

but they are not easy to reconcile with our observations. Further experiments are desirable.

Isotopic rate ratios much larger than 10 are not impossible where tunneling occurs but will not be observed where the energy barrier is low, as in the reactions of 4-NPNM with other imines.⁷ A high value (30 ± 2 at 25 °C) has also been found for the reaction of 4-NPNM with 1,8-bis(dimethylamino)-2,7-dimethoxynaphthalene, where the base has no exchangeable proton, in chlorobenzene.⁸ Values of 30 to 50 have also been reported for other reactions.⁹⁻¹² A full paper is in preparation.

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Circular Dichroism and Absolute Configuration of C₃-Chiral Derivatives of Cyclotrimeratrylene

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Recently, we have described several optically active derivatives of cyclotrimeratrylene (1) (CTV) having C₃ symmetry.^{1,2} In this communication, we report that the absolute configurations of these compounds may be correctly established by means of an exciton analysis of their circular dichroism.

The "crown" is the only stable conformation of CTV;³⁻⁵ that derivatives 2 and 3 behave similarly is indicated by the ¹H NMR spectra and by their optical activity.¹ The only observable conformational change is a slow interconversion between two identical (1) or enantiomeric (2 and 3) crown conformers, which leads to racemization when the compounds involved are optically active. We have measured⁶ the energy barrier for such ring inversion in 3. The value found ($E_a = 27.0 \pm 0.3$ kcal·mol⁻¹) is nearly identical

(1) Collet, A.; Jacques, J. *Tetrahedron Lett.* 1978, 1265-8. Cyclotrimeratrylene is also named 10,15-dihydro-2,3,7,8,12,13-hexamethoxy-5H-tribenzo[*a,d,g*]cyclononene.

(2) Collet, A.; Gabard, J. *J. Org. Chem.* 1980, 45, 5400. The following Arrhenius and Eyring activation parameters for ring inversion of (C₃-CTV-*d*₉) (formula 1, with R' = CD₃) have been measured: $E_a = 26.5 \pm 0.5$ kcal·mol⁻¹, $A = (0.7 \pm 0.5) \times 10^{13}$, $\Delta G_{25}^\ddagger = 26.5 \pm 0.1$ kcal·mol⁻¹, $\Delta H^\ddagger = 25.9 \pm 0.5$ kcal·mol⁻¹, $\Delta S^\ddagger = -1.9 \pm 2$ eu.

(3) (a) Erdtman, H.; Haglid, F.; Ryhage, R. *Acta Chem. Scand.* 1964, 18, 1249-54. (b) Miller, B.; Gesner, B. D. *Tetrahedron Lett.* 1965, 3351-4. (c) Lindsey, A. S. *J. Chem. Soc.* 1965, 1685-92. (d) Cookson, R. C.; Halton, B.; Stevens, I. D. R. *J. Chem. Soc. B* 1968, 767-74. (e) Sato, T.; Uno, K. *J. Chem. Soc., Perkin Trans. 1* 1973, 895-900. (f) Dale, J. *Top. Stereochem.* 1976, 9, 199 (see pp 248-50).

(4) Those CTV derivatives substituted at the methylene positions or at the aromatic positions ortho to the nine-membered ring may adopt flexible "saddle" conformations; see, for examples, ref 3d-f. Owing to their conformational mobility, no stable optical activity is expected for these conformers.

(5) Crystal structure of CTV: Cerrini, S.; Giglio, E.; Mazza, F.; Pavel, N. V. *Acta Crystallogr., Sect. B* 1979, 35, 2605-9.

(6) The racemization of (+)-3 was followed polarimetrically at 436 nm in chloroform solution. From the first-order rate constants at 37, 46, and 55.8 °C the following activation parameters were derived: $E_a = 27.0 \pm 0.3$ kcal·mol⁻¹, $A = (1.4 \pm 0.9) \times 10^{13}$, $\Delta G_{25}^\ddagger = 26.5 \pm 0.1$ kcal·mol⁻¹, $\Delta H^\ddagger = 26.4 \pm 0.3$ kcal·mol⁻¹, $\Delta S^\ddagger = -0.5 \pm 1$ eu.

