dioxide had evaporated, 25 mL of saturated aqueous sodium bisulfate and 25 mL of ether were added followed by 3 mL of concentrated hydrochloric acid or enough to reach pH 2. The layers were separated, the aqueous layer reextracted with 15 mL of ether and the combined organic layers dried (Na_2SO_4). The organic layer was then cooled to 0 °C and stirred while an ethereal solution of diazomethane was added portionwise until TLC showed complete reaction. Removal of solvent by atmospheric distillation followed by flash chromatography (5% ether in pentane), reconcentration, and distillation (bulb-to-bulb, 80 °C, 0.02 mmHg) yielded 110 mg (0.99 mmol 66%) of ester from the ketone. R_f 0.22 (4:1 hexane/ethyl acetate) for the acid, 0.55 for the ester. The following data were obtained on a sample containing 20% of the bridgehead olefin and a 2:1 ratio of methyl epimers: ^{1}H NMR (270 MHz) 6.68 (m, 1 H), 4.98 (m, 0.13 H), 4.93 (q, J = 2, 0.07 H), 4.88 (m, 0.13 H), 4.86 (q, J = 2, 0.07 H), 4.79 (m, 0.36 H), 4.76 (m, 0.44 H), 4.69 (m, 0.8 H), 3.73 (s, 1.6 H), 3.72 (s, 1.4 H), 3.35 (m, 2 H), 2.9–2.6 (m, 2 H), 2.3–2.1 (m, 3 H), 1.14 (d, J = 7, 0.21 H), 1.09 (d, J = 7, 1.32 H), 0.96 (d, J = 7, 1.08 H), 0.86 (d, J = 8, 0.39 H); IR ($CHCl_3$) 2962, 1705, 1636, 1438, 1275, 1100, 900, 632; MS 192 (54), 161 (13), 160 (19), 133 (62), 132 (50), 117 (22), 105 (17), 91 (26). Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.96; H, 8.39; MW, 192.1150. Found: C, 74.79; H, 8.39; MW, 192.1151.

Preparation of 2-Carbomethoxy-6-methyl-7-methylenebicyclo[3.3.0]-oct-7-ene (20). *n*-Butyllithium (0.56 mL, 0.97 mmol of 1.74 M hexane solution) and HMPA (174 mg, 0.97 mmol) were added to a −78 °C solution of 0.85 mL of THF and 98 mg of diisopropylamine (0.97 mmol). After allowing the solution to warm to −30 °C until the solution became homogeneous, the flask was recooled to −78 °C and the ester (125 mg, 0.65 mmol) in 0.94 mL of THF was added dropwise over 10 min. The light yellow solution was allowed to stir for an additional 10 min, then cannulated onto a biphasic ether/saturated aqueous sodium bisulfate solution (5 mL each), to which was added 15 mL of pentane. After separation, the organic layer was washed with aqueous sodium bicarbonate (1 × 2 mL), saturated aqueous cupric sulfate (2 × 3 mL), water (1 × 2 mL), and dried (Na_2SO_4). Solvent removal via atmospheric distillation followed by bulb-to-bulb distillation [80 °C (0.01 mmHg)] yielded 101 mg (0.45 mmol, 69%) of product. ^{1}H NMR (270 MHz) 6.42 (bs, 0.04 H), 6.35 (bs, 0.08 H), 5.90–5.78 (m, 0.88 H), 5.70–5.60 (m, 0.88 H), 4.80–4.60 (m, 2.0 H); four singlets, 3.73, 3.71, 3.70, 3.69 (3 H), 3.01–1.81 (m, 6 H), 1.14 (d, J = 6.8 Hz, 0.88 H), 1.13 (d, J = 6.8 Hz, 1.76 H), 0.95 (d, J = 6.8 Hz, 0.12 H), 0.93 (d, J = 6.8 Hz, 0.24 H). IR ($CHCl_3$): 1729, 1460, 1440 cm^{-1}. These spectral data represent a sample with 12% of the olefin isomer and a 2:1 ratio of methyl epimers.

