OPTICAL STABILITY AND SPECTROSCOPIC STUDIES OF 1,1'-BINAPHTHYL AND RELATED COMPOUNDS.

A thesis submitted to the University of London for the degree of Doctor of Philosophy

by

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ABSTRACT

Previous work on the optical stabilities of substituted 1,1'-binaphthyls has shown that the energy of activation for the racemisation of optically active 1,1'-binaphthyls with planar substituents (-COOH, $-COOCH_3$, -COOEt) in the 8,8'-positions is almost identical with that of unsubstituted 1,1'-binaphthyl. 8'-Methyl-1,1'-binaphthyl-8-carboxylic acid has been prepared, resolved and its Arrhenius parameters and transition state theory functions for racemisation determined.

The values of E, A, $\Delta F^{\neq}$, $\Delta H^{\neq}$, and $\Delta S^{\neq}$ are remarkably close to those of 8-methyl-1,1'-binaphthyl (M. M. Harris and R. Z. Mazengo, _Chem_. _Comm_., 1967, 125; _J_. _Chem_. _Soc_. _C_, 1967, 2575) and it is concluded that here again the -COOH group offers a negligible steric barrier to the transition state for racemisation.

Optically active 2,2'-dimethyl-1,1'-binaphthyl has been synthesised and found to be highly optically stable; this is explained on the basis that its ground state energy is much lower than that of an 8,8'-substituted 1,1'-binaphthyl.

Attention was then turned to an investigation of the ground states of certain of the substituted 1,1'-binaphthyls using U.V., N.M.R., I.R., mass spectra, O.R.D. and C.D. Ultraviolet spectra indicate that the 8,8'-substituted 1,1'-binaphthyls are overall more "planar" than 2,2'-substituted 1,1'-binaphthyls. Nuclear magnetic resonance spectra indicate that the substituents in the 2,2'-positions are further away

from the opposite naphthalene residue than in the case with 8,8'-substituted 1,1'-binaphthyls; this is deduced from the greater shielding of the methyl groups in 8,8'-substituted 1,1'-binaphthyls. Moreover, a second substituent in the 8,8'-position reduces the observable effect (shielding), presumably due to greater distortion, resulting in the "pushing away" of the substituent from the centre of the opposite naphthalene ring.

O.R.D. and C.D. curves have enabled assignment of absolute configurations to several of the 1,1'-binaphthyls.

Optically active 1,1'-binaphthyl-8,8'-dicarboxylic acid had not previously been obtained free from occluded water; a method of preparing the anhydrous acid in a crystalline state enabled a comparison of the infrared spectra of the racemic and optically active acids to be carried out. Striking differences in the spectra in the carbonyl and the hydroxyl regions have, with the aid of molecular models, been attributed to different degrees of hydrogen bonding in the crystals.

The thesis is divided into sections, the first being a general account of evidence for peri-interaction in naphthalene compounds. This is followed by sections describing the application of various techniques in the present investigation, each section having its separate introduction.

THE OBJECT OF THIS WORK.

Previous work on the 1,1'-binaphthyls mainly involved investigations of the optical stabilities of these compounds. To further these investigations, 8'-methyl-1,1'-binaphthyl-8-carboxylic acid was prepared and resolved and its Arrhenius parameters and transition state theory functions for racemisation compared with those of 8-methyl-1,1'-binaphthyl.

Stability to racemisation is concerned with the ground state as well as the transition state for the racemisation. It is, however, not possible to study the transition state for racemisation, alone. Moreover, the differences in the optical stabilities of certain 1,1'-binaphthyls was taken to be due largely to differences in the ground states of these molecules. It was therefore considered desirable to study the ground state of the 1,1'-binaphthyls in the solid form and in solution using all available spectroscopic techniques, since spectroscopic studies are concerned with the ground states of molecules.

GENERAL INTRODUCTION. EVIDENCE FOR peri-INTERACTION IN NAPHTHALENE DERIVATIVES

In some sections discussed in this thesis, peri-interaction in the naphthalene residues of the 1,1'-binaphthyls is offered as an explanation of the observed results. This peri-interaction causes molecular distortions in the 8,8'-disubstituted 1,1'-binaphthyls. It is therefore, appropriate that a discussion on molecular deformation as a result of peri-interaction in naphthalene derivatives, should precede the discussions on the work done by the author.

Bulky substitution at interfering positions causes steric strain which can be relieved by:

(a) Bond stretching

(b) In-plane deflection of the substituent

(c) Out-of-plane deflection of the substituent

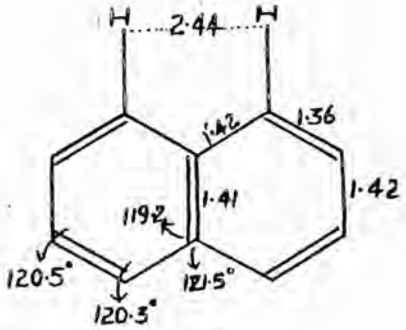
(d) A distortion or buckling of the nucleus itself.

Bond stretching, which obeys Hooke's quadratic law (K. Mislow, Introduction to Stereochemistry, Benjamin Inc., New York, 1965), however small, is associated with large amounts of energy, and for this reason it can be excluded. Whether one or more of the other modes of relief of steric compression operate in a given molecule will depend on the extent of the steric compression in that molecule. "Decentralisation of steric strain" (R.L. Avoyon, A.I. Kitaigorodskii and Yu. T. Struchkov, *J. Struct. Chem.*, U.S.S.R., 1963, **4**, 581) or "distribution over many coordinates" (C.A. Coulson, Ind. Chim. Belge. 1963, 28, 149) refers to the relief of strain by a multiplicity of these atomic motions. There are fewer reported cases of nuclear distortions. When this occurs there is loss in resonance energy due to these nuclear distortions and deviations of substituents from the mean molecular plane, and this competes with the decrease in steric strain energy. Resonance of the substituent with the aromatic skeleton tries to keep the molecule planar, whereas steric repulsion due to nonbonded atoms tend to cause deviation from planarity.

PHYSICAL EVIDENCE:

1. Crystal structure:

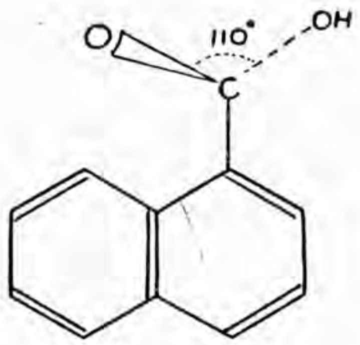
The naphthalene molecule, I, has a planar structure (C.A.Coulson, R.Daudel and J.M.Robertson, Proc. Roy. Soc. (London) 1951, A207, 306) with bond angles and bond lengths accurately determined (D.W.J.Cruickshank, Acta Cryst., 1957 10, 504).



I

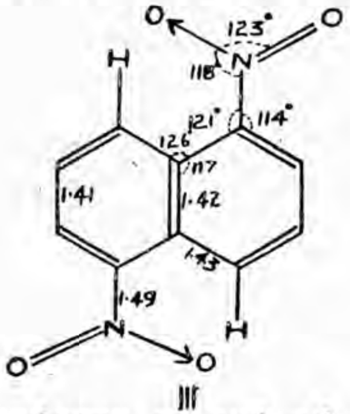
The distance between peri-positions is only about 2.4-2.5Å. In aromatic molecules, the normal nonbonded H----H distance is 2.4-2.5Å and the nonbonded C----C distance is approximately 3.0Å. Therefore any substituent other than hydrogen in peri-positions in the naphthalene molecule will introduce steric interaction. Crystallographic studies of 1-monosubstituted and 2-monosubstituted naphthalenes have revealed the nature of peri-interaction in these molecules and the mechanism by which the steric strain is relieved. In 1-substituted naphthalenes, there is in-plane and/or out-of-plane deformations of substituents because of peri-hydrogen interaction, whereas in 2-substituted naphthalenes these deformations are lacking. 2-Naphthoic acid (J. Trotter, Acta Cryst., 1961, 14, 101) and 2,6-dichloronaphthalene (T.L.Khotsyanova and Yu.T.Struchkov, J. Struct. Chem. U.S.S.R., 1964, 5, 375) have been found to be planar. In 1,3-dichloro-(J. Trotter, Can. J. Chem., 1961, 39, 1964) and 1,4-dibromonaphthalene (J. Trotter, Can. J. Chem., 1961, 39, 1574) the α-halo substituents undergo an out-of-plane deviation of 0.3-0.4Å, which is significant.

With bulkier 1-substituents, the distortions are more significant. J.Trotter (Acta.Cryst., 1960, 13, 732) found that in 1-naphthoic acid, II, the carboxyl group is twisted, the oxygen atoms lying at mean distances of 0.2Å, one above and another below the mean plane. The angle between the aromatic and carboxyl plane is 11°. This partly relieves the steric strain, There is, in addition, a slight in-plane displacement of the (C_{Ar}——CO_2H) bond away from the peri-position and a reduction in the O-C-O angle from approximately 120° to 110°.



II

With the more bulky substituent in 1,1'-binaphthyl, the interplanar angle is estimated as 73° (W.A.C.Brown, J.Trotter and J.M.Robertson, Proc. Chem. Soc., 1961, 115)*. J. Trotter (Acta Cryst., 1960, 13, 95)by studying the structure of 1,5-dinitronaphthalene, III, has found that the molecule as a whole deviates considerably from planarity even though the naphthalene ring itself remains planar.



III

The nitro groups undergo an out-of-plane twisting of 49°

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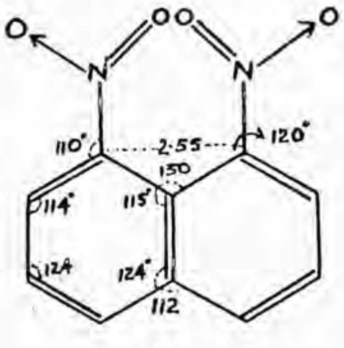
*(The specimen of 1,1'-binaphthyl used in this determination had m.p. 148-149°. Y.Badar, Chau Cheung King Ling, A.S.Cooke and M.M.Harris (J. Chem. Soc., 1965, 1543) obtained the compound in two distinct crystalline forms of m.p.144.5-145°

and 157-159°. Hence it is doubtful whether or not the crystals used by Brown and coworkers were of one form. Their results can therefore be taken as only approximate).

by rotation about the C-N bond. The C-N bond is also displaced within the molecular plane, thus reducing the exocyclic valency angles to 114°. These slight in-plane displacements effectively reduce the extent of the interplanar twisting of the nitro group to 49° as contrasted to 65° in nitromesitylene, 9-nitroanthracene, and 9,10-nitroanthracene.

In 1,8-dinitronaphthalene, IV, steric interactions are expected to be even greater.



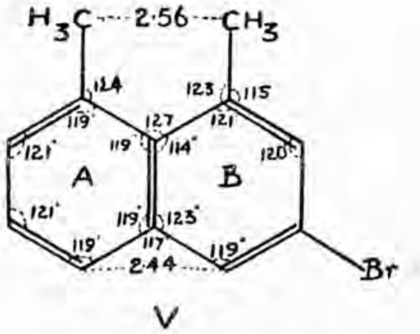
IV

If the molecule were entirely planar, the nonbonded O----O distance would be approximately 0.5Å as against the normal distance of 2.5Å. The steric interaction here is reduced by:

1) Rotation of the nitro group about the C-N axis by 45° in one direction.
2) Splaying apart of the C-N bonds to increase the N----N distance to 2.93Å from 2.24Å in a hypothetically planar model.
3) Deviations of the C-N bonds from the aromatic plane by 0.37Å in opposite directions and

4) Forcing of the carbon atoms attached to the nitro groups out of the plane of the molecule in the direction of the substituents resulting in slight nuclear distortions (~~A. de Aguiar, Ber., 1874, 7, 306.~~) Z. A-Akopyan and Yu. T. Struchov, J. Strukt Chem. USSR, 1964, 5, 457.

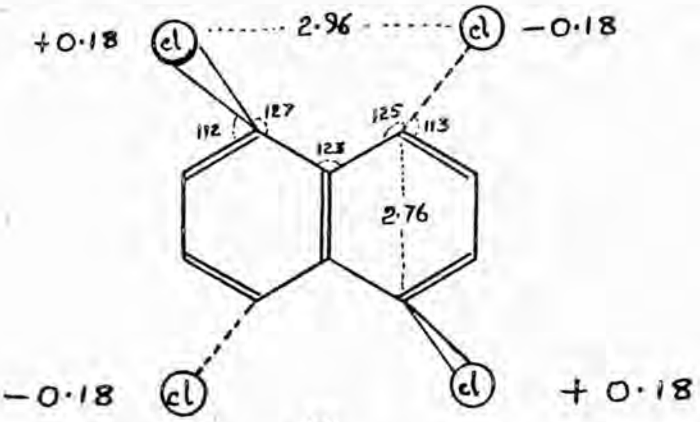
A study of 3-bromo-1,8-dimethyl-naphthalene, V, (M.D.Jameson and B.R.Penfold, J. Chem. Soc., 1965, 528) has proved very interesting in that the observed bond lengths in the molecule are not significantly different from those in similar environments.



V

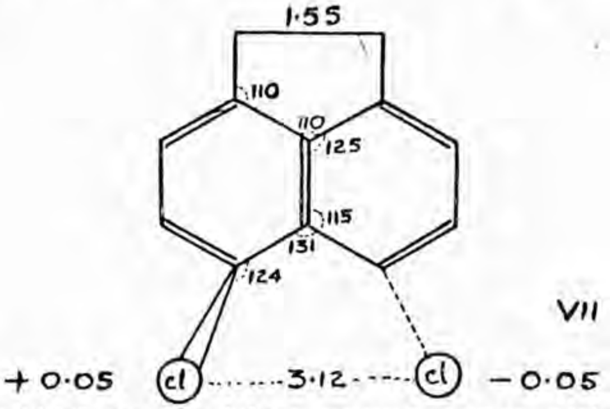
The peri-methyl groups are pushed apart by 0.42Å within the aromatic plane by a 4° in-plane bending of C–CH_3 bonds. This causes deformation of bond angles in the naphthalene portion of the molecule ($\angle C_8C_9C_1=126.8^\circ$, $\angle C_4C_{10}C_5=117.4^\circ$, $\angle C_{Me}C_1C_9=122.9$, $\angle C_{Me}C_8C_9=124.2^\circ$). The nonbonded distance between the methyl groups is increased from 2.44Å (that between C_4----C_5) to 2.56Å. However, the bond angles in ring A do not show any large variation whereas those in ring B show this variation considerably. This is attributed to a buckling of ring A thus enabling bond angles in it to remain more or less unaffected. The heavy bromine atom in ring B militates against any buckling of the ring, which would cause non-planarity of that ring. However, this introduces angle strain in ring B.

Work on 1,4,5,8-tetrachloronaphthalene, VI, (M.A.Davydova and Yu.T.Struchkov, J. Struct. Chem. U.S.S.R., 1961, 2, 63, M.A.Davydova and Yu, T. Struchkow. J. Struct. Chem., U.S.S.R. 1962, 3, 202; 1965, 6, 98; and G.Gafner and F.H.Herbstein, Acta Cryst., 1962, 15, 1081) has shown that the mechanism for the relief of steric strain in this molecule is similar to that in 1,8-dinitronaphthalene.



VI

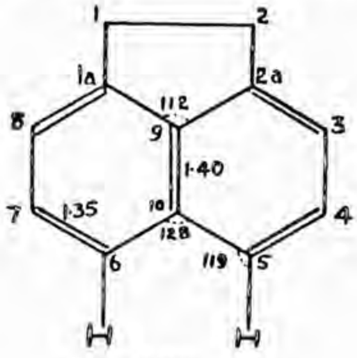
The steric strain, as shown by observed bond lengths and bond angles, is spread over the entire molecule and steeply decreases with increasing distance from the site of its origin. In-plane bending of the peri-halogens is restricted by β-hydrogen atoms The major release of the van der Waals strain, therefore, is a propeller-like arrangement of the C-Cl bonds. The carbon atoms carrying the halogens are also forced in the direction of the displaced halogens and the nucleus thus assumes a chair-like conformation. The elasticity of the naphthalene framework allows nuclear distortions thereby decreasing the C_1----C_4 distance to 2.76Å from the normal distance of 2.90Å in naphthalene. A comparison between this molecule and 5,6-dichloroacenaphthalene, VII, is interesting.



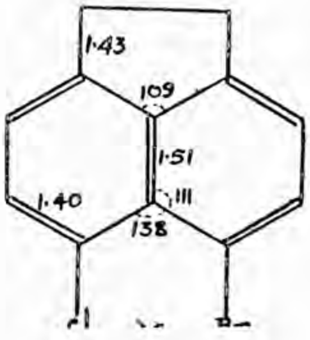
VII

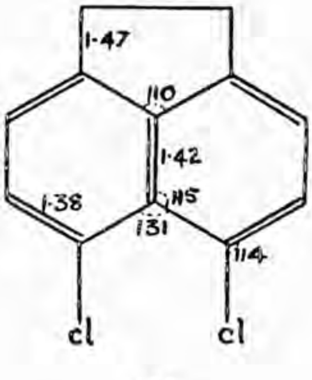
The dimethylene bridge across one set of peri-positions pulls these carbon atoms together, thus widening the angles at the other end (T.W.C.Mak and J.Trotter, Acta Cryst., 17, 367; 1963, 16, 1032). Hence there is a greater in-plane displacement of the halogens and a small out-of-plane deviation (0.05Å as compared to 0.18Å in 1,4,5,8-tetrachloronaphthalene).

An interesting comparison is also provided by the bond angles and distances observed for acenaphthene, VIII, its 5,6-dichloro-, IX, and 5-chloro-6-bromo-, X, derivatives.



VIII

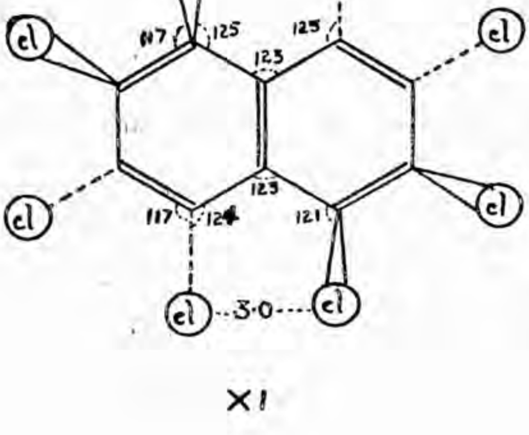




IX

Changes ate observed in C_1-C_{1a} and C_9-C_{10} bond lengths. The C_1-C_{1a} bond length decreases steadily whereas the C_9-C_{10} bond increases in length. A less significant increase is noticed in the C_6-C_7 bond length. However, bond angles involving carbon-halogen bonds show dramatic changes. As the peri-substituent increases in size, the $C_5C_{10}C_6$ angle widens. The carbon-halogen bonds in these molecules and several other sterically hindered molecules are generally longer than the normal C_{Ar}——halogen bonds. This is suggested to be due to a weakening of conjugation of the halogen atoms with the aromatic ring (R.L.Avoyan and Yu.T.Struchkov, J. Struct. Chem., U.S.S.R, 1963, 4, 578; R.L.Avoyan, A.I.Kitaigorodskii and Yu.T.Struchkow, J. Struct. Chem., U.S.S.R. 1964, 5, 390; G.Gafner and F.H.Herbstein, Acta Cryst., 1960, 13, 706).

G.Gafner and F.H.Herbstein (Nature, 1963, 200, 130) have reported a three-dimensional X-ray analysis of octachloronaphthalene, XI.



XI

Deviations of the atoms from the mean molecular plane (in Å)=

C_1	-0.20	Cl_1	-0.60
C_2	-0.13	Cl_2	-0.4-
C_3	+0.11	Cl_3	+0.40
C_4	+0.22	Cl_4	+0.75
C_5	-0.24	Cl_5	-0.79
C_6	-0.14	Cl_6	-0.37
C_7	+0.14	Cl_7	+0.47
C_8	+0.20	Cl_8	+0.54
C_9	-0.20		
C_{10}	+0.01		

As a result of these multiple displacements of the substituents and the nuclear carbon atoms, the molecule is severely deformed. The α- and β-chlorines are displaced out-of-plane in the same direction by 0.54-0.79Å and 0.37-0.47Å respectively and the out-of-plane displacement of each carbon atom is about a third as much and in the same direction as its halogen substitent. The molecule also takes up a propeller-like conformation The non-bonded chlorines are approximately 3.0Å apart.

The above results suggest a need for revision of the findings of D.M.Donaldson and J.M.Robertson, (J. Chem. Soc., 1953, 17) regarding the molecular structure of octamethylnaphthalene. These workers suggest, on the basis of a two-dimensional X-ray analysis that the α-methyl groups undergo an out-of-plane displacement of 0.73Å corresponding to a 28° deviation of the C_{Ar}——CH_3 bond. The β-methyl groups also deviate by 0.25-0.40Å from planarity. In addition these bonds undergo a slight in-plane displacement. However, adjoining methyl groups deviate in opposite directions, one above and the other below the plane of the molecule. The results suggest, but do not give conclusive evidence, that there are slight nuclear distortions. Hence an elaborate solution should await further work on the molecule. It is not possible to make a precise crystal structure analysis due to the difficulty in obtaining crystal of a suitable-size. To retain the trigonal sp^2 geometry at each carbon atom, the nuclear carbon atoms have to move in the direction of the methyl groups and this would mean that despite the serious molecular distortion, the geometry around each nuclear carbon atom is planar. R.L.Avoyan, A.I.Kitaigorodskii and Yu.T.Struchkov (J. Struct. Chem., U.S.S.R., 1964, 5, 390) describe this as "the assembly of curved domes from planar tiles".

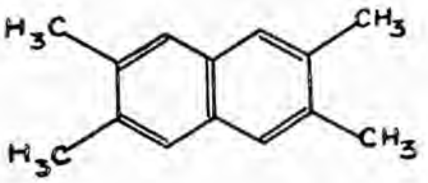
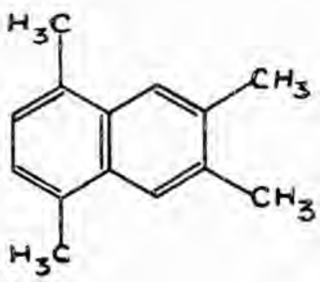
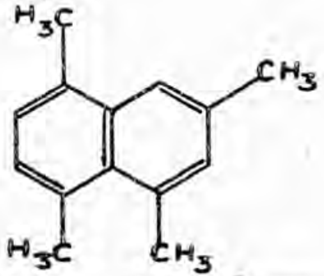
2. Molecular spectra:

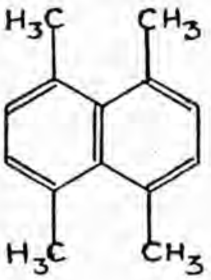
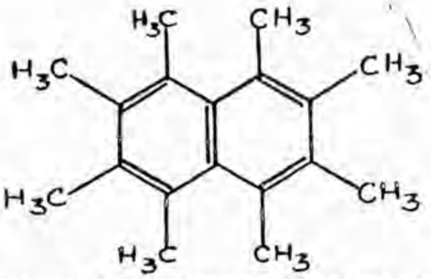
(a) Ultraviolet spectra:

Naphthalene has three absorption bands with λ_{max} at 312, 275 and 220mμ, the respective ϵ_{max} values being 200, 5000 and 100,000. Introduction of substituents modifies the band positions and intensities, and the spectral characteristics depend on whether or not substituents enter into mutual conjugation through the aromatic ring and whether the systems are homo- or heteronuclear. When the substituents occupy positions susceptible to steric effects, interpretation of spectral pattern has to take this into consideration. B.D. Pearson (Tetrahedron, 1961, 12, 32) has made a careful comparison of spectral data on a number of monosubstituted naphthalenes, and shown that α-substitution causes a bathochromic shift of the 275mμ band ('La) which becomes superimposed on the weaker 312mμ band ('La), and that with β-substitution the middle band is unaffected while the 312mμ band is displaced to longer wavelengths.

In disubstituted naphthalenes where conjugation is possible a conjugation band appears at longer wavelengths (e.g., 400-440mμ in nitronaphthylamines in ethanolic solution). The shape and intensity of this band is a measure of the electronic and steric effects in the molecule.

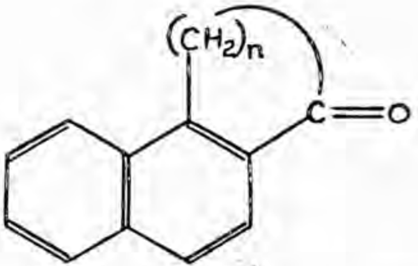
W.L.Mosby, (J. Amer. Chem. Soc., 1953, 75, 3348) observed that in the series 2,3,6,7-, 1,4,6,7-, 1,4,5,7-, and 1,4,5,8-tetramethylnaphthalene, there is a progressive red shift:-

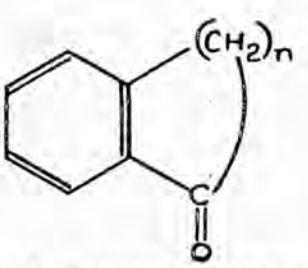
Compound	λ_{max}	ϵ_{max}
	270	4800
	290	6600
	292	7600

	296	8300
	308	5000

In 1,4,5,8-tetramethylnaphthalene, the methyl groups occupy α-positions which possess greater conjugative interaction than the β-positions. Hence the progressive observed red shift may be linked to progressive overcrowding in the peri-positions of the molecule. This view is supported by an even greater red shift for octamethylnaphthalene.

R. Huisgen and U. Rätz (Tetrahedron, 1958, 2, 271) studied the U.V. spectra of cyclic ketones of the type:

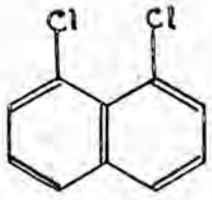


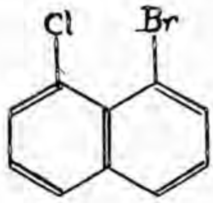


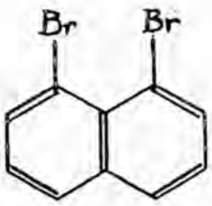
These compounds have an absorption band around 250mμ which is believed to arise from carbo~~x~~nyl group conjugation with the aromatic ring. As one goes from n=5 to n=8 the intensity of this absorption band becomes considerably reduced. This effect is observed much more in the naphthalene series than in the benzene analogues. This difference is attributed to steric effects of peri-hydrogen in the former series.

1-Nitronaphthalene (λ_{max} 243, 342mμ; log ϵ_{max} 4.02, 3.59 in ethanol) undergoes a hypsochromic shift by the introduction of a 5-nitro-group (λ_{max}233, 327mμ; logϵ_{max} 4.32, 3.81), or 8-nitro-group (λ_{max}231, 313mμ; log ϵ_{max} 4.32, 3.81) as has been shown by the work of L.H.Klemm, J.M.Sprague and E.Y.K.Mak (*J. Org. Chem.*, 1957, *22*, 161). In 1,5-dinitronaphthalenes each of the nitro groups is counteracting the conjugative ability of the other and this makes the electronic transition difficult; whereas in 1,8-dinitronaphthalene the effect is more steric in nature.

V.A.Koptyug and V.A.Plakhov, (*J. Gen. Chem.* U.S.S.R. 1962, *32*, 249) determined the absorption spectra of peri-dihalonaphthalenes and showed that in going from 1,8-dichloronaphthalene to 1,8-dibromonaphthalene a distinct bathochromic shift in the region 250-315mμ region is observed.







The average shift is about 3mμ, whereas in the corresponding 1,7-dihalonaphthalenes the red shift is only 1mμ, showing that peri-halonaphthalenes are strained systems.

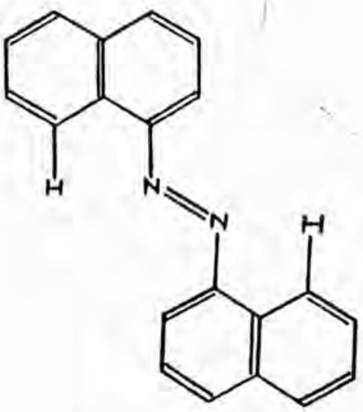
The spectral data of azo- and azoxynaphthalenes (G.M. Badger and R.G.Buttery, *J. Chem. Soc.*, 1953, 2156) also provide strong evidence for steric effects due to peri-substitution. It is assumed that these are all *trans*. In ethanolic solutions, aromatic azo compounds have a strong conjugation band around 320-380mμ. The K band positions in these compounds are in the order:

azobenzene $<$ azotoluene $<$ 2,2'-azonaphthalene $<$ 1,1'-azonaphthalene (table below).

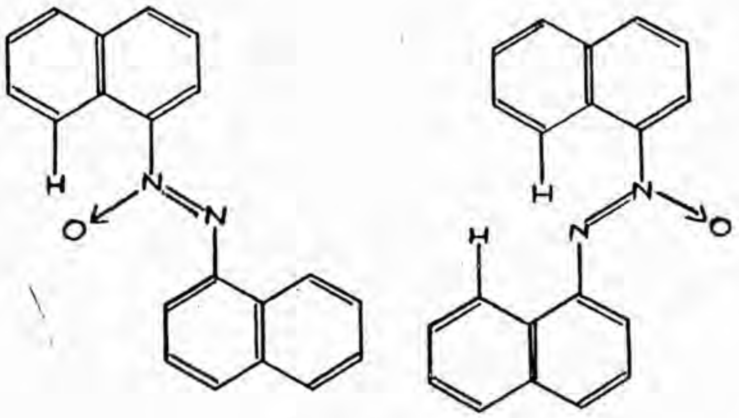
K band of azo and azoxy derivatives in ethanol

Compound	λ_{max}	Log ϵ_{max}
Azobenzene	318	4.32
-2,2'-Azotoluene	332	4.24
2,2'-Azonaphthalene	335	4.37
1,1'-Azonaphthalene	400	4.21
Azoxybenzene	323	4.16
2,2'-Azoxytoluene	313	3.96
2,2'-Azoxynaphthalene	346	4.41
1,1'-Azoxynaphthalene	364	4.06

Increasing conjugation shifts the K band to longer wavelengths. But with corresponding azoxy compounds the order is different. Passing from azobenzene or 2,2'-azonaphthalene to the azoxy compound shows a bathochromic shift whereas a similar change from 2,2'-azotoluene or 1,1'-azonaphthalene to the azoxy compound causes a blue shift. This indicates that steric effects are important in the 1,1'-azoxynaphthalene but not in the azo compound.



Azonaphthalene



Azoxynaphthalene

It is possible that the overlap of the peri-hydrogen with azoxy oxygen is more than that between the peri-hydrogen and azo nitrogen and perhaps changes the preferred conformation about the C-N bonds.

These are but a few of the examples of the U.V. spectroscopic work done on peri-substituted naphthalenes that give evidence on the strained nature of these compounds.

(b) Nuclear magnetic resonance spectra:

Apart from using N.M.R. in structural analysis the organic chemist has applied this method in studies of intramolecular interactions in peri-substituted naphthalenes.

The naphthalene molecule has a spectrum with α- and β- proton resonance signals at τ 2.20 and τ 2.56 respectively (D.C.F.Garbutt, K.G.R.Pachler and J.R.Parish, J. Chem. Soc., 1965, 2324). However, in the presence of other substituents in the naphthalene nucleus, the resonance positions of the remaining protons are affected.

G.O.Dudek, (Spectrochim. Acta, 1963, 19, 691), P.R. Wells (Australian J. Chem., 1964, 17, 967) and P.R.Wells and P.G.E.Alcorn (Australian J. Chem., 1963, 16, 1108) have observed a significant deshielding which results from peri-effects. The peri-proton in 1-nitronaphthalene appears at τ 1.64 as compared to τ 2.20 for the peri-proton in naphthalene itself. Introducing a methyl group ortho to the nitro group i.e., 1-nitro-2-methylnaphthalene, shifts the peri-proton signal to τ 2.23 as against a calculated value of τ 1.69. Hence the deshielding of the peri-proton in 1-nitronaphthalene is due to the nitro group. The reversal of the chemical shift in passing from 1-nitronaphthalene to 1-nitro-2-methylnaphthalene is a result of the non-planar twisting of the 1-nitro group.

G.O.Dudek (Spectrochim. Acta, 1963, 19, 691) has shown that α-substituents e.g., OH, OCH_3 and NH_2 considerably deshield peri-protons, which prefer the trans-arrangement of these substituents. Under such conditions the peri-hydrogen would be within 2.40Å from the lone-pair electrons on the adjacent oxygen or nitrogen. This can be seen as a type of hydrogen bond (normal H-bond distance is 2.70Å) and this would readily explain the downfield shift of the peri-proton signal. The extra proximity of the peri-protons, by virtue of their fixed geometry compensates for the normally poor acceptor ability of the aromatic hydrogen.

Aromatic and methyl proton chemical shifts in dimethylnaphthalenes also show a noticeable variation:

Proton chemical shifts in dimethylnaphthalenes.

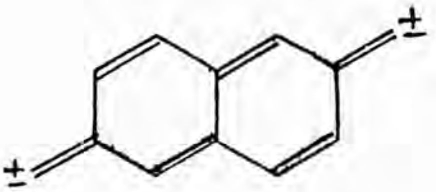
(C. MacLean and E.L.Mackor, Mol. Phys., 1960, 3, 223).

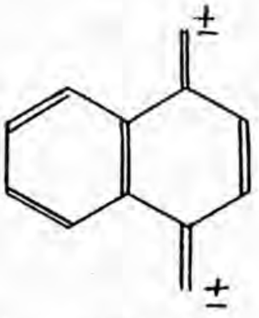
Compound Dimethylnaphthalene	Ring α-protons (c.p.s.)	Aliphatic protons (c.p.s.)
(naphthalene)	-117.0	------
2,3-	-105.0	+99.3
2,6-	-104.6	+94.1
2,7-	-100.8	+94.8
1,4-	-121.0	+88.7
1,5-	-115.2	+86.7
1,8-	------	+78.7

The α-methyl protons in 1,4- and 1,5-dimethylnaphthalenes are deshielded as a result of steric hindrance by the adjoining peri-hydrogen atoms. The downfield shift of the methyl protons in 1,8-dimethylnaphthalene compared to other isomers reflects much greater steric strain in the molecule.

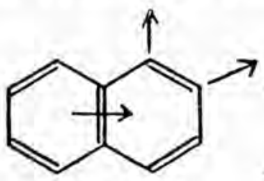
3. Electric dipole moments:

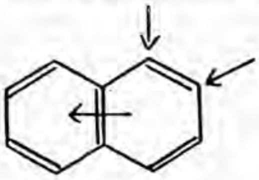
For monosubstituted naphthalenes, the 2-isomer has a greater dipole moment than that of the 1-isomer, irrespective of the type of substituent. This is partly due to a longer conjugated system in the 2-isomer than in the 1-isomer and partly due to the in-plane and/or out-of-plane twisting of the 1-substituent leading to a decreased conjugation of the substituent with the naphthalene system. (A.E.Lustkii and L.A.Kochergina, Russ. J. Phys. Chem., 1959, 37, 238; J.H. Richards, Tetrahedron, 1964, 20, 841).



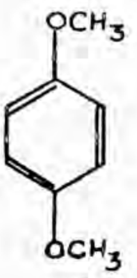


Moreover, the dipole moments of 1-naphthyl compounds are close to those of the corresponding benzene derivatives. This is taken to indicate that steric effects caused by peri-hydrogen are counterbalanced by the dielectric contribution from the other ring in the naphthalene derivative;

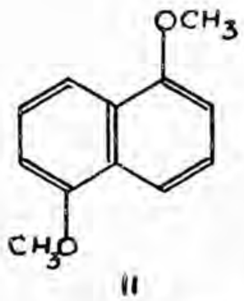




E.B.Everard and L.E.Sutton (J. Chem. Soc., 1949, 2313) have measured the dipole moments of some substituted naphthalenes.



I



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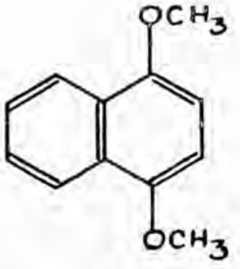
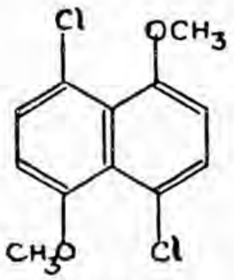


III

I has a dipole moment of 1.73D and this is assumed to be a result of the free rotation of the $-OCH_3$ group, thus allowing the group to take all configurations from cis to trans with equal probability for each configuration. The value 0.67D for II indicates reduced free rotation due to the steric effect of the peri-hydrogen, and the effect of the resonance causing a π-bonding between the C_{Ar}——O bond. Hence the $-OCH_3$ groups are supposed to lie trans to each other. III has a dipole moment of 2.09D which is lower than the calculated value of 2.45D which is taken to indicate that the groups cannot be quite coplanar.



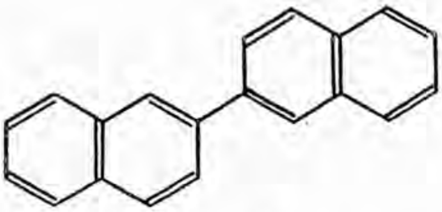
IV

V

In IV and V the halogen dipoles would be expected to cancel and the resultant moment to be that of the parent compound II. But the dipole moments are 0.95D and 0.93D respectively. Scale drawings show considerable interference between the halogens and the oxygen in IV and V and this strain is relieved by in-plane and out-of-plane movements of the substituents. An in-plane movement of the substituent would not explain the dipole moment observed, but an out-of-plane movement of the substituent could give an unsymmetrical configuration possessing a dipole. The angle of deflection calculated from the dipole moment was 18° and the theoretical moment was about 1, which is close to the observed value.

4. Chromatographic adsorption:

Planarity of an organic molecule affects the degree of chromatographic adsorption; the more planar the molecule the more strongly it is adsorbed. M.Orchin and F.Reggel (J. Amer. Chem. Soc., 1947, 69, 505), observed that 2,2'-binaphthyl, I, is much more strongly adsorbed than the twisted 1,2-binaphthyl, II.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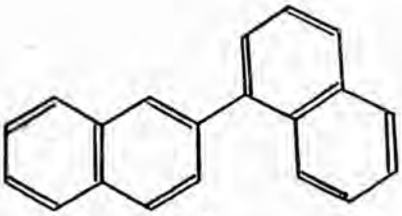
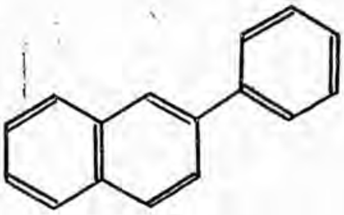

II

L.H.Klemm, D.Reed and C.D.Lind (J. Org. Chem., 1957, 22, 739) employed this method with a set of 1- and 2-phenyl- and Δ^1-cyclohexenylnaphthalenes using an alumina column and found that the 1-isomers eluted first.


III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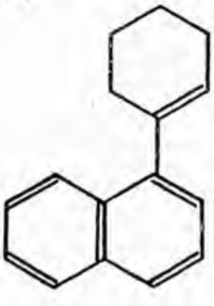
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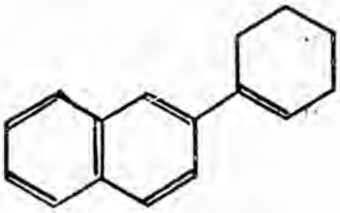
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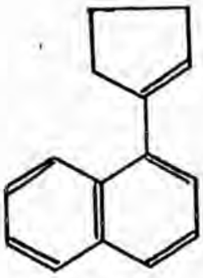
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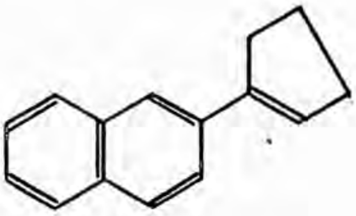

VIII

With the cyclopentenyl- and cyclohexenylnaphthalenes (V, VI, VII, VIII) the difference in the conjugative effects (L.H.Klemm, W. Hodes and W.B.Schaap, J. Org. Chem., 1954, 19, 451) is still insufficient to offset the factor of the twist. So the 1-isomers elute first.

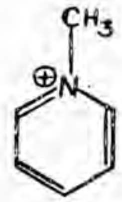
Similar effects have been observed with other polycyclic aromatic hydrocarbons (L.H.Klemm, D.Reed, L.A.Miller and B.T.Ho, J. Org. Chem., 1959, 24, 1468), e.g. in the decreasing order of chromatographic adsorption.

2-phenylanthracene > 1-phenylanthracene > 9-phenylanthrcene;

1,2'-binaphthyl > 1,1'-binaphthyl.

CHEMICAL EVIDENCE

By following the progress of reaction of a series of bases with methyl iodide, in nitrobenzene over a temperature range 10-50°, using conductivity measurements, J.Packer, J.Vaughan and E.Wong (J. Amer. Chem. Soc., 1958, 80, 905) have attempted to estimate the steric strain in the resulting quaternary bases:



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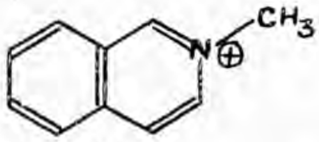

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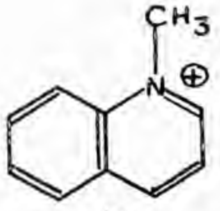

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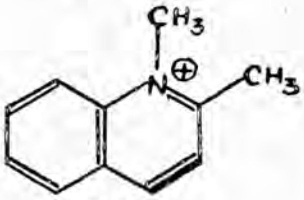

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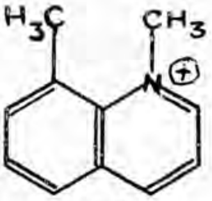


V

Base	10^5k (at 30°)	$\Delta\log A$	$\Delta\Delta H^{\neq}$	$T\Delta\Delta S^{\neq}$
Pyridine	50.7	0.00	0.00	0.00
Isoquinoline	60.0	0.03	-0.14	0.04
Quinoline	8.0	0.00	1.11	0.00
2-methylquinoline	00.677	-0.19	2.34	-0.26
8-methylquinoline	0.0087	-0.06	5.12	0.08

The changes in A, $\Delta H^{\neq}$ and $\Delta S^{\neq}$ are recorded with respect to those of pyridine. The main changes occur in $\Delta H^{\neq}$ and this is taken as the main factor that plays a dominant part in accounting for the observed decrease in rate in going from isoquinoline to 8-methylquinoline. It is taken as a measure of the steric strain in the transition state of the reaction i.e., transition state steric strain energy. $\Delta\Delta H^{\neq}$ is greatest in IV and V where steric strain is greatest. V has the highest value for $\Delta\Delta H^{\neq}$ and this is striking in view of the fact that in this molecule both peri-positions are involved. According to the calculations by H.C.Brown (J. Chem. Soc., 1956, 1248) the steric strain in methylnaphthalenes must be greater and a figure of 7.6.Kcal. mole^{-1} is quoted for 1,8-dimethylnapthalene.

CONCLUSION

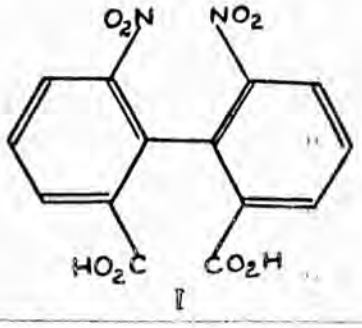
This evidence for peri-interaction in naphthalene derivatives provides every reason to suppose that, even in solution, peri-substituted naphthalenes are distorted; since crystal lattice restricting forces are absent in solution the distortions are expected to be greater than those observed in the solid state. A combination of two distorted naphthalene residues is therefore expected to give a distorted binaphthyl if the interannular bond is in the 1,1′-position.

5. OPTICAL ACTIVITY OF 1,1' - BINAPHTHYLS:

(i) Introduction:

1,1' - Binaphthyls belong to that class of compounds which can show optical activity because of restricted rotation about a single bond: the phenomenon was first noted in substituted biphenyls. J. Kenner (J. Chem. Soc., 1922, 614) interpreted his resolution of 2,2' - dinitro-6,6-diphenic acid, I, as resulting from the folded structure of the biphenyl system, Kaufler's "bent" formular (Annalen 1907, 351, 151; Ber., 1907, 40, 3250, 3253). This explanation was, however, proved not to be correct. F. Bell and J. Kenyon (Chem. and Ind., 1926, 45, 864), W. H. Mills (ibid., 1926, 45, 884, 905) and E. E. Turner and R. J. W. Le Fevre (ibid., 1926, 45, 831) attributed the optical activity in suitably substituted biphenyls to non-planarity of the biphenyl system. Identical 2,2' - substituents, which are large enough to prevent planarity, introduce dissymmetry: with one other substituent in a 3, 5 or 6 position, the molecule is asymmetric. In either case optical activity is possible.

E. E. Turner and R. Adams and their coworkers have done much of the fundamental work on optically active biphenyls.



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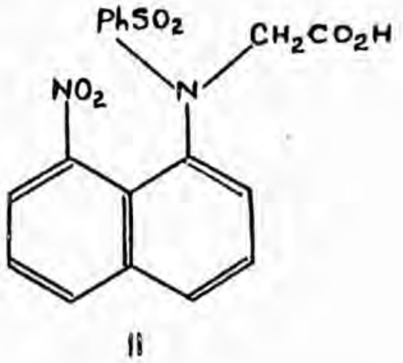

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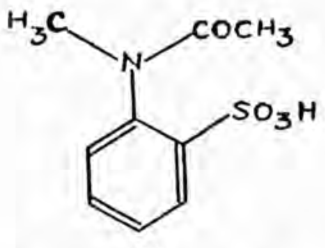
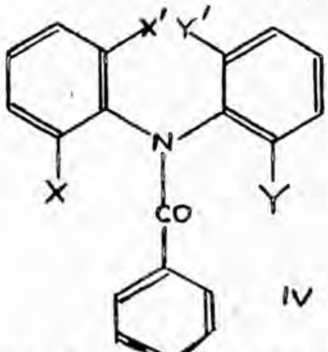


III

Optical activity due to restricted rotation has also been reported by W.H. Mills and K. A. C. Elliot (J. Chem. Soc., 1928, 1291) in N-benzene sulphonyl-8-nitro-1-naphthylglycine, II. W.H. Mills and R. M. Kelham (J. Chem. Soc., 1937, 274) reported optical activity in a substituted benzene, III. E. E. Turner and M. M. Harris obtained optically active N-benzoyl-diphenylamine-2-carboxylic acids of the type represented by IV, while R. Adams and M. W. Miller (J. Amer. Chem. Soc., 1940, 62, 53) resolved substituted stilbenes of the type V.



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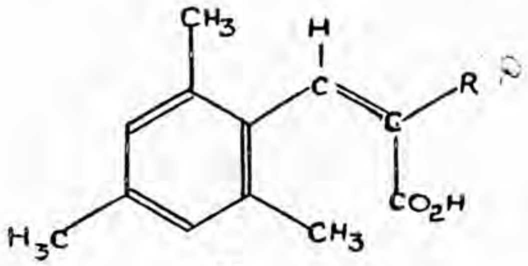
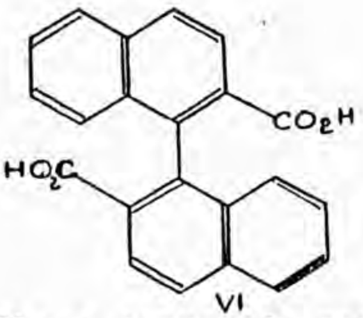


V

R. Kuhn and O. Albrecht (Annalen, 1928, 465, 282) resolved 1,1'-binaphthyl-2-2'dicarboxylic acid, VI, A. Corbellini (Atti Accad. Lincei, 1931, 13, 702), W.M. Stanley (J. Amer. Chem. Soc., 1931, 53, 3104) and J. Meisenheimer and O. Beisswenger (Ber., 1932, 65, 32) reported the resolution of 1,1'-binaphthyl-8,8'-dicarboxylic acid, VII.



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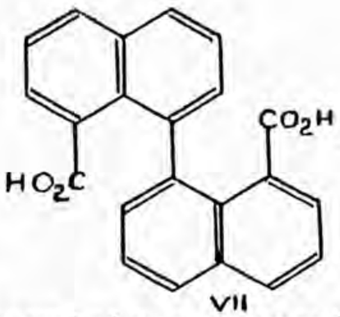


VII

In all these compounds non-bonded repulsions prevent planarity and give rise to molecular asymmetry.

In order to assess the effect of the size of interfering groups on optical stability of structurally similar series it was necessary to study the variation of the ease of racemisation in such series.

R. Kuhn and O. Albrecht (Annalen, 1927, 455, 272) observed that the racemisation of sterically hindered nitrodiphenic acids obeyed the first order reaction rate law given by the equation,

$$k = \frac{2.303}{t} \log \frac{\alpha_0}{\alpha_t}$$

α_0 = initial rotation of the compound

α_t = rotation after time t

R. Adams and his coworkers (J. Amer. Chem. Soc., 1939, 61, 2825) used the first order rate constant $\underline{k}$ and the half life period for racemisation at a given temperature as a measure of optical stability.

The Arrhenius equation;

$$\underline{k} = \underline{A}.e.^{-E/RT}.$$

E = energy of activation
A = probability factor
R = gas constant
T = absolute temperature

has been used in the kinetic studies of racemisation of sterically hindered compounds. The rate constant $\underline{k}$ is determined at different temperatures and E, the energy of activation is obtained from the Arrhenius equation above. E is taken as the energy barrier to racemisation. R. Kuhn and O. Albrecht (*Annalen*, 1927, *455*, 272) used this method to calculate E for the racemisation of nitrodiphenic acids.

A, which can be calculated from the Arrhenius equation gives a measure of the probability that a molecule with sufficient energy will undergo inversion of configuration.

F.W. Cagle and H. Eyring (*J. Amer. Chem. Soc.*, 1951, *73*, 5628) used the Glasstone, Laidler and Eyring's absolute reaction rate theory equation,

$$\underline{k} = \kappa \frac{\underline{\underline{k}}T}{h} e^{-\Delta H^{\neq}/RT} \cdot e^{\Delta S^{\neq}/R}$$

(Glasstone, Laider and Eyring, *The Theory of Rate Processes*, McGraw-Hill, 1941, p. 197)

$\underline{k}$ = rate constant
κ = transmission coefficient
$\underline{\underline{k}}$ = Boltzmann's constant
h = Plank's constant

$\Delta H^{\ddagger}$ = enthalpy of activation

$\Delta S^{\ddagger}$ = entropy of activation

R = gas constant

T = absolute temperature

and calculated $\Delta S^{\ddagger}$ for several optically active compounds and showed that $\Delta S^{\ddagger}$, the entropy ~~for~~ of activation, makes an important contribution to the racemisation velocities of sterically hindered compounds.

$$\Delta H^{\ddagger} = E - RT$$

$\Delta S^{\ddagger}$ can therefore be calculated by substituting the value for $\Delta H^{\ddagger}$ in the absolute reaction rate theory equation.

The free energy of activation $\Delta F^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$ and it reflects the measured quantity $\underline{k}$.

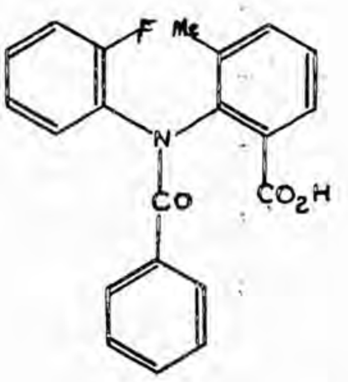
$$\underline{k} = K \frac{\underline{\underline{k}}\ T}{h} \cdot e^{\boxed{\Delta F^{\ddagger}}/RT}$$

Since $\Delta F^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$, $\Delta F^{\ddagger}$ may be brought into the observable region (17Kcal. mole^{-1}) when the negative $\Delta S^{\ddagger}$ factor is large even if $\Delta H^{\ddagger}$ is small. W. H. Mills and R.M.Kelham (J. Chem. Soc., 1937, 274) thought that the lowest limiting value of E for observable optical activity must be about 16 Kcal. mole^{-1} and yet N-benzoyl-2-fluoro-6-methyl-diphenylamine-2-carboxylic acid, obtained optically active had a low E value of 14.9 Kcal. mole^{-1}. Its observable optical activity was attributed to its unusually large negative $\Delta S^{\ddagger}$ of -20.9 e.u.

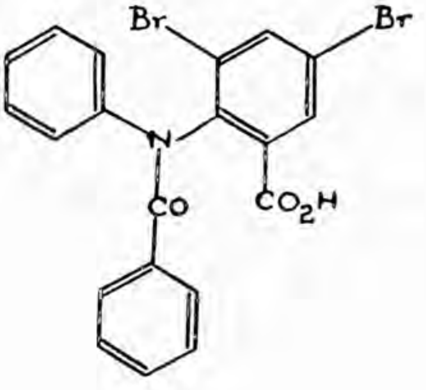
Using values of $\Delta H^{\ddagger}$, A and ΔS^{*} for racemisation, calculated from published racemisation data for a number of compounds, F.W. Cagle and H. Eyring (*J. Amer. Chem. Soc.*, 1951, *73*, 5628) tried to show the influence of structural factors on the entropy term of the absolute rate equation. However, their results were criticised by de la Mare (*Progress in Stereochemistry*, Vol I, Butterworths Scientific Publications, 1954, p. 122) who said he thought the authors should await a considerable extention of the existing information.

In some cases the authors had determined only two rate constants, *k*, at different temperatures, and had perhaps used different solvents for a pair of compounds. However, their approach proved useful in helping the interpretation of some apparently anomalous results.

J. W. Brooks, M. M. Harris and K. E. Howlett (*J. Chem. Soc.*, 1957, 2380) working along these lines made detailed investigations into some N-benzoyldiphenylamine-2-carboxylic acids:



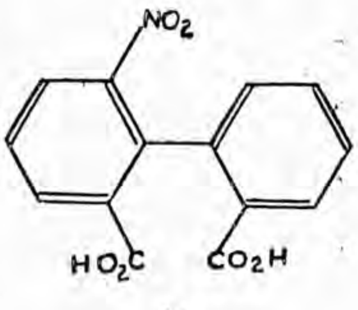
VIII



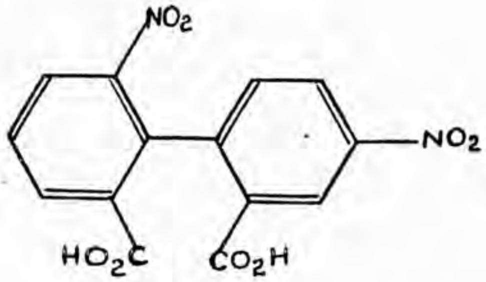
IX

6-Methyl-2'-fluoro-N-benzoyldiphenylamine-2-carboxylic acid VIII, had E = 14.9 Kcal.mole^{-1}, $t_{\frac{1}{2}}^{20}$ = 3.2 minutes whereas 4,6-dibromo-N-benzoyldiphenylamine-2-carboxylic acid, IX, had E = 19.3 Kcal.mole^{-1} and $t_{\frac{1}{2}}^{20}$ = 1.4 minutes. They explained that these differences, as well as being due to steric factors must be due to differences in the entropy of activation, which is -4.1. e.u. for IX and -20.9. e.u. for VIII.

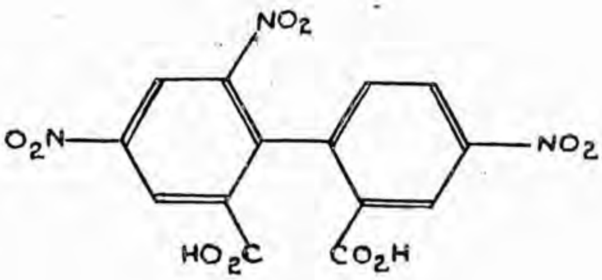
Working along these lines again, J.W. Brooks, M.M. Harris and K.E. Howlett (J. Chem. Soc., 1957, 1934) found that the E values for the racemisation of the nitro-diphenic acids (X-XII) were the same, 22.6 Kcal.mole^{-1}, though their optical stabilities were different, being in the order XII > XI > X.



X



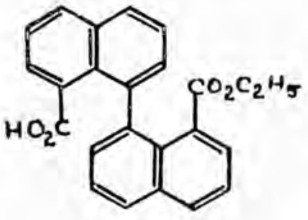
XI



XII

Since the additional nitro group is in a non-blocking position, the increase in the optical stability was attributed to the increase in the entropy factors which are -12.2 e.u. for X, -14.7 e.u. for XI and-16.2 e.u. for XII.

A number of substituted 1,1'-binaphthyls have been resolved and among these are the carboxylic acids: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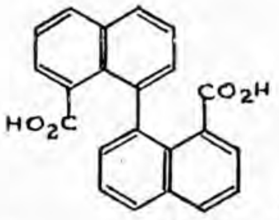
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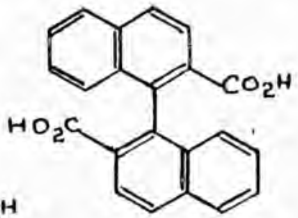
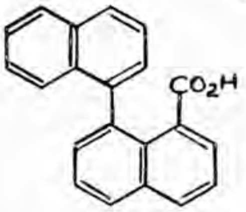
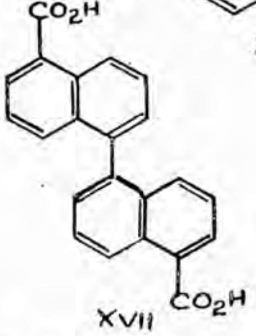

XV


XVI

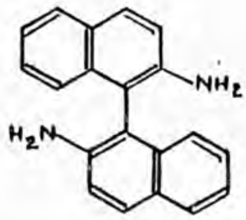

XVII

Whereas in the biphenyls the main factor determining optical stability is the size of ortho-substituents, in the 1,1'-binaphthyls the effect of blocking groups has not yet been easy to interpret. Considering the obstacles to rotation, about the interannular bond, and thinking of the 1,1'-binaphthyl skeleton as a rigid framework, the order of optical stability on the grounds of blocking groups would be expected to be;

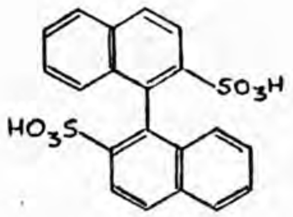
XIII $>$ XIV ——— XV $>$ XVI $>$ XVII as indicated by classical models, but J. Meisenheimer and O. Beissenger (<u>Ber</u>, 1932, <u>65</u>, 32) and D. M. Hall, S. A. Ridgewell and E. E. Turner (<u>J. Chem. Soc.</u>, 1954, 2498) showed that the

2,2'-diacid, XV, was stable to racemisation in aqueous sodium hydroxide. It did not racemise when heated in N,N-dimethylformamide at 170° for 8 hours. This high optical stability has been observed in all 2-substituted and 2,2'-disubstituted 1,1'-binaphthyls.

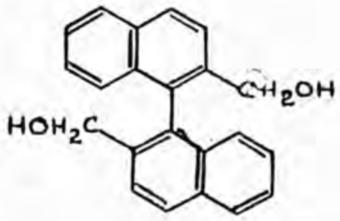
2,2'-Diamino-1,1'-binaphthyl, XVIII, was prepared and resolved by R. Kuhn and P. Goldfinger (Annalen, 1929, 470, 183) and found to be so optically stable that it underwent reactions at 200° without losing its optical activity.



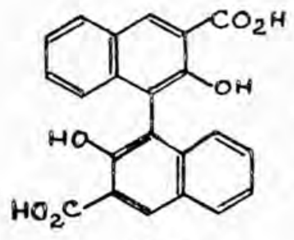
XVIII



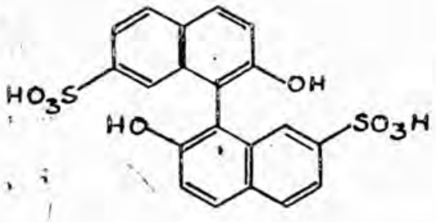
XIX



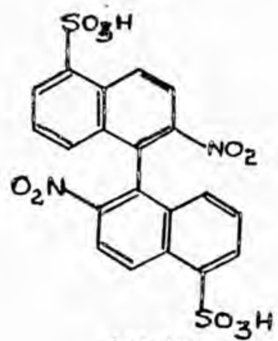
XX



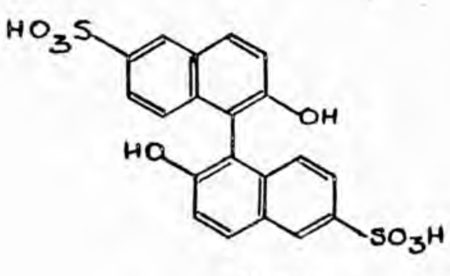
XXI



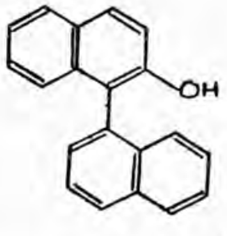
XXII



XXIII



XXIV



XXV

These compounds show high optical stability

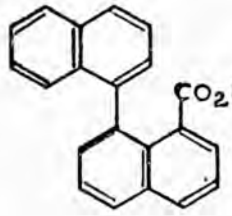
W. L. F. Armarego and E.E. Turner (J. Chem. Soc., 1957, 13) synthesized and resolved 1,1' - binaphthyl - 2,2' disulphonic acid, XIX, and found it to be stable towards racemisation when heated for 10 hours at 200° in aqueous sodium hydroxide in a sealed tube.

D. M. Hall and E.E. Turner (J. Chem. Soc., 1955, 1242) found that 2,2' - bishydroxymethyl-1,1'- binaphthyl XX, was so optically stable that it melted and solidified on cooling without racemising.

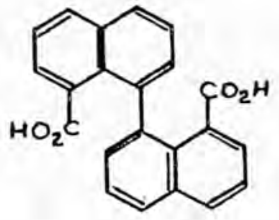
W. M. Stanley and R. Adams (Rec. trav. Chem., 1929, 48, 1035) made 2,2'-dihydroxy-1,1'-binaphthyl-3,3'-dicarboxylic acid, XXI, the Russians I.S. Joffe and I. V. Grachev, (J. Gen. Chem., U.S.S.R., 1935, 5, 950) prepared 2,2'-dihydroxy-1,1'-binaphthyl-7,7'-disulphonic acid, XXII, and 2,2'-dihydroxy-1,1'-binaphthyl-6,6'-disulphonic acid, XXIV, and all these were found to be stable towards racemisation. V. S. Murahashi, (Sci-papers inst. Phys. Chem. Research Tokyo, 1932, 17, 297; C. A., 1932, 26, 2191) prepared barium salts of 2,2'-dinitro, XXIII, and 2,2'-diamino-1,1'-binaphthyl-5,5'-disulphonic acids and resolved them by crystallisation from water with Ph.CH.Me.NH_2 and showed them to be optically stable.

Even 1,1'- binaphthyls singly substituted in the 2-position show a considerable optical stability. An example of this is 2-hydroxy-1,1'binaphthyl, XXV prepared by J. A. Berson and M. A. Greenbaum (J. Amer. Chem. Soc., 1958, 80, 653) and shown to have a half-life period of racemisation of two days in boiling benzene.

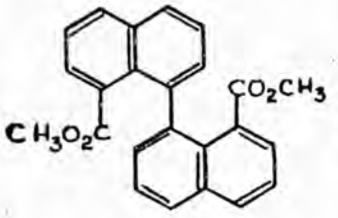
However, 1,1'-binaphthyl itself and the other 1,1'-binaphthyls substituted in positions other than the 2,2'-positions have been found to be optically labile.



