Tetrahedron. Vol. 30, pp. 1671 to 1682. Pergamon Press 1974. Printed in Great Britain

OPTICAL ACTIVITY IN THE BIARYL SERIES

S. F. MASON* and R. H. SEAL
Chemistry Department, King's College, London WC2R 2LS

and

D. R. ROBERTS
Chemistry Department, Open University, Milton Keynes MK7 6AA

(*Received in the UK 5 February 1974*)

Abstract—The relationship between the CD spectra of the chiral biaryls and their stereochemical configuration, as a function of the dihedral angle between the molecular planes of the aromatic moieties, has been investigated for biphenyl, 1,1'-binaphthyl, 1,1'-bianthryl and 9,9'-bianthryl in the exciton approximation and, for the 1,1'-binaphthyls, in the π-SCF approximation. Both methods provide unambiguous assignments of absolute configuration except for biaryls with a critical dihedral angle of $\pi/2$ in those with effective D_2 chromophoric symmetry, or 100–110° in the case of the 1,1'-binaphthyls.

INTRODUCTION

Although Pasteur[1] (1850) instanced the irregular tetrahedron, as well as the helix, as examples of dissymmetric structures and both Butlerow[2] (1862) and Kekulé[3] (1867) envisaged a possible tetrahedral arrangement of the four valencies of a carbon atom, the stereochemical implications of the model remained largely unexplored until 1874. By that time some understanding of the 2-dimensional stereochemistry of benzene and its derivatives had been achieved, notably by the work of Körner[4] based upon Kekulé's principle that a decision between alternative geometric structures for a parent molecule is afforded by the number and type of isomers produced in its substitution reactions. In 1874 a comparable insight into the 3-dimensional structure of aliphatic molecules was attained independently by Le Bel[5a] and van't Hoff,[5b] although the stereochemical consequences of the new model were worked out the more fully by the latter. The work of Le Bel[5a] was largely confined to a rationalisation of existing knowledge. He showed that four different groups attached tetrahedrally to a carbon atom form a dissymmetric structure, nonsuperposable upon its mirror image, and that such molecules are optically-active or are resolvable into optical isomers. Van't Hoff not only rationalised in addition the geometric isomerism of maleic and fumaric acid but also predicted[6] the existence of dissymmetric molecules devoid of an asymmetric carbon atom.

The specific prediction[6] by van't Hoff of optical isomerism in an allene with two inequivalent groups bonded to both the 1- and the 3- carbon atom was verified only sixty years later,[7] although the resolution of 4-methylcyclo-hexylidene-acetic acid, another case exhibiting molecular dissymmetry without an asymmetric carbon atom, was achieved[8] in 1909. Meanwhile another type of molecular dissymmetry, that due to restricted rotation, had emerged from an investigation[9] of the folded "butterfly" structure for biphenyl, postulated by Kaufler[10] from such observations as the facile rearrangement of hydrazobenzene to benzidine. Kenner *et al.* resolved[9] into optical isomers 6,6'-dinitrodiphenic acid, which was thought to be a *trans*-isomer in the Kaufler structure, and subsequently showed[11] that the supposed corresponding *cis*-isomer was in fact 4,6'-dinitrodiphenic acid. The general field of atropisomerism thus opened was extensively studied by the schools of Adams[12] and of Turner,[13] and it was the field in which the determination of the absolute configuration of an organic molecule from its CD spectrum was first attempted.[14]

Coupled oscillator theory of biaryl optical activity

Kuhn and Rometsch[14] recorded the CD spectrum† of (+) - 2,2' - diamino - 6,6' - dimethyl

---

†The CD spectrum illustrated by Kuhn and Rometsch in Fig 14 of *Helv. Chim. Acta* **27**, 1080 (1944) has the same qualitative form as the present CD spectra, consisting of a negative and then a positive CD band at higher frequency, but the magnitude and frequencies of the CD bands are intermediate between the values recorded here for the neutral molecule and the dication (Fig 1). Although the text of Ref 14 refers to the CD spectrum as that of (+)-2,2'-diamino-6,6'-dimethyl biphenyl, and the molecular structure of that compound is illustrated in Fig 14 of the paper, the legend to Fig 14 states that the CD spectrum recorded refers to 2,2'-dichloro-6,6'-dimethyl benzidine in conc sulphuric acid.

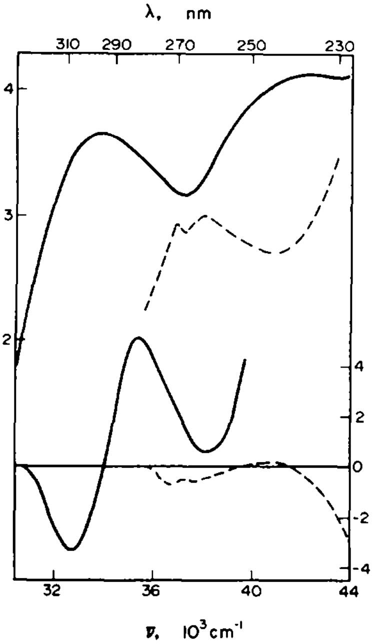


Fig 1. The absorption spectra (upper curves) and CD spectra (lower curves) of (*R*)-(+)-2,2′-diamino-6,6′-dimethyl biphenyl in ethanol (——) and in 1·0 M perchloric acid (- - -).

biphenyl (Fig 1) and the ORD curves of this and related chiral biphenyls, the results being interpreted in terms of a model in which it was assumed that the molecular planes of the two benzene rings have a mutually perpendicular orientation (Fig 2). Not a great deal was then known, in regard to the polarisation directions of electronic transitions in polyatomic molecules, but it was inferred[14] that the lowest-energy transition dipole of each *m*-toluidine chromophore in the molecule was oriented perpendicular to the long axis of the biphenyl and displaced from that axis towards the amino group (Fig 2). The displacement postulated was required to give non-zero Cotton effects for the assumed dihedral angle of $\pi/2$ between the planes of the benzene rings. Coulombic coupling between the lowest-energy transition dipole of the two *m*-toluidine chromophores gave a lower-frequency coupling-mode with the overall form of a left-handed helical charge displacement and a higher-frequency mode giving a right-handed helical displacement of charge for the (*S*)-configuration of the biphenyl (Fig 2). Since the observed lower-frequency negative CD band followed by a higher frequency positive CD band in the region of the lowest-energy absorption band (Fig 1) matched the theoretical model (Fig 2), Kuhn and Rometsch concluded[14] that (+)-2,2′-diamino-6,6′-dimethyl biphenyl has the (*S*)-configuration.

