

Figure 1. Out-of-phase combination of ring breathing modes in bent benzene rings of [2.2]paracyclophane.

ordinary absorption of unsubstituted single crystal [2.2]paracyclophane has been observed at low temperature.^{7,8} A recent reinterpretation of the vibrational analysis⁹ applies the dimer vibronic coupling theory of Fulton and Gouterman¹⁰ and defines a vibrational mode significantly coupled to the electronic structure. The major features of the uv absorption edge are accounted for by theory parameter values¹⁰ of $\epsilon = 1.5$ and $\lambda = 2.0$ for the 235 cm^{-1} coupled vibrational mode⁹ similar to that shown in Figure 1. The theory assumes variation with nuclear position of the *inter*-ring electronic potential to be the primary vibronic interaction. It has been observed previously⁵ that such theory should account for details of band shape in the long wavelength CD of the ring-substituted paracyclophanes.

A more recent extension of the theory by Fulton¹¹ adds consideration of the variation of *intra*-ring electronic structure with such nuclear displacement as is depicted in Figure 1. Extending the right-hand side of eq 38 in ref 11 to include additional states and considering also the transition magnetic dipole form of eq 40 in ref 11, the model of ref 5 yields a vibronic coupling rotatory strength (*cf.* eq 5, ref 5)

$$R_{0,\pm} = \pm \pi \bar{\nu}_{0i} \frac{\partial \mathbf{m}(\mathbf{A})_{0i}}{\partial Q_r^A} \cdot \mathbf{R}(\mathbf{B}) \times \frac{\partial \mathbf{m}(\mathbf{B})_{0i}}{\partial Q_r^B} \xi_r \quad (1)$$

where $\bar{\nu}_{0i}$ is the frequency in cm^{-1} of the zero-order $i \leftarrow 0$ transition. Q_r^A and Q_r^B are modified ring breathing modes shown in Figure 1 with a phase convention such that Q_r^A itself and the *negative* of Q_r^B are depicted, ξ_r is the zero-point mean square displacement of the normal mode. Equation 1 applies to a low temperature limit with no vibrational modes excited in the electronic ground state. Equation 1 can account for 1L_b rotatory strength in [2.2]paracyclophane ring substituted by deuterium.

The extended form of eq 38 in ref 11 will define dipole derivatives that can be deduced as shown in Figure 2. Normal mode displacements have been assumed that would generate the observed 1L_b circular dichroism of (–)-(S)-4-deuterio[2.2]paracyclophane.²

The *vibronic* rotation of transition dipole in ring A is

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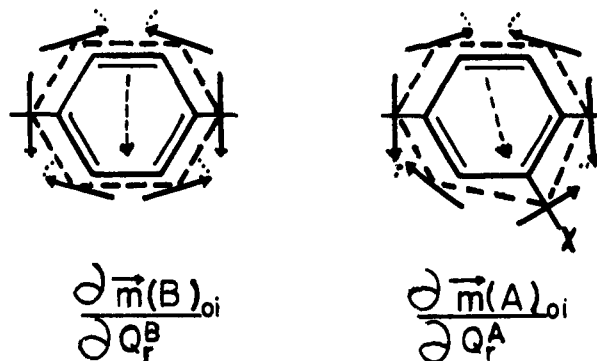


Figure 2. Paracyclophane rings B and A under the distortion (exaggerated) of ring-breathing type modes. The reorientation (dotted arcs) of spectroscopic moment vectors relative to those for equilibrium position rings is shown. The resultant differential increments with vibration (dashed arrows), $\partial \mathbf{m}(\mathbf{B})_{0i} / \partial Q_r^B$ and $\partial \mathbf{m}(\mathbf{A})_{0i} / \partial Q_r^A$, are consistent with more general symmetry arguments.

completely analogous to the electronically induced rotation discussed in ref 5. Thus the vector relationships and the feature of opposite signed rotational strength with equal magnitude in the electronic theory³ is preserved also in the vibronic theory detailed here.

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[2.2]Paracyclophane System Optical Activity.

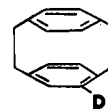
IV. The Circular Dichroism of

(–)-(S)-4-Deuterio[2.2]paracyclophane¹

Sir:

Few examples of CD arising from deuterium-hydrogen chirality have been reported.² We wish to report the first such uv transition CD observed for a system which has a broadly verified model for the origin of transition rotatory strength.

(–)-(S)-4-Deuterio[2.2]paracyclophane (1), $[\alpha]^{25}_{546}$



1

$-4.0 \pm 1.1^\circ$ (c 0.87, chloroform) mp 280–285, was synthesized by deuterolysis of (S)-4-lithio[2.2]paracyclophane which in turn was derived from optically pure (+)-(S)-4-carboxy[2.2]paracyclophane.³ Mass spectral analysis showed 90% deuterium incorporation into the [2.2]paracyclophane.⁴

(1) Taken in part from the Undergraduate Honors Thesis of P. H. Hoffman, Tulane University, 1971.

(2) For a recent review of optically active deuterium compounds, see L. Verbit, *Progr. Phys. Org. Chem.*, **7**, 51 (1970).

(3) A. Guest, P. H. Hoffman, and M. J. Nugent, *J. Amer. Chem. Soc.*, **94**, 4341 (1972).

