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Theoretical Rayleigh Optical Activity of Hexahelicene

Sir:

The very large optical rotation and circular dichroism exhibited by hexahelicene suggests that it might show large Rayleigh optical activity (a difference in the Rayleigh scattered intensity in right and left circularly polarized light¹). Rayleigh optical activity has not yet been observed, although the Raman analog is now well established.²⁻⁴

In a recent article, Barron and Buckingham⁵ presented a simple two-group model in which Rayleigh and Raman optical activity arises through interference between light waves scattered independently from two groups held in a chiral structural unit. This contrasts with the Kirkwood dynamic-coupling theory of optical rotation⁶ in which an unscattered wave interferes with a forward-scattered wave that has suffered sequential scattering from the two groups. The Kirkwood theory was applied to hexahelicene⁷ by summing 15 pairwise interactions of benzenoid rings; the calculated specific rotation (3010°) agrees remarkably well with experiment (3750°) considering the complexity, and a recent X-ray study⁸ has shown that the correct absolute configuration is predicted. Despite the reservations about applying a two-group model to hexahelicene (on account of complete π -electron exchange between the benzenoid rings), the good optical rotation result encourages a calculation of the Rayleigh optical activity.

The components of the Rayleigh CID (circular intensity differential) parallel (Δ_z) and perpendicular (Δ_x) to the scattering plane are, for molecules much smaller than the wavelength of the light¹

$$\Delta_z = \frac{4(3\alpha_{\alpha\beta}G_{\alpha\beta}' - \alpha_{\alpha\alpha}G_{\beta\beta}' - \frac{1}{3}\omega\alpha_{\alpha\beta}\epsilon_{\alpha\gamma\delta}A_{\gamma\delta\beta})}{2c(3\alpha_{\gamma\delta}\alpha_{\gamma\delta} - \alpha_{\gamma\gamma}\alpha_{\delta\delta})} \quad (1a)$$

$$\Delta_x = \frac{2(7\alpha_{\alpha\beta}G_{\alpha\beta}' + \alpha_{\alpha\alpha}G_{\beta\beta}' + \frac{1}{3}\omega\alpha_{\alpha\beta}\epsilon_{\alpha\gamma\delta}A_{\gamma\delta\beta})}{c(7\alpha_{\gamma\delta}\alpha_{\gamma\delta} + \alpha_{\gamma\gamma}\alpha_{\delta\delta})} \quad (1b)$$

(1) L. D. Barron and A. D. Buckingham, *Mol. Phys.*, **20**, 1111 (1971).

(2) L. D. Barron, M. P. Bogaard, and A. D. Buckingham, *J. Amer. Chem. Soc.*, **95**, 603 (1973).

(3) L. D. Barron and A. D. Buckingham, *Nature (London)*, **241**, 113 (1973).

(4) L. D. Barron and E. D. Buckingham, *J. Chem. Soc., Chem. Commun.*, 152 (1973).

(5) L. D. Barron and A. D. Buckingham, *J. Amer. Chem. Soc.*, **96**, 4769 (1974).

(6) J. G. Kirkwood, *J. Chem. Phys.*, **5**, 479 (1937).

(7) D. D. Fitts and J. G. Kirkwood, *J. Amer. Chem. Soc.*, **77**, 4940 (1955).

where ω is the angular frequency, $\alpha_{\alpha\beta}$ is the polarizability tensor, $G_{\alpha\beta}'$ is the electric dipole-magnetic dipole distortion tensor, and $A_{\alpha\beta\gamma}$ is the electric dipole-electric quadrupole distortion tensor. According to Barron and Buckingham,⁵ the required products in eq 1 for two chirally arranged groups *i* and *j* with threefold or higher rotation axes are, neglecting the static and dynamic coupling between the groups

$$\alpha_{\alpha\beta}G_{\alpha\beta}' = \frac{1}{3}\omega\alpha_{\alpha\beta}\epsilon_{\alpha\gamma\delta}A_{\gamma\delta\beta} = -\frac{9}{2}\omega\alpha_i\alpha_j\kappa_i\kappa_j\epsilon_{\beta\gamma\delta}R_{ij\gamma}u_{ja}u_{ia}u_{j\beta}u_{i\delta} \quad (2a)$$