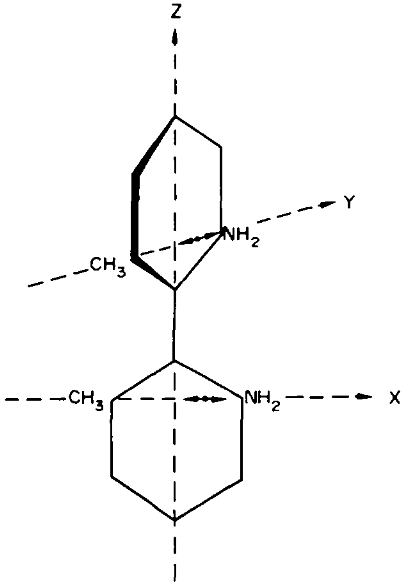


Fig 2. The classical coupled-oscillator model of W. Kuhn and R. Rometsch (*Helv. Chim. Acta* **28**, 1080 (1944)) for the lowest-energy bisignate CD bands of (+)-2,2′-diamino-6,6′-dimethyl biphenyl.

In fact this isomer has the (*R*)-configuration,[15] and the procedure of Kuhn and Rometsch, although sound in principle, rested upon insecure spectroscopic foundations. The polarisation-directions of the electronic transition moments of aromatic hydrocarbons and their derivatives were not well characterised before the 1950's. In the theory of spectroscopic moments Platt showed[16] that the lowest-energy singlet transition in a monosubstituted benzene, giving the α-band in the classification of Clar[17] or the ^1L_b band in that due to Platt,[18] is polarised in the molecular plane perpendicular to the two-fold rotational axis (Fig 3), and that the corresponding transition moment direction in polysubstituted derivatives is given by a simple vectorial addition scheme. The theory is supported by measurements of the single-crystal spectra of 1,4-dimethoxybenzene,[19] durene,[20] and other benzene derivatives.[21]

For the case of (*R*) - (+) - 2,2′ - diamino - 6,6′ - dimethyl biphenyl the theory indicates that the lowest-energy transition moment of each *m*-toluidine chromophore lies at approximately 30° to

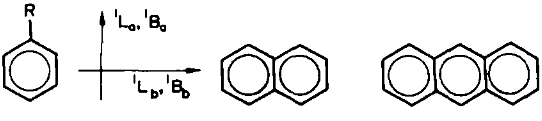


Fig 3. The polarisation directions of the ^1L_b, ^1L_a, ^1B_b, and ^1B_a transitions of a monosubstituted benzene, naphthalene and anthracene.

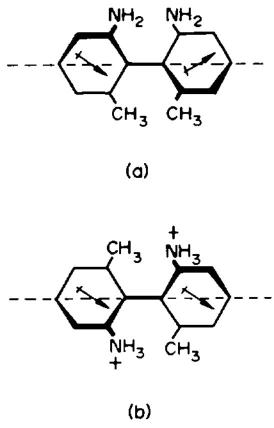


Fig 4. The lower-energy coupling mode of the ^1L_b benzenoid transition moments giving a negative rotational strength in (R)- (+)-2,2′-diamino-6,6′-dimethyl biphenyl for (a) the neutral molecule and (b) the dication.

the long-axis of the biphenyl in both the neutral molecule and the dication (Fig 4). In the neutral molecule the transition moments are largely equivalent to those of two aniline moieties (Fig 4a), the methyl substituents making only a small relative contribution, whereas the dication is equivalent to two toluene chromophores (Fig 4b), since the electronic spectrum of the m-toluidine cation is virtually identical with that of toluene. These moment directions indicate that (R) - 2,2′ - diamino - 6,6′ - dimethyl biphenyl and its dication are expected to give a negative CD band followed by a positive CD band to higher frequencies in the region of the ^1B_b absorption (Fig 4), as is observed for the (+)-isomer (Fig 1). These expectations hold for any sterically-accessible dihedral angle between the molecular planes of the two benzenoid chromophores in the (R)-configuration. Dipole-moment evidence suggests[12] a mean dihedral angle of some 67° for the neutral molecule in benzene solution, and the corresponding angle in the dication is probably larger than $\pi/2$ on account of the repulsion between the charged ammonium groups.

Exciton theory of biaryl optical activity

The classical coupled-oscillator theory of Kuhn[22] transforms with little change in essentials into the quantum-mechanically-based exciton theory of optical activity, as is exemplified above. In applications of the exciton theory to the chiral biaryls it is generally assumed that there is no electron delocalisation between the two bonded aromatic moieties, so that the approximation becomes progressively poorer as the dihedral angle between the two aromatic planes becomes larger or smaller than $\pi/2$. In the simplest approximation only Coulombic interactions between local electronic excitations of the same energy in the two aromatic chromophores are considered, and the corresponding moments are approximated as point transition electric dipoles located at the centre of each chromophore.

For chiral conformations of the biaryls (1–4) a non-zero rotational strength is generated, on the basis of these assumptions, only by local excitations polarised perpendicular to the internuclear bond direction, i.e. the ^1L_b or the ^1B_b transition (Fig 3). The moments of two such excitations, one in each nucleus of the biaryl, couple Coulombically in-phase and out-of-phase to give the respective rotational strengths, R_A and R_B, of equal magnitude and opposite sign (Fig 5). For the (R)-configuration

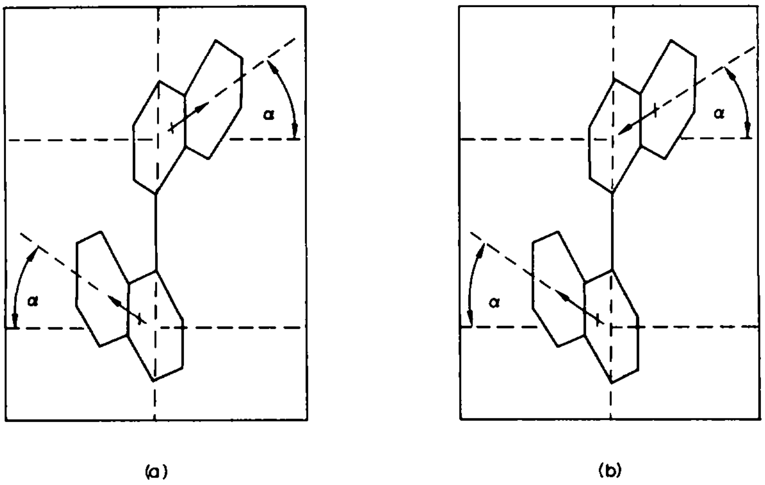


Fig 5. The orientation of the ^1B_b naphthalene transition moments in a 1,1′-binaphthyl with the (S)-configuration for (a) the A coupling mode and (b) the coupling mode. The angle α equals $(\pi-\theta)/2$ where θ is the dihedral angle.

of the biaryls (1–4) the magnitude and signs are,[23]

$$R_A = -R_B = (3/2)\pi\bar{\nu}_0 r_{cc} D_0 \sin\theta \qquad (1)$$

where ν_0 and D_0 are the wavenumber and the dipole strength, respectively, of the transition considered in the monomeric chromophore, r_{cc} is the aromatic carbon–carbon bond length, and θ is the dihedral angle between the aromatic molecular planes in the biaryl.