Preparation of 1-*O*-Methyldehydrologanin Aglucon (21b). A dry stream of O_3/O_2 was bubbled into a −78 °C solution of 39.5 mg (0.18 mmol, 0.21 mmol of combined olefin isomers) of **20** in 4 mL of methylene chloride until a blue color appeared. After removing the excess ozone with a stream of nitrogen, the solvent was removed in vacuo followed by 2 min on a vacuum pump. Reduction was then accomplished by dissolving the bis(ozonide) in 3 mL of acetic acid and adding zinc dust (80 mg, 1.23 mm) in one portion followed by stirring at room temperature for 2 h. The solution was then added to a separatory funnel containing 25 mL each of ether and saturated aqueous sodium bicarbonate. Solid sodium bicarbonate was added until the acetic acid was decomposed. The aqueous layer was extracted further with ether (3 × 25 mL). The combined organic layers were dried ($MgSO_4$) and concentrated to yield crude hydroxyacetal. The oil was dissolved in 3 mL of methanol containing TsOH (17 mg, 0.1 mmol) for 2 days at room temperature. Sodium methoxide (20 mg, 0.37 mm) was then added to the flask in a glovebag and the flask was kept at 2 °C for 18 h. The reaction was neutralized with acetic acid, concentrated in vacuo, extracted with ether, washed with aqueous sodium bicarbonate, dried ($MgSO_4$), and plated (6:4 hexane/ethyl acetate) to yield 12.1 mg (0.05 mm, 28%) of quite pure material which was identical with material obtained from degradation of natural loganin: R_f 0.30 (6:4 hexane/ethyl acetate) for hydroxyacetal, 0.50 for methoxyacetal. Evidently the deconjugated olefin isomer forms a keto acid upon ozonolysis which is lost in the basic workup.

Acknowledgment. We thank the National Science Foundation and the National Institutes of Health, General Medical Sciences, for their generous support of our programs.

Registry No. *exo*-**6**, 79348-44-0; *endo*-**6**, 79390-46-8; **7a**, 79348-40-6; **7b**, 94235-18-4; **7c**, 94235-19-5; **9**, 91495-68-0; **10**, 94235-20-8; (*Z*)-**11**, 94235-21-9; (*E*)-**11**, 94235-22-0; *exo*-**18**, 94235-23-1; *endo*-**18**, 94235-24-2; **19** (isomer 1), 94235-25-3; **19** (isomer 2), 94235-26-4; **20**, 94235-27-5; **20** (bis(ozonide)), 94235-31-1; **21a**, 86342-78-1; **21b**, 50427-62-8; **22**, 94235-28-6; **23** (isomer 1), 94292-76-9; **23** (isomer 2), 94292-77-0; **24** (isomer 1), 94292-78-1; **24** (isomer 2), 94292-79-2; 3-methyl-3-buten-2-ol, 10473-14-0; 2-(trimethylsiloxy)-3-[(trimethylsilyl)methyl]-3-butene, 94235-29-7; 2-(trimethylsiloxy)-3-[(trimethylsilyl)methyl]-4-(trimethylsilyl)-3-butene, 94235-30-0; 3-[(trimethylsilyl)methyl]-3-buten-2-ol, 79348-42-8; 2-[(trimethylsilyl)methyl]propenal, 56407-82-0; 2-cyclopentenone, 930-30-3; [(2,4,6-triisopropylphenyl)sulfonyl]-hydrazine, 39085-59-1.

Supplementary Material Available: General experimental procedures (2 pages). Ordering information is given on any current masthead page.

Exciton Approach to the Optical Activity of C_3-Cyclotriveratrylene Derivatives

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Contribution from the Collège de France, Chimie des Interactions Molêculaires,[§] 11, place Marcelin Berthelot, 75005 Paris, France, and the Universitâ di Bologna, Istituto di Scienze Chimiche, via S. Donato 15, 40127 Bologna, Italy. *Received July 2, 1984*

Abstract: The circular dichroism of chiral C_3-cyclotriveratrylenes **2–12** in which the substitution patterns correspond to various combinations of R_1 and R_2 = H, OH, O$^-$, and OAc, and *O*-alkyl groups has been analyzed in light of the exciton theory, using the concept of spectroscopic moments. From the observed signs and intensities of the B_{2u} couplets, a self-consistent set of polarization angles for this transition in the OH/*O*-alkyl ortho-disubstituted derivatives has been established. The spectroscopic moments of these substituents have been shown to increase on going from the bulkiest (O-*i*-C_3H_7) to the smallest (OH) group, very likely as a consequence of different equilibria between planar and nonplanar conformers. Finally, the experimental B_{2u} and B_{1u} couplets have been satisfactorily reproduced in most of the cases studied by calculations based on the exciton approximation, with limited p–α configuration interaction.

Cyclotriveratrylene (**1**) and its analogues devoid of bulky substituents ortho to the nine-membered ring are rigid, cone-shaped molecules that exhibit stable optical activity at ambient temperature when the achiral C_{3v} symmetry of the parent compound is destroyed by appropriate substitution (e.g., when $R_1 \neq R_2$).[1] With the exception of a C_1-monobenzyl ether which was partially resolved in 1966 by Lüttringhaus,[2] all the optically active

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(1) Collet, A. In "Inclusion Compounds"; Atwood, J. L., Ed.; Academic Press: London, 1984; Vol. II, Chapter 4 and references therein.
(2) Lüttringhaus, A.; Peters, K. C. *Angew. Chem.* **1966**, *78*, 603; *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 593–594.

