THE SYNTHESIS AND STEREOCHEMISTRY OF SOME SUBSTANCES DERIVED FROM 1,1'-BINAPHTHYL-8,8'-DICARBOXYLIC ACID

A THESIS
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ABSTRACT

Experimental data have been accumulated in order to compare the optical stabilities of several 8,8'-disubstituted-1,1'-binaphthyls, thus extending the work already done on the 8,8'-acid and its esters to blocking groups of distinctly different character.

The compounds studied are 1,1'-binaphthyls substituted in 8 and 8' positions by hydroxymethyl, bromomethyl, methyl, methylene quinolinium bromide and methoxy carbonyl groups; in addition benzo-1',2'-7,8-benzanthrone-3'-carboxylic acid and its methyl ester have been prepared. All these compounds have been synthesised for the first time (except benzo-1',2'-7,8-benzanthrone-3'-carboxylic acid and its ester)and have been obtained in their optically active state for the first time. Their rate co-efficients for racemisation have been determined at several temperatures covering the range 30^{0}-40^{0} (except 8,8'-bisbromomethyl and 8,8'-bis(methylenequinolinium bromide)-1,1'-binaphthyls which were decomposed in N,N-dimethylformamide). The solvent used for all the compounds was N,N-dimethylformamide. From the experimental results the Arrhenius Parameters E and $\log_{10}A$ and the Transition State Theory functions $\Delta H^{\neq}$, $\Delta S^{\neq}$ and $\Delta F^{\neq}$ have been calculated using the equations,

$$\underline{k} = A\, e^{-E/RT} \quad ; \quad \Delta H^{\neq} = E - RT \qquad (\text{i})$$

$$\underline{k} = \kappa \frac{\underline{\underline{k}}\, T}{h}\, e^{-\Delta H^{\neq}/RT}\, e^{-\Delta S^{\neq}/R} \qquad (\text{ii})$$

$$\underline{k} = \kappa \frac{\underline{\underline{k}}\, T}{h}\, e^{-\Delta F^{\neq}/RT} \qquad (\text{iii})$$

In the discussion the optical stability of optically labile substituted 1,1'-binaphthyls have been described. A comparison of the racemisation parameters has been made which appears to show that the $-CH_3$ and the $-CH_2OH$ groups, which are rounded (or three dimensional) produce larger angular blocking area to passing than the $-COOH$ and $COOCH_3$ or $COOC_2H_5$ groups do, which are "flat". That is, 8,8'-bishydroxymethyl, 8,8'-dimethyl and 8'-hydroxymethyl-8'-methoxy carbonyl-1,1'-binaphthyls are more stable than 1,1'-binaphthyl-8,8'-dicarboxylic acid and its ester. All these compounds are also concluded to be strained in their ground state as they are much less stable than the 1,1'-binaphthyl-2,2'-dicarboxylic acid. The strain is obvious also from the models.

In the experimental section the syntheses and the methods by which the optical activity was gained have been described.

In the final part some infrared spectral data for 1,1'-binaphthyl-8,8'-dicarboxylic acid, its ester and 1',2'-7,8-(benzanthrone)-3'-carboxylic acid is given. No complete conclusion can be drawn from these spectra, but it may be seen in 1,1'-binaphthyl-8,8'-dicarboxylic acid the (+) and (-) forms have similar infrared spectra and hence have the same molecular configuration apart from the mirror image isomerism, while in (±) acid the infrared spectrum shows distinct differences therefore it probably has a different configuration. The difference could be because of the hydrogen bonding which may be different in the two cases owing to different spatial configuration of the carboxylic acid groups relative to each other.

CONTENTS.

CONTENTS (contd.) Page.

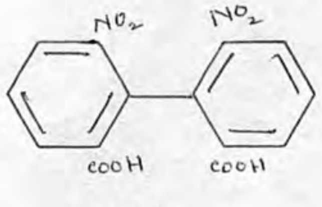
CONTENTS (contd.) Page

Tables.

INTRODUCTION

Optical activity due to restricted rotation about a single bond was first recognised in substituted biphenyls, with the interpretation of Kenner's (J., 1922, 614) resolution of 6,6'-dinitrodiphenic acid by Bell and Kenyon (Chem. and Ind., 1926, 45, 864), Mills (ibid., 1926, 45 884, 905) and Turner and Le Fèvre (ibid., 1926, 45, 831; they rejected Kaufler's "bent" formula (Ann., 1907, 351,151.,Ber. 1907, 40, 3250) in favour of coaxial benzene rings.

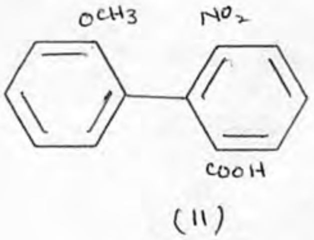
A substituted biphenyl is intrinsically capable of optical activity if each ring carries at least one substituent unsymmetrically placed, and if the molecule is not flat. The "flat" molecule represents the half-way stage between a(+) and a (-) form. Therefore if optical activity is to be observed, flattening under the conditions of observation must be prevented to some extent. This can be done by 4, 3, 2 or 1 obstacles:-



(I)

Christie and Kenner

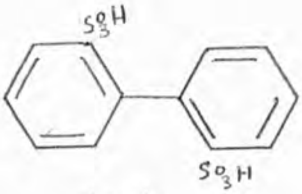
(J.,1922, 121, 614)



(II)

Stoughton and Adams

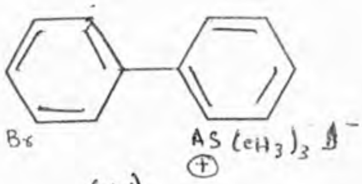
(J.A.C.S., 1932, 54, 4426)



(III)

Lesslie and Turner

(J., 1932, 2394)



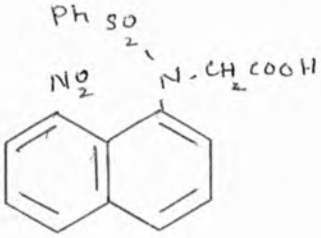
(IV)

Lesslie and Turner

(J.,1933, 1588)

The (+)-camphor sulphonate of 3-bromobiphenyl-2-trimethyl arsonium iodide (IV) shows mutarotations: the arsonium iodide obtained had a very tiny rotation which was ~~gone~~ reduced to zero after heating it at 100° for 2 hours. This shows that the molecule is not planar. This is the only known example of the optical activity depending on only one obstacle. They failed to resolve the corresponding 2-trimethyl-ammonium salts.

There are many other types of compounds where the optical activity in the molecule is produced by restricted rotation. e.g. Mills and Elliott, (J., 1928, 1291) obtained N-benzenesulphonyl-8-nitro-1-naphthyl-glycine (V) in optically active forms. Mills and Kelham (J., 1937, 274) resolved N-acetyl-N-methyl-p-toluene-3-sulphonic acid (XVI). They also prepared a series of 1-alkyl-acyl-amine-8-naphthalene-sulphonic acids and resolved these compounds (VII) (J., 1937, 274).



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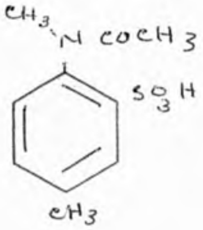
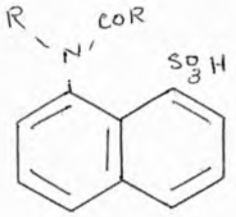
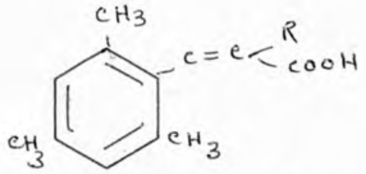


(VI)

Adams and Miller (J.A.C.S.,1940, 62, 53) resolved substituted stilbenes, (VIII).



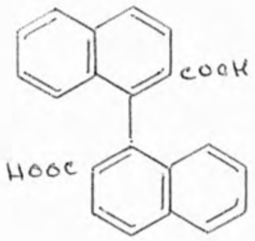
(VII)



(VIII)

$R = CH_3, H$

Kuhn and Albrecht (Ann., 1928, 465, 282) resolved 1,1'-binaphthyl-2,2'-dicarboxylic acid (IX). Corbellini, (Atti Accad, Lincei., 1931, 13 702), Stanley (J.A.C.S., 1931, 53, 3104) and Meisenheimer and Beisswenger (Ber., 1932, 65, 32) almost simultaneously reported the resolution of 1,1'-binaphthyl-8,8'-dicarboxylic acid (X) and recognised as disubstituted biphenyl with the $\underset{/\ \backslash\backslash}{C}$ - COOH groups in the 2 and 2' positions.



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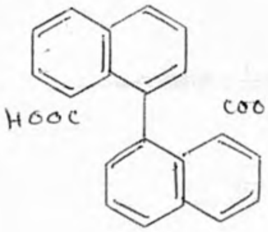
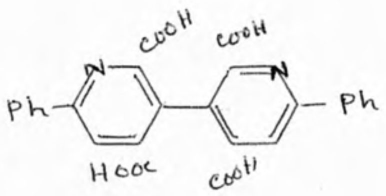
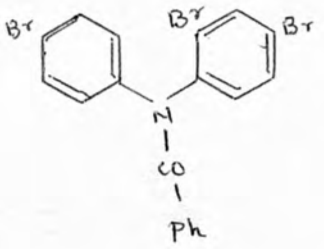


(X)

Jamison and Turner (J. 1938, 1646) obtained (XII) in the optically active state and Woodruff and Adams, (J.A.C.S., 1932, 54, 1977) resolved (XIII).



(XIII)



(XII)

These are only few examples out of many other compounds that have been resolved and have asymmetry due to restricted rotation.

Measurement and Assessment of the Optical Stability of Labile Optically Active Compounds

Racemisation is a transformation of an optically active form into equal quantities of (+) and (-) forms and is found to follow the unimolecular law in sterically hindered compounds. Kuhn and Albrecht (Ann., 1927, 455, 272, 458, 221) were the first to observe that the racemisation of a hindered biphenyl, a nitrodiphenic acid, obeyed the first order reaction rate law in sodium carbonate solution. The rate constant **k** for racemisation may be calculated from the first order rate equation,

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

where α_0 = initial rotation

α_t = rotation after time t.

The first order rate constant **k** and the resulting half life-period for racemisation in a given solvent and at given temperature were used as a quantitative measure of optical stability by Adams and his co-workers (J.A.C.S., 1939, 61, 2825)

The kinetics of racemisation of sterically hindered compounds has also been studied using the Arrhenius relationship,

$$\underline{k} = Ae^{-E/RT}$$

where $\underline{k}$ = rate constant
$\overline{E}$ = energy of activation
A = probability factor
R = gas constant
T = absolute temperature

By measuring values of $\underline{k}$ at different temperatures and using the above equation, E, the energy of activation - i.e. the energy barrier over which the molecule inverts its configuration, and the probability factor, A (PZ) which is related to the probability that the molecule having got sufficient energy will invert may be calculated. The first people who used the Arrhenius relationship for the racemisation of sterically hindered compounds were Kuhn and Albrecht (Ann., 1927, 455, 272). They worked on the racemisation of some dinitro and trinitro diphenic acids and calculated the energy of activation from the rate constants at different temperatures.

Finally Cagle and Eyring (J.A.C.S., 1951, 73, 5628) applied the Glasstone, Laidler and Eyring's absolute reaction rate theory equation for the racemisation of certain sterically hindered compounds, (Glasstone, Laidler and Eyring, "The Theory of Rate Processes", McGraw-Hill, New York, 1941).

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

where $\underline{k}$ = rate constant

κ = transmission co-efficient

$\underline{\underline{k}}$ = Boltzmann's constant

h = Plank's Constant

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

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

R = gas constant

T = Absolute temperature .

From the above equation, $\Delta S^{\neq}$, the entropy of activation may be evaluated on determining the value of $\Delta H^{\neq}$, the enthalpy of activation, from $\Delta H^{\neq} = E - R\,T$.

$\Delta F^{\neq}$, the free energy of activation, may be evaluated from the relationship:

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

The free energy of activation has been often used as a measure of optical stability as it is related to the measured quantity $\underline{k}$.

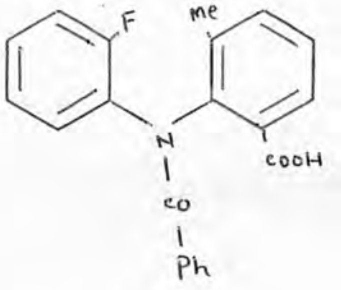
$$\underline{k} = \kappa \frac{\underline{\underline{k}}\,T}{h}\, e^{-\Delta F^{\neq}/RT} \quad (\text{since } \Delta F^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq}$$

Its value could be raised from an unobservable to an observable value by a large negative entropy factor. Rieger and Westheimer (<u>J.A.C.S.</u>, 1950, <u>72</u>, 24) thought for a straight forward unimolecular reaction in solution entropy factor is of the order - 6.0 e.4.

All of these factors $\Delta F^{\neq}$, $\Delta H^{\neq}$ and $\Delta S^{\neq}$, are called the transition state theory functions; these and the Arrhenius factors, E and A have been used to describe the optical stability of any particular compound. If the probability factor (or the entropy factor) were constant, the optical stability would be measured by energy of activation E, the greater the energy of activation the more optically stable the compound. But it is not always so because sometimes the probability factor A (and the entropy of activation $\Delta S^{\neq}$) effects the rate as well as E.

Cagle and Eyring (J.A.C.S., 1951 73, 5628) collected the racemisation data available at the time and calculated $\Delta S^{\neq}$ and $\Delta H^{\neq}$ for a number of compounds in order to try to co-relate the structure and the reaction rate. The data given in their table are not sufficient to make a very profitable discussion, as, in some cases, there are only two values of k at different temperatures with which to plot the graph to calculate $\Delta H^{\neq}$. Besides, the solvent used differed with the different compounds, and the change of solvent makes a difference to the rate of racemisation. P.B.D. de la Mare (Progress in Stereo-chemistry, Vol. 1, p. 122) in his criticism said he thought that "The authors should await a considerable extension of the existing information." However they were the first to point out that $\Delta S^{\neq}$ could be important in racemisations.

Brooks, Harris and Howlett (J., 1957, 2380), worked on a series of substituted N-benzoyl-diphenylamine-2-carboxylic acids and discussed their optical stabilities from the racemisation velocity constants and from the E, A and $\Delta S^{\neq}$ values. They explained that the differnnce in stability between 6-methyl-2'-fluoro-N-benzoyl-diphenylamine-2-carboxylic acid (XIV) having E = 14.9 k calmole^{-1} and $t_{\frac{1}{2}}^{20}$ = 3.2 minutes, and that of 4:6-dibromo-N-benzoyl-diphenylamine-2-carboxylic acid (XV) with E = 19.3 k calmole^{-1} and $t_{\frac{1}{2}}$ = 1.4 minutes apart from the steric factors must be due to the entropy of activation, which is only -4.1 e.u. for (XV) in comparision with -20.9 e.u. for the former(XIV).



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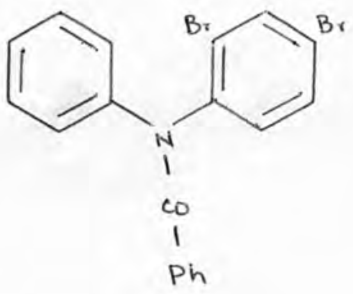
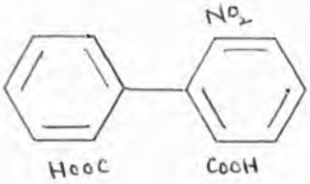


(XV)

Brooks, Harris and Howlett (J., 1957, 1934) also made some interesting investigations along these lines, working on some nitro diphenic acids. They found that the E values for the racemisation of 6-nitro-, 6,4'-dinitro-, and 4,6,4'-trinitro-diphenic acid in sodium carbonate solution were equal, 22.6 k calmole^{-1}.



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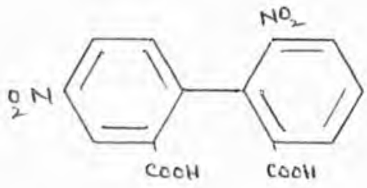
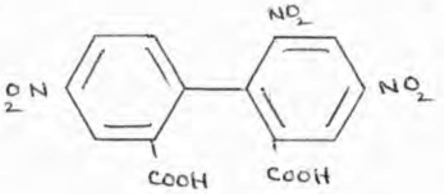


(XVII)



(XVIII)

The half lives were 28, 91 and 208 minutes respectively. The increase in stability on addition of the 4 and 4' nitro groups in which they can have no steric effect, was shown to be due to the $\Delta S^{\neq}$ values, which were respectively -12.2, -14.7 and -16.2 e.4. (or alternatively in A (PZ) values, $10^{10.6}$, $10^{10.1}$ and $10^{9.7}$)

From the collection of the experimental data by Hall and Harris (J., 1960, 490), who were able to compile a table of Arrhenius parameters, and entropies of activation for the racemisation of 34 optically labile compounds, which owe their activity to restricted rotation, it may be seen that the entropy factor may vary in the range between + 9.e.4--20.e.4. and also that E values may spread over a wide range.

Calculation of energy of activation for racemisation.

Mayer and Westheimer (J. Chem. Phys., 1947, 15, 252) were the first who theoretically calculated the energy of activation of a sterically hindered biphenyl, 2,2'-dibromobiphenyl- of 18 k cal.mole^{-1}, by minimising the energy of a planor transition state with respect to bond deformation and Vander Waals interactions. Their method has been applied with some modifications for many other compounds by Howlett (J., 1960, 1055), and by Hall and Turner (J., 1955, 1242 - appendix).

Discussion on Optical Stability in 1,1'-Binaphthyls.

A number of substituted 1,1'-binaphthyls have been obtained in optically active forms, and it was found from the literature that all 2,2'-disubstituted-1,1'-binaphthyls are quite stable towards racemisation, so the substituted optically active 1,1'-binaphthyls may be divided into two classes.

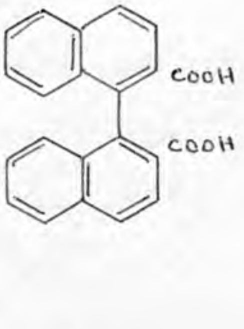
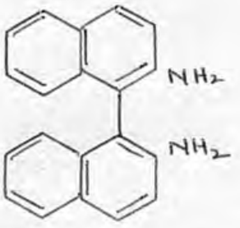
(i) Those which do not racemise or racemise with difficulty.

(ii) Those which racemise fairly easily.

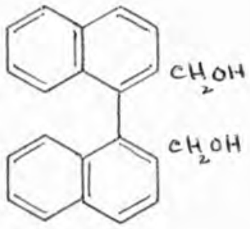
The tables of both types of compound are given below.

TABLE I

All 2,2'-Substituted-1,1'-Binaphthyls, showing high optical stability.

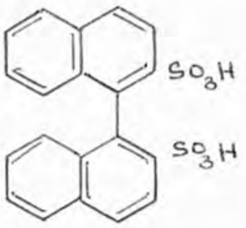
No.	Compounds.	Experiments.	Ref.
1		The rotation was found to be unchanged, when the solution in N-methylformamide was heated at 170°,after 8 hours	1 & 2
2		It is so optically stable that it underwent reaction at 200°, and yet the activity was retained.	3

3.



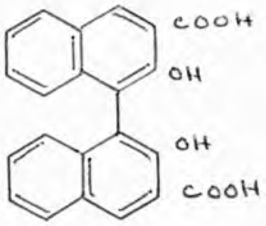
It was found to be so
stable that the melted diol, 9
solidified on cooling,
showed that racemisation
had not occured.

4.



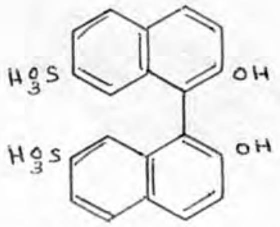
(−) Sodium salt proved to
have high optical stability.
Rotations in aqueous
sodium hydroxide in sealed 4
tubes was unchanged at
190^0-200^0 after 10 hours.

5.



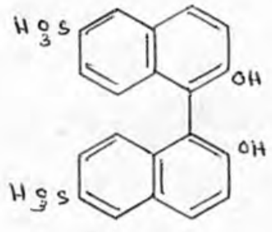
Stable towards racemisation. 5

6.
& 7.



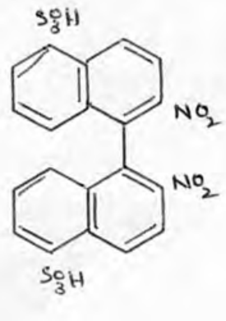
Stable towards any 6
ordinary method of
racemisation.

7.



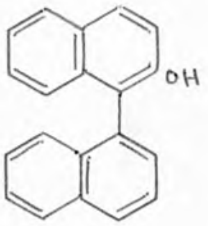
quite stable towards race- 6
misation

8.



Ba salts of 2,2'-dinitro,and 2,2'
diamino-1,1'-binaphthyl-5,5'-
disulphonic acid resolved by 8
crystallization from water
with PhCHmeNH$_2$ proved to be optically
stable. ~~Ph.CHme NH$_2$~~.

9.



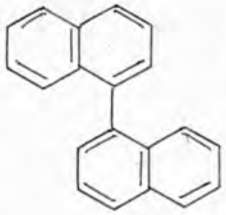
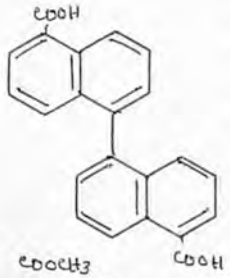
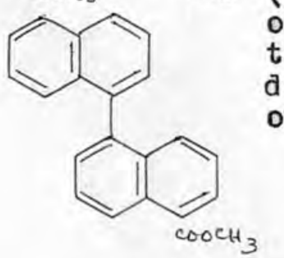
The acid succinate was racemised with difficulty, half life of about 2 weeks at 80°. and (+)2-hydroxy-1,1' binaphthyl under the same conditions had half life of about two days. 7

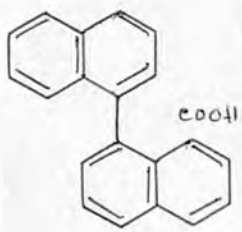
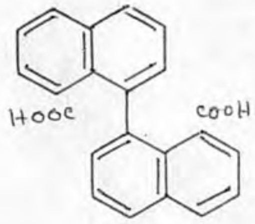
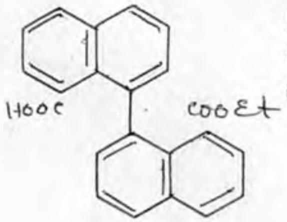
References for Table I

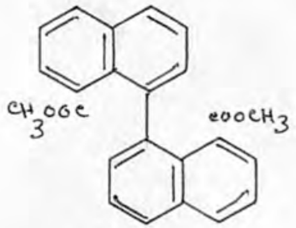
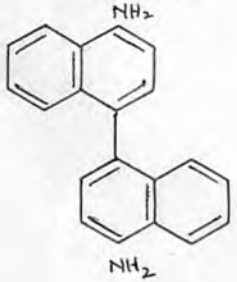
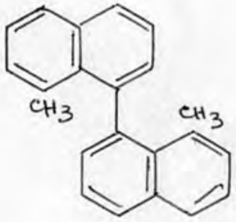
1. Kuhn and Albrecht, *Ann.*, 1928, *465*, 282.
2. Hall, Ridgwell and Turner, *J.*, 1954, 2498.
3. Kuhn and Goldfinger, *Ann.*, 1929, *470*, 183.
4. Armarego and Turner, *J.*, 1957, 13.
5. Stanley and Adams, *Rec. Trav Chem.*, 1929, *48*, 1035
6. Ioffe and Grachev. *J. Gen. Chem. U.S.S.R.* 1935, 1950
7. Berson and Greenbaum *J.A.C.S.*, 1958, *80*, 653.
8. Murahashi, *Sci-papers inst. Phys. Chem. Research Tokyo*, 1932, *17*, 297, *C.A.*, 1932, *26*, 2191.
9. Hall and Turner, *J.*, 1955, 1242.

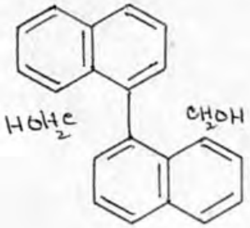
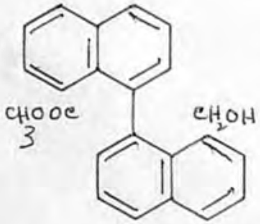
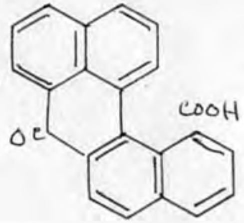
TABLE - 2

Optically labile 1,1' -Binaphthyls.

	Substituted 1,1'-binaphthyls.	Method by which optical activity was gained resolutions or optical activation.	Solvent	E k cal. $^{-1}$ mole	log$_{10}$A sec.$^{-1}$	$\Delta F^{\neq}$ kcal mole^{-1}	$\Delta H^{\neq}$ kcal. mole^{-1}	$\Delta S^{\neq}$ e.u.	$t_{\frac{1}{2}}$ in minutes at 50°	Temp. range	Ref.
(1)		Deamination of (+)-8 at low temperatures using hypophosphorous acid.	$HCONMC_2$	22.5	12.1	23.5	21.6	-5.2	14.5	31-59°	(1)
(2)		Second Order asymmetric transformation with Brucine from aq. ethyl Cellosolve.	$HCONMC_2$ N/10 NaOH	24.1 24.9	12.3 12.9	25.4 24.8	23.5 24.3	-5.9 -1.5	271.5 94	50-70 46-79	(1) & (11)
(3)		(+)form obtained by the action of diazomethane on (+) (2)	$HCONMC_2$	23.8	12.2	24.8	23.5	-5.1	101	49-70	(1)

	Substituted 1,1'-binaphthyls.	Method by which optical activity was gained resolutions or optical activation.	Solvent	E kcal. mole^{-1}	$\log_{10} A$ sec.$^{-1}$	$\Delta F^{\neq}$ kcal mole^{-1}	$\Delta H^{\neq}$ kcal. mole^{-1}	$\Delta S^{\neq}$ e.u.	$t_{\frac{1}{2}}$ in minutes at 50°	Temp. range	Ref.
(4)		Resolved through Brucine salt from ethyl acetate.	H.CON. Me_2	22.4	12.0	23.5	21.8	-5.5	15.4	19-69	(i) & (ii)
(5)		Resolved through Brucine salt from methyl alcohol	H.CO.NMe_2	22.1	11.3	24.4	21.5	-9.1	51.5	14-90	(i) &
			N/10 NaOH	26.0	15.2	22.5	25.4	+9.2	3	17-52	(iii)
(6)		Second Ord. Asym.Trans. with brucine from aqueous ethyl cellasolve	H.CON. Me_2	21.6	11.4	23.7	20.95	-8.4	18.3	30-75	(i)
			N/10 NaOH	25.7	14.0	24.0	25.1	+3.2	31	40-80	& (iii)

	Substituted 1,1'-binaphthyls.	Method by which optical activity was gained resolutions or optical activetion.	Solvent	E kcal. mole^{-1}	$\log_{10}A$ Sec.$^{-1}$	$\Delta F^{\neq}$ kcal mole^{-1}	$\Delta H^{\neq}$ kcal. mole^{-1}	$\Delta S^{\neq}$ e.u	$t_{\frac{1}{2}}$ in minutes at 50°	Temp. range	Ref
(7)		both (+) and (-)antipodes obtained by the action of diazomethane on active forms of (5)	H.CON.Me$_2$	22.0	11.6	23.8	21.4	-7.5	23	30-75	(i)
(8)		Second Ord. Asym. Trans with 2 mols of (+)-bromo-camphorsulphonic acid from 60% aq. ethanol.	Acetone	21.4		22.9	20.8	-7.1	24.6 at 38°C.	10.4-37.9	(IV)
(9)		(+)-form obtained by the action of LiAlH$_4$ on (+)-8,8'-bis(bromo-methyl)-1,1'-binaphthyl.	HCO.NMe$_2$	27.58	11.30	30.44	26.80	-9.3	678.8	100-130	*

	Substituted 1,1'-binaphthyls.	Method by which optical activity was gained resolutions of optical activation.	Solvent	E kcal. $mole^{-1}$	$\log_{10} A$ $sec.^{-1}$	$\Delta F^{\neq}$ kcal $mole^{-1}$	$\Delta H^{\neq}$ kcal. $mole^{-1}$	$\Delta S^{\neq}$ e.4	$t_{\frac{1}{2}}$ in minutes at 50°	Temp. range	Ref.
(10)		(+) and (-) obtained by the action of $LiAlH_4$ on (-) and (+) forms of dimethyl-1,1'-binaphthyl-8,8'-dicarboxylate.	HCO NMe_2	29.2	12.6	29.85	28.4	-3.66	374.5	100-130	*
(11)		(+) and (-)-antipodes by the action of Lithium aluminium hydride on active forms of (7)	HCON Me_2	25.8	11.96	27.2	25.1	-6.2	14.1 (2226.0 at 50°C).	55-95	*
(12)		(+) and (-) forms of (5) treated with H_2SO_4 (conc) in cold	HCO.N.Me_2	23.2	12.1	24.3	22.6	-5.3	48.5	30-75	*

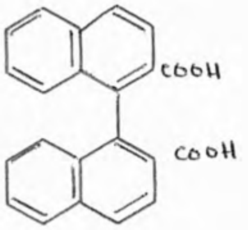
References for table II

* New work.

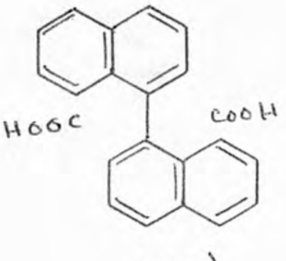
1. Cooke and Harris, *J.*, 1963, 2365
2. Bell, Morgan and Smyth, *Chem. and ind.*, 1951, 634
3. Meisenheimer and Beisswenger, *Ber.*, 1932, **65**, 32.
4. Theilacker and Hopp, *Ber.*, 1959, **92**, 2293

Considering the obstacle to rotation about the 1,1'-bond and examining the classical models of these structurally related acids (XX) (XXI) (XXII) and (XXIII) and the ester (XIV) the order of expected stability would be

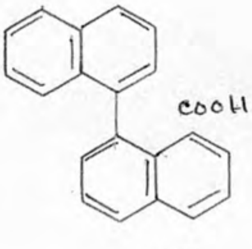
$$\mathrm{XIV} > \mathrm{XX} \simeq \mathrm{XXI} > \mathrm{XXII} > \mathrm{XXIII}$$



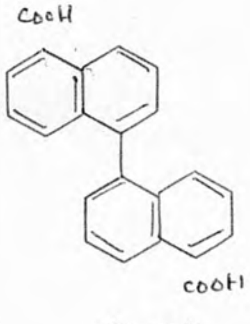
(XX)



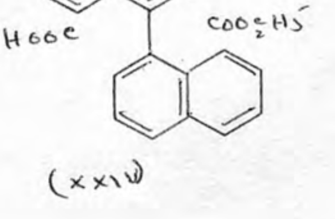
(XXI)



(XXII)



(XXIII)



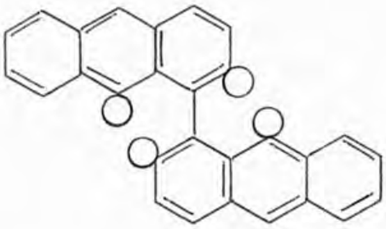
(XXIV)

But it was seen from the results of Meisenheimer and Beisswenger (Ber., 1932, 65, 32) and of Hall, Ridgwell and Turner (J., 1954, 2498) that (XX) was the most optically stable. The rotation was found to be unchanged after a solution of the acid in N-methyl formamide was heated at 170° for 8 hours.

It was rather surprising ~~why~~ that 1,1'-binaphthyl-8,8'-dicarboxylic acid is readily racemised while 1,1'-binaphthyl-2,2'-dicarboxylic acid was quite stable towards racemisation. As it appears from the study of the models, the interference with the free rotation about 1,1'-bond is very similar. Stanley, (J.A.C.S., 1931, 53, 3104) wrote that, "the difference in stability may be due to the fact that the peri-substituted carboxyl groups in 8,8'-dicarboxyl-1,1'-binaphthyl render the molecule more labile and more capable of distortion then when the carboxyl groups are in the 2,2' position". Later an explanation was suggested by Cooke and Harris (J., 1963, 2365) that the peri-substituted naphthlene units are strained in such a way that passing is almost as easy as in unsubstituted binaphthyl.

In the case of 1,1'-binaphthyl-5,5'-dicarboxylic acid, which has no carboxyl group in the blocking position, the only steric hindrance is provided by the overlap of hydrogen atoms. Bell, Morgan and Smyth (Chem and ind., 1951, 634) said that the scale diagram showed there was no restriction to rotation about the 1,1'-bond. However Bell and Waring

(J., 1949, 1579) had obtained 1,1'-bianthryl in its optically active forms, which were completely stable in chloroform at room temperature but were racemised in about 7 hours in boiling xylene solution. The scale diagram made according to Sidgwick (Ann. Report.1932, 29, 70) showed that the interference of the hydrogen atom in position number 9 with that in position 2', (which is same as 8 and 2' hydrogen atoms in 1,1'-binaphthyl) appeared to be less than 0.2A: This seems a very small overlap for such high optical stability.

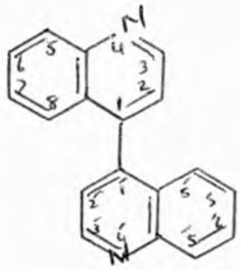


(XXV)

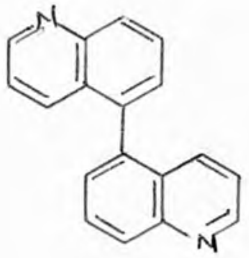
(XXVI)

Theilacker and Hopp (Ber., 1959, 92, 2293) resolved naphthidine. Calculation from the rate of racemisation gave the half life period as three to four hours at room temperature in acetone and E 21.4 k cal.mole^{-1}.

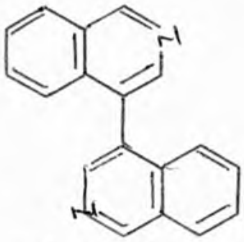
A number of diquinolyl and diisoquinolyls, whose structure is based on 1,1'-binaphthyl, have been obtained in their optically active forms (Crawford and Smyth, J., 1952, 4133; 1954, 3464) the overlapping of the van der Waals radii of the interfering hydrogen atoms appears to be largely



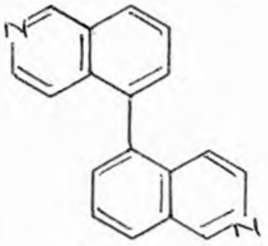
(XXVIII)



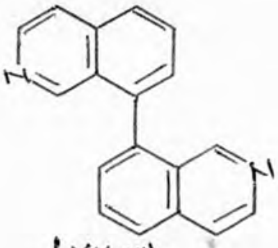
(XXIX)



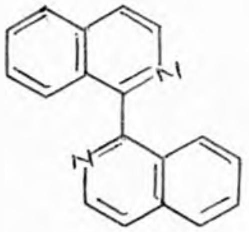
(XXX)



(XXXI)



(XXXII)



(XXXIII)

responsible for the optical stability of these isomers, the approximate half life periods vary from 2.5 hours to 12 minutes, except in 1,1'-biquinolyl (N in 2,2'-position) which was observable only as a tartrate dissolved in aqueous hydrochloric acid. There are no hydrogen atoms in the blocking position 2,2', but these are present during resolution as the substance is in the salt form. In the same way 8,8'-diisoquinonyl(N in 8,8' position) lacks two hydrogen atoms in the blocking position and has not been obtained in its optically active forms. In 8,8' -diisoquinolyl (N in 7,7' position), the absence of a substituent next to the blocking position may account for a rather high rate of racemisation even in acid solution. In 4,4' and 5,5' diquinolyls nitrogen atoms are not in the blocking position. These compounds are therefore comparable with binaphthyl derivatives. The half lives in acid solution were found to be 2.5 and 1.3 hours respectively.