An observable CD absorption depends not only upon the rotational strengths (Eq 1) but also upon the energy separation between the biaryl transitions formed by the coupling modes of A and B symmetry (Fig 5) in the group C_2 of **2** and **3**. Although inexact, the symbols A and B are used here additionally to distinguish the analogous modes of **1** and **4a** which have general D_2 symmetry. The Coulombic potential between the monomer excitation moments, separated by the distance r_{ab} in the biaryl, has the same magnitude but an opposite sign for the two coupling modes so that the A and B biaryl transition energies are displaced symmetrically from the corresponding monomer frequency ν_0 by the exciton energy, V,

$$V = D_0 G_{ab}/(r_{ab})^3 \qquad (2)$$

where G_{ab} is the angular factor for the dipole–dipole potential. For a given biaryl the geometric factors in Eq (2) are functions of the dihedral angle, θ, and for the ^1L_b or ^1B_b monomer excitations of that biaryl the frequency-interval between the A and B biaryl coupling modes at the angle θ may be obtained from the general relations illustrated (Fig 6). These relations between $(\nu_A - \nu_B)$ and θ for 1–4 are normalised to unity at zero dihedral angle (Fig 6), and for a given excitation of a particular biaryl they are quantified by the appropriate frequency interval at zero angle $[2V(0°) = 2D_0/(3r_{cc})^3]$. Similarly the general relation between rotational strength and dihedral angle for the ^1L_b or ^1B_b monomer excitations of 1–4 are normalised to unity at $\theta = \pi/2$ (Fig 6), and R_A and R_B are quantified from the relation by the appropriate value at that angle (Eq 1).

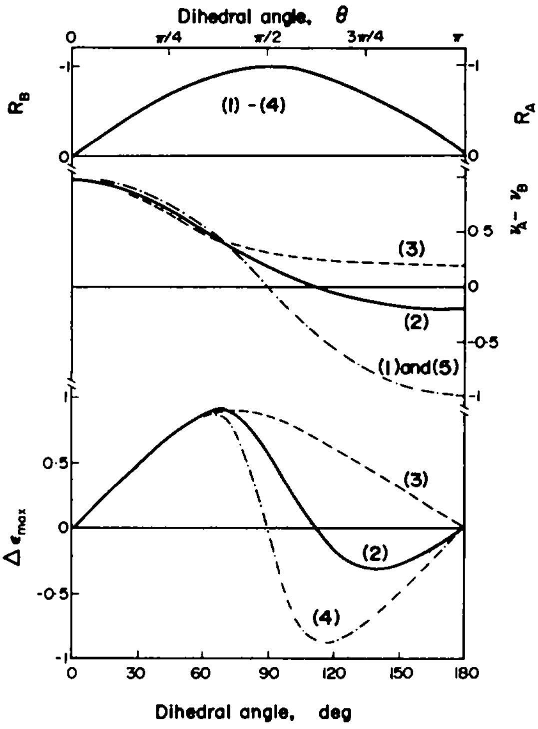
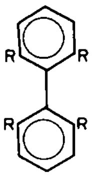


Fig 6. Relationships between the dihedral angle θ in a biaryl with the (*S*)-configuration and (top curve) the rotational strengths R_A and R_B (equation 1) resulting from the coupling of the ^1L_b or ^1B_b excitations in the two constituent aromatic chromophores of (1)–(4), and (middle curves) the frequency interval $(\nu_A - \nu_B)$ between the A and the B coupling modes (2V, Eq 2). The bottom curves give the relations between the dihedral angle θ and the observable maximum CD $\Delta\epsilon_{max}$ (Eq 3) for a half-band width σ of 1500 cm^{-1} resulting from the coupling of the ^1B_b naphthalene excitations in the 1,1′-binaphthyls (2) and of the ^1B_b anthracene excitations in the 1,1′-bianthryls (3) and 9,9′-bianthryls (4). The sign refrs to the lower-frequency CD band for the (*S*)-configuration.

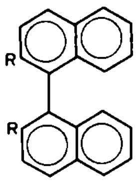
Although the magnitudes of the rotational strengths of **1** and **4a** have a maximum at the dihedral angle of $\pi/2$, these biaryls are achiral at that angle, having D_{2d} symmetry, since the frequency-interval $(\nu_A - \nu_B)$ goes to zero and the mutual cancellation of R_A and R_B (Eq 1) is complete (Fig 6). At other dihedral angles the mutual cancellation is only partial and the A and B coupling modes (Fig 5) give generally an observable CD absorption with smaller band maxima $(\Delta\epsilon_{max})$ than prescribed by Eq (1) and with a larger frequency separation than 2V (Eq 2). On the assumption that the rotational strengths R_A and R_B give rise to Gaussian bands centred on ν_A and $\nu_{B'}$ respectively, with a common half band width, σ, at $(e)^{-1/2}$ maximum height the circular dichroism at the frequency ν is given by,[24]

$$\Delta\epsilon(\nu) = \left[\frac{4N(2\pi)^{5/2}}{3hc\,10^3 \ln 10}\right] \sum_i \left(\frac{R_i\,\nu_i}{\sigma}\right) \exp\left[\frac{-(\nu-\nu_i)^2}{2\sigma^2}\right] \qquad (3)$$

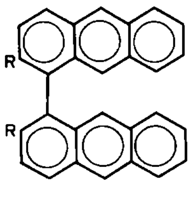
where the sum is taken over the A and B coupling modes of a given monomer excitation in a biaryl. For strong coupling, where $V > \sigma$, the observed CD is expected to consist of two oppositely signed bands with the full magnitude of each term in Eq (3) taken individually, and with a separation of 2V. When $\sigma > V$ the coupling is weak and the two oppositely signed CD bands have a separation of 2σ and they are weaker, $\Delta\epsilon_{max}$ being smaller than the corresponding strong-coupling value at the same dihedral angle by a factor of $[2V/(\sigma\sqrt{e})]$.



1



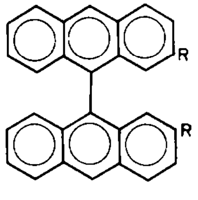
2



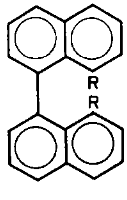
3 R=COOMe

a : R=H
b : R=NH_2
c : R=NH_3^+
d : R=COOH
e : R=COO^-

A



4

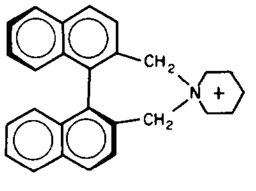


5

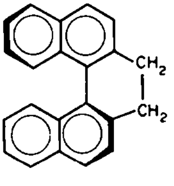
a : R=H
b : R=CooMe

a R=COOH
b : R=COO^-

B



6



7

C

The relations between the dihedral angle θ and the observable $\Delta\epsilon_{max}$ as a fraction of the value expected in the limiting strong-coupling case for an angle of $\pi/2$ are illustrated (Fig 6) for the coupling modes of the ^1B_b transition of naphthalene in **2** and the corresponding excitation of anthracene in **3** and **4**. The ^1B_b transition (Fig 3) lies at 39,000 cm^{-1} and has a dipole strength of 74 square Debye (D^2) in anthracene, and the analogous excitation in naphthalene has the frequency 45,500 cm^{-1} and the dipole strength of 49 D^2. These values give an exciton energy at zero dihedral angle [$V(0°)$] of 3300 cm^{-1} for **2** and 5500 cm^{-1} for **3** and **4** (Eq 2) and rotational strengths at the $\pi/2$ dihedral angle in Debye-magneton of ± 15 for **4** and ± 21 for **3** and **4** (Eq 1).

