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THE ABSORPTION AND CIRCULAR DICHROISM SPECTRA AND THE ABSOLUTE CONFIGURATION OF (+)-1-FLUORO-12-METHYLBENZO[c] PHENANTHRENE

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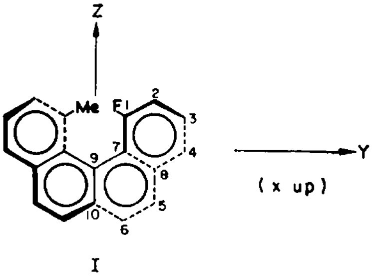
Abstract—The circular dichroism and electronic absorption spectra of (+)-1-fluoro-12-methylbenzo[c]phenanthrene are reported. The results are compared with the theoretical rotational and dipole strengths of the lower-energy $\pi \rightarrow \pi^*$ transitions in the optical isomers of the overcrowded, non-coplanar, benzo[c]phenanthrene molecule. The comparison indicates that (+)-1-fluoro-12-methylbenzo[c]phenanthrene has the stereochemical form of a segment of a right-handed helix (I), viewed in the direction perpendicular to the mean molecular plane.

The aromatic nuclei of benzo[c]phenanthrene are non-coplanar,[1,2] and several derivatives of the hydrocarbon have been resolved into their optical isomers by Newman *et al.*[3-5] The present work reports the electronic absorption and CD spectra of one of these isomers, (+)-1-fluoro-12-methylbenzo[c]phenanthrene[5] (I), the spectra (Fig. 1) being measured with the object of determining the absolute configuration of the isomer non-empirically from the one-electron theory of optical rotatory power.[6,7]



I

The electronic origin of the first three absorption bands of aromatic hydrocarbons, the α-, p-, and β-bands in the nomenclature of Clar,[8] or the ${}^1L_b$, ${}^1L_a$, and ${}^1B_a$ bands in

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[1] F. H. Herbstein and G. M. J. Schmidt, *J. Chem. Soc.* 3302 (1954).
[2] F. L. Hirschfeld, S. Sandler and G. M. J. Schmidt, *J. Chem. Soc.* 2108 (1963).
[3] M. S. Newman and W. B. Wheatley, *J. Amer. Chem. Soc.* **70,** 1913 (1948).
[4] M. S. Newman and R. M. Wise, *J. Amer. Chem. Soc.* **78,** 450 (1956).
[5] M. S. Newman, R. G. Mentzer and G. Slomp, *J. Amer. Chem. Soc.* **85,** 4018 (1963).
[6] E. U. Condon, W. Altar and H. Eyring, *J. Chem. Phys.* **5,** 753 (1937).
[7] A. Moscowitz, *Tetrahedron* **13,** 48 (1961); Thesis, Harvard (1957).
[8] E. Clar, *Chem. Ber.* **69,** 607 (1936); *Polycyclic Hydrocarbons.* Springer, Academic Press, London (1964).

that of Platt,[9] is well-understood.[9,10] The p-band, with a moderate intensity, is due to the promotion of an electron from the highest occupied π-orbital ψ_m to the lowest unoccupied π-orbital ψ_{m+1}, and the low-intensity α-band and the high-intensity β-band, which in general appear at lower and higher frequencies, respectively, than the p-band, arise from the out-of-phase and the in-phase combinations, respectively, of the degenerate single-configuration transitions, $\psi_m \rightarrow \psi_{m+2}$ and $\psi_{m-1} \rightarrow \psi_{m+1}$.