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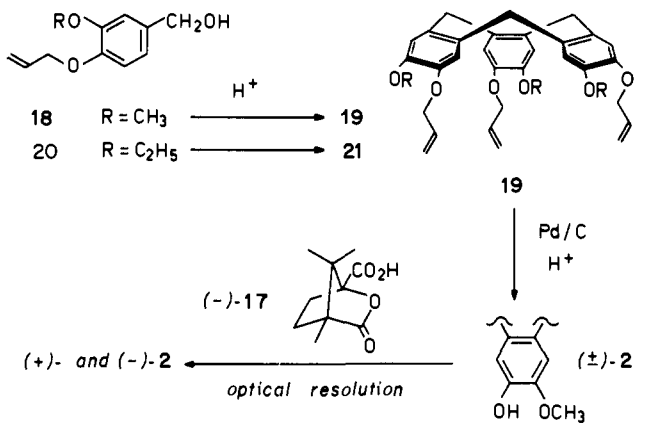
Scheme I



derivatives of **1** known to date belong to the C_3 and D_3 symmetry groups.[3-7]

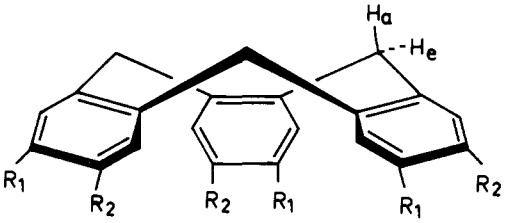
As in the well-known case of the C_2-biaryls,[8] the chiroptical properties of C_3-cyclotriveratrylenes merely originate from through-space interactions of equivalent, intrinsically achiral aromatic subunits, giving rise to well-characterized exciton circular dichroism (CD) spectra. More precisely, the optical activity in these compounds results from more or less important deviations of the long- and short-axis polarized components of the transitions of the phenyl rings from the symmetrical positions, as a consequence of the presence of two substituents R_1 and R_2 having different properties.[9] Due to the favorable (and rigid) geometry and to the relatively strong dipole strengths of the transitions in this system, even a very small distortion yields intense exciton CD, which in turn provides useful information as to the substituent effects on the properties of the aromatic chromophore; this system, as we have shown, is sensitive enough to evidence isotope substitution effects (e.g., in **6** and **13**).[10-12]

In the present article, we analyze in the light of the exciton mechanism the CD properties of a series of C_3-cyclotriveratrylenes, **2–12**, in which the substitution patterns correspond to various combinations of R_1 and R_2 = H, OH, O^-, *O*-alkyl, and *O*-acyl groups. We also describe several new procedures that we have developed since our previous reports[3,5] for the optical resolution of C_3-cyclotriguaiacylene (**2**) as well as for the synthesis and resolution of the ethoxy analogue **3**.

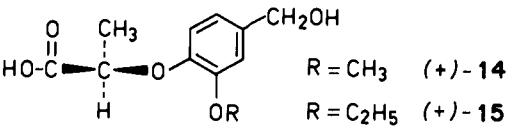
The synthesis and CD spectrum of isotopically chiral C_3-cyclotribenzylene-d_3 (**13**) have been reported separately,[7,12] and the CD of D_3-bis(cyclotriveratrylenyl)[6] and related compounds bearing two cyclotriveratrylene fragments will be discussed in a forthcoming paper.

Results

Syntheses and Absolute Configurations. The absolute configurations of the C_3-cyclotriveratrylenes **2–12**, shown on the stereoformulas with the corresponding *M* or *P* descriptors, are based on the previous X-ray determination of the structure of **22**, bearing a chiral group R_2 of known stereochemistry.[5] This compound was one of the diastereomers formed by acid-catalyzed trimerization of (*R*)-(+)-**15**; after appropriate transformations it afforded (−)-**9** and (−)-**3**, which on methylation gave (−)-**7**. On the other hand,



	R_1	R_2	
1	OCH_3	OCH_3	*achiral*
2	OCH_3	OH	*P*-(−)
3	OC_2H_5	OH	*P*-(−)
4	OCH_3	$OCOCH_3$	*M*-(−)
5	OC_2H_5	$OCOCH_3$	*M*-(−)
6	OCH_3	OCD_3	*M*-(−)
7	OC_2H_5	OCH_3	*P*-(−)
8	OCH_3	OiC_3H_7	*M*-(−)
9	OC_2H_5	OiC_3H_7	*M*-(−)
10	OCH_3	H	*P*-(−)
11	OH	H	*P*-(−)
12	$OCOCH_3$	H	*P*-(−)
13	D	H	*P*-(+)



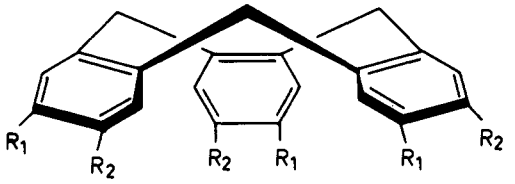
trimerization[3] of (*R*)-(+)-**14** likewise gave, inter alia, diastereomer **23** which by a multistep sequence was converted into cyclotriguaiacylene, (+)-**2**. Since on ethylation the latter also gave (−)-**7**, its absolute configuration was accordingly established as (*M*)-(+) or (*P*)-(−).

