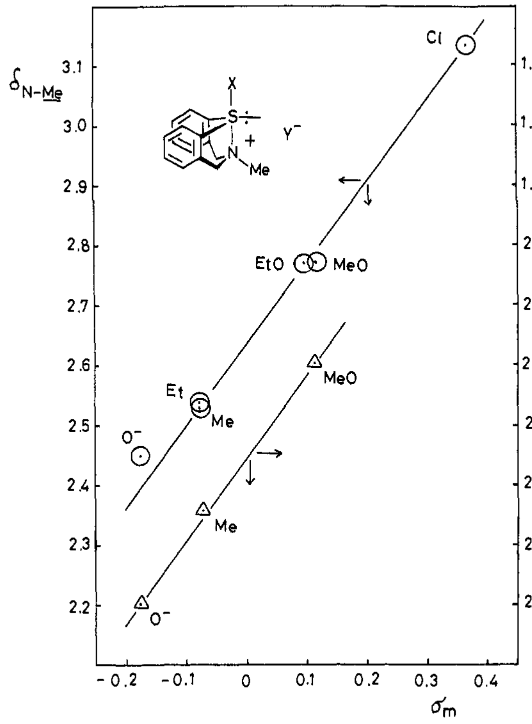


Figure 1. Hammett plot against σ_m of ^1H NMR chemical shifts of the NMe group and S-N bond distances of **3**.

been shown to be more stable and rigid than twist-boat (*TB*) and/or boat-boat (*BB*) conformations. By considering these results, we realized that there is a definite attractive force between the amino and the sulfonio groups of **3** which is strong enough at least to fix the conformation as *TB* or *BB*, exclusively.

A Hammett plot of chemical shifts of NMe of **3** against σ_m shows a very good straight line with positive ρ value ($\delta_{NMe} = 1.35\sigma_m + 2.63$, $r = 0.999$, $n = 5$) as shown in Figure 1. This fact further indicates that these compounds maintain the same conformation in solution and that the electron-withdrawing effect of the substituent at the sulfur is transmitted to the NMe group through the N-S bond.

X-ray crystallographic analysis established the proposed structures of **2**, **3a**, and **3c**.[9] The molecular structure of *S*-methylsulfurane **3a** is shown in Figure 2.[10] Since the geometry around the sulfur is essentially trigonal bipyramidal,[9] **3a** is concluded to be the first example of the stable σ-alkylsulfurane with an apical methyl group.

The S-N bond distances of three compounds also fit the same Hammett relationship as chemical shifts of the NMe group (Figure 1), and the bond distance becomes shorter as the electron-withdrawing effect of X increases.

Formation of iodosulfuranes as intermediates is proposed on the basis of kinetic study of the oxidation of the sulfur of methionine[11] and 5-methyl-1-thia-5-azacyclooctane.[12] The present study offers strong support for these observations.

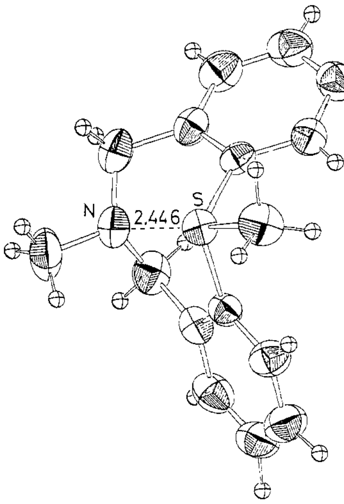


Figure 2. ORTEP drawing of *S*,*N*-dimethylammonioalkylsulfurane **3a**.[10]

Registry No. 2, 87532-42-1; **3a** (Y = PF_6), 87532-44-3; **3b** (Y = PF_6), 87532-46-5; **3c** (Y = $SbCl_6$), 87532-48-7; **3d** (Y = $SbCl_6$), 87532-50-1; **3e**-i (Y = Cl), 87532-51-2; **3e**-ii (Y = $SbCl_6$), 87532-53-4; **3e**-iii (Y = PF_6), 87532-54-5.

Supplementary Material Available: ORTEP drawings of **2**, **3a**, and **3c** and tables of crystal data and bond lengths and angles (6 pages). Ordering information is given on any current masthead page.

---

(8) (a) Gellatly, R. P.; Ollis, W. D.; Sutherland, I. O. *J. Chem. Soc., Perkin Trans. 1* **1976**, 913. (b) Renaud, R. N.; Bovenkamp, J. W.; Franser, R. R.; Roustan, J. L. A. *Can. J. Chem.* **1977**, *55*, 3456. (c) Leonard, N. J.; Ōki, M.; Chiavarelli, S. *J. Am. Chem. Soc.* **1955**, *77*, 6234. (d) Brieaddy, L. E.; Hurlbert, B. S.; Mehta, N. B. *J. Org. Chem.* **1981**, *46*, 1630.