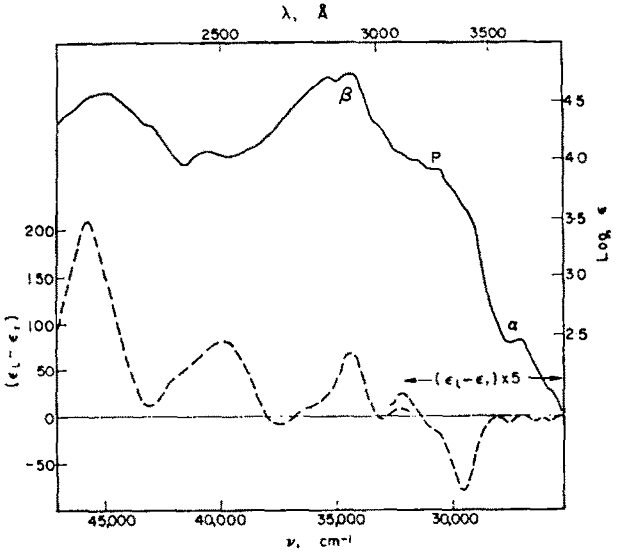

FIG. 1. The CD — — — — and the absorption spectrum ———— of (+)-1-fluoro-12-methylbenzo[c]phenanthrene in cyclohexane solution.

Benzo[c]phenanthrene has nine bonding and nine antibonding π-orbitals so that the p-band, for example, is due to the transition $\psi_9 \rightarrow \psi_{10}$. In 1-fluoro-12-methylbenzo[c]phenanthrene these π-orbitals are not greatly modified by the inductive or mesomeric effects of the substituents or by the additional overcrowding due to the steric effect of those substituents, since the absorption spectrum of (I) (Fig. 1) does not differ substantially from that of the parent hydrocarbon.[11,12] Accordingly the Hückel molecular orbitals of benzo[c]phenanthrene are used in the following analysis of the CD spectrum of the (+)-1-fluoro-12-methyl derivative (I), and it is assumed that the co-ordinates of the nuclear carbon atoms of (I) referred to molecular axes are the same as those of 1,12-dimethylbenzo[c]phenanthrene measured in the X-ray diffraction study of Schmidt *et al.*[2]

The present study is concerned primarily with the calculation of the sign and the order of the magnitude of the rotational strengths, measured experimentally by the sign and the area of the corresponding CD bands, of the electronic transitions responsible for the p- and the β-absorption bands. The α-band is due to a forbidden

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

[10] M. J. S. Dewar and C. H. Longuet-Higgins, *Proc. Phys. Soc.* **67A**, 795 (1954).

[11] H. B. Klevens and J. R. Platt, *J. Chem. Phys.* **17**, 470 (1949).

[12] R. S. Becker, I. S. Singh and E. A. Jackson, *J. Chem. Phys.* **38**, 2144 (1963).

electronic transition which has neither a dipole nor a rotational strength in the zero order. The small but non-zero CD associated with the α-band of (+)-1-fluoro-12-methylbenzo[c]phenanthrene arises from perturbations due to the substituents or, more probably, from a vibronic origin, since the dichroism of the α-band has a marked vibrational structure (Fig. 1) and the unpolarized absorption intensity of the α-band, which measures the dipole strength, is virtually the same in the unsubstituted hydrocarbon as in the isomer (I). The $\pi \rightarrow \pi^*$ electronic transitions of 1-fluoro-12-methylbenzo[c]phenanthrene with a finite dipole strength have an intrinsic non-zero rotational strength, owing to the displacement of charge through a helical path determined by the dissymmetric σ-bond nuclear framework of the molecule, and the signs of the rotational strengths reflect the chirality of that framework. However, only the transitions giving the p- and β-bands of benzo[c]phenanthrene have, as yet, an established electronic provenance.

The dipole and rotational strengths of the p- and the β-bands of benzo[c]-phenanthrene were calculated by the dipole-velocity method used by Moscowitz[7] in his study of the optical rotatory dispersion of hexahelicene. The rotational strength of an electronic transition represents the scalar product of the electric dipole and the magnetic dipole transition moments, and the dipole strength, which is nominally the sum of the squares of all of the dipole and multipole transition moments, is given for the present purpose by the predominant term of the sum, the square of the electric dipole moment. For molecules with closed shells the dipole strength D_{ba} and the rotational strength R_{ba} of the electronic transition between the orbitals ψ_a and ψ_b are,

$$D_{ba} = 2\,|(\psi_a\,|\vec{\nabla}|\,\psi_b)\beta_M/(\pi\bar{\nu}_{ba})|^2 \tag{1}$$

and

$$R_{ba} = 2(\psi_a\,|\vec{\nabla}|\,\psi_b)(\psi_a\,|\vec{r} \times \vec{\nabla}|\,\psi_b)\beta_M{}^2/(\pi\bar{\nu}_{ba}) \tag{2}$$

where β_M is the Bohr magneton, $\bar{\nu}_{ba}$ is the frequency of the transition in wave numbers, $\vec{r}$ is the radius vector of the promoted electron from the origin of coordinates, and $\vec{\nabla}$ is the operator,

$$\vec{\nabla} = \mathrm{d}/\mathrm{d}x + \mathrm{d}/\mathrm{d}y + \mathrm{d}/\mathrm{d}z \tag{3}$$

