

SOME 9-MEMBERED HETEROCYCLIC RINGS INCORPORATING THE  
8- AND 8'- POSITIONS of 1,1'-BINAPHTHYL

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BY

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**TO MY PARENTS**

## ACKNOWLEDGMENTS

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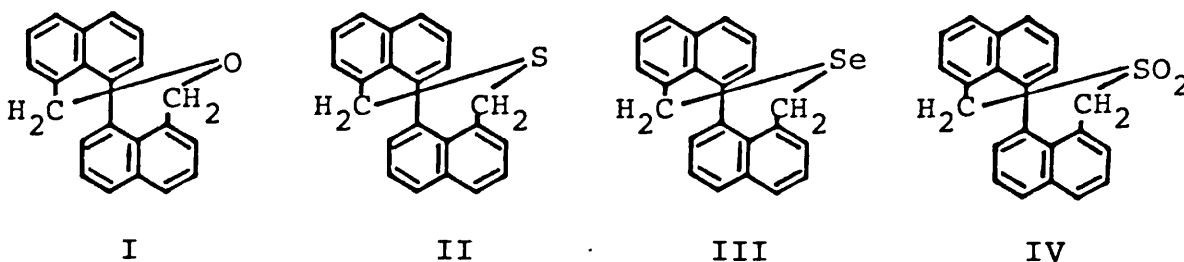
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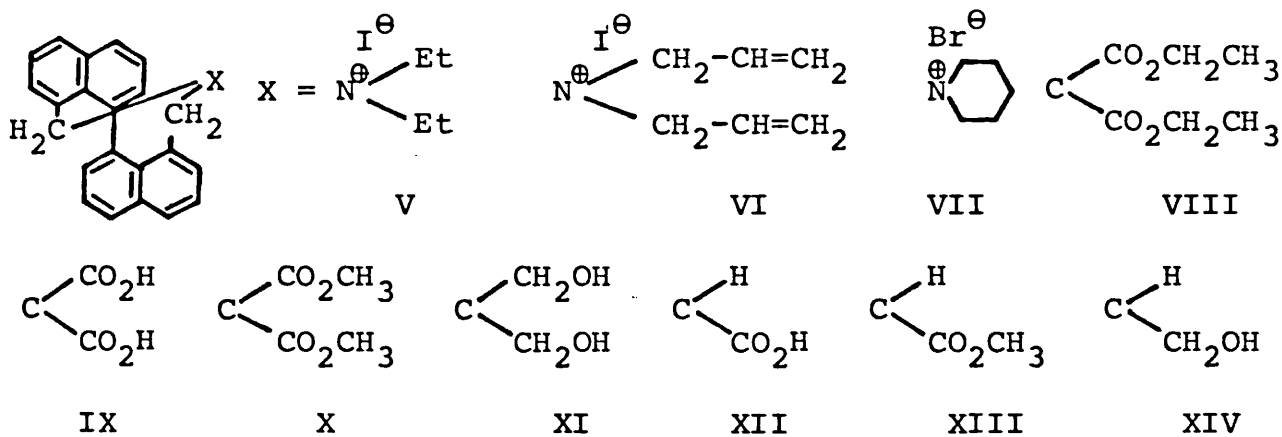
A B S T R A C T

Four, new nine-membered ring compounds, 8,9-dihydro-7H-cyclonona[1,2,3-de:4,5,6-d'e']-dinaphthalenes with heteroatoms in the 8 positions, have been prepared, where the hetero-function is -O-(I), -S-(II), -Se-(III) and -SO<sub>2</sub>(IV), in the racemic and optically active states.



The oxygen-bridged compound (I) was made from 8,8'-bishydroxymethyl-1,1'-binaphthyl while the sulphur (II) and selenium (III) compounds were synthesised from 8,8'-bisbromomethyl-1,1'-binaphthyl; the cyclic sulphone (IV) was prepared by oxidation of the sulphide (II).

The following nine-membered ring heterocyclic and carbocyclic analogues, which had been described previously but were not available in sufficient quantity for further study were also synthesised. 8,8'-Biscyanomethyl-1,1'-binaphthyl



(XIX) was also prepared for further investigation.

The optically active heterocyclic bridged compounds were synthesised from optically active precursors derived from resolved 1,1'-binaphthyl-8,8'-dicarboxylic acid (XV); the carbocyclic ones were prepared from the bridged di-acid (IX), resolved through its quinidine salt.

The absolute configurations of all these compounds are unequivocally assigned through synthetic routes which link them with (+)-2,2'-dihydroxy-1,1'-binaphthyl-3,3'-dicarboxylic acid dimethyl ester established as of (R)-configuration by the x-ray crystallographic method by Akimoto and his coworkers (1971). Thus we find that the new compounds (+)I, (+)II, (+)III, and (+)IV have the (S) configuration; (+)V, (+)VI, (+)VII, (+)VIII, (+)IX, (+)X, (+)XI, (+)XII, (+)XIII, and (+)XIV also have the (S), while (+)XV and its methyl ester (+)XVI have the (R) configuration.

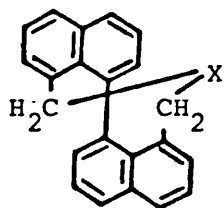
The proton nuclear magnetic resonance spectra of all the bridged compounds show the pairs of diastereotopic geminal methylene protons of the 9-ring to be spin-spin non-equivalent and to have large coupling constants. Shift reagents have assisted in the assignment of signals.

The corresponding geminal methylene protons of 8,8'-dihydroxymethyl-1,1'-binaphthyl, previously found to give a single signal, have been shown as diastereotopic in deuterio-dimethyl sulphoxide and studied at varying temperature.

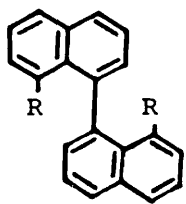
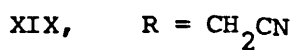
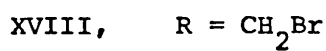
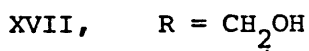
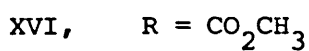
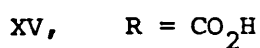
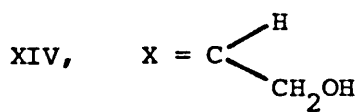
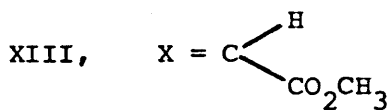
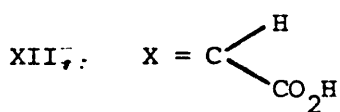
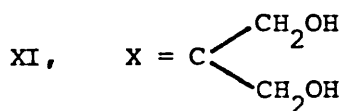
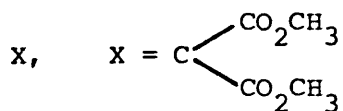
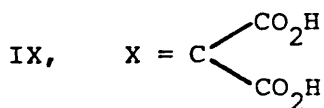
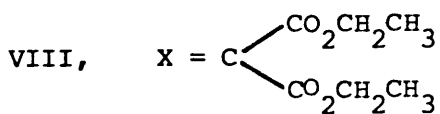
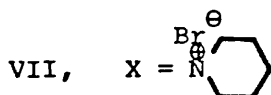
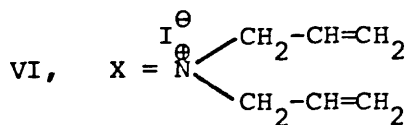
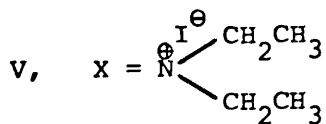
The ultraviolet spectra show the general characteristics of the spectrum of 1,1'-binaphthyl itself. In the series -O-, -SO<sub>2</sub>-, -S-, -Se-, there is a small progressive red shift in the maximum of the short wave band and of a shoulder on the long wave side of it. This band is followed by a minimum; minima show red shifts in the same order as the maxima, and

at the same time become progressively shallower troughs; the minimum for the -O- compound is similar to that of unbridged compounds.

Optical rotatory dispersion and circular dichroism spectra were obtained for the four new compounds (I), (II), (III), (IV), and for the unbridged compound (XIX). The range of wavelength was extended for the previously recorded o.r.d. and c.d. spectra of (V)-(XVIII). Particular attention is paid to the short wave couplet and to the longer wavelength features shown by each compound, and comparisons are drawn between the c.d. spectra of the different types of structure. All the compounds of (S) configuration, except for the 8,8'-bridged ones, have a negative c.d. band in the 285-315 region: in contrast, the (S)-8,8'-bridged compounds show c.d. of opposite sign in this region.



- I, X = O  
 II, X = S  
 III, X = Se  
 IV, X = SO<sub>2</sub>





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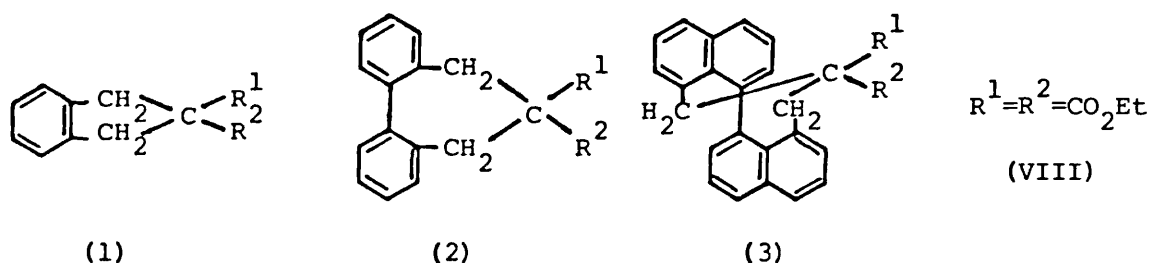
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## 1 HISTORICAL INTRODUCTION : THE PRESENT WORK IN ITS CONTEXT

## 1.1 The Synthesis of Related Bridged Biaryls

In 1913, Kenner first made a 3-carbon bridge across the 2,2'-positions in biphenyl to prepare a seven-membered ring (2); he used 2,2'-bisbromomethylbiphenyl and diethyl sodiomalonate, following Perkin's (Baeyer and Perkin jun., 1884; Perkin jun., 1888) method for preparing a five-membered ring (1) from *o*-xylylene dibromide. It appears that the presence of the two aromatic bonds in the precursor of the seven-membered ring makes it comparable with that of the five-



membered ring containing one aromatic bond; the ease of the cyclisation reaction is very similar in the two systems.

This discovery was followed by the preparation of a whole series of new bridged compounds involving biphenyl (and 2,2'-bridged 1,1'-binaphthyl) compounds with different atoms in the bridges (Hall, 1969): 2,2'-bridged biphenyls have been particularly interesting to the stereochemist because they exist, in many cases, in only two conformations, which are enantiomerically related, and sometimes the energy barrier separating these conformations is conveniently measurable.

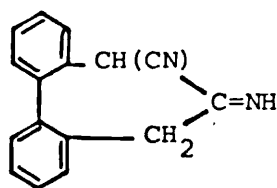
Information obtained from ultraviolet and proton nuclear magnetic resonance spectra, and the study of Cotton effects arising from the inherently dissymmetric chromophores, has provided information about the geometry of the bridged compounds since the spectroscopic properties depend on the twisting forced upon the aromatic systems by the bridge. The fact that the length of the bridge controls the angle between the

aromatic rings created an interest in preparing bridges of different sizes. Eight-membered rings proved very difficult to prepare and so too did nine-membered rings in the 2,2'-biphenyl series (Mislow, Hyden and Schaefer, 1962).

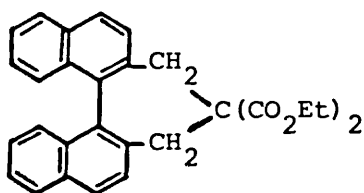
In 1976, Harris and Singh discovered that 8,8'-bisbromomethyl-1,1'-binaphthyl reacted readily with diethyl sodiomalonate forming a nine-membered ring (3) in conditions similar to those used for (1) and (2). It seemed that here again the geometry of the molecule is favourable to ring closure.

### 1.1.1. Seven-membered rings incorporating 2,2'- positions in biphenyl and 1,1'-binaphthyl.

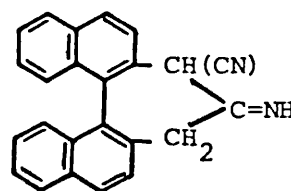
In 1913, Kenner prepared (4) from 2,2'-dicyanomethylbiphenyl by the Thorpe reaction. Mislow and coworkers (1958, 1962), following



(4)

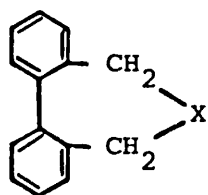


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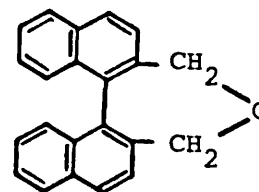


(6)

Kenner's methods as for (2) and (4) prepared (5) and (6). The oxepin (7) has been prepared from 2,2'-bishydroxymethylbiphenyl by reaction



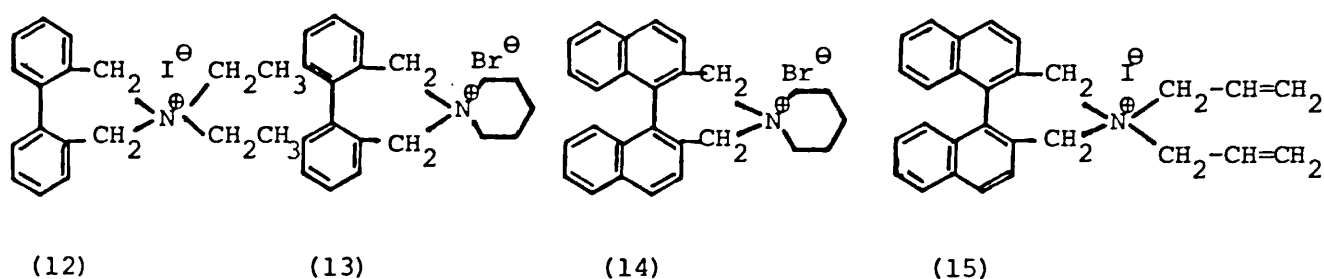
- (7) X = O  
 (8) X = S  
 (9) X = Se  
 (10) X = SO<sub>2</sub>



(11)

with dilute sulphuric acid (Hall and Turner, 1951) or with dilute hydrobromic acid (Wittig, Davis and Koenig, 1951) and from 2,2'-bisbromomethylbiphenyl by treating a solution in aqueous acetone with silver oxide (Mislow, Glass, Hopps, Simon, Wahl jun., 1964). Mislow and co-workers (1962, 1964) also made oxepins (7) and (11) from the

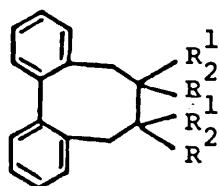
respective 2,2'-bishydroxymethyl compounds by boiling with toluene-p-sulphonic acid in benzene. Truce and Emrick (1956) reported that (8), (9) and (10) could be obtained in nearly quantitative yield, while Wenner (1951) described the preparation of 6,7-dihydro-5H-dibenz(c,e)-azepin derivatives, from 2,2'-bisbromomethylbiphenyl. Turner and his co-workers (Hall and Turner, 1955) prepared several heterocyclic bridged biphenyls (12), (13) and binaphthyls (14), (15) from the respective dibromides.



Many of these seven-rings were prepared in their optically active forms.

### 1.1.2. Eight-membered rings incorporating 2,2'-positions in biphenyl and 1,1'-binaphthyl.

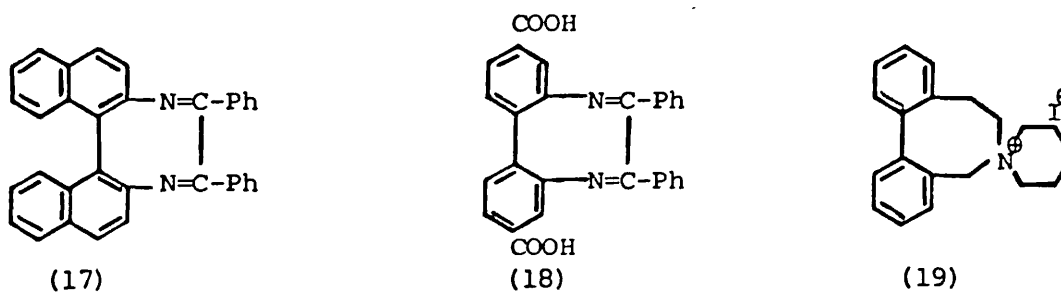
Cope and Smith (1956) made the first carbocyclic ring of this type, 1,2,3,4-dibenzcycloöcta-1,3-diene (16a). Mislow and co-workers (Dvorken, Smyth and Mislow, 1958) prepared and studied the stereochemistry of (16a), (16b), (16c), (16d), (16e), (16f). The diastereomeric forms of the dicarboxylic acid (16e) were resolved and identified as trans and cis by the fact that the optically active forms of the former mutarotate while those of the latter racemise. Kuhn and Goldfinger



- (16a)  $R^1=R^2=H$   
 (16b)  $R^1=R^2=CO_2C_2H_5$   
 (16c)  $R^1=R^2=CO_2H$   
 (16d)  $R^1=R^2=CO_2CH_2C_6H_5$   
 (16e)  $R^1=H; R^2=CO_2H$   
 (16f)  $R^1=H; R^2=CO_2CH_3$

(1929) had prepared the enantiomeric forms of (17) by the interaction of

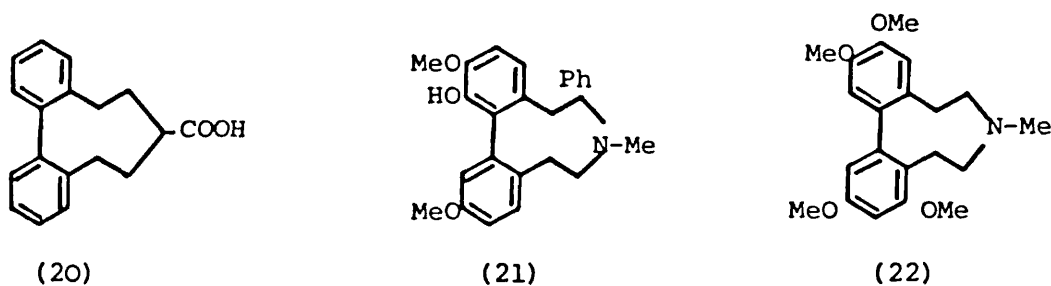
(+) and (-) 2,2'-diamino-1,1'-binaphthyl with benzil, and Bell (1952) prepared the analogue (18) and resolved it by crystallisation of the



brucine salt to give optically stable enantiomers. Ahmed and Hall (1959) made the eight-membered heterocyclic ring 1,2,7,8-tetrahydro-3,4,5,6-dibenzazocine-1-spiro-1'-piperidinium iodide (19).

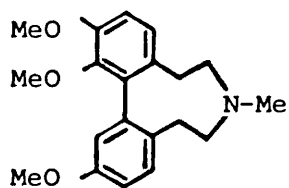
### 1.1.3. Nine-membered rings incorporating 2,2'-positions of biphenyl.

The carbocyclic rings proved difficult: Mislow, Hyden and Schaefer (1962) synthesised a ten-membered ring diketone incorporating a 2,2'-biphenyl system by an acyloin reaction, then the ring was reduced in size by one carbon atom, through its toluenesulphonhydrazone, to the acid (20). They prepared (20) in optically active form by second order

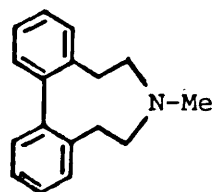


asymmetric transformation and compared its physical and spectroscopic properties with those of seven and eight-membered rings. Bentley and Robinson (1952) reported the nine-membered heterocyclic ring phenyldihydrothebaine (21), derived from natural sources. Pecherer and Brosi (1967) prepared (22). Hall and Manser (1967) and Hall and Hwang (1972) prepared (23) and (24) respectively in optically active form. Compounds with arsenic and phosphorous in the ring are also





(23)



(24)

known (Forbes, Mann, Miller and Moelwyn-Hughes, 1963; Allen, Miller and Mann, 1967).

#### 1.1.4. Nine-membered rings incorporating 8,8'-positions of 1,1'-binaphthyl.

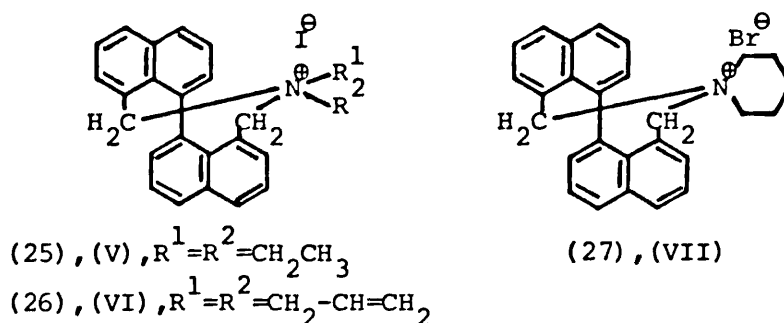
##### 1.1.4.1. Carbocyclic rings:

Harris and Shyam Singh (1976) following the synthetic method used for (1) and (2) prepared diethyl 8,9-dihydro-7H-cyclonona-(1,2,3-de: 4,5,6-d'e')-dinaphthalene-8,8-dicarboxylate ((3), (VIII)). They noted that elimination to olefin is not an alternative as it is in attempting to make the biphenyl nine-ring analogue; the ring was formed, even in the presence of an excess of diethylmalonate, so the internal nucleophilic attack by the substituted diethylmalonate anion on the second  $-\text{CH}_2\text{Br}$  group must be highly favoured by the stereochemistry of the molecule. They also prepared (3a)  $\text{R}^1=\text{R}^2=\text{CO}_2\text{H}$  (IX), (3b)  $\text{R}^1=\text{CO}_2\text{H}$ ,  $\text{R}^2=\text{H}$  (XII), (3c)  $\text{R}^1=\text{R}^2=\text{CO}_2\text{Me}$  (X), (3d)  $\text{R}^1=\text{CO}_2\text{Me}$ ,  $\text{R}^2=\text{H}$  (XIII), (3e)  $\text{R}^1=\text{R}^2=\text{CH}_2\text{OH}$  (XI) and (3f)  $\text{R}^1=\text{CH}_2\text{OH}$ ,  $\text{R}^2=\text{H}$  (XIV); at least one optically active isomer of each of these compounds was obtained and chiroptical properties studied. In the present work we have now made both enantiomers of these compounds and completed the assignment of their absolute configurations by relating them to their synthetic precursors.

##### 1.1.4.2. Nitrogen heterocycles:

Harris and Shyam Singh (1972) prepared the ring compounds ((25), (V)), ((26), (VI)) and ((27), (VII)) from 8,8'-bisbromomethyl-

1,1'-binaphthyl and carried out preliminary investigations on them.



Both enantiomers of these compounds are now described and the assignment of absolute configurations completed. Preliminary experiments on the preparation of the bromide corresponding to ((26), (VI)) had been carried out earlier by Badar, Cooke and Harris (1963-1964, unpublished).

#### 1.1.4.3. Oxygen, Sulphur and Selenium heterocycles:

In the present work four new nine-membered ring heterocyclic bridged compounds, with a hetero atom in the 8-position have been prepared where the hetero function is -O- (I), -S- (II), -Se- (III) and -SO<sub>2</sub>- (IV). The optically active isomers were synthesised from resolved

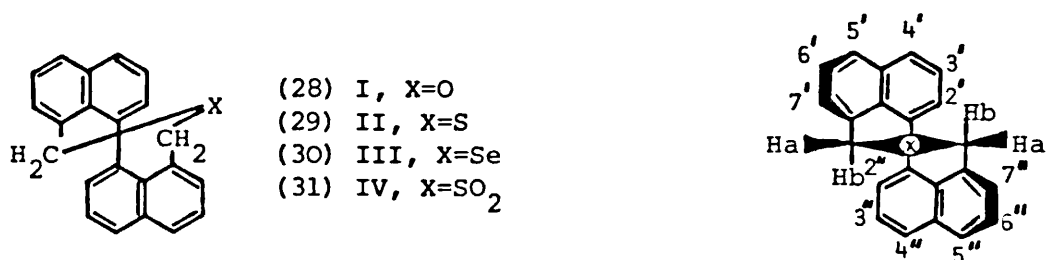


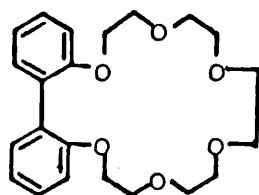
Fig.1 (R)-Configuration

1,1'-binaphthyl-8,8'-dicarboxylic acid, and their absolute configurations assigned by relating them to this precursor. The model indicates that like the carbocyclic bridged compounds the heterocyclic rings are conformationally stable. Configurational inversion is of course not possible without breaking bonds. No indication of racemisation has been found in any of the ring compounds during this work.

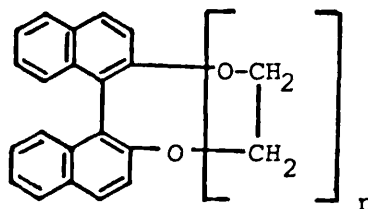
#### 1.1.4.4. Other bridged biaryls

Cram and his co-workers (Kyba, 1977) have prepared larger rings

such as (32) formed by treating 2,2'-dihydroxy-1,1'-biphenyl with pentaethylene glycol ditosylate and sodium hydroxide in dioxane-butanol.



(32)

(33)  $n = 1, 2, 3, 4, 5$ 

They also prepared ring compounds (33) by treating 2,2'-dihydroxy-1,1'-binaphthyl with the various polyethylene glycol ditosylates. Many such compounds are useful crown ethers.

## 1.2. Proton Nuclear Magnetic Resonance Spectra in Related Series:

Mislow and his co-workers (1964) observed that in the bridged biphenyls the two geminal methylene protons on any one of the benzylic carbon atoms are diastereotopic (Mislow and Raban, 1961), i.e. stereochemically non-equivalent. In most of the doubly bridged and dimethyl singly bridged biphenyls investigated they are also magnetically non-equivalent, and the nuclear magnetic resonance spectra show the expected methylene AB pattern. The difference in chemical shifts of the two geminal protons is a general consequence of the difference in shielding by two diastereomeric environments. In some bridged biphenyls they did not find the expected multiplicity, only a single signal was observed; in any one case this could be due to "accidental isochrony" (Abragam 1961), because of very small differences in chemical shifts of the two protons or spin coupling constant effects: rapid conformational interchange of diastereomeric environments was also considered possible. Harris and Singh (1976) reported that the methylene protons ( $\text{CH}_2$ -naphthyl) in nine-membered rings incorporating 8,8'-positions of 1,1'-binaphthyls are diastereotopic: the n.m.r. spectra show an identical pair of well separated methylene protons with large coupling constants, as would be

expected for diastereotopic protons in very different environments.

The proton nuclear magnetic resonance spectrum of the new compound (I) is very simple in the non-aromatic region and shows the pair of doublets ( $\frac{\Delta Hz}{J} = 9-11$ ) at a lower field than normal for methylene protons. These can only be the diastereotopic (Mislow and Raban 1961), spin coupling non-equivalent protons Ha and Hb (Fig. 2). Study of a model and the use of the rules for shielding and deshielding

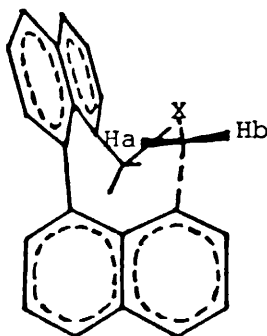


Fig.2

(see p. 84 ) makes it possible to assign signals to Ha and Hb.

The aromatic protons fall into three distinct groups in the numerical ratio 2:3:1; examination of the evidence (see later) assigns these as 4,4',5,5' (4H); 3,3',6,6',7,7' (6H) and 2,2' (2H) respectively.

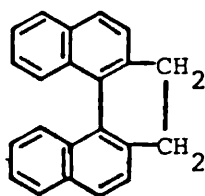
### 1.3. Ultra Violet Absorption Spectra of Related Compounds

The u.v. absorption spectrum of biphenyl shows two bands: a small short wavelength band at 205nm, and a broad high intensity band at approximately 250nm in ethanol called the conjugation band.

The position and intensity of the conjugation band depends on the amount of conjugation between the two benzene rings which again depends upon the dihedral angle between them ( $40^\circ$  in biphenyl itself (Karle and Brockway, 1944; Bastiansen, 1949;  $20^\circ$ , Suzuki, 1967)). When the biphenyl is substituted in the ortho positions, conjugation between the two benzene rings decreases. Few groups are small enough to permit observable conjugation between the benzene rings but 2,2'-dihydroxybiphenyl (Williamson and Rodebush, 1941) and 2,2'-difluorobiphenyl (Beaven and Hall, 1956) show it; in heavily ortho-substituted biphenyls such as bimesityl (Pickett, Walter and France, 1936) and in all molecules with

large ortho-substituents it is absent. When the 2,2'-positions in biphenyl are joined by saturated bridges of two or more carbon atoms, the conjugation band shows progressive shifts to shorter wavelengths as the size of the bridge increases: in a nine-membered ring (five carbon atoms joined to biphenyl) the conjugation band is present only as an inflection at low wavelength. The gradual increase in the dihedral angle reduces gradually the amount of conjugation between the two rings. When the dihedral angle is sufficiently large, the conjugation is greatly reduced and the resulting electronic absorption appears as the sum of the two component parts of the molecule.

9,10-Dihydro-3,4:5,6-dibenzophenanthrene (34) is a similar kind of substance to a substituted bridged biphenyl. Hall and Turner (1955) recorded its u.v. absorption spectrum. It shows a distinct



(34)

conjugation band at 239.5nm; the dihedral angle between the naphthalene rings is ca.  $20^{\circ}$ . Such a band is also found in the spectrum of the relatively unhindered 2,2'-binaphthyl, but not in 1,1'-binaphthyl (Jaffè and Orchin, 1948). Harris, Harris, Mazengo and Shyam Singh (1974) studied the u.v. spectra of several 8,8'-disubstituted 1,1'-binaphthyls; they found that the conjugation band is missing, as in 1,1'-binaphthyl itself, except apparently in 1,1'-binaphthyl-8,8'-dicarboxylic acid (XV) and its methyl ester (XVI). Absence of an observable conjugation band is expected if the dihedral angle between the main planes of the two naphthalene nuclei is  $>60^{\circ}$  (Hall, 1969) and the models indicate that the bulky substituents in many of the compounds keep the planes at even higher mutual angles (Harris, Harris, Mazengo

and Singh, 1974). Le Fèvre and his co-workers (Le Fèvre, Sundaram and Sundaram, 1963) have calculated the dihedral angle in 1,1'-binaphthyl itself, in solution, from molecular Kerr constants, as  $48^{\circ}$ . At this angle a weak conjugation band would be expected: if it exists it must be masked by the strong short wave band at 220 nm (Harris, Harris, Mazengo and Singh, 1974).

#### 1.4. Absolute Configuration

Fitts, Siegel and Mislow (1958), from calculations using the polarizability theory of optical activity, assigned the (S)-configuration to (+)9,10-dihydro-3,4,5,6-dibenzophenanthrene (34) (Hall and Turner, 1955). Assuming this is true, then chemically linked (-)1,1'-binaphthyl-2,2'-dicarboxylic acid also has the (S)-configuration. This assignment has been confirmed by determination of configuration of (-)-<sup>2,2'</sup>bisbromomethyl-1,1'-binaphthyl (Harata and Tanaka, 1973) as (S)-configuration by utilising the anomalous dispersion effect of bromine atoms on the x-ray diffraction pattern.

The large positive increase in optical rotation in forming the bridged compound (34) from the non-bridged compound confirms (S)-configuration in agreement with Fitts, Siegel and Mislow's (1958) use of Freudenberg's optical displacement rule.

Mislow and McGinn (1958) also determined the absolute configuration of (-)1,1'-binaphthyl-2,2'-dicarboxylic acid as (S) on the basis of incomplete asymmetric Meerwein - Ponndorf - Verley reduction of the racemic bridged binaphthyl ketone (45) with (+) (S)-2-octanol. Using the model of known absolute configuration of (+)2-octanol, they deduced that the reduced alcohol (46) has (R)- configuration. The (+)1,1'-binaphthyl-2,2'-dicarboxylic acid must have the same configuration and so (R) was assigned to it.

Following Mislow's generalization for 1,1'-binaphthyls regarding the Cotton effects at longer wavelengths, Badger and his co-workers (1962)

determined the o.r.d. and Grinter and Mason (1964) the c.d. spectra of (-)dimethyl 1,1'-binaphthyl-2,2'-dicarboxylate and assigned the (R)-configuration on the basis of the positive Cotton effect at  $\sim 300\text{nm}$ .

When Akimoto et al. (1968/71) established the (R)-configuration of (+) dimethyl 2,2'-dihydroxy-1,1'-binaphthyl-3,3'-dicarboxylate by the anomalous x-ray diffraction method, the (S)-configuration was established for the synthetically linked (+)1,1'-binaphthyl itself and (-)1,1'-binaphthyl-2,2'-dicarboxylic acid: so this result is in agreement with Mislow's assignment for (-) (S)-1,1'-binaphthyl-2,2'-dicarboxylic acid.

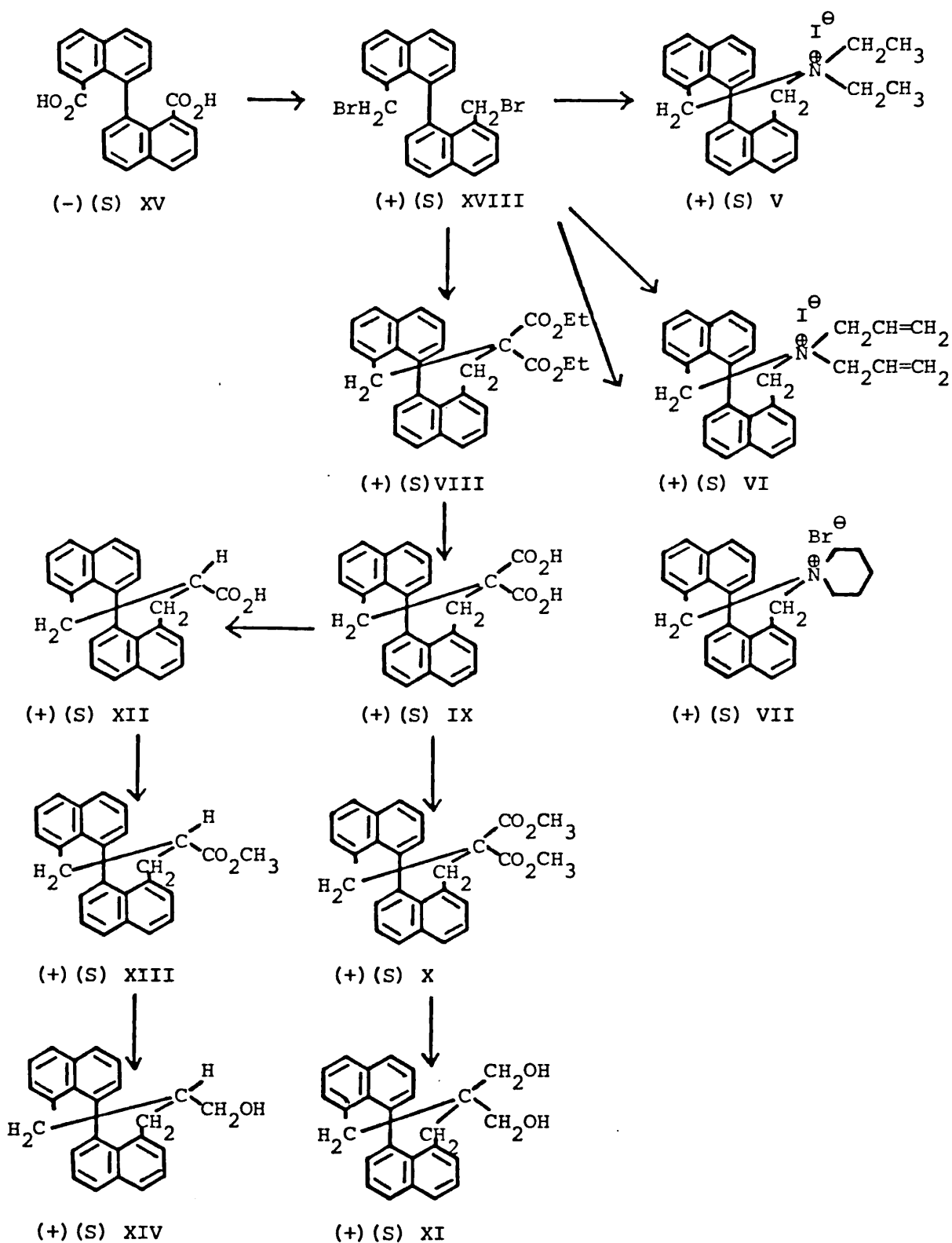
Harris, Harris, Mazengo and Shyam Singh (1974) reported that the o.r.d. and c.d. spectra of (+)2,2'-dimethyl-1,1'-binaphthyl (Mislow et al. 1962, 1963), (+)1,1'-binaphthyl (Brown, Harris, Mazengo and Singh, 1971), and (+) 8,8'-dimethyl-1,1'-binaphthyl are similar; they all show a negative Cotton effect centered near 285 nm and as (+)2,2'-dimethyl-1,1'-binaphthyl and (+) 1,1'-binaphthyl are known to have (S)-configuration, by analogy (+)8,8'-dimethyl-1,1'-binaphthyl also has (S)-configuration. They also reported the o.r.d. and c.d. spectra of (-)1,1'-binaphthyl-8,8'-dicarboxylic acid (XV), (-)dimethyl 1,1'-binaphthyl-8,8'-dicarboxylate (XVI), (+)8,8'-bishydroxymethyl-1,1'-binaphthyl (XVII), and (+)8,8'-bisbromomethyl-1,1'-binaphthyl (XVIII). They are synthetically linked as follows, and all have the same (S)-configuration.

(-) XV  $\rightarrow$  (-) XVI  $\rightarrow$  (+) XVII  $\rightarrow$  (+) XVIII  $\rightarrow$  (+) 8,8'-dimethyl-1,1'-binaphthyl.

These results also agree with Mason, Seal and Roberts' (1974) assignments by calculation of configuration as a function of the dihedral angle between the molecular planes of the aromatic moieties, in the  $\Pi$ -SCF (Self Consistent Field) approximation and in the exciton approximation, of 1,1'-binaphthyl-2,2'-dicarboxylic acid and 1,1'-binaphthyl-8,8'-dicarboxylic acid (XV).

Harris and Shyam Singh (1972, 1976) prepared optically active nine-

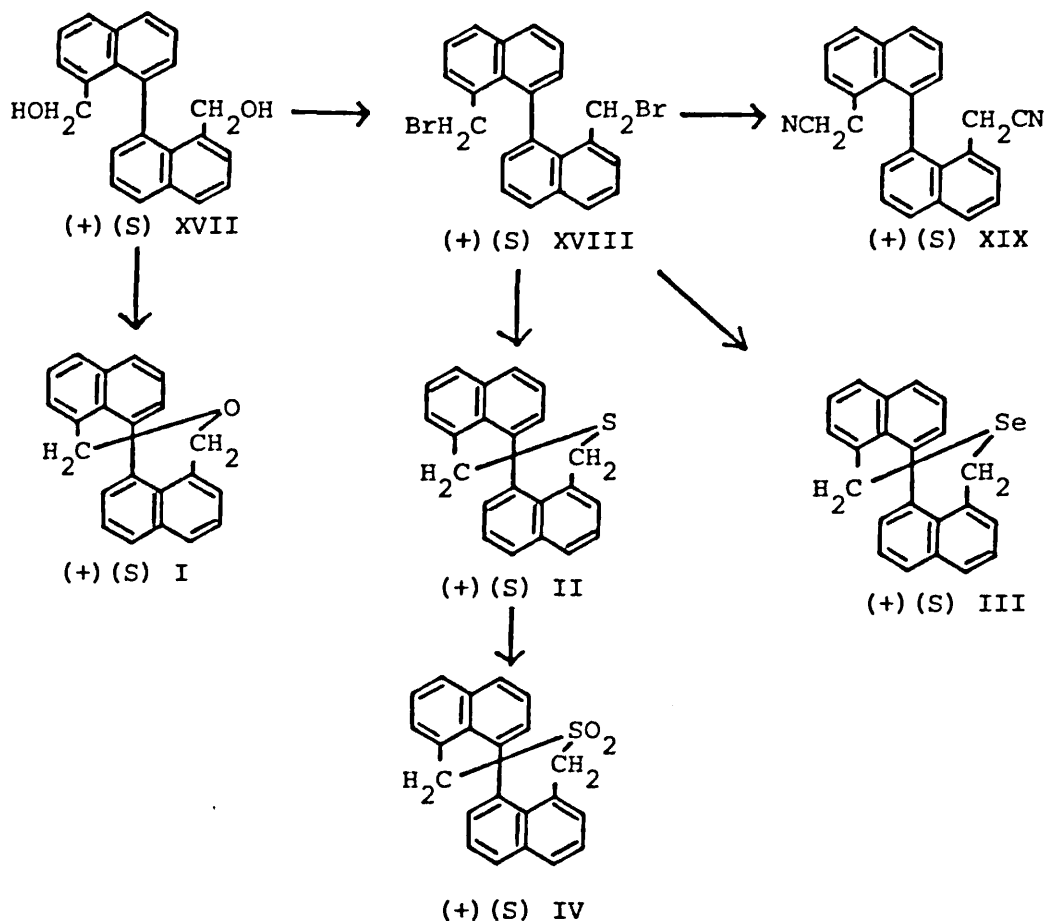
membered ring 8,8'-bridged 1,1'-binaphthyls from (S) (-)1,1'-binaphthyl-8,8'-dicarboxylic acid as follows. They are all (+) rotatory; they must have the (S)-configuration.



Therefore at the start of this work it was known that (-)XV, (-)XVI, (+)XVII, (+)XVIII, (+)V, (+)VI, (+)VII, (+)VIII, (+)IX, (+)X, (+)XI, (+)XII, (+)XIII, (+)XIV were all of the same (S) chirality.



The new compounds I,II,III, and IV and XIX (Browne, Harris, Mazengo, Singh, 1971) have been added to this list and chirality linked to the sign of rotation.



The o.r.d. and c.d. spectra of I, II, III, IV, V, VI, VII, VIII, IX, X, XI, XII, XIII, XIV, XV, XVI, XVIII, XIX have now been determined and (S)-(+)-I-XIV, XVIII, XIX and (-)XV, XVI show the same feature in the short wave region. They have an oppositely signed pair of c.d. bands below 280nm, the negative one at shorter wavelength. The sulphur and selenium compounds show signs of further negative bands at still lower wavelength. The dihedral angle in <sup>the</sup> selenium compound probably approaches the critical angle where Mason's work suggests that the sign of the couplet in the short wave region might reverse. All the bridged compounds (S)-I-XIV show long wave positive c.d. bands at about 300nm while unbridged compounds (S)-XV-XIX show negative c.d. bands at about 300nm.

## 2. SYNTHESIS

### 2.1. Intramolecular Cyclisation : Some General Methods.

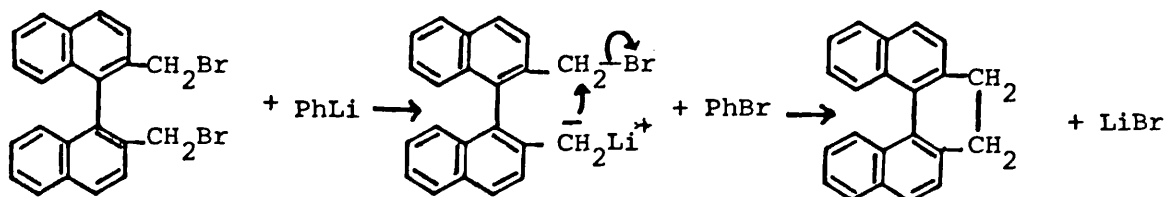
For ring-closure, two reactive ends of a system must be brought together and securely joined. The process depends on entropy and on enthalpy. The entropy factor reflects how often the reacting centres at the ends of a chain come close enough to reacting distance in the proper orientation. The probability of meeting of two ends of a chain of more than six aliphatic carbon atoms decreases with increase in chain length and thus the cyclisation rate decreases; competing intermolecular reactions may then be favoured, so that the yield of the ring is very small. By keeping the concentration very low, the probability of intermolecular collisions can be decreased and the probability of intramolecular collisions can be proportionately increased. Another scheme is to restrict the movement of the reacting end groups by absorption on a surface on which the cyclisation process takes place.

For aliphatic rings the probability of intramolecular cyclisation depends very definitely on the size of the ring to be prepared: many methods are known, but a few of them are frequently and widely used.

#### 2.1.1. Wurtz reaction and Phenyl-lithium reaction

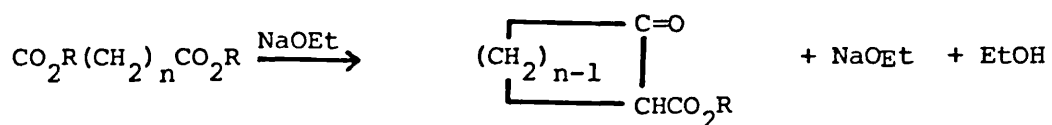
The Wurtz reaction i.e. the reaction of alkyl halides with sodium has limited importance. The mechanism involves first the formation of an organo-sodium compound, which then reacts with a second alkyl halide group: sodium metal is extremely reactive and promotes side reaction, so the yields are usually poor.

Phenyl-lithium as a reagent to replace halogen by alkali metal is less reactive than sodium, so the desired reaction can be carried out in better yield. Hall and Turner (1955) synthesised optically active 9,10-dihydro-3:4,5:6-benzophenanthrene from optically active 8,8'-bisbromomethyl-1,1'-binaphthyl using this process.

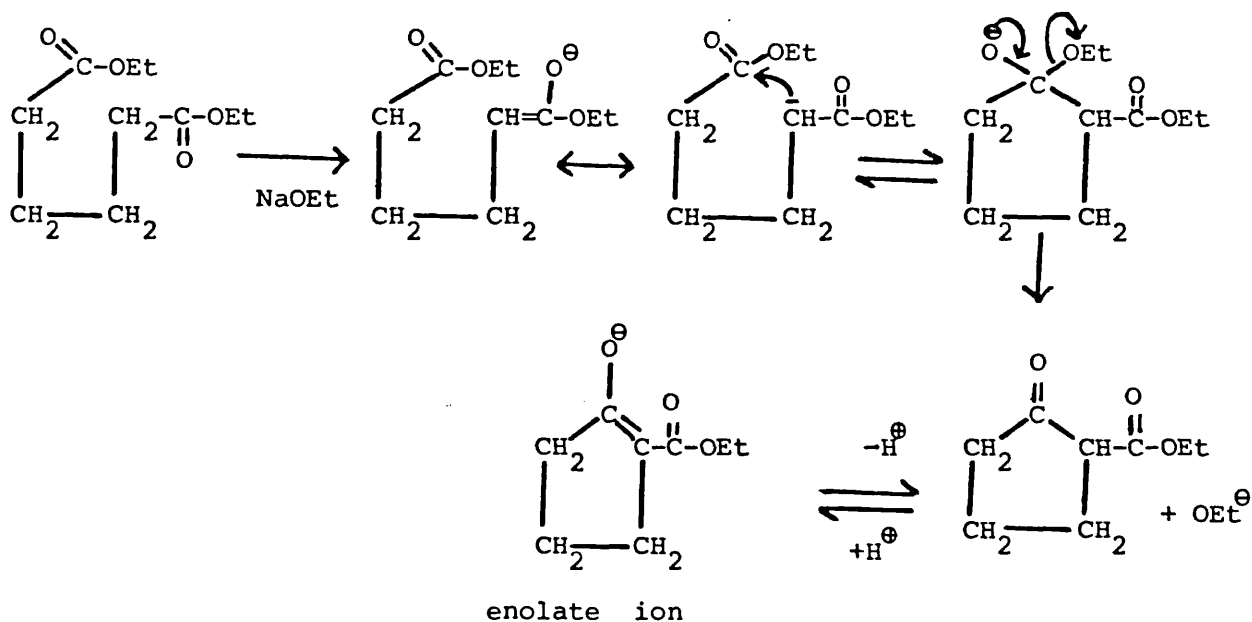


### 2.2.2. Dieckman cyclisation

Dieckman (1901) discovered the cyclisation of esters of dicarboxylic acids to form  $\beta$ -ketoesters.



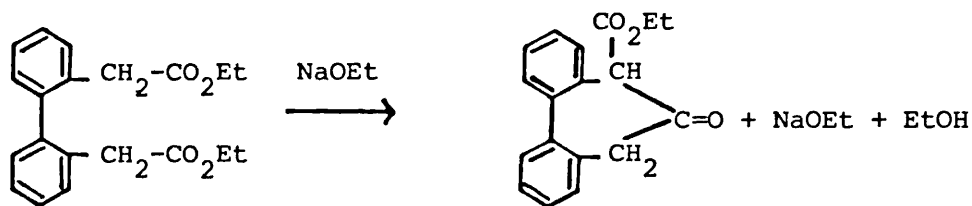
He found that heating adipic esters with sodium and a trace of alcohol led to cyclisation with formation of cyclopentanone carboxylic ester. The mechanism involves first the reversible formation of the enolate ion of the ester and then attack on the other ester function by the enolate ion. Rapid decomposition of the adduct through loss of alkoxide ion followed by formation of the enolate of the  $\beta$ -keto ester completes the reaction.



The reaction depends for its success upon stabilization of the

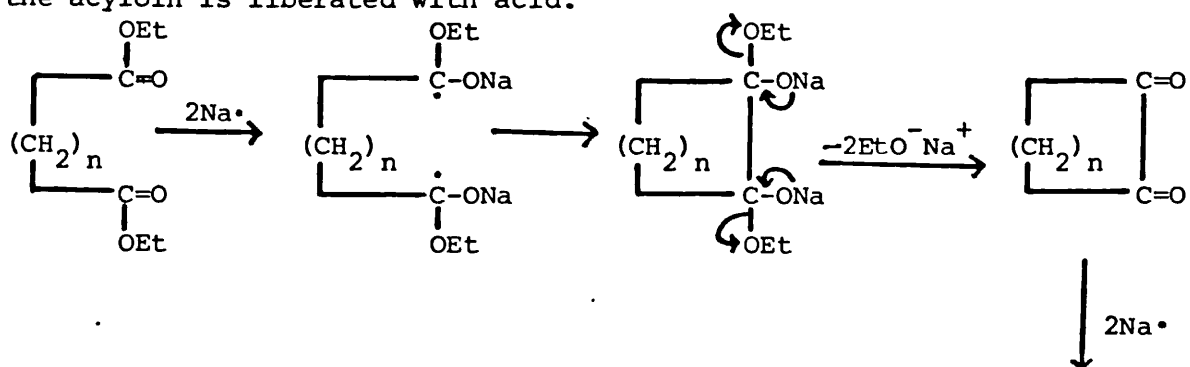
immediate cyclisation product as the enolate anion. Generally five and six-membered alicyclic rings are formed by the Dieckman reaction. A few medium ring compounds (9-14 membered) have been prepared in very low yield.

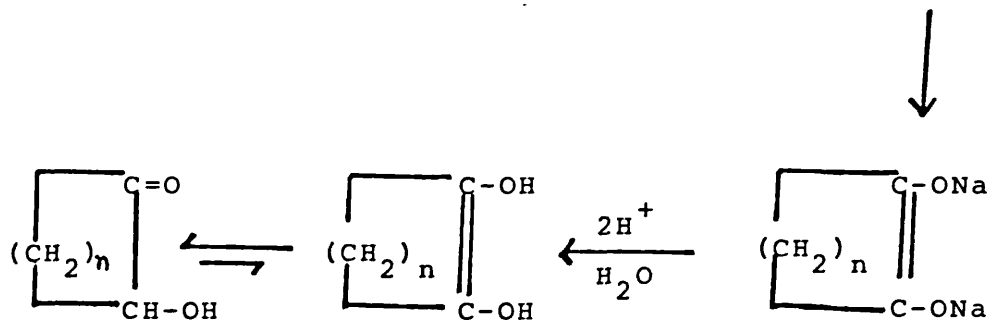
Kenner (1913) prepared a seven-membered ring in 80% yield by heating diethyl 1,1'-biphenyl-2,2'-diacetate with sodium ethoxide.



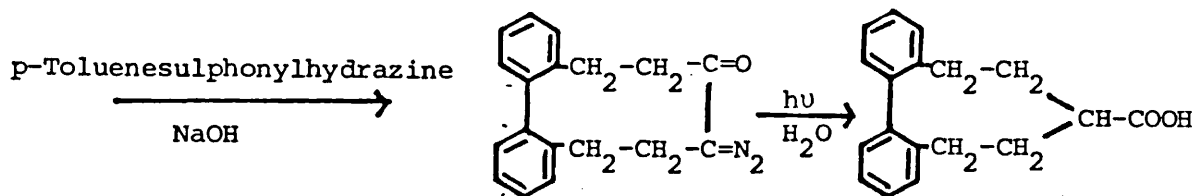
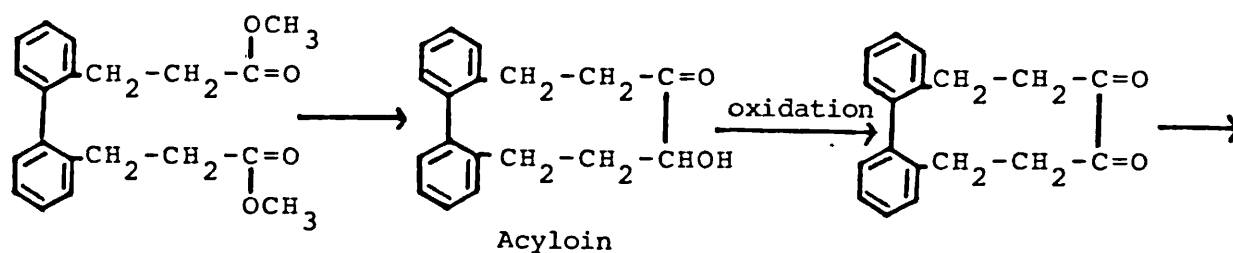
### 2.1.3. Acyloin condensation

Acyloin condensation bears a superficial resemblance to the above reaction. It is the most successful general method for synthesising medium and larger rings. Yields of 60-70% (9-13 membered rings); 70-85% (13-18 membered rings) and ~95% (18-20 or larger rings) can be obtained. Dieckman and Thorpe cyclisation has reversible stages while the acyloin reaction is not reversible. The reactant is again a dicarboxylic ester but the reagent is sodium dispersed in a hydrocarbon solvent (under nitrogen). This small difference in the reagent changes the course of the reaction completely. Sodium is unable to function as a base in hydrocarbon solvents and instead it reacts as a one-electron reducing reagent to produce a radical anion at each carbonyl group, and the resulting radicals dimerize. Then the alkoxide groups are eliminated and further electron-transfer gives the disodium derivative from which the acyloin is liberated with acid.





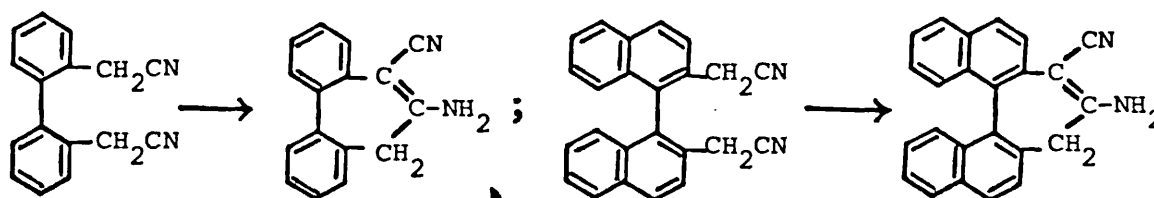
Blomquist, Wheeler and Chu (1955) prepared the nine-membered ring 5,5-dimethylcyclononane and other ring compounds by acyloin condensation. Mislow and co-workers (1962) used the acyloin reaction to prepare a ten-membered ring diketone incorporating 2,2'-biphenyl and then converted it into a nine-membered ring.



#### 2.1.4. Thorpe-Ziegler cyclisation

The intramolecular cyclisation of dinitrile to enamionitrile has

been especially valuable in the synthesis of medium and large-ring compounds. In 1908, Moore and Thorpe reported the base catalysed conversion of *o*-xylylene biscyanide to the five-membered ring 1-cyano-2-iminoindane. Thorpe also observed the intramolecular cyclisation of adiponitrile in the presence of sodium ethoxide to give 1-imino-2-cyanocyclopentane. Ziegler, in 1933, found that the most effective catalyst system was an alkali metal salt of an arylalkylamine e.g. *N*-methylaniline; since then this condensation reaction is generally called Thorpe-Ziegler cyclisation. In the alicyclic series this method was found to be successful for preparing medium (95% for 7-ring; 88% for 8-ring) and large ring compounds (60-80% for >14 ring), except nine- and eleven-membered rings. However in 1934, Ziegler and Aurnhammer synthesised cyclononane, but in very low yield (2.8%). The odd numbered rings are generally formed in lower yields than the even-numbered rings. The cyclisation product is a stable enamionitrile. Sometimes the cyclization appears to be irreversible even in the absence of base sufficiently strong to convert the enamionitrile to its anion. Kenner and Turner (1911) prepared the seven-membered ring ((4)-p2) in good yield by heating 2,2'-biscyanomethylbiphenyl with sodium ethoxide. The mechanism is given on page 25.

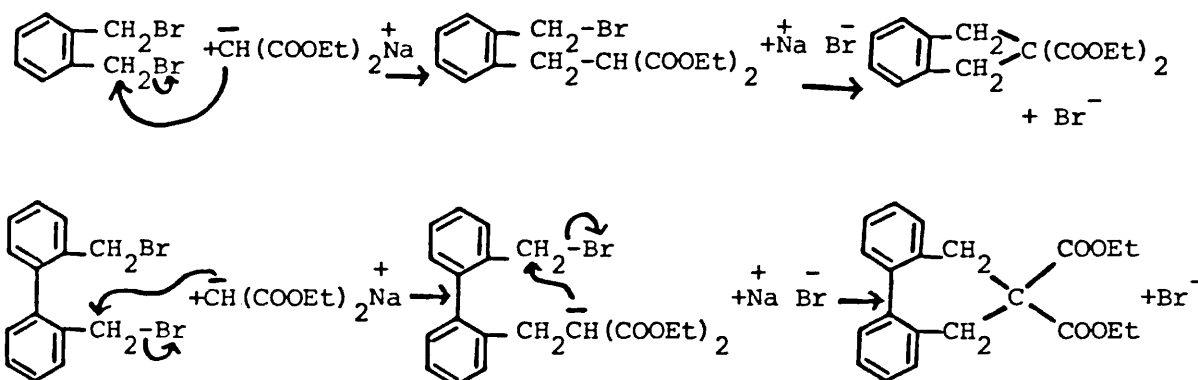


Mislow and co-workers (1958) synthesised seven-membered rings incorporating the 2,2' positions of various substituted biphenyls, including 1,1'-binaphthyl.

### 2.1.5. Malonic ester synthesis:

The classical malonic ester synthesis can be used intramolecularly to make rings for example for the synthesis of three and four membered alicyclic compounds from dibromides: the mechanism involves nucleophilic attack on one alkyl halide group by the carbanion,  $\bar{\text{C}}(\text{COOC}_2\text{H}_5)_2$  and then on the other by  $-\bar{\text{C}}(\text{COOC}_2\text{H}_5)_2$ .

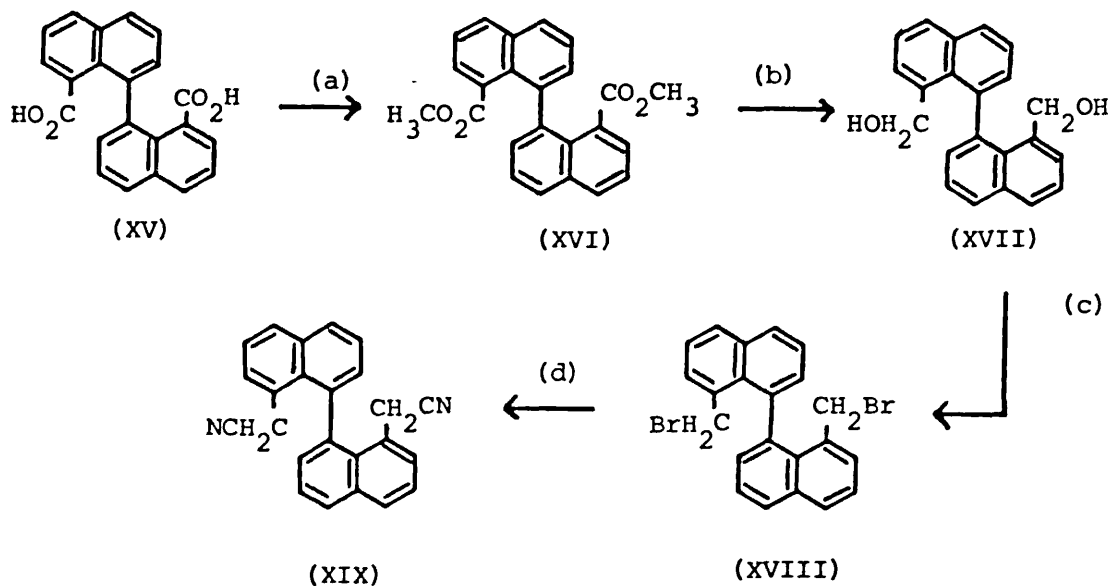
Bayer and Perkin (1884) made the five-membered ring from o-xylylene dibromide and Kenner (1913) prepared a seven-membered ring by heating 2,2'-bisbromomethylbiphenyl with ethylmalonate in presence of sodium ethoxide.



## 2.2. Synthetic Methods Used in the Present Work

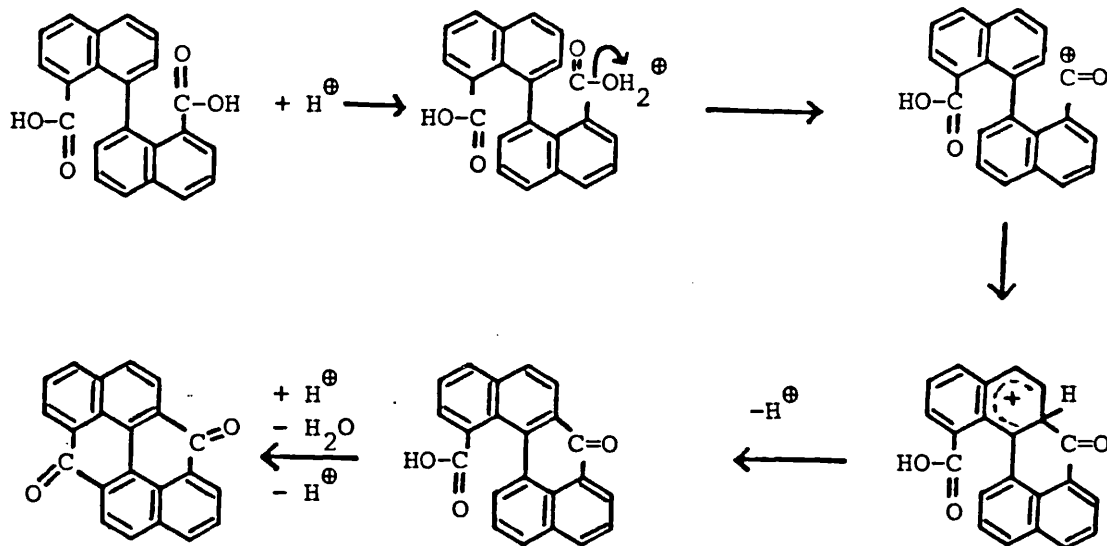
### 2.2.1. Unbridged 8,8'-disubstituted 1,1'-binaphthyls.

These were made from 1,1'-binaphthyl-8,8'-dicarboxylic acid or its ester. The most significant difference made from previous workers was in the esterification of (xv).

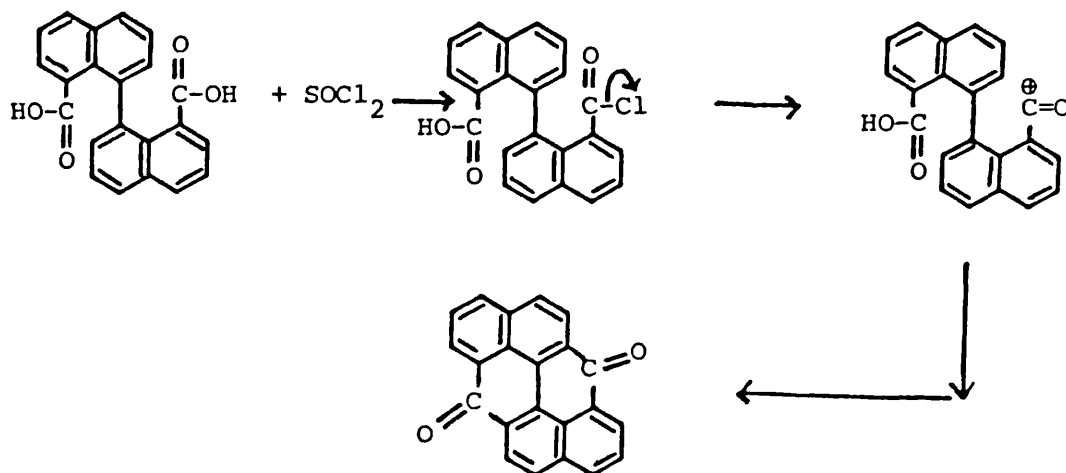


Stage (a): The direct esterification of sterically hindered carboxylic acids is often difficult: the reaction rate may be very slow, or the equilibrium between the acid and the ester may be unfavourable and there may be competing reactions in the acidic conditions.

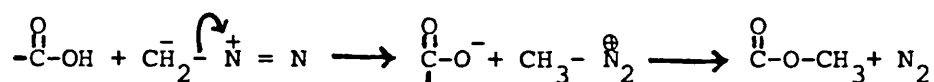
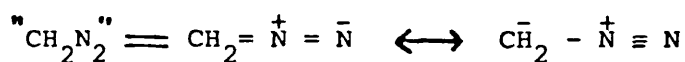
The attempted esterification of 1,1'-binaphthalenyl-8,8'-dicarboxylic acid (XV) using thionyl chloride or in acidic conditions is a total failure as the formation of intermediate carbonium ions results in the formation of anthanthrone (Kalb, 1914).



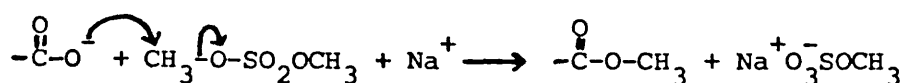
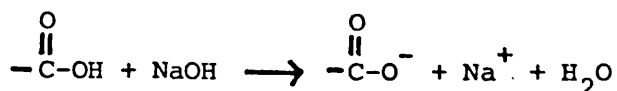




Meisenheimer and Beisswenger (1932) prepared the diethyl ester through the silver salt and Cooke and Harris (1963) prepared the dimethyl ester (XVI) by the use of diazomethane. Both the methods are tedious and diazomethane presents an explosive hazard in addition to its high toxicity, therefore it is used only in small quantities.

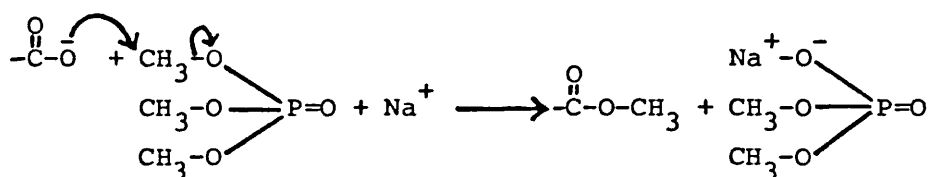


Dimethyl sulphate has long been known to be an effective reagent for the preparation of sterically hindered aromatic carboxylic esters (Grundy, James and Patterson, 1972) but it is very toxic. Esterification of 1,1'-binaphthyl-8,8'-dicarboxylic acid (XV) by dimethyl sulphate in alkaline solution was successful and gave the diester (XVI) in good yield.



Now, we have successfully carried out esterification of (XV) with trimethyl phosphate, which is similar in operation and less unpleasant to handle. It has perhaps been neglected as a reagent for sterically

hindered acids. The normal mode of reaction of trimethyl phosphate in alkaline solution is by fission of a phosphorous-oxygen bond (Ingold, 1969), but in neutral solution carbon-oxygen fission takes place, and  $\text{CO}\bar{\text{O}}$  makes a nucleophilic attack on the carbon of a methyl group rather than on phosphorous. The diacid in a small excess of sodium hydroxide was heated with trimethylphosphate in excess (to compensate for the competing reaction with the alkali): the sodium dimethyl phosphate formed does not react further in these conditions.



Stage (b): The dimethyl 1,1'-binaphthyl-8,8'-dicarboxylate (XVI) was reduced with excess of lithium aluminium hydride in sodium-dried ether to prepare 8,8'-bishydroxymethyl-1,1'-binaphthyl (XVII) (Badar, Cooke and Harris, 1965).

Stage (c): 8,8'-Bisbromomethyl-1,1'-binaphthyl (XVIII) was prepared from the diol (XVII) by heating it with 45% W/V hydrobromic acid (Badar, Cooke and Harris, 1965) in glacial acetic acid or by reaction with phosphorous tribromide (Singh, 1972) which gave a better yield but was less convenient to do.

