

SPECTROSCOPIC PROPERTIES OF SOME DERIVATIVES
OF
CAMPHOR

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A thesis submitted for the degree of Master of Philosophy
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All kinetic measurements have been reviewed by Hargreaves and his co-workers but the studies have been investigated. Cameron has been asked to study the physical and the spectroscopic properties of the

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ABSTRACT

Aliphatic monocyclic imides have been reviewed by Hargreaves and his coworkers but few imides have been investigated. Camphorimide was chosen in order to study the chiroptical and the spectroscopic properties of the imide chromophore.

Camphorimide was prepared from camphoric acid. Some N-substituted alkyl and aryl imides were also made, by opening the ring some amido-acids were prepared.

Camphorquinone was condensed with 1,2-diamines to give camphorquinoxaline and substituted camphorquinoxalines. Dimethyluracil hydrate on condensation with camphorquinone gave pteridine dione. Camphorquinone-p-anisylimine was obtained when only one carbonyl group took part in the reaction with a monoamine.

The infrared spectra of these compounds are discussed with particular reference to the N-H stretching and C=O stretching vibrations as well as to the substitution pattern in aromatics.

The proton nmr spectra revealed some interesting information regarding the shielding of the camphor group methyl protons.

The uv and cd measurements have been found to be in reasonable agreement. Some of the uv bands are not found in the cd spectra, specially in the longer wavelength region.

All the imides showed ord curves with a positive cotton effect. Owing to strong absorption it is not possible to take ord measurements for the quinoxalines below about 350nm, ~~350nm~~.

The pteridine dione and camphorquinone-p-anisylimine showed a high optical rotation in the near uv region.

GENERAL INTRODUCTION

The most important terpene of the camphor group is the bicyclic camphor(1). It is found in (1), (-) and (+) enantiomeric forms. The main source of (+) camphor is the

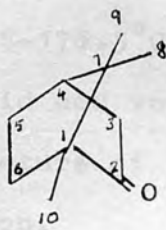
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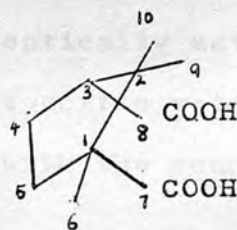


GENERAL INTRODUCTION

The most important terpene of the camphor group is the ketone camphor(a). It is found in (+), (-) and racemic forms. The main source of (+) camphor is the wood of the tree Cinnamomum Camphora Nees which is found in China, Japan and countries within latitudes of $10 - 34^{\circ}$ north. The most extensive forests are in Formosa. It also has been successfully cultivated



(a)



(b)

in subtropical countries. It has been known to the people in the Far East for a long time. It was introduced into the western countries by Arabs.

Because of its medicinal value, alchemists tried to treat it with various reagents. Kosegarten prepared camphoric acid (b) by the action of nitric acid on camphor. Biot found that it had optical activity even in the vapour state. In 1841 Pelouze¹ observed that borneol ($C_{10}H_{18}O$) gave camphor ($C_{10}H_{16}O$) on oxidation.

Gerdardt² suggested that camphor was the aldehyde corresponding to the alcohol borneol. Weyl³ considered that camphor could be a ketone, because when oxidised

by chromic acid it did not give an acid of the formula $C_{10}H_{16}O_2$. Meyer put forward a formula based on Kekule's benzene formula. In 1893 Bredt⁴ after a series of experiments on camphoric acid, suggested structures for camphor and camphoric acid. This structure for camphor was accepted as the correct one after the synthesis of camphoric acid by Komppa⁵ and independently by Perkin and Thorpe.⁶

Camphor has a characteristic odour and crystallises in thin plates. It sublimes at room temperature. The (+) and (-) modifications melt at 178.5-179° C and the racemic form at 178-178.5°C. (+)Camphor is optically active in liquid, solid and vapour states. The specific rotation varies with the nature of the solvent and with the concentration of the solution.

In absolute alcohol the following values are observed.

$$[\alpha]_D = +41.4^\circ(c, 1); +43.6^\circ(c, 5); +44.8^\circ(c, 20); +48.4^\circ(c, 50).$$

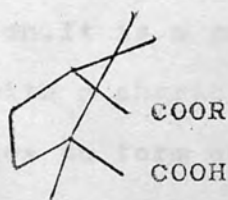
In 75% alcohol:

$$+34^\circ(c, 1); +36.9^\circ(c, 5); +39.8^\circ(c, 20)^7.$$

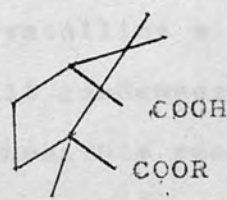
(+) Camphor is an optically active six-membered ring ketone having a gem-dimethyl bridge, locking it in a boat conformation, although the chair form is normally the stable conformation of a cyclohexane ring. Though camphor has two asymmetric carbon atoms, there is only one (\pm) pair. This is because the configurations of the asymmetric atoms are not independent, since

the gem-dimethyl bridge cannot be anything other than cis. The absolute configuration of (+) camphor has been shown to be (1R,4R) by an x-ray diffraction study of (+)-3-bromocamphor.⁸

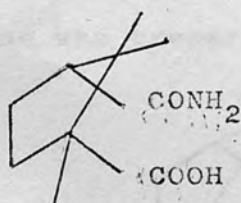
(+)- Camphor on oxidation with nitric acid gives the dicarboxylic acid, (+) cis (1R,3S) camphoric acid (b) which is widely used in experiments. The C-3 and C-2 bonds in camphor breaks open to form the five-membered dicarboxylic acid. The two carboxyl groups differ in reactivity and two isomeric esters can be obtained (c) and (d). Corresponding to the two esters two monoamides have been prepared, α -amide (α -camphoramic acid) (e) and the β -amide (β -camphoramic acid) (f).



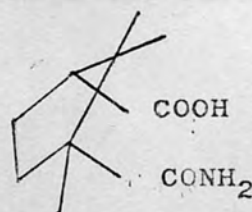
(c)



(d)

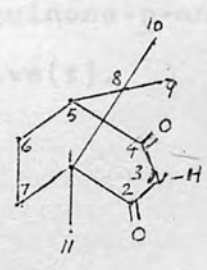


(e)

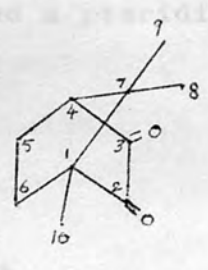


(f)

Bredt and Wornast⁹ prepared camphorimide (g) by distilling camphoric acid in a stream of ammonia. W.C.Evans¹⁰ prepared camphorimide and a few of its N-substituted derivatives. Camphorimide, when treated with dilute sodium hydroxide produces the β -amide (f)¹¹. The N-substituted α -amides can be obtained from the anhydride by the action of primary amines.¹²

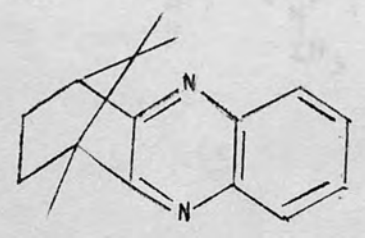


(g)



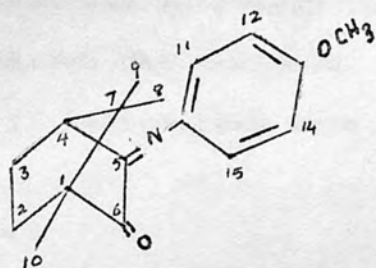
(h)

Camphorquinone (h) is the diketone obtained by the oxidation of camphor with selenium dioxide in acetic acid solution. It is a golden yellow crystalline substance with a characteristic odour. It condenses with diamines to form camphorquinoxalines. This reaction was discovered by Hinsberg.¹³ The name quinoxaline was derived from the structural resemblance of the ring system to quinoline and glyoxal from which the first quinoxaline was prepared.

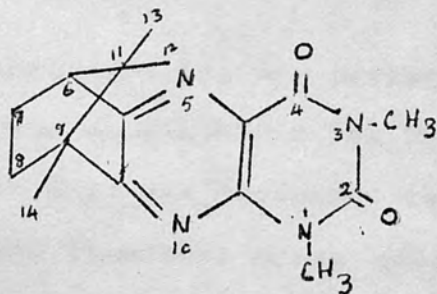


(o)

The present work is a detailed study of some of the spectroscopic and chiroptical properties of camphorimide and its derivatives. Some simple and substituted camphorquinoxalines have been also prepared to study the effect of the bornane structure on the aromatic chromophore. Besides the above mentioned, two more compounds have been prepared, camphorquinone-p-anisylimine(s) and a pteridine derivative(t).



(s)

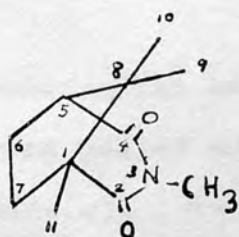


(t)

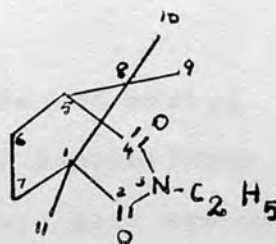
SYNTHESIS

The method used for the preparation of camphorimide (g) was that adopted by W.C. Evans,¹⁰ for the preparation of camphorimide and its N-substituted derivatives.

Camphorimide was prepared by the distillation of camphoric acid (b) in a stream of ammonia. The product was redistilled in a current of ammonia and purified by crystallisation. The N-alkyl derivatives were obtained by the action of alkyl halides on camphorimide in the presence of aqueous potassium hydroxide. Though W.C. Evans method was adopted, a slight modification was made to hasten the reaction. The N-methyl (i) and N-ethyl (j) derivatives were prepared in this manner.

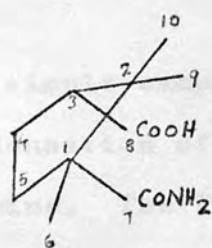


(i)

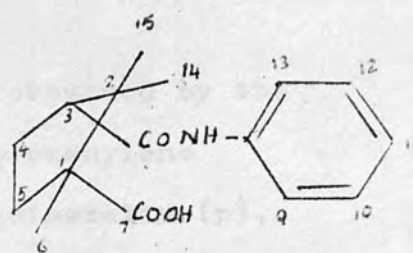


(j)

β -Camphoramic acid (f) was prepared by the action of sodium hydroxide on camphorimide. The preparation of β -Camphoramic acid was a^a prolonged reaction; the position of the 11-methyl group sterically hinders the cleavage of C₂-N₃ bond of camphorimide and thus inhibits formation of the α -acid. At the end of the reaction the sodium salt of β -camphoramic acid was obtained, which was converted into the β -acid.



(f)

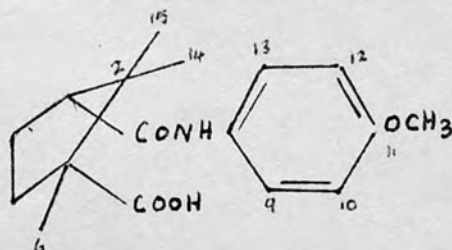


(k)

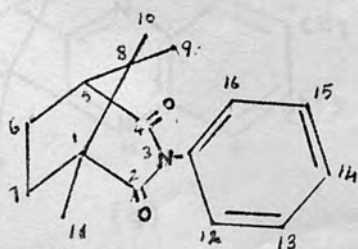
α -camphoranilic acid(k) was prepared by heating camphoric anhydride and aniline under reflux.

However, this method was not suitable for the preparation of α -camphor-p-anisidinic acid(l). So the two reactants, camphoric anhydride and p-anisidine were dissolved separately in dilute alcohol and then allowed to react by heating under reflux. The reaction product was crystallised a few times to get the pure compound.

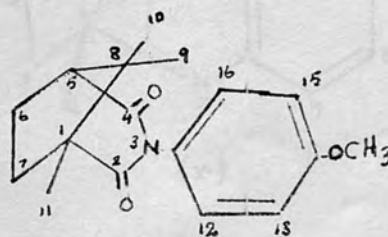
α -camphoranilic acid, acetylchloride and acetic acid were heated under reflux to get N-phenylcamphorimide(m). α -camphor-p-anisidinic acid was used to prepare the N-p-anisylcamphorimide(n).



(l)

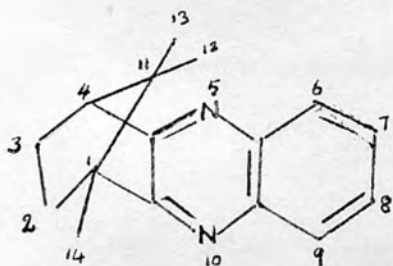


(m)

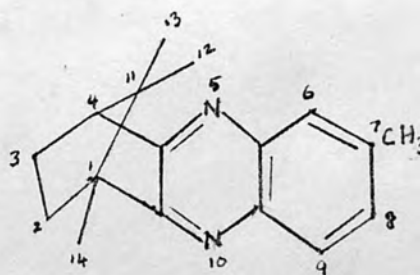


(n)

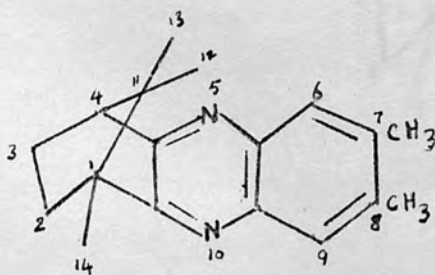
The simple camphorquinoxaline(o) was obtained by the condensation of camphorquinone with *o*-phenylene diamine. The 7 or (8)-methylcamphorquinoxaline(p), 7,8-dimethylcamphorquinoxaline(q) and 7 or (8)-chlorocamphorquinoxaline(r) have been prepared using the corresponding substituted phenylene diamines. Though the reaction proceeded well, the purification was not very easy. Column chromatography proved to be the best tool for the purification of quinoxalines. The reaction products were passed through a column of alumina several times, till no change in the melting point was observed. H.Rao and co-workers have done uv and cd measurements on 7,8-dimethylcamphorquinoxaline.¹⁴



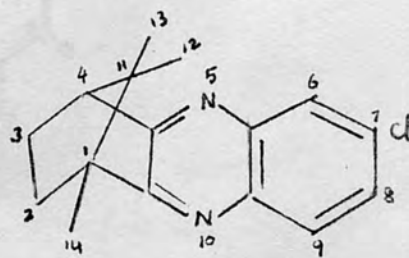
(o)



(p)



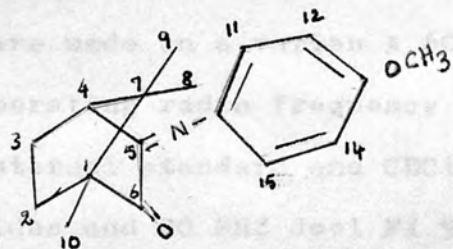
(q)



(r)

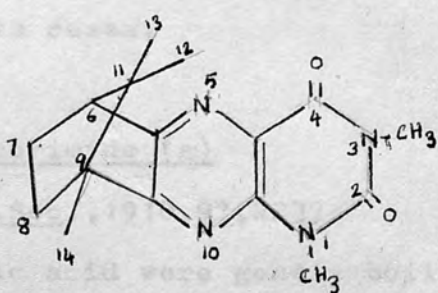
Camphorquinone on condensation with p-anisidine gave camphorquinone-p-anisylimine (s). This compound is indifferant from the quinoxalines in not having three rings. Only one carbonyl group took part in the reaction. The o-compound was reported in the literature.¹⁵

For ultraviolet spectra, a FS-124 Double Beam spectrophotometer was used for the shorter wavelength region. When camphorquinone was treated in the same way, with diamino dimethyl uracil hydrate, the compound obtained was 6,7,8,9-tetrahydro-1,3,9,11,11-pentamethylbenzopteridine-2,4(1H,3H)-dione.(t).



(s)

Ord measurements were done on a Cary Spectrophotometer at North Carolina State University. IR measurements were done at North Carolina State University and UV spectra were measured at North Carolina State University.



(t)

IR measurements were done on a Cary Spectrophotometer at North Carolina State University. IR measurements were done at North Carolina State University and UV spectra were measured at North Carolina State University.

EXPERIMENTAL

Infrared spectra were done on PE 457 spectrometer using KBr discs and nujol or hexachlorobutadiene mulls.

For ultraviolet spectra, a PE 124 Double beam spectrophotometer with a recorder was used. A digital voltmeter attachment was used for taking direct readings. 95% Ethanol was found to be a suitable solvent. 10 mm. cells were used at longer wavelength and 2 mm. cells for the shorter wavelength region.

Nmr measurements were made on a varian A 60 spectrophotometer at an operating radio frequency of 60 MHz, using TMS as the internal standard and CDCl_3 as solvent for the imides and 90 MHz Joel FX 90 Q'FT Nmr spectrometer for the quinoxalines.

Ord measurements were done on a Fica Spectropol I at North East London Polytechnic. Cd measurements were done at Westfield College and 95% ethanol was used as solvent in both cases.

(1R,5S) (+)-Camphorimide (g)

W.C.Evans, J.Chem.Soc., 1910, 97, 2237.

50 G. of camphoric acid were gently boiled in a flask fitted with a long column. The temperature was maintained at 180°C (metal bath), while dry ammonia gas was passed into the reaction vessel. When the

evolution of water vapour had stopped (about $1\frac{1}{2}$ hrs.) the content of the flask were distilled in a current of ammonia. The camphorimide thus obtained had m.p. 245°C . Crystallisation from aqueous acetic acid raised the m.p. to 248°C . (Lit. m.p. 243°C)

Yield 30 g. (66.2%).

(Found: C, 66.4; H, 8.2; N, 7.75. Calc. for $\text{C}_{10}\text{H}_{15}\text{N O}_2$:
C, 66.3; H, 8.3; N, 7.7%)

$[\alpha] = + 4.6^{\circ}$ (c, 6.00, Chloroform).

(1R,3S) (+)- β -Camphoramic acid (f)

W.A. Noyes, Amer. Chem. J., 1894, 16, 310.

5.0 G. of camphorimide were dissolved in 16 ml. of 15% aqueous sodium hydroxide, and heated under reflux on the water bath for $1\frac{1}{2}$ hours. On cooling the sodium salt separated. It was filtered at the pump to remove most of the alkali. Then it was dissolved in a small amount of water and the acid precipitated with concentrated hydrochloric acid. It was crystallised from dilute alcohol, m.p. 180° - 181°C . (Lit. m.p. 182 - 183°C).

Yield 3.0 g. (54.6%)

(Found: C, 59.8; H, 8.6; N, 7.0. Calc. for $\text{C}_{10}\text{H}_{17}\text{N O}_3$:
C, 60.3; H, 8.6; N, 7.0%).

$[\alpha] = + 68^{\circ}$ (c, 0.5, Ethanol).

(1R,5S) (+) N-methylcamphorimide (i)

W.C. Evans, J. Chem. Soc., 1910, 97, 2239.

12 G. of camphorimide, 10 ml. of methyl iodide and 65 ml. of 1.1N potassium hydroxide were allowed to react in the cold by shaking for one hour and then heated under reflux for 2 hours on the water bath. The reaction product was cooled and the oily layer was treated with 10% sodium hydroxide. The precipitate was dried and recrystallised from aqueous alcohol, m.p. 40-42° C.

(Lit. m.p. 40-42° C* ; 46° C).

Yield 4.0 g (31.0%).

(Found: C, 67.8; H, 8.9; N, 7.1 Calc. for $C_{11}H_{17}NO_2$:

C, 67.7, H, 8.9; N, 7.2%)

$[\alpha]_D = + 12.5$ (C, 2.21, Ethanol)

* Hoogwerf Van Dorp, Rec. Trav. Chim., 1893, 12, 12.

(1R,5S) (+) N-ethylcamphorimide (j)

W.C. Evans, J. Chem. Soc., 1910, 97, 2240.

16 G. of camphorimide, 86.8 ml. of 1.1N potassium hydroxide and 12.8 g. of ethyl iodide were mixed together and allowed to react by shaking for an hour. Then the mixture was heated under reflux for 2 hours on the water bath. The reaction product was cooled and the oily layer was separated and treated with 10% sodium hydroxide solution. The white precipitate was dried and crystallised from aqueous ethanol, m.p. 51-52° C.

(Lit. m.p. 51-52° C).

Yield 4.4 g. (23.8%).

(Found: C, 68.8; H, 9.2; N, 6.4. Calc. for $C_{12}H_{19}NO_2$:

C, 68.9; H, 9.1; N, 6.7)

$[\alpha]_D = + 11.2$ (c, 2.02, Ethanol).

Camphoric anhydride

60 G. of camphoric acid and 100 ml. of acetic anhydride were heated under reflux for 2 hours. The anhydride was obtained in the form of white needles. It was crystallised from aqueous ethanol m.p. 220-221° C. (Lit. m.p. 221° C).

α-Camphoranilic acid (k)

Method used by W.O. Wootton, J. Chem. Soc., 1910, 97, 413.

for related compounds.

A mixture of 14.6 g. of camphoric anhydride and 17.3 ml. of aniline was heated under reflux for 15 minutes. After cooling, the product was crystallised from dilute acetic acid and had m.p. 205-206° C, unaltered by further crystallisation.

(Lit. m.p. 209-210° C; 203-204° C*).

Yield 9.0 g. (40.9%).

(Found: C, 70.0; H, 7.7; N, 5.0. Calc. for $C_{16}H_{21}NO_3$:

C, 69.9; H, 7.6; n, 5.1%)

$[\alpha]_D^{25} = + 19.0$ (c, 1.0, Chloroform).

* K. Auvers and F. Schleicher, Ann. 1899, 309, 341.

N-phenylcamphorimide (m)

Method used by W.O.Wootton, J.Chem.Soc., 1910, 97, 415.
for related compounds.

8 G. of camphoranilic acid 24 ml of glacial acetic acid and 31 ml of acetyl chloride were heated together in a flask for 2 hours under reflux, the temperature being maintained between 110 and 120°C. The reaction product was cooled and poured into cold ammonium hydroxide (2N). The white precipitate was filtered dried and crystallised from aqueous ethanol, m.p. 110-112°C.

(Lit. m.p. 117-118°C).^{*}

(Found: C, 74.8; H, 7.4; N, 5.4. Calc. for $C_{16}H_{19}N_2O_2$:
C, 74.7; H, 7.4; N, 5.2%) Yield 7.5 g (100%)

$[\alpha]_D^{25} = + 11.6^\circ$ (C, 1.12, Chloroform).

* B.K.Singh and A.N.Puri, J.Chem.Soc., 1926, 506.

 α -Camphor-p-anisidinic acid (1)

Method used by W.O.Wootton, J.Chem.Soc., 1910, 97, 415.
for related compounds.

9.1 G. of camphoric anhydride and 6.1 g. of p-anisidine were dissolved separately in aqueous ethanol, mixed together and heated under reflux, the temperature being maintained between 160 and 180°C (using metal bath). The reaction mixture was cooled and filtered. It was

crystallised from aqueous ethanol using decolourising charcoal, m.p. 200-202° C.

Yield 4.0 g. (26.2%)

(Found: C, 66.95; H, 7.4; N, 4.7. $C_{17}H_{23}N_4O$ requires:

C, 66.8; H, 7.5; N, 4.6%)

$[\alpha]_D = + 11.6$ (c, 1.0, Chloroform).

N-p-anisylcamphorimide (n)

Method used by W.O. Wootton, J. Chem. Soc., 1910, 97, 415.

for related compounds.

A mixture of 3.2 g. of α -camphor-p-anisidinic acid,

9.6 ml. of glacial acetic acid and 12.5 ml. of

acetyl chloride was heated under reflux for 2 hours,

the temperature being maintained between 125 and 130° C

(using a metal bath). The reaction product was cooled

and poured into cold ammonium hydroxide (2N). The

white precipitate was filtered and dried. It was

crystallised from aqueous alcohol, m.p. 114 - 117° C.

Yield 1.3 g. (43.3%).

(Found: C, 71.3; H, 7.2; N, 4.9; $C_{11}H_{12}N_2O_3$ requires:

C, 71.1; H, 7.3; N, 4.9%)

$[\alpha]_D = + 15.32$ (c, 1.01, Chloroform).

Camphorquinone (h)

H. Rupe and A. Tommasi, Helv. Chim. Acta, 1937, 20, 1078.

100 G. of camphor, 80 ml. of acetic anhydride and 80 g. of selenium dioxide were heated under reflux, while stirring with a mechanical stirrer for 2 hours. 20 G. of selenium dioxide were added and heating continued for 2 hours. Then another 20 g. of selenium dioxide were added and the heating continued for 4 hours. The reaction product was cooled and approximately neutralised with 30% sodium hydroxide and then made alkaline with sodium carbonate solution. It was steam distilled. The product was crystallised from aqueous alcohol m.p. 197-199° C. (Lit. m.p. 198° C).*

Yield 80 g. (73%).

(Found: C, 72.0; H, 8.0; Calc. for $C_{10}H_{16}O_2$:
C, 72.0; H, 8.0%)

* W. C. Evans, J. M. Ridgion and J. L. Simonsen, J. Chem. Soc., 1934, 1, 137.

(1R)-Bornano(2,3-b) quinoxaline (α) · Camphorquinoxaline (β)

A. Heckendorn, Helv. Chim. Acta., 1929, 12, 50.

8 G. of o-phenylene diamine and 12 g. of camphorquinone were dissolved in aqueous alcohol and heated under reflux for 20 minutes. On cooling, the product was obtained as a viscous mass and on rubbing, it turned into solid. It was passed through a column of alumina (Beckmann Grade I) using light petroleum (b.p. 40-60°) as solvent and eluent. It was recrystallised from light petroleum (b.p. 40-60°) m.p. 75-77° C. (Lit. m.p. 74° C).

Yield 9.0 (52.3%).

(Found: C, 80.7; H, 7.5; N, 11.75 Calc. for $C_{16}H_{18}N_2$: C, 80.7;
H, 7.5; N, 11.8%) $[\alpha]_D^{20} = + 33^\circ$ (c, 0.20, Ethanol)

(1R)-Bornano(2,3-b)-7 or(8)-methylquinoxaline(p)

A.Heckendorn,Helv.Chim.Acta.,1929,12,50.

12 G. of 3,4-diaminotoluene and 16 g.of camphorquinone were dissolved in aqueous alcohol and heated under reflux for half an hour.The reaction product was extracted with light petroleum(b.p.40-60°) and passed through a column of alumina (Beckmann grade I) using the same solvent.It was crystallised from light petroleum(b.p.40-60°) m.p.83.- 85° C.
Yield 8 g. (32.9%).

(Found:C,80.75;H,8.0;N,11.0. $C_{11}H_{20}N_2$:Calc.for C,81.0;H,8.0;N,11.0%).

$[\alpha]_D^{25} = + 20.8$ (c,0.11,Ethanol).

(1R)-Bornano(2,3-b)-7 or (8)-Chloroquinoxaline (r)

A.Heckendorn,Helv.Chim.Acta.,1929,12,50.

9.6 G of camphorquinone and 8.4 g. of 4-chloro-*o*-phenelene diamine were dissolved in aqueous alcohol and heated under reflux for an hour.After passing through a column of alumina(Beckmann grade I) using light petroleum(b.p.40-60°) as an eluent.It was crystallised from the same solvent m.p.123-25° C.
Yield 6.6 g.(41.9%).

(Found:C,70.5;H,6.3;N,10.2. $C_{16}H_{17}N_2Cl$:Calc.for C,70.6;H,6.25;N,10.3%).

$[\alpha]_D^{25} = + 19.9$ (c,0.12,Ethanol).

(1R)-Bornano(2,3-b)-7,8-dimethylquinoxaline(q)

A.Heckendorn, Helv.Chim.Acta., 1929, 12, 50.

9.2 G. of camphorquinone and 7.8 g. of 4,5-diamino o-xylene were dissolved in aqueous alcohol and heated under reflux for half an hour. The product was passed through a column in the same way as the other quinoxalines mentioned above and crystallised using the same solvent m.p.81-82° C.

(Lit.m.p.80-81° C)*

Yield 8 g. (54.3%).

(Found:C,81.6;H,8.2;N,10.6 Calc.for C₁₈H₂₁N₂:
C,81.0;H,8.2;N,10.5%)

* H.Rao, O.Schuster and A.Bacher, J.Amer.Chem.Soc., 1974, 96, 3155.

$[\alpha]_D^{25} = + 23$ (c, 0.12, Ethanol).

(1R,4S) (+)- Camphorquinone-p-anisylimine (s)

Method used by A.Heckendorn, Helv.Chim.Acta., 1929, 12, 50 for related compounds.

6.2 G. of p-anisidine and 8.4 g. of camphorquinone were dissolved in aqueous alcohol and heated under reflux for half an hour. The product after filtration was crystallised from ethanol m.p.112° C.

Yield:5 g.(36.4%).

(Found:C,75.0;H,7.8;N,5.0 C₁₇H₂₁N O₂ requires
C,75.3;H,7.7;N,5.2%).

$[\alpha]_D^{25} = + 1730$ (c, 1.01, Ethanol).

6,7,8,9-Tetra hydro-1,3,9,11,11-pentamethylbenzo(g)
pteridine-2,4(1H,3H)dione (t)

Method used by A.Heckendorn,Helv.Chim.Acta.,1929,
12,50.for related compounds.

8.2 G. of 5,6-diamino,2,4-dimethyluracil hydrate
and 8.2 g. of camphorquinone were dissolved in
aqueous alcohol and heated under reflux for half
an hour.The product was passed through a column of
alumina(Beckmann grade I) using acetone as an eluent.
Then it was crystallised from aqueous alcohol m.p.
m.p.200-201° C .

Yield:5.0 g.(33.8%).

(Found:C,63.85;H,6.75;N,18.75 . $C_{16}H_{20}N_4O_2$ requires
C,64.0;H,6.6;N,18.7%).

$[\alpha]_D^{25} = + 42$ (c,1.0,Ethanol).

INFRA-RED SPECTRA

AMIDES

INTRODUCTION

Amides have characteristic bands due to NH modes, as well as the carbonyl groups.

a. NH-stretching modes

Primary and secondary amides are characterised by their NH stretching modes besides the carbonyl absorption. Primary amides show two NH modes corresponding to the asymmetric and symmetric motions of the hydrogen atom. Secondary amides have only a single absorption. The physical state in which these compounds are being examined is important because of the shift in position due to hydrogen bonding in solution.

In the solid state, primary amides show two broad absorption bands near 3350 cm^{-1} and 3180 cm^{-1} . Secondary amides absorb at 3280 cm^{-1} , but some show a weak absorption at 3080 cm^{-1} .¹⁶

b. Carbonyl absorption - Amide I band

All amides show an intense band near 1640 cm^{-1} when examined in the solid state. The precise location of this band is determined by the presence or absence of any substituent on the N atom and by the electronegativity of the substituent if present.

Ring strain also affects the position of this band. Particular attention should be paid to the state in which the material is examined, because the frequency of this band is affected by hydrogen bonding.

Simple primary amides absorb near 1650 cm^{-1} in the solid state. Secondary-N-monosubstituted open-chain amides absorb very close to 1540 cm^{-1} . This band can get shifted to a higher wavenumber upto 1680 cm^{-1} if the nitrogen atom has an electron attracting group attached to it.¹⁷ In tertiary amides the carbonyl absorption is not much influenced by changes in the state, so this band is found near 1550 cm^{-1} .

C. Amide II band

This is shown by primary and secondary amides.

In primary amides, it appears as a weak band on the lower frequency side of the main carbonyl band, between 1650 cm^{-1} and 1620 cm^{-1} . In secondary amides it is observed in the range $1570 - 1510\text{ cm}^{-1}$ in the solid state.¹⁷ This is considered as a mixed vibration due to NH in-plane bending and CN stretching.¹⁸ This is absent in tertiary amides.¹⁹

d. The amide III band

This absorption band occurs in secondary amides in the region $1300-1200\text{ cm}^{-1}$ and is usually weaker than either of the amide I or II bands.¹⁸ It is almost certainly due to a mixed vibration involving OCN and NH modes. It is sensitive to deuteration.¹⁶

e. The amide IV, V and VI bands

Secondary amides have bands in the lower frequency region due to the amide group, which are less important in the correlation work. The amide IV band is found around 620 cm^{-1} which is considered to be due to OCN bending and the amide VI band around 600 cm^{-1} is due to C=O out-of plane bending.¹⁸ The amide V band is around 700 cm^{-1} and is considered as due to NH out of plane deformation.²⁰

CYCLIC IMIDES

The CO-NH-CO group is uncommon in open chain compounds. Cyclic compounds containing this group are the imides, which are the derivatives of dicarboxylic acids. Cyclic carboxylic monoimides have been extensively studied.²¹ This group is found in five and six membered ring compounds such as maleimide, succinimide, and glutarimide (Fig. 1).

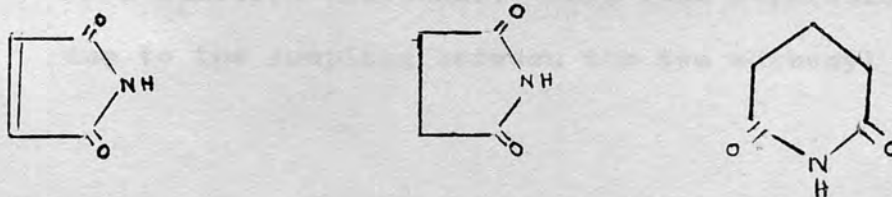


Fig. 1

The free imide group can adopt three different conformations, according to the position of the carbonyl group relative to the group R on the N atom. Because of resonance, the group is essentially planar and this facilitates calculations. It has been proved that only the cis-cis conformation is possible in five and six membered cyclic imides as the C=O groups are farthest apart and the electrostatic repulsion is least.²² (Fig. 2)

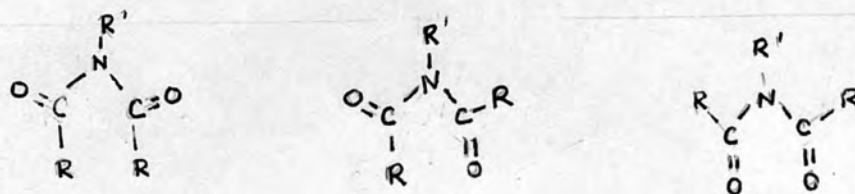


Fig. 2

CIS-CIS

CIS-TRANS

TRANS-TRANS

a. NH stretching vibrations

Imides have two strong and broad bands²¹ in the region $3500-3000\text{ cm}^{-1}$ due to the NH stretching vibrations. This absorption arises from the cis configuration of the CO-NH-CO group.²³

b. Carbonyl bands

The amide I band in imides is found as two widely separated bands due to the vibrational coupling of the two carbonyl groups, in the regions $1700-1670\text{ cm}^{-1}$ in six-membered ring compounds and $1770-1700\text{ cm}^{-1}$ in five membered compounds.²⁴ This band separation is due to the coupling between the two carbonyl groups

which are in the same plane. This coupling depends on the nature of the substituent on the N atom suggesting its electronic origin. Conjugation with the carbonyl group shifts the imide bands to lower frequency while in cyclic imides, in which carbonyl group is part of the ring, ring strain causes a shift to higher frequency.²⁵

c. The amide II band

This band is absent in secondary cyclic amides which are less than nine-membered. In cis systems, due to the high deformation, it is expected to approach very close to the amide I band and may coincide with it.