The factor of two in Eqs (1) and (2) allows for the promotion of either of the two electrons in the orbital doubly occupied in the ground state.

On expanding the molecular orbitals ψ_a and ψ_b over the $2p\pi$ atomic orbitals of the hydrocarbon the factor $(\psi_a\,|\vec{\nabla}|\,\psi_b)$ of Eqs (1) and (2) governing the magnitude of the electric dipole transition moment becomes,

$$(\psi_a\,|\vec{\nabla}|\,\psi_b) = \sum_{r,s} C_{ra}C_{sb}\,\vec{\nabla}_{rs} \tag{4}$$

where C_{ra} is the coefficient of the atomic orbital ϕ_r of the nuclear carbon atom r in the molecular orbital ψ_a and the dipole velocity element $\vec{\nabla}_{rs}$ is,

$$\vec{\nabla}_{rs} = -\vec{\nabla}_{sr} = \int \phi_r\,\vec{\nabla}\phi_s\,\mathrm{d}\tau \tag{5}$$

The charge displacements along bonds provide the major contributions to the transition moments, and only adjacent atoms ($s = r \pm 1$) are considered in the sum of Eq. (4), giving

$$(\psi_a\,|\vec{\nabla}|\,\psi_b) = \sum_{r,s\ \text{adjacent}} P_{rs}^{ab}\ \vec{\nabla}_{rs} \tag{6}$$

where the transitional bond-order change between the atoms r and s in the transition $\psi_a \to \psi_b$ is,

$$P^{ab}_{rs} = C_{ra}C_{sb} - C_{sa}C_{rb} \qquad (7)$$

The dipole velocity element $\vec{\nabla}_{rs}$ is a vector directed along the bond rs in the direction $r \to s$ with the expectation value $\langle \nabla_{rs} \rangle$ which may be calculated[7] or estimated empirically from the absorption spectrum of a reference molecule. For an aromatic carbon–carbon bond with a length of 1·40 Å the calculated value[7] of $\langle \nabla_{CC} \rangle$ is $4{\cdot}184 \times 10^7$ cm^{-1}, and the empirical value estimated from the frequency and the dipole strength of the β-band of benzene[11] is $3{\cdot}55 \times 10^7$ cm^{-1}. In keeping with the general empirical procedure of the Hückel method the latter value is adopted in the present calculations.

The X-ray diffraction study[2] of 1,12-dimethyl benzo[c]phenanthrene gives (Table 8 of Ref. 2) the co-ordinates x_r, y_r, z_r, of the nuclear carbon atoms r referred to molecular axes. From these values are obtained the co-ordinates of the centre of each bond rs, x_{rs}, y_{rs}, z_{rs}, which represent the Cartesian components of the radius vector $\vec{r}$ (Eq. 2) in the present approximation, and the direction cosines, $\cos x_{rs}$, $\cos y_{rs}$, $\cos z_{rs}$, of the centre of each bond rs from the origin of co-ordinates, e.g.,

$$\cos x_{rs} = (x_r - x_s)/R_{rs} \qquad (8)$$

where R_{rs} is the length of the bond rs (Table 1). In terms of the direction cosines the Cartesian components of the dipole velocity element $\vec{\nabla}_{rs}$ have the form $\langle \nabla_{rs} \rangle \cos x_{rs}$ for the x-component and analogous forms for the y- and z-components.