The non-bridged binaphthyls **2** and **5** are likely to have a dihedral angle in the 90 ± 20° range and so to fall into the weak-coupling region (Fig 6) with bisignate CD bands separated by the frequency-interval 2δ. The observed frequency separation between these CD bands in the 210–250 nm region of the spectra of **2** and **5** is 3000 ± 1000 cm^{-1} Figs 7–10), giving σ the approximate value of 1500 cm^{-1}. This empirical half-band width and the theoretical rotational strengths then give from Eq (3) $\Delta\epsilon_{max}$ in the limiting strong-coupling case for the $\pi/2$ dihedral angle the value of ± 750 $1.M^{-1}cm^{-1}$ for **2** and **5** and of ± 970 $1.M^{-1}$ for **3** and **4**, together with the relations between the observable $\Delta\epsilon_{max}$ and the dihedral angle θ illustrated (Fig 6), covering the weak, strong and general intermediate-coupling regions determined by the particular $V(\theta)$ values (Eq 2).

The observed CD spectra of the bianthryls (**3a** and **4b**) in the 260 nm region (Fig 11) suggest that the dihedral angle is near to $\pi/2$ in each case. The measured $\Delta\epsilon_{max}$ of the 1,1'-bianthryl (**3a**) have some 77% of the theoretically observable value, indicating a dihedral angle of approximately 100° (Fig 6), compared with the angle of 110° derived from the corresponding absorption spectrum.[23] The (*R*)-configuration of the (−)-isomer of **3a** deduced[23] from the CD spectrum (Fig 11) has been confirmed recently by an extensive chemical correlation,[25] covering members of the series **1**, **2** and **3**, with (+)-2,2'-dihydroxy-3,3'-bismethoxy-carbonyl-1,1'-binaphthyl, shown to have the (*R*)-configuration by the anomalous X-ray scattering method.[26]

In the case of (−)-2,2'-bismethoxycarbonyl-9,9'-bianthryl[27] (**4b**) the dihedral angle must be close to $\pi/2$ since the CD observed near 260 nm is weak and lacks the characteristic bisignate exciton form (Fig 11). A deviation of the mean dihedral from $\pi/2$ by 5° is expected (Fig 6) to give a bisignate CD absorption readily observable with current instrumentation, although a knowledge of the sense of that deviation would be required to obtain configurational information from the signs and frequency-order of the two CD bands.

The chiral 1,1'-binaphthyls (**2**) are expected to show, for the (*S*)-configuration, a positive CD band followed by a negative CD absorption at higher frequency in the 210–250 nm region for dihedral angles in the range 0–110° and the converse sequence of CD band signs from larger angles (Fig 6). The optical isomers of the 2,2-disubstituted-1,1'-binaphthyls (**2a–3e**) have established configurations[25] and their CD spectra indicate that in all cases the dihedral angle is smaller than the critical value where the bisignate CD absorption changes sign (Fig 7–9). The smallest $\Delta\epsilon_{max}$ values, indicating the

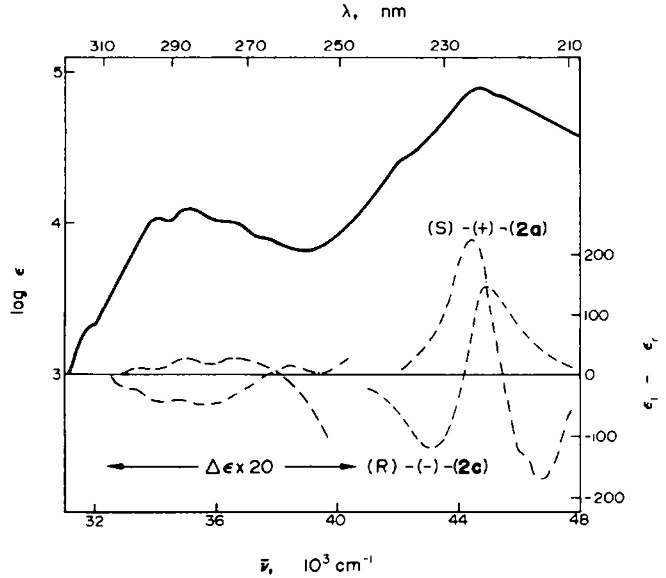


Fig 7. The absorption (——) and the CD spectrum (- - -) of the dication of (*R*)-(+)-2,2′-diamino-1,1′-binaphthyl in 2M perchloric acid solution, and the CD spectrum (-··-) of (*S*)-(+)-1,1′-binaphthyl in ethanol. The latter spectrum was kindly provided by Dr. M. M. Harris.[43]

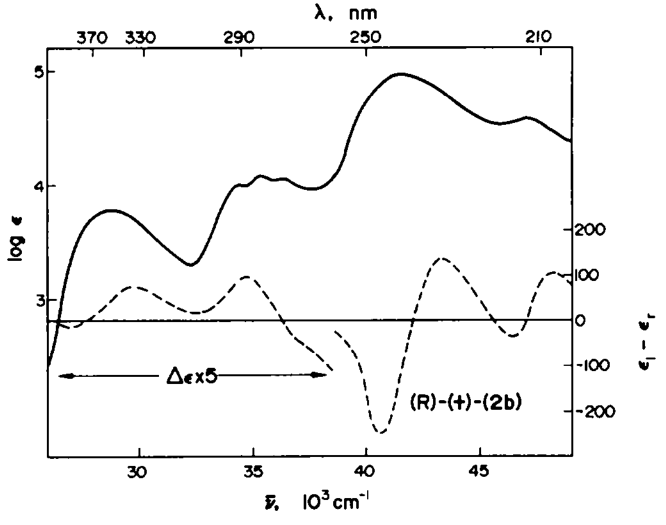


Fig 8. The absorption (upper curves) and CD spectrum (lower curve) of (*R*)-(+)-2,2′-diamino-1,1′-binaphthyl in ethanol.

largest dihedral angle (Fig 6), are observed in the case of (*S*) - (−) - 1,1′ - binaphthyl - 2,2′ - dicarboxylate **2e** (Fig 9). A larger dihedral angle is unlikely in 1,1′ - binaphthyl - 8,8′ - dicarboxylic acid (**5**) and thus the CD spectrum of the (−)-isomer and its dianion (Fig 10) indicate that this antipode has the (*S*)-configuration.[28] The observed $\Delta\epsilon_{max}$ of (−)-**5** in ethanol solution increase by 30% on reducing the temperature from 300 to 200 K (Fig 11), suggesting that the amplitude of the torsional mode about the 1,1′-bond is large at room temperature with one turning-point close to or possibly larger than critical dihedral angle where the bisignate exciton CD goes to zero (Fig 6). In the series of 1,1′-binaphthyls studied the largest $\Delta\epsilon_{max}$ values in the 210–250 nm region are observed for the 7-ring 2,2′-bridged derivative (+)-**6** (Fig 12), which was synthesised[29] from (−)-(**2d**) and thus has the (*S*)-configuration.