AMINO ACIDS AND AMIDO ACIDS

β -Camphoramic acid (*f*) is an amido acid.

α -Camphoranilic acid (*k*) and α -camphor-p-anisidinic acid (*l*) are ^{N-substituted} amido acids. Amido acids show characteristic vibrations of amides and also of amino acids.²⁶

a. NH stretching vibrations

In the solid state these compounds absorb in the range 3390-3260 cm^{-1} .²⁷

b. The Carboxyl group absorption

These compounds absorb in the range 1724-1695 cm^{-1} .²⁷ due to the carbonyl stretching of the carboxyl group.

c. The amide I Band

This is found in the range $1620-1600\text{ cm}^{-1}$ for α -acids and between $1650-1620\text{ cm}^{-1}$ for other acids.^{27,28}

d. The amide II Band

The amide II band falls in the range $1570-1500\text{ cm}^{-1}$.²⁷

9 AROMATIC GROUP FREQUENCIES

The C-H stretching vibrations

The C-H stretching vibrations which are generally three in number are found very close to 3080 cm^{-1} .

The C=C stretching vibrations

The C=C stretching modes of the aromatic system are found in the $1650-1450\text{ cm}^{-1}$ region. Though there are four bands, the ones near 1600 cm^{-1} and 1500 cm^{-1} are more characteristic of the group. Substitution shifts these bands to slightly higher or lower wavelengths.

Substitution pattern in aromatics

The region $1000-650\text{ cm}^{-1}$ is characteristic of C-H out-of plane deformation vibrations. The bands are normally strong in the region except in case of a single hydrogen atom where the intensity is comparatively low due to the reduction in the number of hydrogen atoms.

HETEROCYCLIC GROUP FREQUENCIES

C-H stretching vibrations

The C-H stretching absorption occurs in the region 3100-3000 cm^{-1} . Phenazine (Fig. 3) absorbs near 3050 cm^{-1} ²⁹ and quinazoline (Fig. 3) at 3020 cm^{-1} .³⁰

Ring stretching vibrations

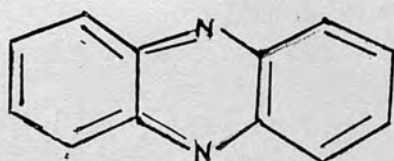
The general range for C=C lies between 1600 and 1300 cm^{-1} . Phenazine has bands between 1625 - 1300 cm^{-1} , quinazoline between 1600- 1300 cm^{-1} , pyrazine 1560-1410 cm^{-1} , pyrimidine 1610-1400 cm^{-1} and pyridazine 1572 - 1414 cm^{-1} respectively. These compounds show characteristic bands, four in number. This vibration arises from the interaction of C=C, C=N and N=N vibrations, so it is difficult to assign them to a particular band frequency.

C-H in-plane deformation

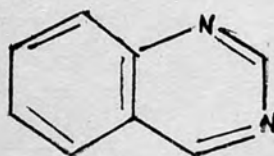
The region 1250 - 1000 cm^{-1} has bands due to the in-plane deformation and ring breathing modes.

C-H out-of- plane deformation

This occurs in the region 900-700 cm^{-1} . The position of these bands varies according to the number of free hydrogen atoms in the ring.



Phenazine



Quinazoline

Fig 3

DISCUSSION

Results for the compounds studied by infra-red spectroscopy, using KBr disc, nujol and hexachlorobutadiene where ever appropriate, are shown in the form of tables, spectra and structures.

1. Camphorimide and its N-substituted derivatives shown in (Table Nos. (1 & 2)), (Spectra Nos. 1, 5, 6, 7, 8, 9, 14 and 15), free NH stretching of the NH group in camphorimide, and the carbonyl frequencies.

2. Amido-acids (Table No. 3), (Spectra Nos. 2, 3, 4, 11, 12, 13, 16 and 17) where the bonded NH group, Characteristic bands for amido-acids as well as the aromatic bands are represented.

3. Camphorquinoxaline and its substituted derivatives (Table No. 4), (Spectra Nos. 18, 19, 20 and 21) showing the substitution pattern more clearly than the other regions.

4. Camphorquinone-p-anisylimine (Table No. 6), (Spectra Nos. 22 and 23) Showing the carbonyl bands as well as the substitution pattern in the aromatic component.

5. Pteridine dione (Table No. 5), (Spectrum No. 10).

NH stretching frequencies

A fairly strong band at 3205 cm^{-1} and a medium side band at 3090 cm^{-1} are attributed to the NH stretching frequencies of camphorimide (Table No.1), (Spectrum No.1). In the solid^{state} imides show a bonded NH near 3250 cm^{-1} . In compounds with a $-\text{CO}-\text{NH}-$ group which forms part of a five or a six-membered ring, the C=O and NH group must lie in a cis configuration showing only one band near 3425 cm^{-1} corresponding to the cis modification.³² Five membered cyclic imides such as maleimide and succinimide in crystalline state show bands in the region $3220-3170\text{ cm}^{-1}$ and another around 3080 cm^{-1} due to NH stretching vibrations.²⁴ The NH frequency range for imides is in the range $3500-3000\text{ cm}^{-1}$.²¹

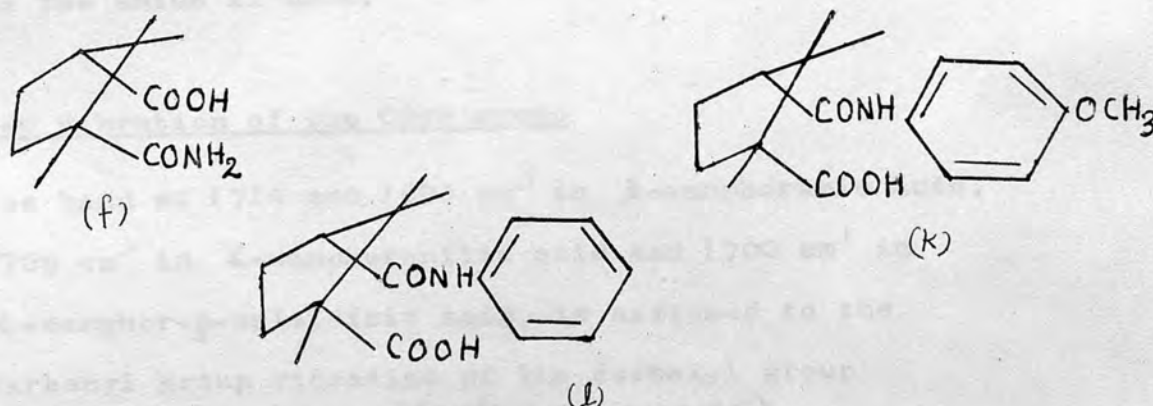
Amido acids (Table No.3, Spectrum No.2) also show NH stretching frequencies in the region $3470-3070\text{ cm}^{-1}$. β -Camphoramic acid has weak and medium bands due to NH stretching vibrations. α -Camphoranilic acid shows medium and weak bands at slightly lower frequency than the former acid (Table No.3, Spectrum No.3). α -Camphor-p-anisidinic acid has one sharp strong band at 3320 cm^{-1} (Table No.3, Spectrum No.4). The range is in agreement with Fuson's work on acids.²⁷

Amide I band

Camphorimide has a strong band at 1685 cm^{-1} with a side band at 1725 cm^{-1} (spectrum No.5). The N-methyl and

N-ethyl camphorimides also have two bands at 1725 cm^{-1} and 1675 cm^{-1} (Spectra Nos. 6 and 7). The N-phenylcamphorimide has its bands at 1725 cm^{-1} and 1680 cm^{-1} (Spectrum No. 8). The N-p-anisylcamphorimide has two bands at 1735 cm^{-1} and 1680 cm^{-1} (Spectrum No. 9).

Five-membered cyclic imides such as maleimide and succinimide (Fig. 1) show carbonyl bands at 1770 and 1700 cm^{-1} in the solid state (KBr_{disc}), while less strained six-membered ring compound, glutarimide (Fig. 1) has a slightly lower wavelength, 1703 and 1669 cm^{-1} . Camphorimide, a seven-membered ring compound, shows band frequencies, nearer to the six-membered ring.



β -Camphoramic acid (f) has a band at 1644 cm^{-1} (Spectrum No. 11), α -camphoranilic acid (k) at 1665 cm^{-1} (Spectrum No. 12) and α -camphor-p-anisidinic acid (l) at 1635 cm^{-1} (Spectrum No. 13). This band in these acids is considered as the amide I band.

The pteridine dione (t) has two strong bands at 1715 cm^{-1} and 1665 cm^{-1} (Spectrum No. 10).

Camphorquinone-p-anisylimine (s) has only one strong

band at 1740 cm^{-1} . The band in both these compounds are due to the carbonyl group vibrations. Since the C=N group also absorb in this region, there will be a mixing of the two (Spectrum No. 23)

The acids are different from the rest of the compounds in absorbing (amide I band) at a shorter wavelength.

Amide II band

This is absent in camphorimide and its N-substituted derivatives. β -camphoramic acid shows a medium band at 1560 cm^{-1} (Spectrum No. 11) which could be assigned to the amide II band.

C=O vibration of the COOH group

The band at 1710 and 1690 cm^{-1} in β -camphoramic acid, 1700 cm^{-1} in α -camphoranilic acid and 1700 cm^{-1} in α -camphor-p-anisidinic acid, is assigned to the carbonyl group vibration of the carboxyl group (Spectrum Nos. 11, 12 and 13)

Gem-dimethyl group

The imides studied here show bands in the region $1365-1355\text{ cm}^{-1}$, with medium intensity. Besides, the alkyl substituted imides have bands in the region $1190-1160\text{ cm}^{-1}$. The acids show medium and weak bands in the region $1390-1370\text{ cm}^{-1}$ and 1200 cm^{-1} . Bellamy¹⁶ specifies the ranges $1385-1380\text{ cm}^{-1}(s)$; $1170_{\pm 5}(s)$, $1170-1140\text{ cm}^{-1}(s)$ and near 800 cm^{-1} for gem-dimethyl groups.

Bands due to aromatic group vibrations

N-phenylcamphorimide, N-p-anisylcamphorimide,

α -camphoranilic acid and α -camphor-p-anisidinic acid

show bands due to aromatic C-H and C=C stretching

vibrations. These compounds also show characteristic

patterns due to substitution. The N-phenylcamphorimide

has a band at 745 cm^{-1} with a side band at 760 cm^{-1} (both strong) and another at 690 cm^{-1} with a side band

(spectrum No. 14). α -camphoranilic acid has two bands

at 755 cm^{-1} and 690 cm^{-1} , both cases indicating mono-substitution (spectrum No. 16). The CH out-of-plane

bending absorption of mono-substituted aromatics is between $770\text{--}730\text{ cm}^{-1}$.³² It is easily recognised being

the strongest in this region of the spectrum. The ^{2nd} band

in mono substituted compounds is almost always with

in $\pm 10\text{ cm}^{-1}$ of 700 cm^{-1} and is regarded by Randall²⁸

as being specific for a monosubstituted phenyl

group. It is essential that both regions should be

examined to confirm the presence of a mono-substituted

compound, because some meta-substituted and tri-

substituted materials also absorb near 700 cm^{-1} .

N-p-anisylcamphorimide and α -camphor-p-anisidinic acid

show characteristic vibrations due to 1,4-di-

substitution. The imide shows a strong band at 820 cm^{-1}

with a side band (Spectrum No. 15). The acid has a

medium band at 828 cm^{-1} with a side band (Spectrum No. 17).

with p-di-substituted compounds, owing to the reduction in the number of free adjacent hydrogen atoms on the ring, the absorption band of the out-of-plane CH vibrations show a further shift to higher wavenumber and a strong band occurs in the range $860-800\text{ cm}^{-1}$ ¹⁶. Results are consistent with the substitution pattern.

C=C and C=N vibrations in heterocyclic compounds

Camphorquinoxaline and the substituted quinoxalines have C=C and C=N vibrations in the $1600-1300\text{ cm}^{-1}$ region.

CH deformations

Camphorquinoxaline has two strong bands at 850 cm^{-1} and 760 cm^{-1} (both strong) (Spectrum No. 18). 2:3 and 2:4-Dimethyl quinoline contain four free hydrogen atoms in the carbocyclic ring. These show their strongest bands in this region at 755 cm^{-1} and 758 cm^{-1} respectively. They also absorb in the $900-850\text{ cm}^{-1}$ range. A band in the region $780-740\text{ cm}^{-1}$ is also shown by quinazolines.

7 or (8)-Chlorocamphorquinoxaline show two medium bands between 840 cm^{-1} and 800 cm^{-1} . It has another medium band at 875 cm^{-1} (Spectrum No 20)

7 or (8)-Methylcamphorquinoxaline has two strong bands of equal intensity at 835 cm^{-1} and 815 cm^{-1} . This compound has a medium band at 880 cm^{-1} . (Spectrum No. 19)

The band in the $840-800\text{ cm}^{-1}$ region in the two substituted quinoxalines^s, resemble those in aromatic compounds with two adjacent hydrogen atoms. The single medium band at 880 cm^{-1} in the methyl derivative and

the band at 875 cm^{-1} in the chloro derivative, is similar to that of a vibration due to a single hydrogen atom.

The 7,8-dimethylcamphorquinoline has one medium band at 870 cm^{-1} . This could be due to the isolated hydrogens in this compound. (Spectrum No. 21).

Camphorquinone-p-anisylimine has a medium and a weak band between 850 and 800 cm^{-1} region for its two adjacent hydrogen atoms. (Spectrum No. 22).

2970 cm	2970 cm	2970 cm	C-H asymmetric and symmetric modes of CH ₃ and CH ₂ groups.
2880 cm	2880 cm	2880 cm	
2840 cm	-	-	
1725 cm	1725 cm	1725 cm	Carbonyl band
1680 cm	1675 cm	1675 cm	
1192 cm	1170 cm	1162 cm	gem-dimethyl group.
725 cm	-	-	Out-of-plane deformation.

TABLE NO. I

Infrared spectra of aliphatic imides using KBr discBands in wavenumber cm^{-1}

Camphor.- imide	N-methyl- camphor. imide	N-ethyl- camphor. imide	Assignments
3205 cm			
3090 cm	-	-	Bonded N-H
2970 cm	2970 cm	2970 cm	C-H asymmetric and symmetric modes of CH ₃ and CH ₂ groups.
2880 cm	2880 cm	2880 cm	
2840 cm	-	-	
1725 cm	1725 cm	1725 cm)	Amide I band C=O stretching
1680 cm	1675 cm	1675 cm)	
1192 cm	1170 cm	1162 cm	Gem-dimethyl group.
728 cm	-	-	N-H out-of- plane deformation.

TABLE NO. 2

Infrared spectra of aromatic imides using KBr discsBands in wavenumber cm^{-1}

<u>N-phenyl</u> <u>-camphorimide</u>	<u>N-p-anisyl-</u> <u>camphorimide</u>	<u>Assignments</u>
3050 cm	3060	Aromatic C-H stretching.
2970 (s) 2880 (w) 2940	2970 2940 (w) 2880 2840	C-H asymmetric and symmetric modes due to CH_3 and CH_2 groups.
1735(w) 1680 (s)	1735 (w) 1680 (s)	Amide I band. C=O stretch.
1600 1500 1480 1455	1610 1510 1455	Aromatic C-C vibrations
1190	1190	Gem-dimethyl group.
745 690	822	
Mono-substituted aromatics.	Two adjacent hydrogen atoms.	

TABLE NO. 3

(Infrared spectra of acids using KBr disc)

Band in wavenumber cm^{-1}

β -Camphoramic acid	α -Camphor-anilic acid	α -Camphor-p-anisidinic acid	Assignments
* 3479	* 3250	* 3320	N-H stretching
* 3418	3130		
* 3320			
* 3240			
* 3190			
** 1710			C=O vibration of the COOH group
** 1690	1695	1700	
1644	1665	1635	C=O Amide I band
1560	1600	1600	Aromatic group vibrations.
Amide II band	1400	1400	
	Aromatic group vibrations.	Aromatic group vibrations	
	755	828	p-di-substitution.
	690		
	Mono-substitution.		

* Hexachlorobutadiene

** Nujol

TABLE NO. 4

Infrared spectra of quinoxalines using KBr discBands in wavenumber cm^{-1}

Camphor- quinoxaline	7 or(8)-methyl camphor- quinoxaline	7,8-Dimethyl camphor quinoxaline	7 or(8)-Chloro camphor quinoxaline
-------------------------	---	--	--

3060	3040	3040	3060
------	------	------	------

C-H aromatic stretching

1610	1600	1600	1600
1560	1510	1500	1510

Bands due to C-C stretching vibrations in aromatic compounds.

1269	1265	1270	1265
1172	1198	1180	1170
	1172		1160

Gem-dimethyl group

* 850 (s)	885 (w)	** 880	875
* 760 (s)	one isolated	one isolated	one isolated
Four adjacent hydrogen atoms	hydrogen atom	hydrogen atom	hydrogen atom
	835		840
	815		810
	Two adjacent hydrogen atoms		Two adjacent hydrogen atoms

**

Nujol

*Hexachlorobutadiene

TABLE NO. 5

Infrared spectra of Pteridine dione

Bands in wavenumber in cm^{-1}	Assignments
1715 1665 equal intensity	C=O stretching, amide I band.
1580	C=N stretching
1490-1450	N-CH ₃ stretching
1380	Gem-dimethyl group

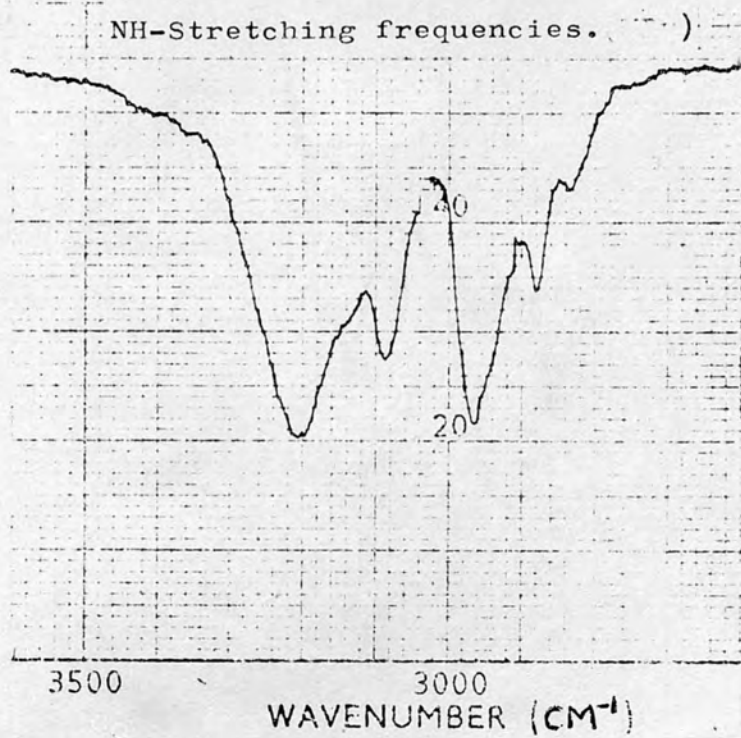
TABLE NO 6

Infrared spectra of camphorquinone-p-
anisylimine using KBr disc.

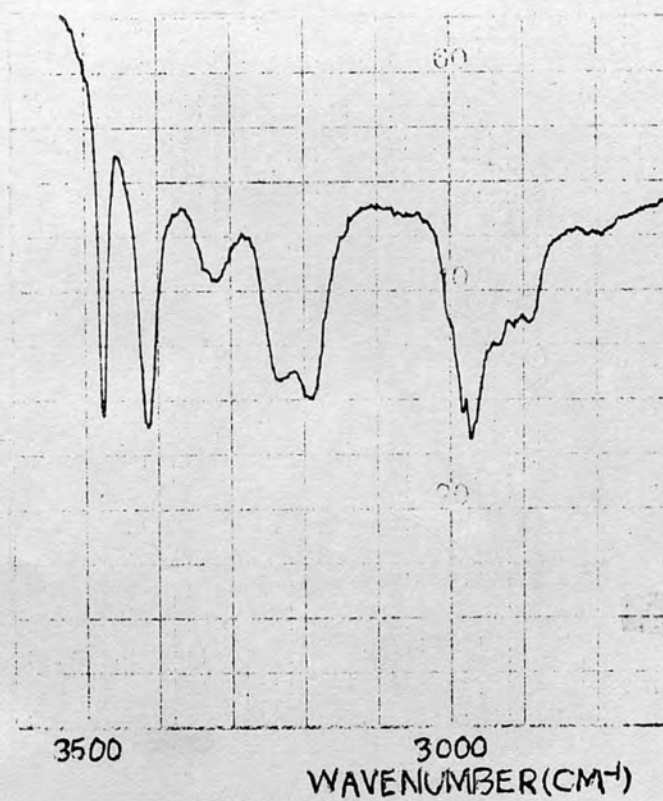
Wavenumber in cm^{-1}	Assignments
1740 (s)	C=O
1640 (s)	C=N stretching vibrations.
1590)	One band split into four.
1495)	
1445)	
1430)	
1165	Gem-dimethyl group.
1175	
** 850 (s)	p-disubstitution
** 815 (m)	

** Nujol

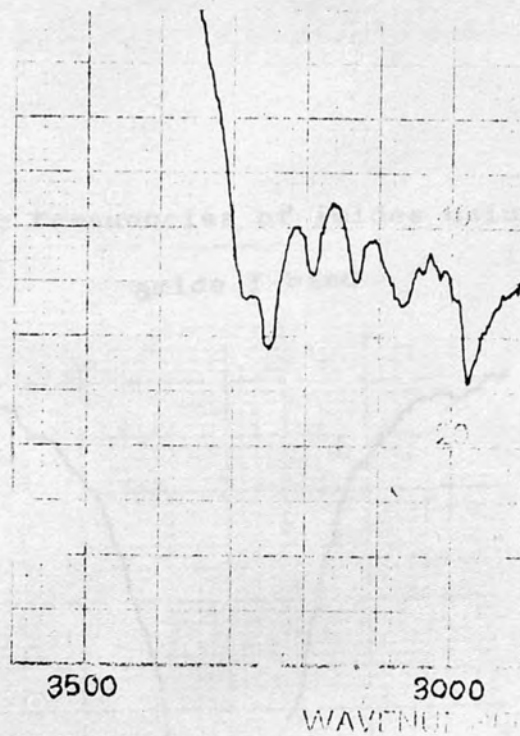
INFRARED SPECTRA



Camphorimide - Spectrum No.1

 β -Camphoramic acid - Spectrum No.2

NH-Stretching frequencies in Hexachlorobutadiene



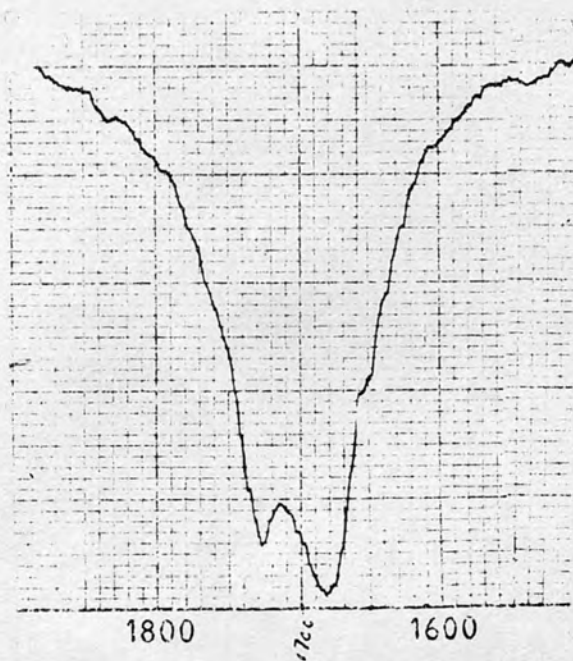
α -Camphoranilic acid
Spectrum No.3



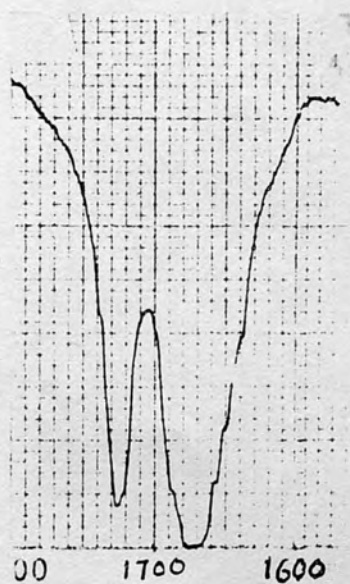
α -Camphor -p- anisidinic acid
Spectrum No.4

Carbonyl group frequencies of imides using KBr disc

amide I band



Camphorimide - Spectrum No. 5

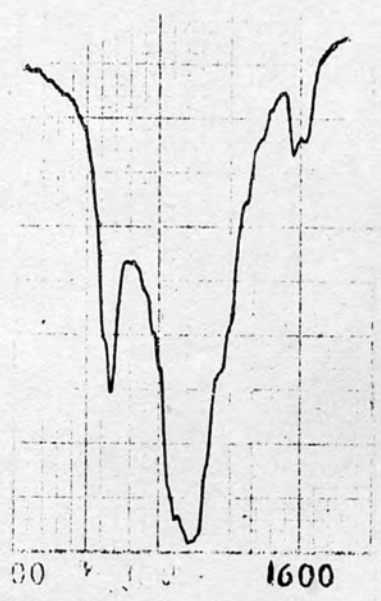


N-methylcamphorimide
Spectrum No. 6

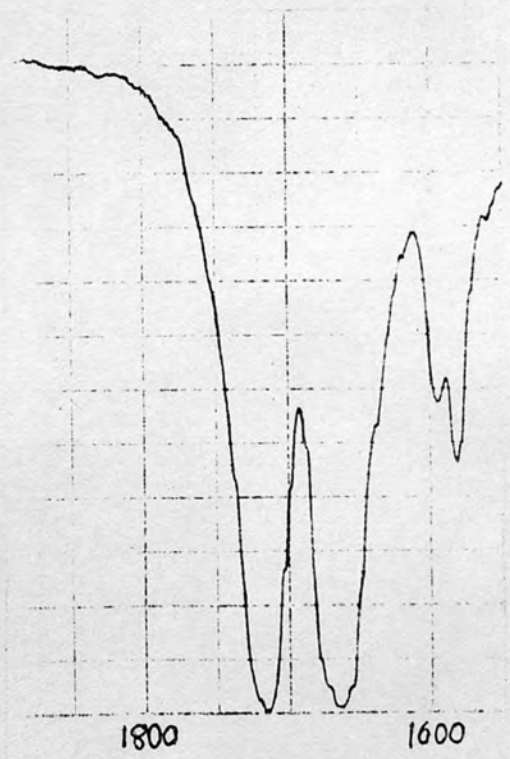


N-ethylcamphorimide
Spectrum No. 7

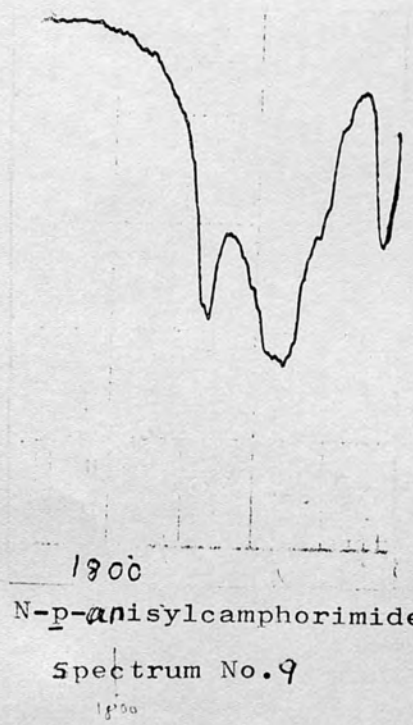
using
Carbonyl group frequencies, KBr disc - Amide I band



N-phenylcamphorimide
Spectrum No. 8

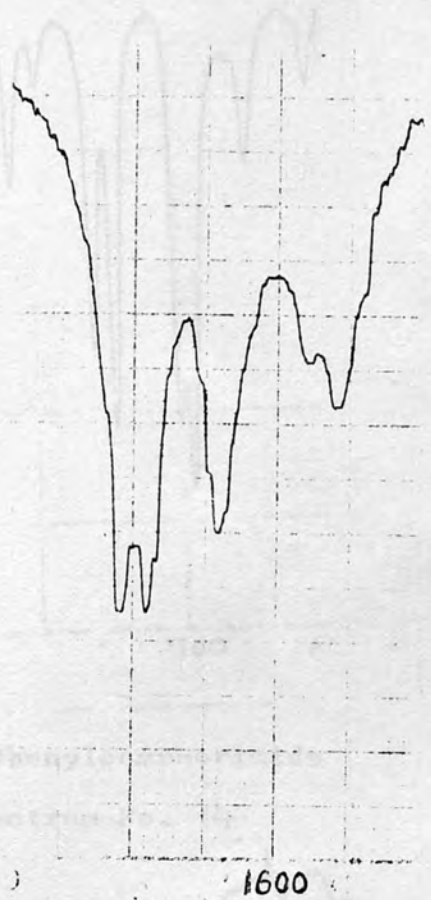


Pteridine dione
Spectrum No. 10

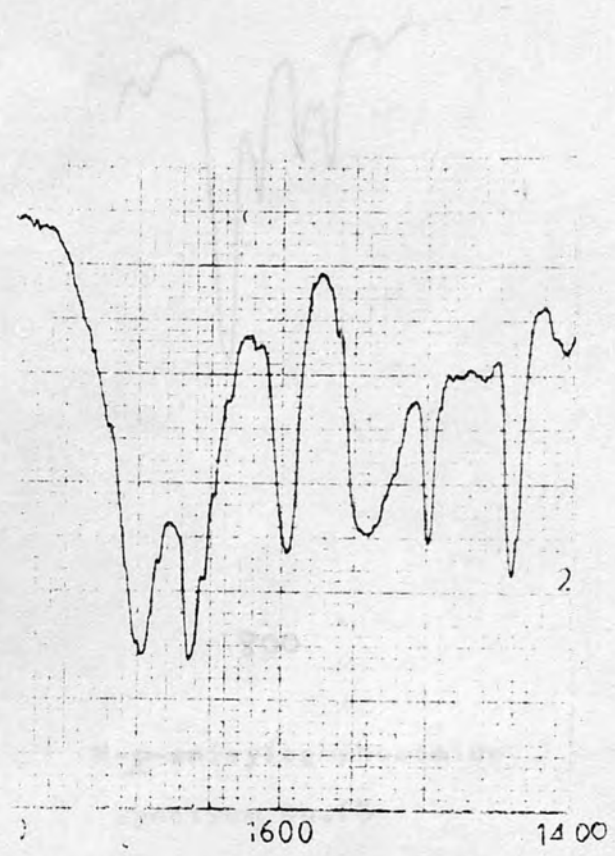


N-p-anisylcamphorimide
Spectrum No. 9

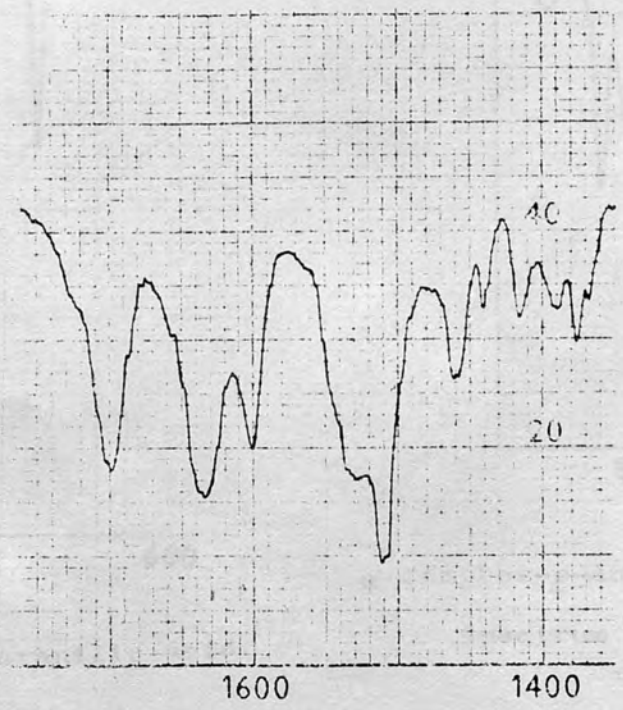
Substituted p-phenylene diamine
C=O stretching of the carboxyl group and amide I band



β -Camphoramic acid
Spectrum No. 11



α -Camphoranilic acid
Spectrum No. 12



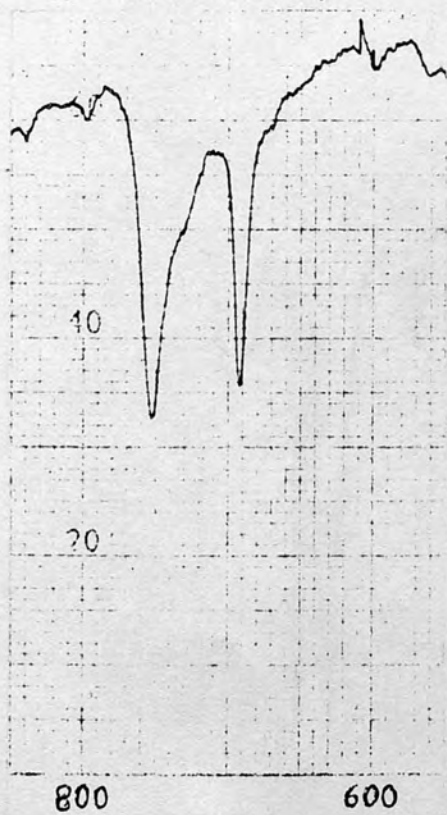
α -Camphor-p-anisidinic acid
Spectrum No. 13

Substitution pattern - Aromatic N-substituted imides
and acids.