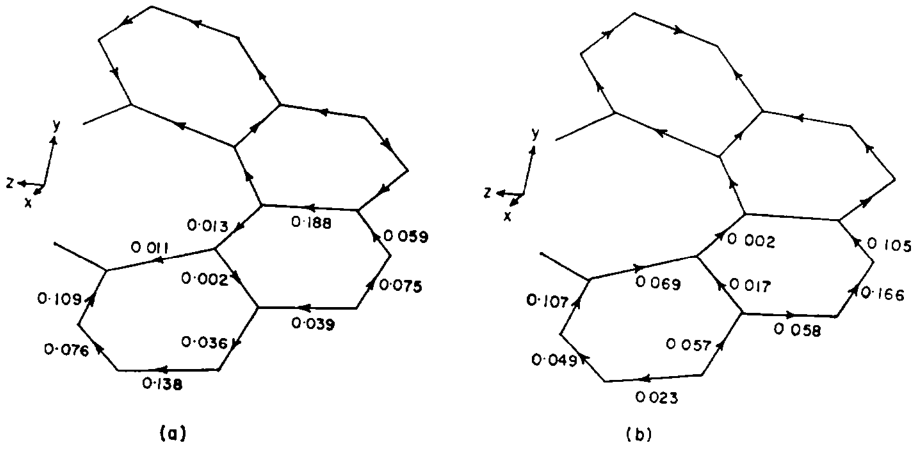

FIG. 2. The magnitudes and the directions of the transitional bond-order changes (Eq. 7) for the $\pi \to \pi^*$ transitions giving (a) the p-band, and (b) the β-band, of benzo[c]-phenanthrene.

For a z-polarized transition, such as that giving rise to the p-band of benzo[c]-phenanthrene (Fig. 2a), the elements (Eqs 1 and 2) governing the contributions of the transition moments to the dipole and rotational strength are,

$$(\psi_a | \vec{\nabla} | \psi_b)_z = \sum_{\text{bonds}} P^{ab}_{rs} \langle \nabla_{rs} \rangle \cos z_{rs} \qquad (9)$$

for the electric moment and,

$$(\psi_a | \vec{r} \times \vec{\nabla} | \psi_b)_z = \sum_{\text{bonds}} P^{ab}_{rs} \langle \nabla_{rs} \rangle (x_{rs} \cos y_{rs} - y_{rs} \cos x_{rs}) \qquad (10)$$

for the magnetic moment. Expressions analogous to Eqs (9) and (10), obtained by cyclic permutation of the Cartesian co-ordinates, hold for the x- and y-polarized transitions, such as that responsible for the β-band of benzo[c]phenanthrene (Fig. 2b).

The transitional bond order changes calculated (Eq. 7) in the Hückel approximation for the transition $\psi_9 \rightarrow \psi_{10}$, giving the p-band of benzo[c]phenanthrene (Fig. 2a), and for the transition $\psi_9 \rightarrow \psi_{11}$ and $\psi_8 \rightarrow \psi_{10}$, responsible for the β-band (Fig. 2b), give, together with the co-ordinates of the bond-centres and the direction cosines of the bonds (Table 1), the theoretical dipole strengths (Eq. 1) and rotational strengths (Eq. 2) recorded (Table 2). The magnitudes of the calculated dipole strengths are in satisfactory agreement with experiment, and the signs of the theoretical rotation strengths calculated for the P configuration[*] of benzo[c]phenanthrene in which the molecule has the stereochemical form of a segment of a right-handed helix (I) viewed in the direction perpendicular to the mean molecular plane, correspond to those observed for (+)-1-fluoro-12-methylbenzo[c]phenanthrene (Table 2, Fig. 1).

The magnitudes of the theoretical rotational strengths are not in good agreement with experiment (Table 2), owing mainly to the optical overlap of adjacent CD bands with opposed signs and to the sensitivity of the magnitudes of the calculated rotational strengths to the particular values of the displacements of the nuclear carbon atoms from the mean molecular plane of benzo[c]phenanthrene. If two CD bands having opposed signs are adjacent, they mutually cancel to a degree dependent on the widths of the bands and the frequency interval between them, so that the observed rotational strengths are smaller than the intrinsic strengths.