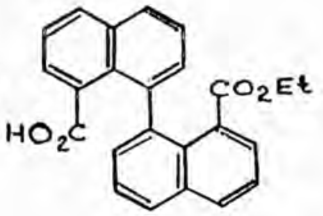
XXIX



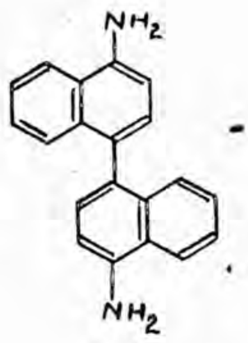
XXX



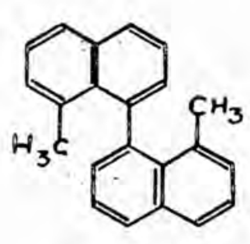
XXXI



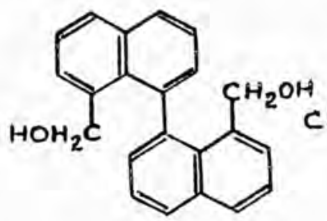
XXXII



XXXIII



XXXIV



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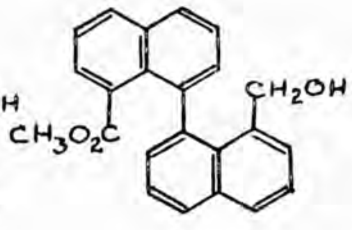
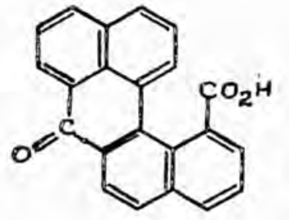
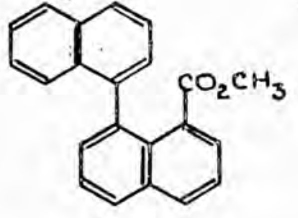


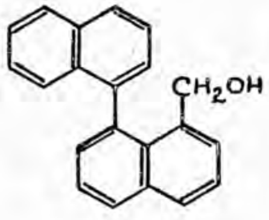
XXXVI



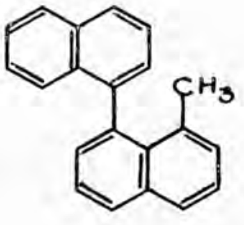
XXXVII



XXXVIII



XXXIX



XL

These compounds have been obtained in the optically active state and their Arrhenius parameters and transition state theory functions determined.

TABLE I

Compound	Solvent	E Kcal mol^{-1}	$log_{10}A$ sec^{-1}	$\Delta F^{\ddagger}$ Kcal mol^{-1}	$\Delta H^{\ddagger}$ Kcal mol^{-1}	$\Delta S^{\ddagger}$ e.u.	Ref.
XXVI	$H.CO.N.Me_2$	22.5	12.1	23.5	21.6	-5.2	1
XXVII	$H.CO.N.Me_2$	24.1	12.3	25.4	23.5	-5.9	1
	0.1N NaOH	24.9	12.9	24.8	24.3	-1.5	2
XXVIII	$H.CO.N.Me_2$	23.8	12.2	24.8	23.5	-5.1	1
XXIX	$H.CO.N.Me_2$	22.4	12.0	23.5	21.8	-5.5	1&2
XXX	$H.CO.N.Me_2$	22.1	11.3	24.4	21.5	-9.1	1
	0.1N NaOH	26.0	15.2	22.2	25.4	+9.2	3
XXXI	$H.CO.N.Me_2$	22.0	11.6	23.8	21.4	-7.4	
XXXII	0.1 NaOH	25.7	14.0	24.0	25.1	+3.2	3
XXXIII	$CH_3.CO.CH_3$	21.4		22.9	20.8	-7.1	4
XXXIV	$H.CO.N.Me_2$	27.58	11.3	30.44	26.8	-9.3	5
XXXV	$H.CO.N.Me_2$	29.2	12.6	29.85	28.4	-3.66	5
XXXVI	$H.CO.N.Me_2$	25.8	11.96	27.2	25.1	-6.5	5
XXXVII	$H.CO.N.Me_2$	23.2	12.1	24.3	22.6	-5.3	6
XXXVIII	$H.CO.N.Me_2$	23.6	12.5	24.1	22.9	-5.3	7

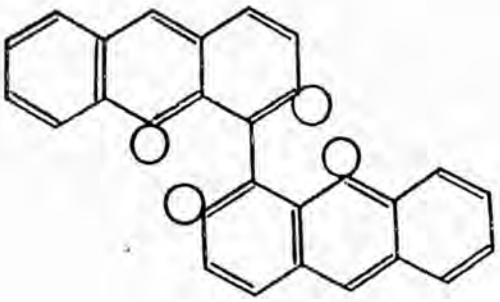
XXXIX	$H.CO.N.Me_2$	26.0	12.4	26.7	25.3	-3.8	7
XL	$H.CO.N.Me_2$	25.3	11.7	27.2	24.6	-7.3	7

References:

1. A.S.Cooke and M.M.Harris, J. Chem. Soc., 1963, 2365.
2. Bell, Morgan and Smyth, Chem. and Ind. 1951, 634
3. J. Meisenheimer and O. Beisswenger, Ber. 1932, 65, 32
4. Theilacker and Hopp, Ber., 1959, 92, 2293.
5. Y. Badar, A.S.Cooke and M.M.Harris, J. Chem. Soc.,1965,1412.
6. Y. Badar, A.S.Cooke and M.M.Harris, J.Chem.Soc., 1966, 1315.
7. A.S.Cooke and M.M.Harris, J. Chem. Soc., 1967, 988.

It is therefore clear that 2,2'-disubstituted 1,1'-binaphthyls are optically stable whereas 8,8'-disubstituted 1,1'-binaphthyls are optically labile. That 1,1'-binaphthyl-8,8'-dicarboxylic acid~~s~~ racemises whereas 1,1'-binaphthyl-2,2'-dicarboxylic acid is quite stable led W.M.Stanley (J. Amer. Chem. Soc., 1931, 53, 3104) to state that this difference in stability is due to the fact that, in peri-positions, carboxyl groups in the 8,8'-diacid are strained in such a way that passing is as easy as it is in an unsubstituted 1,1'-binaphthyl.

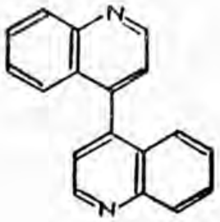
In some 1,1'-binaphthyls, steric hindrance to rotation is provided by the overlap of the hydrogen atoms in the 2- and 8- positions, which might appear to be insufficient barriers. F. Bell, W.H.D.Morgan and I.F.B.Smyth (Chem. and Ind., 1951, 634) made scale drawings which showed that in 1,1'-binaphthyl-5,5'-dicarboxylic acid there was no restriction to rotation about the interannular bond. F. Bell and D.H. Waring (J. Chem. Soc., 1949, 1579) considered that in 1,1'-bi~~naphthyl~~anthryl, XLI, the overlap of the 2'- and 9- hydrogen atoms, which is the same as the 2'- and 8-hydrogen atoms in 1,1'-binaphthyl, to be less than 0.2Å.



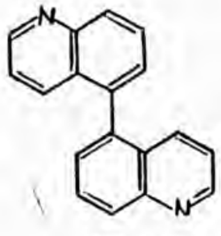
XLI

However, they resolved it and showed it to be optical stable at room temperature and racemised after 7 hours in boiling chloroform.

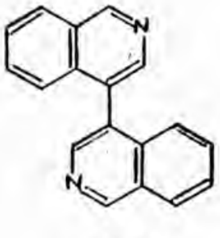
Another example is naphthidine, XXXIII, which was resolved by W. Theilacker and R. Hopp (Ber. 1959, 92, 2293) and shown to have a half-life period for racemisation of 3 to 4 hours at room temperature in acetone, and E of 21.4 Kcal. mole^{-1}. M. Crawford and I.F.B.Smyth (J. Chem. Soc., 1952, 4133; 1954, 3464) made and resolved a number of diquinolyls and diisoquinolyls whose structures are similar to that of 1,1'-binaphthyl and suggested that although the overlap of the atoms themselves (i.e., the part within the atomic radius) is the most effective in hindering rotation, the overlap of van der Waals envelopes should also be considered as largely responsible for the steric hindrance in these isomers.



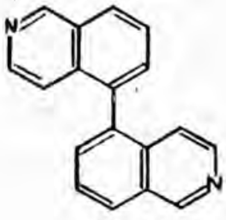
XLII



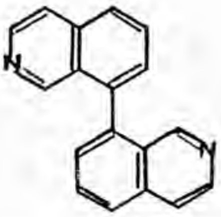
XLIII



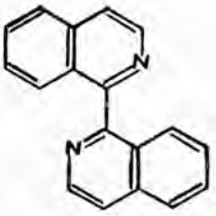
XLIV



XLV



XLVI



XLVII

The half-life periods of these isomers vary from 2-5 hours to 12 minutes at room temperature, except for 1,1'-diisoquinolyl, XLVII, which was only observed to mutarotate when the ~~as a~~ tartrate was dissolved in aqueous hydrochloric acid. The free base could not be obtained optically active because it lacks hydrogen atoms in the blocking positions.

M.M.Harris and A.S.Mellor (Chem. and Ind. 1961, 1082) prepared 1,1'-binaphthyl itself in the optically active state. The half-life period of racemisation was 14.5 minutes at 50° and $E_{rac.}$ was 22.5 Kcal. mole^{-1}.

These experimental observations show that hydrogen atoms in the blocking positions in the 1,1'-binaphthyls produce enough steric hindrance to cause observable optical activity. Hence, the optical activity of the 5,5'-diacid and of the 4,4'-diamine.

Low optical stability of 8,8'-substituted 1,1'-Binaphthyls.

A.S.Cooke and M.M.Harris (J. Chem. Soc., 1963, 2365), determined the Arrhenius parameters and transition state theory functions of optically labile substituted 1,1'-binaphthyls and observed that the entropy factor could not satisfactorily account for the optical lability of these compounds even in aqueous sodium hydroxide solution where ΔS^{*} is large and positive. The variation of the entropy factors in NN-dimethylformamide solution is small and not in accordance with the variation of the optical labilities of these compounds. This led them to the conclusion that the optical lability of these compounds, such as the 8,8'-diacid, is caused by intramolecular overcrowding which induces a state of strain in the molecule. This strain is relieved by molecular distortions, the effect of which is to favour optical inversion by reducing the rotational energy barrier through increase of the ground state energy. They discussed the energy barrier to racemisation, E_{rac} in terms of E_{steric}, E_r and E_{gs}, where E_{steric} represents the energy due to strain and compression in the transition state, E_r the gain in resonance energy in the transition state and E_{gs} the ground state energy. The relationship can be written as:

$$E_{rac} = E_{steric} - E_r - E_{gs}$$

E_r is considered to be insignificantly small. Hence, the difference in E_{rac} between the 8,8'- and the 2,2'- dicarboxylic acids must be due to the differences in E_{steric} and E_{gs}, and since E_{rac} in the optically labile acids does not vary by more than 3 K cal. mole^{-1} the only factor determining the closeness of their stabilities and their difference from the optically stable 2,2'-diacid is the ground state strain, and it is this E_{gs} that reduces the observed E_{rac} in the 8,8'-substituted 1,1'-binaphthyls.

A.S. Cooke and M.M. Harris (*J. Chem. Soc.*, 1963, 2365) have discussed the strained conformations of 8,8'-disubstituted 1,1'-binaphthyls. They state that any peri-substituted naphthalene, 1,8-$C_{10}H_6XY$, the C_8-X and C_1-Y bonds are forced out of plane with one of them above and the other below the mean plane of the nucleus. These can be represented theoretically in two diastereoisomeric structures *d* and *l*;

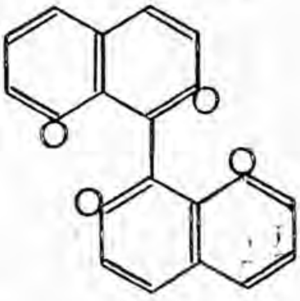
(d)

(l)

When these deformed units combine to make 1,1'-binaphthyl, there can be three readily interconvertible forms, (dd), (ll) and (dl). Each of these can in turn lead to *R* and *S* configurational isomers by rotation about the 1,1'-bond. The inversion of such structures of 8,8'-disubstituted 1,1'-binaphthyl derivatives is most probably through the "*trans*-route" the 8-COOH passing the 2'-H and the 8'-COOH passing the 2-H. The 8,8'-carboxyl groups in the 8,8'-diacid undergo an out-of-plane bending and hence the passing between these and the hydrogen atoms is easy and hence a lower energy barrier to racemisation equal to that of the ground state. However, in the 2,2'-diacid where the carbon atom of the -COOH is 2.9Å distant from the 1-carbon atom, deformation is unlikely and so the energy barrier to racemisation is high. Cooke and Harris suggested a value of approximately 15 K cal.mole^{-1} as the lower limit for the ground-state strain energy in the 8,8'-diacid.

Mesoid and Racemoid Transition Paths:

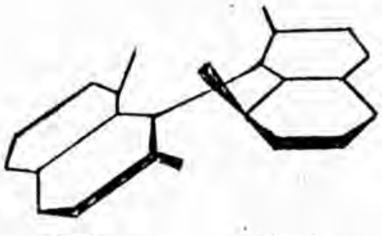
A.S. Cooke and M.M. Harris (*J. Chem. Soc.*, 1963, 2356) suggest that because of the deformations (d) and (l) there are three possible "*trans*" transition states for the R $\rightleftharpoons$ S change, two of which are, R(dd) $\rightleftharpoons$ S(dd) and R(ll) $\rightleftharpoons$ S(ll), the racemoid ones.



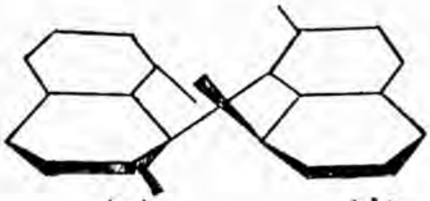
Trans-passing

Cis-passing

These are mirror images of each other, with equal energy barriers and in each, 8-COOH passes 2'-H at the same time as 8'-COOH passes 2-H. There is a single energy barrier and the transition state is still asymmetric. The other path is R(dl) $\rightleftharpoons$ S(dl), the mesoid one, in which passing of the obstacles is not simultaneous. Between the two energy barriers lies the minimum representing the intermediate state (ii) with a configuration neither R nor S, nor is it flat, but has a centre of symmetry.



(1) (1)
Racemoid
(i)



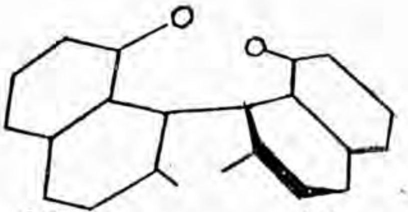
(d) (l)
Mesoid
(ii)

Since it requires less energy, this will be the path used.

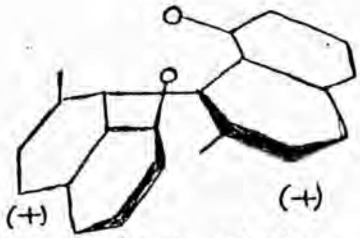
$$R(dd) \rightleftharpoons R(dl) \rightleftharpoons R(ll)$$

$$S(dd) \rightleftharpoons S(dl) \rightleftharpoons S(ll)$$

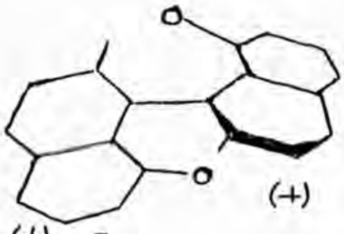
Configurational inversion in the racemoid molecules



R

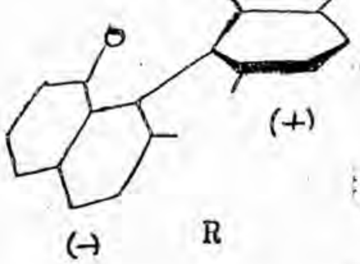


Transition State
or
Intermediate

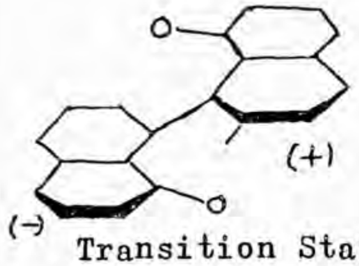


S

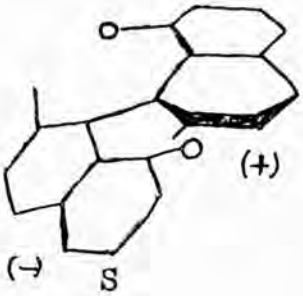
Configurational inversion in the mesoid molecule:



R



Transition State
or
Intermediate



S

(ii) Object of the present work:

Work has been done on substituted 1,1'-binaphthyls containing planar and tetrahedral substituents in the blocking positions and it has been observed that the carboxyl and ester groups do not present as high an energy barrier to racemisation as do the tetrahedral substituent groups. It was therefore decided to synthesise 8'-methyl-1,1'-binaphthyl-8-carboxylic acid and see how its Arrhenius parameters and transition state theory functions compare with those of other 1,1'-binaphthyls.

Work on 2,2'-dimethyl-1,1'-binaphthyl was undertaken on the grounds that, this compound, being a hydrocarbon, should be chemically more stable than the acids, amines and diols substituted in the 2,2'-position. Racemisation was therefore tried at temperatures much higher than those used for other 2,2'-substituted 1,1'-binaphthyls. Moreover, since the hydrocarbon has a low melting point it seemed interesting to try and racemise it in the molten state.

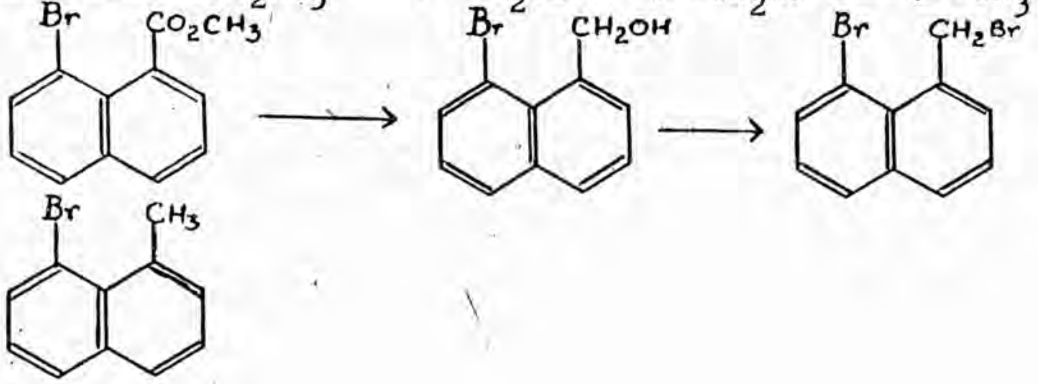
(iii) DISCUSSION:

A. 8'-Methyl-1,1'-binaphthyl-8-carboxylic acid:

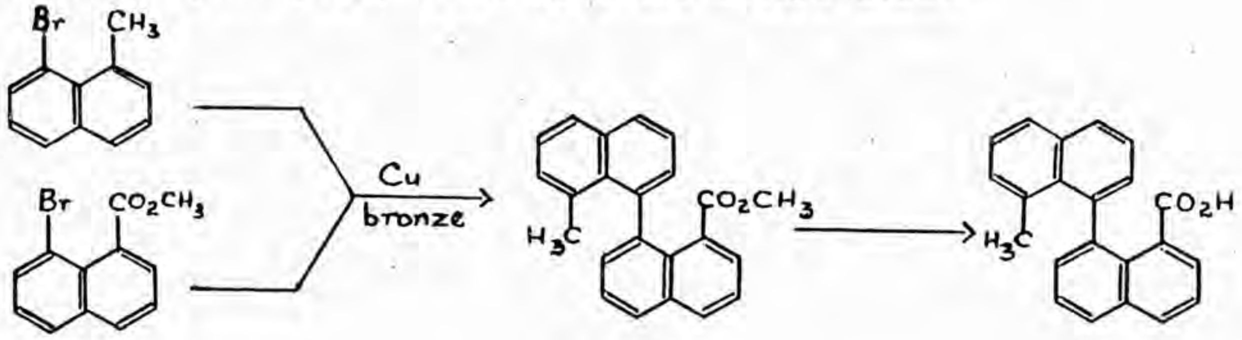
I. Synthesis:

Two routes were considered available for the synthesis of 8'-methyl-1,1'-binaphthyl-8-carboxylic acid, the starting material being 8-bromo-1-naphthoic acid (H.G.Rule, W. Pursell and R.H.Brown, J. Chem. Soc., 1934, 168)

(a) Half the bromo acid would be converted, as its methyl ester, into 1-bromo-8-methylnaphthalene through the series $-CO_2CH_3 \longrightarrow -CH_2OH \longrightarrow -CH_2Br \longrightarrow -CH_3$

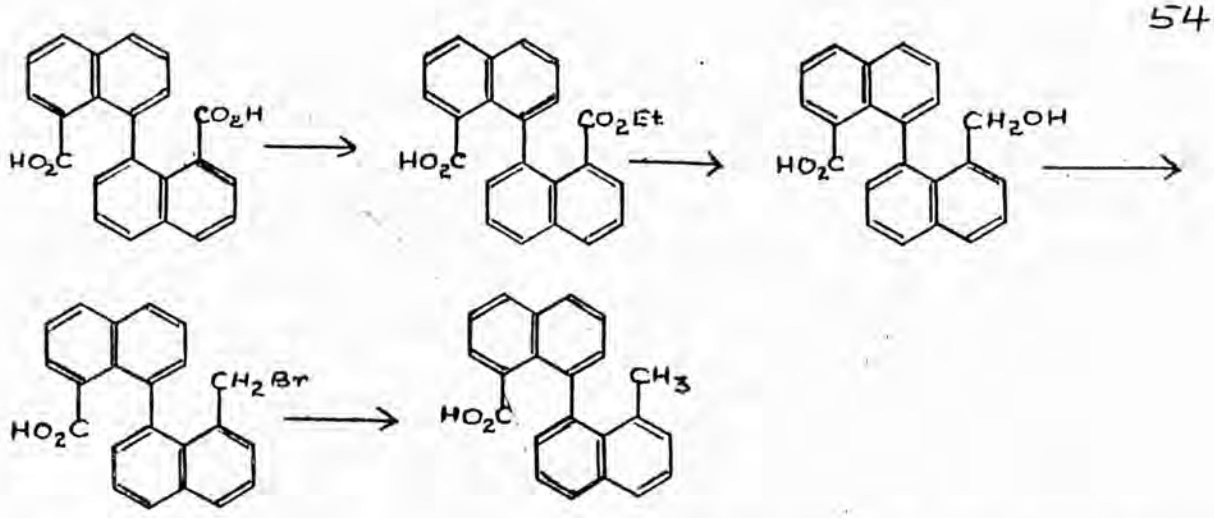


which could then be subjected to a mixed Ullman reaction with the other half to give the ester of the methyl acid which on hydrolysis, would give the methyl acid:



This route proved impracticable because the bromine was lost in the reduction stages. This is possibly a result of the fact that the bromine atom is forced out-of-plane as a result of peri-interaction, and that the carbon-bromine bond is longer than the normal C_{Ar}——Bromine bond, which makes the loss of the bromine easy.

(b) 1,1'-Binaphthyl-8,8'-dicarboxylic acid could be initially prepared from 8-bromo-1-naphthoic acid and then one acid group converted into a methyl group:



The methyl hydrogen dicarboxylate was found to be as insoluble in ethanol as the 8,8'-diacid and could not be easily isolated from a mixture. Therefore, ethoxycarboxyl-1,1'-binaphthyl-8-carboxylic acid was the preferred intermediate in the synthesis.

(II) <u>Proof of constitution</u> (Orientation in particular)

Group migration is known in the naphthalenes. G. Suld and A.P. Stuart (J. Org. Chem., 1964, 29, 2923) have investigated the isomerisation of di- and monomethylnaphthalenes in the system anhydrous hydrofluoric acid-boron trifluoride and shown that the concentrations of these in the isomerates depend on the amount of boron trifluoride and that the experimental rate data are in agreement with the postulated intramolecular 1,2-methyl shift. The barriers to the intramolecular methyl shift between adjacent β-β as well as between the peri-positions are rationalised in terms of the unfavourable high-energy complexes required for these migrations.

V.A. Koptying, V.G. Shubin and V.A. Plakhov (Zh. Obshch.

Khim., 31, 4023) have investigated the isomerisation of 1,8-dihalonaphthalenes in the presence of anhydrous β-naphthalene sulphonic acid. They have shown that heating 1,8-$C_{10}H_6Cl_2$ or 1,8-$C_{10}H_6Br_2$ with 2-$C_{10}H_7SO_3H$ at 110° resulted in an irreversible migration of one halogen atom to the adjacent β-position.

It was therefore considered reasonable to establish evidence for the orientation of the methyl and carboxylic acid groups.

The evidence is as follows:

a) The acid is synthesized from 1,1'-binaphthyl-8,8'-dicarboxylic acid which can itself be easily converted into anthanthrone (H.G.Rule and F.R.Smith, J. Chem. Soc., 1937, 1096; Y.Badar, A.S.Cooke and M.M.Harris, J. Chem. Soc., 1966, 1315).

b) The methyl acid, in quinoline, was refluxed with copper bronze to decarboxylate the acid. The infrared spectrum and m.p. of the hydrocarbon thus obtained were found to be identical with those of 8-methyl-1,1'-binaphthyl, for which the orientation of the methyl group to the 8-position has been established (A.S.Cooke and M.M.Harris, J. Chem. Soc., C. 1967, 988). A mixed m.p. with a specimen prepared from 1,1'-binaphthyl-8-carboxylic acid confirmed that the hydrocarbon was 8-methyl-1,1'-binaphthyl.

c) On boiling the acid with acetic anhydride under reflux for 5 hours a mixed anhydride was obtained. Longer boiling gave a small quantity of 13-methyl-7-oxodibenz (a. kl) anthracene which shows a major peak in the infrared spectrum at the low value of 1633 cm^{-1} corresponding to that at 1637 cm^{-1} attributed to the carboxyl group in phenalene-1-one (N.H.Cromwell and G.C. Hudson, J. Amer. Chem. Soc., 1953, 75, 872; D.H.Reid and R.G.Sutherland, J. Chem. Soc., 1963, 3295) and at approximately 1640 cm^{-1} in 7-oxodibenz (a,kl) anthracene (Y. Badar, A.S.Cooke and M.M.Harris, J. Chem. Soc., C. 1966, 1315; N.H.Cromwell and G.V. Hudson, J. Amer. Chem. Soc., 1963, 3295). Ring shutting is relatively inhibited in this compound, in comparison with the 8- or 8,8'-carboxylic acids, and this is probably due to the steric influence of the methyl group. The carboxyl peak in the methyl acid itself is at 1689 cm^{-1}.

This chemical evidence, as well as the synthesis from the 8,8'-diacid firmly establish the situation of the methyl and the carboxyl groups in the 8- and 8'-positions.

(III). Resolution.

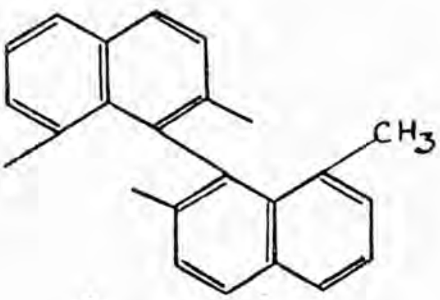
The resolution of the methyl acid was achieved through its brucine salts. Arrhenius parameters and transition state theory functions for racemisation in N,N-dimethylformamide solution have been determined and compared with those for optically active 1,1'-binaphthyl and its relevant substitution products (Table III).

(IV). Comparative optical stabilities.

The racemisation of optically active 1,1'-binaphthyl-8,8'-dicarboxylic acid and some of its esters and of 1,1'-

binaphthyl have already been followed (A.S.Cooke and M.M. Harris, J. Chem. Soc., 1963, 2365 and references therein). There has been observed a striking similarity in the Arrhenius parameters (and transition state theory functions) for these compounds. The low optical stability of these compounds, in comparison with those of the 2- and 2,2'-substituted 1,1'-binaphthyls may be partly explained on the basis of molecular deformation in the ground state with a consequent increase in energy, thereby, lowering the observed activation energy for racemisation, E_{rac}. That the similarity of the Arrhenius parameters of the 8,8'-diacid, the 8-acid and their esters to those of 1,1'-binaphthyl itself depends upon some peculiar property of the carboxyl and ester groups, as well as the overall distorted geometry of the molecule is apparent from a comparison of the Arrhenius parameters of these compounds with those of optically active compounds with the tetrahedral obstacles $-CH_3$ and $-CH_2OH$ in the 8,8'-positions (Y.Badar, A.S.Cooke and M.M.Harris, J. Chem. Soc., 1965, 1412). The methyl and hydroxymethyl groups present a higher energy barrier to inversion than the groups $-CO_2H$, $-CO_2Me$ and CO_2Et which have a similar "planar" structure as obstacles. However, the optical stability does not approach that of the 2,2'-disubstituted compounds and this is taken as evidence that the observed E_{rac} in all 8,8'-disubstituted compounds is substantially lowered by the ground state energy. The obstacle effect of these groups is enhanced by the fact that they are forced by their very nature to subtend a larger angle at the 1,1'-pivot bond than do the planar substituent groups. This introduces an element of higher compression into the mesoid transition state through which these compounds are presumed to racemise. This mesoid transition state, therefore, can be reached by a further deformation.

It appears as if the ground state deformation in the acids and esters is such that the compounds reach the transition state as easily as if the substituent groups were not there at all. On the other hand methyl and hydroxymethyl groups provide effective barriers. Work on singly substituted 1,1'-binaphthyls (A.S.Cooke and M.M.Harris J. Chem. Soc., C, 1967, 988) has also shown that the increment in E_{rac} based upon the parameter E_{rac} for 1,1'-binaphthyl itself is significant for $-CH_3$ and $-CH_2OH$ whereas $-CO_2H$ or CO_2Me in the same positions show no effect (Table II). It has been found in general that two substitutions with $-CH_3$ and $-CH_2OH$ show increments in E_{rac} which are approximately the sums of those observed for one substitution and this is probably connected with the use of symmetrical bending of the type shown below in an exaggerated form, in which release of pressure on one side does not set up additional pressure on the other; the two releases being mutually helpfull.



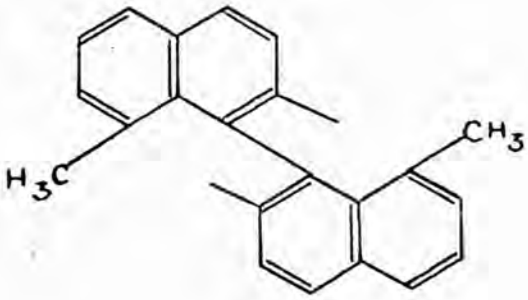


TABLE II

Racemisation of substituted 1,1'-binaphthyls in N,N-dimethylformide solution; increase in Arrhenius parameters and transition-state theory functions on substitution.

8-subst.	H	H	H	H	H	CO_2H	CO_2Me	CH_2OH	CH_3	CO_2H	CH_2OH
8'-subst.	H	CO_2H	CO_2Me	CH_2OH	CH_3	CO_2H	CO_2Me	CH_2OH	CH_3	CO_2Et	CO_2Me
E_{racem}	0	-0.1	+1.1	+3.5	+2.8	-0.4	-0.5	+6.7	+5.1	-0.9	+3.3
$\log_{10}A$-	0	-0.1	+0.4	+0.3	-0.4	-0.8	-0.5	+0.5	-1.1	-0.7	-0.1
$\Delta F^{\neq}$	0	0.0	+0.6	+3.2	+3.7	+0.9	+0.3	+6.3	+6.9	+0.2	+4.3
$\Delta H^{\neq}$	0	-0.1	+1.0	+3.4	+2.7	-0.4	-0.5	+6.5	+4.9	-0.95	+3.2
$\Delta S^{\neq}$	0	-0.3	+1.7	+1.4	-2.1	-3.9	-2.5	+2.2	-4.2	-3.2	-1.0

Table III

Arrhenius Parameters and Transition-state Theory Functions For Racemisation in N,N-Dimethylformamide Solution:

	$E_{rac.}$ Kcal $mole^{-1}$	$Log_{10}A$	$\Delta F^{\neq}$	$\Delta H^{\neq}$	$\Delta S^{\neq}$
a) 1,1'-Binaphthyl	22.5	12.1	23.5	21.9	-5.2
b) 1,1'-Binaphthyl-8-carboxylic acid	22.4	12.0	23.5	21.8	-5.5
c) 1,1'-Binaphthyl-8,8'-dicarboxylic acid	22.1	11.3	24.4	21.5	-9.1
d) 8-Methyl-1,1'-binaphthyl	25.3	11.7	27.2	24.6	-7.3
*e) 8'-Methyl-1,1'-binaphthyl-8-carboxylic acid	25.3(5)	11.6	27.4	24.6	-7.7

* The present work.

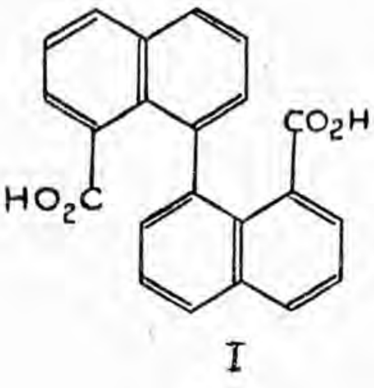
The lateral bending depicted here, is accompanied by out-of-plane bending.

These observations were compared with those of 8'-methyl-1,1'-binaphthyl-8-carboxylic acid: Table III, shows that the Arrhenius and transition-state theory functions for 8'-methyl-1,1'-binaphthyl-8-carboxylic acid are virtually identical with those for 8-methyl-1,1'-binaphthyl. This means that the contribution to E_{rac} is from the methyl groups only. Both the methyl and the carboxyl groups have an effect on the ground state energy of the molecule, but it is only the methyl group that has an appreciable contribution to the transition state energy. In other words in the <u>trans</u> passing position the carboxyl group offers a negligible steric retardation.

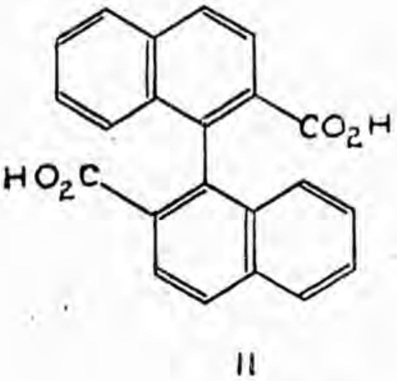
B. 2,2'-Dimethyl-1,1'-binaphthyl:

2,2'-Dimethyl-1,1'-binaphthyl, like other 2,2'-disubstituted binaphthyls was found to be highly optically stable.

Using classical models similar resistance to passing from the R- to the S- configuration is found for 1,1'-binaphthyl-8,8'-dicarboxylic acid (I), and 1,1'-binaphthyl-2,2'-dicarboxylic acid (II)



I



II

Small differences are observed, such as the ability of the carboxyl groups of the 8,8'-acid to form internal hydrogen bonds, or each to be coplanar with and conjugated with the naphthalene nucleus to which it is attached. However, the major difference observed is in the distance between the carbon atoms $C_{(a)}$ and $C_{(b)}$. In acid (1) the $C_{(a)}-C_{(b)}$ distance is 2.4Å, whereas in acid (11), the $C_{(a)}-C_{(b)}$ distance is 2.9Å, these figures being obtained from a scale diagram, using bond lengths and angles by J. Trotter (Acta. Cryst., 1960, 13, 732) for 1-naphthoic acid.

E. Harnik, F.H. Herbstein, G.M.J. Schmidt and F.L. Hirshfeld (J. Chem. Soc., 1954, 3288) stated that overcrowding begins when the unperturbed structures bring the carbon atoms (aliphatic or aromatic) to within 3.0Å. The strain resulting from such an overcrowding is relieved by an out-of-plane distortion which tends to be spread over the whole molecule rather than by stretching of particular bonds.

In 1,1'-binaphthyl-8,8'-dicarboxylic acid where the -COOH group is 2.4Å distant from the 1'-carbon atom, there must be deformation in the ground state, but this deformation is not likely to be large in the 2,2'-acid and other 2,2'-disubstituted 1,1'-binaphthyls, where the $C_{(a)}-C_{(b)}$ distance is 2.9Å.

It seems, therefore, reasonable to conclude that 2,2'-dimethyl-1,1'-binaphthyl has a smaller deformation in the ground state than 8,8'-dimethyl-1,1'-dinaphthyl (Y. Badar, A.S. Cooke and M.M. Harris (J. Chem. Soc., 1965, 1412). Hence its high optical stability. The attempt to racemise it at higher temperatures was made to see if there is a temperature above which the compound begins to racemise, but no racemisation could be observed below temperatures high enough to cause decomposition.

6. THE ULTRAVIOLET SPECTRA OF THE 1,1'-BINAPHTHYLS

(i) Introduction

the absorption of ultraviolet or visible light by organic molecules is accompanied by the excitation of valency electrons to higher energy levels, the frequency ν of the light being related to the difference ΔE, between these energy levels by the equation, $\Delta E = h\nu$ where h is Planck's constant and ν is the frequency of the light absorbed or emitted. Since $\nu = \frac{c}{\lambda}$, $\Delta E = \frac{hc}{\lambda}$.

π-π^* Electron transitions, i.e. transitions in which a π-electron is excited to an antibonding π-orbital, give rise to absorption in the region λ=200mμ to λ=1000mμ. Hence a study of the ultraviolet spectra in this region can provide information regarding the distribution of unsaturated linkages within a molecule.

If a molecule contains two unsaturated linkages which are separated by more than one single bond, the resultant effect on the absorption spectrum of the molecule is additive; but when such chromophores are separated by a single bond, the absorption spectrum shows other characteristics that are typical of all conjugated systems. As the number of double bonds in a conjugated system increases, the absorption comes to progressively longer wavelengths. This is readily understood by a consideration of the type of resonance in various molecules.

For ethylene, the ground state and the most stable of the excited states can be discussed on the basis of resonance among structures I, II and III.

$H_2C = CH_2$

I

$\overset{\oplus}{H_2C} - \overset{\cdot\ominus}{CH_2}$

II

$\overset{\cdot\ominus}{H_2C} - \overset{\oplus}{CH_2}$

III

For 1,4-pentadiene, which contains a pair of isolated double bonds, there are nine such structures, IV-XII:-

$H_2C = CH - CH_2 - CH = CH_2$

IV

$H_2C = CH - CH_2 - \overset{\oplus}{CH} - \overset{\cdot\cdot\ominus}{CH_2}$

V

$H_2C = CH - CH_2 - \overset{\cdot\cdot\ominus}{CH} - \overset{\oplus}{CH_2}$

VI

$\overset{\oplus}{H_2C} - \overset{\cdot\cdot\ominus}{CH} - CH_2 - CH = CH_2$

VII

$\overset{\oplus}{H_2C} - \overset{\cdot\cdot\ominus}{CH} - CH_2 - \overset{\oplus}{CH} - \overset{\cdot\cdot\ominus}{CH_2}$

VIII

$\overset{\oplus}{H_2C} - \overset{\cdot\cdot\ominus}{CH} - CH_2 - \overset{\cdot\cdot\ominus\,\oplus}{C} - CH_2$

IX

$\overset{\cdot\cdot\ominus\,\oplus}{H_2C - CH} - CH_2 - CH = CH_2$

X

$\overset{\cdot\cdot\ominus\,\oplus}{H_2C - CH} - CH_2 - \overset{\oplus}{CH} - \overset{\cdot\cdot\ominus}{CH_2}$

IX

$\overset{\cdot\cdot\ominus\,\oplus}{H_2C - CH} - CH_2 - \overset{\cdot\cdot\ominus\,\oplus}{CH - CH_2}$

XII

As a result of the insulating effect of the central methylene group, the two double bonds are nearly as independent of each other as if they belong to two separate molecules. Hence the molecule absorbs at about the same wavelength as does 1-pentene, but with twice the intensity (L. Bateman and H.P.Koch, J. Chem. Soc., 1944, 600).

With 1,3-butadiene, as well as the nine structures analogous to IV-XII, three additional structures can be written:-

$\underbrace{H_2C - CH = CH - CH_2}$

XIII

$\overset{\oplus}{H_2C} - CH = C - \overset{\cdot\cdot\ominus}{CH_2}$

XIV

$H_2\overset{\cdot\cdot\ominus}{C} - CH = CH - \overset{\oplus}{CH_2}$

XV

These three structures have no close analogues in the unconjugated systems. In this molecule the double bonds are less independent of each other and its spectrum is therefore different from that of 1,4-pentadiene. Considering the effect of the respective possibilities of resonance, it can be said that, with 1,3-butadiene, the effect of the additional structures XIII-XV will be to lower both the energy of the ground state and that of the lowest excited state. The magnitude of this stabilization in the ground state is equal to the resonance energy of the substance, (3.5 Kcal.mole^{-1}). This stabilization is rather small and this accords with the view that the structures XIII-XV, are relatively unstable and that the actual state of the normal butadiene molecule can be represented by the conventional structure XVI, the analogue of IV.

$$H_2C = CH - CH = CH_2$$

XVI

However, the stabilization of the excited state should be appreciably greater than that of the ground state since, in comparison with the high energy of the former state, structures XIII-XV are not extremely unstable. These latter structures therefore, make significant contributions so that the resonance energy is fairly large and the true state of the excited molecule can only be represented by a "resonance hybrid". Hence the energy of the excited state is lowered by the conjugation more than is the ground state, and therefore the excited energy must be decreased by the conjugation and hence the absorption will be displaced to lower energy i.e. to longer wavelengths, as is observed,

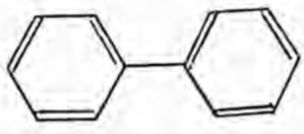
The above simple and qualitative viewpoint can also be used to interpret another feature of the spectra of unconjugated 1,4-pentadiene and that of the conjugated, 1,3-butadiene. With 1,4-pentadiene, there are two excited states having nearly the same energy (i.e. one state for each double bond); and the observed intensity is the sum of the intensities for the two almost completely independent transitions. With 1,3-butadiene, the absorption at 210mμ is presumed to be due a transition to a single electronically excited state; hence the intensity would be expected to be only half as great as with 1,4-pentadiene. However, the values both of ϵ_{max} and the integrated intensity appear to be approximately equal for the two compounds. This unexpected observation is explained on the basis of the exceptionally large dipole moments that are associated with structures XIV and XV. The complete equivalence of these two structures ensures that their effects upon the net dipole moment of the molecule must exactly cancel each other in both the ground and excited states. However, it has been shown (R.S. Mulliken, J. Chem. Phys., 1939, 7, 121, 364, 570; L. Pauling, Proc. Natl. Acad. Sci., U.S. 1939, 25, 577) that the large moments of the individual structures, or, more precisely, the large differences between the corresponding average distributions of charge, must lead to intense absorption of light. The fact that the absorption due to the one electronic transition in 1,3-butadiene is considerably more than half as intense as is that due to the two transitions in 1,4-pentadiene, can therefore be explained on the grounds that the dipole moments of the structures XIV and XV are larger than are those of the corresponding structures V-XII.

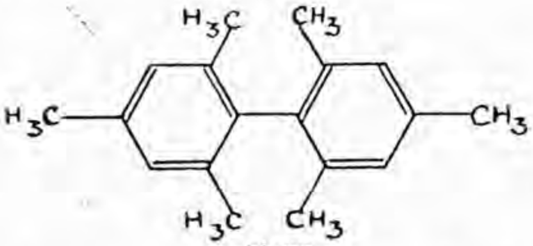
(ii) Ultraviolet spectra in the Biphenyl series:

Benzene has two main absorption bands, the first one has a high intensity (ϵ about 8,000) and appears in the region of 198mμ which is outside the limit of the usual quartz spectrophotometer. This band corresponds to that found in other conjugated systems. The other region of absorption is between 230 and 270mμ and the band is of a low intensity (ϵ about 230) and exhibits considerable fine structures. The biphenyl molecule, XVII, however, has a spectrum which is different from that of benzene. Maximum absorption occurs at 255mμ and the intensity is increased (ϵ 18,000) and fine structure is lacking. The spectrum bears no resemblance to the spectrum of the partial benzenoid chromophores. This is attributed to conjugation between the aromatic rings. The spectra of biphenyls, substituted in positions other than the ortho positions exhibit this conjugation band. On the other hand, the spectra of biphenyls substituted in the ortho positions show a reversion of the benzenoid type.

G.H. Beaven and E.A. Johnson (*Proceedings of the Conference on Molecular Spectroscopy*, Ed. E. Thornton and H.W.Thompson, Pergamon Press, 1959) have discussed the absorption spectra of the methylbiphenyls and they state that the effect of progressively introducing substituents into blocking positions has been most conveniently studied with methyl groups, as these groups have the least perturbing effect on the electronic absorption spectrum of the parent biphenyl chromophore, and their auxochromic properties, in the benzenoid chromophore are also well known (R.N. Jones, *Chem.* Rev., 1943, *32*, 1; R.A. Freidel and M. Orchin, *Ultraviolet Absorption Spectra of Aromatic Compounds*, pp. 13-27, Wiley, New York, 1951)

A classical example of the effect of complete methyl substitution in the four *ortho* positions on the ultraviolet spectrum of biphenyl is the 2,2'-4,4'-6,6'-symmetrical hexamethyl derivative (dimesityl), XVIII.


XVII



XVIII

The spectrum of this compound was shown to be comparable especially in the 250-290mμ region, with that expected for two molecules of the corresponding 1,3,5-trimethylbenzene (mesitylene), absorbing additively (M.T.O'Shaughnessy and W.H. Rodebush, *J. Amer. Chem. Soc.*, 1940, *62*, 2906). The intense conjugation band which appears at 248mμ in biphenyl

ϵ_{max} 17,000 was not evident in bimesityl. L. Pauling (The Nature of the Chemical Bond, 1st Ed., Cornell University Press, New York, 1939) emphasized the importance of coplanarity as a condition for maximum conjugation in linked systems of olefinic and aromatic double bonds and pointed out that in biphenyl itself the "steric interference" between ortho positions determines the actual degree of conjugation between the phenyl groups.

The effect of methyl groups in the 3- or 4- positions of biphenyl is small and the same as that on other aromatic chromophores. The increase in the absorption intensity caused by a 4-methyl group is presumed to be due to hyperconjugation participating in the total conjugation through the 1,1'-bond. However, a single methyl group in the ortho position caused a reduction in intensity and a blue shift of the conjugation band, which allows the poorly resolved low intensity long-wave band to be seen as an inflection. In 2,2'-dimethylbiphenyl, the second ortho methyl group has a striking effect. The conjugation band is further shifted to shorter wavelengths as an unresolved inflection, overlapped by the more intense band system at about 200mμ. The long-wave band becomes more definite, and has fine structure. 2,6-Dimethylbiphenyl, which is asymmetrically substituted shows differences, especially at long wavelengths, from 2,2'-dimethylbiphenyl. However, the spectra are similar at short wavelengths which suggests that the degree of conjugation between the rings is the same in the two isomers.

2,6,2'-Trimethyl- and 2,6' - 2'6 -tetramethyl - biphenyls show a progressive development of the long-wave band, and increasing blue shift and reduced intensity of the conjugation band, until in the tetramethyl derivative when the conjugation band is overlapped by the short-wave band system. L.W. Picket, G.F. Walter and H. France (*J. Amer. Chem. Soc.*, 1936, *58*, 2296) have shown that 2,2'-4,4'-6,6'-hexachloro-biphenyl has a spectrum of substantially the type observed for trichlorobenzene.

It was at one time thought that conjugation across the 1,1'-bond was possible only when the biphenyl system was planar. It was assumed that biphenyl molecules lacking in *ortho* substituents were planar, with complete conjugation between the benzene nuclei, this giving rise to spectral changes from the benzenoid type, a bathochromic shift on the main absorption band, a considerable increase in intensity and a loss of fine structure. Progressive introduction of substituents in the blocking positions would give rise to hypsochromic shifts, decrease in intensity of the conjugation band and increase in fine structure of the long-wave band, the spectrum therefore, reverting to the spectrum of the individual benzenoid chromophore.

P.M. Everitt, D.M. Hall and E.E. Turner (*J. Chem. Soc.*, 1956, 2286) determined the ultraviolet absorption spectra of a number dialkylbiphenyls (2,2'-diethyl-,2,2'-diisopropyl-and 2,2'-di-tert-butylbiphenyl). The ultraviolet spectrum of 2,2'-ditolyl (G.H. Beaven, G.R. Bird, D.M. Hall, E.A. Johnson, J.E. Ladbury, M.S. Lesslie and E.E. Turner, J. Chem. Soc., 1955, 2708) was re-examined and found to show slight conjugation between the two benzene rings, in spite of the steric effect of the *ortho* methyl groups; the inflection at about 227mμ being regarded as a vestigal conjugation band displaced to shorter wavelengths. The spectra of 2,2'-ditolyl-,2,2'-diethyl-, 2,2'-diisopropyl, and 2,2'-di-tert-butylbiphenyl show a progressive decrease in conjugation with increasing size of the alkyl groups until with the last compound, no trace of a discrete conjugation band remains. In the other compounds the inflection at 227mμ is apparent, its intensity decreasing slightly from methyl to isopropyl.

Ultraviolet spectra of 2,2'-dialkylbiphenyls:

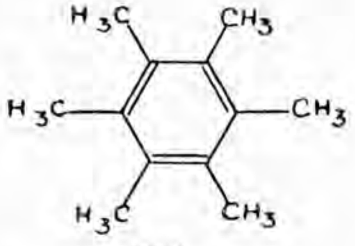
Compounds	λ(inflection)	ε	λmin.	ε
2,2'-Dimethyl	(ca.227)	6800	260.5	770
2,2'-Diethyl	(ca.227)	6000	258.5	685
2,2'-Diisopropyl-	(ca.227)	5500	254	630
2,2'-Di-t-butyl			249.5	290

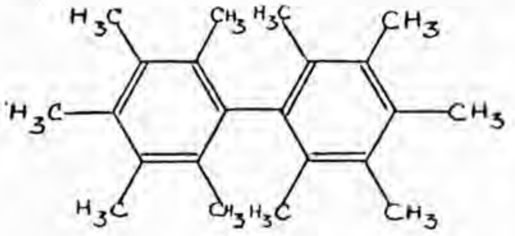
Moreover, the absorption minimum in di-t-butylbiphenyl moves to progressively longer wavelengths.

The influence of *ortho* substituents on free rotation about the interannular bond determines the rate of thermal racemisation of optically active biphenyls. As the size of the *ortho* substituent decreases, the compounds become less optically stable. With much smaller groups in blocking positions, the compounds become unresolvable although their ultraviolet spectra may still imply a lack of or a decrease in conjugation. This can be explained on the basis that optical activity depends upon the easiness of rotation about the 1,1'-bond in a substituted biphenyl whereas the degree of conjugation, observed spectroscopically is determined by the mean interplanar angle of the biphenyl system. A small substituent may cause a lack or a decrease in conjugation, but it may present a very small barrier to optical inversion of a biphenyl and therefore make the compound unresolvable.

G.H. Beaven and D.M. Hall, (J. Chem. Soc., 1956, 4637) have shown that the introduction of even a single fluorine substituent into one of the ortho-positions of biphenyls results in a detectable blue shift and reduction in intensity of the conjugation band. In the series 2,2'-dihalogenbiphenyls the blue shift and intensity reduction are progressively larger from fluorine to bromine, in 2,2'-diiodobiphenyl the spectrum does not show a conjugation band. In the same series, the absorption contributions due to unconjugated halogenobenzene chromophores appear with increasing distinctness as the conjugation band is inhibited, and progressively approach the expected intensity for an additive system of such absorbing units. The ultraviolet absorption spectra of diphenyls containing fluorine substituents in the meta- and para-positions show them to be "perturbed" biphenyls, in which small changes in the conjugation band are accompanied by the appearance of low-intensity unresolved contributions from the phenyl chromophores. These minor spectroscopic effects are caused by non-steric, electronic interactions of the substituent groups with the biphenyl chromophore.

A compar~~a~~is~~i~~on between decamethylbiphenyl, XX, and the completely methylated benzene, XIX is interesting,


XIX


XX

The extinction coefficients from the two compounds compare in an interesting way. These two compounds have identical substitution symmetry of the phenyl groups. The location and fine structure of the long wave bands of the two compounds are strikingly similar. If the extinction coefficients of hexamethylbenzene in the spectrum are for two moles, it is found that the extinction coefficients of decamethylbiphenyl is consistently higher down to 207mμ. The minimum absorption in the region 200-247mμ. is much higher in decamethylbiphenyl than in hexamethylbenzene. This additional absorption provides some evidence in support of the theorectical analysis of H.A. Longuet-Higgins and J.N. Murrell (Proc. Phys. Soc. A, 1955, 68, 601; J. Chem, Soc. 1955, 2552) that electronic transitions involving both phenyl groups in biphenyls can occur by an interaction process, that is apparently independent of the coplanarity condition.

It is generally believed that the biphenyl molecule is planar in the solid phase and non-planar in the vapour phase and in solution although the molecular configuration in the liquid phase and in solution are not known with certainty. The molecular configuration of biphenyl in the solid state was first established more than 30 years ago by X-Ray crystal analysis. G.L. Clark and L.W. Picket (Proc. Nat. Acad. Sci. U.S.A. 1930, 16, 20) found the biphenyl ~~molecule in the~~ molecule in the crystal to be planar, or very nearly planar. J. Dhar (Indian.J.Phys. 1932, 7, 43), showed that the two phenyl rings are flat and in the same plane. The C–C distance in the ring is 1.48°A.

A later study of the intensities of the X- Ray reflections (J. Dhar. Proc. Nat. Inst. Sci.India, 1949, 15, 11) was not sufficiently detailed to provide further accurate information about the molecular configuration of biphenyl.

More recently J. Trotter (Acta. Cryst., 1961, 14, 1135) showed, by X-Ray diffraction methods, that the carbon skeleton of the biphenyl molecule is completely planar within the limits of experimental error, the maximum deviation from the mean molecular plane being only 0.007°A and that the hydrogen atoms are situated on the plane of the carbon atoms, but that there are small in-plane displacements of the ortho hydrogen atoms from idealized positions, which reduce steric strain.

A. Hargreaves and S. Hasan Rizvi (Acta. Cryst. 1962, 15, 365) agree with Trotter and suggest that the great length of the interannular bond (1.50°A with estimated standard deviation of 0.017°A) indicates that there is no conjugation between the rings; they consider that crystal forces are responsible for the rings taking up the coplanar configuration.

In 2,2'-dichlorobenzidine (D.L. Smare, Acta. Cryst., 1948, 1, 150) the aromatic rings were shown to be at an angle of 72° to each other. A similar situation was found with 2,2'-dimethylbenzidine (F. Foweather and A. Hargreaves, Acta. Cryst, 1950, 3, 81) These results refer to the configuration in the crystal state where cohesive forces, absent in the vapour state and in solution, are operating. The earliest electron diffraction investigation of biphenyl vapour (L.O. Brockway and I.L. Karle, J. Amer. Chem. Soc., 1944, 66, 1974) was interpreted as indicating a non-coplanar structure, although this conclusion was not based entirely on the experimental evidence, since a completely planar arrangement agreed equally well with the data.

O. Bastiansen, from electron diffraction evidence (Acta. Chem. Scand., 1949, 3, 408) has suggested that the mean interplanar angle of biphenyl in the vapour state is 45° ± 10° and that the length (about 1,48°A) of the 1,1'-bond corresponds to about 10% double bond character. He also suggested that the mean interplanar angles of 3,3'-dichlorobenzidine and 3,3'-dibromobiphenyl are 53° ± 10° and 54° ± 5°

respectively. The non-planarity of the biphenyl molecule in the vapour phase has been attributed to the hydrogen-hydrogen repulsive interactions (A. Almeningen and O. Bastiansen, *Det. Kgl. Norske Videnskabers Selskabs Skrifter*, 1958, No. 4.)

Dipole moment measurements support the non-coplanar form in 2,2'-disubstituted biphenyls in solution (G.G. Hampson and A. Weissberger, *J. Amer. Chem. Soc.*, 1936, *58*, 2111; R.J.W. Le Fevre and H. Vine, *J. Chem. Soc.*, 1938, 867).

A.C. Littlejohn and J.W. Smith (*J. Chem. Soc.*, 1953, 2456) determined the dipole moments of mono-chloro-, -bromo-, -iodo- and -nitro- biphenyls in benzene solution. The moments of the 2-substituted biphenyls were found in all cases to be greater than the values to be expected with the rings coplanar to one another, and except for 2-bromo biphenyl, were approximately equal to the calculated values for a configuration with the rings in planes at right angles to one another. As an increased mesomeric effect would not be expected to alter these moments very much, it was inferred that the mean position of the rings is nearer to the perpendicular than the coplanar arrangement.

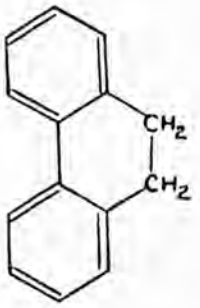
These same workers (*J. Chem. Soc.*, 1954, 2553) determined the dipole moments of 2,2'-difluoro-, 2,2'-dichloro-, 2,2'-dibromo-, 2,2'-diiodo- and 2,2'-dinitro- derivatives of biphenyl and of 3,3'-dinitrobiphenyl in benzene solution. On the assumption that the primary moments of the substituted groups, and the induced moments that they produce in the rings in which they are present, are the same as in the monosubstituted benzenes, the moments induced by each substituent in the opposite ring and in the other substituent were calculated for various angles of inclination of the planes of the rings. It was found that, so long as the rings were coaxial, the observed moments of the 2,2'-disubstituted biphenyls were in accord with the calculated values only if the substituent groups had preferred slightly-cis-disposition. For 3,3'-dinitrobiphenyl, the dipole moment suggested preference for a slightly-trans-configuration.

Dipole moment studies of certain unsymmetrical 4,4'-disubstituted biphenyls (C.G. Le Fevre and R.J.W. Le Fevre, J. Chem. Soc., 1936, 1130) have shown that there is interaction between the rings (e.g. in 4-amino-4'-nitrobiphenyl).

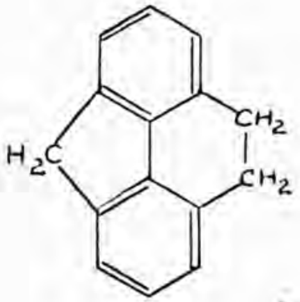
Bridged biphenyls

Compounds have been prepared in which the biphenyl skeleton forced to assume a more or less rigid non-coplanar configuration by joining of the 2,2'-positions to produce a strainless multiplanar bridge (G.H. Beaven, D.M. Hall, M.S. Lesslie and E.E. Turner, J. Chem. Soc., 1952, 854). The ultra-violet absorption spectra of these compounds indicate decreased conjugation between the two benzene rings of the biphenyl skeleton.

R.N. Jones (J. Amer. Chem. Soc., 1941, 63, 1658) reports the absorption spectra of 9,10-dihydrophenanthrene XXI, and of 4,5-methylene-9,10-dihydrophenanthrene XXII in which the biphenyl rings are restricted severely in such a manner as to hold the phenyl groups close to a planar configuration.



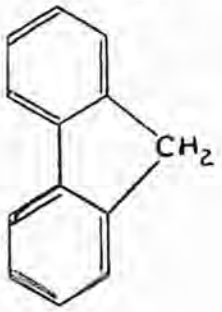
XXI



XXII

Assuming an aliphatic bond length (1.54Å) for the co-planar linkage and normal bond angles and lengths in the remainder of the molecule (M.T. O'Shaughnessy and W.H. Rodebush, J. Amer. Chem. Soc., 1940, 62, 2906), the dimethylene bridge of XXI can be acoommodated with the minimum strain if the aromatic rings are rotated through an angle of 15° 2' about the common axis. The absorption spectrum of 9,10-dihydrophenanthrene agrees in shape and intensity (ϵ_{max} 18,000) with that of the biphenyl curve (ϵ_{max} 18,000) allowance being made for the bathochromic effect of the alicyclic bridge (λ_{max} 249mμ for biphenyl and about 264mμ for 9,10-dihydrophenanthrene). However, fluorene (2,2'-methylene-biphenyl), XXIII, is a strained molecule and evidence from dipole moments favours an approximately planar structure with phenyl groups not symmetrical about an axis through the 4,4'-positions. J.W. Cook and J. Iball (Chem. and Ind., 1936, 55, 467) suggested that in the crystalline form, fluorene is non-planar, but recently, D.M. Burns and J. Iball (Nature, 1954, 173, 635) made a detailed quantitative crystal analysis of fluorene, and determined all bond lengths and angles and found that all carbon atoms lie on a plane, and stated that because of its planarity, fluorene cannot exhibit optical isomerism.

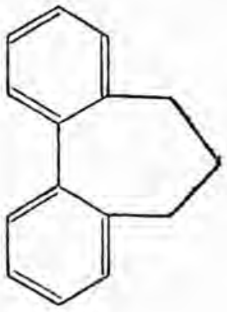
Since 9,10-dihydrophenanthrene and fluorene are effectively planar as indicated by ultraviolet absorption spectra and other evidence provided above, 4,5-methylene-9,10-dihydrophenanthrene, XXII, is also expected to be planar. This is confirmed by the observation that its ultraviolet spectrum resembles that of biphenyl.



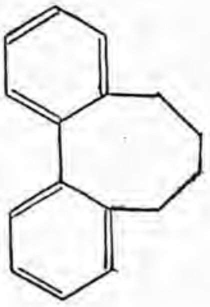
XXIII

The previous three compounds are examples of coplanar biphenyl derivatives.

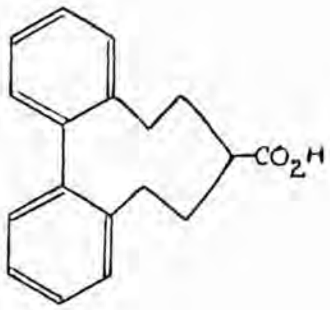
A.C. Cope and R.D. Smith (J. Amer. Chem. Soc., 1956, 78, 1012) have shown that 1,2,3,4-dibenz-1,3-cycloheptadiene XXIV, has an ultraviolet spectrum which shows an absorption maxim~~a~~um at 247mμ (ϵ 15,700) and that 1,2,3,4-dibenz-1,3-cycloclooctadiene, XXV, has an ultraviolet spectrum having an absorption maximum at 235mμ (ϵ 9,680) and two points of inflection at 265 and 275mμ. Hence the conjugation band in XXV has undergone a hypsochromic shift.



XXIV



XXV



XXVI

K. Mislow, S. Hyden and H. Schaefer (*J. Amer. Chem. Soc.*, 1962, *84*, 1449) prepared the nine-membered ring bridged biphenyl XXVI, and found that its ultraviolet spectrum showed a pronounced hypsochromic shift and drop in extinction of the vestigial biphenyl conjugation band (inflection at 231mμ, ϵ 5550). The long wavelength features are now clearly resolved, and the spectrum of this compound is nearly superimposable on that of its open chain analogue. They therefore concluded that conjugation is more severely inhibited and that the angle of torsion is greater in XXVI than in the lower homologues, XXI, XXIV, and XXV. It is observed that the conjugation band suffers a hypsochromic shift and decreases in intensity as the size of the bridge and therefore the angle of torsion (θ) increase.

Derivatives of XXIV and XXV have been obtained in optically active form (D.C. Iffland and H. Siegel, *J. Amer.*

Chem. Soc., 1958, 80, 1947; L.V. Dvorken, R.B. Smyth and K. Mislow, J. Amer. Chem. Soc., 1958, 80, 486). The optical stability of these systems ($t_{\frac{1}{2}}^{31.5}$ = 85 min. E = 22.8 Kcal. mole^{-1} for β-1,2,3,4-dibenz-1,3-cyclooctadiene-6,7-dicarboxylic acid in absolute ethanol and E = 20.8 - 26.2 Kcal. mole^{-1}, $t_{\frac{1}{2}}^{32.5}$ = 80 min. for 6,6'-dicarbethoxy-1,2,3,4-dibenz-1,3-cycloheptadiene in cyclohexane) is a reflection of the angle strain (i.e. the biphenyl system is not planar) and nonbonded interactions which are introduced in the transition state conformation for racemisation.

