THE SYNTHESIS AND STEREOCHEMISTRY OF SOME 8,8'-DISUBSTITUTED 1,1'-BINAPHTHYLS, BRIDGED AND UNBRIDGED

A Thesis submitted to the University of London
for the Degree of Doctor of Philosophy

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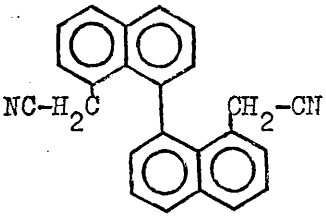
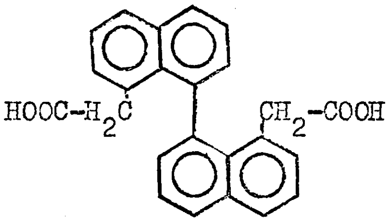
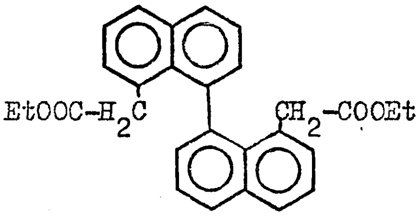
(SHYAM SINGH)

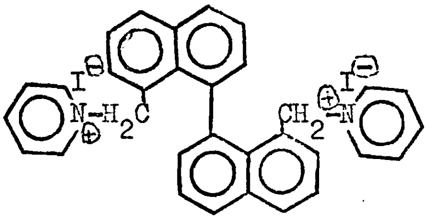
ABSTRACT

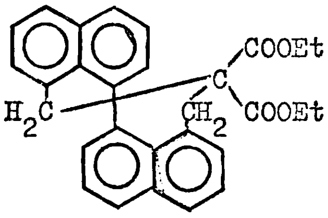
In the present work, starting from 8,8'-bisbromomethyl-1,1'-binaphthyl, the following new compounds were prepared.

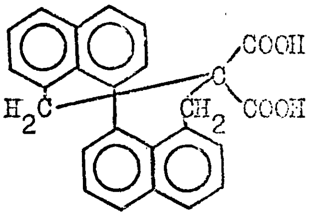


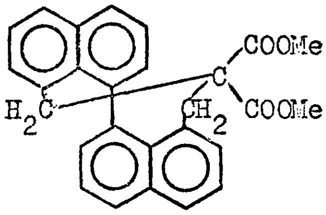


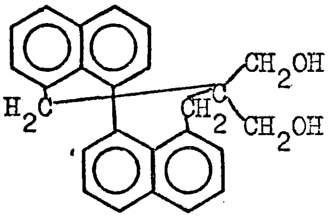


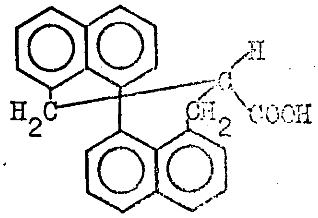


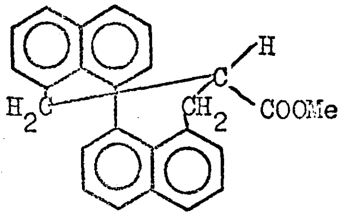


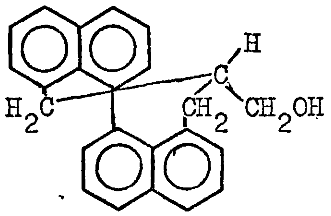


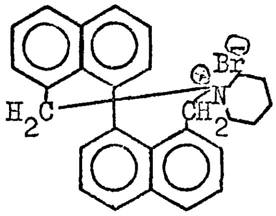


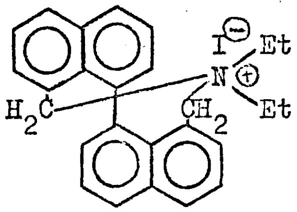


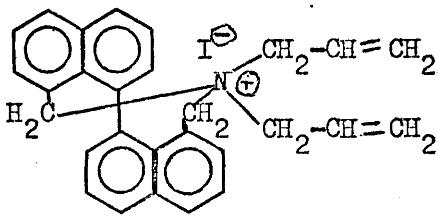












1,1'-Binaphthyl-8,8'-diacetic acid was resolved through its quinine salt and Arrhenius parameters and Transition State Theory Functions for racemisation were determined for it. Another unbridged compound, 1,1'-binaphthyl-8,8'-bis(methylenepyridinium)diiodide, was obtained optically active from optically active 8,8'-bisbromomethyl-1,1'-binaphthyl.

8,8'-Bridged carbocyclic compounds were obtained in optically active forms from the resolved dinaphtho [8,1-ab, 1',8'-de] -cyclonona-2,4-diene-8,8-dicarboxylic acid. All these optically active carbocyclic compounds were found to be optically stable even when melted.

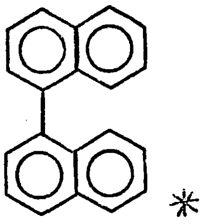
8,8'-Bridged N-heterocyclic compounds were obtained optically active by using as optically active precursor the 8,8'-bisbromomethyl-1,1'-binaphthyl and were also found optically stable up to their decomposition points.

The main features of the ultra-violet absorption spectra in 95%

ethanolic solution of all 8,8'-bridged 1,1'-binaphthyls correspond with those of the parent compound, 1,1'-binaphthyl.

Optical rotatory dispersion(o.r.d.) and circular dichroism(c.d.) spectra of the optically active compounds were studied in 95% ethanol. From these chiroptical studies, and by correlation with other workers' assignments, it is shown that absolute configuration can be assigned in the short-wave region below the short-wave ultra-violet absorption band. A short-wave positive Cotton effect (o.r.d.) corresponds to the S-configuration and a negative Cotton effect corresponds to the R-configuration.

Compounds with S-configuration:



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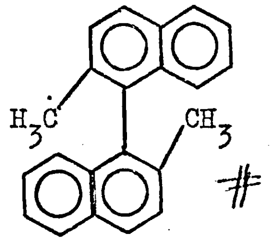

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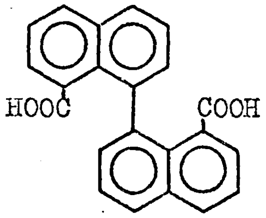

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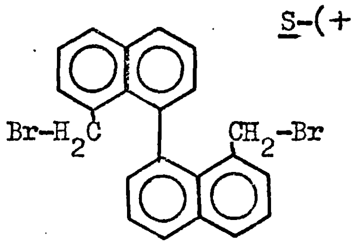

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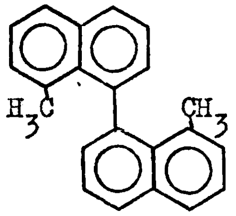

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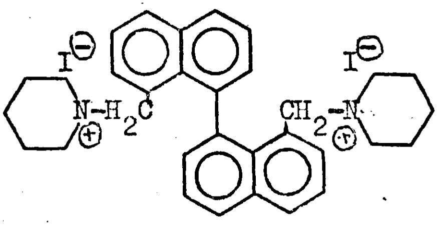

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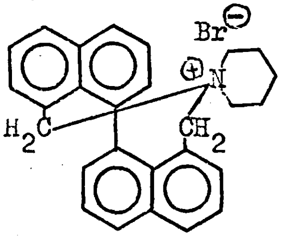

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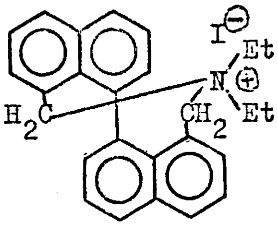
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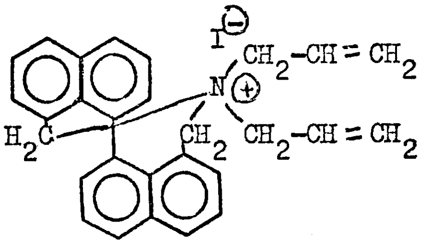
Et
N⊕
Et
H2C
CH2

S-(+)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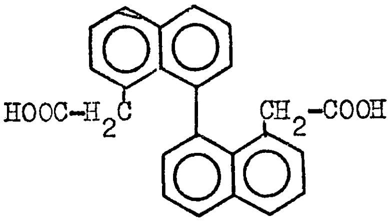
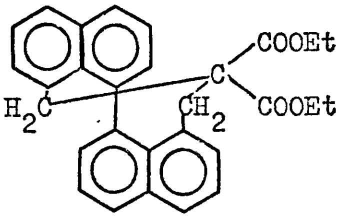
N⊕
CH2-CH=CH2
H2C
CH2

S-(+)


HOOC-H2C
CH2-COOH

S-(+)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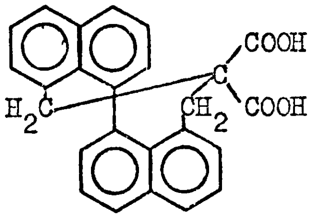
C
COOEt
H2C
CH2

S-(+)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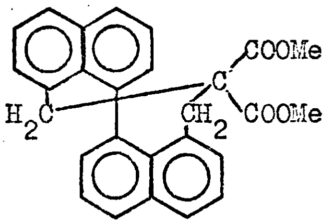
C
COOH
H2C
CH2

S-(+)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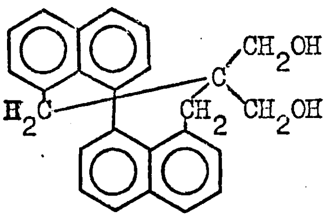
C
COOMe
H2C
CH2

S-(+)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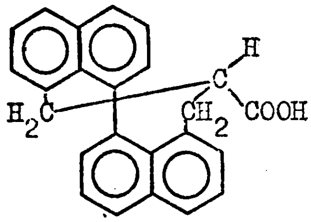
C
CH2OH
H2C
CH2

S-(+)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CH2

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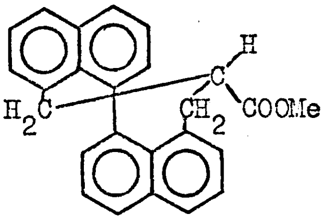
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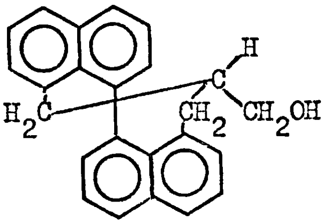
C
COOMe
H2C
CH2

S-(+)


H
C
CH2OH
H2C
CH2

S-(+)

✳ Previously assigned by chemical correlation from a compound of known absolute configuration by X-ray crystal analysis (Akimoto, Shioiri, Iitaka and Yamada, 1968).

Previously assigned by chemical correlation with a compound whose configuration was assigned after asymmetric reduction of a ketone with a reagent of known absolute configuration (Mislow and McGinn, 1958).

Our optical rotatory dispersion and circular dichroism observations are related to these absolute assignments, and hence the configurations of the new optically active compounds are determined.

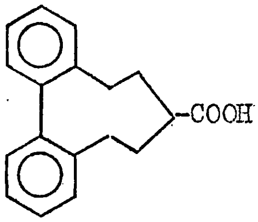
1. INTRODUCTION

For a long time nine-membered ring compounds remained very hard to synthesise, but the discovery of the acyloin method of ring closure made it easy to synthesise saturated carbocyclic compounds. The stereochemistry of the acyclic molecule is such that it cannot easily adopt the conformation required for cyclisation by other methods.

An interesting discovery of Kenner (1913) for the synthesis of seven-membered ring compounds in the 2,2'-bridged biphenyl series using Perkin's method led to the knowledge that double bonds in an acyclic molecule to be cyclised improves the chances of its cyclisation. However, the use of Perkin's method to synthesise similar but nine-membered ring compounds did not succeed: Mislow, Hyden and Schaefer (1962) attempted the diethylmalonate condensation with 2,2'-bisbromoethylbiphenyl under a variety of experimental conditions but the method failed to give a nine-membered ring. The authors were successful in synthesising a nine-membered ring acid (1) by carrying out an acyloin reaction on the appropriate dimethyl ester to form a ten-membered ring ketone incorporating a 2,2'-biphenyl system: the ten-membered ring was then reduced in size by one carbon atom, through its toluenesulphonhydrazide.

Few heterocyclic compounds in this category are known; Bentley and Robinson (1952) reported the preparation of phenyldihydrothebaine (2) which has an asymmetric carbon atom and exists in four diastereomeric forms, they were all isolated by Small, Sargent and Bralley (1947).

Bentley and Robinson (1952) described the preparation of (3) for which Hall and Manser (1967) found the activation energy for racemisation to be 31.5 kcal mol^{-1}. Compound (4) is reported to be optically stable at 150^{o} (Forbes, Mann, Millar and Moelwyn-Hughes, 1963). A phosphonium compound (5) is reported optically active by Allen, Millar and Mann (1967). Pecherer and Brosi (1967) reported the preparation of (6) but attempts to bring about optical resolution failed. Recently, Hwang (1972) obtained optically active the nine-membered ring 2,2'-bridged biphenyl(7). It appears that nine-membered ring bridged biphenyls,



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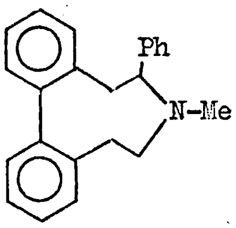

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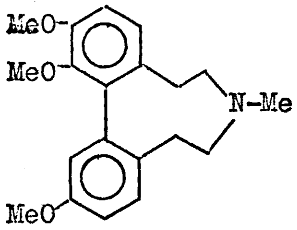

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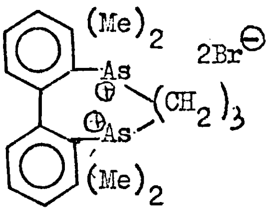

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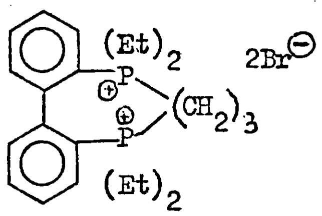

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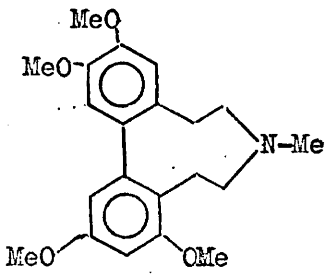

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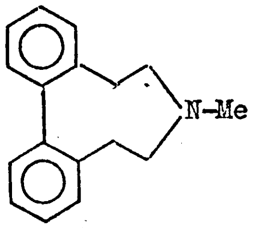


(7)

owing to the non-bonded interactions in the ring, require much more energy to invert their configurations than the lower homologues, and thus are optically stable.

In the present work, nine-membered carbocyclic and heterocyclic compounds incorporating the 8,8'-positions of 1,1'-binaphthyl were synthesised in very good yields: they could be prepared in optically active form and were found to be optically stable up to their melting points: no mechanism can be envisaged for their configurational inversion. Models suggest that they are probably conformationally as well as configurationally stable molecules and this assessment adds interest to their spectroscopic properties. Observation of chiroptical properties down to shorter wavelengths than have previously been studied has led to finding <u>two</u> Cotton effects of opposite signs below the β-band of the unpolarised absorption spectrum: this has led to proposing new criteria for absolute configurational assignment in 1,1'-binaphthyls. The validity of these assignments rests upon some compounds of known absolute configuration determined by standard methods. $(+)_{578}$-1,1'-Binaphthyl has been assigned <u>S</u>-configuration (Akimoto, Shiroiri, Iitaka and Yamada, 1968) by its chemical correlation with $(+)_{578}$-2,2'-dihydroxy-3,3'-bismethoxycarbonyl-1,1'-binaphthyl for which the <u>R</u>-configuration was assigned by the X-ray crystallographic method. $(+)_{578}$-2,2'-Dimethyl-1,1'-binaphthyl has been classified as <u>S</u> on the basis of the asymmetric reduction method (Mislow and McGinn, 1958). These two compounds also show Cotton effects of the same nature in this region of shorter wavelength which correspond with those of our new compounds.

2. SYNTHETIC WORK

2.1 General Introduction to Synthetic Work

a. Methods of ring closure. For the preparation of the nine-membered carbocyclic and heterocyclic compounds incorporating the 8,8'-positions of 1,1'-binaphthyl, 8,8'-bisbromomethyl-1,1'-binaphthyl (8) (Badar, Cooke and Harris, 1965) was selected as a starting material and from it cyclised products were obtained in very good yields. For the last 80 years chemists have been interested in the preparation and properties of cyclic molecules but only for the last 30 years have the medium ring compounds(containing 8 to 11 atoms in the ring) been the subject of particular interest and systematic investigation; use has been made of the observation that in certain cases a given type of intermolecular condensation reaction can be made to take place intramolecularly, depending largely upon the size of the resulting ring compound.

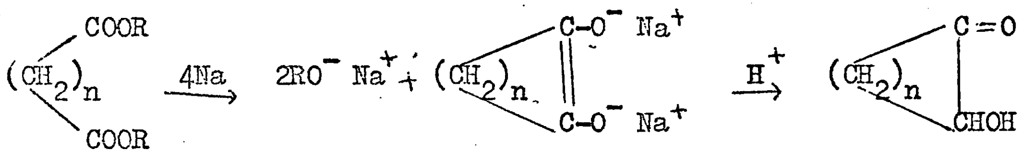
A number of methods of ring closure can be found in the literature; the following are among those which have been frequently used.

(1). Pyrolysis of the heavy metal salts of $\alpha\omega$-alkyldicarboxylic acids (Ruzicka, Stoll and Schinz, 1926); yields of up to eight-membered ring compounds were very good, but for nine-, ten- and eleven-membered ring ketones yields were negligible. The failure to obtain nine to eleven membered ring ketones by this method is explained by the rings, although puckered, being highly congested and strained. Marvel and Glass (1938) were able to synthesise a cyclononanone by using this method (they attempted to resolve it but failed).

(2). In 1909, Thorpe discovered the intramolecular cyclisation of adiponitrile in the presence of sodium ethoxide, ~~leading to~~ that led to a five-membered ring enaminonitrile. Ziegler, Eberle and Ohlinger (1933) extended the procedure of Thorpe by (a) using high dilution, (b) using diethyl ether as solvent, and (c) using an amide as the catalysing base. Later Ziegler and his associates found that an alkali metal derivative of an aralkyl amine such as N-methylaniline, is a most effective catalyst. This method was found effective for the preparation of 5 to 33 membered ring compounds, except for the 9 and 11 membered rings. Ziegler and Aurnhammer (1934) prepared a cyclononanone using this method but with only 2.8% yield.

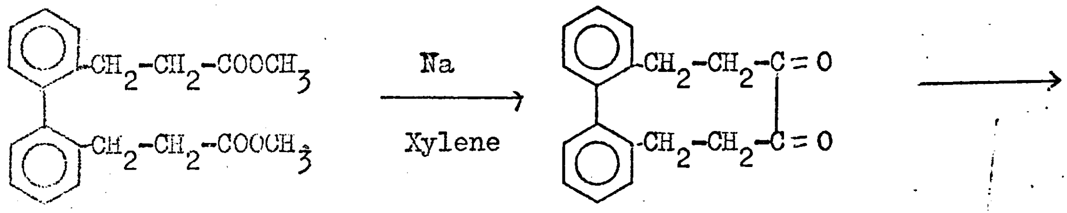
(3). The cyclisation of esters of dicarboxylic acids leading to keto-esters: Dieckmann (1894) discovered that adipic or pimelic esters on heating with sodium in the presence of traces of ethanol give a cyclopentanone or a cyclohexanone. This method also did not give satisfactory yields for the medium-sized ring compounds, only a few cyclooctanones have been prepared by it. Blicke, Azuara, Doorenbos and Hotelling (1953) used sodium hydride as the base catalyst and reported 61% yield of an eight-membered ring keto-ester. Leonard and Schimelpfenig (1958) obtained a 15% yield of an eight-membered ring compound by using potassium t-butoxide as a base. Borgan and Dale (1970) reported the preparation of 4,4,7,7-tetramethylcyclononanone (30% yield). However, even using high dilution, the compounds containing nine and eleven atoms in the ring are obtain in very poor yields or not at all, which is probably due to destabilisation of the preferred conformation for cyclisation by transannular steric interaction.

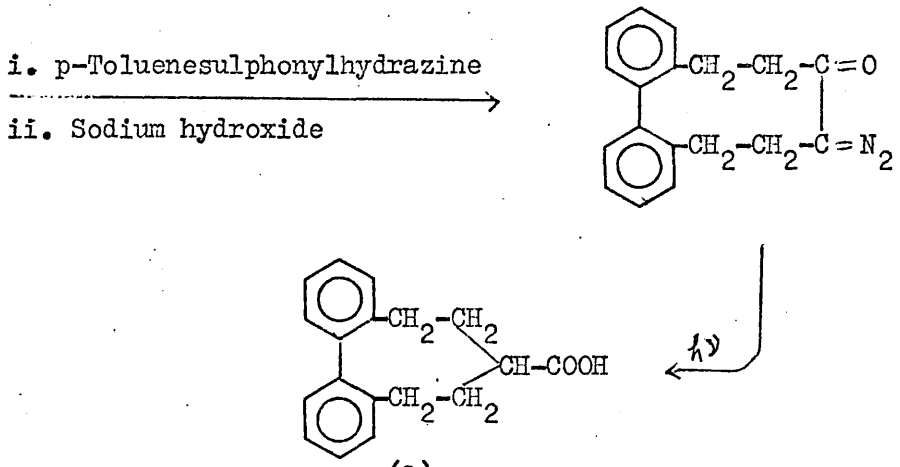
(4). The best and often the only method of selection for the preparation of medium-sized ring ketones is the acyloin condensation. In this method the two ester groups of a diester are reduced to a hydroxyketone by a dispersion of molten sodium droplets in xylene. The actual reaction product is an ene-diol which gives acyloin after acidification, the ene-diols are very sensitive to oxygen and therefore this reaction is carried out in an atmosphere of nitrogen.



The majority of the nine-membered ring compounds made by the acyloin method are found in the work of Blomquist, Wheeler and Chu (1955).

(5). Mislow, Hyden and Schaefer (1962) attempted the malonic ester condensation for the preparation of a nine-membered ring biphenyl compound bridged in the 2,2'-positions, but this method failed to give the desired product. They then succeeded in preparing a nine-membered ring acid (1) by carrying out an acyloin condensation on the ester of a dicarboxylic acid, followed by ring contraction in a series of reactions.





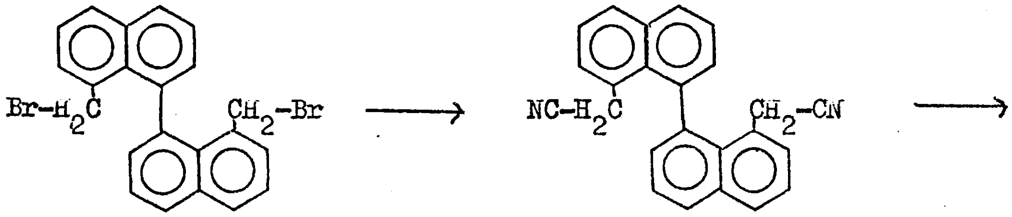
(1)

(6). One cyclononanone has been reported by Kohler, Tischler, Potter and Thompson (1939) prepared by the ring expansion reaction of cyclooctanone with diazomethane in 61% yield.

(7). Rabinovitz, Gazit and Bergmann (1970) reported the synthesis of a nine-membered ring compound, dibenzocyclononatetraene(5%) by carrying out a Wittig reaction between biphenyl-2,2'-dialdehyde and the bisphosphorane derived from trimethylene bromide in the presence of sodium methoxide in dimethyl formamide in an atmosphere of argon.

b. Schemes of new work. The new work described in this Thesis is summarised in the following schemes.

Scheme 1: Unbridged 8,8'-disubstituted 1,1'-binaphthyls.



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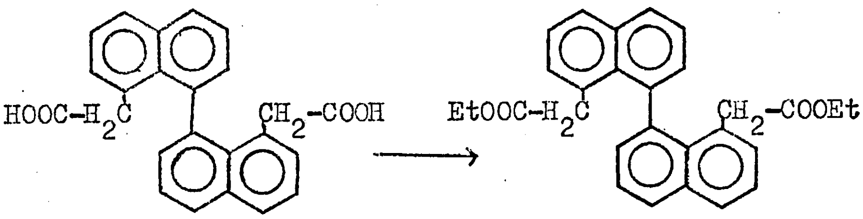
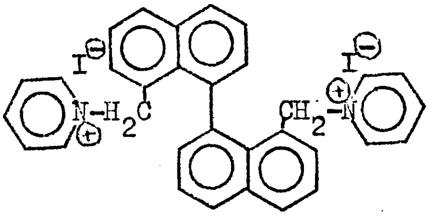


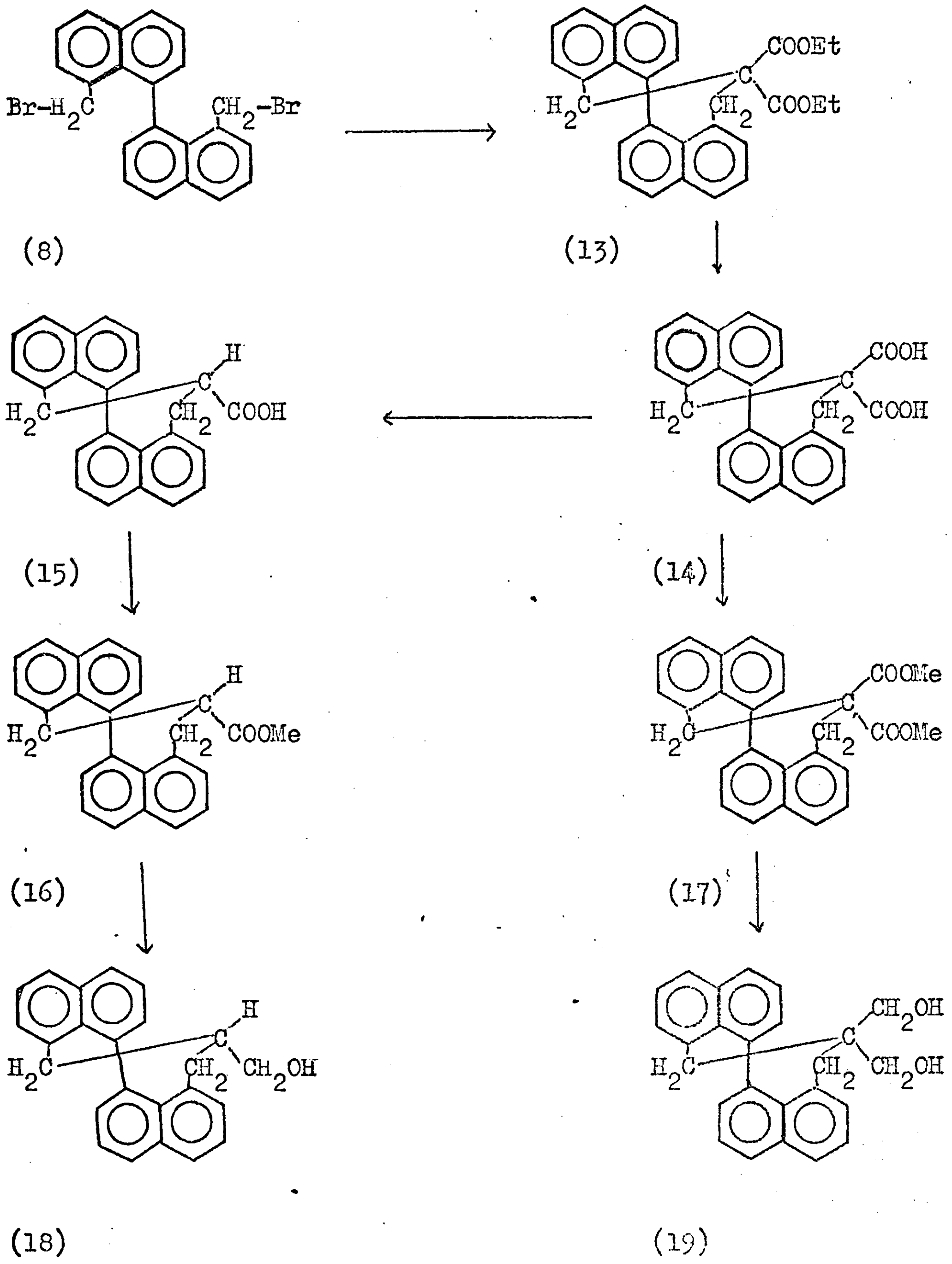
(10) (11)

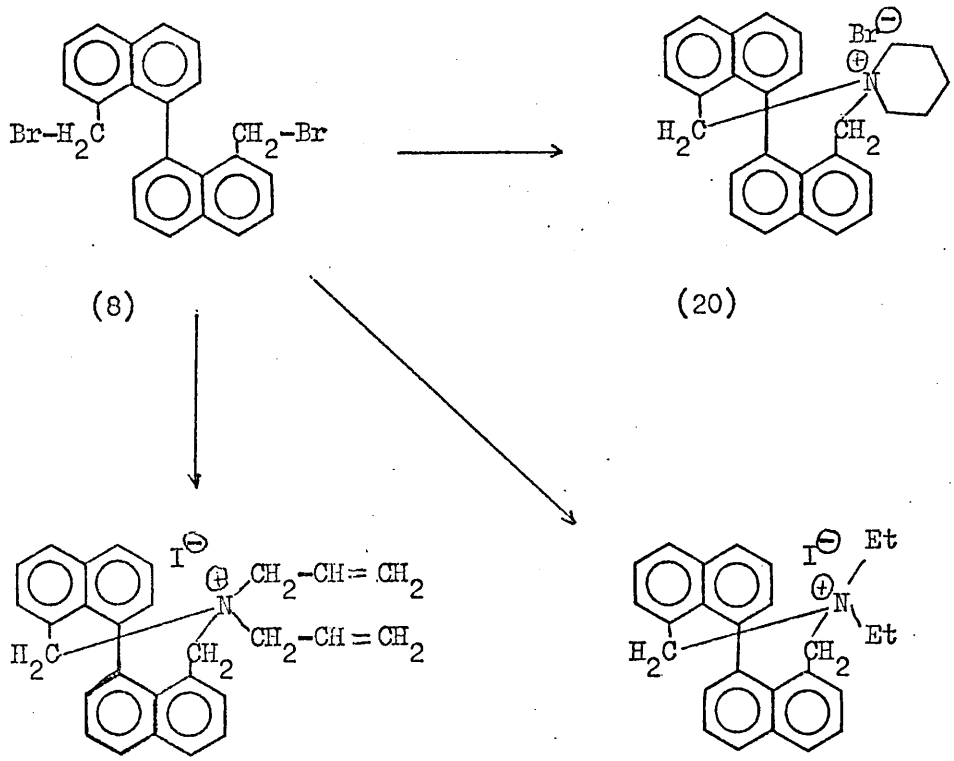
(8) →



(12)

Scheme 2: 8,8'-Bridged 1,1'-binaphthyls.




Br-H$_2$C
CH$_2$-Br
Br$^\ominus$
$\oplus$N
H$_2$C
CH$_2$
I$^\ominus$
$\oplus$N
CH$_2$-CH = CH$_2$
CH$_2$-CH = CH$_2$
H$_2$C
CH$_2$
I$^\ominus$
Et
$\oplus$N
Et
H$_2$C
CH$_2$

(8)

(20)

(22)

(21)

2.2 Discussion of Synthetic Work

a. The starting material (8,8'-Bisbromomethyl-1,1'-binaphthyl).
8,8'-Bisbromomethyl-1,1'-binaphthyl (8) was prepared first (Badar, Cooke and Harris, 1965). 8,8'-Bishydroxymethyl-1,1'-binaphthyl was dissolved in warm glacial acetic acid and hot hydrobromic acid added to it with stirring; a gum like product was obtained which eventually gave a 80% yield of the bisbromomethyl compound(8). Two modifications of the method were tried:

(i) Since halide formation is reversible, and water liberated during the reaction, an equivalent amount of acetic anhydride was added to the diol dissolved in hot glacial acetic acid before adding hot hydrobromic acid; this gave an 86% yield of a purer product.

(ii) Phosphorous tribromide was used in place of acetic acid/acetic anhydride and hydrobromic acid; the phosphorous tribromide acts as reagent and as solvent. This method, which gave a yield of 99% was adopted for subsequent preparation of the bisbromomethyl compound (8), as the yield is excellent and the product is stable when stored.

The bisbromomethyl compound (8) has advantages as synthetic precursor; the weakly basic halide ions are easily replaced by a wide variety of nucleophiles: this work describes reactions with cyanide ion, a tertiary amine, sodiomalonic ester and secondary amines.

b. The new synthetic work is divided into two main classes:

A. Unbridged 8,8'-disubstituted 1,1'-binaphthyls

(i) Open chain carbon compounds

(ii) Open chain quaternary ammonium salt

B. 8,8'-Bridged 1,1'-binaphthyls

(i) Carbocyclic compounds

(ii) Heterocyclic compounds with nitrogen in the bridge

A. Unbridged 8,8'-disubstituted 1,1'-binaphthyls

Several compounds with methyl and substituted methyl groups in the 8,8'-positions of 1,1'-binaphthyl have been synthesised and their stereochemistry studied (Badar, Cooke and Harris, 1965), some spectroscopic (IR, NMR, u.v. and mass spectra) observations have been reported (Mazengo, 1968; Dixon, Harris and Mazengo, 1971; Harris and Mazengo, 1967)

(i) Open chain carbon compounds: To prepare 1,1'-binaphthyl-8,8'-diacetic acid (10), the bisbromomethyl compound (8) was treated with aqueous ethanolic potassium cyanide. The colour of the reaction became brick red. After three hours heating under reflux and working up, the biscyanomethyl compound (9) was obtained in 77.5% yield. It was easily hydrolysed to (10) by heating with 50% ethanolic potassium hydroxide. Purification before and after acidifying with hydrochloric acid gave colourless 8,8'-diacetic acid (10), m.p. 320°d. This acid is not appreciably soluble in ethanol, methanol, carbon tetrachloride or chloroform; good solvents for it are dimethylformamide and dimethylsulphoxide. Other examples of aromatic dicarboxylic acids having high melting point and being sparingly soluble are terephthalic acid (300° subl.) and 1,1'-binaphthyl-8,8'-dicarboxylic acid (303 - 324°d.).

The ethyl ester (11) of the acid (10) was prepared (with a view to attempting a Dieckmann reaction) by the reaction of thionyl chloride in benzene solution, followed by ethanol. This ester was very soluble in chloroform and in methanol and failed to crystallise from either of them; it crystallised from a very concentrated ethanolic solution with m.p. 95-96°. Such a low melting point is surprising while its precursor acid decomposed at 320°.

(ii) A bis(methylenepyridinium) iodide: The reaction of pyridine with the bisbromomethyl compound (8) took place smoothly to give 1,1'-binaphthyl-8,8'-bis(methylenepyridinium) dibromide. This salt was hygroscopic and very soluble in water: it was converted into the iodide by treatment with a hot aqueous solution of potassium iodide.

B. 8,8'-Bridged 1,1'-binaphthyls

(i) The following general reactions were attempted

1. Thorpe-Ziegler reaction: This reaction has proved satisfactory for the preparation of seven-membered ring enaminonitriles in the biphenyl and 2,2'-bridged 1,1'-binaphthyl series but in the present work the 8,8'-biscyanomethyl compound (9) gave only recovered starting material. IR and NMR spectra, m.p., mixed m.p. and elemental analysis were all unchanged. Another attempt was made using the sodio-derivative of N-methylaniline as a catalyst but it also failed to give the desired cyclic product.

2. Dieckmann reaction: Diethyl 1,1'-binaphthyl-8,8'-diacetate (11) was treated with sodium ethoxide in Dieckmann conditions; this reaction also failed to give a nine-membered ring compound and the starting material was recovered completely.

3. Perkin method of cyclisation: Although it is unusual for the preparation of a nine-membered ring compound by the reaction of an $\alpha\omega$-alkyldihalide with diethylmalonate to succeed, in this case the attempt met with success, the cyclic ester (13) was formed in 97% yield. To test the possibility of forming the 8,8'-disubstituted product, two equivalents of sodiomalonic ester were used, but this excess did not affect the excellent yield of the cyclic product.

This ester (13) was easily hydrolysed to the dicarboxylic acid (14). Care was taken to minimise the chances of decarboxylation. This acid is very soluble in ethanol and in dimethylformamide but very sparingly soluble in chloroform and carbon tetrachloride. It melted with a brisk effervescence at 235-236°, resolidified quickly and melted again at 252-254°. Decarboxylation of (14) on a preparative scale gave monocarboxylic acid (15), m.p. 252-254°.

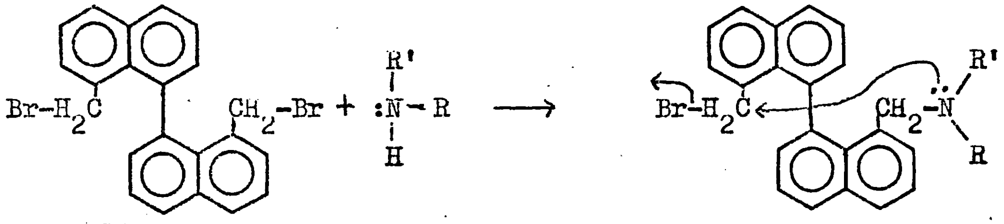
Methyl esters of cyclic dicarboxylic acid (14) and monocarboxylic acid (15): To obviate the risk of decarboxylation during esterification, the methyl ester of the diacid (14) was prepared by adding the powdered acid in small portions to a cold ethereal solution of diazomethane. Crystallisation of the purified product from benzene gave 92.6% of dimethyl ester (17), m.p. 258-260°.

The monocarboxylic acid (15) is not appreciably soluble in benzene, but it goes into solution as it reacts with thionyl chloride: treatment with methanol gave the methyl ester, m.p. 186-188°.

The alcohols corresponding to the monomethyl ester (16) and dimethyl ester (17) were made by reduction with lithium aluminium hydride;

the alcohol (18) crystallised from chloroform, m.p. 74-76° (92%) yield. The diol (19) crystallised from benzene in shining needles, m.p. 196° (75% yield).

(ii) Heterocyclic compounds containing nitrogen in the bridge: The success of the reaction of sodiodiethylmalonate with the bisbromomethyl compound (8) to give a good yield of a nine-membered ring ester (13) encouraged us to attempt the reaction with secondary amines. Secondary amines can be alkylated twice to form quaternary salts, so the second stage of reaction could be intramolecular.



The following secondary amines were tried.

(1) Piperidine: Piperidine (2 mole) dissolved in chloroform, was added to a solution of the bisbromomethyl compound (8) (1 mole) in chloroform at room temperature and then warmed up to 50°, a 67% yield of the cyclic bromide (20) was obtained after purification.

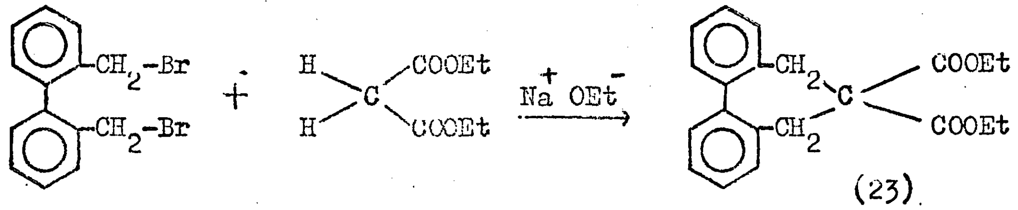
(2) Diethylamine and (3) Diallylamine: Quaternary diethyl and diallyl ammonium bromides were prepared; both of them were very soluble in water and failed to crystallise. These bromides were converted into the corresponding iodides (21) and (22), which crystallised from aqueous solution. Beaven, Hall, Lesslie and Turner (1952) reported the high solubility of 1,1-diethyl-2,7-dihydro-4',1"-dimethoxy-3,4,5,6-dibenzoazepinium bromide in water but that the iodide could be crystal-

lised.

2.3 Ring Size and Ease of Formation

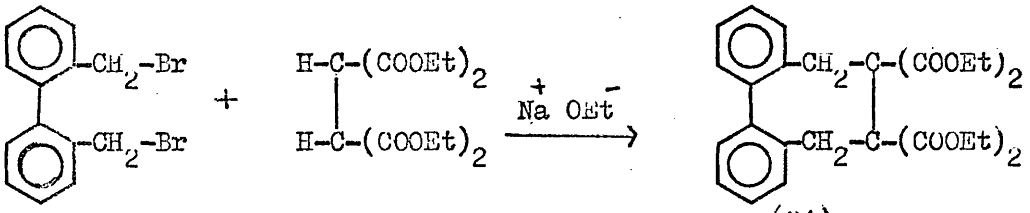
Nine-membered carbocyclic and heterocyclic compounds in the present work were formed very easily and in very good yields. Such an ease of formation of nine-membered rings by chemical methods (except by the acyloin method) is unusual. The common difficulty of formation of nine-membered and other medium-sized rings is attributed to an excessive trans-annular strain; the effect of this strain is said to be favourable to the ring closure as the size of the ring increases from 3 to 6 membered, is less favourable for the seven-membered ring and most unfavourable for medium-sized rings, but after that the van der Waal's repulsion forces across the ring become constant making closure easier for these large sized rings (Sicher, 1962).

In aliphatic molecules, five- and six-membered rings are easily formed, but seven-membered are formed with difficulty. Introduction of aromatic groups into the chain results in remarkable ease of formation of the seven-membered rings in the biphenyl series; Kenner (1913) prepared a seven-membered ring by condensation between 2,2'-bisbromomethylbiphenyl and sodiomalonic ester (23)



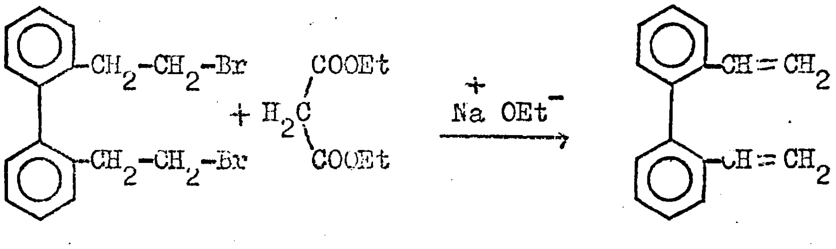
(23).

He also observed that the condensation between the bisbromomethylbiphenyl and two molecular proportions of malonic ester in the presence of sodium ethoxide led only to the same cyclic product. Using ethyl ethane-1,1,2,2-tetracarboxylate in the presence of sodium ethoxide in ethanol he was able to prepare an eight-membered ring ester (24). The



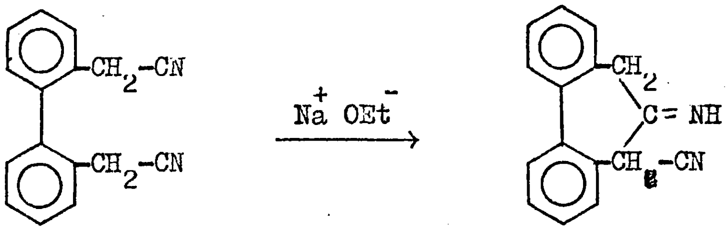
(24)

interaction of 2,2'-bisbromomethylbiphenyl and ethyl propane-1,1,3,3-tetracarboxylate in the presence of sodium ethoxide (Beaven, Bird, Hall, Johnson, Ladbury, Lesslie and Turner, 1955) failed to give the nine-membered carbocyclic compound. The attempt of Mislow, Hyden and Schaefer, 1962) to prepare a nine-membered ring compound by condensation between 2,2'-bisbromoethylbiphenyl and diethylmalonate in the presence of sodium ethoxide also met with no success, giving 2,2'-divinylbiphenyl (25) as a result of the elimination reaction.



(25)

The product of a Thorpe-Ziegler reaction from 2,2'-biscyanomethylbiphenyl (Kenner and Turner, 1911) led to good yields of a seven-membered ring iminonitrile (26). Kenner (1913) suggested that the cause of this



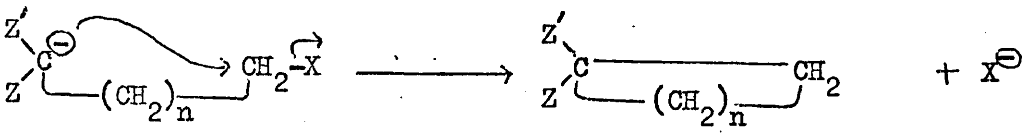
(26)

ease of formation of seven-membered ring compounds is that the two aromatic double bonds minimise the strain and make the chain comparable with the saturated n-pentane. Another important feature of formation of these seven-membered ring compounds in the biphenyl series is the absence of β-hydrogens in the 2,2' substituents in the chain, thus precluding elimination reactions.

Reactions leading to cyclisation can be divided into two classes:

(i) Where only one carbon-carbon bond is formed at a time, and

(ii) where two carbon-carbon bonds are formed at the same time (concerted reactions). In the present work reactions used belong to class (i) and are of intramolecular-nucleophilic-displacement type, where the nucleophile and the leaving groups both are present in the same molecule, e.g.



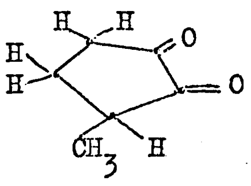
In the malonic ester condensation the nucleophilic centre is a carbanion and both the groups Z and Z' are strongly electron withdrawing, able to stabilise the negative charge. The leaving group $X^{\ominus}$ is a halide ion. A conformation is required in which the reacting end groups will be close together and properly in line for an S_N2 reaction. The presence of rigid groups such as double bonds, aromatic rings or bulky substituents in the chain of the compound being cyclised decreases the possibility of intermolecular rotations and hence the number of possible unfavourable conformations; as a result favourable conformation becomes more probable, and increases the possibility and the yield of cyclised product.

In general, high dilution technique minimises the probability of the intermolecular reactions and the chance of intramolecular cyclisation improves; but in the present work the conditions of high dilution were not required, which suggests unusual ease of formation of the nine-membered rings; thus a major contribution to ease of reaction comes from the stereochemistry of 8,8'-bisbromomethyl-1,1'-binaphthyl (8) and the cyclised product. Secondly, the presence of two naphthyl groups prevents vigorous intermolecular rotations of the chain and encourages the preferred conformation for cyclisation. Third, this bisbromomethyl compound does not have β-hydrogens in the chain to be cyclised, so that the alternative of olefin formation is not available.

2.4 NMR Spectroscopy and Stereochemistry

a. Introduction. NMR spectroscopy is younger than u.v. and IR spectroscopy, but in a very short period it has advanced as a very important tool for organic chemists. The use of NMR spectroscopy to a stereochemist, apart from the determination of gross molecular structure lies in determination of configuration and conformation.

(1) Elucidation of structure of unknown compounds: The proton NMR spectrum tells some most important features about the structure of a molecule: first, the chemical nature of protons, observed by the use of chemical shift (τ). Protons in similar chemical environments have similar chemical shifts. Second, integration of the NMR spectrum tells the ratio of numbers of protons of each kind. Third, spin-spin splitting gives information about how many protons are on each carbon atom adjacent to any atom bearing one or more protons. For example, a mono-enol derived from (27) could possibly be (28) or (29). To find which is correct, the



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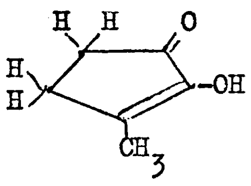

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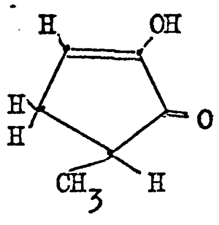
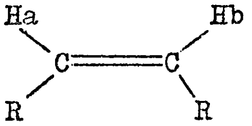


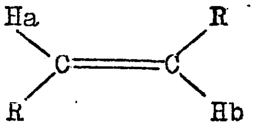
(29)

chemical shift is used (Bredenberg, 1959); the signal at τ 3.25 is an hydroxyl group signal, at 7.57 is a methylene and at 7.97 a methyl signal. The integration suggests the ratio of protons 1:4:3, which could be explained with structure (28) and not (29). Structure (29) would give five signals in an integrated ratio 1:1:1:2:3. The methyl signal is unsplit suggesting that there is no proton present on the adjacent carbon atom.

(2) Determination of configuration: Protons in geometrically isomeric situations have different chemical shifts, for example,



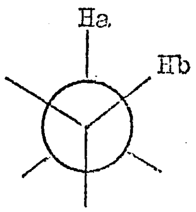
cis-



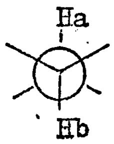
trans-

The cis- protons resonate at lower magnetic field than the trans- protons.

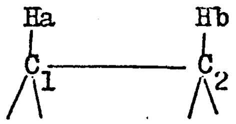
(3) Determination of conformation: If a given proton is in different environments in different conformations, it will give a signal corresponding to each environment; and the relative peak areas of these signals reflect the relative populations of the conformations, for example cyclohexane at -110° shows two signals: the chair form is by far the major conformer present and one signal is due to axial protons and another due to equatorial protons. The size of the coupling constant (J) between protons Ha and Hb on a pair of adjacent carbon C_1 and C_2 depends on the planes C_1C_2Ha and C_1C_2Hb. Trager, Vincenzi and Huitric (1962) after the study of many cyclohexane derivatives reported the use of the coupling



J_{HaHb} 2-4 cps



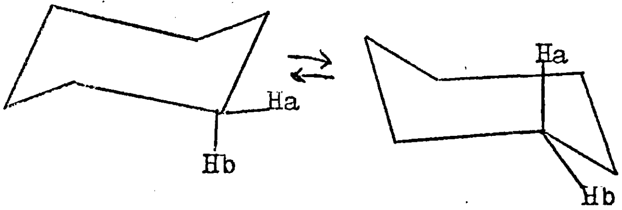
J_{HaHb} 5-12 cps



constant for conformational determination; the coupling constant is two to three times as large between anti protons (axial) as between gauche (axial-equatorial or equatorial-equatorial) protons.

Theoretical calculations of Karplus (1963) show that the coupling constant should depend upon the cosine of the dihedral angle. The coupling constant therefore would be zero for a dihedral angle of 90° and increase to a moderate value from 90° to 0° and increase to a high value from 90° to 180° (see page 44).

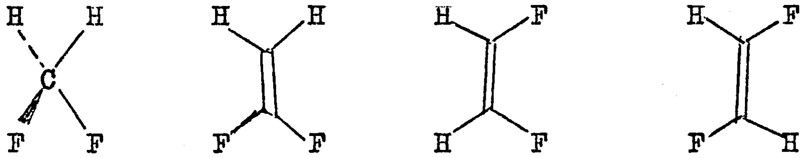
In molecules which are readily interconvertible rotamers, several conformations are probable, and any proton in the molecule can occupy all possible positions in a very short time; the NMR spectrum represents an average position. This phenomenon has been observed in many open chain molecules and in some cyclic compounds, for example: cyclohexane (30); the chair-chair interconversion of cyclohexane is so rapid at room temperature that the NMR spectrum shows only a single sharp signal.



(30)

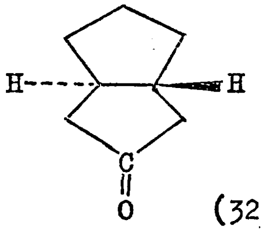
Apart from the classification of protons based upon their chemical nature, Mislow and Raban (1961) classified protons of conventional stereoisomers into three main classes.

(i) Equivalent protons: Protons whose positions in the molecule are interconvertible by rotation about an axis of rotation to give an indistinguishable structure from the original structure are known as "equivalent". The necessary requirement for proton equivalence is interconversion by axis of rotation C_n and not by an S_n operation, e.g. in these difluoro compounds, each has a set of two equivalent fluorine atoms



(31)

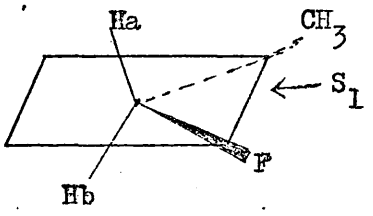
and a C_2 axis. Secondly, molecular dissymmetry does not preclude equivalence of protons, for example compound (32), where the methine protons are equivalent.



(32)

Equivalent protons can be found in molecules which belong to the axial point group (excluding $C_{\infty v}$); molecules belonging to non-axial point groups (C_1, C_i and C_s) cannot show proton equivalence.

(ii) Enantiotopic protons: In enantioisomeric environments the protons are called "enantiotopic". Enantiotopic protons could be interchanged only by a rotation-reflection operation (S_n) and not by a rotation (C_n, $n > 1$). This S_n operation gives an indistinguishable structure from the original. The environments of enantiotopic protons are nonsuperimposable, for example; compounds (33) and (34). In these molecules, the



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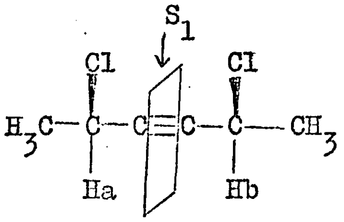
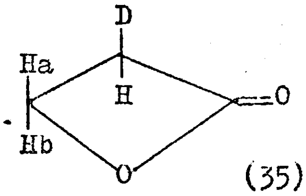


(34)

proton Ha is the reflection of Hb in the mirror planes (S_1). Only non-linear and achiral molecules can have enantiotopic protons. Asymmetric molecules (point group C_1) are nonaxial and chiral, which means that asymmetric molecules cannot have equivalent or enantiotopic protons. The only difference between equivalent and enantiotopic protons is that enantiotopic protons in a chiral solvent or reagent exhibit their distinctiveness as they are then in diastereoisomeric situations.

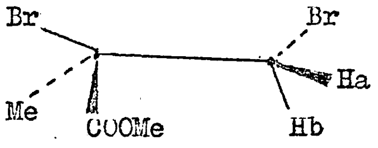
(iii) Diastereotopic protons: When the stereochemical environments of protons are diastereoisomeric, the protons are said to be "diastereotopic". The necessary requirement for diastereotopic protons is that they must not be interchanged by any symmetry operation. An asymmetric molecule (point group C_1) cannot have equivalent or enantiotopic protons but can have diastereotopic protons, for example: propiolactone-2-D (35).



(35)

In this compound Ha and Hb are diastereotopic.

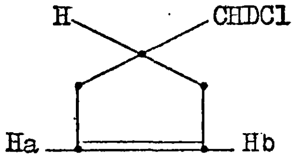
The presence of asymmetry in a molecule containing a methylene group makes the methylene protons non-equivalent; for example in the compound (36) Ha and Hb are diastereotopic protons; the environment of Hb is diastereotopic with the environment of Ha, a situation which is



(36)

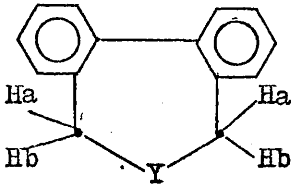
independent of conformation (Mislow, 1966).

The two diastereotopic protons may be on two different carbon atoms, for example compound (37): the two olefinic protons Ha and Hb in this asymmetric molecule are diastereotopic and show two signals.



(37)

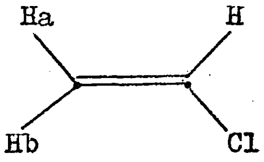
Dissymmetric nonasymmetric molecules may also have diastereotopic situations, for example (38), this belongs to point group (C_2), there



(38)

are two equivalent methylene groups each containing two diastereotopic protons. When $Y = S$, the spectrum shows an AB doublet (Mislow, Glass, Hopps, Simon and Wahl. jr., 1964). Kurland, Rubin and Wise (1964) in the case where Y = O observed an AB quartet for the diastereotopic methylene protons in carbondisulphide at -105^{o} and the four lines merge into one at 43^{o}.

Molecular asymmetry is not necessary for diastereoisomeric situations: an achiral molecule (39) contains diastereotopic protons Ha and Hb. In the chiral molecule *trans*-1,2-dichlorocyclopropane (40) Ha and Ha' are equivalent, Hb and Hb' are equivalent.



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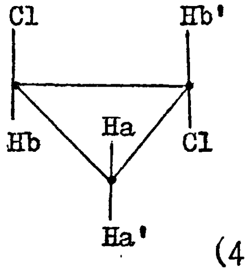
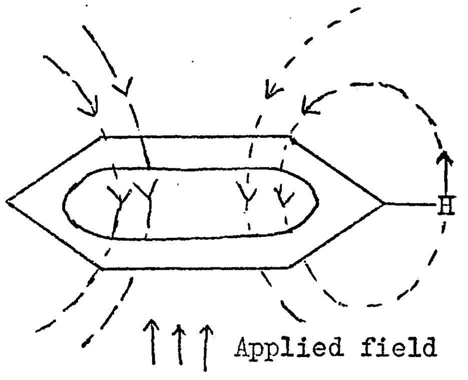


(40)

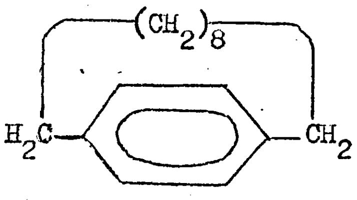
The two parameters, chemical shift and coupling constant are useful to determine the equivalence or non-equivalence of protons in a molecule.