1,1'-Binaphthyl itself was obtained in its optically active form by Harris and Mellor, (Chem. and Ind., 1961, 1082). The half life at 50° was 14.5 minutes and E 22.5 k cal.mole^{-1}, so it was concluded from the above examples that the interference provided by the overlap of hydrogen atoms is sufficient to cause observable optical activity and the optical stability of 1,1'-binaphthyl - 5,5' - dicarboxylic acid was not surprising.

Conclusions.

It may be seen from the table that all 8- and 8,8'-substituted binaphthyls investigated previously to this work have $\Delta F^{\neq}$ and E values very close to that of 1,1'-binaphthyl itself, the 4,4'-diamino compound, and the 5,5'-dicarboxylic acid, i.e. the energy barrier alters very little when the two COOH groups or $COOCH_3$ or $COOC_2H_5$ groups are put in.

Suggested explanation of low optical stability from Cooke and Harris. (J.,1963, 2365-2373).

Cooke and Harris who measured the rate constants and calculated Arrhenius parameters and the transition state theory functions for all the compounds given in table II, (except No. 8 which was measured by Theilacker and Hopp), said the entropy factors could not explain the unexpected lability of 8,8'-substituted 1,1'-binaphthyls. As the entropy factors in all the compounds given in the table vary only to a small degree and not in such a way as could be responsible for the order in which the stabilities lie. When the racemisation of the acids were carried out in sodium hydroxide solution, the values of $\Delta S^{\neq}$ were positive or slightly negative.

They concluded that enough evidence existed as to the probability of molecules of 8,8'-substituted-1,1'-binaphthyls being strained and consequently less optically stable than would be expected.

Reasons why Peri-substituted naphthalenes thought to be strained.

Ground state strain:-

When the molecule passes from R to S configuration, if the ground state of the molecule is strained i.e. if the molecule is already in a high energy state, the experimental energy of racemisation will be

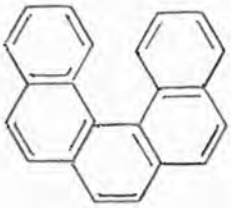
$$E_{rac} = E_{ster} - E_{gs}$$

Where E_{ster} is the energy due to strain and compression in the transition state, and E_{gs} is the ground state energy the difference in E_{rac} between 8,8' and 2,2'-dicarboxylic acids must be due to the differences in E_{ster} and E_{gs}. Since the E_{rac} in all the optically labile acids does not vary by more than 3 k cal.mole^{-1}, the factor ground state strain could be responsible for the closeness of their stabilities and the striking difference from 2,2'-dicarboxylic acid.

As the strain energy required in bending the group out of the plane makes it easy for the molecule to racemise, the energy barrier will be reduced by the strain energy, that is why the observed E is very small.

Deformations which might arise as a consequence of strain in peri-substituted binaphthyl.

Over-crowding sets in when the unperturbed structure would bring two carbon atoms to with in 3.0° A (Harnik, Herbstein, Schmidt, and Hershfield, *J.*, 1954, 3288) and when there is overcrowding it finds relief principally by an out of plane distortion, which tends to be spread over the whole molecule rather than by stretching of particular bonds. e.g. Robertson, McIntosh, Vand (*Nature.*, 1952, *169*, 322) by X-ray crystallography found a distance of 3.0 Å between nearest non bonded carbon atoms in 3:4:5:6 dibenzophenthrene.



(XXXIV)

Cooke and Harris concluded that 1,1'-binaphthyl-8,8'-dicarboxylic acid and its ester are overcrowded molecules, as there are two C-C distances of 2.4 Å and which comprises two serious compressions and also a small CO compression which finds relief by an out of plane distortion of COOH groups.

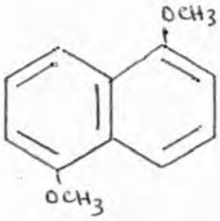
There is some evidence of out of plane distortion in substituted naphthalenes for example (a) Donaldson and Robertson (*J.*, 1953, 17) examined the crystal structure of octamethylnaphthalene by X-ray analysis and showed that the 1 and 8 methyl groups are displaced from the mean plane by about 0.73 Å. This corresponds to the deviation of about 28° of the $C-CH_3$ bond from the mean molecular plane and the

the β-methyl groups are displaced in an opposite direction probably between 0.25-0.4Å.

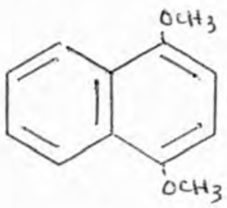
(b) Dipole moment evidence

There is also some evidence from dipole moments of steric repulsion between the substituents in 1,8 positions in naphthalenes. Everard and Sutton (J.,1949, 2312) made some dipole moment measurements of some methoxynaphthalenes and halogenomethoxynaphthalenes.

(XXXV)



(XXXVI)

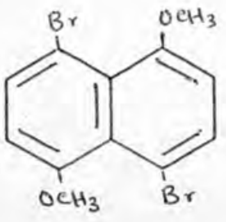


(XXXVII)

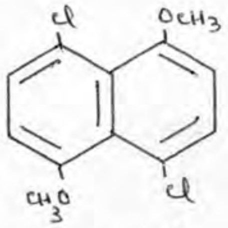
The dipole moment of (XXXV), 1.73D, is regarded as arising from the free rotation of the methoxy group about the C_{aryl} - O bond giving all the configurations from cis to trans with equal probability, while in (XXXVI) the value 0.67 shows that the free rotation is much reduced because of the resonance effect involving the use of π bond between the oxygen and the ring, and the steric effect of the peri-hydrogen atom so the methoxy groups lie trans to each other.

This explanation was tested by measuring the dipole moment of (XXXVII). The result of 2.09 was found to be lower than that of the calculated 2.45. This was supposed to indicate that the groups cannot quite lie in coplanar configuration.

The dipole moments of (XXXVIII), 0.95, and (XXXIX), 0.93D, were found to be greater than that of the parent compounds (XXXVI). Scale diagram showed that there is some considerable interference between the oxygen atom and the chlorine atom, and the resulting strain can be relieved by movements of the substituents in two directions-one in the plane of the ring and one out of the plane. The in-plane movement would not account for the moment observed, but an out of plane movement would give an unsymmetrical configuration which would possess a dipole moment. They found the out of plane deflection to be 18°, and theoretical moment to be 1.0, which is very near to the observed value.

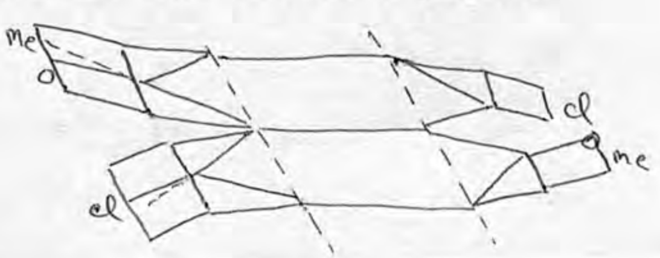


(XXXVIII)



(XXXIX)

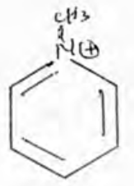
Diagram from Everard and Sutton's paper.



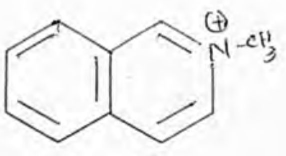
(c) Packer, Vaughan, and Wong (J.A.C.S., 1958, 80, 905) measured the rates of reaction in nitrobenzene solution of methyl iodide with pyridine, quinoline, isoquinoline, 2-methyl quinoline and 8-methyl-quinoline (over a range of 10-50°) to estimate the steric strain present in the activated complex of these reactions by comparing the heats of activation. The results are given in the table:-

Base	10^5k(at 30°)	log A	$\Delta H^{\neq}$ kcal.mole^{-1}	$T\Delta S^{\neq}$ kcal.mole^{-1}
Pyridine	50.7	0.00	0.00	0.00
isoquinoline	69.0	0.03	-0.14	0.04
quinoline	8.00	0.00	1.11	0.00
2-methyl "	0.677	-0.17	2.34	-0.26
8-methyl "	0.00877	-0.06	5.12	-0.08

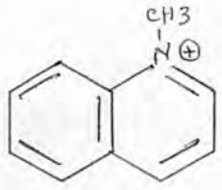
The factor $\Delta H^{\neq}$ accounts for the observed decrease in rate and is used as a quantitative measure of the steric strain in the transition state of the reaction. The steric strain energy is 5.1 kcal.mole in 8-methyl quinoline (XLIV) where both of the peri-positions are involved.



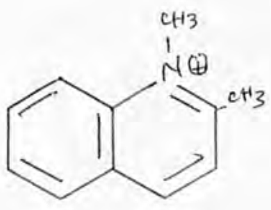
(XL)



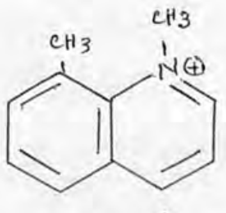
(XLI)



(XLII)



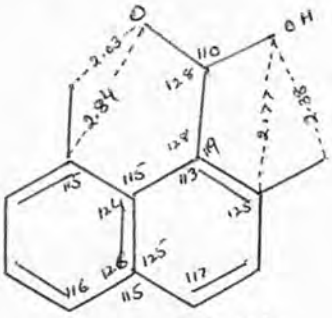
(XLIII)



(XLIV)

Following the calculations of Brown (J., 1956, 1248), they estimated the strain present in the structures corresponding to methylnaphthalenes must be even greater. They estimated the strain in 1,8-dimethylnaphthalene to be 7.6 k cal.mole^{-1}.

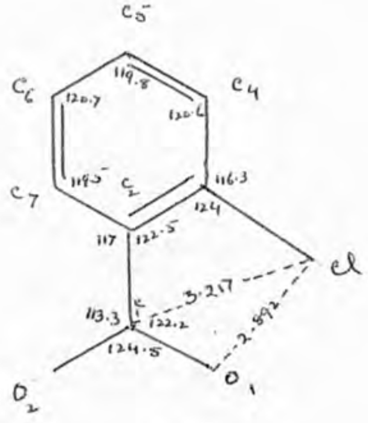
(d) Trotter (Acta Cryst., 1960, 13, 732) studied the crystal structure of 1-naphthoic acid and found that in addition to an out of plane twisting of carboxyl group, there is a significant inplane displacement of the Caromatic-Carboxyl bond away from the peri-position.



(XLV)

Diagram shows that the deviation of the carbon atom from the mean plane is not significant but the oxygen atoms lie one above and one below the aromatic plane at a mean distance of about 0.20 Å, and the carbonyl group is twisted about the Caromatic-Carboxyl bond, the angle between the aromatic and corbonyl plane being 11°; the strain in The coplanar model however is partially relieved by these deviations from coplanarity and partly by in plane deviations. However this molecule has no 8-substituent, if there was an 8-substituent, it would probably force the - COOH group out of the plane.

(e) Ferguson and Sim (Acta. Crysta., 1961, 1262) studied the crystal structure of o - Chloro benzoic acid.



(XLVI)

The Cl --- O_1 (2.892A°) and Cl -----C_1 (3.217 Å°) intramolecular separations are appreciably shorter than the sum of the Van der Waals radii (3.20A and 3.40A°) respectively. The molecule may therefore by expected to be subject to same strain.

The displacements ofthe atoms C_1 and Cl from the benzene plane are -0.058 Å and + 0.036Å respectively corresponds to the C-Cl bond and the exocyclic c-c bond bending in the opposite directions out of the main plane of the benzene ring through an angle of 1.2° and 2.2° respectively.

The carboxyl group is rotated about the exocyclic C-C bond, the angle between the plane of the carboxyl group and the aromatic ring is 13.7°, and there is significant in plane displacement of C-Cl and exocyclic C-C bonds away from each other so that the two of the exocyclic valency angles are increased from the normal value of 120^{o} to 122.5^{o} and 124.7^{o} while the adjacent angles are decreased to 117^{o} and 116.3^{o}. which must also contribute towards relieving the strain.

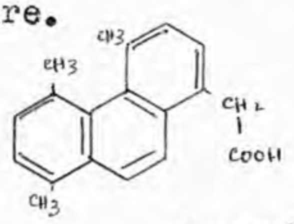
The exocyclic C_2-C_1 bond leading to the carboxyl group is 1.521Å in length which is larger than the standard single bond distance between carbon atoms, 1.479 (Dewar and Schmelsing, *Acta cryst.*, (1959) and found to be very close to the length of the central bond in oxalic acid dihydrate, 1.53A (Shrivastava and Speakman, *Acta. Cryst.*, 1960). This is because the *peri-bond* in the latter molecule is longer than might be expected and has been attributed to repulsion between overcrowded hydrogen atoms and the cis-interaction of C-C bonds. The length of the exocyclic C-C bond in *o* - chlorobenzoic acid is probably related to the intermolecular overcrowding.

Ferguson and Sim (*Acta. Cryst.*, 1962, 346) also studied the crystal structure of *o*-bromobenzoic acid and found that the carboxyl group is rotated about the exocyclic C-C bond 18.3^{o} out of the plane of the benzene ring, the exocyclic substituents are deflected in opposite directions out of the aromatic plane, the bromine atom by + 0.064Å and the exocyclic carbon atom by -0.057A^{o} and the exocyclic C-C and C-Br bonds are displaced sideways so that the normal valency angles of 120° are increased to 123.4° and 124.9° respectively.

These effects are very similar to though larger than those of *o* -chlorobenzoic acid.

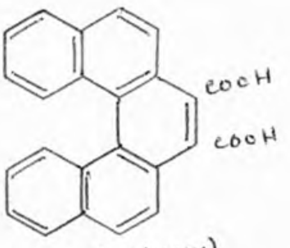
Optically labile overcrowded compounds.

There is some evidence that the optically active compounds which owe their asymmetry to molecular overcrowding are optically more labile than would be expected. Although the Arrhenius parameters and other racemisation data are not yet available for such compounds, but several instances of optical unstability have been reported. For example 4,5,8-trimethyl-1-phenanthryl-aceticacid (XLVII) was prepared and resolved by Newman and Hussey (*J.A.C.S.*, 1947, *69*, 3023). Both the salt and the acid racemised *fairly easily* in solution in solution at room temperature.

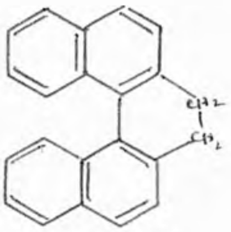


(XLVII)

Another well known example is of 3,4:5,6-dibenzphenanthrene-9,10-dicarboxylic acid (XLVIII) (Bell and Waring, *J.*, 1949, 2689). The morphine salt was found to exhibit rapid mutarotation in solution and the acid recovered from the alkaloidal salt was optically inactive. Whereas (+)-9,10-dihydro-3:4,5:6,-dibenzophenanthrene (XLIX) in which the overcrowding is relieved by twisting is optically stable (Hall and Turner, J., 1955, 1242). The compound racemised very slowly in benzene at 100° in a sealed tube.

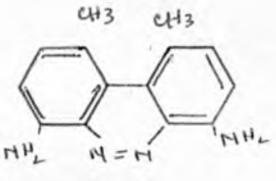


(XLVIII)

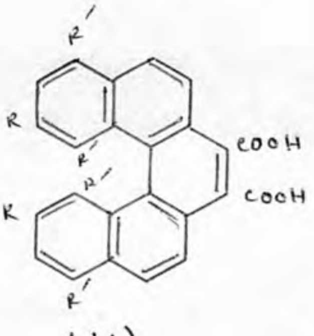


(XLIX)

Another compound, 1,8-diamino-4,5-dimethylbenzocinnoline (L), was prepared and resolved by Theilacker and Baxmann (Ann., 1953, 581, 117) which racemised very quickly in boiling methyl alcohol.



(L)



(LI)

R' = H

A number of 3,4,5,6-dibenzanthrene like (LI) have been prepared by Bell and Waring R = CH_3 (J.,1949, 2689) and by Crawford R=Br. (J., 1959, 2807). R = OCH_3 (J.,1960, 3313). All these compounds are overcrowded and racemise more easily than would be expected.

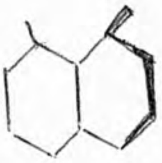
Strained Conformations of 8,8',Substituted 1,1'-Binaphthyl.

Possibility of mesoid transition state.

(Cooke and Harris, J., 1963, 2365-2373)

A peri-substituted naphthalene unit with its 1 and 8 bonds directed out of the main plane in opposite direction can exist into two diastereoisomeric conformations (d) and (l).

(d)

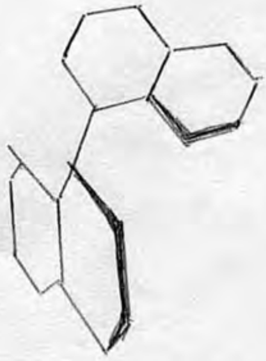


(l)

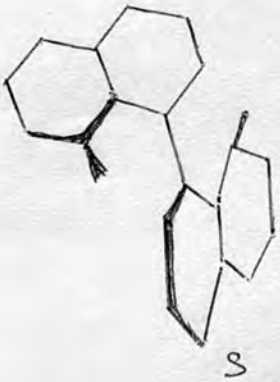
When two of these deformed units are combined, there result three possible structures, (d)⊐(d), (l)(l), and (d)⊐(l). Each of these structures by rotation about 1,1'- bond can exist in its **R** and S configuration; the passage from R- to the S- configuration will be by the "trans" route, 8-COOH passing 2'-H and 8'-COOH passing 2-H.

R

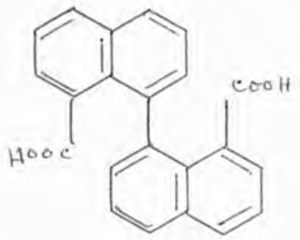
S



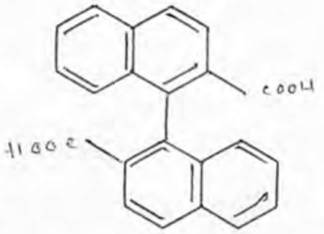
R



S



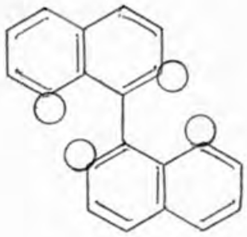
In 1,1'-binaphthyl-8,8'-dicarboxylic acid the 8,8'-carboxy groups are bent out of the mean plane and such out of plane bending would make it easier for the 8,8' carboxyl groups to pass ~~through~~ the relevant hydrogen atoms and also would lower the energy barrier to racemisation by a amount equal to the energy in the ground state. In the 2,2'-acid, there is no appreciable ground state strain, as the carbon atom of the 2-COOH group is 2.9 Å distant from the 1' carbon atom the energy barrier to racemisation will be very high.



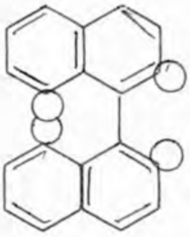
Cooke and Harris suggested that the lower limit for the ground state strain energy in 1,1'-binaphthyl-8,8'-dicarboxylic acid is about 15 k cal.mole^{-1}, on the basis of the work of Packer, Vaughan, and Wong (*J.A.C.S.*, 1958, *80*, 905).

Mesoid and Racemoid Transition Paths.

When there is out of plane bending of C-COOH bond, inversion R→S by "trans" route must go through one of the three trans transition paths. Two of them are:-



Trans passing

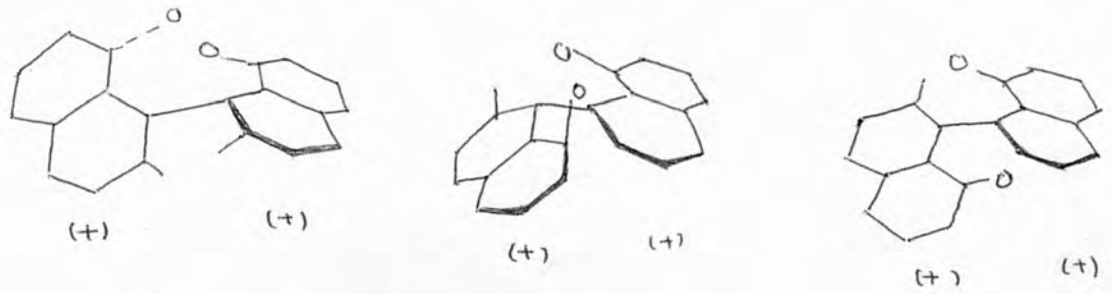


cis passing

R (dd)$\rightleftarrows$S(dd) or R(ll)$\rightleftarrows$S(ll), the racemoid ones which are the mirror images of each other and have equal energy barriers, in each of them 8-COOH passes 2'-H at the same time as 8'-COOH passes 2-H. There is a single high energy barrier and the transition state still retains asymmetry. The third one is R (dl)$\rightleftarrows$S(dl), the mesoid route the 8-COOH does not pass 2'-H at the same time as 8'-COOH passes 2-H, but one after another. Between the two energy barriers lies an energy of minimum representing an intermediate state the configuration of which is neither R nor S, nor it is flat., it has a centre of symmetry. As less energy will be required for a mesoid inversion, this will be the path used.

$$\begin{tikzcd}
R\ (dd) \arrow[r, shift left] & R\ (dl) \arrow[l, shift left] \arrow[r, shift left] \arrow[d, shift left] & R(ll) \arrow[l, shift left] \\
S(dd) \arrow[r, shift left] & S\ (dl) \arrow[l, shift left] \arrow[r, shift left] \arrow[u, shift left] & S(ll) \arrow[l, shift left]
\end{tikzcd}$$

Configurational inversion in the racemoid molecule.

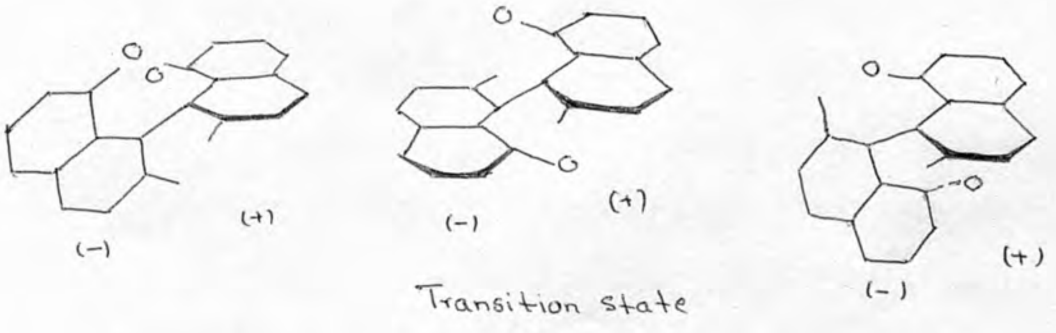


R

Transition state
Or
Intermediate

S

Configurational inversion in the mesoid molecule.



Transition state
Or
Intermediate

R

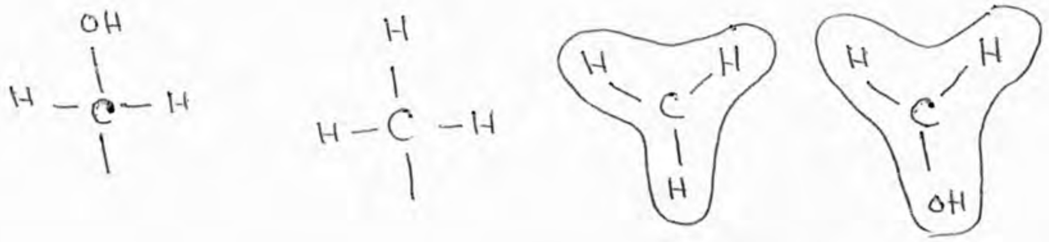
S

Reason for undertaking the present work.

The reason for undertaking the present work is that only $COOH$, $COOCH_3$, $COOC_2H_5$, groups have been tried in the 8,8'-positions, these are all "flat" groups.

viewed from above

We wanted to try some more "three dimensional groups", which would present larger angular blocking area to passing. CH_2OH, CH_2Br and CH_3 groups were tried.

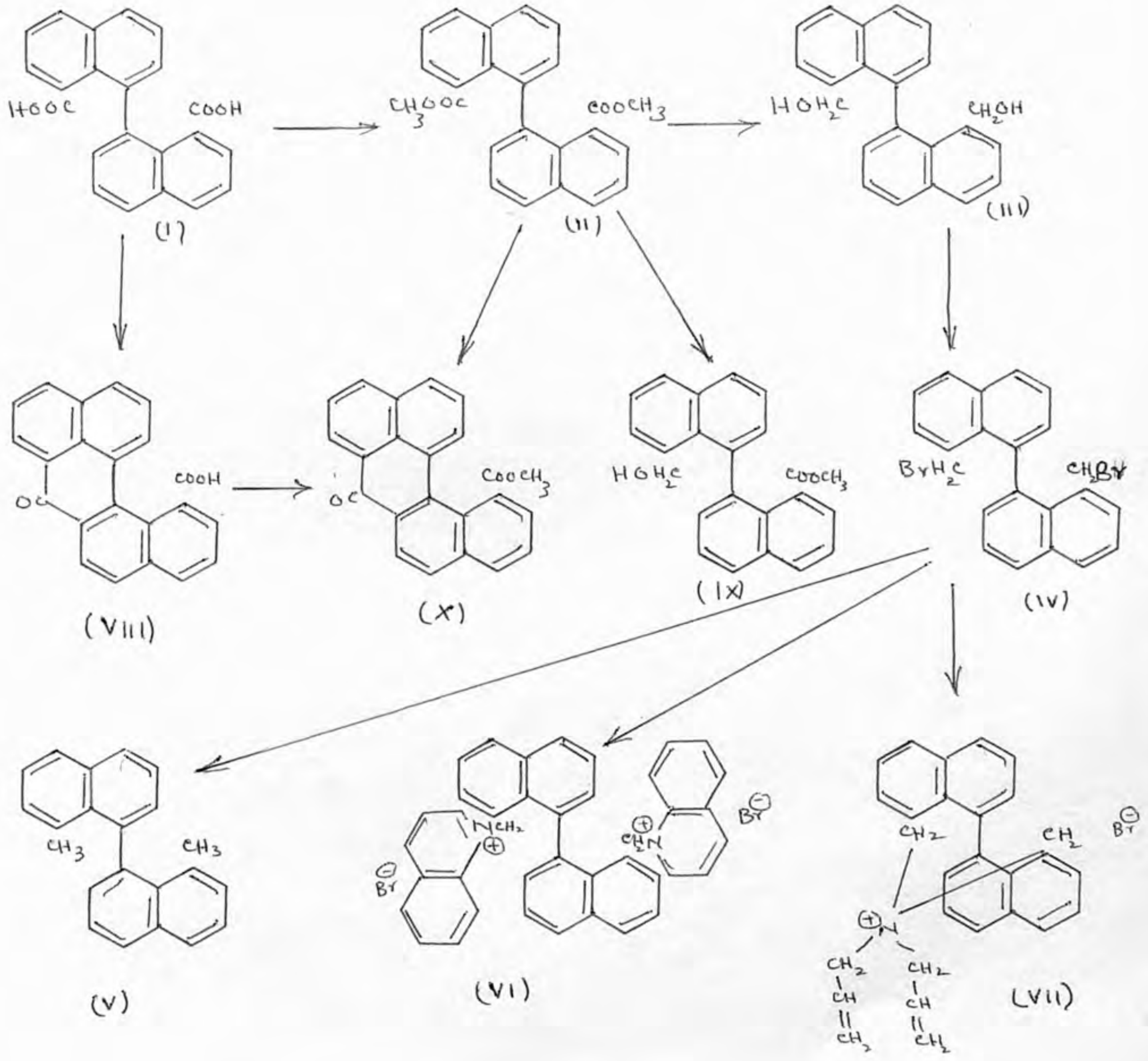


viewed from above

During the synthetic work various other interesting compounds were indicated and their syntheses followed up.

Discussion of the present results

The following 8,8'-derivatives of 1,1'-binaphthyls have been prepared. The starting material was optically active 1,1'-binaphthyl-8,8'-dicarboxylic acid and the scheme followed is shown below (rotations in N,N-dimethyl formamide) details are presented in the experimental section.



The 1,1'-binaphthyl-8,8'-dicarboxylic acid was first prepared optically active almost simultaneously by Stanley (*J.A.C.S.*,1931, *53,* 3104), Corbellini. (*Atti Accad Lincei.*, 1931, *13,* 702) and Meisenheimer and Beisswenger (*Ber.*,1, 1932, *65*, 32), and its Arrhenius parameters and the transition state theory functions for racemisation were determined by Cooke and Harris (*J.*, 1963, 2365). The dimethyl ester was also prepared in its optically active form by them (Cooke and Harris), and the Arrhenius parameters and transition state theory functions were also calculated by them.

Now all the compounds have been obtained in their optically active forms and the rate of racemisation of (III), (V), (VIII) and (IX) have been measured in N,N-dimethylformamide at several temperatures, covering the range of about 30-40° in each case. First order kinetics was observed for all rate measurements and Arrhenius parameters and transition state theory function were calculated. The results are given in the table (Page 51).

Attempts for the racemisation of 8,8'-bis-(bromomethyl)-1,1'-binaphthyl (IV) and 8,8' bis-(methylene quinolinium bromide 1,1'-binaphthyl (VI) failed because of the decomposition in N,N-dimethyl-formamide. The compound (VII) was found to be so optically stable that it did not racemise when heated at 130° for two hours, but the rotation increased in the opposite direction. However this could not be racemisation;the reason is not yet understood.

TABLE

8,8'-substituents in 1,1'-binaphthyl	Solvent	Temp. range.	No. of rates	$t_{\frac{1}{2}}$ at 100^0 in min.	E kcal. $mole^{-1}$	$\log_{10} A$	$\Delta H^{\neq}$ kcals $mole^{-1}$	$\Delta S^{\neq}$ e.u	$\Delta F^{\neq}$ kcal. $mole^{-1}$
CH_2OH CH_2OH	N,N.D.M.F	95-130°	6	374.5	29.2	12.6	28.4	-3.66	29.9
CH_3 CH_3	"	100-130	7	678.8	27.6	11.3	26.8	-9.3	30.4
CH_2OH $COOCH_3$	"	55- 95	9	14.1 2226.8 at 50 C	25.8	11.96	25.1	-6.1	27.2
$\rangle$CO COOH	"	30- 75	10	48.5 at 50°	23.2	12.1	22.6	-5.3	24.3

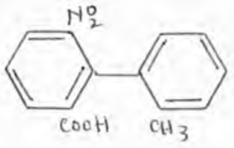
The values of $\log_{10}A$, $\Delta S^{\neq}$, $\Delta H^{\neq}$ and $\Delta F^{\neq}$ given in the table are the averages taken over the whole range of temperature. The Arrhenius parameters E and $\log_{10}A$, and the transition state theory functions have been used to describe the optical stability of each compound, and also the half life period which is a direct measure of optical stability of any compound at given temperature.

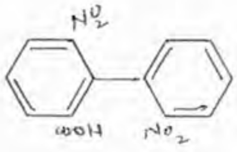
If we examine the values of E for 8,8'-bis(hydroxymethyl)-1,1'-binaphthyl (29.2), 8,8'-dimethyl-1,1'-binaphthyl(27.6) and 8-methoxycarbonyl-8'-hydroxymethyl-1,1'-binaphthyl (25.8), all are found to be much higher than those of 1,1'-binaphthyl-8,8'-dicarboxylic acid and its dimethyl ester (22.0). This is what would be expected, as the CH_2OH and CH_3 groups are "three dimensional" groups and present a larger angular blocking area to passing than the carboxyl and the ester groups, which are all "flat" groups and hence present smaller blocking area to passing.

It can be seen from the following examples, as they appear from the half life periods, that the capacity of ortho substituents to interfere with the planar transition state in biphenyl would be in the order of:-

$$Br > CH_3 > NO_2 > COOH > OCH_3$$

(Adam and Yuan, Chem. Reviews., 1933, 12, 300)





Substituents in 2'-nitro-6-carboxyl biphenyl	Solvent	$t_{\frac{1}{2}}$ in mins.	temp.
2 - CH_3	Acetic acid	179	118°
2 - NO_2	"	125	118°
2 - COOH	"	91	118°
2 - OCH_3	"	25	25°

Racemisation tests in other solvents practically showed the same order.

There is some spectroscopic evidence for the steric effect of the methyl group (O'Shaugnnessy and Rodebush, J.A.C.S., 1940, 62, 2906).

A great effect in the absorption is to be anticipated from ortho substituents which interfere with the rotation of the two rings in biphenyl. If the interference is slight the two rings may still retain coplanarity, since this gives a state of low energy, but considerable interference may turn the ring out of coplanarity and prevent conjugation between the two rings and thus greatly reduce the absorption.

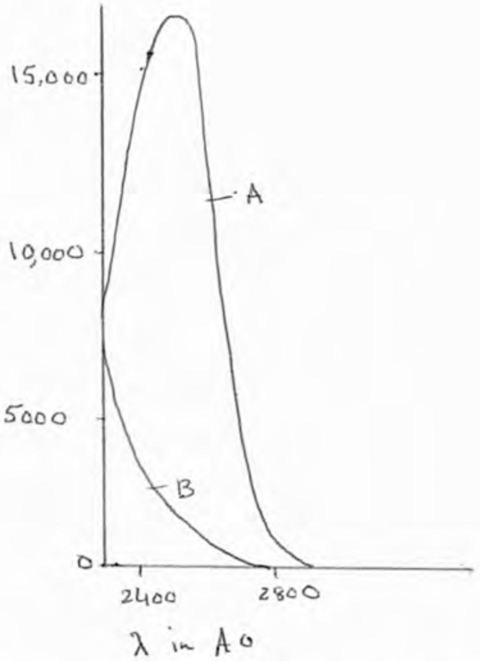
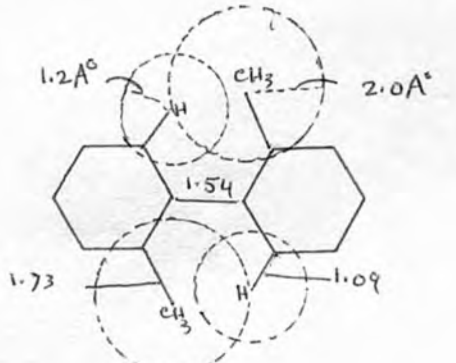


FIG I

In fig. I , The curve A shows the absorption curve for 1,1'-biphenyl, and the curve B shows the absorption for 2,2'-dimethylbiphenyl. It shows a large reduction in the amount of absorption. It was explained that the methyl groups interfere with the hydrogen to such an extent as to turn the two rings well out of plane and destroy all resonance between them.

Fig II , where a plot of van der Waals radii of the ortho groups shows considerable overlap when the benzene rings are coplanar.

FIG II

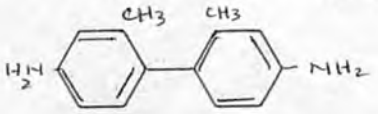


valuesdue to Pauling (1940). The Nature of the Chemical Bond Cornell University Press (*Progress in stereochemistry* Vol. I P.361. *Appendix*).

Vander Waal's radii of atoms		bond length	
H	1.2Å	C-H	1.09
O	1.4Å	C-OH	1.45
Br	1.95Å	C-COOH	1.56
CH_3	2.0Å	C-CH_3	1.73
C-COOH	2.0Å	C-Br	1.86

Howlett (*J.*, 1960, 1055) said that the dipolar studies on steric inhibition of mesomerism, (Smith, *J.*, 1957, 4050) indicate that the methyl group is on the average sterically equivalent to bromine. However two methyl group have not yet been shown to be capable of causing observable optical activity in the biphenyl series until buttressed.

Fowsweather (*Acta.*, *cryst.*, 1952, *5*, 820) studied the crystal structure of *m-* tolidine and found that



the mean displacements of the atoms from the mean plane of two phenyl ring being 0.03Å, the angle between the mean plane of two phenyl rings is 86° which makes the methyl-methyl separation 3.86A°. This is in reasonable agreement with Paulings (The Nature of the Chemical Bond Cornell University Press 1940) value of about 4.0 Å in m-tolidine hydrochloride, where the two rings are inclined at an angle of 70.6°.

When the COOH and $COOCH_3$ groups in the blocking position were compared the stability was found to be of the same order, as can be seen from the work of Graybill and Leffler (J. Phys. Chem., 1959, 63, 1461), who worked on 2,2'-dimethoxy-6,6'-dicarboxydiphenyl and derivatives to see the solvent effects in the racemisation. They determined the rates and the Arrhenius parameters for racemisation in 24 solvents for the acid, and in 23 solvents for the corresponding dimethylester, some of the results are given below.

