* smaller c values. These criteria may lead to already known force fields, however it should be pointed out that GREEN's function and the partitioning method would yield a *consistent* set of force fields (for the molecules being studied) distinct from those provided by other methods and also give information about the molecular vibrations of the isotopic molecule.

The above procedure of selecting the c values (as listed in Table II) is still ambiguous with respect to its sign. Instead of giving the precise *magnitude* of the mixing parameter for the dichlorides $^{12}CCl_2$, $SiCl_2$, $GeCl_2$ and $PbCl_2$, we have used a few of the nearest possible small values of the absolute mixing parameter, *viz.* (2.26, 4.63), (2.175, 2.4), (0.024, 0.02) and (0.4, 0.5, 0.55), respectively. For the rest of the molecules under consideration, the determination of precise c values is quite straightforward *via* the modified expressions reported by us in this paper and elsewhere [10], employing the procedure of DEWAMES *et al.* [8]. Hence there is no need to employ the above two criteria for these molecules when determining their c values.

(3) An exact knowledge of the mixing parameter is possible if the complete set of the isotopic frequencies of a molecule is available. In certain cases, as those studied in this paper, rough estimates of experimental ω_1^i (or ω_2^i) frequency assignments might be available. In such cases, we have a third criterion for fixing the correct ω_2^i value, which would yield real mixing parameters.

3.2. *Force Field Ellipses*

The force field ellipses of the molecules under consideration are generated by varying the mixing parameter in steps of 0.251, starting from the value indicated by a cross on the respective curves of the Figs 1, 2 and 3, and using the modified expressions [11] for F_{11} and F_{12}. The ellipses for $SiCl_2$ resemble closely those reported in this paper and hence are not shown. The ellipses given in the figures are marked with the same serial numbers as of Table I. For comparison, the force field ellipses obtained without considering lone pair effects are also shown for a few molecules by dotted lines. Clearly, the lone pair contribution decreases the inclination of a given ellipse with the F_{11} axis, though not appreciably, as observed in our earlier studies [10] of the $SnCl_2$ molecule. A smaller angle of inclination of the ellipse, according to TORKINGTON's analysis [7], implies an enhanced mass of the central atom. Further, the lone pair electron contribution causes a typical ellipse to contract along its major axis (F_{12}) and elongate along its minor axis (F_{11}), a feature of the type noted recently [11] in force field ellipses of water molecule coordinated to a titanium atom. MULLER *et al.* [13] comment that two extremal properties, *viz.* F_{11} = max. and F_{22} = min., can be simultaneously fulfilled provided m_x (mass of the central atom) is very large. Thus elongation along the F_{11} axis due to the lone pair contribution shifts the F_{11} (max.) point (of the XY_2 structure without a lone pair) to higher values. This also indicates that the lone pair electron contribu-

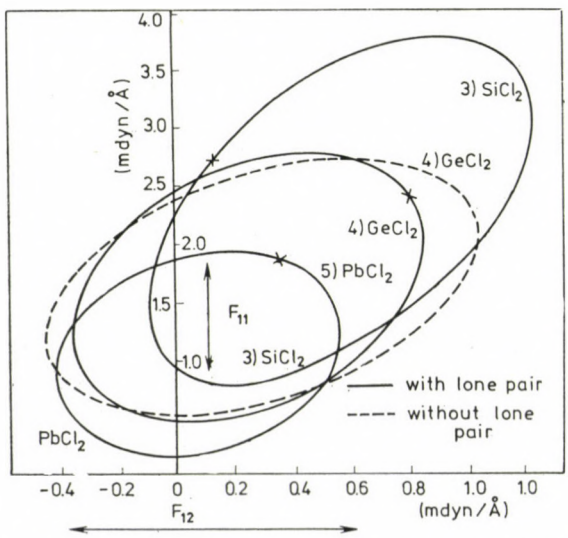


Fig. 1. F_{11} as a function of F_{12}; the cross indicates starting value of the mixing parameter

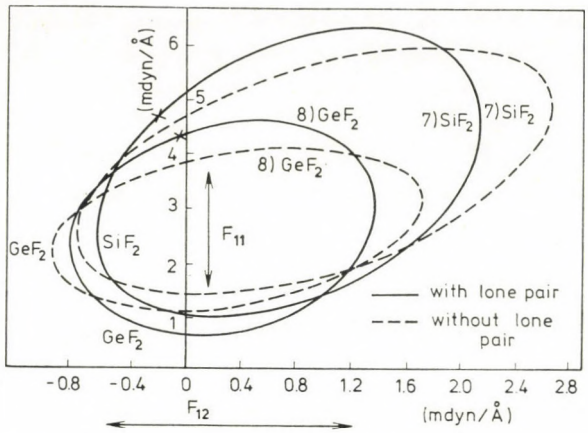


Fig. 2. F_{11} as a function of F_{12}; the cross indicates starting value of the mixing parameter

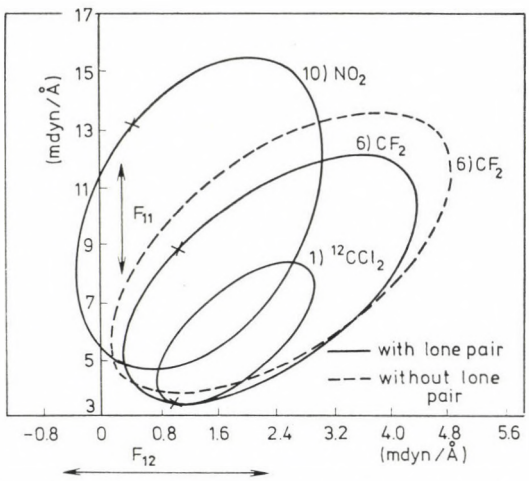


Fig. 3. F_{11} as a function of F_{12}; the cross indicates starting value of the mixing parameter

tion increases apparent mass of the central atom. Again it may be pointed out here that the interaction term of the G matrix, *viz.* G_{12}, is inversely proportional to the mass of the central atom, *i.e.* $G_{12} \propto \mu_x$ for XY_2 molecules without the lone pair electrons. The angle of inclination defined by TORKINGTON's equation

$$\Theta = \frac{1}{2} \tan^{-1} \left(\frac{2G_{12}}{G_{11} - G_{22}} \right) \tag{3}$$

becomes smaller with G_{12} vanishingly small. Consequently, lone pair contri-

Table II

Molecular force constants (mdyn/Å) and G_{12} elements for lone pair dihalides and NO_2

No.	Molecule and angle	c	F_{11}	F_{22}	F_{12}	F_{33}	G_{12}	Ref.
1	$^{12}CCl_2$	2.26	3.75	1.26	1.4	2.31		
		−2.26	5.46	0.69	1.0		−0.0693	this work
		4.63	3.63	1.08	1.07	2.34		
		−4.63	4.59	0.76	0.85			
	100°	—	3.13	—	—	2.59		[19]
2	$^{13}CCl_2$	2.5375	3.7	1.2	1.28			
						2.36	−0.0669	this work
		−2.5375	5.16	0.71	0.94			
	100°	—	3.12	—	—	2.59		[19]
3	$SiCl_2$	2.175	0.82	0.84	0.19			
						2.95		
		−2.175	2.54	0.27	0.19		−0.0535	this work
		2.4	0.84	0.8	0.15			
						2.87		
		−2.4	2.41	0.28	0.15			
	90°	—	1.89	0.35	−0.123	2.31		[27]
	120°	—	2.71	0.23	−0.096	1.89		
4	$GeCl_2$	0.024	2.3	0.43	0.83	1.94		
		−0.024	2.4	0.4	0.81		−0.0372	this work
		0.020	2.3	0.43	0.83			
		−0.020	2.38	0.4	0.81			
	90°	—	2.23	—	—	1.95		
	100°	—	2.36	—	—	1.84		[19]
5	$PbCl_2$	0.4	0.62	0.54	0.47	1.61		
		−0.4	1.77	0.15	0.4		−0.0329	this work
		0.5	0.5	0.56	0.42			
		−0.5	1.83	0.12	0.34			
		−0.55	1.86	0.11	0.3			
	90°	—	1.63	—	—	1.59		
	100°	—	1.88	—	—	1.54		[19]
6	CF_2	1.70753	3.83	2.48	1.68			
						5.19	−0.104	this work
		−1.70753	8.67	0.87	0.93			
		—	6.77	0.81	0.5	5.22	—	[28]
7	SiF_2	1.759597	1.15	1.54	0.48	4.87	−0.0793	this work
		−1.759597	4.7	0.35	−0.35			
		—	5.329	0.44	1.174	4.71		[21]
8	GeF_2	1.357072	0.65	1.4	−0.024			
						4.2	−0.0646	this work
		−1.357072	4.21	0.22	−0.025			
		—	4.29	0.32	0.0	3.85		[22]

Table (cont).

No.	Molecule and angle	c	F_{11}	F_{22}	F_{12}	F_{33}	G_{12}	Ref.
9	SnF_2	1.382833	0.39	1.10	−0.068)	)	—	
					)	3.21)	−0.0602	this work
		−1.382833	3.28	0.14	−0.18)	)		
		—	3.55	0.2	0.0	3.27		[23]
10	NO_2	0.77666	7.61	2.74	3.38)	)		
					)	11.05)	−0.0981	this work
		−0.77666	13.16	0.89	0.53)	)		
		—	12.965	0.785		8.89		[26]

butions may be considered to increase the mass of the central atom. Since the ratio of the major and minor axes, a/b, tends to unity in the limiting case of elongation along F_{11} and contraction along F_{12}, the ellipse tending to be more circular, we again arrive at the conclusion that the mass coupling term tends to be small with the lone pair electron contributions taken into account explicitly. A physical aspect of this low mass coupling term is that the lone pair certainly influences nature of chemical bonding in XY_2 molecules [13].

As opposed to the consideration of lone pair electron contributions in a chosen molecule, an entirely different study would be to examine the force field ellipses for a set of molecules (with lone pair electrons) in the increasing order of central atom masses. With the mass of the other atom Y decreasing in a set of dichlorides to that of difluorides and the mass of the central atom X increasing (in a given set), it would be interesting to see if F_{12} tends to become more negative, *e.g.* to examine the sets ($SiCl_2$, $GeCl_2$) and (SiF_2, GeF_2). The physical significance of this will be discussed. We would then find that the dichloride and difluoride groups of ellipses individually tend to shift so as to have a more negative F_{12} and minimum F_{11} values.

3.3. *Force Field Constants*

The molecular force constants evaluated by utilizing the positive and negative mixing parameters estimated from isotopic frequency data and the modified formulas [11] are reported in Table II. The force constants estimated by earlier workers without considering the lone pair effects are also included. A comparative study reveals that of the two possible values of the mixing parameter mostly negative values seem to be physically reasonable, giving

rise to force constant values close to those reported by others. However, for the molecules $^{12}CCl_2$, $^{13}CCl_2$ and $GeCl_2$, the positive mixing parameters yield better results. In general, there seems to be a gradual decrease in each of the symmetry force constants with increasing mass of the central atom of the dihalides, *e.g.* for negative mixing parameters in a given set of dihalides. This trend, however, is not followed by $SiCl_2$, for which a less negative value of the mixing parameter, such as -1.29 (see Table I), would be more likely to yield a set of force constants consistent with the above observation. In the event of such a conjectured value, it is interesting to note that the F_{12} values for SiF_2, GeF_2 and SnF_2, evaluated with negative mixing parameters, turn out to be negative in contrast to both the positive and zero values reported by others.

The claim of FADINI [14] that the sign of the interaction term F_{12} is opposite to that of the term G_{12} and this is generally valid for problems even with $\nu_1 = \nu_2$ (a rule called "Vorzeichenregel") is regarded by PEACOCK *et al.* [15] as the reason why the approximation $L_{12} = 0$ has a physical significance. Under this approximation F_{12} is proportional to $-G_{12}$, which implies that G_{12} is positive for negative F_{12} values. Without the lone pair contribution, the G_{12} values in fact tend to zero at large m_X. With lone pair electron contributions, from the G_{12} values given in Table II, it is evident that G_{12} is no longer small for large central atom masses. In conclusion we state that for small mass coupling with the lone pairs the approximation methods may not yield exact force field estimates [15]. From Table II we see that this conclusion is valid, however, only for SiF_2, GeF_2 and SnF_2 since here the F_{12} values are negative in spite of the negative values of G_{12} [16, 17]. A more negative F_{12} implies that the lone pair favours a decrease in the bond angle and so to some extent outweighs the repulsive forces between the non-bonded atoms. For other cases, where F_{12} is positive, we agree with the conclusions of SMITH and LINNET [18] that other effects (due to a lone pair or an interaction between bonds) either influence this constant so weakly that they do not outweigh the X–X repulsion or they make a positive contribution too.

In Tables III, IV and V are listed, respectively, the Coriolis coupling coefficients, symmetrized mean square amplitudes and potential energy distribution matrix elements evaluated by using positive and negative mixing parameters for each of the molecules under consideration. It is pointed out in the discussion of force constants that negative mixing parameter values seem to be more reasonable for the set of dihalides with the exception of $^{12}CCl_2$, $^{13}CCl_2$ and $GeCl_2$, a fact that should be borne in mind in the subsequent discussion of other symmetry quantities.

Table III

Coriolis coupling coefficients

No.	Molecule	Mixing parameter	ξ_1	ξ_2	ξ_1^2	ξ_2^2
1	$^{12}CCl_2$	2.26	−1.2589	0.2083	1.5850	0.0434
		−2.26	1.4155	1.1195	2.0037	1.2532
		4.63	−1.2815	−0.0511	1.6423	0.0026
		−4.63	1.1462	0.5754	1.3138	0.3311
2	$^{13}CCl_2$	2.5375	−1.2772	0.1469	1.6315	0.0216
		−2.5375	1.0341	0.764	1.069	0.5837
3	$SiCl_2$	2.170	−1.3636	0.0805	1.8593	0.0065
		−2.170	0.8247	1.0889	0.6800	1.1858
		2.40	−1.3597	0.1310	1.8487	0.0172
		−2.40	0.8644	1.0572	0.7472	1.1178
4	$GeCl_2$	0.024	−0.5961	1.1411	0.3554	1.3021
		−0.024	−0.5407	1.1684	0.2924	1.3651
		0.020	−0.5916	1.1435	0.3500	1.3076
		−0.020	−0.5454	1.1662	0.2975	1.3601
5	$PbCl_2$	0.4	−1.0761	0.6287	1.1580	0.3953
		−0.4	−0.3456	1.1974	0.1195	1.4339
		0.5	−1.1246	0.5372	1.2647	0.2886
		−0.5	−0.2450	1.2220	0.0600	1.4933
		−0.55	−0.1969	1.2307	0.0388	1.5146
6	CF_2	1.707,5307	−1.2914	0.2230	1.6677	0.0497
		−1.707,5307	0.8262	1.0172	0.6828	1.0347
7	SiF_2	1.759,597	−1.2811	0.1324	1.6413	0.0175
		−1.759,597	0.7693	1.0329	0.5919	1.0670
8	GeF_2	1.357,0715	−1.2683	−0.0600	1.6086	0.0036
		−1.357,0715	0.3183	1.2292	0.1013	1.5109
9	SnF_2	1.382,8327	−1.2410	−0.0697	1.5401	0.0049
		−1.382,8327	0.3225	1.2004	0.1040	1.4410
10	NO_2	0.776,6597	−1.0813	0.7433	1.1693	0.5526
		−0.776,6597	0.4526	1.2317	0.2048	1.5170

Table IV

Symmetrized mean square amplitudes in (Å)²

Molecule	Mixing parameter	Σ_{11}		Σ_{22}		Σ_{33}		Σ_{12}	
		0 K	298 K	0 K	298 K	0 K	298 K	0 K	298 K
$^{12}CCl_2$	2.26	0.002436	0.002846	0.009836	0.026874	0.003087	0.003283	−0.003310	−0.003624
	−2.26	0.001832	0.001939	0.011649	0.061229	0.003087	0.003283	−0.002887	−0.002989
	4.63	0.002244	0.002558	0.009709	0.024469	0.003056	0.003250	−0.002964	−0.003105
	−4.63	0.001907	0.002052	0.010720	0.043628	0.003056	0.003250	−0.002728	−0.002751
$^{13}CCl_2$	2.5375	0.0023135	0.002697	0.009446	0.010073	0.002940	0.003147	−0.003052	−0.003325
	−2.5375	0.0018064	0.001930	0.010966	0.012372	0.002940	0.003147	−0.002698	−0.002788
$SiCl_2$	2.17	0.003547	0.006082	0.006366	0.01108	0.001736	0.002075	−0.001850	−0.001946
	−2.17	0.002121	0.002519	0.010644	0.03833	0.001736	0.002075	−0.001850	−0.001946
	2.40	0.003466	0.005879	0.006404	0.004811	0.001736	0.002075	−0.001744	−0.001681
	−2.40	0.002134	0.002551	0.010401	0.006723	0.001736	0.002075	−0.001743	−0.001680
$GeCl_2$	0.024	0.002729	0.006294	0.012788	0.032717	0.001913	0.002670	−0.003738	−0.011412
	−0.024	0.002619	0.005895	0.013119	0.033914	0.001913	0.002670	−0.003665	−0.011146
	0.020	0.002720	0.006261	0.012816	0.032820	0.001913	0.002670	−0.003733	−0.011392
	−0.020	0.002628	0.005929	0.013093	0.033818	0.001913	0.002670	−0.003671	−0.011171
$PbCl_2$	0.4	0.005002	0.021058	0.008324	0.002954	0.001843	0.002987	−0.003575	−0.018299
	−0.4	0.002368	0.006276	0.016227	0.004095	0.001843	0.002987	−0.003093	−0.015595
	0.5	0.005203	0.022188	0.007513	0.009982	0.001843	0.002987	−0.003199	−0.016186
	−0.5	0.002148	0.005040	0.016679	0.027603	0.001843	0.002987	−0.002640	−0.013050
	−0.55	0.002058	0.004536	0.016841	0.027916	0.001843	0.002987	−0.002409	−0.011753
CF_2	1.7075307	0.002611	0.002806	0.006680	0.013511	0.002106	0.002125	−0.002323	−0.002406
	−1.7075307	0.001576	0.001585	0.009783	0.037222	0.002106	0.002125	−0.001838	−0.001833
SiF_2	1.759597	0.003488	0.005074	0.006111	0.008229	0.001778	0.001832	−0.001565	−0.001933
	−1.759597	0.001613	0.001761	0.011747	0.025106	0.001778	0.001832	−0.000252	0.000387
GeF_2	1.3570715	0.004074	0.007141	0.004851	0.005206	0.001565	0.001698	−0.000362	−0.000151
	−1.3570715	0.001617	0.001735	0.012223	0.021425	0.001565	0.001698	−0.000361	−0.000495
SnF_2	1.3828327	0.005039	0.011425	0.005281	0.005980	0.001764	0.002002	−0.000077	0.000490
	−1.3828327	0.001770	0.002079	0.015087	0.034020	0.001764	0.002002	0.000321	0.001629
NO_2	0.7766597	0.002213	0.002305	0.007987	0.027516	0.001495	0.001496	−0.002619	−0.002737
	−0.7766597	0.001239	0.001246	0.010908	0.052422	0.001495	0.001496	−0.001644	−0.001676

Table V

Potential energy distribution (PED) matrix elements

Molecule	Mixing parameter	PED_{11}	PED_{12}	PED_{21}	PED_{22}	PED_{33}
$^{12}CCl_2$	2.26	0.3280	1.3817	1.6077	1.1020	1.00
	−2.26	1.3323	0.0308	0.5567	0.8064	1.00
	4.63	0.4980	0.9197	1.4125	0.0052	1.00
	−4.63	1.0290	0.2337	0.7973	0.4654	1.00
$^{13}CCl_2$	2.5375	0.3501	1.2426	1.5481	0.0446	1.00
	−2.5375	1.2530	0.0671	0.6030	0.7170	1.00
$SiCl_2$	2.17	0.1247	0.9299	1.0391	0.0155	1.00
	−2.17	1.0389	0.0155	0.1248	0.9297	1.00
	2.40	0.1395	0.8935	0.9936	0.3940	1.00
	−2.40	0.9934	0.0395	0.1396	0.8933	1.00
$GeCl_2$	0.024	0.4490	2.7821	0.1377	3.0934	1.00
	−0.024	0.5114	2.6144	0.1055	3.0202	1.00
	0.020	0.4541	2.7691	0.1348	3.0885	1.00
	−0.020	0.5061	2.6293	0.1080	3.0275	1.00
$PbCl_2$	0.4	0.0470	2.9717	0.6640	2.3547	1.00
	−0.4	0.7887	1.6751	0.0196	2.4442	1.00
	0.5	0.0239	2.5537	0.7648	1.8128	1.00
	−0.5	0.8747	1.1480	0.0080	2.0150	1.00
	−0.55	0.9094	0.9189	0.0045	1.8238	1.00
CF_2	1.7075307	0.1027	1.3223	1.2958	0.1293	1.00
	−1.7075307	1.1236	0.0059	0.1860	0.9435	1.00
SiF_2	1.759597	0.0160	1.1334	1.0786	0.0707	1.00
	−1.759597	0.7685	0.3109	0.0894	0.9899	1.00
GeF_2	1.3570715	0.0096	0.9911	0.9854	0.0153	1.00
	−1.3570715	0.9853	0.0154	0.0096	0.9911	1.00
SnF_2	1.3828327	0.0042	1.0064	0.9825	0.0281	1.00
	−1.3828327	0.9428	0.1363	0.0085	1.0707	1.00
NO_2	0.7766597	0.7072	2.2063	0.8748	1.3387	1.00
	−0.7766597	1.1653	0.0831	0.050	1.1985	1.00

3.4. *Coriolis Coupling Coefficients*

Table III reveals that with increasing mass of the central atom, the absolute values of ξ_1 decrease and those of ξ_2 gradually increase for both sets of dihalides. This is not true for the SnF_2 molecule. For the NO_2 molecule the most appropriate ξ_1 and ξ_2 values are those listed against the negative mixing parameter value given in Table III.

3.5. *Symmetrized Mean Square Amplitudes*

It is apparent from Table IV that the Σ_{22} elements of the symmetrized mean square amplitude are relatively temperature sensitive with the exception of $GeCl_2$ and $PbCl_2$. Generally, the elements for these two molecules are found to vary appreciably with the temperature. In this context the small values of the mixing parameter for these two molecules should be noted.

3.6. *Potential Energy Distribution Matrices*

The PED_{11} elements listed in Table V for the molecules $^{12}CCl_2$, $^{13}CCl_2$, $GeCl_2$ and $PbCl_2$ are found to be smaller than the corresponding PED_{12} elements, while the reverse is true for rest of the molecules. Surprisingly, the PED_{12} elements of $GeCl_2$ and $PbCl_2$ are greater than the corresponding PED_{11} elements, a feature independent of the signs of the mixing parameter adopted. A comparative study of PED_{21} and PED_{22} elements shows that the former are greater than the latter in the case of $^{12}CCl_2$, $^{13}CCl_2$, $GeCl_2$ and $PbCl_2$, while the reverse holds for the remaining molecules. Again, for $GeCl_2$ and $PbCl_2$, the PED_{22} elements predominate over the PED_{21} elements for both the positive and negative mixing parameters considered in the Table. As the PED_{33} element refers to a pure symmetry coordinate, its value is unity for all the molecules.

4. Conclusions

In summary, the following conclusions have been drawn: (1) A test of the reality of the mixing parameters by the appropriate sum and product rules may be useful in the experimental frequency assignments of XY_2 type molecules and their isotopic substitutes. (2) Inclusion of the lone pair electrons effectively increases the mass of the central atom, thereby changing the sizes of the ellipses and their inclinations with the F_{11} axis as well their shift in a set of dichlorides or difluorides. (3) In general, all the symmetry force constants decrease gradually with increasing mass of the central atom (with lone pair effect) for XY_2 molecules belonging to a dichloride or difluoride group

(4). All the Σ elements for $GeCl_2$ and $PbCl_2$ are found to be very temperature sensitive. Also the PED elements for these two molecules behave exceptionally as compared with those for other molecules.

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KINETICS OF PLATINUM CATALYZED HYDROCARBON TRANSFORMATIONS

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Yields of isomerization, cyclization and hydrogenolysis of 3-methylpentane as well as ring opening of methylcyclopentane over platinum black catalyst show maxima as a function of hydrogen pressure, both in circulation and pulse systems, whereas a Langmuir-Hinshelwood type behaviour has been found as a function of hydrocarbon pressure. A kinetic treatment has been put forward in terms of singly and multiply dissociated hydrocarbon species, the former being active intermediate of isomerization, cyclization and ring opening whereas the latter obstructing these reactions. Assuming that hydrogen effect is mainly suppressing the formation of the latter, we can explain the maximum curves theoretically. Kinetic data are discussed and used as additional evidences in the interpretation of the mechanisms of various surface processes.

Introduction

It has been found earlier that — as opposed to dehydrogenation being the main reaction in helium — in the presence of hydrogen, C_6 alkanes may undergo a great variety of catalytic reactions over platinum black, including C_5-cyclization, hydrogenolysis, isomerization [1, 2]. The yields of these reactions show, as a rule, maxima as a function of the hydrogen pressure [3]. A possible reaction mechanism for skeletal rearrangement has been suggested the main pathway of isomerization involving C_5-cyclic intermediates in hydrogen the formation of which would take place through half-hydrogenated surface species [4].

Whereas the pulse system applied for these studies was excellent to trace intermediates and follow up the changes of catalyst activity [5—7], no quantitative data could be obtained with respect to the kinetic parameters of the reactions due to the basically transient character of the pulse reactor. A static system would be a more suitable experimental device for this purpose, as shown by the studies of hydrogenolysis and H—D exchange of various hydrocarbons (ethane, propane, butane etc.) [8, 9].

It seemed reasonable to compare the transformations of selected model substances in pulse and static systems under experimental conditions as close to each other as possible.

Such a comparison could help us to decide whether the maximum yields of most of these reactions as a function of the hydrogen pressure [4—8] can be

attributed to the special characteristics of the pulse system or to more general regularities governing the behaviour of the system containing hydrogen and hydrocarbon in the presence of platinum catalyst. If the latter were true, the phenomena could be interpreted theoretically; this can be done easier if quantitative kinetic parameters are available. These data could also be useful evidences in elucidating the mechanisms of various reactions.

Experimental

The pulse-microcatalytic system has been described in details earlier [5, 6]. The description of the static (circulation) apparatus as well as the method of calculation of kinetic parameters can also be found in the literature [8, 9].

The platinum black catalyst was precipitated from H_2PtCl_6 with HCHO at 20—25 °C in the presence of KOH [10]. The same batch of platinum was used for the pulse and static experiments, the hydrogen pretreatment prior to use [11] was, however, carried out separately; the specific surface of platinum used in static studies was 2.1 m^2/g; (measured with N_2-adsorption by BET method), that of Pt for pulse studies 1.6 m^2/g; ageing decreased this latter value to 1.1 m^2/g. Regeneration was carried out by air and subsequent hydrogen treatment of the catalyst; thus only a slight activity decrease could be observed over a lengthy period of the catalyst lifetime [5].

Product analysis was carried out gas chromatographically; using squalane columns in both cases.

Contact times in the circulation apparatus were 5 or 10 minutes. In pulse system, the average hydrocarbon/hydrogen ratio can be estimated to be about 1 : 10, and the approximate contact time about 1/30 s.

Results

Comparison of data obtained in pulse and static systems

Table I contains comparative data on product compositions obtained from 3-methylpentane and methylcyclopentane in pulse and static systems. In spite of the very different contact times, basically similar product spectra are produced. It is not surprising that results obtained at higher hydrocarbon pressures are closer to those of the pulse system. Both methylcyclopentane and 3-methyl-2-pentene (which is basically a by-product of C_5-cyclization [4], accumulated with longer contact times in the circulation apparatus.

Table I gives some indication on effect of hydrogen on product composition; for more clear direct comparison, the percentage of methylcyclopentane formed from 3-methylpentane in pulse and static system has been selected to demonstrate the similar hydrogen dependence and also the similar temperature effects (Figures 1a and 1b). The analogy can be observed for the yields of isomerization, hydrogenolysis and ring opening, too.

On the basis of our data, it seems to be clear that results obtained with 1/30 and 120 s contact times cannot be as similar as shown in Figures 1a and 1b due to mere coincidence. If it is so, the phenomenon must belong intrinsically to the catalytic reaction (and not to the pulse reactor) and its theoretical explanation may be possible.

Table I

Product patterns of 3-methylpentane and methylcyclopentane conversion measured in pulse and circulation apparatus

Catalyst; system	Starting hydrocarbon	t, °C	Hydrocarbon: hydrogen ratio*	Effluent composition %										2MP/nH ratio
				$< C_6$	2,2-DMB	3M1P =	2MP	3MP	nH	c + t 3M2P =	MCP	Bz	1-MCP=	
0.157 g Pt;	3MP	300	5 : 20	0.86	—	0.01	0.41	94.91	0.03	1.15	2.50	0.12	—	13.7
static			5 : 300	1.08	0.03	—	4.90	91.74	0.63	0.01	1.27	—	—	7.7
$\tau = 10$ min			30 : 160	0.36	0.02	0.02	1.57	95.08	0.22	0.08	2.30	—	—	7.1
		330	5 : 50	3.89	—	0.08	1.09	89.60	0.04	0.06	3.40	0.66	—	27.3
			5 : 200	13.14	—	—	11.54	65.87	4.20	0.37	3.93	0.73	—	2.7
			5 : 500	9.91	0.15	—	17.60	66.01	3.83	—	2.21	—	—	4.6
			30 : 400	1.69	0.09	—	7.04	85.96	0.82	0.13	3.74	—	—	8.6
		360	5 : 125	11.28	—	0.23	3.57	71.18	0.42	2.31	8.24	1.73	—	8.5
			5 : 300	17.64	0.19	—	21.42	48.17	6.95	0.04	4.46	0.72	—	3.1
0.157 g Pt; static	MCP	300	5 : 180	0.18	—	—	2.69	0.98	0.72	0.16	94.50	—	0.75	3.7
$\tau = 5$ min		330	5 : 300	0.56	—	—	6.22	2.54	1.91	0.35	87.22	—	1.19	3.3
0.4 g Pt	3MP	300	1 : 10	0.40	0.03	—	1.38	96.02	0.13	0.09	1.96	—	—	10.6
pulse		330	1 : 10	2.63	0.17	—	7.47	86.25	1.32	0.25	1.89	—	—	5.7
$\tau \sim 1/30$ s		360	1 : 0.5	5.21	0.01	0.13	1.52	87.35	0.31	1.74	1.92	1.18	0.62	4.9
			1 : 10	10.29	0.21	0.05	13.33	68.62	2.84	0.44	3.95	0.15	0.18	4.7
	MCP	300	1 : 10	0.37	—	—	6.28	2.12	0.48	—	90.70	—	0.11	3.0
		330	1 : 10		—	—	17.51	6.51	1.24	0.04	73.67	—	0.17	2.7

* The numbers shown are actual hydrocarbon and hydrogen pressures for static system and approximate values for the pulse system where the carrier gas pressure was about 1000 torr with 3 μl pulses of giving just above 100 torr pressures in their maximum. Hydrogen pressures were adjusted by using ready-made hydrogen-helium mixtures as carrier gases [6].

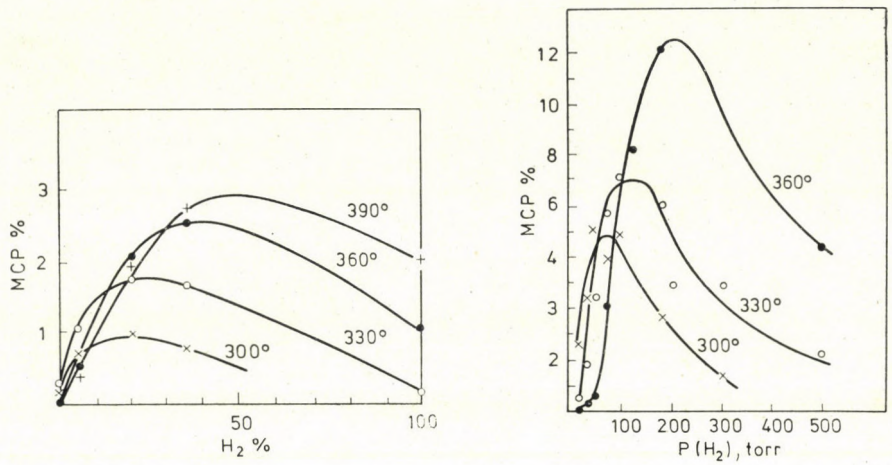


Fig. 1. Methylcyclopentane yield from 3-methylpentane as a function of the hydrogen pressure. a) Pulse system; b) Circulation system. Reaction conditions are given in Table I.

Determination of kinetic parameters

The logarithms of the reaction rates of various groups of reactions determined in the circulation apparatus were plotted as a function of the logarithm of the hydrogen pressure at various temperatures. Figure 2 shows the corresponding data for isomer and methylcyclopentane formation from 3-methylpentane.

Both these curves and the plots for hydrogenolysis of 3-methylpentane (Fig. 3) have maxima. The ring opening of methylcyclopentane (Fig. 3) proceeds at a much higher rate. Every reaction enumerated has its own (temperature dependent) optimum hydrogen pressure.

The rates of various reactions plotted as a function of the hydrocarbon pressure (Fig. 4) increase monotonically. Results shown were obtained under conditions where for most of the reactions the order in respect to hydrogen was near to zero, *i.e.* at the maximum of the curves on Figures 2 and 3.

Whereas the reaction rates do not vary considerably in function of the hydrocarbon pressure, hydrogen (either as stoichiometric or non-stoichiometric component [12]), affects the rates very strongly. In pulse system, the conditions, as a rule, result in zero order in respect to hydrocarbon but the order in respect to hydrogen may be positive, zero or negative, depending on the hydrogen pressure and temperature. Consequently, activation energy determinations in the pulse system based on the conversion values [13] at constant hydrogen pressure should be treated with extreme caution, since due to the shift of the maximum reaction rates as a function of hydrogen pressure, Arrhenius plots tend to deviate from the straight lines at higher temperatures (Table II).

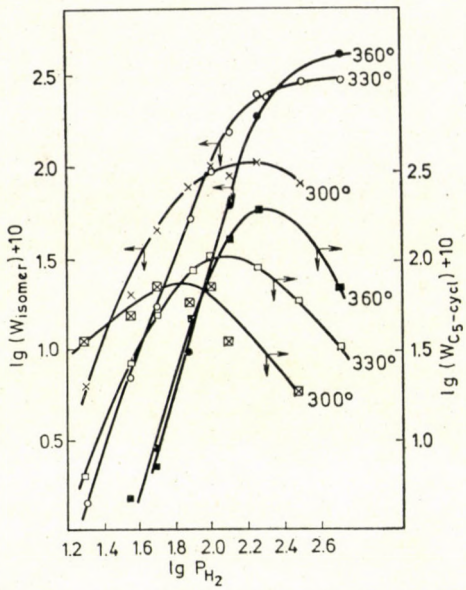


Fig. 2. Rates of 3-methylpentane isomerization and cyclization as a function of the hydrogen pressure. Symbols: ×, ○ and ●: isomerization at 300, 330 and 360 °C, respectively; ⊠, □ and ■: methylcyclopentane formation at 300, 330 and 360 °C, respectively. Hydrocarbon pressure: 5 torr.

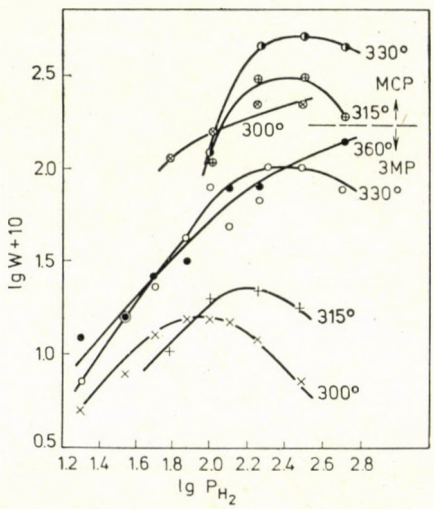


Fig. 3. Rates of 3-methylpentane hydrogenolysis and methylcyclopentane ring opening as a function of the hydrogen pressure. Symbols: ×, +, ○ and ●: 3-methylpentane hydrogenolysis at 300, 315, 330 and 360 °C, respectively. ⊗, ⊕ and ◐: methylcyclopentane ring opening at 300, 315 and 330 °C, respectively. Hydrocarbon pressure: 5 torr.

Experiments in circulation apparatus permit more accurate calculation (Table II). Hydrogen effects were eliminated by plotting reaction rate values in the range where the order in respect to hydrogen is zero corresponding to optimum hydrogen coverages but not to constant hydrogen pressures.

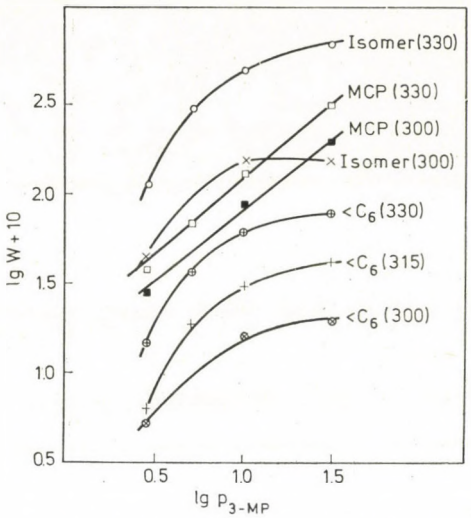


Fig. 4. Rates of various reactions of 3-methylpentane as a function of hydrocarbon pressure. Symbols: ⊗, + and ⊕ : hydrogenolysis at 300, 315 and 330 °C, respectively, × and ○ : isomerization at 300 and 330 °C, respectively, □ and ■ : methylcyclopentane formation at 300 and 330 °C, respectively. Hydrogen pressure: 300 °C: 160 torr, 315°: 260 torr, 330°: 400 torr.

Table II

Activation energy values determined in pulse and static system (determined between 270 and 360 °C)

System	Catalyst	E_A kcal/mole		
		MCP ring opening	3MP hydrogenolysis*	3MP isomerization
Static	Fresh Pt	23.5	34.8	21.5
Pulse	Fresh Pt	26.5	40.3 (27.0)	bending down
Pulse	Aged Pt	—	19.7 (11.4)	23.8

* Values in parentheses obtained at higher (330—375 °C) temperatures.

Discussion

Discussion of the kinetic curves

Our approach is based on the suggestion [14] that reacting hydrocarbons suffer at least two types of dissociative adsorption, one of them losing one, the other *a* hydrogen atoms, respectively. In addition to these processes — formally shown by Eqs (1) and (2) — the dissociative adsorption of hydrogen must be considered (3):

$$C_6H_{14}(g) + 2\,M \overset{K_{CH}}{\rightleftharpoons} C_6H_{13}M + HM \tag{1}$$

$$C_6H_{14}(g) + 2\,aM \overset{K_X}{\rightleftharpoons} C_6H_{14-a}M_a + a\,HM \tag{2}$$

$$H_2(g) + 2\,M \overset{K_H}{\rightleftharpoons} 2\,HM \tag{3}$$

Let us assume Reactions (1) — (3) to be in equilibrium and express the surface concentrations (Θ_{CH}, Θ_X and Θ_H, respectively) of their products by means of the equilibrium constant and the gas pressure. Let us assume, further, that (under our conditions, in the excess of hydrogen) Θ_H is governed by the hydrogen pressure only (*i.e.* the hydrogen coverage from dissociative adsorption is negligible)

$$\Theta_H = \sqrt{K_H p_H} \tag{4}$$

Then, hydrogen can be substituted into the equations for Θ_X and Θ_{CH} from Equation (4):

$$\Theta_{CH} = \frac{K_{CH} p_{CH}}{\sqrt{K_H p_H}} \tag{5}$$

$$\Theta_X = \frac{K_X p_{CH}}{(\sqrt{K_H p_H})^a} \tag{6}$$

Experimental evidence indicate that the assumption of at least two types of chemisorption (leading to exchange and hydrogenolysis) describes the situation adequately [9]. The formation of deactivating deposits was found to be a very rapid process even in hydrogen atmosphere and the surface fraction occupied by them was controlled by the actual hydrogen pressure; the activity of the catalyst decreased subsequently rather slowly [7].

SINFELT's kinetic analysis for ethane hydrogenolysis was based on the assumption that multiply dissociated species are active intermediates [15, 16]. In cyclization and isomerization of 3-methylpentane, the half-hydrogenated product of reaction (1) (denoted by subscript "CH") is the active intermediate [4]. The presence of any other, multiply dissociated species (subscript X) is unfavourable. Thus, the kinetic equation will be the following (using a Langmuir-Hinshelwood approximation; *cf.* Fig.4):

$$W = k\frac{\Theta_{CH}}{1 + \Theta_H + \Theta_{CH} + \Theta_X} = k\frac{\dfrac{K_{CH} p_{CH}}{\sqrt{K_H p_H}}}{1 + \sqrt{K_H p_H} + \dfrac{K_{CH} p_{CH}}{\sqrt{K_H p_H}} + \dfrac{K_X p_{CH}}{(\sqrt{K_H p_H})^a}} \tag{7}$$

According to (4), the term corresponding to Θ_X will respond most sensivitely to a change in hydrogen pressure (since it is very probable that $a \gg 2$). At lower hydrogen pressures, therefore, everything else can be neglected in the denominator and the expression will give a positive hydrogen order:

$$W = k \frac{K_{CH}}{K_X} K_H p_H^{\frac{a-1}{2}} \tag{8}$$

At higher hydrogen pressures, the term characterizing Θ_X can be neglected ("hydrogen suppresses multiple dissociation") and the expression will be the following:

$$W = k \frac{K_{CH} p_{CH}}{\sqrt{K_H p_H} + K_H p_H + K_{CH} p_{CH}} \tag{9}$$

resulting in a negative hydrogen exponent between 0.5 and 1. The reaction rate will have a maximum as a function of the hydrogen pressure.

The treatment can be extended to other reactions involving multiply dissociated active intermediates (losing b hydrogen atoms per molecule). This must be the situation for hydrogenolysis [15, 16]. We are presumably right to suggest that surface species leading to hydrogenolysis lose less hydrogen atoms than those resulting in carbonaceous deposits, thus $a > b > 1$. Then, the rate of hydrogenolysis at low hydrogen pressures can be expressed by an equation similar to (8) but the hydrogen exponent will be $\frac{a-b}{2} < \frac{a-1}{2}$ *i.e.* lower than for isomerization or cyclization. At higher hydrogen pressures, SINFELT's original treatment can be applied.

As for the hydrocarbon order, Eq. (7) suggests a conventional Langmuir-Hinshelwood behaviour. This is in agreement with earlier results on hydrogenolysis and isomerization of lower alkanes [9] and with data in Fig. 4.

Due to the several approximations included, no further mathemathical treatment of the data has been attempted, instead, the agreement between theory and experimental data will be evaluated.

— The above treatment gives a theoretical explanation for the dual behaviour of hydrogen, inhibiting in lower concentrations the formation of poisonous deposits but in higher concentrations, even the useful reaction.

— The hydrogen exponent in the positive range is equal to $\frac{a-1}{2}$ and can be used to estimate the average degree of dissociation *(a)* of multiply adsorbed species deactivating the surface. Numerical values of hydrogen exponents and a values calculated on their basis are shown in Table III. They show that dissociation leading to catalyst deactivation is very deep, indeed: it may involve the splitting off up to 8 hydrogen atoms from 3-methylpentane.

Table III

Hydrogen and hydrocarbon exponents for various reactions

Reaction	Temperature °C	Hydrogen exponent before the maximum	Hydrogen exponent after the maximum	Position of maximum, p_{H_2} torr	a	b	Hydrocarbon exponent
3MP hydrogenolysis	300	1	1	80—100		4 (1)*	$\sim 1 \rightarrow 0$
	315	1	1	130—180		4—5 (5—6)	$>1 \rightarrow 0$
	330	1	1	200—300		5 (5—6)	$>1 \rightarrow 0$
	360	1	—	not reached			—
3MP isomerization	300	2.5	1	120—180	6		$\sim 1.5 \rightarrow 0$
	330	2.5—3	—	400—500	6—7		$2 \rightarrow 0$
	360	3	—	>500	7		
3MP C_5-cyclization	300	<1 (~0.7)	1	50—100	2—3		1
	330	3—3.5	1	100—130	7—8		1
	360	3—3.5	1	~200	7—8		1
MCP ring opening	285	<1 (~0.5)	—	not reached	2		—
	300	<1 (~0.5)	—	not reached	2		—
	315	2	—	200—300	5		—
	330	3	—	300	7		—

* Values in parentheses calculated from a (cyclization), others from a (isomerization).

— The empirical fact that at higher temperature the extent of dissociation must increase has obtained a quantitative support.

— The positive order in respect to hydrogen of C_6H_{14} hydrogenolysis is lower indeed, as compared with cyclization and isomerization, the b values (calculated from a values) indicate that interactions leading to hydrogenolysis involve species with the loss of 4—5 hydrogen atoms.

— The order in respect to hydrocarbon found corresponds to the predicted behaviour, except for methylcyclopentane formation from 3-methylpentane, whose concentration is, however, governed by the reactions of its formation and decomposition.

Conclusions concerning the reaction mechanism

The comparison of kinetic behaviour of different reactions may allow to draw conclusions with respect to their mechanism, too.

Every reaction has its optimum hydrogen coverage; at higher temperatures K_H decreases and higher and higher hydrogen pressures are required to maintain this; the positions of maxima correspond to the same order of hydrogen sensitivity of individual reactions as pointed out earlier [17]. Various hydrogen sensitivities can be interpreted in terms of the constants in Eq. (4) for individual reactions being different.

The different kinetics of isomerization and hydrogenolysis can resolve the apparent contradiction that with increasing hydrogen pressures the selectivity increases in favour of isomerization and the relative importance of hydrogenolysis — although it involves stoichiometric hydrogen uptake — decreases. The energy barrier for hydrogenolysis is higher (*cf.* Table II); therefore, at higher temperatures it becomes more and more predominating.

The kinetic behaviour of C_5-cyclization and ring opening is identical giving thus an additional support that they must involve similar surface intermediates probably at the same sites. On the other hand, the ring opening is a process basically different from hydrogenolysis as indicated by the facts that (i) the rate of ring opening is considerably higher and its activation energy is lower as compared with hydrogenolysis, (ii) they show different positive orders and hydrogen sensitivities (in agreement with recent literature data [18]), (iii) cyclopentane formation from methylcyclopentane is negligible as compared with ring opening, (iv) the selectivity for ring opening vs. hydrogenolysis is very high and increases with the hydrogen pressure [19].

The cause of the difference lies not only in the hindered geometry of the cyclopentane ring [20] but evidently the ring opening involves a less dissociated intermediate. At higher temperatures the positive orders of the two processes approximate each other as though a change in the mechanism would manifest itself.

The positive hydrogen exponents for C_5-cyclization and isomerization of 3-methylpentane are not identical, especially at lower temperatures, and the 2-methyl-pentane/*n*-hexane ratios from 3-methylpentane are much higher than the analogous value obtained from methylcyclopentane ring opening (Table I). All these support that under these conditions bond shift (producing only 2-methylpentane and no *n*-hexane from 3-methylpentane) must play a not negligible role in isomerization. All these confirm our previous conclusions that bond shift mechanism is favoured by hydrogen-deficient conditions [2—4], but its rate is not high as compared with C_5-cyclic isomerization.

*

The authors wish to express their gratitude to Mrs. DOBROVOLSZKY for her active participation in performing pulse experiments as well as to Dr. A. SÁRKÁNY for valuable discussions.

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SOME 3-SUBSTITUTED-4-HYDROXYCARBOSTYRILS

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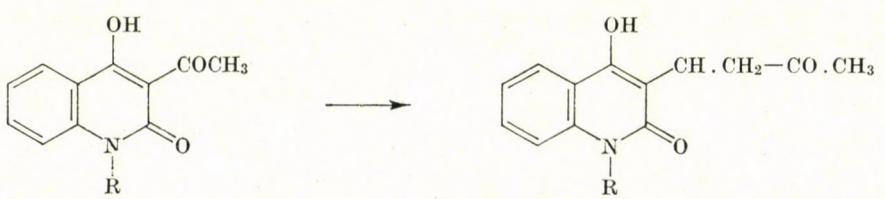
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Several new 4-hydroxycarbostyril derivatives having heterocyclic substituent and a long acyl chain in the 3-position have been synthesized from 3-acetyl-1-alkyl-(or phenyl)-4-hydroxy-carbostyrils (**I**). The monobromoderivative of **Ia** was made and its structure established.

Compounds containing the 4-hydroxycarbostyril system are of particular biological importance [1]. Many of these compounds proved to be active insecticides [2], antiparasitic agents [3], antimalarials [4], tranquilizers, hypnotics and muscle relaxants [5, 6]. In the course of the present work several new 4-hydroxycarbostyrils substituted in the 3-position have been synthesized from 3-acetyl-1-alkyl-(or phenyl)-4-hydroxycarbostyrils **Ia-c**. Compounds **Ia-c** were prepared by the Fries rearrangement of 4-acetoxy-1-alkyl-carbostyrils [1], or by the alkaline hydrolysis of 5,6-dihydro-4-hydroxy-2,5-dioxo-6-alkyl-(or phenyl)-2*H*-pyrano-(3,2-*C*)-quinolines [7, 8, 9].

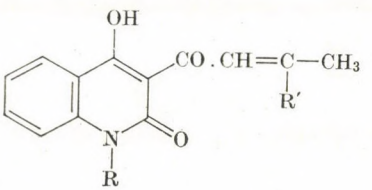
The 3-acetoacetyl-1-alkyl (or phenyl)-4-hydroxycarbostyrils **IIa-c** were synthesized by the Claisen condensation of **I** with ethyl acetate in the presence of metallic sodium.



I	R	**II**	R
a	CH_3	**a**	CH_3
b	C_2H_5	**b**	C_2H_5
c	C_6H_5	**c**	C_6H_5

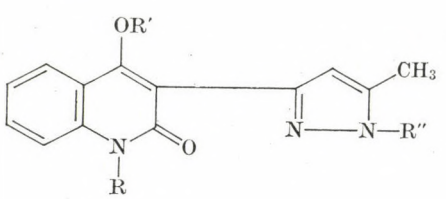
IIa when kept in contact with aqueous NaOH regenerates **Ia**. The IR spectrum of **IIb** shows stretching frequencies at 1720 cm^{-1} ($3-\gamma-C=0$), 1660 cm^{-1} (C = 0 at 2-position), 1630 cm^{-1} ($3-\alpha-C=0$) and νOH absorption at 2800—2500 cm^{-1}.

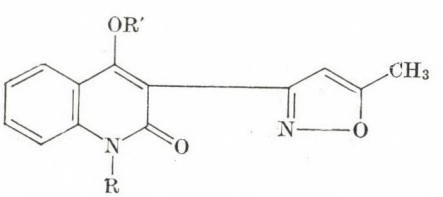
Compounds **IIa-c** condense with one mole of amines to give the enamine derivatives **IIIa-k**. Substitution by the amine, as in many analogous β-diketones [10], occurred at the $3-\gamma-$position in **II**, since the IR spectrum of **IIIc** taken as example reveals the absence of the band at 1720 cm^{-1}.



III	R	R′
a	CH_3	NH · C_6H_5
b	CH_3	NH · $C_6H_4CH_3(p)$
c	CH_3	NH · $CH_2C_6H_5$
d	CH_3	NH · C_6H_{11}
e	CH_3	N · C_5H_{10}(piperidyl)
f	C_2H_5	NH · C_2H_5
g	C_2H_5	NH · C_4H_9(n)
h	C_2H_5	NH · C_6H_5
i	C_6H_5	NH · C_2H_5
j	C_6H_5	NH · C_4H_9(n)
k	C_6H_5	NH · C_6H_5

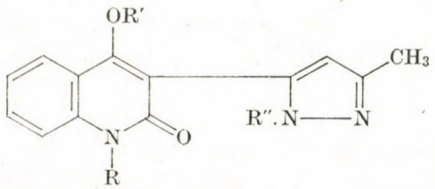
The condensation of **IIa-c** with hydrazines and hydroxylamine led to the formation of products, resulting from the elimination of two molecules of water, ass hown by their elemental analyses. Based on the reaction of β-diketones with hydrazines [10] and hydroxylamine [11] giving pyrazole and isooxazole derivatives, respectively the products obtained from the reaction of **IIa-c** with these reagents may have formulas **IV** and **V**, or possibly their isomeric formulas **IVi** and **Vi**.



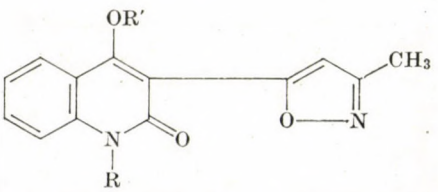


IV	R′	R′	R″
a	CH_3	H	H
b	CH_3	H	C_6H_5
c	C_2H_5	H	H
d	C_2H_5	H	C_6H_5
a	C_6H_5	H	H
f	C_6H_5	H	C_6H_5
g	CH_3	H	COC_6H_5
h	CH_3	COC_6H_5	COC_6H_5

V	R	R′
a	CH_3	H
b	C_2H_5	H
c	C_6H_5	H
d	CH_3	COC_6H_5



IVi

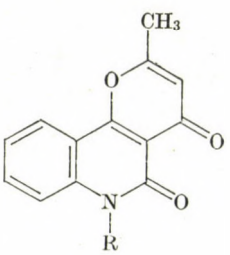


Vi

The structures of compounds **IV** and **V** find support in the IR data, which show bands at 3160 cm^{-1} (NH), 3100 cm^{-1} (OH) and 1620 cm^{-1} (C = N) in the spectrum of **IVa**, and bands at 3100 cm^{-1} (OH) and 1620 cm^{-1} (C = N) in the spectrum of **Va**. Further support for structures **IV** and **V** is the formation of their mono- (**IVg** and **Vd**) and dibenzoyl (**IVh**) derivatives.

The IR spectrum of **IVh** and **Vd** each displays no OH absorption, but exhibits a band at 1720 cm^{-1} due to the C = 0 ester group. The spectrum of **IVh** has no NH band, but shows absorption at 1720 (C = 0, benzoyl).

It is well known that *o*-hydroxy-*β*-diketones cyclize readily when acted upon by dehydrating agents to give 2-methylchromones [11, 12]. When the dicarbonyl compound **IIb** and **IIc** were treated with cold conc. sulfuric acid, or with boiling ethanolic hydrochloric acid, or boiling acetic acid, a product was obtained believed to have structure **VI**, since the OH group in the 4-position in analogous compounds has been reported to take part in a similar cyclization reaction [9, 13].



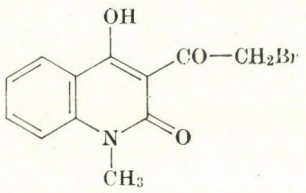
	R
a	C_2H_5
b	C_6H_5

VI

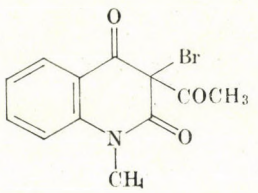
Compounds **VIa** and **VIb**, responding positively to the known potassium hydroxide test of chromones [14] are readily hydrolyzed with 2*N* sodium hydroxide into **Ib** and **Ic**; they react with appropriate amines, hydrazine hydrate, phenyl hydrazine and hydroxylamine giving products identical with **III*f*-k**, **IVc-*f***, **Vb** and **Vc**, respectively. The diketones **IIb** and **IIc** may be intermediate products in these reactions. The IR spectrum of **VIa** and **VIb** each revealed the presence of two carbonyl frequencies at 1680 and 1700, which are in agreement

with the values observed for the C = 0 group of chromones [15] and C = 0 of 2-quinolones (fused oxygen rings in the 3,4 positions [16]).

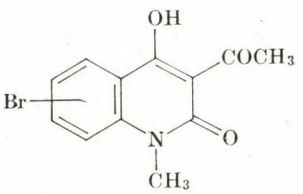
Bromination of **Ia** with bromine in acetic acid or chloroform resulted in the formation of a monobromo derivative. There are three possible structures for this compound:



VII



VIII



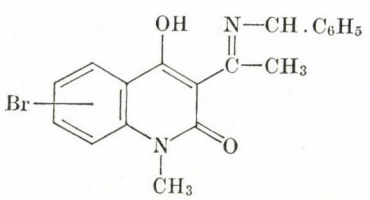
IX

Structures **VII** and **VIII** were eliminated by consideration of the chemical properties of the product:

a the refluxing of the monobromo derivative with alcoholic KOH left the material unchanged giving positive *m*-dinitrobenzene test [17];

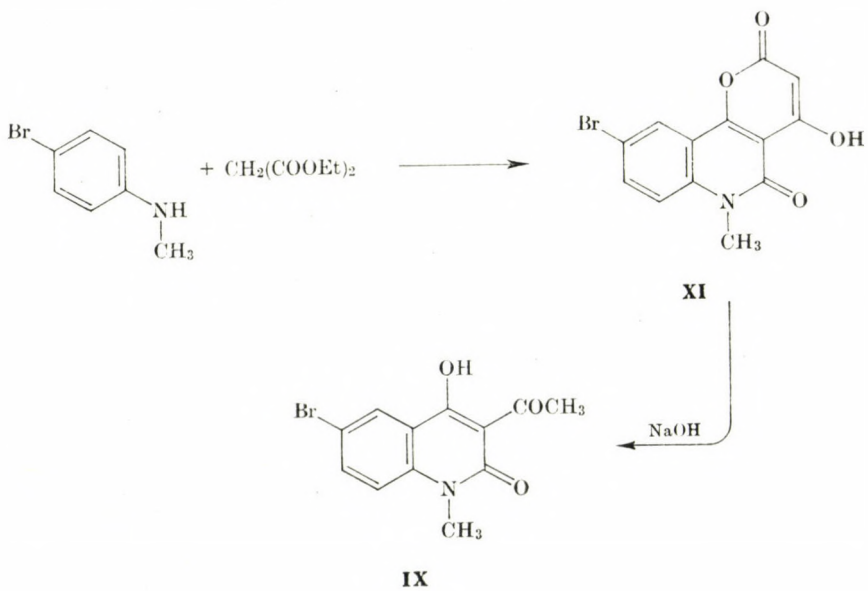
b the bromo derivative condensed with one molecule of benzylamine in boiling ethanol to give a product containing bromine. The latter was readily reconverted to the starting material by boiling with dilute HCl. This evidence suggested that substitution by the bromine atom took place in the aromatic ring and that the product obtained in the reaction of the monobromo derivative with benzylamine was a Schiff base having formula **X** [18].

The bromine atom was found to occupy the 6-position in the bromo derivative **IX**. This was established by synthesis according to the procedure describ-



X

ed for the preparation of **Ia** [8, 9]; thus when *p*-bromomethylaniline was condensed with malonic ester in nitrogen atmosphere and at the boiling point of the reaction mixture, **XI** was isolated, which upon hydrolysis with 2*N* sodium hydroxide yielded **IX** (m.p. and mixed m.p.).



Experimental

M.p.'s are uncorrected. The IR spectra were obtained with a Perkin-Elmer Infracord Spectrophotometer Model 1378. using KBr wafer technique.

3-Acetoacetyl-1-alkyl-(or phenyl)-4-hydroxycarbostyrils, II a—c

A mixture of **Ia—c** (0.03 mole), finely devided sodium metal (0.15 mole) and dry ethyl acetate (0.68 mole) was refluxed for 4 hrs. The reaction mixture was kept at room temperature overnight, then poured into dilute acetic acid. The solid which formed was collected, washed thoroughly with water and crystallized from an appropriate solvent to obtain yellow crystals of **IIa—c**.

3-Acetoacetyl-4-hydroxy-1-methylcarbostyril (IIa) crystallized from ethanol, m.p. 142—143 °C; yield 76%. (Found: C 65.07; H 5.11; N 5.41. $C_{14}H_{13}NO_4$ requires: C 65.21; H 5.00; N 5.40%.)

3-Acetoacetyl-1-ethyl-4-hydroxycarbostyril (IIb) crystallized from ethanol, m.p. 143—144 °C; yield 74%. (Found: C 65.56; H 5.58; N 5.29. $C_{15}H_{15}NO_4$ requires: C 65.93; H 5.49; N 5.12%.)

3-Acetoacetyl-4-hydroxy-1-phenylcarbostyril(IIc) crystallized from methanol, m.p. 176—177 °C, yield 65%. (Found: C 71.08; H 4.75; N 3.93. $C_{19}H_{15}NO_4$ requires: C 71.02; N 4.67; N 4.36%.)

Action of sodium hydroxide on IIa

A solution of 0.5 g of **IIa** in 2*N* sodium hydroxide (5 ml) was allowed to stand at room temperature for 48 hrs. It was then acidified with dilute hydrochloric acid and the solid which formed was filtered off and crystallized from methanol to give **Ia** in 93% yield (m.p. and mixed m.p.).

3-(β-Alkyl- or arylaminocrotonyl)-1-alkyl-(or phenyl)-4--hydroxycarbostyrils, III

A solution of each of **IIa—c** (0.002 mole) in ethanol (5 ml) was treated with an excess of the appropriate amine and kept at room temperature for 1 hr (in the case of aromatic amines the reaction mixture was refluxed for 3 hrs). The crystalline products formed were filtered off and recrystallized from an appropriate solvent to give **IIIa-k** as yellow crystallized (*cf.* Table I).

Table I

3-(β-Alkyl- or arylaminocrotonyl)-1-alkyl-(or phenyl)-4-hydroxycarbostyrils **(III)**

Compound III	Yield, %	M.p., °C	Solvent of crystn.	Formula	Analysis					
					Carbon		Hydrogen		Nitrogen	
					calcd.	found	calcd.	found	calcd.	found
a	73	163—4	methanol	$C_{20}H_{18}N_2O_3$	71.85	71.65	5.38	5.22	8.38	8.32
b	70	186—7	ethanol	$C_{21}H_{20}N_2O_3$	72.41	72.35	5.74	6.15	8.04	8.24
c	72	184—5	ethanol	$C_{21}H_{20}N_2O_3$	72.41	72.62	5.74	5.71	8.04	8.04
d	75	176—7	ethanol	$C_{20}H_{24}N_2O_3$	70.51	70.21	7.05	7.13	8.23	8.13
e	59	274	methanol	$C_{19}H_{22}N_2O_3$	69.93	69.94	6.74	6.40	8.58	8.45
f	62	167	methanol	$C_{17}H_{20}N_2O_3$	68.00	67.86	6.66	6.60	9.33	9.40
g	71	153	methanol	$C_{19}H_{24}N_2O_3$	69.51	69.50	7.31	7.52	8.53	8.23
h	80	180	ethanol	$C_{21}H_{20}N_2O_3$	72.41	72.12	5.74	5.94	8.04	8.27
f	88	219—20	ethanol	$C_{21}H_{20}N_2O_3$	72.41	72.21	5.74	6.04	8.04	7.78
j	84	218—9	ethanol	$C_{23}H_{24}N_2O_3$	73.40	73.20	6.39	6.21	7.44	7.58
k	83	240	dioxan	$C_{25}H_{20}N_2O_3$	75.75	75.96	5.05	5.34	7.07	6.95

4-Hydroxy-1-alkyl-(or phenyl)-3 [5(or3)-methyl-1-substituted pyrazol-3(or 5)-yl]-carbostyrils, IV

Each of **IIa—c** (0.002 mole) was treated with hydrazine hydrate (or phenyl hydrazine) (0.002 mole) in acetic acid or ethanol (5 ml), and the reaction mixture was refluxed for 4 hrs. The solid which deposited after cooling was filtered off and crystallized from an appropriate o vent to afford colourless crystals of **IVa—f** (*cf.* Table II).
s

Table II

4-Hydroxy-1-alkyl (or phenyl)-3-[5 (or 3)-methyl-1-substituted pyrazol-3 (or 5)-yl]-carbostyrils **(IV)**

Compound IV	Yield, %	M.p., °C	Solvent of crystn.	Formula	Analysis					
					Carbon		Hydrogen		Nitrogen	
					calcd.	found	calcd.	found	calcd.	found
a	74	309	ethanol	$C_{14}H_{13}N_3O_2$	65.88	66.07	5.09	5.00	16.47	16.47
b	63	294—5	acetic	$C_{20}H_{17}N_3O_2$	72.50	72.39	5.13	5.38	12.68	12.65
c	80	268	anisol	$C_{15}H_{15}N_3O_2$	63.15	63.31	5.26	5.27	14.73	15.03
d	72	229	benzene	$C_{21}H_{19}N_3O_2$	73.04	73.20	5.50	5.85	12.17	11.88
e	93	312	dimethyl-formamide	$C_{19}H_{15}N_3O_2$	71.92	71.76	4.73	4.86	13.24	13.13
f	75	307—9	ethanol	$C_{25}H_{19}N_3O_2$	76.33	75.52	4.83	4.88	10.68	11.00

Benzoylation of IVa

A mixture of **IVa** (0.5 g) in pyridine (5 ml) and one equivalent of benzoyl chloride was shaken for 10 min. at room temperature. The reaction mixture was then poured into cold dilute HCl, and the product obtained was crystallized from acetone to give white crystals of **4-hydroxy-1-methyl-3-[5(or (or 3)-methyl-1-benzoylpyrazol-3 (or 5)-yl]-carbostyril, IVg,** m.p. 253—254 °C, yield 41%. It gave a dark colour with aq. $FeCl_3$. (Found: C 70.22; H 4.77; N 11.58. $C_{21}H_{17}N_3O_3$ requires C 70.19; H 4.73; N 11.69%.)

When **IVa** (0.4 g) was refluxed with two equivalents of benzoyl chloride in pyridine (5 ml) for 3 hrs, the product obtained on crystallization from acetone was white crystals of **4-benzoyloxy-1-methyl-3-[5(or 3)-methyl-1-benzoylpyrazol-3 (or 5)-yl]-carbostyril, IVh,** m.p. 173—174 °C; yield 89%. It gave no colour with aq. $FeCl_3$. (Found: C 72.84; H 4.79; N 9.25. $C_{28}C_{28}H_{21}N_3O_4$ requires C 72.57; H 4.53; N 9.06%.)

4-Hydroxy-1-alkyl (or phenyl)-3-[5(or 3)-methylisoxazol-3(or 5)-yl]-carbostyrils, V

To a solution of each of **IIa—c** (0.002 mole) in ethanol or pyridine (5 ml) hydroxilamine hydrochloride (0.002 mole) was added, and the mixture was refluxed for 3 hrs. The solid which separated on cooling was filtered off and crystallized from an approptiate solvent to give yellow crystals of **Va—c** (*cf.* Table III).

Table III

4-Hydroxy-1-alkyl (or phenyl)-3-[5 (or 3)-methylisoxazol-3 (or 5)-yl]-carbostyrils, **V**

Compound, V	Yield, %	M.p., °C	Solvent of crystn.	Formula	Analysis					
					Carbon		Hydrogen		Nitrogen	
					calcd.	found	calcd.	found	calcd.	found
a	66	230—1	ethanol	$C_{14}H_{12}N_2O_3$	65.62	65.88	4.68	4.91	10.93	10.88
b	91	184	ethanol	$C_{15}H_{14}N_2O_3$	66.66	66.65	5.18	5.33	10.37	10.54
c	75	270	acetic	$C_{19}H_{14}N_2O_3$	71.69	71.56	4.41	4.51	8.80	8.68

4-Benzoyloxy-1-methyl-3-[5(or 3)-methylisoxazol-3(or 5)-yl]-carbostyril, Vd

This compound was obtained by refluxing equimolecular quantities of **Va** and benzoyl chloride in pyridine (5 ml) for 4 hrs. It was recrystallized from acetone to obtain colourless crystals, m.p. 197—198 °C, yield 84%. It gave no colour with aq. $FeCl_3$. (Found: C 69.62; H 4.81; N 7.38. $C_{21}H_{16}N_2O_4$ requires C 70.00; H 4.44; N 7.77%.)

Cyclization of IIb and IIc

IIb and/or **IIc** (0.5 g) was shaken with conc. sulfuric acid (6 ml) for 15 min. The reaction mixture was poured into ice-cool water, and the solid which formed was filtered off and crystallized from a suitable solvent.

6-Ethyl-2-methyl-4-oxo-[4H]-pyrano-[3.2-C]-carbostyril, VIa

This compound crystallized from benzene as a colourless substance, m.p. 208 °C, yield 83%. (Found: C 70.69; H 5.23; N 5.22. $C_{15}H_{13}NO_3$ requires C 70.58; H 5.09; N 5.49%.)

2-Methyl-6-phenyl-4-oxo[4H]pyrano-[3,2-C]-carbostyril, VIb

VIb was obtained from methanol as colourless crystals, m.p. 270 °C. (Found: C 74.92; H 4.60; N 4.35. $C_{19}H_{13}NO_3$ requires C 75.24; H 4.29; N 4.62%.)

Cyclization was achieved in good yields when **IIb** and/or **IIc** was refluxed with glacial acetic acid for 3 hrs, or with ethanol–hydrochloric acid mixture for 1 hr.

Action of sodium hydroxide on VIa and VIb

VIa and/or **VIb** (0.1 g) was refluxed with of 2*N* NaOH (8 ml) for 30 min; the mixture was then cooled, acidified with dilute HCl and the product which separated was filtered off to give **Ib** and **Ic** in 90—92% yields (m.p. and mixed m.p.).

Action of amines on VIa and VIb

To a solution of **VIa** or **VIb** (0.001 mole in 2 ml of ethanol) the appropriate amine (0.001 mole) was added and the reaction mixture was heated for 5 min, allowed to stand 1 hr at room temperature (or refluxed for 3 hrs when using aniline). The yellow crystals of the product were identified as **IIIf—k** (m.p. and mixed m.p.). (*Cf.* Table I.)

The reactions of VIa or VIb with hydrazine hydrate, phenyl hydrazine and with hydroxylamine

These reactions were carried out under conditions similar to those of the reactions of 3-acetoacetyl-carbostryril **IIb** and **IIc** with the above reagents and gave products identified as **IVc—f**, **Vb** and **Vc** (m.p. and mixed m.p.). (*Cf.* Tables II and III.)

Preparation of 3-acetyl-6-bromo-4-hydroxy-1-methyl-carbostyril (IX)

(1) *By bromination of* **Ia**: — To a solution of **Ia** (0.005 mole) in glacial acetic acid (5 ml). bromine (0.005 mole) was added dropwise, with shaking. The reaction mixture was let to stand at room temperature overnight, and the yellow crystals which formed were collected washed with ethanol and recrystallized from acetic to give (**IX**) in 75% yield, m.p. 197 °C. It developed an orange red colour with aq. $FeCl_3$. (Found: C 48.50; H 3.50; N 5.27; Br27.32. $C_{12}H_{10}NO_3Br$ requires C 48.64; H 3.37; N 4.72; Br 27.73%.)

From p-bromo-N-methylaniline and diethyl malonate:

A mixture of *p*-bromo-N-methylaniline (5 ml) and diethyl malonate (25 ml) was heated in nitrogen atmosphere for 6 hrs. The ethanol formed was allowed to escape freely through a short column. The reaction mixture was cooled and the solid precipitate washed with petroleum ether. It was then stirred in boiling ethanol (20 ml) and the insoluble material was separated by filtration and crystallized from dioxan to give 2 g of **9-bromo-5,6-dihydro-4-hydroxy-2,5-dioxo-6-methyl-2H-pyrano 3,2-C-quinoline (XI)** as colourless crystals, m.p. 306—309 °C. (Found: C 49.08; H 2.67; Br 24.69. $C_{13}H_8NO_4Br$ requires C 48.44; H 2.48; Br 24.84%.) **XI** (1 g) was refluxed with 10 ml of 2*N* NaOH for 2 hrs. After cooling, the reaction mixture was filtered from any insoluble material, acidified with dilute hydrochloric acid, and the solid product was crystallized from acetic acid to give **X** (0.8 g) (m.p. and mixed m.p.).

Action of alcoholic KOH on IX

A mixture of **IX** (0.45 g) and potassium hydroxide (1 g) dissolved in a minimum amount of water (1 ml) and ethanol (9 ml) was refluxed for 4 hrs. The precipitated solid was filtered off, washed with dilute hydrochloric acid and crystallized from ethanol; **IX** was recovered unchanged (m.p. and mixed m.p.).

Action of amines on IX

IX (0.0013 male) was treated with benzylamine (0.002 mole) in ethanol (5 ml) and the mixture was heated till it became clear, then allowed to stand at room temperature overnight. The yellowish white crystals formed were filtered off and recrystallized from ethanol to obtain pale yellow needles of the Schiff base **X**, m.p. 211—212 °C; yield 74%. (Found: C 59.45; H 4.68; N 7.03. $C_{19}H_{17}N_2O_2Br$ requires C 59.22; H 4.41; N 7.27%.)

On refluxing **X** (0.2 g) in ethanol (7 ml) with conc. HCl (3 ml) for 4 hrs., the product obtained after crystallization from acetic acid was identified as **IX** (m.p. and mixed m.p.); yield 96%.

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CONTRIBUTIONS TO THE STUDY OF HETEROCYCLES, XLIII

A COMPARATIVE STUDY BETWEEN THE 2*P*(X)-PHENYL-4(R)-OXAZOLE AND 2*P*(X)-PHENYL-4(R)-THIAZOLE. QUANTUM-CHEMICAL CALCULATIONS

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We performed a comparative study between the thiazole and the oxazole nucleus in the series I and II; we concluded that the chemical character of the thiazole derivaties is more aromatic than the oxazole ones. Therefore ϱ (the reaction constant of the Hammett equation) is greater in the oxazole series than in the thiazole one.

The reactivity indices are in good agreement with the rate constants, and the calculated molecular parameters with the experimental data.

There results prove the coplanarity of the two nucleus.

In dealing with the hetero-aromatic compounds we payed a special attention to the reactivity of the 2-aryl-thiazole (**I**) and 2-aryl-oxazole (**II**) frameworks [1, 2].

Quantum-chemical studies tried to complete our knowledge on the structure of the series I [3, 4, 5]. The HMO calculations are in good agreement with the experiments, that means the reactivity indices, especially the superdelocalization, showed that position five is the most reactive one. The logarithm of the rate constants could be correlated with the corresponding electrophylic superdelocalization indices.

The SCF-MO method [5] acknowledged both the aromatic nature of the thiazole and the coplanarity of the two rings.

GALASSO and TRINAJSTIC by EHT calculation [6] found an about 40° twist angle between the two rings in the 2-phenyl-thiazole, and at the same time they found that the calculated potential barrier is low, 0.3 eV. The authors mention that this unplanar conformation is a surprising one and it may be due to the exaggerated steric factor in EHT method.

One of our main aims being the comparative study of the aryl-thiazole, respectively, aryl-oxazole system, the present paper deals with the quantum-chemical studies and the experimental determinations concerning series I and II: a) aromaticity indices; b) the indices of reactivity for electrophylic substitution; c) some molecular properties (electronic transitions, dipole moment).

Calculations

The HMO and DEL RE parameters have been chosen from STREITWIESER [7] respectively, from DEL RE [8] and A. PULLMAN [9].

In our first HMO calculations [4] in the series I, the chosen coulomb integral for the sulphur atom gives a q_s too positive. That is why we have reconsidered the choice of these parameters in the present paper as follows:

$$\alpha_S = \alpha_C - 1.7\,\beta;\ \beta_{CS} = 0.8\,\beta$$

The values of the ionisation potentials, electron affinities and the resonance integrals β_{ij}, in the PPP-CI (limited CI) method have been taken from METZGER [10].

The atomic distances have been calculated from the HMO bond orders with the well-known formula:

$$d_{rs} = \frac{3.25}{z}(1.52 - 0.19p_{rs})$$

where d_{rs} = interatomic distance; $z = (z_r + z_s)/2$ and $z_r = z_r^0 - 0.35q_r$ (z_r = effective nuclear charge of the bonded atom; z_r^0 = effective nuclear charge of the neutral atom; q_r = net π charge); p_{rs} = HMO bond order.

The calculations have been performed on a Felix C–256 computer, based on programmes as follows: the HMO and the DEL RE programme done by R. D. POP; for the PPP–CI we used a programme from R. Boskovic Institute, Zagreb. We have used a programme of the Texas University in order to calculate the angles of the cycles. The geometry of the molecule already known we calculated the atom coordinates using a PRO–XYZ programme, obtained from the QCPE, University of Indianapolis.

Experimental

The UV spectra were recorded on a VSU 2P spectrometer (GDR), between 200–380 nm in heptane, methanol and dimethyl formamide (DMF) solutions. The dielectric constants have been determined by a Universal dielectrometer OH–309 (Hungary), the refraction indices with a Carl-Zeiss Jena Refractometer (GDR). As solvent we used benzene, chloroform and CCl_4 at 25 ± 0.2 °C (Hoeppler termostat).

The dipole moment was calculated according the DEBYE, HALVERSTADT-KUMLER, GUGGENHEIM and, respectively, the HIGASHI formulas, using a programme from the literature [11].

Table I

Aromaticity indices

X	HMO D.E. in β units		A_j^*		$\Delta A_j^* = A_{jX} - A_{jH}$		Hammett constants
	series I	series II	series I	series II	series I	series II	σ
$-NH_2$	—	—	0.8090	0.7958	0.028	0.0258	−0.30
$-CH_3$	3.386	3.319	0.8037	0.7901	0.033	0.0316	−0.13
$-H$	3.750	3.720	0.8374	0.8216	—	—	0.00
$-Cl$	3.896	3.830	0.7955	0.7868	0.041	0.0348	0.24
$-Br$	3.886	3.870	—	—	—	—	0.27
$-NO_2$	5.946	5.400	—	—	—	—	0.78; (1.25)

Regression equations:

			n	R
1)	D.E. $= 1.797\ \sigma + 3.608$	(series I)	5	0.993
2)	D.E. $= 1.405\ \sigma + 3.597$	(series II)	5	0.993
3)	$\Delta A_j = -0.237\ \sigma - 0.355$	(series I)	3	0.997
4)	$\Delta A_j = -0.154\ \sigma - 0.317$	(series II)	3	0.932

n = the number of the already studied substances

R = the regression coefficient.

* Calculated by the PPP-CI method.

Results and discussion

The HMO delocalization energies and the A_j aromaticity indices [12] in both series are in Table I. This table makes clear that the values of DE depend upon the nature of the substituents in both series of heterocycles. For both series we have succeeded in establishing a quantitative linear relationship between DE and the Hammett substituent constants (regression equations 1 and 2).

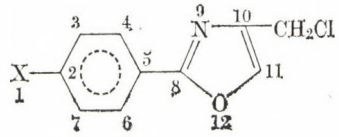
Because some authors [13] have criticized the DE capacity to reflect the aromatic character, we have calculated one more index of aromaticity, A_j, introduced by JULG [12].

We have noticed that both the DE and the A_j indices of the compounds in the 2-aryl-oxazole series are smaller than the corresponding indices in the 2-aryl-thiazole series. This proves that the thiazolic ring has a stronger aromatic character than the oxazole as it was expected. The $\Delta A_j = A_{jX} - A_{jH}$ values can be correlated with σ constants too (regression Eqs. 3 and 4).

By means of the HMO and PPP—CI methods we have calculated the following indices: net charge, electrophylic superdelocalization, bond order; their values are shown in the Tables II and III.

Both methods show in good agreement with the kinetic studies [14], position five as beeing the most reactive in both series I and II. The HMO reactivity indices (superdelocalization) show the following reactivity concerning the competitive positions: $C_{11} > C_{4,6} > C_2 > C_{3,7}$ (according to our notations, Tables II and III).

Table II

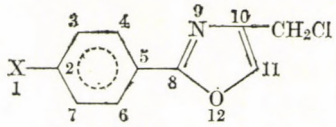


Reactivity indices of series I

X	Position	—NH_2	—CH_3		—H		—Br	—Cl		—N(1)<O$_{13}$ O$_{14}$
Indices		a	a	b	a	b	b	a	b	b
Q_r	1	0.036	0.027	—	—	—	0.013	0.023	0.024	0.991
	2	0.022	0.024	0.021	0.012	0.008	0.014	0.023	0.022	0.003
	3, 7	−0.169	−0.014	−0.075	0.002	−0.001	−0.008	−0.013	0.013	0.018
	4, 6	0.020	0.019	0.019	0.016	0.010	0.010	0.019	0.010	0.009
	5	−0.022	−0.021	−0.049	−0.013	−0.009	−0.013	−0.020	−0.017	0.006
	8	0.135	0.135	0.090	0.134	0.084	0.086	0.135	0.086	0.085
	9	−0.026	−0.262	−0.293	−0.259	−0.282	−0.278	−0.262	−0.280	−0.270
	10	0.013	0.013	0.098	0.013	−0.053	−0.097	0.013	−0.095	−0.094
	11	−0.044	−0.043	0.001	−0.042	−0.017	0.013	−0.043	0.012	0.020
	12	0.119	0.119	0.250	0.120	0.252	0.257	0.119	0.253	0.256
	13, 14	—	—	—	—	—	—	—	—	−0.523
p_{rs}	1—2	0.190	0.166	—	—	—	0.112	0.154	0.149	0.265
	2—3, 2—7	0.650	0.653	0.643	0.661	0.658	0.654	0.654	0.651	0.632
	3—4, 6—7	0.678	0.677	0.685	0.675	0.679	0.681	0.676	0.682	0.685
	4—5, 5—6	0.624	0.623	0.605	0.626	0.610	0.610	0.624	0.609	0.605
	5—8	0.344	0.343	0.406	0.341	0.401	0.401	0.343	0.403	0.404
	8—9	0.817	0.817	0.704	0.818	0.702	0.707	0.817	0.706	0.706
	9—10	0.380	0.380	0.531	0.381	0.539	0.535	0.380	0.534	0.539
	10—11	0.908	0.908	0.803	0.908	0.799	0.797	0.908	0.799	0.794
	11—12	0.260	0.251	0.410	0.252	0.407	0.415	0.251	0.415	0.420
	8—12	0.308	0.309	0.421	0.309	0.424	0.420	0.308	0.421	0.420
	1—13, 1—14	—	—	—	—	—	—	—	—	0.677
S_r^E	2	—	—	—	—	0.906	—	—	—	
	3, 7	—	—	0.975	—	0.828	0.849	—	0.865	0.814
	4, 6	—	—	0.918	—	0.923	0.923	—	0.923	0.920
	11	—	—	1.335	—	1.327	1.270	—	1.275	1.237

a) PPP-CI; b) HMO
where Q_r = net π charge; p_{rs} = bond order; S_r^E = electrophylic superdelocalization index.

Table III



Reactivity indices of the series II

X		Position	—NH_2	—CH_3		—H		—Br	—Cl		—N(1)<O_{13} O_{14}
Indices			a	a	b	a	b	b	a	b	b
Q_r		1	0.036	0.027	—	—	—	0.013	0.023	0.013	0.992
		2	0.022	0.024	0.021	0.013	0.014	0.017	0.024	0.024	0.005
		3, 7	−0.017	−0.014	−0.074	0.002	0.008	−0.008	−0.012	−0.016	0.071
		4, 6	0.020	0.016	0.018	0.005	0.012	0.013	0.018	0.013	0.011
		5	−0.026	−0.025	−0.051	−0.016	−0.009	−0.014	−0.024	−0.018	0.004
		8	0.134	0.134	0.104	0.133	0.099	0.099	0.134	0.100	0.133
		9	−0.243	−0.243	−0.286	−0.240	−0.269	−0.271	−0.243	−0.272	−0.262
		10	0.008	0.008	−0.091	0.008	−0.089	−0.089	0.008	−0.089	−0.089
		11	−0.031	−0.031	0.009	−0.029	0.022	0.021	−0.031	0.020	0.029
		12	0.097	0.097	0.210	0.097	0.213	0.213	0.097	0.213	0.210
		13, 14	—	—	—	—	—	—	—	—	−0.525
p_{rs}		1−2	0.191	0.166	—	—	—	0.112	0.153	0.150	0.264
		2−3, 2−7	0.649	0.655	0.646	0.662	0.658	0.654	0.654	0.650	0.632
		3−4, 6−7	0.678	0.677	0.687	0.674	0.679	0.680	0.678	0.681	0.686
		4−5, 5−6	0.624	0.628	0.605	0.629	0.609	0.608	0.627	0.607	0.605
		5−8	0.329	0.328	0.410	0.326	0.404	0.404	0.328	0.405	0.407
		8−9	0.833	0.832	0.713	0.834	0.717	0.719	0.833	0.716	0.716
		8−12	0.275	0.275	0.389	0.275	0.390	0.388	0.275	0.389	0.414
		9−10	0.376	0.376	0.522	0.376	0.527	0.527	0.376	0.532	0.530
		10−11	0.911	0.910	0.813	0.910	0.808	0.839	0.910	0.809	0.805
		11−12	0.236	0.236	0.376	0.236	0.383	0.382	0.236	0.381	0.359
		13−1, 1−14	—	—	—	—	—	—	—	—	0.677
S^E		2	—	—	—	—	0.897	—	—	—	—
		3, 7	—	—	0.974	—	0.829	0.809	—	0.886	0.814
		4, 6	—	—	0.914	—	0.918	0.917	—	0.829	0.916
		11	—	—	1.345	—	1.289	1.270	—	1.275	1.237

a) PPP-CI; b) HMO
where Q_r = net π charge; S_r^E = electrophylic superdelocalization index; p_{rs} = bond order.

Table IV

Energy levels in eV (PPP-CI)

—X	2*p*(X)-aryl-thiazole		2*p*(X)-aryl-oxazole	
	HOMO	LEMO	HOMO	LEMO
$-NH_2$	−9.3486	−2.0229	−9.5108	−1.9093
$-CH_3$	−9.3785	−2.0318	−9.5471	−1.9184
—Cl	−9.3936	−2.0404	−9.5636	−1.9272
—H	−9.4888	−2.1041	−9.6689	−1.9943

Following the superdelocalization indices, S_{11}^{E}, from the 5th position of thiazole, respectively, oxazole, we noticed that their values depend upon the nature of the substituent X, therefore the order of electrophylic reactivity is the following: $CH_3 > Br > Cl > NO_2$. This order runs parallel the values of the rate constants determined experimentally [14].

The bond orders of the oxazole ring underline the more pronounced dienic character of this heterocycles compared with the corresponding thiazolic derivatives, in good agreement with the values of the DE and A_j index.

The quite high value of the internuclear bond order ($C_5 - C_8$) in accordance both with the HMO and the PPP—CI, plead for the planarity of the two nucleus.

We have calculated the HOMO and LEMO indices (Table IV). The higher occupied energy level (HOMO) of the thiazole derivatives shows the more electrondonating character of the thiazole compared with the oxazole. In our future studies we shall deal with experiments concerning the ability of the thiazolic derivatives to form molecular complexes more facile than the oxazolic ones.

In tables V and VI are given the electronic transitions, calculated by the PPP—CI method. They are compared with the experimental data.

From the positive solvatochromie and especially from the high value of the molar extinction coefficient ($\log \varepsilon \simeq 4$) it results that the transitions are $\pi \rightarrow \pi^*$.

It is obviously a good agreement of the theoretical values with the experimental ones. For a comparative study there have been taken only those values which have a high oscillator strength. For example in the case of the unsubstituted derivative, transition $\Psi_m \rightarrow \Psi_{m+1}$, $\Psi_m \rightarrow \Psi_{m+2}$ respectively, transition $\psi_{m-1} \rightarrow \psi_{m+1}$ have been noticed as being the principal components of the 200—380 nm spectra range.

We have correlated the λ_{max} of the experimental absorption spectra to the $\sigma_{pK_{UV}}$ index, introduced by P. Tomasik [13]. The regression equations are:

$$5.\ \lambda_{max} = 0.0518\ \sigma_{pK_{UV}} + 0.2857 \qquad n = 4;\ r = 0.937 \text{ (thiazole)}$$

Table V

Calculated and experimental electronic transitions of series I

X		Calculated			Experimental (nm)			The contribution of different transitions %
		eV	Oscillator strength	nm	heptane	methanol	DMF	
$-NH_2$	Singlet	4.45	0.922	278.90				99.1[a]
		4.87	0.010	254.68				
		5.74	0.012	216.34	—	—	—	— —
		6.03	0.551	205.89				58.8[b]; 41.0[c]
		6.43	0.224	193.14				
	Triplet	2.83						
		3.52						
		3.95						
		4.25						
		4.93						
$-CH_3$	Singlet	4.46	0.914	277.98	294	296	303	99.0[a]
		4.89	0.014	253.47				
		5.79	0.011	214.24				
		6.05	0.548	205.11	218	220	—	61.0[b]; 38.5[c]
		6.44	0.244	192.86				
	Triplet	2.81						
		3.51						
		3.97						
		4.25						
		4.99						
$-H$	Singlet	4.49	0.881	276.26	291	295	302	98.9[a]
		4.94	0.033	251.40				
		5.88	0.009	211.35				
		6.09	0.525	203.73	218	220	—	65.8[b]; 32.0[c]
	Triplet	2.76						
		3.52						
		4.03						
		4.22						
		5.14						
$-Br$		—	—	—	296	301	305	—
					220	223	—	—
$-Cl$	Singlet	4.47	0.911	277.66				99.0[a]
		4.90	0.016	253.10				
		5.90	0.010	213.70	—	—	—	
		6.06	0.545	204.87				61.7[b]; 37.6[c]
		6.44	0.250	192.78				
	Triplet	2.81						
		3.51						
		3.98						
		4.25						
		5.01						
$-NO_2$		—	—	—	325	335	347	—
					243	248	—	

[a] $\psi_m \rightarrow \psi_{m+1}$ transition
[b] $\psi_m \rightarrow \psi_{m+2}$ transition
[c] $\psi_{m-1} \rightarrow \psi_{m+1}$ transition

Table VI

Calculated and experimental electronic transitions of series II

X	Calculated			Experimental (nm)			The contribution of different transitions %
	eV	Oscillator strength	nm	heptan	methanol	DMF	
Singlet	4.70	0.860	263.91				98.1[a]
	4.89	0.015	253.55				
	5.88	0.021	210.99	—	—	—	
	6.17	0.628	201.23				56.5[b]; 43.3[c]
$-NH_2$	6.55	0.342	189.58				
Triplet	3.04						
	3.67						
	4.01						
	4.24						
	4.93						
Singlet	4.72	0.852	262.76	270	272	—	98.1[a]
	4.92	0.018	252.04				
	5.94	0.017	208.86				
	6.19	0.625	200.33	—	—	—	58.9[b]; 40.7[c]
$-CH_3$	6.55	0.358	189.39				
Triplet	3.03						
	3.66						
	4.02						
	4.99						
	6.35						
Singlet	4.76	0.822	260.75	267	270	—	98.0[a]
	4.97	0.037	249.29				
	6.02	0.012	206.09				
	6.24	0.589	198.96	—	—	—	64.7[b]; 33.8[c]
$-H$	6.57	0.404	188.97				
Triplet	2.99						
	3.64						
	4.04						
	4.23						
	5.17						
$-Br$	—	—	—	278	281	—	—
Singlet	4.73	0.851	262.40	276	277	—	98.1[a]
	4.93	0.020	251.53				
	5.96	0.016	208.36				
	6.20	0.620	200.04	—	—	—	59.8[b]; 39.7[c]
$-Cl$	6.56	0.365	189.34				
Triplet	3.03						
	3.66						
	4.03						
	4.25						
	5.02						
$-NO_2$	—	—	—	305	310	327	—

[a] $\psi_m \rightarrow \psi_{m+1}$ transition
[b] $\psi_m \rightarrow \psi_{m+2}$ transition
[c] $\psi_{m-1} \rightarrow \psi_{m+1}$ transition.

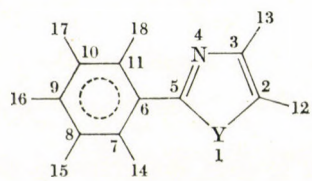
6. $\lambda_{max} = 0.065\ \sigma_{pK_{UV}} + 0.2617$ $\quad n = 4;\ r = 0.939$ (oxazole)

The slope (ϱ = reaction constant in the Hammett equation) of the regression equations 5 and 6, are in good agreement with the observations of PERJESSY [15] and KRYGOWSKI [16] that the decrease of aromaticity increases the sensitivity of the system against the substituent effects.

The calculated value (HMO method indicated by JAFFE [17]) $\varrho_{thiazole} = 0.484$ is indeed smaller than $\varrho_{oxazole} = 0.819$.

In order to obtain the theoretical value of the dipolemoment of the two unsubstituted derivative, 2-phenyl-4-chloromethyl-thiazole, respectively, 2-phenyl-4-chloromethyl-oxazole, we have calculated the electronic densities by the DEL RE method.