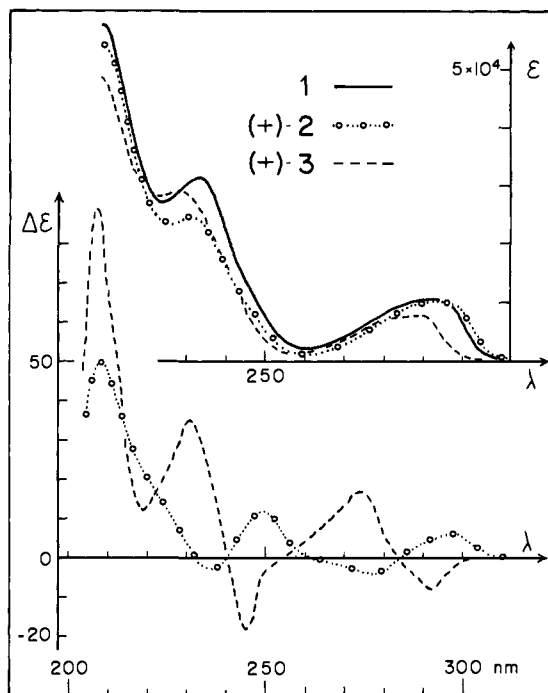
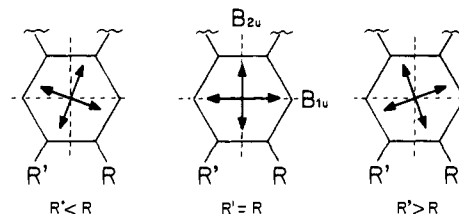
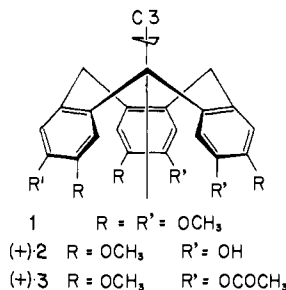


Figure 1. Isotropic absorption spectra and circular dichroism spectra in methanol.¹⁷

Scheme I



with that observed² for (C₃)-cyclotrimeratrylene-*d*₉ (26.5 ± 0.5 kcal·mol⁻¹); the rate constants for the (+) → (-) process are close to 10⁻⁷ s⁻¹ at 20 °C in both cases, indicating a mean half-life of the order of 10⁶-10⁷ s for a given crown at room temperature. In view of these data, it may be assumed that the circular dichroism (CD) spectra discussed here originate from homogeneous populations of such C₃ conformers.



The CD spectra of the triphenol (+)-2 and of its triacetate (+)-3 (Figure 1) show two exciton patterns centered at ca. 284 and 240 nm, which are connected to the benzene B_{2u} and B_{1u} transitions, respectively. A striking feature of these spectra is that acetylation of the triphenol reverses the signs of these CD couplets.

The intensities of the B_{2u} and B_{1u} transitions of aromatic derivatives are currently interpreted in terms of spectroscopic moments.^{7,8} For the CTV derivatives 2 and 3, the presence of two different substituents R and R' causes in each of the phenyl rings a rotation of the electric dipole transition moments with respect

(7) (a) Platt, J. R. *J. Chem. Phys.* 1951, 19, 263. (b) Petruska, J. *Ibid.* 1961, 34, 1120.

(8) (a) Sagiv, J. *Tetrahedron* 1977, 33, 2303. (b) *Ibid.* 1977, 33, 2315.

to the short (B_{2u}) and long (B_{1u}) axes of the rings. The sense and the extent of the rotation depend critically on the relative magnitude of the spectroscopic moments of R and R', as shown in Scheme I.