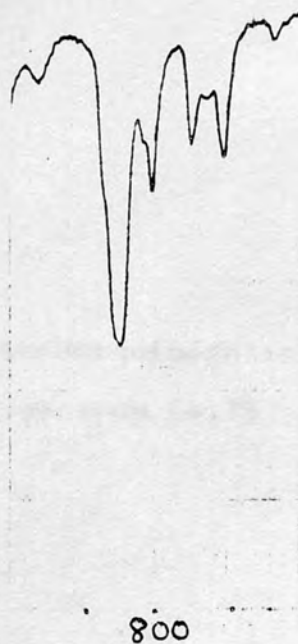
N-phenylcamphorimide

Spectrum No. 14



α -Camphoranilic acid

Spectrum No. 16



N-p-anisylcamphorimide

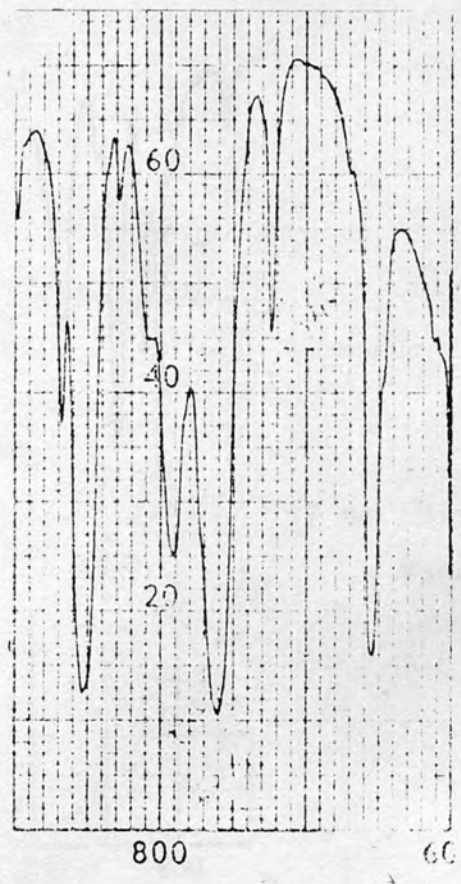
Spectrum No. 15



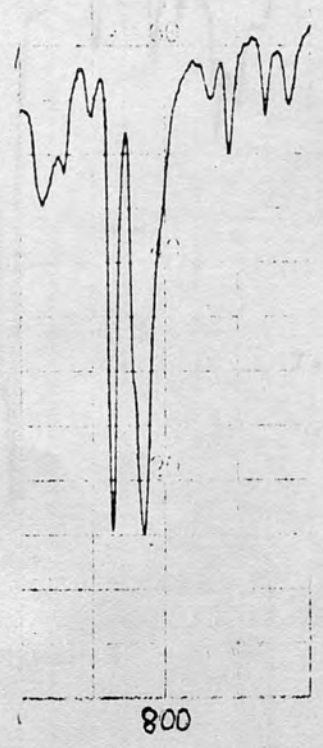
α -Camphor-p-anisidinic acid

Spectrum No. 17

Substitution pattern - Quinoxalines



Camphorquinoxaline
Spectrum No. 18



7 or (8)-Methylcamphorquinoxaline
Spectrum No. 19

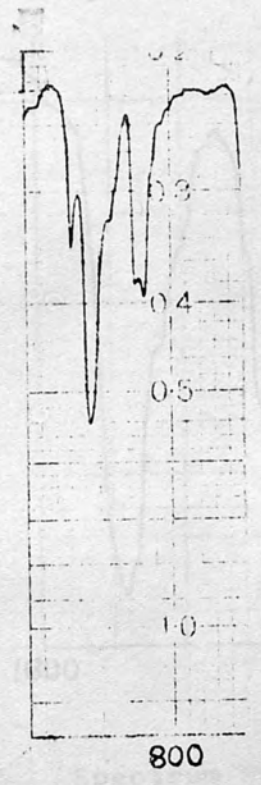


7 or (8)-Chlorocamphorquinoxaline
Spectrum No. 20

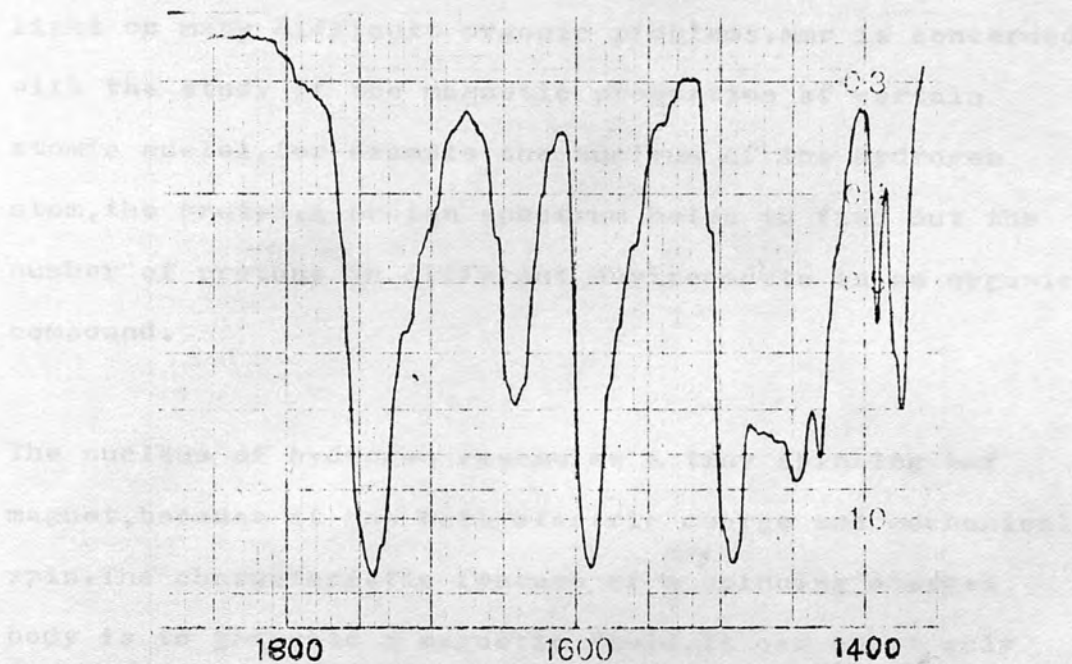


7,8-Dimethylcamphorquinoxaline
Spectrum No. 21

Camphorquinone-p- anisylimine(nujol mull)
p-disubstitution pattern - Spectrum No.22



The development of IR spectroscopy is now recognized
 as one of the most important developments in the last
 50 years. C=O, C=N and aromatic C=C stretching frequencies
 of various compounds. Camphorquinone -p- anisylimine



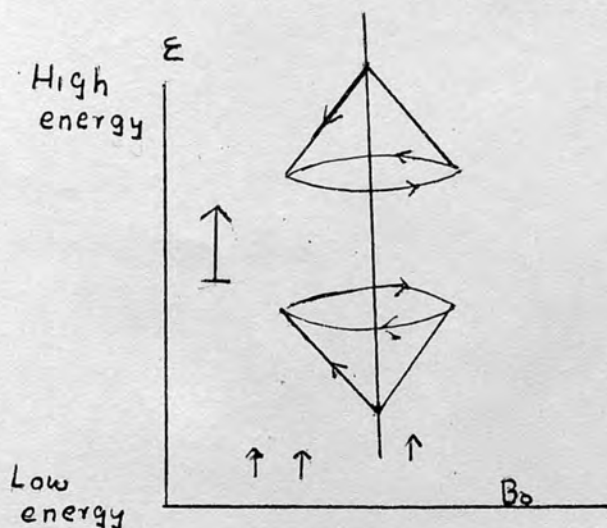
Spectrum No. 23

NUCLEAR MAGNETIC RESONANCE

INTRODUCTION

The development of nmr spectroscopy is now recognised as one of the most important developments in the last fifty years for the advancement of the understanding of organic chemistry. Nmr techniques are throwing new light on many difficult organic problems. Nmr is concerned with the study of the magnetic properties of certain atomic nuclei, for example the nucleus of the hydrogen atom, the proton. A proton spectrum helps to find out the number of protons in different environments in an organic compound.

The nucleus of hydrogen resembles a tiny spinning bar magnet, because it has both electric charge and mechanical spin. The characteristic feature of ^{any} spinning charged body is to generate a magnetic field. It can adopt only two orientations with respect to the external magnetic field, either aligned with the field (low energy state) or opposed to the field (high energy state). (Fig. 4)



Representation of Precessing nuclei

Fig. 4

The precessional frequency γ , is directly proportional to the strength of the external field B_0 .

$$\gamma \propto B_0$$

When a proton is precessing in the aligned orientation it absorbs energy and passes to the opposed orientation and relaxes in the aligned orientation. If the precessing nuclei are irradiated with a beam of radio frequency energy equal to that of the proton's precessing frequency this may be absorbed by the low energy nuclei to attain a higher energy state. Then the nucleus and the radio frequency beam are said to be in resonance, hence the term nuclear magnetic resonance.

The precessional frequency of protons differ⁶ in different chemical environments. This was first observed by Packard in 1951. He found different values for the precessional frequency of the proton for different chemical environments. E.g. for ethanol he found three different precessional frequencies of the protons corresponding to the three different environments (CH_3 , CH_2 and CH). Thus the term chemical shift came into use.

The precessional frequencies are measured with respect to some reference group. The universally accepted reference is tetramethylsilane (Tms). This is chemically inert and gives an intense sharp signal at low concentrations, and can be removed from the sample easily, and it is soluble in most solvents, so it is used as an internal standard.

The nmr spectrometer scans from low-field to high-field. The low-field values on the left and high-field on the right (Fig 5)

$$\delta = \frac{\nu_{\text{Sample}} - \nu_{\text{reference}}}{\text{Oscillator frequency (HZ)}} \times 10^{-6}$$

Chemical shift positions are expressed in ' δ ' units, which are the differences in ppm from TMS.

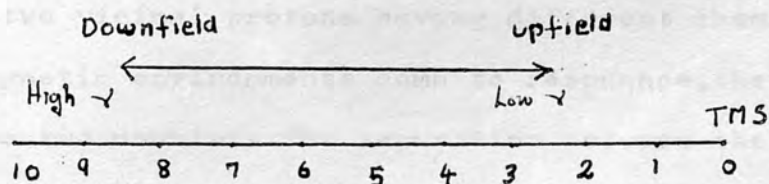


Fig.5

TMS has a sharp signal at δ '0' and most of the signals for protons appear to the left of the TMS signals or ppm downfield from TMS. Larger values of ' δ ' indicates a greater separation from TMS. In other words these protons that have high ' δ ' values are less shielded.

Chemical shift

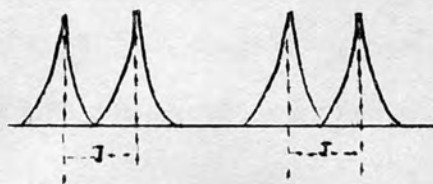
It is known that the field experienced by a nucleus in an atom is not precisely equal to the applied field because the nucleus is to some extent shielded by the extra nuclear electrons associated with it and by the neighbouring nuclei. The electron shielding in atoms and nuclei is due to the motion of electrons in a magnetic field. This is the origins of diamagnetism and the chemical shift.

Splitting of Nmr signals

In an nmr spectrum we may see the spectral lines split. This is due to the coupling interaction between adjacent protons and it is related to the number of possible spin orientation that these two can adopt. The number of lines appearing in a signal is related to the number of neighbouring protons.

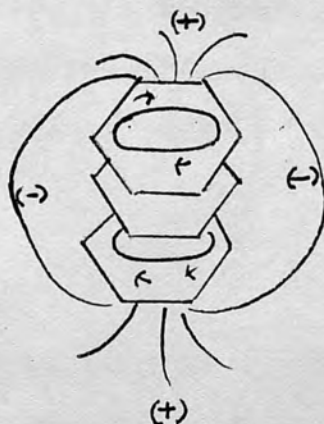
Coupling constant

When two vicinal protons having different chemical and magnetic environments come to resonance, they give rise to two doublets. The separation between the two lines of each doublet is equal. This spacing is called the coupling constant J .



Aromatic system

In an aromatic system the ' π ' electrons are cyclically delocalised in a magnetic field and are induced to circulate over the ring forming a ring current. Fig 6



Electron density, ring currents and magnetic lines of forces about a benzene ring.

Fig. 6

Protons around the periphery of the ring experience a magnetic field greater than the applied field and come to resonance at high δ '. Protons held above or below the plane of the ring come to resonance at low δ '. For example in toluene, the methyl protons resonate at δ 2.43, whereas a methyl group attached to an acyclic conjugated alkene appears at δ 1.95.³³

Aromatic Protons

The signal for ring protons are found in the low field region due to the strong deshielding effect of the ring. For example in benzene the ring protons are found at δ 7.27 ppm and in substituted benzenes, between δ 6.5 and δ 8.00 depending on the substituents.

Heterocyclic Protons

The signals for the heterocyclic protons in six-membered nitrogen containing rings are in the region between δ 6.9 and δ 8.5 ppm.

Double bond

In an alkene system, any group held above or below the plane of the double bond will experience a shielding, whereas those in the plane of the double

bond are deshielded.

An example is α -pinene. Fig. 8

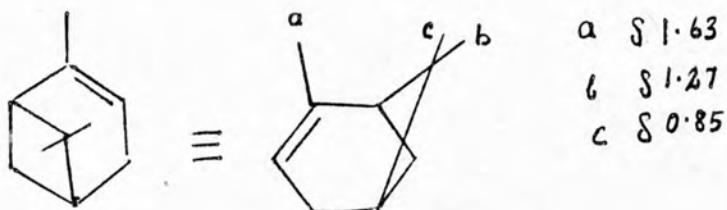
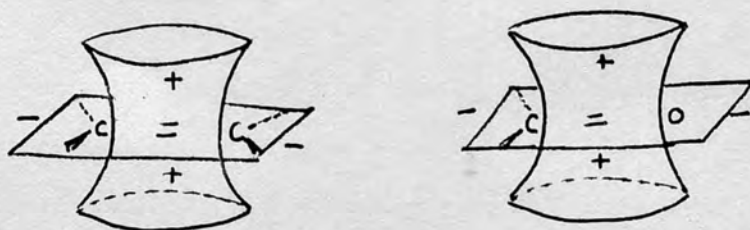


Fig. 8

In α -pinene one of the geminal methyl group is held in such a shielded position and comes to resonance at a significantly lower ' δ ' than its twin methyl group. The third methyl group appears at higher ' δ ' since it lies in the plane of the double bond and is deshielded.³³

Carbonyl group

Shielding and deshielding in compounds containing carbonyl groups are similar to that in olefinic compounds. Aldehydic protons appear at a higher value whereas others held above or below the plane come to resonance at low ' δ '. Fig. 7



The shielding region about an olefinic double bond and a carbonyl double bond.

Fig. 7

Methyl Protons

A methyl group has the freedom to rotate at room temperature about its threefold axis of symmetry. The methyl protons are magnetically equivalent and exhibit a three-proton signal in an nmr spectrum. In cases where the deshielding effect of neighbours is negligible, the methyl protons show signals at highfield. An electron attracting group in the molecule, within three bonds of the methyl group, has a ^{de} shielding effect on the methyl proton signals.

Methoxyl and N-methyl Protons

Due to the electron withdrawing effect, methoxyl protons show a sharp singlet between δ 3.20-3.40 region, in the case of acyclic systems. In cyclic systems it gets shifted to even lower fields.

The deshielding effect of nitrogen is less than that of oxygen, so the signal for N-methyl protons in saturated acyclic systems, is in the region δ 2.00-2.20. Presence of a heterocyclic ring causes a further downfield shift by about δ 0.7-0.9 ppm.

Methylene Protons

Protons in methylene group are less shielded than methyl protons and therefore absorb at lower frequency. In an acyclic system sharp bands are observed, but in cyclic systems, the complex spin-spin coupling of adjacent protons yields a broad multiplet.

Methine protons

The signals for methine protons appear further downfield. Due to the presence of only one H atom the intensity is comparatively low, which helps to distinguish the signals from those of methylene protons.³⁵

NH protons

Protons attached to a nitrogen atom experience a deshielding effect. When a proton is bound to a nitrogen atom, the signals are broadened. In certain cases it is difficult to distinguish the signal from the noise.³⁵ This is due to the fact that the nitrogen atom has a quadrupole moment which gives rise to a strong relaxation mechanism, if the electron charge distribution around it is sufficiently asymmetric.³⁶

Amides - Rotation about the double bond

The C-N bond in amides has partial double bond characters and this results in restricted rotation about the C-N bond.

So the two substituents show separate signals. In the case of dimethyl formamide (Fig. 9) at room temperature, Annet and Bown³⁴ have shown by the use of the nuclear overhauser effect, that the methyl group cis to the carbonyl group (CH_3^a) is more shielded than the methyl group trans to the carbonyl group (CH_3^b). But only one signal was observed at a higher temperature.

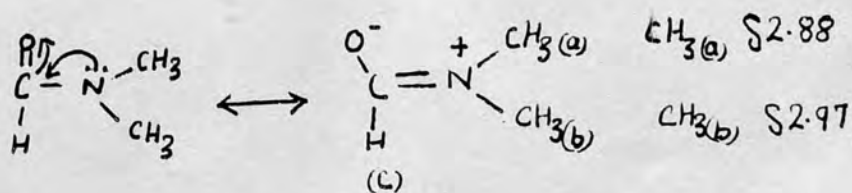


Fig. 9

DISCUSSION

Proton chemical shift values are represented in the form of tables. The spectra show the various chemical shift positions.

1. Camphorimide and its alkyl derivatives are represented in Table No.7, Spectra (25,26,27)

2. N-phenyl and N-p-anisylcamphorimide:-

Table No.8, Spectra No.(28,29).

3. Quinoxalines:-

Table No.9, Spectra No.(30-33).

4. Pteridine dione and Camphorquinone-p-

anisylimine:- Table No.10, Spectra No.(34+35).

TMS was used as an internal standard.

Solvent: CDCl_3

Methyl protons

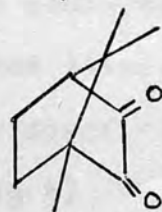
Camphor has three signals for its three methyl protons.

(Fig. a)



(a)

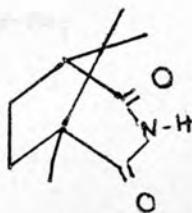
³⁷Hinkley has used lanthanide shift reagents to find out the different chemical shift positions for camphor group protons. The assignments are δ 0.86 (10-methyl group), δ 0.83 (8-methyl group) and δ 0.95 (9-methyl group) protons. The maximum lanthanide induced shift was shown by the 10-methyl group and the medium shift by the 8-methyl group. The 9-methyl group was not affected because of its distance from the carbonyl group so the signal remained unchanged. Connolly and McCrindle³⁸ have previously assigned (δ 0.91 for 10-methyl, δ 0.83 for 8-methyl and δ 0.97 for 9-methyl group), which is also in agreement with Hinkley's assignment when solvent change from CH_2Cl_2 to CCl_4 is taken into account.



(h)

Camphorquinone (Fig. h) Spectrum No. 24) has three signals at δ 1.09, δ 1.06, δ 0.92 respectively for its three methyl groups. The signal at δ 1.06 could be due

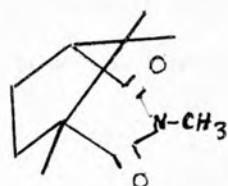
to the 8-methyl group, since the model shows that it is outside the cone of the carbonyl group which experiences shielding. The resonance at δ 1.09 was assigned to the 10-methyl group which is in the plane of the carbonyl group. The signal upfield at δ 0.92 was assigned to the least affected 9-methyl group.



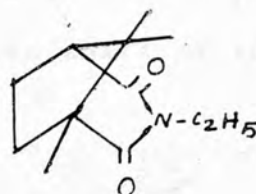
9

Camphorimide (Fig. 9, Spectrum No. 25) has three signals at δ 1.14, δ 1.02 and δ 0.96 for its three methyl groups. The maximum downfield shift could be due to the 11-methyl group, the medium shift to the 9-methyl group and the resonance at δ 0.96 for 10-methyl group. Being a seven-membered ring, it has more flexibility and this probably accounts for the different values compared to those of camphor and camphorquinone. The introduction of the nitrogen atom could be contributing to the downfield shift of the 11-methyl group protons. The shift is 0.05ppm downfield compared to that of camphorquinone (Fig. h)

The N-methylcamphorimide (Fig. i, Spectrum No.26) Shows only two signals for its three methyl group protons.



(i)



(j)

δ 1.20 (11-methyl), δ 0.98 (9-methyl and 10-methyl) groups protons. The 11-methyl group shows a deshielding of δ 0.06 ppm more than that of camphorimide. The 9-methyl signal could have shifted upfield coinciding with the signal for 10-methyl, so only one signal is observed at δ 0.98.

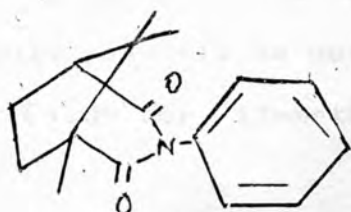
The N-ethylcamphorimide (Fig. j), Spectrum No.27) also has two signals for its three methyl group protons.

δ 1.21 (11-methyl) and δ 0.97 for (9 and 10-methyl) group protons. Integration shows two sets of protons for the signal upfield and one set for the signal downfield.

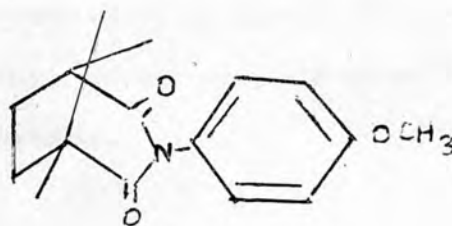
The N-phenylcamphorimide (Fig. m, Spectrum No. 28), has three signals^s for its three methyl groups.

δ 1.25 (11-methyl), δ 1.20 (9-methyl) and δ 1.04 for (10-methyl) group protons.

The N-p-anisylcamphorimide (Fig. n, Spectrum No. 29) has three signals at δ 1.22 (11-methyl), δ 1.20 (9-methyl) and δ 1.00 (10-methyl) groups. In these compounds the further down field shift compared to the aliphatic imides, is due to the paramagnetic shift of the aromatic ring.



(m)



(n)

The three signals shown by the quinoxalines for their three methyl groups are as follows:-

Camphorquinoxaline (Fig. o, Spectrum No. 30) has its signals at δ 0.62, δ 1.10 and δ 1.14 respectively.

7 or (8)-methylcamphorquinoxaline (Fig. p, Spectrum No. 31) has its signals at δ 0.62, δ 1.11 and δ 1.43 respectively.

7,8-dimethylcamphorquinoxaline (Fig. q, Spectrum No. 33) has δ 0.62, δ 1.09 and δ 1.42.

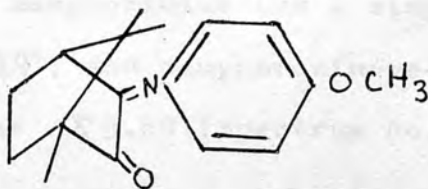
7 or (8)-chlorocamphorquinoxaline (Fig. r, Spectrum No. 32) shows three signals at δ 0.65, δ 1.11 and δ 1.45 respectively.

One of the methyl signals in the quinoxaline is shielded. Since the 12-methyl group is above the heterocyclic ring, it is possible for it to experience a shielding effect due to the electron sheath below it. So that the signal upfield between δ 0.62 and δ 0.65 in these compounds could be for the 12-methyl group.

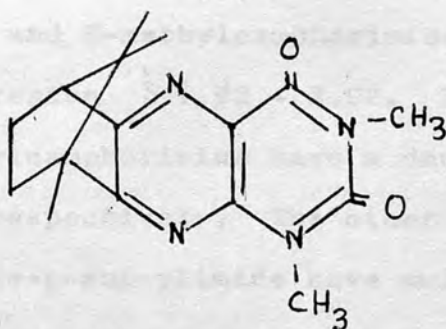
The signal downfield between $\delta 1.14$ and $\delta 1.45$ could be assigned to the 14-methyl group due to its proximity to the nitrogen atom. The signal in between $\delta 1.09$ and $\delta 1.11$ can be assigned to the least affected 13-methyl group.

The pteridine dione (Fig. t, Spectrum No. 35) also has one methyl group shielded, appearing at $\delta 0.61$, which could be assigned to the 12-methyl protons. The signal at $\delta 1.36$ could possibly be due to 14-methyl group and the signal at $\delta 1.09$ for 13-methyl group protons.

Camphorquinone-*p*-anisylimine (Fig. s, Spectrum No. 34) has its chemical shift values for its methyl protons similar to those of camphor.



(s)



(t)

Since, the 10-methyl group is in the plane of the carbonyl double bond, the signal at $\delta 0.87$ was assigned to it. The signals at $\delta 0.99$ and $\delta 1.10$ are assigned to the 9- and 8- methyl protons respectively.

Methyl protons attached to nitrogen atom

N-methylcamphorimide has a signal at δ 3.04 for its N-methyl protons (Spectrum No.26). The pteridine compound (t) has two sharp signals at δ 3.61 and δ 3.84 (Spectrum No.35).

Methyl protons in the aromatic ring

The 7 or (8)-methyl camphorquinoxaline has a singlet at δ 2.67 and the 7,8-dimethyl camphorquinoxaline has a singlet at δ 3.42 (Spectra Nos. 31 and 33)

Methoxy protons

The N-p-anisyl camphorimide has a singlet at δ 3.78 (Spectrum No.29), and camphorquinone-p-anisylimine has a singlet at δ 3.80 (Spectrum No.34).

Methylene protons

Camphorimide and N-methylcamphorimide show a multiplet in the region δ 1.92 - 2.02. The N-phenyl and N-p-anisylcamphorimide have a doublet at δ 2.10 and δ 2.05 respectively. The other compounds except camphorquinone-p-anisylimine have multiplet in the δ 2.0 - 2.2 region, which is not distinguishable from the noise. Camphorquinone-p-anisylimine has two signals with a midpoint at δ 1.85.

The methylene protons in N-ethylcamphorimide appear as a quartet with its midpoint at δ 2.73 (Spectrum No.27)

Methine protons

In camphorimide, the signals appear in the δ 2.65-2.68 region as an ill defined band. But in the rest of the N-substituted derivatives this signal is in the region δ 2.73 - 2.85 as a doublet. In quinoxalines this signal is found in the region δ 3.10, the pteridine dione at δ 3.25 and in camphorquinone-p-anisylimine at δ 2.9 respectively.

N-H protons

Camphorimide has a broad signal at δ 8.50 for its NH proton.

Aromatic protons

The N-phenylcamphorimide (Fig. m, spectrum no. 28) has a multiplet with its midpoint at δ 7.45. The set downfield was assigned to protons H-16 and H-12, and the set upfield to the protons H-13, H-14 and H-15 respectively.

The N-p-anisylcamphorimide (Fig. n, Spectrum No. 29) has only one signal at δ 6.99.

In N-phenylcamphorimide, the downfield shift of the signals is considered as due to the proximity of the nitrogen atom. In the N-p-anisyl compound the two protons nearer to the nitrogen must be shielded to the same extent as those nearer to the methoxy group so we see only one signal.

The camphorquinoxaline (Fig. 0, Spectrum No. 30) shows two sets of multiplets. The signals downfield at $\delta 7.94-8.10$ are assigned to the protons H-6 and H-9, the signals upfield at $\delta 7.56-7.70$ to the protons H-7 and H-8 respectively.

The 7 or(8)-methylcamphorquinoxaline (Fig. p, Spectrum No. 31) has two sets of signals for its aromatic protons. The signals downfield at $\delta 7.82$ and $\delta 7.87$ are assigned to the protons H-6 and H-9, the signal at $\delta 7.50$ for H-8.

The 7,8-dimethylcamphorquinoxaline (Fig. q, Spectrum No. 33) has two signals for its aromatic protons H-6 and H-9 at $\delta 7.73$ and $\delta 7.80$ due to their different chemical environment.

The 7 or(8)-chlorocamphorquinoxaline (Fig. r, Spectrum No. 32) has two sets of signals for its aromatic protons. The set downfield at $\delta 8.02$ and $\delta 8.05$ are assigned to the proton (6-H) which shows only meta coupling. The signal at $\delta 7.97$ and $\delta 7.87$ are for (9-H), which shows only ortho coupling. The signals upfield at $\delta 7.59$ and 7.62 , $\delta 7.52$ and $\delta 7.49$ for (8-H) which is showing an ortho and meta coupling.

Black and Heffernan³⁹ have studied the spectrum of quinoxaline in acetone and in carbon tetrachloride solution. They consider the signals downfield of the spectrum are due to the deshielding effect of nitrogen atoms proximate to the protons in the ring.

TABLE 7

Proton Chemical Shift Data for Alkyl Imides
in CDCl_3

x The values are in δ' (ppm) from TMS

Compounds	CH_3	CH_2	CH	N- CH_3	N- CH_2CH_3
Camphori- mide	0.96(s) 1.02(s) 1.14(s)	1.92- 2.02	2.60		
N-methyl- camphori- mide	0.98(s) 1.20(s)	1.82- 2.01	2.77	3.04 (s)	
N-ethyl- camphori- mide	0.97(s) 1.21(s)	1.86 2.02	2.73		3.73(q)

TABLE 8

Proton Chemical Shift Data for Aryl Imides
in CDCl_3

Compounds	CH_3	CH_2	CH	O- CH_3	Aromatic Protons
N-phenyl- camphori- mide	1.04(s) 1.20(s) 1.25(s)	2.10 (m)	2.85		7.05(m) 7.45
N-p-anisyl- camphori- mide	1.00(s) 1.20(s) 1.22(s)	2.05 (m)	2.82	3.78	6.99(s)

s = singlet, m = multiplet, q = quartet.

TABLE 9

Proton Chemical Shift Data for quinoxalines in CDCl_3 The values are in δ (ppm) from TMS

Compounds	CH_3	CH_2	CH_3 (ring)	CH	Aromatic Protons
Camphor- quinoxala- line	0.62(s) 1.10(s) 1.44(s)	2.26(m) 2.31		3.04(d) 3.08	7.56 7.70 7.94 8.10
7 or (8)- methyl- camphor- quinoxala- line	0.62(s) 1.11(s) 1.43(s)	1.60(m) 2.20	2.55 (s)	3.01(d) 3.05	7.51 (8H) 7.82(m) 7.87 (6-H and 9-H)
7 or (8)- chloro- camphor- quinoxala- line	0.65(s) 1.11(s) 1.45(s)	1.97(m) 2.31		3.07(d) 3.12	7.49 7.52 7.59 7.62 7.97 8.02 8.05
7,8-dime- thyl- camphor- quinoxala- line	0.62(s) 1.09(s) 1.42(s)	1.60(m) 2.0	2.42 (s)	2.99(d) 3.04	7.73 7.80

s = singlet, d = doublet, m = multiplet

TABLE 10

Proton Chemical Shift Data for Pteridine dione and
Camphorquinone-p-anisylimine in CDCl_3

The values are in δ' (ppm) from TMS

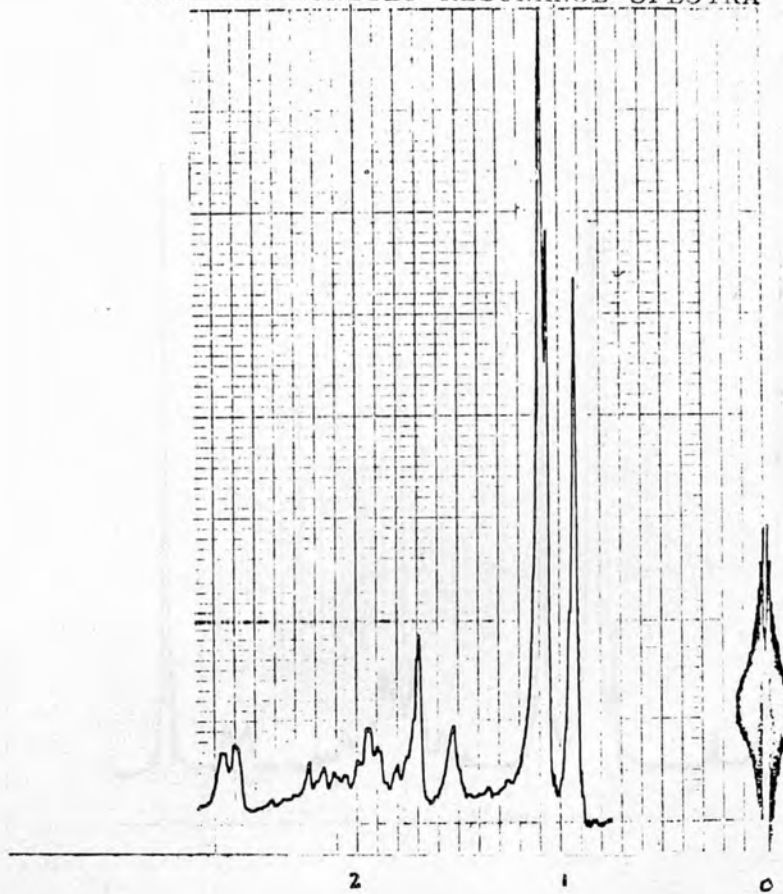
Compounds	CH_3	CH_2	CH	N- CH_3	O- CH_3	Aromatics
Pteridine	0.61 (s)			3.53		
dione	1.09 (s)	2.16	3.14	3.75		
	1.36 (s)	(m)	(d)	(s)		
Camphor-	0.87 (s)	1.59	2.90		3.80	6.94 (s)
quinone-	0.99 (s)	1.89	2.95		(s)	6.96
<u>p</u> -anisyl-	1.09 (s)	(m)	(d)			
imine						

s = singlet

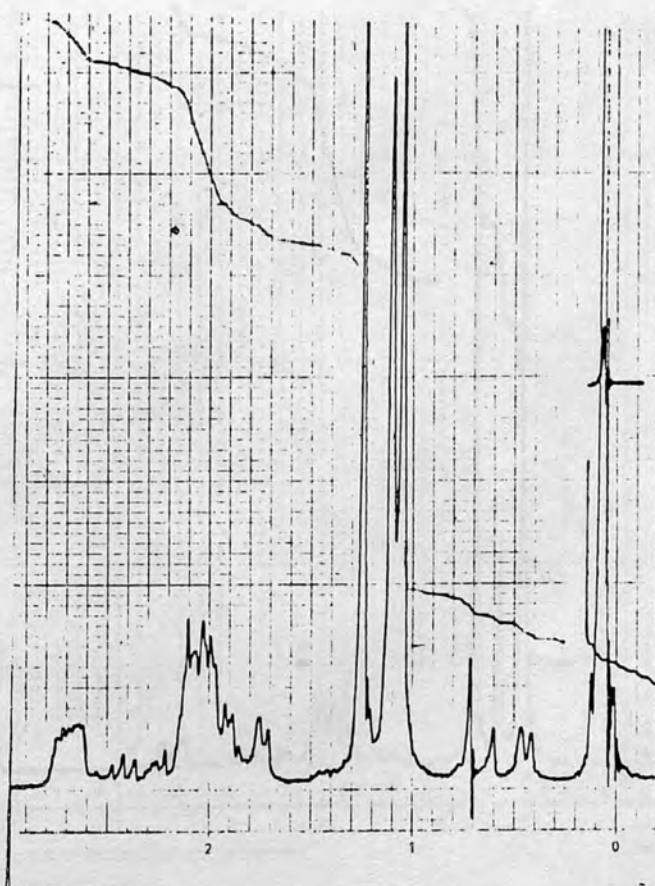
d = doublet

m = multiplet.