K. Mislow, S. Hyden and H. Schaefer (loc. cit.) obtained XXVI optically active and found that its optical stability (E = 24.0 Kcal.mole^{-1} in o-xylene) reflects a large angle strain in the transition state.

There are some indications that the degree of interaction between the benzene rings in biphenyl, as calculated using the Molecular Orbital Theory, and the interplanar angle are related by a cos θ or cos^2 θ law (M.J.G. Dewar, J. Amer. Chem. Soc., 1952, 74, 3345; J. Guy, J. Chim. Phys., 1940, 46, 469)

(IV). Naphthalenes:

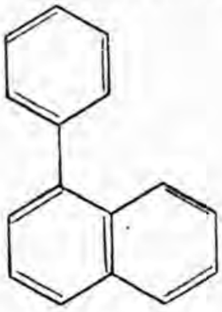
Naphthalene has an ultraviolet spectrum which shows three main absorption bands:

1) A weaker band, λ_{max} = 312, $\epsilon = 10^2$-10^3 possessing some vibrational structure.
2) A moderately intense band, λ_{max} = 275, $\epsilon = 10^4$.

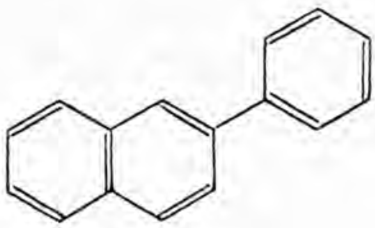
showing a very regular vibrational structure.

3) A strong band, $\lambda_{max} = 220$, $\epsilon = 10^5$, without any vibrational structure.

R.A. Friedel, M. Orchin and L. Reggel (*J. Amer. Chem. Soc.*, 1948, *70*, 199) have done some work on phenylnaphthalenes and other naphthalene derivatives. 1-Phenylnaphthalene, XXVII, was shown to have an absorption spectrum resembling that of naphthalene, indicating strong steric hindrance to planarity. However, there are bathochromic shifts of the ultraviolet absorption bands and a great decrease in fine structure, this indicates appreciable contributions from coplanar structures, i.e. a certain degree of conjugation between the naphthalene and benzene rings. The spectrum of 2-phenylnaphthalene, XXVIII, differs from that of naphthalene; this molecule can become planar as easily as biphenyl can.



XXVII

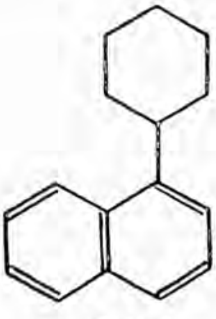


XXVIII

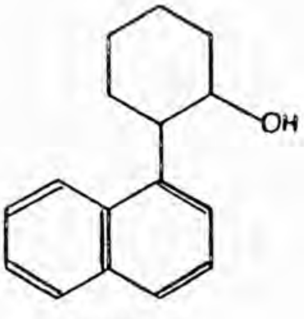
Substituting the groups $-CH_3$, $-OCH_3$ and $-OH$ in the *ortho* positions of the phenyl group of 1-phenylnaphthalene has an appreciable effect on the ultraviolet absorption bands. The methyl group in 1-*o*-tolynaphthalene produces in the 280mμ region, a weaker, narrower band with typical naphthalene fine structure, including the band at 314mμ. Thus it has increased the steric hindrance in the molecule. The methoxy and hydroxy groups hardly affect the absorption bands and so cause only slight additional steric hindrance over that already present in 1-phenylnaphthalene.

In comparison, the relative hindrance produced by the groups $-CH_3$ and -OH in the *ortho* positions of the phenyl group of 2-phenylnaphthalene is striking. The methyl group in 2-*o*-tolylnaphthalene causes the two absorption bands at 250 and 212mμ in the spectrum of 2-phenylnaphthalene to appear as a wide band around 230mμ, with a doublet splitting. The long-wave band undergoes a hypsochromic shift from 286 to 274mμ. The hydroxy derivative has the same spectral structure indicating, surprisingly, that *both* methyl and hydroxy groups show an appreciable and similar increase in steric hindrance over the parent compound.

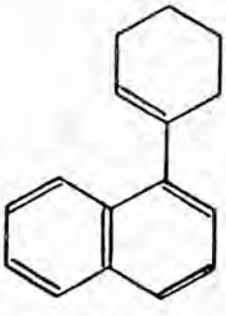
The spectra of 1-cyclohexylnaphthalene, XXIX, and 2'-hydroxy-1-cyclohexylnaphthalene, XXX, are typical of naphthalene derivatives with one saturated substituent. The spectra are almost identical with that of the strongly hindered 1-*o*-tolylnaphthalene. The spectrum of the tetrahydro-compound, 1-(2',3',4',5')-tetrahydrophenylnaphthalene XXXI, shows band widening, decreased fine structure and increased intensity.



XXIX



XXX



XXXI

This shows that there is some conjugation between the naphthalene nucleus and the double bond.

Measurements:

The ultraviolet absorptions were measured using a Unicam spectrophotometer (SP 500).

96% ethanol was used as the solvent.

Optical density measurements were taken using 0.2cm. cells for the region 205-255mμ and 1.0cm. cells for the region beyond 250mμ.

The main feature of the spectra determined are recorded in the tables following,

(Some of these spectra have been accepted for publication in the D.M.S.Atlas (Butterworths)).

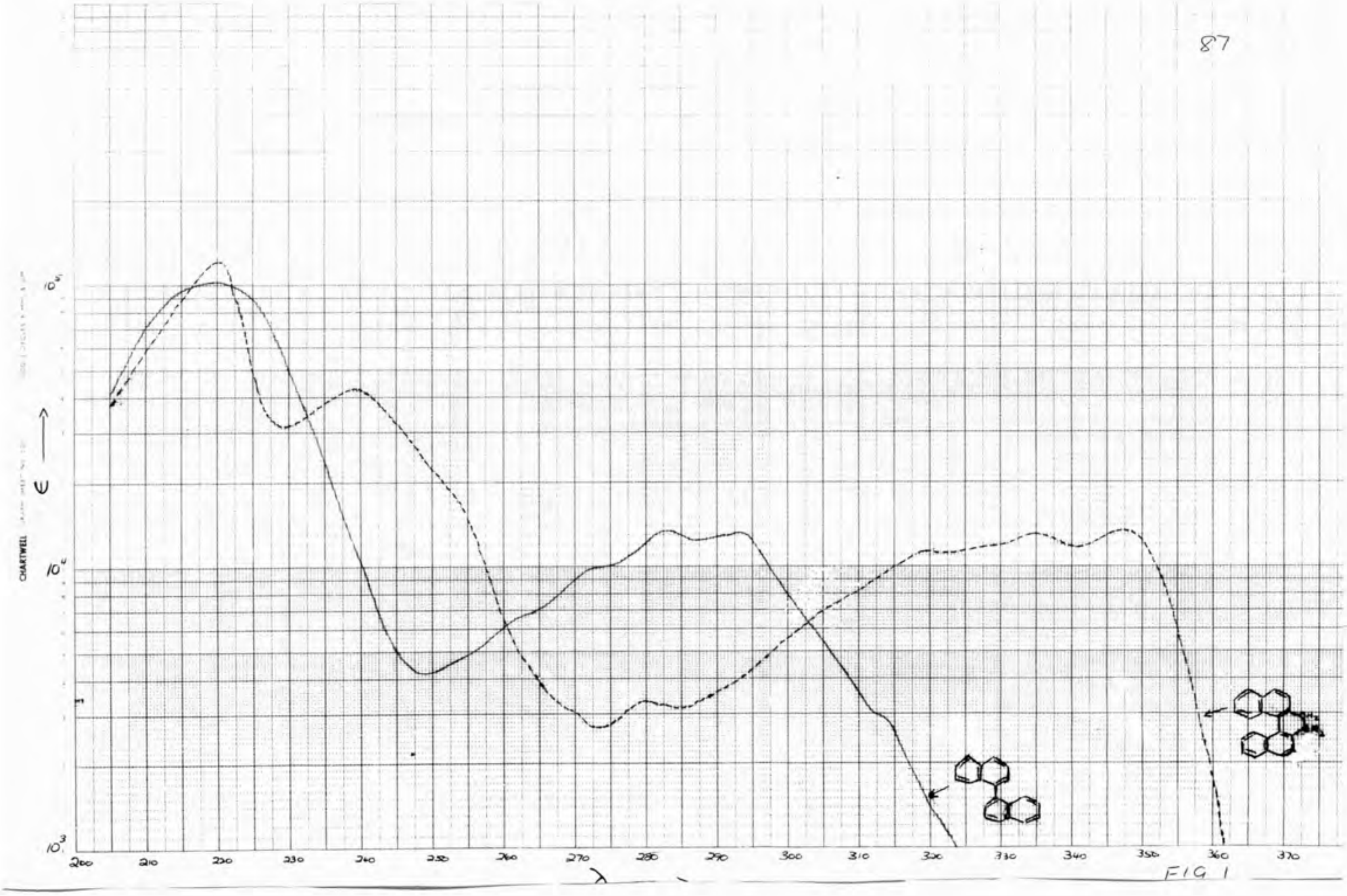

CHARTWELL
10^5
10^4
10^3
ε ⟶
200
210
220
230
240
250
260
270
280
290
300
310
320
330
340
350
360
370
λ

FIG 1

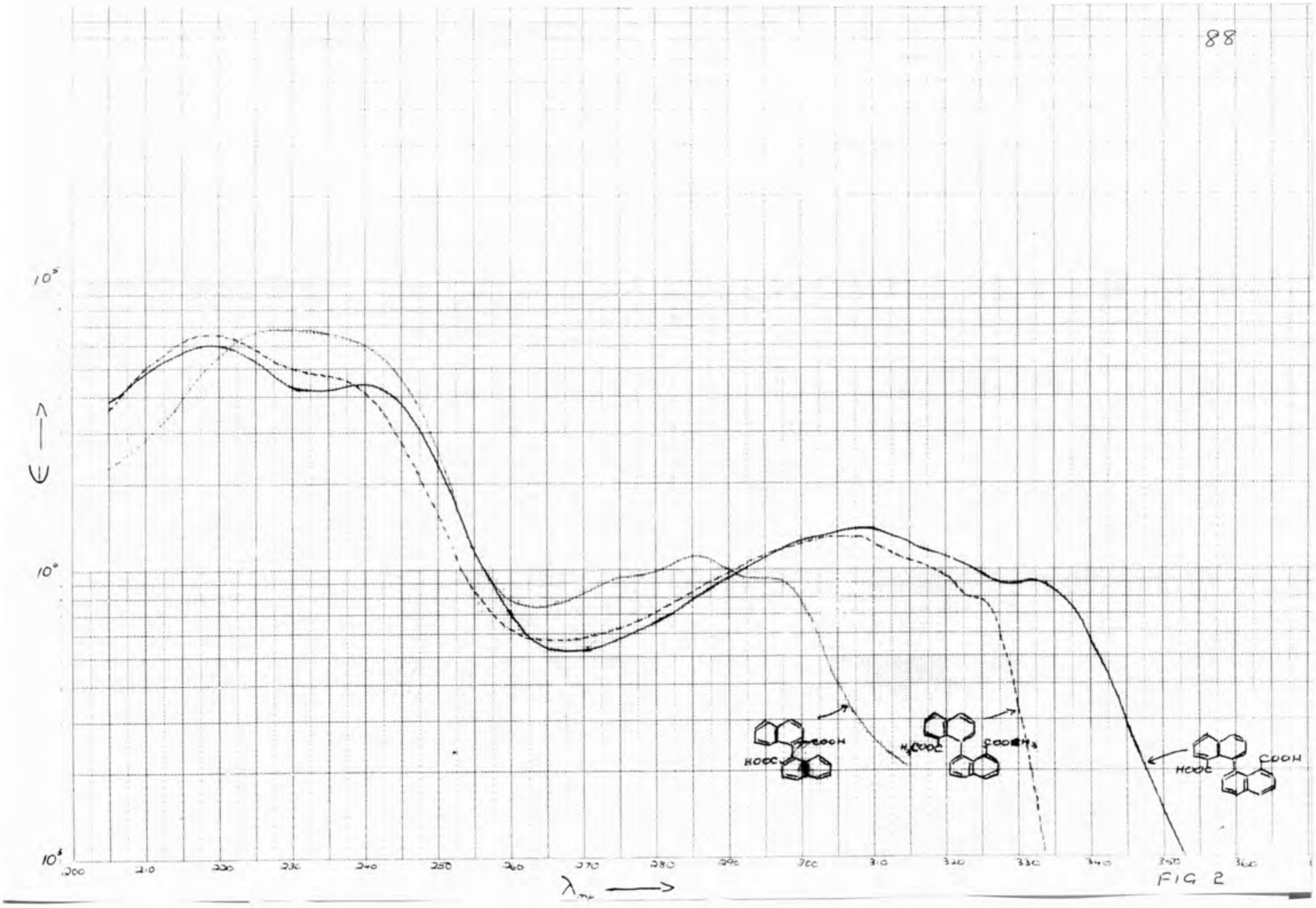

10^5
10^4
10^3
ε →
200
210
220
230
240
250
260
270
280
290
300
310
320
330
340
350
360
$\lambda_{m\mu}$ →
COOH
HOOC
H_3COOC
$COOCH_3$
HOOC
COOH

FIG 2

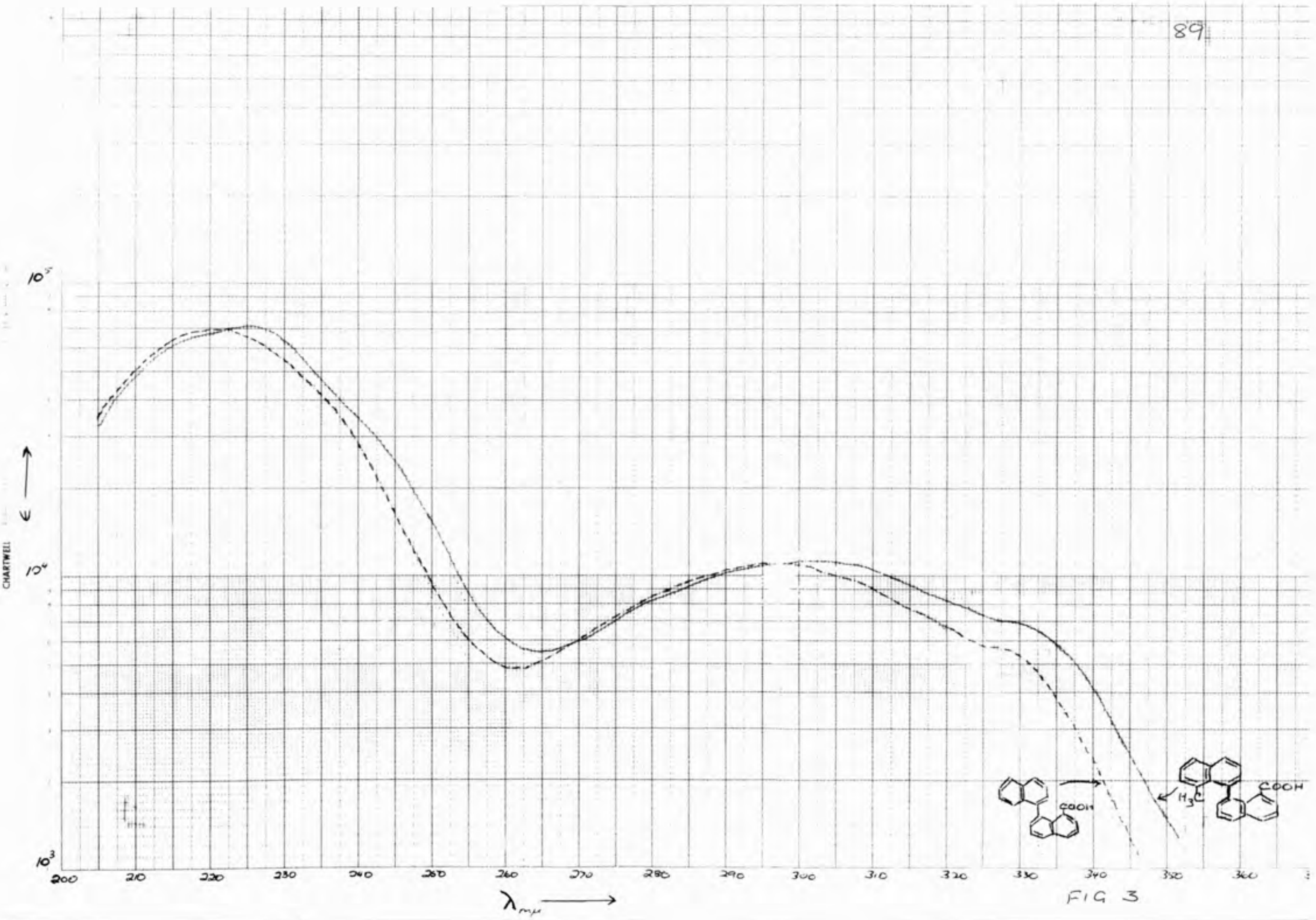

10^5
10^4
10^3
ε →
CHARTWELL
200
210
220
230
240
250
260
270
280
290
300
310
320
330
340
350
360
λ mμ →
COOH
H_3C
COOH

FIG 3

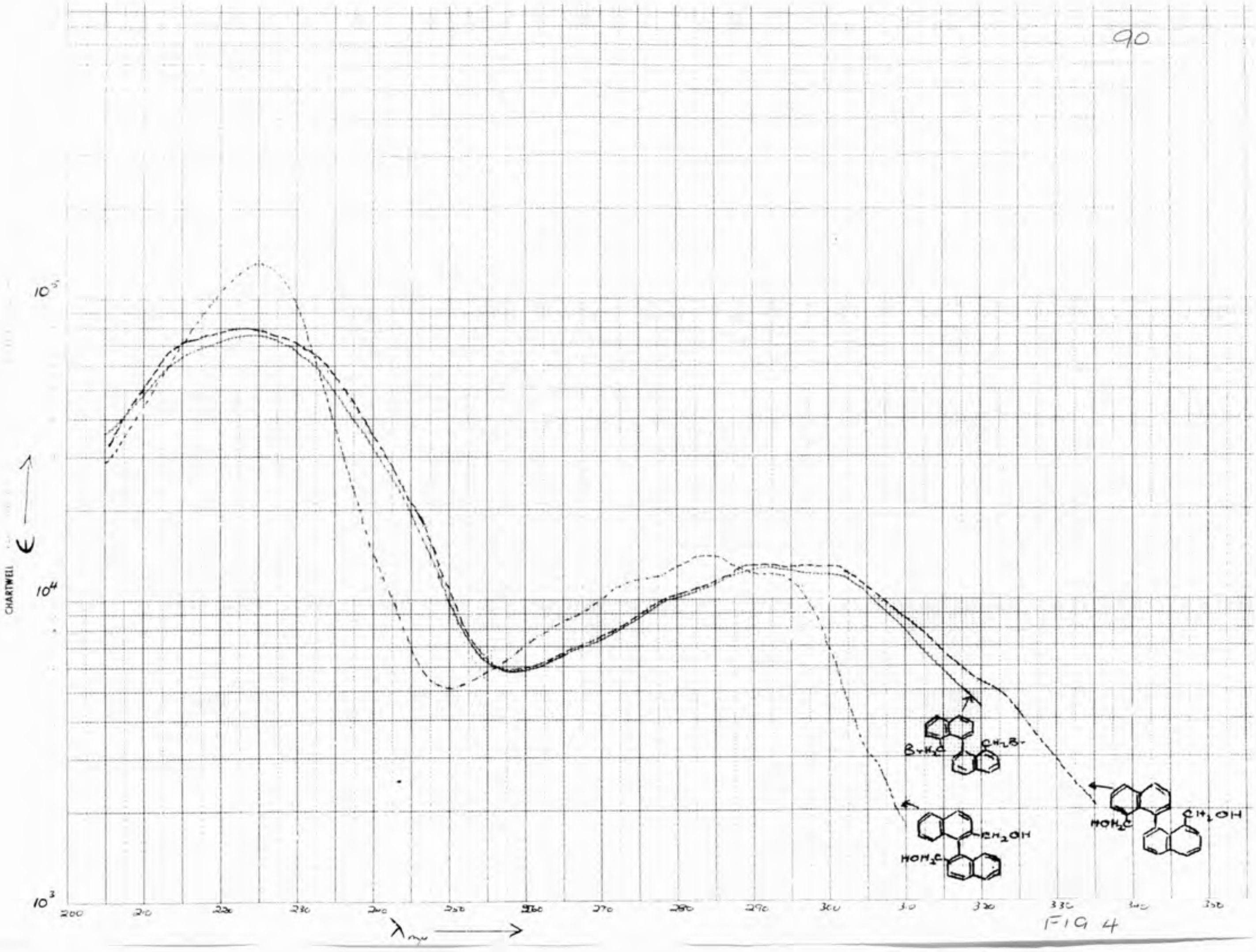

CHARTWELL
ε ⟶
10^5
10^4
10^3
200
210
220
230
240
250
260
270
280
290
300
310
320
330
340
350
λ mμ ⟶
BrH₂C
CH₂Br
CH₂OH
HOH₂C
HOH₂C
CH₂OH

FIG 4

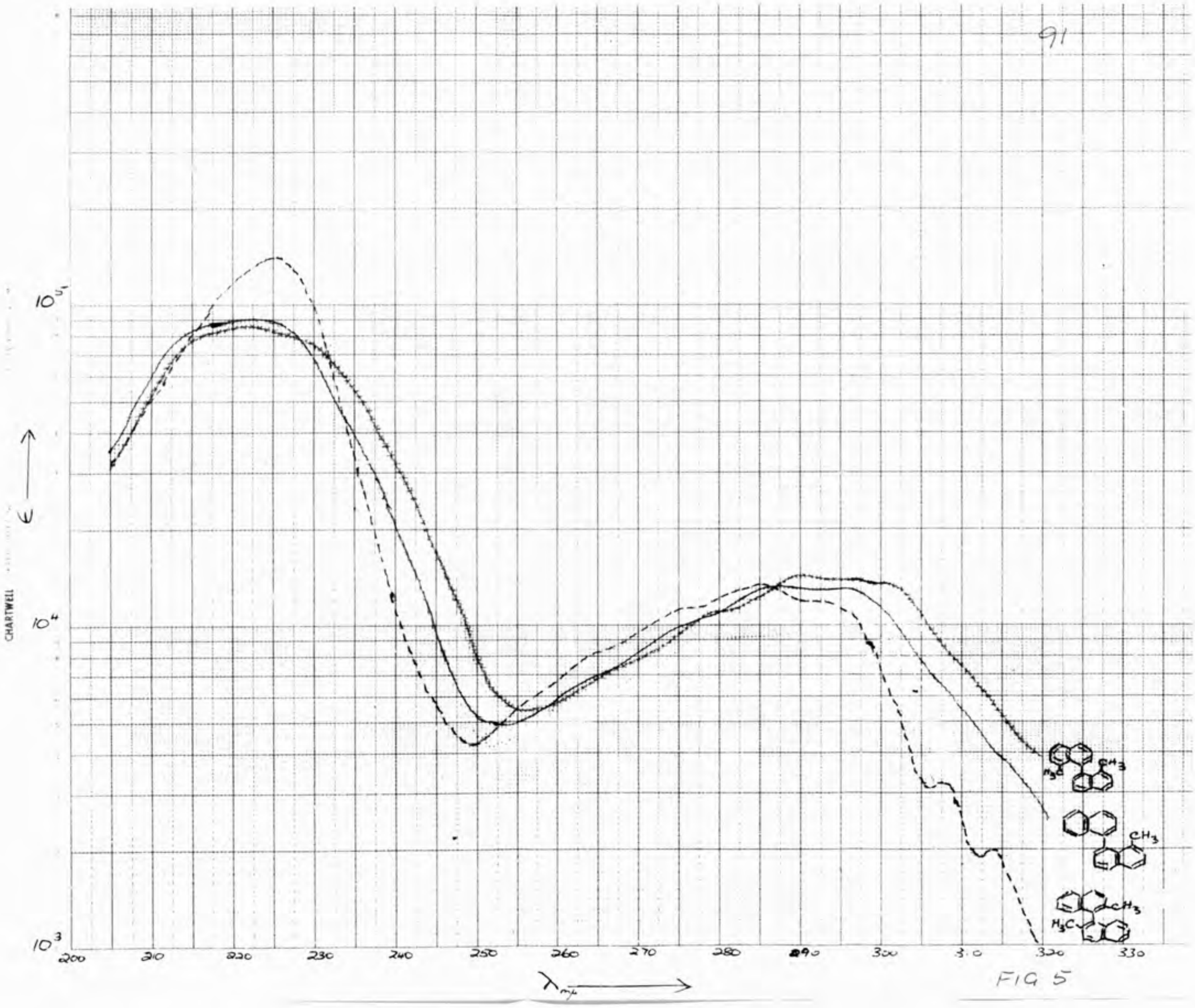

10^5
10^4
10^3
ε ⟶
200
210
220
230
240
250
260
270
280
290
300
310
320
330
$\lambda_{m\mu}$ ⟶
CH_3
H_3C
CH_3
CH_3
H_3C

FIG 5

DATA FOR THE ULTRAVIOLET SPECTRA OF 1,1'-BINAPHTHYLS.

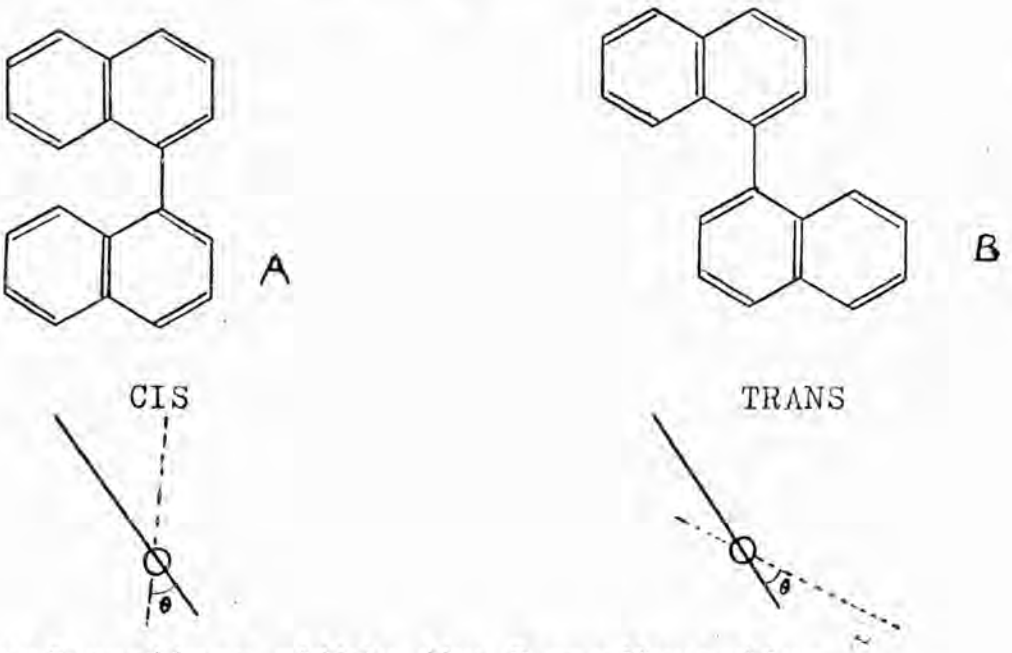
Fig.	Compound	Shortwave band λ_{max}	ϵ_{max}	λ_{min}	ϵ_{min}	Conjugation band λ_{max}	ϵ_{max}	λ_{min}	ϵ_{min}	Longwave band λ_{max}	ϵ_{max}
I	1,1-Binaphthyl	220	110,000	249	4,200	–	–	–	–	262.5(Inf.) 272.5(Inf.) 283 293 313,5(Inf.)	6,600 9,800 13,000 13,000 2,900
	9,10-Dihydro-3,4-5,6-dibenzophenanthrene	220	120,000	229.5	31,000	239.5	42,000	473.5	2,700	279.5 320 334.5 347	3,300 11,000 13,000 13,400
II	1,1-Binaphthyl-8,8'-dicarboxylic acid	219.5 239.5(sh.)	60,000 44,000	267.5	5,200	–	–	–	–	309 332(sh.)	14,000 9,100
	1,1-Binaphthyl 2,2'-dicarboxylic acid	230	69,000	263.5	7,200	–	–	–	–	275(sh.) 285.5 297(sh.)	9,400 12,000 9,200
	Dimethyl 1,1'-Binaphthyl-8, 8'-dicarboxylate	219.5 235(sh.)	65,000 47,000	266.5	5,700	–	–	–	–	305 320(sh.)	13,000 9,400
III	1,1'-binaphthyl-8,carboxylic acid	221.5	69,000	261.5	4,800	–	–	–	–	296 325(sh.)	11,000 5,800
	8'-Methyl-1,1'-binaphthyl-8-carboxylic acid	225.5	70,000	264.5	5,500	–	–	–	–	303 330(sh.)	11,000 6,900

Fig.	Compound	Shortwave band				Conjugation band				Longwave band	
		λ_{max}	ϵ_{max}	λ_{min}	ϵ_{min}	λ_{max}	ϵ_{max}	λ_{min}	ϵ_{min}	λ_{max}	ϵ_{max}
IV	8,8'-Dimethyl-1,1'-binaphthyl	221.5	85,000	256	5,600	–	–	–	–	280(sh) 290 300	11,000 14,000 13,000
	2,2'-Dimethyl-1,1'-binaphthyl	225.5	140,000	248	4,400	–	–	–	–	265(Inf.) 275(sh) 285 292 307.5 314	8,200 11,000 13,000 12,000 3,000 2,000
	8-Methyl-1,1'-binaphthyl	221	90,000	253.5	5,000	–	–	–	–	287.5 296	13,000 13,000
V	8,8'-Bishydroxy-methyl-1,1'-binaphthyl	223.5	80,000	258	5,800	–	–	–	–	279(Inf.) 290 300 322.5(Inf.)	10,000 13,000 10,000 5,000
	2,2'-Bishydroxy-methyl-1,1'-binaphthyl	225	135,000	250	5,100	–	–	–	–	260(Inf.) 275(sh) 284 292.5 305.5	8,500 12,000 14,000 12,000 3,000
	8,8'-Bisbromo-methyl-1,1'-binaphthyl	224.5	76,000	258.5	5,800	–	–	–	–	280(Inf.) 290 300 322.5	10,000 13,000 12,000 4,900

(V) Discussion:

The interpretation of the ultraviolet spectra of 1,1'-binaphthyls is complicated in the following way:-

(a) 1,1'-Binaphthyl itself, which has a much higher steric barrier to rotation about the 1,1'-bond ($E = 22.5$Kcal. mole^{-1}) than biphenyl ($E \sim 4$Kcal.mole^{-1} to 10.8Kcal.mole^{-1}, estimated from calculations) has almost certainly two preferred conformations within each R and S configuration.



Two conformations within the S-configuration.

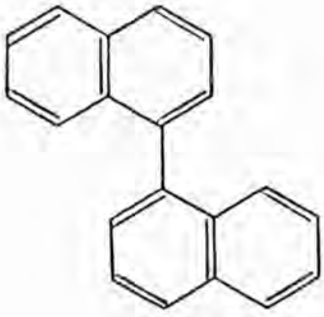
(Structures A and B are drawn as extremes; they are not intended to represent flat states).

In solution it is probable that both conformations are present, and whether one is preferred over the other is so far not known.

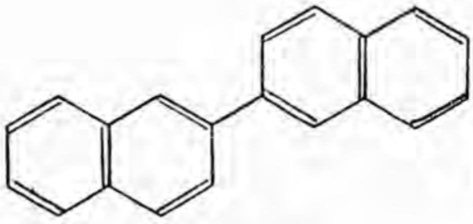
(b) Substituents in the naphthalene residues will affect the separate naphthalene conjugation patterns, but they may at the same time (when in the 2,2'- and 8,8'-positions) change the geometry of the binaphthyl system both by distorting it and also by changing the distribution of molecules in the two conformations (e.g. *S-cis* and *S-trans*).

It is therefore not possible to attribute the 1,1'-binaphthyl spectral features to a particular conformation.

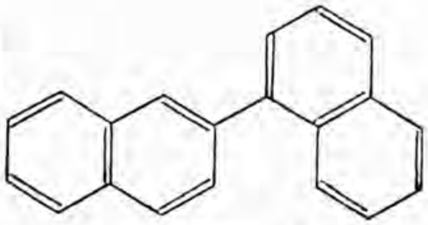
R.A. Friedel, M. Orchin and L. Reggel (*J. Amer. Chem. Soc.*, 1948, *70*, 199) have discussed the spectra of 1,1'-binaphthyl, XXXII, 2,2'-binaphthyl, XXXIII, and 1,2'-binaphthyl, XXXIV.



XXXII



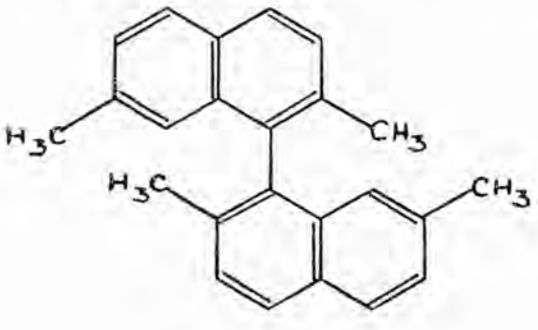
XXXIII



XXXIV

1,1'-Binaphthyl shows the greatest non-planarity in that its spectrum is closest to that of naphthalene. However, the spectrum shows that some resonance structures involving coplanarity exist because its spectrum is not simply that of two naphthalene residues; fine structure is diminished and the minimum in naphthalene at 235mμ has increased in intensity and undergone a bathochromic shift to 249mμ. The interaction here is not merely of the type described by H.C. Longuet-Higgins and J.N. Murrell (*loc.cit.*,) which is due to electronic transitions which are independent of the coplanarity conditions, since a bathochromic shift of the absorption minimum is observed, and the fine structure of the long-wave band is reduced. 2,2'-Binaphthyl which is as free from steric hindrance as biphenyl has a spectrum showing a structure radically different from that of naphthalene. The spectrum has an intense conjugation band at 254mμ, a weaker broad band at 305mμ and a short wavelength band at 212mμ. 1,2'-Binaphthyl was found to be intermediate between the other two compounds. Its spectrum is more similar to that of 1,1'-binaphthyl but intensities are greater, fine structure is diminished and bands are considerably broader.

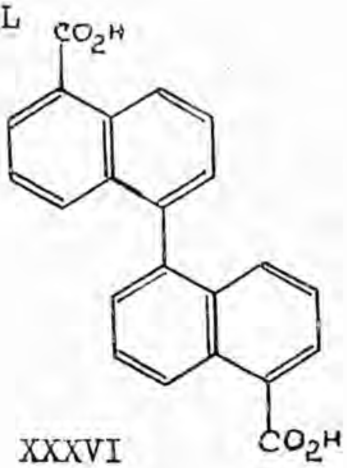
However, the spectrum of 2,2'-7,7'-tetramethyl-1,1'-binaphthyl, XXXV, shows that the molecule is even further from planarity than 1,1'-binaphthyl, since fine structure is developed, the typical naphthalene band appears at 319mμ and intensities are approximately twice those of naphthalene. This observation shows that substituents in the blocking positions (in this case the 2,2'-methyls) in the 1,1'-binaphthyl system affect the residual conjugation in the system.



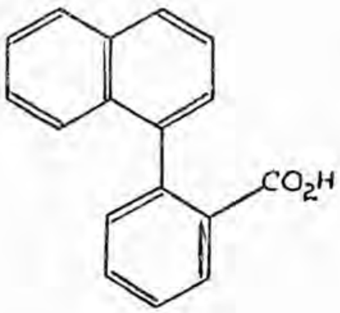
XXXVI

The new work discussed here was undertaken to see the effect, on the 1,1'-binaphthyl spectrum, of the increase in size of substituents in 8,8'-positions in 1,1'-binaphthyls. Moreover, it was considered interesting to see how the spectra of 8,8'-substituted 1,1'-binaphthyls compare with those of the corresponding 2,2'-substituted 1,1'-binaphthyls (i.e. try to cast some light on the 1,1'-binaphthyls in the ground state). Classical models show similar steric interference to rotation about the inter-annular bond in both 8,8'-substituted and 2,2'-substituted 1,1'-binaphthyls but the low optical stability of 8,8'-substituted 1,1'-binaphthyls has been attributed to greater deformation in the ground states of these compounds (A.S. Cooke and M.M. Harris, J. Chem. Soc., 1963, 2365). Any deformation would be small in the 2,2'-substituted 1,1'-binaphthyls. The results obtained in this work could serve as an assessment of the difference in the total ground state deformation in the two classes of compounds, the comparison being based on fine structure, absorption intensities and band positions.

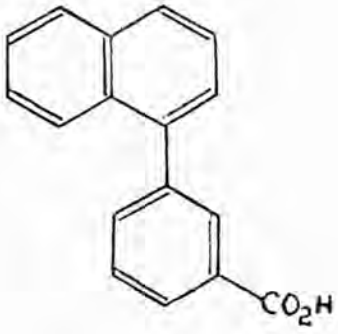
D.M. Hall, S. Ridgewell and E.E. Turner (J. Chem. Soc., 1954, 2498) examined the ultraviolet spectra of compounds XXXVI - XL



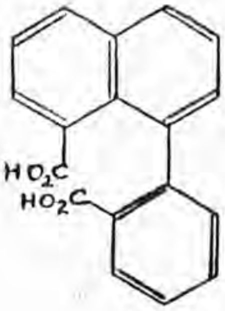
XXXVI



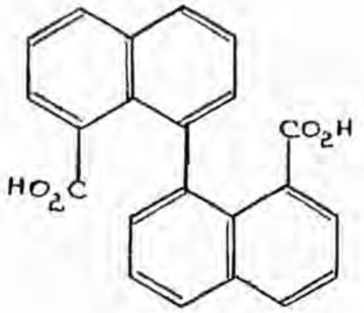
XXXVII



XXXVIII



XXXIX



XL

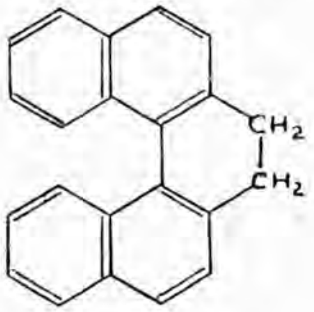
They found that the spectra of compounds XXXVI and XL differ from that of 1,1'-binaphthyl and those of XXXVII, XXXVIII and XXXIX from that of 1-phenylnaphthalene. The difference is consistent with the expected effects of substituents on the spectra of parent compounds (Y. Hirshberg and R.N.Jones, Canad. J. Res., 1949, 27B, 437) and on the steric hindrance to coplanarity across the interannular bond. They found a poor correlation between the relative degree of conjugation across the interannular bond, as deduced from the spectra, and the relative optical stabilities of the optically active compounds. Secondary effects of substituents on conjugation, and hence on the length of the interannular bond, do not appear to have any further influence on the ease of rotation about the bond. These workers therefore suggested that the lack of correlation between the spectra and optical stabilities of the compounds may be associated with the possibility that some of the compounds have non-planar ground states and coplanar excited states (c.f. E.A.Braude, F.Soudheimer and W.F.Forbes, Nature, 1954, 173, 117) so that the substituents affect the spectra by altering the transition possibilities for the excited states and have little effect on the ground states. In these compounds the steric distortion has given rise to a change in the absorption intensities but not to the wavelength of the absorption bands. Braude and his co-workers (ibid) suggested that when only intensity changes occur, the substituent has produced a distortion of the ground state but not the excited state (the reduced intensity was then thought to follow from the Franck-Condon principle), but if changes in wavelength also occur then the excited state has also been distorted. But it is not clear why the first case should give no wavelength changes (J.N.Murrell, Theory of Electronic Spectra of Organic Molecules, p.238, Methuen 1963). Also the intensity of the constant wavelength absorption band is not temperature dependent, as it should be for one arising from a Franck-Condon forbidden transition (Waight and Erskine, Steric Effects in Conjugated Systems, p.73, ed. Gray, Butterworths 1958).

A correlation between spectra and optical stabilities is, however, not satisfactory, because spectral features are determined by the interplanar angle whereas optical stabilities depend upon the easiness with which substituents pass each other in the transition state for racemisation. This is observed with 9,10-dihydro-3,4-5,6-dibenzophenanthrene, XLI, which possesses a conjugation band (λ_{max}=239.5mμ) but is much more optically stable (ΔE =34K.cal.mole^{-1}.) than the less planar 1,1'-binaphthyl which is less optically stable (ΔE =22.5K.cal.mole^{-1}.) but exhibits no conjugation band.

The lack of correlation between the spectra and optical stabilities of the 8,8'-substituted 1,1'-binaphthyls is therefore not surprising.

9,10-Dihydro-3,4-5,6-dibenzophenanthrene: Fig. I.

This compound, XLI, formed by bridging the 1,1'-binaphthyl system with two methylene groups shows a spectrum similar to those of the bridged biphenyls, 9,10-dihydrophenanthrene and 4,5-methylene-9,10-dihydrophenanthrene.

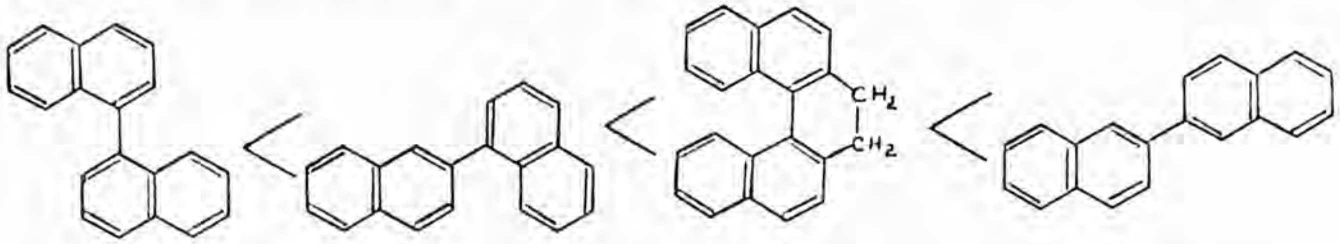


XLI

This bridging, as is expected, brings the naphthalene residues in the molecule, to a nearly planar necessarily cisoid conformation.

The spectrum shows a structure much different from that of 1,1'-binaphthyl. It has an intense conjugation band at 239.5mμ and the longwavelength band has undergone a bathochromic shift (in comparison with that of 1,1'-binaphthyl) and has fine structure, which is due to the effect of the dimethylene bridge. The spectrum is typical of a conjugated binaphthyl system. However, the intensity of the conjugation band for this compound (ϵ 42,000) is less than that for 2,2'-binaphthyl (ϵ 94,000) whereas in 1,1'-binaphthyl the band is overshadowed by the shortwave band. Moreover, it has undergone a hypsochromic shift, relative to the position of the conjugation band for 2,2'-binaphthyl. This observation is consistent with the fact 9,10-dihydro-3,4-5,6-dibenzophenanthrene is capable of observable optical activity (D.M.Hall and E.E.Turner J. Chem. Soc., 1955, 1242) whereas 2,2'-binaphthyl is not as its rotational barrier is too small.

Hence according to the degree of planarity, as revealed by the ultraviolet spectra, the following compounds can be written in the order:-



9,10-Dihydro-3,4-5,6-dibenzophenanthrene and 2,2'-binaphthyl show the typical naphthalene conjugation band.

1,1'-Binaphthyl-8,8'-dicarboxylic acid, dimethyl 1,1'-binaphthyl-8,8'-dicarboxylate and 1,1'-binaphthyl-2,2'-dicarboxylic acid: Fig. II.

In the spectrum of the 8,8'-diacid, the long wavelength band has been shifted to longer wavelengths, it is broad and lacks the fine structure present in the spectrum of 1,1'-binaphthyl. This does not necessarily mean that there is conjugation across the 1,1'-bond. The bathochromic shift and loss of fine structure may be due to conjugation between the carboxyl group and the naphthalene residues. J. Fujita, K.Koshimizu and T.Mitsui, (Tetrahedron, 1966, 22, 1587) have worked on the ultraviolet spectra of substituted 1-naphthoic acids. They have observed that the long wavelength band positions reflect the degree of conjugation between the naphthalene ring and the carboxyl group, in particular for those compounds in which rotation of the carboxyl group is hindered by a nearby second substituent. The spectra of the 2- and 8- methyl- and -halo- substituted derivatives of 1-naphthoic acid, except for the 2-fluoro-acid, possess fine structure which consists of three peaks or shoulders observed at shorter wavelengths than for any of the acids substituted at other positions. This fact would mean a lower degree of conjugation between the carboxyl group and the ring owing to twisting of the carboxyl group caused by steric interaction of the vicinal substituent. For the 2-fluoro-acid, the long wavelength band is devoid of fine structure and the spectrum resembles that of 1-naphthoic acid. This fact suggests that the carboxyl group is not so hindered as those of other 2- substituted acids because the small atomic radius of fluorine is so small. However, the spectrum of the 8,8'-diacid still shows conjugation between the carboxyl groups and the naphthalene residues (as shown by loss of fine structure and bathochromic shift of the long-wave band). This extra conjugation shows the effect the substituents have on the conjugation between the naphthalene residues in the molecule.

However, it is observed that the long-wave band is shifted bathochromically more than that of 1-naphthoic acid. This suggests additional contribution by the 1,1'-binaphthyl system to the overall conjugation in the molecule, (this could be consistent with a fairly planar conformation of the carboxylic acid group with its attached naphthalene unit).

With the 2,2'-diacid, the short wavelength band has undergone a hypsochromic shift (λ=229) relative to that of 2-naphthoic acid (λ=233) (R.A. Friedel and M. Orchin, Ultra-Violet Spectra of Aromatic Compounds, Wiley and Sons. Inc., New York) and the intensity ($\in$ 69,000) approaches that of the band in the naphthalene partial chromophores and is higher than that of the 8,8'-diacid ($\in$ 60,000). There is increased fine structure, compared to the spectrum of 1,1'-binaphthyl. However, a comparison between the spectra of the 2,2'-diacid and the 8,8'-diacid is complicated by the greater conjugative effects of the carboxyl groups in the 8,8'-diacid, which overshadow the fine structure in the spectrum of the 8,8'-diacid as it does in 1-naphthoic acid.

The spectrum of dimethyl-1,1'-binaphthyl-8,8'-dicarboxylate resembles that of the 8,8'-diacid. Hence the factors operating in the two compounds are similar. This suggests that steric considerations, rather than internal hydrogen bonding (say of an OH-π electron type) govern the choice of conformation.

1,1'-Binaphthyl-8-carboxylic acid and 8'-methyl-1,1'-binaphthyl-8-carboxylic acid: Fig. III.

These two compounds have ultraviolet spectra resembling that of 1,1'-binaphthyl except that bands are broader and the long wavelength bands have undergone a bathochromic shift, presumably due to conjugation between the carboxyl groups and the naphthalene residues as in the 8,8'-diacid.

8,8'-Dimethyl-, 8-methyl- and 2,2'-dimethyl-1,1'-binaphthyl: Fig. V.

The spectrum of 8,8'-dimethyl-1,1'-binaphthyl resembles that of 1,1'-binaphthyl in fine structure. However, the spectrum of 2,2'-dimethyl-1,1'-binaphthyl shows more developed fine structure and the appearance of the typical naphthalene band at about 314mμ. The absorption minimum has been shifted hypsochromically and its intensity is lower than that of 8,8'-dimethyl-1,1'binaphthyl. This suggests that the whole binaphthyl skeleton is more nearly planar in 8,8'-dimethyl-1,1'-binaphthyl than in the 2,2'-dimethyl-1,1'-binaphthyl molecule, although individual naphthalene units may be more distorted in the 8,8'-compound. Models confirm that this suggestion is possible. The spectrum of 8-methyl-1,1'-binaphthyl resembles that of the 8,8'-dimethyl derivative.

8,8'-Bishydroxymethyl-1,1'-binaphthyl, 2,2'-bishydroxy-1,1'-binaphthyl and 8,8'-bisbromomethyl-1,1'-binaphthyl: Fig. IV.

The substituent $-CH_2OH$ has essentially the same effect on spectra as the simple alkyl substituent. This is due to the fact that the auxochromic group $-OH$, is insulated from the aromatic chromophore by a methylene group. The spectra of the hydroxymethyl compounds can therefore be compared to those of the methyl compounds. The spectrum of 8,8'-bishydroxymethyl-1,1'-binaphthyl resembles those of 1,1'-binaphthyl and 8,8'-dimethyl-1,1'-binaphthyl, but it differs from that of 2,2'-bishydroxymethyl-1,1'-binaphthyl which shows increased fine structure, with a development of the naphthalene long wavelength band at 305mμ. The spectrum of the latter compound has a minimum with a lower intensity than that of the former and it resembles that of 2,2'-dimethyl-1,1'-binaphthyl. This also indicates that 8,8'-bishydroxymethyl-1,1'-binaphthyl has a more planar binaphthyl skeleton than 2,2'-bishydroxy-methyl-1,1'-binaphthyl.

8,8'-Bisbromomethyl-1,1'-binaphthyl has a spectrum which resembles that of 1,1'-binaphthyl, 8,8'-dimethyl-, and 8,8'-bishydroxymethyl-1,1'-binaphthyl in fine structure and intensities of the absorption bands.

It is therefore apparent that increasing the size of the substituent in the 8,8'-positions in 1,1'-binaphthyl does not have a great effect on the degree of non-planarity in the overall system as far as can be deduced from the ultraviolet spectra. However, substitution in the 2,2'-positions increases the non-planarity of the 1,1'-binaphthyl system.

It is, in general observed that with 8,8'-substituted 1,1'-binaphthyls, the shortwave band has a lower intensity, the absorption minimum has a higher intensity and is shifted bathochromically and the longwave band has less fine structure and is also shifted bathochromically, than is the case with 2,2'-substituted 1,1'-binaphthyl.

In the case of the 8,8'-substituted 1,1'-binaphthyls there is peri-interaction which causes in-plane and out-of-plane deflection of substituents. This "pushing out" of substituents appears to allow greater interaction between the naphthalene residues in these compounds. This is not so with 2,2'-substituted 1,1'-binaphthyls. The lack of deflection of substituents in 2,2'-substituted 1,1'-binaphthyls gives rise to increased non-planarity of the binaphthyl system, thus reducing the interaction between the naphthalene residues in the system.

The possibility of in-plane deflections of the substituents in 8,8'-substituted 1,1'-binaphthyls, reduces the degree of out-of-plane deviations of the substituents, thus allowing some conjugation between the carboxyl (and ester) groups and the naphthalene residues. Without such deformations the net result would be a system as non-planar as the 2,2'-substituted 1,1'-binaphthyl system and the ultraviolet spectral differences between the two classes of compounds would not be observed. Hence these spectral differences between the 8,8'-substituted and 2,2'-substituted-1,1'-binaphthyls are likely to be due to differences in the effects the substituents have on the ground states of the molecules.

7. CONFIGURATIONAL CORRELATIONS OF THE 1,1'-BINAPHTHYL SERIES USING OPTICAL ROTATORY DISPERSION AND CIRCULAR DICHROISM.

(i)Introduction:

Dissymmetric substances have an ability to refract and absorb right and left circularly polarized light to different extents (i.e. optical activity or optical rotatory power).

A beam of light is associated with varying electrical and magnetic fields. In a beam of plane polarized light, the electrical vector, E, is restricted to one plane and its magnitude at a given point in the beam varies periodically In a beam of circularly polarized light, the magnitude of the vector remains unchanged, but its direction at a given point rotates either clockwise (right circularly polarized) or anticlockwise (left circularly polarized light). Crudely speaking, plane polarized light corresponds to an ordinary wave in one plane, while circularly polarised light corresponds to movement along a right or left handed helix. Plane polarized light can be considered to be the resultant of two circularly polarized in-phase beams of the same frequency and amplitude. The electric vectors, E_R (R = right) and E_L (L = left) trace out helical paths of opposite chiralities so that circularly polarized light is dissymmetric. A diastereoisomeric relationship occurs between right circularly polarized light passing through a dissymmetric medium of given chirality, and left circularly polarized light passing through the identical medium. Hence a dissymmetric medium can distinguish between the two beams of opposite chirality, the distinction taking the form of differences in refractive indices of the two beams ($n_R \neq n_L$) and differences in molar extinction coefficients ($\epsilon_R \neq \epsilon_L$). The former is referred to as circular birefringences and the latter as circular dichroism.

For a given solute, solvent, wavelength λ, and temperature T, the magnitude of the measured angle of rotation is proportional to the number of molecules in the path of the light (Biot's law). The proportionality constant is the specific rotation, $[\alpha]$ or the molecular rotation $[\phi]$ depending on units of concentration.

For solutions,

$$[\alpha]^T_\lambda = \frac{\alpha^T_\lambda \times 100}{l \times c}$$

where α = rotation in degree
l = path length
c = grams. per c.c.
M = molecular weight

$$[\phi]^T_\lambda = \frac{M\ [\alpha]^T_\lambda}{100}$$

$[\alpha]^T_\lambda$ or $[\phi]^T_\lambda$ vary with wavelength and this can be understood in terms of the dependence of refractive index on wavelength which in a dissymmetric medium, follows a different course for n_R and n_L. At a given wavelength the rotation is proportional to the difference between n_R and n_L. Therefore the dependence of specific (or molecular) rotation on wavelength (optical rotatory dispersion or ORD) follows a course dictated by that difference inclusive of sign. This behaviour, together with the wavelength dependence of circular dichroism (described below) constitute the Cotton effect.

Where $n_L > n_R$, $[\alpha]_\lambda^T$ is positive and where $n_L < n_R$, $[\alpha]_\lambda^T$ is negative.

When $n_L = n_R$, $\alpha_\lambda^T = 0$, and this occurs at a wavelength (λ_o) ideally corresponding to the λ_{max} of the relavent absorption band. At wavelengths far removed from λ_o, the dependence of optical rotation on wavelength is given by the Drude equation,

$[\alpha]_\lambda^T = A/(\lambda^2 - \lambda^2_o)$, A being a constant characteristic of the solvent - solute system.

ORD curves ($[\phi]$ plotted against λ) are classified into two main types:

(a) Plain curves

(b) Cotton effect curves

Compounds which do not possess an optically active absorption band within the region studied, generally give curves showing no maxima and are termed plain curves. These can either be positive or negative depending on whether the rotation of the compound becomes more positive or more negative with decreasing wavelength. Cotton effect curves show maxima and minima known as peaks and troughs which are collectively referred to as extrema. A curve with one peak and trough is called a single Cotton effect curve and it is classified as positive depending on whether the extremum at longer wavelengths is a peak or trough. The algebraic difference between the molecular rotations at the peak and the trough is known as the molecular amplitude. Curves having more than one extremum of the same type are called Multiple Cotton effect curves.

Circular Dichroism

There are small differences in the molar extinction coefficients $\in_L$ and $\in_R$ of circularly polarized components of plane-polarized light and these differences are expressed by the molecular ellipticity;

$$\left[\theta\right]_{\lambda}^{T} = 3300\ (\in_L - \in_R).$$

The ellipicity arises from the fact that as one of the circularly polarized beams is absorbed more than the other, the resultant vector E no longer oscillates in a plane (whose projection is a line) but instead traces out a flattened helix (whose projection is an ellipse). Circular dichroism and circular birefringence occur together and therefore it is not strictly the plane of polarization that is rotated but the "major plane" of the flattened helix (whose projection is the major axis of the ellipse). Since $[\theta]$ is extremely small, the distinction is not necessary. The CD curve has a positive or negative sign over the whole wavelength range and by convention, when $\in_L > \in_R$, $[\theta]$ is positive.

A CD curve has an appearence and shape closely similar to the absorption curve of the relevant electronic transition, the positions of maximum absorptions of the "reduced" or isolated curves (curves free from overlapping neighbouring bands) correspond almost exactly. However, a CD curve is signed (positive or negative), the sign being that of the Cotton effect.

Structure and Optical Rotatory Power:

A given molecule may have several chromophores and one or more electronic transitions corresponding to each of these, e.g. a molecule may possess a nitrobenzene ring system and a carbonyl system separated by methylene groups. The chromophores and their various transitions give rise to several Cotton effects, positive and negative. In general a complex molecule may have numerous optically active transitions (i.e. transitions having Cotton effects). These can also be referred to as optically active chromophores.

According to A. Moscowitz (Tetrahedron, 1961, 13, 48) there are two limiting types of optically active transitions: "asymmetrically perturbed symmetric" and "inherently dissymmetric". the former (e.g. the carbonyl group of (+)-3-methylcyclohexanone) are chromophores which on grounds of local symmetry are symmetric (i.e. nondissymmetric) and optically inactive. Such groups may be attached to other groups e.g. alkyl groups, whose electronic transitions are far removed in energy and therefore mix only slightly with the chromophores themselves. Such symmetric chromophores may be symmetrically or dissymmetrically perturbed by the extrachromophoric environment. Rotational strengths of such chromophores are low (less than 10) and molecular amplitude of Cotton effects are generally less than 10^4.

On the other hand, some chromophores are themselves dissymmetric, and such inherently dissymmetric chromophores are accompanied by relatively large rotational strengths (i.e. 25 or greater) and large Cotton effect amplitudes (10^5 or greater). Since Cotton effects accessible by current instrumentation are those in which the relevant transitions involve π^* excited states, the structual feature most closely identified with this chromophore is the twisted dissymmetric, π-system e.g. skewed biphenyls.

The sign of the Cotton effect of an inherently dissymmetric chromophore directly depends upon the chirality of the chromophore itself whereas that of a dissymmetrically perturbed symmetric chromophore depends on the chirality of the perturbing environment.

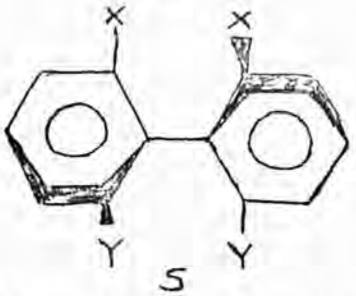
However, K. Mislow (Introduction to Stereochemistry, p. 66, Benjamin Inc., New York 1965) points out that this classification of optically active chromophores is purely a matter of convenience since, theoretically either outlook leads to the same result. These viewpoints refer to limiting situations separated by a continuum of possibilities.

(ii) Absolute Configuration of twisted biphenyls

Configuration refers to the relative position or order of arrangement of atoms in space which characterises a particular stereoisomer. Absolute configuration refers to the position or order of arrangement of the ligand atoms in space in relation to a commonly agreed upon macroscopic standard of chirality e.g. a right-handed helix. Absolute configurations are specified as R (Rectus = right) and S (Sinister = left), designation proposed by R.S. Cahn, C.K. Ingold and V. Prelog (Experientia, 1958, 12, 81). For skewed biphenyl itself, the configurations are:

R

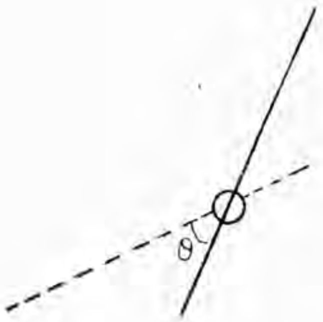
S



S

To the general sequence rule, for assigning configurations to biphenyls, there has to be added the particular rule for biphenyls; "near groups precede far groups". The R configuration for 1,1'-binaphthyl can therefore be drawn as:

R (cisoid)

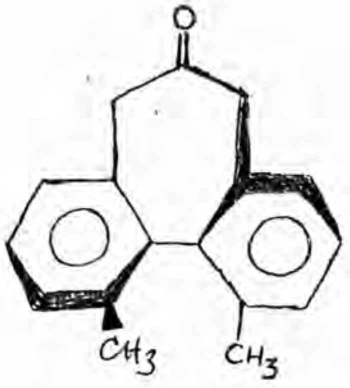


R (transoid)

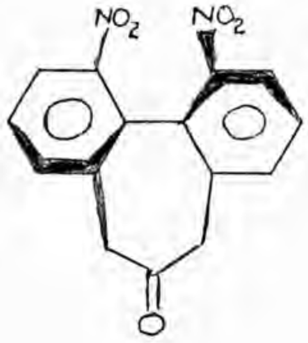
Configurational Assignment from first principles. Biphenyls

Configurational intercorrelations of some inherently dissymmetric chromophores have been determined by chemical correlation with an established standard and by thermal analysis. First it was necessary to establish the configuration of at least one biphenyl with certainty.

K. Mislow and P. Newman (J. Amer. Chem. Soc., 1957, 79, 1769) and K. Mislow (Annals of the New York Academy of Sciences, 1962, 93, 457) report a general direct chemical method for correlating the configuration of a biphenyl with that of a centrally asymmetric compound and hence for the establishment of absolute configuration in the biphenyl series. It was shown that the partial asymmetric Meerwein-Ponndorf-Verley reductions of (±)-I and of the related dimethyl ketone (±)-II with (S)(+)-2-octanol in the presence of $Al(t\text{-}BuO)_3$ leave unreduced I and II enriched in the (+)- and (-)- enantiomer, respectively.



(S)(-)-II

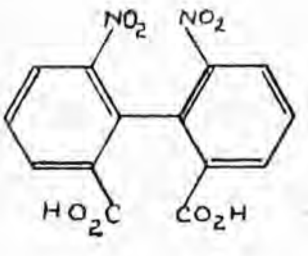


(S)(+)-I

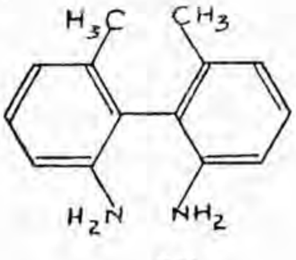
On inspecting models of (S)-I and (S)-II, they observed that hydrogen transfer to the carbonyl carbon via a Meerwein-Ponndorf-Verley type of transition state (W. von E. Doering and R.W. Young, J. Amer. Chem. Soc., 1950, 72, 631) on either face of the carbonyl group will be rendered energetically unfavourable owing to the necessity of accommodating the bulky butyl group on the side of the jutting phenyl, whereas for the R-isomers, only the much smaller nitro and methyl groups need thus be crowded. Accordingly, the S-configuration was assigned to (-)-II and (+)-I.

Configurational assignment by correlation: Biphenyls.

The absolute configuration of 6,6'-dinitro-2,2'-diphenic acid, III and 6,6'-dimethyl-2,2'-diphenyldiamine, IV, have been established by correlation with those of the known compounds (K. Mislow, P. Rutkin and A.K. Lazarus, ibid, 1957, 79, 2974)

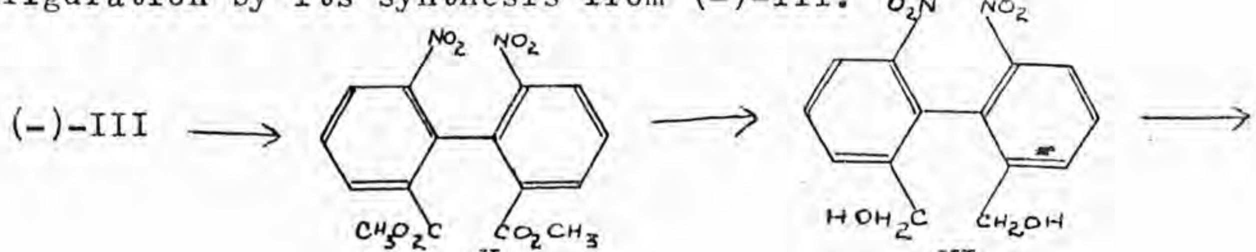


III

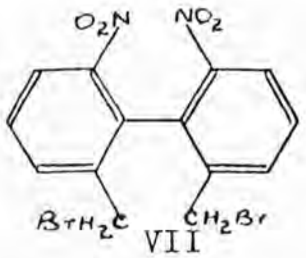


IV

(-)-III was converted into (+)-I. Since (+)-I has been shown to have the S-configuration, (-)-III was also taken as having the S-configuration. (-)-IV was shown to have the S-configuration by its synthesis from (-)-III.