Soon after this work was published we found[11,12] a more straightforward access to multigram quantities of the key triphenol (±)-**2**, by trimerization of the phenolic allyl ether of vanillyl alcohol (**18**) to the derivative **19**, which in turn was converted into **2** in high yield (Scheme I). We have now extended this route to the preparation of optically active **2**, by resolving the diastereomer mixture of **24** and **25** obtained from the racemate and (−)-ω-camphanic acid (**17**). The diastereomeric triesters were completely separated by chromatography and crystallization, and their reductive cleavage gave back triphenols (+)- and (−)-**2** which exhibited the rotations indicated in Table I. Several preparations, using either the above procedure or the earlier synthesis,[3] afforded enantiomers, having $[\alpha]_D$ 271° (±4%) in chloroform. Recrystallization of partially resolved samples (e.g., $[\alpha]_D$ 205°) also raised the rotation to the same value, which therefore very likely represents the maximum rotation (±4%) of **2**.

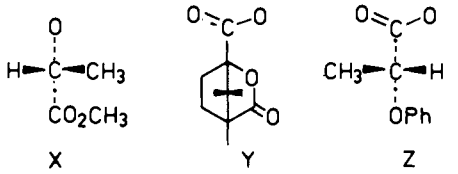
We also attempted to apply the sequence of Scheme I to the synthesis of **3**. However, the phenolic allyl ether **20** did not trimerize satisfactorily under the conditions in which **18** gave **19**,[13]

(3) Collet, A.; Jacques, J. *Tetrahedron Lett.* **1978**, 1265–1268.
(4) Collet, A.; Gabard, J. *J. Org. Chem.* **1980**, *45*, 5400–5401.
(5) Collet, A.; Gabard, J.; Jacques, J.; Cesario, M.; Guilhem, J.; Pascard, C. *J. Chem. Soc., Perkin Trans. 1* **1981**, 1630–1638.
(6) Gabard, J.; Collet, A. *J. Chem. Soc., Chem. Commun.* **1981**, 1137–1139.
(7) Canceill, J.; Collet, A. *J. Chem. Soc., Chem. Commun.* **1983**, 1145–1147.
(8) Mason, S. F.; Seal, R. H.; Roberts, D. R. *Tetrahedron* **1974**, *30*, 1671–1682.
(9) Collet, A.; Gottarelli, G. *J. Am. Chem. Soc.* **1981**, *103*, 204–205.
(10) Collet, A.; Gottarelli, G. *J. Am. Chem. Soc.* **1981**, *103*, 5912–5913.
(11) Canceill, J.; Gabard, J.; Collet, A. *J. Chem. Soc., Chem. Commun.* **1983**, 122–123.
(12) Canceill, J.; Collet, A.; Gottarelli, G. *J. Am. Chem. Soc.* **1984**, *106*, 5997–6003.

(13) The phenolic allyl ether of ethylvanillyl alcohol (**20**) (mp 32 °C) on reaction with 65% perchloric acid in methanol or acetic acid solution invariably afforded trimer **21** (mp 116 °C) in ca. 15% yield, instead of 50% for the similar conversion of **18** into **19**.[12] The reasons for this difference are not entirely clear; as a matter of fact, acid-catalyzed condensation of 3,4-disubstituted benzyl alcohols only rarely afford cyclotriveratrylenes in good yield. These reactions are extremely sensitive to the nature of the substituents as well as the experimental conditions. However, it is likely that the solubility of the trimer is one of the factors determining the yield. When the latter crystallizes off during the course of the reaction (this is the case of **19**), it is protected from side reactions which can occur under the strongly acidic conditions employed, and the yield is eventually better.



	R_1	R_2	$[\alpha]_D$ ($CHCl_3$)
22	OC_2H_5	X	-16.1°
23	X	OCH_3	+ 74°
24	OCH_3	Y	- 52°
25	Y	OCH_3	+ 47°
26	OC_2H_5	Z	+ 37°
27	Z	OC_2H_5	+ 99°



X Y Z

and this circumstances led us to adopt the alternative route summarized in Scheme II. Ethylation of the phenol group of vanillyl alcohol furnished the starting compound **30**, which on reaction with 65% perchloric acid gave (±)-**7** in ca. 50% isolated yield. Cleavage of the methyl ethers in **7** could then be effected in a totally selective manner, by reaction with lithium diphenylphosphide,[14] providing the desired triphenol (±)-**3** in 78% yield.