NUCLEARMAGNETIC RESONANCE SPECTRA

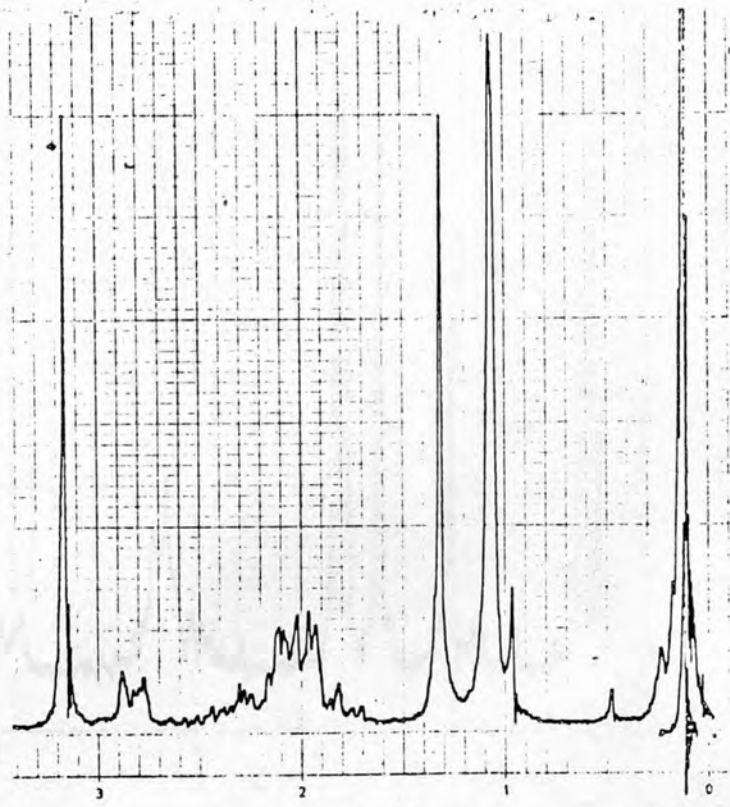


Camphorquinone
Spectrum No. 24

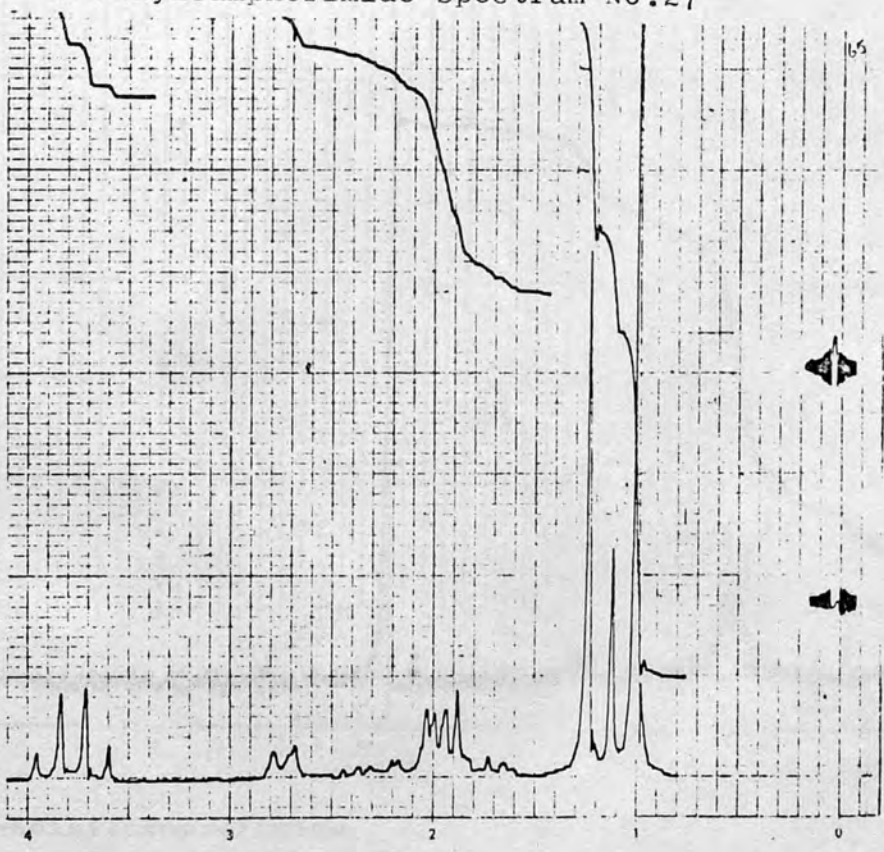


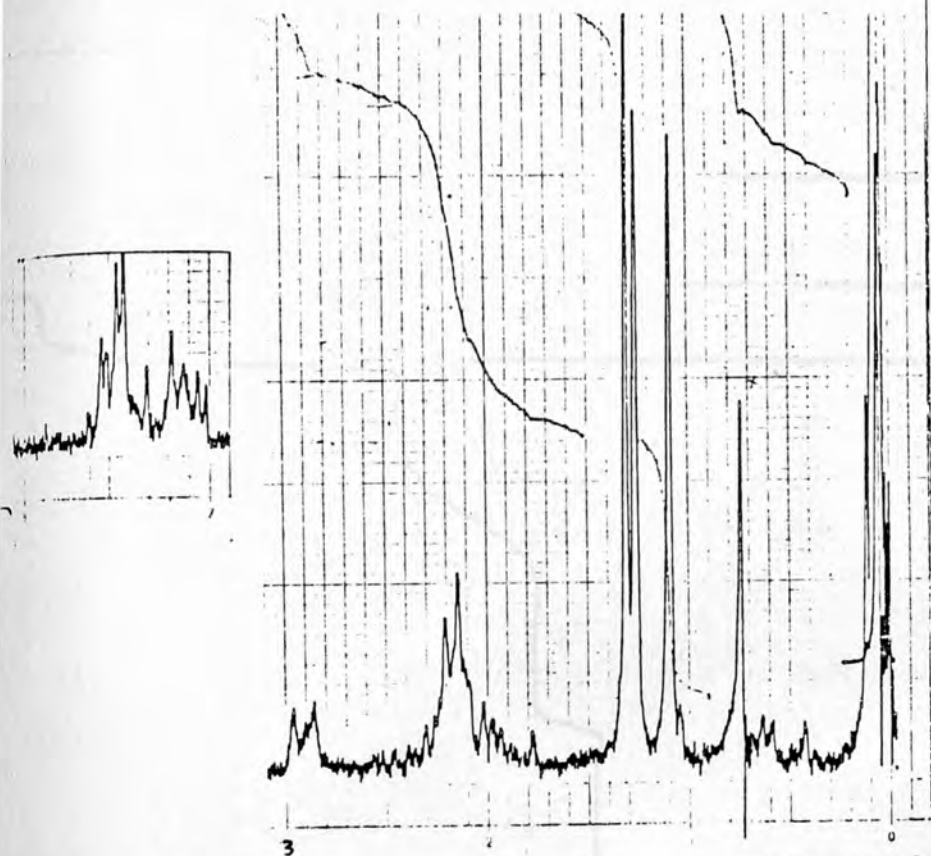
Camphorimide
Spectrum No. 25

N-methylcamphorimide Spectrum No.26



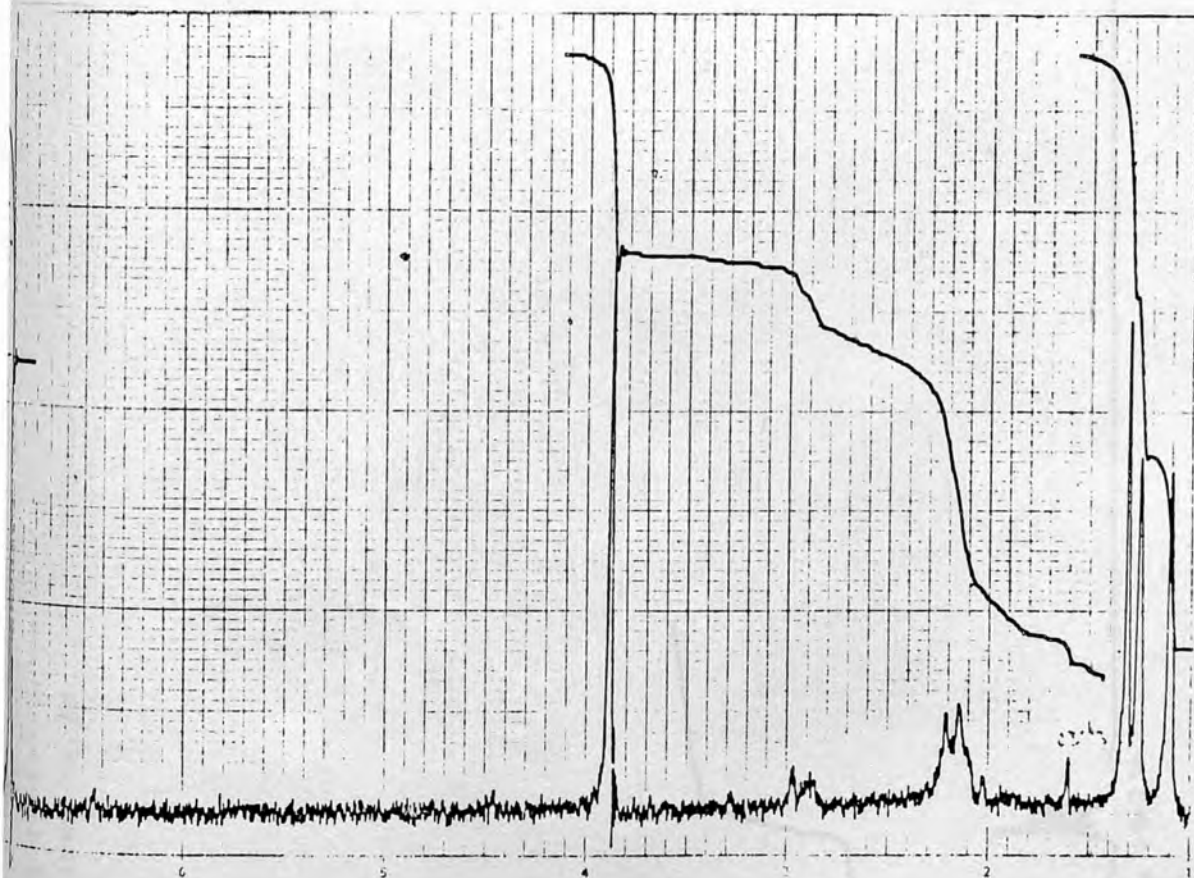
N-methylcamphorimide Spectrum No.27





N-Phenylcamphorimide

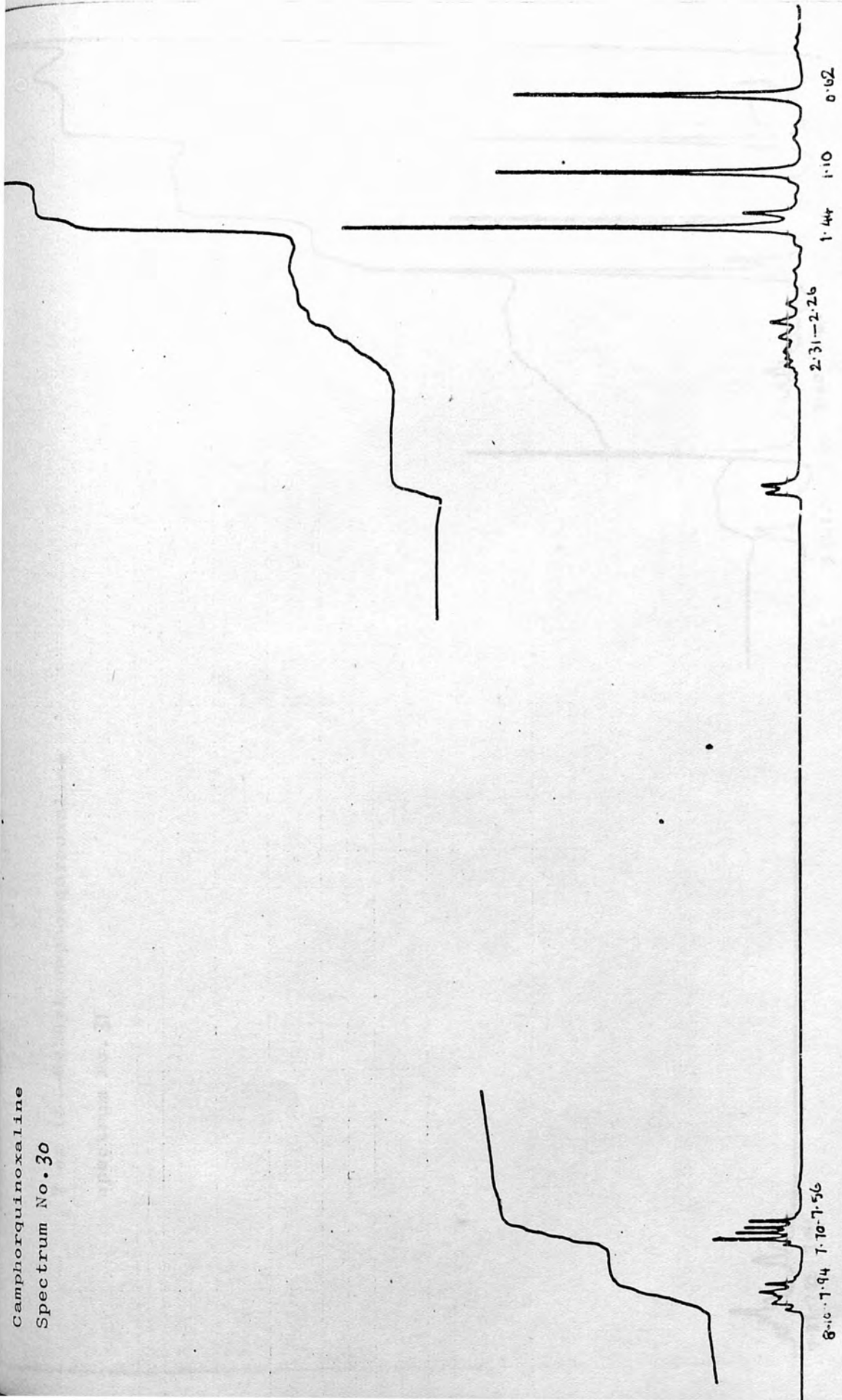
Spectrum No. 28



N-p-anisylcamphorimide

Spectrum No. 29

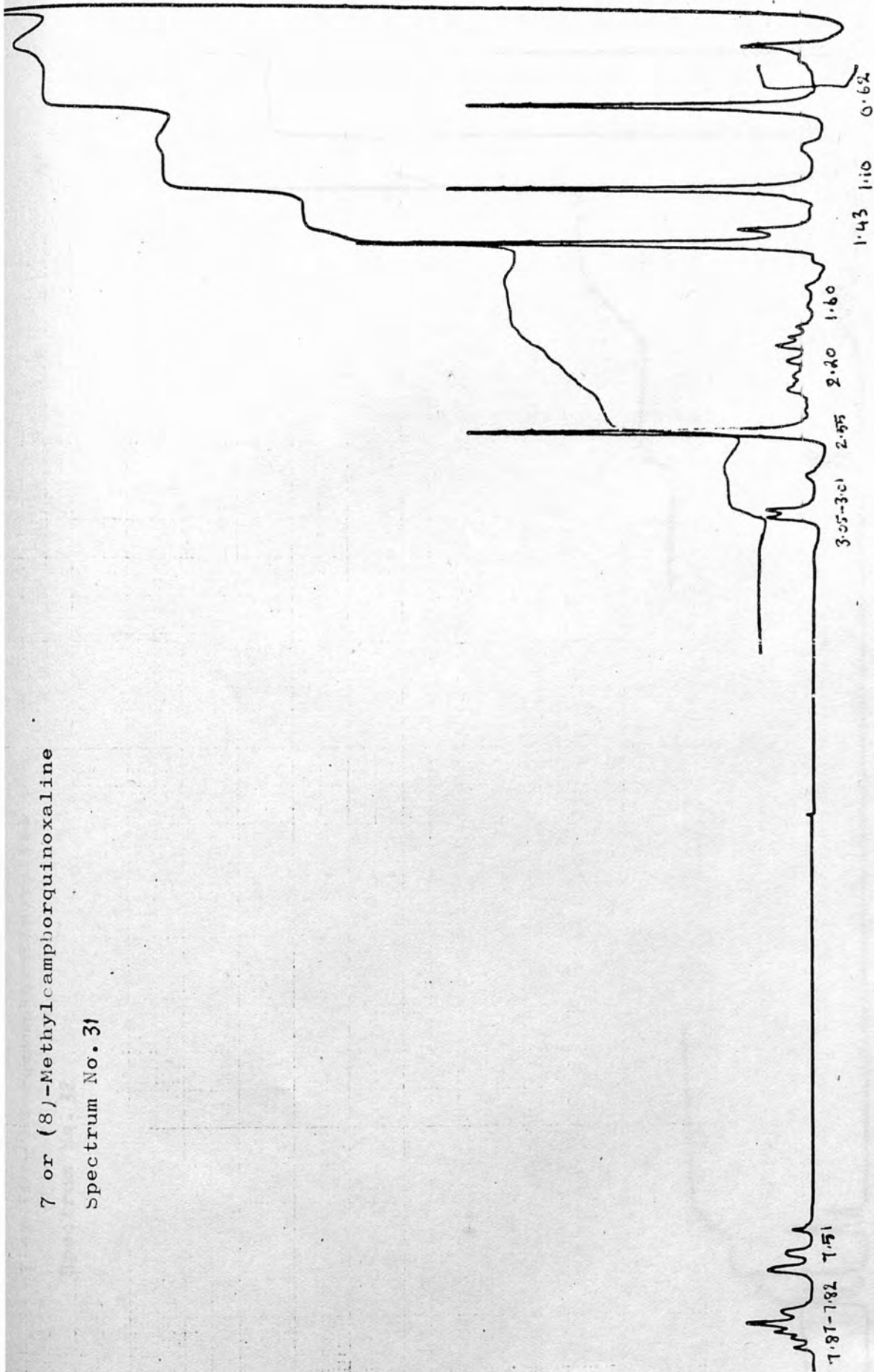
Camphorquinoxaline
Spectrum No. 30



δ (ppm)

7 or (8)-Methylcamphorquinoline

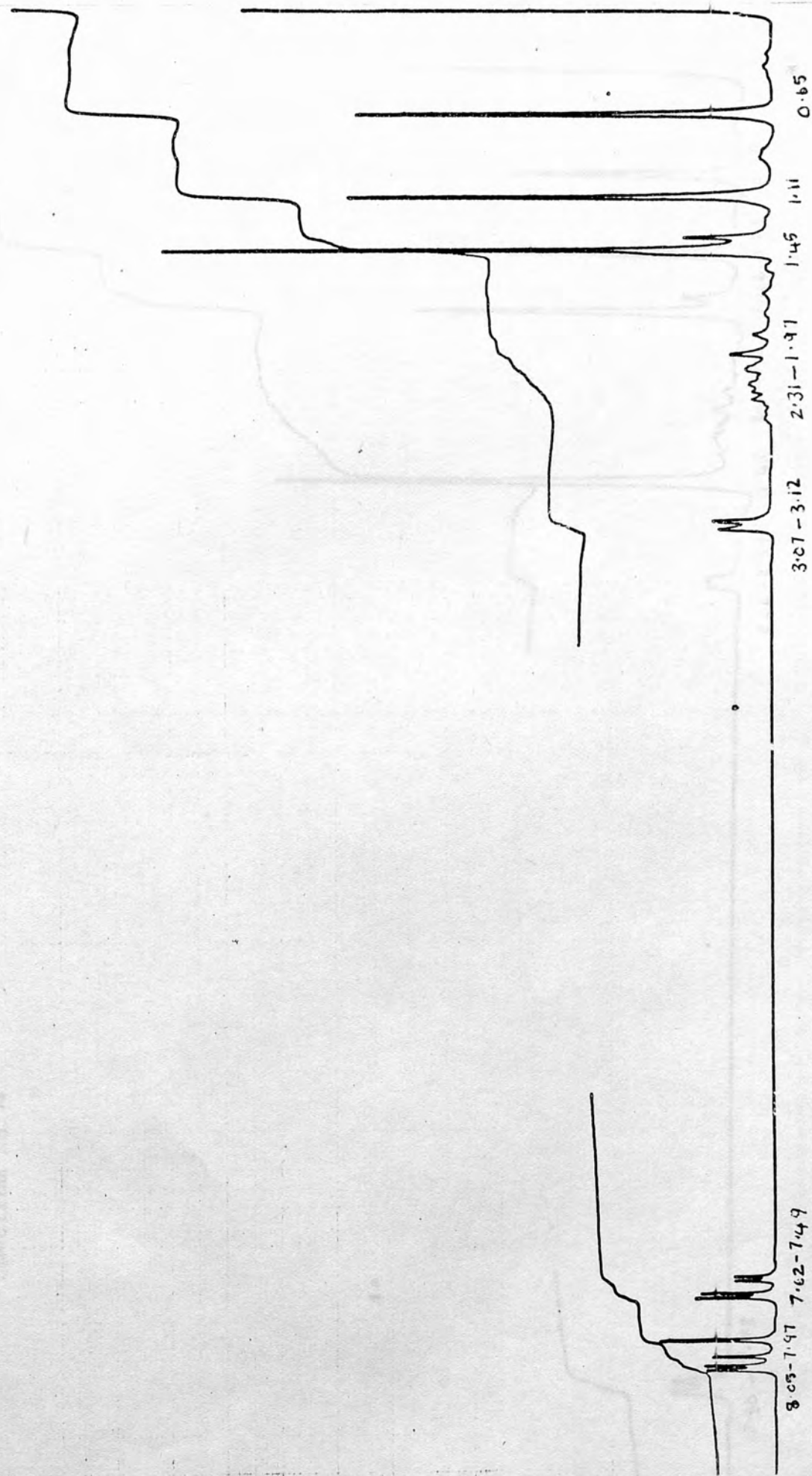
Spectrum No. 31



δ (ppm)

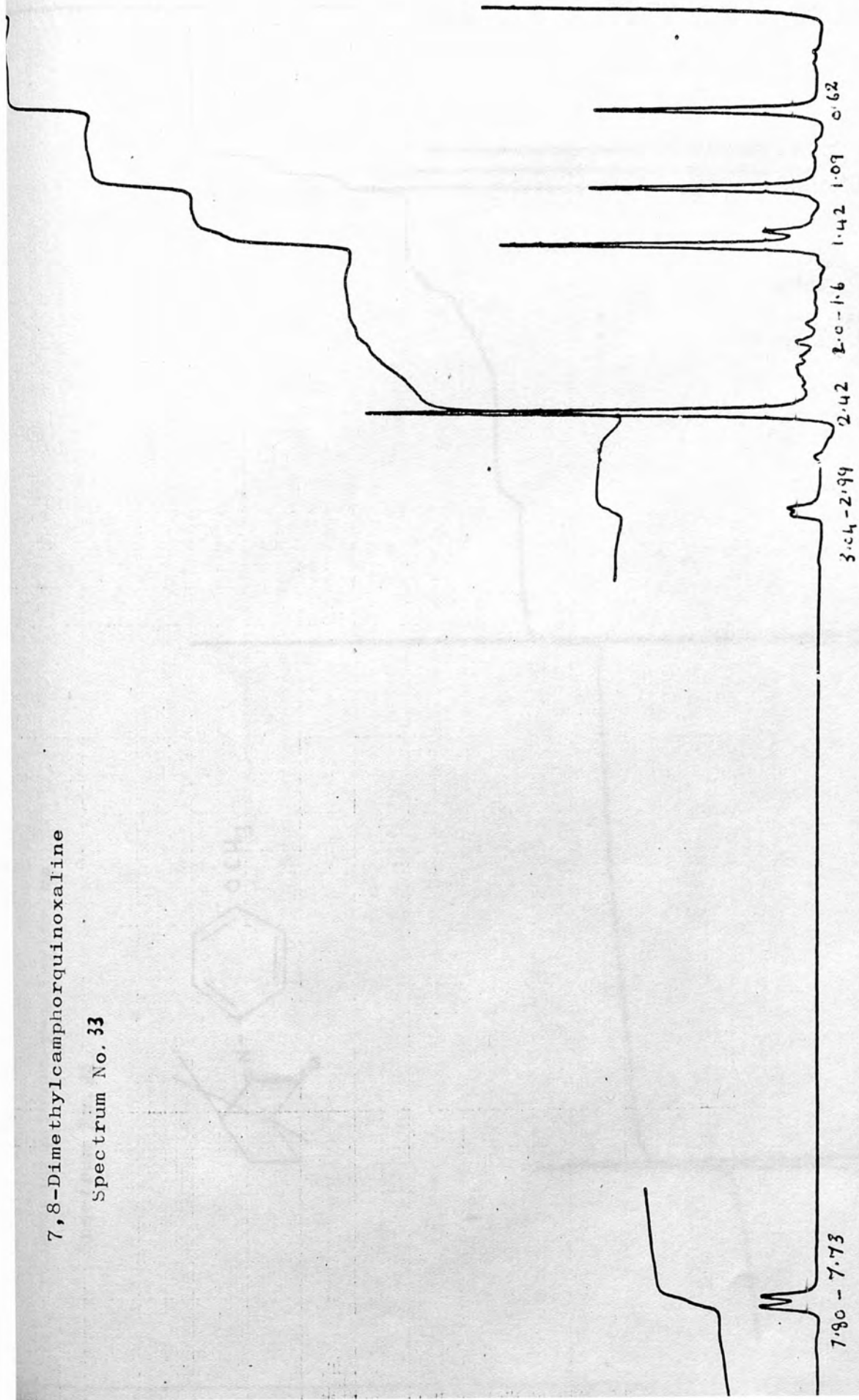
7 or (8)-Chlorocamphorquinoxaline

Spectrum No. 32



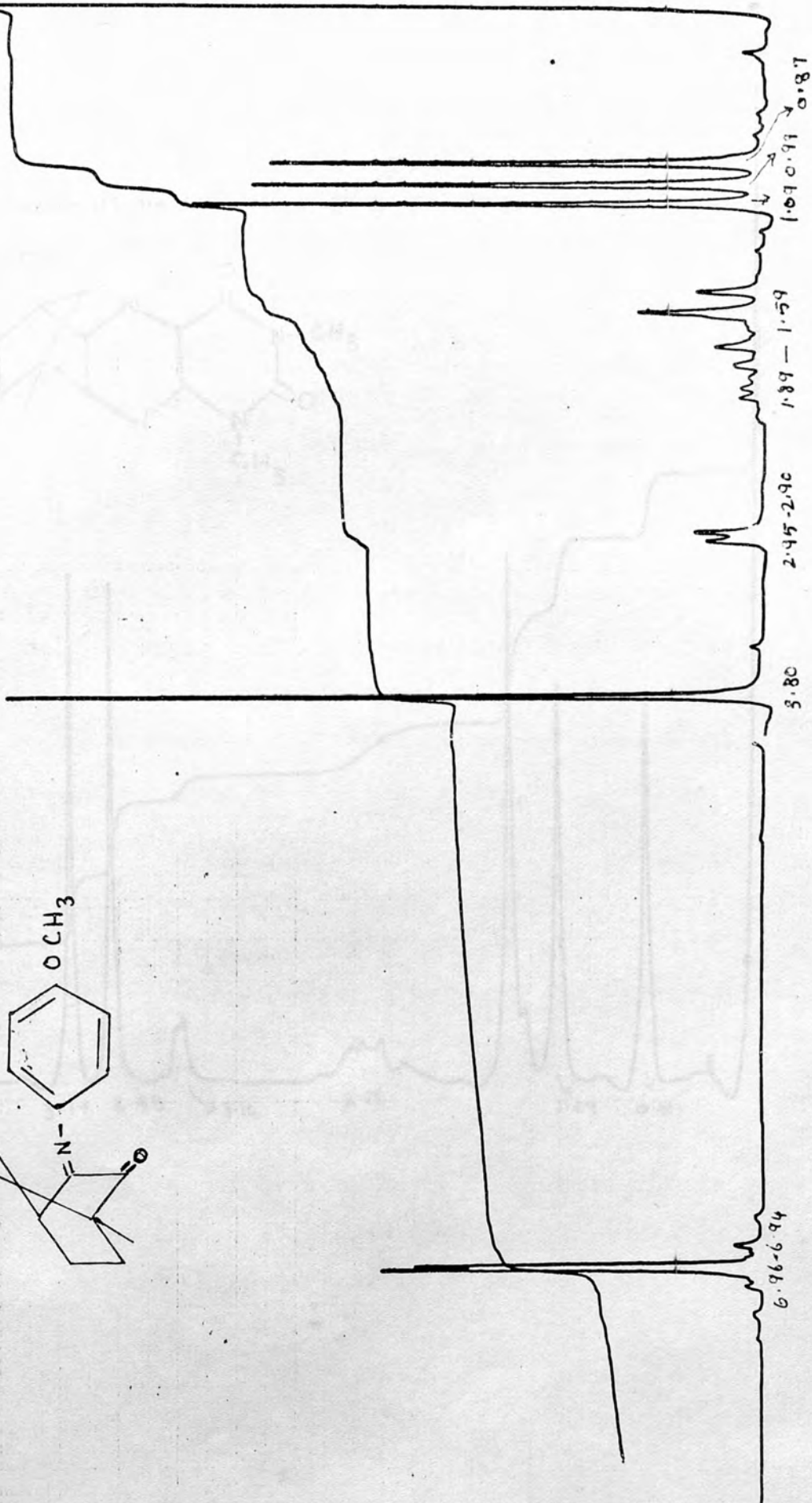
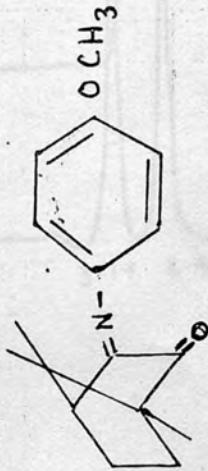
7,8-Dimethylcamphorquinoline

Spectrum No. 33



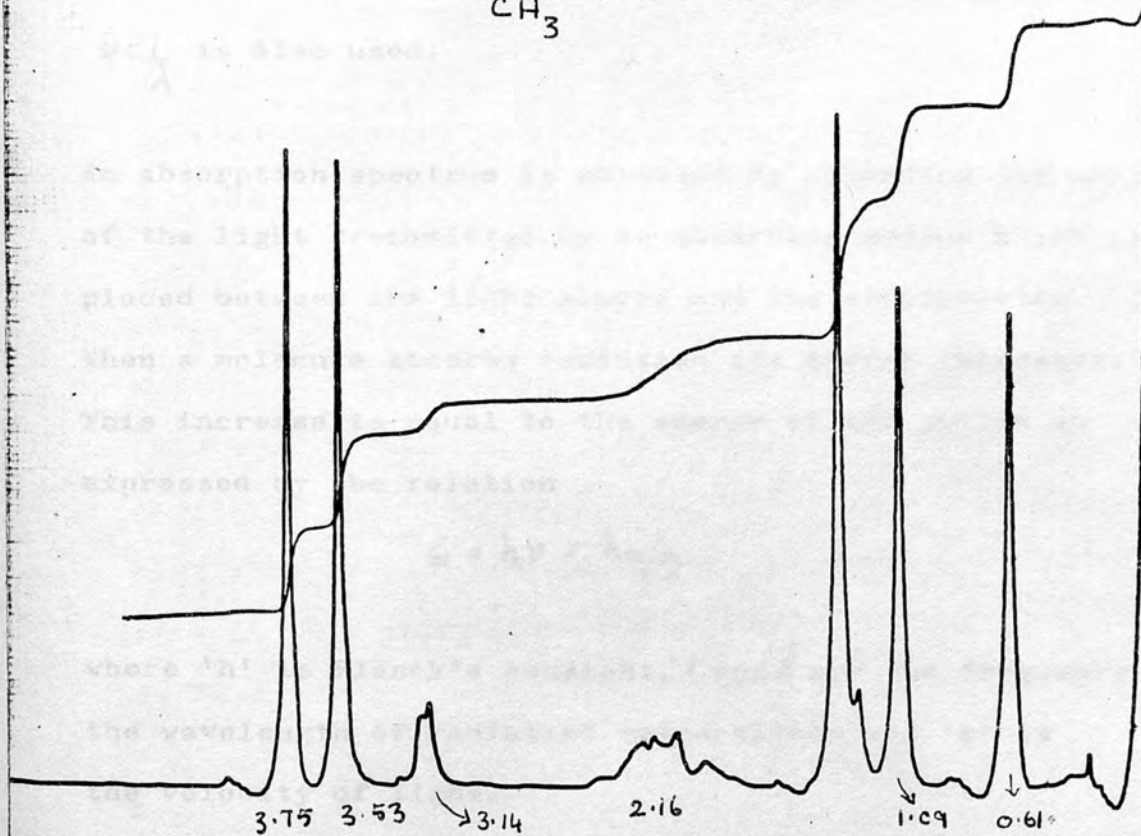
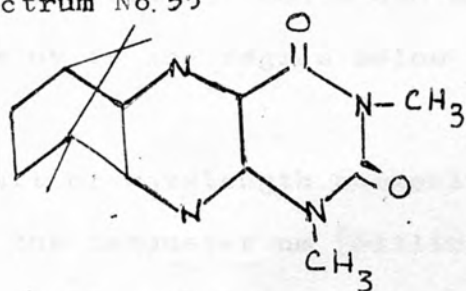
Camphorquinone-p-anisylimine

Spectrum No. 34



Pteridine dione

Spectrum No. 35



ULTRAVIOLET SPECTRA

The electronic spectrum covers a wide range of wavelengths between 100 - 800 nm. The visible region to which the human eye is sensitive, corresponds to the wavelengths range between 400 - 800 nm. The near uv region is between 200 - 400 nm and the far uv or vacuum uv is the region below 200 nm.