$$\alpha_{\alpha\alpha}G_{\beta\beta}' = 0 \quad (2b)$$

$$\alpha_{\alpha\beta}\alpha_{\alpha\beta} = \alpha_{i\alpha\beta}\alpha_{i\alpha\beta} + \alpha_{j\alpha\beta}\alpha_{j\alpha\beta} + 2\alpha_{i\alpha\beta}\alpha_{j\alpha\beta} \quad (2c)$$

$$\alpha_{i\alpha\beta}\alpha_{j\alpha\beta} = 3\alpha_i\alpha_j + 3\alpha_i\alpha_j\kappa_i\kappa_j(3u_{ia}u_{ja}u_{i\beta}u_{j\beta} - 1) \quad (2d)$$

where u_i is the principal axis of the *i*th group, α_i and κ_i are its mean polarizability and polarizability anisotropy, and $R_{ij} = R_i - R_j$.

The centers of the six benzenoid rings in hexahelicene are placed on a right-handed cylindrical helix $X = a \cos \theta$, $Y = a \sin \theta$, and $Z = b\theta$ at $\theta = 30, 90, 150, 210, 270$, and 330° . The radius vector of the *i*th benzenoid ring is

$$R_{i\alpha} = I_\alpha a \cos \theta_i + J_\alpha a \sin \theta_i + K_\alpha b \theta_i \quad (3)$$

where **I**, **J**, **K** are unit vectors along the internal axes, *X*, *Y*, *Z*, of the molecule. The principal axis of the *i*th group is

$$u_{i\alpha} = (a^2 + b^2)^{-1/2}(I_\alpha b \sin \theta_i - J_\alpha b \cos \theta_i + K_\alpha a) \quad (4)$$

These geometrical relations are derived more fully in a recent article on the optical rotation of oriented hexahelicene.⁹ If a bond length of 1.40 Å is adopted, the radius *a* is 2.42 Å. An X-ray analysis of hexahelicene¹⁰ reports a distance $2\pi b = 3.05$ Å between the closest pair of nonbonded carbon atoms in the terminal rings.

By summing independently the numerators and denominators of eq 1 over all 15 pairs of benzenoid rings, it is found that the resulting expressions are functions of $\theta_{ij} \equiv \theta_i - \theta_j$ only

$$\Delta_z = \frac{2\pi b \sum_{i>j=1}^6 [2(1 - \cos \theta_{ij}) + \gamma^2 \theta_{ij} \sin \theta_{ij}](1 + \gamma^2 \cos \theta_{ij})}{3\lambda \left[-3(1 + \gamma^2)^2 + \sum_{i>j=1}^6 (1 + \gamma^2 \cos \theta_{ij})^2 \right]} \quad (5a)$$

$$\Delta_x = \frac{8\pi\kappa^2 b \sum_{i>j=1}^6 [2(1 - \cos \theta_{ij}) + \gamma^2 \theta_{ij} \sin \theta_{ij}](1 + \gamma^2 \cos \theta_{ij})}{\lambda \left[3(1 + \gamma^2)^2(20 - 7\kappa^2) + 7\kappa^2 \sum_{i>j=1}^6 (1 + \gamma^2 \cos \theta_{ij})^2 \right]} \quad (5b)$$

(8) D. A. Lightner, D. T. Hefelfinger, T. W. Powers, G. W. Frank, and K. N. Trueblood, *J. Amer. Chem. Soc.*, **94**, 3492 (1972).

(9) L. D. Barron, *J. Chem. Soc., Faraday 2*, in press.

(10) I. R. Mackay, J. M. Robertson, and J. G. Sime, *Chem. Commun.*, 1470 (1969).

where $\gamma \equiv b/a$. For the values $a = 2.42 \text{ \AA}$, $b = 0.486 \text{ \AA}$, $\lambda = 5000 \text{ \AA}$, and $|\kappa| = 0.18$ (for 6328 \AA),¹¹ the CID components are found to be $\Delta_z \sim 0.62 \times 10^{-3}$ and $\Delta_x \sim 0.41 \times 10^{-4}$. These estimates apply only to gaseous samples; in liquids a significant reduction in Rayleigh scattering occurs through interference, the isotropic contribution being suppressed much more than the anisotropic contribution.