Chemical Shift: A proton in a molecule is always shielded by electrons and the field strength at a constant frequency necessary for resonance is not the same for protons in different environments. Equivalent protons will resonate at the same value of the applied magnetic field but non-equivalent protons as they are differently shielded will require different values of the applied magnetic field to resonate, i.e. with the variation in the magnetic field, signals will appear at separate and suitable places for each non-equivalent proton. This dependence of signal position on the environment of the proton is known as "chemical shift", measured as the distance of its signal from a standard (e.g. tetramethylsilane). In an applied magnetic field the electrons circulating around the nuclei produce a field known as the secondary field: if the secondary field opposes the applied magnetic field; then the effect on a proton in the field is known as shielding and the signal is shifted upfield.

For benzene, when the applied field is perpendicular to the plane of the ring a ring current is set up, and the secondary field at the protons is parallel to the main applied field and in the same direction at the site of the aromatic proton. The resulting field at the proton is increased which brings about its resonance at lower applied magnetic field, i.e. it is de-shielded. But in the case where a proton lies



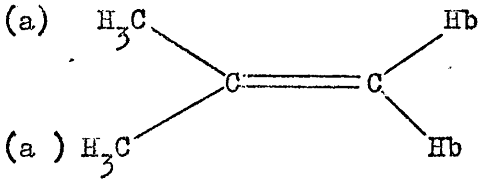
directly above the plane of the ring current, it is shielded. For example, the NMR spectrum of (41) is reported by Waugh and Fessenden (1957);



(41)

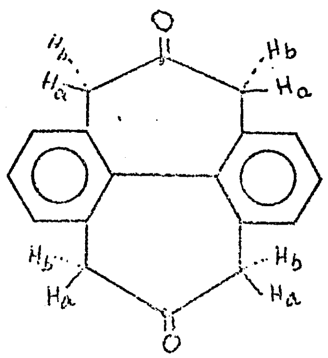
the CH_2 protons which are lying over the benzene ring resonate at higher magnetic field (i.e. are shielded) than those directly attached to the benzene ring.

Equivalent or enantiotopic protons are equally shielded and must exhibit the same NMR chemical shift: for example isopropyl chloride CH_3———CHCl———CH_3 shows only two NMR signals. Similarly,
(a) (b) (a)



shows only two NMR signals, one for methyl and another for methine protons. Protons which show equal chemical shifts are termed as 'isochronous' by Abragam (1961).

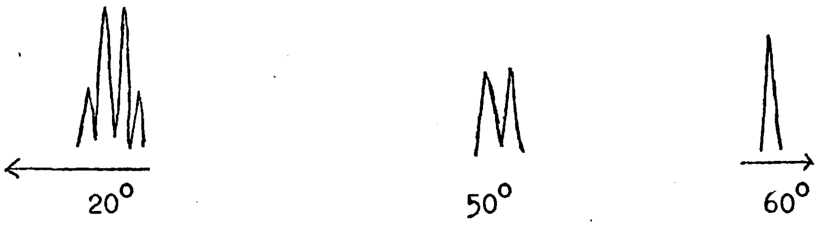
Diastereotopic protons must have different chemical shifts and are said to be 'anisochronous'. They are chemically non-equivalent and must be magnetically non-equivalent. Sometimes the non-equivalence is not sufficiently large to show detectably different chemical shifts. For example a doubly bridged biphenyl (42) (point group D_2) has four equi-



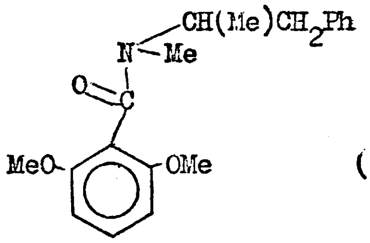
(42)

valent methylene groups each containing geminal diastereotopic (i.e. non-equivalent) protons Ha and Hb, but does not show different chemical shifts for these protons under normal conditions (Mislow, Glass, Hopps, Simon and Wahl jr., 1964).

The effect of temperature change on conformationally labile diastereotopic protons may be to show a qualitative change in the spectrum: a quartet at room temperature may become a singlet at higher temperatures; a singlet at room temperature may appear as a quartet; at lower temperatures, for example, the NMR spectrum of 15H-dibenzo [c,e] benzimidazo-[1,2-a]-azepine, shows a doublet at 50°, a fine quartet at 20° and lower temperatures and a singlet at 60° and above (Hwang, 1972). The temperature at which the peaks merge into one is known as the "coalescence temperature". Temperature variation and coalescence temperature observations in suitable cases help in the determination of the free energy of inversion $\Delta F^{\neq}$, energy of inversion E_{inv} and enthalpy of inversion $\Delta H^{\neq}$ (Anderson, 1965).



The substituted benzamide (43) exhibits four methoxyl signals in



(43)

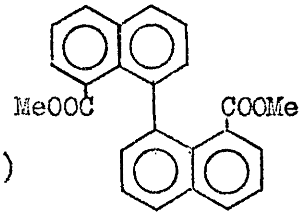
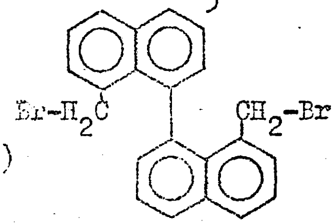
t-butylbenzene solution at 60° and these signals coalesce first into two at 130° and then into a singlet at 165°. From this information Siddall and Garner (1966) determined the separate rotation barriers about the carbonyl-nitrogen and aryl-carbonyl bond, both are above 20 kcal mol^{-1}.

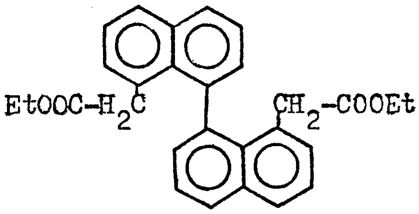
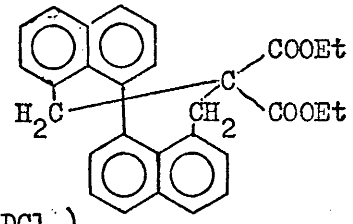
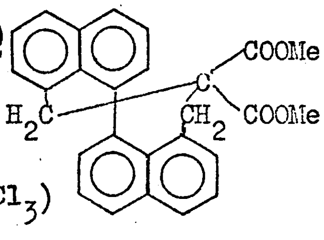
Coupling Constant: Spin-spin coupling occurs between chemically non-equivalent protons. Diastereotopic protons because of their differences in environment and relationships, must have different coupling constants (J) with respect to any nucleus in the same molecule.

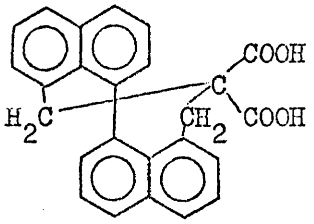
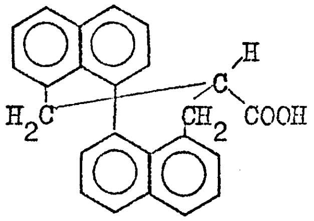
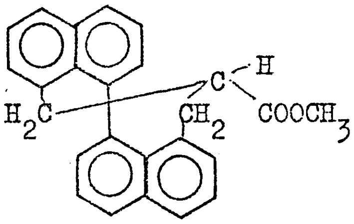
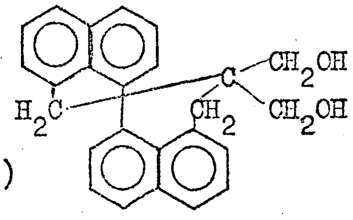
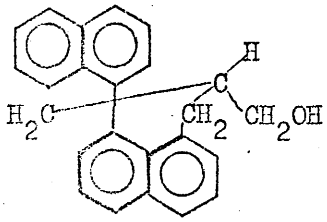
In two sets of two equivalent or enantiotopic protons, if one of the nuclei in the first set and one of the nuclei in the second set are in diastereoisomeric situations, then one set of enantiotopic or equivalent nuclei can couple with the other, for example in *trans*-1,2-dichlorocyclopropane (40), the two methylene hydrogens Ha and Ha' are equivalent and similarly Hb and Hb'. There are two types of vicinal methylene methine couplings, one *trans*- coupling between Ha and Hb or between Ha' and Hb' and second *cis*- coupling between Ha and Hb' or between Ha' and Hb.

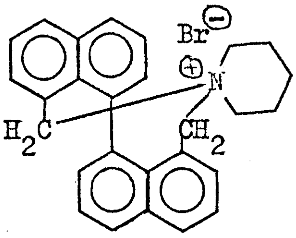
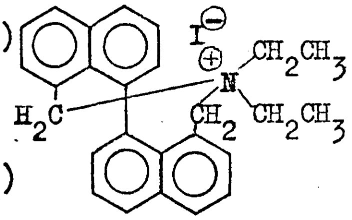
b. NMR spectra, results and discussion

The NMR characteristics of 8,8'-disubstituted unbridged and 8,8'-bridged 1,1'-binaphthyls at room temperature are collected in Table I and the supposed source of the signal given.(60 MHz, TMS)

Compound and solvent	Aromatic proton τ (ppm)	Other proton τ (ppm)
(I) 1-Methoxycarbonylnaphthalene (CDCl$_3$)	2.00-3.10 (7H)	6.3 -COOCH$_3$ (3H)
(II) 8-Bromo-1-methoxycarbonyl-naphthalene (CDCl$_3$)	2.15-2.95 (6H)	6.1 -COOCH$_3$ (3H)
(III)  (CDCl$_3$)	2.03-2.85 (12H)	7.33 -COOCH$_3$ (6H)
(IV) 1-Naphthylcarbinol (CDCl$_3$)	2.00-2.95 (7H)	5.17 -CH$_2$ (2H) 7.57 -OH (1H)
(V) 8,8'-Bishydroxymethyl-1,1'-binaphthyl (CDCl$_3$)	2.10-2.95 (12H)	6.03 -CH$_2$ (4H) 8.25 -OH (2H)
(VI) 1-Bromomethylnaphthalene (CDCl$_3$)	1.90-3.05 (7H)	5.30 -CH$_2$ (2H)
(VII)  (CDCl$_3$)	2.05-2.80 (12H)	5.74 5.90 5.99 6.15 5.94 -CH$_2$ (4H)

Compound and solvent	Aromatic proton τ (ppm)	Other proton τ (ppm)
(VIII) 8,8'-Biscyanomethyl-1,1'-binaphthyl ($CDCl_3$)	2.00-2.75 (12H)	5.75 5.92 6.00 6.17 5.96 $-CH_2$ (4H)
(IX) Diethyl 1,1'-binaphthyl-8,8'-diacetate ($CDCl_3$)	2.00-3.00 (12H)	6.75 $-CH_2$ (4H) attached to naphthalene rings.
		6.20 6.30 6.43 6.53 6.36 $-COOCH_2-$ (4H)
		8.93 9.04 9.15 CH_3 (6H)
(X)  ($CDCl_3$)	2.15-3.38 (12H)	5.90 6.14 6.80 7.04 6.47 $-CH_2$ (4H) attached to naphthalene rings.
	3.23 3.26 3.35 3.38 (2H)	5.98 6.10 6.22 6.34 6.16 $-COOCH_2-$ (4H)
		8.83 8.94 9.05 CH_3 (6H)
(XI)  ($CDCl_3$)	2.16-3.38 (12H)	5.89 6.13 6.80 7.04 6.46 $-CH_2$ (4H) attached to naphthalene rings.
	3.23 3.26 3.35 3.38 (2H)	6.64 $-COOCH_3$ (6H)

Compound and solvent	Aromatic proton τ (ppm)	Other proton τ (ppm)
(XII)  (DMF)	3.28 3.30 3.38 3.40 (2H)	Not observed due to the absorption of dimethylformamide (solvent)
(XIII)  (DMF)	3.27 3.29 3.31 3.38 3.40 3.42 (2H)	Not observed
(XIV)  ($CDCL_3$)	2.20-3.40 (12H) 3.25 3.27 3.31 3.38 3.40 3.42 (2H)	A very complicated multiplet (doublets become triplets) 6.67 $-COOCH_3$ (3H)
(XV)  ($CDCl_3$)	3.24 3.28 3.36 3.40 (2H)	This compound shows a complicated multiplets and was not appreciably soluble.
(XVI)  ($CDCl_3$)	2.20-3.46 (12H) 3.30 3.32 3.34 3.42 3.44 3.46 (2H)	A very complicated set of complex multiplets was observed, which made difficult to label signals (see NMR spectrum No. 2)

Compound and solvent	Aromatic proton τ (ppm)	Other proton τ (ppm)
(XVII)  (CDCl$_3$)	2.18-3.39 (12H)	4.71 4.94 4.99 5.22 4.96 -CH$_2$ (4H) attached to naphthalene rings.
	3.25 3.27 3.37 3.39 (2H)	7.05 -CH$_2$ (4H, aliphatic)
		8.25 -CH$_2$ (6H, aliphatic)
(XVIII)  (CDCl$_3$)	1.9-3.39 (12H)	4.79 5.03 5.12 5.36 5.07 -CH$_2$ (4H) attached to naphthalene rings.
	3.25 3.27 3.37 3.39 (2H)	7.06 7.19 7.29 7.42 7.24 -CH$_2$ (4H) attached to methyl groups.
		8.75 8.87 8.99 CH$_3$ (6H)

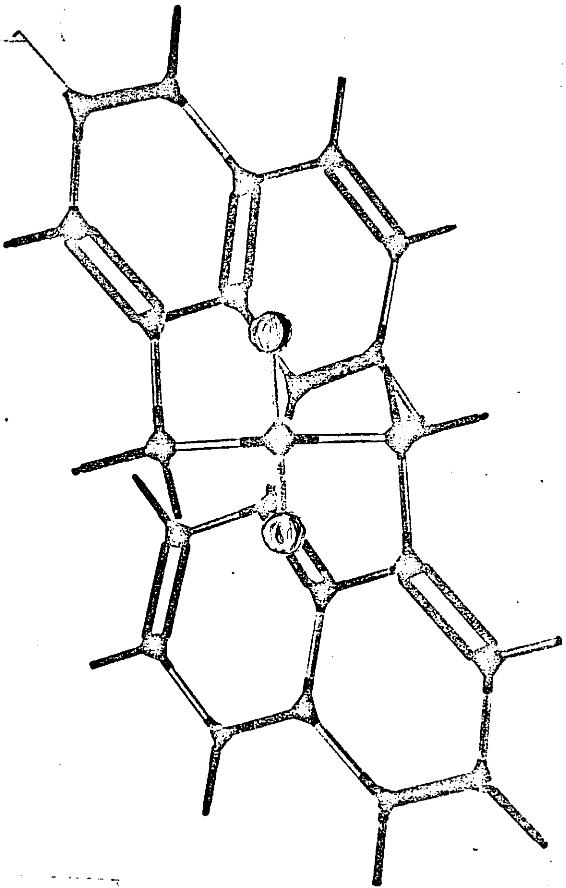
Discussion of the NMR spectra in Table I

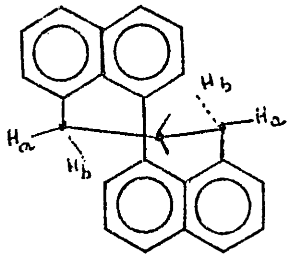
(Roman numerals in parentheses refer to Table I)

(i) Shielding: A comparative study of NMR characteristics of mono and disubstituted naphthalenes, 8-substituted and 8,8'-disubstituted-1,1'-binaphthyls has shown that the groups in the 8,8'-positions of 1,1'-binaphthyl are shielded. In compound (I) the methoxycarbonyl protons show a sharp singlet at τ 6.3 but the same protons in compound (III) resonate at 7.33. Similarly for compound (IV) a single signal for methylene (attached to naphthalene ring) protons appeared at 5.17, but when the two units of (IV) are joined to make the 8,8'-disubstituted 1,1'-binaphthyl system (V) the methylene protons resonate upfield at 6.03. Shielding is also observed in going from (VI) to (VII), and in the latter compound there is the additional feature that the singlet of (VI) at 5.30 is replaced in (VII) by a quartet centred at 5.94 ppm. Dixon, Harris and Mazengo (1971) observed the methyl-proton resonance in NMR spectra of some mono- and disubstituted methyl 1,1'-binaphthyls. In 8-methyl-1,1'-binaphthyl, the methyl group is held above the plane of the opposite naphthalene ring which causes long-range shielding for the methyl proton to resonate upfield (τ 8.32) in comparison with 1-methylnaphthalene (7.47). The steric repulsion between substituents in the 8,8'-positions and naphthalene rings is enhanced by a second methyl group and reduces the long-range shielding by opposite naphthalene rings a little (8.25). In 2,2'-dimethyl-1,1'-binaphthyl, the methyl proton resonates upfield compared with 2-methylnaphthalene, again showing the presence of long-range shielding of the methyl protons by the opposite naphthalene rings, but long-range shielding in this molecule is less than that for the 8,8'-dimethyl compound. The difference between the chemical shifts of 2,2'-dimethyl-1,1'-binaphthyl and 2-methylnaphthalene is 0.42, whereas that between 8,8'-dimethyl-1,1'-binaphthyl and 1-methylnaphthalene is 0.78; this suggests that each methyl group in the 2,2'-dimethyl compound is farther away from the opposite naphthalene ring centre than in 8,8'-dimethyl compound. From this data, with some assumptions, the average dihedral angles for 2,2'-dimethyl and 8,8'-dimethyl compounds are calculated to be 85-90° and 55-60° respectively (Dixon, Harris and Mazengo, 1971).

(ii) Equivalence and non-equivalence: Methylene protons in unbridged 8,8'-disubstituted 1,1'-binaphthyls (V, VII, VIII) are diastereotopic and they should in principle show observable geminal coupling, but in compound (V) the non-equivalence was not detectable and the geminal methylene protons appeared as a single signal. In compounds (VII) and (VIII) these diastereotopic geminal methylene protons appeared as a quartet at room temperature (J= 11 cps) and (J= 10 cps) respectively in 60MHz spectra. The non-equivalence of methylene protons in the 8,8'-positions in the ethyl ester of 1,1'-binaphthyl-8,8'-diacetic acid also was not observable. The methylene protons in this ester (IX) resonated at τ 6.75 as averaged singlet.

In all 8,8'-bridged 1,1'-binaphthyls the diastereotopic geminal methylene protons Ha and Hb in compounds (X) to (XVIII) were observed to be spin coupling non-equivalent. 8,8'-Bridged 1,1'-binaphthyls with a twofold axis of symmetry (C_2) show large J values, for example the compound (X) shows $J = 14$ cps as centered at τ 6.47. Such a large





(Fig 1.)

separation of peaks was expected as can be seen from the model (Fig. 1) that the environments of the diastereotopic geminal methylene protons are remarkably different. Each Ha is in the plane of a naphthalene ring and must be de-shielded, while Hb is pointing to the second naphthalene ring and must be comparatively shielded due to the long-range shielding effect, thus as a result they show~~ing~~ a large difference in chemical shifts (see spectrum No. 1)

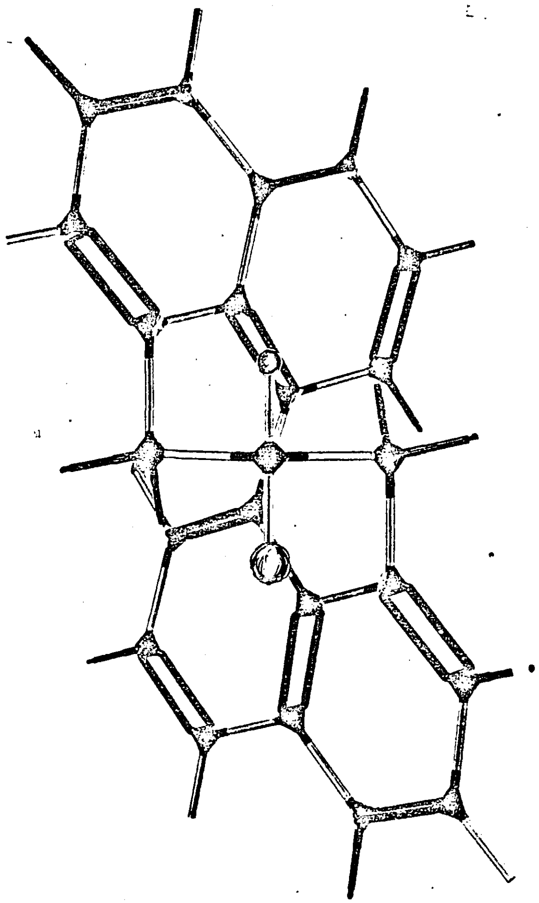
Effect of replacing one group by hydrogen atom on bridge (central carbon atom): The observed spin coupling non-equivalence of geminal methylene protons must be a function of angle φ ($\angle$HCH) as well as of their different chemical shifts. Karplus (1963) extended this concept to vicinal protons, considering the dihedral angles instead of $\angle$HCH of geminal protons: he emphasises the difficulties involved. The introduction of a hydrogen atom instead of one -COOEt (or other group) substituent increases the complexity of molecule. It also therefore increases the complexity of the spectrum (see spectrum No. 2). To solve such NMR spectrum and to describe the placement of each new peak some other parameters (distances and angles) will be needed; the spectrum would depend on all of these parameters in some specific ways.

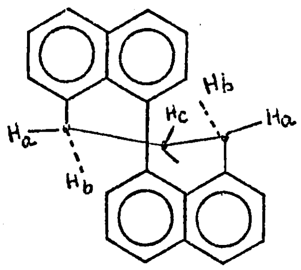
For tetrahedral bond angles and normal bond distances, the vicinal coupling constant is given by

$$J_{vic} = A + B\cos\varphi + C\cos 2\varphi$$

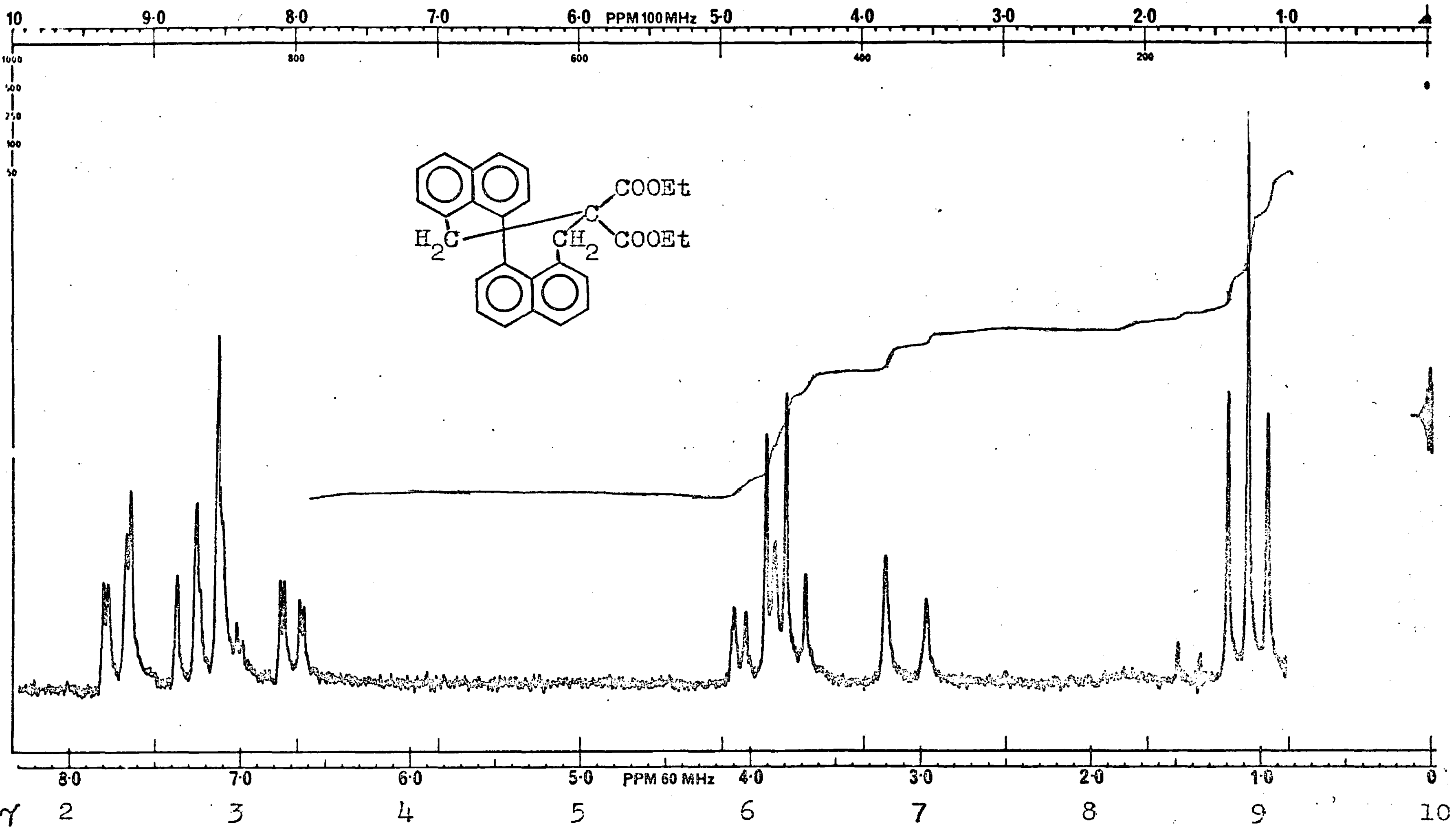
where $A = 4$cps, $B = -\frac{1}{2}$cps and $C = 9/2$cps. Karplus (1963) explains that the close values of constants A and C signify that the coupling will be small when $\varphi = 90^\circ$ and large when $\varphi = 0^\circ$ or 180°. The negative sign of B implies $J_{vic}(180^\circ) > J_{vic}(0^\circ)$. Thus $J_{vic}(0^\circ)$ and $J_{vic}(180^\circ)$ are positive.

The introduction of proton Hc at the central atom of the bridge incorporating the 8,8'-positions of 1,1'-binaphthyl gives a compound (Fig. 2) which belongs to point group (C_1): we have a situation with added vicinal coupling, making the spectrum more complicated than with only geminal coupling (see for example spectrum No. 2). There are a larger number of parameters involved than in a compound of point group (C_2), but at

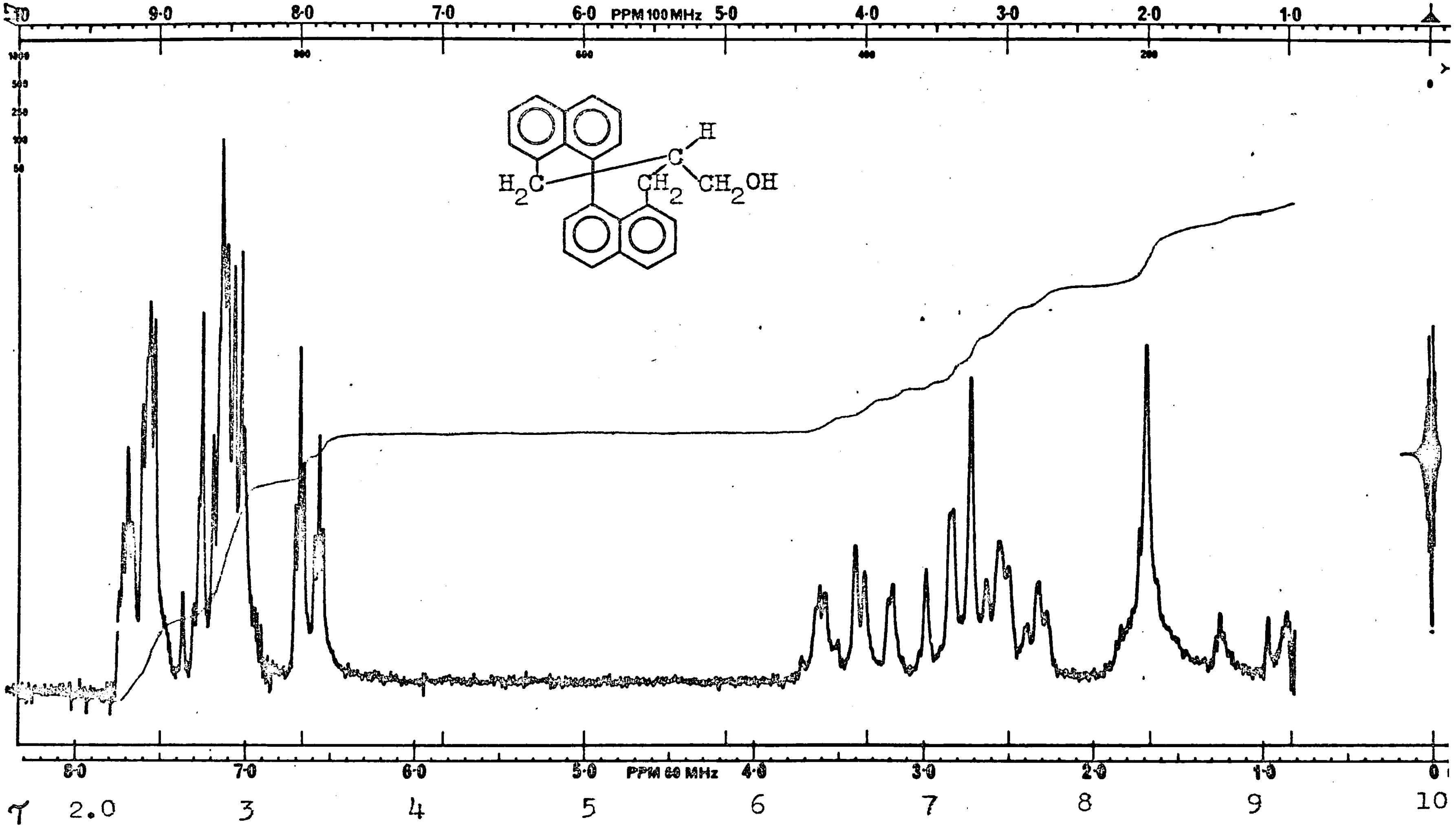




(Fig. 2.)



NMR SPECTRUM No.1

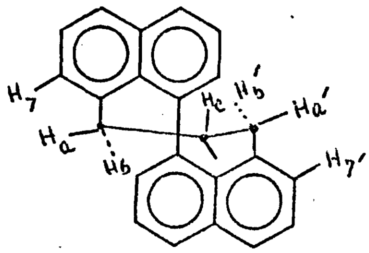


NMR SPECTRUM No. 2.

present it is not certain in what ways.

(iii) Aromatic Protons: Splitting of binaphthyl aromatic protons was observed in two well separated complex multiplets for unbridged 8,8'-disubstituted 1,1'-binaphthyls. On the other hand the splitting of binaphthyl aromatic protons in 8,8'-bridged compounds was found to be into three complex groups of multiplets in the integrated ratio of 2:3:1 (4H, 6H and 2H). One group of multiplets for two protons was observed in between τ 3.2-3.45 for all the 8,8'-bridged 1,1'-binaphthyls. 8,8'-Bridged 1,1'-binaphthyls with a twofold axis of symmetry (C_2), for example compound (X) show two doublets of nearly equal peak heights in this region corresponding two protons (see spectrum No.1). These doublets could be due to the coupling relationship between two non-equivalent protons Ha and Hb with the 7,7'- protons of 1,1'-binaphthyl system.

In the compounds belonging to point group (C_1) where one of the two substituents at the central carbon atom of the bridge is hydrogen Hc, the doublets (2H) for compounds belonging to point group (C_2) appeared as two triplets (1:2:1) (2H). The coupling constant is very small, roughly 1.5 cps. In these cases spin coupling interactions could be between the 7-proton and one non-equivalent. Ha, and two nearly equivalent protons, Hb and Hc.



Another observation was that the signals for aromatic protons, while still in three separated sets of multiplets, were rather more complicated than for compounds of point group (C_2). There is equivalence between pairs Ha, Ha', Hb, Hb' and H_7, $H_{7'}$ in molecules with C_2 symmetry (central bridging carbon atom carrying like substituents). When Hc replaces one substituent on the central carbon atom, there is C_1 symmetry and all the pairs lose equivalence. Proton Hc has an equal relationship with Hb' and Ha' (e,e) but a different relationship with the Ha and Hb methylene protons (a,e). All these factors together, and perhaps more, are responsible for the complications of the observed NMR spectrum.

2.5 Mass Spectra and Structure Elucidation

a. Introduction. The most important applications of mass spectroscopy to organic chemistry are to determine the molecular weight and to elucidate the molecular structure. On electron bombardment of a molecule M a number of processes may occur:

$$M + e^- = M^- \quad \ldots (1)$$

$$M + e^- = M^{\overset{+}{\cdot}} + 2e^- \quad \ldots (2)$$

$$M + e^- = M^{n+} + (n+1)e^- \ldots (3)$$

of which the (2) is the commonest. At high energy fragmentation can take place in various ways:-

$$ABCD + e^- \longrightarrow ABCD^{\overset{+}{\cdot}} + 2e^-$$

$$ABCD^{\overset{+}{\cdot}} \longrightarrow A^{\overset{+}{\cdot}} + BCD^{\cdot}$$

$$ABCD^{\overset{+}{\cdot}} \longrightarrow AB^{\overset{+}{\cdot}} + CD^{\cdot}$$

$$B^{\overset{+}{\cdot}} + A^{\cdot} \longleftarrow AB^{\overset{+}{\cdot}} \longrightarrow A^{\overset{+}{\cdot}} + B^{\cdot}$$

$$AD^{\overset{+}{\cdot}} + BC^{\cdot};\quad CD^{\overset{+}{\cdot}} + AB^{\cdot},\ \text{etc.}$$

In ~~an~~ applied magnetic and electric fields the positive ions with different mass-to-charge ratios can be separated and their m/e values and relative abundance measured. Corresponding to $[M]^{\overset{+}{\cdot}}$ the accurate molecular weight, and the rest of the fragmentation pattern give~~s~~ clues to elucidate the structure of the molecule.

When the rate of decomposition of the molecular ion to fragments is very fast, the ion will decompose before reaching the accelerating plate; the fragments of the molecular ion will be accelerated and recorded, therefore the spectrum would consist only of fragment ion peaks and no peak for the molecular ion.

As the ion takes about 10^{-6} sec. to reach the accelerating region and 10^{-4} sec. to become fully accelerated, a metastable transition could be observed in such a case where the half-life of the ion lies in between 10^{-6} to 10^{-4} sec., and the corresponding peak appears as a broad peak (hump) which can be recognised by careful inspection of the spectrum. The corresponding mass m^* for a metastable peak is related to the mass of the original ion m_1, and the mass of the product ion m_2 by the following equation

$$m^* = \frac{(m_2)^2}{m_1} .$$

b. Mass spectra, results and discussion

(1). Mass spectra of unbridged 8,8'-disubstituted 1,1'-binaphthyls:

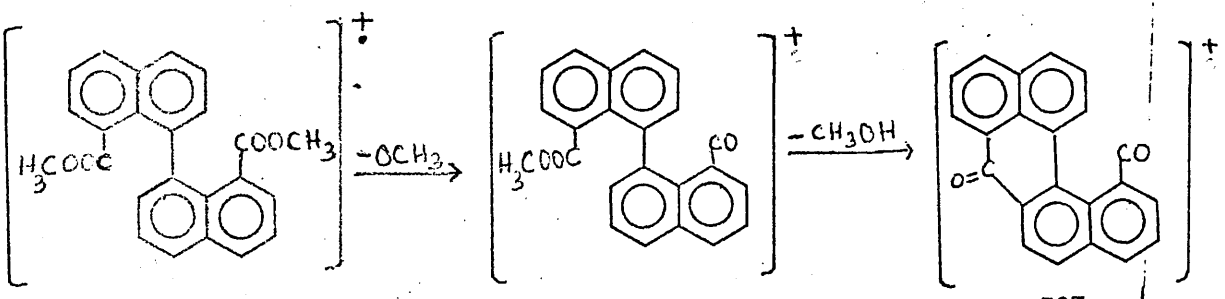
(i) Mass spectrum of 8,8'-bismethoxycarbonyl-1,1'-binaphthyl.

McLafferty and Gohlke (1959) suggested that in aromatic esters the principal ions arise by cleavage at the acyl bond or at the alkyloxy bond with rearrangement of one or two hydrogen atoms.

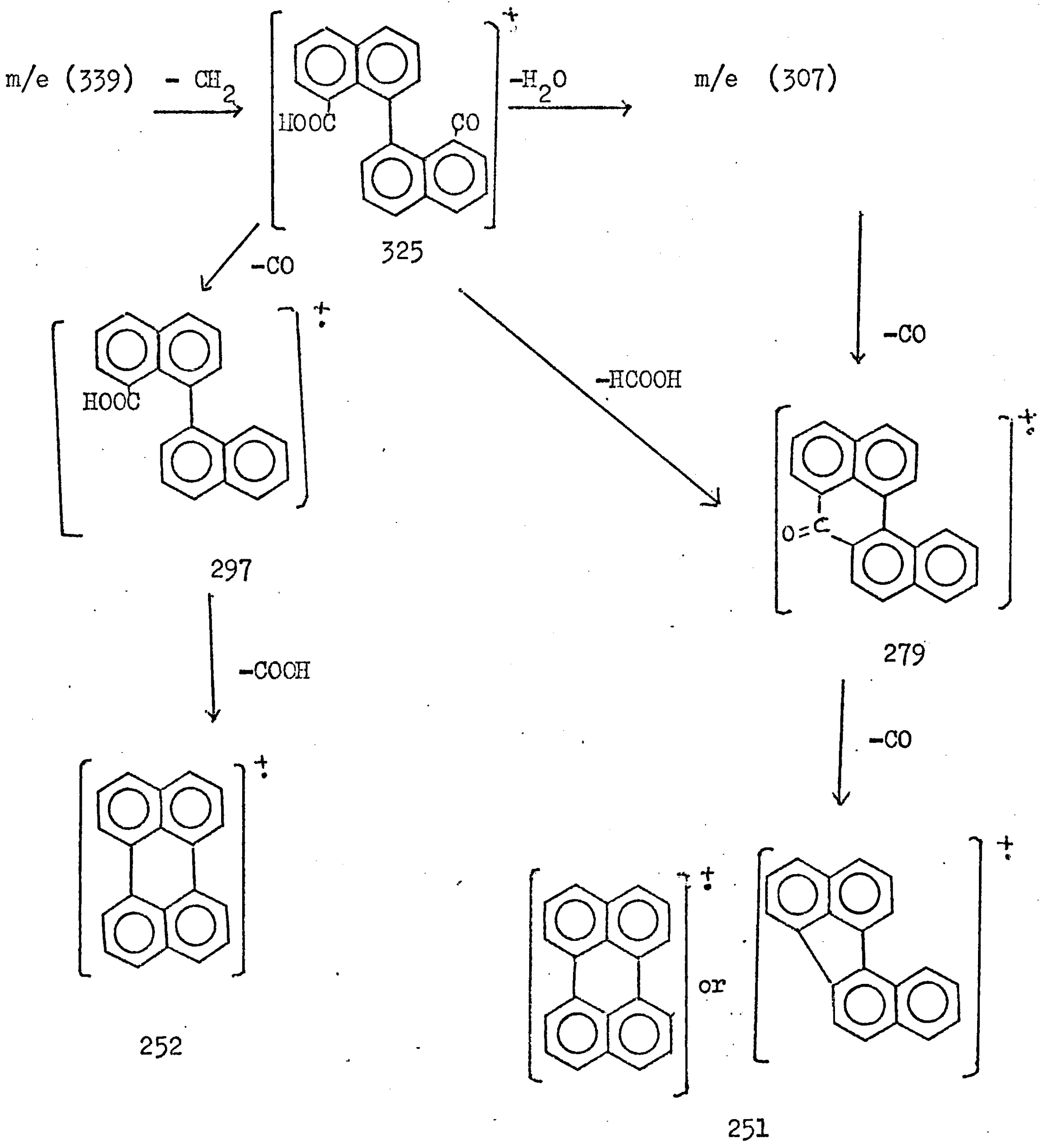
$$\overset{\dot{+}}{\mathrm{ArCO}} \wr \mathrm{OR} \longrightarrow \mathrm{ArC}\overset{+}{\mathrm{O}}{}^{\circ} + \mathrm{RO}^{\bullet}$$

$$\overset{+}{\mathrm{ArCO}}\text{—}\mathrm{OR} \longrightarrow \overset{\dot{+}}{\mathrm{ArCOOH}} + \mathrm{R(-H)}$$

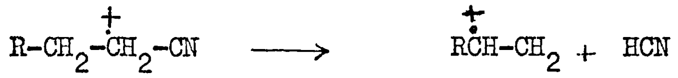
The mass spectroscopic determination of the molecular weights of the two crystal forms of 8,8'-bismethoxycarbonyl-1,1'-binaphthyl agrees with $C_{24}H_{18}O_4$ (see page 67); the molecular ion peak appeared at m/e 370 and the base peak at m/e 252. Badar, Cooke and Harris (1966) reported the formation of a six-membered ring keto-ester, by the treatment of 8,8'-bismethoxycarbonyl-1,1'-binaphthyl with sulphuric acid; the mass spectrum of the ester has also suggested the formation of this six-membered ring keto-ester (see below). No difference was observed between the spectra of the two crystalline forms. The following is a possible interpretation of the fragmentation pattern:



370 339 307

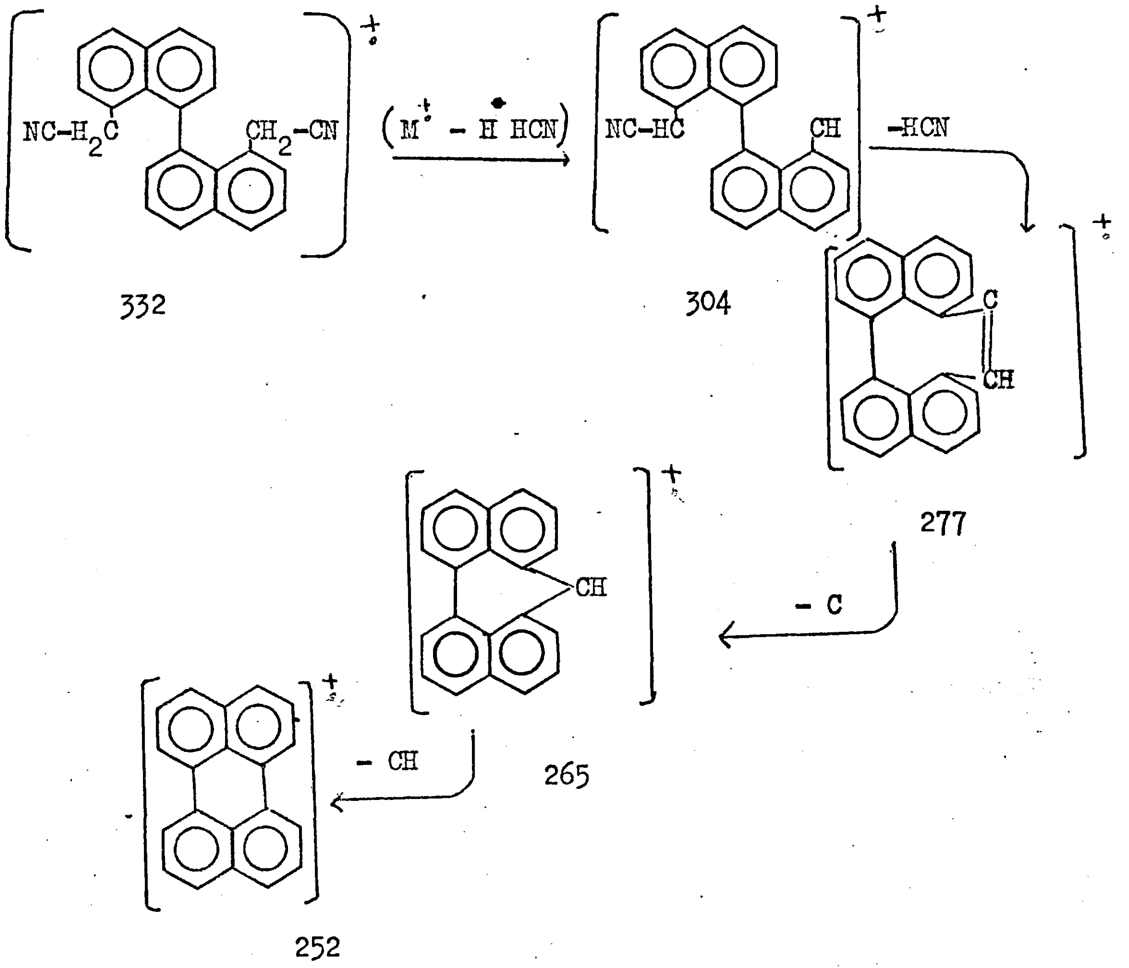

m/e (339)
- CH2
HOOC
CO
325
-H2O
m/e (307)
-CO
-HCOOH
-CO
HOOC
297
-COOH
252
O=C
279
-CO
or
251

(ii) Mass spectrum of 8,8'-biscyanomethyl-1,1'-binaphthyl. Aliphatic nitriles break usually at the α-bond with the accompanied transfer of a hydrogen atom.

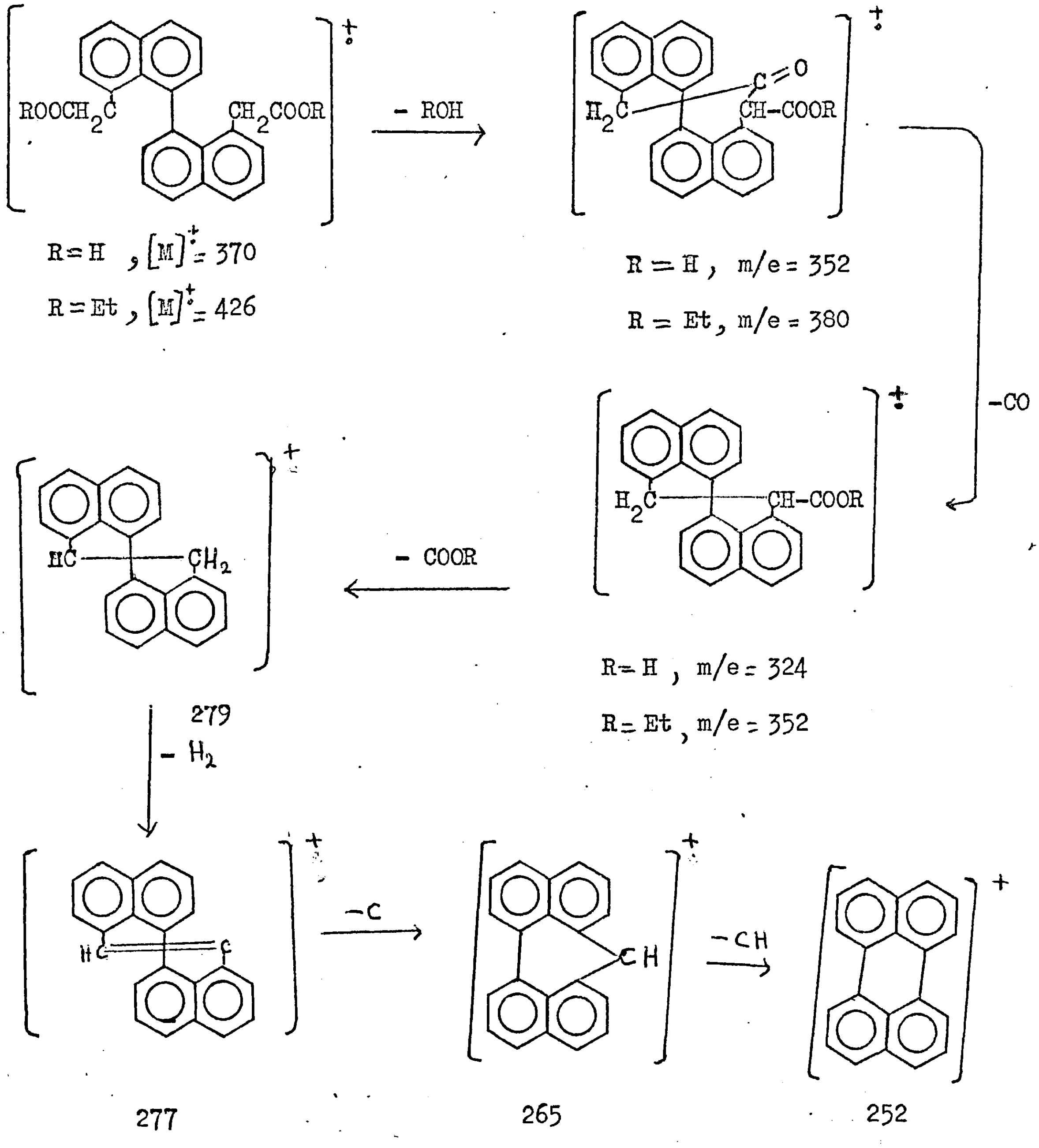


$$R\text{-}CH_2\text{-}\overset{+}{\dot{C}}H_2\text{-}CN \longrightarrow R\overset{+}{\dot{C}}H\text{-}CH_2 + HCN$$

For 8,8'-biscyanomethyl-1,1'-binaphthyl, the fragmentation of the molecular ion (100%) started with the elimination of a hydrogen atom and hydrogen cyanide molecule followed by the elimination of neutral hydrogen cyanide, giving m/e 277 (22%). The formation of a seven-membered ring in the fragmentation process was supported by the appearance of m/e 265. Proposed route of the fragmentation:



(iii) Mass spectrum of 1,1'-binaphthyl-8,8'-diacetic acid and its diethyl ester. The common fragments for these compounds give peaks at m/e 279, 277, 265 (100%) and 252. The appearance of peaks at m/e 352 for the acid (10) and at 380 for the diethylacetate (11) are the first decomposition fragments, correspond to the formation of a nine-membered ring system (see below) in the acid and diethylacetate respectively. An accurate determination of the mass of the molecular ion and of some other fragment ions occuring in the fragmentation of 1,1'-binaphthyl-8,8'-diacetic acid suggested the molecular formula $C_{24}H_{18}O_4$, which are fitted with the results obtained from elemental microanalysis (see page 72). A peak at m/e 352 for which mass measured 352.1092 fits the formula $C_{24}H_{16}O_2$ (calculated mass 352.1100). This peak correspond to a nine-membered ring keto-carboxylic acid incorporating the 8,8'-positions of 1,1'-binaphthyl system. There is a second peak at m/e 324 (mass measured 324.1158 and mass calculated 324.1150) fitting the formula $C_{23}H_{16}O_2$ corresponding to an eight-membered ring carboxylic acid. The third peak at 279, could be formed by the elimination of -COOH, fitting the formula $C_{22}H_{15}$ (mass measured 279.1171, mass calculated 279.1174). The next fragment occuring is after the elimination of a hydrogen molecule at m/e 277 with formula $C_{22}H_{13}$ (mass measured 277.1013, mass calculated 277.1017). This fragment loses one carbon atom giving a seven-membered ring hydrocarbon with 100% relative abundance for which the formula is $C_{21}H_{13}$ (mass measured 265.1017, mass calculated 265.1017). The next fragment ion formed is due to the elimination of a methine group leaving $C_{20}H_{12}$ a pentacyclic aromatic hydrocarbon (the most characteristic fragment in the 1,1'-binaphthyl series). A similar pattern for the diethyl acetate (11) was observed as shown in the following scheme:

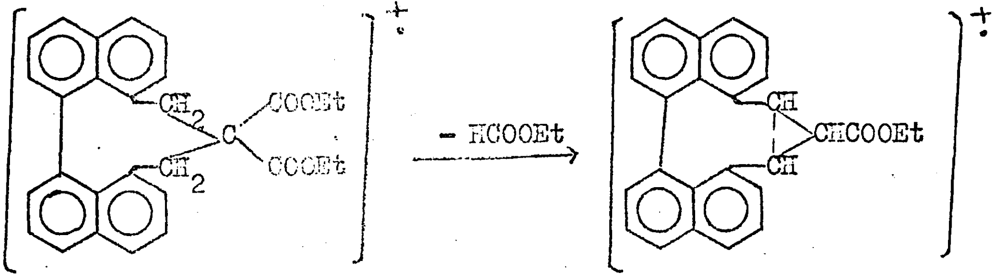


(2) Mass spectra of 8,8'-bridged 1,1'-binaphthyls:

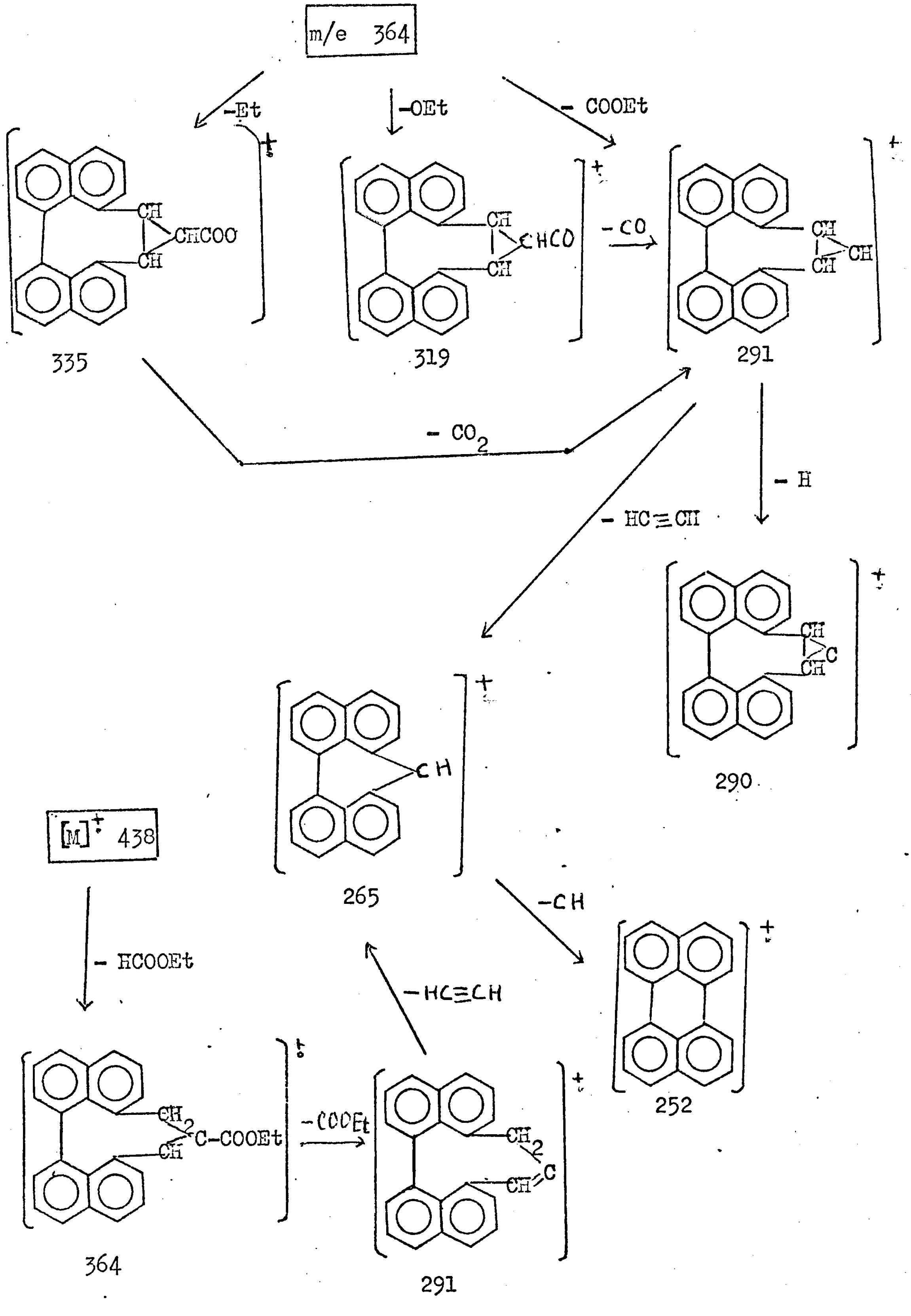
(i) Mass spectra of carbocyclic compounds

In the carbocyclic compounds the most common peaks appeared for m/e values of 291, 290, 279, 277, 265 and 252. The formation of a peak at m/e 291 in the carbocyclic compounds suggested that the bridging ring was very stable and the fragmentation of the ring system did not occur till the substituent groups at the central carbon atom of the bridging ring were completely eliminated; and in addition to this evidence there is the appearance of the doubly charged species (corresponding to m/e 290) which shows a peak at m/e 145, Bleankney (1930) has suggested that the removal of two or more electrons without resulting in fragmentation, is especially characteristic of compounds having a strong ring structure.