Table VII



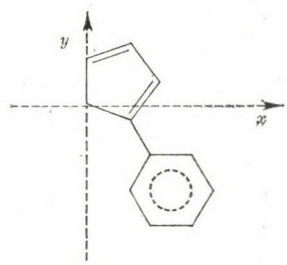
σ and total charges

Positions	Series I (Y = S)		Series II (Y = O)	
	Q_σ	Q_T	Q_σ	Q_T
1	−0.18587	−0.06611	−0.41668	−0.31958
2	0.00491	−0.03656	0.12963	0.10050
3	0.10780	0.12120	0.10270	0.11030
4	−0.27685	−0.53580	−0.28475	−0.52460
5	0.17353	0.30740	0.30246	0.43580
6	0.03394	0.02100	0.02970	0.01290
7	−0.05135	−0.03560	−0.05179	−0.04730
8	−0.05282	−0.05100	−0.05287	−0.05110
9	−0.05297	−0.04100	−0.05298	−0.04030
10	−0.05282	−0.05100	−0.05287	−0.05110
11	−0.05135	−0.03560	−0.05179	−0.04730
12	0.07441	0.07441	0.07038	0.07038
13	0.06403	0.06403	0.06353	0.06353
14	0.05317	0.05317	0.05313	0.05313
15	0.05303	0.05303	0.05303	0.05303
16	0.05302	0.05302	0.05302	0.05302
17	0.05303	0.05303	0.05303	0.05303
18	0.05317	0.05317	0.05313	0.05313

$Q_T = Q_\sigma + Q_{\pi PPP-CI}$

Table VII also contains the total Q_T, electronic densities obtained by summing q_σ and $q_{\Pi_{PPP\text{-}Cl}}$.

Table VIII



Experimental and calculated dipole moment (in Debye)

μ experimental				μ calculated			
(2-phenyl-4-chloromethyl-thiazole)				(2-phenyl-thiazole)			
solvents	method	μ	±Δ		components		angles
	D	1.289	0.173				
Benzene	H.K	1.126	0.131	μ_{PPP_Cl}	X	−0.896	65° 44′
	G	1.158	0.160				
	H	1.310	0.031	2.181	Y	−1.988	24° 16′
	D	0.966	0.037				
Carbon	H.K	0.873	0.035	μ_σ	X	−0.028	88° 14′
tetrachloride	G	0.890	0.044				
	H	1.023	0.011	0.906	Y	0.906	1° 46′
	D	1.157	0.166				
Cyclohexane	H.K	1.208	0.112	$\mu_T =$	X	−0.924	49° 30′
	G	1.256	0.105	$\mu_{PPP_Cl} + \mu_\sigma$			
	H	1.401	0.008	1.423	Y	−1.082	40° 30′
(2-phenyl-4-chloromethyl-oxazole)				(2-phenyl-oxazole)			
	D	1.540	0.297	μ_{PPP_Cl}	X	−1.050	59°
				2.040	Y	−1.750	31°
Benzene	H.K	1.334	0.114		X	0.317	75° 58′
				μ_σ	Y	1.233	14° 42′
	G	1.371	0.134	1.273	X	−0.733	35° 12′
	H	1.449	0.020	$\mu_T =$	Y	−0.517	54° 48′
				$\mu_{PPP_Cl} + \mu_\sigma$			

D — DEBYE; H.K — HALVERSTADT and KUMLER; G — GUGGENHEIM; H — HIGASHI

In Table VIII are given the calculated and experimental dipole moment values of 2-phenyl-4-chloromethyl-thiazole and of 2-phenyl-4-chloromethyl-oxazole. The calculations have been made for unsubstituted 2-phenyl-thiazole, respectively, 2-phenyl-oxazole, as we do not have the absolute configuration of R = $-CH_2Cl$ group.

As it appears from Table VIII, the calculated value is in good agreement with the experiments, determined by different methods.

It also agrees with the determination of GALASSO and TRINAJSTIC [16] concerning 2-phenyl-thiazole.

Kinetic measurements, the internuclear bond order, both in PPP—CI method and in HMO method, the value of the calculated dipole moment for a planar conformation near to the experimental one, suggest a planar conformation for the studied systems.

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REACTION OF SUGAR DERIVATIVES WITH α-DIHALOGENO ETHERS

SYNTHESIS OF GLYCOSYL CHLORIDES WITH THE REAGENT DICHLOROMETHYL METHYL ETHER–TIN TETRACHLORIDE

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Per-O-acetates of mono- and disaccharides can be converted into the more stable anomeric glycosyl chloride derivatives with dichloromethyl methyl ether–$SnCl_4$ in high yields. According to polarimetric measurements, the reaction follows first-order kinetics. On this basis, a reaction mechanism is proposed.

In an earlier paper [1] the possibility of converting mono- and disaccharide per-0-acetates in high yield into the more stable anomeric glycosyl chloride derivatives with dichloromethyl methyl ether-$ZnCl_2$ was reported. When BF_3-etherate catalyst is used, only acetates with 1,2-*trans* configuration react to yield the corresponding 1,2-*trans* per-0-acetylglycosyl chlorides in this stereoselective reaction; this method can generally be applied to the synthesis of less stable β-chlorosugars [2, 3].

In search of other catalysts, tin tetrachloride, a compound with pseudo Lewis acid character, was found to have good catalytic action in the reaction of sugar acetates with dichloromethyl methyl ether, and the more stable anomers of the corresponding glycosyl chloride derivatives could be isolated in excellent yields. The reaction is carried out with an excess of dichloromethyl methyl ether in the presence of 10% tin tetrachloride in a suitable solvent (dichloromethane or chloroform) or without solvent, at 20 °C. The reaction mixture was processed in the usual manner. Detailed data concerning the synthesis are summarized in Table I. The reaction can be reproduced on large scale, also giving high yields. Another advantage of the method is that — in contrast to the reaction catalyzed by $ZnCl_2$ — it takes place in dichloromethane solution, in homogeneous phase. Thus kinetic studies of the processes catalyzed with $ZnCl_2$ were not feasible and the mechanism of the reaction was concluded only from other data (*e.g.*, the by-products formed).

The reaction of sugar acetates with dichloromethyl methyl ether in dichloromethane solution in the presence of $SnCl_4$ catalyst made possible the determination of the kinetic order of the reaction. The reaction rate was determined by the polarimetric technique. The measurements were carried out with

Table I

Synthesis of α-acetochlorosugars with dichloromethyl methyl ether/$SnCl_4$

Sugar acetate*	Reaction time (min) at 20 °C		Isolated α-acetochlorosugar **1-10**								
			Yield %	M.p. °C			$[\alpha]_D$ ($CHCl_3$)			Cl %	
				Found.	Lit.		Found	Lit.		Found	Calcd.
Tetra-0-acetyl-β-D-xylopyranose	40	**1**	65	104	105	[8]	+173.6	+171.2	[8]	11.84	12.03
Penta-0-acetyl-α-D-glucopyranose	180	**2**	79	73—74	76	[8]	+167.1	+166	[8]	9.55	9.66
Penta-0-acetyl-β-D-glucopyranose	30	**2**	80	74	76	[8]	+172.0	+166	[8]	9.57	9.66
Penta-0-acetyl-β-D-galactopyranose	60	**3**	89	78—79	78—79	[9]	+178.5	+177.5	[9]	9.67	9.66
Penta-0-acetyl-β-D-mannopyranose	30	**4**	91	80	81	[8]	+88.3	+90.6	[8]	9.73	9.66
Tetra-0-acetyl-L-ramnose**	30	**5**	74	73	73	[8]	−125.6	−127	[8]	11.54	11.48
Octa-0-acetyl-β-lactose	30	**6**	97	143—144	144	[10]	+89.7	+85.7	[10]	5.64	5.41
Octa-0-acetyl-β-maltose	60	**7**	91	124	125	[11]	+162.4	+159.15	[11]	5.45	5.41
Octa-0-acetyl-α-cellobiose	45	**8**	80	193—194	178	[12]	+71.1	+71.3	[12]	5.57	5.41
					186—187			+73			
					200—201						
Octa-0-acetyl-β-genciobiose	30	**9**	77	143	137	[13]	+84.1	+80.5	[13]	5.48	5.41
					142—143			+89.2			
					148						
Hepta-0-acetyl-β-rutinose	30	**10**	73	150	150—150.5 [14]		+67.7	+66.5	[14]	5.88	5.94

* In the experiments, 1 g acetate was processed in each case
** Syrupy product.

Table II

Rate constants for the reaction of penta-O-acetyl-β-D-glucopyranose and dichloromethyl methyl ether/$SnCl_4$ in dichloromethane solution at 27 °C
(Concentration of dichloromethyl methyl ether: 0.4 mole/l.
Concentration of $SnCl_4$: 0.01 mole/l)

Conc. of sugar acetate	$k \cdot 10^{-2} \cdot min^{-1}$
0.05	4.97
0.10	5.32
0.15	5.17
0.20	5.21
0.25	5.25

penta-0-acetyl-β-D-glucopyranose. The reaction rate was examined first as a function of the sugar acetate concentration in 0.05—0.25 mole/liter dichloromethane solution. (In all cases, the concentration of tin tetrachloride and dichloromethyl methyl ether was 0.01 and 0.4 mole/liter, respectively.)

As shown in Fig. 1, the reaction rate increased with increasing concentration of the sugar acetate; the value of the rate constant, k, was calculated according to the correlation given for first-order reactions, and it proved to be nearly constant (Table II). Accordingly, the correlation $2.303 \log \frac{\alpha_\infty - \alpha_0}{\alpha_\infty - \alpha_t}$ plotted *versus* time yielded a straight line (Fig. 2). Changes in the dichloromethyl methyl ether concentration did not affect the reaction rate (Fig. 3), that is, the reaction is of zero-order in respect of the reagent. All these facts prove unambiguously that α-acetochlorosugars are formed in a kinetically first-order reaction. However, this simple kinetic order belongs to a complex reaction.

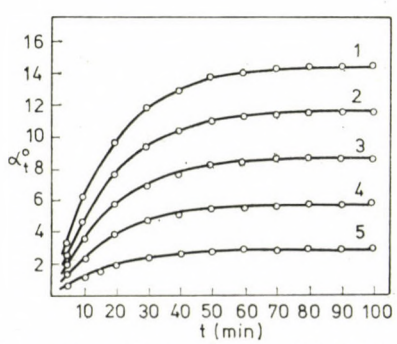


Fig. 1. Reaction of penta-O-acetyl-β-D-glucopyranose with dichloromethyl methyl ether in the presence of $SnCl_4$ catalyst in dichloromethane solution at 27 °C. Conc. of sugar acetate: (1) 0.25 mole/l; (2) 0.20 mole/l; (3) 0.15 mole/l; (4) 0.10 mole/l; (5) 0.05 mole/l
Conc. of catalyst: 0.01 mole/l
Conc. of reagent: 0.4 mole/l

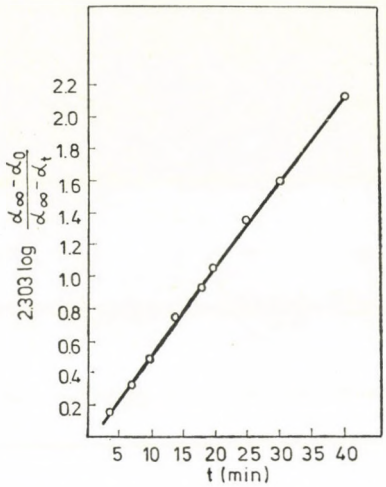


Fig. 2. Reaction of penta-O-acetyl-β-D-glucopyranose with dichloromethyl methyl ether/$SnCl_4$ in dichloromethane at 27 °C

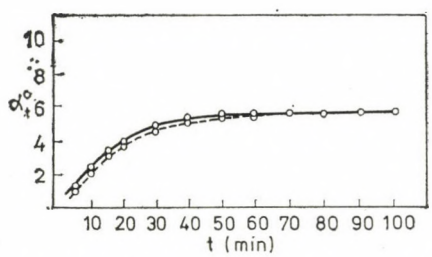


Fig. 3. Reaction of penta-O-acetyl-β-D-glucopyranose (0.10 mole/l) with dichloromethyl methyl ether (0.3—1.2 mole/l) catalysed with $SnCl_4$ (0.01 mole/l) in dichloromethane at 27 °C

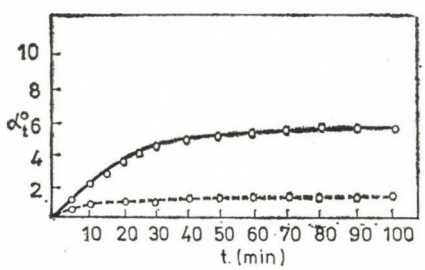
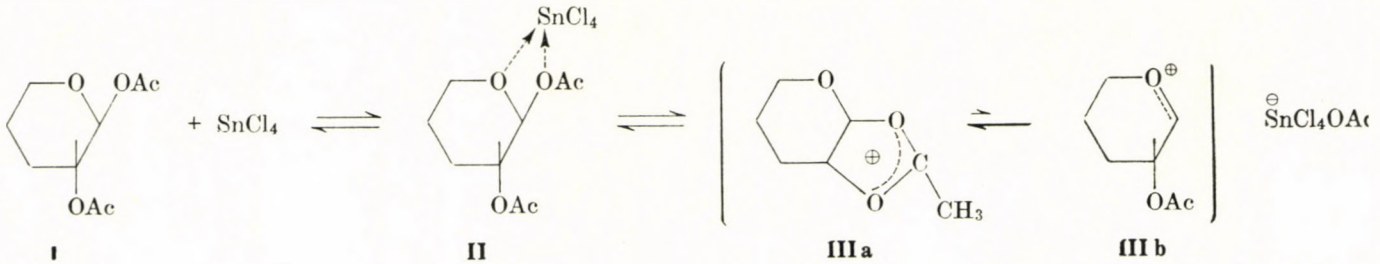
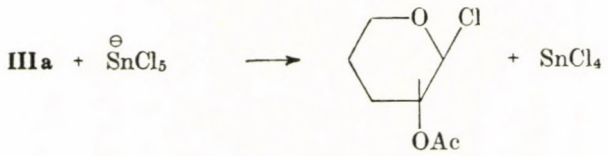


Fig. 4. Anomerization of tetra-O-acetyl-β-D-glucopyranosyl chloride (0.1 mole/l) with $SnCl_4$ (0.01 mole/l) in dichloromethane at 27 °C (———) Anomerization of penta-O-acetyl-β-D-glucopyranose (0.2 mole/l) with $SnCl_4$ (0.01 mole/l) in dichloromethane at 27 °C (– – – – –)

In order to obtain information on the part-processes, anomerization of tetra-O-acetyl-β-D-glucopyranosyl chloride with $SnCl_4$ was examined under identical conditions, and a curve exactly identical with the reaction of sugar acetate was obtained (Fig. 4). Therefore the reaction is assumed to consist of two part-processes: in the first, tetra-O-acetyl-β-D-glucopyranosyl chloride is formed









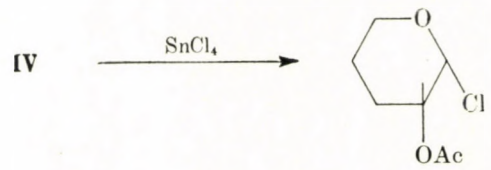


Fig. 5. The proposed mechanism of the reaction *1,2-trans* sugar acetates with dichloromethyl methyl ether catalyzed by tin tetrachloride

involving the participation of the C_2-acetoxy group, and the product of the first reaction undergoes isomerization in a second, slower part-process, yielding the thermodynamically more stable anomer. LEMIEUX and BRICE [4] arrived at the same conclusion in the kinetic examination of the reaction between penta-O-acetyl-β-D-glucopyranose and $TiCl_4$.

The assumption of a first, rapid part-process is supported by the observation that under identical conditions but using BF_3-etherate catalyst, acetates with 1,2-*trans* configuration yield 1,2-*trans* halogeno-sugars [2].

Furthermore, non-desired anomerization of penta-O-acetyl-β-D-glucopyranose with $SnCl_4$ [5] is, in practice, completely suppressed under the experimental conditions (Fig. 4).

As shown by preparative studies and polarimetric measurements, penta-O-acetyl-α-D-glucopyranose having 1,2-*cis* configuration reacts far more slowly (by another mechanism), in accordance with the expectations [6].

On the basis of kinetic studies and observations in connection with analogous reactions, the mechanism shown in Fig. 5 is assumed for the reaction of 1,2-*trans* sugar acetates with dichloromethyl ether–$SnCl_4$. The $SnCl_4$ complexes formed in the reaction were not examined in detail; the structure of II was given on the basis of literature data [7].

Experimental

Synthesis of α-acetochlorosugars

The sugar acetate (1 g) was allowed to react with dichloromethyl methyl ether (1 ml) and tin tetrachloride (0.1 ml) under the conditions given in Table I. In the cases of **6**—**10**, the components were dissolved in chloroform (2—4 ml).

After the accomplishment of the reaction, the mixture was evaporated to dryness in vacuum on a water bath at 50 °C, the residue was dissolved in chloroform, made neutral with 10% $KHCO_3$ and, after drying over $MgSO_4$, it was again evaporated to dryness in vacuum. The syrupy residue was recrystallized from ether–petroleum ether (**1**—**5**, **7**), anhydrous ethanol (**6**, **10**), anhydrous benzene (**8**) or chloroform–ether (**9**).

Penta-O-acetyl-β-D-glucopyranose (10 g) and octa-O-acetyl-α-cellobiose (10 g) were allowed to react under the conditions given in Table I and processed as described above; **2** and **8** were obtained in 85% and 80% yield, respectively.

In the *reaction kinetic measurements*, penta-O-acetyl-β-D-glucopyranose dried in vacuum over phosphorus pentoxide at 40 °C was used (0.5—2.5 mmole); the required amount of a stock solution of dichloromethyl methyl ether and $SnCl_4$ in dichloromethane was added, and the solution was made up to 10 ml with dichloromethane. (Dichloromethane was freshly distilled from P_2O_5.)

The dichloromethyl methyl ether stock solution was prepared from 1.78 ml (2.299 g) of dichloromethyl methyl ether, and this was made up to 10 ml with dichloromethane. There was 1 mmole (115 mg) of dichloromethyl methyl ether in 0.5 ml of the stock solution.

Anhydrous $SnCl_4$ (1.15 ml) was dissolved in dichloromethane and made up to 50 ml; 0.52 ml of this stock solution contained 0.1 mmole (26 mg) of $SnCl_4$.

Polarimetric measurements were carried out with a Schmidt-Haensch visual polarimeter in a 10-cm tube at 27 °C.

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CONVERSIONS OF TOSYL AND MESYL DERIVATIVES OF THE MORPHINE GROUP, XX*

SYNTHESIS OF MESYL ESTERS

(SHORT COMMUNICATION)

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A simple and convenient method had been developed for the preparation of dihydro derivatives of morphine alkaloids. In this way, 3-O-ethyldihydromorphine was obtained in crystalline form. This compound is described in the literature as an oily product. Several 6-O-mesyl derivatives have been synthesized in good yields also on a larger scale from the dihydro compounds by the use of Crossland's method.

Procedures for the synthesis of mesyl esters listed in Tables I and II have been published earlier [1—9]. In these procedures the widely applied methods for the preparation of alkyl and arylsulfonic esters (pyridine, sulfonic acid chloride, 24 hrs) have been adopted. The disadvantage of this method is that it can only be used if the end products are not too sensitive and therefore in the present case relatively low yields were obtained, furthermore, difficulties arise when applying it to a large-scale synthesis.

In some of the compounds examined, a tertiary alcoholic hydroxyl group (C—14) is also present, in addition to the secondary alcoholic hydroxyl group (C—6) (**Ic**, **IId**, **IIe**). The phenolic hydroxyl group (C—3) was protected by acetylation before mesylation in each case.

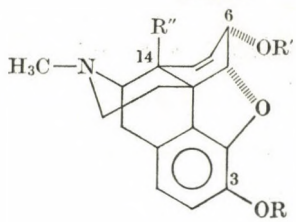
CROSSLAND *et al.* [10] recently reported the preparation of mesyl esters, even with tertiary alcoholic hydroxyl groups, in a fast reaction and in high yields, under very simple experimental conditions (dichloromethane, methanesulfonyl chloride, triethylamine). Using this method, we examined the mesylation of 14-hydroxymorphine derivatives.

In these compounds, however, the tertiary alcoholic hydroxyl group (C—14) did not undergo mesylation, but the mesyl esters of the C—6-alcoholic hydroxyl group was formed in high yields.

In view of these results, it was considered necessary to re-examine the preparation of the 6-O-mesyl esters also of other compounds, which are of theoretical and practical importance of our work; the results are shown in Tables I and II.

*Part XIX: MAKLEIT, S., KNOLL, J., BOGNÁR, R., BERÉNYI, S., SOMOGYI, G., KISS G.: Acta Chim. (Budapest) (In press) and Magyar Kém. Folyóirat **82**, 434 (1976)

Table I



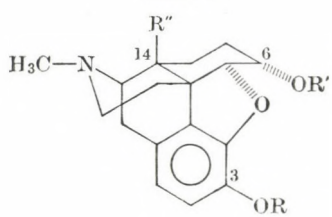
I

I

No.	R	R′	R″	Compound	Ref.	Yield, %	Lit. Yield, %
Ia	CH_3CO	CH_3SO_2	H	3-0-acetyl-6-0-mesyl-morphine*	[1, 3, 4, 6]	71	20
Ib	CH_3	CH_3SO_2	H	6-0-mesylcodeine	[1, 2, 4, 5]	79	16.4
Ic	CH_3	CH_3SO_2	OH	6-0-mesyl-14-hydroxy-codeine	[7, 8]	64	66.7

* 3-acetoxy-4,5α-epoxy-6α-methanesulfonyloxy-7,8-didehydro-17-methylmorphinan

Table II



II

No.	R	R′	R″	Compound	Ref.	Yield, %	Lit. Yield, %
IIa	CH_3CO	CH_3SO_2	H	3-0-acetyl-6-0-mesyl-dihydromorphine	[1, 3, 4, 6]	65.5	47.5
IIb	CH_3	CH_3SO_2	H	6-0-mesyl-dihydrocodeine	[1, 2, 4, 5]	80	23
IIc	C_2H_5	CH_3SO_2	H	6-0-mesyldihydroethyl-morphine	[9]	80	66
IId	CH_3CO	CH_3SO_2	OH	3-0-acetyl-6-0-mesyl-14-hydroxydihydro-morphine	[9]	63	44
IIe	CH_3	CH_3SO_2	OH	6-0-mesyl-14-hydroxy-dihydrocodeine	[7, 8]	80	20

In connection with these studies it may be mentioned that a simple and reliable method has been developed for the synthesis of the dihydro derivatives (dihydromorphine, dihydrocodeine, dihydroethylmorphine, 14-hydroxy-dihydrocodeine). (14-Hydroxydihydromorphine was prepared according to the method suggested by WEISS [11]. According to our method, the unsaturated compounds ($\Delta^{7,8}$) are hydrogenated in 5—10% methanolic or ethanolic solutions in the presence of 20% Raney Ni at room temperature, under atmospheric pressure. Hydrogenation takes place rapidly and quantitatively, which cannot be achieved with 10% Pd/C or even with PtO_2 catalysts.

This method made possible the preparation of 3-O-ethyldihydromorphine in crystalline state, which compound had been described [12] as an oil in the literature; m.p. 94—95 °C (from *n*-hexane), $[\alpha]_D$ —131° (c = 1.0, anhydrous ethanol).

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A NEW AND EFFICIENT METHOD FOR THE PREPARATION OF NEOPINE

(PRELIMINARY COMMUNICATIONS)

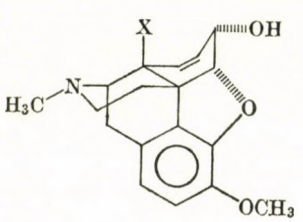
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Received April 15, 1977

The first synthesis of neopine (**4**) was achieved by CONROY [1] as follows: thebaine (**1**) was brominated with N-bromosuccinimide to yield 14-bromocodeinone (**2a**) in 85% yield; the product was reduced catalytically under special conditions resulting in neopinone (**3**) in 81% yield and this compound was reduced with sodium tetrahydridoborate(III), when neopine was obtained (the paper did not specify the yield of the last step). (See the scheme on the next page).

CONROY developed another variation of the method, too [1]: **2a** was reduced with sodium tetrahydridoborate(III) to 14-bromocodeine (**5a**) in 76% yield in the 0—5 °C temperature range, and the product was reduced further with the same reagent at 40 °C to **4**; the yield was not stated.

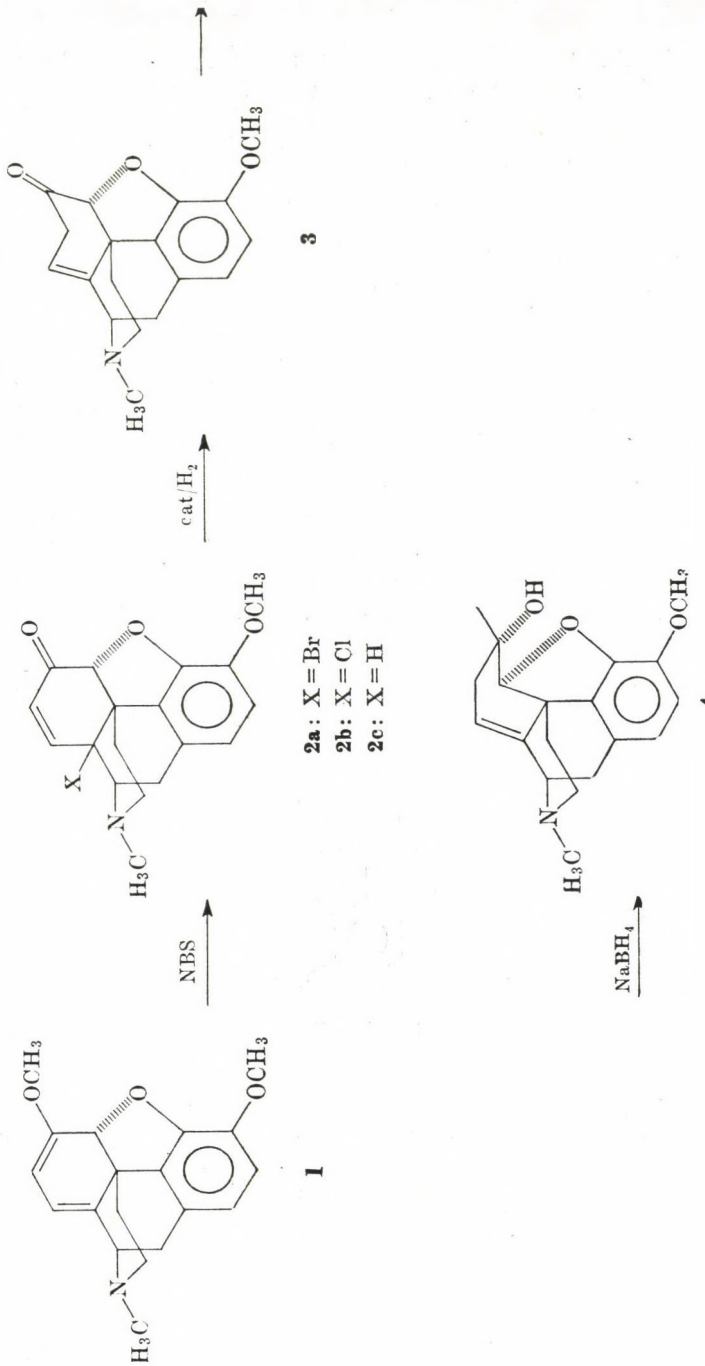


5a: X = Br
5b: X = Cl

Lather methods, varying the reducing agents and reaction conditions, and starting from **2a** or **5a**, gave the following results: KRAUSZ and RÜLL [2] used lithium tetrahydridoaluminate(III) and **2a** (47% yield); **5a** and the same reducing agent gave a yield of 34,7%; finally in the catalytic reduction of **5a** the yield was 42% neopine, calculated for thebaine.

OKUDA, TSUDA and JAMAGUCHI [3] started from **5a** applying CONROY's method, and isolated neopine in 25% yield (calculated for thebaine).

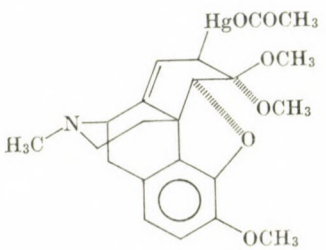
In 1976, BARBER and RAPOPORT [4] reported a fundamentally different method for the preparation of neopinone in high yield: **1** was converted with


OCH3
OCH3
H3C
N
O
1
NBS
X
2a: X = Br
2b: X = Cl
2c: X = H
cat/H2
3
NaBH4
OH
4

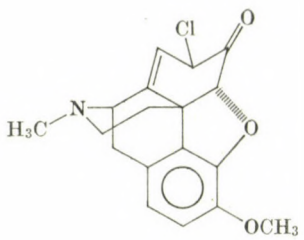
mercury(II) acetate into a mercury derivative (**6**) consisting mainly of the β-isomer, and this could by hydrolyzed with acetic acid to **3** in 93—100% yield (calculated for thebaine) without previous isolation.

The value of the method is affected by the fact that, on one hand, it yields neopinone containing codeinone (**2c**) when carried out without proper carefulness, as mentioned by the authors themselves; on the other hand, there is no data in the literature regarding the yield of the reductive conversion of neopinone to neopin. Furthermore, the non-stereospecific nature [3] of the reduction of neopinone with sodium tetrahydridoborate(III) also indicates that the method can hardly be evaluated in respect of the preparation of neopine.

The preparation of the chloro derivative (**2b**) of type **2a** was described by BRADLEY and LUTZ [5]; the compound was obtained from thebaine with phenyl iodide dichloride in 80% yield. In 1975, HOLMES [6] questioned the correctness of the structure given for the compound and supposed a 7-chloro-neopine structure (**7**).



6



7

According to our investigations, the compound can be prepared in another reaction path, too [7] and its structure definitely corresponds to **2b** (IR and NMR evidence). Its reduction with sodium tetrahydridoborate(III) at 0 °C gives compound **5b**, unknown up to now, in 90% yield. This product has a structure of allyl alcohol and allyl halide character, similar to **5a**, however, it is more stable than **5a** and its conversion reactions are more controllable and more selective.*

Of these reactions, in the present paper only the reduction resulting in neopine is reported**, which takes place quantitatively with sodium dihydro--bis-[2-methoxyethoxy]aluminate. Since **5b** is obtained from thebaine in 72% yield, this method, in comparison with other reaction routes, can be regarded as the most convenient and best reproducible preparation of neopine in the highest yield.

* Some reactions of **5b** were described by ABE, NAKAMURA and ONDA [8].

** Other reactions of **5b**, as well as the results of further conversion studies on neopine will be published in the near future.

In summing up, a simple, convenient and reliable method has been developed for the preparation of neopine. Starting with thebaine, compound **2b** was made and the structure of the product, disputed in the literature, was elucidated. This compound was reduced with sodium tetrahydridoborate(III) to **5b**, a new compound, in 90% yield. Reduction of this product with sodium dihydro-bis-[2-methoxyethoxy]aluminate yielded neopine quantitatively. The over-all yield, calculated for thebaine was 72% in this procedure.

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APPLICATION OF 8-HYDROXYQUINOLINE IN THE SYNTHESIS OF SEMI-SYNTHETIC β-LACTAM ANTIBIOTICS AND THEIR ESTERS

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Substituted (4-methyl, 6-methyl-, 5-ethyl-, 5-acetyl- and 5-nitroso-8-quinolyl esters of penicillin G, penicillin V and of several semi-synthetic penicillins (**I**—**X**) have been prepared. The compounds proved to be effective *in vitro* against *Mycobacterium tuberculosis* $H_{37}R_v$ and other INH- and streptomycin-resistant tuberculosis strains. It has been verified that these compounds are not only biologically but also chemically active. The 8-quinolyl esters of various carboxylic acids have been successfully applied in the synthesis of 3-methyl-7-acylamino-ceph-3-em-4-carboxylic acids (**XVa**–e) and their trichloroethyl esters (**XVIa**–e).

Of the numerous known penicillin esters, mainly the dialkylamino [1] and acyloxyalkyl esters [2] of penicillin G possess pharmacological importance. By the *per os* application of the acetoxymethyl ester of penicillin G (*Penamecillin, Maripen*) a high antibiotic level can be attained in the organism (serum, urine, tissue), and unlike the simple alkyl esters of penicillins, this compound in hydrolyzed by the human esterase enzymes [3].

Lately Hardy *et al.* [4] prepared esters having considerable antituberculotic and antifungal activity, by the reaction of penicillins with 8-hydroxyquinolines substituted by chlorine, alkyl, acyl, aralkyl, and alkoxy groups.

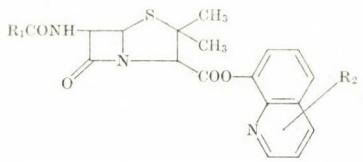
In the expectation of obtaining similar biological activity, we used 4-, as well as 6-methyl-, 5-ethyl-, 5-nitroso- and 5-acetyl-8-hydroxyquinoline and various penicillins as starting materials, to synthesize the esters **I**—**X** (*cf.* Table I) in dichloromethane (0—4 °C, 12 hrs) by means of dicyclohexylcarbodiimide or diisopropylcarbodiimide. Of these compounds, **II** and **IV**—**VI** were isolated as crystals, the others as amorphous materials.

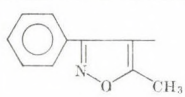
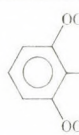
The penicillin- and semi-synthetic penicillin esters **II**—**VIII** inhibited *in vitro* the growth of *Mycobacterium tuberculosis* $H_{37}R_v$ at a concentration of 1—5 μg/ml, and they also had biological activity against tuberculosis strains resistant to isonicotinic acid hydrazide (*Isonicid*) and streptomycin. At the same time the 8-(5-nitroso-quinolyl) ester of penicillin V (**IX**) was effective only at a concentration as high as 20—50 μg/ml, and the 8-(6-methylquinolyl) ester of penicillin V (**X**) at a still higher concentration.

8-Quinolyl esters of amino acids are known to have found wide-spread application in peptide chemistry [5], like many other active esters. Thus the

Table I

Substituted 8-quinoline esters of penicillins and semi-synthetic penicillins



No.	R_1	R_2	M.p., °C	Yield, %	Cryst. or precip.	Analysis			
						Caled.		Found	
						S%	N%	S%	N%
I*		H	133—135	34.4					
II		4-Me	119—120	71	ethyl acetate petroleum ether	6.53	8.54	6.46 6.35	8.53 8.50
III		4-Me	83—87	32	petroleum ether	5.89	10.33	5.74 5.78	10.11 10.13
IV		4-Me	166—168	31.5	dichloromethane–petroleum ether	6.73	8.84	6.53 6.48	8.80 8.89
V		4-Me	150—152	11.4	dichloromethane–petroleum ether	13.29	8.72	12.91 12.81	8.70 8.77
VI		4-Me	177—178	38.7	dichloromethane–petroleum ether	6.15	8.07	5.61 5.50	8.35 8.46
VII		5-Ac	78—81	38	petroleum ether	6.17	8.09	5.94 5.93	8.03 8.12
VIII		5-Et	78—82	22	petroleum ether	6.34	8.32	6.37 6.42	8.23 8.13
IX		5-NO	80—82	35.7	ether	6.33	11.08	5.70 5.57	10.15 10.04
X		6-Me	80—82	35.7	ether	6.53	8.54	6.55 6.41	8.48 8.34

*First prepared by HARDY *et al.* [4] M.p. 133—135 °C

penicillin 8-quinolyl esters shown in Table I may be of interest not only because of their biological but also their chemical activity.

To verify this statement, the 8-(4-methylquinolyl) ester of penicillin V (**II**), as a model compound, was allowed to react with the well crystallizable 1-[N-glycylamino)] adamantane [6], in ethyl acetate (room temperature 24 hrs) (Fig. 1). 1-[V-Penicillyl-glycylamino] adamantane (**XIb**) and the

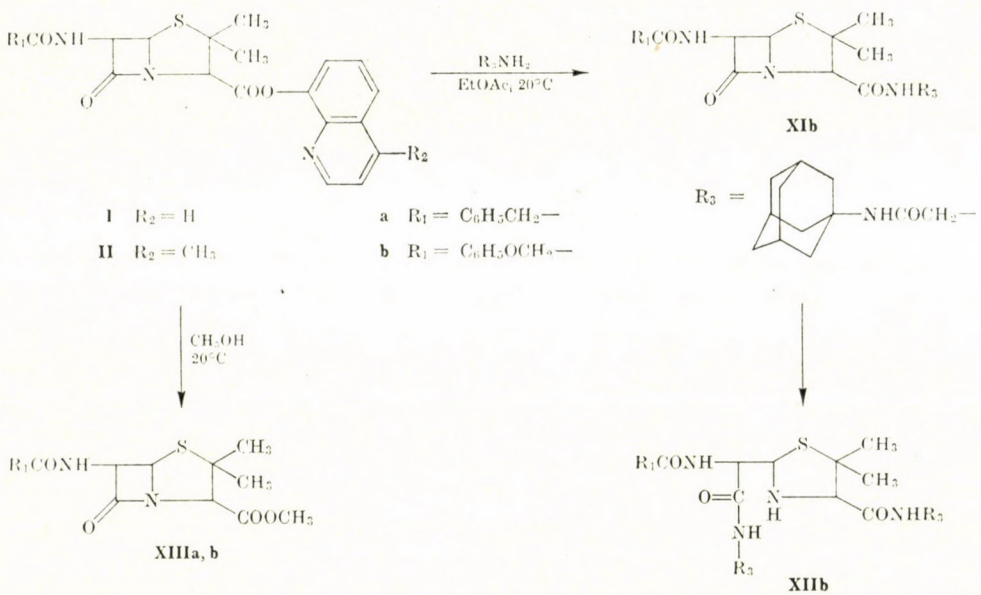


Fig. 1. Reactions of the 8-(4-methylquinolyl) esters of penicillin V

α- and β-biscarboxamide of V-penicilloic acid (**XIIb**), resulting from cleavage of the β-lactam were isolated from the reaction mixture. Besides the data of elementary analysis, the presence of the β-lactam carbonyl group was confirmed by the intense ν C=O band at 1778 cm^{-1} in the IR spectrum of **XIb**. This band was entirely missing in the IR spectrum of **XIIb**.

For the sake of comparison, **XIb** was also prepared from penicillin V and 1-[N-glycylamino] adamantane with dicyclohexylcarbodiimide; the product was identical with the compound obtained as described above. However, under these reaction conditions **XIIb** did not form (Fig. 1). The isolation of **XIb** in the course of the reaction affords evidence to show that the penicillin ester **II** behaves as an "active ester". On the other hand, the appearance of **XIIb** along with **XIb** indicates a difference in the reaction rates between acylation and β-lactam ring opening. In our opinion, this difference may also play an important part in the biological effect of penicillin-8-quinolyl esters.

The transesterification of the above mentioned penicillin-8-quinolyl esters occurs similarly to the reaction of other esters of 8-hydroxyquinoline [7] (Fig. 1). Thus, *e. g.*, **I** and **II** gave, on standing in abs. methanol (room temp., 12 hrs the methyl esters of penicillin G and V (**XIIIa** and **b**), which were identical in every respect (m. p., $[\alpha]_D$, TLC, IR spectrum) with the authentic samples [8, 9] prepared by methylation with diazomethane. The transesterification of **I** and **II** in ethanol and *n*-propanol was followed by TLC.

For the preparation of semi-synthetic β-lactam antibiotics, besides the acid chloride, mixed anhydride, ketene and carbodiimide methods, lately the use of the activated ester method has also been attempted. Thus several semi-synthetic penicillins have been prepared by the acylation of 6-aminopenicillanic acid (in the following: 6-APA) with 3-pyridyl- [10], cyanomethyl- [11], pentachlorophenyl- [12] and 8-quinolyl esters [13] of various carboxylic acids. 4-Nitro- and 2,4-dinitrophenyl esters [14] have been used for the acylation of both 6-APA and 7-aminocephalosporanic acid.

Semi-synthetic penicillins had been prepared in our laboratory by the 8-quinolyl ester procedure even before the corresponding patent [13] was known to us, moreover this method has been extended to the synthesis of deacetoxycephalosporin derivatives as well (Fig. 2). The esters **XIVa**–e, synthesized from the appropriate carboxylic acid and 8-hydroxyquinoline in dichloromethane with dicyclohexylcarbodiimide (0—4 °C, 20 hrs.) were used partly without isolation, and in the isolated form.

The sodium salt of 7-aminodeacetoxycephalosporanic acid (7-ADCA–Na) and the trichloroethyl ester of 7-aminodeacetoxycephalosporanic acid (7-ADCA–TCE) were acylated with the esters **XIVa**–e at room temperature in a mixture of tetrahydrofuran and water (4:1) and in dichloromethane, respectively. With the non-isolated esters **XIVa**–e yields of 30—40% were obtained. However, when the isolated, crystalline ester **XIVa** was used, the yield of acylation was as high as 65%.

The main advantage of this procedure is that the 8-hydroxyquinoline liberated during the acylation can be quickly and conveniently separated by extraction with dilute acid; thus, if required, it can be recovered. Furthermore, when the acylation is effected with an optically active amino acid derivative (**XIVe**), no racemization occurs.

The 3-methyl-ceph-3-em-4-carboxylic acids (**XVa**–e) and their trichloroethyl esters (**XVIa**–e) prepared with the 8-quinolyl esters of the above carboxylic acids proved to be identical with the authentic compounds synthesized from 7-ADCA (**XIIa**) and 7-ADCA–TCE (**XIIb**) by the acid chloride or dicyclohexylcarbodiimide method. Identity was established by elementary analysis, m. p., mixed m. p., TLC, and IR spectroscopy. Elimination of the trichloroethyl- and trichloroethylcarbonyl group of **XVIa**–e with metallic zinc in formic acid [15] gave compounds **XVa**–e.

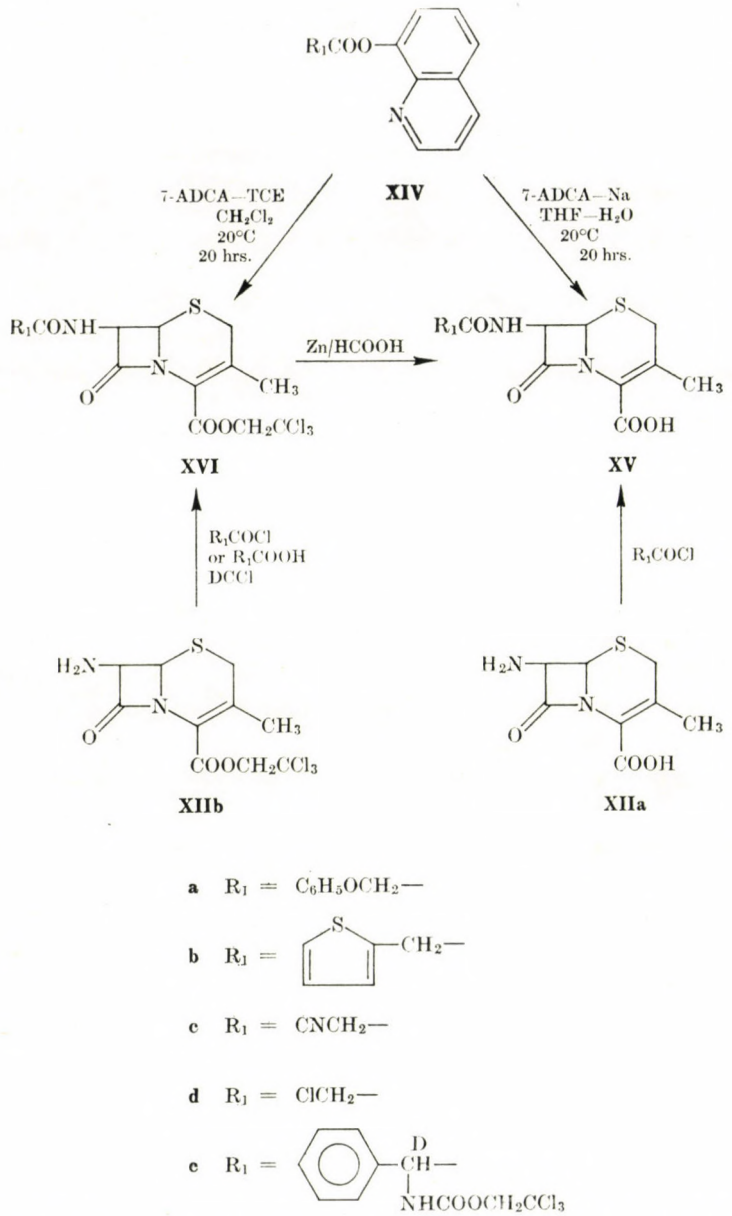


Fig. 2. Acylation of 7-ADCA and 7-ADCA—TCE with 8-quinolyl esters of carboxylic acids

Experimental

M.p.'s were determined by the capillary tube method, and are uncorrected. The IR spectra were obtained in KBr pellets with a UNICAM SP 200 G spectrophotometer. Thin-layer chromatographic investigations were made on 0.4 mm thick silicagel G layer on glass, in benzene–ethyl acetate–glacial acetic acid (7:3:1) (system A) or ethyl acetate–benzene (1:1) (system B); the spots were visualized by means of iodine vapour.

8-Quinolyl esters of penicillin and semi-synthetic penicillins (I—X)

Dicyclohexylcarbodiimide (or diisopropylcarbodiimide) (0.01 mole) was added to a solution of the 8-hydroxyquinoline derivative (0.01 mole) and penicillin (0.01 mole) (or penicillin-Na, K salt and 0.01 mole of pyridine hydrochloride) in dry dichloromethane (35 ml). The solution was allowed to stand 12 hrs at 0—4 °C. The precipitated dicyclohexyl urea was filtered off and washed with a small amount of dichloromethane. The organic solution was shaken successively with 5% hydrochloric acid (10 ml), water (10 ml), 5% sodium hydrogen carbonate (10 ml) and water, and dried over magnesium sulfate. The drying agent was removed by filtration and the solution evaporated to dryness. The residue was recrystallized from an appropriate solvent (*cf.* Table I), or rubbed with petroleum ether to obtain an amorphous material.

Reaction of the 8-(4-methylquinolyl) ester of penicillin V (II) with 1-(N-glycylamino)adamantane (a) 1-(V-penicillylglycyamino) adamantane (XIb)

A solution of V-penicillin-8-(4-methylquinolyl) ester (0.49 g; 0.001 mole) and 1-(N--glycylamino) adamantane (0.20 g; 0.001 mole) in ethyl acetate (15 ml) was let to stand 24 hrs at room temperature. The solution was extracted successively with water (5 ml), 5% HCl (5 ml), water, 5% sodium hydrogen carbonate (5 ml) and water, and dried over anhydrous $MgSO_4$. The solution was then evaporated to dryness and the remaining oil recrystallized from a mixture of carbon tetrachloride and ether, to obtain 93 mg (17.2%) of **XIb** m. p. 135—138 °C.

This product proved to be identical with **XIb** prepared by the dicyclohexylcarbodiimide condensation method, as shown by TLC, IR spectra, elementary analysis and m.p. measurements.

$C_{28}H_{36}N_4O_5S$ (540.6). Calcd. S 5.91; N 10.33%. Found S 5.75; 5.63; N 9.68, 9.45%.

R_f (system A): 0.30.

IR spectrum (KBr): νNH (amide) 3400; νC=O (β-lactam) 1778, νC=O (amide I) 1660, (amide II) 1520; νCH_2 2916, 2858 cm^{-1}.

(b) α- and β-bis-XIIb-Carboxamide of V-penicilloic acid

The compound was obtained as crystal separating from the reaction mixture of **XIb** after standing for 2 days. Yield: 180 mg (49%); m. p. 195.

$C_{40}H_{57}N_6O_6S$ (733.9). Calcd. S 4.28; N 11.22%. Found S 4.30, 4.31; N 11.30, 11.42%.

IR spectrum (KBr): νNH (amide) 3315; νC=0 (amide I) 1660, (amide II) 1530; νCH_2 2905, 2848 cm^{-1}.

Transesterification of I and II in methanol

I or **II** (0.002 mole) were dissolved in dry methanol (20 ml) and the solution was allowed to stand 12 hrs at room temperature. The solution was then evaporated to dryness and the residue dissolved in dichloromethane (30 ml). The organic solution was ewashed with 5% HCl (10 ml) and water (10 ml), dried over anhydrous $MgSO_4$, and evaporated to dryness.

XIIIa: 550 mg (79%). $[\alpha]_D^{20}$ +172° (c = 1, $CHCl_3$); lit. [8] $[\alpha]_D^{20}$ +172° (c = 1, $CHCl_3$). M.p. 90—91 °C; lit. [8] m.p. 89.5—92.2 °C and 97—98 °C.

IR spectrum (KBr): νNH (amide) 3359; νC=O (β-lactam) 1785; νC=O (amide I) 1676, νC=O (ester) 1740 cm^{-1}.

According to TLC (system A, R_f = 0.68) the compound is identical with the authentic product prepared from G-penicillin-K by the mixed anhydride method [8].

XIIIb: 610 mg (83%). $[\alpha]^{25} + 142.1°$ ($c = 1.22$, acetone); lit. [9] $[\alpha]^{25} +150.2°$ ($c = 1.3725$, acetone).

In TLC (system A, $R_f = 0.5$) it was identical with the authentic compound prepared from penicillin V by means of diazomethane [9].

The transesterification of **I** and **II** in ethanol and *n*-propanol to **XIIIa** and **XIIIb** was followed by TLC (system A). The spot **I** or **II** disappeared from the reaction mixture, and the spots of the ethyl and *n*-propyl esters and the liberated 8-hydroxyquinoline and 4-methyl--8-hydroxyquinoline, respectively, appeared. **I**: $R_f = 0.57$; 8-hydroxyquinoline: $R_f = 0.24$; ethyl ester of penicillin-G: $R_f = 0.71$; *n*-propyl ester of penicillin G: $R_f = 0.77$. **II**: $R_f = 0.50$; 4-methyl-8-hydroxyquinoline: $R_f = 0.17$; ethyl ester of penicillin V: $R_f = 0.68$; *n*-propyl ester of penicillin V: $R_f = 0.72$.

Acylation of 7-ADCA with 8-quinolyl esters of carboxylic acids

A solution of the appropriate carboxylic acid (0.01 mole), 8-hydroxyquinoline (0.01 mole) and dicyclohexylcarbodiimide (0.01 mole) in dichloroethane (50 ml) was let to stand at 0—4 °C for 20 hrs. After filtering off the dicyclohexylurea the solution was ecvaporated to dryness. The residue was dissolved in tetrahydrofuran (40 ml) and a solution of 7-ADCA (2.14 g; 0.01 mole) and sodium hydrogen carbonate (0.84 g; 0.01 mole) in water (10 ml) was added. The mixture was stirred for 24 hrs, then for removal of the tetrahydrofuran it was extracted with ethyl acetate (2 × 20 ml). The aqueous phase was then acidified with 5% HCl to pH 2, and extracted with ethyl acetate (3 × 10 ml). After drying over Na_2SO_4 the solution was evaporated to dryness, and the residue was rubbed with ether.

XVb: 1.0 g (29%), m.p. 178 °C; R_f (system A) = 0.40. According to TLC, m.p. and IR, the product was identical with **XVIb** prepared with metallic Zn in formic acid (54%), m.p. 177—178 °C (see below).

$C_{14}H_{14}N_2O_4S$ (338.4). Calcd. S 18.95, N 8.25. Found S 19.11, 19.20; N 7.92, 7.85%.

IR (KBr): νNH (amide) 3267; νC=0 (β-lactam) 1768; νC=O (amide I) 1660; νC=0 (COOH) 1708 cm^{-1}.

XVd: 0.82 g (28.3%), m.p. 174 °C, R_f (system A) = 0.41. According to TLC, m.p. and IR, the product proved to be identical with an authentic sample prepared from **XIIa** with chloroacetyl chloride, m.p. 174 °C (64%).

$C_{10}H_{11}N_2O_4S$ Cl. (291.0). Calcd. S 11.01, N 9.62, Cl 12.19%. Found S 11,05, 11.23; N 9.51, 9.40; Cl 12.22, 12.44%.

IR (KBr): νNH (amide) 3301; νC=O (β-lactam) 1765; νC=O (amide I) 1679; C=O (COOH) 1710 cm^{-1}.

8-Quinolyl ester of phenoxyacetic acid (XIV)

A solution of phenoxyacetic acid (1.52 g; 0.01 mole), 8-hydroxyquinoline (1.44 g; 0.01 mole) and dicyclohexylcarbodiimide (2.0 g; 0.01 mole) in dichloroethane (60 ml) was allowed to stand at 0—4 °C for 20 hrs. The precipitated dicyclohexylurea was filtered off, the solution was extracted with 5% HCl (10 ml), water (10 ml), 5% $NaHCO_3$ (10 ml) and water, and dried over $MgSO_4$. After filtration, the solution was evaporated to dryness. The residual colourless oil was crystallized from a mixture of ethyl acetate and petroleum ether.

1.55 g (55.8%), m.p. 126—129 °C, R_f (system B) = 0.60.

$C_{17}H_{13}NO_3$ (279.2). Calcd. N 5.03. Found N 4.95, 4.83%.

Acylation of 7-ADCA-TCE- with 8-quinolyl esters of carboxylic acids

A solution of the appropriate carboxylic acid (0.01 mole), 8-hydroxyquinoline (0.01 mole) and dicyclohexylcarbodiimide (0.01 mole) in dichloromethane (60 ml) was allowed to stand for 20 hrs at 0—4 °C. The dicyclohexylurea which precipitated was filtered off and a solution of 7-ADCA—TCE hydrochloride (0.01 mole) and triethylamine (0.01 mole) in dichloromethane (40 ml) was added to the filtrate. The reaction mixture was then let to stand 20 hrs at room temperature, extracted with 5% HCl (20 ml), water (20 ml), 5% $NaHCO_3$ solution (20 ml) and water (20 ml), and dried over $MgSO_4$. After removal of the drying agent by filtration, the solution was evaporated to dryness and the residue rubbed with ether. In the case of **XVIe**, the product was crystallized from carbon tetrachloride.

XVIa: 1.83 g (39.6%), m.p. 113—116 °C, lit [16] m.p. 114—116 °C, R_f (system A) = = 0.80.

If the acylation was carried out with the isolated 8-quinolyl ester of phenoxyacetic acid, the yield was 3.03 g (65.1%), m.p. 115—117 °C, R_f (system A) = 0.80.

XVIb: 0.85 g (16%), m.p. 146—8 °C, R_f (system A) 0.72.

According to TLC and IR, the product was identical with the pure compound prepared by the acylation of **XIIb** with 2-thienylacetyl chloride (77%).

$C_{16}H_{15}N_2O_4S_2Cl_3$ (469.8). Calcd. S 13.64, N 5.96, Cl 22.85%. Found S 13.60, 13.47; N 5.94, 5.86; Cl 22.78, 22.90%.

IR (KBr): νNH (amide) 3320; νC=O (β-lactam) 1768; νC=O (amide I) 1682; νC=O (ester) 1732 cm^{-1}.

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RECENSIONES

B. LINDMAN, S. FORSÉN: *Chorine, Bromine and Iodine NMR Physico-Chemical and Biological Applications.*

Springer Verlag, Berlin, Heidelberg, New York, 1967 (368 p.)

This book is the 12th volume of the series "NMR Basic Principles and Progress" started in 1969 (Editors: P. DREHL, E. FLUCH, R. KOSFELD). Previous volumes dealt with special fields of NMR spectroscopy, being devoted mainly to theoretical and physical aspects. Due to the increasing importance of this method, in the preface of the present volume the editors express their intention to devote more attention to the problems of applied spectroscopy in further issues.

This aim was realized in Volume 12, in which the authors illustrate the theoretical considerations with practical results.

The special scope allowed a complete treatment of the relevant literature practically up to the time the manuscript was sent to press (several, previously unpublished data appeared in this volume) and, as a result of the extremely short printing time, the volume offers the reader up-to-date review of halogen (except fluorine) NMR.

The concise first chapter (21 pp.) applies the NMR theory to halogens, *i.e.* deals briefly with the NMR properties of halogen atoms which possess particular features because of their nuclear quadrupole moments. The phenomena of quadrupole splitting, nuclear shielding and spin-spin coupling, quadrupole and other relaxation mechanisms, chemical exchange effects and the experimental aspects for determining the NMR parameters of halogens are shortly discussed.

Relaxation processes in molecules or ions with covalently bonded halogens and evaluation of the correlation time are described in Chapter 2 (38 pp.).

Chapter 3 (24 pp.) discusses the chemical shift of covalent halogen compounds, halide ions in crystals and aqueous solutions using numerous experimental data. Methods for approximate calculations of nuclear shielding and medium effects on shielding values are described too.

Spin coupling constants of halogens and the effects which contribute or determine them are reported in Chapter 4 (18 pp.).

The lengthy Chapter 5 (100 pp.) is devoted to the relaxation of halide ions. The theoretical treatment of the electrostatic and electronic distortion model for infinitely dilute aqueou solutions of alkali halides and several other compounds containing paramagnetic species are illustrated by experimental results. This chapter is completed with the NMR study of liquid exchange mechanisms of inorganic halide complexes.

Shielding values of halide ions can be found in Chapter 6 and the quadrupole splitting values in liquid crystals in Chapter 7 (30 and 16 pp., respectively).

Chapter 8 (77 pp.) deals with biological systems containing halide ions referring to the connections between chemical structure, relaxation and chemical exchange processes. In subchapters the data referring to small molecules of biological interest, polypeptides, proteins and other compounds are summarized.

NMR parameters of perchlorate ions are described in Chapter 9 (12 pp.)

Chapter 10 informs about recent work and trends.

At the end of the book more than 500 references and a subject index (6 pp.) are given.

This concentrated, complete, up-to-date work may provide much useful information for research workers engaged in this field.

P. SOHÁR

Atlas of Thermoanalytical Curves (TG, DTG, DTA curves recorded simultaneously) Volume 5

Edited by G. LIPTAY
Akadémiai Kiadó, Budapest, and Heyden and Son Ltd., London, New York, Rheine, 1976
(169 pages, 75 diagrams)

The methods of thermal analysis were extensively developed during the last two decades simultaneously with widening applications. The series Atlas of Thermoanalytical Curves plays a special role in thermal analysis literature because of the wide scale of selected material and uniform treatment of the results obtained.

The greater part of the investigations reported in this volume is by Hungarian contributors but there are also several diagrams recorded abroad.

Volume 5, containing diagrams no. 276—350, is arranged similarly to the previous volumes. Each material was measured under two conditions of unified parameters:

a) samples of small initial mass, slow heating (red curves in the diagrams)

b) samples of greater initial mass, rapid heating (black curves in the diagrams)

Simultaneous measurements carried out with a Derivatograph (MOM) and a Mettler Thermoanalyzer, in some cases, like in Volume 4, were supplemented by TG/DTG, DTA and DSC curves obtained separately with a Du Pont 990 Thermal Analysis System, using milligram samples. The instruments are described in appendices.

Carefully compiled diagrams published in Volume 5 concern 41 pure inorganic and 22 organic compounds, and 4 natural coals. The judgement of the Editor should be praised for including 9 standards selected by the International Confederation for Thermal Analysis for temperature calibration. Simultaneous and supplemental DSC, DTA and TG/DTG curve of ICTA standards offer an opportunity to check various thermoanalitical instruments.

Another interesting group of the material selected, refers to different inorganic and organic salts of rare-earth metals, which are of great importance in several practical fields.

The diagrams are clear and uniform. Description of the sample and experimental parameters, the notes explaining the processes indicated on the curves and references are concise and valuable. So this volume certainly is useful for experts working in this field or for those applying thermoanalytical results.

Presentation of the volume is faultless, demonstrating the careful work of the Publishers.

Gy. POKOL

G. S. HAMMOND, J. OSTERYOUNG, T. H. CRAWFORD and H. B. GRAY: *Modellvorstellungen in der Chemie.*

Walter de Gruyter, Berlin, New York, 1976. (XVI. 526 pp.)

Numerous chemistry text books of introductory nature have been published during the past 20 years. These books have sought the best didactic possibility for the presentation of the laws of chemistry, and for the description of the most important chemical substances (elements and their compounds). The proportions devoted to the general principles and to an account of the more practical subject matter differ considerably from book to book. The trend at present is for less and less space to be occupied by chemistry of a "descriptive" nature; it has become a fashion to regard a knowledge of substances as a necessary, or even an unnecessary evil in education. The book in question falls in this category. The work is the German translation (translator: H. W. SICHTING) of the book which appeared in English in 1971.

The book has some undoubtedly advantageous features. It is useful that the various concepts, summarized separately at the end of the chapters, are explained individually. As the discussion progresses, certain concepts are dealt with again, now analyzed more deeply. The problems have been well selected, are stimulating and suitable for beginners to test themselves as to whether they have really understood the text. The Figures are generally clear and well arranged.

However, this exhausts the good that can be said of the book. The space devoted to the knowledge of matter is inadmissibly insufficient. The intention to introduce the more complex concepts in a simple way is often overdone. The infantile "story" concocted to present the law of mass action is hardly likely to become widespread in teaching.

It is difficult to define precisely just who the book is written for. Definitely not for beginners who wish to become acquainted with the elements of chemistry. It may be useful for those delivering introductory chemical lectures as a standby in the selection of examples, and in the moulding of clear concepts.

The typographical production of the book is exemplary.

M. T. BECK

Arno HÖPFER: *Irreversible Thermodynamik für Chemiker*, Sammlung Göschen 2611

Walter de Gruyter, Berlin—New York, 1976 (182 pp.)

In this little book an elementary treatment of the theory of irreversible thermodynamics with applications for discontinuous macroscopic systems of particular importance for chemists is presented. In the first chapter the basic concepts of phenomenological and statistical thermodynamics are briefly summarized. In the next four chapters the fundamentals of the linear Onsagerian theory are presented and applied to systems representative of the most relevant problems of physical chemistry. In the seventh chapter the thermodynamic theory of stationary systems is analyzed and applied to simple system models in the traditional form adequate to Prigogine's original formulation, which is, at least nowadays, a little obsolate. In the following the Glansdorff-Prigogine macroscopic evolution criterion is dealt with and applied to catalytic reactions and chemical oscillations. The last three chapters are devoted to fundamental and interesting problems of thermodiffusion, thermodynamic stability and to some important biophysical problems of living organisms.

Although the book is very elementary, it might be useful for those not yet familiar with the modern theory of thermodynamics. It is particularly recommended for chemists, biophysicists and biologists.

I. GYARMATI

Structure and Bonding, Vol. 27.

Springer-Verlag, Berlin, Heidelberg, New York, 1976 (217 pp.)

The volume contains reviews of three fields:

1. M. SIMONETTA, A. GAVEZOTTI: Extended Hückel Investigation of Reaction Mechanisms (pp. 1—43).

The authors review the more recent calculations based on the Extended Hückel Theory (EHT), an approximate quantum-chemical method first described in 1962—1963. The review touches three topics: a discussion of organic reaction mechanisms, calculations relating to coordination compounds of heavy metals, and the applications of the EHT to describe surface phenomena on solids.

A large proportion of the results obtained with the calculations cannot be checked experimentally. The results are in agreement with the Woodward-Hoffmann rules when it is possible to make a comparison.

The review provides a good picture of the efforts being made to extend the range of application of the EHT method, and urges the checking of the reliability of the calculations with further experimental studies.

2. K. D. WARREN: Ligand Field Theory of Metal Sandwich Complexes (pp. 45—159).

Since the discovery of ferrocene (1951), intensive research has been carried out with regard to the preparation and theoretical investigation of similar transition metal π-complexes.

After an account of the ligand field theory for the d configurations, the author deals in turn with the most important experimental methods used to study complexes, and examines the extent to which the experimental results can be explained in terms of the ligand field theory. Different sections are devoted to electronic spectra resulting from d-d transitions, magnetic susceptibility measurements, and ESR, charge-transfer and photoelectronic spectra.

At present, quantum chemistry can describe these compounds containing many atoms and many electrons only to a rather rough approximation. *Ab initio* calculations giving a good approximation are used only rarely, as they are very expensive. The semiempirical methods have not been appropriately developed for metal atoms.

With 180 references, the review gives a very good picture of the rapid advances in this new field of chemistry.

3. O. ERMER: Calculation of Molecular Properties using Force Fields. Application in Organic Chemistry (pp. 161—211).

The approximate method described permits calculation of the equilibrium geometry and force constants of a family of molecules. As a starting point it is necessary to know the average geometry and force constants for the type of molecule studied. The potential energy of the molecule examined can then be given as a function of the nuclear coordinates. The equilibrium geometry is obtained by displacing the nuclei from the initial positions, with the aid of computer programs, until the derivatives of the potential energy with respect to the nuclear coordinates vanish. The force constants are given by the second derivatives of the potential functions thus obtained.

The author describes the parameters serving to characterize the geometry of the molecules, and gives an account of the various force constant systems, the methods for determining these from the experimental data, and the procedures suitable for energy minimization. An example of the application of the method is also presented. Finally, the most important areas of application are discussed: calculation of the force constants of saturated hydrocarbons, hydrocarbons with isolated or conjugated double bonds, amides, peptides and crystals, the solution of conformational problems, and the structures of transition states. The review is complete with 113 references.

Little is said about comparison of the quantumchemical equilibrium geometries and the force constants calculated by this method, though it is likely that this would be very instructive.

F. TÖRÖK

J. U. KELLER and C. G. STOJANOFF: *Journal of Non-Equilibrium Thermodynamics*

Walter de Gruyter, Berlin—New York, 1976 Vol. 1. No. 1. pp. 1—78

The Journal of Non-Equilibrium Thermodynamics (JNETD) is the first international journal devoted to the publication of original research concerned with both the physical foundatiions and the engineering applications of the modern discipline, the thernodynamics of irreversble processes. This includes many fields of science and technology based on exact physical laws, *e.g.* thermomechanics, fluid dynamics, rheology, various parts of physical chemistry (especially; diffusion, electrochemistry, reaction kinetics etc.), with numerous aspects of plasma physics, general energetics, mechanical, chemical and power engineering, and so on.

The main aim of JNETD is to reduce the gap between today's theoretical advances and urgent practical needs in many fields of science and engineering which deal with non-equilibrium phenomena. The Editors wish to make JNETD a broadly based communication medium of high standards for all aspects of non-equilibrium thermodynamics. The Editors and the members of the Editorial Advisory Board (EAB) are all prominent scientists active in experimental and theoretical research and will act according to the principle of unprejudiced valuation.

JNETD will publish selected articles solicited by the Editors and the EAB, as well as original papers and short communications not exceeding 25 type-written pages and 1000 words respectively. The submitted papers will be refereed by the EAB. As a rule, for a paper to be accepted it is necessary to obtain the recommendation of two referees, one of which should be a member of the EAB.

In the first volume one review article, six original papers and one book review are published. In the review by BRANDT and NEUER (Stuttgart) more than 300 publications have been used for discussing the thermal conductivity and the thermal radiation properties of UO_2. In a paper by BATAILLE and KESTIN (Lyon), the various forms of the dissipation inequality are analyzed. It is surprising, however, that certain special forms of the traditional formulation of the second law in the form of the classical (Onsagerian) thermodynamics of irreversible processes are considered as new results of "rational thermodynamics" may perhaps be "rational" as a pure mathematical subject, but it is not a real physical theory. The paper of HIERNAUX and BABLOYANTZ (Bruxelles) is devoted to the problem of embryogenesis, and "nonlinear thermodynamics" is used to evaluate dissipation during embryogenesis. However, we cannot find anything about non-linearities in this paper. The paper of PICCIRELI and IM (Detroit) deals with the acoustic propagation constant at high frequencies from experimental and theoretical points of view. WEN-JEI YANG (Ann Arbor) analyzes the motion of a spherical gas bubble in the flow around a flat disk which rotates about an axis perpendicular to its plane in a fluid at rest or in axial flow. In a paper by MUSCHIK and SZER (West Berlin) it is shown that

the matrix of the Onsagerian laws may be symmetrized also for systems with a magnetic field, consequently, the variational principle of GYARMATI can be applied to systems with magnetic fields. KELLER (West Berlin) discusses the fundamental inequality of MEIXNER in the case of a simple model of a discontinuous system.

The reviewer is convinced that the Journal of Non-Equilibrium Thermodynamics will become an international medium for facilitating the exchange of basic ideas and applications of non-equilibrium thermodynamics. The first number of the journal is very attractively printed at a price of DM 45.

J. SÁNDOR

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РЕЗЮМЕ

Сенсибилизированная флуоресценция нафтацена 3,4-бензпиреном и ее аналитическое применение

И. ХОРНЯК

Под влиянием УФ света 3,4-бензпирен на ватмановской бумаге испускает спектр флуоресценции, состоящий из широкой полосы. При температуре 77°К полоса расщепляется на три полосы. Твердый 3,4-бензпирен сенсибилизирует флуоресценцию нафтацена; это явление хорошо объяснимо на основе механизма замедленного перехода триплет—триплет. Описывается применение этого явления для количественного определения нафтацена.

Свойства смесей спирт-амин, XIV

Исследование средней степени ассоциации

Ф. РАТКОВИЧ и Т. ШАЛАМОН

Была определена плотность смесей 1-бутанола с моно-, ди- и три(н-бутил)-аминами при 20°С, а также исследована их динамическая вязкость в интервале температур 20—40°С. Из вискозиметрических данных была определена энтальпия активации ламинарного течения в зависимости от средней степени ассоциации смесей и состава. Заключения, полученные из результатов, пополняют более ранние сведения относительно ассоциации смесей спирт — амин. Было доказано, что энталпия образования водородных мостиков в случае O—H . . . N больше, чем в случаях O—H . . . O и N—H . . . N. Были сделаны также качественные заключения относительно вероятности образования различных структур смешанных ассоциатов спирт — вода.

Вклад свободной пары электронов в эллипсы силового поля и спектроскопические константы дигалоидов элементов группы IV A и NO_2

К. Л. НАРАЯНА и М. К. СОУДАГАР

Вклад свободной пары электронов в молекулярные константы и эллипсы силового поля некоторых дигалоидов элементов группы IV A и NO_2 исследовали, принимая во внимание формализм функций Грина и используя технику разложения. По существу, считается, что свободная пара находится при атоме Z структуры типа XY_2Z, полагаемой для таких молекул. Приводятся также рассчитанные силовые постоянные, симметричные среднеквадратичные амплитуды, константы Кориолиса, матрицы распределения потенциальной энергии и генерированные эллипсы силового поля. Все они подвергаются сравнению и обсуждению.

Кинетика превращений углеводородов, катализированных платиной

З. ПАЛ, К. МАТУШЕК и П. ТЕТЕНИ

Выходы изомеризации, циклизации и гидрогенолиза 3-метилпентана, а также раскрытие кольца метилциклопентана на катализаторе платиновой черни дают максимумы в зависимости от давления водорода как в циркуляционной, так и в импульсной системе, а поведение типа Лангмюра-Хиншельвуда наблюдается в зависимости от давления углеводорода. Кинетическая обработка производилась; исходя из углеводородных частиц, образующихся в однократной и многократной диссоциации, причем первые являются активными промежуточными продуктами изомеризации, циклизации и раскрытия кольца, а последние препятствуют этим реакциям. Полагая, что эффект водорода в основном проявляется в подавлении образования последних, могут быть объяснены теоретические кривые с максимумом. Кинетические данные обсуждаются, а также используются как дополнительные свидетельства в интерпретации механизмов различных поверхностных процессов.

Исследование некоторых 3-замещенных 4-гидроксикарбостирилов

А. А. САЕД, С. М. САМИ, А. ЭЛЬФАЙОУМИ и Э. А. МОХАМЕД

Некоторые новые производные 4-гидроксикарбостирила, обладающие гетероциклическим заместителем и длинной ацильной цепочкой в положении 3, были синтезированы из 3-ацетил-1-алкил(или фенил)-4-гидроксикарбостирила I. Было получено монобромное производное Ia и определена его структура.

Исследование в области гетероциклов, XLIII

Сравнительные исследования 2p(X)-фенил-4(R)-оксазола и 2p(X)-фенил-4(R)-тиазола. Квантово-химические расчеты

И. ШВАРЦ, Р. Д. ПОП и И. СИМИТИ

Было проведено сравнительное исследование тиазольных и оксазольных колец в сериях I и II. Было заключено, что по химическому характеру тиазольные производные более ароматичны, чем оксазольные. Так, σ (константа реакционности в уравнении Гаммета) больше в оксазольной серии, нежели в тиазольной.

Индексы реактивности находятся в хорошем согласии с константами скоростей, а рассчитанные молекулярные параметры с экспериментальными данными.

Результаты указывают на копланарность двух колец.

Взаимодействие производных сахаров с α-дигалогеновыми эфирами

Синтез гликозилхлоридов с помощью реагента дихлорметилметилового эфира/четыреххлористое олово

И. ФАРКАШ, И. Ф. САБО, М. М. МЕНЬХАРТ, Е. Р. ДАВИД и Р. БОГНАР

Перекисные ацетаты моно- и дисахаридов с дихлорметилметиловым эфиром/$SnCl_4$ могут быть превращены в стабильные производные аномерного гликозилхлорида с очень хорошим выходом. Согласно поляриметрическим измерениям, кинетически реакция протекает по закону первого порядка. На основе этого предлагается вероятностный механизм реакции.

Использование 8-гидроксихинолина в синтезе антибиотиков полусинтетических β-лактамов и их эфиров

Ф. СТАРИЧКАИ, И. МИШКОЛЬЦИ, Р. Е. ФАРКАШ и Р. БОГНАР

Были получены G- и V-пенициллин, а также 4- и 6- метил-, 5-этил-, 5-ацетил- и 5-нитрозохинолил-8-эфиры полусинтетического пенициллина (I—X), которые оказались эффективными in vitro по отношению к Mycobacterium tuberculosis $H_{37}R_v$, а также к тем породам туберкулеза, которые устойчивы к INH и стрептомицину. Было доказано, что эти соединения являются активными не только биологически, но и химически. Различные 8-эфиры карбоновых кислот хинолила были использованы в синтезе 3-метил-7-ациламиноцеф-3-ем-4-карбоновых кислот (XVa—e) и их трихлорэтильных эфиров (XVIa—e).

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ABHÄNGIGKEIT DER LEISTUNGSFÄHIGKEIT DER SPEKTROCHEMISCHEN METHODEN VOM AUFLÖSUNGSVERMÖGEN DER SPEKTROGRAPHEN, II*

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Eingegangen am 26. Oktober 1976

Es wurde die Abhängigkeit der Wertungsparameter der spektrochemischen analytischen Methoden vom theoretischen Auflösungsvermögen untersucht. Bei den Untersuchungen wurde vorher die Untergrundschwärzung optimalisiert. Die Veränderung des theoretischen Auflösungsvermögens wurde mittels Ordnungsänderung, Gitterfurchenzahländerung und schließlich durch Anwendung des sog. doppelten Strahlendurchganges erreicht.

In einer früheren Arbeit [1] wurde gezeigt, daß die Wertungsparameter der spektrochemischen analytischen Methoden durch die Veränderung des theoretischen Auflösungsvermögens von Gitterspektrographen beeinflußt werden können. Diese Untersuchung wurde aber bei konstanten Belichtungszeiten für alle vier angewendete Ordnungen durchgeführt, was bei den Spektren mit steigender Ordnungszahl von einer prägnanten Verminderung der Untergrundschwärzung begleitet wird. Sogar in Spektren, die für die vierte Ordnung mit Hilfe eines Vorzerlegers aufgenommen wurden, war es sehr problematisch, meßbare Untergrundschwärzungswerte zu erreichen. Selbstverständlich wurden unter diesen Bedingungen die Möglichkeiten einer weiteren Optimalisierung der Leistungsfähigkeit der spektrochemischen Methoden schon sehr begrenzt. Deshalb wurden bei den neukonzipierten Untersuchungen in erster Linie die experimentellen Bedingungen, nämlich die Untergrundschwärzung, nach den von DOERFFEL und DEMUTH [2] festgelegten Regeln optimalisiert.

Experimenteller Teil

Unterschiedliche Bedingungen für das theoretische Auflösungsvermögen und damit unterschiedliche reziproke Dispersionswerte wurden durch Anwendung von vier Gittern mit den in Tabelle I angegebenen Leistungsparametern geschaffen. In Tabelle II sind die allgemeingültigen und die veränderlichen experimentellen Versuchsbedingungen zusammengefaßt.

In Rahmen der veränderlichen experimentellen Bedingungen wurden wechselsweise Graphit- und quasiamorphe Kohleelektroden, 60 und 90 Sekunden lange Belichtungszeiten

* Vorgetragen auf der Sitzung des Spektrochemischen Arbeitskomitees der Ungarischen Akademie der Wissenschaften, Budapest, Dezember 1975.

Tabelle I

Leistungsparameter der angewendeten Gitter

Untersuchungsmodell	1a	1b	2	3a	3b	4
Gesamtfurchenzahl	45600		91000	45600		45600
Furchenzahl pro Millimeter	651		1302	651		651
λ_{blaze} [nm]	320		270	280		350
Ordnung der Diffraction, m	1	1	1	1	2	3
Strahlungsdurchgangsart *	E	D	E	E	D	E
Strahlungsanteil [%]	87	41	80	67	31	57
Reziproke Dispersion $\times 10^{-6}$	0,737	0,368	0,368	0,368	0,184	0,246
Theoretisches Auflösungsvermögen $\times 10^5$	0,451	0,902	0,911	0,922	1,845	1,368

**Bemerkung*: E — einfacher, D — doppelter Durchgang

Tabelle II

Experimentelle Versuchsbedingungen

A. Allgemeine, optische und Anregungsbedingungen

Spektrograph	Gitterspektrograph PGS—2, C. Zeiss, Jena
Abbildungsart	dreilinsig mit Zwischenabbildung
Spaltbreite	0,040 mm
Elektrodenmaterial	Graphit (SU) und Kohle (SW), VEB Elektrokarbon, Topolčany, Tschechoslowakei
Elektrodenabstand	5,0 mm
Emulsion	VEB ORWO, Wolfen, DDR
Entwickler	VEB ORWO, F—43; 10 Minuten bei 20 °C
Anregungsart	elektronisch gesteuerter Abreißbogen
Anregungsquelle	Generator BIG—100
Primärspannung	220 V
Primärintensität	7,2 A
Polarität	$\pm$
Zündungspunkt	$\lambda/4$
Zündungszahl	100 pro Sekunde

B. Veränderliche experimentelle Angaben

Untersuchungsmodell	1a	1b	2	3a	3b	4
Emulsion	WU—3	WU—3	WU—3	WU—3	WU—2	WU—2
Trägerelektrode	SU—304	SU—304	SU—304	SU—304	SW—304	SW—304
Gegenelektrode	SU—201	SU—201	SU—201	SU—201	SW—201	SW—201
Abbildungsblende [mm]	5	5	12	12	12	5
Belichtungszeit [s]	60	60	60	90	90	90

sowie zwei unterschiedliche Öffnungen der Abbildungsblende angewendet, um die optimale Untergrundschwärzung im Durchschnitt zu gewährleisten. Kombinationen dieser Bedingungen bildeten dann die sechs (1a, 1b, 2, 3a, 3b und 4) Untersuchungsmodelle.

Die gemessenen Schwärzungswerte wurden anhand der 1-Transformationsprozedur [3] in I-Werte umgesetzt. Die nötigen Transformationsparameter wurden mittels des Programmes GAMA/KA—LM—70 ermittelt [4].

Hier ist zu erwähnen, daß bei der Ermittlung der R_{theor}-Werte für die Fälle, bei denen der doppelte Durchgang zur Anwendung gelangt, eine gewisse Unsicherheit besteht. Theoretisch muß dieser Wert das Doppelte des dem einfachen Durchgang entsprechenden Wertes sein. Die aktuelle optische Anordnung (z. B. Gitterblenden) kann aber diesen Wert unkontrollierbar herabsetzen.

Für die Beurteilung des erörterten Problemenkreises wurden ausschließlich solche Parameter der analytischen Eichgeraden angewendet, deren linearer Verlauf durch Testprüfungen [5] gesichert wurde. Bei der Ermittlung der ΔY-Werte wurden die Intensitäten der analytischen Linien konsequent mit der Untergrundintensität korrigiert, wobei die Ergebnisse früherer Arbeiten [6, 7] berücksichtigt wurden. Für die Festlegung der analytischen Eichgeraden wurde das Rechenprogramm KF—FLM—72 angewendet [8].

Diskussion

Die angewendeten sechs Kombinationen der experimentellen Untersuchungsmodelle erlauben in weiten Grenzen zu beurteilen, wie sich die Wertungsparameter der analytischen Methoden in Abhängigkeit von den Werten der reziproken Dispersion, des theoretischen Auflösungsvermögens, der aktuellen Strahlungsanteilwerte sowie bei Anwendung des doppelten Strahlendurchganges ändern. Die Teilergebnisse sind zweckmäßig in der folgenden Reihenfolge zu diskutieren.

A. Einfluß der Verminderung der reziproken Dispersion durch Anwendung von mehreren Gittern mit unterschiedlichem »blaze« Winkel unter gleichzeitiger Verbesserung des theoretischen Auflösungsvermögens (Tab. III).

B. Einfluß der Anwendung des sog. doppelten Strahlendurchganges für zwei Gitter mit unterschiedlichen »blaze« Winkeln (Tab. IV).

C. Einfluß der Erhöhung der Strahlungsanteile unter Konstanthaltung der reziproken Dispersion und des theoretischen Auflösungsvermögens (Tab. V).

Tabelle III

Wertungsparameter der Cr/Pd-, Mn/Pd- und V/Pd-Linienpaare

Parameter	Analytische Linienpaare								
	Cr 302,16 / Pd 302,79			Mn 278,27 / Pd 302,79			V 318,40 / Pd 302,79		
Untersuchungsmodell	1a	3a	4	1a	3a	4	1a	3a	4
B_X	0,88	0,83	1,04	0,90	0,92	0,92	0,99	0,96	0,98
$t_{B_X} = 1$ $P = 95\%$	⊖	⊖	⊕	⊖	⊖	⊖	⊕	⊕	⊕
$s_{c_{X,r}}$ [%]	±16,4	±6,4	±5,3	±14,8	±4,7	±13,3	±6,9	±11,6	±8,7
$c_L \cdot 10^4$ [%]	1,1	0,31	0,47	1,6	1,7	0,63	1,0	0,22	0,32
$s_{c_L} \cdot 10^4$ [%]	± 0,2	±0,1	±0,1	± 0,6	±0,9	± 0,1	±0,4	± 0,01	±0,1

Tabelle IV

Wertungsparameter der Mn/Pd- und V/Pd-Linienpaare

Parameter	Analytische Linienpaare							
	Mn 280,11 / Pd 302,79		V 318,40/ Pd 302,79		Mn 280,11 / Pd 302,79		V 318,40 / Pd 302,79	
Untersuchungs-modell	1a	1b	1a	1b	3a	3b	3a	3b
B_X	0,90	0,87	0,82	0,85	0,82	0,90	0,93	0,92
$t_{B_X} = 1$ $P = 95\%$	⊖	⊖	⊖	⊖	⊖	⊖	⊕	⊕
$s_{c_{X,r}}$ [%]	±14,8	±13,4	±9,3	±11,5	±12,6	±21,8	±7,3	±12,7
$c_L \cdot 10^4$ [%]	1,6	0,6	0,4	0,2	0,3	0,2	0,1	0,2
$s_{c_L} \cdot 10^4$ [%]	± 0,6	± 0,3	±0,06	± 0,1	± 0,1	± 0,1	±0,03	± 0,08
Strahlungs-durchgangsart	E	D	E	D	E	D	E	D

E = einfacher Durchgang; D = doppelter Strahlungsdurchgang

Für die weitere Diskussion ist es notwendig, zuerst zu klären, welche Faktoren die ermittelten Werte der Nachweisgrenzen beeinflussen. Die allgemein verbreitete Behauptung [9], daß durch sukzessive Verringerung der reziproken Dispersion bis zur vollkommenen Auflösung der physikalischen Breite der Spektrallinie immer günstigere Nachweisgrenzen erreicht werden, gilt nur begrenzt. Durch die Verringerung der reziproken Dispersion wird die Untergrundschwärzung immer geschwächt, aber nicht deren Fluktuationscharakter. Die Werte der Nachweisgrenzen werden, wenn man keine Untergrundkorrektion vornimmt, folgendermaßen ermittelt [10, 11]:

$$c_L = 10^{(\Delta Y_N - A_{X,B})\frac{1}{B_X}} \tag{1}$$

$$\Delta Y_N = \log\,(\bar{I}_{X,U} + 3\,s_{I_{X,U}}) - Y_{R,L+U}\,. \tag{2}$$

Das bedeutet aber, daß der c_L-Wert die folgende Funktionsabhängigkeit aufweist:

$$c_L = f[\bar{I}_{X,U};\ s_{I_{X,U}};\ A_{X,R};\ B_X]\ . \tag{3}$$

Falls man aber die Intensität der analytischen Linie mit der Untergrundintensität korrigiert, was hauptsächlich bei der Spurenanalyse der häufigste Fall ist, ändert sich die Funktionsabhängigkeit der c_L-Werte (3) wie folgt:

$$c_L = f[s_{I_{X,U}};\ A_{X,R};\ B_X]\,, \tag{4}$$

da der ΔY_N-Wert in diesem Fall aus der modifizierten Gleichung (5) ermittelt wird [11, 12]:

$$\Delta Y_N = \log\,(3\ s_{I_{X,U}}) - Y_{R,L+U}\ . \tag{5}$$

Falls man auch die Bezugslinienintensität mit der Untergrundintensität korrigiert, gilt die Abhängigkeit (4) weiter, aber in der Gleichung (5) wird anstatt des Gliedes $Y_{R,L+U}$ der mit der Untergrundintensität korrigierte Y_R-Wert eingesetzt.

Selbstverständlich müssen die $A_{X,R}$- und B_X-Grundparameterwerte der analytischen Eichgeraden für die angewendete Ermittlungsart der ΔY-Werte getrennt berechnet werden.

Da bei der Auswertungsmodifikation (5) das Glied $\bar{I}_{X,U}$ entfällt, ist der c_L-Wert vor allem durch die $s_{I_{X,U}}$-Standardabweichung bedingt. Deshalb muß bei den Auswertungsvarianten, wo man die Linienintensitäten mit der Untergrundintensität korrigiert, die Verminderung der reziproken Dispersion nicht immer zur Verbesserung der Nachweisgrenzen führen.

A. *Einfluß der Verminderung der reziproken Dispersion*

Die Auswirkung der Verminderung der reziproken Dispersion auf die Wertungsparameter ist aufgrund der Parameter einiger Cr/Pd-, Mn/Pd- und V/Pd-Linienpaare in Tabelle III dargestellt, da diese Werte als typische Beispiele angesehen wurden.

Aus dieser Tabelle ist ersichtlich, daß die Verminderung der reziproken Dispersion, die von einer gleichzeitigen Steigerung der theoretischen Auflösung begleitet ist, bei den relativen Empfindlichkeitswerten (Parameter B_X) immer eine Verbesserung hervorrufen. Dieser Wert ist im Optimalfall meistens signifikant gleich 1 oder mindestens höher als 0,80.

Die relative Genauigkeit der Konzentrationsbestimmung (Parameter $s_{c_{X,r}}$) erreicht meistens bei einer theoretischen Auflösung von ca. 10^5, die einer reziproken Dispersion von $0{,}368 \cdot 10^{-6}$ entspricht, den optimalen Wert.

Die Nachweisgrenzen c_L weisen eine gute Konformität mit der relativen Genauigkeit der Konzentrationsbestimmung auf. Bemerkenswert ist auch die Tatsache, daß man bei der reziproken Dispersion von $0{,}368 \cdot 10^{-6}$ auch die günstigsten Standardabweichungen s_{c_L} für die Nachweisgrenzen erreicht. Bei Gittern, die bei der gegebenen reziproken Dispersion einen höheren Strahlungsanteil (ca 85%) besitzen, ist sicherlich eine weitere Verbesserung der Wertungsparameter zu erwarten.

B. *Einfluß der Anwendung des doppelten Strahlendurchganges*

Diese Untersuchung wurde ausschließlich unter Anwendung von Gittern mit einer Furchenzahl von 651 pro Millimeter, aber nicht nur in der ersten, sondern auch in der zweiten Ordnung durchgeführt. Die Auswirkung des doppelten Strahlendurchganges wird durch die Veränderungen der Parameter der Mn/Pd- und V/Pd-Linienpaare in der Tabelle IV veranschaulicht.

Es zeigt sich auf den ersten Blick, daß die relativen Empfindlichkeiten am wenigsten von der Einschaltung des doppelten Strahlendurchganges betroffen werden. Diese Werte sind fast immer größer als 0,80, aber die Differenz zwischen den zwei verglichenen Wertereihen ist nicht signifikant.

Die Werte der relativen Genauigkeit der Konzentrationsbestimmung haben sich bei der Einschaltung des doppelten Strahlendurchganges mit nur einer Ausnahme verschlechtert. Dieses Teilergebnis widerspricht aber nicht den Erwartungen da sich durch den doppelten Strahlengang die Störungsfaktoren (z. B. Streulichtanteil) vermehren, die die endgültigen Standardabweichungen $s_{\Delta Y}$ beeinflussen.

Die Werte der Nachweisgrenzen haben sich im ersten Fall ($m = 1$) bei der Anwendung des doppelten Strahlendurchganges ganz prägnant verbessert. Im zweiten Fall ($m = 2$), wo der Wert des theoretischen Auflösungsvermögens von $0{,}922 \cdot 10^5$ auf $1{,}844 \cdot 10^5$ angehoben wurde, kann man jedoch nicht von einer solchen eindeutigen Verbesserung sprechen.

Bemerkenswert ist auch der Vergleich der Untersuchungsmodelle 1b und 3a, wonach bei gleichen Werten der reziproken Dispersionen und des theoretischen Auflösungsvermögens wiederum bei einfachem Strahlendurchgang (Fall 3a) günstigere Wertungsparameter erreicht wurden.

C. *Einfluß der Werte der Strahlungsanteile der Gitter*

Die Bedeutung der Werte der Strahlungsanteile der Reflexionsgitter wurde bei quasikonstantem theoretischen Auflösungsvermögen sowie konstanten reziproken Dispersionen untersucht. Es wurden drei Gitter angewendet, u. zw. ein Gitter mit einem »blaze« Winkel für die erste Ordnung, aber unter Anwendung des doppelten Strahlendurchganges, ein Gitter mit gleicher

Tabelle V

Wertungsparameter der Cr/Pd-, Mn/Pd- und V/Pd-Linienpaare

Parameter	Analytische Linienpaare								
	Cr 302,16 / Pd 302,79			Mn 280,11 / Pd 302,79			V 318,54 / Pd 302,79		
Untersuchungs-modell	1b	3a	2	1b	3a	2	1b	3a	2
B_X	0,51	0,83	0,96	0,87	0,82	0,83	0,85	0,96	0,93
$t_{B_X} = 1$ $P = 95\%$	⊖	⊖	⊕	⊖	⊖	⊖	⊖	⊕	⊕
$sc_{X,r}$ [%]	±15,1	±6,4	±3,2	±13,4	±12,6	±9,1	±11,5	±11,6	±7,3
$c_L \cdot 10^4$ [%]	1,7	0,3	0,2	0,6	0,3	0,1	0,2	0,2	0,1
$sc_L \cdot 10^4$ [%]	± 0,1	±0,06	±0,1	± 0,3	± 0,1	±0,01	± 0,1	± 0,01	±0,03

Furchenzahl wie das erste, welches jedoch einen »blaze« Winkel für die zweite Ordnung hat, und schießlich ein Gitter mit doppelter Furchenzahl und in erster Ordnung eingesetzt. Die Ergebnisse dieser Vergleichsstudien sind anhand der Parameter der Cr/Pd-, Mn/Pd- und V/Pd-Linienpaare in Tabelle V veranschaulicht.

Die relativen Empfindlichkeitswerte sind entweder für die drei untersuchten Fälle signifikant gleich (Mn/Pd) oder steigen parallel mit der Hebung der Strahlungsanteile bis zum Optimalwert ($B = 1$) an. Die günstigsten Werte für die relative Genauigkeit der Konzentrationsbestimmung wurden in dieser Untersuchungsserie immer bei dem Untersuchungsmodell 2, das die höchsten Strahlungsanteilwerte aufweist (80%), erhalten. Einen durchaus konformen Verlauf zeigen auch die Nachweisgrenzen.

Schlußfolgerungen

Bei der Verringerung der reziproken Dispersion, womit gleichzeitig eine Erhöhung des theoretischen Auflösungsvermögens einhergeht, verbessern sich die relativen Empfindlichkeitswerte und erreichen den Optimalwert. Die optimale relative Genauigkeit der Konzentrationsbestimmung und auch die niedrigsten Nachweisgrenzen erreicht man dagegen schon bei dem theoretischen Auflösungsvermögen von $R_{\text{theor}} = 10^5$. Eine weitere Verbesserung dieser Werte kann im allgemeinen bei gegebener Anregungsart nicht durch Erhöhung des theoretischen Auflösungsvermögens erreicht werden, da dies keinen weiteren Einfluß auf die Verringerung der Standardabweichung der Untergrundintensitäten ausübt.