These Rayleigh CID components of hexahelicene are disappointingly small; in solution they will be even smaller due to the Rayleigh intensity from the solvent and could probably not be detected at present. The calculated Rayleigh CID of a biphenyl twisted at 45° is rather larger ($\Delta_z \sim 1.3 \times 10^{-3}$, $\Delta_x \sim 0.6 \times 10^{-4}$).⁵ In contrast, the calculated specific rotation (using the dynamic coupling model) of the twisted biphenyl (863°) is rather smaller than that of hexahelicene (2650°).⁹ This is because each pairwise CID contribution is "weighted" by a corresponding polarizability, whereas each pairwise optical rotation contribution is purely additive. Thus a molecule with a large specific rotation will not necessarily show a large Rayleigh CID. Raman CID's associated with certain normal vibrational coordinates of hexahelicene should be rather larger than the Rayleigh CID, but a detailed analysis will take some time.

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(11) N. J. Bridge and A. D. Buckingham, *Proc. Roy. Soc., Ser. A*, **295**, 334 (1966).

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Models for Chiral Recognition in Molecular Complexation¹

Sir:

Optically pure host compounds **5**² and **8** have been examined for their abilities to complex selectively and make extractable from water into chloroform the enantiomers of α -amino ester hexafluorophosphate salts as guest compounds. Racemic 3,3'-bishydroxymethyl-2,2'-dihydroxy-1,1'-binaphthyl (**2**)³ with hydrogen bromide in glacial acetic acid gave (90%) 3,3'-bisbromomethyl-2,2'-dihydroxy-1,1'-binaphthyl, mp $211\text{--}213^\circ \text{ dec.}$ ⁴ With LAH, the bromo compound gave (87%) (\pm)-**3**,⁴ mp $204\text{--}205^\circ$. Optically pure (*R*)-**3**⁴ was obtained (25% overall) by resolution of the cinchonine salt of the phosphoric acid diester⁴ of (\pm)-**3**.⁵ From dihydropyran and 2-(2'-chloroethoxy)-

(1) This work was supported by a grant from the National Science Foundation, GP33533X, and by the U. S. Public Health Service, Research Grant No. GM12640-10 from the Department of Health, Education and Welfare.

(2) E. P. Kyba, K. Koga, L. R. Sousa, M. G. Siegel, and D. J. Cram, *J. Amer. Chem. Soc.*, **95**, 2692 (1973).

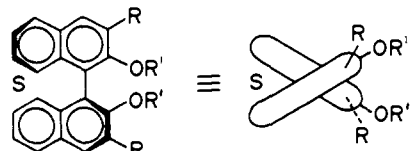
(3) (a) R. C. Helgeson, J. M. Timko, and D. J. Cram, *J. Amer. Chem. Soc.*, **95**, 3023 (1973); (b) R. C. Helgeson, K. Koga, J. M. Timko, and D. J. Cram, *ibid.*, **95**, 3021 (1973).

(4) (a) Carbon and hydrogen analyses were within 0.30% of theory. Pmr spectra were consistent with assigned structures. (b) Mass spectra exhibited molecular ions.

(5) The procedure resembled that applied to 2,2'-dihydroxy-1,1'-binaphthyl: J. Jacques and C. Fouquay, *Tetrahedron Lett.*, 4617 (1971).

ethanol was produced (96%) 2-(2'-chloroethoxy)ethyl 2'-tetrahydropyranyl ether,⁴ bp $87\text{--}88^\circ$ (0.5 mm), which with sodium hydroxide, butanol, and optically pure (*S*)- and (*R*)-2,2'-dihydroxy-1,1'-binaphthyl² (**1**) at reflux for 20 hr gave pyranyl ethers that by conventional procedures were converted to ditosylates, (*S*)-**4** and (*R*)-**4**, respectively (Chart I). Treatment