The unit of wavelength commonly used in uv or visible uv is the nanometer nm (millimicrons $m\mu$). The wavenumber $\bar{\nu} = \frac{1}{\lambda}$ is also used.

An absorption spectrum is obtained by recording the analysis of the light transmitted by an absorbing medium which is placed between the light source and the spectrometer. When a molecule absorbs radiation its energy increases. This increase is equal to the energy of the photon as expressed by the relation

$$E = h\nu = hc/\lambda$$

where 'h' is Planck's constant, ν and λ are the frequency and the wavelength of radiation respectively and 'c' is the velocity of light.

If the energy absorbed by a molecule from radiation is very intense as in the case of ultraviolet light, changes in the electronic, vibrational and rotational energies will take place.

The Beer-Lambert law states that the fraction of incident light absorbed is proportional to the number of molecules in the path. That is, if a substance is dissolved in a solvent, the absorption by the solution will be proportional to the molecular concentration provided the solvent itself does not have any absorption in that region. Absorbance = ϵcl where ' ϵ ' is the absorption coefficient, 'c' is the concentration in moles and 'l' is the path length in cm. The data on absorption are usually presented as absorption curves. The units of absorption are plotted as ordinates and the unit of wavelength as abscissae, that is ϵ or $\log \epsilon$ against wavelength nm.

Ultraviolet absorption spectra result from the interaction of light quanta with electrons. Under favourable conditions these interactions raise the potential energy of the electrons. The system containing such electrons is referred to as the excited state. For example in formaldehyde the electrons are in three types of orbitals. σ , π and n (Fig. 10)

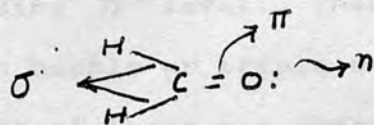
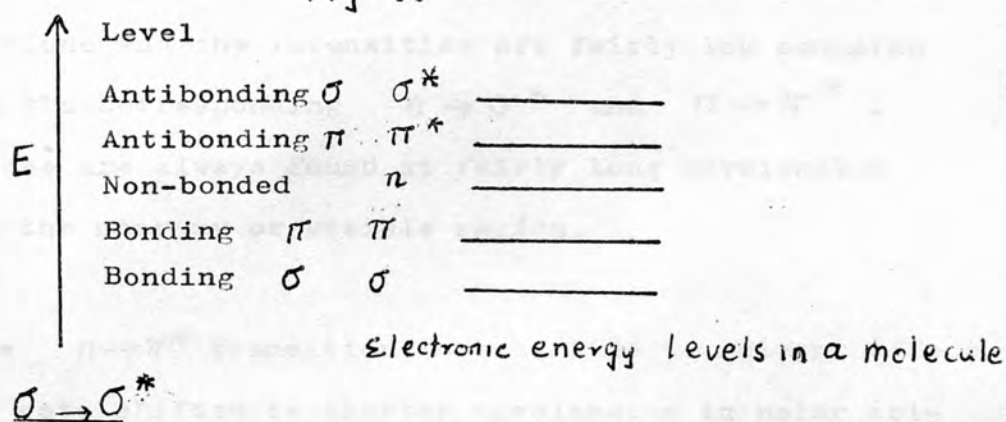


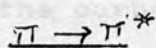
Fig. 10

Bonding electrons are more strongly bound than the non-bonded electrons. In the bonding electrons, σ electrons are more strongly bound than the π electrons. While in the antibonding level, the σ^* level has higher energy than the π^* level, which is shown below.

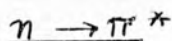
Fig. 11



σ electrons are found in saturated hydrocarbons. These are strongly bound and the excitation of these to antibonding σ^* level requires very large energies which can be obtained in the far uv region.

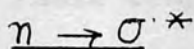


The transition in which a π -electron is excited to an antibonding π^* level. These are found in compounds with double or triple bonds or aromatic rings. Some of these are observed in the far uv, most of these in the near uv.



The transition in which an 'n'-electron in a non-bonding atomic orbital (lone pair) is excited to an antibonding π^* orbital. These occur with compounds which contain double bonds involving hetero atoms. e.g. C=O, -N=N- etc. These are the forbidden transitions and the intensities are fairly low compared to the corresponding $n \rightarrow \sigma^*$ and $\pi \rightarrow \pi^*$. These are always found at fairly long wavelengths in the near uv or visible region.

The $n \rightarrow \pi^*$ transition is sensitive to solvent effect. It gets shifted to shorter wavelengths in polar solvents (hypsochromic shift). This is a characteristic feature which differentiates the $n \rightarrow \pi^*$ from $\pi \rightarrow \pi^*$ bands. This hypsochromic shift is due to the oxygen atom of the hydroxyl group of the solvent conjugating with the carbonyl group donating electrons to the carbonyl carbon atom raising the energy of the π^* orbital with reference to the orbital occupied by the 'n' electrons in the ground state. The $n \rightarrow \pi^*$ transition energy is therefore raised and the absorption shifts to shorter wavelengths.⁴⁰



This is the transition from a non-bonding 'n' orbital to an antibonding σ orbital. The absorption is generally found in the region around 200nm.

AMIDES

Amides show characteristic absorption bands due to $n \rightarrow \pi^*$ transition around 220nm. In polar solvents it shows a blue shift.⁴¹ Amides have bands also due to $n \rightarrow \sigma^*$ and $\pi \rightarrow \pi^*$ transitions. Turner⁴² has recorded the spectra of amides and some cyclic imides in the region (175-200nm) which is not normally accessible to most spectrometers.

IMIDES

Imides have bands due to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions. Simple imides absorb in the far uv near 178nm (ϵ 8,000) and, this band is shifted in succinimide to about 194nm and in N-methyl succinimide to 204nm.²² This transition in imides could probably be and $N \rightarrow V$ transition because it gets displaced to longer wavelength due to N-substitution, also the intensity is high. The high intensity and location of the band at about 200nm in imides is entirely consistent with the $\pi \rightarrow \pi^*$ transition in the C=O group in conjugation with the lone-pair 'p' electrons of the nitrogen atom.²¹

BENZENOID AROMATICS

These compounds exhibit three main bands which are designated α , ρ and β bands.⁴³ Benzene exhibits two intense bands at about 180 and 200nm and a weak band around 260nm. All the three bands are associated

with the π electron system of benzene. The 260 nm band is mainly affected by resonance and inductive effects. Alkyl substitution intensifies and shifts the 260 nm band to longer wavelength.

HETEROCYCLIC COMPOUNDS

Heterocyclic nitrogen compounds with six membered rings have spectra which closely resemble those of their benzenoid counterparts, except that the intensity of the forbidden long wavelength $\pi \rightarrow \pi^*$ (or β -band) transition is considerably higher. The doubly bound N atom (=N-) has similar properties to those of an aromatic carbon atom (=CH-). Introduction of more nitrogens does not drastically alter the original spectrum even in polycyclic systems. The heterocyclic molecule, however, may show an additional band or inflection for the $n \rightarrow \pi^*$ transition at longer wavelengths. This may be hidden under the $\pi \rightarrow \pi^*$ band but can be revealed if the polarity of the solvent is decreased. ⁴⁴Hirt ⁴⁵and coworkers have studied the weak bands in the near uv region in quinoxaline. Simple quinoxaline in methanol has a band at 315 nm with an ϵ 6850 and another at 233 nm with ϵ 28,250, which are considered as due to the first and second $\pi \rightarrow \pi^*$ transitions. The presence of nitrogen atom introduces an $n \rightarrow \pi^*$ band at longer wavelength in case of pyridazine and pyrazine. ⁴⁶The $\pi \rightarrow \pi^*$ bands are not greatly affected in di-aza-naphthalenes ⁴⁵compared to naphthalenes.

DISCUSSION

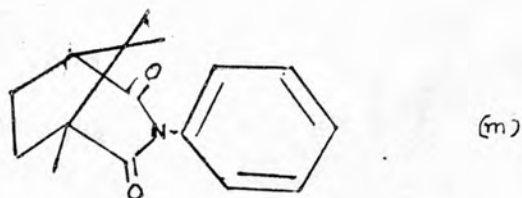
IMIDES

Camphorimide (Fig. 9, Spectrum No. 37) has a broad maximum at λ 255nm, ϵ 153, an inflection at λ 235nm, a maximum at λ 230nm, ϵ 260 and an intense band at λ 201 nm, ϵ 14,000.

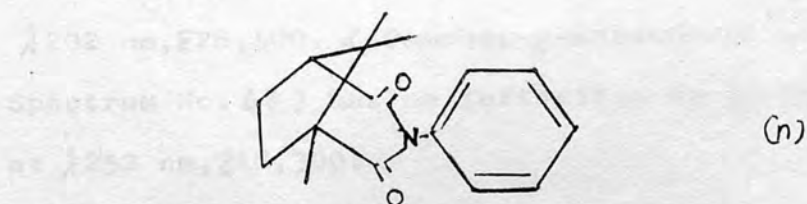
The bands in the longer wavelength with low intensity are due to symmetry-forbidden (weak) $n \rightarrow \pi^*$ transitions. The one at λ 201 nm with its high intensity could be due to $\pi \rightarrow \pi^*$ or symmetry allowed $n \rightarrow \pi^*$, similar to those of succinimide and glutarimide.

N-methylcamphorimide (Fig. i, Spectrum No. 37), has a broad shoulder at λ 255, ϵ 158, and inflection at λ 238nm and a maximum at λ 209nm, ϵ 14,200.

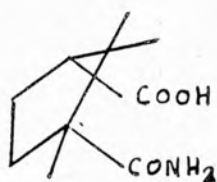
N-ethylcamphorimide (Fig. j, Spectrum No. 38) has a broad shoulder at λ 257nm, ϵ 175, an inflection at λ 240nm and a maximum at λ 209nm, ϵ 13,500. The longer wavelength bands are in the form of inflections. The λ 230nm band is replaced by another at a slightly longer wavelength in substituted imides. There is a bathochromic shift in the shorter wavelength band as well as the longer wavelength bands compared to the parent imide, which is considered as due to N-substitution.



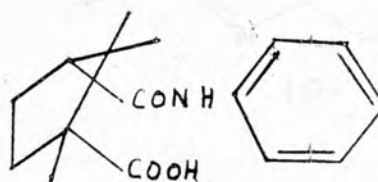
N-phenylcamphorimide (Fig. m, Spectrum No. 39) has a broad shoulder at $\lambda 262$ nm, $\epsilon 430$, a maximum at $\lambda 258$ nm, $\epsilon 450$ and another at $\lambda 250$ nm, $\epsilon 480$. The three bands in the longer wavelength region corresponds to the 260 nm band in benzene, but the intensity is fairly high, so it is possible that there is some mixing of the $n \rightarrow \pi^*$ bands with the $\pi \rightarrow \pi^*$ bands. It is not possible to obtain the lower wavelength band due to instrument limitation.



N-p-anisylcamphorimide (Fig. n, Spectrum No. 40) has two maxima at $\lambda 280$ nm, $\epsilon 1130$ and $\lambda 273$ nm, $\epsilon 1430$. It has an inflection at $\lambda 265$ nm and a maximum at $\lambda 225$ nm, $\epsilon 13,490$. In this compound, the introduction of a OCH_3 group in the p-position has shifted the absorption bands to the red and increased the intensity.



(f)

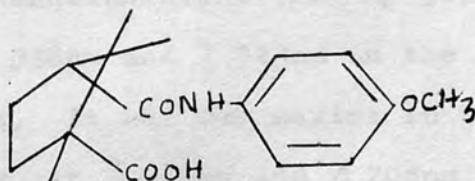


K

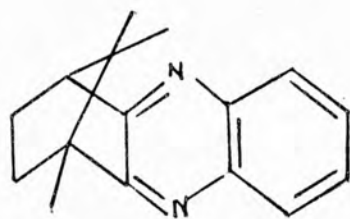
Acids

β -Camphoramic acid (Fig. f, Spectrum No. 41) has two broad shoulders, one at λ 270 nm, ϵ 50 and other at λ 215 nm, ϵ 620. These two low intensity bands can be due to $n \rightarrow \pi^*$ transition of the carbonyl group. α -Camphoranilic acid (Fig. K, Spectrum No. 42) has an inflection at λ 282 nm a maximum at 245 nm, ϵ 15,400 and another intense one at λ 202 nm, ϵ 28,500. α -Camphor-p-anisidinic acid (Fig. L, Spectrum No. 43) has an inflection at λ 290 nm and a maximum at λ 252 nm, ϵ 18,300.

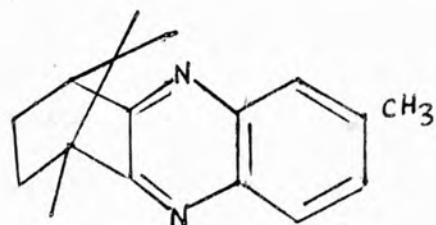
The transition in the latter two aromatic acids can be a mixed kind due to a $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$, except the λ 202 band which is rather intense for a $\pi \rightarrow \pi^*$ band. There is an overlapping of aromatic and carbonyl bands in this region.



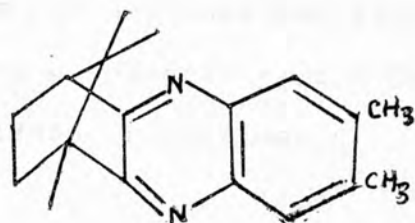
(L)



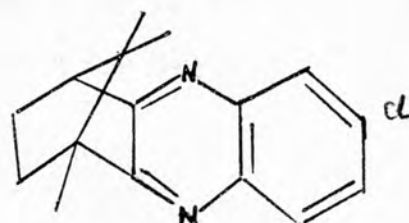
(o)



(p)



q



(r)

Camphorquinoxalines

Camphorquinoxaline (Fig. o , Spectrum No. 44) has a shoulder at λ 325nm, and λ 245nm, inflections at λ 305nm and λ 240nm, maxima at λ 315 nm, λ 241. nm and λ 202nm respectively.

The 7 or (8)-methylcamphorquinoxaline (Fig. p , Spectrum No. 45) has a broad shoulder in the λ 330-335nm region, as well as λ 249nm. It has an inflection at λ 305nm and λ 241 nm, maxima at λ 319 - 320nm, λ 245nm and λ 207nm respectively. The 7,8-dimethylcamphorquinoxaline (Fig q , Spectrum No. 47) has two maxima λ 338nm and λ 323nm in the longer wavelength region. It has two maxima in the shorter wavelength region, at λ 248nm and λ 208nm with shoulders and inflections at λ 252nm and λ 243nm respectively. The 7 or (8)-chlorocamphorquinoxaline (Fig. r , Spectrum No. 46) has a shoulder in the region

λ 330-332 nm, a maximum at λ 319 nm, an inflection at λ 309 nm, another shoulder at λ 248 nm, and maxima at λ 244 nm and λ 207 nm respectively.

Two $n \rightarrow \pi^*$ transitions are expected in diazines in the longer wavelength region due to the allowed and forbidden transitions.

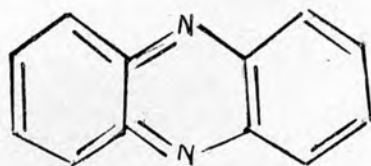
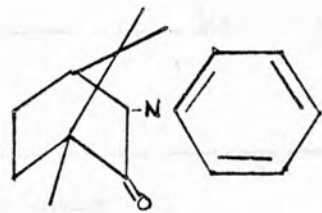


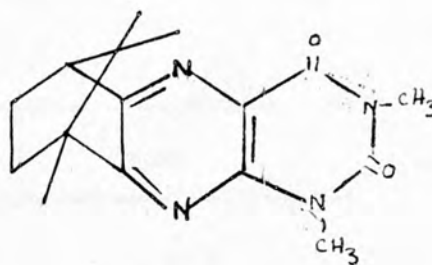
Fig 12

Quinoxaline (Fig.12) has bands in the longer wavelength region λ 374 nm and λ 339 nm with low intensity due to the $n \rightarrow \pi^*$ transitions. The bands between λ 317 nm and λ 310 nm with moderate intensities are due to the first $\pi \rightarrow \pi^*$ and λ 232 nm and λ 229 nm with high intensities for the second $\pi \rightarrow \pi^*$ cyclohexane. But in ethanol it has only two bands, first $\pi \rightarrow \pi^*$ λ 315 nm and the second at λ 233 nm.⁴⁶

The longer wavelength bands in quinoxaline and substituted quinoxalines could be due to the first $\pi \rightarrow \pi^*$ and the $n \rightarrow \pi^*$ in the form of shoulders. The bands in the λ 250 - 230 nm can be compared to the second $\pi \rightarrow \pi^*$ bands. Besides, these compounds have a band between λ 208 nm and λ 202 nm with high intensity.



(S)



(t)

In the pteridine dione (Fig. t, Spectrum No. 49), the nitrogen atom as well as the carbonyl group contribute towards the transitional frequencies. This compound has an inflection at λ 350 nm, λ 320 nm, a shoulder at λ 255 nm and a maxima at λ 338 nm, ϵ 21,380, λ 240 nm, ϵ 21,580, and λ 214 nm, ϵ 20,000.

In this compound the contributions are from the carbonyl as well as the diaza groups. The intensity in the longer wavelength bands are rather moderate. We can consider the bands as due to the allowed and forbidden $n \rightarrow \pi^*$ transitions.

Camphorquinone-p-anisylimine (Fig. s Spectrum No. 48) has moderately intense bands. It has an inflection at λ 382 nm a broad maximum at λ 345 nm another at λ 277 nm and another maximum at λ 227 nm. In this compound there should be some overlapping between the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ bands.

TABLE NO.11

Ultraviolet spectra of alkyl and aryl imides
using 95% ethanol

Compounds	λ max(nm)	ϵ max.
Camphorimide	255(sh.)	153
	235(infl.)	213
	230	262
	201	14,000
N-methyl- camphorimide	255(sh.)	158
	238(infl.)	320
	209	14,200
N-ethyl- camphorimide	257(sh.)	175
	240(infl.)	328
	209	13,500
N-phenyl- camphorimide	262(sh.)	430
	258	450
	250	480
N-p-anisyl- camphorimide	280	1,130
	273	1,430
	265(infl.)	1,240
	225	13,490

TABLE NO.12

Ultraviolet spectra of acids using
95% ethanol

Compounds	$\lambda_{\max}(\text{nm})$	$\epsilon_{(\max)}$
β -camphoramic acid	270-260 (br.sh.)	50
7 or (8)-methyl- camphor- quinoxaline	215-214 (br.sh.)	620
δ -camphoranilic acid	282(infl.) 245 202	61.8 15,400 28,500
δ -camphor-p- anisidinic acid	290(infl.) 252	2,250 18,300
7,8-diacetyl- camphor- quinoxaline	238 203 252(infl.) 246 243(infl.) 207-208	12,200 12,300 27,800 27,300 26,500 68,200

TABLE NO. 13

Ultraviolet spectra of quinoxalines using 95% ethanol

Compounds	$\lambda_{\max}(\text{nm})$	$\epsilon(\text{max})$
Camphor- quinoxaline	325(sh.)	6,980
	315	9,400
	305(infl.)	7,900
	245(sh.)	23,500
	241	24,840
	240(infl.)	23,000
	202	47,900
7 or (8)-methyl- camphor- quinoxaline	335-330(sh.)	7,200
	319-320	9,000
	305(infl.)	6,250
	249(sh.)	23,600
	245	25,500
	241(infl.)	23,000
	207	39,000
7 or(8)-chloro- camphor quinoxaline	330-332(sh.)	7,400
	319	9,200
	309(infl.)	7,100
	248(sh.)	24,160
	244	24,800
	207	25,280
7,8-dimethyl- camphor- quinoxaline	338	12,900
	323	13,300
	252(sh.)	27,800
	248	29,800
	243(infl.)	26,600
	207-208	68,200

TABLE NO. 14

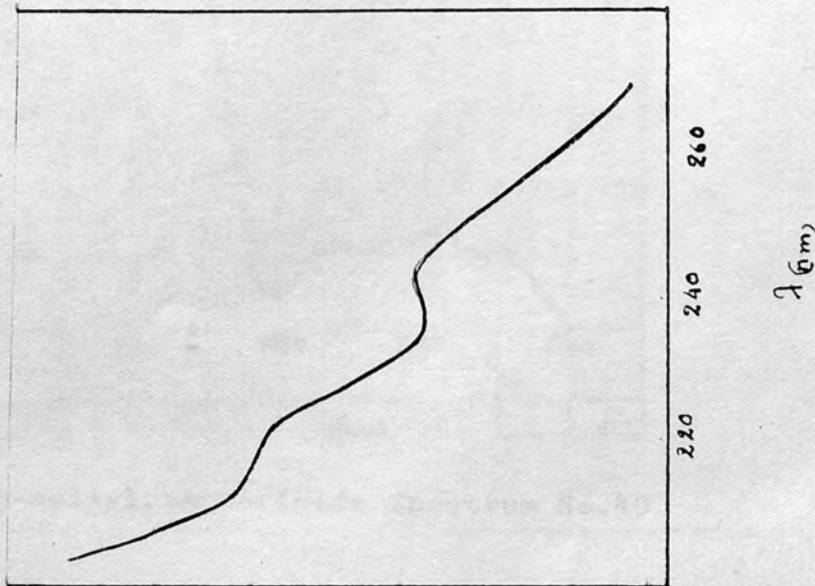
Ultraviolet spectra of pteridine-dione and
camphorquinone-p-anisylimine using 95%
ethanol

Compounds	λ_{max} (nm)	ϵ (max)
Pteridine-dione	350(infl)	19,000
	338	21,380
	320(infl.)	16,200
	255(sh.)	17,800
	240	21,600
	214	20,000
Camphorquinone- <u>p</u> -anisylimine	382(infl.)	2,840
	345-340	5,030
	277-270	4,260
	227	9,800

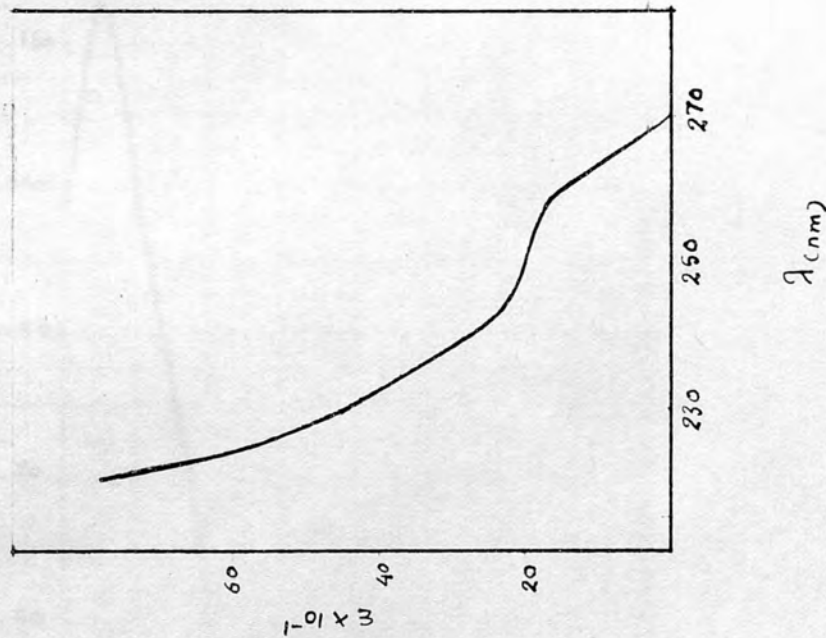
ULTRAVIOLET ABSORPTION SPECTRA

Aliphatic imides

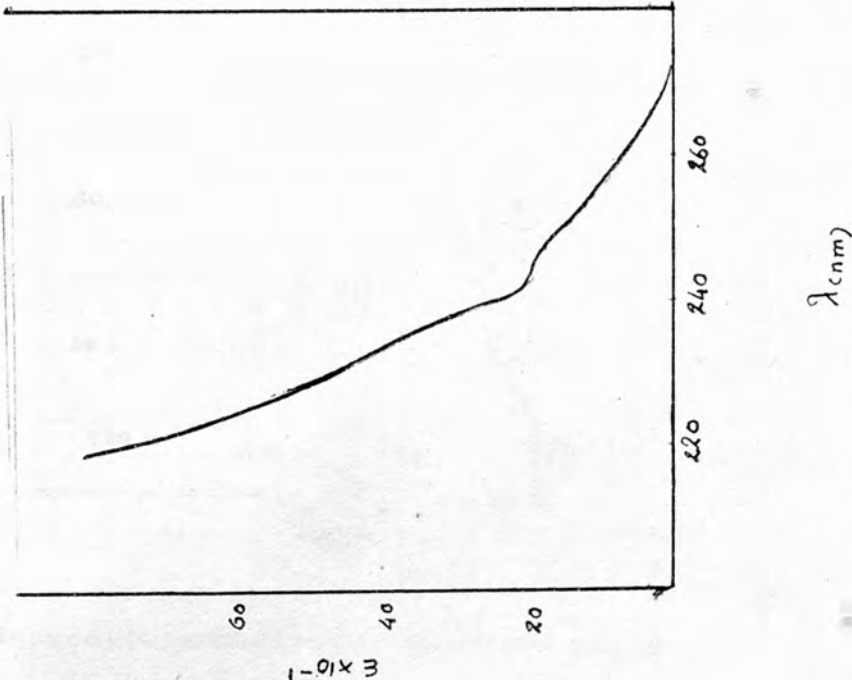
Camphorimide
Spectrum No. 36



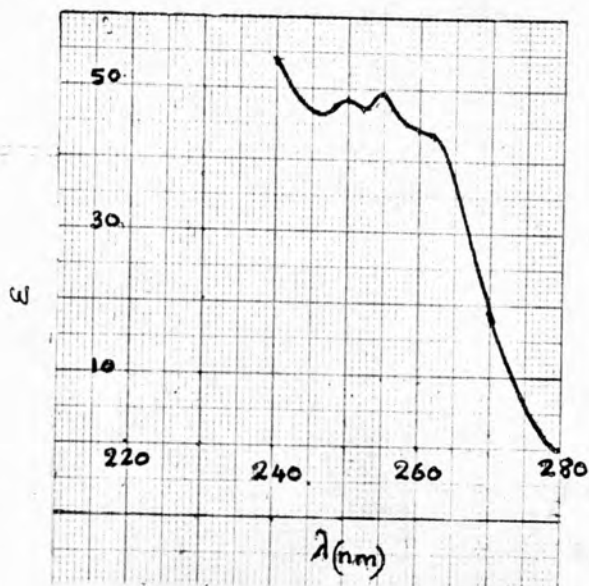
N-methylcamphorimide
Spectrum No. 37



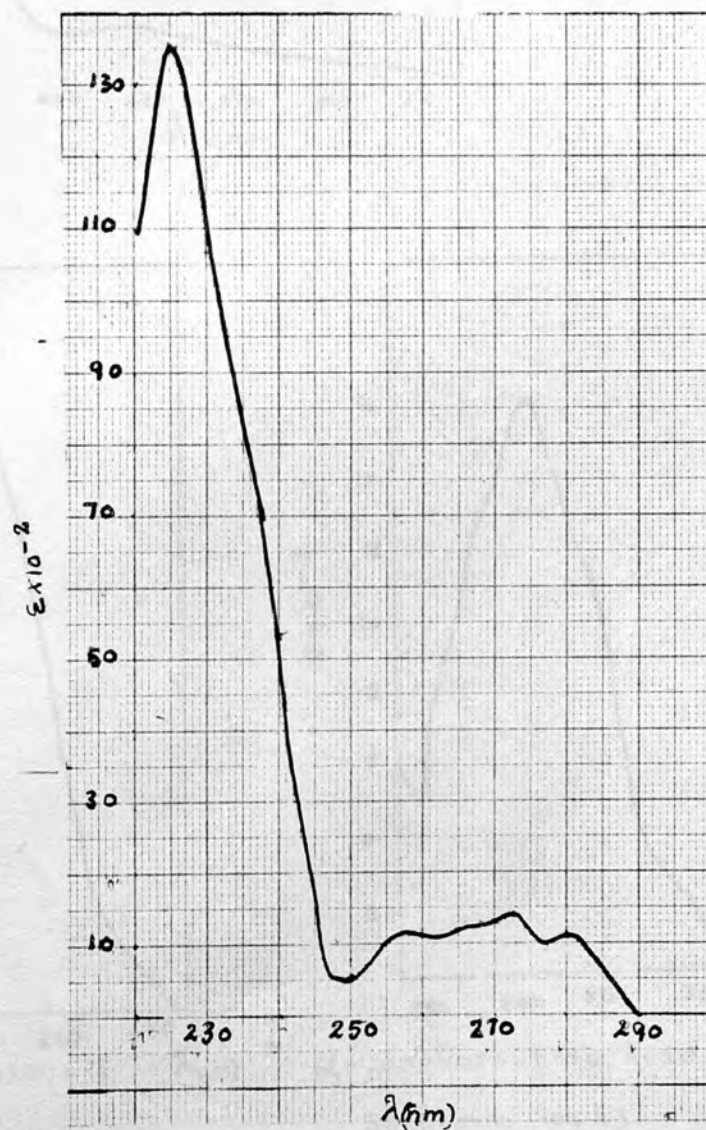
N-ethylcamphorimide
Spectrum No. 38



Ultraviolet absorption curves of aromatic imides

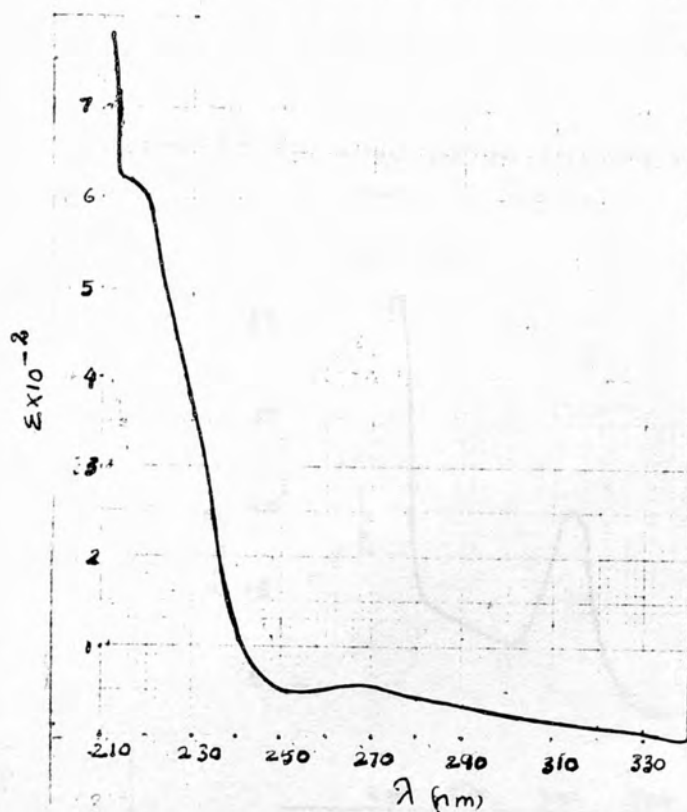


N-phenylcamphorimide Spectrum No.39

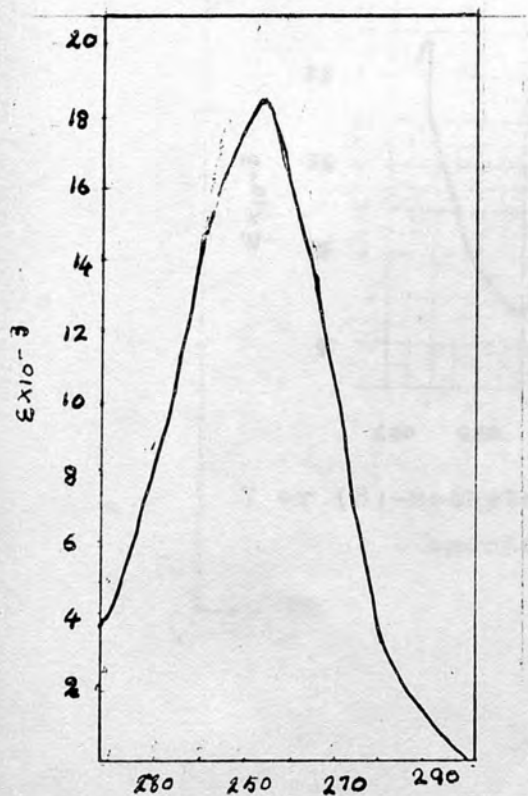


N-p-anisylcamphorimide Spectrum No.40

Ultraviolet absorption curves of acids.