Die Anwendung des doppelten Strahlendurchganges bei dem Gitterspektrographen PGS-2 ermöglicht auf ziemlich einfache Weise die Verringerung der reziproken Dispersion, wobei allerdings die Verbesserung der Wer-

tungsparameter der analytischen Methoden nicht so ausgeprägt ist, wie bei Verwendung von Gittern mit »blaze«-Winkeln für höhere Ordnungen, hauptsächlich für die zweite und dritte Ordnung.

Die Wertungsparameter der spektrochemischen analytischen Methoden werden am wirksamsten von folgenden zwei Faktoren beeinflußt: von der Zahl der Gitterfurchen pro Millimeter und vom aktuellen Strahlungsanteil. Die Vergrößerung dieser zwei Werte wirkt sich immer positiv auf die Wertungsparameter, in erster Linie auf die Nachweisgrenzen und auf die relative Genauigkeit der Konzentrationsbestimmung aus.

*

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Erläuterung der Symbole, die im Text und in den Tabellen nicht definiert wurden

$A_{X,R}$	— Parameter der modifizierten Lomakin-Scheibe-Gleichung
B_X	— Richtungstangente der analytischen Eichgerade; relative Empfindlichkeit
$s_{c_{X,r}}$	— relative Genauigkeit der Konzentrationsbestimmung in %
c_L	— Nachweisgrenze
s_{c_L}	— Standardabweichung der Nachweisgrenze
R_{theor}	— theoretisches Auflösungsvermögen
D	— reziproke Dispersion
$\bar{I}_{X,U}$	— arithmetischer Mittelwert der Untergrundintensität
$s_{I_X,U}$	— Standardabweichung der Untergrundintensität
$Y_{R,L+U}$	— unkorrigierter Y-Wert der Bezugslinie
Y_R	— korrigierter Y-Wert der Bezugslinie
m	— Ordnung der Diffraktion
P = 95%	— statistische Sicherheit des Testverfahrens

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COMPLEXES OF Co(II), Ni(II), Zn(II) AND Hg(II) WITH THE CHELATING TRIDENTATE LIGAND ETHYL 2-CYANO-3,4-DIPHENYL-4-HYDROXYCROTONATE

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Complexes of the composition ML_2, where M is Co(II) or Ni(II), and MLCl, where M is Zn(II) or Hg(II), and L is the tridentate ethyl 2-cyano-3,4-diphenyl-4--hydroxycrotonate (obtained from the condensation of benzoin and cyanoacetic ester) have been synthesized. The Co(II) and Ni(II) complexes are octahedral, whereas the Zn(II) and Hg(II) complexes are tetrahedral as inferred from analytical conductance, magnetic susceptibility, IR and electronic spectral data.

Introduction

The tridentate nitrogen donor ligand terpyridil is known to form five-coordinated complexes with Ni(II), Cu(II) and Zn (II) halides [1]. To achieve this rare coordination number, many new tridentate ligands were synthesized and their complexation behaviour was studied. More recently BHATTACHARYA *et al.* [2, 3] have reported complexes with triazene-N-oxide. Though a number of complexes have been synthesized using benzoin [4] or benzoin monoxime as ligands, no attempts have been made to prepare a tridentate ligand from benzoin. It was, therefore, thought worthwhile to synthesize a new tridentate ligand (ethyl 2-cyano-3,4-diphenyl-4-hydroxycrotonate) by condensing benzoin and cyanoacetic ester and to study its complexation with some divalent transition and nontransition metal ions like Co(II), Ni(II), Zn(II) and Hg(II), respectively.

Experimental

All chemicals used were of AnalaR grade.

Preparation of ligand

An ethanolic solution of benzoin (2.12 g) and cyanoacetic ester (1.13 ml) was treated with piperidine (2—3 ml) and the solution refluxed for about 2 hrs on a water bath. The hot solution was poured into a beaker containing ice cold water, when a yellow precipitate separated out immediately. It was allowed to stand overnight, filtered and washed with water. On crystallization in alcohol a yellowish crystalline precipitate of the ligand separated out (melting point 112 °C). ($C_{19}H_{17}O_3N$. Calcd: C 74.26; H 5.53; N 4.56. Found: C 73.84; H 5.07; N 4.17%.) Elemental analysis gave the composition $C_{19}H_{17}O_3N$ and the IR spectra the presence of functional groups according to the structure given.

Preparation of the complexes

To an ethanolic solution of a metal chloride, the ligand was added in 1 : 2 ratio, followed by the addition of dropwise NH_4OH under stirring till a precipitate formed. This was filtered off, washed with absolute ethanol and ether and dried in vacuum.

Metals in the complexes were estimated by complexometric EDTA titration using Eriochrome Black-T as indicator at pH 10. Conductance was neasured in *M*/1000 acetone solution using a Toshniwal conductivity bridge. Magnetic susceptibility measurements were made on solid samples at room temperature by the Gouy method using $Hg[Co(SCN)_4]$ as the calibrant. Infrared spectra were recorded in KBr pellets on Perkin Elmer 237 and 521 spectrometers. Electronic spectra were recorded on a Hilger-Watt Uvispeck Photometer with *M*/100 (chloroform–ligand) solutions of the complexes. The relevant analytical data are given in Table I and the spectral data in Table II.

Table I

Analysis of m.p., conductance and magnetic susceptibility data of the complexes studied

Compound	Colour and form	M.p. (°C)	Conductance (mho, cm²)	μ_{eff} B.M.	Metal %		Chlorine %	
					Found	Calcd.	Found	Calcd.
CoL_2	Pink crystalline	167	8.5	4.9	9.34	9.67	—	—
NiL_2	Reddish-brown crystalline	198	10.8	2.9	9.51	9.64	—	—
ZnL Cl	White crystalline	260	10.5	—	19.47	19.76	8.02	8.59
HgL Cl	White crystalline	202	9.8	—	43.65	43.50	6.27	6.46

Table II

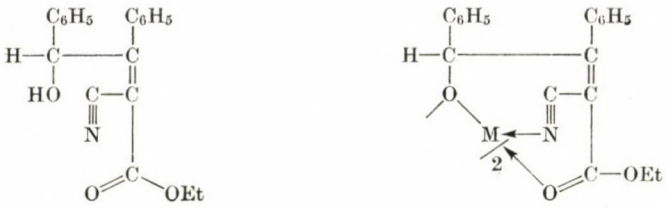
IR spectra (cm^{-1}) and electronic spectral data of the complexes studied

Compounds	ν(C—O)	ν (C=O)	ν(C=C)	ν(C≡N)	ν(O—H)	ν(M—N)	ν(M—O)	$\nu_{max}^{(cm^{-1})}$	D_q (cm^{-1})	β
Ligand	1210	1600	1660	2260	3400	—	—			
CoL_2	1200	1580	1650	2240	—	520	450	7,600 (15) 20,700 (19)	865	0.85
NiL_2	1200	1590	1650	2230	—	520	460	8,300, (9.3) 13 400 (6) 24,680 (19)	830	0.85
ZnL Cl	1200	1580	1650	2240	—	515	420	—	—	
HgL Cl	1200	1580	1650	2230	—	510	455	—	—	

Result and discussion

Complexes reported in the present investigation have the compositions ML_2, where M = Co(II), Ni(II), and MLCl, where M = Zn(II), Hg(II) and L is the tridentate ligand. Zinc and mercury complexes are white, whereas cobalt and nickel complexes are pink and reddish-brown, respectively. These

have fairly low melting points and are soluble in acetone, giving low molar conductance values, which indicates (Table I) the non-electrolytic nature of the complexes. The ligand and complex are represented as follows:



It can function as a tridentate chelating ligand with the carboxyl oxygen, the hydroxy oxygen and the cyano nitrogen as the bonding sites. Infrared spectra provide evidence for these bonding sites. Upon bonding, the ν (C≡N), ν (C=O) and ν (C—O) frequencies should decrease and the ligand ν (O—H) should disappear in the case of chelates. Further when the cyano nitrogen and the carboxy oxygen are bonded, C=C may be polarized and ν (C=C) should be shifted to lower frequencies. The assignment of IR spectra has been performed according to NAKAMOTO [5] and SILVERSTEIN *et al.* [6] in conformity with the above assumptions. The ligand bands at 2260, 1660, 1600 and 1210 cm^{-1} are attributable to ν (C≡N), ν (C=C), ν (C=O) and ν (C—O), respectively.

All these bands are shifted to lower frequencies in the chelates and the disappearance on complexation of the 3400 cm^{-1} band (occurring at a lower frequency than usual, probably because of hydrogen bonding) attributable to ν (O—H) of the ligand provides conclusive evidence for bonding of these three sites to the metal ions. This has been further substantiated by the observation of ν (M—N) and ν (M—O) at about 520 and 460 cm^{-1}, respectively.

Three bands were observed in the visible electronic spectrum of the nickel(II) complexes, *viz.* at 8300 (9.3), 13 400 (6) and 24 680 (19) cm^{-1}, attributable [7] to $^3A_{2g} \rightarrow {}^3T_{2g}$, $^3A_{2g} \rightarrow {}^3A_{2g} \rightarrow {}^3T_{1g(F)}$ and $^3A_{2g} \rightarrow {}^3T_{1g(P)}$ transitions, respectively. Calculations [8] of ligand field parameters like D_q and β and the agreement between calculated (on the basis of these parameters) and experimental values for the $^3A_{2g} \rightarrow {}^3T_{1g(F)}$ transition show the symmetry to be Oh rather than D_{4h}. According to magnetic measurements the μ_{eff} is 2.9 B. M., indicating the presence of two unpaired electrons and a spin-free octahedral configuration for the complex.

In case of the cobalt(II) complex absorption bands appear at 7600 (15) and 20 700 (19), assignable [9] to $^4T_{1g(F)} \rightarrow {}^4T_{2g(\nu_2)}$ and $^4T_{1g(F)} \rightarrow {}^4T_{1g(P)(\nu_3)}$ transitions, respectively. Three transitions are expected for Co(II) complexes of Oh symmetry. The $^4T_{1g(F)} \rightarrow {}^4A_{2g(F)}$ transition involving a two-electron process gives rise to a weak band on the high frequency side of the $^4T_{1g(P)}$

band. The low intensity combined with closeness to the $^4T_{1g(P)}$ transition renders it unobservable in the present case. The calculation of ligand field parameters and the agreement between the calculated and experimental values for the ν_2 and ν_3 bands provide evidence for an Oh symmetry. The μ_{eff} value of 4.9 B. M. is in conformity with the spin-free octahedral geometry of the complex.

The Zn(II) and Hg(II) complexes with one molecule of the tridentate ligand bind one chloride in the fourth coordination position, probably giving rise to a tetrahedral geometry for these complexes.

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SCHIFF BASE COMPLEXES OF TITANIUM(III) AND VANADIUM(III)

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The complexes of titanium(III) with bis(2-methoxy benzalidene) dianisidine, bis(2-methoxybenzalidene) benzidine, bis(benzalidene) benzidine, bis(acetylacetone) benzidine, bis(acetyl acetone) ethylene diimine and bis(acetyl acetone) dianisidine and vanadium(III) with bis(benzalidene) *o*-phenylene diimine and bis(2-methoxy benzalidene) *o*-phenylene diimine have been synthesized and characterized by their elemental analyses, melting points, molar conductances, thermogravimetric analysis and infrared spectra. All the complexes show 1 : 1 ratio (Schiff base metal salt) and only one chloride is in the outer coordination sphere.

The preparation and characteristics of the complexes of titanium(IV) [1—3] and vanadium(IV) [4—6] with Schiff bases have been reported in the literature. However, the interaction of titanium(III) and vanadium(III) has been studied very vaguely. We have recently reported a number of titanium(III) complexes with Schiff bases [7]. The present communication deals with the complex formation between titanium(III) chloride and Schiff bases—bis(2--methoxybenzalidene) dianisidine, bis(2-methoxy benzalidene) benzidine, bis(benzalidene) benzidine, bis(acetylacetone) benzidine, bis(acetylacetone) dianisidine, and bis(acetylacetone) ethylene-diimine and between vanadium(III) chloride and Schiff bases — bis(benzylidene)-*o*-phenylenediimine and bis(2--methoxybenzalidene), *o*-phenylene-diimine. The complexes were isolated, subjected to elemental analysis for carbon, hydrogen, nitrogen and chlorine, their thermograms, molar conductances and infrared spectra taken and melting points determined.

Experimental

Benzidine (Reanal, Hungary), dianisidine (E. Merck, Germany), ethylenediamine (Riedel, Germany), *o*-phenylene-diamine (Xenon, Poland), benzaldehyde (Riedel, Germany), 2-methoxybenzaldehyde (Norda, U.S.A.), $TiCl_3 6H_2O$ [8], acetylacetone (B.D.H.) and vanadium(III) chloride (B.D.H., England) were used in these studies. 2-Methoxybenzaldehyde was distilled and benzidine, *o*-phenylenediamine were recrystallized before use.

The respective aldehydes and amines were taken in a mole ratio of 2 : 1 in benzene, stirred for about 3—4 hours and the resulting precipitate was washed with ethanol and recrystallized. The ligands were subjected to elemental analysis for carbon, hydrogen and nitrogen to establish their identity.

Preparation of the complexes

The complexes of Schiff bases with titanium(III) chloride and vanadium(III) chloride were prepared by reacting the metal and Schiff base in the mole ratio of 1 : 1 in dry tetrahydrofuran. The precipitate obtained was filtered in a Buchner base in dry tetrahydrofuran to remove any excess of the ligand. As titanium(III) and vanadium(III) chlorides are prone to oxidation and the complexes are highly hygroscopic, the whole process of preparation was done in an inert dry atmosphere. For this purpose a glove bag with constant flow of pure and dry nitrogen was improvized. After the washing of the complex was completed the precipitate was transferred quickly into a vacuum desiccator and dried. Since the complexes are insoluble in usual organic solvents, it was not possible to crystallize them. The complexes were analysed for carbon, hydrogen and nitrogen at the microanalytical section of this department. A given amount of the complex was fused with pure potassium carbonate in a platinum crucible, dissolved in dilute nitric acid solution and the chloride determined as silver chloride. The results are given in Table I.

Table I

Sl. No.	Complex	Carbon	Hydrogen	Nitrogen	Chloride	Colour	Solubility	λM Ohm^{-1} cm^{2}mole^{-1}
1.	Dichloro bis(2-methoxy--benz) dian Ti(III) Cl	56.76	4.45	4.41	16.75	Light	DMSO	27.4
	$[(C_{30}H_{28}N_2O_4Cl_2)Ti]$ Cl	(56.89)	(4.38)	(4.43)	(15.17)	brown		
2.	Dichloro bis(2-methoxy-benz) bn Ti(III) Cl	58.51	4.21	4.87	18.50	Light	DMSO	61.2
	-$[(C_{28}H_{24}N_2O_2Cl_2)$ Ti] Cl	(68.48)	(4.14)	(4.89)	(18.47)	yellow		
3.	Dichloro bis(benz) bn Ti(III) Cl	60.67	3.92	5.44	20.66	Yellow	DMSO	58.3
	$[(C_{26}H_{20}N_2Cl_2)$ Ti] Cl	(60.31)	(4.01)	(5.11)	(20.49)			
4.	Dichloro bis(acac) bn Ti(III) Cl	52.56	4.81	5.57	21.45	Yellow	DMSO	71.1
	$[(C_{22}H_{24}N_2O_2Cl_2)$ Ti] Cl	(52.54)	(4.79)	(5.54)	(21.15)			
5.	Dichloro bis(acac) dian Ti(III) Cl	51.22	5.02	4.98	18.90	Yellow	DMSO	70.9
	$[(C_{24}H_{28}N_2O_4Cl_2)]$ Ti Cl	(51.23)	(4.87)	(4.87)	(18.89)			
6.	Dichloro bis(acac) en Ti(III) Cl	38.07	5.33	7.40	28.10	Yellow	DMSO	70.8
	$[(C_{12}H_{20}N_2O_2Cl_2$ Ti] Cl	(38.88)	(5.23)	(7.45)	(28.09)			
7.	Dichloro bis(benz) *o*-phene-bis tetrahydrofuranato V(III) Cl							
	$[(C_{20}H_{16}N_2Cl_2 \cdot$	57.40	5.51	4.78	—	Light	DMSO	52.3
	$2\ C_4H_8O)$ V] Cl	(57.94)	(5.31)	(4.68)		pink		
8.	Dichloro bis(2-methoxy--benz) *o*-phene V(III) Cl dihydrate							
	$[(C_{22}H_{20}N_2O_2\ Cl_2)$ V]	49.14	4.50	5.21	—	Dirty	DMSO	27.6
	$2\ H_2O$	(48.99)	(4.41)	(5.13)		white		

(The observed percentages for carbon, hydrogen, nitrogen and chlorine are given in parentheses)

Abbreviations used: en = ethylenediimine, dian = dianisidine, bn = benzidine, *o*-phene = *o*-phenylenediimine, benz = benzalidene, acac = acetylacetone.

Physico-chemical measurements

For the measurements of molar conductance, Philips conductivity bridge model PR9500 with a dip type conductivity cell was employed. Thermograms were taken at the Regional Research Laboratory, Hyderabad, India, for the complexes containing water, between room temperature and 500 °C in an inert atmosphere.

The i.r. spectra of the complexes and the ligands were taken in KBr phase between 4000 cm^{-1} and 700 cm^{-1}.

Results and discussion

Elemental analysis of carbon, hydrogen, nitrogen and chlorine give formulas for the titanium(III) and vanadium(III) Schiff base complexes (given in Table I) where the mole ratio between metal and the Schiff base is 1 : 1. Some of the hydrogen analyses are quite high because the complexes readily absorb moisture when exposed to air during microanalysis.

Since the complexes are very much susceptible to oxidation from atmospheric oxygen and prone to absorb moisture very readily and also because very small amounts of the samples were available, it was not possible to measure their magnetic susceptibility by the Gouy method.

The molar conductances of the complexes of titanium at 10^{-3} *M* concentration lie in the range of 27.4—71.1 $ohm^{-1} cm^2 mole^{-1}$, in dimethyl sulphoxide and for the complexes of vanadium(III) lie between 27.6 and 52.3 $ohm^{-1} cm^2 mole^{-1}$, which are compatible with 1 : 1 electrolytes [9]. It is therefore concluded that two of the three chlorides present are inside the coordination sphere leaving one outside.

The two complexes of vanadium(III) chloride with bis(benzylidene) *o*-phenylenediimine and bis(2-methoxybenzylidene) *o*-phenylenediimine which had indications of the presence of tetrahydrofuran or water were subjected to thermogravimetric analyses. The bis(benz) *o*-phenylenediimine complex shows the removal of the two tetrahydrofuran molecules at 225 °C (observed weight loss = 26%, theoretical for two tetrahydrofuran molecules = 25.03%). The total weight loss is 93% at about 460 °C. The bis(2-methoxybenzylidene) *o*-phenylenediimine complex shows that the removal of two water molecules is completed at only 50 °C (observed weight loss is 5.6%, theoretical 6.38%). The total observed weight loss is 99.5% at 425 °C. Since the total weight losses are 93% and 99.5% it is possible that during heating complex species is formed which volatilizes leaving little residue in the thermogravimetric balance. The two tetrahydrofuran molecules in the bis(benz) *o*-phene complex must be coordinated and the two water molecules in the vanadium(III) chloride complex of bis(2-methoxybenz) *o*-phene are present as lattice water.

The i.r. spectra of titanium(III) complexes in the region of 4000—2800 cm^{-1} in general contain bands in metal chelates of bis(acetylacetone)-ethylenediimine and related compounds [10] for the hydrogen bonded C–H or N–H. The hydrogen bonding between nitrogen and hydrogen is very weak and hence only in a few cases some bands have appeared in the region of 3700 and 3000 cm^{-1}. The bis(acetylacetone) benzidine, bis(acetylacetone) dianisidine and bis(acetylacetone) ethylenediimine show bands at 2950—3300 (b), 2980 (w) and 3450 (b) cm^{-1}, respectively. The titanium(III) complex with bis(acetylacetone) benzidine has a broad band at 2950 and that of bis(acetylacetone) ethylenediimine at 2750 whereas the complex of bis(acetylacetone) dianisidine

does not show any band in this region. These bands may be due to weak hydrogen bonding.

In the region of 1700—800 cm^{-1} the most important absorption is that of the C=N stretching. BIRADAR and KULKARNI [11] have reported that the C=N stretching vibration occurs at 1625—1630 cm^{-1} and is shifted to higher frequencies, *i.e.* 1630—1650 on complexation. This absorption occurs at 1605 (s), 1630 (s), 1613 (s), 1610 (s), 1606 and 1603 (s) in the ligands and is shifted to higher frequencies on complexation, that is to 1640 (vs), 1635 (m), 1618 (s), 1615 (s), 1618 (s) and 1632 (s), respectively, in the order given in Table I. The other bands in this region are due to phenyl ring and CH_3 and CH_2 deformation vibrations.

The complexes of Schiff bases, derived from acetylacetone and three amines, benzidine, dianisidine, and ethylenediamine show bands at 1365 (m), 1510 (s); 1355 (s) 1520 (m); 1380 (s) 1580 (m) which were present at 1345 (s), 1510 (m); 1325 (s), 1510 (s); 1350 (m) in their ligands, respectively. The bands show shifts to higher frequency thus signifying that coordination also occurs through the oxygen of the carbonyl groups of the Schiff bases derived from acetylacetone [12].

The most important feature of i.r. spectra of the complexes of vanadium(III) Schiff bases is the reduction in the number of bands of the ligands on complexation.

The bands of tetrahydrofuran do not appear in the IR spectra of dichloro bis(benzalidene) *o*-phenylenediimine bis tetrahydrofuranato vanadium(III) chloride. Tetrahydrofuran absorbs at 1076 cm^{-1}. Perhaps this band very much decreases in intensity and thus disappears as a result of coordination of tetrahydrofuran with the metal.

The complex bis(2-methoxybenzalidene) *o*-phenylenediimine vanadium(III) contains two water molecules. The i.r. spectra show a strong band at 1651 cm^{-1} and a broad band at 3280—3350 cm^{-1}, signifying the presence of lattice water [13].

The i.r. spectra of the complexes do not have any bands which may be assigned to V=O vibration. This is a clear proof of the fact that the complexes have been well protected from the atmospheric oxygen and are not oxidized.

The most important i.r. absorptions in the ligands occur at 1630 (s) and 1612 (s) cm^{-1} which shift to higher or lower frequencies on complexation, *i.e.* to 1605 (s), and 1630 (v—s) in the complexes of vanadium(III) with bis-(benz)*o*-phene and bis(2-methoxy benz)*o*-phene, respectively. This is due to C=N stretching [10].

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MAGNETIC AND SPECTRAL STUDIES ON SOME TRANSITION METAL COMPLEXES OF DL-α-AMINOBUTYRIC ACID

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Magnetic and spectral (IR, UV and reflectance spectra) investigations have been carried out on Cu(II), Ni(II), Zn(II) and Pd(II) complexes of DL-α-aminobutyric acid which coordinates through amino nitrogen and carboxylate oxygen. Cu(II) and Ni(II) complexes are paramagnetic with magnetic moments of 1.92 and 3.28 B.M., respectively. Spectral studies suggest hexacoordinated Cu(II) and Ni(II) and tetracoordinated Zn(II) and Pd(II). It also indicates the presence of two coordinated water molecules in the Ni(II) complex possibly having a distorted octahedral structure. Pd(II) complex is square planar.

The formation and stability of some transition metal as well as other metal complexes of α-aminobutyric acid have been studied earlier in solution by several workers [1—7]. GRADDON and MUNDAY [8] studied the spectral properties of its Cu(II) complex and found that this complex crystallizes anhydrous from aqueous solution and possibly C : O—Cu linkages are involved in the coordination. MCAULIFFE and PERRY [9] studied the dehydration of nickel(II)-α-aminobutyrate dihydrate complex and observed that in the resulting anhydrous complex nickel(II) is hexacoordinate and contains tridentate ligands in which the carboxylate group is both bidentate and a bridge ligand. SHARMA *et al.* [10] pointed out a correlation between the NH stretching frequency and the stability of complexes of α-aminobutyric acid. They also studied the absorption spectra of Ni(II) complex in solution and observed that in it Ni(II) is in octahedral coordination. The present paper deals with systematic magnetic and spectral (IR, UV and reflectance) study of some transition metal [Cu(II), Ni(II), Zn(II) and Pd(II)] complexes of DL-α-aminobutyric acid.

Experimental

Materials

Copper sulfate (AnalaR), nickel sulfate (AnalaR), zinc sulfate (AnalaR), palladium chloride (Chempure), DL-α-aminobutyric acid (B.D.H.) and sodium hydroxide (E. Merck).

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Preparation and isolation

The solutions of metal ions and DL-α-aminobutyric acid were mixed in the mole ratio of 1 : 2 and the pH of the mixture solutions was adjusted to an appropriate value [4.0 for Cu(II), 6.0 for Ni(II) and Zn(II) and 3.2 for Pd(II)] by adding alkali. The mixture solutions were then concentrated over an electric water-bath and allowed to crystallize. The products were filtered, thoroughly washed first with distilled water and then with alcohol and dried in a vacuum desiccator. Analytical data are presented below: Bis(DL-α-amino- butyrato) copper(II): Deep blue, shining, crystalline, soluble in water on heating. Calcd. for $Cu(OOC\ CH(NH_2)CH_2\ CH_3)_2$: Cu, 23.54; C, 35.88; H, 6.02; N, 10.46%; found: Cu, 23.66; C, 36.01; H, 6.13, N, 10.22%. Bis(DL-α-aminobutyrato) nickel(II) dihydrate: Blue powder, soluble in water. Calcd. for $Ni(OOC\ CH(NH_2)\ CH_2\ CH_3)_2.2H_2O$: Ni, 19.70; C, 32.11; H, 6.74; N, 9.36%; found: Ni, 19.54; C, 32.30; H, 6.90; N, 9.61%.

It loses its water molecules and an anhydrous green product is obtained by heating at 110 °C in an air oven for 2—3 hours.

Bis(DL-α-aminobutyrato) zinc(II): colourless, shining, crystalline, soluble in water on heating. Calcd. for $Zn(OOC\ CH(NH_2)\ CH_2\ CH_3)_2$: Zn, 24.26; C, 35.63; H, 5.98; N, 10.39%; found: Zn, 24.17; C, 35.84; H, 6.13; N, 10.39%.

Bis(DL-α-aminobutyrato) palladium(II) : Light yellow, shining, crystalline, insoluble in water and other common organic solvents. Calcd. for $Pd(OOC\ CH(NH_2)\ CH_2\ CH_3)_2$: Pd, 34.33; C, 30.91; H, 5.19; N, 9.01%; found: Pd, 34.58; C, 31.10; H, 5.39; N, 9.18%.

Magnetic measurements were done at room temperature by Gouy's method. A semi-micro Sartorius balance was employed and mercury(II) tetrathiocyanatocobaltate(II) was used as a standard for calibration.

IR measurements were carried out on a Perkin-Elmer grating infrared spectrophotometer model-337 in the range 4000—700 cm^{-1} in KBr discs. The UV spectra measurements were done on a Cary model-14 recording spectrophotometer in aqueous solutions. Reflectance spectra were recorded in MgO on a VSU—2P spectrophotometer in the range of 200—1000 mμ.

Results and discussion

Magnetic studies: Magnetic studies show that copper(II) and nickel(II) complexes are paramagnetic whereas zinc(II) and palladium(II) complexes are diamagnetic. The magnetic moments are: Cu(II) complex: 1.92 B. M. at 304 °K and Ni(II) complex: 3.28 B. M. at 306 °K. It thus suggests the presence of one and two unpaired electrons, respectively, in the Cu(II) and Ni(II) complexes.

IR studies: Table I contains the important characteristic frequencies of diagnostic value in the i.r. spectra of DL-α-aminobutyric acid and its complexes. The i.r. spectra of α-aminobutyric acid has been studied by LEIFER and LIPPINCOTT [11] who attributed a band at ~3050 cm^{-1} to $\overset{+}{N}H_3$ and at ~1600 cm^{-1} to ionized carboxyl group. As a zwitter ion, DL-α-aminobutyric acid may be written as:

$$CH_3-CH_2-\underset{\displaystyle \overset{+}{N}H_3}{\underset{|}{CH}}-COO^-$$

Thus it should show all the characteristic bands of an amino acid (*i.e.*, $\overset{+}{N}H_3$ and COO^- groups). Band assignments in Table I for the i.r. spectra of DL-α-

Table I

IR frequencies of diagnostic value of DL-α-*aminobutyric acid and its metal complexes* (cm^{-1})

DL-α-amino-butyric acid	Metal complexes				Band assignments
	Pd(II)	Cu(II)	Ni(II)	Zn(II)	
	3200 s	3285 s	3330 s	3330 s	$\nu(NH_2)$
—	3130 s	3146 w. sh.	3280 w. sh.	3270 w. sh.	coordinated
				3120 w. sh.	
3065 m	—	—	—	—	$\nu(\overset{+}{N}H_3)$
2660 w. sh.					weak bands of amino
2600 w	—	—	—	—	acid
2100 w. b.					
1640 w. sh.	—	—	—	—	$\delta_d(\overset{+}{N}H_3)$ amino acid I band
1608 s	1640 s	1620 s	1590 s	1580 s	$\nu_{as}(COO^-)$
—	1603 s	1610 s	1605 s	1613 s	$\delta(NH_2)$
1520 m	—	—	—	—	$\delta_s(\overset{+}{N}H_3)$ amino acid II band
1427 s	1370 s	1389 s	1405 s	1400 s	$\nu_s(COO^-)$

s = strong; m = medium; w = weak; b = broad; sh = shoulder.

aminobutyric acid and its metal complexes have been done on this basis [12, 13]. IR frequencies ascribable to $\overset{+}{N}H_3$ group ($\nu\overset{+}{N}H_3$ at 3065 cm^{-1} and $\overset{+}{N}H_3$ deformation frequencies at 1640 and 1520 cm^{-1}) present in DL-α-aminobutyric acid vanish in the case of its metal complexes, indicating coordination through nitrogen of the primary amino group. Instead some new bands appear in the region 3330—3100 cm^{-1} which may be attributed to coordinated NH_2 group and solid state effects. The deformation frequency of the NH_2 group (δNH_2) is at $\sim$1610 cm^{-1}. Further DL-α-aminobutyric acid shows a very strong sharp band at 1608 cm^{-1} due to ionized carboxyl group, ascribed as its antisymmetric stretching frequency. The symmetric stretching frequency of the COO^- group appears at 1427 cm^{-1}. In metal complexes the $\nu_{as}(COO^-)$ appears at $\sim$1600 cm^{-1} and is in the order of increasing frequency with the increasing stability of metal complexes *i.e.*, Zn < Ni < Cu < Pd. But the symmetric frequency $\nu_s(COO^-)$ is considerably lowered on coordination and the extent of lowering also increases in the same order. Thus the separation in $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ stretching frequencies may be correlated with the increasing stability of the metal complexes. As suggested by NAKAMOTO *et al.* [14] it indicates the increasing covalent nature of the M—O bond. DL-α-aminobutyric acid also shows some weak bands at 2660, 2600 and 2100 cm^{-1} which are absent in its metal complexes and are thus assigned as weak bands

of amino acids. It thus appears that in the metal complexes, DL-α-aminobutyric acid shows bidentate behaviour and coordinates through amino nitrogen and carboxylate oxygen. Further in Ni(II) complex, two characteristic absorption bands are also observed at 1632 and 840 cm^{-1} which may be assigned to deformation and rocking frequencies of coordinated water molecules [15—17].

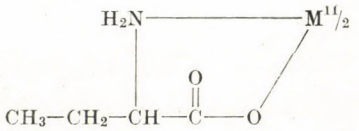


Fig. 1. Transition metal DL-α-aminobutyrate complex

UV spectra: Table II contains the principal bands observed in the UV spectra of DL-α-aminobutyric acid and its metal complexes. The UV spectra of amino acids have been studied earlier by a number of workers notably LEY and ARENDS [18] and SAIDEL *et al.* [19]. SAIDEL *et al.* have shown that in amino acids the main absorber is the carboxylate group. BARNES and SIMPSON [20] have assigned this band as $\pi \rightarrow \pi^*$ transition whereas the absorptivity of α-ammonium group is rather small.

The UV spectrum of DL-α-aminobutyric acid shows a strong absorption band at 47180 cm^{-1} ascribable to CO group whereas the weaker transitions observed at 51810 and 52360 cm^{-1} may correspond to amino (*i.e.*, $\overset{+}{N}H_3$) group. The UV spectra of Cu(II), Ni(II) and Zn(II) complexes show in all cases one principal absorption band at 42020 cm^{-1} (Cu^{II}); 47850 cm^{-1} (Ni^{II}) and 49030 cm^{-1} (Zn^{II}) which can be attributed to a charge transfer from the carboxyl group to the metal [21, 22]. In addition there are some bands at 50000—52000 cm^{-1}, which may be taken to correspond to charge transfer from amino group to metal and some transitions within the ligand itself, *e.g.*, carboxyl $\pi \rightarrow \pi^*$ transitions.

Table II

UV Spectra of DL-α-*aminobutyric acid and its Cu(II), Ni(II) and Zn(II) complexes*

Compound	Bands (cm^{-1})
DL-α-aminobutyric acid	48180 (main band); 48180; 50510; 51810; 52360
Bis(DL-α-aminobutyrato) copper(II)	42020 (main band); 50510; 51540; 52360
Bis(DL-α-aminobutyrato) nickel(II) dihidrate	47850 (main band); 50510; 51680; 52360
Bis(DL-α-aminobutyrato) zinc(II)	49030 (main band); 50510; 51680; 52360

Reflectance spectra

Copper(II) complex: The reflectance spectrum of Cu(II) complex shows a very broad absorption band in the visible region, λ_{max} being observed at $\sim$623 mμ (15 800 cm^{-1}). This is assigned as $^2E_g \rightarrow {}^2T_{2g}$ transition and its energy may be taken as equivalent to 10 Dq [23]. It may be noted that according to HARE *et al.* [24] a band at $\sim$620 mμ in Cu(II) complexes corresponds to a transmodel. Thus the present evidences suggest a hexacoordination for Cu(II) in this complex possibly with a distorted octahedral structure. However, since Cu(II) complex is anhydrous and contains only two α-aminobutyrate rings, the hexa coordination of Cu(II) atoms, as suggested by GRADDON and MUNDAY [8] is possibly completed by weak intermolecular C=O·····Cu linkages.

Palladium(II) complexes: Palladium(II) with $4d^8$ configuration is usually tetracoordinated, diamagnetic and square planar [25, 26]. The reflectance spectra of Pd(II) complex show main absorption bands at 40000, 28570, 22730, 20000, 18180, 16660, 12820 and 11 360 cm^{-1}. Out of these the more intense bands at 40000 and 28570 cm^{-1} are charge transfer bands. The bands in the visible region at 22730, 20000 and 18180 cm^{-1} can be taken as spin-allowed d—d transitions. The remaining weaker bands may correspond to spin-forbidden singlet—triplet transitions. Thus the present evidences indicate that Pd(II) complex has a square planar structure.

Nickel(II) complex: As already stated, in Ni(II) complex i.r. study has shown the presence of coordinated water molecules in addition to two α-aminobutyrate rings. Thus it is evident that in this complex Ni(II) is hexacoordinated. It gets further support from magnetic measurement (μ = 3.28 B. M.), a value corresponding to spin-free octahedral Ni(II) complexes. The reflectance spectra of Ni(II) complex show three principal absorption bands at 11100, 16940 and 25970 cm^{-1} and for an octahedral Ni(II) complex these may be taken to correspond to three spin-allowed transitions ν_1, ν_2 and ν_3 [26, 27]. Besides there is also a shoulder on the ν_2 band at 16130 cm^{-1}, which may correspond to a spin-forbidden transition. However, when an attempt is made to estimate its 10 Dq and B values from these transitions (by TANABE SUGANO's diagram [28] and transition energy ratio diagrams of LEVER [26]) it leads to a rather low value of B (B = 617 cm^{-1}, *i.e.*, the covalency factor β = 0.59) which does not seem feasible for a Ni(II) complex with N and O as donor atoms. The calculated 10 Dq value also comes to be somewhat higher (10 Dq = 11100 cm^{-1}) than expected for a (NiN_2O_4) chromophore group. In the spectrochemical series its position should lie in between the oxygen donor and nitrogen donor ligands. If $[Ni(H_2O)_6]^{2+}$ and $[Ni(NH_3)_6]^{2+}$ are taken as two such representative species, the 10 Dq value for an octahedral amino acid Ni(II) complex is expected to lie in between them, *i.e.*, in the range

of 8500—10700 cm^{-1} (10 Dq for $[Ni(H_2O)_6]^{2+} = 8500$ cm^{-1} and for $[Ni(NH_3)_6]^{2+} = 10700$ cm^{-1} [29]. It thus appears that the present bis(DL-α-aminobutyrato) nickel(II) dihydrate complex does not possess a regular octahedral structure. Possibly it possesses a distorted octahedral structure of $[NiX_4Y_2]$ type [26]. Such complexes are known to have a visible spectrum typical of regular octahedral complexes, *i.e.* ν_2 and ν_3 bands are not affected by the lowering of the symmetry. But ν_1 band is frequently split into two bands. In the present case the splitting of ν_1 band could not be observed due to the limitations of the apparatus (spectral measurements being limited up to 1000 mμ only) but it appears that the band observed at 11100 cm^{-1} represents one of the components of the splitted ν_1 band, whereas the other component may appear in the near infrared region. Thus the present evidences suggest a distorted octahedral structure for this bis(DL-α-aminobutyrato) nickel(II) dihydrate complex.

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LIGATIONAL BEHAVIOUR OF THIOSEMICARBAZIDE AND THIOSEMICARBAZONE, I

TETRAGONAL COMPLEXES OF NICKEL(II) DERIVED FROM 4-BENZYLAMIDOTHIOSEMICARBAZIDE AND ITS THIOSEMICARBAZONE

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Some new complexes of nickel(II) of the type NiL_2X_2 (where L = BTSC and FBTS and X = Cl, Br, I, NO_3 and NCS) have been prepared with 4-benzylamidothiosemicarbazide (BTSC) and 1-(α-) furyl-4-benzylamidothiosemicarbazone (FBTS) and characterized by conventional chemical and physical measurements. Tetragonal symmetry has been proposed on the basis of magnetic and electronic spectral studies. The various tetragonal ligand-field parameters Dq(E), Dq(A) and Dt and molecular orbital parameters d_σ and d_π have been evaluated. The presence of the anions in the coordination sphere and the bidentate nature of the ligands have been confirmed on the basis of the additional Ni–N, Ni–S and Ni–X frequencies observed in the far infrared spectra. The nitrato and thiocyanato groups act as monodentate ligands and are coordinated through oxygen and nitrogen atoms, respectively.

Introduction

The substituted thiosemicarbazides and thiosemicarbazones, which contain nitrogen and sulphur as potential donor atoms are well known for their versatile chelating ability, form square-planar, octahedral and pseudo-octahedral nickel(II) complexes [1–4] depending upon the experimental conditions. CAMPBELL *et al.* [4] have recently reported some tetragonally distorted nickel(II) complexes of thiosemicarbazones with various nickel(II) salts, but no systematic attempts were made to ascertain the nature of distortion, degree of distortion and causes of distortion, therefore, no significant conclusion could be drawn for such type of the complexes. In the present communication a number of tetragonally distorted nickel(II) complexes of 4-benzylamidothiosemicarbazide and 1-(α-) furyl-4-benzylamidothiosemicarbazone are described and attempts have been made in the direction of elucidating the structure of these complexes.

Results and discussion

The analytical data show that all the complexes have a general formula of the type NiL_2X_2 (where L = BTSC and FBTS and X = Cl, Br, I, NO_3 and NCS). All these complexes, as expected for sulphur-nitrogen donor set [5],

Table I

Magnetic data of $Ni(BTSC)_2Cl_2$ at various temperatures

Temperature (°K)	$X_{M'} \times 10^6$ c.g.s.	μ_{eff} B.M.
80	13,352	2.93
96	11,306	2.96
118	9,066	2.97
157	7,019	2.98
202.5	5,286	2.99
295	3,886	3.04

are sparingly soluble in non-polar solvents and possess no sharp melting points. They do, however, decompose on heating above 250 °C.

The magnetic moments of all the nickel(II) complexes of BTSC and FBTS have been measured at room temperature which lie between 2.95—3.27 B. M. The ground term, $^3A_{2g}$, of nickel(II) in cubic ligand field is almost unaffected by low symmetry components as orbital degeneracy is not lifted. The magnetic anisotropy observed, when this $^3A_{2g}$ term lies lowest, is small and arises as a consequence of the splitting of the higher lying $^3T_{2g}$ term by the low symmetry field since the higher term is not split in these complexes. Magnetic moment values are similar to those observed in octahedral fields. As a representative complex, the chloro complex of the BTSC was subjected to low temperature magnetic measurements. These data reveal obeyance of Curie-Weiss law ($\Theta = -14$ °K).

The electronic spectra of all the complexes show a characteristic marked splitting of the first spin-allowed band (ν_1) because of the lowering of symmetry. The four absorption bands are observed in the regions 8290—7650 cm^{-1}, 11,720—10,950 cm^{-1}, 15,700—14,250 cm^{-1} and 27,770—25,640 cm^{-1}. The first two bands could consequently be assigned to transitions $^3B_{1g} \rightarrow {}^3B_{2g}$ and $^3B_{1g} \rightarrow {}^3E_g$ which are the consequence of the splitting of the $^3T_{2g(F)}$ (ν_1) (component of O_h environment). The other two bands are assigned to the spin-allowed transitions $^3B_{1g} \rightarrow {}^3T_{1g(F)}$ (ν_2) and $^3B_{1g} \rightarrow {}^3T_{1g(P)}$ (ν_3) and are not greatly affected by the low symmetry environment on account of the fact that the levels concerned are $^3T_{1g(F)}$ and $^3T_{1g(P)}$ terms which give rise to ($^3A_{2g} + {}^3E_g$) in D_{4h} symmetry. These two levels split in the reverse sense in the strong field limit, the splittings tend to cancel out. Similar results have been obtained by various workers [6, 7] and only one band (ν_1) has been found to split into two levels while the rest of the two bands (ν_2) and (ν_3)

remain unsplit by the presence of low-symmetry components. The tetragonal ligand field parameters, Dq(E), (ligand field strength in xy-direction), Dq(A) (ligand field strength in z-direction) for different anions and Dt (magnitude of distortion) have been evaluated with the aid of the equations suggested by LEVER [8]. The distorted octahedral stereochemistry is further supported by the fact that the ratio ν_2/ν_1 comes out to be $\sim$1.5 whereas in octahedral field [9] this should have been $\sim$1.8. The values of Dt, which are the measure of tetragonality, have been found to increase from halo complexes to thiocyanato complexes via nitrato complexes and minimum in chloro complexes and maximum in thiocyanato complexes. If a series is drawn on the basis of 10 Dq(E), it comes out as $Cl < Br < I < NO_3 < NCS$. The difficulty in evaluating the value of Ds (kind of distortion) arises due to the fact that higher terms $^3T_{1g(F)}$ and $^3T_{1g(P)}$ do not split in the present studies.

If the molecular orbital interpretation as developed by MCCLURE [10] and YAMATRA [11] is applied then the splitting of the triplet state can be expressed in terms of two parameters, d_σ and d_π, where d_σ (or d_π) is the measure of the difference between σ (or π) antibonding ability of the axial (z-directional) and in-plane (xy-directional) ligands. In the present studies the d_σ should be negative due to the weaker field in z-direction than in xy-plane (due to BTSC and FBTS) and d_π positive since the anions have antibonding lone pairs.

Infrared spectral studies

The assignments for the bands particularly in thiosemicarbazide and thiosemicarbazone complexes are difficult because of the extensive mixing of internal mode of the ligand. The absorption bands in the regions 3,290—3,040 cm^{-1} in the infrared spectra of BTSC only have been assigned to the NH_2 and NH frequencies on the basis of similar observations by MASHIMA [12]. Most of these bands are shifted to lower frequencies as a result of the drainage of the electrons from terminal nitrogen atom of the NH · NH_2 group to the metal ion which indicates that this terminal nitrogen is taking part in coordination. A strong band at 1625 cm^{-1} in BTSC has been observed due to the amide I and NH_2 bands [2]. On complexation this band shifts slightly (10—20 cm^{-1}) to lower frequency, as contribution of the NH_2 group to this band is reduced which suggests the participation of the NH_2 group in coordination. On the other hand since the NH_2 group disappears during the thiosemicarbazone formation the amide I band is expected to be relatively free from the contribution of NH_2 band and therefore it is observed at 1615 cm^{-1} in FBTS (instead of 1625 cm^{-1} as in BTSC). Furthermore no change in the position of this band

has been observed in FBTS complexes. Another strong band at 1565 cm^{-1} in BTSC and 1575 cm^{-1} in FBTS has been assigned to the amide II and ν(CN) stretching vibrations [12]. In case of BTSC there is no change in the position of this band on complexation whereas in FBTS complexes this band shifts either to low frequency up to 20 cm^{-1} or weakens in intensity (in few cases weakening and shift both occur). This indicates that the contribution of CN stretch has been reduced as the nitrogen of CN group is involved in bond formation to the metal ion. The bands observed at $\sim$1230 cm^{-1}, $\sim$750 cm^{-1} and 650 cm^{-1} have been assigned to the amide III [2], amide IV [13] (due to the major contribution of NCO) and amide VI [13] (due to the contribution of C=O out of plane bending), respectively. The coordination through amino group can be excluded as no appreciable change in the position of all the bands due to this vibration has been observed in the infrared spectra of all the complexes of both the ligands.

The bands around 1290 cm^{-1} and 730 cm^{-1} which may be assigned to ν(CS) vibrations, do change either in energy or in intensity; generally intensity decreases as also the energy is lowered on complexation. These vibrations are not free from the other vibrations, especially CN vibration. The contribution of CN is smaller to band observed at 1290 cm^{-1} and greater to that observed at $\sim$730 cm^{-1} since the former changes to a greater extent than the latter. These changes in the ν(CS) vibrations are suggestive of the participation of sulphur atom of thioketo group in chelation [14, 15].

The coordination through the terminal nitrogen atom of hydrazinic group (in BTSC only) and the same nitrogen atom of CN groups (in FBTS only) and thioketo sulphur is further substantiated by the appearance of additional M—N and M—S vibrations in the low energy infrared spectra of the complexes. The metal-nitrogen and metal-sulphur vibrations have been observed [16, 17] in all the complexes in the regions 490—450 cm^{-1} and 430—405 cm^{-1}, respectively. In the present studies the bands that have been observed at 315,288 cm^{-1}, 242,248 cm^{-1} and 208,210 cm^{-1} have been assigned to ν(Ni—Cl) [18], ν(Ni—Br) [18] and ν(Ni—I) [19], respectively. In the nitrato complexes the bands observed in the regions 1535—1510 cm^{-1}, 1290—1265 cm^{-1}, 995—1005 cm^{-1} and 808—790 cm^{-1} have been assigned to asymmetric $-NO_2$ stretching, symmetric $-NO_2$ stretching, NO stretching and out-of-plane NO_2 rocking vibrations. These vibrations indicate that nitrate is a monodentate ligand [20]. One additional band is also observed in the region of 1800—1700 cm^{-1} which has been found to split. The magnitude of splitting, 23 cm^{-1} and 20 cm^{-1} in BTSC and FBTS complexes, further suggests the monodentate mode of coordination of nitrato group. The N-bonded mode of coordination of thiocyanato group has been confirmed because of the appearance of bands around 2075 cm^{-1}, 870 cm^{-1} and 480 cm^{-1} which are assignable [21] to (Ni—N) stretching of NCS group, (C—S) stretching of NCS group and NCS bending vibrations, respectively.

Experimental

(i) Preparation of the ligands*

The 4-benzylamidothiosemicarbazide (BTSC) was prepared by the hydrazinolysis of 5-benzyl 1,3,4-oxadiazole 2(3H) thione and 1-(α-) furyl-4-benzylamidothiosemicarbazone was prepared by the condensation of the BTSC with furfuraldehyde (1 : 1) in the mixture of glacial acetic acid and ethanol (1 : 4).

(ii) Preparation of the complexes

(a) *Dihalobis (BTSC) nickel(II), dinitratobis(BTSC) nickel(II) and corresponding complexes with FBTS*

A general method was employed for the preparation of these complexes.

When 50 ml of nickel(II) salt (1.0 mmole) in ethanol was added to 125 ml of the ethanolic solution of the ligand (2.5 mmole), a green coloured solution was obtained. This mixture was refluxed on a water bath for two hours and finally concentrated to a small volume. On cooling, a precipitate was obtained which was filtered off, washed with hot ethanol and ether, and dried at 110 °C. Yield ~70 per cent. The analyses of the complexes give the following general formulas: $Ni(C_9H_{12}N_4OS)_2X_2$ and $Ni(C_{14}H_{14}N_4O_2S)_2X_2$ where X = Cl, Br, I and NO_3.

(b) *Dithiocyanatobis (BTSC) nickel(II) and dithiocyanatobis (FBTS) nickel(II) complexes*

An ethanolic solution of ammonium thiocyanate (3.5 g) was added to the green solution obtained as a result of mixing nickel(II) chloride and the ligand in procedure (a). On stirring the mixture, a white precipitate of ammonium chloride separated which was discarded after filtration. The green coloured filtrate was condensed to about half of its volume by refluxing for about two hours and evaporating on a water bath. A green coloured precipitate was obtained on cooling. It was filtered off, washed successively with hot ethanol and ether and dried in an oven at 110 °C. Analysis of the complexes revealed the general formula $Ni(L)_2(NCS)_2$ where L = BTSC and FBTS.

Physical measurements

Magnetic measurements were made on powder forms of the complexes employing Gouy's balance using mercury(II) tetrathiocyanatocobaltate(II) as calibrant. The electronic spectra of all the complexes were recorded on Beckmann DK-2 by reflectance technique and vibrational spectra in the range 4000—200 cm^{-1} of the ligands as well as their complexes on Perkin Elmer — 471 in KBr discs. The Beckmann IR-12 instrument was used for recording the exclusive low energy vibrational spectra in the range of 650—200 cm^{-1} in nujol mull. The sparingly soluble nature of these complexes has prevented the determination of molecular weight, conductivity and solution absorption spectral measurement which might have given more information regarding their structure.

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Conclusions

(i) The tetragonality decreases from thiocyanate complexes to halo complexes *via* nitrato complexes. The order of the tetragonality is as follows: $Cl < Br < I < NO_3 < NCS$.

(ii) The ligand field strength in xy-plane, Dq(E), for a given ligand is not constant but depends largely on the nature of axial ligands and follows the same order as observed for tetragonal geometry.

(iii) The difference, Dq(E)—Dq(A), runs parallel with the difference, $d_\pi - d_\sigma$, which is a theoretical expectation.

(iv) The values of d_π and d_σ also run parallel with changing anions which is also expected theoretically.

*

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Table II

Electronic spectral data of Ni(II) complexes of BTSC and FBTS

Complex	$^3B_{1g} \rightarrow$				Dq(E)	Dq (A)	Dt	d_σ	$d\pi - d_\sigma$	$d\pi$
	$^3E_g(\nu_1)$	$^3B_{2g}(\nu_1)$	$^3T_{1g(F)}$ (ν_2)	$^3T_{1g(P)}$ (ν_3)						
$Ni(C_9H_{12}N_4OS)_2\ Cl_2$	8200	10.700	15.150	27.020	1070	571	285	833	1247	414
$Ni(C_9H_{12}N_4OS)_2\ Br_2$	8150	10.850	15.150	26.320	1085	546	308	900	1397	497
$Ni(C_9H_{12}N_4OS)_2\ I_2$	7650	10.950	14.250	25.640	1095	436	377	1100	1649	549
$Ni(C_9H_{12}N_4OS)_2\ (NO_3)_2$	8150	11.480	15.350	25.810	1128	463	380	1100	1662	552
$Ni(C_9H_{12}N_4OS)_2\ (NCS)_2$	8290	11.720	15.440	27.270	1172	486	392	1143	1715	572
$Ni(C_{14}H_{14}N_4O_2S)\ Cl_2$	8230	11.750	15.500	26.320	1075	571	288	840	1260	420
$Ni(C_{14}H_{14}N_4O_2S)\ Br_2$	8290	10.840	15.700	27.770	1084	565	291	850	1273	423
$Ni(C_{14}H_{14}N_4O_2S)\ I_2$	7680	10.990	14.320	25.970	1099	480	354	1103	1546	443
$Ni(C_{14}H_{14}N_4O_2S)\ (NO_3)_2$	8150	11.430	15.150	27.020	1143	487	375	1093	1548	455
$Ni(C_{14}H_{14}N_4O_2S)\ (NCS)_2$	8290	11.680	15.350	27.270	1168	491	387	1130	1568	438

Table III

Infrared spectral bands of the complexes of nickel(II) with BTSC

BTSC (1)	$Ni(BTSC)_2Cl_2$ (2)	$Ni(BTSC)_2Br_2$ (3)	$Ni(BTSC)_2I_2$ (4)	$Ni(BTSC)_2(NO_3)_2$ (5)	$Ni(BTSC)_2(NCS)_2$ (6)	Tentative assignment (7)
3290 (s)	3240 (m)	3200 to	3200 to	3290 to	3270 (m)	
3245 (s)	3200 (m)	3060 (br. m)	3065 (br. m)	3030 (br. m)	3237 to	ν (NH) and ν (NH_2)
3160 (s)	3150 (m)		3050 (m)		3157 (br.m)	stretch.
3090 (s)	3070 (m)				3070 (m)	
3040 (s)	3030 (m)	3030 (m)	3020 (m)		3030 (m)	
2940 (m)	2935 (m)	2940 (m)	2930 (m)	2935 (s)	2940 (m)	ν (CH_2)
—	—	—	—	—	2075 (v.s)	ν(CN) of *N*CS
—	—	—	—	1775 (m)	—	
				1752 (m)		Unidentate nitrate
1625 (s)	1605 (s)	1612 (s)	1610 (s)	1615 (s)	1605 (m)	Amide I & NH_2 bend
1565 (s)	1562 (s)	1560 (s)	1565 (s)	1567 (s)	1562 (s)	ν Amide II & ν(CN)
1495 (s)	1490 (s)	1495 (s)	1497 (s)	1535 (m)	1560 (s)	
				1495 (s)	1490 (s)	
1450 (s)	1450 (s)	1455 (s)	1452 (s)	1460 (s)	1448 (s)	
1420 (s)	1425 (m)	1430 (s)	1425 (m)	1427 (m)	1427 (m)	
1365 (m)	1370 (m)	1365 (m)	1370 (s)	1370 (m)	1365 (m)	
1335 (s)	1330 (m)	1328 (s)	1332 (m)	1337 (m)	1335 (m)	
1315 (m)	1310 (m)	1320 (sh.m)	1310 (w)	1315 (m)	1317 (m)	
1290 (s)	1270 (m)	1275 (s)	1277 (m)	1270 (m)	1272 (m)	ν CS and CN stretch.
1320 (m)	1235 (m)	1232 (m)	1230 (m)	1232 (m)	1228 (m)	ν Amide III
1200 (w)	1205 (w)	1202 (w)	1200 (w)	1205 (w)	1207 (w)	
1080 (m)	1085 (w)	1085 (m)	1075 (m)	1080 (m)	1075 (m)	
1070 (sh.m.)	1075 (sh.w)	—	1067 (w)	—	—	
1050 (s)	1037 (m)	1035 (m)	1035 (w)	1040 (w)	1032 (m)	N—C—N stretch &
1035 (sh.s)	1020 (sh.m)	1025 (sh.m)	—	1030 (w)	1015 (m)	C = S stretch.
				992 (w)		
970 (m)	970 (w)	972 (m)	968 (s)	965 (m)	972 (m)	
955 (s)	—	960 (m)	950 (m)	947 (m)	950 (m)	
920 (w)	925 (w)	—	920 (w)	925 (w)	925 (w)	N—N stretch.
900 (w)	—	915 (w)	—	—	865 (m)	
795 (m)	790 (m)	785 (m)	792 (m)	789 (m)	792 (m)	
755 (m)	752 (m)	755 (m)	750 (m)	752 (m)	758 (m)	ν (NCO)
730 (s)	732 (s)	728 (s)	730 (s)	732 (s)	730 (s)	CS & CN stretch.
715 (s)	705 (s)	710 (s)	707 (s)	710 (m)	700 (s)	

Table III (cont.)

BTSC (1)	$Ni(BTSC)_2Cl_2$ (2)	$Ni(BTSC)_2Br_2$ (3)	$Ni(BTSC)_2I_2$ (4)	$Ni(BTSC)_2(NO_3)_2$ (5)	$Ni(BTSC)_2(NCS)_2$ (6)	Tentative assignment (7)
685 (s)	690 (s)	692 (s)	687 (s)	690 (s)	685 (m)	
670 (s)	668 (s)	670 (m)	667 (m)	—	667 (m)	
658 (m)	655 (m)	652 (s)	654 (s)	655 (s)	658 (s)	C = O out of plane
632 (s)	—	600 (s)	598 (s)	625 (m)	600 (s)	bending
				604 (s)	590 (sh.s)	
572 (s)	578 (s)	580 (s)	574 (s)	568 (m)	570 (m)	ν(C=S)
542 (s)	540 (m)	548 (m)	540 (w)	542 (w)	555 (w)	ν(C—C)
—	512 (m)	492 (m)	496 (w)	512 (w)	490 (m)	(Ni—N) stretch.
487 (s)	482 (m)	480 (w)	478 (w)	475 (w)	475 (w)	
480 (sh.m)	472 (m)	470 (m)	468 (m)	462 (m)	462 (m)	ring deformation
	432 (w)	440 (w)	442 (w)	445 (w)	442 (w)	
			418 (w)		430 (w)	
378 (m)	385 (w)	378 (w)	380 (w)	402 (w)	378 (w)	
340 (w)	355 (w)	342 (w)	340 (w)	358 (w)	328 (w)	
300 (m)	315 (w)	300 (w)	—	315 (w)	312 (w)	
—	290 (w)	280 (m)	273 (w)	285 (w)	280 (m)	(Ni—S) stretch.
—	276 (w) (Ni—Cl)	—	—	—	265 (w)(Ni—*N*CS)	
—	—	242 (w) (Ni—Br)	—	—	—	
—	—	—	208 (w) (Ni—I)	—	—	

Table IV

Infrared spectral bands of the complexes of nickel(II) with FBTS

FBTS (1)	$Ni(FBTS)_2Cl_2$ (2)	$Ni(FBTS)_2Br_2$ (3)	$Ni(FBTS)_2I_2$ (4)	$Ni(FBTS)_2(NO_3)_2$ (5)	$Ni(FBTS)_2(NCS)_2$ (6)	Tentative assignment (7)
3140 (s)	3120 (s)	3120 (s)	3190 (s)	3100 (s)	3120 (m)	
3090 (s)	3080 (s)	3085 (m)	3080 (s)	3060 (s)	3060 (s)	ν(NH)
3040 (s)	3060 (s)	3060 (m)	3035 (s)	3025 (sh.m)	3035 (s)	
	3025 (s)	3025 (m)				
2935 (m)	2940 (m)	2942 (m)	2937 (m)	2935 (m)	2940 (m)	$\nu(CH_2)$
—	—	—	—	—	2076 (s)	ν(CN) of (*N*CS)
—	—	—	—	1770 (m)		
				1750 (m)	—	Unidentate nitrate
1615 (s)	1612 (s)	1615 (s)	1618 (s)	1615 (s)	1617 (s)	Amide—I
1575 (s)	1550 (m)	1550 (m)	1542 (m)	1558 (m)	1555 (m)	Amide—II +(CN)
1500 (m)	1495 (m)	1497 (m)	1492 (m)	1505 (m)	1495 (m)	
1475 (s)	1475 (m)	1467 (sh.m)	1480 (m)	1475 (m)	1478 (s)	
1455 (s)	1445 (m)	1440 (s)	1455 (m)	1455 (sh.m)	1452 (sh.m)	
1430 (m)	1425 (sh.m)	—	1442 (m)	1440 (m)	1445 (m)	
1415 (s)	1410 (w)	1420 (sh.m)	1420 (sh.m)	—	1425 (sh.m)	
1395 (s)	1390 (m)	1392 (s)	1395 (m)	1390 (s)	1290 (s)	
1390 (m)	1355 (m)	1365 (m)	1350 (w)	1360 (m)	1357 (m)	
1325 (w)	1335 (m)	1337 (m)	1330 (w)	1332 (w)	1330 (w)	
1280 (s)	1280 (m)	1267 (br.m)	1265 (br.m)	1267 (m)	1260 (m)	CS & CN stretch.
1235 (w)	1225 (w)	1230 (w)	1235 (w)	1232 (sh.w)	1235 (sh.m)	Amide—III
1200 (m)	1195 (s)	1205 (m)	1195 (m)	1192 (m)	1197 (m)	
1155 (m)	1158 (sh.m)	1160 (m)	1152 (m)	1152 (m)	1150 (m)	
1100 (w)	—	—	1150 (sh.m)	—	—	
1070 (s)	1075 (m)	1075 (m)	1078 (m)	1072 (m)	1070 (m)	
1025 (m)	1018 (m)	1020 (s)	—	1018 (m)	1022 (m)	N—C—N stretch. &
1015 (s)	—	—	1018 (s)	1005 (w)	1000 (w)	C = S stretch.
				990 (m)		
950 (m)	960 (sh.m)	957 (w)	952 (w)	952 (m)	950 (w)	
935 (s)	935 (s)	937 (s)	937 (s)	932 (s)	935 (s)	N—N stretch.
905 (w)						
885 (s)	882 (s)	885 (s)	882 (s)	885 (m)	882 (m)	
845 (s)	842 (w)	845 (w)	840 (m)	840 (m)	870 (w)	
835 (sh.m)	832 (m)	830 (m)	827 (m)	828 (m)	840 (w)	
					825 (m)	

Table IV (cont.)

FBTS (1)	$Ni(FBTS)_2Cl_2$ (2)	$Ni(FBTS)_2Br_2$ (3)	$Ni(FBTS)_2I_2$ (4)	$Ni(FBTS)_2(NO_3)_2$ (5)	$Ni(FBTS)_2(NCS)_2$ (6)	Tentative assignment (7)
				795 (w)		
750 (s)	755 (s)	750 (s)	752 (s)	757 (m)	745 (s)	ν(NCO)
735 (s)	730 (s)	725 (s)	730 (m)	730 (m)	730 (m)	C=S and C=N
705 (s)	697 (m)	697 (s)	700 (w)	705 (m)	697 (s)	stretch.
694 (s)	685 (m)	688 (m)	682 (m)	688 (m)	680 (m)	
650 (s)	665 (m)	652 (m)	655 (m)	648 (m)	650 (m)	C=O out of plane bend
592 (s)	590 (m)	595 (m)	592 (m)	596 (m)	590 (m)	
580 (sh.m)	582 (sh.m)	585 (sh.m)	585 (sh.m)	582 (sh.m)	582 (sh.m)	ν(C=S)
548 (s)	540 (m)	537 (w)	560 (m)	547 (m)	545 (m)	ν(C−C)
498 (s)	505 (w)	512 (m)	487 (m)	482 (m)	492 (m)	
					485 (w)	
—	465 (m)	478 (m)	465 (m)	467 (m)	472 (m)	(Ni−N) stretch.
437 (m)	445 (w)	448 (w)	437 (w)	430 (w)	455 (w)	
	407 (w)	425 (m)	427 (w)	420 (w)	437 (w)	ring deformation
			420 (w)			
387 (m)	380 (w)	832 (w)	—	400 (w)	390 (w)	
346 (m)	342 (w)	338 (w)	345 (w)	335 (w)	350 (w)	
330 (m)		300 (w)	325 (w)	—	—	
—	288 (m) (Ni−Cl)			290 (m)		
	270 (m)	285 (m)	282 (m)	272 (m)	275 (m)	(Ni−S) stretch.
255 (w)						
—	—	—	248 (m) (Ni−Br)	—	265 (Ni−NCS)	
—	—	—	—	210 (w) (Ni−I)	—	

Table V

Analytical data of nickel (II) complexes

Complex	Observed percentage					Calculated percentage				
	C	H	N	M	X	C	H	N	M	X
$Ni(C_9H_{12}N_4OS)_2$ Cl_2	37.42	4.08	19.42	10.02	12.13	37.39	4.15	19.39	10.16	12.27
$Ni(C_9H_{12}N_4OS)_2$ Br_2	32.67	3.69	16.78	8.76	24.17	32.41	3.60	16.80	8.81	23.98
$Ni(C_9H_{12}N_4OS)_2$ I_2	28.27	3.01	14.69	7.84	33.94	28.40	3.15	14.73	7.72	33.37
$Ni(C_9H_{12}N_4OS)_2$ $(NO_3)_2$	34.48	3.89	22.02	9.42	—	34.25	3.80	22.20	9.31	—
$Ni(C_9H_{12}N_4OS)_2$ $(NCS)_2$	38.47	3.98	22.59	9.42	—	38.53	3.85	22.48	9.43	—
$Ni(C_{14}H_{14}N_4O_2S)_2$ Cl_2	42.97	3.72	14.39	8.12	9.54	43.43	3.82	14.48	8.00	9.66
$Ni(C_{14}H_{14}N_4O_2S)_2$ Br_2	41.06	3.52	13.67	7.10	19.54	40.84	3.41	13.62	7.14	19.43
$Ni(C_{14}H_{14}N_4O_2S)_2$ I_2	36.79	3.08	12.18	6.29	28.03	36.66	3.05	12.22	6.40	27.69
$Ni(C_{14}H_{14}N_4O_2S)_2$ (NO_3)	42.23	3.53	17.68	7.45	—	42.71	3.56	17.79	7.46	—
$Ni(C_{14}H_{14}N_4O_2S)_2$ $(NCS)_2$	46.01	3.57	18.82	7.59	—	46.22	3.60	17.97	7.54	—

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STEREOCHEMISTRY OF THE REACTIONS OF BIOPOLYMERS, VI*

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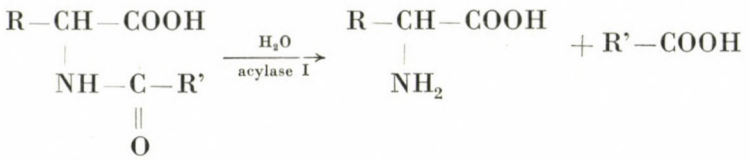
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The stereospecificity of acylase I catalyzed dipeptide hydrolysis has been studied and interpreted. If the α-carbon atom of the N-terminal acyl moiety has D-configuration, the R group is closer to the catalytic site of the enzyme than in the case of compounds in L-configuration. Steric hindrance of the R group in the reaction between the catalytic moiety of the enzyme and the CO group of the substrate is much greater in the case of substrates containing peptides with N-terminal amino acids of D-configuration, than for substrates of L-configuration. Consequently, the rate of hydrolysis of the former is lower by several orders of magnitude.

Interpretation of the stereospecificity is based on a fixed conformation of the enzyme–substrate complex. Owing to the fixed position of the terminal amino group and the amide carbonyl group, the α-H atom and R group of the acyl moiety are in reversed positions in the two diastereomeric compounds.

Introduction

Acylase I (N-acylamino acid amidohydrolase, EC 3.5.1.14), which has a wide range of substrate specificity [1—4], catalyzes the following process:



In the knowledge of the mechanism [5] and a recently reported new free energy relationship [6], the stereochemistry of the reaction can be interpreted.

Peptides are considered one of the most important groups of substrates. The hydrolysis of dipeptides [7—10] catalyzed by acylase I is highly stereospecific depending on the configuration of the C- and N-terminal amino acids. The aim of this paper is an interpretation of the specificity, including stereospecificity of the peptide hydrolysis, in relation to the structure of the N-terminal amino acid.

* Part V: L. Ötvös, E. Moravcsik and F. Kraicsovits: Tetrahedron Letters, **29**, 2485 (1975).

Experimental

All m.p.'s were determined with a Boetius hot-stage apparatus and are uncorrected. Compounds were checked for purity by elemental analysis, thin-layer chromatography (Kieselgel HF_{254}, Merck; detection with iodine vapour or ninhydrin reagent).

Structures were confirmed by IR spectra recorded in KBr pellets on a Perkin-Elmer spectrophotometer Model 137. Optical rotations were measured with a Schmidt-Haensch polarimeter.

Materials and methods

Acylase I was purchased from the Sigma Chemical Company. The specific activity of the enzyme was determined according to BRUNS and SCHULZE [11]. The substrates applied were different dipeptides containing L-norvaline as the C-terminal amino acid. As the N-terminal amino acid, glycine, the L- and D-stereoisomer of alanine, valine, as well as norvaline were applied. The enantiomeric amino acids with high optical purity (min. 99.5%) required for the synthesis of peptides were obtained by resolution of the N-acyl-DL-amino acids through the action of acylase I [2]. Glycyl-L-norvaline was prepared by amination of chloroacetyl-L-norvaline according to ROBINSON *et al.* [12]. The different diastereomeric dipeptides were obtained by the reaction of carbobenzoxy derivatives of the amino acids with L-norvaline ethyl ester in a toluene–chloroform mixture, using isovaleryl chloride as the condensation reagent [9, 13]. Overall yields were 50–65% of the theoretical. All materials were purified up to a constant melting point and optical rotation. Rotation values and analytical results are collected in Table I.

Table I

Optical rotations and analyses

$[\alpha]_D^t$ was measured in H_2O using a 1-dm polarimeter tube

Compound (-L-norvaline)	$[\alpha]_D^t$	t	c	Calcd.			Found		
				N	C	H	N	C	H
	degree	°C	%	%			%		
Glycyl-	−27.3[a]	25	2	16.09	48.27	8.10	15.92	48.20	7.98
L-alanyl-	− 5.1[b]	23	2	14.89	51.06	8.51	14.81	50.94	8.50
D-alanyl-	−47.1[c]	24	2	14.89	51.06	8.56	14.83	51.01	8.38
L-norvalyl-	+18.9	25	1	12.96	55.51	9.32	12.87	55.49	9.20
D-norvalyl-	−71.0	25	1	12.96	55.51	9.32	12.91	55.48	9.21
L-valyl-	+13.3	24	0.9	12.96	55.51	9.32	12.87	55.38	9.16
D-valyl-	−74.1	24	1	12.96	55.51	9.32	12.92	55.48	9.18

[a] Lit. [11] $[\alpha]_D^t$ −27.6 °C (in water)
[b] Lit. [14] $[\alpha]_D^{25}$ − 5.0 °C (in water)
[c] Lit. [9] $[\alpha]_D^{25}$ −47.4 °C (in water)

Kinetic procedure

Enzymatic hydrolysis of the dipeptides was carried out at pH 7.15 at 37 ± 0.1 °C in 0.1 *M* phosphate buffer. The cleavage rate was determined on a UNICAM SP 500 spectrophotometer by measuring the colours at 570 nm obtained from the reaction of the liberated amino acids with ninhydrin reagent, according to ROSEN [15].

In evaluating the initial velocities of the enzyme-catalyzed reactions, we used the conventional graphic method [16], applying only a small segment of the kinetic curve on the one hand, and for the analysis of the entire curve an integrated rate equation (1) derived by JOHNSTON and DIVEN [17], on the other. The validity of latter procedure was recently studied by ZERVOS [18], who claimed that it can only be applied for a few types of enzyme-catalyzed reactions, under certain experimental conditions. On the basis of our investigations, however, the procedure proved to be applicable also for acylase-catalyzed dipeptide hydrolysis, since the initial velocities evaluated by the conventional graphic method [16] and those obtained by JOHNSTON and DIVEN's procedure [17] are identical.

$$\ln\left(1 - \frac{[P]}{[P]_{eq}}\right) = -\frac{v.t}{[P]_{eq}} \qquad (1)$$

K_m(app) and V_{max} were determined from the Lineweaver-Burk plot between $1/v$ and $1/S$. The k_{cat} values were calculated from the relationship $k_{cat} = V_{max}/E$. Enzyme concentrations in the experiments ranged between $3.2 \cdot 10^{-8}$ *M* and $3.2 \cdot 10^{-7}$ *M* based on 76,500 molecular weight [11] and the specific activity values for N-acetyl-L-methionine of the pure enzyme [11]. In the range studied, the initial rate of hydrolysis was found to change linearly with the enzyme concentration. The initial substrate concentration varied between 1.0 m*M* and 10.0 m*M*.

Results and discussion

Kinetic data of the hydrolysis of the dipeptides (formula **I**) catalyzed by acylase I are presented in Table II.



I

R = H, CH_3, *n*-C_3H_7, *i*-C_3H_7

In the course of our previous studies [5] the decomposition of the enzyme–substrate complex was found to be the rate determining step of the reaction, where K_m(app) is equal to K_S. Accordingly, K_m(app) is characteristic of the binding strength between the substrate and the enzyme.

Table II

Kinetic data of the acylase I catalyzed hydrolysis of dipeptides

Compound (-L-norvaline)	K_m(app) mM	k_{cat} sec^{-1}	k_{cat}/K_m(app) $mM^{-1}sec^{-1}$	$\bar{Q}_e$
Glycyl-	3.2±0.4	170 ±30	53	
L-alanyl-	2.2±0.3	155 ±18	70	
D-alanyl-	3.2±0.4	0.67± 0.1	0.21	333
L-norvalyl-	2.7±0.2	102 ± 8.4	38	
D-norvalyl	2.2±0.2	0.13± 0.01	0.06	633
L-valyl-	2.0	1.2	0.6	
D-valyl-	—	0	0	

$\bar{Q}_e$ in the last column is the stereospecificity factor:

$$\bar{Q}_e = \frac{k_{cat}/K_m(\text{app})_L}{k_{cat}/K_m(\text{app})_D}$$

The K_m(app) values of the compounds studied were found to be nearly identical, irrespective of the configuration of the acyl moiety and the nature of the side chain. It has been concluded therefore that all substrates are bound to the enzyme practically in the same way, considering the fact that the substrates differ only in the structure of one of the alkyl groups. It may be presumed that the conformation of the substrate in the enzyme–substrate complex is mainly due to interaction between the C-terminal amino acid moiety (L-norvaline) and the amino group of the acyl moiety on the one hand, and the corresponding bindig sites of the enzyme, on the other (Fig. 1).

The above consideration may also provide an explanation for the stereospecificity depending on the acyl moiety.

In addition to the fixed amino and amide carbonyl groups, there are two substituents attached to the α–carbon of the N-terminal amino acid moiety: an α-hydrogen atom and a side chain.

Since the amino group of the diastereoisomers is bound in the enzyme–substrate complex at the same site (position "B" in Fig. 2), the acyl moiety of the two diastereomeric substrates differs only in the positions of the hydrogen

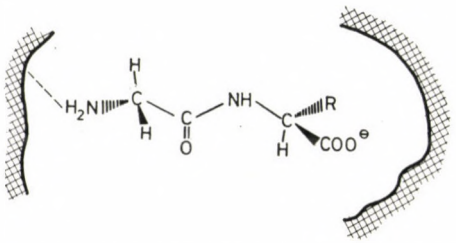


Fig. 1. Attachment between enzyme and substrate in the enzyme–substrate complex

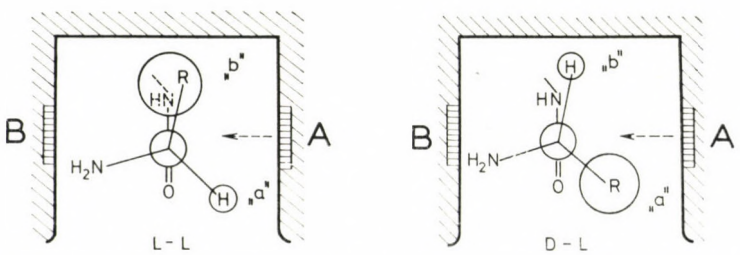


Fig. 2. Conformation of the acyl moiety of diastereomers in the enzyme–substrate complex: A: catalytic site; B: amino binding site

atom and the side chain related to the catalytic site of the enzyme (position "A" in Fig. 2).

Since the two substituents are not in symmetrical positions related to the catalytic site of the enzyme, the reversed positions in the two diastereomeric compounds show different steric hindrance towards the catalytic site and thus involve different reactivities. Fig. 2a shows the case, where position "a" near the catalytic site is occupied by a hydrogen atom and position "b", farther away from it, is taken by an "R" group. This steric arrangement is characteristic of the conformation of substrates in the enzyme–substrate complex where the acylating amino acid has L-configuration. As the unbranched alkyl groups of the L-acyl moieties do not exert considerable steric hindrance in position "b", the slight difference in polarity of the methyl and *n*-propyl groups causes hardly any difference in the k_{cat} values of L-alanyl-L-norvaline and L-norvalyl-L-norvaline. According to these results, in the case of glycyl-L-norvaline (Fig. 3), where two hydrogen atoms are bound to the α-carbon atom, reactivity was found to be nearly the same as observed for L-alanyl- and L-norvalyl derivatives.

Figure 2b shows the conformation of diastereomeric substrates containing a D-acyl component. Here, position "a", which is near the catalytic site, is occupied by an "*R*" group. Since the alkyl groups are much bulkier than the hydrogen atom, the catalytic site is more hindered. The difference between

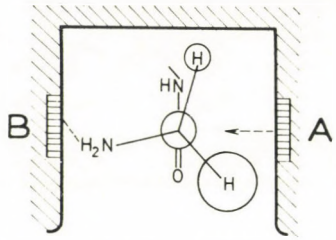


Fig. 3. Conformation of the acyl moiety of glycyl-L-norvaline in the enzyme–substrate complex: A: catalytic site; B: amino binding site

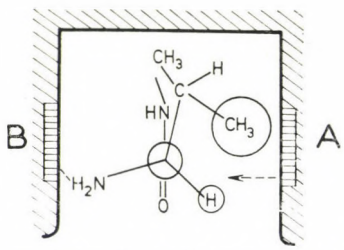


Fig. 4. Conformation of the acyl moiety of L-valyl-L-norvaline in the enzyme–substrate complex: A: catalytic site; B: amino binding site

steric hindrance by the hydrogen atom and the alkyl groups in position "a" results in great stereospecificity.

Accordingly the differences in stereospecificity depending on the structures of the side chains of various N-terminal amino acids can also be well interpreted, as it may be expected that steric hindrance near the catalytic site becomes more effective. It follows that the considerable differences observed in the stereospecificity of compounds within a homologous series are due to the different reactivities of the substrates containing D-acyl groups. According to the experimental data, the reactivity is more than six times as high in the case of D-alanyl-L-norvaline, which contains an α-methyl group in the acyl moiety as found for the D-norvalyl-L-norvaline, which has an *n*-propyl group in the same position. The greater steric hindrance of the *n*-propyl group can be interpreted by the twisted conformation of the side chain. For the same compounds in L-configuration, the steric hindrance of the *n*-alkyl group of N-terminal amino acids is rather low.

The steric effect greatly increases, however, if the side chain is a branched alkyl group (Fig. 4).

It is not surprising, therefore, that the rate of hydrolysis for L-valyl-L-norvaline was found to be lower by two orders of magnitude than in the case of the above substrates with unbranched acyl moieties in L-configuration. Owing to the great steric hindrance of the same structure in D-configuration, hydrolysis takes place at an extremely low rate.

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SEARCH FOR NEW LOCAL ANAESTHETIC AGENTS, III

SYNTHESIS OF 2-ALKYL-ARYLAMINO-ACETYLAMINO-4-PHENYLTHIAZOLES

P. K. SRIVASTAVA,* R. D. SHARMA and S. K. RAI

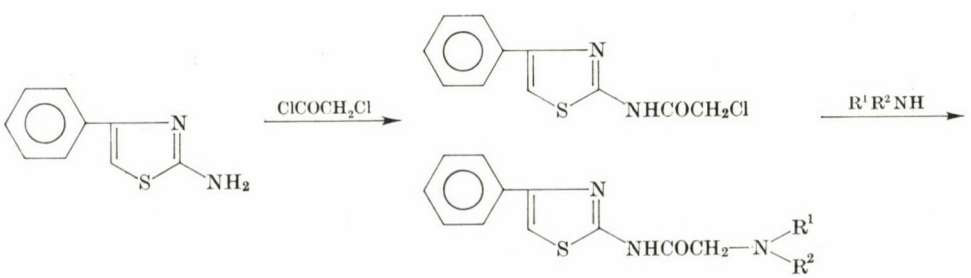
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A series of various 2-alkyl-arylamino-acetylamino-4-phenylthiazoles have been synthesized and tested for local anaesthetic activity.

Thiazole and imidazole groups are of great importance in biological systems. Following the local anaesthetic screening reports of some derivatives of benzothiazoles, search for better local anaesthetic agents in this series has gained momentum [1]. Recently, numerous derivatives of benzothiazole and benzimidazole have been shown to possess notable local anaesthetic activity [2].

Since the essential structure requirements [3, 4] for a local anaesthetic are the presence of a lipophilic end containing an aromatic nucleus, a hydrophilic end consisting of a tertiary amino group, and an intermediate alkyl or substituted alkyl chain, it was thought worthwhile to synthesize some 2-alkyl-arylamino-acetylamino-4-phenylthiazoles. These compounds were prepared by condensation of chloroacetyl chloride with 2-amino-4-phenylthiazole followed by treatment with various primary and secondary amines.



The structures of these compounds have been established on the basis of their analytical results and infrared spectra. The IR spectra of these compounds show characteristic strong absorption peaks at 1650—1625 cm^{-1} and

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1370—1360 cm^{-1} corresponding to C=O and C—N bands, respectively. An absorption band at 3200—3150 cm^{-1} indicates the NH stretching frequency. A strong absorption peak in the region 1700—1670 cm^{-1} shows the amide ($-\overset{\overset{O}{\|}}{C}-N<$) band.

Experimental

2-Amino-4-phenylthiazole was prepared by adopting the procedure suggested by DODSON and KING [5]. Chloroacetyl-2-amino-4-phenylthiazole was made by the known procedure [2].

Preparation of 2-morpholinoacetylamino-4-phenylthiazole

To an ethanolic solution (20 ml) of chloroacetyl-2-amino-4-phenylthiazole (5.04 g; 0.02 mole), morpholine (1.74 g; 0.02 mole) was added slowly with constant shaking. After the addition, the reaction mixture was refluxed for 6 hrs. Unreacted morpholine was recovered by distillation, and the residue was washed with sodium hydrogen carbonate to remove any acid impurities. The final product was crystallized from ethanol to yield 4.2 g (70%) of the product, m.p. 115 °C. The compound was shown to be homogeneous (single spot on TLC, silica gel).

IR $\sim$1630 cm^{-1} (C=O); $\sim$1365 cm^{-1} (C—N); $\sim$3150 cm^{-1} (NH, stretching) and $\sim$1675 cm^{-1} ($-\overset{\overset{O}{\|}}{C}-N<$).

$C_{15}H_{17}N_3O_2S$. Calcd. C 59.41; H 5.61; N 13.86; S 10.56. Found C 59.08; H 5.50; N 13.62; S 10.03%.

This base was converted into its hydrochloride for biological evaluation by passing dry hydrogen chloride gas in its ethereal solution.

Similarly, dimethylaminoacetyl-, diethylaminoacetyl-, dipropylaminoacetyl-, isopropylaminoacetyl-, 4-diethylaminophenylaminoacetyl-, piperazinoacetyl-, piperidinoacetyl-, pyrimidine-2-aminoacetyl-, and 2-(pyridine-2-amino-)acetylamino-4-phenylthiazoles were prepared and their hydrochlorides isolated (Table I).

Bioassay

In the present studies all the three actions, *viz.* surface anaesthesia [6], infiltration anaesthesia [7] and conduction anaesthesia [7] exhibited by the synthesized compounds were determined by employing the methods given in literature. Procaine hydrochloride was used as standard drug.

The results of biological testing are listed in Table II (a, b, c). 2-(Diethylaminophenyl-4-amino-)acetylamino-4-phenylthiazole (Compd. No. 7 in Table IIa) was found quite active when tested for surface anaesthesia. Of all the compounds in Table IIb, compound No. 7 was the most active. The duration of anaesthesia of 2-dipropylaminoacetylamino-4-phenylthiazole (Table IIc, Compd. No. 3) is comparable with the standard drug procaine hydrochloride. It is clear from these results that the compounds containing a saturated (*e.g.*, piperidino-) and branched (*e.g.*, N,N-dimethylanilino-) hydrophilic moiety exhibit enhanced activity.

*

The authors are thankful to Prof. K. N. UDUPA, Director, Institute of Medical Sciences, B. H. U., Varanasi, for providing the necessary laboratory facilities. Financial assistance from C.S.I.R., New Delhi, is also gratefully acknowledged.

Table I

2-Alkyl-arylamino-acetylamino-4-phenylthiazoles



No.	R_1 / R_2 (or H)	Yield, %	M.p., C°	Formula	Analysis, %					M.p., °C (hydrochloride)
						C	H	N	S	
1	Dimethyl	72	134	$C_{13}H_{15}N_3OS$	Found Calc.	59.92 59.77	5.76 5.74	15.99 16.09	12.19 12.26	175—76
2	Diethyl	70	129	$C_{15}H_{19}N_3OS$	Found Calc.	62.35 62.28	6.64 6.57	14.48 14.53	10.97 11.07	195—96
3	Dipropyl	65	108	$C_{17}H_{23}N_3OS$	Found Calc.	64.67 64.35	7.15 7.25	13.17 13.24	10.02 10.09	182—83
4	Isopropyl	68	123	$C_{15}H_{19}N_3OS$	Found Calc.	62.15 62.28	6.61 6.57	14.45 14.53	11.00 11.07	185—86
5	Pyridyl	75	100	$C_{16}H_{14}N_4OS$	Found Calc.	61.98 61.93	4.53 4.51	17.98 18.06	10.25 10.32	140—41
6	Pyrimidino	60	90	$C_{15}H_{13}N_5OS$	Found Calc.	57.61 57.88	4.22 4.18	22.43 22.51	10.24 10.29	125—26
7	4-Diethylaminophenyl-amino	55	45	$C_{21}H_{21}N_4OS$	Found Calc.	66.52 66.31	6.35 6.31	14.78 14.74	8.44 8.42	127—28
8	Piperidino	75	106	$C_{16}H_{19}N_3OS$	Found Calc.	63.88 63.78	6.35 6.31	13.89 13.95	10.57 10.63	175—76
9	Piperazino	60	120	$C_{15}H_{18}N_4OS$	Found Calc.	59.82 59.60	5.89 5.96	18.40 18.54	10.48 10.59	148—49
10	Morpholino	70	115	$C_{15}H_{17}N_3O_2S$	Found Calc.	59.08 59.41	5.50 5.61	13.62 13.86	10.03 10.56	200—201

Table II

Screening results of 2-alkyl-arylamino-acetylamino-4-phenylthiazoles

No.*	a Surface anaesthesia			b Infiltration anaesthesia			c Conduction anaesthesia			
	Concn. of drug, %	Intensity	Duration, min	Concn. of drug, %	Intensity	Duration, min	Concn. of drug, %	Onset of anaesthesia (min) in HCl of strength		
								0.05 *N*	0.1 *N*	0.2 *N*
1	2	Complete	5	0.2	Nil		0.2	20	21	22
2	2	Complete	6	0.2	Complete	5	0.2	22	22	23
3	2	Complete	3	0.2	Nil		0.2	16	17	17
4	2	Nil		0.2	Complete	2	0.2	20	22	22
5	2	Nil		0.2	Complete	6	0.2	18	19	19
6	2	Nil		0.2	Complete	2	0.2	18	18	19
7	2	Complete	27	0.2	Complete	30	0.2	12	13	13
8	2	Complete	20	0.2	Complete	18	0.2	9	10	11
9	2	Complete	10	0.2	Complete	15	0.2	8	9	9
10	2	Complete	8	0.2	Complete	8	0.2	11	12	13
Procaine hydrochloride	2	Complete	15	0.2	Complete	12		15	16	17

* Numbers correspond to those in Table I.

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N-(3-QUINAZOLINIO)-AMIDATES, IV *

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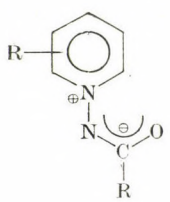
Irradiations (high-pressure Hg lamps, Pyrex filter) of the title compounds **8a-g** (R^2, R^4 = H, Me; R = OEt, OCH_2Ph, Ph) in ethanol and benzyl alcohol furnish in addition to the amides **15** corresponding to the acyl groups of the starting amidates, six types of heterocyclic transformation products: 4-acyl-5-alkoxy-4,5-dihydro-3*H*-1,3,4--benzotriazepines (**9**), quinazolines (**10**), 1,2-di(4-quinazolinyl) ethanes (**11**), *N*-(4-quinazolinylmethyl)-carbamates (**12**, R = OEt), 4-alkoxyquinazolines (**13**) and 3-acylamino--4(3*H*)-quinazolinones (**14**). The yields of the compounds **9**—**15** markedly depend on the nature of the substituents present in the starting amidates **8**, as well as whether oxygen is present during the irradiations or not. The formation of products analogous to the type **11**—**14** compounds has never yet been observed in phototransformations of heterocyclic ammonioamidates. Rationales for the formation of all of the products **9**—**15** are presented.

The photochemistry of electron deficient heterocyclic ammonioamidates, *viz.* of *N*-(1-pyridinio)-amidates (**1**) and -sulfonamidates (**2**) has been first studied by STREITH *et al.* [4—9]. Following the pioneering work of the French authors, a large number of simple [10—15] and condensed *N*-(1-pyridinio)--amidates and -sulfonamidates, including *N*-(1-quinolinio)- [16—18], *N*-(2-isoquinolinio)- [17—20] and *N*-(5-phenanthridinio)-amidates [2] have been irradiated. In general, the monocyclic compounds undergo ring expansions (yielding the corresponding 1*H*-1,2-diazepine derivatives, **3**) and the condensed compounds undergo photoisomerisation under (formal) [1,2]-shifts of the acylnitrene groups (giving rise to compounds such as 2-acylaminoquinolines, 1-acylaminoisoquinolines and 6-acylaminophenanthridines). In addition to these processes, acyl- or sulfonylnitrene eliminations occur leading to the formation of the parent heterocycles. Until now only a single case of a [1,2] acylnitrene shift has been reported in the monocyclic series: irradiation of *N*-(3,5-dimethyl-1-pyridinio)-toluenesulfonamidate furnished 3,5-dimethyl-2--toluenesulfonamidopyridine [14]; and two cases are known, in which irra-

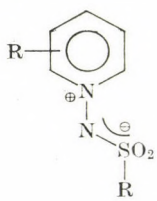
* Part XIII of "Electron Deficient Heteroaromatic Ammonioamidates". For Parts III and XII, see Ref's [1] and [2], respectively. The results presented in this paper have earlier been described in three lectures delivered by one of the authors (see Ref. [3]). For a preliminary communication of part of the results, see Ref. [26]

** Chinoin Pharmaceutical Works (Budapest) research fellow, 1975—1977.

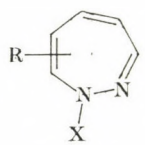
diation of condensed *N*-(1-pyridinio)-amidates effects ring expansions: *N*-(1-quinolinio)-acetamidate in methanol furnishes, in addition to the acylnitrene elimination product, the 1,2-benzodiazepine derivative **4** [16], and *N*-(1-quinolinio)-ethoxyformamidate in ethanol gives rise, among other products to the related compound **5** [18]. In both cases the ring expansions are accompanied by addition of one molecule of the nucleophilic solvent, conserving the aromaticity of the benzene ring. Simple ring expansions to **7** have been observed on irradiation of the *N*-(1-quinolinio)-amides **6** in methylene chloride or acetone [21].



1

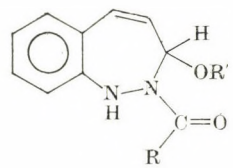


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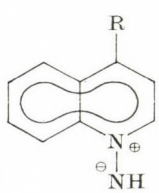
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(X = R—CO—, R—SO_2—)

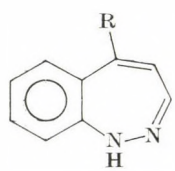


4: R = R′ = Me

5: R = OEt, R′ = Et



6



7

(R = H, Me)

The literature on the photochemistry of both simple and condensed *N*-(diazinio)-amidates is rather scarce. *N*-(5-Benzo[*c*]cinnolinio)-amidates have been found to suffer acylnitrene eliminations on irradiation [22, 23], as is also the case with *N*-(1,4-diphenyl-2-phthalazinio)-benzamidate if the irradiation is carried out in deaerated solution [24]. However, when the latter compound is irradiated in the presence of air, *o*-dibenzoylbenzene is formed as the result of a photooxidation process [24]. Irradiation of an *N*-(1-quinoxalinio)-amidate has been found to yield the corresponding 2-acylaminoquinoxaline *via* a [1,2] acylnitrene shift [25], and preliminary communications on the photochemistry of a series of *N*-(3-quinazolinio)-amidates in various solvents have recently been published [1, 26]. During the preparation of the present paper the ring contraction with concomitant fragmentation of *N*--ethoxycarbonyl-*N*-(1-pyrazinio)-amides to yield 1-ethoxycarbonylpyrazoles and nitriles has been described [40].