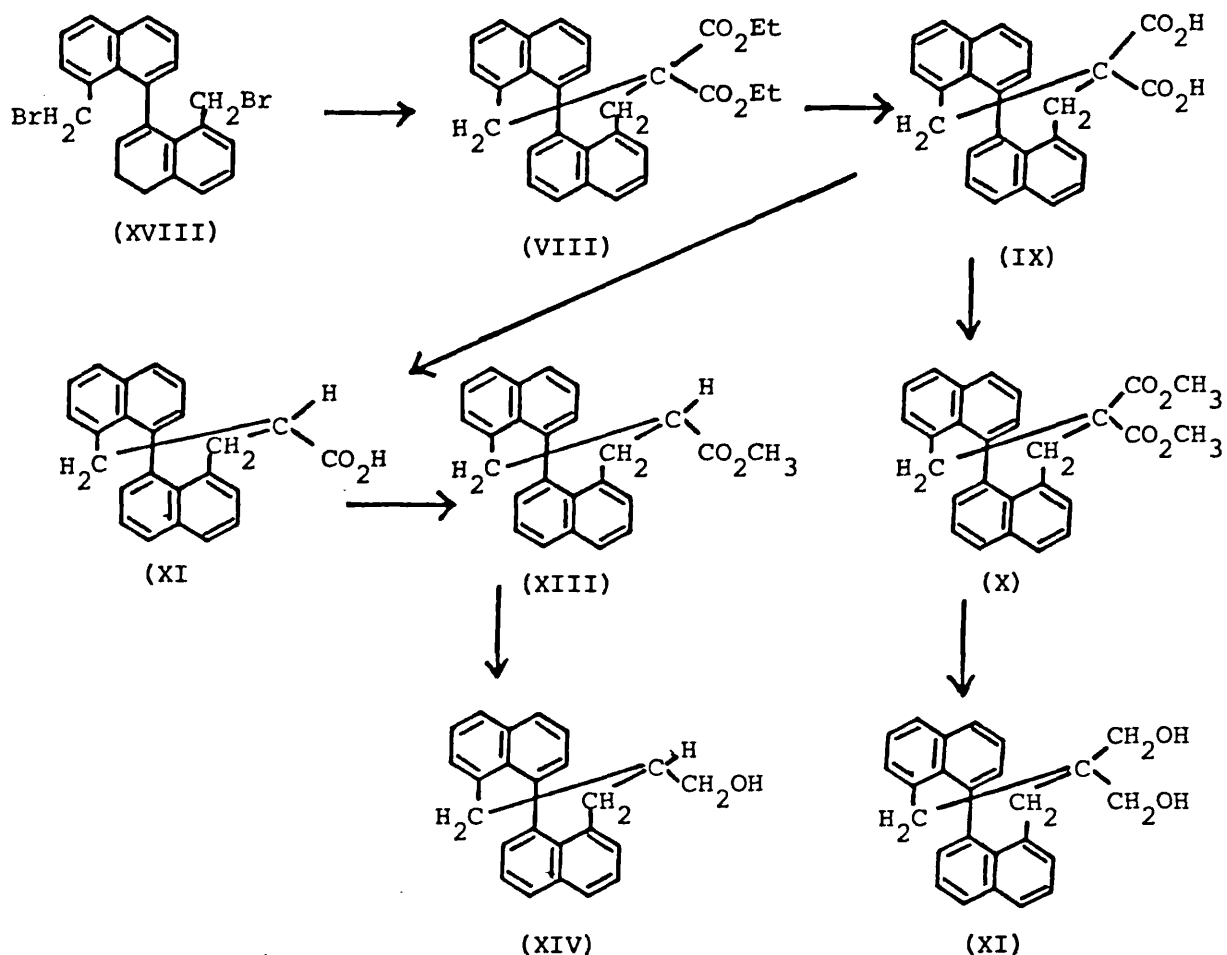
Stage (d):

The dibromo compound (XVIII) was boiled under reflux with potassium cyanide in ethanol to prepare 8,8'-biscyanomethyl-1,1'-binaphthyl (XIX) in good yield (Harris, Harris, Mazengo, Singh, 1974).

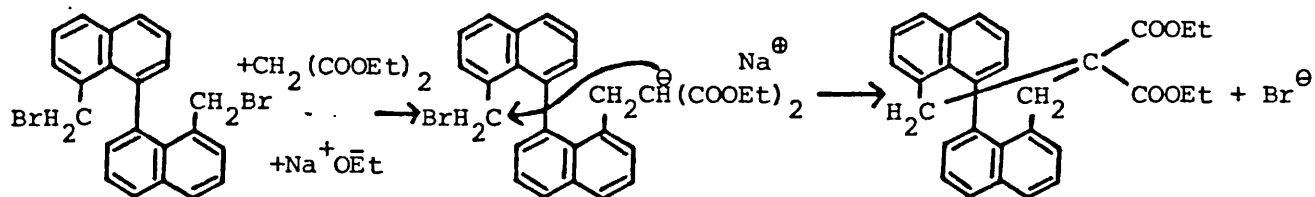
## 2.2.2. Bridged 8,8'-disubstituted-1,1'-binaphthyls

### 2.2.2.1. Carbocyclic rings

The carbocyclic nine-membered ring compounds were prepared according to the following scheme, as described by previous workers (Harris and Singh, 1976)



8,8'-Bisbromomethyl-1,1'-binaphthyl was heated under reflux with diethyl disodiummalonate in absolute ethanol to obtain the cyclic diethyl-ester (VIII) in excellent yield.



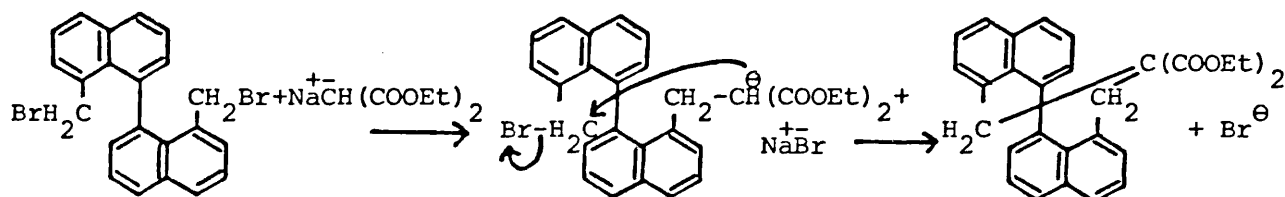
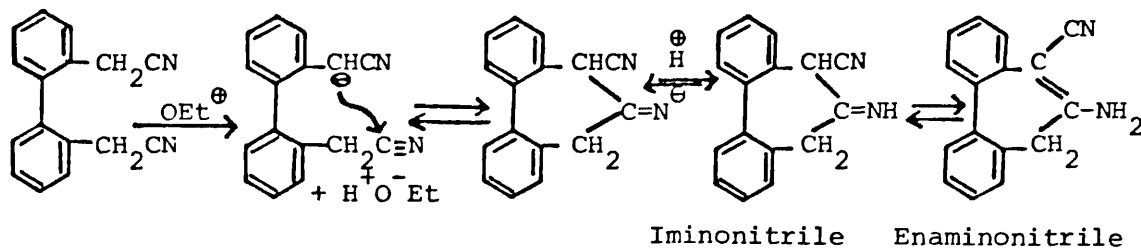
Hydrolysis of the diethyl ester by 60% potassium hydroxide gave the dicarboxylic acid (IX), with one molecule of water; <sup>it melts</sup> at 235-236° with brisk effervescence, then solidifies and remelts at 253-255°. This effervescence is not only loss of water but also of carbon dioxide as the diacid (IX) decarboxylates to give the monocarboxylic acid (XII); after crystallisation from ethanol this melts at 255-257°.

The dimethyl ester (X) of the cyclic dicarboxylic acid (IX) was obtained by treating with cold ethereal diazomethane. The monocarboxylic acid (XII) was heated with thionyl chloride in benzene and methanol was added to obtain the methyl ester (XIII). The methyl esters were reduced by lithium aluminium hydride in ether to give the corresponding alcohols (XI) and (XIV).

An attempt at Thorpe-Ziegler cyclization of 8,8'-biscyanomethyl-1,1'-binaphthyl (XIX) to obtain the nine-membered cyano-enamine ring failed. The biscyanomethyl compound (XIX) was heated with sodium ethoxide in ethanol for up to 75h in a nitrogen atmosphere, but after normal working up only starting material was recovered. Its m.p., i.r. and n.m.r. spectra were unchanged. This method of cyclization was successful for preparing seven-membered ring compounds from 2,2'-biscyanomethylbiphenyl (Kenner and Turner, 1911) and from 2,2'-biscyanomethyl-1,1'-binaphthyl (Newman, Rutkin and Mislow, 1959; Mislow and McGinn, 1958). Kenner (1913) suggested that the two aromatic double bonds in his biphenyl compounds e.g. 2,2'-(bisbromomethyl)biphenyl undergoing cyclization could increase the frequency of the reacting sites coming together in comparison with a five carbon chain.

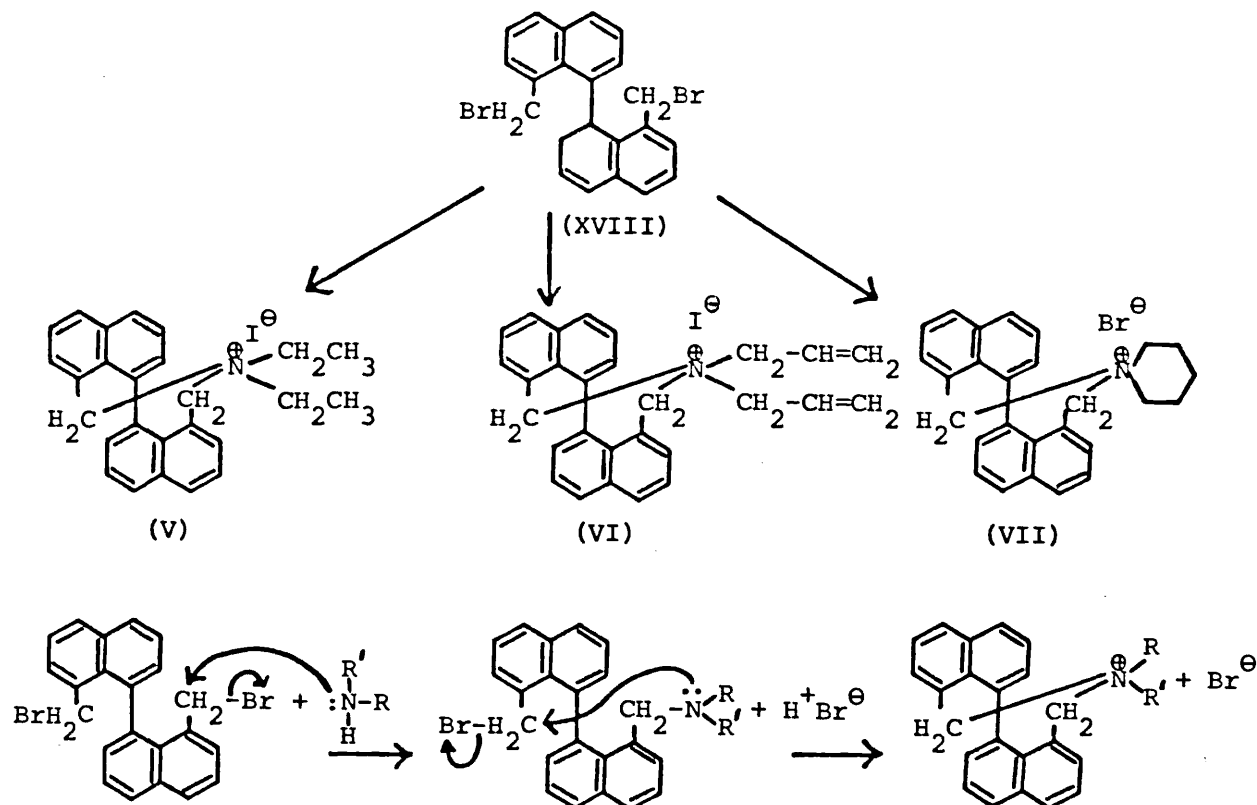
We should now say that unfavourable entropy is decreased by limiting the conformational range. In the 1,1'-binaphthyl series, using the 8 and 8'-positions, in the malonic ester synthesis we saw that the four aromatic bonds of the binaphthyl have a similar conformational effect in forming a 9-membered ring as the two aromatic double bonds of the biphenyl in forming the 7-membered ring. The situation seems to be different for a Thorpe-Ziegler cyclisation. A model of the nine-membered ring compound in which the 8,8'-positions of 1,1'-binaphthyl are linked by  $\text{CH}_2\text{CR}_2\text{CH}_2$  shows that it could not contain a further double bond, as required by an enolate or cyano-enamine system, without enormously increasing the strain. This reaction is reversible at a stage which forms the ring but does not complete the reaction, so the strain operates

adversely, while the reaction between the bromo compound and diethylmalonate is not reversible, the ring forming stage is a final stage.



#### 2.2.2.2. Nitrogen heterocycles

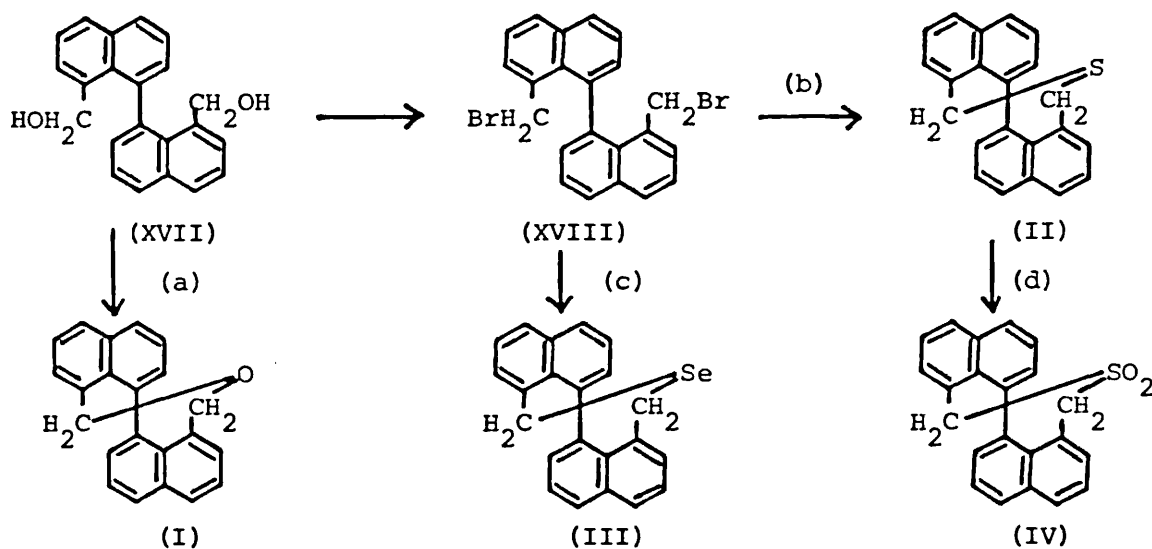
These compounds were prepared as described by previous workers (Singh, 1972); (Badar, Cooke and Harris, 1963-64) by condensation of 8,8'-bisbromomethyl-1,1'-binaphthyl (XVIII) and secondary amines:-



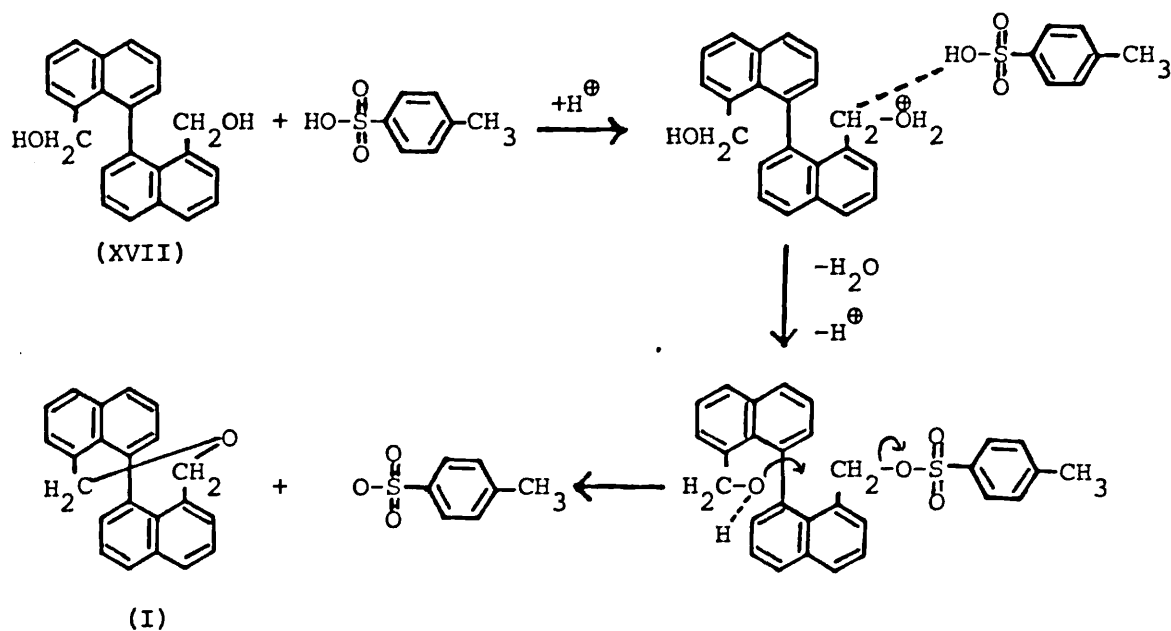
Freshly distilled diethylamine or diallylamine (2.2equiv) were heated with the dibromo compound (XVIII) in benzene to prepare the quaternary diethyl and diallylammonium salts. Both the salts were very soluble in water and failed to crystallise, so the bromides were converted into the corresponding iodides (V) and (VI) which then crystallised from water in good yields.

The piperidinium compound (VII) was prepared by using piperidine in chloroform; in this case the bromide crystallised from water.

### 2.2.2.3. Oxygen, Sulphur and Selenium heterocycles

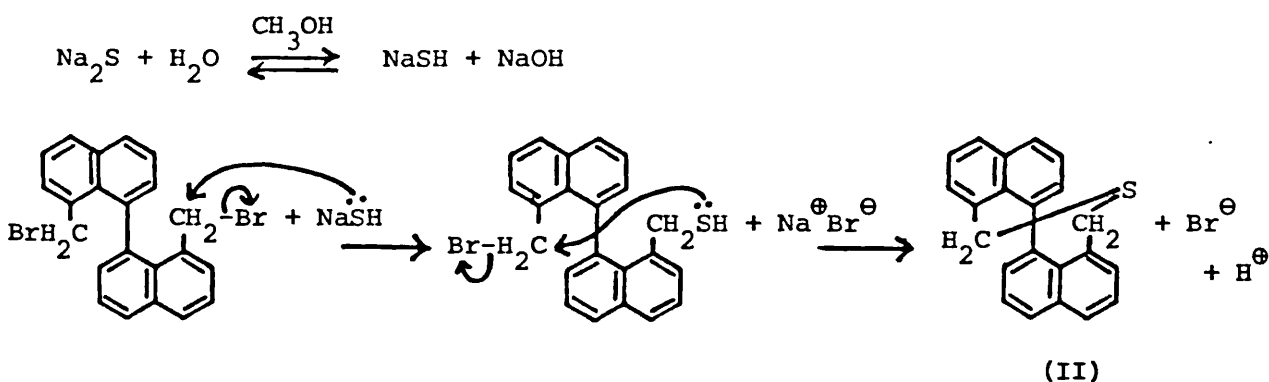


Both 50%  $\text{H}_2\text{SO}_4$  (Hall and Turner, 1951) and 24%  $\text{HBr}$  (Wittig, Davis and Koenig, 1951) have been successful reagents to prepare seven-membered ring oxepins in the biphenyl series, but they both failed to give the desired cyclic product in the binaphthyl series when 8,8'-bisbromomethyl-1,1'-binaphthyl (XVIII) was treated with them. Freshly prepared silver oxide in aqueous acetone, successful in the biphenyl series (Mislow *et.al.*, 1964) also failed to give (I). However, the second method of these authors, the synthesis from (XVII) and toluene-p-sulphonic acid (Mislow *et.al.*, 1962, 1964) in benzene met with success after heating under reflux for 16h, to give (I) in very reasonable yield.



An attempt to prepare optically active 8-oxa-8,9-dihydro-7H{1,2,3-de:4,5,6-d'e'-dinaphthalene}cyclononane (I) by treating 8,8'-bishydroxymethyl-1,1'-binaphthyl (XVII) with optically active camphor-10-sulphonic acid in benzene also failed: it did not form in 21 hours of boiling.

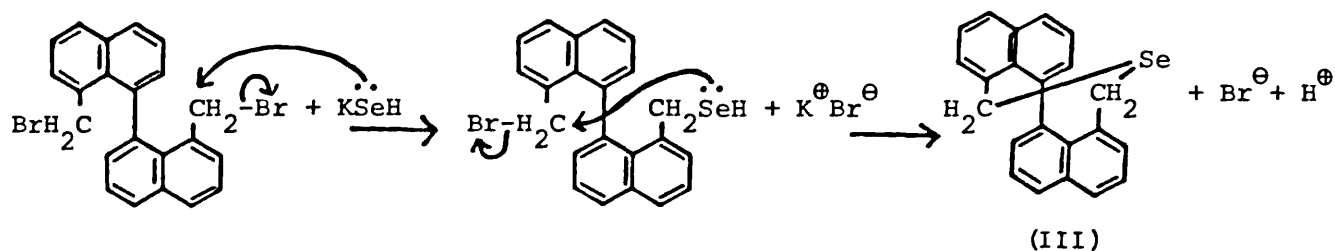
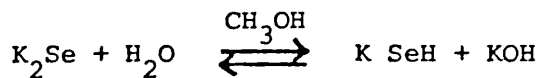
8,8'-Bisbromomethyl-1,1'-binaphthyl (XVIII) heated for 24h with sodium sulphide nonahydrate in methanol, the reagent used by Truce and Emrick (1956) in the biphenyl series, was successful in giving a nearly quantitative yield of compound (II).



An attempt to resolve 8-thia-8,9-dihydro-7H{1,2,3-de:4,5,6-d'e'-dinaphthalene}cyclononane (II) by column chromatography, using optically active acetyl cellulose as absorbent in dry benzene and sodium dried ether as eluent, failed, though it had been successful for the resolution

of 4,5,6,7-dibenzo-1,2-dithiocyclooctadiene (Luttringhaus, Hess and Rosenbaum, 1967).

The corresponding selenium compound (III) was prepared from the dibromo-compound (XVIII) using potassium selenide in methanol, again adapting Truce and Emrick's (1956) procedure,



Oxidation of the thiopin (II) with hydrogen peroxide in glacial acetic acid produced the cyclic sulphone (IV) as in the biphenyl series.

Clearly some of the methods applicable in the 7-ring biphenyl series work just as well in the 8,8'-disubstitued-1,1'-binaphthyl series, but others do not.



Notes

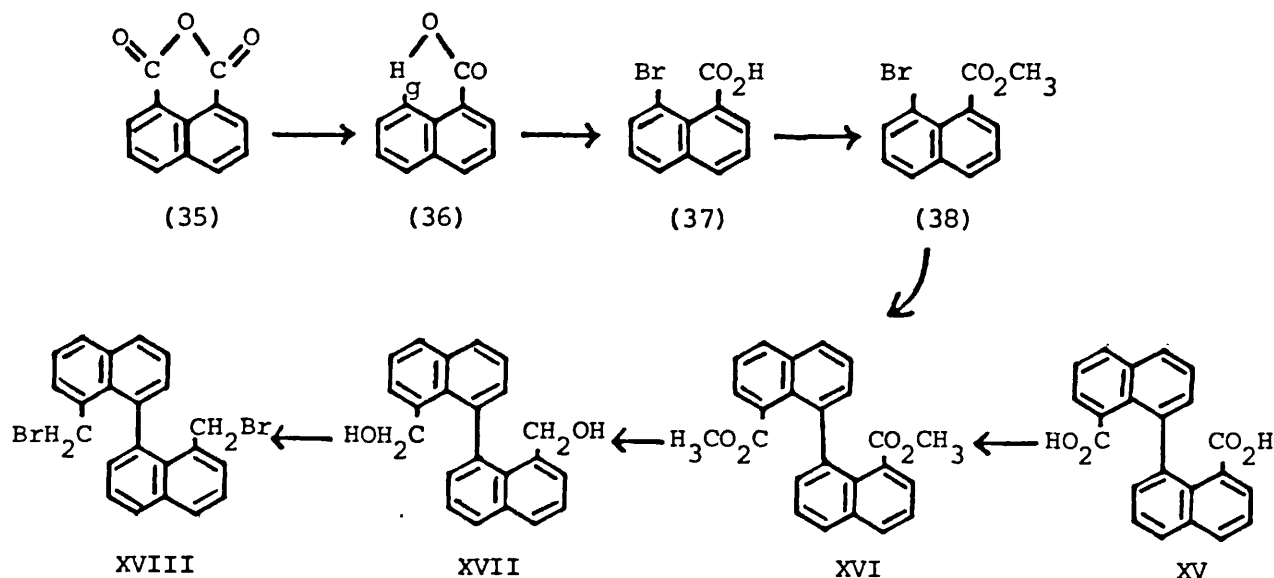
1. Melting points were determined in an oil bath and are corrected.
2. Nuclear magnetic resonance spectra at 60 MHz were determined on a Varian A60 instrument in this Department, and those at 100 MHz and 220 MHz by the P.C.M.U., Harwell. Chemical shifts are recorded on the  $\delta$  scale relative to TMS  $\delta = 0$  as internal standard.
3. Infrared spectra were determined on a Perkin-Elmer 457 instrument.
4. Ultraviolet absorption spectra were determined in 96% ethanol on a Unicam SP 500 manual spectrophotometer using quartz cells.
5. Some preliminary mass spectra were obtained in this Department but those given in this Thesis were determined by P.C.M.U., Harwell.
6. Microanalyses were carried out by Alfred Bernhardt.
7. Optical rotations were measured on a Carl Zeiss Photoelectric Precision Polarimeter and on a Perkin-Elmer 241 Polarimeter, at room temperature.
8. Optical rotatory dispersion spectra and circular dichroism measurements were determined in 95% ethanol on a Fica Spectropol-1 at the Polytechnic of North East London and on a Jasco J-40-CS Spectropolarimeter at King's College, London.
9. Material for optical rotations, u.v. and Circular dichroism was weighed to an accuracy of four decimal places on a Stanton B.20 balance and made up to the required volume in a standard flask at room temperature.
10. Geminal coupling constants are given negative signs in the tables by analogy with those for similar compounds (Jackman and Sternhell, 'Application of N.m.r. Spectroscopy in Organic Chemistry, 1969).

3      EXPERIMENTAL : PREPARATION OF RACEMIC AND OPTICALLY ACTIVE COMPOUNDS.\*

3.1      COMPOUNDS PREVIOUSLY KNOWN

3.1.1      8,8'-Disubstituted 1,1'-Binaphthyls, Unbridged

3.1.1.1      Preparation of 8,8'-bishydroxymethyl-1,1'-binaphthyl (XVII) and 8,8'-bisbromomethyl-1,1'-binaphthyl (XVIII)



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

(Rule and Barnett, 1932).

From naphthalic anhydride :- Methyl 8-bromo-1-naphthoate (38), (50 g) by the Ullmann reaction (Hall, Ridgwell and Turner, 1954; Cooke and Harris, 1963; Badar, 1964; Mazengo, 1968; Singh, 1972) gave 8,8'-dimethoxycarbonyl-1,1'-binaphthyl, m.p. 144-6°, 25 g (71%) (158-9°, 76.5%, Badar, 1964; 157-8°, 78.6%, Mazengo, 1968; Cheung King Ling and Harris, 1962 found two crystalline forms, m.p. 145-7° and 155-7°).

From 1,1'-binaphthyl-8,8'-dicarboxylic acid (XV) using dimethyl sulphate :- 1,1'-binaphthyl-8,8'-dicarboxylic acid (3.42 g; 0.01 mole) was dissolved in 10ml of 10% sodium hydroxide. Dimethyl sulphate (3.8 ml;  $d$ , 1.32; 0.04 mole) was added and the mixture shaken well. It became warm, deposition of solid began and was completed on warming on a water-bath. The excess of dimethyl sulphate was decomposed by shaking with a further 20 ml of 10% sodium

\* See Notes, p.28A.

hydroxide. The solid was filtered off, washed with water and dried on a boiling water-bath (3.6 g, 97.7%) m.p. 143-44<sup>o</sup>, after recrystallisation from ethanol, m.p. 157-158<sup>o</sup>.

From 1,1'-binaphthyl-8,8'-dicarboxylic acid (XV) using trimethyl phosphate:- (Harris and Patel, 1973)

1,1'-Binaphthyl-8,8'-dicarboxylic acid (3.42 g, 0.01 mole) was dissolved in 10 ml of 10% sodium hydroxide and shaken with trimethyl phosphate (7 ml;  $d$ , 1.21; 0.06 mole). The mixture became warm spontaneously. Deposition of solid soon began and was completed on warming on a water-bath. The excess of trimethyl phosphate was decomposed by shaking with a further 40 ml of 10% sodium hydroxide. The solid was filtered off, washed with water and dried on a boiling water-bath giving 3.34 g (90%), m.p. 157<sup>o</sup>. Crystallisation from ethanol gave two crystalline forms as before.

I.r. (Nujol mull): a sharp strong band at  $1700\text{cm}^{-1}$  confirms the presence of the carbonyl group of an ester. (Bellamy, 1958).

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

(Badar, Cooke and Harris, 1965).

Lithium aluminium hydride (1.5 g; 6 equiv.) was weighed in the fume cupboard and quickly covered with sodium dried ether (500 ml) in a three-necked three-litre flask equipped with a condenser and a dropping funnel. A suspension of 8,8'-dimethoxycarbonyl-1,1'-binaphthyl (5 g; 1 equiv.) in one litre of sodium dried ether was then washed in and the mixture boiled on a water-bath for four hours. Wet ether and water were added dropwise, to decompose the excess of lithium aluminium hydride, until no bubbles were observed, and dilute sulphuric acid (2N) was then added. The ether layer was separated and the aqueous layer extracted once with ether, the combined ether layers were washed twice with water, dried over calcium chloride and the ether distilled off. The crystalline compound obtained together with some sticky material (4.8 g in all) was dissolved in benzene, boiled with charcoal and filtered. After some time

crystals separated (3.6 g) and were recrystallised from benzene.

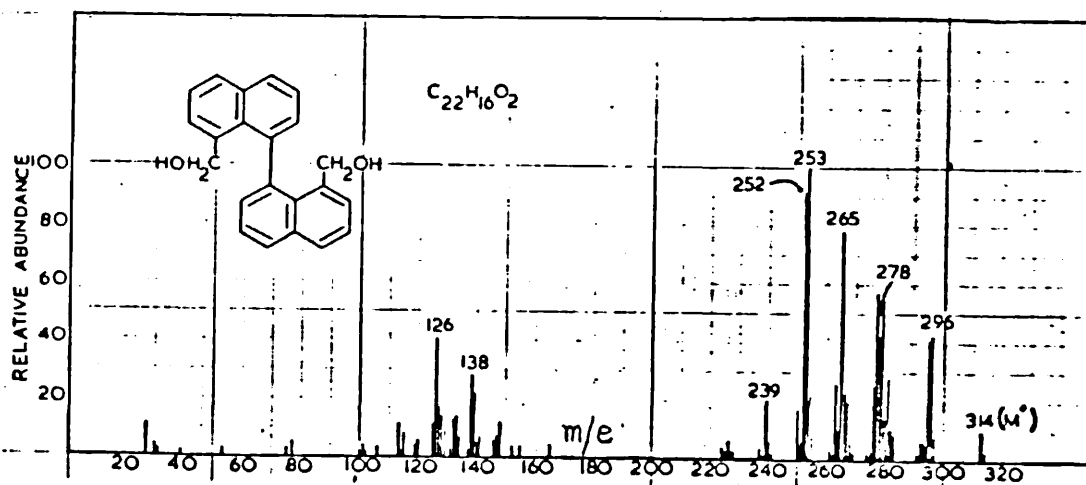
This gave the diol in the form of two molecular proportions with one of benzene; vacuum-drying over phosphorous pentoxide for two hours at  $100^{\circ}$  removed the benzene (2.1766 g of diol lost 0.2360 g of benzene; calc. for  $(C_{22}H_{18}O_2)_2C_6H_6$ , 0.2406 g {Found: C, 85.0; H, 5.7; O, 8.95.  $(C_{22}H_{18}O_2)_2C_6H_6$  requires C, 85.0; H, 6.0; O, 9.0%}.

I.r. (Nujol mull): strong bands at  $3420\text{ cm}^{-1}$  and  $3545\text{ cm}^{-1}$  confirm the presence of the hydroxyl groups.

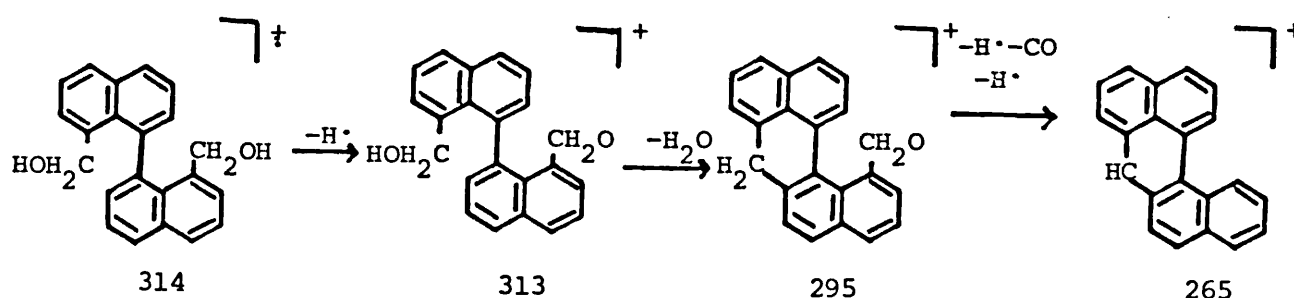
N.m.r. ( $Me_4Si$ ;  $CDCl_3$ ; 60MHz) at room temperature:  $\delta$  7.12-8.0 (12H, complex multiplet, aromatic);  $\delta$  4.02 (4H, s,  $CH_2$ ) and  $\delta$  1.78 (2H, s, OH).

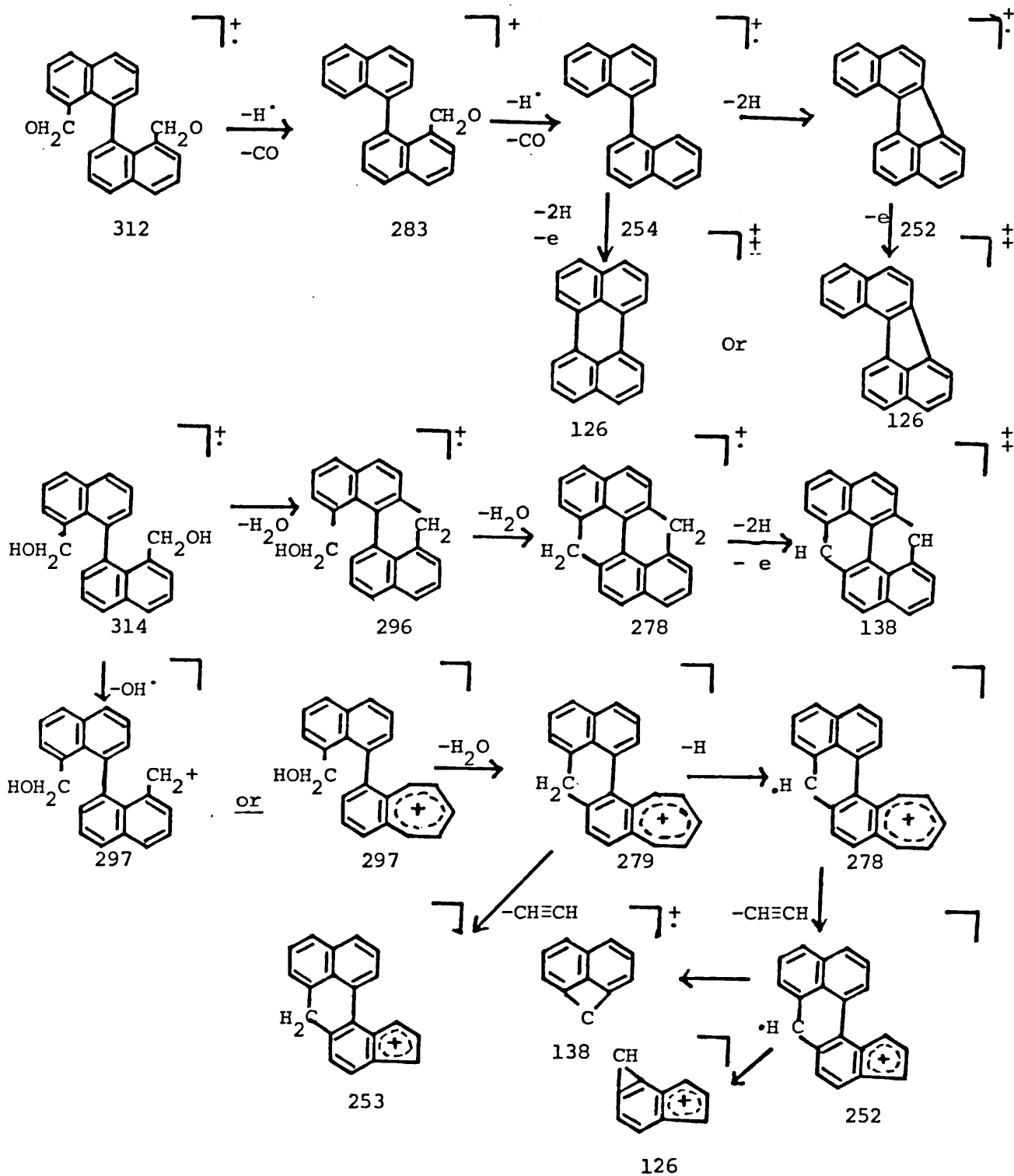
{ Sometimes the diol was contaminated by some half-reduced product, i.e. 8-hydroxymethyl-8'-methoxycarbonyl-1,1'-binaphthyl, m.p.  $120-22^{\circ}$ , the i.r. spectrum (Nujol mull) showing strong bands at  $3420\text{ cm}^{-1}$  (OH) and  $1700\text{ cm}^{-1}$  (CO) confirming the presence of both groups: such samples were neglected}.

Mass spectrum: mass measured, 314.1305, calc. for  $C_{22}H_{18}O_2$  314.1307



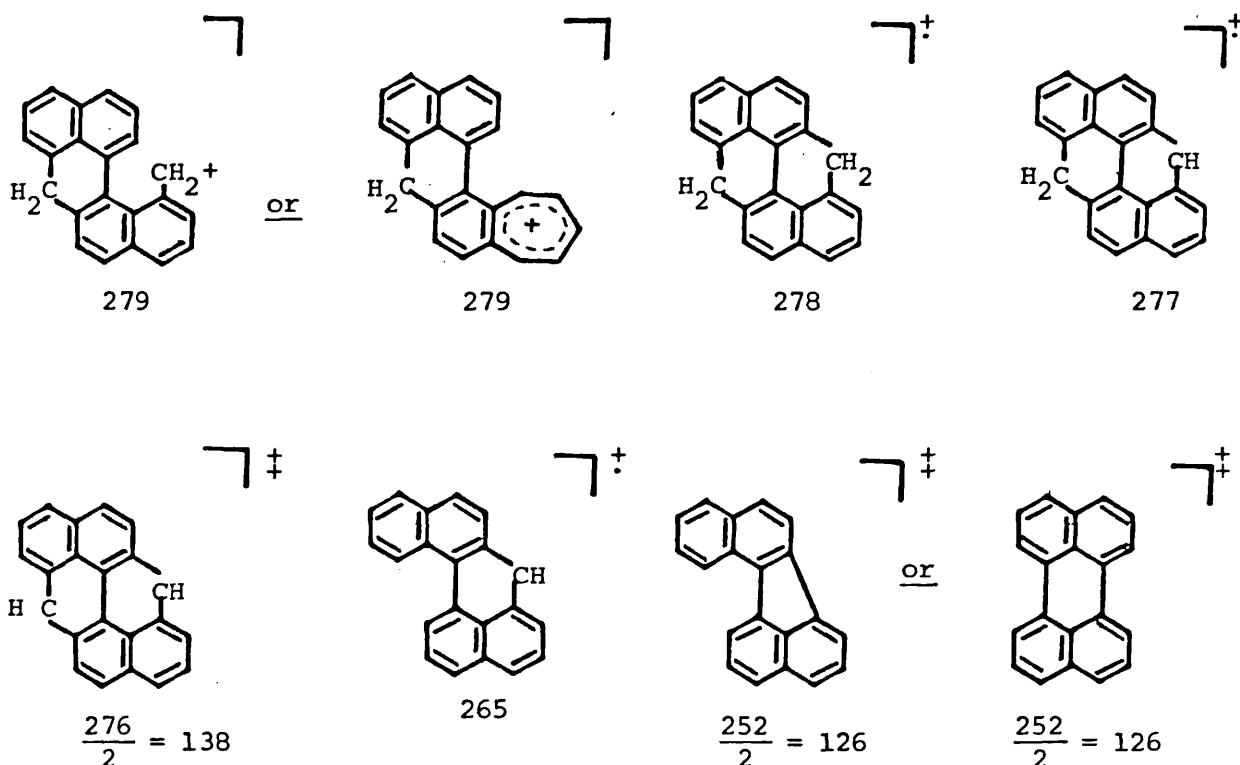
Possible fragmentations may be as follows:





In the binaphthyl compounds certain fragments occur rather commonly: these are  $m/e$  279, 278, 277, 276, 275, 252, 138 and 126. The structures of these fragments may be as below: doubly charged fragments appear at  $m/2e$ .

Fused ring aromatic fragments may have two positive charges,  $P^{++}$  (Beynon, Saunders and Williams, The Mass Spectra of Organic Molecules, 1968, p.129) which is significant as an alternative reason for the presence of signals at 138 and 126.



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

Using Hydrobromic acid: (Badar, Cooke and Harris, 1965)

8,8'-Bishydroxymethyl-1,1'-binaphthyl (5 g) was dissolved in boiling glacial acetic acid (125 ml) and boiling hydrobromic acid (60 ml;  $d$ , 1.49) added; the solution became cloudy and a light yellow crystalline compound separated. More hydrobromic acid (25 ml) was added. After cooling the solid was filtered, washed well with water and dried (7 g). It crystallised from chloroform in very light yellow crystals, m.p.189-191 $^{\circ}$ , 5.55 g, 81%. (m.p.190-191.5 $^{\circ}$ , 82%, Badar, 1964; m.p.191.5-192 $^{\circ}$ , 82%, Mazengo, 1968; m.p.191-192,86%, Singh, 1972). Alternatively a solution of hydrogen bromide in glacial acetic acid (35 ml, 45% $^{w/v}$ ) was added to 8,8'-bishydroxymethyl-1,1'-binaphthyl (5 g) and heated for about fifteen minutes under reflux. Then it was cooled, filtered and worked up as before, m.p.189-90 $^{\circ}$ , 5.5 g, 81%.

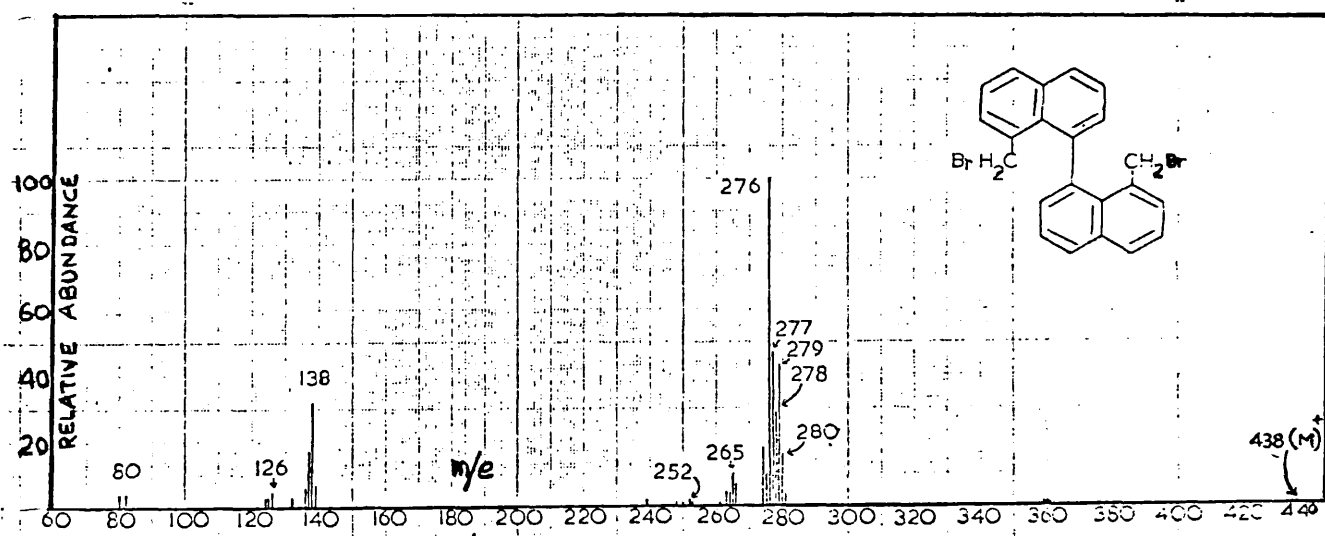
Using phosphorous tribromide (Singh, 1972)

8,8'-Bishydroxymethyl-1,1'-binaphthyl (5.0 g, 0.0159 mole) was added in small portions at room temperature to magnetically stirred phosphorous tribromide (25 g, 0.092 mole; freshly distilled, under nitrogen to prevent

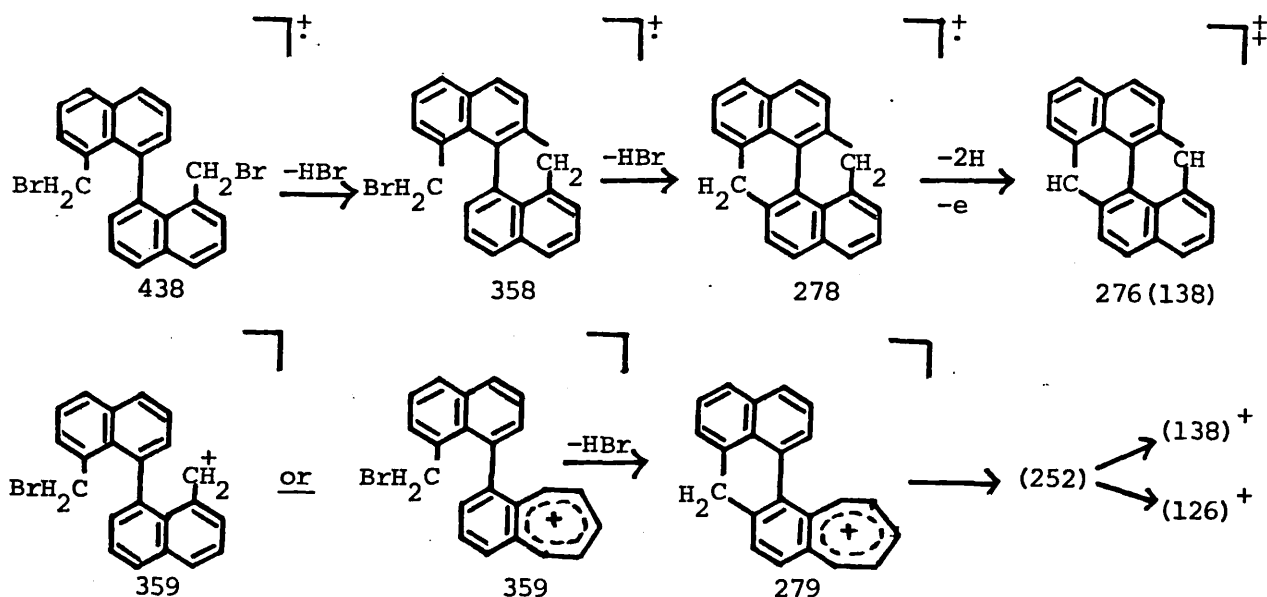
air-oxidation, b.p.168-71<sup>o</sup>) in a 100 ml round bottomed flask fitted with a calcium chloride tube. The reaction was vigorous. After the addition was complete, stirring was continued for another 25 minutes. Then the reaction mixture was poured into a vigorously stirred ice-water mixture and the yellow precipitate worked up as before, m.p.189-90<sup>o</sup>, 5.7 g, 82%, (m.p.191-192<sup>o</sup>, 99% Singh, 1972).

N.m.r. (Me<sub>4</sub>Si; CDCl<sub>3</sub>; 100MHz) :  $\delta$  7.99-7.35 (12H, complex multiplet, aromatic) and  $\delta$  4.26, 4.18; 4.07, 3.95 (4H, q, CH<sub>2</sub>).

Mass spectrum: Mass measured 437.9609, calc. for C<sub>22</sub>H<sub>16</sub>Br<sub>2</sub> 437.9598.



Possible fragmentations may be as follows:



### 3.1.1.2 (±)1,1'-Binaphthyl-8,8'-dicarboxylic acid. (XV)

(Corbellini, 1931; Meisenheimer and Beisswenger, 1932;

Stanley and Adams, 1929).

By hydrolysis of 8,8'-bismethoxycarbonyl-1,1'-binaphthyl:

Hydrolysis of 8,8'-bismethoxycarbonyl-1,1'-binaphthyl (5 g) with 30% alcoholic potassium hydroxide gave 1,1'-binaphthyl-8,8'-dicarboxylic acid, m.p.320-322<sup>o</sup>, 4 g, 86.6% (m.p.300-304<sup>o</sup>, Hall, Ridgwell and Turner, 1954).

Purification of commercial 1,1'-binaphthyl-8,8'-dicarboxylic acid,

(Mazengo, 1968).

The light brown commercial acid (Fluka AG Chemische Fabrik), m.p.303<sup>o</sup> (50 g) was dissolved in a minimum amount of 10% sodium hydroxide and 30% sodium hydroxide added to precipitate the sodium salt. It was filtered off, dissolved in water and stirred with charcoal for one hour. The charcoal was filtered off and the diacid precipitated with dilute hydrochloride acid. The process was repeated and the precipitate then boiled with water, filtered, washed with hot water and ethanol and dried on a boiling water-bath, 39.8 g, 79.6%, m.p.317-18<sup>o</sup>. It crystallised from dimethylformamide on dropwise addition of water. {Found: C, 76.2; H, 4.2. (C<sub>22</sub>H<sub>14</sub>O<sub>4</sub>)<sub>4</sub>H<sub>2</sub>O requires C, 76.2; H, 4.2%}. After drying at 100<sup>o</sup>/2mm for two hours the water was lost. {Found: C, 77.0; H, 4.0. C<sub>22</sub>H<sub>14</sub>O<sub>4</sub> requires C, 77.2; H, 4.1%} Some of the product was recrystallised from ethanol and had m.p.321-22<sup>o</sup>.

### 3.1.1.3 Preparation of optically active 8,8'-bishydroxymethyl-1,1'-binaphthyl (XVII) and 8,8'-bisbromomethyl-1,1'-binaphthyl (XVIII)

The starting materials for the synthesis of optically active compounds were (+) and (-) 1,1'-binaphthyl-8,8'-dicarboxylic acid.

#### Resolution of 1,1'-binaphthyl-8,8'-dicarboxylic acid (XV)

(Meisenheimer and Beisswenger, 1932)

(±)-1,1'-Binaphthyl-8,8'-dicarboxylic acid (2.0 g) was added to a methanolic



solution of brucine (2.8 g of  $C_{23}H_{26}O_4N_2 \cdot 4H_2O$  in 60 ml). The solution was boiled until all the acid dissolved: then filtered and evaporated down to about 400 ml. On standing, the solution deposited needles, 1.7 g, m.p. 252-258°;  $\alpha_{546} -3.32^\circ$ .  $\{\alpha\} -520.6^\circ$  (c, 1.275; l, 0.5; chloroform).

The mother liquor was evaporated to dryness and the residue dissolved in boiling ethylacetate and filtered hot. The filtrate was concentrated to about 250 ml; on standing crystals separated, 2.1 g, m.p. 229-245°;  $\alpha_{546} +3.49^\circ$ ,  $\{\alpha\}_{546} +558.4^\circ$  (c, 1.25; l, 0.5; chloroform).

Liberation of optically active acids:-

The (-) brucine salt (1.37 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 trace of chloroform, and filtered, The filtrate was acidified with dilute hydrochloric acid to precipitate the active acid, which was filtered off, washed with water and dried in an evacuated desiccator, 0.52 g, m.p. 310-320°d;  $\alpha_{546} - 4.705^\circ$ ,  $\{\alpha\}_{546} -707^\circ$  (c, 1.33; l, 0.5; N,N-dimethylformamide) {C, 75.7; H, 4.3; O, 19.7%}.

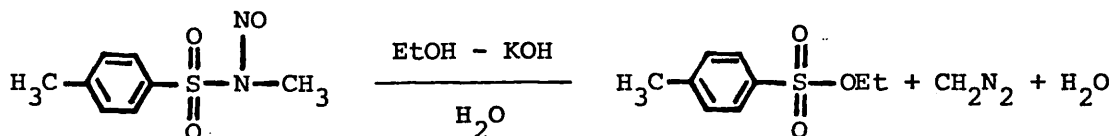
The (+) diacid was obtained from the brucine salt  $\{\alpha\}_{546} + 558.4^\circ$  in a similar way, 0.60 g; m.p. 308-319°d;  $\alpha_{546} +4.9^\circ$ ,  $\{\alpha\}_{546} +736.8^\circ$  (c, 1.33; l, 0.5; N,N-dimethylformamide). {Found: C, 75.8; H, 4.4; O, 19.8} These specimens of optically active acid are clearly hydrated.

3.1.1.4 Optically active 8,8'-dimethoxycarbonyl-1,1'-binaphthyl

(XVI)

(Cooke and Harris, 1963).

Preparation of diazomethane,  $CH_2N_2$ , from N-methyl-N-nitroso-p-toluene-4-sulphonamide (Fieser and Fieser, 1967).



In a round bottomed flask were placed 5 g potassium hydroxide, 8 ml water and 25 ml of 95% ethanol and kept at 60-70° on a water bath: (all joints were fitted with PTFE sleeves). N-Methyl-N-nitroso-p-toluenesulphonamide

(21.5 g) dissolved in 150 ml of ether was added from a dropping funnel. There were two receiving flasks in series; the second one which contained 40-60 ml of sodium dried ether acted as a trap for any diazomethane which might escape. After the addition, a further 50 ml of ether was added and the distillation continued until the distillate was colourless. The ethereal solution  $\approx$  160 ml was used immediately and was assumed to contain 2.6-2.7 g of diazomethane.

(+) - Dimethyl 1,1'-binaphthyl-8,8'-dicarboxylate:- Powdered (+)-1,1'-binaphthyl-8,8'-dicarboxylic acid 4.30 g,  $\{\alpha\}_{546} +727^{\circ}$ , N,N-dimethylformamide, was added slowly to the cold ethereal solution of diazomethane (1.3 g in 75 ml). There was effervescence and the di-ester crystallised as a white solid: it was filtered off, washed with aqueous sodium bicarbonate solution and then with water and dried, 3.0 g, m.p.156-158 $^{\circ}$ ,  $\alpha_{546} +1.304^{\circ}$ ,  $\{\alpha\}_{546} +196^{\circ}$  ( $\underline{c}$  1.33;  $\underline{l}$ , 0.5; N,N-dimethylformamide.) { Found: C, 77.7; H, 5.0; O, 17.35.  $C_{24}H_{18}O_4$  requires C, 77.8; H, 4.9; O, 17.3%}.

(-) Dimethyl 1,1'-binaphthyl-8,8'-dicarboxylate:- Use of (-)-1,1'-binaphthyl-8,8'-dicarboxylic acid (4.5 g),  $\{\alpha\}_{546} -704^{\circ}$ , ( $\underline{c}$  1.0;  $\underline{l}$  0.5; N,N-dimethylformamide) gave 3.13 g of di-ester, m.p.155-158 $^{\circ}$ ,  $\alpha_{546} -0.97^{\circ}$ ;  $\{\alpha\}_{546} -194^{\circ}$  ( $\underline{c}$  1.0;  $\underline{l}$  0.5; N,N-dimethylformamide). { Found: C, 77.6; H, 4.85; O, 17.35.  $C_{24}H_{18}O_4$  requires C, 77.8; H, 4.9; O, 17.3%}.

#### Preparation of (-)-8,8'-bisbromomethyl-1,1'-binaphthyl. (XVIII)

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

(The procedure of Badar, Cooke and Harris (1965) was used).

Lithium aluminium hydride (6.0 g) in 600 ml of sodium dried ether was heated under reflux for 10 min, and (+)-dimethyl 1,1'-binaphthyl 8,8'-dicarboxylate 7.3 g, ( $\{\alpha\}_{546} +158^{\circ}$ ,  $\{\alpha\}_{546} +161^{\circ}$ ,  $\{\alpha\}_{546} +179^{\circ}$ ; N,N-dimethylformamide) suspended in 1L of sodium dried ether was added portionwise during half an hour. After 90 min. boiling under reflux and decomposition of excess  $LiAlH_4$  with dilute sulphuric acid, the

etheral layer yielded 5.44 g of crude diol. Crystallization from benzene gave colourless crystals 1.2 g, m.p. 146-148° followed by non-crystalline (-)-rotatory material (4.0 g),  $\alpha_{546} -0.11^\circ$ ,  $\{\alpha\}_{546} -22^\circ$  (c 1.0;  $\underline{1}$  0.5; N,N-dimethylformamide). {Found: C, 83.95; H, 5.7; O, 10.3.  $C_{22}H_{18}O_2$  requires C, 84.1; H, 5.7; O, 10.2%}

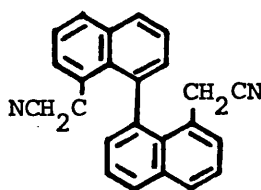
(-)-8,8'-Bisbromomethyl-1,1'-binaphthyl:— The non-crystalline (-)-diol (4.0 g) obtained from the mother liquor was dissolved in 120 ml of glacial acetic acid and warm hydrobromic acid (70 ml) added to it. The yellow precipitate (4.6 g, m.p. 170-174°,  $\{\alpha\}_{546} -380^\circ$ ) was dissolved in chloroform and petroleum ether (40-60°) added to give 4.0 g, m.p. 180-182°,  $\alpha_{546} -2.14^\circ$ ,  $\{\alpha\}_{546} -428^\circ$  (c 1.0;  $\underline{1}$  0.5; N,N-dimethylformamide). {Found: C, 60.2; H, 3.6; Br, 36.1.  $C_{22}H_{16}Br_2$  requires C, 60.3; H, 3.65; Br, 36.1%}

Preparation of (+)-8,8'-bisbromomethyl-1,1'-binaphthyl. (XVIII)

(+)-8,8'-Bishydroxymethyl-1,1'-binaphthyl:— (-)-Dimethyl 1,1'-binaphthyl-8,8'-dicarboxylate 5.9 g  $\{\alpha\}_{546} -189^\circ$ ,  $\{\alpha\}_{546} -127^\circ$ , N,N-dimethylformamide) treated as for the (-)-diol gave 1.1 g, m.p. 146-148° and sticky material 3.0 g;  $\alpha_{546} +0.065^\circ$ ,  $\{\alpha\}_{546} +13^\circ$  (c 1.0;  $\underline{1}$  0.5; N,N-dimethylformamide). {Found: C, 83.0; H, 5.9; O, 10.3%}

(+)-8,8'-Bisbromomethyl-1,1'-binaphthyl:— The oily (+)-diol (3.0 g) gave the dibromo compound 4.0 g, m.p. 168°-174°,  $\alpha_{546} +1.93^\circ$ ,  $\{\alpha\}_{546} +386^\circ$  (c 1.0;  $\underline{1}$  0.5; N,N-dimethylformamide). {Found: C, 60.7; H, 3.6; Br, 35.6%} ( $\{\alpha\}_{546} +470^\circ$ , N,N-dimethylformamide, Shyam Singh, 1972).

3.1.1.5  
Preparation of 8,8'-biscyanomethyl-1,1'-binaphthyl (XIX)—



(This compound has been described previously but there was some doubt about the authenticity of specimens. Mislow *et. al.*, (1958)

attempting to prepare the biphenyl analogue found that the Thorpe cyclisation product was easily obtained.) 8,8'-Bisbromomethyl-1,1'-binaphthyl (3.2 g) was added to a boiling solution of potassium cyanide (1.2 g in 85 ml of n-propyl alcohol and 17 ml of water) and boiled for three hours; the solid was filtered off, dried and crystallised from benzene giving 2.0 g (82%), m.p.230-232° Singh, 1972).

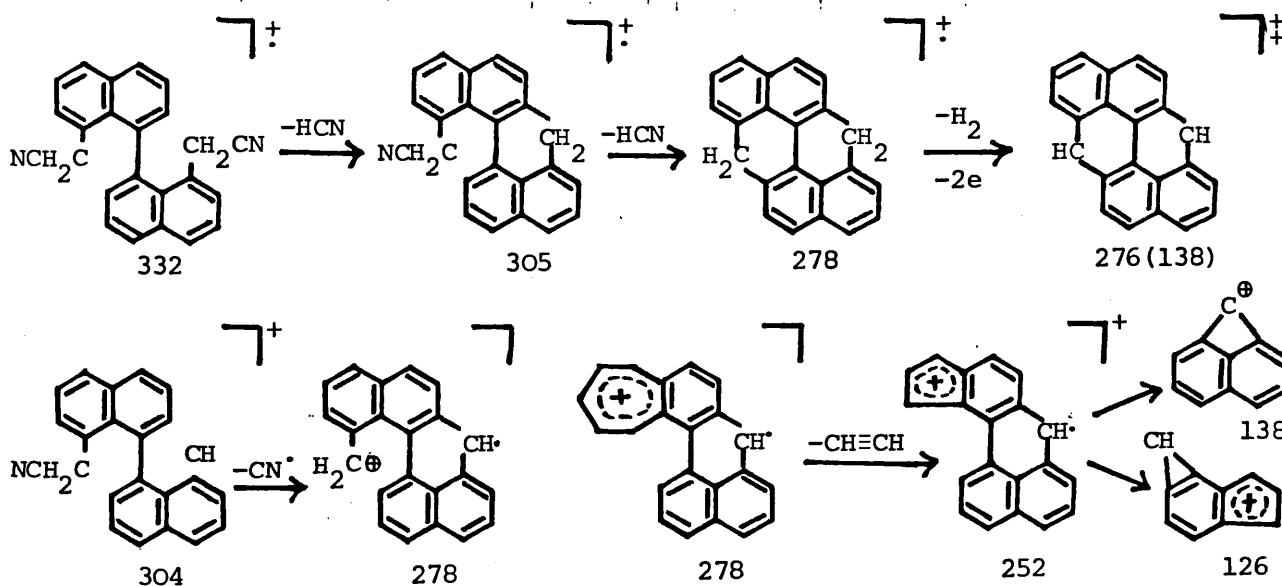
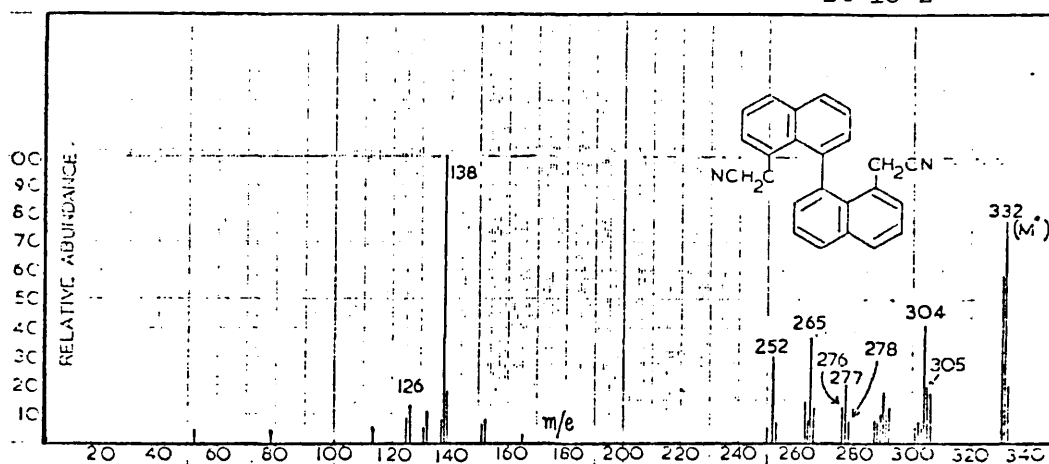
{Found: C, 86.7; H, 4.9; N, 8.3.  $C_{24}H_{16}N_2$  requires C, 86.8; H, 4.8; N, 8.4%}

I.r.(Nujol mull):  $2250\text{ cm}^{-1}$  (sharp, C≡N stretching).

N.m.r.( $CDCl_3$ ):  $\delta$  8.06-7.33 (12H, complex multiplet, aromatic);

$\delta$  3.34, 3.15; 3.07, 2.88 (4H, q,  $CH_2CN$ ).

Mass spectrum: Mass measured 332.1289, calc. for  $C_{24}H_{16}N_2$  332.1313.



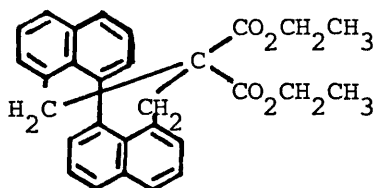
Preparation of (+)-(XI.X) - (+)-8,8'-Bisbromomethyl-1,1'-binaphthyl

(1.5 g,  $[\alpha]_{546}^{+351^{\circ}}$ , N,N-dimethylformamide), in 20 ml of 95% ethanol was boiled under reflux with potassium cyanide (1.0 g in 6 ml of 95% ethanol and 2 ml of water). Normal working up and crystallisation from ethanol gave 0.85 g, m.p. 224-225 $^{\circ}$ ,  $\alpha_{546}^{+0.71^{\circ}}$ ,  $[\alpha]_{546}^{+297^{\circ}}$  ( $c$  0.478;  $l$  0.5; N,N-dimethylformamide). {Found: C, 86.7; H, 4.9; N, 8.4%}.

Preparation of (-)-(XIX). (-)-8,8'-Bisbromomethyl-1,1'-binaphthyl (1.5 g,  $[\alpha]_{546}^{-259^{\circ}}$ , N,N-dimethylformamide), treated with potassium cyanide as above gave 0.84 g, m.p. 224-225 $^{\circ}$ ,  $\alpha_{546}^{-0.515^{\circ}}$ ,  $[\alpha]_{546}^{-284^{\circ}}$  ( $c$  0.362;  $l$  0.5; N,N-dimethylformamide) {Found: C, 86.6; H, 4.9; N, 8.5%}.

### 3.1.2 9-Membered Ring 8,8'-Bridged 1,1'-Binaphthyls, Carbocyclic

3.1.2.1 Preparation of diethyl 8,9-dihydro-7H-cyclonona{1,2,3-de:4,5,6-d'e'}-dinaphthalene-8,8'-dicarboxylate (VIII):  
(Harris and Singh, 1976).



8,8'-Bisbromomethyl-1,1'-binaphthyl (4.12 g, 1 equiv.) was suspended in dioxan (10 ml) in a well dried three-necked flask, fitted with dropping funnel, a stopper and a water condenser and stirred magnetically. Diethyl disodiummalonate (prepared 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, 1.4 equiv.) added dropwise. The reaction mixture was heated under reflux with occasional swirling for three hours; on cooling to room temperature a solid separated. Water was added to complete the precipitation of the product, which was filtered, washed, and crystallised from benzene (charcoal) to give 4.0 g (97%), m.p. 270-271 $^{\circ}$  (263-264 $^{\circ}$  Singh, 1972). {Found: C, 79.5; H, 5.95; O, 14.5.  $C_{29}H_{26}O_4$  requires C, 79.4; H, 6.0; O, 14.6%}.

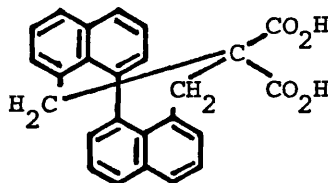
I.r. (Hexachlorobutadiene mull): 1720  $cm^{-1}$  ( $s$ ; ethoxycarbonyl group) and

3050, 2990, 2970 (s), 2950, 2930, 2890  $\text{cm}^{-1}$  ( $\text{CH}, \text{CH}_2$  and  $\text{CH}_3$  stretching).  
 N.m.r. ( $\text{CDCl}_3$ ):  $\delta$  7.92-6.72 (12H, complex multiplet, aromatic),  $\delta$  4.16, 3.92; 3.26, 3.08 (4H, q,  $\text{CH}_2$  attached to naphthalene); 4.09, 3.97, 3.86, 3.73 (4H, q,  $\text{COOCH}_2$ ); 1.22, 1.10, 0.98 (6H, t,  $\text{CH}_3$ ).

Preparation of (+)-(VIII).- (+)-8,8'-Bisbromomethyl-1,1'-binaphthyl (1.0 g,  $[\alpha]_{546}^{25} +254^\circ$ ) in sodium dried ether and diethyl disodiummalonate in ethanol were refluxed for 3h. After normal working up, the product was crystallised from benzene. The first fraction (0.2 g) was optically inactive diester, m.p.265-267 $^\circ$ . The filtrate was evaporated to dryness and the residue crystallised from ethanol to give 0.46 g, m.p.142-143 $^\circ$ ,  $\alpha_{546}^{25} +0.375^\circ$ ,  $[\alpha]_{546}^{25} +307^\circ$  (c 0.244; l 0.5; N,N-dimethylformamide).  
 {Found: C, 79.2; H, 6.0; O, 14.7%}

Preparation of (-)-(VIII).- The (-)-(VIII) was prepared in a similar way from (-)8,8'-bisbromomethyl-1,1'-binaphthyl (1.5 g,  $[\alpha]_{546}^{25} -380^\circ$ ). Crystallisation from benzene gave some optically inactive diester, m.p.266-267 $^\circ$  as before. Crystallisation of the remainder from ethanol gave 0.80 g, m.p.141-142.5 $^\circ$ ,  $\alpha_{546}^{25} -0.80^\circ$ ,  $[\alpha]_{546}^{25} -320^\circ$  (c 0.5; l 0.5; N,N-dimethylformamide). {Found: C, 79.3; H, 6.0; O, 14.7%}.