Optical resolution of **3** was then achieved by converting this compound into the mixture of triesters **26** and **27**, by reaction with (*R*)-(+)-2-phenoxypropionic acid (**16**).[15] Chromatographic separation followed by reductive cleavage of each pure diastereomer finally afforded *crystalline* enantiomers of **3**, having rotations (Table I) 12% greater than previously reported[5] for a *glassy* sample of (−)-**3** obtained from **22** by the earlier method.[5]

Finally, acetates **4** and **5** were obtained from the corresponding triphenols **2** and **3** by reaction with acetyl chloride in pyridine at 0–20 °C, and reaction of the sodium salt of **2** with CD_3I or $(CH_3)_2CHBr$ in HMPA at 20 °C provided **6** and **8**. The synthesis of **10–13** from **2** was effected as described in detail elsewhere.[12] The specific rotations assembled in Table I correspond to the values observed for recrystallized samples and very likely represent the maximum rotations (±~5%) of these substances.[12]

As previously noted,[1,12] chiral cyclotriveratrylenes racemize on heating, via crown inversion, over a barrier of 110–115 kJ/mol. The rate constant for the inversion process at room temperature is about 10^{-7}–10^{-8} s^{-1}, which corresponds to a 1% rotation decrease over 12–48 h in solution. These compounds can, therefore, be considered optically stable and conformationally homogeneous[1] in the conditions in which the CD measurements discussed below were recorded.

Exciton Approach to the Optical Activity of 2–12. In the exciton approximation,[16] the wave functions of cyclotriveratrylene derivatives having C_3 symmetry can be expressed as eq I, where indexes 1, 2, and 3 label each benzene ring and the asterisk indicate excitation. For each "monomer" transition, there are, thus, in the "trimer" three excitations, two of which (E) are degenerate.

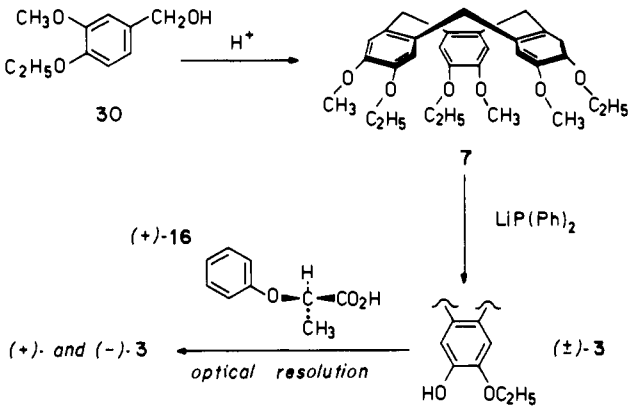
$$\psi_o = \chi_1\chi_2\chi_3$$

$$\psi_A = (1/3^{1/2})(\chi_1^*\chi_2\chi_3 + \chi_1\chi_2^*\chi_3 + \chi_1\chi_2\chi_3^*)$$

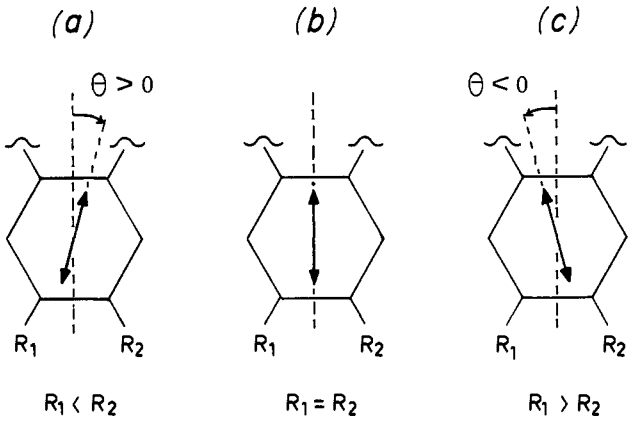
$$\psi_E = (1/2^{1/2})(\chi_1^*\chi_2\chi_3 - \chi_1\chi_2\chi_3^*)$$

$$\psi_E = (1/6^{1/2})(2\chi_1^*\chi_2\chi_3 - \chi_1\chi_2^*\chi_3 - \chi_1\chi_2\chi_3^*) \quad (I)$$