(9) X-ray data of **2**, **3a**, and **3c** concerning the following items are shown below: (i) the distance between the sulfur and the nitrogen, (ii) the distance between the sulfur and the X atom, (iii) the angle ∠X-S-N, (iv) the angle ∠N-S-C_e, (v) the angle ∠C_e-S-C_e. **2** (i) 2.609 Å, (ii) 1.501 Å, (iii) 179.4°, (iv) 75.6°, (v) 98.9°; **3a** (i) 2.446 Å, (ii) 1.804 Å, (iii) 176.9°, (iv) 79.7°, (v) 104.6°; **3c** (i) 2.206 Å, (ii) 1.658 Å, (iii) 175.3°, (iv) 81.7°, (v) 107.7°. Sum of the van der Waals radii of S and N is 3.35 Å. There are several interesting points in these structures, and full details will be published elsewhere by F. Iwasaki and K. Akiba.

(10) Johnson, C. K. ORTEP Report ORNL-3794, 1965, Oak Ridge National Laboratory, TN.

(11) Young, P. R.; Hsieh, L. S. *J. Am. Chem. Soc.* **1978**, *100*, 7121.

(12) Doi, J. T.; Musker, W. K. *J. Am. Chem. Soc.* **1981**, *103*, 1159. Doi, J. T.; Musker, W. K.; deLeeuw, D. L.; Hirschon, A. S. *J. Org. Chem.* **1981**, *46*, 1239.

(13) All new compounds **3a-e** except **3e**-i (Y = Cl) gave correct elemental analyses. The melting point (°C) and yield (%) of **3** are listed: **3a**, 195-197, 16; **3b**, 195-198, 35; **3c**, 148-151, 49; **3d**, 176-178, 61; **3e**-ii, 170-173, 57; **3e**-iii, 145-155 dec, 34.

(14) Partial support of this work was provided by a Grant-in Aid for Scientific Research (No. 57430006) administered by the Ministry of Education, Science and Culture of Japanese Government.

Optical Activity due to Exciton Interaction between ^1B Transitions of Benzene Chromophores

Keiji Shingu,* Seiichi Imajo,[1] and Hiroko Kuritani

Department of Chemistry, Faculty of Science
Osaka University, Toyonaka, Osaka, 560 Japan

Sanji Hagishita and Kaoru Kuriyama*

Shionogi Research Laboratories, Shionogi & Co., Ltd.
Sagisu, Fukushima-ku, Osaka, 553 Japan

Received June 15, 1983

Dipole-dipole interactions between the ^1B_b transitions of naphthalene or anthracene chromophores[2] in chiral molecules have been shown to cause distinct CD couplets in agreement with expectations from the exciton theory. However, the exciton approach has thus far been regarded as unsuitable for analyzing CD spectra associated with the ^1B transition of *benzene chromophores*[3]

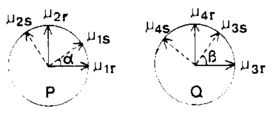
---

[1] Present address: Suntory Institute for Biomedical Research, Wakayamadai, Shimamoto-cho, Mishima-gun, Osaka, 618 Japan.

(2) (a) Mason, S. F.; Seal, R. H.; Roberts, D. R. *Tetrahedron* **1974**, *30*, 1671. (b) Harada, N.; Takuma, Y.; Uda, H. *J. Am. Chem. Soc.* **1978**, *100*, 4029. (c) Shingu, K.; Imajo, S.; Kuritani, H. *J. Am. Chem. Soc.* **1982**, *104*, 4272.

(3) See, e.g.: Snatzke, G.; Kajtar, M.; Snatzke, F. In "Fundamental Aspects and Recent Developments in Optical Dispersion and Circular Dichroism"; Ciardelli, F., Salvadori, P., Eds.; Heiden and Son: London, 1973; p 148. They pointed out also that some molecules containing only one benzene chromophore show couplet features in the ^1B region. We think, however, that such features are possibly caused by the small splitting of the degenerate levels due to the perturbation effect of the substituents. Only a positive CD was observed for (*S*)-3-*tert*-butyl-1,1-dimethylindan, which is the monomer of the spiro compounds illustrated in this paper. Its intensity was much weaker than the CDs arising from the exciton coupling of two benzene chromophores.[7]

Scheme I



because no definite assignment of the polarization directions of local transition moments can be made due to the degenerate character of the ^{1}B transition.[4] We report here that the degeneracy does not prevent the exciton approach since any choice of polarization directions gives the same final result of calculation.