Mass spectrum of 8,8-diethoxycarbonyl [dinaphtho(8,1-ab, 1',8'-de)] - cyclonona-2,4-diene: A careful determination of molecular weight and m/e values for the fragment ions of this compound supported the presence of a nine-membered ring in the system. A suggested explaination of the abundance ratios of the fragment ions for this compound is:

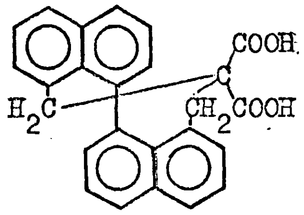


$[M]^{+\cdot} = 438$ 364

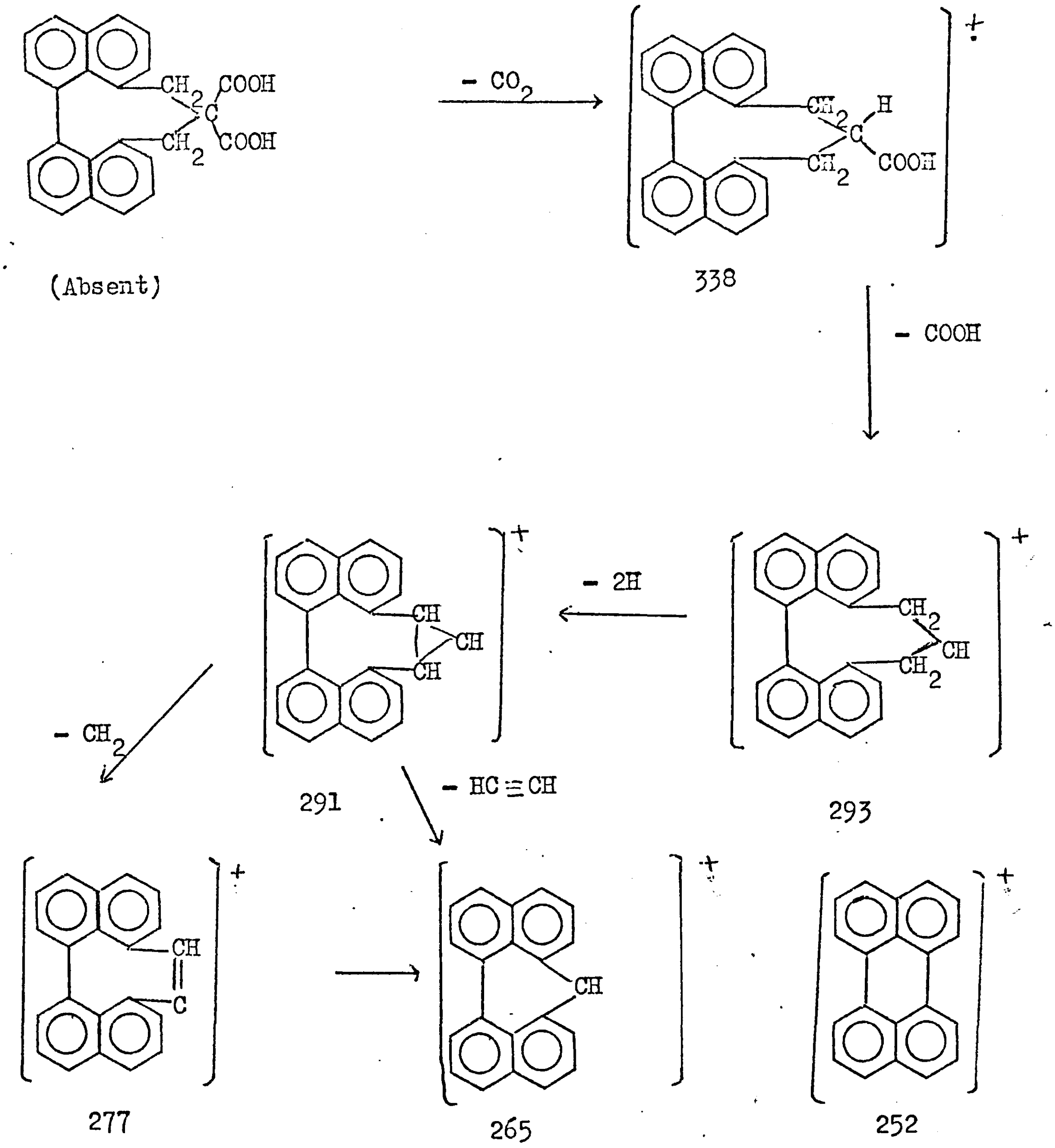

m/e 364
-Et
-OEt
- COOEt
CH
CHCOO
CH
CHCO
- CO
CH
CH
335
319
291
- CO2
- HC≡CH
- H
290
265
CH
C
[M]+ 438
- HCOOEt
-CH
252
-HC≡CH
CH2
C-COOEt
-COOEt
CH2
CH
C
364
291

The elimination of HCOOEt from the molecular ion is supported by the appearance of a metastable peak at m/e 302.5, i.e. $m^{*} = (364)^2/438$. The formation of the fragment ions m/e 364, 291, 265 and 252 were rechecked (High resolution mass measurement). The peak at m/e 364 corresponds to $C_{26}H_{20}O_2$ (mass measured 364.1470, mass calculated 364.1463). The most stable fragment in the process m/e 291, obtained after the elimination of carboethoxy groups which fits the formula $C_{23}H_{15}$ (mass measured 291.1172, mass calculated 291.1174). The next and most common fragments, found in all these new compounds at m/e 265, fits the formula $C_{21}H_{13}$ (mass measured 265.1011, mass calculated 265.1017). The next fragment the formation of a pentacyclic aromatic hydrocarbon $C_{20}H_{12}$ is supported by the mass measured 252.0929 (mass calculated 252.0939). This spectrum along with other evidence confirmed the proposed structure of this compound.

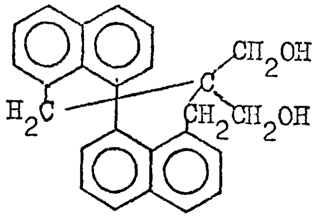
Mass spectrum of (14)



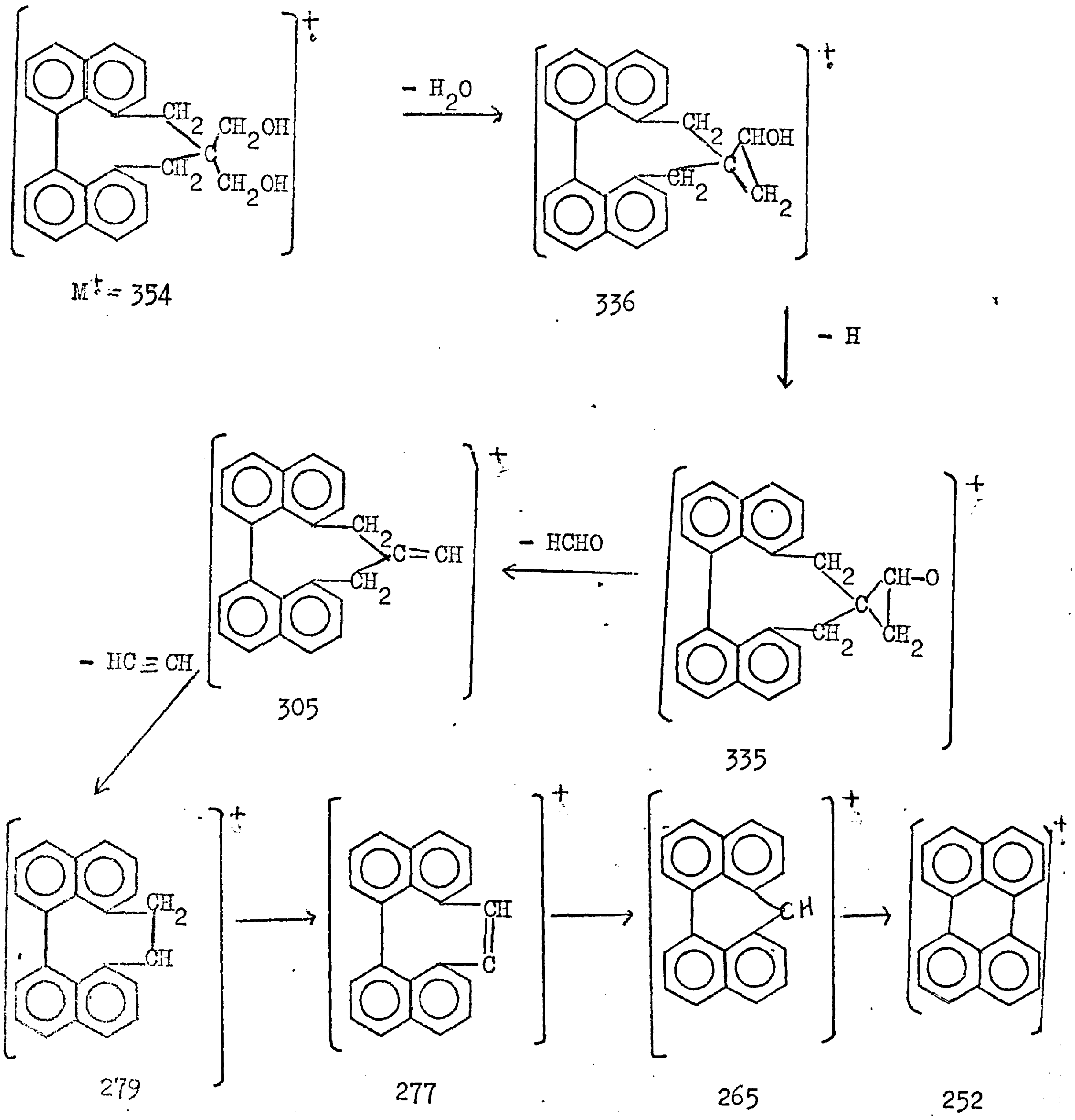
The mass spectrum was observed at 220° (see page 81) which is a sufficiently high temperature to decarboxylate this acid before the formation of the molecular ion, and to explain the reason for the absence of molecular ion peak at 380. The parent peak in the spectrum was the base peak at m/e 338; which determines the molecular weight of the monocarboxylic acid (15). The proposed route of fragmentation is:


CH$_2$
COOH
C
CH$_2$
COOH
(Absent)
- CO$_2$
CH$_2$
H
C
CH$_2$
COOH
338
- COOH
CH$_2$
CH
CH$_2$
293
- 2H
CH
CH
CH
291
- CH$_2$
- HC≡CH
CH
C
277
CH
265
252

Mass spectrum of (19)

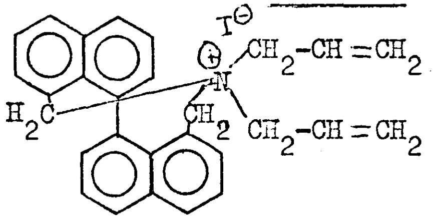


A suggested explaination of the abundance of the fragment ions for this compound is:



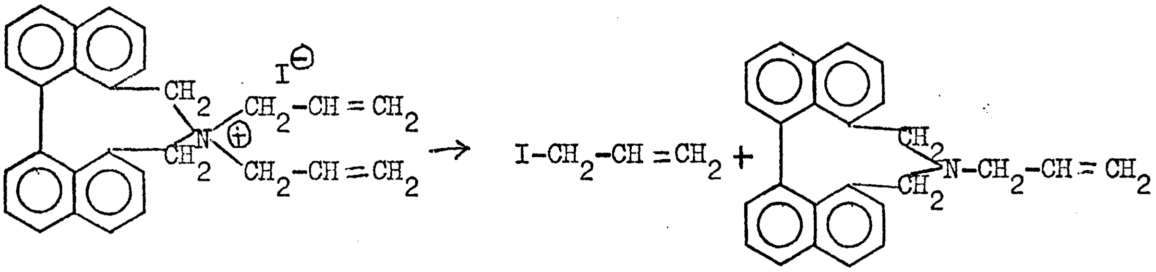
(ii) Mass spectrum of 8,8'-bridged N-heterocyclic compound:

Mass spectrum of 8,8-diallyl dinaphtho(8',1'-ab, 1",8"-de) -cyclonona-2,4-diene-8-azepinium iodide.

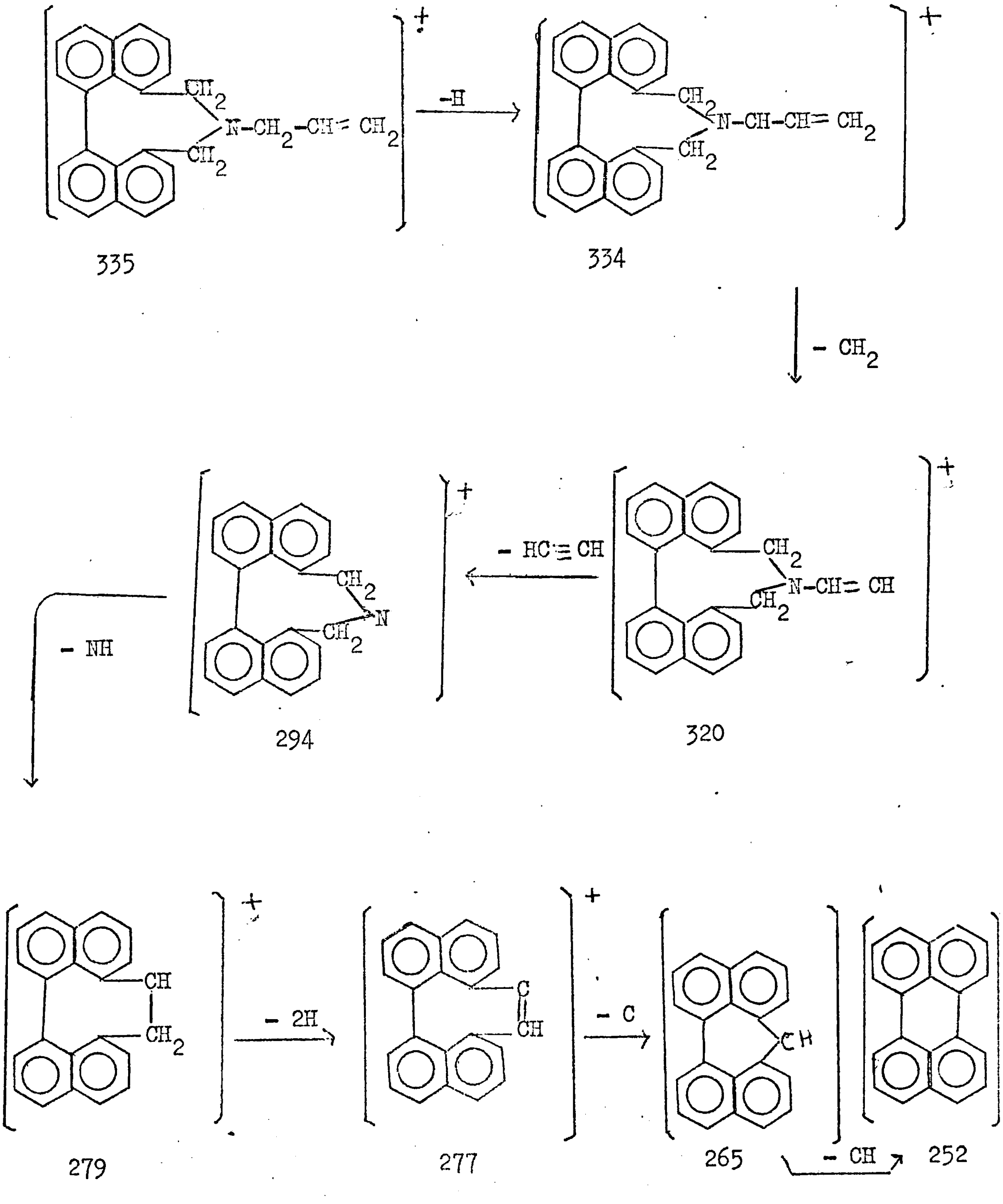


The mass spectrum of this compound did not show a peak at m/e 291 but showed 294 and 293 as expected for the replacement of a carbon atom by a nitrogen atom in the ring. The base peak was observed at m/e 41, probably allyl ion, as it has two equivalent resonance structures, which increases its stability. $H_2C=CH-CH_2^+ \longleftrightarrow -H_2\overset{+}{C}-CH=CH_2$

The next most abundant fragment ions are at m/e 168 (allyl iodide) and at m/e 335. The molecular weight of this compound was observed less by 168. This first ion peak in the spectrum is at m/e 335, the tertiary amine. So the fragmentation observed started from this tertiary amine,



a daughter molecular ion (m/e 335) which is α-branched, therefore the first most abundant fragment would be expected by the elimination of a hydrogen atom. The supposed fragmentation is:


CH2
N-CH2-CH= CH2
CH2
335
-H
CH2
N-CH-CH= CH2
CH2
334
- CH2
CH2
N-CH= CH
CH2
320
- HC≡CH
CH2
N
CH2
294
- NH
CH
CH2
279
- 2H
C
CH
277
- C
CH
265
- CH
252

2.6 Experimental: Syntheses

Preparation of 8,8'-bisbromomethyl-1,1'-binaphthyl

(Badar, Cooke and Harris, 1965)

Purification of 1,8-naphthalic anhydride

Commercial 1,8-naphthalic anhydride (200 g) was dissolved in 2.5% aqueous sodium hydroxide solution by heating in a stainless steel beaker and filtered. The filtrate was boiled with decolourising charcoal and kept hot for one hour and filtered. The filtrate was boiled and acidified while hot with dilute hydrochloric acid; the precipitated acid anhydride was filtered off, washed with water and dried. Crystallisation from acetic anhydride gave long needles (188 g), m.p. 272-273°. It showed no change in appearance before it melted.

Mercuration of 1,8-naphthalic anhydride

(Rule and Barnett, 1932)

Purified 1,8-naphthalic anhydride (188 g) was dissolved by heating in 2.5% aqueous sodium hydroxide and filtered into a 20 litre flask using a glasswool plug. The filtrate was heated under reflux for 15 min. Mercuric oxide (208 g, red) was dissolved in glacial acetic acid (151 ml) and water (560 ml). The mercuric acetate solution was added to the boiling solution of naphthalic acid solution, the reaction mixture was made acidic by the addition of glacial acetic acid and heating under reflux continued for about 100 hours, swirling from time to time, during which carbon dioxide came off. The completeness of reaction was checked by dipping a shining copper wire into the reaction mixture, and finding no mercury deposition; a test portion with sodium hydroxide gave a clear solution. The reaction product was cooled, filtered, washed with water, ethanol and finally with ether and dried. The cream coloured product weighed 305 g (87%).

Preparation of 8-bromo-1-naphthoic acid

(Rule and Barnett, 1932)

The mercuri-compound (95 g) was suspended in 300 ml of glacial acetic acid and 50 ml of water. The mixture was stirred mechanically and cooled down to -10° in a solid carbon dioxide/acetone bath. The brominating solution was prepared by adding 11 ml of bromine in 150 ml of 50% aqueous sodium bromide solution; this was added dropwise to the mecuri-compound keeping the temperature below 0°; then the reaction mixture was allowed to warm to room temperature and heated to 90°, poured into three litres of boiling water and filtered quickly. The bromo acid, precipitated out on cooling, was filtered off, washed with water and dried. The procedure was repeated with the rest of mercuri-compound. Crystallisation from benzene gave 68% yield, m.p. 173-174°.

Preparation of 8-bromo-1-methoxycarbonylnaphthalene

(Rule, Pursell and Brown, 1934)

8-Bromo-1-naphthoic acid (75 g) was dissolved in 510 ml of benzene by heating under reflux and freshly distilled thionyl chloride (23 ml) added dropwise. The reaction mixture was boiled under reflux for 4.5 hours, cooled, freshly prepared anhydrous methanol (75 ml) was added dropwise and boiling under reflux continued for an additional hour. The reaction mixture was cooled, washed with water, with aqueous sodium carbonate and finally with water. The benzene layer was dried over calcium chloride and the benzene distilled off. A syrupy residue obtained was distilled between 156-160°/1 mm. The distillate was stirred in an ice bath and gave a colourless solid which on crystallisation from petroleum ether (b.p. 40-60°) gave 55 g of the ester (73% yield), m.p. 35-36°.

Preparation of 8,8'-bismethoxycarbonyl-1,1'-binaphthyl

(Cooke and Harris, 1963)

8-Bromo-1-methoxycarbonylnaphthalene on Ullmann reaction at 200°, with copper bronze gave 8,8'-bismethoxycarbonyl-1,1'-binaphthyl. It crystallised from ethanol in two crystalline forms, plates and prisms as previously described (Cooke and Harris, 1963).

The first crystalline form: plate, melted at 156-158° if taken slowly, but when the m.p. was determined in an apparatus preheated up to 140°, it melted at 145-147°. The second crystalline form: prism, melted at 156-158^{6}, no change observed if the m.p. was taken in a preheated apparatus.

IR spectrum (nujol mull): a sharp strong band at 1700 cm^{-1} confirmed the presence of carbonyl groups in both forms of the ester.

The NMR spectra of these two forms observed in $CDCl_3$ solution at room temperature did not show any differences, and exhibited a complex multiplet between 2.03-2.85 ppm (12H, aromatic) and a singlet at τ 7.33 (6H, methoxycarbonyl) for these forms.

Mass spectra: mass measured for plates, 370.1204; for prisms, 370.1206. $C_{24}H_{18}O_4$ requires 370.1205. The relative abundances obtained for these two forms show small differences for the same values of m/e, and are shown below (Ion source, 180°; Trap current, 100μA)

m/e	Relative abundance (%)		m/e	Relative abundance (%)	
	Plates	Prisms		Plates	Prisms
370	97	80	251	12	11
339	6	5	250	25	24
311	6	7	168	4	5
307	33	32	127	17	20
279	26	27	125	22	22
254	4	5	115	11	12
253	24	25	28	11	17
252	100	100			

Preparation of 8,8'-bishydroxymethyl-1,1'-binaphthyl

(Badar, Cooke and Harris, 1965)

Powdered lithium aluminium hydride (1.5 g) was suspended in 400 ml of anhydrous diethyl ether in a well dried three-necked flask fitted with a dropping funnel, stopper and a water condenser fitted with calcium chloride tube at the top. A solution of 8,8'-bismethoxycarbonyl-1,1'-binaphthyl was added slowly using a dropping funnel to the refluxing suspension of lithium aluminium hydride. After the complete addition of ester, boiling under reflux was continued for four hours and cooled; the excess of reagent was decomposed by using wet ether, a little water and finally with dilute sulphuric acid. The ethereal layer was washed with water, dried over anhydrous sodium sulphate and ether distilled off. The residue was dissolved in hot benzene from which it crystallised on cooling. The crystalline diol was heated at 100° for two hours in a vacum drier to remove benzene of crystallisation. Yield 3.5 g (88.8%), m.p. 151-152°.(lit., 151-152°).

Preparation of 8,8'-bisbromomethyl-1,1'-binaphthyl

(Badar, Cooke and Harris, 1965)

8,8'-Bishydroxymethyl-1,1'-binaphthyl was dissolved in warm acetic acid and hot hydrobromic acid added to it with vigorous stirring; a gum like product was obtained. The method was then modified.

(a) The diol (1 g) was dissolved in a little glacial acetic acid by warming and an equivalent amount of acetic anhydride added. Warm hydrobromic acid (18 ml) was added slowly to the vigorously stirred solution; a violent exothermic reaction occured during which special care was needed. When the yellow solid started separating the remainder of the hydrobromic acid was added all at one time and the reaction mixture stirred for another 15 min. It was poured quickly in to an ice-water mixture, stirred, the solution decanted, the solid washed several times with water, filtered and dried in an evacuated desiccator. Crystallisation from chloroform gave shining yellow powder 1.2 g (86%), m.p. 191-192° (lit., 191-192°).

(b) The diol (5 g) was added in small portions at room temperature to magnetically stirred phosphorous tribromide (25 g, 6 mole) in a 100 ml round bottom flask fitted with a calcium chloride tube. The reaction was vigorous. After the addition was complete, stirring was continued for another 15 min. The reaction mixture was poured into a vigorously stirred ice-water mixture and the precipitated yellow solid was filtered, washed several times with water, aqueous sodium bicarbonate and finally with water and dried. Crystallisation from chloroform gave shining yellow powder 7 g (99%), m.p., 191-192°.

The NMR spectrum in $CDCl_3$ solution exhibited a complex multiplet at τ 2.1-2.80 (12H, aromatic) and a (1:4:4:1) quartet at 5.74, 5.90, 5.99, 6.15 centered at 5.94 (4H, methylene).

Preparation of new 8,8'-disubstituted 1,1'-binaphthyls

Preparation of 8,8'-biscyanomethyl-1,1'-binaphthyl (9)

8,8'-Bisbromomethyl-1,1'-binaphthyl (7.3 g, 1 mole) was suspended in 100 ml of 95 per cent ethanol and added over a period of two hours to a refluxing solution of potassium cyanide (2.6 g, 2.4 mole) in 6 ml of water and 17.3 ml of ethanol. During the addition of bisbromomethyl compound the colour of the reaction turned to brick red. After an additional three hours of heating under reflux, the solution was cooled, diluted with water to complete the precipitation of the product, filtered, washed with water and dried. Crystallisation from benzene gave dark red crystals 4.5 g (77.5%), m.p., 218-223°d.; using an apparatus preheated at 220°, m.p. 230-232°.

(Found: C, 86.4; H, 4.8; N, 8.5. $C_{24}H_{16}N_2$ requires C, 86.7; H, 4.8; N, 8.4%).

IR spectrum (nujol mull): a sharp band at 2250 cm^{-1} confirms the presence of nitrile groups ($-C\equiv N$ stretching, 2240-2260 cm^{-1} (sharp), Bellamy, 1957).

NMR spectrum in $CDCl_3$ solution at room temperature; a complex multiplet between τ 2.00-2.75 (12H, aromatic) and a (1:4:4:1) quartet centered at τ 5.96 (4H, methylene).

Mass spectrum: mass measured 332.1313; calculated for $C_{24}H_{16}N_2$, 332.1314. The relative abundances of the fragments are

m/e	R.A. (%)	m/e	R.A. (%)	m/e	R.A. (%)
333	26	304	43	263	13
332	100	302	13	252	30
331	51	292	17	250	8
330	8	291	13	152	6
317	4	290	21	151	6
316	4	289	13	139	17
315	4	277	21	138	21
307	8	276	13	131	13
306	21	266	13	83	13
305	26	265	39		

333 represents M+1; its presence is due to ^{15}N.

Preparation of 1,1'-binaphthyl-8,8'-diacetic acid (10)

8,8'-Biscyanomethyl-1,1'-binaphthyl (5 *g*) was suspended in ethanol and heated under reflux and 100 ml of 50% aqueous ethanolic potassium hydroxide solution added; heating was continued until the evolution of ammonia gas ceased. The reaction mixture was cooled, the solid salt was dissolved in water, and the solution boiled with decolourising charcoal and filtered. The filtrate was acidified with 3N hydrochloric acid to precipitate the 8,8'-diacetic acid which was filtered off, washed with water and dried. The acid obtained was greyish white in colour; it was dissolved in boiling methanol, treated with decolourising charcoal and filtered. Colourless crystals appeared, 4.5 *g* (81.8%), m.p. 320°*d*. (Found: C, 77.7; H, 5.0; O, 17.2. $C_{24}H_{18}O_4$ requires C, 77.8; H, 4.9; O, 17.3%).

The IR spectrum (nujol mull) shows a strong band at 1700 cm^{-1} consistent with the presence of a carboxylic acid group.

NMR spectrum: unfortunately this acid is not appreciably soluble in chloroform and carbon tetrachloride; NMR spectra were observed in dimethylformamide and in dimethylsulphoxide but could not give reliable information about the molecule because of their own signals in the regions of interest.

Mass spectrum; mass measured 370.1195; calculated for $C_{24}H_{18}O_4$ 370.1205. The relative abundances of fragments are:

m/e	R.A. (%)	m/e	R.A. (%)	m/e	R.A. (%)
370	28	279	56	263	16
352	8	278	24	253	8
326	8	277	28	252	20
325	10	276	20	239	8
324	14	267	20	140	8
323	8	266	36	139	24
281	12	265	100	138	24
280	16	264	12		

Accurate determination of the mass of the molecular ion and of some other fragment ions:

Measured mass	Possible formulae	Calculated mass
370.1195	$C_{24}H_{18}O_4$	370.1205
352.1092	$C_{24}H_{16}O_2$	352.1100
324.1158	$C_{23}H_{16}O_2$	324.1150
279.1171	$C_{22}H_{15}$	279.1174
277.1013	$C_{22}H_{13}$	277.1017
265.1017	$C_{21}H_{13}$	265.1017
252.0941	$C_{20}H_{12}$	252.0939

Preparation of diethyl 1,1'-binaphthyl-8,8'-diacetate (11)

1,1'-Binaphthyl-8,8'-diacetic acid (1 g) was dissolved in 100 ml of anhydrous benzene (dried over calcium chloride) by heating under reflux. Freshly distilled thionyl chloride (0.5 ml) was added to the boiling benzene solution and heating under reflux continued for another three hours; the mixture was cooled and absolute ethanol (5 ml),added dropwise. After a further hour of heating, the reaction mixture was cooled, washed with water. The separated benzene layer was dried over calcium chloride and distilled off. The residue was cooled in an ice bath while stirring. A yellow crude product obtained was dissolved in hot ethanol, boiled with decolourising charcoal and filtered. From the concentrated filtrate the diethyl ester crystallised, 1 g (87%), m.p. 95-96°. (Found: C, 78.7; H, 6.1; 0,15.0.$C_{28}H_{26}O_4$ requires C,79.0 ; H, 6.1; 0, 15.0%).

The IR spectrum (nujol mull) shows a strong band at 1740-1725 cm^{-1} as expected for an ethoxycarbonyl group (Bellamy, 1957).

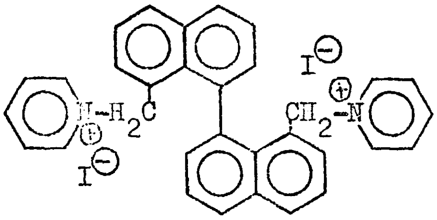
The NMR spectrum in $CDCl_3$ solution at room temperature, shows a complex multiplet at τ 2.00-3.00 isolated in two groups for 4H and 8H (aromatic). A singlet at 6.75 (4H, methylene protons attached to naphthalene rings), a (1:3:3:1) quartet centered at τ 6.36 (4H, methylene protons of ethoxycarbonyl groups) and a (1:2:1) triplet centered at 8.94 (6H, methyl protons of the ethoxycarbonyl groups).

Mass spectrum: mass measured 426.1820, $C_{28}H_{26}O_4$ requires 426.1831. Relative abundances of fragment ions are given below. There is a metastable transition at 339.

m/e	R.A. (%)	m/e	R.A. (%)	m/e	R.A. (%)
426	6	324	5	276	19
381	5	323	23	266	16
380	13	305	11	265	100
354	3	280	13	264	8
353	11	279	54	252	11
352	24	278	46	239	5
351	5	277	43	139	8

$$339 = \frac{(380)^2}{426}$$

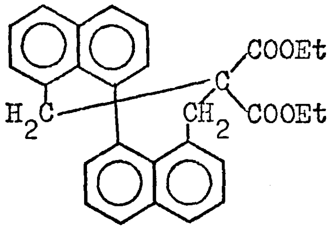
Preparation of 1,1'-binaphthyl-8,8'-bis(methylenepyridinium) diiodide (12)



8,8'-Bisbromomethyl-1,1'-binaphthyl (1 g) was added to an excess of hot anhydrous pyridine (dried over potassium hydroxide), stirring magnetically. With in a few minutes a solid appeared. The reaction mixture was cooled, filtered and washed with light petroleum (b.p. 40-60°); it quickly absorbed water from the atmosphere. It was dissolved in water in which it is very soluble and boiled with decolourising charcoal, filtered and the filtrate was concentrated, but the salt did not crystallise out. A hot aqueous solution of potassium iodide was added, and on concentration the iodide precipitated, which was again dissolved in water, boiled with decolourising charcoal, and filtered. Crystallisation from the filtrate afforded yellow crystals 1.4 g (87.5%) of the dihydrate, m.p., loses water around 165° and decomposes at 196°. (Found: C, 52.9; H, 4.2; N, 3.8; I, 34.8; O, 4.3 (by difference). $C_{32}H_{26}N_2I_2.2H_2O$ requires C, 52.8; H, 4.2; N, 3.8; I, 34.8; O, 4.3%).

The IR spectrum (nujol mull) shows a band at 3500-3420 cm^{-1}, which is consistent with the presence of water of crystallisation and explains the change in appearance when taking the melting point.

Preparation of 8,8-diethoxycarbonyl [dinaphtho(8,1-ab, 1',8'-de)]-cyclonona-2,4-diene (13)



8,8'-Bisbromomethyl-1,1'-binaphthyl (4.12 g, 0.047 mole) was suspended in dioxan (10 ml) in a well dried three-necked flask, fitted with a dropping funnel, a stopper and a water condenser and stirred magnetically. Sodioethylmalonate, prepared in a dried and stoppered flask by dissolving 0.64 g of freshly cut sodium metal in 40 ml of absolute ethanol and adding it to the diethylmalonate (2.06 g, 0.07 mole) was added dropwise to the magnetically stirred dioxan suspension at room temperature. The reaction mixture was heated under reflux with occasional swirling for three hours and cooled down to room temperature, when the reaction mixture contained a solid. Water was added to complete the precipitation of the product, which was filtered, washed with water and dried. The crude product was dissolved in benzene by boiling, treated with decolourising charcoal and filtered. Crystallisation from the filtrate gave 4.8 g (96%), m.p. 263-264°.

(Found: C, 79.3; H, 5.9; O, 14.7. $C_{29}H_{26}O_4$ requires C, 79.4; H, 6.0; O, 14.6%).

Molecular weight (Mechrolab Osmometer, in benzene solution) found 437.7; required, 438.

The IR spectrum (hexachlorobutadiene mull), shows a sharp strong band at 1715 cm^{-1}, as expected for ethoxycarbonyl groups, and 3050, 3030, 2990, 2975 (strong), 2950, 2930, 2890 cm^{-1} for CH, CH_2 and CH_3 stretchings.

The NMR spectrum in $CDCl_3$ solution at room temperature exhibited a very complicated multiplet between τ 2.15-3.38 (12H, aromatic) in three isolated sets. An octet, mixture of two quartets, analysed by comparing with compound (17) ; one quartet (1:2:2:1) centered at τ 6,47 (4H, methylene protons attached to naphthyl residues) and another quartet (1:3:3:1) centered at τ 6.16 (4H, methylene proton of ethoxycarbonyl groups), and a triplet (1:2:1) centered at 8.94 (6H, methyl protons of ethoxycarbonyl groups).

Mass spectrum: mass measured 438.1826; $C_{29}H_{26}O_4$ requires 438.1831. The relative abundances for the fragment ions are:

m/e	R.A. (%)	m/e	R.A. (%)	m/e	R.A. (%)
438	81	292	31	266	25
365	3	291	100	265	37
364	6	290	50	252	12
335	12	289	62	145	6
320	6	278	19	78	18
319	25	277	37	44	31
318	18	276	37	32	50

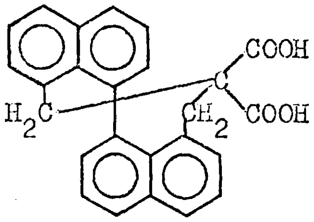
There is a metastable peak at 302.5 $\cong (364)^2/438$.

Accurate determination of masses of some fragment ions:

Measured mass	Possible formulae	Calculated mass
364.1470	$C_{26}H_{20}O_2$	364.1463

Measured mass	Possible formulae	Calculated mass
291.1172	$C_{23}H_{15}$	291.1174
265.1011	$C_{21}H_{13}$	265.1017
252.0929	$C_{20}H_{12}$	252.0939

Preparation of [dinaphtho(8,1-ab, 1',8'-de)]-cyclonona-2,4-diene-8,8-dicarboxylic acid (14)



The diethyl ester (13) (6 g) was placed in a 500 ml round bottomed flask fitted with a water condenser and heated under reflux with 50 ml of ethanol. Ethanolic potassium hydroxide (40 ml) was added and heating under reflux continued for three hours with magnetic stirring. The potassium salt came out during the reaction. The mixture was cooled and the potassium salt was dissolved in water, boiled with decolourising charcoal and filtered. The filtrate was cooled down and acidified with cold dilute hydrochloric acid to precipitate the diacid (14), filtered, washed with water and dried in an evacuated desiccator; m.p. 235-236° with a brisk effervescence, solidifying and remelting at 252-254°. Yield 4.8 g (92.3%).

(Found: C, 74.9; H, 5.0; O, 19.8. $C_{25}H_{18}O_4.H_2O$ requires C, 75.0; H, 5.0; O, 20.0%).

The effervescence observed between 235-236° and subsequent solidification can be explained by decarboxylation and loss of a molecule of water of crystallisation.

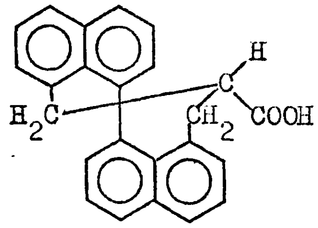
IR spectrum (hexachlorobutadiene mull): a sharp strong band at 1700 cm^{-1} as expected for carboxyl group, a broad band at 3500 cm^{-1} for water molecule.

NMR spectrum: This acid is not soluble in chloroform or carbon tetrachloride; the best solvents are ethanol and dimethylformamide. To locate the presence of shielded aromatic protons the spectrum was run in NN-dimethylformamide, the two sets of doublets appeared at τ 3.28, 3.30; 3.38, 3.40 (2H, aromatic).

Mass spectrum: mass measured 338.1301, this is too small for the acid prepared but the result fits the formula $C_{24}H_{18}O_2$ for the decarboxylated acid (15), mass calculated 338.1307. The mass spectrum was observed at 220° with a trap current 70 eV; the result is consistent with the easy decarboxylation of the diacid (14). The relative abundances of the fragment ions are

m/e	R.A. (%)	m/e	R.A. (%)	m/e	R.A. (%)
380	absent	276	31	152	6
338	100	266	37	145	22
337	6	265	56	138	30
293	25	264	12	132	12
292	21	263	15	131	16
291	30	252	21	123	12
289	15	250	5	119	6
279	12	239	6	112	5
278	18	224	5	44	68
277	37	165	9	29	16

Preparation of [dinaphtho(8,1-ab, 1',8'-de)] -cyclonona-2,4-diene-8-carboxylic acid (15)

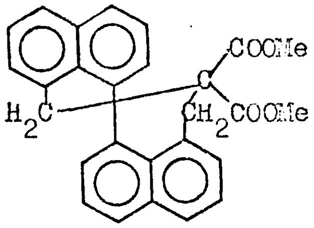


The cyclic dicarboxylic acid (14), (4 g) was heated in a hard glass tube immersed in a metal bath at 230-240° for 15 min., when the diacid started melting, a brisk effervescence was observed and after that it again solidified and remelted; it was cooled, dissolved in 2.5% aqueous sodium hydroxide solution and filtered. The filtrate was boiled with decolourising charcoal, filtered. The filtrate was acidified with 3N hydrochloric acid to precipitate the acid (15), filtered, washed with water and dried. Yield 3.0 g (85.7%), m.p. 252-254°.
(Found: C, 85.1; H, 5.4; O, 9.3. $C_{24}H_{18}O_2$ requires C, 85.2; H, 5.3; O, 9.4%).

The IR spectrum (KBr disc) shows a sharp band at 1700 cm^{-1} as expected for the carboxylic group .

NMR spectrum; this acid is not appreciably soluble in chloroform or carbon tetrachloride; the best solvents for it are ethanol and NN-dimethylformamide. To locate the presence of shielded aromatic protons the spectrum was run in NN-dimethylformamide, and the two sets of triplets (1:2:1); one at τ 3.27, 3.29 and 3.31 and another at τ 3.38, 3.40 and 3.42 were observed in place of two doublets in the diacid.

Preparation of 8,8-dimethoxycarbonyl-[dinaphtho(8,1-ab, 1',8'-de)] - cyclonona-2,4-diene (17)

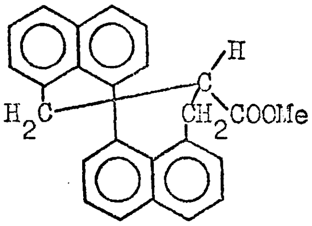


The cyclic dicarboxylic acid (1 g) was added to a cold ethereal solution of freshly prepared diazomethane (0.3 g) with continuous swirling; when the effervescence was over the ethereal solution was washed with aqueous sodium carbonate and finally with water. The ethereal layer was dried over anhydrous sodium sulphate and distilled off. Crystallisation from benzene gave 1 g of the ester (92.6%), m.p. 258-260°. (Found: C, 78.9; H, 5.2; O, 15.7. $C_{27}H_{22}O_4$ requires C, 79.0; H, 5.3; O, 15.6%).

IR spectrum (nujol mull): a sharp strong band at 1720 cm^{-1} as expected for methoxycarbonyl groups.

NMR spectrum: The NMR spectrum was observed in $CDCl_3$ solution at room temperature. It exhibited a complex multiplet from τ 2.16-3.38 (12H, aromatic) in three isolated sets of multiplets. One set is shielded and appears in two sets of doublets, each set corresponding to one proton. There is a singlet at τ 6.64 (6H, methoxycarbonyl protons) and a (1:2:2:1) quartet centered at τ 6.46 (4H, methylene protons attached to naphthalene rings).

Preparation of 8-methoxycarbonyl-[dinaphtho(8,1-ab, 1',8'-de)]-cyclonona-2,4-diene (16)



The cyclic monocarboxylic acid (15), (3 g), was suspended in anhydrous benzene (100 ml) in a well dried three-necked round bottomed flask fitted with a dropping funnel, stopper, and a water condenser carrying a calcium chloride tube, and heated under reflux (it did not dissolve). Freshly distilled thionyl chloride (1 ml) was added dropwise to the magnetically stirred benzene suspension of the acid (15), and the whole heated under reflux for three hours; the solution became clear, was cooled, 5 ml of freshly prepared anhydrous methanol added and the mixture heated under reflux for another 30 min.; it was cooled, washed thrice with water, thrice with aqueous sodium carbonate and finally with water (1.5 g of the acid was recovered). The benzene layer was dried over calcium chloride and benzene distilled off. The brown residue was stirred in light petroleum (b.p. 40-60°), a greyish white solid filtered off. Crystallisation from ethyl acetate/ethanol gave 1.4 g (90%), m.p. 186-188°.

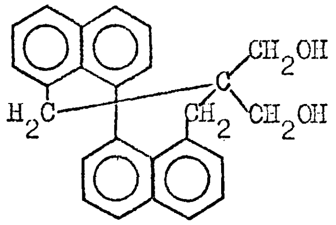
Molecular weight determined in the Mechrolab Osmometer using ethyl acetate as a solvent: found 351, required 352.

(Found: C, 85.1; H, 5.7; O, 9.2. $C_{25}H_{20}O_2$ requires C, 85.2; H, 5.7; O, 9.1%).

IR spectrum (nujol mull), a strong band at 1728 cm^{-1} is in accord with the expected band for methoxycarbonyl group.

The NMR spectrum observed in $CDCl_3$ solution at room temperature has shown characteristic complicated multiplets between 2.20-3.40 (12H, aromatic) and a sharp singlet at τ 6.67 (3H, methoxycarbonyl protons)

Preparation of 8,8-bishydroxymethyl-[dinaphtho(8,1-ab, 1',8'-de)]-cyclonona-2,4-diene (19)



Lithium aluminium hydride (0.5 g) was placed in a well dried three-necked round bottomed flask, fitted with a dropping funnel, stopper and a dried water Jacketted condenser carrying a calcium chloride tube, and 250 ml of anhydrous diethyl ether added. The lithium aluminium hydride suspension was heated under reflux, stirring magnetically. The powdered diethyl ester (1 g) suspended in 100 ml of anhydrous diethyl ether, was added over a period of 30 min. and heating continued for 5 hours: after cooling the excess pf reagent was destroyed by adding a few drops of water and 50 ml pf dilute sulphuric acid and then heated under reflux for another 30 min.; during this period the reaction mixture became clear, and was then cooled. The ethereal layer was separated, washed with water and dried over anhydrous sodium sulphate and ether distilled off. Crystallisation from benzene gave colourless needles 0.6 g (75%), m.p. 196°.

(Found: C, 84.6; H, 6.3: O, 9.0. $C_{25}H_{22}O_2$ requires C, 84.7; H, 6.3; O, 9%).

The IR spectrum (hexachlorobutadiene mull) shows a strong band at 3340 cm^{-1} as expected for the presence of a hydroxyl group and at 3060, 3050, 3000, 2960, 2950 (sharp), 2920, 2890 (sharp and strong), 2860 and

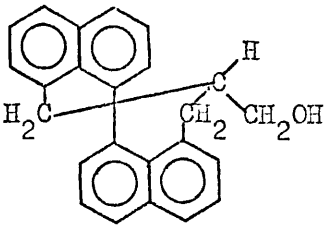
2790 cm^{-1} for CH and CH_2 and aromatic CH stretching.

The NMR spectrum: this diol is not appreciably soluble in chloroform or carbon tetrachloride, and therefore integration was not satisfactory. The shielded aromatic protons appeared in two sets of doublets at 3.24 and 3.28 and another at 3.36 and 3.40 as is characteristic of these cyclic compounds.

Mass spectrum: mass measured 354.1615; calculated for $C_{25}H_{22}O_2$ 354.1620. The relative abundances for the ions involved in the fragmentation

m/e	R.A. (%)	m/e	R.A.(%)	m/e	R.A. (%)
355	27	280	11	165	2
354	100	279	44	153	5
336	2	278	17	145	3
335	2	277	29	138	3
317	5	267	29	83	7
305	19	265	12	44	2
291	12	252	14	28	22
290	12	239	2	18	13
289	27				

Preparation of [dinaphtho(8,1-ab, 1',8'-de)] -cyclonona-2,4-diene-8-carbinol (18)

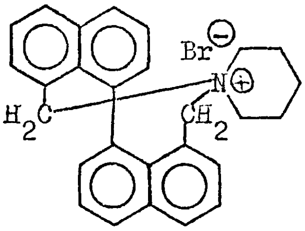


The cyclic monomethyl ester (16), (3 g), was placed in a well dried Soxlet extractor, and 0.75 g of powdered lithium aluminium hydride was suspended in 1000 ml of anhydrous diethyl ether in the dried three-necked two litre round bottomed flask below; the apparatus was then heated under reflux for three hours, stirring magnetically. The excess of the reagent was decomposed by treatment with wet ether, a little water, and dilute sulphuric acid; heating was continued for another hour and then the mixture cooled. The ethereal layer was washed with water, dried over anhydrous sodium sulphate and ether distilled off. The crude product was dissolved in cyclohexane and boiled with decolourising charcoal, filtered and crystallised from the filtrate, m.p. 47-49°. The elemental analysis showed that the desired compound was not pure, so it was recrystallised from chloroform, m.p. 74-76°. Yield, 2.7 g (92.6%). (Found: C, 88.6; H, 6.3: O, 5.0. $C_{24}H_{20}O$ requires C, 88.8; H, 6.2; O, 4.9%).

The IR spectrum (hexachlorobutadiene mull) shows 3600 (weak), 3350 cm^{-1} (broad) bands as expected for the presence of hydroxyl group.

The NMR spectrum determined in $CDCl_3$ solution at room temperature, exhibits two sets of triplets for shielded aromatic protons (see NMR spectrum No. 2).

Preparation of [dinaphtho(8',1'-ab, 1",8"-de)]-cyclonona-2,4-diene-8-azepinium-1-spiro-[5,8]tetradecane-1"'-piperidinium bromide (20)



8,8'-Bisbromomethyl-1,1'-binaphthyl (5 g, 1 mole) was dissolved in 50 ml of chloroform and a solution of piperidine (2.3 ml, 2 mole) in chloroform (50 ml) added dropwise while stirring magnetically. The reaction mixture was warmed to 50° over a water bath and kept at this temperature for 90 min. It was cooled and ether added to precipitate the bromide, which was filtered off and dried by suction. The crude product, 5 g, was dissolved in water, boiled with decolourising charcoal and filtered. The filtrate was concentrated and the bromide crystallised out, 4.6 g (67.6%), m.p. 280-290°d., melted at 314-316° in an apparatus preheated to 300°.

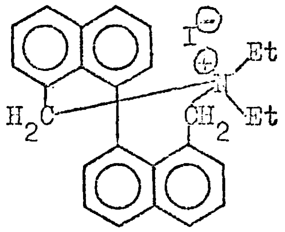
(Found: C, 72.8; H, 5.9; N, 3.1; Br, 18.0. $C_{27}H_{26}NBr$ requires C, 73.0; H, 5.9; N, 3.1; Br, 18.0%).

The IR spectrum (hexachlorobutadiene mull) shows bands at 3040, 3010 (strong), 2990, 2980, 2970, 2940 (broad), 2900 (weak), 2860 cm^{-1} for CH, CH_2 atretching.

The NMR spectrum in $CDCl_3$ solution at room temperature exhibited a complicated multiplet from 2.18 to 3.39 (12H, aromatic), separated into three complex sets of multiplets. Two doublets centered at 3.26 and 3.38, each with a separation of less than 0.1 ppm are characteristic of the cyclic system.

A quartet centered at 4.96 (4H, methylene protons attached to naphthalene rings). A broad singlet at τ 7.05 (4H, piperidine) and another broad singlet at τ 8.25 (6H, piperidine).

Preparation of 8,8-diethyl [dinaphtho(8,1-ab, 1',8'-de)] -cyclonona-2,4-diene-8-azepinium iodide (21)

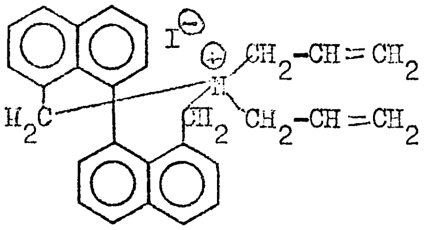


8,8'-Bisbromomethyl-1,1'-binaphthyl (4 g, 1 mole) was dissolved in anhydrous benzene by heating. Freshly distilled diethylamine (1.08 g, 2.2 mole) was added over 20 min. to the magnetically stirred benzene solution of the bisbromomethyl compound. Precipitation of the bromide salt was completed by adding petroleum ether (b.p. 40-60°); it was filtered by suction, but quickly absorbed water from the atmosphere. It was dissolved in water in which it is very soluble and boiled with decolourising charcoal, filtered and the filtrate concentrated, but the salt did not crystallise out. A hot aqueous solution of potassium iodide was added, and on concentration the iodide precipitated, which was again dissolved in water, boiled with decolourising charcoal and filtered. Crystallisation from the filtrate afforded the monohydrate in needles 4 g (88.8%) had m.p. 210-212°; it changes its appearance between 155-160°. (Found: C, 62.7; H, 5.7; N, 2.9; O, 3.2; I, 25.4. $C_{26}H_{26}NI.H_2O$ requires C, 62.8; H, 5.7; N, 2.8; O, 3.2; I, 25.5 %).

The IR spectrum (hexachlorobutadiene mull) shows band between 3500-3450 (broad) indicating the presence of water and explaining the change in appearance when taking the melting point.

The NMR spectrum in CDCl$_3$ solution at room temperature exhibited three isolated sets of multiplets at 1.9 to 3.39 (12H, aromatic). A quartet centered at τ5.07 (4H, methylene attached to naphthalene rings), another quartet centered at τ7.24 (4H, methylene protons) and a triplet (6H, methyl protons).

Preparation of 8,8-diallyl-[dinaphtho(8,1-ab, 1',8'-de)] -cyclonona-2,4-diene-8-azepinium iodide (22)



8,8'-Bisbromomethyl-1,1'-binaphthyl (2 g, 1 mole) was dissolved in dried (calcium chloride) benzene by heating and freshly distilled diallylamine (1 g, 2.2 mole) was added while stirring magnetically. The reaction mixture was heated under reflux for 30 min., after 10 min. a solid appeared. The reaction mixture was cooled, petroleum ether (b.p. 40-60°) added to complete the precipitation, and filtered. The solid bromide was dissolved in water in which it is very soluble and boiled with decolourising charcoal, filtered, and the filtrate was concentrated, but the bromide failed to crystallise out. A hot aqueous solution of potassium iodide was added and on concentration the iodide precipitated out, which was again dissolved in water, boiled with decolourising charcoal and filtered. Crystallisation from the concentrated filtrate afforded long needles, 1.6 g (72.7%), m.p. 182-184°. (Found: C, 66.6; H, 5.2; N, 2.7; I, 25.7. $C_{28}H_{26}NI$ requires C, 66.8; H, 5.2; N, 2.8; I, 25.3%). Further gravimetric determination of iodine, 25.2%.

The IR spectrum (hexachlorobutadiene mull) shows bands at 3080, 3040, 3000 (strong), 2980 (weak), 2940, 2890 (weak) for CH and CH_2 stretching.

This compound dissolves in chloroform at room temperature and then immediately precipitates out from this solution, and does not dissolve again; thus we failed to observe the NMR spectrum.

Mass spectrum: mass measured for the second peak 334.1593; calculated for $C_{25}H_{20}N$ 334.1596. 335 could be a tertiary base. We could not work on it further due to its unpleasant physiological properties. The parent peak in the spectrum at m/e 335 is explained by the elimination of one molecule of allyl iodide (m/e 168) before the rest of the fragmentation started, leaving $C_{25}H_{21}N$. The relative abundances for the respective ions are

m/e	R.A. (%)	m/e	R.A. (%)	m/e	R.A. (%)
335	30	277	22	147	3
334	23	276	17	146	3
320	3	266	7	142	5
306	3	265	17	139	5
295	3	264	5	138	5
294	13	263	13	134	6
293	13	252	6	132	8
292	7	250	3	127	6
291	5	208	53	41	100
290	5	194	3	39	46
280	8	168	83		
279	22	166	19		
278	8				

8,8-Diallyl [dinaphtho(8',1'-ab, 1",8"-de)]-cyclonona-2,4-diene-8-azepinium iodide (20) was sent to Chester Beatty Research Institute, Institute of Cancer Research: Royal Cancer Hospital, London, S.W.3, (Dr. T.A.Connors). It was tested for tumour inhibiting properties. The report follows:

TUMOUR: R_1 Lymphoma

Cell Innoculum ..... 1.9 10^6. Site of Transplant ..... s.c. (inguinal).

Sex & Strain of Mice ..... ♀ CBA/LAC

Vehicle..... Arachis oil. Route of injections ..... i.p.

Dosage Schedule ...... Single dose.

Maximum effective dose...-... Minimum effective dose .....-.

Dose mg/Kg	Number of animals	Days of Treatment	Days of death	Range of days of death	Average	% Increase in survival time over control
control	10	-	9,9,9,9,9, 9,9,10,10,11	9-11	9.4	-
25	5	3	5,9,9,9,9	5-9	8.2	-12.8
50	5	3	5,5,6,6,6	5-6	5.6	-40.4
100	5	3	4,4,4,4,4,	4	4.0	-57.4
200	5	3	4,4,4,4,4.	4	4.0	-57.4
400	5	3	4,4,4,4,4.	4	4.0	-57.4
800	5	3	4,4,4,4,4.	4	4.0	-57.4

At doses as low as 50 mg/Kg, deaths are due to drug toxicity. At 25 mg/Kg, however, there is one early death due to drug toxicity while the remaining four deaths are due to the tumour. Under these conditions the compound exerts no anti-tumour effect. It is a compound which is very toxic.

3. OPTICAL WORK

3.1 Introduction to Preparative Optical Work

The present work includes two classes of new optically active compounds:

a. Unbridged 8,8'-disubstituted 1,1'-binaphthyls

b. 8,8'-Bridged 1,1'-binaphthyls

A brief summary of preparative optical work is shown in the schemes on the following pages.

a. Unbridged 8,8'-disubstituted 1,1'-binaphthyls

(i) Optically active 1,1'-binaphthyl

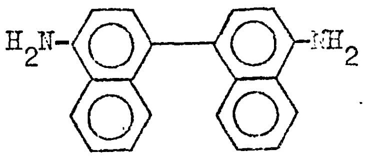
(Harris and Mellor, 1961; Cooke and Harris, 1963)

Optically active 1,1'-binaphthyl was prepared by using the method of Cooke and Harris (1963) from the optically active $(+)_{578}$-1,1'-binaphthyl-4,4'-diamine. The 4,4'-naphthidine was obtained optically active following the procedure of Theilacker and Hopp (1959). The 1,1'-binaphthyl is optically labile, therefore special precautions were taken to prevent loss of optical activity. Higher values of optical rotation, in various solvents, were found than before; in benzene $[\alpha]_{578}$ was $+268^{\circ}$ ($[\alpha]_{578}$ $+245^{\circ}$, Cooke and Harris, 1963). In tetrahydrofuran $[\alpha]_{578}+107^{\circ}$ ($[\alpha]_{589}+104^{\circ}$, Akimoto, Iitaka, Shioiri and Yamada, 1968). In ethanol $[\alpha]_{578}+223^{\circ}$, however, if the binaphthyl was dissolved at room temperature and the rotation read as quickly as possible, $[\alpha]_{578}$ was $+203^{\circ}$.