V VI



VII $\longrightarrow$ (-)-IV

M. Siegel and K. Mislow (*J. Amer. Chem. Soc.*, 1957, *80*, 473) have used the method of thermal analysis (a method introduced by J. Timmermans *Rec. trav. chim.*, 1929, *48*,) in the configurational intercorrelation of optically active biphenyls. These workers used S(-)-6,6'-dinitro-2,2'-diphenic as the absolute standard in the configurational intercorrelation of 6,6'-dichloro- and 6,6'-dimethyl-2,2'-diphenic acids. These compounds are optically stable and similarly constituted No peculiarities were observed in the thermal analysis of mixtures of these three racemates with the corresponding optically active forms. The phase diagrams exhibited simple eutectics, with evidence of partial solid solution formation and no evidence of partial racemate formation; the only compound formed between enantiomeric species is the 1:1 racemate

The phase diagrams of (+)-6,6'-dimethyl-2,2'-diphenic acids *vs* (+)- and (-)-6,6'-dichloro-2,2'-diphenic acids, (+)-6,6'-dimethyl-2,2'-diphenic- acid *vs* (+)- and (-)-6,6')-dinitro-2,2'-diphenic acid and (+)-6,6'-dichloro-2,2'-diphenic acid *vs* (-)- and (+)- 6,6'-dinitro-2,2'-diphenic acid showed that the quasi-enantiomeric pair forms a congruent and pronounced 1:1 compound (quasi-racemate) while the other, configurationally related pair, exhibits continuous solid solution formation. From these results, the above workers concluded that (+)-6,6'-

dimethyl-, (-)-6,6'-dichloro- and (-)-6,6'-dinitro-2,2'-diphenic acids have the same configuration. Accordingly (+)-6,6'-dimethyl- and (-)-6,6'-dichloro-2,2'-diphenic acids have the S-configuration,

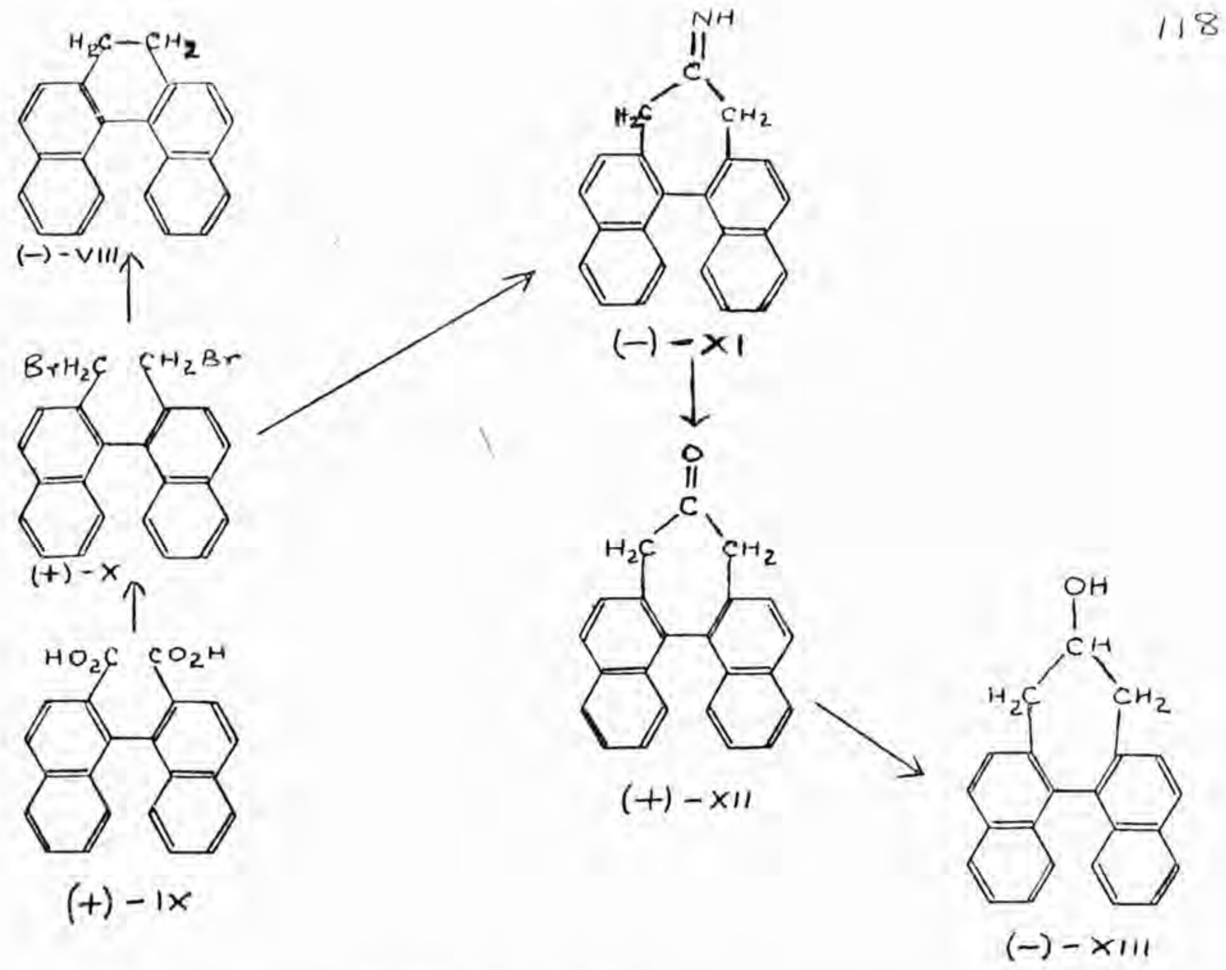
The method of thermal analysis was also successfully applied to the series of 2,2'-~~bis(hydroxymethyl)~~-biphenyls.

The results obtained from thermal analysis were confirmed by the method of chemical correlations (F.A. McGinn, A.K.Lazarus, M.Siegel, J.E.Ricci and K. Mislow, *J. Amer. Chem. Soc.*, 1957, *80*, 476). This was achieved by transformation of 6,6'-dinitro-2,2'-diphenic acid into 6,6'-dimethyl-2,2'-biphenyldiamine and conversion of the latter into 6,6'-dichloro- and 6,6'-dicyano-2,2'-dimethylbiphenyl which were also obtained from 6,6'-dichloro- and 6,6'-dimethyl-2,2'-diphenic acid respectively. The absolute configuration of the relay compound , 6,6'-dimethyl-2,2'-biphenyldiamine, had already been established (K. Mislow, P. Rutkin and A.K.Lazarus, *loc. cit.*)

Configurational assignment from first principles to 1,1'-binaphthyls: chemical correlations.

Determination of the absolute configuration by asymmetric Meerwein- Ponndorf- Verley reduction was also applied to restricted 1,1'-binaphthyls (K. Mislow and P.A.Grasemann, *ibid.*, 1958, *80*, 6036)

In a sequence of transformations, starting with (+)-IX, there was obtained, in order, (+)-X, (-)-XI, (+)-XII and (-)-XIII. (+)-IX also gave (-)-VIII.



All these have the R- configuration.

The racemic bridged binaphthyl ketone XII was reduced by (S)(+)-2-octanol in the presence of Al $(t\text{-BuO})_3$ and the alcohol (-)-XIII was produced and (-)-XII left. These two compounds are therefore of opposite configurations.

Following the arguments previously used (P. Newman, P. Rutkin and K. Mislow, <u>loc</u>. <u>cit</u>.) the authors assigned the S-configuration to (-)-XII, the unreacted ketone, and the R-configuration to (-)-XIII, the produced alcohol; (+)-IX, the synthetic precursor of (-)-XIII as well as to the structurally symmetrical derivatives of (+)-IX, including (-)- (-)VIII.

These results, as well as those described earlier (P. Newman, P. Rutkin and K. Mislow, <u>loc</u>. <u>cit</u>.) furnished an experimental test for the explicit assumption that the nature of the blocking substituent in the biaryl has a negligible effect on the direction and stereospecificity of the asymmetric reduction, and that the correlation method is therefore a generally applicable one,

It was expected that the method of thermal analysis ~~method~~ could be used in the assignment of absolute configuration to the series of 2,2'-substituted 1,1'-binaphthyls. The phase behaviour of mixtures of (-)-2,2'-bis-(hydroxymethyl)-1,1'-binaphthyl with (+)- and (-)-6,6'-dimethyl-2,2'-bis-(hydroxymethyl)-biphenyl was investigated and it was found that the phase diagrams are indistinguishable, simple eutectics being formed in both cases. Hence the difference in structures and geometry of these compounds apparently limit the applicability of this method, which unfortunately proves not to be of any use in the 1,1'-binaphthyls.

Optical Displacement Principle:

D.D.Fitts, M. Seigel and K.Mislow (J. Amer. Chem. Soc., 1958, 80, 483) proposed a general optical displacement rule which allows absolute configurational assignments in the biaryl series on the basis of characteristic rotation shifts accompanying 2,2'-bridge formation. They investigated the possibility that like shifts in rotation in related derivatives of biaryls having the same configuration might constitute the basis for a correlation akin to Freudenberg's Displacement Rule in the centrally asymmetric series of optically active compounds (K. Freudenberg in "Stereochemie"

Franz Deuticke, Leipzig, 1933, 699).

By using the polarizability theory of optical activity, the authors assigned the S-configuration to (+)-9,10-dihydro-3,4,5,6-dibenzophenanthrene, VIII. Synthetic precursor (-)-IX therefore also had the S-configuration. This was confirmed by the method of chemical correlation (already described, K.Mislow and P.A.Grasemann, loc. cit.,).

The authors examined the rotations of some 2,2'-bridged biaryls of known configuration. All bridged compounds prepared from S(-)-6,6'-dinitro- and S(-)-6,6'-dichloro-2,2'-diphenic acids are more strongly dextrorotatory than the parent acids. The bridged compounds prepared from S(+)-6,6'-dimethyl-2,2'-diphenic acid are considerably more dextrorotatory than the parent acid and most of its unbridged derivatives. They anticipated that the change from an open to a bridged system, involving as it must a dramatic change in Θ (the interplanar angle) might be reflected in a characteristic manner in the sign and magnitude of the optical rotation. They therefore proposed the general Optical Displacement Rule that "a symmetrically substituted hindered biaryl has the S-(resp. R-) configuration if, in going from an open to a bridged system, the optical activity suffers a marked shift in the positive (resp. negative) direction". The rule was also applied to restricted 2,2'-biaryldiamines, and it was found that compounds the R-configuration gave bridged biaryls that are more levorotatory.

Use of the Cotton Effect to relate unknown to known configurations

K. Mislow (Angew. Chem., 1958, 70, 683) recognised that scrutiny of optical rotatory dispersions would be likely to furnish correlative information of greater general significance. The usefulness of O.R.D. in this connection had been established by C. Djerassi (Optical Rotatory Dispersion. McGraw-Hill Book Co., Inc., New York, N.Y. 1960) who through a series of brilliant researches, had been able to demonstrate that the sign and shape of an O.R.D. curve, particularly of a Cotton effect, significantly reflect the stereochemistry, including absolute configuration, of the immediate environment of the optically active chromophore. These investigations were mainly concerned with ketones since optically active ketones of known absolute configuration are abundantly available from natural sources, and the region of the carbonyl $\underline{n}$ — π^* transitions (near 290mμ) is of low extinction and thus spectropolarimetrically penetrable. This work led to the formulation, from symmetry principles, of the Octant rule which relates the sign and amplitude of the Cotton effect exhibited by saturated ketones to the disposition of atoms in space about the carbonyl groups of the ketones (i.e. the relationship between the absolute configuration or conformation of the perturbing environment and the sign of the carbonyl n — π^* Cotton effect). The rule states that "the sign of the contribution which a given atom at point $P(x, y, z)$ makes to anomalous rotatory dispersion will vary as the simple product, x. y. z of its coordinates (W. Moffitt, R.B. Woodward, A. Moscowitz, W. Klyne and C. Djerassi, J. Amer. Chem. Soc., 1958, 83, 4013).

K. Mislow, M.A.W. Glass, R.E. O'Brien, P. Rutkin, D.H. Steinberg, J. Weiss and C. Djerassi (J. Amer. Chem. Soc., 1962, 84, 1955) initiated an investigation of the O.R.D. of biphenyls. Spectral (ultraviolet and O.R.D.) information was gathered for a series of suitably substituted biaryls whose absolute configurational assignments had been done by other methods or could be inferred from those of starting materials.

The O.R.D. curves are found to be dependent on conformation and configuration. The change from open to 2,2'-bridged seven-membered ring biaryls give rise to characteristic changes in O.R.D. which are interpreted as reflecting changes in conformation. In the 2,2'-dinitrobiphenyls bridging results in a reversal of the sign of the Cotton effect which, together with the red-shift of the B-band (long-wave band), is taken to signal a change in the interplanar angle.

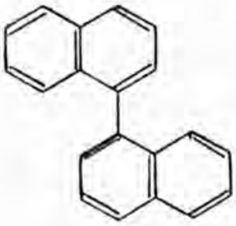
With 2,2'-dimethyl- and 2,2'-dichlorobiphenyls, bridging gives rise to appearance of high-amplitude Cotton effects centred at the biphenyl conjugation band. It was also demonstrated that the position of this Cotton effect changes with change of θ.

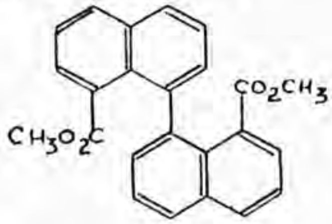
In the 1,1'-binaphthyls, the change from (a) unbridged to (b) seven-membered ring bridged to (c) six-membered ring bridged 1,1'-binaphthyl is accompanied by an enhancement in amplitude of the O.R.D.

For each set of these compounds, two or three Cotton effects were observed, corresponding to various groups of bands in the ultraviolet spectrum. The Cotton effects at shorter wavelengths had higher amplitudes. It was found that the absolute configuration uniquely determines the sign of each Cotton effect. The sign of several Cotton effects in each O.R.D. curve were usually not the same, so that the transition (or band group) associated with the particular Cotton effect had to be specified for the purpose of configurational assignment. Accordingly, the authors summarised the results as follows: For 2,2'-bridged biaryls having the R-configuration, the sign of the long-wave Cotton effect is negative for 6,6'-dinitro-derivatives, positive for 6,6'-dimethyl- and 6,6'-dichloro- derivatives and 1,1'-binaphthyls. The long wavelength Cotton effect of the 2,2'-bridged biaryls is generally accompanied by a Cotton effect at shorter wavelength, of opposite sign and greater amplitude, which often dominates the sign of rotation in the visible.

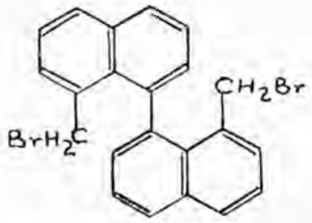
Present work and results:

This work was done in order to assign absolute configurations to the following 1,1'-binaphthyls and to see the effect the substituents and their positions in the binaphthyl system, have on the absolute configurations of the 1,1'-binaphthyl system.

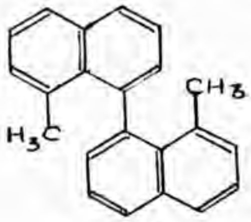

XIV



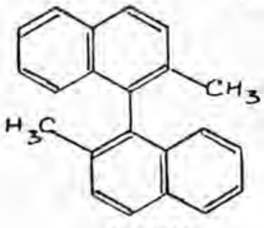
XV



XVI



XVII



XVIII

OR.D. and C.D. curves were obtained using the Polarmatic 62 Spectropolarimeter and the Jouan Dichrograph respectively. Methanol was used as the solvent in both cases.

The results are shown in Figures I - X.

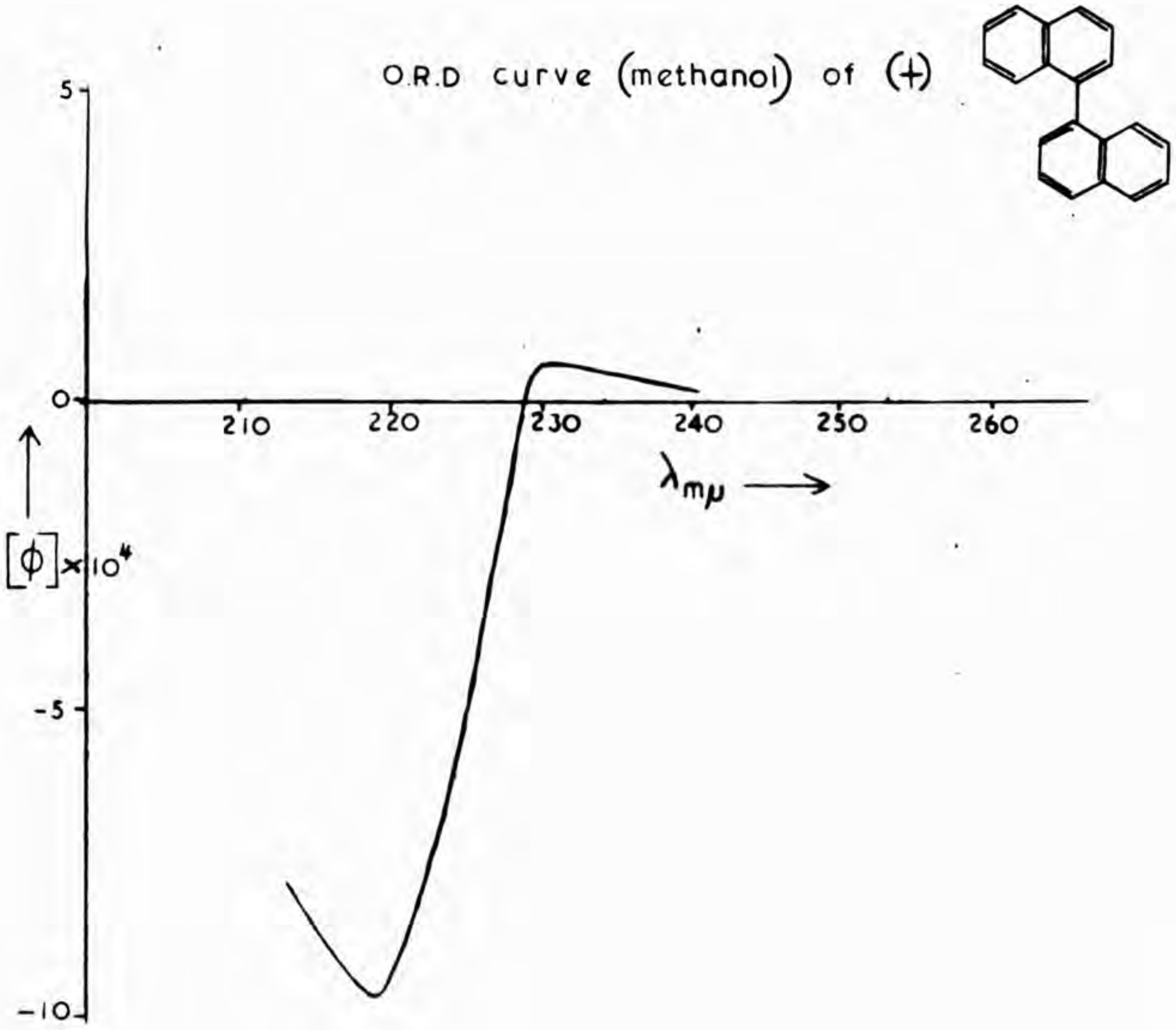

O.R.D curve (methanol) of (+)
5
0
-5
-10
210
220
230
240
250
260
$\lambda_{m\mu}$ →
↑ $[\phi] \times 10^4$

FIG. I

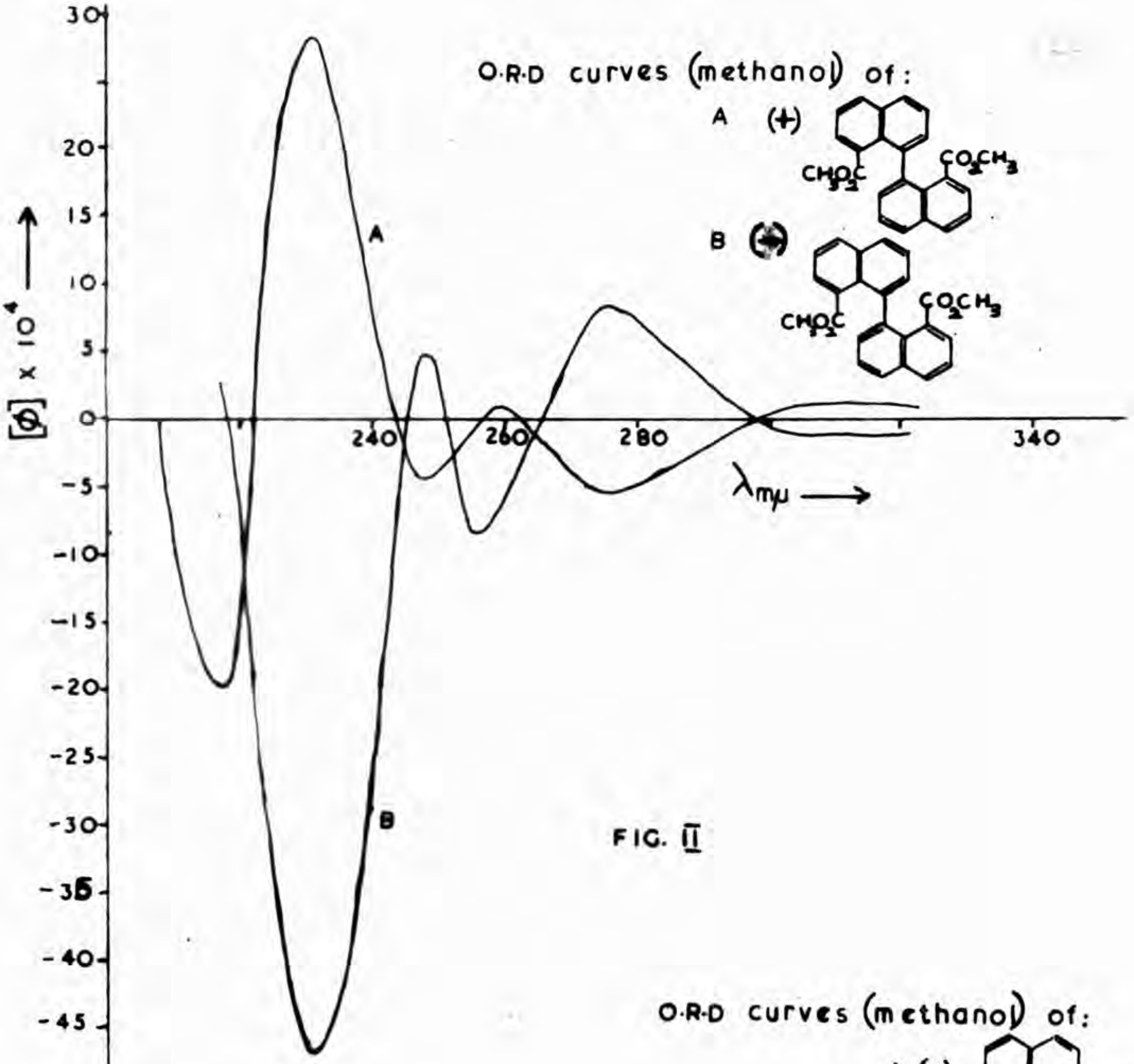


FIG. II

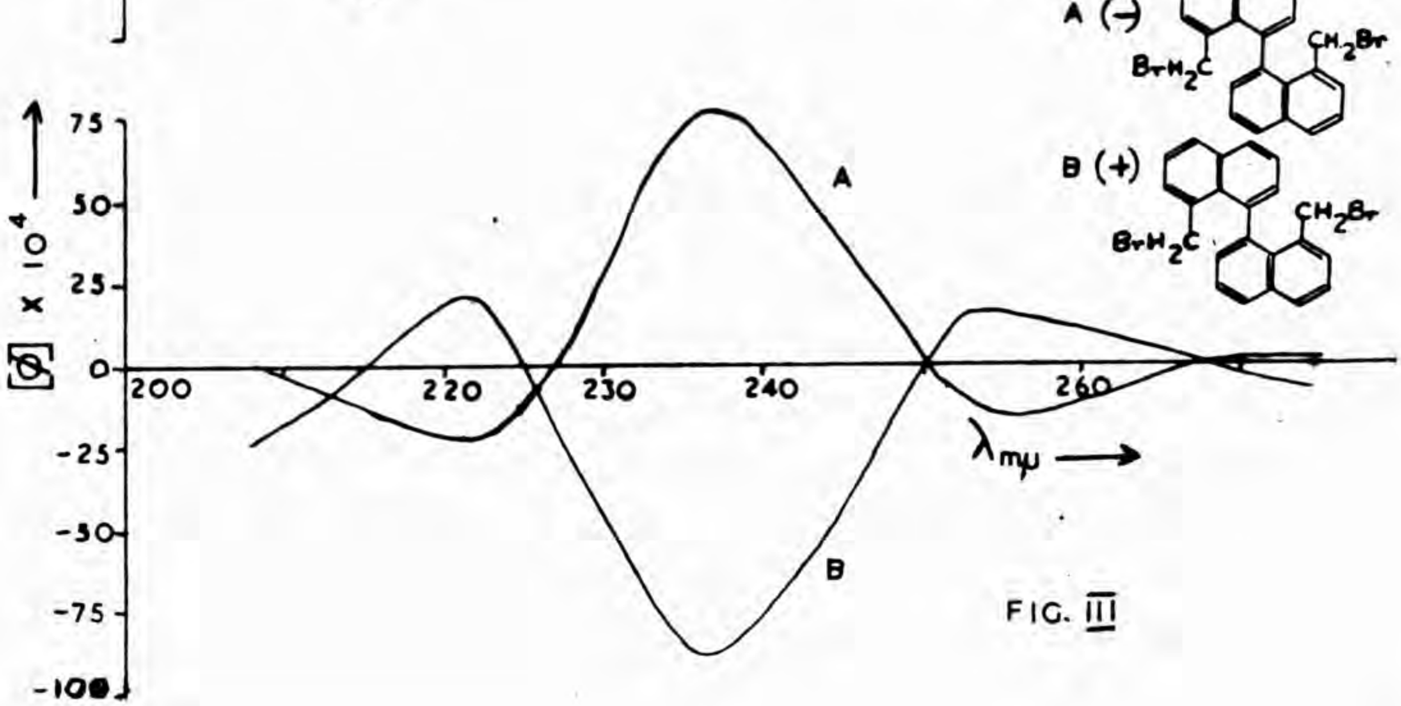


FIG. III

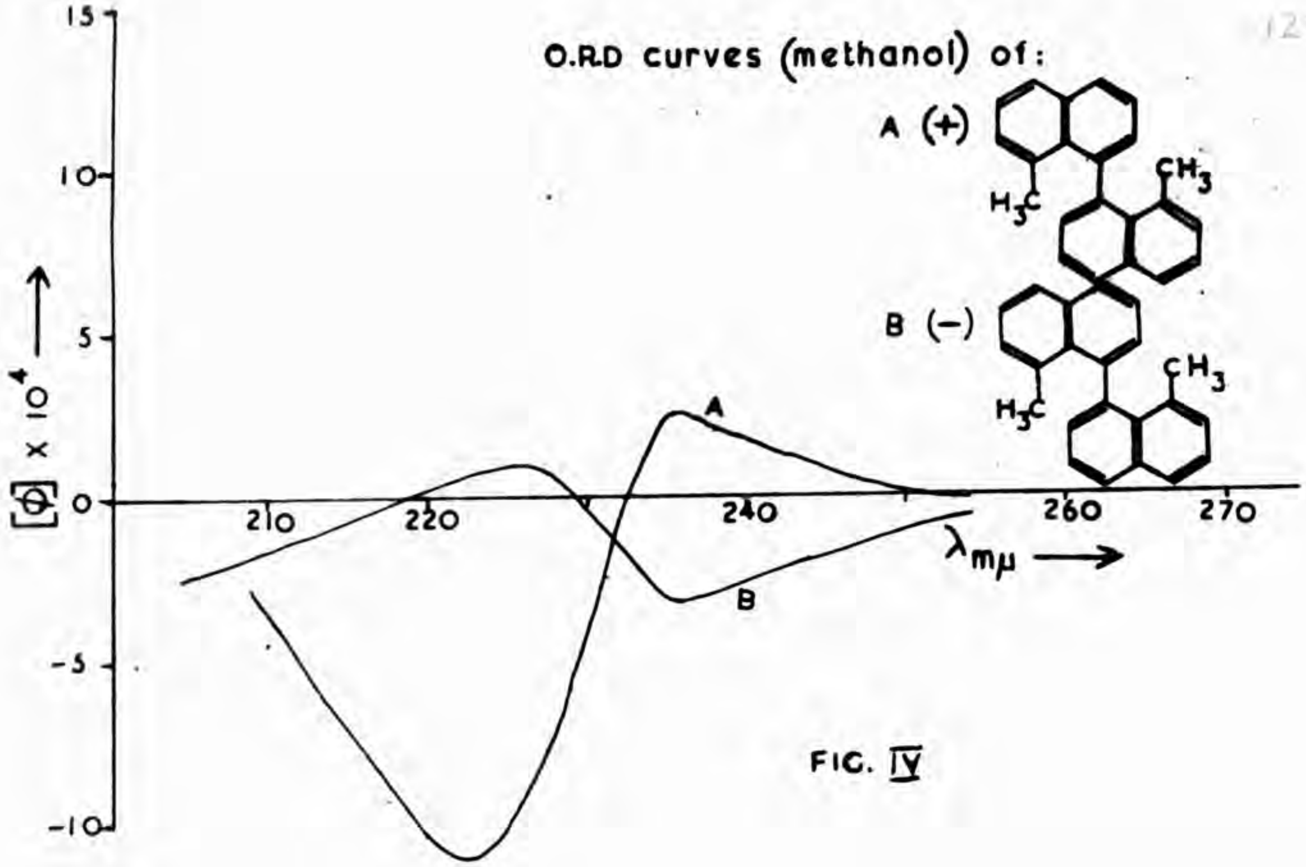

O.R.D curves (methanol) of:
A (+)
B (−)
H₃C
CH₃
[Φ] x 10⁴ →
15
10
5
0
-5
-10
210
220
240
260
270
λmμ →
A
B

FIG. IV

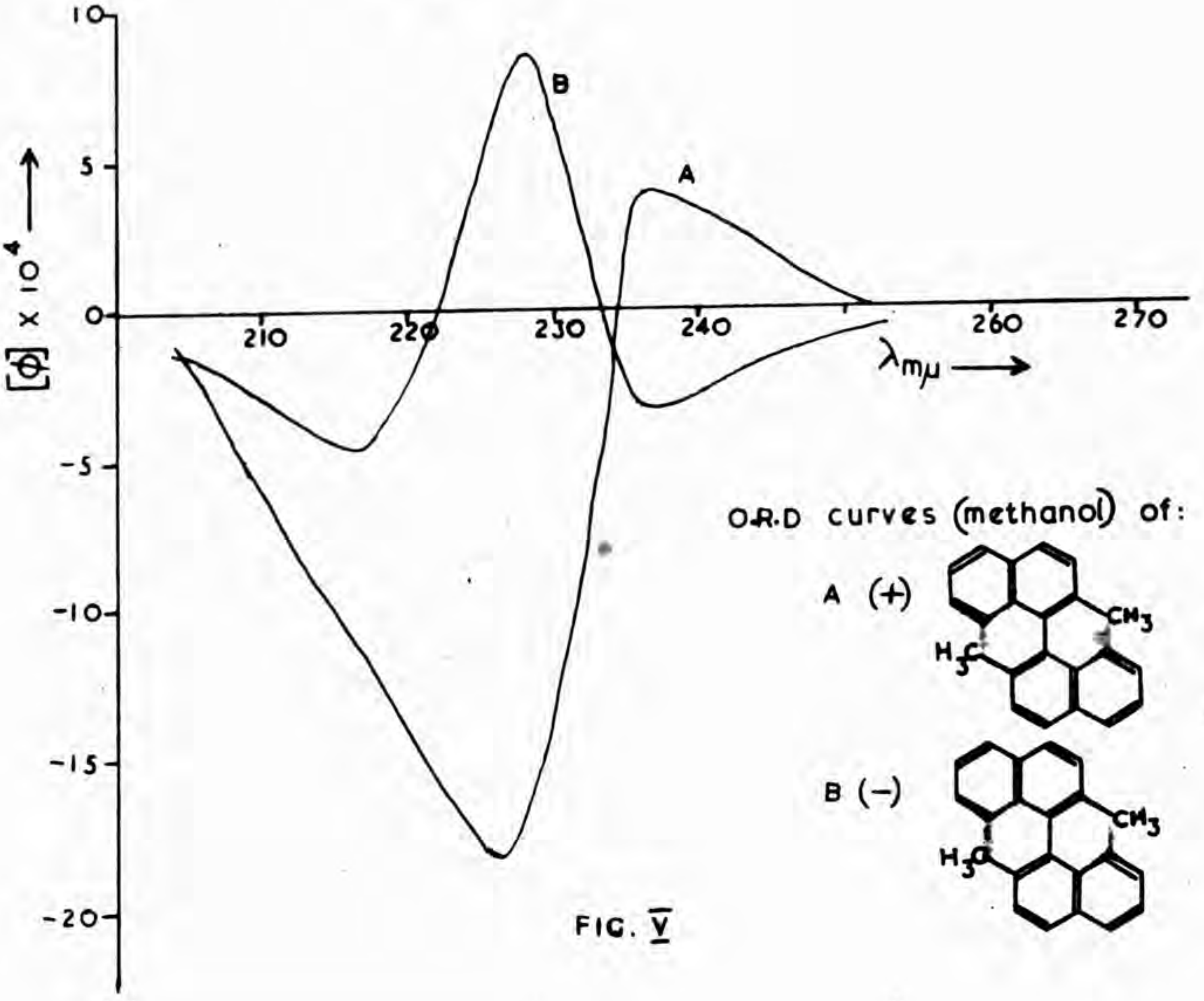

O.R.D curves (methanol) of:
A (+)
B (−)
H₃C
CH₃
[Φ] x 10⁴ →
10
5
0
-5
-10
-15
-20
210
220
230
240
260
270
λmμ →
A
B

FIG. V

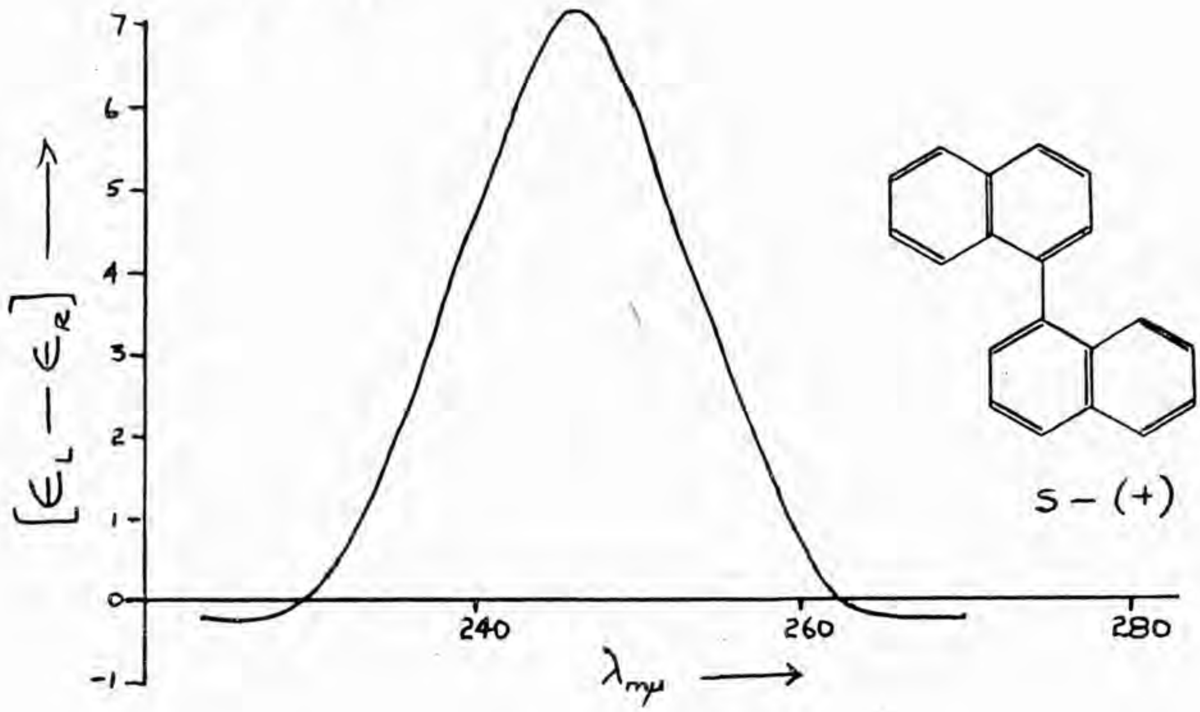
Optical Rotatory Dispersion results

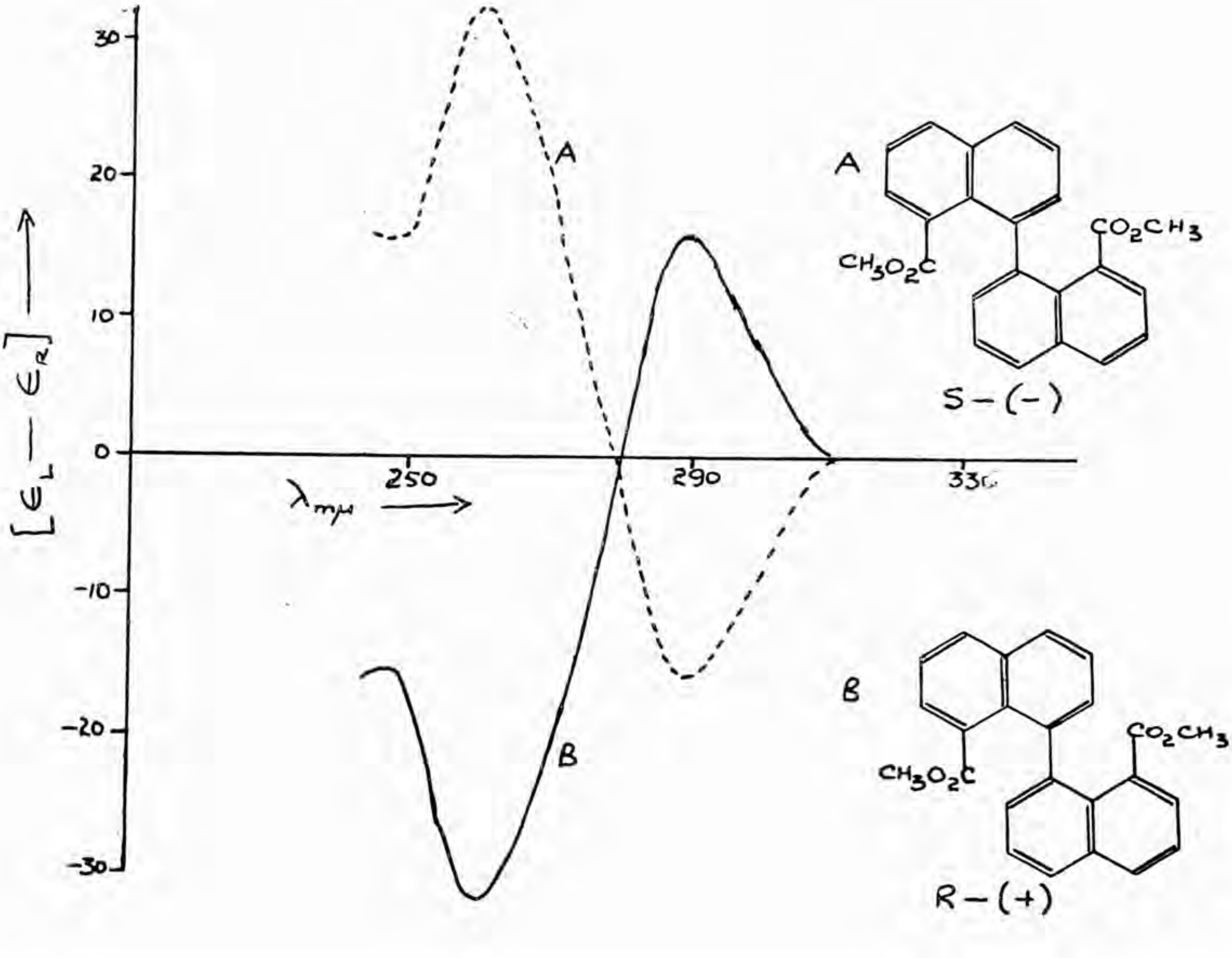
TABLE I

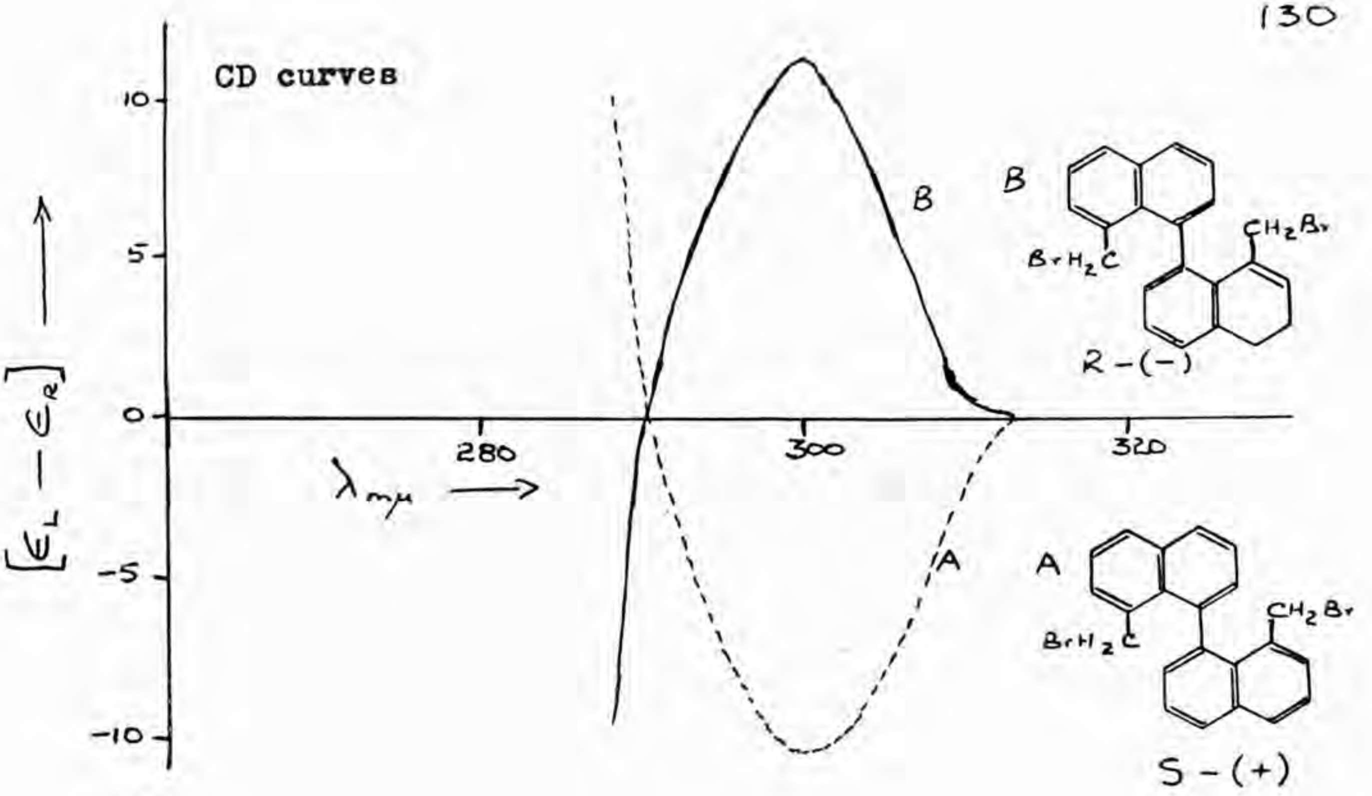
Compound (with assigned configuration)	Molecular rotations
S-(+)-XVI	$[\phi]_{230}$ + 12,700; $[\phi]_{219}$ - 95,000.
S-(-)-XV	$[\phi]_{275}$ - 56,200; $[\phi]_{256}$ - 8,480; $[\phi]_{248}$ + 48,750
	$[\phi]_{231}$ -469,000; $[\phi]_{217}$ + 30,700
R-(+)-XV	$[\phi]_{275}$ - 56,200; $[\phi]_{258}$ + 7,400; $[\phi]_{248}$ - 45,900
	$[\phi]_{231}$ +281,000; $[\phi]_{217}$ -197,000
S-(+)-XVI	$[\phi]_{253}$ + 15,900; $[\phi]_{236}$ - 89,500; $[\phi]_{221}$ + 22,100
R-(-)-XVI	$[\phi]_{255}$ - 15,700; $[\phi]_{236}$ + 78,500; $[\phi]_{221}$ - 23,600
S-(+)-XVII	$[\phi]_{235}$ + 27,200; $[\phi]_{222}$ 109,000
R-(-)-XVII	$[\phi]_{286}$ 0 $[\phi]_{235}$ - 26,800; $[\phi]_{226}$ + 10,200
S-(+)-XVIII	$[\phi]_{236}$ + 41,500; $[\phi]_{226}$ -184,000;
R-(-)-XVIII	$[\phi]_{236}$ - 33,000; $[\phi]_{228}$ + 87,000

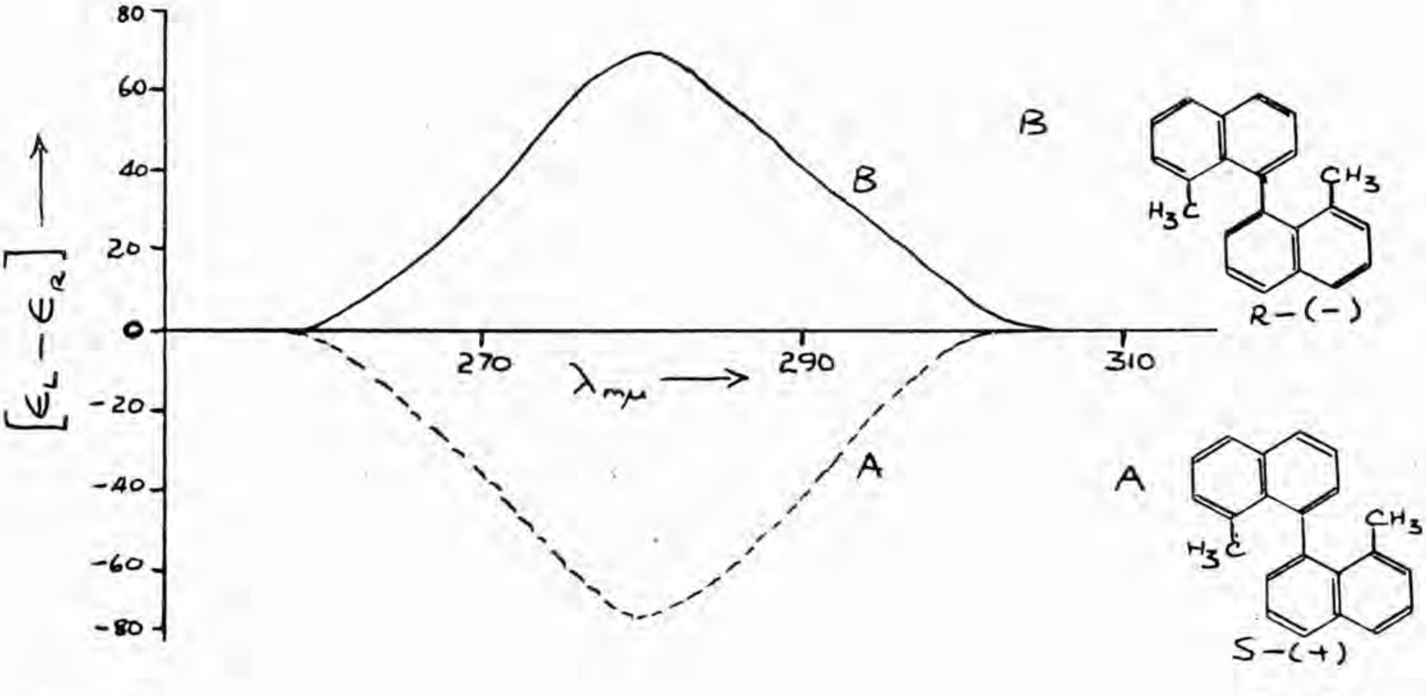
These compounds were prepared from optically active 1,1'-binaphthyl-8,8'-dicarboxylic acid, and they are optically labile. They are, therefore, not optically pure. Hence the molecular rotations of two optical isomers are not equivalent.

CD curves


7
6
5
4
3
2
1
0
-1
$[\epsilon_L - \epsilon_R] \longrightarrow$
240
260
280
$\lambda_{m\mu} \longrightarrow$
S – (+)


30
20
10
0
-10
-20
-30
$[\epsilon_L - \epsilon_R] \longrightarrow$
250
290
330
$\lambda_{m\mu} \longrightarrow$
A
B
A
CO_2CH_3
CH_3O_2C
S – (–)
B
CO_2CH_3
CH_3O_2C
R – (+)


CD curves
[ε_L − ε_R] →
10
5
0
-5
-10
280
300
320
λ_mμ →
B
A
B
R-(−)
CH₂Br
BrH₂C
A
S-(+)
CH₂Br
BrH₂C


[ε_L − ε_R] →
80
60
40
20
0
-20
-40
-60
-80
270
290
310
λ_mμ →
B
A
B
R-(−)
CH₃
H₃C
A
S-(+)
CH₃
H₃C

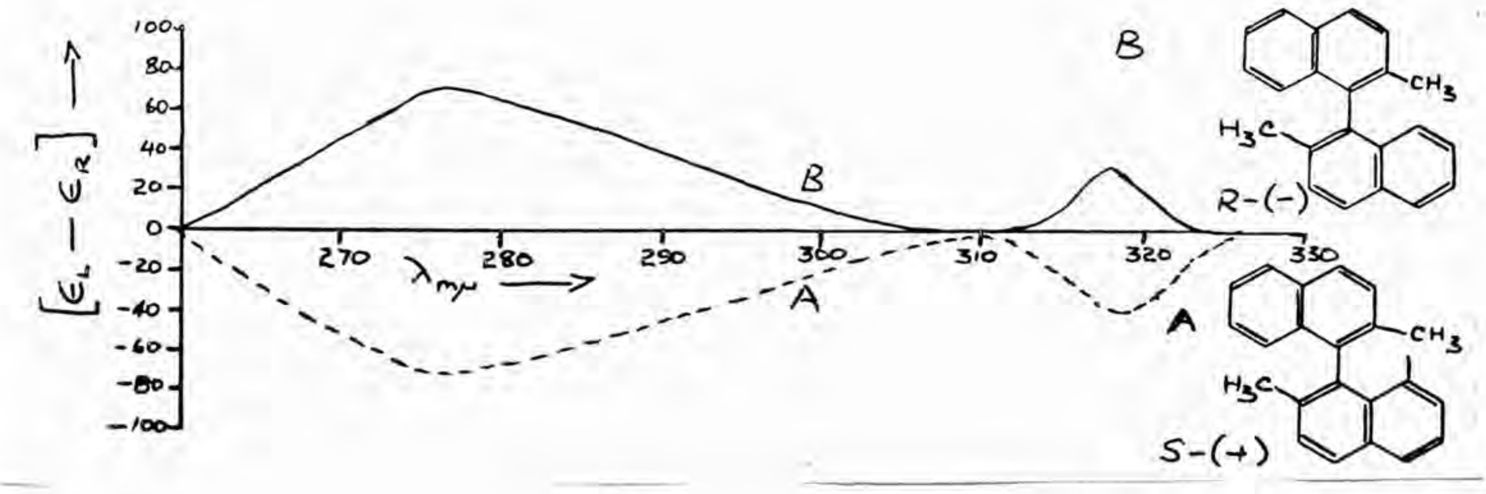

[ε_L − ε_R] →
100
80
60
40
20
0
-20
-40
-60
-80
-100
270
280
290
300
310
320
330
λ_mμ →
B
A
B
R-(−)
CH₃
H₃C
A
S-(+)
CH₃
H₃C

TABLE II

Circular Dichroism results

Compound	Molecular Ellipticity
*	
S-(+)-XIV	$[\epsilon_L - \epsilon_R]_{254} + 7.2$
S-(-)-XV	$[\epsilon_L - \epsilon_R]_{290} - 16.2 [\epsilon_L - \epsilon_R]_{260} + 32.4$
R-(+)-XV	$[\epsilon_L - \epsilon_R]_{290} + 16.0; [\epsilon_L - \epsilon_R]_{260} - 32.0$
S-(+)-XVI	$[\epsilon_L - \epsilon_R]_{300} - 11.0$
R-(-)-XVI	$[\epsilon_L - \epsilon_R]_{300} + 12.5$
S-(+)-XVII	$[\epsilon_L - \epsilon_R]_{280} - 71.5$
R-(-)-XVII	$[\epsilon_L - \epsilon_R]_{280} + 70.0$
S-(+)-XVIII	$[\epsilon_L - \epsilon_R]_{318} - 40.1; [\epsilon_L - \epsilon_R]_{276} - 70.5$
R-(-)-XVIII	$[\epsilon_L - \epsilon_R]_{318} + 39.3; [\epsilon_L - \epsilon_R]_{276} + 72.1$

* Configurations as assigned from ORD curves

Discussion; Assignments related to previous work.

The complex absorption spectra of unbridged 1,1'-binaphthyls are dominated by maxima at 285 and about 230mμ (as can be observed from the ultraviolet spectral work already discussed and results obtained by V.L.Frampton, J.D.Edwards Jr., and H.R.Henze, J. Amer. Chem. Soc., 1948, 70, 2284). Correspondingly, K. Mislow, M.A.W.Glass, R.E. O'Brian P. Rutkin, D.H.Steinberg, J. Weiss and C. Djerassi (loc. cit.) observed that the complex O.R.D. curves of these compounds are dominated by Cotton effects centred at 285 and below 250mμ respectively. In all cases a positive 285mμ Cotton effect was taken to correspond to the R-configuration.

In contrast the O.R.D. curves of 1,1'-binaphthyls bridged by a three atom chain in the 2,2'-positions have absorption spectra dominated by maxima at 220, 232 and 306mμ. There is a red shift in the O.R.D. curves which now have two Cotton effects of opposite sign, centered near 300 and below 240mμ. A positive 300mμ Cotton effect was taken to correspond to the R-configuration.

From the present work, it is observed that only 1,1'-binaphthyls with substituents that are chromophoric (e.g. CO_2CH_3) give multiple Cotton effect curves. Thus dimethyl 1,1'-binaphthyl-8,8'-dicarboxylate has two peaks at 275 and 248mμ and two troughs at 256 and 231mμ. With substituents that are not chromophoric (e.g. $-CH_3$), the curves have a single Cotton effect below 250mμ. Hence the Cotton effects below 250mμ have to be taken into consideration in the configurational correlation of the 1,1'-binaphthyls discussed herein.

K. Mislow and P.A.Graseman (<u>loc. cit.</u>) has assigned the S-configuration to (+)-9,10-dihydro-3,4-5,6-dibenzophenanthrene and its parent compound (-)-1,1'-binaphthyl-2,2'-dicarboxylic acid. This was also confirmed by application of the Optical Displacement principle (D.M.Fitts, M.Siegel and K.Mislow, <u>loc. cit.</u>) The S-configuration was also assigned to (+)-2,2'-dimethyl-1,1'-binaphthyl derived from S-(-)-1,1'-binaphthyl-2,2'-dicarboxylic acid.

The configuration assignment of the 1,1'-binaphthyls discussed herein is based on those of (+)-2,2'-dimethyl-1,1'-binaphthyl (K. Mislow and P.A. Graseman, <u>loc. cit.</u>) and 1,1'-binaphthyl (author's work) itself. The O.R.D. curve of (+)-1,1'-binaphthyl has one Cotton effect with maximum and minimum at 230 and 219mμ respectively.

With the (+)-dimethyl 1,1'-binaphthyls it is found that the O.R.D. curves are simple and resemble that of (+)-1,1'-binaphthyl. This indicates that the $-CH_3$ groups do not affect absolute configuration of the 1,1'-binaphthyl system. It is observed that the O.R.D. curve of (+)-2,2'-dimethyl-1,1'-binaphthyl resembles that of 1,1'-binaphthyl, and (+)-8,8'-dimethyl-1,1'-binaphthyl indicating that they all have the same S-configuration, and that the positions of the methyl groups either in the 2,2'- or 8,8'- positions in the 1,1'-binaphthyl system have no effect on the total absolute configuration of the whole system. It is also seen that the aromatic chromophore in these compounds has a positive Cotton effect with a peak about 236mμ and trough at 225mμ.

(+)-8,8'-Bisbromomethyl-1,1'-binaphthyl, from which S-(+)-8,8'-dimethyl-1,1'-binaphthyl was prepared, should also have the S-configuration. The aromatic chromophore has a positive Cotton effect with a peak at 255mμ and trough at 239mμ and the long-wave maximum at 253mμ. This red shift allows the appearence of the short-wave Cotton effect at 221mμ.

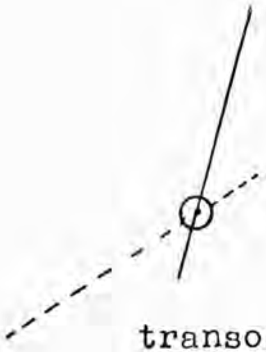
(-)-Dimethyl-1,1'-binaphthyl-8,8'-dicarboxylate from which the above compounds were prepared should also have the S-configuration. Its O.R.D. curve shows two distinct Cotton effects (with maxima at 275 and 248mμ, and minima at 256 and 231mμ, that at 231 and 248mμ being due to the aromatic chromophore. The second long-wave Cotton effect is simple and can be due to the $-COOCH_3$ interacting with the asymmetric chromophore (aromatic). The fact that it is a single Cotton effect suggests that the $-COOCH_3$ groups are in equivalent environments, or that the Cotton effects overlap in such a way that they are indistinguishable.

(+)-Dimethyl-1,1'-binaphthyl-8,8'-dicarboxylate and its synthetic precursor, the (+)-8,8'-diacid and the compounds prepared from it, (-)-2,2'-dimethyl-1,1'-binaphthyl prepared from R-(+)-1,1'-binaphthyl-2,2'-dicarboxylic acid therefore have the R-configuration. The aromatic chromophore has a negative Cotton effect in the same region as that of the above compounds. However, molecular rotations of these compounds do not correspond with those of their optical isomers already discussed (and shown on table I) and this is due to differences in optical purity.

For each configuration, R and S, there are two possible conformations i.e. <u>cis</u> and <u>trans</u>, and there may be an equilibrium between them; or one of the two conformations could be the preferred one.

R-configuration:

cisoid



transoid

S-configuration:

cisoid

transoid

However, a conclusion as to whether the cis or trans conformation is the preferred one, cannot be drawn from the~~re~~se O.R.D. and C.D. results.

Absorption spectra, circular dichroism and optical rotatory dispersion curves can be used simultaneously for configurational assignments, since C.D. and O.R.D. phenomena are complementary manifestations of the Cotton effect associated with a particular electronic transition. However, on certain occasions, circular dichroism measurements have distinct advantage over rotatory dispersion, whose background rotation may hide weak Cotton effects. Circular dichroism can be used in identifying relatively weak optically active transitions, especially in the longer wavelength region, where their presence may be obscured in both ultraviolet absorption and O.R.D. spectra by broad, overlapping neighbouring bands.

The O.R.D. spectra of 1,1'-binaphthyls discussed above do not show the long wavelength Cotton effects. These are observed in the C.D. curves. However, C.D. measurements could not be done in the shorter wavelength region (below 240mμ) due to an instrumental limitation. Hence the long-wave Cotton effects had to be considered in the configurational correlations.

From table II, it is observed that optically active 2,2'-dimethyl-1,1'-binaphthyl has two C.D. Cotton effects, one at 318 and the other at 276mμ. The Cotton effect at 318mμ corresponds to the typical naphthalene absorption band (which appears in the U.V. spectrum of the 2,2'-dimethyl-1,1'-binaphthyl at about 310mμ). The Cotton effect at 276mμ is the same as those of the other compounds, XVII, XVI, and XV centred at 280, 300 and 290mμ respectively. Compounds with the S-configuration have <u>negative</u> circular dichroism Cotton effects at these wavelengths; the other optical isomers, with <u>positive</u> CD Cotton effect at these wavelengths have the R-configuration.

For S-(+)-1,1'-binaphthyl, the positive Cotton effect at 254mμ corresponds to the absorption minimum (centred at 260mμ) of its U.V. spectrum. If it were a Cotton effect corresponding to those at about 280mμ for XVIII, XVII, XVI and XV having the S-configuration, it should be negative. The same is true of the Cotton effect of XV centred at 260mμ.

8. INFRA-RED SPECTRA of RACEMIC and OPTICALLY ACTIVE 1,1'-BINAPHTHYL-8,8'-CARBOXYLIC ACIDS:

Introduction:

Infrared spectroscopy has been extensively used in organic chemistry for the recognition and quantitative analysis of structural units in unknown compounds.

Electromagnetic radiation of the near-infrared and infrared region (0.8 - 30mμ) is absorbed to various extents by all substances, and the energy so absorbed appears as heat. The absorption process involves excitation of the molecule to higher vibrational states and it is therefore quantised. The vibrations increase in amplitude when electromagnetic radiation (infrared) of the same frequency reaches the molecule and raises it to the next vibrational level. The infrared spectrometer measures this absorption at each frequency and so produces an infrared spectrum. The presence of numerous rotational levels for each vibrational level gives rise to the rotational fine structure observed when small molecules are examined in the vapour state. However, for the average complex organic molecule in solution or in the solid state, these rotational lines are so close together and blurred by collision and other interactions that they cannot be distinguished. The result for a single vibrational band is a smooth peak of about 5 - 30cm^{-1} half-band width.

Infrared spectra can be used to obtain fundamental data on the mechanics of simple molecules, and this makes it possible to assess to some extent the likelihood of frequency shifts occuring with changes in the local environment of a group. However, with more complex materials such studies are complicated by frequencies associated with several various structural units. In the interpretation of spectra the chemist relies largely upon the empirical data, published in Correlation charts, which need to be properly used to be of great value. An infrared spectrum can give an indication of the presence of such groups as $C=O$, $O-H$, NH_2 etc.; the position of the absorption band of a group such as $C=O$ can indicate whether it forms part of an anhydride, ketone, ester, aldehyde or lactone, if the circumstances are sufficiently ordinary.

Sampling methods are available for solids, liquids and solutions:-

Solid state:

Three methods are available for examining solids:

1) Nujol mulls: More spectra are recorded in this form than with any other form. This is because a mull is simple to prepare and mount, and the method is suitable for all solids. The substance is ground in a drop of medicinal liquid paraffin (Nujol) and the paste thus obtained is pressed between two salt plates and placed in the beam. Nujol serves to immerse the minute particles of the substance in a transparent medium of similar refractive index and so prevents the severe scattering of radiation which would otherwise occur. Nujol bands have to be marked off on the spectrum to avoid misinterpretation. If information is required in the OH region

hexachlorobutadiene can be used as the mulling substance.

2) Melt: A gumlike substance and a substance with a melting point less than 150°, can be melted between two salt plates and the resulting solid or molten film examined.

3) Halide disc: A finely ground mixture of the substance and anhydrous KCL or KBr powder is subjected to pressure for about 5 minutes in an evacuated metal die, and the resulting transparent alkali halide disc containing the dispersed substance gives an excellent spectrum free from other absorption and with little scatter.