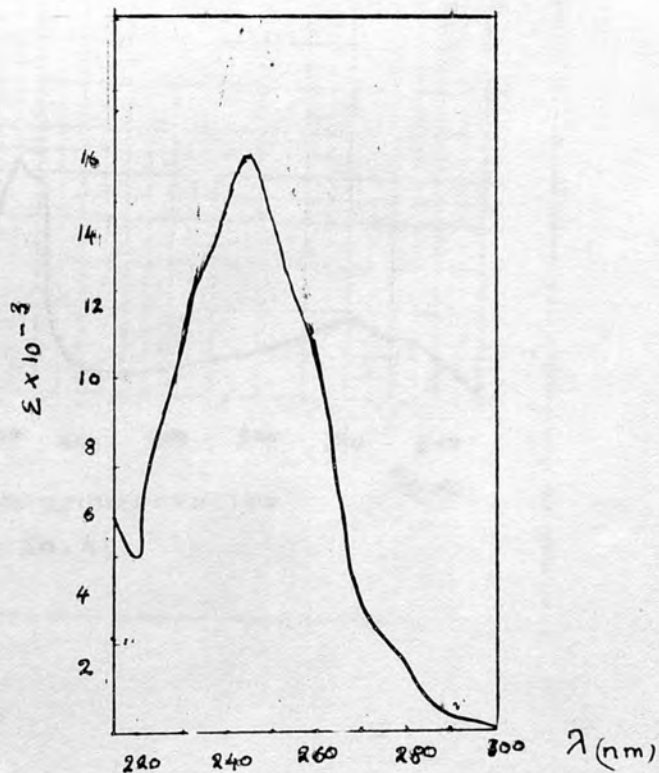


β -Camphoramic acid
Spectrum No. 41



α -Camphor-p-anisidinic acid
 λ (nm)

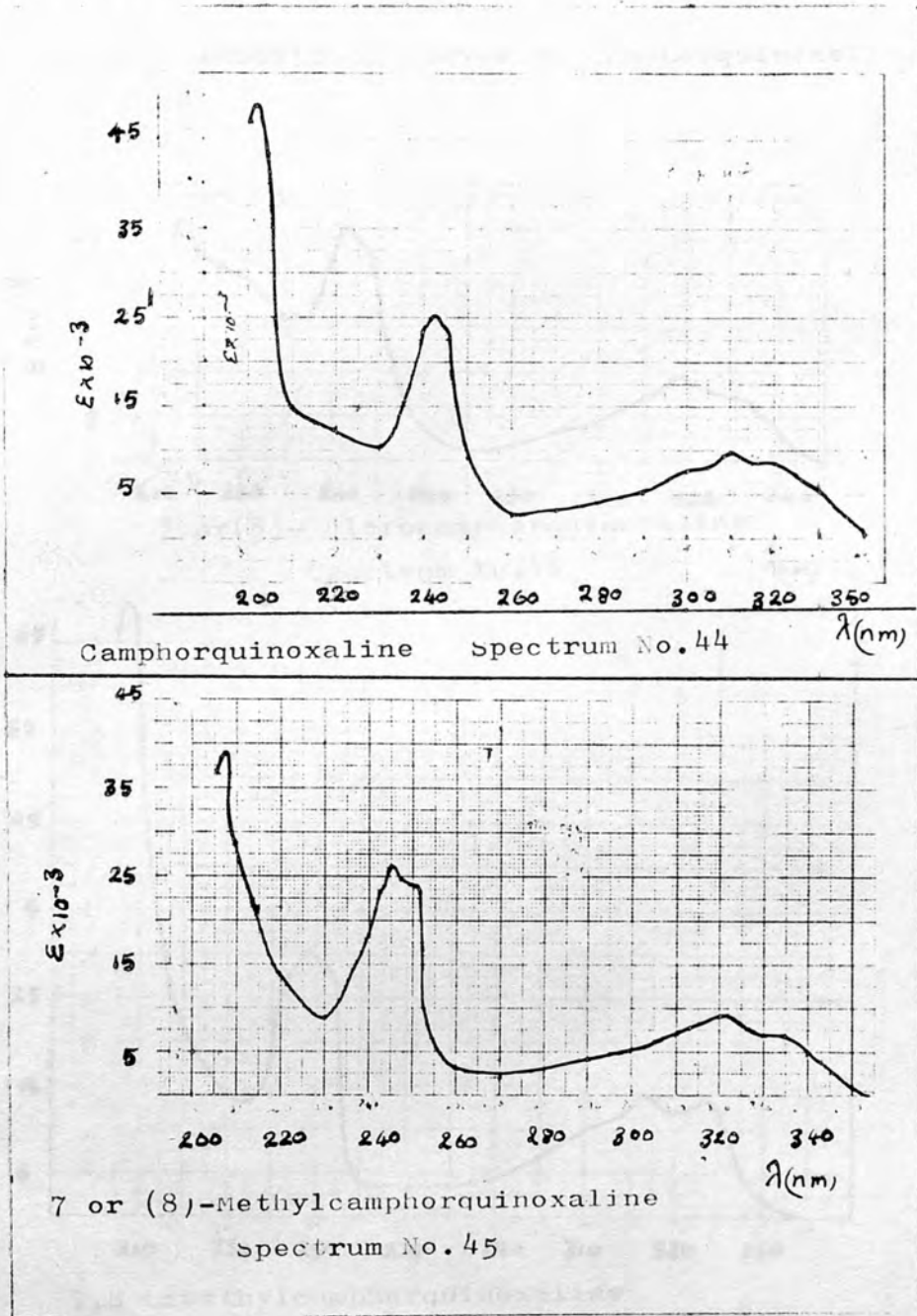
Spectrum No. 42



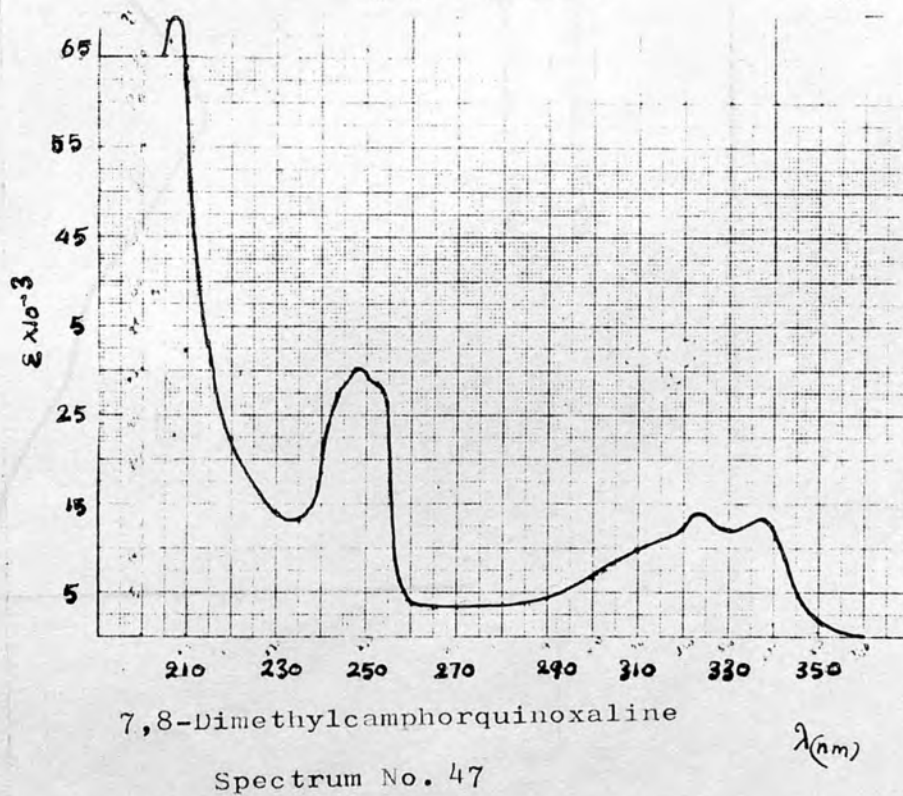
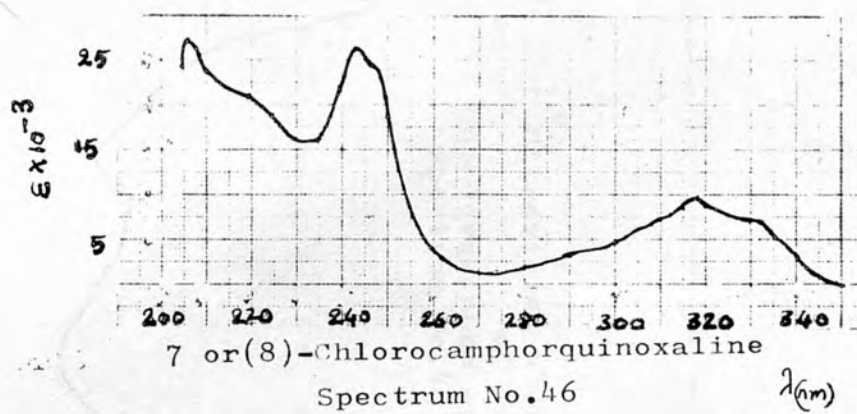
α -Camphoranilic acid
 λ (nm)

Spectrum No. 43

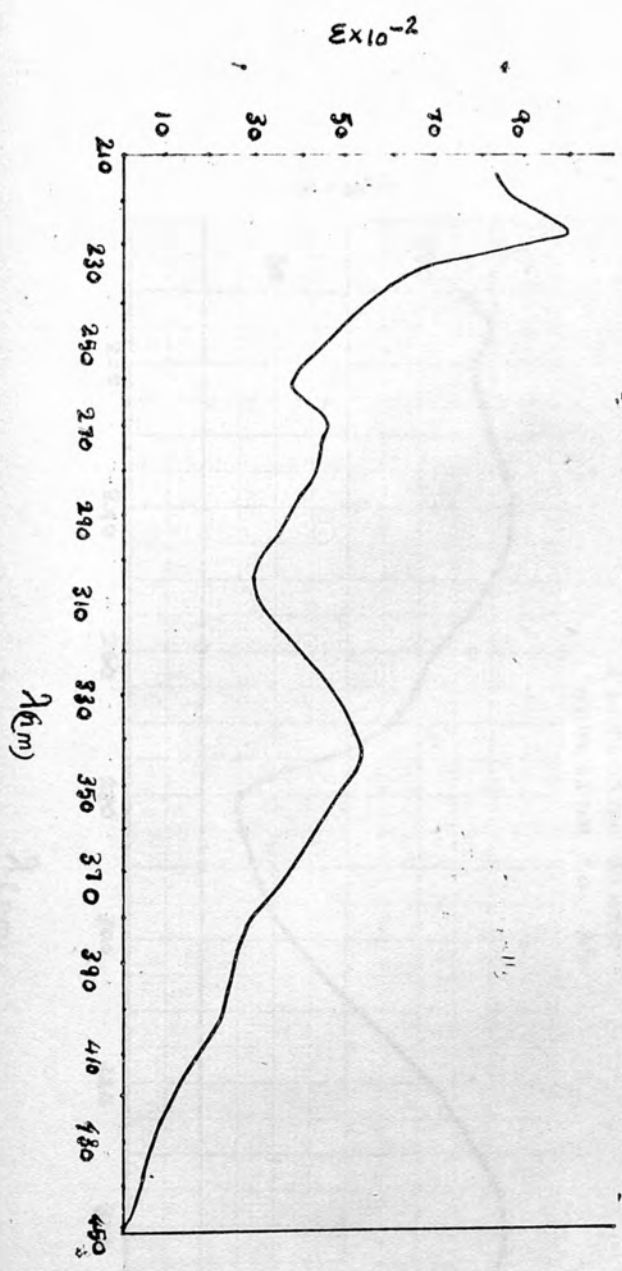
Ultraviolet absorption curves of camphorquinoxalines

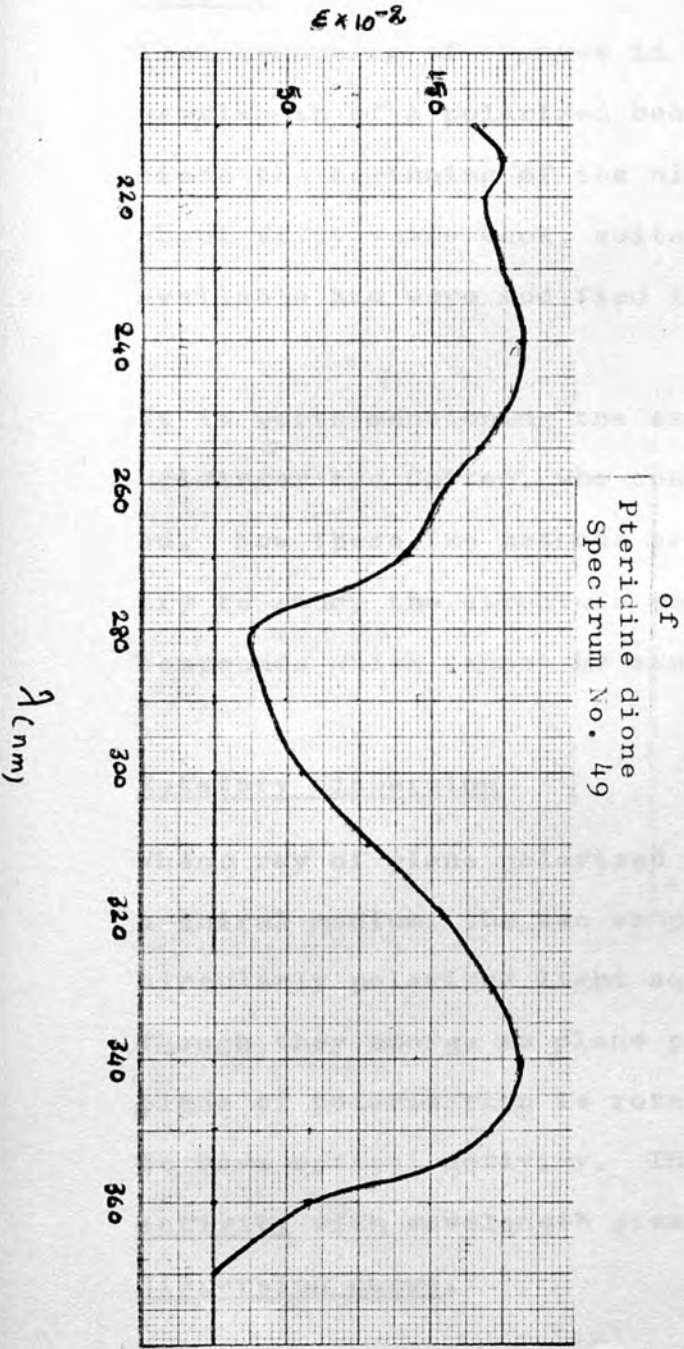


Ultraviolet absorption curves of camphorquinoxalines



Ultraviolet absorption curve
of
Camphorquinone -p-anisylimine
Spectrum No. 48





OPTICAL ROTATORY DISPERSION AND CIRCULAR DICHROISM

INTRODUCTION

History

The phenomenon of changes in optical activity with wavelength of a polarized beam of light has been known since the beginning of the nineteenth century.⁴⁷ But about fifty years back, suitable instruments became available and were modified in due course.

It is worth mentioning the early works of Arago, Biot, Haidinger and Cotton, who contributed towards ord and cd. Now these two methods are used in organic chemistry to study the structure and stereochemistry of many compounds which cannot be studied by other methods.

Rotatory dispersion

When a ray of plane polarized light is passed through a chiral medium, the two components left and right circularly polarized light acquire different speed. Though they emerge as plane polarized light, the plane of polarization is rotated. The medium is said to have optical activity. The variation of optical activity with wavelength gives an optical rotatory dispersion curve.

Circular dichroism

When a medium, besides transmitting two component (left and right) circularly polarized rays with unequal

velocity, also shows an unequal absorption of the two components, then not only is the plane of polarization rotated at an angle but the resulting light is also elliptically polarized and the medium is said to exhibit circular dichroism.⁴⁸

Cotton effect

The combination of unequal absorption (circular dichroism) and unequal velocity of transmission (optical rotation) of left and right circularly polarized light in the region in which optically active absorption bands are observed is a phenomena called the "Cotton effect". Cotton at the end of the last century observed that optically active compounds show abnormal behaviour of their rotatory power in the region where absorption bands appear, so the anomalous curves are called "Cotton effect curves".⁴⁷

Ord and cd curves

The rotatory dispersion curves can be divided into three groups.

1. Plain curves
2. Complex curves
3. Cotton effect curves.

I. Plain curves

These have the rotatory power increase with decreasing wavelength. They do not have a maximum or minimum within the spectral range under obser-

vation. (Fig. 13). When they show positive values with decreasing wavelength, they are positive curves and when they show negative values, they are negative curves.

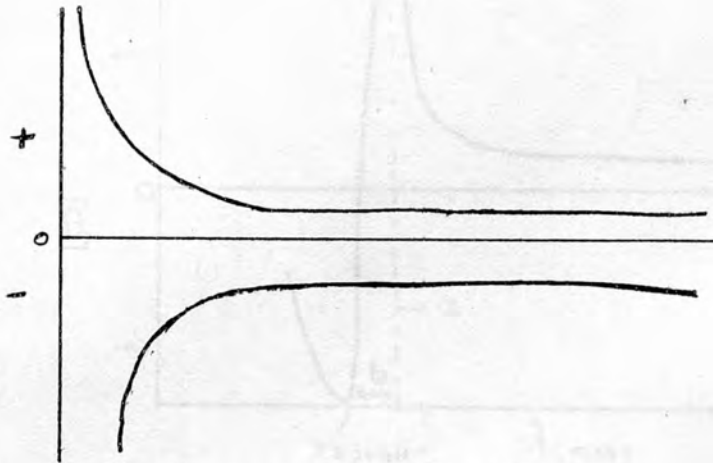


Fig. 13

2. Complex or anomalous curves

When ord curves show changes in sign, maxima or minima or inflection points due to super imposition of plain curves of different signs, they are complex curves.

3. Cotton effect curves

47, 49

When there are anomalies associated with the presence of optically active absorption bands, they are called Cotton effect curves.

To this class belong the single Cotton effect curves and the multiple Cotton effect curves.

a. A single Cotton effect curve has one maximum called the peak, one minimum called the trough. (Fig. 14).

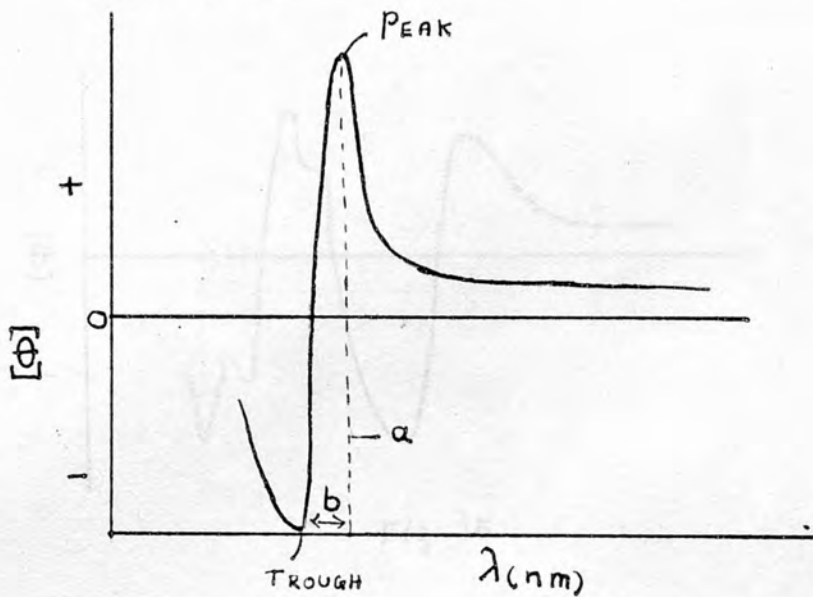


Fig. 14

In a positive Cotton effect curve the peak occurs at a higher wavelength than the trough. The reverse happens in a negative Cotton effect curve. The vertical distance between the peak and the trough is called the molecular amplitude 'a'. The molecular amplitude is the difference between the molecular rotation at the extremum (peak or trough) of longer wavelength $[\Phi]_1$ and the molecular rotation at the extremum of the shorter wavelength $[\Phi]_2$ divided by 100.

$$a = \frac{[\Phi]_1 - [\Phi]_2}{100}$$

b. A multiple Cotton effect curves

A combination of single Cotton effect curves is called the multiple Cotton effect curve. (Fig. 15)

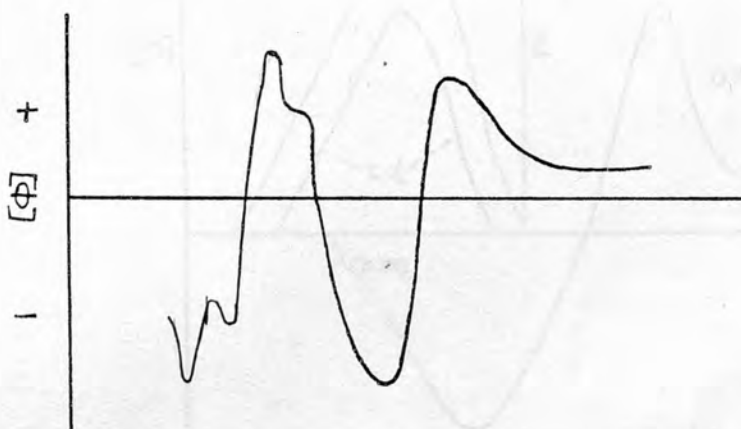


Fig. 15

Comparison of rotatory dispersion curves with those of absorption spectroscopic curves

The term "peak" and "trough" have been used to distinguish the ord curves from the absorption spectroscopic curves. Cd curves are known as positive maximum, positive inflection point, positive minimum and negative minimum, negative inflection point, and negative minimum.

The midpoint between the extrema of a positive or negative cotton effect ord curve coincides roughly with the absorption maximum of the chromophore. In cd the wavelength of the extremum of the cd curve almost coincides with the maximum of the absorption spectrum Fig. 16).

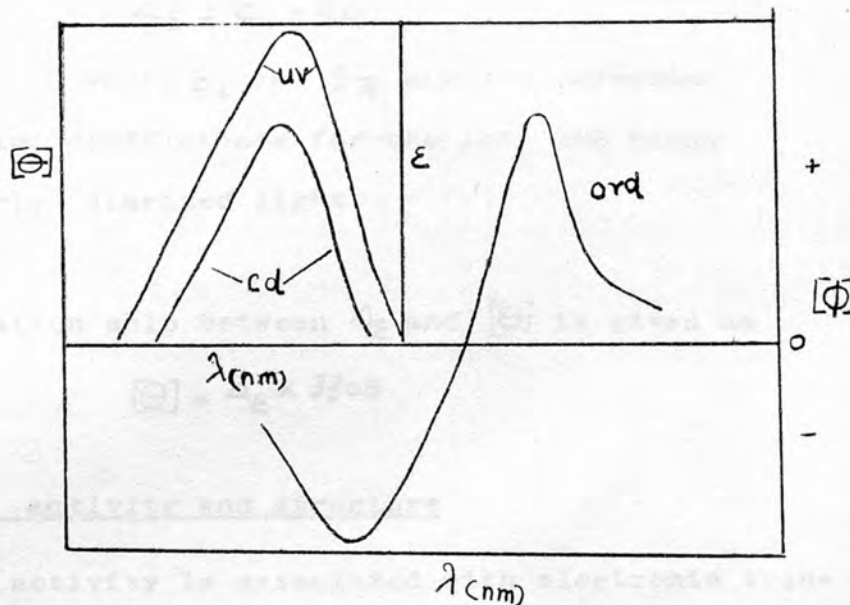


Fig. 10

The advantages and disadvantages of ord and cd curves

Although ord and cd give equivalent information, there are points which differentiate the two techniques. Ord has specific features which are due to the near and far Cotton effects. In cd the absence of background effect simplifies the curves. So it is more easy to resolve the overlapping bands in cd than those in ord.

The presentation of ord and cd curves

The ord curves are plotted with the wavelengths in nanometers (nm) on the abscissa against molecular rotations $[\Phi]$ on the ordinate. The cd curves are plotted with the wavelengths in (nm) on the abscissa

against either $[\Theta]$ molecular ellipticity or $\Delta\varepsilon$ differential dichroic absorption.

$$\Delta\varepsilon = \varepsilon_L - \varepsilon_R$$

where ε_L and ε_R are the molecular extinction coefficients for the left and right circularly polarized light.

The relationship between $\Delta\varepsilon$ and $[\Theta]$ is given as

$$[\Theta] = \Delta\varepsilon \times 3300$$

Optical activity and structure

Optical activity is associated with electronic transitions occurring in a chiral environment. In many cases, the electrons involved in a given transition belong to the chromophore. Optically active chromophores have been divided into two main classes by Moscovitz.⁵⁰

1. Inherently symmetric but dissymmetrically perturbed chromophores.
2. Inherently dissymmetric chromophores.

Carbonyl group belong to the 1st class. But when asymmetrically surrounded as in a steroid or a terpene it is asymmetric. Hexahelicene belongs to the 2nd class of compounds. The inherently dissymmetric chromophores show rotational strength, hundred times larger than inherently achiral chromophores.⁵¹

DISCUSSION

Cd of imides, acids and quinoxalines

Imides

Camphorimide (Spectrum No. 61) has a cd maximum at

$[\theta]_{255} + 1950$, which corresponds to a peak in the uv spectrum. The cd minimum at $[\theta]_{225} - 2240$ does not have a corresponding uv band, but there is a uv maximum at λ_{230} .

N-methylcamphorimide (Spectrum No. 62) has the

$[\theta]_{255} + 1220$ band in cd as well as the uv spectrum. It has a negative cd band at $[\theta]_{225} - 2640$, in the same region as uv.

N-ethylcamphorimide (Spectrum No. 63) has a cd maxi-

mum at $[\theta]_{257} + 1250$. This band is seen in the uv as an inflection. The two negative bands, $[\theta]_{232} - 1450$ and $[\theta]_{212} - 2480$ are not seen in the uv spectrum, but the uv has an inflection at λ_{232} and a maximum at λ_{209} .

N-phenylcamphorimide (Spectrum No. 64) has two positive

cd maxima at $[\theta]_{264} + 460$ and $[\theta]_{258} + 500$ with an inflection at $[\theta]_{252} + 360$. The uv of this compound has a band at λ_{262} and λ_{250} . The negative inflection at $[\theta]_{233} - 1420$ and a negative minimum at $[\theta]_{218} - 1950$ are shown in the cd spectrum are not found in the uv spectrum.

N-p-anisylcamphorimide (Spectrum No. 65) has three positive maxima at $[\theta]_{264} +530$, $[\theta]_{258} +730$ and $[\theta]_{219} +1820$. The uv spectrum has only an inflection at λ_{265} corresponding to the cd band. The λ_{280} , λ_{273} and λ_{225} bands are not seen in the cd spectrum, but it has a negative band at $[\theta]_{232} -2210$.

The aliphatic imides have a higher molecular ellipticity than the aromatic imides.

Acids

β -camphoramic acid (Spectrum No. 66) has a cd band at $[\theta]_{219} +3894$, where as the uv band is at a slightly shorter wavelength. $\lambda_{215-214nm}$. It has a broad shoulder, which is not visible in the cd spectrum.

α -camphoranilic acid (Spectrum No. 67) has a cd band at $[\theta]_{264} +759$, $[\theta]_{245} +1419$, $[\theta]_{230} +5775$ and at $[\theta]_{204} +6897$. The uv spectrum shows only the λ_{245nm} and λ_{202nm} band. The inflection at λ_{282} is not seen in its cd spectrum.

α -camphor-p-anisidinic acid (Spectrum No. 68) has cd bands at $[\theta]_{262} +666$; $[\theta]_{250} +8910$; $[\theta]_{230} +5775$ and $[\theta]_{204} +6897$. The uv of this compound shows only a maximum at λ_{252nm} .

All three acids have only positive cd bands. The aromatic acids have more bands than the aliphatic acid.

Camphorquinoxalines

Camphorquinoxaline (Spectrum No. 69) has one positive and two negative cd bands at $[\epsilon]_{242} +2770$; $[\epsilon]_{230} -4160$ and $[\epsilon]_{220} -6040$ respectively. The uv spectrum of this compound has a band at $\lambda 240$ and an inflection at $\lambda 241$. The longer wavelength uv bands are not found in the cd spectrum.

7 or (8)-methylcamphorquinoxaline (Spectrum No. 70) has a cd band at $[\epsilon]_{244} +2500$; $[\epsilon]_{234} -1650$ and $[\epsilon]_{230} -5410$. The uv spectrum shows only a band at $\lambda 245$ corresponding to the positive cd band.

7,8-dimethylcamphorquinoxaline (Spectrum No. 72) has a positive and a negative cd band at $[\epsilon]_{245} +2050$ and $[\epsilon]_{220} -7260$. The uv maximum is found at $\lambda 248 \text{ nm}$.

7 or (8)-chlorocamphorquinoxaline (Spectrum No. 71) has only negative cd bands, a broad shoulder at $[\epsilon]_{260-255} -760$, $[\epsilon]_{235} -8180$ and $[\epsilon]_{213} -3500$. The uv spectrum does not show any band in this region except the intense band at $\lambda 207 \text{ nm}$.

Pteridine dione (Spectrum No. 74) has a cd band at $[\epsilon]_{320} +7590$ and another at $[\epsilon]_{236} +2840$. The uv spectrum shows two bands at $\lambda 320$ and $\lambda 240$. Besides, it has two negative bands at $[\epsilon]_{262} -4950$ and $[\epsilon]_{218} -48,200$. The corresponding uv band is found at $\lambda 214 \text{ nm}$.

Camphorquinone-p-anisylimine (Spectrum No. 73) has two positive and three negative cd bands at

$[\theta]_{392}^{+54,580}$, $[\theta]_{344}^{+21,850}$; $[\theta]_{269}^{-36,400}$; $[\theta]_{223}^{-14,550}$ and $[\theta]_{204}^{-25,480}$ respectively. The uv spectrum shows an inflection at λ 382, broad bands at λ 345-340 nm λ 277-270 and a maximum at λ 227 respectively.

It is interesting to note that most of the positive cd bands are found in the same wavelength as their uv bands in camphorimide and its alkyl imides. In the aromatic acids, the lower wavelength bands are found in both uv and cd spectra.

The quinoxalines show cd bands only in the lower wavelength region corresponding to the uv bands.

Cd bands have corresponding uv bands in pteridine dione and camphorquinone-p-anisylimine. In some cases, especially the bands in the longer wavelength region, the cd bands are not shown corresponding to the uv spectrum. This may be due to the weak cd bands or the two bands cancelling each other.

Ord of imides, acids and quinoxalines

Imides

Ord of the imides show a positive Cotton effect.

The parent imide has a low ^{er} positive rotation than its N-substituted imides. Camphorimide (Spectrum No. 50) has a rotation at $[\phi]_{270} +362$. The ord of the substituted imides are as follows:

N-methyl camphorimide (Spectrum No. 51) $[\phi]_{270} +660^{\circ}$;
 N-ethyl camphorimide (Spectrum No. 52) $[\phi]_{268} +689^{\circ}$;
 N-phenyl camphorimide (Spectrum No. 53) $[\phi]_{270} +464^{\circ}$ and
 the N-p-anisylcamphorimide (Spectrum No. 54) $[\phi]_{290} +400^{\circ}$
 (inflection) and $[\phi]_{270} +820^{\circ}$ (peak). The substituted aromatic imide has a higher rotation compared to the other imides, but not the expected high $[\phi]$ value for aromatic compounds. This must mean that the contribution from the aromatic compound is in ^{the} opposite sense and therefore cancelling some of $[\phi]$ values.

All the imides except the N-phenyl camphorimide, show a negative rotation in the range λ 240-245 with a value of $[\phi]$ between 1000° ^{and} 1800° . The N-phenyl-camphorimide has a ^{smaller} negative trough $[\phi]_{245} -580^{\circ}$.

Acids

The acids have positive Cotton effect. β -camphoramic acid (Spectrum No. 55) has inflections at $[\phi]_{310} +580$;
 $[\phi]_{270} +1140$ and $[\phi]_{230} +4353$.
^{a maximum at}

1
 α -Camphoranilic acid (Spectrum No.56) has only an inflection $[\Phi]_{310} + 1000$ and a peak $[\Phi]_{270} + 4300$.

α -Camphor-p-anisidinic acid (Spectrum No.57) has an inflection at $[\Phi]_{320} + 942$ and a peak at $[\Phi]_{270} + 5322$.

Camphorquinoxalines

It is not possible to take measurements in camphorquinoxalines below $\lambda 350$ nm because of high absorption and instrument limitations. 7 or (8)-Chlorocamphorquinoxaline has a measurable negative rotation (Spectrum No. 58).

Pteridine dione has a positive maximum at $[\Phi]_{350} + 4900$ with inflections at $\lambda 420$ nm and $\lambda 400$ nm . It has a negative shoulder at $[\Phi]_{300} - 7500$ and a negative trough at $[\Phi]_{272} - 8900$ (Spectrum No. 60).

Camphorquinone-p-anisylimine(Spectrum No. 59) has ^{two} ~~a~~ positive maxima at $[\Phi]_{470} + 9000$ and $[\Phi]_{415} + 39,000$ with a negative inflection at $[\Phi]_{360} - 40,000$. It has a broad negative maximum at $[\Phi]_{295} - 57,000$.

The latter two compounds show a remarkably high rotation.

The cd maxima of these compounds coincide with the midpoint of the ord curve where it crosses the zero line.