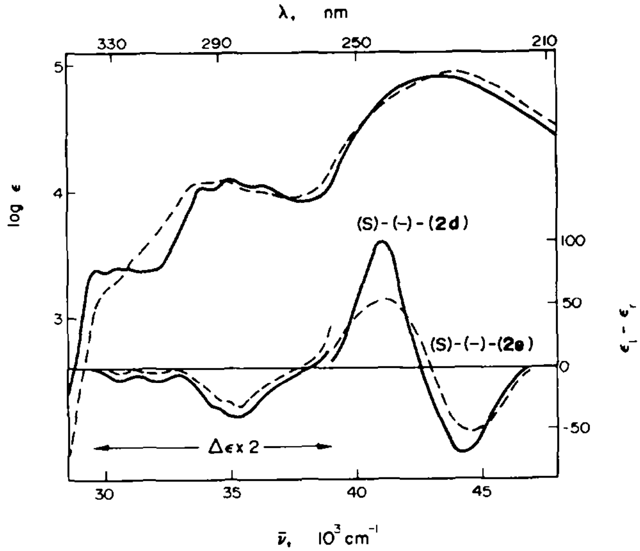


Fig 9. The absorption (upper curves) and CD spectra (lower curves) of (*S*)-(−)-1,1′-binaphthyl-2,2′-dicarboxylic acid in ethanol (——) and in M/100 sodium hydroxide (- - -).

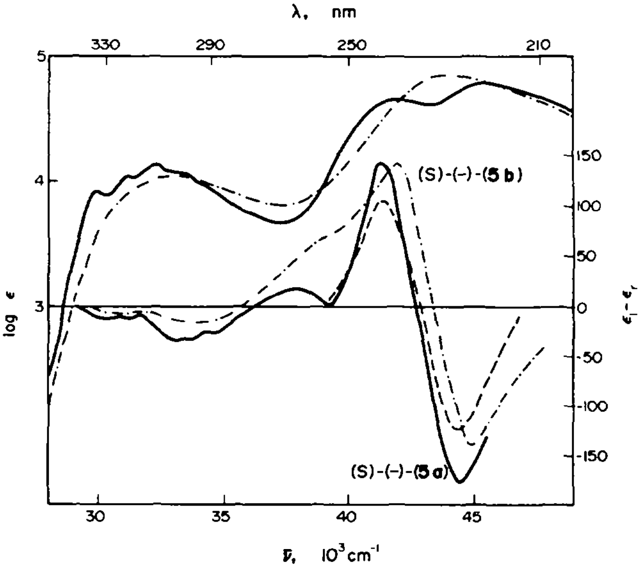


Fig 10. The absorption (upper curves) and CD spectra (lower curves) of (*S*)-(−)-1,1′-binaphthyl-8,8′-dicarboxylic acid in ethanol at 200 K (——) and at 300 K (- - -) and in M/100 sodium hydroxide (-·-·-).

The large $\Delta\epsilon_{max}$ measured suggest that the dihedral angle of **6** lies near to that of the maximum in the observable $\Delta\epsilon_{max}$ vs θ relation (70°) (Fig 6), although the exciton approximation is not likely to be good for such an angle. The approximation is worse, and cannot account for the qualitative features of the CD spectrum of the 6-ring 2,2′-bridged derivative[29], (*S*)-(+)-**7**, (Fig 13), with a substantially smaller dihedral angle.

The simplest form of the exciton theory, where only the Coulombic coupling of isoenergetic excitations in the two aromatic chrompohores is considered, does not account for the relatively weak long-wavelength CD absorption of the biaryls **2** and **3** Figs 7–13), due to the ^1L_a transition of the parent aromatic hydrocarbon (Fig 3). The local ^1L_a excitation of each aromatic chromophore in **2** or **3** is polarised parallel to the 1,1′-bond direction, and

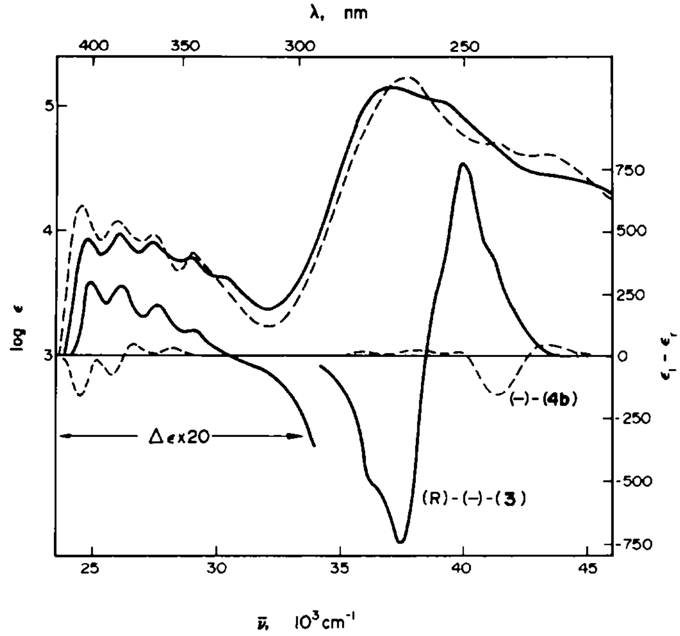


Fig 11. The absorption (upper curves) and CD spectra (lower curves) of (*R*)-(−)-2,2′-bismethoxycarbonyl-1,1′-bianthryl (——) and of (−)-2,2′-bismethoxycarbonyl-9,9′-bianthryl (- - -) in cyclohexane.