Liquid state:

Pure liquids are examined by merely placing a drop of a liquid between two plates or inserting the liquid into a narrow thin cell.

Solution spectra:

These are not always easily obtained but they give the most precise information. Detailed comparisons between related compounds can be made but the same solvent has to be used for each compound. Useful spectral data can be obtained only in the "window regions" where solvent absorption does not exceed 95%. Solvent such as CCL_4, CS_2, $CHCl_3$ and CH_2Cl_2 can be used and the entire range 2 - 15μ can be covered, if the substance under investigation is sufficiently soluble.

Factors affecting group frequencies:

Infrared correlation charts show that a particular structural group e.g. C=O, produces an absorption band somewhere within a considerable wavelength range, and as more compounds are examined, these uncertainty ranges increase. This is considered to be due to the modification of a group vibration by the rest of the molecule.

Resonance:

The frequency of vibration along a covalent bond X - Y in a simple molecule obeys Hooke's law:

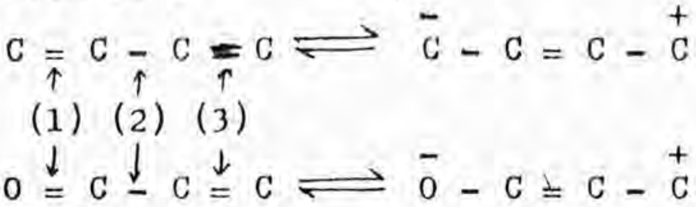
$$\nu = \frac{1}{2\pi c} \quad \left(\frac{K}{\mu}\right)$$

where ν = frequency of vibration
c = velocity of light
K = force per unit displacement of the bond (usually called the force constant) and
μ = reduced mass of the system ($\frac{1}{\mu} = \frac{1}{M_X} + \frac{1}{M_Y}$ where M_X and M_Y are the atomic weights in grams of X and Y respectively).

The frequency, ν , is proportional to the square root of the force constant; this is a factor of 2 or 3 higher for double and triple bonds respectively. Any electronic displacement due to inductive or mesomeric effects in the molecule which increases the number of electrons partaking in the bond, will increase the frequency of the bond. Reduction in the number of bonding electrons will have the opposite effect, and the band tends towards lower frequency (single bond character).

Conjugation:

Conjugation of double bonds produces resonance structures such as:-

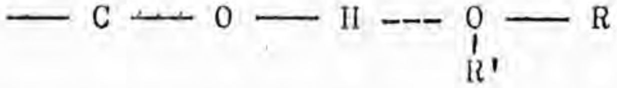


$$\begin{array}{l} C = C - C = C \rightleftharpoons \overset{-}{C} - C = C - \overset{+}{C} \\ \quad\uparrow\quad\uparrow\quad\uparrow \\ \;(1)\;(2)\;(3) \\ \quad\downarrow\quad\downarrow\quad\downarrow \\ O = C - C = C \rightleftharpoons \overset{-}{O} - C = C - \overset{+}{C} \end{array}$$

This resonance decreases the double bond character of bonds (1) and (3) and thus the stretching vibrations of these bonds will absorb at lower frequencies than they would if unconjugated. The opposite is the case for bond (2).

Hydrogen bonding:

Alcohols have a characteristic OH absorption near to 3.0μ. However, the position of this band is affected by hydrogen bonding or association, an effect which can be explained in the same manner as the resonance effect. When a hydrogen bond is formed between a hydroxyl group and a neighbouring oxygen atom the bond length of the O - H bond is increased and the bond force constant is reduced.



$$— C — O — H --- \underset{\displaystyle R'}{\underset{|}{O}} — R$$

This reduced the frequency of the hydroxyl stretching vibration, i.e. the hydroxyl stretching vibration will absorb at lower frequencies. The shift of the absorption band is of the order of about 200cm^{-1}.

For many organic chemists the most vital single attribute of infrared spectroscopy is the ability first to detect and then to distinguish the different types of carbonyl groups.

The group is polar,

$$\overset{\delta+}{>C} = \overset{\delta-}{O}$$ and may be regarded in terms of relative contributions of the hypothetical canonical structures,

$$>C = O \longleftrightarrow >C^{+} - O^{-}$$

Hence any effect which will tend to increase the contribution of the single bond form will lower the force constant of the $C = O$ bond and will result in a fall in frequency of the stretching vibration $\nu C = O$.

An acidic hydrogen e.g. that of $-OH$ can hydrogen-bond with a basic centre such as $O<$, $O = C<$, $N<$ etc.

$$\text{e.g.}\ >C = O --- H - \overset{\overset{O}{\|}}{C} - R$$

When a carboxyl group is involved, as is the case with the carboxylic acids, $\nu C = O$ falls. Such bonding can be intermolecular or intramolecular.

Strain:

If a carbonyl group is part of a ring, the carbonyl frequency increases as the size of the ring decreases. This has been observed with cyclic ketones, lactones and lactams.

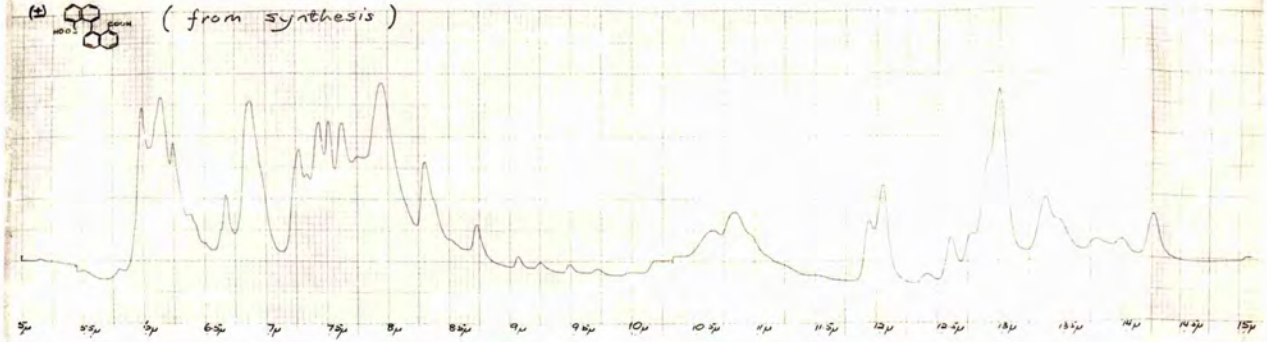
Spectra of 1,1'-Binaphthyl-8,8'-dicarboxylic Acids.

Preparation of Specimens:

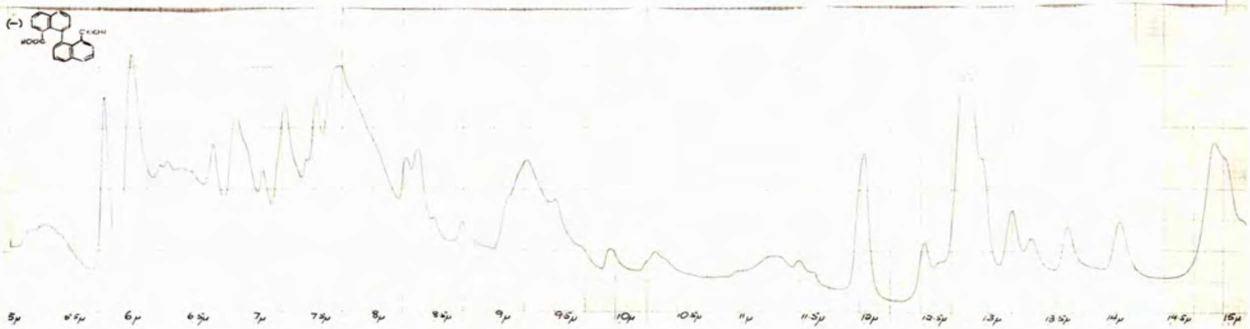
Racemic 1,1'-binaphthyl-8,8'-carboxylic acid was purified and recrystallised from NN-dimethylformamide as described in the Synthetic Experimental Section. For the optically active acids recrystallisation was done quickly to prevent

I.R. SPECTRA

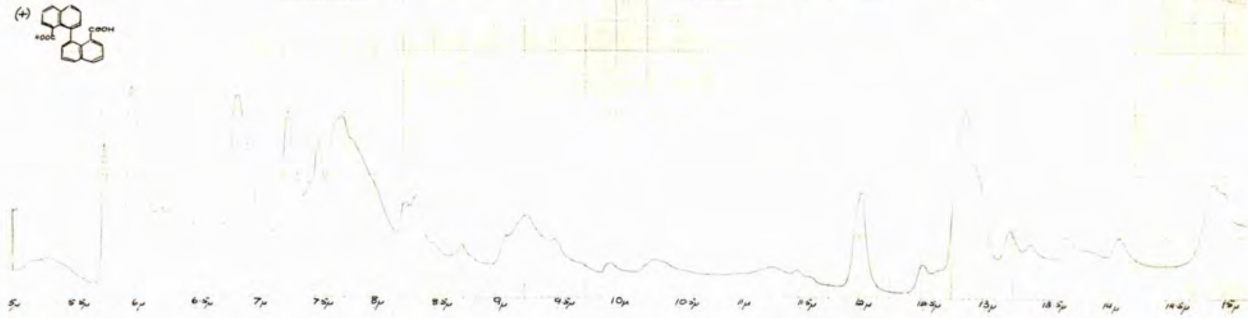
(±) (from synthesis)



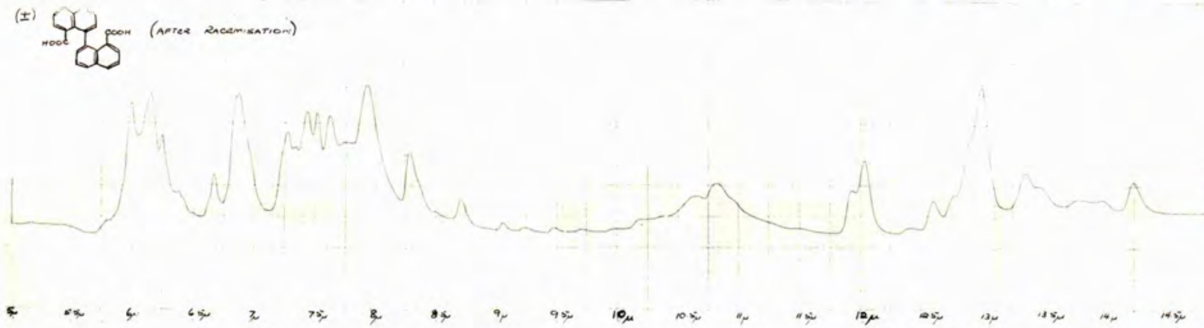
(−)



(+)



(±) (AFTER RACEMISATION)



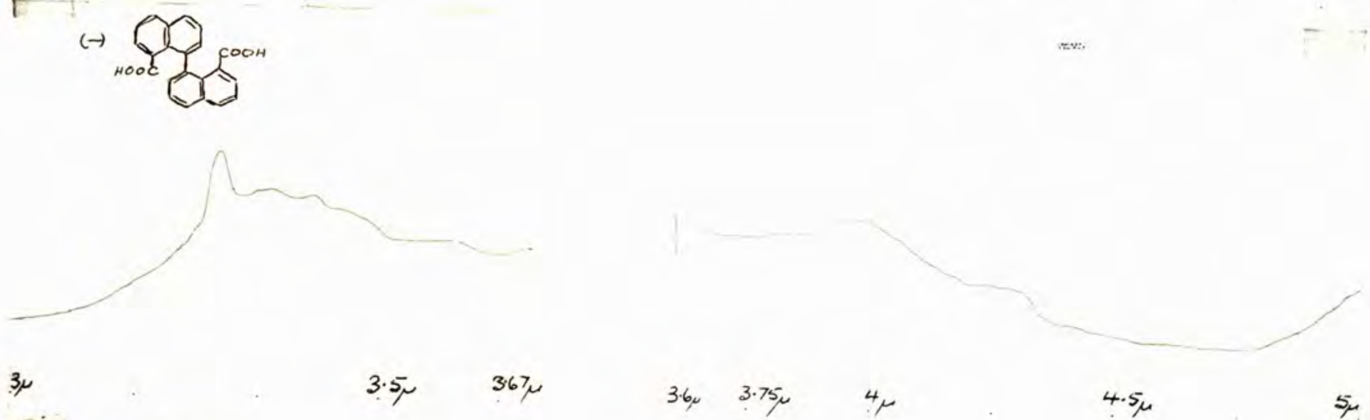
I.R. SPECTRA

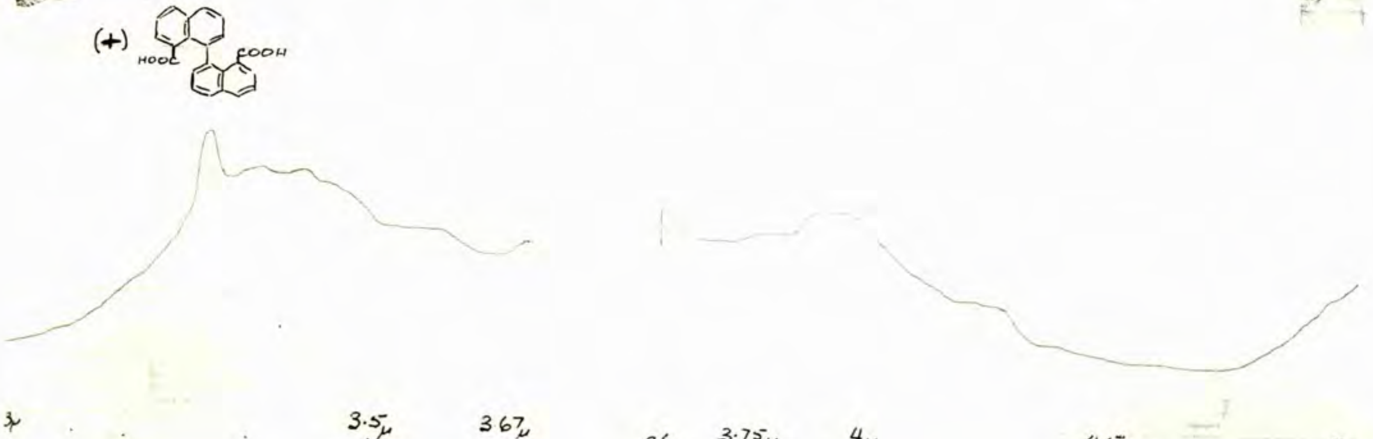
(±) (RACEMIC)

(−)

(+)

I.R. SPECTRA (OH REGION)





loss of optical activity. The optically active acid was also boiled in the same solvent until it had fully racemised, after which it was crystallized, to give another specimen of the racemic acid. The recrystallised products were dried at 100° under reduced pressure.

The Nujol mull method was used between 5 and 20μ and hexachlorobutadiene was used for the hydroxyl region.

It was not possible to obtain solution spectra because the acid is virtually insoluble in all available solvents. NN-dimethyl-formamide, in which the acid dissolves, could not be used because it does not possess "window regions" in the regions to be examined. NaCl plates were used for the region below 15μ and KBr plates were used for the region beyond 15μ.

Results: Wavelengths of bands in microns (μ)

(±) from synthesis	(+)	(-)	(±) after racemisation
-	5.78 s	5.78 s	-
5.99 one	6.01 s	6.01 s	5.99
6.15 strong	-	-	6.15 s
6.25 band	6.24v.w.	6.24v.w.	6.25
-	6.30v.w.	6.30v.w.	-
6.675 v.w.	6.675m.w.	6.675m.w.	6.675m.w.
-	7.08 w	7.08 w	-
7.325m.w.	-	-	7.325

$(\pm)$ from synthesis	(+)	(-)	$(\pm)$ after racemisation
7.325m.w.	-	-	7.325m.w.
7.43 m.w.	7.44 sh	7.44 sh	7. 43m.w.
7.51 m.w.	7.525m.w.	7.525m.w.	7.51 m.w.
7.62 m.w.	-	-	7.62 m.w.
-	7.73 s	7.73 s	-
7.95 s	-	-	7.95 s
8.28 m.s.	8.27) m	8.27) m	8.28 m.s.
-	8.32)	8.32)	-
-	8.50 sh	8.50 sh	-
8.71 m.w.	8.73 w	8.73 w	8.71 m.w.
9.05 w	-	-	9.05 w
9.22 w	9.20 m.s	9.20m.s	9.22 w
9.475w	9.49 sh	9.49 sh	9.475w
9.70v.w.	-	-	9.70v.w.
-	9.95 w	9.95 w	-
-	10.30 w	10.30 w	-
10.65 w	-	-	10.65 w
10.80 m.w.	-	-	10.80 m.w.
-	11.30 w	11.30 w	-
-	11.41 w	11.41 w	-
11.91) m.s.	-	-	11.91) m.s.
12.025)	12.00 s	12.00 s	12.025)
12.39 w	-	-	12.39 w
12.59 m.w.	12.50 w	12.50 w	12.59 m.w.
12.75 sh	12.85 v.s.	12.85 v.s.	12.75 sh

(±) from synthesis	(+)	(-)	(±) after racemisation
12.97 s	12.95 s.h.	12.95 s.h.	12.97 s
-	13.20 m.w.	13.20 m.w.	-
13.35 m	13.35 w	13.35 w	13.35 m
13.72 w	13.65 m.w.	13.65 m.w.	13.72 w
13.97 w	14.075m	14.075m	13.97 w
14.22 m.w.	-	-	14.22 m.w.
-	14.875s	14.875s	-
15.17 w	15.125w	15.125w	-
-	15.27 w	15.27 w	-
	15.44 w	15.44 w	
15.575s	-	-	
-	15.90 w	-	-
16.15			
-	15.33 s	15.33 s	
16.53 s	-	-	
17.52 v.w.	17.63w	17.63 w	
18.32 w	-	-	
	18.50 m	18.50 m	
18.725w	-	-	
-	20.00	20.00	

s=strong, m=medium, w=weak, v=very, s=shoulder.

(±) from synthesis	(+) and (-)
Broad OH absorption band (3.2 - 4.5μ). A slight increase in intensity around 4μ	OH absorption band is broad (3.2 - 4.5μ) with increase in intensity around 4μ. However a a sharp and obvious band occurs at 3.29μ.

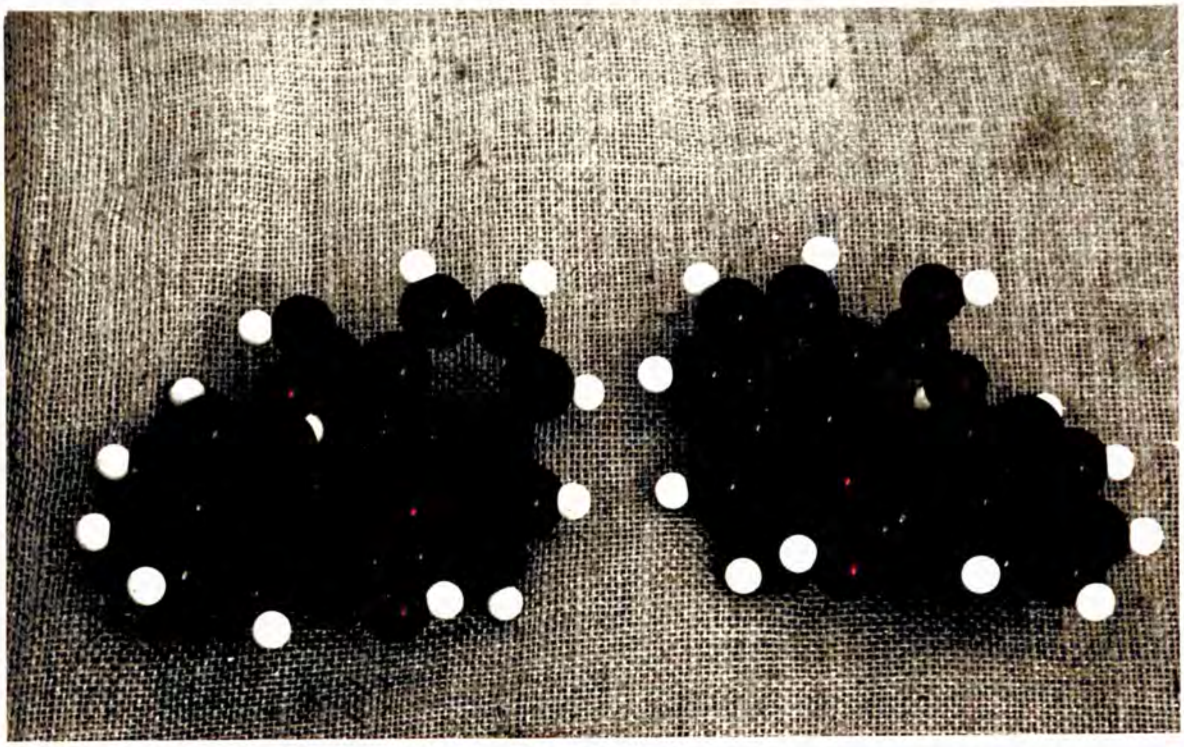
Discussion:-

Previous workers were unable to purify the optically active 1,1'-binaphthyl-8,8'-dicarboxylic acids by crystallization, as was shown by poor elemental analyses. The acids contained occluded water and this made a comparative study of the hydroxyl region impossible. In the present work, NN-dimethylformamide proved to be a suitable solvent from which the acids could be crystallized without much loss in optical activity. The elemental analyses were good, and therefore a comparison of the i.r. spectra of the acids could be made.

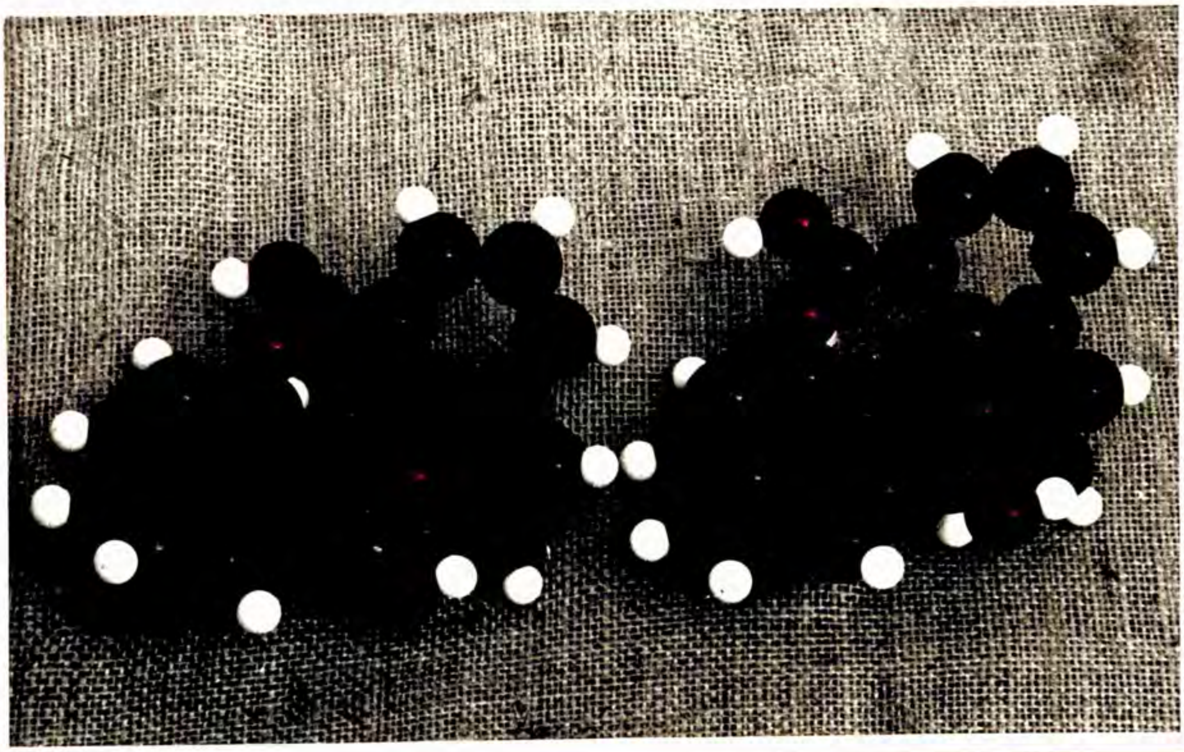
It can be observed from fig. 1, 2 and 3 that the spectrum of racemic 1,1'-binaphthyl-8,8'-dicarboxylic acid differs from that of the optically active isomers which themselves have identical spectra. Since the spectra were done on the solid acid, the differences can be due to differences in the influence of the molecules on one another in the two compounds. Such differences give rise to differences in crystal structure in the two cases so that there will be differences in crystal forces, and dipolar interactions in the crystals.

The racemic acid contains equimolecular amounts of the (+) and (-)-isomers. Since the infrared spectrum of the (+) acid is identical with that of the (-)-acid, an equimolecular mixture of the two isomers might be expected to give the same spectrum as that of the individual optical isomers. The difference in the spectra, therefore, provides every reason to suppose that the differences observed here are due to differences in intermolecular factors.

FIG I



Mirror image isomers of 1,1'-binaphthyl-8,8'-dicarboxylic acid.



Two molecules of one isomer of optically active 1,1'-binaphthyl-8,8'-dicarboxylic acid.

The fact that the OH absorption bands of the racemic acid and optically active isomers are broad and appear at low frequencies, clearly shows the presence of hydrogen bonding; the differences in the OH absorption bands of the racemic and the optically active acids, shows that the hydrogen bonding is intermolecular, since if there were intramolecular hydrogen bonding in the racemic acid, and the optically active acids (which have identical spectra), these differences would not be observed.

It has already been stated that if the carbonyl group e.g. that of a carboxylic acid, is involved in hydrogen bond formation, $\nu C = O$ falls. Hence if both carbonyl groups in the 8,8'-diacid are involved in hydrogen bonding, they will give a peak at a lower ~~a~~ frequency than that of a free carbonyl group. But should only one carbonyl group be involved, there will be two carbonyl peaks, one at lower frequencies (for the C=O group involved in hydrogen bonding) and the other at higher frequencies (for the free C=O group). This is what is observed in the case of the optically active acid. The racemic acid has one carbonyl peak, at the lower frequency, showing that both carboxyl groups are involved in hydrogen bonding. Examination of models (fig. 11) shows that intramolecular hydrogen bonding between mirror-image molecules in the racemic acid takes place in such a way that there will be two carboxyl groups on opposite "sides" free to form hydrogen bonds with other molecules, without causing much overcrowding. However, with the (+)- or (-)-acid (fig. 11), the two carboxyl groups will be on the same "side" and will not be able to form hydrogen bonds with other molecules without serious overcrowding, and so they will remain free. These carboxyl groups give a C=O band at a higher frequency, (absorption band at 5.78μ). The free OH also gives a sharp band at 3.29μ. These two peaks are not observed in the case of the racemic acid in which both carbonyl groups are equally involved in hydrogen bonding (C=O band has secondary maxima at 5.99, 6.15, 6.25μ). the bonded C=O group in the (+)- or (-)-isomers absorbs at lower frequencies (6.01μ).

Arrangements of the classical models (bearing in mind the fact that the -COOH groups have to approach each other linearly) indicates that the involvement of both carboxyl groups in the racemic acid could be easier than in the (+)- and (-)-isomers where only one carboxyl group appears to be free.

Hence these differences in hydrogen bonding in the crystalline acid, racemic and optically active, give rise to differences between the infrared spectrum of the racemic acid and the optically active acid.

Unfortunately, the insolubility of these acids in suitable spectroscopic solvents precludes investigation of the i.r. spectra in solution. This high insolubility can be attributed to strong intermolecular forces in the solid acids. The acids were found to be soluble in NN-dimethylformamide and dimethyl sulphoxide, which are strong enough to break the intermolecular forces in the solid acids. However, these solvents absorb in the carbonyl and hydroxyl regions, thus making i.r. spectral studies of the acids impossible.

If the spectral differences should disappear when the spectra are obtained using a suitable solvent, it can be correct to suppose that the above observations are due to differences in some factors prevailing in the crystals of these acids.

9. NUCLEAR MAGNETIC RESONANCE SPECTRA OF SUBSTITUTED 1,1'-BINAPHTHYLS

Introduction:

LONG-RANGE SHIELDING.

The abnormal shielding of certain methylene groups in polymethylene benzenes (discussed later), the difference between the shielding of methylene groups in cyclic and acyclic systems, and the dependence of the frequencies of protons in substituted ethanes on the populations of conformations, suggest that proton shielding may be controlled by the nature of neighbouring groups as well as their orientation with respect to the proton. Therefore, nuclear magnetic resonance spectroscopy can be applied to investigations of sterochemical problems.

L.M.Jackman (Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry. p. 112. Pergamon Press, London, 1959). has considered the shielding of a proton which arises from a group of electrons, G, not directly associated with the proton. The local diamagnetic circulations of G (where G consists of electrons of an isolated atom, assuming the atom has a closed shell configuration so that there is no resultant electron spin), gives rise to an induced field which is independent of the direction of the applied field because G is spherically symmetrical, The orientation of the proton relative to G determines the component of the induced field at the proton as shown in fig. I.

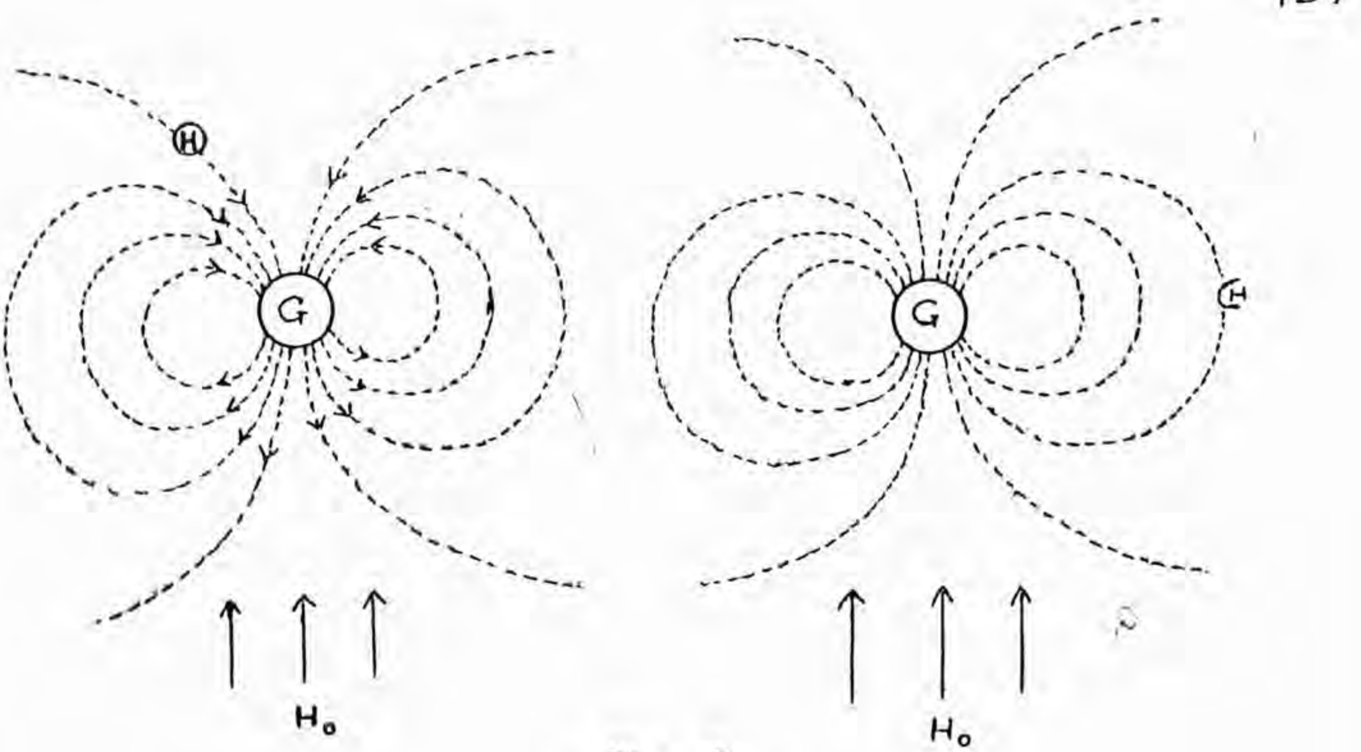
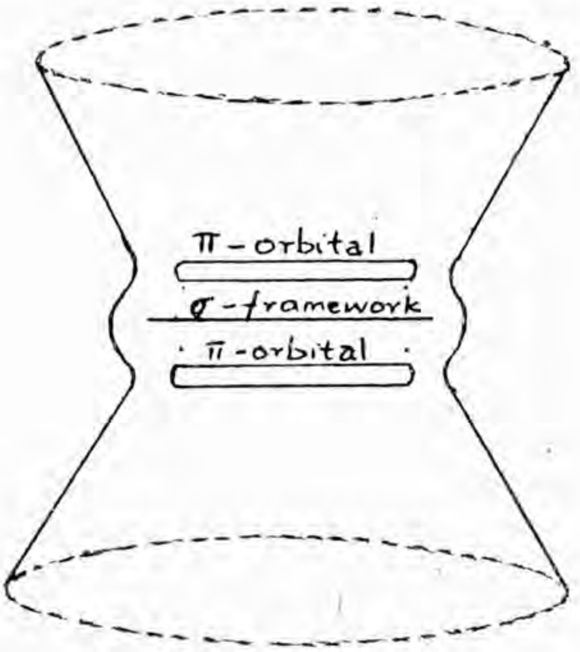


Fig. I.

If the relative orientations of the proton and G vary randomly over a period of time, as would be the case if they were part of the same molecule in the liquid or gaseous state, the average field produced by G at the proton is zero. If G is not spherically symmetrical, the component of the induced field, averaged over all orientations, will have a finite value, because the strength of the induced field will no longer be independent of the applied field. Hence a group of electrons can only contribute to the shielding of a remote proton if the group is magnetically anisotropic. For this reason, long-range shielding effects are best discussed in terms of diamagnetic anisotropies of groups of electrons.

In aromatic and pseudo-aromatic rings, the π-electrons are cyclically delocalized. These rings allow induced circulation of the π-electrons over all the ring atoms. This induces considerable ring currents which produce correspondingly large magnetic fields. Such systems are not spherically symmetrical (i.e. they are markedly anisotropic) and therefore the effects of the induced field at a point in the surrounding space do not average to zero for all possible orientations of the ring with respect to the applied field. Hence aromatic rings provide a strong source of long-range shielding and deshielding. The induced field and resulting shielding zones for the benzene molecule can be pictured as in fig. II, (L.M.Jackman, <u>loc</u>. <u>cit</u>.)



Long-range shielding by the benzene ring. The magnitu~~t~~de increases towards the π-orbitals rather than towards the electrical centre of gravity of the π-electrons.

<u>Fig. II.</u>

The induced magnetic field is opposed to the applied field at the centre of the ring, but in the same direction as the applied field outside the ring, in the plane of the ring where benzene protons lie. The benzene protons are therefore deshielded as shown in fig. III.

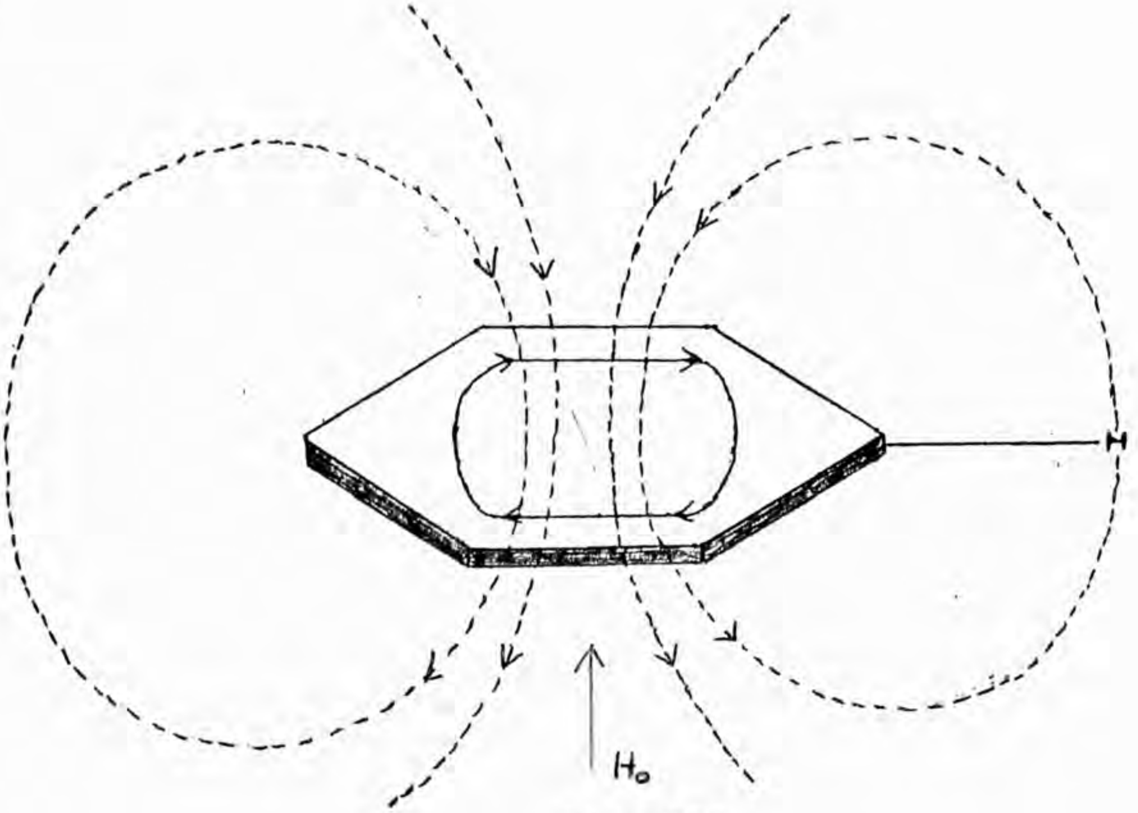
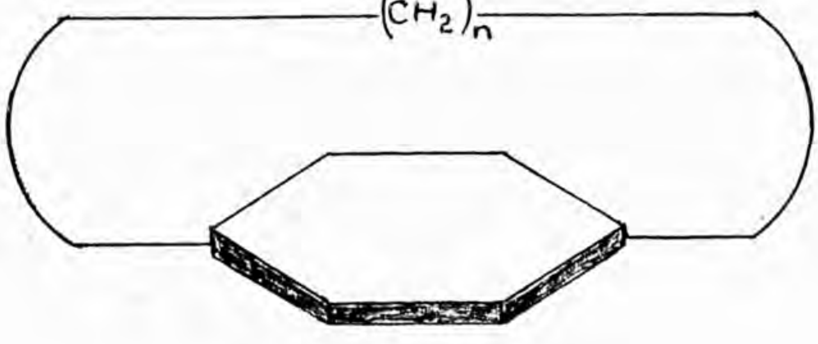


Fig. III.

The deshielding of aromatic protons.

Hence the aromatic protons resonate at a lower value of the applied field than they otherwise would. However, a proton held over the centre of the benzene ring is shielded, because in this region the induced field opposes the applied field, and resonates at a higher frequency.

J.S.Waugh and R.W.Fessenden (J. Amer. Chem. Soc., 1957, 79, 846) have predicted the high resolution nuclear spectra of 1,4-polymethylenebenzene (Fig. IV), using the classical free electrical model of Pople. They state



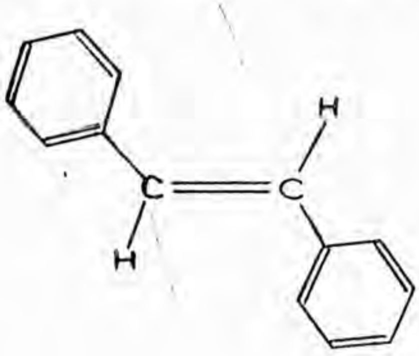
that in the lower members of the series ($n \geqslant 8$) the centre CH_2-groups are confined to a region near the centre of the aromatic nucle~~a~~us, and are therefore expected to experience a free electron field of appreciable magnitude and of a sign opposite to that associated with aromatic protons. The spectra for cases n=10 and n=12 were predicted as follows:

1) The aromatic protons are expected to give a single line at about the same position as in p-xylene.

2) The α-CH_2-protons one expected to experience nearly the same combination of chemical effects and free electron field as the corresponding protons in ethylbenzene. Hence a triplet is predicted.

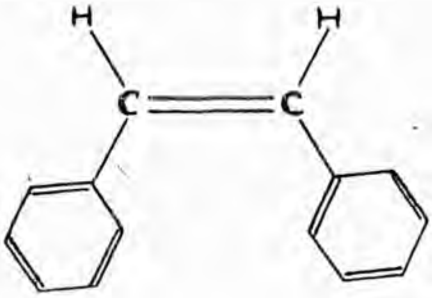
3) The remaining (β, γ, ----) protons should have chemical shifts characteristic of saturated, unstrained cyclic hydrocarbons modified by the free electron field. These methyl protons have, in fact, been observed to give signals more upfield than do the CH_2-protons in other compounds, in the compound n=10 we find the central methylene protons of the bridging chains have τ 9.20 as compared with τ 8.75 in a normal aliphatic chain.

When in a complex molecule, an aromatic ring is not coplanar with another part of the molecule, th~~a~~en there will be differential long-range effects. D.Y. Curtin, H. Gruen and B.A. Shoulders (Chem. and Ind., 1958, 1205) have examined several pairs of *cis*-*trans* isomers involving phenyl substituents. They have observed quite large frequency shifts arising from long-range shielding by the aromatic rings. Hence the olefinic protons frequencies of cis- and trans-stilbene (II and III) indicate that in the trans isomer the two rings are essentially coplanar with the double bond and so deshield the protons.



II

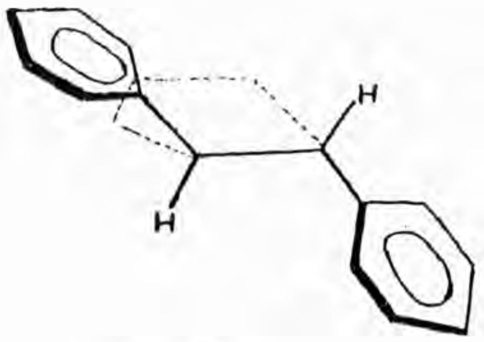
The olefinic protons in II have τ 3.01. Each proton lies in the plane of the two phenyl groups and is therefore deshielded.



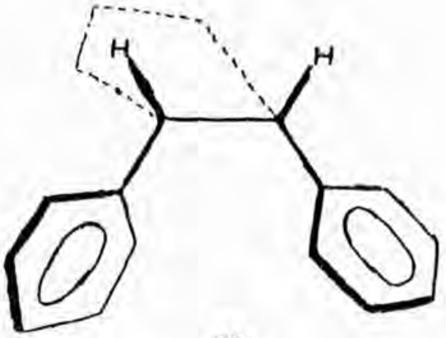
III

In III, the olefinic protons have τ3.51. The aromatic rings in this molecule are tilted and the deshielding of the olefinic protons is therefore reduced.

However, the frequencies of the protons α to the phenyl groups in trans and cis 1,2-diphenyl cyclopentane, IV ahd V, show that in both isomers the phenyl groups are not planar.



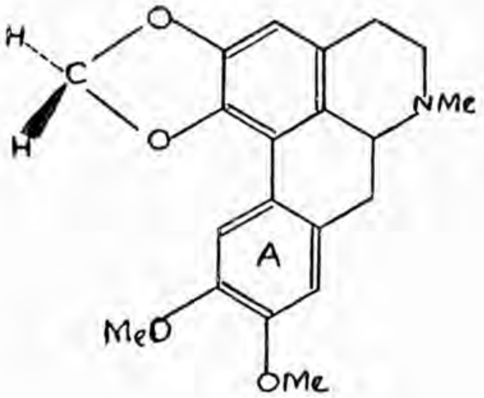
IV
τ 7.11



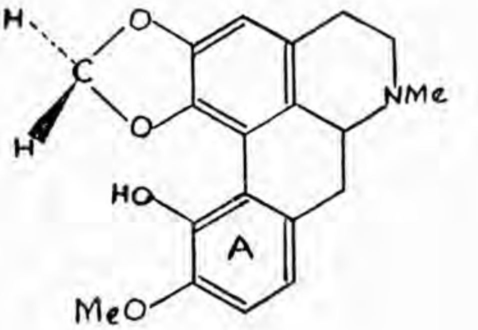
V
τ 6.71

In IV each proton lies above the plane of the vicinal phenyl group and is therefore shielded whereas in V, each proton is further removed from the vicinal phenyl group and the ~~de~~shielding is therefore less than it is in V.

S. Goodwin, J.N. Shoolery and L.F. Johnson (Proc. Chem. Soc., 1958, ~~263~~ 306) have reported data for decentrine (VI) and bulbocapnine (VII), two alkaloids of the aporphine group possessing non-planar diphenyl systems.

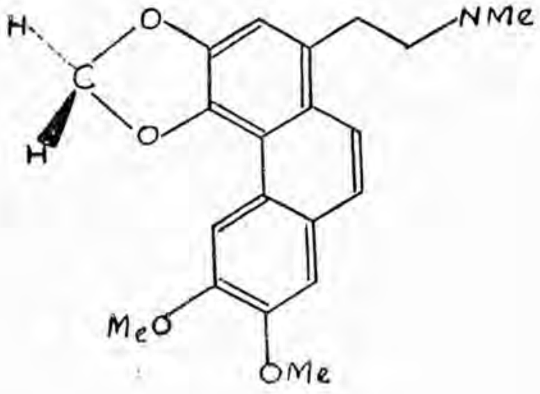


VI



VII

There is unequal deshielding of the two protons of methylenedioxy groups by the benzene ring A, because the plane of this ring does not bisect the $-C\genfrac{}{}{0pt}{}{\diagup H}{\diagdown H}$ group. The spectrum therefore is of an AB type, (AB is a two spin system of interacting nuclei, B having a higher chemical shift than A). In the Emde degradation product, VIII, there is coplanarity and the methylenedioxy protons show a single resonance line because they are now equivalent, being equally deshielded by the aromatic ring.



VIII

The above examples are helpful in that they provide a means of understanding the approximate spatial geometry of the long-range shielding and deshielding zones in aromatic rings.

In view of the above considerations it was considered that the relative degrees of shielding of substituent protons in suitably substituted 1,1'-binaphthyls would give an approximate measure of the relative spatial orientation of the substituents.

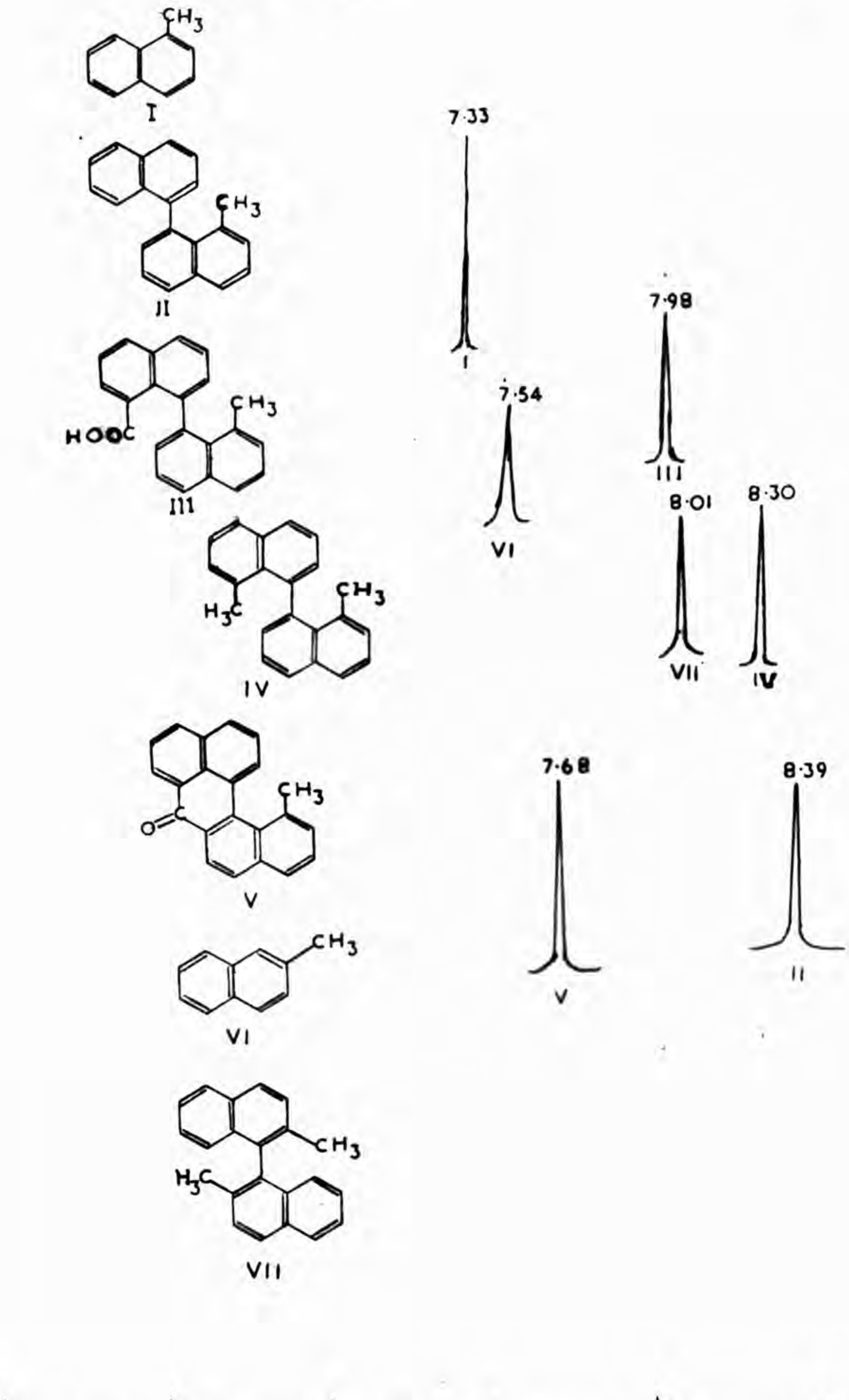
Results from present work:

Nuclear magnetic resonance spectra were done in deuterated dimethylsulphoxide because this was found to be the best solvent for the set of compounds.

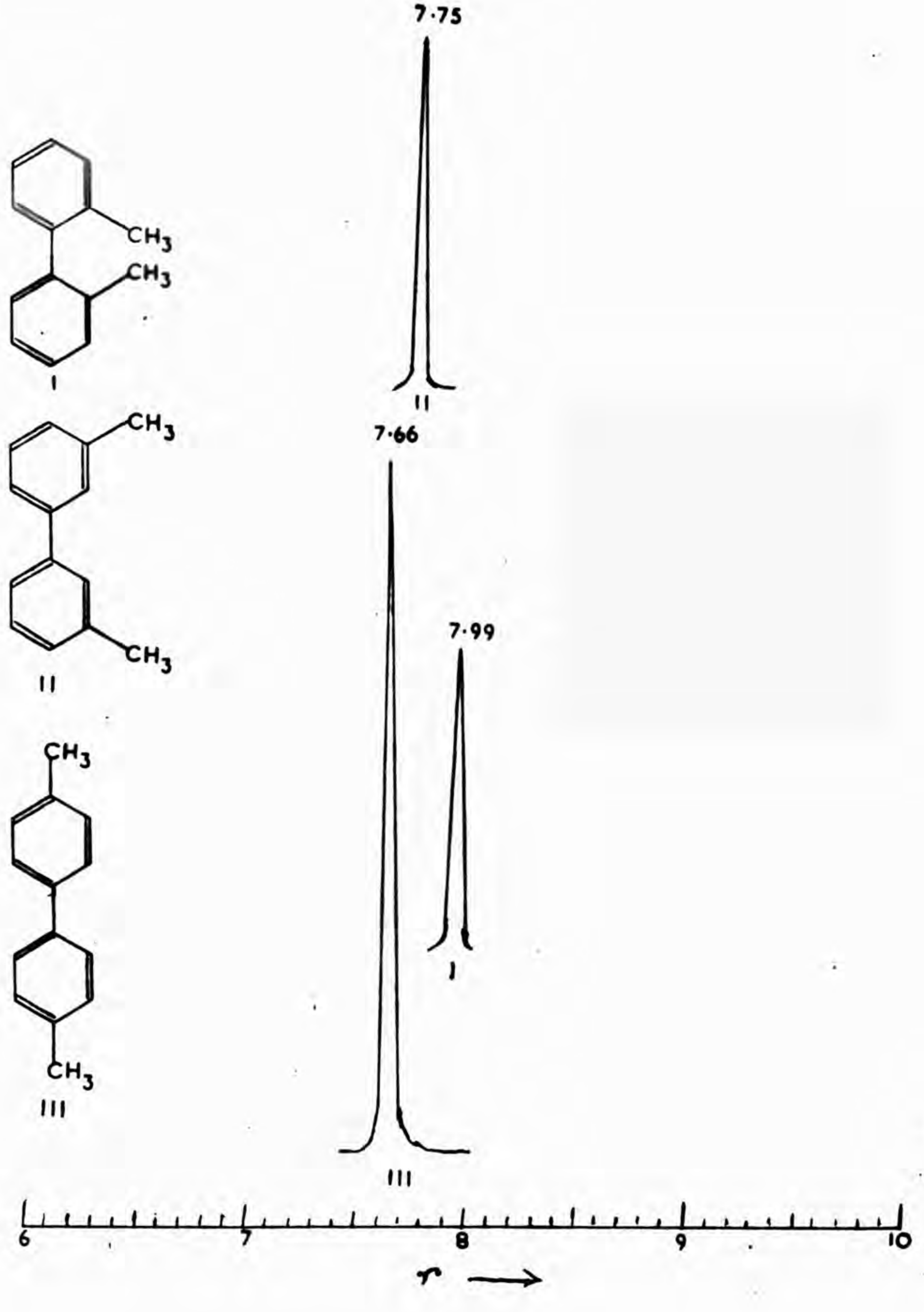
Compounds with the methyl group as a substituent, gave the most satisfactory results, since complications such as hydrogen bonding and proton exchange with solvent do not arise as they do in the case of groups with hydroxylic protons. The results are compared with those of toluene and the ditolyls whose nuclear magnetic resonance spectra were done in carbon tetrachloride.

Freshly opened deuterated dimethylsulphoxide was used as the solvent for the carboxylic acid, because the solvent which has been standing for some time contained water and as a result of the rapid proton exchange between the carboxylic acids and the water, there appeared one sharp signal around the H_2O proton signal and no detectable proton signal was observed.

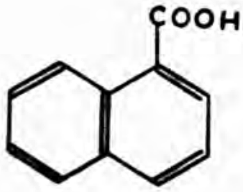
Methyl proton signals.

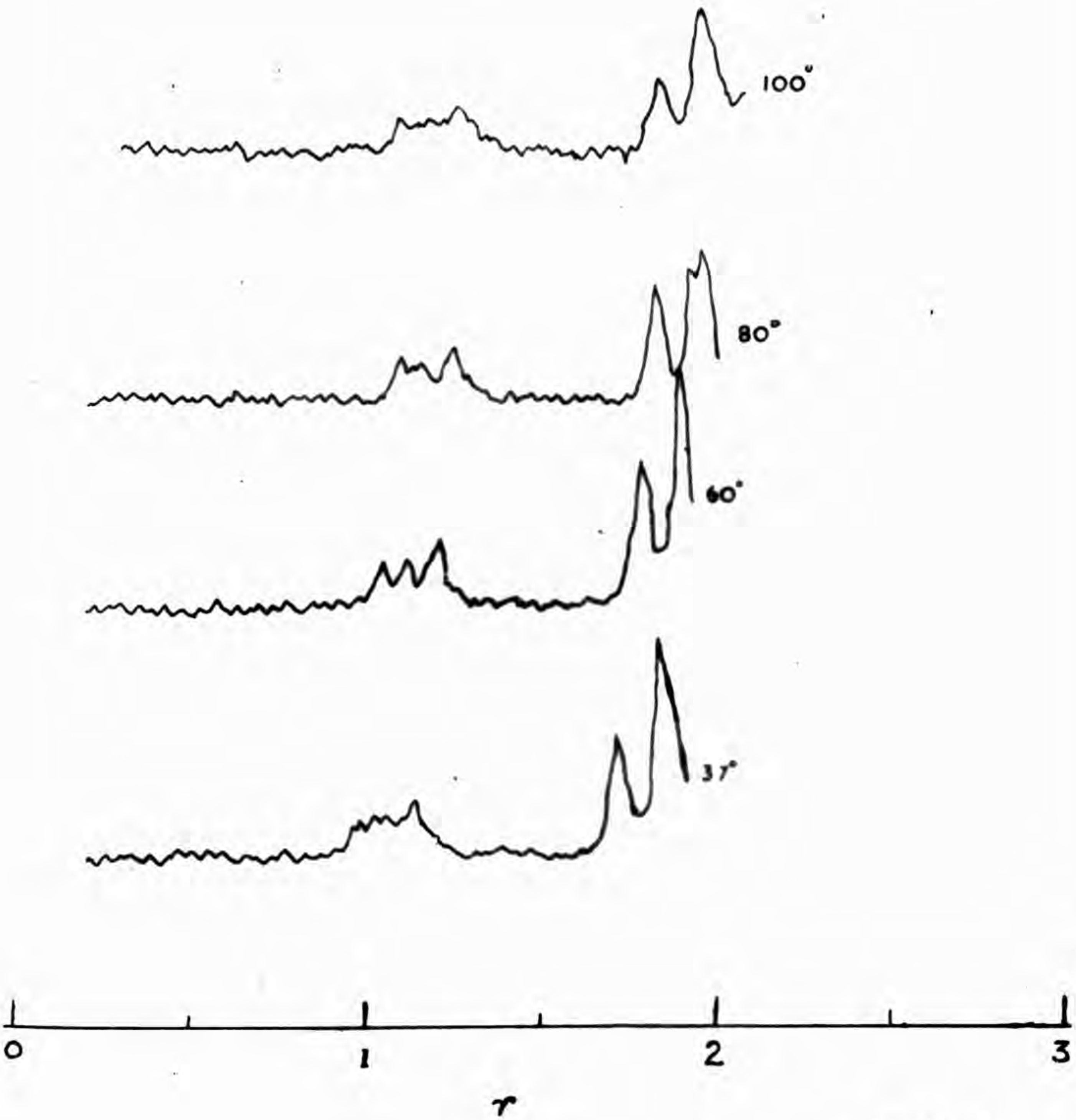


Methyl proton signals.