3.1.2.2 Preparation of 8,9-dihydro-7H-cyclonona {1,2,3-de: 4,5,6-d'e'}-dinaphthalene-8,8 -dicarboxylic acid (IX)  
 (Harris and Singh, 1976).



95% Ethanol (S.V.R.) was boiled under reflux with sodium metal and then distilled: 100 ml of it was used to dissolve 60 g of KOH pellets. The diethylester (VIII) (11.0 g) was added all in one portion and heating under reflux, while stirring mechanically, continued for 3 h. until a test portion dissolved completely in water (potassium salt

formed). It was cooled, water added to dissolve the salt, boiled with decolourising charcoal and filtered. The cooled filtrate was acidified with dilute hydrochloric acid to precipitate the diacid which was filtered, washed with water and dried in an evacuated dessicator, 8.7 g, 83.3%, m.p. 235-236° with a brisk effervescence, solidifying and remelting at 253-255°. {Found: C, 75.1; H, 5.0; O, 19.8  $C_{25}H_{18}O_4 \cdot H_2O$  requires C, 75.0; H, 5.0; O, 20.0%}

I.r. (Hexachlorobutadiene mull): 1710  $cm^{-1}$  (strong, carbonyl group), and 3570, 3440  $cm^{-1}$  (broad, water).

N.m.r. (N,N-dimethylformamide):  $\delta$  8.07-6.72 (12H, Complex multiplet, aromatic);  $\delta$  4.11, 3.87; 3.30, 3.06 (4H, q,  $CH_2$ -naphthyl). (The diacid is not soluble in  $CDCl_3$  or  $CCl_4$ ).

#### Resolution of (IX)

Quinidine (5.67 g) was boiled in ethanol (250 ml) and the diacid (7.0 g) dissolved in ethanol (250 ml) added slowly. On standing overnight needles separated which were filtered off washed in ethanol and dried in an evacuated desiccator. 5.5 g, m.p. 199-205°,  $\alpha_{546} -0.28^\circ$ ,  $\{\alpha\}_{546} -56^\circ$  ( $\underline{c}$  1.0;  $\underline{l}$  0.5; N,N-dimethylformamide). {Found: C, 75.1; H, 6.0; N, 4.0; O, 14.7.  $C_{45}H_{42}N_2O_6 \cdot \frac{1}{2}H_2O$  requires C, 75.5; H, 6.0; N, 3.9; O, 14.5%}.

Second crop: 2.25 g, m.p. 180-188° (hydrated)  $\alpha_{546} + 0.98^\circ$ ,  $\{\alpha\}_{546} + 196^\circ$  ( $\underline{c}$  1.0;  $\underline{l}$  0.5; N,N-dimethylformamide). {Found: C, 75.0; H, 5.9; N, 3.8; O, 14.9%}.

Third crop: 3.52 g of unhydrated salt, m.p. 200-205°.  $\alpha_{546} + 0.87^\circ$ ,  $\{\alpha\}_{546} + 174^\circ$  ( $\underline{c}$  1.0;  $\underline{l}$  0.5; N,N-dimethylformamide). {Found: C, 76.3; H, 6.1; N, 3.85; O, 13.7  $C_{45}H_{42}N_2O_6$  requires C, 76.5; H, 6.0; N, 4.0; O, 13.6%}.

Liberation of active acids:- The (-) quinidine salt,  $\{\alpha\}_{546} -56^\circ$  (5.5 g) was suspended in chloroform and extracted with dilute aqueous sodium hydroxide. The extract was washed with chloroform and then air bubbled through to remove traces of chloroform. Acidification with cold dilute hydrochloric acid precipitated the active acid, which was filtered,

washed with water and dried in an evacuated desiccator, 2.85 g, m.p. 180-90° with effervescence, solidifying and remelting at 232-236°,  $\alpha_{546} -1.775^\circ$ ,  $\{\alpha\}_{546} -355^\circ$  ( $\underline{c}$  1.0;  $\underline{l}$  0.5; 95% ethanol). {Found: C, 78.7; H, 4.8; O, 16.65  $C_{25}H_{18}O_4$  requires C, 78.5; H, 4.7; O, 16.7%}.

The (+) quinidine salt  $\{\alpha\}_{546} +196^\circ$  (2.0 g) decomposed to give diacid, 1.10 g, m.p. 172-176° with effervescence, solidifying and remelting at 228-231°,  $\alpha_{546} +1.55^\circ$ ,  $\{\alpha\}_{546} +310^\circ$  ( $\underline{c}$  1.0;  $\underline{l}$  0.5; 95% ethanol). {Found: C, 78.4; H, 4.90; O, 16.6.  $C_{25}H_{18}O_4$  requires C, 78.5; H, 4.7; O, 16.7%}.

The (+) quinidine salt,  $\{\alpha\}_{546} +164^\circ$ , (3.40 g) gave diacid 1.55 g, m.p. 224-230°,  $\alpha_{546} +1.31^\circ$ ,  $\{\alpha\}_{546} +262^\circ$  ( $\underline{c}$  1.0; 0.5; 95% ethanol).

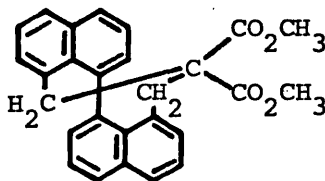
Preparation of (+)-(IX). - Hydrolysis of (+)-(VIII), 1.40 g,  $\{\alpha\}_{546} +293^\circ$ , by boiling with ethanolic potassium hydroxide for 4½ h. gave the potassium salt which was dissolved in water and acidified with dilute hydrochloric acid to give diacid, 1.07 g, m.p. 173-179° with effervescence, solidifying and remelting at 232-234°,  $\alpha_{546} +0.35^\circ$ ,  $\{\alpha\}_{546} +208^\circ$  ( $\underline{c}$  0.336;  $\underline{l}$  0.5; N,N-dimethylformamide). {Found: C, 76.5; H, 4.9; O, 18.3.  $C_{25}H_{18}O_4 \cdot \frac{1}{2}H_2O$  requires C, 76.7; H, 4.9; O, 18.4%}.

Preparation of (-)-(IX). - (-)-(IX) was similarly prepared by hydrolysis of (-)-(VIII), 1.5 g,  $\{\alpha\}_{546} -298^\circ$ , 1.11 g, m.p. 173-179° with effervescence, solidifying and remelting at 232-234°,  $\alpha_{546} -0.435^\circ$ ,  $\{\alpha\}_{546} -218^\circ$  ( $\underline{c}$  0.396;  $\underline{l}$  0.5; N,N-dimethylformamide). {Found: C, 76.6; H, 4.9; O, 18.2%}.

### 3.1.2.3 Preparation of dimethyl 8,9-dihydro-7H-cyclonona

#### (1,2,3-de:4,5,6-d'e')-dinaphthalene-8,8-dicarboxylate (X)

(Harris and Singh, 1976)



The cyclic dicarboxylic acid (1.0 g) was added to a cold ethereal solution of freshly prepared diazomethane (0.35 g) with continuous



swirling; when effervescence was over, the ethereal solution was washed with aqueous sodium carbonate and with water, dried over anhydrous sodium sulphate and the ether distilled off. Crystallisation from benzene gave 0.92 g (85.7%), m.p. 258-259°. {Found: C, 79.4; H, 5.3; O, 5.3.  $C_{27}H_{22}O_4$  requires C, 79.0; H, 5.4; O, 15.6%}.

I.r. (Hexachlorobutadiene mull):  $1760\text{ cm}^{-1}$  (strong,  $-CO.OCH_3$ ).

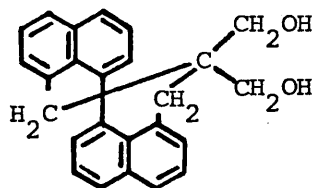
N.m.r. ( $CDCl_3$ ):  $\delta$  7.91-6.72 (12H, complex multiplet aromatic); 4.18, 3.93; 3.24, 3.00 (4H, q,  $CH_2$ -naphthyl); 3.44 (6H, t,  $CH_3$ ).

Preparation of (+)-(X). (+)-(IX) 2.5 g,  $\{\alpha\}_{546}^{+237^\circ}$ , with diazomethane gave the dimethyl ester which was crystallised from methanol, 2.0 g, m.p. 164-166°,  $\alpha_{546}^{+0.92^\circ}$ ,  $\{\alpha\}_{546}^{+368^\circ}$ , (c 0.5; l 0.5; N,N-dimethylformamide). {Found: C, 79.1; H, 5.35; O, 15.5%}.

Preparation of (-)-(X). (-)-(IX), 3.0 g,  $\{\alpha\}_{546}^{-216^\circ}$ , similarly treated gave 2.7 g of (-)di-ester, m.p. 165-167°,  $\alpha_{546}^{-91^\circ}$ ,  $\{\alpha\}_{546}^{-364^\circ}$  (c 0.5; l 0.5; N,N-dimethylformamide). {Found: C, 78.8; H, 5.4; O, 15.6%}.

#### 3.1.2.4. Preparation of 8,8-bishydroxymethyl-8,9-dihydro-7H-cyclonona-(1,2,3-de:4,5,6-d'e')-dinaphthalene (XI).

(Harris and Singh, 1976).



Lithium aluminium hydride (1.5 g, 6 equiv.) and 750 ml of anhydrous diethyl ether were heated under reflux, stirring magnetically for 1½ h. The diethyl ester (X) (3.0 g, 1 equiv. suspended in 300 ml of anhydrous diethyl ether) was added over a period of 45 minutes and heating continued for 5 h. It was cooled, the excess of reagent was destroyed by adding a few drops of water and 150 ml of dilute sulphuric acid and heating continued for another one hour; during this period the reaction mixture became clear. It was cooled, the ethereal layer was separated,

washed with water and dried over anhydrous sodium sulphate and the ether distilled off. Crystallisation from benzene gave 2.0 g, (82.5%), m.p.198-199°. {Found: C, 84.7; H, 6.3; O, 9.1.  $C_{25}H_{22}O_2$  requires C, 84.7; H, 6.3; O, 9.0%}.

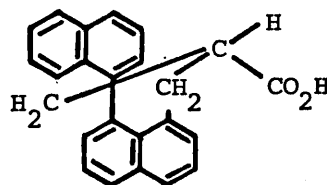
I.r. (Hexachlorobutadiene mull):  $3340\text{ cm}^{-1}$  (strong OH), 3060,3050, 3000,2970,2950 (sharp), 2930,2890 (sharp and strong) 2865 and  $2790\text{ cm}^{-1}$  (CH and  $CH_2$  stretching).

N.m.r.( $CDCl_3$ ):  $\delta$  7.92-6.68 (12H, complex multiplet, aromatic); 3.48, 3.24; 2.60,2.36 (4H, q,  $CH_2$ -naphthyl); 2.85 (4H, s,  $CH_2OH$ ) and 1.76 (2H, s, OH).

Preparation of (+)-(XI).-(+)-Dimethyl ester (X) 1.0 g,  $\{\alpha\}_{546} +368^\circ$ , was reduced as for the racemic compound; crystallisation from chloroform gave the (+)-diol, 0.45 g, m.p.187-188° (155-157°, Singh, 1972),  $\alpha_{546} +0.727^\circ$ ,  $\{\alpha\}_{546} +591^\circ$  (c 0.123; l 1.0;  $CHCl_3$ ). {Found: C, 84.7; H, 6.3; O, 8.95%}.

Preparation of (-)-(XI). (-) Dimethyl ester (X) 1.5 g,  $\{\alpha\}_{546} -364^\circ$  similarly reduced gave 0.99 g, m.p.187-188° (155-156° Singh, 1972),  $\alpha_{546} -0.895^\circ$ ,  $\{\alpha\}_{546} -721^\circ$  (c 0.124; l 1.0;  $CHCl_3$ ). {Found: C, 84.6; H, 6.3; O, 9.0%}.

3.1.2.5 Preparation of 8,9-dihydro-7H-cyclonona {1,2,3-de: 4,5,6-d'e'} dinaphthalene-8-carboxylic acid (XII). (Harris and Singh, 1976).



The cyclic dicarboxylic acid (4.0 g) was heated in a hard glass tube immersed in a metal-bath at  $230-240^\circ$  for about 15 minutes; it melted, effervesced and then solidified. It dissolved in 2.5% aqueous sodium hydroxide solution, but then precipitated as sodium salt, so more sodium hydroxide solution was added to complete the precipitation.

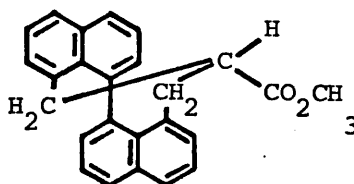
The salt was filtered off, dissolved in water and acidified with 3N hydrochloric acid giving 3.23 g (91.5%), of (XII) m.p.255-257°; after crystallisation from ethanol, 2.85 g, m.p.255-256° (252-254°, Singh, 1972). { Found: C, 85.1; H, 5.4; O, 9.4.  $C_{24}H_{18}O_2$  requires C, 85.2; H, 5.4; O, 9.45% }.

I.r (Hexachlorobutadiene mull):  $1690\text{ cm}^{-1}$  (strong, carboxylic acid group) and 3050, 3030, 2990, 2950, 2890  $\text{cm}^{-1}$  (CH, CH<sub>2</sub> stretching).

Preparation of (+)-(XII).- A specimen of the (+)-dicarboxylic acid (IX) 1.0 g ( $\{\alpha\}_{546}^{+310^\circ}$  and  $\{\alpha\}_{546}^{+208^\circ}$ ) treated as above gave 0.75 g, m.p.227-229° (220-222°, Singh, 1972),  $\alpha_{546}^{+0.55^\circ}$ ;  $\{\alpha\}_{546}^{+423^\circ}$  ( $\underline{c}$  0.13;  $\underline{l}$  1.0; 95% ethanol). { Found: C, 83.6; H, 5.6; O, 10.6. ( $C_{24}H_{18}O_2$ )<sub>3</sub>H<sub>2</sub>O requires C, 83.7; H, 5.5; O, 10.8% }.

Preparation of (-)-(XII).- Three specimens of -(IX), ( $\{\alpha\}_{546}^{-216^\circ}$ ,  $\{\alpha\}_{546}^{-221^\circ}$ ,  $\{\alpha\}_{546}^{-355^\circ}$ , N,N-dimethylformamide) 2.5 g combined, were treated as above. Crystallisation from ethanol gave (XII) m.p.225-228° (220-222°, Singh, 1972)  $\alpha_{546}^{-11.23^\circ}$ ,  $\{\alpha\}_{546}^{-527^\circ}$  ( $\underline{c}$  1.06;  $\underline{l}$  2.0; 95% ethanol). { Found: C, 83.1; H, 5.6; O, 11.3. ( $C_{24}H_{18}O_2$ )<sub>2</sub>H<sub>2</sub>O requires C, 83.0; H, 5.6; O, 11.5% }.

3.1.2.6 Preparation of methyl 8,9-dihydro-7H-cyclonona  
{ 1,2,3-de:4,5,6-d'e' }-dinaphthalene-8-carboxylate (XIII).  
(Harris and Singh, 1976).



(The procedure of Harris and Shyam Singh (1976) was followed with very careful precautions against water. The yield of ester was almost quantitative, while the previous workers recovered half of the original acid.)

The powdered acid (XII) 3.0 g was suspended in anhydrous benzene

(100 ml) in a three-necked round bottomed flask fitted with a dropping funnel, stopper and a water condenser carrying a calcium chloride tube and heated under reflux for about 30 minutes. Freshly distilled thionyl chloride (2 ml) was added dropwise to the magnetically stirred suspension and boiled for 3½ hours: the solution became clear. It was cooled and 10 ml of anhydrous methanol added and the mixture heated under reflux for another hour. It was cooled, washed three times with water, three times with aqueous sodium carbonate and finally with water. The crude ester after removal of benzene (3.05 g, m.p.188-190°) was recrystallised from a mixture of ethyl acetate and ethanol (1:1) and dried under vacuum at 80° for two hours, 2.92 (93.4%), m.p.190-192° (186-188° Singh, 1972). {Found: C, 85.1; H, 5.7; O, 9.25. C<sub>25</sub>H<sub>20</sub>O<sub>2</sub> requires C, 85.2; H, 5.7; O, 9.1%}.

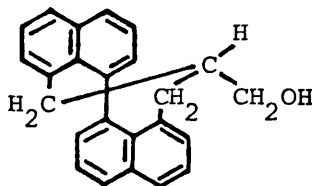
I.r. (Hexachlorobutadiene mull): 1835 cm<sup>-1</sup> (strong, methoxycarbonyl group) and 3055,3035,3000,2955,2910,2895,2840 cm<sup>-1</sup> (CH and CH<sub>2</sub> stretching).

N.m.r. (CDCl<sub>3</sub>): δ 7.90-6.75 (12H, complex multiplet, aromatic); δ 3.90,3.66;2.98,2.73 (4H, q, CH<sub>2</sub>-naphthyl); 3.38(3H, s, -COOCH<sub>3</sub>).

Preparation of (+)-(XIII). The (+) acid (XII) 2.0 g, {α<sub>546</sub>+327°, was esterified by treatment with ethereal diazomethane and crystallised from methanol, 1.66 g, m.p.111-113°, α<sub>546</sub>+0.728°, {α<sub>546</sub>+644° (c 0.113; l 1.0; CHCl<sub>3</sub>). {Found: C, 85.0; H, 5.8; O, 9.1%}. ({α<sub>546</sub><sup>21</sup>+444°, 95% ethanol, m.p.111-112°, Singh, 1972).

Preparation of (-)-(XIII). The (-) acid (XII) 2.5 g, {α<sub>546</sub>-531°, esterified as above and crystallised from methanol gave 2.25 g, m.p. 111-113°, α<sub>546</sub>-1.009°, {α<sub>546</sub>-638° (c 0.158; l 1.0; CHCl<sub>3</sub>). {Found: C, 85.0; H, 5.7; O, 9.0%}. ({α<sub>546</sub><sup>21</sup>-478°, 95% ethanol, m.p.110-112°, Singh, 1972).

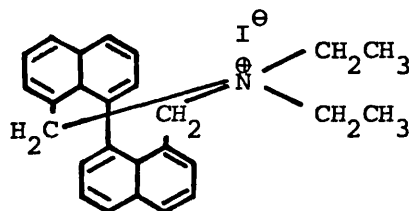
3.1.2.7. Preparation of 8-hydroxymethyl-8,9-dihydro-7H-cyclonona{1,2,3-de:4,5,6-d'e'}-dinaphthalene (XIV). -  
(Harris and Singh, 1976)



The ester (XIII) is only slightly soluble in ether therefore it (1.0 g) was placed in the thimble of a Soxhlet extractor which had been oven-dried, with 0.45 g of powdered lithium aluminium hydride suspended in 400 ml of anhydrous diethyl ether in the flask. After heating for three hours, stirring magnetically, the excess of the reagent was decomposed with wet ether, a little water, and dilute sulphuric acid; heating was continued for another hour and the ethereal layer then washed with water, dried over anhydrous sodium sulphate and the ether distilled off. The crude product after boiling in cyclohexane with decolourising charcoal crystallised, 0.62 g, m.p. 74-76°. {Found: C, 87.9; H, 7.0; O, 5.0.  $C_{24}H_{20}O$  requires C, 88.75; H, 6.2; O, 4.9%}. I.r. (Hexachlorobutadiene mull): 3580 (weak), 3330 (broad, OH) and 3055, 3005, 2930, 2880  $cm^{-1}$  (CH and  $CH_2$  stretching).

3.1.3 9-Membered Ring 8,8'-Bridged-1,1'-Binaphthyls with Nitrogen in the Ring.

3.1.3.1 Preparation of 8-diethylazonium-8,9-dihydro-7H-{1,2,3-de:4,5,6-d'e'}-dinaphthalene}cyclononane iodide (V). -  
(Singh, 1972)



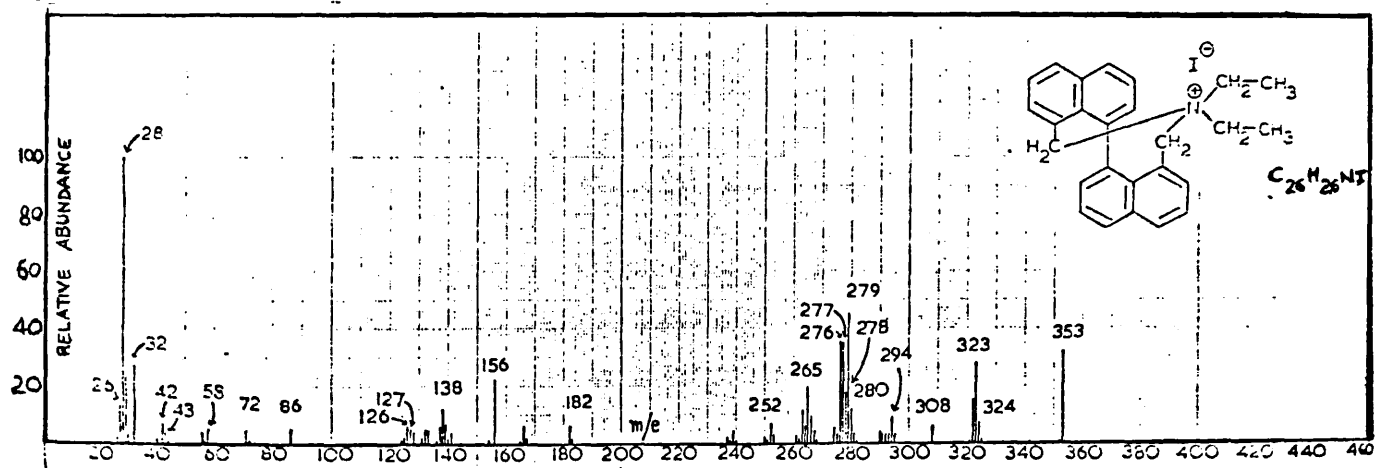
8,8'-Bisbromomethyl-1,1'-binaphthyl (2.0 g) was dissolved in anhydrous

benzene by heating. Freshly distilled diethylamine (0.74 g, 2.2 equiv.) was added during 20 minutes and heating continued for another 15 minutes. Precipitation of the bromide was completed by adding petroleum ether (b.p.40-60°). It was filtered off, but quickly absorbed water from the atmosphere. It was dissolved in water and boiled with decolourising charcoal, but failed to crystallise. Addition of hot aqueous potassium iodide precipitated the corresponding iodide. The monohydrate crystallised from water in needles, 1.8 g (79%), m.p. 210-212°. {Found: C, 62.8; H, 5.8; N, 2.7; O, 3.05; I, 25.6.  $C_{26}H_{26}NI \cdot H_2O$  requires C, 62.8; H, 5.6; N, 2.8; O, 3.2; I, 25.55%}

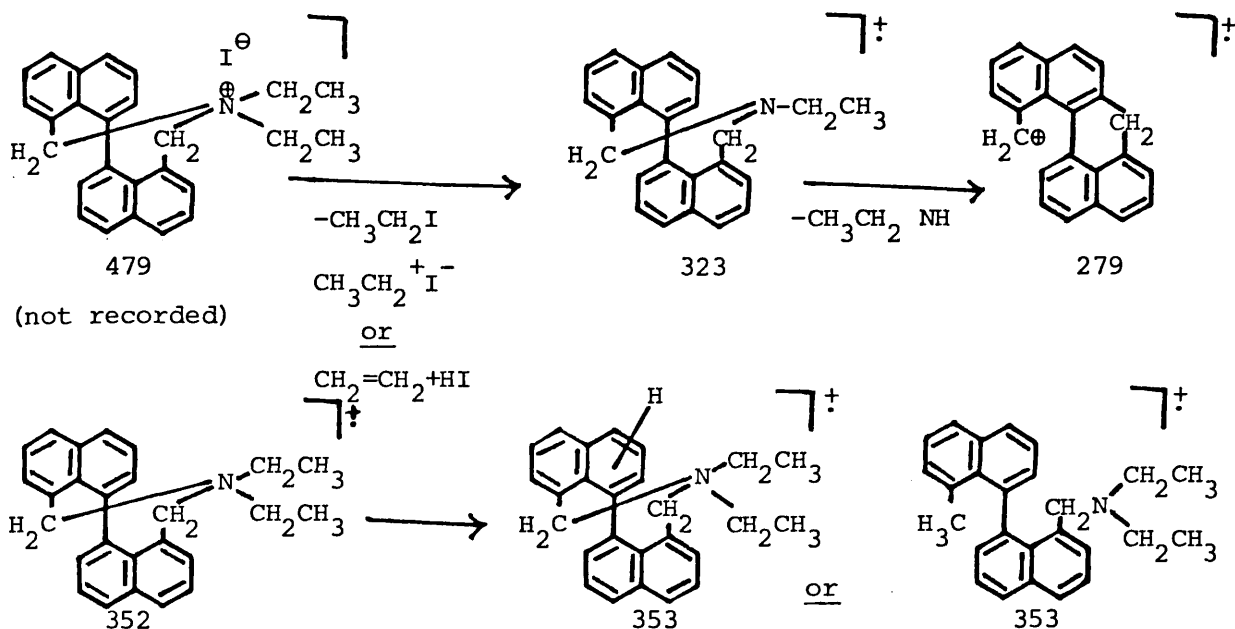
I.r. (Hexachlorobutadiene mull): 3480, 3430  $cm^{-1}$  (water); 3025, 3010, 2985, 2960, 2895  $cm^{-1}$  ( $CH_2, CH_3$  stretching).

N.m.r. ( $CDCl_3$ ):  $\delta$  8.16-6.75 (12H, complex multiplet, aromatic); 5.30, 5.06; 4.88, 4.64 (4H, q,  $CH_2$ -naphthyl); 3.01, 2.89; 2.78, 2.66 (4H, q,  $CH_2$  ethyl group); 1.28, 1.17, 1.05 (6H, t,  $CH_3$  ethyl group).

Mass spectrum: Mass measured 352.2063, calc. for  $C_{26}H_{26}N$  352.2065.



Amines may produce a  $(P+H)^+$  ion by ion-molecule reaction. Some of the fragments may be as follows:



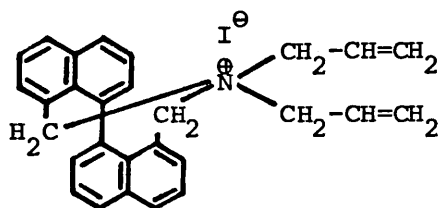
Preparation of (+)-(V). - (+)-8,8'-Bisbromomethyl-1,1'-binaphthyl 2.0 g,  $\{\alpha\}_{546} +386^\circ$ , and freshly distilled diethylamine (0.74 g) in anhydrous benzene (25 ml) treated as above gave colourless needles of (+)-(V) monohydrate, 1.0 g, m.p. 200-202 $^\circ$ ,  $\alpha_{546} +2.10^\circ$ ,  $\{\alpha\}_{546} +420^\circ$ , ( $c$  1.0;  $l$  0.5; N,N-dimethylformamide). { Found: C, 62.8; H, 5.6; N, 2.8; O, 3.2; I, 25.3% }.

Preparation of (-)-(V). (-)-(V) was similarly prepared from (-)-8,8'-bisbromomethyl-1,1'-binaphthyl 1.5 g,  $\{\alpha\}_{546} -409^\circ$  and diethylamine (0.55 g) gave 0.6 g of unhydrated crystals, m.p. 199-202 $^\circ$ ,  $\alpha_{546} -0.395^\circ$ ,  $\{\alpha\}_{546} -379.8^\circ$  ( $c$  0.208;  $l$  0.5; N,N-dimethylformamide).

{ Found: C, 64.1; H, 5.7; N, 3.2; I, 27.0% }

### 3:1.3.2 Preparation of 8-diallylazonium-8,9-dihydro-7H-[1,2,3-de:4,5,6-d'e']-dinaphthalene} cyclononane iodide (VI).

(Badar, 1964; Singh, 1972).



8,8'-Bisbromomethyl-1,1'-binaphthyl (2.0 g) reacted similarly in benzene with diallylamine (1 g, 2.2 equiv.). The precipitated bromide

was dissolved in water, boiled with charcoal, filtered and concentrated. Hot aqueous potassium iodide was added; on concentration the iodide crystallised, and was recrystallised from water, giving needles, 1.5 g (65.3%), m.p.183-185°.

{Found: C, 66.6; H, 5.3; N, 2.7; I, 25.15.  $C_{28}H_{26}NI$  requires C, 66.8; H, 5.2; N, 2.8; I, 25.2%}.

I.r.(Hexachlorobutadiene mull): 3550,3470  $cm^{-1}$ (water); 3080  $cm^{-1}$  (R-CH=CH<sub>2</sub>), 3045,3000,2970,2940  $cm^{-1}$  (CH,CH<sub>2</sub> stretching).

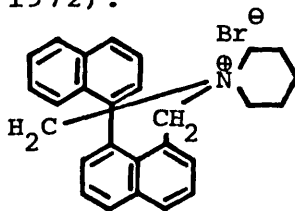
N.m.r.(CDCl<sub>3</sub>):  $\delta$  8.22-6.81 (12H, complex multiplet, aromatic): 5.36, 5.13; 4.81, 4.58 (4H, q, CH<sub>2</sub>-naphthyl); 5.84, 5.59 (2H, two doublets, CH); 4.46,4.25;3.37,3.14 (4H,CH<sub>2</sub>, four doublets, CH<sub>2</sub> attached to  $>N^{\oplus}$ ); 5.44, 5.28, 5.14, 5.00 (4H, CH<sub>2</sub>-allyl CH=CH<sub>2</sub>).

Preparation of (+)-(VI). - (+)-8,8'-Bisbromomethyl-1,1'-binaphthyl, 2.0 g,  $[\alpha]_{546}^{+386^{\circ}}$ , and diallylamine (1 g) treated as above gave colourless needles. 1.05 g, m.p.179-183°,  $\alpha_{546}^{+1.225^{\circ}}$ ,  $[\alpha]_{546}^{+245^{\circ}}$  (c 1.0; l 0.5; N,N-dimethylformamide). {Found: C, 66.7; H, 5.1; N, 2.7; I, 25.1%}.

Preparation of (-)-(VI). (-)-8,8'-Bisbromomethyl-1,1'-binaphthyl, 2.0 g,  $[\alpha]_{546}^{-409^{\circ}}$ , was treated similarly with diallylamine and the bromide  
: analysis showed that this conversion was incomplete.  
converted into iodide. Crystallisation from water gave needles 0.7 g, m.p.176-178°,  $\alpha_{546}^{-1.33^{\circ}}$ ,  $[\alpha]_{546}^{-266^{\circ}}$  (c 1.0; l 0.5; N,N-dimethylformamide). {Found: C, 69.5; H, 5.6; N, 2.6; I, 11.4; Br, 10.7%}.

### 3.1.3.3. Preparation of 8-spiropiperidinium-8,9-dihydro-7H-

{1,2,3-de: 4,5,6-d'e'-dinaphthalene} cyclononane bromide  
(VII). - (Singh, 1972).



8,8'-Bisbromomethyl-1,1'-binaphthyl (2.0 g) was dissolved in 20 ml of chloroform and a solution of piperidine (1 ml,2.2 equiv) in 20 ml of

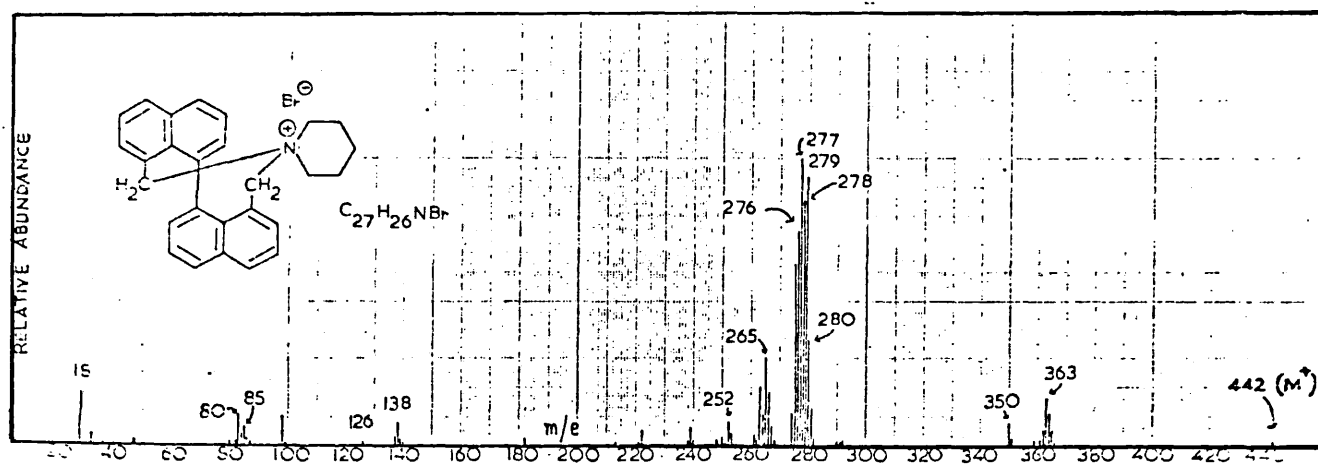


chloroform added dropwise while stirring magnetically. The reaction mixture was heated under reflux for 90 minutes, cooled, and petroleum ether (b.p.40-60°) added to complete the precipitation. The solid bromide was dissolved in water, boiled with decolourising charcoal, filtered and the solution concentrated; the bromide crystallised, 1.5 g (74 %), m.p.267-269°<sub>d</sub>. {Found: C, 73.1; H, 5.9; N, 3.05; Br, 17.8. C<sub>27</sub>H<sub>26</sub>N Br requires C, 73.0; H, 5.9; N, 3.15, Br. 18.0%}.

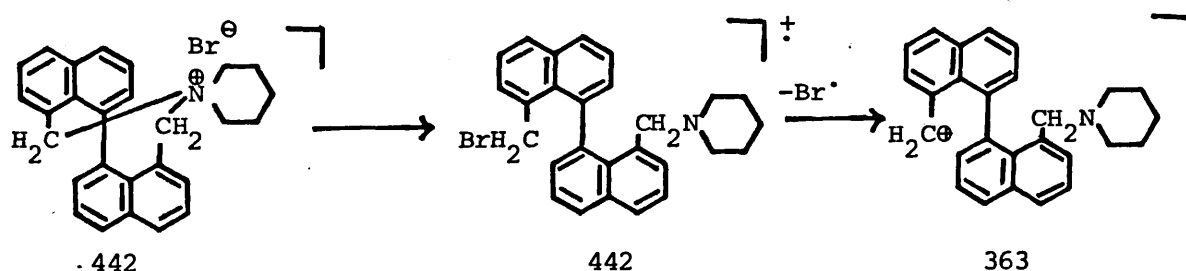
I.r. (Hexachlorobutadiene mull): 3040,3010 cm<sup>-1</sup> (strong),2990,2980, 2970,2940,2900,2860 cm<sup>-1</sup> (CH, CH<sub>2</sub>, stretching)

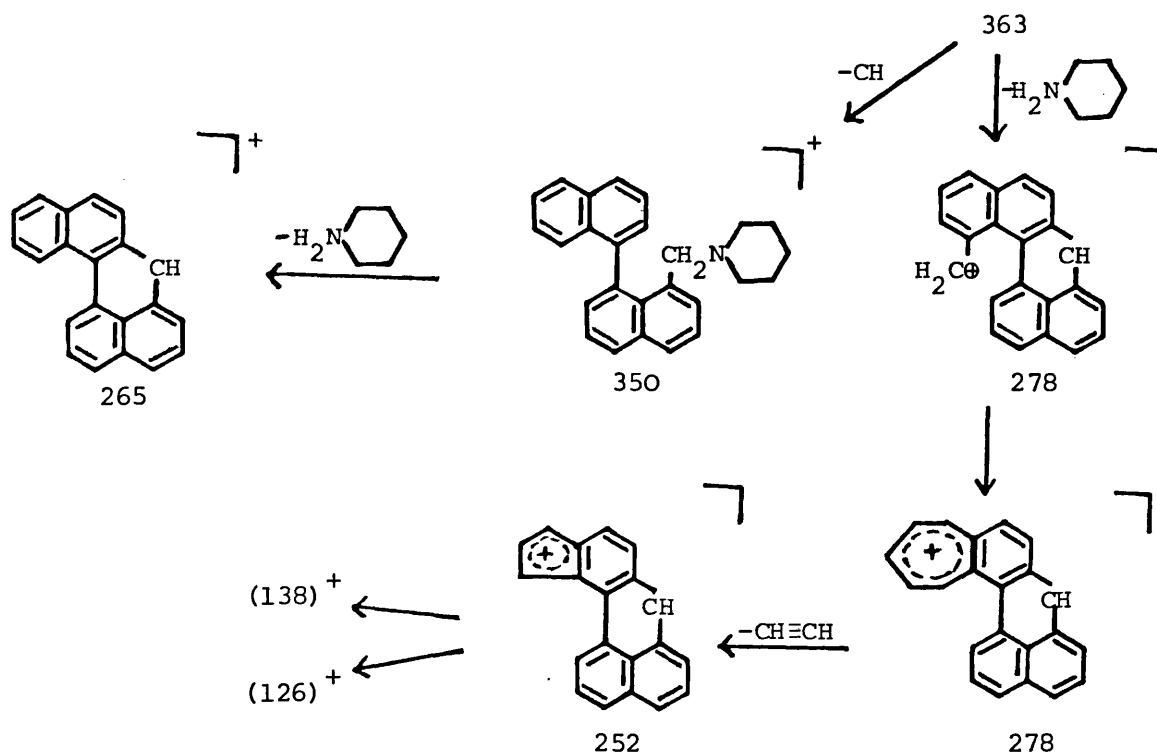
N.m.r. (CDCl<sub>3</sub>, 220 MHz) δ 8.20-6.80(12H, complex multiplet, aromatic); 5.18, 5.11; 5.07, 5.00(4H, q, CH<sub>2</sub>-attached to naphthyl); 3.01 (4H, s, CH<sub>2</sub>->N<); 1.82 (6H, s, CH<sub>2</sub>,N<CH<sub>2</sub>>CH<sub>2</sub>).

Mass spectrum: Mass measured 442.1184, calc. for C<sub>27</sub>H<sub>25</sub>N<sup>79</sup>Br 442.1171.



Quaternary ammonium salts may undergo thermal decomposition into neutral particles which then are vaporised and ionised; in the present case an ion with the molecular weight of the original ammonium salt will be encountered (Budzikiewicz, Djerassi and Williams, Mass spectrometry of Organic Compounds, 1967, p.330).





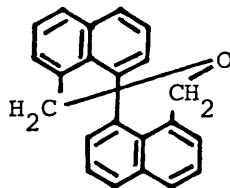
Preparation of (+)-(VII).-(+)-8,8'-Bisbromomethyl-1,1'-binaphthyl

1.0 g,  $\{\alpha\}_{546}^{+280^\circ}$  and piperidine in benzene similarly gave (+)-(VII) monohydrate 0.58 g, m.p. 241-244 $^\circ$ ,  $\alpha_{546}^{+1.285^\circ}$ ,  $\{\alpha\}_{546}^{+514^\circ}$  ( $c$  0.5;  $l$  0.5 N,N-dimethylformamide). { Found: C, 70.2; H, 6.1; N, 2.9; Br, 17.2; O, 3.3.  $C_{27}H_{26}N Br \cdot H_2O$  requires C, 70.1; H, 6.1; N, 3.0; Br, 17.3; O, 3.5% }.

Preparation of (-)-(VII).-(-)-8,8'-Bisbromomethyl-1,1'-binaphthyl

2.0 g  $\{\alpha\}_{546}^{-380^\circ}$  and piperidine treated as above gave (-)-(VII) monohydrate 1.20 g, m.p. 241-244 $^\circ$ ,  $\alpha_{546}^{-1.315^\circ}$ ,  $\{\alpha\}_{546}^{-526^\circ}$  ( $c$  0.5;  $l$  0.5; N,N-dimethylformamide). { Found: C, 70.3; H, 6.1; N, 2.9; Br, 17.5; O, 3.3% }.

## 3.2. NEW COMPOUNDS

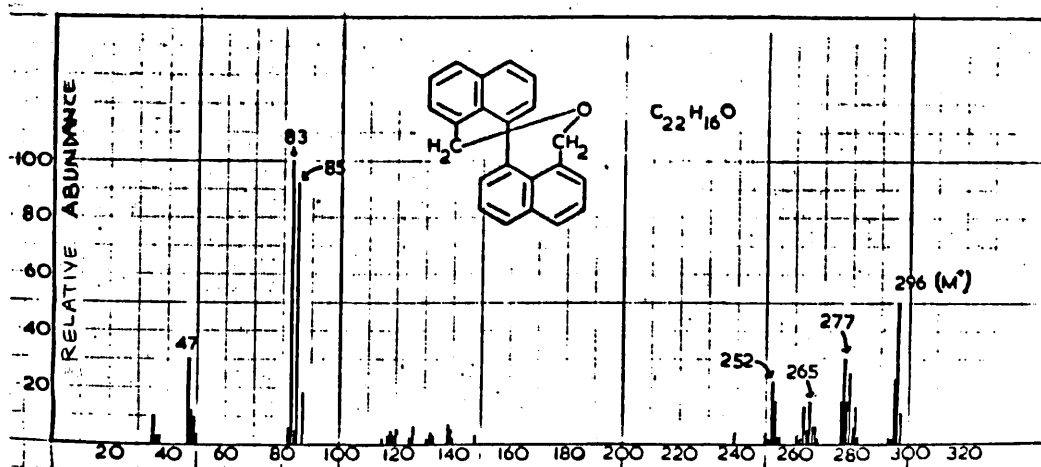
3.2.1. 9-Membered Ring 8,8'-Bridged-1,1'-Binaphthyls with Oxygen, Sulphur, and Selenium in the Ring3.2.1.1 Preparation of 8-Oxa-8,9-dihydro-7H-[1,2,3-de:4,5,6-d'e'-dinaphthalene]cyclononane (I).

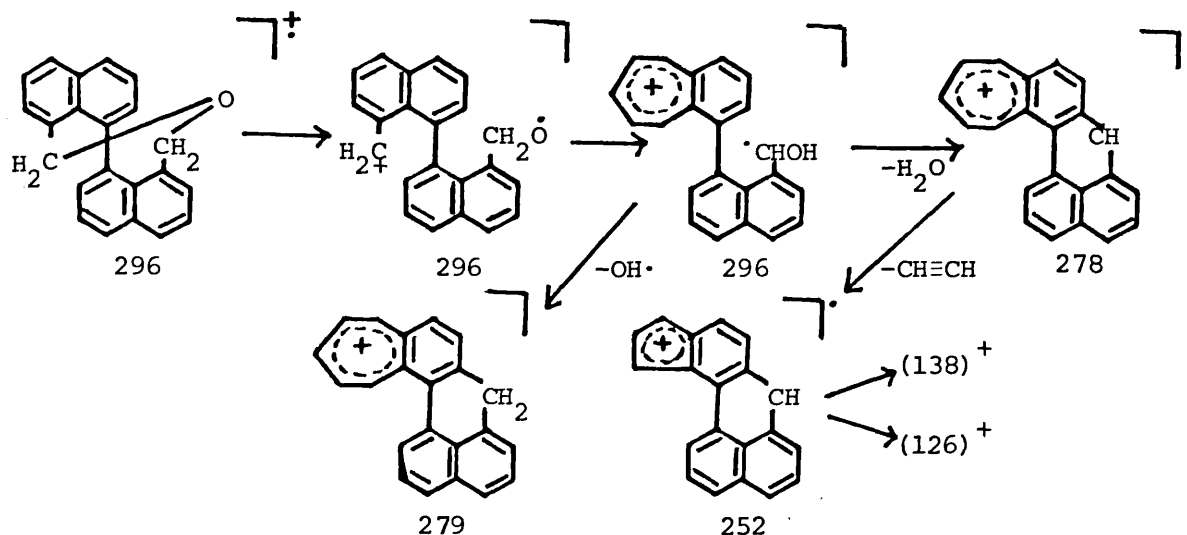
A solution of 8,8'-bishydroxymethyl-1,1'-binaphthyl (10 g in 120 ml of benzene) and toluene-*p*-sulphonic acid monohydrate (0.8 g, in 960 ml of benzene) was heated under reflux for 16 h in a three necked round bottomed flask which had been fitted with a Dean-Stark water trap. The benzene solution was washed with 5% sodium carbonate and solvent was removed under reduced pressure. The residual solid was dissolved in benzene and purified by chromatography on alumina using ether-benzene as eluent. It was recrystallised from benzene (5.5 g, 58%) m.p.169-170<sup>o</sup>, {Found: C, 89.0; H, 5.4; O, 5.5. C<sub>22</sub>H<sub>16</sub>O requires C, 89.2; H, 5.4; O, 5.4%}~

I.r. (Nujol mull): 1071,1098 cm<sup>-1</sup> (-CH<sub>2</sub>-O-CH<sub>2</sub>,cyclic).

N.m.r.(CDCl<sub>3</sub>): δ 7.96-6.85 (12H,complex multiplet, aromatic); 5.53,5.40; 4.33,4.20 (4H, *q*, CH<sub>2</sub>-naphthyl).

Mass spectrum: Mass measured, 296.1194, calc. for C<sub>22</sub>H<sub>16</sub>O 296.1201

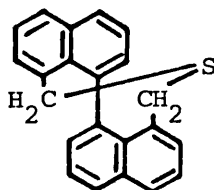




Preparation of (+)-(I), (-)-Dimethyl 1,1'-binaphthyl-8,8'-dicarboxylate (XVI) ( $\alpha_{546} -0.532^\circ$ ;  $\{\alpha\}_{546} -305.7^\circ$ ;  $c$  0.174;  $l$  1.0;  $CHCl_3$ ) (8.0 g) was reduced to (+)-8,8'-bishydroxymethyl-1,1'-binaphthyl 1.8 g, m.p. 145-147 $^\circ$  ( $\alpha_{546} +0.037^\circ$ ,  $\{\alpha\}_{546} +13^\circ$ ;  $c$  0.276;  $l$  1.0;  $CHCl_3$ ) but mainly yellow sticky material of higher rotation. Approximately 6.0 g of the sticky material was heated under reflux with toluene-*p*-sulphonic acid monohydrate (0.6 g) in benzene (270 ml) for 21 h and worked up as for the racemic compound. After three crystallisations from benzene, it gave 0.32 g of (+)-(I), m.p. 196-197.5 $^\circ$ ;  $\alpha_{546} +1.31^\circ$ ,  $\{\alpha\}_{546} +1119^\circ$  ( $c$  0.117;  $l$  1.0;  $CHCl_3$ ). {Found: C, 89.0; H, 5.5; O, 5.5%}: further fractions had  $\{\alpha\}_{546} +51^\circ$ ; +660 $^\circ$ ; 972 $^\circ$ ; +1271 $^\circ$ .

Preparation of (-)-(I). (+)-Dimethyl 1,1'-binaphthyl-8,8'-dicarboxylate ( $\alpha_{546} +0.861^\circ$ ,  $\{\alpha\}_{546} +284^\circ$ ;  $c$  0.303;  $l$  1.0;  $CHCl_3$ ) (8.0 g) was reduced to (-)-8,8'-bishydroxymethyl-1,1'-binaphthyl 4.1 g, m.p. 145-147 $^\circ$ ,  $\alpha_{546} -0.007^\circ$ ,  $\{\alpha\}_{546} -3.6^\circ$  ( $c$  0.19;  $l$  1.0;  $CHCl_3$ ) and some sticky material. Treated as above, this gave 0.30 g of (-)-(I), m.p. 190-192 $^\circ$ ,  $\alpha_{546} -1.167^\circ$ ,  $\{\alpha\}_{546} -1100^\circ$  ( $c$  0.106;  $l$  1.0;  $CHCl_3$ ). {Found: C, 89.2; H, 5.5; O, 5.4%}.

3.2.1.2 Preparation of 8-thia-8,9-dihydro-7H-[1,2,3-de:4,5,6-d'e'-dinaphthalene]-cyclononane (II). -



(This method was adapted from that used by Truce and Emrick (1956) and by Mislow and co-workers (1964) to prepare cyclic 7-membered rings in the 2,2'-disubstituted-biphenyl and 2,2'-disubstituted 1,1'-binaphthyl series).

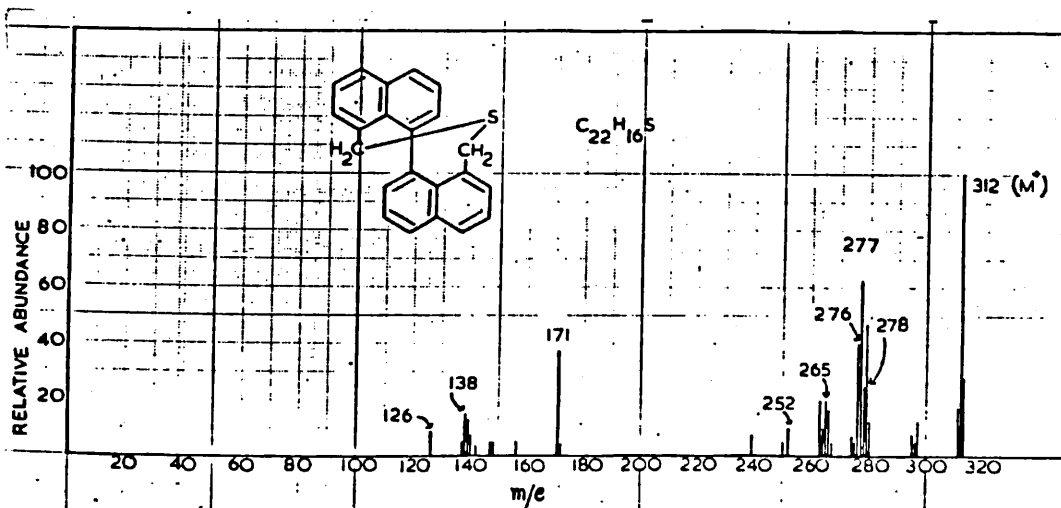
A mixture of 320 ml of methanol, 16 ml of distilled water, 8,8'-bisbromomethyl-1,1'-binaphthyl (7.74 g, 0.0176 mole) and sodium sulphide nonahydrate ( $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ , 12.72 g, 0.053 mole) was heated under reflux with vigorous stirring for 24 hr. After distilling off most of the methanol and treating the residue with ice-water, the crude product was filtered off and washed with water and a little methanol. After boiling in ethanol with decolourising charcoal it formed colourless crystals, 5.0 g, (91%), m.p. 240-241 $^{\circ}$ . {Found: C, 84.8; H, 5.2; S, 10.1.  $\text{C}_{22}\text{H}_{16}\text{S}$  requires C, 84.6; H, 5.1; S, 10.25%}.

I.r. (Nujol mull): 625, 658, 705  $\text{cm}^{-1}$  (C-S stretch).

N.m.r. ( $\text{CDCl}_3$ ):  $\delta$  7.91-6.78 (12H, complex multiplet, aromatic); 4.83, 4.68;

3.41, 3.26 (4H, q,  $\text{CH}_2$ -naphthyl).

Mass spectrum: Mass measured 312.0970, calc. for  $\text{C}_{22}\text{H}_{16}\text{S}$  312.0972.

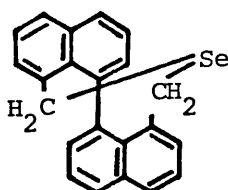


Many of the fragmentations are analogous to those for compound (I).  
Preparation of (+)-(II). (+)-8,8'-Bisbromomethyl-1,1'-binaphthyl 2.5 g,  $\{\alpha\}_{546} +351^{\circ}$ , N,N-dimethylformamide) and sodium sulphide nonahydrate (8.0 g) in 100 ml of methanol and 5 ml of distilled water was boiled under reflux for 24 h. Methanol was distilled off and the crude solid product filtered, washed with water and dried. Crystallisation from ethanol gave colourless crystals, 1.5 g, m.p.194-195 $^{\circ}$ ,  $\alpha_{546} +1.065^{\circ}$ ,  $\{\alpha\}_{546} +832^{\circ}$ ; ( $c$  0.256;  $l$  0.5; N,N-dimethylformamide). {Found: C, 84.6; H, 5.2; S, 10.2%}.

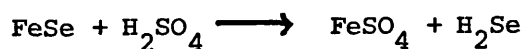
Preparation of (-)-(II). (-)-(II) was similarly prepared from (-)-8,8'-bisbromomethyl-1,1'-binaphthyl 1.5 g,  $\{\alpha\}_{546} -396^{\circ}$ . Crystallisation from ethanol gave colourless crystals. 0.8 g, m.p.190-191 $^{\circ}$ ,  $\alpha_{546} -0.505^{\circ}$ ,  $\{\alpha\}_{546} -855^{\circ}$  ( $c$  0.059;  $l$  1.0; N,N-dimethylformamide). {Found: C, 84.6; H, 5.1; S, 10.3%}, other reactions had  $\{\alpha\}_{546} -593^{\circ}$ .

3.2.1.3. Preparation of 8-Selena-8,9-dihydro-7H-{1,2,3-de:4,5,6-d'e'-dinaphthalene}-cyclononane (III)

(Truce and Emrick, 1956)

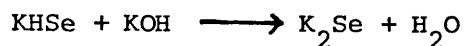
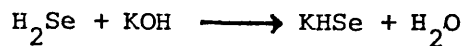


(a) Preparation of Hydrogen Selenide-



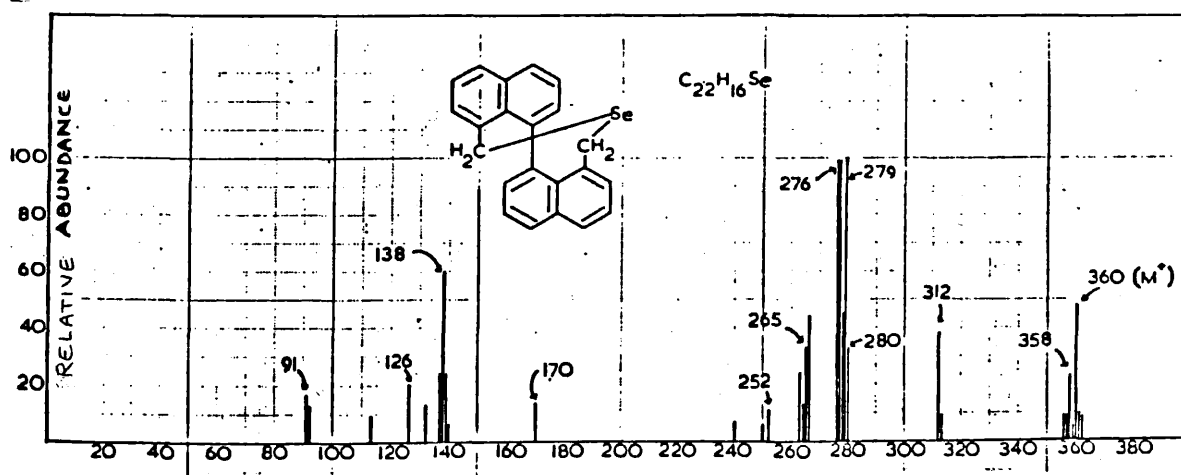
Ferrous selenide was prepared by heating to redness an intimate mixture of equimolar quantities of powdered selenium (3.66 g) and iron filings (2.6 g) under nitrogen. Hydrogen selenide gas was generated by the action of warm sulphuric acid (15.4 ml) upon the powdered ferrous selenide.

(b) Potassium selenide solution was prepared as follows:



Potassium hydroxide pellets (2.6 g) were dissolved in water (12 ml) and the cooled solution saturated with excess of hydrogen selenide gas under nitrogen. This was followed by the addition of a cold solution of 2.6 g of potassium hydroxide pellets in 4 ml of water.

(c) The potassium selenide solution (18 ml, 0.044 mole) was added to 8,8'-bisbromomethyl-1,1'-binaphthyl (5.2 g, 0.012 mole) suspended in 320 ml of methanol under nitrogen. It was boiled under reflux with rapid stirring for 24 h. About 275 ml of methanol was distilled off. The remaining solid was filtered off and washed with water. It was put on to an alumina column in benzene and eluted using petroleum ether benzene, thus removing some dark red material. The solvent was removed on the rotatory evaporator, and the residue boiled in petroleum ether (b.p. 80-100°) with decolourising charcoal; it formed colourless crystals, 2.6 g (61%), m.p. 240-241°. {Found: C, 73.65; H, 4.6; Se, 21.8.  $\text{C}_{22}\text{H}_{16}\text{Se}$  requires C, 73.5; H, 4.5, Se, 22.0%}. N.m.r. ( $\text{CDCl}_3$ ):  $\delta$  7.86-6.77 (12H, complex multiplet, aromatic) 4.94, 4.81; 3.55, 3.42 (4H, q,  $\text{CH}_2$ -naphthyl). Mass spectrum: Mass measured 360.0424, calc. for  $\text{C}_{22}\text{H}_{16}\text{Se}$  360.0417.

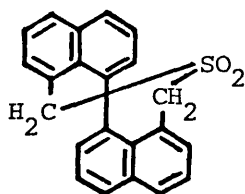


Many of the fragmentations are analogous to those compounds (I) and (II).

Preparation of (+)-(III). (+)-8,8'-Bisbromomethyl-1,1'-binaphthyl- (2.0 g),  $\{\alpha\}_{546} +420.5^{\circ}$ , and potassium selenide solution (10 ml) heated as above gave colourless crystals of (+)-(III), 0.83 g, m.p.232-234 $^{\circ}$ ,  $\alpha_{546} +0.59^{\circ}$ ,  $\{\alpha\}_{546} +472^{\circ}$ . ( $\underline{c}$  0.25;  $\underline{l}$  0.5; N,N-dimethylformamide). {Found: C, 73.3; H, 4.5; Se, 21.7%}.

Preparation of (-)-(III). (-)-8,8'-Bisbromomethyl-1,1'-binaphthyl (1.5 g),  $\{\alpha\}_{546} -396^{\circ}$  and potassium selenide solution (8 ml) heated as above gave 0.65 g, m.p.232-234 $^{\circ}$ ,  $\alpha_{546} -0.835^{\circ}$ ,  $\{\alpha\}_{546} -417^{\circ}$  ( $\underline{c}$  0.20;  $\underline{l}$  1.0; N,N-dimethylformamide). {Found: C, 73.5; H, 4.5; Se, 21.7%}

#### 3.2.1.4 Preparation of 8-thiadioxy-8,9-dihydro-7H-{1,2,3-de: 4,5,6-d'e'-dinaphthalene}cyclononane (IV).



The thiopin (II) (2.5 g, 0.0072 mole), 30% hydrogen peroxide (20 ml, 0.092 mole) and 25 ml of glacial acetic acid were boiled under reflux for about 90 minutes. The solution was cooled to -5 $^{\circ}$  and then cooled below 1 $^{\circ}$  overnight. The resulting white needles were filtered off, washed with cold glacial acetic acid and recrystallised from ethanol. 2.45 g, (89%), m.p.300-302 $^{\circ}$ . {Found: C, 76.7; H, 4.7; S, 9.3; O, 9.4.  $C_{22}H_{16}SO_2$  requires C, 76.7; H, 4.7; S, 9.3; O, 9.3%}.

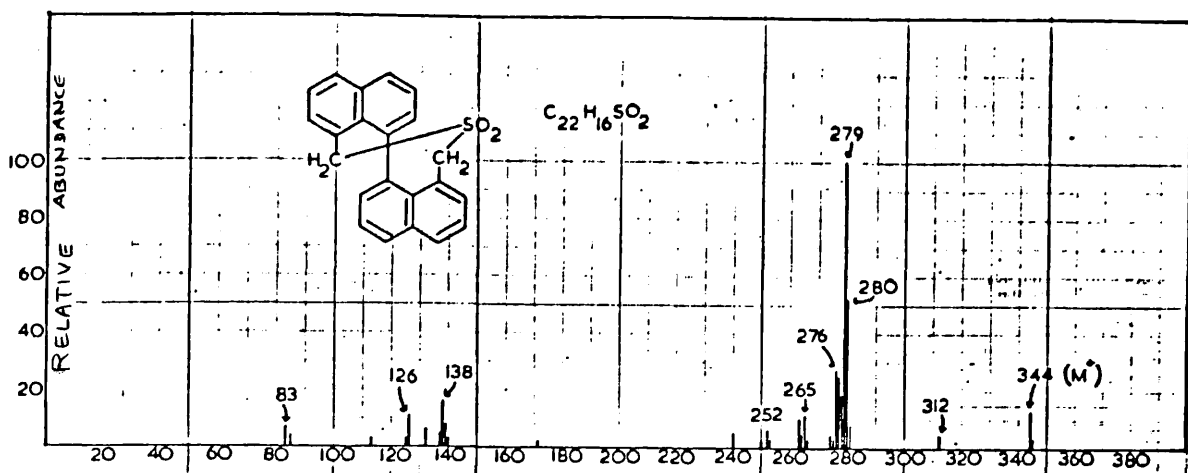
I.r. (Nujol mull): 1150,1310,1330  $cm^{-1}$  ( $\nu_{SO_2}$ ).

N.m.r. ( $CDCl_3$ ):  $\delta$  8.06-6.84 (12H, complex multiplet, aromatic),

5.13,4.99; 3.86, 3.72 (4H, q,  $CH_2$ -naphthyl).

Mass spectrum: Mass measured 344.0874, calc. for  $C_{22}H_{16}SO_2$  344.0871.





Many of the fragmentations are analogous to those for (I), (II) and (III).

Preparation of (+)-(IV). The (+) thiepin (II) (0.50 g),  $[\alpha]_{546}^{+832^{\circ}}$ , 30% hydrogen peroxide (5 ml) and glacial acetic acid (10 ml) were boiled under reflux for two hours and worked up as for the racemic compound to give 0.40 g, m.p. 277-280<sup>o</sup>,  $\alpha_{546}^{+0.535^{\circ}}$ ,  $\{\alpha\}_{546}^{+438^{\circ}}$  ( $\underline{c}$  0.244;  $\underline{l}$  0.5; N,N-dimethylformamide). { Found: C, 76.6; H, 4.6; O, 9.4; S, 9.3% }.

Preparation of (-)-(IV). The (-) thiepin (II) (0.50 g),  $[\alpha]_{546}^{-593^{\circ}}$ , similarly treated gave 0.45 g, m.p. 275-279<sup>o</sup>,  $\alpha_{546}^{-0.855^{\circ}}$ ,  $\{\alpha\}_{546}^{-365^{\circ}}$  ( $\underline{c}$  0.468;  $\underline{l}$  0.5; N,N-dimethylformamide). { Found: C, 76.6; H, 4.6; O, 9.4; S, 9.4% }.

## 4 PROTON NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

### 4.1 Introduction: General Description and Relevance to Stereochemistry

Proton n.m.r. spectroscopy is very useful to the organic stereochemist. It can give information about the spatial arrangement of functional groups containing hydrogen atoms and of hydrocarbon residues. The important features of the n.m.r. spectra are: (a) the chemical shift of protons:- i.e. the difference between the position of the resonance signal in cycles per second (cps or Hz) and the signal of a standard, often tetramethylsilane (TMS): a spectrum is normally calibrated in  $\delta$  units and  $\delta$  is field independent,

$$\delta = \frac{\text{observed shift (cps)}}{\text{oscillator frequency in MHz}}$$

Some workers use the T scale, where  $T = 10 - \delta$ : (b) Integration:- this allows the estimation of the number of protons associated with a particular resonance: (c) Spin-Spin Coupling:- coupling occurs between certain chemically non-equivalent protons. The patterns show the number and kind of protons on adjacent carbon atoms: (d) Coupling Constant:- the coupling constant J is the separation in cps between the peaks formed by splitting of the signal of one proton by another, due to coupling of the spins. Coupling constants are dependent upon the structural situation of the protons concerned. They are independent of the frequency used.

#### 4.1.1. Chemical Shift

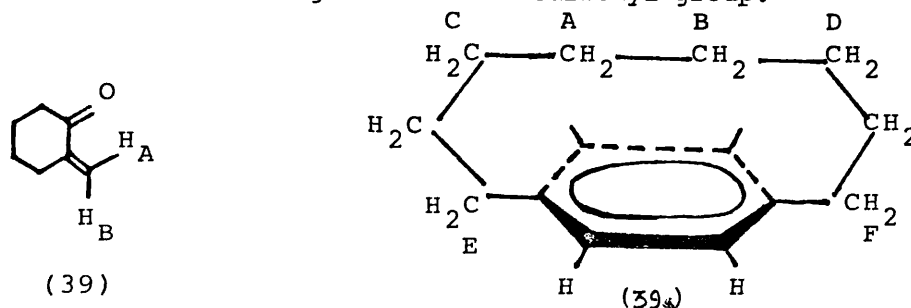
All protons in identical situations have the same chemical shift.

Chemical shifts are found to be affected by

Inductive effects: these operate through bonds. Electron withdrawing groups deshield (shift to lower field) adjacent protons, electron repelling groups cause shielding.

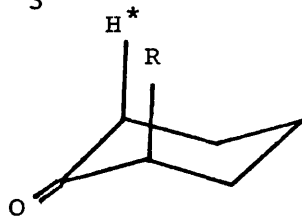
Magnetic anisotropy: in compounds with  $\pi$ -electrons, circulation of electrons generates a field that can either oppose or reinforce the applied field at the proton. Thus in compound (39) the proton labelled  $H_A$  absorbs

at lower field than the very similar proton  $H_B$ , because the former  $H_A$  lies in the deshielding zone of the carbonyl group.



In (39a) the  $\pi$  electrons acting as a ring current cause the large deshielding of benzene ring protons which resonate at  $\delta$  7.27 (39a) (ref. TMS) by the reinforcing induced field: the groups labelled A and B are however shielded because they lie in an opposing induced field area, and signals appear at a much higher field than those marked C and D, whereas the methylene protons marked E and F, being adjacent to the ring are deshielded and absorb at lower field.

Van der Waals deshielding: if protons attached to different atoms are brought sufficiently close together for van der Waals repulsion to occur there will be mutual deshielding e.g. proton  $H^*$  in a conformationally rigid cyclohexane chair system will resonate at lower field when  $R=CH_3$  than when  $R=H$ .



Solvent: the chemical shifts of a set of protons may be different in different solvents (Bothner-By & Glick, 1957; Reeves and Schneider, 1957). Thus a change of solvent may remove accidental equivalence. The solvent shift arises principally from the formation of collision complexes between solvent and solute, involving the formation and breaking of bonds; there is an equilibrium between the complexed and the uncomplexed species, resulting in observation of averaged signals whose position is concentration dependent. The bonding is associated

with specific geometry, the various protons of the solute molecule will have different spatial relationships to the solvent molecule and therefore different magnetic environments associated with long-range effects. Disc-like solvents such as benzene interact at an electron deficient site and the solute proton will show an upfield shift (Buckingham, 1960), while rod-like solvents e.g. carbon disulphide cause a down-field shift. Pyridine (Slomps and McKeller, 1960) and dimethylformamide are useful solvents especially when solubility in other solvents is low. Dimethylsulphoxide- $d_6$  is particularly good for alcohols. Alcohols are often sparingly soluble in other solvents and their hydroxyl protons are detectable only by their effect on methylene and methyl groups. The trace of acid always present in these solvents catalyses proton exchange so that spin-spin splitting of hydroxyl peaks is rarely observed. In dimethylsulphoxide- $d_6$  solution, strong hydrogen bonding to the solvent shifts the hydroxyl resonance downfield ( $\delta$  4.0 or lower) and reduces the rate of proton exchange sufficiently to permit observation of hydroxyl proton splitting (Chapman and King, 1964).

Temperature: the chemical shifts of protons bonded directly to electronegative atoms e.g. OH, SH and NH groups, exhibit a marked dependence on temperature. The chemical shift of the hydroxylic proton of ethanol moves to higher field at higher temperature, while the  $CH_2$  and  $CH_3$  protons are unaffected (Arnold and Packard, 1951). The effect of temperature change on conformationally labile molecules may be a qualitative change in the spectrum. In cyclohexane the transformation of one chair form into another <sup>involves</sup> rotation about single bonds. In any chair conformation there are two kinds of protons : six equatorial protons and six axial protons, yet there is a single sharp n.m.r. signal for all twelve at room temperature, since their average environments are identical. As it is cooled down, the single sharp peak is seen to broaden and then, at about  $-70^\circ$ , to split into two peaks, which at  $-100^\circ$

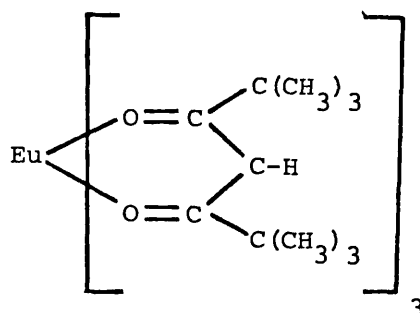
are clearly separated: one peak is due to axial protons, and the other is due to equatorial protons.

Shift reagents: shift reagents are useful to resolve overlapping signals to simplify interpretation of the spectrum. Lanthanide ions can increase their co-ordination number by interaction with lone pairs of electrons: changes of chemical shift are then observed for nuclei that neighbour functional groups such as  $-\text{NH}_2 > -\text{OH} > -\text{C}=\text{O} > -\text{O}- > -\text{CO}_2\text{R} > -\text{CN}$  which give characteristic shift magnitudes in this order. Shift reagents are normally used in non-polar solvents such as  $\text{CDCl}_3, \text{CCl}_4, \text{C}_6\text{D}_6$ . The displacement of peaks from the original position is called the induced shift.