Scheme a. Unbridged 8,8'-disubstituted 1,1'-binaphthyls

(i) Optically active 1,1'-binaphthyl

(Harris and Mellor, 1961; Cooke and Harris, 1963)

(±)- 

+ 2(Ammonium-(+)-bromocamphor-π-sulphonate)

↓

(+)-4,4'-Naphthidine(ammonium-(+)--bromocamphor-π-sulphonate)

$\downarrow$ Ammonium hydroxide

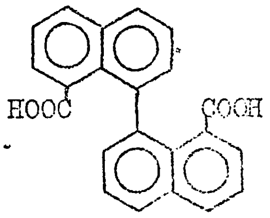
(+)-4,4'-Naphthidine + 2(Ammonium-(+)-bromocamphor-π-sulphonate)

(+)-4,4'-Naphthidine $\xrightarrow[\text{(ii) Hypophosphorous acid}]{\text{(i) HCl/NaNO}_2}$ (+)-1,1'-Binaphthyl

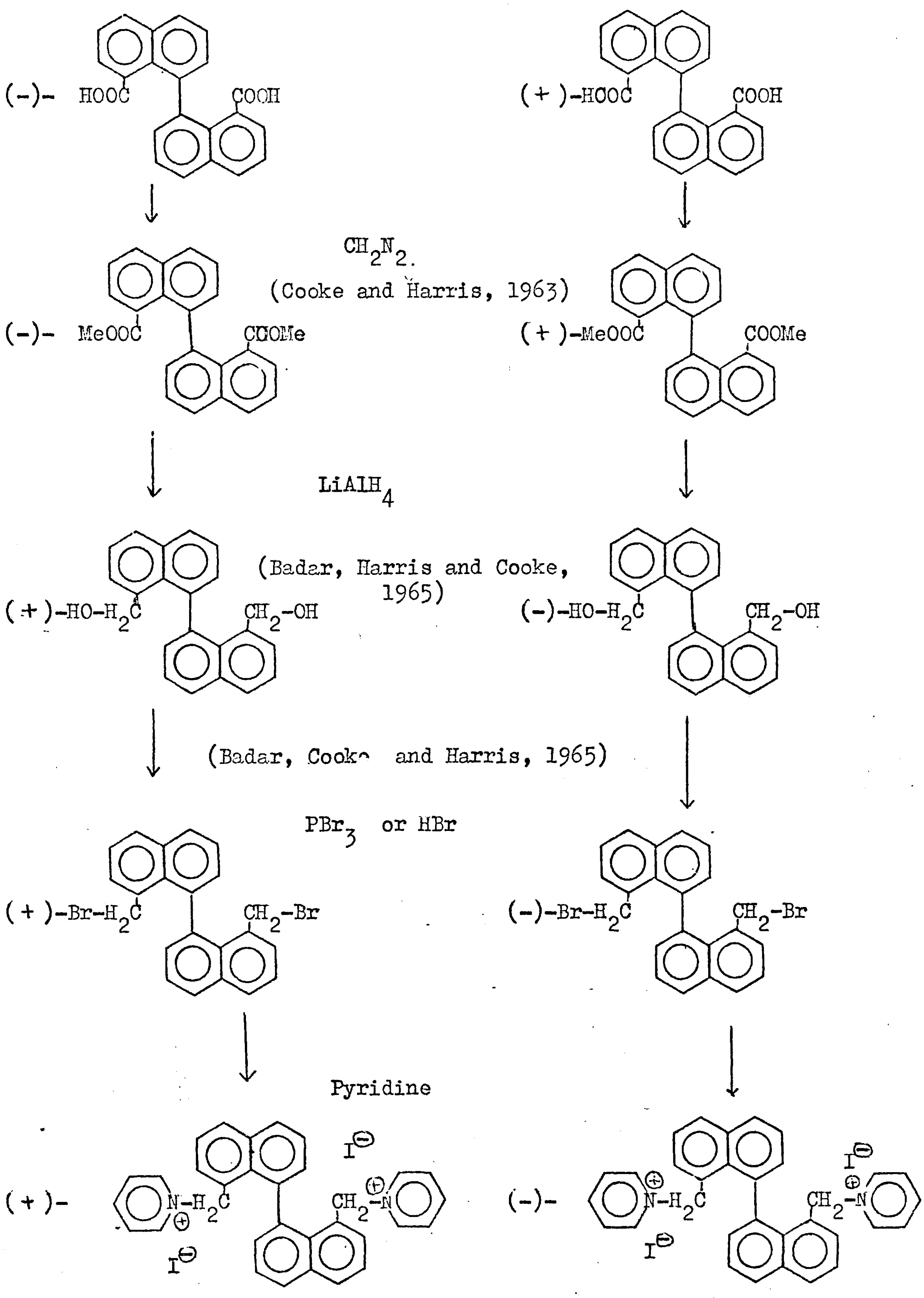
(ii) Optically active 1,1'-binaphthyl-8,8'-dicarboxylic acid and substances derived from it.

Optically active 1,1'-binaphthyl-8,8'-dicarboxylic acid

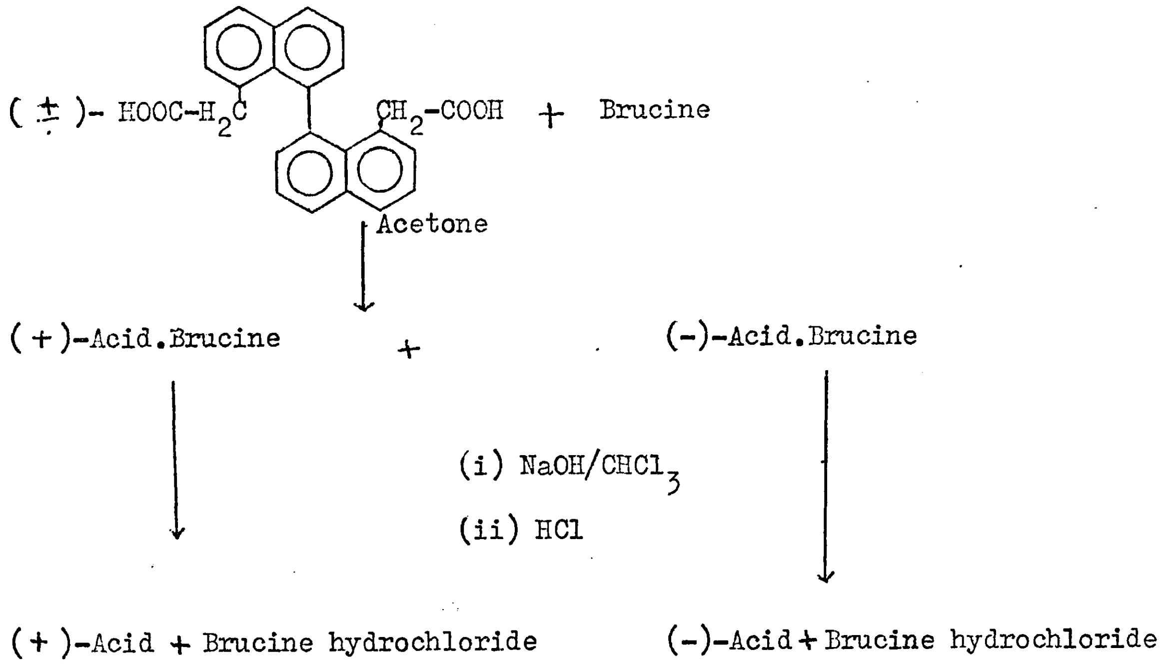
(Meisenheimer and Beisswenger, 1932)

(±)- 

$\xrightarrow[\text{(ii) NaOH/HCl}]{\text{(i) Brucine/MeOH}}$

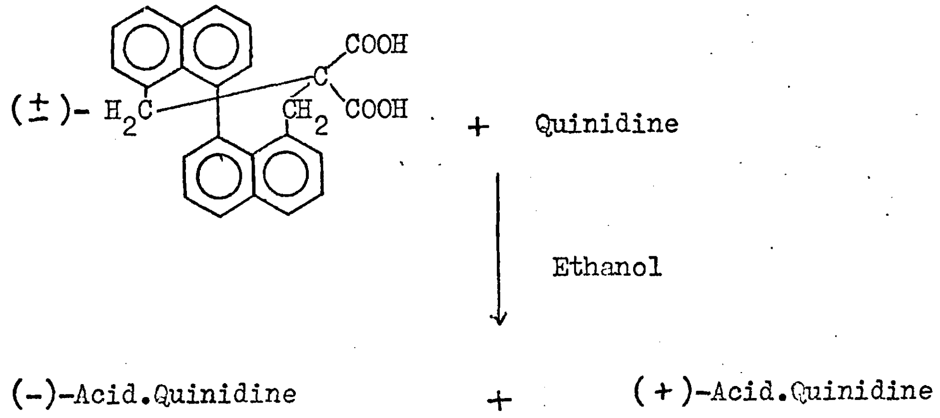

(-)- HOOC
COOH
(+)-HOOC
COOH
CH2N2.
(Cooke and Harris, 1963)
(-)- MeOOC
COOMe
(+)-MeOOC
COOMe
LiAlH4
(Badar, Harris and Cooke, 1965)
(+)-HO-H2C
CH2-OH
(-)-HO-H2C
CH2-OH
(Badar, Cooke and Harris, 1965)
PBr3 or HBr
(+)-Br-H2C
CH2-Br
(-)-Br-H2C
CH2-Br
Pyridine
(+)-
N-H2C
CH2-N
I⊖
I⊖
(-)-
N-H2C
CH2-N
I⊖
I⊖

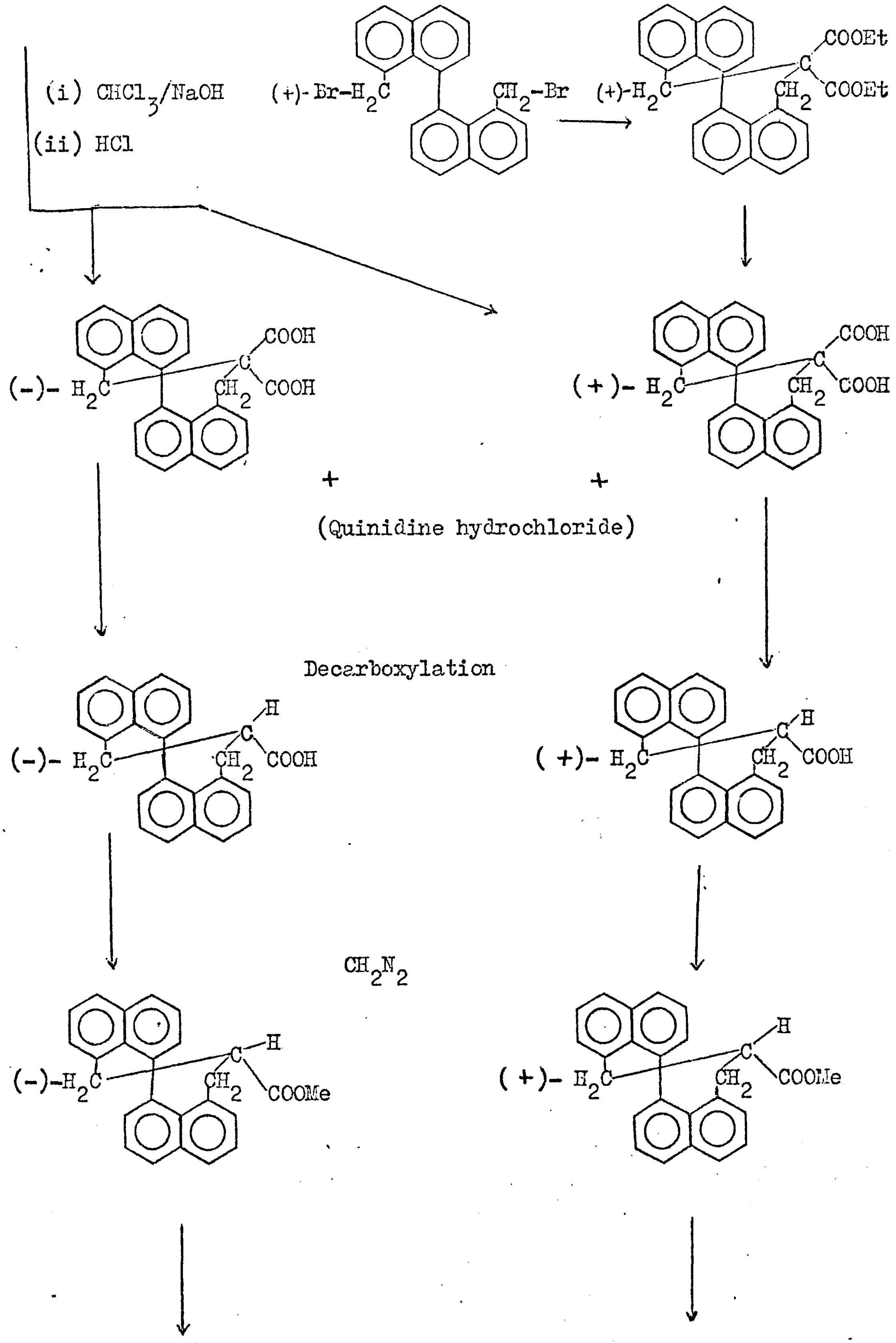
(iii) Optically active 1,1'-binaphthyl-8,8'-diacetic acid

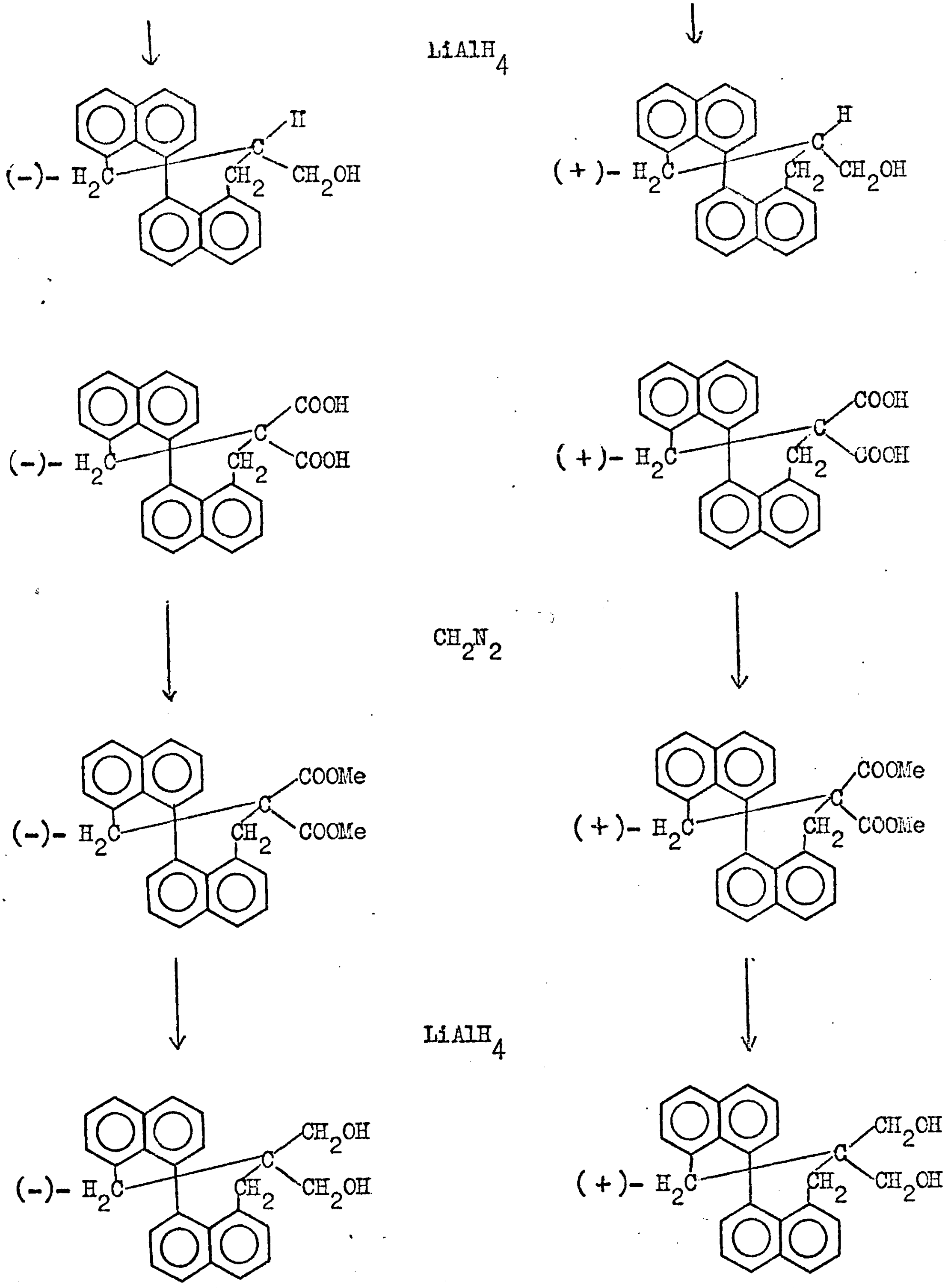


Scheme b. Optically active 8,8'-bridged 1,1'-binaphthyls

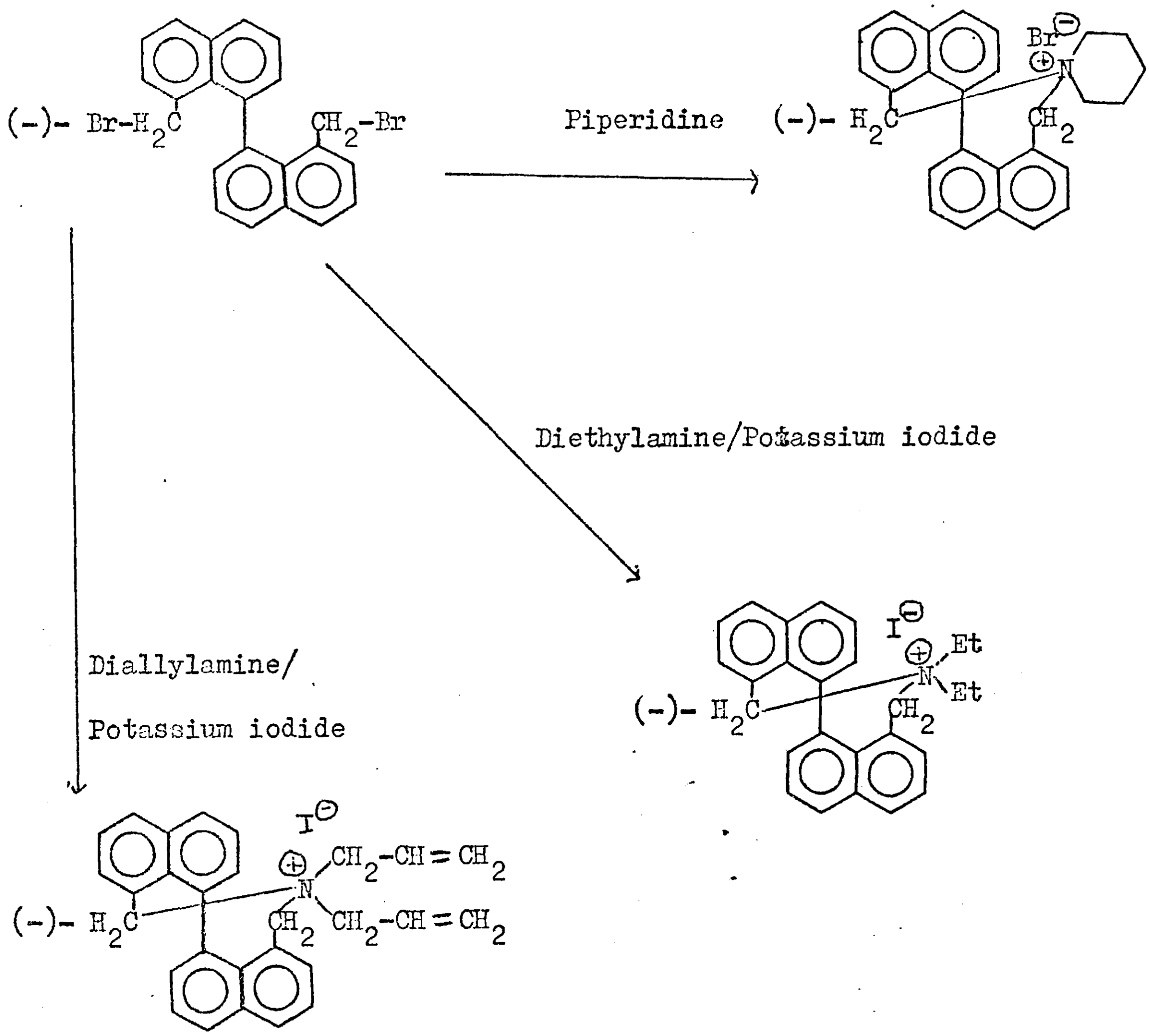
(i) Carbocyclic Compounds




(i) CHCl3/NaOH
(ii) HCl
(+)-Br-H2C
CH2-Br
(+)-H2C
COOEt
COOEt
CH2
(-)- H2C
COOH
COOH
CH2
(+)- H2C
COOH
COOH
CH2
+
+
(Quinidine hydrochloride)
Decarboxylation
(-)- H2C
H
CH2
COOH
(+)- H2C
H
CH2
COOH
CH2N2
(-)-H2C
H
CH2
COOMe
(+)- H2C
H
CH2
COOMe


LiAlH$_4$
(−)- H$_2$C
CH$_2$
H
CH$_2$OH
(+)- H$_2$C
COOH
COOH
CH$_2$N$_2$
COOMe
COOMe
LiAlH$_4$
CH$_2$OH
CH$_2$OH

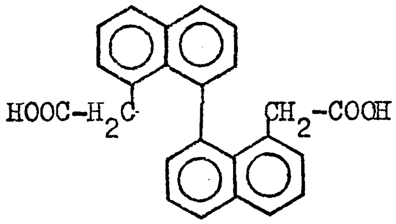
(ii) 8,8'-Bridged N-heterocyclic compounds



(ii) Optically active 1,1'-binaphthyl-8,8'-dicarboxylic acid, and substances derived from it

1,1'-binaphthyl-8,8'-dicarboxylic acid was optically activated by the crystallisation of its diastereomeric brucine salts from methanol using the method of Meisenheimer and Beisswenger (1932). Optically active 8,8'-bismethoxycarbonyl-1,1'-binaphthyls were prepared from the optically active acids (Cooke and Harris, 1963). These optically active methyl esters were reduced to the respective 8,8'-diols (with change in sign of optical rotation), converted into the 8,8'-bisbromomethyl compounds (8) following the procedure of Badar, Cooke and Harris (1965). Optically active (8) was used to prepare quaternary ammonium halides (12, 20, 21 and 22). In the preparation of optically active compounds derived from optically active (8) no change in sign of optical rotation was observed.

(iii) Optically active 1,1'-binaphthyl-8,8'-diacetic acids (10)



The resolution of 1,1'-binaphthyl-8,8'-diacetic acid (10) was attempted with brucine, quinidine and quinine in methanol, ethanol and acetone. The acid itself was not appreciably soluble in methanol or ethanol but in the presence of the alkaloid it went into solution.

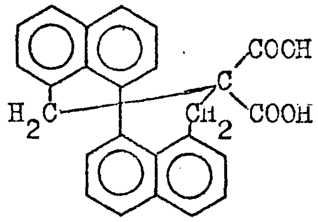
When equimolecular amounts of (±) -acid and quinidine were dissolved in ethanol and left to stand, long needles crystallised out; however m.p. and mixed m.p. with quinidine and optical rotation of these needles showed that it was only quinidine itself. With brucine in methanol and also in ethanol crystallisation did not occur; on slow evaporation at room temperature a gel was obtained.

On crystallisation of the salt with quinine from ethanol the first crop was optically inactive acid. On concentration of the filtrate from the first crop and on standing overnight a quinine salt with negative optical rotation crystallised out which on decomposition liberated the laevorotatory acid; but on repeating the same procedure, it failed to crystallise. The solvent ethanol was then replaced by acetone, from which the first (+)-rotatory quinine salt crystallised. The filtrate was concentrated and gave quinine salt with negative optical rotation.

Racemisation of the $(+)_{546}$ acid was carried in 0.1N aqueous sodium hydroxide between 111-137°. No decay in the degree of optical activity was observed below 98°. The optical stability was as expected in the range of 8,8'-dimethyl-1,1'-binaphthyl and 8,8'-bishydroxymethyl-1,1'-binaphthyl compounds which have been reported fairly stable at room temperature (Badar, Cooke and Harris, 1965).

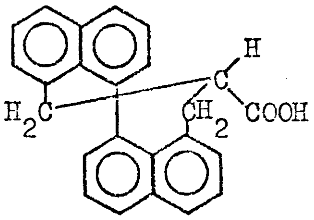
b. Optically active 8,8'-bridged 1,1'-binaphthyls

Resolution of [dinaphtho(8,1-ab, 1',8'-de)] -cyclonona-2,4-diene-8,8-dicarboxylic acid (14)



The resolution was carried out using equimolecular proportions of the acid and quinidine. The racemic acid was known to decarboxylate, and therefore to minimise the risk of decarboxylation of the optically active acid during resolution, the solutions were not heated; where it was necessary to remove the solvent, a rotatory film evaporator was used. Both the acid and quinidine were dissolved in ethanol separately, filtered and mixed together gently: vigorous stirring of the mixed solutions resulted in the appearance of racemic diastereomeric salts. In a few minutes time after mixing the solutions short needles started to crystallise which on standing overnight took the shape of white flowers. The filtrate was concentrated on a rotatory film evaporator, and gave optically impure salt. Crystallisation of first crop gave (-)$_{546}$-salt, the filtrate from the second crop gave (+)$_{546}$-salt. After the third crop, the remainder was left as a gel. (-)$_{546}$-Salt on decomposition gave (-)-acid and (+)$_{546}$-salt gave (+)-acid. When the resolution was carried out on a large scale, optically active acids were not obtained with such high rotations as obtained from smaller amounts.

Optically active [dinaphtho(8,1-ab, 1',8'-de)] -cyclonona-2,4-diene-8-carboxylic acid (15)



Optically active acids (14) were heated separately in pyrex glass tubes placed in a preheated metal bath up to 220-225° in order to obtain (+) and (-) optically active acids (15). Decarboxylated products were extracted with dilute aqueous sodium hydroxide, boiled with decolourising charcoal, filtered and precipitated from the hot filtrate acidified with dilute hydrochloric acid. The signs of optical rotations corresponded to their precursors, but the amount of rotation was approximately doubled. This may be connected with the disappearance of C_2 symmetry in (15) which was present in (14). This decarboxylation of optically active acid (14) shows that it is an optically stable compound and does not permit the inversion of its configuration.

Methyl esters of the optically active acids were prepared by reaction with diazomethane in cold ethereal solutions.

Optically active alcohols: Optically active methyl esters (16) and (17) were reduced to corresponding optically active alcohols (18) and (19).

The sign of optical rotations for the alcohols here remained the same as for their precursor esters.

Preparation of optically active 8,8-diethoxycarbonyl [dinaphtho(8,1-ab, 1',8'-de)] -cyclonona-2,4-diene (13) and dinaphtho[8,1-ab, 1',8'-de)] -cyclonona-2,4-diene-8,8-dicarboxylic acid by another method:

For the purpose of chemical correlation to derive absolute configurations, $(+)_{546}$-bisbromomethyl compound (8) was treated with sodiodiethylmalonate in anhydrous diethyl ether to obtain optically active ester (13). Crystallisation gave 33% of optically inactive ester (13), the filtrate was evaporated to dryness, dissolved in ethanol and filtered. Crystallisation from the filtrate gave 50% of $(+)_{546}$-diethyl ester (13). This ester was hydrolysed to obtain optically active diacid (14). The $(+)_{546}$-acid obtained has a little higher optical rotation than the one obtained by resolution. Results of the racemisation experiments are discussed later.

3.2 Experimental: Preparation of optically active compounds and racemisation of one optically active compound

Preparation of optically active 1,1'-binaphthyl-8,8'-diacetic acid

(1) Quinine (1.2 g, 1 mole) was placed in 300 ml of ethanol and 1,1'-binaphthyl-8,8'-diacetic acid (1.4 g, 1 mole) was added, and the solution was heated until all the solid dissolved, filtered and the filtrate concentrated down to 100 ml. On standing over-night it gave needles, which were filtered, washed with a little ethanol and dried. Yield 0.5 g, m.p. 307°d. In ethanol as well as in N-dimethylformamide solution it did not show any optical rotation; this was racemic acid recovered.

The filtrate was again concentrated down to 50 ml and after standing over-night, a white crystalline product deposited was filtered, washed with a little ethanol and dried. Yield 0.5 g, m.p. 123-127°. $\alpha_{546}-0.395^{\circ}$, $[\alpha]^{20}_{546}-176^{\circ}$ (c = 0.448; l = 0.5; NN-dimethylformamide). (Found: C, 71.6; H, 6.8; O, 15.8; N, 5.6. The mono quinine salt $C_{44}H_{42}O_6N_2$ requires C, 76.1; H, 6.1; O, 13.8; N, 4.0%). This salt was supposed to be the mono salt of quinine but it has some extra quinine. No second crop of the quinine salt crystallised.

Liberation of optically acive acid (10)

The quinine salt $[\alpha]_{546}-176^{\circ}$ was dissolved in chloroform and shaken with dilute aqueous sodium hydroxide. The alkaline layer was separated and washed with chloroform several times and air was bubbled through to remove traces of chloroform and the solution filtered. The filtrate was acidified with dilute hydrochloric acid, the precipitated acid was filtered, washed with water and dried in an evacuated desiccator, m.p. 308°. α_{546} $-0.08°$, $[\alpha]^{20}_{546}$ $-307°$ (c = 0.052, l = 0.5, 95% ethanol). (Found: C, 77.7; H, 5.0; O, 17.3. $C_{24}H_{18}O_4$ requires C, 77.8; H, 4.9; O, 17.3%). This procedure on repetition did not give a crystalline quinine salt, and therefore it was decided to change the solvent.

(2) Quinine (0.8 g, 1 mole) was dissolved in 150 ml of acetone and 1,1'-binaphthyl-8,8'-diacetic acid (1 g, 1 mole) added to it; the solution was heated until all dissolved and then filtered. On standing, after a few hours colourless solid crystallised out, which was filtered and washed with a little acetone and dried, yield 0.7 g, m.p. 120-128°. α_{546} $+0.05°$, $[\alpha]^{20}_{546}$ $+138°$ (c = 0.072, l = 0.5, N,N-dimethylformamide). (Found: C, 73.7; H, 6.3: N, 3.6. The monohydrate of quinine salt $C_{44}H_{42}O_6N_2.H_2O$ requires C, 74.2; H, 5.9; N, 3.9%).

The filtrate was concentrated up to 50 ml and on standing overnight it gave 0.6 g, m.p. 119-125°. α_{546} $-0.06°$, $[\alpha]^{20}_{546}$ $-142°$ (c = 0.084, l = 0.5, N,N-dimethylformamide).

(Found: C, 73.8; H, 6.3; N, 3.5. The monohydrate of quinine salt $C_{44}H_{42}O_6N_2.H_2O$ requires C, 74.2; H, 5.9; N, 3.9%). Stoichiometric composition of these quinine salts is evidently not simple.

Liberation of optically active acids

The procedure used was the same as on page 109 . The quinine salt $[\alpha]^{20}_{546}$ + 138° gave the acid, m.p. 308-310°. α_{546} + 0.205°, $[\alpha]^{18}_{546}$ + 227° (c = 0.18, l = 0.5, N,N-dimethylformamide).

(Found: C, 78.1; H, 5.1. $C_{24}H_{18}O_4$ requires C, 77.8; H, 4.9%).

The quinine salt $[\alpha]^{20}_{546}$ -142° gave the acid, m.p. 309-310°, α_{546} -0.26°, $[\alpha]^{20}_{546}$ -245° (c = 0.212, l = 0.5, N,N-dimethylformamide). Unfortunately the material was insufficient to try for greater optical purity.

Racemisation of (+)-1,1'-binaphthyl-8,8'-diacetic acid in 0.1N aqueous sodium hydroxide solution

(+)-1,1'-Binaphthyl-8,8'-diacetic acid (0.1868 g) was dissolved in 50 ml of decinormal aqueous sodium hydroxide and portions of this solution sealed in pyrex glass ampoules, kept in an oil thermostat at selected temperatures, withdrawn at suitable intervals, cooled immediately to room temperature and optical rotation measured. α^{20}_{546} + 0.465° $[\alpha]^{20}_{546}$ + 248.9° (time = 0)

Temperature (°C)	Time (min.)	α (°)	Temperature (°C)	Time (min.)	α (°)
111	15	0.430	123	120	0.060
	30	0.395	133	15	0.235
	45	0.360		30	0.130
	60	0.335		45	0.065
	90	0.280		60	0.035
123	15	0.365	137	15	0.135
	30	0.280		30	0.035
	45	0.225		35	0.022
	60	0.155		45	0.000
	90	0.100			

The ultra-violet absorption spectrum (Perkin-Elmer Double Beam Spectrophotometer 124) of the recovered acid was found identical with the u.v. spectrum of the original racemic acid in 0.1N aqueous sodium hydroxide solution.

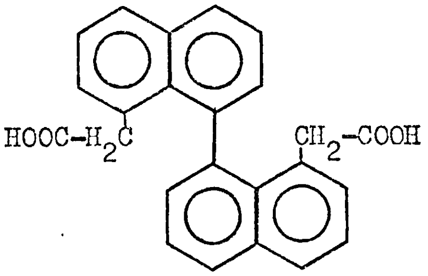
Calculation of Arrhenius parameters for racemisation

The rate constant k was determined at each temperature using the first order rate equation;

$$\underline{k} = \frac{1}{t} \log_e \frac{\alpha_0}{\alpha_t}.$$

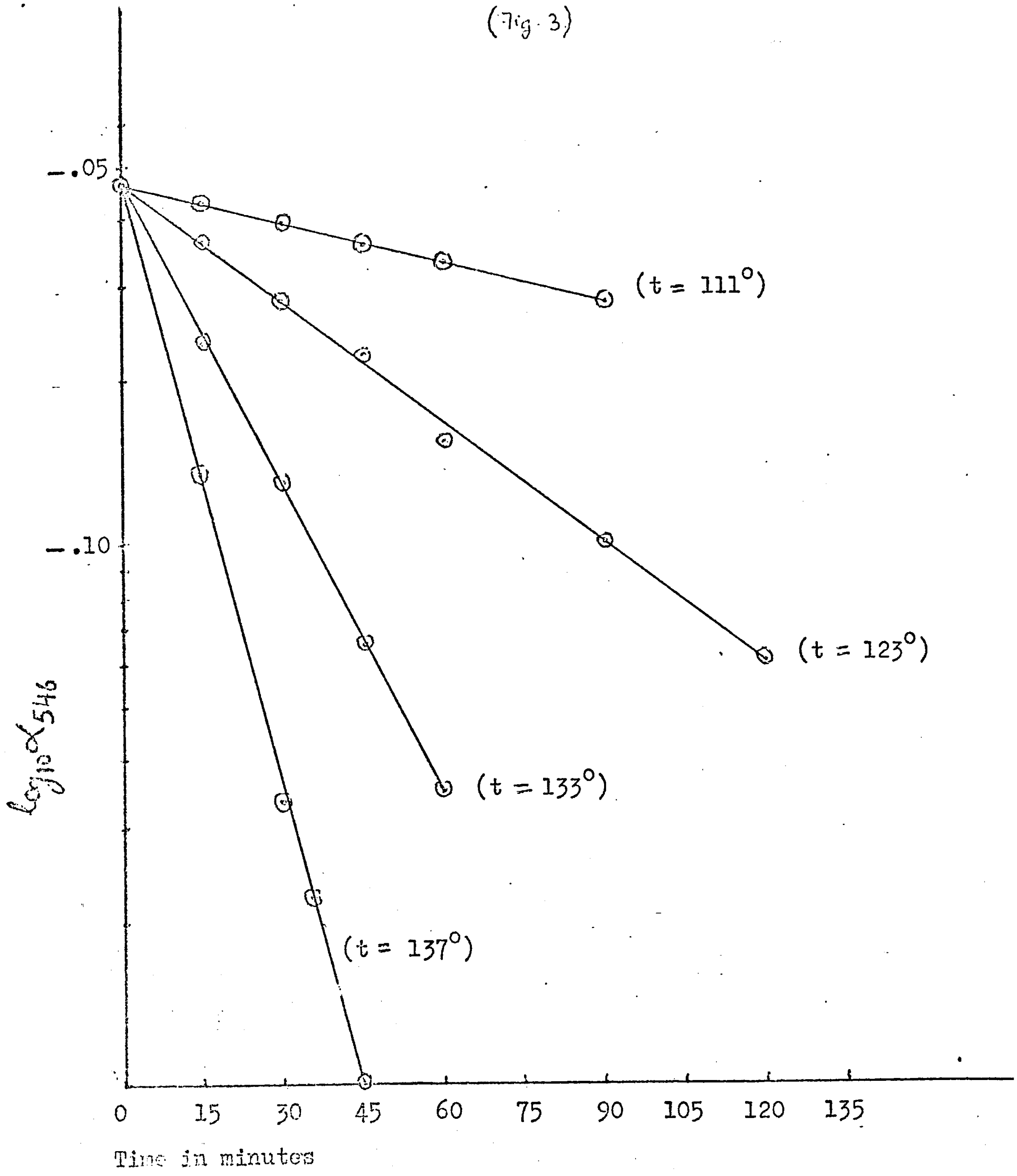
The energy of activation for racemisation E_{rac} was found graphically as well as using the method of least squares;

Racemisation of (+)-

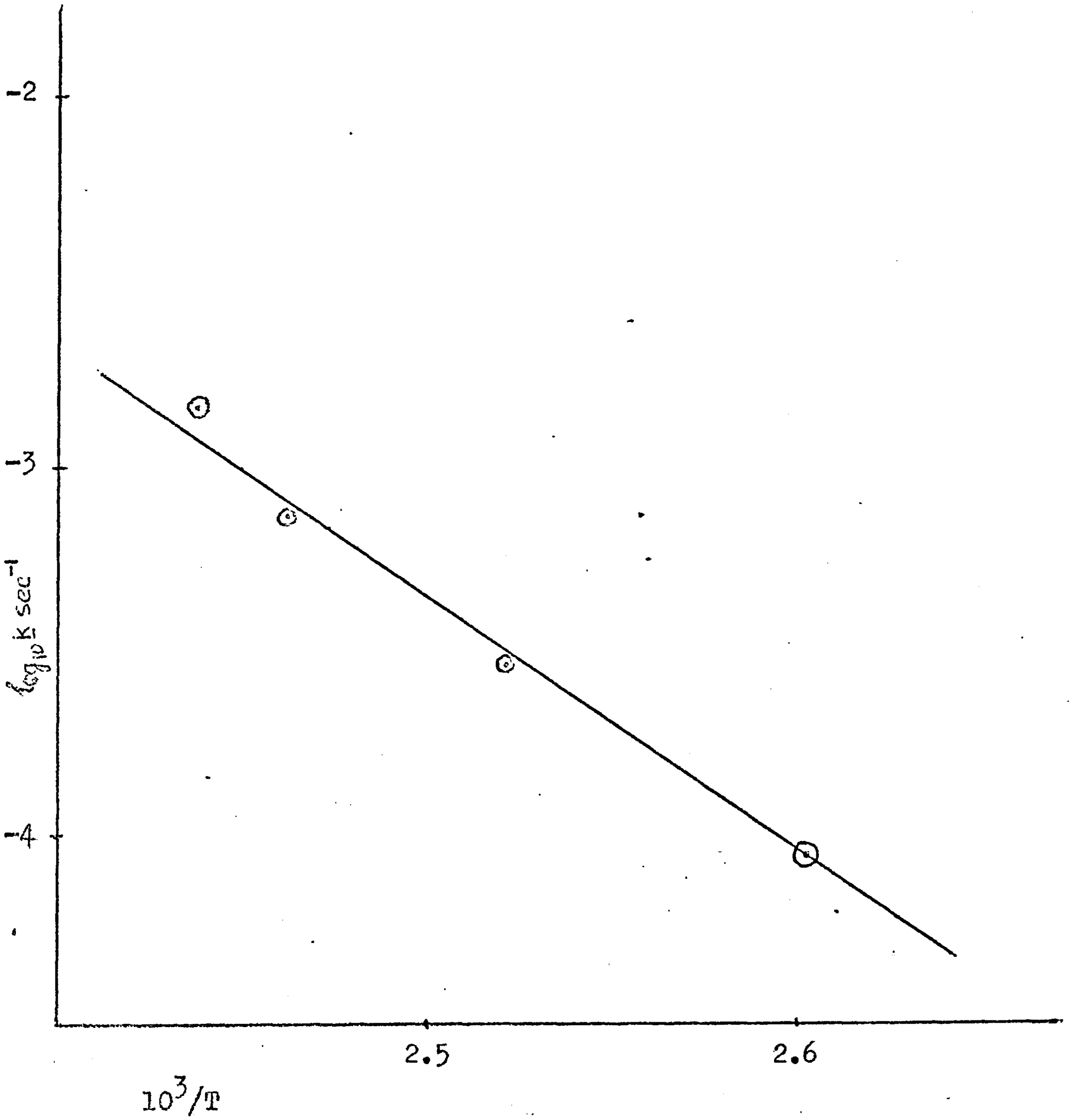


in 0.1N NaOH

(Fig. 3)



Arrhenius plot for (+)-1,1'-binaphthyl-8,8'-diacetic acid in 0.1 N NaOH (aqueous)



(Figure 4)

(i) Graphical determination of E_{rac}: Data used (also used for least squares method), hence figures retained till end.

T^oK	$10^3/T$ (x)	k sec^{-1}	$\log_{10}k$ sec^{-1} (y)
384.2	2.6028110	0.0000915	-4.03858
396.2	2.5239777	0.0002823	-3.54929
406.2	2.4618414	0.0007285	-3.13757
410.2	2.4378352	0.0014217	-2.84720

The slope of the line (figure 4) is, 0.200/0.029 = 6.89(655)

E_{rac} = 6.89(655) x 2.303 x 1.988 = 31.5(4) kcal mol^{-1}.

(ii) Calculation of E_{rac} by least squares method

The equation $k = Ae^{-E/RT}$ (where k is rate constant, A probability factor, R the gas constant (1.988) and T absolute temperature) can be written as $\log_{10}k = \log_{10}A - E/2.303RT$ ... ... (1). In the equation $y = a + bx$ ... ... (2), (Hammett, 1941) on fitting a series of measurements of the values of x and y, the best values of a and b can be evaluated by the relationships;

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

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

If the variable y is taken as $\log_{10}k$ and the variable x as $10^3/T$, then the slope b (a constant) will be equivalent to $-E/2.303R$ and the equation constant a will be equivalent to $\log_{10}A$ from equation (1).

Calculation of b and a:

xy	x^2
-10.5116604	6.7746251
- 8.9583288	6.3704634
- 7.7241997	6.0606631
- 6.9410044	5.9430405

$\Sigma x = 10.0264653$, $\Sigma y = -13.57264$, $\Sigma xy = -34.1351933$

$\Sigma x^2 = 25.1487921$, $4\Sigma x^2 = 100.5951684$, $(\Sigma x)^2 = 100.5300064$

$4\Sigma xy = -136.5407732$, $\Sigma x \Sigma y = -136.0856040$, $n = 4$.

Putting these values in the stastical equation to determine the slope of the line, b is -6.9852.

$E_{rac} = -b \times 2.303 \times 1.988 = 6.9852 \times 2.303 \times 1.988$

$= 31.99 = 32.0 \text{ kcal mol}^{-1}$.

Calculation of $\log_{10}A$ at 111°C: Putting the values of y, x and b in equation (2), $a = -4.03858 - (-6.978221)(2.6041666)$

$\log_{10}A = 14$

i.e. $E_{rac} = 32 \text{ kcal mol}^{-1}$ $\log_{10}A = 14$

Calculation of Transition State Theory Functions ($\Delta S^{\neq}$, $\Delta H^{\neq}$, $\Delta F^{\neq}$)

Cagle and Eyring (1951) suggested the application to racemisation of the absolute reaction rate theory equation (Glastone, Laidler and Eyring, 1941),

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

where $\underline{k}$ is rate constant, κ transmission coefficient (unity), K is Boltzmann constant, h Planck's constant, $\Delta H^{\neq}$ enthalpy of activation, $\Delta S^{\neq}$ entropy of activation, R gas constant and T absolute temperature; they showed that the entropy of activation $\Delta S^{\neq}$ makes an important contribution to the racemisation velocities of atropisomers. In fact every process depends upon two terms $\Delta H^{\neq}$ and $\Delta S^{\neq}$, and a change occurring in the process is favoured if $\Delta H^{\neq}$ is small or $\Delta S^{\neq}$ is positive, which corresponds with a small energy or an increase in disorder in the transition state respectively. Whenever the temperature is not very high, both the terms $\Delta H^{\neq}$ and $T \Delta S^{\neq}$ are important. However in all cases a process leads to the minimum possible value of $\Delta H^{\neq} - T \Delta S^{\neq}$, for the system and this minimum value is known as free energy of activation $\Delta F^{\neq}$ thus the absolute reaction rate theory equation can be written as;

$$\underline{k} = \frac{KT}{h} . e^{-\Delta F^{\neq}/RT}$$

$\Delta H^{\neq}$ was calculated using the relation $\Delta H^{\neq} = E - RT$ for each temperature and the mean of the four values taken giving 31.2 kcal mol^{-1}.

$\Delta F^{\neq}$ was calculated from equation,

$\Delta F^{\neq} = 47.22T - 4.576T.\log_{10}(\underline{k}_{rac}/T)$ (Hall and Harris, 1960) for each temperature and the mean value obtained 29.6 kcal mol^{-1}.

$\Delta S^{\neq}$ was calculated from the equation $\Delta F^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq}$ for each temperature and the average value was determined $+3.6$ e.u. The half-life at 111°C is 126 min.

Hence, $\Delta F^{\neq} = 29.6$ kcal mol^{-1}; $\Delta H^{\neq} = 31.2$ kcal mol^{-1}; $\Delta S^{\neq} = 3.6$ e.u.

(+)-1,1'-Binaphthyl-4,4'-diamine

(Theilacker and Hopp, 1959)

4,4'-Naphthidine (2.8 g, 1 mole) was dissolved in 50 ml of hot acetone and this solution was then poured into 400 ml of water. N.Hydrochloric acid (40 ml) was added to the naphthidine solution followed immediately by a solution of ammonium (+)-α-bromocamphor-π-sulphonate (6.5 g, 2 mole). On standing the precipitate was filtered off and dried away from the light in a vacuum. It was crystallised from 60% aqueous ethanol. First crop gave pinky crystals, yield 2.5 g, m.p. 330-332°. α^{20}_{579} +0.44°, $[\alpha]^{20}_{579}$ + 98.0° (c = 0.2232, l = 2, 60% acetone)

$[\alpha]_D$ + 75°, 60% acetone (Theilacker and Hopp, 1959).

Second crop: yield 2.0 g, m.p. 330-333°, α^{20}_{546} + 0.18°, $[\alpha]^{20}_{546}$ +115.8°
This probably contains (+)-acid.

Liberation of the optically active naphthidine

The bromocamphor-π-sulphonate (5 g) was suspended in 60 ml of ethanol and a few pieces of ice added. The solution was made alkaline with ammonium hydroxide, when the amine was precipitated, filtered, washed with water and dried in an evacuated desiccator. Yield 1.5 g, m.p. 198-200°. $[\alpha]^{23.5}_{578}$ + 45.0° (c = 0.168, l = 0.5, acetone).

$[\alpha]^{22}_{D}$ + 42 ± 1°, acetone (Theilacker and Hopp, 1959).

Optically active 1,1'-binaphthyl

(Cooke and Harris, 1963)

The (+) - naphthidine (0.5 g) was dissolved in cold hydrochloric acid. Aqueous sodium nitrite (0.25 g) was added with the help of a dropping pipette keeping the temperature below 0°. The reaction mixture was poured into 20% aqueous hypophosphorous acid (10-15 ml) stirring magnetically; a deep yellow precipitate appeared, which was filtered off, washed with cold water, with cold dilute hydrochloric acid and finally with water, and dried over a suction pump. The product was extracted with cold benzene (35 ml), the solid residue was rejected and the deep red solution was kept cold and washed with ice-cold aqueous sodium hydroxide solution, water, hydrochloric acid and finally with water, The benzene layer was shaken with calcium chloride and filtered, and diluted with 35 ml of ice-cold petroleum ether (b.p. 40-60°).

An alumina column was prepared with ice-cold alumina packeted in a 1" wide column surrounded with a water jacket through which ice-cold water was circulated to maintain the temperature as low as possible during the elution period. The benzene-petroleum mixture was run through this column and eluted with ice-cold 90% petroleum ether (b.p. 40-60°) in 10% ether solution. The solvent was removed by bubbling a stream of dried air, keeping the solution container in an ice bath. The colourless product, m.p. 157-158° was dried in an evacuated desiccator. (Previous workers gave m.p. 157-159° and $[\alpha]^{22}_{579} + 245.3^\circ$, benzene-petroleum ether).

Measurement of optical rotation:

$\alpha^{23.5}_{578} + 0.05^\circ$, $[\alpha]^{23.5}_{578} + 268^\circ$ ($\underline{c} = 0.038$, $\underline{l} = 0.5$, benzene)

($\underline{c} = 0.344$, $\underline{l} = 0.5$, dioxan)

λ	578	546	436	405	365
α	$+0.18^\circ$	$+0.21^\circ$	$+0.39^\circ$	$+0.535^\circ$	$+0.765^\circ$
$[\alpha]_{\lambda}^{23.5}$	$+104^\circ$	$+122^\circ$.	$+226^\circ$.	$+311^\circ$	$+433^\circ$

($\underline{c} = 0.0336$, $\underline{l} = 1$, 95% ethanol)

α	$+0.075^\circ$	$+0.085^\circ$	$+0.140^\circ$	$+0.195^\circ$	$+0.295^\circ$
$[\alpha]_{\lambda}^{7}$	$+223^\circ$	$+252^\circ$.	$+416^\circ$.	$+580^\circ$	$+877^\circ$.

($\underline{c} = 0.028$, $\underline{l} = 0.5$, tetrahydofuran)

$[\alpha]_{589}^{23} + 107^\circ$.

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

(Meisenheimer and Beisswenger, 1932)

(±)-1,1'-binaphthyl-8,8'-dicarboxylic acid (2 g) was added to a methanolic solution of brucine (2.8 g, in 600 ml). The solution was boiled until all the acid dissolved, filtered and evaporated down to about 400 ml. On standing the solution deposited needles, 2.2 g, m.p. 220-235°. α_{546} -1.81°, $[\alpha]^{20}_{546}$ -472°. ($c = 0.1912$, $l = 2$, chloroform). $[\alpha]_{D}$-395° (Meisenheimer and Beisswenger, 1932) and $[\alpha]^{21.4}_{546}$ -481° (Cooke and Harris, 1963).

The mother liquor was evaporated down to dryness and the residue was dissolved in ethyl acetate by boiling and filtered hot. The filtrate was concentrated to 250 ml, on standing crystals obtained 2.4 g, m.p. 210-225°. α_{546}+2.00, $[\alpha]^{21}_{546}$+469° ($c = 0.2128$, $l = 2$, chloroform). $[\alpha]_{546}$+ 483° (Cooke and Harris, 1963).

Liberation of optically active acids

The (-)-brucine salt (2 g) was dissolved in chloroform and the active acid was extracted with cold aqueous sodium hydroxide. The alkaline solution was washed with chloroform, air was bubbled through to remove the traces of chloroform, and filtered, The filtrate was acidified with dilute hydrochloric acid to precipitate the active acid, which was filtered, washed with water and dried in an evacuated desiccator, m.p. 318-319°d. α_{546}-0.94°, $[\alpha]^{21}_{546}$ -839° ($c = 0.056$, $l = 2$, chloroform). [$[\alpha]^{20.5}_{546}$ -740.7°, in N,N-dimethylformamide, m.p. 319-322° (Mazengo, 1968)]

The (+)-acid was obtained from the brucine salt $[\alpha]_{546}$ +469.9° in a similar way, m.p. 318-319°d. α_{546} +0.68°, $[\alpha]_{546}^{21}$ +900° (c = 0.0376, l = 2, chloroform). $[\alpha]_{546}^{20.5}$ +738.9°, N,N-dimethylformamide (Mazengo, 1968).

Preparation of optically active 8,8'-bismethoxycarbonyl-1,1'-binaphthyl

(Cooke and Harris, 1963)

(-)-8,8'-Bismethoxycarbonyl-1,1'-binaphthyl $[\alpha]$ -839°

Finely ground (-)-1,1'-binaphthyl-8,8'-dicarboxylic acid (5 g) was added to a cold ethereal solution of diazomethane (1.3 g in 100 ml). With a brisk effervescence the portions of the acid added were dissolved and the ester separated. The ether was evaporated and the solid product was shaken well with aqueous sodium carbonate, filtered and washed with water and dried in an evacuated desiccator, m.p. 123-125°. $[\alpha]_{546}^{20}$ -217.5°, (N,N-dimethylformamide) (Cooke and Harris reported the same m.p.).

(+)-8,8'-Bismethoxycarbonyl-1,1'-binaphthyl was prepared in a similar way from the acid $[\alpha]_{546}$ +900°, m.p. 124-125°, solidified and remelted at 157°. $[\alpha]_{546}^{20}$ + 210°, (N,N-dimethylformamide) (Cooke and Harris reported the same m.p.).

Preparation of optically active 8,8'-bishydroxymethyl-1,1'-binaphthyl

(Badar, Cooke and Harris, 1965)

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

(-)-8,8'-Bismethoxycarbonyl-1,1'-binaphthyl (5 g, 1 mole) suspended in anhydrous ether (1 L) was added to lithium aluminium hydride (1.5 g, 3 mole) and heated under reflux for 90 min. The excess of lithium aluminium hydride was decomposed by treatment with a few drops of water and then dilute sulphuric acid, the ether layer was separated and washed with water, dried over anhydrous sodium sulphate in the refrigerator and the ether distilled off. Crystallisation from benzene gave (+)-diol, m.p. 148°. α_{546} +0.25° $[\alpha]^{23}_{546}$ + 96°. ($\underline{c}$ = 0.52, $\underline{l}$ = 0.5, 95% ethanol).

[$[\alpha]_{546}$ +45° N,N-dimethylformamide (Badar, Cooke and Harris, 1965).]

(-)-8,8'-Bishydroxymethyl-1,1'-binaphthyl was obtained from (+)-8,8'-bismethoxycarbonyl-1,1'-binaphthyl in a similar way, m.p. 145-146°. α_{546} -0.24°, $[\alpha]^{22.5}_{546}$ -95° ($\underline{c}$ = 0.504, $\underline{l}$ = 0.5, 95% ethanol).

[$[\alpha]_{546}$ -32° N,N-dimethylformamide (Badar, Cooke and Harris, 1965)]

Preparation of optically active 8,8'-bisbromomethyl-1,1'-binaphthyl

(Badar, Cooke and Harris, 1965)

The (+)-diol (6 g) was powdered and added in portions to stirred phosphorous tribromide (30 g, 6 mole). After the addition was complete, the stirring was continued for another 15 minutes and the reaction mixture was poured into vigorously stirred ice-cold water, the yellow solid separated, was filtered and washed with aqueous solution of sodium bicarbonate, then with water and dried in an evacuated desiccator. Yield 7.5 g, m.p. 180-182°. $[\alpha]^{20}_{546}$ +348° (N,N-dimethylformamide) $[\alpha]_{546}$ + 470° (Badar, Cooke and Harris, 1965).

The (-)-8,8'-bisbromomethyl-1,1'-binaphthyl was prepared in a similar way, m.p. 179-182°, $[\alpha]^{20}_{546}$ -337° (N,N-dimethylformamide). $[\alpha]_{546}$ -466.6° (Badar, Cooke and Harris, 1965).