Scheme II

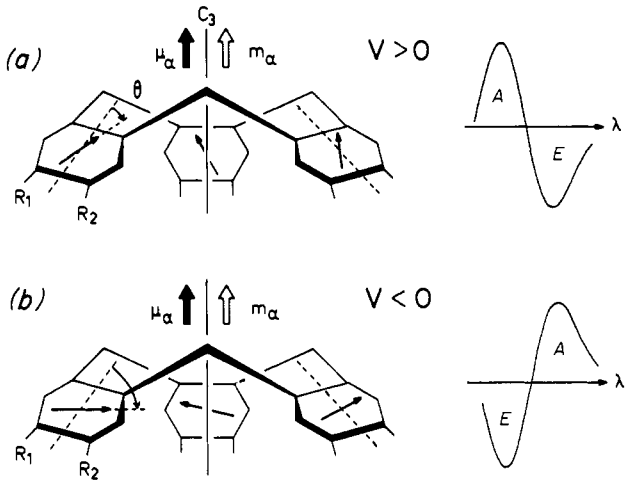


Scheme III. Polarization Direction θ of the B_{2u} Transition Dipoles as a Function of the Spectroscopic Moments of the Substituents R_1 and R_2[a]



[a] View from the exo side of the molecule. The corresponding B_{1u} transition dipoles should be found at $\theta^* = \theta + 90°$.

Scheme IV. In-phase (A) Coupling of the B_{2u} Transition Dipoles[a]



[a] (a) $0 < \theta < \sim 45°$, repulsive interaction; (b) $\sim 45° < \theta < 90°$, attractive interaction.

(14) (a) Ireland, R. E.; Walba, D. M. *Org. Synth.* **1977**, *56*, 44–48. (b) Vedejs, E.; Fuchs, P. L. *J. Am. Chem. Soc.* **1973**, *95*, 822–825.

(15) Fourneau, E.; Sandulesco, G. *Bull. Soc. Chim. Fr.* **1922**, *31*, 988–993. Fredga, A.; Matell, M. *Ark. Kemi* **1952**, *4*, 325–330. Sjöberg, B.; Sjöberg, S. *Ark. Kemi* **1964**, *22*, 447–450. The (*R*)-(+)-2-phenoxypropionic acid that we used had $[\alpha]^{25}_D$ +39.7° in absolute ethanol and was enantiomerically pure. This resolving agent can also be prepared by reaction of the *O*-*p*-toluenesulfonate of *S*-(−)-ethyl lactate with phenol and potassium carbonate in acetonitrile (5-h reflux), followed by alkaline hydrolysis of the ester. This simple procedure affords the (*R*)-(+)-acid with ee 70%, and recrystallization of the *n*-propylamine salt from ethyl acetate raises the ee to 100%.

(16) Mason, S. F. In "Optical Activity And Chiral Discrimination"; Mason, S. F., Ed.; Reidel: New York, 1979; pp 1–24.

Table I. Specific Rotations of **2–12**

compound	solvent	concentration, per 100 mL	$[\alpha]^{25}$, deg[e] 589	578	546	436	365	error range[c], (±)	C,H analysis
2 (*M*)-(+)	*a*	0.1–0.3	+271	+284	+329	+619	+1160	4%	$C_{24}H_{24}O_6$, $1H_2O$
(*P*)-(−)	*a*	0.1–0.3	−272	−285	−329	−619	−1162	3%	$C_{24}H_{24}O_6$, $1H_2O$
3 (*M*)-(+)	*a*	0.3	+293	+306	+354	+667	+1265	*d*	$C_{27}H_{30}O_6$
(*P*)-(−)	*a*	0.3	−293	−307	−354	−670	−1270	*d*	
4 (*M*)-(−)	*a*	0.25	−169	−177	−205	−386	−697	3%	$C_{30}H_{30}O_9$
5 (*M*)-(−)	*a*	0.1	−218	−223	−255	−473	−849	*d*	$C_{33}H_{36}O_9$
6 (*P*)-(+)	*a*	2	+3.1	+3.3	+4.0	+8.2	+17.7	5%	*f*
(*M*)-(−)	*a*	1	−3.4	−3.4	−4.0	−7.6	−15.6	10%	*f*
7 (*P*)-(−)	*a*	0.2	−20.0	−21.0	−23.2	−47	−99	5%	$C_{30}H_{36}O_6$
8 (*P*)-(+)	*a*	0.7	+14.2	+14.3	+14.8	+14.0	−28.1	*d*	
(*M*)-(−)	*a*	0.7	−14.1	−14.1	−14.8	−14.4	+23.2	*d*	$C_{33}H_{42}O_6$
9 (*M*)-(−)	*a*	0.6	−47	−49	−56	−98	−155	*d*	$C_{36}H_{48}O_6$
10 (*M*)-(+)	*a*	0.25	+161	+168	+192	+354	+630	*d*	
(*P*)-(−)	*a*	0.25	−165	−173	−201	−370	−656	6%	$C_{24}H_{24}O_3$, $^1/_2H_2O$
11 (*M*)-(+)	*b*	0.25	+207	+215	+251	+476	+882	*d*	$C_{21}H_{18}O_3$, $2H_2O$
(*P*)-(−)	*b*	0.25	−199	−208	−241	−456	−846	4%	
12 (*M*)-(+)	*a*	0.5	+190	+200	+227	+405	+685	*d*	$C_{27}H_{24}O_6$