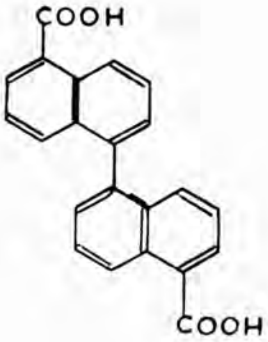
N.M.R. spectra (hydroxylic region) of

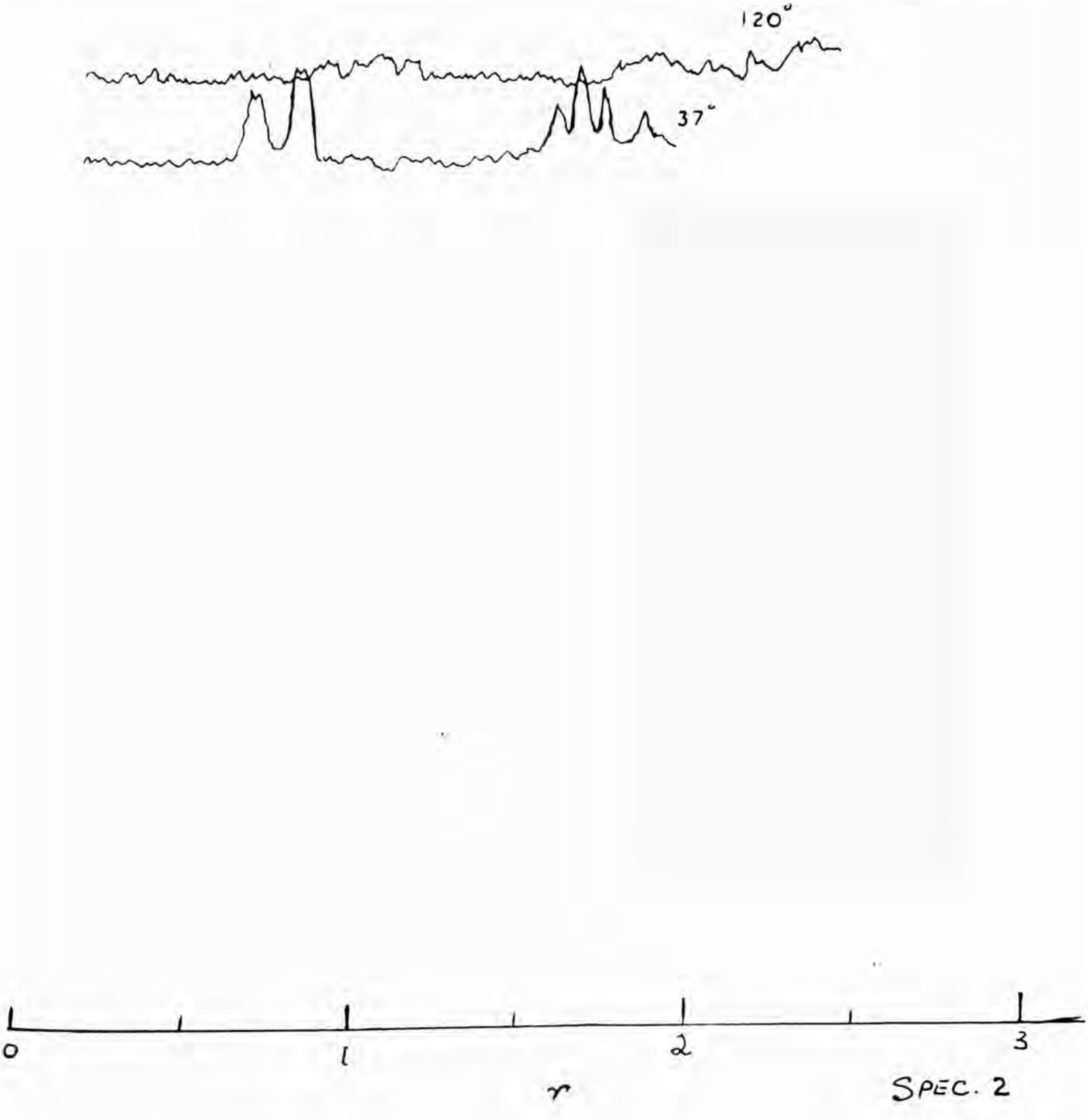




SPEC. I

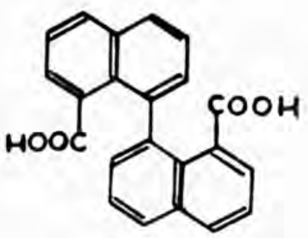
N.M.R. spectra (hydroxylic region) of

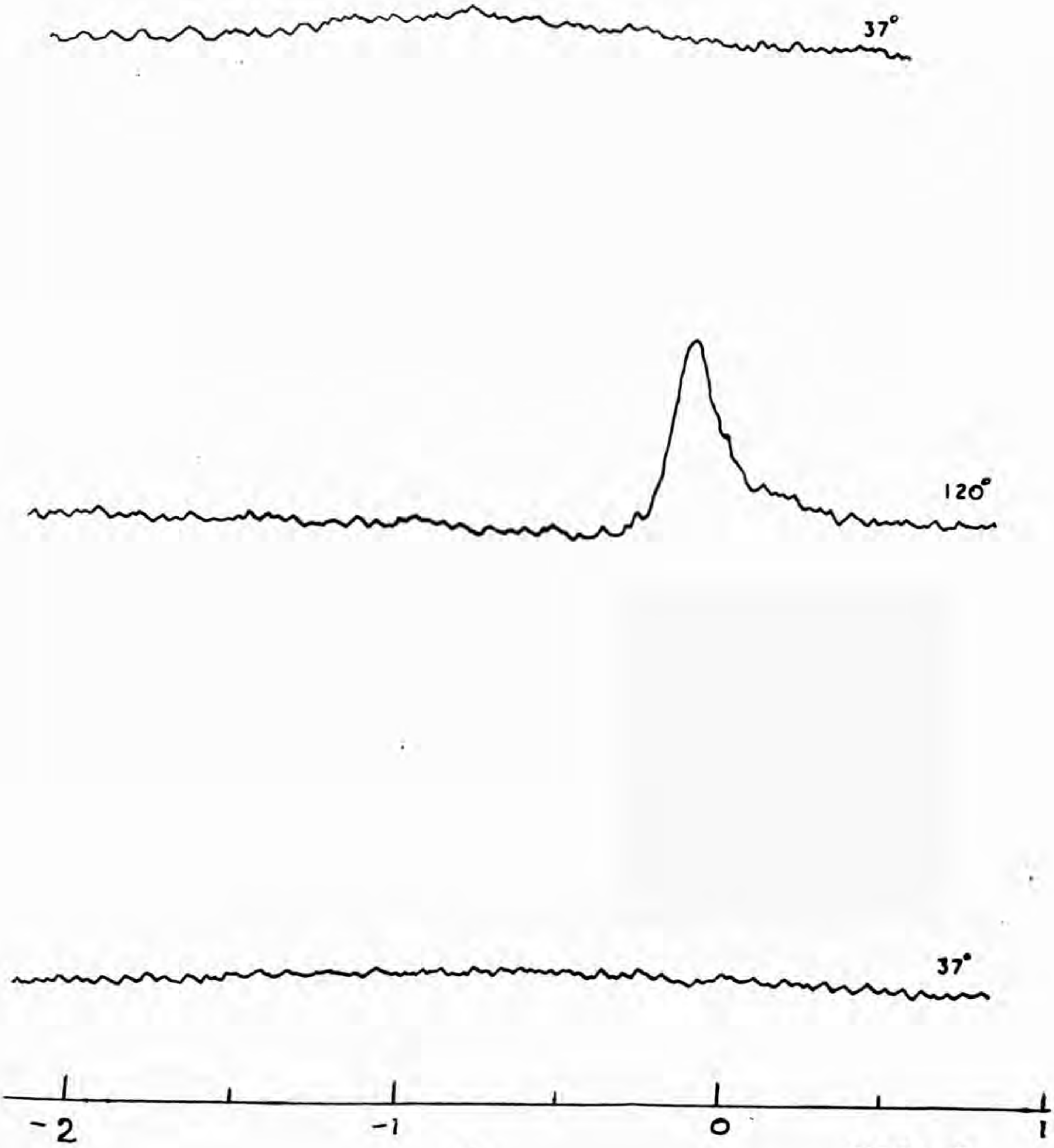




SPEC. 2

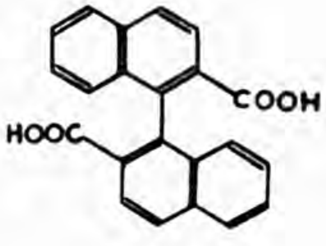
N.M.R. spectra (hydroxylic region) of

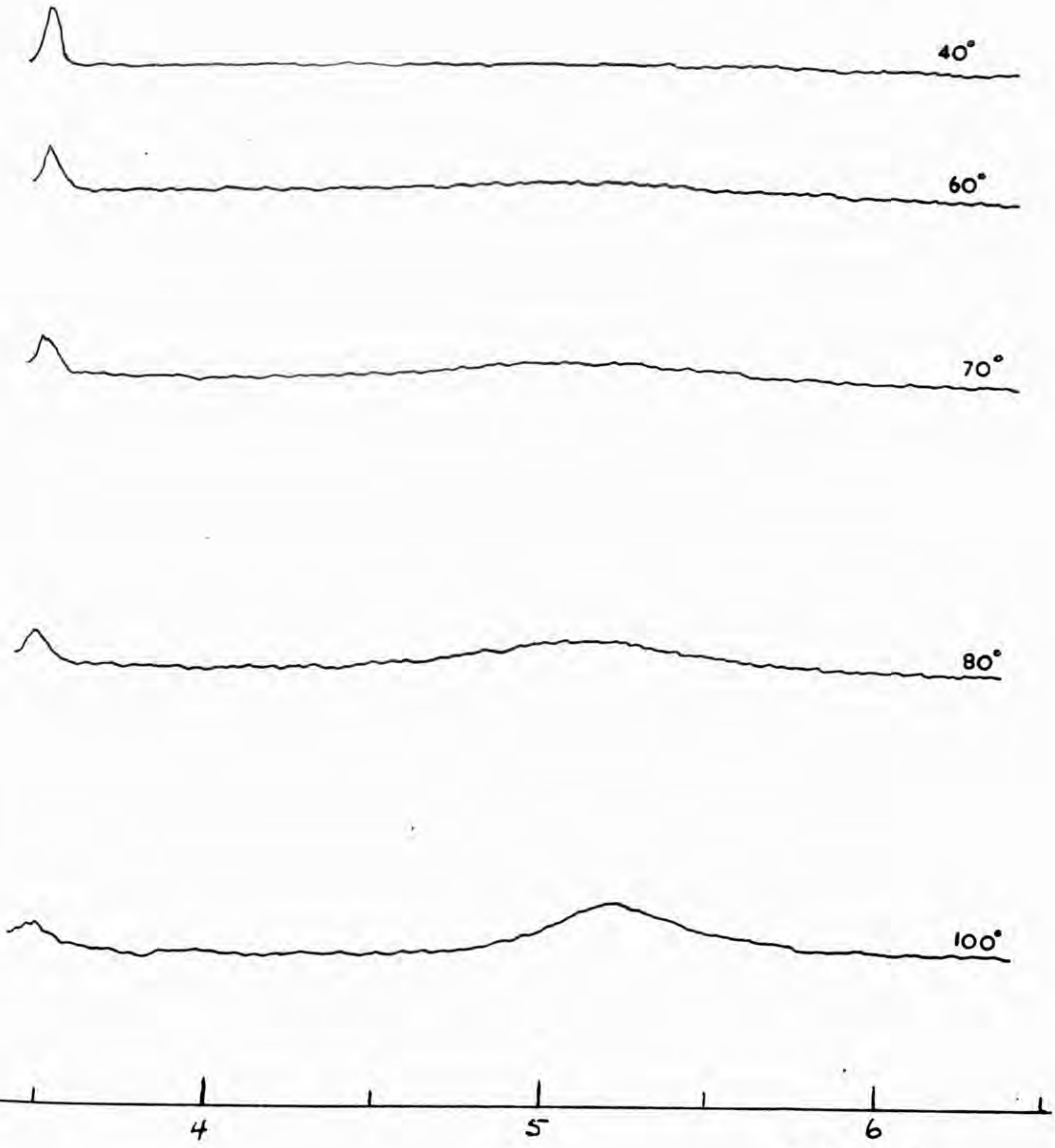




SPEC. 3

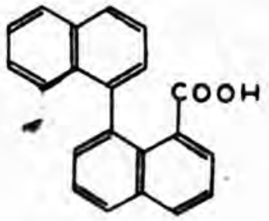
N.M.R. spectra (hydroxylic region) of

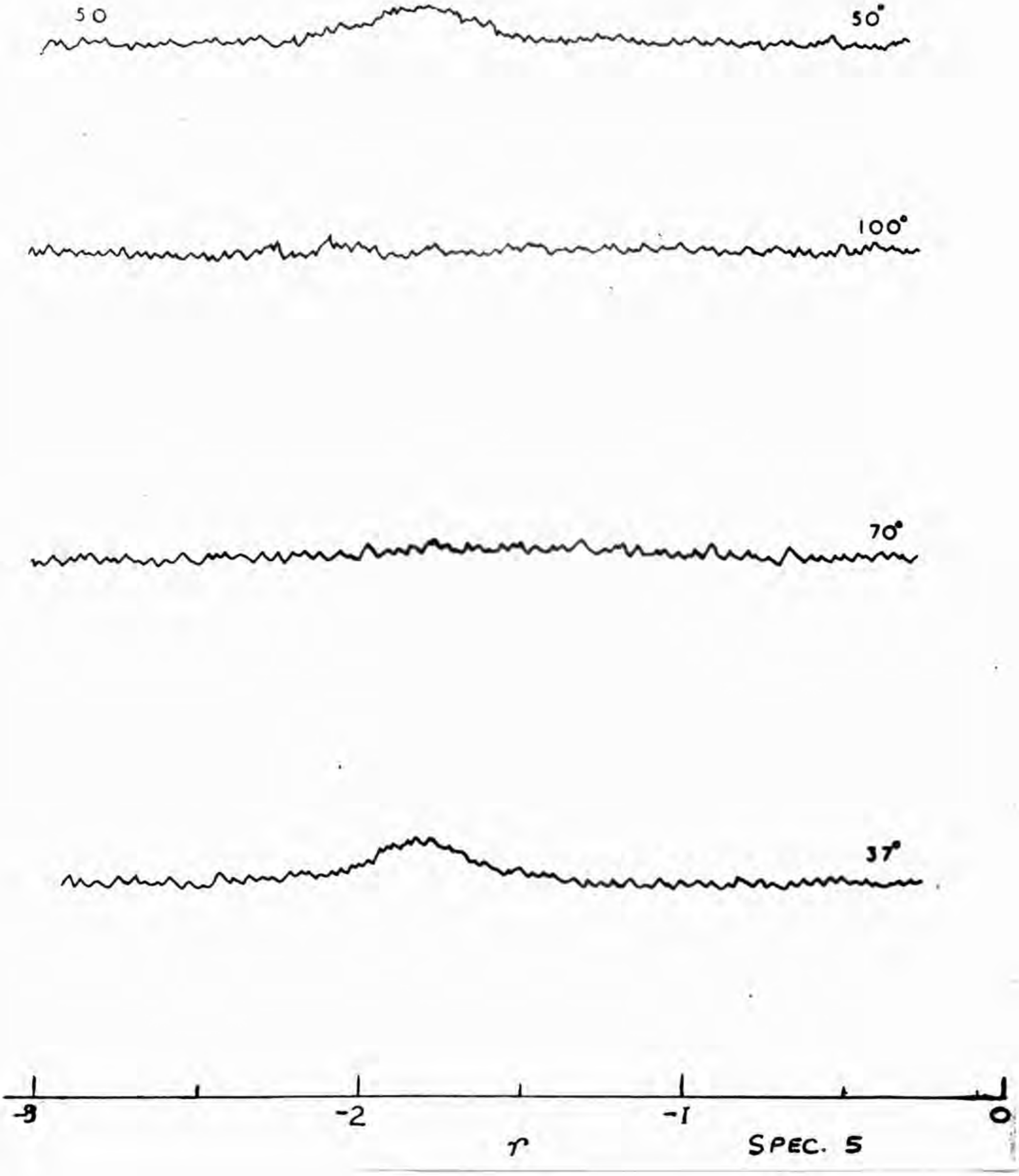




SPEC. 4

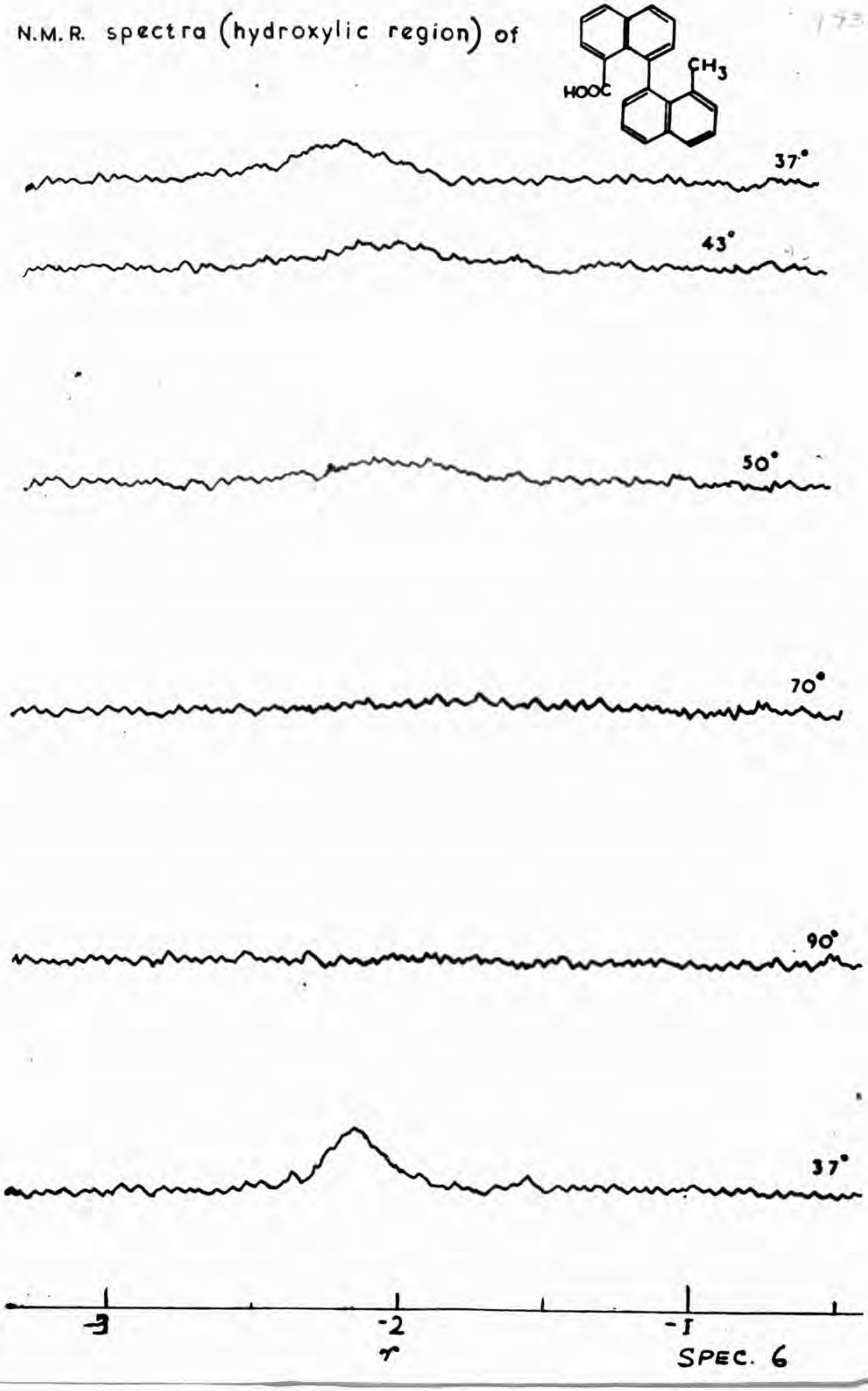
N.M.R. spectra (hydroxylic region) of





SPEC. 5

N.M.R. spectra (hydroxylic region) of

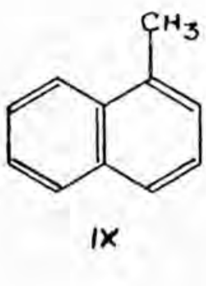


SPEC. 6

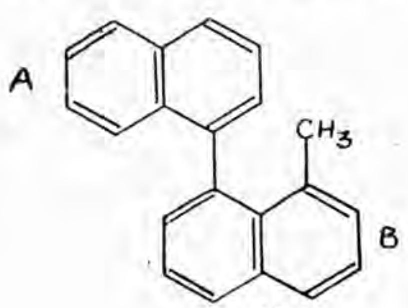
Discussion

The methyl protons, in the absence of deshielding effects induced by neighbouring atoms or groups, are usually the most highly shielded of all the common organic types. In saturated hydrocarbons the methyl proton signal appears between τ 9.05 and τ 9.15. In rigid cyclic systems the signal can appear at slightly higher frequencies (up to about τ9.40). However, the methyl groups joined to aromatic systems absorb at lower frequencies as a result of the deshielding by the ring current fields. The methyl proton signal for α-methylnaphthalene, IX, appears at τ 7.33 in deutero-dimethylsulphoxide as the solvent.

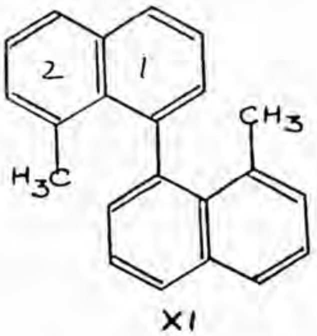
However, 8-methyl-1,1'-binaphthyl, X, gives the methyl proton signal at τ 8.39. Steric repulsion between the naphthalene residue A and the methyl group causes bond deformation resulting in deshielding of the methyl group (this effect has been observed in the dimethylnaphthalene series by C. MacLean and E.L. Mackor, Mol. Phys., 1960, 3, 223) by changing its relationship with ring B.



IX



X



XI

Because of this the methyl proton signal would be expected to appear downfield relative to that in α-methylnaphthalene

The fact that it appears upfield relative to that in α-methylnaphthalene is due to long-range shielding of the methyl group by the opposite naphthalene residue A. The two naphthalene residues in the molecule are not coplanar, and so the methyl group is held above the opposite naphthalene portion of the molecule and the methyl protons are therefore shielded. Since the naphthalene residues in the molecule are assumed to be trans, the methyl group is held above ring I.

With 8,8'-dimethyl-1,1'-binaphthyl, XI, the methyl protons would be expected to give a signal at the same position as that for the $-CH_2$ protons in 8-methyl-1,1'-binaphthyl, if the in-plane and out-of-plane deflections of the $C-CH_3$ bonds in the two molecules were the same. But if these distortions should increase in the case of 8,8'-dimethyl-1,1'-binaphthyl, due to increased peri-interaction, the signal should come downfield, relative to that of 8-methyl-1,1'-binaphthyl since the interaction increases the deshielding of the methyl protons by the aromatic ring current field. This is what is observed; the $-CH_3$ proton signals in 8,8'-dimethyl-1,1'-binaphthyl appear at τ 8.30. Moreover the increased in-plane and out-of-plane deflection of the methyl groups in 8,8'-dimethyl-1,1'-binaphthyl reduces the long range shielding of the methyl groups by the opposite naphthalene residues since in this molecule, each $-CH_3$ group is held further away from the opposite naphthalene residue than is the

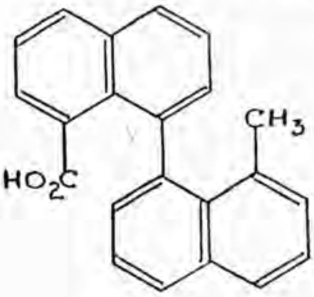
$-CH_3$ group in 8-methyl-1,1'-binaphthyl. With one methyl substituent in the 8-position in 1,1'-binaphthyl, the 1,1'-bond is distorted in-plane and out-of-plane. The second methyl group in the 8'-position causes additional distortion thus bringing the methyl groups even further away from the opposite naphthalene residues.

Hence, in 8,8'-dimethyl-1,1'-binapthyl, increased peri-interaction between each $-CH_3$ group and the opposite naphthalene residues increases the deshielding of the $-CH_3$ protons by the naphthalene nucleus to which the methyl group is attached, and reduces the long range shielding of these protons by the opposite naphthalene nucleus.

Equivalence of methyl protons.

An interesting observation is that all the protons in each methyl group give a single signal indicating that they are equivalent. Hence the distortions in the molecule are large enough to allow rotation of the methyl groups. Moreover, the two methyl groups in 8,8'-dimethyl-1,1'-binaphthyl give one signal indicating that they are in equivalent environments. This suggests that one conformation is substantially preferred.

In 8'-methyl-1,1'-binaphthyl-8-carboxylic acid, XII, the -COOH group can be considered to be larger than the $-CH_3$ group if it is rotating. On the present evidence, it seems that it is, since it increases in-plane and out-of-plane distortions in the molecule thus bringing the $-CH_3$ group even further away from the opposite naphthalene residue (although a study of space filling models makes a rotating carboxyl group seem highly improbable). The methyl proton signal therefore appears downfield, τ 7.98 relative to that of the $-CH_3$ protons in 8,8'-dimethyl-1,1'-binaphthyl.

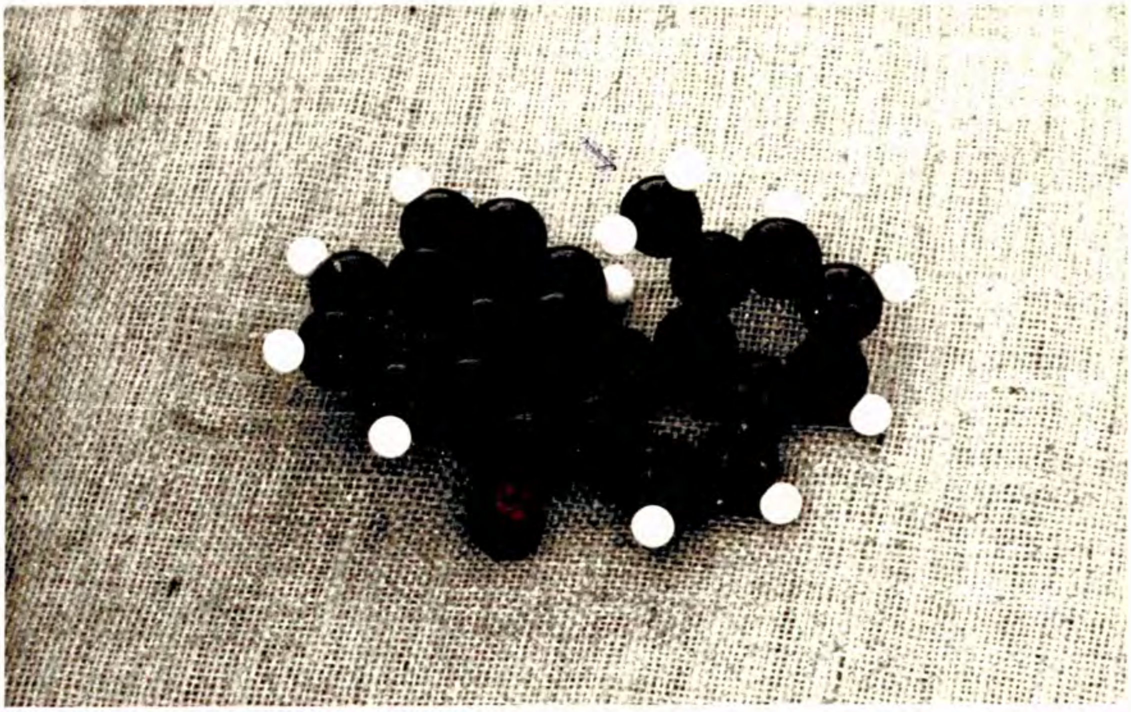


XII

It may be thought that the secondary magnetic field set up by the induced circulation of π-electrons in the $>C=O$ of the carboxyl group, will deshield the $-CH_3$ protons when they are adjacent to the end of the double bond. However, if the group rotates the $-CH_3$ protons also come near the centre of the double bond and they would be therefore relatively shielded. Hence the two effects cancel each other. Therefore the only apparent cause of the downfield shift of the methyl proton signal is the effectively large size of the carboxyl group.

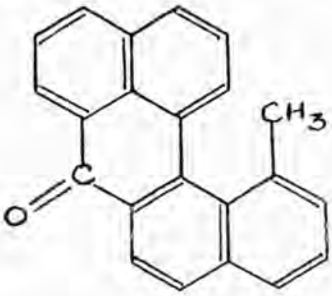
That the downfield shift of the $-CH_3$ proton signal is a result of additional distortion in the molecule, which brings the $-CH_3$ group further away from the opposite naphthalene nucleus, is evident from the $-CH_3$ proton signal of 13-methyl-7-oxodibenz (a, kl) anthracene, XIII, which appears at τ 7.68. Ring shutting on one side of the molecule puts the $-CH_3$ group further away from the naphthalene nucleus A

13-Methyl-7-oxodibenz [a, kl] anthracene



Ring closure on one side, pulls the methyl group further away from the centre of the opposite naphthalene ring.

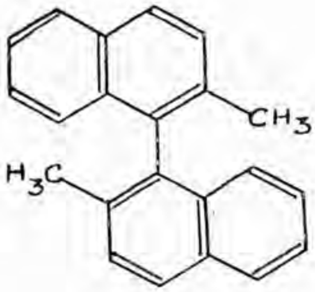
but nearer into its plane. Hence the long-range shielding of the $-CH_3$ group is reduced and the deshielding is increased. The $-CH_3$ proton signal therefore comes further downfield compared to that in the



XIII

compounds considered above.

2,2'-Dimethyl-1,1'-binaphthyl, XV, gives a methyl proton signal at τ 8.01, whereas β-methylnaphthalene has a $-CH_3$ proton signal at τ 7.54. Hence there is long-range shielding of the methyl protons in 2,2'-dimethyl-1,1'-binaphthyl. This molecule is not coplanar; each $-CH_3$ group is held above the opposite naphthalene nucleus.

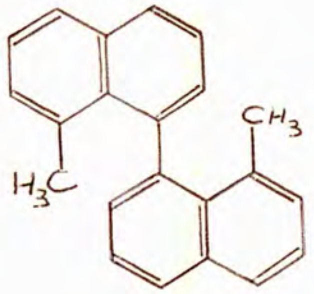


XV

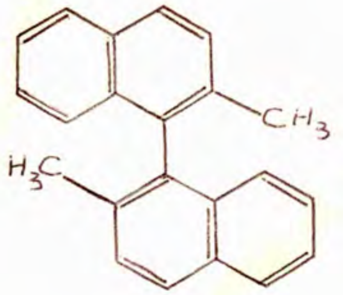
The difference between the chemical shifts of 2,2'-dimethyl-1,1'-binaphthyl and β-methylnaphthalene is 0.47 whereas that between the chemical shifts of 8,8'-dimethyl-1,1'-binaphthyl and α-methylnaphthalene is 1.06. This indicates

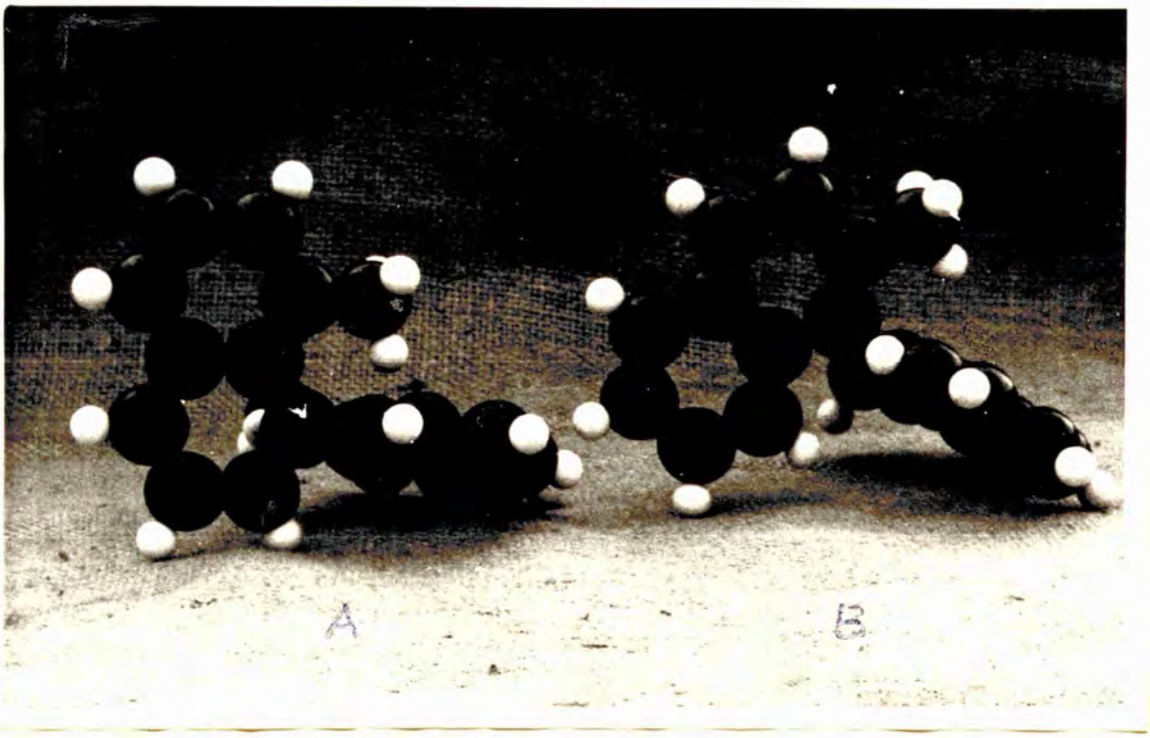
Trans conformations of

A



B

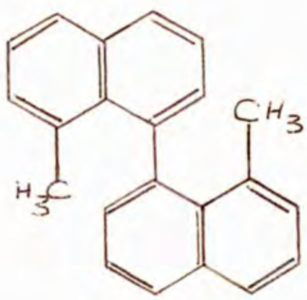




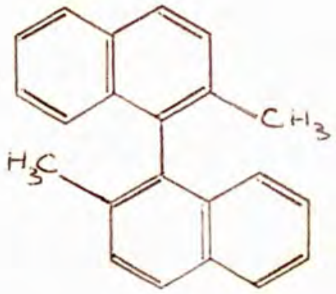
The methyl groups in 8, 8'-dimethyl-1,1'-binaphthyl (A) are nearer the centres of opposite naphthalene residues than are those of 2, 2'-dimethyl-1,1'-binaphthyl (B).

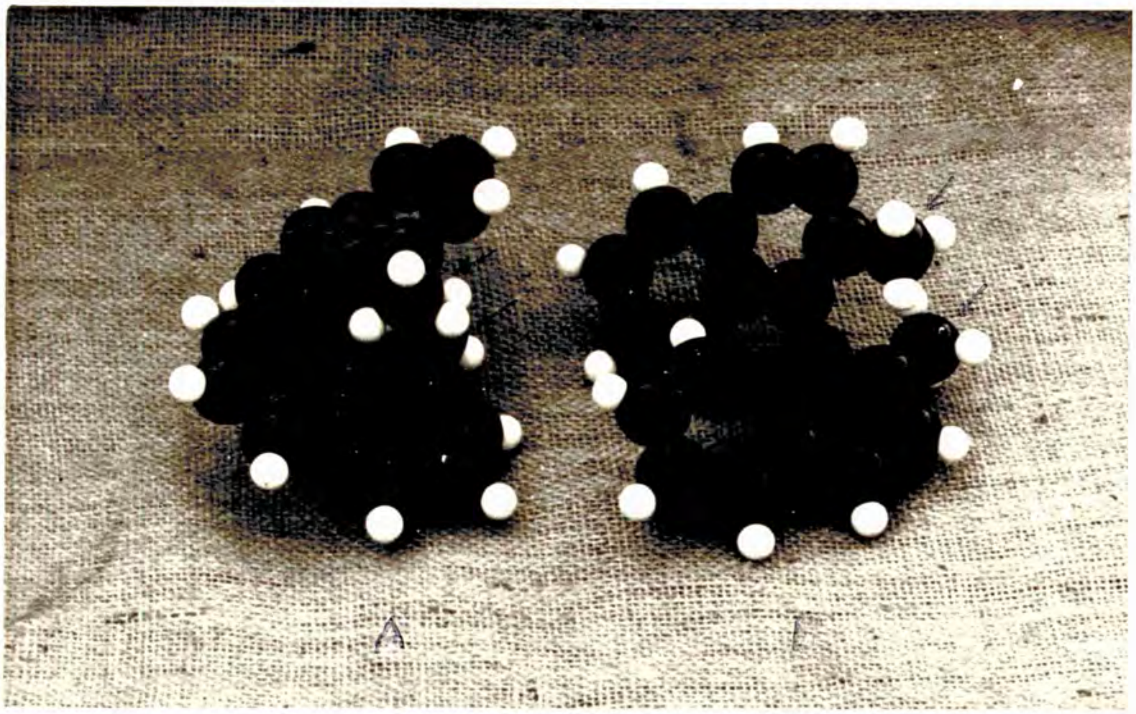
<u>Cis</u> conformations of

A



B



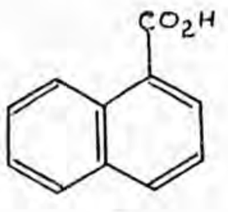


In this conformation it is found that the methyl groups in 8,8'-dimethyl-1,1'-binaphthyl are held above and nearer the centre of the opposite naphthalene ring than those of 2,2'-dimethyl-1,1'-binaphthyl.

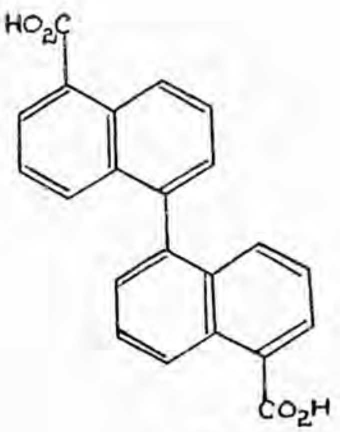
that there is less long-range shielding in 2,2'-dimethyl-1,1'-binaphthyl than in 8,8'-dimethyl-1,1'-binaphthyl. Classical models show that each methyl group in the former compound is further away from the ring centre of the opposite naphthalene nucleus than in the latter compound. This explains the lower long-range shielding in 2,2'-dimethyl-1,1'-binaphthyl.

The effects of the distance of a proton from the aromatic nucleus, on the long-range shielding is clearly shown by the ditolyls. 2,2'-Ditolyl, XVII, gives a $-CH_3$ proton signal at τ 7.99 whereas toluene gives this signal at τ 7.66. There is, therefore, long-range shielding of the $-CH_3$ protons by the benzene ring current fields. However, in 3,3-ditolyl, XVIII, each methyl group is further away from the opposite ring and hence there is less long-range shielding and the $-CH_3$ proton signal appears at τ 7.76. 4,4'-Ditolyl; XIX, gives a $-CH_3$ proton signal at τ 7.66, as does toluene, thus indicating the absence of long-range shielding of the $-CH_3$ protons in the molecule.

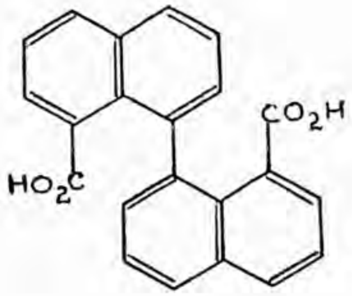
Carboxylic acids:



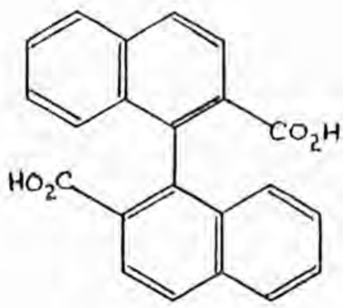
I



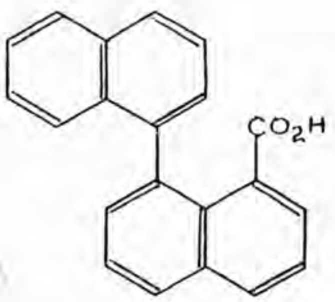
II



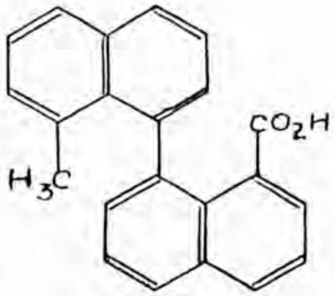
III



IV



V



VI

In non-polar solvents (e.g. CCl_4) the carboxylic proton frequencies are invariant with the concentration (C.M.Huggins, G.C.Pimentel and J.N.Shoolery, J. Phys. Chem., 1956, 60, 1311; A.D.Cohen and C.Reid, J. Chem. Phys., 1956, 25, 790). This is the result of the tendency of the carboxylic acids to form stable dimers. However, in polar aprotic solvents, particularly those which can act as proton acceptors, the dimers are less stable and the carboxylic proton frequencies are concentration dependent. Since a polar solvent was used for the above acids, a valid comparison of the positions of the hydroxylic proton signal in the series could not be made.

J.T.Arnold and M.E.Packard (J. Chem. Phys., 1951, 19, 1608) observed that the chemical shift of the proton signal of the ethanol OH group was temperature dependent whereas under the conditions of resolution employed in the experiment no temperature dependence of the CH_2 and CH_3 proton signals was observed. They found that an increase of temperature from 160 to 350°K caused the OH proton signal to shift towards that of the CH_2 group i.e. to higher fields. They also found that dilution by solvents had an effect similar to that of raising the temperature e.g. for a 10% solution of ethanol in carbon tetrachloride the chemical shift difference between the OH and CH_2 signals was very nearly that of pure alcohol at its boiling point.

These results were interpreted by U. Liddel and N.F. Ramsey (J. Chem. Phys., 1951, 19, 1608) on the basis that the existence of a temperature dependence of the resonance signal can be understood if there are alterative molecular states whose energy separation is of the order of kT. Since alcohol forms hydrogen bonds involving the hydrogen of the OH group, this hydrogen should experience a different magnetic shielding in the associated and unassociated states. If the correlation time related to the lifetimes of the two states is sufficiently small (less than a millisecond), the hydrogen resonance will be observed at the frequency corresponding to the average shielding for the two states. Since temperature changes will alter the population of the associated and unassociated states, the resonance frequency will be temperature dependent . Solvent dilution, because it also causes dissociation of the hydrogen bonds, will have an effect equivalent to that of raising the temperature.

The temperature dependence of the hydroxylic protons of the acids, I-VI is interesting. The hydroxyl proton signal of α-naphthoic acid, I (SPEC I) was not affected by the increase in temperature. This suggests lack of intermolecular association and proton exchange with the solvent (deuterated dimethylsulphoxide). The hydroxylic proton signal of 1,1'-binaphthyl-5,5'-dicarboxylic acid, II (SPEC.2.) is also not affected by increase in temperature, indicating the lack of intermolecular association and proton exchange. Intramolecular hydrogen bonding is not possible with II since the situation of the carboxyl groups in not favourable to this. Since the carboxyl group in these two compounds, I and II, are not as sterically hindered as those in the acids III-VI, any difference in the behaviour of the carboxylic protons in these two groups of compounds, is a result of some intramolecular effects, e.g. intramolecular hydrogen bonding, Any intermolecular effect will affect I and II much more than III, IV, V and VI in which the -COOH groups are in sterically hindered positions.

The hydroxylic protons in 1,1'-binaphthyl-8,8'-dicarboxylic acids, III (SPEC .3.) and the 2,2'-diacid, IV, (SPEC. 4.) give rise to a broad (hump-like) signal at lower temperatures. As the temperature is raised, the signal sharpens and shifts to higher fields. On lowering the temperature (SPEC. 3. for the 8,8'-diacid) broadens again. However, with 1,1'-binaphthyl-8-carboxylic acid, V (SPEC. 5.) and 8'-methyl-1,1'-binaphthyl-8-carboxylic acid, IV (SPEC. 6.), each of which has one carboxyl group in the 8-position, raising the temperature has the effect of broadening the signal and shifting it to lower fields. On lowering the temperature the signal sharpens. It is therefore observed that the temperature dependence behaviour of the hydroxylic protons of V and VI is the opposite of that of the hydroxylic protons of III and IV. This can be a result of possible differences in the nature of hydrogen bonding in these compounds. It is possible that in III and IV, there is intermolecular hydrogen bonding between the carboxyl groups, whereas in the V and VI, the hydrogen bonding is between the carboxyl hydrogen and the π-electron system of the opposite naphthalene nucleus. It might be possible to establish the exact nature of the differences between the carboxyl proton frequencies of III and IV and those of V and VI by a thorough investigation of the temperature and concentration dependence of these protons.

10. MASS SPECTRA OF 2,2'-DIMETHYL- AND 8,8'-DIMETHYL-1,1'-BINAPHTHYL

(i) Introduction:

Mass spectrometry has become increasingly important in Organic chemistry. The functions of the Mass Spectrometer are to produce positive ions from the substance under investigation, to resolve these ions into a series of ion beams which are homogeneous with respect to their mass/charge ratio, and to measure the relative abundance of the ions in these beams.

Theory and operation:

The substance under investigation is introduced into the ionisation chamber of the spectrometer where it is bombarded with an electron beam of variable energy (50-70-eV). The material is ionised by electron impact forming positive ions in accordance with the equation:

$$e + XY \longrightarrow XY^{+} + 2e$$

This ion formation occurs in the neighbourhood of a positively charged plate, the ion-accelerating plate, whose potential is also variable, but customarily kept at 2KV. The ions are repelled from this plate in accordance with the equation governing electrostatic repulsion:

$$\tfrac{1}{2}\,Mv^{2} = eV \qquad \ldots\ldots\ (1)$$

where M is the mass of the ion, e the electronic charge, V the potential of the ion-accelerating plate and v the velocity of the particale. As it passes through the source the beam of ions is focused on an exit slit by means of subsidiary, charged plates. The ions now pass between the poles of an electromagnet where they are deflected along a circular path according to the relation:

$$\frac{Mv^2}{r} = Hev \quad \ldots\ldots (2)$$

where r is the radius of the path and H is the field strengh of the magnet.

From equations (1) and (2)

$$\frac{M}{e} = \frac{H^2r^2}{2V} \quad \ldots\ldots (3)$$

From equation (3) it follows that, for given values of H and V ions having different values of M/e follow different paths in the intrument. The magnetic deflection also has a focusing effect upon the ion beams, and beams that are homogeneous with respect to their mass/charge ratio converge to the same focus.

The ion-accelerating voltage and the magnetic field are so adjusted that a selected beam of ions passes through a slit, placed at its focus, and falls on the collector - a Faraday cage which is behind the slit.

Equation (3) shows that the values of the ion-accelerating voltage and the field strength of the magnet will determine the mass/charge ratio of the ion beam received at the collector.

A spectrometer of this type, in which the ions, once formed, are focused only by the action of the magnetic field are known as single-focusing instruments.

With double-focusing instruments, the ion beam is brought to a focus following electrostatic repulsion and before the ions are magnetically deflected.

Time-of-flight instruments have recently been introduced. In such instruments the ions formed by electron bombardment of thematerial are admitted to the analyser by means of an electron device which allows a sample of all the ions present to enter at the same instant. The analyser is a tube at the end of which is the collector. An electronic shutter is in front of the collector, and hte opening and closing of this shutter is controlled by a devise for admitting the ions to the analyser. The ions entering the tube, having different masses, will travel down the tube with different velocities by reason of the law of electronic repulsion (equation (1)). The time taken for an ion of any given mass/charge ratio to arrive at the shutter in front of the collector can be determined, and the time delay between admitting the ions and the opening of this shutter can be adjusted to allow ions of selected mass/charge ratio to reach the collector. By varying the time lag all the ions are allowed in turn to arrive at the collector. The number of ions of each M/e arriving at the collector may be computed.

In order to produce an ion by electron bombardment the electron must strike the molecule with sufficient energy to expel another electron. Since the energy of the electron beam can be varied, it is possible to determine the minimum energy necessary to produce ions from a given material (ionisation potential). This can be done by observation of the ion current at various electron energies.

As the ionisation potential energy is increased, the abundance of the molecular ion also increases, until the energy is sufficient to cause dissociation of the molecular ion, a dissociation which begins at a definite energy value (the appearance potential of the fragment ion) to yield an ion and a neutral radical. This process can be represented thus:

$$e + XY \longrightarrow XY^{+} + 2e$$

$$XY^{+} \longrightarrow X^{+} + Y \text{ or } X + Y^{+}$$

Given sufficient energy both possibilities occur, but normally one of these dissociations will have a lower appearance potential and it will therefore be the one favoured.

Cracking patterns

As the electron energy is further increased, the fragmentation of the molecule becomes more and more extensive until the energy imparted to the molecule becomes sufficient to allow fragmentation of any bond, and under such conditions organic molecules fragment in very many ways to give a great variety of ions of different abundances. This is the cracking pattern and individual compounds have distinct cracking patterns, if not in the mass/charge ratios of the ions at least in their relative intensities.

Application of mass spectrometry.

To the organic chemist, the most interesting application of mass spectrometry is its use in the determination of molecular structure.

It can be used to determine molecular weights, deduce molecular formulae, elucidate structural details (functional groups) and to decide between alternative structures.

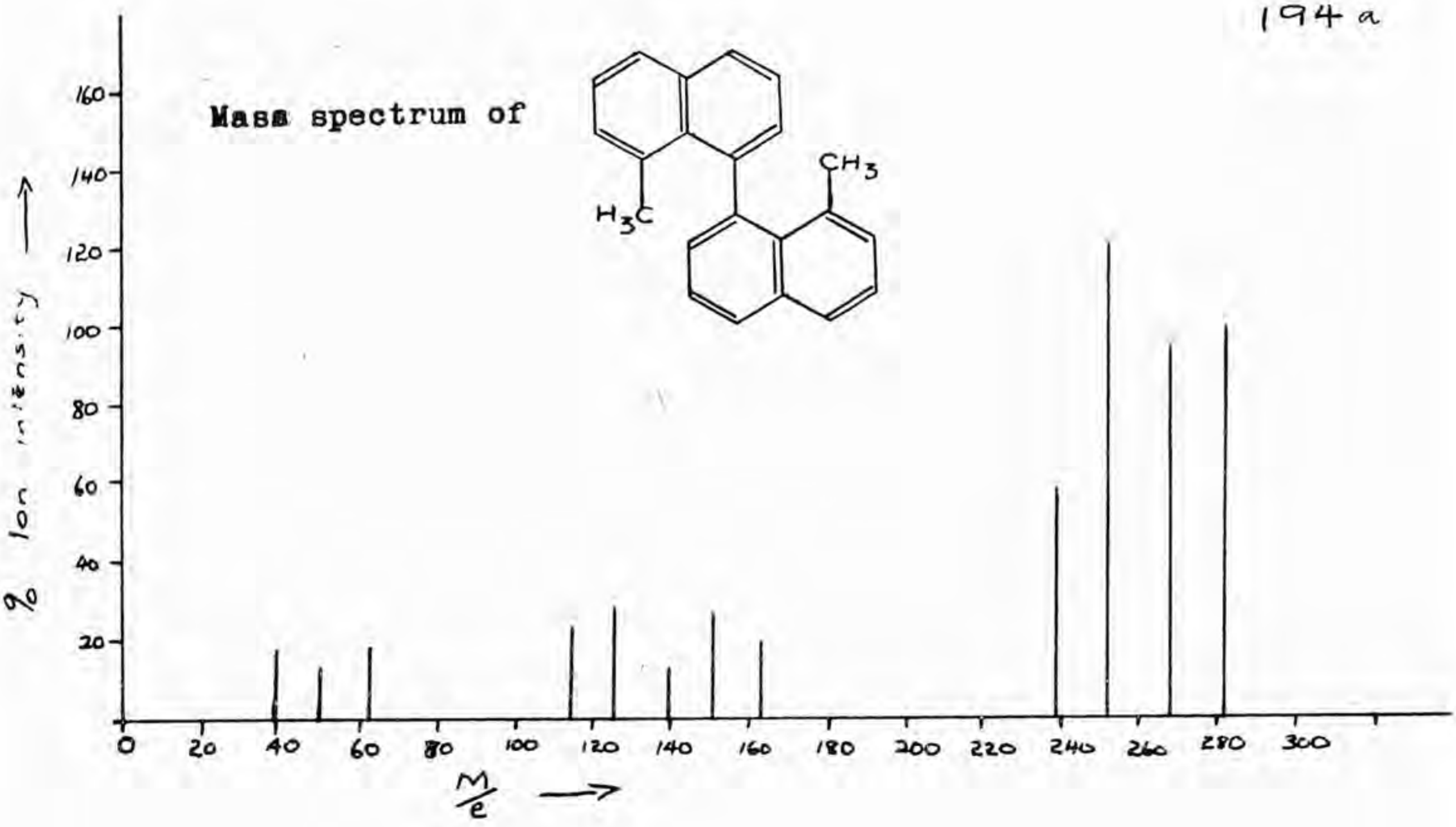
The data can be presented in a tabular form, listing the mass numbers of the peaks and their intensities. The latter are expressed in relation to the most intense peak of the spectrum which is assigned an arbitrary value of 100.

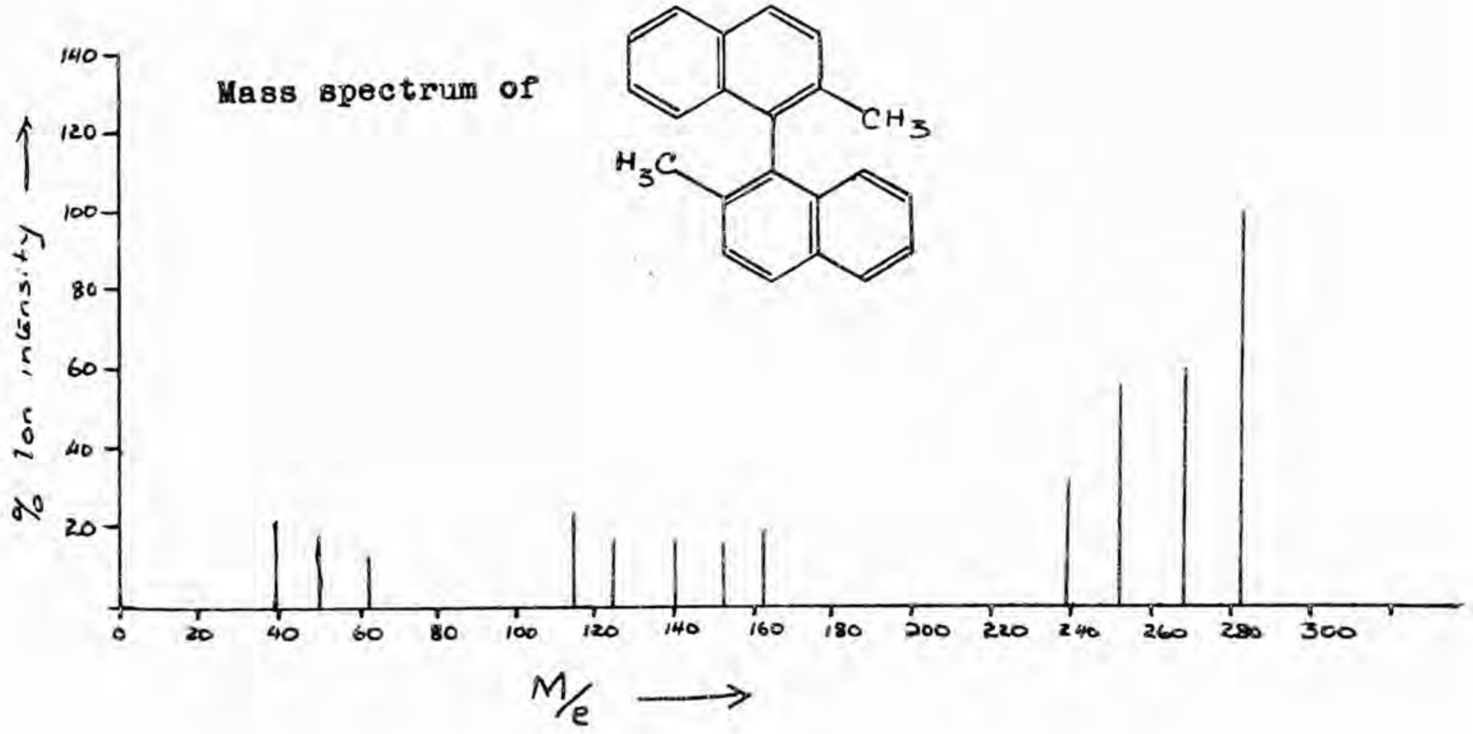
The mass spectrum can also be presented in the form of a drawing of relative abundance (ordinate) of the fragments to their mass-to-charge ratio (abscissa). The relative intensities of the peaks are thus clearly recognisable as are their masses.

In comparing individual spectra, the relationship between the intensity of a given peak and the total intensity of the spectrum i.e. the sum of the intensities of all peaks is important. The intensity of a peak, in per cent of the total ionisation then indicates the extent to which the initially formed molecular ions decompose to this fragment. This type of intensity is normally required in the interpretation of spectra. To obtain this value, it is necessary to measure all peaks for this summation. However, this is not possible if the spectrum was not scanned over the entire range for M/e =1 to the molecular weight.

Object of present work:

The mass spectra of 2,2'-dimethyl- and 8,8'-dimethyl-1,1'-binaphthyl were determined in order to compare the fragmentation patterns of these two compounds which differ in the orientation of the methyl groups. The difference in the orientation of the methyl groups gives rise to differences in the steric strain in the molecules. It was thought that steric strain might influence the ease of fragmentation at C_{Ar} —— CH_3 bonds and at the interannular bond.


Mass spectrum of
CH3
H3C
% Ion intensity →
160
140
120
100
80
60
40
20
0
20
40
60
80
100
120
140
160
180
200
220
240
260
280
300
M/e →


Mass spectrum of
CH3
H3C
% Ion intensity →
140
120
100
80
60
40
20
0
20
40
60
80
100
120
140
160
180
200
220
240
260
280
300
M/e →

Results

% Intensities of ions of different masses:

	8,8'-Dimethyl-1,1'-binaphthyl	2,2'-Dimethyl-1,1'-binaphthyl
M/e	268.3	268.3
% Intensity	93.3	60.0
M/e	252.3	252.3
% Intensity	120.0	54.5
M/e)	141.2	141.2
% Intensity	11.1	16.4
M/e	126.2	126.2
% Intensity	26.7	18.2

The intensities tabulated above were more important in the discussion on this work and they were calculated as a percentage of the intensity of the molecular ion of M/e 282.2 (taken as 100%). However, in the spectrum, the other minor peaks are also given. Using the 1,1'-binaphthyl 10n as the 100% intensity peak for the 8,8'-dimethyl-1,1'-binaphthyl would make the comparison between the two compounds difficult.

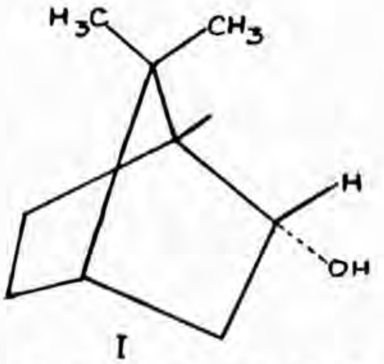
(iii) DISCUSSION OF RESULTS: recognition of steric strain.

K. Beimann (*Mass Spectrometry*, 1962, p.144, McGraw-Hill Book Company, Inc.,) has discussed the mass spectra of isomeric compounds. The mass spectra of optical isomers and of the corresponding racemic compounds, are identical. This is due to the fact that in the both *d*-form and *l*-form all bond energies and all fragments that can be formed from them are identical.

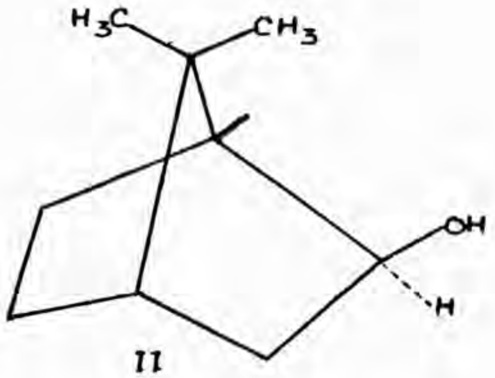
The mass spectra of aliphatic diastereoisomers are usually also similar and this is taken to be due to a large extent to the ease of rotation along the bonds attached to the asymmetric centres.

However, the mass spectra of some aliphatic compounds show significant differences and it is possible in certain cases to deduce the stereochemistry of the molecule from the mass spectra. K. Biemann and J. Seibl (*J. Amer. Chem. Soc.*, 1959, *81*, 3149) investigated the mass spectra of epimeric cyclic alcohols and they observed that the spectra of epimers, which are in general very similar as is to be expected, differ distinctly in the abundance of the molecular ion, M^+. This peak was found to be more intense in the spectrum of the less crowded epimer (equatorial hydroxyl) of secondary alcohols, whereas in tertiary alcohols, the epimer with the axial hydroxyl and equatorial alkyl group exhibits the more intense M^+ peak.

For borneol I, the intensity of this peak was found to be 0.17 percent, while it is only 0.14 percent for isoborneol, 11.



I



II

The authors interpreted this effect as a consequence of a different rate of decomposition into fragments of the molecular ion (M^+), formed on electron impact, which is slower in the case of the more stable ion M^+.

These findings were best explained on the assumption that the strain relief experienced by the molecular ion upon fragmentation provides a greater driving force in the more crowded molecular ion than in the less crowded one. The two other steps in the overall reaction,

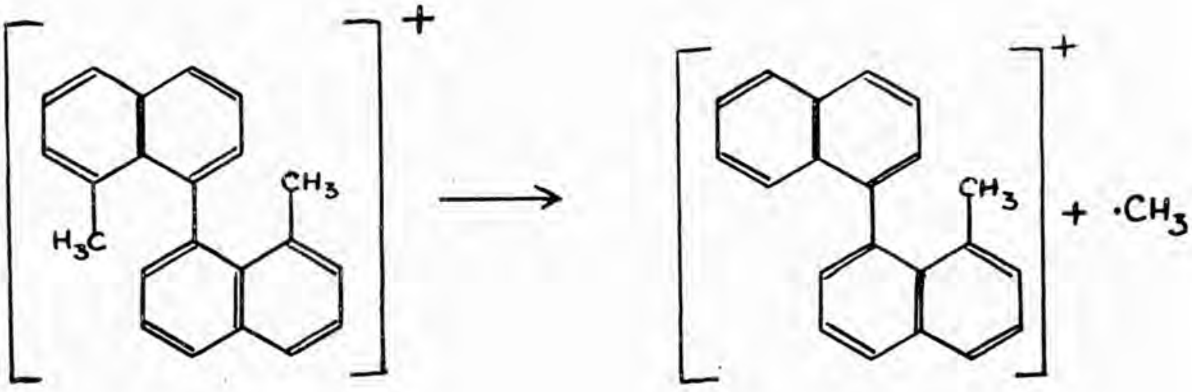
$$M \longrightarrow M^+ \longrightarrow F^+$$

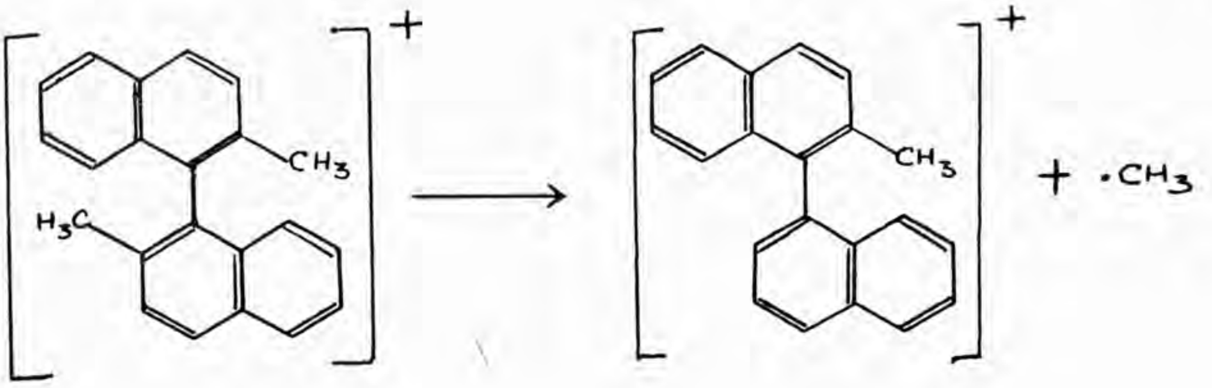
i.e. the ionisation of the molecule and the driving force due to the energies of the fragments, must be the same in both epimers because the stability of the fragments produced must be the same since the fragments themselves are identical in both cases, as evidenced by the otherwise great similarity of the mass spectra. Hence a secondary alcohol with the hydroxyl group in the more crowded position will yield a molecular ion which has a greater tendency to decompose (and show less intense M^+ peak) than its less crowded epimer. Since a hydroxyl group requires less space than an alkyl group, the situation is reversed in the case of tertiary alcohols.

The authors also found that the spectra of the acetates of secondary alcohols show the same effect, enhanced due to the larger size of the acetoxy group compared with hydroxyl. The main difference in the decomposition of M^+ appeared to be in the path leading to the fragment of M-18 (or M-60 for the acetates) whose abundance was in turn greater for the more crowded epimer.

It can therefore be observed that the method of comparing intensities can be used to compare the magnitude of steric strain in two molecules, and therefore the ground states of such strained systems.

The results from the present work show that the percentage intensity of the ion formed from the molecular ion M^+, by loss of a methyl group relative to that of the parent ion itself, is 93.3 for 8,8'-dimethyl-1,1'-binaphthyl and 60.0 for 2,2'-dimethyl-1,1'-binaphthyl. This stage can be represented as:





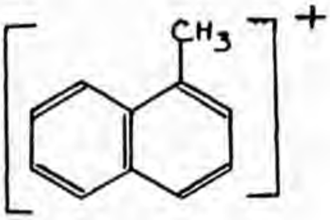
However, the spectra are similar, indicating that the fragmentation process is the same in both compounds. The above observations, therefore indicate that the molecular ion formed from 8,8'-dimethyl-1,1'-binaphthyl and the strain relief experienced by the molecular ion upon fragmentation provides the greater driving force in the case of 8,8'-dimethyl-1,1'-binaphthyl than in the latter.

Methyl groups in α-positions possess greater conjugative interaction than do those in β-positions. It should therefore be easier to remove β-methyl groups from the naphthalene residues, than it is with α-methyl groups. It is therefore reasonable to suppose that the above observation is due to greater steric strain in 8,8'-dimethyl -1,1'-binaphthyl.

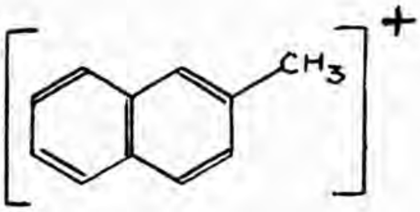
Moreover, there is more 1,1'-binaphthyl ion produced from 8,8'-dimethyl-1,1'-binaphthyl than is the case with 2,2'-dimethyl-1,1'-binaphthyl. This follows from the fact that the loss of the second methyl group is easier in the former compound than is in the latter and it is also consistent with the greater abundance of the 8-methyl-1,1'-binaphthyl ion. It should be noted that this ion, formed from 8,8'-dimethyl-1,1'-binaphthyl by loss of one methyl group is more sterically strained than that formed from 2,2'-dimethyl-1,1'-binaphthyl. This is due to the fact that the remaining CH_3 group, in the 8-position induces greater steric strain in the molecule than it does when in the 2-position.

The fragments which are lost as free radicals, do not give rise to peaks. Hence methyl groups which show no observed peak on the spectra, are lost as free radicals.