2,2'-dimethoxy-6,6'-dicarboxybiphenyl.

Solvent	$K\times10^{-6}$ — 100°	Sec^{-1} 79.4°	$\Delta H^{\neq}$ $\mathrm{Kcal.\ mole}^{-1}$	$\Delta S^{\neq}$ e.u
Dimethylformamide	138	1.81	25.12	-13.91
Ethanol	15.0	2.18	23.88	-17.06
Methanol	16.55	2.55	23.24	-18.58
Acetic acid	16.0	2.21	24.41	-15.51
t.butylalcohol	5.93	0.709	26.31	-12.37
N,N-dimethylethanolamine	10.91	1.52	22.14	-27.29
Acetone	15.4	2.03	25.07	-13.81
Ethyleneglycol	13.6	1.78	25.14	-13.87
Pyridine	8.43	1.15	24.66	-16.11

The solvents effects are quite complicated in acid the enthalpy and entropy are roughly co-related with each other. The range in rate const. is a factor of four, while $\Delta H^{\neq}$ and $\Delta S^{\neq}$ vary by 3.3 kcal mole^{-1} and 8 e.u. respectively. There is some tendency for the reaction to be faster in the more polar solvents.

Dimethyl-2,2'-dicarboxy-6,6'-dicarboxylate.

Solvent	$k \times 10^{-6}$ — sec.$^{-1}$ 100°	 79.4°	$\Delta H^{\neq}$ kcal. mole^{-1}	$\Delta S^{\neq}$, e.u
Dimethyl formamide	15.6	2.19	24.25	-16.0
Ethanol	14.0	1.95	24.41	-15.76
Methanol	13.7	1.94	24.12	-16.58
Acetic acid	13.6	1.91	24.26	-16.24
_t_-butylalcohol	13.7	2.07	23.32	-18.73
Acetone	14.2	2.00	24.21	-16.23
ethyleneglycol	12.9	1.81	24.3	-16.23
Pyridine	11.5	1.60	24.35	-16.31

The ester is less influenced by change of solvent than the acid ~~e.g.~~ the rates vary by about a factor of 2 and the enthalpy and entropy have ranges of 2.1 k cal. mole^{-1} and 4.4 e.u the higher enthalpies of activation tend to be associated with less negative entropy factor.

The solvents methanol, acetic acid, acetone, ether and dimethyl formamide give points on the isokinetic line for both the ester and the acid of these five the dimethyl formamide gives the slowest reaction for the acid and fastest for the ester, while methanol is fastest for acid and slowest for ester i.e. the racemisation of the acid is slowest in the solvents which are hydrogen bond acceptors and the racemisation of ester is slowest in the solvents which are hydrogen bond donors. It was suggested that the hydrogen bond between the ground state of biphenyls and solvent may be an important factor influencing the racemisation rate.

When we compare the optical stability of dimethyl-1,1'-binaphthyl-8,8'-dicarboxylate, 8-methoxycarbonyl-8'-hydroxymethyl-1,1'-binaphthyl and 8,8'-bishydroxymethyl-1,1'-binaphthyl the expected order of stability would be

diol > hydroxy ester > dimethyl ester,

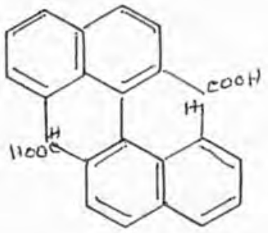
which is what is observed.

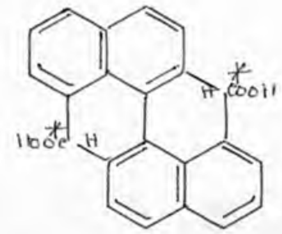
The E value for the diol, 29.2, is greater than than of 8,8'-dimethyl-1,1'-binaphthyl, 27.6. The rate of racemisation of the diol in N,N-dimethyl formamide is much quicker and the E value does not fall in with the order of stability by half life period. It must be because of the $\Delta S^{\neq}$ values which are -9.3 for 8,8'-dimethyl-1,1'-binaphthyl and -3.66 for the diol. Presumably the diol is more associated with the solvent in the ground state than the dimethyl compound is.

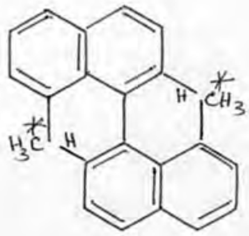
Study of the models.

It was not possible to construct the 1,1'-binaphthyl -8,8'-dicarboxylic acid, its dimethylester and 8-methoxycarbonyl-8'-hydroxymethyl-1,1'-binaphthyl using the Leybold models which show the Vander Waals overlap. The pieces fell apart when the groups in the 8,8'-positions were tried to be introduced. Using these models we could just make 8,8'-bishydroxymethyl-1,1'-binaphthyl, 8,8'-bisbromomethyl-1,1'-binaphthyl, and 8,'8-dimethyl-1,1'-binaphthyl, they fell into pieces when we tried to do anything. However they are very easily made using the Bedford College classical models in which no vander Waals overlap is introduced.

When these compounds are compared with 1,1'-binaphthyl-8,8'-dicarboxylic acid on classical diagrams, the same type of interference was found as in 1,1'-binaphthyl-8,8'-dicarboxylic acid.







The groups COOH, $COOCH_3$, CH_2OH, CH_2Br, and CH_3 when in the 8,8'-position all have the same $\overset{*}{C}-C_1$ or $\overset{*}{C}-C_1'$ interference. Variation in interference between these groups are due to the attached atoms or groups. On a scale drawing the distance $\overset{*}{C} - C_1 = \overset{*}{C} - C_1' = 2.4A^o$.

However as already described it has been found in general that non bonded carbon atoms cannot approach closer than $3.0A^o$ (Harnik, Herbstein, Schmidt and Herschfield, J., 1954, 3288). Thus if the geometry of the molecule is such that it will be overcrowded, the resulting strain will find relief by an out of plane distortion of the substituents and by the bending of the nucleus.

There are evidences of this kind of out of plane distortion in substituted naphthalenes. (Donaldson and Robertson, J., 1953, 17, Everard and Sutton, J., 1949, 2312, Packer, Vaugham and Wong, J.A.C.S., 1958, 80, 905, and Ferguson and Sim, Acta crysta., 1961, 1262) (see page 35-42)

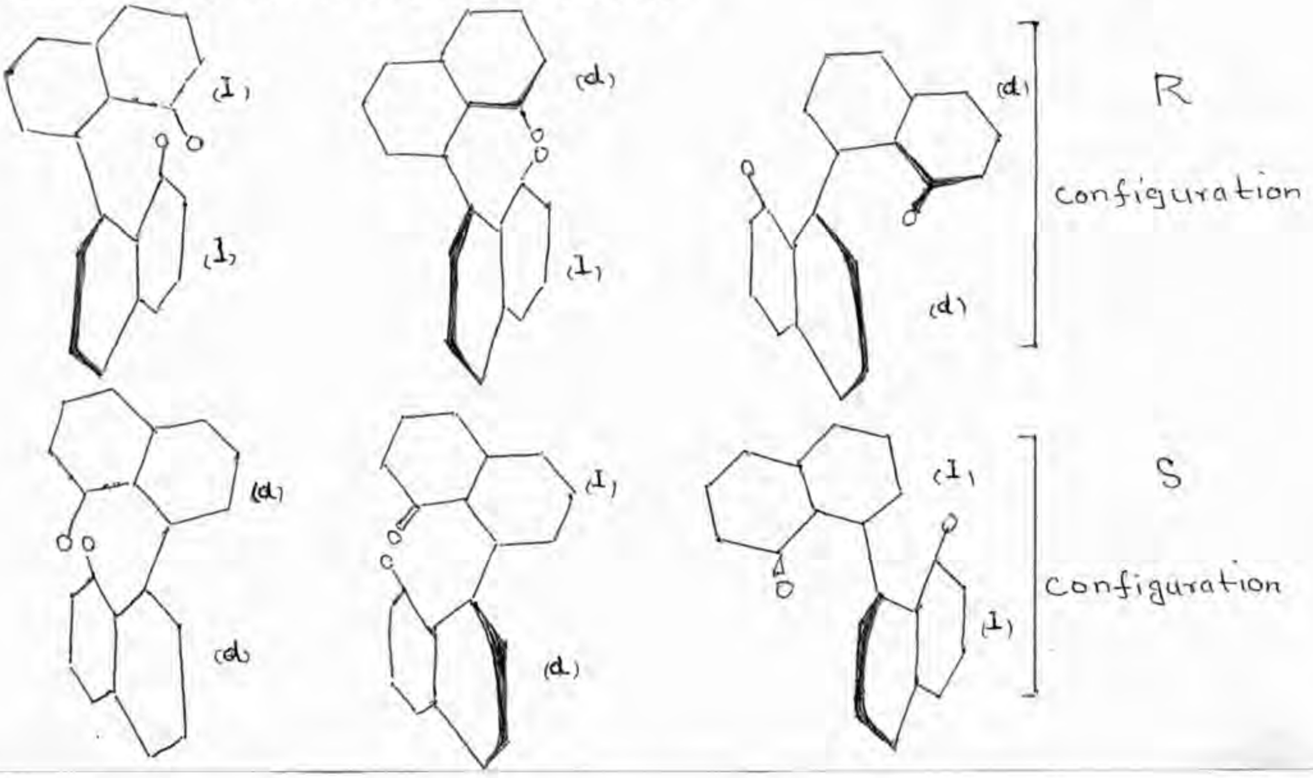
There is also some evidence that the intramolecular overcrowded compounds in general have lower optical stability than one might expect, and have very small E values: (Newman and Hussey, J.A.C.S., 1947, 69, 3023, Bell and Waring, J., 1949, 2689, Hall and Turner, J., 1955, 1242, Theilacker and Boxmann, Ann., 1953, 584, 117, and Crawford, J., 1959, 2807, 1960, 3133) (see page 42)

The 8,8'-bishydroxymethyl-1,1'-binaphthyl, 8-methoxycarbonyl-8'-hydroxymethyl-1,1'-binaphthyl and 8,8'-dimethyl-1,1'-binaphthyl will be considered as overcrowded molecules as they all have two $2.4A^o$ C - C distances i.e.

they are under strain and find relief by an out of plane distortion of the substituents and the bending of the nucleus.

It seems probable that in solution peri-substituted naphthalene units are even more distorted than in the solid phase. (In biphenyl the individual benzene units are more out of plane in the solution than in the solid state)

The stereochemistry of 8,8'-bishydroxymethyl-1,1'-binaphthyl, 8,8'-dimethyl-1,1'-binaphthyl and 8-methoxycarbonyl-8'-hydroxymethyl-1,1'-binaphthyl can be considered in a similar way to 1,1'-binaphthyl-8,8'-dicarboxylic acid. So there are three possible conformations for each of these molecules in the ground state. (l)(l), (d)(d) and (d)(-), each of these structures about the 1,1'- bond can exist in R and S configurations. Structures about the 1,1'-bond can exist in R and S configurations.



The inversion of each unit, (d)→(l) and (l)→(d), can take place within the frame work of each R and S configuration, and it is probable that the conformational inversion is faster than the configurational inversion as the measurement of velocity constants, made over a wide range of temperature for the diol, hydroxy ester and the dimethyl binaphthyl. The k plots and the Arrhenius plots are good straight lines. In 1,1'-binaphthyl-8,8'-dicarboxylic acid there is no significant deviation in the Arrhenius plot and k plot so it is the only R → S process which is under observation in the polarimeter. The conformational changes being too fast to be detectable at the temperature used.

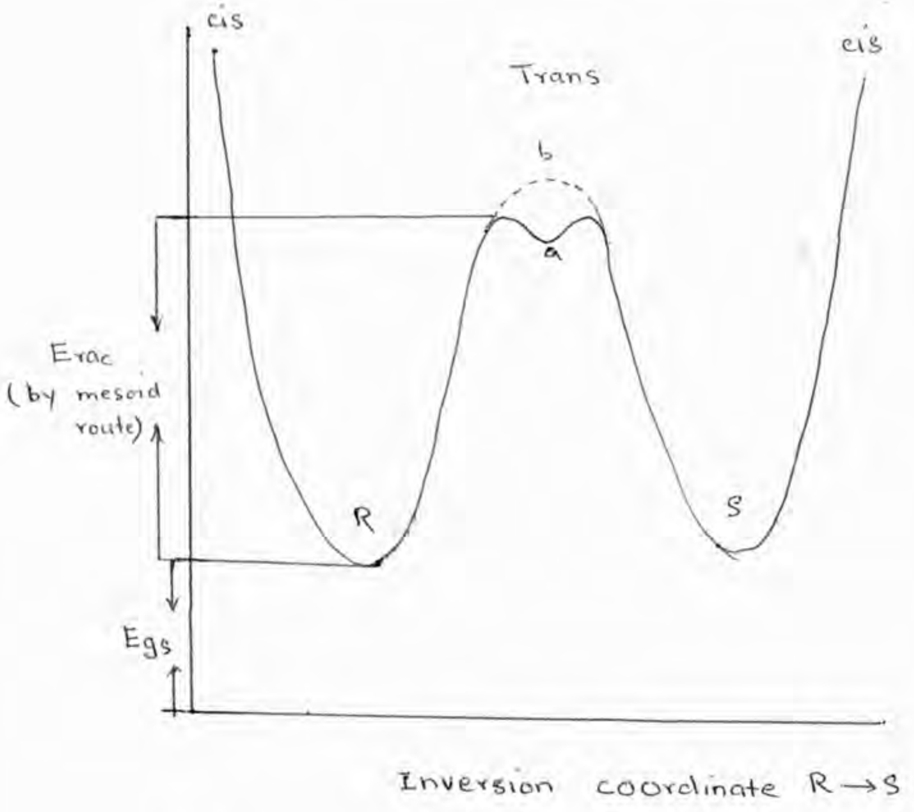
However it is clear that if the substituents in the peri positions are bent out of the main plane and they can pass the relevent hydrogen atom more easily in the transition state this explains the unexpected lability of 8,8'-substituted binaphthyl. As the strain energy makes it more easy for a molecule to racemise, the energy barrier for racemisation will be reduced by the strain energy that is why the measured E values are small. On the basis of Packer, Vaughan and Wong's estimation of strain energy of 7.9 kcal.mole^{-1} for 1,8-dimethyl-naphthalene, we can only approximately suggest that the steric strain in 8,8'-dimethyl-1,1'-binaphthyl, diol and the hydroxy ester to be about 15 k cal.mole^{-1}, because there are two similar kind of compressions involving carbon atoms attached in the 1 and 8 positions.

If we take the strain energy to be 15 k cals. and add it to the experimental value for E in dimethyl formamide. The E value would be about 44.2 k cal.mole^{-1} for the diol, 43.6 k cal.mole^{-1} for 8,8'-dimethyl-1,1'-binaphthyl and 40.8 k cal.mole^{-1} for the 8-methoxycarbonyl-8'-hydroxymethyl-1,1'-binaphthyl. These large values one would expect for the optically stable compounds and such compounds once optically active should not racemise at all. These high values are what one would expect for the 8,8'-substituted-1,1'-binaphthyls if they are not distorted in any way.

Mesoid and Racemoid Paths.

As in 1,1'-binaphthyl-8,8'-dicarboxylic acid, the mesoid one will be favoured in this configurational inversion as less energy is required for the mesoid inversion.

$$\begin{tikzcd}
R(dd) \arrow[r, shift left] & R(dl) \arrow[l, shift left] \arrow[r, shift left] \arrow[d, shift left] & R(ll) \arrow[l, shift left] \\
S(dd) \arrow[r, shift left] & S(dl) \arrow[l, shift left] \arrow[r, shift left] \arrow[u, shift left] & S(ll). \arrow[l, shift left]
\end{tikzcd}$$



Schematic energy diagram representing optical inversion path for 8,8'-disubstituted 1,1'-binaphthyls.

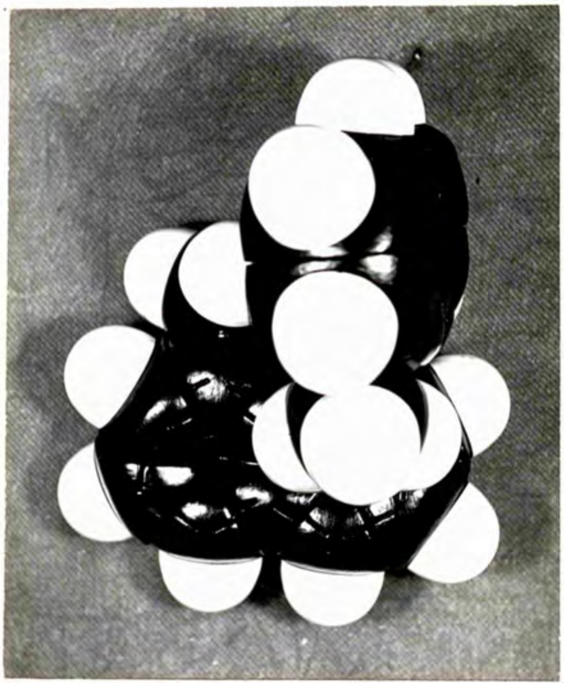
Conclusions from the above results.

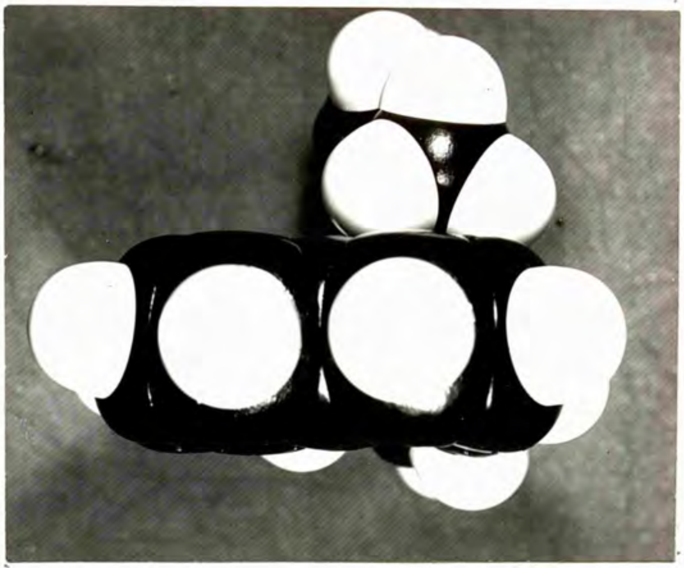
1. Even with $-CH_2OH$ and $-CH_3$ groups the 8,8'-substituted 1,1'-binaphthyls are still more labile than the 2,2'-disubstituted compounds (listed in table).

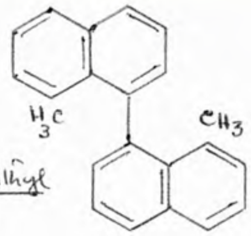
2. The "rounded" groups $-CH_2OH$ and $-CH_3$ lead to greater optical stability than the groups $-COOH$ and $-COOCH_3$ which are effectively flat.

3. The ground state of these new molecules is strained, and the ground state energy lowers E_{racem}.

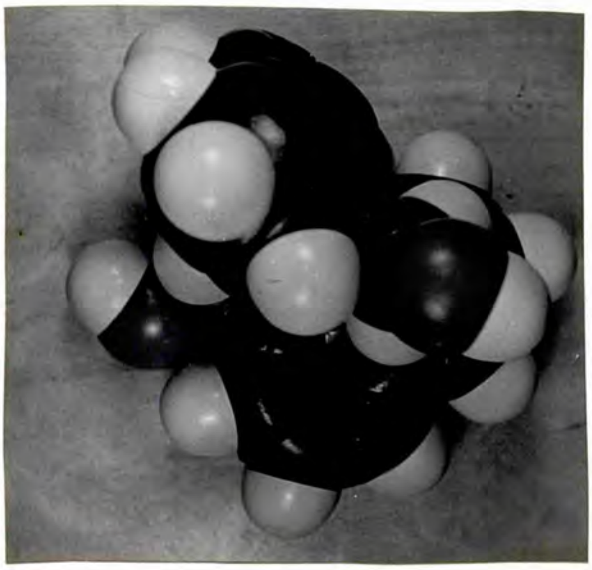
LEYBOLD MODELS

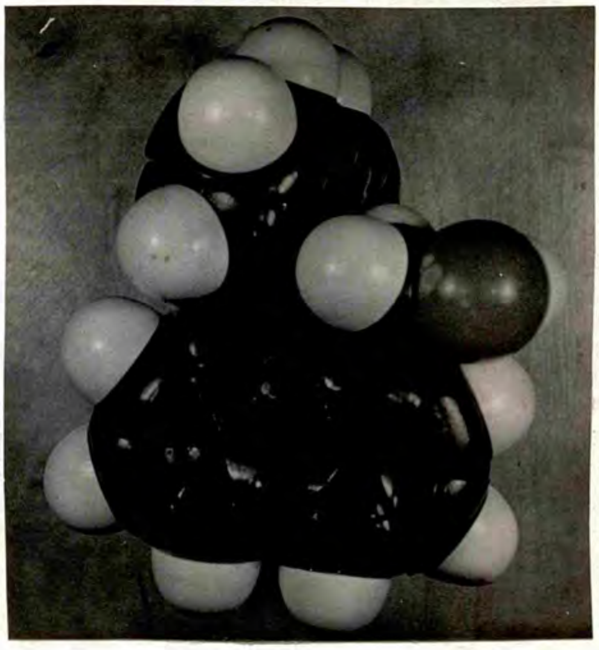


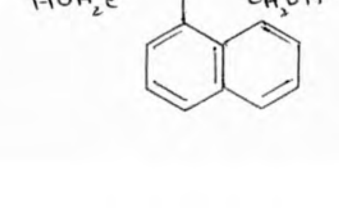




8,8'-Dimethyl-1,1'-binaphthyl

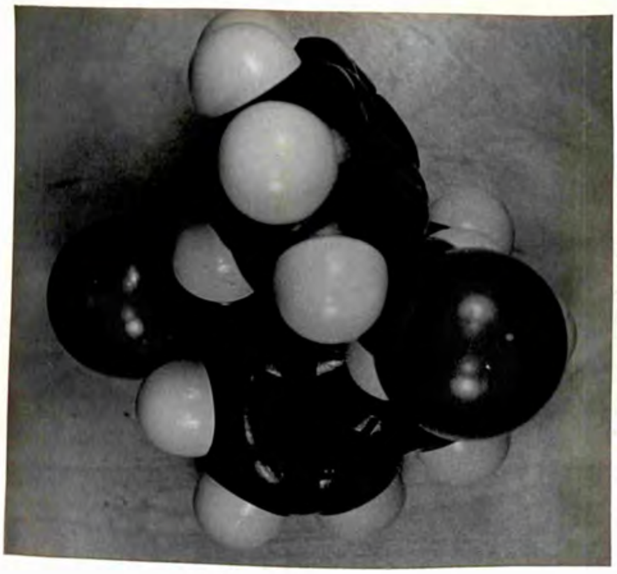


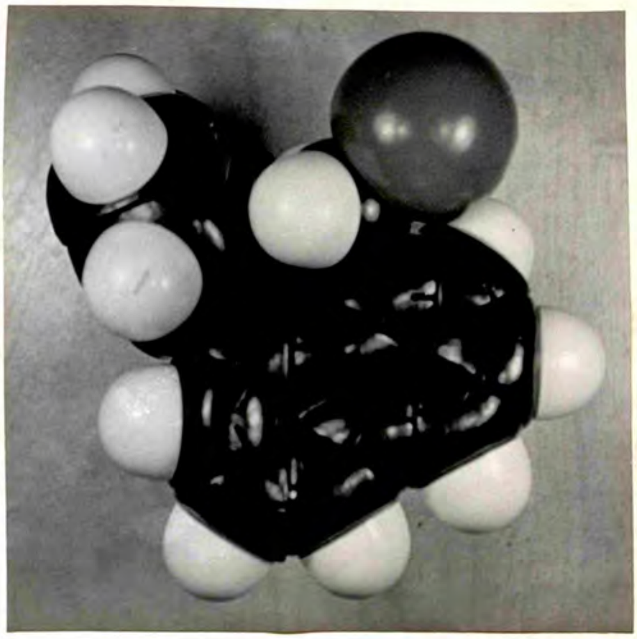


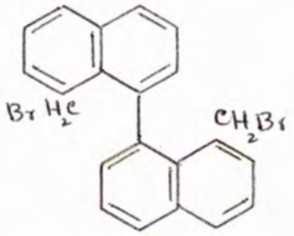


8,8'-Bis(hydroxymethyl)-1,1'-binaphthyl

LEYBOLD MODELS



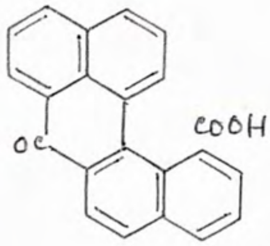


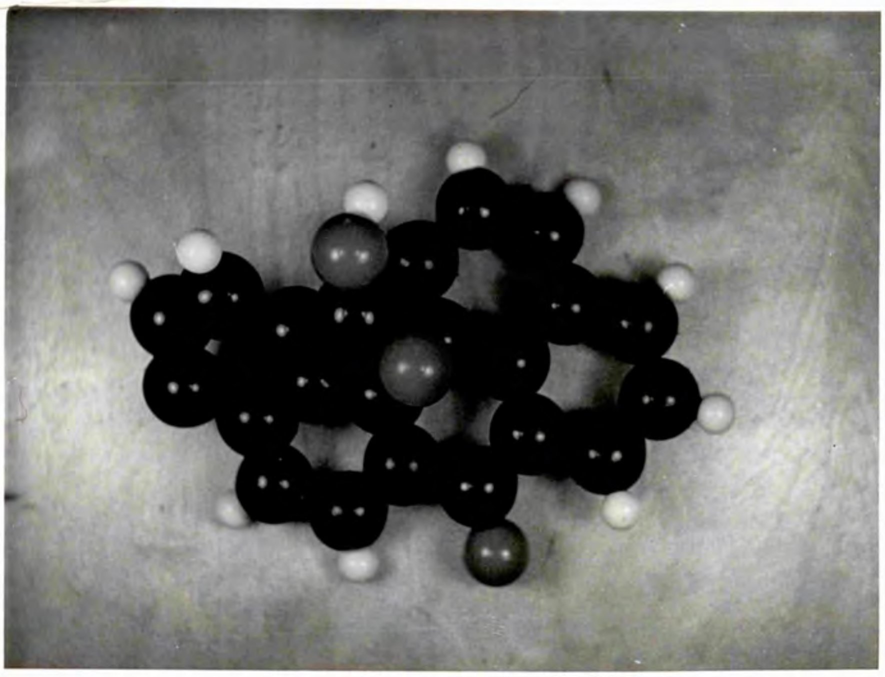


8,8'-Bis(bromomethyl)-1,1'-binaphthyl.

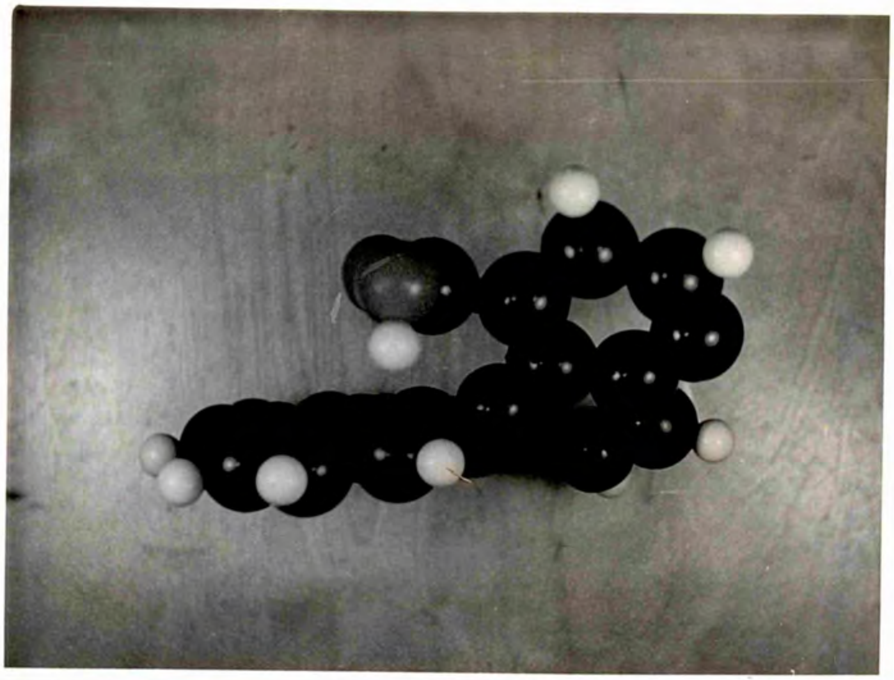
It is very difficult to construct 8,8'-bis(hydroxymethyl)-1,1'-binaphthyl, 8,8'-bis(bromomethyl)-1,1'-binaphthyl, and 8,8'-dimethyl-1,1'-binaphthyl using these Leybold models which show van der Waals overlap; it was just possible to construct these models. However, 1,1'-binaphthyl-8,8'-dicarboxylic acid could not be made using these models, so it seems probable that the acid or its ester are more strained than the above compounds.

BALL MODELS





Front view



Side view

Benzo-1',2'-7,8-(benzanthrone)-3'-Carboxylic acid

EXPERIMENTAL

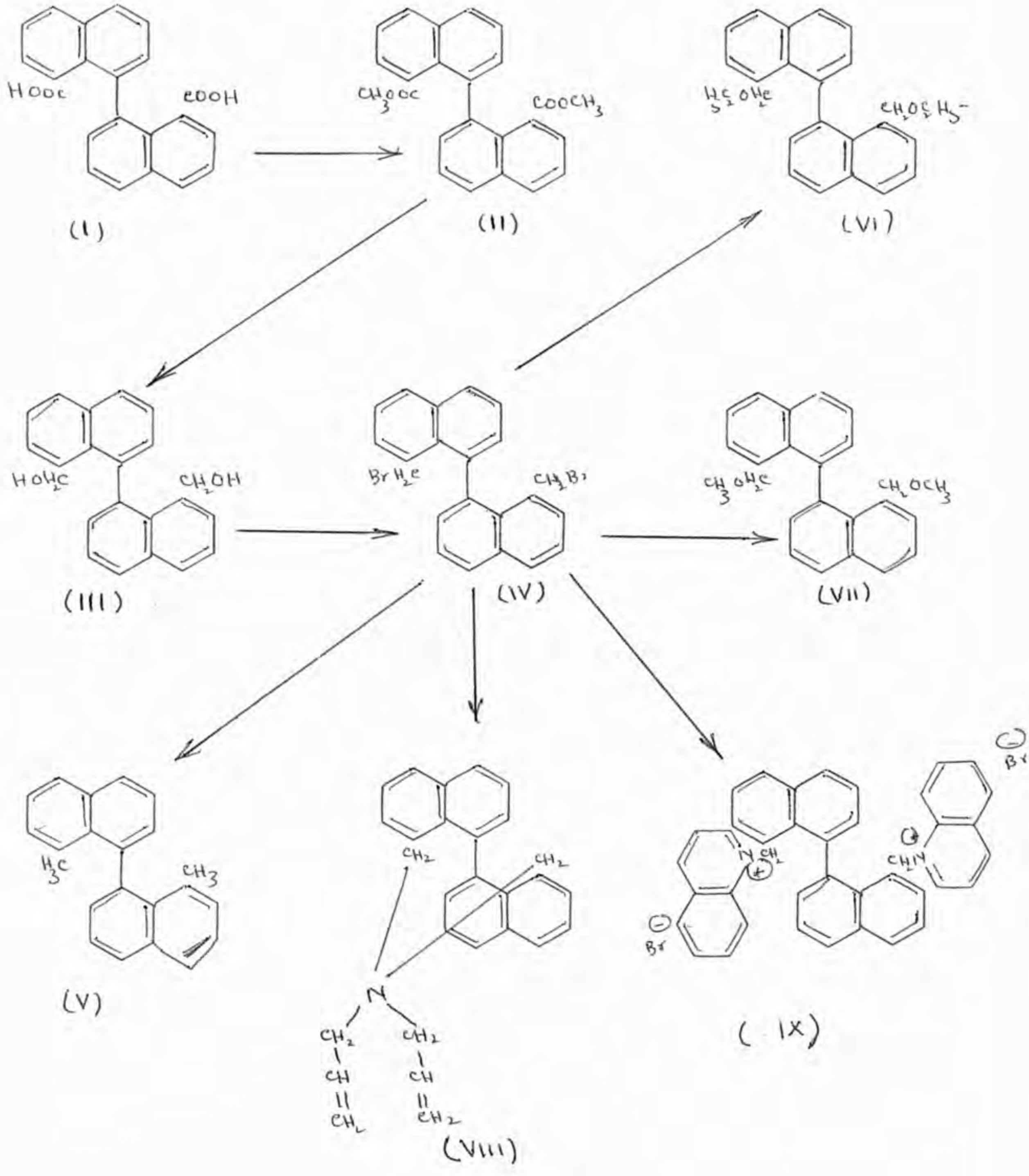
PART I

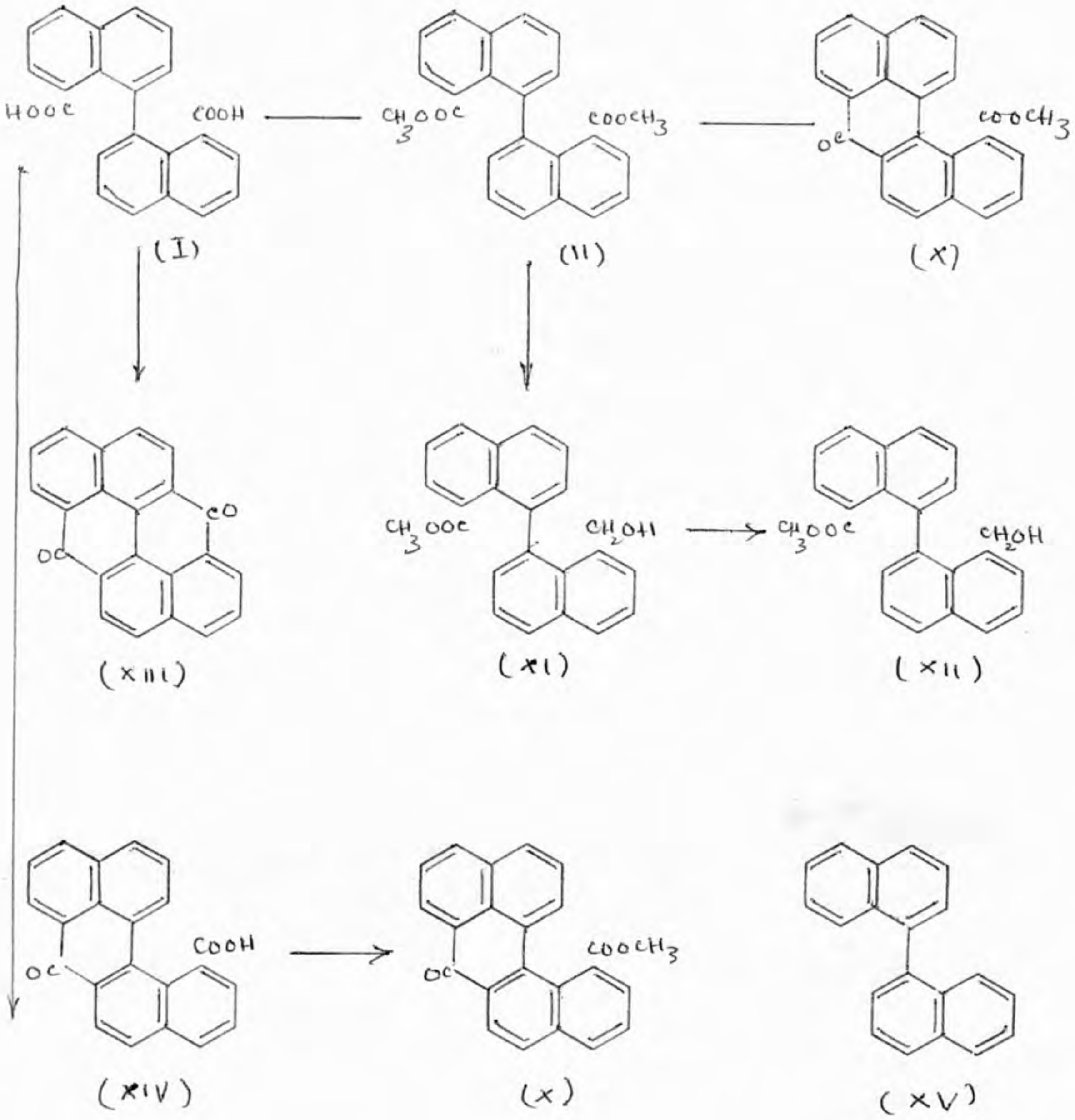
(1) Synthesis of 1,1'-binaphthyl compounds substituted in the 8,8'-positions.