There are two mechanisms by which paramagnetic species cause chemical shifts; contact shifts arise from delocalization of unpaired electrons through bonds and pseudocontact shifts originate from the secondary magnetic fields generated by the magnetic moment of the paramagnetic ions: these shifts depend only on distance and geometry, while contact shifts depend on covalent bonding. In the lanthanide complexes pseudocontact interaction occurs.

Hinckley (1969) reporting on the use of the lanthanide shift reagent tris(2,2,6,6-tetramethylheptane-3,5-dionato)europium(III) dipyridine adduct  $\{\text{Eu}(\text{DPM})_3\text{PY}_2\}$ , observed that the shifts for protons close to the point of association are larger than those for protons further removed and that the magnitude of the shifts are dependent upon the concentration of reagent:

Williams and Sanders (1970) obtained effectively first-order spectra of benzyl alcohol and of cyclohexanol in carbon tetrachloride solution using a pyridine-free  $\text{Eu}(\text{DPM})_3$  complex which they found to be a superior reagent as it co-ordinates more effectively: shifts may be increased by a factor of 4. The signal from the t-butyl group of  $\text{Eu}(\text{DPM})_3$  tris-

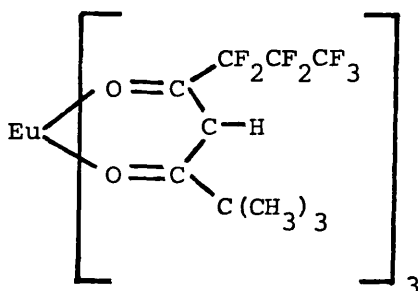


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(2,2,6,6-tetramethylheptane-3,5-dionato) europium (III) appears at a higher field than TMS and does not interfere with the spectra as most induced shifts are towards the lower field.

Praseodymium complexes (Briggs, Frost, Hart, Moss, Staniforth, 1970) show shifts which are usually reverse in direction and about triple in magnitude to the europium counterparts. The capability of producing shifts in either direction by use of the Eu or the Pr complex greatly increases the scope of this method.

Partially fluorinated (Rondeau and Sievers, 1971) complexes tris-(1,1,1-2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionato) europium  $\{Eu(FOD)_3\}$  or praseodymium  $\{Pr(FOD)_3\}$ , are stronger Lewis acids because



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of the electron withdrawing effect of the fluorine atoms, and also they have very considerable advantage in being highly soluble in solvents such as chloroform and carbon tetrachloride.

Lanthanide induced shifts are temperature dependent (Bennett and Schaster, 1972). It has been reported that the resonance of internal standards such as solvents (Cockerill and Rackman, 1970; Katritzky and Smith, 1971; Hart and Staniforth, 1971) and TMS (Hertz, Rodriguez and Joseph Nathan, 1971) are shifted to a small extent in the presence of LSR because of changes in the bulk susceptibility of the solution: the

induced shift of internal TMS may be up to about +1.4ppm.

Analysis of a series of spectra obtained on successive additions of the shift reagent gives most information. Information may be expressed in tabular or in graphical form relating the induced shift to the ratio of  $\{(\text{LSR}) / (\text{Substrate})\}$ ; shifts do not always change linearly over the entire range from 0 to 1 for  $\{(\text{LSR}) / (\text{Substrate})\}$ .

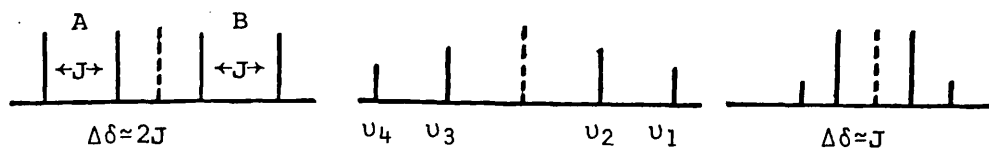
4.1.2 Integration: The area under an n.m.r. signal is directly proportional to the number of protons giving rise to the signal and is measured by the height of an integration line, drawn by the instrument, over the signal.

4.1.3 Spin-spin coupling. This is of most interest in getting the overall structure of the molecule. Splitting reflects the environment of the absorbing protons, with respect to other nearby protons. The n.m.r. signal of a proton is split into a doublet by one nearby proton, and into a triplet by two (equivalent) nearby protons. In general, a set of  $n$  equivalent protons will split an n.m.r. signal into  $n+1$  peaks: spin-spin splitting is observed only between non-equivalent neighbouring protons. Spin-spin splitting occurring between the protons on the same carbon atom is called geminal, between the proton on adjacent carbon atoms is called vicinal and there may also be long-range coupling. Long-range coupling is usually observable in  $\pi$ -systems.

The spin-spin coupling is of first order when the chemical shift difference between interacting nuclei is large compared with the coupling constant; the ideal condition is  $\Delta\delta \gg 6J$  and when each proton in one group is coupled equally to each and every proton in the second group. An AX system is one of first order coupling. The separation is the difference in chemical shift of the two unperturbed signals (centres of the doublets). As the chemical shift difference between two interacting nuclei approaches



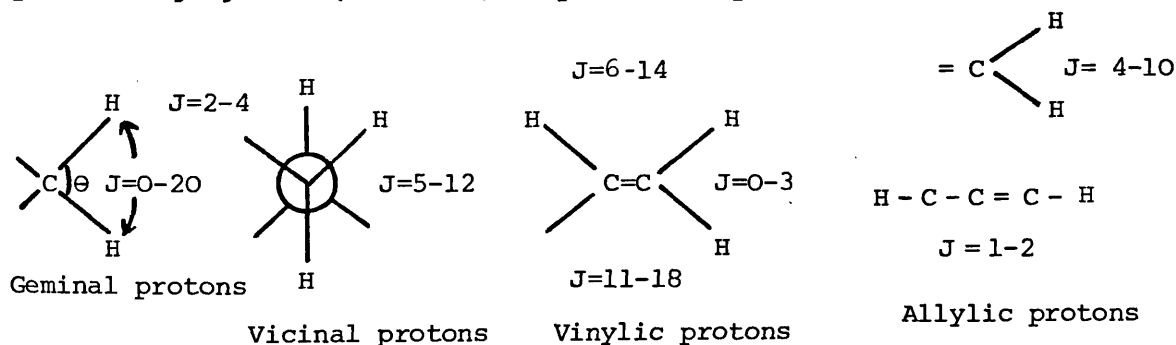
the value of the coupling constant between them, the first order rule no longer applies and the result is called an AB system. The patterns



of the multiplets becomes unsymmetrical, the inner member of each doublet increases in intensity at the expense of the outer members. In this case the chemical shift separation between the protons must be calculated by the equation  $\delta A - \delta B = \sqrt{\{\nu_4 - \nu_1\}\{\nu_3 - \nu_2\}}$  where  $\nu$  is frequency. In some cases the outer lines may be so weak that they are not observed at all.

In an ABX system, where X is chemically well shifted from A and B and coupled to both, the four AB lines will each be split into a doublet whereas the X proton should occur as four lines of approximately equal intensity.

4.1.4 Coupling Constant. The size of the coupling constant depends markedly on the structural relationship between the coupled protons e.g. geminal, vicinal, vinylic or allylic.



Geminal coupling: When a methylene group ( $-\text{CH}_2-$ ) with no protons on adjacent carbon atoms is part of an aliphatic chain in which there is restricted rotation, or is part of a ring system, or adjacent to an asymmetric centre, the possibility of non-equivalence of the two protons arises, and the protons will exhibit geminal coupling.  $J_{\text{gem}}$  markedly increases on increasing the angle  $\theta$  between the interacting C-H bonds. In systems of the type  $\text{RCH}_2\text{-X}$ , the value of  $J_{\text{gem}}$  increases algebraically with increase in the electronegativity of X, whereas in systems of the

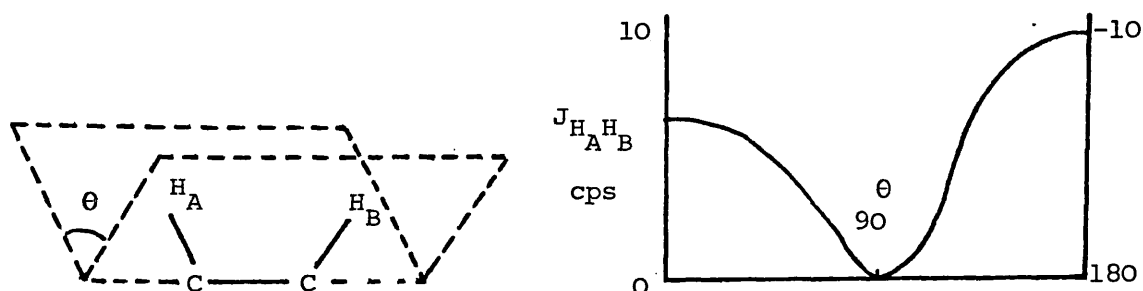


type  $R-CH_2-\overset{\overset{|}{I}}{\underset{\underset{|}{I}}{C}}-X$  an increase in the electronegativity of X leads to a fall in  $J_{gem}$ . This illustrates that changes in J are not simply attributed to the direct inductive effect of the substituent.  $J_{gem}$  is also greatly dependent on the number of  $\pi$ -bonds adjacent to the methylene group; if the geminal protons can assume all possible rotational conformations with respect to the adjacent  $\pi$ -systems, then it is found that the geminal coupling constant is increased by about 1.9 cps for each adjacent  $\pi$ -bond.  $J_{gem}$  may be as large as 21 cps.

Vicinal coupling: the vicinal coupling constant between the protons on adjacent saturated carbon atoms decreases (1) with an increase in the electronegativity of substituents (2) with an increase in carbon-carbon bond length, and (3) with increase in the angle between the bonds to the protons and the carbon-carbon bond. Karplus derived theoretically (Williams and Fleming, Spectroscopic methods in Organic Chemistry, 1966) an equation for the relationship between the vicinal coupling constant and the dihedral angle ( $\theta$ ) between the planes  $H_A-C-C$  and  $C-C-H_B$  (see fig.)

$$J = 8.5 \cos^2 \theta - 0.28, \quad 0^\circ \leq \theta \leq 90^\circ$$

$$J = 9.5 \cos^2 \theta - 0.28, \quad 90^\circ \leq \theta \leq 180^\circ$$



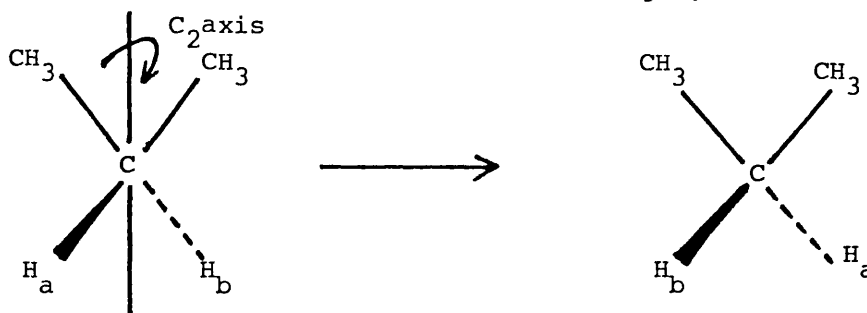
The Karplus equation can also be applied to vicinal coupling in olefins.

Long-range couplings:- these are usually found in conjugated systems e.g.  $J_{HH}$  (para) and  $J_{HH}$  (meta) in benzene are about 0-1 cps and 1-3 cps respectively.

#### 4.1.5. Geminal coupling in Equivalent, Enantiotopic and Diastereotopic protons:

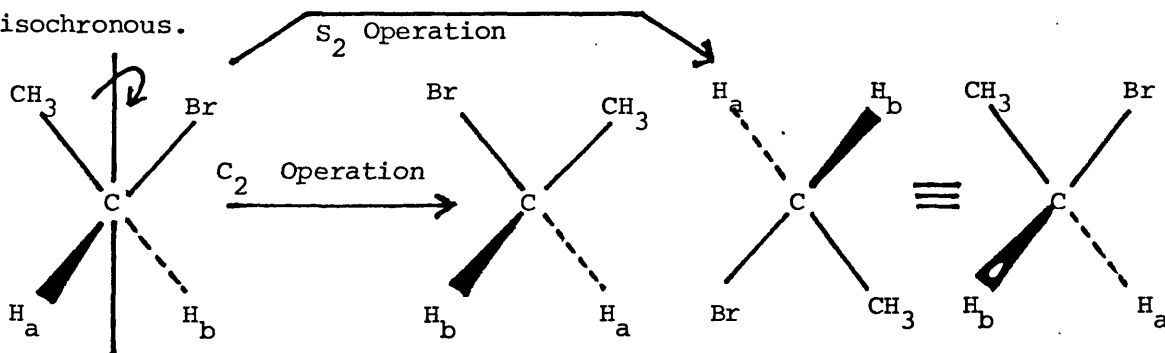
Mislow and Raban (1961) have divided hydrogen atoms of molecules into three classes: (1) equivalent (2) enantiotopic and (3) diastereotopic.

Equivalent protons:- they are in identical environments and interchangeable by rotation about an axis of rotation ( $C_n$ ) and not by an ( $S_n$ ) operation, to give an indistinguishable structure from the original e.g. in propane, the two methylene protons  $H_a$  and  $H_b$  are equivalent and are interchangeable by  $C_2$  rotation. They have identical chemical shifts: they are 'isochronous' (Abraham, 1961).

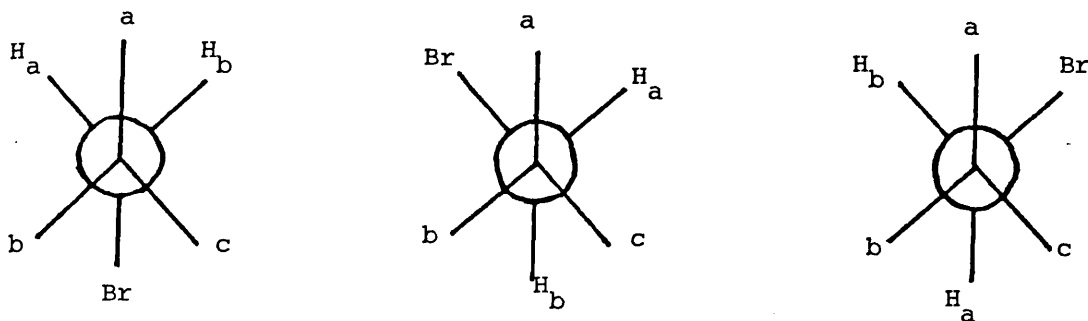


Enantiotopic protons:- the environments of enantiotopic protons are non-superposable, they are enantiomeric. The protons are interchangeable only by a rotation reflection operation ( $S_n$ ) and not by a simple rotation operation ( $C_n$ ). In bromoethane the protons  $H_a$  and  $H_b$  are interchangeable by an  $S_2$  operation but not by a  $C_2$  operation.

Enantiotopic protons have the same n.m.r. chemical shift: they are isochronous.



Diastereotopic protons:- Protons in diastereomeric environments cannot be interchanged by any symmetry operation, e.g.  $CabcCH_2Br$ .  $CabcCH_2Br$  is shown below in 3 conformations. No symmetry operation can interconvert the diastereomers, nor can it make the protons,  $H_a$  and  $H_b$  equivalent. In none of the conformations is the environment of the two protons the same;



nor there is a pair of mirror image conformations to balance out their environments. Even when a group such as  $-\text{CH}_2\text{Br}$  can rotate about the C-C bond in a structure such as  $\text{Cabc}-\text{CH}_2\text{Br}$ , the diastereotopic methylene protons still have different environments and they give distinct signals. It is only when the groups are rotating fast enough to average out their environments that they give a single averaged signal. An asymmetric molecule ( $\text{C}_1$ ) may contain diastereotopic protons; but molecular asymmetry is not necessary for the diastereoisomeric condition.

The two diastereotopic protons need not be situated on the same carbon atom. Dissymmetric molecules may have diastereoisomeric environments, for example 2,2'-bridged biphenyls which belong to point group  $\text{C}_2$  contain two equivalent methylene groups and each methylene group contains diastereotopic protons:-



Diastereotopic protons have different chemical shifts and are called "anisochronous". Sometimes there are compensating structural features which result in diastereotopic protons having indistinguishable signals, then these are called accidentally isochronous and may be separated by shift reagents. The situation in which e.g.  $-\text{CH}_2\text{Br}$  or  $-\text{CH}_2\text{OH}$  rotates relative to an asymmetric group has already been described. The situation in which  $\text{R} \rightleftharpoons \text{S}$  conformations are equally interconvertible as in some chiral biphenyls can also give an averaged signal.

#### 4.1.6. Conformationally Labile Compounds:-

If the compound is conformationally labile, the rapid change of conformation (perhaps inversion of configuration) may make the protons magnetically equivalent on a time-averaged basis and give rise to a sharp singlet. For example, in singly bridged biphenyls where  $Y=O, CO, CH_2, NCH_3$ , the enantiomeric conformations suffer rapid interconversion and give sharp singlets while the thiepin,  $Y=S$ , gives a multiplet which is resolved into the expected methylene AB pattern with  $\Delta\delta=0.22\text{ppm}$  and  $J=12.5\text{cps}$  (Mislow and co-workers, 1964). Additional information about two conformations in equilibrium can be obtained from low or high temperature n.m.r. spectra. The compound may show a low temperature spectrum which is really the separate spectra of the two conformations superimposed, and a high temperature spectrum which is a single spectrum of the averaged conformations. The transition from the low temperature spectrum to the high temperature spectrum occurs gradually, but over a relatively small temperature interval, from which a coalescence temperature can be estimated. The coalescence temperature can be used to give the activation energy and more detailed study of the change of shape of lines with temperature reveal other thermodynamic parameters of activation of conformationally labile molecules.

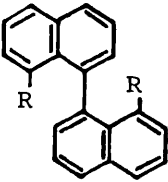
4.2 Proton Nuclear Magnetic Resonance Spectra of Unbridged and Bridged 8,8'-Disubstituted 1,1'-Binaphthyls.  
Results and Discussion.

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

The nuclear magnetic resonance spectra of 8,8'-disubstituted unbridged 1,1'-binaphthyls (XVI), (XVII), (XVIII) and (XIX) which have a two fold axis of symmetry ( $C_2$ ) were determined in deuterated chloroform (Table 1). Some preliminary work on n.m.r. spectra of these compounds has been previously carried out (Shyam Singh, 1972) but the present investigation has carried the assignments into much greater detail.

Table 1

Chemical shifts ( $\delta$ ; Me<sub>4</sub>Si; CDCl<sub>3</sub>) of aromatic and methylene protons. 60 MHz

Compound	Aromatic protons		Methylene protons
	4,4',5,5'	2,2',3,3',6,6',7,7'	
XVI, R=CO <sub>2</sub> CH <sub>3</sub>	8.12-7.73	7.70-7.37	2.71 (6H, CH <sub>3</sub> , s)
XVII, R=CH <sub>2</sub> OH	8.00-7.70	7.53-7.13	4.02 (4H, CH <sub>2</sub> , s) 1.78 (2H, OH, s)
XVIII, R=CH <sub>2</sub> Br	7.99-7.87	7.58-7.35	4.28, 4.18; 4.07, 3.97 (4H, CH <sub>2</sub> , q)
XIX, R=CH <sub>2</sub> CN	8.06-7.93	7.67-7.33	3.34, 3.15; 3.07, 2.88 (4H, CH <sub>2</sub> , q)

In these compounds the aromatic protons give two complex multiplets in the integrated ratio of 1:2(4H, 8H) at about  $\delta$ 8.12-7.70ppm and  $\delta$ 7.70-7.13 ppm respectively. The deshielded complex multiplet of four protons is assigned to 4,4' and 5,5' protons and the complex multiplet of eight to 2,2',3,3',6,6',7,7' protons. The chemical shifts of 4,4' and 5,5' protons are downfield from the 2,2',3,3',6,6',7,7' protons as expected for  $\alpha$ -protons

in naphthalene (Jackman and Sternhell, Application of N.m.r. Spectroscopy in Organic Chemistry, 1969). More evidence of this assignment of the downfield signals comes from a comparison of the n.m.r. spectra of 2,2', 8,8'- (Fitts, Siegel and Mislow, 1958; Dixon, Harris and Mazengo, 1971; Badar, Cooke and Harris, 1965) and 4,4'-dimethyl-1,1'-binaphthyls (Clar, Sanigok and Zander, 1957). In all three the aromatic protons fall into two groups; for the 2,2'- and 8,8'-disubstituted compounds the integration ratio of the two complex multiplets at lower to higher field is 4:8; while for the 4,4'-disubstituted 1,1'-binaphthyl it is 2:10, confirming that the 4,4'-protons, when present, are in the lower field multiplet.

In 8,8'-bismethoxycarbonyl-1,1'-binaphthyl (XVI) the methyl protons resonate at  $\delta$ 2.71 ppm as a singlet. In compounds (XVII), (XVIII) and (XIX) the geminal methylene protons are diastereotopic and non-equivalent and might be expected to give two signals. The hydroxyl protons in compound (XVII) give a singlet at  $\delta$ 1.78 ppm and the geminal methylene protons also give only one singlet, at  $\delta$ 4.02 ppm, while in compounds (XVIII) and (XIX), they appear as an AB quartet, with  $J=11$ cps and 19cps respectively. The observed large coupling constant of methylene protons of biscyanomethyl-1,1'-binaphthyl is expected owing to the C $\equiv$ N bonds adjacent to the methylene groups. All these three compounds (XVII), (XVIII) and (XIX) were examined at different temperatures. The 8,8'-bishydroxymethyl-1,1'-binaphthyl (XVII) was examined at lower than ambient temperatures at 220MHz and the results are collected in (Table 2).

Table 2 Chemical shifts ( $\delta$ ; Me<sub>4</sub>Si; CDCl<sub>3</sub>) of methylene and hydroxylic protons of (XVII) 220 MHz

Temperature °C	Methylene protons CH <sub>2</sub> (4H) $\delta$ ppm	Hydroxyl protons OH(2H) $\delta$ ppm
22	4.02	1.82
5.2	3.98	
0.0	3.99	
-7.5	3.99, 3.93, 3.86	
-12.5	4.02, 3.96, 3.87	
-19	3.99, 3.92; 3.90, 3.87	
-27	3.98, 3.92; 3.89, 3.83	2.74
-34	3.94, 3.88; 3.84, 3.78	2.89
-56	3.92, 3.85; 3.79, 3.73	3.32

The result at  $>0^{\circ}$  shows the presence of conformational isomers. It is known that the main binaphthyl structure cannot be inverting its configuration at these temperatures, therefore restricted rotation of the hydroxymethylene groups is responsible for the change of pattern with temperature. At the highest temperature ( $22^{\circ}\text{C}$ ) the rotation is sufficiently fast to give the average of the methylene proton signals. The rate of rotation becomes slower with decreasing temperature and is slow enough at  $-7.5^{\circ}$  and  $-12.5^{\circ}$  to reveal the separate resonances of the geminal diastereotopic protons at  $\delta 3.99, 3.93, 3.86$  (triplet) and between  $-19^{\circ}$  and  $-56^{\circ}$  as a quartet  $3.92, 3.85, 3.79, 3.73$ . (Figure 1)

When the spectrum was determined in dimethyl sulphoxide the geminal protons appeared, at  $22^{\circ}$  as an AB quartet and each peak split into a doublet,  $\delta 4.02, 4.00; 3.95, 3.93; 3.79, 3.77; 3.73, 3.70$  a result at first surprising. However, this solvent has a pronounced effect on the hydroxylic protons also: the signal is not only shifted downfield but is also split into a triplet ( $4.97, 4.94, 4.92$ ). It appears that the dimethylsulphoxide associates with the  $-\text{CH}_2\text{OH}$  groups; this will make them effectively larger and slow down the conformational rotation,

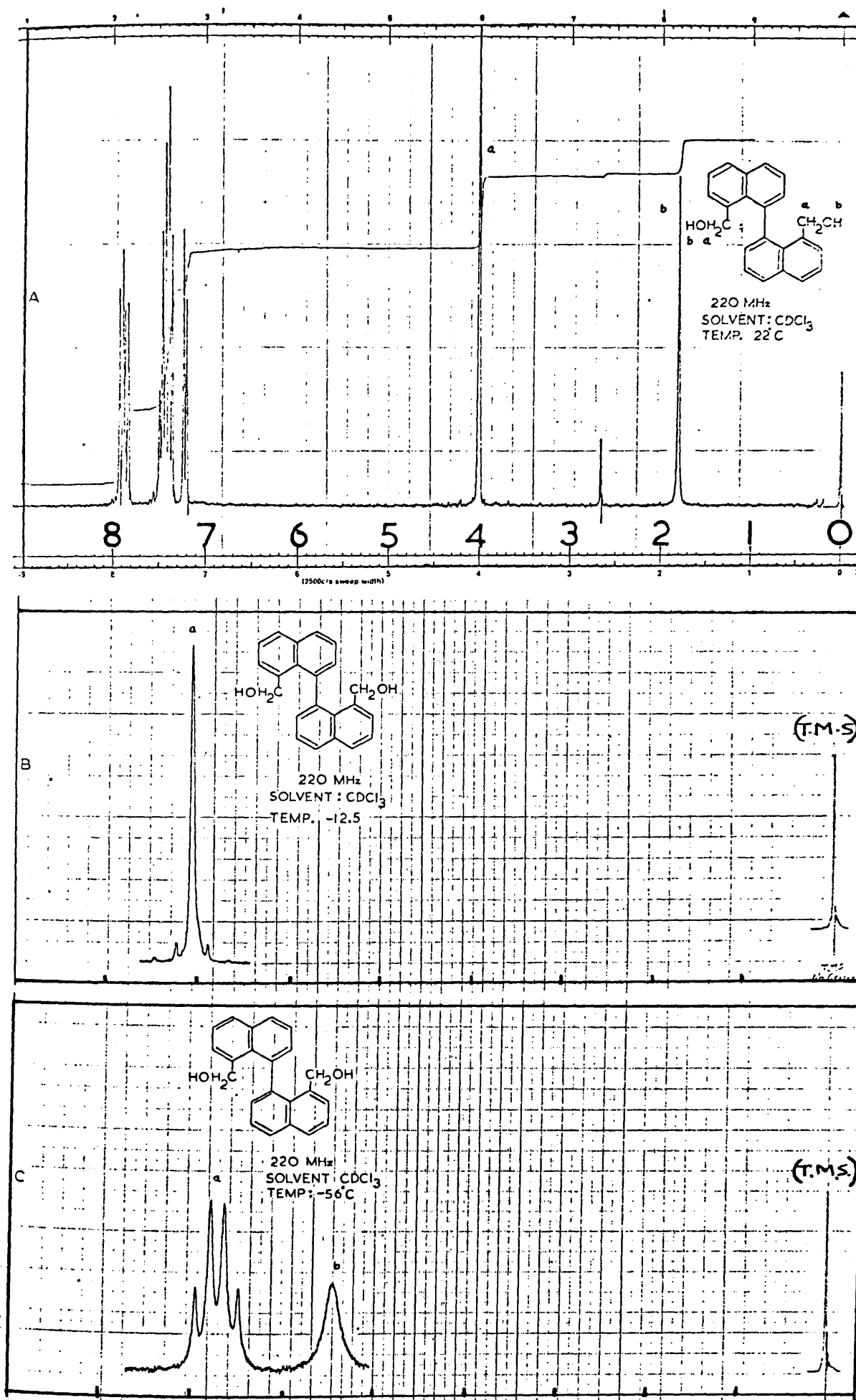


Figure 1



resulting in observable signals at ordinary temperature. Hydroxyl protons of alcohols dissolved in dimethyl sulphoxide give well resolved signals and permit the detection of H-C-O-H coupling, thus accounting for the doublets and for the triplet (Figure 2).

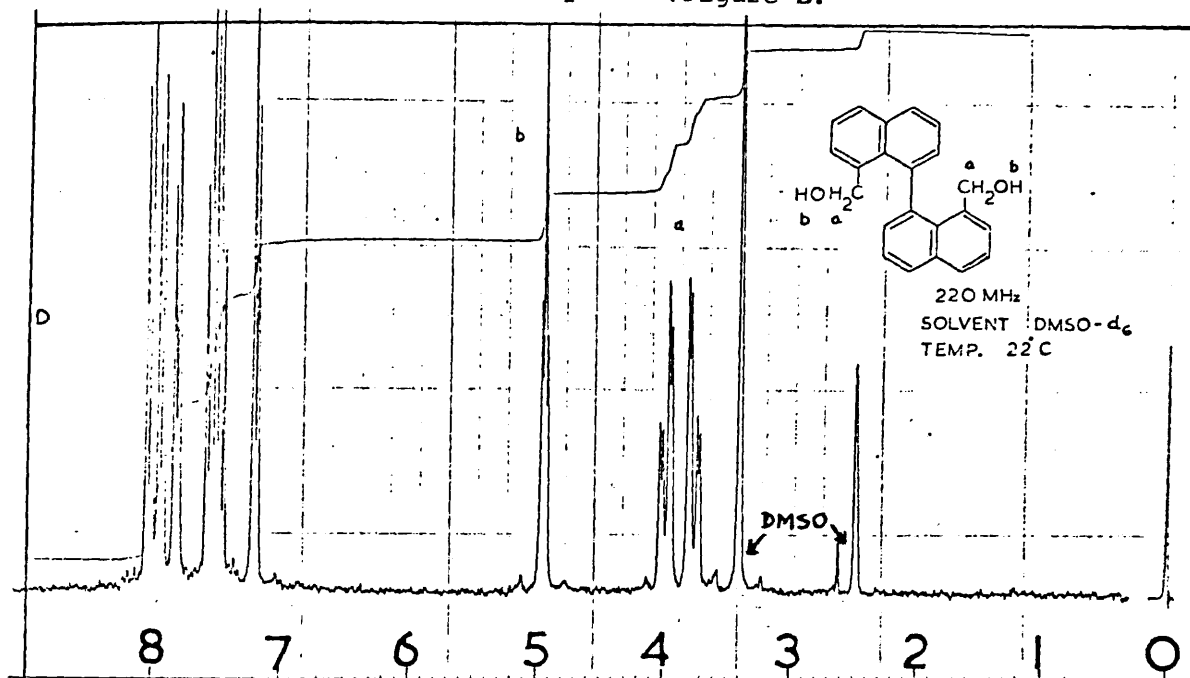


Figure 2

8,8'-Bisbromomethyl-1,1'-binaphthyl (XVIII) and 8,8'-biscyanomethyl-1,1'-binaphthyl (XIX), which show quartets at room temperature, were examined at raised temperatures (Tables 3 and 4) but even at  $\sim 140^\circ$  they do not show any averaging of the signals. This indicates that while in compound (XVII), the smaller hydroxymethyl group undergoes rapid conformational change at ordinary temperature, the bromomethyl and cyanomethyl groups are large enough to prevent rapid rotation.

Table 3: 8,8'-Bisbromomethyl-1,1'-binaphthyl: chemical shifts

( $\delta, \text{Me}_4\text{Si}$ ) of methylene protons. 100 MHz

Temperature C	Solvent	Methylene protons	$\Delta\delta$	JHz	$\frac{\Delta \text{ in Hz}}{J}$
$\sim 30^\circ$	$\text{CDCl}_3$	4.26, 4.18; 4.07, 3.95	2.1	-10	2.1
$65^\circ$	$\text{CDCl}_3$	4.27, 4.16; 4.07, 3.97	1.95	-11	1.9
$100^\circ$	$\text{CCl}_4$	4.16, 4.05; 3.99, 3.88	1.7	-11	1.6
$120^\circ$	$\text{CCl}_4$	4.16, 4.05; 3.99, 3.88	1.7	-11	1.6
$140^\circ$	$\text{CCl}_4$	4.16, 4.05; 4.00, 3.89	1.6	-11	1.5

Table 4: 8,8'-Biscyanomethyl-1,1'-binaphthyl chemical shifts ( $\delta, \text{Me}_4\text{Si}$ )Methylene protons 100 MHz

Temperature C	Solvent	Methylene protons	$\Delta\delta$	JHz	$\frac{\Delta \text{ in Hz}}{J}$
$\sim 30^\circ$	$\text{CDCl}_3$	3.32, 3.14; 3.06, 2.86	2.7	-19	1.42
$70^\circ$	$\text{CDCl}_3$	3.32, 3.13; 3.06, 2.87	2.6	-19	1.35
$120^\circ$	$\text{CCl}_4$	3.20, 3.01; 2.95, 2.76	2.6	-19	1.35
-	$\text{CDCl}_3$ (220 MHz)	-	4.8	-19	2.5

The chemical shifts and coupling constants in both the above tables show little variation over a large temperature range.

The geminal methylene protons of compound (XVII) were also revealed, in  $\text{CDCl}_3$ , by use of the lanthanide shift reagent  $\text{Eu}(\text{FOD})_3$ . This enabled the geminal coupling constant to be observed. The singlet, on progressive addition of  $\text{Eu}(\text{FOD})_3$  separates into two signals to yield eventually an AB quartet with  $J=14$  cps. The effect on the chemical shift of progressively adding the shift reagent for methylene protons and the hydroxyl protons of (XVII) ( $6.23 \times 10^{-5}$  mole in 0.6ml  $\text{CDCl}_3$ ) are collected (Table 5), and the figure<sup>3</sup> shows the spectrum before and after addition of 0.184 moles of  $\text{Eu}(\text{FOD})_3$  per mole of compound (XVII) at 60 MHz (reference TMS).

Table 5: Addition of  $\text{Eu}(\text{FOD})_3$  to 8,8'-bishydroxymethyl - 1,1'-binaphthyl  
Chemical Shifts ( $\delta, \text{Me}_4\text{Si}, \text{CDCl}_3$ ) 60 MHz.

$\frac{\text{Moles of Eu}(\text{FOD})_3}{\text{Moles of XVII}}$	Methylene protons $\delta$ ppm	Hydroxyl protons $\delta$ ppm
1 -	4.15	1.51
2 0.017	4.24	2.00
3 0.042	4.49	2.88
4 0.074	4.80	4.00
5 0.086	4.93	4.45
6 0.102	5.35, 5.09, 5.85	
7 0.142	5.72, 5.49; 5.41, 5.17	6.27
8 0.161	5.87, 5.62; 5.52, 5.30	6.72
9 0.181	6.05, 5.81; 5.69, 5.46	7.39

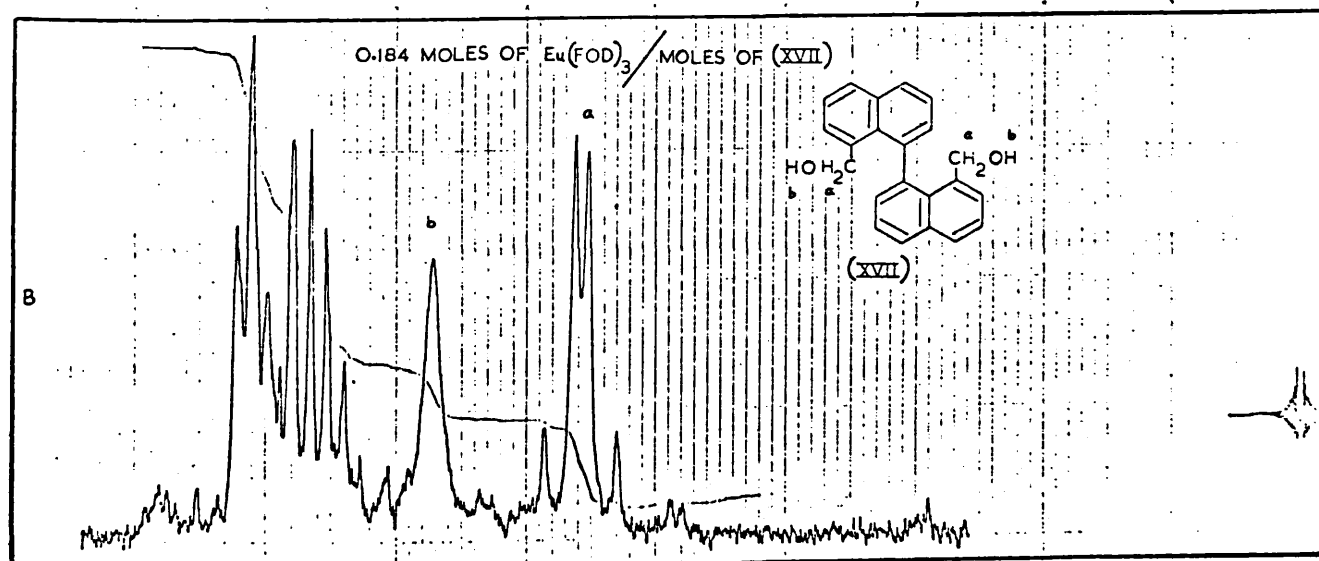
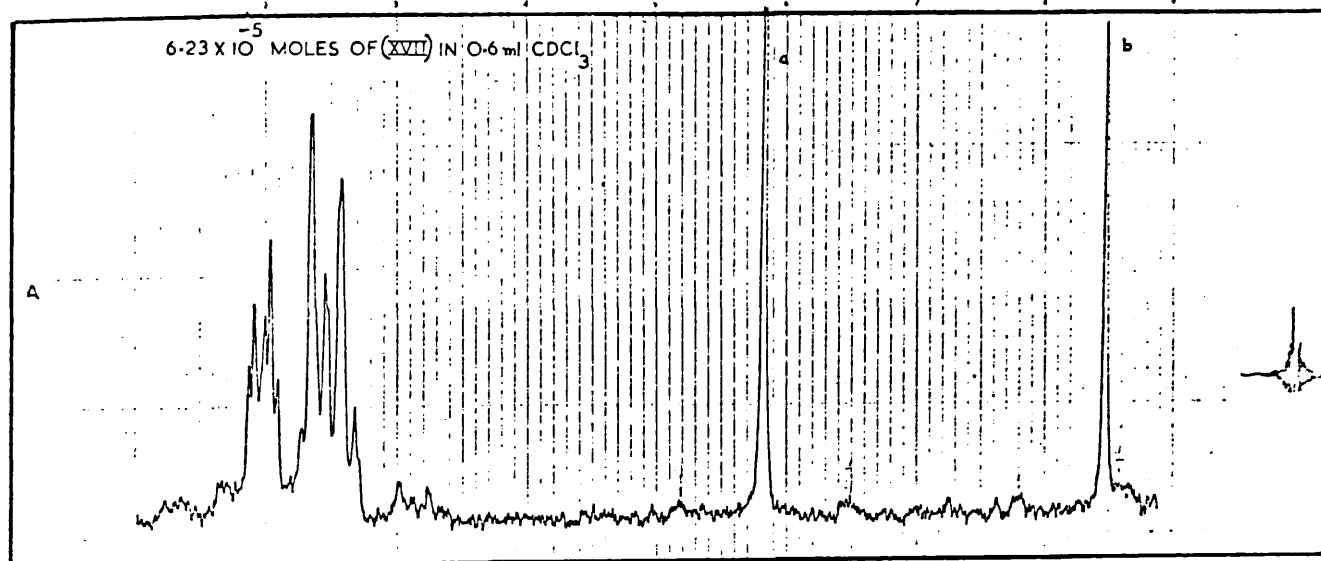


Figure 3

#### 4.2.2 Heterocyclic Compounds Containing Oxygen, Sulphur and Selenium.

These 8,8'-bridged 1,1'-binaphthyls have a twofold axis of symmetry ( $C_2$ ). The splitting of the aromatic protons is here found to be into three groups of complex multiplets in the integrated ratio (4H:6H:2H). The complex multiplet of four protons at lowest field corresponds to 4,4' and 5,5' protons as explained for these protons in unbridged 1,1'-binaphthyls; the six-proton complex multiplet corresponds to 3,3',6,6' and 7,7' protons while the remaining multiplet is assigned to the 2,2' protons. These two protons give doublets of a doublet with  $J \approx 7\text{Hz}$ , ortho coupling, and  $J = 2\text{Hz}$ , meta coupling (Jackman and Sternhell, Application of N.m.r. Spectroscopy in Organic Chemistry, 1969): they lie near in space to the opposite naphthalene nucleus, so they must be shielded while the 7,7'-protons are near one of the geminal protons so they must be deshielded, by the Van der Waals deshielding effect. Further confirmation of the assignment of these 2,2'-protons was obtained by using the lanthanide shift reagent  $\text{Pr}(\text{FOD})_3$  (Rondeau and Sievers, 1971). When portions of  $\text{Pr}(\text{FOD})_3$  are added stepwise to the oxonin (I) and to the thiadioxy compound (IV) there is a progressive upfield shift in the spectrum, and a doublet separates out from the central multiplet and crosses over the doublet assigned to 2,2' protons. The 7,7'-protons are nearest to the bridging atom i.e. nearest to the lanthanide complex both through bonds and through space, and so it seems reasonable to consider that they are more sensitive to the shift reagent. The signal positions, after each addition of a small portion of  $\text{Pr}(\text{FOD})_3$  are collected (Tables 6 and 7) before and after the addition of shift reagent  $\text{Pr}(\text{FOD})_3$  follow.

During the addition the  $\text{Me}_4\text{Si}$  signal also shifted upfield; after the addition of  $5.42 \times 10^{-5}$  moles of  $\text{Pr}(\text{FOD})_3$  per mole of thiadioxy compound (IV), the  $\text{Me}_4\text{Si}$  signal had shifted upfield by 2.53 ppm. (Figure 4 and 5)

Table 6 Chemical Shifts ( $\delta$ ; Me Si; CDCl<sub>3</sub>) of aromatic protons of 8-oxa-8,9-dihydro-7H-{1,2,3-de : 4,5,6-d'e'-dinaphthalene} cyclononane (I). 60 MHz.  
Addition of Pr (FOD)<sub>3</sub> to 0.0211g, 7.1 x 10<sup>-5</sup> mole, in 0.6 ml CDCl<sub>3</sub> solution.

Moles of Pr (FOD) <sub>3</sub>	Aromatic protons		
	4,4'H; 5,5'H	3,3'H; 6,6'H; 7,7'H	2,2'H
1. -	8.08 8.02 7.95 7.84	7.69 7.58 7.52 7.47 7.42	7.02 6.90
2. 0.237	7.96 7.81 7.71 7.61	7.50 7.38	6.75 6.64
3. 0.399	7.90 7.78 7.62	7.48 7.31 7.20 7.05	6.59 6.47
4. 0.495	7.88 7.73 7.60 7.47	7.33 7.14 7.03	6.51 6.38
5. 0.717	7.82 7.68 7.54 7.45	7.18 7.05 6.91	6.32 6.20
6. 0.915	7.79 7.67 7.53 7.47	7.11 6.98 6.84	6.24 6.08 6.00
7. 1.86	7.67	6.89 6.76 6.66	5.74 5.63
8. 2.81	7.48 7.34 7.20	6.73 6.61 6.49	5.47 5.35
9. 5.40	7.39 7.13 7.00	6.47 6.35 6.22	4.94 4.83
10. 6.16	7.34	7.04 6.91	4.78 4.66
		6.37 6.24 6.11	5.34 5.24
			4.84 4.73
			3.92 3.87
			7.7'H

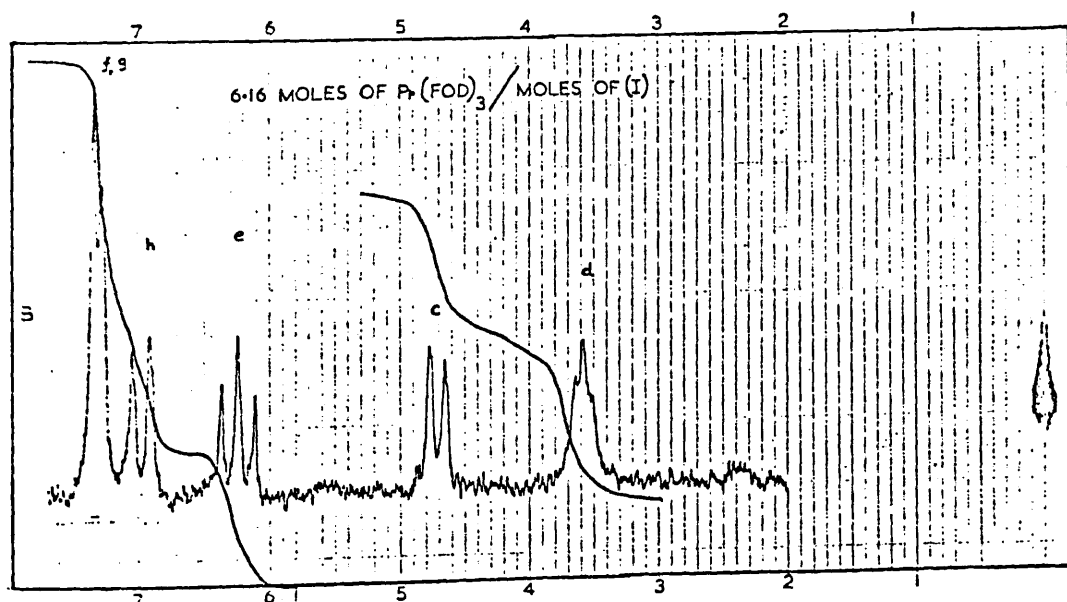
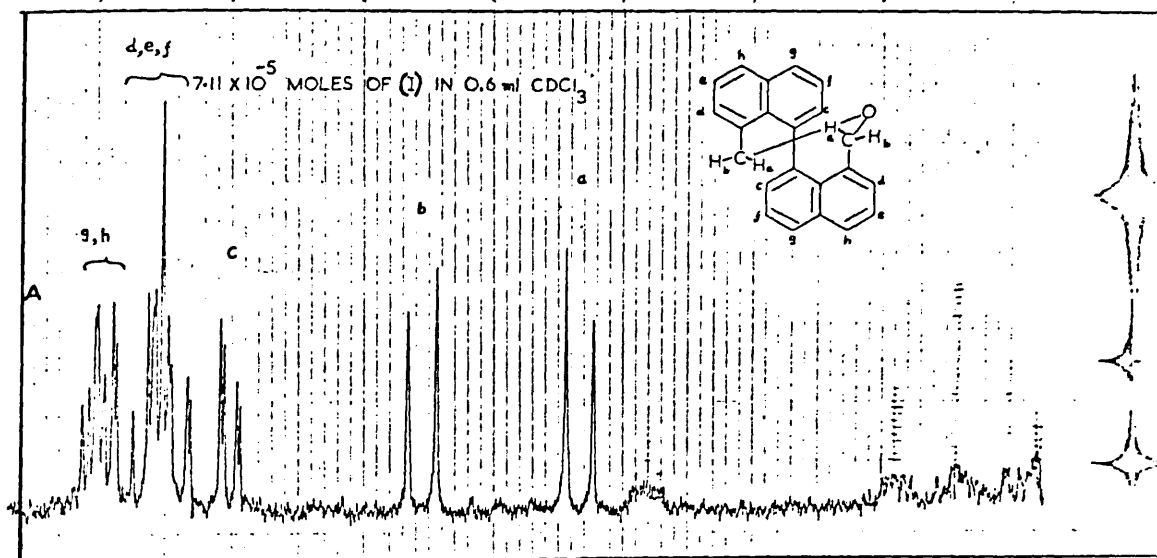


Figure 4

Table 7 (Chemical Shifts ( $\delta$ ; Me<sub>4</sub>Si; CDCl<sub>3</sub>) of aromatic protons of 8-thiadioxy -8,9- dihydro-7H-  
 {1,2,3-de : 4,5,6-d'e'-dinaphthalene} cyclononane (IV). 60 MHz.  
 Addition of Pr (FOD)<sub>3</sub> to 0.0179<sub>g</sub>, 5.72 x 10<sup>-5</sup> Mole in 0.65 ml CDCl<sub>3</sub> solution.

Moles of Pr(FOD) <sub>3</sub>	Aromatic protons			Methylene protons attached to naph.ring		
	4,4',5,5'H	3,3',6,6',7,7'H	7,7'H	Ha	Hb	TMS
1. 0.00	8.13 8.03 7.98 7.92 7.77 7.64 7.58 7.53 7.47 7.33	7.77 7.64 7.58 7.53 7.47 7.33	7.00 6.89	5.22 4.98	3.93 3.69	0.00
2. 0.213	8.00 7.94 7.87 7.80 7.63 7.51 7.35 7.22 7.11	7.63 7.51 7.35 7.22 7.11	6.81 6.69	4.53 4.29	3.22 2.98	0.22
3. 0.474	7.93 7.88 7.80 7.72 7.57 7.46 7.29 7.15 6.93 6.81	7.57 7.46 7.29 7.15 6.93 6.81	6.66 6.55	3.92 3.68	2.60 2.33	0.28
4. 0.752	7.86 7.80 7.73 7.68 7.50 7.39 7.34 7.24 7.09	7.50 7.39 7.34 7.24 7.09	6.71 6.55 6.44	3.50 3.25	2.11 1.88	0.44
5. 1.25	7.77 7.64	7.41 7.27 7.13 7.00	6.40 6.30	2.94 2.71	1.55 1.30	0.67
6. 1.91	7.72 7.59	7.38 7.24 7.11 6.95	6.33 6.19 6.07	2.51 2.27	1.06 0.82	1.04
7. 3.02	7.65 7.54	7.30 7.17 7.03 6.92	6.21 6.08	5.92 5.79	2.01 1.77	1.55
8. 4.23	7.62 7.50	7.25 7.13 7.00 6.87	6.13 6.00	5.71 5.60	1.67 1.42	2.07
9. 5.42	7.55 7.45	7.23 7.10 6.93 6.81	6.05 5.93	5.59 5.47	1.43 1.20	2.53

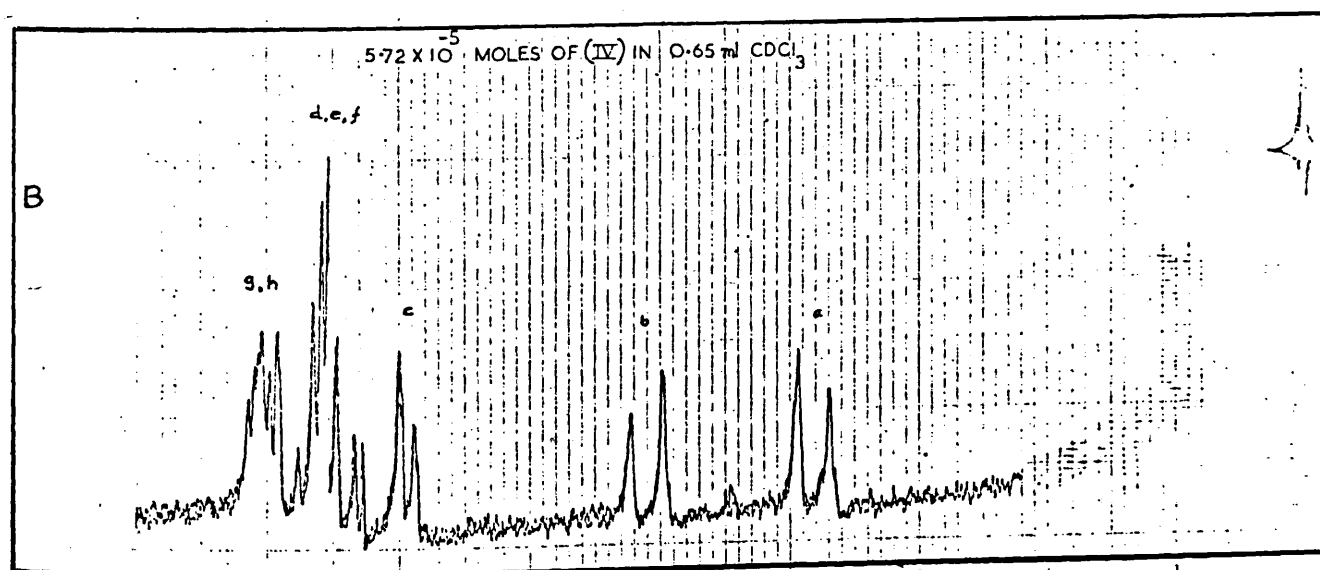
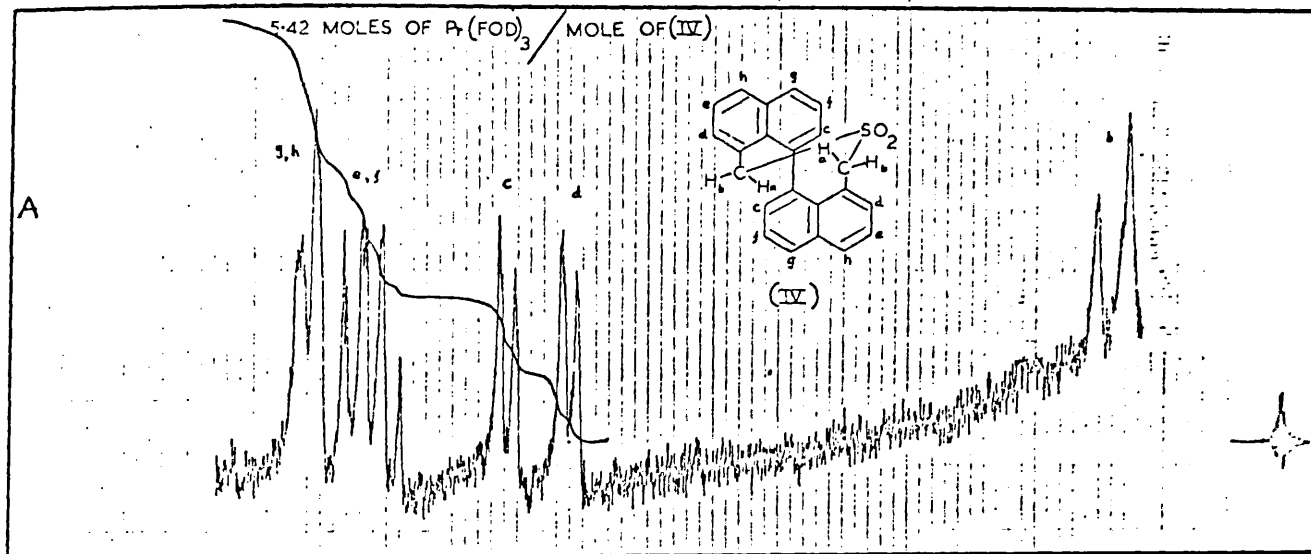
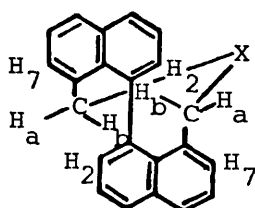


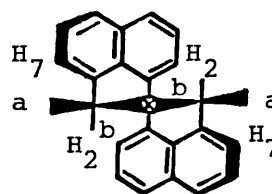
Figure 5



The nine-membered ring compounds are conformationally very stable (Harris and Singh, 1976). The model shows the different environments of the diastereotopic methylene protons Ha and Hb. The spectra in deuteriochloroform have clearly defined groups of signals, in an AB system of two well separated doublets. The coupling constant is large, e.g.  $J=15\text{cps}$  for compound (II),  $\Delta\text{Hz}/J=9-11$ . The model indicates that both Ha and Hb while not exactly in the "main plane" of the aromatic ring to which the methylene group is joined are probably in its deshielding zone. They are brought nearer to this "main plane" by the distortion due to peri-repulsion in 1,8-disubstituted naphthalenes (Harris and Mellor, 1961; Cooke and Harris, 1963; Balasubramanian, 1966; Anderson, Frank and Mandella, 1972; Carter and Liljefors, 1976). Each Ha, a little closer to being in the plane of the attached naphthalene ring than Hb, must be the more deshielded; Hb must also be subject to shielding by the long range effect of the naphthalene system towards which it is pointing. Ha must be again further deshielded by the van der Waals deshielding effect of the nearby 7,7'-aromatic protons.



(I) X=O



In the heterocyclic compounds O(I), S(II), Se(III), SO<sub>2</sub>(IV) the signals for Ha and Hb are shifted downfield, in comparison with the carbocyclic compounds, because of the inductive effect of the bridging atom; electronegativity decreases in the order O>SO<sub>2</sub>>S≈Se and the methylene proton signals (Table 8) show it. Chemical shifts, which are affected by the overall geometry of the molecule, will also depend on the size of the heteroatom, which influences the dihedral angle between

the naphthalene planes. In the carboxylic analogues (Harris and Singh, 1976) bridged by  $>C(CO_2H)_2$ ,  $>C(CO_2Et)_2$ ,  $>C(CO_2Me)_2$ ,  $>C(CH_2OH)_2$ , the methylene protons appear at higher field,  $\delta$ 3.99,3.18;  $\delta$ 4.03,3.13;  $\delta$ 4.05,3.12;  $\delta$ 3.28,2.49 respectively. As the inductive effect operates through the chemical bonds, the Ha and Hb signals must be shifted equally by the electronegativity of the bridging atom; the difference in their signals is due to their different spatial relationships with the aromatic nuclei, large  $\Delta\delta$  and  $\Delta Hz/J$  values are observed.


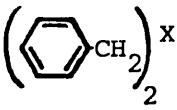
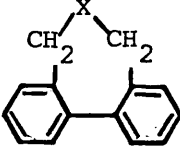
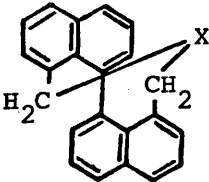
Table 8: Proton N.m.r. spectra of (I), (II), (III), (IV)

Chemical shifts ( $\delta$ ; Me<sub>4</sub>Si; CDCl<sub>3</sub>) of aromatic and methylene protons: 100MHz

X	Aromatic protons			Methylene protons				
	4',4'',5'5'' 4H,m	3',3'',6',6'',7',7'' 6H,m	2',2'' 2H,m	Ha 2H,d	Hb 2H,d	$\Delta\delta$	J Hz	$\Delta Hz/J$
1. O	7.96-7.77	7.57-7.35	6.94-6.85	5.47	4.27	1.20	-13	9.2
2. S	7.91-7.77	7.54-7.24	6.86-6.78	4.76	3.34	1.42	-15	9.5
3. Se	7.86-7.77	7.50-7.19	6.86-6.77	4.80	3.49	1.39	-13	10.7
4. SO <sub>2</sub>	8.06-7.89	7.66-7.34	6.93-6.84	5.06	3.79	1.27	-14	9.1

The chemical shift data (Table 9) of methylene protons for oxygen and sulphur compounds in different but chemically related situations shows that oxygen always promotes a larger downfield shift than sulphur.

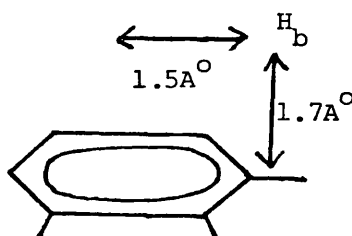
Table 9: Chemical shift ( $\delta$ ; Me<sub>4</sub>Si; CDCl<sub>3</sub>) of methylene protons in comparable situations.

X	Chemical structures				Ha	Hb
						
O	3.52	4.55	4.34	5.47	4.27	
S	2.57*	3.61	3.44, 3.35**	4.76	3.34	

\* Jackman and Sternhell, Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry, 1969, p.199

\*\* Mislow and co-workers, 1964.

Working out from the scale models, approximately, for the oxepin compound (I), an H<sub>b</sub> proton lies  $1.7\text{\AA}$  above the plane of the opposite naphthalene nucleus and  $1.5\text{\AA}$  from the centre of its nearest benzene moiety. Using the magnetic field contour diagram of Johnson and Bovey (1958) which gives the shielding value for protons in the neighbourhood of a benzene ring, one can see that the long range shielding of H<sub>b</sub> would be expected to be at least one p.p.m. greater than that of H<sub>a</sub>.



In these nine-membered heterocyclic ring compounds the geometry is not as precisely known as it is in the seven membered ring biphenyl series where the angles of torsion have been calculated,  $44.1^\circ$  in the oxepin, and  $56.6^\circ$  in the thiepin compound (Mislow and co-workers, 1964; Hall, 1969). From the model, it seems probable that in nine-membered carbocyclic rings incorporating the 8,8'-positions of 1,1'-binaphthyls the dihedral angle is near to  $90^\circ$  (Harris and Singh, 1976; Allinger and Miller, 1964). The following bond lengths and angles are quoted for the bridging atom in cyclic systems:- C-O (in 1,4-dioxan)  $1.44 \pm 0.03\text{\AA}$ ,  $\angle\text{C-O-C } 112 \pm 5^\circ$ ; C-S (in 1,4-dithian)  $1.80\text{\AA}$ ,  $\angle\text{C-S-C } 100^\circ$ ; C-Se (in 1,4-diselenan)  $1.99 \pm 0.04\text{\AA}$ ,  $\angle\text{C-Se-C } 97.6 \pm 3.5^\circ$ ; C-SO<sub>2</sub> (various, mean taken)  $1.75\text{\AA}$ ,  $\angle\text{C-SO}_2\text{-C } 107^\circ$  (Sutton, Interatomic Distances, 1965). Using these data, the distances between the carbon atoms C<sub>7</sub> and C<sub>9</sub> are calculated as (I)  $2.3\text{\AA}$ , (II)  $2.84\text{\AA}$ , (III)  $3.0\text{\AA}$ , (IV)  $2.85\text{\AA}$ , and  $2.5\text{\AA}$  for the carbocyclic compound if CH<sub>2</sub> is used as X in the bridge. From these data, the angle of torsion for nine-membered ring compounds cannot be precisely calculated because the naphthalene rings are not planer. The calculated angles subtended by the C<sub>7</sub>-C<sub>9</sub> distances at the centre of the pivot bond are near to  $52^\circ$  for (I);  $63^\circ$  for (II),  $68^\circ$  for (III),  $63^\circ$  for (IV) and  $55^\circ$  for X=CH<sub>2</sub>. Now if the presumption of near orthogonality is correct for

the carbocyclic rings then the oxonin (I) has a dihedral angle a little less than  $90^\circ$ , the thionin (II) and dioxothionin (IV) has a little greater than  $90^\circ$  and the selenonin (III) approaches, but does not pass an angle of  $\approx 110^\circ$ .

Solvent variation: The n.m.r. spectra of these ring compounds (I), (II), (III) and (IV) were recorded in different solvents and the results are collected in Table 10.

Table 10: Chemical Shift ( $\delta_{Me_4Si}$ ) of methylene protons. 60MHz

Compound	solvent	Methylene protons		$\Delta\delta$	$J_{Hz}$	$\Delta Hz/J$
		Ha	Hb			
(I)	$CDCl_3$	5.47	4.26	1.21	12.9	5.62
	$CCl_4$	5.34	4.12	1.22	12.9	5.67
	$C_6H_6$	5.62	4.24	1.38	12.9	6.41
	$CS_2$	5.27	4.08	1.19	13	4.59
	Nitrobenzene	5.48	4.27	1.21	13	5.58
	Pyridine	5.56	4.32	1.23	13	5.69
(II)	$CDCl_3$	4.78	3.34	1.44	15	5.7
	$CCl_4$	4.65	3.21	1.44	15	6.76
	$C_6H_6$	4.82	3.07	1.75	15	7.0
	$CS_2$	4.62	3.19	1.43	14	6.11
	Nitrobenzene	4.73	3.32	1.41	14	6.07
	(III)	$CDCl_3$	4.88	3.48	1.40	13.2
$CCl_4$		4.80	3.40	1.40	13.5	6.22
$C_6H_6$		4.96	3.19	1.77	13.2	8.04
$CS_2$		4.76	3.34	1.41	13	6.54
Nitrobenzene		4.88	3.46	1.42	13	6.57
Pyridine		4.98	3.56	1.42	13	6.57
(IV)	$CDCl_3$	5.08	3.80	1.28	14.4	5.48
	$CCl_4$ )	Insoluble				
	$C_6H_6$ )					
	$CS_2$ )					
	Nitrobenzene					

The average Ha and Hb value is found to be lowest in  $CS_2$  and highest in pyridine for (I), (II) and (III) compounds. The  $\Delta\delta$  and  $\frac{\Delta \text{ in Hz}}{J}$  values are higher in  $C_6H_6$  for (I), (II) and (III) in the order of (III) > (II) > (I).

### 4.2.3. Heterocyclic Compounds Containing Nitrogen

The aromatic protons of the compounds (V), (VI) and (VII) appear at lower field from those of the other heterocyclic and carbocyclic analogue. (Table 11) The aromatic protons of the compound (VII) integrate in the ratio 6:4:2 in contrast to 4:6:2 for all the other ring compounds (see below).

Table 11: Chemical shift ( $\delta$ ; Me<sub>4</sub>Si; CDCl<sub>3</sub>) of aromatic protons and methylene protons in the 9-membered N-heterocyclic ring in (V)<sup>†</sup>, (VI), (VII)<sup>†</sup>. 60MHz

Compound	Aromatic protons			Methylene protons		$\Delta\delta$	J	$\Delta\text{Hz}/J$
	4H	6H	2H	Naph-CH <sub>2</sub> -N Ha Hb	N-CH <sub>2</sub> -C			
(V)	8.24-8.09	7.93-7.29	6.98-6.87	5.27 4.70	3.09, 2.95; 2.82, 2.70 (4H, <u>t</u> , CH <sub>2</sub> CH <sub>3</sub> ) 1.28, 1.16, 1.03 (6H, <u>t</u> , CH <sub>3</sub> )	0.82	14.4	3.41
VI	8.22-8.09	7.95-7.30	6.95-6.81	5.25 4.70	4.46, 4.25; 3.37, 3.14 5.84 ( <u>d</u> ) 5.59 ( <u>d</u> ) 5.44, 5.28; 5.14, 5.00	0.55	13.8 13.0	2.39
VII	8.29-8.01 (6H)	7.88-7.32 (4H)	6.89-6.74	5.11 <u>s</u>	3.09 1.81			
VII*	8.20-7.92	7.56-7.39	7.80 5.14	5.03	3.01 1.82	0.11	15.4	1.57
VII DMSO-d <sub>6</sub>	8.41-7.41		7.00-6.87	5.06 4.63	3.29 1.64	0.43	14.0	1.84

\* 220MHz

† Less detailed spectra (60MHz) were obtained previously (Singh, 1972).

In compound (V), the geminal methylene protons Ha and Hb show an AB quartet centred at  $\delta$ 4.99; the -CH<sub>2</sub>-protons of the ethyl groups are also diastereotopic and show an AB quartet at  $\delta$ 2.89. The methyl protons show a

triplet at 1.28, 1.16, 1.03. In dimethylsulphoxide at 220MHz, the methylene protons of the ethyl groups show two well separated sextets, and AB pattern further split by the methyl groups. Figures 6 and 7 show the spectrum at 60MHz in  $\text{CDCl}_3$  and at 220MHz in  $\text{DMSO-d}_6$ .

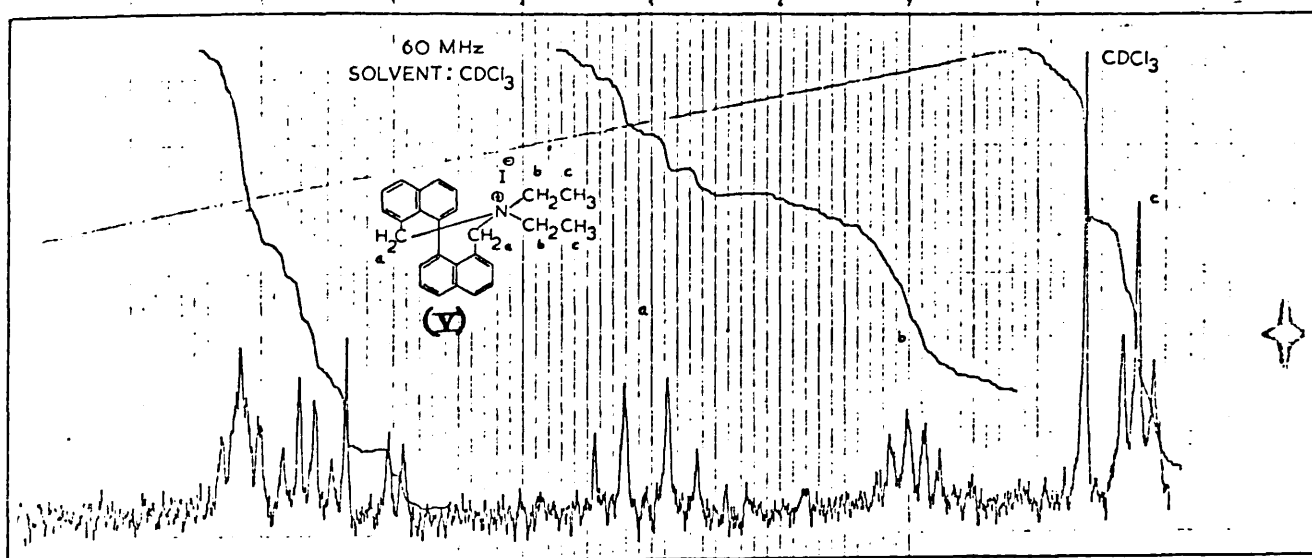


Figure 6

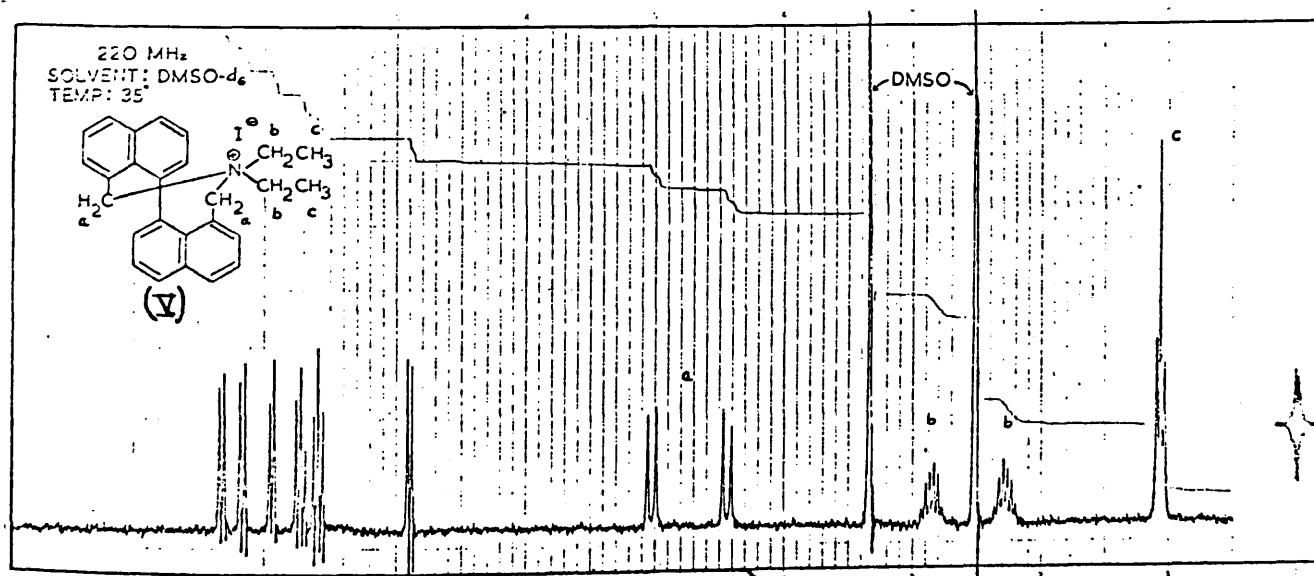


Figure 7

The diallyl compound (VI) shows a very complex spectrum (Figure 8, 9 & 10). The diastereotopic geminal methylene protons attached to the naphthalene ring appear to give an AB system quartet centred at  $\delta 4.96$ . The diastereotopic allylic methylene protons attached to nitrogen show an AB quartet, and

each peak split into doublets ( $J=6\text{cps}$ ) by the adjacent methine protons. The methine protons split into two doublets ( $J=2.5\text{cps}$ ) centred at  $\delta 5.84$  and  $\delta 5.59$  ( $J=14.7$ ). The remaining diastereotopic allylic methylene protons also show an AB system quartet centred at  $\delta 5.22$  ( $J=9\text{cps}$ ). In deuterated dimethylformamide and in dimethylsulphoxide- $d_6$  this compound shows a similar but not as well defined spectrum.