Preparation of optically active 1,1'-binaphthyl-8,8'-bis(methylenepyridinium) diiodide.

(-)-1,1'-Binaphthyl-8,8'-bis(methylenepyridinium) diiodide

(-)-8,8'-Bisbromomethyl-1,1'-binaphthyl (1 g) $[\alpha]^{20}_{546}$ -180° * interacted with anhydrous pyridine at room temperature on stirring them together for 30 min. The solid was separated, filtered and washed with petroleum ether (b.p. 40-60°). The bromide was dissolved in water and hot aqueous potassium iodide added to precipitate the iodide, which was again dissolved in water and warmed with decolourising charcoal, filtered. The filtrate was slowly concentrated. Crystallisation gave 0.5 g of (-)-1,1'-binaphthyl-8,8'-bis(methylenepyridinium) diiodide, m.p. 198-203°. α_{546} -0.020°, $[\alpha]^{22}_{546}$ -27.7° (c=0,144, l= 0.5, 95% ethanol). (Found: C, 54.3; H, 3,7; N, 3.9; I, 35.3. $C_{32}H_{26}N_2I_2 \cdot 2H_2O$ requires C, 52.8; H, 4.2; N, 3.8; I, 34.8%).

(+)- 1,1'-Binaphthyl-8,8'-bis(methylenepyridinium) diiodide was prepared in a similar way from (+)-8,8'-bisbromomethyl-1,1'-binaphthyl $[\alpha]_{546}$ + 348.7°, m.p. 200-204°. α_{546} + 0.40°, $[\alpha]^{18}_{546}$ + 202.8° (c = 0.396, l = 0.5, 95% ethanol).

(Found: C, 52.9; H, 4.2; N, 3.8; I, 35.2. $C_{32}H_{26}N_2I_2 \cdot 2H_2O$ requires C, 52.8; H, 4.2; N, 3.8; I, 34.8%).

* The specimen available of the (-)-bisbromomethyl compound was much less optically pure than of the (+)-bisbromomethyl compound.

Resolution of [dinaphtho(8,1-ab, 1',8'-de)]-cyclonona-2,4-diene-8,8-dicarboxylic acid (14)

Quinidine (4.25 g, 1 mole) was dissolved in ethanol (200 ml) and the acid (5.0 g, 1 mole) dissolved in ethanol (200 ml) added slowly to the quinidine solution. On standing for a little time needles started separating, after standing over-night the crystals were filtered, washed with ethanol and first dried on suction pump and then in an evacuated desiccator, yield 4.0 g, m.p. 198-200°. α_{546}^{21} -0.08°, $[\alpha]_{546}^{21}$ -42° (c = 0.38, l = 0.5, N,N-dimethylformamide).

(Found: C, 76.3; H, 6.1; N, 4.0; O, 13.7. $C_{45}H_{42}N_2O_6$ (the mono quinidine salt) requires C, 76.5; H, 5.9; N, 4.0; O, 13.6%).

Second crop: The filtrate was concentrated by solvent evaporation on a rotatory film evaporator and filtered, the filtrate on standing gave a solid, filtered, washed with ethanol and dried, yield 1.5 g, m.p. 185-192°, $[\alpha]_{546}^{21}$ + 44.1° , which on decomposition gave an acid of optical rotation $[\alpha]_{546}$ -51.3° (ethanol).

Third crop: The filtrate from the second crop was kept over-night and gave a crystalline quinidine salt, which when filtered, washed with ethanol and dried, yield 3.00 g, m.p. 198-201°, α_{546} + 0.195°, $[\alpha]_{546}^{21}$ + 187.5° (c = 0.208, l = 0.5, N,N-dimethylformamide).

(Found: C, 74.4; H, 6.0; N, 4.0; O, 15.3. The monohydrate of quinidine salt, $C_{45}H_{42}N_2O_6.H_2O$ requires C, 74.6; H, 6.1; N, 3.9; O, 15.5%).

Liberation of active acids

The (−)-quinidine salt, $[\alpha]_{546}$ -42.1° (1 g) was suspended in chloroform and the acid was extracted with dilute aqueous solution of sodium hydroxide. The alkaline solution was washed with chloroform to remove the traces of quinidine, and finally air was bubbled through this solution to remove the traces of chloroform, and filtered. The filtrate was acidified with cold dilute hydrochloric acid to precipitate the active acid, which was filtered, washed with water and dried in an evacuated desiccator, yield 0.5 g, m.p. 195-198°, α_{546} -0.54°, $[\alpha]^{19}_{546}$ -318.3° ($\underline{c}$ = 0.0848, $\underline{l}$ = 2, 95% ethanol).
(Found: C, 74.9; H, 5.2; O, 19.9. $C_{25}H_{18}O_4.H_2O$ requires C, 75.0; H, 5.0; O, 20.0%).

The (+)-quinidine salt $[\alpha]_{546}$ $+187.5^{\circ}$ (1 g) was decomposed in a similar way to give an acid which melted at 195-200°. α_{546} $+0.72^{\circ}$, $[\alpha]^{21}_{546}$ $+349.5^{\circ}$ ($\underline{c}$ = 0.412, $\underline{l}$ = 0.5, 95% ethanol).
(Found: C, 74.8; H, 5.2; O, 19.9. $C_{25}H_{18}O_4.H_2O$ requires C, ~~75;~~ 75.0 H, 5.0; O, 20.0%).

Summary:	salt	acid
	-42.1°	-318.3°
	$+44.1^{\circ}$	-51.3°
	$+187.5^{\circ}$	$+349.5^{\circ}$

Because of the small amounts, optically active compounds were not further optically purified.

Preparation of optically active dinaphtho(8,1-ab, 1',8'-de) -cyclonona-2,4-diene-8-carboxylic acid (15)

The (-)-dicarboxylic acid (5 g) $[\alpha]_{546}$ -235.3° in a hard glass tube immersed in a metal bath was heated up to 220-225°, and stirred with a thermometer. When it was all melted, it was cooled and extracted with dilute aqueous sodium hydroxide. The alkaline solution was boiled with decolourising charcoal, filtered and acidified with dilute hydrochloric acid to precipitate the acid, the precipitated acid was filtered, washed with water and dried. Crystallisation from ethanol gave 3.9 g, m.p. 220-222°. α_{546} -0.34°, $[\alpha]^{22}_{546}$ -515° ($\underline{c} = 0.132$, $\underline{l} = 0.5$, 95% ethanol).

(Found: C, 85.1; H, 5.3; O, 9.5. $C_{24}H_{18}O_2$ requires C, 85.2; H, 5.3; O, 9.5%).

The (+)-dicarboxylic acid $[\alpha]_{546}$ $+257.5^{\circ}$ was decarboxylated in a similar way and the monocarboxylic acid after crystallisation from ethanol obtained had m.p. 220-222°. α_{546} $+0.115^{\circ}$, $[\alpha]^{22}_{546}$ $+522^{\circ}$ ($\underline{c} = 0.044$, $\underline{l} = 0.5$, 95% ethanol).

(Found: C, 85.0; H, 5.5; O, 9.3. $C_{24}H_{18}O_2$ requires C, 85.2; H; 5.3; O, 9.4%).

Preparation of optically active 8,8-dimethoxycarbonyl[dinaphtho(8,1-ab, 1',8'-de)]-cyclonana-2,4-diene (17)

Preparation of (-)-dimethyl ester

The (-)-dicarboxylic acid (1 g), $[\alpha]_{546}$ -235° was added in small portions to a cold ethereal solution of diazomethane. All portions of the acid dissolved with a brisk effervescence. The ethereal layer was washed with aqueous sodium carbonate solution and finally with water and dried over anhydrous sodium sulphate and the ether distilled off. The methyl ester was crystallised from methanol, 0.8 g, m.p. 165-167°, α_{546} -0.095°, $[\alpha]^{21}_{546}$ -263° (c = 0.072, l = 0.5, 95% ethanol). (Found: C, 78.9; H, 5.4; O, 15.7. $C_{27}H_{22}O_4$ requires C, 79.0; H, 5.4; O, 15.6%).

Preparation of (+) -dimethyl ester

The (+)-dimethyl ester was obtained in a similar way to the (-)-dimethyl ester, from (+)-dicarboxylic acid (1 g), $[\alpha]_{546}$ +257°. Crystallisation from methanol gave 0.7 g, m.p. 164-165°. α_{546} + 0.075°, $[\alpha]^{21}_{546}$ + 234°. (c = 0.064, l = 0.5, 95% ethanol). (Found: C, 79.0; H, 5.3; O, 15.7. $C_{27}H_{22}O_4$ requires C, 79.0; H, 5.4; O, 15.6%).

Preparation of 8-methoxycarbonyl[dinaphtho(8,1-ab, 1',8'-de)] -cyclonona-2,4-diene (16)

Preparation of (-)-monomethyl ester

The (-)-monocarboxylic acid (1 g), $[\alpha]_{546} -515^{\circ}$ was esterified by the treatment with ethereal diazomethane in a similar way and crystallised from methanol, yield 0.9 g, m.p. 110-112°, $\alpha_{546} -0.335^{\circ}$, $[\alpha]^{21}_{546} -478^{\circ}$. (c = 0.14, l = 0.5, 95% ethanol).

(Found: C, 85.1; H, 5.6; O, 9.0. $C_{25}H_{20}O_2$ requires C, 85.2; H, 5.7; O, 9.1%).

Preparation of (+)-monomethyl ester

The (+)-monomethyl ester was obtained in a similar way as above from (+)-monocarboxylic acid (1 g), $[\alpha]_{546} +522^{\circ}$. Crystallisation from methanol gave 0.8 g, m.p. 111-112°, $\alpha_{546} + 0.08^{\circ}$, $[\alpha]^{21}_{546} + 444^{\circ}$. (c = 0.036, l = 0.5, 95% ethanol).

(Found: C, 85.1; H, 5.5; O, 9.1. $C_{25}H_{20}O_2$ requires C, 85.2; H, 5.7; O, 9.1%).

Preparation of optically active 8,8-bishydroxymethyl [dinaphtho(8,1-ab, 1',8'-de)] -cyclonona-2,4-diene (19)

Preparation of (-)-diol

Powdered (-)-dimethyl ester (0.5 g), $[\alpha]_{546}$ -263° was heated under reflux in 100 ml of anhydrous ether in dry conditions. 0.25 g of lithium aluminium hydride suspended in 100 ml of anhydrous ether was added slowly and heating continued for four hours; after cooling the excess of lithium aluminium hydride was destroyed by adding a few drops of water and 100 ml of dilute sulphuric acid, and heating for another 30 minutes. The ethereal layer was separated, washed with water and dried over anhydrous sodium sulphate and the ether distilled off. The crude product was crystallised from chloroform, yield 0.25 g, m.p. 155-156°. α_{546} -0.31, $[\alpha]^{21.5}_{546}$ -378° (c = 0.164, l = 0.5, 95% ethanol). (Found: C, 84.6; H, 6.2. $C_{25}H_{22}O_2$ requires C, 84.7; H, 6.2%).

Preparation of (+)-diol

The (+)-diol was prepared in a similar way from (+)-dimethyl ester $[\alpha]_{546}$+234°. M.p. 155-157°, α_{546} + 0.17°, $[\alpha]^{20}_{546}$+320° (c = 0.106, l = 0.5, 95% ethanol).

(Found: C, 84.6; H, 6.4. $C_{25}H_{22}O_2$ requires C, 84.7; H, 6.3%).

Preparation of optically active 8-bishydroxymethyl[dinaphtho(8,1-ab, 1',8'-de)]-cyclonona-2,4-diene (18)

Preparation of (-)-alcohol

Powdered (-)-monomethyl ester (0.5 g), $[\alpha]_{546}$-478°, was reduced in a similar was as used for dimethyl esters. Crystallisation from chloroform gave, 0.2 g, m.p. 80-84° (effervescence). α_{546} -0.51°, $[\alpha]^{22}_{546}$ -554°. (c = 0.184, l = 0.5, 95% ethanol). (Found: C, 87.8; H, 6.2. $C_{24}H_{20}O$ requires C, 88.8; H, 6.2%).

Preparation of (+)-alcohol

Powdered (+)-monomethyl ester (0.5 g), $[\alpha]_{546}$+444°, was reduced in a similar way and crystallised from chloroform, yield 0.3 g, m.p. 81-84° (effervescence). α_{546}+ 0.13°, $[\alpha]^{21.5}_{546}$+ 500°(c = 0.052, l = 0.5, 95% ethanol).
(Found: C, 88.6; H, 6.2. $C_{24}H_{20}O$ requires C, 88.8; H, 6.2%).

Preparation of optically active 8,8-diethoxycarbonyl [dinaphtho(8,1-ab, 1',8'-de)] -cyclonona-2,4-diene (Reaction of (+)-8,8'-bisbromomethyl-1,1'-binaphthyl with diethyl malonate)

(+)-8,8'-Bisbromomethyl-1,1'-binaphthyl (1 g, 0.047 mole) $[\alpha]_{546}+348^{\circ}$ was suspended in anhydrous ether (10 ml) in a well dried three-necked flask, fitted with a dropping funnel, a stopper and a water condensor and stirred magnetically. Sodiomalonic ester, prepared in a dried and stoppered flask by dissolving 0.16g of freshly cut sodium metal in 10 ml of absolute ethanol and adding this to the diethylmalonate (0.5 g, 0.07 mole), was added dropwise to the stirred ether suspension at room temperature. The reaction mixture was heated under reflux for 15 minutes, cooled down to room temperature, when it contained solid. Water was added to complete the precipitation of the product which was filtered off washed with water and dried. The crude product was dissolved in benzene by boiling , treated with decolourising charcoal and filtered. Crystallisation from the filtrate gave 0.3 g , m.p. 263°, which was found to be optically inactive (mixed m.p. with racemic ester, 263-264°). The filtrate of this inactive ester was evaporated to dryness and dissolved in ethanol treated with decolourising charcoal, filtered and crystallisation from the filtrate gave 0.5 g of the ester, m.p. 128-130°. $\alpha_{546}+0.34^{\circ}$, $[\alpha]^{21.5}_{546}+317^{\circ}$ ($\underline{c}=0.214$, $\underline{l}=0.5$, 95% ethanol)

(Found: C, 79.2; H, 5.9. $C_{29}H_{26}O_4$ requires C, 79.4, H, 6.0%).

(+)-Diethyl ester $[\alpha]_{546}+317^{\circ}$ was hydrolysed to dicarboxylic acid using potassium hydroxide in a similar way as was used for racemic ester hydrolysis. After normal working up the acid obtained had m.p. 198-200°(effervescence) and remelted at 219-220°, m.p. and mixed m.p. with acid prepared by resolution were found the same.

$\alpha_{546}+0.57^{\circ}$, $[\alpha]_{546}^{19.5}+356^{\circ}$ ($\underline{c}=0.08$, $\underline{l}=2$, 95% ethanol).

Preparation of optically active [dinaphtho(8',1'-ab, 1",8"-de)]-cyclonona-2,4-diene-8-azepinium-1-spiro[5,8]tetradecane-1"'-piperidinium bromide (20)

(i) 8,8'-Bisbromomethyl-1,1'-binaphthyl (1 g, 1 mole), $[\alpha]_{546}$ -180°*, was dissolved in 10 ml of dry benzene and a solution of piperidine (0.5 ml, 2 mole) in 10 ml of dry benzene added dropwise at room temperature, stirring magnetically. Later the temperature was raised up to 50°, a solid product appeared, was filtered, washed with petroleum ether (b.p. 40-60°) and dried by suction; it was dissolved in water, boiled with decolourising charcoal, filtered. Crystallisation gave 0.8g of bromide, m.p. 250-255°d. α_{546} -0.15°, $[\alpha]^{20}_{546}$ -156° ($\underline{c}$ = 0.192, $\underline{l}$ = 0.5, 95% ethanol).

(Found: C, 72.9; H, 5.8; N, 3.2; Br, 17.9. $C_{27}H_{26}NBr$ requires C, 73.0; H, 5.9; N, 3.1; Br, 17.9%).

(ii) 8,8'-Bisbromomethyl-1,1'-binaphthyl (1 g, 1 mole), $[\alpha]_{546}$ +348° was treated with piperidine in a similar way. Crystallisation from water gave 0.75 g of the cyclic piperidinium bromide, m.p. 251-255°. α_{546} + 0.52°, $[\alpha]^{21}_{546}$ + 481° ($\underline{c}$ = 0.216, $\underline{l}$ = 0.5, 95% ethanol)

(Found: C, 69.4; H, 6.1; N, 3.0; Br, 18.1. $C_{27}H_{26}NBr.H_2O$ requires C, 70.1; H, 6.1; N, 3.0; Br, 17.3%).

Preparation of optically active 8,8-diethyl[dinaphtho(8,1-ab, 1',8'-de)]-cyclonona-2,4-diene-8-azepinium iodide (21)

(i) (-)-8,8'-Bisbromomethyl-1,1'-binaphthyl (1 g), $[\alpha]_{546} -180^{\circ}$* was dissolved in anhydrous benzene and freshly distilled diethylamine (0.25g, 2.2 mole) was added at room temperature. After the addition of diethylamine was completed the reaction mixture was warmed to 60°; a solid separated and petroleum ether (b.p. 40-60°) was added in order to complete the precipitation. The bromide was filtered, washed with petroleum ether and traces of solvent removed by suction, It was dissolved in water and boiled with decolourising charcoal, filtered and the filtrate concentrated, but salt did not crystallise. When a hot aqueous solution of potassium iodide was added, a precipitate separated which was redissolved by heating, treated with decolourising charcoal and filtered. Crystallisation from the filtrate geve, 0.9 g of the iodide, m.p. 150-155°. α_{546} -0.115°, $[\alpha]^{21}_{546}$ -287° (c = 0.08, l = 0.5, 95% ethanol)
(Found: C, 61.3; H, 5.5; N, 2.8; I, 26.4. Calculated for $C_{26}H_{26}NI.H_2O$ C, 62.8; H, 5.6; N, 2.8; I, 25.5%).

(ii) The (+) iodide was prepared in a similar way from (+)-bisbromomethyl compound $[\alpha]_{546}+348^{\circ}$ and crystallised from water, m.p. 152-155°, $\alpha_{546}+0.4^{\circ}$, $[\alpha]^{21}_{546}+363^{\circ}$ (c = 0.22, l = 0.5, 95% ethanol)
(Found: C, 63.6; H, 5.6; N, 2.9; I, 25.4. $C_{26}H_{26}NI.H_2O$ requires C, 62.8; H, 5.6; N, 2.8; I, 25.5%).

Preparation of 8,8-diallyl [dinaphtho(8,1-ab, 1',8'-de)]-cyclonona-2,4-diene-8-azepinium iodide (22)

(i) Reaction of (-)-8,8'-bisbromomethyl-1,1'-binaphthyl with diallylamine: (-)-8,8'-Bisbromomethyl-1,1'-binaphthyl, $[\alpha]_{546}-180^{\circ *}$ was treated with diallylamine in a similar way as with diethylamine, and the bromide formed was converted into the iodide. Crystallisation from water gave iodide, m.p. 170-173°, $\alpha_{546} -0.29^{\circ}$, $[\alpha]_{546}^{21.4} -140^{\circ}$ (c = 0.412, l = 0.5, 95% ethanol).

(Found: C, 66.4; H, 5.2; N, 2.7; I, 24.4. $C_{28}H_{26}NI$ requires C, 66.8; H, 5.2; N, 2.8; I, 25.3%)

(ii) Reaction of (+)-8,8'-bisbromomethyl-1,1'-binaphthyl with diallylamine: (+)-8,8'-bisbromomethyl-1,1'-binaphthyl, $[\alpha]_{546}+348^{\circ}$ was treated with anhydrous benzene solution of diallylamine in a similar way and the bromide formed was converted to iodide by the treatment with a hot aqueous solution of potassium iodide. Crystallisation from water gave iodide, m.p. 169-171°, $\alpha_{546}+0.695^{\circ}$, $[\alpha]_{546}+279^{\circ}$ (c = 0.064, l = 0.5, 95% ethanol)

(Found: C, 64.7; H, 5.2; N, 2.7; I, 24.6. $C_{28}H_{26}NI$ requires C, 66.8; H, 5.2; N, 2.8; I, 25.3%)

3.3 Discussion: Optical Activity and Optical Stability in 8,8'-Disubstituted 1,1'-Binaphthyls

a. Optical activity in unbridged 8,8'-disubstituted 1,1'-binaphthyls

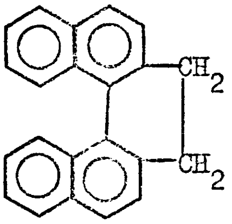
After the problem of the origin of optical activity in biphenyls was solved (Turner and LeFevre, 1926; Bell and Kenyon, 1926 and Mills, 1926) , Kuhn and Albrecht (1928) applied the principles to 1,1'-binaphthyls. They are "atropisomers", and under normal conditions the achievement of planarity becomes improbable and thus/they possess optical activity. The phenomenon of optical activity in the 1,1'-binaphthyl series was first realised in 1928 by Kuhn and Albrecht. These authors demonstrated the resolution of 1,1'-binaphthyl-2,2'-dicarboxylic acid. About 40 years ago, Stanley (1931) and Corbellini (1931) and a year lat~~t~~er Meisenheimer and Beisswenger (1932) prepared optically active 1,1'-binaphthyl-8,8'-dicarboxylic acid and remarked on its low optical stability. In 1949, Bell and Waring and in 1954, Crawford and Smyth; Bell and Morgan; Hall, Ridgwell and Turner investigated the strange fact that 1,1'-binaphthyl-5,5'-dicarboxylic acid which has no carboxylic group in the interfering positions is more optically stable than that of 8,8'-dicarboxylic acid. Another similar example where the amino groups are not substituted in the interfering positions of 1,1'-binaphthyl is 4,4'-naphthidine, obtained optically active by Theilacker and hopp (1959). By its deamination Harris and Mellor (1961) , Cooke and Harris (1963) were able to obtain optically active 1,1'-binaphthyl (half-life 13 min. at 50° in N,N-dimethylformamide). Recently Pincock and Wilson (1971) reported the spontaneous crystallisation of optically active 1,1'-binaphthyl from its racemic melt. The degree of optical stability of these chiral binaphthyls depends mainly upon the effective size of the blocking barriers but the 8,8'-dicarboxylic acid and its esters are exceptional.

1,1'-Binaphthyls with identical substituents in the 2,2'-, 4,4'- 5,5'-, 6,6'-, 7,7'- and 8,8'-positions have twofold axes of symmetry and belong to point group (C_2); i.e. they are dissymmetric nonasymmetric molecules. The C_2 axis passes through the centre of the 1,1'-bond and bisects the dihedral angle between like substituents.

Monosubstituted 1,1'-binaphthyls are examples of point group (C_1). These molecules lack all symmetry elements and are therefore asymmetric.

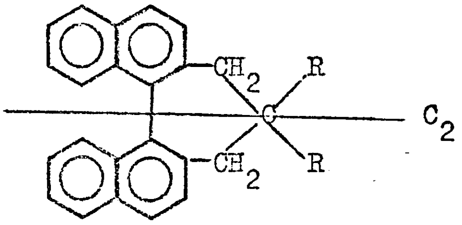
b. <u>Optical activity in bridged 1,1'-binaphthyls</u>

A large number of optically active compounds in the biphenyl series and some in 1,1'-binaphthyl series with a bridge running from one ring to the other have been reported during the last 20 years from the Schools of Professor E.E.Turner and Dr. D.M.Hall in England and Professor K.Mislow in United States. The overlapping of the substituents is not the only principal cause of restricted rotation, the angular strain in the transition state of racemisation is also responsible. Up to now the 2,2'-bridged 1,1'-binaphthyls are known optically active which have been made by a link between the naphthalene rings by means of a chain in such a manner as to form a ring larger than five-membered. A six-membered 2,2'-bridged 1,1'-binaphthyl (44) obtained in optically active form was reported by Hall and Turner (1955) with E_{rac} 30.8 kcal mol^{-1}. This is a dissymmetric nonasymmetric molecule (C_2).



(44)

When the 2,2'-positions are joined with a saturated chain with three atoms, the compounds are more optically stable than those with six-membered rings. When the 2,2'-positions are bridged by three atoms and they have two identical functional groups at the central atom of the bridge they are dissymmetric nonasymmetric molecules (C_2), but when the two groups at the bridge are not identical (other things remaining the same), the molecules lack all elements of symmetry and are therefore asymmetric (C_1)



(C_2 axis passes through the centre of 1,1'-bond of 1,1'-binaphthyl and the central atom of the bridge).

c. Optical stability in unbridged 1,1'-binaphthyls

The present work is mainly concerned with the optical stability of 1,1'-binaphthyls with two identical substituents in the 8,8'-positions (C_2). In these compounds the rotation about the 1,1'-bond of binaphthyl is prevented by the interference of the blocking substituents in the 2 and 8', and 2' and 8 positions. An extensive work on the stereochemistry of 8- and 8,8'-disubstituted 1,1'-binaphthyls has been done during last 19 years in the school of Dr. M.M.Harris (Harris and Mellor, 1959; 1961; Harris and Ling, 1962; Cooke and Harris, 1963; Badar, Cooke and Harris, 1965; Badar and Harris, 1964; Harris, Mazengo and Cooke, 1967; Dixon, Harris and Mazengo, 1971; Browne, Harris, Mazengo and Singh, 1971). Earlier, Stanley (1931) suggested That the reason for the low optical stability of the 8,8'-dicarboxylic acid may be ~~due to the fac~~t that the carboxylic groups in this acid are in the <u>peri</u>-positions. Distortions are less likely in the 2,2'-positions and thus the 2,2'-diacid shows optical stability. Cooke and Harris (1963) calculated that the entropy factor of transition-state theory functions is not sufficient to explain the lower optical stability in these compounds although it accounts for much of the optical instability of the 8,8'-diacid in aqueous alkali. Following the observations of Hernik, Herbstein, Schmidt and Hershfield (1954) that the overcrowding in a molecule arises when the distance between two non-bonded carbon atoms lie below 3Å ; Cooke and Harris (1963) suggested that in the 8,8'-diacid, the bond distance between the two <u>peri</u>- substituted carbon

Table II

No.	Compound	E kcal/mol	$\log_{10}A$	$\Delta F^{\neq}$ kcal/mol	$\Delta H^{\neq}$ kcal/mol	$\Delta S^{\neq}$ e.u.	Ref.
	8.8'						
1.	H,H	22.5	12.1	23.5	21.9	-5.2	27
2.	H,COOH	22.4	12.0	23.5	21.8	-5.5	27
3.	COOH,COOH	22.1	11.3	24.4	21.5	-9.1	27
4.	COOMe,COOMe	22.0	11.6	23.8	21.4	-7.5	27
5.	COOH,COOMe	21.6	11.4	23.7	20.9(5)	-8.4	27
6.	CH_2OH,CH_2OH	29.2	12.6	29.8	28.4	-3.4	7
7.	CH_2OH,COOMe	25.8	12.0	27.2	25.1	-6.2	7
8.	CH_3,CH_3	27.6	11.0	30.4	26.8	-9.4	7
9.	COO^-,COO^-	26.0	15.2	22.5	25.4	+9.2	27
10.	COO^-,COOEt	25.7	14.0	24.0	25.1	+3.2	27
11.	H,COOMe	23.6	12.5	24.1	22.9	-3.5	28
12.	H,CH_2OH	26.0	12.4	26.7	25.3	-3.8	28
13.	H,CH_3	25.3	11.7	27.2	24.6	-7.3	28
14.	$COOH,CH_3$	25.3	11.6	27.4	24.6	-7.7	55

Table II (contd.)

No.	Compound	E kcal/mol	$\log_{10}A$	$\Delta F^{\neq}$ kcal/mol	$\Delta H^{\neq}$ kcal/mol	$\Delta S^{\neq}$ e.u.	Ref.
	5,5'						
15.	COOH,COOH	24.1	12.3	25.4	23.5	-5.9	16, 27
16.	COO^-,COO^-	24.9	12.9	24.8	24.3	-1.5	16,27
17.	COOMe,COOMe	23.8	12.2	24.8	23.2	-5.1	27
18.	(compound 44 in text)	30.8	13.4	29.9	30.0	+0.3	44

Table III

No.	Compound	Reference
1.	2,2' $COOH,COOH$	Kuhn and Albrecht (1928) Hall and Turner (1955)
2.	2,2' NH_2,NH_2	Kuhn and Goldfinger (1929)
3.	2,2' CH_2OH,CH_2OH	Hall and Turner (1955)
4.	2,2' SO_3H,SO_3H	Armarego and Turner (1957)
5.	2,2' OH,OH; 3,3' $COOH,COOH$	Stanley and Adams (1929)
6.	2,2' OH,OH; 7,7' SO_3H,SO_3H	Ioffe and Grachev (1935)
7.	2,2' OH,OH; 6,6' SO_3H,SO_3H	" " " "
8.	2,2' NO_2,NO_2; 5,5' SO_3H,SO_3H	Murahashi (1932)

atoms is very small (2.4 Å) and there are two serious compressions. The way to find relief from these compressions without decomposition is the out-of-plane distortions of the 8,8'-carboxylic groups, which allows them to pass through the planar transition-state. In 1965, Badar, Cooke and Harris reported work on ~~some~~ 8,8'-disubstituted 1,1'-binaphthyls which have comparatively larger effective volumes of the substituents than those previously reported, and found a considerable increase in their optical stability, but did not reach the degree of stability observed for 2,2'-disubstituted 1,1'-binaphthyls.

On the basis of optical stability 1,1'-binaphthyls studied previous to the present work can be divided into two catagories:

1: Those which racemise (Table II)
2. Those which do not racemise (Table III) .

In the present work two 8,8'-disubstituted 1,1'-binaphthyls, 1,1'-binaphthyl-8,8'-diacetic acid (10) and 1,1'-binaphthyl-8,8'-bis(methylenepyridinium) diiodide (12) were obtained in optically active form, the former by resolution while the latter was synthesised from its optically active precursor, 8,8'-bisbromomethyl-1,1'-binaphthyl (8). As the pyridinium compound (12) decomposed in hot solvents the racemisation could not be studied. In the diacetic acid (10) the passing barriers are methylene groups and it was assumed that it would possess the degree of optical stability of the order similar to 8,8'-dimethyl and 8,8'-bishydroxymethyl-1,1'-binaphthyl (Badar, Cooke and Harris, 1965). The activation energy of racemisation and the Transition State Theory functions are given below in Table IV.

Table IV

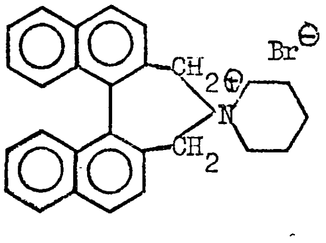
Compound 8,8'-	E_{rac} (kcal/mol)	$\log_{10}A$	$\Delta F^{\neq}$ (kcal/mol)	$\Delta H^{\neq}$ (kcal/mol)	$\Delta S^{\neq}$ (e.u.)	Solvent
CH_3 CH_3	27.6	11.0	30.4	26.8	-9.4	DMF
CH_2OH CH_2OH	29.2	12.6	29.8	28.4	-3.4	DMF
CH_2COOH CH_2COOH	31.9	14.0	29.6	31.2	+3.58	0.1N NaOH

The correlation of optical stabilities suggests that the steric situations in these compounds are probably very similar.

d. Optical stability in bridged 1,1'-binaphthyls

The optical stability of 9,10-dihydro-3,4,5,6-dibenzophenanthrene (44) cannot fairly be compared with that of 1,1'-binaphthyl, because the trans-passing route is not available.

The enlargement of the bridging ring from six atoms to seven atoms has shown a greater optical stability in this series of compounds. Hall and Turner (1955) reported some seven-membered ring compounds in the 2,2'-bridged 1,1'-binaphthyl series: $(+)_{546}$-2,7-dihydro-(2',1',3,4)(1",2",5,6)-azepinium-1-spiro-1"'-piperidinium bromide (45), a seven-membered ring compound obtained from $(-)_{546}$-2,2'-bisbromomethyl-1,1'-binaphthyl, has half life of 26 hours at 172° in ethylene glycol. The low optical stability is in fact a dramatic change in the 2,2'-disubstituted 1,1'-binaphthyl series as the corresponding unbridged binaphthyls are completely optically stable. The reason for the low stabil-



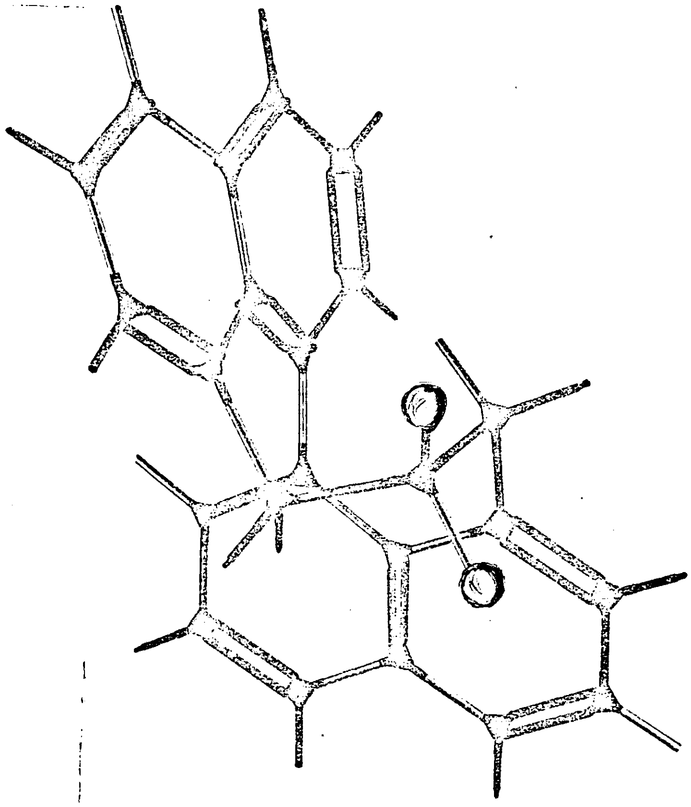
(45)

ities in these ring compounds, suggested by Hall and Turner (1955), is that the passage through the planar transition state of the 2,2'-bridged 1,1'-binaphthyls is mainly due to the considerable reduction in the ~~degree of~~ inter-planar angle in their ground state compared with the unbridged ones, thus the molecule requires less energy to pass through the transition state.

No seven or eight-membered ring compounds in the 8,8'-bridged 1,1'-binaphthyl series has yet been reported ~~to form.~~ In the present work the 8,8'-bridged carbocyclic and heterocyclic (nine-membered ring) compounds were obtained in optically active state, they are optically stable and failed to racemise. For example, after they had been heated up to melting and kept at that temperature for half hour, then cooled down slowly to solidify, they were recovered unchanged chemically and with the same rotation. The N-heterocyclic (quaternary ammonium salts) compounds also did not show any sign of racemisation, they decomposed on melting.

A theoretical treatment for the optical stability and the energy required to bring the cyclononadiene system into the transition state to invert the configuration seems a very complicated task, which could not be very likely to give an accurate answer. Looking at the photograph of the model, the distortion is really spread over the whole molecule, all the bonds, even the main 1,1'-bond of 1,1'-binaphthyl, and the naphthalene rings are distorted and it will be difficult to work out the real amount of energy for this molecule which could bring it into the planar transition state. A crudest calculation on the lines followed by Mislow, Hyden and Schaefer (1962) gives a value of approximately 75-80 kcal mol^{-1} (from calculation 208 kcal mol^{-1}), an impossibly high figure.

In the ground state of these nine-membered ring compounds, only one conformation ~~was~~ is observed to be possible; the Drieding models



suggest a possibility of a highly overcrowded second conformation, made by applying a very great strain, which is very unlikely: the central atom of the bridge and the functional groups have to make a home in the moiety of the aromatic system, and they feel severe overcrowding. The interplanar angle between the two naphthalene rings is approximately orthogonal. A huge amount of energy (see page 148) would be required to bring the molecule into a <u>cis</u>-planar conformation, which would break the bonds before it happens to occur~~e~~. As none of the passing transition mechanisms looks favourable, the complete optical stability of the nonacyclodiene system in the present work seems perfactly reasonable.

4. ULTRA-VIOLET ABSORPTION SPECTRA OF 1,1'-BINAPHTHYLS

4.1 Introduction

Ultra-violet absorption spectra are frequently used in stereochemistry to study the steric effects in biaryls. The bond joining two aryl units, called the 'interannular bond', has partial double bond character, and may show a typical absorption spectrum of the whole molecule. When two or more chromophores have maximum conjugation, the π-electrons across the interannular bond will have a maximum overlap, which results in resonance between the two chromophores; thus the absorption band shows a bathochromic shift with an increased intensity of absorption.

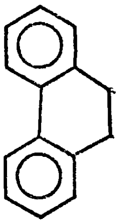
The angle between the π-planes of two chromophores is called the 'dihedral angle', and a gradual increase in the degree of dihedral angle up to 90° reduces gradually the π-electron overlapping across the interannular bond, and reduces the amount of resonance between the two chromophoric groups. When the dihedral angle is sufficiently large, the π-electron overlap across the interannular bond is greatly reduced and the resulting electronic absorption appears as the sum of two component parts of the molecule. This is the case with highly hindered molecules.

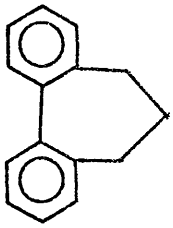
An extensive study has been made in the biphenyl series on the relation between conformation and conjugation. Benzene mainly absorbs u.v. light in two regions; one around 198 nm, an intense band (ε max, 8000), and another between 230-270 nm. The absorption spectrum of biphenyl is quite different from that of benzene, the maximum absorption band is shifted bathochromically to 255 nm (ε max, 18000) and the fine structure has disappeared; these effects are due to the presence of resonance between the two benzene rings through the interannular bond, the absorption band of biphenyl at 255 nm is known as the 'conjugation band'.

Dhar (1932) Robertson (1961), Trotter (1961), Hargreaves and Rizvi (1962) using X-ray crystallography suggested a coplanar structure for biphenyl in crystalline state, and later Braude (1945) among others suggested a dihedral angle nearer to 45° in solution.

In compounds where the suitable positions of biphenyl are substituted with bulky substituents giving steric hindrance to planarity, and the two benzene rings are kept apart from the resonance across the interannular bond, the conjugation band disappears; for example, the electronic absorptions of 2,2',4,4',6,6'-hexamethylbiphenyl appears as the sum of the absorption by two 1,3,5-trimethylbenzene units (O'Shaughnessy and Rodebush, 1940), the conjugation band of biphenyl does not appear. Biphenyls in solution have an infinite number of conformations, and which one has been involved in the electronic transitions exhibited in the absorption spectrum it is difficult to know. To overcome this uncertainty in the ground state, the 2,2'-positions of biphenyl have been joined with a saturated bridge of one or more atoms; in these cases the planes of two benzene rings can have a certain fixed dihedral angle (in non-flexible molecules) producing a strainless multiplanar ring, provided that normal bond lengths and angles obtain in the ground state.

Beaven, Hall, Lesslie and Turner (1952) reported the u.v. absorption spectrum of 9,10-dihydrophenanthrene (46) which has a linear biphenyl structure ~~molecule~~ and shows a high intensity typical biphenyl band at 264 nm (ε max, 17000) and broad low intensity band at 299.5 nm (ε max, 4450). The appearance of these absorption bands separate from the unconjugated phenyl chromophores made it reasonable to think about a lesser dihedral angle in this compound than biphenyl itself.


(46)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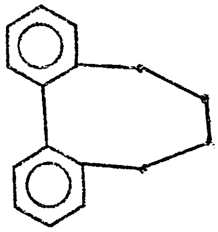

(48)

Hall and Minhaj (1957) with the use of normal covalent radii and bond angles calculated the dihedral angle for (46) as 15°. A group with Professor E.E.Turner at Bedford College and others reported u.v. absorption spectra of several seven-membered ring compounds obtained by joining the 2,2'-positions of biphenyl. The u.v. absorption spectrum of (47) was reported by Cope and Smith (1956) for which Beaven and Hall (1956) calculated dihedral angle 49° from scale models. On increasing the size of the bridging ring by four atoms (48), Cope and Smith (1956) observed its u.v. absorption spectrum and found a hypsochromic shift of the biphenyl conjugation band at 255 nm (ε max, 9680) and long-wave inflections at 265 nm and 275 nm. The appearance of long-wave absorption as inflections and the hypsochromic shift of the absorption maximum with reduced intensity suggest a comparatively large departure from the π-electron overlap across the interannular bond. Beaven and Hall (1956) measured a dihedral angle 59° (and 75°) for this compound. from a scale model.

In 1962, Mislow, Hyden and Schaefer reported the u.v. absorption spectrum of (1) a flexible multiplanar ring compound; the biphenyl conjugation band appears as an inflection at 251 nm (ε max 5550) with long-wave bands appearing at 265 nm (ε max 800) and 273 nm (ε max 600) suggesting a larger departure from resonance between the two benzene rings through the interannular bond. Suzuki (1967) by using LCAO-MO method calculated the dihedral angle for this acid (1) to be 68°.

From this series of bridged biphenyl compounds in their ground state it is concluded that as the bridge is enlarged, the dihedral angle increases, the degree of conjugation across the interannular bond decreases, and the molecule possesses a more and more strainless multiplanar configuration. 1,1'-Binaphthyl is a next higher analogue of biphenyl, formed by the linear annelation of benzene rings and therefore similar generalisations could be applied to bridged 1,1'-binaphthyls.

4.2 Ultra-violet Absorption Spectra, Results and Discussion

1: Instrument	Unicam Spectrophotometer (SP 500)
2: Source of radiation	340 nm to 320 nm Tungsten lamp, below 320 nm hydrogen lamp
3: Cell	2 mm silica cell
4: Solvent	95% ethanol

Ultra-violet absorption characteristics are given in the following table and spectra are in figure 5 – 8.

Ultra-violet absorption spectra characteristics: (λ nm)

Compound and concentration	Short-wave band				Long-wave band	
	λmax	εmax	λmin	εmin	λmax	εmax
(9)	224.5	54800	265	5000	(280)	7890
0.2-0.02					302	12370
(10)	222.5	83100	257	5500	269	7300
0.12-0.012					279	10000
					290	12700
					301	1200
					324	2430
(11)	223	87300	257	5550	267	7300
0.12-0.012					277	9900
					290	13100
					301	12100
					324	2200
(12)	221.5	139400	274	11200	285	12560
0.144-0.0144					293	13400
(14)	223.5	79550	255.5	4850	272	8880
0.176-0.0176					285	14100
					293	17400
					302	14100
					319	1900
(15)	224	82600	256	4680	273	8900
0.176-0.0176					283	13800
					293	17800
					304	14000
					319	2000

Compound and concentration	Short-wave band				Long-wave band	
	λmax	ε max	λmin	ε min	λmax	ε max
(16)	223.5	85500	255	5100	272	9350
0.12-0.012					282	13900
					293	18300
					303	14800
					319	2100
(17)	223	75900	255	4750	272	8770
0.108-0.00864					282.5	13200
					292.5	16670
					302.5	13100
					319	1800
(18)	225	88700	255	4290	273	9550
0.28-0.00168					284	15000
					293	18900
					303	15500
					319	2300
(19)	225	87500	257	5100	274	8990
0.52-0.0054					284	13240
					294	16600
					305	12900
					320	1970
(20)	223	85500	255	4200	286	15000
					297	17600
					303	14500
					321	2200

Compound and concentration	Short-wave band				Long-wave band	
	λmax	ε max	λmin	ε min	λ max	ε max
(21)	222	89960	255.5	4180	273	8600
0.26-0.026					287	13670
					296.5	15900
					301	13700
					319	2750
(22)	223	93200	254.5	4200	285	14260
0.41-0.0164					297	17000
					305	13000
					320	2800

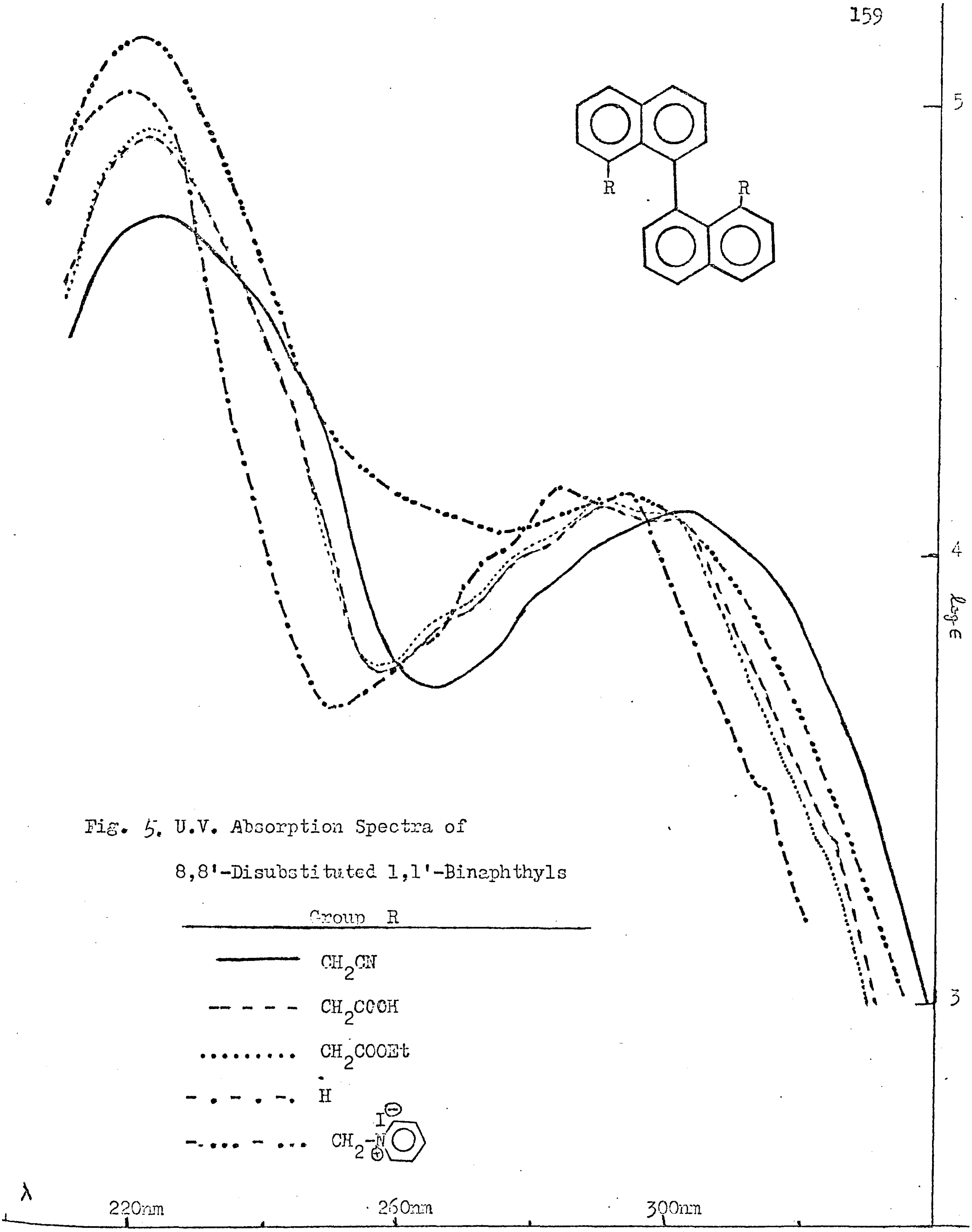


Fig. 5. U.V. Absorption Spectra of 8,8'-Disubstituted 1,1'-Binaphthyls

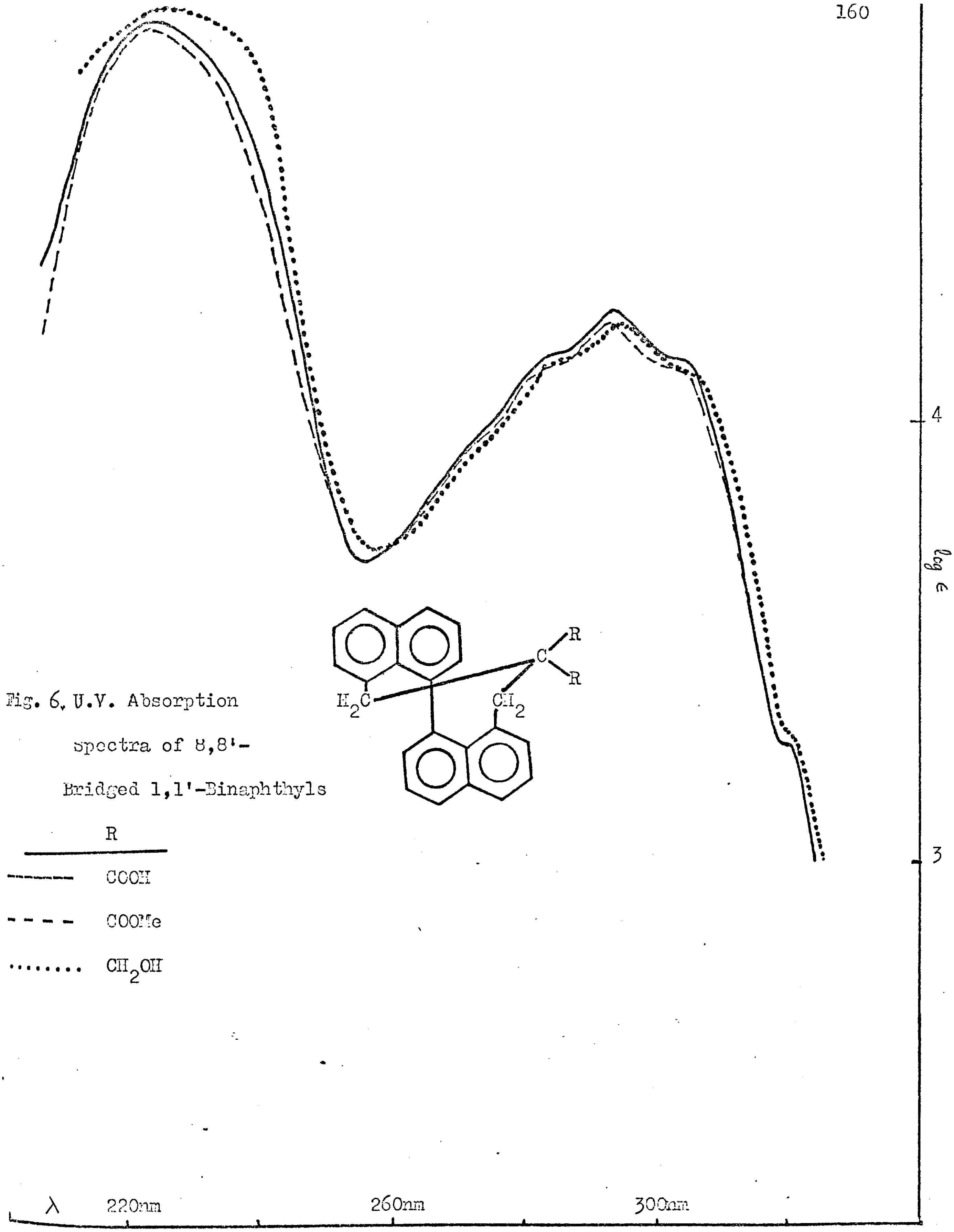


Fig. 6. U.V. Absorption spectra of 8,8'-Bridged 1,1'-Binaphthyls

	R
———	COOH
- - - -	COOMe
....	CH_2OH

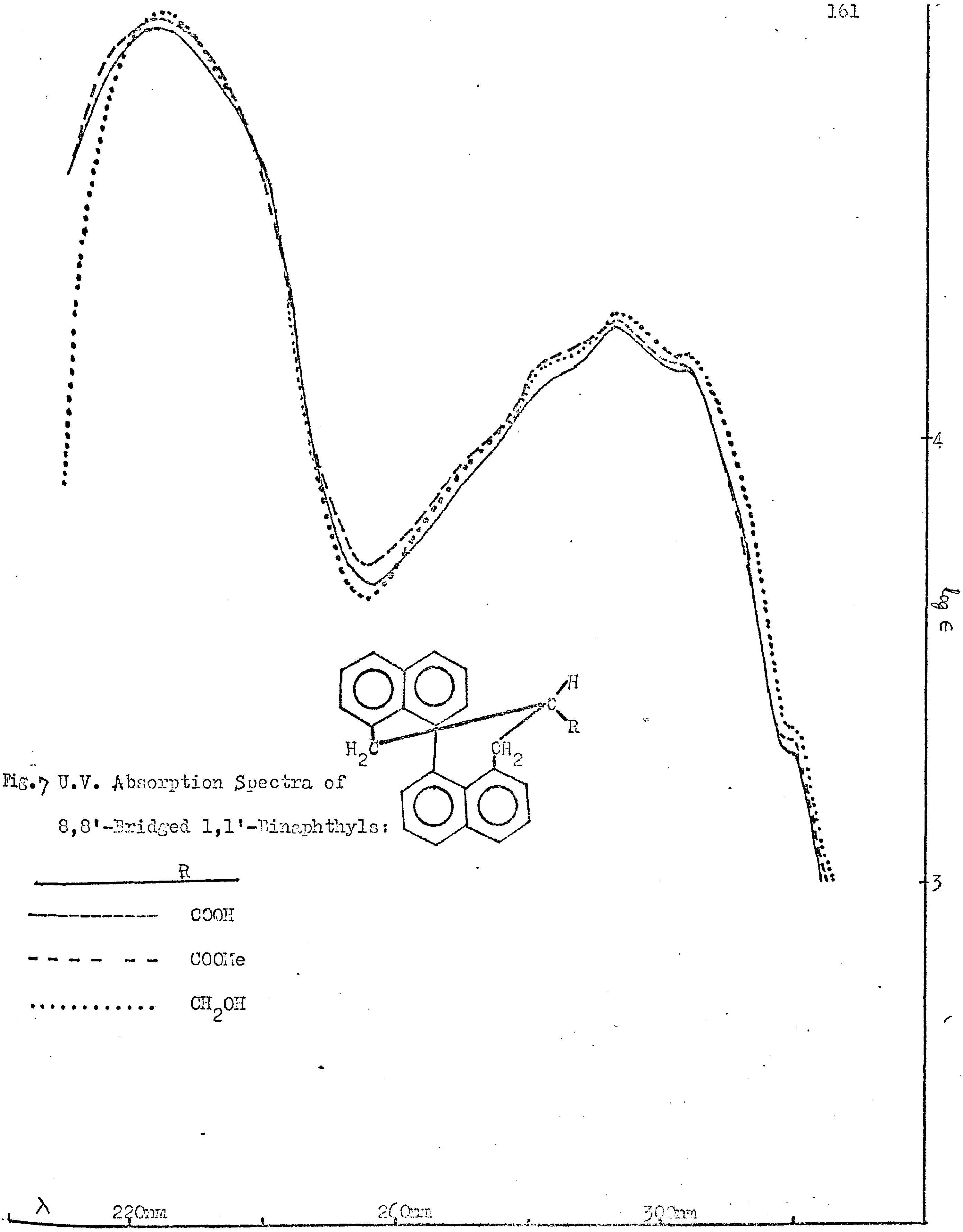


Fig.7 U.V. Absorption Spectra of 8,8'-Bridged 1,1'-Binaphthyls:

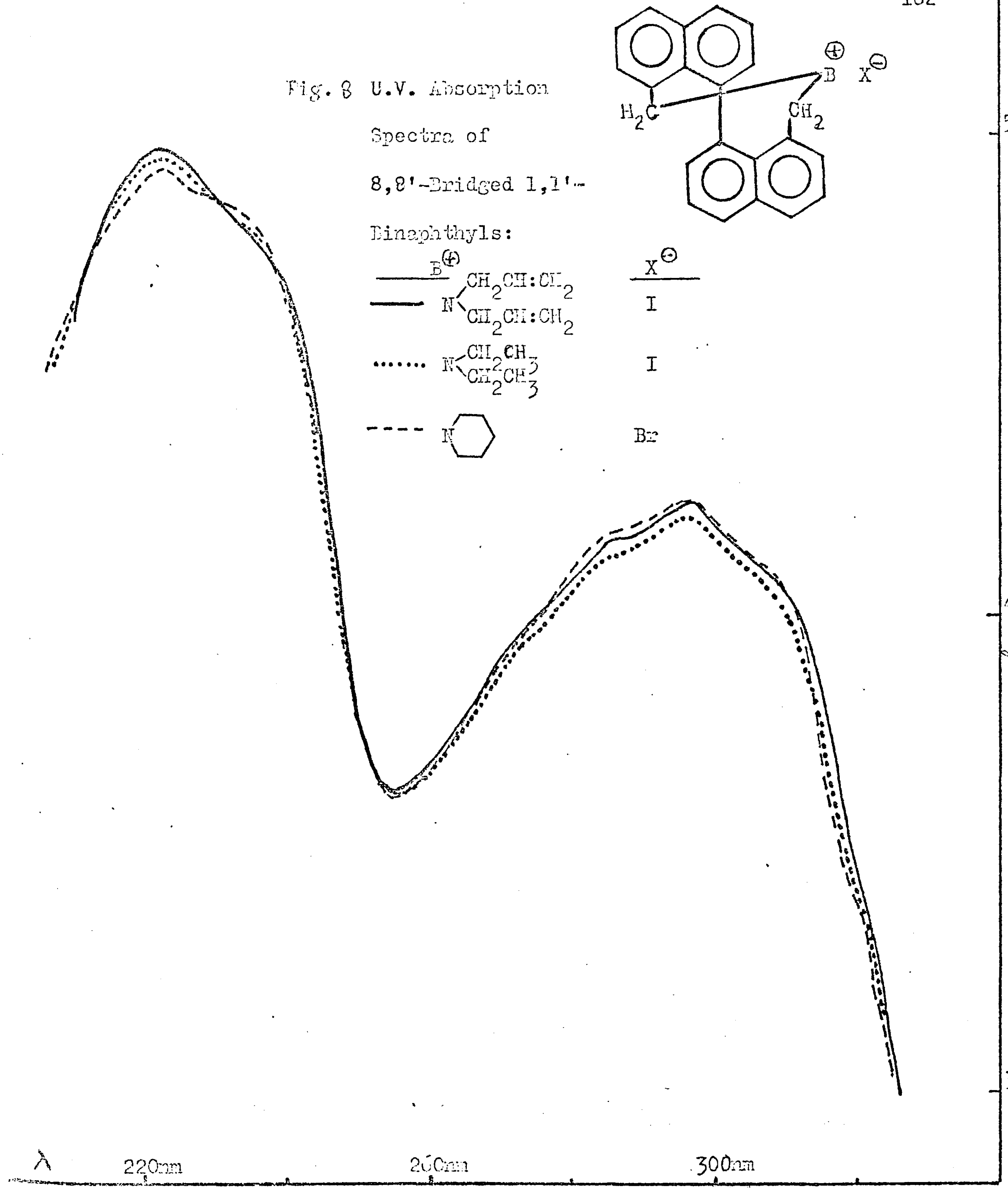


Fig. 8 U.V. Absorption Spectra of 8,8'-Bridged 1,1'-Binaphthyls:

Discussion of the ultra-violet absorption spectra of 1,1'-binaphthyls

a. Unbridged 8,8'-disubstituted 1,1'-binaphthyls

(i) Open chain carbon compounds:

Naphthalene possesses dihedral symmetry and in equilibrium the nuclear configuration of naphthalene in ground electronic state belongs to point group (D_{2h}), and shows a u.v. absorption spectrum with a low intensity band at 312 nm (εmax ~ 100-1000) with fine structure; the second absorption is of intermediate intensity around 275 nm (ε ~ 10,000) with well resolved structure. The third absorption band is an intense band at 220 nm ($\varepsilon \sim 10^5$). When the two naphthalene units are joined together to make 1,1'-binaphthyl, an inherently dissymmetric chromophore, the parent hydrocarbon in the series of substituted 1,1'-binaphthyls, its u.v. absorption spectrum resembles to a certain extent that of naphthalene. Friedel, Orchin and Reggel (1948) reported the u.v. absorption spectrum of 1,1'-binaphthyl (95% ethanol) and said that it does not show a separate conjugation band as does biphenyl. The fine structure features in the 1,1'-binaphthyl spectrum are of intermediate order, this suggests that this molecule no longer planar ; partly on this basis Harris and Mellor (1961) became confident in its optical activity and were able to obtain it in optically active form.