Let us suppose a molecule contains two benzene chromophores P and Q which are not conjugated. The local ^1B_a and ^1B_b transition moments (denoted by $\vec{\mu}_1$ and $\vec{\mu}_2$ for P and $\vec{\mu}_3$ and $\vec{\mu}_4$ for Q), lying mutually perpendicular within the benzene plane, are equal in magnitude and located at the center of each benzene ring. Let us arbitarily choose two different polarization modes, r and s, and use μ_r and μ_s for the set of local transition moments in each mode (Scheme I).

$$\mu_r = (\vec{\mu}_{1r}\ \vec{\mu}_{2r}\ \vec{\mu}_{3r}\ \vec{\mu}_{4r}) \qquad \mu_s = (\vec{\mu}_{1s}\ \vec{\mu}_{2s}\ \vec{\mu}_{3s}\ \vec{\mu}_{4s}) \tag{1}$$

Since μ_r can be transformed into μ_s by its rotation through angles α and β within the benzene planes P and Q, respectively, μ_s is interrelated with μ_r by orthogonal matrix $\boldsymbol{\theta}$. Thus,

$$\theta = \begin{pmatrix} \cos\alpha & -\sin\alpha & 0 & 0 \\ \sin\alpha & \cos\alpha & 0 & 0 \\ 0 & 0 & \cos\beta & -\sin\beta \\ 0 & 0 & \sin\beta & \cos\beta \end{pmatrix} \tag{2}$$

$$\mu_s = \mu_r\theta \quad \text{or} \quad \mu_s{}^T = \theta^T\mu_r{}^T = \theta^{-1}\mu_r{}^T \tag{3}$$

where the superscripts T and −1 denote the transposed and inverse matrices, respectively. The interaction energies between the local transitions for polarization mode r are represented by symmetric matrix $\mathbf{H}_r$.

$$\mathbf{H}_r = \mu_r{}^T|H|\mu_r \tag{4}$$

where $|H|$ is the Hamiltonian energy operator, the diagonal elements, $\vec{\mu}_{ir}|H|\vec{\mu}_{ir}$ $(i = 1\text{–}4)$, are the equal energy levels of the local transitions, and the off-diagonal elements, $\vec{\mu}_{ir}|H|\vec{\mu}_{jr} = \vec{\mu}_{jr}|H|\vec{\mu}_{ir} = {}^rV_{ij}$ $(i \neq j)$, are the interaction energies between local transitions evaluated by using the point–dipole–point–dipole approximation[6] (${}^rV_{12}$ and ${}^rV_{34}$ are zero because of orthogonality). If we can find, through the variational method, eigenvector matrix $\mathbf{C}_r$ (mixing coefficients of local transitions) and eigenvalue matrix $\mathbf{E}_r$ (energy levels of the mixed states) for $\mathbf{H}_r$, then

$$\mathbf{C}_r{}^{-1}\mathbf{H}_r\mathbf{C}_r = \mathbf{E}_r \tag{5}$$

Expressions for polarization mode s, which are similar to (4) and (5), are transformed as follows using relation (3).

$$\mathbf{H}_s = \mu_s{}^T|H|\mu_s = \theta^{-1}\mu_r{}^T|H|\mu_r\theta = \theta^{-1}\mathbf{H}_r\theta \tag{6}$$

$$\mathbf{C}_s{}^{-1}\mathbf{H}_s\mathbf{C}_s = \mathbf{C}_s{}^{-1}\theta^{-1}\mathbf{H}_r\theta\mathbf{C}_s = \mathbf{E}_s \tag{7}$$

Since only one $\mathbf{C}_r$ and only one $\mathbf{E}_r$ should exist for $\mathbf{H}_r$, we obtain the following relation by comparison of (5) with (7).

$$\mathbf{C}_s = \theta^{-1}\mathbf{C}_r \quad \text{and} \quad \mathbf{E}_s = \mathbf{E}_r \tag{8}$$

Thus the energy levels of the mixed states are not influenced by the choice of the polarization modes of the local transitions.

Furthermore, the electric transition moments ($\vec{m}_{jr}$) of the jth state $(j = 1\text{–}4)$ resulting from polarization mode r are represented by

$$\vec{m}_{jr} = {}^rC_{1j}\vec{\mu}_{1r} + {}^rC_{2j}\vec{\mu}_{2r} + {}^rC_{3j}\vec{\mu}_{3r} + {}^rC_{4j}\vec{\mu}_{4r} \tag{9}$$

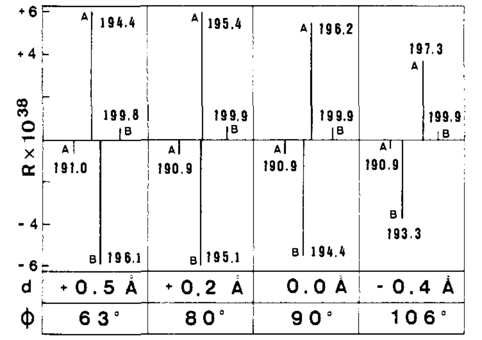


Figure 1. Illustration of conformation dependence of the rotational strength calculated for (1*S*)-1,1′-spirobiindan. *d* is the deviation of the flap atom of the cyclopentene ring, and ϕ is the dihedral angle between two benzene planes.