The theoretical rotational strengths are calculated from the co-ordinates of the bond centres and the direction cosines of the nuclear carbon–carbon bonds in 1,12-dimethyl-benzo[c]phenanthrene[2] (Table 1), but the Van der Waals radius[13] of a fluoro-substituent (1·35 Å) is somewhat smaller than that of a methyl group (2·0 Å), so that the out-of-plane distortions of the nuclear carbon atoms in 1-fluoro-12-methylbenzo[c]phenanthrene are probably not so large as those in the corresponding 1,12-dimethyl derivative. The magnitudes of the theoretical rotational strengths whether x-, y-, or z-polarized in (I) are sensitive to the particular values of the out-of-plane co-ordinates, x_{r_s}, or the corresponding direction cosines, $\cos x_{r_s}$, and thus these magnitudes are overestimated in the present calculations, although the signs of the calculated rotational strengths are correct for (I) if the general method is valid.

The magnitudes of the dipole strengths with y- and z-polarization in (I) are not sensitive to small displacements of the nuclear carbon atoms from the mean molecular plane in benzo[c]phenanthrene, although the dipole strength with x-polarization is strongly dependent upon the particular values of those displacements. However, for the out-of-plane distortions which have been determined by X-ray diffraction[1,2] or which are physically probable in benzo[c]phenanthrene derivatives the contribution of the out-of-plane x-polarized component to the total dipole strength of any given $\pi \rightarrow \pi^*$ transition is relatively minor, and the satisfactory agreement between the theoretical and the observed dipole strengths supports the validity of the method of calculation adopted.

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[*] The use of P (plus) and M (minus) to describe the chirality, respectively, of a right- and a left-handed helical structure follows the recommendation of R. S. Cahn, C. K. Ingold and V. Prelog, *Angew Chem.*, 1965 to be published.

[13] L. Pauling, *The Nature of the Chemical Bond*, p. 189. Cornell University Press (1940).

Accordingly, it is concluded that (+)-1-fluoro-12-benzo[c]phenanthrene has the *P* configuration (I). Although the signs of the rotational strengths of both bands, calculated for the *P* configuration, agree with those observed (Table 2, Fig. 1), the sign of the CD of the p-band is probably more reliable than that of the β-band for the identification of the absolute configuration of (I) and of overcrowded benzo[c]-phenanthrene derivatives generally. The sign of the rotational strength of the p-band depends upon the chirality of the σ-bond framework of the benzo[c]phenanthrene molecule as a whole, whereas the overall rotational strength of the β-band is the sum of two components, R_x and R_y (Table 2), which have opposed signs and magnitudes dependent upon the particular values of the co-ordinates of the nuclear carbon atoms.

For similar reasons the sign of the CD of the β-band should be the more reliable for the determination of the absolute configuration of dissymmetric phenanthrene[14] and 3,4,5,6-dibenzophenanthrene derivatives.[15,16] The rotational strength of the

TABLE 1. THE CO-ORDINATES x_{rs}, y_{rs}, AND z_{rs} OF THE CENTRE OF EACH BOND BETWEEN THE NUCLEAR CARBON ATOMS *r* AND *s* OF THE *P*(PLUS, RIGHT-HANDED) CONFIGURATION OF 1,12-DIMETHYL BENZO[C]-PHENANTHRENE AND THE DIRECTION COSINES, COS x_{rs}, COS y_{rs}. COS z_{rs} (E.G. EQ. 8) OF THE BONDS TAKEN IN THE DIRECTION $r \rightarrow s$ FROM THE MOLECULAR ORIGIN OF CO-ORDINATES. THE AXES ARE AS IN (I) AND AS IN TABLE 8 OF REFERENCE (2) FROM WHICH THE DATA BELOW WERE CALCULATED