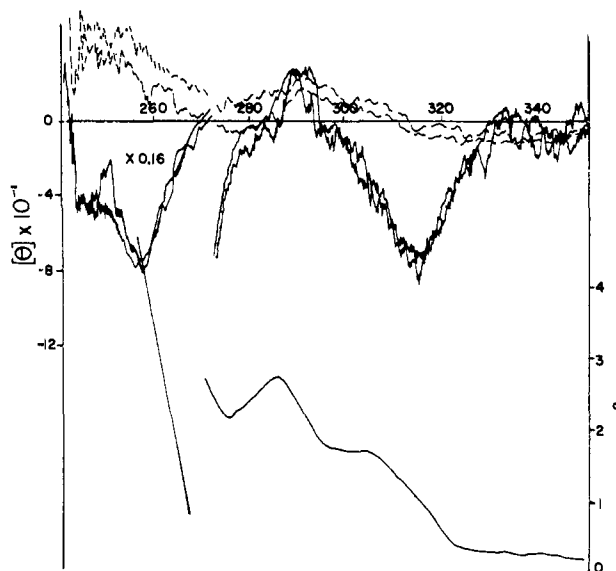


Figure 1. The molecular ellipticity $[\theta]$ (left-hand scale) and ordinary absorption ϵ (right-hand scale) of (–)-(S)-4-deuterio[2.2]paracyclophane in methanol. The base line for ellipticity shown by the broken lines was obtained by replacing the sample with the same concentration of [2.2]paracyclophane.

A large number of published CD spectra for 4-substituted [2.2]paracyclophanes^{5,6} show that the sign and magnitude of long wavelength rotatory strength for a given chirality vary with the transition electric dipole direction in the trisubstituted benzene ring.⁷ Platt's spectroscopic moments⁸ adequately predict this direction. Therefore, the perturbation that gives rise to rotatory strength in these 4-substituted [2.2]paracyclophanes must have an electronic origin. That such electronic effects would be absent for **1** can be concluded from the observation that the long wavelength uv vapor spectrum of deuteriobenzene, like benzene, lacks a 0–0 band.⁹ Alternatively a vibronic coupling model can be defined¹⁰ which again accounts for a turning of the benzene transition dipole direction.

The experimental circular dichroism for compound **1**¹¹ shown in Figure 1 has a number of notable features. The magnitude of molecular ellipticity^{12,13} in the ¹L_b bands (280–330 nm) is about 1/100 of that for (+)-(S)-4-methyl[2.2]paracyclophane.⁵ The vibronically induced CD in more massively substituted [2.2]paracyclophanes is probably larger. But unless the vibronic CD contribution varies as an inordinately high power of the

(4) Mass spectra were kindly furnished by Professor W. Weber at the University of Southern California.

(5) M. J. Nugent and O. E. Weigang, Jr., *J. Amer. Chem. Soc.*, **91**, 4556 (1969).

(6) H. Falk, P. Reich-Rohrwig, and K. Schloegl, *Tetrahedron*, **26**, 511 (1969).

(7) O. E. Weigang, Jr., and M. J. Nugent, *J. Amer. Chem. Soc.*, **91**, 4555 (1969).

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(11) Compound **1** was purified by recrystallization and tlc on silver nitrate-coated silica gel until the CD was constant. Measurements were carried out on a Cary 60 spectropolarimeter with a 6001 CD accessory. The uv spectrum of **1** is identical with that of [2.2]paracyclophane.

(12) The observed order of magnitude is the same as found for 1-deuterio- α -fenchocamphoronequinone.¹³

(13) W. C. M. C. Kokke, Doctoral Thesis, University of Leiden, 1973.

mass, this contribution would be much too small to account for the CD of the ¹L_b bands observed previously.^{5,7} This result is consistent with the evidence that an electronic perturbation, operative even in a vibrationless molecule, is responsible for the optical activity in these cases. The shorter wavelength component of the ¹L_b band pair appears as a positive contribution to the edge of the highly negative ¹L_a region. As in some other instances^{5,6} the sign of the ¹L_a band dominates.

The ¹L_a region (240–280 nm) in Figure 1 shows a signed CD that is reversed from the unchanging sign for the same transition in other S-4-substituted [2.2]paracyclophanes.^{5,6,14} If the CD of these shorter wavelength bands is indeed dominated by vibronic rather than purely electronic perturbations,⁷ it may be relevant that Figure 1 shows the one CD where the mass at the 4 position is much less than the ethylene bridges.

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(14) This observation shows that trace amounts of optically active S-substituted [2.2]paracyclophane contaminants are not responsible for the CD of **1**.

(15) NSF-URP Fellow 1971.

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Preparation and Properties of Iron(III)–Amino Acid Complexes. Iron(III)–Alanine, a Possible Ferritin Analog

Sir:

Spiro, Saltman, and coworkers have shown that it is possible to produce an iron-containing polymer of a molecular weight of approximately 150,000 from bicarbonate-hydrolyzed ferric nitrate solutions.^{1–4} A similar result is found for hydrolyzed iron–citrate solutions.^{5,6} The physical properties of the polymer, Tables I and II, suggest that its constitution is essentially that of the ferritin core. Based primarily upon low angle X-ray scattering work, Brady, *et al.*,³ have suggested that the structure of the iron-containing polymer and thus the ferritin core consists of polymerically bound tetrahedral [FeO₂(OH)₂] units. Gray⁷ has taken issue with this model pointing out that in the electronic spec-

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