[a] In spectrometric grade chloroform, stabilized with 0.5–0.8% ethanol. [b] In spectrometric grade dioxane. [c] Mean deviation of the observed rotation of several samples obtained from different syntheses. [d] Only one sample available, estimated accuracy ±2%. [e] In the case of **2**, **10**, and **11** which form crystalline hydrates, the rotations indicated in the table are *not* corrected for the water content. [f] See ref 4.

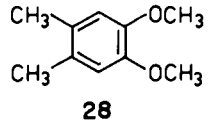
The splitting ($\Delta\tilde{\nu} = 3V/hc$) between the A and E components can be semiquantitatively evaluated by the point-dipole approximation, $V = d_{12}^{-3}\,[\mu_1\cdot\mu_2 - 3d_{12}^{-2}\,(\mu_1\cdot d_{12})(\mu_2\cdot d_{12})]$, where μ_1 and μ_2 are the transition moment vectors, located at the centers of benzene rings 1 and 2, separated by $d_{12} = 4.79$ Å.[5] The theoretical rotational strengths R of the A and E coupling modes are evaluated as $R_{om} = \mathrm{Im}\{\langle\psi_o|\hat{\mu}|\psi_m\rangle\cdot\langle\psi_m|\hat{m}|\psi_o\rangle\}$, where $\hat{\mu}$ and $\hat{m}$ are the electric and magnetic dipole moment operators, respectively. In an achiral derivative in which $R_1 = R_2$, such as **1**, the B_{2u} and B_{1u} transitions are polarized along the short and long axes of the aromatic rings, respectively, as sketched in Scheme IIIb, whereas in the chiral compounds the presence of substituents R_1 and R_2 of different nature causes a rotation θ of the transition moments with respect to the symmetrical positions (Scheme IIIa and c). The above expressions of the interaction potential and rotational strengths accordingly become eq II and III, respectively, where Φ is the angle

$$V = (D_{mon}/d_{12}^3)(\cos^2\theta\cos^2\Phi + {}^7/_4\cos^2\theta\sin^2\Phi - {}^5/_4\sin^2\theta) \quad \text{(II)}$$

$$R_A = 3^{1/2}\pi\tilde{\nu}d_{12}D_{mon}\cos\theta\sin\theta\cos\Phi = -2R_E \quad \text{(III)}$$

between the plane of each benzene ring and the C_3 axis ($\Phi = 43°$),[5] and $D_{mon} = \mu^2$ is the dipole strength of the transition; the latter can be experimentally evaluated from the absorption (UV) spectrum of the trimer or, alternatively, of an appropriately substituted benzene ring (e.g., 4,5-dimethylveratrole (**28**) or guaiacol (**29**)) as the monomer model.[37]

The intensities of the B_{2u} and B_{1u} transitions of aromatic derivatives are currently interpreted in terms of the spectroscopic moments of the substituents,[18,19] and the rotation θ of the electric dipole transition moment in C_3-cyclotriveratrylenes should then depend on the nature of R_1 and R_2 as indicated in Scheme III.



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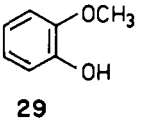

29

For the absolute configuration depicted, one obtains, when the spectroscopic moment of R_2 is greater than that of R_1 ($R_2 > R_1$), a clockwise rotation ($\theta > 0$) which is inverted when $R_1 < R_2$. Accordingly, the signs of the exciton CD bands should depend critically on the relative magnitude of the spectroscopic moments, the signs of θ and of the interaction potential being the important factors in determining the actual sequence of the signs of the B_{2u} and B_{1u} couplets. As shown in Scheme IV, the in-phase A coupling of the B_{2u} transition moment vectors for $0 < \theta < 90°$ generates overall parallel electric and magnetic transition moments along

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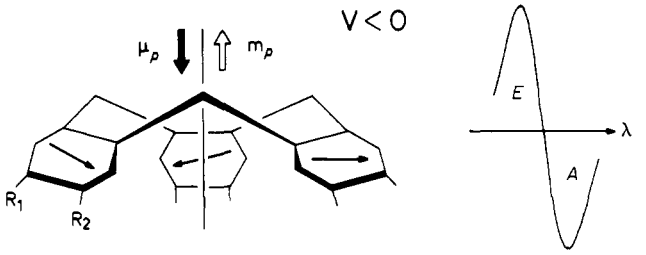
(37) Experimental dipole strengths and rotational strengths were evaluated from the UV and CD band areas: $D_{mon} \sim 91.8 \times 10^{-40}(1/\lambda)\int\epsilon\,d\lambda$ and $R \sim 22.8 \times 10^{-40}(1/\lambda)\int\Delta\epsilon\,d\lambda$, respectively.