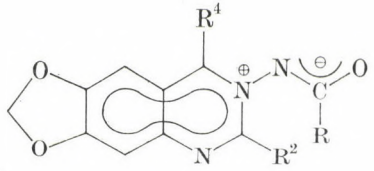
In the present paper we wish to describe the photochemical transformations of the *N*-(3-quinazolinio)-amidates **8a–f** [27] and **8g** in ethanol and benzyl alcohol.

Identification and some reactions of the phototransformation products

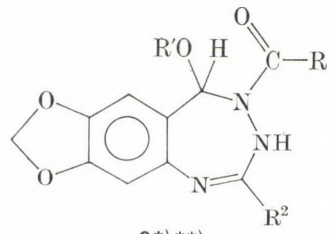
The irradiations were performed in argon-flushed solutions with high-pressure mercury immersion lamps through Pyrex, until the starting compounds **8** were completely used up according to TLC. Some irradiations were carried out under oxygen. The necessary reaction times varied strongly with the nature of the substituents R^2, R^4 and R (Table V). The resulting mixtures were worked up by chromatographic methods combined with fractional crystallizations. Six different types **9**—**14** of heterocyclic transformation products were obtained in the yields indicated in Table I, in addition to the amides **15** corresponding to the amidate groups of the starting compounds. Compounds **11**—**14** are of types which have never been isolated yet on irradiation of heterocyclic ammonioamidates.

The structures of the new compounds among the products were derived from their IR, mass (see below), NMR (Table II) and UV spectra (Table III), and were corroborated at least for one compound of each type either by synthesis or by X-ray molecular structure determination. The structure elucidation of the ring expansion products **9** may serve as an example. The type of the chromophore present in **9b** (R' = Et) followed from the similarity of its UV spectrum to that of the model compound **16** (X = NHCOOEt) [27]. This was further substantiated by the identity of the positions of several signals in the NMR spectra of these two compounds. The IR spectrum of compound **9b** (R' = Et) revealed the presence of an NH group, a urethane grouping and of a C=N bond. The site of attachment of the EtOOC group was deduced from the comparatively low wave number (1690 cm^{-1}) of the urethane band which would be incompatible with the presence of the $-N=C-N-COOR$ grouping required if the EtOOC group were attached to N-3 rather than to N-4 as shown. This conclusion was supported by an important difference between the ^{1}H-NMR spectra (in DMSO-d_6) of compounds **9a** (R' = Et) and **9b** (R' = Et): while in the first case the coupling of the C-2 proton with a vicinal NH proton could be observed, there was no such coupling in the second case. Final proof of structure for the ring expansion products came from the X-ray structure determination of compound **9d** (R' = Et) (see below).

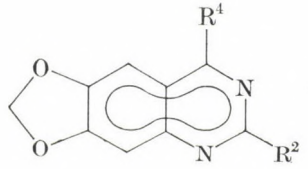
The benzotriazepine **9b** (R' = Et) remained completely unchanged, according to TLC and IR spectra, when irradiated 1.25 times the reaction time necessary for complete conversion of **8b**.



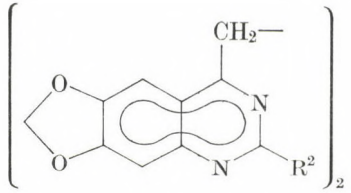
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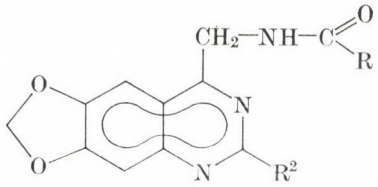
9*) **)



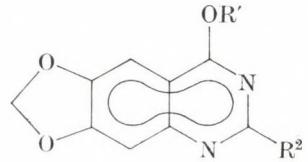
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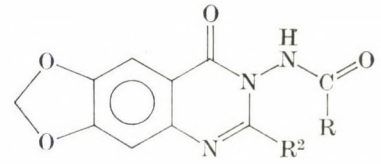
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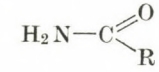
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13**)



14

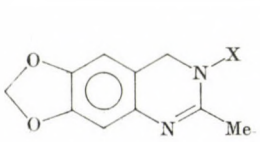


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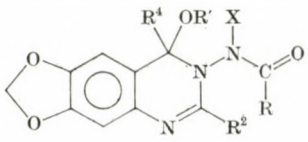
8—15

	R^2	R^4	R
a	H	H	OEt
b	Me	H	OEt
c	Me	H	OCH_2Ph
d	Me	H	Ph
e	H	Me	OEt
f	Me	Me	OEt
g	Me	Me	Ph

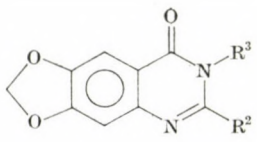
* Potentially tautomeric compound
** R'O is the alkoxy group corresponding to the solvent alcohol



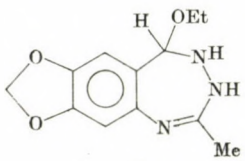
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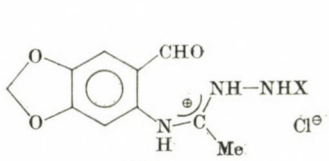
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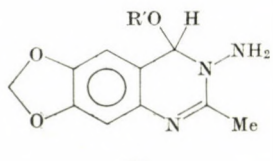
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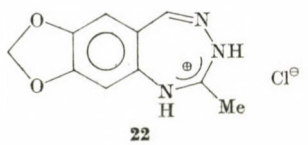
19



20



21



22

The hydrochlorides of the benzotriazepines **9b** (R' = $PhCH_2$) and **9c** (R' = Et) were — in contrast to the free bases **9b** (R' = $PhCH_2$, Et) and the hydrochloride of the latter — smoothly reduced in EtOH solution at room temperature in the presence of a Pd/C catalyst to yield, under ring contraction, the hydrochlorides [27] of **16**, X = NHCOOEt and X = NH_2, respectively. These reductive ring contractions may be rationalized by assuming the intermediacy of **9b**·HCl (R' = H), **20** (X = COOEt), **8b**·HCl and/or its type **17**·HCl adducts (R^2 = Me, R^4 = X = H, R = Et, R' = H, Et) which are known [27] to be reduced under the conditions applied to **16**·HCl (X = NHCOOEt), and of **19**·HCl, **22**, **20** (X = H) and **21**·HCl, respectively.

9d (R' = Et) proved insensitive to methanolic HCl at room temperature but was converted under ring contraction into the hydrochloride of the MeOH adduct **17** (R^2 = R' = Me, R^4 = X = H, R = Ph) [27] of **8d** when refluxed with the above reagent.

Mass spectra

A general feature of the mass spectra of the compounds **9** is the ready elimination of the R'O· radical from the molecular ion with the formation of abundant ions (base peaks in the spectra of **9a** and **9b**, R' = Et). This process initiates the predominant fragmentation modes in the case of compounds **9a** (R' = Et) and **9b** (R' = Et, $PhCH_2$) (Fig. 1, where all decompositions given

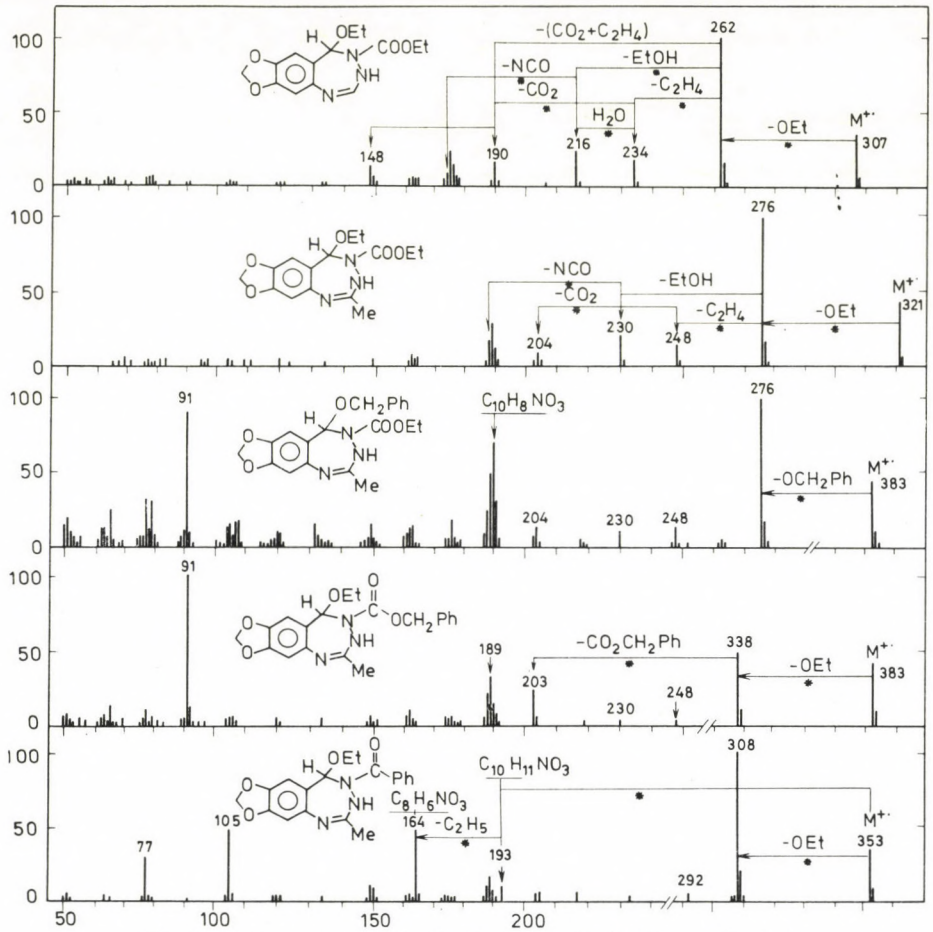
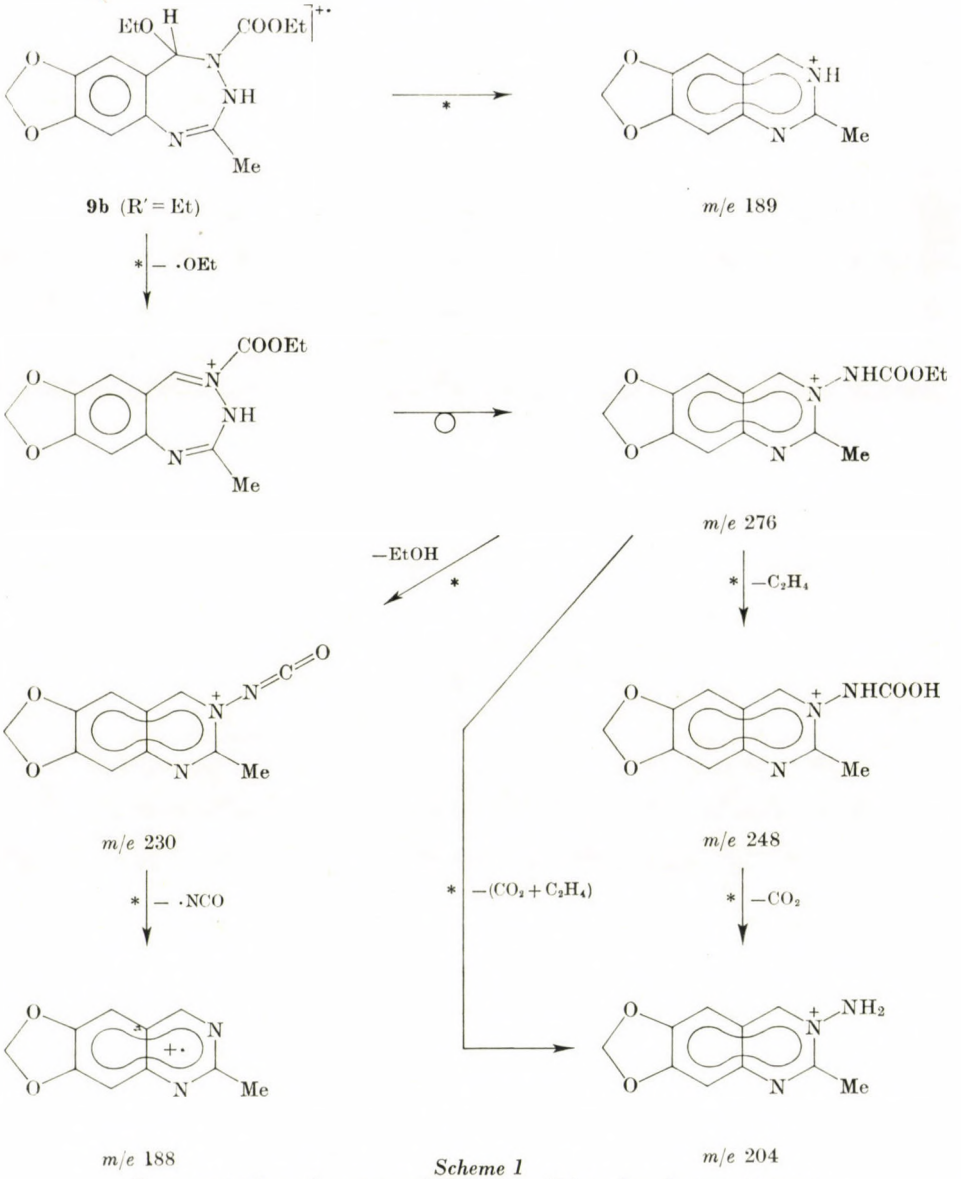


Fig. 1. Mass spectra of the the phototransformation products **9**

are supported by metastable ion data). In the case of **9b** (R' = Et) elemental compositions of important ions have been determined by exact mass measurements, and possible structures are suggested in Scheme 1. The ring contraction to a quinazoline structure assumed for the $[M - OEt]^+$ ion (*m/e* 276) is based on a comparison with the fragmentation of the $[M-CH_2COCH_3]^+$ ion (*m/e* 276) in the spectrum of **28** (R^2 = Me) [28]. The decompositions associated with metastable ions of the *m/e* 276 ions in the two compounds give rise to identical DADI spectra suggesting the same structure for these ions. In the MS of **9b** (R' = $PhCH_2$) an alternative fragmentation mode of the molecular ion gives rise to the formation of the abundant *m/e* 190 ion whose elemental composition corresponds to $C_{10}H_8NO_3$. Metastable defocussing has indicated the molecular ion as well as *m/e* 264 (3%) and *m/e* 281 (< 1%) as precursors. This suggests that the *m/e* 190 ion is generated by losses — both

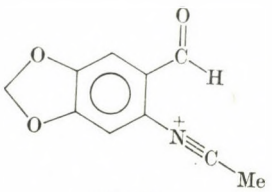


Scheme 1

Fragmentation of compound **9b** (R' = Et) under electron impact

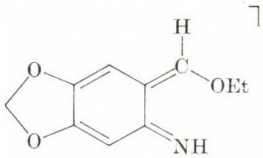
stepwise and concerted — of $Ph\dot{C}H_2$ and HN=N—COOEt from the molecular ion. A possible structure for the *m/e* 190 ion is shown below.

The MS of **9c** (R' = Et) exhibits, in addition to the ions corresponding to those of Scheme 1, an abundant ion at *m/e* 203 formed by loss of $\cdot CO_2CH_2Ph$ from the $[M-OEt]^+$ ion. This latter ion is also the precursor of the tropylium ion which forms the base peak of the spectrum.

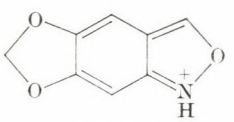


m/e 190

The molecular ion of **9d** (R' = Et) offers an additional fragmentation path giving rise to the ions at *m/e* 193 and 164: $C_{10}H_{11}NO_3$ and $C_8H_6NO_3$, respectively. Metastable defocussing has revealed the sequence $M \rightarrow 193 \rightarrow$ $\rightarrow 164$. Possible structures for the two ions may be **a** and **b**, respectively.

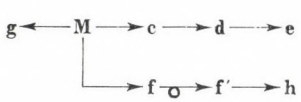


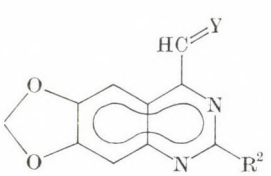
a (*m/e* 193)



b (*m/e* 164)

The mass spectra of the photoisomers **12e** and **12f** are shown in Fig. 2. Metastable peaks indicate the decomposition modes (identical for both compounds) shown in Scheme 2. This fragmentation scheme can be rationalized by assuming the structures **c**—**h**.



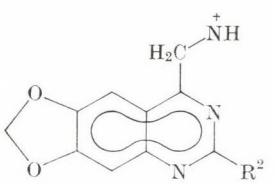


c: Y = $\overset{+}{N}$H—COOEt

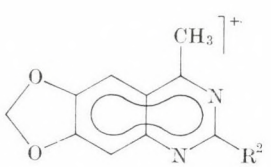
d: Y = $\overset{+}{N}$H—COOH

e: Y = $\overset{+}{N}$=C=O

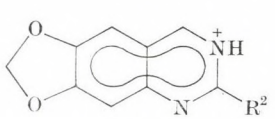
f': Y = $\overset{+}{N}H_2$



f



g



h

Scheme 2
Fragmentation of compounds **12e** and **12f** under electron impact

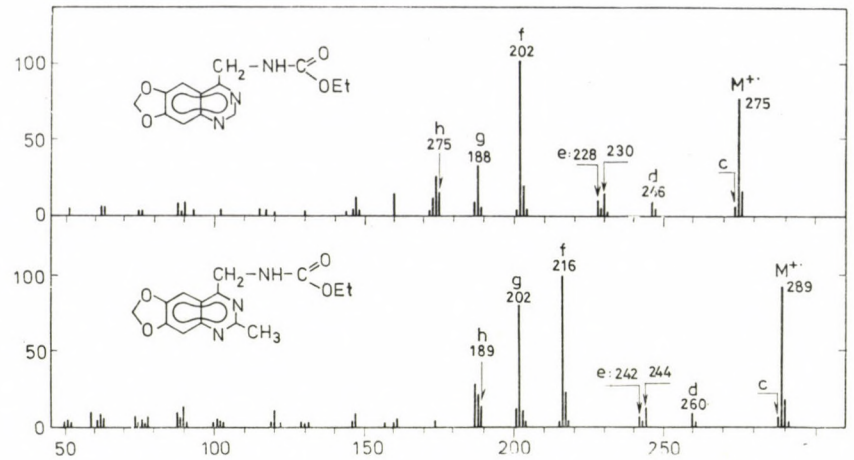


Fig. 2. Mass spectra of the photoisomers **12e** and **12f**

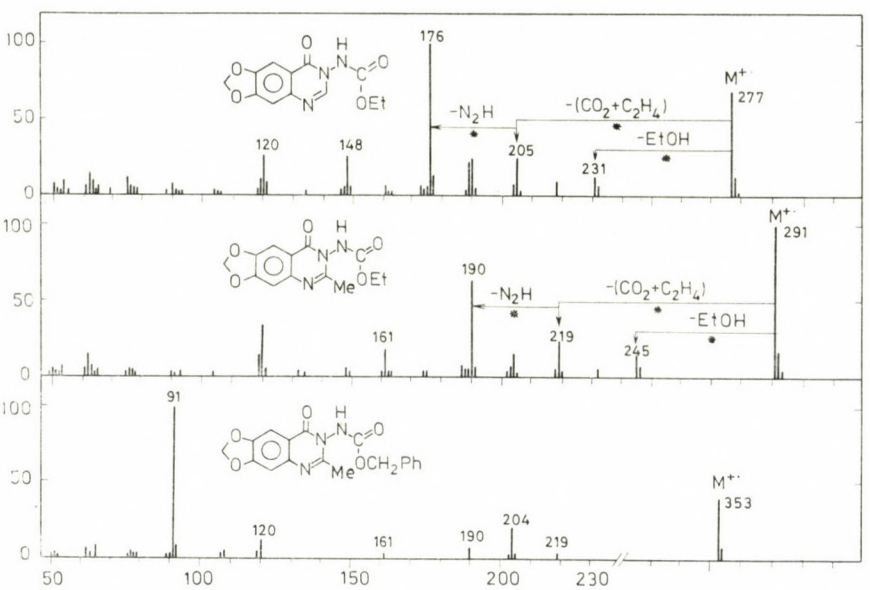
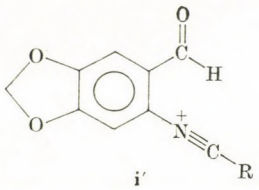
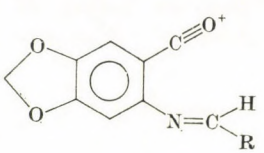


Fig. 3 Mass spectra of the phototransformation products **14a–c**

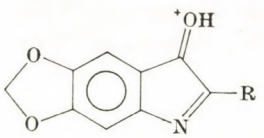
The mass spectra of the phototransformation products **14a—c** are shown in Fig. 3 together with the predominant fragmentation routes. Characteristic features of the spectra of **14a** and **14b** are the abundant peaks at *m/e* 176 ($C_9H_6NO_3$) and at *m/e* 190 ($C_{10}H_8NO_3$), respectively. Application of the metastable defocussing technique has revealed their precursors to be *m/e* 205 and *m/e* 219, respectively (loss of $\cdot N_2H$). The alternative structures **i'**, **i''** or **i'''**



i'



i''



i'''

(R = H, Me)

are suggested for these ions (*cf.* the *m/e* 190 ion in the spectrum of **9b**, R' = = $PhCH_2$). In the case of **14a**, **i** is further decomposed by two successive losses of 28 mass units (CO and CH_2N, respectively) yielding *m/e* 148 and *m/e* 120. In the spectrum of **14b** *m/e* 190 eliminates CHO followed by MeCN yielding *m/e* 161 and *m/e* 120. The spectrum of **14c** exhibits the tropylium ion *m/e* 91 as the base peak; the fragment ion at *m/e* 204 corresponds to $[M-NCO_2CH_2Ph]^+\cdot$.

X-Ray molecular structure determination of the ring expansion product 9d (R' = Et)

In order to grow suitable crystals, compound **9d** (R' = Et) had to be recrystallized from a methanol–benzene mixture, the former component, apparently, containing traces of water, since the compound crystallized with one molecule each of water and methanol.

Bond distances and angles for the non-hydrogen atoms are given in Table V. A diagram of the molecule indicating the numbering applied is shown in Fig. 4. The water and the methanol molecules are linked to the seven-membered ring by hydrogen bonding (N1. . . .O6: 3.12; H(N1). . . .O6: 2.03 and N2. . . .O5: 3.08 Å). A double bond is found between atoms N2 and C9 (1.28 Å)

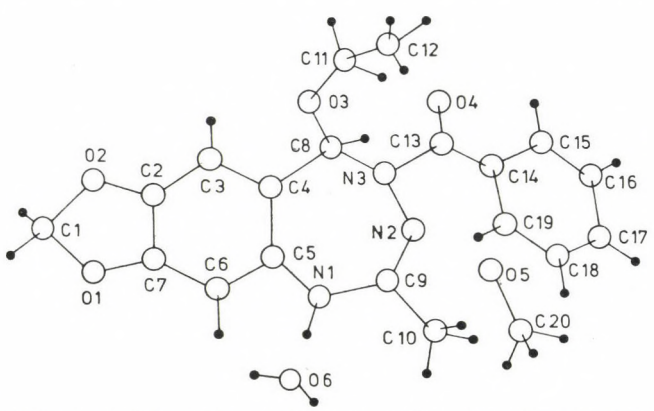


Fig. 4. Diagram of the molecule **9d** (R' = Et) + MeOH + H_2O indicating the numbering applied

in the seven-membered ring. Thus, the tautomeric structure of the compound is different in the crystalline state from that in solution where, as shown by the UV spectra (Table III) the double bond is between atoms N1 and C9, and the hydrogen is attached to N2 rather than to N1 (notations of Fig. 4).

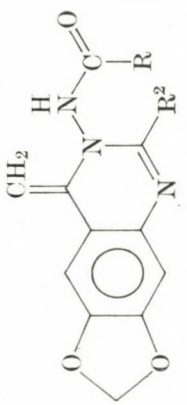
Least squares plane: The atoms C1, O1, O2, C2, C3, C4, C5, C6, C7, C8, N1 and C9 form a plane with an average deviation of 0.03 Å. Atoms N2 and N3 are positioned from this plane at a distance of 0.90 and 0.48 Å, respectively.

Rationale of formation of the phototransformation products

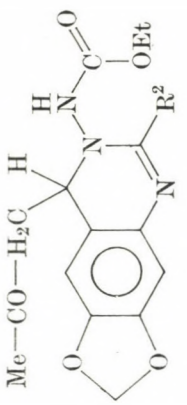
As shown by their NMR spectra, the quinazolinioamidates **8** do exist in CD_3OD solutions as equilibrium mixtures of the amidate forms themselves and their CD_3OD adducts **17** (R' = CD_3, X = D). The positions of the equilibria are dependent on the nature of the substituents R^2, R^4 and R; in particular, replacement of hydrogen attached to C-4 by methyl stabilizes the amidate with respect to the adduct forms, probably as a result of the combined electronic and steric effects of the methyl group [27]. Essentially the same situation may be assumed to prevail in such solvents as ethanol and benzyl alcohol, although the increasing bulk of the substituent R' will tend to destabilize the adducts **17** (R' = Et and $PhCH_2$, X = H). In an attempt to rationalize the formation of the phototransformation products **9**—**15**, the presence of both the amidate (**8**) and the adduct forms **17** in the reaction mixtures has to be taken into account.

The ring expansion products **9** are thought to arise from the excited amidate forms through the intermediacy of the condensed diaziridines **23** which, upon nucleophilic attack of one molecule of the solvent at the original C-4 atom, are converted into the end-products. Ring closure in the alternative direction, which would lead to the isomeric diaziridines **24**, apparently does not take place because the aromaticity of both six-membered rings would thereby be destroyed. In the case of the amidates **8e**—**g**, the 4-methyl group apparently either prevents formation of the type **23** diaziridines or causes them to revert rapidly to the starting material (*cf.* the effect of the 4-methyl group on the formation of dimers and adducts of the amidates **8**, see above and Ref. [27]), or renders nucleophilic attack of the solvent more difficult; as a result, no ring expansion products are obtained from **8e**—**g**.

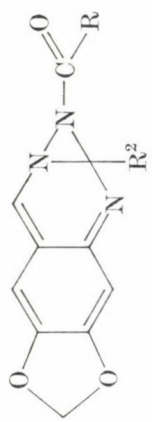
The parent quinazolines (**10**), too, are transformation products of the free amidates **8**; they may be derived by acylnitrene eliminations either from the excited amidates, or from the excited diaziridines **23**. The acylnitrenes are recovered in the form of the corresponding amides **15**, *i.e.* ethyl carbamate from **8b** and **8f**, benzyl carbamate from **8c** and benzamide from **8d** and **8g**. (For an alternative mode of formation of the amides, see below.) The formation



25



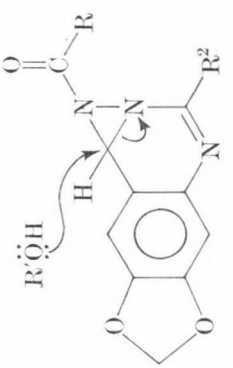
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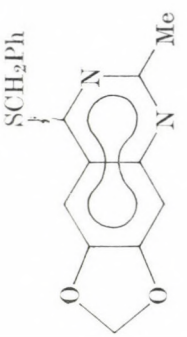
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27



23



26

of the type **15** carbamates as the sole transformation products of the acylnitrenes is not surprising, since no thermal or photo-Curtius rearrangements have been observed with azidoformates, either [33, 34]. Photolysis of alkanoyl and aroyl azides, on the other hand, is known to yield isocyanates as a result of photo-Curtius rearrangements [33, 34]; a search for products such as ethyl *N*-phenylcarbamate and carbanilide, eventually formed through the intermediacy of phenyl isocyanate has therefore been undertaken in the mixtures resulting from irradiation of compounds **8d** and **8g** in EtOH. However, all attempts to isolate such products failed. The photolyses of **8d** and **8g** are, therefore, analogous to that of *N*-(trimethylammonio)-dodecanamidate [35] (leading through triplet dodecanoylnitrene to dodecanamide) rather than to the photolyses of alkanoyl and aroyl azides.

The formation of the type **11** products from **8e—g** may be explained by assuming that the intermediate acylnitrenes are capable of abstracting hydrogen atoms from the 4-methyl groups of the quinazoline fragments **10** (*cf.* Ref. [36]). Subsequent recombination of the resulting 4-quinazolinylmethyl radicals would then lead to the products. There are indications [28] that the quinazolinylmethyl radicals might, alternatively, be directly formed by photo-induced homolysis of the N—N bond of the type **25** tautomers (see below) of the amidates.

The formation of the type **12** photoisomerization products* is without precedence in the photochemistry of heterocyclic ammonioamidates, and there is only a single comparable reaction known in the related *N*-oxide series, *viz.* photoisomerization in the vapour phase of 2-picoline-*N*-oxide into 2-pyridinemethanol, induced by irradiation with 3261 Å light [30]. Two mechanisms may be considered in order to explain the formation of the type **12** products: (*a*) photolysis of the N—N bond of the starting compound **8**, and insertion of the resulting excited singlet nitrene into a C—H bond of the 4-methyl group of the quinazoline fragment **10**; (*b*) tautomerization of the starting compound and subsequent [1, 3] sigmatropic shift of the ethoxycarbonylamino group of the resulting type **25** (R = OEt) tautomers. In connection with mechanism (*b*) it should be pointed out that the hydrogen atoms of the 4-methyl group of **8e** and **f** are rapidly exchanged in perdeuteriomethanol solution at room temperature [27] and that UV irradiation is known to be capable of shifting tautomeric equilibria (see Ref's [31] and [32]). The second step of mechanism (*b*) may, in principle, take place both as a dark reaction and a light-induced process, depending on whether inversion takes place at the migrating nitrogen atom or not. Experiments to test these various mechanisms are in progress. In the light of our preliminary observation that **12f** becomes the main product if irradiation of **8f** is performed in acetone, mechanism (*a*), however, appears to be less likely.

* The isomerization does not take place in the dark, at least not at room temperature.

The 4-ethoxyquinazolines **13** (R^2 = H, Me; R' = Et) are thought to arise through Type II processes from the adducts **17** (R' = Et, X = H). The necessary condition for such processes is that R^4 is hydrogen; accordingly, no type **13** products are obtained from **8e—g**. The non-heterocyclic by--products of these Type II processes are the imidic acid tautomers of the amides **15** which rapidly tautomerize into the amides themselves. Support for the suggested mode of formation of the type **13** products comes from the observation that compound **16** (X = NHCOOEt) is similarly photolyzed to yield, among other products, **10b** and ethyl carbamate.

The mechanism of formation of the 4-ethoxyquinazolines **13** is completely different from that of the 4-ethoxyisoquinolines obtained by Japanese authors as one type of photoproducts on irradiation of *N*-(2-isoquinolinio)-amidates [18]; and the compounds **13** are the first photolysis products of heterocyclic ammonioamidates in general which do arise through adducts of the amidates with nucleophiles.

In contrast to the related compound **26** whose photolysis furnishes the thione **27** (X = H) [26], the compounds **13** appear to be photostable since no type **18** (R^3 = H) products could be detected by TLC in the mixtures obtained by irradiation of compounds **8a—d**.

It appears, therefore, rather unlikely that the pathway of formation of the compounds **14a—c** is a photochemically induced homolysis of the Et—O bond of the type **17** (R^4 = H, R' = OEt, X = H) ethanol adducts of the amidates **8a—c**, followed by loss of the hydrogen atom initially attached to C-4 {which would be analogous to the probable pathway of formation of compound **27** (X = NHCOOEt) during irradiation of compound **8b** in α-toluenethiol–$CHCl_3$ mixtures [26]}. Alternatively, formation of the type **14** compounds could be assumed to involve the intermediacy of the type **17** (R^4 = R' = X = H) hydrates of the starting amidates **8a—c** (formed as a result of the presence of traces of water), and the photooxidation of the latter by traces of oxygen (or perhaps even their dehydrogenation by acylnitrenes formed as a result of concurrent processes, see above). Some support for this assumption came from the significant increase in the yields of **14a** and **14b** when the amidates **8a** and **8b**, respectively, were irradiated in non-anhydrous solvents and/or in the presence of oxygen.

Experimental

IR and UV spectra were obtained on a Spectromom 2000 IR spectrometer (Hungarian Optical Works, Budapest), and on Carl Zeiss (Jena, GDR) Type Specord, Unicam Type SP 700 and MOM 201 (Hungarian Optical Works) UV spectrometers, respectively. The NMR spectra were recorded at 60 MHz on a Perkin-Elmer R 12 spectrometer. The mass spectra were obtained on a Varian MAT 311A (Grant No. 511—3809 from the Danish Science Research Council) by electron impact (70 eV) and using the direct insertion system.

N-(2,4-Dimethyl-6,7-methylenedioxy-3-quinazolinio)-benzamidate (8g)

This compound was made similarly to its analogues **8e** and **f**, described earlier [27]. Yields, physical and microanalytical data of the intermediates and the final product were as follows.

4,5-Methylenedioxy-6-nitroacetophenone benzoylhydrazone, 79.5% yield, m.p. 181 °C (from EtOH).

$C_{16}H_{13}N_3O_5$ (327.28). Calcd. C 58.71; H 4.00; N 12.84. Found C 58.73; H 4.26; N 13.04%.

6-Amino-4,5-methylenedioxyacetophenone benzoylhydrazone, 40% yield, m.p. 212 °C (from EtOH).

$C_{16}H_{15}N_3O_3$ (297.30). Calcd. C 64.64; H 5.01; N 14.13. Found C 64.62; H 5.19; N 13.88%.

6-Acetamino-4,5-methylenedioxyacetophenone benzoylhydrazone, 47% yield, m.p. 284—286 °C (from BuOH).

$C_{18}H_{17}N_3O_4$ (339.34). Calcd. C 63.71; H 5.05; N 12.38. Found C 63.46; H 5.29; N 12.54%.

Compound **8g**, 64% yield, colourless needles, m.p. 196 °C.

$C_{18}H_{15}N_3O_3$ (321.32). Calcd. C 67.28; H 4.70; N 13.08. Found C 66.58; H 4.87, N 13.16%.

IR (KBr): highest band in the double bond region 1590 cm^{-1} (sh's at 1630 and 1610) which precludes the presence of appreciable amounts of the dimeric form, *cf.* Ref. [27].

MS (170 °C): *m/e* 321 (13%, $M^{+\cdot}$), *m/e* 306 (100%, $[M-Me]^+$), *m/e* 244 (3%, $[M-Ph]^+$), *m/e* 218 (4%, $[M-PhCN]^{+\cdot}$), *m/e* 217 (4%), *m/e* 203 (14%), *m/e* 202 (28%), *me* 188 (5%), *m/e* 187 (10%), *m/e* 175 (6%), *m/e* 121 (6%), *m/e* 120 (6%), *m/e* 105 (20%, $PhCO^+$), *m/e* 103 (7%), *m/e* 77 (23%, Ph^+).

Irradiation of the compounds 8* and isolation of the products

The starting compounds were dissolved, under gentle heating, in the selected solvents, and the resulting colourless solutions were irradiated with a high-pressure mercury immersion lamp (Philips, HPK-125) through pyrex at room temperature under argon or oxygen until, according to TLC, the starting compound was completely used up (Table IV). If any crystalline product was formed in the course of the irradiation, it was filtered off at this point (Fraction *A*). Silica (Kieselgel 60, Merck, size 0.063—0.200 mm) (2.0 g) was added to the clear brown photolysis mixtures or filtrates, and the solvents were evaporated in vacuum. The residues were transferred onto columns (diameter 1.5—2.0 cm), prefilled with silica (50 g) which has been introduced in the form of suspensions in benzene–acetone (4 : 3), and chromatographed with the same solvent. 5—10 ml fractions were collected and, on the basis of their TLC's, combined into 5—8 main fractions. The latter were evaporated to dryness in vacuum, and the residues were worked up by recrystallization (α), preparative TLC (β) or sublimation in vacuum (γ). 20×20 cm plates, coated with 1.5 mm layers of Kieselgel $PF_{254+366}$ were used for TLC of the product mixtures (0.15 g or less). Those products which were formed in trace amounts were identified on the basis of the identity of their R_f values and, wherever possible, their IR spectra, with those of authentic samples. The following compounds, listed in decreasing order of their R_f values in benzene–acetone (4 : 3), were obtained.

Run No. 1

14a (α, from MeOH, and β, solvent: benzene–EtOAc, 1 : 1), 89 mg (5.6%), m.p. 224—225 °C (from MeOH).

$C_{12}H_{11}N_3O_5$ (277.24). Calcd. C 51.99; H 3.99; N 15.16. Found C 52.06; H 4.08; N 14.99%.

IR (KBr): 3180 (NH), 1745 (carbamate), 1660 (ring carbonyl).

MS (150 °C): Fig. 3.

13a (R' = Et) (β, solvent: benzene–EtOAc, 1 : 1), traces.

9a (R' = Et) (α, from benzene–light petroleum), 0.62 g (35%), m.p. 123—124 °C.

$C_{14}H_{17}N_3O_5$ (307.30). Calcd. N 13.68. Found 13.39%.

IR (KBr): 3400—2800 (NH), 1690 (carbamate), 1650 (C=N). 1235, 1070, 1030 (ester + methylenedioxy group).

MS (120 °C): Fig. 1.

* The starting compounds actually exist as mixtures of variable compositions of the amidate forms **8** and their dimers, *cf.* Ref. [27].

In addition, 95 mg (5.6%) of compound **28** (R^2 = H) (α, from MeOH), m.p. 193—195 °C, was obtained which is apparently an artefact formed in the course of the column chromatography work-up of the reaction mixture from unreacted **8a** with acetone.

$C_{15}H_{17}N_3O_5$ (319.31). Calcd. C 56.42; H 5.37; N 13.16. Found C 56.17; H 5.31; N 13.39%. For spectral data and the proof of structure, see Ref. [28].

Run No. 2

14a (α, from MeOH, and β, solvent benzene–acetone, 1 : 1), 203 mg (13.4%). No attempt was made to isolate further products.

Run No. 3

15b (γ; bath temperature 100—110 °C, 15—20 torr), 0.12—0.15 g (25—30%), m.p. 45—48 °C, lit. [41] m.p. 49 °C.

14b (β, solvent: benzene–MeOH, 10 : 1), traces.

13b (R' = Et) (β, solvent: benzene–MeOH, 10 : 1), 50 mg (4%), m.p. 124—126 °C.

MS: see below.

9b (R' = Et) (α, from benzene–ether, and β, solvent benzene–acetone, 1 : 1), 455 mg (26%), m.p. 174—175 °C (from benzene).

$C_{15}H_{19}N_3O_5$ (321.32). Calcd. C 56.07; H 5.96; N 13.08. Found C 55.85; H 6.02; N 13.05%.

IR (KBr): 3335 (NH), 1690 (carbamate), 1640 (C=N), 1485 (NH), 1240, 1080, 1035 (ester + methylenedioxy group).

MS (120 °C): Fig. 1.

HCl salt, m.p. 215 °C (from MeOH–Et_2O).

IR (KBr): 3400 and 2750, b (⊕NH), 1730 (carbamate), 1630, b (C=N), 1250, 1100, 1040 (ester + methylenedioxy group). The MS was identical with that of the free base.

10b (α, from benzene–light petroleum, and β, solvent: benzene–acetone, 1 : 1), 0.41 g (40%), m.p. and lit. [27] m.p. 180 °C.

Run No. 4

14b (β, solvent: ether), 22 mg (4.15%). No attempt was made to isolate further products.

Run No. 5

14b (β, solvent: benzene–EtOAc, 5 : 1), 41 mg (2.6%), m.p. 153—155 °C (from aq MeOH).

9b (R' = Et) (β, solvent: benzene–EtOAc, 1 : 1), 160 mg (9.2%), m.p. 165—168 °C (crude product).

No traces of **10b** could be detected by TLC.

Runs Nos 6—7

14b (β, solvent: ether, and benzene–EtOAc, 1 : 1, respectively), 32 mg (6%) and 130 mg (8.2%), respectively. No attempts were made to isolate further products.

Run No. 8

9b (R' = $PhCH_2$) (β, solvent: benzene–acetone, 1 : 1), 82 mg (4%), m.p. 90—93 °C (from benzene–ether).

MS (130 °C): Fig. 1.

10b (β, solvent: benzene–acetone, 1 : 1), 118 mg (11.5%), m.p. 176—179 °C (from benzene–light petroleum).

Run No. 9

13c (R' = Et) (= **13b**, R' = Et) (β, solvent: benzene–MeOH, 10 : 1), 12 mg (1.1%,) m.p. 110 °C (crude product).

15c (β, solvent: benzene–MeOH, 10 : 1), 155 mg (23%), m.p. 85 °C (from MeOH), lit. [37] m.p. 86 °C.

14c (β, solvent: benzene– MeOH, 10 : 1), 22 mg (1.5%), m.p. 197 °C (from MeOH).

IR (KBr): 3170 (NH), 1730 (carbamate), 1650 cm^{-1} (ring carbonyl).

MS (150 °C): Fig. 3.

9c (R' = Et) (α, from benzene–ether, and β, solvent benzene–acetone, 1 : 1), 309 mg (21%), m.p. 105—107 °C.

$C_{20}H_{21}N_3O_5$ (338.31). Calcd. C 62.66; H 5.52; N 10.96. Found C 62.71; H 5.58; N 10.87%.

IR (KBr): 3380 (NH), 1700 (carbamate), 1650 (C=N), 1495 (NH), 1240, 1080, 1040 (ester + methylenedioxy group).

MS (155 °C): Fig. 1.

HCl salt: m.p. 166 °C (from MeOH–Et_2O).

IR (KBr): 3400 and 2750, b (NH), 1735 (carbamate), 1630 (C=N), 1250, 1140, 1100 and 1040 (ester + methylenedioxy group). The MS was identical with that of the free base.

10c (= **10b**) (β, solvent: benzene–acetone, 1 : 1), 280 mg (33.4%), m.p. 178—179 °C.

Run No. 10

13d (R' = Et) (= **13b**, R' = Et) (β, solvent: benzene–MeOH, 10 : 2), 103 mg (9%), m.p. 127 °C (from EtOH).

9d (R' = Et) (α, from benzene), 625 mg (36%), m.p. 197 °C (from benzene).

$C_{19}H_{19}N_3O_4$ (353.30). Calcd. C 64.57; H 5.30; N 11.89. Found C 64.48; H 5.46; N 11.79%.

MS (190 °C): Fig. 1.

10d (= **10b**) (β, solvent: benzene–EtOAc, 1 : 1), 65 mg (7%), m.p. 175—178 °C (crude).

15d (β, solvent: benzene–EtOAc, 1 : 1), 211 mg (23%), m.p. 128—130 °C, lit. m.p. 130 °C.

Run No. 11

Fraction **A**: **11e**, 75 mg (11%), m.p. > 300 °C.

$C_{20}H_{14}N_4O_4$ (374.34). Calcd. C 64.17; H 3.77; N 14.97. Found C 63.91; H 3.80; N 14.75%.

MS (190 °C): *m/e* 374 (92%, $M^{+\cdot}$), *m/e* 373 (12%), *m/e* 359 (18%), *m/e* 345 (5%), *m/e* 344 (9%), *m/e* 275 (11%), *m/e* 201 (100%), *m/e* 188 (45%), *m/e* 187.5 (3.5%), *m/e* 187 (26%, M^{++}).

12e (α, from MeOH), 67 mg (6.7), m.p. 178—180 °C.

$C_{13}H_{13}N_3O_4$ (257.27), Calcd. C 56.73; H 4.76; N 15.27. Found C 56.24; H 4.75; N 15.24%.

IR (KBr): 3400 (NH), 1725, 1210,1035 cm^{-1} (carbamate).

MS (100 °C): Fig. 2.

10e (α, from MeOH), 0.158 g (23%), m.p. 165 °C.

$C_{10}H_8N_2O_2$ (188.18). Calcd. C 63.88; H 4.29; N 14.89. Found C 63.55; H 4.39; N 15.29.

MS (100 °C): *m/e* 188 (100%, $M^{+\cdot}$), *m/e* 187 (27%), *m/e* 173 (4%), *m/e* 160 (3%), *m/e* 143 (2%), *m/e* 130 (5%), *m/e* 120 (6%).

Run No. 12

Fraction **A**: **11f**, 200 mg (29%), m. p. > 300 °C.

$C_{22}H_{18}N_4O_4$ (402.41). Calcd. N 13.92. Found N 13.88%.

MS (185 °C): *m/e* 402 (85%, $M^{+\cdot}$), *m/e* 401 (10%), *m/e* 387 (5%), *m/e* 373 (4%), *m/e* 372 (3%), *m/e* 215 (100%), *m/e* 202 (12%), *m/e* 201.5 (4%), *m/e* 201 (14%, M^{++}).

15f (= **15b**) (γ, bath temperature 100—110 °C, 15—20 torr), 210 mg (45%), m.p. 46—48 °C, lit. [41] m.p. 49 °C.

12f (α, from MeOH, and β, solvent: benzene–acetone, 1 : 1), 66 mg (5%), m. p. 168—170 °C.

$C_{14}H_{15}N_3O_4$ (289.28). Calcd. C 58.11; H 5.23; N 14.53. Found C 58.36; H 5.38; N 14.19%.

IR (KBr): 3420 (NH), 1730, 1225, 1035 cm^{-1} (carbamate).

MS (100 °C): Fig. 2.

10f (α, from MeOH, and β, solvent: benzene–acetone, 1 : 1), 455 mg (43%), m.p. 185–186 °C (from MeOH).

$C_{11}H_{10}N_2O_2$ (202.21). Calcd. C 65.33; H 4.98; N 13.86. Found C 65.20; H 4.86; N 13.77%.

Run No. 13

Fraction **A**: **11g** (= **11f**), 10 mg (1%), m.p. > 300 °C.
15g (= **15d**) (α, from benzene), 490 mg (86.5%), m. p. 128–130 °C.
10g (= **10f**) (α, from MeOH), 547 mg (57%), m.p. 185–186 °C.

X-Ray molecular structure determination of the ring expansion product 9d (R' = Et)

Crystal data: $C_{19}H_{19}O_4N_3 \cdot CH_3OH \cdot H_2$, formula wt. 403.44, $a = 8.989(3)$, $b = 11.886(4)$, $c = 19.161(4)$ Å, $\beta = 91.28(2)°$, $V = 2046.71$ Å^3, $Z = 4$, $D_m = 1.302$, $D_x = 1.309$ gcm^{-3}, $F(000) = 856$, monoclinic space group $P2_1/c$, μ for Mo-K_α($\lambda = 0.7107$ Å) 0.55 cm^{-1}. Intensity data were collected on a Syntex $P2_1$ automatic four-circle diffractometer with Mo-K_α radiation. The structure was solved by direct methods. The water and the methanol molecule, as well as the proton attached to the N1 atom were located in difference-Fourier maps. The hydrogen atom of the methanol —OH group has not been revealed. Other hydrogen atoms were introduced at the beginning of the refinement. The C14—. . .—C19 phenyl group was converted into a regular hexagon with C—C and C—H bond lengths of 1.395 and 1.08 Å, respectively. This segment together with the methyl group has been treated as rigid groups so far. The structure was refined in isotropic mode to an R-value of 0.089 for the 1607 strongest reflexions out of the 1905 observed ones. The refinement was performed for "blocked" segments of the molecule using the program SHEL-X written by SHELDRICK [29]. Further refinement is in progress.

Photolysis of compound 16 (X = NHCOOEt)

A solution of the title compound [27] (0.30 g) in EtOH (150 ml) was irradiated under the conditions described for the irradiation of the compounds **8a-g**. The starting compound was used up after 12 hrs. The mixture was evaporated to dryness and the residue worked up by preparative TLC (20×20 cm plates; adsorbent: Kieselgel $PF_{254+366}$, Merck; solvent: benzene–MeOH, 2 : 1) to yield 8 mg (4.5%) of **10b**, identical, according to the IR spectra, with an authentic product.

Reactions of the benzotriazepines 9

(*a*) A methanolic (10 ml) solution of **9b** (R' = $PhCH_2$) (53 mg; 0.14 mmole), which had been previously acidified with methanolic HCl, was catalytically reduced at room temperature and ordinary pressure in the presence of a 8% Pd/C catalyst. The catalyst was filtered off, the filtrate evaporated to dryness, the residue was dissolved in water, and the solution made alkaline with 10% aq. NaOH. The product was extracted with $CHCl_3$ to yield, after the usual work-up, an oil which, when triturated with a few drops of benzene, turned into 20 mg (53%) of a colourless powder, m.p. 143 °C; this was found identical with compound **16** (X = NHCOOEt), lit. [27] m.p. 145 °C.

(*b*) The methanolic (10–15 ml) solution of **9c** (R' = Et) (65 mg; 0.17 mmole), which had been acidified with methanolic HCl, was catalytically reduced as described above. The catalyst was filtered off, and part of the solvent evaporated. Ether was added to precipitate a crude product (0.40 g) which was recrystallized from methanol–ether to yield 0.25 g (63%) of the hydrochloride of **16** (X = NH_2), m.p. 268–270 °C, lit. [27] m. p. 273–274 °C.

(*c*) The anhydrous ethanolic (10 ml) solution of **9d** (R' = Et) (0.10 g; 0.28 mmole), which had been previously acidified with methanolic HCl, was refluxed for 30 min. The resulting red solution was evaporated to dryness in vacuum and the residue recrystallized from

MeOH–ether to yield 0.08 g (83%) of the hydrochloride of compound **17** (R^2 = R' = Me; R^4 = H; R = Ph; X = H), m.p. 238–240 °C, lit. [27] m. p. 244 °C (d.).

Reduction of the dimer of compound 8a (*cf.* Ref. [27])

A solution of the title compound (1.0 g; 3.8 mmoles) in EtOH (100 ml) was refluxed for 5 hrs in the presence of Raney-Ni (10 g). The catalyst was filtered off and the greenish brown filtrate evaporated to dryness. The residue (0.7 g) was dissolved in hot EtOH (10 ml). On cooling 50 mg (5%) of **16** (X = NHCOOEt, with H replacing the 2-Me group), m.p. 165–167 °C (from EtOH) separated.

IR (KBr): 1730 cm^{-1} (carbamate).

NMR: see Table II.

The ethanolic filtrate of the above product was evaporated to dryness, and the residue was triturated with ether (5 ml) to yield 0.4 g (58%) of compound **10a**, m. p. 170–171 °C (from EtOH).

$C_9H_6N_2O_2$ (174.16). Calcd. C 62.06; H 3.47; N 16.09. Found C 61.59; H 3.43; N 16.04%.

MS (100 °C): *m/e* 174 (100%, $M^{+\cdot}$), *m/e* 173 (75%), *m/e* 147 (3%), *m/e* 143 (3%), *m/e* 120 (15%).

6-Nitropiperonylamide

A mixture of 6-nitropiperonylic acid [38] (42.2 g; 0.20 mole), anhydrous dioxane (150 ml) and $SOCl_2$ (45 ml; 0.60 mole) was refluxed for 1 hr and then evaporated to dryness in vacuum. The oily residue was dissolved in dioxane (80 ml), and conc. aq. NH_4OH (420 ml) was added under stirring and ice-cooling; the temperature was throughout maintained below 10 °C. The mixture was allowed to warm up to room temperature under stirring, to yield 36.1 g (89%) of the title compound, m.p. 202–203 °C (from EtOH).

$C_8H_6N_2O_5$ (210.15). Calcd. C 45.72; H 2.88; N 13.33. Found C 45.91; H 3.06; N 13.61%.

IR (KBr): 3380, 3220, 3120 (NH), 1660 (C=O).

6-Aminopiperonylamide

The above compound (12.6 g; 60 mmoles) was reduced in ethanolic (500 ml) suspension at room temperature and ordinary pressure in the presence of an 8% Pd/C catalyst (6 g). The resulting solution was evaporated to 1/5 its original volume to yield 8.6 g (77%) of the title compound on cooling, m.p. 187 °C (from EtOH).

$C_8H_8N_2O_3$ (180.16). Calcd. C 53.33; H 4.48; N 15.43. Found C 53.44; H 4.74; N 15.43%.

6-Formylamino- and 6-acetylaminopiperonylamide

Acetic-formic anhydride (8.5 ml, 0.1 mole) and acetic anhydride (5.0 ml; 53 mmoles), respectively, were added by drops to the boiling mixtures of the 6-amino derivative (9.0 g; 50 mmoles) in CH_2Cl_2 (180 ml). After refluxing for another 20 min., the mixtures were allowed to cool. 7.5 g (72%) of the formyl derivative, m.p. 193–194 °C (from EtOH), and 8.35 g (75%) of the acetyl derivative, m.p. 215–216 °C (from EtOH), respectively, were obtained.

Formyl derivative, $C_9H_8N_2O_4$ (208.17). Calcd. C 51.92; H 3.87; N 13.47. Found C 51.18; H 3.94; N 13.12%.

IR (KBr): 3400, 3200 (NH), 1680 and 1635 cm^{-1} (Amide I).

Acetyl derivative, $C_{10}H_{10}N_2O_4$ (222.20). Calcd. C 54.05; H 4.54; N 12.61. Found C 53.90; H 4.67; N 12.78%.

IR (KBr): 3350, 3180 NH, 1660 and 1630 cm^{-1} (Amide I).

Ring closures

The above compounds (50 mmoles) were heated under argon* to 245–250 °C and kept for 20 min. at this temperature. Melts were initially formed which, after the evolution of water vapours had subsided, gradually resolidified. The products were allowed to cool and were

* Extensive colouration took place in the presence of air.

triturated with ethanol to yield 8.9 g (94%) of **18** ($R^2 = R^3 = H$), and 9.5 g (93%) of **18** ($R^2 = Me$, $R^3 = H$), respectively, both melting above 300 °C (from DMF).

18 ($R^2 = R^3 = H$), $C_9H_6N_2O_3$ (190.15). Calcd. C 56.84; H 3.18; N 14.73. Found C 56.66; H 3.50; N 14.63%.

IR (KBr): 3200—2500 (NH), 1660 (Amide I), 1635 cm^{-1} sh (Amide I, 1,4-dihydro-4--oxo tautomer?).

18 ($R^2 = Me$, $R^3 = H$), $C_{10}H_8N_2O_3$ (204.18). Calcd. C 58.82; H 3.95; N 13.72. Found C 59.11; H 4.03; N 14.22%.

IR (KBr): 3150—2500 (NH), 1650 (Amide I), 1630 cm^{-1} sh (Amide I, 1,4-dihydro-4--oxo tautomer?).

Alkylations of the quinazolinones 18 (R^2=H, Me; R^3=H)

(*a*) Mixtures of the title compounds (1.0 mole), DMF or nitromethane (10 ml), dry Ag_2O (freshly prepared from 4.0 mmoles of $AgNO_3$) and EtI (2.0 ml) were stirred at room temperature until, according to TLC, the starting compounds **18** were completely used up (30—40 hrs.). The inorganic compounds were filtered off, the filtrates evaporated to dryness and worked up by preparative TLC to yield the following products:

Product	M.p., °C	Yield, %	Formula (Mol. wt.)	Calcd. / found		
				C%	H%	N%
13a (R' = Et)	134—135	41[a]	$C_{11}H_{10}N_2O_3$	60.54	4.62	12.84
			(218.21)	59.91	4.57	12.43
13b (R' = Et)	127	62[a]		62.06	5.21	12.07
		traces[b]	$C_{12}H_{12}N_2O_3$	61.70	5.05	12.32
			(232.24)			
18 (R^2 = Me, R^3 = Et)	156	18[a]		62.06	5.21	12.07
		65[b]		61.82	5.02	11.84

[a] In nitromethane

[b] in DMF

13a (R' = Et), MS (50 °C): *m/e* 218 (100%, $M^{+\cdot}$), *m/e* 217 (7%), *m/e* 203 (74%), *m/e* 190 (75%), *m/e* 189 (45%), *m/e* 174 (28%), *m/e* 173 (10%), *m/e* 163 (6%), *m/e* 147 (17%.)

13b (R' = Et), IR (KBr): 1605 (sh's at 1640 and 1620), 1500, 1470 vs; MS (50 °C): *m/e* 232 (91%, $M^{+\cdot}$), *m/e* 231 (8%), *m/e* 218 (100%), *m/e* 204 (84%), *m/e* 203 (20%), *m/e* 188 (25%), *m/e* 187 (10%), *m/e* 163 (13%), *m/e* 147 (22%).

18 (R^2 = Me, R^3 = Et), IR (KBr): 1650 cm^{-1}; MS (60 °C): *m/e* 232 (100%, $M^{+\cdot}$), *m/e* 204 (80%), *m/e* 203 (13%), *m/e* 190 (9%), *m/e* 163 (5%), *m/e* 149 (16%).

(*b*) A mixture of **18** (R^2 = Me, R^3 = H) (0.3 g; 1.5 mmole), nitromethane (15 ml), benzyl iodide (0.21 ml; 1.65 mmole) and dry Ag_2O (freshly prepared from 3.5 mmoles of $AgNO_3$) was stirred for 10 hrs at room temperature, and worked up as described under (*a*) (solvent used for TLC: benzene–acetone, 1 : 1) to yield 80 mg (18%) of **13b** (R' = $PhCH_2$), colourless crystals, m. p. 149—150 °C (from MeOH).

$C_{17}H_{14}N_2O_3$ (294.31). Calcd. C 69.39; H 4.79; N 9.52. Found C 69.29; H 4.76; N 9.17%.

IR (KBr): 1630 w (sh at 1640), 1600, 1500, 1460 vs.

Ethyl N-(2-methyl-6,7-methylenedioxy-4-oxo-3,4-dihydro-3-quinazolinyl)-carbamate 14b) (authentic product).

Ethyl chloroformate (0.19 g; 2.0 mmoles) was added by drops under ice-cooling and stirring to a mixture of compound **18** (R^2 = Me, R^3 = NH_2) [39] (0.44 g; 2 mmoles) and anhydrous pyridine (10 ml). The mixture was gradually heated to the boiling point and refluxed for 4 hrs.; after 2 hrs another portion of the chloroformate (0.19 g) was added. At the end of this period, the starting compound **18** was, according to TLC, completely used up. The dark mixture was poured into water (20 ml), and the resulting aqueous solution was extracted with $CHCl_3$ (three portions, 5—10 ml, each). The combined $CHCl_3$ solutions were dried ($MgSO_4$), concentrated to a small volume and worked up by preparative TLC (solvent: benzene–MeOH, 10 : 2) to yield 0.11 g (19%) of **14b**, m.p. 156 °C (from aq. MeOH).

$C_{13}H_{13}N_3O_5$ (291.25). Calcd. C 53.61; H 4.50; N 14.43. Found C 53.53; H 4.60; N 14.10%.

IR (KBr): 3180 (NH), 1750/1740, d (carbamate), 1680/1660 cm^{-1}, d (Amide I).

*

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Table I

Phototransformation products of the N-(3-quinazolinio)-amidates **8** *obtained in argon-flushed solutions*

Starting compound[a]	Solvent	Products and yields, %[b]						
		9[c]	**10**	**11**	**12**	**13**[c]	**14**	**15**
8a	EtOH	35	—	X	X	+	5.6	—
8b	EtOH	26	40	X	X	4	+	25—30
8b	$PhCH_2OH$	4	11.5	X	X	—	—	—[d]
8c	EtOH	21	33	X	X	1.1	1.4	23
8d	EtOH	36	7.2	X	X	9.1	?	23
8e	EtOH	X	23	11	6.7	X	X	—?
8f	EtOH	X	43.5[e]	29	5	X	X	45.5
8g	EtOH	X	57	1	—	X	X	86

[a] The starting compounds were introduced as mixtures of variable compositions of the monomeric amidate and the dimeric forms, *cf.* Ref. [27]. For the forms actually present in the solutions, see below.

[b] +: Traces detected by TLC and identified by the IR spectrum
—: Nothing detectable by TLC
X: In principle impossible products

[c] R' = Et and $PhCH_2$, depending on whether ethanol or benzyl alcohol were used as the solvents

[d] Four additional photoproducts of not yet identified structures, differing from the hitherto known type **9**—**15** products, have also been isolated in this case.

[e] The yield of 86% stated in Ref. [26] was erroneous.

Table II

NMR Spectra of the phototransformation products **9**—**14** *and of some model compounds*

Compound	Solvent	Reference	Chemical shifts (δ scale)						
			R²	R	5-H[a]	R'	ArH's[a]	OCH_2O	NH
9a (R'=Et)	$CDCl_3$	TMS	6.73, d[b] $J = 4$ Hz	1.30, t + 4.27, q $J = 7.5$ Hz	6.35, s	1.25, t + ~ 3.7, m[c] $J = 7.5$ Hz	6.35, s + 6.70,s	5.90, s	8.10, d $J = 4$ Hz
9a (R'=Et)	DMSO-d_6	DSS	6.58, d $J = 5$ Hz	1.20, t + 4.06, q $J = 7$ Hz	6.23, s	1.13, t + ~ 3.4, m $J = 7$ Hz	6.40, s + 6.77s	5.92, s	9.00, d $J = 5$ Hz
9a (R'=Et)	CD_3OD	CHD_2OD = 3.35	6.77, s[d]	1.29, t + 4.24, q	6.36, s	1.21, t + ~ 3.6, m	6.44, s + 6.75, s	5.94, s	—
9b (R'=Et)	$CDCl_3$	TMS	2.15, s	1.35, t + 4.30, q $J = 7.1$ Hz	6.35, s	1.28, t + ~ 3.6, q $J = 7.1$ Hz	6.40, s + 6.70,s	5.95, s	7.05, br
9b (R'=Et)	DMSO-d_6	DMSO-d_5 = 2.50	1.96, s	1.14, t + 4.10, q $J = 7.3$ Hz	6.27, s	1.08, t + ~ 3.45, q $J = 7.3$ Hz	6.60, s + 6.89, s	6.01, s	8.84, s
9b (R'=Et)	CD_3OD	CHD_2OD = 3.35	2.10, s	1.28, t + 4.22, q $J = 7$ Hz	6.22, s	1.21, t + ~ 3.6, q $J = 7$ Hz	6.49, s + 6.70, s	5.91, s	—
9b (R'=Et)	CD_3OD + TFA	CHD_2OD = 3.35	2.54, s	1.27, t + 4.21, q $J = 7$ Hz	6.07, s	1.21, t + ~ 3.8, q $J = 7$ Hz	6.87, s + 6.98, s	5.87, s	—
9b (R'= = $PhCH_2$)	$CDCl_3$	TMS	2.12, s	1.29, t[e] $J = 7$ Hz	6.25, s	7.33, s[e]	6.31, s + 6.58, s	5.88, s	
9c (R' = Et)	$CDCl_3$	TMS	2.05, s	5.20 + 5.35, both d, $J_{AB} = 13$ Hz;[f] + 7.40, s	6.32, s	1.22, t + 3.7, q (+ 3.55, q),[f] $J = 7$ Hz	6.32, s + 6.70, s	5.91, s	
HCl salt	CD_3OD	CHD_2OD = 3.35	2.55, s	5.19 + 5.28[f,g] + + 7.42, s	6.22, s	1.29, t + 3.7, q $J = 7$ Hz	6.85, s + 6.96, s	6.08, s	—
9d (R'=Et)	$CDCl_3$	TMS	2.0, s	7.64 br, m (*o*-H's) + 7.37 br, m (*m*-+*p*-H's)	6.36, s	1.27, t + ~ 3.6 br, m, $J = 7$ Hz	6.80, s	5.87, s	

Table II (continued)

Compound	Solvent	Reference	Chemical shifts (δ scale)				
			2-Me	COOEt	4-H	ArH's	OCH_2O
16[h] (X = NHCOOEt)	$CDCl_3$	TMS	7.30,[h] s	1.35, t + 4.30, q J = 7 Hz	4.65, s, 2H	6.38, s + 6.70, s	5.93, s
16 (X = NHCOORt) [27]	$CDCl_3$	TMS	2.15, s	1.30, t + 4.20, q J = 7 Hz	4.60, s, 2H	6.30, s + 6.70, s	5.90, s
16 (X = NHCOOEt) [27]	CD_3OD	CHD_2OD = 3.35	2.10, s	1.30, t + 4.25, q J = 7 Hz	4.65, s, 2H	6.50, s + 6.55, s	5.95, s
17 (R^2 = Me, R^4 = H, R = OEt, R' = CD_3, X = D) [27]	CD_3OD	CHD_2OD = 3.35	2.22, s	1.30, t + 4.22, q J = 7 Hz	5.92, s	6.70, s	5.95, s
			R^2	R^4		ArH's	OCH_2O
10a	$CDCl_3$	TMS	9.25, s	9.25, s		7.20, s + 7.38, s	6.23, s
10b [27]	$CDCl_3$	TMS	2.80, s	9.0, s		7.05, s + 7.20, s	6.12, s
10e	$CDCl_3$	TMS	9.06, s	2.86, s		7.30, s	6.20, s
10f	$CDCl_3$	TMS	2.88, s	2.88, s		7.44, s + 7.47, s	6.33, s
11e	TFA	TMS (ext.)	8.85, s	3.75, s		7.10, s + 7.40, s	5.95, s
11f	TFA	TMS (ext.)	2.40, s	3.62, s		6.95, s + 7.30, s	5.90, s
12e	DMSO-d_6 + $CDCl_3$	TMS	8.97, s	1.20, t + 4.07, q, J = 7 Hz; 4.75, s + d, J = 3.5 Hz, CH_2NH, with NH partially deuterated; s, after addition of D_2O		7.29, s (8-H) + 7.60, s (5-H)	6.25, s
12f[i]	$CDCl_3$	TMS	2.85, s	1.35, t + 4.30, q, J = 7 Hz; 4.87, d, J = 4.5 Hz; s, after addition of D_2O		7.35, s	6.20, s

Table II (continued)

Compound	Solvent	Reference	Chemical shifts (δ scale)				
			R^2	R^2	ArH's	OCH_2O	
13a (R' = Et)	$CDCl_3$	TMS	8.73, s	1.50, t + 4.65, q J = 7.3 Hz	7.30, s + 7.48, s	6.15, s	
13b (R' = Et)	$CDCl_3$	TMS	2.70, s	1.50, t + 4.65, q J = 7.3 Hz	7.25, s + 7.45, s	6.15, s	
			R^2	R	ArH's	OCH_2O	NH
14a	$CDCl_3$ + CD_3OD	TMS	7.96, s	1.31, t + 4.22, q J = 7 Hz	7.00, s (8-H) + 7.55, s (5-H)	6.08, s	
14b	$CDCl_3$	TMS	2.54, s	1.28, t + 4.25, q J = 7.3 Hz	7.02, s (8-H) + 7.50, s (5-H)	6.12, s	8.2, br, s
			R^2	R	ArH's	OCH_2O	
18 (R^2 = Me, R^3 = Et)	$CDCl_3$	TMS	2.63, s	1.37, t + 4.20, q J = 7.1 Hz	7.05, s (8-H) + 7.67, s (5-H)	6.15, s	

[a] The correct assignment of the 5-H and ArH signals may be reversed
[b] The upfield peak of the d is merged with the signal at δ 6.70
[c] All peaks of the q are slightly split (hindered rotation?)
[d] The correct assignment of the 2-H and the low-field ArH signal may be reversed
[e] The methylene parts of the R and R' signal furnish a complex multiplet pattern between δ 4.00 and 5.06 ppm
[f] Hindered rotation
[g] The two central peaks of an AB spectrum
[h] H replacing 2-Me
[i] NH: 6.45 bs

Table III

UV Spectra of the phototransformation products **9**—**14** *and of some model compounds in ethanol*

Compound	λ_{max} (log ε)
9a (R' = Et)	212 (4.40); 224 (4.30), sh; 307 (3.96)
9b (R' = Et)	209 (4.56); 220 (4.40), sh; 300 (4.00)
9b (R' = $PhCH_2$)	210; 223, sh; 302
9c (R' = Et)	209 (4.74); 222 (4.50), sh; 300 (4.10)
9d (R' = Et)	206 (4.54); 216 (4.50), sh; 315 (4.05)
16 (X = H) [27]	214 (4.25); 221 (4.27), sh; 316 (3.88)
16 (X = NH_2) [27]	212 (4.23); 319 (3.89)
16 (X = NHCOOEt) [27]	204 (4.28); 316 (3.90)
10a	226 (4.39), sh; 233 (4.41); 317 (3.79); 330 (3.86)
10b [27]	224 (4.52), sh; 234 (4.54); 322 (3.90); 332 (3.96)
10e	225 (4.38), sh; 234 (4.44); 315 (3.75), sh; 328 (3.85)
10f	226 (4.51), sh; 233 (4.55); 318 (3.80), sh; 331 (3.87)
11e	227 (4.07), sh; 236 (4.13); 318 (3.51), sh; 330 (3.63)
11f	227 (4.43), sh; 234 (4.45); 322 (3.82), sh; 334 (3.89)
12e	228 (4.11), sh; 237 (4.70); 321 (3.86), sh; 331 (3.96)
12f	226 (4.47), sh; 233 (4.48); 322 (3.82), sh; 333 (3.92)
13a (R' = Et)	231 (4.60); 243 (4.35), sh; 260 (3.62); 307 (3.75); 314 (3.71), sh; 320 (3.85)
13b (R' = Et)	230 (4.67); 240 (4.41), sh; 260 (3.75); 310 (3.83); 318 (3.78), sh; 323 (3.88)
13b (R′ = $PhCH_2$)	232 (4.68); 242 (4.68), sh; 260 (3.77); 310 (3.87); 317 (3.83), sh; 325 (3.93)
14a	241 (4.59); 290 (3.68); 311 (3.70); 324 (3.62)
14b	240 (4.67); 288 (3.76); 316 (3.72); 327 (3.65)
14c	239 (4.61); 287 (3.65); 314 (3.64); 326 (3.56)
18 (R^2 = R^3 = H)	236 (4.17); 286 (3.20); 309 (3.28); 323 (3.25)
18 (R^2 = H, R^3 = Bu) [28]	240 (4.58); 288 (3.56); 310 (3.58); 323 (3.50)
18 (R^2 = Me, R^3 = H)	236 (4.52); 284 (3.59); 314 (3.63); 327 (3.57)
18 (R^2 = Me, R^3 = Et)	239 (4.56); 287 (3.70); 314 (3.64); 326 (3.56)
18 (R^2 = Me, R^3 = Bu) [28]	240 (4.54); 287 (3.69); 314 (3.57); 322 (3.49)

Table IV

Irradiation of the quinazolinioamidates **8**[a]

Run No.	Starting compound	g (mmole)	Solvent (ml)	Flushing gas	Time of irradiation, hr
1	**8a**	1.50 (5.75)	EtOH (150)	argon	80
2	**8a**	1.50 (5.75)	dioxane + H_2O (75–75)	oxygen	40
3	**8b**	1.50 (5.45)	EtOH (150)	argon	40
4	**8b**	0.50 (1.82)	EtOH + H_2O (50–50)	argon	20
5	**8b**	1.50 (5.45)	EtOH (150)	oxygen	20
6	**8b**	0.50 (1.82)	EtOH (100)	oxygen	20
7	**8b**	1.50 (5.45)	dioxane + H_2O (75–75)	oxygen	25
8	**8b**	1.50 (5.45)	$PhCH_2OH$ (150)	argon	8
9	**8c**	1.50 (4.45)	EtOH (150)	argon	40
10	**8d**	1.50 (4.88)	EtOH (150)	argon	60
11	**8e**	1.00 (3.62)	EtOH (100)	argon	30
12	**8f**	1.50 (5.18)	EtOH (150)	argon	5
13	**8g**	1.50 (4.68)	EtOH (100)	argon	3

[a] The starting compounds were introduced as mixtures of variable compositions of the monomeric amidate and the dimeric forms, *cf.* Ref. [27]. As to the forms actually present in the solutions, see above.

Table V

Bond distances and bond angles of compound **9d** *(R' = Et) + MeOH +* H_2O

Bond distances:

C1—O1	1.421(11) Å	C3—C4	1.396(10) Å	N3—N2	1.417(7) Å
O1—C7	1.393(9)	C4—C5	1.394(9)	N2—C9	1.281(8)
C7—C2	1.365(10)	C5—C6	1.405(9)	C9—N1	1.346(9)
C2—O2	1.393(9)	C6—C7	1.340(10)	N1—C5	1.412(9)
O2—C1	1.413(11)	C4—C8	1.491(9)	C9—C10	1.503(10)
C2—C3	1.356(10)	C8—N3	1.471(9)	C8—O3	1.396(9)

O3—C11	1.436(10) Å
C11—C12	1.510(13)
N3—C13	1.350(9)
C13—O4	1.247(8)
C13—C14	1.470(8)
O5—C20	1.389(13)

C—C in the phenyl group 1.395(6) Å

Bond angles:

O1—C1—O2	108.9(7)°	C4—C8—N3	109.7(5)°
C1—O1—C7	105.8(6)	C4—C8—O3	109.3(6)
C2—O2—C1	105.2(6)	N3—C8—O3	109.6(5)
O2—C2—C3	127.8(7)	C8—N3—N2	118.4(5)
O2—C2—C7	110.3(6)	C8—N3—C13	121.6(5)
C3—C2—C7	121.9(7)	C13—N3—N2	117.9(5)
C2—C3—C4	117.1(7)	N3—N2—C9	115.8(5)
C2—C7—O1	109.1(6)	N2—C9—N1	130.6(6)
C2—C7—C6	123.1(7)	N2—C9—C10	115.4(6)
O1—C7—C6	127.8(7)	C10—C9—N1	113.9(6)
C7—C6—C5	117.0(6)	C9—N1—C5	133.5(6)
C6—C5—C4	120.2(6)	C8—O3—C11	113.3(6)
C6—C5—N1	115.9(6)	O3—C11—C12	108.1(7)
N1—C5—C4	123.9(6)	N3—C13—O4	119.5(6)
C5—C4—C3	120.8(6)	N3—C13—C14	119.2(5)
C3—C4—C8	118.3(6)	C14—C13—O4	121.3(6)
C5—C4—C8	120.9(6)	C—C—C in the phenyl group	120.0(4)°

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CARBOHYDRATE METHYL ETHERS, IX*

AN IMPROVED SYNTHESIS OF 2-O-, 2,6-di-O AND 2, 4, 6-tri-O-METHYL-D-MANNOSE

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Hydrogenolysis of benzyl *exo*-2,3 : 4,6-di-O-benzylidene-α-D-mannopyranoside (**2**) with 1.1 mole of $LiAlH_4$–$AlCl_3$ reagent gave benzyl 3-O-benzyl-4,6-O-benzylidene-α-D-mannopyranoside (**3**). Catalytic hydrogenation of **6**, obtained from **3** by methylation resulted in 2-O-methyl-D-mannose (**7**). Hydrogenolysis of the 4,6-O-benzylidene ring of **6** gave **8** from which **10** was obtained by successive methylation and catalytic hydrogenation. Hydrogenation of **12**, obtained from **11** by methylation, gave **13**.

Introduction

In the course of our research programme in the field of lipopolysaccharides and mannanes, experiments have been performed to synthesize higher oligosaccharides (so-called repeating-units). For the structure investigation of the compounds prepared, various carbohydrate methyl ethets were required. In our present paper the synthesis of the three title compounds is described. For the preparation of 2-O-methyl-D-mannose various methods have been published [2—7] while 2,6-di-O-methyl-D-mannose was identified as the carbohydrate component of two antibiotics (avilamycin [8] and curamycin [9]). The latter compound has also been synthesized in three different ways [6, 10—11]. 2,4,6-Tri-O-methyl-D-mannose was for the first time isolated as one of the hydrolysis products of methylated mannanes [12] and it was also synthesized [13] in 1971.

Results and discussion

The improved synthesis of the three title compounds was performed using our recently published method [14—15] for the reductive ring cleavage of the 2-phenyl-1,3-dioxolane derivatives of carbohydrates. It has been established that the direction of cleavage of the benzylidene ring is determined by the steric relation of the phenyl and pyranosyl rings. In the case of the *exo*-derivatives (in which the two rings are quasi antiparallel) the reagent attacks

* For Part VIII see Ref. [1].

the *axial* oxygen atom of the dioxolane ring, while in the case of the *endo*-derivatives (containing the two rings in a quasi parallel relation), it attacks the *equatorial* oxygen atom. This rule has already been supported by our experiments with various derivatives in the D-manno- and L-rhamno- (2,3-*cis*-*axial-equatorial* OH groups) as well as in the D-galacto-, D-fuco- and D-arabino-(3,4-*cis-equatorial-axial* OH groups) series. The cleavage of the dioxolane ring is very fast (the reaction is complete within 15 minutes) and using a stoichiometric amount of the reagent, the 4,6-O-benzylidene acetal rings (2-phenyl--1,3-dioxanes) which are also present in the molecule, remain intact during the reaction.

Benzyl α-D-mannopyranoside (**1**), the starting material of our synthesis, was prepared by a modified method of GORIN and PERLIN [16] (see Experimental). Benzylidenation of **1** with benzaldehyde and $ZnCl_2$ gave benzyl 2,3 : 4,6-di-O-benzylidene-α-D-mannopyranoside (**2**) in 85—90% yield. The NMR spectrum of the crude product contained only two singlets of 1 : 1 intensity ($\delta = 6.22$ and 5.56 ppm), from which the one appearing at the higher field ($\delta = 5.56$ ppm) and the other at $\delta = 6.22$ ppm could be assigned to the C*H*-Ph proton of the 4,6-O-benzylidene- and the 2,3-O-benzylidene ring, respectively. On the basis of this NMR spectrum the other isomer could not be detected, and even if it formed under the reaction conditions applied, its yield must have been below 1—2%.

Compound **2** has recently been isolated by JEANLOZ *et al.* [26] as a by-product in the synthesis of benzyl 4,6-O-benzylidene-α-D-mannopyranoside, in a low yield (20%).

On the basis of the investigation of FOSTER [17], the benzylidene proton of the *exo*-isomers always resonates at a lower field than that of the *endo*-isomers. Comparing the NMR data of our compound **2** with the data of FOSTER [17] and other authors [18—19], formula **2** could also be assigned to an *exo*-isomer. This was also supported by the high yield of formation of **2**, as well as by its hydrogenolysis detailed below.

Reaction of **2** with 1 mole of the $LiAlH_4$–$AlCl_3$ reagent gave benzyl 3-O-benzyl-4,6-O-benzylidene-α-D-mannopyranoside (**3**) within 15 minutes in nearly quantitative yield. On the basis of TLC examination, the other isomer, benzyl 2-O-benzyl-4,6-O-benzylidene-α-D-mannopyranoside (**4**) formed maximally in 2—3% yield; however, its isolation by means of short column chromatography gave only a few tenth per cents. Its physical data proved to be identical with those of the product described by ALFREDSSON *et al.* [20].

The structure of **3** was unequivocally supported by the experimental fact that the product obtained after the removal of the benzylidene acetal by acetic acid was resistant during the periodate oxidation reaction, so it proved to be benzyl 3-O-benzyl-α-D-mannopyranoside (**5**).

The OCH_3 signal in the NMR spectrum of **6** obtained from **3** upon methyl-

ation, appears at a high δ-value (3.54 ppm) and the catalytic hydrogenation of **6** resulted in crystalline 2-O-methyl-D-mannose (**7**). Acetic acid hydrolysis of **6** gave crystalline benzyl 3-O-benzyl-2-O-methyl-α-D-mannopyranoside (**11**).

Similarly to our earlier results for the 3-O-benzyl-4,6-O-benzylidene-D-gluco-, D-manno- and D-galactopyranoside derivatives [21—22], the hydrogenolysis of the 4,6-O-benzylidene ring of **6** resulted in the C_4-O-benzyl derivative with free C_6-OH, namely, benzyl 3,4-di-O-benzyl-2-O-methyl-α-D-mannopyranoside (**8**) as the main product in 80—90% yield. The isolation of the by-product appearing in a few percentages was not attempted.

According to its IR spectrum, compound **9** — obtained from **8** upon methylation — proved to be a completely blocked derivative containing two OCH_3 signals (δ = 3.50 and 3.41 ppm) in its NMR spectrum. Catalytic hydrogenation of **9** gave syrupy **10** whose 2,6-di-O-methyl-D-mannose structure was unequivocally proved by its oxidation reaction with periodate: it consumed 2 moles of periodate [23] accompanied by the formation of 1 mole of formic acid [24] and the lack of formation of formaldehyde during the reaction.

The NMR spectrum of **12** — obtained from **11** by methylation — contained three OCH_3 signals at δ = 3.55, 3.44 and 3.40 ppm; its IR spectrum had no band assignable to a free hydroxyl group. Catalytic debenzylation of **12** gave crystalline 2,4,6-tri-O-methyl-D-mannose (**13**).

The chemical purity of **7**, **10** and **13** was also checked by gas chromatography on 10% OV-1 column and the purity grades were found to be 95—98%.

Experimental

M.p.'s were determined on a Kofler hot-stage apparatus and are uncorrected. Optical rotations were measured with a Polamat (Zeiss) automatic photoelectric polarimeter. IR spectra were recorded in KBr pellets using a Perkin-Elmer 700 instrument. NMR spectra were obtained on a Jeol MH-100 (100 MHz) instrument using TMS as internal standard. The thin-layer chromatographic examination and the short column chromatographic separations were carried out on silica gel (Kieselgel G; E. Merck, Darmstadt) using benzene–methanol mixtures the proportion of which are given in brackets where R_f-values are stated. 50% sulfuric acid was used for detection. GLC was performed with a Hewlett-Packard 5830 A instrument using helical stainless steel columns.

Benzyl α-D-mannopyranoside (1)

D-Mannose (10 g) was added to benzyl alcohol (80 ml) containing dissolved hydrochloric acid gas (7 g) at 55 °C with stirring. After the dissolution of D-mannose, the reaction mixture was neutralized with solid $NaHCO_3$ and diluted with methanol (80 ml). The solution was filtered, concentrated in vacuum and the excess of benzyl alcohol removed by distillation (bath temperature 130—140 °C). The residue was dissolved in water and extracted with ethyl acetate (10 × 50 ml). After the concentration of the organic layer to about 40 ml spontaneous crystallization of **1** was observed. The product was recrystallized from ethyl acetate to give pure **1** (8.5 g; 56.6%), m.p. 130—135 °C, $[\alpha]_D$ + 75.5° (c = 1.5, water), (lit. [16] m.p. 132—135 °C, $[\alpha]_D$ + 73.5° (c = 1.5, water)).

Benzyl exo-2,3:4,6-di-O-benzylidene-α-D-mannopyranoside (2)

Compound **1** (10 g) was treated with benzaldehyde (100 ml) and freshly fused $ZnCl_2$ (10 g) for 24 hrs. The reaction mixture was washed with ice-water (3×100 ml) and petroleum ether (5×10 ml) and filtered. The crystalline residue was recrystallized from acetone (190 ml). to yield **2** (11.2 g; 87%), m.p. 188 — 189 °C (lit. [26] m.p. 174 — 176°C); $[\alpha]_D$ + 34° (c = 1.0, chloroform);

NMR: δ = 7.60—7.10 (m, 15H, aromatic); 6.22 (s, 1H, dioxolane); 5.56 (s, 1H, dioxan) 5.12 (s, 1H, C_1-H); 4.80—3.60 (m, 8H, benzyl and skeleton protons).

Benzyl 3-O-benzyl-4,6-O-benzylidene-α-D-mannopyranoside (3)

To a solution of **2** (3.0 g) in 1 : 1 abs. ether–dichloromethane mixture (60 ml) $LiAlH_4$ (150 mg) was added, followed by the dropwise addition of $AlCl_3$ (500 mg) in abs. ether (12 ml) over a period of 2 min. The mixture was stirred at 45 °C for 15 min. After cooling, the excess of the reagent was decomposed with ethyl acetate (2 ml) and water (4 ml), the mixture was diluted with dichloromethane (50 ml) and the $Al(OH)_3$ precipitated was filtered off. The filtrate was washed with water (3×30 ml), dried over Na_2SO_4 and concentrated. Recrystallization of the crystalline residue from ethanol (15 ml) gave pure **3** (2.28 g; 76%), m.p. 88—89 °C, $[\alpha]_D$ +55.4° (c = 0.5, chloroform). R_f 0.70 (95 : 5).

NMR (in $CDCl_3$): δ = 7.44—7.08 (m, 15H, aromatic); 5.51 (s, 1H, C*H*-Ph); 4.84 (s, 1H, C_1-H); 4.67 and 4.50 (q, 4H, 2 benzyl); 4.24—3.60 (m, 6H, skeleton protons); 2.52 (broad, 1H, OH).

$C_{27}H_{28}O_6$ (448.5). Calcd. C 72.30; H 6.29. Found C 72.65; H 6.21%.

From the mother liquor of **3** a component of higher chromatographic mobility (R_f 0.75 (95 : 5)) was also isolated by short column chromatography. This compound appeared only in a few percentages and it was proved to be benzyl 2-O-benzyl-4,6-O-benzylidene-α-D-mannopyranoside (**4**) (12.2 mg; 0.4%), m.p. 98—99 °C (lit. [20] m.p. 97—98 °C), $[\alpha]_D$ + 40° (c = 0.2, chloroform) (lit. [20] $[\alpha]_D$ + 39° (c = 0.3, chloroform)); mixed m.p. 98—99 °C.

Benzyl 3-O-benzyl-α-D-mannopyranoside (5)

Compound **3** (200 mg) was hydrolyzed in 50% aqueous ethanol (10 ml) containing 0.04 ml of conc. H_2SO_4 at 100 °C for 3 hrs. After neutralization with $BaCO_3$ and filtration, the filtrate was concentrated to give syrupy **5** (132 mg; 75.8%), $[\alpha]_D$ + 65° (c = 1.2, ethanol).

$C_{20}H_{24}O_6$ (360.4). Calcd. C 70.56; H 7.05. Found C 71.02; H 6.98%.

Compound **5** (5 mg) was dissolved in a mixture of 50% aqueous ethanol (2 ml) and $NaIO_4$ (20 mg). After standing for 3 hrs only unchanged **5** could be detected by TLC.

Benzyl 3-O-benzyl-4,6-O-benzylidene-2-O-methyl-α-D-mannopyranoside (6)

Compound **3** (2.9 g) was methylated with methyl iodide (2 ml) in N,N-dimethylformamide (15 ml) in the presence of Ag_2O (2 g). After stirring for 18 hrs the mixture was worked up in the usual manner. The syrupy product was purified by chromatography on 100 g of Kieselgel G using a benzene–methanol (95 : 5) mixture as the eluant, to yield 2.7 g of syrupy **6** (93%), $[\alpha]_D$ + 62.6° (c = 0.77, chloroform), R_f 0.77 (95 : 5).

NMR (in $CDCl_3$): δ = 7.54—7.12 (m, 15H, aromatic); 5.60 (s, 1H, C*H*-Ph); 4.94 (s, 1H, C_1-H); 4.78 and 4.58 (2 q, 4H, 2 benzyl), 4.26—3.62 (m, 6H, skeleton protons); 3.54 (s, 3H, OCH_3).

$C_{28}H_{30}O_6$ (462.5). Calcd. C 72.70; H 6.53. Found C 73.01; H 6.41%.

2-O-Methyl-D-mannose (7)

Compound **6** (1.0 g) was hydrogenated in a mixture of ethyl acetate–ethanol (1 : 1) (200 ml) and in the presence of Pd/C-10% (500 mg) for 18 hrs. After the reaction was complete, the catalyst was filtered off and the filtrate concentrated. Crystallization of the residue from a small amount of ethanol gave **7** (266 mg; 80%), m.p. 132—134 °C; $[\alpha]_D$ + 8.5° (c = 0.5, water). (Lit. [7] m. p. 136—138 °C; $[\alpha]_D$ + 11° (c = 1.0, water)). R_f 0.26 (8 : 2), R_T 12.27 min.

Benzyl 3,4-di-O-benzyl-2-O-methyl-α-D-mannopyranoside (8)

$LiAlH_4$ (0.6 g) was added to a solution of **6** (1.7 g) in 1 : 1 ether–dichloromethane (60 ml) and it was warmed up to 45 °C. After the dropwise addition of $AlCl_3$ (1.8 g) in ether (10 ml) during 2 min. the mixture was boiled for an additional 30 min. It was then cooled and the excess of the reagent decomposed with ethyl acetate (5 ml) and water (8 ml); the mixture was then diluted with dichloromethane (100 ml) and filtered. The filtrate was washed with water (3×50 ml), dried over Na_2SO_4 and evaporated. The residue was chromatographed on Kieselgel G (100 g) using benzene–methanol (95 : 5) solvent system to yield syrupy **8** (0.86 g; 50%), $[\alpha]_D$ + 51.3° (c = 0.5, chloroform), R_f 0.51 (95 : 5).

IR (KBr): 3440—3240 cm^{-1} (broad, polymeric OH); 734 and 697 cm^{-1} (phenyl).

$C_{28}H_{32}O_6$ (464.5). Calcd. C 72.39; H 6.96. Found C 72.51; H 7.02%.

Benzyl 3,4-di-O-benzyl-2,6-di-O-methyl-α-D-mannopyranoside (9)

Methylation of **8** (0.73 g) with methyl iodide (1 ml) and Ag_2O (1 g) in N,N-dimethylformamide (10 ml), as described for **6**, resulted in chromatographically homogeneous syrupy **9** (0.6 g; 80%), $[\alpha]_D$ + 54.6° (c = 0.42, chloroform), R_f 0.72 (95 : 5).

NMR (in $CDCl_3$): δ = 7.32—7.12 (m, 15H, aromatic); 4.99 (d, 1H, C_1-H, $J_{1,2}$ = 1.5 Hz); 4.88—3.53 (m, 18H, benzyl and skeleton protons); 3.50 and 3.41 (2 s, 6H, 2 OCH_3).

$C_{29}H_{34}O_6$ (490.5). Calcd. C 72.78; H 7.16. Found C 72.67; H 7.11%.

2,6-Di-O-methyl-D-mannose (10)

Compound **9** (0.5 g) was hydrogenated in ethyl acetate (100 ml) in the presence of Pd/C-10% (0.5 g) for 18 hrs. The catalyst was removed by filtration and the filtrate evaporated to give **10** as a thick syrup (202 mg; 91%), $[\alpha]_D$ + 26.8° (c = 1.0, water), R_f 0.38 (7 : 3), R_T 10.37 min. (lit. [6] $[\alpha]_D$ + 2 2.4° (c = 3.5, water)).

Compound **9** (10 mg) and $NaIO_4$ (30 mg) were dissolved in water and the solution was diluted to 20 ml. It was allowed to stand in the dark at 4 °C for 24 hrs. Aliquot 1-ml portions of the solution were found to consume 1.82 mole of periodate accompanied by the formation of 0.87 mole of formic acid (measured by the iodometric method). Using the method of UNRAU and SMITH [25], the formation of formaldehyde could not be detected.

Benzyl 3-O-benzyl-2-O-methyl-α-D-mannopyranoside (11)

Compound **6** (1.25 g) was hydrolyzed with 50% aqueous acetic acid (50 ml) with stirring at 80 °C. After hydrolysis was complete (the transformation was monitored by TLC (95 : 5)), the mixture was concentrated in vacuum and the residue was subjected to azeotropic distillation with abs. ethanol and abs. benzene to remove the last traces of water and acetic acid. The product was crystallized from ethanol (4 ml) and 0.70 g of **11** (70%) was obtained, m.p. 93—95 °C, $[\alpha]_D$ + 46° (c = 0.5, ethanol), R_f 0.37 (85 : 15).

IR (KBr): 3450, 3440—3240 cm^{-1} (OH), 736 and 698 cm^{-1} (phenyl).

$C_{21}H_{26}O_6$ (374.4). Calcd. C. 67.36; H 7.00. Found C 68.01; H 6.89%.

Benzyl 3-O-benzyl-2,4,6-tri-O-methyl-α-D-mannopyranoside (12)

Compound **11** (0.49 g) was methylated with 2 ml of methyl iodide and Ag_2O (2 g) in N,N-dimethylformamide (10 ml). After the work-up of the reaction mixture in the usual manner, 0.45 g (86.5%) of syrupy **12** was obtained, $[\alpha]_D$ + 71.1° (c = 0.24, chloroform), R_f 0.71 (96 : 4).

NMR (in $CDCl_3$): δ = 7.40—7.20 (m, 10H, aromatic); 4.94 (d, 1H, C_1-H, $J_{1,2}$ = 1.5 Hz); 4.68 (s, 2H, benzyl); 4.58 (q, 2H, benzyl); 3.90—3.60 (m, 6H, skeleton protons); 3.55, 3.44 and 3.40 (3 s, 9H, 3 OCH_3).

$C_{23}H_{30}O_6$ (402.4). Calcd. C 68.62; H 7.51. Found C 68.10; H 7.38%.