(2) Synthesis of substituted benzo-1',2'-7,8-benzanthrone.

(3) Synthesis of anthanthrone and 1,1'-binaphthyl as reference compounds.

SUMMARY OF SYNTHETIC WORK

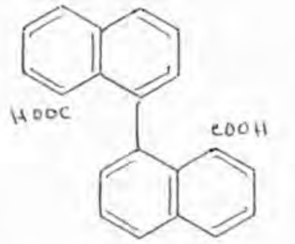




(1) III, IV, V, VI, VII, VIII, IX, XI, XII are new compounds.

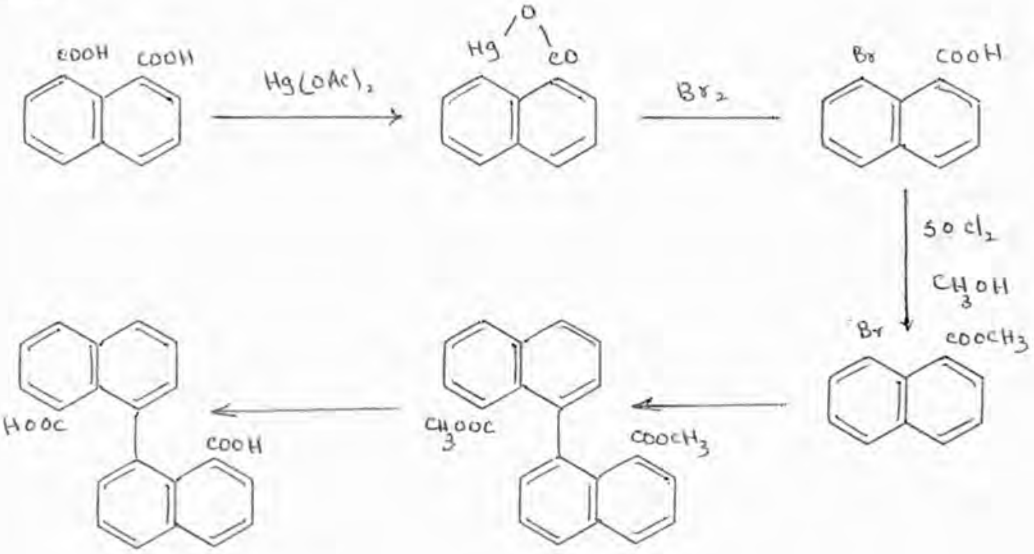
(2) I, II, III, IV, V, VIII, IX, X, XI, XIV were prepared optically active,
III, IV, V, VIII, IX, X, XI, XIV for the first time.

Preparation of (±) - 1,1'-binaphthyl-8,8'-dicarboxylic acid



This compound has been prepared by two methods, but the method number (1) was preferred because of the better yield.

Scheme I



1. 8 - Bromo-1-naphthoic acid

(Rule, Pursell and Brown, J., 1934,168)

Mercuri-compound

Naphthalic acid (260 g., 1 M.) was dissolved in aqueous sodium hydroxide (155 g. in 6 litres of water) by heating, and the solution filtered into a 20 litre flask in a large heating mantle and boiled under reflux for 15 minutes.

Mercuric oxide (275g., 1.1M.) dissolved in 200 ml. of glacial acetic acid and 750 ml. of water was then added and the reaction mixture made acidic with glacial acetic acid. The solution was then heated for 90 hours. The reaction was finished when a sample gave a clear solution with sodium hydroxide and no mercury was deposited on a clean copper wire held in this solution.

The product was filtered off, washed with water, alcohol and ether and then dried, a pale cream coloured solid was obtained. Yield, 515.5g. 91.1%
(A.S. Mellor, Ph.D Thesis (London) 1961, 81.0%)

2. Introduction of bromine

The mercuri-compound (95g.) was suspended in a mixture of 300 ml. of glacial acetic acid and 50 ml. water, and cooled to -10°.

Bromine (14g.) in aqueous sodium bromide solution (150 ml. of 50% solution) was added gradually with constant stirring, using a mechanical stirrer, keeping the temperature below 0°.

The reaction was then allowed to warm to room temperature and then heated to 90° and poured into three litres of boiling water. The solution was filtered as hot as possible. The residue was extracted with boiling water and again filtered hot. The combined filtrate on cooling deposited a shining crystalline solid, which was sucked off and dried (50.5g.). Crystallization from benzene gave 41.5g.(81%) of 8 - bromo-1-naphthoic acid. m.p. 174-175° (shrinking at 170°.

3. Methyl -8- bromo -1- naphthoate

This was prepared by the method of Rule and Barnet (**J.**, 1932,175), with a modified method of purification.

8 - Bromo-1-naphthoic acid (75g.) was dissolved in benzene (510 ml.) by boiling under reflux. Thionyl chloride (22 ml.) was added slowly to the boiling solution and the mixture boiled for 4½ hours. Methyl alcohol (75 ml.) was then added very slowly and cautiously and boiled for further 45 minutes.

The benzene solution was washed twice with water, twice with aqueous sodium carbonate solution and finally with water. It was then dried over calcium chloride, benzene removed (distillation from a water bath). The residue, dark brown in colour, was distilled off under reduced pressure (1. m/m.) using an air condenser. At

At 180-200° a pale yellow oily compound was obtained. It was allowed to cool (ice). It did not solidify. It then crystallized on rubbing with a rod under light petroleum (b.p. 40-60°). A very light coloured crystalline compound was obtained. Yield 46g. (76.6%), m.p. 38°.

4. Ullmann reaction.

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

This preparation was carried out according to the procedure of Hall, Ridgwell and Turner (J., 1954, 2498), except that the reaction was tried out at much lower temperature of 200°, while the internal temperature was 220°, with 76.5% yield. Previously it was done at 260°, and the internal temperature was 300°, and the yield was 55%.

Copper bronze (40g.) was added gradually to methyl -8--bromo-1-naphthoate (40g.) contained in a hard glass tube immersed in a metal-bath kept at 200°. During addition the internal temperature rose to 220°, after addition of the whole copper bronze it was heated at 195° for about 15 minutes. It was then allowed to cool, the cooled mass was extracted with acetone in a Soxhlet apparatus. The solution obtained was then boiled with charcoal until light pale yellow, filtered and then concentrated to about 150 ml. A very light cream coloured crystalline compound was obtained (thick needles).

Yield. 21g. 76.5%, m.p. 158-159°. (Cooke and Harris, (J., 1963, 2370.) obtained two crystalline forms, (i) needles m.p 155-157° and(ii)plates m.p 145-147°).

5. Hydrolysis of the above methyl ester.

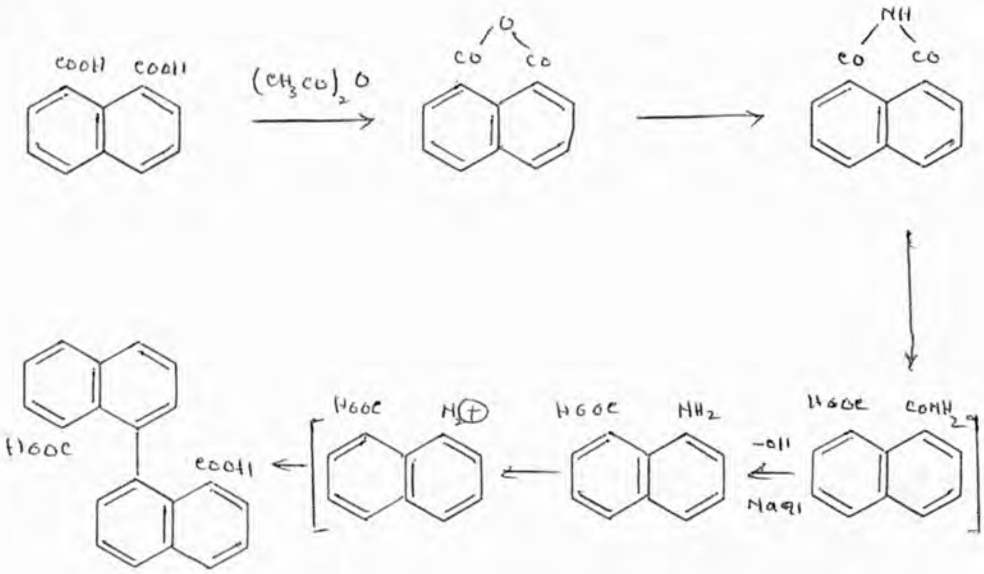
(Hall, Ridgwell and Turner, J., 1954, 2498)

The ester (17g.) was boiled under reflux with 30% alcoholic potassium hydroxide (500 ml.) for 30 minutes on a metal-bath. The alcohol was then distilled off, and the residue heated at 130-140° for about half an hour.

The residue was extracted with boiling water and filtered. The cooled filtrate was acidified with dilute hydrochloric acid and the precipitate filtered off, washed with water and dried. This precipitate was 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 the white crystalline acid was obtained (14.1g. 90%) m.p. 318-320° (decomp.). Recrystallization from methylated spirit raised the melting point to 324-325° (decomp.).

(Hall, Ridgwell and Turner. (J., 1954, 2498) gave m.p. 300-304°. Meisenheimer and Beisswenger. (Ber., 1932, 65, 32) gave m.p 304°. Stanley, J.A.C.S., 1931, 53.3104),306-307°, and Cooke and Harris (J;, 1963, 2372) reported that the acid was melted with decomposition at 306 - 324°, depending upon the crystallinity of the sample and the rate of heating).

Scheme 2



1. Naphthalic anhydride.

Naphthalic acid (10g) was heated under reflux with acetic anhydride (50 ml) for two hours. It was then filtered hot. On cooling needle shaped crystals were obtained (9g) m.p. 273.5-276°, 97.15%.

2. Naphthalimide.

(A.P. Karishin and D.M.Kustol, State pedagog inst. poltavazhur. Obschchei Khim., 1958, 28, 692 - C.A.,52, 17197 a)

Naphthalic anhydride (5.00g) and 8 ml. of 16% ammonium hydroxide were heated on a steam bath for 30 minutes. (final temperature 90°). It was then diluted with water, filtered, washed well with water and dried. (4.93g. 99%). m.p. 299-300°.

3. 1,1' - Binaphthyl - 8,8' - dicarboxylic acid.

(A.P. Karishin and D.M. Kustol. Zhur Obschei Khim., 1959, 29, 1928, C.A., 1960, 54, 8748c.).

Naphthalimide (9.4g.) was heated under reflux with 200 ml of distilled water and 24 ml of 30% potassium hydroxide to solution. It was then cooled to 20° and 40 ml. of 30% potassium hydroxide and 75 ml. of freshly prepared sodium hypochlorite solution added and stirred for two hours at 25°. Excess hypochlorite was decomposed by adding a dilute solution of sodium bisulphite. This was then added to 70 ml. of 30% sulphuric acid below 5°.

The mixture was cooled to - 4°, and treated with 3.0g. of sodium nitrite in 20 ml. of water. It was stirred 20 minutes below 2°, and neutralized with saturated sodium carbonate solution until barely acid to congo red. This gave the diazonium salt solution.

Preparation of Catalyst.

(Vorländer; Annalen, 1902, 320 138)

Copper sulphate (35.5g.) was dissolved in 200 ml. of water and 100 ml. of ammonia (d = 0.880) was added. The solution was cooled, 80 g. of powdered sodium metabisulphite and 80 ml. of ammonia (d = 0.880) was added, the solution turned brown and a heavy precipitate appeared. Ammonia caused some blue colour owing to oxidation. It was then cooled to 15°.

The diazo solution was added slowly to the catalyst by means of a dropping funnel, keeping the temperature below 15°, and stirring vigorously throughout the addition. Nitrogen was evolved.

Ferric chloride (50 g.) was dissolved in water (80 ml.) filtered through Buchner funnel and 260 ml. of concentrated hydrochloric acid was added. This solution was then added to the reaction product, the solution turned brown and 1,1' - binaphthyl -8,8' - dicarboxylic acid precipitated. It was filtered, washed throughly with water and dried, dissolved in methylated spirit, boiled with charcoal and filtered. It was concentrated to about $\frac{1}{4}$ of its volume. On cooling the crystalline acid separated. m.p. 323-325° (decomp.).

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

The 1,1' - binaphthyl - 8,8' - dicarboxylic acid (10 g), dark brown in colour, was dissolved in 3 litres of boiling methylated spirit. It was then boiled with charcoal and filtered. A light pale yellow coloured solution was obtained. Methylated spirit was then distilled off leaving about 1¼ litre of solution. On cooling white colourless crystalline acid was obtained, m.p. 318 - 320° (decomp). Yield (7.6g.). It was recrystallized from methylated spirit, m.p. 320 - 323° (decomp.).

(The infra red spectrum is very closely similar to that of the acid obtained from the first two experiments).

Preparation of the dimethyl ester of 1,1' - binaphthyl - - 8,8' - dicarboxylic acid.

This describes the general procedure for the preparation of the (±)- , (+) - and (-) - esters.

Diazomethane.

(Org. Synth., 1956, 36, 16)

$$\underline{p} - CH_3C_6H_4SO_2N(NO)\,CH_3 + R.OH$$

$$CH_2N_2 + \underline{p} - CH_3.\,C_6H_4SO_2\,.\,OR + H_2O$$

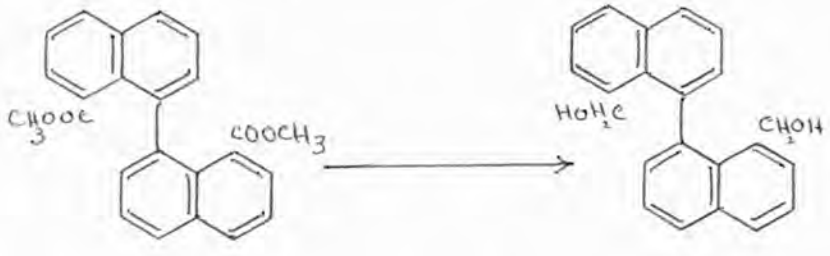
The joints of the apparatus were fitted with plastic sleeves to limit the possibility of explosion.

In a round botommed flask were placed 5g. potassium hydroxide, 8 ml. water and 25 ml. of 95% ethanol. N-methyl-N-nitroso-p-toluene-sulphonamide (21.5g.) dissolved in 150 ml. of ether was placed in a dropping funnel. There were two receiving flasks in series and the second one which contained 40-60 ml. ether acted as a trap for any diazomethane which might escape. The N-methyl-N-nitroso-p-toluene-sulphonamide was added from the dropping funnel to the potassium hydroxide solution in the flask, which was on water-bath kept at 60-70°. After the addition a further 50 ml. of ether was added, and the distillation continued until the distillate was colourless. The ethereal solution was used immediately and was assumed to contain 2.6-2.7g. of diazomethane.

(±)-Dimethyl - 1,1' - binaphthyl - 8,8' - dicarboxylate.
(Cooke and Harris, J., 1963, 2365 - 2373).

Powdered 1,1' - binaphthyl - 8,8' - dicarboxylic acid (5 g.) was added slowly to the cold ethereal solution of diazomethane (70 ml. - 1.22 g). There were effervences, and as the reaction proceded a white solid crystallized at the bottom of the flask. When the reaction was complete, the solid was filtered off, washed throughly with aqueous sodium carbonate solution and then with water and dried. A white crystalline product was obtained (4.5 g.) m.p 156-158°. It was then dissolved in methylated spirit, filtered and concentrated to about half the volume. On cooling two types of crystals were obtained (i) thick needles m.p. 158-159° and (ii) plates m.p. 158-159°. When the plates were dissolved in methylated spirit and allowed to stand, thick needles were obtained m.p. 158-159°.

8,8' - Bis(hydroxymethyl) - 1,1' - binaphthyl.



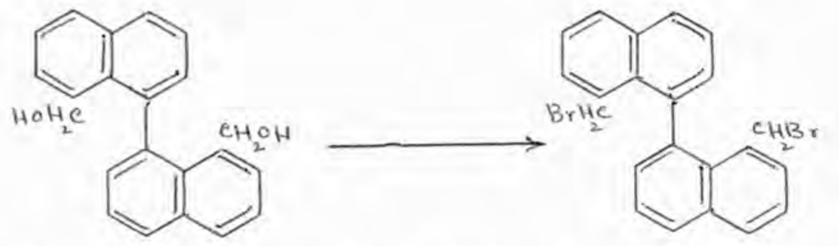
This method was adapted from Bergmann and Szuskovicz, (J.A.C.S., 1951, 73, 5135,), and Hall and Turner (J.,1955, 1242), who used it for different compounds.

Lithium aluminium hydride (1.5g. - 6 M.) was weighed in the fume cupboard and quickly covered with sodium dried ether (500 ml.) in a three necked, three litre flask equipped with a condenser and a dropping funnel. A suspension of dimethyl - 1,1' - binaphthyl - 8,8' - dicarboxylate (5g.1M.) in 1000 ml. of sodium-dried ether was then washed in.

The mixture was then heated on a water-bath for 3-4 hours. Wet ether and then water (½ - 1 drop at a time) was added, to decompose the excess of lithium aluminium hydride, until no bubbles were observed, and dilute sulphuric acid (2 N.) was then added. The ether layer was separated. The aqueous layer was extracted once with ether and the combined ether layers were washed twice with water and dried over calcium chloride. The calcium chloride was removed by filtration and washed twice, with small portions of dry ether. The ether was then distilled off. A quantitative yield of the crystalline compound m.p. 145 - 150° together with a little sticky substance was obtained. It was dissolved in benzene, boiled with a little charcoal and filtered. After some time colourless hexagonals crystals separated, (3.9 g.), mp 150-151.5°, and were recrystallized from benzene, m.p. 151-152°. After drying in a vacuum over phosphorous pentoxide for two hours at 100°, m.p. 152 - 153°.

(Found: C, 83.9; H, 5.7; O, 10.40, $C_{22}H_{18}O_2$ requires C 84.05; H, 5.8; O, 10.2%.).

8,8' - Bis(bromomethyl)-1,1' - binaphthyl.



8,8' - Bis(hydroxymethyl) - 1,1' - binaphthyl (5g.) was dissolved in boiling acetic acid (125 ml.) and then boiling hydrobromic acid (60 ml. d = 1.5) was added. The solution cleared on shaking then become cloudy, and a light yellow crystalline compound separated. More hydrobromic acid (25 ml.) was added. After cooling, the solid was filtered, washed well with water and dried (8g.) m.p. 178 - 1 90°. Crystallization from chloroform gave very light yellow crystals, (5.7g. 82%), m.p. 190 - 191.5°.

(Found: C, 60.2; H, 3.6; Br, 36.5, $C_{22}H_{16}Br_2$ requires C, 60.0; H, 3.7; Br, 36.3%).

Estimation of bromine by Parr bomb method.

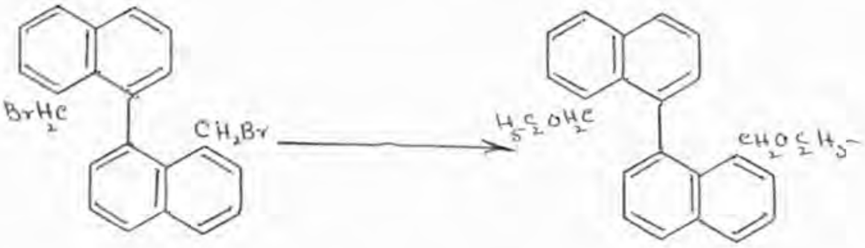
The bromocompound (0.3211 g.) was weighed directly into the fusion cup, and 0.5g of cane sugar, 1.5g. of potassium nitrate followed by 15 g of sodium peroxide added, Immediately the lid was placed on the fusion cup, screwing the union tightly into place. The contents of the bombs were mixed throughly by shaking it and the bomb was placed inside the fusion guard. Some distilled water was placed in the top of the cap union. The bomb was heated with a bunsen flame till the water on the top boiled. The bomb was allowed to cool under the tap. After cooling, the bomb was dismantled and the fusion cup was placed in a beaker containing 200 ml. of hot water. The beaker was covered with a watch glass. When the evolution of gas ceased the cup was removed and rinsed well. The solution was acidified with nitric acid and the silver nitrate solution was added slowly with constant stirring till no further precipitate was obtained. The solution was then allowed to stand for one hour and then filtered through sintered glass crucible, washed with dilute nitric acid and dried in an oven until constant weight was obtained (0.2744 g of AgBr)

$$\text{Percentage of bromine} = \frac{0.2744 \times 42.55}{0.3211} = 36.35\% .$$

8,8' - Bis(hydroxymethyl) - 1,1' - binaphthyl from 8,8' - bisbromomethyl - 1,1' - binaphthyl:

8,8' - Bisbromomethyl - 1,1' - binaphthyl (2g.) was dissolved in boiling acetone. Aqueous silver nitrate was added and the silver bromide filtered off. The filtrate was extracted with benzene and the extract was washed well with water twice and dried over calcium chloride. The benzene was removed by distillation and the residue obtained (1.35 g., 94.7%) was crystallized from benzene (1.05g.,73.5%) m.p. 147 - 149°. On recrystallization from benzene the melting point was raised to 150 - 151°. (The infrared spectrum was very closely similar to that of 8,8' - bis(hydroxymethyl)- - 1-1' -binaphthyl previously prepared (see p.84) and there was no depression when the mixed melting point with this diol was taken).

8,8' - Bis(ethoxy-methyl)-1,1'-binaphthyl.



(a) 8,8' - Bisbromomethyl - 1,1' - binaphthyl (5 g.) was boiled with alcoholic potassium hydroxide in which it dissolved. After cooling and filtering off potassium bromide, the mother liquor was evaporated on water-bath, the residue was washed well with water, dissolved in ether and dried over calcium chloride. Ether was removed by distillation and the brown sticky residue dissolved in alcohol: on cooling needle shaped crystals were obtained (2.1 g., 67.74%) m.p. 78 - 80°. Recrystallization from alcohol after boiling with charcoal gave colourless thick needles. m.p. 80 - 81°.

(Found: C, 84.45; H, 7.05; O, 8.5. $C_{26}H_{26}O_2$ requires C, 84.3; H, 7.1; O.8.6%)

(b) 8,8' - Bis(bromomethyl)-1,1'- binaphthyl (2.273g.) was dissolved in boiling methylated spirit, and aqueous silver nitrate was added slowly till no further precipitate was obtained. On cooling the precipitate of silver bromide was filtered off, washed with water, alcohol, ether and benzene and dried in the oven until the weight was found constant (1.9002 g., calculated for 2 M. AgBr, 1.938 g. 98.45%). The organic solvents in the mother liquor were vaporised off on a water bath, the residue was dissolved in benzene and dried over calcium chloride. Benzene was distilled off from the solution leaving behind the compound - a brownish sticky substance (1.79 g., 94%). It solidified under ethanol, was filtered and dried (0.85 g., 44.9%) m.p. 77 - 80°. Recrystallisation from alcohol raised the m.p. to 80 - 81°.

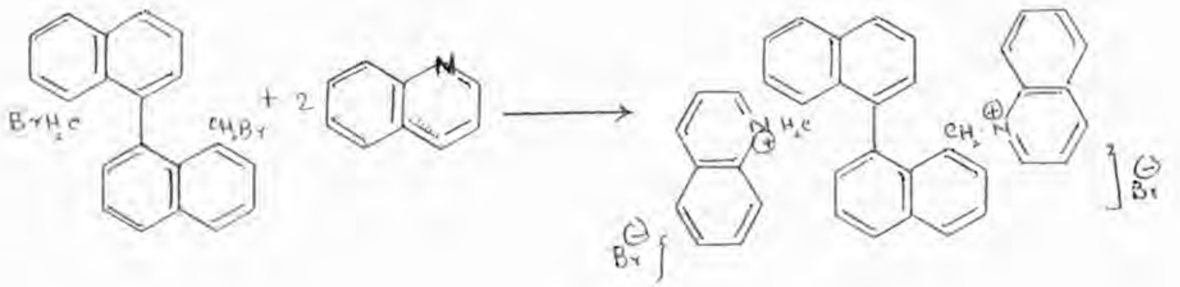
Mixed melting point with the material from the first preparation, 80 - 81°. The infrared spectrum was also very closely similar.

8,8' - Bis(methoxymethyl) - 1,1'-binaphthyl

8,8' - Bis(bromomethyl) - 1,1' - binaphthyl (2g.) was dissolved in boiling methyl alcohol and excess of silver nitrate was added. On cooling the precipitate of silver bromide was filtered off, washed with water, ether, alcohol and benzene respectively. The filtrate was evaporated on a water-bath and the residue obtained was extracted with benzene. The benzene solution was washed with water twice and dried over calcium chloride. The benzene was then removed by distillation and the oily residue obtained was solidified on trituration with methyl alcohol (1.512g.) m.p. 63-68°. Crystallization from methylated spirit gave colourless plates. m.p. 72 - 73°. It was then recrystallized from methylated spirit. m.p. 72 - 73°.

(Found: C, 84.5; H, 6.4; O, 9.2. $C_{24}H_{22}O_2$ requires C, 84.2; H, 6.5; O, 9.3%).

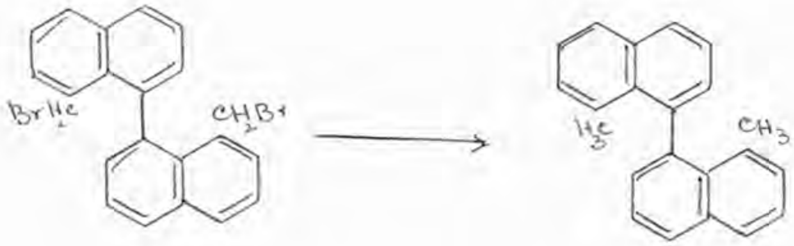
8,8' - Bis(methylenequinolinum bromide) - 1,1'-binaphthyl.



8,8' - Bis(bromomethyl) - 1,1' - binaphthyl (1g.) was dissolved in hot quinoline (10 ml.). It was then allowed to stand overnight, needle shaped crystals were obtained, which were filtered, washed well with benzene and dried (1.65g. m.p. 190 - 195°. It was then recrystallized from water (0.9g) m.p. 203 - 205° (decomp.).

(Found: C, 68.7; H, 4.5; N, 3.9; Br, 23.0. $C_{40}H_{30}O_2Br_2$ requires C, 68.8; H, 4.3; N, 4.0; Br, 22.9%).

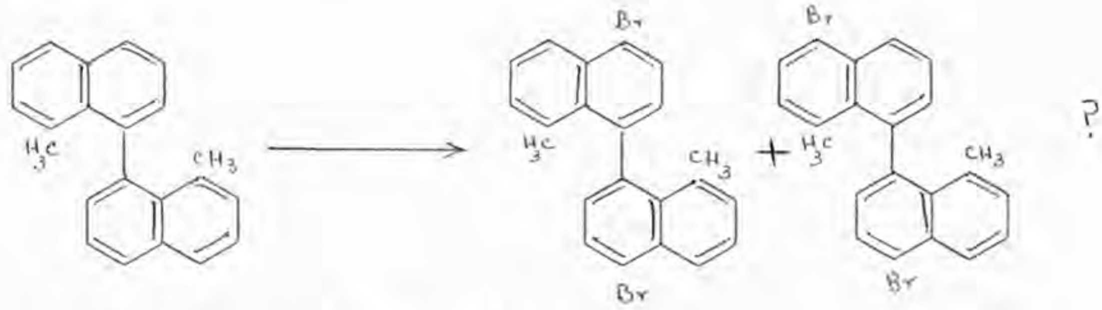
(±) - 8,8' - Dimethyl - 1,1'-binaphthyl



8,8' - Bis(bromomethyl)-1,1' - binaphthyl (5g. 1M.) in sodium dried ether (500 ml.) was added to a well stirred solution of lithium aluminium hydride (1.4g - 6 M) in the same solvent (1500 ml.) and the mixture was heated under reflux for two hours. The excess of lithium aluminium hydride was decomposed with ethyl acetate and excess of potassium hydroxide was added. The ether layer was separated and the aqueous layer was extracted with a benzene - ether mixture. The combined organic layers were washed well with water twice and dried over magnesium sulphate. Magnesium sulphate was removed by filtration and washed twice with ~~a~~ small portions of dry ether. The solution was distilled almost to dryness. The residue, crystalline thick needles (3.15g - 100%) was obtained. m.p. 123 - 127°. Recrystallization from ether gave colourless crystals mp.130.5 - 131°.

(Found: C, 93.5; H, 6.4. $C_{22}H_{18}$ requires
C, 93.6; H, 6.4%).

Bromination of 8,8' - dimethyl - 1,1' - binaphthyl.



Bromine (0.75 ml.) in 200 ml. of carbon tetrachloride was added during 2¼ hours to a well stirred solution of 8,8' - dimethyl-1,1' - binaphthyl (2g.) in 25 ml. of carbon tetrachloride, with a small amount iron and iodine, at -7°. Stirring was continued for further 1½ hours at -7° and the mixture was then left for two hours.

As the temperature rose the excess of bromine was removed by adding 2N sodium hydroxide and water. The mixture was evaporated on a water-bath, the residue obtained was extracted with chloroform and then dried over calcium chloride. The chloroform was removed by distillation and the residue was extracted with ether. The ether insoluble matter (0.6g.) was crystallized from benzene and then from acetone. Needle shaped crystals were obtained. m.p. 241 - 242°.

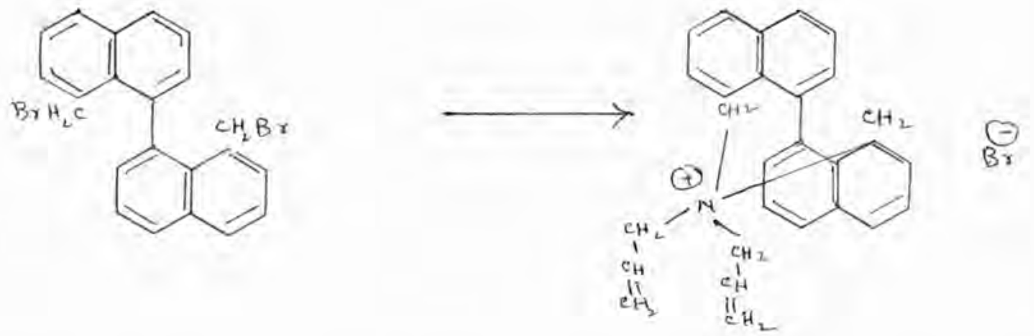
(Found: C, 60.15; H, 3.7; Br, 36.14. $C_{22}H_{16}Br_2$ requires C, 60.0; H, 3.7; Br, 36.3%).

The ether soluble portion was evaporated to dryness. A brownish residue was obtained (1.95g.), m.p. 105 - 112°, which was dissolved in methylated spirit, boiled with charcoal and filtered; light yellow coloured plates separated, m.p. 112 - 115° (clear at 120°). It was then recrystallized from methylated spirit. m.p. 123 - 125.5°.

(Found: C, 61.88; H, 3.9; Br, 34.14. $C_{22}H_{16}Br_2$ requires C, 60.0, H, 3.7; Br, 36.3%).

Note:- Most probably the above compounds are 4,4'-dibromo, and 5,5' - dibromo - 8,8' - dimethyl-1,1'-binaphthyl, but there are also other possibilities.

The condensation of 8,8'-bisbromomethyl-1,1'-binaphthyl with diallylamine



8,8'-Bis(bromomethyl)-1,1'-binaphthyl(2g.) dissolved in benzene, and diallylamine were allowed to react at 50-55° (over hot plate) for 2-3 hours. A white crystalline compound separated, which was filtered, washed with benzene and dried (2.2g.) m.p. 165-184°. Recrystallization from water gave white long needles m.p. 190-191°.

Found: C, 72.2; H, 5.84; N, 3.15, Br, 18.4. calculated for $C_{28}H_{26}N.Br$. C, 73.6; H, 5.74; N, 3.1, Br. 17.5%

Methyl benzo-1',2'-(benzanthrone)-3'-Carboxylate

This compound has been prepared by Rule and Smith (J., 1937, 1096). The yield was only 50% so it was tried to prepare ~~it~~ this at room temperature, and the yield was found to be very good. It was also prepared by the action of diazomethane on benzo- 1,2' -(benzanthrone) - 3'-carboxylic acid.

(a) Concentrated sulphuric acid (25 ml.) was added to well powdered dimethyl - 1,1' - binaphthyl - 8,8'-dicarboxylate (2g.) with constant stirring with the rod. It was then left at room temperature for about 20 - 30 minutes, the colour changed from brown to dark bright red. This red coloured product was poured into ice cold water, an orange yellow precipitate resulted, which was filtered, washed well with water, with sodium carbonate and then again with water and dried.

The residue was extracted with acetone, leaving a dark orange insoluble residue of anthanthrone (0.1g.) The acetone solution was then evaporated to dryness, from the residue an orange-yellow crystalline compound (1.6g.) was obtained m.p. 149-157°. It was then recrystallized from methylated spirit, m.p. 158-159°. Yield (1.42g.).

(Found: C, 81.5; H, 4.2; O,14.2. $C_{23}H_4O_3$ requires C, 81.6; H, 4.2; O.14.2%).

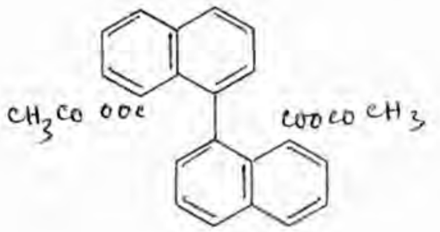
(b) Benzo-1',2'-7,8-benzanthrone-3'-Carboxylic acid, (0.5g) was added slowly to the cold ethereal solution of diazomethane (10 ml ≈ 0.125g). It dissolved with effervescence. When the reaction was complete, the ether was evaporated and the resulting yellow product was washed well with sodium carbonate, and then with water, and dried (0.47g). It was then dissolved in methylated spirit, filtered, and concentrated to about half of its volume. A yellow crystalline compound separated (0.3g) m.p. 155-158°. It was recrystallized from methylated spirit. m.p. = 157.5 - 159°.

There was no depression when the mixed melting point with the compound previously obtained was taken. The infra red spectrum was also very closely similar.

Benzo-I',2'-7,8-(benzanthrone)-3'-carboxylic acid

This compound has been prepared in low yield by Rule and Smith (J.,I937,I096) and by Sutcliffe (J.,I952,I247),therefore modified methods of preparation were developed, and the yields were found to be very good.

I,I'-Binaphthyl-8,8'-dicarboxylic acid(I0g.) was heated under reflux with acetic anhydride (I50 ml.) for two hours. A clear yellow solution was obtained which was filtered and concentrated to a very small volume which on cooling gave a yellow needle shaped crystalline compound,m.p. I56 I57, which on recrystallisation from methylated gave m.p. I56-I57 , This compound was thought to be mixed anhydride.(A.S.Mellor Ph.D Thesis (London) I96I,I27). because the infrared spectrum showed peak at I808 cm^{-1} and I72I cm^{-1} which is a characterstic of an ~~anhydri~~ anhydride,



This compound when heated above its melting point ~~it~~ bubbled and went cloudy and at about 1 90 - 200° it solidified as an orange solid: heating was continued and it melted with decomposition at 280 - 300°.