Brown and Monteath Robertson (1961) by X-ray crystallographic studies made a preliminary observation of the angle between the two naphthalene planes as 73° for crystalline state. Later, Kerr and

Monteath Robertson (1969) also by X-ray crystallography found that its cis-conformation exists with a dihedral angle 68°.

According to molecular orbital theory, whatever is the degree of dihedral angle there would be at least some π-electron overlapping across the interannular bond. If there is some π-electrons interaction then it must have a conjugation band in its absorption spectrum resulting from the resonance between the two naphthalene units, but this might be overshadowed by the short-wave strong absorption band at 220 nm (Browne, Harris, Mazengo and Singh, 1971). The vibrational fine structure and the appearance of long-wave typical naphthalene band at 313 nm (3160, shoulder) correspond to the nonplanar structure of 1,1'-binaphthyl. LeFevre, Sundaram and Sundaram (1963) from molar Kerr constant determinations calculated the dihedral angle in solution for 1,1'-binaphthyl of 48°, it would be probable that there is still some degree of resonance between the naphthyl units through the interannular bond and weak π-electron interaction resulting in weaker intense absorption band which is certainly overlapped by a strong absorption band at 220 nm.

The substitution of groups in the 8,8'-positions of 1,1'-binaphthyl introduces some molecular overcrowding which is relieved by introducing distortions (Harris and Mellor, 1961; Cooke and Harris, 1963) making possible passing of these substituents in the planar transition state of racemisation; the same substituents in the 2,2'-positions do not need these distortions as they are less crowded and thus are optically stable. These distortions change the geometry of the molecule and could explain why the u.v. absorption spectra of the 8,8'-disubstituted 1,1'-binaphthyls differ substantially from those of 2,2'-substituted compounds. Mazengo (1968), Harris and Mazengo (1967) reported the u.v. of some 8,8'-disubstituted, 8-substituted and 2,2'-disubstituted 1,1'-binaphthyls and concluded that in 2,2'-disubstituted 1,1'-binaphthyls the degree of twist around the interannular bond in the ground state may be larger than in 8,8'- and 8-substituted 1,1'-binaphthyls. The absorption minimum in 2,2'-disubstituted compounds shows a hypsochromic shift and decreased intensity together with developed fine structure and appearance of the long-wave typical naphthalene band compared with the 8,8' compounds, for example, (Mazengo, 1968)

Compound	λ min	εmin
2,2'-dimethyl-1,1'-binaphthyl	248 nm	4400
8,8'-dimethyl-1,1'-binaphthyl	256 nm	5600
2,2'-bishydroxymethyl-1,1'-binaphthyl	250 nm	5100
8,8'-bishydroxymethyl-1,1'-binaphthyl	258 nm	5800

1,1'-Binaphthyl-8,8'-dicarboxylic acid and its methyl ester show an absorption band at short-wave length 219.5 nm (εmax 60000) and 239.5 nm (shoulder, 44000) and for the methyl ester 219,5 nm (εmax 65000) and 238 nm (47000). This splitting of the short-wave band does not appear in the spectrum of the 2,2'-dicarboxylic acid. The splitting of the short-wave band in 8,8'-diacid and its methyl ester was suggested (Mazengo, 1968) to be due to the conjugation between carboxylic acid group and the corresponding naphthyl residues and not between the two naphthalenes.

The replacement of these carboxylic groups in the 8,8'-positions of 1,1'-binaphthyl by bulkier groups (methyl, bishydroxymethyl and bisbromomethyl) show developed fine structure and the absence of a split band at 239.5 nm of the 8,8'-dicarboxylic acid; the spectra resemble more closely the spectrum of 1,1'-binaphthyl itself. The study was made of the effect of carboxylic acid and ester groups isolated by methylene groups from the naphthyl units in the 8,8'-positions; the spectra of 1,1'-binaphthyl-8,8'-diacetic acid (10) and its ethyl ester (11) and 8,8'-biscyanomethyl-1,1'-binaphthyl (9) were observed in 95% ethanol.

The spectra of (10) and (11) resemble those of 1,1'-binaphthyl itself and 8,8'-disubstituted (methyl and bishydroxymethyl) compounds, which suggests that the carboxylic groups do not effect the absorption pattern in these compounds (10 and 11) as they are isolated from the aromatic nuclei. The positions of the absorption minima in (10) and (11) at 257 nm (εmax 5500) and (5550) respectively are very close to those of the 8,8'-dimethyl-1,1'-binaphthyl and 8,8'-bishydroxymethyl-1,1'-binaphthyl; these findings suggest that dihedral angle in (10) and (11) corresponds to that of 8,8'-disubstituted methyl and bishydroxymethyl compounds, and the steric situations in these compounds are probably the same.

The absorption spectrum of 8,8'-biscyanomethyl-1,1'-binaphthyl (9) did not resemble that of its diacid (10); a long-wave length shift of the spectrum was observed with reduction in intensity of the absorption maximum at short-wave length. The fine structure feature of p-band disappeared and the absorption minimum bathochromically shifted.

(ii) U.v. absorption spectrum of 1,1'-binaphthyl-8,8'-bis(methylenepyridinium) diiodide (12):

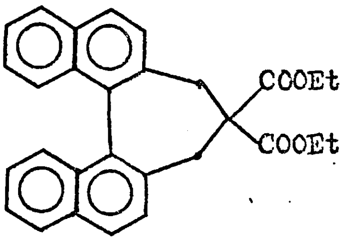
The u.v. absorption spectrum of (12) did not resemble the other compounds in this series and did not show vibrational fine structure; at the same time the long-wave band of naphthalene disappeared. The absorption minimum was observed at 274 nm (εmin 11,200) and the short-wave unsplit intense band at 221.5 nm (139,400). It can be supposed that this molecule has the same dihedral angle as in other 8,8'-disubstituted 1,1'-binaphthyls. The shift of absorption minimum towards long-wavelength at 274 nm (usually around 257-258 nm) with a comparatively high intensity could be due to the pyridine absorption band resulting from the $\pi - \pi^*$ transition at 252nm; also some shoulders at the long-wave end of this band (Gillam and Stern, 1957); thus this observed minimum is not the real minimum for the main 1,1'-binaphthyl nucleus. Organic cations normally have an excited state less polar than their ground state and show a large blue shift of charge transfer absorption on changing from a less polar to more polar solvent. In this molecule, the u.v. spectrum observed in 95% ethanol and in chloroform did not show any shift of the absorption bands. This again could be due to the charge stabilisation, which the increased polarity of the solvent could not effect or it could be due to the two ends of the molecule having positive charge and hence the (+)-(+) repulsions. Another reason might be found in that the positively charged nitrogen atom is lying over the π-cloud of the opposite naphthalene ring.

b. Ultra-violet absorption spectra of 8,8'-bridged 1,1'-binaphthyls

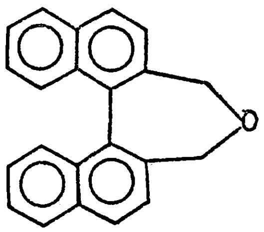
In the ground state bridging makes these 1,1'-binaphthyls multiplanar with one preferred conformation.

(i) Carbocyclic compounds:

Hall and Turner (1955) reported the preparation of 9,10-dihydro-3,4,5,6-dibenzophenanthrene (44). The u.v. spectrum of this compound (Hall and Mazengo, 1967) shows a strong conjugation band at 239 nm (ε max 42000). This molecule is nearly planar as the bridging methylene groups reduce the dihedral angle. This molecule is ~~a~~ dissymmetric and has a twofold axis of symmetry (C_2). Compounds in this series with three atoms in the bridge (Mislow, Glass, O'Brien, Rutkin, Steinburg, Weiss and Djerassi, 1962) also show splitting of the short-wave maximum absorption band. Compound (49) show an absorption maximum at 220 nm (112,200) and 232 nm (74,000); similarly an oxepin (50) shows this side



(49)



(50)

band at 231 nm (72400)

Ultra-violet absorption spectra of 1,1'-binaphthyl-8,8'-bridged carbocyclic compounds

The dicarboxylic acid (14) belongs to point group (C_2) and monocarboxylic acid (15) to point group (C_1), but the main u.v. absorption characters of both acids were found to be very close (see figure 6+7). The two spectra possess fine structure and the long-wave typical naphthalene band appeared at 319 nm (shoulder, 1900–2000). A slight reduction in the intensity of absorption minimum and blue shift compared with unbridged compounds suggests that the twist about the 1,1'-bond in the bridged compounds is larger. A marked difference between the spectra of open and bridged compounds was found in that the carboxylic acid groups of the latter did not effect the spectrum of the main skeleton, this is presumably because they are isolated by carbon atoms from the aromatic ring system. The spectra of their methyl esters (16) and (17) resemble the acids suggesting that the factors involved in the transitions were very similar.

The replacement of the methoxycarbonyl groups by bishydroxymethyl groups on the central carbon atom of the bridge did not alter very much the spectra of their synthetic precursors. The effect of hydroxyl groups was found similar to the 8,8'-bishydroxymethyl or 2,2'-bishydroxymethyl 1,1'-binaphthyls and the aliphatic chain. Owing to its auxochromic nature, a slight increase in intensity of the absorption bands were found; for example the dimethyl ester (17) shows absorption maximum at 223 nm (εmax 75,900) and the dialcohol (19) at 225 nm (εmax 87,500) but the appearance of this band in both mono- and dialcohols (18) and (19) are distinctly similar, in both cases maximum absorption occurs at 225 nm, thus the steric situations in these carbocyclic (8,8'-bridged 1,1'-binaphthyls) compounds are presumably approximately the same.

(ii) Ultra-violet absorption spectra of 8,8'-bridged N-heterocyclic compounds

The absorption spectrum of the compound (20) shows an intense short-wave band at 223 nm (εmax 85,500) very close to that of the carbocyclic compounds. Fine structure features were slightly diminished and the long-wave typical naphthalene band appeared as shoulder at 321 nm (εmax 2200). Splitting of the β-band was observed (see figure 8) this might be due to the positive charge or to the presence of halide ion in the solution.

The absorption spectra of the compounds (21) and (22) resemble (20); their absorption maximum appeared at 222 nm (εmax 90000) and 223 nm (εmax 93000) respectively, other features of their spectra were remained very close to each other. The position of the absorption minimum in these three quaternary ammonium halides were found at 255 nm (4200), 255.5 nm(4200) and 254.5 nm (4200), which is explained by the dihedral angles in these compounds being the same and other steric situations are also very close to each other. Variations in the length of the substituents at the bridge carbon atom and also on the azepinium nitrogen did not effect the main chromophoric transition characteristics of the spectra.

5. CHIROPTICAL EFFECTS AND STEREOCHEMICAL CORRELATIONS

5.1 Introduction

From very begining of stereochemistry it has been realised that the optical activity of a molecule is a function of the arrangement of atoms or groups distributed in the space within the molecule, and this close relation between optical activity and the molecular geometry is reflected in the refinement of the study of absolute stereochemistry. The optical activity of an organic molecule necessarily requires chiral structure of the molecule, together with the chiral distribution of valence electrons which are present in the individual chromophores of the electronic spectra. On this basis it could be imagined that the molecule is a framework of electronic oscillators, all of them contribute to the total optical activity; as a result the optical activity in a molecule is the sum of rotation of plane-polarised light contributions both by the intensity and anisotropy of each absorption band.

A dissymmetric molecule which has several chromophores of different nature, where one or more than one electronic transition can occur corresponding to each chromophore, shows Cotton effects (defined later). Professor A.Moscowitz (1961, 1962) classified optically active chromophores into two classes:

(i) Inherently dissymmetric chromophores, and

(ii) Dissymmetrically perturbed symmetric chromophores.

In the inherently dissymmetric chromophores, electrons occupy an enantiomeric configuration even in an achiral environment and have very high optical activity and show intense Cotton effects,

The sign of the Cotton effect of an inherently dissymmetric chromophore is directly related to the chirality of the chromophore itself, but the sign of Cotton effect of a symmetric chromophore perturbed in a chiral environment, e.g. a keto group, depends on the chirality of the perturbing medium.

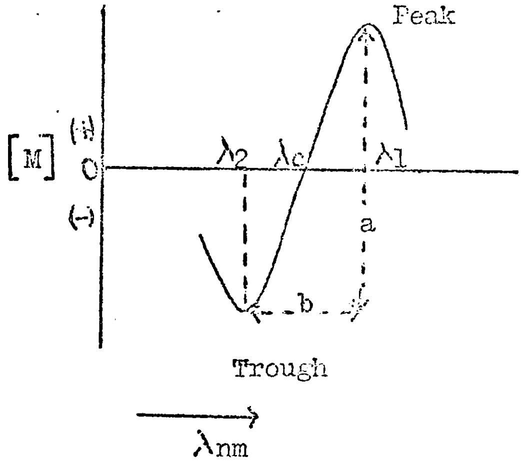
The optical activity of a molecule can be assessed by two effects on polarised light: circular birefringence and circular dichroism. The former is studied by measuring the rotation of the plane of polarisation of the plane-polarised light, or in other words the difference in velocity of the right- and left-circularly polarised beam, as a function of the energy of radiation.A plot of molecular rotation of the oscillating plane of linearly polarised light against wavelength (nm) gives an optical rotatory dispersion (o.r.d.) curve. For compounds which do not absorb in a particular region of wavelength, the plot is a "plain curve", but if the molecule absorbs radiation as a result of an electronic transition an anomalous curve or "Cotton effect" is observed. The sign and amplitude of a Cotton effect curve give significant information about the real arrangement of the ligands in space (i.e., the absolute configuration) of the molecule. When the positive extremum of the o.r.d. curve (the peak) is at longer wavelength than the negative extremum (the trough), the Cotton effect is positive; when the negative extremum is at longer wavelength than the positive extremum, the Cotton effect is negative.

Units and definitions of optical rotatory dispersion parameters

Molecular rotation $[M]$ is defined as

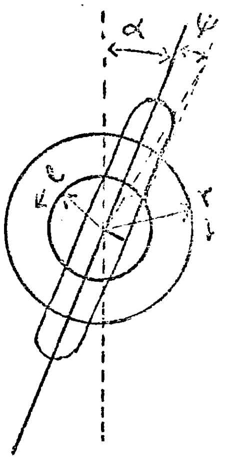
$$[M] = \frac{M[\alpha]}{100} \text{ (in degrees)}$$

where M is the molecular weight of the optically active compound and $[\alpha]$ the specific rotation.



The amplitude $\underline{a} = ([M]$ for extremum of long wavelength $- [M]$ for extremum of shorter wavelength$)/100$, expressed in degrees. The horizontal distance $\underline{b}$ (breadth of the Cotton effect is defined as $\underline{b} = \lambda_1 - \lambda_2$, where λ_1 and λ_2 are the wavelength of peak and trough respectively and expressed in nanometers (nm). λ_0 is the wavelength where the curve changes its sign and rotation is zero.

When the radiation has a frequency close to an absorption band, both the refractive indices and the extinction coefficients for left- and right-circularly polarised beams which make up the plane polarised light will not be identical and therefore after passing through the optically active substance the two waves will not recombine to make plane-polarised light but will result in an elliptically polarised vibration form, making an angle α between its major axis and the original plane of polarisation. The medium is said to exhibit circular dichroism. The ellipticity of the wave is defined as the angle whose tangent is the ratio of the minor to the major axis of the ellipse.



(The rotation α and ellipticity ψ of plane-polarised light emerging from an optically active solution in the absorption region)

Units and definitions of c.d. parameters

Molar ellipticity $[\theta]$ is defined as

$$[\theta] = 3300\,\Delta\varepsilon$$

where $\Delta\varepsilon = (\varepsilon_l - \varepsilon_r) =$ differential absorption. The amplitude $\underline{a}$ is $40.28\,\Delta\varepsilon$ or $\underline{a} = 0.0122[\theta]$

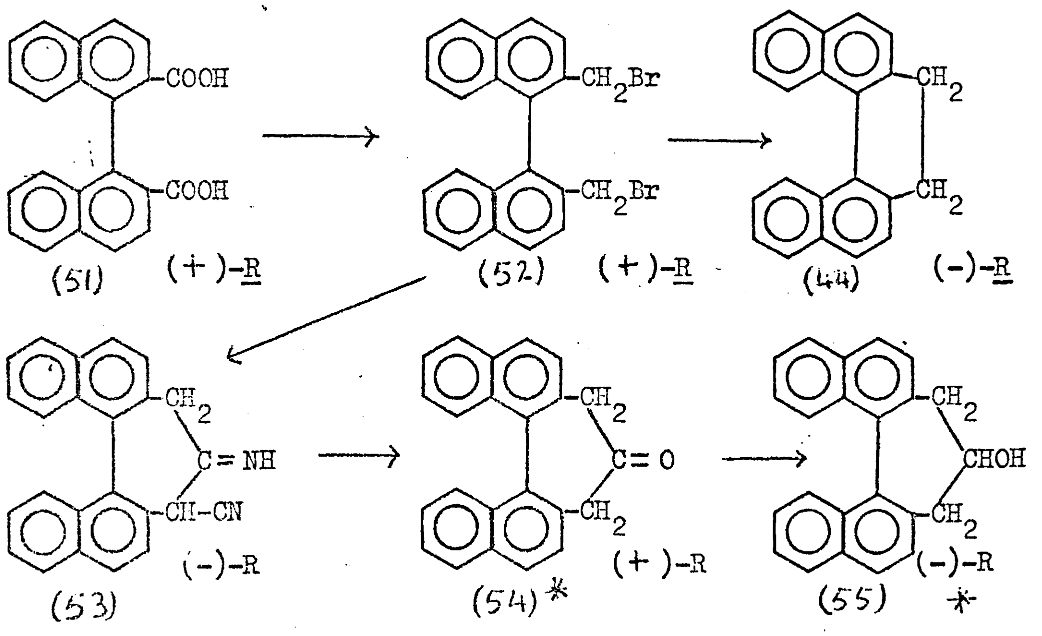
A plot of molar ellipticity against wavelength (nm) gives a circular dichroism (c.d.) curve.

5.2 Stereochemical Correlations:

The following methods have been applied to skewed biaryls (inherently dissymmetric) to determine absolute configuration

(1) Asymmetric Synthesis:- In this method asymmetry in introduced in the course of a reaction, which involves the preferential formation of one or other diastereoisomer in the reaction of (±)-substance with an unsymmetrical reagent. The reagent approaches the part of the molecule to be reduced from the less hindered side. Meerwein-Ponndorf-Verley reduction of a keto group has proved effective as suggested by Woodward, Wendler and Brutschy (1945). A biphenylic ketone has been reduced by centrally asymmetric alcohols of known absolute configuration by Newman, Rutkin and Mislow (1958) and resulted in configurational determination of biphenyls and later of 1,1'-binaphthyls (Mislow and McGinn, 1958). The stereospecificity of this method is generally applicable one.

R-configurations assigned on the basis of asymmetric synthesis and chemical correlation: (Mislow and McGinn, 1958)



*configuration assigned to which the others are related. The compound (54) differs from ketones (RR'C=O) in the classical Meerwein-Ponndorf-Verley reduction in two ways: (a) It can exist in enantiomeric forms, (b) hydrogen transfer to either face of the carbonyl group in a given enantiomer produces the same alcohol (55), i.e. *R*-(54) only gives *R*-(55) on reduction; this is because compound (54) is a dissymmetric nonasymmetric molecule and has a twofold axis of symmetry C_2, and the compound (55) is an asymmetric molecule (C_1). Compounds with three atoms in the bridging in the 2,2'-positions of 1,1'-binaphthyls are fairly highly optically stable. Hydrogen can be transfered by a given enantiomer of (RR'CHOH) i.e. *S*-(+)-2-octanol to either face of the carbonyl carbon of (54). From inspecting models of the transition state, it was expected that reduction of the *R*-isomer by *S*-octanol would take place quicker than that of the *S*-isomer. As *S*-(+)-2-octanol produces *R*-(-)-(55), which is related to (+)-1,1'-binaphthyl-2,2'-dicarboxylic acid (51), thus gives the *R*-configuration for the optical isomers of the compounds shown above.

(2) Configurational correlation of biaryls by Optical Displacements:- Fitts, Siegel and Mislow (1958) argued that the success of Freudenberg's Displacement Rule in the centrally asymmetric optically active compounds depends on the similarity in size and shape of the molecules to be compared. The authors said that like shifts in optical rotation will take place in related derivatives of biaryls of the same configuration,

and make a basis for a chemical correlation. Using the polarisability theory of optical activity, the authors assigned the S-configuration to (+)-9,10-dihydro-3,4,5,6-dibenzophenanthrene (44). Therefore its synthetic precursor, (−)-2,2'-diacid (51) has also S-configuration. The Absolute configurations of these compounds already reported (Mislow and McGinn, 1958) confirm the validity of this rule. Fitts, Siegel and Mislow (1958) observed the optical rotations of several 2,2'-bridged biaryls of known configuration. 2,2'-Bridged compounds derived from S-(−)-6,6'-dinitro-2,2'-diphenic acids and S-(−)-dichloro-2,2'-diphenic acids have stronger dextrorotatory power than their parent unbridged acids. 2,2'-Bridged compounds derived from S-(+)-6,6'-dimethyl-2,2'-diphenic acids again show considerably larger dextrorotation. On the basis of these findings it has been proposed by Fitts, Siegel and Mislow (1958) that going from unbridged to 2,2'-bridged biaryls, involving a change in the interplanar angle, reflects a characteristic change in the sign and magnitude of the optical rotation, and follows a general 'Optical Displacement Rule', i.e. a symmetrically substituted hindered biaryl has the S- (resp. R-) configuration, if in going from an unbridged to a bridged system, the optical activity suffers a marked shift in the positive (resp. negative) direction. This rule is permissive but not obligatory: as the authors also said, "we would also hesitate at this time to come to firm conclusions unless the 'marked shift' in our rule involved both a change in sign and reasonably large change in magnitude of rotation".

(3) Chiroptical effects:- Mislow (1958) proposed that the detailed study of optical rotatory dispersion will furnish useful information about configurational assignment.

C. Djerassi (1960) established the usefulness of o.r.d. curves for configurational assignment in optically active ketones of known absolute configuration. Mislow, Bunnenberg, Records ~~Richards~~, Wellman and Djerassi (1963) found that the circular dichroism (c.d.) curves of skewed biaryls (inherently dissymmetric chromophores) are of extreme usefulness in separating the individual electronic transitions responsible for the total Cotton effect.

From the results of these two optical properties of chiral molecules it is generalised: correlating the sign and shape of Cotton effects can correlate the configuration of compounds. An enantiomeric pair of molecules have identical Cotton effects of opposite sign.

5.3 Optical Rotatory Dispersion and Absolute Configuration of 1,1'-Binaphthyls

a. Introduction. - Spectroscopic observations were collected by Mislow, Glass, O'Brien, Rutkin, Steinberg, Weiss and Djerassi (1962)for a series of suitably substituted unbridged and bridged biphenyls, 2,2'-disubstituted unbridged and bridged 1,1'-binaphthyls, and their configurations related to those compounds whose absolute configurations were already assigned by some other standard methods. They also found that change in conformation brings about a characteristic change in o.r.d. Cotton effect curve. The longwavelength Cotton effect of the 2,2'-bridged biaryls is generally accompanied by a Cotton effect at shorter wavelength, of opposite sign and greater amplitude, which usually dominates the sign of rotation in the visible region. For 2,2'-bridged biaryls having the *R*-configuration, the sign of the longwavelength Cotton effect is negative for 6,6'-dinitro derivative, positive for 6,6'-dimethyl and 6,6'-dichloro derivative and 2,2'-disubstituted 1,1'-binaphthyls.

Unbridged 1,1'-binaphthyls possess complex u.v. absorption spectra dominated by maxima at 285 nm and about 230 nm (Frompton, Edwards,Jn. and Henze, 1948) which correspond to the complex o.r.d. spectra. Mislow *et al.*(1962) recorded two o.r.d. Cotton effects for 1,1'-binaphthyls with -CH$_2$OH, -CH$_2$Br, -CH$_3$, -COOH, -COOMe, -CONH$_2$ groups substituted in the 2,2'-positions, centered at 285 nm and below 250 nm respectively. In all cases a positive 285 nm Cotton effect corresponded to the *R*-configuration.

Bridging with a saturated chain containing *two* atoms incorporating the 2,2"-positions of 1,1'-binaphthyls (i.e. compound 44) changes the u.v. absorption pattern with a marked red-shift compared with the unbridged hydrocarbon spectrum; in particular, at long-wavelengths, bands at 320 nm, 328 nm, 335 nm and 348 nm (Hall and Mazengo, 1967) appear. This compound shows a red-shift of Cotton effect which is associated with its u.v. absorption red-shift: its Cotton effect is of enormous amplitude (1570000°) centered near 250 nm.

In contrast, the o.r.d. curves of bridged compounds containing *three* atoms in the bridge joining the 2,2'-positions of 1,1'-binaphthyl have u.v. absorption spectra dominated by maxima at 220 nm, 232 nm and 306 nm. The red-shift of the longwavelength absorption band at 283 nm and 293.5 nm of 1,1'-binaphthyl itself, in comparison with these bridged compounds, also appears in o.r.d. curves yielding two Cotton effects of opposite sign, centered around 300 nm and below 240 nm respectively. Mislow *et al*. (1962) suggested that a positive 300 nm Cotton effect corresponds to the *R*-configuration.

b. Optical rotatory dispersion spectra, results and discussion of 8,8'-disubstituted unbridged and bridged 1,1'-binaphthyls in the present work

Instrument: Perkin-Elmer Spectrophotopolarimeter (P 23)

Slit: 3 mm; Gain: 3; Damp: 7; Ordinate: 0.1°.

Solvent: 95% Ethanol

Formula applied in calculations:

$$[M] = \frac{[\alpha] \times M}{100}$$

where M is molecular weight of the chiral compound, $[\alpha]$ is specific rotation(in degrees) and is defined as αobs/*c* *l*.

l = 0.01 (length of cell), *c* is concentration of chiral compound in g/100 ml. α obs. (observed optical rotation) = 0.001 x observed deflection (in divisions of the chart paper), where 0.001 is least count.

Optical rotatory dispersion data (nm, [α] in parentheses).

a amplitude of short-wavelength Cotton effect(Note: the compounds are not necessarily optically pure.)

(-)-1,1'-Binaphthyl-8,8'-dicarboxylic acid (c 0.1296-0.0011184)
546 (-839°), 490 (-2160°), 340 (-5780°), 320 (-2500°), 312 (-3900°),
304.5 (0°), 270 (+10,825°), 259 (+4,614°), 249.5 (+16,100°), 242 (0°),
233 (-563,890°), 230 (-537,500°), 215 (-295,000°); (a = 1,984,000°).

(+)-8,8'-Bisbromomethyl-1,1'-binaphthyl (c = 0.0304-0.001824)
546 (+348°), 320 (+986°), 295 (+10360°), 290 (+12500°), 285 (+13900°),
258 (+25000°), 255 (+23500°), 248 (0°), 238-235 (-82000°), 277 (-93000°),
220 (-46700°); (a = 514500°)

(+)-8,8'-dimethyl-1,1'-binaphthyl (c=0.014-0.0028)
546 (+250°), 330 (+714°), 325 (+1420°), 320 (+714°), 313 (0°), 295-291.5 (-4600°), 288 (0°), 275 (+23600°), 270 (+25700°), 265 (+27800°),
260 (+28200°), 250 (+41000°), 245-242 (+42500°), 235 (+85700°),
228 (0°), 222.5-220 (-35700°), 215 (-48000°), 205 (-8900°)
(a = 377600°).

(+)-2,2'-Dimethyl-1,1'-binaphthyl (c = 0.572-0.00092)
546 (+22°), 352 (0°), 327 (-297°), 321.5 (0°), 319 (+220°), 315 (0°),
305 (-890°), 298 (0°), 275 (+15100°), 265 (+16000°), 260 (+13000°),
245 (+39000°), 233.5 (+185000°), 230 (0°), 224.5 (-266000),
220 (-152000), 216 (-10800°); (a = 1054000°).

(+)-1,1'-Binaphthyl (c = 0.056-0.0007)

578 (+203°), 320 (+550°), 315(+800°), 310 (+500°), 300 (+300°), 293 (+4900°), 290 (+5700°), 285 (+11500°), 283 (+12000°), 272 (+15000°), 255 (+9900°), 230 (+98000°), 225 (0°), 220 (-180000°), 219 (-185000°), 217 (-160000°), 214 (0°), 208 (+78000°), (a = 518800°)

(+)-1,1'-Binaphthyl-8,8'-diacetic acid (10) (c = 0.0512-0.002048)

546 (+227°), 340 (+1270°), 335 (+1170°), 328 (+2100°), 320 (+500°), 315 (+780°), 310 (+490°), 306 (0°), 300 (-590°), 293 (-490°), 291 (0°), 280 (+7300°), 277 (+7400°), 269 (+10000°), 265 (+12200°), 260 (+12700°), 252 (+20500°), 247.5 (+37000°), 239 (0°), 227 (-80500°), 225 (-73000°), 213 (-36600°); (a = 434600°)

(-)-1,1'-Binaphthyl-8,8'-diacetic acid (10) (c = 0.056-0.00112)

546 (-307°), 400 (-700°), 330 (-2300°), 311 (0°), 307 (+1200°), 293 (0°), 280 (-11300°), 276-273 (-13600°), 270 (-15400°), 268 (-16500°), 260 (-19000°), 254 (-48000°), 250 (-49000°), 248 (-55300°), 239 (0°), 228 (+134000°), 220 (+22000°), 217.5 (0°); (a = 5186000°).

(+)-1,1'-Binaphthyl-8,8'-bis(methylenepyridinium) diiodide (12)

(c = 0.0512-0.0031)

546 (+202°), 340 (+780°), 328 (+1270°), 320 (+290°), 315 (0°), 304 (-390°), 301 (0°), 290 (+7300°), 275-270 (+10700°), 250 (+34000°), 231.5 (0°-), 220 (-40000°), 217 (-48000°), 210 (-40000°), (a = 600000)

(+)-(13)* (c = 0.0163-0.000326)

546 (+317°), 436 (+700°), 405 (+962°), 365 (+1620°), 330 (+2400°), 310 (+6500°), 300 (+4600°), 275-270 (+113000°), 263 (+13000°), 260 (+12600°), 243 (+49000°), 235 (+26000°), 233 (0°), 227.5 (-330000°), 215 (-150000°); (a = 1659000).

(+)-(14)* (c = 0.033-0.00132)

546 (+356°), 340 (+1500°), 310 (+8000°), 295 (+4700°), 284 (+7600°), 275 (+9000°), 270 (+8800°), 247 (+74800°), 242.5 (+77000°), 232.5(0°), 222 (-190000°), 214 (0°), 208 (+91000°), (a= 1170000).

(-)-(14)* (c = 0.204-0.000816)

546 (-318°), 340 (-1900°), 320 (- 3200°), 310 (-3900°), 299 (-2200°), 271 (-9300°),,266 (-7600°), 260 (-9000°), 245 (-30600°), 233 (0°), 222 (+290000°), 212 (+ 160000°), (a = 1300000°).

(+)-(17)* (c = 0.0168-0.00336)

546 (+257°), 310 (+7400°), 297 (+4200°), 243 (+55000°), 233 (0°), 225-223 (-148800°), 218 (-107000°), 213 (0°), (a = 836000°).

(-)-(17)* (c = 0.01968-0.0023616)

564 (-264°), 310 (-9000°), 293 (-7600°), 273-270 (-15000°), 260 (-15500°), 244 (-67000°), 233 (0°), 230 (+440000°), 221 (+165000°), 214 (+114000°), (a = 950000°).

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* Numbers refer to p.14-16

(+)-(19)* (*c* = 0.03504-0.0014016)

546 (+ 320°), 320 (+ 2000°), 311 (+ 3400°), 295 (+ 7000°), 244 (+ 52800°), 234.5 (0°), 225 (-235000°), 215 (0°), 210 (+ 50000°), (*a* = 1020000°).

(-)-(19)* (*c* = 0.02048-0.00328)

546 (- 378°), 310 (-5000°), 295 (-3600°), 268 (-11000°), 268 (-9500°), 245-242 (-50000°), 235 (0°), 230 (+56600°), 224 (+ 96000°), 215 (+ 68000°), (*a* = 520000°),

(+)-(15)* (*c* = 0.022-0.0011)

546 (+523°), 320 (+ 6000°), 300 (+ 8600°), 290 (+ 6000°), 270 (+ 10600°), 264 (+ 11000°), 244 (+ 66000°), 235.5 (0°), 222 (-91000°), 220-215 (-1000000°), 212 (-68000°), (*a* = 560000°).

(-)-(15)* (*c* = 0.0304-0.00475)

546 (-515°), 320 (-5900°), 313 (-6900°), 305 (-6000°), 295 (-7000°), 290 (-7200°), 246 (-61000°), 235.5 (0°), 230 (+ 82000°), 220-217 (+126000°), 215 (+116000°), 205 (+42000°), (*a* = 630000°).

(+)-(16)* (*c* = 0.056-0.001064)

546 (+444°), 320 (+ 5800°), 306 (+ 8500°), 273-269 (+11600°), 240 (+86000°), 232 (0°), 225 (-94000°), 220 (-70000°), 216 (-56000°), (*a* = 630000°).

(-)- (16)* (*c* = 0.023-0.00046)

546 (-478°), 320 (-4100°), 307 (-5400°), 300 (-4000°), 269 (-12600°), 264 (-12000°), 242.5 (-67000°), 232 (0°), 221 (+88000°), 217 (+91000°), 210 (+76000°), (*a* = 558000°).

(+)-(18)* (*c* = 0.02-0.0004)

546 (+500°), 320 (+5000°), 310 (+8200°), 296 (+6200°), 255 (+23000°), 243 (+44000°), 233 (0°), 230 (-250000°), 220 (-460000°), 216 (-440000°), (*a* = 1640000°).

(-)-(18)* (*c* = 0.084-0.001344)

546 (-554°), 320 (-5400°), 315 (-6800°), 297 (-1800°), 260 (-12500°), 245 (-61000°), 235 (0°), 230 (+253000°), 222.5 (+390000°), 215 (+160000°), (*a* = 1400000°).

(+)-(20)* (*c* = 0.08-0.008)

546 (+481°), 340 (+1500°), 313 (+4600°), 297 (0°), 290 (-2250°), 279 (0°), 243 (+44000°), 235 (0°), 230 (-230000°), 225 (-250000°), 215 (0°), (*a* = 1300000°).

(-)-(20)* (*c* = 0.0808-0.001616)

546 (-156°), 340 (-1000°), 315 (-2400°), 297 (0°), 291 (+1200°), 289 (0°), 245 (-31000°), 243 (-31000°), 235 (0°), 227 (+77000°), 220 (+62000°), 210 (+31000°), (*a* = 480000°).

(+)-(21)* (c = 0.044-0.001584)

546 (+363°), 340 (+2730°), 314 (+7200°), 298 (0°), 293 (-2400°), 285 (-680°), 279 (0°), 265 (+8400°), 250 (+8500°), 243 (+43000°), 237 (0°), 222.5 (-205000°), 218 (-160000°), (a = 1180000°).

(-)-(21)* (c = 0.0021-0.000084)

546 (-287°), 330 (-4000°), 315 (-6000°), 298 (0°), 293 (+2000°), 280 (0°), 246 (-44000°), 238 (0°), 230 (+210000°), 225.5 (+226000°), 220 (+150000°), 215 (+120000°), (a = 1040000°).

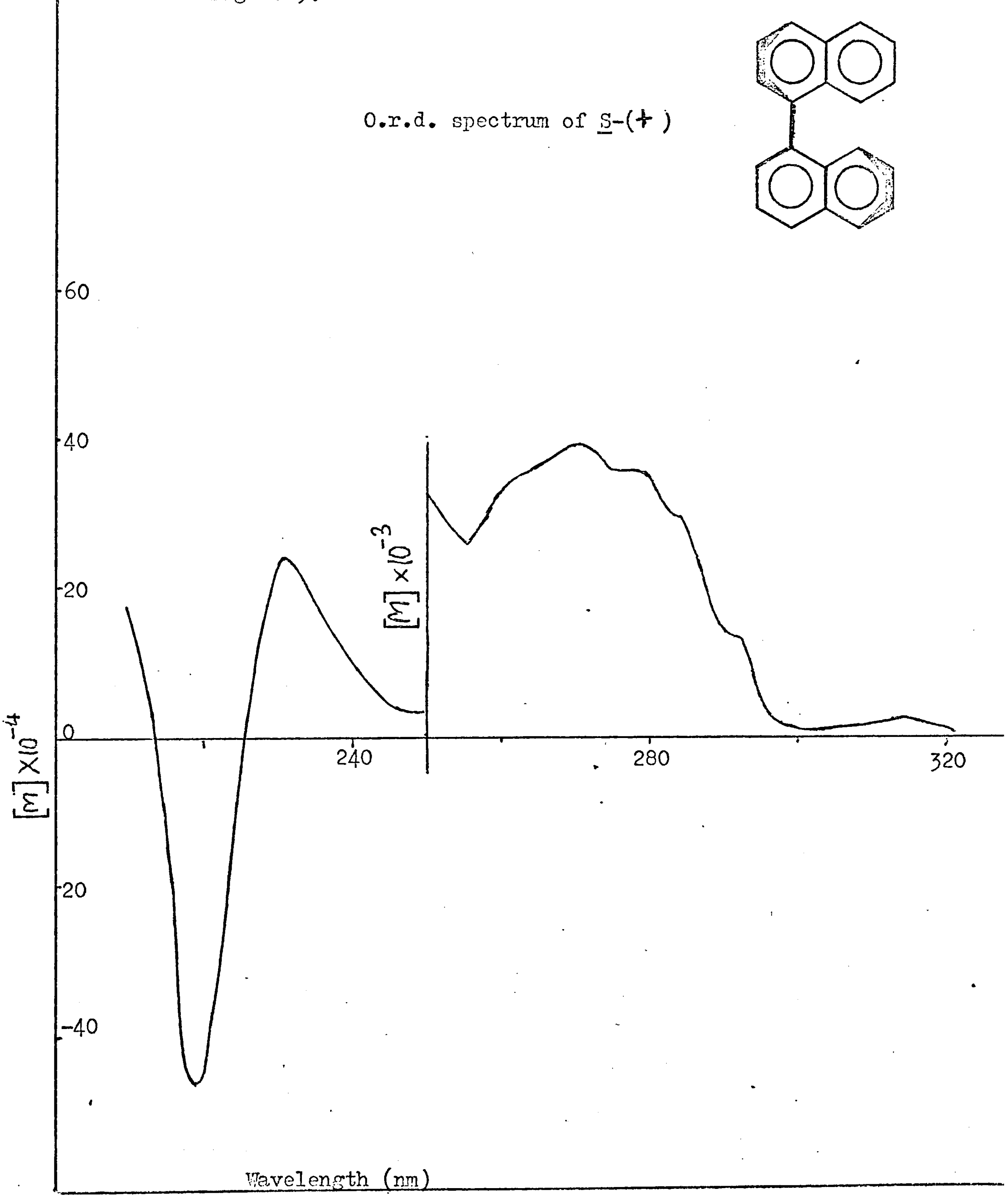
(+)-(22)* (c = 0.058-0.00116)

546 (+279°), 340 (+2600°), 312.5 (+7700°), 295 (0°), 292.5 (-1400°), 282 (0°), 246 (+60000°), 239 (0°), 225 (-280000°), 210 (-146000°), (a = 1700000°).

(-)-(22)* (c = 0.0412-0.0049)

546 (-140°), 340 (-1900°), 314 (-4200°), 300 (-600°), 298.5 (0°), 295 (+1700°), 283 (0°), 245 (-36000°), 238 (0°), 225 (+90000°), 223 (+91000°), 205 (+60000°), (a = 646000°).

Figure 9.



O.r.d. spectrum of S-(+)

Figure 10 O.r.d. spectra of S- 1,1'-Binaphthyls

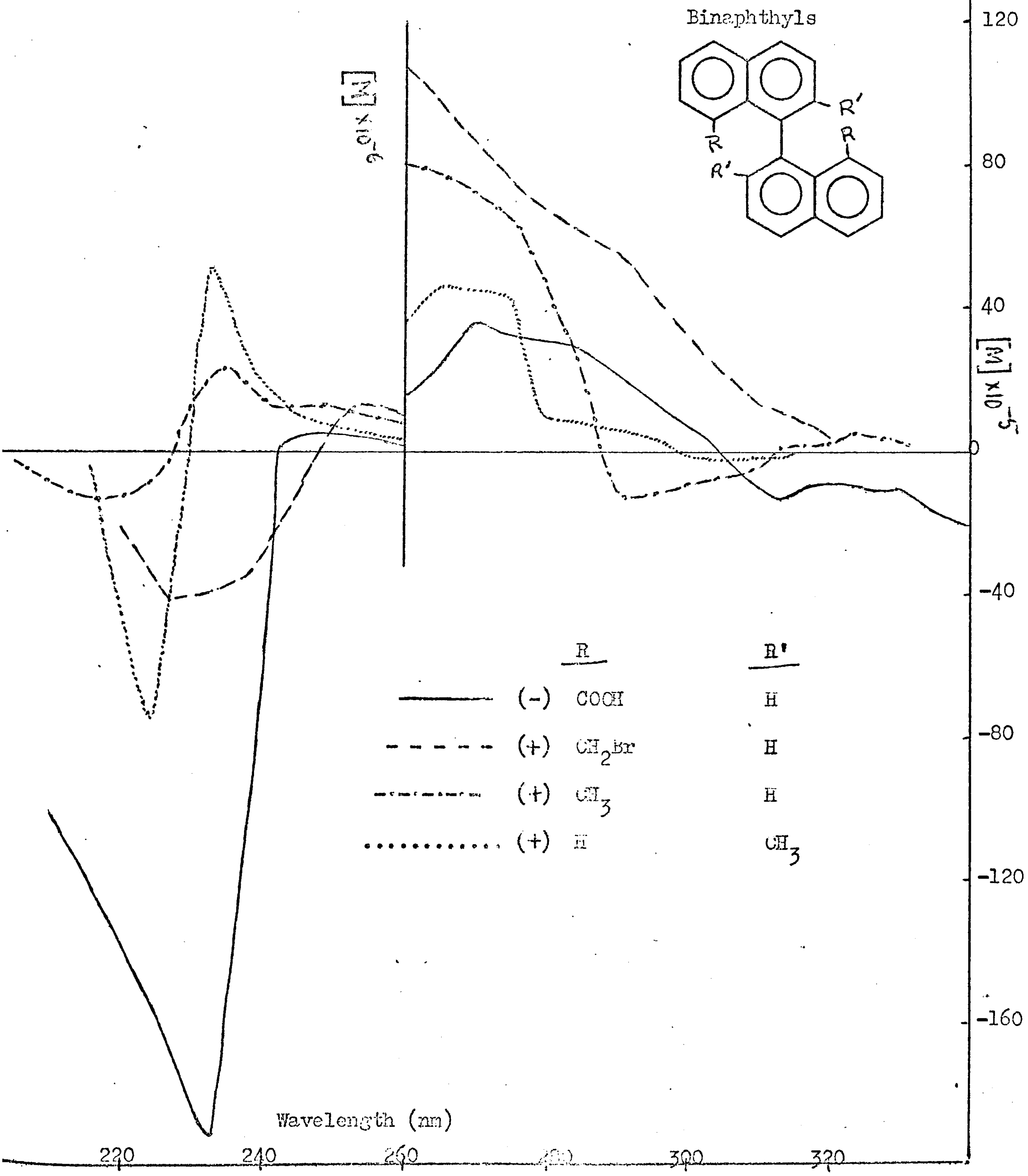


Figure 11

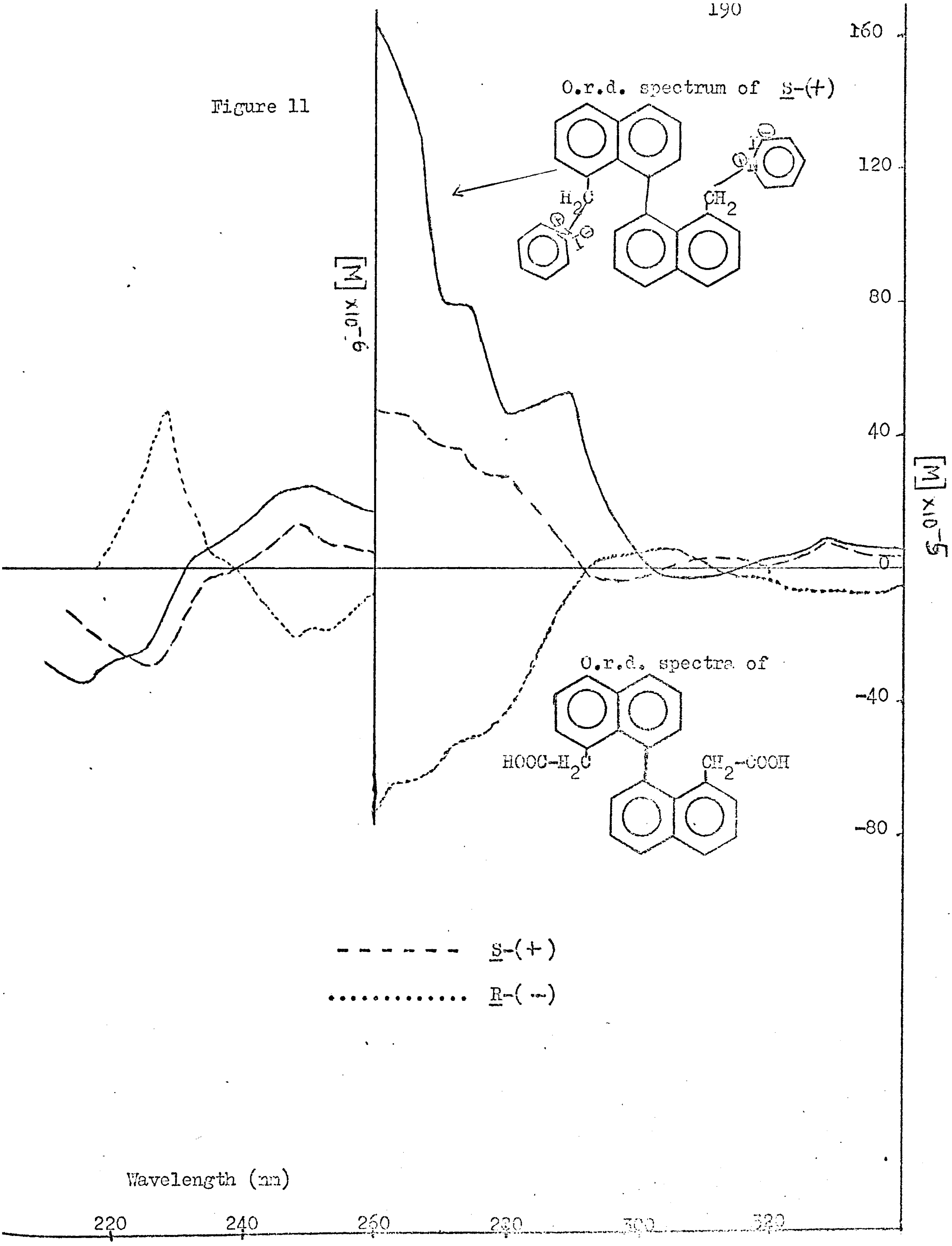
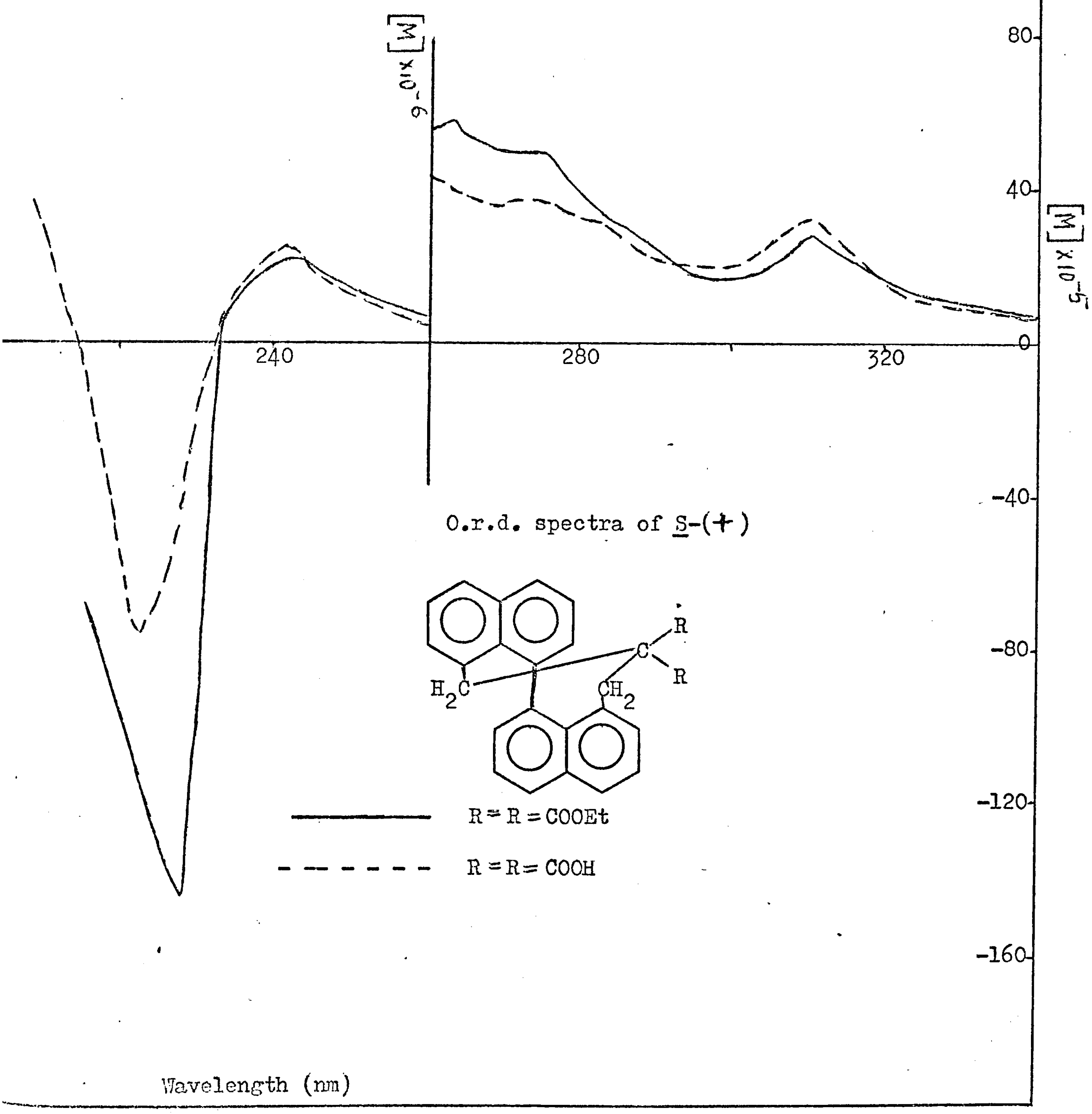
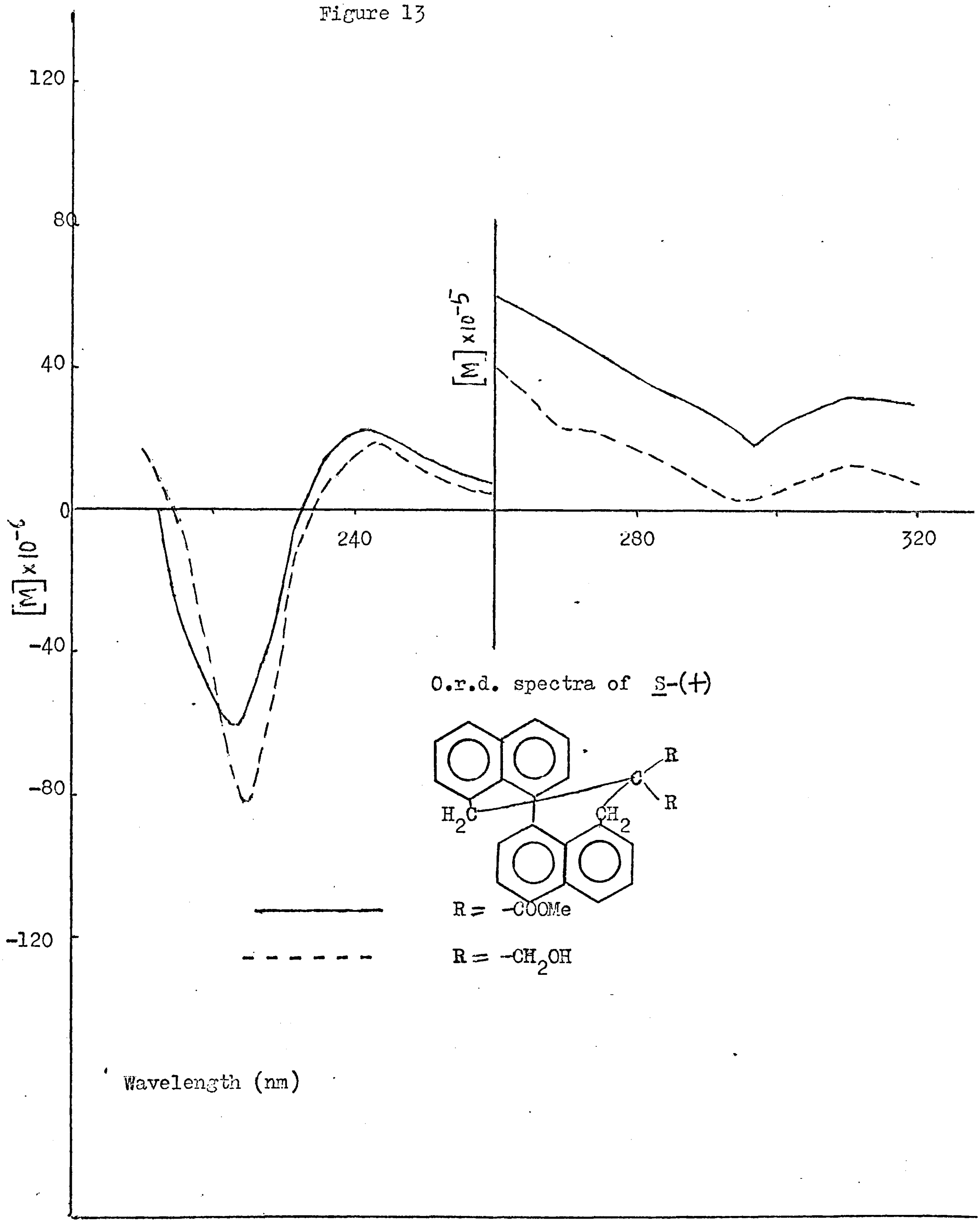