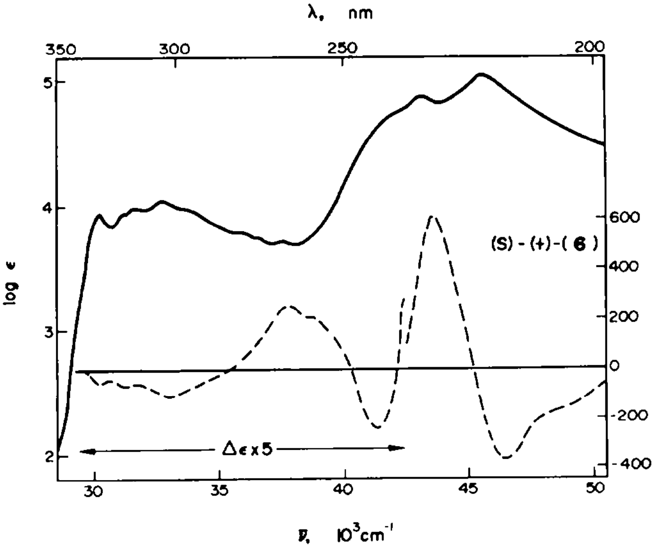


Fig 12. The absorption (upper curves) and CD spectrum (lower curve) of (*S*)-(+)-2,7-dihydrodinaptho [2′, 1′-3, 4]-4[1″,2″-5,6]-azepinium-1-spiro-1-piperidinium bromide (6) in water.

they couple to give solely a magnetic dipole moment in the A-mode and only an electric dipole moment in the B-mode.[23] Thus neither of these two coupling modes is optically-active in the degenerate exciton approximation. However the Coulombic potential between the ^1L_a moment of one aromatic chromophore and the ^1B_b moment of the other in **2** or **3** is non-zero (Fig 14) and coupling modes of the same symmetry derived from the ^1L_a and the ^1B_b monomer excitations are mixed by the potential.[30] For the biaryls (**2** and **3**) the mixing gives the perturbed A and B coupling modes of the two ^1L_a

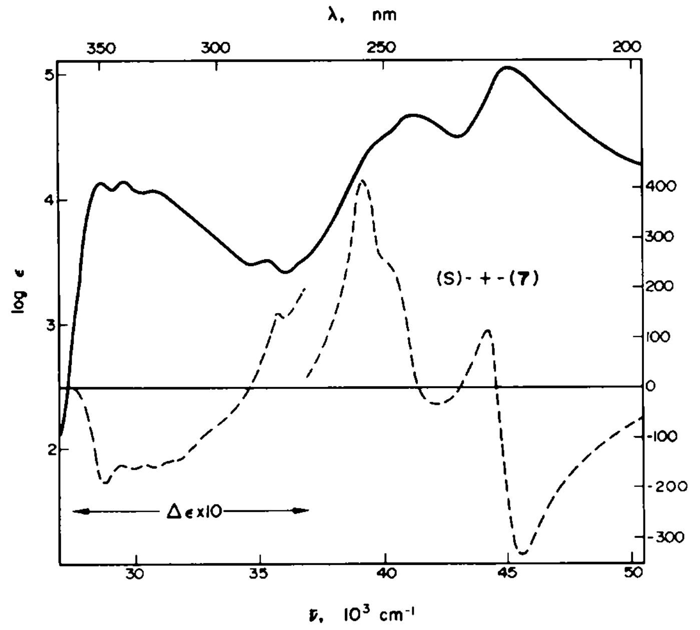


Fig 13. The absorption (upper curve) and CD spectrum (lower curve) of (*S*)-(+)-9,10-dihydrodibenzo [c, g] phenanthrene (7) in cyclohexane.

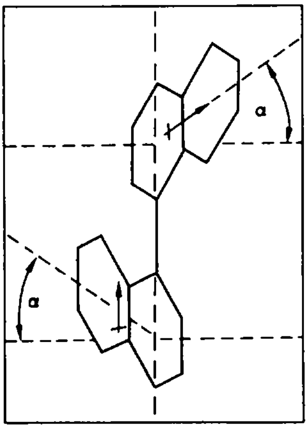


Fig 14. The coupling mode of a ^1L_a excitation in one naphthalene chromophore with the ^1B_b excitation in the other of a 1,1′-binaphthyl with the (*S*)-configuration generating a negative rotational strength in the ^1L_a absorption region.

excitations a rotational strength of the same sign. The sign is opposite to that of the lower-frequency CD band in the bisignate pair resulting from the coupling of the ^1B_b monomer-excitations, i.e., positive for the (*R*)-configuration and negative for the (*S*)-configuration of **3** over all dihedral angles, and of **2** over the 0–110° dihedral angle range. The rotational strength in the ^1L_a absorption region of **2** and **3** is estimated to be an order of magnitude smaller than that of the ^1B_b region. These expectations are generally observed (Figs 7–11).

π-SCF treatment of 1,1′-*binaphthyl optical activity*

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 π-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 π-electron delocalisation across the internuclear bond, both types becoming excitations of the biaryl chromophore as a whole.

The π-SCF treatment[31] provides the energies and dipole and rotational strengths of such biaryl excitations, and the calculated quantities transform through Eq (3) and its analogue[24] for dipole strengths into theoretical absorption and CD spectra to afford a more direct comparison with experiment. Representative theoretical spectra of the 1,1′-binaphthyl chromophore (**2a**) with (*S*)-configuration are presented (Fig 15) from the set computed for dihedral angles over the range 20° to 120° at 10° intervals, reduced to 5° for the critical range 90–110° where the bisignate CD absorption in the ^1B_b region is expected to change sign. The π-SCF spectra of 1,1′-binaphthyl (Fig 15) support the general expectations of the corresponding exciton treatment for dihedral angles in the 70°–120°

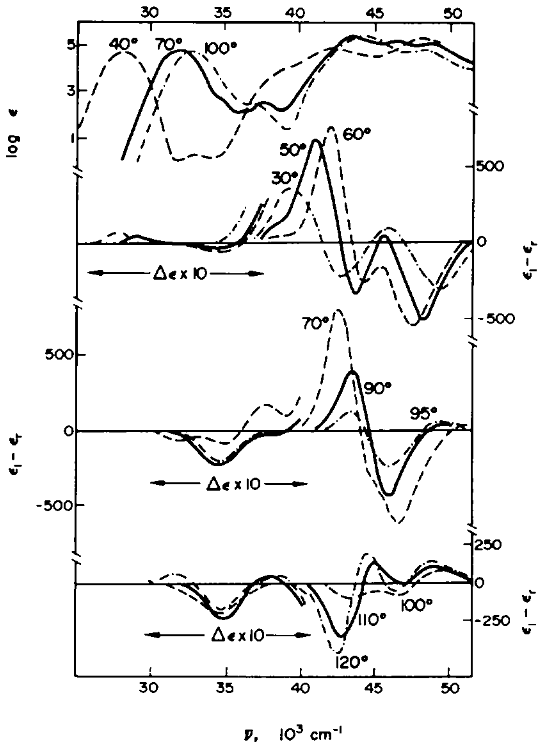


Fig 15. Theoretical π-SCF spectra of a 1,1′-binaphthyl with the (*S*)-configuration for dihedral angles in the range 30° to 120°. Top curves refer to absorption spectra and the lower curves to CD spectra.