where ${}^rC_{ij}$ $(i = 1\text{–}4)$ are the jth column elements of matrix $\mathbf{C}_r$. If we use $\mathbf{M}_r$ for the set of $\vec{m}_{jr}$, then

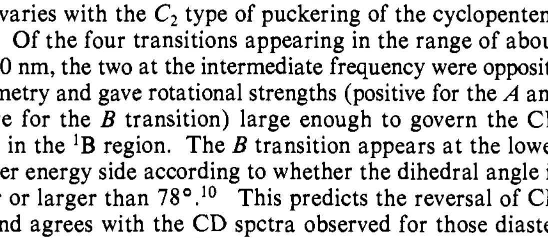
$$\mathbf{M}_r = (\vec{m}_{1r}\ \vec{m}_{2r}\ \vec{m}_{3r}\ \vec{m}_{4r}) = \mu_r\mathbf{C}_r \tag{10}$$

A similar expression for polarization mode s is transformed as follows from relations (3) and (8).

$$\mathbf{M}_s = \mu_s\mathbf{C}_s = \mu_r\theta\theta^{-1}\mathbf{C}_r = \mu_r\mathbf{C}_r = \mathbf{M}_r \tag{11}$$

This means that the electric transition moment and, consequently, the dipole strength of each mixed state are independent of the choice of polarization modes. That is also the case with the magnetic transition moment and accordingly the rotational strength, as long as the degenerate local transition moments are located at the same position. Thus it is clear that the exciton approach is applicable to the case of the degenerate transition as well.

On the basis of the foregoing arguments, we calculated the dipole and rotational strengths of the diastereomers of 3,3′-di-*tert*-butyl-1,1′-spirobiindan reported previously[7] using the three different polarization modes a, b, and c.[8] In accordance with expectations, all polarization modes led to the same calculation result for each diastereomer. Figure 1 illustrates the conformation dependence of the rotational strength calculated for (1*S*)-1,1′-spirobiindan in which the dihedral angle between two benzene planes varies with the C_2 type of puckering of the cyclopentene rings.[9] Of the four transitions appearing in the range of about 190–200 nm, the two at the intermediate frequency were opposite in symmetry and gave rotational strengths (positive for the *A* and negative for the *B* transition) large enough to govern the CD feature in the ^{1}B region. The *B* transition appears at the lower or higher energy side according to whether the dihedral angle is smaller or larger than 78°.[10] This predicts the reversal of CD signs and agrees with the CD spctra observed for those diastereomers in the ^{1}B regions.[7,9]



---

[4] Linear dichroism measurements have shown that the strong, allowed ^{1}B transition moments of substituted benzenes are usually degenerate in energy and of the same order of magnitude.[5]

[5] Sagiv, J. *Tetrahedron* **1977**, *33*, 2303.

[6]

$$V_{ij} = \frac{1}{R^3}\left[\vec{\mu}_i\cdot\vec{\mu}_j - \frac{3(\vec{\mu}_i\cdot\vec{R})(\vec{\mu}_j\cdot\vec{R})}{R^2}\right]$$

where R is the distance between the centers of two benzene rings P and Q.

[7] Imajo, S.; Kato, A.; Shingu, K. *J. Chem. Soc., Chem. Commun.* **1978**, 810; **1979**, 25.

[8] The values of 6.35 eV (195 nm) and 1.59 × 10^{-35} cgs, respectively, were adopted as the energy level and the dipole strength of the local ^1B_a and ^1B_b states.

[9] ^{1}H NMR spectroscopy showed that the dihedral angles between two benzene planes are ca. 65°, 90°, and 105° for the 1*S*,3*R*,3′*R*, 1*S*,3*R*,3′*S*, and 1*S*,3*S*,3′*S* isomers, respectively, owing to the puckering of the cyclopentene rings in which the *tert*-butyl groups tend to assume quasi-equatorial orientations for each diastereomer.[7] While the 1*S*,3*R*,3′*S* isomer does not belong to the point group C_2, its calculated rotational strength was found to be almost the same as that for the nonpuckered C_2 conformer (d = 0 Å, ϕ = 90°).

[10] Even if the ^1L_a and ^1L_b transition moments are taken into account for this calculation, the results in the ^{1}B region are almost unchanged. A similar type of inversion of the energy levels of *A* and *B* coupling was observed for the ^1B_b transition of 1,1′-spirobi[benz[*g*]indan].[2c]