

The Circular Dichroism and Configuration of Benzo[*c*]phenanthrene Derivatives

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HEXAHelicene,¹ and derivatives of phenanthrene,² 3,4-benzo-,³⁻⁵ and 3,4,5,6-dibenzo-phenanthrene^{6,7} have been resolved into optical isomers, and *X*-ray-diffraction studies show that the aromatic nuclei of 3,4-benzo-⁸ and 3,4,5,6-dibenzophenanthrene⁹ are non-coplanar, these molecules having the form of a segment of a helix. The present work reports the measurement of the circular dichroism spectra of (-)-1,12-dimethylbenzo[*c*]phenanthrene-5-acetic acid⁴ and (+)-1-fluoro-12-methylbenzo[*c*]phenanthrene⁵ (Figure), and an analysis which shows that the former has the *M*-(minus, left-handed) (I) and the latter the *P*-(plus, right-handed) helical configuration (II) viewed in the direction perpendicular to the mean molecular plane.

The electronic origins of the first three absorption bands of aromatic hydrocarbons, the α -, p -, and β -bands in the nomenclature of Clar¹⁰ or the ¹L_b, ¹L_a, and ¹B_a bands in that of Platt,¹¹ are well understood.^{11,12} 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 excitations $\Psi_m \rightarrow \Psi_{m+2}$ and $\Psi_{m-1} \rightarrow \Psi_{m+1}$. The circular dichroism and the unpolarized absorption of the α -band of (I) and (II) is weak, as this band is due to a forbidden electronic transition. However, the electronic transitions responsible for the p - and β -bands of (I) and (II) are allowed and they have a substantial intrinsic rotational strength, owing to the displacement of π -electron charge through a helical path determined by the dissymmetric σ -bond framework of the molecule.

The rotational strengths of the p - and the β -bands of 1,12-dimethylbenzo[*c*]phenanthrene have been calculated from the co-ordinates of the nuclear carbon atoms of the molecule given by the *X*-ray-diffraction study of Schmidt and co-workers,⁸ using the Hückel molecular π -orbitals of the parent hydrocarbon and the dipole-velocity method adopted by Moscowitz¹³ for the calculation of the optical rotatory dispersion of hexahelicene. The p -band of benzo[*c*]phenanthrene is due to a

¹ M. S. Newman and D. Lednicer, *J. Amer. Chem. Soc.*, 1956, **78**, 4765.

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³ M. S. Newman and W. B. Wheatley, *J. Amer. Chem. Soc.*, 1948, **70**, 1913.

⁴ M. S. Newman and R. M. Wise, *J. Amer. Chem. Soc.*, 1956, **78**, 450.

⁵ M. S. Newman, R. G. Mentzer, and G. Slomp, *J. Amer. Chem. Soc.*, 1963, **85**, 4018.

⁶ F. Bell and D. H. Waring, *J. Chem. Soc.*, 1949, 2689.

⁷ M. Crawford, R. A. M. MacKinnon, and V. R. Supanekar, *J. Chem. Soc.*, 1959, 2807.

⁸ F. L. Hirshfeld, S. Sandler, and G. M. J. Schmidt, *J. Chem. Soc.*, 1963, 2108.

⁹ A. O. McIntosh, J. M. Robertson, and V. Vand, *J. Chem. Soc.*, 1954, 1661.

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¹¹ J. R. Platt, *J. Chem. Phys.*, 1949, **17**, 484.

¹² M. J. S. Dewar and C. H. Longuet-Higgins, *Proc. Phys. Soc.*, 1954, **67**, A, 795.