2,4,6-Tri-O-methyl-D-mannose (13)

Compound **12** (330 mg) was hydrogenated in ethyl acetate (60 ml) in the presence of Pd/C-10% (300 mg) for 24 hrs. After completion of the reduction the catalyst was filtered off and the filtrate evaporated to dryness. The syrupy residue was crystallized from ether containing 20% of cyclohexane (2 ml) to obtain **13** (164 mg; 90%), m. p. 53—54 °C (lit. [13] m.p. 53—57 °C, $[\alpha]_D + 16°$ (c = 1.0, water) lit. [13] $[\alpha]_D + 15.1°$ (c = 0.8 water)), R_f 0.43 (8 : 2), R_T 9.45 min.

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SYNTHESIS AND EXAMINATION OF ACYL MIGRATION OF PARTIALLY BENZOYLATED BENZYL 4,6-O-BENZYLIDENE-α-AND β-D-GLUCOPYRANOSIDE DERIVATIVES

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Benzoylation of benzyl 4,6-O-benzylidene-β-D-glucopyranoside **(1)** with 1.1 mole of N-benzoylimidazole resulted in the corresponding 3-O-benzoyl- **(2)** and 2-O-benzoyl- **(3)** derivatives in 30% yield each. The α-anomer of **1** **(7)** under the same conditions gave the 2-O-benzoate **(8)** as the main product in a yield of 50% and the 3-O-benzoate **(9)** in 10% yield. In alkaline acetone **2** and **8** transformed into **3** and **9**, respectively, presumably *via* orthoester-type intermediates. The structures of the products were proved by IR and NMR spectra.

Our recently published results on the synthesis of 2,6-di-O-glycosyl-hexosides with different interglycosidic anomeric configuration [1] starting from 3-O-acyl- or 3-O-benzyl-4,6-O-benzylidene-α,β-hexopyranosides required the elaboration of an improved synthesis of these starting materials. The synthesis of trisaccharides was accomplished by the extension of our stereoselective method for the reductive cleavage of the benzylidene ring of benzyl 3-O-benzyl-4,6-O-benzylidene-hexopyranosides [2, 3] to di- [4] and trisaccharide [5] derivatives.

In the case of the three most frequently occurring hexose components of oligosaccharides (glucose, mannose and galactose) the syntheses of the required derivatives may meet difficulties in some cases. In the simplest case, for galactose, the Chittenden method [6] — including the benzoylation of benzyl 4,6-O-benzylidene-β-D-galactopyranoside with N-benzoylimidazole — offers a good possibility to obtain the corresponding 3-O-benzoate in 89% yield.

In the case of mannose, a new method giving excellent yields has been elaborated by us for the synthesis of benzyl 3-O-benzyl-4,6-O-benzylidene-α-D-mannopyranoside, including the stereoselective hydrogenolytic cleavage of the dioxolane-type acetal ring of benzyl *exo*-2,3 : 4,6-di-O-benzylidene-α-D-mannopyranoside [7].

The synthesis of such derivatives is most problematic in the glucose series. The published synthesis of benzyl 3-O-benzyl-4,6-O-benzylidene-β-D-glucopyranoside [8] is very difficult and its reproducibility seems to be doubtful.

According to the above mentioned results of CHITTENDEN [6], it seemed to be interesting to examine the partial benzoylation of benzyl 4,6-O-benzylidene-α- and β-D-glucopyranosides.

Partial benzoylation of methyl 4,6-O-benzylidene-α-D-glucopyranoside has already been investigated in detail by different authors. In 1935 ROBERTSON and GRIFFITH [9] published the favoured reactivity of C_2-OH in the benzoylation reaction using benzoyl chloride and pyridine. Using the same reaction conditions, 24% of 2-O-benzoate and 6% of 3-O-benzoate were isolated by JEANLOZ [10], while according to BOLLENBACK and PARRISH [11], the ratio of the two products was 59 : 9.8, respectively.

The formation of the 3-O-benzoate was found to be more favoured in the case of the β-anomer (35%) but a considerable amount of the 2-O-benzoyl isomer (18%) was also isolated by COLLINS *et al.* [12].

Considerably higher selectivity was attained in the case of the α-anomer using the N-benzoylimidazole method established by STAAB [13]. In agreement with the results of COLLINS [12], COREY and HODGSON [14] reported a yield of 78% for the 2-O-benzoate. The 2-O-benzoate was also prepared by ABBAS and HAINES [15] in 62% yield using benzoyl cyanide as the acylating agent introduced by HOLY and SOUCEK [16] for the selective benzoylation of nucleosides. The corresponding 3-O-benzoate formed only in traces in this reaction.

Re-examining the known benzoylation methods, KÖNIG and WEIDMANN [17] found the system triethylamine–benzoyl chloride to be a selective reagent for benzoylation. The 2-O-benzoyl derivative of the α-anomer formed in 60% yield, while the yield of the 3-O-benzoyl derivative was only 5%. In the case of the β-anomer, the formation of the 3-O-benzoate was found to be more favoured (43%), accompanied by 12% of the 2-O-benzoyl derivative.

According to recent examinations by STANEK and JARY [18], in the reaction with N-benzoylimidazole the formation of the 3-O-benzoyl derivative of the β-anomer is kinetically more favoured, but at a later stage of the reaction this compound transforms into the more stable 2-O-benzoate.

To our knowledge, the partial benzoylation of benzyl 4,6-O-benzylidene-D-glucopyranosides has not been examined yet.

Benzoylation of benzyl 4,6-O-benzylidene-β-D-glucopyranoside (**1**) with 1.1 mole of N-benzoylimidazole in chloroform for 18 hours resulted in a mixture of 20% of the unreacted **1**, 20% of the di-O-benzoyl derivative (**4**) and in 30% each of the two monobenzoylated derivatives (**2** and **3**) of different chromatographic mobilities in the benzene–methanol (99 : 1) solvent system used. After separation of this mixture by short column chromatography, the crystalline mono-O-benzoate (**2**) of higher R_f value (0.25) melted at 167—169 °C and the carbonyl frequency in its IR spectrum could be assigned at 1728 cm^{-1}. The IR spectrum of the crystalline compound **5** — obtained from **2** upon methyl-

ation with diazomethane — did not contain the OH absorption band at 3400—3200 cm^{-1}, while the carbonyl frequency remained unchanged at 1728 cm^{-1}. The mono-O-methyl-glucose isolated from the saponification of **5** followed by acid hydrolysis, proved to be 2-O-methyl-D-glucose by TLC examination as well as by gas chromatography in the form of the alditol acetate obtained on reduction and acetylation. Thus, compound **2** was unequivocally identified as benzyl 3-O-benzoyl-4,6-O-benzylidene-β-D-glucopyranoside.

The carbonyl band of the other crystalline compound of lower chromatographic mobility (R_f 0.19; m.p. 154—156 °C) contained two split maxima at 1730 and 1710 cm^{-1}. From the crystalline **6** — obtained from **3** by methylation with diazomethane — 3-O-methyl-D-glucose was isolated, thus **3** proved to be benzyl 2-O-benzoyl-4,6-O-benzylidene-β-D-glucopyranoside.

Experiments were also made to effect acyl migration of the benzoyl group in both **2** and **1**, in alkaline medium. In the case of the 2-O-benzoate (**3**) acyl migration did not occur, while the 3-O-benzoyl derivative (**2**) transformed into **3** within 10—15 minutes, but it also suffered saponification to a considerable extent during the experiment. An unusual direction of acyl migration was observed in this case, because in the majority of cases the movement of acyl group is toward the primary hydroxyl group. Acyl migration was also shown to occur with the crude reaction mixture, and **3** was isolated in about 50% yield.

Thus, benzoylation of benzyl 4,6-O-benzylidene-β-D-glucopyranoside gave similar results to the benzoylation of the methyl 4,6-O-benzylidene-β-D-glucopyranoside known from the literature. However, acyl migration made possible the preparation of the 2-O-benzoyl derivative (**3**) in a good yield.

The partial benzoylation of benzyl 4,6-O-benzylidene-α-D-glucopyranoside (**7**) was also examined under the same reaction conditions. A one-step synthesis of **7** —which served as our starting material — has ben achieved by INCH *et al.* [19] with a yield of 20%, but the yield of our reproduction experiments has never been higher than 10%. Thus benzyl α-D-glucopyranoside [20] was directly benzylidenated to give **7** in a good yield. Benzoylation of **7** in the same manner resulted in a mixture of the unchanged **7** (30%), 10% of the di-O-benzoate (**10**) and in the two mono-O-benzoates (**8** and **9**). All yields given in brackets are based on TLC estimation. Isolated yields are given in Experimental. From among the latter the yield of the compound (**8**) with lower chromatographic mobility (R_f 0.23) was about 50% and it had a sharp carbonyl band in the IR spectrum at 1720 cm^{-1}. The IR spectrum of the fully protected **11** — obtained from **8** by methylation — had the carbonyl frequency at 1720 cm^{-1} and, after saponification, followed by hydrolysis, 3-O-methyl-D-glucose was obtained; thus **8** proved to be benzyl 2-O-benzoyl-4,6-O-benzylidene-α-D-glucopyranoside. The carbonyl band of the product of higher chromatographic mobility (R_f 0.30) was at 1700 cm^{-1}. This band appeared

at 1720 cm^{-1} in the IR spectrum of **12**, obtained from **9** by methylation with diazomethane, just as in the case of **11**. After the saponification of **12**, followed by hydrolysis, 2-O-methyl-D-glucose was identified.

On the basis of the NMR spectra it was easy to assign the position of the benzoyl group of **9** and the methylated **12**. In the spectrum of **9** the C_3-H proton gave a triplet at $\delta = 5.51$ ppm as a result of *axial-axial* coupling. In the case of the methylated **12**, this proton gave also a triplet at $\delta = 5.73$ ppm.

The acyl migration experiment with the 2-O-benzoyl derivative (**8**) showed a fast transformation; after 1—2 minutes only the 3-O-benzoate (**9**) could be detected and, contrary to the observed saponification of the β-anomers, only traces of **7** could be identified.

The favoured formation of **8** in the case of the 2-O-benzoate (**7**) can be presumably explained by the formation of a hydrogen bond between C_2-OH and C_1-O-aglycone. Owing to the existence of this hydrogen bond, the nucleophilic character of C_2-O—H → O increases, which is equivalent to increased reactivity towards the carbonyl cation. In the case of the β-anomer there is no possibility for the formation of such hydrogen bond and this fact explains well the formation of the 1 : 1 mixture of the two mono-O-benzoylated derivatives.

Experimental

M. p.'s were determined on a Kofler hot-stage apparatus and are uncorrected. Optical rotations were measured with a Polamat (Zeiss) automatic photoelectric polarimeter. IR spectra were recorded in KBr pellets using a Perkin-Elmer 700 instrument. NMR spectra were obtained with a Jeol MH-100 (100 MHz) instrument using TMS as internal standard. The thin-layer chromatographic examinations and the short column chromatographic [21] separations were carried out on silica gel (Kieselgel G; E. Merck, Darmstadt) and charring with 50% sulfuric acid. GLC was performed with a Hewlett-Packard 5830 A instrument using a helical stainless steel column (2 m; i.d. 4 mm) of 10% OV-1 on Chromosorb W (60—80 mesh) with flame-ionization detection, an injection-block temperature of 250 °C, nitrogen as carrier gas (20 ml/min.) and with a temperature programme of 150 to 220 °C at 5 °C/min.

Benzoylation of benzyl 4,6-O-benzylidene-β-D-glucopyranoside (1)

A solution of imidazole (3.47 g; 51 mmoles) in chloroform (38 ml) was treated with 3.59 g (25.5 mmoles) of freshly distilled benzoyl chloride in chloroform (13 ml) at 5 °C with stirring. Imidazole hydrochloride was filtered off and washed with chloroform (13 ml). The combined chloroform solution was added to **1** (9.3 g; 25.5 mmoles) dissolved in chloroform (100 ml) and the mixture was boiled for 18 hrs. After cooling, the mixture was successively washed with saturated $NaHCO_3$ solution (2×25 ml) and water (2×25 ml), dried (Na_2SO_4) and evaporated. The crystalline residue (9 g) was separated by short column chromatography on Kieselgel G (210 g) using a benzene–methanol (99 : 1) solvent system as the eluant.

R_f 0.81 fraction: **Benzyl 2,3-di-O-benzoyl-4,6-O-benzylidene-β-D-glucopyranoside (4)**. 1.6 g (11%), m.p. 170—171 °C (from ethanol), $[\alpha]_D$ −20.6° (c = 0.95, chloroform).

$C_{34}H_{30}O_8$ (566.6). Calcd. C 72.07; H 5.33. Found C 72.25; H 5.42%.

R_f 0.25 fraction: **Benzyl 3-O-benzoyl-4,6-O-benzylidene-β-D-glucopyranoside (2)**. 2.20 g (18.4%) m.p. 167—169 °C (from methanol), $[\alpha]_D$ −103.5 ° (c = 1.19, chloroform).

IR (KBr): 1728 cm^{-1} (carbonyl).

$C_{27}H_{26}O_7$ (462.5). Calcd. C 70.11; H 5.67. Found C 70.81; H 5.81%.

R_f 0.19 fraction: **Benzyl 2-O-benzoyl-4,6,O-benzylidene-β-D-glucopyranoside (3).** 1.80 g (15%), m. p. 154—156 °C (from methanol), $[\alpha]_D$ −96.4° (c = 0.44, chloroform).

IR (KBr): 1710 and 1730 cm^{-1} (carbonyl).

$C_{27}H_{26}O_7$ (462.5). Calcd. C 70.11; H 5.67. Found C 70.92; H 5.75%.

Benzyl 3-O-benzoyl-4,6-O-benzylidene-2-O-methyl-β-D-glucopyranoside

To a cold mixture of **2** (50 mg) in dichloromethane (2 ml) and boron trifluoride etherate (0.04 ml) a dichloromethane solution of diazomethane (prepared from 250 mg of nitrosomethylurea) was added at −5 °C and the solution was allowed to stand at 0 °C for 1 hr. It was then diluted with dichloromethane (10 ml), filtered and the filtrate washed with $NaHCO_3$ solution and water. After drying (Na_2SO_4) the solution was evaporated and the residue crystallized from ethanol (1 ml) to obtain pure crystalline **5** (26 mg; 50%), m.p. 150—152 °C, $[\alpha]_D$ −88.2° (c = 0.38, chloroform). R_f 0.70 (benzene–methanol, 98 : 2).

IR (KBr): 1720 cm^{-1} (carbonyl). In the interval of 3500—3200 cm^{-1} there was no OH absorption band.

2 mg of **5** was successively saponified, hydrogenated in the presence of Pd/C-10%, reduced with $NaBH_4$, and acetylated. R_T 11.69 min. (1,3,4,5,6-penta-O-acetyl-2-O-methyl-D-sorbit).

Benzyl 2-O-benzoyl-4,6-O-benzylidene-3-O-methyl-β-D-glucopyranoside (6)

Compound **3** (230 mg) was methylated in dichloromethane (5 ml) as described above, for **5**. The crystalline residue was recrystallized from ethanol (3 ml) to give **6** (115 mg; 49%), m.p. 170—172 °C, $[\alpha]_D$ −58.9° (c = 0.2, chloroform). R_f 0.68 (benzene–methanol, 98 : 2).

IR (KBr): 1730 cm^{-1} (carbonyl).

2 mg of **6** was converted into the corresponding alditol acetate. R_T 12.18 min. (1,2,4,5,6-penta-O-acetyl-3-O-methyl-D-sorbit).

Examination of acyl migration in benzyl 3-O-benzoyl-4,6-O-benzylidene-β-D-glucopyranoside (2)

A solution of **2** (0.5 g) in 25 ml of acetone was mixed with 0.05*M* NaOH solution (25 ml), and the mixture was allowed to stand at room temperature for 15 min. It was then poured into ice-water (150 g), filtered and the crystalline product obtained was washed until neutral and recrystallized from methanol to afford benzyl 2-O-benzoyl-4,6-O-benzylidene-β-D-glucopyranoside **(3)** (0.23 g; 46%), m.p. 153—156 °C, $[\alpha]_D$ −95° (c = 0.40, chloroform).

Benzyl 4,6-O-benzylidene-α-D-glucopyranoside (7)

Benzyl α-D-glucopyranoside (5.35 g) was shaken with freshly fused $ZnCl_2$ (4.30 g) and benzaldehyde (15 ml) for 20 hrs. It was then poured into ice-water and the solid material which precipitated was washed with n-hexane (30 ml) to remove the excess of benzaldehyde. The crude product was crystallized from ethanol (50 ml) to give pure **7** (5.63 g; 79.4%), m. p. 155—157 °C (lit. [19] m.p. 152 °C), $[\alpha]_D$ +99.8° (c = 0.58, chloroform) (lit. [19] $[\alpha]_D$ +51° (c = 3.0, chloroform)).

$C_{20}H_{22}O_6$ (358.4). Calcd. C 67.02; H 6.18. Found C 66.90; H 6.25%.

Benzoylation of benzyl 4,6-O-benzylidene-α-D-glucopyranoside (7)

Compound **7** (5.0 g) was benzoylated with N-benzoylimidazole (prepared from 1.94 g of imidazole and 1.90 g of benzoyl chloride in 60 ml of chloroform) as described above for **1**. The crystalline product (4.9 g) was chromatographed on Kieselgel G (150 g) using a benzene–methanol (99 : 1) system as the eluant.

R_f 0.84 fraction: **Benzyl 2,3-di-O-benzoyl-4,6-O-benzylidene-α-D-glucopyranoside (10).** 0.75 g (9.5%), m.p. 121—123 °C (from ethanol), $[\alpha]_D$ +98.1° (c = 0.5, chloroform).

$C_{34}H_{30}O_8$ (566.6). Calcd. C 72.07;H 5.33. Found C 72.15; H 5.40%.

R_f 0.23 fraction: **Benzyl 2-O-benzoyl-4,6-O-benzylidene-α-D-glucopyranoside (8).** 2.55 g (40%) m.p. 63—64 °C (from ethanol), $[\alpha]_D$ +109.5° (c = 0.82, chloroform).

IR (KBr): 3400 cm^{-1} (hydroxyl), 1720 cm^{-1} (carbonyl).
$C_{27}H_{26}O_7$ (462.5). Calcd. C 70.11; H 5.67. Found C 70.85; H 5.78%.

R_f 0.30 fraction: **Benzyl 3-O-benzoyl-4,6-O-benzylidene-α-D-glucopyranoside (9).** 0.75 g (11.8%) m.p. 182—183 °C (from ethanol), $[\alpha]_D$ +46° (c = 0.53, chloroform).
IR (KBr): 1700 cm^{-1} (carbonyl).
NMR (in $CDCl_3$): δ = 7.89—7.26 (m, 15H, arom.); 5.51 (t, 1H, C_3-H); 5.38 (s, 1H, C*H*-Ph); 4.94 (d, 1H, C_1-H, $J_{1,2}$ = 1.8 Hz); 4.58 (q, 2H, benzyl); 4.46—3.48 (m, 5H, skeleton protons); 2.38 (broad, 1H, C_2-OH).
$C_{27}H_{26}O_7$ (462.5). Calcd. C 70.11; H 5.67. Found C 70.89; H 5.85%.

Benzyl 2-O-benzoyl-4,6-O-benzylidene-3-O-methyl-α-D-glucopyranoside (11)

Compound **8** (100 mg) was methylated with diazomethane in dichloromethane (2 ml) in the presence of boron trifluoride etherate (0.08 ml) as described above for **5**. Recrystallization of the crystalline residue from ethanol (5 ml) gave **11** (50 mg; 48%), m.p. 108—109 °C, $[\alpha]_D$ +133° (c = 0.38, chloroform), R_f 0.42 (benzene–methanol, 99 : 1).
IR (KBr): 1720 cm^{-1} (carbonyl).
5 mg of **11** was converted into 1,2,4,5,6-penta-O-acetyl-3-O-methyl-D-sorbit in the usual manner (R_T 12.15 min).

Benzyl 3-O-benzoyl-4,6-O-benzylidene-2-O-methyl-α-D-glucopyranoside (12)

Compound **9** was methylated with diazomethane as described above for **11**. 60 mg of **12** was obtained after crystallization of the syrupy crude product from ethanol (5 ml) (58%), m.p. 184—185 °C, $[\alpha]_D$ +55° (c = 0.44, chloroform), R_f 0.58 (benzene–methanol, 99 : 1).
IR (KBr): 1720 cm^{-1} (carbonyl).
NMR (in $CDCl_3$): δ = 7.89—7.26 (m, 15H, arom.); 5.73 (t, 1H, C_3-H); 5.40 (s, 1H, C*H*-Ph); 5.02 (d, 1H, C_1-H, $J_{1,2}$ = 1.4 Hz); 4.68 (q, 2H, benzyl); 4.25—3.42 m, 5H, skeleton protons); 3.32 (s, 3H, C_2-OCH_3).
5 mg of **12** was converted into 1,3,4,5,6-penta-O-acetyl-2-O-methyl-D-sorbit in the usual manner (R_T 11.66 min).

Examination of acyl migration in benzyl 2-O-benzoyl-4,6-O-benzylidene-α-D-glucopyranoside (8)

A solution of **8** (0.50 g) in acetone (25 ml) was mixed with 0.05*M* NaOH solution (25 ml) and the mixture was allowed to stand at room temperature for 1 min. It was then poured into ice-water, filtered and the solid which precipitated was washed with water until neutral: it was then recrystallized from ethanol (9 ml) to afford 375 mg (75%) of benzyl 3-O-benzoyl-4,6-O-benzylidene-α-D-glucopyranoside. (**9**), m.p. 182—183 °C, $[\alpha]_D$ + 46.8 ° (c = 0.62, chloroform). R_f 0.31 (benzene–methanol, 99 : 1).
IR (KBr): 1700 cm^{-1} (carbonyl).

*

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POLYMERIZATIONS IN LIQUID CRYSTALS, I

VINYL OLEATE

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Kinetics of polymerization of vinyl oleate was studied in the liquid, liquid crystalline (two types of smectic), and solid crystalline states. It was established that the rate of polymerization was the lowest, but the polymer showed the most regular structure in the smectic liquid crystalline state being a high-molecular weight crystalline product. In the liquid states, only oligomers are formed because of the dominating degradative chain transfer. In solid state the polymerization proceeded probably by ionic mechanism producing lower molecular weight products.

In the investigations of solid-state polymerizations, it was established in our laboratories that, besides a favourable prearrangement of the molecules, a suitable molecular mobility was required for the polymerization processes. It was observed that polymerizations proceeded more rapidly in the supercooled liquid state since a prearrangement before the crystallization and an appropriate molecular mobility were simultaneously realized [1]. In the light of these observations, it seemed particularly promising to discover the regularities of polymerization processes in the mesomorphous liquid crystalline state [2]. As a result of our previous studies, polymerizations of cetyl vinyl ether [3] and cholesteryl acrylate [4, 5] in the solid and liquid crystalline state were reported.

Studies on the synthesis and characterization of liquid crystalline monomers were opened with vinyl oleate as model compound in 1965. Just as the experimental work was completed, AMERIK and KRENTSEL [6, 7] published their results on the polymerization of vinyl oleate which delayed the presentation of our results. Since that time, however, a lot of our experimental work has accumulated about the polymerization processes in the liquid crystalline state. It led us to the conception to present the observations concerning vinyl oleate before the publication of these results.

Experimental

Vinyl oleate was prepared by transesterification of vinyl acetate by oleic acid according to ADELMAN [8]. Characteristics of the product are as follows: boiling point: 205 °C at 4 torr, $n_D^{30} = 1.4533$, $d_4^{30} = 0.8725$ g · cm^{-3}. $R_M = 95.32$ (theoretical: 95.28), C% = 77.80 (theoretical: 77.60%), H% = 11.25 (theor: 11.37%)

* Included some notable results of her graduation thesis prepared at the Department of Plastics and Rubbers, Technical University of Budapest, in 1967.

Characteristic transformation temperatures of vinyl oleate were determined by optical (using Zeiss polar microscope), differential thermal analytical, and viscometric (in Höppler consistometer) methods [3, 4, 9]. Changes in the density were detected by dilatometry of 25 g of the material.

Polymerizations were carried out in glass ampoules under N_2 atmosphere desoxygenated by freezing either by Co γ ray or by AZBN initiation. Conversions were determined gravimetrically by precipitation of the polymer from the petroleum ether solution of the irradiated samples using methanol at -78 °C. Molecular weight of the polymers was measured by cryoscopy in benzene solutions.

X-ray diffractograms were recorded in Debye-Scherrer camera with radian diameter by Cu K-α radiation filtered by Ni. The sample preparations were sucked into 0.2 mm dia. capillary tubes and were temperated axially by air cooled in a dry ice/acetone bath. The temperature of the cooling air was monitored at the outlet by a copper-constantan thermocouple.

Results and discussion

DTA, dilatometric, polar optical, and viscometric results for the vinyl oleate monomer are shown in Fig. 1. It can be seen that vinyl oleate is an isotropic liquid above -8 °C; between -8 and -26 °C, it is in smectic I state; between -26 and -36 °C in smectic II state; below -36 °C, it is crystalline. Fig. 2 shows that the vinyl oleate can be characterized by batonet structure in the smectic I state at -10 °C while it has a focal-conic structure in the smectic II state at -30 °C. At -59 °C it is microcrystalline. These observations differ from those of AMERIK and KRENTSEL [6, 7] concerning their temperature values. They used only DTA measurements observing one transformation at -18 °C from isotropic liquid into crystalline liquid and another one at -45 °C into the crystalline structure, in the cooling period.

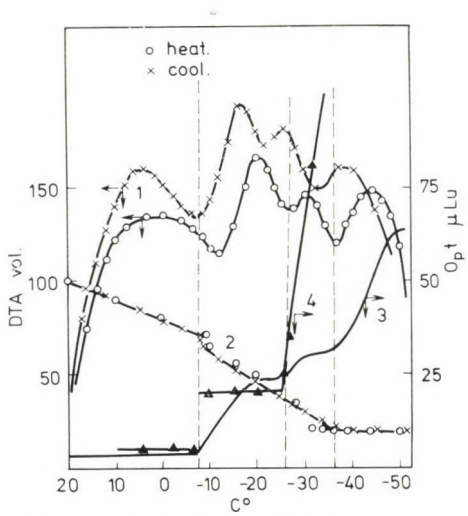


Fig. 1. Phase conditions of vinyl oleates. 1. DTA, 2. dilatometric, 3. depolarized light intensity, 4. viscosity change by the temperature

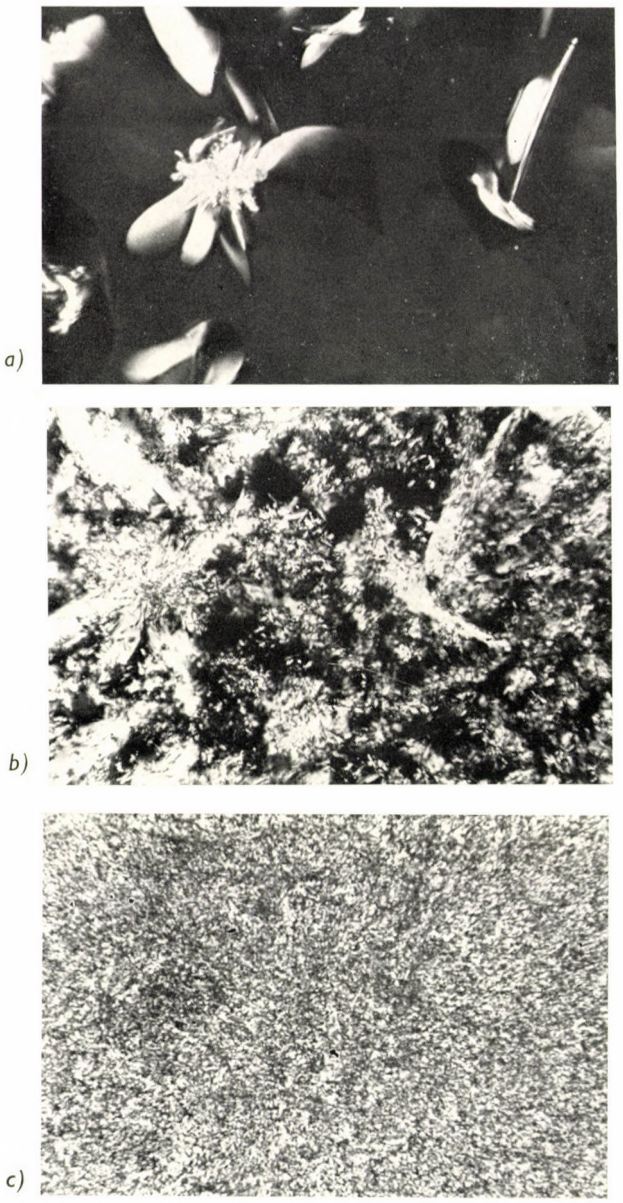


Fig. 2. The polaroptical pattern of vinyl oleate. a) −10 °C, b) −30 °C, c) −59 °C Magnification: ×150

During heating, one transformation was recorded, from the crystalline into the liquid crystalline state at −32 °C. They failed to present the structure and type of the liquid crystalline state. FARINKA-MARTINS [10] also detected two mesomorphous states.

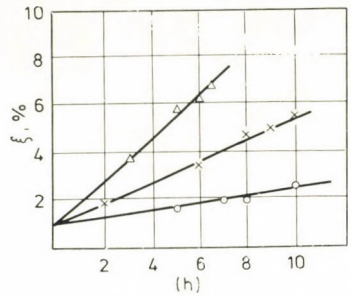


Fig. 3. The kinetic curves of vinyl oleate in the liquid state at 80 °C (△), 72 °C (×) and 60 °C (○) initiated by 0.5% w/w of azobis-(isobutyronitrile)

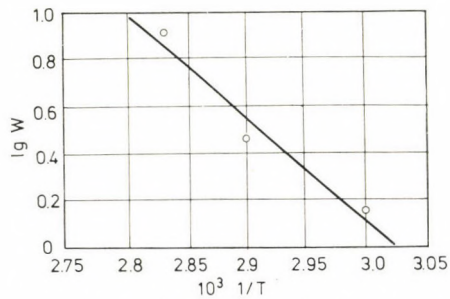


Fig. 4. The temperature dependence of the polymerization rate of vinyl oleate initiated by azobis-(isobutyronitrile) in liquid state

We found a shift in the range of the liquid crystalline state in the presence of polymer. At a polymer content of 3%, the range of the liquid crystalline state is between —18 and —43 °C (in agreement with the values given by AMERIK and KRENTSEL) while for 30% of polymer, these limit values are —21 and —52 °C.

Figure 3 presents the kinetic curves for the polymerization of vinyl oleate in the liquid state initiated by 0.5% w/w azobis-(isobutyronitrile). The rates of liquid-phase polymerizations are shown in Fig. 4 as a function of temperature. The overall activation energy of the polymerization is 80 kJ/mole. The polymer prepared is a light yellow transparent soft material, at room temperature suggesting amorphous structure and low molecular weight.

Figure 5 shows the kinetic curves for the gamma-ray-induced polymerizations of vinyl oleate at various temperatures. It can well be observed that the rate of polymerization is the highest in the liquid state at 40 °C than in the solid state at —196 and —78 °C. The next one in the order of the polymerization rates is that at 0 °C, *i.e.* the polymerization in the liquid state followed by those in the liquid crystalline state coinciding the rates of polymerizations

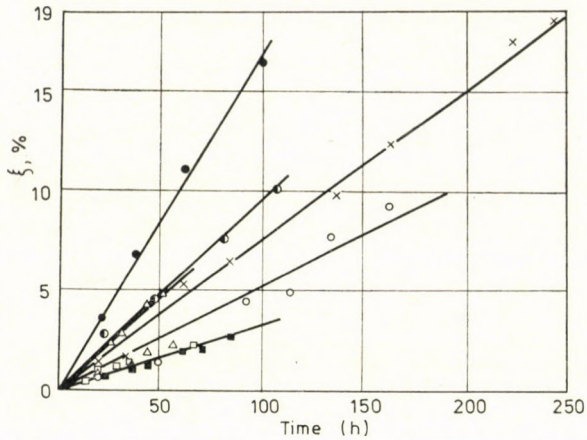


Fig. 5. The polymerization kinetical curves of vinyl oleate initiated by γ-rays at 0 °C (○), 25 °C (◐), 40 °C (●), −12 °C (△), −25 °C (■), −34 °C (□), −78 °C (×) and −196 °C (▲). Dose rate: $6.6 \cdot 10^4$ rad/h

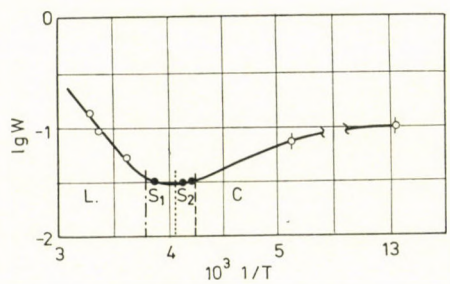


Fig. 6. The temperature dependence of the polymerization rate of vinyl oleate initiated by Co γ rays. ○ = liquid, ● = liquid crystalline, ⊖ = solid state

measured at three different temperatures practically on the same straight line. Fig. 6 illustrates the temperature dependence of the polymerization rates. The overall activation energy of the radiation-induced liquid-state polymerization is 24 kJ/mole. It is in fair agreement with the overall activation energy of the polymerization initiated by azobis-(isobutyronitrile) considering that the activation energy of the thermal decomposition of azobis-(izobutyronitrile) is about 130 kJ/mole.

Even the rates of polymerizations presented here deviate from those found by AMERIK and KRENTSEL. They measured the highest polymerization rate at −25 °C, *i.e.* in the liquid crystalline state. They observed lower rate at 0 °C in the liquid state and the lowest value at −78 °C in the solid state. This considerable difference may be caused by the fact that AMERIK and KRENTSEL followed the conversion by measuring the changes in the refraction

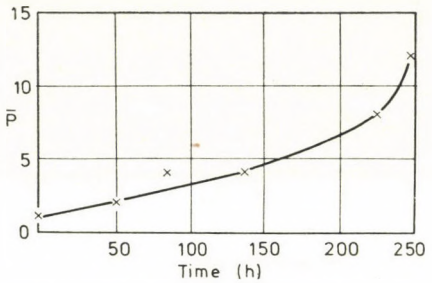


Fig. 7. The conversion dependence of the molecular weight of poly vinyl oleate prepared in the solid state at −78 °C by γ-ray initiation. Dose rate: $6.6 \cdot 10^4$ rad/h

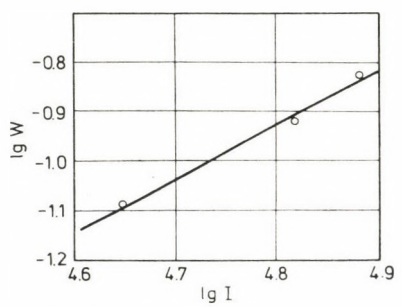


Fig. 8. The dose rate dependence of the solid state polymerization of vinyl oleate at −78 °C

index of the polymerizing system in contrast with our gravimetric measurements of the prepared polymer. Molecular weight and structure of the polymers formed in the three different states differ considerably from each other. Consequently, it is probable that the changes in the refraction index detect not only the conversion but they reflect the regular or irregular structure of the polymer product and its isomorphism with the monomer too.

During the liquid-state polymerization of vinyl oleate, only oligomers are formed. It may be attributed to the enhanced mobility of methylene groups in alpha position to the double bond of the unsaturated fatty acid substituent, thus the substitution reaction of the propagating radical with the mobile hydrogens (degradative chain transfer) may compete with the propagation reaction at a commensurable rate. It can be supported by earlier investigations on vinyl oleate [11, 12] where the inhibiting effect of 10% of vinyl oleate was revealed on the polymerization of vinyl stearate.

In the solid-state polymerization of vinyl oleate, essentially oligomers are formed as well. Fig. 7 shows the dependence of the degree of polymerization on the conversion for polymers obtained at −78 °C. The rate of the radia-

Table I

X-ray diffraction identity periods of vinyl oleate in A units and of poly (vinyl oleates) formed in different phases

Subst.	VO (—20 °C)	VO (20 °C)	PVO—L	PVO—LQ	PVO—S
m. p. °C	—8(S1), —16(S2) —36(C)		—20	38—40	25—30
d(001)	?	?	27.7	?	?
d(003)	—	—	—	8.83 m	8.30 m
d(100)	—	5.50 v.s.	—	—	—
d(110)	—	—	4.45 v.s.	4.58 v.s.	4.45 v.s.
d(111)	4.15 v.s.	—	4.15 v.s.	4.15 s	4.14 s
d(020)	3.68 m	3.66 m	—	—	—
	—	3.30 m	3.30 m	3.31 m	—
	—	—	—	3.16 w	3.16 m
	—	—	3.10 w	3.09 w	—
	—	—	—	2.47 w	—
	—	—	—	2.21 v.w.	—
	—	—	—	2.11 v.w.	—

? = Non appraisable because of shielding by the screening shade
v.s. = very strong,
s = strong,
m = medium,
w = weak,
v.w. = very weak.

tion-induced solid-state polymerization is proportional to the 1.1 power of the dose rate which appears to exclude the possibility of a bimolecular termination (Fig. 8).

Polymers obtained in the smectic liquid crystalline state have higher molecular weight and crystalline structure. The principal characteristics of oligomers and polymers produced in different ways are collected in Table I. It is well perceptible from the data that the structural differences are reflected both in melting points and in X-ray diffraction angles recorded at ambient and subambient temperatures. It should be noted that polymers obtained either in the solid or in the smectic state are birefringent and have sharp melting point. According to the X-ray diffraction measurements, the polymer produced in the solid state represents a smectic structure exhibiting ortho-

rhombic subcells whereas that from the liquid crystalline state shows an orthorhombic crystalline structure identical to that of the paraffins. A similar structure was indicated for the cetyl vinyl ether below −12 °C [3].

The structure of smectic materials was discussed by SACKMANN and DEMUS [13], CHISTYAKOV [14], DE VRIES and FISCHEL [15], and DOUCHET *et al.* [15]. By a comparison with their X-ray diffractograms, the diffraction patterns of vinyl oleate and poly(vinyl oleate) suggest that the structure of the monomer in the smectic I and II states is S_A and S_C, respectively, while that of the polymer formed in the liquid and solid state is S_A again and S_E, respectively.

It should be noted now that the monomer encapsulated in the capillary tube was reheated to +20 °C after its chilling at −20 °C. The X-ray diffraction pattern of this sample was amazing showing sharp reflexions (*cf.* Row 2 of Table I). An exact interpretation of this phenomenon cannot be given at present.

As a conclusion of these experimental results, the prevalence of the topotactic factor has well been evinced by the polymerizations in three states. In the liquid state, the allylic double bonds in the carbon chain can get into contact with the radicals formed on the vinyl ester which hinders the formation of high-molecular polymer chains. In the liquid crystalline states the double bonds in the side chain and on the vinyl ester are sterically separated, due to the gathering of molecules into layers, so polymers with higher molecular weight are formed. In solid state the activation energy of polymer formation is negative, the molecular weights turn to be decreased. The topochemical behaviour did not change markedly by this transformation, therefore it seems to be highly probably that the process is mainly ionic.

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RECENSIONES

L. Barcza: *The hydrogen bond* (In Hungarian)
A kémia újabb eredményei 31. kötet

(Editor: Csákvári Béla)

Akadémiai Kiadó, Budapest, 1976. 175. pages, 10 figures

The author deals with the physical-chemical phenomena accompanying the development of inter- and intramolecular hydrogen bonds, the nature of the hydrogen bond, its thermodynamical characteristics, and the theoretical results and problems connected with the above-mentioned topics are also surveyed.

In the introductory part (22 pages), the definition, the problems involved in it and the preconditions of the formation of the hydrogen bond are considered, then the systematic classification of inter- and intramolecular bonds is given.

In the second part of the book, the author gives a very interesting and valuable summary of the phenomena accompanying the formation of the hydrogen bond, as well as the respective experimental methods (90 pages). The simple physical-chemical anomalies are discussed appearing in the gas and liquid phase and in mixtures (solution) due to the formation of hydrogen bonds (in density, solubility, melting point, boiling point, surface tension, viscosity, etc.). Methods suitable for studying the nature of hydrogen bonds, including techniques based on the measurement of simple physical properties, as well as the results and possibilities provided by the various spectroscopic techniques (IR, UV, NMR), are reviewed.

Thermodynamics of hydrogen bond is discussed in about 10 pages, with particular attention to the correlation of enthalpy and entropy values. Hydrogen bonds in solid state are shortly mentioned, then the bond theory is applied to the problems discussed in previous chapters of the book.

The book provides a comprehensive information. The 236 references indicate the wide field discussed. A particular value of the book is the presentation of 60 tables which allows evaluation of the results of various authors, methods and thus gives a good summary of valuable information. The book calls attention to a field rather neglected but gaining an increasing importance now.

F. Ratkovics

Structure and Bonding. Volume 25. *Rare Earths.*

Springer-Verlag, Berlin—Heidelberg—New York, 1976. 154 pages

Volume 25 of this very successful book series deals with the problems of the structure of compounds of lanthanides and actinides, and presents three reviews.

In a short monograph (consisting of 18 pages) by C. K. Jørgensen on "Narrow Band Thermoluminescence of Rare Earths in Auer Mantles" the author active in this field

gives a comprehensive survey of researches dealing with the "narrow band thermoluminescence" of the rare earth metals. The author presents a number of facts of importance both from theoretical and practical aspects on the light emission of the mixed oxides of lanthanides at high temperature which emission occurs in a way similar to that of Auer mantles. The comparison with the d-group elements, the discussion of the hypersensitive transitions and the chapter treating the problems of the applicability of burners of this type in illuminating engineering are of particular interest.

The structural layout of the monograph, however, is not fortunate. First of all, the theoretical introduction is objectionable. The author begins the discussion with elementary, historical spectroscopical concepts (such as Fraunhofer lines, activity of BUNSEN and KIRCHOFF) From this one might conclude that the monograph is intended for readers hardly versed in this field. However, in this case it would be necessary to clearly define at least the concept of luminescence and within this that of thermoluminescence mentioned in the title of the monograph since this latter term is used by the author *not* in its most widespread sense. (Release of stored energy originating from an earlier energy transfer, *e.g.* from radioactive radiation, in the form of light, on the effect of heating.) This is mentioned only at the end of the monograph, and that is too late from the aspect of understandability, alluding to the remark by Professor REISFELD point to the use of the term in question. It would have been more unequivocal to denote the discussed phenomenon by the alternative name "narrow spectral band incandescence" given at the end of the text.

The 46-page review by E. C. BAKER, G. W. HALSTEAD and K. N. RAYMOND entitled "The Structure and Bonding of 4f and 5f Series Organometallic Compounds" presents an excellent survey of the synthesis, kinetic stability and other chemical properties of the compounds mentioned in the title, and the structural data concerning these compounds are given in detail. It is pointed out by the authors that the formal coordination number is a function of the ligand system. The structural parameters and chemical properties of the organometallic compounds of the 4f and 5f series indicate that these compounds are representing a transition between the compounds of covalent character of the d-groups and the properties of the carbocyclic alkali metal salts of ionic character. The rules derivable from the VSEPR theory are essentially well applicable to the molecular geometry of the discussed compound (it would have been fortunate if the authors had mentioned this circumstance in their text!). For the group of the organometallic compounds of isostructural lanthanides and actinides empirical relationships are presented by the authors as regards the bond distances and coordination numbers.

The 81-page detailed review by S. P. SHINHA entitled "Structure and Bonding in Highly Coordinated Lanthanide Complexes" deals with the properties of lanthanide compounds with low and high coordination numbers. Obviously, coordination numbers below six are rather rare among the lanthanides, and thus the aim set by the author, *i.e.* the study of the relationship between the structural parameters and the chemical bond, is attained in fact in the knowledge of the data concerning the compounds having a higher coordination. According to the VSEPR theory, no given preferred structure can be expected in the case of compounds having higher coordination numbers; data of the literature confirm actually the existence of structures having diversified symmetries. The most valuable feature of this study is the full and detailed presentation of the literature of the discussed field of themes.

B. CSÁKVÁRI

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РЕЗЮМЕ

Зависимость продуктивности спектрохимических методов от разрешающей способности спектрографов, II

К. ФЛОРИАН и М. МАТЕРНИ

Параметрами, характеризующими спектрохимические методы анализа, являются относительная чувствительность, относительная точность определения концентрации и предел обнаружения. Изучалась их зависимость от увеличения теоретической разрешающей способности спектрографа. Прежде всего, были получены оптимальные величины почернения фона. Изменение теоретической разрешающей способности было достигнуто изменением порядка дифракции, использованием решеток с разным числом штрихов на 1 мм и, наконец, использованием, так называемого, двойного перехода луча спектрографом.

Было установлено, что повышение теоретической разрешающей способности от приблизительно $4 \cdot 10^4$ до $1{,}8 \cdot 10^5$, связанное со снижением обратной линейной дисперсии, ведет к постепенному повышению относительной чувствительности, вплоть до достижения оптимального значения ($B_x = 1$). Наиболее высокие значения относительной точности определения концентрации и предела обнаружения были получены при теоретической разрешающей способности $R_{теор.} = 10^5$. Теоретически обосновано, а также доказано на практических результатах, что дальнейшее повышение разрешающей способности не ведет к дальнейшему улучшению результатов. Хотя использование двойного перехода луча уменьшает в два раза обратную линейную дисперсию, однако, улучшения результатов аналитических методов не удалось достигнуть в ожидаемой мере, т. к. имеет место эффект светорассеяния. Переход к спектрам более высоких порядков и использование решетки с большим числом штрихов на 1 мм более значительно повышают точность результатов аналитических методов.

При постоянной теоретической разрешающей способности спектрографа наиболее эффективно на результаты анализа влияет коэффициент отражательной способности решетки.

Комплексы Co(II), Ni(II), Zn(II) и Hg(II) с хелатным тридентатным лигандом этил 2-циан-3,4-дифенил-4-гидроксикротонатом

Б. Б. МОХАПАТРА, Б. К. МОХАПАТРА и С. ГУРУ

Были синтезированы комплексы с составом ML_2, где M = Co(II), Ni(II) и с составом MLCl, где M = Zn(II) и Hg(II), а L-тридентатный лиганд — этил 2-циан-3,4-дифенил-4-гидроксикротонат (полученный конденсацией бензоина с эфиром цианоуксусной кислоты). Согласно данным анализа, проводимости, магнитной восприимчивости, ИК и электронным спектрам, комплексы Co(II) и Ni(II) являются октаэдрическими, а комплексы Zn(II) и Hg(II) — тетраэдрическими.

Комплексы шиффовых оснований с титаном(III) и ванадием(III)

С. Ф. Х. РИЗВИ и Н. АХМАД

Комплексы титана(III) с бис-(2-метоксибензилиден)-дианизидином, бис-(2-метоксибензилиден)-бензидином, бис-(бензилиден)-бензидином, бис-(ацетилацетон)-бензидином, бис (ацетилацетон)-этилендиимином и бис-(ацетилацетон)-дианизидином, а также ванадия(III) с бис-(бензилиден)-о-бенилендиимином и бис-(2-метоксибензилиден)-о-фенилендиимином были синтезированы и охарактеризованы на основе данных элементарного анализа, точек плавления, молярной проводимости, термогравиметрического анализа и ИК-спектров. Для всех комплексов было обнаружено отношение 1 : 1 (шиффово основание: металлическая соль) и лишь один хлор находится вне координационной сферы.

Магнитные и спектральные исследования комплексов переходных металлов с DL-α-аминомасляной кислотой

ДЖ. П. Н. СРИВАСТАВА и М. Н. СРИВАСТАВА

Были проведены магнитные и спектральные (ИК, УФ и спектры отражения) исследования комплексов Cu(II), Ni(II), Zn(II) и Pd(II) с DL-α-аминомасляной кислотой, которая координируется через аминовый азот и карбоксилатный кислород. Комплексы Cu(II) и Ni(II) парамагнитны; магнитный момент последних равен 1,92 и 3,28 В. М., соответственно. Исходя из спектральных исследований было заключено, что комплексы Cu(II) и Ni(II обладают шестикратной координацией, а комплексы Zn(II) и Pd(II) — четырехкратной. Это также указывает на присутствие двух координированных молекул воды в комплексе Ni(II), обладающем, вероятно, искаженной октаэдрической структурой. Комплекс Pd(II) имеет квадратно-планарную структуру.

Комплексообразующее поведение тиосемикарбазидов и тиосемикарбазонов, I

Тетрагональные комплексы никеля(II) с 4-бензиламидотиосемикарбазидом и подобным тиосемикарбазоном

М. С. ДЖЭЙН и П. С. ДЖЭЙН

Были приготовлены некоторые новые комплексы никеля(II) с 4-бензиламидотиосемикарбазидом (БТСК) и 1-(α-фурил)-4-бензиламидотиосемикарбазоном (ФБТС) с кобще формулой NiL_2X_2 (где L = БТСК и ФБТС, а X = Cl, Br, J, NO_3 и NCS). Они были исследованы обычными химическими и физическими методами. Тетрагональная симметрия полагалась, исходя из данных магнитных и электроноспектральных измерений. Были рассчитаны различные параметры тетрагонального лигандного поля Dq(E), Dp(A) и Dt и параметры молекулярных орбиталей d_σ и d_π. Присутствие анионов в координированной сфере и биденатная природа лигандов подтверждались на основе дополнительных частот Ni—N, Ni—S и Ni—X, наблюдаемых в далекой ИК-области. Нитратная и тиоцианатная группы ведут себя как монодентаты и координированы через атомы кислорода и азота, соответственно.

Стереохимия реакций биополимеров, VI

Интерпретация стереоспецифичности гидролиза дипептида, катализированного ацилазой-I

Л. ЁТВЁШ, Э. МОРАВЧИК, ДЬ. МАДИ, Х. ТЮДЁШ и Ю. ТЕЛЕГДИ

Была исследована интерпретируется стереоспецифичность гидролиза дипептидов, катализированного ацилазой-I. В случае, когда α-углеродный атом N-концевой ацильной группы находится в D-конфигурации, группа R расположена ближе к каталитической

части фермента, нежели в случае L-соединаний. Стерические препятствия группы в реакции между каталитической частью фермента и группой CO субстрата намного большие в случае субстратов, содержащих пептиды с N-концевыми аминокислотами в D-конфигурации чем для тех же субстратов в L-конфигурации. В результате этого, скорость гидролиза первых на несколько порядков ниже скорости последних.

Полученные результаты интерпретируются на основе фиксированной конформации субстрата в фермент-субстратном комплексе. Вследствие закрепленного расположения концевой аммонийной группы и амиднокарбонильной группы, в двух диастереоизомерных соединениях взаимно изменяют свое положение лишь атом α-водорода и R-группа ацильного фрагмента.

Поиски новых местноанестезирующих препаратов, III

Синтез 2-алкилариламиноацетиламино-4-фенилтиазолов

П. К. СРИВАСТАВА, Р. Д. ШАРМА и С. К. РАИ

Были синтезированы серии различных 2-алкилариламиноацетиламино-4-фенилтиазолов и проверена их местноанестезирующая активность.

N-(3-Хиназолинио)-амидаты, IV

Фотохимия N-(3-хиназолинио)-амидатов в первичных спиртах

И. ФЕТТЕР, К. ЛЕМПЕРТ, Г. БАРТА-САЛАИ, Й. МЕЛЛЕР и Л ПАРКАНИ

Облучение соединений, упомянутых в заглавии *(8а—д)*, в этиловом и бензиловом спиртах приводит к образованию шести типов гетероциклических продуктов превращений *(9—14)*, наряду с амидами типа *15*. Выход соединений *9—15* в значительной степени зависит от природы заместителей в исходных амидатах *(8)*, а также от того, что облучение происходит в присутствии или в отсутствии кислорода. Образование процуктов, аналогичных типам *11—14*, до сих пор еще не наблюдали при облучении гетероциклических аммониоамидатов. Предлагается интерпретация образования всех типов фотопродуктов.

Метиловые эфиры углеводов, IX

Усовершенствованный синтез 2-O-, 2,6-ди-O- и 2,4,6-три-O-метил-D-маннoз

А. ЛИПТАК, А. БОБАК и П. НАНАШИ

Гидрогенолиз бензил *экзо*-2,3 : 4,6-ди-O-бензилиден-α-D-маннопиранозида *(2)* с помощью 1,1 моля реагента $LiAlH_4—AlCl_3$ дает бензил 3-O-бензил-4,6-O-бензилиден-α-D-маннопиранозид *(3)*. Каталитическое гидрирование соединения *6*, полученного метилированием *3*, приводит к образованию 2-O-метил-D-маннозы *(7)*. Гидрогенолиз 4,6-O-бензилиденового кольца соединения *6* дает соединение *8*, из которого путем успешного метилирования и каталитического гидрирования было получено соединение *10*. Гидрирование соединения 12, полученного метилированием 11, приводит к образованию соединения 13.

Синтез и исследование миграции ацила в частично бензоилированных производных бензил 4,6-O-бензилиден-α- и -β-D-глюкопиранозидов

А. ЛИПТАК, Э. ЧИК и П. НАНАШИ

Бензоилирование, бензил 4,6-O-бензилиден-β-D-глюкопиранозида *(1)* с помощью 1,1 моля N-бензоилимидазола приводит к образованию 3-O-бензоильных *(2)* и 2-O-бензоильных *(3)* производных с выходом 30—30%. α-Аномерсоединения *1 (7)* при тех же самых

условиях дает 2-О-бензоат *(8)* в качестве основного продукта с выходом 50% и 3-О-бензоат *(9)* с выходом 10%. В щелочном ацетоне *2* и *8* превращаются в *3* и *9*, соответственно, вероятно через промежуточные продукты типа ортоэфира. Структура продуктов подтверждалась на основе их ИК и ЯМР спектров.

Полимеризация в жидких кристаллах, I

Винилолеат

ДЬ. ХАРДИ, Ф. ЧЕР, Н. ФЕДОРОВА и М. БАТКИ

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QUANTITATIVE DETERMINATION OF TRACE ELEMENTS IN SILICATE BASED SUBSTANCES BY SPECTROGRAPHIC METHODS USING CONTINUOUS SOLUTION FEED, 1

STUDY OF SEVERAL FACTORS AFFECTING THE PROPERTIES OF THE RADIATING PLASMA+

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For the quantitative determination of components at low concentrations in silicate matrices three spectrographic techniques of solutions have been selected and the optimum working conditions for these have been established. The influence of the gas atmosphere has been studied. The interelement effects most significant in the analysis of solutions are discussed. The analytical efficiency of the techniques studied can be enhanced by the use of an argon atmosphere. This is true first of all with the rotating disk technique. The tube-electrode spray method, and the rotating disk technique are less sensitive to the changes of the concentration of alkali metal additives introduced with the sample than is the stabilized d.c. arc excitation method.

Introduction

The importance of the quantitative determination of trace amounts of elements present in silicate based substances is steadily increasing, notably in the service of endeavours to utilize best the raw materials available, to study the qualities of special commercial products, to intensify and increasingly chemicalize agricultural production. For these determinations emission spectrography has proved suitable because this method has the following advantageous characteristics.

— Several, in principle any number of elements simultaneously present can be determined.

— No previous separation processes are generally needed, *i.e.* the work required for the preparation of a sample is not laborious.

— Spectrography produces a record of the analyses the evaluation of which can be repeated at any time or can be repeated with some other purposes in view.

There are several aspects which make the dissolving of the solid sample expedient:

+ The substance of this series of papers forms part of the doctoral thesis of A. DOMBI, prepared at the University of Chemical Engineering, Veszprém, 1975.

— the sample prepared is homogeneously distributed;

— the differences due to structural diversities (crystal structures) of the various samples are eliminated;

— it is possible to prepare standard reference samples with the same physical and chemical properties;

— the interelement effects are less pronounced, respectively, these can be counterbalanced more easily.

Selection of technique, and of experimental conditions

A continuous feed of the sample solution has been practised in these investigations. At a suitable and uniform rate of solution feed stationary processes are attained in the course of excitation, and, generally, such processes are more advantageous for quantitative work than the phenomena that produce emission variable in space and time when batchwise sample feeding is practised [1]. When selecting among methods, we considered the need that the selected one should be applicable to serial routine analyses in a wide range of practical cases, that it should not require highly sophisticated equipment, and that it should be simple to carry out.

On the basis of these considerations the following three techniques have been selected:

— rotating disk technique [2]

— tube-electrode spray method according to ERDEY—GEGUS—KOCSIS [3],

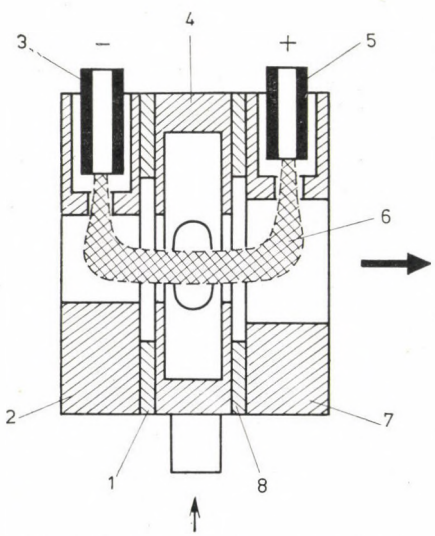


Fig. 1. Radiation source worked by stabilized d.c. arc excitation according to MARINKOVIČ: 1, 8: Isolator disks; 2, 7: water-cooled brass segments; 3: carbon cathode; 4: chamber for the introduction of the aerosol; 5: graphite anode; 6: arc plasma

— low current d.c. arc excitation stabilized by ag as stream, proposed by MARINKOVIČ [4].

In this selection we have arc excitation that generally shows better detection power, and we have also spark excitation that assures better reproducibility, thus the comparison of the methods in respect also to these features comprises a wider range.

In the cases of all these three radiation sources the spectrograms were recorded at the following optical, and photographical parameters.

Spectrograph: plane-grating, Ebert arrangement (Zeiss PGS 2), with 290 nm blaze-wavelength in the 1st order (651 grooves/mm).
Illumination: intermediate, achromatic.
Slit width: 0.020 mm.
Three-step filter: 100/50/10 per cent.
Emulsion: fine-grain, hard (Agfa-Gevaert Scientia 34B50).
Developing: Kodak D—19, 4 min, at 20°C.
Densitometry: with a micro-photometer, S-scale (Zeiss G II).
Blackening transformation: *l*-transformation [5].
The optimum excitation conditions found for the several radiation sources are the following.
For the tube-electrode spray method,
atomizing: with a pneumatic nebulizer, type EGK-G [1], argon, or nitrogen gas at 160 .. 200 litre/hour volume rates; electrode system: lower tube-electrode (6 mm o.d., 4 mm bore), hemispherical counter-electrode (4.5 mm dia.), from spectrographically pure graphite (type RW 103); excitation: high-voltage spark according to Feussner, $U_{eff} = 12$ kV, $C = 12$ nF, $L = 1.5$ mH (Zeiss HFO-2); pre-sparking time: 60 s (while atomizing); exposure time: 120 s.
For the rotating disk technique,
electrode system: lower disk electrode, 20 mm o.d., 3 mm bore, 4 mm disk breadth (type SU 401), upper tube-electrode, 6 mm o.d., 2.5 mm bore (type SU 104); electrode gap: 2.5 mm; disk revolution: 10 min^{-1}; gas introduction: Ar (He, N_2) gas, 80 litre/hour volume rate, through the bore of the upper electrode; excitation: as in the case of the tube-electrode spray technique; pre-sparking time: in gas stream, without the solution, 60 s, then, with the solution, 90 s; exposure time: 120 s.
For stabilized d.c. arc technique,
electrode system: tubular form of both electrodes, 6 mm o.d., 3 mm bore, anode made of spectrographically pure graphite type RW 103, cathode of spectral pure carbon, type RW 203; electrode coolant: argon gas at 50 ... 80 litres per hour volume rate; stabilizing of the arc column: with argon gas at 160...220 litres per hour volume rate; stabilizer disk cooling with water at 40...80 litres per hour volume rate; atomizing: EGK—G type modified nebulizer, by the gas stream used for the stabilizing of the arc column; excitation: d.c. are 150 V and 4...6 A, over a loading resistor, voltage drop across electrodes about 80 V; pre-arcing time: while atomizing, 60 s; exposure time: 120 s.

Results and discussion

Among the factors that affect the behaviour of the radiating plasma we have studied the most important effects, from the point of view of trace analysis, of the changes of parameters due to the composition of the samples to be analysed and to the method of how the solutions are prepared, and further to the qualitative change of the gas atmosphere that forms the main substance of the plasma.

For these studies we chose elements of divergent physical, and chemical characteristics, thus our model solutions contained arsenic, boron, copper, cobalt, manganese, molybdenum, and zinc. The quantitative determination of these elements is important first of all for soil studies. Of each element a stock solution at a concentration of 0.1 g/litre in about a 7% (by weight) solution of hydrochloric acid was prepared.

The effect of the gas atmosphere

It is with the rotating disk technique that the effect of the qualitative change of the plasma-atmosphere is most important [6]. Use of a noble gas (Ar) atmosphere instead of air leads to the diminution of background radiation [7], to a better stability of the plasma [8], and a more effective excitation of the particles introduced into the plasma [9].

Under the experimental conditions described, in the rotating disk technique we introduced argon, or helium, or nitrogen gas through the bore of the upper electrode. The changes of the intensity-logarithms referred to figures recorded without a gas stream are shown in Table I.

Table I

Enhancement of the logarithmic intensity of several elements, due to gas flow, in the rotating disk technique

Element studied	Wavelength (nm) I atom line II ion line	Excitation energy (eV)	ΔY		
			Ar	He	N_2
As	I 234.9	6.59	0.883	0.876	0.152
	I 237.1	6.77	0.795	0.848	0.137
	I 303.3	6.40	0.427	0.412	0.120
Mo	II 281.6	6.06	0.915	0.944	0.143
	I 317.0	3.91	0.567	0.553	0.157
	II 329.2	6.91	0.848	0.869	0.161
B	I 249.6	4.96	0.745	0.685	0.086
	II 345.1	12.70	0.577	0.740	0.103

The following conclusions can be drawn from data in Table I.

— The gas stream increases intensity; noble gases do this in a substantially higher measure than does nitrogen.

— The intensity-increasing effect of the noble gases is enhanced by the increase of the excitation energy of the spectrum lines.

The cause of this phenomenon resides in the energy transmission role of the metastable excitation levels of the noble gases and also in the heat-transport differences due to different conductivities [10].

No substantial change (one greater than half an order of magnitude) was found with the tube-electrode spray method. Most probably the rate of the atomizing gas is much too high to allow the previously described phenomena to emerge. In an indirect way this seems to be proven by the finding that also with the rotating disk technique the line intensities decrease when the protecting gas velocity surpasses the optimum value (Fig. 2).

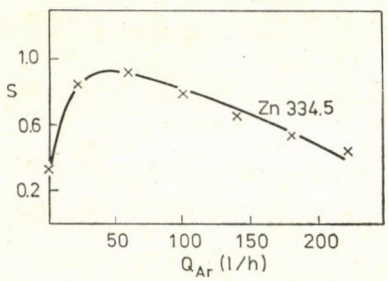


Fig. 2. Effect of the volume rate of the protective gas on the blackening of the spectrum lines in the case of the rotating disk technique

With low intensity stabilized arc excitation only argon gas is appropriate since some other stabilizing gas spoils the uniform performance of the radiation source.

Interelement effects

Among the foreign elements introduced in high quantities with the sample into the plasma generally the metals of low ionization energies play an important role [11, 12]. When non-conducting solid samples are brought into solution, a high amount of alkali metals gets into the solution, generally due to fusion. We studied the effect on the intensity of spectrum lines of increased concentrations of sodium as of an element of low ionization energy, in all the three techniques.

In spark excitation the increase of the concentration of sodium decreases slightly the intensity of the lines studied (Fig. 3). This experience might be kept in mind when solid samples are brought into solution. Increased concentrations of alkali metal additives increase the level and the scattering of background radiation, thereby the detection power of the methods is reduced.

In the case of stabilized, low intensity arc excitation the increase of the concentration of the sodium additive generally increases the intensity of the spectrum lines of the elements studied (Fig. 4).

The measure of this increase can be linked to the ionization energies of the elements studied. Irrespective of the excitation energies of the lines studied,

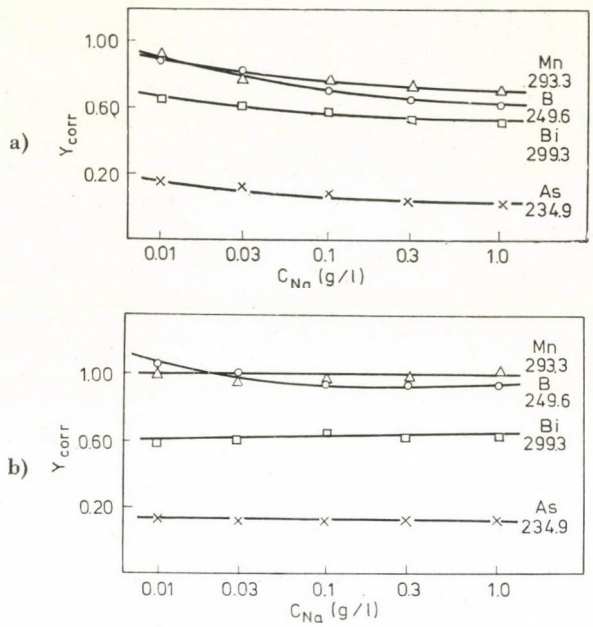


Fig. 3. Effect of the change of concentration of the sodium additive on line-intensities (Y_{corr}: intensity-logarithm corrected to background); a) tube-electrode spray method; b) rotating disk technique

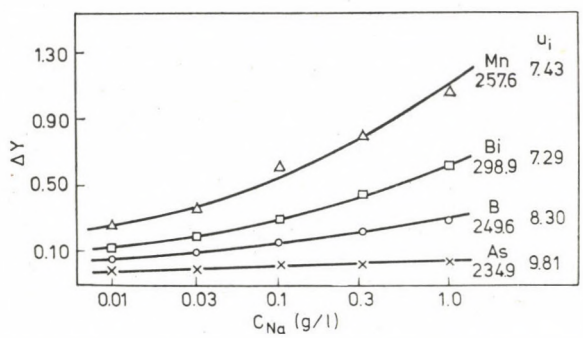


Fig. 4. Effect of the change of concentration of the sodium additive on line intensity changes in stabilized d.c. arc excitation ($\Delta Y = Y - Y_{C_{Na}=0}$; U_i : ionization energy, eV)

the intensity of the line of an element with a high ionization potential (As) remains practically unchanged, while with elements of low ionization energies the increase is substantial (highest in the case of Mn). An explanation of these phenomena might be sought in the changes of plasma parameters (temperature, ion-, and electron-pressure), further in the supervention of optimum excitation conditions for the elements studied. High amount of an element of low ionization energy lowers the temperature of the plasma, which increases the probability that low energy transitions will occur (increase of

intensity of atom lines). Another of our findings seems to support this: increasing the amount of the stabilizer and carrier gas increased the intensity of lines (Fig. 5).

The measure of this increase (rise of the slope) is greater for elements of lower ionization energies. Also in this case the lowering of the temperature of the plasma can be the cause of this change: a greater volume of gas and a greater amount of solvent cool the plasma in a greater measure.

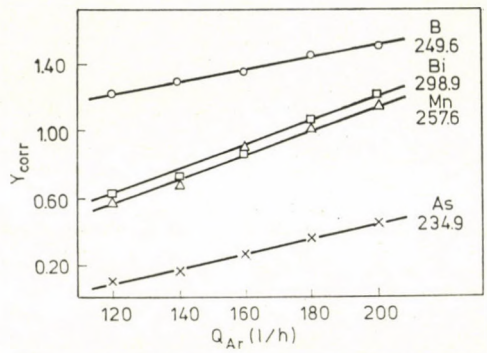


Fig. 5. Effect of the volume rate of the carrier gas on line intensities in stabilized d.c. arc excitation

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QUANTITATIVE DETERMINATION OF TRACE ELEMENTS IN SILICATE BASED SUBSTANCES BY SPECTROGRAPHIC METHODS USING CONTINUOUS SOLUTION FEED, II

CONSTRUCTION OF A COMPUTER PROGRAM FOR THE EVALUATION OF ANALYTICAL RESULTS AND FOR THE COMPARISON OF TECHNIQUES+

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A computer program for the statistical evaluation of quantitative spectrographic analysis was written. Besides the evaluation of measured data this program includes the computation of

— the standard deviation of the data recorded,
— the parameters of the analytical straight and their deviations,
— the relative, complete standard deviation of concentration data,
— the fit of the data recorded, to the analytical straight.

This computer program is suitable for use also in the assessment of other methods of chemical analysis.

Introduction

Nowadays the performance of chemical analytical methods suitable for quantitative determinations is assessed in several senses. The methods can be classified according to the type, or according to the number of the elements or compounds being determined; they can be characterized on ground of their detection power (absolute, and relative detection limits, precision accuracy, etc.) or according to the rapidity of their execution, the amount of work demanded by them, and the apparatus required.

The choice of a method of chemical analysis for a given task depends upon the demands made, and the means available. This selection narrows the field within which the analytical performance of the method can be assessed. A further narrowing of the remaining many possibilities is due to the requirements, or to the order of importance of the requirements a given method has to meet. According to this last feature the various characteristics of analytical performance can be variously weighed [1].

Computation of analytical results

A comparative assessing of the tube-electrode spray, the rotating disk, and the gas-stabilized d.c. arc excitation techniques, for samples in solution,

+The substance of this series of papers forms part of the doctoral thesis of A. DOMBI, prepared at the University of Chemical Engineering, Veszprém, 1975.

of the analysis of trace elements in silicate based substances has been carried out [2]. The following characteristics were considered:

a) limit of detection;
b) precision characterized by the standard deviations of
   1. the points plotted,
   2. the parameters of the analytical straight,
   3. concentration (as relative complete scattering);
c) study of the suitability of the analytical straight;
d) concentration sensitivity;
e) accuracy.

For such a comparison of the methods many-sided statistical cross-checkings and very many measurements are required, thus for their evaluation and assessing a computer program has been elaborated. Among those listed before, the establishing of the limit of detection was considered to be a separate task and was not included in present endeavours; the next characteristics b), c), and d) logically and practically constitute one unit, calculation work required for these is great, therefore the evaluation of these characteristics was carried out by computer.

With this program (Fig. 1) the s reduced blackening values independent of spectrum plate were calculated from line and background blackening values fed in, and from the γ gradation values of the photographic emulsion, as previously determined. In the next step Y intensity-logarithm values, calculated by l-transformation and corrected for background radiation, were obtained. (The need of transformation, and of correction, is decided upon by the computer.)

The $Y_x - Y_r = \Delta Y$ difference between related intensity-logarithms of the studied and of the reference element can be formed according to the instructions given.

After averaging the parallel measurements, the $s_{\Delta Y_j}$ standard deviations of the ΔY_{ij} values pertinent to the same concentrations of the elements were calculated.

Incidental outlying points of measurement may falsify the most probable value that can be regarded as the real value. In deciding on such outliers we cancelled (according to statements of GRAF and HENNING [3]) the $|\overline{\Delta Y}_j - \Delta Y_{ij}| > 4\, s_{\Delta Y_j}$ values. (The computer repeats this operation till an outlier crops up, but not more often than three times.)

In spectrography, the analytical curve is approximately a straight line. Its general form is

$$\Delta Y = a + b \lg c \,.$$

One of the best methods for the approximate computation of the equation of a straight line is the method of least squares; here the values of con-

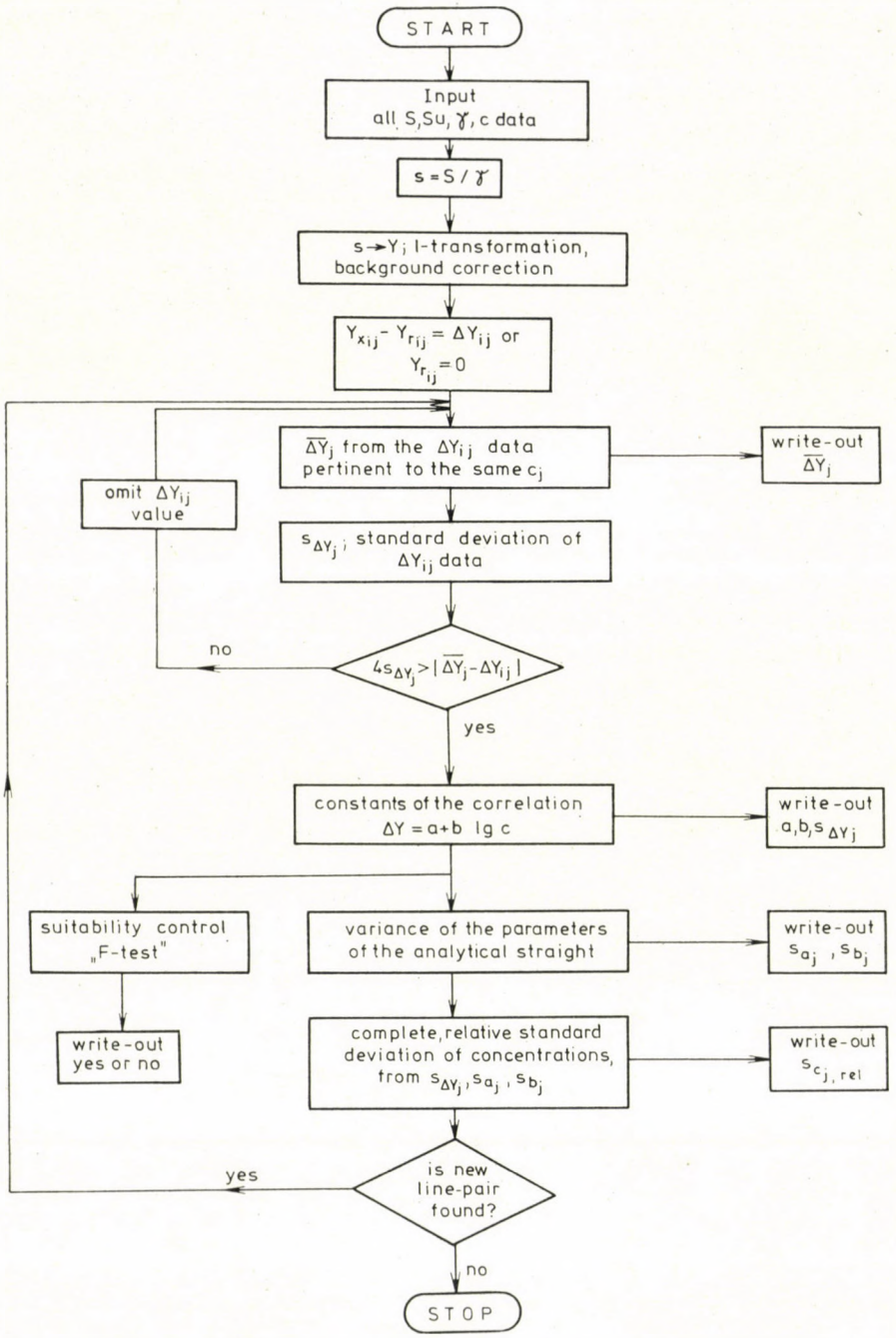


Fig. 1. Block scheme of the computer program

stants a and b can be calculated by finding the minimum value of the expression $Q = \sum_{j=1}^{k} (\overline{\Delta Y}_j - a - b \lg c_j)^2$, where k is the number of concentration points (reference samples used).

This method of calculation is allowed only provided the several average figures of measured results are derived from a series of points normally distributed, and the standard deviations in each series of points are the same. In our case the ΔY figures are of acceptably normal distribution; however, the scatterings in the several series of points pertinent to the several average figures are not the same in every case. Therefore the previous summation must be weighed by the square of standard deviations

$$Q = \sum_{j=1}^{k} \frac{1}{s^2_{\Delta Y_j}} (\overline{\Delta Y}_j - a - b \lg c_j)^2 .$$

There is no need to consider the deviations of $\lg c_j$ because this is zero since parallel tests were made with the same solution.

Also the parameters of the analytical straight show scatterings (incertitude) since no fixed values form their origin. In the next step the standard deviations linked to the various concentrations were calculated:

$$s_{a_j} = \sqrt{\frac{\sum_{i=1}^{n} (\lg c_i)^2}{n \sum_{i=1}^{n} (\lg c_i - \lg c_j)^2} s^2_{\Delta Y}}$$

$$s_{b_j} = \sqrt{\frac{s^2_{\Delta Y_j}}{\sum_{i=1}^{n} (\lg c_i - \lg c_j)^2}}$$

The control of the suitability of the analytical curve can be carried out by using the FISHER—SNEDECOR "F-distribution" [4] which describes the relation of normal distributions. When a high number of measured values is available the deviations between ΔY_{cj} obtained from theoretical relations and $\overline{\Delta Y}_j$ got as the average of measured values show normal distribution. As mentioned before, ΔY_{ij} measured values show a similar distribution also around the $\overline{\Delta Y}_j$ average values. The divergence from the analytical straight is correctly described in practice — at relatively small number of measured data — by the following equation:

$$s_1^2 = \frac{n \sum_{j=1}^{k} (\Delta Y_{c,j} - \overline{\Delta Y}_j)^2}{k - 2}$$

(Owing to the calculation of the parameters of the straight line two degrees of freedom are lost.)

The deviation of the average values severally pertinent to various concentrations can be characterized by the so-called 'residual' variance:

$$s_r^2 = \frac{\sum_{j=1}^{k} \sum_{i=1}^{n} (\Delta Y_{ij} - \overline{\Delta Y}_j)^2}{k(n-1)}$$

For deciding on the suitability of the analytical curve the quotient of the two variances was compared with F-distribution values, tabelled into the program, pertaining to a certain level of significance (statistical reliability) and to the degree of freedom determined by the system [5].

The equation according to which the computer calculated the complete, relative standard deviation of concentrations, which is a good characterization of the precision of the method, and also includes the standard deviation of the several points and of the analytical curve, is the following:

$$s_{cj,\,\mathrm{rel}} = \frac{2.30}{b_j} \sqrt{s^2 \Delta Y_j + s_{aj}^2 + (s_{bj} \cdot \lg c_j)^2}$$

The limit of detection of the elements studied was determined by estimation on the basis of a comparison of the blackening of the lines with that of their background density. We eschewed accurate calculation [6] because this, in spite of its being rather elaborate when samples of variable basic composition are to be dealt with, does not tell us more than a correct estimate [7].

The accuracy of the techniques compared is characterized by the pertinent systematic errors. A systematic error we consider to be the divergence of the result obtained by the technique studied from the most probable value.

The computer program devised seems to be suitable for a comparative assessment of the analytical chemical performance of emission spectrographic techniques, *i.e.* of their characteristics that are important from the point of view of trace analysis. Some parts of this program can be used separately for the solution of several tasks as, *e.g. l*-transformation, background correction, calculation of standard deviation, determination of the congruence of data in known correlations, etc.

Besides its use in spectrography this computer program may be applicable to the evaluation of other methods of chemical analysis, first of all when the recorded signal is a function of the logarithm of concentration.

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QUANTITATIVE DETERMINATION OF TRACE ELEMENTS IN SILICATE BASED SUBSTANCES BY SPECTROGRAPHIC METHODS USING CONTINUOUS SOLUTION FEED, III

COMPARISON OF THE ANALYTICAL PERFORMANCE OF THE VARIOUS METHODS OF DETERMINATION+

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The spectrographic techniques with continuous solution feed are suitable for the quantitative determination of metallic components present in minute quantities in silicate based substances. In the course of these studies it was found that

1. the detection power of spark excitation techniques is enhanced by the application of an argon atmosphere,
2. the precision of the techniques studied meets the general requirements of trace analysis,
3. low current gas-stabilized d.c. arc excitation assures higher precision, but this technique is more sensible to changes in the composition of the matrix, thus its analytical chemical accuracy is less than that of the spraying or rotating disk techniques.

By the use of a computer the evaluation of the spectra and the results is rapid and precise.

Introduction

In previous papers [1, 2] we have dealt with several characteristics of the spectrochemical solution techniques, selected for the quantitative determination of trace impurities in silicate based substances; on the ground of experimental findings we have discussed the characteristics suitable for indicating the analytical performance of these techniques.

For model substances, samples of arable soils of various base composition were selected for the comparative studies carried out with the help of an evaluating computer program. With respect to the importance of practical applications, and owing to their various physical and chemical properties, these samples allow adequate comparisons to be made.

Experimental

In order to dissolve the samples they were digested with hydrogen fluoride since using other methods great excess of alkali ions are introduced and these interfere with the determinations. Accordingly, three different series of stock solutions (Table I) were prepared, respectively, from calciferous, acidic, and intermediate type soils, marked A, B, and C.

+The substance of this series of papers forms part of the doctoral thesis of A. DOMBI, prepared at the University of Chemical Engineering, Veszprém, 1975.

Table I

Solutions with a base composition (SiO_2 omitted) to accord with various types of soil

Main component	Concentration,* % by weight		
	Calciferous "A"	Acidic "B"	Intermediate "C"
Al_2O_3	43.0	75.0	60.1
Fe_2O_3	16.3	3.8	7.6
CaO	16.0	9.2	22.3
MgO	3.8	0.4	0.7
K_2O	5.5	8.0	6.4
Na_2O	15.4	3.6	2.9

* without SiO_2.

To these stock solutions the elements to be analysed, viz. arsenic, boron, cobalt, copper molybdenum, manganese, and zinc, were introduced at various concentrations in the form of their soluble salts. The reference element was bismuth in a concentration of 0.5 g Bi per litre.

Spectrograms were recorded under the experimental conditions described earlier [1]. With all the three techniques a stabilizing, protecting, respectively, atomizing gas atmosphere of argon was maintained. In the case of the spray method, the effect of Ar, and of N_2, as atomizing gas upon the analytical chemical efficiency was studied.

For the plotting of the analytical curves, three times three parallel spectrograms were taken of the solutions of various concentrations of the elements studied (six-membered series).

The analysis lines selected are listed in Table II.

Table II

The analysis lines of elements tested

Element	Ionization energy eV	Wave-length nm	Excitation energy eV
As	9.81	234.98	6.59
B	8.30	249.68	4.96
Bi	7.29	240.09	7.07
		298.90*	5.50
		299.33	5.55
		302.46	6.00
Co	7.88	345.35	4.02
Cu	7.72	327.40	4.78
Mn	7.43	257.61*	4.81
		293.31	5.41
Mo	7.38	317.03	3.91
		379.83	3.26
Zn	9.39	334.50	7.78

* for d.c. arc excitation only

Results and discussion

In connection with the detection limits for a given element of the various techniques we have found [1] that the difference of the intensities of the analysis lines depends on the ionization potential of the element in question. In the case of elements with ionization potentials below 8 eV (Mn, Mo, Cu, Co) there is no significant divergence of the results of spark excitation techniques while, in the given range of concentrations, stabilized arc excitation technique gives more feeble analysis signals. Elements with ionization potentials above 8 eV (As, B, Zn) do not show a deviation of this kind.

Table III

Estimated limits of detection for the various spectrographic techniques
(1 mg/litre in the initial sample corresponds to 50 ppm)

Element	Estimated limits of detection, mg/litre			
	Spray method		Rotating disk	Stabilized arc
	Ar gas	N_2 gas	Ar gas	Ar gas
As	2	2	2	2
B	0.5	1	0.5	5
Co	0.1	0.7	0.1	0.7
Cu	0.05	0.05	0.05	0.1
Mn	0.2	0.2	0.2	0.5
Mo	0.1	0.7	0.3	0.1
Zn	0.5	2	0.2	2

Estimated concentration values of detection limits of the several elements are shown in Table III.

The best detection power was found with the argon-gas spray method, and with the rotating disk argon blow-in technique. Stabilized arc excitation and nitrogen-gas spray method did not perform so well when assessed in this respect. The worse detection power of the two latter techniques might be perhaps ascribed, besides the decrease of plasma temperature, to the emergence of interfering molecule bands and to increased background fluctuation.

In the course of our matrix effect study we found that the character of the analysis curves pertinent to the variable base composition does not show significant divergency in the case of the spark excitation techniques (Figs 1, and 2). The tendency is discernible for the values of absolute line intensities to become lowest with the acidic type soil (mark B in the Figures). In the case of the stabilized arc excitation technique, and testing the elements of lower ionization energies, the absolute values of line intensities are lower, while relative intensities, *i.e.* those referred to Bi, are similar to those found

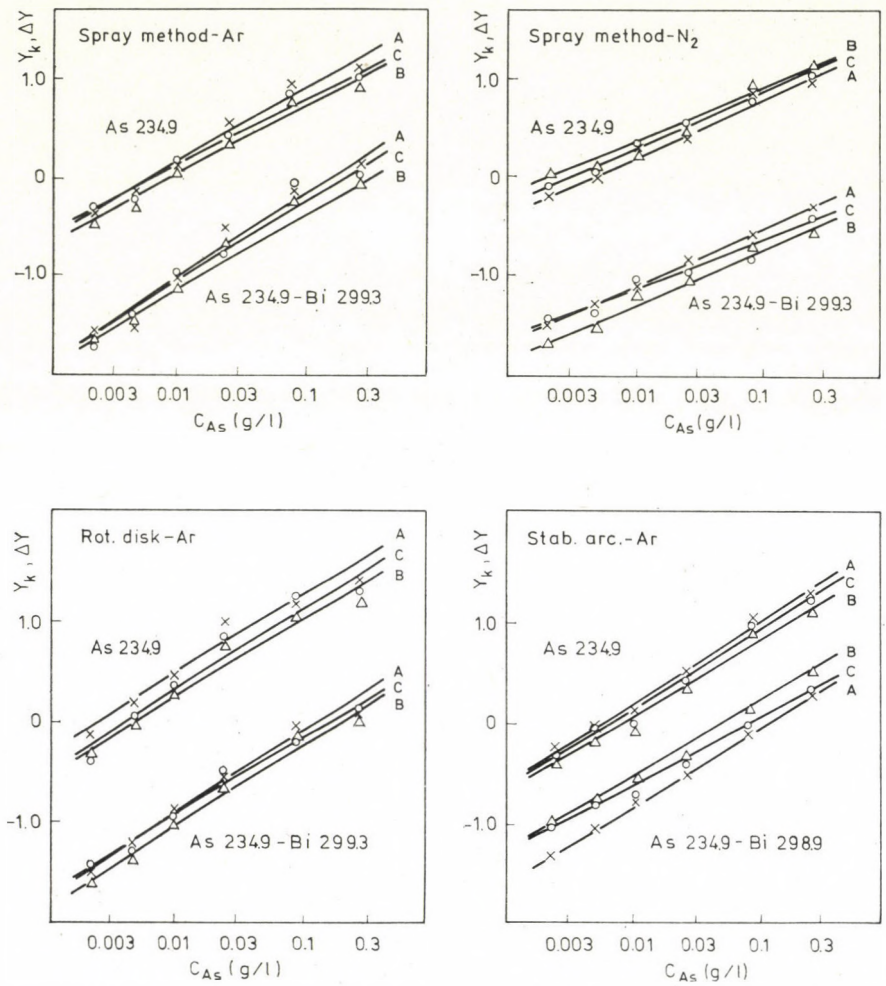


Fig. 1. Effect of the change in base composition on analytical curves in the case of an element of relatively high ionization energy (As)

with spark excitation. In the case of stabilized arc excitation it is inappropriate to compare the intensity of the lines of elements of higher ionization potentials with that of the lines of bismuth which is of a lower ionization potential, and thus a great divergence will be apparent between the substances of various base compositions.

Considering the accuracy of these techniques, a general finding is that the relative, complete standard deviation of concentration is least in the middle section of the concentration ranges studied. Also unaffected by the technique used, the highest figures of standard deviation are found for samples of calciferous composition (Tables IV and V).

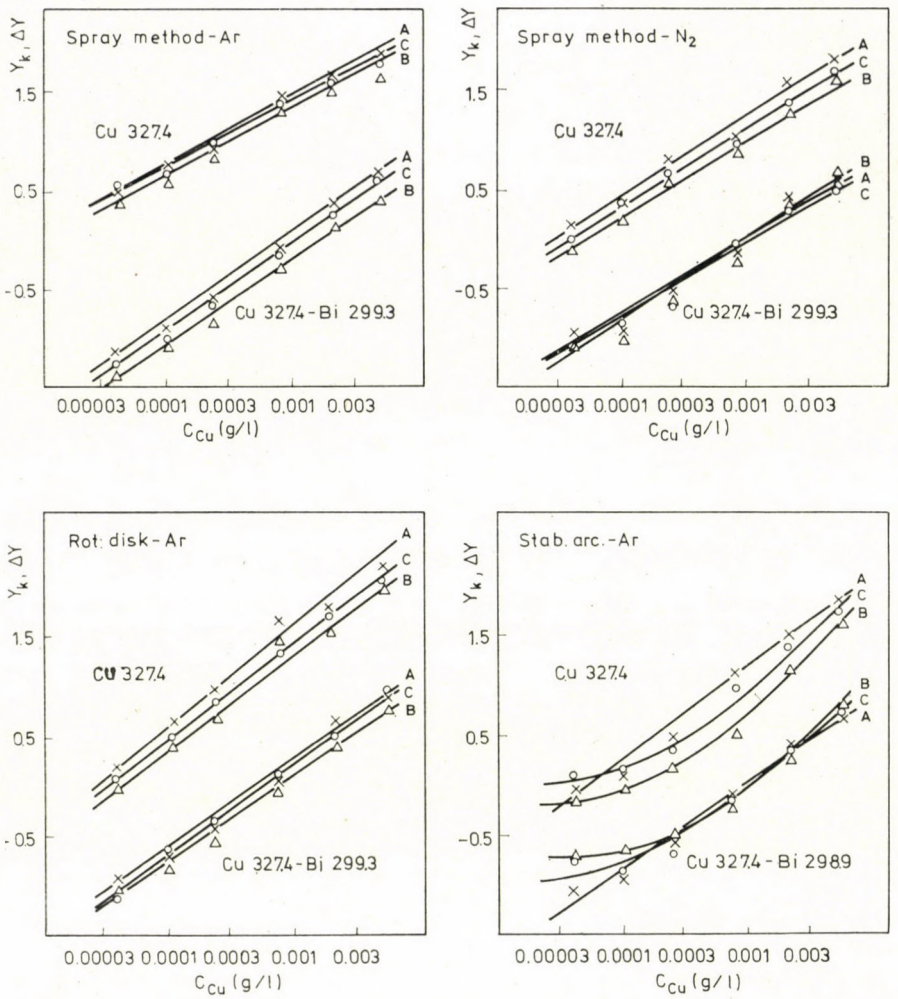


Fig. 2. Effect of the change in base composition on analytical curves in the case of an element of relatively low ionization energy (Cu)

By comparing the standard deviations of the several methods it was found that the best data were furnished by the stabilized arc excitation technique. Nearly equal performances are due to argon-blow spark excitation techniques, while spraying with nitrogen seems to be the least advantageous.

Besides those discussed earlier in connection with techniques, and with the comparison of various base substances [1] no further significant divergencies were found when the analytical sensitivity (slope) was studied.

Table IV

Various analytical parameters characteristic of the several spectrographic techniques

Line pair	Base composition	Characteristic parameter		Tube-electrode spray method		Rotating disk	Stabilized d.c. arc
				Ar gas	N_2 gas	Ar gas	Ar gas
Mn 299.3 resp. 257.6	A	$s_{c,\,rel.}$ %	a	68.7	61.4	29.6	50.9
			b	9.3	34.0	11.3	7.5
			c	61.7	45.0	16.2	13.2
		Anal. sens.		0.91	0.89	0.89	0.99
		Linearity		+	+	+	−
	B	$s_{c,\,rel.}$ %	a	73.7	61.0	31.0	61.3
			b	19.0	20.0	10.6	4.7
			c	42.3	63.3	12.2	9.7
		Anal. sens.		0.91	0.96	0.86	0.97
		Linearity		+	+	+	−
	C	$s_{c,\,rel.}$ %	a	42.6	105.0	28.0	50.5
			b	22.7	14.1	12.0	18.0
			c	22.6	76.4	17.3	11.3
		Anal. sens.		0.97	0.89	0.86	0.92
		Linearity		+	+	+	−
Mn 293.3 resp. 257.6 Bi 299.3 resp. 298.9	A	$s_{c,\,rel.}$ %	a	14.3	41.3	14.3	34.8
			b	5.8	29.9	6.2	4.8
			c	26.5	75.0	10.1	11.1
		Anal. sens.		0.84	0.86	0.91	0.97
		Linearity		+	+	+	−
	B	$s_{c,\,rel.}$ %	a	40.6	40.8	16.1	61.8
			b	11.9	30.9	6.8	3.9
			c	12.9	36.8	9.9	12.5
		Anal. sens.		0.90	0.99	0.90	0.99
		Linearity		+	+	+	−
	C	$s_{c,\,rel.}$ %	a	55.5	86.3	13.7	45.4
			b	7.1	10.2	8.4	14.2
			c	22.5	43.4	20.8	16.5
		Anal. sens.		0.87	0.91	0.88	0.93
		Linearity		−	+	+	−

a = 0.2 mg/litre; b = 2.5 mg/litre; c = 22.5 mg/litre

Table V

Various analytical parameters characteristic of the several spectrographic techniques

Line pair	Base composition	Characteristic parameter		Tube-electrode spray method		Rotating disk	Stabilized d.c. arc
				Ar gas	N_2 gas	Ar gas	Ar gas
As 234.9	A	$s_{c,\,rel.}$ %	a	55.9	29.3	38.2	25.2
			b	9.4	18.9	7.9	3.5
			c	26.1	32.8	6.1	12.8
		Anal. sens.		0.90	0.81	0.88	1.04
		Linearity		—	+	+	+
	B	$s_{c,\,rel.}$ %	a	89.5	96.2	45.1	30.2
			b	12.9	34.0	19.5	1.7
			c	12.1	22.9	22.7	20.0
		Anal. sens.		0.89	0.73	0.88	1.04
		Linearity		—	—	+	+
	C	$s_{c,\,rel.}$ %	a	33.9	81.2	24.8	17.0
			b	11.2	21.3	8.4	5.7
			c	28.5	31.5	28.9	11.2
		Anal. sens.		1.23	0.85	0.94	1.00
		Linearity		+	+	+	—
As 234.9	A	$s_{c,\,rel.}$ %	a	44.6	67.4	23.9	13.3
			b	6.4	32.5	8.6	3.4
			c	33.1	37.5	4.9	16.2
		Anal. sens.		1.10	0.87	0.85	0.99
		Linearity		+	+	—	—
Bi 299.3 resp. 298.9	B	$s_{c,\,rel.}$ %	a	56.2	34.5	12.3	31.2
			b	7.2	19.8	6.6	5.1
			c	27.2	35.1	26.9	22.1
		Anal. sens.		1.03	0.92	0.96	1.00
		Linearity		—	+	—	+
	C	$s_{c.\,rel.}$ %	a	24.7	33.6	16.8	28.8
			b	7.0	16.5	7.3	3.1
			c	24.5	24.3	40.5	12.7
		Anal. sens.		1.14	0.89	0.94	0.96
		Linearity		—	+	+	—

a = 2 mg/litre; b = 25 mg/litre; c = 200 mg/litre

For the majority of the elements studied, analytical straights best approximate the theoretical correlations in the case of the argon-blow spark excitation techniques.