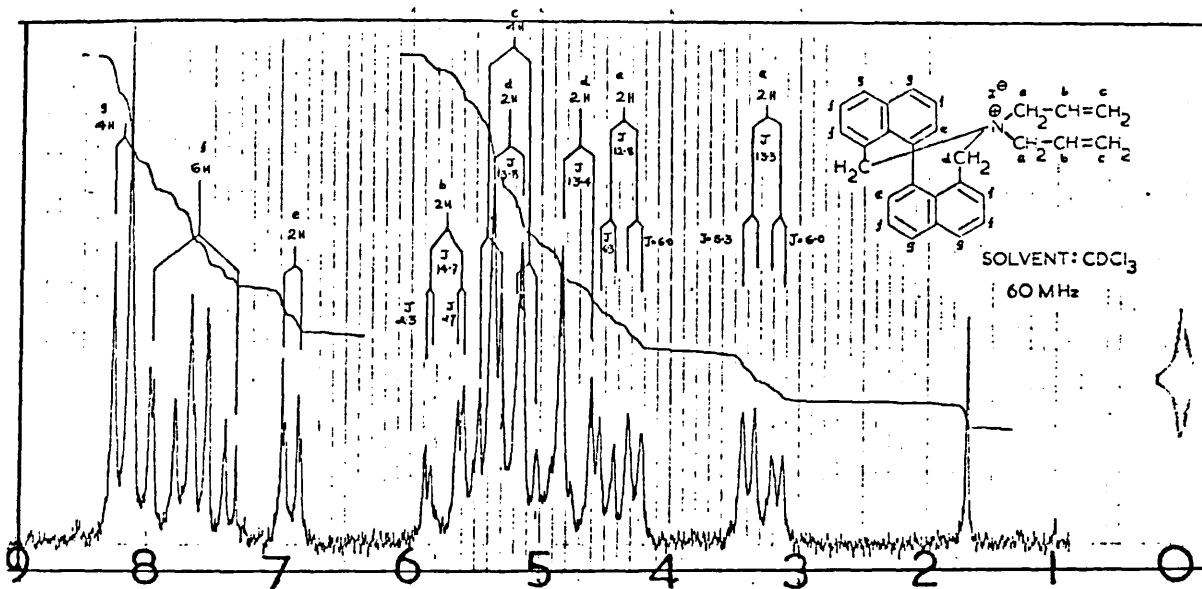


Figure 8

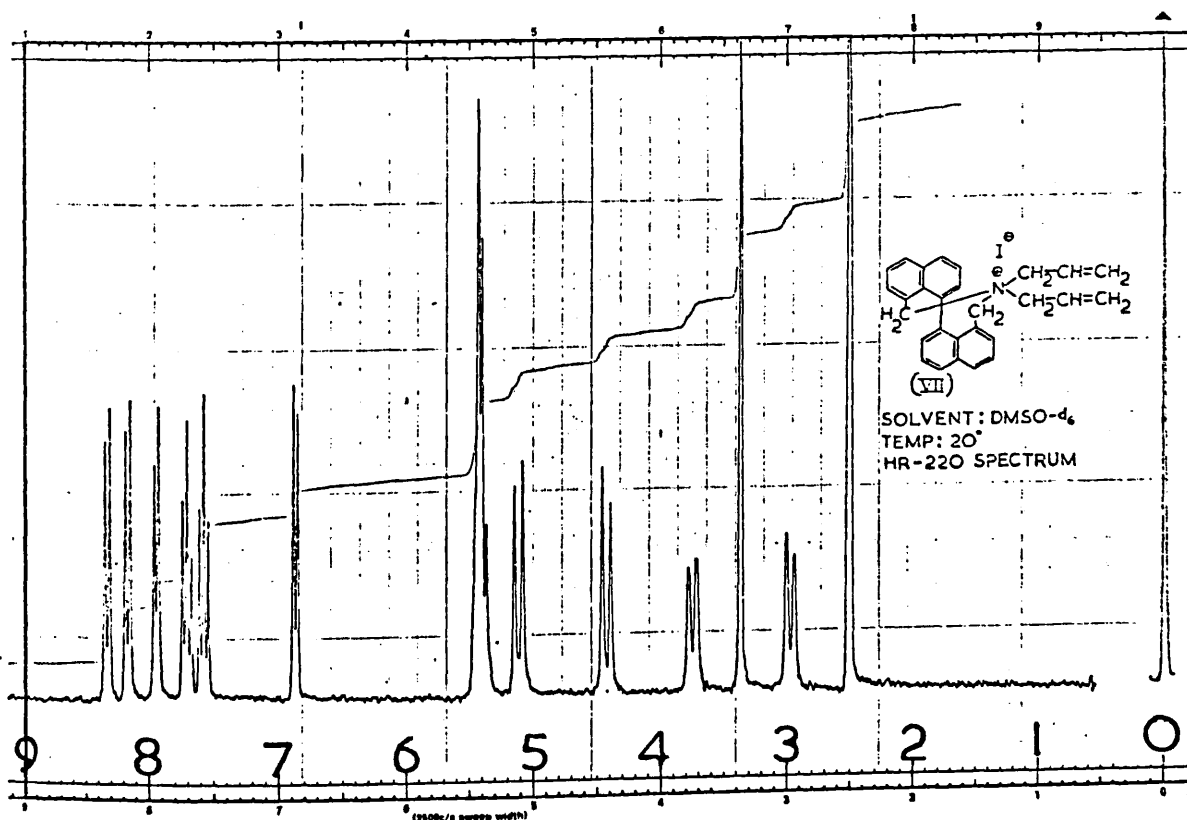


Figure 9

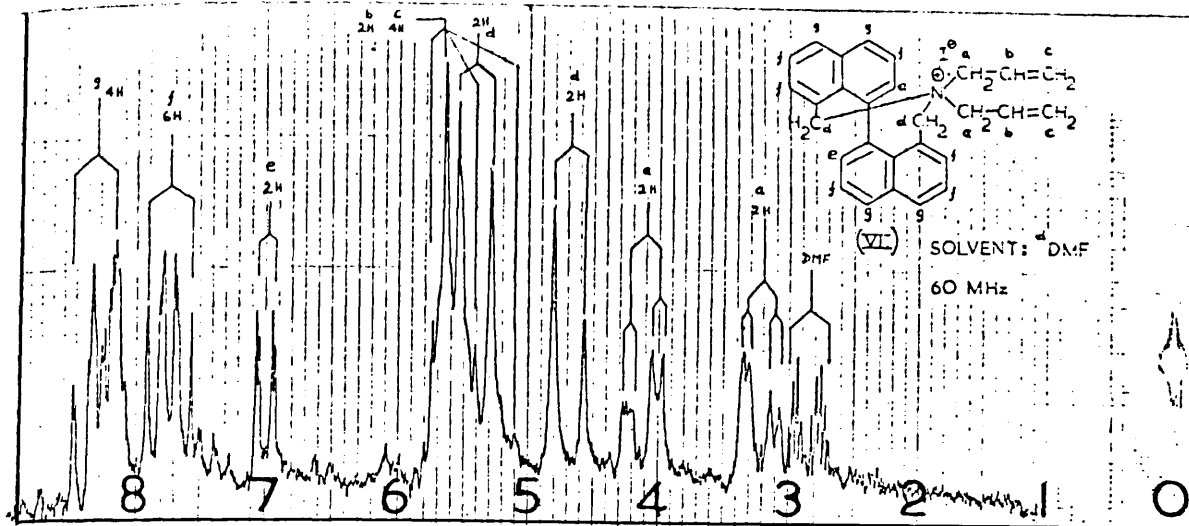
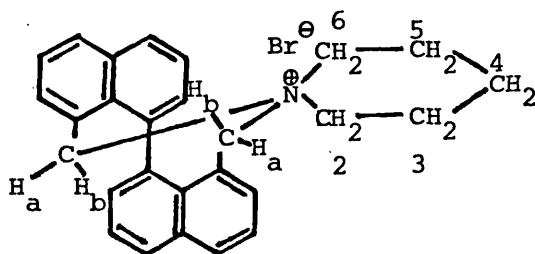


Figure 10

In the piperidinium compound (VII) the aromatic protons integrate in the ratio 6:4:2 and the diastereotopic geminal methylene protons of  $\text{CH}_2$  attached to a naphthalene ring, in deuteriochloroform at 60MHz, show (Fig. 11) only one singlet at  $\delta 5.11$ , this seems to be a case of accidental isochrony; the methylene protons of the piperidine ring attached to nitrogen show only one singlet at lower field,  $\delta 3.09$ , while the remaining three methylene protons also show only one singlet at  $\delta 1.81$ . But the diastereotopic geminal methylene protons are separated into an AB system, centred at  $\delta 5.09$ , in  $\text{CDCl}_3$  at 220MHz at room temperature; in dimethylsulphoxide a quartet is found at 60MHz and at 220MHz. The geminal methylene protons attached to naphthalene are in a fixed conformation but chair-chair conformational inversion in the piperidine ring is possible and expected to be fast. In this case the C-3 axial protons of the piperidine ring come nearer to the 7,7' protons of the aromatic rings and cause them to shift to lower field (van der Waals deshielding). This may be the reason for the change in the aromatic integration from 4:6:2 to 6:4:2.

The n.m.r. spectra of (VII) at different temperatures in  $\text{CDCl}_3$  were obtained to study the conformational changes of the piperidine protons. The results are interesting in a way that by lowering the temperature to





$-33^{\circ}$ , the AB system of the methylene protons Ha and Hb, disappears to a broad singlet at  $\delta 5.09$ ; the singlet of the piperidine methylene protons next to nitrogen (C-2,C-6) broadens at  $\delta 3.01$ ; but the singlet of the remaining piperidine methylene protons splits into a doublet at  $\delta 1.88$  (4H,C-3,C-5) and at  $\delta 1.79$  (2H,C-4). In  $\text{DMSO-d}_6$ , increasing the temperature causes peaks to sharpen and become more defined. At room temperature (60MHz) the methylene protons Ha and Hb show a quartet centred at  $\delta 4.84$ ; the piperidine methylene protons (C-2,C-6) show a singlet at  $\delta 3.29$ , and the remaining methylene protons (C-3,C-4,C-5) also show a singlet at  $\delta 1.64$ . At room temperature ( $24^{\circ}$ ) at 220MHz the methylene protons Ha and Hb show

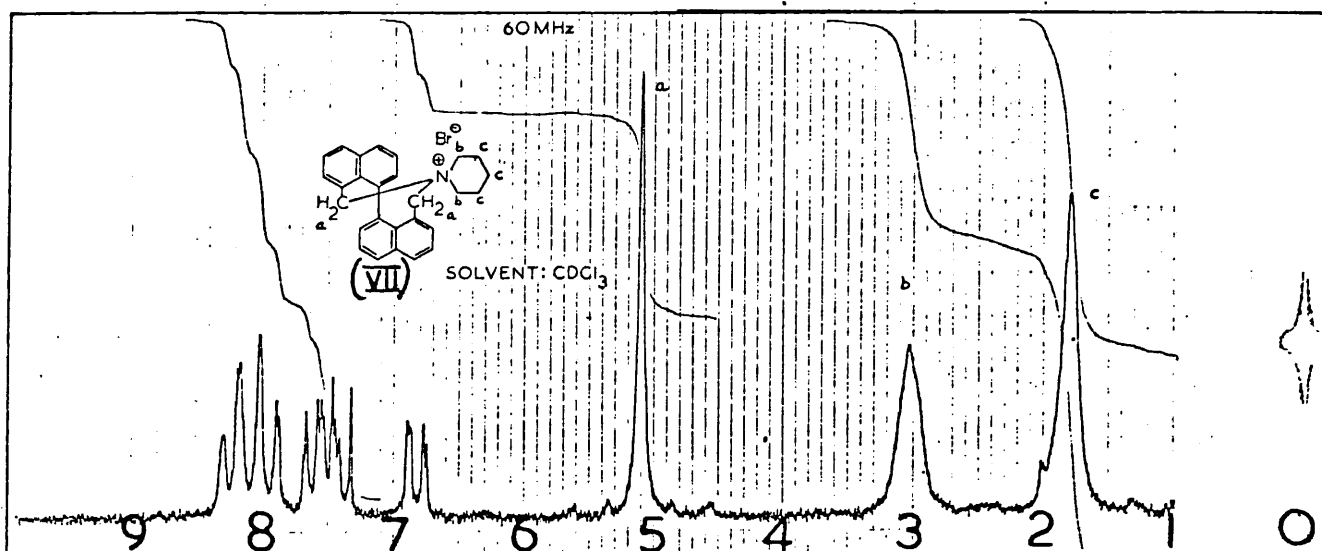


Figure 11

a quartet centred at  $\delta 4.84$ ; the piperidine methylene protons (C-2,C-6) show a doublet at  $\delta 2.74$  and  $\delta 2.60$ ; the remaining methylene protons also give a doublet at  $\delta 1.77$  (4H,C-3,C-5) and at  $\delta 1.51$  (2H,C-4). By raising the temperature to  $99^{\circ}$ , the methylene protons Ha and Hb become a quartet centred at  $\delta 4.87$ ; the piperidine methylene protons (C-2,C-6) split into two multiplets centred at  $\delta 2.81$  and at  $\delta 2.61$ ; the methylene protons (C-3,C-5) show a broad multiplet centred at  $\delta 1.80$ ; and the methylene protons (C-4) split into a quartet centred at  $\delta 1.58$ . The results are collected in Table 12 and the spectra at different temperatures are shown in figure 12

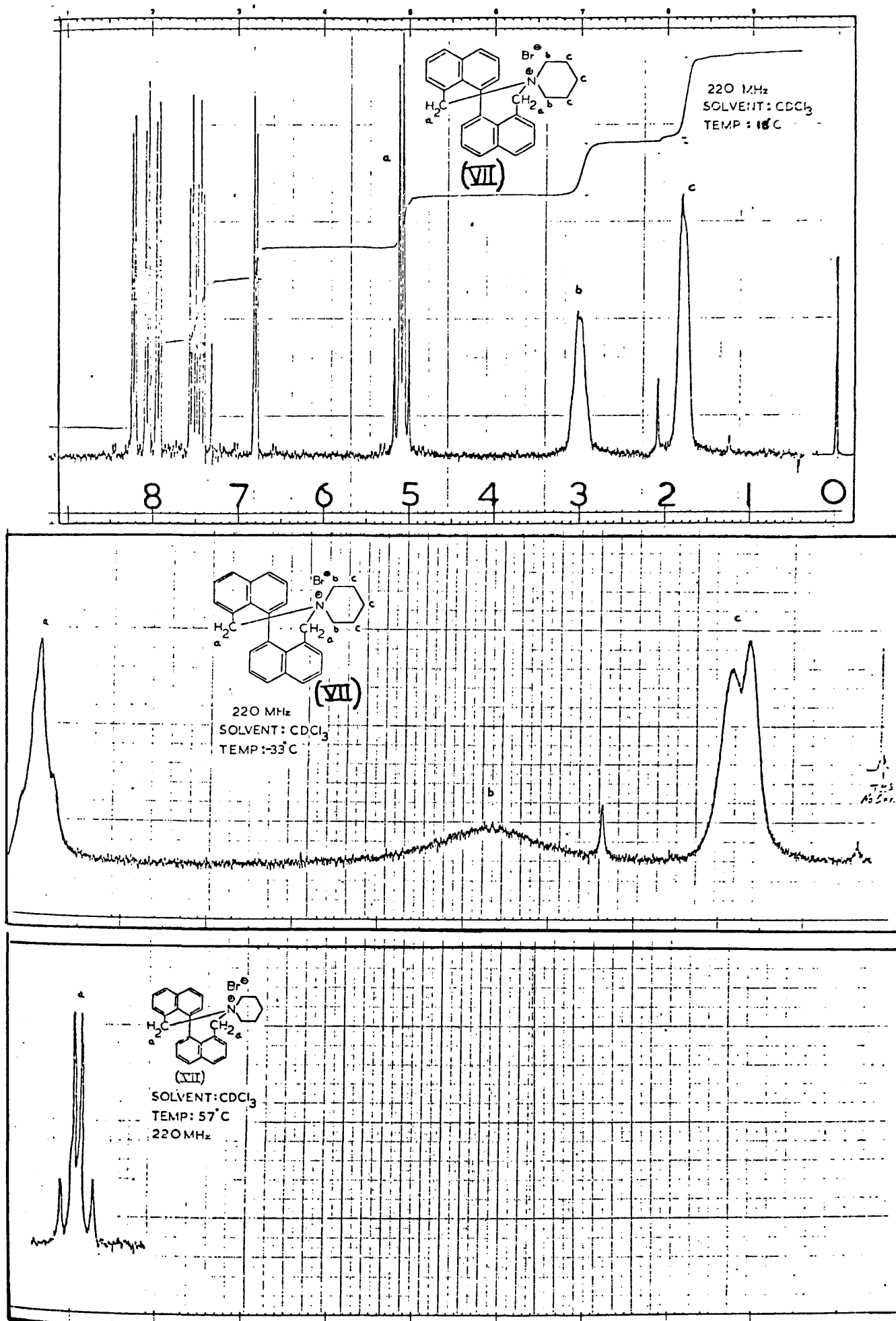


Figure 12

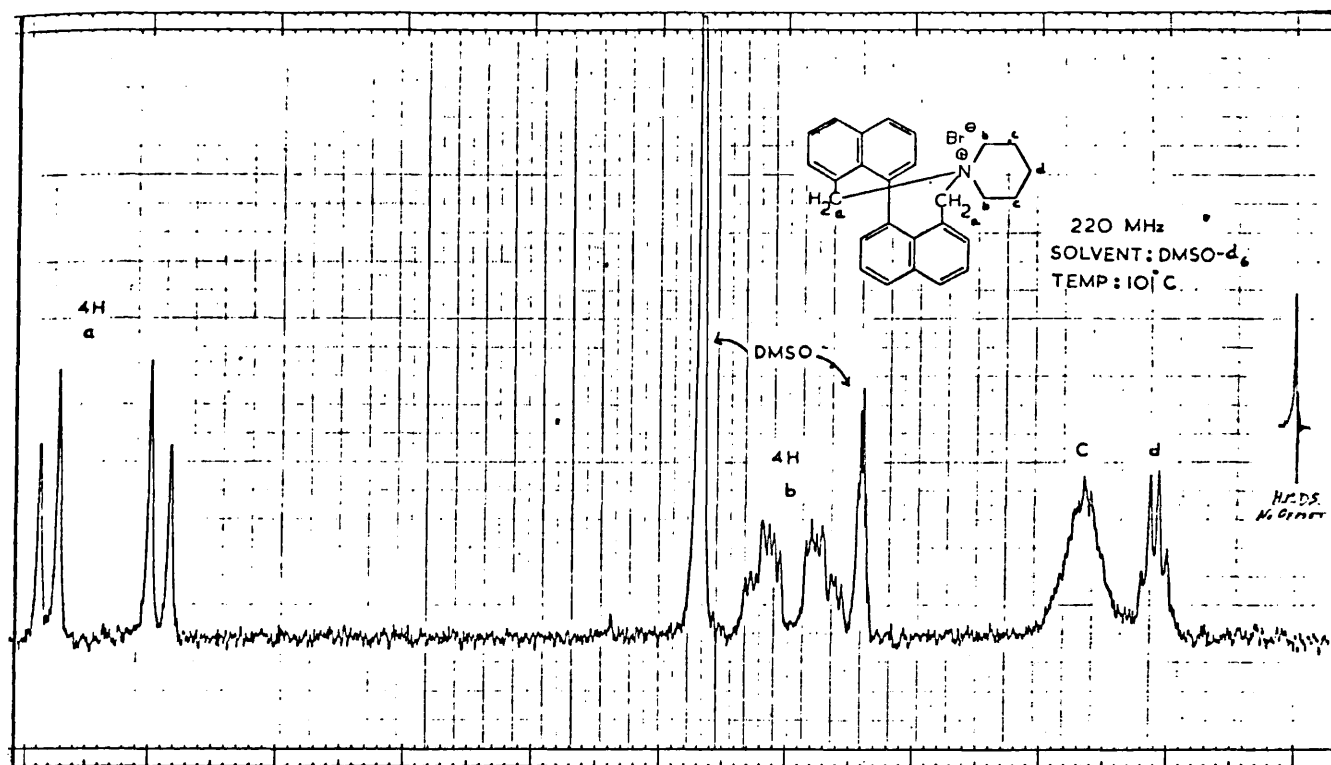


Figure 12

It seems that in this complicated situation accidental isochrony is operative again. The spectra were taken at room temperature, lower temperature, higher temperature and again at room temperature in order to confirm that there is no chemical change of the compound after heating at high temperature. In compound (V), change of temperature in  $\text{DMSO-d}_6$  did not change the spectrum significantly. (Fig. 13).

Table 12 : 9-spiropiperidinium 8,9-dihydro-7H-[1,2,3-de:4,5,6-d'e'-dinaphthalene]-cyclononanebromide (VII)

Chemical shifts ( $\delta$ ; Me<sub>4</sub>Si) methylene protons 220MHz

	Solvent	Temperature	Methylene protons		Piperidine methylene protons		
			Ha	Hb	4H 2,2',6,6'H	6H 3,3',5,5',4,4'H	4,4'H
1	$\text{CDCl}_3$	18°	5.14	5.03	3.01 (s)	1.82 (s)	
2	$\text{CDCl}_3$	5°	5.16	5.06	3.01	1.83 (s)	
3	$\text{CDCl}_3$	-24°	5.16	5.06	3.01	1.84 (s)	1.77 (s)
4	$\text{CDCl}_3$	-33°	5.08 (s)		3.01	1.88 (s)	1.79 (s)
5	$\text{CDCl}_3$	57°	5.16	5.06	-	-	
6	$\text{DMSO-d}_6$	99°	5.03	4.66	2.78 (m), 2.60 (m)	1.77 (d)	1.55 (d)
7	$\text{DMSO-d}_6$	101°	5.06	4.69	2.81 (m), 2.61 (m)	1.80 (m)	1.62, 1.59 1.56, 1.54 (q)
8	$\text{DMSO-d}_6$	23°	4.98	4.69	2.67 (d)	1.64 (d)	

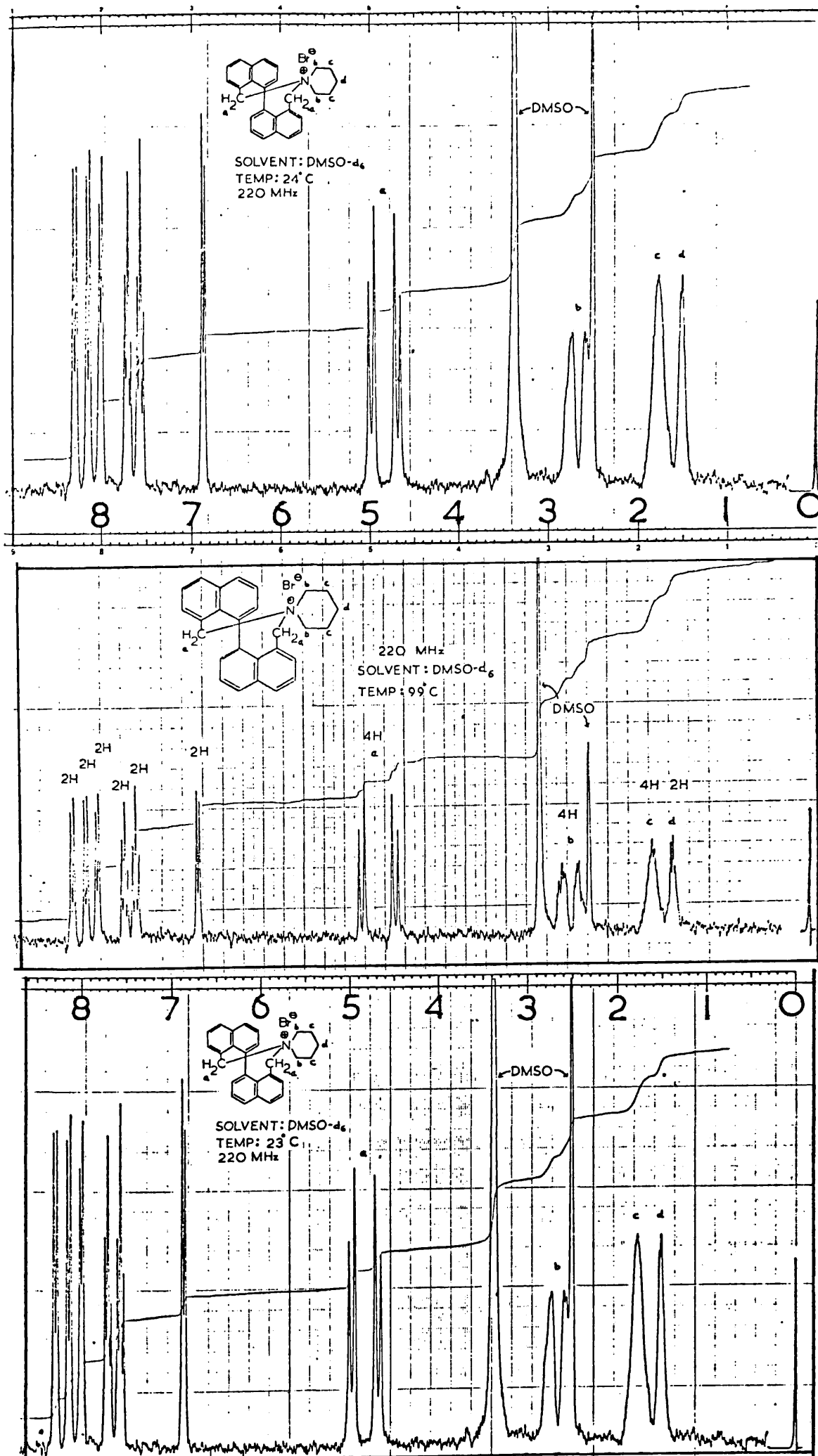
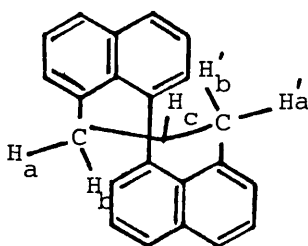


Figure 13

#### 4.2.4 Carbocyclic Compound

The n.m.r. spectra of the carbocyclic compounds (Harris and Singh, 1976) (VIII), (IX), (X), (XI) having a  $C_2$  axis are similar to those of the heterocyclic bridged compounds. The 9-ring geminal methylene protons show an AB system with  $J \approx 14\text{Hz}$ . The compounds (XII), (XIII) belong to the point group  $C_1$ , where one of the two substituents at the central carbon atom of the bridge is hydrogen, Hc. The equivalent protons of the  $C_2$  structure lose their equivalence and show a more complicated spectrum. The proton Hc



on the bridging carbon atom has an equal relationship with  $\text{Ha}'$  and  $\text{Hb}'$  methylene protons but different relationships with Ha and Hb methylene protons. The results are collected in Table 13.

Table 13: Proton n.m.r. spectra of (VIII), (IX), (X), (XI), (XII), (XIII)

Compound	<u>Chemical shifts</u> ( $\delta, \text{Me}_4\text{Si}, \text{CDCl}_3$ ) <u>of aromatic and methylene protons.</u> 60MHz			Methylene protons		Other protons	$\Delta\delta$	J	$\Delta\text{Hz}/J$
	Aromatic Protons			Ha	Hb				
(VIII)	7.92-7.77	7.49-7.10	6.87-6.72	4.04	3.13	4.03(d) (4H, $\text{CH}_2$ , q, $\text{CH}_2\text{CH}_3$ ) 1.10(6H, t, $\text{CH}_2\text{CH}_3$ )	0.91	-14.7	3.7
(IX)	8.07-7.91	7.62-7.33	6.85-6.72	3.99	3.18		0.81	-14.7	3.3
DMF									
(X)	7.91-7.75	7.50-7.06	6.87-6.72	4.05	3.12	3.42(6H, $\text{CH}_3$ , s)	0.93	-14.6	3.8
(XI)			6.82-6.68	3.38	2.49	2.85(4H, s, $\text{CH}_2\text{OH}$ ) 1.78(2H, s, OH)	0.89	-14.7	3.6
(XII)	8.06-7.91	7.59-7.34	6.89-6.76	4.00	3.18		0.82	-14.7	3.3
(DMF)									
(XIII)	7.90-7.74	7.54-7.03	6.87-6.76	3.78	2.85	3.38(3H, s, $\text{CH}_3$ )	0.93	-14.5	3.8

## 5. ULTRA-VIOLET ABSORPTION SPECTROSCOPY

5.1. General Introduction: The u.v. absorption spectra of organic compounds are associated with transitions between electronic energy levels. The transitions are generally between a bonding or lone pair orbital and an unfilled non-bonding or antibonding orbital. The principal characteristics of an absorption band are its position and intensity. The position of absorption corresponds to the wavelength of radiation whose energy is equal to that required for the electronic transition. The absorption intensity of any wavelength depends on the probability of the transition and the structure and size of the absorbing chromophore.

Beer and Lambert proposed laws of absorption: their combined form states that the fraction of the incident light absorbed is independent of the intensity of the source and is proportional to the number of absorbing molecules. It is expressed by the equation  $a = \log_{10} \frac{I_0}{I} = \epsilon \cdot l \cdot c$ . where  $a$  is the absorbance,  $I_0$  and  $I$  are the intensities of the incident and transmitted light respectively,  $l$  is the path length of the absorbing solution in centimeters,  $c$  is the concentration in moles/litre and  $\epsilon$  is the molar extinction coefficient. The Beer-Lambert law is obeyed if the absorbance of a solution remains constant as long as the product of the concentration and the path length is constant: obedience shows that the molecular species under investigation is not changed by dilution.

Steric effect: Rotation about bonds between chromophores may have a profound effect on the absorption spectrum: it may increase or decrease or cause new electronic interactions. Steric hindrance to coplanarity about a single bond between chromophores gives rise to a marked decrease in intensity compared with a planar conformation: the hindering substituent may also cause a shift of the band.

## 5.2. Historical Introduction: Ultra-Violet Spectra of Biaryls

5.2.1. Biphenyl: Biphenyl itself (in ethanol) shows a broad high intensity conjugation band (Hall, 1969) at about 250 nm because of the electronic transition between the two benzene rings through the interannular bond, and another band at short wave, 205 nm. The degree of conjugation between the two benzene rings depends upon the dihedral angle between them. The biphenyl molecule is found to be planar only in the crystal (Dhar, 1932; Robertson, 1961; Trotter, 1961; Hargreaves and Rizvi, 1962). Various estimations from physical measurements of the mean interplanar angle of biphenyl in the vapour or solution range from 40 to 45° (Karle and Brockway, 1944; Bastiansen, 1949).

5.2.1.1. Substituted biphenyls: The u.v. spectra of biphenyl and its derivatives have proved particularly interesting because of the relationship between the wavelength of maximum absorption and the dihedral angle. Some ortho substituents are small enough to allow some conjugation between the benzene rings e.g. in 2,2'-dihydroxybiphenyl and 2,2'-difluorobiphenyl which show a conjugation band shifted hypsochromically i.e. to shorter wave length (Williamson and Rodebush, 1941; Beaven and Hall, 1956). When biphenyl is substituted in the ortho positions by larger groups its dihedral angle departs further from coplanarity and effective conjugation decreases.

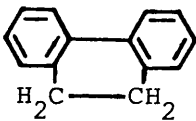
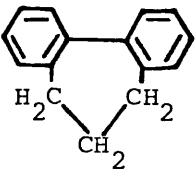
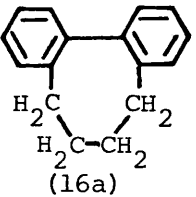
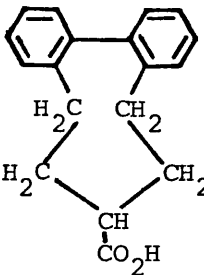
### 5.2.1.2

Carbocyclic 2,2'-bridged biphenyls: When the 2,2' positions in biphenyl are joined to form a bridge, the interplanar angle of the benzene rings has a fixed value. As the length of the bridging ring increases, the dihedral angle  $\theta$  increases and the electronic interaction between the aromatic rings decreases (Hall, 1969); the conjugation band and long wave band shift to shorter wave lengths with decrease in intensity. Table 14 (Hall, 1969) shows that bridging rings containing 6, 7 or 8 atoms allow the appearance of a separate conjugation band.

When there are nine atoms in the ring (i.e. five atoms in the bridge) the conjugation band is diminished to an inflection at low wave length.

$\theta$  is the dihedral angle estimated from scale models.

Table 14 (Hall, 1969)

Compound	No. of atoms in bridging ring	$\theta$	Conjugation band		Longwave band	
			$\lambda_{\max}, \text{nm}$	$\epsilon_{\max}$	$\lambda_{\max}, \text{nm}$	$\epsilon_{\max}$
	6	15.3	264	17,000	299.5 289.5 inf	4,450 4,200
 (2)	7	50.6	247	15,700		
 (16a)	8	59	235	9,680	265 inf 275 inf	
 (20)	9	68	231 inf	5,550	265 273	ca.800 ca.600

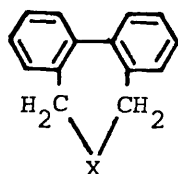
### 5.2.1.3. Heterocyclic 2,2'-bridged biphenyls:- Beaven, Hall,

Lesslie and Turner (1952) studied the u.v. spectra of biphenyls with hetero-atoms O and N in the bridges. They found that the dihydrobenzoxepin (7) is spectroscopically about as conjugated as biphenyl itself and the dihydrodibenzazepinium salt (13) is only marginally less conjugated (Table 15). Truce and Emrick (1956) studied 7-membered heterocyclic 2,2'-bridged biphenyls, where the heterofunction is sulphur, sulphone, selenium, methylselenium etc. The wave lengths of the absorption maxima lay in the reverse order of the sizes of the hetero atoms:



these compounds show shifts of the conjugation bands towards shorter wave lengths and a decrease in the extinction coefficient in comparison with the corresponding carbocyclic rings and the other seven membered  $o,o'$ -bridged biphenyls. The order shows that larger heteroatoms allow less  $1,1'$ -biphenyl conjugation than smaller ones (Table 15)

Table 15



		Conjunction band			
		$\theta$	$\lambda_{\max}$	$\epsilon_{\max}$	solvent
(7)	X=O	44.1 *	250	17,000	iso-octane
		47	250	16,500	Ethanol
		43 **			
(13)	X=N <sup>+</sup> NMe <sub>2</sub>	49	248	15,000	Ethanol
		47			
		NMe	45.8		
(2)	X=CH <sub>2</sub>	50.6	247	15,700	
(8)	X=S	56.6	244	10,200	iso-octane
			245	10,000	Ethanol
(10)	X=SO <sub>2</sub>		243	13,000	Ethanol
(9)	X=Se		247	6,250	Ethanol

\* Mislow et.al., 1964

\*\* Hall and Minhaj, 1957

Braude and Forbes (1955) looked for a relationship between the cosine of the mean interplanar angles of bridged biphenyls in their ground states and maximum absorption, using the formula  $\epsilon/\epsilon_0 = \cos^2 \theta$ : this proved of very limited value. Suzuki (1967) calculated the angle  $\theta$  of biphenyls by using the LCAO molecular orbital method: his result for biphenyl itself in solution was about  $20^\circ$ . He also reported calculated values of the angle of twist of  $44.5^\circ$  in the oxepin (7),  $47.3^\circ$  in

the azepinium bromide (13),  $58-61.5^\circ$  in compounds with 8-membered homocyclic bridging rings (16a) and  $68^\circ$  for compounds with 9-membered bridging rings (20).

5.2.2 The 1,1'-binaphthyl Series: 1,1'-Binaphthyl is an example of a 2,2'-disubstituted biphenyl. Friedel, Orchin and Reggel (1948) studied the u.v. spectra of biphenyl, 2,2'-binaphthyl and 1,1'-binaphthyl and found that 2,2'-binaphthyl is comparable with biphenyl while 1,1'-binaphthyl has a spectrum resembling naphthalene itself with three main bands: a short-wave band with high intensity at 220 nm ( $\epsilon$  100,000) and long wave bands at 275 (5,000) and 312 nm (200); they concluded that the mean dihedral angle is too great for conjugation between the rings.

Brown, Trotter and Robertson (1961), by the x-ray diffraction method, found a dihedral angle of  $73^\circ$  between the two naphthalene rings in the crystals of the form m.p.  $148-149^\circ$ . In 1969, Kerr and Robertson, found that the dimensions of the two naphthalene rings are not significantly different from those of naphthalene itself, that the conformation is cis with an interplanar angle of  $68^\circ$ . LeFevre, Sundaram and Sundaram (1963), working with solutions, calculated a dihedral angle of  $48^\circ$ , from molecular Kerr constant. Unlike biphenyl, 1,1'-binaphthyl is not flat even in the crystal.

Harris and Mellor (1961) obtained optically active 1,1'-binaphthyl; the energy of activation for racemization in solution being 22.5 Kcal. showing that attainment of the "flat" conformation is infrequent. Browne, Harris, Mazengo and Shyam Singh (1971) recorded the u.v. spectrum of 1,1'-binaphthyl in 96% ethanol which shows absorption maxima at 220 ( $\epsilon$  108,000); 249 (4,760); 262 inf (6,210); 272 inf (9,720); 283 (14,300); 293.5 (14,000) and 313 nm, sh (3,160).

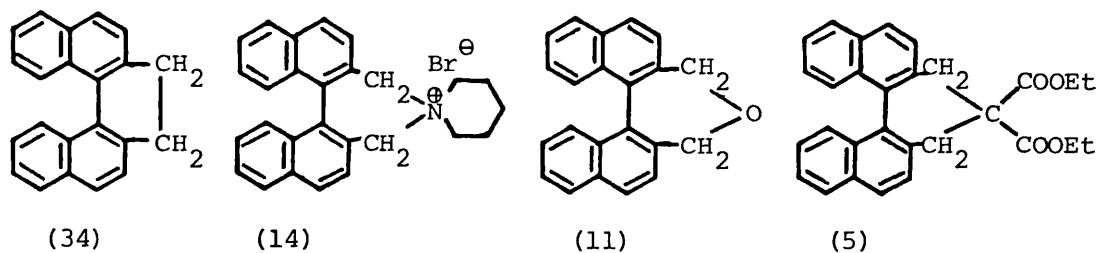
5.2.2.1. Substituted 1,1'-binaphthyls: The preferred conformation of the substituted 1,1'-binaphthyls depends mainly upon the steric

effect of the substituting groups. The absorption spectrum of 2,2',7,7'-tetramethyl-1,1'-binaphthyl shows fine structure and a typical naphthalene band at 319 nm (Friedel, Orchin and Reggel, 1948). In 8,8'-disubstituted 1,1'-binaphthyls, the substituting groups cause greater molecular overcrowding which is relieved by {Harris and Mellor 1961; Harris and Cooke, 1963} distortions (peri-naphthalene forces) which cause bathochromic (to longer wave length) shifts with increased intensity. But in 2,2'-disubstituted 1,1'-binaphthyls, the same substituents cause very much less molecular overcrowding and do not produce similar distortion. Harris and Mazengo (1967) studied the u.v. absorption spectra of 2,2' and 8,8'-dimethyl-1,1'-binaphthyls. They found that the spectrum of 8,8'-dimethyl-1,1'-binaphthyl resembles that of 1,1'-binaphthyl, while the absorption spectrum of 2,2'-dimethyl-1,1'-binaphthyl gives fine structure with a typical naphthalene band at 314 nm. The hypsochromic shift and the lower intensity of the absorption minimum of 2,2'-dimethyl compared with 8,8'-dimethyl indicates that the overall binaphthyl structure may be more nearly planar in 8,8'-dimethyl than 2,2'-dimethyl-1,1'-binaphthyl, although individual naphthalene units may be more distorted. This means that the twist about the interannular bond in the ground state may be more in 2,2'-dimethyl-1,1'-binaphthyl than in 8,8'-dimethyl-1,1'-binaphthyl. Mason, Seal and Roberts (1974) considered that 1,1'-binaphthyl-2,2'-dicarboxylic acid may have a larger dihedral angle than 1,1'-binaphthyl-8,8'-dicarboxylic acid as it has a smaller  $\Delta\epsilon$  max value.

#### 5.2.2.2.

2,2'-Bridged 1,1'-binaphthyl: Hall and Mazengo (1967) recorded the u.v. spectrum of a six ring 2,2'-bridged compound, 9,10-dihydro-3,4:5,6-dibenzophenanthrene (34). This compound has a dihedral angle of about  $20^\circ$ . It shows a strong band at  $\lambda$  239.5 nm ( $\epsilon=42,000$ ) attributed to conjugation between the naphthalene rings. The seven-membered heterocyclic ring compounds (14) (Hall and Turner,

1951, 1955; Beaven, Hall, Lesslie and Turner, 1952), (11) (Mislow, 1962, 1964) and the carbocyclic ring compound (5) (Mislow, 1958, 1962) also show conjugation bands, at slightly longer wavelength than the common short wave band at about 232 nm, with high extinction coefficients ( $\epsilon \approx 74,000$ ): a blue shift (to shorter wavelength) of the conjugation band takes place with increase in intensity by enlarging the bridging ring; this is different from the biphenyl cases:



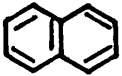
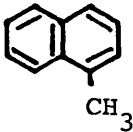
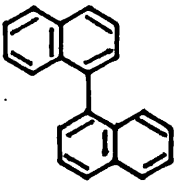
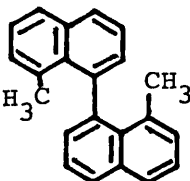
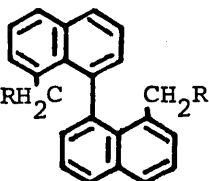
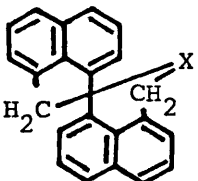
Mason, Seal and Roberts (1974) carried out a set of  $\pi$ -SCF calculations to correlate  $\epsilon_{\max}$  and the c.d. spectra of 1,1'-binaphthyls at different dihedral angles.  $\epsilon_{\max}$  is greatest for compound (14), predicted to have a dihedral angle of  $70^\circ$ : its c.d. spectrum resembles that of 1,1'-binaphthyl.

### 5.3 Ultraviolet absorption spectra of Unbridged and Bridged 8,8'-disubstituted 1,1'-binaphthyls. Results and discussion:

This section consists mainly of the discussion of the results in Tables 17,18, 19 and 20. The spectra of 9-membered ring 8,8'-bridged 1,1'-binaphthyls I, II, III, IV and VIII are reported here for the first time; 8,8'-disubstituted 1,1'-binaphthyls XV, XVII and XVIII were previously studied by Richard Mazengo 1968, Harris, Harris, Mazengo, Singh, 1974 and those of the 9-membered ring 8,8'-bridged 1,1'-binaphthyls V, VI, VII, IX, X, XI, XII and XIII by Shyam Singh 1972 (the figures for compound XIX previously reported are now known to be in error, on account of the mistaken identity of the specimen used; an erratum notice has been submitted for publication with the 1977, Index J.C.S. Perkin II). All of the syntheses and the spectra have now been repeated, for the purpose of comparison and as a preliminary to investigating the c.d. spectra. In the Tables the figures in curved brackets ( ) were obtained by Richard Mazengo and those in square brackets { } by Shyam Singh.

The comparison of the spectra of the 8,8'-disubstituted unbridged and bridged 1,1'-binaphthyls with 8,8'-dimethyl-1,1'-binaphthyl and 1-methylnaphthalene is interesting as they have so much common molecular structure (Table 16):-

Table 16

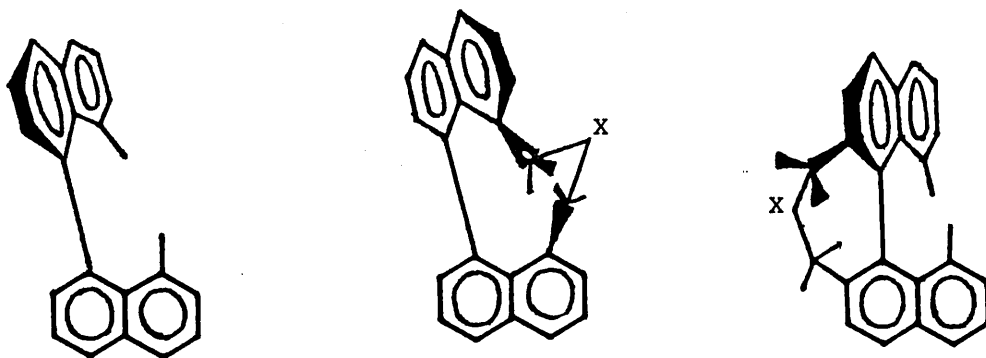
					
$\lambda_{\max}$ 220	$\lambda_{\max}$ 224	$\lambda_{\max}$ 220	$\lambda_{\max}$ 221.5	$\lambda_{\max}$ 222.5-224.5	$\lambda_{\max}$ 221-225-230.5
$\epsilon_{\max}$ 117,000	$\epsilon_{\max}$ 60,000	$\epsilon_{\max}$ 101,000	$\epsilon_{\max}$ 85,000	$\epsilon_{\max}$ 76,500-85,900	$\epsilon_{\max}$ 78,000-93,800
$\lambda_{\min}$ 235	$\lambda_{\min}$ 240	$\lambda_{\min}$ 240	$\lambda_{\min}$ 255	$\lambda_{\min}$ 257-259	$\lambda_{\min}$ ~255
		$\epsilon_{\min}$ 4,760	$\epsilon_{\min}$ 5,600	$\epsilon_{\min}$ 4,600-6,300	$\epsilon_{\min}$ 4,400-10,200

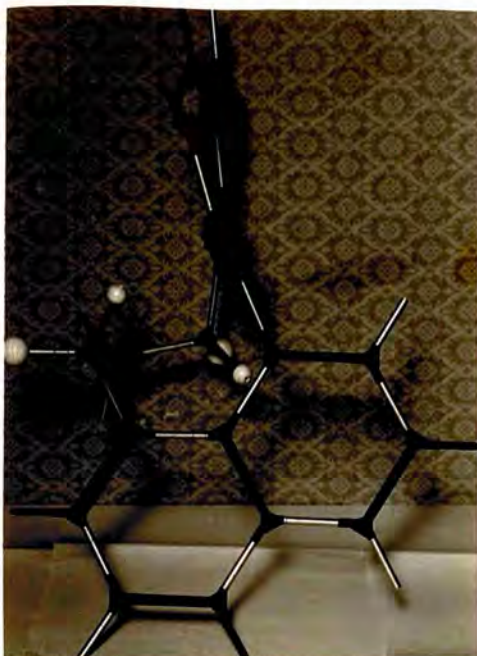
All the spectra show general characteristics to be found in naphthalene and in 1,1'-binaphthyl. When the 1-position in naphthalene is substituted by a methyl group the short wave absorption maximum shifts to longer wave length, with decrease in intensity, and the absorption minimum also shifts to longer wave length, with increase in intensity. Similarly in 8,8'-dimethyl-1,1'-binaphthyl the short wave maximum shifts to longer wave length with decrease in intensity and the minimum shifts to longer wave length with increase in intensity compared to 1,1'-binaphthyl. The other unbridged and bridged 1,1'-binaphthyls also show red shifts of the short wave absorption maxima with decrease in intensity compared to 1,1'-binaphthyl and are very closely similar to 8,8'-dimethyl-1,1'-binaphthyl: the long wave absorptions are similar to this compound also.

Inspection of the u.v. spectra of 8,8'-disubstituted unbridged (Harris, Harris, Mazengo and Singh, 1974) and 9-membered ring (Shyam Singh, 1972) 8,8'-bridged 1,1'-binaphthyl compounds reveals that a separate band corresponding to the "conjugation band" of the biphenyl series is absent; (the 8,8'-dicarboxylic acid and its esters are left out of this generalisation, as they have special features which are not fully understood); models indicate that in 9-membered ring 8,8'-bridged binaphthyl compounds, the dihedral angle is about  $90^{\circ}$ . Mason, Seal and Roberts (1974), from  $\pi$ -SCF calculations, considered that the non-bridged 1,1'-binaphthyls are likely to have dihedral angles in the  $90+20^{\circ}$  range. The six-membered 2,2'-bridged compound 9,10-dihydro-3,4:5,6-dibenzophenanthrene (34) has a dihedral angle of about  $20^{\circ}$  and does show a conjugation band, at 239.5 nm ( $\epsilon 42,000$ ), while the nine-membered bridged biphenyl (20), which has a dihedral angle of about  $65-68^{\circ}$  in one of its conformations, shows a conjugation band only as an inflection at low wave length 231 nm ( $\epsilon 5,500$ ). Mason, Seal and

Roberts (1974) say " a biaryl with a dihedral angle of  $\pi/2$  has not only local electronic excitations within each aromatic chromophore but also charge-transfer excitations arising from the promotion of a  $\pi$ -electron from an occupied orbital of one aromatic residue to an unoccupied orbital of the other. These charge transfer excitations are devoid of dipole and rotational strength but with a change of dihedral angle from  $\pi/2$  they mix with the local excitations, and a distinction between the two types is largely lost when there is appreciable  $\pi$ -electron delocalisation across the internuclear band, both types becoming excitations of the biaryl chromophores as a whole." This indicates that at all dihedral angles smaller or larger than  $90^\circ$ , some interaction between the rings is still expected to occur, but it may be masked by a shorter wave length absorption.

The  $\pi$ SCF calculations are carried out using a model with flat naphthalene units and equal aromatic bond lengths. This approximation may mean that the results of calculations are not strictly applicable in the peri-substituted cases because the peri-repulsion distorts the naphthalene residues away from planarity. The diagrams (taken from Harris and Mellor, Chem. and Ind., 1961, 557), and figure show the distortions in unbridged compound and 8,8'-bridged 9-membered ring compound compared with a 2,2'-bridged 7-membered ring compound.





5.3.1 9-Membered ring 8,8'-bridged 1,1'-binaphthyls with Oxygen, Sulphur and Selenium in the ring (I, II, III, IV, fig.14 Table 17.)

The spectra of the 8,8'-bridged heterocyclic compounds show the general characteristics of 1,1'-binaphthyl itself. Along the series -O-, -SO<sub>2</sub>-, -S-, -Se-, there is a small progressive red shift of the short wave band with a decrease in intensity in the same order, more marked in the selenium compound:  $\lambda_{\max}$  221 ( $\epsilon$ , 93,000), 223.5 (91,400), 227.5 (91,000), 230.5nm (78,000) respectively, the latter being a second maximum, the first being at 220 nm (75,000). The short wave band overlaps a band at slightly longer wavelength which appears as a shoulder at increasing wavelength and with decrease in intensity in the same order. The absorption minima show red shifts in the same order as the maxima with increasing intensity;  $\lambda_{\min}$  254 ( $\epsilon$  5,600), 257 (6,600), 267 (7,000), 272nm (10,200) respectively; the minimum for the oxonine is similar to that of unbridged 8,8'-bishydroxymethyl-1,1'-binaphthyl (XVII). The oxonine and sulphone compounds show more resolved bands at longer wavelength centered at  $\lambda$  292.5 ( $\epsilon$  19,700) and 295nm (19,500) respectively while the sulphur and selenium compounds show broad longwave bands at  $\lambda$  302 ( $\epsilon$  16,600) and 306nm



(17,400) respectively. The oxonine and sulphone compounds show naphthalene bands at  $\lambda_{319}(\epsilon_{2,400})$  and  $319\text{nm}(3,400)$  respectively which are absent in the sulphur and selenium compounds. In general, as the size of the heteroatom in the bridge increases, the whole spectrum shifts toward longer wavelength. The low intensity of the short wave band in the selenium compound is as predicted by Mason, Seal and Roberts (1974), the smallest  $\lambda_{\text{max}}$  indicating the largest dihedral angle.

5.3.2 9-Membered ring 8,8'-bridged 1,1'-binaphthyls with nitrogen in the ring (V,VI,VII,fig. 15 Table 18)  
(Shyam Singh, 1972)

The spectra of the N-heterocyclic quaternary ammonium halides V,VI and VII are similar to each other as would be expected since the dihedral angle and other steric situations in these compounds resemble each other closely; the short wave band is followed by another band as a shoulder at slightly longer wavelength. They show intense short wave bands at  $\lambda_{\text{max}}$  222( $\epsilon_{90,300}$ ), 223(93,800), 223nm (80,800) respectively. The absorption minima are also very close to each other:  $\lambda_{\text{min}}$  255.5(4,400), 255.5(4,600), 255nm(4,800) respectively. The long wave band is centered at  $\lambda_{295.5}(\epsilon_{15,800})$ , 297(17,400), 297nm(16,400) respectively and there is a typical naphthalene band at  $\lambda_{319}(\epsilon_{2,900})$ , 320(3,100), 322nm(2,200) respectively.

5.3.3 9-Membered ring 8,8'-bridged 1,1'-binaphthyls, Carbocyclic. (VIII,IX,X,XI,XII,XIII,fig.16,17Table 19)  
(Shyam Singh, 1972).

The general characteristics of the spectra of the 9-ring dicarboxylic acid, monocarboxylic acid and their respective esters and related alcohols are similar to each other and again similar to that of 8,8'-dimethyl binaphthyl and to 1,1'-binaphthyl itself. They show slight red shifts of the short wave band with decreased intensity of absorption in

comparison with the N-heterocycles. In comparison with their unbridged precursors the short wave bands are red shifted with increased intensity, and the minima blue shifted with reduction in intensity. Unlike unbridged 1,1'-binaphthyl-8,8'-dicarboxylic acid and its methyl ester, the bridged diacid and its ester did not show any splitting of the short wave band, probably because the carboxyl groups are separated by carbon atoms from the aromatic ring system. Harris, Harris, Mazengo and Shyam Singh (1974) found that 1,1'-binaphthyl 8,8'-diacetic acid and its ethyl ester do not show any splitting of the short wave band suggesting that the carboxylic acid groups do not effect the absorption pattern in these compounds as they are isolated from the aromatic nuclei. The long wave bands show red shifts compared with unbridged compounds, with more resolved structure and of higher intensity. They all show long wave typical naphthalene bands at about 319-320nm. The dihedral angles in all these compounds must be very close to each other; groups beyond the CH<sub>2</sub> have very little influence (hence resemblance to CH<sub>3</sub>).

In general, all the bridged compounds in Table 17, 18 and 19 show similar characteristic spectra to 8,8'-dimethyl-1,1'-binaphthyl; the heterocyclic compounds II and III show the largest shifts to longer wavelength.

#### 5.3.4. Unbridged compounds: (XV, XVI, XVII, XVIII, XIX, fig.18 Table 20.)

(Harris, Harris, Mazengo and Shyam Singh, 1974)

The absorption spectra of 1,1'-binaphthyls substituted at 8,8'- positions by CH<sub>2</sub>OH, CH<sub>2</sub>Br, and CH<sub>2</sub>CN are also similar to that of 8,8'-dimethyl-1,1'-binaphthyl and to 1,1'-binaphthyl itself, but the diacid (XV) and its dimethyl ester (XVI) show marked difference. The absorption maxima of the short wave bands of XV and XVI show blue shifts with reduction in intensity and the absorption minima and the long wave bands show red shifts compared to other unbridged compounds,

(XVII, XVIII, XIX) and to 1,1'-binaphthyl. The short wave band in the diacid and its dimethyl ester is followed by another band at  $\lambda 239.5\text{nm}$  ( $\epsilon 44,000$ ) and  $\lambda 235\text{nm}$  ( $\epsilon 47,800$ ) respectively, which is very tempting to ascribe to the COOH group but (34) has a band at this position too, this may just be a coincidence. Mason, Seal and Roberts (1974) suggested a dihedral angle larger than  $70^\circ$  for 1,1'-binaphthyl-8,8'-dicarboxylic acid as the c,d, spectrum of its (-) isomer resembles qualitatively the theoretical  $\pi$ -SCF spectrum for a  $70^\circ$  dihedral angle but has smaller  $\epsilon_{\text{max}}$  value. They (XV and XVI) also show typical naphthalene bands at longer wavelength with high intensity,  $\lambda 332\text{sh}$  ( $\epsilon 9,100$ ) and  $\lambda 329\text{nm}$  (8,100) respectively.

Table 17 U.V. absorption spectra of 8,8'-bridged heterocyclic 1,1'-binaphthyls in 95% ethanol.

	Short wave band			Long wave band			$\lambda$	$\epsilon$	$\lambda$	$\epsilon$				
	$\lambda_{max}$	$\epsilon_{max}$	$\lambda_{min}$	$\epsilon_{min}$	$\lambda$	$\epsilon$					$\lambda$	$\epsilon$		
I X=O	221	93,000	254	5,600	274	11,200	284	15,400	292.5	19,700	302.5	16,200	319	2,400
II X=S	227.5	91,000	267	7,000					302	16,600				
III X=Se	230.5	78,000	272	10,200					306	17,400				
	220	75,000												
IV X=SO <sub>2</sub>	223.5	91,400	257	6,600	273	11,000	285.5	16,000	295	19,500	302.5	15,600	319	3,400

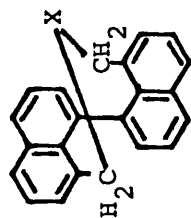


Table 18 U.V. absorption spectra of 8,8'-bridged N-heterocyclic 1,1'-binaphthyls in 95% ethanol.

V R=R'=CH <sub>2</sub> CH <sub>3</sub>	222	90,300	255.5	4,400	273	8,900	287	13,600	295.5	15,800	301	13,600	319	2,900
	(222)	(89,960)	(255.5)	(4,180)	(273)	(8,600)	(287)	(13,670)	(296.5)	(15,900)	(301)	(13,700)	(319)	(2,750)
VIR R'=CH <sub>2</sub> -CH=CH <sub>2</sub>	223	93,800	255.5	4,600			285	14,700	297	17,400	305	13,400	320	3,100
	(223)	(93,200)	(254.5)	(4,200)			(286)	(14,260)	(297)	(17,000)	(305)	(13,000)	(320)	(2,800)
VII N <sub>10</sub>	223	80,800	255	4,800			286	14,200	297	16,700	303	13,500	322	2,200
	(223)	(85,500)	(255)	(4,200)			(286)	(15,000)	(297)	(17,600)	(303)	(14,500)	(321)	(2,200)

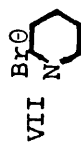
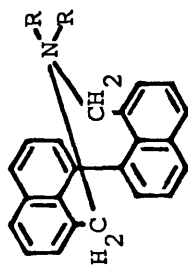
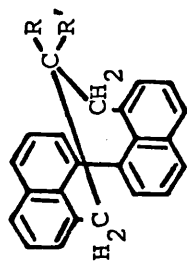
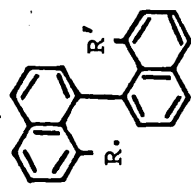


Table 19 U.v. absorption spectra of 8,8'-bridged carbocyclic compounds in 95% ethanol.

	Short wave band				Long wave band									
	$\lambda_{\max}$	$\epsilon_{\max}$	$\lambda_{\min}$	$\epsilon_{\min}$	$\lambda$	$\epsilon$	$\lambda$	$\epsilon$						
VIII R=R'=COOEt	223.5	81,000	255.5	5,900	269	9,300	282	15,100	292.5	19,100	302.5	15,400	319	2,400
IX R=R'=COOH	223.5	82,800	255.5	5,900	274	10,900	285	14,800	293	18,200	302.5	14,600	319	2,300
	(223.5)	(79,550)	(255.5)	(4,800)	(272)	(8,800)	(285)	(14,100)	(293)	(17,400)	(302)	(14,100)	(319)	(1,900)
X R=R'=COOCH <sub>3</sub>	223	92,000	255	6,100	272	10,700	282.5	15,900	292.5	20,000	302.5	16,000	319	2,500
	(223)	(75,900)	(255)	(4,750)	(272)	(8,770)	(282.5)	(13,200)	(292.5)	(16,670)	(302.5)	(13,100)	(319)	(1,800)
XI R=R'=CH <sub>2</sub> OH	225	88,200	256.5	5,500	274	10,400	284.	15,200	294.5	18,900	304.5	14,900	320	2,000
	(225)	(87,500)	(257)	(5,100)	(274)	(8,990)	(284)	(13,240)	(294)	(16,600)	(305)	(12,900)	(320)	(1,970)
XII R=H; R'=CO <sub>2</sub> H	224	93,400	256	6,300	273	11,000	283	15,900	293	20,000	303	16,200	319	2,900
	(224)	(82,600)	(256)	(4,680)	(273)	(8,900)	(283)	(13,800)	(293)	(17,800)	(304)	(14,000)	(319)	(2,000)
XIII R=H, R'=CO <sub>2</sub> CH <sub>3</sub>	224	85,800	255	5,800	272	10,000	282	14,800	293	18,800	303	15,300	319	2,500
	(223.5)	(85,500)	(255)	(5,100)	(272)	(9,350)	(282)	(13,900)	(293)	(18,300)	(303)	(14,800)	(319)	(2,100)

Table 20 U.v. absorption spectra of 8,8' - disubstituted 1,1' - binaphthyls in 95% ethanol.