¹³ A. J. Moscowitz, *Tetrahedron*, 1961, **13**, 48; Thesis, Harvard, 1957.

transition which involves only the linear displacement of charge along the two-fold rotation axis, the z -axis of (I) and (II), in the planar molecule. Owing to the non-coplanarity of the nuclear carbon atoms, this transition gives rise additionally to a rotatory charge displacement about the z -axis in the overcrowded molecules (I) and (II). The resulting magnetic-dipole transition moment is parallel to the electric moment for the M -configuration (I) and antiparallel for the P -configuration (II), giving a positive and a negative

the y -axis. The rotational strength of the β -band of benzo[c]phenanthrene derivatives thus has x - and y -polarized components, and for the M -configuration (I) they have the theoretical values $R_x = +95$ and $R_y = -132$ in units of 10^{-40} c.g.s., giving a negative overall rotational strength. In the same units the experimental rotational strengths of the β -band are -26 for (–)-1,12-dimethylbenzo[c]phenanthrene-5-acetic acid and $+48$ for (+)-1-fluoro-12-methylbenzo[c]phenanthrene, supporting the assignment, based on the sign of the circular dichroism of the p -band, of the M - (I) and the P -configuration (II) to these isomers, respectively.

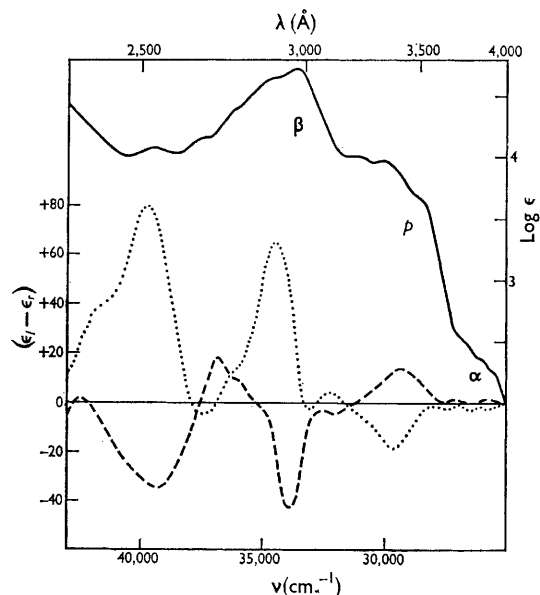
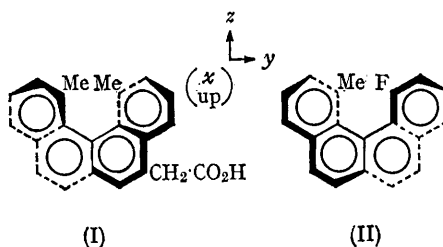


FIGURE. The absorption spectrum ——— and the circular dichroism of (–)-1,12-dimethylbenzo[c]phenanthrene-5-acetic acid, and the circular dichroism ——— of (+)-1-fluoro-12-methylbenzo[c]phenanthrene in cyclohexane.

rotational strength, respectively. The theoretical magnitude of the rotational strength of the p -band is 102 in units of 10^{-40} c.g.s., compared with the experimental values, obtained from the areas of the corresponding circular dichroism bands, of $+20$ for (I) and -15 for (II) in the same units.

The transition responsible for the β -band of benzo[c]phenanthrene is y -polarized in the planar molecule, but in the overcrowded derivatives (I) and (II) the transition gives rise additionally to charge displacements along and about the x -axis as well as a rotatory charge displacement around



The sign of the circular dichroism of the p -band is more reliable than that of the β -band for the identification of the absolute configuration of overcrowded benzo[c]phenanthrene derivatives, since the relative magnitudes of the components R_x and R_y , and thus the sign of the overall rotational strength of the β -band, are sensitive to the particular values⁸ of the co-ordinates of the nuclear carbon atoms. The sign of the rotational strength of the p -band depends primarily on the chirality of the molecule as a whole, although the magnitude of that rotational strength, which is overestimated in the present calculation, is sensitive to the detailed atomic displacements from the mean molecular plane. For similar reasons the sign of the circular dichroism of the β -band should be the more reliable for the determination of the absolute configuration of dissymmetric phenanthrene³ and 3,4,5,6-dibenzophenanthrene derivatives,^{6,7} as the rotational strength of the β -band of these molecules has only one component, R_z , where z is the two-fold rotation axis of the parent hydrocarbon, and that of the p -band has two components, R_x and R_y , which may have opposed signs.

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