The mixed anhydride was again dissolved in acetic anhydride and concentrated to dryness. An orange product was obtained, which was dissolved in alkali, filtered and the filtrate acidified with dilute hydrochloric acid. The resulting yellow precipitate was filtered, washed with water and dried (7.2g.). It was then crystallized from toluene, m.p. 290 - 291.5°. This is, presumably, the required product. (Found: C,81.45; H, 4.09; O,14.55, $C_{22}H_{12}O_3$ requires C,81.47; H, 3.73; O,14.79%).
Bradley and Sutcliffe, J., 1952, 1247, Rule and Smith J.,1937, 1096, and A.S. Mellor (Ph.D. Thesis London, 1961.127) gave m.p. 279 -280°.

(b) Sulphuric acid (25 ml. 75%) was cooled in ice and added to finely powdered 1,1' - binaphthyl - 8,8' - dicarboxylic acid (5g.) More concentrated acid (cooled) was added. The dark red coloured solution resulted, which was kept 10 minutes in the ice mixture and then 15-20 minutes at room temperature. The dark red coloured solution was poured into ice cold water: an orange precipitate was obtained, which was filtered and washed throughly with water. The residue obtained was dissolved in alkali, and filtered from the dark orange coloured insoluble material (anthanthrone).

The filtrate was precipitated with dilute hydrochloric acid and the yellow product obtained was filtered, washed with water and dried (4.2g.) m.p. 288 - 292°. It was then recrystallized from methylated spirit. m.p. 291 - 292.5°. (Found: C,81.3; H,3.9; O,14.8. $C_{22}H_{12}O_3$ requires C,81.5; H,3.7; O,14.8%).

Preparation of anthanthrone from 1,1' - binaphthyl -8,8'-dicarboxylic acid.

(J.Chem. Soc, Japan.,1952, 55, 485.).

The powdered 1,1' - binaphthyl - 8,8' - dicarboxylic acid (1.5g.) and concentrated sulphuric acid (5 ml.) were heated on water bath for one hour. The colour changed from brown to red and then to dark green. After cooling the reaction mixture was poured into ice cold water. A dark orange precipitate resulted, which was filtered, washed with water, washed with sodium carbonate solution to remove any carboxylic acid and filtered. It was then washed well with water and dried at 110° (1.65g.). The crude material was crystallized from nitrobenzene. Fine yellow orange needles were obtained m.p. >350°.

The infra red spectrum ~~was~~ resembled very closely ~~to~~ that of anthanthrone purchased from Lights and Co. and that given in infra-red spectrum data, American petroleum institute research project No. 44 (2322).

8-Methoxycarbonyl-8'-hydroxymethyl-1,1'-binaphthyl.

A suspension of dimethyl-1,1'-binaphthyl-8,8'-dicarboxylate (5g.) in 750 ml. of sodium dried ether was added to a well stirred solution of lithium aluminium hydride (1g.) in 750 ml. of the same solvent. The stirring was continued for a further one hour at room temperature .

The excess of metal hydride was decomposed by adding water ($\frac{1}{2}$ - 1 drop at a time) and dilute sulphuric acid was added. The two layers were separated. The aqueous layer was extracted with ether and the combined ether extract was washed twice with water and dried over calcium chloride. The calcium chloride was removed by filtration and washed twice with small portions of dry ether. The ether was then distilled off and the residue a sticky substance (4.7 g.) was solidified by trituration with benzene (4.2g.).It melted partly at I0I-I09° and cleared at I20°. It was a mixture of dimethyl ester , hydroxyester and the diol(by the investigation of this mixture by thin layer chromatography).The mixture was separated by passing it through a column packed with alumina using ether/benzene mixture (I:I0) as an eluting solvent. Dimethyl ester (0.I2g.) was collected from the first few fractions,and than hydroxyester was collected (2.3g.) m.p. I27-I30°.The diol came out in the last. The hydroxy ester was crystallised from benzene. The needle shaped crystals melted at I30.5-I3I.5°

Found: C, 81.7 H, 5.3 O, 12.8 $C_{23}H_{18}O_{3}$ requires C, 80.7 H, 5.3 O, 14.0 %.

8,8' - Bis(hydroxymethyl)- 1,1' - binaphthyl obtained by the reduction of 8 - methoxycarbonyl - 8' - hydroxymethyl- 8' - hydroxymethyl - 1,1' - binaphthyl.

8 - Methoxycarbonyl - 8' - hydroxymethyl - 1,1' - binaphthyl (0.6g.) in 150 ml. of sodium dried ether was added to a well stirred solution of lithium aluminium hydride (0.5g.) in 200 ml. of the same solvent. The reaction mixture was then heated under reflux for three hours.

Excess of lithium aluminium hydride was decomposed carefully first with water and then with dilute sulphuric acid. The two layers were separated, the aqueous layer was extracted twice with ether and the combined ether layers were washed twice with water. It was then dried over calcium chloride, and the ether was removed by distillation. The residue obtained was dissolved in benzene, boiled with a little charcoal and filtered. Colourless hexagonal crystals separated (0.25g.) m.p. 150-151°. Mixed melting point with the diol previously prepared 150-151°*. The infra red spectrum was also very closely similar ~~with~~ to that of the diol.

* See page 84

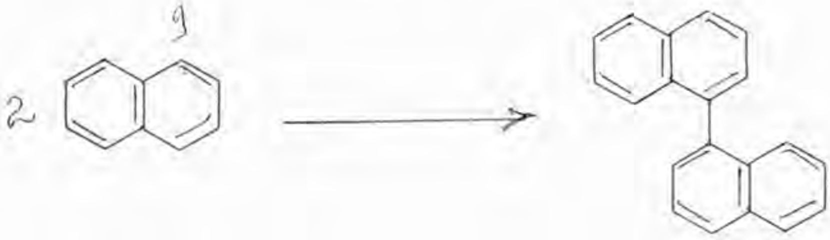
8 - Methoxycarbonyl - 8' - bromomethyl-1,1'-binaphthyl

8 - Methoxycarbonyl - 8'-hydroxymethyl-1,1'-binaphthyl (0.3g.) was dissolved in hot glacial acetic acid (10 ml.) and 10 ml. of hydrobromic acid (d = 1.5) was added. The yellow compound obtained thereby was filtered, washed thoroughly with water and dried (0.25g.) m.p. 120-124°. It was crystallized from acetone m.p. 128.5 - 130°.

(Found: C,68.5; H, 4.3; Br, 20.8. $C_{23}H_{17}O_2Br_2$ requires C,68.2; H, 4.2; Br, 19.8%).

(±) - 1,1' - Binaphthyl.

(Nathan Kornblum and David L. Kendall, J.A.C.S., 1952, 74, 5782.) This compound was prepared in order to have its infrared spectrum for comparison purposes.



α - Iodonaphthalene (20g.) and dimethyl formamide (100 ml.) were placed in 200 ml. 3 - necked flask equipped with reflux condenser and the Tantalum-Hershberg type stirrer. The solution was heated to boiling and 20 g. of copper powder were added in one portion; heating at boiling point was continued for six hours after which another 20 g. portion of the copper powder was added and the heating was continued for another 18 hours period.

After cooling the reaction mixture was poured into two litres of water to remove dimethyl formamide and then filtered. The solid was extracted with benzene and the residue was washed well with benzene. The benzene was then distilled off; the residue (7.59 g.) was crystallized from glacial acetic acid. The shining crystals melted at 144 - 145°*. Yield 3.02 g.

Acknowledged in Cooke and Harris paper J., 1963, 2365

(±)-1,1'-<u>Binaphthyl</u>

(b) (Schoepfle, <u>J.A.C.S.</u>, 1923, <u>45</u>, 1566)

Bromonaphthalene (75g) copper bronze (28g) and iodine (1.9g) were heated for 4-5 hours in a metal bath, which was kept at a temperature of 280-285°. The mixture was stirred occassionally. On cooling the reaction product was extracted with benzene. The residue was washed well with benzene. It was very difficult to filter that so to facilate the filtering of the finely powdered cuprous bromide Kieselguhr salt was used. The filtrate was concentrated: benzene was removed, the residue was washed well with a small quantity of methylated spirit to remove the sticky substance and the remainder was then dried and weighed (2.5g) the crude binaphthyl was crystallized from methylated spirit (19.5g) m.p. 135-140, it was recrystallized from acetic acid (12.6g) m.p. 143-144°. This crystalline compound was dissolved in petroleum ether (40-60°) under reflux. On standing two types of crystals were obtained (9.8g). (1) m.p. 154° (ii) m.p. 159°. (Schoepfle gave the m.p. 157°. James Forrest, <u>J.</u>, 1960, 566 gave 155-156° and, Kursanov and Blokhina, <u>J.Gen</u>. <u>Chem</u>. (U.S.S.R.), 1938, <u>8</u> , 1786 gave 157-158°.

EXPERIMENTAL

PART II

(1) Obtaining optically active material.

(2) Determination of Velocity Constants for Racemisation.

(3) Calculation of Arrhenius Parameters and Absolute Reaction Rate Theory Constants.

(4) Racemisation data.

Description of polarimetric technique

Polarimetric equipment.

All the polarimetric readings were taken on the mercury green line $\lambda = 5461\ \mathring{A}$ using a visual spectropolarimeter made by Bellingham and Stanley.

A thermostat bath containg Ucepal (from F.W. Berk, England) was used when the measurements were made at higher temperature than 80°. A thermometer was fitted in there to read the temperature throughout the experiment. The temperature was read nearest to 0.1°. Portions of the solution were sealed in glass tubes and kept in the thermostat bath and were removed at suitable intervals of time, cooled quickly and the readings were taken using a 1 dm. micro polarimeter tube.

In the case of 8 - methoxycarbonyl-8'-hydroxymethyl -1,1'-binaphthyl, the rates of racemisation below 80° were measured using a 2 dm. centre-filling jacketed polarimeter tube (Hilgers) and the temperature was kept constant by a fast stream of water pumped from the thermostat bath (circotherm) through the jacket. A thermometer was fitted in the polarimeter tube to read the temperature and a clock marked in minutes and hundredth parts of a minute was used and was fully wound at the beginning of each experiment.

Solvent.

The rotations of brucine salts were taken in B.P. chloroform and of other compounds in N,N-dimethyl formamide. All the rates of racemisations were followed in dimethyl formamide purchased from Hopkin and Williams, (refractive index 1.4290 at 25^{o}).

Procedure.

When the rates of racemisations were to be measured at higher temperatures, the solvent was added at t = 0, the solution was filtered and one reading was taken at room temperature, then sealed into tubes in 1.5 ml. portions and kept in the thermostat bath. The tubes were removed at suitable intervals of time, cooled quickly under the tap and readings were taken. The average values of the reading were used to plot the graph of $\log_{10}(\alpha_0 - \alpha_t)$ against time and good straight lines were obtained.

When the rates of racemisations were measured below 80^{o}, at t = 0 the solvent was added and the solution filtered into the polarimeter tube. The temperature was noted and the readings were started as soon as possible. An observation was always made much later to ensure that the final rotation had gone to zero.

Over six rate co-efficients at different temperature covering the range 30 - 45^{o} were obtained for all the racemisations of each compound in the given solvent.

The compound was always recovered from the solutions after racemisations and the melting points and the infrared spectrum were taken.

Calculations.

The logarithm of the angle of rotation was plotted against time t, and the slope of the straight line obtained was used to calculate the rate constant **k** using the first order rate equation:-

$$\underline{k} = \log_e \frac{\alpha_0 - \alpha_t}{\alpha_t - \alpha_\infty}$$

$$= \frac{2.303}{t} \log \frac{\alpha_0 - \alpha_t}{\alpha_t - \alpha_\infty}$$

Where **k** = rate constant
t = time in seconds
α_o = initial rotation.
α_t = rotation after time t.

and the half life periods were calculated from the corresponding rate coefficient, using the equation,

$$\underline{k} = \frac{2.303}{t} \log_{10} \frac{a}{a - x} \quad \text{where } x = a/2$$

$$t_{\frac{1}{2}} = \frac{2.303}{\underline{k}} \log 2.$$

The logarithm of the rate constant $\underline{k}$ was plotted against the reciprocal of the absolute temperature (0°C was taken as 273.2°K) and the slope of the straight line obtained was used to calculate the Arrhenius parameters E and $\log_{10}A$ using the relationship,

$$\underline{k} = Ae^{-E/RT}$$

where E = energy of activation for racemisation.

A = the probability factor

R = gas constant.

T = absolute temp.

$$\log_{10}\underline{k} = \frac{-E}{2.303\,R} \cdot \frac{1}{T} + \log_{10} A.$$

$$\text{therefore } E = 2.303\ RT \times \log_{10} \underline{k} - \log_{10}A.$$

As well as using the graphical method to obtain E from a series of values of $\underline{k}$ and T, the energy of activation was also calculated by the method of least squares (see

Introduction to the study of physical chemistry. Hammett, New York, Mc Graw Hill,1941, P.140), which states that for an equation of the form,

$$Y = a + bx$$

where a and b are constants, and x and y are variable,

$$b = \frac{n\sum xy - \sum x . \sum Y}{n\sum x^2 - (\sum x)^2}$$

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

writing the Arrhenius equation in the above form we have,

$$\frac{1}{T} = \log_{10} A - \frac{2.303\ R}{E} - \log_{10} k$$

where $Y = \frac{1}{T}$, $a = \log_{10} A$, $b = \frac{-2.303R}{E}$, $x = \log_{10} k$

$$\text{therefore } E = \frac{2.303\ R}{b}$$

$$= 4.576 \times \frac{n\sum x^2 - (\sum x)^2}{n\sum xy - \sum x . \sum y}$$

where n = the number of points.

$$\log_{10} A = \frac{\sum x2 . \sum y - \sum x . \sum yx}{n\sum x^2 - (\sum x)^2}$$

calculation of the Transition State Theory functions, $\Delta F^{\neq}$, $\Delta H^{\neq}$, and $\Delta S^{\neq}$ from the absolute reaction rate theory equation (Glasstone, Laidler and Eyring, "<u>The Theory of Rate Processes</u>" McGraw Hill, New York 1941) in the forms,

$$\underline{k} = k \frac{\underline{\underline{k}}\,T}{h}\, e^{\frac{-\Delta H^{\neq}}{RT}}\, e^{\frac{-\Delta S^{\neq}}{R}} \qquad \text{(i)}$$

$$\underline{k} = k \frac{\underline{\underline{k}}\,T}{h}\, e^{\frac{-\Delta F^{\neq}}{RT}} \qquad \text{(ii)}$$

where $\underline{k}$ = rate constant.

$\underline{\underline{k}}$ = Boltzmann constant

k = transmission co-efficient

h = Plank's constant.

$\Delta H^{\neq}$ = enthalpy of activation for racemisation

$\Delta F^{\neq}$ = the change in standard free energy in racemisation.

$\Delta S^{\neq}$ = the entropy of activation for racemisation.

R = gas constant.

T = absolute temperature.

$\Delta H^{\neq}$, the enthalpy of activation was calculated from the relationship,

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

E being obtained experimentally

and from the equation (i)

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

$$\log_{10} k = \log_{10} \kappa \frac{\underline{k}}{h} + \log_{10} T - \frac{\Delta H^{\neq}}{2.303\ RT} + \frac{\Delta S^{\neq}}{2.303\ R}$$

$$\log_{10} k/T = \log_{10} \kappa \frac{\underline{k}}{h} - \frac{\Delta H^{\neq}}{4.576T} + \frac{\Delta S^{\neq}}{4.576}$$

when the transmission co-efficient was taken as unity and

$\underline{k} = 1.380 \times 10^{-6}$ erg/deg. and $h = 6.624 \times 10^{-27}$ erg-sec.

$$\log_{10} k/T = 10.319 + \frac{\Delta S^{\neq}}{4.576} - \frac{\Delta H^{\neq}}{4.576} \times \frac{1}{T}$$

$$4.576 \log_{10} k = 10.319 \times 4.576 + \Delta S^{\neq} - \frac{\Delta H^{\neq}}{T}$$

$$4.576 T \log_{10} k = 47.22T + \Delta S^{\neq} T - \Delta H^{\neq}$$

$$\Delta H^{\neq} = -4.576T \log_{10} k + 47.22\ T + \Delta S^{\neq}\ T$$

~~$\Delta H^{\neq} = -4.576\ T \log_{10} k + 47.22T + \Delta S^{\neq}\ T$~~

$\Delta S^{\neq}$, the entropy of activation for racemisation was calculated from the equation,

$$\Delta S^{\neq} = 4.576 \log_{10} k/T + \frac{E}{T} - 49.2$$

$$\log_{10} k/T = 10.319 + \frac{\Delta S^{\neq}}{4.576} - \frac{\Delta H^{\neq}}{4.576} \cdot \frac{1}{T}$$

$$4.576 \log_{10} k/T = 10.319 \times 4.576 + \Delta S^{\neq} - \frac{\Delta H^{\neq}}{T}$$

$$\Delta S^{\neq} = 4.576 \log_{10} k/T + \frac{\Delta H^{\neq}}{T} - 47.22$$

$$= 4.576 \log_{10} k/T + \frac{E-RT}{T} - 47.22 \quad (\Delta H^{\neq} = E-RT)$$

$$\Delta S^{\ddagger} = 4.576 \log_{10} k/T + \frac{E}{T} - \frac{RT}{T} - 47.22$$

$$= 4.576 \log_{10} k/T + \frac{E}{T} - R - 47.22$$

$$= 4.576 \log_{10} k/T + \frac{E}{T} - 1.987 - 47.22$$

~~$= 4.576 \log_{10} k/T + \frac{E}{T} - 1.987 - 47.22$~~

$$= 4.576 \log_{10} k/T + \frac{E}{T} - 49.207$$

(2) $$\underline{k} = k \frac{\underline{k}\, T}{h} \; e^{\frac{-\Delta H^{\ddagger}}{RT}} \; e^{\frac{\Delta S^{\ddagger}}{R}}$$

$$= k \frac{\underline{k}\, T}{h} \; e^{\frac{RT - E}{RT}} \; e^{\frac{\Delta S^{\ddagger}}{R}} \quad (\text{since } \Delta H^{\ddagger} = E - RT$$

$$= k \frac{\underline{k}\, T}{h} \; e^{\frac{RT}{RT}} \times e^{\frac{-E}{RT}} \; e^{\frac{\Delta S^{\ddagger}}{R}}$$

$$= k \frac{\underline{k}\, T}{h} \; e^{1} \times e^{\frac{-E}{RT}} \; e^{\frac{\Delta S^{\ddagger}}{R}}$$

substituting the values of $\underline{k}$, h

$$\log_{10+} \underline{k} = \log_{10} k \frac{\underline{k}}{h} + \log_{10} T + \log e^{1} - \frac{E}{eRT} + \frac{\Delta S^{\ddagger}}{e\, R}$$

$$= \log_{10} \left(\frac{1.38 \times 10^{-16}}{6.624 \times 10^{-2}} \right\} + \log_{10} 1/2.303 + \log_{10} T - \frac{E}{2.303\, RT} + \frac{\Delta S^{\ddagger}}{2.30312}$$

$$= 10.3187 + 0.4342 + \log_{10} T - \frac{E}{4.576\, T} + \frac{\Delta S^{\ddagger}}{4.576}$$

$$\log_{10} k/T = 10.7529 - \frac{E}{4.576T} + \frac{\Delta S^{\ddagger}}{4.576}$$

$$4.576 \log_{10} k/T = 10.7529 \times 4.576 - \frac{E}{T} + \Delta S^{\ddagger}$$

$$\Delta S^{\ddagger} = 4.576 \log_{10} k/T + \frac{E}{T} - 49.205$$

$\Delta F^{\neq}$, the change in standard free energy was calculated from the equation,

$$\underline{k} = \frac{k\,\underline{k}\,T}{h}\; e^{\frac{-\Delta F^{\neq}}{RT}}$$

$$\log_{10}\underline{k} = \log_{10}\frac{k\,\underline{k}}{h} + \log_{10} T - \frac{\Delta F^{\neq}}{2.303\,RT}$$

$$\log_{10}\frac{\underline{k}}{T} = \log_{10}\frac{k\,\underline{k}}{h} - \frac{\Delta F^{\neq}}{2.303\,R}\cdot\frac{1}{T}$$

$$\log_{10}\underline{k}/T = 10.319 - \frac{\Delta F^{\neq}}{4.576}\cdot\frac{1}{T}$$

$$4.576\log_{10} * \underline{k}/T = 4.576 \times 10.319 - \frac{\Delta F^{\neq}}{T}$$

$$T.4.576\log_{10}\underline{k}/T = 4.576 \times 10.319\,T - \Delta F^{\neq}$$

$$\Delta F^{\neq} = 47.22T - 4.576\,T\log_{10} k/T$$

It was also calculated from the relationship,

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

$$\underline{k} = \frac{k\,\underline{k}\,T}{h}\; e^{\frac{-\Delta H^{\neq}}{RT}}\; e^{\frac{\Delta S^{\neq}}{R}}$$

$$\log_{10}\underline{k} = \log_{10}\frac{k\,\underline{k}}{h} + \log_{10} T - \frac{\Delta H^{\neq}}{2.303\,R}\cdot\frac{1}{T} + \frac{\Delta S^{\neq}}{2.303\,}$$

$$\log_{10}\underline{k}/T = \log_{10}\frac{k\,\underline{k}}{h} - \frac{\Delta H^{\neq}}{2.303\,R}\cdot\frac{1}{T} + \frac{\Delta S^{\neq}}{2.303\,R}$$

$$\log_{10}\underline{k}/T = 10.319 - \frac{\Delta H^{\neq}}{4.5.76}\cdot\frac{1}{T} + \frac{\Delta S^{\neq}}{4.576}$$

$$4.576\log_{10}\underline{k}/T = 10.319 \times 4.576 - \frac{\Delta H^{\neq}}{T} + \Delta S^{\neq}$$

$$T.4.576\log_{10}\underline{k}/T = 10.319 \times 4.576\,T - \Delta H^{\neq} + T\Delta S^{\neq}.$$

$$\Delta F^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq} = 47.22\,T - 4.576\,T\log_{10} k/T$$

1,1'-Binaphthyl-8,8'-dicarboxylic acid.

Preparation of (+) - and (-)- Salts with brucine

(Cooke and Harris, (J., 1963, 2365), Meisenheimer and Beisswenger, Ber., 65, 1932, 65, 32, and Corbellini, C.A., 26., 1277)

1,1'-Binaphthyl-8,8'-dicarboxylic acid (2g., 1M.) was dissolved in boiling methyl alcohol (2 litres) and the solution filtered hot. Brucine (2.8 g. 1M.) was dissolved in 50 ml. of methyl alcohol and added to the solution of the acid. Methyl alcohol was then distilled off leaving about 400 ml. of the solution. On standing (-) acid brucine salt as colourless opaque prims was obtained (≈ 2 g.) m.p. 260 - 268°. $[\alpha]^{175} = -499°$.
(Cooke and Harris gave the m.p. 260-275°, $[\alpha]^{214}_{5461} = -481$, and Meisenheimer and Beisswenger gave m.p. 255 - 262°.).

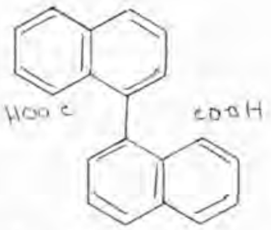
The mother liquor was evaporated to dryness and the residue was dissolved in boiling ethyl acetate (1.5 litre.). The solution was filtered and concentrated to about 400 ml. (+) acid-brucine salt (1.8g.) was obtained as colourless needles, m.p. 223-233° $[\alpha]^{20} = +477°$.

(Cooke and Harris gave m.p. 220-250°. $[\alpha]^{21.4} = +483°$ and Meisenheimer and Beisswenger gave m.p. 228-234° and $[\alpha]_D = +377°$)

(Note:- When the mother liquor from the (-)-acid-brucine salt was concentrated to a small volume and allowed to cool, colourless needle shaped crystalline (+)-acid brucine salt with as good rotations as from the other method were obtained.)

1. Optically active acids.

(-) - 1,1' - binaphthyl - 8,8' - dicarboxylic acid.



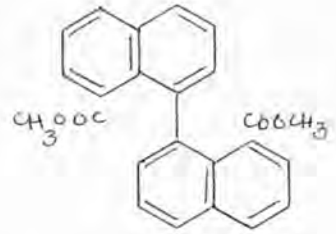
The (-) -alkaloidal salt (5^{0}g.) was dissolved in chloroform and this solution was extracted with aqueous sodium hydroxide. ~~The sodium hydroxide.~~ The sodium hydroxide layer was washed well with chloroform and then with ether, and the optically active acid was precipitated with dilute hydrochloric acid. It was then filtered, washed thoroughly with water and dried. (2.25g.) m.p. 318 - 320° $[\alpha] = -660°$ in dimethyl formamide.

2. (+)-1,1'-binaphthyl - 8,8' - dicarboxylic acid.

The (+)-alkaloidal salt (5.0g.) was dissolved in chloroform, extracted with aqueous sodium hydroxide. The sodium hydroxide layer was washed with chloroform and then with ether and dilute hydrochloric acid was added. The precipitate obtained was filtered, washed with water and dried (2.2g.) m.p. 318 - 320° $[\alpha] = + 650°$.

Preparation of optically active esters.

(Cooke and Harris, J., 1963, 2365)



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

The (-)-1,1'-binaphthyl-8,8'-dicarboxylic-acid (2.50g.) was added slowly to the cold ethereal solution of diazomethane (50 ml ≈ 0.63 g of CH_2N_2) there was effervescence and as the reaction proceded a white solid crystallized at the bottom of the flask. When the reaction was finished, the solid was filtered off, washed with aqueous sodium carbonate and water and dried. A white crystalline compound was obtained (2.1g.) m.p. 123-126°, solidified and melted again at 157-158.5° $[\alpha]^{19.5} = 197^{\circ}$.

2. (+) Dimethyl-1,1'-binaphthyl-8,8'-dicarboxylate.

The (+)-1,1'-binaphthyl-8,8'-dicarboxylic acid (5 g.) was added to the cold ethereal solution of diazomethane (100 ml, 1.25 g CH_2N_2). When the reaction was finished, the solid was filtered, washed with aqueous sodium carbonate and then with water and dried (4.4g.) m.p. 124° - 126° $[\alpha]^{19} = +177^{\circ}$

Note:- It is not possible to measure the specific rotation of an optically pure optically labile compound. The rotations vary slightly with different specimens. Variation in concentration and speed of crystallization of brucine salts can make unavoidable difference in optical purity. The acid itself would racemise to some extent during warming to dissolve it in a solvent. A collection of readings of different specimens of brucine salts and of the acids and esters obtained from them is given below.

Crops of Brucine Salt mixed [α] at room temp.	(-)-8,8'-acid [α]	(-)-Dimethyl ester. [α]
-499.0°	-660°	-197°
-490		
-490	-657	-180
-492		
-490		
-485		
-480	-649	-175.5
-490		
-485		
-495	-705	-207
-499		
-498		

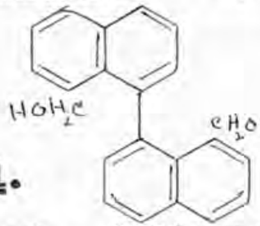
2. Crops of brucine (+)-8,8' - acid (+)dimethyl ester.

+477°	+ 620	+177
+ 470		
+ 459		

Crops of brucine salt mixed	(+)-8,8'-acid	(+)-methyl ester.
+ 511° + 510° + 531°	+ 650	+ 195
+ 394°	+ 478	+154°

Optically active diols.

Preparation of (+) and (-)-8,8' - bishydroxymethyl - 1,1'-binaphthyl.



1. (+)-8,8'-Bishydroxymethyl - 1,1'-binaphthyl.

The (-)- dimethyl - 1,1'- binaphthyl - 8,8' -dicarboxylate (5.0g) was treated with lithium aluminium hydride in the same way as given in the synthetic section, except that it was heated under reflux only for 1½ hour and the ether was removed under reduced pressure from a water bath kept below 50°. Yield (0.9g, m.p. 142.5-145°. $[\alpha]''$ = +45°.

Treatment of mother liquor, from the above experiments.

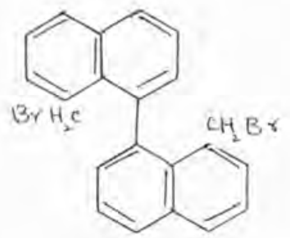
The mother liquor was evaporated; the residue, a sticky substance, was dissolved in benzene and passed through a column packed with alumina using benzene-ether mixture (9:1) as an eluting solvent. A sticky substance was obtained from all the fractions except the first few. This sticky substance could not be crystallized, so it was dissolved in hot glacial acetic acid and hot hydrobromic acid (d = 1.5) was added. The yellow bromocompound separated some more hydrobromic acid was added. The bromocompound was filtered washed with water and dried. It was then recrystallized from chloroform m.p. 184-186° $[\alpha]^{19}$ + =470°

2. (-) 8,8' - Bishydroxymethyl - 1,1' - binaphthyl.

Powdered (+) -dimethyl - 1,1'-binaphthyl-8,8' - dicarboxylate (7.5g.) in 1 litre of sodium dried ether was added slowly during about half an hour to the hot solution of lithium aluminium hydride in a litre of the same solvent. The mixture was then heated under reflux for 1½ hours. The rest of the procedure is exactly the same as for the (±)-diol in the synthetic section, except that the ether was removed under reduced pressure from a waterbath kept below 50°. Crystallized from benzene (1.4g.) m.p. 143-145°. $[\alpha]^{17} = -32^\circ$.

The mother liquor was evaporated. the Residue, a sticky substance had 8-methoxycarbonyl-8'-hydroxymethyl-1,1'-binaphthyl in traces (thin layer chromatography). So it was dissolved in benzene and passed through a column packed with alumina. All fractions except the first few were mixed and evaporated. The sticky substance obtained could not be crystallized; so to see if it gives the bromocompound with very high rotation as in the first experiment, it was dissolved in hot glacial acetic acid (100 ml.) and hot hydrobromic acid(125 ml., d = 1.5) was added. The bromo compound obtained was filtered, washed with water and dried (4.5 g.) crystallized from chloroform m.p. 184-186°. $[\alpha]^{19} - 466.6^\circ$

(+)-8,8' - Bisbromomethyl - 1,1'- binaphthyl



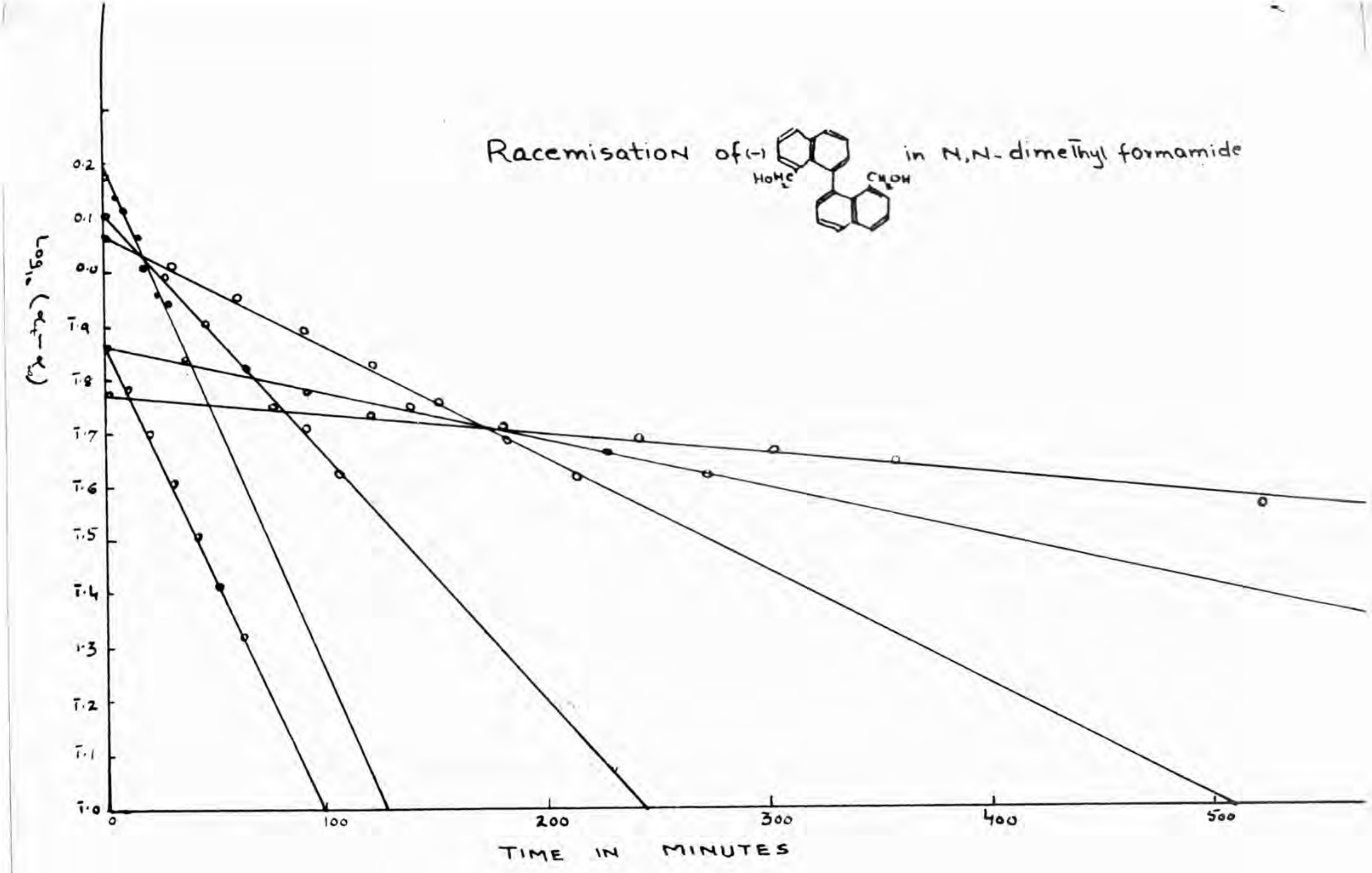
The (+) -8,8' - bis(hydroxymethyl)-1,1'-binaphthyl (0.5g.) was dissolved in hot glacial acetic acid (10 ml.) and hot hydrobromic acid (5 ml. d = 1.5) was added, a yellow solid separated and some more hydrobromic acid (3 ml.) was added. After cooling the solution was filtered off, and the solid washed thoroughly with water and dried (0.45g.) It was crystallized from chloroform, m.p. 183-185°.

$[\alpha]^{17.5^o} = +185^o$.

Determination of rate co-efficient for the racemisation
of 8,8' - Bis(hydroxymethyl) - 1,1' - binaphthyl.
Solvent:- N, N' - dimethyl formamide.