The accuracy of the analytical methods was checked by analysis of real soil samples. Accepting the results obtained by atomic absorption spectroscopy (AAS) as the most probable values, it could be stated that, judged on the basis of systematic error, the spark excitation techniques are the "more reliable" ones (Table VI).

Table VI

Systematic errors, $\delta_{rel,\%}$, of the several techniques of spectrographic analysis

Element	Sample marked	AAS, ppm	Tube-electrode spray method				Rotating disk		Stabilized d.c. arc	
			Ar		N_2					
			c (ppm)	δ (%)	c (ppm)	δ (%)	c (ppm)	δ (%)	c (ppm)	δ (%)
Mn	1	948	940	−0.84	954	+0.64	970	+2.1	1080	+13.9
	2	510	490	−3.9	488	−4.3	500	+1.9	540	+5.9
	3	590	620	+5.1	625	+5.9	605	+2.4	640	+8.5
Cu	1	37.2	34	−8.6	34.5	−7.2	36.1	−2.9	38.8	+4.3
	2	25.0	22	−12.0	—	—	24.5	−2.0	—	—
	3	21.4	21	−1.8	—	—	21.0	−1.8	—	—

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THE THERMAL ANALYSIS OF POLYPROPYLENE FIBRES

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During the heat treatment of PP fibres a process of recrystallization occurs. Isothermal heat treatment was performed in a DSC instrument and the process of recrystallization was detected in the form of an exothermal peak. The measurements were carried out both in the melting range and below it.

The double fusion peak observed in polypropylene fibres and the new endothermal peak found in the DSC curves of polymers subjected to isothermal heat treatment have been interpreted on the basis of a recrystallization process. The DSC curves of polymers with metastable structures should always be regarded as the resultant of simultaneous exothermal and endothermal processes.

Introduction

The great significance of thermal analysis in the investigation of polymers is well known. Valuable information may be obtained on the structures of polymers by studying the thermal effects which accompany structural changes or the changes in the thermal behaviour of polymers which follow these structural changes.

So far only a few authors have carried out DSC measurements in polypropylene (PP) materials [1—4]. These studies have furnished numerous pieces of information, which are, however, insufficient to obtain a uniform picture.

Experimental

In our tests two different fibres, prepared from isotactic PP fibre, were employed:

1. Daplen 708 C (OSW)	M_W	= 300 000
	M_W/M_n	= 2.9
	Melt index*	= 16.1
2. Hostalen PPU 1080	M_W	= 620 000
	M_W/M_n	= 9.5
	Melt index*	= 10.6

Fibres were made from both polymers under nearly identical operating conditions. The fibres were very slightly oriented so-called non-stretched fibres. The non-stretched fibres

* According to ASTM 1238—57 T.

made of Daplen 708 C and Hostalen PPU 1080, respectively, had very different structures: the as-spun Daplen fibre possessed a so-called smectic structure, with a density of 0.890 g/cm^3, whereas the fibre obtained from the Hostalen with higher molecular weight had a density of 0.902 and a monoclinic structure. The X-ray diffractograms show the structural differences between the two non-stretched fibres (Fig. 1).

The DSC measurements were carried out on a Perkin-Elmer DSC-IB type instrument. Silicon grease was introduced between the sample holder and the sample carrier head to improve thermal contact. We used samples of 6—10 milligrams.

In the case of polymers one must take into account that substantial structural changes may occur upon heating. If they are neglected, completely false conclusions can be reached during evaluation. Moreover valuable information can be obtained on the nature and rate of these processes at the same time by plotting the DSC curves for several heating rates.

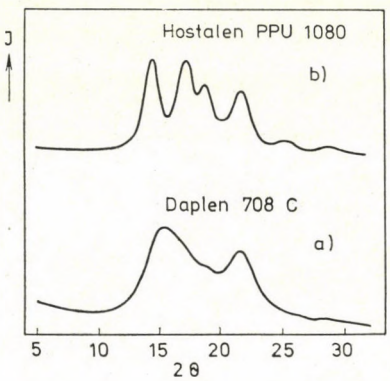


Fig. 1. X-ray diffractogram of non-stretched fibres of Daplen 708 C (a) and Hostalen PPU (b)

X-ray measurements have been performed on a Philips Mikro-Müller 111 type apparatus with CuKα-radiation. For wide angle measurements we used a Philips diffractometer and for small angle measurements a Rigaku-Denki small angle camera. For the SAXS measurements we used a step-scanning method, with a measuring period of 100 seconds between each step.

The fibre density was measured with the floating method in a CCl_4-toluene mixture.

Results

Detection of processes occurring in the melting range

At certain heating rates the non-stretched Daplen fibre exhibited a double or multiple fusion peak (Fig. 2). With increasing heating rate the maxima at the fusion peaks increasingly overlap although the double character of the peaks is still recognizable at a heating rate of 8 °C/min.

The position of the peaks belonging to lower temperatures does not change much with increasing heating rates, but its height increases while that of the higher temperature peak decreases.

This double or multiple nature of the fusion peaks is very frequent with polymers and the influence of the heating rate is also similar [5—10].

However, the opinions are substantially different in the interpretation of this effect. Some authors explain it with two different structures existing in the original substance, even in polymers which are known to possess one crystalline modification only (polyesters, polyethylene). According to others the difference may be due to the coexistence of crystals with folded and stretched chains [5] and still others claim that there is a difference in the crystal sizes [9].

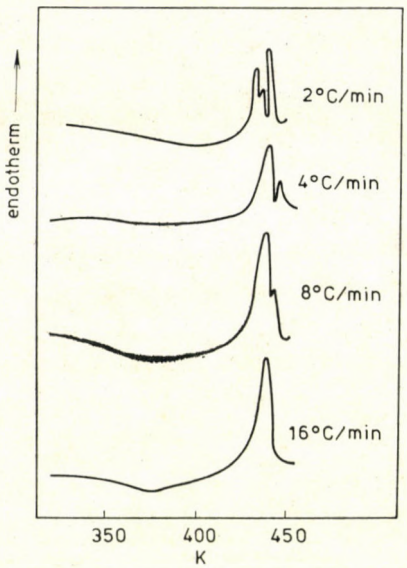


Fig. 2. DSC curves of a non-stretched Daplen 708 C fibre at various heating rates

ROBERTS [10] has pointed out that for a correct interpretation it is absolutely necessary to consider the processes that take place in the sample during the DSC measurement, more particularly the possibility of recrystallization or reordering processes occurring in the fusion range, which tend to increase the melting point of the reordered structure.

All these factors must be taken into account in the interpretation of the fusion curves for Daplen 708 C non-stretched fibres. During the DSC measurement, structural changes due to heating are indicated by the fact that the area under the peak belonging to the higher melting point increases definitely in parallel with the time of the DSC measurement (*i.e.* with the decrease in the heating rate) both in the absolute sense and related to the total area under the fusion peak.

A relationship between the shape of the fusion peak and the properties of the polymer (molecular weight and structure) is indicated by the absence of double fusion peak in non-stretched fibres prepared from polypropylene with higher molecular weight (Hostalen PPU 1080).

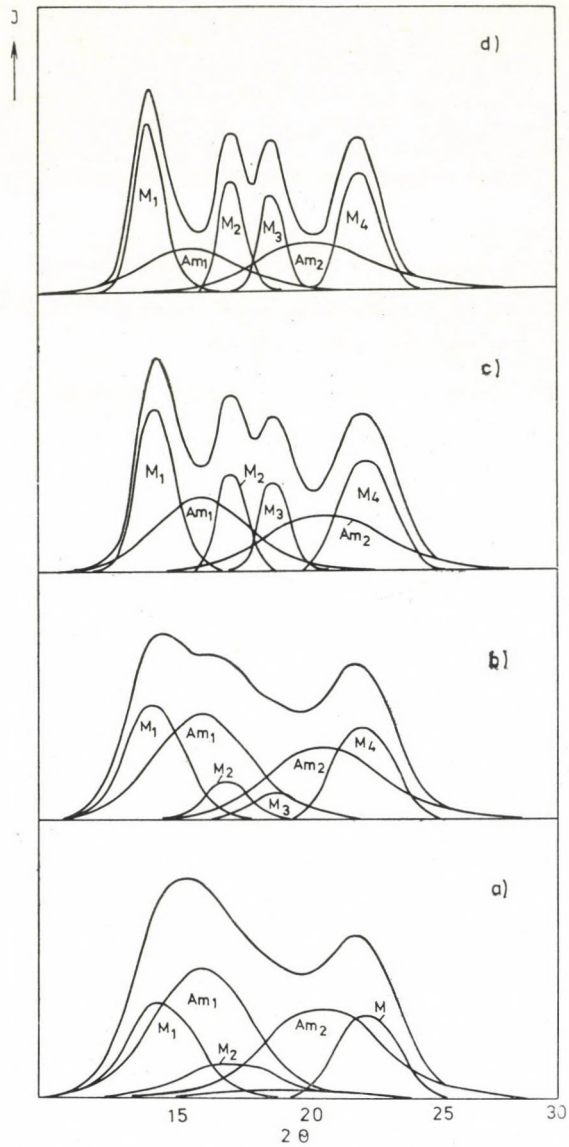


Fig. 3. Wide angle X-ray diffractograms of the non-stretched Daplen 708 C fibre, after heat treatment at various temperatures: a) without heat treatment; b) 80 °C; c) 110 °C; d) 140 °C heat treatment

Our original hypothesis that the double fusion peak of the Daplen sample is related to the smectic structure had to be discarded, since the shape of the fusion peak did not change by heat treatment at 140 °C, although the X-ray diffraction curve (Fig. 3c) and the density (0.9088 g/cm^3) indicated a change of structure into monoclinic.

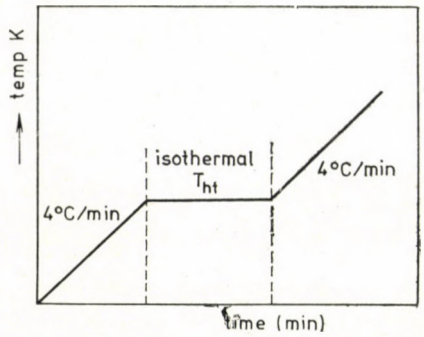


Fig. 4. DSC programme for studying the processes in the melting range

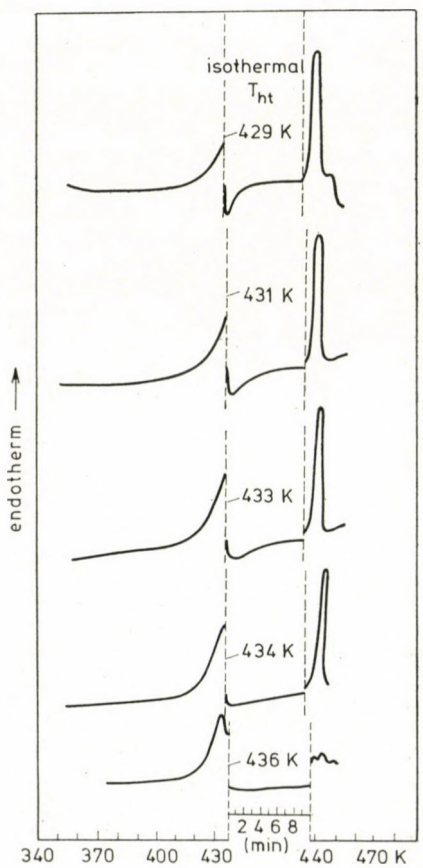


Fig. 5. DSC curves of Daplen 708 C fibres; an isothermal stage was inserted into the melting range

We decided to perform further measurements on the nature of the double fusion peak, especially to clarify the existence and nature of exothermal processes in the temperature range of melting. The heating programme (4 °C/min) was interrupted at various temperatures in the melting range and heating was resumed after an isothermal stage of 10 min (Fig. 4). Figure 5 shows the DSC curves of a non-stretched pre-oriented Daplen 708 C fibre obtained with the above programme at different temperatures. It can be seen from the figure

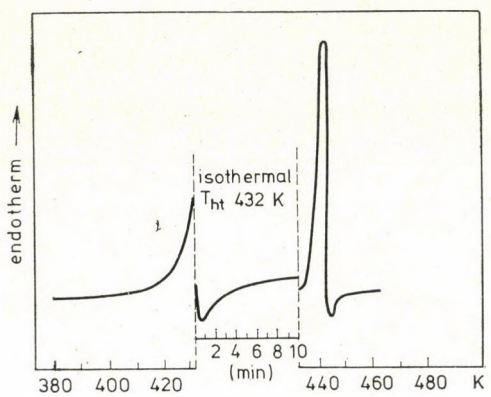


Fig. 6. DSC curve of Hostalen PPU fibre; an isothermal stage was inserted into the melting range

that an exothermal process occurs in the isothermal stage with a duration of several minutes. This phenomenon has also been observed by ROBERTS [10] on polyethylene fibres. According to our measurements the exothermal heat of transformation decreases with an increase in the temperature of the isothermal stage and becomes zero at 163 °C (436 K).

No double fusion peak was obtained for the Hostalen PPU 1080 fibre, as mentioned already. Nevertheless, we assumed that fusion occurs in a similar way as with non-stretched Daplen 708 C and therefore we performed the

Table I

Temperature of heat treatment and the positions of the fusion peaks

Daplen 708 C	Temperature of heat treatment (K)	—	428.0	431.0	433.0	434.0	436.0
	Peak maximum (K)	436.2	436.5	439.5	441.5	443.5	443.2
Hostalen PPU 1080	Temperature of heat treatment (K)	—	432.0	434.0	435.0	436.0	
	Peak maximum (K)	435.0	440.0	442.5	444.6	446.1	

measurement with the above programme with this fibre, too. Figure 6 shows one of the curves obtained.

According to the figures, when heating is continued after the isothermal stage, only one endothermal peak appears. The higher the temperature of the isothemal heat treatment, the higher the temperature of this peak (Table I).

Extension of the investigations to temperatures below the melting range

Several literature data refer to an extra endothermal peak appearing in polymers subjected to an isothermal heat treatment below the melting range [6, 8, 11—16]. This also holds for the PP fibre studied here, as shown by the DSC curves for non-stretched fibres with very slight orientation, annealed at 80, 110 and 140 °C (Fig. 7). The heat treatment had no influence on the shape of the fusion peak or on the melting point; however, a new, small endothermal peak appeared on the curve in the vicinity of the temperature of heat treatment.

This phenomenon has been observed on different polymers by various authors but their calorimetric measurements were restricted to the re-heating of heat treated and cooled samples and to measuring or detecting the fusion occurring during this process.

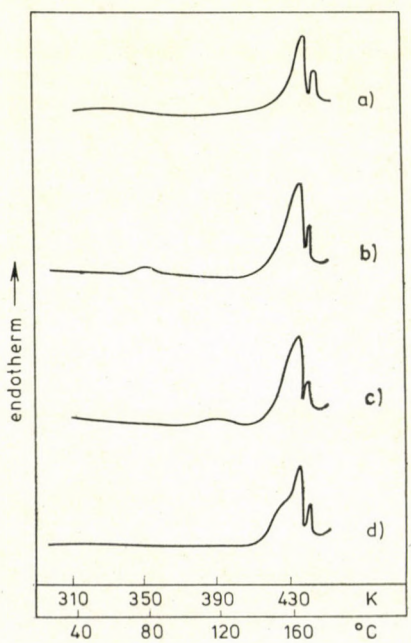


Fig. 7. Change in the DSC curve of the non-stretched fibre after heat treatments at various temperatures (4 °C/min)

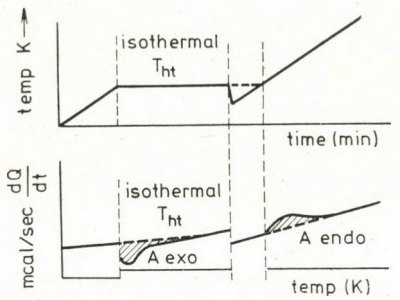


Fig. 8. Programme of heat treatment in the DSC and a typical DSC curve obtained with this programme

To study the nature of the low-temperature endothermal process more closely the heat treatment was carried out in the DSC instrument itself, similarly to the measurements performed in the melting range. Heating was interrupted, and isothermal stages of several minutes' duration were inserted into the programme; then the sample was cooled rapidly — at a rate of about 80 °C/min — to about 20 °C below the temperature of heat treatment. The further part of the DSC curve was recorded again with a heating rate of 4 °C/min. Figure 8 shows this programme and the DSC curve obtained.

The measurements indicate that an exothermal process occurs in the temperature range of isothermal heat treatment and substantially below the melting point; the process appears as a measurable peak on the DSC curve.

In the repeated heating of the heat treated fibre an endothermal peak appears with an initial temperature which is identical with the temperature of heat treatment.

The areas under the peaks belonging to the exothermal and endothermal processes were measured in arbitrary units by planimetry. The values of A_{exo} and A_{endo} are given in Table II. The extent of the exothermal process

Table II

Area of exothermal and endothermal peaks in arbitrary units, as a function of the temperature of heat treatment

	Temperature of heat treatment					
	353 K		383 K		413 K	
	A_{exo}	A_{endo}	A_{exo}	A_{endo}	A_{exo}	A_{endo}
Non-stretched Daplen fibre	1.31	1.31	1.48	1.93	3.14	3.14
Non-stretched Hostalen fibre	0.87	0.63	1.66	1.66	2.77	2.85
Daplen granules	0.83	1.25	1.67	2.25	4.73	4.16

increases with the increasing temperature of the heat treatment, and the areas under the peaks corresponding to the exothermal and endothermal processes are approximately equal.

The sizes of the endotherm peaks of samples heat-treated below the melting range were independent of the cooling rate.

We have also investigated Daplen granules and obtained similar results, as shown in Table II.

Attempts were made to obtain the exothermal peak at a given temperature T_{ht} after a prior heat treatment of the fibre at a higher temperature.

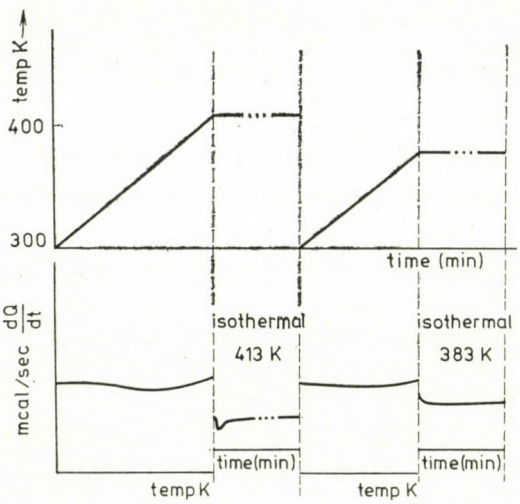


Fig. 9. DSC programme for heat treatment at 140 and 110 °C and the resultant DSC curve

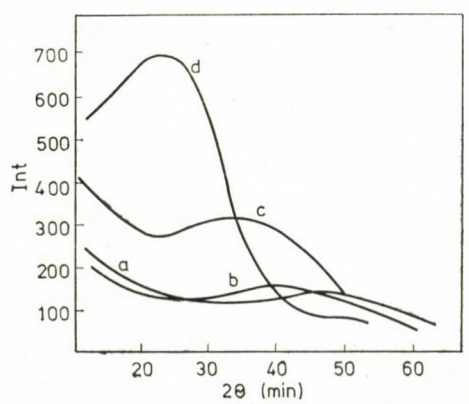


Fig. 10. Small angle X-ray diffractogram of the Daplen 708 C non-stretched fibre after heat treatments at various temperatures: a) without heat treatment; b) 80 °C; c) 110 °C; d) 140 °C heat treatment

For this reason the DSC curve was recorded after a heat treatment at 140 °C, according to the programme given in Fig 9. No exothermal peak was found at 110 °C after this heat treatment.

The exothermal peak obtained during heat treatment in the DSC instrument indicates some kind of recrystallization process. The structural changes accompanying this process were studied by X-ray and density measurements. Figure 3 shows the wide angle X-ray diffractograms and Fig. 10 the small angle X-ray diffractograms. The changes in the structural characteristics are summarized in Table III.

Table III

Changes in structural characteristics after heat treatment in non-stretched Daplen fibre

T_{ht} K	Density g/cm³	Crystalline %		Cryst. particle size Å	Small angle period Å
		from density	from X-ray diffract.		
Untreated	0.8900	50.5	40	29	104
353	0.8940	52.5	45	35	124
383	0.9038	63.4	56	52	152
413	0.9088	70.9	69	67	220

Discussion

In linear homopolymers able to crystallize, the crystallites with stretched chains and large lateral dimension have the lowest free energy and this is therefore the final stage of thermodynamical equilibrium [17].

In crystallization from a melt or a solution, the structure obtained is always unstable thermodynamically since the formation of the equilibrium structure is kinetically hindered.

The smaller the mobility of the molecular chains during crystallization, the lower the temperature of crystallization of the polymer, and the more defect-inducing sites are present in the polymer (atactic chains or chain segments, contaminations, chain ends) the farther is the structure formed from the equilibrium state.

In fibre formation crystallization occurs at steadily decreasing temperatures and accordingly the structure is homogeneous in distribution.

When linear macromolecules with sufficient flexibility crystallize without or at low stress, crystallites with folded chains are obtained. Under the conditions of fibre formation the crystalline phase is composed of crystallites with folded chains which crystallize into the nuclei with stretched chains oriented in the direction of the stress [18, 19].

At rising temperature the mobility of the molecular chains increases and the structure transforms toward a thermodynamically stable equilibrium. This change proceeds, through an increase in the chain folding period, toward the formation of crystallites with stretched chains.

Simultaneously with the above process the crystal size grows, the number of defect sites in the crystalline structure decreases, and the amorphous chains on the folding surfaces may be built into the crystal lattice.

The extent of change can be characterized numerically by a variation in the size of crystalline particles obtained from wide angle X-ray measurements, in the large period obtained from small angle X-ray diffractograms and in the percentage of crystallinity obtained by various methods.

This change is irreversible, *i.e.* the structure remains unchanged until the temperature of formation of the given state is exceeded. This is the basis of fixing the shape and structure of polymers by heat treatment.

According to our DSC studies this transformation can be detected in the form of an exothermal heat effect already far below the melting point. The exothermal process detected during isothermal heat treatment at a given temperature is a recrystallization always involving structural elements formed by crystallization at temperature below the temperature of the given heat treatment.

This interpretation explains the increase in size of the exothermal peak in parallel with the temperature of heat treatment.

The process of recrystallization at a temperature T_{ht} results a change in the so far homogeneous distribution; the crystallites with lower temperatures of crystallization assume a structure stable at T_{ht}. The proportion of the structure belonging to T_{ht} increases accordingly, as proved by the endothermal peak starting at T_{ht} upon re-heating. This peak corresponds to a partial melting of the structure stable at T_{ht}.

Therefore during the continuous increase of the temperature — when recording the DSC curve — a recrystallization process takes place much below the melting point. This consists of a partial melting and a recrystallization.

The melting curves of polymers should always be considered as the resultant of endothermal and exothermal processes occurring in parallel, both in the melting range and below it. The DSC measurements discussed above also prove that partial melting must be taken into account already far below the melting point, due to the wide melting range of semicrystalline polymers. So far this phenomenon has been studied indirectly through the percentage of the crystallinity [20].

The double or multiple fusion peaks frequently occurring with polymers and the endothermal peaks in the DSC curves of polymers subjected to isothermal heat treatment can therefore be explained by studying the exothermal

recrystallization processes taking place simultaneously with the melting process.

New endothermal peaks appearing on the DSC curves of polymers subjected to isothermal heat treatment indicate a melting of zones which have already recrystallized up to the given temperature. The thermal energy liberated during recrystallization is the same as the energy required for melting these zones, and therefore the areas under the exothermal and endothermal peaks are nearly identical.

The phenomenon of recrystallization is independent of the state of the sample (non-stretched fibre or granule); however, the crystallinity increases only in chains already slightly stretched, whereas in completely non-oriented material the crystallinity is constant, as shown before [21].

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ELECTRON DIFFRACTION INVESTIGATION OF THE MOLECULAR STRUCTURE OF DIPHENYL SULFIDE*

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A gas-phase electron diffraction study of diphenyl sulfide yielded the bond lengths (r_a) S–C 1.771±0.005 Å, C–C 1.399±0.003 Å, C–H 1.089± 0.008 Å and the angle C—S—C 103.7±1.3°. At least two conformations are in agreement with the experimental data.

Introduction

This investigation is an extension of our studies on the molecular structures of sulfur compounds. Our primary purpose was to compare the sulfur bond configuration in diphenyl sulfide with those in other sulfides, *e.g.* $(CH_3)_2S$ [1], $[(CH_3)_2N]_2S$ [2] on the one hand, and with the structures of diphenyl sulfoxide and sulfone, on the other. The structure analysis of the latter two substances is in progress in this laboratory. As seen on similar compound series of SX_2, SOX_2, and SO_2X_2 [X = F, Cl, CH_3, or $(CH_3)_2N$], interesting geometrical variations appear in the sulfur bond configurations (see *e.g.* [3]), which may have important implications concerning the bonding properties. In addition, the elucidation of the conformational behaviour of the diphenyl derivatives is challenging, although it was clear from the beginning that only a very limited amount of information can be obtained in this respect at the present time.

Experimental

The sample of diphenyl sulfide was obtained from Dr. I. KAPOVITS and the purity of the sample was confirmed by mass spectrometry [4]. The electron diffraction patterns were obtained with an EG-100A apparatus [5, 6] using a so-called membrane nozzle system [5] at nozzle temperatures around 130—143 °C. The wavelength of the electron beam was determined from TlCl diffraction patterns [7]. The intensity data intervals were $1.75 \leq s \leq 13.50$ and $6.25 \leq s \leq 31.5$ Å^{-1} for the 50 cm and 19 cm camera ranges, respectively, with a data step of $\Delta s = 0.25$ Å^{-1}. The total experimental intensity values are tabulated in the Appendix. The experimental molecular intensities were obtained as usual [8, 9] and are shown in Fig. 1.

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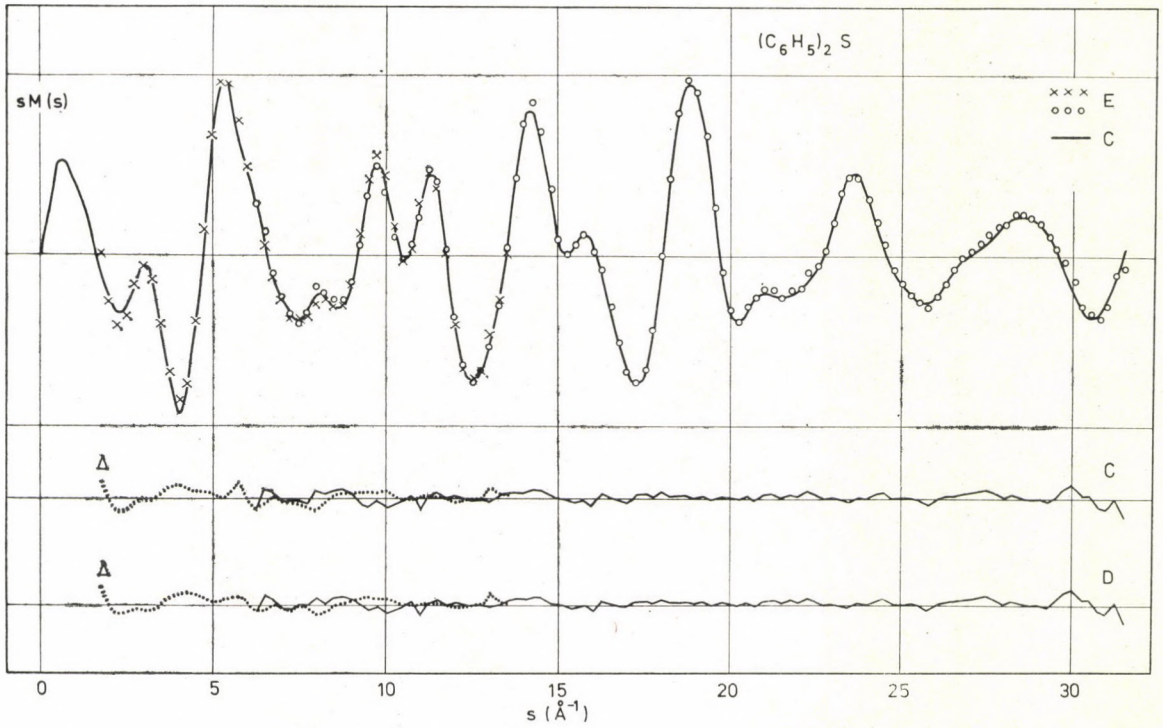


Fig. 1. Experimental (E) molecular intensities $sM^E(s)$ for the two camera ranges, theoretical molecular intensities $sM^T(s)$ for model C and difference curves $\Delta = sM^E(s) - sM^T(s)$ for models C and D. All scaled to the 19 cm experimental data

Structure analysis

The geometry of models used in the structure analysis is defined by bond lengths C–C, C–H, S–C, bond angle C–S–C and the angles of rotation of the phenyl rings about the S–C bonds (φ_1, φ_2). $\varphi_1 = \varphi_2 = 0$ when both rings are coplanar with the C–S–C plane, $\varphi_1 = \varphi_2 \neq 0$ corresponds to models with symmetry C_2 (Fig. 2).

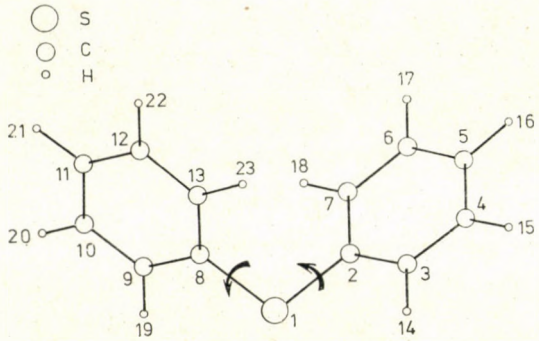


Fig. 2. A model with C_2 symmetry and the numbering of atoms

Our general procedure of structure analysis is described in Ref. [9]. The same coherent and incoherent scattering amplitudes were used as in Ref. [10].

Initial parameter values for the least-squares refinements were estimated mainly from three sources: the experimental radial distribution (Fig. 3), structural data for similar molecules and calculated mean vibrational amplitudes (l) for benzene sulfonyl chloride [10]. First the bond r and l values were refined. Since they proved to be insensitive to conditions of refinements (*e.g.* to values of other parameters), they were fixed in most of the subsequent calculations.

Information on angle C–S–C and the rotational angles is hidden in the range above 2.5 Å of the radial distribution. Curve F of Fig. 3 illustrates that the preponderant part of contributions comes from distances that are independent of the angle parameters.*

Four conformations** were chosen with rotational angles and symmetry (90°, 90°) C_{2v}, (0°, 90°) C_s, (45°, 45°) C_2 and (45°, −45°) C_s to test C–S–C angles in a wide range (85 to 145°). Models with $\varphi_1 = \varphi_2 = 0°$ were excluded in view of steric hindrance. None of the radial distributions calculated for models

* It may be striking that curve F runs above the experimental curve in some regions, although the former does not contain all contributions. Since negative values of $f(r)$ have not been compensated, an interatomic distance r_{ij} may have a positive contribution to $f(r)$ in the vicinity of r_{ij} and a negative contribution in farther regions.

** A conformation is denoted by (φ_1, φ_2).

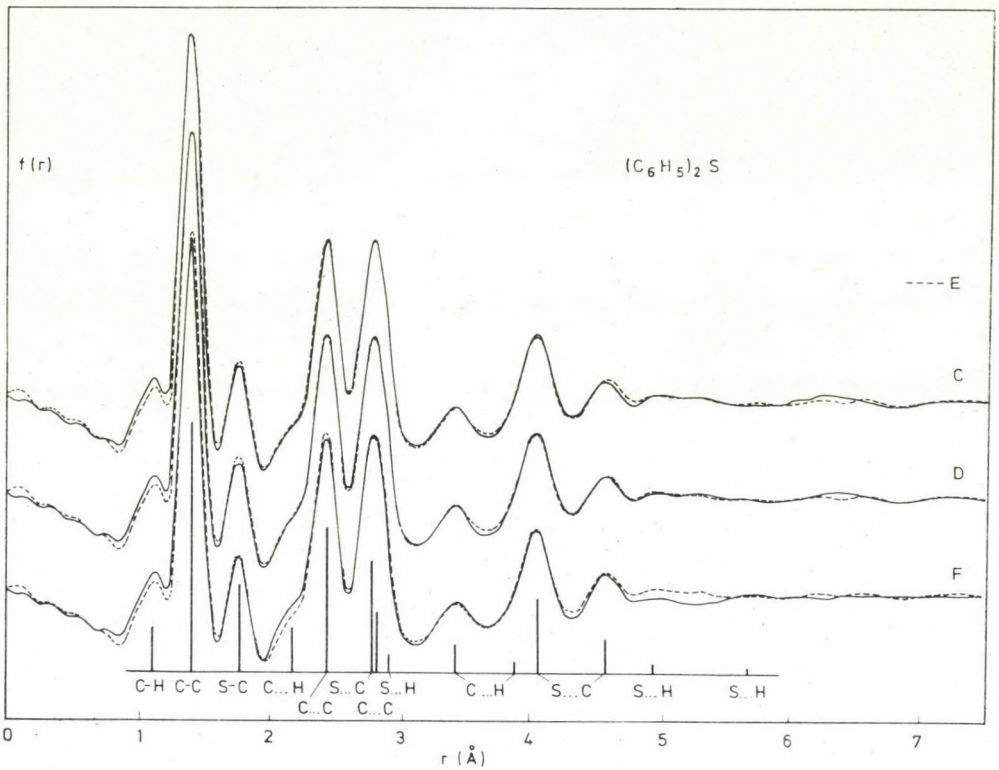


Fig. 3. Experimental (E) radial distribution and theoretical curves for models C and D. Curve F includes only those contributions that are independent of both the C–S–C angle and the rotational angles. Contributions from angle- and rotation-independent interatomic distances r_{ij} are indicated by vertical bars with lengths proportional to $m_{ij}Z_iZ_j/r_{ij}$, m_{ij} multiplicity of the distance, Z_i Z_j atomic numbers. $s_{min} = 0$, $s_{max} = 31.5$ Å^{-1}, damping constant $a = 0.002$ Å^2. Model C was used to extrapolate experimental data to $s = 0$

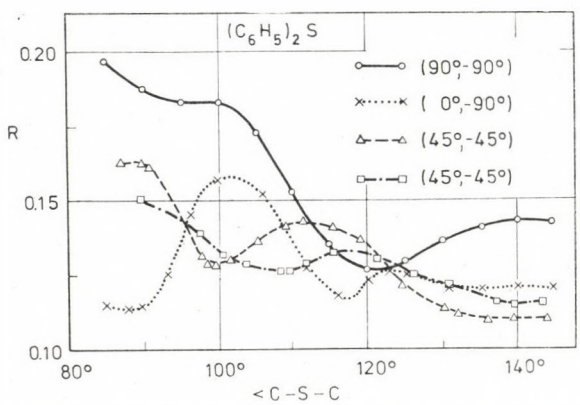


Fig. 4. Variation of the R-factor with the C–S–C angle. $R = \{\Sigma \Delta^2/\Sigma[sM^E(s)]^2\}^{1/2}$

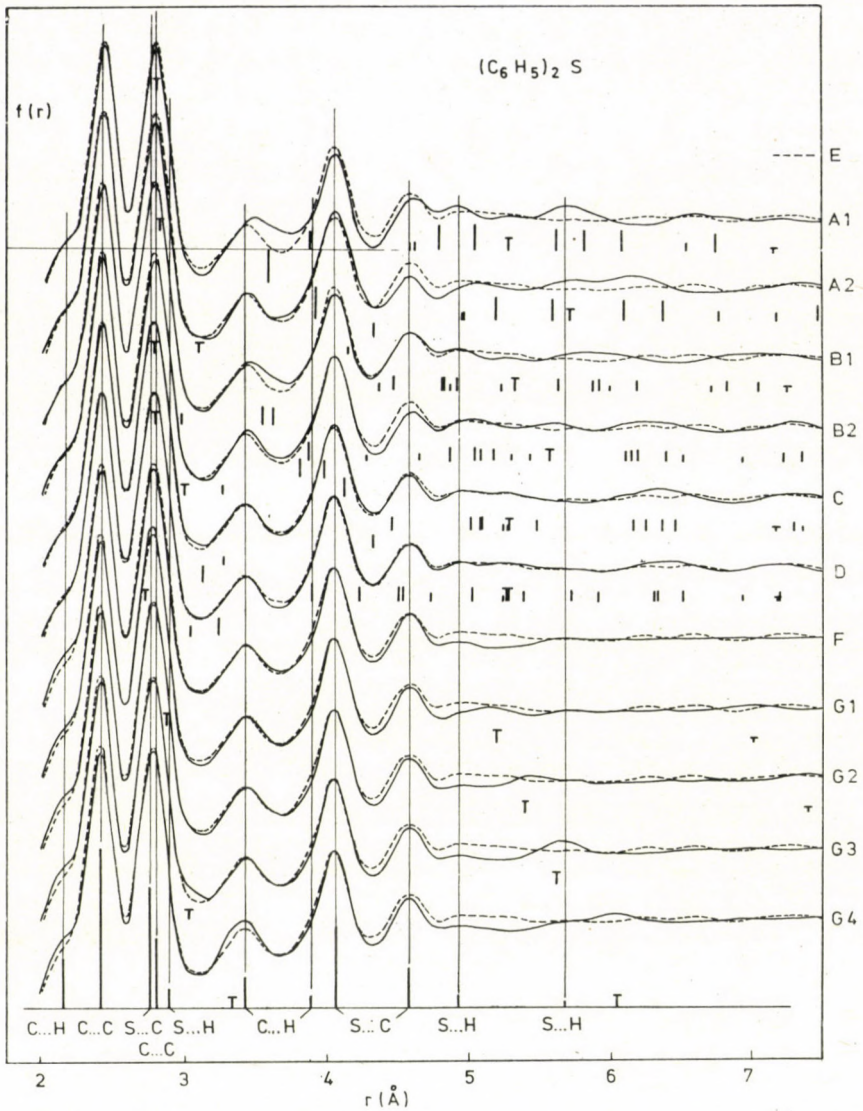


Fig. 5. Experimental (*E*) and theoretical radial distribution curves. *F* angle- and rotation-independent contributions only, *G1* to *G4* rotation-independent contributions only. Unlabelled bars show contributions from C...C distances, hooded bars represent rotation-independent C...C distances

Model	*A1*	*A2*	*B1*	*B2*	*C*	*D*
(φ_1, φ_2)	(90°, 90°)		(0°, 90°)		(43°, 43°)	(56°, 56°)
⟨ C–S–C	103°	121°	105°	115°	104°	104°
R-factor	0.119	0.101	0.098	0.090	0.085	0.082

Model	*F*	*G1*	*G2*	*G3*	*G4*
⟨ C–S–C	—	100°	108°	117°	139°

corresponding to the minima on the *R*-factor *vs.* C–S–C angle curves (Fig. 4) provided satisfactory agreement with the experimental data. It is emphasized, however, that relatively small assumed vibrational amplitudes were used in these calculations for the rotation-dependent distances. Note also that most *R*-factor *vs.* C–S–C angle curves show improving agreement with the experimental data as the bond angle increases to presumably unreasonably large values. This may in turn suggest that the inter-ring distances have a more dispersed contribution, *i.e.* apparently larger l values than anticipated.

Curves *G* in Fig. 5 illustrate some calculations in which the rotation-dependent distances were ignored. Here, in addition to the parameters used to calculate curve *F* of Figs 3 and 5, the following amplitudes were assumed: l (C2 . . . C8) = 0.07 Å, l (C2 . . . C11) = 0.11 Å, l (C5 . . . C11) = 0.13 Å. Values of ⟨C–S–C were chosen to represent the minima shown in Fig. 4. Since the distributions with ⟨C–S–C = 117° or 139° (curves *G3* and *G4*) display considerable discrepancies from the experimental distribution, and these cannot be compensated by adding the rotation-dependent contributions, no refinement was carried out starting with values larger than 117°. The resulting values of ⟨C–S–C were about 103.5° in these refinements.

In subsequent refinements the rotation-dependent distances were included again. In order to spread their contribution over a wider range of r, large initial l values (0.16 to 0.27 Å) were assumed for the rotation-dependent C . . . C distances. They were then refined in appropriate groups together with other l values. In several cases some amplitudes had to be fixed because they reached too high values to allow further refinement cycles. The following conformations and initial C–S–C angles were tried:

(90°, 90°): ⟨C–S–C = 103° did not change significantly when refined (see Fig. 5, curve *A1* for the radial distribution of this model), ⟨C–S–C = 120° to 123° refined to 121° (curve *A2*), the agreement was not satisfactory.

(0°, 90°): Angles 112° to 120° refined to 116° (curve *B2*), 103° refined to 105° (curve *B1*), the agreement was not satisfactory.

(45°, 45°): An initial 120° tended towards larger values and amplitudes became too large. Angles 100° to 110° refined to about 104° (curve *C*), and satisfactory agreement was achieved. Angles of rotation were also allowed to vary in these refinements but they were restricted to be equal. The final values remained close to (45°, 45°) within estimated standard deviations.

(45°, −45°): These models behaved like the previous conformer. Angle C–S–C refined to about 104° and the rotational angles to (56°, −56°) when the model was constrained to have C_s symmetry (curve *D*), and the agreement was satisfactory.

Table I presents the results for the two models (*cf.* *C* and *D*, Fig. 5) which gave satisfactory agreement with the experimental data (less important C . . . H and H . . . H distances are not listed). Error estimates of the most

Table I

Some results of the refinements[a]

	Model *C*		Model *D*	
	r_a (Å)	l (Å)	r_a (Å)	l (Å)
	Independent parameters			
S–C	1.7711(16)	0.0489(24)	1.7715(17)	0.0489(23)
C–C	1.3991(5)	0.0460(11)	1.3992(4)	0.0460(11)
C–H	1.0888(46)	0.0806(50)	1.0899(45)	0.0809(49)
∠C–S–C	103.6(8)°		103.7(9)°	
φ_1[b]	43.5(25)°		55.6(24)°	
φ_2[b]	43.5°		−55.6°	
	Dependent distances			
S....C3	2.752(1)	0.079(2)[d]	2.752(1)	0.079(2)[i]
S....C4	4.055(1)	0.078(4)	4.056(1)	0.077(4)
S....C5	4.569(1)	0.081(8)	4.570(1)	0.084(9)
S....H14	2.890(1)	0.146[e]	2.891(1)	0.146[e]
S....H15	4.912(3)	0.080[e]	4.913(3)	0.080[e]
S....H16	5.658(3)	0.100[e]	5.660(3)	0.100[e]
C2...C4	2.423(1)	0.057(1)	2.424(1)	0.058(1)
C2...C5	2.798(1)	0.070[d]	2.798(1)	0.070[i]
C2...H14	2.160(3)	0.118(7)	2.161(3)	0.117(7)
C2...H15	3.410(3)	0.096(11)	3.411(3)	0.096(9)
C2...H16	3.887(3)	0.095[e]	3.888(3)	0.095[e]
C2...C8	2.784(10)	0.078[e]	2.787(10)	0.078[e]
C2...C9	3.975(13)	0.300(80)[e]	3.892(19)	0.144(46)[j]
C2...C10	5.083(13)	0.307(62)[f]	5.020(18)	0.235(64)[k]
C2...C11	5.275(13)	0.140[e]	5.279(14)	0.140[e]
C2...C12	4.448(18)	0.454(184)[g]	4.526(13)	0.359(81)[l]
C2...C13	3.121(20)	0.216(44)[h]	3.230(14)	0.232(49)[m]
C3...C9	5.243(13)	0.267[i]	4.734(39)	0.265[k]
C3...C10	6.355(17)	0.220[e]	5.898(41)	0.270[e]
C3...C11	6.448(20)	0.220[e]	6.317(30)	0.220[e]
C3...C12	5.467(21)	0.357[f]	5.714(17)	0.220[e]
C3...C13	4.122(18)	0.370[e]	4.502(12)	0.269[l]
C4...C10	7.362(22)	0.220[e]	6.935(45)	0.270[e]
C4...C11	7.312(23)	0.220[e]	7.198(34)	0.220[e]
C4...C12	6.238(23)	0.270[e]	6.499(20)	0.220[e]
C4...C13	5.010(19)	0.357[f]	5.378(16)	0.235[k]
C5...C11	7.183(25)	0.160[e]	7.190(27)	0.160[e]
C5...C12	6.151(33)	0.270[e]	6.297(24)	0.270[e]
C5...C13	5.095(31)	0.357[f]	5.267(23)	0.285[k]
C6...C12	5.266(53)	0.357[f]	5.243(32)	0.285[k]
C6...C13	4.325(52)	0.454[g]	4.231(30)	0.234[j]
C7...C13	3.255(56)	0.216[h]	3.042(30)	0.232[m]
k_{50}	1.006(14)		1.000(13)	
k_{19}	1.029(19)		1.029(19)	
R	0.085		0.082	

[a] Standard deviations from the least-squares refinement are given in parentheses and refer to the last digit of the parameter value. — k_{50} and k_{19} scale theoretical molecular intensities to the experimental data

[b] Only one of the rotational angles is actually independent in these models

[c] Fixed value

[d–m] Amplitudes refined in groups

important parameters (Table II) were obtained first separately for models *C* and *D* as described in Ref. [8], then the larger of them was increased by the difference between the corresponding parameter values.

Table II

Structural parameters of diphenyl sulfide[a]

	r_a (Å)	l (Å)
S—C	1.771(5)	0.049(4)
C—C	1.399(3)	0.046(2)
C—H	1.089(8)	0.081(8)
⟨C—S—C	103.7(13)°	

[a] Error limits in parentheses refer to the last digit of the value given

Discussion

This structure analysis has not provided an unambiguous elucidation of the conformation of diphenyl sulfide. We have found at least two conformers (models *C* and *D*, Table I) that agree with the experimental data. It was an important restriction, however, that in all models except the (0°, 90°) models, the absolute values of φ_1 and φ_2 were confined to be equal. Our findings do not conflict with the interpretation of vibrational spectra, according to which the two phenyl groups are nonequivalent in diphenyl sulfide [11]. EHT calculations on the conformation of diphenyl sulfide yielded a (35°, 35°) conformer [12]. An X-ray study of crystalline poly-*p*-phenylene sulfide gave (45°, 45°) for the dihedral angles and 110° for the C–S–C angle [13]. The molecules of diphenyl sulfide probably cannot be characterized by a fixed conformation in the vapour phase: there may be a mixture of several conformers and/or the phenyl rings perform large amplitude torsional vibrations.

Although the conformation of diphenyl sulfide could not be ascertained, it is important that the bond parameters and the sulfur bond angle proved to be independent of the assumed conformation of the model. The mean values of the most important parameters from columns *C* and *D* of Table I are given in Table II, and are considered to be a fair representation of the results of this structure analysis. As for the C–S–C angle, it must be noted that values close to the preferred 103.7° were obtained in most of the refinement schemes, and this choice is strengthened by evidence from the radial distributions,

yet larger angles, 116°, 121°, emerged in some schemes, and they were ruled out only by qualitative arguments based on the radial distribution curves. The bond lengths in Table II can be regarded reliable, since their correlation with other parameters is small.

The bond lengths and the C–S–C angle of diphenyl sulfide given in Table II are in accordance with those in similar molecules (Table III). Thus, r_g(C–C) = = 1.399±0.001 Å and r_g(C–H) = 1.101±0.005 Å in benzene [20]. (See also Ref. [10] for the parameters of benzene sulfonyl chloride.) In thianthren,

Table III

Bond lengths S–X and angles X–S–X in some sulfides SX_2 and sulfones SO_2X_2[a]

X	r(S—X) (Å)		⟨X—S—X (deg.)		Reference	
	SX_2	SO_2X_2	SX_2	SO_2X_2	SX_2	SO_2X_2
F	1.589[b]	1.530(3)[b]	98.3[b]	96.1(2)[b]	[14][b]	[15][b]
Cl	2.006(4)[c]	2.011(5)	103.0(4)	100.0(7)	[16]	[17]
CH_3	1.810(4)	1.771(4)	99.2(6)	102.6(9)	[1]	[9]
$(CH_3)_2N$	1.688(6)	1.651(3)	114.5(16)	110.5(13)	[2]	[18]
C_6H_5	1.771(5)	1.768[e]	103.7(13)	104.1(1)[e]	[d]	[19][e]

[a] Unless noted otherwise, the values are r_a parameters from electron diffraction studies. Error limits in parentheses refer to the last digit of the value given
[b] Microwave study, r_0 value
[c] Electron diffraction study, r_g value
[d] This work
[e] X-ray diffraction, crystalline phase, average r(S–C) value

r_g(S–C) = 1.770±0.003 Å and <C–S–C = 104.1° [21]. r_a(S–C) is shorter in diphenyl sulfide than in dimethyl sulfide, and the difference is smaller than it is for the corresponding carbon-oxygen bonds: in anisole, $r_a(C_{ar}–O)$ = = 1.361±0.015 Å, r_a(C–O) = 1.423±0.015 Å [22] and in dimethyl ether, r(C–O) = 1.416±0.003 Å [23].

Finally, we should like to call attention to a few features of the data in Table III. The bond S–X is shorter in the sulfone SO_2X_2 than in the corresponding sulfide SX_2 when X = F, CH_3 or $(CH_3)_2N$,whereas little or no difference is observed in the case of Cl and C_6H_5. Angle X–S–X in a sulfone is similar to that in the corresponding sulfide. Angle N–S–N is considerably larger than the other values in Table III.

Comparison of the structures of diphenyl sulfide, sulfoxide, and sulfone will be possible after completing the studies on the other two compounds.

Appendix

Diphenyl sulfide. Total experimental intensities for camera ranges of **50** *cm and* **19** *cm and an accelerating voltage of* **60** *kV.*

$s = (4\pi/\lambda) \sin(\vartheta/2)$ is in $Å^{-1}$ units, λ wavelength, ϑ scattering angle; the intensity is in arbitrary units

s	.00	.25	.50	.75	s	.00	.25	.50	.75
50 *cm*					**19** *cm (continued)*				
1				4084	11	5074	5081	4990	4785
2	3866	3933	4359	4983	12	4574	4421	4345	4331
3	5400	5408	5119	4790	13	4341	4383	4452	4530
4	4666	4919	5496	6196	14	4582	4573	4485	4354
5	6789	7068	6963	6636	15	4246	4192	4172	4156
6	6291	6000	5715	5488	16	4103	4047	3968	3893
7	5296	5141	5051	5010	17	3828	3794	3786	3816
8	5000	4956	4885	4836	18	3886	3951	3999	4008
9	4861	4964	5075	5097	19	3967	3894	3793	3706
10	5006	4834	4715	4712	20	3643	3609	3603	3589
11	4785	4822	4754	4584	21	3576	3553	3523	3507
12	4393	4264	4223	4228	22	3490	3481	3467	3460
13	4280	4323	4398		23	3463	3465	3458	3441
					24	3406	3369	3334	3299
19 *cm*					25	3272	3248	3225	3203
					26	3195	3190	3182	3176
6		7938	7486	6972	27	3164	3153	3144	3133
7	6603	6320	6107	5993	28	3122	3114	3101	3083
8	5910	5790	5637	5527	29	3068	3046	3028	3010
9	5486	5519	5574	5571	30	2987	2960	2944	2930
10	5406	5204	5057	5035	31	2926	2932	2923	

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ELECTRON DIFFRACTION INVESTIGATION OF THE MOLECULAR STRUCTURE OF VINYLSULFONYL CHLORIDE

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The molecular structure of vinylsulfonyl chloride has been studied in the vapour phase by electron diffraction. There may be three conformers present as regards rotation around the C–S bond, characterized by rotation angles (C=C–S–Cl) 60, 80 and 160—180° (0° corresponds to *anti* form). The following bond lengths (r_a) and bond angles were determined:

C=C	1.357±0.018	C–C–S	121.3±1.7
S–C	1.744±0.005	C–S–Cl	100.2±0.6
S=O	1.420±0.006	C–S=O	109.8±0.4
S–Cl	2.035±0.005	O=S=O	122.0±1.0
		Cl–S=O	106.4±0.5

The overall sulfur bond configuration is consistent with the geometries determined in other simple sulfone molecules. The C=C bond is among the longest observed in substituted ethylenes. The S–C bond is shorter than in other sulfonyl chlorides.

Introduction

In the course of our structural studies on simple sulfone molecules including sulfonyl halides, the following compounds have recently been investigated employing electron diffraction:

Compound	Reference
FSO_2OCH_3	[1]
FSO_2CH_3	[2]
$ClSO_2OCH_3$	[3]
$ClSO_2Cl$	[4]
$ClSO_2CH_3$	[5]
$ClSO_2C_6H_5$	[6]
$ClSO_2N(CH_3)_2$	[7]
$CH_3SO_2CH_3$	[8]
$(CH_3)_2NSO_2N(CH_3)_2$	[9]

The main purpose of these studies is to determine the geometrical configurations at the sulfur atom and to correlate the variations in the geometrical parameters with bonding properties. In addition, some of the compounds mentioned seem to possess interesting conformational properties which can be most completely investigated in the vapour phase.

Vinylsulfonyl chloride, $CH_2=CH-S(O_2)Cl$, was chosen for an electron diffraction study to examine the influence of the vinyl group on the configuration of the sulfonyl chloride moiety as compared with those of other substituents. Also, it was hoped to gain some information on the conformational properties of this compound. We are aware of no structural data in the literature for sulfone molecules in which the vinyl group is adjacent to the SO_2 group. The lack of such information, and in particular that of vibrational spectroscopic data, was a limiting factor for this investigation concerning the conformational analysis.

Experimental

The purity of the vinylsulfonyl chloride sample used in this investigation was confirmed by mass spectrometry [10]. The electron diffraction patterns were taken with the Budapest apparatus [11, 12], a modified EG-100A unit, by essentially the same technique as in some other studies mentioned above [2, 5, 8]. The temperature of the nozzle of the so-called membrane nozzle system [11] was about 60 °C during the exposures. The wavelength of the electron beam was determined from the diffraction pattern of thallium(I) chloride. The ranges of intensity data used were $1.75 \leq s \leq 13.00$ Å^{-1} and $6.50 \leq s \leq 35.25$ Å^{-1} with $\Delta s = 0.25$ Å^{-1}. The total experimental intensity values are listed in the Appendix. The experimental molecular intensities corresponding to the two camera ranges were obtained as before [2, 5, 8]. The scaled and averaged molecular intensities, $sM^E(s)$, are shown in Fig. 1.

Structure analysis

A molecular model with numbering of the atoms is shown in Fig. 2. The following comments are needed to clarify the model used in this analysis: (*i*) The H_2CCHS part of the molecule was assumed to be planar. (*ii*) The bond angles H–C–H and S–C–H were kept equal to 120° (in fact it proved to be impossible to refine them), however, these parameters were included into the final refinement scheme which was used to establish the standard deviations of the parameters. (*iii*) The same r(C–H) and l(C–H) values were used for all C–H bonds. (*iv*) It was assumed that the bond lengths and bond angles are the same for all rotational forms. This assumption was then tested by examin-

ing the changes in these parameters as obtained for very different conformational ratios.

A number of conformers are *a priori* possible for vinylsulfonyl chloride. They can be characterized by forms shown in Fig. 2.

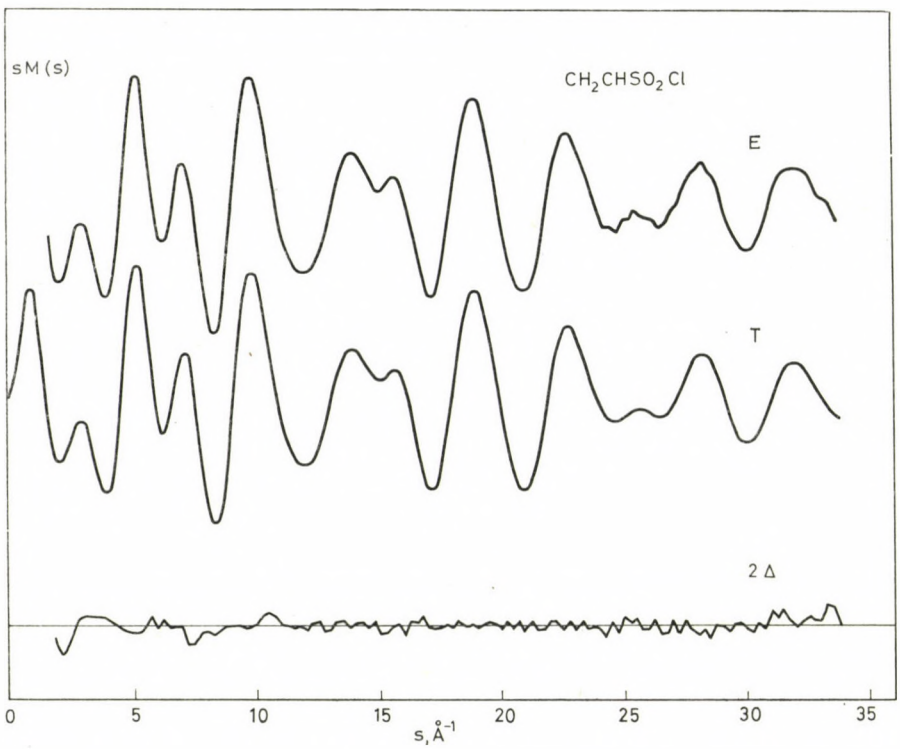


Fig. 1. Experimental (E) and theoretical (T) molecular intensities. The latter was calculated from the parameters given in Column *a* of Table III. Twice the differences between the experimental and theoretical values are also shown [$\Delta = sM^{E}(s) - sM^{T}(s)$]

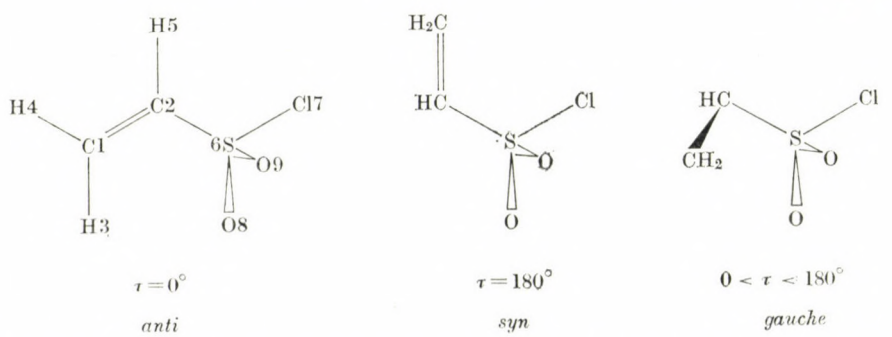


Fig. 2. Models of the *anti*, *syn*, and *gauche* conformers of vinylsulfonyl chloride. The numbering of atoms and the definition of the angle of rotation (τ) are also shown

The radial distributions are shown in Fig. 3. The bond distances C=C and S=O contribute to the maximum appearing at about 1.42 Å. The maxima at 1.75 and 2.03 Å can be unambiguously assigned to the bonds S–C and S–Cl, respectively, although some other distances with small contributions are also present in this region. The maximum around 2.78 contains primarily the contribution of the non-bond distances through one bond angle. However, some important rotation-dependent distances may be expected to be as small as to appear under this maximum. The broad maximum in the region between 3.4 and 4.1 Å contains the contribution from the rest of the most important rotation-dependent distances. Unfortunately, the experimental radial distribution of vinylsulfonyl chloride provides little information concerning the rotational forms present.

The structure refinement has been performed in a similar manner as before (*e.g.* [6, 7]). The least squares method was applied to the molecular intensities [13]. The coherent and incoherent scattering amplitudes were taken from published tables ([14] and [15], resp.).

Spectroscopic calculations were used to obtain the mean square parallel amplitudes of vibration (l values) and also the K values ($K = [<(\Delta x)^2> + <(\Delta y)^2>]/2r$, where $<(\Delta x)^2>$ and $<(\Delta y)^2>$ are the mean square perpendicular amplitudes of vibration and r is the internuclear distance for a given atomic pair). A very tentative force field was constructed from a combination of the force fields of ethylene [16] and the SO_2Cl part of methane sulfonyl chloride [17]. The calculated mean amplitudes of vibration are presented in Tables I and II for the rotation-independent and rotation-dependent distances,

Table I

Calculated mean amplitudes of vibration (Å)
*Rotation-independent distances**

Bonds	l (Å)	K (Å)	Non-bond distances	l (Å)	K (Å)
C=C	0.040	0.005	S... C	0.061	0.002
C–H, average	0.078	0.024	Cl... C	0.064	0.001
S–C	0.044	0.001	O... C	0.066	0.002
S=O	0.036	0.003	S... H3	0.141	0.013
S–Cl	0.051	0.001	S... H4	0.096	0.008
			S... H5	0.097	0.010
			Cl... O	0.076	0.002
			O... O	0.069	0.003
			Cl...H5	0.101	0.015
			C2...H3	0.098	0.020

* The numbering of atoms is given in Fig. 2; the H...H distances are not listed
** average

Table II

Calculated mean amplitudes of vibration
*Rotation-dependent distances**

	l (Å)				K (Å)			
τ(°)	0	60	90	180	0	60	90	180
Cl... C	0.068	0.084	0.095	0.100	0.001	0.001	0.001	0.001
O8...Cl	0.093	0.103	0.104	0.086	0.002	0.002	0.002	0.001
O9...Cl	0.093	0.075	0.068	0.086	0.002	0.002	0.001	0.001
Cl... H3	0.134	0.172	0.198	0.176	0.007	0.007	0.007	0.016
Cl... H4	0.118	0.133	0.141	0.131	0.005	0.005	0.006	0.007
Cl... H5	0.129	0.145	0.141	0.097	0.009	0.006	0.006	0.006
O8...H3	0.184	0.180	0.185	0.169	0.010	0.014	0.014	0.009
O8...H4	0.128	0.127	0.129	0.126	0.007	0.008	0.008	0.006
O8...H5	0.123	0.098	0.100	0.131	0.007	0.007	0.007	0.008
O9...H3	0.184	0.155	0.140	0.169	0.010	0.009	0.008	0.009
O9...H4	0.128	0.118	0.113	0.126	0.007	0.006	0.006	0.006
O9...H5	0.123	0.137	0.134	0.131	0.007	0.008	0.008	0.008

* The numbering of atoms is given in Fig. 2

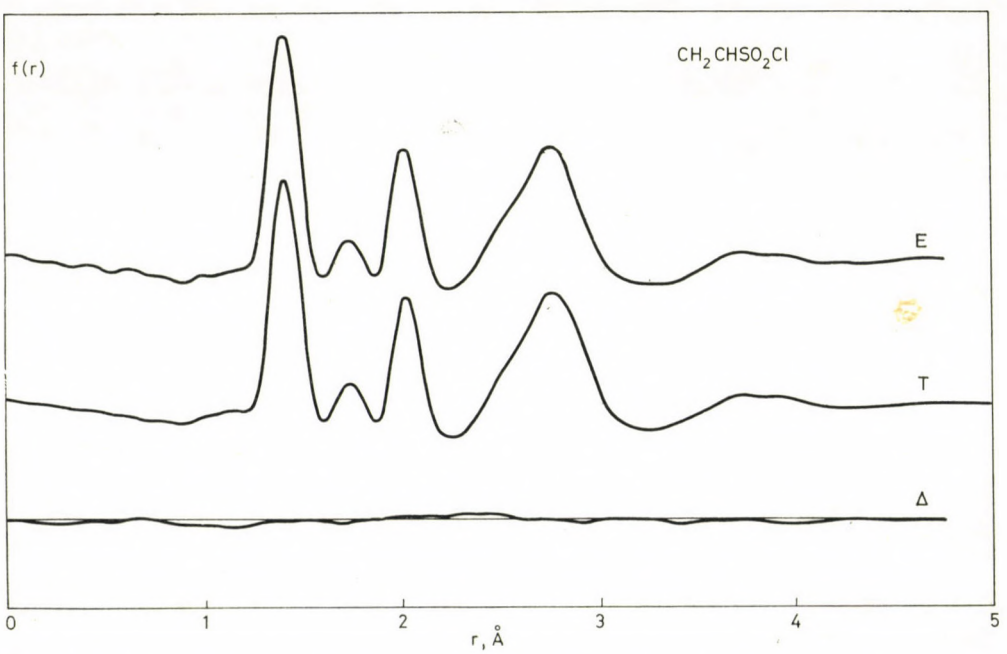


Fig. 3. Experimental (E) and theoretical (T) radial distributions and the difference curve (Δ). The theoretical distribution was calculated from the parameters given in Column *a* of Table III. The constant $a = 0.0015$ Å^2 was used in the damping factor

respectively. Although attempts have been made to refine the l values for both the bond and important non-bond distances, the results for the latter could not be considered reliable because of the strong correlations involving the vibrational and geometrical parameters and those characterizing the conformational properties. Thus in the final stages of this analysis the bond amplitudes, except l(C–H), were treated as independent parameters while all the others were assumed from the spectroscopic calculations.

Concerning the rotational forms and their relative abundance, at the beginning, models containing only one form were tested. Three minima occurred in the quantities of $\sum_i W_i \Delta_i^2$ (where W_i are the weights and Δ_i are the differences between the experimental and the calculated theoretical molecular intensities). These three minima corresponded to rotational angles of about 60, 90, and 160 to 180°. In these calculations the bond distances and bond angles were also refined. It is important to note that already in these calculations these geometrical parameters showed very little sensitivity towards changes in the rotational angles.

In the later stages in this analysis, mixtures of two (τ_1 and τ_2 in the vicinity of 60 and 160 to 180°, respectively) and then three forms were used to further refine the bond distances and bond angles and to determine both the rotational angles and the relative abundance of the conformers.

Two refinement schemes were constructed in the investigation of the conformational ratios. In one (*a*) the sum of the conformers was forced to be 100%, while in the other scheme (*b*) no such constraint was imposed upon the sum of the rotation-dependent contribution. The latter scheme was thought to be useful for testing purposes. In fact, the unconstrained refinement scheme (*b*) never provided results which added up to 100%, although various starting amounts and l values for the rotation-dependent distances were tried in these calculations. Typical results for the two schemes, in which three rotational forms were considered, are compiled in Table III as a representation of the findings of this analysis.

In connection with the conformational analysis of vinylsulfonyl chloride, we would like to summarize our comments in the following points:

(*i*) The contribution from the rotation-dependent distances to the total scattering is relatively very small, thus an accurate picture of the conformational properties of this system is not to be expected.

(*ii*) The situation is further complicated by the fact that the contribution from the rotation-dependent distances is little sensitive to changes in the rotational angles in relatively large intervals of the latter. This insensitivity comes not only from the insensitivity of the rotation-dependent distances to the rotational angle but also from the fact that the various rotation-dependent distances exchange their places of appearance on the radial distribution

Table III

Results of least squares refinements for a mixture of three conformers

	a		*b*	
Bond distances	*r*	σ	*r*	σ
C=C*	1.356	0.016	1.356	0.019
C—H**	[1.120]	0.011	[1.118]	0.011
S—C*	1.744	0.002	1.745	0.002
S=O*	1.419	0.003	1.419	0.004
S—Cl*	2.035	0.001	2.035	0.001
Bond amplitudes	*l*	σ	*l*	σ
C=C*	0.038	0.021	0.040	0.023
C—H**	[0.078]	0.010	[0.078]	0.010
S—C*	0.051	0.002	0.052	0.002
S=O*	0.040	0.003	0.040	0.004
S—Cl*	0.050	0.001	0.050	0.001
Bond angles	$\langle$	σ	$\langle$	σ
C—C—S*	121.3	1.0	121.3	1.2
C—S—Cl*	100.0	0.3	100.3	0.3
C—S=O*	109.9	0.2	109.8	0.2
O=S=O*	122.2	0.6	121.8	0.6
H—C—H**	[120]	9	[120]	10
S—C—H**	[120]	8	[120]	8
Cl—S=O***	106.2	0.2	106.5	0.2
Some non-bond distances (independent of rotation)	*r*	σ	*r*	σ
S...C***	2.709	0.005	2.710	0.005
Cl...C***	2.900	0.006	2.908	0.006
O...C***	2.595	0.004	2.595	0.004
Cl...O***	2.787	0.003	2.791	0.003
O...O***	2.484	0.011	2.479	0.012
Angles of rotation (°)	τ	σ	τ	σ
τ_1*	58	4	60	4
τ_2*	167	5	177	29
τ_3*	80	13	82	13
Amount of conformers (%)	α	σ	α	σ
α_1*	45	10	33	10
α_2*	38	10	17	13
α_3	17***	—	17*	9

* Independent parameters
** Assumed
*** Dependent parameters

curve. This point is illustrated by Fig. 4 where the variations of the most important rotation-dependent distances are shown as a function of the rotational angle.

(*iii*) The mean amplitudes of vibration for the rotation-dependent distances cannot be determined from this study, although they would be important since they certainly strongly correlate both with the parameters characterizing the conformational composition and the rotational angles. In this study the values tentatively obtained for an assumed force field were used in the final calculations as fixed parameters. This fact has to be further considered when judging the reliability of the results from this study concerning the conformational properties of vinylsulfonyl chloride.

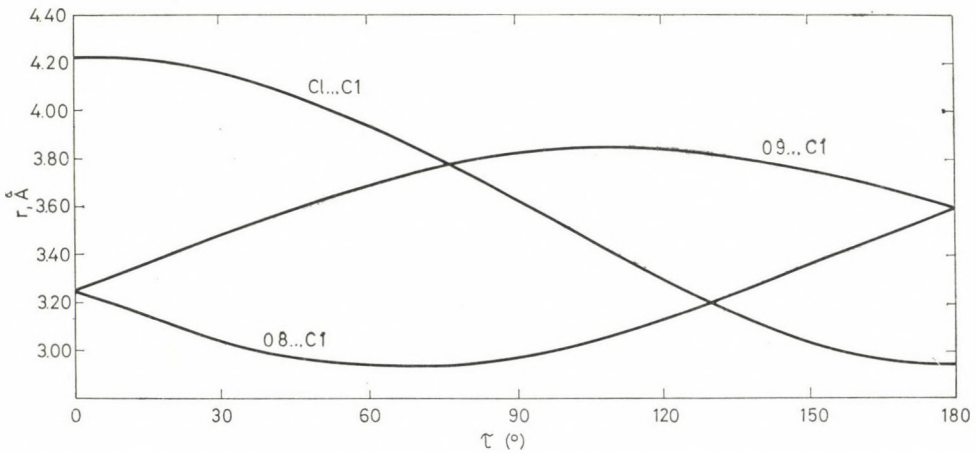


Fig. 4. Variations of the most important rotation-dependent distances as a function of the angle of rotation (τ). For the numbering of atoms and the definition of τ, see Fig. 2

(*iv*) The geometrical parameters such as bond distances and bond angles and also the amplitudes of vibration for the bond distances were very stable under the various conditions used in the refinements and were strongly insensitive to the conformational properties of the models for which the calculations were carried out.

Discussion

The electron diffraction data indicate that three conformers may be present in the gas phase of vinylsulfonyl chloride characterized by rotational angles in the vicinity of 60, 80 and 160—180°, respectively. The two forms with angles of rotation of 60 and 80° could probably be substituted by one intermediate form with somewhat larger vibrational amplitudes for the

rotation-dependent distances. Because of the relatively small contribution of the rotation-dependent distances to the total molecular scattering and the lack of vibrational spectroscopic data, it is not possible to obtain a detailed picture of the conformational composition from the experimental information available at this time.

The bond lengths and bond angles with their total uncertainties are given in the summary. These parameters and also the bond mean amplitudes of vibration determined in this study were found to be insensitive to changes in the relative amounts of the conformers considered in the models.

The C=C bond of vinylsulfonyl chloride is among the longest in substituted ethylenes, as illustrated in Table IV. As noted by YOKOZEKI and BAUER [25], the C=C distances, except for the fluorinated compounds, are longer than that in ethylene; $(CF_3)_2C{=}CH_2$ seems to be the only exception (*cf.* Table IV).

Table IV

*Lengths of the C=C bonds in ethylene and some substituted derivatives**

Compound	r_g(C=C), Å	Ref.
$H_2C{=}CH_2$	1.337±0.002	[18]
$F_2C{=}CF_2$	1.311±0.007	[19]
$FHC{=}CF_2$	1.309±0.006	[19]
$F_2C{=}CH_2$	1.316±0.006	[19]
$(CF_3)_2C{=}CH_2$	1.374±0.013	[26]
$H_2C{=}CHSCH_3$	1.342±0.003	[20]
$H_2C{=}C(SCH_3)_2$	1.349±0.005	[21]
$H_2C{=}C(CH_3)_2$	1.342±0.003	[22]
$(CH_3)_2C{=}C(CH_3)_2$	1.351±0.003	[23]
$CH_3CH{=}CHCH_3$ *cis*	1.347±0.003	[24]
trans	1.348±0.003	[24]
$H_2C{=}CHSO_2Cl$	1.357±0.018	this work

* Vapour phase data

The S–C bond of vinylsulfonyl chloride is somewhat shorter than those in other sulfonyl chlorides, *viz.*

$$C_6H_5SO_2Cl \quad r(S{-}C) = 1.765 \pm 0.009 \text{ Å} \qquad [6]$$

$$CH_3SO_2Cl \quad r(S{-}C) = 1.764 \pm 0.005 \text{ Å} \qquad [5]$$

The length of the S–Cl bond in vinylsulfonyl chloride is intermediate among those in sulfonyl chlorides determined so far and listed in Table V. As the O. . . Cl non-bond distances are also given, it can be seen that the S–Cl bond distances show a larger variation than the non-bond distances which may be an indication of the importance of oxygen . . . chlorine non-bond interactions in the structures of the SO_2Cl moieties.

Table V

*The S—Cl bond and O. . .Cl non-bond distances and O—S—Cl bond angles in some simple sulfonyl chlorides**

Compound	r_g(S—Cl), Å	O—S—Cl,°	r(O. . .Cl), Å	Ref.
$ClSO_2Cl$	2.001	107.7	2.781	[4]
CH_3OSO_2Cl	2.023	106.3	2.779	[3]
$CH_2{=}CHSO_2Cl$	2.035	106.3	2.789	this work
$C_6H_5SO_2Cl$	2.047	105.5	2.780	[6]
CH_3SO_2Cl	2.046	107.1	2.816	[5]
$(CH_3)_2NSO_2Cl$	2.064	105.8	2.806	[7]

* Vapour phase data

A more striking example of the possible importance of non-bond interactions in the simple sulfone molecules is shown by the remarkable constancy of the r(O. . . O) values (2.48—2.49 Å) while the S=O bonds and O=S=O bond angles show the variations consistent with the predictions of the V.S.E.P.R. model. This has been discussed by us repeatedly and the data of vinylsulfonyl chloride are completely consistent with these observations (for a compilation of the data of the S=O, O. . . O distances and O=S=O angles in sulfones, see HARGITTAI and BRUNVOLL [7]).

Appendix 1

Numerical values of the total experimental intensities, 50 cm camera range, $s_{min} = 1.75$ Å^{-1}, $s_{max} = 13.00$ Å^{-1}, $\Delta s = 0.25$ Å^{-1}; the table develops horizontally

0.4811	0.4982	0.5602	0.6379	0.7100
0.7584	0.7815	0.7877	0.7914	0.8079
0.8475	0.9066	0.9658	1.0034	1.0079
0.9805	0.9359	0.8888	0.8695	0.8703
0.8846	0.8929	0.8865	0.8636	0.8343
0.8057	0.7900	0.7912	0.8052	0.8256
0.8451	0.8601	0.8653	0.8612	0.8495
0.8331	0.8157	0.8007	0.7895	0.7812
0.7755	0.7728	0.7724	0.7731	0.7736
0.7770				

Appendix 2

Numerical values of the total experimental intensities, 19 cm camera range, $s_{min} = 6.50$ Å^{-1}, $s_{max} = 35.25$ Å^{-1}, $\Delta s = 0.25$ Å^{-1}; the table develops horizontally

1.1151	1.1276	1.1138	1.0909	1.0589
1.0200	0.9831	0.9540	0.9456	0.9512
0.9668	0.9865	0.9978	1.0010	0.9926
0.9759	0.9546	0.9325	0.9122	0.8971
0.8850	0.8771	0.8684	0.8646	0.8620
0.8599	0.8616	0.8640	0.8647	0.8622
0.8582	0.8516	0.8437	0.8373	0.8301
0.8261	0.8233	0.8188	0.8110	0.8030
0.7923	0.7828	0.7739	0.7692	0.7683
0.7703	0.7736	0.7779	0.7802	0.7808
0.7783	0.7734	0.7662	0.7566	0.7465
0.7383	0.7301	0.7247	0.7216	0.7186
0.7185	0.7198	0.7213	0.7224	0.7215
0.7197	0.7153	0.7110	0.7052	0.7001
0.6954	0.6908	0.6883	0.6851	0.6839
0.6813	0.6794	0.6761	0.6732	0.6705
0.6669	0.6646	0.6634	0.6613	0.6607
0.6590	0.6568	0.6548	0.6514	0.6484
0.6442	0.6399	0.6363	0.6330	0.6301
0.6279	0.6268	0.6256	0.6254	0.6242
0.6232	0.6211	0.6187	0.6160	0.6130
0.6095	0.6063	0.6040	0.6016	0.5994
0.4016	0.3049	0.3045	0.3029	0.3021
0.2032				

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ALKALOIDS CONTAINING THE INDOLO[2,3-c]QUINAZOLINO [3,2-a]PYRIDINE SKELETON, VI*

PREPARATION OF *CIS*- AND *TRANS*-HEXAHYDRORUTECARPINE**

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Similarly to the synthesis of rutecarpine [1], 1,2,3,4-tetrahydro-1-oxo-β-carboline (**3**) was condensed with *cis* (**1**) and *trans*-2-aminocyclohexanecarboxylic acid (**2**). The end products were two stereoisomers: *cis*- (**4**) and *trans*-hexahydrorutecarpine (**5**). The structures of (**4**) and (**5**) were proved by the UV, IR, NMR and MS spectra.

cis- (**6**) and *trans*-Hexahydrorutecarpic acids (**7**) regarded as intermediates in the condensation reaction have also been synthesized; these compounds also give (**4**) and (**5**) by ring closure.

In our earlier papers [1—5] rutecarpine derivatives containing an aromatic ring E have been discussed. In the present work, rutecarpine derivatives having a hydrated ring E are dealt with. These compounds are the starting materials in the synthesis of derivatives with 14-azayohimbane skeleton.

Since, according to our earlier experience, ring E in rutecarpine cannot be hydrogenated [1], a 2-aminocyclohexanecarboxylic acid with given stereochemical properties was required for the synthesis. The following literature data were found in this connection. *cis*-2-Aminocyclohexanecarboxylic acid (**1**) can be prepared by the catalytic reduction of 2-aminocyclohexene-1-carboxylic acid ester as described by HÜNIG and KAHANEK [9], or by the addition of ammonia to cyclohexene-1-carboxylic acid, according to PLIENINGER and SCHNEIDER [10]. EINHORN [6, 7] and ORTHNER and HEIN [8] prepared *trans*-2-aminocyclohexanecarboxylic acid (**2**) by the sodium amylate reduction of anthranilic acid, followed by proper purification.

In our work, EINHORN's method [6, 7] was applied in the preparation of *trans*-2-aminocyclohexanecarboxylic acid (**2**). The *cis* compound (**1**) was also successfully made directly from anthranilic acid in our experiments. In contrast with earlier findings [11, 12], it was found that the hydrogenation of anthranilic acid in the presence of Adams catalyst at room temperature in a

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mixture of glacial acetic acid and concentrated hydrochloric acid gave directly *cis*-2-aminocyclohexanecarboxylic acid (**1**).

In the next step, 1,2,3,4-tetrahydro-1-oxo-β-carboline (**3**) was subjected to condensation with the *cis* and *trans* compounds (**1**) and (**2**) under the conditions established by us [1], to obtain two stereoisomeric compounds, *cis*- (**4**) and *trans*-hexahydrorutecarpine (**5**), respectively. Both isomers could be crystallized after the processing of the reaction mixture; (**4**) was crystallized from methanol, and acetone–ethanol mixture was suitable for (**5**). Compound (**4**) contained 1 mole methanol of crystallization, which was removed by heating the substance in vacuum at the boiling point of toluene (Fig. 1).

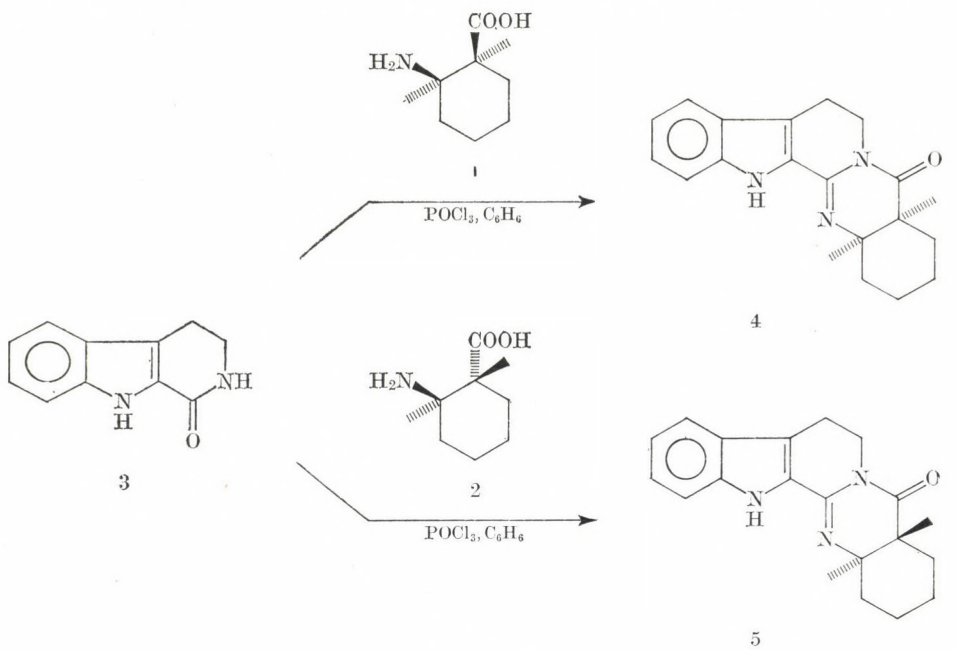


Fig. 1

The UV spectra of (**4**) and (**5**) are nearly identical, and characteristic of a double bond conjugated with the indole chromophore [(**4**) λ_{max} 306 (log ε 4.31); (**5**) λ_{max} 306 (4.34)]. In the IR spectra, the lactam CO vibrations (1690 cm^{-1}) and the C=N bands (1640 cm^{-1}) can be identified.

The structures of the two products (**4**) and (**5**) obtained in the process shown in Fig. 2 were also confirmed by the low and high resolution mass spectral data. Their molecular weights and molecular formulas are identical and agree with the expected values. The fragments and the fragmentation patterns are also identical in the two mass spectra, only the intensity ratios differ significantly.

Great differences can be observed particularly in the intensities of the molecular ions and in their stabilities, in accordance with the different thermodynamical stabilities of the *cis* and *trans* isomers. In the case of the *trans* compound (**5**), the molecular ions make up about 50% of the total ion current, whereas this is hardly 20% for the *cis* isomer (**4**) (see Σ% data).

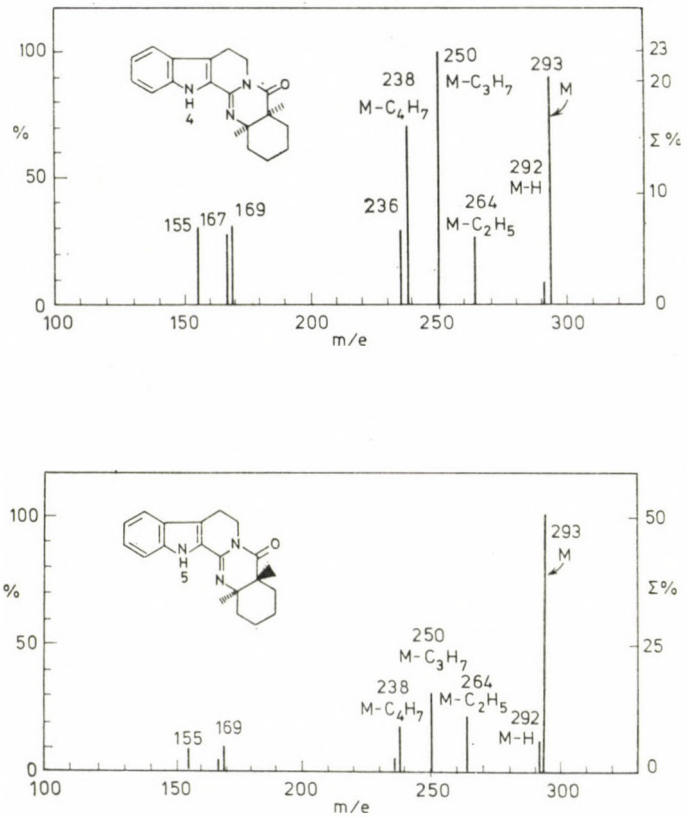


Fig. 2

In both compounds, the main fragmentation path is connected with the cleavage of ring E, in contrast with rutecarpine, where fragmentation of ring C is predominating [4].

The most important fragment ions are: *m/e* 264, *b* (M–C_2H_5); *m/e* 250, *c* (M—C_3H_7) and *m/e* 238, *d* (M—C_4H_7), and the interpretation of their formation is shown in Fig. 3. In some of the ionized molecules with odd electron number, the bond C(15)—C(16) in β-position with respect to N(14) in ring E is broken yielding intermediate *a*; this becomes stabilized through parallel steps of free radical elimination hydrogen migration processes. The driving force in these processes is the extension of conjugation and the formation of immonium ions with even electron numbers.

The intensity differences of the fragments *b*, *c* and *d* in the two stereoisomers can be explained by the difference in the frequency of formation of *a* (cleavage of ring E). The intermediates *a* formed from (**4**) and (**5**) are structurally identical from the mass spectrometric point of view, as it is confirmed by the intensity ratio of the three kinds of fragment ion species discussed

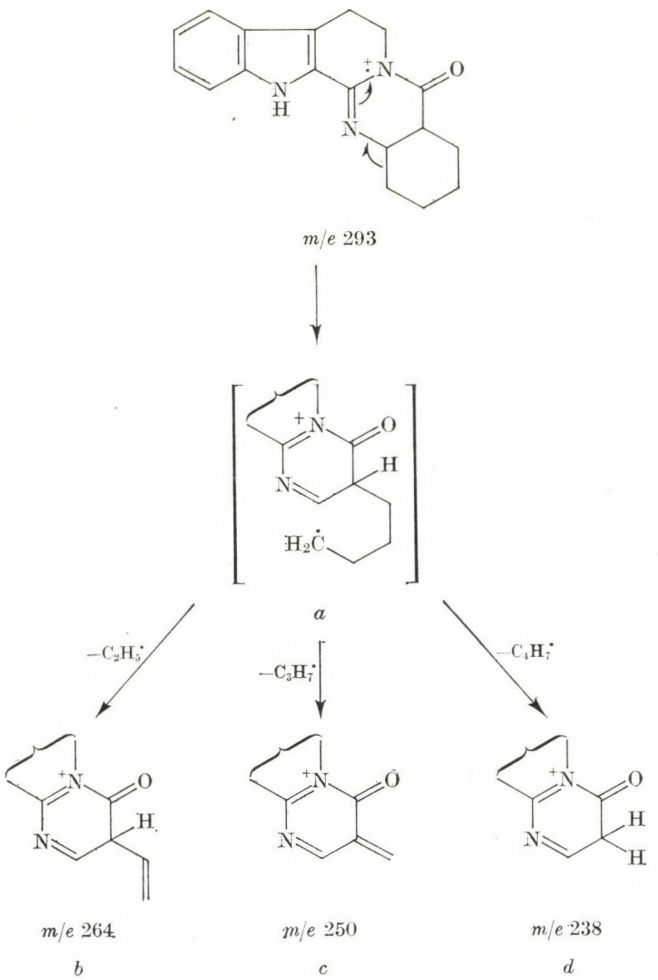


Fig. 3

above (*b*, *c*, *d*) being nearly identical in the two spectra, furthermore, by the identical intensity ratio of the metastable peaks representing the formation of these ion species in the field-free section 2 (metastable characteristics method [13]).

However, in the ^{1}H-NMR spectra, the above similarity has not been observed; the spectra of (**4**) and (**5**) were rather different (Fig. 4).

In the case of (**4**), the methylene protons H_2–C(5) and H_2–C(6) appeared in the usual range (4.22 *t* and 3.04 *t*), as triplets of A_2X_2 type. This means that ring C is flexible resulting in averaging of the chemical shifts of the *axial* and *equatorial* protons. The peak H–C(15) appears at 3.76, and the structure of the quartet also proves the existence of the *cis* isomer (of the two possible

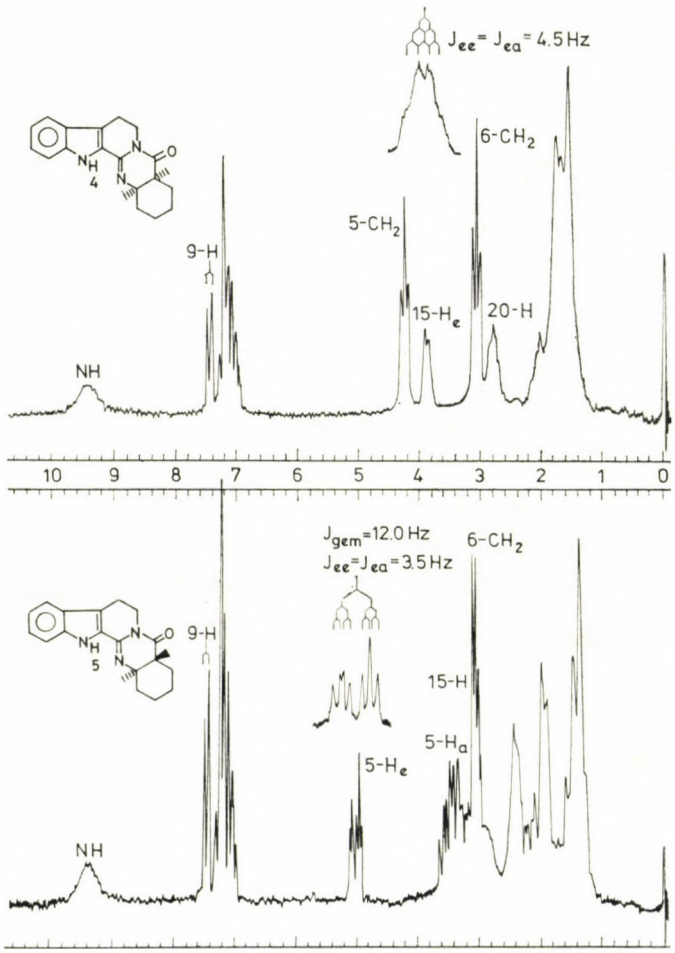


Fig. 4

structures) with *α*-position of H–C(15) and *equatorial* in ring E ($J_{ee} = 4.5$ Hz, $J_{ea} = 5.0$ Hz). On the basis of the multiplet of the neighbouring H–C(20) appearing at 2.76, this proton is really in *axial* position ($J_{aa} = 7.5$ Hz, $J_{ae} =$ $= 5.0$ Hz and 3.0 Hz). Double resonance experiments made possible the identification of the band of H_2–C(19) at 1.98, but the other alicyclic protons strongly overlap in the range 1.2—1.9, and this could not be analyzed further. A similar

strongly coupled band system was produced by the H–C(10, 11 and 12) protons between 6.9 and 7.35, while H–C(9) appears separately at 7.46 as a doublet.