For a given absolute configuration, one obtains, when the spectroscopic moment of R is greater than that of R' ($R > R'$), a helical relationship of the electric transition moments, whose chirality is inverted when $R < R'$. It follows that the signs of the exciton CD bands in (+)-2 and (+)-3 should be determined by the relative magnitude of the spectroscopic moments of R and R'.

In the exciton approximation, the wave functions of CTV derivatives having C_3 symmetry can be expressed as^{9,10}

$$\psi_0 = \chi_1 \chi_2 \chi_3$$

$$\psi_A = \frac{1}{\sqrt{3}}(\chi_1^* \chi_2 \chi_3 + \chi_1 \chi_2^* \chi_3 + \chi_1 \chi_2 \chi_3^*)$$

$$\psi_E = \frac{1}{\sqrt{2}}(\chi_1 \chi_2^* \chi_3 - \chi_1 \chi_2 \chi_3^*)$$

$$\psi_E = \frac{1}{\sqrt{6}}(2\chi_1^* \chi_2 \chi_3 - \chi_1 \chi_2^* \chi_3 - \chi_1 \chi_2 \chi_3^*)$$

where 1, 2, and 3 label each benzene ring and the star indicates excitation. In the trimer we have thus, for each benzene transition, three excitations, two of which (E) are degenerate. The splitting ($3V$) between the A and the E components can be semiquantitatively evaluated by using the point-dipole/point-dipole approximation

$$V = \frac{1}{d^3} \mu_1 \cdot \mu_2 - \frac{3(\mu_1 \cdot d)(\mu_2 \cdot d)}{d^5}$$

where μ 's are the transition moment vectors and d is the distance between their centers (in the present case, the point dipoles are located at the centers of the benzene rings and are separated by $d = 4.79 \text{ \AA}$).¹¹

The rotational strengths are evaluated as

$$R_A = 3\pi\nu r D_{\text{mon}} \cos \theta \sin \theta \cos \phi = -2R_E$$

where ϕ is the angle between the plane of a benzene ring and the C_3 axis ($43 \pm 2^\circ$),¹² θ represents the rotation of the transition moment of each benzene ring with respect to the short-axis direction, r is the distance of the centers of each benzene ring from the C_3 axis (2.78 \AA) and D_{mon} is the dipole strength of the individual aromatic chromophore, evaluated from absorption spectra.¹³

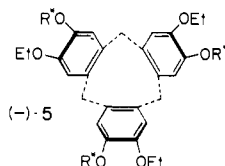
Several values of substituent spectroscopic moments are reported in the literature.^{7,8,14} The most recent data are those of Sagiv,⁸ which were evaluated from linear dichroism spectra, taking into account vibrational components. In particular, the acetoxy group

(9) Bosnich, B. *Acc. Chem. Res.* **1969**, *2*, 266.

(10) Mason, S. F. *Inorg. Chim. Acta* **1968**, *2*, 89.

(11) We emphasize that the exact location of the point dipole does not represent a critical problem in this system. The value of d given is taken from ref 12.

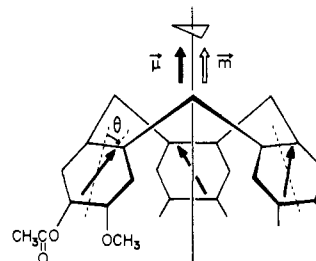
(12) Cesario, M.; Collet, A.; Gabard, J.; Guilhem, J.; Jacques, J.; Pascard, C., submitted for publication. We have determined by single-crystal X-ray analysis the structure of compound (-)-5, which incorporates the chiral group $R^* = \text{CH}(\text{CH}_3)\text{CO}_2\text{CH}_3$ of known absolute configuration as an internal reference; (+)-2 was chemically related to (-)-5 and its absolute stereochemistry so established unambiguously.



(13) Dipole strength is defined as $D = 91.8 \times 10^{-40} \int \epsilon/\nu \, d\nu$. Experimental rotational strength was evaluated as $R = 22.9 \times 10^{-40} \int \Delta\epsilon/\nu \, d\nu$.