Bond $r \rightarrow s$	z_{rs} (Å)	y_{rs} (Å)	x_{rs} (Å)	cos z_{rs}	cos y_{rs}	cos x_{rs}
1 → 2	+1·605	+2·158	+0·565	−0·4040	−0·9111	+0·0759
2 → 3	+1·5705	+3·3185	+0·1805	+0·4545	−0·7530	+0·4760
3 → 4	+0·610	+3·7555	−0·3865	+0·9319	+0·1266	+0·3408
4 → 8	−0·350	+3·0385	−0·5585	+0·4469	+0·8903	−0·0898
5 → 8	−1·374	+2·3635	−0·616	−0·9840	−0·0632	−0·1681
5 → 6	−2·414	+1·746	−0·564	+0·4857	+0·8368	−0·2531
7 → 1	+0·684	+1·407	+0·309	−0·8881	−0·1598	−0·4294
7 → 8	−0·3555	+1·8505	−0·2475	+0·5078	−0·7899	+0·3500
7 → 9	−0·2865	+0·646	0	+0·4566	+0·8998	0
6 → 10	−2·389	+0·587	−0·1955	−0·4996	+0·8215	−0·2736
9 → 10	−1·325	0	0	+1·000	0	0

TABLE 2. THE CD AND ABSORPTION SPECTRA OF (+)-1-FLUORO-12-METHYL BENZO[C]PHENANTHRENE AND THE ROTATIONAL AND DIPOLE STRENGTHS OF THE α-, p-. AND β-BANDS CALCULATED IN THE HÜCKEL APPROXIMATION FROM THE DATA OF TABLE 1. THE FREQUENCY ν_{CD}, MAXIMUM DIFFERENTIAL EXTINCTION COEFFICIENT $(\epsilon_l - \epsilon_r)$ AND THE ROTATIONAL STRENGTH *R* OF THE CIRCULAR DICHROISM, AND THE FREQUENCY ν_{abs}, MAXIMUM EXTINCTION COEFFICIENT ϵ AND DIPOLE STRENGTH *D* OF THE UNPOLARIZED ABSORPTION. THE THEORETICAL ROTATIONAL STRENGTHS REFER TO THE *P* CONFIGURATION (I) AND, TOGETHER WITH THE THEORETICAL DIPOLE STRENGTHS, THEY ARE DIRECTED ALONG THE CO-ORDINATE AXES GIVEN IN (I)

	Experimental						Theoretical	
Band	ν_{CD} (cm^{-1})	$(\epsilon_l - \epsilon_r)$ (M^{-1} cm^{-1})	*R* (10^{-40} c.g.s.)	$\nu_{abs.}$ (cm^{-1})	ϵ (M^{-1} cm^{-1})	*D* (10^{-36} c.g.s.)	*R* (10^{-40} c.g.s.)	*D* (10^{-36} c.g.s.)
α	26,000	−0·5	−0·3	25,800	300	0·2	0	0
p	29,700	−16·5	−15	29,500	9000	9	−102(z)	7·2(z)
β	34,500	+68	+56	34,500	57,500	46	+132(y) −95(x)	38·2(y) 2·9(x)

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[14] M. S. Newman and A. S. Hussey, *J. Amer. Chem. Soc.* **69** 3023 (1947).

[15] F. Bell and D. H. Waring, *J. Chem. Soc.* 2689 (1949).

[16] M. Crawford, R. A. M. MacKinnon and V. R. Supanekar, *J. Chem. Soc.* 2807 (1959).

β-band of these molecules has only one component, R_z, where z is the two-fold rotation axis of the parent hydrocarbon, and the sign of R_z is determined by the chirality of the molecule as a whole, whereas the rotational strength of the p-band is the sum of two components, R_x and R_y, which have magnitudes dependent upon the detailed atomic displacements from the mean molecular plane and have, in general, opposed signs.

EXPERIMENTAL

The CD and absorption spectra of (+)-1-fluoro-12-methylbenzo[c]phenanthrene in cyclohexane solution (Fig. 1) were measured with a Jouan Dichrograph and a Unicam SP 700, respectively. The experimental dipole D and rotational strengths R (Table 2) were obtained in c.g.s. units from the appropriate band areas by means of the expressions,[17]

$$D = 91{\cdot}8 \times 10^{-40} \int (\varepsilon/\nu)\, d\nu$$

and

$$R = 22{\cdot}9 \times 10^{-40} \int [(\varepsilon_1 - \varepsilon_r)/\nu]\, d\nu$$

where the frequency ν is in cm^{-1} and the decadic molar extinction coefficient ε is in M^{-1} cm^{-1}.

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[17] S. F. Mason, *Quart. Rev.* **17**, 20 (1963).