It is also observed that fission of the interannular bond is less easy with 8,8'-dimethyl-1,1'-binaphthyl than it is with 2,2'-dimethyl-1,1'-binaphthyl, as seen from the percentage intensities of the ion of Mass = 141 of the fragments:



and



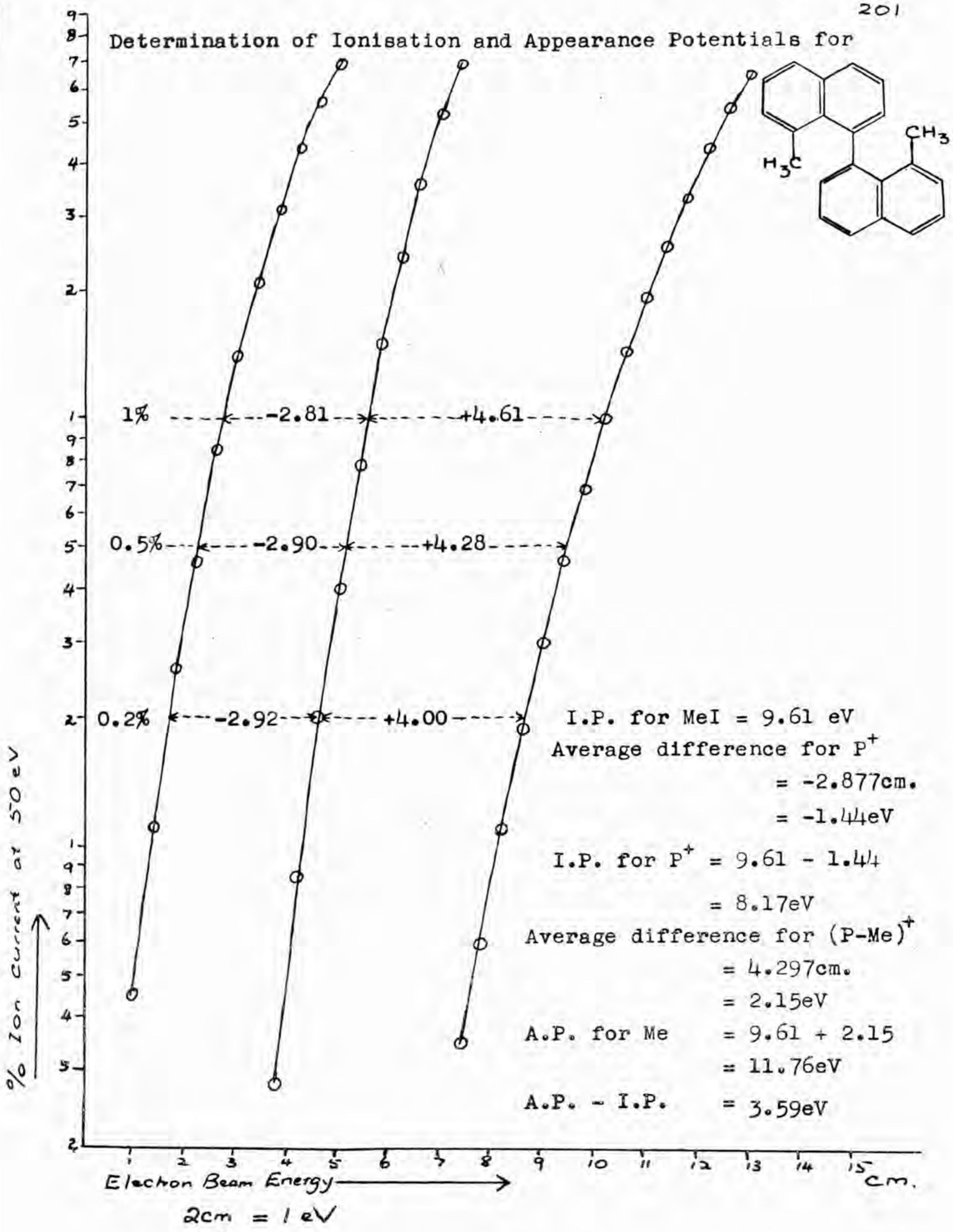
The percentage intensities are 11.1 and 16.4 respectively. This difference can be explained on the basis that greater ease of loss of a methyl group from the molecular ion, M^+, of 8,8'-dimethyl- makes this step much faster than it does in the case of 2,2'-dimethyl-1,1'-binaphthyl, and because of this, the intensity of the fragment of Mass = 141 is less in the spectrum of the former compound.

The ion at M/e = 126.2 (the naphthalene ion) formed from 8,8'-dimethyl-1,1'-binaphthyl has a 26.2% intensity whereas that for 2,2'-dimethyl-1,1'-binaphthyl has an intensity of 18.2%. This can be due to greater abundance of the 1,1'-binaphthyl ion in the former case, which can fragment to give more of the naphthalene ion than in the latter case.

Determination of appearance potentials would be helpful in showing the difference in the easiness of loss of methyl groups from the two compounds and this might help to confirm the greater steric strain in 8,8'-dimethyl-1,1'-binaphthyl in its ground state.

Interpretation of results below M/e = 100 is not easy because the fragmentation pattern is not well known. But it is observed that the ratio of the intensities of the peaks for one compound, are reversed in the other compound.

Determination of Ionisation and Appearance Potentials for



I.P. for MeI = 9.61 eV

Average difference for P^+

= -2.877cm.

= -1.44eV

I.P. for P^+ = 9.61 - 1.44

= 8.17eV

Average difference for $(P-Me)^+$

= 4.297cm.

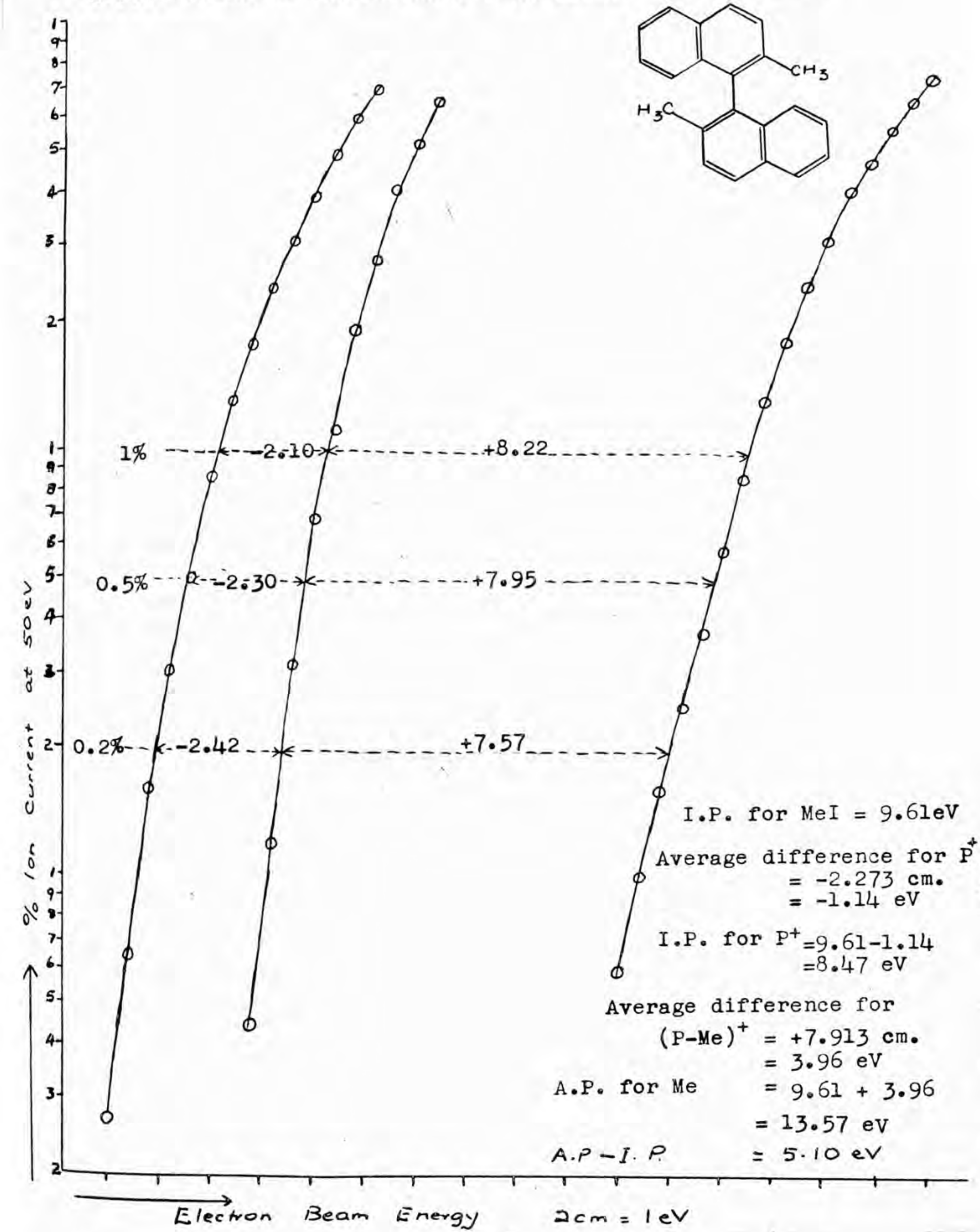
= 2.15eV

A.P. for Me = 9.61 + 2.15

= 11.76eV

A.P. - I.P. = 3.59eV

Determination of Ionisation and Appearance Potentials for



I.P. for MeI = 9.61eV

Average difference for P^+
= -2.273 cm.
= -1.14 eV

I.P. for P^+=9.61-1.14
=8.47 eV

Average difference for
$(P-Me)^+$ = +7.913 cm.
= 3.96 eV

A.P. for Me = 9.61 + 3.96
= 13.57 eV

A.P – I. P. = 5.10 eV

Ionisation and appearance potentials for the methyl groups in 2,2'-dimethyl-1,1'-binaphthyl and 8,8'-dimethyl-1,1'-binaphthyl.

Results:

	2-2'-Dimethyl-1,1'-binaphthyl	8,8'-Dimethyl-1,1'-binaphthyl
Ionisation Potential (I.P)	8,47eV	8.17eV
Appearance Potential (A.P)	13.57eV	11.76eV
A.P.-I.P. =	5.10eV	3.59eV

The results are shown on the graph on p. 201 and 202 each of which is a plot of percentage ion current at 50eV against electron beam energy.

Discussion

It is observed that the I.P. for 2,2'-dimethyl-1,1'-binaphthyl (8.47eV) is higher than that for 8,8'-dimethyl-1,1'-dinaphthyl and this is taken to indicate that in the former compound there is less electron delocalisation as a result of less planarity, and the removal of the electron is therefore more difficult than is the case with the latter compound, which as a result of greater planarity has greater delocalisation.

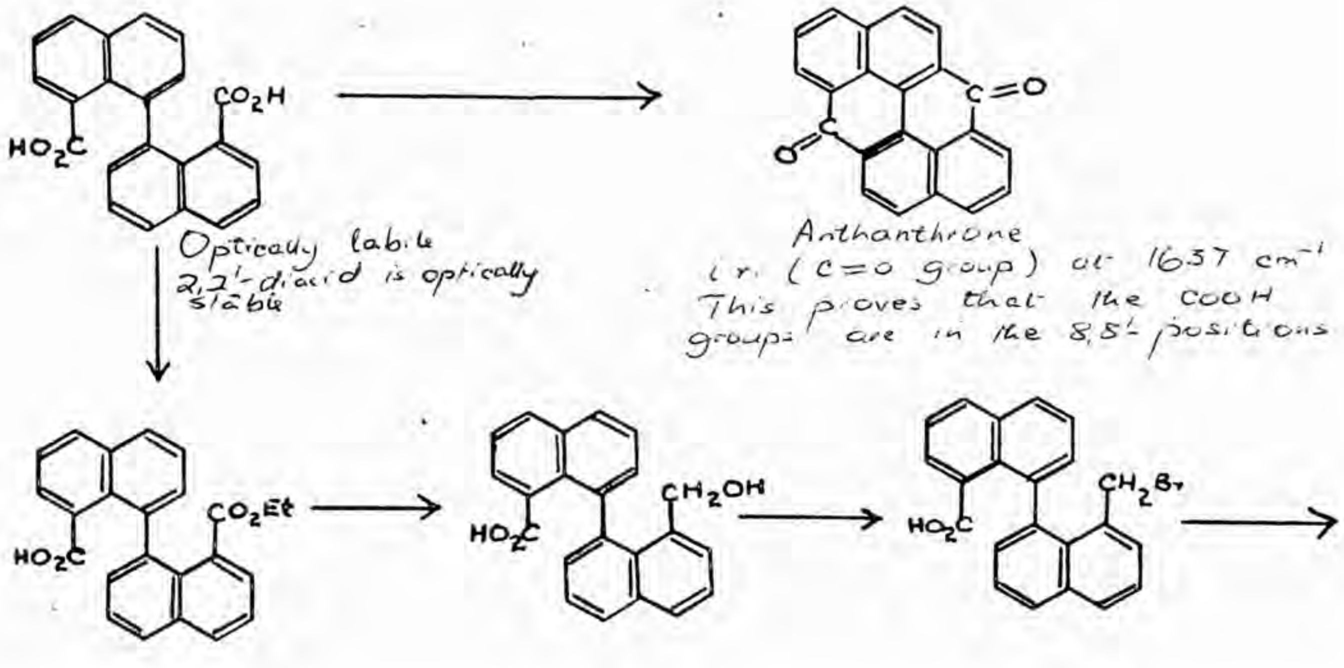
Moreover, the difference between the I.P. and A.P. (A.P. for the methyl group) is 5.10eV for 2,2'-dimethyl-1,1'-binaphthyl and it is larger than that for 8,8'-dimethyl-1,1'-binaphthyl (3.59eV). This indicates that more energy is required to remove a $-CH_3$ group from the 2,2'-dimethyl-1,1'-binaphthyl ion (to give the $P-CH_3$ ion) than is the case with the 8,8'-dimethyl-1,1'-binaphthyl ion. This is consistent with the idea that 8,8'-dimethyl-1,1'-binaphthyl is a much more sterically strained molecule than 2,2'-dimethyl-1,1'-binaphthyl and it therefore can lose its $-CH_3$ group much more easily than 2,2'-dimethyl-1,1'-binaphthyl can.

These results confirm the deductions obtained from the comparison of the percentage intensities obtained from the mass spectra.

(11) GENERAL CONCLUSIONS

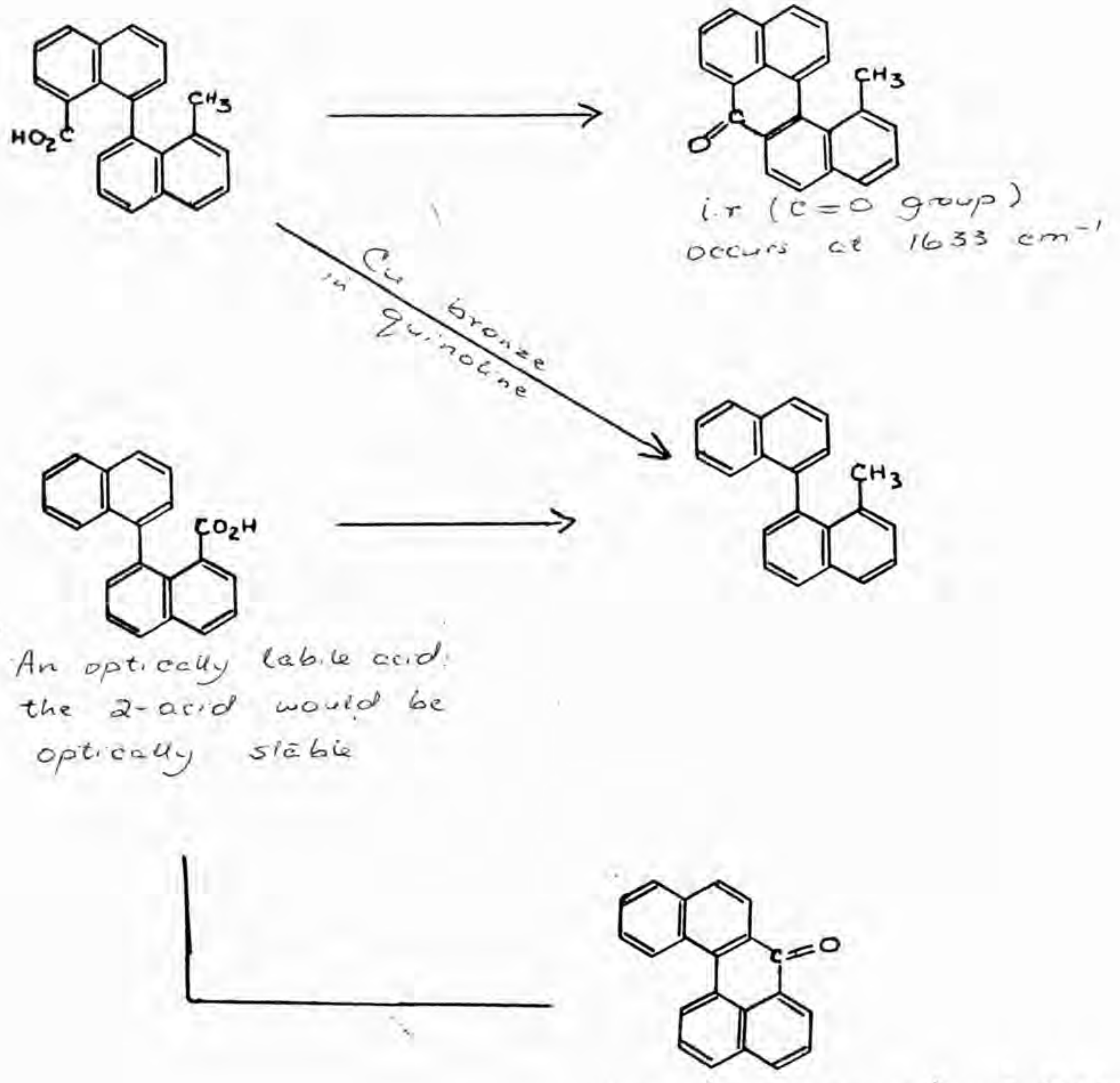
The optical stability study of 8'-methyl-1,1'-binaphthyl-8-carboxylic acid and comparison with that of 8-methyl-1,1'-binaphthyl has led to the conclusion that the carboxyl group affects the steric pressures in the ground state of the molecule but not further in the transition state for racemisation. Differences in the ground state strain of the molecules had already been offered as a partial explanation for differences observed between the optical stabilities of 8,8'-substituted and 2,2'-substituted 1,1'-binaphthyls and the present work supports this conclusion.

The remarkable near-identity of the racemisation parameters of the compounds with and without the carboxylic acid group, made confirmation of the orientation of this group a necessity. The following raction sequences do this:-



Optically labile
2,2'-diacid is optically stable

Anthanthrone
i.r. (C=O group) at 1637 cm⁻¹
This proves that the COOH groups are in the 8,8'-positions



i.r (C=O group) occurs at 1633 cm^{-1}

An optically labile acid: the 2-acid would be optically stable

i.r. (C=O group) at 1640 cm^{-1} Proves that the COOH group is in the 8-position

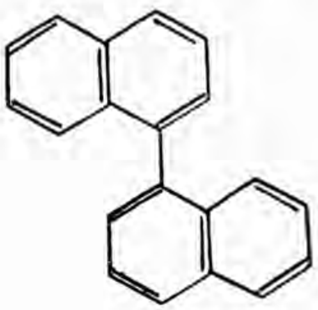
2,2'-Dimethyl-1,1'-binaphthyl did not racemise even when kept at 290° for about 40 hours. At this temperature it started to decompose. This result is striking in comparison with the E for racemisation (27.58Kcal. mole^{-1}.) for the 8,8'-isomer.

From ultraviolet and nuclear magnetic spectral results, it can be concluded that the ground state of 8,8'-substituted 1,1'-binaphthyls is much more strained than that of 2,2'-substituted 1,1'-binaphthyls, and that in order to relieve this steric strain the substituents undergo in-plane and out-of-plane distortions. As a result of these distortions, the naphthalene residues in the 8,8'-substituted 1,1'-binaphthyls lie nearer to a planar state than those of the 2,2'-substituted 1,1'-binaphthyls. Moreover, a second substituent increases the distortions.

Mass spectral results, show that the C_{Ar}—CH_3 bond breaks more easily in 8,8'-dimethyl-1,1'-binaphthyl compared to that in 2,2'-dimethyl-1,1'-binaphthyl and shows that the former has greater ground state strain than the latter.

The results obtained from O.R.D. and C.D. curves has enabled, by relation to previously established configurations, assignments of configurations to the 1,1-binaphthyls.

The following compounds have been newly assigned the S-configuration:



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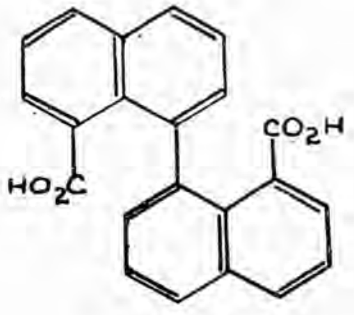

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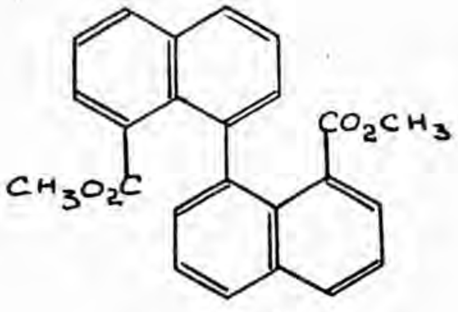

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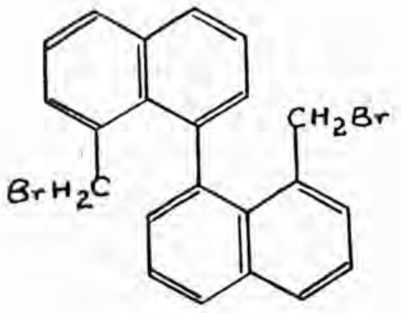

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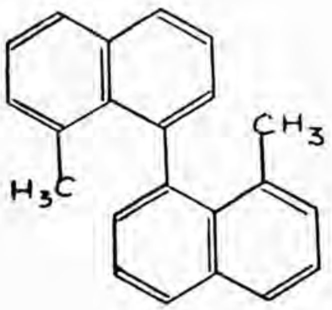


(+)

It has been observed that the nature of substituents does not alter the sign of the Cotton effect of the 1,1'-binaphthyl system, in the region 220 - 231mμ. Moreover, positions of substituents on the naphthalene nucleus do not affect the sign of the Cotton effect of the 1,1'-binaphthyl system. 1,1'-Binaphthyls with the same configurations and having non-chromophoric groups have optical rotations of the same sign. Chromophoric groups appear to change the sign of optical rotation of substituted 1,1'-binaphthyls.

It can therefore be said that substituents affect the ground states of 1,1'-binaphthyls but do not alter the sign of the Cotton effect of the 1,1'-binaphthyl system (hence they do not alter the configurations of these compounds).

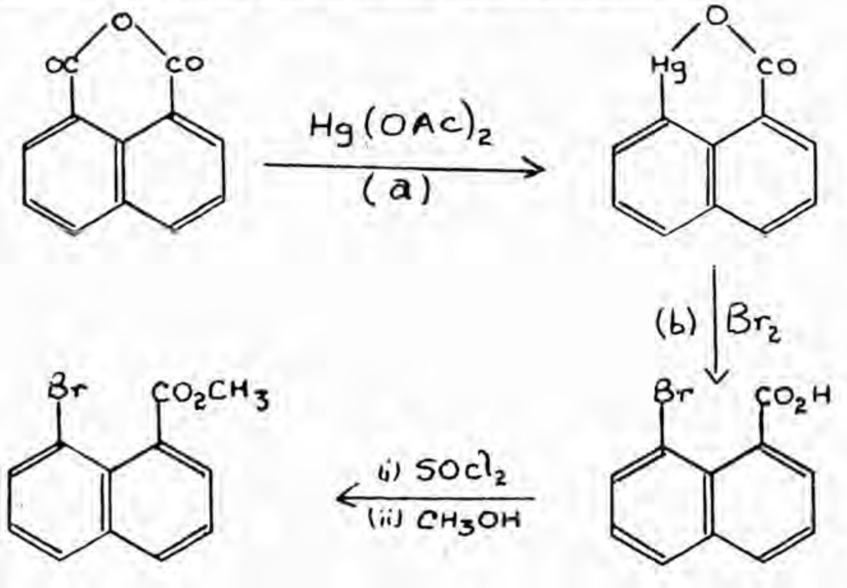
Infrared spectra of pure crystalline racemic and optically active 8,8'-diacids show that a mixture of molecules of opposite configuration (racemic mixture) gives rise to crystals that differ from those formed from molecules of the same configuration, (optically active isomers).

The differences are most obvious in the hydroxyl and carboxyl regions and are taken to be due to differences in hydrogen bonding.

SYNTHETIC EXPERIMENTAL.

Preparation of methyl-8-bromo-1-naphthoate.

Scheme:



8-Bromo-1-naphthoic acid

H.G.Rule, W.Pursell and R.R.H.Brown (*J. Chem. Soc.*, 1934, 168).

A.S.Mellor, *Ph. D. Thesis* (Lond.) 1961.

Y. Badar, *Ph. D. Thesis* (Lond.) 1964.

(a) Mercuri-compound.

Naphthalic anhydride (248g. 1M) was dissolved in aqueous sodium hydroxide (155g. in 6 litres of water) and the solution was filtered through glass wool into a 20 litre flask on a large boiling mantle, and boiled under relux for 15 minutes.

Mercuric oxide (275g. 1.014M) dissolved in diluted acetic acid (200c.c. glacial acetic acid) and 750c.c. of water) was then added and the reaction mixture made acid with glacial acetic acid.

The reaction mixture was then boiled for 90 hours, when no further carbon dioxide was evolved and no mercury was deposited on a copper wire dipped into the reaction mixture, indicating completion of reaction. The product was filtered off, washed with water, and ethanol, then ether and dried. A pale cream coloured solid (445g., 96%) was obtained; (A.S.Mellor, loc. cit., 81.0%).

(b) Bromination of the mercuri-compound:

A stirred suspension of the mercuri-compound (95g.) in acetic acid (300c.c. acetic acid in 50c.c. water) was cooled in a freezing mixture to -10°. To this was added a solution of bromine (34g.) in aqueous sodium bromide solution (150c.c. of a 50% solution), gradually with constant stirring, using a mechanical stirrer. The addition took 2 hours, the temperature being kept below 0°C.

The reaction mixture was allowed to warm to room temperature and then heated slowly to 90°C, after which it was poured into 3 litres of boiling water and filtered as hot as possible. The residue was extracted by boiling with a further 1 litre of water, filtered hot and the filtrate added to the first filtrate.

8-Bromo-1-naphthoic acid was deposited on cooling (51g.) m.p. 169-171°. Recrystallization from benzene gave the bromo acid, 42g. (65.3%) m.p. 174-176° (with shrinkage at 170°).

Conversion of 8-bromo-1-naphthoic acid into methyl-8-bromo-1-naphthoate:

H.G. Rule and A.J.G. Barnet, J. Chem. Soc., 1932, 175.
A.S. Mellor, Ph. D. Thesis (Lond.) 1961.
Y. Badar, Ph. D. Thesis (Lond.) 1964.

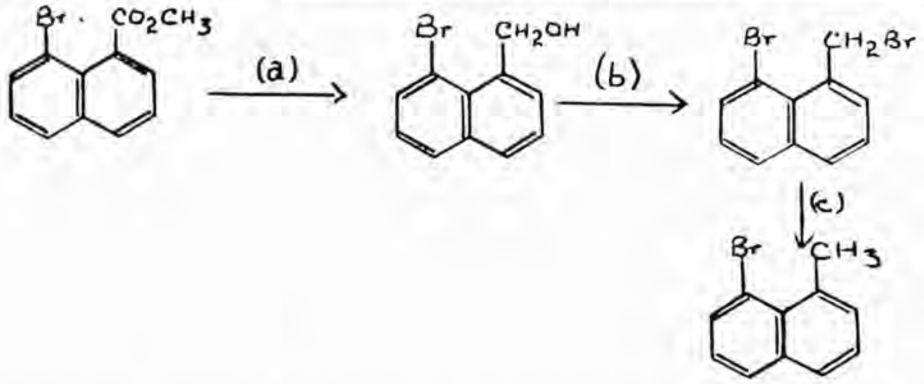
8-Bromo-1-naphthoic acid (109g.) was dissolved in benzene (750c.c.) by boiling under reflux. Thionyl chloride (40c.c.) was added slowly to the boiling solution and the mixture boiled for 4½ hours,

Methyl alcohol (270c.c.) was then added, very cautiously, and the mixture boiled for a further 45 minutes. The benzene solution was then washed twice with water, twice with 10% aqueous sodium carbonate, and again with water. After drying with anhydrous magnesium sulphate, the benzene was distilled off and the ~~reamineder~~ remainder distilled under reduced pressure (4 mm.) using an air condenser. Methyl 8-bromo-1-naphthoate distilled over at 180-200°/4mm. as a pale yellow oily liquid which solidified on cooling and leaving to stand overnight, to give a pale granular solid.

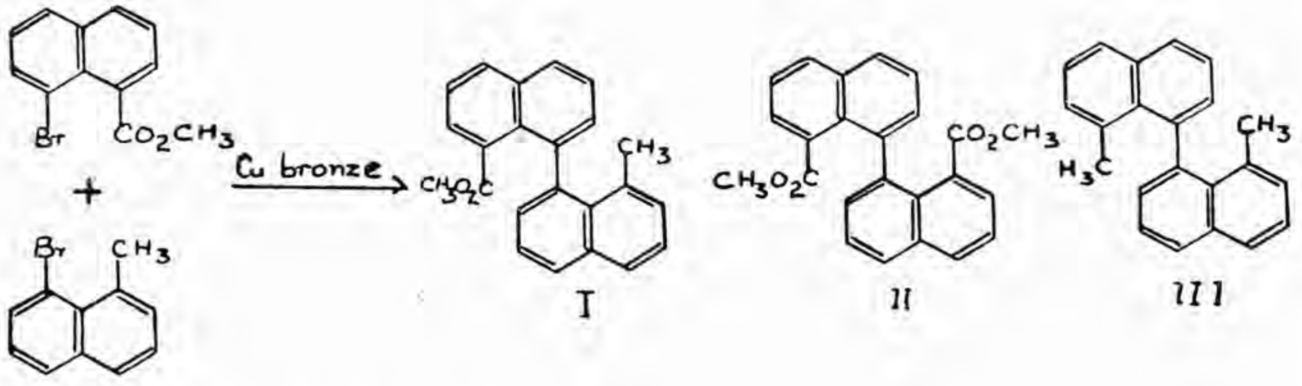
Yield 93g. (80.0%), m.p. 38-39°.

Attempted preparation of 8-methyl-1-bromonaphthalene:

Scheme:



This preparation was following a report by J. Karabatos, R.L. Shore and S.E. Scheppele (Tet. Letts., 1964, 2113) on lithium aluminium hydride reductions of esters containing an aromatic halogen. (An Ullman reaction between 8-methyl-1-bromonaphthalene and methyl-8-bromo-1-naphthoate was expected to give the following mixture of products;



from which I could be isolated.)

However, an attempt to prepare 8-methyl-1-bromonaphthalene gave α-methylnaphthalene. This is possibly due to peri-interaction which forces the bromine out of the plane of the aromatic nucleus thus rendering it susceptible to replacement by hydrogen. For comparison α-methylnaphthalene was prepared from 1-naphthoic acid and the product gave identical gas chromatograms.

(a) Attempted conversion of Methyl 8-bromo-1-naphthoate into 8-hydroxymethyl-1-bromonaphthalene:

J. Karabatsos, R.L. Shore and S.E. Scheppele, *Tet. Letts.*, 1964, 2113.

E.D. Bergman and J. Szuskovicz, *J. Amer. Chem. Soc.* 1951, *73*, 5153.

D.M. Hall and E.E. Turner, *J. Chem. Soc.*, 1955, 1242.

Lithium aluminium hydride (29g. 3M) was weighed in the fume cupboard and quickly covered with sodium-dried ether (750c.c.) in a three litre, three neck flask equipped with a condenser and a dropping funnel. Methyl-8-bromo-1-naphthoate (6.6 g.) in sodium-dried ether was added, adding 1L of ether in all (making 1750c.c. ether in the flask).

The mixture was then heated on a water bath for 1½ hours. In order to decompose excess $LiAlH_4$, wet ether and then water, a drop at a time, was added, until no further bubbles were observed. Dilute sulphuric acid (2N) was then added. The ethereal layer was separated, the aqueous layer extracted with ether and the extract added to the major ethereal solution. After washing the combined ethereal solution with water, it was dried over anhydrous magnesium sulphate, and the ether was distilled off, to leave a liquid product. Thin layer chromatography indicated two products in unequal proportions.

(b) The total product from (a) was dissolved in boiling glacial acetic acid (100c.c.). Boiling hydrobromic acid (30c.c.) was added and a yellowish liquid separated. More hydrobromic acid (20c.c.) was added and the reaction mixture allowed to cool. It was then extracted with benzene, and the benzene solution washed twice with water; after drying over anhydrous magnesium sulphate, the benzene was distilled off and a yellow liquid obtained.

(c) The product from (b) in sodium-dried ether (500c.c.) was added to lithium aluminium hydride (1.4g.) in in sodium-dried ether (750c.c.).

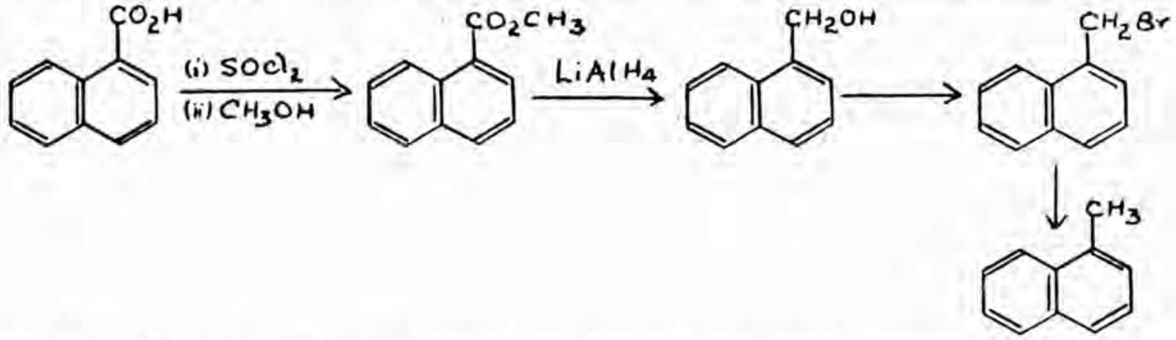
The mixture was heated under reflux for 2 hours. Excess lithium aluminium hydride was decomposed with ethyl acetate and excess potassium hydroxide solution was added, the ethereal layer was separated and the aqueous layer extracted with benzene-ether mixture. The combined organic layers were washed well with water and dried over anhydrous magnesium sulphate.

The solution was filtered and the filtrate decolorized with charcoal. The organic solvents were distilled off and a pale yellow liquid, 2.1g., was obtained.

This product was not 8-methyl-1-bromonaphthalene which is a solid, m.p. 78° (V. Vesety, F. Stursa, H. Olejnicak and E. Rein, Chem. Abstracts, 1930, <u>24</u>, 3009). It was shown, by means of gas and thin layer chromatography, to be α-methylnaphthalene.

A parallel synthesis using α-naphthoic acid gave the same product (α-methylnaphthalene) as the one above, obtained from 8-bromo-1-naphthoic acid.

Scheme for the synthesis of α-methylnaphthalene:



<u>Thin layer chromatographic analysis of the products from methyl-8-bromo-1-naphthoate and 1-naphthoic acid</u>:

This was done using alumina as the absorbent. The two products had the same R_f value as a specimen of pure α-methylnaphthalene, kindly provided by Dr.H. Suzuki.

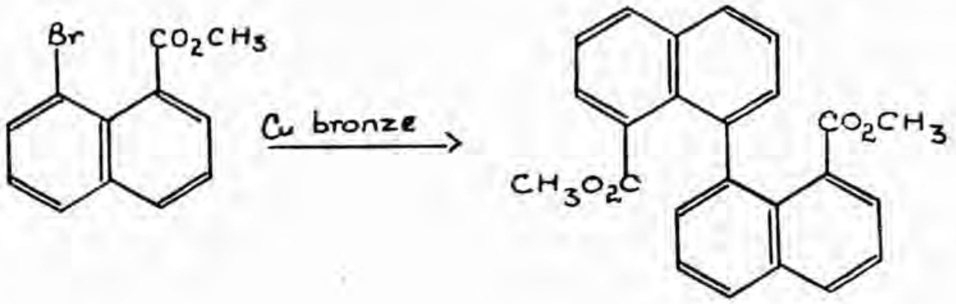
<u>Gas chromatographic analysis of the products from methyl 8-bromo-1-naphthoate and 1-naphthoic acids</u>:

The two products were subjected to gas chromatography separately, and were found to have equal retention times. Each of them gave a single peak indicating that they were pure. A mixture of equal quantities of the two products, on gas chromatography, gave a single peak showing that they were the same. They were shown on gas chromatography with a known sample to be α-methyl naphthalene.

Hence in the attempted conversion of methyl 8-bromo-1-naphthoate into 8-methyl-1-bromonaphthalene there was a debromination and a conversion of the ester group into the methyl and α-methylnaphthalene was obtained as the final product.

The synthesis of 8'-methyl-1,1'-binaphthyl-8-carboxylic acid was therefore tried, starting from dimethyl-1,1'-binaphthyl-8,8'-dicarboxylate and 1,1'-binaphthyl-8,8'-dicarboxylic acid.

(±) - Dimethyl-1,1'-binaphthyl-8,8'-dicarboxylate:



The preparation was carried out according to the procedures of D.M. Hall, S. Ridgewell and E.E. Turner, (J. Chem. Soc., 1954, 2498); A.S. Mellor, Ph.D. Thesis (Lond.) 1961; Y. Badar, Ph.D. Thesis (Lond.) 1964; the reaction being carried out at 200°, with a modification in the method of extraction of the diester.

Copper bronze (51g.) was gradually added to methyl 8-bromo-1-naphthoate (51g.) contained in a hard glass tube immersed in a metal bath kept at 200°. During the addition, which took about 40 minutes, the internal temperature rose from 190° to 230°. After the addition of all copper bronze the reaction mixture was heated at 200° for another 15 minutes and allowed to cool. The cooled mass was boiled with ethanol, to extract the diester, and the solution filtered off from copper. On cooling, a light cream coloured crystalline compound separated as plates (26g.), m.p. 157°-158°. The mother liquor was concentrated and cooled to give needle-like crystals (2g.), m.p. 157°-158°. Total yield 28g. (78.6%; previous optimum yield 76.5%, Y. Badar Ph.D. Thesis (Lond.) 1964).

Hydrolysis of (±) -dimethyl-1,1'-binaphthyl-8,8'-dicarboxylate

D.M. Hall, S. Ridgewell and E.E. Turner, J. Chem. Soc., 1954, 2498.

The diester (5g.) was boiled for ½ hour under reflux with 30% alcoholic potassium hydroxide (1960c.c.), (previously prepared by dissolving potassium hydroxide (30g.) in ethanol (100c.c.) by washing) in a metal bath. Ethanol was distilled off and the residue heated at 130-140° for about ½ hour.

The residue was then extracted with boiling water and filtered. The filtrate was allowed to cool, and acidified with dilute HCl and the precipitated acid was filtered off, washed with water and dried. The precipitate was then extracted with a large amount of methylated spirit in a Soxhlet apparatus. The yellow coloured solution obtained was boiled with charcoal, filtered, and concentrated to a small volume. On standing, a white crystalline product was obtained (4.2g.; 93.6%) m.p. 320-321°. (decomposition). Recrystallisation from methylated spirit gave a product of m.p. 322-324° (decomp.).

Purification of 95% pure 1,1'-binaphthyl-8,8-dicarboxylic acid purchased from Lights and Co.

The impure acid (65g.) was dissolved in a minimum amount of 10% NaOH and 30% NaOH was added to precipitate the acid as the sodium salt. The precipitate was filtered and dissolved in water.

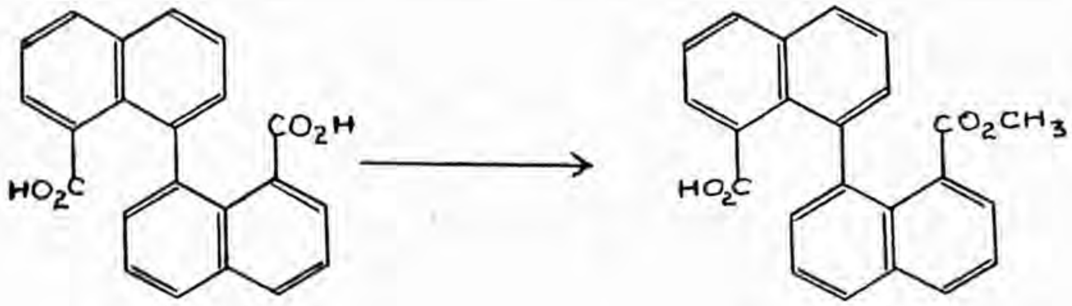
Charcoal was added to the stirred solution, to decolourize it. After an hour, the charcoal was filtered off and the filtrate acidified with dilute HCl to precipitate the diacid. The process was repeated and the precipitate was then boiled with water and filtered. It was washed with water and a little ethanol and dried.

Yield; 43g. (66.2%), m.p. 317-318° (decomp.)

Some of the product was recrystallized from methylated spirit and this gave pale yellow crystals, m.p. 320-321° (decomp.).

A second purification was carried out but in the final precipitation of the acid, instead of adding dilute HCl to the sodium salt solution, the sodium salt solution was added to dilute HCl. The product was the same as the one above (m.p. 317-318°).

Methyl hydrogen 1,1'-binaphthyl-8,8'-dicarboxylate:



1,1-Binaphthyl-8,8'-dicarboxylic acid (50g.) was dissolved in N NaOH (146c.c. exactly one equivalent), stirred and warmed to dissolve all acid. It was necessary to add water to keep the sodium salt in solution. The solution was filtered, and to the cooled filtrate a normal silver nitrate solution (146c.c. exact equivalent) was added with stirring. The precipitated silver salt was filtered, sucked well and allowed to dry away from light.

Yield of the silver salt: 69.5g.

The dry silver salt was boiled under reflux for 2 hours with excess methyl iodide (200g.). Excess methyl iodide was distilled off and the residue extracted:-

(a) with sodium carbonate solution to extract the acids.

(b) with acetone to extract the diester.

Solution (a) was acidified with dilute HCl and the precipitate was filtered and dried. Yield; 25g. It was then taken up in ethanol and the insoluble product (expected to be the diacid) was filtered off. The filtrate was concentrated and allowed to cool when a white crystalline compound was obtained. The process was repeated.

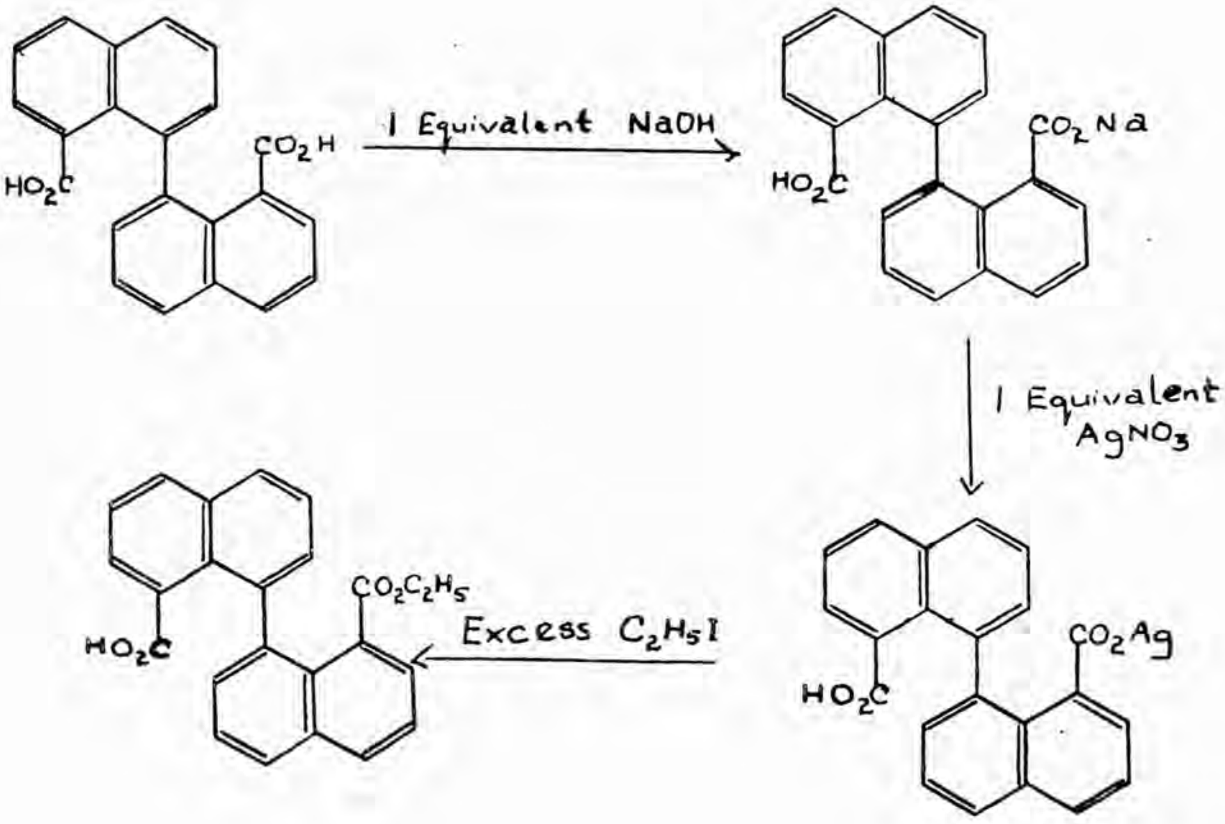
Yield; 3.5g. m.p. 236 (shrinkage) -295°, with slight decomposition. This product contained some of the diacid. Attempts to purify it further resulted in a little yield (0.9g.) m.p. 236-237°, (Found: C, 77.4; H, 4.6; O, 18.15; $C_{23}H_{16}O_4$ requires C, 77.5; H, 4.5; O, 18.0%).

Solution (b) was concentrated and allowed to cool when the dimethyl ester separated as yellowish plates. Recrystallisation from methanol gave 11.0g. of a mixture of plates and needles, m.p. 157-158°.

Meisenheimer made the <u>ethyl</u> half-ester this way and because it is more soluble in ethanol than the 8,8'-diacid, the yield was satisfactory.

<u>Ethyl hydrogen 1,1'-binaphthyl-8,8'-dicarboxylate.</u>

J. Meisenheimer and O. Beisswenger, <u>Ber.</u>, 1932, <u>6</u>, 32



1,1'-Binaphthyl-8,8'-dicarboxylic acid (50g.) was dissolved in N NaOH (146c.c. - exact equivalent). The solution was stirred and warmed to dissolve all acid. The solution was allowed to cool and N $AgNO_3$ solution (146c.c. - exact equivalent) was added slowly with stirring. The fine white precipitate so formed was filtered off, sucked well and allowed to dry away from light.

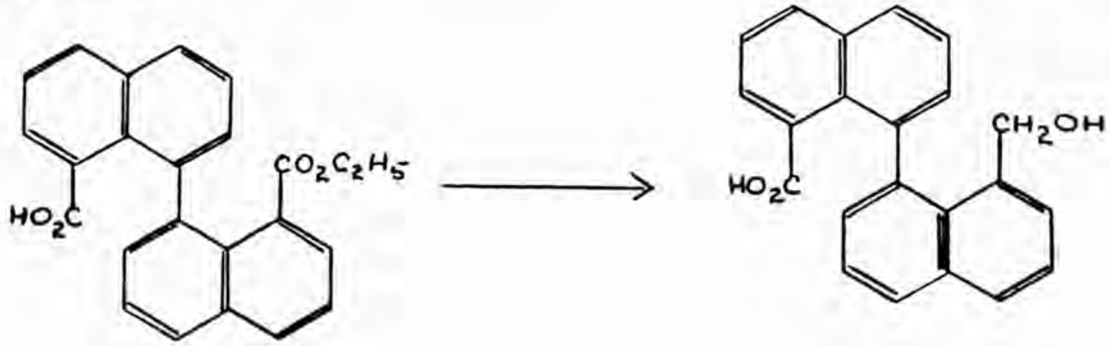
Yield of silver salt: 69g.

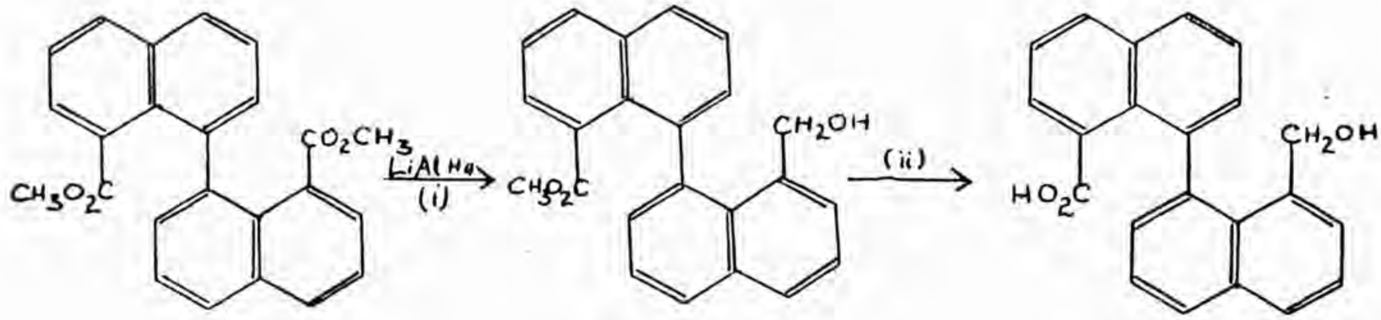
The dry finely powdered silver salt, and excess ethyl iodide (200g.) were heated together under reflux for 2 hours. The excess ethyl iodide was distilled off and the residue extracted with aqueous sodium carbonate.

The cooled sodium carbonate extract was acidified with dilute HCl and the precipitated crude acid was crystallised from ethanol. After two recrystallizations the acid was obtained as a white crytalline compound, m.p. 193-195° (lit. m.p. 194-195°). Yield 12.3g.

Preparation of 8'-hydroxymethyl-1,1'-binaphthyl-8-carboxylic acid.

Two routes were available for the synthesis of this compound:





(a) Conversion of ethyl hydrogen-1,1'-binaphthyl-8,8'-dicarboxylate into 8'-hydroxymethyl-1,1'-binaphthyl-8-carboxylic acid.

Ethyl hydrogen-1,1'-binaphthyl-8,8'-dicarboxylate (5g.) suspended in a 50% mixture of sodium - dried ether and benzene (300c.c.) was added to a solution of lithium aluminium hydride (5g.) in 450c.c. of the same solvent mixture. The mixture was heated under reflux for 2 hours.

The excess of metal hydride was decomposed by adding water, a drop at a time, and dilute sulphuric acid was added with stirring to remove the white suspension. The two layers were separated. The aqueous layer was extracted with ether and the combined solvent extracts washed with water and extracted with sodium carbonate solution to extract the hydroxymethyl acid. The sodium carbonate solution was acidified with dilute HCl and the precipitate filtered off.

Yield of the crude hydroxymethyl acid: 3g.

The crude product was dissolved in alcohol, and the solution decolorised with charcoal and filtered.

The filtrate was concentrated and cooled. The hydroxymethyl acid separated as a white crystalline compound, m.p.219-220°. Yield; 2.5g. (Found: C, 80.1; H, 4.9; O, 15.3; $C_{22}H_{16}O_3$ requires C, 80.47; H, 4.91; O, 14.62%).

(b) (i) Conversion of dimethyl-1,1'-binaphthyl-8,8'-dicarboxylate into 8'-hydroxymethyl-8-methoxycarbonyl-1,1'-binaphthyl:

Dimethyl 1,1'-binaphthyl-8,8'-dicarboxylate (5g.) suspended in dry ether (750c.c.) was added, with stirring, to lithium aluminium hydride (1g.) suspended in dry ether (75c.c.). The mixture was stirred at room temperature for 1 hour.

The unreacted metal hydride was decomposed by adding water, a drop at a time, and dilute H_2SO_4 was added to the stirred solution. The ethereal layer was separated, washed with water, dried over anhydrous $MgSO_4$ and the ether distilled off. The residue was dissolved in benzene run on to an alumina column, and eluted with 10% ether/benzene mixture. This gave some unchanged dimethyl ester (0.1g.).

Elution with ether gave 8'-hydroxymethyl-8-methoxycarbonyl-1,1'-binaphthyl (2.4g.), m.p. 122 - 125°.

Further elution with methanol gave 8,8'-bishydroxymethyl-1,1'-binaphthyl, m.p. 151°.

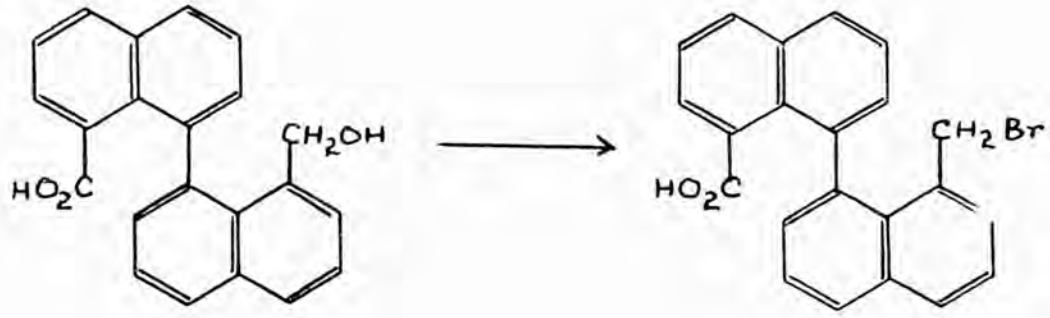
(ii) Hydrolysis of 8'-hydroxymethyl-8-methoxycarbonyl-1,1'-binaphthyl.

The acid ester (2.4g.) was boiled for ½ hour under reflux with 30% alcohol potassium hydroxide (40c.c.) in a metal bath. The alcohol was distilled off and the residue heated at 130-140° for about ½ hour.

The residue was then extracted with boiling water and filtered. The filtrate was allowed to cool, it was then acidified with dilute HCl and the precipitate was filtered, washed with water, dried and recrystallized from ethanol, after decolorising with charcoal. A white crystalline compound (1.9g.)m.p. 219-220° was obtained.

The I.R. spectra of the two acid products from routes (a) and (b) were identical. A mixed m.p. determination also showed no depression.

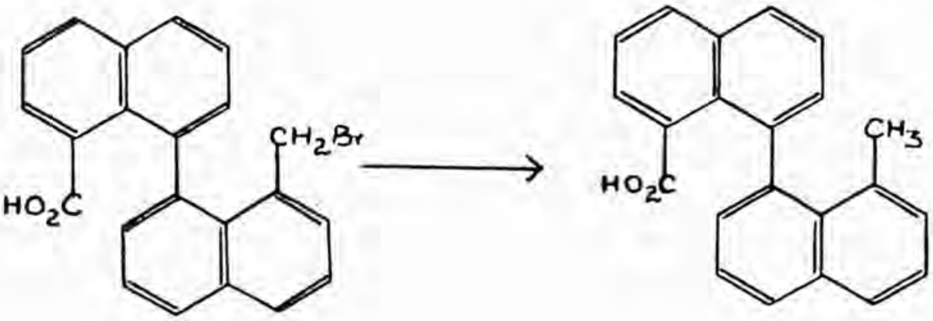
8'Bromomethyl-1,1'-binaphthyl-8-carboxylic acid:



8'-hydroxymethyl-1,1'-binaphthyl-8-carboxylic acid (3g.) was dissolved in glacial acetic acid (60c.c.) by boiling and the solution was allowed to cool. Cold hydrobromic acid (30c.c.) was slowly added with stirring and a crystalline compound separated out. More hydrobromic acid (30c.c.) was slowly added with stirring and a crystalline compound separated out. More hydrobromic acid (15c.c.) was added and the solution allowed to stand for 1 hour.

The precipitate was filtered off and crystallized from glacial acetic acid. A pale yellow crystalline compound (3.1g.), m.p. 180-190° (decomp) was obtained. (Found: C, 67.5; H, 4.05; O, 8.2; Br, 20.4. $C_{22}H_{15}O_2Br$ requires C, 67.5; H, 3.9; O, 8.2; Br, 20.4%).

(±) 8'-methyl-1,1'-binaphthyl-8-carboxylic acid:



8'-Bromomethyl-1,1'-binaphthyl-8-carboxylic acid (5g.) in sodium-dried ether/benzene (200c.c. ether, 50c.c. benzene) was added to lithium aluminium hydride (5g.) in sodium-dried ether/benzene (400c.c. ether, 10c.c. benzene). The mixture was gently reluxed for 1½ hours.

The unreacted metal hydride was decomposed by dropwise addition of water and dilute sulphuric acid (2N) was added. The ether/benzene was separated off and the aqueous layer extracted with ether. The combined organic solvent extracted was washed with water and extracted with sodium carbonate solution. The sodium carbonate solution was acidified with dilute HCl and the precipitated acid filtered off, washed with water and dried.

Yield of crude product; 3g.

The crude product was dissolved in alcohol and the solution was decolorised with charcoal, filtered and concentrated. On cooling, 8'-methyl-1,1'-binaphthyl-8-carboxylic acid (2.1g.), m.p. 252-254° separated. (Found: C, 84.15; H, 5.33; O, 10.63; $C_{22}H_{16}O_2$ requires C, 84.59; H, 5.16; O, 10.24%).

<u>Determination of the equivalent weight of 8'-methyl-1,1'-binaphthyl-8-carboxylic acid</u>:

This determination was carried out by a back titration between an approximately decinormal solution of potassium hydrogen phthalate and 0.09996N NaOH.

The volume of an approximately 0.1N potassium hydrogen phthalate equivalent to a known volume of 0.09996N NaOH was determined by a direct titration.

Then a known volume of 0.09996N NaOH was added to a known weight of 8'-methyl-1,1'-binaphthyl-8-carboxylic acid. The excess sodium hydroxide was titrated against potassium hydrogen phthalate solution. ~~The amount of sodium hydroxide solution equivalent to that of potassium hydrogen phthalate solution.~~ The amount of sodium hydroxide solution equivalent to that of potassium hydrogen phthalate used in the titration was calculated and its difference from the volume of the originally added sodium hydroxide solution was the amount required to neutralise the acid.

Phenolphthalein was used as indicator in these titrations.

<u>Results:</u>

10c.c. approximately o.1N C_6H_5(COOK)COOH were titrated against 0.09996N NaOH.

	1st. Run.	2nd. Run.
Titres (NaOH) in c.c.	10.05	10.05

40 Therefore 40.00 ~~10.05~~c.c. 0.09996N NaOH were added to 0.2798g. 8'-methyl-1,1'-binaphthyl-8-carboxylic acid.

Volume of approx. 0.1N. C_6H_5(COOK)COOH required for titration against the excess 0.09996N NaOH = 30.30c.c., 30.30c.c. approx. 0.1N. C_6H_5(COOK)COOH = 30.45c.c. 0.099$\overset{9}{/}$6N. NaOH.

Therefore the amount of 0.09996N.NaOH required to neutralize 0.2798g. of the methyl acid = 40.00 - 30.45 = 9.55c.c.

Weight of NaOH equivalent to 0.2798g. of the methyl acid
= 0.04 x 0.09996 x 9.55 = 0.3819.

Therefore 40g. NaOH = $\frac{40\ x\ 0.2798}{0.3819}$

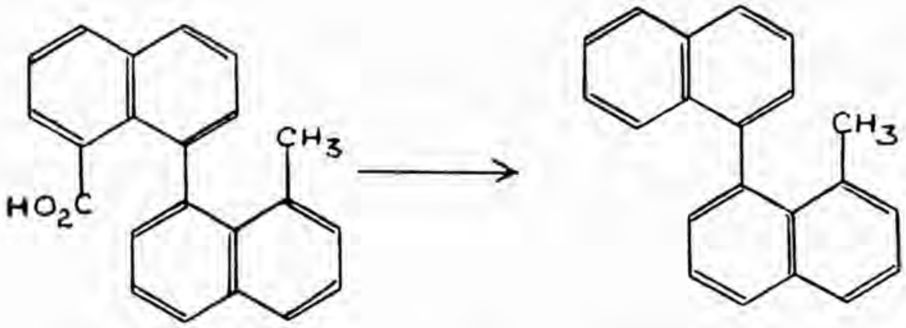
i.e. 293g.

The molecular weight of the methyl acid is 312. Therefore the acid has ONE equivalent, and is therefore monobasic.

A second determination gave the equivalent wt. of the acid as 295.

The results are rather low, perhaps because steric hindrance in the molecule lowers the acidity. However, these approximate results confirm the presence of one carboxyl group in the molecule.

Decarboxylation of 8'-methyl-1,1'-binaphthyl-8-carboxylic acid:



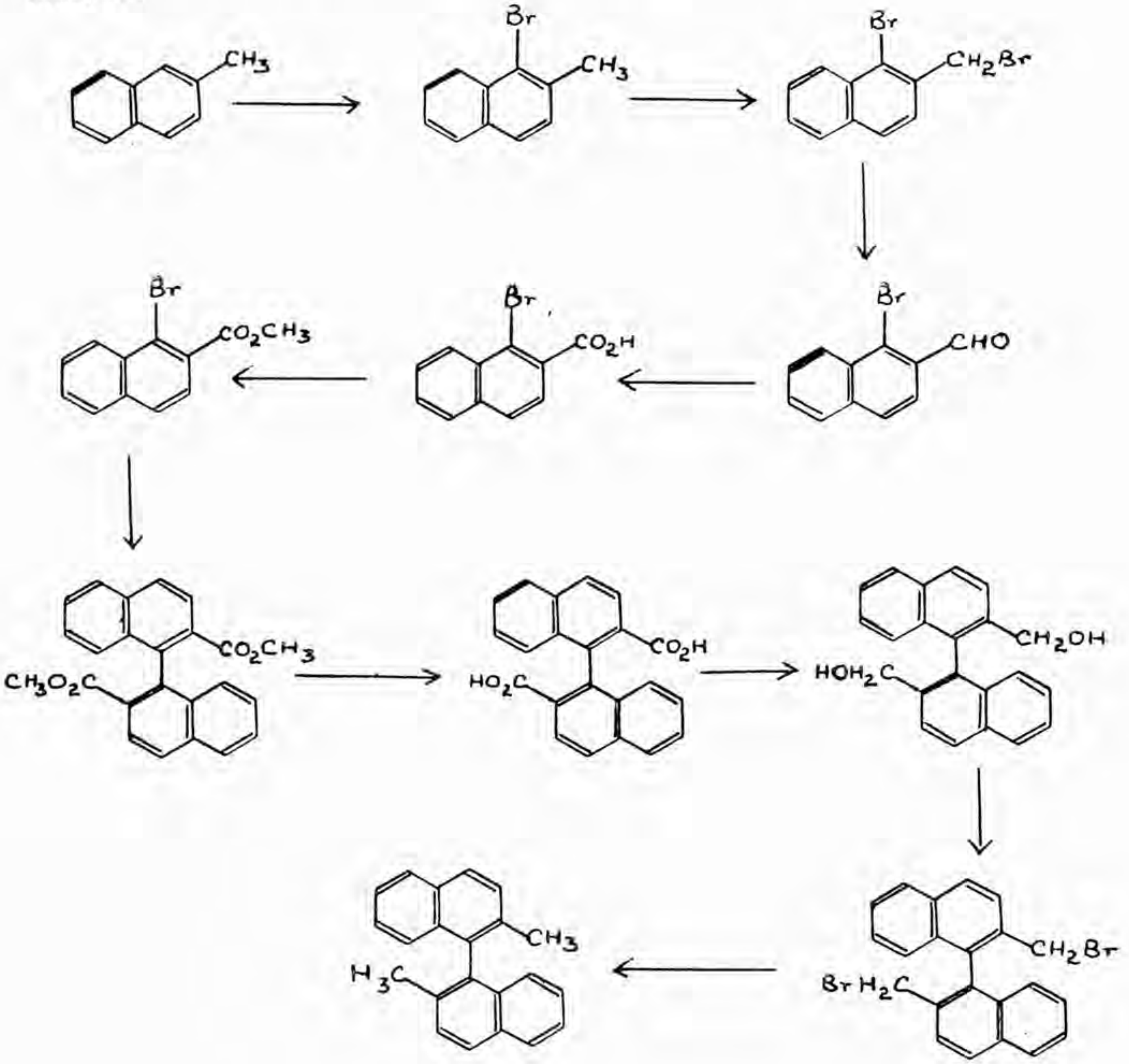
The (±) - acid (1g.) was dissolved in quinoline and copper bronze was added. The reaction mixture was boiled under reflux for 20 minutes. On cooling, the reaction mixture was extracted with dilute hydrochloric acid to remove all quinoline. The insoluble residue was extracted with sodium carbonate to remove any remaining methyl acid. The insoluble residue was then boiled with petroleum ether (b.p. 40 - 60°) and copper bronze filtered off. The petroleum ether solution was concentrated and cooled in an ice bath. 8-Methyl-1,1'-binaphthyl (0.3g.), m.p. 113-115°, was obtained as a white crystalline compound.