TABLE NO.15

Circular Dichroism and Optical Rotatory
Dispersion of imides

Compounds	Cd			Ord	
	λ_{nm}	$\Delta \epsilon$	$[\theta]$	λ_{nm}	$[\Phi]$
Camphor- imide	255	+0.59	+1950	275	+362
	225	-0.75	-2480	260	Nil
				240	-1810
N-methyl- camphor- imide	255	+0.37	1220	270	+669
	225	-0.80	2640	260	0
				242	-1760
N-ethyl- camphor- imide	257	+0.38	+1250	268	+689
	232	-0.44	-1450	257	0
	212	-0.75	-2480	240	-1314
N-phenyl- camphor- imide	264	+0.14	+460	270	+460
	258	+0.15	+500	254	0
	252	+0.11	+360	245	-580
	233	-0.43	-1420		
	218	-0.59	-1950		
N-p-anisyl- camphor- imide	264	+0.16	+530	290	+400
	258	+0.22	+730	270	+750
	232	-0.67	-2210	255	0
	218	+0.55	+1820	242	-1025

TABLE NO.16

Circular Dichroism and Optical
Rotatory Dispersion of acids

Compounds	Cd			Ord	
	$\lambda_{(nm)}$	$\Delta\epsilon$	$[\theta]$	$\lambda_{(nm)}$	$[\Phi]$
β -Camphor- amic acid	219	+1.18	+3894	310	+580
				270	+1140
				230	+4353
α -Camphor- anilic acid	264	+0.23	+759	310	+1000
	245	+0.43	+1419	270	+4300
	230	+0.45	+1485		
	204	+0.98	+3234		
α -Camphor- p-anisi- dinic acid	263	+2.02	+6666	320	+942
	250	+2.70	+8910	270	+5322
	230	+1.75	+5775		
	204	+2.09	+6897		

TABLE NO. 17

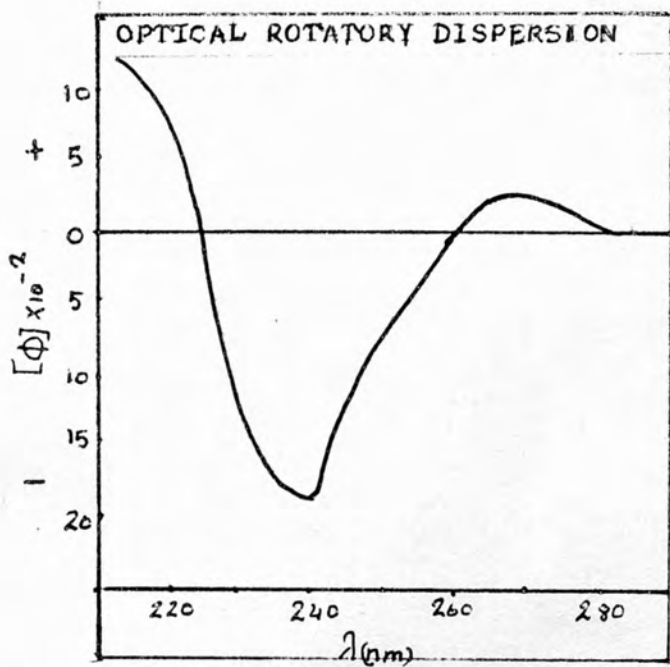
Circular Dichroism and Optical Rotatory
Dispersion of Camphor quinoxalines

	Cd			ORD	
	λ (nm)	$\Delta\epsilon$	$[\theta]$	λ (nm)	$[\Phi]$
Camphor-	242	+0.84	+2770	350	+700
quinox-	234	-1.26	-4160		
aline	220	-1.83	-6040		
7 or (8)-	244	+0.76	+2500	340	+1200
methyl-	234	-0.50	-1650		
camphor-	220	-1.64	-5410		
quinox-					
aline					
7,8-di-	245	+0.62	+2050	350	+690
methyl-	220	-2.20	-7260		
camphor-					
quin-					
oxaline					
7 or (8)-	260-	-0.21	-760	350	+1000
chloro-	255				
camphor-	235	-2.48	-8180	310-300	-1000
quin-	213	-10.85	-3500		
oxaline				(br.Tr)	
				280	-820

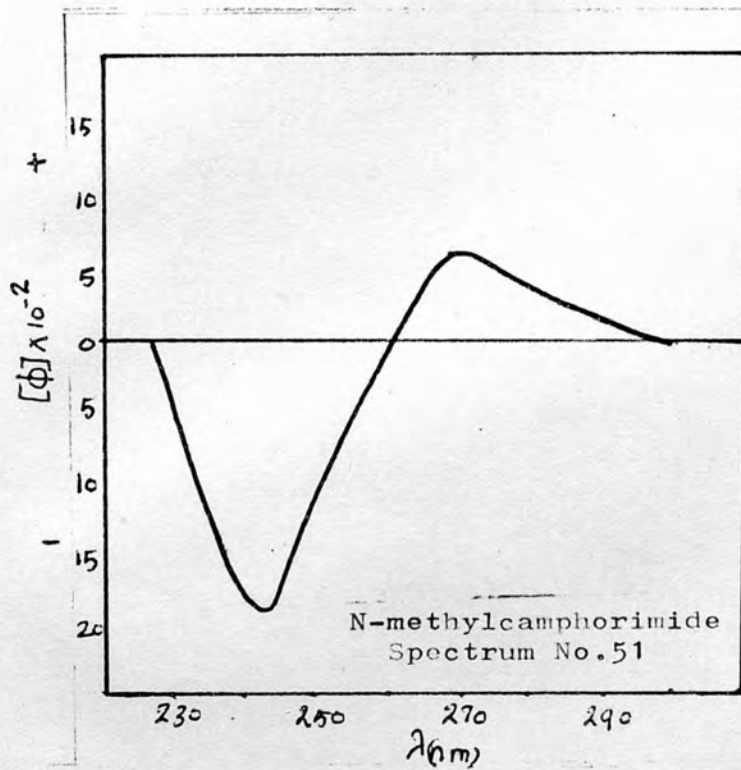
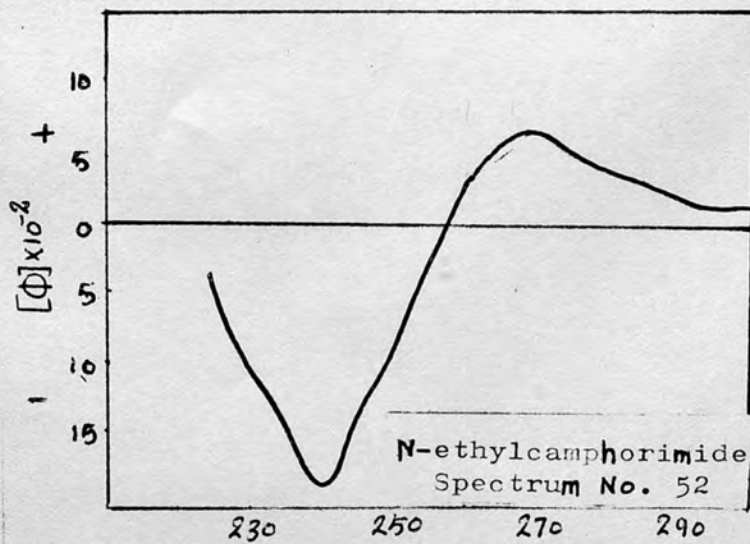
TABLE NO. 18

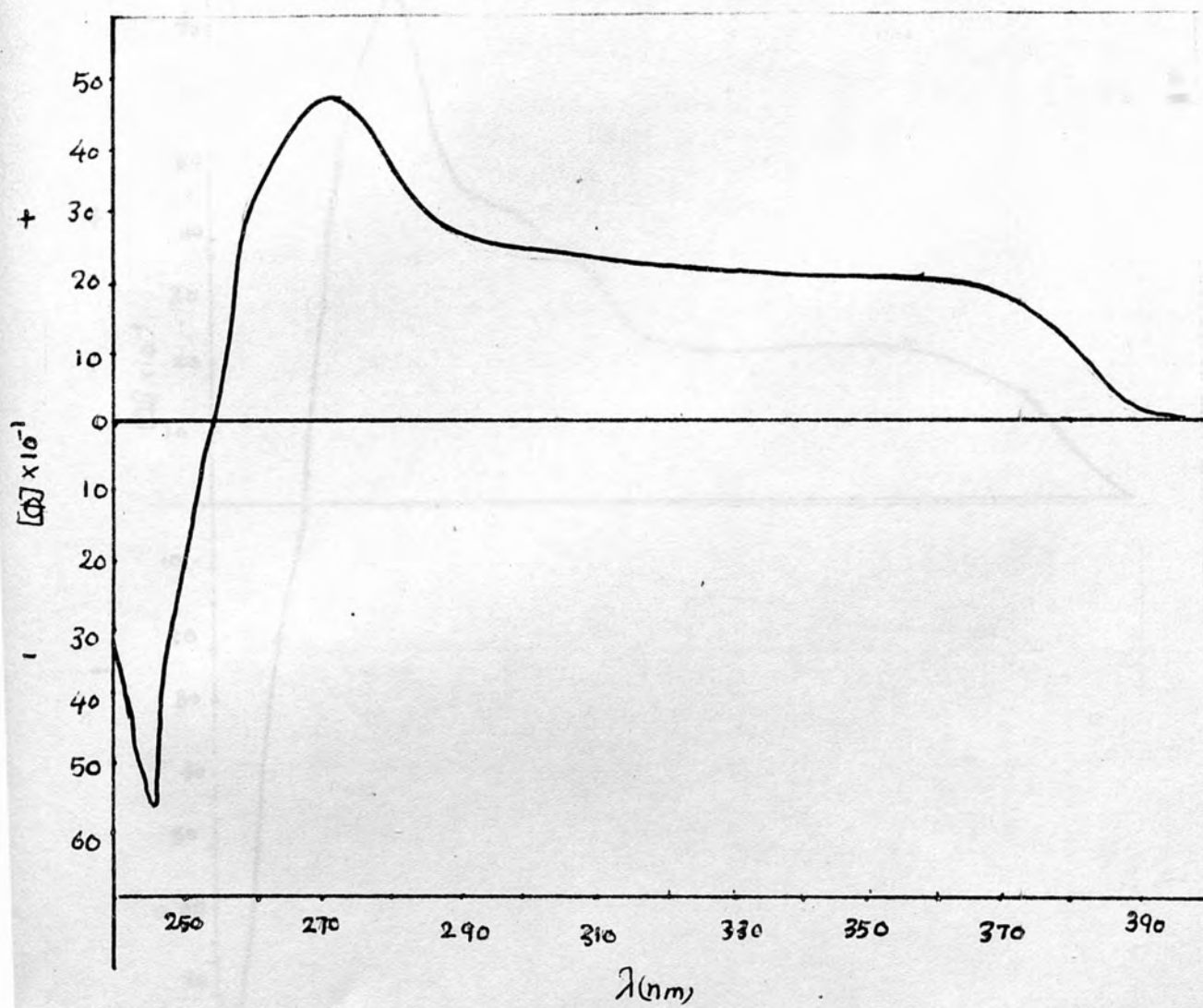
Circular Dichroism and Optical Rotatory
Dispersion of Pteridine dione and
Camphorquinone-p-anisylimine

	cd			ord.	
	$\lambda_{(nm)}$	$\Delta\varepsilon$	$[\theta]$	λ_{nm}	$[\phi]$
Pteridine dione	320	+2.36	+7,590	420	+700
	262	-1.50	-4,950	400	+900
	236	+0.86	+2,840	350	+4,900
	218	-14.60	-48,200	330	+1,300
				325	Nil
				320	-1,500
				300	-7,500
			272	-8,900	
Camphor- quinone- p-anisyl- imine	392	+16.54	+54,580	415	+39,000
	344	+6.62	+21,850	390	-
	269	-11.03	-36,400	360	-40,000
	223	-4.41	-14,550	295	-57,000
	204	-7.72	-25,480		

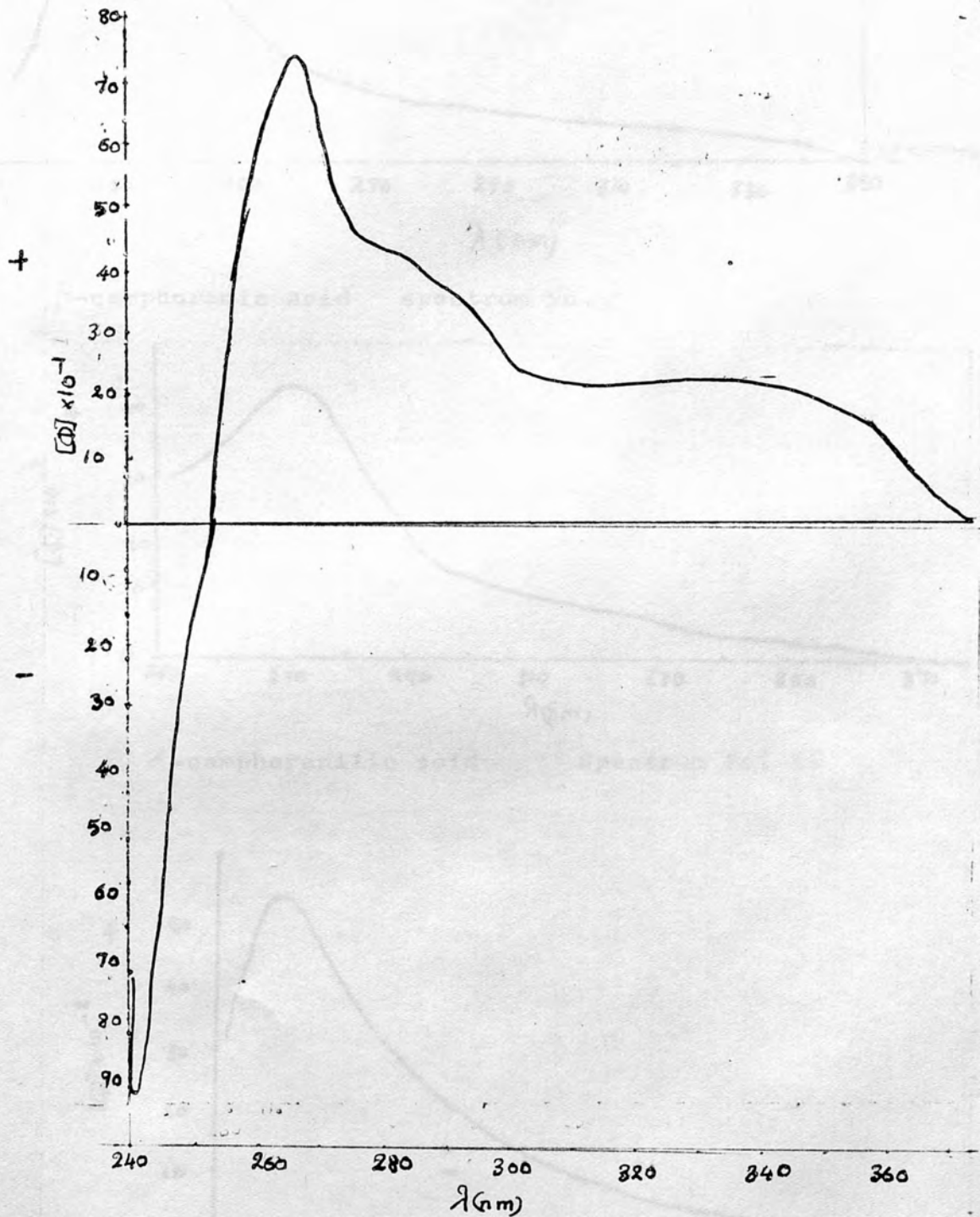


Camphorimide Spectrum No. 50

N-methylcamphorimide
Spectrum No. 51N-ethylcamphorimide
Spectrum No. 52

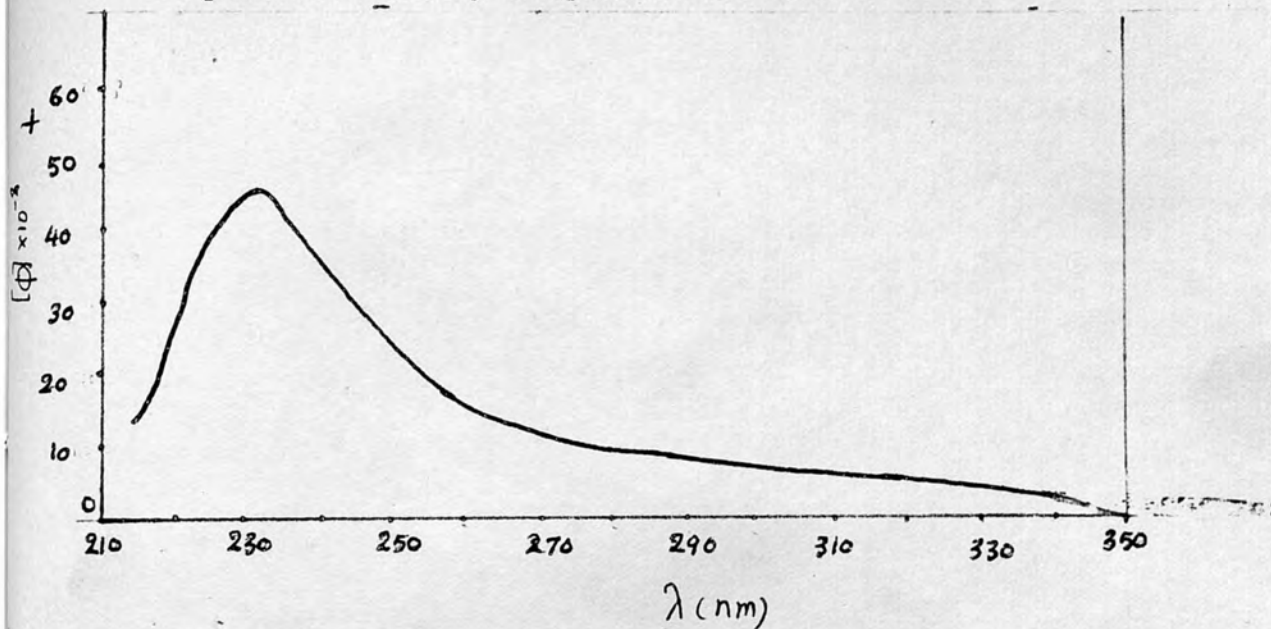
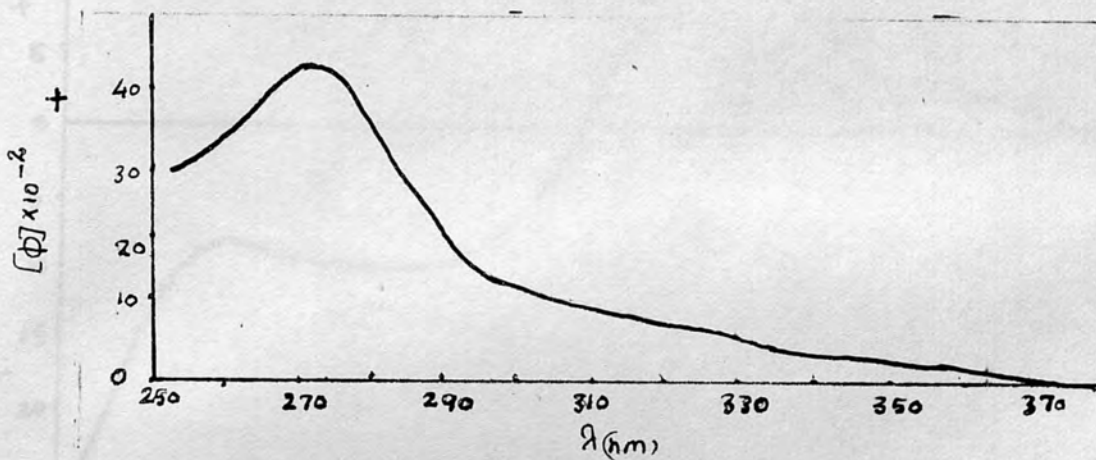
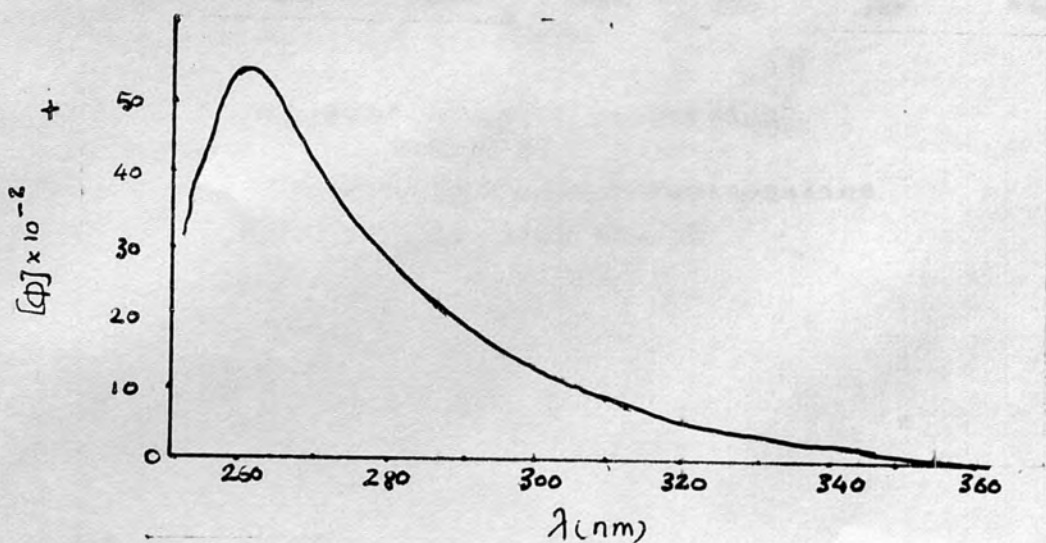


Optical rotatory dispersion curve of N-phenylcamphorimide
Spectrum No.53

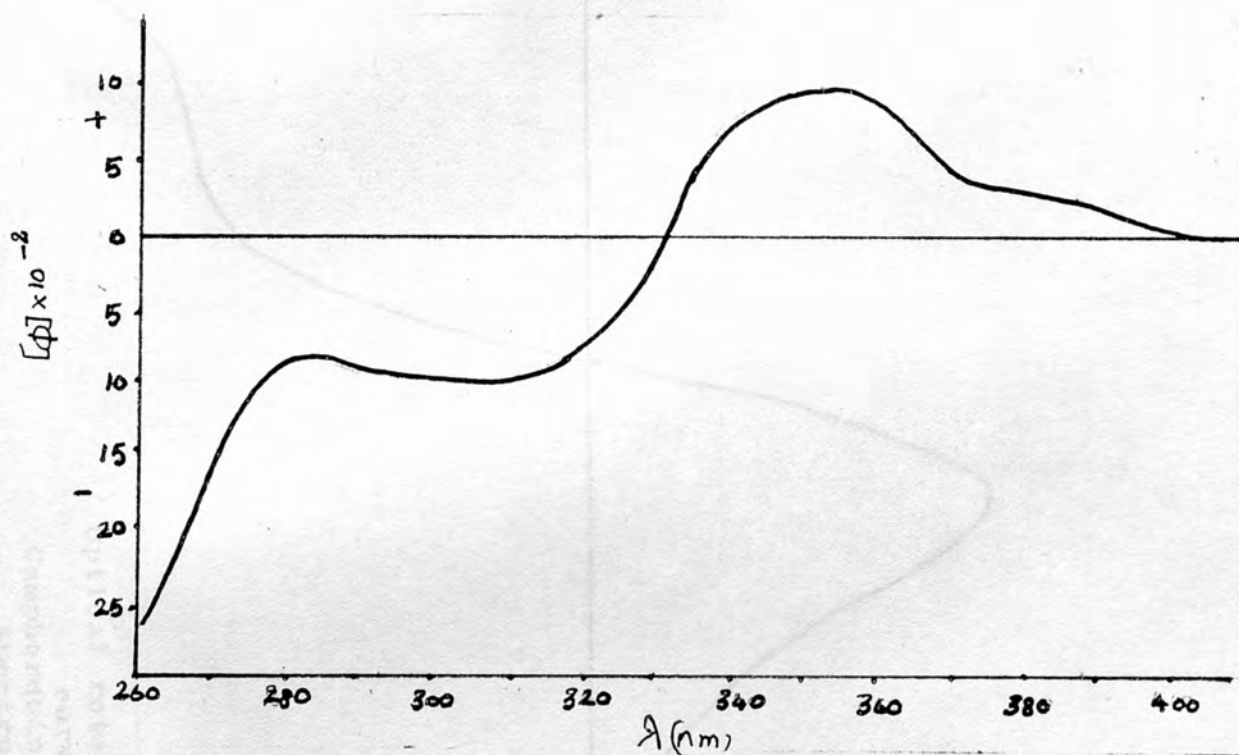


Optical rotatory dispersion curve of N-p-anisylcamphorimide
Spectrum No. 54

Optical rotatory dispersion of acids

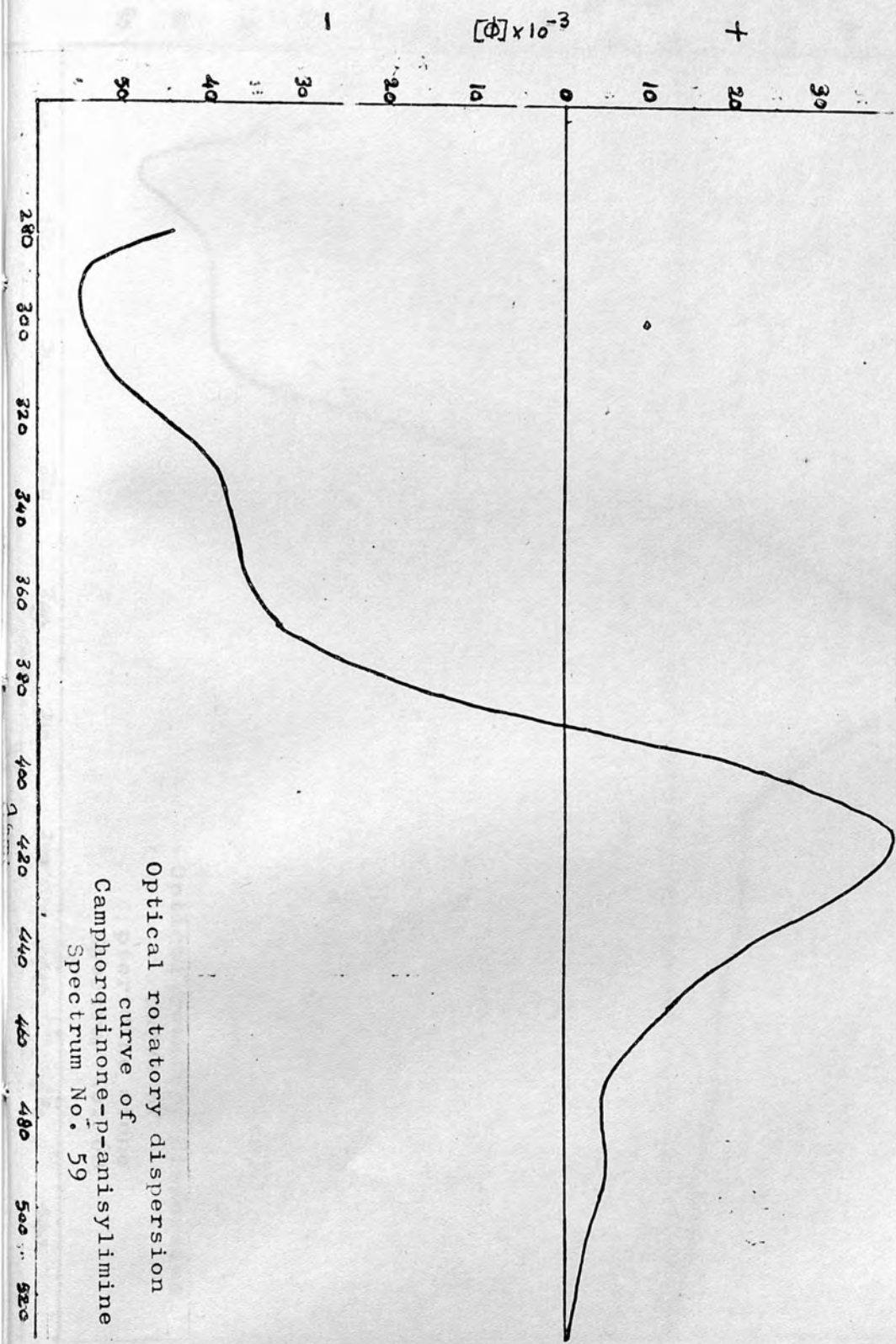
 β -camphoramic acid spectrum No. 55 α -camphoranilic acid Spectrum No. 56

L-camphor-p-anisidinic acid Spectrum No. 57

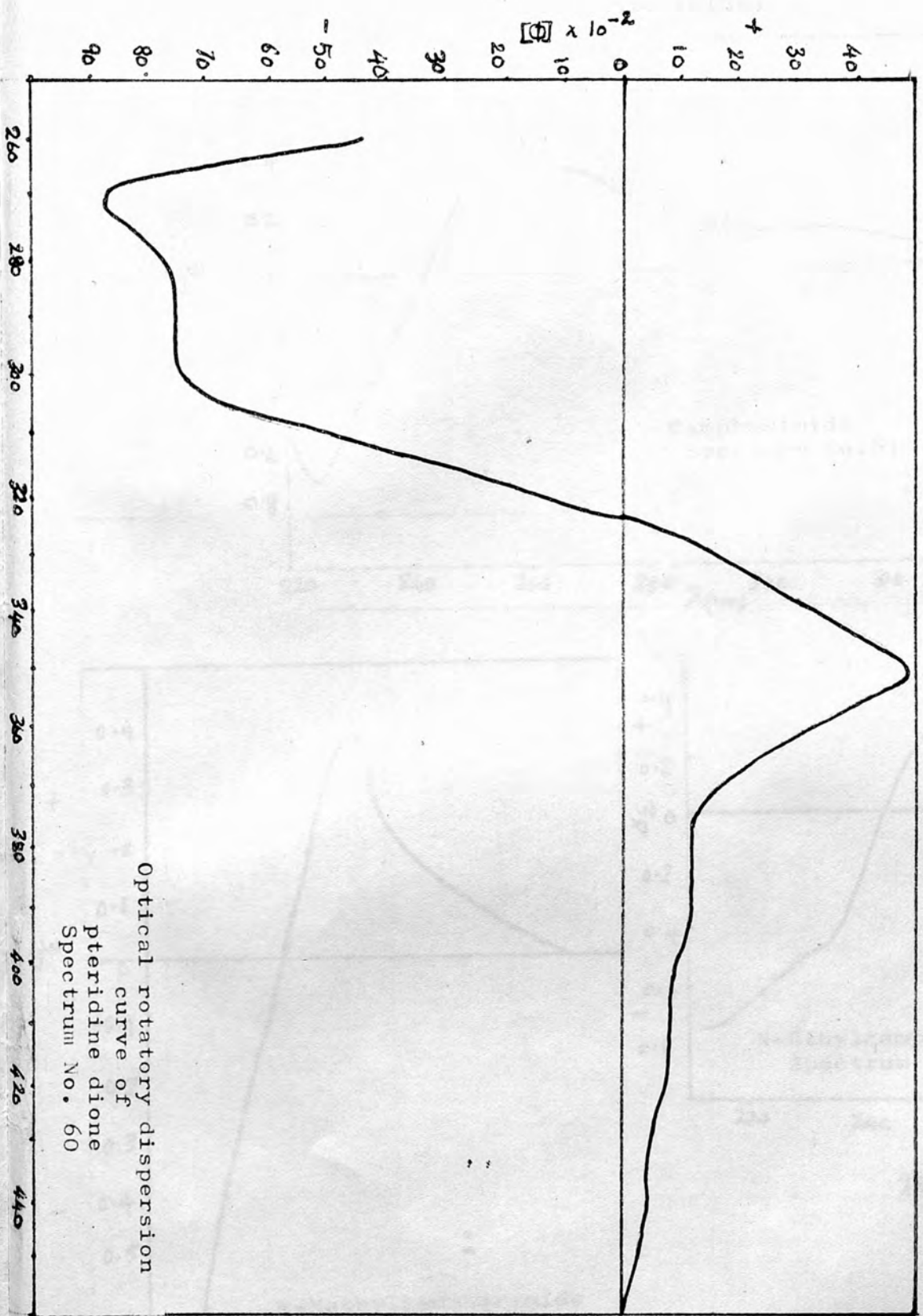


Optical rotatory dispersion
curve of

7or(8)-chlorocamphorquinoxaline
Spectrum No. 58



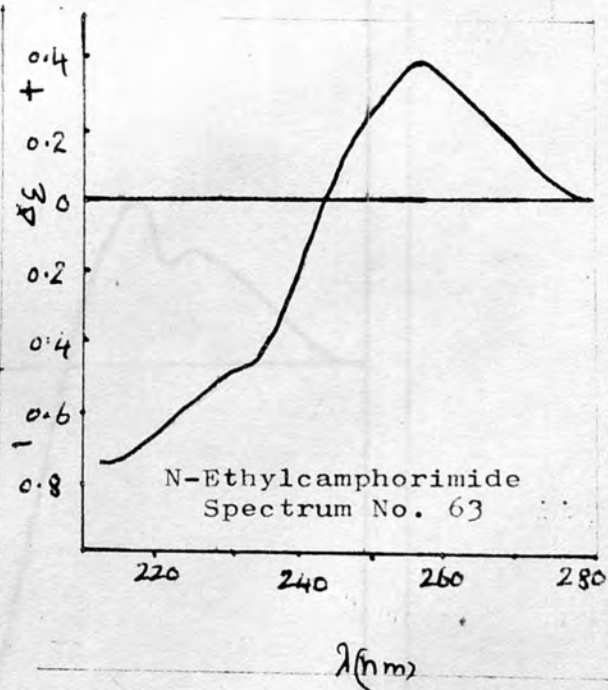
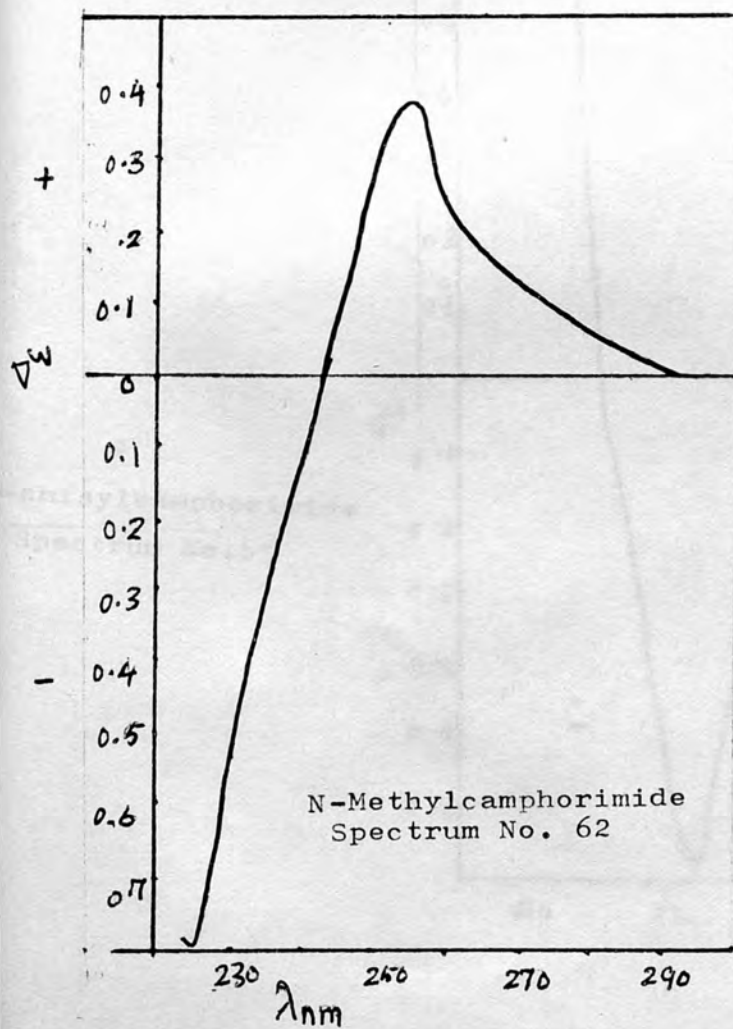
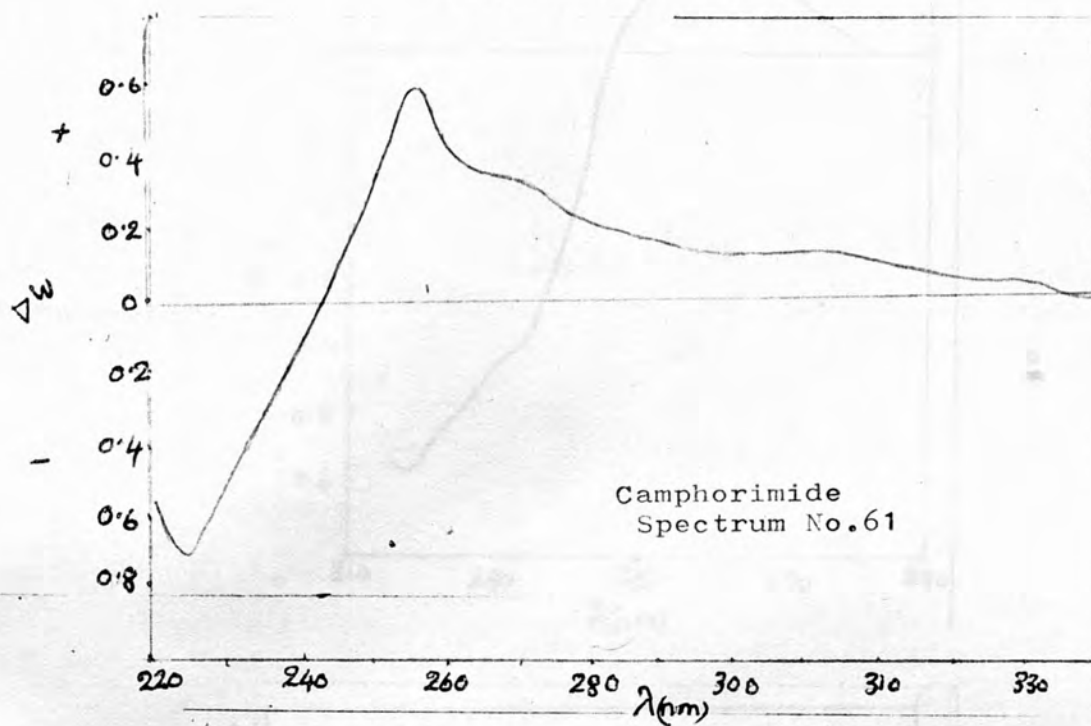
Optical rotatory dispersion
 curve of
 Camphorquinone-p-anisylimine
 Spectrum No. 59