These data are in all respects consistent with the structure proposed for (**4**).

The ^{1}H-NMR spectrum of (**5**) is much less distinct; only the *dt* (doublet showing further triplet splitting) band of 1-proton intensity can be observed separately at 4.99. The assignment of this band was not, however, possible without further examination, since, if it belongs to H–C(15), the multiplicity of the band cannot be explained, although the 1-proton intensity and comparison with (**4**) would suggest this interpretation. It seemed to be justified to consider another pathway of ring closure different from the assumed one, involving acylation of the indole ring. In the IR spectrum an amide C=O band of similar frequency would appear in this case, too, like in vincamone and hexahydrocantinone containing the analogous structural unit. Likewise, the UV spectrum does not exclude the above structural alternative either. However, the seven-membered ring structure can be refused unambiguously on the basis of the fact that in the ^{1}H-NMR spectra of the two latter compounds the chemical shift of the H–C(12) aromatic proton in *peri* position is very large (between 8.2 and 8.3), owing to the well-known magnetic anisotropy of the carbonyl group, while no band is found in this range for (**5**) and (**4**).

In order to simplify the spectrum, the shift reagent $Eu(dmp)_3$ was tried, but unsuccessfully, since even increased amounts of $Eu(dpm)_3$ did not separate the individual bands. It could be stated that the Eu complex was bound simultaneously to the groups N(14) and C=O, and this is responsible for the fact that the bands of the alicyclic CH protons did not separate. The LIS $\Delta\delta$ values could be determined only for the H–C(5) and H–C(9, 10, 11 and 12) protons, and these were found to be 12.8, 0.85, 0.70, 0.75 and 1.25 ppm, respectively, by means of graphical interpolation.

In the next step, assignment of the band at 4.99 was attempted by comparison of the chemical shifts of (**5**), measured in $CDCl_3$ and CF_3COOH. If the band should be assigned to H–C(15), a considerable change of the chemical shift is expected in the salt [15]. In the case of (**4**) an increase of 0.55 ppm was really found in the salt; however, there was a shift of 0.35 observed for H_2–C(5), too, indicating substantial delocalization of the positive charge within the acylamidine structural unit. In the case of (**5**), the chemical shift of the band examined increased only by 0.12 in the salt, thus assignment to H–C(15) can be excluded. Finally, double resonance measurements proved unambiguously that the band belongs to H_2–C(5), and the large chemical shift is caused by the C=O group in *peri* position. The band of H_a–C(5) appearing at 3.4 is partly overlapped by the multiplets of H–C(15) (3.3) and H_2–C(6) (3.0); similarly, the H–C(20) band (2.15) is merged with the bands of the other protons of ring E.

In view of these facts it can be stated that ring closure took place in this case, too, its way being analogous to the reaction path in (**4**). However, while the flexibility of ring C in (**4**) allows averaging of the two conformers, compound (**5**) has only one, definite conformation.

In order to decide, whether the hindrance of ring inversion is responsible for the absence of the averaging of chemical shifts of the H_e–C(5) and H_a–C(5)

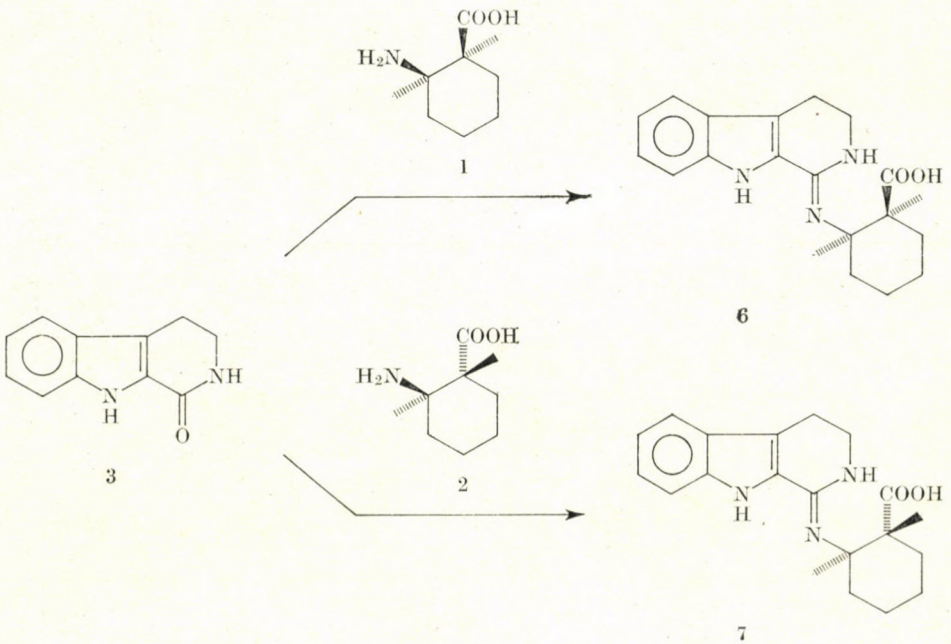


Fig. 5

protons, temperature dependence measurements were carried out. No averaging was observed in $C_6D_5NO_2$ up to $+200$ °C, thus certainly ring C is not rigid in this case either, but the most stable conformer is where the H_e–C(5) proton and C=O group are coplanar.

Further confirmation of the structures of (**4**) and (**5**) was obtained by means of the ^{13}C-NMR spectra [16].

In the preparation of (**4**) and (**5**), one mole of 1,2,3,4-tetrahydro-1-oxo-β-carboline (**3**) was allowed to react with 10 moles of $POCl_3$. When decreasing the amount of $POCl_3$, the open-chain aminocarboxylic acids (**6**) and (**7**), regarded as intermediates, also appeared. This product crystallized first on processing the reaction mixture and crystallization. After filtering off (**6**) and (**7**), the separation of the cyclic lactams, (**4**) and (**5**), slowly started. When the amount of $POCl_3$

was reduced to 3 moles, the main products were the open-chain aminocarboxylic acids, *cis*- (**6**) and *trans*-hexahydrorutecarpic acid (**7**) (Fig. 5).

The UV spectra of (**6**) and (**7**) have maxima at 226 and 315 nm. In the IR spectra, a broad band between 3200 cm^{-1} and 2400 cm^{-1}, as well as the carbonyl stretching frequency at 1720 cm^{-1} verify the open-chain aminocarboxylic acid structure.

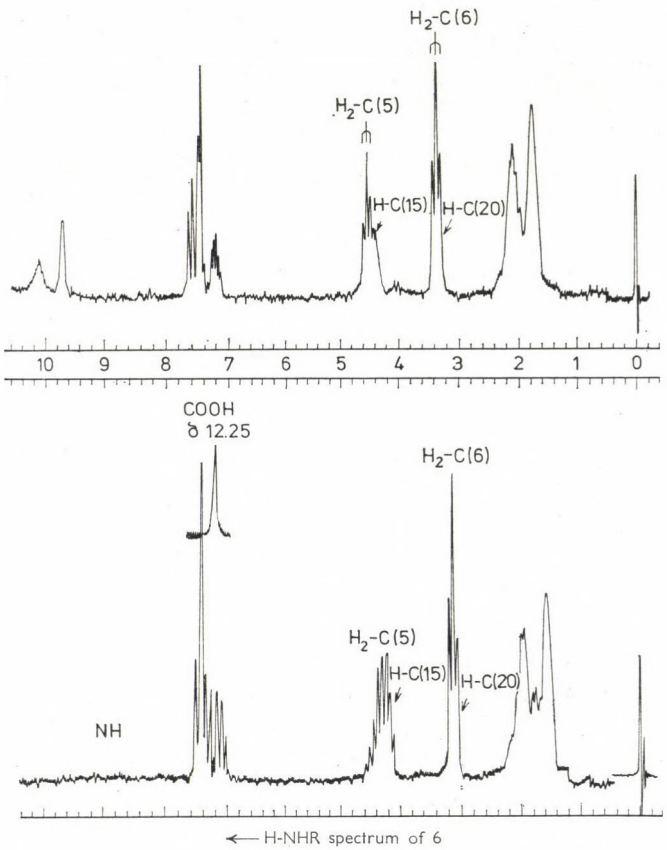


Fig. 6

Another evidence for the aminocarboxylic acid structure is provided by the ^{1}H-NMR spectrum of (**6**.) In $CDCl_3$, the band due to the proton of the carboxylic acid appears at 12.25, in addition to the NH band of 2H intensity (8.8) (Fig. 6).

When irradiating the triplet of H_2–C(6), the bands of H_2–C(5) transform into a quartet of type AB, and the geminal coupling constant was obtained from this (12.6 Hz). Considering that H_2–C(6) appears as a triplet, ring C must be flexible and undergoes rapid inversion at room temperature. At the same time, the deviation in the chemical shift of the methylene protons at

C(5) indicates that the N_b atom does not undergo inversion, that is, it behaves as a chiral centre; consequently, the methylene protons at C(5) are not enantiotopic, they are diastereotopic [14]. In order to confirm this statement, (**6**) was also examined in CF_3COOH. In this medium the chiral character of N_b is eliminated owing to protonation, thus the chemical non-equivalence of the C(5) methylene protons must be eliminated. In the spectrum, as expected, both H_2–C(6) and H_2–C(5) appear as triplets at 3.37*t* (2H) and 4.55*t* (2H), respectively.

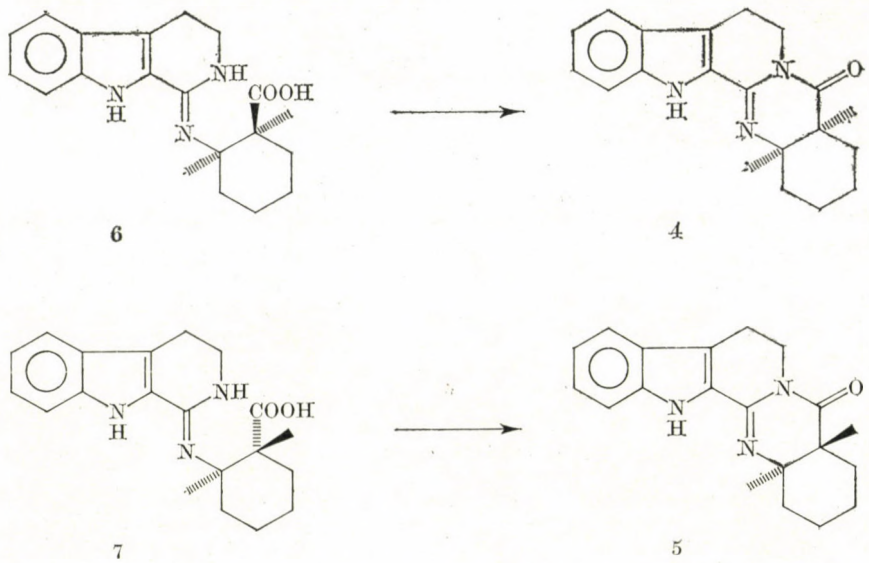


Fig. 7

Owing to the poor solubility of (**7**), NMR measurements in DMSO and TFA could not be effected.

The mass spectra of (**6**) and (**7**) were found to be identical with those of (**4**) and (**5**), respectively. This fact, as well as the appearance of significant water peaks indicate thermal transformation of (**6**) and (**7**) into (**4**) and (**5**), respectively, during examination, prior to the evaporation.

During the cyclization of *cis*- (**6**) and *trans*-hexahydrorutecarpic acid (**7**), compounds (**4**) and (**5**) were again obtained. Cyclization was effected with $POCl_3$ in benzene or with $POCl_3$ and polyphosphoric acid (Fig. 7).

Experimental

M.p.'s were measured with a Boetius M. micro-hot-stage. UV spectra were recorded with a Unicam SP-500, the IR spectra were taken on a Unicam SP-1200 spectrophotometer. The NMR spectra were obtained with a Jeol PS-100 instrument at 100 Hz, with TMS as internal standard; the chemical shifts are given according to the convention $\delta_{TMS} = 0$ ppm. An AEI-902 instrument was used for recording the mass spectra (70 eV).

cis-2-Aminocyclohexanecarboxylic acid (1)

Adams catalyst (0.67 g; 0.003 mole) was prehydrogenated in glacial acetic acid (18 ml). A solution of anthranilic acid (1.40 g; 0.01 mole) in a mixture of glacial acetic acid (35 ml) and conc. hydrochloric acid (11 ml) was then added and hydrogenation was continued at room temperature for 15 hrs. The catalyst was filtered off, and the filtrate evaporated to dryness in vacuum. The pale oily residue was dissolved in absolute ethanol (15 ml) and some ether was added to it dropwise. White crystals precipitated (1.05 g; 60%).

The base from the hydrochloride was obtained on Dowex 50X2—100 resin as follows. The resin (20 g) was activated with 0.5*M* HCl (40 ml) for 5 min, and a column was packed with it; this was washed until neutral with water, then *cis*-2-aminocyclohexanecarboxylic acid · HCl (1.0 g) was dissolved in water (15 ml) and transferred onto the column, which was then washed with water until neutral reaction was obtained. Elution of the base was begun with dilute ammonia (20 ml of conc. NH_4OH and 180 ml of water). When the eluate became alkaline, 20 ml fractions were taken. Evaporation of the first 20 ml gave a pale solid (0.70 g; 88%). After recrystallization from aqueous acetone, the m.p. was 232—234 °C (lit. m.p. 235 °C [9]). The other fractions were combined and evaporated to dryness, but practically no residue was obtained.

trans-2-Aminocyclohexanecarboxylic acid (2)

Anthranilic acid (10 g; 0.07 mole) was processed in absolute amyl alcohol (400 ml) by subjecting it to reduction with metallic sodium (32 g; 0.4 mole) according to the method suggested by EINHORN and MEYENBERG [6, 7]. The product (5.5 g; 50%) had m. p. 267—270°C (lit. m. p. 273°C).

cis-15,16,17,18,19,20-Hexahydrorutecarpine (4)

(*a*) Absolute benzene (250 ml) and $POCl_3$ (60 ml) were poured to tetrahydro-1-oxo-β-carboline **(3)** (7.4 g; 0.04 mole), and the mixture was refluxed on a water bath for about 10 min. First a solution was obtained, then a red oil separated. 2-Aminocyclohexanecarboxylic acid **(1)** (7.1 g; 0.05 mole) was added and the mixture refluxed, with stirring, for 5 hrs, then evaporated in vacuum on a water bath. The reaction mixture was made alkaline with conc. NH_4OH while cooling in ice-water and extracted with 1×200 ml, then with 2×100 ml of chloroform. After drying, the solution was evaporated to dryness. The residue was a slowly solidifying oil that was crystallized from methanol; m.p. 155—157 °C (from methanol) (8.0 g; 68%).

The filtrate was evaporated to dryness and purified on Kieselgel 60H preparative layers. The developing solvent system was benzene : methanol (25 : 2). The substance having an R_f value of 0.68 was eluted with absolute ethanol. After evaporation and crystallization, 1.4 g (80%) of the product was obtained.

$C_{18}H_{19}N_3O$ (293). Calcd. C 73.72; H 6.48; N 14.66. Found C 73.62; H 6.30; N 14.50%.

UV (EtOH: λ_{max}(log ε): 226 (4.32), 306 (4.34); (0.1*M* HCl): 246 (4.12), 340 (4.45)

IR (KBr: 3300 (νNH indole), 1670 (νC=O lactam)
1640 cm^{-1} (νC=N)

$CHCl_3$ 3470 cm^{-1}, 3300 cm^{-1} (νNH indole)
1690 (νC=O lactam), 1640 (νC=N) cm^{-1}

^{1}H-NMR ($CDCl_3$): δ = H_2—C(5) 4.22*t* (2H); H_2—C(6) 3.04*t* (2H)
J = 6.5 Hz; H_e—C(15) 3.84*q* (1H) J_{ee} = 4.5 Hz,
$J_{e,a}$ = 5.0 Hz; H_a—C(20) 2.76*m* (1H), J_{aa} = 7.5 Hz,
J_{aa} = 5.0 Hz, and 3.0 Hz, resp.; H_e—C(19)
1.98*m* (1H), H—C(9) 7.46*d* (1H) J = 0.8 Hz.
(CF_3COOH): H_2—C(5) 4.75*t* (2H), H_2—C(6) 3.39*t* (2H),
H_e — C(15) 4.37*m* (1H), H_a—C(20) 2.98*m* (1H).

MS: $M^+_{measured}$ = 293.1530, $C_{18}H_{19}N_3O$ ($M^+_{calcd.}$ = 293.1528).

(*b*) An "adduct" was prepared from tetrahydro-1-oxo-β-carboline **(3)** (0.90 g; 0.005 mole) and $POCl_3$ (9 ml) [1]. The mixture was stirred with *cis*-2-aminocylohexanecarboxylic acid **(1)** (0.71 g; 0.005 mole), absolute benzene (20 ml) was added, and the mixture was refluxed, with stirring, on a water bath for 3 hrs. The reaction mixture was processed as given under (*a*) to obtain 0.90 g (62%) of the product.

trans-15,16,17,18,19,20-Hexahydrorutecarpine (5)

(*a*) Absolute benzene (250 ml) and $POCl_3$ (60 ml) were poured to tetrahydro-1-oxo-β-carboline (**3**) (7.5 g; 0.04 mole) and the mixture was refluxed on a water bath for 10 min. First the substance dissolved, then a red oil separated. *trans*-2-Aminocyclohexanecarboxylic acid (**2**) (7.1 g; 0.05 mole) was added and the mixture refluxed, with stirring, on a water bath for 5 hrs. The solution was evaporated in vacuum to dryness, the residue was made alkaline with conc. NH_4OH while cooling in ice-water, and then extracted with chloroform (1×200, 2×100 ml). After drying, the solution was evaporated to dryness, and the oily residue was crystallized from a 1 : 1 mixture of methanol and acetone, to obtain 8.20 g (70%) of the product. After recrystallization from absolute ethanol, the m.p. was 208—210 °C.

The filtrate from the crystals was evaporated to dryness, the residue dissolved in chloroform and purified on Kieselgel 60H preparative layers. The developing mixture was benzene : methanol (25 : 2). The substance with an R_f value of 0.86 was eluted with absolute ethanol, evaporated to dryness and crystallized to give 1.60g (84%) of the substance.

$C_{18}H_{19}N_3O$ (293). Calcd. C 73.72; H 6.48; N 14.66. Found C 73.66; H 6.66; N 14.65%.

UV (EtOH): λ_{max}(log ε): 226 (4.27), 306 (4.31)
(0.1*M* HCl): 246 (4.04), 340 (4.35)

IR (KBr) 3370, 3160 cm^{-1} (νNH indole), 1690 cm^{-1} (νC=O lactam), 1640 cm^{-1} (νC=N)
$CHCl_3$: 3465, 3300 (νNH indole), 1690 (νC=O lactam), 1640 (νC = N) cm^{-1}

^{1}H-NMR ($CDCl_3$): H_e—C(5) 4.99*dt* (1H), J_{gem} = 12.0 Hz,
$J_{ea} \approx J_{ee}$ = 3.5 Hz; H_a—C(5) 3.4*m* (1H),
H_2—C(6) 3.0*m* (2H); H_a—C(15) 3.3*m* (1H);
H_a—C(20) 2.15*m* (1H); H—C(9) 7.45*d* (1H)
J = 8 Hz.
(CF_3COOH): H_e—C(5) 5.12*dt* (1H), H_2—C(6) 3.4
(2H) H_a—C(5) and H_a—C(15) 3.9 (2H).

MS: $M^+_{measured}$ = 293.1532; $C_{18}H_{19}N_3O$ ($M^+_{calcd.}$ = 293.1528).

(*b*) An "adduct" was prepared from tetrahydro-1-oxo-β-carboline (**3**) (0.90 g; 0.005 mole) and $POCl_3$ (9 ml) [1]. This was thoroughly mixed with *trans*-2-aminocyclohexanecarboxylic acid (**2**) (0.71 g; 0.005 mole), then refluxed in absolute benzene (20 ml) for 3 hrs, and processed as described under (*a*) to obtain 0.94 g (65%) of the product.

cis-15,16,17,18,19,20-Hexahydrorutecarpic acid (6)

1,2,3,4-Tetrahydro-1-oxo-β-carboline (**3**) (0.20 g 0.001 mole) was refluxed with absolute benzene (10 ml) and $POCl_3$ (0.84 g) on a water bath for 10 min. *cis*-2-Aminocyclohexanecarboxylic acid (**1**) (0.14 g; 0.001 mole) was added, and the mixture was refluxed for 5 hrs, then evaporated to dryness in vacuum. Under cooling in ice-water, the solution was adjusted to pH 7 with 2*M* NH_4OH, and extracted with chloroform (1×20, 2×10 ml), dried and evaporated to dryness. The oily residue was crystallized from methanol (0.20 g; 68%). After recrystallization from methanol, the m.p. was 195—198°C.

$C_{18}H_{21}N_3O_2$ (311). Calcd. C 69.45; H 6.75; N 13.50. Found C 69.57; H 6.82; N 13.45%.

UV (EtOH): λ_{max}(log ε): 228 (4.24), 315 (4.19)

IR (KBr): 3430 cm^{-1} (νNH sec.), 3200—2400 cm^{-1}
(νNH, COOH), 1715 cm^{-1} (νC=O acid),
1660 cm^{-1} (νC=N), 755, 740 cm^{-1} (γCH, *ortho*-disubst.)
($CHCl_3$): 3450 cm^{-1}(νNH sec.), 3200—2500 cm^{-1}
(νNH, COOH), 1730 cm^{-1} (νC=O acid), 1640 cm^{-1}(νC=N).

NMR ($CDCl_3$): H_2—C(16,17,18,19) 1.4—2.3*m* (8H), H—C(20)
3.1*m* (1H), H_2—C(6) 3.12*t* (2H) J = 6.5 Hz,
H_a—C(5) 4.25 *dd* (1H), H_e—C(5) 4.43*dd* (1H),
J_{gem}= 12 Hz, H—C(15) 4.24*m* (1H), H—C(9,11,12)
7.25—7.55*m* (3H), H—C(10) 7.10*t* (1H)
J_{ortho} = 8 Hz, NH 8.8, broad (2H), COOH 12.25*s* (1H).
(CF_3COOH): H_2—C(16,17,18,19) 1.6—2.3*m* (8H), H—C(20)
3.3 (1H), H_2—C(6) 3.37*t* (2H), J = 7 Hz,
H—C(15) 4.4 (1H), H_2—C(5) 4.55*t* (2H),
H—C(9,1011,12) 7.2—7.7 (4H).

trans-15,16,17,18,19,20-Hexahydrorutecarpic acid (7)

1,2,3,4-Tetrahydro-1-oxo-β-carboline (**3**) (0.20 g; 0.001 mole) and *trans*-2-aminocyclohexanecarboxylic acid (**2**) (0.14 g; 0.001 mole) were allowed to react as described for compound (**6**) to yield 0.24 g (80%) of a product. After recrystallization from a 2 : 1 mixture of methanol and acetone, the m.p. was 222—224 °C.

$C_{18}H_{21}N_3O_2$ (311). Calcd. C 69.45; H 6.75; N 13.50. Found C 69.30; H 6.42; N 13.41%.

UV (EtOH: λ_{max}(log ε): 228 (4.22), 315 (4.11).

IR (KBr): 3430 cm^{-1} (νNH indole), 3200—2400 cm^{-1} (νNH, COOH), 1720 cm^{-1} (νC=O acid), 1640 cm^{-1} (νC=N), 755, 745 cm^{-1} (γCH, *o*-disubst.)

Cyclization of cis-15,16,17,18,19,20-hexahydrorutecarpic acid (6)→(4)

(*a*) *cis*-Hexahydrorutecarpic acid (**6**) (0.30 g; 0.001 mole) was refluxed, with stirring, in absolute benzene (20 ml) with $POCl_3$ (1 ml; 0.003 mole) on a water bath for 3 hrs. The solution was evaporated to dryness in vacuum, cooled in ice-water, the oily residue was made alkaline with conc. NH_4OH and extracted with chloroform (1 × 30, 2 × 20 ml). After drying, the solution was evaporated to dryness, and the residue was crystallized from a mixture of methanol and acetone (1 : 1) (0.24 g; 82%), m. p. 155—157 °C.

(*b*) *cis*-Hexahydrorutecarpic acid (**6**) (0.30 g; 0.001 mole) was heated with $POCl_3$ (1 ml, 0.003 mole) and polyphosphoric acid (0.07 g) on a paraffin bath at 140 °C for 2 hrs. The reaction mixture was cooled in ice-water, absolute ethanol (5 ml) was added to it dropwise, followed by dilution with water (20 ml). The mixture was made alkaline with conc. NH_4OH, then extracted with chloroform (1 × 30, 2 × 20 ml). After drying, the solution was evaporated to dryness. Crystallization gave 0.20 g, (68%) of the product.

Cyclization of trans-15,16,17,18,19,20-hexahydrorutecarpic acid (7)→(5)

(*a*) *trans*-Hexahydrorutecarpic acid (0.30 g; 0.001 mole) (**7**) was made to react as given for the *cis* compound (0.22 g; 75%). M. p. 208—210 °C.

(*b*) *trans*-Hexahydrorutecarpic acid (**7**) (0.30 g; 0.001 mole) was treated as given for the *cis* compound (0.16 g; 55%).

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THE FORMATION OF 1,3-BENZOTHIAZOLE DERIVATIVES FROM 2,2'-DIAMINODIPHENYL DISULFIDE

SULFOCYANATION OF 2,2'-DIAMINODIPHENYL SULFIDE AND ITS REACTION WITH N-ARYL ISOTHIOCYANATES

E. VINKLER and F. KLIVÉNYI

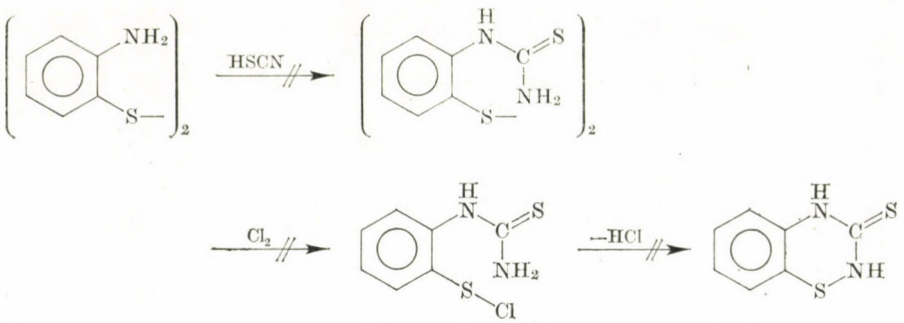
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In the reaction of 2,2'-diaminodiphenyl disulfide with hydrogen thiocyanide, 2-aminobenzothiazole and 2-benzothiazolinethiol derivatives are simultaneously formed. With aryl isothiocyanates only the 2-amino derivative is obtained. The course of the reaction and the ratio of the products formed were investigated. The structures of the benzothiazole derivatives were proved by IR spectroscopy.

In the course of research on sulfenyl chlorides in our laboratory it appeared possible to prepare thioxobenzothiadiazine derivatives containing three heteroatoms by the sulfenylation of *o*-thioureido disulfides and intramolecular ring closure.

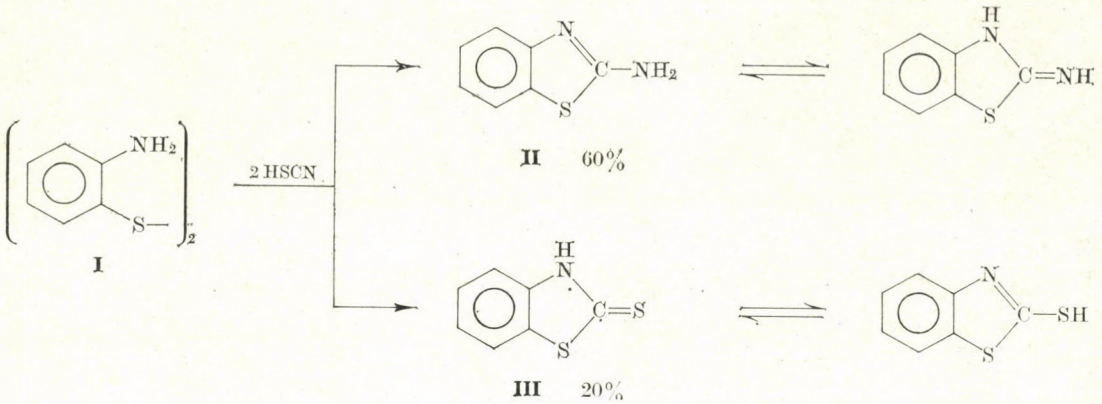
The proposed reaction route was the following:



Scheme 1

Reaction of compound I with hydrogen thiocyanide

We intended to form the thioureido group by the reaction of 2,2'-diaminodiphenyl disulfide (**I**) with hydrogen thiocyanide [1]. However, instead of the expected bis-thioureidodiphenyl disulfide, 2-aminobenzothiazole (**II**) and 1,3-benzothiazolinethion (**III**) were isolated in a total yield of 80%. Sixty per cent of the mixture, separated by chromatography, was the amino, and 20% the thion derivative (Scheme 2).



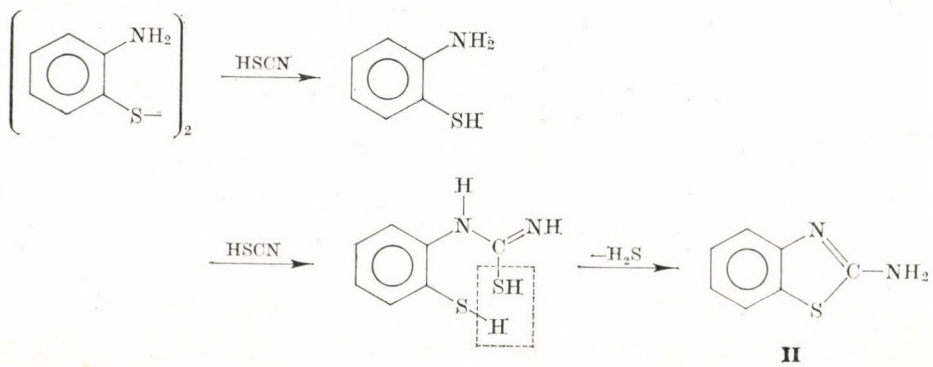
Scheme 2

It is known from several data in the literature (*e.g.* [2—5]) that aniline derivatives with a sulfur-containing substituent in *ortho* position, thus primarily 2-aminothiophenol, close a benzothiazole ring with various compounds (acetic anhydride, formic acid, carbon disulfide, nitriles, etc.).

From compound **I** only the formation of 2-methyl- and 2-mercaptobenzothiazole has been reported, in low yields, by reaction with acetic anhydride and carbon disulfide, respectively.

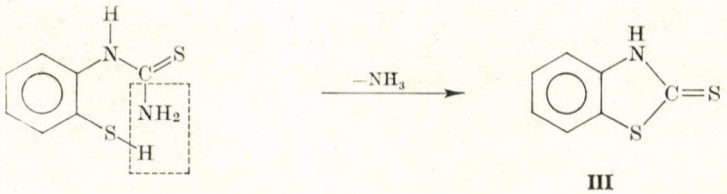
Model experiments have been made in our laboratory to elucidate the course of the reaction according to Eq. (1) in Scheme 1. It was found that hydrogen thiocyanide, or the hydrogen sulfide formed in the reaction, reduces the disulfides to thiophenol. Thus, in our case 2-aminothiophenol is formed, which, on reaction with hydrogen thiocyanide is closed to a benzothiazole ring, with the loss of ammonia and hydrogen sulfide. Simultaneously with the reduction, presumably the intermediate thiourea derivative is also formed.

The formation of 2-aminobenzothiazole may proceed by the following reaction route (Scheme 3):



Scheme 3

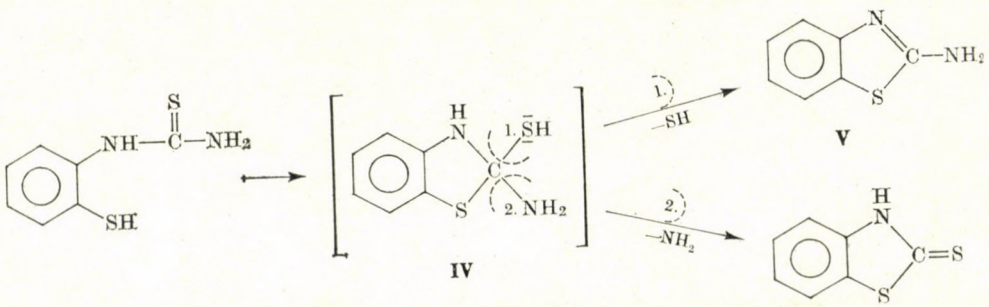
The formation of benzothiazolinethion* from 2-mercapto-N-phenylthiourea, formed as an intermediate, can be explained by ring closure with the elimination of ammonia (Scheme 4).



III

Scheme 4

The bidirectional course of the reaction can be rationalized by the formation of the benzothiazoline derivative (**IV**) as intermediate, produced by attack of the thiol group, attached to the aromatic ring, on the electrophilic carbon atom of the thiourea part. On the other hand, the steric positions of the two ligands attached to the carbon atom are independent of the original conformation of the (2-mercapto-N-phenyl)thiourea molecule. Thus, the bidirectional reaction is a consequence of the fact that both the NH_2 and the SH groups are able to split off as nucleofuges and are converted by proton uptake into ammonia and hydrogen sulfide, respectively. The ratio of the reaction products is determined by the circumstance that hydrogen sulfide is a better leaving group than ammonia (Scheme 5).



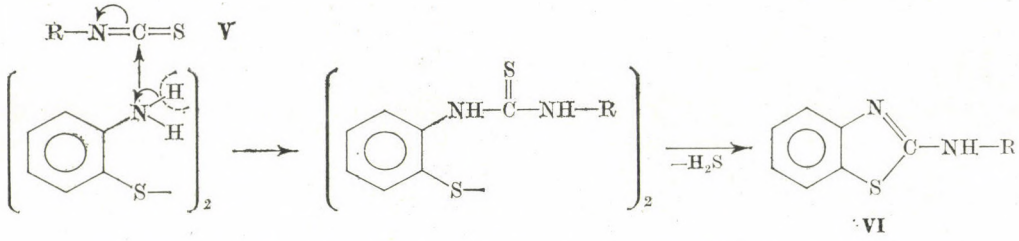
IV V

Scheme 5

The synthesis of the thioureido group has also been attempted with N-aryl isothiocyanates [6]. The reaction gave again 2-N-alkyl- and aryl-benzothiazole derivatives in almost theoretical yield. The reaction can be

* On the basis of its NMR and IR spectra, compound **III** has a thioamide structure, i. e. equilibrium is shifted in the direction of the thion tautomer. NMR spectrum: δ Ar—H(4H) 420—460 Hz multiplet, δ NH(H) $\sim$ 10.2 ppm.

explained by the splitting off of hydrogen sulfide from the bis-thioureido-diphenyl disulfide, formed as an intermediate, and this hydrogen sulfide reduces the disulfide bond to thiol; the ring is then closed by proton transfer (Scheme 6).



Scheme 6. R = (a) phenyl; (b) *p*-chlorphenyl; (c) *p*-bromphenyl; (d) methyl

Experimental

The IR spectra were taken in KBr pills with a Spectromom 2000 Spectrometer, the NMR spectra with a Varian A-60D Spectrometer in $CDCl_3$ solvent, using TMS as internal standard.

Reaction of 2,2'-diaminodiphenyl disulfide (1) with hydrogen thiocyanide

Compound **I** (49.6 g; 0.2 mole) was dissolved in a mixture of 200 ml of water and 40 ml of conc. hydrochloric acid with stirring and 30.4 g (0.4 mole) of ammonium thiocyanate was added, in portions, to the solution. The solution was then heated for 1 hr on a steam bath. The reaction mixture was filtered, and the solid dissolved in benzene. The aqueous filtrate was neutralized with sodium hydrogen carbonate, and the substance which separated was dissolved in the benzene solution. After evaporation of the solvent, the residue (50.5 g) was chromatographed on a silica gel column, and successively eluted with petroleum ether, benzene, and finally methanol.

The evaporation residue of the fractions in benzene was 12 g (20%) of a yellow crystalline substance. Recrystallization from methanol–benzene (3 : 1) gave 2-benzothiazoline-2-thion (**III**), m.p. 179—180 °C.

The evaporation residue of the methanolic eluate consisted of 38.1 g (80%) of colourless plates. Recrystallization from benzene yielded 2-aminobenzothiazole (**II**), m. p. 130—131 °C (Table I).

Reaction of 2,2'-diaminodiphenyl disulfide (1) with N-aryl isothiocyanates

A solution of 0.02 mole of compound **I** in 50 ml of alcohol was heated under strirring with 0.04 mole of compounds **Va, b, c, d**, respectively, for 1 hr on a steam bath. The corresponding benzothiazole derivative separated from the hot solution. The products were recrystallized from an alcohol–benzene (3 : 1) mixture (Table I). The yields were 90—95% for compounds **VIa, b, c**, and 80% for compound **VId.**

*

The authors' thanks are due to Prof. Dr. P. Sohár, D. Sc., for his valuable advice in evaluating the IR and NMR spectra.

Table I

	M.p., °C	Formula (mol. wt.)	Analysis		Calcd. %	Found %
II	130—131	$C_7H_6N_2S$	C 55.9	H 4.02	N 18.6	S 21.3
		(150.20)	C 56.3	H 3.80	N 18.3	S 21.2
II	266—267	$C_{13}H_9O_7N_5S$			N 18.4	S 8.4
picrate		(379.31)			N 18.5	S 8.6
III	179—180	$C_7H_5NS_2$	C 50.28	H 3.01	N 8.37	S 38.3
		(167.25)	C 49.91	H 2.96	N 8.37	S 38.7
VIa	156—158	$C_{13}H_{10}N_2S$			N 12.3	S 14.1
		(226.30)			N 12.0	S 14.3
VIa	233	$C_{18}H_{13}O_7N_5S$			N 15.4	S 7.0
picrate		(455.41)			N 15.3	S 6.9
VIb	206—208	$C_{13}H_9N_2SCl$	C 59.81	H 3.48	N 10.7	S 12.3
		(260.74)	C 59.74	H 3.62	N 10.4	S 12.7
VIc	216—217	$C_{13}H_9SBr$	C 51.15	H 2.97	N 9.2	S 10.5
		(305.20)	C 51.34	H 3.09	N 9.4	S 10.7
VId	138—140	$C_8H_8N_2S$	C 58.50	H 4.91	N 17.0	
		(164.23)	C 58.31	H 5.06	N 17.3	

Main bands in the IR spectra of compounds **II—VI**

	νNH	νC=N	Thioamide B and C	γ $C_{Ar}H$ (*ortho*-di)	γ $C_{Ar}H$ (*para*-di)	γ $C_{Ar}H$ $C_{Ar}C_{Ar}$ (mono)
II	3200—2570	1640	—	740	—	—
III	3200—2560	—	1500—1480[1] 1440—1400[1]	750	—	—
VIa	3300—2570	1610	—	750	—	710
VIb	3200—2550	1610	—	740	820	—
VId	3300—2700[2]	1610	—	750	—	—

[1] Overlapping with the aromatic skeletal vibrations
[2] Overlapping with the aliphatic skeletal vibrations

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REACTIONS OF MONO- AND DIARYLIDENECYCLOALKANONES WITH THIOUREA AND AMMONIUM THIOCYANATE, II*

SYNTHESIS OF 4-ARYL-2-IMINO-1,2,5,6,7,8-HEXAHYDRO-4*H*-3,1-BENZOTHIAZINE SALTS AND 4-ARYL-2-IMINO-1,2,4,5,6,7-HEXAHYDROCYCLOPENTA[d] [1,3] THIAZINE SALTS

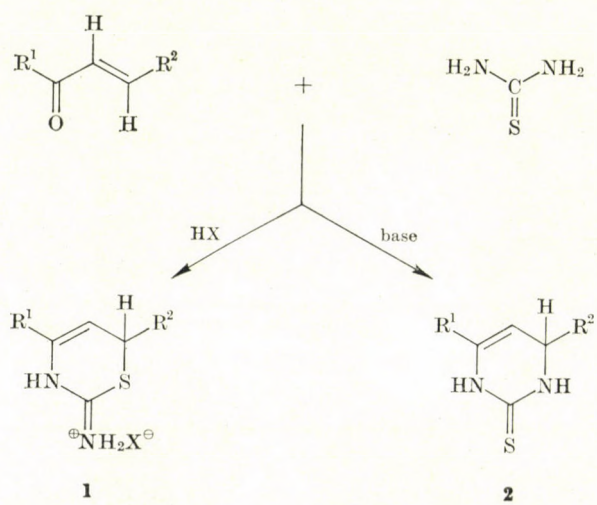
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In acid media, 2-arylidenecyclohexanones react with thiourea to yield 4-aryl-2-imino-1,2,5,6,7,8-hexahydro-4*H*-3,1-benzothiazine salts (**Ia–c**), while the reaction of 2-arylidenecyclopentanones results in the 4-aryl-2-imino-1,2,4,5,6,7-hexahydrocyclopenta[d] [1,3] thiazine salts. Similarly, 2,6-diarylidenecyclohexanones and 2,5-dibenzylidenecyclopentanone give the corresponding thiazine derivatives (**IIIa–d** and **IV**, respectively).

In the reaction of vinyl ketones with thiourea two different reaction paths are possible depending on the conditions [1, 2] (Fig. 1).



1 **2**

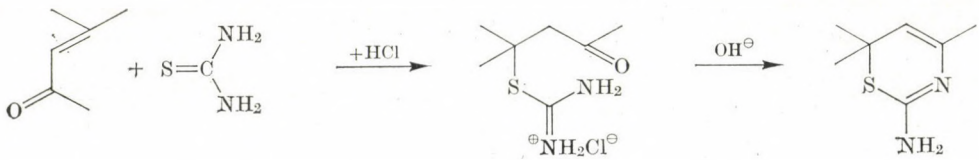
Fig. 1

In base-catalyzed reactions of mono- and diarylidenecycloalkanones and thiourea, 2-thionoquinazolines and 2-thionocyclopentapyrimidines are formed, as it was reported in our previous paper [3].

* Part I, see Ref. [3]

In the present paper, acid-catalyzed reactions of some mono- and diarylidenecycloalkanones and thiourea are discussed. In these reactions the expected thiazine derivatives were obtained.

In acid-catalyzed reactions of α,β-unsaturated ketones with thiourea, the polarized sulfur atom of thiourea will attack the ketone in the β position [1]. The open-chain isothiuronium salt intermediate (**3**) formed in the first step from mesityl oxide was isolated by WILLEMS and VANDENBERGHE [4], and it was converted into the iminothiazine (**4**) in alkaline medium.



3 **4**

Fig. 2

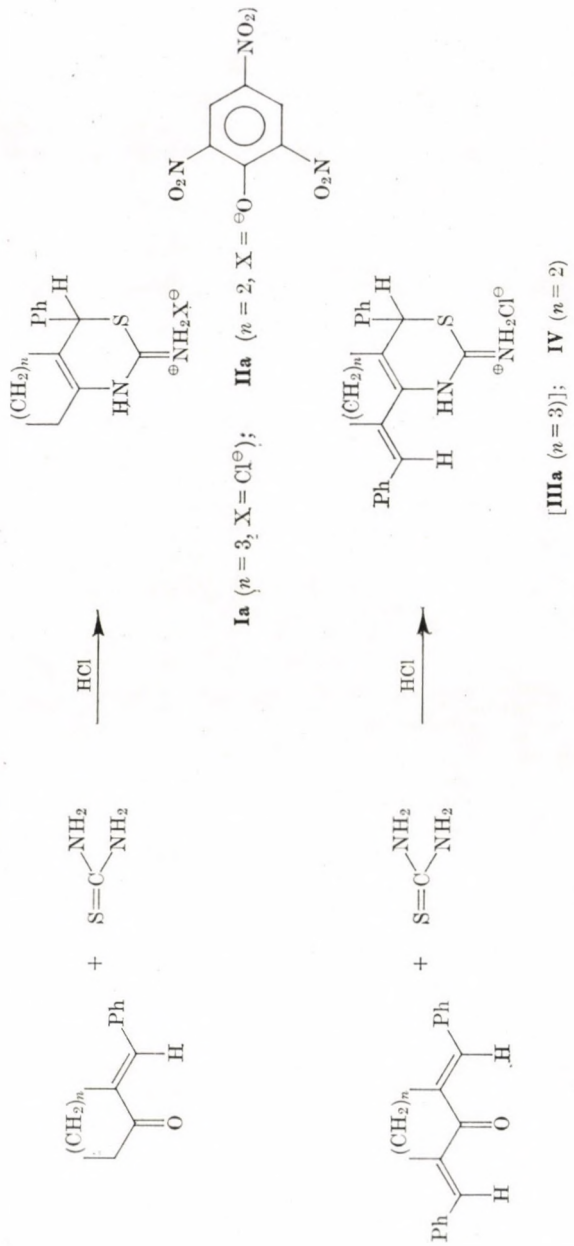
KHACHATRIAN *et al.* [5] observed similar conversions in reactions of substituted divinylketones.

In hydrochloric acid medium, 2-arylidenecyclohexanones, when allowed to react with thiourea, yield 4-aryl-2-imino-1,2,5,6,7,8-hexahydro-4*H*-3,1-benzothiazine hydrochloride (**Ia—c**). In the analogous reactions of 2-arylidenecyclopentanones, the products were isolated as picrate salts (**IIa, b**). The open-chain isothiuronium salt intermediate could not be isolated.

In the reaction of 2-benzalcyclohexanone and ammonium thiocyanate in acid medium, no 1,3-thiazine derivative was formed; the starting ketone degraded into a tar during the reaction. 2,6-Diarylidenecyclohexanones as well as 2,5-dibenzylidenecyclopentanone reacted with two moles of thiourea in acid medium to give 4-aryl-8-arylidene-2-imino-1,2,5,6,7,8-hexahydro-4*H*-3,1-benzothiazine hydrochloride (**IIIa—d**) and 7-benzylidene-4-phenyl-2-imino-1,2,4,5,6,7-hexahydrocyclopenta [d] [1, 3] thiazine hydrochloride (**IV**), respectively. (**Ia** and **IIIa** were also converted into the corresponding bases **Iα** and **IIIα**.)

The spectral properties of the compounds prepared are discussed below.

In the IR spectra of compounds **Ia—c, IIa—b, IIIa—d, IV** (Table II) a broad band appears in the 2400—3400 cm^{-1} range, with partial maxima assignable to the $=NH_2^+$ and NH groups. (The band due to the endocyclic NH group can be recognized at 3200 cm^{-1} in the broad band mentioned.) The imine salt character is confirmed by the very intense $\nu C{=}N$ band between 1642 and 1660 cm^{-1}. In **Ia—c**, the isolated $\nu C{=}C$ band could be identified at relatively high wavenumber values (1695—1705 cm^{-1}), similarly to the case of 2-thionohexahydroquinazolines [3].

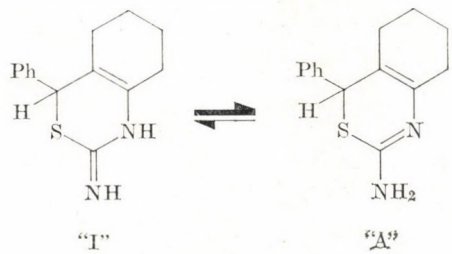


Ia ($n = 3$, $X = Cl^{\ominus}$); **IIa** ($n = 2$, $X = {}^{\ominus}O$–$C_6H_2(NO_2)_2$–NO_2)

[**IIIa** ($n = 3$)]; **IV** ($n = 2$)

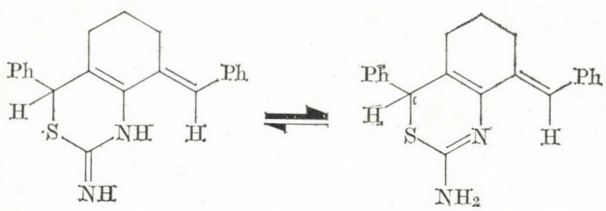
Fig. 3

In the IR spectra of **Iα** and **IIIα** (Table II) the doublets at high wavenumber (3450 and 3275 cm^{-1}; 3490 and 3380 cm^{-1}) suggest the presence of the amino tautomeric form ("A") in contrast with the imino tautomer ("I"). This is also confirmed by the IR spectra recorded in chloroform solution (**Iα** : ν_{as} NH_2 3503 cm^{-1}, $\nu_s NH_2$ 3393 cm^{-1}; **IIIα** : $\nu_{as}NH_2$ 3505 cm^{-1}, $\nu_s NH_2$ 3395 cm^{-1}). When applying the correlation derived for the asymmetric and symmetric vibration wavenumbers of the NH_2 group [6], the calculated value for $\nu_s NH_2$ in **Iα** is 3413 cm^{-1}, that in **IIIα** is 3415 cm^{-1}, being in acceptable agreement with the found values. In **Iα** and **IIIα**, the $\nu C{=}N$ band appears at a lower frequency than in the spectra of the corresponding **Ia** and **IIIa** compounds (**Ia**: $\nu C{=}N$ 1640 cm^{-1}, **Iα**: $\nu C{=}N$ 1630 cm^{-1}; **IIIa**: $\nu C{=}N$ 1645 cm^{-1}, **IIIα**: $\nu C{=}N$ 1625 cm^{-1}), indicating the imine salt structure in **Ia** and **IIIa**.



"I" "A"

Iα



IIIα

Fig. 4

The phenomenon of tautomerism in **Iα** was also examined by UV spectroscopy. DESHPANDE *et al.* [7] carried out the reaction of mesityl oxide with thiourea in acid medium, and the structure of the thiazine derivative (**4**) formed was also proved by the UV spectra. The maximum at 298 nm was assigned to the chromophore system C=N—C=C. The UV spectra of **Iα** and **Ia** were recorded in pure ethanol and 20% ethanol solutions at different pH values (Tables I and II).

Table I

Absorption of **Ia** *and* **Iα** *in the 280—360 nm range, in 20% ethanol solution*

Compound	pH	λ_{max}(nm)	log ε
Ia	2.08	294	3.46
	6.40	294	3.46
	7.00	296	3.40
	9.00	303	3.46
Iα	1.98	295	3.45
	7.00	296	3.47
	7.60	301	3.41
	9.00	303	3.47

According to the measurements, the conjugated tautomer "A" is present in the alcohol solution (λ_{max} = 301 nm, in both cases, being in good agreement with the results reported by DESHPANDE *et al.*) In 20% ethanol, **Ia** is converted into the amino form ("A") when the pH exceeds 7; at lower pH the protonated form of tautomer "I" exists in the solution. The process is reversible, **Iα** exists in the protonated form "I" in the acid range and the conjugated form "A" is present when the pH is higher than 7.

The PMR spectrum of **Iα** (Table II) was compared with the PMR spectrum of the isomeric 2-thionohexahydroquinazoline derivative prepared earlier [3], and a significant difference was found in the chemical shift of the C-4 proton: the signal for the proton in the vicinity of the more electronegative nitrogen atom appeared at δ = 4.8 ppm, while that being beside the sulfur atom was found at δ = 4.3 ppm. While two singlet NH signals are found in the isomeric 2-thionohexahydroquinazoline (δ = 8.0 and 6.9 ppm), the NH_2 group gives rise to one signal at δ = 5.1 ppm in **Iα**. A similar effect is observed in **III** α and the isomeric 2-thionohexahydroquinazoline derivative.

Experimental

The IR spectra were recorded with a Zeiss UR 10 spectrophotometer, the PMR spectra were obtained with a Perkin-Elmer R-12 spectrometer. The UV spectra were recorded with a Perkin-Elmer 402 instrument.

The mono- and diarylidenecycloalkanones were prepared by aldol condensation catalyzed with NaOH [8]. All the starting ketones were the *trans* isomers [9].

4-Phenyl-2-imino-1,2,5,6,7,8-hexahydro-4H-3,1-benzothiazine hydrochloride (Ia)

An ethanolic solution (30 ml) of 2-benzylidene-cyclohexanone (7.44 g; 0.04 mole) and thiourea (6.08 g; 0.08 mole) was treated with conc. hydrochloric acid (3 ml) and the reaction mixture was warmed on a water bath at 50 °C for 6.5 hrs. The solution was evaporated to

Table II

Compound Ar	M.p., °C	Formula M. w. Yield, %	Analysis, % Calcd.	 Found
Ia C_6H_5—	165 (d.)	$C_{14}H_{17}ClN_2S$ 280.83 35	C 59.88 H 6.10 N 9.98 S 11.42	59.62 5.92 10.26 11.34
Iα C_6H_5—	144 (d.)	$C_{14}H_{16}N_2S$ 244.36 77	C 68.82 H 6.60 N 11.47 S 13.12	68.90 6.63 11.18 13.24
Ib 4—CH_3—C_6H_4—	156 (d.)	$C_{15}H_{19}ClN_2S$ 294.86 26	C 61.10 H 6.50 N 9.50 S 10.88	60.96 6.48 9.21 10.89
Ic 4—CH_3O—C_6H_4—	154 (d.)	$C_{15}H_{19}ClON_2S$ 310.86 15	C 57.96 H 6.16 N 9.01 S 10.32	57.79 6.36 8.83 10.33
IIa C_6H_5—	180 (d.)	$C_{19}H_{17}N_5O_7S$ 459.45 51	C 49.67 H 3.73 N 15.25 S 6.98	49.74 4.01 15.02 7.22
IIb 4—CH_3O—C_6H_4—	185 (d.)	$C_{20}H_{19}N_5O_8S$ 489.48 28	C 49.08 H 3.91 N 14.31 S 6.55	49.09 4.08 14.05 6.69
IIIα C_6H_5—	138—141	$C_{21}H_{20}N_2S$ 332.47 35	C 75.87 H 6.06 N 8.43 S 9.66	75.60 6.28 8.20 9.88
IIIb 4—CH_3—C_6H_4—	164 (d.)	$C_{23}H_{25}ClN_2S$ 396.99 27	C 69.59 H 6.35 N 7.06 S 8.08	69.79 6.38 6.90 8.12
IIIc 4—CH_3O—C_6H_4—	193 (d.)	$C_{23}H_{25}ClN_2O_2S$ 428.99 31	C 64.40 H 5.87 N 6.53 S 7.48	64.27 5.94 6.28 7.48

UV (ethanol)		IR, cm^{-1} (KBr pellet)		PMR δ ppm, $CDCl_3$			
λ_{max}, nm	log ε						
207	4.13	$\nu{=}NH_2^+$ }	2400—3400[a]	1.2—2.8	m	8H	CH_2
247	3.77	$\nu N{-}H$ }		4.6	s	1H	CH
301	3.31	$\nu C{=}C$	1695	7.3	s	5H	Ar
		$\nu C{=}N$	1640	8.2—10.0	s	2—3H	NH, $=NH_2^+$[b,d]
207	4.08		3450	1.0—2.6	m	8H	CH_2
247	3.74	νNH_2	3275	4.3	s	1H	CH
301	3.32		3210[h]	5.1	s	2H	NH_2[d]
		$\nu C{=}N$	1630	7.2	s	5H	Ar
207	4.19	$\nu{=}NH_2^+$ }	2400—3400[a]	1.2—2.2	m	8H	CH_2
225	4.09	$\nu N{-}H$ }		2.3	s	3H	CH_3
250	3.86	$\nu C{=}C$	1700	4.6	s	1H	CH
310	3.42	$\nu C{=}N$	1645	7.2	s	4H	Ar
				8.5—10.0	s	2—3H	NH, $=NH_2^+$[b,d]
206	4.25	$\nu{=}NH_2^+$ }	2400—3400[a]	1.3—2.6	m	8H	CH_2
233	4.12	$\nu N{-}H$ }		3.8	s	3H	OCH_3
259	3.98	$\nu C{=}C$	1705	4.6	s	1H	CH
313	3.44	$\nu C{=}N$	1645	7.1	q	4H	Ar J=9.0Hz
		$\nu_{as}C{-}O{-}C$	1260	8.8—10.0	s	2—3H	NH, $=NH_2^+$[b,d]
		$\nu_s C{-}O{-}C$	1040				
213	4.43	$\nu{=}NH_2^+$ }	2400—3400[a]	1.5—2.9	m	6H	CH_2
239	4.25	$\nu N{-}H$ }		5.3	s	1H	CH
360	4.14	$\nu C{=}C$	1700 (sh)	7.3	s	5H }	Ar
		$\nu C{=}N$	1650	8.6	s	2H }	
				9.0—10.0	s	2—3H	NH, $=NH_2^+$[b,c,d]
208	4.50	$\nu{=}NH_2^+$ }	2400—3400[a]	1.5—2.8	m	6H	CH_2
235	4.44	$\nu N{-}H$ }		3.6	s	3H	OCH_3
360	4.24	$\nu C{=}C$	1705 (sh)	5.2	s	1H	CH
		$\nu C{=}N$	1660	7.0	q	4H	Ar J=9.0Hz
		$\nu_{as}C{-}O{-}C$	1260	8.6	s	2H	Ar
		$\nu_s C{-}O{-}C$	1035	8.9—9.8	s	2—3H	NH, $=NH_2^+$[b,c,d]
207	4.39		3490	1.2—3.0	m	6H	CH_{2e}
224	4.22	νNH_2	3380	3.7—4.9	s	2H	NH_2
278	4.36	$\nu C{=}N$	1625	4.4	s	1H	CH
325	3.95			7.3	d	11H	Ar, =CH J=6.0Hz
207	4.43	$\nu{=}NH_2^+$ }	2400—3320[a]	1.0—2.5	m	6H	CH_2
229	4.22	$\nu N{-}H$ }		1.9	s	6H	CH_3
282	4.41	$\nu C{=}N$	1645	4.3	s	1H	CH
321	4.08			6.5	s	1H	=CH
				6.8	s	8H	Ar
				7.0—7.6 } 9.4 }	s	2—3H	NH, $=NH_2^+$[f,g]
207	4.46	$\nu{=}NH_2^+$ }	2400—3320[a]	1.1—2.7	m	6H	CH_2
234	4.26	$\nu N{-}H$ }		3.5	s	6H	OCH_3
286	4.47	$\nu C{=}N$	1645	4.4	s	1H	CH
324	4.17	$\nu_{as}C{-}O{-}C$	1260	6.8	q	9H	Ar, =CH J=10.0Hz
		$\nu_s C{-}O{-}C$	1040	7.1—8.0 } 9.5 }	s	3H	NH, $=NH_2^+$[f,g]

Table II

Compound Ar	M.p., °C	Formula M. w Yield, %	Analysis, % Calcd.	 Found
IIId 4—Cl—C_6H_4—	203 (d.)	$C_{21}H_{19}Cl_3N_2S$ 437.84 72	C 57.61 H 4.37 N 6.40 S 7.32	57.48 4.15 6.10 7.23
IV C_6H_5—	195 (d.)	$C_{20}H_{19}ClN_2S$ 354.91 54	C 67.69 H 5.40 N 7.89 S 9.03	67.76 5.57 7.70 9.06

dryness and the red oil obtained was dissolved in some acetone. After cooling, colourless crystals separated, which were recrystallized from a mixture of acetone and methanol.

The synthesis of **Ib** and **c** colourless crystals was effected in a similar way.

2-Amino-4-phenyl-5,6,7,8-tetrahydro-4H-3,1-benzothiazine Iα

Compound **Ia** (5.6 g; 0.02 mole) was dissolved in hot methanol, and a methanolic solution of KOH (1.68 g; 0.03 mole) was added to it. The solution was concentrated and poured into water. The precipitate was filtered off and washed with water until neutral. The colourless product was crystallized from benzene.

Other data for **Iα**, **a**, **b**, **c** are given in Table II.

4-Phenyl-2-imino-1,2,4,5,6,7-hexahydrocyclopenta[d] [1,3] thiazine picrate IIa

IIa was prepared in a manner similar to **Ia**. The red oil obtained after evaporation could not be crystallized. An alcoholic solution of picric acid (9.16 g; 0.04 mole) was added to the hot alcoholic solution of the substance. After cooling, yellow crystals separated from the solution, which were recrystallized from ethanol.

Compound **IIb** (a green crystalline substance) could be isolated as the picrate, similarly to compound **IIa**.

Other data for **IIa**, **b** are given in Table II.

2-Amino-8-benzylidene-4-phenyl-5,6,7,8-tetrahydro-4H-3,1-benzothiazine (IIIα)

A suspension of 2,6-dibenzylidenecyclohexanone (8.22 g; 0.03 mole) and thiourea (4.56 g; 0.06 mole) in ethanol (150 ml) was treated with conc. hydrochloric acid (4 ml). The reaction mixture was stirred at 50 °C for 14 hrs. Meanwhile, a colourless precipitate separated. The precipitate was filtered off, washed with ethanol, then with water until neutral reaction. Some precipitate was also obtained from the mother liquor after evaporation. The hydrochloride of the product (**IIIa**) was crystallized from acetone or acetic acid, however, the solvent could not be completely removed. Therefore, similarly to the case of **Iα**, the corresponding base (**IIIα**) was prepared and crystallized from benzene.

Preparation of **IIIb**, **c**, **d** and **IV** (colourless crystals) was accomplished in a similar way. **IIIb–d** and **IV** were crystallized from methanol and ethanol respectively.

Other data for **IIIα**, **b–d** and **IV** are shown in Table II.

*

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UV (ethanol)		IR, cm^{-1} (KBr pellet)		PMR δ ppm, $CDCl_3$			
λ_{max}, nm	log ε						
207	4.47	ν=NH_2^+	2400—3300[a]	1.1—2.7	m	6H	CH_2
231	4.28	νN—H		4.4	s	1H	CH
285	4.42	νC=N	1645	6.5	s	1H	=CH
327	4.08			6.9	s	8H	Ar
				7.2—8.1	s	3H	NH, $=NH_2^+$[f,g]
				9.6			
207	4.31	ν=NH_2^+	2400—3320[a]	2.1—3.1	m	4H	CH_2
286	4.44	νN—H		5.6	s	1H	CH
331	4.12	νC=N	1642	7.0	s	1H	=CH
				7.4	s	10H	Ar
				9.5—10.7	s	2—3H	NH, NH_2^+[c,d]

[a] broad band with partial maxima
[b] broad band
[c] recorded in DMSO-d_6
[d] disappears on the effect of D_2O
[e] the methine signal overlaps the NH_2 signal, the broad NH_2 band disappears on the effect of D_2O
[f] recorded in trifluoroacetic acid
[g] disappear on the effect of D_2O
[h] weak band

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AMINOPHTHALAZINONE DERIVATIVES, II

SYNTHESIS OF 4-(HYDROXYALKYLAMINO)-1(2H)-PHTHALAZINONES FROM HYDROXYALKYLPHTHALIMIDES

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4-(Hydroxyalkylamino)-1(2H)-phthalazinones (**6**) can be prepared in good yields from variously substituted 1,2- and 1,3-aminoalcohols by the pathway **1**→**6** leading through the cyclic imino-ether (**5**). The present work has shown that an earlier method developed by us for ethanolamine and 3-amino-1-propanol [2, 3] can be generalized and greatly improved by some modifications, so that even in the case of aminoalcohols sterically shielded at the N-terminal, *e.g.* 2-amino-2-methyl-1-propanol, excellent yields (about 90%) are obtained. An anomalous tosylation reaction occurs with 3-hydroxypropylphthalimide, in the course of which 3-chloropropylphthalimide (**4**) is formed instead of the tosyl ester (**3**). Monosubstituted alkylhydrazines react with the cyclic intermediate (**5**) to yield the 2-N-substituted derivatives (**7**).

In the first part of this series [1] we have reported that aminoalcohols fairly readily react with chlorophthalazinone to give 4-(hydroxyalkylamino)-1(2H)-phthalazinones (**6**). The extent of conversion is, however, greatly affected by the steric arrangement on the N-terminal group of the aminoalcohol; thus, *e.g.* the usual yield of 70 or 90% is reduced to 4.2% in the case of 2-amino-2-methyl-1-propanol.

In our earlier studies we found [2, 3] that the oxazoline **5** (M = —) prepared from ethanolamine and 3-amino-1-propanol by the reactions **1**→**2**→**5**, and the dihydro-1,3-oxazine (M = —CH_2—) derivative, readily react with hydrazine to give 4-(2-hydroxyethylamino)-1(2H)-phthalazinone (**6a**) and 4-(3-hydroxypropylamino)-1(2H)-phthalazinone (**6b**), respectively. Apart from practical purposes, a study of the general applicability of this synthesis is justified as it is yet unknown whether an effect similar to steric hindrance and reducing the yield in the reaction of chlorophthalazinone with aminoalcohols, is in operation also in processes **1**→**6**, or not.

GABRIEL *et al.* [4, 5] have recognized that the cyclization of 2- and 3-halogenoalkylcarboxylic acid amides in alkaline media gives C(2)-substituted oxazoline and dihydro-1,3-oxazine derivatives, respectively. According to GLICK [6], this ring closure is still more readily effected when the appropriate tosyloxyalkylcarboxylic acid amides are used. Generally, there is no difficulty in preparing hydroxyalkylphthalimides from aminoalcohols, but — depending on the substituent in the aromatic ring and on the distance between the hydroxyl group and the imide nitrogen — the hydroxyl–halogen exchange

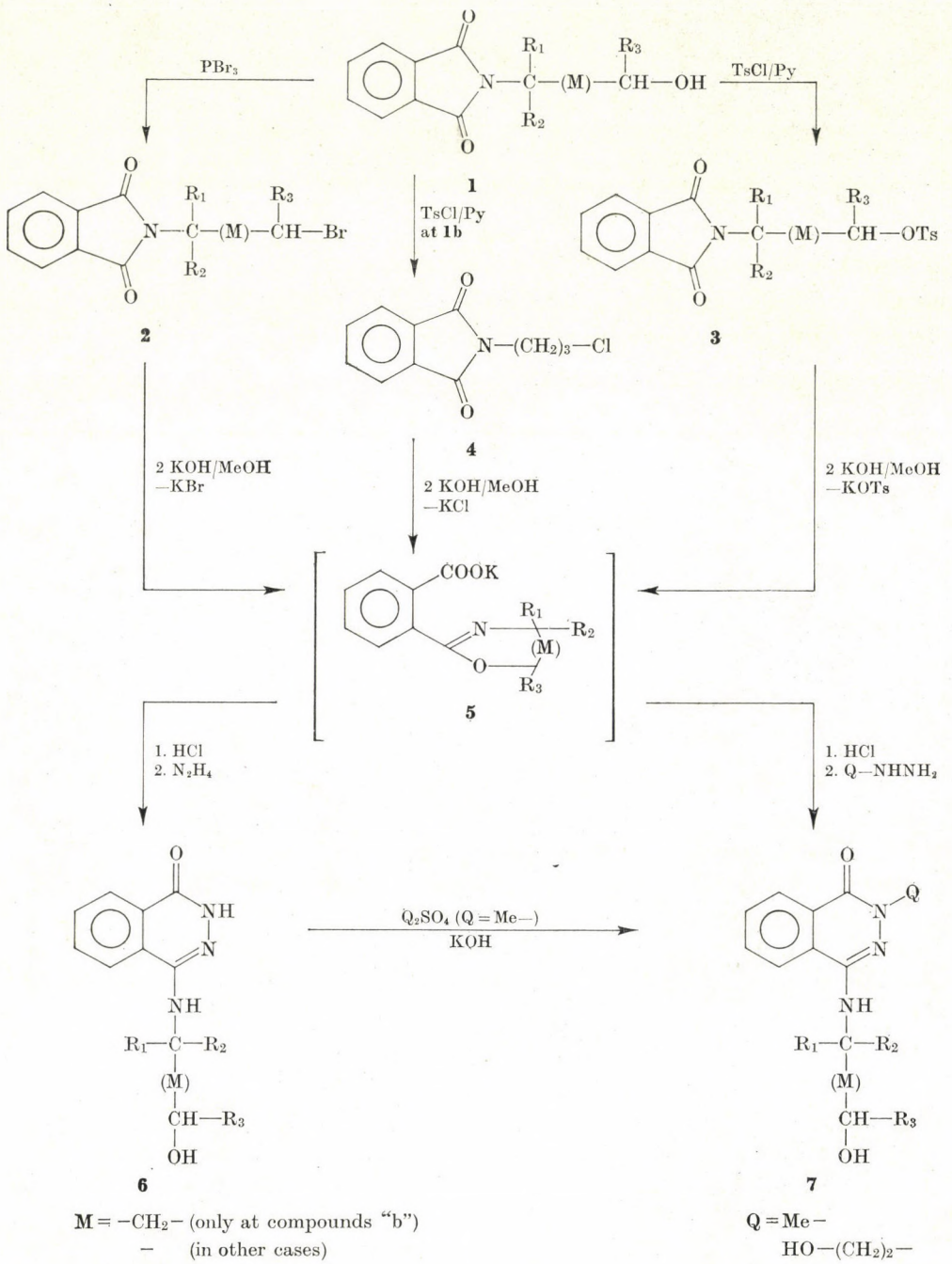

PBr3
TsCl/Py
1
TsCl/Py at 1b
2
3
4
2 KOH/MeOH —KBr
2 KOH/MeOH —KCl
2 KOH/MeOH —KOTs
COOK
5
1. HCl 2. N2H4
1. HCl 2. Q—NHNH2
Q2SO4 (Q = Me—) KOH
6
7
M = —CH2— (only at compounds "b")
— (in other cases)
Q = Me—
HO—(CH2)2—

Fig. 1

1→2 may meet with some obstacles. Thus, *e.g.* 2-hydroxyethyl-m-hemipinimide can be halogenated with phosphorus tribromide only to a few per cents, its tosylation, however, is a smooth process [7]. The convenient preparation of the tosyl esters and their higher reactivity both suggest that 4-(hydroxyalkylamino)-1(2H)-phthalazinones (**6**) are better synthesized starting from the tosyl esters, *i.e.* following the sequence **1→3→5→6**.

Hydroxyalkylphthalimides (**1**) can be esterified with tosyl chloride in dry pyridine in good yields **1→3** (*cf.* Table I). An irregular behaviour is observed in the case of 3-hydroxypropylphthalimide, which does not yield a tosyl ester (**3**), but is converted into 3-chloropropylphthalimide (**4**). (The cause of this will be discussed in a following communication.)

Table I

Synthesis of tosyloxyalkylphthalimides (**3**)

Product (3)	Yield %	Crystallization		M.p., °C	Empirical formula	Mol. wt.	Analysis	
		solvent	cryst. form				Calcd. S,%	Found S,%
a	87	EtOH	needles	141—142 (lit.: 144.5 [13])	$C_{17}H_{15}NO_5S$	345.4	9.3	9.2
c	92	EtOH	needles	157—158	$C_{18}H_{17}NO_5S$	359.4	8.9	8.7
d	88	EtOH	needles	116—117	$C_{19}H_{19}NO_5S$	373.4	8.6	8.7
e	78	EtOH	prisms	120—121	$C_{19}H_{19}NO_5S$	373.4	8.6	8.5
f	83	C_6H_6–pentane	needles	130—132	$C_{24}H_{21}NO_5S$	435.5	7.4	7.4

The separation of the intermediates **5** formed from the tosyl esters **3** in alkaline medium was not attempted in the course of the present work, but their presence is unequivocally proved by the smoothly proceeding hydrazinolysis yielding in each case the end-products **6** and **7**. When the isolation of **5** is omitted, not only the procedure of the synthesis is simplified, but also there is a considerable improvement of the yield (Tables II and III), which

←

(1, 3, 6)	R_1	R_2	R_3	M	(7)	Q	(7)	Q
a	H	H	H	—	**a**	Me	**g**	$-(CH_2)_2-OH$
b*	H	H	H	CH_2	**b**	Me	**h**	$-(CH_2)_2-OH$
c	H	H	Me	—	**c**	Me	**i**	$-(CH_2)_2-OH$
d	Et	H	H	—	**d**	Me	**j**	$-(CH_2)_2-OH$
e	Me	Me	H	—	**e**	Me	**k**	$-(CH_2)_2-OH$
f	Me	H	Ph	—	**f**	Me	**l**	$-(CH_2)_2-OH$

* **3b** is unknown

Table II

Yields of the methods of preparing of 4-(hydroxyalkylamino)-1(2H)-phthalazinones (**6**)

Product (6)	Method and yield, %			
	A	*B*	*C*	*D*
a	76.5 [2]	96.5	97.0	88.0
b	33.0 [3]	70—84	—	69.0
c	—	—	86.8	82.3
d	—	—	91.5	70.0
e	—	—	92.7	4.2
f	—	—	91.5	—

A From halogenoalkylphthalimide (with isolation of the intermediate **5**)
B From halogenoalkylphthalimide (without the isolation of **5**)
C From tosyloxyalkylphthalimide (without the isolation of **5**)
D Synthesis from chlorophthalazinone and aminoalcohol [1]

Table IV

Synthesis of hydroxyalkylaminophthalazinones (**7**)

Product (7)	Reaction time, hr.	Method and yield, %	Crystallization	
			solvent	form
a 2-Methyl-4-(2-hydroxyethylamino)-1(2H)-phthalazinone	1	A 82.2 B 94.0	water	needles
b 2-Methyl-4-(3-hydroxypropylamino)-1(2H)-phthalazinone	3	A 54.9 B 86.7	water	(α) needles (β) plates
c 2-Methyl-4-(2-hydroxy-2-methylethylamino)-1(2H)-phthalazinone	1	A 65.6 B 90.9	water	needles
d 2-Methyl-4-(1-ethyl-2-hydroxyethylamino)-1(2H)-phthalazinone	1	A 51.0 B 87.8	water	(α) needles (β) needles
e 2-Methyl-4-(1,1-dimethyl-2-hydroxyethylamino)-1(2H)-phthalazinone	5	A 28.3 B 96.0	water	needles
f 2-Methyl-4-(1-methyl-2-hydroxyphenethylamino)-1(2H)-phthalazinone	6	A 19.4 B 32.4	EtOH	needles
g 2-(2-Hydroxyethyl)-4-(2-hydroxyethylamino)-1(2H)-phthalazinone	1 24 (20 °C)	A 84.3 A 78—84	water	needles
h 2-(2-Hydroxyethyl)-4-(3-hydroxypropylamino)-1(2H)-phthalazinone	1	A 79.9	water	needles
i 2-(2-Hydroxyethyl-4-(2-hydroxy-2-methyl-ethylamino)-1(2H)-phthalazinone	1 3 5 10	A 43.7 A 51.1 A 61.6 A 62.0	water	needles
j 2-(2-Hydroxyethyl)-4-(1-ethyl-2-hydroxyethylamino)-1(2H)-phthalazinone	1	A 61.4	water	needles
k 2-(2-Hydroxyethyl)-4-(1,1-dimethyl-2-hydroxyethylamino)-1(2H)-phthalazinone	1	A 67.5	water	prisms
l 2-(2-Hydroxyethyl)-4-(1-methyl-2-hydroxyphenethylamino)-1(2H)-phthalazinone	1 4	A 46.0 A 48.0	aqueous EtOH	prisms

Table III

Synthesis of hydroxyalkylaminophthalazinones (**6**) *from tosyloxyalkylphthalimides*

Product (6)	Reaction time, hr.	Yield, %	Crystallization		M.p., °C	Empirical formula	Mol. wt.
			solvent	cryst. form			
a	1	96.0* 97.0	water	needles	254—256	$C_{10}H_{11}N_3O_2$	205.2
b	1	70—84**	water	needles	193—194	$C_{11}H_{13}N_3O_2$	219.2
c	1	86.8	water	needles	231—233	$C_{11}H_{13}N_3O_2$	219.2
d	1	91.5	water	plates	246	$C_{12}H_{15}N_3O_2$	233.3
e	1	92.7	water	micr. prisms	270—271	$C_{12}H_{15}N_3O_2$	233.3
f	1	91.5	water	needles	204—206	$C_{17}H_{17}N_3O_2$	295.4

* From 2-bromoethylphthalimide
** From 3-bromopropylphthalimide

Analysis: According to the m.p's and IR spectra, compounds **6a**—**6e** are identical with samples synthesized in another way [1]. **6f**, 4-(1-methyl-2-hydroxyphenethylamino)-1(2H)-phthalazinone, $C_{17}H_{17}N_3O_2$ (295.4). Calcd. C 69.1; H 5.8; N 14.2. Found: C 68.9; H 5.7; N 14.3%.

by total synthesis (A) and by alkylation (B)

M.p., °C	Empirical formula	Mol. wt.	Analysis					
			Calcd.			Found		
			C%	H%	N%	C%	H%	N%
170—171	$C_{11}H_{13}H_3O_2$	219.2	According to m.p. and IR spectra, this is the same compound as prepared in other ways [3, 9]					
129—131	$C_{12}H_{15}N_3O_2$	233.3	61.8	6.5	18.0	61.9	6.5	18.1
135—136 178—179	$C_{12}H_{15}N_3O_2$	233.3	61.8	6.5	18.0	61.8	6.5	18.2
142—143	$C_{13}H_{17}N_3O_2$	247.3	63.1	6.9	17.0	63.0	6.8	17.1
152—153 173—175	$C_{13}H_{17}N_3O_2$	247.3	63.1	6.9	17.0	62.9	6.9	17.0
192—193	$C_{18}H_{19}N_3O_2$	309.4	69.9	6.2	13.6	69.7	6.1	13.7
175	$C_{12}H_{15}N_3O_3$	249.3	57.8	6.1	16.9	57.8	6.2	17.0
152—153	$C_{13}H_{17}N_3O_3$	263.3	59.3	6.5	16.0	59.5	6.4	16.1
170—171	$C_{13}H_{17}N_3O_3$	263.3	59.3	6.5	16.0	59.3	6.6	16.2
157—159	$C_{14}H_{19}N_3O_3$	277.3	60.6	6.9	15.2	60.5	6.9	15.3
158—161	$C_{14}H_{19}N_3O_3$	277.3	60.6	6.9	15.2	60.6	6.8	15.3
192—193	$C_{19}H_{21}N_3O_3$	339.4	67.2	6.2	12.4	67.2	6.3	12.5

is explained by the instability of the substances of the type **5**. In the earlier method [2, 3] proceeding *via* the separated intermediary compounds **5**, the yield of **6a** was 76% at best; the modification enhanced this to 96—97%. Still more pronounced is this enhancement in the case of **6b** where a yield of 33% could be raised to 70—84% in this way.

N(2)-substituted hydroxyalkylaminophthalazinones (**7**) can be prepared by the N-alkylation (**6**→**7**) of the parent compounds [3, 9, 10], and also by total synthesis when the intermediate (**5**) is made to react with monosubsti-

Table V

Important bands in the infrared spectra of tosyloxyalkylphthalimides (**3**) *(KBr pellets)*

	νCO_{imide}	νSO_2 as.	νSO_2 sym.	δSO_2	1,4-disubst. Ar ring	1,2-disubst. Ar ring	Mono-subst. Ar ring
3a	1775	1392	1192	580	820	769	—
	1712	1361	1179	554			
3c	1772	1350	1192	578	818	770	—
	1710		1180	556			
3d	1770	1366	1190	555	827	729	—
	1710		1179	532			
3e	1770	1362	1191	572	819	718	—
	1709		1179	556			
3f	1770	1360	1191	569	811	721	703
	1713		1178	552			

tuted alkylhydrazines (**5**→**7**) instead of hydrazine. The effecting of the ring closure with methylhydrazine and 2-hydroxyethylhydrazine gave the alkylated derivatives in various yields (Table IV). The data show that the total synthesis **5**→**7** gives lower yields than alkylation **6**→**7**, yet for the introduction of specific substituents (*e.g.* Q = 2-hydroxyethyl group) total synthesis is preferable.

In the cases of **7b** and **7d** crystal dimorphism was detected; the two forms of **7b** were: α = small needles, m.p. 129—131 °C; β = well developed plates m.p. 135—136 °C. Both modifications of **7d** crystallized in needles; α with m.p. 143—144 °C, β with m.p. 152—153 °C; the infrared spectral data are given in Table VI. The α-modification is metastable and heating below the melting point accelerates its transformation; in such cases always the higher m.p. of the β-form is observed, therefore unequivocal identification of the modifications should be based on the infrared spectra recorded with solid samples. Crystal dimorphism is rendered probable also by the fact that the solutions in chloroform of these modifications have identical infrared spectra.

A summing up of our observations suggests that the processes **1**→**5** do not depend upon steric conditions, and that within this sequence the reactions **2**→**5** and **3**→**5** occur practically quantitatively. The lower yields

Table VI

Important bands in the infrared spectra of some new 4-[2(3)-hydroxyalkylamino]-1(2H)-phthalazinone derivatives (**6f*** *and* **7b—7l**) *(KBr pellets)*

	νNH νOH	νCO_{amide} νC=N	δNH	νC—O	1,2-disubst. Ar ring	Monosubst. Ar ring
6f	3500—2850	1660	1529	1030 1038	770	707
7b	3470—3130	1632	1534	1073	737	—
(α)	3340	1574		1044		
7b	3342 (NH)	1630	1539	1072	738	—
(β)	3245 (OH)	1574		1044		
7c	3450—3200	1630 1571	1540	1063	736	—
7d	3400 (shoulder)	1637	1540	1052	736	—
(α)	3363 3375	1580				
7d	(shoulder)	1633	1534	1065	735	—
(β)	3350	1571				
7e	3390	1636 1578	1532	1053	738	—
7f	3340	1630 1577	1529	1056 1035	738	710 690
7g	3450—3000 3290 3382	1639 1578	1537	1055 1049	744	—
7h	(shoulder) 3350 3440	1637 1573	1538	1057 1040	740	—
7i	(shoulder) 3355 3540 (OH)	1628 1564	1535	1062 1073	739	—
7j	3352 (shoulder)	1629 1567	1532	1053 1020	733	—
7k	3300 3412	1622 1565	1533	1060 1039	748	—
7l	3315 3405 3340	1619 1555	1530	1060 1040 1030	741	705 696

* For **6a—6e**, see Part I, Table II [1]

found, in turn, for the concluding reactions **5**→**6** and **5**→**7**, not yet studied in detail but certainly composed of several steps, must be due to the character of these reactions. This decrease of the yield is substantial chiefly in the cyclization **5**→**7** effected with monosubstituted alkylhydrazines. The two ways of synthesizing N(2)-substituted derivatives, total synthesis and alkylation, always lead to products of the same structure.

According to their infrared spectra (δNH 1540 to 1529 cm^{-1}), compounds **6** and **7** made as described above are probably the tautomers containing endocyclic C=N group as shown in the formulas. The most important infrared spectral data are collected in Tables V and VI.

Experimental

M.p.'s were determined on a Boetius microapparatus. Infrared spectra were recorded in KBr pellets or in chloroform solution with a UR-10 (Zeiss, Jena) spectrophotometer.

Synthesis of hydroxyalkylphthalimides (1)

Equimolar quantities of phthalic anhydride and the aminoalcohol were mixed and heated in an open flask on an oil bath at 200 °C till the elimination of water ceased (from 30 to 60 min). In the case of **1a**, **1b** and **1f**, the fused mass solidified on cooling. **1f** was crystallized from ethanol to obtain colourless needles (m. p. 154 °C, identified as the erythro compound described in the literature [11]; **1f** was prepared from a DL-norephedrine not further specified, sold by the Aldrich Chem. Co., Inc.). Substances **1c** and **1e** were difficult to crystallize and substance **1d** was obtained as a thick syrup [12]. The tosyl esters were prepared from the crude hydroxyalkylphthalimides. Derivatives **1a**—**1f** are compounds described in the literature.

Tosylation reaction 1→3

The crude hydroxyalkylphthalimide (**1a**—**1f**) (0.1 mole) was dissolved in dry pyridine (100 ml) and treated with tosyl chloride (28.5 g; 0.15 mole). The solution became slightly warm. It was allowed to stand overnight in a stoppered flask and diluted with water to 1000 ml whereupon the tosyl ester separated as an oil which slowly solidified. The crystalline substance was filtered off, washed until free of chloride, and recrystallized as specified in Table I. (Compound **3a** is described in the literature [13].) These tosyl esters were colourless compounds which crystallized readily. Owing to an anomalous reaction, tosylation of **1b** gave the 3-chloropropylphthalimide.

3-Chloropropylphthalimide (4)

3-Hydroxypropylphthalimide (20.5 g; 0.1 mole) was dissolved in pure pyridine (100 ml) and mixed with tosyl chloride (28.5 g; 0.15 mole). Slight warming of the mixture was observed. The next day some water was added to the mixture and the pyridine removed in a rotating evaporator. The oily residue was dissolved in chloroform, washed with water, dried over magnesium sulfate, then the filtrate was evaporated to dryness to leave a yellowish oil which crystallized on standing to give 15.6 g (43%) of the product. According to elementary analysis no sulfur was present in the crude product obtained by extraction with chloroform. Colourless needles (from ethanol), m.p. 68—69 °C.

$C_{11}H_{10}ClNO_2$ (223.7). Calcd. Cl 15.9. Found Cl 15.9, 16.0%.

Preparation of hydroxyalkylaminophthalazinones (6 and 7) by total synthesis (A) and by alkylation (B)

Method (A)

The tosyl ester (**3a**, **3c**—**3f**) (10 mmoles) and the appropriate halogenoalkylphthalimide (2-bromoethyl- and 3-bromopropylphthalimide) (10 mmoles) were suspended in methanol (100 ml) and mixed with a methanolic solution (30 ml) of potassium hydroxide (1.34 g; 24 mmoles). The mixture was refluxed for 30 min. Chilling in ice-water caused potassium tosylate to separate in crystal platelets; slight acidification with conc. hydrochloric acid in the presence of methyl orange followed. In order to prepare **6** (*cf.* Table III), a 72% solution (3 ml) hydrazine hydrate was added, whereas derivatives of the type **7** (*cf.* Table IV) were made by adding methylhydrazine (0.92 g; 20 mmoles) and 2-hydroxyethylhydrazine (1.52 g; 20 mmoles), respectively, and boiling the mixture for the period noted in Table IV. After dilution with some water the solution was evaporated to dryness in a rotary evaporator, the residue was taken up in some water and neutralized with hydrochloric acid. The solid was collected on a filter and purified by recrystallization.

Method (B)

10 mmoles of the hydroxyalkylaminophthalazinone (**6a**—**6f**) were dissolved in methanol (300 ml) containing potassium hydroxide (11.2 g), in a flask fitted with a stirrer; dissolution was promoted by slight warming. The mixture was cooled to room temperature, the intensive

mechanical stirring was started and, over a period of 15 to 20 min, dimethyl sulfate (10 ml) was added in portions. After standing for a short time, methanol was removed in a rotary evaporator, the residue was taken up in some water, the solid collected by filtration, washed with water, dried, and recrystallized as specified in Table IV. From the alkaline mother liquor of the crude product the unchanged starting material was recovered by neutralization. Compounds **6a**—**6e** were rather scarcely soluble in methanolic potassium hydroxide; compound **6f** was an exception as it readily dissolved in the cold solvent. Methylation, in general, proceeded to give excellent yields, with the exception of compound **6f**, which even with a great excess of dimethyl sulfate was methylated only in about 30%.

*

The author's thanks are due to Dr. F. RUFF for his help in recording and interpreting infrared spectra. Elementary analyses were made in the Microanalytical Laboratory of the Institute, under the leadership of Dr. H. MEDZIHRADSZKY. The starting materials used in these studies were made available by the Bristol Laboratories, Syracuse, N.Y., U.S.A.; this generous support is gratefully acknowledged.

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CRYSTALLINE HYDROGEN HALIDE COMPLEXES OF CYCLODEXTRINS

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One molecule of β-cyclodextrin forms a crystalline inclusion complex with 1.5—2.0 molecules of HCl. The yield calculated for β-cyclodextrin is 72—74%. The fact of complex formation is confirmed by the crystal form, thermoderivatographic, X-ray diffraction and mass spectral data. The HBr and HI complexes of β-cyclodextrin, and the HI complex of α-cyclodextrin were prepared in crystalline form. These complexes are stable at room temperature.

In the presence of acetone, a ternary complex is formed in which the molar ratio of β-CD : acetone : HCl is 1 : 1 : 1.

Acetone also gives a complex with β-CD; the molar ratio is 1 : 1.

Cyclodextrins, also known as Schardinger dextrins, cycloamyloses or cycloglucanes, are cyclic oligosaccharides, the best known representatives being α-cyclodextrin consisting of six anhydroglucopyranose units (diameter of the internal cavity: about 6 Å), and β-cyclodextrine constructed of seven anhydroglucopyranose units (the cavity diameter is about 8 Å). The glucopyranose units are linked by α-1,4-glycosidic linkages.

In consequence of the C1 conformation of the glucopyranose units, cyclodextrins possess a particular steric structure: on one edge of the torus-like molecule are localized the C_6—OH primary hydroxyl groups, on the other one the secondary C_2- and C_3-hydroxyls. As a result of the unshared electron pairs of the glycosidic oxygen bridges, which form an internal "lining" of the cyclic molecule, the cyclodextrin cavity may be regarded as a topochemical base, and in solution it accelerates the base-catalyzed reactions of such compounds which are capable of being incorporated into the cavity [1].

Cyclodextrins give crystalline inclusion complexes with a great variety of aromatic and aliphatic compounds and also with gases. The lattice structure of these crystalline complexes may be stable even if a part of the cavities remains unoccupied.

Previous studies [2] led to the conclusion that the activation energy of acid hydrolysis of the α-1,4 glycosidic linkages participating in the building of the macrocycle is significantly higher than those of α-1,4 glycosidic bonds in the comparable linear dextrins. Another interesting observation was that the rate of hydrolysis in $2N$—$5N$ hydrochloric acid at room temperature, or below, was slower than it could be anticipated by extrapolating the results

of hydrolyses effected at higher temperatures, or with a lower concentration of acid.

These results led to the inference that not only hydrolysis, but also complex formation takes place in $2N-5N$ hydrochloric acid solutions at room temperature or below.

According to CRAMER [3], β-cyclodextrin, in consequence of the diameter of its internal cavity, forms crystalline complexes only with Br_2 and I_2, but not with Cl_2. Concerning the α-cyclodextrin–HI complex it has to be mentioned that, according to JAMES *et al.* [4], α-cyclodextrin forms an iodine complex without the participation of iodide ion.

By treating solid amylose with HCl gas in vacuum, PANZICA *et al.* [5] prepared the hydrochloric acid complex of amylose, which, however, being a macromolecule does not form a crystalline compound of well defined composition. The HCl content is between 3.8 and 7.2%, *i.e.* one mole HCl per 4—6 glucopyranose units.

The present paper deals with the preparation of HI, HBr and HCl complexes of β-cyclodextrin, as well as the HI complex of α-cyclodextrin. The β-cyclodextrin–HCl complex has been more thoroughly studied because of its potential industrial application.

Preparation and investigation of the β-cyclodextrin–HCl complex

β-Cyclodextrin (10%) was dissolved in water at 80—90 °C (a nearly saturated solution at this temperature) and added immediately to the same volume of $10N$ hydrochloric acid (conc. HCl), with vigorous stirring. The resulting $5N$ hydrochloric acid solution of β-cyclodextrin was cooled quickly to 0 °C, allowed to stand for 30 min, and then stored between —5 and —10 °C for 48 hrs. The crystals which separated were filtered off cold, rinsed with the cold mother liquor, and dried over solid KOH pellets in vacuum for 72 hrs at room temperature. The yield was between 72 and 74% calculated for β-cyclodextrin. Acid hydrolysis of cyclodextrin occurring during the preparation of the complex is insignificant. The reducing sugar determined in the mother liquor by Somogyi–Nelson method and expressed as glucose, is 1.5% of the total β-cyclodextrin. The further "loss", *i.e.* any β-cyclodextrin–HCl complex remaining in the hydrochloric acid mother liquor, may be hydrolyzed at 100 °C during 1 hr to glucose, and may be then determined by the Somogyi–Nelson method.

Figure 1 schematically illustrates the assumed structure of the crystalline β-cyclodextrin–HCl complex and the process of its formation.

According to alkalimetric and argentometric titrations and chloride microanalysis, the HCl content of the freshly prepared complex was on the average 1.8 mole HCl per mole of β-cyclodextrin (Table I).