Action of acetic anhydride on 8'-methyl-1,1'-binaphthyl-8-carboxylic acid:

The acid (1g.) was boiled under reflux with acetic anhydride (20c.c.) for 5 hours. On cooling, the solution deposited colourless needle-like crystals of a mixed anhydride (0.7g.), m.p. 120-121°. (Found: C, 81.5; H, 4.9; O, 13.6. $C_{24}H_{18}O_3$ requires C, 81.3; H, 5.1; O, 13.5%). The yellow acetic anhydride solution was boiled for a further 5 hours and concentrated. 13-Methyl-7-oxodibenz(*a*, *kl*) anthracene separated as yellow crystals, m.p. 158-159°. (Found: C89.75; H, 4.6; O. 5.5. $C_{22}H_{14}O$ requires C, 89.75; H, 4.8; O, 5.45%). The infrared spectrum showed a strong carbonyl peak at 1633cm.$^{-1}$. (This peak is at a rather lower value compared to that of dibenz(*a*, *kl*) anthracen-7-one, which shows a major infrared peak at 1637cm^{-1}. This could be a result of the steric strain induced by the methyl group in 13-methyl-7-oxodibenz(*a*, *kl*) anthracene).

Synthesis of 2,2'-dimethyl-1,1'-binaphthyl:

Scheme:



1-Bromo-2-methylnaphthalene:

R. Adams and L.O.Binder, J. Amer. Chem. Soc., 1941, 63, 2773.

To a solution of 2-methylnaphthalene (142g. 1.0M). in carbon tetrachloride (300c.c.) were added a crystal of iodine and a pinch of iron powder. The flask and contents were cooled to 0°. The flask was covered with aluminium foil to exclude light and bromine (160g. 1.0M.) in carbon tetrachloride was added with mechanical stirring over a period of 8 hours without allowing the temperature to rise above 5°. After standing overnight, the carbon tetrachloride solution was washed thoroughly with 10% aqueous sodium hydroxide, then with water and dried over anhydrous calcium chloride. The solution was then filtered and the carbon tetrachloride distilled off. The 1-bromo-2-methylnaphthalene was distilled under reduced pressure, b.p. 174-177°/23m.m.

1-Bromo-2-bromomethylnaphthalene:

M.S.Newman and A.I.Kosak, J. Org. Chem. 1949, 14 , 375.

A mixture of 1-bromo-2-methylnaphthalene (210g. 0.95M) N-bromosuccin~~a~~imide (160g. 0.90M), benzoyl peroxide (1g.) and carbon tetrachloride (250c.c.) was refluxed for 2½ hours. The warm product was filtered after addition of carbon tetrachloride, the residue being washed several times with solvent. The solution was concentrated and allowed to cool when 1-bromo-2-methylnaphthalene separated as colourless crystals (231g.) m.p. 104-106°.

1-Bromo-2-naphthaldehyde:

D.M.Hall and E.E.Turner, J. Chem. Soc., 1955, 1242.

1-Bromo-2-bromomethylnaphthalene (90g.) was dissolved in chloroform (400c.c.) and powdered hexamine (46.5g.) added in several lots to the boiling solution. The hexamine salt separated in a few minutes and was filtered off and then boiled in 50% acetic acid (650c.c.) for 1 hour. Concentrated hydrochloric acid (105c.c.) was added and the solution boiled for a further 5 minutes. The aldehyde (41.5g. 59%), m.p. 119-120°. (Previous workers, 58%; m.p. 119-120°).

1-Bromo-2-naphthoic acid:

D.M.Hall and E.E.Turner, loc. cit.

A solution of 1-bromo-2-naphthaldehyde (11g.) in acetone (275c.c.) was heated in a water bath kept at 60-68°, a hot aqueous solution of potassium permanganate (14g. in 330c.c. water) was added during ½ hour and heating was continued for a further ½ hour. Sulphur dioxide was passed in at once and the clear solution poured into water (1.5L) and cooled in ice. The acid was filtered off. The crude acid from 8 oxidations was collected and worked up together as follows:-

It was dissolved in dilute ammonia (based on a slight excess of 0.88 ammonia very much diluted.) The small amount of insoluble material was filtered off. The acid was precipitated, as a thick paste, from the filtrate with hydrochloric acid. It was filtered on a large Buchner funnel and dried over a water bath. The acid (87g.), m.p. 190-191° was used for the next stage without recrystallisation.

Methyl-1-bromo-2-naphthoate:

A mixture of 1-bromo-2-naphthoic acid (84g.) methanol

(800c.c.) and concentrated sulphuric acid (80g.) was boiled under reflux for 5 hours. The reaction mixture was poured into water (2 l) and left in a refrigerator overnight. The solution was filtered and the solid was recrystallized from methanol (400c.c.) to give the ester (85g., m.p. 60-61.5°).

(±)-Dimethyl-1,1'-binaphthyl-2,2'-dicarboxylate:

(D.M.Hall and E.E.Turner, loc. cit.)

Methyl 1-bromo-2-naphthoate (40g.) was heated with copper bronze at 270-280° for about 20 minutes. While still hot the mixture was extracted with toluene; the filtrate deposited crystals on cooling. A further crop was obtained by removal of some of the solvent. After one recrystallization from ethanol, the ester had a m.p. 157.5 - 158° (yield 77.5%).

(±)-1,1'-Binaphthyl-2,2'-dicarboxylic acid:

(D.M.Hall and E.E.Turner, loc. cit).

This was obtained by hydrolysis of the diester. A very little water was added to potassium hydroxide (22g.) and the mixture heated untill all the KOH went into solution. Ethanol was added and then the solid diester (37g.). More ethanol was added until the solution was clear when hot (170c.c. of ethanol was added altogether). The reaction mixture was boiled under reflux for 3/4 hour. The potassium salt soon separated. The reaction mixture was cooled and water was added followed by dilute hydrochloric acid. The precipitated acid was filtered, dried and dissolved in aqueous potassium carbonate (the potassium salt being more soluble than the sodium salt). Any remaining solid was filtered off.

The filtrate was acidified with 50% hydrochloric acid (effervescence!) and the precipitated acid was filtered off using a large Buchner funnel and sucked dry. Crystallisation from ethanol gave the acid in a solvated form. The anhydrous acid (m.p. 272-273°) was obtained through prolonged heating of the solvated acid on a steam bath.

(±)-2,2'-Bishydroxymethyl-1,1'-binaphthyl:

(D.M.Hall and E.E.Turner, loc. cit.)

Methyl 1,1'-binaphthyl-2,2'-dicarboxylate (20g. 1M) was ground and washed with ether (500c.c.) into lithium aluminium hydride (5.4g. 2.6M.) in ether (350c.c.) The mixture was boiled under reflux for ½ hour. It was then treated with water to decompose excess lithium aluminium hydride. Sulphuric acid (2N). was added and the ether distilled off. The diol was filtered off from the residual aqueous solution and crystallised from ethanol. Yield 16.1g., m.p. 190.5 - 92°.

(±)-2,2'-Bisbromomethyl-1,1'-binaphthyl:

The previous diol (10g.) was dissolved in glacial acetic acid (250c.c.) by boiling and boiling hydrobromic acid (d 1.49; 75c.c.) was added. After one minute, the dibromide separated as an oil. The mixture was boiled and more hydrobromic acid (50c.c.) was added and boiling continued for ½ hour, when the oil solidified. The solid was separated and crystallized from ethyl methyl ketone (yield 11.9g.) m.p. 152 - 155° (D.M.Hall and E.E.Turner loc. cit., m.p. 151 - 153°).

(±)-2,2'-Dimethyl-1,1'-Binaphthyl:

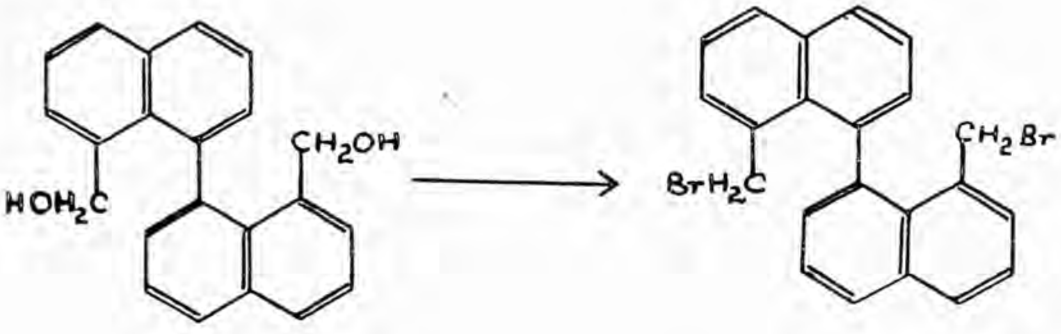
The dibromide (10g.) in sodium-dried ether (500c.c.) was added to lithium aluminium hydride (12g.) and heated under reflux for 2½ hours. To decompose excess lithium aluminium hydride, wet ether was added, followed by a dropwise addition of water, until no further bubbles were observed. Dilute sulphuric acid was added and the reaction mixture was well shaken. The ethereal layer was separated and dried over anhydrous calcium chloride. The solution was filtered and all ether was evaporated off. The highly viscous residue was dissolved in a minimum amount of ethanol and allowed to stand overnight. 2,2'-Dimethyl-1,1'-binaphthyl was obtained as a white crystalline compound (yield 4.5g., m.p. 70 - 71°). Found: C, 93.4; H, 6.35; $C_{22}H_{18}$ requires C, 93.6; H, 6.4%).

(±)-8,8'-Bishydroxymethyl-1,1'-binaphthyl:

Y. Badar, A.S. Cooke and M.M. Harris, J. Chem. Soc., 1965, 1412.

Dimethyl 1,1'-binaphthyl-8,8'-dicarboxylate (5g. 1M). suspended in sodium-dried ether (1L) was added to lithium aluminium hydride (1.5g. 3M). The reaction mixture was heated under reflux for 4 hours. Excess lithium aluminium hydride was decomposed with wet ether, water (added dropwise) and then sulphuric acid (2M.) was added. The ethereal layer was separated, washed with water and dried over anhydrous magnesium sulphate. The ether was distilled off and the residue crystallized from benzene and vacuum dried for 2 hours at 100° to give the diol (4g.)m.p. 151.5 - 152°. (Previous workers, 151-152°).

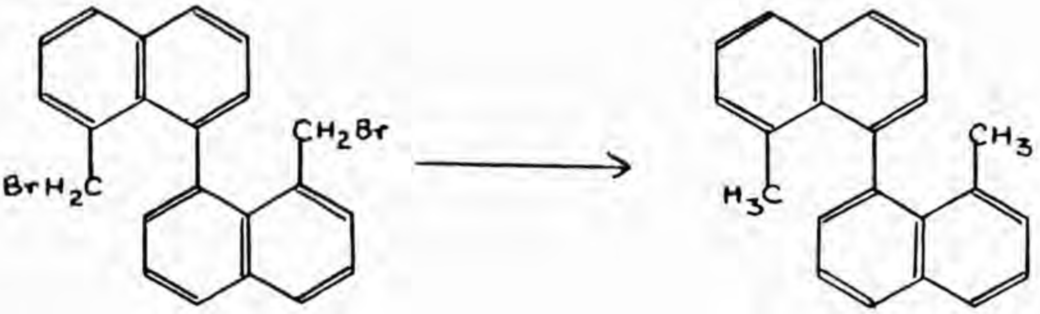
(±)-8,8'-Bisbromomethyl-1,1'-binaphthyl:



The diol (5g.) was dissolved in glacial acetic acid (125c.c.) by boiling. Boiling hydrobromic acid (d 1.49; 60c.c.) was added. After a few minutes the solution became cloudy and pale yellow crystals separated. More hydrobromic acid

(25c.c.) was added. After cooling the solid was filtered, washed well with water and dried. The product was crystallized from chloroform to give light yellow crystals (5.7g.) m.p. 190-191.5°. (Y. Badar, A.S. Cooke and M.M. Harris, loc. cit., 191-192°).

(±) 8,8'-Dimethyl-1,1'-binaphthyl:



The dibromo-compound (5g. 1M) in sodium-dried ether (500c.c.) was added to lithium aluminium hydride (1.4g. 6M) in sodium-dried ether (1.5L) and the mixture was heated under reflux for two hours. Excess lithium aluminium hydride was decomposed by a dropwise addition of ethyl acetate. Excess potassium hydroxide was added. The ethereal layer was separated and the aqueous layer extracted with ether/benzene mixture. The combined organic solution was washed twice with water, dried over magnesium sulphate, concentrated to a small volume and allowed to cool. Thick crystalline plates (3.0g.) were obtained, m.p. 123-127°. Recrystallisation from ether gave colourless crystals m.p. 130-131°. (Y. Badar, A.S. Cooke and M.M. Harris, loc. cit., 129-130°).

OPTICAL EXPERIMENTAL

Resolution of 8'-methyl-1,1'-binaphthyl-8-carboxylic acid:

The (±)-acid (2.0g.) was dissolved in ethanol (300c.c.) and to it was added a solution of brucine (3.0g., 1.2M) in ethanol (300c.c.). The solution was evaporated down to 150c.c. and allowed to cool slowly to room temperature. The brucine (-)-acid salt (A) crystallized out (1.8g.), m.p. 161-163°, $[\alpha]^{21.5}_{578}$ - 239.9° (in chloroform).

The mother-liquor from (A) was concentrated to half-volume and a further 0.5g. of the brucine salt (B) separated, m.p. 161-162.5°, $[\alpha]^{21.5}_{578}$ -211.8°

(A) and (B) together constitute 50% of the brucine salt, based on the quantity of (±)-acid used.

The mother-liquor contained the brucine (+)-acid salt. Cool evaporation of this mother liquor from (B) gave a non-crystalline residue (C) which failed to crystallize from a large variety of solvents.

Liberation of the optically active acids:

(-) - Acid:

The brucine salt (A) was dissolved in chloroform and extracted twice with N-sodium hydroxide and the alkaline extract washed twice with chloroform and once with ether, then acidified with dilute hydrochloric acid. This gave the (-)-acid (0.55g.), m.p. 247.5-248°, $[\alpha]^{21.5}_{578}$ - 253.5°

(in chloroform).

(+) - Acid:

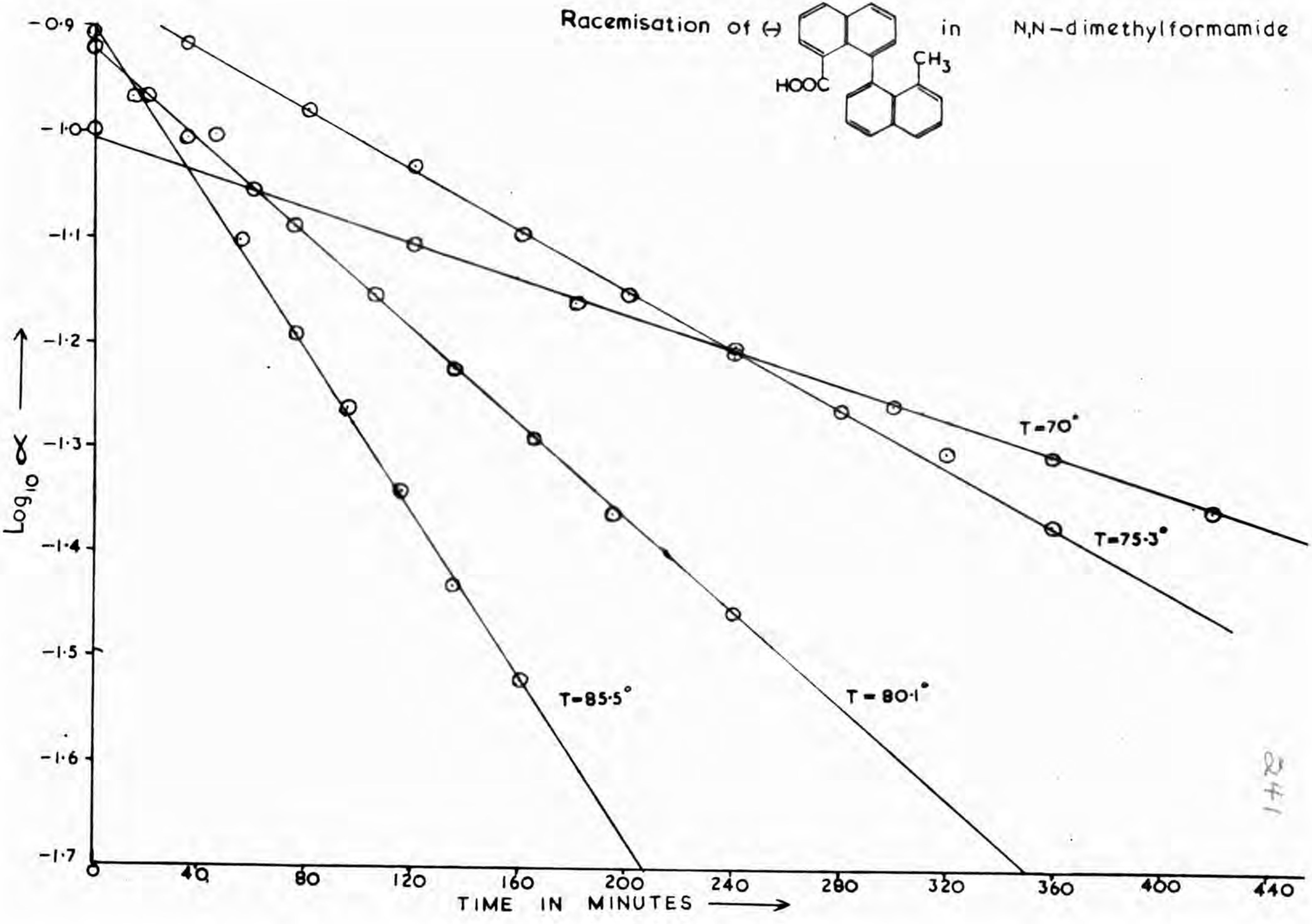
The residue (C) was dissolved in chloroform and the solution treated as described for salt (A). The (+)-acid thus obtained had m.p. 247.5-248°, $[\alpha]_{578}^{21.5}$ +250.2°

(in chloroform).

The (–)-acid racemised when heated under reflux in sodium hydroxide for several hours. The (±)-acid recovered was identical (m.p., mixed m.p. and infrared spectrum) with the (±)-acid used for the resolution.

Polarimetric work:

Optical rotations were measured on the "Carl Zeiss Photoelectric Precision Polarimeter 0.005°" at λ = 578mμ. Portions of a solution of the optically active 8'-methyl-1,1'-binaphthyl-8-carboxylic acid were sealed in glass tubes kept in an oil thermostat, withdrawn at suitable intervals immediately cooled to room temperature, and optical rotations read.

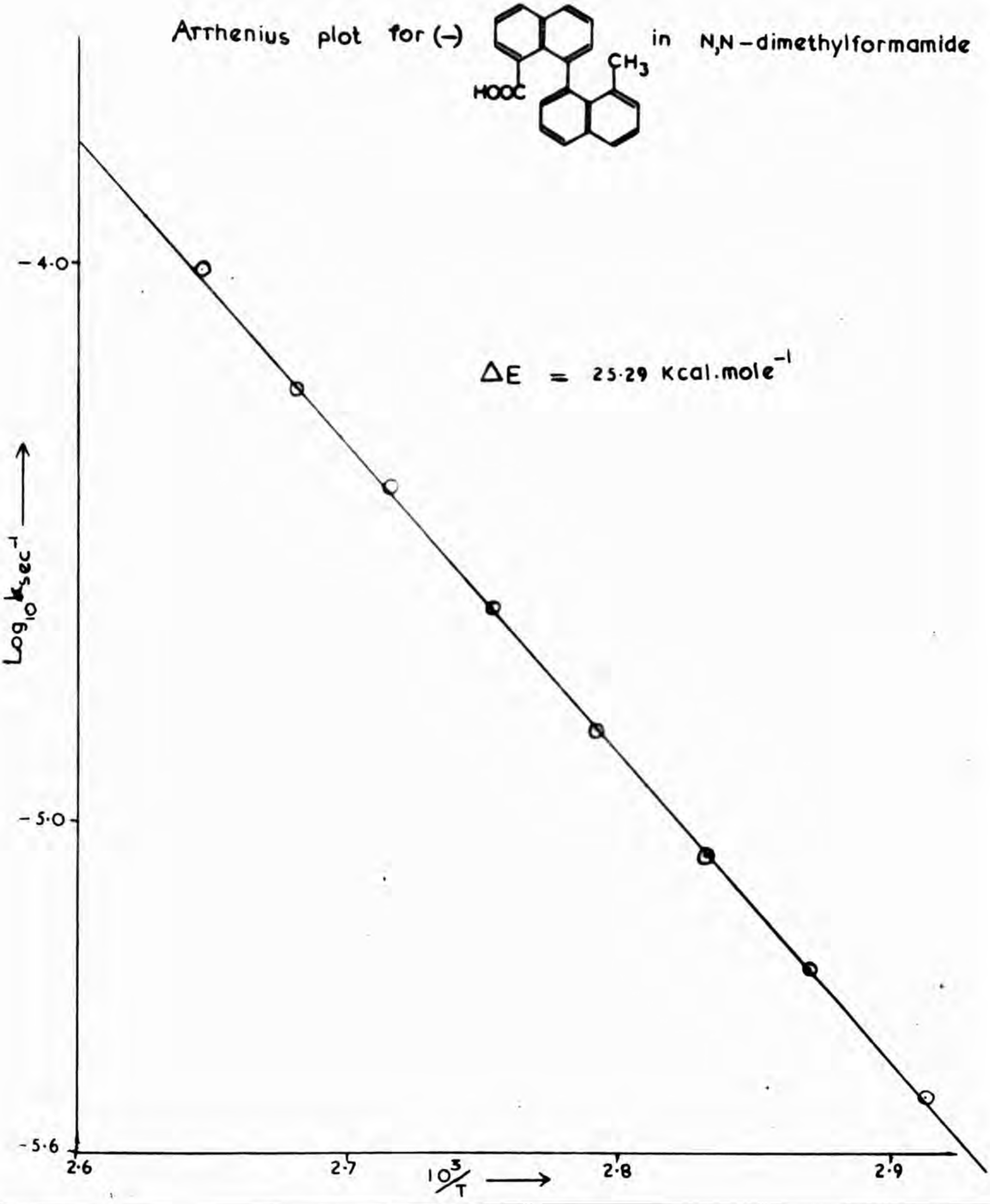


Racemisation of (–) in N,N-dimethylformamide

Determination of the rate coefficients for racemisation of 8'-methyl-1,1'-binaphthyl-8-carboxylic acid in N,N-dimethylformamide.

Temperature in °C.	First Reading	No. of Readings.	Time over which readings were taken in mins.	$k_{\text{min}^{-1}}$.
70	-1.005°	8	420	1.9×10^{-3}
75.3	-1.410°	10	360	3.26×10^{-3}
80.1	-1.210°	10	280	5.2×10^{-3}
85.05	-1.245°	10	195	8.8×10^{-3}
90	-1.255°	10	145	1.2×10^{-2}
95	-1.170°	10	105	2.4×10^{-2}
100	-1.735°	10	80	3.6×10^{-2}
105	-1.365°	10	45	5.9×10^{-2}

Racemisation could not be followed in 0.1N, NaOH because in this solvent, the methyl acid had too small an optical rotation for accurate measurement.


Arrhenius plot for (–) in N,N-dimethylformamide
HOOC
CH_3
ΔE = 25·29 Kcal.mole^{-1}
$Log_{10} k_{sec^{-1}}$ →
$\frac{10^3}{T}$ →
–4·0
–5·0
–5·6
2·6
2·7
2·8
2·9

Determination of the Arrhenius parameters and transition state theory functions in N,N-dimethylformamide:

T(abs.)	$\frac{1}{T} \times 10^3$	$k_{min.}$	$\log_{10} k_{sec^{-1}}$
343.2	2.913	1.919×10^{-3}	$\bar{5}.5049$
348.5	2.87	3.26×10^{-3}	$\bar{5}.7351$
353.3	2.831	5.187×10^{-3}	$\bar{5}.9367$
358.25	2.791	8.790×10^{-3}	$\bar{4}.1658$
363.2	2.753	1.466×10^{-2}	$\bar{4}.3878$
368.2	2.715	2.405×10^{-2}	$\bar{4}.6030$
373.2	2.680	3.588×10^{-2}	$\bar{4}.7767$
378.2	2.645	5.91×10^{-2}	$\bar{4}.9934$

Graphical determination of ΔE (p.   )

$\frac{1}{T}$ was plotted against $\log_{10} k_{sec^{-1}}$.

The slope of the graph = $\frac{1.32}{0.239}$

Therefore $\Delta E = \frac{1.32}{0.239} \times 1.9885 \times 2.303 = 25.3$ Kcal. mole^{-1}.

Calculation of ΔE by least squares method:

In the equation $y = a + bx$

y is taken as the temperature and x as $\log_{10} k_{sec^{-1}}$.

$$a = \frac{\sum x^2 \sum y - \sum x \sum xy}{n \sum x^2 - (\sum x)2}$$

$$b = \frac{n \sum xy - \sum x \sum y}{n \sum x^2 - (\sum x)^2}$$ i.e. the slope of the graph.

$$x = 5 + \log_{10} k_{sec^{-1}}.$$

$$y = \frac{10^3}{T}$$

T	y	x	xy	x^2
343.2	2.91375	0.5049	1.47115	0.25492
348.5	2.86944	0.7351	2.10933	0.54037
353.3	2.83045	0.9367	2.65128	0.87741
358.25	2.79135	1.1658	3.25416	3.15909
363.2	2.75330	1.3878	3.82103	1.92599
368.2	2.71592	1.6030	4.35362	2.56961
373.2	2.67953	1.7745	4.75483	3.14885
378.2	2.64410	1.9938	5.27181	3.97524

$\sum y = 22.19784$

$\sum x = 10.10160$

$\sum xy = 27.68721$

$\sum x^2 = 14.65148$

$n = 8$

$$b = \frac{8 \times 27.68721 - 10.10160 \times 22.19784}{8 \times 14.65148 - (10.10160)^2} = 0.180363$$

Therefore $\Delta E = \frac{1.9885 \times 2.303}{0.180363} = 25.39$Kcal. mole^{-1}.

Average value of ΔE = <u>25.3</u> Kcal. mole^{-1}.

Half-life period at 100° $= \frac{0.3010}{1.0125} \times 65 = 19.3(2)$ minutes.

Calculation of $\log_{10}A$, $\Delta S^{\neq}$, $\Delta H^{\neq}$, and $\Delta F^{\neq}$

(e.f. D.M.Hall and M.M.Harris, *J. Chem. Soc.*, 1960, 490).

$\log_{10}A$ was calculated for each temperature, using the equation:

$$\log_{10}A = \frac{\Delta E}{2.303 \times 1.9885 \times T_{abs.}} + \log_{10}K_{sec^{-1}}.$$

The average value of $\log_{10}A$ = <u>11.6</u> sec^{-1}.

$\Delta S^{\neq}$ was calculated for each temperature, using the equation:

$$\Delta S^{\neq} = 2.303 \times R \log_{10} K_{rac}/T + \frac{E}{T} - 49.20$$

The average value of $\Delta S^{\neq}$ = <u>-7.7</u>e.u.

$\Delta H^{\neq} = \Delta E - RT$

at 100°, $T_{abs} = 373.2$

Therefore, $\Delta H^{\neq} = 25340 - 1.9885 \times 373.2$

$= $ <u>24.6</u>K. mole^{-1}.

$\Delta F^{\neq} = \Delta H^{\neq} - T\,\Delta S^{\neq}$

At 100° $\Delta F^{\neq}$ = <u>27.5</u>K. mole^{-1}.

(14) Synthetic Optical

Resolution of 1,1'-binaphthyl-2,2'-dicarboxylic acid:

(D.M. Hall and E.E. Turner, J. Chem. Soc., 1955, 1242)

The de-solvated acid (46.8g., 1M) and anhydrous quinine (44.3g., 1M) were dissolved together in ethanol (455c.c.) and ether (455c.c.) was added. The solution was kept in the refrigerator and it eventually deposited a salt (58g.) which was subsequently recrystallized 3 times from ethanol to constant specific rotation. The mother-liquor from the first crop was evaporated to dryness and the residue crystallized from ethanol. The more soluble salt was crystallized from highly concentrated ethanolic solutions. Intermediate crops were repeatedly recrystallized. Altogether 29.5g. of the less soluble salt, and 15g. of the more soluble salt were obtained. The less soluble quinine salt had m.p. 177-178° (decomp.),

$[\alpha]^{22.5}_{578}$ - 93.4° in acetone.

(D.M. Hall and E.E. Turner, loc. cit., 178° (decomp.),

$[\alpha]^{23}_{5791}$ - 89.8° in acetone.

The more soluble salt had m.p. 185-188° (decomp.),

$[\alpha]^{22.5}_{578}$ + 15.1 in acetone.

(D.M. Hall and E.E. Turner, J. Chem. Soc., 1955, 1242 quote m.p. 184-190° (decomp.),

$[\alpha]^{22}_{5791}$ + 8.6° in acetone

(-) -1,1'-Binaphthyl-2,2'-dicarboxylic acid:

A solution of the less soluble quinine salt (35g.) in chloroform (350c.c.) was extracted 3 times with normal potassium hydroxide solution. The combined extracts were washed with chloroform and poured into dilute hydrochloric acid. The precipitated acid was crystallized from aqueous acetone (yield 16.5g.) and had m.p. 120-121° (decomp.), $[\alpha]^{22}_{578}$ - 81.4° in approximately 0.1N. NaOH (D.M. Hall and E.E. Turner, loc. cit., $[\alpha]^{22}_{5791}$ - 108.6°). It was heated on a water bath for some hours to drive off the water of crystallization.

(+) -1,1'-Binaphthyl-2,2'-dicarboxylic acid:

Similar decomposition of the more soluble quinine salt gave the (+)-diacid, m.p. 119-120° (decomp.), $[\alpha]^{22}_{578}$ + 132.4° in approximately 0.1N NaOH (D.M. Hall and E.E. Turner, loc. cit., $[\alpha]^{20}_{5791}$ + 107.2°).

(-) -2,2'-Bishydroxymethyl-1,1'-binaphthyl:

(-) -1,1'-Binaphthyl-2,2'-dicarboxylic acid (12g,) dissolved in sodium-dried ether (400c.c.) was added to lithium aluminium hydride (5.1g. 4M) in ether (300c.c.) The mixture was boiled for 1½ hours. Ethyl acetate was added, followed by water and sulphuric acid (2N). The ethereal layer was separated, the solvent removed, and the residue crystallized twice from benzene. (–)-Bishydroxymethyl-1,1'-binaphthyl (9.5g.) was obtained as hexagonal plates, m.p. 168.5-169°,

$[\alpha]^{22}_{578}$ – 75.0° in acetone.

(D.M. Hall and E.E. Turner, *loc. cit.*, m.p. 168-169°,

$[\alpha]_{5791}$ – 72.3° in acetone).

(+) -2,2'-Bishydroxymethyl-1,1'-binaphthyl:

Similar reduction of the (+) -acid (12g.) gave the (+) -diol (9.4g.), m.p. 168-169°,

$[\alpha]^{22}_{578}$ + 74.1° in acetone.

(–)-2,2'-Bisbromomethyl-1,1'-binaphthyl:

The (–) – diol (7.85g.) was dissolved in boiling glacial acetic acid (195c.c.) and boiling hydrobromic acid (d 1.49; 60c.c.) was added. The solution cleared on shaking, then became cloudy and, after a few minutes' boiling, crystals separated. More hydrobromic acid (40c.c.) was added and heating was continued for a total time of 7 minutes after the first addition of hydrobromic acid. After cooling, the solid was filtered off, washed with water and sucked dry. The crude dibromide (10.9g. 98.5%) had m.p. 184 – 188°.

$[\alpha]^{22}_{578}$ – 155.9° in benzene, (D.M.Hall and E.E.Turner, *loc. cit.*, m.p. 184 - 186°

$[\alpha]^{23}_{5791}$ - 169.4° in benzene)

and was used without further purification.

(+)-2,2'-Bisbromomethyl-1,1'-binaphthyl:

Similar treatment of the (+) - diol (7.8g.) gave the (+)-dibromide (10.9g.), m.p. 184 - 188°,

$[\alpha]^{22}_{578}$ + 155.9° in benzene.

(+)-2,2'-Dimethyl-1,1'-binaphthyl:

(-)-2,2'-Bisbromomethyl-1,1'-binaphthyl (10g.) was treated as already described for the optically inactive compound. (+)-2,2'-Dimethyl-1,1'-binaphthyl was obtained as a white crystalline compound (4.5g.) m.p. 70 - 71°,

$[\alpha]^{22.5}_{436}$ + 40.0°, $[\alpha]^{22.5}_{578}$ + 21.0° in methanol.

(D.D.Fitts, M. Siegel and K.Mislow, *J. Amer. Chem. Soc.*, who made the compound using the same method quote m.p. 64 - 67°,

$[\alpha]^{22}_{D}$ + 19° in methanol.

(-)-2,2'-Dimethyl-1,1'-binaphthyl:

Similar treatment of the (+)-dibromide (10g.) gave (-)-2,2'-dimethyl-1,1'-binaphthyl (4.6g.), m.p. 69 - 70°,

$[\alpha]^{22.5}_{436}$ - 40.0, $[\alpha]^{22.5}_{578}$ - 21.0 in methanol

Attempted racemisation of 2,2'-dimethyl-1,1'-binaphthyl:

1) in solution:

<u>Method</u>: Portions of a solution of 2,2'-dimethyl-1,1'-binaphthyl in suitable solvents were sealed in glass tubes and kept in an oil thermostat. After a number of hours, the glass tubes were withdrawn and cooled to room temperature and optical rotations measured.

Racemisations were tried as follows:

(a) A solution of (+)-2,2'-dimethyl-1,1'-binaphthyl in m-xylene, having α^{20}_{578} + 0.030, was sealed in a glass tube and kept at 136° in an oil thermostat for 9 hours. It then had α^{20}_{578} + 0.030 showing that no racemisation had taken place.

(b) A solution of the hydrocarbon in α-methylnaphthalene having α^{20}_{578} + 0.360 was sealed in a glass tube and kept at 240° in an oil thermostat for 15 hours. It then had α^{20}_{578} + 0.360 showing that it had not racemised. A similar attempt at 290° gave a dark solution which could not be seen through. Hence there must have been a decomposition of 2,2'-dimethyl-1,1'-binaphthyl. α-Methyl naphthalene without the binaphthyl remained clear at this temperature.

<u>Molten hydrocarbon</u>:

2,2'-Dimethyl-1,1'-binaphthyl having $[\alpha]^{20}_{578}$ + 21.0°

(in ethanol) was sealed in a glass tube and kept at 290° in an oil thermostat, for about 40 hours. It was then withdrawn and cooled to room temperature. The molten hydrocarbon was dark. Crystallization from ethanol gave dirty brown crystals, m.p. 52 - 54°

$[\alpha]^{20}_{578}$ + 11.0°. An infrared spectrum of this product was not identical with that of the 2,2'-dimethyl-1,1'-binaphthyl used in the attempted racemisation. Hence the hydrocarbon had decomposed. The pure hydrocarbon obtained from the decomposition product had $[\alpha]^{20}_{578}$ + 21.0° showing that it had not racemised

Resolution of 1,1'-binaphthyl-8,8'-dicarboxylic acid:

A. S. Cooke and M. M. Harris, J. Chem. Soc., 1963, 2365.
J. Meisenheimer and O. Beisswenger, Ber. 1932, 65, 32.
A. Corbellini, C.A., 26, 1277.

1,1'-Binaphthyl, 8,8'-dicarboxylic acid (4g.) was added to brucine (5.6g.) dissolved in methyl alcohol (1.2litres). The solution was boiled until all acid dissolved. It was then evaporated down to about 800c.c. On standing the solution deposited the (-)-acid brucine salt as colourless prisms (4.1g.), m.p. 262 - 275°,

$[\alpha]^{21.5}_{546}$ - 497.2°.

(Cooke and Harris quote m.p. 260 - 275°,

$[\alpha]^{21.4}_{5461}$ - 481

and Meisenheimer and Beisswenger quote m.p. 255 - 262°

$[\alpha]^{26}_{D}$ - 395°)

The mother liquor was exaporated to dryness and the residue dissolved in ethyl acetate (2 litres) by boiling The solution was filtered hot and concentrated to about 1/4 of the original volume. On cooling, the (+)-acid brucine salt (3.7g.) was obtained as feather-like crystals, m.p. 220 - 240°,

$[\alpha]^{21.5}_{546}$ - 535.3

(Cooke and Harris quote m.p. 220 - 250, $[\alpha]^{21.4}_{5461}$ + 483°

and Meisenheimer and Beisswenger quote m.p. 228 - 234°, $[\alpha]_D^{27}$ + 377°.

Optically active acids:

(-)-1,1'-Binaphthyl-8,8'-dicarboxylic acid:

The (-)-acid brucine salt (10g.) was dissolved in chloroform (200c.c.) and the solution was extracted with chilled aqueous sodium hydroxide. The sodium hydroxide was washed twice with chloroform and once with ether, and immediately poured into chilled dilute hydrochloric acid. The precipitated diacid was throughly washed with water and dried.

Yield : 4.5g., m.p. 319-322° (decomp.), $[\alpha]_{546}^{20.5}$ - 740.7°

Crystallization from NN-dimethylformamide:

The (-)-diacid (1g.) was quickly added to boiling NN-dimethylformamide (5c.c.) and the solution shaken until all acid dissolved. Ethyl alcohol (10 drops) was added and the solution quickly cooled under a tap, when the (-)-diacid (0.3g.) was deposited as micro-crystals, m.p. 320-321° (decomp.), $[\alpha]_{546}^{21}$ - 620.1°

(Found: C, 77.05; H, 4.21; O, 18.64.
calculated for $C_{22}H_{14}O_4$ C, 77.20; H, 4.10; O, 18.70.

(+)-1,1'-Binaphthyl-8,8'-dicarboxylic acid:

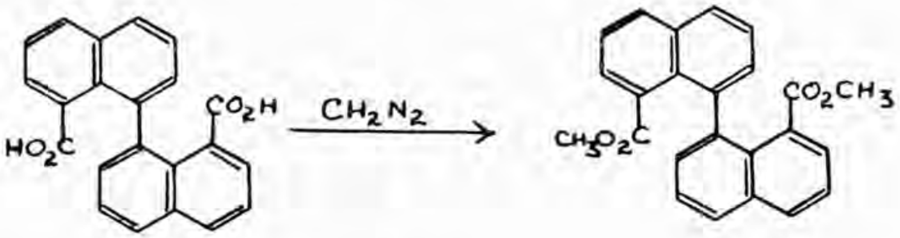
Treatment of the (+)-acid brucine salt (10g.) as above gave the (+)-diacid (4.5g.), m.p. 319-322° (decomp.)

$[\alpha]^{20.5}_{546}$ + 738.9°

Crystallization from NN-dimethylformamide gave the (+)-diacid m.p. 320-322° (decomp.), $[\alpha]^{20.5}_{546}$ + 601°

(found: C, 77.18; H, 4.24; O, 18.85 Calc. for $C_{22}H_{14}O_4$:
C, 77.2; H, 4.1; O, 18.7%).

Preparation of optically active esters:



Preparation of diazomethane:

Org. Synth., 1956, 36, 16.

$p\text{-}CH_3C_6H_4SO_2N(NO)CH_3$ + ROH —— CH_2N_2 +
$p\text{-}CH_3C_6H_4SO_2,OR$ + H_2O

Quickfit apparatus was used and the joints were fitted with plastic sleeves to limit the possibility of an explosion.

Potassium hydroxide (5g.), water (8c.c.) and 95% ethanol (25c.c.) were placed in a round bottomed flask. Two receiving flasks were placed in series with each other and 40 - 60c.c. was put into the second flask, to trap any diazomethane which might escape N-methyl-N-nitroso-p-toluene-sulphonamide (21.5g.) dissolved in ether (150c.c.) was added from a dropping funnel to the potassium hydroxide solution in the flask, which was on a water-bath kept at 60-70°. When addition was complete a further 50c.c. of ether was added and the distillation continued until the distillate was colourless. The distillate, containing diazomethane (2.6 - 2.7g.) was used immediately.

(-)-Dimethyl-1,1'-binaphthyl-8,8'-dicarboxylate:

The (-)-diacid (5g.) was slowly added to a cold ethereal solution of diazomethane (100c.c. - containing 1.3g. CH_2N_2) The reaction proceeded with an effervescence and a white solid crystallized out. When the reaction was complete, the solid was filtered off, washed with aqueous sodium carbonate, water and dried.

Yield: 4.5g., m.p. 124 - 126°

$[\alpha]^{20}_{546}$ - 217.5°.

(Found: C, 77.9; H, 4.93; O, 17.39. Calc. for $C_{24}H_{18}O_4$: C, 77.8; H, 4.9; O, 17.3%).

(+)-Dimethyl-1,1'-binaphthyl-8,8'-dicarboxylate:

Treatment ofthe (+)-diacid (5g.) as above gave the (+)-diester (4.5g.), m.p. 124-126°, $[\alpha]^{20}_{546}$ + 177.2°

(Found: C, 77.79; H, 4.81; O, 17.21. Calc. for $C_{24}H_{18}O_4$: C, 77.8; H, 4.9; O, 17.3%)

(+)-8,8'-Bisbromomethyl-1,1'-binaphthyl:

The mother liquor from above (containing the (+)-diol) was evaporated to dryness and the residue dissolved in hot glacial acetic acid. Hot hydrobromic acid (d=1.5) was added and a yellow dibromide separated out. More hydrobromic acid was added and the reaction mixture allowed to cool. The dibromide was filtered off, washed well with water and dried. Recrystallization from chloroform gave a yellow crystalline compound, m.p. 185-186°, $[\alpha]^{20}_{546}$ + 447.7°

(Found: C, 60.14; H, 3.76; Br, 36.37. Calc. for $C_{22}H_{16}Br_2$: C, 60.0; H, 3.7; Br, 36.3%)

(+)-8,8'-Bishydroxymethyl-1,1'-binaphthyl:

(-)-Dimethyl-1,1'-binaphthyl-8,8'-dicarboxylate (7.5g.) was reduced with lithium aluminium hydride as given in the synthetic section, except that the reaction mixture was refluxed for 1½ hours and the ether removed under reduced pressure from a water bath kept below 50°.

Yield: 1.5g., m.p. 143-145°, $[\alpha]^{20}_{546}$ + 16.5°

(Found: C, 83.7; H, 5.96; O, 10.29. Calc. for $C_{22}H_{18}O_2$: C, 84.05; H, 5.8; O, 10.2%)

(-)-8,8'-Bishydroxymethyl-1,1'-binaphthyl:

This was prepared in the same way as the (+)-diol, from (+)-dimethyl ester (7.5g.). The (-)-diol (1.4g.) had m.p. 143-145°, $[\alpha]^{20.5}_{546}$ - 13.5°

(Found: C, 83.7; H, 6.12; O, 10.26. Calc. for $C_{22}H_{18}O_2$: C, 84.05; H, 5.8; O, 10.2%)

(-)-8,8'-Bisbromomethyl-1,1'-binaphthyl:

The mother liquor from the preparation of the (-)-diol was evaporated to dryness and the residue dissolved in hot glacial acetic acid. Hot hydrobromic acid (d=1.5) was added and the dibromide separated out. More hydrobromic acid was added and the reaction mixture allowed to cool. The dibromide was filtered off, washed with water, dried and recrystallized from chloroform to give a yellow crystalline compound, m.p. 185-186°, $[\alpha]^{20}_{546}$ - 437.7°

(Found: C, 60.19; H, 3.8; Br, 36.45. Calc. for $C_{22}H_{16}Br_2$: C, 60.0; H, 3.7; Br, 36.3%)

<u>(+)-8,8'-Dimethyl-1,1'-binaphthyl:</u>

(+)-8,8'-Bisbromomethyl-1,1'-binaphthyl (5g.) $[\alpha]^{20}_{546}$ +447.7° in sodium dried ether (750c.c.) was added with stirring, to lithium aluminium hydride (1.4g.) in the same solvent (500c.c.) and the reaction mixture heated under reflux for one hour. Excess metal hydride was decomposed by dropwise addition of ethyl acetate and the excess potassium hydroxide was added. The organic layer was washed with water and dried over magnesium sulphate. The solvent was removed under reduced pressure and the residue crystallizes from ether.

Yield: 2.7g. m.p. 129-130°, $[\alpha]^{20}_{546}$ + 257.5°

(Found: C, 93.5; H, 6.38; Calc. for $C_{22}H_{18}$: C, 93.6; H, 6.4%)

<u>(-)-8,8'-Dimethyl-1,1'-binaphthyl:</u>

Treatment of the (-)-8,8'-bisbromomethyl-1,1'-binaphthyl $[\alpha]^{20}_{546}$ - 437.7° as above, gave the (-)-dimethyl compound, m.p. 129-130°, $[\alpha]^{20}_{546}$ - 198.8°

(Found: C, 93.49; H, 6.48. Calc. for $C_{22}H_{18}$: C, 93.6; H, 6.4%)

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Racemisation Parameters for 8′-Methyl-1,1′-binaphthyl-8-carboxylic Acid. Negligible Steric Retardation by the Carboxylic Acid Group

By MARGARET M. HARRIS and R. Z. MAZENGO

(*Department of Chemistry, Bedford College, London, N.W.*1)

THE Arrhenius parameters and transition-state theory functions for racemisation in *NN*-dimethylformamide solution of optically active 1,1′-binaphthyl, 1,1′-binaphthyl-8-carboxylic acid, and 1,1′-binaphthyl-8,8′-dicarboxylic acid are remarkably alike.[1]

The racemisation of optically active 8-methyl-1,1′-binaphthyl has recently been studied.[2] We have now resolved 8′-methyl-1,1′-binaphthyl-8-carboxylic acid[3] through its brucine salt and observed its racemisation in *NN*-dimethylformamide solution at eight temperatures between 70° and 105°. The racemisation parameters calculated from the velocity constants are almost identical with those for the 8-methyl-1,1′-binaphthyl:—

The 8-carboxylic acid group appears to make no significant measurable steric contribution to the energy barrier to racemisation. One possible explanation is that it is equally effective in its steric influence on the energy of the ground state and of the transition state; this is not the case for the methyl group.[2]

Proof of the situation of the methyl group and the carboxylic acid group in the 8- and 8′-positions rests on (a) the synthesis from 1,1′-binaphthyl-8,8′-dicarboxylic acid, (b) ready decarboxylation to 8-methyl-1,1′-binaphthyl, and (c) formation of a mixed anhydride (with acetic anhydride) accompanied by ring closure to form 13-methyl-7-oxodibenz[*a,kl*]anthracene on long boiling.

	E_{rac} (k.cal. mole^{-1})	$\log_{10} A$	$\Delta F^{\ddagger}$	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$ (e.u.)
			(k.cal. mole^{-1})		
1,1′-Binaphthyl[1]	22·5	12·1	23·5	21·9	−5·2
1,1′-Binaphthyl-8-carboxylic acid[1]	22·4	12·0	23·5	21·8	−5·5
1,1′-Binaphthyl-8,8′-dicarboxylic acid[1]	22·1	11·3	24·4	21·5	−9·1
8-Methyl-1,1′-binaphthyl[2]	25·3	11·7	27·2	24·6	−7·3
8′-Methyl-1,1′-binaphthyl-8-carboxylic acid	25·3	11·6	27·4	24·6	−7·7

(*Received, December* 15*th*, 1966; *Com.* 995.)

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[1] A. S. Cooke and M. M. Harris, *J. Chem. Soc.*, 1963, 2365.

[2] A. S. Cooke and M. M. Harris, submitted for publication.

[3] The (±)-acid was prepared in 1965 by A. S. Cooke and M. M. Harris (unpublished).

Negligible Steric Retardation by the Carboxy-group in the Racemisation of 8′-Methyl-1,1′-binaphthyl-8-carboxylic Acid[1]

By **Margaret M. Harris,*** **R. Z. Mazengo,** and (in part) **Ann S. Cooke,** Chemistry Department, Bedford College, Regent's Park, London N.W.1

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Negligible Steric Retardation by the Carboxy-group in the Racemisation of 8′-Methyl-1,1′-binaphthyl-8-carboxylic Acid[1]

By **Margaret M. Harris**,* **R. Z. Mazengo**, and (in part) **Ann S. Cooke**, Chemistry Department, Bedford College, Regent's Park, London N.W.1

8′-Methyl-1,1′-binaphthyl-8-carboxylic acid has been synthesised and resolved into its enantiomeric forms. Arrhenius parameters and transition-state theory functions for racemisation in *NN*-dimethylformamide solution have been determined and are compared with those for optically active 1,1′-binaphthyl and its relevant substitution products.

IN the 1,1′-binaphthyl series, where all members are inherently capable of optical activity, substitution in the 2- and 2′-positions confers much greater resistance to optical inversion than does substitution in the 8- and 8′-positions.[2] While 1,1′-binaphthyl-2,2′-dicarboxylic acid is optically stable, the 8,8′-acid is easily optically labile; this difference has been attributed to the ground-state energy of *peri*-substituted naphthalenes, resulting from steric compression and being accompanied by distortion which is favourable to configurational inversion.[2,3] Moreover, the Arrhenius parameters for racemisation of the 8- and 8,8′-substituted carboxylic acids and esters are strikingly like those for 1,1′-binaphthyl itself;[2] in other words, the molecules reach the transition state for optical inversion as easily as if the substituents were not present.

Unlike the acid and ester groups, which show this steric peculiarity, methyl and hydroxymethyl groups in the 8- and 8′-positions make a substantial addition to the energy of activation for racemisation;[3,4] here the increment difference, $E'_{(\text{transition state})} - E'_{(\text{ground state})}$, is positive, while for acid and ester groups it is effectively zero.

To complete the investigation of this series of 1,1′-binaphthyls, we have prepared optically active 8′-methyl-1,1′-binaphthyl-8-carboxylic acid and determined its racemisation parameters in *NN*-dimethylformamide solution. The starting material for synthesis is 8-bromo-1-naphthoic acid;[5] this might in principle afford two routes: (*a*) one in which half the material was reduced (as its methyl ester)[6] to 1-bromo-8-methylnaphthalene, followed by a mixed Ullmann reaction with the other half; or (*b*) the binaphthyl dicarboxylic acid could be prepared initially and then one acid (or ester) group reduced to the methyl group, leaving the other. Route (*a*) proved impractical at the reduction stage, but (*b*) was effective. 8′-Ethoxycarbonyl-1,1′-binaphthyl-8-carboxylic acid as an intermediate is preferable to the corresponding methyl ester, which it is more difficult to separate from the di-acid. The monoethyl ester was converted into 8′-hydroxymethyl-1,1′-binaphthyl-8-carboxylic acid by lithium aluminium hydride reduction, thence into the bromomethyl compound which with lithium aluminium hydride yielded 8′-methyl-1,1′-binaphthyl-8-carboxylic acid.* A slightly different route to the same compound led through the alkaline hydrolysis of 8-hydroxymethyl-8′-methoxycarbonyl-1,1′-binaphthyl.

Resolution was accomplished by crystallisation of the brucine salt from ethanol, the (−)-acid being obtained from the least soluble salt and the (+)-acid from the mother-liquor. Racemisation was followed in *NN*-dimethylformamide solution at eight temperatures between 70 and 105°.

Arrhenius parameters and transition-state theory functions for racemisation in *NN*-dimethylformamide solution

	E_{rac} (kcal. mole^{-1})	$\text{Log}_{10} A$	$\Delta F^\ddagger$ (kcal.	$\Delta H^\ddagger$ mole^{-1})	$\Delta S^\ddagger$ (e.u.)
1,1′-Binaphthyl	22·5	12·1	23·5	21·9	−5·2
1,1′-Binaphthyl-8-carboxylic acid[3]	22·4	12·0	23·5	21·8	−5·5
1,1′-Binaphthyl-8,8′-dicarboxylic acid[2]	22·1	11·3	24·4	21·5	−9·1
8-Methyl-1,1′-binaphthyl[3]	25·3	11·7	27·2	24·6	−7·3
8′-Methyl-1,1′-binaphthyl-8-carboxylic acid	25·3(5)	11·6	27·4	24·6	−7·7

Reference to the Table shows that the racemisation parameters for 8′-methyl-1,1′-binaphthyl-8-carboxylic acid are almost identical with those for 8-methyl-1,1′-binaphthyl; the overall increment (compared with 1,1′-binaphthyl) is that of the methyl group alone.

Group migration is not unknown in the naphthalene series;[7,8] therefore it is reasonable to look closely at the proof of the orientation of the methyl acid. The evidence is as follows: (*a*) the acid is prepared from 1,1′-binaphthyl-8,8′-dicarboxylic acid which is itself easily converted into anthanthrone;[9,10] (*b*) when boiled in

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* The (±)-acid was first prepared in 1965 by A. S. Cooke and M. M. Harris (unpublished) from (±)-8′-ethoxycarbonyl-1,1′-binaphthyl-8-carboxylic acid.

[1] Preliminary communication, M. M. Harris and R. Z. Mazengo, *Chem. Comm.*, 1967, 125.

[2] A. S. Cooke and M. M. Harris, *J. Chem. Soc.*, 1963, 2365, and references therein.

[3] Y. Badar, A. S. Cooke, and M. M. Harris, *J. Chem. Soc.*, 1965, 1412.

[4] A. S. Cooke and M. M. Harris, *J. Chem. Soc.* (*C*), 1967, 988.

[5] H. G. Rule, W. Pursell, and R. R. H. Brown, *J. Chem. Soc.*, 1934, 168.

[6] G. J. Karabatsos, R. L. Shone, and S. E. Scheppele, *Tetrahedron Letters*, 1964, 2113.

[7] G. Suld and A. P. Stuart, *J. Org. Chem.*, 1964, **29**, 2939.

[8] V. A. Koptyug, V. G. Shubin, and V. A. Plakhov, *Zhur. obshchei Khim.*, 1961, **31**, 4023.

[9] H. G. Rule and F. R. Smith, *J. Chem. Soc.*, 1937, 1096.

[10] Y. Badar, A. S. Cooke, and M. M. Harris, *J. Chem. Soc.* (*C*), 1966, 1315.

quinoline with copper-bronze the acid lost carbon dioxide and left a hydrocarbon identical (infrared spectrum, melting point, and mixed melting point) with 8-methyl-1,1′-binaphthyl;[4] (*c*) on boiling the acid with acetic anhydride under reflux for 5 hours a mixed anhydride was formed; longer boiling gave a small quantity of 13-methyldibenz[*a,kl*]anthracen-7-one, which shows a major infrared peak at the low value of 1633 cm.$^{-1}$ corresponding to that at 1637 cm.$^{-1}$ attributed to the carbonyl group in phenalen-1-one [11,12] and at 1640 cm.$^{-1}$ in dibenz[*a,kl*]anthracen-7-one.[10-12] Ring closure is evidently relatively inhibited in this compound, in comparison with the 8- or 8,8′-carboxylic acids, probably owing to the steric influence of the methyl group. The carbonyl peak in the methyl acid itself is at 1689 cm.$^{-1}$.

EXPERIMENTAL

Optical rotations were measured on the 'Carl Zeiss Photoelectric Precision Polarimeter 0·005°' and refer to $\lambda = 578$ mμ. Portions of a solution of optically active 8′-methyl-1,1′-binaphthyl-8-carboxylic acid were sealed in glass tubes, kept in an oil thermostat, withdrawn at suitable intervals, immediately cooled to room temperature, and the optical rotation was read at 21·5°. Material recovered after complete racemisation was identical in m. p., mixed m. p., and infrared spectrum with the original (±)-acid.

Action of Lithium Aluminium Hydride on Methyl 8-*Bromo*-1-*naphthoate*.—Methyl 8-bromo-1-naphthoate[5] (6·6 g.) was dissolved in sodium-dried ether, added to lithium aluminium hydride (2·9 g.) in sodium-dried ether, and heated under reflux for 1½ hr. Normal work-up gave a liquid product which thin-layer chromatography on alumina showed to be mainly a single substance, containing a small quantity of a second one. The whole was dissolved in boiling glacial acetic acid and hydrobromic acid added at the boiling point; the yellow liquid which separated was extracted with benzene and treated with lithium aluminium hydride. Normal work-up gave 1-methylnaphthalene containing no trace of a second product (thin-layer chromatography).

(±)-8′-*Hydroxymethyl*-1,1′-*binaphthyl*-8-*carboxylic Acid*.—*Method A*. (±)-Ethyl hydrogen 1,1′-binaphthyl-8,8′-dicarboxylate[13] (5·0 g.) suspended in sodium-dried ether and benzene (1 : 1) (300 c.c.) was added to lithium aluminium hydride (5·0 g.) in the same mixed solvent (450 c.c.) and heated under reflux for 2 hr. Normal work-up gave the *product* (2·5 g.), m. p. 219—220° (from ethanol) (Found: C, 80·1; H, 4·9; O, 15·3. $C_{22}H_{16}O_3$ requires C, 80·5; H, 4·9; O, 14·6%).

Method B. (±)-8-Hydroxymethyl-8′-methoxycarbonyl-1,1′-binaphthyl[3] (2·4 g.) was boiled with 30% ethanolic potassium hydroxide (40 c.c.) for ½ hr. The ethanol was then removed and the residue heated at 130—140° for ½ hr. Normal work-up gave the (±)-hydroxy-acid (1·9 g.), m. p. 219—220°, identical with the product from method A.

(±)-8′-*Bromomethyl*-1,1′-*binaphthyl*-8-*carboxylic Acid*.—The above hydroxymethyl acid (3·0 g.) was dissolved in boiling glacial acetic acid (60 c.c.) and allowed to cool for a few minutes. Hot hydrobromic acid was added, with stirring. After 1 hr. the solution had deposited pale yellow crystals; recrystallisation from glacial acetic acid gave the *product* (3·1 g.), m. p. 180—190° (decomp.) (Found: C, 67·5; H, 4·05; Br, 20·4; O, 8·2. $C_{22}H_{15}BrO_2$ requires C, 67·5; H, 3·9; Br, 20·4; O, 8·2%).

(±)-8′-*Methyl*-1,1′-*binaphthyl*-8-*carboxylic Acid*.—The above bromomethyl acid (5·0 g.) in sodium-dried ether (200 c.c.) and benzene (50 c.c.) was added to lithium aluminium hydride (5·0 g.) in the same mixed solvent (500 c.c.) and heated under reflux for 1½ hr. Normal work-up gave the *product* (2·1 g.), m. p. 252—254° (from ethanol) (Found: C, 84·4; H, 5·3; O, 10·2. $C_{22}H_{16}O_2$ requires C, 84·6; H, 5·2; O, 10·2%); major infrared peak at ~1689 cm.$^{-1}$.

Resolution of (±)-8′-*Methyl*-1,1′-*binaphthyl*-8-*carboxylic Acid*.—The resolution was effected by crystallising the brucine salt from ethanol; various conditions were tried and the optimum procedure was as follows. The (±)-acid (2·0 g.) was dissolved in ethanol (300 c.c.) and to it was added a solution of brucine (3·0 g., 1·2 mol.) in ethanol (300 c.c.). The solution was evaporated down to 150 c.c. and allowed to cool slowly to room temperature; 1·8 g. of brucine (−)-acid salt (A) crystallised, m. p. 161—163°, $[\alpha]^{21\cdot5}$ −239·9° (in $CHCl_3$). Concentration of the mother-liquor from (A) to half-volume gave a further 0·5 g. of brucine salt (B), m. p. 161—162·5°, $[\alpha]^{21\cdot5}$ −211·8°; (A) and (B) together represent a 50% yield of brucine salt, based on the quantity of (±)-acid used. The salt (A) was dissolved in chloroform and twice extracted with N-sodium hydroxide; the alkaline extract was washed twice with chloroform and once with ether, and acidified with hydrochloric acid, to give 0·55 g. of the (−)-*acid*, m. p. 247·5—248°, $[\alpha]^{21\cdot5}$ −253·4° (in $CHCl_3$). Cool evaporation of the mother-liquor from (B) gave a non-crystalline residue (C) which failed to crystallise from any of a large variety of solvents. It was therefore dissolved in chloroform and the (+)-*acid* extracted from it as described for salt (A). It had m. p. 247·5—248°, $[\alpha]^{21\cdot5}$ +250·2° ($CHCl_3$).

The (−)-acid racemised when heated under reflux in sodium hydroxide solution; the (±)-acid recovered was identical with the (±)-acid used for the resolution (m. p., mixed m. p., infrared spectrum). Racemisation was not followed polarimetrically in sodium hydroxide solution, as the rotation of the sodium salt in water is inconveniently small in comparison with that of the acid in *NN*-dimethylformamide.

Racemisation of (+)- *and* (−)-8′-*Methyl*-1,1′-*binaphthyl*-8-*carboxylic Acid in* NN-*Dimethylformamide Solution*.—Racemisation took place according to the first-order kinetic law. Calculation of E, $\log_{10} A$, $\Delta F^‡$, $\Delta H^‡$, and $\Delta S^‡$ was carried out according to the procedure previously outlined.[14]

	70·0°	75·3°	80·1°	85·05°
c	0·5029	0·6200	0·5515	0·5580
10^5k (sec.$^{-1}$)	3·2	5·4	8·65	14·65
	90·0°	95·0°	100·0°	105·0°
c	0·5500	0·5240	0·7010	0·5740
10^5k (sec.$^{-1}$)	24·1	40·1	59·5	98·5

whence $E = 25\cdot3$ kcal. mole^{-1} (graphical), 25·4 (least-squares calculation); $\log_{10} A = 11\cdot6$. $\Delta F^‡ = 27\cdot4$ kcal. mole^{-1}; $\Delta H^‡ = 24\cdot6$ kcal. mole^{-1}; $\Delta S^‡ = -7\cdot7$ e.u.

Decarboxylation of (±)-8′-*Methyl*-1,1′-*binaphthyl*-8-*carboxylic Acid*.—The (±)-acid (1·0 g.) was boiled in quinoline with copper-bronze for about 20 min. Normal work-up

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[11] N. H. Cromwell and G. V. Hudson, *J. Amer. Chem. Soc.*, 1953, **75**, 872.

[12] D. H. Reid and R. G. Sutherland, *J. Chem. Soc.*, 1963, 3295.

[13] J. Meisenheimer and O. Beisswenger, *Ber.*, 1932, **65**, 32.

[14] D. M. Hall and M. M. Harris, *J. Chem. Soc.*, 1960, 490.

and crystallisation from light petroleum (b. p. 40—60°) gave 8-methyl-1,1′-binaphthyl, m. p. 113—115° (0·3 g.).[4]

Action of Acetic Anhydride on (±)-*8′-Methyl-*1,1′-*bi-naphthyl-*8-*carboxylic Acid.*—The acid (1·0 g.) dissolved in acetic anhydride (20 c.c.) was boiled for 5 hr. On cooling, the *mixed anhydride*, colourless needles (0·7 g.), m. p. 120—121°, was deposited (Found: C, 81·5; H, 4·9; O, 13·6. $C_{24}H_{18}O_3$ requires C, 81·3; H, 5·1; O, 13·5%). If boiling of the above solution was continued for 10 hr. in all, on concentration 13-*methyldibenz*[a,kl]*anthracen*-7-*one*, m. p. 158—159°, was deposited (Found: C, 89·75; H, 4·6; O, 5·5. $C_{22}H_{14}O$ requires C, 89·75; H, 4·8; O, 5·4%); strong infrared peak at 1633 cm.$^{-1}$.

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