Temp. ^{o}C	First Reading	No. of Readings.	Time during which reading were taken in minutes.	$kx10^{-5}$	$t_{\frac{1}{2}}$ in minutes.
95	- 0.585	8	540	1.573	734.14
100	- 0.717	7	270	3.146	374.1
110	- 1.161	8	210	7.782	148.5
120	- 1.30	8	105	18.46	62.6
125	- 0.712	7	60	33.830	34.14
130	- 1.74	8	35	44.223	26.1

Racemisation of (−) in N,N-dimethyl formamide

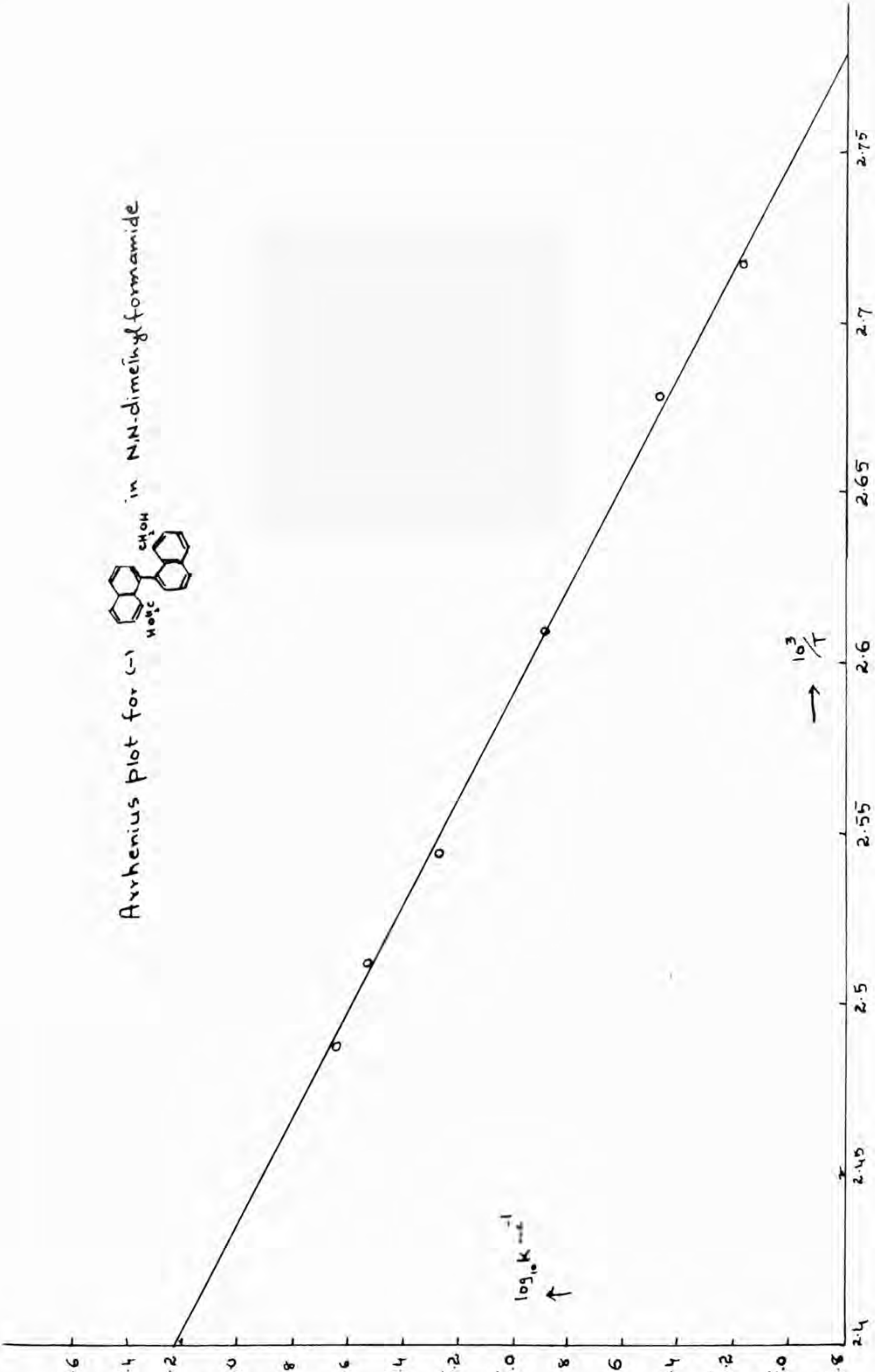


Determination of Arrhenius parameters E and $\mathrm{Log}_{10}A$ and transition state theory function: $\Delta H^{\neq}$, $\Delta F^{\neq}$ and $\Delta S^{\neq}$ for the racemisation of 8,8' - bis(hydroxymethyl) - 1,1' - binaphthyl.

T.	$10^3/T$	$K \times 10^{-5}$ Sec^{-1}	$\log_{10} K$ $\mathrm{sec.}^{-1}$
368.2	2.7159	1.573	$\bar{5}.1967$
373.2	2.6795	3.146	$\bar{5}.4977$
383.2	2.6096	7.782	$\bar{5}.8911$
393.2	2.5432	18.460	$\bar{4}.2662$
398.2	2.5113	33.830	$\bar{4}.5293$
403.2	2.48016	44.223	$\bar{4}.6456$

The best straight line taken graphically (see page 129) gives:-

$$E = 29.2 \ \mathrm{Kcal.mole}^{-1}$$



Arrhenius plot for (–) [structure] in N,N-dimethylformamide

Mean Square Calculations.

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

T	X =	$Y = 10^3/T$	XY	X^2
95	1.1967	2.715915	3.2501170	1.43209
100	1.4977	2.679528	4.0131291	2.24311
110	1.8911	2.609603	4.936930	3.57645
120	2.2662	2.543234	5.7634769	5.135662
125	2.5293	2.511300	6.357100	6.39736
130	2.6456	2.480158	6.5615606	6.99919
	12.0266	15.539738	30.8822591	25.78386

Graphical method

$E = 29.2 \text{ k cal.mole}^{-1}$ $\quad \log_{10} A = 12.6$

$\Delta H^{\neq} = 28.43 \text{ k cal.mole}^{-1}$ $\quad \Delta S^{\neq} = -3.66 \text{ e.u.}$

$\Delta F^{\neq} = 29.85 \text{ k cal.mole}^{-1}$

Mean square calculations.

$\Sigma x = 12.0266$ $\quad \Sigma xy. \ 30.882259$

$\Sigma y = 15.539738$ $\quad \Sigma x^2 = 25.78386$

$\Sigma x . \Sigma y = 186.889227$ $\quad (\Sigma x)^2 = 144.618907$

$n = 6$

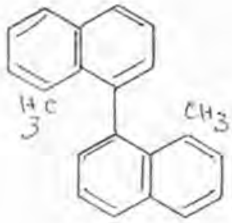
$$b = \frac{(6 \times 30.882259) - 186.889227}{(6 \times 25.78386) - 144.618907}$$

$$= \frac{-1.585672}{10.084252}$$

$$E = \frac{2.303 \times 1.987 \times 10.084252}{1.585672}$$

$$= 29.1 \text{ k cal. mole}^{-1}$$

<u>Preparation of</u> (+) - <u>and</u> (-) 8,8' - <u>dimethyl-1,1'-binaphthyl</u>



1. (+)8,8'-<u>Dimethyl</u>-1,1'-<u>binaphthyl</u>.

The (+) -8,8' - dibromomethyl - 1,1'-binaphthyl $[\alpha]^{19} = +470^{\circ}$ (2.0g.) in 750 ml. of sodium dried ether was added to a well stirred solution of lithium aluminium hydride (0.75g.) in 500 ml of the same solvent. The mixture was heated under reflux for one hour. Excess of metal hydride was destroyed by adding ethyl acetate and then excess of potassium hydroxide was added. The organic layer was washed with water and dried over magnesium sulphate. The solvent was removed under reduced pressure. The residue (1.3g.) was crystallized from ether rectangular crystals were obtained m.p. 127-129°.

$[\alpha]^{17.5} = + 231^{\circ}$.

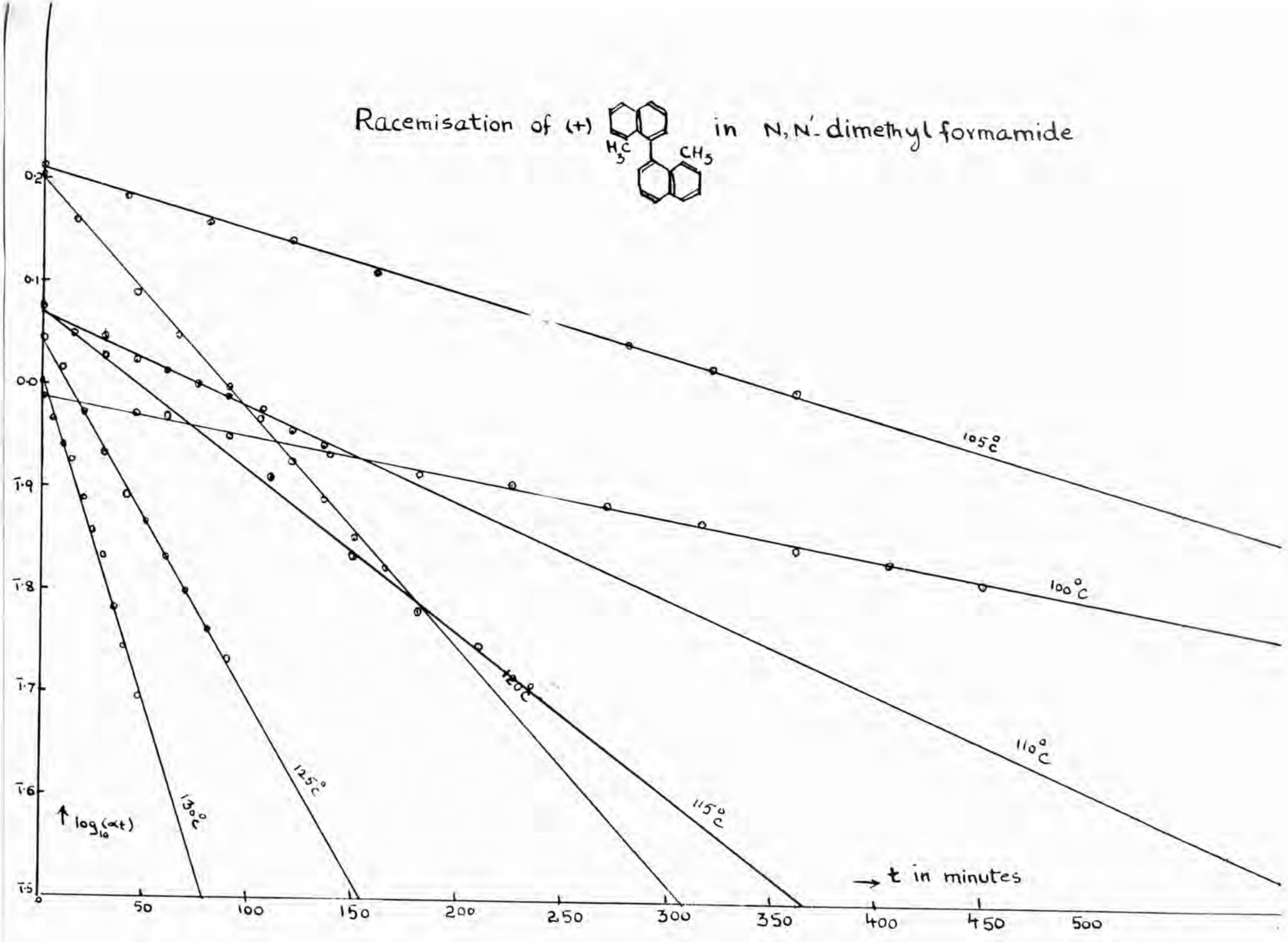
2. (-)-8,8' - <u>Dimethyl</u>-1,1'-<u>binaphthyl</u>.

The (-)-8,8'-dibromomethyl - 1,1'-binaphthyl(1.0g.) $[\alpha]^{19} = -446$ in ether was added to a well stirred solution of lithium aluminium hydride in ether. The mixture was heated under reflux for one hour. After decomposing the excess of metal hydride with ethylacetate and potassium hydroxide, the ether layer was dried over magnesium sulphate. Ether was removed under reduced pressure the residue obtained was crystallized from ether $[\alpha]^{21} = -252^{\circ}$.

Determination of rate co-efficient for the racemisation of 8,8' - dimethyl-1,1' -binaphthyl.

Solvent:- N,N'-dimethyl formamide.

No.	Temperature °C	First Reading.	No.of Readings	Time during which readings were taken in minutes.	$k10^{-5}$ $sec.^{-1}$	$t_{\frac{1}{2}}$ in minutes.
1	100	+ 0.97°	11	450	1.50	678.8
2	105	+ 1.63	10	360	2.32	498.8
3	110	+ 1.195	10	136	3.84	301.0
4	115	+ 1.195	9	240	6.8	190.1
5	120	+ 1.620	12	165	8.80	131.4
6	125	+ 1.113	11	100	13.82	83.6
7	130	+ 1.00	11	50	24.3	48.2



Racemisation of (+) in N,N'-dimethyl formamide

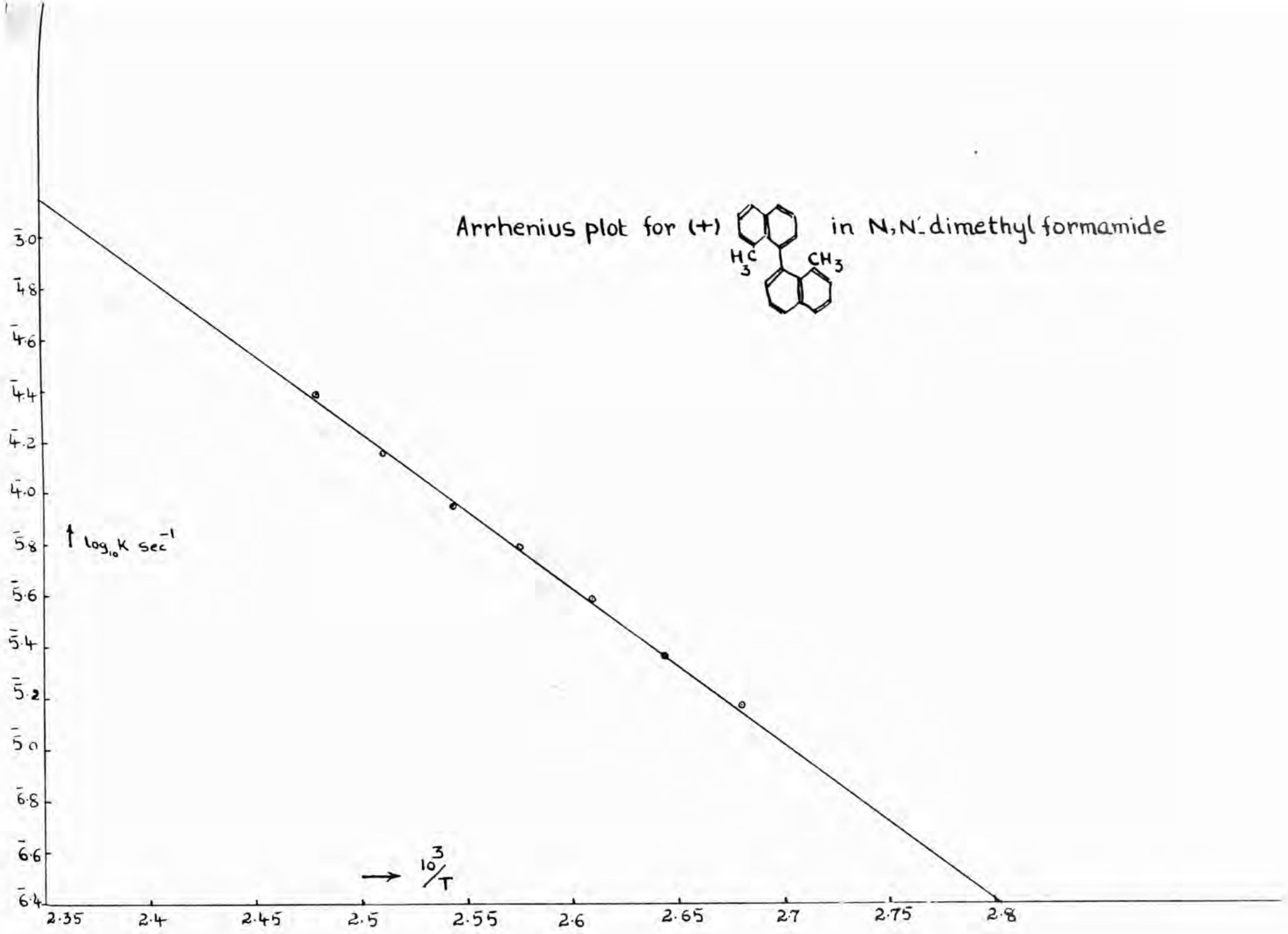
Determination of Arrhenius parameters E and $\text{Log}_{10}A$, and transition state theory functions $\Delta H^{\neq}$, $\Delta S^{\neq}$ and $\Delta F^{\neq}$ for the racemisation of 8,8' - dimethyl - 1,1' - binaphthyl.

	T	103/T	10^5 Sec.$^{-1}$	Log_{10} k Sec^{-1}
100	373.2	2.6795	1.5037	$\bar{5}$.1771
105	378.2	2.6441	2.3157	$\bar{5}$.304
110	383.2	2.6095	3.8383	$\bar{5}$.5841
115	388.2	2.5759	6.0773	$\bar{5}$.7837
120	393.2	2.5432	8.7961	$\bar{5}$.9443
125	398.2	2.5113	13.818	$\bar{4}$.1405
130	403.2	2.4801	24.229	$\bar{4}$.3843.

The best straight line taken graphically (See page 136) gives

$$E = 27.58 \text{ k cals. mole}^{-1}$$

Arrhenius plot for (+) in N,N'-dimethyl formamide



Mean Square Calculations.

Determination of Arrhenius Parameters E and $\log_{10} A$ and Transition State Theory Functions for the racemisation of 8,8' - dimethyl-1,1'-binaphthyl.

T.	$X = + \log k$	$Y = 10^3/T$	XY	X^2
373.2	0.1761	2.6795	0.4719	0.03100
378.2	0.3588	2.6441	0.9487	0.12874
383.2	0.5841	2.6095	1.5242	0.34117
388.2	0.7837	2.5759	2.0187	0.61420
393.2	0.9443	2.5432	2.4015	0.89170
398.2	1.1405	2.5113	2.8641	1.3007
403.2	1.3843	2.4801	2.4332	1.9163
	5.3718	18.0436	13.6623	5.2238

Graphical method.

$E = 27.6 \text{ kcal. mole}^{-1}$ $\log_{10}A = 11.30$

$\Delta H^{\neq} = 26.8 \text{ kcal. mole}^{-1}$ $\Delta S^{\neq} = -9.3$ eu.

$\Delta F^{\neq} = 30.4 \text{ Kcal. mole}^{-1}$

Mean Square Calculations.

$\Sigma x = 5.3718$ $\Sigma Y = 18.0436$

$\Sigma x^2 = 5.2238$ $\Sigma XY = 13.6623$

$n = 7$

$\Sigma X . \Sigma Y = 96.9266$ $n . \Sigma XY = 95.6361$

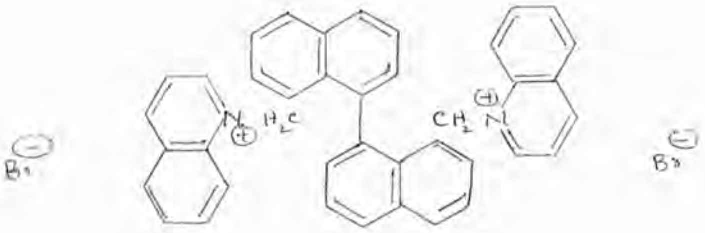
$(\Sigma x)^2 = 28.8562$ $n . \Sigma X^2 = 36.5666$

$$b = \frac{95.6361 - 96.9266}{36.5666 - 28.8562}$$

$$E = \frac{4.576 \times 7.7104}{1.2905}$$

$$= 27.35 \text{ kcal. mole}^{-1.}$$

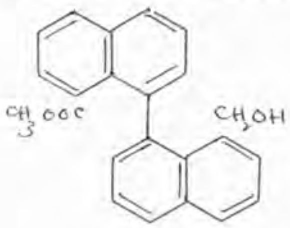
(+) - 8,8' - Bis(methylene quinolium bromide)-1,1'-binaphthyl.



The (+) - 8,8' - Bisbromomethyl - 1,1'-binaphthyl $[\alpha]^{19}=+470^{\circ}$ (0.5g) was dissolved in not quinoline (5 ml.) On standing the solution a needle shaped crystalline compound was obtained which was filtered, washed with benzene and dried (0.75 g) m.p. 221-224°. $[\alpha]^{17} = +294^{\circ}$.

NOTE:- Racemisation experiments on the above quinolinium bromide failed because of the decomposition in hot N, N, - dimethyl formamide.

1. (-)-8-Methoxycarbonyl - 8'-hydroxymethyl-1,1'-binaphthyl.



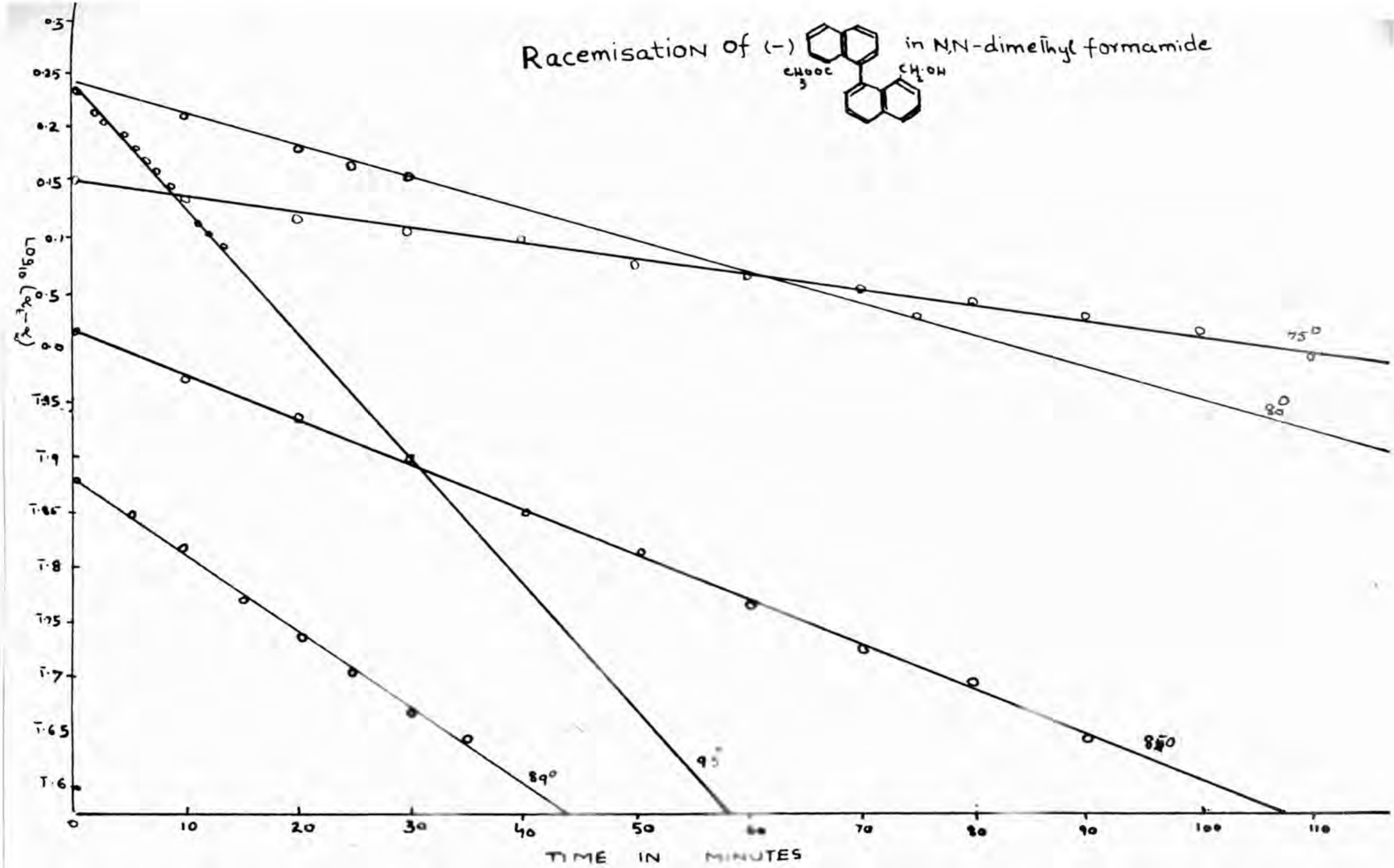
This compound was prepared from (-)-dimethyl-1,1'-binaphthyl-8,8'-dicarboxylate. The procedure is the same as described in the synthetic experimental section. After separation the mixture of the diol and the hydroxyester by chromatography, the hydroxy ester obtained was crystallized from benzene. Needle shaped crystals were obtained m.p. 128 - 130°. (shrinking at 122°). $[\alpha]^{17.5} = -145.0^{\circ}$.

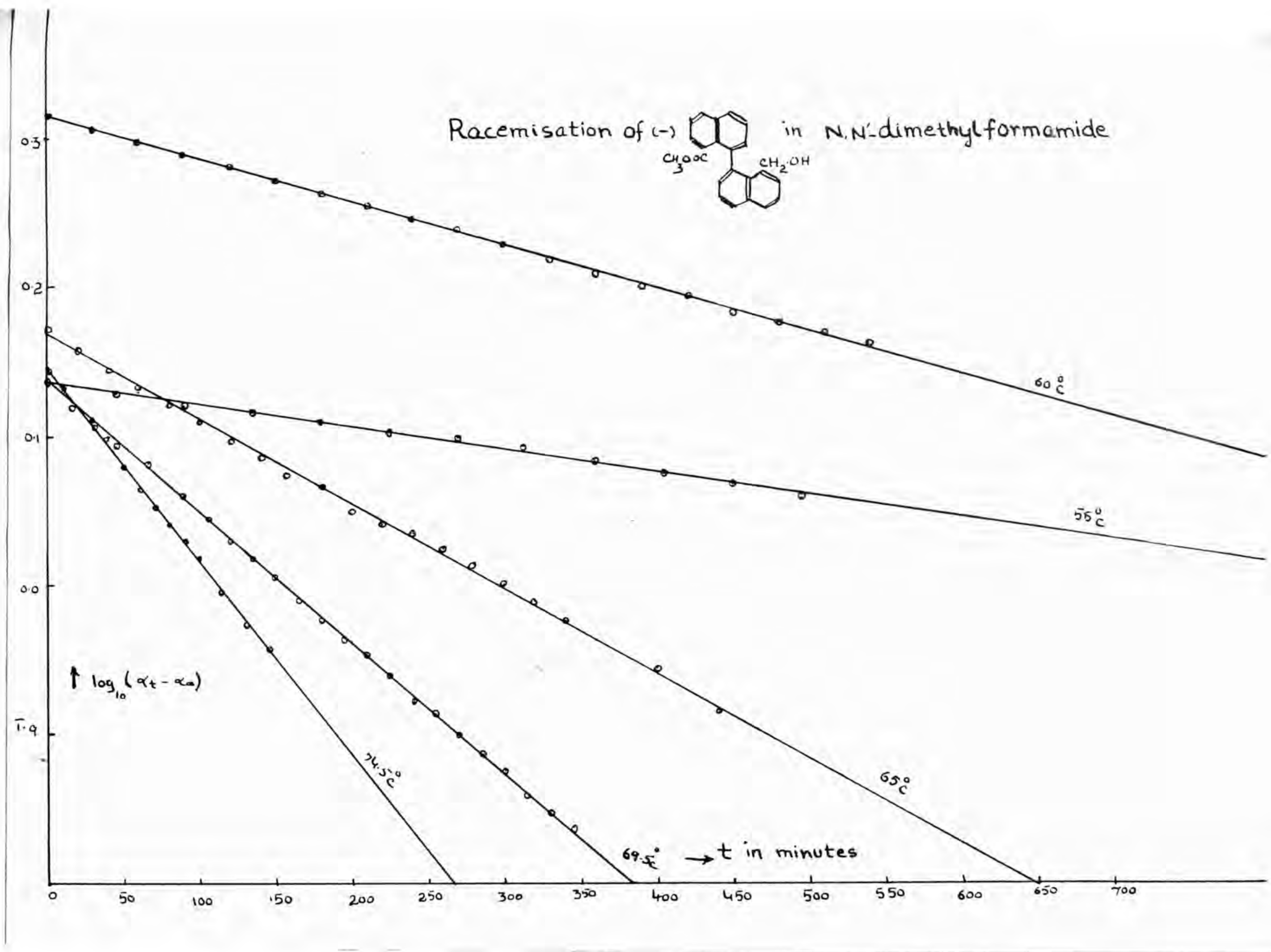
Determination of rate co-efficients for the racemisation of (-) - 8-methoxycarbonyl-8'-hydroxymethylene-1,1'-binaphthyl.

Solvent: N, N - dimethyl formamide.

No.	Temperature	First Reading	No. of readings	Time during which readings were taken in minutes.	$k10^5$ $Sec.^{-1}$	$t_{\frac{1}{2}}$ in minutes.
1	55°C	-1.37	12	495	0.59	1949.4
2	60	-2.07	19	540	1.13	1014.0
3	65	-1.49	25	480	2.14	540.3
4	69.5	-1.40	24	345	3.40	339.49
5	74.5	-1.44	18	190	5.405	215.0
6	80	-1.78	10	75	11.09	104.2
7	85	-0.93	10	90	15.57	74.2
8	89	-0.76	8	40	25.58	45.2
9	95	-1.67	14	13	46.58	24.8

Racemisation of (-) in N,N-dimethyl formamide





Racemisation of (-) in N,N'-dimethylformamide

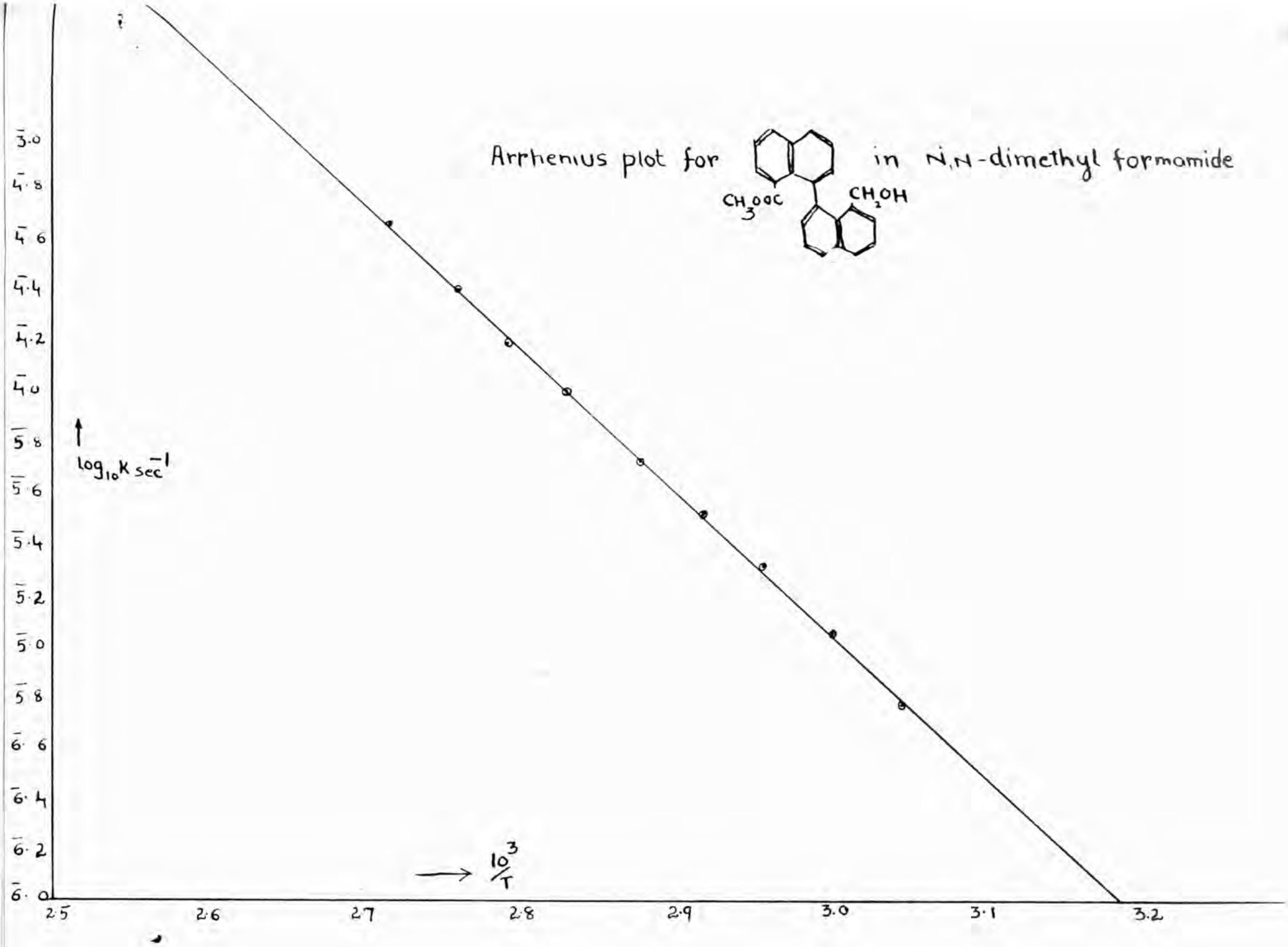
Determination of Arrhenius parameters E and logA, and Transition State Theory Functions $\Delta H^{\neq}$, $\Delta S^{\neq}$, and $\Delta F^{\neq}$ for the racemisation of 8 - methoxy carbonyl- -8' - hydroxymethyl - 1,1' - binaphthyl.

t	T	$10^3/T$	10^4 k Sec.$^{-1}$	$\log_{10}k$ Sec.$^{-1}$
55	328.2	3.0461	0.05927	$\bar{6}.7728$
60	332.2	3.0012	0.1139	$\bar{5}.0565$
65	338.2	2.9568	0.21385	$\bar{5}.3309$
69.5	342.7	2.9180	0.34033	$\bar{5}.5319$
74.5	347.7	2.8760	0.5405	$\bar{5}.7328$
80	353.2	2.8312	1.1093	$\bar{4}.0448$
85	358.2	2.7917	1.5566	$\bar{4}.1919$
89	362.2	2.7609	2.558	$\bar{4}.4079$
95	368.2	2.7159	4.658	$\bar{4}.6682$

The best straight line taken graphically (see page 145)

gives:-

$$E = 25.8 \text{ k cals. mole}^{-1}$$



Arrhenius plot for [structure] in N,N-dimethyl formamide

Mean Square Calculations.

(-) - 8 - methoxy-carbonyl - 8' - hydroxy methyl-1,1'-binaphthyl.

T	$X = 6 + \log k$	$Y = 10^3/T$	XY	X^2
328.2	0.7728	3.0461	2.3540	0.59722
332.2	1.0565	3.0012	3.1708	1.1162
338.2	1.3309	2.9568	3.9352	1.7713
342.7	1.5319	2.9180	4.4701	2.3467
347.7	1.7328	2.8760	4.9835	3.0026
353.2	2.0448	2.8312	5.7892	4.1812
358.2	2.1919	2.7917	6.1191	4.8044
362.2	2.4079	2.7609	6.6480	5.7980
368.2	2.6682	2.7159	7.2466	7.1193
	15.7373	25.8978	44.7165	30.7369

Graphical Method.

$E = 25.8$ k cals. mole^{-1} $\log_{10}A = 11.96$

$\Delta H^{\neq} = 25.1$ k cal. mole^{-1} $\Delta S^{\neq} = -6.2$ e.u.

$\Delta F^{\neq} = 27.2$ k cal. mole^{-1}

Mean Square Calculations.

$\sum X = 15.7373$ $\sum Y = 25.8978$

$\sum X^2 = 30.7369$ $\sum XY = 44.7165$

$n = 9$

$\sum X . \sum Y = 407.572$ $n\sum XY = 402.4485$

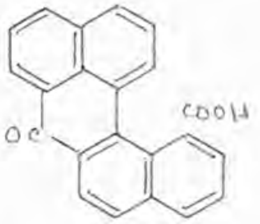
$(\sum x)^2 = 247.675$ $n\sum X^2 = 276.632$

$$b = \frac{402.4485 - 407.572}{276.632 - 247.675} = \frac{-5.1235}{28.957}$$

$$E = \frac{4.576 \times 28.957}{5.1235}$$

$$= 25.86 \text{ k cal. mole}^{-1}$$

Optically active benzo-1',2'-7,8-(benzanthrone) - 3' - Carboxylic Acid.



1. (-)-Benzo-1',2'-7,8-benzanthrone -3'-carboxylic acid.

(-)-1,1' - binaphthyl - 8,8' - dicarboxylic acid (2.og.) was treated with concentrated sulphuric acid in the same way as described in the synthetic sections and 1.40 g of optically active acid was obtained m.p. 177-180°. $[\alpha]^{22} = -164°$.

The acid recovered after racemisation was treated with cold ethereal solution of diazo methane and its methl ester prepared the ester obtained melted at 157-159°. There was no depression when the mixed melting point with methyl benzo - 1'-2'-7,8'-benzanthrone-3'-carboxylate and the infra red spectrum was also very closely similar.

2. (+) Benzo-1',2'- 7,8'-benzanthrone -3'-Carboxylic acid.