	Short wave band				Long wave band			
	$\lambda_{\max}$	$\epsilon_{\max}$	$\lambda_{\min}$	$\epsilon_{\min}$	$\lambda$	$\epsilon$	$\lambda$	$\epsilon$
XV R=CO <sub>2</sub> H	219.5	60,500	268	4,800	309	13,800	332 <sub>sh</sub>	9,100
	{ 219.5 }	{ 60,000 }	{ 267.5 }	{ 5,200 }	{ 309 }	{ 14,000 }	{ 332 <sub>sh</sub> }	{ 9,100 }
	239.5	44,000						
	{ 239.5 }	{ 44,000 }						
XVI R=CO <sub>2</sub> CH <sub>3</sub>	219.5	64,900	266.5	5,700	305	13,300	319	10,300
	{ 219.5 }	{ 65,000 }	{ 266.5 }	{ 5,700 }	{ 305 }	{ 13,000 }	{ 320 }	{ 9,400 }
	235 <sub>sh</sub>	47,800						
	{ 235 <sub>sh</sub> }	{ 47,000 }						
XVII R=CH <sub>2</sub> OH	223	85,900	258.5	4,600	291	12,900	299.5	12,500
	(223.5)	(80,000)	(258)	(5,800)	(290)	(13,000)	(300)	(10,000)
								(322.5 <sub>inf</sub> )
								(5,000)
XVIII R=CH <sub>2</sub> Br	224.5	76,500	259	6,300	290.5	13,200	301	12,800
	(224.5)	(76,000)	(258.5)	(5,800)	(290)	(13,000)	(300)	(12,000)
XIX R=CH <sub>2</sub> CN	222.5	84,900	257	6,200	289.5	14,000	301.5	12,400
	(224.5)	(54,800)	(265)	(5,000)	(280)	(7,890)	(302)	(12,370)
	(221.5)	(85,000)	(256)	(5,600)	(280 <sub>inf</sub> )	(11,000)	(300)	(13,000)
R=CH <sub>3</sub>	(220)	110,000	262.5 <sub>inf</sub>	6,600	272.5 <sub>inf</sub>	9,800	283	13,000
R=H	(249)	4,200						
								313.5
								2,900



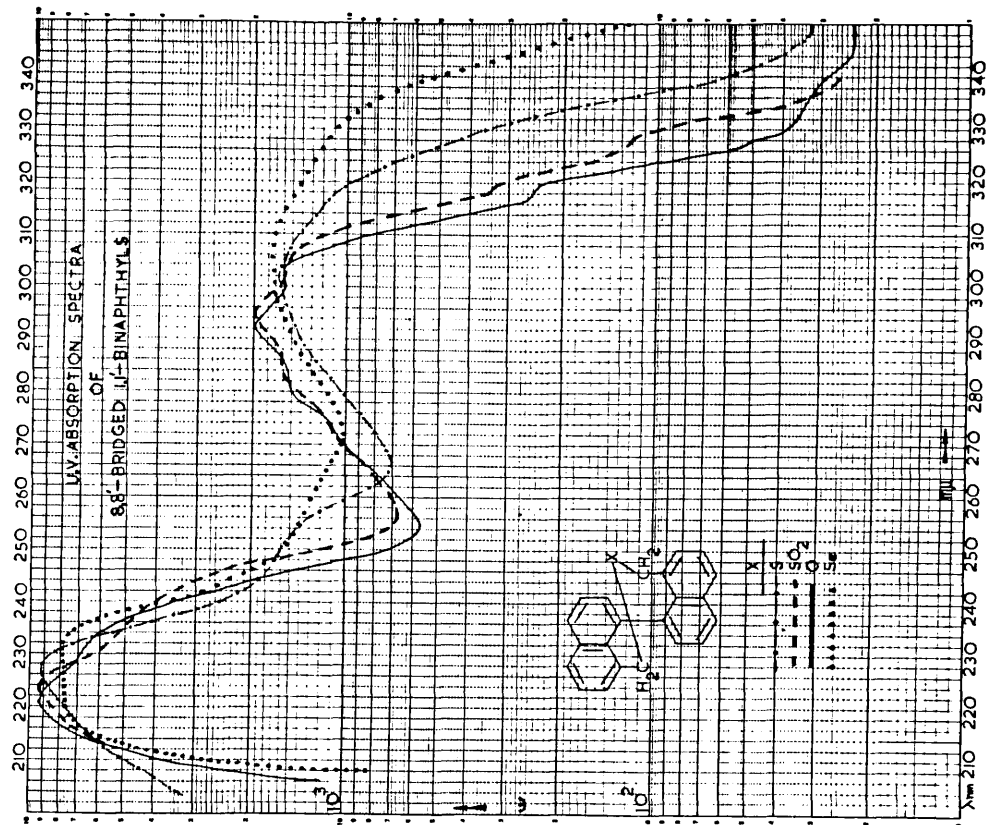


Figure 14

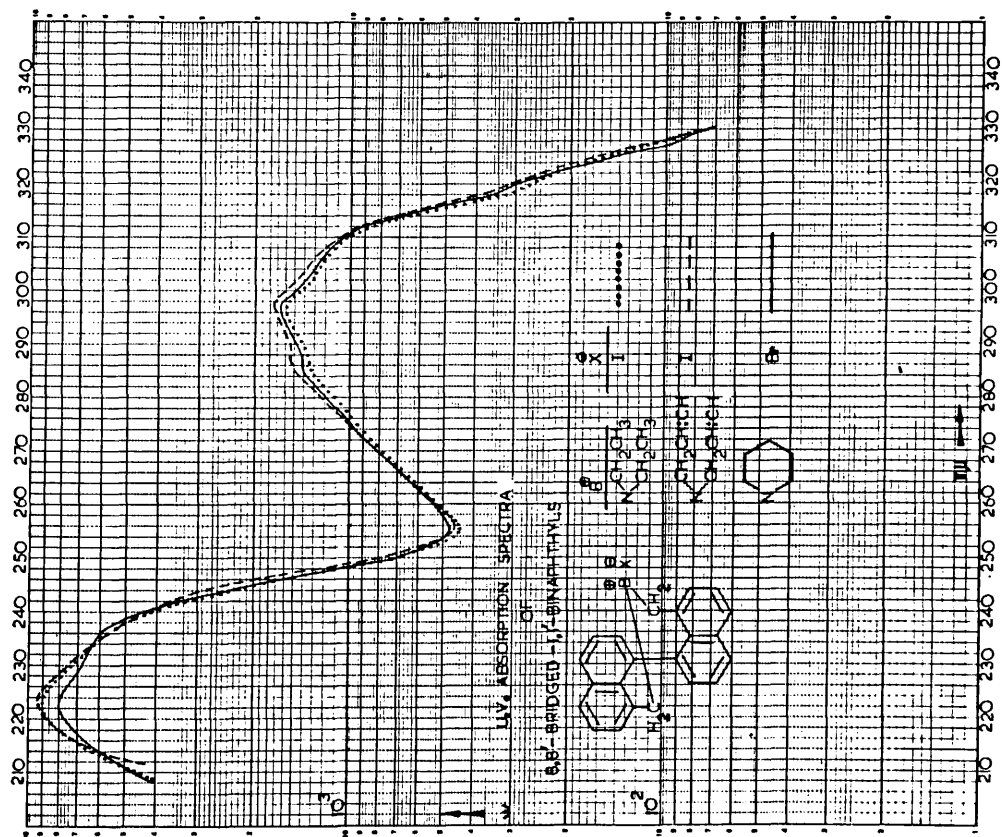


Figure 15

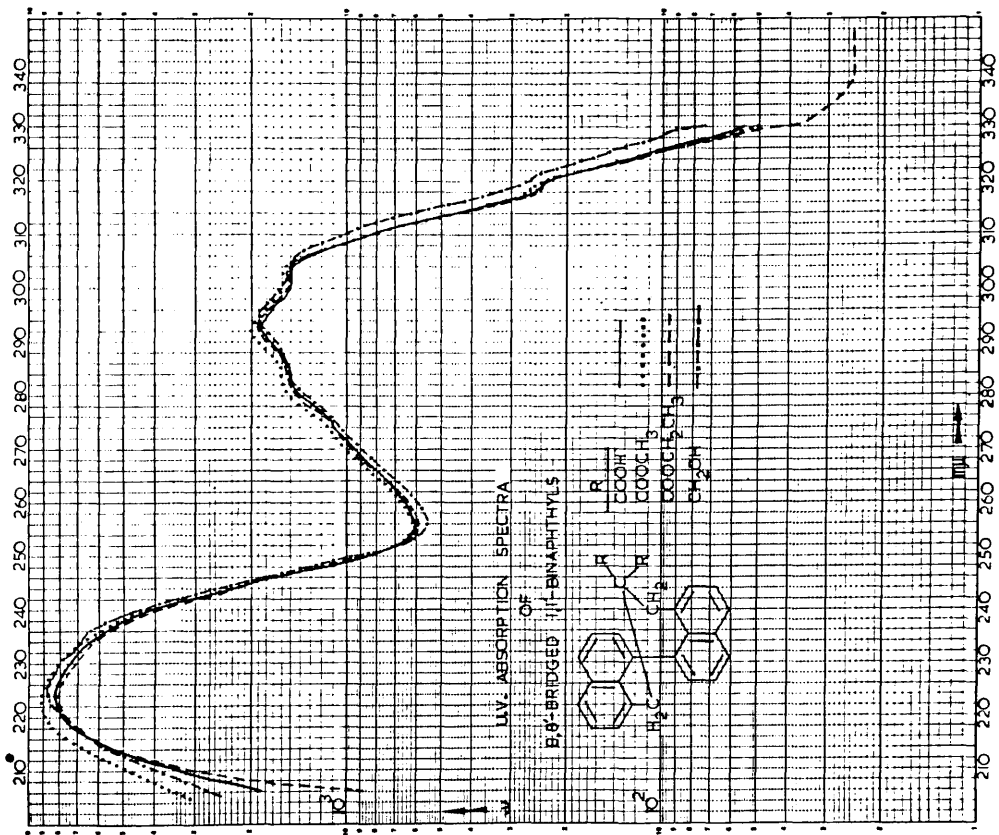


Figure 16

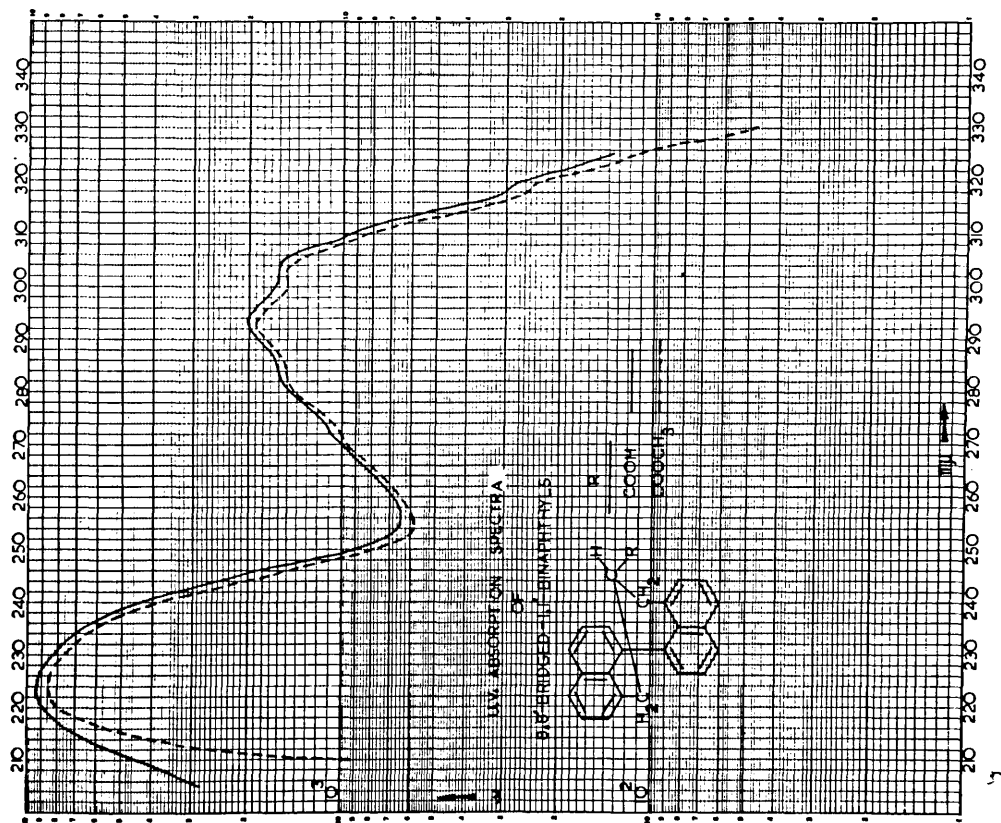


Figure 17



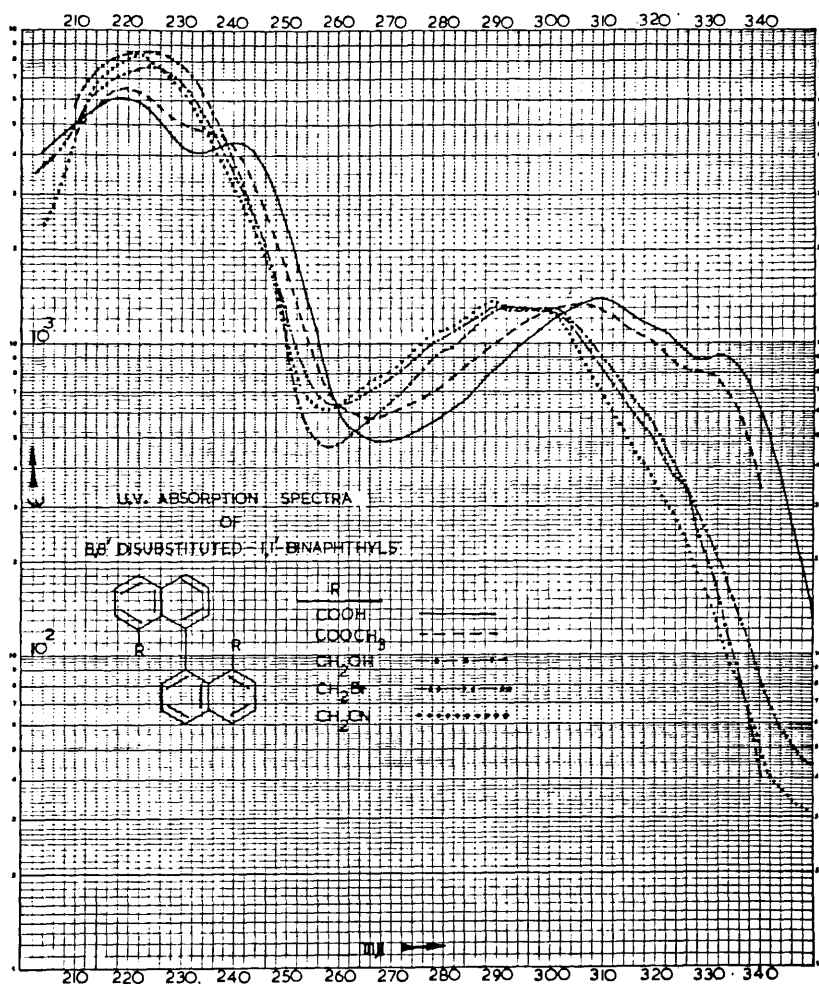


Figure 18

## 6 CHIROPTICAL EFFECTS. O.R.D. AND C.D. SPECTRA.

### 6.1. Optical Rotatory Dispersion and Circular Dichroism: Introduction.

According to Professor Moscowitz (1961,1962) optically active chromophores can be classified into two types:(1)the inherently dissymmetric chromophores and(2) the inherently symmetric, but asymmetrically perturbed, chromophores.

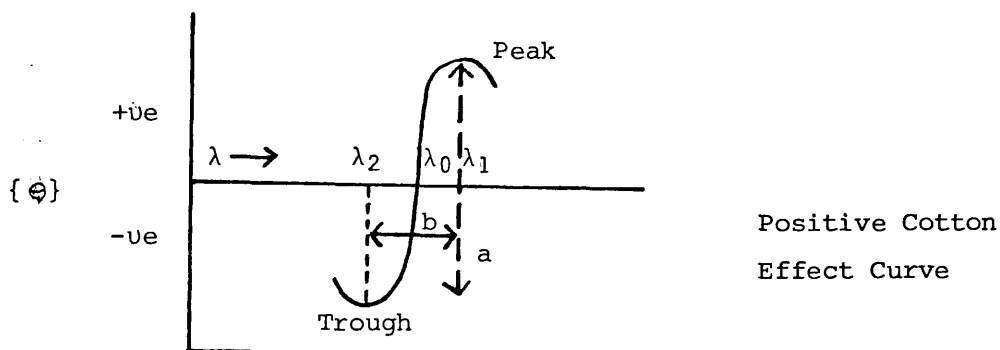
In the inherently dissymmetric chromophores the optical activity is very intense because it is due to the intrinsic geometry of the chromophore itself and the electrons are part of a chiral configuration even in an achiral environment. The structural features most closely identified with these chromophores are twisted  $\pi$ -systems e.g. twisted biaryls.

In the second type, the inherently symmetric but asymmetrically perturbed chromophores, the chromophore itself is optically inactive, but if it lies in a dissymmetric molecular environment, its transitions become optically active; the carbonyl function in aldehyde, ketone, acid and ester becomes optically active in this way. The intensity of the optical activity is usually weaker than in the inherently dissymmetric chromophores.

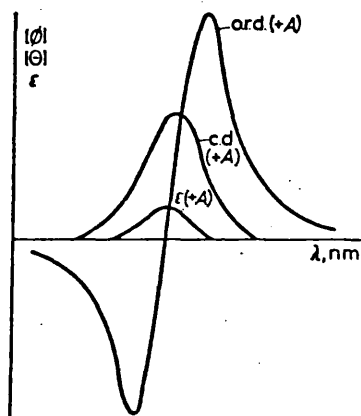
#### 6.1.1 Optical rotatory dispersion (O.r.d.):-

If an absorption in the electronic spectrum is related to a transition which is dissymmetric, plotting optical rotation against wavelength gives an o.r.d. curve. For a compound devoid of chromophores, the optical activity progressively increases numerically as the wavelength decreases. A plain positive or plain negative dispersion curve is obtained, depending upon whether the optical rotation rises or falls with decreasing wavelength. For a compound with one or more optically active absorption bands (i.e. chromophores) within the

spectral range, the dispersion curve is anomalous and shows one or more 'extrema'. A single Cotton effect O.r.d. curve presents one maximum and one minimum extremum called peak and trough respectively. When the peak occurs at higher wavelength than the trough the curve shows a positive Cotton effect. Conversely, when the trough occurs at higher wavelength, the curve shows a negative Cotton effect.



All curves are plotted with the wavelength in nanometers (nm) on the abscissa against molecular rotation  $\{\theta\}$  on the ordinate. Molecular rotation  $\{\theta\}$  is defined as  $\{\theta\} = \frac{M\{\alpha\}}{100}$  (in degrees) where  $M$  is the molecular weight of the optically active compound and  $\{\alpha\}$  is the specific rotation. The point  $\lambda_0$  of rotation  $\{\theta\}=0$ , where the curve inverts its sign, corresponds roughly to the wavelength of an ultraviolet absorption band. The vertical distance between the peak and trough in molecular rotation is called the amplitude  $a$ , and the molecular amplitude is the difference between the molecular rotation  $\{\theta\}$  for the extrema of longer and shorter wavelengths divided by 100,  $a = \frac{\{\theta\}_1 - \{\theta\}_2}{100}$ . The horizontal distance  $b$  is called the breadth of the Cotton effect curve, expressed in nanometers (nm). In multiple Cotton effect curves two or more peaks with corresponding troughs are observed.



Relationship of u.v. o.r.d. and c.d. curves (ideal). (Klyne and Scopes, 1969)

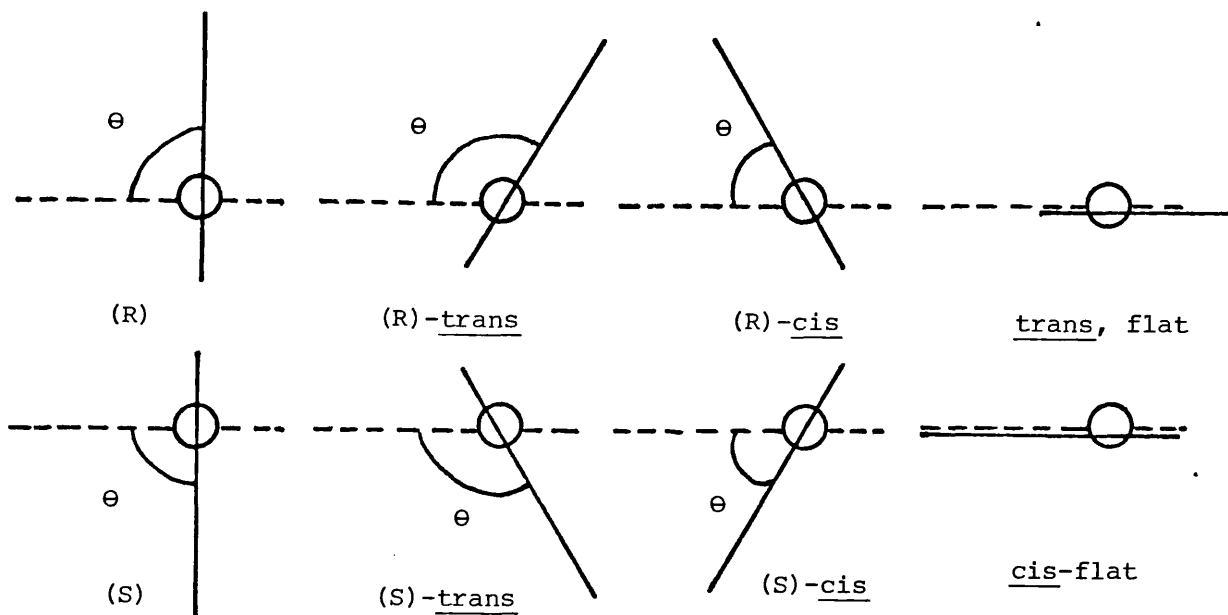
### 6.1.2 Circular dichroism (C.d.):

While O.r.d. measurements are significant over all the range of the spectrum, c.d. is apparent only in the neighbourhood of an absorption band. In the spectral region in which optically active absorption bands are present the two components, the right and left polarised rays, show circular birefringence and are also differentially absorbed. Hence, when an optically active medium is traversed by plane polarized light in the spectral range in which an optically active chromophore absorbs, not only does the plane of polarization rotate by an angle  $\alpha$ , but the resulting light is also elliptically polarized: the medium exhibits circular dichroism. The plot of molecular ellipticity against wavelength (nm) gives a circular dichroism curve. The molecular ellipticity is defined by  $\{\Theta\} = 3300 (\Delta\epsilon)$ , where  $\Delta\epsilon$  is the differential absorption.

Circular dichroism curves plotted in molecular ellipticity units have the advantage of allowing an easy comparison of the intensity of the Cotton effect with the molecular rotation of rotatory dispersion; since in both approximately equal orders of magnitude are encountered. An expression which relates the molecular amplitude  $\underline{a}$ , of an optical rotatory dispersion curve to the dichroic absorption  $\Delta\epsilon$  of its circular dichroism curve is  $\underline{a} = 40.28 \times \Delta\epsilon$  In term of molecular ellipticity  $\{\Theta\}$ ,  $\underline{a} = 0.0122 \times \{\Theta\}$ .

### 6. 2 Absolute Configuration in 1,1'-Binaphthyls

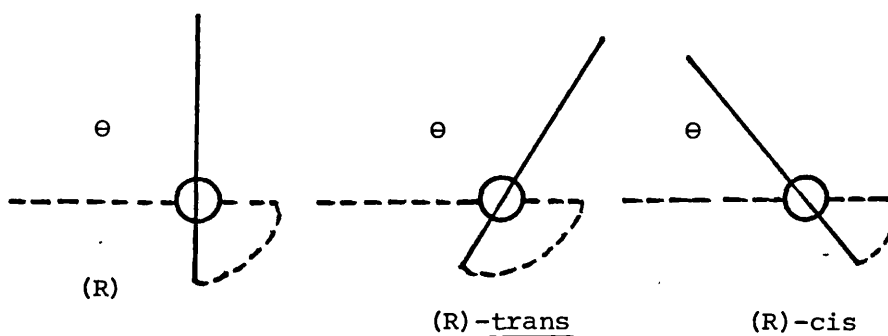
The chirality of 1,1'-binaphthyl is designated about an axis containing the 1,1'-bond. Each absolute configuration (R) or (S) can be in an infinite number of conformations of which those with  $\theta > 90^\circ$  are called trans as shown in the Newman projections below. (In these diagrams each naphthalene nucleus is considered as flat).



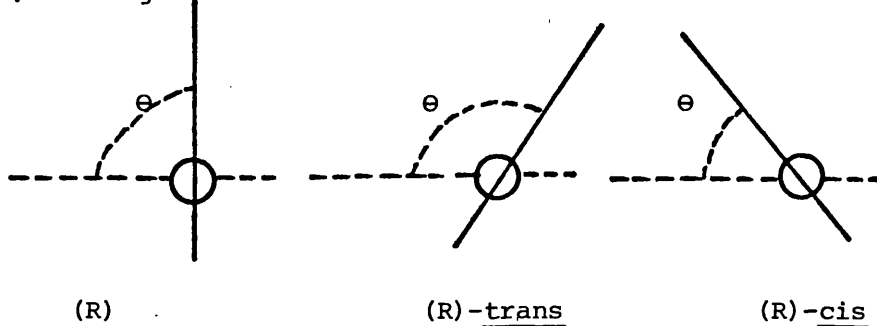
The orthogonal conformations ( $\theta=90^\circ$ ) are chiral, and the two conformations with  $\theta=180^\circ$  are achiral: all other conformations are chiral.

In the 2,2'- and 8,8'-disubstituted-1,1'-binaphthyl bridged compounds, conformations { (R)-configuration } are shown; the length of the bridge determines  $\theta$ . For the seven-membered ring 2,2'-bridged-1,1'-binaphthyl, the only possible conformation is cis; for the nine-membered ring 8,8'-bridged-1,1'-binaphthyl, the possible conformations are near to  $\theta=90^\circ$ , cis or trans.

#### 2,2'-bridged



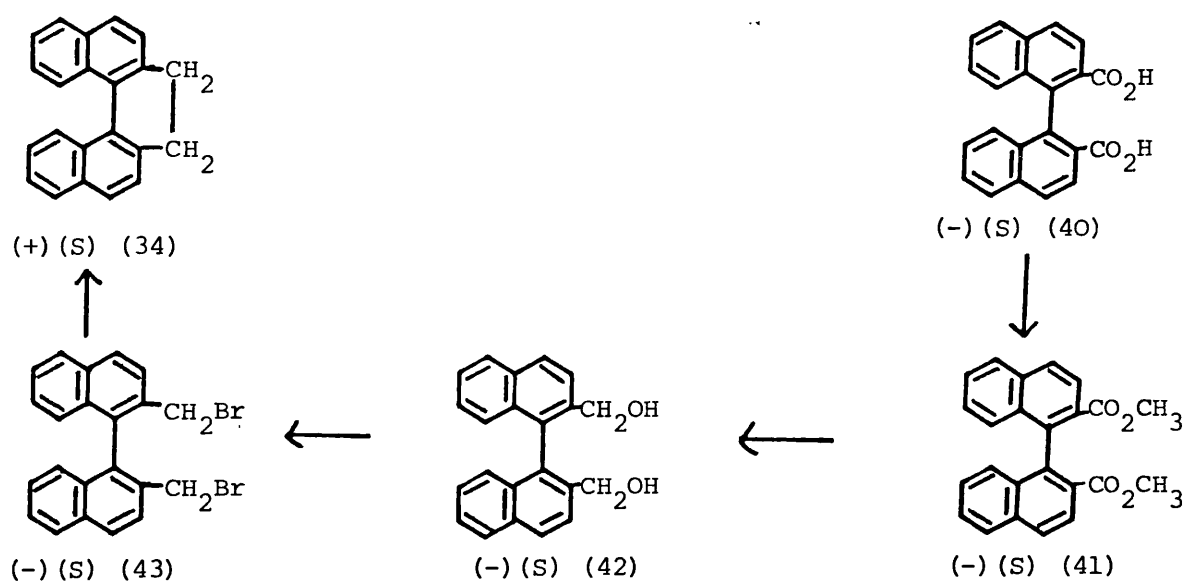
#### 8,8'-bridged



### 6.2.1. Determination of absolute Configuration

#### Polarisability theory :-

In 1958, Fitts, Siegel and Mislow, using the polarizability theory of optical activity, assigned the (S)- configuration to (+) 9,10-dihydro-3,4,5,6-dibenzophenanthrene (34) (Hall and Turner, 1955). Assuming this is true, then (-)-1,1'-binaphthyl-2,2'-dicarboxylic acid (40) and the compounds in Hall and Turner's reaction sequence (41), (42) and (43) also have the (S)- configuration.



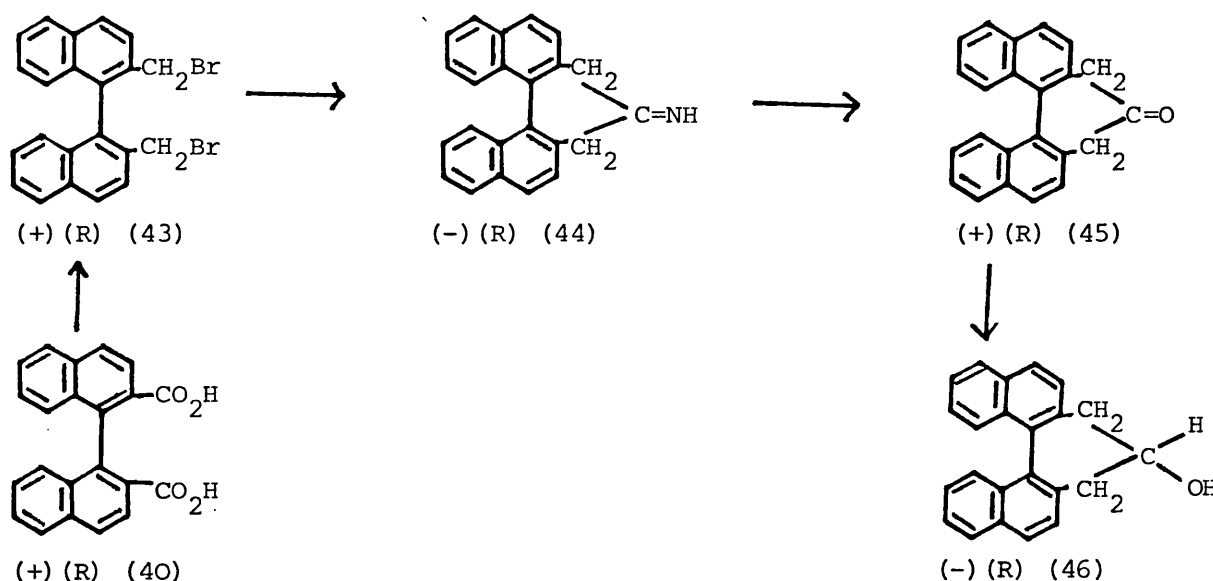
#### Optical displacement rule:-

The large positive increase in optical rotation in forming (34) from (40) agrees with Fitts, Siegel and Mislow's (1958) use of Freudenberg's optical displacement rule, although these workers later proved it to be of limited application. Reduction of (-) (43) with  $\text{LiAlH}_4$  gave (+) 2,2'-dimethyl-1,1'-binaphthyl, therefore it too has (S)-configuration.

#### Asymmetric Meerwein - Ponndorf-Verley reduction:-

Mislow and McGinn (1958) determined the absolute configuration of several 1,1'-binaphthyls by the scheme previously employed by Newman, Rutkin and Mislow (1958) for biphenyls. In this method asymmetry

is introduced in the course of a reaction, which involves the preferential formation of one or other diastereomer in the transition state of the reaction of the (+) substance with an unsymmetrical reagent of known absolute configuration. Incomplete Meerwein-Ponndorf-Verley-reduction of the racemic bridged binaphthyl Ketone (+) (45) with (+) (S)-2-octanol, in the presence of aluminium-t-butoxide, gave (-)-alcohol (46), along with unreduced (-)-(45). Using the model



of known absolute configuration of (S) (+)-2-octanol they deduced that the alcohol<sup>(-)</sup>(46) has (R) configuration. The synthetic precursor of (-) (46), the (+)-1,1'-binaphthyl-2,2'-dicarboxylic acid (40), must have the same relative configuration, and so (R)- configuration was assigned to it.

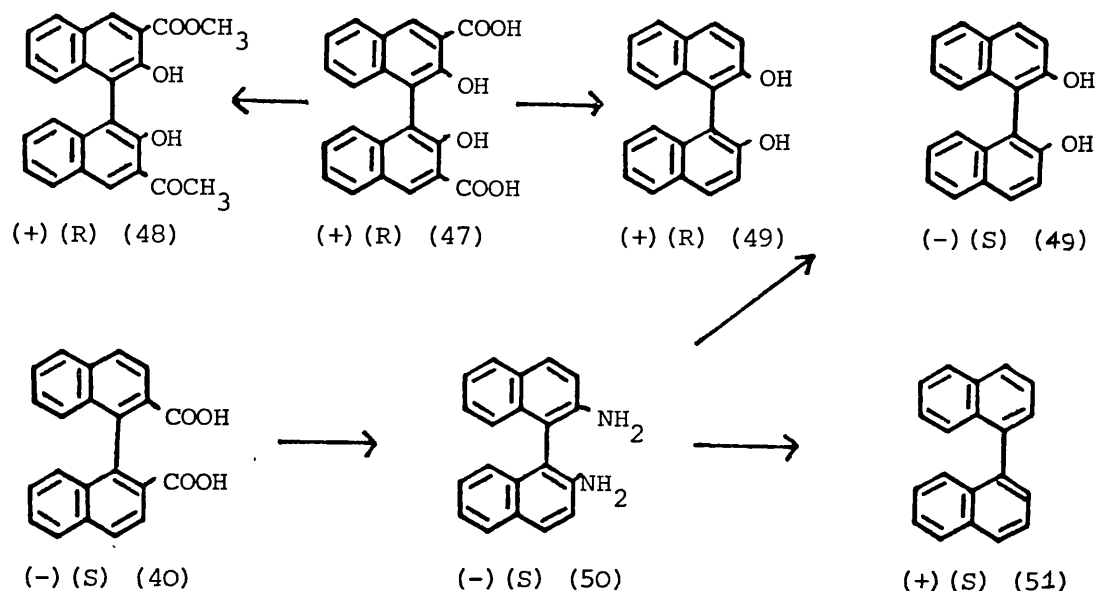
#### Chiroptical Correlation:-

Badger and his co-workers (1962) determined the O.r.d. spectrum of (-)dimethyl-1,1'-bianthryl-2,2'-dicarboxylate and found it to have two Cotton effects of opposite sign, a large negative one centered at 271 nm and a small positive one centered at 377 nm. Following 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. Grinter and Mason (1964) recorded the

c.d. absorptions of opposite sign in the short wave region, where the u.v. spectrum showed two split components.

Anomalous x-ray diffraction:-

(1968, Akimoto et.al. /1971) established the (R) configuration of (+) dimethyl-2,2'-dihydroxy-1,1'-binaphthyl-3,3'-dicarboxylate (48) by the anomalous x-ray diffraction method and therefore established the configuration of optically active binaphthyls linked with it synthetically as follows:



From this reaction sequence, (S)-configuration was established for (+)-1,1'-binaphthyl itself and for (-)-1,1'-binaphthyl-2,2'-dicarboxylic acid. So this result is in agreement with Mislow's assignment for (-)-(S)-1,1'-binaphthyl-2,2'-dicarboxylic acid. This assignment has been confirmed by determination of configuration of (-) bisbromomethyl-1,1'-binaphthyl (Harata and Tanaka, 1973) as (S) by utilising the anomalous dispersion effect of bromine atoms on the x-ray diffraction pattern.

6.3 Optical Rotatory Dispersion, Circular Dichroism and Configuration: Disubstituted-1,1'-Binaphthyls. Background to the Present Work.

Mislow and Djerassi and co-workers made fundamental observations on u.v., o.r.d. and c.d. of some unbridged and bridged 2,2'-disubstituted-



1,1'-binaphthyls of established absolute configuration (Mislow, 1962a; Mislow 1962b; Mislow,1963). They found that o.r.d. curves are dependent on conformation as well as on configuration, and that chemical change from open to 2,2'-bridged seven-membered ring biaryls gives rise to characteristic changes in the o.r.d. curves; c.d. curves are associated with o.r.d. curves and u.v. absorption maxima and are useful in the identification of the electronic transitions which are responsible for the individual cotton effects. The sign of a c.d. curve corresponds to the sign of the related o.r.d. curve. C.d. spectra do not have as extensive overlapping tails as do the o.r.d. curves and so permit the identification of weakly optically active transitions whose Cotton effects were previously unsuspected because they were hidden by high amplitude Cotton effects centered at short wavelengths.

1,1'-Binaphthyl itself was known (Frampton, Edward,jr and Henze, 1948; Friedel, Orchin and Reggel, 1948) to have u.v. absorption maxima at approximately 230nm and about 285nm. Mislow and his co-workers found that the 2,2'-disubstituted compounds with substituents  $\text{CO}_2\text{H}$ ,  $\text{CO}_2\text{CH}_3$ ,  $\text{CH}_2\text{OH}$ ,  $\text{CH}_2\text{Br}$ , and  $\text{CH}_3$  have similar u.v. maxima; the o.r.d. and c.d. curves are dominated by two Cotton effects, centered below 250 and at about 285nm ( $\sim 220$  can now be added to these); a positive 285nm Cotton effect corresponds to the (R)-configuration.

In the 2,2'-disubstituted-1,1'-binaphthyls, they found that the change from unbridged to bridged compounds (6-ring bridged) shows a red shift of o.r.d. and c.d. with enhancement in amplitude, in common with the absorption spectra. The six-membered ring 2,2'-bridged-1,1'-binaphthyl, 9,10-dihydro-3,4,5,6-dibenzophenanthrene, shows a marked red shift of o.r.d. and c.d. bands corresponding to the red shift of the absorption maxima at 320,335 and 348nm compared with 1,1'-binaphthyl: it also shows short wave o.r.d. and c.d. bands with enormously high amplitude centered near 250 nm, which swamp the long-wave length negative Cotton effect and dominate the visible region: it

has bands  $\sim 220\text{nm}$  as in 1,1'-binaphthyl.

They also found that the absorption spectra of seven-membered ring 2,2'-bridged-1,1'-binaphthyls (where the bridging atom or group is -O-, -CO-, >CHOH, >C(CO<sub>2</sub>C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>, >CHOCOCOC<sub>6</sub>H<sub>5</sub>) are dominated by maxima at 220, 232 and 306nm. The o.r.d. and c.d. curves are dominated by two Cotton effects of opposite sign, centred below 240nm and near 300nm; a positive 300nm Cotton effect corresponds to the (R) configuration.

### 6.3.1 2,2'-Dimethyl-1,1'-binaphthyl; 1,1'-binaphthyl and 8,8'-dimethyl-1,1'-binaphthyls:-

Harris, Harris, Mazengo and Shyam Singh (1974) reported that o.r.d. and c.d. spectra of (+)-2,2'-dimethyl-1,1'-binaphthyl (Mislow *et. al.* 1962, 1963); (+)-1,1'-binaphthyl (Browne, Harris, Mazengo and Shyam Singh, 1971) and (+)-8,8'-dimethyl-1,1'-binaphthyl are similar; they all show a negative Cotton effect centred near 285nm and as (+)-2,2'-dimethyl-1,1'-binaphthyl and (+)-1,1'-binaphthyl are known to have (S)-configuration, by analogy (+)-8,8'-dimethyl-1,1'-binaphthyl was assigned the (S)- configuration. They suggested that a pair of c.d. bands of opposite signs and of high rotational strengths which appear in the short wave region, could provide a more useful criterion for assigning chirality to the binaphthyl skeleton. A short wave negative c.d. band is accompanied by a positive band at slightly longer wavelength for (S)-configuration: this "couplet" is characteristic of 1,1'-binaphthyl spectra. (It is possible that this generalisation holds true only for dihedral angles of less than a certain maximum value.-see below).

### 6.3.2 8,8'-Disubstituted-1,1'-binaphthyls:-

Harris, Harris, Mazengo and Shyam Singh (1974) have published o.r.d. and c.d. spectra of (-)-1,1'-binaphthyl-8,8'-dicarboxylic acid (XV), (-)dimethyl-1,1'-binaphthyl-8,8'-dicarboxylate (XVI), (+)-8,8'-bishydroxymethyl-1,1'-binaphthyl (XVII), and (+)-8,8'-bisbromomethyl-1,1'-binaphthyl (XVIII).

The change of sign of the c.d. bands (the couplet) corresponds with neither of the u.v. maxima, but is not far removed. As (-)-1,1'-binaphthyl-8,8'-dicarboxylic acid and (+)-8,8'-dimethyl-1,1'-binaphthyl are linked synthetically as follows, they both have the same (S)-configuration. (-) (XV) → (-) (XVI) → (+) (XVII) → (+) (XVIII) → (+)-8,8'-dimethyl-1,1'-binaphthyl, as do the intermediate compounds.

### 6.3.3 1,1'-Binaphthyl-2,2'-dicarboxylic acid and 1,1'-binaphthyl-8,8'-dicarboxylic acid.

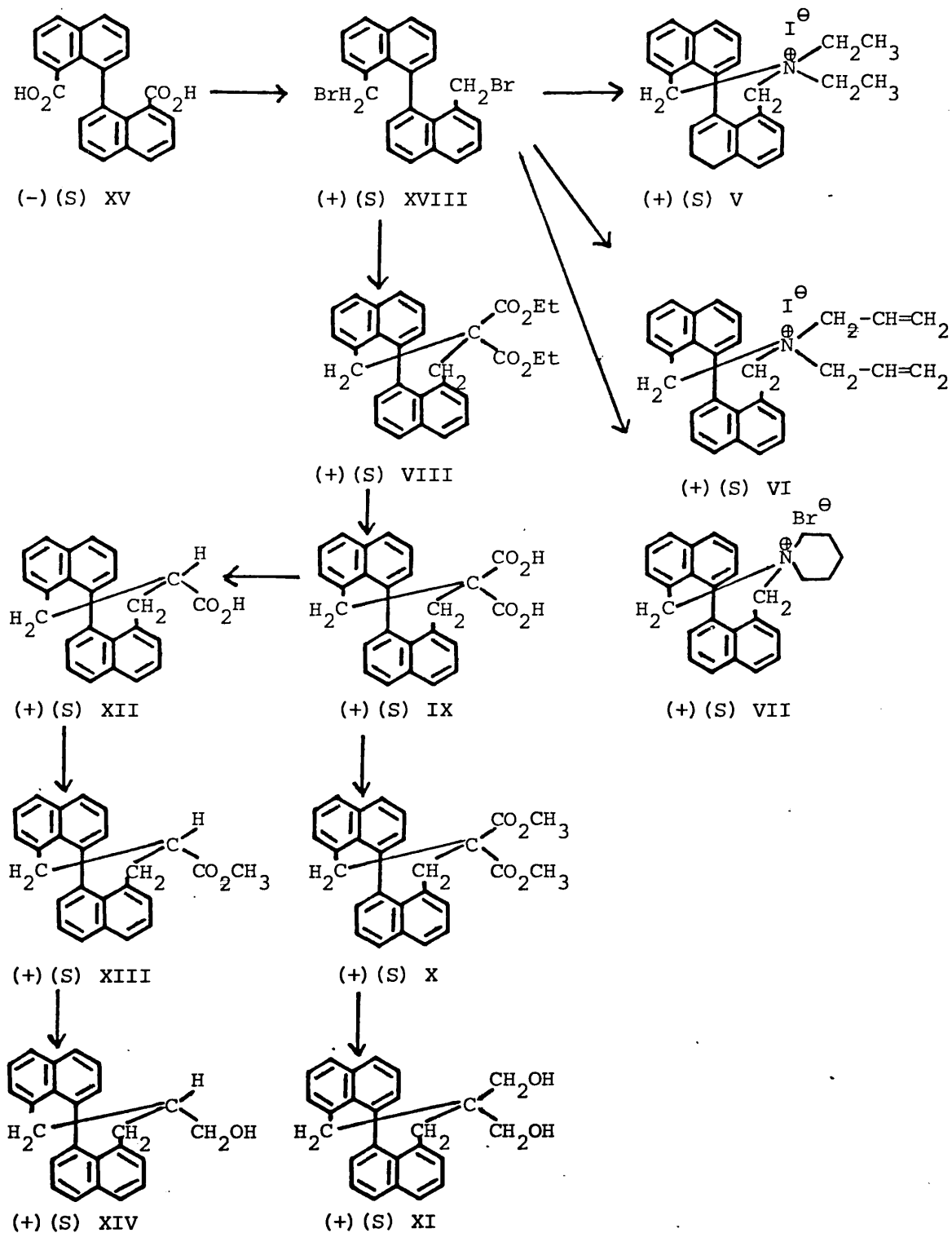
Mason, Seal and Roberts (1974) obtained a set of theoretical c.d. spectra of chiral 1,1'-binaphthyls from  $\pi$ -SCF calculations, { for either (R) or (S) molecules } for different values of the dihedral angle between the molecular planes of the aromatic moieties; at angles near to  $110^\circ$ , the short wave "couplet" would change its sign. Known optical isomers of 2,2'-disubstituted-1,1'-binaphthyls have established configurations (Mislow *et al.* 1962, 1963; Akimoto, 1971), and according to this treatment, their c.d. spectra indicate that in all cases the dihedral angle is smaller than the critical value where the change of sign would take place; the smallest  $\Delta\epsilon_{\text{max}}$  value, observed for (S)-1,1'-binaphthyl-2,2'-dicarboxylate anion, indicates the largest dihedral angle: they consider that a still larger dihedral angle is unlikely in 1,1'-binaphthyl-8,8'-dicarboxylic acid and if this is so, the c.d. spectrum of (-)-1,1'-binaphthyl-8,8'-dicarboxylic acid shows that it has (S)-configuration. They expect that the non-bridged-1,1'-binaphthyls disubstituted at 2,2'-and 8,8'-positions have dihedral angles in the range  $90 \pm 20^\circ$ .

Fitts, Siegel and Mislow (1958) earlier came to a similar conclusion to Mason's in relating change of sign rotation to conformational change in a study of (R)-6,6'-dichloro-2,2'-diethylbiphenyl; their calculations were based on polarisability theory.

### 6.3.4 9-Membered ring-8,8'-bridged-1,1'-binaphthyls.

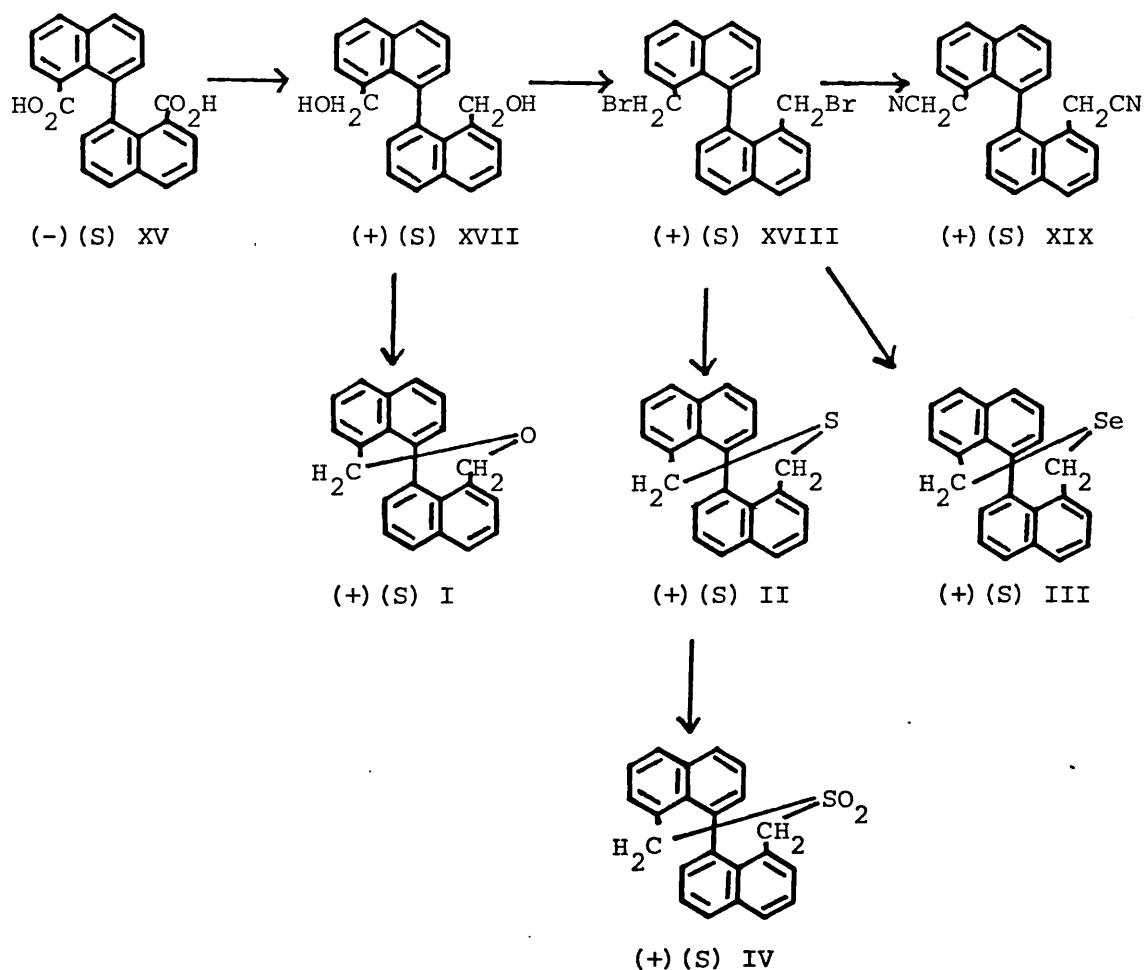
Harris and Shyam Singh (1972, 1976) prepared optically active

nine-membered ring 8,8'-bridged-1,1'-binaphthyls from (S)(-)-1,1'-binaphthyl-8,8'-dicarboxylic acid as follows. They are all (+)-rotatory and they must have the (S)-configuration.



They also found that all the compounds show similar short wave Cotton effects: all (S)-(+)-rotatory compounds show a short wave negative c.d. band followed by a positive band at slightly longer wave length. The mono carboxylic acid (XII), its ester (XIII) and alcohol (XIV) also show similar spectra.

In the present work 8,8'-biscyanomethyl-1,1'-binaphthyl and four new heterocyclic nine-membered ring 8,8'-bridged-1,1'-binaphthyls have been prepared from (-)(S)-1,1'-binaphthyl-8,8'-dicarboxylic acid as follows: they are all (+) rotatory and they must have the same configuration as the original acid. Their o.r.d. and c.d. spectra have been recorded and discussed (in the later section).



#### 6.4 O.r.d. and C.d. Spectra of Bridged and Unbridged 1,1'-Binaphthyls: Results and Discussion. Relation of Spectral Features to Absolute Configuration.

This section mainly consists of discussion of the o.r.d. and c.d. spectra now obtained of the bridged and unbridged-1,1'-binaphthyls in Tables 29-36 and 21-28 respectively. O.r.d. and c.d. spectra of (+) and (-) 9-membered ring 8,8'-biscyanomethyl-1,1'-binaphthyl (XIX) are reported here for the first time; those of 9-membered ring 8,8'-bridged 1,1'-binaphthyls V,VI,VII,VIII,IX,X,XI,XII, XIII and XIV were first studied by Harris and Shyam Singh (1972); those of the unbridged 8,8'-disubstituted-1,1'-binaphthyls by Harris and Mazengo (1968) and by Harris and Shyam Singh (1972); Harris, Harris, Mazengo and Shyam Singh (1974). O.r.d. and c.d. spectra of the 2,2'-bridged -1,1'-binaphthyl oxepin (Mislow et.al. 1962) have now been recorded at shorter wavelengths than before. 1,1'-Binaphthyl,2,2'-dimethyl-1,1'-binaphthyl and 8,8'-dimethyl-1,1'-binaphthyl were studied by Harris, Harris, Mazengo and Shyam Singh (1974).

All these spectra have now been repeated. In the Tables the figures in brackets were obtained by Shyam Singh (1972).

O.r.d. and c.d. are two manifestations of the same phenomenon: for reasons already given o.r.d. and c.d. data are reported here, but the detailed discussion is in terms of the c.d.

##### 6.4.1 Circular dichroism spectra: description

##### 6.4.1.1 (+) (S) oxygen, sulphur and selenium heterocycles:

They all have an oppositely signed pair of c.d. bands below 280nm, the negative one at shorter wavelength and the centre of the pair moving to longer wavelength in the order O,SO<sub>2</sub>,S,Se. The negative maximum of the short wave member of the pair corresponds closely with the u.v. maximum and is larger in molecular rotation than the positive

band. The sulphur and selenium compounds show signs of further negative bands at lower wavelength; the extra selenium band corresponds with its extra shorter wave u.v. absorption maximum. They all have positive c.d. bands at about 300nm.

All (-) (R) compounds show similar but opposite features.

#### 6.4.1.2 (+) (S) Nitrogen heterocycles:

They all have an oppositely signed pair of bands below 250nm. The negative maximum is larger in molecular rotation and is at shorter wavelength than the positive maximum, and at slightly shorter wavelength than the u.v. maximum. They all have a positive c.d. absorption at about 300 nm.

The spectra of (-) (R) compounds (V) and (VII) are similar but opposite in sign.

#### 6.4.1.3 (+) (S) Carbocyclic compounds:

All have two oppositely signed bands below 250nm, the negative maximum at shorter wave length than the positive maximum. In contrast to the heterocyclic compounds, they all have the positive maximum larger in optical rotation than negative maximum. While the negative maximum lies at somewhat lower wavelength than the u.v maximum, the wavelength at which c.d. rotatory power is zero lies near to the u.v. maximum. They all have a small positive band at about 260nm and another one at about 300nm.

The (-) (R) compounds show similar but opposite features.

#### 6.4.1.4 (+) (S) Unbridged 8,8'-disubstituted-1,1'-binaphthyls: (except for 8,8'-diacid XV and 8,8'-dimethyl ester XVI where (-) (S) ).

All have an oppositely signed pair of bands below 250nm, the negative one being at shorter wavelength. The magnitude of the positive band is greater than the negative band, sometimes by only a little margin.

The amplitudes are smaller than in the other groups except for the dimethyl compounds. The short wave maxima for (-)-8,8'-diacid XV, negative at 223.5 and positive at 239.5nm, correspond with the u.v. maxima at 219.5 and 239.5nm. Similarly short wave maxima for (-)-8,8'-dimethyl ester (XVI), negative at 222 and positive at 237.5 corresponds with the u.v. maxima at 219.5 and 235nm. For the remainder of the compounds, the negative maxima lie at a little shorter wavelength than the u.v. maxima. The 8,8'-diacid (XV) and diester (XVI) have positive bands at about 260nm. They all have negative bands between 280 and 300nm.

(R) compounds show similar but opposite features.

#### 6.4.1.5 (+)(S) 2,2'-Oxepin:

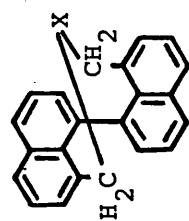
A negative band of large magnitude at 216nm is followed by two oppositely signed bands below 250nm, the positive band of large magnitude at 228nm and the negative band of small magnitude at 239.5nm. A long wave positive band at 262-3 is followed by a negative band at about 300nm.

#### 6.5. Conclusion:

Comparison of the c.d. spectra of this large number of bridged and unbridged 1,1'-binaphthyls shows that all the (S)-configuration compounds have a common short wave pattern, but that in the longer wave region there are differences which are related to their structure. The unbridged compounds and the 2,2'-bridged compounds have negative maxima in the 280-315 nm region, while the 8,8'-bridged compounds have positive ones.

The (R) compounds, where available, show these features with opposite sign.



Table 21 C.d spectra of 8,8' -bridged heterocyclic 1,1' binaphthyls (S-configuration) in 96% ethanol.  $\lambda$  nm ( $\epsilon \times 10^{-3}$ )

											<u>a</u>		
(+)	I	X=O	219	225	232	255	270	280	291.5	302.5	322.5	1,159	
			(-)	1,020	0.0	(+)	1,139	(+)	59	(+)	44	(+)	5.1
(+)	II	X=S	228	237.5	251		270	285	295.5	313	328		
			(-)	1,316	0.0	(+)	368	(+)	54.8	(+)	30.9	(+)	23.1
				215									
			(-)	211									
(+)	III	X=Se	232	242.5	256		277		297	331	338		
			(-)	749	0.0	(+)	199	(+)	72	(+)	19.8	(-)	19.8
				221									
			(-)	159									
				210									
			(-)	618									
(+)	IV	X=SO <sub>2</sub>	222	227	237	261	270	282-3	296.5	302-3			
			(-)	1,591	0.0	(+)	1,250	(+)	58.9	(+)	59.7	(+)	2,841
				228	235.5	239.5	246	262-3	300	339			
			(+)	2,340	0.0	(-)	430	0.0	(-)	71.6	0.0		
				216									
			(-)	2,110									

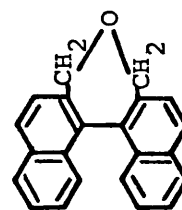
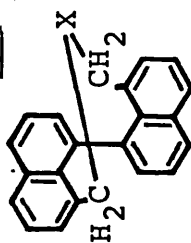
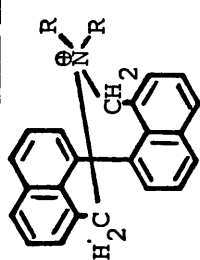


Table 22 C.d. spectra of 8,8'-bridged heterocyclic 1,1'-binaphthyls (R-Configuration) in 96% ethanol.  $\lambda_{nm}$  ( $\epsilon \times 10^{-3}$ )



a

(-) I, X=O	219	225	232	255	267.5	281	291	322.5	
	(+) 1,088	0.0	(-) 1,149	(-) 52	(-) 61	(-) 57	(-) 55	(-) 4.8	2,237
(-) III, X=S	228.5	234.5	247		272	283	297.5	312	328
	(+) 735	0.0	(-) 511		(-) 32.4	(-) 44	(-) 54.2	(-) 32.1	(-) 22.7
	221.5								1,246
	0.0								
	217								
(-) 299									
(-) III, X=Se	232	239.5	253-7		277		297	331	339
	(+) 717	0.0	(-) 279		(-) 55.9		(-) 96.7	(-) 28	(+) 24.9
	225								1,196
	0.0								
	220								
(-) 154									
(-) IV, X=SO <sub>2</sub>	223	228	239	264	272-4	284	296	304	2,118
	(+) 1,149	0.0	(-) 969	(-) 5.4	(-) 9.8	(-) 22.5	(-) 47.5	(-) 48.9	

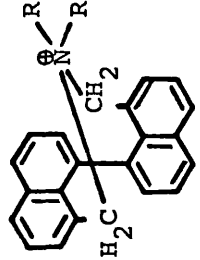
Table 23 c.d. spectra of 8,8'-bridged N-heterocyclic 1,1'-binaphthyls (S-configuration) in 96% ethanol.  $\lambda_{nm}(\phi \times 10^{-3})$ 


(+) V, R =  $\text{CH}_2\text{CH}_3$

Wavelength (nm)	Sign	Wavelength (nm)	Sign	Wavelength (nm)	Sign	Wavelength (nm)	Sign	Wavelength (nm)	Sign	Wavelength (nm)	Sign	Wavelength (nm)	Sign
215	(-)	228	(+)	276-7.5	(+)	281	(+)	294.5	(+)	301-3	(+)	322	(+)
1,125 (218)	(-)	903 (234)	(+)	13.7 (260)	(+)	17.2	(+)	38 (292)	(+)	33.2 (306-10)	(+)	5.0	(+)
1,200	(-)	530	(+)	6.0	(-)	0.0	(-)	20	(+)	18	(+)		
220	(-)	234	(+)	274-7	(+)	285	(+)	298	(+)	304	(+)	324	(+)
1,511 (215)	(-)	940 (232-6)	(+)	15.2 (280)	(+)	23.9	(+)	50 (300)	(+)	46.1	(+)	8.7	(+)
970	(-)	440	(+)	30	(+)	0.0	(-)	58	(+)				
218	(-)	225	(+)	277	(+)	286	(+)	297	(+)	305	(+)	324	(+)
1,231 (216)	(-)	915 (233)	(+)	11.7 (280)	(+)	17.6 (291)	(+)	33.5 (300-10)	(+)	31	(+)	5.4	(+)
900	(-)	520	(+)	35	(-)	0.0	(-)	15	(+)				

(+) VII,  $\text{N}^{\oplus}$

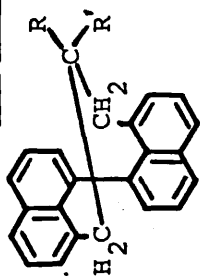
Table 24 c.d. spectra of 8,8'-bridged N-heterocyclic 1,1'-binaphthyls (R-configuration) in 96% ethanol.



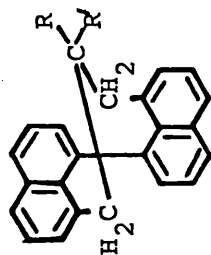
(-) V, R =  $\text{CH}_2\text{CH}_3$

Wavelength (nm)	Sign	Wavelength (nm)	Sign	Wavelength (nm)	Sign	Wavelength (nm)	Sign	Wavelength (nm)	Sign	Wavelength (nm)	Sign	Wavelength (nm)	Sign
219	(+)	225	(-)	275	(-)	283.5-5.5	(-)	296	(-)	304	(-)	318	(-)
887 (218)	(+)	649 (226)	(-)	11.3 (255)	(-)	14.9	(-)	33.6 (300)	(-)	31.3	(-)	7.4	(-)
230	(+)	250	(-)	18	(+)	0.0	(-)	18	(+)				
218	(+)	225	(-)	277.5	(-)	285	(-)	296	(-)	304	(-)	324	(-)
1,199 (218)	(+)	853 (234)	(-)	14.8 (225)	(-)	17.7 (289)	(-)	38.2	(-)	34.1 (306)	(-)	4.9	(-)
300	(+)	170	(-)	16	(+)	0.0	(-)	4.0	(-)				

(-) VII,  $\text{N}^{\oplus}$

Table. 25 c.d. spectra of 8,8' bridged carbocyclic 1,1'-binaphthyls (S-configuration) in 96% ethanol.  $\lambda_{nm} (\epsilon \times 10^{-3})$ 

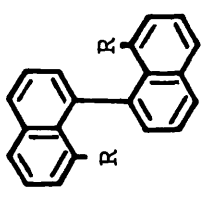
Structure	219	224.5	230.5	256	263	286.5	296.5	302	317	$\lambda_{nm}$
(+) VIII, $\text{R}=\text{R}'=\text{CO}_2\text{Et}$	(-) 976 (215)	0.0 (222.5)	(+) 1,003 (229)	(+) 50.3 (254)	(+) 53 (290)	(+) 11.5 (290)	(+) 20.8 (300)	(+) 21.4	(+) 6.0	1,979
(-) IX, $\text{R}=\text{R}'=\text{CO}_2\text{H}$	215-7.5 (-) 563 (217)	222.5 0.0 (223.5)	229 (+) 667 (232)	256 (+) 32.6 (255)	264 (+) 34.2 (263.5)	285.5 (+) 11.4 (285)	293 (+) 14.8 (292.5)	301.5 (+) 15 (302)	316 (+) 4.0	323 (+) 3.3
(+) X, $\text{R}=\text{R}'=\text{CO}_2\text{CH}_3$	215.5 (-) 492 (218)	220.5 0.0 (223)	228 (+) 1,156 (230.5)	254.5 (+) 33.8 (255)	262 (+) 37.4 (265)	286 (+) 1.6 (288)	293.5-6.5 (+) 11.2 (293-5)	301.5-3 (+) 13.3 (303)	315 (+) 2.3 (318)	1,648
(+) XI, $\text{R}=\text{R}'=\text{CH}_2\text{OH}$	218 (-) 549 (220)	223.5 0.0 (226)	230 (+) 947 (231.5)	254-5 (+) 17.8 (255.5)	266 (+) 22.3 (270)	286 (+) 8.4 (288)	295 (+) 16.5	301 (+) 16.3 (302)	316 (+) 1.1	1,496
(+) XII, $\text{R}=\text{H}$ $\text{R}'=\text{CO}_2\text{H}$	215 (-) 447 (216)	221 0.0 (223)	230 (+) 862 (231)	253 (+) 48 (255)	262 (+) 55.4 (260)	289 (+) 19 (287)	293 (+) 26 (293-5)	300.5 (+) 23 (300)	323.5 (+) 8.0	1,309
(+) XIII, $\text{R}=\text{H}$ $\text{R}'=\text{CO}_2\text{CH}_3$	216 (-) 823 (216)	222 0.0 (223.5)	229 (+) 1,252 (230.5)	257 (+) 53 (255)	260 (+) 59 (265)	287 (+) 13.4 (287)	294 (+) 23 (296)	302.5 (+) 22 (303)	322 (+) 7.0 (323)	2,075
(-) 600 (-) 600	0.0 0.0	(+) 720	(+) 66	(+) 10	(+) 7.2 (+) 9.4	(+) 11 (+) 12	(+) 9.7 (+) 8.5	(+) 11 (+) 11	(+) 2.5 (+) 2.5	

Table 26 c.d. spectra of 8,8'-bridged carbocyclic 1,1'-binaphthyls (R-configuration) in 96% ethanol.  $\lambda_{\text{nm}}$  ( $\times 10^{-3}$ )

a

(-) VIII, R=R'=CO <sub>2</sub> Et	215 (+) 822	222 0.0	229 (-) 931	254 (-) 34	262.5 (-) 35.9	285-7 (-) 1.5	296 (-) 14.4	302.5 (-) 16.8	316 (-) 1.7	1,753
(-) IX, R=R'=CO <sub>2</sub> H	215 (+) 707 (218)	221.5 0.0 (224.5)	229 (-) 719 (232)	257 (-) 29.8 (255-60)	261.5 (-) 31.8 (264)	287.5 (-) 8.7 (287)	295 (-) 15.3 (296.5)	301.5 (-) 16.7 (303.5)	316.5 (-) 2.6 (317)	323 (-) 2.1
(-) X, R=R'=CO <sub>2</sub> CH <sub>3</sub>	215 (+) 600 (217.5)	220.5 0.0 (223)	228.5 (-) 1,108 (231)	253.6 (-) 28.1	261 (-) 30.7 (264)	285.5-8.5 (+) 0.8 (288)	294 (-) 10.9 (295)	303 (-) 14.1 (304)	315 (-) 1.4 (318)	1,708
(-) XI, R=R'=CH <sub>2</sub> OH	217 (+) 738 (215)	222 0.0 (225)	230 (-) 1,060 (235)	255 (-) 26.3 (252)	268 (-) 27.4 (260)	287 (-) 16 (298)	296.5 (-) 25.1 (298)	304.5 (-) 25.3 (306)	318 (-) 3.2 (322.5)	1,798
(-) XII, R=H R'=CO <sub>2</sub> H	215 (+) 680 (215)	222 0.0 (223)	230 (-) 992 (230)	255 (-) 39 (252)	262.5 (-) 43 (260)	286.5 (-) 11.4 (286.5)	294 (-) 21 (293-7)	303 (-) 18 (306)	319-22 (-) 3.1 (322.5)	1,672
(-) XIII, R=H R'=CO <sub>2</sub> CH <sub>3</sub>	214.5 (+) 965 (216)	223 0.0 (223)	228 (-) 1,139 (230)	252 (-) 38.9 (255)	259 (-) 49 (262)	287 (-) 10.4 (289)	295 (-) 23 (295)	301.5 (-) 20 (304)	321 (-) 4.0 (322)	2,104
(+) 500	(-) 870	(-) 33	(-) 7.0	(-) 16	(-) 4.0	(-) 16	(-) 4.0	(-) 16	(-) 4.0	

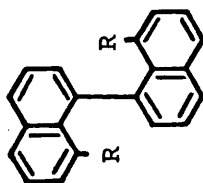
Table 27 c.d. spectra of 8,8'-disubstituted 1,1'-binaphthyls (S-configuration) in 96% ethanol.  $\lambda_{nm} (\epsilon \times 10^{-3})$



Structure	223.5	229	239.5	252	260-4	276	300	313	324	894
(-) XV, R=CO <sub>2</sub> H	(-) 410 (223)	0.0 (232.5)	(+) 484 (240)	0.0	(+) 46.9 (270)	0.0 (281)	(-) 77.8 (289-96)	(-) 39.4 (326)	(-) 35 (326)	
(-) XVI, R=CO <sub>2</sub> CH <sub>3</sub>	221 (-) 397	227.5 0.0	237.5 (+) 399	250 (+) 47.7	260 (+) 106	278.5 0.0	296.5 (-) 60.4	315 (-) 28	325 (-) 23.5	796
(+) XVII, R=CH <sub>2</sub> Br	226.5 (-) 390 (228)	233.5 0.0 (238)	243 (+) 490 (241)	258 (+) 162 (260)	283.5 0.0	299-300 (-) 28 (300)	327.5 (-) 3.5			880
(+) XIX, R=CH <sub>2</sub> CN	219 (-) 396	223.5 0.0	229 (+) 687	238.5 (+) 295	268 0.0	284.5 (-) 51	312 (+) 5.0			1,083
(+) R=CH <sub>3</sub>	215-7 (-) 474 (218)	224 0.0 (222.5)	229.5-30 (+) 966 (229.5)	270.5 0.0 (269.5)	286.5 (-) 41 (287)	307.5 (+) 6.0 (306.5)	322.5 (+) 3.4 (321)	326.5 (-) 3.8 (325.5)		1,440
(+) R=H	214 (-) 394 (214)	221 0.0 (220)	226 (+) 666 (225)	245 (+) 12	250 (+) 17 (260)	258 (+) 19 (280)	287.5-90 (-) 8.6 (285)	312 (+) 1.6		2,408
(+) 2,2'-CH <sub>3</sub>	223-23.5 (-) 979 (221)	226.5 0.0 (224.5)	230 (+) 1,429 (228.5)	260 0.0 (259)	282.5 (-) 33 (283)	306.5 (-) 3.2 (306.5)	327.5 (-) 2.5			1,060

a

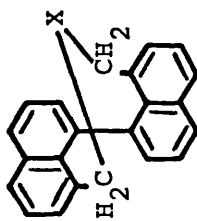
Table 28 c.d. spectra of 8,8'-disubstituted 1,1'-binaphthyls (R-Configuration) in 96% ethanol.  $\lambda_{nm}$  ( $\epsilon \times 10^{-3}$ )



a

(+) XV, R=CO <sub>2</sub> H	222.5 (+) 565	231.5 0.0	240 (-) 342	252 0.0	261.3 (-) 39.2	274 0.0	296-300 (+) 79.5	312.5 (+) 38.6	325 (+) 36.9	907
(+) XVI, R CO <sub>2</sub> CH <sub>3</sub>	221 (+) 320	226.5 0.0	236.5 (-) 368	249.5 (-) 32.8	258.5-260 (-) 66.6	276.5 0.0	295 (+) 47.2	311 (+) 24.8	326 (+) 20	688
(-) XVIII, R=CH <sub>2</sub> Br	223.5 (+) 455	232 0.0	242.5 (-) 472	239 (-) 263	281 0.0	284 (+) 43	297 (+) 29.3	330 (+) 3.9		927
(-) XIX, R=CH <sub>2</sub> CN	217 (+) 363	223 0.0	228 (-) 614	239 (-) 263	269 0.0	284 (+) 43	302 0.0	309 (-) 5.3		977

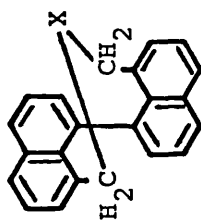
Table 29 o.r.d. spectra of 8,8'-bridged heterocyclic 1,1'-binaphthyls (S-configuration) in 96% ethanol.  $\lambda_{nm}$  ( $\times 10^{-3}$ )



a

(+) I, X=O	224.5	234.5	243	273	283	288	295	305.5		
	(-) 1,405	0.0	(+) 380	(+) 39	(+) 41	(+) 35	(+) 47	(+) 55		1,785
(+) II, X=S	228	235	254	260	283		305	318	331	
	0.0	(-) 1,054	0.0	+197	(+) 6.5		(+) 42	(+) 44	(+) 45	1,251
	217									
	0.0									
	212									
	(-) 159									
(+) III, X=Se	227	231.5	238	264	269	277.5	286	296	311.5	320
	(+) 378	0.0	(-) 652	0.0	(+) 44.2	0.0	(-) 20.5	0.0	(+) 649	(+) 62
										334
(+) IV, X=SO <sub>2</sub>	227.5	241.5	246			277	280	291	311	
	(-) 2220	0.0	(+) 522			0.0	(-) 8.0	(-) 19	(+) 62	
	222									
	0.0									
	216									
(+) 1,230										
(+) 2,2', X=O	220.5	229.5	234	252	277		318	327		3,748
	(-) 2,351	0.0	(+) 1,397	(+) 18	(+) 170		0.0	(-) 15		

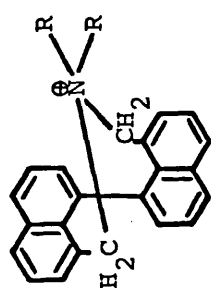


Table 30 o.r.d. spectra of 8,8'-bridged heterocyclic 1,1'-binaphthyls (R-configuration) in 96% ethanol.  $\lambda_{nm}(\epsilon \times 10^{-3})$ 

a

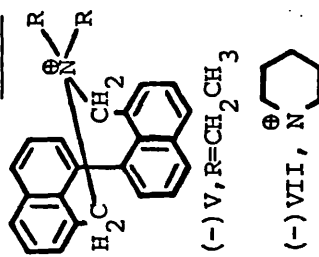
(-) I, X=O	223	227.5	234	242.5	281.5	287.5	296	305.5		
	(+) 1,644	0.0	(-) 355	0.0	(-) 41	(-) 35	(-) 52	(-) 60		1,999
(-) II, X=S	223	227.5	234	253	281.5-85	306.5	319	331.5		
	(-) 570	0.0	(+) 1,200	0.0	(-) 7.8	(-) 46	(-) 49	(-) 52		1,495
	216									
	0.0									
	212									
	(+) 190									
(-) III, X=Se	228	232.5	239.5	264	277.5	285	296.5	313	319-22	897.7
	(-) 474	0.0	(+) 843	0.0	(-) 54.7	0.0	0.0	(-) 81.6	(-) 77.4	335
	219.5									(-) 59.3
	0.0									
	217									
	(+) 181									
(-) IV, X=SO <sub>2</sub>										
		227	242.5	246.5	276.5	283-6	291	297	311.5	2,428
		(+) 2,030	0.0	(-) 398	0.0	(+) 11.6	(+) 20	0.0	(-) 52	

Table 31 o.r.d. spectra of 8,8'-bridged N-heterocyclic 1,1'-binaphthyls (S-configuration) in 96% ethanol.  $\lambda$  nm ( $\epsilon \times 10^{-3}$ )

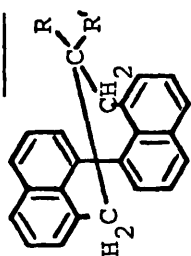


	226.5	238	244.5	292.5	312	325	$\epsilon$
(+) V, R=CH <sub>2</sub> CH <sub>3</sub>	(-) 1,588	0.0	(+) 463	(+) 1.4	(+) 44.4	(+) 30.6	2,051
(+) VI, R=CH <sub>2</sub> -CH=CH <sub>2</sub>	226	238.5	244	290-2	312	322	
	(-) 1,557	0.0	(+) 343	(-) 10.3	(+) 41	(+) 29	1,900
(+) VII, N <sup>+</sup>	226.5	237	243	292	311.5	324	
	(-) 1,626	0.0	(+) 419	(+) 3.6	(+) 44.2	(+) 31.1	2,045

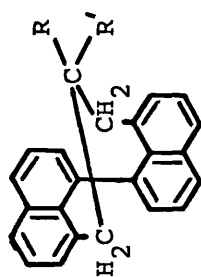
Table 32 o.r.d. spectra of 8,8'-bridged N-heterocyclic 1,1'-binaphthyls (R-configuration) in 96% ethanol.  $\lambda$  nm ( $\epsilon \times 10^{-3}$ )