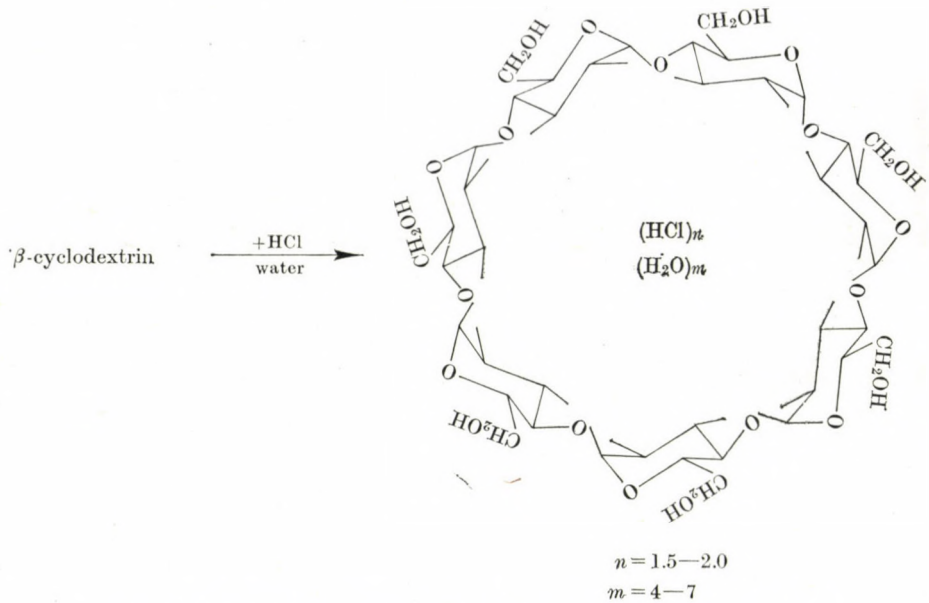


Fig. 1. The assumed structure of the β-cyclodextrin–HCl complex

Table I

Microanalytical data

	Determined, % (depending on H_2O cont.)	Recalculated for anhydrous substance, %
C	37—40	41—42
H	6.2—6.5	5.8—6.00
O	48—51	46—46.6
Cl	4.9—5.2	5.3—5.7

β-cyclodextrin : HCl ratio $\sim$ 1 : 1.8

According to microanalysis, the ionic chloride content of the complex stored in a stoppered flask at room temperature is 5.14%, *i.e.* 1.73 mole HCl per mole of β-cyclodextrin after 2 weeks, 4.5% = 1.46 mole after 3 months, and 1 mole HCl per mole of β-cyclodextrin after 8 months; this value remained unaltered also after 18 months. The complex stored in sealed ampoules at room temperature contained its original (1.8 mole) HCl-content also after 18 months.

Determination of moisture content was carried out according to the Karl Fischer method in dimethylformamide solution. Under the given conditions the water content of the product was between 8 and 10%, *i.e.* 4 to 7 mole of water per mole of β-cyclodextrin.

The crystal form of complex is significantly different from that of β-cyclodextrin. Figure 2 shows the microscopic picture (magnification $\times 70$) of β-cyclodextrin (A) and its HCl complex (B). The diameter of the crystals of the complex is about 0.5 mm on the average.

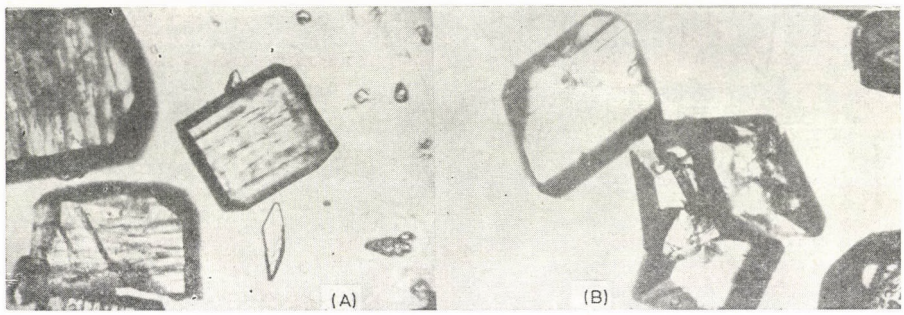


Fig. 2. Crystal photos of β-cyclodextrin (A) and its hydrochloric acid complex (B). $70\times$)

The X-ray crystallographic dimensions and space groups were determined from Buerger-type precession and WEISSENBERG films [9]. As shown by Table II, the space groups for crystalline β-cyclodextrin and for its HCl complex are identical, and the cell dimensions are very similar, too. The two crystals are considered to be isomorphous, their morphology, however, is different. In the case of β-cyclodextrin *b* represents the longitudinal axis, whereas for the HCl complex *a* is the rotational axis. The powder patterns are also very similar; nevertheless, some significant discrepancy can be observed in Fig. 3.

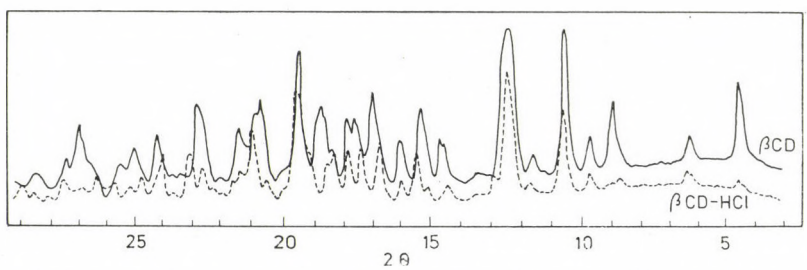


Fig. 3. X-ray powder pattern of β-cyclodextrin and its hydrochloric acid complex

Figure 4 illustrates the **thermoderivatograms**. As seen in the TG curves, β-cyclodextrin will lose about 8% of its moisture content at a temperature between 80 and 100 °C; its weight will remain then constant until the beginning of the decomposition at about 300 °C. The β-cyclodextrin–HCl complex loses water and HCl progressively; after this, also the decomposition is progressive.

Comparing the DTG curves, in addition to water, also the peak corresponding to the loss of hydrogen chloride is clearly visible.

The time and temperature dependence of the **mass spectrum** was also studied. The main peaks in the mass spectrum of the substances evaporating from the β-cyclodextrin–HCl complex at 80—200 °C were as follows: *m/e* 17;

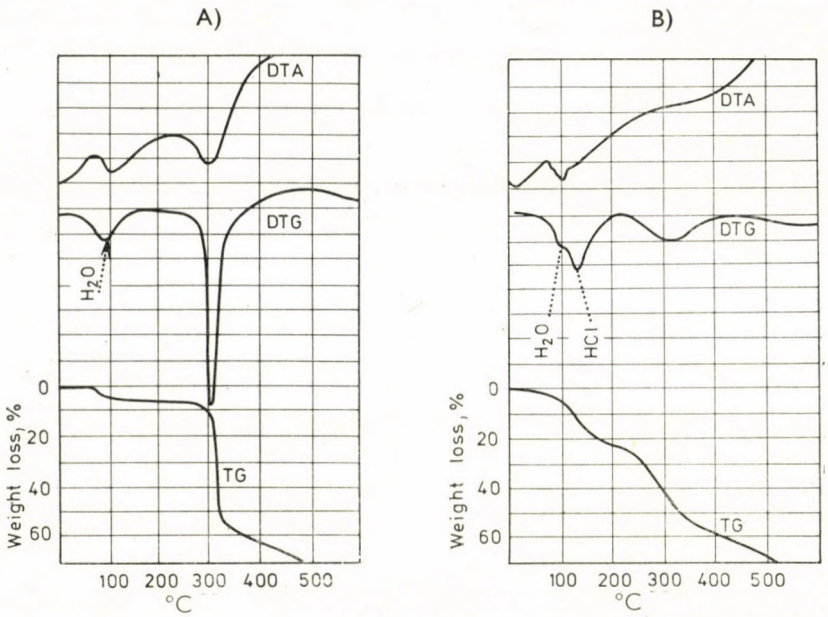


Fig. 4. Thermoderivatograms of β-cyclodextrin (A) and its hydrochloric acid complex (B)

18 (water); 36; 38 (HCl) and 139; 221; 226. The latter three peaks must have resulted from a single component, as it is proved by the metastable transitions. Table III contains the temperature of the sample as a function of time, the intensity of the hydrochloric acid peak in percentage of the total ion current, as well as the total ion current compared with the initial state. The hydrochloric acid peak is always intense, even at about 250 °C at which the thermal

Table II

The cell dimension and space groups for β-cyclodextrin and its HCl complex

	β-cyclodextrin	HCl complex
a	15.18 Å	15.04 Å
b	10.25	10.27
c	21.12	20.75
β	111.6°	109.0°
space group	$P2_1$	$P2_1$

decomposition of β-cyclodextrin begins. These data indirectly confirm that the sample contains hydrochloric acid rather in the form of inclusion complex than adsorbed. β-Cyclodextrin examined for comparison loses chiefly water when recording the mass spectrum; the intensities of the peaks $m/e = 266$; 222 and 139 are very weak.

Table III

Mass spectrum data of the β-cyclodextrin–HCl complex

Min	Temperature °C	HCl (as % of total ion current)	Total ion current
0	80	0.44	1
8	80	11	1
15	90	42	3/4
26	100	23	1/2
40	110	10	1/4
55	150	10	1/4
80	200	7	1/4
90	250	0.8	3/4

Other hydrogen halide complexes

On the analogy of the β-cyclodextrin–HCl complex also the following crystalline complexes were prepared:

β-cyclodextrin–hydrobromic acid complex; it contains 13 to 14.7% bromine as bromide ion, *i.e.* 2.13 to 2.45 mole HBr per mole of β-CD;

β-cyclodextrin–hydrogen iodide complex; the iodide content is 25.25%, *i.e.* 3 mole HI per mole of β-CD.

In the α-cyclodextrin–hydrogen iodide complex the iodide content is 27 to 29%, *i.e.* 2.85 to 3.1 mole HI per mole of α-CD.

These values have been calculated from the results of elemental microanalyses.

The preparation and examination of the ternary complex of β-cyclodextrin, HCl and acetone

In the course of a study of the complex formation of cyclodextrins and diethyl ether, TAKEO and KUGE [6] became aware of the 'Einschleppeffekt' ('pull-in effect'), which may result in ternary complexes. This means that

molecules, which in themselves do not form complexes, may be incorporated into the cyclodextrin cavity together with another molecule, to give stable complexes. For instance, diethyl ether alone is not an appropriate guest molecule for β-cyclodextrin, nevertheless, together with anthracene, it forms a **ternary complex.**

In order to improve the yield of the crystalline β-cyclodextrin–HCl complex, instead of cooling alone, solvent precipitation was also tried. However, it was not possible to attain the object with the solvents tested (ethanol, methanol, *n*-butanol, *t*-butanol, isopropanol, carbon tetrachloride, dimethylformamide, toluene, ethylacetate). A ternary complex separated, if acetone was applied.

β-Cyclodextrin (10%) was dissolved in water at 80—90 °C, and to this solution first the same volume of 10*N* HCl was added, thereafter two and a half volumes of acetone until further crystal separation did not occur. This mixture was stored in a refrigerator for 24 hours, then the fine crystalline powder was filtered off on a G4 glass filter, rinsed with acetone and dried in a vacuum exsiccator at room temperature over solid KOH. The yield calculated for β-cyclodextrin was 65—70%.

The product consists of colourless, odourless snow-white small crystals. The taste is sour and the aqueous solution smells definitely of acetone. As in the case of the β-cyclodextrin–HCl complex, the hydrochloric acid content was determined by alkalimetric and argentometric titration as well as by elemental microanalysis, showing the composition of 1 mole hydrochloric acid per mole of β-CD.

For the determination of the acetone content 5% of the ternary complex was dissolved in 0.1*N* NaOH and about three-quarters of the solution were distilled over. The distillate contained the acetone (but no HCl). The acetone was determined by gas chromatography.

In this manner the acetone content was found to be 1.5 mole of acetone per mole of β-CD, *i.e.* the product contained 8% acetone. The cyclodextrin content of the product was determined by the methyl orange method [7], as well as with the Somogyi–Nelson method after total hydrolysis, the value of 82% (5% moisture content) was found.

Thus, the composition of the ternary complex is 1 : 1.5 : 1 mole β-CD : acetone : HCl. If the complex is stored in vacuum at 60 °C for 2 hours, the acetone content decreases and approximates the molar ratio of β-CD : acetone : HCl 1 : 1 : 1. The thermoderivatogram of the product was similar to that illustrated in Fig. 4; the loss of acetone and hydrochloric acid practically takes place simultaneously.

The β-cyclodextrin–acetone complex was prepared under similar conditions as in the case of the β-cyclodextrin–acetone–HCl complex at 80—90 °C; to a 10% aqueous solution of β-cyclodextrin acetone was added until the

separation of crystalline precipitate ceased (about three volumes of acetone). This mixture was stored in a refrigerator for 24 hours. The separated fine crystal powder was filtered off and dried. The yield for β-cyclodextrin was 63 –65%.

The **acetone content** of the β-cyclodextrin–acetone complex was determined directly by means of gas chromatography. The acetone content was found to be 2 moles acetone per mole of β-CD. If the product was stored in vacuum at 60 °C for 2 hours, the acetone content decreased to 1 mole acetone per mole of β-CD.

Practical applications [8]

The β-cyclodextrin–HCl complex is suitable for the preparation of tablets. One tablet containing 1 g of the β-cyclodextrin–HCl complex dissolved in 150 ml of water gives a 0.01N hydrochloric acid solution. Thus, the β-cyclodextrin–HCl complex may have the following applications:

— supplying gastric acid in tablet form,
— storage of hydrochloric acid in solid form, easy to dose,
— hydrochloric acid may be introduced, for instance as catalyst, into anhydrous media,
— it may be used as a minor constituent of vehicle for tablets, if slightly acid medium is required.

*

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ELECTRON DEFICIENT HETEROAROMATIC AMMONIOAMIDATES, XIV*

THE SYNTHESIS AND SOME REACTIONS OF 9,10-DIMETHOXY-2*H*[1,3,4]-THIADIAZINO[3,2-*c*]QUINAZOLIN-5-IUM-3-OLATES

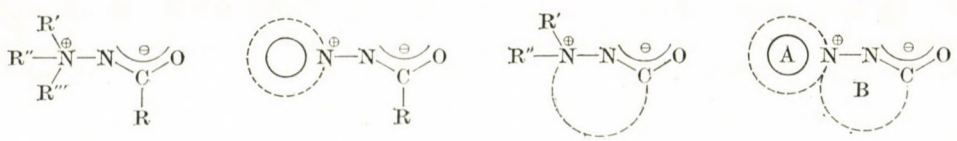
M. LEMPERT-SRÉTER,[a] K. LEMPERT,[b] P. BRUCK[c] and G. TÓTH[d]

([a]Department of Organic Chemistry, Eötvös Loránd University, Budapest, [b]Department of Organic Chemistry, Technical University, Budapest, [c]Central Research Institute for Chemistry of the Hungarian Academy of Sciences, Budapest and [d]Department of Organic Chemistry, Pharmaceutical Faculty, Semmelweis Medical University, Budapest)

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Ring closures of the 2-(2-acylaminophenyl)-4*H*-1,3,4-thiadiazin-5(6*H*)-ones **15d** and **15f** furnished the first members (**16a** and **16b**, respectively) of a novel class (type **4**) of electron deficient heteroaromatic ammonioamidates. Alkaline hydrolysis of the 2*H*-[1,3,4]thiadiazino[3,2-*c*]quinazolin-5-ium-3-olate **16a** gave, in addition to minor amounts of compounds **15d** and the 4(3*H*)-quinazolinone **17a**, the 3-mercapto-acetamido-4(3*H*)-quinazolinone **18b**, which is in equilibrium with its ring-chain tautomer **18a**, the stable tetrahedral intermediate of the reaction **16a**→**18b**. Photolysis (HPK-125 lamp, Pyrex, N_2) of **16a** furnished the 4(3*H*)-quinazolinethione **17d** and minor amounts of the 3-acetamido-4(3*H*)-quinazolinone **17b**.

Starting with the two basic types of *N*-ammonioamidates, the purely aliphatic (**1**) [1, 2] and the heteroaromatic members (**2**) [1—3] of this class of compounds, it is possible to derive two further types, **3** [1, 2, 4, 5] and **4** of ammonioamidates by incorporation of the amidate nitrogen and carbon and of the ammonio nitrogen atoms into a second ring which may or may not contain additional hetero atoms.

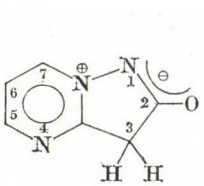


1 **2** **3** **4**

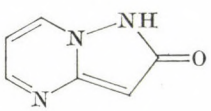
A very limited number of type **4** compounds has been known so far, their majority being derivatives of the pyrazolo[1,5-*a*]pyrimidine ring system [6—10]. These compounds are potentially tautomeric and may be formulated either as the *C*— H (**5**) or the *N*—H (**6**) or the *O*—H forms (**7**) and have, actually, invariably been formulated as the *O*—H forms, although the IR spectrum

* For Part XIII, see Ref. [14]

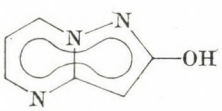
(KBr) of the 3-ethyl-5,7-dimethyl derivative (3300—2300, XH; 1650, 1640 and 1540, b) [9] rules out the presence of significant amounts of the *N*—H form only, but not of the *C*—H form. Support for the postulate of the non-existence of the *C*—H forms may, however, be derived from the analogous situation found for the related 1-substituted 3-pyrazolols (**8**—**10**) where, in spite of extensive studies [11—13], no evidence for the existence of the dipolar *C*—H forms **8** could be obtained.*



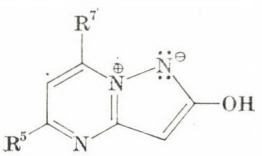
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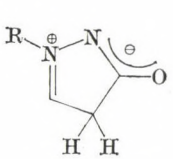
6



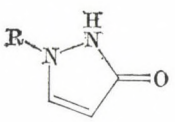
7



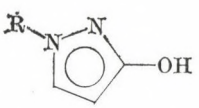
7a



8



9



10

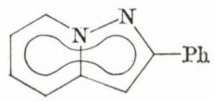
Probably as a consequence of their being *N*-pyrimidiniohydroxy-vinylamides (*cf.* limiting structure **7a**) rather than true *N*-pyrimidinioamidates (which, as type **2** compounds, should be photoactive [14]**) both 5,7-dimethyl- and 7-methyl-5-phenylpyrazolo[1,5-*a*]pyrimidin-2-ol [9] (type **7**) proved, in our hands, photoinactive even if irradiated in quartz vessels. This is in agreement with our observation that the related 2-phenylpyrazolo[1,5-*a*]pyridine **11** [15] is also stable towards irradiation under all conditions tested (with or without Pyrex filters, both in the presence and absence of oxygen and benzophenone, respectively).

Another type **4** compound, the [1, 3, 4]oxadiazolo[3,2-*a*]pyridine derivative **12** [16] has also proved stable when irradiated with 300 and 350 nm light, both in the absence and presence of benzophenone [17], which may be the

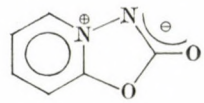
* *Added in proof:* For the analogous situation with the potentially tautomeric pyrazolo-[1,5-*a*]pyridin-2-ols which, in solution, exist at least predominantly as such, see Ref. [25].

** It should be pointed out in this connection that, as shown by the photostability of compound **21** [21], the presence of the ammonioamidate moiety may not be regarded as a sufficient condition of photoreactivity. Studies with the aim to elucidate the effect of the presence and the structure of ring B on the photoreactivity of type **4** ammonioamidates are in progress.

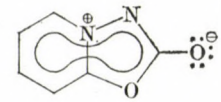
consequence of its actual electronic structure closely approaching that shown in **12a**.



11

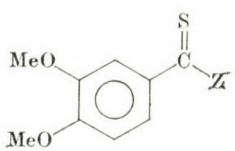


12

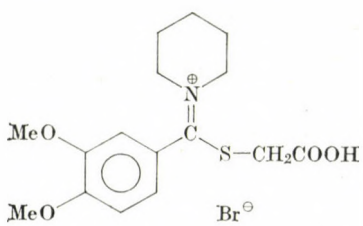


12a

In order to avoid complications due to the potential aromaticity of ring B in type **4** compounds, we have started studies into the chemistry of such compounds containing various six-membered and larger rings B, and wish to describe in the present paper our experiences with 9,10-dimethoxy-6--methyl-2*H*-[1,3,4]thiadiazino[3,2-*c*]quinazolin-5-ium-3-olate (**16a**) and the 6--phenyl analogue **16b**. The key intermediate for the synthesis of the compounds **16**, *viz.* 2-(2-amino-4,5-dimethoxyphenyl)-4*H*-1,3,4-thiadiazin-5(6*H*)-one (**15c**) was obtained starting with 3,4-dimethoxybenzaldehyde *via* *N*-(3,4-dimethoxythiobenzoyl)piperidine (**13a**), *N*-(α-carboxymethylthio-3,4-dimethoxybenzylidene)piperidinium bromide (**14**), *S*-(3,4-dimethoxythiobenzoyl)thioglycolic acid (**13b**), 3,4-dimethoxythiobenzohydrazide (**13c**), 2-(3,4-dimethoxyphenyl)-(**15a**) and 2-(4,5-dimethoxy-2-nitrophenyl)-4*H*-1,3,4-thiadiazin-5(6*H*)-one (**15b**), in part by applying methods described earlier for the syntheses of the *p*-methoxy analogs of **13b** [18] and of **13c** [19]. Acetylation of **15c** furnished, depending on the conditions, either the mono- (**15d**) or the diacetyl derivative (**15e**);* benzoylation of **15c** gave the monobenzoyl derivative (**15f**) which could be acetylated to **15g**.* The ring closures of **15d** and **15f** to yield the perchlorates of **16a** and **16b**, respectively, were effected with perchloric acid



13



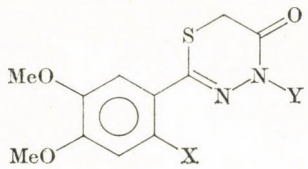
14

a; $Z =$ 

b: $Z =$ —SCH_2COOH

c: $Z =$ —$NHNH_2$

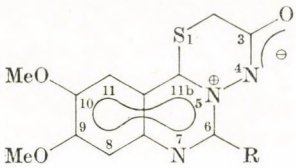
* The structures of the diacyl derivatives **15e** and **15g** were deduced from their IR and NMR spectra.



15

15

	X	Y
a	H	H
b	NO_2	H
c	NH_2	H
d	NHAc	H
e	NHAc	Ac
f	NHBz	H
g	NHBz	Ac



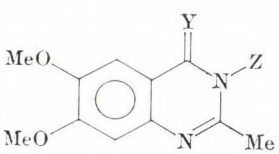
16

a: R = Me

b: R = Ph

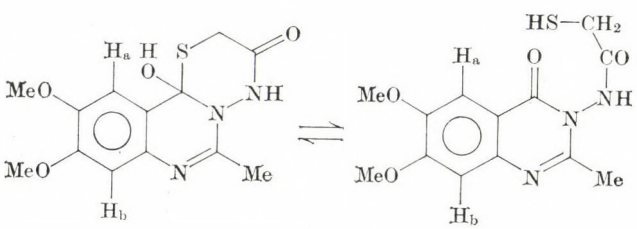
and acetic anhydride in methylene dichloride. The zwitterionic free base **16a** was liberated from the perchlorate by treatment with Amberlite IRA-4B ($OH^{\ominus}$ form) in water; this method is superior to that using Na_2CO_3 as the base because, according to exploratory tests, with the latter reagent a certain amount of the hydrolysis product 3-amino-2-methyl-4(3*H*)-quinazolinone (**17a**) is always formed in addition to **16a**. The solubilities both of **16b** and its perchlorate in water are so slight that the Amberlite method could not be used for the liberation of **16b** from its perchlorate.

Treatment of **16a** with aqueous $NaHCO_3$ furnished two isomeric products, *viz.* compound **15d** and the tautomeric compound **18**, by attack of $OH^{\ominus}$ at C-6 and C-11b, respectively. While the former is insoluble in aqueous alkalies, the latter can be extracted from its chloroform solutions with excess 10% aqueous NaOH in the form of its sodium salt. This salt is apparently a derivative of the tricyclic form **18a** since the IR spectrum of the solid, obtained on evaporation of the aqueous alkaline solution to dryness, had no C=O band. The salt is reconverted into **18** when chromatographed over silica. The UV



17

	Y	Z
a	O	NH_2
b	O	NHAc
c	O	H
d	S	H
e	S	NHAc



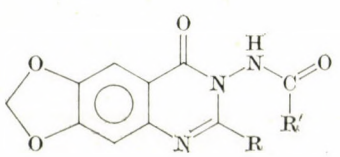
a **18** **b**

spectrum of **18** in ethanol is essentially identical with those of the type **19** model compounds [14] demonstrating that in ethanolic solution the compound exists as the practically pure "open-chain" form **18b**. In chloroform solution, however, as shown by the typical AB pattern of the methylene group in the NMR spectrum, the compound exists as the pure tricyclic tautomer **18a**. Elevation of the temperature caused slight broadening of the individual peaks of the methylene dd. Addition of about 0.25 parts (v/v) of CD_3OD to the $CDCl_3$ solution resulted in significant changes of the NMR spectrum. At room temperature the signal of H_a (which is a sharp s at δ 7.42 in $CDCl_3$) is split into two singlets (δ 7.44 and 7.47, total intensity 1H); and the intensity of the methylene dd decreases to about 1H. At 40 °C the two H_a singlets coalesce, as does also, at 75 °C, the methylene dd. All this may be interpreted as demonstrating the coexistence in $CDCl_3/CD_3OD$ 4 : 1 (v/v) of the tricyclic (**18a**) and the "open-chain" (**18b**) tautomers;* elevation of the temperature favours the formation of the "open-chain" form (to a lesser degree even in $CDCl_3$ solution), the mean enthalpy of activation of the process **18a** $\rightleftharpoons$ **18b**, as calculated on the basis of both coalescence phenomena, being about 17 kcal/mole.

Compound **18a** may be viewed as the stable tetrahedral intermediate of the alkaline hydrolysis reaction of the tricyclic imidothioate **16a**, leading to the cyclic amide **18b**.

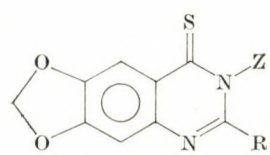
Treatment of compound **16a** with aqueous NaOH gave, in addition to compounds **15d** and **18**, the hydrolysis product **17a**.

Irradiation of compound **16a** (high pressure mercury immersion lamp, Pyrex) in water under nitrogen furnished 4,5-dimethoxy-2-methyl-4(3*H*)--quinazolinethione (**17d**) as the main product, and a small amount of 3-acetamido-4,5-dimethoxy-2-methyl-4(3*H*)-quinazolinone (**17b**). The structures of these products were derived from their spectral properties, in particular from the close resemblance of their UV spectra to those of the model compounds **20a** [20] and **19** [14], respectively, and were substantiated by comparison with



19

(R = H, Me; R' = OEt, OCH_2Ph, Ph)



20

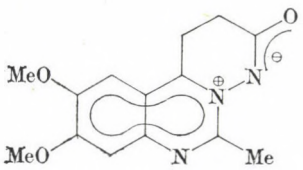
a: R = Me, Z = H

b: R = H, Z = NHCOOEt

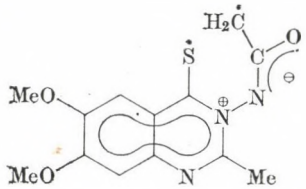
* It is noteworthy that the combined deshielding effect of the OH group and the S atom on H_a of **18a** is almost identical with the deshielding effect of the carbonyl group on H_a of **18b**.

authentic samples. The photoproducts, at least compound **17b**, could in principle be formed either from **16a** itself or from the hydroxyl adduct **18**; that the latter is actually *not* the case is shown by the stability of compound **18** towards prolonged irradiation in aqueous acetonitrile.

Since the closely related compound **21** is known to be photoinactive [21], it is assumed that photolysis of **16a** is initiated by homolysis of the S—CH_2 bond to yield **22** as the first intermediate. (For an analogous process, see Ref. [22].) Hydrogen rearrangement under elimination of 2-azirinone (or its equivalent) should then lead to **17d**. The formation of **17b** is probably the result of a photo-oxidative process. A likely intermediate for this process is compound **17e** (which could be formed from **22** by double H-abstraction from the solvent). The closely related compound **20b** [20] was, however, found to be unaffected by prolonged irradiation in aqueous acetonitrile. It is therefore the diradical **22** which is assumed to be photo-oxidized by traces of oxygen present in the solvent.



21



22

Experimental

UV spectra were obtained with a Carl Zeiss (Jena, GDR) type Specord UV spectrometer, IR spectra with Carl Zeiss (Jena, GDR) type 10 and Hungarian Optical Works (Budapest) type Spektromom 2000 IR spectrometers, PMR spectra with a Bruker type X90 NMR spectrometer operating at 90 MHz in the FT mode and with Perkin-Elmer type R 12 and Jeol type RS-100 NMR spectrometers operating at 60 and 100 MHz, respectively, in the CW mode, using TMS as the internal reference compound. Mass spectra were obtained, except where noted, at 70 eV with an AEI MS-902 mass spectrometer using direct sample insertion.

N-(3,4-Dimethoxythiobenzoyl)piperidine (13a)

A mixture of 3,4-dimethoxybenzaldehyde (1.66 g; 10 mmoles), piperidine (1.5 ml; 15 mmoles) and sulfur (0.48 g; 15 mmoles) was refluxed for 1 hr under an efficient hood. The resulting brown solution was diluted with water and acidified with conc. HCl (2 ml), and the gummy precipitate was crystallized from EtOH to yield 2.36 g (89%) of **13a**, m.p. 107—108 °C.

$C_{14}H_{19}NO_2S$ (265.3). Calcd. N 5.31. Found N 5.28%.

N-(α-Carboxymethylthio-3,4-dimethoxybenzylidene)piperidinium bromide (14)

Bromoacetic acid (0.62 g; 45 mmoles) was added to the anhydrous benzene solution of compound **13a** (1.0 g; 3.8 mmoles). The resulting gummy precipitate was triturated on the next morning with dry ether (15 ml) to yield 1.24 g (81%) of a crystalline product, m.p. 174—176 °C (from ethanol–ether).

$C_{16}H_{22}BrNO_4S$ (404.3). Calcd. C 47.53; H 5.49; N 3.46. Found C 47.14; H 5.80; N 3.28%.

S-(3,4-Dimethoxythiobenzoyl)thioglycolic acid (13b)

H_2S was introduced for 8 hrs into an ice-cold anhydrous ethanolic (120 ml) solution of compound **14** (6.0 g; 15 mmoles). The mixture was kept overnight in a refrigerator and evaporated to dryness in vacuum. The residue was extracted with hot benzene until the insoluble material turned colourless. The benzene solution was concentrated and chilled to yield 4.0 g (98%) of orange red crystals, m.p. 143—145 °C.

$C_{11}H_{12}O_4S_2$ (272.3). Calcd. C 48.51; H 4.44; S 23.55. Found C 48.38; H 4.29; S 23.68%.

3,4-Dimethoxythiobenzohydrazide (13c)

Compound **13b** (2.7 g; 10 mmoles) was added to a mixture of 1 *N* aqueous NaOH (14 ml) and 70% hydrazine hydrate (3 ml). The resulting faint yellow solution was acidified under cooling with acetic acid (4.5 ml). The aqueous layer was decanted and the oily product dried by azeotropic distillation with benzene and crystallized from benzene to yield 1.46 g (69%) of compound **13c**, m.p. 111—112 °C.

$C_9H_{12}N_2O_2S$ (212.2). Calcd. N 13.21. Found N 13.15%.

2-(3,4-Dimethoxyphenyl)-4H-1,3,4-thiadiazin-5(6H)-one (15a)

Compound **13c** (1.06 g; 5 mmoles) and, subsequently, ethyl bromoacetate (0.56 ml; 5 mmoles) were added to an ethanolic (15 ml) solution of Na (0.13 g; 5.6 mmoles) to yield 0.88 g (69%) of a crystalline product, m.p. 184—185 °C (from AcOH).

$C_{11}H_{12}N_2O_3S$ (252.3). Calcd. C 52.36; H 4.80; N 11.11. Found C 52.35; H 5.40; N 11.46%.

IR (KBr): 3200, 3100, 1675, 1520 cm^{-1}.

NMR ($CDCl_3$): δ 3.5, s, 2H, CH_2CO; 3.9, s, 6H, $(MeO)_2$; 6.9, d, $J = 9.5$ Hz, 1H, 5-H of Ar; 7.47, dd, $J = 9.5$ and 2 Hz, 1H, 6-H of Ar; 7.47, d, $J = 2$ Hz, 1H, 2-H of Ar; 9.75, bs, 1H, N–H.

2-(4,5-Dimethoxy-2-nitrophenyl)-4H-1,3,4-thiadiazin-5(6H)-one (15b)

Conc. HNO_3 (3 ml) was added to a suspension of compound **15a** (2.5 g; 10 mmoles) in AcOH (10 ml). Under gentle evolution of heat a transient clear yellow solution was formed from which precipitation of the yellow crystalline product soon started. (In some cases the reaction had to be initiated by placing the mixture for a short time into a luke-warm water bath. If larger batches are run, external cooling may become necessary.) Yield: 2.7 g (91%), m.p. 238—240 °C (from AcOH).

$C_{11}H_{11}N_3O_5S$ (297.3). Calcd. N 13.82. Found N 13.65%.

IR (KBr): 3220, 3100, 1675, 1530 cm^{-1}.

2-(2-Amino-4,5-dimethoxyphenyl)-4H-1,3,4-thiadiazine-5(6H)-one (15c)

A mixture of compound **15b** (1.0 g; 3.4 mmoles), pyridine (50 ml) and of an aqueous (12 ml) solution of $Na_2S_2O_4$ (3.0 g) was stirred for 5 hrs at 90—95 °C. The resulting solution was concentrated, and diluted with water to yield 0.82 g (88%) of **15c**, m.p. 208—210 °C (from EtOH).

$C_{11}H_{13}N_3O_3S$ (267.3). Calcd. N 15.81. Found N 15.72%.

IR (KBr): 3460, 3340, 3170, 3085, 1670, 1530 cm^{-1}.

Acetylation

(*a*) A suspension of compound **15c** (0.2 g; 0.75 mmole) in a mixture of dry benzene (8 ml) and pyridine (2 ml) was treated at 0—5 °C with acetyl chloride (0.2 ml; 2.7 mmoles). The mixture was kept for 2 hrs at this temperature, and the solvents were removed below 30—35 °C in vacuum. The residue was taken up in water to yield 0.2 g (86%) of 2-(2-acetamido-4,5-dimethoxyphenyl)-4*H*-1,3,4-thiadiazin-5(6H)-one (**15d**), m.p. 216—218 °C (from AcOH).

$C_{13}H_{15}N_3O_4S$ (309.3). Calcd. N 13.59; S 10.27. Found N 13.53; S 10.12%.

IR (KBr): 3400—2800 with local maxima at 3230 and 3130; 1670, 1660 sh, 1530 cm^{-1}.

NMR (DMSO-d_6): δ 2.05, s, 3H, Ac; 3.58, s, 2H, CH_2CO; 3.78, s, 6H, $(MeO)_2$; 7.12 and 7.68, both s, 1H, each, ArH's; 10.35, bs, and 11.6, bs NH's.

UV (EtOH): 2.48 (4.40); 259 (4.30), sh; 296 (3.92), sh; 326 (3.97); 338 (3.98).

MS (75 eV): *m/e* 309 ($M^{+\cdot}$, 100%); 267 ($M-C_2H_2O$, 32%); 252 (63.7%); 224 ($267-C_2H_3O$, 7.6%).

(*b*) Compound **15c** was allowed to react with acetyl chloride as described above but without cooling, to yield 76% of 4-acetyl-2-(2-acetamido-4,5-dimethoxyphenyl)-4*H*-1,3,4--thiadiazin-5(6*H*)-one (**15e**), m.p. 218—220 °C (from AcOH).

$C_{15}H_{17}N_3O_5S$ (351.4). Calcd. N 11.96. Found N 11.94%.

IR (KBr): 3250, 1730, 1710, 1690, 1530 cm^{-1}.

NMR ($CDCl_3$): δ 2.39, s, 3H, AcNH; 2.75, s, 3H, 4-Ac; 3.62, s, 2H, CH_2CO; 3.94, s, 3H and 4.00, s, 3H, (MeO_2); 7.42, s, and 8.64, s, both 1H, ArH's.

Benzoylation

A suspension of compound **15b** (0.5 g; 1.9 mmoles) in a mixture of dry benzene (10 ml) and pyridine (5 ml) was treated with benzoyl chloride (0.7 ml; 6 mmoles) at room temperature. After 30 min the solvents were distilled off, and water was added to obtain 0.7 g (98%) of 2-(2-benzamido-4,5-dimethoxyphenyl)-4*H*-1,3,4-thiadiazin-5(6*H*)-one (**15f**), m.p. 269—270 °C (from DMF).

$C_{18}H_{17}N_3O_4S$ (371,4). Calcd. N 11.31; S 8.63. Found N 11.31, S 8.35%.

IR (KBr): 3400—2800 with local maxima at 3180 and 3100; 1665, 1530 cm^{-1}.

Acetylation of compound 15f

Compound **15f** (0.37 g; 1 mmole) was refluxed for 2.5 hrs with acetic anhydride (5 ml) to yield 0.32 g (78%) of 4-acetyl-2-(2-benzamido-4,5-dimethoxyphenyl)-4*H*-1,3,4-thiadiazin--5(6*H*)-one (**15g**), m.p. 205—207 ° C (from AcOH).

$C_{20}H_{19}O_5S$ (413,4). Calcd. N 10.02. Found N 10.13%.

IR (KBr): 3275, 1730, 1710, 1675, 1530 cm^{-1}.

NMR ($CDCl_3$): δ 2.75, s, 3H, Ac; 3.75, s, 2H, CH_2CO; 4.08, s, 3H, and 4.16, s, 3H, $(MeO)_2$; 7.4—7.8, m, 4H, Bz, *m*- and *p*-H's, + ArH; 7.95—8.25, m, 2H, Bz, *o*-H's; 8.55, s, 1H, ArH.

9,10-Dimethoxy-6-methyl-3-oxo-3,4-dihydro-2H-[1,3,4]thiadiazino[3,2-c]quinazolin--5-ium perchlorate (16a · $HClO_4$)

A mixture of Ac_2O (0.2 ml) and 70% $HClO_4$ (0.2 ml) was added under continuous stirring to an ice-cold suspension of compound **15d** (0.2 g; 0.65 mmole) in CH_2Cl_2 (3 ml). The mixture was kept for 2 hrs at room temperature. Anhydrous EtOH (about 5 ml) was added, and the mixture was boiled up to yield 0.19 g (75%) of yellow crystals, m.p. 247—251 °C.

$C_{13}H_{14}ClN_3O_7S$ (391.8). Calcd. C 39.84; H 3.34; Cl 9.05; N 10.75. Found C 40.02; H 3.81; Cl 9.27; N 10.41%.

IR (KBr): 1710, 1100 cm^{-1}.

9,10-Dimethoxy-6-methyl-2H-[1,3,4]thiadiazino[3,2-c]quinazolin-5-ium-3-olate (16a)

The above perchlorate (0.8 g; 2 mmoles) was stirred with Amberlite IRA-4B ($OH^{\ominus}$ form) for 1 hr in water (80 ml). The resin was filtered off and thoroughly washed with water. The combined filtrate and washings were evaporated to dryness in vacuum to yield 0.5 g (86%) of **16a**, m.p. 223—225 °C (from EtOH).

$C_{13}H_{13}N_3O_3S$ (291.3). Calcd. N 14.45; S 11.08. Found N 14.20; S 10.89%.

IR (KBr): *no* C=O band, *no* $ClO_4^{\ominus}$ band.

UV (H_2O): 226 (4.19); 283 (4.41); 361 (4.21), sh; 380 (4.25).

NMR (TFA): δ 3.25, s, 6-Me; 4.17, s, $(2\text{-H})_2$; 4.29, s, +4.36, s, $(MeO)_2$; 7.60, s, 8-H; 7.79, s, 11-H.

MS (200 °C): *m/e* 291 ($M^{+\cdot}$, 100%); 276 (M—Me, 9%); 263 ($M^{+}-CO$, 52%); 249 (M—NCO, 32%); 236 (14%); 218 ($249^{+}-MeO$, 40%); 217 ($263^{+}-CH_2S$, 52%); 203 ($249-CH_2S$; 56%).

9,10-Dimethoxy-3-oxo-6-phenyl-3,4-dihydro-2H-[1,3,4]thiadiazino[3,2-c]quinazolin-5--ium perchlorate (16b · $HClO_4$)

A mixture of Ac_2O (2.7 ml) and 70% $HClO_4$ (2 ml) was added, with continuous stirring, to an ice-cold suspension of compound **15f** (2.7 g; 7.3 mmoles) in CH_2Cl_2 (50 ml). An oily product

deposited. After 30 min the CH_2Cl_2 was evaporated in vacuum. Anhydrous EtOH (10 ml) was added, and the mixture was boiled up to yield 2.0 g of the yellow perchlorate, m.p. 246—250 °C. A second crop (0.5 g; total yield: 68%) was obtained by concentration of the mother liquor.

$C_{18}H_{16}ClN_3O_7S$ (453.8). Calcd. N 19.19; S 7.09. Found N 9.26; S 7.07%.
IR (KBr): 3290, b; 1725, 1100 cm^{-1}.

9,10-Dimethoxy-6-phenyl-2H-[1,3,4]thiadiazino[3,2-c]quinazolin-5-ium-3-olate (16b)

A suspension of the above perchlorate (0.9 g; 2 mmoles) in CH_2Cl_2 (10 ml) was treated with NaOEt, obtained by dissolving Na (0.06 g; 2.6 mmoles) in anhydrous EtOH (1.5 ml) and evaporation of the excess solvent. The resulting clear solution was evaporated to dryness and the residue triturated with water and extracted with boiling EtOH (20 ml) to yield 0.65 g (92%) of compound **16b**, m.p. 214—215 °C.

$C_{18}H_{15}N_3O_3S$ (353.4). Calcd. N 11.89; S 9.07. Found N 11.76; S 8.92%.
IR (KBr): *no* C=O, *no* $ClO_4^{\ominus}$ band.

Reactions of compound 16a with bases

(*a*) Compound **16a** (1.0 g; 3.44 mmoles) was stirred with 3% aqueous $NaHCO_3$ solution (50 ml) at 50—60 °C until the starting compound was, according to TLC (Kieselgel $GF_{254+366}$, Merck; EtOAc–EtOH, 4 : 1), completely used up (about 10 hrs; a clear solution was obtained after 2 hrs). Extraction with $CHCl_3$ furnished 0.16 g of a crude product which was purified by TLC (Kieselgel $PF_{254+366}$, Merck; EtOAc) to yield 0.1 g (9.9%) of **15d**, identical with an authentic sample (see above).

The aqueous solution was saturated with CO_2 and again extracted with $CHCl_3$. The extract was taken up in CH_2Cl_2 to yield, after being allowed to stand for a few minutes, 0.33 g of compound **18** which was purified by extraction of its contaminants with boiling EtOAc: m.p. 250—252 °C. A further 0.15 g (total yield 48%) of compound **18** was obtained by TLC work-up (Kieselgel $PF_{254+366}$; EtOAc–EtOH, 4 : 1) of the CH_2Cl_2 mother liquor.

$C_{13}H_{15}N_3O_4S$ (309.3). Calcd. N 13.59; S 10.35. Found N 13.48; S 10.53%.
IR (KBr): 3250, b; 1680, b; 1610, 1500 cm^{-1}.
UV (EtOH): 243 (4.69); 293 (3.83), sh; 310 (3.73); 322 (3.65). Model compounds **19** (EtOH): 239—241 (4.59—4.67); 287—290 (3.67—3.76); 311—316 (3.64—3.72); 324—326 (3.56—3.65) [14].
NMR ($CDCl_3$), 25 °C: δ 1.62, s, 1H, exchangeable, OH; 2.59, s, 3H, *C*–Me; 3.72, d, and 4.24, d, J = 15.5 Hz, 1H, each, CH_2 of the tricyclic form; 3.97, s, 6H, $(MeO)_2$; 7.04, s, 1H, H_b; 7.42, s, 1H, H_a; 11.02, s, 1H, NH. 75 °C: 1.46, s, 1H, OH; 2.58, s, 3H, *C*–Me; 3.75, d, and 4.21, d, both slightly broadened, 1H, each, CH_2; 3.97, s, 6H, $(MeO)_2$; 7.05, s, 1H, H_b; 7.47, s, 1H, H_a; 10.75, bs, 1H, NH.
NMR ($CDCl_3$—CD_3OD, 4 : 1, v/v), 25 °C: δ 2.59, s, 3H, *C*–Me; 3.66, d, and 3.90, d, J = 14.5 Hz, *total* intensity $\approx$ 1H, CH_2 of the tricyclic form;* 4,00, s, 4,02, s and 4,09, s, total intensity 6H, MeO's of the two tautomeric forms; 7.02, s, 1H, H_b; 7.44, s, and 7,47, s, total intensity 1H, H_a's of the two tautomeric forms; 10.97, bs, 0.5H, NH, partly exchanged. 75 °C: 2.55, s, 3H, *C*–Me; 3.82, bs, CH_2; 3.95, s, and 3.98, s, 6H, $(MeO)_2$; 7.04, s, 1H, H_b; 7.46, s, 1H, H_a.
MS (75 eV): *m/e* 309 ($M^{+\cdot}$, 62.6%); 262 (M—CH_2SH, 50.4%); 235 (M—$COCH_2CH$+H, 64%); 220 (M—$NHCOCH_2SH$ + H, 100%); 206 (30.1%); 205 (220—Me, 33.5%); 177 (205—CO, 12.8%); 136 (dimethoxybenzyne$^{+\cdot}$, 22.2%).
(*b*) Compound **16a** (1.0 g; 3.44 mmoles) was stirred with 1% aqueous NaOH (10 ml) at room temperature until the starting compound was, according to TLC, completely used up (about 3 hrs; a clear solution was obtained after 30 min). The solution was evaporated to dryness and the residue extracted with EtOH. The extract was boiled up with EtOAc to yield 0.12 g (9.5%) of the sodium salt of compound **18.** The mother liquor of the latter was evaporated to dryness, the residue was taken up in a mixture of MeOH and CH_2Cl_2, transferred onto a TLC plate (Kieselgel) and chromatographed twice with EtOAc to yield 0.07 g (6.8%) of compound **15d**, 0.07 g (8.6%) of compound **17a**, m.p. 217—219 °C, identical with an authentic sample (see below), and an impure product of very low R_f. The latter was chromatographed with EtOAc–EtOH (4 : 1) to yield 0.08 g (9%) of **18.**

Irradiation of compound 16a

A nitrogen-purged aqueous (150 ml) solution of compound **16a** (0.15 g; 0.52 mmole) was irradiated with a high pressure mercury immersion lamp (HPK-125) for 14 hrs through

* The CH_2 signal of the "open-chain" form is merged with the OH signal of the solvent.

Pyrex, and evaporated to dryness. The residue was taken up in CH_2Cl_2 (about 2 ml). The insoluble residue, 0.04 g, m.p. 281—283 °C (from DMF), proved identical with an authentic sample (see below) of 6,7-dimethoxy-2-methyl-4(3*H*)-quinazolinethione (**17d**). The CH_2Cl_2 soluble material was worked up by preparative TLC (20 × 20 cm; Kieselgel $PF_{254+366}$, Merck; benzene–$CHCl_3$–EtOAc, 1 : 1 : 1, and subsequently EtOAc) to yield 0.01 g of **17a** (total yield 42%) and 0.005 g (3.5%) of 3-acetamido-6,7-dimethoxy-2-methyl-4(3*H*)-quinazolinone (**17b**), m.p. 255—256 °C (from EtOH) which proved identical with an authentic sample (see below).

2-Acetamido-4,5-dimethoxybenzamide

A mixture of 4,5-dimethoxy-2-nitrobenzamide [23] (1.0 g: 4.8 mmoles), AcOH (30 ml) and Ac_2O (3 ml) was reduced in the presence of a 10% Pd-C catalyst at ordinary pressure and room temperature. The catalyst was filtered off and the filtrate evaporated to dryness. The residue was boiled up with EtOAc (20 ml) (only part of the product went into solution) to yield, after cooling, 0.78 g (69%) of the title compound, m.p. 224—227 °C.

$C_{11}H_{14}N_2O_4$ (238.2). Calcd. C 55.45; H 5.92; N 11.76; O 26.87. Found C 55.15; H 6.03; N 11.60; O 26.97%.

IR (KBr): 3450—2450, with local maxima at 3400, 3370 and 3200; 1680, 1625 cm^{-1}.

6,7-Dimethoxy-2-methyl-4(3H)-quinazolinone (17c)

The above product (0.6 g; 25 mmoles) was heated for 10 min at 240 °C under nitrogen to yield 0.52 g (93%) of the title compound, which was recrystallized from AcOH. The product sublimes around 270—280 °C without melting, and may be conveniently purified by sublimation in vacuum.

$C_{11}H_{12}N_2O_3$ (220.2). Calcd. C 59.99; H 4.90; N 12.77. Found C 60.04; H 5.30; N 14.52%.

IR (KBr): 3200—2700, b; 1670 cm^{-1}.

6,7-Dimethoxy-2-methyl-4(3H)-quinazolinethione (17d)

A mixture of compound **17c** (0.22 g; 1 mmole), P_2S_5 (0.24 g; 1.1 mmole) and dry pyridine (3 ml) was refluxed for 8 hrs and poured into water (7 ml). 10% aqueous NaOH (2 ml) was added and the mixture was acidified with AcOH to yield 0.15 g (64%) of **17d**, m.p. 281—283 °C.

$C_{11}H_{12}N_2O_2S$ (236.3). Calcd. N 11.86; S 13.57. Found N 11.75; S 13.28%.

UV (EtOH): 226 (4.66), sh; 231 (4.82); 255 (4.11); 274 (4.13); 351 (3.99), sh; 367 (4.21); 383 (4.18). Model compound **20a**: 223 (4.47), sh; 228 (4.49); 260 (4.12), sh; 271 (4.18); 354 (4.04), sh; 370 (4.22); 383 (4.15) [20].

MS (130 °C): *m/e* 236 ($M^{+\cdot}$, 100%); 221 (M—Me, 12%); 203 (M—SH, 16%); 118 (8%); 57 (7%).

Methyl 2-acetamido-4,5-dimethoxybenzoate

A suspension of methyl 4,5-dimethoxy-2-nitrobenzoate [24] (1.0 g; 4.1 mmoles) in AcOH (30 ml) was reduced in the presence of a 10% Pd-C catalyst at ordinary pressure and room temperature. The catalyst was removed, and the red solution was evaporated to dryness. The residue was refluxed for 1 hr with Ac_2O (1 ml) in CH_2Cl_2 (4 ml). The CH_2Cl_2 was distilled off and the solution was poured into water to yield 0.82 g (79%) of the title compound, m.p. 159—160 °C (from EtOH).

$C_{12}H_{12}NO_5$ (253.2). Calc. N 5.53, Found: N 5.42%

IR (KBr): 3305 (w), 3270, 1690, 1680 cm^{-1}.

3-Amino-6,7-dimethoxy-2-methyl-4(3H)-quinazolinone (17a)

The above ester (0.2 g; 0.8 mmole) was refluxed for 1.5 hr with a mixture of pyridin (1 ml) and 98% hydrazine hydrate (0.5 ml) to yield 0.16 g (85%) of compound **17a**, m.p. 219—220 °C (from AcOH).

$C_{11}H_{13}N_3O_3$ (235.2). Calc. C 56.40; H 5.57; N 17.86. Found C 56.62; H 5.72; N 17.70%.

IR (KBr): 3270, 3180, 1665, 1625 cm^{-1}.

MS (130 °C): *m/e* 235 ($M^{+\cdot}$, 100%); 220 (M^{*}—Me, 29%); 206 (M^{*}—N_2H, 51%); 191 (220^{*}—N_2H and 206^{*}—Me, 10%); 190 (9%); 162 (191^{*}—HCO, 12%); 136 (dimethoxybenzyne$^{+\cdot}$, 12%).

3-Acetamido-6,7-dimethoxy-2-methyl-4(3H)-quinazolinone (17b)

Compound **17a** (0.4 g; 1.7 mmole) was refluxed with a mixture of pyridine (5 ml) and Ac_2O (0.8 ml). The dry residue of the reaction mixture was triturated with water to yield 0.52 g (96%) of the 3-diacetylamino compound, m.p. 223—225 °C (from AcOH).

$C_{15}H_{17}N_3O_5$ (319.3). Calcd. C 56.40; H 5.37; N 13.16; O 25.05. Found C 56.25; H 5.27; N 13.35; O 25.07%.

IR (KBr): 1735, 1690, 1605, 1500 cm^{-1}.

Partial deacetylation of this product (0.2 g) was effected by refluxing with EtOH (2 ml) containing a trace of NaOEt. The solvent was distilled off, the residue was dissolved in water, and CO_2 was introduced to precipitate 0.14 g (79%) of the title compound, m.p. 255—256 °C (from EtOH).

$C_{13}H_{15}N_3O_4$ (277.3). Calcd. C 56.32; H 5.40; N 15.15. Found C 56.05; H 5.90; N 15.32%.

IR (KBr): 3200—2700, b; 1670 cm^{-1}, b.

UV (EtOH): 241 (4.80); 283 (3.94); 310 (3.89); 323 (3.83). For the spectra of the model compounds **19**, see above.

MS (140 °C): *m/e* 277 ($M^{+\cdot}$, 9%); 235 (M—Ac+H, 15%); 220 (M—AcNH + H, 100%); 205 (220—Me, 50%); 177 (205—CO, 24%); 175 (18%); 136 (dimethoxybenzyne$^{+\cdot}$, 25%); 134 (29%).

*

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ISOXAZOLES, I

THE CRYSTAL AND MOLECULAR STRUCTURE AND SOME REACTIONS OF A NOVEL TYPE CONDENSATION PRODUCT OF ETHYL 2-ETHOXY-2-IMINOPROPIONATE AND HYDROXYLAMINE

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A 2 : 1 condensation product of structure **2** is formed in the reaction of ethyl 2-ethoxy-2-iminopropionate in the presence of sodium hydroxide. The crystal and molecular structure of the product was solved by the direct method and refined by least-squares calculations to R 0.057 for 1724 observed reflexions collected on a Syntex $P2_1$ four-circle automatic diffractometer using a graphite monochromator. The dimers of the molecules form infinite sheets maintained by hydrogen bonding.

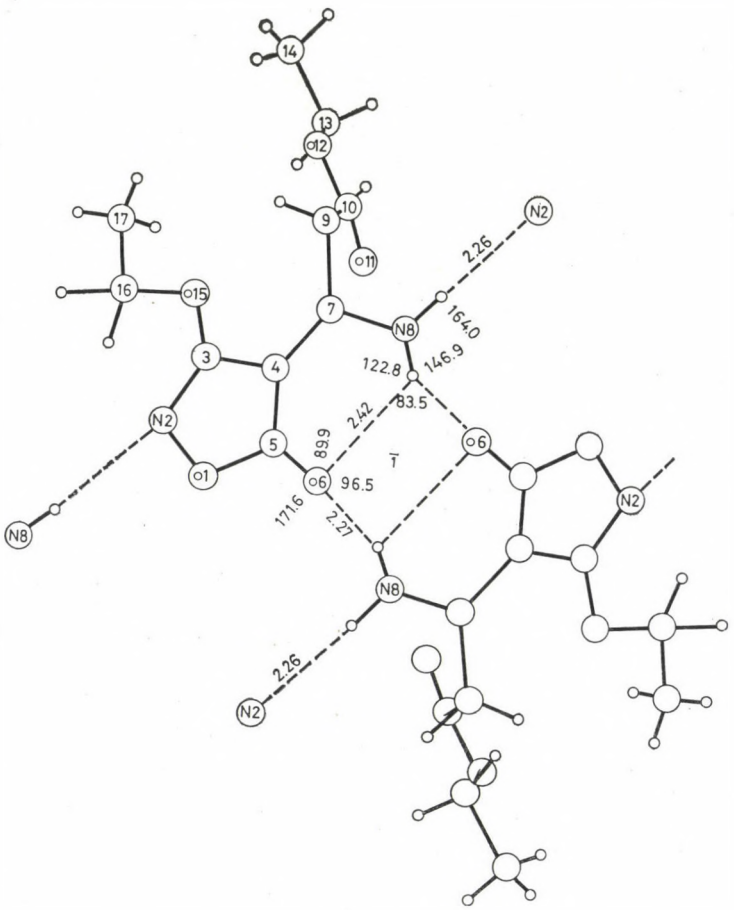
Condensation of ethyl 2-ethoxy-2-iminiopropionate chloride (**1**) [1] with hydroxylamine in the presence of alkali furnished, instead of the expected 1 : 1 condensation product, 3-ethoxy-5-isoxazolol (or tautomeric forms), a 2 : 1 condensation product, $C_{10}H_{14}N_2O_5$. The structure of this compound which, according to its IR and NMR spectra, had one NH_2, one CH_2, two C=O and two OEt groups, was revealed by X-ray structure determination (see below) to be **2**. The tautomeric structure, in the crystalline state, of this potentially tautomeric compound agrees with the tautomeric structures of related compounds both in the crystalline state and in solutions, as established earlier by IR and NMR spectroscopic methods [2].

As a result of its various functional groups and active sites, the reactions of compound **2** are manifold.

Treatment of **2** with dry hydrogen chloride in boiling ethanol caused selective hydrolysis of the ethoxy group attached to the ring. Treatment of **2** with a hot mixture of hydrochloric and acetic acids, on the other hand, resulted in hydrolysis of both the ethoxy and the ester groups, and treatment of the resulting acid with copper powder effected smooth decarboxylation to **3**. Direct deethoxycarbonylation of **2** to **4** was brought about by treatment with sodium chloride in aqueous DMSO (*cf.* [3]). Attack of electrophilic reagents, such as nitrous acid and bromine, took place at the methylene group and furnished compounds **5** and **6**, respectively. The latter was obtained also on

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NBS treatment of compound **2**. When treated with boiling acetic anhydride, compound **5** was acetylated both at the hydroxyimino and the amino groups to yield compound **7**. Attack of the nucleophilic hydrazine took place at the α-position of the side chain of compound **2** furnishing, after acidification, the pyrazolylisoxazole derivative **8** (or tautomeric forms).



Crystal and molecular structure determination of 2

Crystal data. From single-crystal diffractometry, using Mo-K_α radiation ($\lambda = 0.7069$ Å), $a = 13.317(3)$, $b = 6.988(2)$, $c = 25.797(4)$ Å, $\beta = 102.42(2)°$, space group $C2/c$ (from the structure determination), $D_X = 1.37$ g.cm^{-3} for $Z = 8$.

Intensity data, structure determination and refinement

Intensities of 2227 independent reflexions were collected on a Syntex $P2_1$ automatic four-circle single-crystal diffractometer from a graphite monochromator. The structure was solved by an XTL version of program MULTAN [4] and Fourier techniques. The full-matrix refinement of the non-hydrogen atoms with a weighting scheme of $w = 1/\delta\,(F)^2$ led to a final R value of 0.057 for 1724 observed $[F_0 \geqslant 3.9\sigma\,(F_0)]$ and 0.073 for all reflexions. Hydrogen

Table I

Atomic coordinates ($\times 10^4$) and anisotropic temperature factors for the non-hydrogen atoms Temperature factors are of the form exp $(1/4\sum_{ij} a_i^* a_j^* h_i h_j B_{ij})$ with B_{ij} in Å²

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
O(1)	4942(2)	2107(3)	415(1)	3.2(1)	2.6(1)	4.6(1)	−0.9(1)	0.9(1)	−0.5(1)
N(2)	4398(2)	3410(4)	695(1)	2.8(1)	3.2(1)	4.1(1)	−0.8(1)	1.0(1)	−0.3(1)
C(3)	4998(2)	4893(5)	804(1)	2.8(1)	3.1(1)	2.9(1)	−0.4(1)	0.6(1)	0.0(1)
C(4)	5934(2)	4740(4)	619(1)	2.4(1)	2.5(1)	2.8(1)	−0.5(1)	0.5(1)	0.1(1)
C(5)	5872(2)	2901(4)	376(1)	2.7(1)	2.6(1)	3.3(1)	−0.6(1)	0.6(1)	0.2(1)
O(6)	6451(2)	2049(3)	152(1)	4.2(1)	3.0(1)	4.9(1)	−0.5(1)	1.8(1)	−0.8(1)
C(7)	6715(2)	6059(4)	629(1)	2.9(1)	2.7(1)	2.3(1)	−0.7(1)	0.4(1)	−0.1(1)
N(8)	7536(2)	5639(4)	451(1)	3.0(1)	3.2(1)	4.3(1)	−1.0(1)	1.7(1)	−0.5(1)
C(9)	6624(2)	8067(4)	815(1)	3.6(1)	2.6(1)	3.0(1)	−1.1(1)	0.8(1)	−0.2(1)
O(10)	6781(2)	8297(5)	1409(1)	3.4(1)	3.0(1)	3.1(1)	−0.9(1)	0.4(1)	−0.3(1)
O(11)	7138(2)	7134(4)	1733(1)	7.1(2)	4.2(1)	3.3(1)	1.0(1)	−0.3(1)	0.2(1)
O(12)	6480(2)	10044(3)	1515(1)	5.4(1)	3.4(1)	3.0(1)	0.1(1)	0.8(1)	−0.5(1)
C(13)	6579(3)	10540(6)	2071(1)	5.9(2)	5.1(2)	2.9(1)	−0.4(2)	0.9(1)	−0.9(1)
C(14)	6049(3)	12414(7)	2084(2)	5.9(2)	5.9(2)	5.0(2)	0.2(2)	1.5(2)	−2.0(2)
O(15)	4791(2)	6413(3)	1073(1)	3.0(1)	3.7(1)	4.7(1)	−0.8(1)	1.5(1)	−1.1(1)
C(16)	3825(2)	6419(6)	1247(2)	2.7(1)	5.5(2)	5.1(2)	−0.1(1)	1.5(1)	−0.8(2)
C(17)	3871(3)	8146(8)	1607(2)	4.9(2)	7.8(3)	7.8(3)	−0.3(2)	3.2(2)	−3.8(2)

Table II

Positional parameters and isotropic temperature factors (Å²) and C–H distances (Å) for the hydrogen atoms

	x	y	z	B	C–H		x	y	z	B	C–H
H(8a)	804	643	45	2.9	0.87*	H(14b)	528	1227	192	4.8	1.03
H(8b)	768	464	36	2.9	0.77*	H(14c)	634	1341	193	4.8	0.93
H(9a)	593	855	65	2.9	0.99	H(16a)	374	524	146	3.8	1.01
H(9b)	712	886	73	2.9	0.93	H(16b)	322	645	95	3.8	0.99
H(13a)	732	1066	226	4.0	1.01	H(17a)	437	792	188	5.0	0.87
H(13b)	627	957	227	4.0	0.99	H(17b)	333	833	167	5.0	0.78
H(14a)	608	1287	246	4.8	1.01	H(17c)	417	917	146	5.0	0.94

* N—H

atoms of the two methyl groups and those attached to the N(8) atom were located in a difference map. Other hydrogens were geometrically generated. No hydrogen parameters were refined. All hydrogen atoms were involved in the structure factor calculations, however. Final atomic parameters are shown in Tables I and II.

All calculations have been performed on a NOVA minicomputer with the XTL structure determination program package supplied by Syntex.

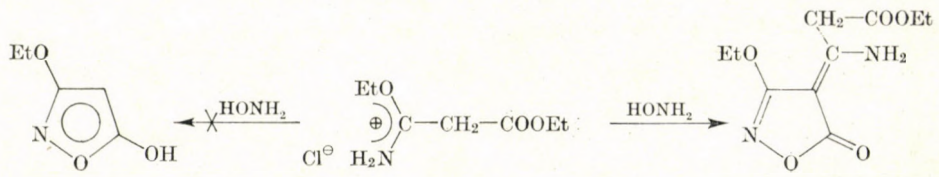
Discussion of the molecular structure

The atomic numbering used, together with the hydrogen bond network are shown in Fig. 1. The bond lengths and angles with their e.s.d.'s are given in Table III. The non-hydrogen atoms of the molecule except the C(9), C(10),

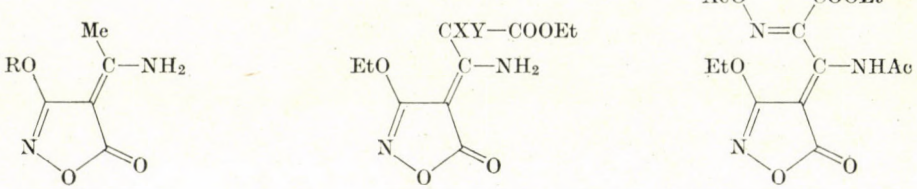
Table III

Bond lengths (Å) and angles (°) with their e.s.d.'s in parentheses

		mean [5]			mean [5]
O(1)—N(2)	1.451(3)	1.422	C(5)—O(1)—N(2)	109.6(2)	108.1
N(2)—C(3)	1.302(3)	1.324	O(1)—N(2)—C(3)	104.9(2)	105.7
C(3)—C(4)	1.431(4)	1.425	N(2)—C(3)—C(4)	114.0(3)	111.0
C(4)—C(5)	1.424(4)	1.352	C(3)—C(4)—C(5)	104.0(3)	104.8
C(5)—O(1)	1.380(4)	1.352	C(4)—C(5)—O(1)	107.4(3)	110.4
C(3)—O(15)	1.330(4)		N(2)—C(3)—O(15)	124.1(3)	
O(15)—C(16)	1.450(4)		C(4)—C(3)—O(15)	121.9(3)	
C(16)—C(17)	1.516(7)		C(3)—O(15)—C(16)	117.5(3)	
C(4)—C(7)	1.386(4)		O(15)—C(16)—C(17)	105.7(3)	
C(7)—N(8)	1.308(4)		C(3)—C(4)—C(7)	130.4(3)	
C(7)—C(9)	1.496(4)		C(5)—C(4)—C(7)	125.5(3)	
C(9)—C(10)	1.509(4)		C(4)—C(7)—N(8)	121.7(3)	
C(10)—O(11)	1.189(4)		C(4)—C(7)—C(9)	121.2(3)	
C(10)—O(12)	1.332(4)		N(8)—C(7)—C(9)	117.1(3)	
O(12)—C(13)	1.454(4)		C(7)—C(9)—C(10)	115.0(3)	
C(13)—C(14)	1.491(6)		C(9)—C(10)—O(11)	126.0(3)	
C(5)—O(6)	1.215(4)		C(9)—C(10)—O(12)	108.9(3)	
			O(11)—C(10)—O(12)	125.0(3)	
			C(10)—O(12)—C(13)	117.0(3)	
			O(12)—C(13)—C(14)	106.7(3)	
			O(1)—C(5)—O(6)	120.6(3)	
			C(4)—C(5)—O(6)	132.0(3)	



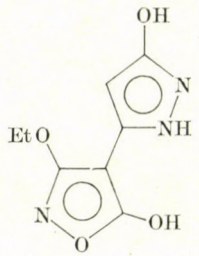
1 2



3: R = H
4: R = Et

5: X + Y = HO—N =
6: X = Br, Y = H

7



8*

*Tautomeric structure not known

Fig. 1. The projection of the molecular dimer perpendicular to the c^* axis with atomic numbering and hydrogen bonds. Geometry of the hydrogen bonds are also given. The bare numbers are for carbon atoms, while the smaller circles represent H atoms

O(11), O(12), C(13), C(14) and C(17) atoms form a planar arrangement as shown in Table IV. The conformations of the 3-ethoxy- and the 4-β-aminoethylpropionate moieties are described by the torsion angles (Table V). The nearly planar carbethoxy group is twisted from the best-plane of the five-membered ring around the C(7)–C(9) bond [*cf.* C(4)–C(7)—C(9)—C(10) = = 75.9°]. The bond lengths and angles in the five-membered ring show only slight differences from the average values (*cf.* Table III) calculated for seven isoxazole rings discussed by SIMON *et al.* [5] in connection with the structure analysis of 5-diacetylamino-3,4-diphenylisoxazole. Only the C(4)—C(5) bond

is considerably longer (1.424 Å) than the mean value of 1.352 Å; this is presumably due to the vicinity of the C(4) – C(7) and C(5) —O(6) multiple bonds. The exocyclic bond lengths are comparable with the corresponding data in the literature. As can be seen from Fig. 1, the molecular dimers with a centre of symmetry are maintained by the hydrogen bonds N(8)—H . . . O(6). These dimers are linked together by weak hydrogen bonds N(8) —H . . . N(2) and, thus, form infinite sheets.

Table IV

Least-squares plane of the isoxazole ring and deviation of atoms from this plane

Plane equation: 0.4424X— 0.4152Y+0.7949Z = 1.9636 where X,Y and Z are in Å and related to orthogonal axes: a,* b, c.

Isoxazole ring	d (Å)	Other atoms	d (Å)
O(1)	—0.006	C(9)	—0.33
N(2)	0.001	C(10)	0.88
C(3)	0.003		
C(4)	—0.006	O(11)	2.00
C(5)	0.007	O(12)	0.48
		C(13)	1.51
Atoms within 0.1 Å	d (Å)	C(14)	0.81
O(6)	—0.003	C(17)	0.31
C(7)	—0.097		
N(8)	—0.055		
O(15)	0.042		
C(16)	0.061		

Table V

Torsion angles

(a) Torsion angles within the isoxazole ring

O(1)— N(2)— C(3)— C(4)	0.0°
N(2)— C(3)— C(4)— C(5)	—0.9
C(3)— C(4)— C(5)— O(1)	1.3
C(4)— C(5)— O(1)— N(2)	—1.2
C(5)— O(1)— N(2)— C(3)	0.0

(b) Torsion angles related to the isoxazole ring

O(1)— N(2)— C(3)— O(15)	—178.3°
N(2)— C(3)— C(4)— C(7)	175.1
N(2)— O(1)— C(5)— O(6)	180.0
O(15)— C(3)— C(4)— C(5)	177.6
O(15)— C(3)— C(4)— C(7)	—6.3
C(3)— C(4)— C(5)— O(6)	180.0
C(7)— C(4)— C(5)— O(1)	—175.1
C(7)— C(4)— C(5)— O(6)	3.0

(c) Torsion angles outside the isoxazole ring

C(3)—C(4)—C(7)—N(8)	178.2°
C(3)—C(4)—C(7)—C(9)	—5.5
C(5)—C(4)—C(7)—N(8)	—6.5
C(5)—C(4)—C(7)—C()9)	169.8
C(4)—C(7)—C(9)—C(10)	75.9
N(8)—C(7)—C(9)—C(10)	—107.7
C(7)—C(9)—C(10)—O(11)	14.1
C(7)—C(9)—C(10)—O(12)	—167.6
C(9)—C(10)—O(12)—C(13)	180.0
O(11)—C(10)—O(12)—C(13)	—1.3
C(10)—O(12)—C(13)—C(14)	—171.4
C(4)—C(3)—O(15)—C(16)	180.0
N(2)—C(3)—O(15)—C(16)	—1.0
C(3)—O(15)—C(16)—C(4)	171.7

Experimental

Condensation of ethyl 2-ethoxy-2-iminopropionate chloride (1) with hydroxylamine

An aqueous (180 ml) solution of NaOH (16.5 g; 412 mmoles) was added under continuous stirring to the suspension of compound **1** [1] (60 g; 305 mmoles) in ether (400 ml), placed into an ice-salt bath, at such a rate that the temperature never exceeded 0 °C. The ethereal layer was separated and added to the aqueous (40 ml) solution of hydroxylammonium chloride (11.5 g; 165 mmoles). The mixture was stirred for 10 min at 0 °C and then for 1 hr at room temperature. The layers were separated and the aqueous layer was extracted with two portions (80 ml each) of ether. The combined ethereal solutions were dried ($MgSO_4$), the solvent was evaporated and the residue kept for several days in an exsiccator whereby most of it turned crystalline. The crude crystalline product was filtered off, washed with ether and recrystallized from ethanol to yield 27.7 g (58%) of **ethyl 3-amino-3-(3-ethoxy-5-oxo-2-isoxazolin-4-ylidene)propionate (2)**, m.p. 120—122 °C (EtOH).

$C_{10}H_{14}N_2O_5$ (242.2). Calcd. C 49.58; H 5.81; N 11.57. Found C 50.01; H 5.94; N 11.84%.

IR (KBr): 3350, 3210, 3000, 1745, 1725, 1665, 1590 cm^{-1}.

NMR ($CDCl_3$): δ 9.2 and 8.1, both bs, 1H each, NH_2; 4.35 and 4.26, both qu, 2H, each, +1.43 and 1.32, both tr, 3H, each, $J = 7$ Hz for both, 2 EtO groups; 3.84, s, 2H, CH_2. NMR ($CDCl_3$ + TFA): δ 9.4 and 8.76, both bs, 1H each, NH_2; $\sim$ 4.28, *two* qu, 4H, + 1.46 and 1.32, both tr, 3H, each, $J \approx 7$ Hz for both, 2 EtO groups: 3.92, s, 2H, CH_2.

Ethyl 3-amino-3-(3-hydroxy-5-oxo-2-isoxazolin-4-ylidene)-propionate

Dry HCl gas was introduced for 1 hr into the refluxing solution of compound **2** (2.42 g; 10 mmoles) in anhydrous EtOH (25 ml). The mixture was evaporated to dryness in vacuum. When triturated with 5% aqueous $NaHCO_3$ solution, the oily residue turned crystalline. Recrystallization of this product gave 1.2 g (56%) of the title compound, m.p. 150—152 °C.

$C_8H_{10}N_2O_5$ (214.18). Calcd. C 44.86; H 4.71; N 13.39. Found C 45.10; H 4.70; N 13.50%.

IR (KBr): 3350, 3200, 1730, 1710, 1670, 1635, 1560 cm^{-1}.

NMR (DMSO-d_6): δ 9.55, bs, 2H and 9.05, bs, 1H, NH_2 + OH; 4.10, qu, 2H, + 1.15, tr, 3H, $J = 7.2$ Hz, COOEt; 3.83, s, 2H, CH_2.

3-Amino-3-(3-hydroxy-5-oxo-2-isoxazolin-4-ylidene)-propionic acid

A mixture of compound **2** (2.42 g; 10 mmoles), AcOH (30 ml) and conc. hydrochloric acid (15 ml), was stirred for 3 hrs at 75—80 °C and evaporated to dryness in vacuum. Water (30 ml) was added to the dry residue and the resulting mixture was again evaporated to dryness in vacuum. The residue was recrystallized from water to yield 1.3 g (70%) of the title compound.

$C_6H_6N_2O_5$ (186.13). Calcd. C 38.71; H 3.25; N 15.05. Found C 38.55; H 3.22; N 14. 79%.

4-(1-Aminoethylidene)-3-hydroxy-2-isoxazolin-5-one (3)

The above compound (1.86 g; 10 mmoles) was stirred with pyridine (15 ml) in the presence of a catalytic amount of copper powder at room temperature until the evolution of CO_2 ceased. The mixture was evaporated to dryness, and the residue was triturated with ether to yield 1.0 g (54%) of compound **3**, m.p. 152—153 °C (d.; from *i*-PrOH).

$C_5H_6N_2O_3$ (142.12). Calcd. C 42.35; H 4.26; N 19.72. Found C 42.12; H 4.08; N 20.01%.

IR (KBr): 3310, 3110, 1690, 1590 cm^{-1}.

4-(1-Aminoethylidene)-3-ethoxy-2-isoxazolin-5-one (4)

A mixture of compound **2** (2.42 g; 10 mmoles), NaCl (0.7 g), water (0.4 ml) and DMSO (20 ml) was stirred at 150 °C. When the evolution of CO_2 had ceased, the mixture was poured onto ice, and the product was extracted with two portions of ether (25 ml each). The combined ethereal solutions were washed with water (two portions, 10 ml each), dried ($MgSO_4$) and evaporated to dryness. The residue was recrystallized from water to yield 0.6 g (36%) of **4**, m.p. 158—160 °C.

$C_7H_{10}N_2O_3$ (170.17). Calcd. C 49.40; H 5.92; N 16. 47. Found C 49.04; H 5.60; N 16.50%.

IR (KBr): 3250, 3050, 1670, 1570 cm^{-1}.

NMR (DMSO-d_6): δ 9.35 and 9.05, both bs, NH_2; 4.20, qu, 2H + 1.30, t, 3H, $J = 7.3$ Hz, EtO; 2.26, s, 3H *C*–Me.

Ethyl 3-amino-3-(3-ethoxy-5-oxo-2-isoxazolin-4-ylidene)-2-hydroxyimino propionate (5)

An aqueous (5 ml) solution of $NaNO_2$ (0.84 g; 10 mmoles) was added by drops under stirring and ice-cooling to a mixture of compound **2** (2.42; 10 mmoles), acetic acid (30 ml) and water (5 ml) at such a rate that the temperature did not exceed 10 °C. The mixture was stirred for another 30 min at this and for 1 hr at room temperature. The residue obtained after evaporation to dryness was recrystallized from water to yield 2.5 g (92.5%) of compound **5**, m.p. 212 °C (d.).

$C_{10}H_{13}N_3O_6$ (271.22). Calcd. C 44.28; H 4.83; N 15.59. Found C 44.10; H 4.92; N 15.79%.

IR (KBr): 3100, b, with sh's at 3300 and 2850; 1720, 1690, 1640, 1575 cm^{-1}.

NMR (DMSO-d_6): δ 13.2 and 13.05, both s, total intensity 1H, oxime-OH, *E* and *Z* isomer; 9.4 and 9.0, both, bs, NH_2; 4.25 and 4.05, both qu, 2H, each, + 1.25 and 1.20, both tr, 3H, each, $J = 7$ Hz for both, two EtO groups.

Acetylation

A mixture of the above product (1.35 g; 5 mmoles) and acetic anhydride (25 ml) was refluxed for 2.5 hrs and evaporated to dryness. The residue was triturated with water and extracted with three portions of $CHCl_3$ (15 ml each). The combined $CHCl_3$ solutions were washed with water (two portions, 5 ml each), dried ($MgSO_4$) and evaporated to dryness. The oily residue was triturated with ether to yield 1.0 g (56%) of the *O*,*N*-diacetyl derivative **7**, m.p. 127 °C (from EtOH).

$C_{14}H_{17}N_3O_8$ (355.30). Calcd. C 47.32; H 4.72; N 11.83. Found C 47.20; H 4.77; N 11.68%.

Ethyl 3-amino-2-bromo-3-(3-ethoxy-5-oxo-2-isoxazolin-4-ylidene)propionate (6)

(*a*) A mixture of Br_2 (0.486 ml) and $CHCl_3$ (5 ml) was added by drops under continuous stirring at ambient temperature to a solution of compound **2** (2.42 g; 10 mmoles) in $CHCl_3$ (50 ml). The mixture was washed with two portions of 5% aqueous $NaHCO_3$ solution (25 ml each) and twice with water (20 ml, each) and dried ($MgSO_4$). The oily residue, obtained after evaporation of the solvent, furnished on scratching 2.4 g (75%) of a yellow powder, m.p. 114—116 °C (from *i*-PrOH).

$C_{10}H_{13}BrN_2O_5$ (321.14). Calcd. C 37.40; H 4.08; Br 24.88; N 8.72. Found C 37.63; H 4.06; Br 24.49; N 8.99%.

IR (KBr): 3350, 3200, 2900, 1740, 1720, 1610, 1570 cm^{-1}.

NMR ($CDCl_3$): δ 5.73, s, 1H, CH; 4.37 and 4.32, both qu, 2H, each, + 1.46 and 1.35, both tr, 3H, each, $J = 7$Hz for both, two EtO groups.

(*b*) A mixture of compound **2** (2.42 g; 10 mmoles), dry CCl_4 (50 ml), NBS (2.4 g; 13.5 mmoles) and dibenzoyl peroxide (0.2 g) was refluxed for 1.5 hr and allowed to cool. The succinimide was filtered off, the filtrate evaporated to dryness and the resulting oily product was worked up as described above, to yield 1.92 (60%) of a product which, according to its m.p. (114—116 °C, from *i*-PrOH) and IR spectrum proved identical with the product described under (*a*).

3-Ethoxy-4-(5-hydroxy-3-pyrazolyl)-5-isoxazolol (8)

(or tautomeric forms)

A mixture of compound **2** (2.42 g; 10 mmoles), 100% hydrazine hydrate (1.5 ml) and EtOH (10 ml) was refluxed for 15 min to yield, after being allowed to cool, 2.4 g (99%) of the hydrazine salt of the title compound, m.p. 195—196 °C (d.).

The latter (1.2 g; 5 mmoles) was dissolved in water (6 ml) and acidified with acetic acid to yield 0.8 g (73%) of the title compound, m.p. 162—163 °C (d.; after thorough drying over P_2O_5 in vacuum).

$C_8H_9N_3O_4$ (211.18). Calcd. C 45.50; H 4.29; N 19.90. Found C 45.31; H 4.01; N 19.68%.

NMR(DMSO-d_6) (of the non-anhydrous product): δ 5.65, s, 1H, pyrazole *C*-H; 4.15, qu, 2H + 1.28, tr, 3H, $J = 7$ Hz, EtO.

IR spectra were obtained on a MOM (Hungarian Optical Works) spectrometer, type Spectromom 2000; NMR spectra were obtained at 60 MHz on a Perkin-Elmer spectrometer, type R 12.

*

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РЕЗЮМЕ

Количественное определение следов элементов в силикатных матрицах спектрографическими методами с непрерывной подачей растворов, III

Сравнение аналитической эффективности различных экспериментальных методов

А. ДОМБИ, Э. ГЕГУШ и К. ФАРКАШ-УЙХИДИ

Описанные спектроаналитические методы, основанные на постоянном введении растворов в источник света, пригодны для количественного определения низкоконцентрационных компонентов металлического характера в материалах на силикатной основе.

В ходе исследований были сделаны следующие заключения:

— чувствительность методов, использующих искровое возбуждение, может быть повышена применением атмосферы аргона;

— точность испытанных методов удовлетворяет требованиям, предъявляемым в анализе следов элементов;

— метод стабилизированной дуги низкоамперного прямого тока обеспечивает большую точность по сравнению с методами искрового возбуждения, но более чувствителен к изменениям состава матрицы, вследствие чего приводит к меньшей аналитической надежности по сравнению с методами распыления и вращающегося диска.

Использование программы расчета на ЭВМ ускоряет процесс обработки спектров и результаты получаются быстрее и аккуратнее.

Количественное определение следов элементов в силикатных матрицах спектрографическими методами с непрерывной подачей растворов, I

Исследование некоторых параметров, влияющих на характер изучающей плазмы

А. ДОМБИ, К. ФАРКАШ-УЙХИДИ и Э. ГЕГУШ

Для количественного определения некоторых низкоконцентрационных компонентов материалов с силикатной основой были выбраны три спектрографических метода, а также установлены оптимальные условия их использования. Было изучено влияние окружающей атмосферы, а также интерелементный эффект (влияние «третьих элементов»), являющийся наиболее значительным фактором при анализе растворов.

Аналитическая эффективность методов может быть повышена применением атмосферы благородного газа (Ar). Это влияние наиболее сильно выражено в методе вращающегося диска. Метод распылен я с применением трубчатого электрода и метод вращающегося диска являются менее чувствительными к изменению содержания щелочного металла в растворе пробы, вводимой в разряд, чем техника стабилизированной дуги постоянного тока.

Количественное определение следов элементов в силикатных матрицах спектрографическими методами с непрерывной подачей растворов, II

Программа расчета на ЭВМ для обработки результатов анализа и сравнения методов

А. ДОМБИ и Э. ГЕГУШ

Была разработана программа расчета на ЭВМ для статистической оценки количественного спектрографического анализа.

Помимо осуществления процесса оценки полученных данных, в программу также входит определение

— стандартных отклонений от результатов опыта,
— параметров аналитических кривых (градупровочных прямых) и их стандартных отклонений,
— относительного суммарного стандартного отклонения концентрации,
— совпадения данных с аналитическими кривыми (градуировочными прямыми).

Программа для расчета на ЭВМ применима также и для оценки данных, полученных другими методами.

Термический анализ полипропиленового волокна

М. ЛЕНДЬЕЛ, К. МАТЭ и Г. БОДОР

В ходе термообработки полипропиленового волокна наблюдается процесс пере кристаллизации. Изотермическая термообработка была произведена на приборе ДСК и процесс перекристаллизации был детектирован в форме экзотермического пика. Измерения проводились в области плавления и ниже ее.

Двойной пик плавления, наблюдаемый для полипропиленового волокна, и новый эндотермический пик, обнаруживаемый на кривых ДСК для полимеров, подвергнутых изотермической термообработке, интерпретируется на основе процесса перекристаллизации. Кривые ДСК для полимеров с метастабильной структурой всегда следует рассматривать как результат параллельно протекающих экзотермических и эндотермических реакций.

Электронографическое исследование строения молекулы дифенилсульфида

Б. РОЖОНДАИ, ДЖ. Х. МУР, Д. С. ГРЕГОРИ и И. ХАРГИТТАИ

Методом газовой электронографии определены структурные параметры дифенилсульфида. Длины связей (r_a) S—C 1,771 ± 0,005 Å, C—C 1,399 ± 0,003 Å, C—H 1,089 ± ± 0,008 Å и угол C—S—C 103.7 ± 1,3°. По крайней мере две формы относительно вращения около S—C связей находятся в согласии с экспериментальными данными.

Электронографическое исследование строения молекул винилсульфонилхлорида

Й. БРУНВОЛЛ и И. ХАРГИТТАИ

Электронографическим методом было исследовано строение молекул винилсульфонилхлорида в парообразной фазе. Три конформера относительно вращения вокруг связи S—C могут обковяем угщсуствова сосуществовать. Эти формы характеризуются углами вращения (C=C—S—Cl) 60, 80 и 160–180°, а угол 0° соответствует форме *анти*. Были определены следующие длины связей (r_a) и валентные углы:

C=C	1.357±0.018	C—C—S	121.3±1.7
S—C	1.744±0.005	C—S—Cl	100.2±0.6
S=O	1.420±0.006	C—S=O	109.8±0.4
S—Cl	2.035±0.005	O=S=O	122.0±1.0
		Cl—S=O	106.4±0.6

Конфигурация связей атома серы, в целом, находится в согласии с молекулярными геометриями в других простых сульфонах. Связь C=C оказывается одной из длиннейших среди производных этилена, а связь S—C несколько короче, чем в других хлористых сульфонилах.

Алкалоиды со скелетом индоло[2,3-с]хиназолино[3,2-а]пиридина, VI

Получение цис- и транс-гексагидрорутекарпина

К. ХОРВАТ-ДОРА, Г. ТОТ, И. ТАМАШ и О. КЛАУДЕР

Подобно синтезу рутекарпина, 1,2,3,4-тетрагидро-1-оксо-β-карболин (3) конденсировали с цис- и транс-2-аминоциклогексанкарбоновой кислотой. В качестве конечного продукта было получено два стереоизомера: цис- (4) и транс-гексагидрорутекарпин (5). Строение соединений (4) и (5) было доказано на основе УФ, ИК, ЯМР и МС спектров.

Были изолированы также и промежуточные продукты конденсации, цис- (6) и транс-гексагидрорутекарпкислота (7), которые дальнейший циклизацией был превращены в продукты (4) и (5).

Образование производных 1,3-бензтиазола из 2,2-диаминодифенилдисульфида

Роданирование 2,2'-диаминодифенилдисульфида и реакция с N-арилизотиоцианатом

Э. ВИНКЛЕР и Ф. КЛИВЕНИ

При взаимодействии 2,2'-диаминодифенилдисульфида с тиоциановой кислотой одновременно образуются производные 2-аминобензтиазола и 2-бензтиазолинтиона. С арилизотиоцианатами образуется лишь 2-аминопроизводное. Был исследован ход реакции, а также отношение одновременно образующихся производных. Строение производных бензтиазола определяли, исходя из их ИК спектров.

Реакции моно- и диарилиденциклоалканонов с тиокарбамидом и роданидом аммония, II

Синтез солей 4-арил-2-имино-1,2,5,6,7,8-гексагидро-4Н-3,1-бензотиазина и 4-арил-2-имино-1,2,4,5,6,7-гексагидроциклопента [d] (1,3)-тиазина

Т. ЛОРАНД и Д. САБО

2-Арилиденциклогексаноны в кислых средах с тиокарбамидом дают соли 4-арил-2-имино-1,2,5,6,7,8-гексагидро-4Н-3,1-бензотиазина (*I*а—с), а 2-арилиденциклопентаноны дают соли 4-арил-2-имино-1,2,4,5,6,7-гексагидроциклопента[d][1,3] тиазина. 2,6-Диарилиденциклогексаноны и 2,5-дибензилиденциклопентанон подобным образом дают соответствующие тиазиновые производные (*III*а—d и IV, соответственно).

Производные аминофталазинона, II

Синтез 4-(гидроксиалкиламино)-1(2Н)-фталазинонов из гидроксиалкилфталимидов

К. КЁРМЕНДИ

4-(Гидроксиалкиламино)-1(2Н)-фталазиноны (6) с хорошим выходом могут быть получены из 1,2- и 1,3-аминоспиртов, замещенных различным образом, через циклический иминоэфир *5* по схеме реакций 1 → 6. Ранее разработанный метод (для этаноламина и 3-амино-1-пропанола) [2,3], согласно последним исследованиям может быть обобщен и с помощью целесообразных модификаций в большой степени может быть уточнен, так что даже в случае аминоспиртов, стерически экранированных на конечном азоте (напр., 2-амино-2-метил-1-пропанол), получается превосходный выход (около 90%). 3-Гидроксипропилфтальимид имеет аномальную реакцию тозилирования, аименно вместо тозильного эфира (3) образуется 3-хлорпропилфтальимид (4). Циклический промежуточный продукт *5*, взаимодействуя с монозамещенными алкилгидразинами, дает 2-N-замещенные производные (7).

Кристаллические галогенводородные комплексы циклодекстринов

Й. СЕЙТЛИ и Ж. БУДАИ

Одна молекула β-циклодекстрина образует кристаллический комплекс с включением 1,5—2,0 молекул HCl. Выход по отношению к циклодекстрину составляет 72—74%. Образование комплекса было подтверждено его кристаллической формой, термодериватографическими, рентгенодиффракционными и масс-спектрометрическими данными. Были также приготовлены в кристаллической форме и комплексы β-циклодекстрина (β-ЦД) с HBr и HJ, и α-циклодекстрина с HJ. Они оказались стабильными при комнатной температуре.

В присутствии ацетона образуются третичные комплексы с молярным отношением β-ЦД: ацетон: HCl = 1 : 1 : 1.

Ацетон, в свою очередь, также дает комплекс с β-ЦД с молярным отношением 1 : 1.

Гетероароматические аммониоамидаты с электронным дефицитом, XIV

Синтез и некоторые реакции 9,10-диметокси-2H-[1,3,4]тиадиазино[3,2-c]хинезолин-5-ий-3-олатов

М. ЛЕМПЕРТ-ШРЕТЕР, К. ЛЕМПЕРТ, П. БРУК и Г. ТОТ

Циклизация 2-(2-ациламино фенил)-4*H*-1,3,4-тиадиазин-5(6*H*)-онов (*15*d, *15f*) приводит к первым представителям (*16a*, *16b*) новой группы (тип *4*) электронодефицитных гетероароматических аммониоамидатов. Шелочной гидролиз 2*H*- [1, 3,4]тиадиазино[3,2-c]-хиназолин-5-ий-3-олата (*16a*) приводит к образованию в качестве основных продуктов помимо соединений *15d* и 4(3*H*)-хиназолинона (*17a*), также и 3-меркаптоацетамидо-4(3*H*)-хиназолинона;(*18b*), который находится в равновесии с таутомером цикл-цепь (*18a*), т.е. тетраэдрическим стабильным промежуточным продуктом реакции *16a* → *18b*. При фотолизе соединения *16a* (лампа НРК-125, Пирекс, N_2) в качестве основного продукта имеем 4(3*H*)-хиназолинтион (*17d*) и в небольших количествах 3-ацетамидо-4(3*H*)-хиназолинон (*17b*).

Изоксазоли, I

Кристаллическая структура, а также некоторые реакции нового продукта конденсации этил 2-этокси-2-иминопропионата с гидроксиламином

П. ЛУГОШИ, Г. ДОЛЕШАЛ, Л. ПАРКАНИ и А. КАЛМАН

Продукт конденсации состава 2 : 1 и структуры *2* может быть получен в реакции этил 2-этокси-2-иминопропионата в присутствии (NaOH). Кристаллическая и молекулярная структуры продукта были определены прямым методом, а уточнены с помощью метода наименьших квадратов до R = 0,057 для 1724 наблюдаемых рефлексий, наблюдаемых на четырехконтуром автоматическом дифрактометре с графитным монохроматором марки Syntex $P2_1$. Димеры молекул образуют бесконечные листы, удерживаемые водородными мостиками.

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