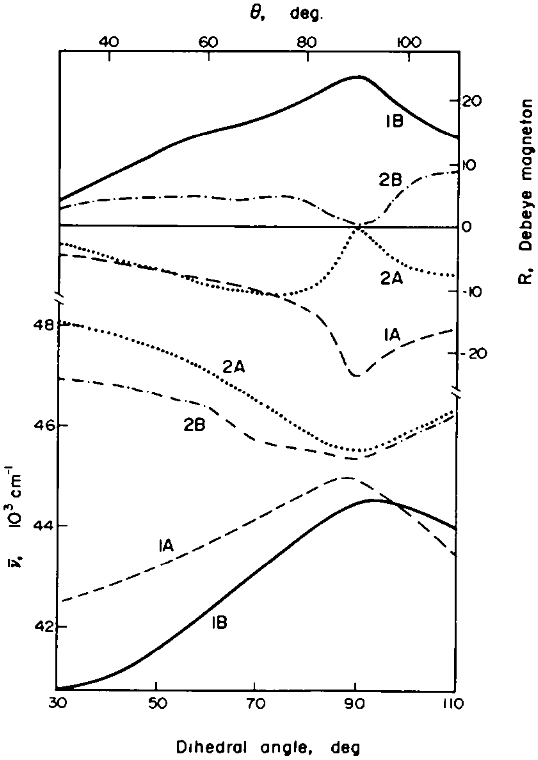


Fig. 16. The relationship between the dihedral angle θ of a 1,1′-binaphthyl with the (*S*)-configuration and the rotational strengths R and frequencies ν of the four principal electronic transitions in the π-SCF approximation giving absorption and CD in the ^1B_b region.

range (Fig 6), although they place the dihedral angle at which the bisignate CD vanishes at 100°, rather than 110°.

Over the 20°–50° dihedral angle range the π-SCF spectra reproduce the four strong CD bands of alternating sign observed in the 210–260 nm region of the spectrum (Fig 13) of (*S*)-(+)-9,10-dihydrodibenzo[c, g]phenanthrene (7). These four CD bands represent the rotational strengths of four principal excitations which correspond at the π/2 dihedral angle to the A and B coupling modes (Fig 5) of the local ^1B_b excitations in each naphthalene chromophore (1A and 1B, Fig 16) and to internuclear charge transfer excitations of A and B symmetry (2A and 2B, Fig 16). The latter are identified by trial calculations in which the electron repulsion integrals between centres on different naphthalene nuclei are set to zero. The charge-transfer excitations then move to a high energy, corresponding to the π-SCF energy difference between the π-orbitals connected by the transition. For even small deviations, 5°–10°, from the π/2 dihedral angle the charge-transfer and local excitations mix extensively, and the former acquire thereby an appreciable rotational strength. However, the frequency intervals between these four principal excitations remain small relative to the band width (Fig 16) and it is not until the dihedral angle is reduced to approximately 50° that four CD bands in the 200–260 nm region of the theoretical spectra become apparent (Fig 15).

From the π-SCF spectra of 1,1′-binaphthyl the largest observable $\Delta\epsilon_{max}$ is expected for a dihedral angle near to 70° (Fig 15) as in the corresponding exciton case (Fig 6). The largest observed $\Delta\epsilon_{max}$ is that of the 7-ring 2,2′ - bridged - 1,1′ - binaphthyl (*S*)-(+)-**6**, which has a CD spectrum (Fig 12) resembling that expected for a 70° dihedral angle (Fig 15) except for the additional negative CD band at 41,400 cm⁻¹. The CD spectrum of (−) - 1,1′ - binaphthyl - 8,8′ - dicarboxylic acid **5a** (Fig 10) also resembles qualitatively the theoretical spectrum for a 70° dihedral angle, but the observed $\Delta\epsilon_{max}$ in the 210–250 nm region are substantially smaller, suggesting a larger angle.

The major shortcoming of the π-SCF calculations is the failure to account for even the sign of the weak CD absorption in the ^1L_a region of the binaphthyl spectrum near 300 nm for dihedral angles smaller than 60°. The observed sign is negative for the (*S*)-configuration in all of the 1,1′-binaphthyls studied, as the non-degenerate exciton theory requires, whereas the π-SCF spectra exhibit a weak positive CD band in the ^1L_a region for this configuration at a dihedral angle of 50° or less (Fig 15). The sign and the magnitude of the CD band in the ^1L_a region is sensitive to the degree of configurational interaction considered in the π-SCF treatment. The recorded spectra (Fig 15) refer to interaction over 48 configurations, whereas the non-degenerate exciton treatment considers only 4 configurations, these being derived from the local ^1L_a and ^1B_b excitations of each of the two naphthalene chromophores.

π-SCF *calculations*

These followed the procedure previously described for the helicene series[32] with the following modifications, which were introduced to bring the systematically-high transition energies calculated earlier into closer agreement with experiment. Following Nishimoto[33] the electron affinity of the trigonal carbon atom was set to zero and the ionisation potential, and thus the one-centre electron repulsion integral, was taken as 9·6 eV. The two-centre electron repulsion integrals were estimated from the Nishimoto–Mataga relation.[34] A resonance integral, β, of $-2{\cdot}371$ eV from Pariser[35] was employed for all the carbon–carbon bonds of 1,1′-binaphthyl except the 1–1′ bond where the standard value was reduced through the cos θ relationship, θ being the dihedral angle.

The 1,1′-binaphthyl geometry assumed in the calculations consisted of two planar naphthalene residues with all carbon–carbon bonds 1·397 Å long, and all bond angles 120°, joined by a 1,1′-bond 1·48 Å long. One calculation was based upon the atomic coordinates of dibenzo[c, g]phenanthrene determined by X-ray crystallography[36] with the resonance integral of the 9–10 bond set to zero in order to simulate the π-electron structure of the 9,10-dihydro derivative (7) in a more realistic σ-bond framework with the carbon atoms of each naphthalene nucleus non-coplanar. The dibenzo[c, g]phenanthrene structure[36] has an average dihedral angle of 25° and the theoretical spectrum resulting from that structure with a zero $\beta_{9\cdot10}$ differed little from that afforded by the general idealised geometry for the same or a larger (30°) dihedral angle (Fig 15).

The excited states of 1,1′-binaphthyl were obtained by considering the interaction between the lowest 48 one-electron excited π-configurations constructed from the π-SCF orbitals. The dipole and rotational strengths of transitions to those excited states were calculated by the dipole-velocity procedure,[32] and were transformed into theoretical spectra through equation (3) and its analogue[24] for the extinction coefficient with a curve-plotter using the empirical half-band width relation.

$$\sigma_i = 0{\cdot}025\,\nu_i \qquad (4)$$

which was found to give theoretical spectra resembling more closely those observed than the relation previously employed.[24]

EXPERIMENTAL

We are indebted to the following colleagues for specimens of optical isomers used in this study. To Dr. D. M. Hall[29] for (*S*)-(−)-**2d**, (*S*)-(+)-**6**, and (*S*)-(+)-(**7**). To Dr. L. H. Schwartz and Dr. C. Koukotas[27] for (−)-**4b**, and to Professor G. M. Badger *et al.*[37] for the (*R*)-(−)-**3**.