(14) Quantitative data of spectroscopic moments are pertinent only to B_{2u} transitions.

Scheme II. In-Phase Coupling of B_{2u} Electric Transition Moments in (+)-3 ($\theta > 0$)



has a spectroscopic moment of $+10 \text{ (cm}\cdot\text{mol}\cdot\text{L}^{-1})^{-1/2}$, which is unambiguously smaller than that of the methoxy group (from $+26$ to $+36 \text{ (cm}\cdot\text{mol}\cdot\text{L}^{-1})^{-1/2}$). However, the data available do not allow us to distinguish between the relative magnitudes of those of methoxy and hydroxy groups.¹⁵ The isotropic absorption spectra of 1 and 2 (Figure 1) do not give any more information on this point.

This ambiguity is ruled out by considering the CD spectra of (+)-2 and (+)-3. Once the spectroscopic moment of OCOCH_3 (R') is established as smaller than that of OCH_3 (R), it follows that OH should have a moment *greater* than OCH_3 .

The absolute configuration of (+)-2 and (+)-3 is that indicated in the structural formula.^{16,17} In fact, when θ is positive ($\text{OCOCH}_3 < \text{OCH}_3$), in-phase A coupling of the electric moments produces for the B_{2u} transition *parallel* electric and magnetic resultant transition moments, collinear with the C_3 axis, leading to *positive* CD at higher energy (Scheme II). Out-of-phase E coupling leads to *antiparallel* moments perpendicular to the C_3 axis, giving a *negative* CD at lower energy.

For the B_{1u} transition, the vectors must be rotated by 90° . A coupling causes a negative CD at lower energy, while the E coupling gives a positive CD at higher energy. The CD spectrum of (+)-3 actually exhibits this sequence of signs. Given the above, a mirror-image relationship of the CD spectrum obtains when $R' = \text{OH}$, $R = \text{OCH}_3$ (θ negative).

Quantitative calculations were carried out only for the B_{2u} transition of compound (+)-3, since only in this case are accurate values of spectroscopic moments available.⁸ The value of θ was estimated to ca. 28° . Calculated values of the rotational strengths ($R = +$ and -50×10^{-40} cgsu from low to high energy) are in fairly satisfactory agreement with experimental data (-6×10^{-40} and $+20 \times 10^{-40}$), taking into account the usual cancellation of the exciton couplets. The splitting between the two exciton components is calculated to be ca. 300 cm^{-1} . The experimental value from the CD spectrum (2300 cm^{-1}) is certainly overestimated on account of the above-mentioned band cancellation.

In the case of compound (+)-2, a value of θ in the range of -3 to -4° must be adopted in order to obtain agreement between experimental and calculated rotational strengths. This leads to values of the spectroscopic moments for OH and OCH_3 not far from those given by Platt.^{7a}

The absolute configurations deduced from the exciton analysis of the CD spectra of (+)-2 and (+)-3 were confirmed by an X-ray crystal structure determination.¹² It may be concluded from the above analysis that the study of the CD of (C_3)-cyclotrimertrylene derivative should provide a sensitive differential measurement of the relative magnitude of nearly equivalent spectroscopic transition moments.

(15) The following values (in Platt's units) have been reported for OH and OCH_3 , respectively: Platt^{7a} $+34$ and $+31$; Petruska^{7a} $+32$ and $+33.6$; Sagiv⁸ $+33 \pm 3$ for both.

(16) These absolute configurations should be designated as $M(+)-2$ and $P(+)-3$, in accordance with the IUPAC rules. We are particularly indebted to Professor V. Prelog for this specification, which is discussed in detail in ref 12.

(17) The samples of (+)-2 and (+)-3 examined had $[\alpha]_{D}^{25} +268$ and $+162^\circ$, respectively (in chloroform). Since they derive from a diastereomerically pure precursor,¹ it may be expected that their enantiomeric purity is in the range 90–100%.