	226.5	238	244	292	312	325	$\epsilon$
(-) V, R=CH <sub>2</sub> CH <sub>3</sub>	(+) 1,298	0.0	(-) 303	(+) 4.0	(-) 35.2	(-) 24.2	1,601
(-) VII, N <sup>+</sup>	226	237	243	290	312	323-4	
	(+) 1,417	0.0	(-) 391	(+) 2.4	(-) 39.7	(-) 28.2	1,808

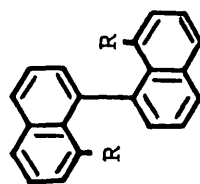
Table 33 o.r.d. spectra of 8,8'-bridged carbocyclic 1,1'-binaphthyls (S-configuration) in 96% ethanol.  $\lambda_{nm}$  ( $\text{ex}10^{-3}$ )

	224	233.5	243	270-2	292.5	306.5-310	320-3	$\lambda_{nm}$ ( $\text{ex}10^{-3}$ )
(+) VIII, R=R'=CO <sub>2</sub> Et	(-) 1,274	0.0	(+) 226	(+) 49	(+) 14.6	(+) 23.2	(+) 16.8	1,500
(+) IX, R=R'=CO <sub>2</sub> H	224.5	234	244	272	292.5	308	320-2	1,488
(+) X, R=R'=CO <sub>2</sub> CH <sub>3</sub>	(-) 1,196	0.0	(+) 292	(+) 41.9	(+) 16.7	(+) 26.9	(+) 18.4	1,696
(+) XI, R=R'=CH <sub>2</sub> OH	223.5	233	242	274	293	310	319-23	1,743
(+) XII, R=H, R'=CO <sub>2</sub> H	(-) 1,437	0.0	(+) 259	(+) 54	(+) 18.2	(+) 8.5	(+) 20.9	1,092
(+) XIII, R=H, R'=CO <sub>2</sub> CH <sub>3</sub>	226	235	242	292	292	308.5	323	1,591
(+) XIV, R=H, R'=CO <sub>2</sub> H	(-) 1,419	0.0	(+) 324	(+) 21.8	(+) 16	(+) 36.1	(+) 24.2	1,591
(+) XV, R=H, R'=CO <sub>2</sub> CH <sub>3</sub>	222.5	235.5	246	275	292	308	325	1,591
(+) XVI, R=H, R'=CO <sub>2</sub> CH <sub>3</sub>	(-) 882	0.0	(+) 210	(+) 36.7	(+) 16	(+) 21	(+) 15.3	1,591
(+) XVII, R=H, R'=CO <sub>2</sub> CH <sub>3</sub>	224	235	243	271	294	307.5	320-5	1,591
(+) XVIII, R=H, R'=CO <sub>2</sub> CH <sub>3</sub>	(-) 1,214	0.0	(+) 277	(+) 53	(+) 22.9	(+) 28	(+) 19.3	1,591

Table 34 o.r.d. spectra of 8,8'-bridged carbocyclic 1,1'-binaphthyls (R-configuration) in 96% ethanol.  $\lambda_{nm}(\text{ex } 10^{-3})$ 

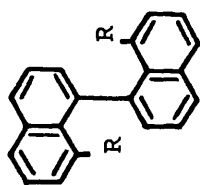
a

(-) VIII, R=R'=CO <sub>2</sub> Et	223.5 (+) 1,803	234 0.0	240.5-45 (-) 316	272 (-) 55.8	292-5 (-) 16.4	307-10 (-) 26.5	322 (+) 18.7	2,119
(-) IX, R=R'=CO <sub>2</sub> H	224 (+) 1,121	235 0.0	244-6 (-) 233	273 (-) 39	296 (-) 17.6	310 (-) 24.9	323 (-) 16.3	1,354
(-) X, R=R'=CO <sub>2</sub> CH <sub>3</sub>	223 (+) 1,437	223.5 0.0	242.5 (-) 225	272 (-) 51	292 (-) 15.6	309 (-) 25.2	319-23 (-) 17.2	1,662
(-) XI, R=R'=CH <sub>2</sub> OH	226 (+) 1,450	235.5 0.0	242-4 (-) 355	280-3 (-) 31.5	292 (-) 17.7	308 (-) 34.3	324-7 (-) 21	1,805
(-) XII, R=H R'=CO <sub>2</sub> H	222.5 (+) 979	235 0.0	244.5 (-) 212		296 (-) 22.2	307.5 (-) 26	320-5 (-) 18.2	1,191
(-) XIII, R=H R'=CO <sub>2</sub> CH <sub>3</sub>	223 (+) 1,313	235 0.0	242.5 (-) 314		297 (-) 29.4	307.5 (-) 34	320 (-) 24.6	1,627

Table 35 o.r.d. spectra of 8,8' - disubstituted 1,1' - binaphthyls (S-configuration) in 96% ethanol.  $\lambda$  nm ( $\times 10^{-3}$ )

	218	224	233	243	248.5	258	278	304	310	318	342	<u>a</u>
(-) XV R=CO <sub>2</sub> H	(+)491	0.0 (-)619	222	229	240.5	245	254	274	308-11	313-5	335	1,110
(-) XVI R=CO <sub>2</sub> CH <sub>3</sub>		0.0 (-)600	218	229	240.5	245	254	274	308-11	313-5	335	
(-) XVII R=CH <sub>2</sub> Br	219.5	224	234	247	255							944
(-) XIX R=CH <sub>2</sub> CN	(+)286	0.0 (-)658	219.5	224	234	247	255					
		0.0 (-)848	211	225	231.5	233.5	248	291	300	310	326	
			0.0 (-)848	0.0 (+)35	0.0 (+)35	(+)186		0.0	(-)11	0.0	(+)7.6	

Table 36 o.r.d. spectra of 8,8' - disubstituted 1,1' - binaphthyls (R-configuration) in 96% ethanol.  $\lambda_{nm}$  ( $\times 10^{-3}$ )



(+) XV	R=CO <sub>2</sub> H	217 (-)410	225.5 0.0	(+)599	231.5	242.5 0.0	248.5 (-)172	259 (-)33.9	279 (-)105	304 0.0	310 (+)25	317 (+)16.9	342 (+)33.6	<sup>a</sup> 1,009
(+) XVI	R=CO <sub>2</sub> CH <sub>3</sub>	225.5 0.0	229.5 (+)480	241 0.0	246 (-)84.4	255 (-)4.7	276 (-)92.3	303 0.0	309 (+)11.5	315 (+)9.0	335 (+)19.1			
(-) XVIII	R=CH <sub>2</sub> Br	221 (-)236	224 0.0	234 (+)689	247.5 0.0	257 (-)175				325 (-)4.5	329 (-)6.5			925
(-) XIX	R=CH <sub>2</sub> CN		225 (+)920	233.5 0.0	234 (-)22	250 (-)186		291 0.0	300 (+)9.3	309.5 0.0	326 (-)9.3			