O.r.d. spectrum of S-(+)
H_2C
CH_2
O.r.d. spectra of
HOOC-H_2C
CH_2-COOH
[M] x10^{-6}
[M] x10^{-5}
160
120
80
40
0
-40
-80
S-(+)
R-(−)
Wavelength (nm)
220
240
260
280
300
320

Figure 12



O.r.d. spectra of S-(+)

Figure 13



O.r.d. spectra of S-(+)

Figure 14

O.r.d. spectra of R-(−)

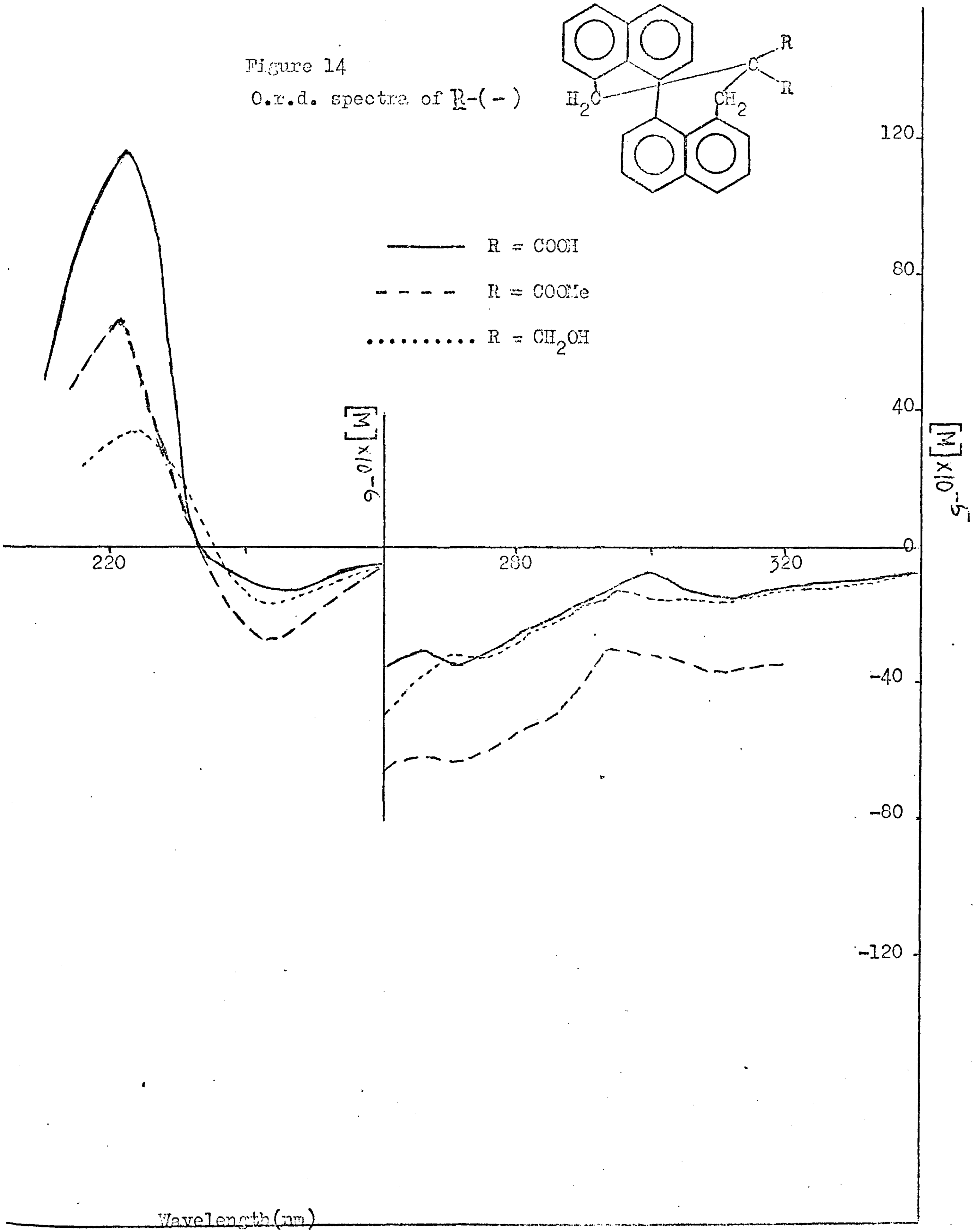
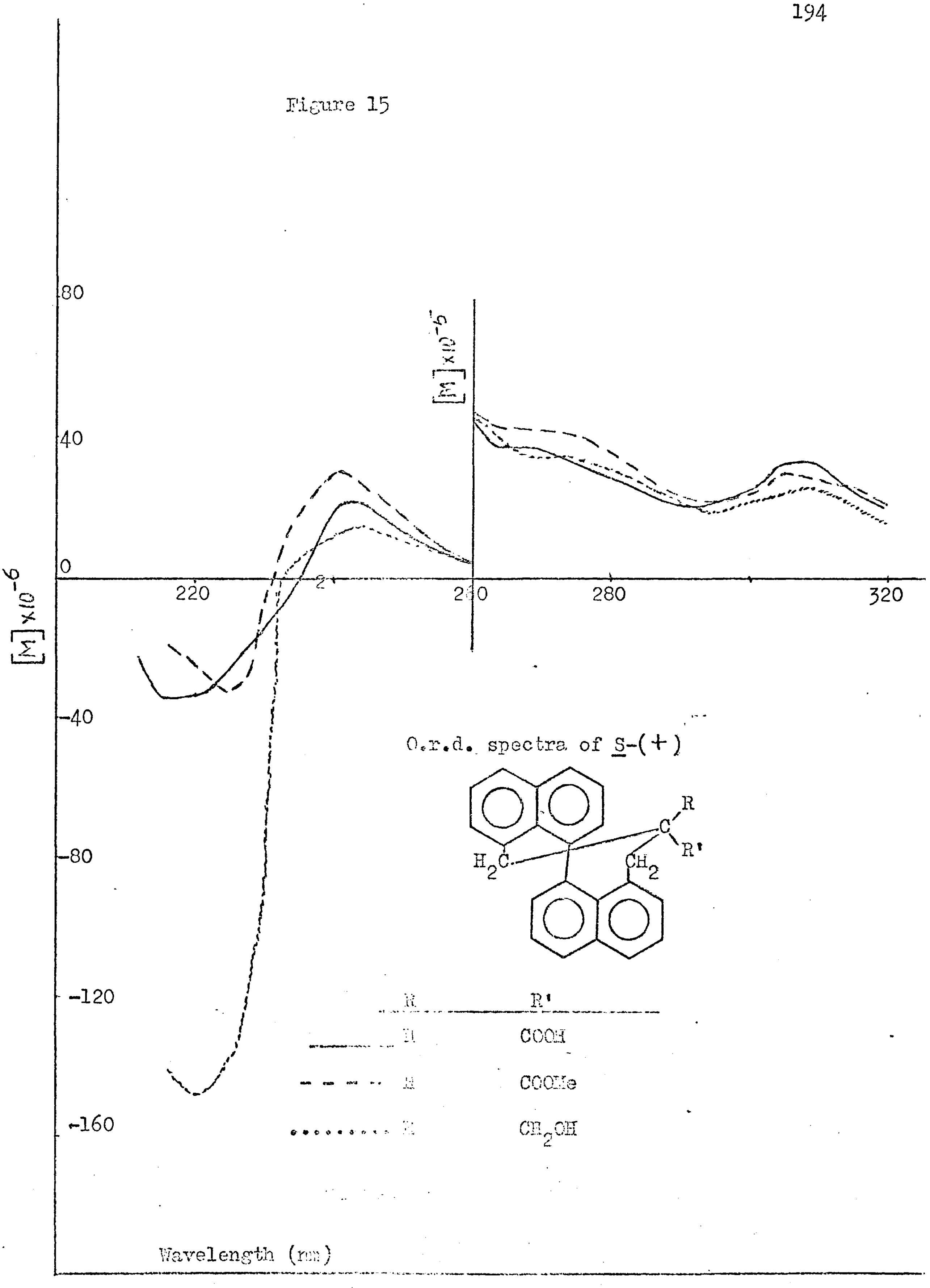


Figure 15



O.r.d. spectra of S-(+)

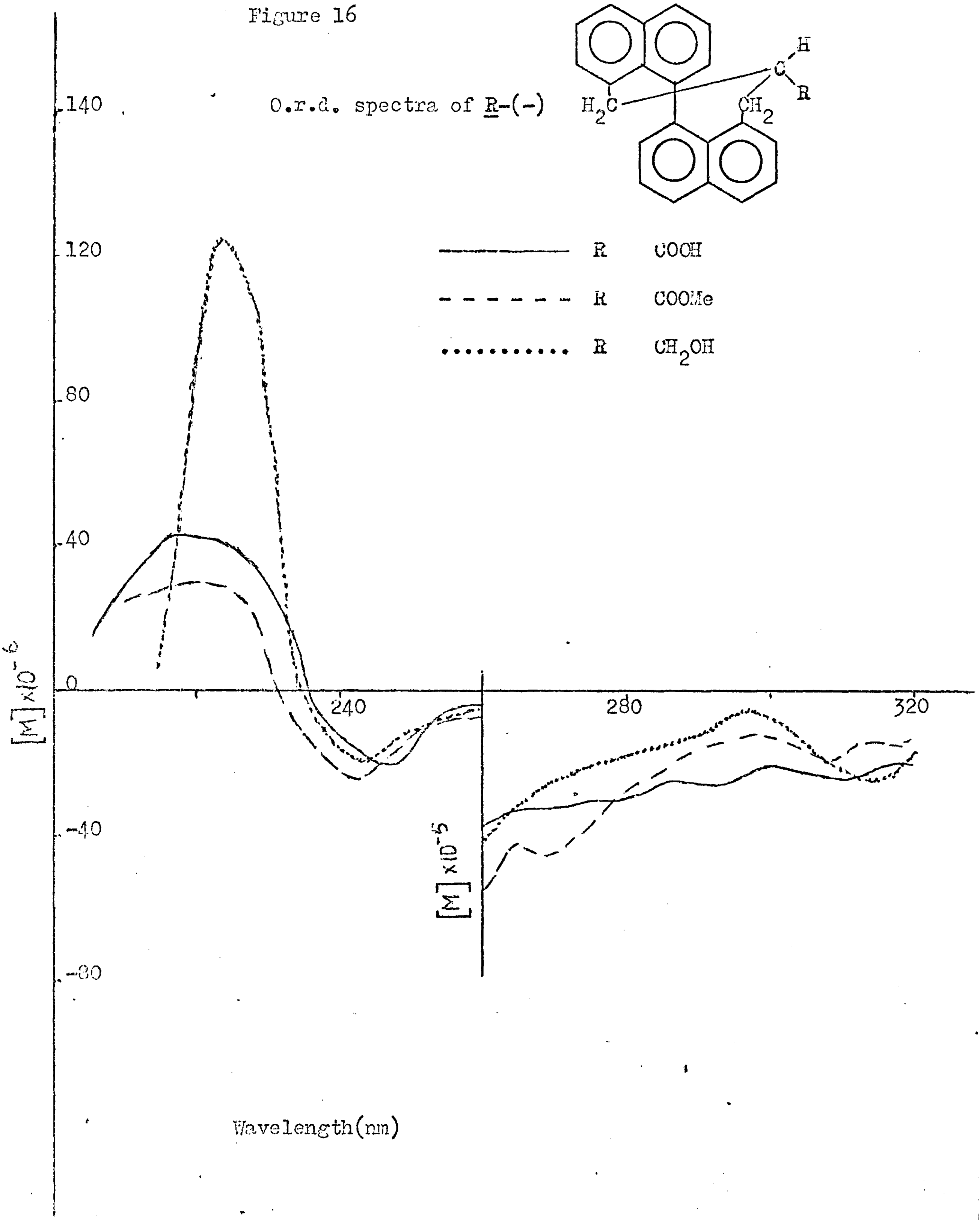


Figure 16

O.r.d. spectra of R-(-)

Figure 17

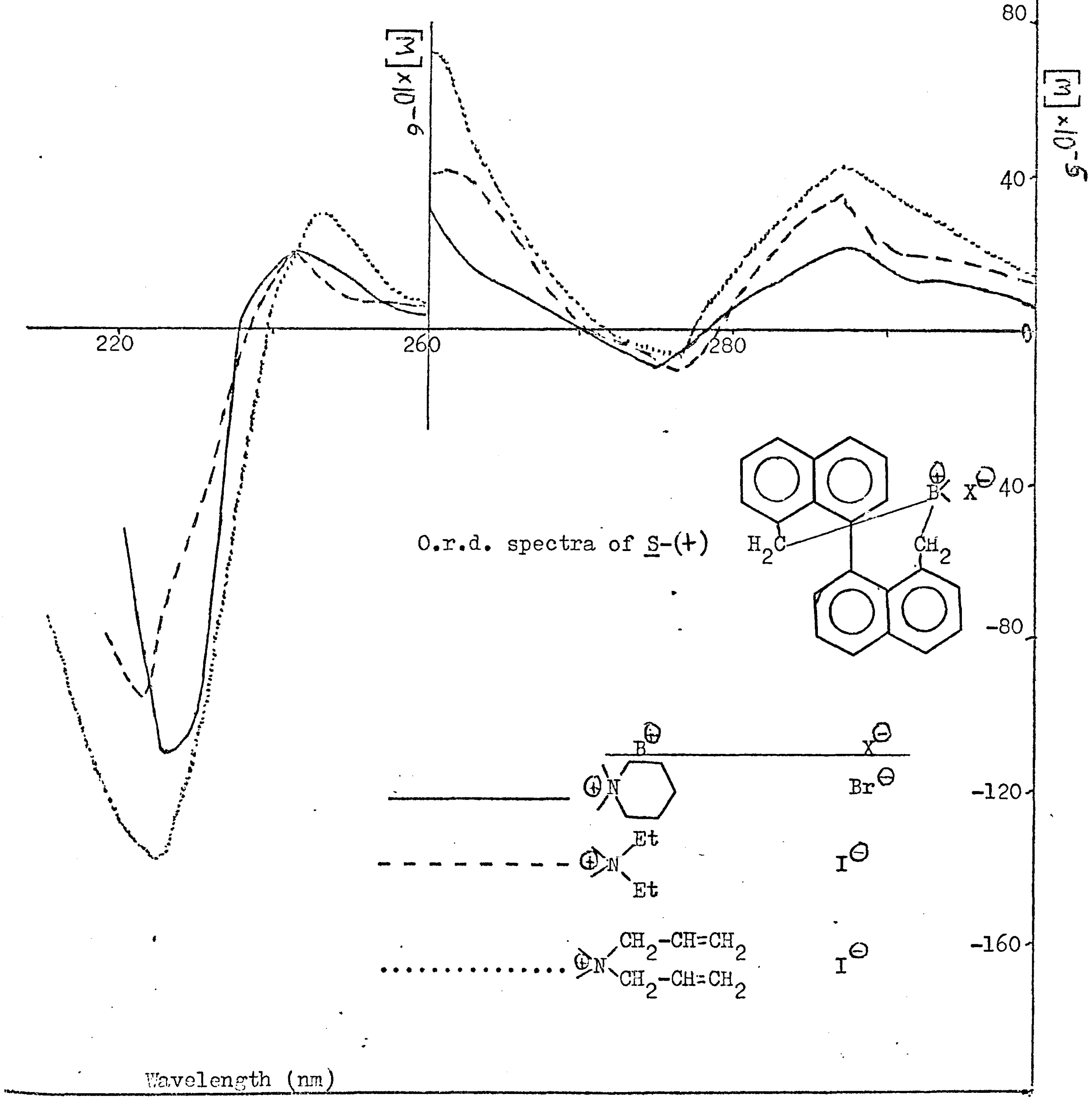
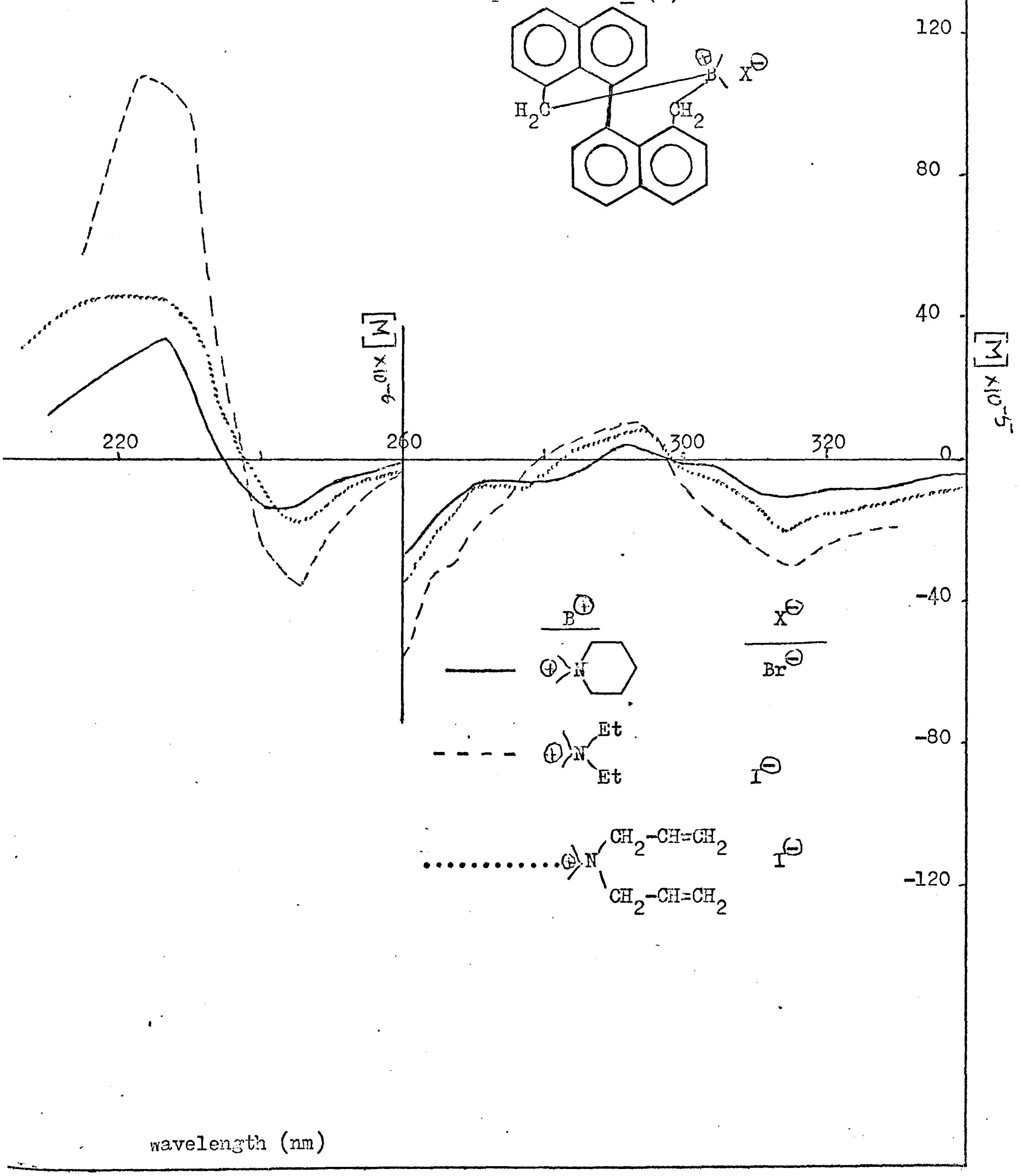

[M] × 10⁻⁶
[M] × 10⁻⁵
80
40
0
-40
-80
-120
-160
220
260
280
Wavelength (nm)
O.r.d. spectra of S-(+)
H2C
CH2
B⊕ X⊖
B⊕
X⊖
Br⊖
Et
Et
I⊖
CH2-CH=CH2
CH2-CH=CH2
I⊖

Figure 18

O.r.d. spectra of R-(-)



Discussion: Recognition of short-wave Cotton effect for configurational assignment

(1) Optical rotatory dispersion spectra of unbridged 8,8'-disubstituted 1,1'-binaphthyls:- 1,1'-Binaphthyl itself exhibits absorption maxima at 220 nm (β-band), 283 nm and 293.5 nm (ρ-band) which correspond with the complex o.r.d. Cotton effects. A short-wave positive Cotton effect of very high amplitude (718800°) centered near 225 nm and the corresponding shape of the long-wave Cotton effect curve with its u.v. absorption spectrum characterises it as an inherently dissymmetric chromophore.

Naphthalene absorbs at 220 nm (β-band), 275 nm (ρ-band) and a weaker band at 312 nm (α-band). The small Cotton effect 315 nm is assigned to the weaker absorption band. The comparatively large positive Cotton effect maximum at 272 nm of 1,1'-binaphthyl can be assigned to the ρ-band and finally the short-wave positive Cotton effect centered at 225 nm can be assigned with confidence to the β-band.

Badger, Drewer and Lewis (1962) concluded that a negative Cotton effect associated with the β-band of 1,1'-binaphthyls indicates R-configuration and a positive Cotton effect here an S-configuration. $(+)_{546}$-1,1'-Binaphthyl has been assigned the S-configuration by X-ray crystallographic methods (Akimoto, Shioiri, Iitaka and Yamada, 1968). These authors reported the R-configuration of $(+)_{578}$-2,2'-dihydroxy-3,3'-bismethoxycarbonyl-1,1'-binaphthyl, and then correlated some other 1,1'-binaphthyls including 1,1'-binaphthyl itself with it through chemical relationships which were already known.

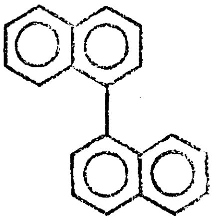
$(+)_{546}$-2,2'-Dimethyl-1,1'-binaphthyl: This compound is completely optically stable and has been assigned the S-configuration on the basis of a negative Cotton effect near 285 nm (Mislow, Glass, O'Brien, Rutkin, Steinberg, Weiss and Djerassi, 1962) and asymmetric synthesis (Mislow and McGinn, 1958) and X-ray crystallographic method (Akimoto, Shioiri, Iitaka and Yamada, 1968). By analogy with 2,2'-disubstituted 1,1'-bianthryls (Badger, Brewer and Lewis, 1962) a positive Cotton effect associated with short-wave u.v. absorption maximum relates to S-configuration of this compound, (see figure 10.).

$(+)_{546}$-8,8'-Dimethyl-1,1'-binaphthyl: This shows three Cotton effects (see figure 10.). A weak positive Cotton effect which could be due to optically active transitions of the long-wave typical naphthalene band: a strong negative Cotton effect near 285 nm which can be assigned to the p-band of u.v. absorptions and a strong positive Cotton effect centered near 230 nm due to β-band of the u.v. absorption. This step-by-step observation of o.r.d. curve of $(+)_{546}$-8,8'-dimethyl-1,1'-binaphthyl shows that it resembles the o.r.d. curves of (+)-1,1'-binaphthyl and (+)-2,2'-dimethyl-1,1'-binaphthyl.

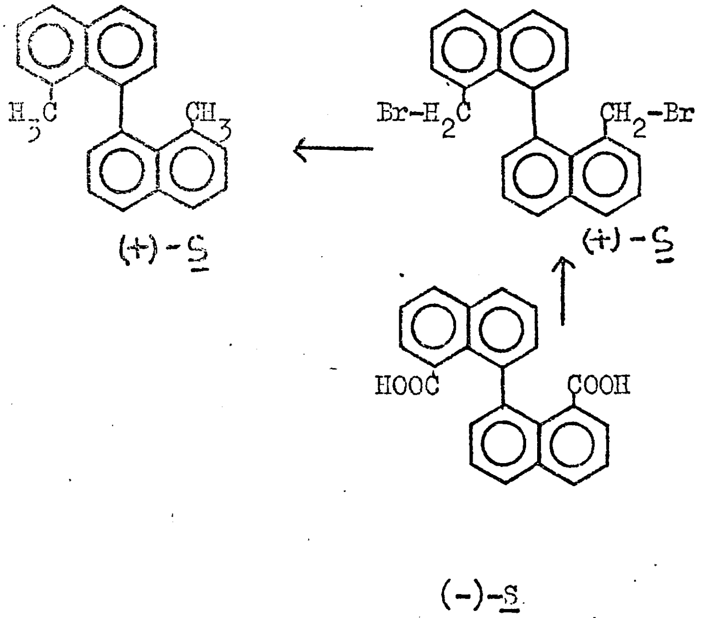
As the optically active transitions in all these three compounds are of the same nature, this fact led us to assign S-configuration to the (+)-isomer of 8,8'-dimethyl-1,1'-binaphthyl.

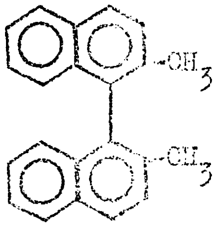
$(+)_{546}$-8,8'-Bisbromomethyl-1,1'-binaphthyl: This is a synthetic precursor of (+)-8,8'-dimethyl-1,1'-binaphthyl. It shows one positive Cotton effect with inflection near 290 nm and 316 nm, which are dominated by long-wave u.v. absorption bands. This did not show any negative long-wave Cotton effect but a clear strong positive Cotton effect associated with its β-absorption band suggesting its *S*-configuration (see fig. 10).

$(-)_{546}$-1,1'-Binaphthyl-8,8'-dicarboxylic acid: This acid shows two Cotton effects of opposite sign. A long-wave negative Cotton effect dominated by transitions of a broad u.v. absorption band at 309 nm and a very weak absorption band at 332 nm. The long-wave transitions appear in the o.r.d. spectrum (see figure 10). A short-wave strong positive Cotton effect of enormously high amplitude (1,983,700°) associated with the u.v. absorption band at 239.5 nm suggests its *S*-configuration. On the basis of a strong positive Cotton effect associated with the β-band *S*-configuration can be assigned to unbridged 8,8'-disubstituted 1,1'-binaphthyls, and other compounds derived from (-)-8,8'-dicarboxylic acid.



(+)-*S*





(+)-*S*

(+)- and (-)-1,1'-Binaphthyl-8,8'-diacetic acids (10)

The u.v. absorption spectrum of (±)-1,1'-binaphthyl-8,8'-diacetic acid (10) resembles that of (±)-8,8'-dimethyl-1,1'-binaphthyl with fine structure features of the p-band and the appearance of typical naphthalene band at 324 nm. In the o.r.d. spectrum, three Cotton effects were observed (see figure 11) for each of the enantiomers. A long-wave Cotton effect averaging near 310 nm could be assigned to the optically active transitions of inflection in the u.v. absorption spectrum at 324 nm. A second intense Cotton effect centered near 290 nm can be due to the p-absorption band and a short-wave strongest Cotton effect is certainly due to the β-band of u.v. spectrum. From the inspection of the u.v. absorption spectrum it is concluded that chromophoric nature of carboxylic acid groups in the 8,8'-positions of 1,1'-binaphthyl are insulated from the aromatic chromophores. The fine structure features of the p-band are also observed in the o.r.d. spectra. A positive Cotton effect associated with the β-absorption band assigns S-configuration to $(+)_{546}$-1,1'-binaphthyl-8,8'-diacetic acid and a negative Cotton effect here R-configuration to the $(-)_{546}$-1,1'-binaphthyl-8,8'-diacetic acid.

$(+)_{546}$-1,1'-Binaphthyl-8,8'-bis(methylenepyridinium) diiodide (12):

This compound was derived from $(+)_{546}$-8,8'-bisbromomethyl-1,1'-binaphthyl which has the S-configuration. This also has shown three Cotton effects of opposite signs, and a positive Cotton effect with fine structure. The positive Cotton effect associated with the short-wave absorption band of the u.v. spectrum centered near 231 nm also is a evidence for its S-configuration (see figure 11.).

(2) Optical rotatory dispersion spectra of 8,8'-bridged 1,1'-binaphthyls

(a). Carbocyclic compounds:

The $(+)_{546}$-8,8-diethoxycarbonyl[dinaphtho(8,1-ab, 1',8'-de)] - cyclonona-2,4-diene (13) was synthesised from $(+)_{546}$-8,8'-bisbromomethyl-1,1'-binaphthyl to which the S-configuration was assigned on the basis of a positive short-wave Cotton effect. A point of interest arises here: Mislow and McGinn (1958) and Fitts, Siegel and Mislow (1958) from their work proposed a general Optical Displacement Rule; in the present work the rule was not obeyed. This compound shows one strong positive Cotton effect of enormously high amplitude (+ 1,659,300°) associated with the β-band (see figure 12.). A long-wave positive Cotton effect corresponds to the optically active transitions due to the typical naphthalene band, and the fine structure features with inflections correspond to the ρ-band. The o.r.d. spectrum resembles that of 1,1'-binaphthyl itself, very closely in the short-wave region. S-configuration is assigned to this compound.

This ester on hydrolysis gave optically active dicarboxylic acid (14). The o.r.d. spectrum is very close to the o.r.d. spectrum of its precursor diethyl ester (13). Secondly, (±)-(14) was resolved and (+)- and (-)-acids were decarboxylated to their corresponding monocarboxylic acids (15). Methyl esters of (+)- and (-)- mono- and dicarboxylic acids were reduced to the corresponding alcohols. O.r.d.

characters of these compounds were observed to be the same (see figure 13,14,15,16). No additional Cotton effect was seen in the case of mono-derivatives with point group (C_1), i.e. during decarboxylation the hydrogen atom can replace either of the carboxylic acid groups, thus these molecules lack all elements of symmetry. The Cotton effects observed in these compounds, both disubstituted (C_2) and monosubstituted (C_1) are probably due only to optically active aromatic chromophores. All these related compounds to which S-configuration is assigned show positive rotation in the visible region, which is dominated by the strong short-wave positive Cotton effect. Isomers showing a negative strong Cotton effect associated with short-wave u.v. absorption maxima are assigned the R-configuration.

(b) 8,8'-Bridged N-heterocyclic compounds:

The o.r.d. spectrum of compounds (20), (21) and (22) differed from the carbocyclic compounds in one sense, that they show multiple Cotton effects. All these quaternary ammonium compounds (20) to (22) were obtained in their optically active form from optically active 8,8'-bisbromomethyl-1,1'-binaphthyl. In their u.v. spectra (see figure 8) a split component of the short-wave β-band was observed, which could show a negative Cotton effect averaged near 280 nm (see figure 17). A long-wave positive Cotton effect is due to weak transitions. All these compounds show strong Cotton effects associated with the short-wave absorption band. A strong positive Cotton effect in this region again is an evidence for S-configuration and a negative Cotton effect for the R-configuration. $(+)_{546}$-isomers in this series are assigned S and $(-)_{546}$-isomers R-configuration.

These findings of o.r.d. spectra in the present work made us confident to propose: A strong positive Cotton effect associated with the short-wave u.v. absorption band relates to S-configuration and a negative Cotton effect relates to R-configuration.

5.4 Circular Dichroism and Absolute Configuration of 1,1'-Binaphthyls

a. Introduction. Mislow, Bunnenberg, Records, Wellman and Djerassi (1963) reported that c.d. curves of twisted biphenyls are of extreme usefulness to identify the electronic transitions which are solely responsible for the individual Cotton effects. Intensity of c.d. curves parallels high extinction coefficients of the absorption spectrum, and high amplitude in the o.r.d. curve; all together they characterise the internal chirality of chromophores present in a molecule. The signs of the c.d. curves correspond to the signs of the related o.r.d. curves. The great advantage of c.d. over o.r.d. is that the overlapping tails of o.r.d. bands dominated by short-wave Cotton effects are reduced in c.d. which assists in the identification of unsuspected weak optically active transitions. They applied these generalisations to some 1,1'-binaphthyls. Unbridged 2,2'-disubstituted 1,1'-binaphthyls have u.v. absorption maxima around 285 nm and 230 nm. A negative 285 nm Cotton effect relates to R-configuration of these compounds.

1,1'-Binaphthyls bridged in the 2,2'-positions have in common c.d. spectra at 270 nm and 310 nm of opposite signs which correspond to the oppositely signed o.r.d. curves centered near 265 nm and 300 nm respectively. A positive 300 nm Cotton effect relates to the R-configuration(Mislow, Bunnenberg, ~~Richards~~ Records, Wellman and Djerassi, 1963).

b. Circular dichroism spectra, results and discussion of 8,8'-disubstituted unbridged and bridged 1,1'-binaphthyls in the present work

Instrument: (i) Fica Spectropol-I (c.d. attachment)

cell = 1 mm, sensitivity = 0.1

Formula used in calculations:

$\Delta\varepsilon$ (coefficient of extinction)

$$= \frac{2.5 \times \text{recorded deflection} \times \text{sensitivity}(0.1) \times 10^{-4} \times \text{M.W.}}{\underline{c}(\text{g/L}) \times \underline{1}\ (\text{cm})}$$

(ii) Roussel-Jouan Dichrograph

cell = 1 mm, sensitivity = 1.5

Formula used in calculations:

$$\Delta\varepsilon = \frac{\text{recorded deflection} \times \text{sensitivity}\ (1.5) \times 10^{-4} \times \text{M.W.}}{\underline{c}(\text{g/L}) \times \underline{1}\ (\text{cm})}$$

Solvent: 95% ethanol

Circular dichroism data (nm, $[\theta]$ in parentheses)

(-)-1,1'-Binaphthyl-8,8'-dicarboxylic acid (c = 0.6-0.024)
340 (-1900), 334 (-32000), 330 (-33800), 326 (-37000), 324 (-32000), 296-289 (-50500), 281 (0), 270 (+176000), 251 (+35000), 250 (+140000), 240 (+420000), 232.5 (0), 223 (-500000), 214 (0).

(+)-8,8'-Bisbromomethyl-1,1'-binaphthyl (c = 0.5-0.02)
340 (0), 300 (-35000), 270 (-22000), 265 (-26000), 260 (0), 241 (+142000), 238 (0), 228 (-760000), 218 (-380000).

(+)-8,8'-Dimethyl-1,1'-binaphthyl (c = 0.23-0.0046)
335 (0), 330 (-1400), 325.5 (-4400), 323 (0), 321 (+1600), 318 (+800), 316 (+1000), 313 (+800), 306.5 (+3200), 302 (0), 300 (-1600), 290 (-26000), 287 (-35000), 285 (-35200), 269.5 (0), 257.5-255.5 (+32000), 250 (+33000), 229.5 (+1200000), 222.5 (0), 220 (-200000), 218 (-320000), 215 (-220000), 210 (0).

(+)-2,2'-Dimethyl-1,1'-binaphthyl (c = 0.418-0.00836)
340 (0), 335-325 (-220), 320 (-2900), 312 (-890), 306.5 (-2500), 305-304 (-2200), 283 (-29800), 280 (-28900), 259 (0), 228.5 (+1240000), 224.5 (0), 222 (-545000), 221 (-590000), 213 (0).

(+)-1,1'-Binaphthyl (c = 0.124-0.0124)

310 (0), 305 (-2300), 300 (-3600), 295 (-7000), 290 (-7600), 285 (-7800), 280 (-8100), 265 (0), 260 (+3700), 255 (+1000), 250 (+ 2000), 245 (~0), 240 (~0), 225 (+825000), 220 (0), 218 (-370000), 216 (-430000), 214 (-590000), 208 (-59000).

(+)-(13)* (c = 0.204-0.0408)

320 (+2600), 300 (+24000), 290 (+10000), 254 (+66000), 248 (+48000), 229 (+720000), 222.5 (0), 215 (-900000), 212 (-740000).

(+)-(14)* (Obtained from 13) (c = 0,84-0.0336)

330 (0), 302 (+23500), 285-280 (+5900), 260 (+23000), 230 (+620000), 223 (0), 215 (-1060000), 213 (-940000).

(+)-(14)* (Obtained by resolution) (c = 0.23-0.023)

340-330 (-34000), 320 (-1600), 319 (-19000), 312 (0), 302 (+94000), 297 (+70000), 295-292 (+72000), 289 (+38000), 287 (+44000), 285 (+34000), 283 (+44000), 265 (+230000), 263.5 (+240000), 255 (+200000), 232 (+5800000), 223.5 (0), 217 (-6000000), 210 (-3400000).

(-)-14* (c = 0.176-0.0176)

340 (+29000), 317 (0), 303.5 (-130000), 299 (-90000), 296.5 (-107000), 287 (-8000), 264 (-240000), 260-255 (-200000), 232 (-6100000), 224.5 (0), 218 (+7000000), 210 (+4200000).

Numbers refer to p. 14 to 16

(+)-(15)* (*c* = 0.13-0.013)

340 (-1000), 325 (0), 301 (+ 9000), 300 (+ 8500), 295-293 (+ 9700), 287 (+ 7400), 260 (+ 27000), 255 (+24000), 231 (+ 580000), 223 (0), 216 (-500000), 210 (-330000), 205 (-300000), 200 (-170000).

(-)-(15)* (*c* = 0.08-0.008)

340 (-1400), 322.5 (-5500), 320 (-4200), 306 (-17000), 301 (-15000), 300 (-16000), 297-293 (-16700), 286.5 (-11000), 250 (-54000), 230 (-760000), 223 (0), 215 (+ 630000), 212 (+ 540000), 210 (+ 280000).

(+)-(16)* (*c* = 0.18-0.0108)

330 (+ 640), 323 (+ 2500), 318 (+ 1300), 303 (+ 11000), 298 (+ 9000), 296 (+ 10000), 287 (+ 7000), 265 (+ 34000), 255 (+ 30000), 230.5 (+ 850000), 223.5 (0), 216 (-600000), 205 (-170000).

(-)-(16)* (*c* = 0.36-0.014)

335 (-800), 322 (-4000), 318.5 (-3000), 304 (-16000), 300 (-13000), 295 (-16000), 289 (-7000), 265 (-35000), 262 (-36000), 255 (-33000), 230 (-870000), 223 (0), 216 (+ 500000), 205 (+ 160000).

(+)- (17)* (*c* = 0.186-0.0186)

320 (+ 3600), 318 (+ 3000), 303 (+ 12000), 295-293 (+ 11000), 288 (+ 6500), 265 (+30000), 255 (+ 27000), 230.5 (+ 630000), 223 (0), 218 (-460000), 215 (-430000), 208 (-180000).

(-)-(17)* (c = 0.29-0.0232)

330 (-3700), 321 (-6300), 318 (-5600), 304 (-18000), 300 (-15000), 297 (-16000), 295 (-15000), 283 (-4600), 264 (-35000), 260 (-34000), 231 (-700000), 223 (0), 217.5 (+ 480000), 205 (+150000).

(+)-(18)* (c = 0.1652-0.01982)

320 (0), 300 (+ 19000), 290 (+ 7000), 264 (+30000), 260 (+ 14000), 256 (+9700), 230-228 (+400000), 224 (0), 218 (-600000), 212 (-300000).

(-)-(18)* (c = 0.38 -0.019)

340 (-2000), 325 (- 5000), 323-321 (-5000),318 (-4700), 304 (-18000), 301 (-17000), 300-299 (-17500), 297 (-19000), 288 (-12000), 264 (-30000), 230 (-800000). 223 (0), 217 (+ 560000), 205 (+ 250000).

(+)-(19)* (c = 0.48-0.024)

335 (+240), 324 (+1700), 302 (+ 13000), 301 (+ 11000), 300 (+12000), 288 (+8000), 281 (+ 14000), 275 (+ 14000), 270 (+ 16000), 255.5 (+ 13000), 231.5 (+580000), 226 (0), 220 (-430000), 210-205 (-130000).

(-)-(19)* (c = 0.0576-0.0069)

330 (0), 333 (-15000), 270 (-90000), 260 (-98000), 252 (-75000), 235 (-680000), 225 (0), 215 (+ 700000), 210 (+ 600000), 207 (0).

(+)- (20)* (*c* =0.71-0.071)

320 (0), 310-300 (+15000), 291 (0), 280 (-35000), 276 (-15000), 260-256 (-120000), 244 (0), 233 (+520000), 225 (0), 216 (-900000), 210 (-700000).

(-)-(20)* (*c* = 0.54-0.0378)

320 (0), 306 (-4000), 289 (0), 280 (+8000), 270 (+2000), 255 (+16000), 244 (0), 234 (-170000), 225 (0), 218 (+300000), 216 (+150000), 213 (0).

(+)-(21)* (*c* = 0.4-0.08)

320 (+9000), 310-306 (+18000), 292 (+200000), 280 (0), 260 (-60000), 248 (0), 234 (+530000), 226 (0), 218 (-1200000), 214 (-1150000).

(-)-(21)* (*c* = 0.4-0.056)

320 (-3000), 300 (-18000), 279 (0), 255 (+18000). 249 (0), 233 (-250000), 226 (0), 218 (+230000), 212 (0).

(+)- (22)* (*c* = 0.1183 -0.059)

320 (+20000), 300 (+58000), 280 (+30000), 236-232 (+440000), 226 (0), 215 (-970000), 214 (-800000).

(+)-(12)* (*c* = 0.71 -0.142)

340 (0), 320 (-5000), 296 (-40000), 293 (-35000), 286 (-55000), 266 (0), 234 (+260000), 231 (+280000), 222.5 (0), 220 (-280000), 214 (-940000).

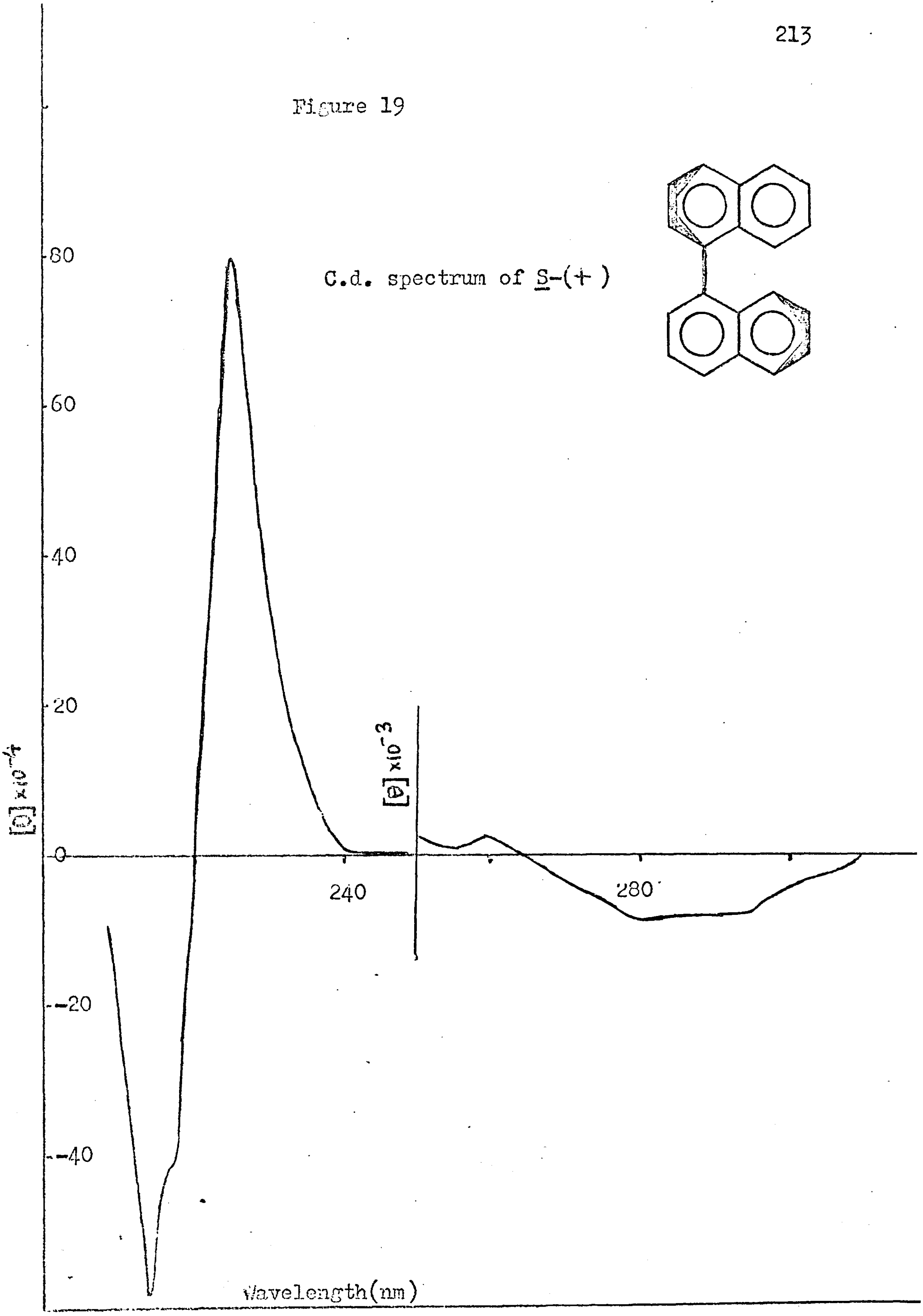
(+)-(10)* (*c* = 0.54-0.054)

310 (-1700), 286 -280 (-18000), 250 (0), 230 (+135000), 226 (0), 220 (-340000), 214 (-130000).

(-)-(10)* (*c* = 0.0.4-0.04)

300 (0), 284-280 (+10000), 270 (+13000), 250 (0), 231 (-110000), 226 (0), 222 (+260000), 220 (+250000), 217 (0).

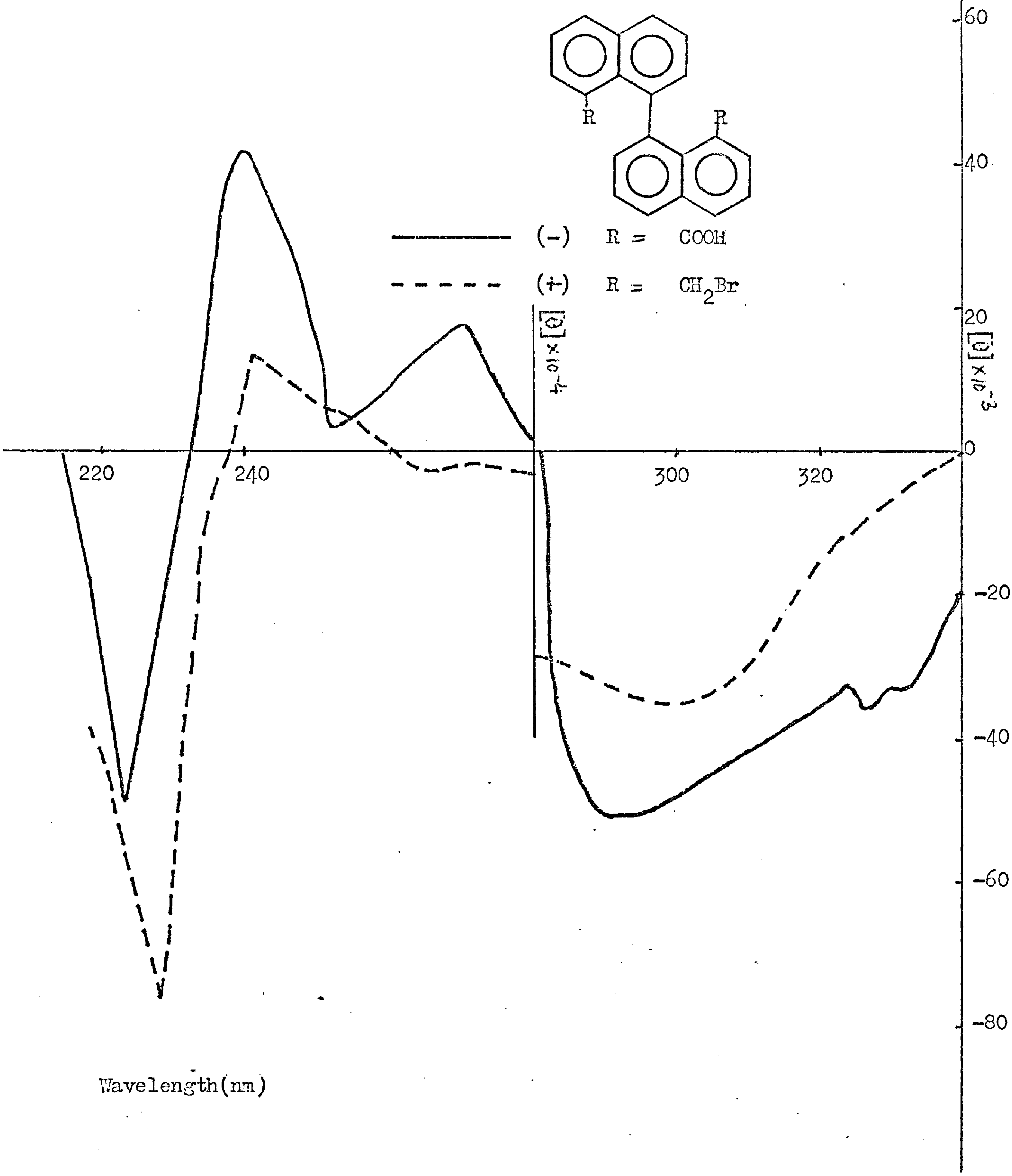
Figure 19



C.d. spectrum of S-(+)

Figure 20

C.d. spectra of S̲- 1,1'-binaphthyls



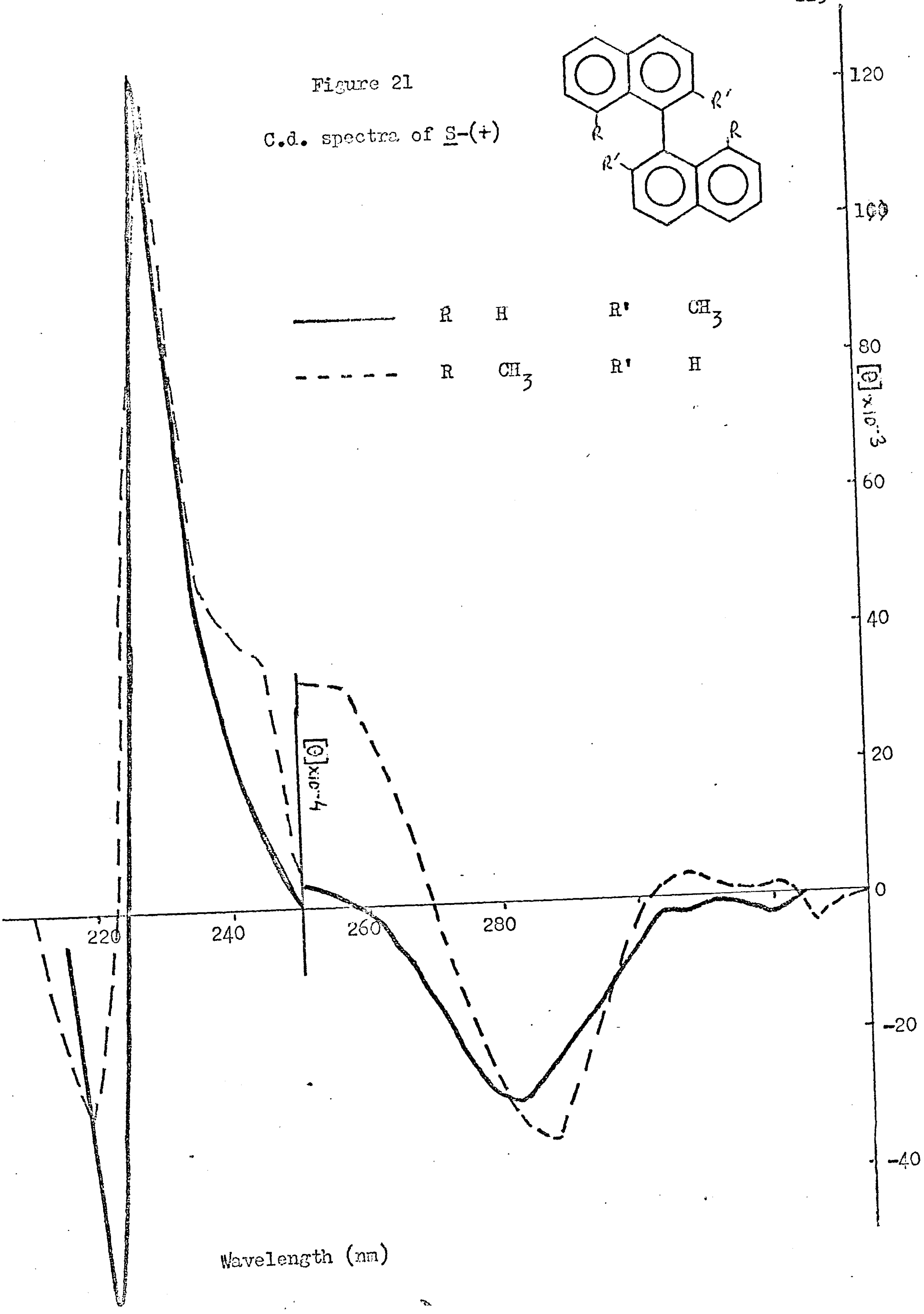
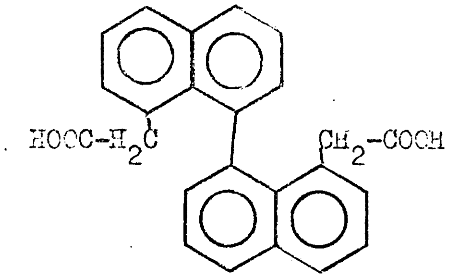


Figure 21

C.d. spectra of S-(+)

Figure 22

C.d. spectra of



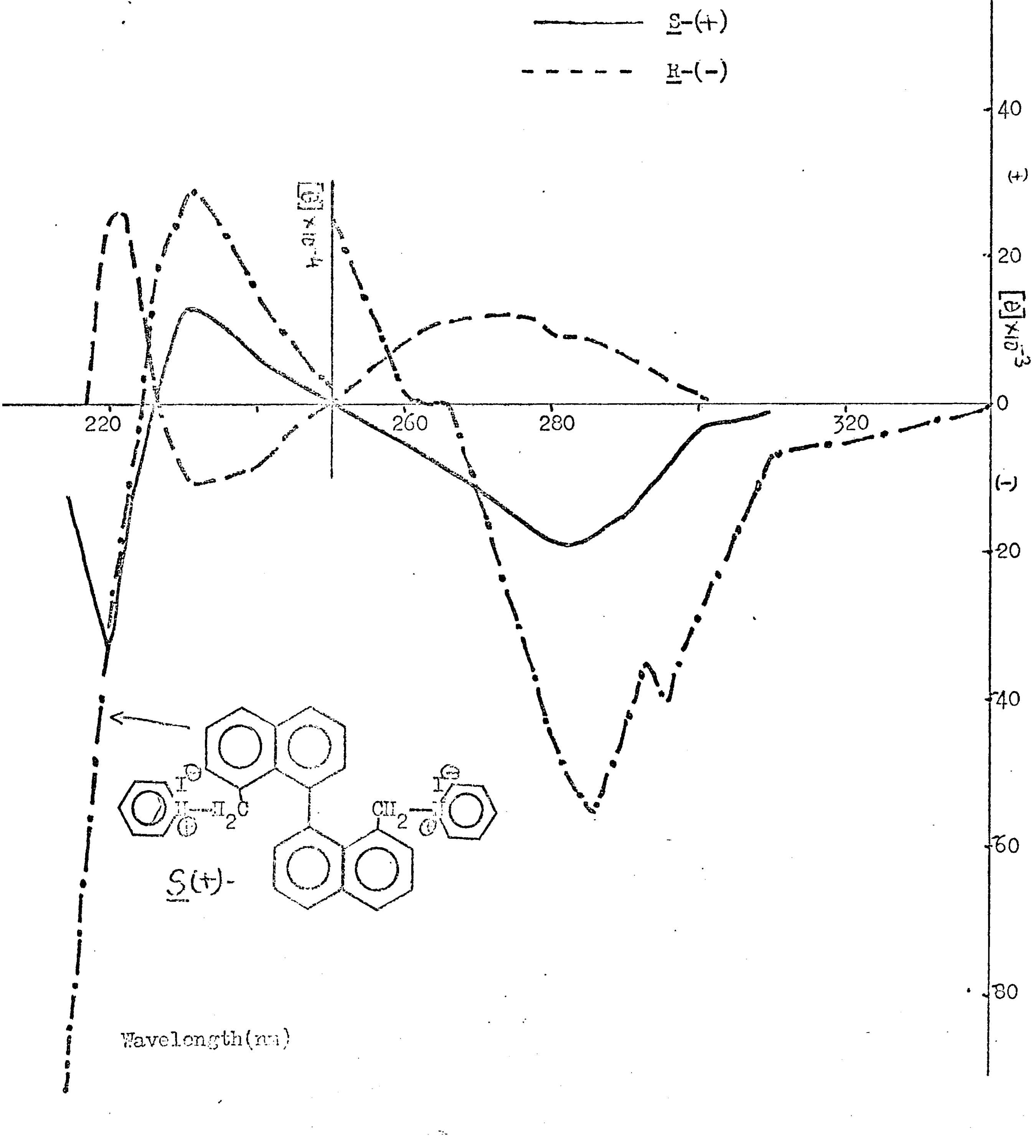


Figure 23

C.d. spectra of S-(+)