(*R*)-(+)-2,2′-Diamino-6,6′-dimethyl biphenyl was prepared by the method of Carlin and Foltz[38] and resolved with (+)-tartaric acid as described by Meisenheimer and Höring.[39] (*R*)-(+)-**2b** was obtained by the method of Clemo and Dawson[40] and resolved with (+)-camphor-10-sulphonic acid as described by Kuhn and Goldfinger.[41] (−) - 1,1′ - Binaphthyl - 8,8′ - dicarboxylic acid **5** was resolved with brucine following Meisenheimer and Beisswenger.[42]

Absorption spectra were measured with a Cary 14 or 17 and CD spectra with a Jouan Dichrograph Model A or CD 185.

We thank Dr. M. M. Harris for the CD spectrum[43] of (*S*) - (+) - 1,1′ - binaphthyl and of 8,8-disubstituted derivatives[28] in advance of publication, Dr. G. W. Vane,[44] Dr. W. S. Brickell,[45] Dr. A. F. Drake, and Dr. G. Gottarelli for spectroscopic measurements, and the SRC for research support.

REFERENCES

[1] L. Pasteur, *C. R. Acad Sci. Paris*, **31**, 480 (1850); *Alembic Club Reprint* p. 30 f No. 14, Livingstone, Edinburgh (1948)

[2] A. M. Butlerow, *Zt, f. Chem.* **5**, 297 (1862)

[3] F. A. Kekulé, *Ibid.* **10**, 214 (1867)

[4] W. Körner, *Gazz. Chim. Ital*, **4**, 305 (1874)

[5a] J. A. Le Bel, *Bull. Soc. Chim. Fr* [2], **22**, 337 (1874); [b] J. H. van't Hoff. *Arch. Néerlandaises des Sciences Exactes et Naturelles*, **9**, 445 (1974); Eng. trans. in *Classics in the Theory of Chemical Combination*, (Edited by O. T. Benfey) Dover, New York (1963)

[6] J. H. van't Hoff, *Chemistry in Space*, trans. J. E. Marsh, Oxford (1891)

[7] P. Maitland and W. H. Mills, *Nature* **135**, 994 (1935); E. P. Kohler, J. T. Walker, and M. Tishler, *J. Am. Chem. Soc.* **57**, 1743 (1935)

[8] W. H. Perkin, W. J. Pope and O. Wallach, *J. Chem. Soc.* **95**, 1789 (1909)

[9] G. H. Christie and J. Kenner, *Ibid.* **121**, 614 (1922)

[10] F. Kaufler, *Dtsch. Chem. Ges.* **40**, 3250 (1907)

[11] G. H. Christie, A. Holderness and J. Kenner, *J. Chem. Soc.* 671 (1926)

[12] R. Adams and H. C. Yuan, *Chem. Rev.* **12**, 261 (1933); R. L. Shriner, R. Adams and C. S. Marvel, *Organic Chemistry* (2nd Edn Edited by H. Gilman) Chap 4. Wiley, New York (1943)

[13] E. E. Turner *Steric Effects in Conjugated Systems* (Edited by G. W. Gray) Chap 1 Butterworths, London (1958); E. E. Turner and M. M. Harris, *Organic Chemistry* Ch. 29 Longmans, Green London, (1952)

[14] W. Kuhn and R. Rometsch, *Helv. Chim. Acta* **27**, 1080 and 1346 (1944)

[15] K. Mislow, *Trans. N. Y. Acad. Sci.* **19**, 298 (1957); *Ann. N. Y. Acad. Sci.* **93**, 457 (1962)

[16] J. R. Platt, *J. Chem. Phys.* **19**, 263 (1951)

[17] E. Clar, *Polycyclic Hydrocarbons*, Academic Press, London (1964)

[18] J. R. Platt, *J. Chem. Phys.* **17**, 484 (1949)

[19] A. C. Albrecht and W. T. Simpson, *Ibid.* **23**, 1480 (1955)

[20] L. E. Lyons, *J. Chem. Soc.* 1347 (1958); O. Schnepp and D. S. McClure, *J. Chem. Phys.* **30**, 874 (1959)

[21] S. C. Sirkar and T. N. Misra, *Indian J. Phys.* **33**, 45 and 376 (1959); J. Tanka, *Bull. Chem. Soc. Japan* **16**, 833 (1963)

[22] W. Kuhn, *Trans. Faraday Soc.* **26**, 293 (1930)

[23] R. Grinter and S. F. Mason, *Ibid.* **60**, 274 (1964)

[24] W. S. Brickell, S. F. Mason and D. R. Roberts, *J. Chem. Soc.* (B), 691 (1971)

[25] H. Akimoto and S. Yamada, *Tetrahedron* **27**, 5999 (1971)

[26] H. Akimoto and Y. Iitaka, *Acta Cryst.* **B25**, 1491 (1969)

[27] C. Koukotas and L. H. Schwartz, *J. Chem. Soc. Chem. Comm.* 1400 (1969)

[28] H. E. Harris, M. M. Harris, R. Z. Mazengo and S. Singh, *J. Chem. Soc.* Perkin I, forthcoming

[29] D. M. Hall and E. E. Turner, *Ibid.* 1242 (1955)

[30] G. Gottarelli, S. F. Mason and G. Torre, *Ibid.* (B), 1349 (1970)

[31] J. A. Pople, *Trans. Faraday Soc.* **49**, 1375 (1953); R. Pariser and R. G. Parr, *J. Chem. Phys.* **21**, 466 (1953)

[32] A. Brown, C. M. Kemp and S. F. Mason, *Molec. Phys.* **20**, 787 (1971); *J. Chem. Soc.* (A), 751 (1971); W. S. Brickell, A. Brown, C. M. Kemp and S. F. Mason, *Ibid.* (A), 756 (1971)

[33] K. Nishimoto, *Theor. Chim. Acta* **5**, 74 (1966)

[34] K. Nishimoto and N. Mataga, *Z. Physik. Chem. Frankfurt* **12**, 335 (1957)

[35] R. Pariser, *J. Chem. Phys.* **24**, 250 (1956)

[36] A. O. McIntosh, J. Montheath Robertson and V. Vand, *J. Chem. Soc.* 1661 (1954)

[37] G. M. Badger, R. J. Drewer and G. E. Lewis, *Ibid.* 4268 (1962)

[38] R. B. Carlin and G. E. Foltz, *J. Am. Chem. Soc.* **78**, 1997 (1956)

[39] J. Meisenheimer and M. Höring, *Ber. Dtsch. Chem. Ges.* **60B**, 1425 (1927)

[40] G. R. Clemo and E. C. Dawson, *J. Chem. Soc.* 1114 (1939)

[41] R. Kuhn and P. Goldfinger, *Liebigs Ann.* **470**, 183 (1929)

[42] J. Meisenheimer and O. Beisswenger, *Ber. Dtsch. Chem. Ges.* **65**, 32 (1932)

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

[44] G. W. Vane, Thesis, Exeter (1965)

[45] W. S. Brickell, Thesis, University of East Anglia (1970