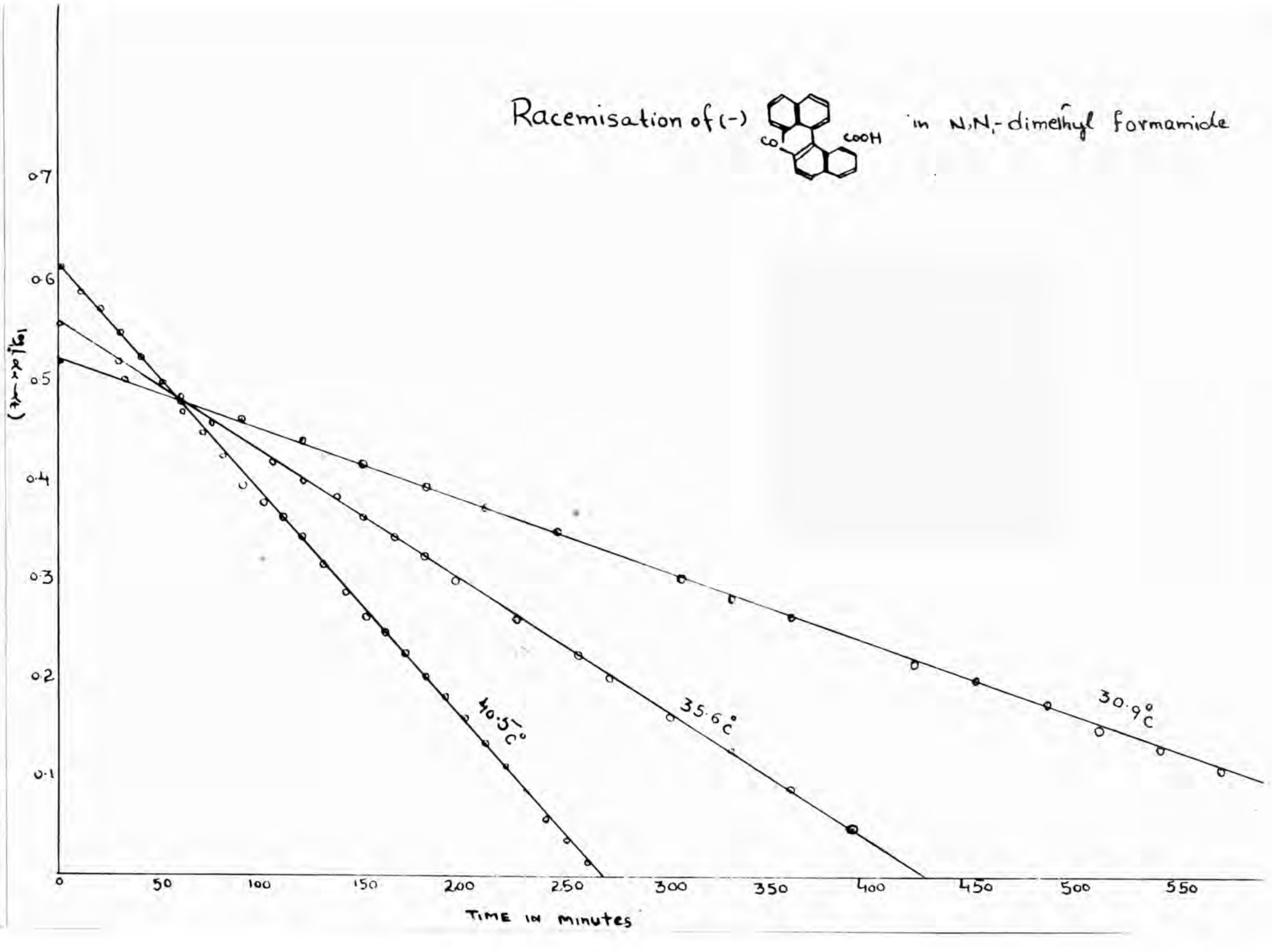
(+)-1,1' - binaphthyl - 8,8'-dicarboxylic acid (1.5 g.) was treated with sulphuric acid, (procedure same as described in the synthetic section). One gram of the (+)-acid was obtained, m.p. 279-281°. $[\alpha]^{22.5}$ + 124°.

Determination of rate co-efficients for the racemisation

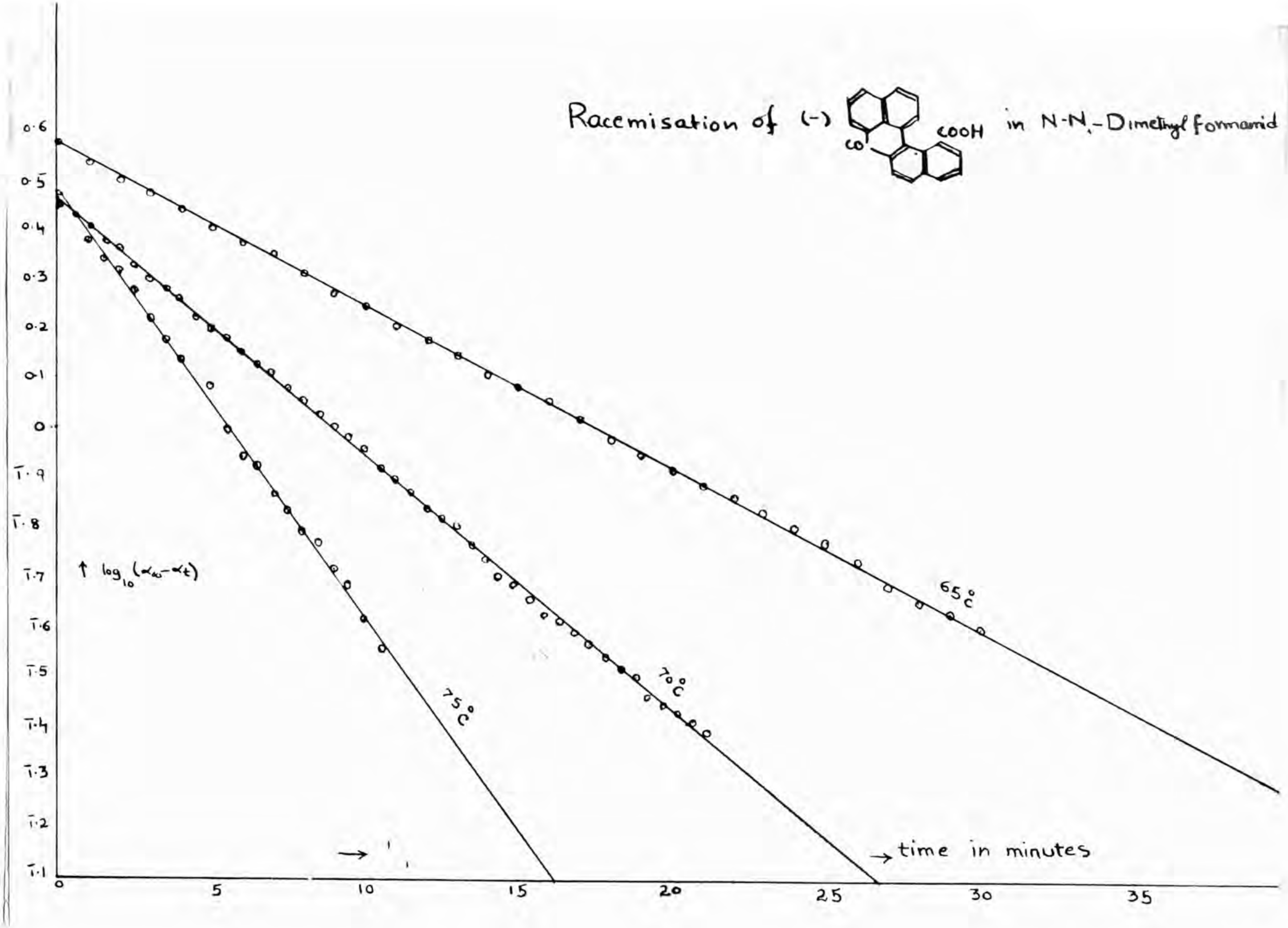
of (-)-Benzo-1',2'-7,8-benzanthrone-3'-Carboxylic acid.

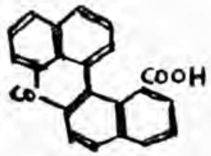
Solvent: N, N-dimethyl formamide.

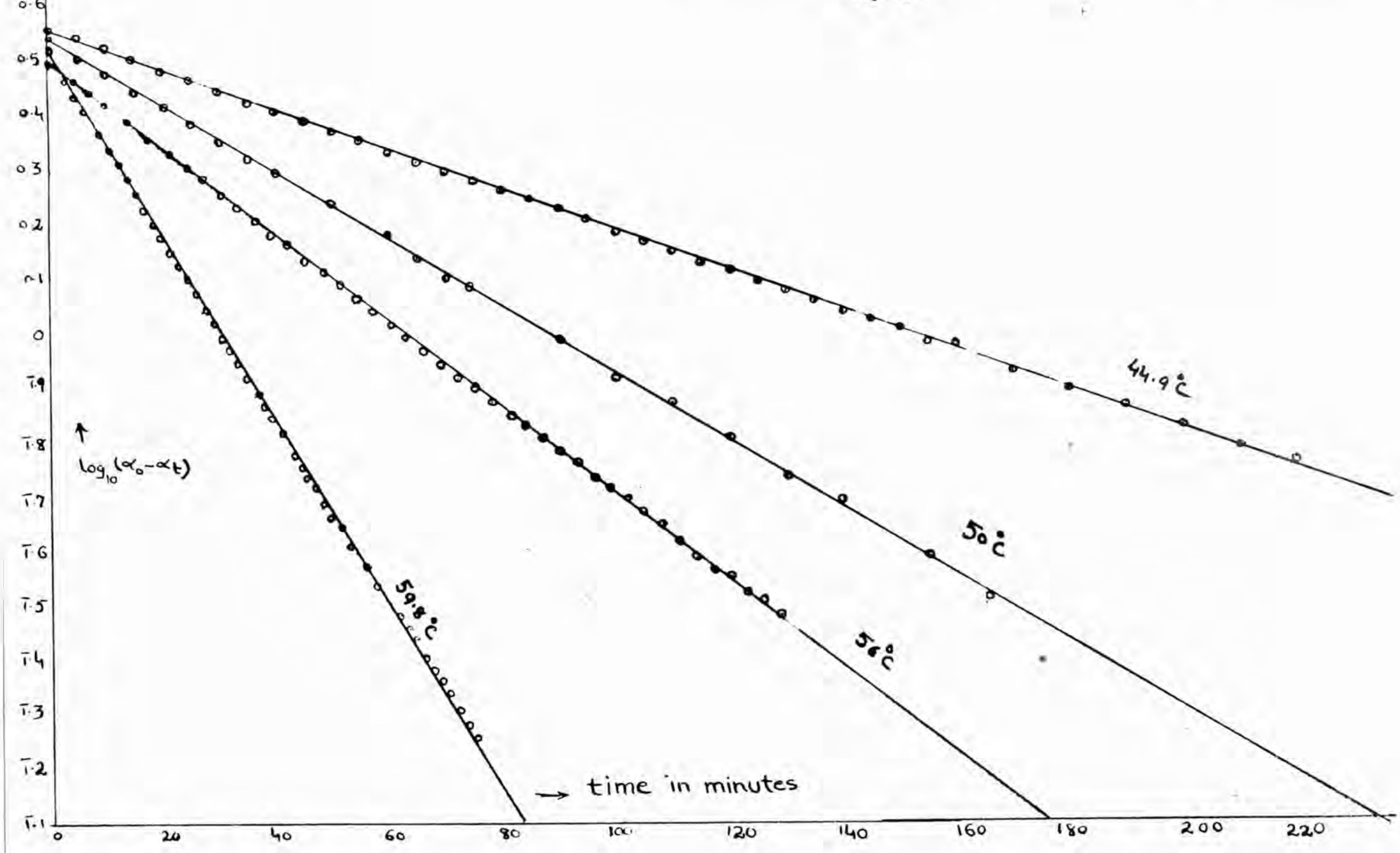
No.	Temp. ^{o}C	First Reading	Time of 1st reading	No. of Readings	Time during which Readings were taken.	K_{10}^{-4} Sec.$^{-1}$	$t_{\frac{1}{2}}$ in minutes.
1	30.9	-3.33	4	21	600	2.795	413.3
2	35.6	-3.26	5	27	390	5.00	231.21
3	40.5	-4.03	4	31	300	8.81	131.13
4	44.9	-3.52	5	38	220	14.185	84.4
5	50	-3.40	5	19	165	23.44	48.5
6	56	-3.07	5	45	86	45.16	25.58
7	59.8	-3.29	6	45	66	65.8	17.56
8	65	-3.66	6	31	30	123.11	9.38
9	70	-2.74	$4\frac{1}{2}$	45	22	202.5	6.2
10	75	-2.85	5	21	10.30	343.8	3.5



Racemisation of (-) in N,N,-dimethyl formamide


Racemisation of (-) in N-N,-Dimethyl formamid

Racemisation of (-)  in N.N.-dimethyl Formamide



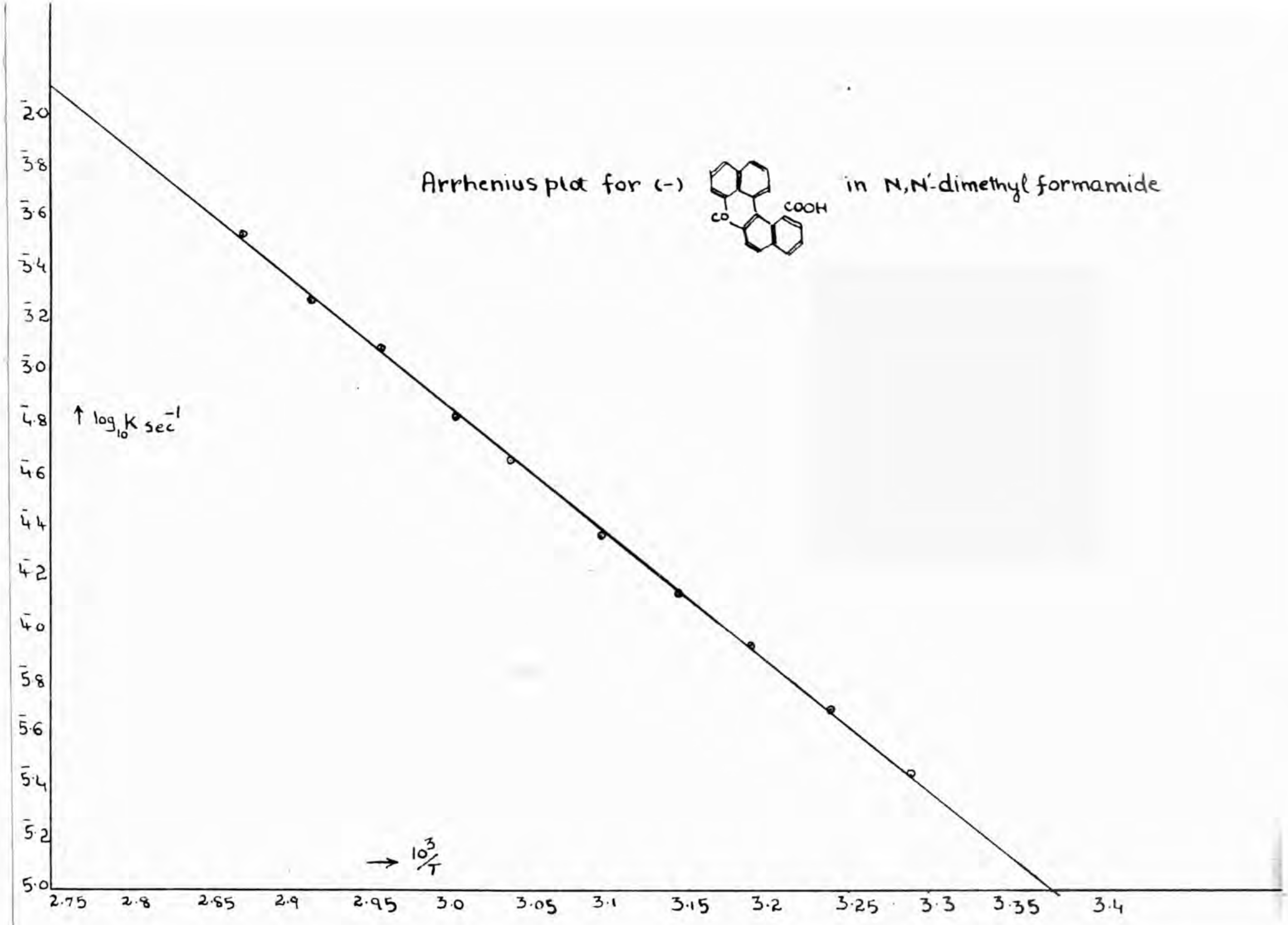
Determination of Arrhenius Parameters E and $\log_{10}A$ and transition state theory functions $\Delta H^{\neq}$, $\Delta F^{\neq}$ and $\Delta S^{\neq}$ for the racemisation of (-)-Benzo-1',2'-7-8-(benzanthrone)-3'-Carboxylic Acid.

T	$10^3/T$	10^4 k $\sec.^{-1}$	$\log_{10}k$ $\sec.^{-1}$
304.1	3.2884	0.2795	$\bar{5}.4464$
308.8	3.2383	0.4997	$\bar{5}.6987$
313.7	3.18775	0.8811	$\bar{5}.9450$
318.1	3.14366	1.4185	$\bar{4}.1515$
323.2	3.09406	2.344	$\bar{4}.3699$
329.2	3.03766	4.5348	$\bar{4}.6565$
333.0	3.0030	6.58	$\bar{4}.8182$
338.2	3.9568	12.311	$\bar{3}.0899$
343.2	2.91375	20.25	$\bar{3}.3065$
348.2	2.8719	34.38	$\bar{3}.5363$

The best straight line taken graphically (see page 154)

gives:

$$E = 23.2 \text{ k cal. mole}^{-1}$$



Arrhenius plot for (-) in N,N'-dimethyl formamide

Mean Square Calculations:

(-)-Benzo-1,2' - 7,8-(Benzanthrone)-3'-Carboxylic acid.

T	$X = 6 + \log k$	$Y = \frac{10^3}{T}$	XY	X^2
3041	1.4464	3.2884	4.7563418	2.092073
308.2	1.6987	3.2383	5.5009002	2.8855817
313.7	1.9450	3.18775	6.2001738	3.783025
318.1	2.1515	3.14366	6.7635845	4.6289523
323.2	2.3772	3.09046	7.3466415	5.6510798
329.2	2.6565	3.03766	8.069544	7.056993
333.0	2.8182	3.0030	8.4630546	7.9422512
338.2	3.0899	2.95683	9.136309	9.547482
343.2	3.3065	2.91375	9.6343144	10.932942
348.2	3.5363	2.8719	10.155899	12.5054177
	25.0262	30.73171	76.02676	67.357981

Graphical method

$E = 232 \text{ k cal. mole}^{-1}$ $\qquad$ $\log_{10}A = 12.1$

$\Delta H^{\neq} = 22.6 \text{ k cal. mole}^{-1}$ $\qquad$ $\Delta S^{\neq} = -5.34 \text{ e.u.}$

$\Delta F^{\neq} = 24.3 \text{ k cal. mole}^{-1}$

Mean Square Calculations.

$\sum X = 25.0262$ $\qquad$ $\sum Y = 30.73171$

$\sum X^2 = 67.0357981$ $\qquad$ $\sum XY = 76.02676$

$n = 10$

$\sum X . \sum Y = 769.0979$ $\qquad$ $n. \sum XY = 760.2676$

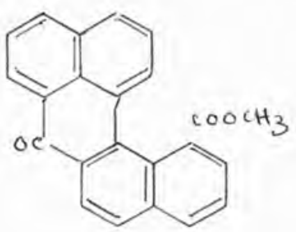
$(\sum X)^2 = 626.31068$ $\qquad$ $n. \sum X^2 = 670.357987$

$$b \quad \frac{-8.8219}{44.0473}$$

$$\text{therefore } E = \frac{4.576 \times 44.0473}{8.8219}$$

$$E = 22.8 \text{ k cal. mole}^{-1}$$

(+) Methyl-1',2'-7,8-benzanthrone-3'-carboxylate.

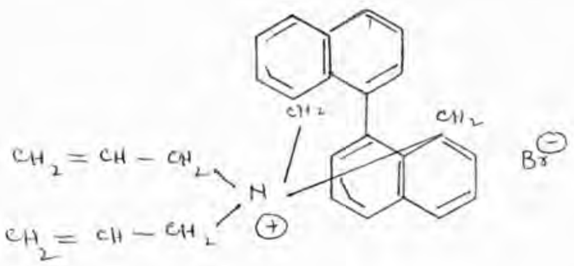


(+)-Benzo-1',2'-7,8-benzanthrone-3'-carboxylic acid (0.5g) was added slowly to the cold ethereal solution of diazomethane. It dissolved with effervescence. When the reaction was complete the ether was evaporated and the resulting product was washed with sodium carbonate and then with water, and dried (0.4g) m.p. 122-125°

$$[\alpha]^{22} = +\ 33.4^{\circ} \text{ in chloroform.}$$

Racemisation experiments were not tried, because the solution in N,N'-dimethylformamide was not very clear.

Condensation of (-)-8,8'-bisbromomethyl-1,1'-binaphthyl with diallylamine



(-)-8,8'-Bisbromomethyl-1,1'-binaphthyl (0.5g. $[\alpha]^{18}$ = -446.6) was dissolved in hot benzene and diallylamine was added. It was then allowed to react at 50-55° (over hot plate) for 2-3 hours. The crystalline compound obtained was filtered, washed with benzene and dried (0.51 g.). Recrystallized from water, m.p. 187-189°. $[\alpha]^{18.2}$ = -287.7°.

Attempted racemisation experiments in N,N-dimethylformamide $[\alpha]$ = -2.71.

(a) at 80° $[\alpha]$ = - 2.72 after two hours.

(b) at 110° $[\alpha]$ = - 2.88 " " "

(c) at 130° $[\alpha]$ = - 4.58 " " "

Since rotations increases this is not racemisation.

EXPERIMENTAL PART III

INFRARED SPECTRA.

Introduction:

Infra-red spectroscopy has found extensive use for the study of molecular structure and for the qualitative and quantitative analysis of very wide range of organic molecules. Most rotational and vibrational spectra lie in the infra-red region, and the term infra-red spectroscopy is synonymous with molecular absorption spectroscopy. Practically all infra-red molecular studies have been made by absorption, because of the low dissociation energies of organic molecules.

Qualitative analysis by infrared method is carried out by identification of characteristic absorption bands and band systems. Because of a large number of bands usually given by any one compound as a result of the sum of all the molecular and atomic interaction occuring with-in it, a unique molecular "fingerprint" is produced upon which the identification of the molecule can be based.

Substances may be studied in either the gaseous, liquid or solid state. Solutions may also be used, but great care must be taken in choosing a solvent that will not absorb in the region in which to study the absorptions. By preparing the solutions in CCl_4, CS_2, $CHCl_3$ and CH_2Cl_2 in cells the entire range from $2-15\mu$ can be covered.

A common practice for studing solid involves the mull technique using a purified oil such as Nujol; hexachlorobutadiene can be used as a mulling agent when it was desired to study frequency ranges in which Nujol absorption bands appear. The mull is made by grinding the sample in a few drops of oil, and placing the suspension between two sodium chloride plates. The grinding is essential in order to obtain a homogeneous mixture of the sample and the oil. comparison of spectra of large numbers of pure compounds have shown that absorption bands occuring at certain frequencies can be co-related with certain bands or atomic groups with-in the molecule. For example the position of the absorption band of a carbonyl group indicates in general whether it forms part of anhydride, ester, ketone, aldehyde or acid. A glance at an absorption spectrum of a simple molecule gives an indication of the presence of such group as O-H, NH, or C = O etc.

The appearance and analysis of the absorption spectrum can often be used to determine The structure or to verify the spatial configuration of atoms within the molecule: examples are cis-trans isomers, ortho, para, meta, isomers, the planarity of rings, keto-enol tautomers, and hydrogen bonding.
In a molecule where there is a restricted rotation about the single band, a number of positions of the rotating groups are possible having different symmetries. The isomers are sometime spectrosespically distinguishable but the chemical separation is difficult. In case of a complex molecule a number of isomers are possible, because at each single bond

two or three configurational states can exist and when the number of rotational isomers increases, the energy difference between the forms decreases and many absorption bands due to the vibration of the same group are different for different isomers. These bands become closer together and form one broad absorption band, this is thought to occur in higher paraffins, acids and long chain alcohols. The near-infra red has assumed great importance in chemical research because of the high specific absorption of chemical compounds at these wavelengths. The characteristic bands for more groups occurs between 2.5 - 15.0 μ . For the wave length of infrared energy the unit micron is universally used.

$$1\mu = 10^{-4}\ \text{cm} = 10^{4}\ \text{Angstrom}\ (\text{Å}).$$

The frequency of radiation is often used instead of wavelength to differentiate the parts of the spectrum. The number of waves per centimeter is the reciprocal of the wavelength in centimeters and is known as wavenumber.

$$\text{Wave number}\ \text{cm}^{-1} = \frac{10^{4}}{\text{Wavelength in micron.}}$$

$$10{,}000\ \text{cm}^{-1} = 1\mu$$

Factors influencing group frequencies.

Hydrogen bonding:- The spectra of alcohols are characterised by an absorption band at 3.0μ, corresponding to the O-H stretching vibration. The exact position of this band depends to a large extent upon the degree of hydrogen bonding or association to which the hydroxy group is subjected. Upon association, the energy and the force constant of the O-H bond decreases, and the absorption band is therefore shifted to lower frequencies by about 200 cm^{-1}.

Resonance:- The effect of resonance is to decrease the bond order of double bonds and to decrease the vibrational frequencies (bathochromatic shift), and to increase the bond order and frequencies of single bonds.

Effect of Strain:- If the carbonyl is a part of a ring the carbonyl frequency increases as the size of the ring diminishes, found in cyclic ketones, lactones, and lactams.

Experimental

The infra red spectra of (+), (-) and (±) 1,1'-binaphthyl-8,8'-dicarboxylic acids, its dimethyl ester, 1,1'-binaphthyl, and other compounds have been studied.

A Grubb Parsons spectrometer fitted with potassium bromide and calcium fluoride prisms was used.

The solid samples, whose spectra were desired in 2.5-15.5μ region, and the Nujol were ground together in a small morter with a pestle, the paste when ground sufficiently was placed, with the aid of a small spatula along the one edge of the sodium chloride plate, the other sodium chloride plate then put over it and squeezed down spreading the paste evenly between the two plates. The plates were then mounted in the holder and then placed in the sample beam path. Hexachlorobutadiene was used when the absorption bands were to be studied in the region in which Nujol bands appear.

The infra-red spectrum of Nujol contains only four absorption bands between 2.5-15.5μ, a strong doublet at 3.43μ and 3.51μ and two strong absorptions at 6.85μ and 7.27μ.

Table I Comparison of peaks - "carbonyl region" in Nujol

Substituents in 1,1'-binaphthyl					μ	
$\overset{H}{8\text{-COOH}}$	$\overset{H}{8'\text{-COOH}}$(+)	5.90(s)	5.98(m)	6.12(s)	6.22(w)	633
"	" (-)	5.90(s)	5.98(m)	6.12	6.22(w)	
"	" (±)		6.0	6.14	6.22(w)	
* 8H	8'-COOH	5.95 (s)		6.21		6.31
5-COOH	5'-COOH	5.90(s)			6.2	6.35
* 4-COOH	4'-COOH	5.95(s)				6.35
2-COOH	2'-COOH	5.92(s)		6.18	6.27	6.38
8-$COOCH_3$	8'-$COOCH_3$(+)	5.88(s)				
"	" (-)					
"	" (±) Needles	5.88(s)				
"	" (±) Plates	5.88(s)				
5-$COOCH_3$	5'-$COOCH_3$	5.88(s)			6.21(w)	6.37(w)
* 8-$COOC_2H_5$	8'-COOH	5.79		6.02		
Methyl-1-bromonaphthalene -8-carboxylate.		5.80				
8-CH_2OH	8'-$COOCH_3$	5.81(s)		6.22(w)	6.29(w)	6.38(w)
8-CH_2Br	8'-$COOCH_3$	5.81(s)		6.22(w)	6.29(w)	6.38(w)

* The writer thanks Dr. A.S. Cooke for this value.

Comparison with condensed compounds

Compounds				
Anthanthrone	6.08(s)	6.27(w)	6.36	
* Benzo-1',2'-7,8-benzanthrone	6.1(s)	6.21	6.28	6.36
Benzo-1',2'-7,8-benzanthrone-3'-Carboxylic acid (Yellow)	5.98(s)	6.11(s)	6.28	6.32
" " (Orange)≠	5.88(s)		6.31	6.4
Benzo-1,2'-7,8-benzanthrone-methyl-3'-carboxylate.	5.83(s)	6.1(s)	6.28	6.38

(≠ Crystallized from methylated spirit). The wave lengths for all the absorptions are given in microns, and the intensities are indicated with them for absorption bands observed in the spectrum. The intensity symbols have the following meaning:-

v.s. very strong, s strong, m., medium, w, weak, v.w. very weak sh- shoulder).

It seems reasonable from the study of the table to assign values about 5.80-5.85μ to CO in esters, 5.80-5.95μ in acids and the value of about 6.1μ to CO ~~reference~~ (see page 165) in the condensed compounds. However (±) 8,8'-dicarboxylic acid is evidently anomalous; it is possible that different conformations of these molecules have different degrees of internal hydrogen bonding and different restrictions on $C = O$ streching vibrations.

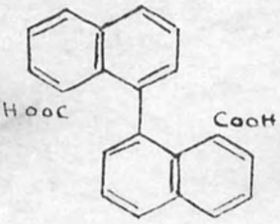
The peak about 6.33μ appears in 1,1'-binaphthyl itself, this band always occurs at 6.3-6.35μ when there is a conjugated phenyl group in the molecule.

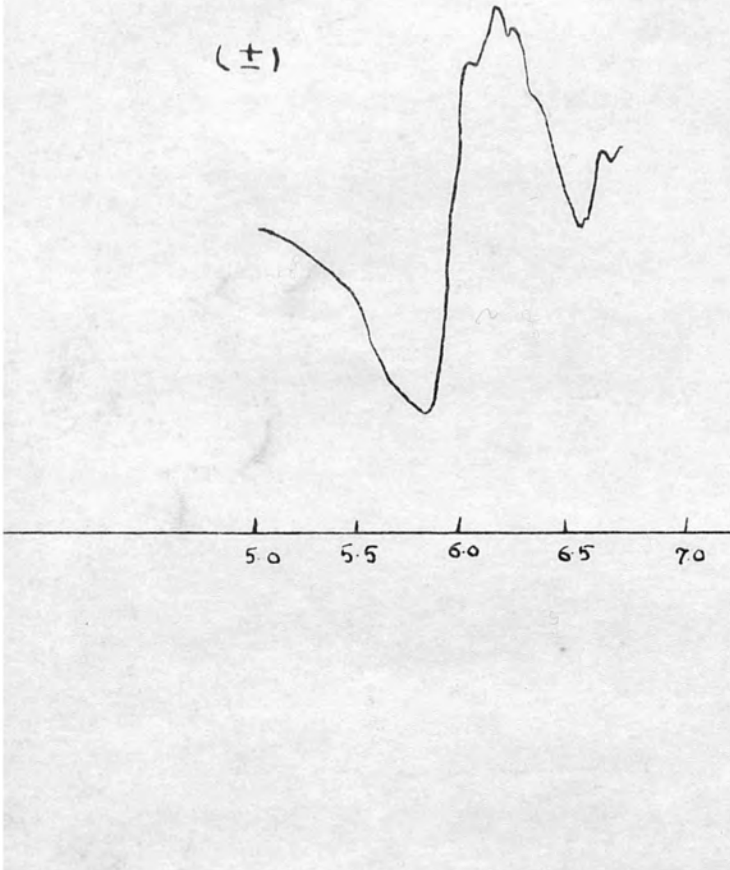
1,1'-binaphthyl-8,8'-dicarboxylic acid:-

It is possible that in 1,1'-binaphthyl-8,8'-dicarboxylic acid, as the restricted rotation occurs about the 1,1'-bond, a number of positions of rotating groups are possible having different symmetries, and the isomer obtained can produce the broad absorption band ~~and~~ 6.0 μ - 6.21μ, due to the vibration of the COOH group.

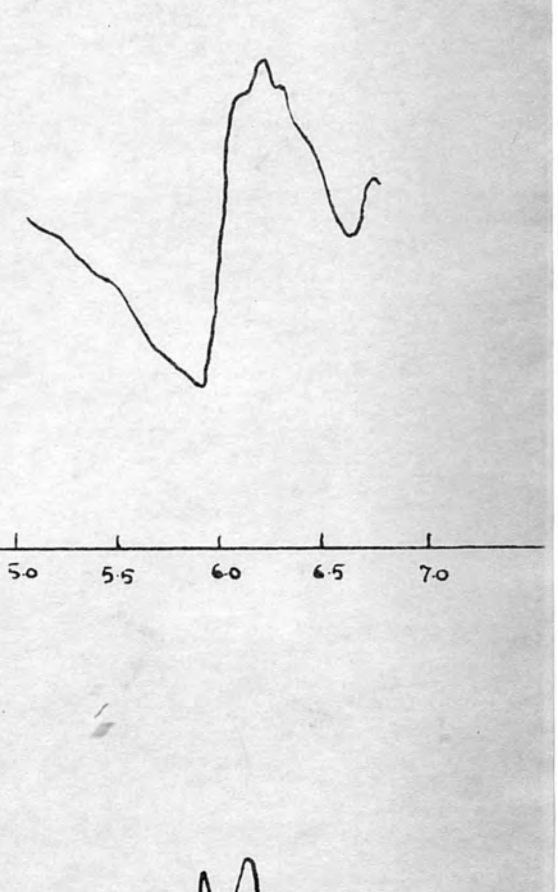
The reason why the (+),(-) and (±) isomers are so different in the carbonyl region and also in 8-8.5μ and 10.8μ regions could be because of any change in the geometrical arrangement of atoms and the force constant of each interatomic bond will alter the infra red spectra. For example the band near 10.82μ, which is strong in (±) acid as synthesised and in the acid recovered after racemisation, but is weak in (+) and (-) isomers, arises from the O-H deformations, and would be expected to the marked changes associated with the change of state, which may alter the degree of hydrogen bonding. The wavelength range of this band is usually between 10.64-11.1μ and the band is usually broad and ill defined when examined in the solid state. (see page 170).