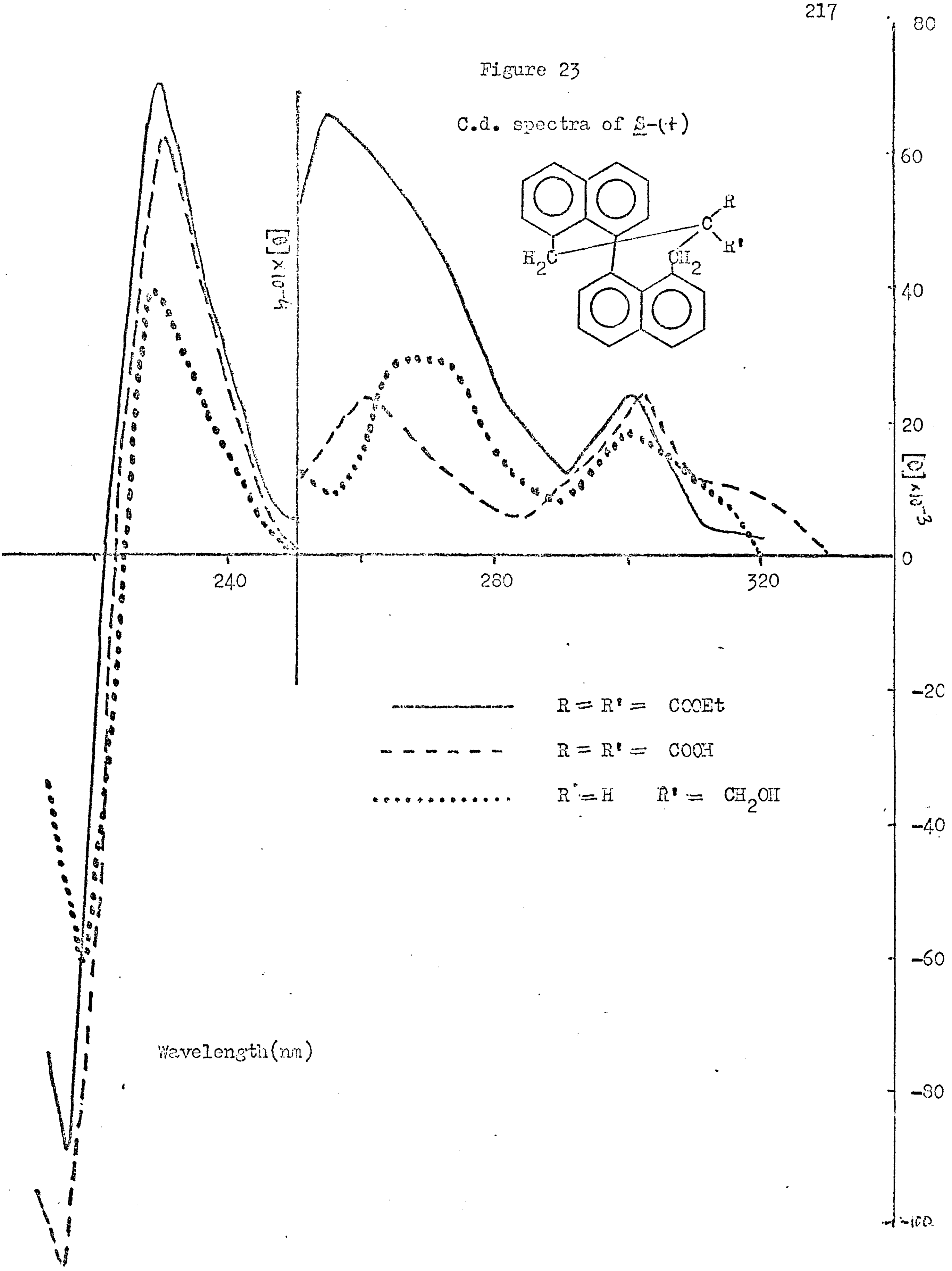


Figure 24

C.d. spectra of S-(+)

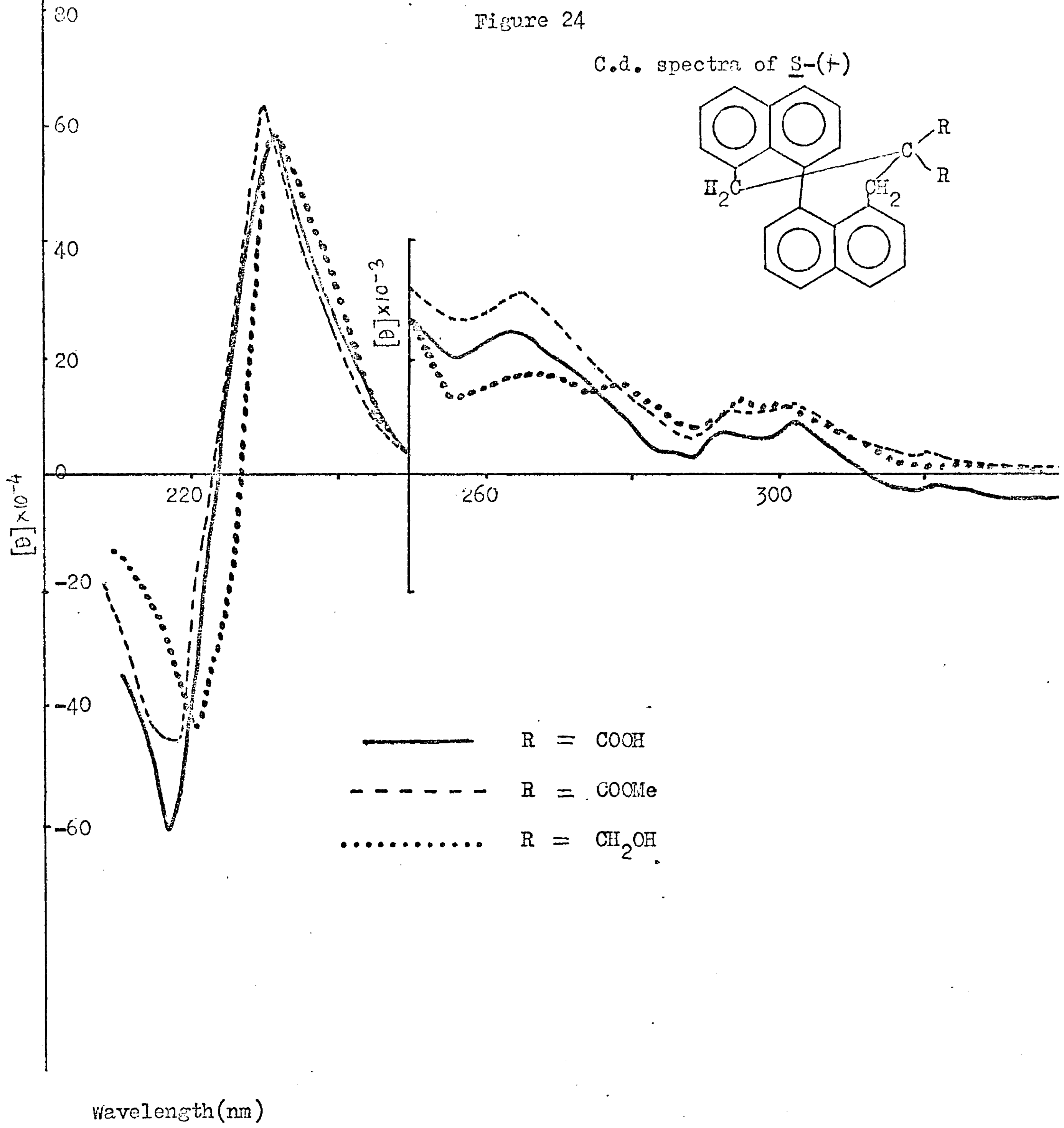


Figure 25

C.d. spectra of R-(-)

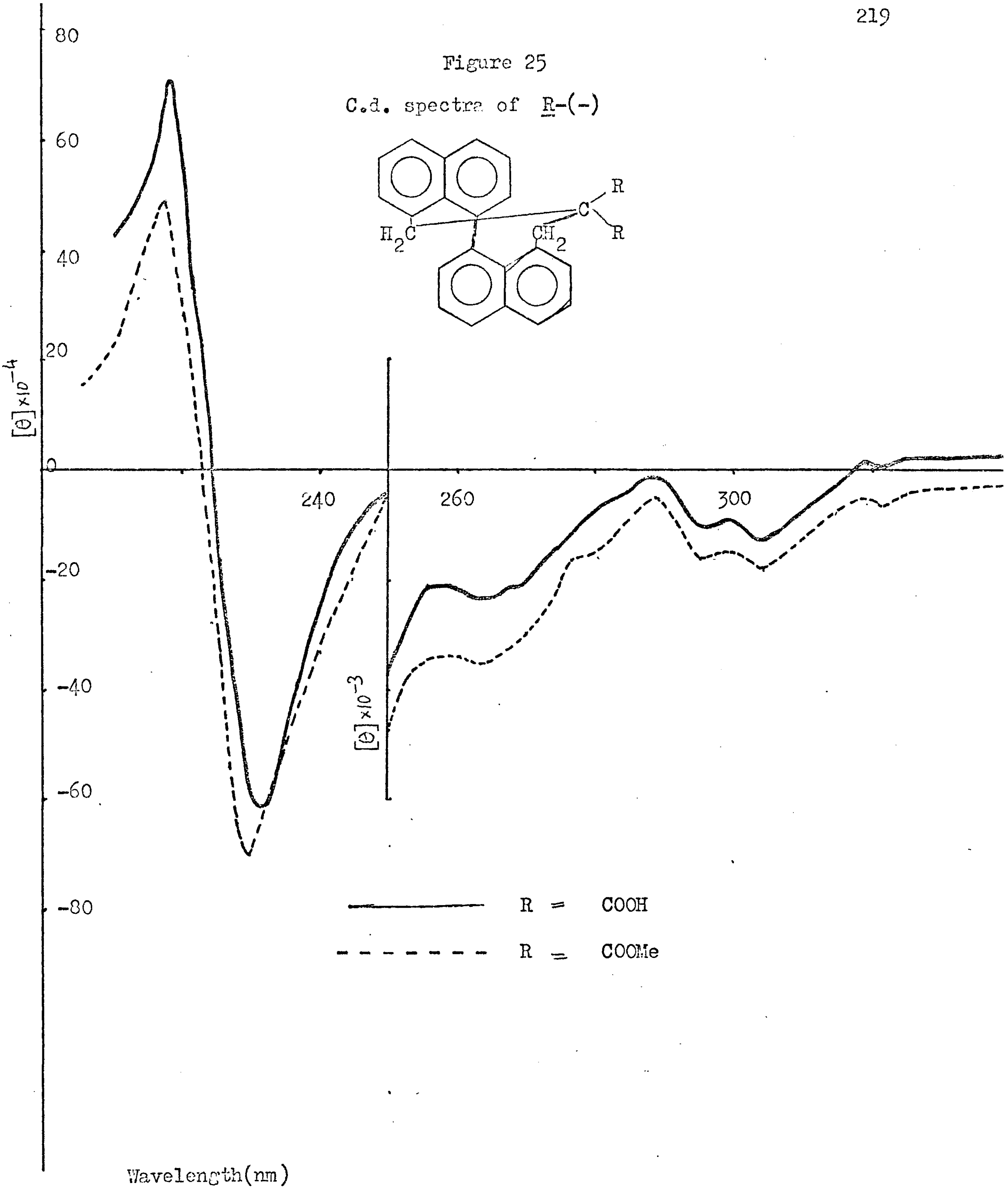


Figure 26

C.d. spectra of R-(-)

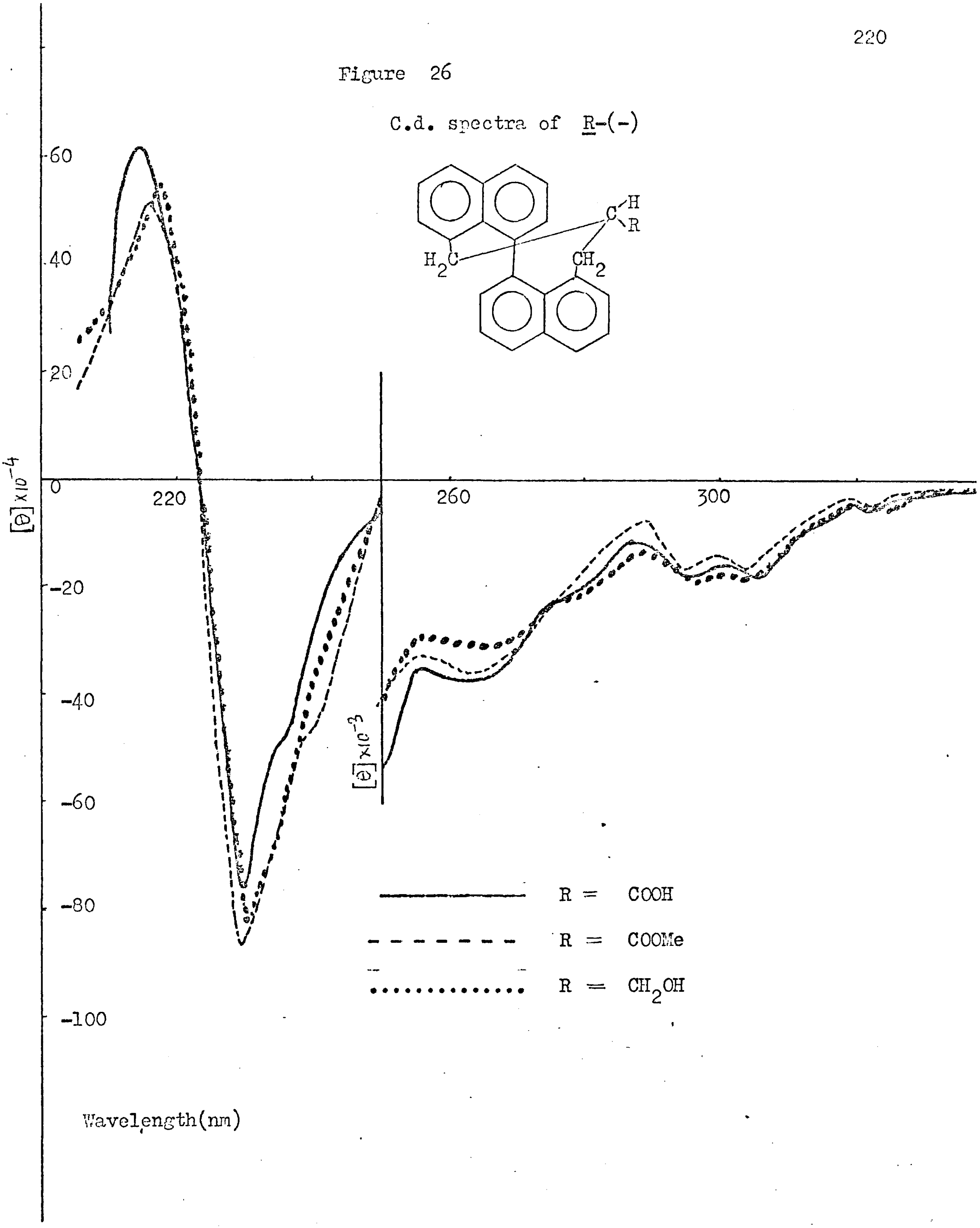
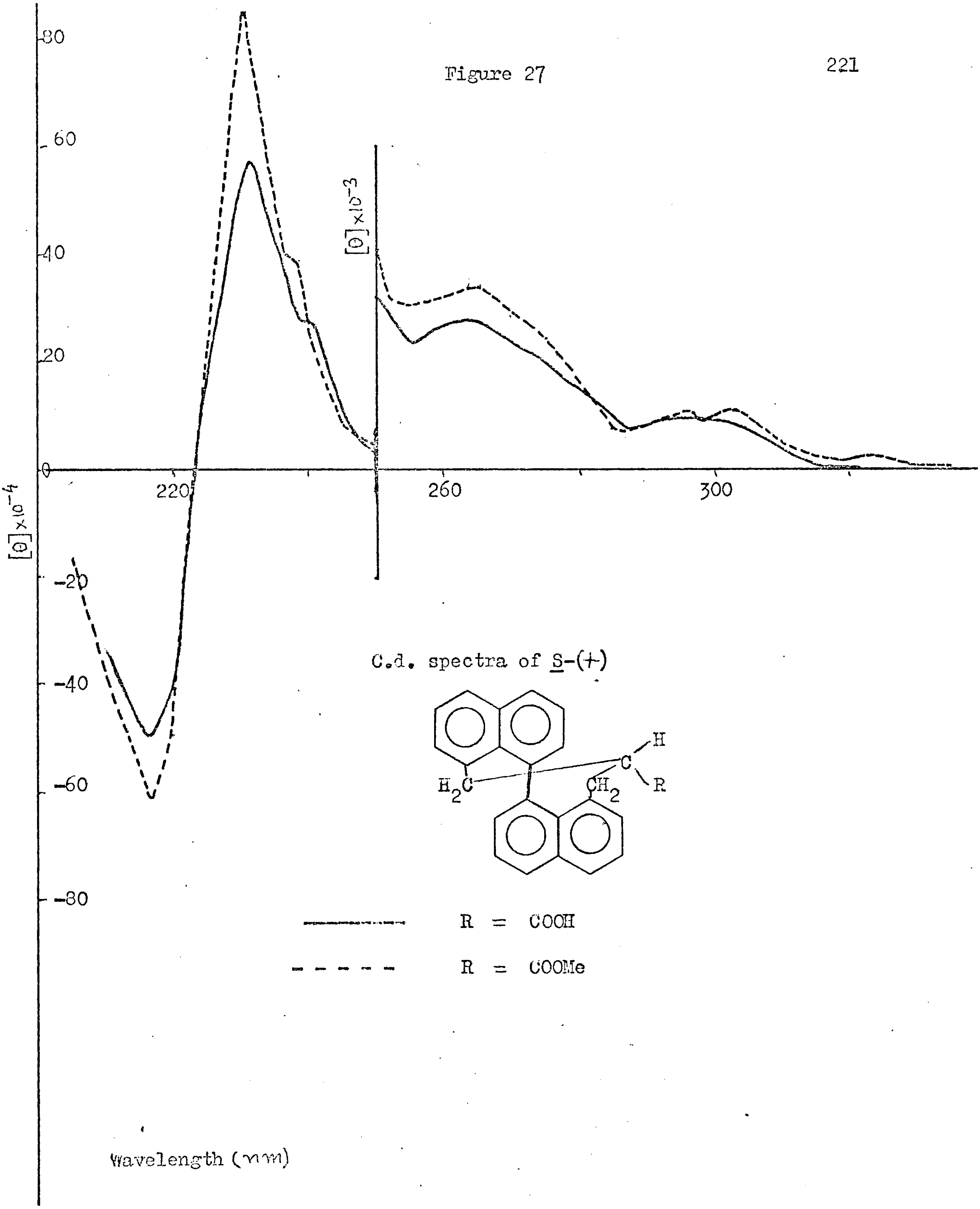
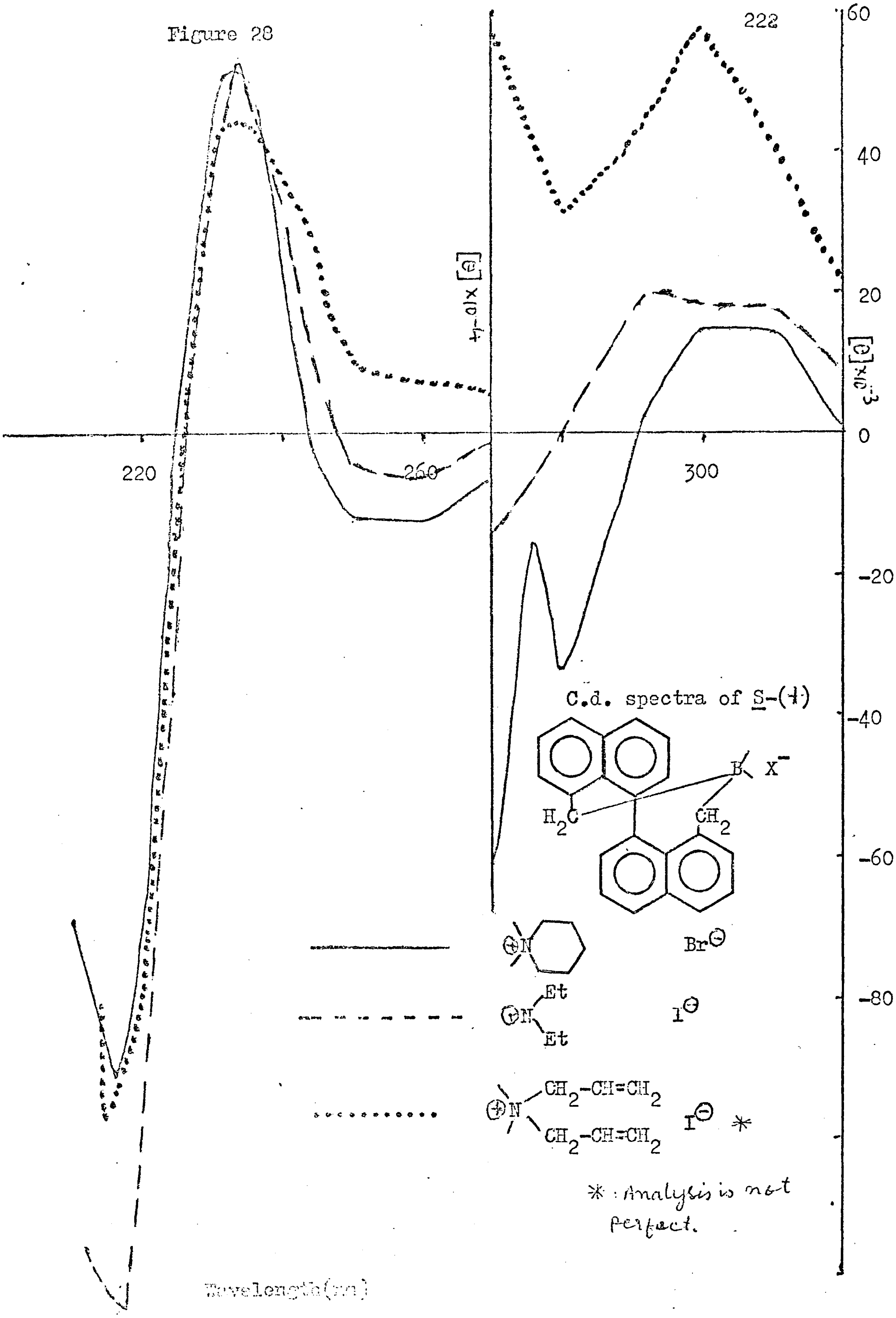


Figure 27



C.d. spectra of S-(+)

Figure 28

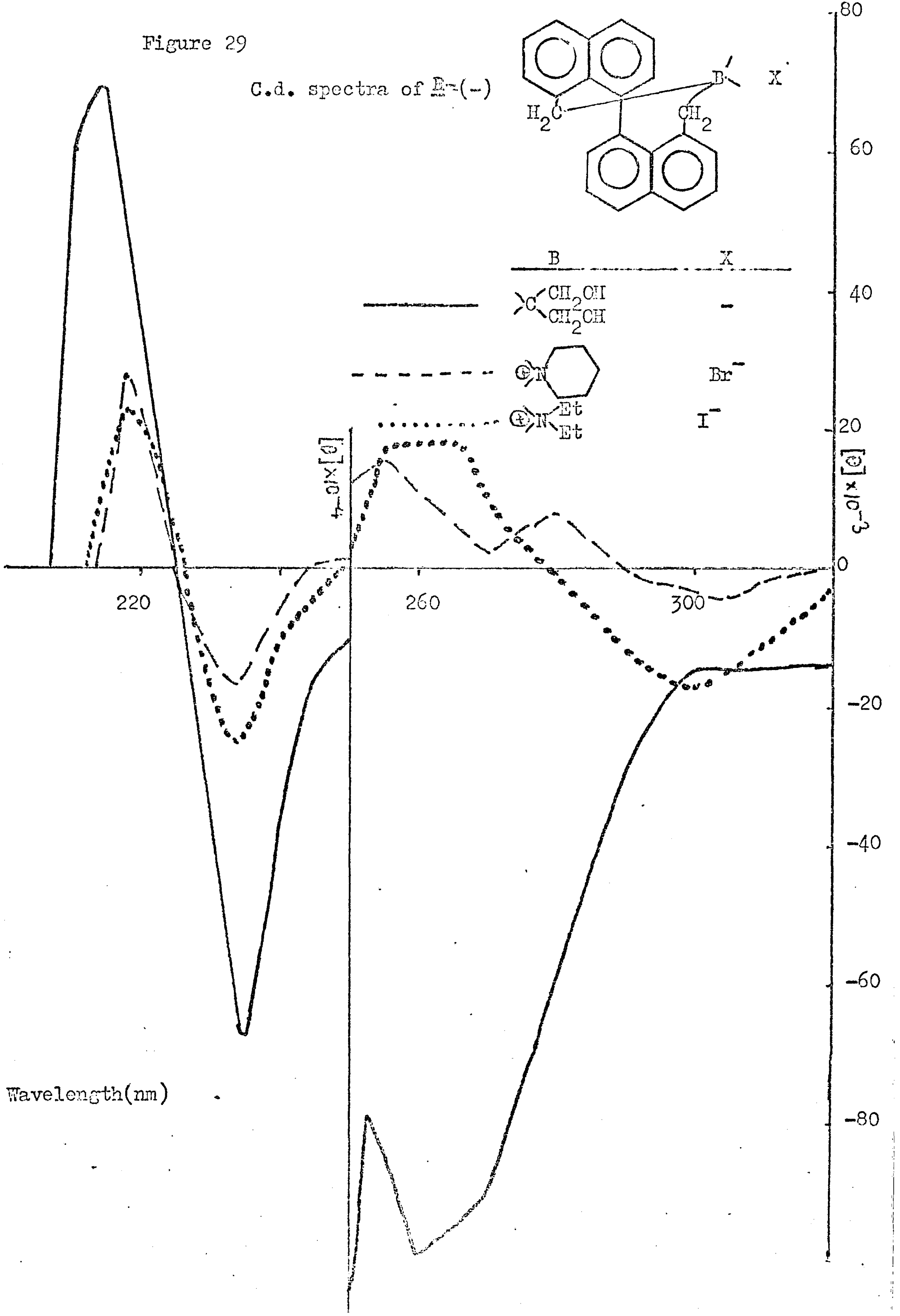


C.d. spectra of S-(+)

* : Analysis is not perfect.

Figure 29

C.d. spectra of B-(-)



Discussion

Circular dichroism spectrum of $(+)_{546}$-1,1'-binaphthyl:- The c.d. spectrum of this compound added to the details of the o.r.d. by revealing two important bands of opposite sign, the negative with a distinct shoulder, in the short-wavelength. This corresponds with the two c.d. bands of opposite signs associated with the short-wave u.v. absorption spectrum in $(-)_{546}$-1,1'-bianthryls, to which (Grinter and Mason, 1964) assigned the R-configuration. The Cotton effects of (+)-1,1'-binaphthyl bear a distinct resemblance to those of the (-)-1,1'-bianthryls except that they appear at shorter wavelengths and refer to the enantiomer of opposite chirality. Therefore a positive c.d. Cotton effect (225 nm) and a negative at (216 nm) relates to S-configuration in 1,1'-binaphthyl.

Circular dichroism spectrum of $(+)_{546}$-2,2'-dimethyl-1,1'-binaphthyl:- Mislow, et al. (1963) determined the c.d. spectrum of this compound above 240 nm and assigned S-configuration on the basis of the presence of a negative 285 nm Cotton effect. A further observation of its c.d. spectrum in the present work down to 208 nm revealed a new Cotton effect which corresponds with its o.r.d. Cotton effect. The two c.d. bands of opposite sign resemble those of $(+)_{546}$-1,1'-binaphthyl suggesting that the aromatic chromophores causing these optically active transitions in these two compounds are of a similar nature.

Circular dichroism spectrum of $(+)_{546}$-8,8'-dimethyl-1,1'-binaphthyl:- The c.d. spectrum of this compound was observed under similar conditions.

It shows a strong long-wave negative c.d. band about 285 nm and in addition to it shows two bands of opposite signs associated with its u.v. absorption short-wave band. Such a fine correspondence between the c.d. bands of (+)-8,8'-dimethyl and (+)-2,2'-dimethyl compounds in addition to (+)-1,1'-binaphthyl made us think about the importance of these short-wave Cotton effects for configurational assignments. The (+)-8,8'-dimethyl-1,1'-binaphthyl was assigned *S*-configuration.

Circular dichroism spectra of (+)-8,8'-bisbromomethyl-1,1'-binaphthyl and (-)-1,1'-binaphthyl-8,8'-dicarboxylic acid:- The c.d. spectrum of the (+)-8,8'-bisbromomethyl compound resembles that of (+)-1,1'-binaphthyl, (+)-2,2'-dimethyl-1,1'-binaphthyl and (+)-8,8'-dimethyl-1,1'-binaphthyl: a negative short-wave c.d. band and positive one at slightly longer wavelength relates it to *S*-configuration.

The (-)-8,8'-dicarboxylic acid showed multiple c.d. bands, in agreement with Mason (1968). The short-wave region c.d. bands resemble that of (+)-8,8'-bisbromomethyl compound. Thus all the unbridged 1,1'-binaphthyls showing a negative c.d. band in the short-wave region and a positive one at slightly longer wavelengths have *S*-configuration.

Circular dichroism spectra of (+)- and (-)-1,1'-binaphthyl-8,8'-diacetic acids:- The c.d. spectra of these enantiomers show a 280 nm Cotton effect and two c.d. bands of opposite signs associated with the u.v. absorption β-band. A negative 280 nm c.d. band of the (+)-enantiomer relates it to *S*-configuration, which in addition a short-wave negative c.d. band confirms (Fig. 22). Similarly the (-)- enantiomer has R-configuration.

Circular dichroism spectrum of 1,1'-binaphthyl-8,8'-bis(methylenepyridinium) diiodide:- This compound also shows an intense 285 nm c.d. band, and as it was derived from S-(+)-8,8'-bisbromomethyl-1,1'-binaphthyl, it would have S-configuration. The short-wave c.d. negatively signed absorption is very intense.

Circular dichroism spectra of 8,8'-bridged 1,1'-binaphthyls

(i) Carbocyclic compounds

Circular dichroism curves obtained for this class of compounds were found to correspond with their o.r.d. curves.

From the synthesis of 8,8-dimethoxycarbonyl [dinaphtho(8,1-ab, 1',8'-de)] -cyclonona-2,4-diene (13) the $(+)_{546}$- isomer of this compound is assigned S-configuration. It shows fine structure corresponding to the u.v. transitions of the β-band and strong c.d. Cotton effect (see figure 23) composed of two oppositely signed bands under the short-wave u.v. absorption band. This ester on hydrolysis gave (+)-dicarboxylic acid, which shown the same c.d. Cotton effect. The short-wave negative and positive c.d. bands of this acid were found to correspond with those obtained by resolution of (+)-(14).

The (+)-dicarboxylic acid (14), and (+)-monocarboxylic acid (15) their methyl esters, and corresponding alcohols all shown the same c.d. Cotton effect; their (-)-enantiomers showed opposite Cotton effects.

(ii) N-Heterocyclic 8,8'-bridged compounds

Dinaphtho(8',1'-ab, 1",8"-de) -cyclonona-2,4-diene-8-azepinium-1-spiro [5,8]·tetradecane-1'''-piperidinium bromide (20) and 8,8-diethyl [dinaphtho(8',1'-ab, 1",8"-de)] -cyclonona-2,4-diene-8-azepinium iodide (21) show multiple Cotton effects. A long-wave positive Cotton effect and a pair of short-wave positive and negative c.d. bands are in correspondence with their o.r.d. curves. 8,8-Diallyl [dinaphtho(8',1'-ab, 1",8"-de)] -cyclonona-2,4-diene-8-azepinium iodide (22) did not show a negative Cotton effect which was seen for the other two compounds near 260 nm (see figure 28, 29), but two strong positive and negative bands associated with their u.v. short-wave absorption band were found characteristic for all these compounds (with positive rotation in visible region) which relate these (+)-enantiomers to S-configuration.

Conclusion: A negative c.d. band at shortest wavelength (~ 220 nm) and a positive one 15-20 nm higher, is characteristic of S-configuration.

6. References

1. Abragam, A., " The Principles of Nuclear Magnetism ", Oxford, 1961.

2. Akimoto, H., Shiroiri, T., Iitaka, Y. and Yamada, S., Tetrahedron Letters, 1968, 97.

3. Allen, D.W., Millar, I.T. and Mann, F.G., J.Chem.Soc.(C), 1967, 1869.

4. Anderson, J.E., Q.Rev.Chem.Soc., 1965, 19, 426.

5. Armarego, W.L.F. and Turner, E.E., J.Chem.Soc., 1956, 3668.

6. Armarego, W.L.F. and Turner, E.E., J.Chem.Soc., 1957, 13.

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

8. Badar, Y., Cooke, A.S. and Harris, M.M., J.Chem.Soc. (C), 1966, 1315.

9. Badar, Y. and Harris, M.M., Chem. and Ind., 1964, 1426.

10. Badger, G.M., Drewer, R.J. and Lewis, G.E., J.Chem.Soc., 1962, 4268.

11. Beaven, G.H., Bird, G.R., Hall, D.M., Johnson, E.A.. Ladbury, J.E., Lesslie, M.S. and Turner, E.E., J.Chem.Soc., 1955, 2708.

12. Beaven, G.H. and Hall. D.M., J.Chem.Soc., 1956, 4637.

Beaven. G.H., Hall, D.M., Lesslie, M.S. and Turner, E.E., J.Chem.Soc., 1952, 854.

14. Bell, F. and Kenyon, J., Chem. and Ind., 1926, 45 , 864.

15. Bell, F. and Morgan, W.H.D., J.Chem.Soc., 1954, 1716.

16. Bell, F., Morgan, W.H.D. and Smyth, L.E.B., Chem. and Ind., 1951, 634.

16a. Bentley, K.W. and Robinson, R., J. Chem. Soc., 1952, 947

17. Bleankney, W., Phys. Rev., 1930, 35, 139.

18. Blice, F.F., Azuara, J., Doorenbos, N.J. and Hotelling, E.B., J.Amer.Chem.Soc., 1953, 75, 5418.

19. Blomquist, A.T., Wheeler, E.S. and Chu, Y., J.Amer.Chem.Soc., 1955, 77, 6307.

20. Borgan, G. and Dale, J., Chem.Commun., 1970, 1105.

21. Braude, E.A., Ann.Reports, 1945, 42, 105.

22. Braude, E.A. and Forbes, W.F., J.Chem.Soc., 1955, 3776.

23. Bredenberg, J.B-Son, Acta.Chem.Scand., 1959, 13, 1733.

24. Brown, W.A.C. and Monteath Robertson, J., Proc.Chem.Soc., 1961, 115.

25. Browne, P.A., Harris, M.M., Mazengo, R.Z. and Singh, S, J.Chem.Soc.(C), 1971, 3990.

26. Cagle,Jr., F.W. and Eyring, H., J.Amer.Chem.Soc., 1951, 73, 5628.

27. Cooke, A.S. and Harris, M.M., J.Chem.Soc., 1963, 2365.

28. Cooke, A.S. and Harris, M.M., J.Chem.Soc.(C), 1967, 988.

29. Cope, A.C. and Smith, R.D., J.Amer.Chem.Soc., 1956, 78, 1012.

30. Corbellini, A., Atti.Accad.Lincei, 1931, 32, 702.

31. Crawford, M. and Smyth, L.E.B., Chem. and Ind., 1954, 346.

32. Dhar, J., Indian J.Phys., 1932, 7, 43.

33. Dieckmann, W., Ber., 1894, 27, 102.

34. Dixon, W., Harris, M.M. and Mazengo, R.Z., J.Chem.Soc. (B), 1971, 775.

35. Djerassi, C., "Optical Rotatory Dispersion", McGraw-Hill, Inc. New York, N.Y., 1960.

36. Fitts, D.D., Siegel, M. and Mislow, K., J.Amer.Chem.Soc., 1958, 80, 480.

37. Forbes, M.H., Mann, F.G., Millar, I.T. and Moelwyn-Hughes, E.A., J.Chem.Soc., 1963, 2833.

38. Freudenberg, K.,"Stereochemie", Franz Deuticke, Leipzig, 1933, p 699.

39. Friedel, R.A., Orchin, M. and Reggel, L., J.Amer.Chem.Soc., 1948, 70, 199.

40. Frampton, V.L., Edwards,Jr., J.D. and Henze, H.R., J.Amer.Chem.Soc., 1948, 70, 2284.

41. Gillam, A.E. and Stern, E.S., "An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry", 2nd ed., Edward Arnold, London, 1957.

42. Glasstone, S., Laidler, K.J. and Eyring, H., "The Theory of Rate Processes", McGraw-Hill, 1941, p 197.

43. Grinter, R. and Mason, S.E. , *Trans.Faraday Soc.*, 1964, *60*, 274. (see also Mason, S.F., "Optical Rotatory Dispersion and Circular Dichroism in Organic Chemistry", ed. Snatzke, Heydon, 1967, ch. 4.

44. Hall, D.M., *J.Chem.Soc.*, 1956, 3674.

45. Hall, D.M. and Harris, M.M., *J.Chem.Soc.*, 1960, 490.

46. Hall, D.M. and Manser, W.W.T., *Chem.Commun.*, 1967, 112.

47. Hall, D.M. and Mazengo, R.Z., *DMS U.V. Atlas*, *III*, Butterworths, 1967.

48. Hall, D.M. and Minhaj, F., *J.Chem.Soc.*, 1957, 4584.

49. Hall, D.M., Ridgwell, S. and Turner, E.E., *J.Chem.Soc.*, 1954, 2498.

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

51. Hammett, L.P., "Introduction to the Study of Physical Chemistry", McGraw-Hill, New York, 1941, p 410.

52. Hargreaves, A. and Rizvi, S.H., *Acta Crystallographica*, 1962, *15*, 365.

53. Harris, M.M. and Ling, C.K., *Chem. and Ind.*, 1962, 1378.

54. Harris, M.M. and Mazengo, R.Z., *DMS U.V. Atlas*, *III*, Butterworths, 1967.

55. Harris, M.M., Mazengo, R.Z. and Cooke, A.S., *J.Chem.Soc.(C)*, 1967, 2575.

56. Harris, M.M. and Mellor, A.S., *Chem. and Ind.*, 1959, 949.

57. Harris, M.M. and Mellor, A.S., *Chem. and Ind.*, 1961, 557; 1082.

58. Hwang, H.Y., *Ph.D. (Thesis)*, London, 1972.

59. Karplus, M., J.Amer.Chem.Soc., 1963, 85, 2870.

60. Kenner, J., J.Chem.Soc., 1913, 613.

61. Kenner, J. and Turner, E.G., J.Chem.Soc., 1911, 2101.

62. Kerr, K.A. and Monteath Robertson, J., J.Chem.Soc.(B), 1969, 1146.

63. Kohler, E.P., Tischler, M., Potter, H. and Thompson, H.T., J.Amer. Chem.Soc., 1939, 61, 1057.

64. Kuhn, R. and Albrecht, O., Ann., 1928, 465, 282.

65. Kuhn, R. and Goldfinger, P., Ann., 1929, 470, 183.

66. Kurland, R.J., Rubin, M.B. and Wise, W.B., J.Chem.Phys., 1964, 40, 2426.

67. LeFevre, R.J.W., (Mrs) Sundaram, A. and Sundaram, K.M.S., J.Chem.SOC., 1963, 3180.

68. Leonard, N.J. and Schimelpfenig, C.W., J.Org.Chem., 1958, 23, 1708.

69. Marvel, C.S. and Glass, D.B., J.Amer.Chem.Soc., 1938, 60, 1051.

70. Mason, S.F., 1968, "Private Communication to Dr. M.M.Harris."

71. Mazengo, R.Z., Ph.D. (Thesis), London, 1968.

72. McLafferty, F.W. and Gohlke, R.S., Anal.Chem., 1959, 31, 2076.

73. Meisenheimer, J. and Beisswenger, O., Ber., 1932, 6B, 32.

74. Mills, W.H., Chem. and Ind., 1926, 45, 884; 905.

75. Mislow, K., Angew. Chem., 1958, 70, 683.

76. Mislow, K., "Introduction to Stereochemistry", Benjamin, New York, 1965.

77. Mislow, K., Bunnenberg, E., Records, R., Wellman, K. and Djerassi, J.Amer.Chem.Soc., 1963, 85, 1342.

78. Mislow, K., Glass, M.A.W., Hopps, H.B., Simon, E. and Whal, Jr., G.H., J.Amer.Chem.Soc., 1964, 86, 1710.

79. Mislow, K., Glass, M.A.W., O'Brien, R.E., Rutkin, P., Steinburg, D.H., Weiss, J. and Djerassi, C., J.Amer.Chem.Soc., 1962, 84, 1455.

80. Mislow, K., Hyden, S.,and Schaefer, H., J.Amer.Chem.Soc., 1962, 84, 1449.

81. Mislow, K. and McGinn, F.A., J.Amer.Chem.Soc., 1958, 80, 6036.

82. Mislow, K. and Raban, M., "Topics in Stereochemistry", I, ed. Allinger and Eliel, Interscience Publishers, New York, 1961.

83. Moscowitz, A., Tetrahedron, 1961, 13, 48.

84. Moscowitz, A., "Advances in Chemical Physics", I, Prigogine, Ed., Interscience, New York, 1962, p 67.

85. Murahashi, S., C.A., 1932, 26, 2191.

86. Newman, P., Rutkin, P. and Mislow, K., J.Amer.Chem.Soc., 1958, 80, 465.

87. O'Shaughnessy, M.T. and Rodebush, W.H., J.Amer.Chem.Soc., 1940, 62, 2906.

88. Pecherer, B. and Brossi, A., J.Org.Chem., 1967, 32, 2350.

89. Pincock, R.E. and Wilson, K.R., J.Amer.Chem.Soc., 1971, 93, 1291.

90. Rabinovitz, M., Gajit, A. and Bergmann, E., Chem.Commun., 1970, 1430.

91. Robertson, G.B., Nature, 1961, 593.

92. Rule, H.G. and Barnett, A.J.G., J.Chem.Soc., 1932, 175.

93. Rule, H.G., Pursell, W. and Brown, R.R.H., J.Chem.Soc., 1934, 168.

94. Ruzicka, L., Stoll, M. and Schinz, H., Helv., 1926, 9, 249.

95. Sicher, J., "Progress in Stereochemistry", III, ed. de la Mare, P.B.D. and Klyne, W., Butterworths, London, 1962.

96. Siddall, T.H. and Garner, R.H., Tetrahedron Letters, 1966, 3513.

97. Small, L., Sargent, L. and Bralley, J.A., J.Org.Chem., 1947, 12, 839.

98. Stanley, W.M., J.Amer.Chem.Soc., 1931, 53, 3104.

99. Stanley, W.M. and Adams, R., Rec.Trav.Chem., 1929, 48, 1035.

100. Suzuki, H., "Electronic Absorption Spectra and Geometry of Organic Molecules", Academic Press, London, 1967, ch. 12.

101. Theilacker, W. and Hopp, R., Ber., 1959, 2293.

102. Thorpe, J.F., J.Chem.Soc., 1909, 901.

103. Trager, W.F., Vincenzi, F.W. and Huistric, A.C., J.Org.Chem., 1962, 27, 3006.

104. Trotter, J. Acta Crystallographica, 1961, 14, 1135.

105. Turner, E.E. and LeFevre, R.J.W., Chem. and Ind., 1926, 45, 831.

106. Waugh, J.S. and Fessenden, R.W., J.Amer.Chem.Soc., 1957, 79, 846.

107. Woodward, R.B., Wendler, N.L. and Brutschy, F.J., J.Amer.Chem.Soc., 1945, 67, 1425.

108. Ziegler, K. and Aurnhammer, R., Ann., 1934, 513, 43.

109. Ziegler, K., Eberle, H. and Ohlinger, H., Ann., 1933, 504, 94.

Optical Rotatory Dispersion and Circular Dichroism Spectra of Optically Active 1,1′-Binaphthyl

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Optical Rotatory Dispersion and Circular Dichroism Spectra of Optically Active 1,1′-Binaphthyl

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The o.r.d. and c.d. spectra of 1,1′-binaphthyl in ethanol solution have been determined in the region 208—320 nm. Comparison of the curves with those of substituted 1,1′-binaphthyls of established chirality leads to the conclusion that the dextrorotatory (λ = 589 nm) enantiomer of this, the parent, compound has the *S*-configuration. This result is in accord with that arrived at by chemical correlation with a substituted 1,1′-binaphthyl in which the configuration was assigned by *X*-ray crystallographic methods.

ON account of its optical lability, the specific rotation of optically pure 1,1′-binaphthyl in solution cannot be known accurately: the highest values previously quoted by different workers are $[\alpha]_{578}^{20}$ +245° in benzene–light petroleum,[1] $[\alpha]_{589}$ +192° in benzene,[2] $[\alpha]_{589}$ +104° in tetrahydrofuran,[3] $[\alpha]_{436}$ +250° in dimethylformamide,[4] $[\alpha]_{589}$ +220° in benzene.[5] The last two values refer to specimens obtained by spontaneous enantiomeric crystallisation from a melt, the others from de-amination of an optically active diamine. Since it seems that the original preparative method[1] is as effective and as reliable as any, we have continued to use it. On this occasion the starting material was (+)-4,4′-diamino-1,1′-binaphthyl, $[\alpha]_{578}^{23}$ +45·7° (c = 0·164, l = 0·5, acetone); since this compound is also optically labile, it was kept in solution for as short a time as possible with the working temperature kept as low as was practically feasible (*ca.* 0°) during the preparation and purification of the product. When the 1,1′-binaphthyl (m.p. 158°) obtained was shaken at 0° for 1·5 h in 96% ethanol, a solution was prepared which showed the following specific rotations, $[\alpha]_{578}^{7}$ +223°, $[\alpha]_{546}^{7}$ +253°, $[\alpha]_{436}^{7}$ +417°, $[\alpha]_{405}^{7}$ +580°, $[\alpha]_{365}^{7}$ +878° (c = 0·0336, l = 1). However, if the binaphthyl was dissolved at room temperature and the rotation read as quickly as possible, $[\alpha]_{578}^{23}$ was +203° (c = 0·064, l = 0·5, 96% ethanol). In dioxan solution the variation with wavelength was $[\alpha]_{578}^{23}$ +105°, $[\alpha]_{546}^{23}$ +122°, $[\alpha]_{436}^{23}$ +227°, $[\alpha]_{405}^{23}$ +311°, $[\alpha]_{365}^{23}$ +433° (c = 0·344, l = 0·5). In benzene $[\alpha]_{578}^{23}$

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[1] Margaret M. Harris and Ann S. Mellor, *Chem. and Ind.*, 1961, 1082; Ann S. Cooke and Margaret M. Harris, *J. Chem. Soc.*, 1963, 2365.

[2] A. K. Colter and L. M. Clemens, *J. Phys. Chem.*, 1964, 68, 651; *J. Amer. Chem. Soc.*, 1965, 87, 847.

[3] H. Akimoto, T. Shioiri, Y. Iitaka, and S. Yamada, *Tetrahedron Letters*, 1968, 97.

[4] R. E. Carter and L. Dahlgren, *Acta Chem. Scand.*, 1969, 504.

[5] R. E. Pincock and K. R. Wilson, *J. Amer. Chem. Soc.*, 1971, 93, 1291.

was +268° ($c = 0{\cdot}038$, $l = 0{\cdot}5$) and in tetrahydrofuran $[\alpha]_{578}^{23}$ was +107° ($c = 0{\cdot}028$, $l = 0{\cdot}5$).

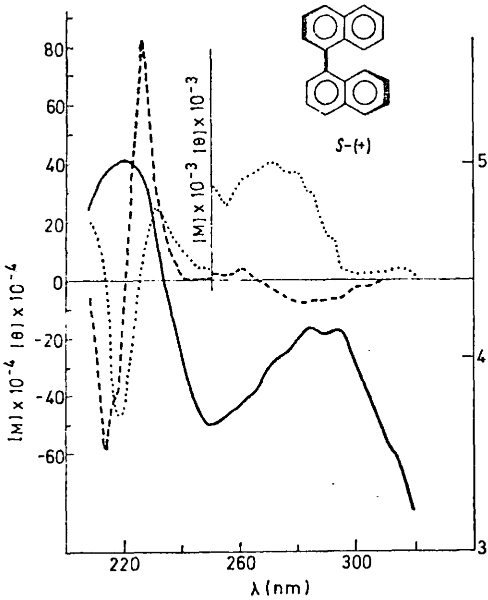
The correspondence between these values and those previously published leads to the speculation that, in the crystallisation of optically impure 1,1′-binaphthyl from solution, there is an element of spontaneous optical purification, as has been observed from the melt, and that these specific rotations represent a fairly close approximation to optical purity, apart from the loss due to racemisation whilst the rotation is measured. We have used this sample to determine the o.r.d. and c.d. spectra, precautions being taken to conserve the optical activity of solutions before and during the determinations; even so, the values for o.r.d. and c.d. given by the spectra are always less than would be given by an optically pure specimen.

The u.v. spectrum of 1,1′-binaphthyl was cited in 1948 as evidence for the non-planarity of the molecule; maxima at 226,[6] 285, and 295 nm[7] were reported and the absence of a separate band corresponding with the 'conjugation band' of biphenyl was noted. Redetermination of the spectrum between 208 and 320 nm in 96% ethanol, has revealed more detail: 220 (ε 108,000), 249 (4760), 262infl. (6210), 272infl. (9720), 283 (14,300), 293·5 (14,000), and 313sh nm (3160). Naphthalene itself has a strong band $\lambda_{max.}$ 220 nm, a moderately intense band at 275 nm and a weaker band at 312 nm.

The o.r.d. spectrum was determined at 8° in 96% ethanol and the c.d. spectrum at 7° in ethanol. The c.d. spectrum adds to the detail of the o.r.d. (see Figure) by revealing two important bands of opposite sign, one carrying a distinct shoulder, in the short wavelength region.

Mislow and his co-workers have studied extensively the o.r.d.[8] and c.d.[9] spectra of several substituted 1,1′-binaphthyls, recognising the twisted systems as inherently disymmetric chromophores: they make the generalisation that a positive Cotton effect centred at 285 nm corresponds with the *R* configuration in this series. Using their criterion, the c.d. spectrum of 1,1′-binaphthyl [(+)-rotatory at λ_{589}] shows a negative Cotton effect in the 285 nm region and hence has the *S*-configuration. This conclusion is in agreement with the recent assignment, based on chemical correlation with an optically active substituted 1,1′-binaphthyl, which was found to have the *S*-configuration by *X*-ray crystallographic methods.[3]

The other published data which are interesting for comparison in the short wavelength region relate to (−)-dimethyl-1,1′-bianthryl-2,2′-dicarboxylate. Badger and his co-workers[10] determined the o.r.d. spectrum of this compound and found it to have two Cotton effects of opposite sign, a large negative one centred at 271 nm and a small positive one centred at 377 nm. By analogy with Mislow's generalisation for 1,1′-binaphthyls regarding the Cotton effect at the longer wavelength, positive in this case, they assigned the *R*-configuration to the (−)-enantiomer. Shortly after, Grinter and Mason[11] determined the c.d. spectrum of the same compound; they found the expected positive c.d. absorption in the region of the long wave band, and in the short wave region where the u.v. spectrum showed split components, found two strong circular dichroism absorptions, of opposite sign. The Cotton effects of the (+)-1,1′-binaphthyl bear a distinct resemblance to those of the (−)-1,1′-bianthryldicarboxylic ester except that they appear at shorter wavelengths and refer to the enantiomer of opposite chirality.



U.v. (——), o.r.d. (······), and c.d. (– – – –) spectra of 1,1′-binaphthyl, $[\alpha]_{578}$ + 223°; the low-intensity parts of the o.r.d. and c.d. spectra are plotted on a ten-fold augmented scale

Hence all the available evidence leads to the conclusion that the enantiomer of 1,1′-binaphthyl which is (+)-rotatory in the visible region has the *S*-configuration.

EXPERIMENTAL

Optical rotations in the region 365—578 nm were taken with a Zeiss photoelectric precision polarimeter, with temperature control.

The u.v. spectrum was determined on a Unicam spectrophotometer (SP 500) in 96% ethanol; $c = 0{\cdot}188$—$0{\cdot}0188$ g/l. 2 mm cell.

The o.r.d. spectrum was determined on a Perkin-Elmer spectrophotometer (P.23), with temperature control at 8°

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[6] R. A. Friedel, M. Orchin, and L. Reggel, *J. Amer. Chem. Soc.*, 1948, **70**, 199.

[7] V. L. Frampton, J. D. Edwards, jun., and H. R. Henze, *J. Amer. Chem. Soc.*, 1948, **70**, 2284.

[8] K. Mislow, M. A. W. Glass, R. E. O'Brien, P. Rutkin, D. H. Steinberg, J. Weiss, and C. Djerassi, *J. Amer. Chem. Soc.*, 1962, **84**, 1455.

[9] K. Mislow, E. Bunnenberg, Ruth Richards, K. Wellman, and C. Djerassi, *J. Amer. Chem. Soc.*, 1963, **85**, 1342.

[10] G. M. Badger, R. J. Drewer, and G. E. Lewis, *J. Chem. Soc.*, 1962, 4268.

[11] R. Grinter and S. F. Mason, *Trans. Faraday Soc.*, 1964, **60**, 274 (see also S. F. Mason, 'Optical Rotatory Dispersion and Circular Dichroism in Organic Chemistry,' ed. Snatzke, Heyden, London, 1967, ch. 4.

in 96% ethanol, c = 0·56—0·007 g/l, 1 mm cell. O.r.d. data ($[\alpha]^8$ in parentheses): 208 (+78,000°), 214 (0°), 217 (−160,000°), 219 (−185,000°), 220 (−180,000°), 225 (0°), 230 (+98,000°), 255 (+9900°), 272 (+15,000°), 283 (+12,000°), 285 (+11,500°), 290 (+5700°), 293 (+4900°), 300 (+300°), 310 (+500°), 315 (+800°), and 320 nm (+550°).

The c.d. spectrum was determined on a Fica Spectropol I, with temperature control at 7°, in ethanol, c = 0·124—0·0124 g/l, 1 mm cell. C.d. data (molar ellipticity [θ] in parentheses): 208 (−59,000), 214 (−590,000), 216 (−430,000), 218 (−370,000), 220 (0); 225 (+825,000), 240 (~0), 245 (~0), 250 (+2000), 255 (+1000), 260 (+3700), 265 (0), 280 (−8100), 285 (−7800), 290 (−7600), 295 (−7000), 300 (−3600), 305 (−2300), and 310 nm (~0).

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