Chart I

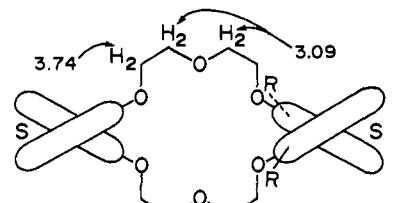


| Compd no. | R | R' | Mp, °C | $[\alpha]_{D}^{25}$, deg | Solvent ^a | Yield, % |
|-------------------------------------|--------------------|---|---------|---------------------------|-----------------------------------|----------|
| (<i>S</i>)- 1 ² | H | H | 207–208 | –34.3 ^b | (CH ₂) ₄ O | Ref 2 |
| (<i>R</i>)- 1 ² | H | H | 207–208 | +34.1 ^b | (CH ₂) ₄ O | Ref 2 |
| (<i>R</i>)- 2 ³ | CH ₂ OH | H | 192–195 | +64.1 | (CH ₂) ₄ O | Ref 3 |
| (<i>R</i>)- 3 ⁴ | CH ₃ | H | 202–204 | +30.2 | CHCl ₃ | 25 |
| (<i>S</i>)- 4 ⁴ | H | (CH ₂ CH ₂ O) ₂ Ts | Oil | –30.7 | (CH ₂) ₄ O | 70 |
| (<i>R</i>)- 4 ⁴ | H | (CH ₂ CH ₂ O) ₂ Ts | Oil | +31 | (CH ₂) ₄ O | 68 |

^a c, 1.0. ^b Sodium D line.

of (*R*)-**3** with (*R*)-**4** and potassium hydroxide in THF and water at reflux for 100 hr gave (*RR*)-**8**. Similarly, (*S*)-**4** and (*S*)-**1** gave (*SS*)-**5**, and (*R*)-**4** and (*R*)-**1** gave (*RR*)-**5**. Reaction of (*R*)-**4** with optically pure (*R*)-**2**³ gave (*R,R*)-**6**, which with SOCl₂ gave (*R,R*)-**7**, which with LAH gave (*R,R*)-**8** (Chart II). The known absolute

Chart II



| Compd no. | R | Mp, °C | $[\alpha]_{D}^{25}$, deg | Solvent ^a | Yield, % |
|---------------------------------------|--------------------|--------------------------------|---------------------------|---------------------------------|-----------------|
| (<i>S,S</i>)- 5 ² | H | 123–126 (solvate) ² | –221 | CH ₂ Cl ₂ | 31 ^b |
| (<i>R,R</i>)- 5 ² | H | 123–126 (solvate) ² | +221 | CH ₂ Cl ₂ | 22 ^b |
| (<i>R,R</i>)- 6 ⁴ | CH ₂ OH | Oil | +170 | CHCl ₃ | 28 ^b |
| (<i>R,R</i>)- 7 ⁴ | CH ₂ Cl | Oil | +122 | CHCl ₃ | 76 |
| (<i>R,R</i>)- 8 ⁴ | CH ₃ | Oil | +152 | CHCl ₃ | 80 |
| (<i>R,R</i>)- 8 ⁴ | CH ₃ | Oil | +152 | CHCl ₃ | 32 ^b |

^a c, 0.8–1.0. ^b Yields on ring closure.

configurations of **2**^{3b} and **1**² indicate the absolute configurations of **5**–**8**.

Optically pure diastereomeric complexes, (*R,R*)-**5**·(*R*)-**9** and (*S,S*)-**5**·(*R*)-**9**, were prepared by extracting at -3° a 1.25 *M* solution of the hexafluorophosphate salt of 6 equiv of (*R*)-phenylglycine methyl ester ((*R*)-**9**) in D₂O (1.25 *M* in NaPF₆) with a 0.16 *M* solution (1-equiv) of each enantiomeric cycle in CDCl₃.⁶ The pmr spectra of the solutions were taken, and indicated $[\text{guest}]/[\text{host}] = 0.8$. Comparisons of the chemical shifts (δ) of **5** alone (CH₂OCH₂, 3.09; ArOCH₂, 3.74) and of each

(6) In the absence of cycle, no detectable ester salt was extracted.