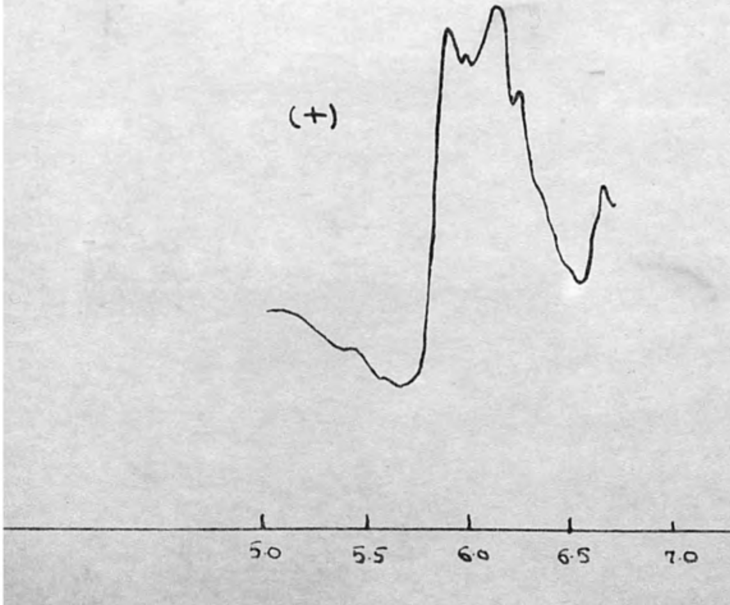
The O-H absorption in the (±) (+), (-) acid and in the acid recovered after racemisation occurs near 3.9μ. ~~The~~

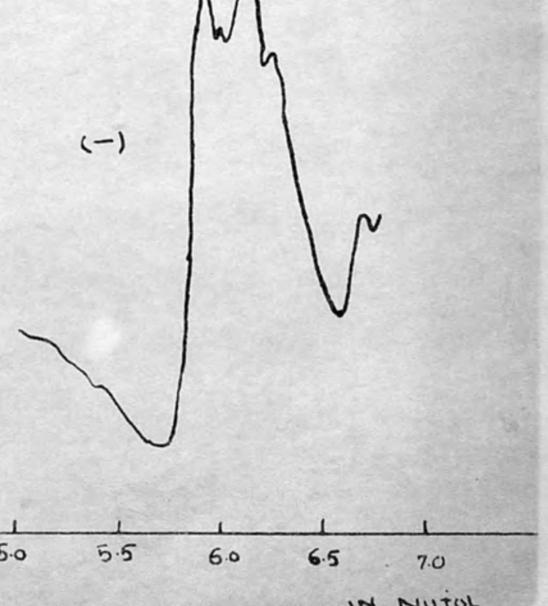



(±)

after racemisation

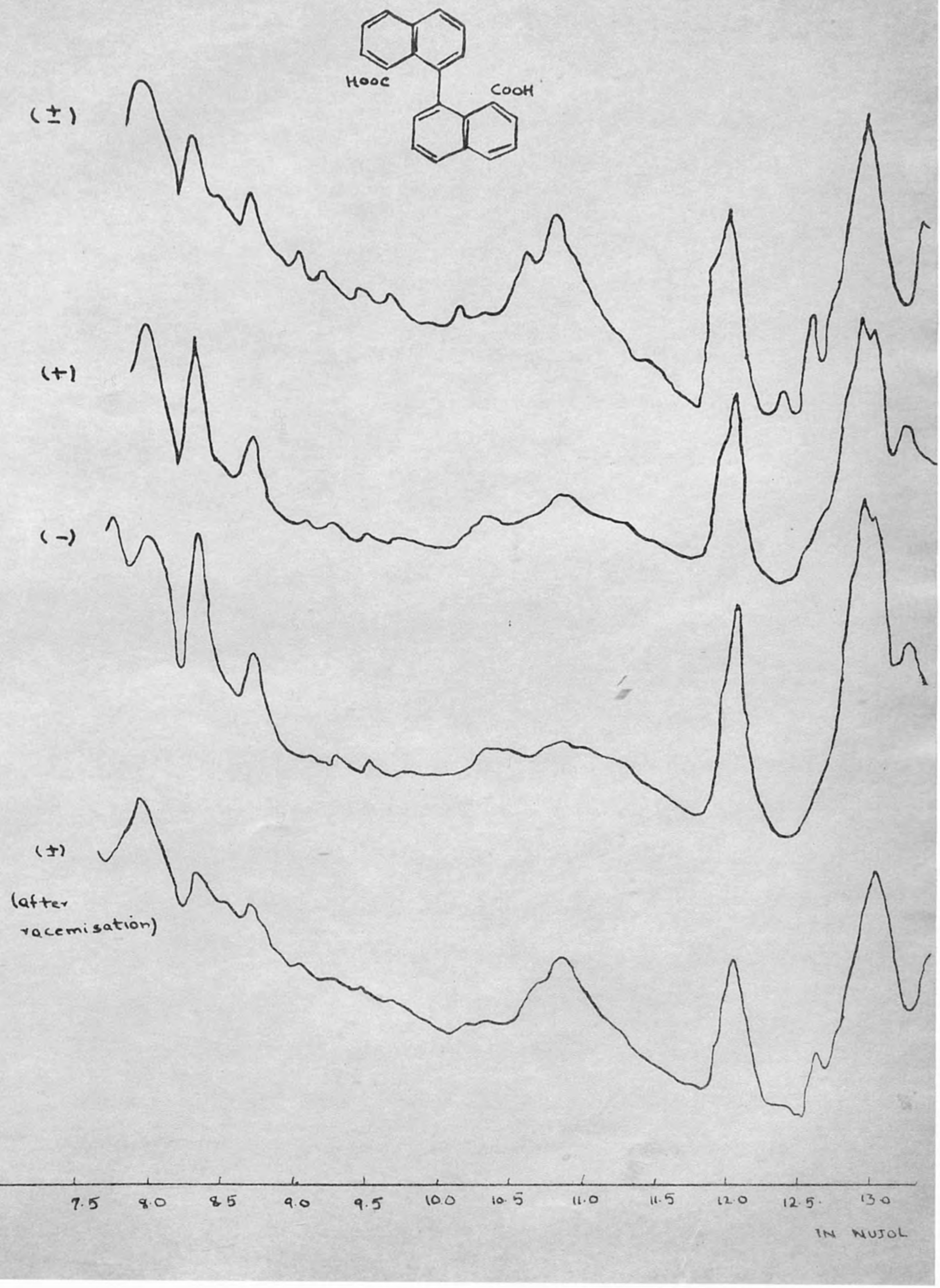



(+)


(−)

IN NUJOL

the band is very broad in all of them. The usuall position for the alcoholic OH Peak is 2.9-3.0 μ, but this is shifted to a higher value in carboxylic acid groups. The intramolecular hydrogen bond occurs near 4.0 μ, but in the present spectra the band is too broad to show up any difference which may exist between (±) and (+) or (-) acid. The carbonyl frequency in the (±) acid as synthesised, and in the (±) acid recovered after racemisation, is shifted to a much greater extent than is usual in hydrogen bonding, to 6.0-6.15 μ.


HOOC
COOH
(±)
(+)
(−)
(±)
(after racemisation)
7.5
8.0
8.5
9.0
9.5
10.0
10.5
11.0
11.5
12.0
12.5
13.0
IN NUJOL

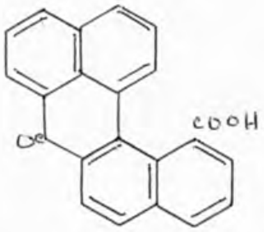
1,1'-Binaphthyl-8,8'-dicarboxylic acid in Nujol

(±) from Synthesis	(+)	(-)	after racemisation of (-) acid.
-	5.9 S	5.9 S	-
6.0	5.99 V.W.	5.98 V.W.	6.0-1
6.15 S	6.12 S	6.12 S	6.14-5 S
6.22 W	6.22 W	6.22 W	6.22 W
6.87	7.87	6.87	6.88
7.26-7	7.27	7.27	7.27
-	7.31 Sh	7.31 Sh	-
7.42 V	7.41 V	7.41	7.42
7.51 V	7.5 V.W.	7.5	7.51
7.61-2 M	7.6	7.6	7.62
X -	7.7 M	7.7 M	-
7.95 S	7.96	7.93-4	7.93-4, S
8.3 M	8.3 S	8.29 S	8.3 M
8.7 M	8.7 M	8.7 M	8.7 M
9.04 V.W.	9.04-5	9.05	9.03
10.62 W	10.3 V.W.	10.3 V.W	-
10.82 S	10.8 W	10.8 W	10.82-5
11.93 Sh	11.92-3 Sh	11.92-3 Sh	11.92 Sh
12.02 S	12.02-3 S	12.01 S	12.02 S
12.4 W	-	-	12.4 W
12.6 M	12.6 V.W.	12.6 V.W.	12.61 M
-	12.89-9 V.S.	12.89 V.S.	-

(±) from Synthesis	(+)	(-)	after racemisation of (-) acid.
13.0 V.S.	13.0 Sh	13.0 Sh	13.02 V.S.
13.38 M	13.22 M	13.2 M	13.38 M
13.52 Sh	13.38 W	13.68 W	13.55
13.99 W			13.99 W
14.26 M	14.22 M	14.22 M	14.25 M

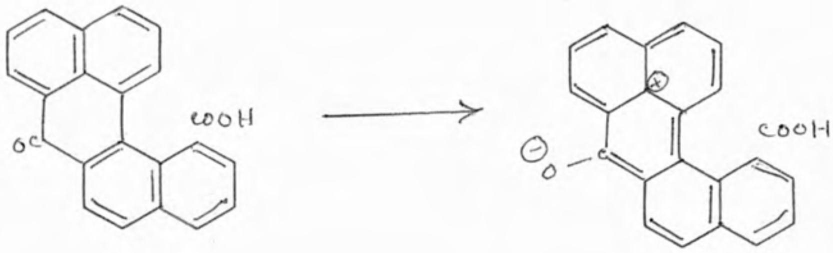
Benzo-1',2'-7,8-benzanthrone-3'-carboxylic acid.

Two types of crystalline compounds were obtained (i) yellow m.p. 190-191.5° from toluene, acetone, and chloroform, and (ii) Orange m.p. 191-192° from methylated spirit. Both the crystalline forms of the acid have been analysed and the analysis is the two cases was found to be very good, but the infra red spectra show distinct differences (see page 175).

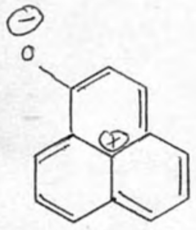


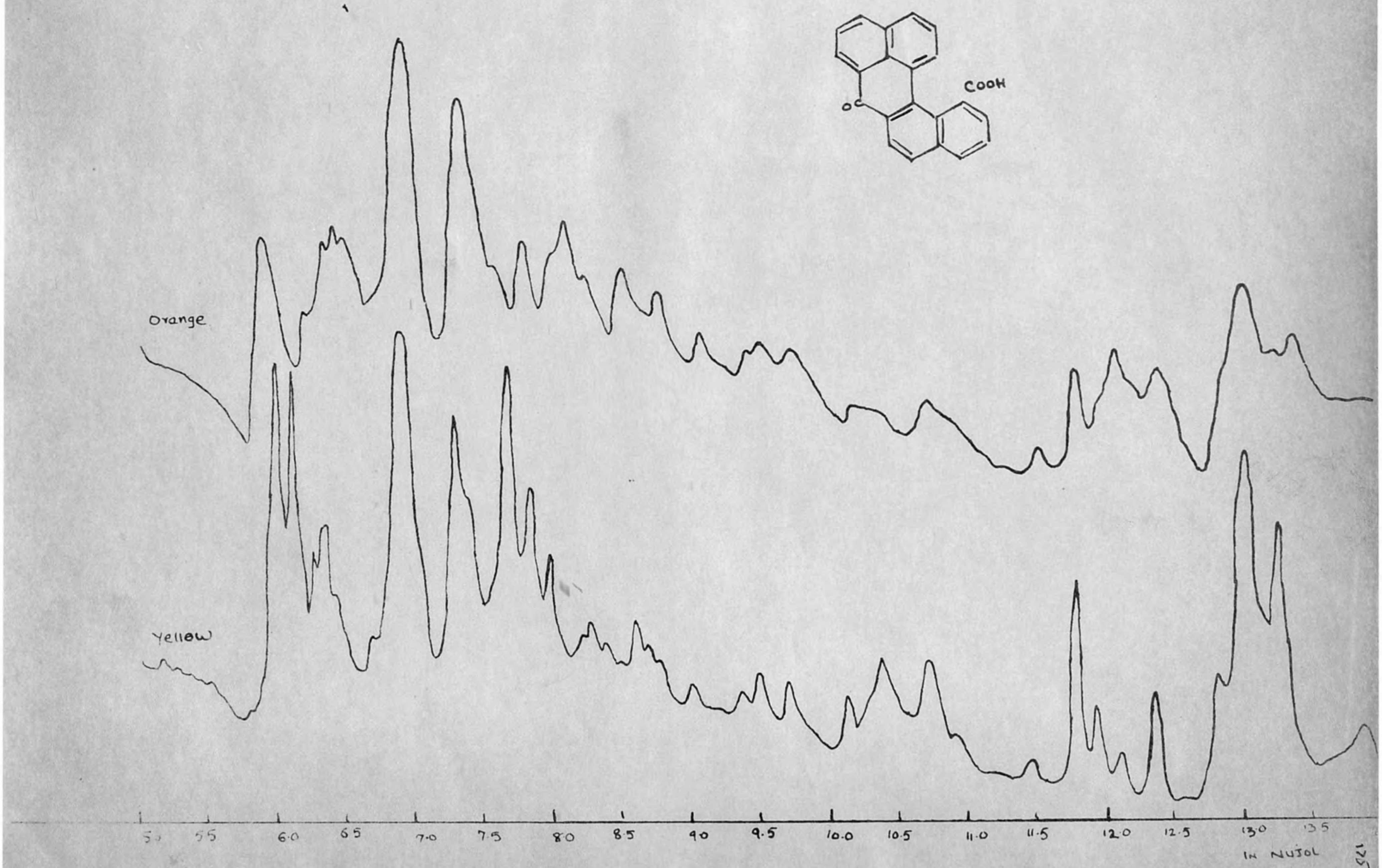
The C-O absorption band 6.1 μ which is present in all the compounds given in the table is the characteristic one for this type of compounds. This value was also reported by Cromwell and Hudson (J.A.C.S., 1953, 75, 872).

In case of benzo-1',2'-7,8-benzanthrone-3'-carboxylic **acid**, the yellow crystalline form shows very strong absorption at 5.97 μ for the carbonyl group of the carboxyl group, and a very strong C-O absorption at 6.09 μ for the carbonyl group in the ring. In the orange crystalline form the C-O absorption band of the carboxyl group is shifted to 5.88 μ and it does not show any C-O absorption at 6.1 μ corresponding to the condensed compound. ( ) Instead of this band the bands 6.4 μ and 6.46 μ were observed. This absorption may arise from the carbonyl which has had its double bond character reduced by resonance of the type:-



Reid and Sutherland (J., 1963, 3295) also reported in a some what similar case of Phenalenium oxide that the abnormal low infra/red carbonyl frequency 1637 cm^{-1} (6.1 μ) and the very high dipole moment are indicative of the considerable polarisation :-



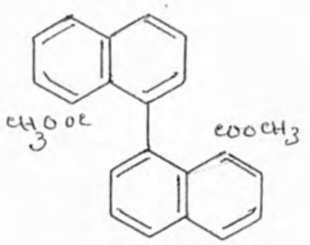

COOH
O
Orange
Yellow
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
10.5
11.0
11.5
12.0
12.5
13.0
13.5
IN NUJOL

Benzo-1',2'-7,8-benzanthrone-3'-carboxylic acid in Nujol

Yellow	Orange
5.97 (v.s)	5.88 (s)
6.09 (v.s)	6.17 (w)
6.26 (w)	
6.31 (w)	6.31 (w)
6.86	6.4 (m)
7.27	6.46 (s)
	6.88
	7.29
7.56 (v.w)	7.56 (v.w)
7.64 (v.s)	
7.82 (m)	7.77 (m)
7.97.8 (m)	7.95 (Sh)
8.28 (w)	8.07 (m)
	8.22 (w)
8.61 (w)	8.49 (m)
9.5(v.w)	8.73 (w)
	9.04 (w)
9.71 (w)	9.46 (w)
	9.7 (w)
10.12.3 (w)	10.14 (w)
10.4 (m)	10.67 (m)

10.72-3 (m)	11.51 (w)
11.78 (s)	11.75 (m)
11.94 (w)	12.09 (s)
12.1 (w)	12.35 (m)
12.35 (m)	
13.0 (v.s)	12.96 (v.s)
13.25 (s)	13.32 (w)
13.9 (w)	

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

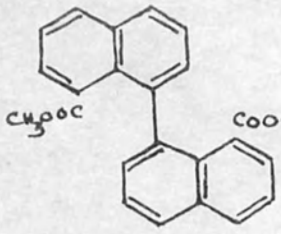


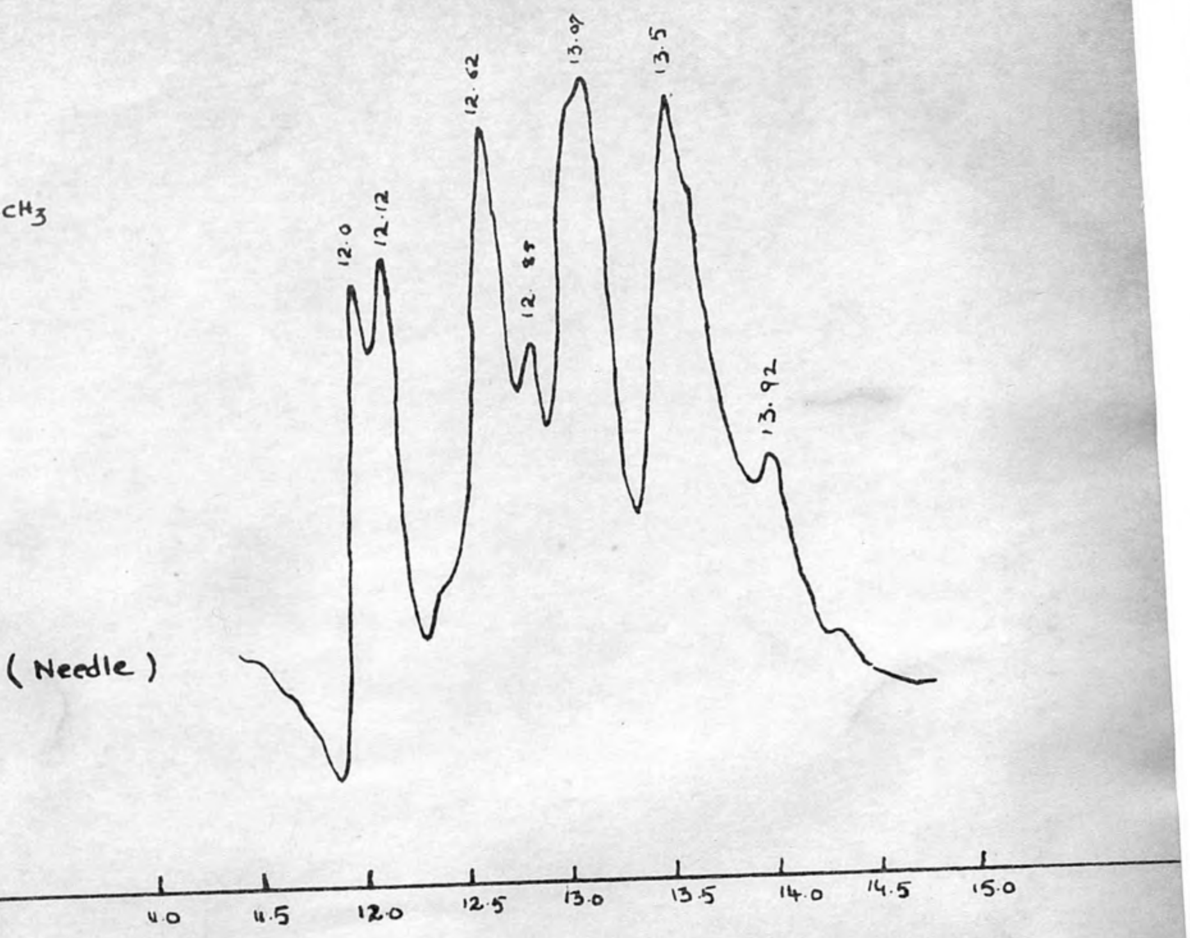
When 1,1'-binaphthyl-8,8'-dicarboxylic acid was treated with a cold ethereal solution of diazomethane, and the product was crystallized from methylated spirit, two types of crystals were obtained (P. 120). (1) Needles m.p. 158-159° and (ii) the plates m.p. 158-159°.

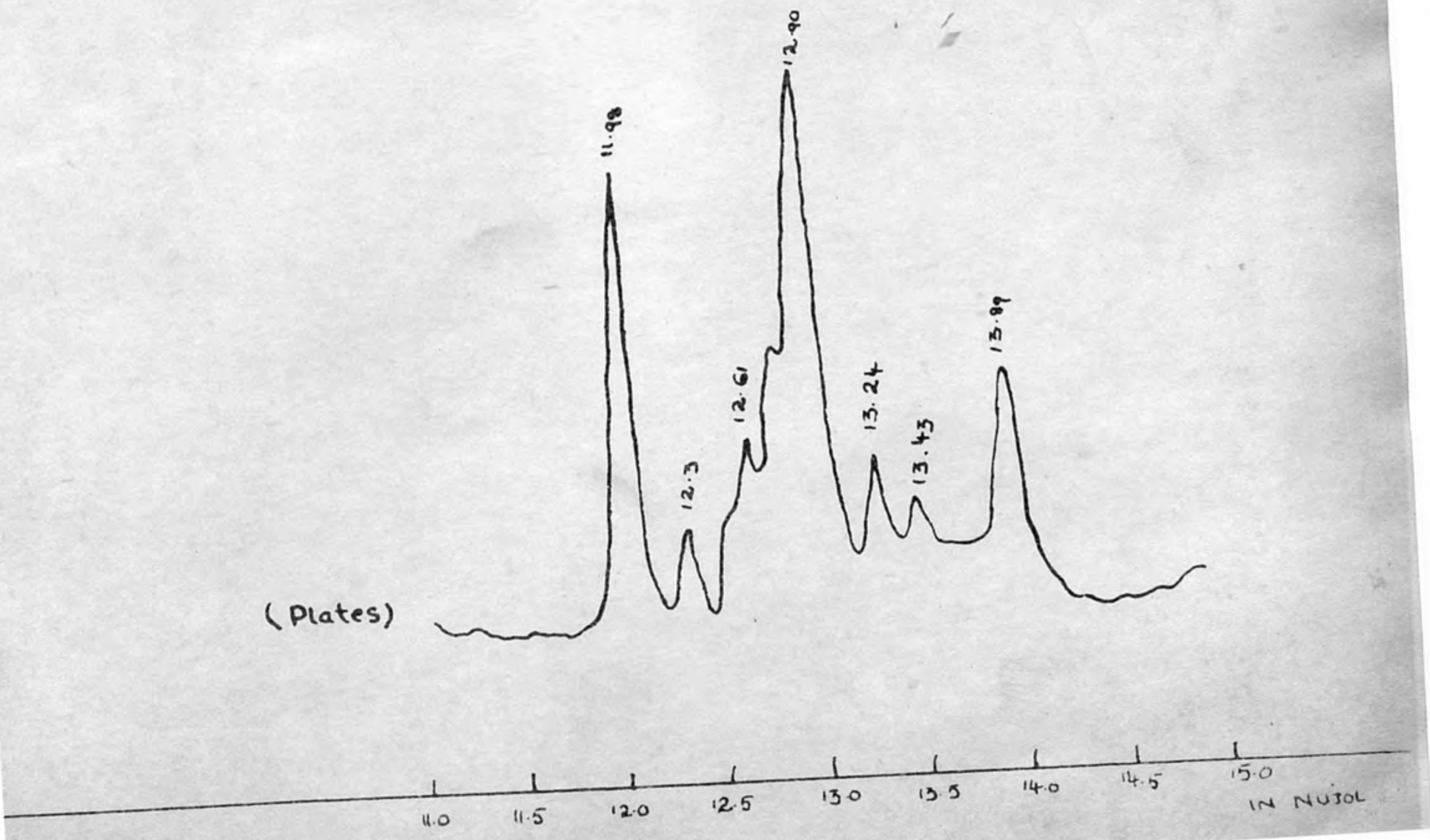
The absorption band in the carbonyl region for both the forms was at 5.88 µ, but the spectra were very different in 11.5-14µ and 7-10 µ regions.

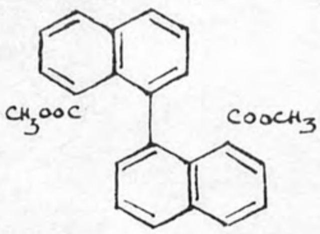
Dimethyl, 1,1'-binaphthyl,8,8'-dicarboxylate iw Nujol		1,1'-binaphthyl in Nujol	
plates	Needles	m.p. 159°	m.P. 144°
μ	μ	μ	μ
5.9 v.s	5.86 v.s.	-	-
6.2 v.w.	6.21 v.w.	-	-
6.31 v.w.	6.3 v.w.	6.32 v.w.	6.3 v.w.
6.66 v.w.	6.66 v.w.	6.66 v.w.	6.66 v.w.
6.89	6.88	6.9	6.86
7.28	7.27	7.29	7.27
7.43 v.w.	7.49 v.w.	-	-
7.53 m	7.57 v.w.	-	-
7.72 m	7.9 s	-	-
7.86 v.s.	7.94	7.97 w	7.97 w
8.3 v.s.	8.23	8.3 w	8.27 w
8.46 v.w.	8.36 Sh, 8.44 S	8.52 v.w.	-
8.72 s	-	8.63 w	8.6 w
8.77 Sh	8.77 s	8.88 w	8.87 v.w.
9.05 v.w.	9.03	-	-
9.13	9.16	9.31 v.w.	9.33 v.w.
9.45 s	9.44 s	9.52 w.	9.45 w
9.72 v.w.	9.83 m	9.91 m	9.89 m
9.86 w	10.15 w	-	-
10.04 w	10.4 v.w.	10.3 w	10.34 w
10.51 w	10.5 v.w.	10.5	10.5
11.98 v.s.	12. v.s.	10.64	10.64
12.3 w	12.13 s	-	11.52

Plates	Needles	m.p. 159°	m.p. 154°, 144
12.5 Sh	-	12.54 s	12.47
12.61 m	12.61 s	12.8 v.s.	-
12.74	12.84 v.w.	12.87	12.82 v.s.
12.89 v.s.	13.0 Sh	-	13.0 s
13.24 v.w.	13.07 s	-	-
13.43 w	13.5 s	13.6 w	13.58 w
13.9 m	13.92 w		

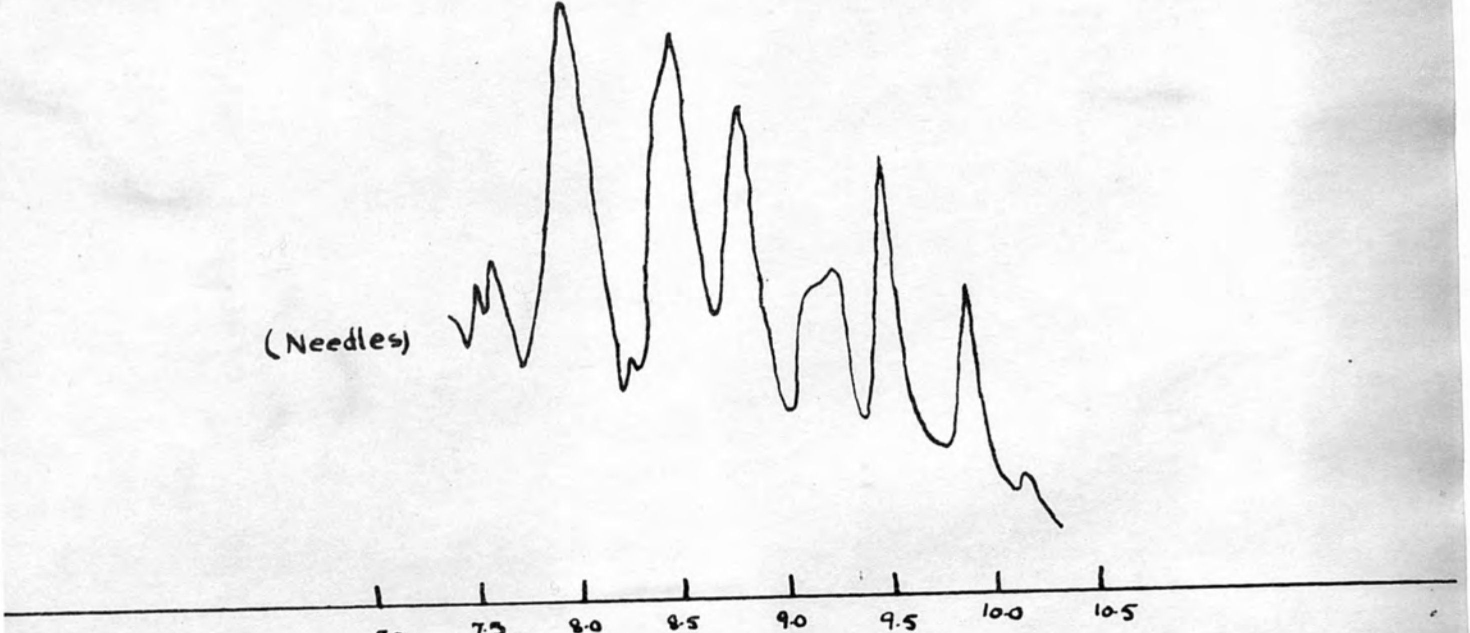



(Needle)

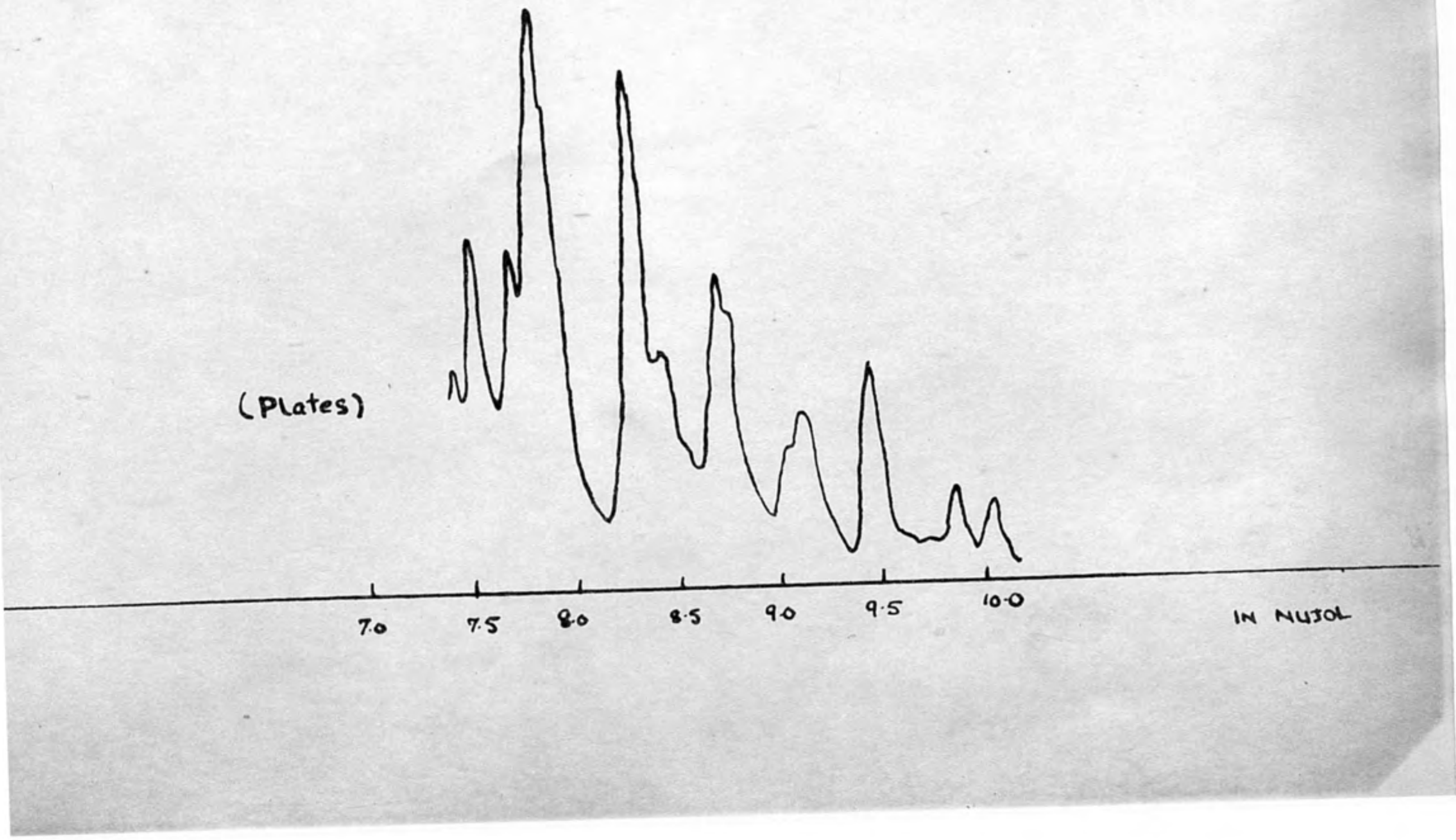

(Plates)

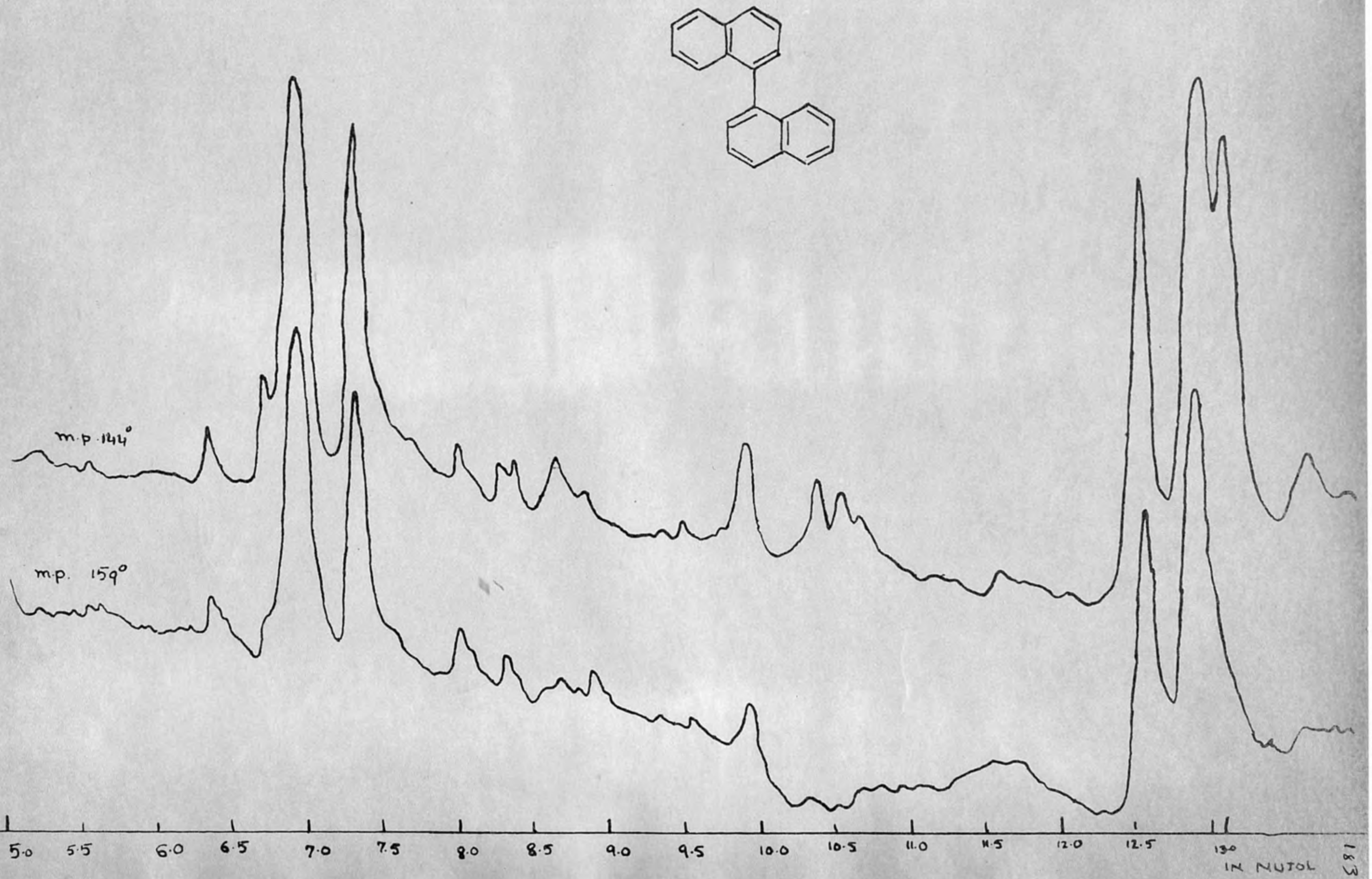


(Needles)



(Plates)




m.p. 144°
m.p. 159°
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
10.5
11.0
11.5
12.0
12.5
13.0
IN NUJOL

No complete conclusions could be drawn from these spectra, but it may be seen that in I,I-binaphthyl-8,8'-dicarboxylic acid the (+) and(-) forms have similar infrared spectra and have the same molecular configuration apart from the mirror image isomerism, while in (±) acid the infrared spectrum shows distinct differences,therefore it probably has a different configuration. The difference could be because of the hydrogen bonding which may be different in the two cases owing to different configuration of the carboxylic acid group relative to each other.