Optical rotatory dispersion
curve of
pteridine dione
Spectrum No. 60

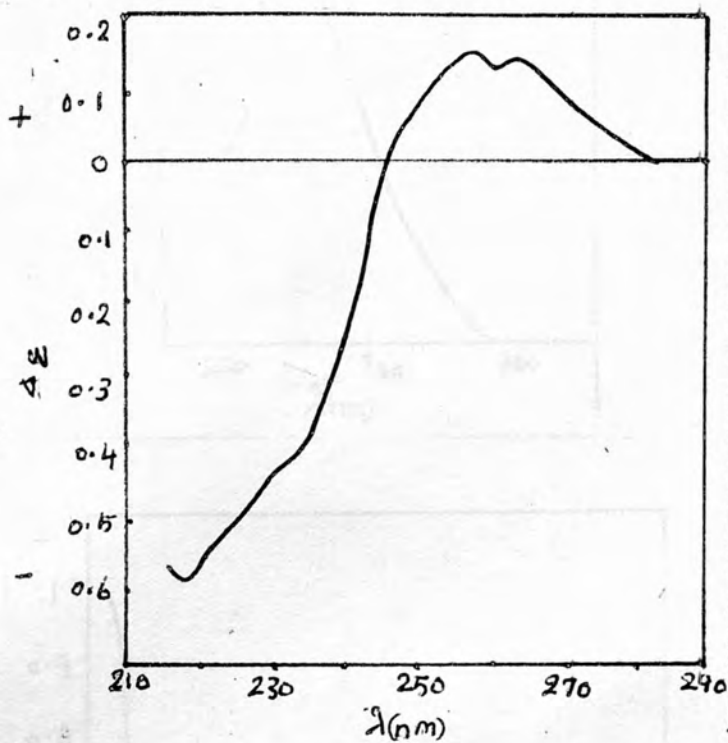
CIRCULAR DICHROISM CURVES

Aliphatic imides

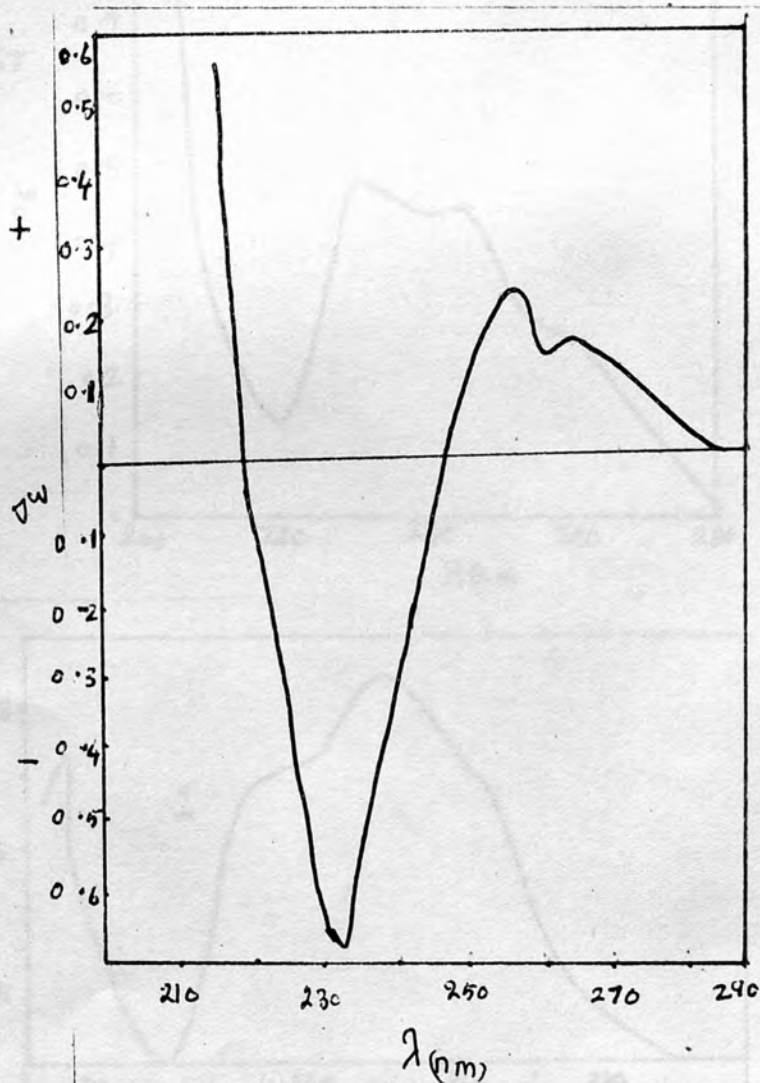


Circular dichroism curves of aromatic imides

N-phenylcamphorimide
Spectrum No. 64

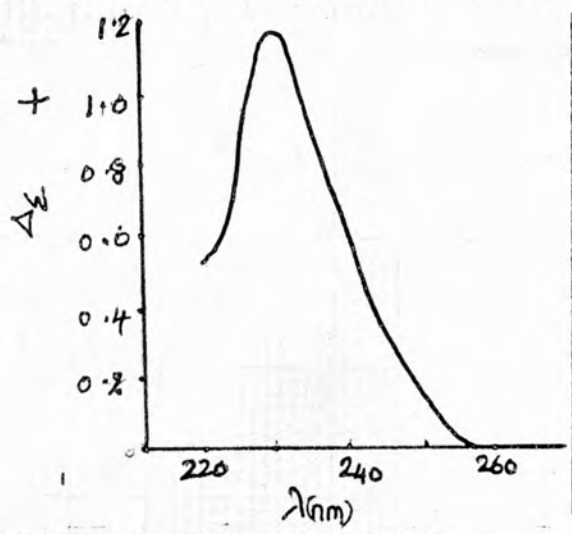


p-anisylcamphorimide
Spectrum No. 65

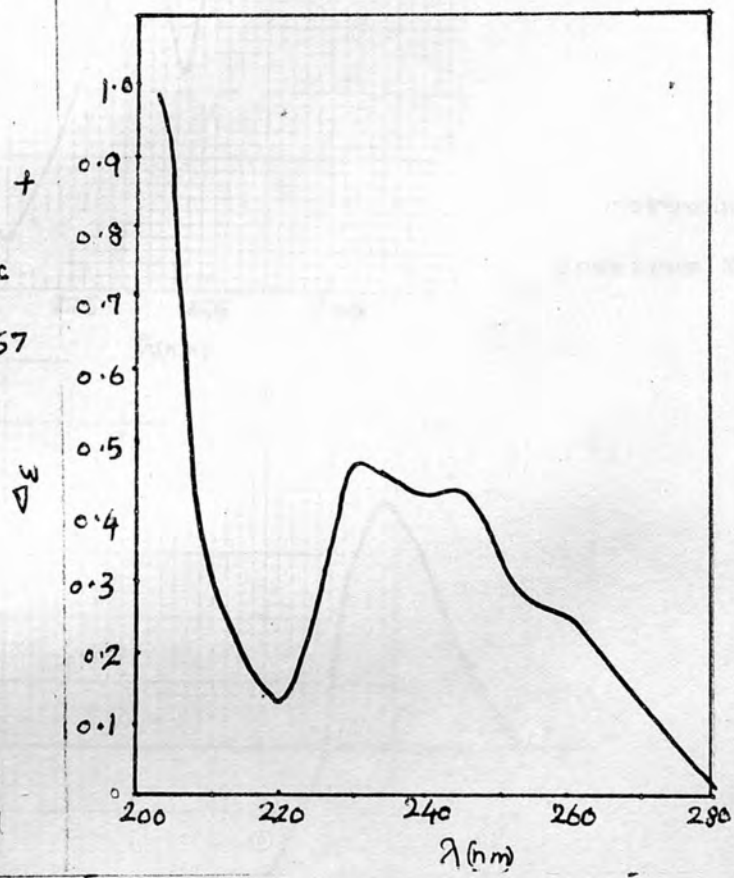


Circular Dichroism curves of acids

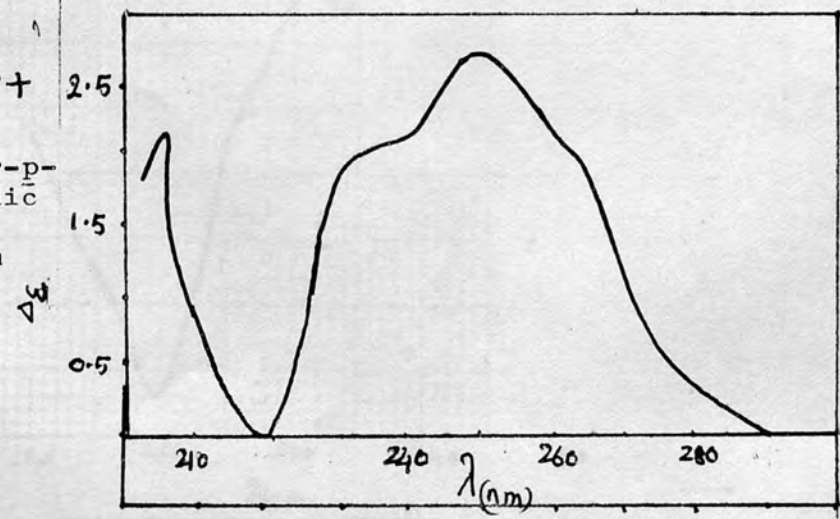
β -Camphoramic acid
Spectrum No.66



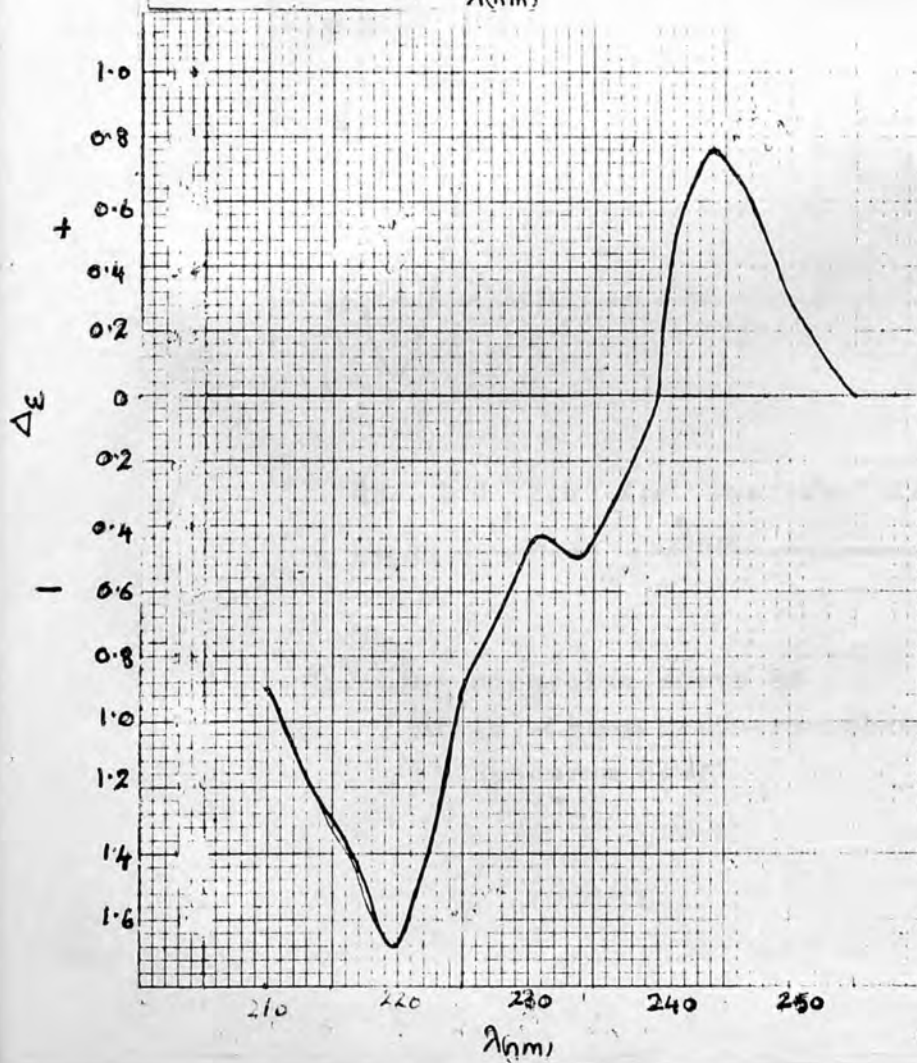
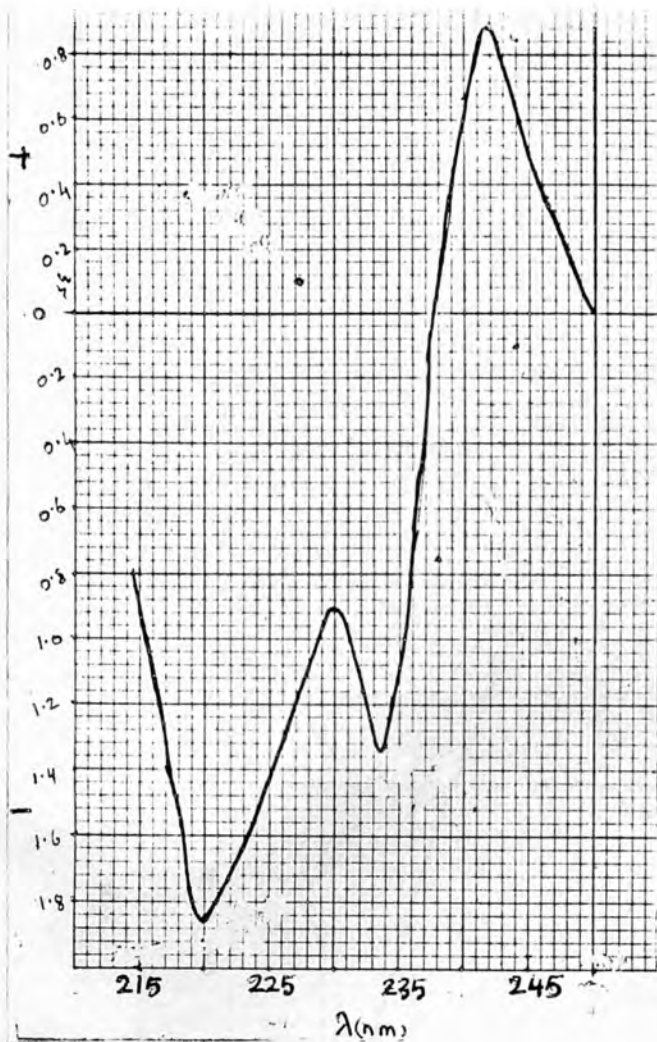
α -Camphoranilic acid
Spectrum No.67

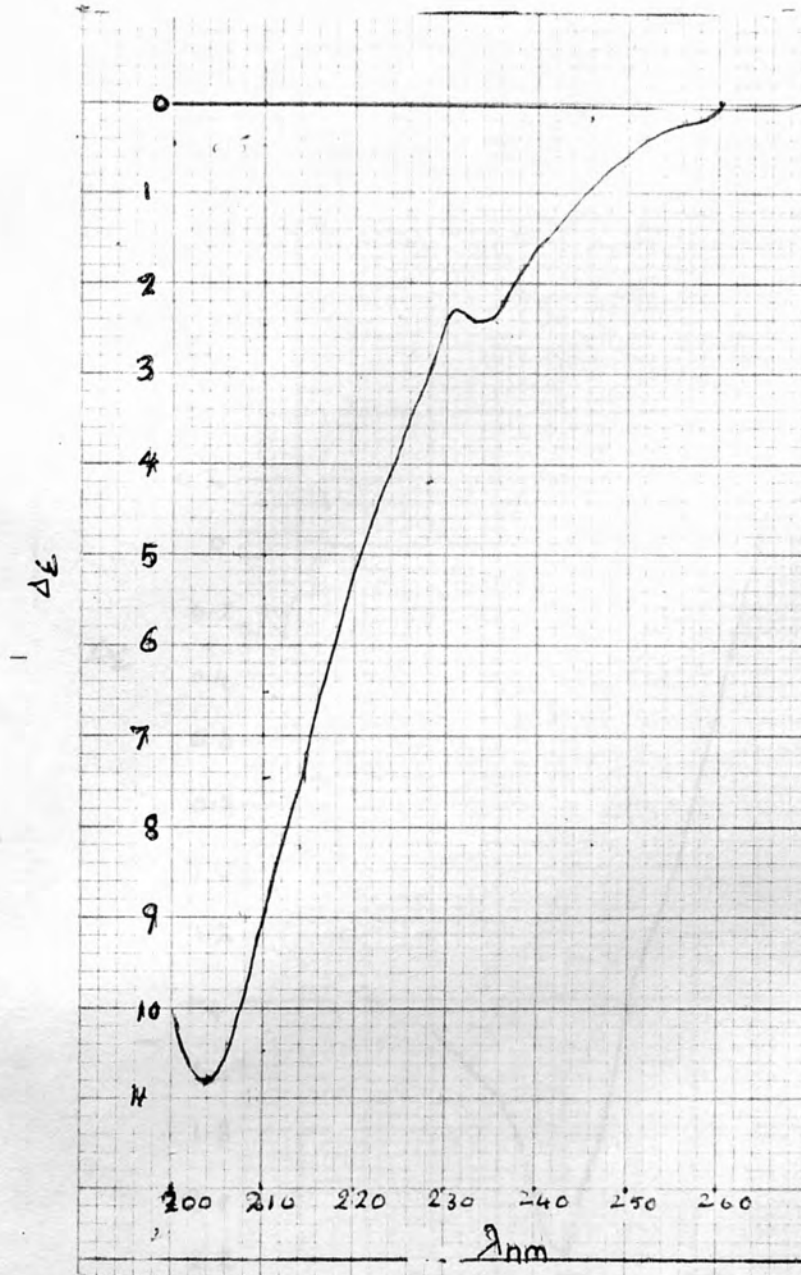


α -Camphor-p-anisidinic acid
Spectrum No.68

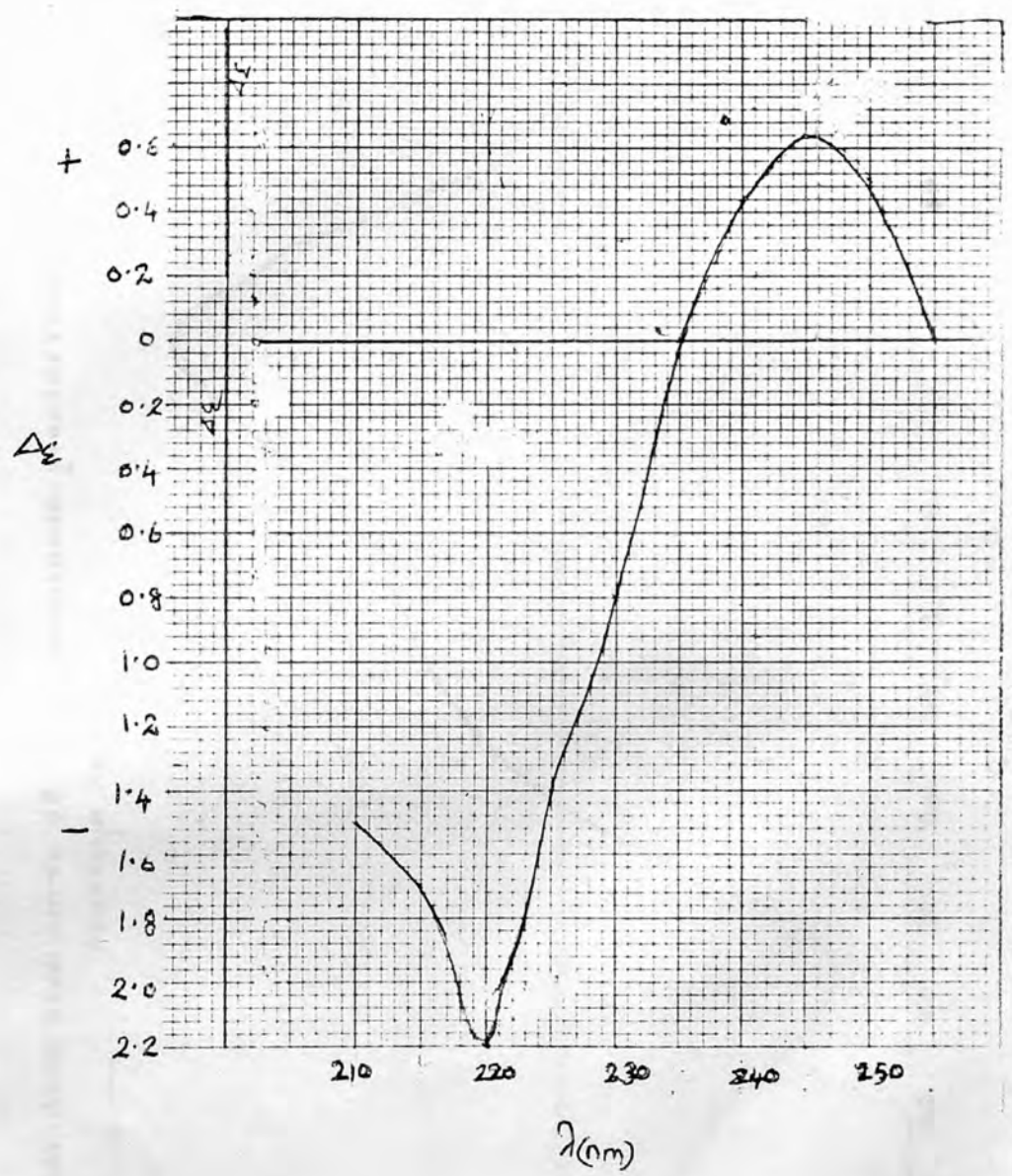


Circular dichroism
curves of
camphorquinoxalines



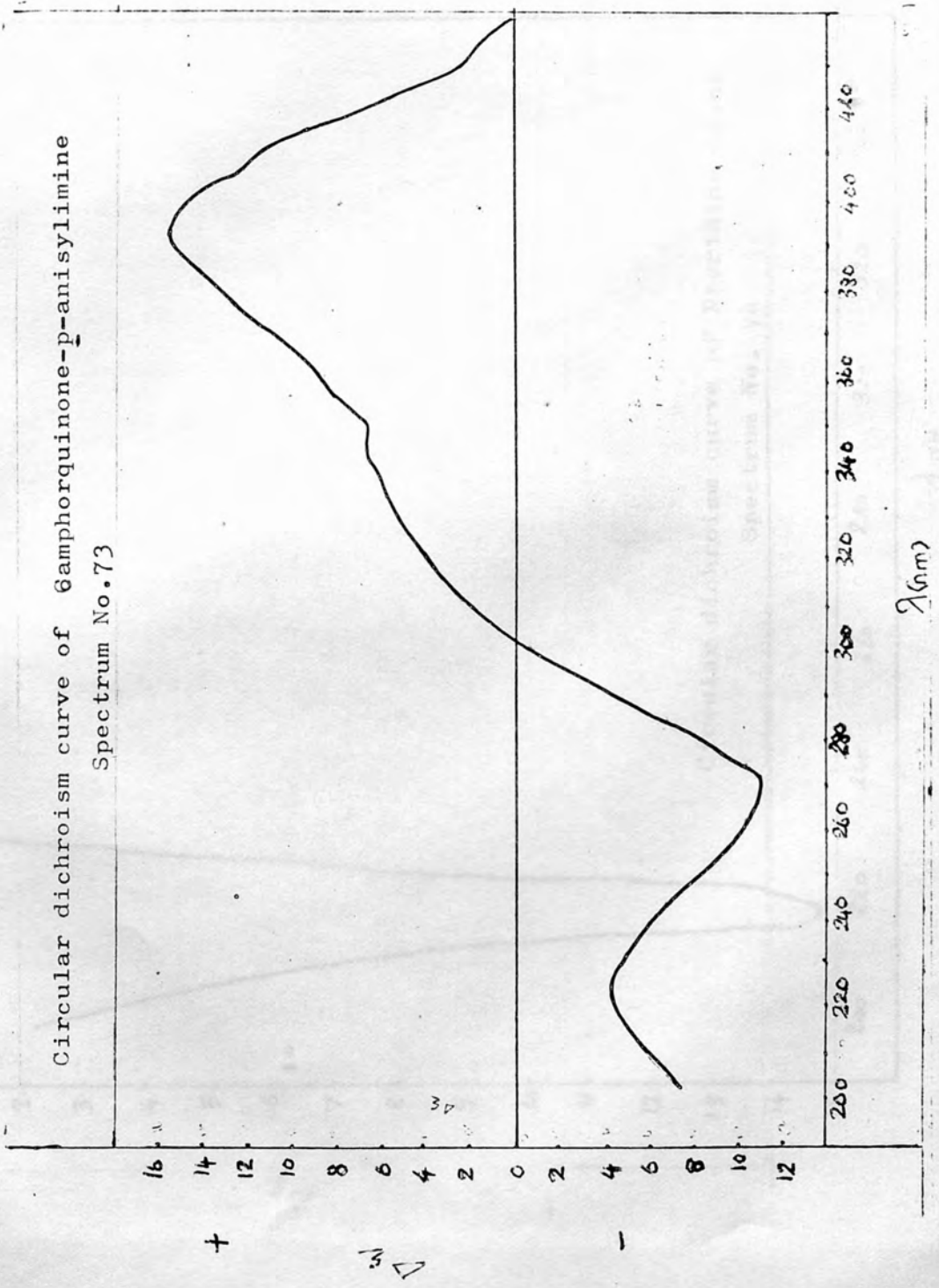


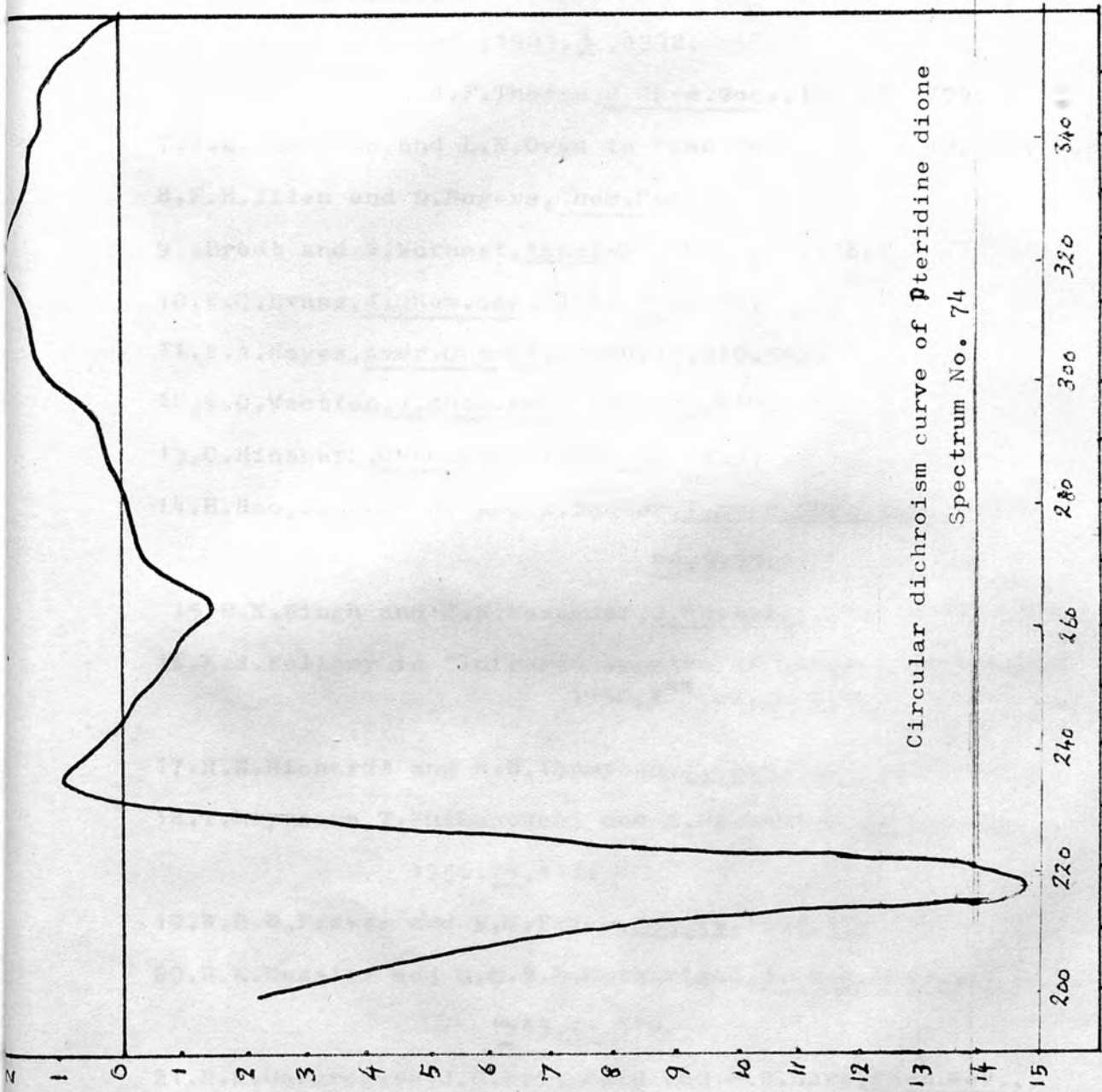
Circular dichroism curve of
7 or (8)-~~Chloro~~ camphorquinoxaline
Spectrum No.71



Circular dichroism curve of
7,8 - dimethylcamphorquinoxaline
Spectrum No. 72

Circular dichroism curve of Gamphorquinone-p-anisylimine
Spectrum No. 73





λ nm

+

Δε

-

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