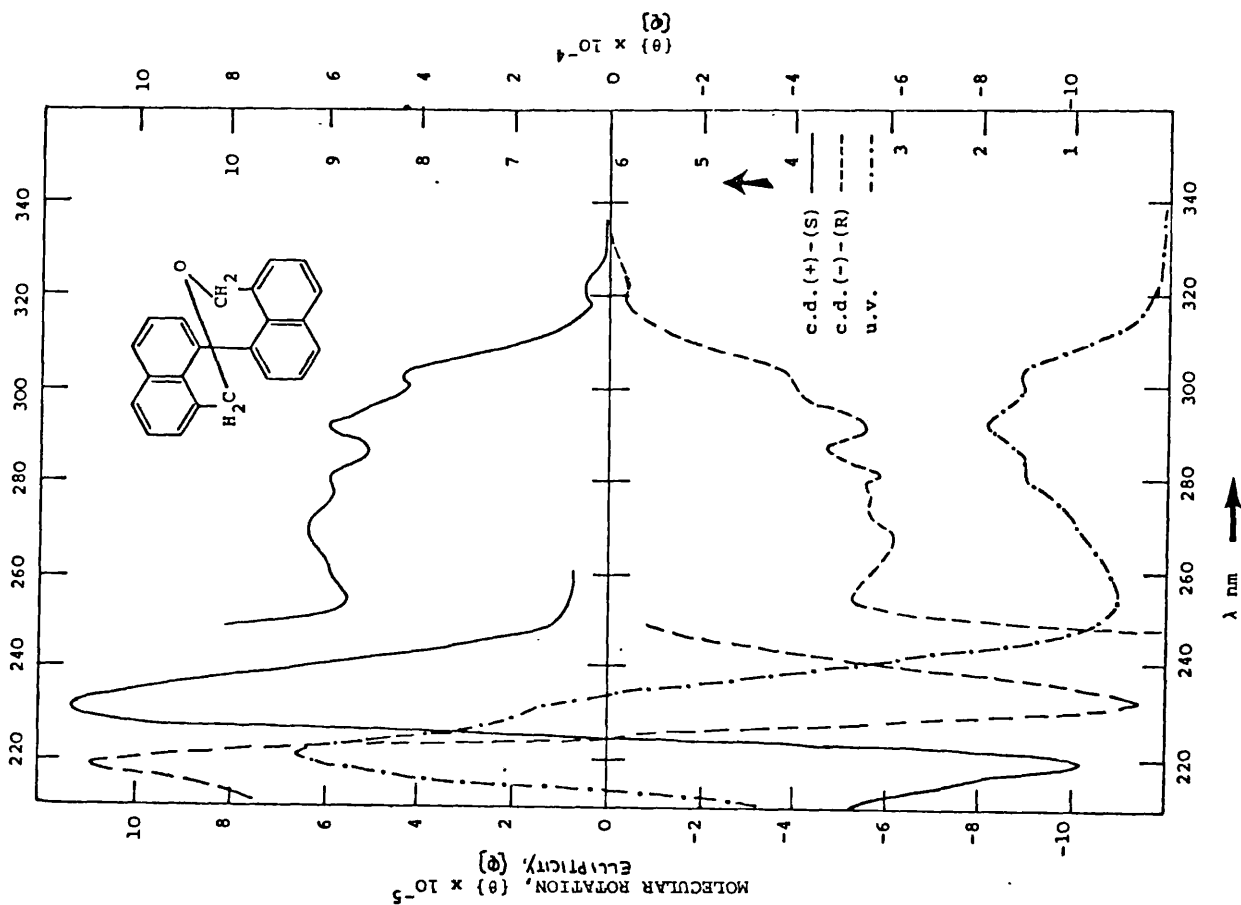


Figure 19

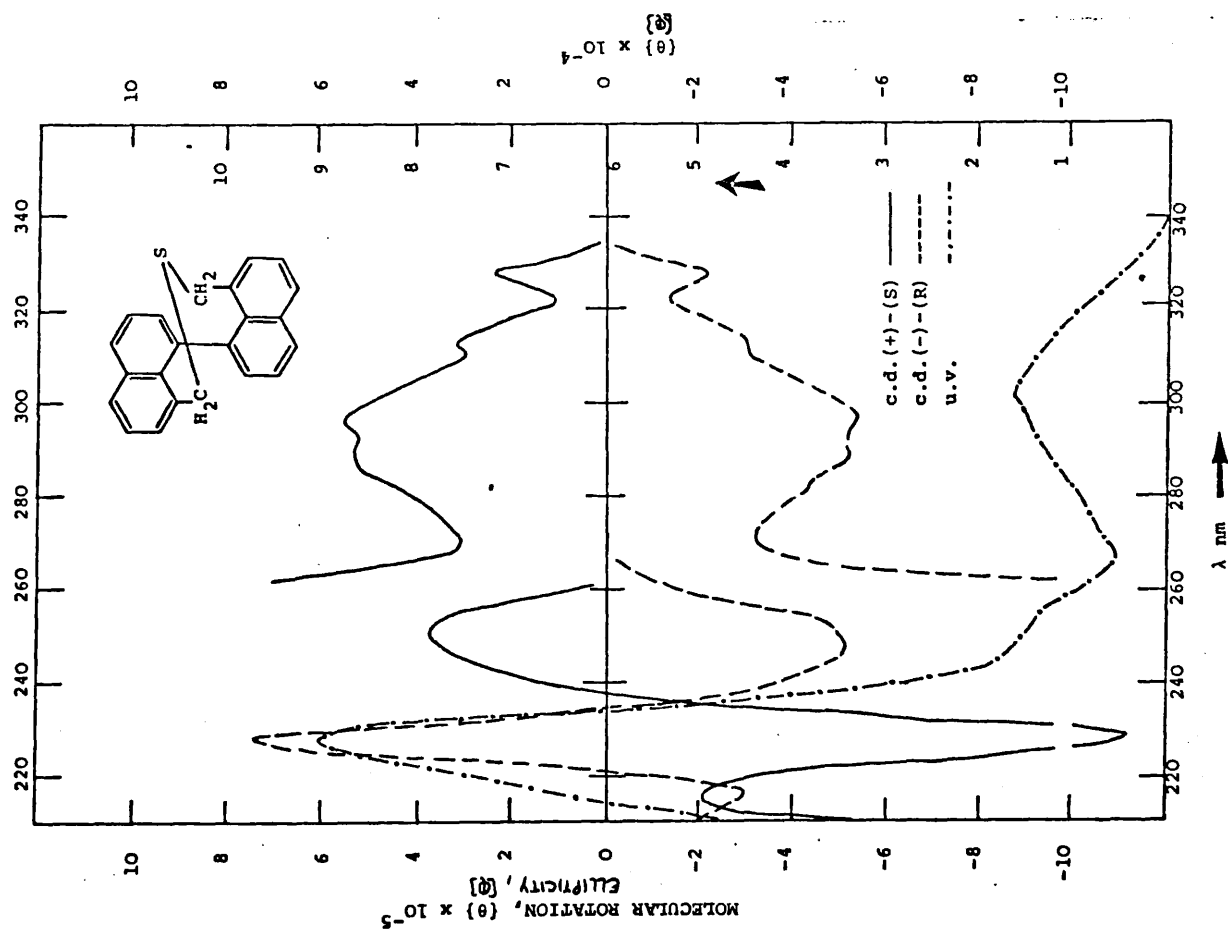


Figure 20

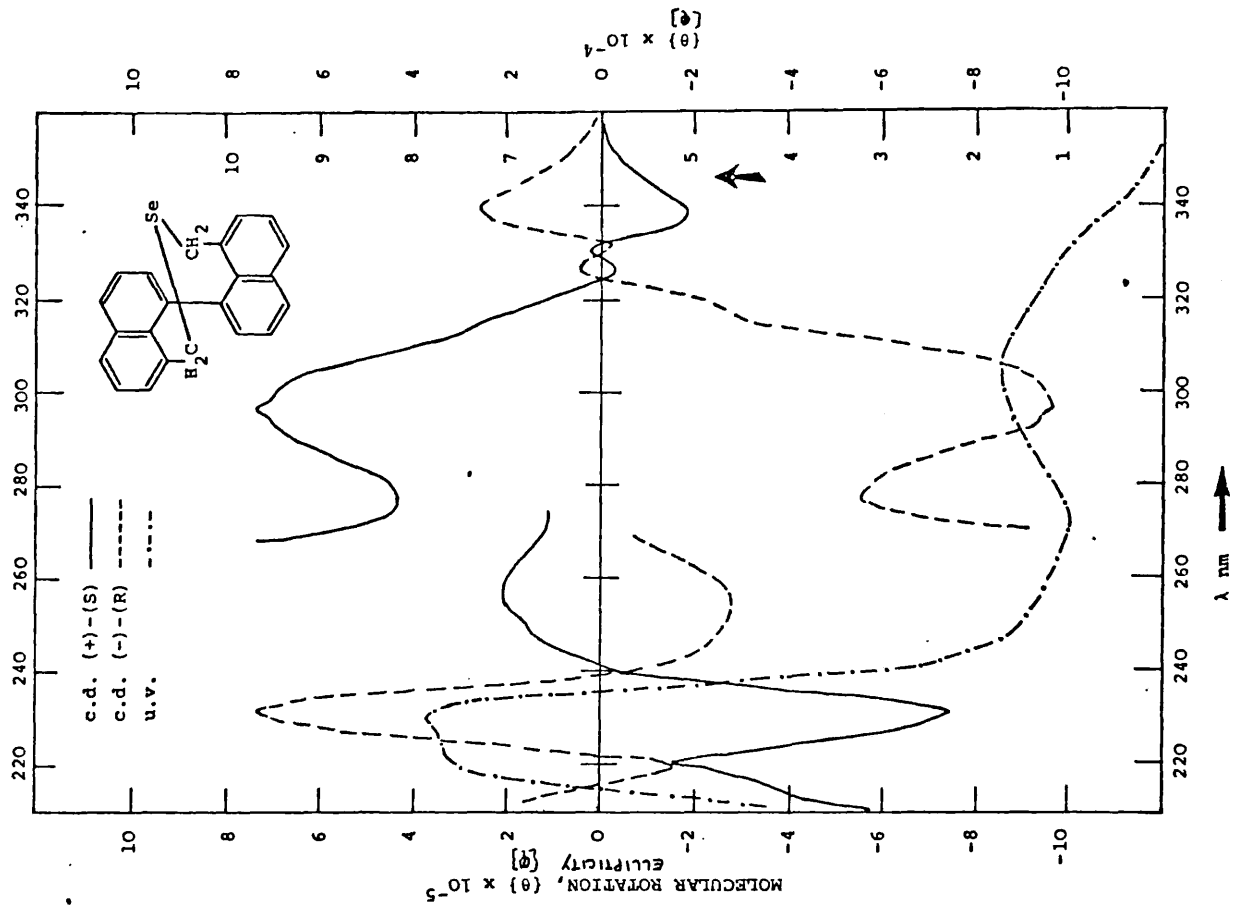


Figure 21

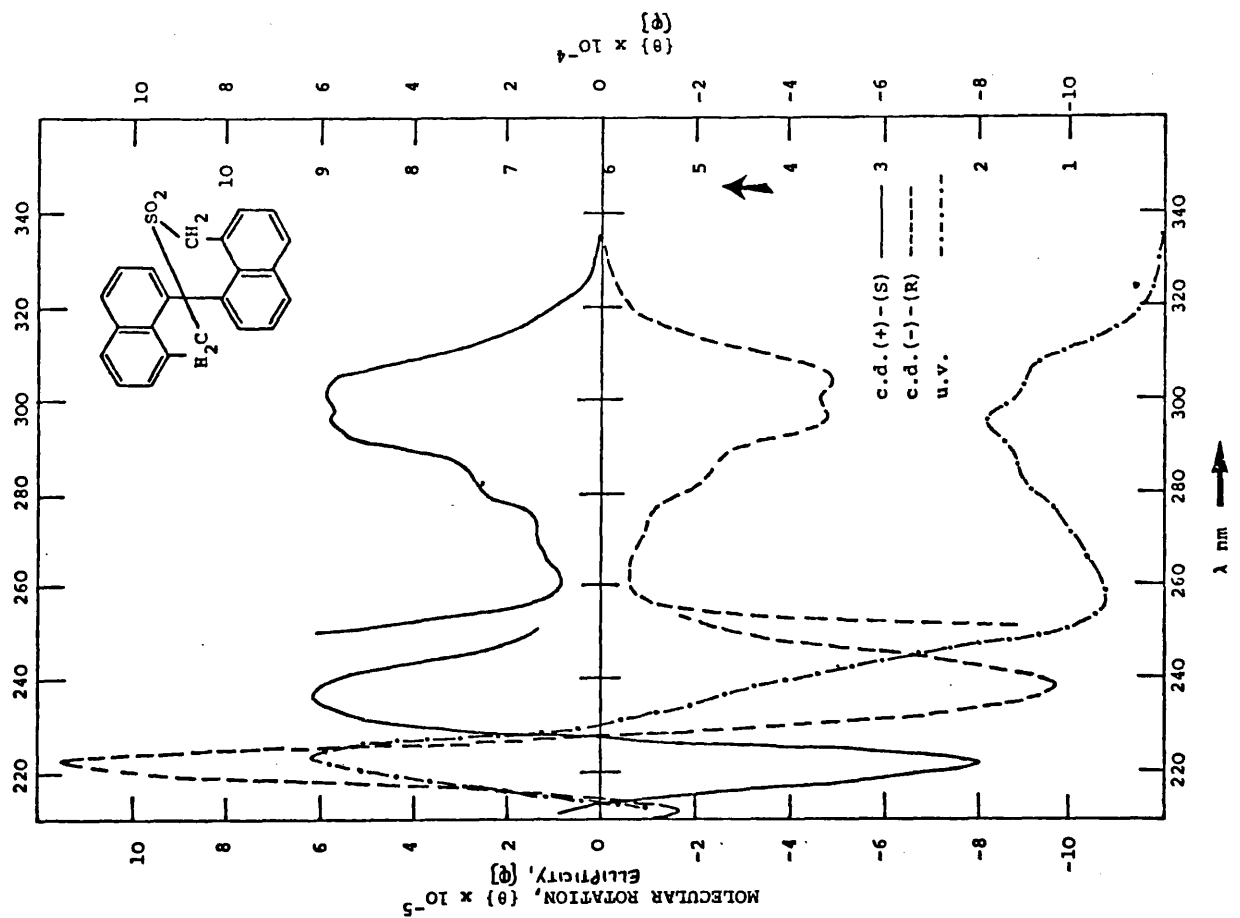


Figure 22



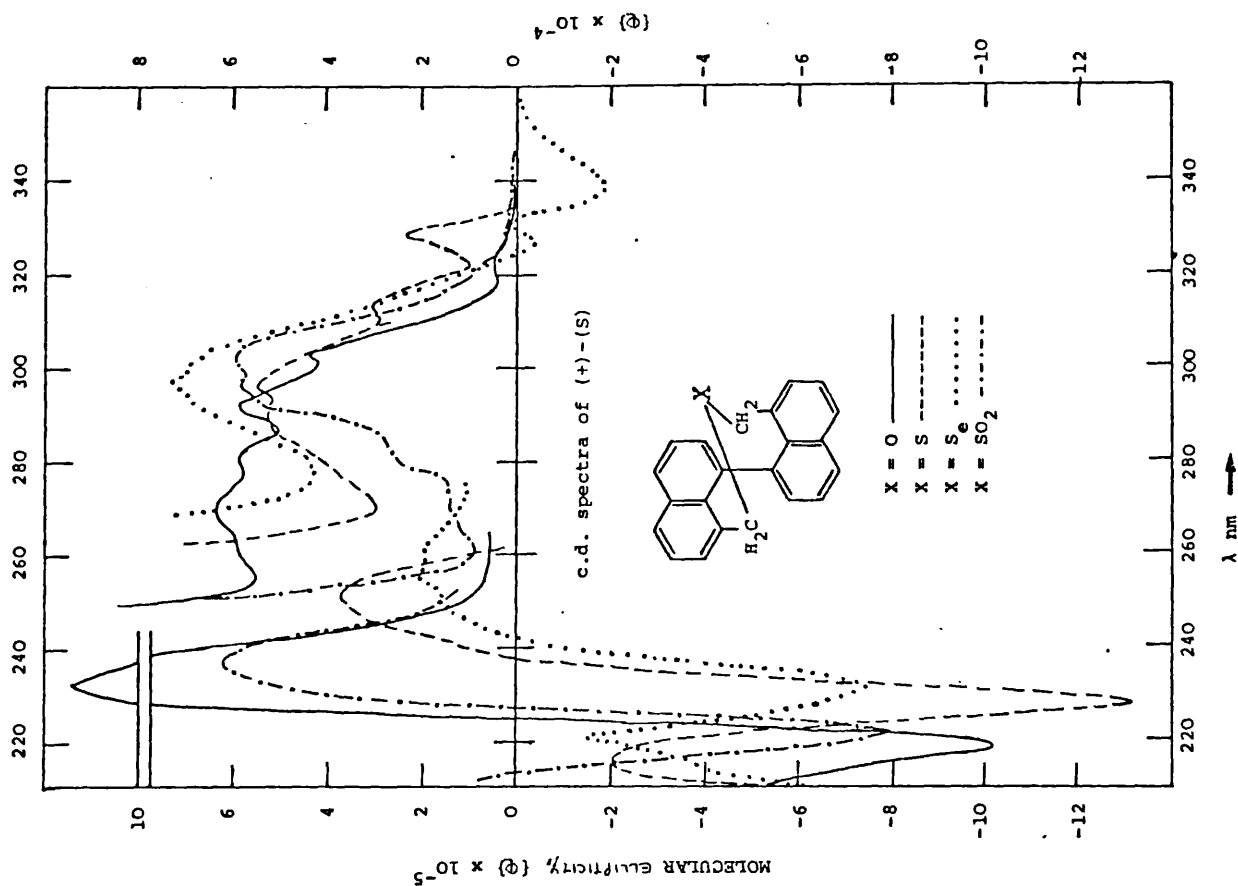


Figure 23

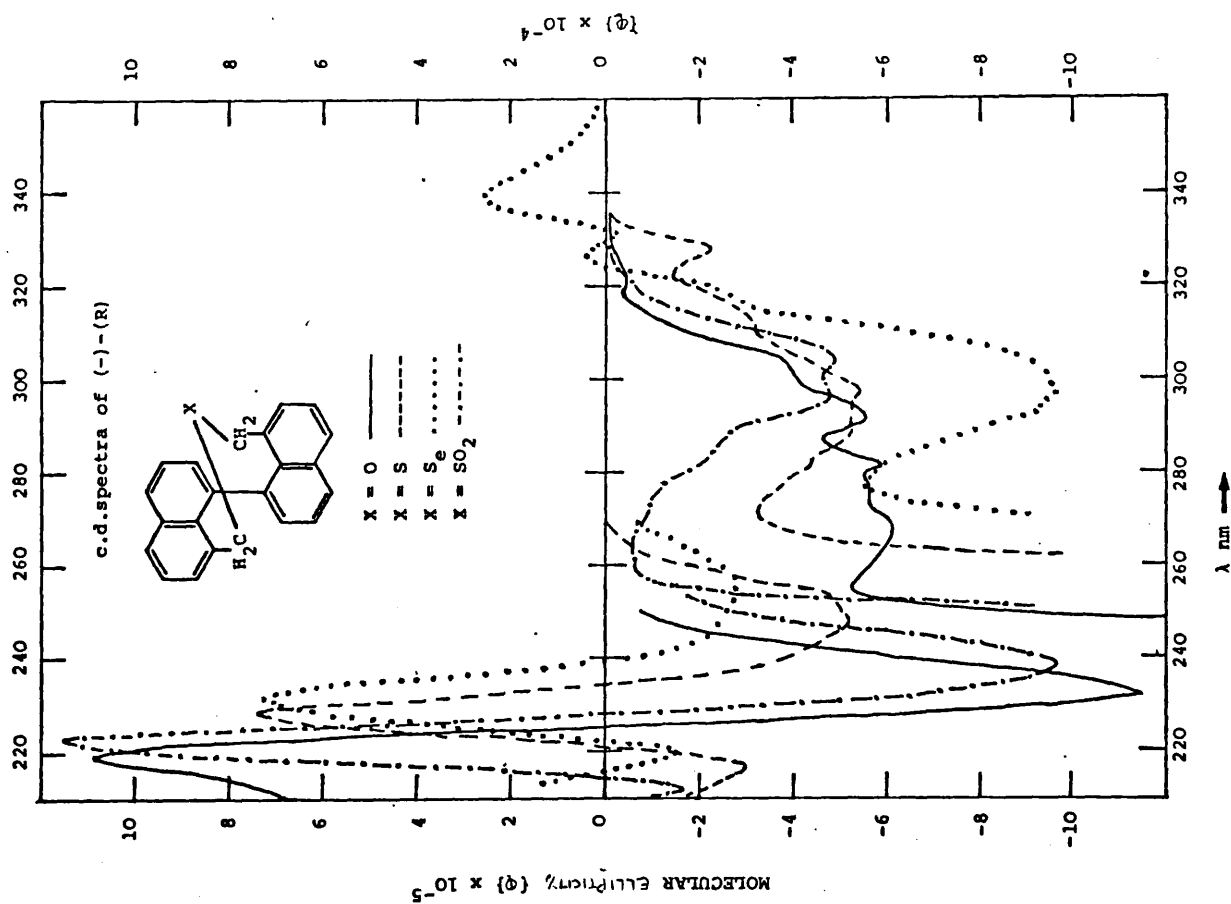


Figure 24

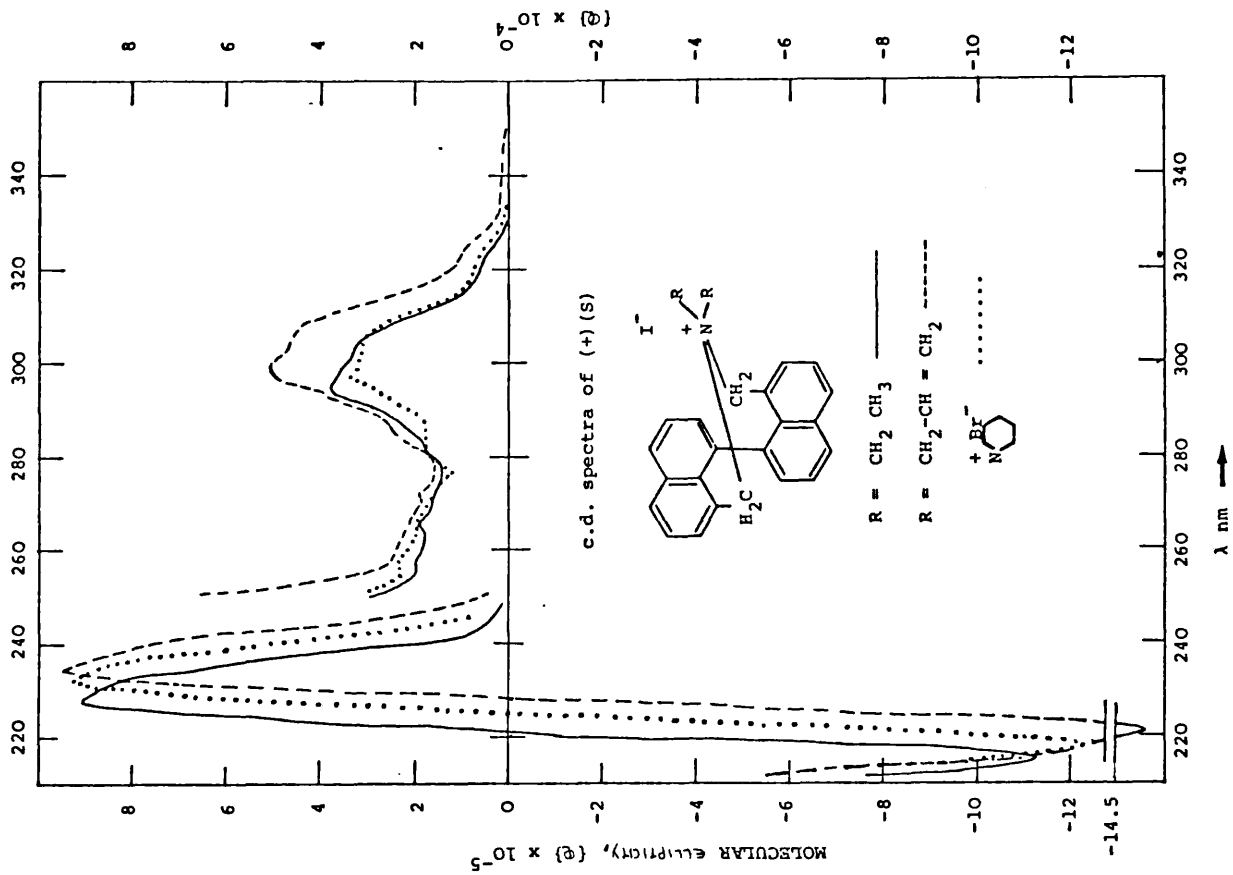


Figure 25

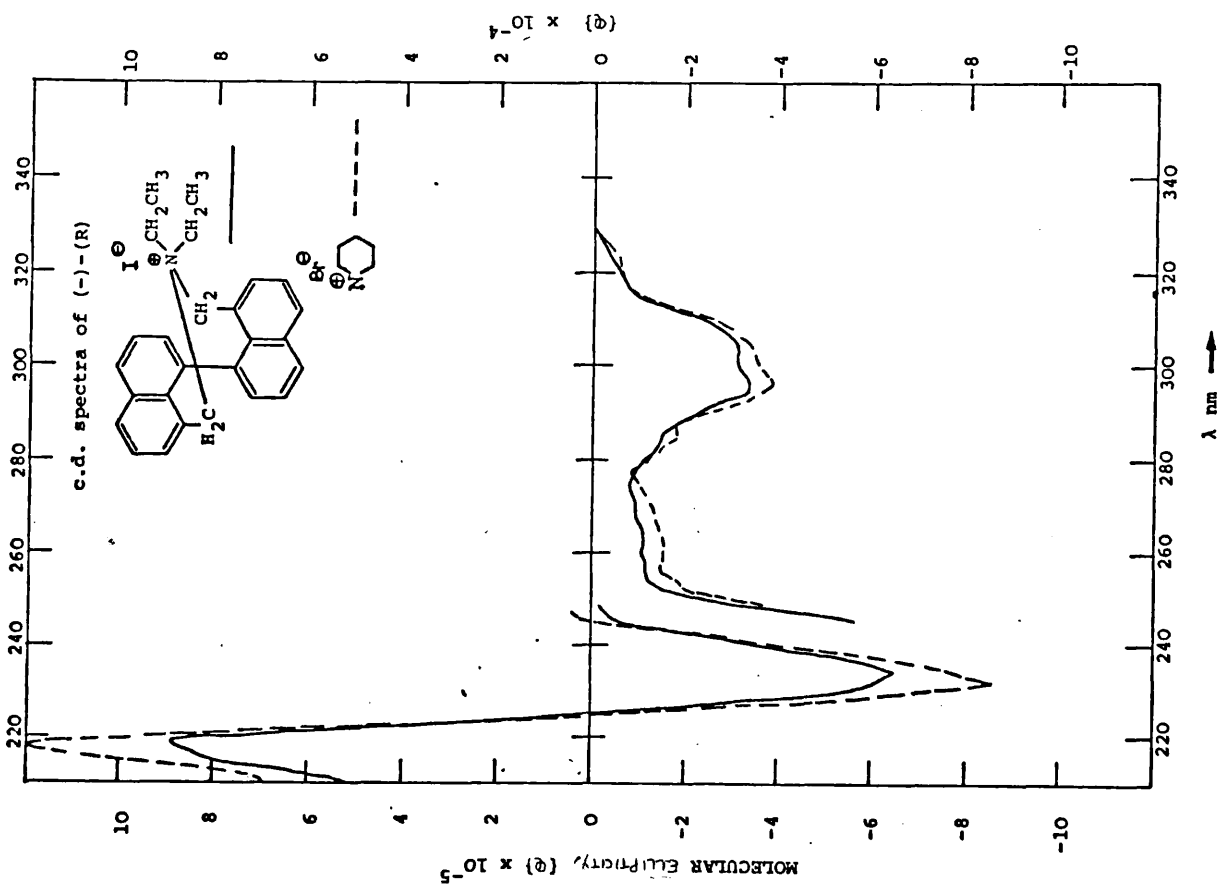


Figure 26

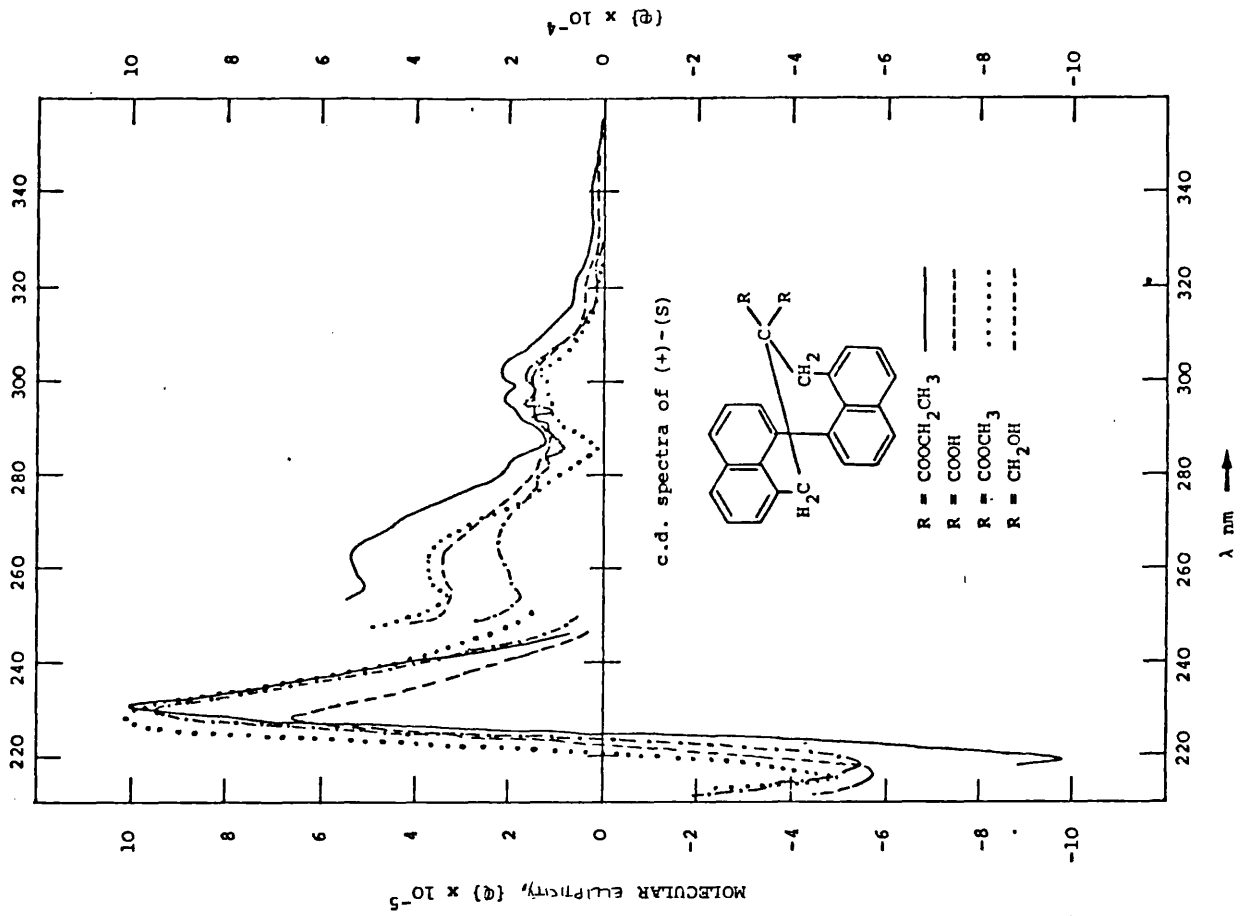


Figure 27

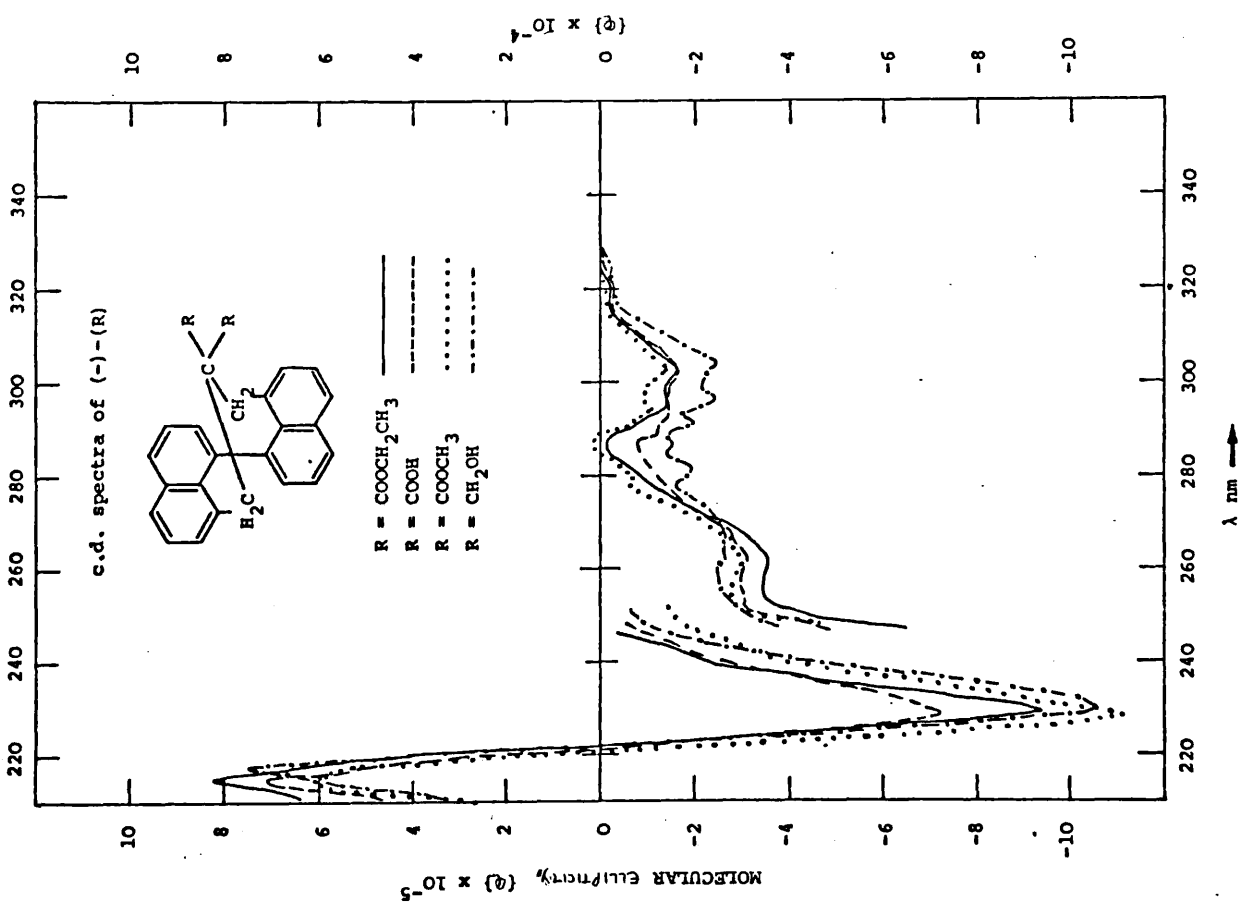


Figure 28

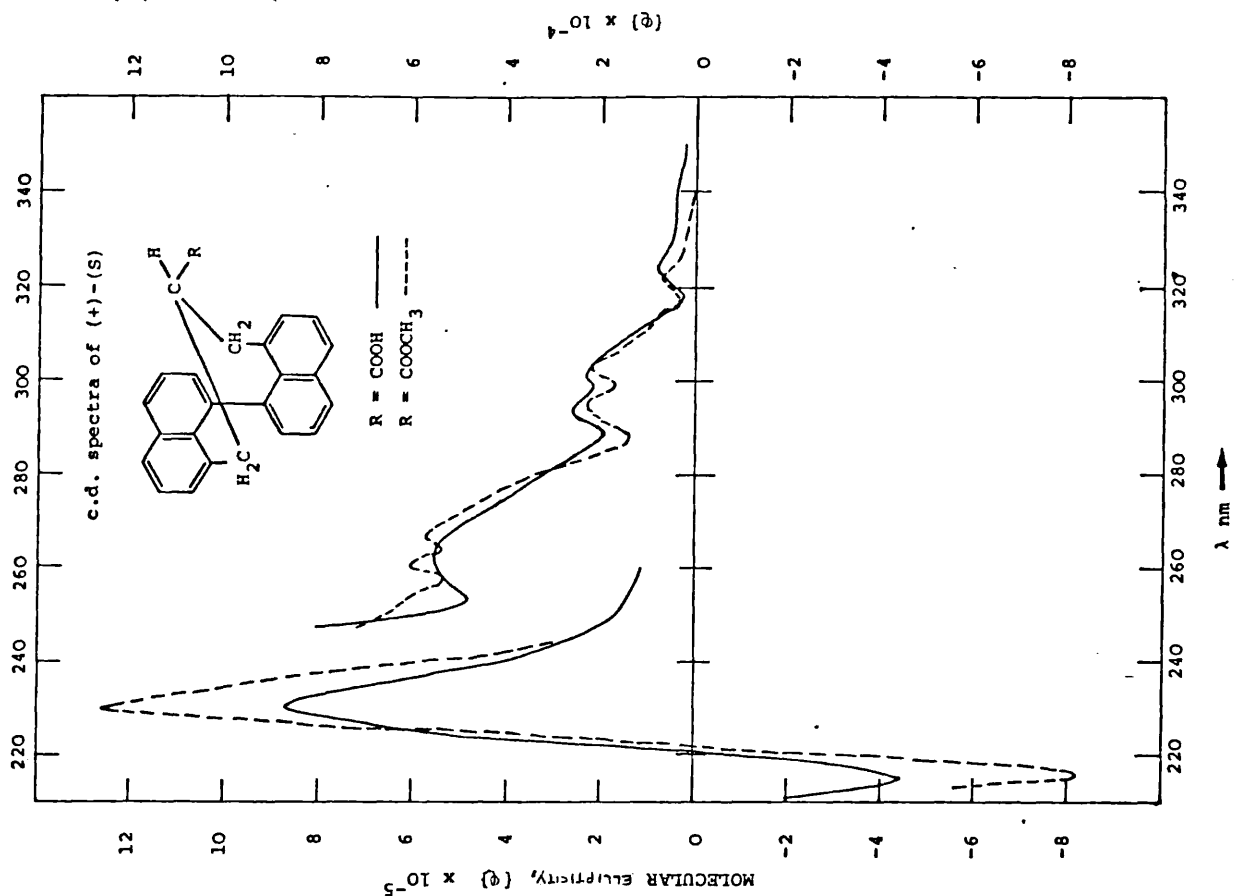


Figure 29

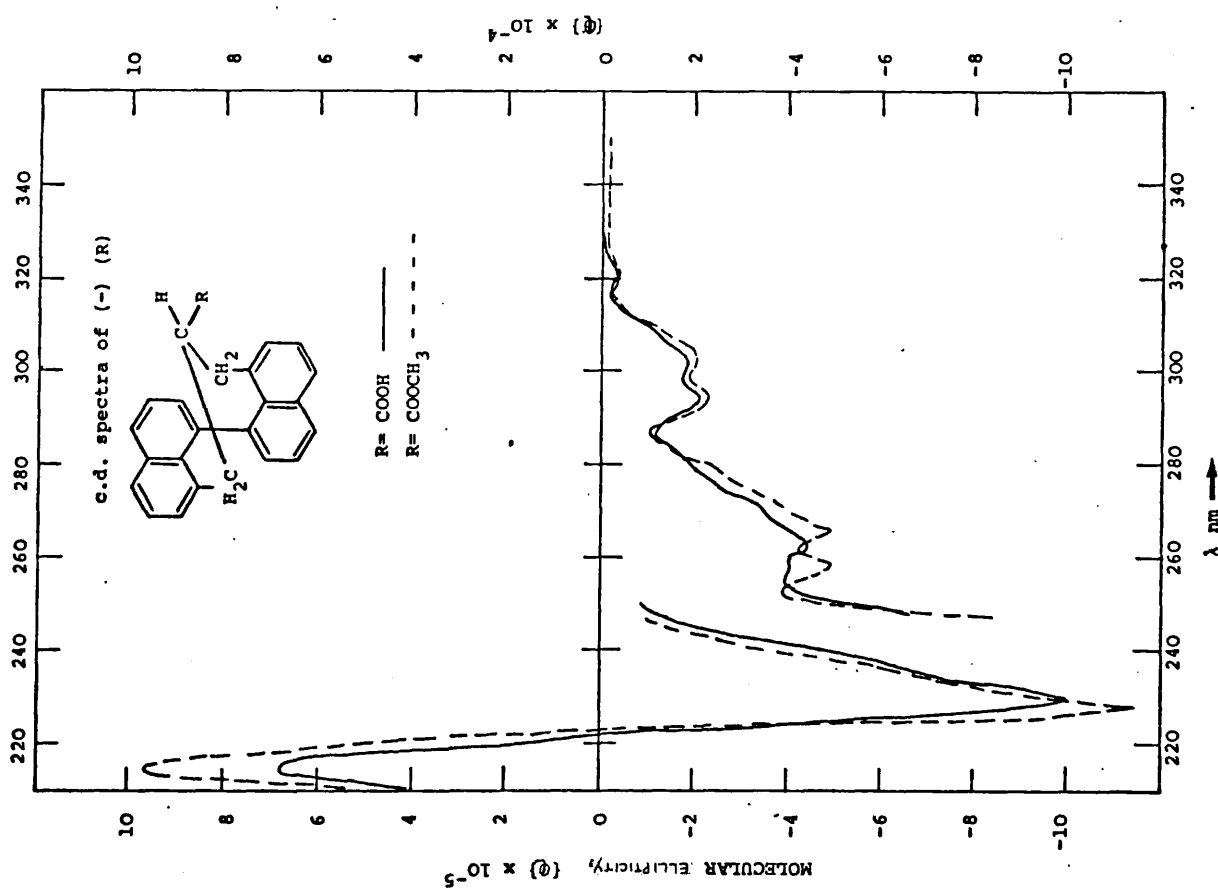


Figure 30

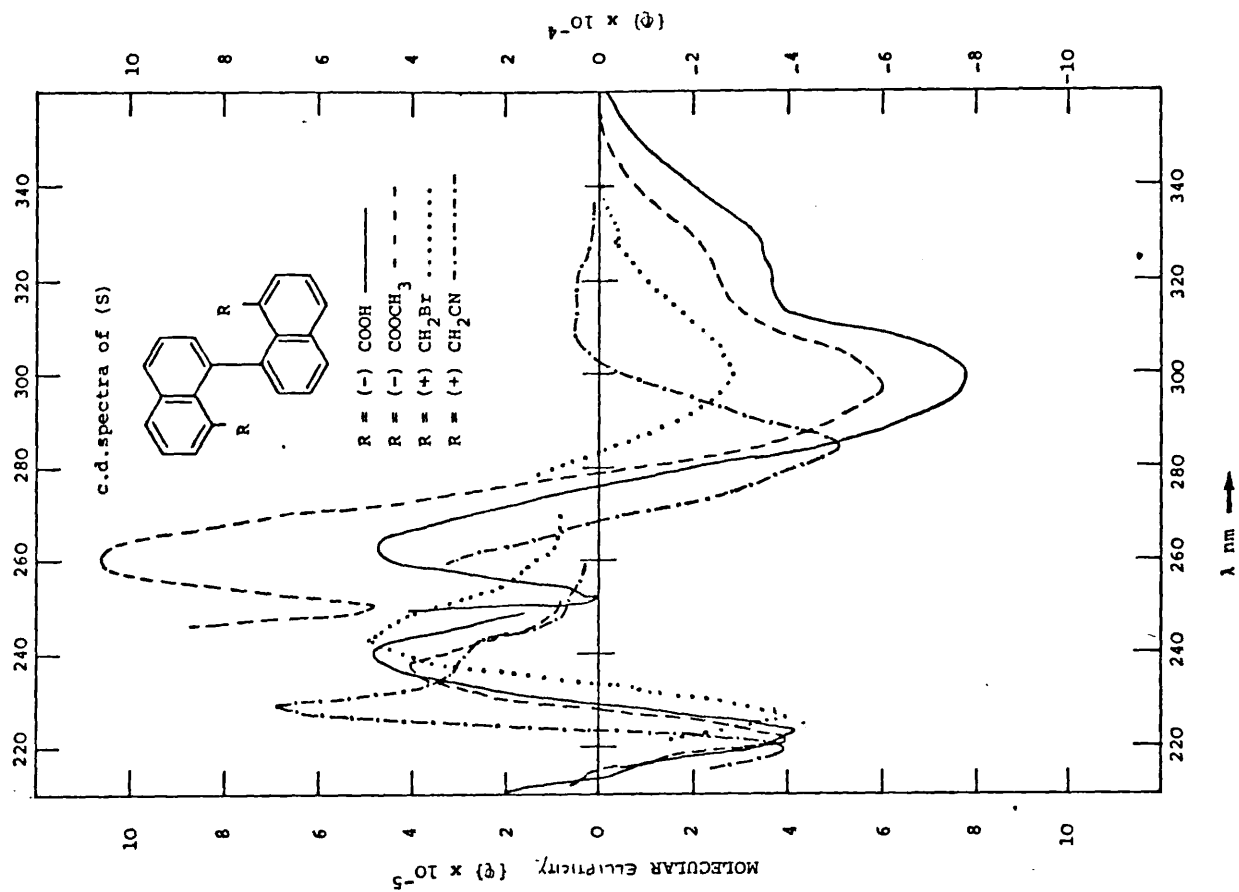


Figure 31

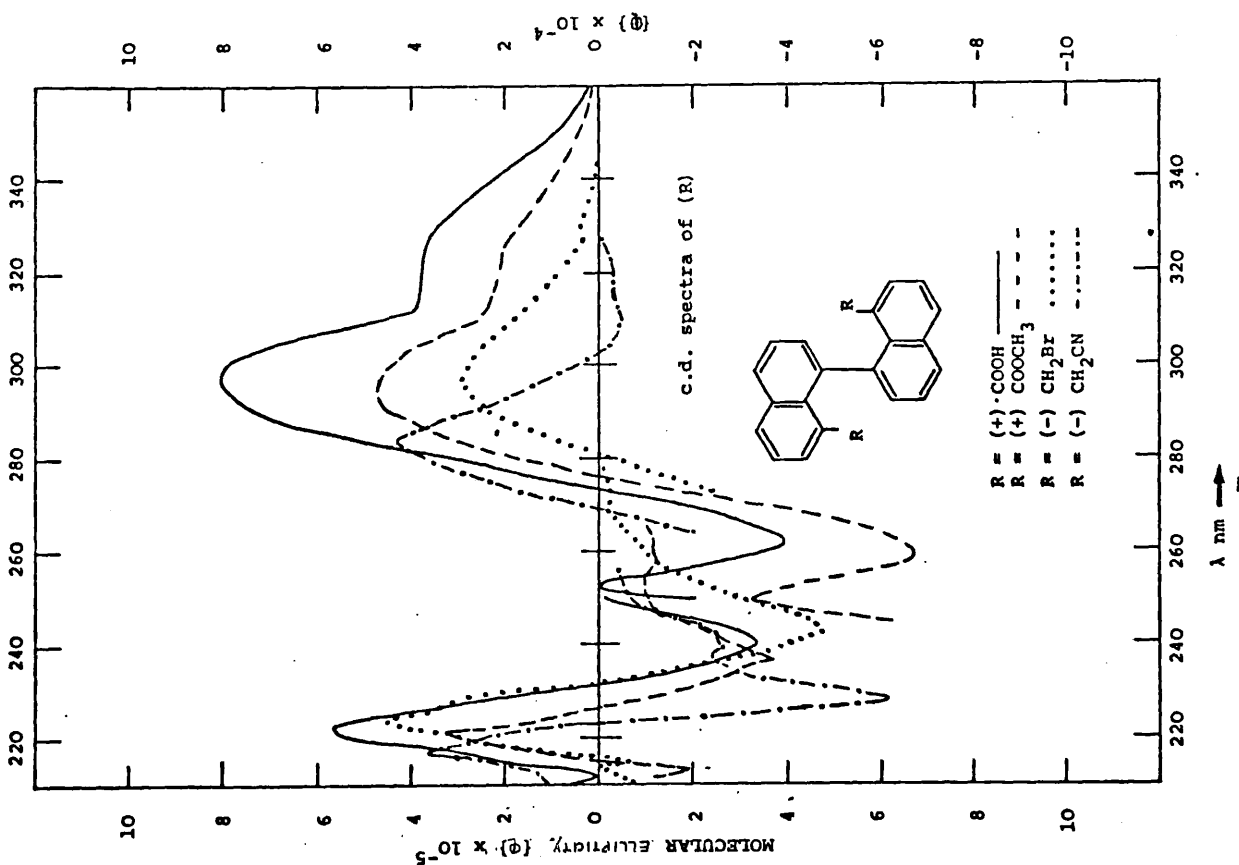


Figure 32

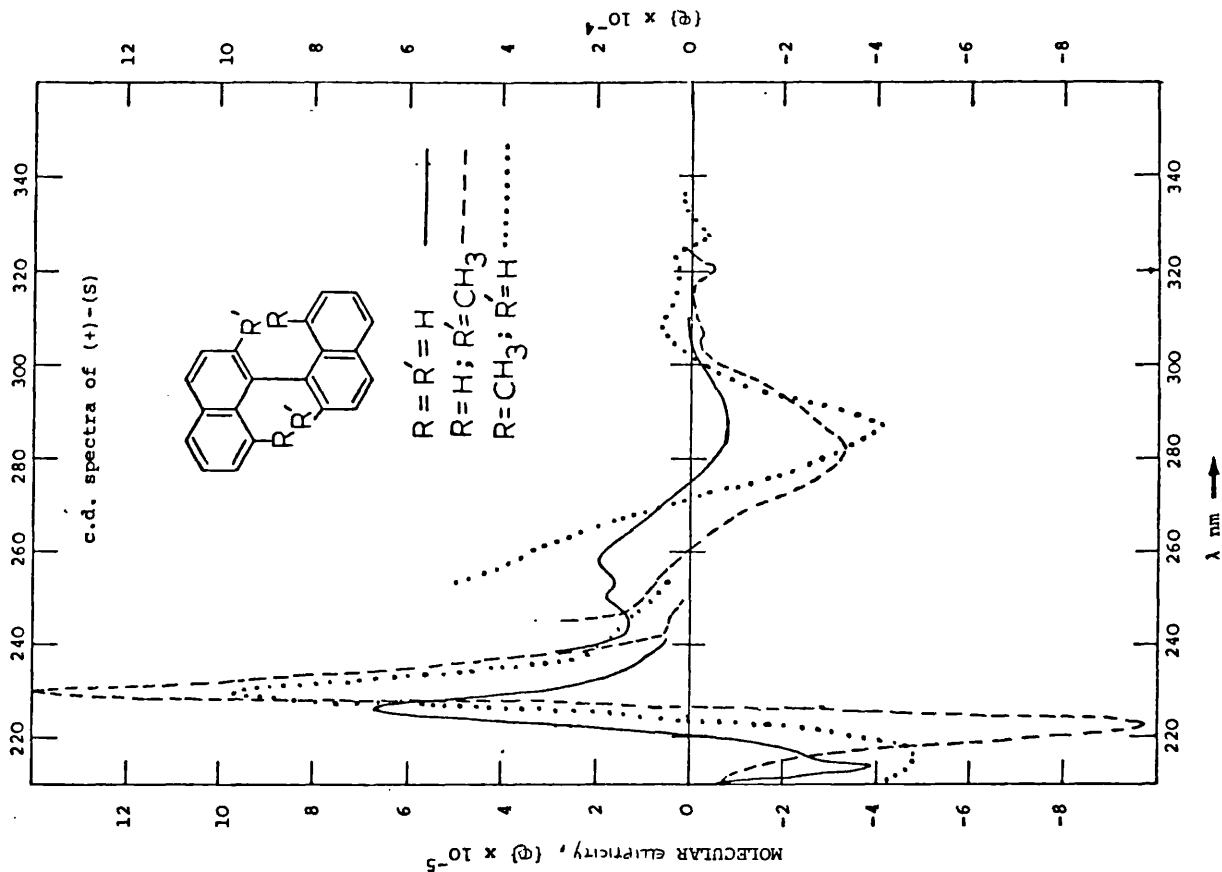


Figure 33

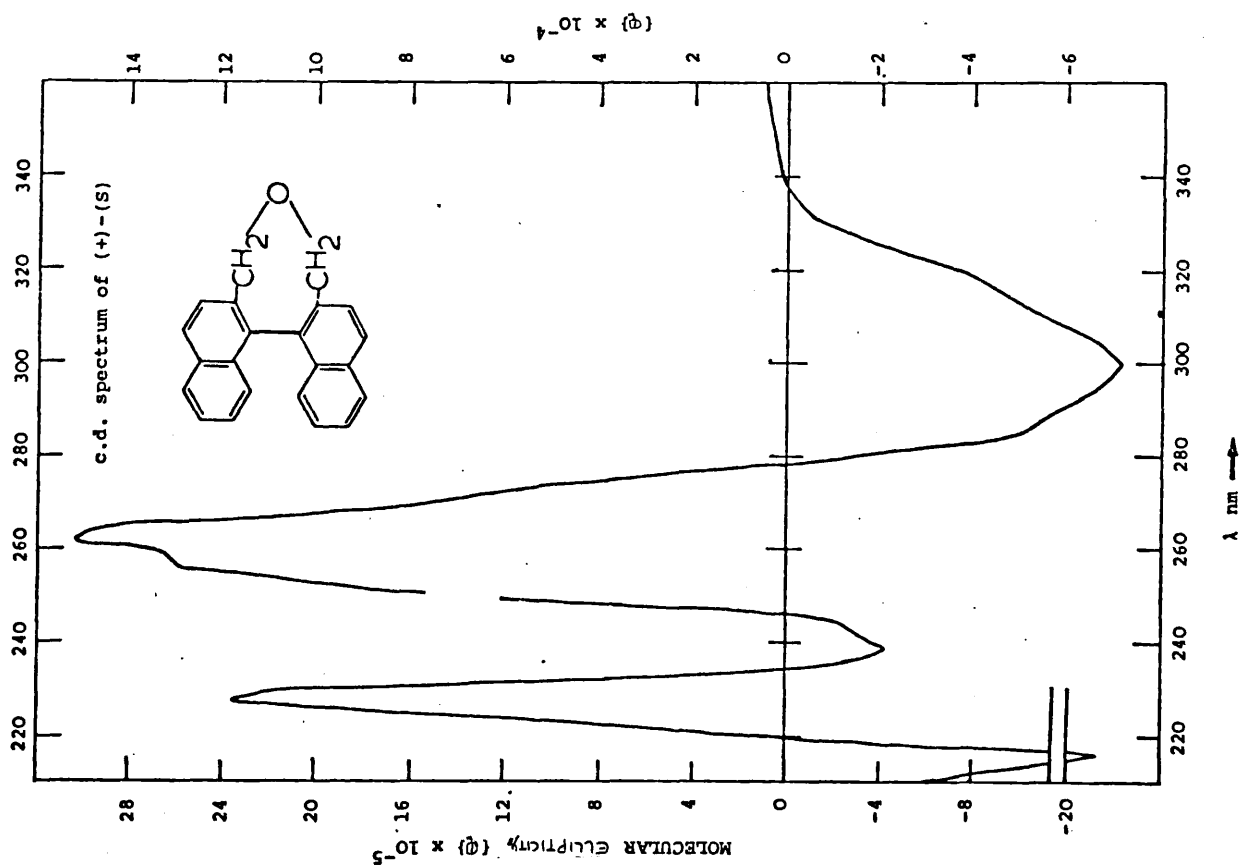


Figure 34

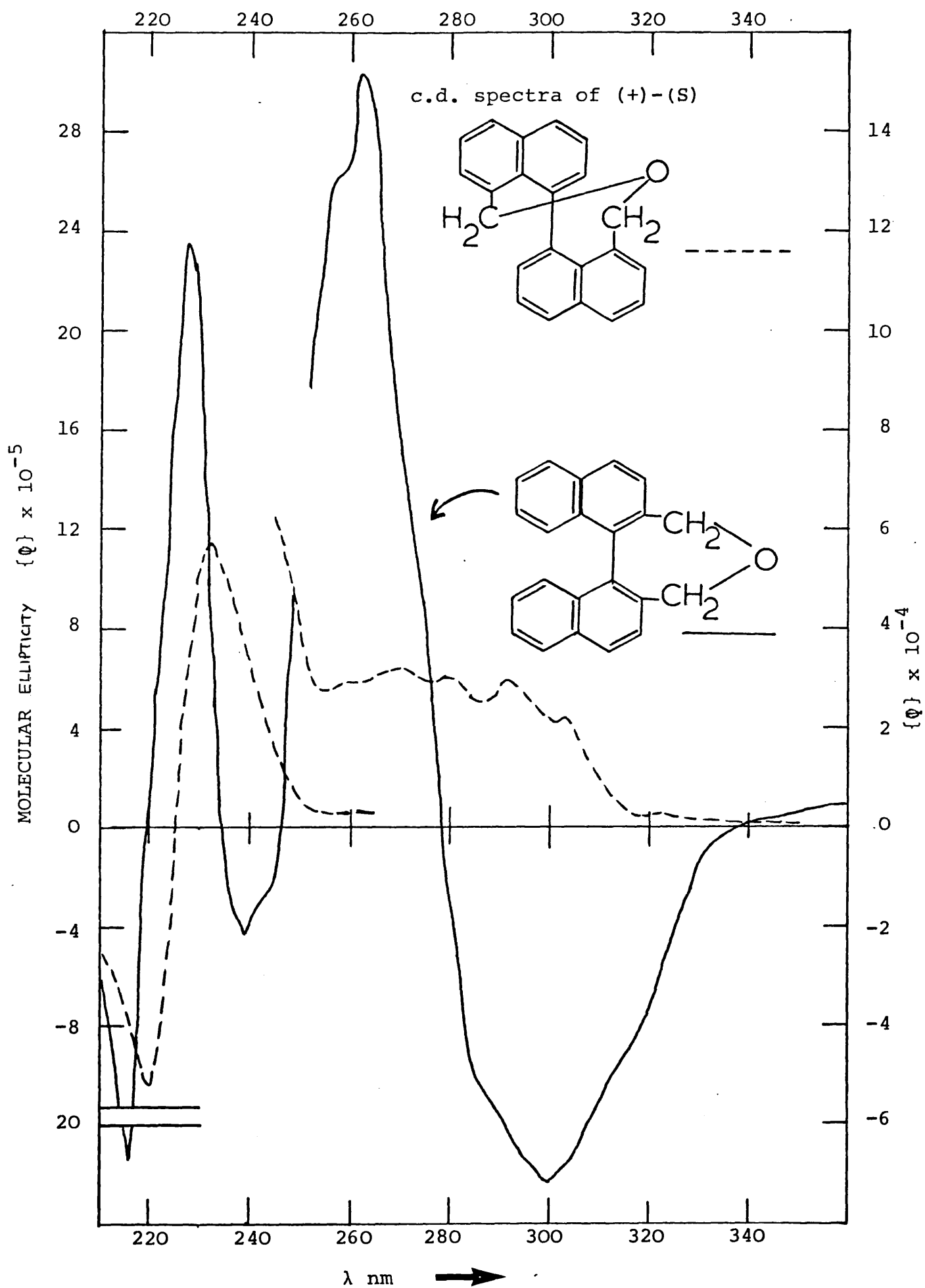


Figure 35

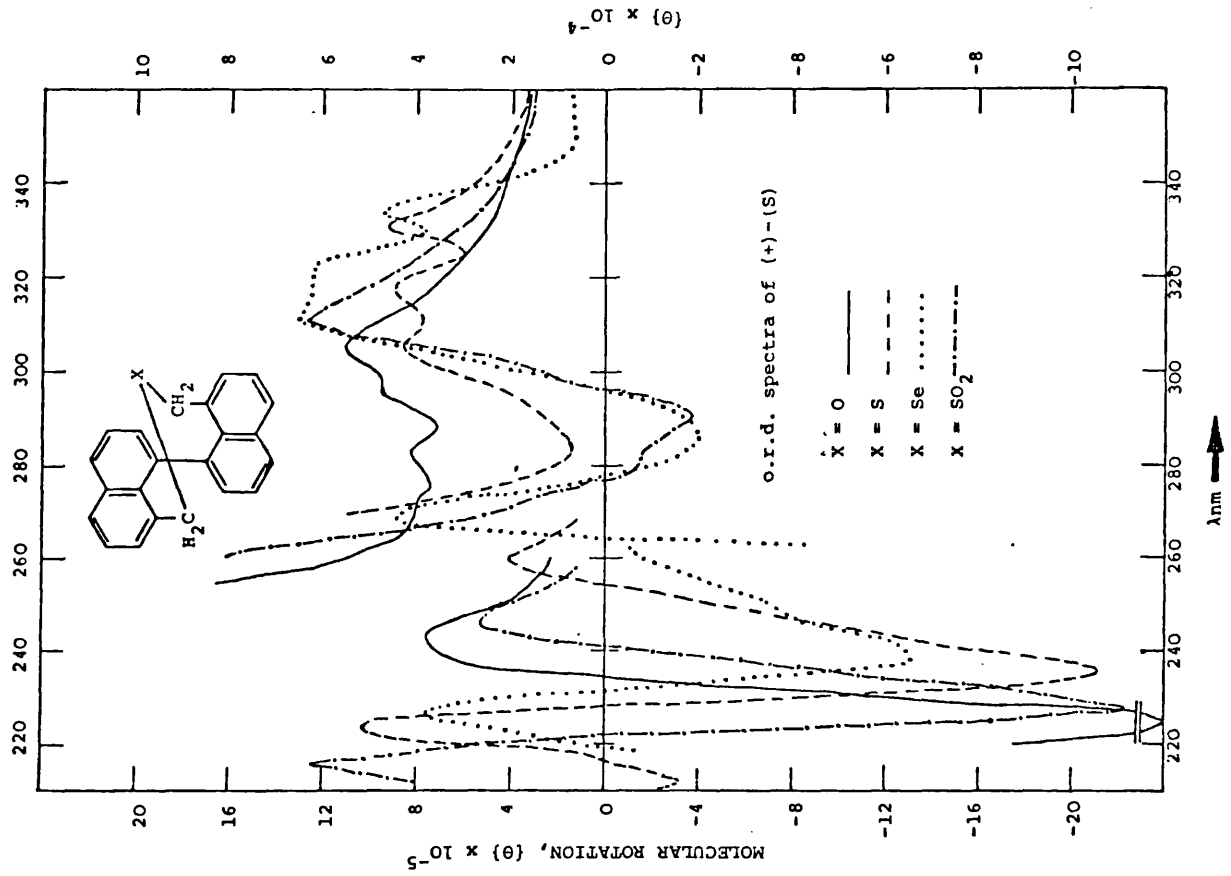


Figure 36

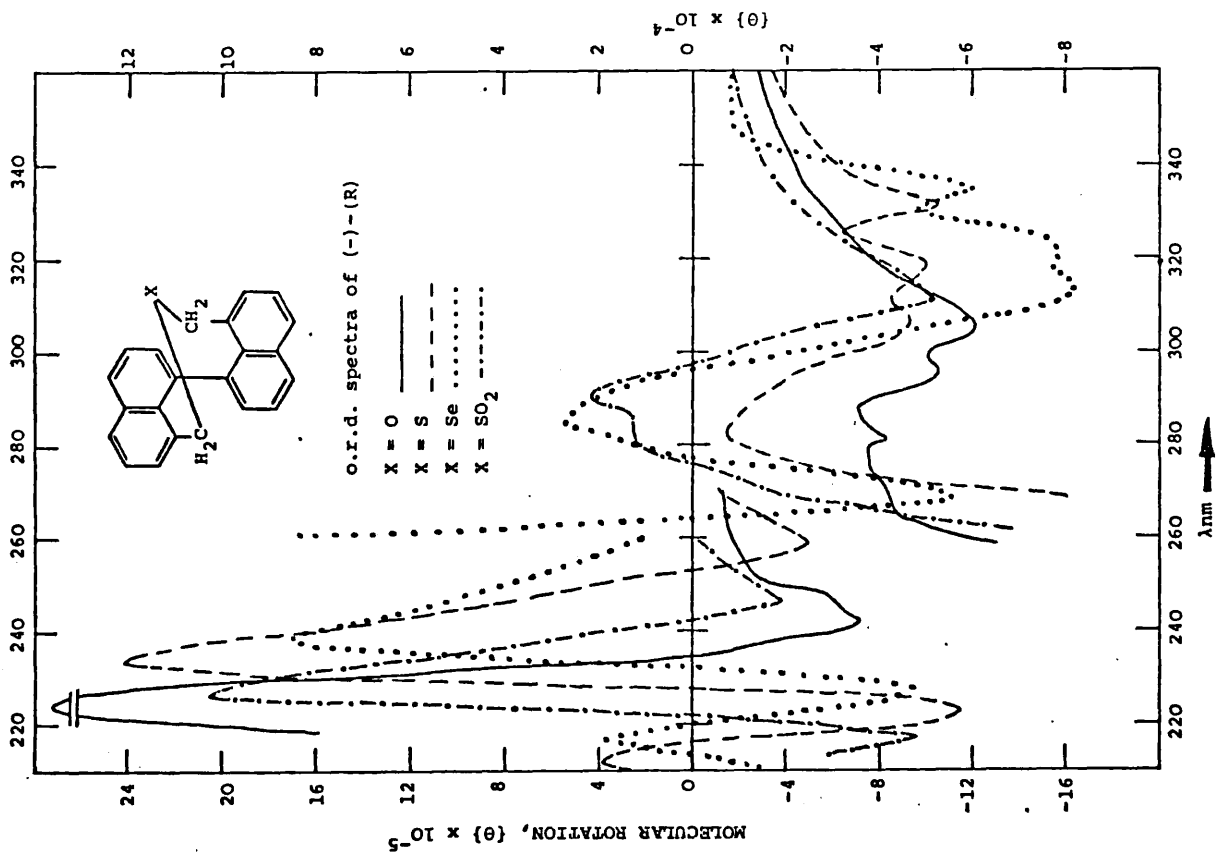


Figure 37



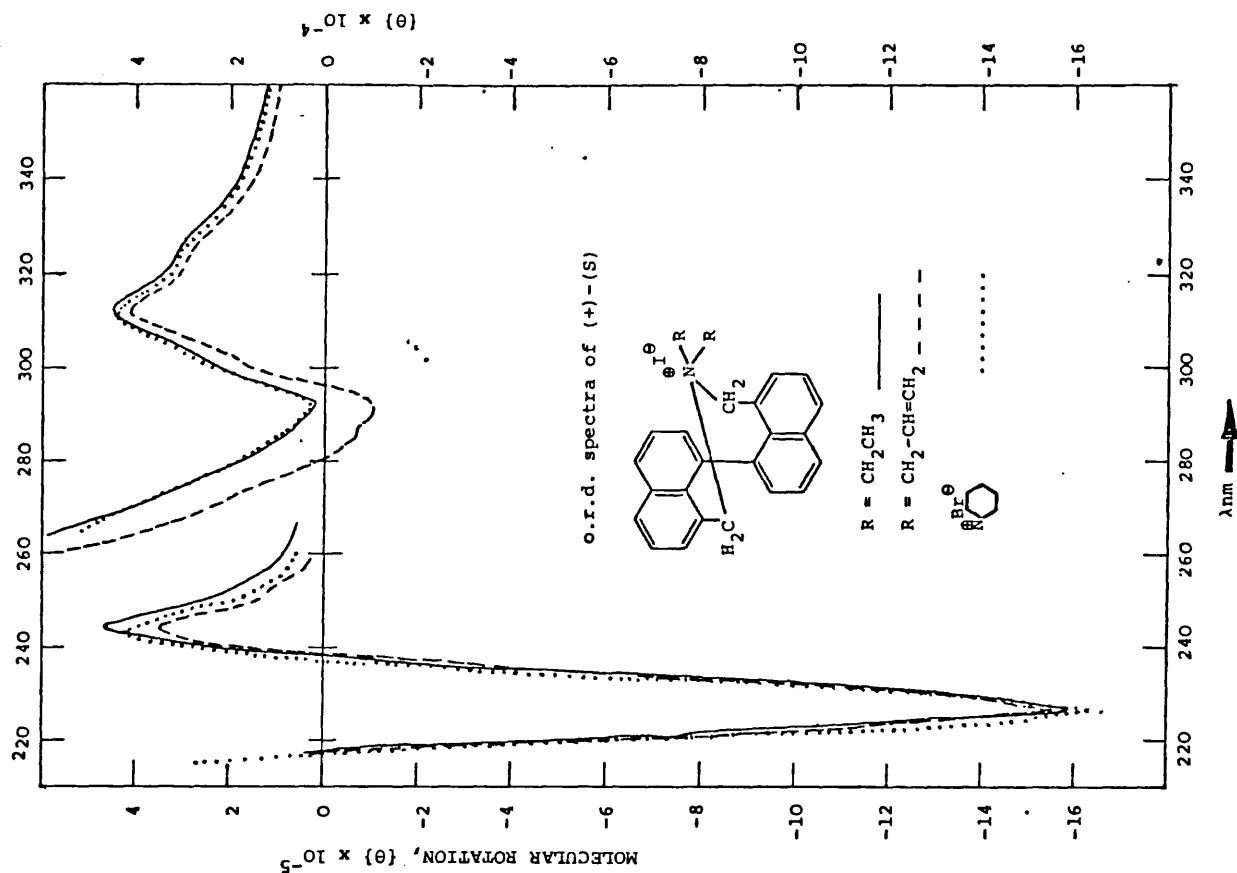


Figure 38

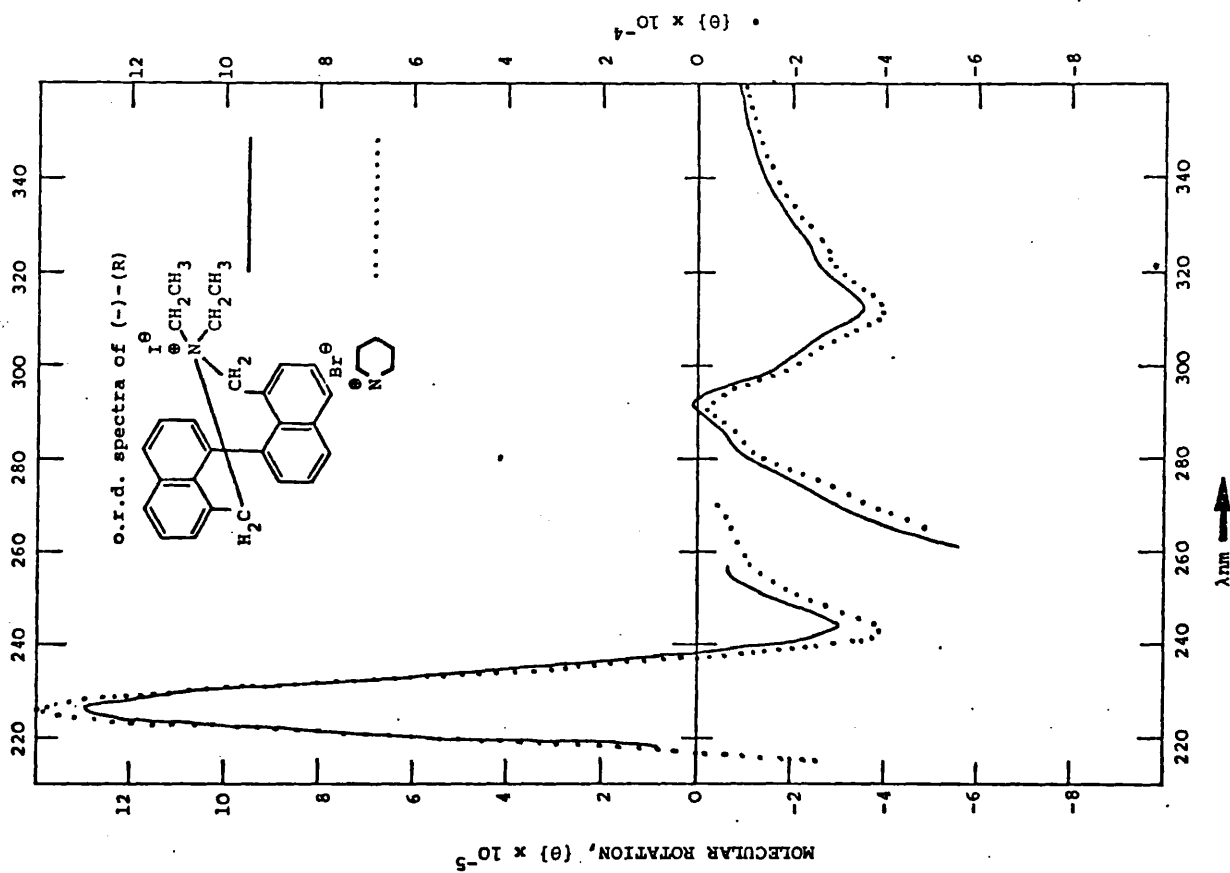


Figure 39

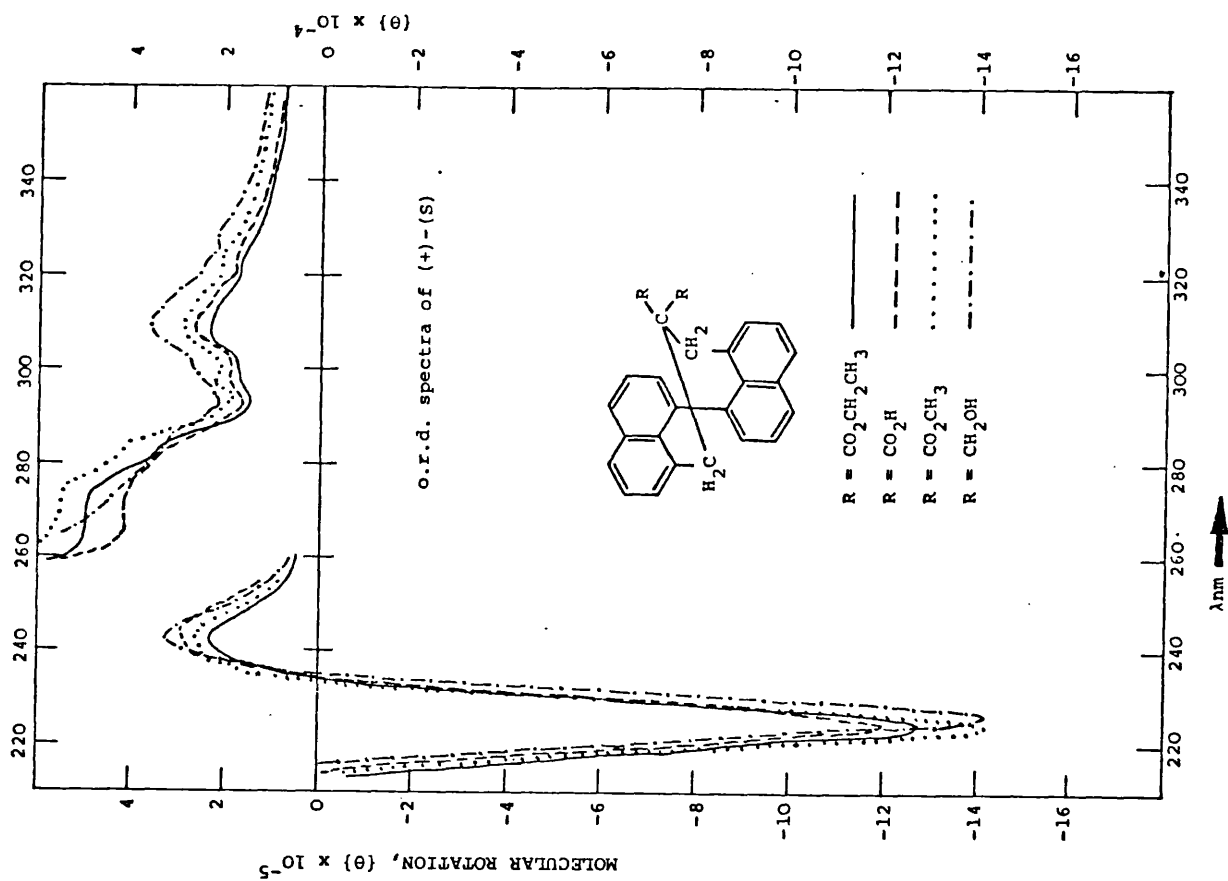


Figure 40

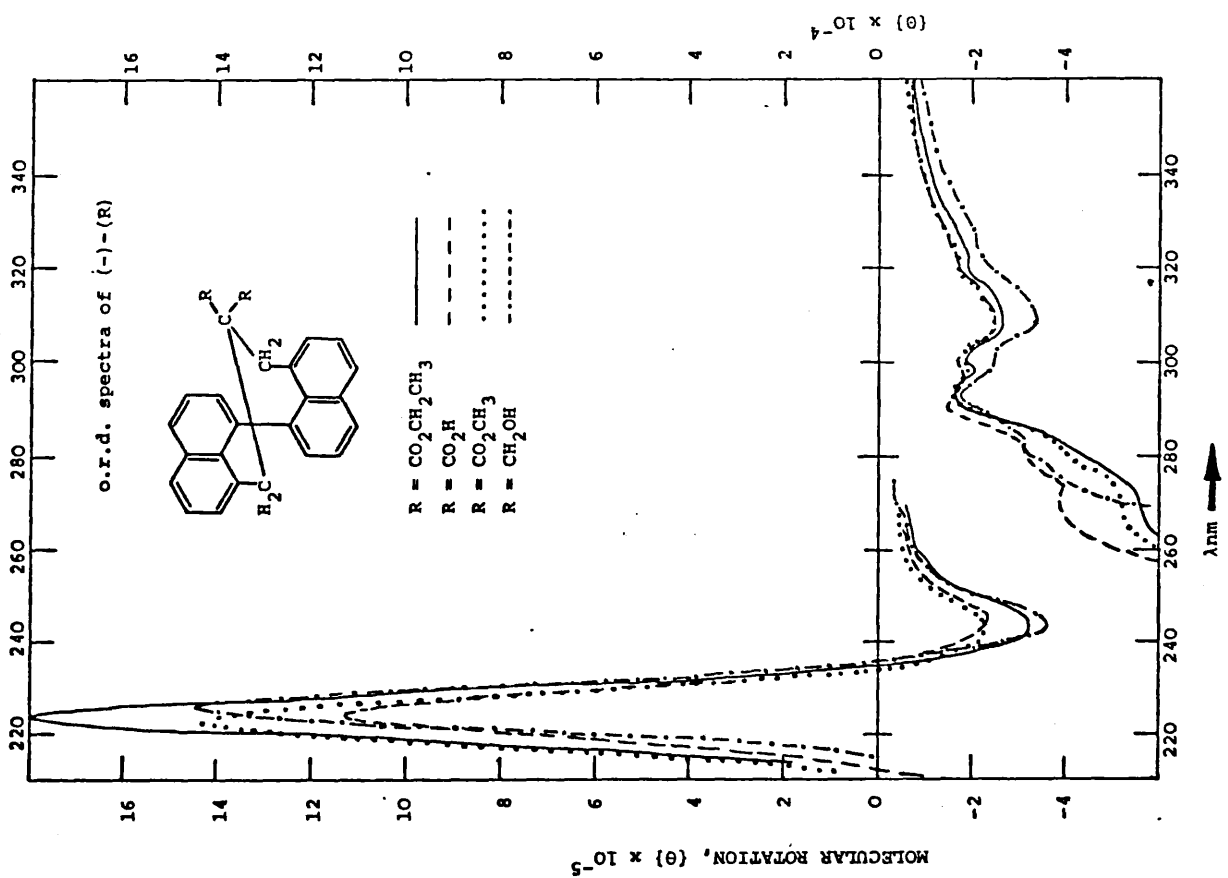


Figure 41

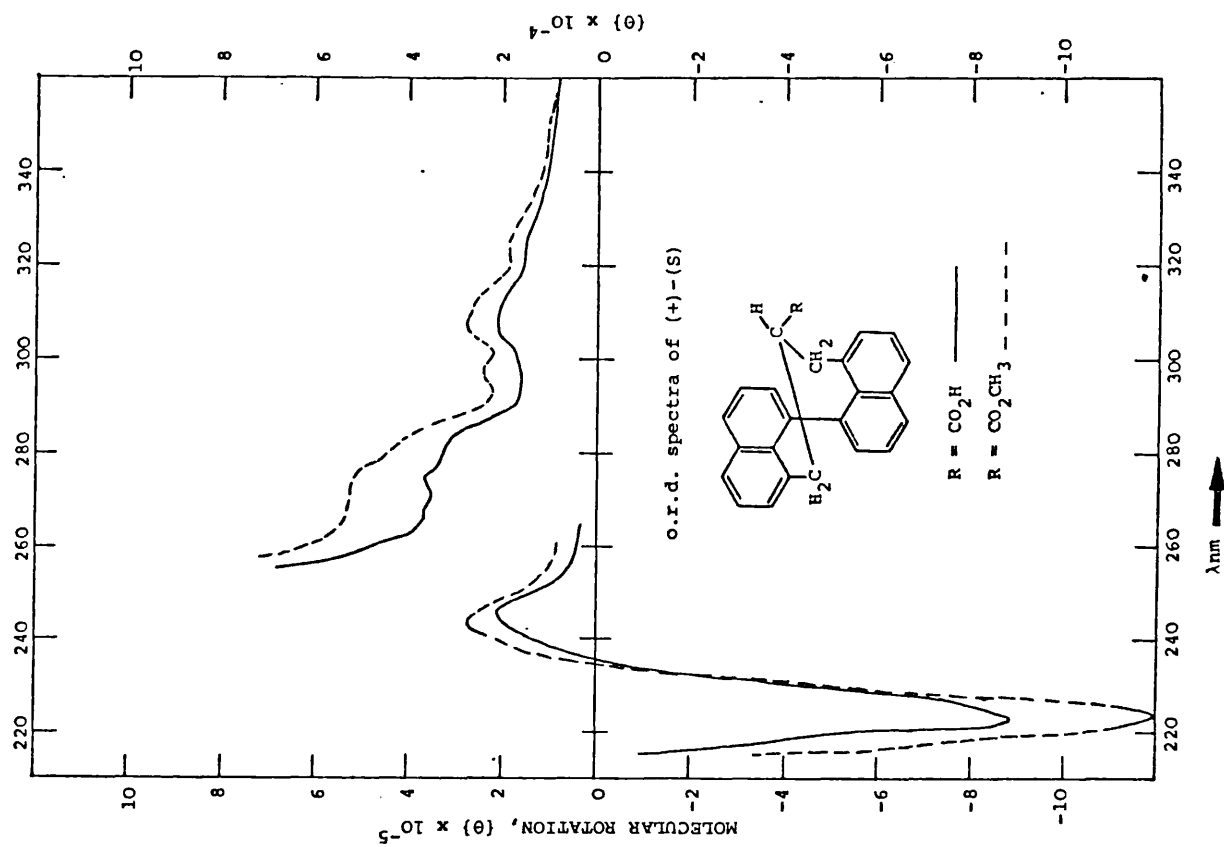


Figure 42

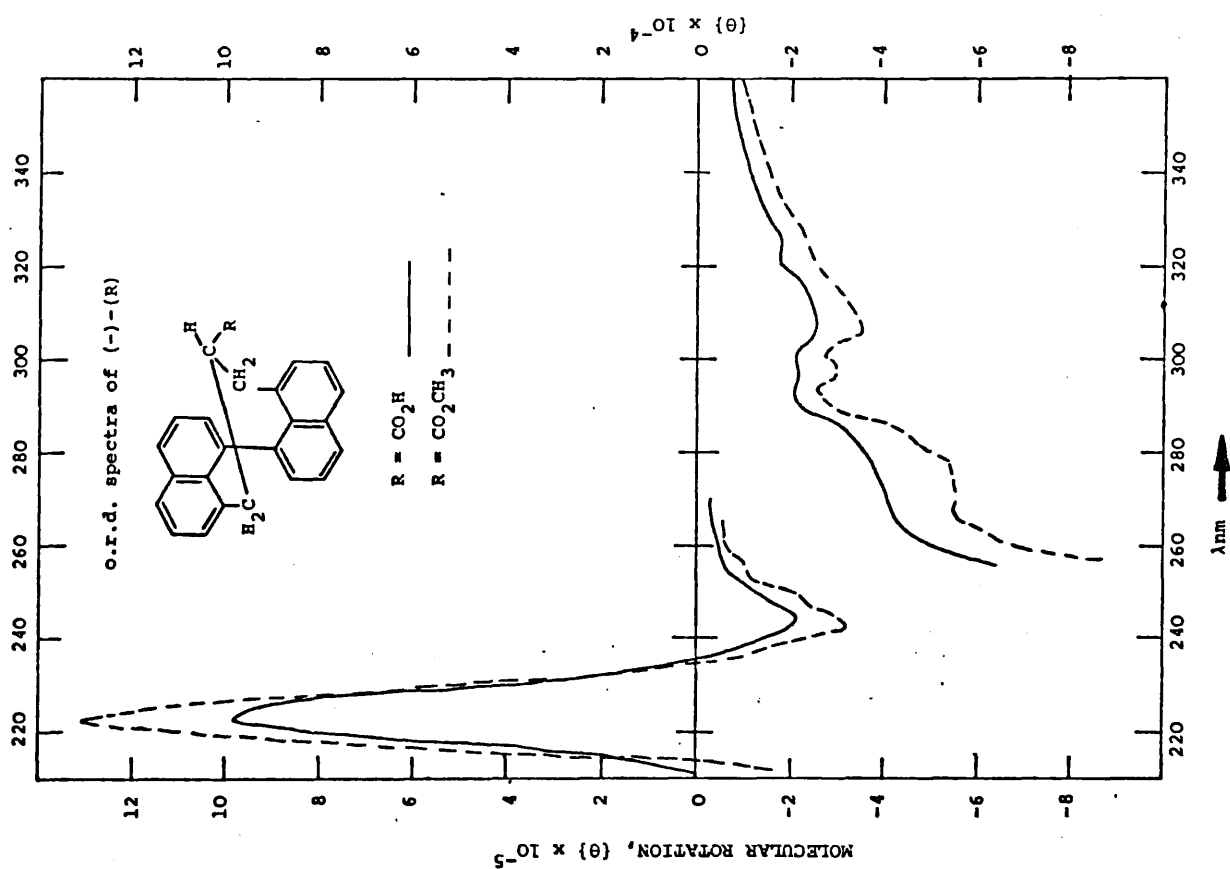


Figure 43

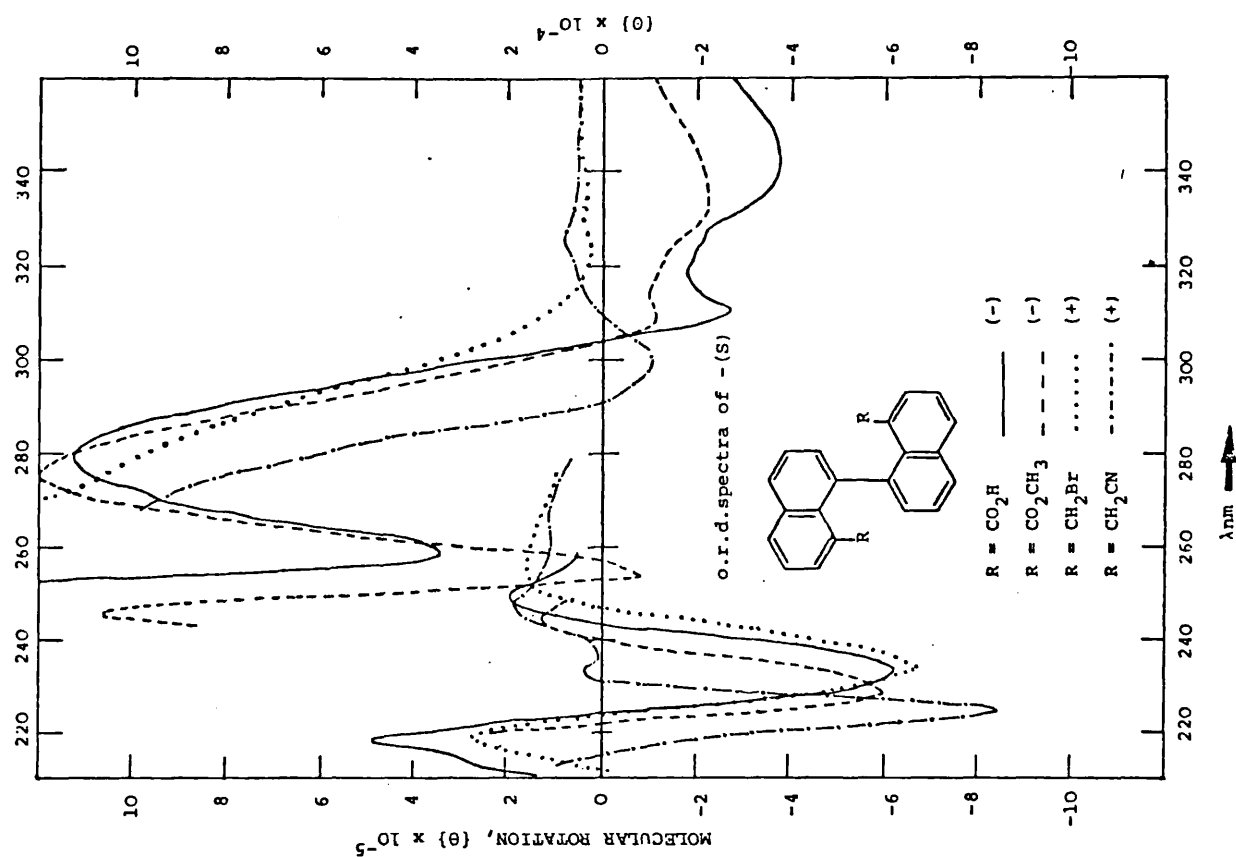


Figure 44

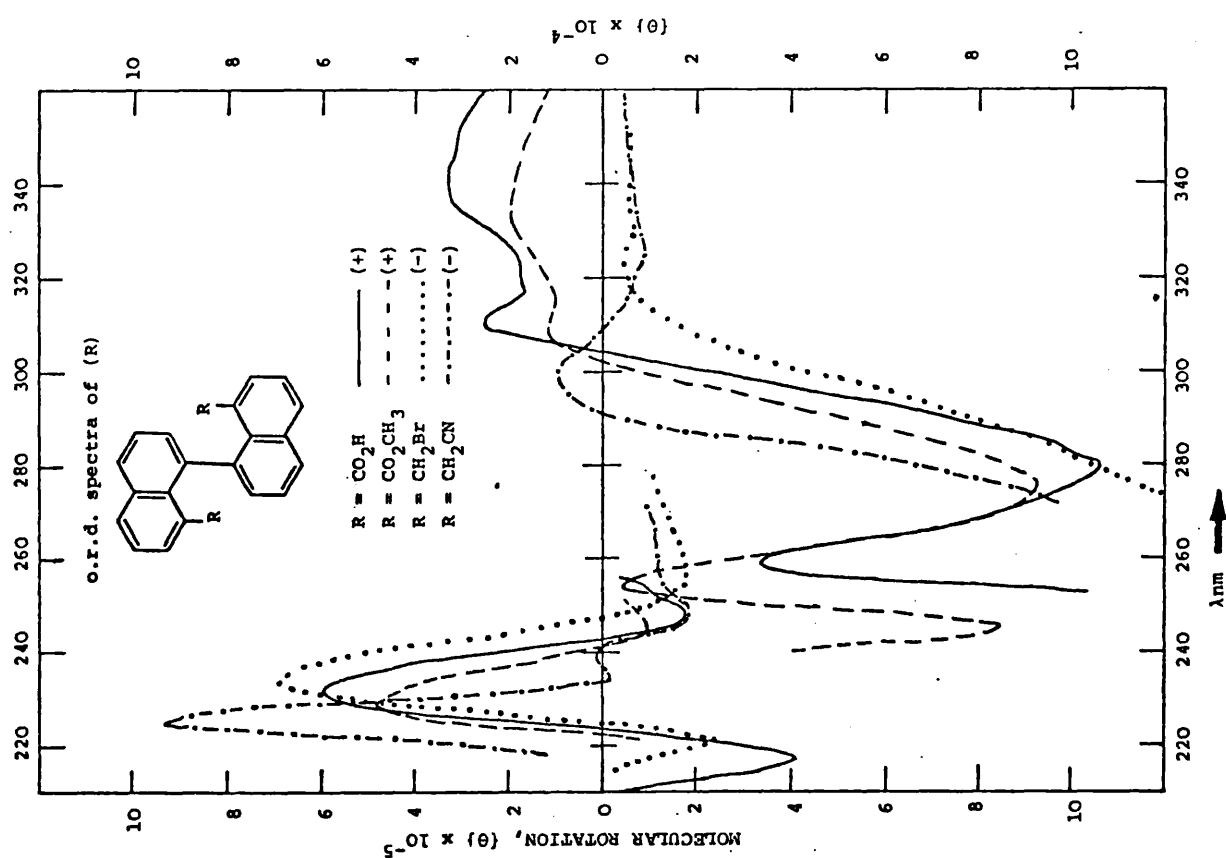


Figure 45

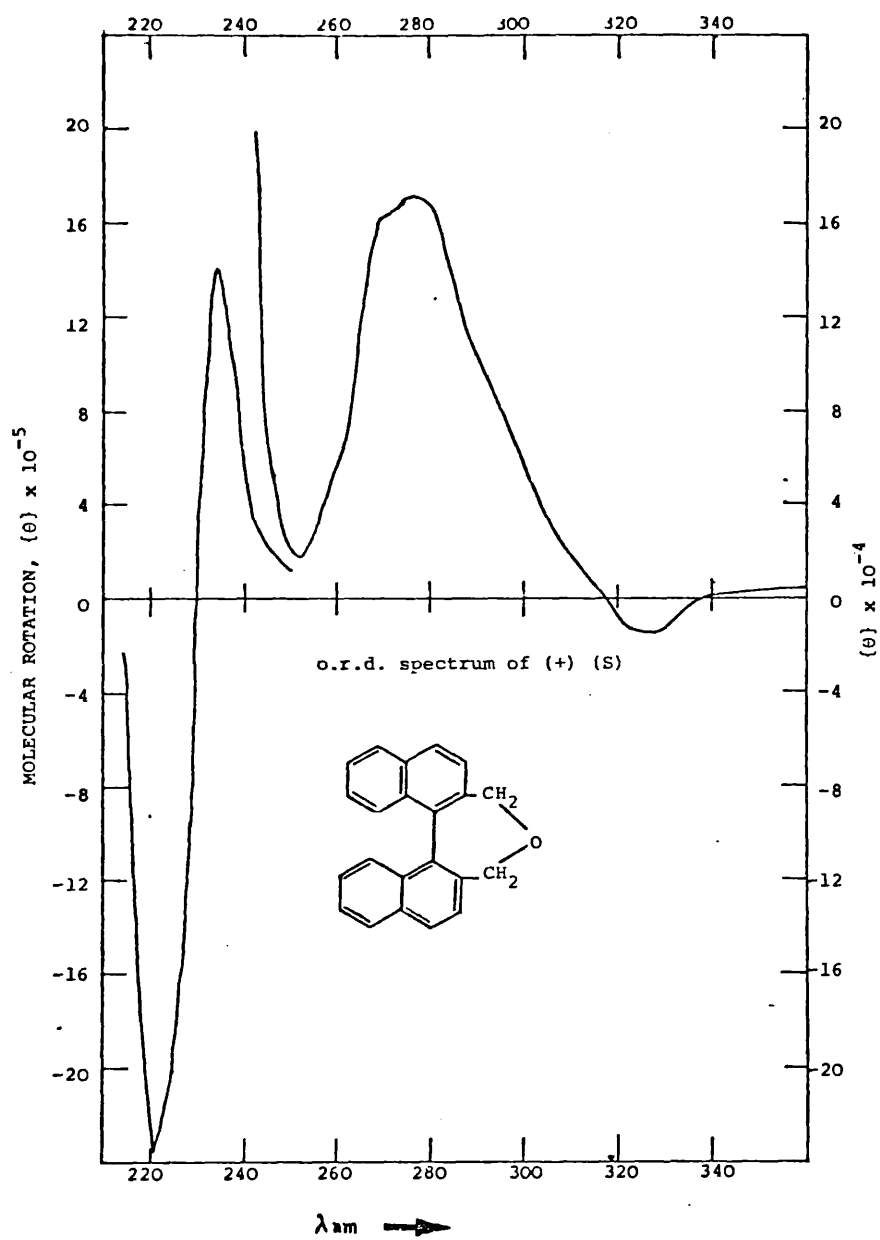


Figure 46

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# Esterification of sterically hindered carboxylic acids using trimethyl phosphate

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Dimethyl sulphate has long been known to be an effective reagent for the preparation of methyl esters of sterically hindered aromatic carboxylic acid groups<sup>1</sup>: a variety of methods which rely upon the formation of an alkyl-oxygen bond, as this one does, have recently been summarised.<sup>2,3</sup> A reagent which is similar in operation and less unpleasant to handle, trimethyl phosphate, is neglected in modern practical treatises and reviews and so we are prompted to record our experience of its use to esterify the sterically protected carboxylic acid groups of 1,1'-binaphthyl-8,8'-dicarboxylic acid. This acid and its esters present the additional difficulty<sup>4-6</sup> that treatment with mineral acid or with thionyl chloride leads to the formation of anthanthrone. Esters have been prepared through silver salts<sup>5</sup> or by the use of diazomethane,<sup>7</sup> both somewhat tedious methods.

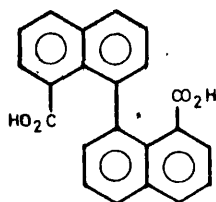
alkali; only one methyl group per molecule is operative for ester preparation, sodium dimethyl phosphate does not react further in these conditions): the mixture became warm spontaneously. Deposition of solid soon began and was completed on warming on a water bath: the excess of trimethyl phosphate was decomposed by shaking with further 10 per cent sodium hydroxide. The yield of ester, after purification, was 33.4g (>90 per cent), mp 157°C.<sup>7</sup>

The normal mode of reaction of trimethyl phosphate in alkaline solution is by fission of a phosphorus-oxygen bond,<sup>8</sup> i.e. attack of OH<sup>-</sup> at phosphorus: however, carbon-oxygen fission is known to take place in neutral solution. The latter mode of reaction appears to be dominant in the conditions here described, -COO<sup>-</sup> making a nucleophilic attack on the carbon of a methyl group rather than on phosphorus.

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In a typical preparation, the acid (34.2g, 0.1mole, 2equiv.) was dissolved in 100cm<sup>3</sup> of 10 per cent sodium hydroxide (2.5equiv.) and shaken with 70cm<sup>3</sup> of trimethyl phosphate (excess, to compensate for the competing reaction with

## Optically Active Nine-membered Rings incorporating the 8- and 8'-Positions of 1,1'-Binaphthyl. Part 2.<sup>1</sup> Oxygen, Sulphur, and Selenium Heterocycles. Synthesis, <sup>1</sup>H Nuclear Magnetic Resonance Spectra, and Absolute Configuration

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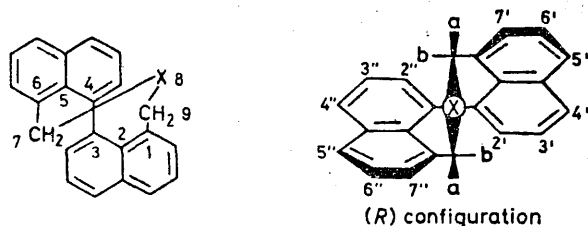
The preparation of 8-oxa-, 8-thia-, 8-selena-, and 8-dioxothia-8,9-dihydro-7*H*-cyclonona[1,2,3-*de*:4,5,6-*d'e'*]dinaphthalene, racemic and optically active, is described. Enantiomeric forms were synthesised from optically active precursors of known absolute configuration, thus the absolute configurations of the new compounds are established. <sup>1</sup>H N.m.r. spectra are discussed.

8,8'-BISBROMOMETHYL-1,1'-BINAPHTHYL reacts with sodiodiethyl malonate to form a nine-membered ring<sup>1</sup> in the same manner as 2,2'-bisbromomethylbiphenyl reacts to give a seven-membered ring. This indication that the geometry of the nucleophilic displacement which closes the ring is favourable for both the substrates has led us to explore further nine-membered ring closures using 8,8'-disubstituted 1,1'-binaphthyls, experimenting with methods previously found successful in the biphenyl seven-membered ring series<sup>2-8</sup> (nine-membered rings incorporating 2,2'-biphenyl are in quite a different category).<sup>7</sup>

2,2'-Bishydroxymethylbiphenyls react with dilute sulphuric acid<sup>2</sup> or with dilute hydrobromic acid<sup>3</sup> to give oxepins, and 2,2'-bisbromomethylbiphenyl forms an oxepin when a solution in aqueous acetone is treated with silver oxide;<sup>5</sup> these conditions failed to give cyclic products from 8,8'-disubstituted 1,1'-binaphthyls: however, 8,8'-bishydroxymethyl-1,1'-binaphthyl did follow the reaction mode of the biphenyl (and 2,2'-disubstituted 1,1'-binaphthyl) series<sup>5,6</sup> when boiled with toluene-*p*-sulphonic acid in benzene and gave the oxonin (1). Little adaptation of the methods used for seven-membered rings<sup>4-6</sup> was needed in order to prepare the nine-membered rings with sulphur (2) or selenium (3) as heteroatom. The dioxothia compound (4) was prepared from (2) by oxidation using hydrogen peroxide.

By starting with the optically active bisbromomethyl-1,1'-binaphthyls or bishydroxymethyl-1,1'-binaphthyls<sup>9</sup> it was possible to prepare both enantiomers of each of the new ring compounds. The substrates are optically labile, but are sufficiently resistant to racemisation to yield optically active cyclic products; the rings when formed are optically stable. The absolute configuration of the optically active precursors is already estab-

lished<sup>10</sup> by notionally stringing together various pieces of synthetic work with optically active compounds into pathways which lead to compounds whose absolute



- (*R*) configuration
- (1) X = O
  - (2) X = S
  - (3) X = Se
  - (4) X = SO<sub>2</sub>

configuration is known from asymmetric Meerwein-Ponndorf-Verley reduction<sup>11</sup> or from anomalous X-ray diffraction structure determination,<sup>12,13</sup> or by close correspondence of chiroptical properties within a set of related compounds.<sup>6,10,14,15</sup> In this way (+)-(1), (+)-(2), (+)-(3), and (+)-(4) are shown all to have the (*S*)-configuration.

<sup>1</sup>H N.m.r. Spectra.—Conformational mobility of these nine-membered rings is improbable.<sup>1</sup> The spectra at 100 MHz in deuteriochloroform show clearly defined groups of signals (Table I). Two well separated doublets [ $\Delta$ (in Hz)/*J* 9–11] affirm the chemical shift non-equivalence of the two pairs of diastereotopic<sup>16</sup> geminal protons H<sub>a</sub> and H<sub>b</sub> (in contrast with the spectra of singly-bridged, otherwise unsubstituted biphenyls which show a sharp singlet in the methylene region, except for the thiepin where there is a small separation,  $\Delta\delta$  0.22

<sup>1</sup> M. M. Harris and S. Singh, *J.C.S., Perkin II*, 1976, 793 is taken as Part I.

<sup>2</sup> D. M. Hall and E. E. Turner, *J. Chem. Soc.*, 1951, 3072.

<sup>3</sup> G. Wittig, P. Davis, and G. Koenig, *Chem. Ber.*, 1951, 84, 627.

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<sup>7</sup> K. Mislow, S. Hyden, and H. Schaefer, *J. Amer. Chem. Soc.*, 1962, 84, 1449.

<sup>8</sup> R. E. Buntrock and E. C. Taylor, *Chem. Rev.*, 1968, 68, 209.

<sup>9</sup> Y. Badar, A. S. Cooke, and M. M. Harris, *J. Chem. Soc.*, 1965, 1412.

<sup>10</sup> H. E. Harris, M. M. Harris, R. Z. Mazengo, and S. Singh, *J.C.S. Perkin II*, 1974, 1059.

<sup>11</sup> K. Mislow and F. A. McGinn, *J. Amer. Chem. Soc.*, 1958, 80, 6036.

<sup>12</sup> H. Akimoto, T. Shioiri, Y. Iitaka, and S. Yamada, *Tetrahedron Letters*, 1968, 97.

<sup>13</sup> S. Yamada and H. Akimoto, *Tetrahedron Letters*, 1968, 3967; H. Akimoto and S. Yamada, *Tetrahedron*, 1971, 6999.

<sup>14</sup> D. M. Hall, *Progr. Stereochem.*, 1969, 4, 1.

<sup>15</sup> W. Klyne and J. Buckingham, 'Atlas of Stereochemistry, Absolute Configuration of Organic Molecules,' Chapman and Hall, London, 1974.

<sup>16</sup> K. Mislow and M. Raban, *Topics Stereochem.*, 1967, 1, 1.

p.p.m. at 100 MHz;<sup>5</sup> six-membered ring *peri*-naphthalenes with similar bridges also show the methylene protons as singlets<sup>17</sup>). The aromatic protons in the new bridged binaphthyl compounds fall into three distinct groups in the numerical ratio 2 : 3 : 1.

its deshielding zone: they are brought nearer to this 'main plane' by the out-of-plane *peri*-distortion of 1,8-disubstituted naphthalenes.<sup>20-24</sup> The extent of the consequent deshielding is best appreciated by looking at H<sub>a</sub> (although H<sub>a</sub> is further deshielded by the nearby

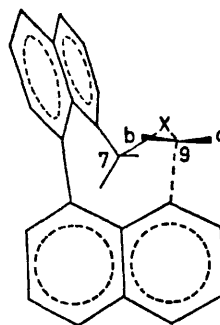
TABLE I

Chemical shifts ( $\delta$ ; 100 MHz; Me<sub>4</sub>Si; CDCl<sub>3</sub>) of aromatic and methylene protons of compounds (1)–(4)

Compound	Aromatic protons			Methylene protons				$\Delta$ (in Hz)/ J
	4',4'',5',5'' (4 H, m)	3',3'',6',6'',7',7'' (6 H, m)	2',2'' (2 H, m)	H <sub>a</sub> (2 H, d)	H <sub>b</sub> (2 H, d)	$\Delta\delta$	J/Hz	
1	7.96–7.77	7.57–7.35	6.94–6.85	5.47	4.27	1.20	-13	9.2
2	7.91–7.77	7.54–7.24	6.86–6.78	4.76	3.34	1.42	-15	9.5
3	7.86–7.77	7.50–7.19	6.86–6.77	4.88	3.49	1.39	-13	10.7
4	8.06–7.89	7.66–7.34	6.93–6.84	5.06	3.79	1.27	-14	9.1

**Methylene protons.** The differences  $\Delta\delta$  between the chemical shifts of H<sub>a</sub> and H<sub>b</sub> are all large in the compounds now studied: in the 6,6'-disubstituted 2,2'-bridged biphenyls there is a wide variation in  $\Delta\delta$  which in some cases is too small to observe.<sup>14</sup> The separate signals for H<sub>a</sub> and H<sub>b</sub> are shifted downfield by the electronegativity of the bridging atom, increasing in the order Se  $\approx$  S < SO<sub>2</sub> < O:<sup>18</sup> Table 2 gives examples of the effect of oxygen and sulphur in different but related chemical situations. In the carbocyclic analogues bridged by  $>C(CO_2Et)_2$ ,  $>C(CO_2Me)_2$ , and  $>C(CH_2OH)_2$ <sup>1</sup> the methylene protons all appear at higher field ( $\delta$  3.93 and 3.11;  $\delta$  3.98 and 3.09;  $\delta$  3.32 and 2.46 respectively). The H<sub>a</sub> and H<sub>b</sub> signals must be shifted equally by the electronegativity factor from the bridging atom in so far as it operates along bonds: the inequalities must spring from their different spatial relationships with the aromatic nuclei<sup>19</sup> and with groups (if any) attached to

7' or 7'' aromatic proton, the van der Waals deshielding effect); in H<sub>b</sub>, shielding by the opposing naphthalene



Proton shielding in compounds (1)–(4)

TABLE 2

Chemical Shifts ( $\delta$ ; Me<sub>4</sub>Si; CDCl<sub>3</sub>) of methylene protons in situations comparable to those of (1) and (2)

(2,6)		
O 3.52	4.55	4.34
S 2.57	3.61	3.44 3.35
(Ref. 25a)		(Ref. 5)

the bridge. Models indicate that both H<sub>a</sub> and H<sub>b</sub>, while not exactly in the 'main plane' of the aromatic system to which the methylene group is joined, are probably in

system has a compensating influence. For (1), in a rough approximation, working from scale models, H<sub>b</sub> lies 1.7 Å above the plane of the opposite naphthalene nucleus and 1.5 Å from the centre of its nearest benzene ring; the procedure of Johnson and Bovey<sup>19</sup> then leads to the conclusion that the long range shielding of H<sub>b</sub> could be expected to be at least 1  $\delta$  unit greater than that of H<sub>a</sub>, shifting the signal upfield.

The coupling constants  $J_{ab}$  are quoted in Table I with negative values by analogy with those in similar situations.<sup>25b</sup>

The geometry is not as precisely known as it is in the seven-membered ring biphenyl series where angles of torsion have been calculated, 44.1° in the oxepin and 56.6° in the thiopin.<sup>5,14</sup> It seems probable that in nine-membered carbocyclic rings incorporating the 8,8'-positions of 1,1'-binaphthyl the dihedral angle is near to 90°.<sup>1,26</sup> Bond lengths and angles quoted for the bridging

<sup>17</sup> A. Biezais-Zirmis and A. Fredga, *Acta Chem. Scand.*, 1971, **25**, 1171.

<sup>18</sup> E. S. Gould, 'Mechanism and Structure in Organic Chemistry,' Holt, Rinehart, and Winston, New York, 1969, p. 39.

<sup>19</sup> C. E. Johnson, jun. and F. A. Bovey, *J. Chem. Phys.*, 1958, **29**, 1012.

<sup>20</sup> M. M. Harris and A. S. Mellor, *Chem. and Ind.*, 1961, 557.

<sup>21</sup> A. S. Cooke and M. M. Harris, *J. Chem. Soc.*, 1963, 2365.

<sup>22</sup> V. Balasubramanian, *Chem. Rev.*, 1966, **66**, 587.

<sup>23</sup> J. E. Anderson, R. W. Frank, and W. L. Mandella, *J. Amer. Chem. Soc.*, 1972, **94**, 4608.

<sup>24</sup> R. E. Carter and T. Liljefors, *Tetrahedron*, 1976, 2915.

<sup>25</sup> L. M. Jackman and S. Sternhell, 'Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry,' Pergamon, Oxford, 2nd edn., 1969, (a) p. 199; (b) p. 276; (c) p. 205; (d) p. 306.

<sup>26</sup> N. L. Allinger, and M. A. Miller, *J. Amer. Chem. Soc.*, 1964, **86**, 2811.

atoms in cyclic situations are: C-O (in 1,4-dioxan)  $1.44 \pm 0.03$  Å, C- $\hat{O}$ -C  $112 \pm 5^\circ$ ; C-S (in 1,4-dithian) 1.80 Å, C- $\hat{S}$ -C  $100^\circ$ ; C-Se (in 1,4-diselenan)  $1.99 \pm 0.04$  Å, C- $\hat{Se}$ -C  $97.6 \pm 3.5^\circ$ ; C-SO<sub>2</sub> (various, mean taken) 1.75 Å, C- $\hat{SO}_2$ -C  $107^\circ$ .<sup>27</sup> If it is permissible to use these data for the nine-membered rings, the calculated distances between C-7 and -9 are (1) 2.3, (2) 2.84, (3) 3.0, and (4) 2.85 Å: if CH<sub>2</sub> is used as X in the bridge the figure is 2.5 Å. The angle of torsion cannot be precisely defined because the naphthalene rings are not planar, but it can be said that the angle subtended by the C-7—C-9 distances at the centre of the pivot bond are near to (1) 52, (2) 63, (3) 68, and (4) 63° and where X = CH<sub>2</sub>, 55°. The approximate nature of these calculations can hardly be over-stressed, but if the presumption of near orthogonality is correct for the carbocyclic rings then the oxepin (1) has a dihedral angle a little less than 90°, and the others a little greater; the selenium compound approaches, but does not pass, the critical angle of *ca.* 110° at which Mason<sup>28</sup> predicts that the sign of the shortwave circular dichroism would reverse. It is beyond the scope of this work to do more than to indicate the magnitude of these changes in the geometry of the molecules and to observe that the signals for H<sub>a</sub> and H<sub>b</sub> will be affected by them.

*Aromatic protons.* The chemical shifts assigned to 4',4'' and 5',5'' protons (Table 1) are in the region expected for  $\alpha$ -positions in naphthalene;<sup>25c</sup> the value for (4) is at somewhat lower field, an observation which can probably be linked with the inductive effect of the *p*-CH<sub>2</sub>SO<sub>2</sub> substituent; the upfield shift of aromatic protons *para*- to a methyl group has been attributed to an inductive effect of opposite direction.<sup>29</sup> Further evidence for this assignment of the lowest field signals comes from a comparison of the n.m.r. spectra of 2,2',-8,8',<sup>30</sup> and 4,4'-dimethyl-1,1'-binaphthyls.<sup>31</sup> In all three the aromatic protons fall into two groups; for the 2,2'- and 8,8'-disubstituted derivatives the integration ratio lower : higher field is 4 : 8, while for the 4,4'-disubstituted it is 2 : 10, showing that the 4,4'-protons when present are in the lower field group (these protons are labelled 4',4'' in the nine-membered ring series).

Two of the eight  $\beta$ -protons appear upfield from the other six which make up the central multiplet: their signal is a doublet of doublets, *J* 7—7.5 (*ortho*-coupling of two  $\beta$ -positions)<sup>25a</sup> and 2 Hz (*meta*-coupling). These we take to belong to 2',2'' protons rather than 7',7'' because they lie nearer in space to the opposite (shielding) naphthalene nucleus. Also, they are less influenced by the lanthanide shift reagent Pr(fod)<sub>3</sub> [tris(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octadionato)praesodymium].<sup>32</sup> When portions of Pr(fod)<sub>3</sub> are added stepwise to (1) in CDCl<sub>3</sub> solution there is a progressive

<sup>27</sup> 'Interatomic Distances,' ed. L. E. Sutton, The Chemical Society, London, 1958; 'Supplement, Special Publication, No. 18,' 1965.

<sup>28</sup> S. F. Mason, R. H. Seal, and D. R. Roberts, *Tetrahedron*, 1974, **30**, 1671.

<sup>29</sup> C. MacLean and E. L. Mackor, *Mol. Phys.*, 1960, **3**, 223.

upfield drift in the spectrum; a doublet separates out from the central multiplet and crosses over the doublet assigned to 2',2'' to  $\delta$  3.58; meanwhile the presumed 2',2'' signal moves from  $\delta$  6.96 to 4.72. The 7',7'' protons are nearer to the oxygen atom both through bonds and through space than are the 2',2'', and so it seems reasonable to consider that they are more sensitive to the shift reagent. While these shifts are taking place the lowest field signals (assigned to 4',4'' and 5',5'') move upfield by *ca.* 1  $\delta$  unit. The spectrum of the dioxothia-compound behaves in a similar way in the presence of Pr(fod)<sub>3</sub>.

U.v. and c.d. of these compounds are currently under investigation.

#### EXPERIMENTAL

8-Oxa-8,9-dihydro-7H-cyclonona[1,2,3-de:4,5,6-d'e']-dinaphthalene (1).—8,8'-Bishydroxymethyl-1,1'-binaphthyl<sup>9</sup> (10 g) and toluene-*p*-sulphonic acid monohydrate (0.8 g) in benzene (1 080 cm<sup>3</sup>) were boiled for 16 h under a Dean-Stark water trap. The solution was washed with 5% sodium carbonate solution and benzene was evaporated off: the residue was purified by chromatography on alumina, using ether-benzene as eluant, and crystallised from benzene to give the oxonin (1) (5.5 g, 58%), m.p. 169—170° [Found: C, 89.0; H, 5.4; O, 5.5%; *M*, 296.119 4 (mass spectrum). C<sub>22</sub>H<sub>16</sub>O requires C, 89.2; H, 5.4; O, 5.4%; *M*, 296.120 1],  $\nu_{\max}$  (Nujol) 1 071 and 1 098 cm<sup>-1</sup> (CH<sub>2</sub>-O-CH<sub>2</sub>, cyclic<sup>33</sup>), for <sup>1</sup>H n.m.r. spectrum at 100 MHz see Table 1. The signals [ $\delta$ ; tetramethylsilane as standard; 60 MHz; 0.021 1 g (7.1  $\times 10^{-5}$  mol) in 0.6 cm<sup>3</sup> CDCl<sub>3</sub>] moved progressively upfield with the addition of successive quantities of Pr(fod)<sub>3</sub>. After the addition of 0.449 g (6.16 mole per mole of oxonin) of the shift reagent the signals were at  $\delta$  7.34, 7.04, and 6.91 (6 H, 3',3'',4',4'',5',5''), 6.37, 6.24, and 6.11 (2 H, 6'6''), 4.78 and 4.66 (2 H, 2',2''), and 3.58 (2 H, 7',7''). During the addition the Me<sub>4</sub>Si signal shifted upfield; the  $\delta$  values reported are measured from the locked Me<sub>4</sub>Si signal at the start of the measurements.

*Optically Active* (1).—(a) (–)-Dimethyl 1,1'-binaphthyl-8,8'-dicarboxylate<sup>21</sup> ( $[\alpha]_{546} -305.7^\circ$ , chloroform) was reduced to (+)-diol<sup>9</sup> which failed to crystallise but treated as above gave (+)-(1), m.p. 196—197.5°,  $[\alpha]_{546} +1 119^\circ$  (*c* 0.117; *l* 1.0; chloroform) (Found: C, 89.0; H, 5.5; O, 5.5%); further fractions had  $[\alpha]_{546} +51$ , +660, +972, and +1 271°.

(b) A similar preparation from (+)-dimethyl 1,1'-dinaphthyl-8,8'-dicarboxylate gave (–)-(1), m.p. 190—192°,  $[\alpha]_{546} -1 100^\circ$  (*c* 0.106; *l* 1.0; chloroform); further fraction  $[\alpha]_{546} -1 215^\circ$ .

8-Thia-8,9-dihydro-7H-cyclonona[1,2,3-de:4,5,6-d'e']-dinaphthalene (2).—8,8'-Bisbromomethyl-1,1'-binaphthyl<sup>9</sup> (7.74 g, 0.017 6 mol) and sodium sulphide nonahydrate (12.72 g, 0.053 mol) in methanol (320 cm<sup>3</sup>) and water (16

<sup>30</sup> D. D. Fitts, M. Siegel, and K. Mislow, *J. Amer. Chem. Soc.*, 1958, **80**, 480; W. Dixon, M. M. Harris, and R. Z. Mazengo, *J. Chem. Soc.*, (B), 1971, 775; Y. Badar, A. S. Cooke, and M. M. Harris, *J. Chem. Soc.*, 1965, 142.

<sup>31</sup> E. Clar, V. Sanigök, and M. Zander, *J. Chem. Soc.*, 1957, 4616.

<sup>32</sup> R. E. Rondeau and R. E. Sievers, *J. Amer. Chem. Soc.*, 1971, **93**, 1522.

<sup>33</sup> L. J. Bellamy, 'The Infrared Spectra of Complex Molecules,' Methuen, London, 2nd edn., 1958.

cm<sup>3</sup>) were boiled with stirring for 24 h. The bulk of the methanol was distilled off, ice-water added to the residue, and the crude product boiled in ethanol with charcoal: the ethanol solution deposited 5.0 g (91%) of the *thionin* (2), m.p. 240–241° [Found: C, 84.8; H, 5.2; S, 10.1%; *M*, 312.0970 (mass spectrum). C<sub>22</sub>H<sub>16</sub>S requires C, 84.6; H, 5.1; S, 10.25%; *M*, 312.0972],  $\nu_{\max}$  (Nujol) 625, 658, and 705 cm<sup>-1</sup> (C–S stretch).<sup>33</sup>

*Optically Active* (2).—(a) Repetition of the above preparation using (+)-8,8'-bisbromomethyl-1,1'-binaphthyl<sup>9</sup> (2.5 g,  $[\alpha]_{546} +351^\circ$ ) gave (+)-(2) (1.5 g) m.p. 194–195°,  $[\alpha]_{546} +832^\circ$  (*c* 0.256; *l* 0.5; *NN*-dimethylformamide).

(b) (–)-8,8'-Bisbromomethyl-1,1'-binaphthyl (1.5 g;  $[\alpha]_{546} -396^\circ$ ) gave (–)-(2) (0.80 g), m.p. 190–191°;  $[\alpha]_{546} -855^\circ$  (*c* 0.059; *l* 1.0; *NN*-dimethylformamide). In another preparation bisbromomethyl compound of  $[\alpha]_{546} -353^\circ$  gave (–)-(2),  $[\alpha]_{546} -593^\circ$ .

8-Selena-8,9-dihydro-7H-cyclonona[1,2,3-de:4,5,6-d'e']-dinaphthalene (3).—Aqueous potassium selenide was prepared as follows. A cold solution of potassium hydroxide (2.6 g) in water (12 cm<sup>3</sup>) was saturated with hydrogen selenide gas under nitrogen and further potassium hydroxide added (2.6 g); 18 cm<sup>3</sup> of this solution (0.044 mol) was added to a suspension of 8,8'-bisbromomethyl-1,1'-binaphthyl (5.2 g, 0.012 mol) in methanol (320 cm<sup>3</sup>) under nitrogen and boiled for 24 h with stirring. The solid, remaining after most of the methanol was distilled off, was purified from dark red material on an alumina column with benzene–light petroleum (b.p. 40–60°) as eluant. The residue, after removing the solvent, was boiled with charcoal in light petroleum (b.p. 80–100°). *Compound* (3) crystallised from this solution (2.6 g, 61%), m.p. 240–241° [Found: C, 73.65; H, 4.6; Se, 21.8%; *M*, 360.0424 (mass spectrum). C<sub>22</sub>H<sub>16</sub>Se requires C, 73.5; H, 4.5; Se, 22.0%; *M*, 360.0417].

*Optically Active* (3).—(a) (+)-8,8'-Bisbromomethyl-1,1'-

binaphthyl (2.0 g;  $[\alpha]_{546} +420.5^\circ$ ) and potassium selenide solution (10 cm<sup>3</sup>) treated as above gave (+)-(3) (0.83 g), m.p. 232–234°,  $[\alpha]_{546} +472^\circ$  (*c* 0.25; *l* 0.5; *NN*-dimethylformamide).

(b) (–)-8,8'-Bisbromomethyl-1,1'-binaphthyl (1.5 g;  $[\alpha]_{546} -396^\circ$ ) and potassium selenide solution (8 ml) similarly treated gave (–)-(3) (0.65 g), m.p. 232–234°,  $[\alpha]_{546} -417^\circ$  (*c* 0.200; *l* 1.0; *NN*-dimethylformamide).

8-Dioxothia-8,9-dihydro-7H-cyclonona[1,2,3-de:4,5,6-d'e']-dinaphthalene (4).—The *thionin* (2) (2.5 g, 0.0072 mol) in acetic acid (25 cm<sup>3</sup>) was boiled with 30% hydrogen peroxide (20 cm<sup>3</sup>) for 90 min. The solution was cooled to –5 °C and kept below 1 °C overnight. Colourless *needles* of (4) separated and were recrystallised from ethanol to give 2.45 g (89%), m.p. 300–302° [Found: C, 76.7; H, 4.7; O, 9.3; S, 9.4%; *M*, 344.0874 (mass spectrum). C<sub>22</sub>H<sub>16</sub>O<sub>2</sub>S requires C, 76.7; H, 4.7; O, 9.3; S, 9.3%; *M*, 344.0871],  $\nu_{\max}$  (Nujol) 1150, 1310, and 1330 cm<sup>-1</sup> (>SO<sub>2</sub>).<sup>34</sup>

*Optically Active* (4).—(a) The (+)-*thionin* (2) (0.5 g;  $[\alpha]_{546} +832^\circ$ ) treated as above gave (+)-(4) (0.40 g), m.p. 277–280°,  $[\alpha]_{546} +438^\circ$  (*c* 0.244; *l* 0.5; *NN*-dimethylformamide).

(b) (–)-(2) (0.5 g;  $[\alpha]_{546} -593^\circ$ ) similarly treated gave (–)-(4) (0.45 g) m.p. 275–279°,  $[\alpha]_{546} -365^\circ$  (*c* 0.468; *l* 0.5; *NN*-dimethylformamide).

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<sup>34</sup> L. J. Bellamy and R. L. Williams, *J. Chem. Soc.*, 1957, 863.



THE CHIRALLY TWISTED NAPHTHALENE CHROMOPHORE IN 1,1'-BINAPHTHOLS

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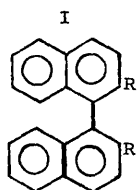
and (the late) D.L. Marshall

Polytechnic of North East London, West Ham, London E.15

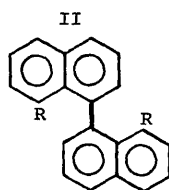
Evidence is here presented that comparison of the CD spectra of a large number of substituted 1,1'-binaphthyls of the same overall configuration reveals a band or bands whose sign can be related, albeit empirically, to the M or P twisted chirality of individual naphthalene units.

CD spectra of 1,1'-binaphthyls substituted in the 2 and 2'-positions<sup>1,2</sup> (I), in the 8 and 8'-positions<sup>2,4</sup> (II), with 2,2'-bridges<sup>1,2</sup> (III), and of 1,1'-binaphthyl itself<sup>3</sup> are already available. We now add the spectra of thirteen 1,1'-binaphthyls bridged across the 8,8'-positions (IV): syntheses of both enantiomers of these (except for IV e, f and g) are published<sup>5,6</sup>. The absolute configuration of all of the 1,1'-binaphthyls has been established by theoretical treatment of the 1,1'-binaphthyl chromophore<sup>2,7,8</sup>, by asymmetric reduction<sup>13</sup> by similarity of Cotton Effects<sup>1,4</sup>, by anomalous X-ray diffraction<sup>10</sup> and by chemical correlations<sup>5,6,7,9</sup>.

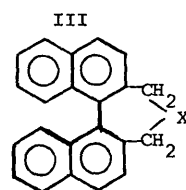
Naphthalene shows three major UV bands<sup>11</sup> in the normally accessible region,  $\lambda$  max 221, 286 and 312 nm. The main characteristics of the CD spectra of 1,1'-binaphthyls are a 'couplet' in the short-wave region, the shorter wavelength lobe being negative for (S) configuration (for conformations of dihedral angle up to  $\sim 110^\circ$ <sup>2,6,8</sup>): they all show chiral absorption near and beyond 280 nm: some of them in addition show a band  $\sim 260$  nm, interpreted as a conjugation or charge-transfer band<sup>1,2,8</sup>.



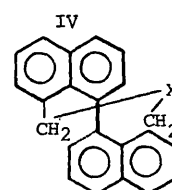
- (a) R=CH<sub>3</sub>
- (b) R=CO<sub>2</sub>H
- (c) R=CO<sub>2</sub>Me
- (d) R=CONH<sub>2</sub>
- (e) R=CH<sub>2</sub>Br
- (f) R=CH<sub>2</sub>OH



- (a) R=H
- (b) R=CH<sub>3</sub>
- (c) R=CO<sub>2</sub>H
- (d) R=CO<sub>2</sub>Me
- (e) R=CH<sub>2</sub>Br
- (f) R=CH<sub>2</sub>CN



- (a) X=O
- (b) X=C(CO<sub>2</sub>Et)<sub>2</sub>
- (c) X=CO
- (d) X=CHOH



- (a) X=O
- (b) X=SO<sub>2</sub>
- (c) X=S
- (d) X=Se
- (e) X=N<sup>+</sup>Et<sub>2</sub>
- (f) X=N<sup>+</sup> (cyclic)
- (g) X=N<sup>+</sup>(allyl)<sub>2</sub>
- (h) X=C(CO<sub>2</sub>H)<sub>2</sub>
- (i) X=C(CO<sub>2</sub>Me)<sub>2</sub>
- (j) X=C(CO<sub>2</sub>Et)<sub>2</sub>
- (k) X=C(CH<sub>2</sub>OH)<sub>2</sub>
- (l) X=CHCO<sub>2</sub>H
- (m) X=CHCO<sub>2</sub>Me

Circular Dichroism in the long wave region, Types I, II and III.

I.  $\lambda_{nm}$  ( $\epsilon \times 10^{-3}$ ) in dioxane, (S) configuration unless otherwise stated<sup>1</sup>.

(+) I(a)	(-) I(b)	(-) I(c)	(-) I(d)	(-) I(e)	(+) I(f) (R)
285(-16)	285(-53)	288(-71)	287(-42)	289(-46)	284(+41)
300(0)	290(-46)	305(-5)	310(0.0)	305(-6)	313(+5)

II.  $\lambda_{nm}$  ( $\epsilon \times 10^{-3}$ ) in 95% EtOH<sup>16</sup>, (S) configuration<sup>1,2,3</sup>.

(+) II(a)	(+) II(b)	(-) II(c)	(-) II(d)	(+) II(e)	(+) II(f)
280-9(-8)	287(-41)	300(-78)	296(-60)	299(-28)	284(-51)
305(-2)	307(+6)	313(-39)	315(-28)		312(+5)

III.  $\lambda_{nm}$  ( $\epsilon \times 10^{-3}$ ) in dioxane, (S) configuration unless otherwise stated<sup>1</sup>.

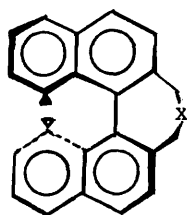
(+) III(a)	(+) III(b)	(+) III(c) (R) (in iso-octane)	(-) III(d) (R)
	285(-35)	287(+85)	291 inf. (+37)
305(-51)	305(-69)	293(+105), 300(+155)	305(+54)

All the above compounds show negative maxima in the 280-315 region, for (S) configuration, a generalisation first noted by Mislow in 1962<sup>1</sup>. In contrast, the Table below shows that (S) 8,8'-bridged compounds have oppositely signed bands in this region. Data for III(a), in 96% ethanol are appended.

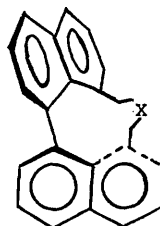
IV.  $\lambda_{nm}$  ( $\epsilon \times 10^3$ ) in 96%<sup>16</sup> EtOH. (S) Configuration. All (+)-.

IV(a)	219(-1020)	232(+1139)	270(+64)	291.5(+59)	302.5(+44)
(b)	222(-1591)	237(+1250)		296.5(+59)	302.5(+60)
(c)	228(-1316)	251(+368)		295.5(+55)	
(d)	232(-749)	256(+199)		297(+72)	
(e)	215(-1125)	228(+903)		294.5(+38)	
(f)	218(-1231)	232.5(+915)		297(+33.5)	
(g)	220(-1511)	234(+940)		298(+50)	
(h)	215-7(-563)	229(+667)		293(+15)	301.5(+15)
(i)	215.5(-492)	228(+1156)		295(+11)	302(+13)
(j)	219(-967)	230.5(+1003)		296.5(+21)	302(+21)
(k)	218(-549)	230(+947)		295(+16.5)	301(+16)
(l)	215(-447)	230(+862)		293(+26)	300.5(+23)
(m)	216(-823)	229(+1252)		294(+23)	302.5(+22)

III(a) 216(-2110) 228(+2340) 262,3(+151) 283 (sh)-51 300(-72)



(S) overall  
(P) naphthalene helix



(S) overall  
(M) naphthalene helix

Calculated CD spectra of 1,1'-binaphthyls<sup>2,8</sup> have been based on flat naphthalene units although this has long been thought to be an approximation<sup>12</sup>. When flexible models are used it is clear that (S) III-type have naphthalene units with (P) helicity while (S) IV-type have (M). Judging by the sense of the 'couplet' (and assuming that the dihedral angles are not greater than  $\sim 110^\circ$ <sup>2,6,8</sup>) (S) I and (S) II-types also have naphthalene units of (P) helicity, distortion being brought about by perinaphthalene forces. Consideration of these factors may help to elucidate some of the imbalance and other peculiarities of individual 'couplets'.

Chirally perturbed naphthalene units have been detected by CD spectra in polymers and in (+)-(S)-2-( $\alpha$ -naphthyl)butane<sup>14</sup> which resemble those of types I  $\rightarrow$  III.

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