Scheme V. In-phase (A) Coupling for the B_{1u} Transition when $90° < \theta^* < \sim 135°$ (Attractive)



the C_3 axis, hence positive rotational strength. However, the interaction potential V which is positive (repulsive) for small values of θ (a), becomes clearly negative (attractive) for the larger ones (b); the "magic angle" θ_m at which $V = 0$ is calculated[20] to be $\sim 45°$ from eq II. It follows that the positive A component of the CD couplet should be found, in the first case, (a) at higher energy and, in the second case, (b) at lower energy, with inversion of the spectrum. Analogous considerations for the B_{1u} transition are straightforward.

While this simple picture of conservative CD adequately accounts for several of the experimental spectra (those of **2**, **3**, and **6–9**), other derivatives (**4**, **5**, and **10–12**) show in the B_{2u} region relatively large differences in the intensities of the two components, and in three cases (**12** and ionized **2** and **11**) only a single component is present. These differences can be semiquantitatively explained by taking into account interactions between different excitations in the three benzene rings.[21,22] Restricting the interaction only to the B_{2u} (α) and B_{1u} (p) transitions,[23] the corrected A symmetry trimer state is expressed as eq IV, where the mixing coefficient λ given by eq V can be calculated as the sum of the pairwise interactions between benzene rings undergoing different (α or p) excitations. In the point-dipole approximation, the

$$\Psi_A{}^\alpha = (\psi_A{}^\alpha + \lambda\psi_A{}^p)/(1 + \lambda^2)^{1/2} \quad \text{(IV)}$$

$$\lambda = \langle\psi_A{}^\alpha|V|\psi_A{}^p\rangle/(E_\alpha - E_p) \quad \text{(V)}$$

interaction potential (eq V) becomes eq VI and is zero for $\theta = 0$ and 90°, being attractive between these values and reaching its maximum at $\theta = 45°$. The corrected rotational strength $R_A{}^\alpha(i)$

$$\langle\psi_A{}^\alpha|V|\psi_A{}^p\rangle = -(3/2d_{12}{}^3)\mu_{1\alpha}\mu_{2p} \sin\theta\cos\theta\,(3 + \sin^2\Phi) \quad \text{(VI)}$$

has the form of eq VII, where μ and m are now the overall electric

$$R_A{}^\alpha(i) = R_A{}^\alpha + \lambda(\mu_\alpha\cdot m_p + \mu_p\cdot m_\alpha) + \lambda^2 R_A{}^p \quad \text{(VII)}$$

and magnetic transition moments of the trimer and $R_A{}^\alpha$ and $R_A{}^p$ are the zero-order rotational strengths for the in-phase coupling mode of the B_{2u} and B_{1u} transitions, respectively, which can be evaluated from eq III; since $\lambda \ll 1$, the term $\lambda^2 R_A{}^p$ in eq VII can be neglected. The term $\lambda(\mu_\alpha\cdot m_p + \mu_p\cdot m_\alpha) = R(\text{int})$, recently called[22] the "interference term", is responsible for the inequality of the areas, as it does not change its sign on going from symmetric (A) to antisymmetric (E) states. In this specific case (z-polarized components), it has, in principle, the form of eq VIII. As a

$$R(\text{int}) = -\frac{3(3^{1/2})}{2}\frac{D_{mon}{}^\alpha D_{mon}{}^p}{hc(\tilde\nu_\alpha - \tilde\nu_p)d_{12}{}^2}\pi\tilde\nu_\alpha \sin\theta\cos\theta\cos\Phi\,(3 + \sin^2\Phi)(1 - 2\sin^2\theta) \quad \text{(VIII)}$$

pictorial example, we consider the interaction between the B_{2u} and B_{1u} transitions in the case of $0 < \theta < 45°$. The A coupling of the B_{2u} transition (Scheme IVa) corresponds to positive electric (μ_α) and magnetic (m_α) moments along the C_3 axis, giving positive CD at higher energy. The same coupling mode for the B_{1u} transition (Scheme V) originates positive m_p and negative μ_p moments along the C_3 axis, giving rise to negative CD at lower energy. The zero-order spectrum therefore consists of a conservative sequence of bands of alternating signs as depicted in Figure 1. Allowing interaction of the two transitions, we expect an increase of the positive exciton component of the B_{2u} couplet

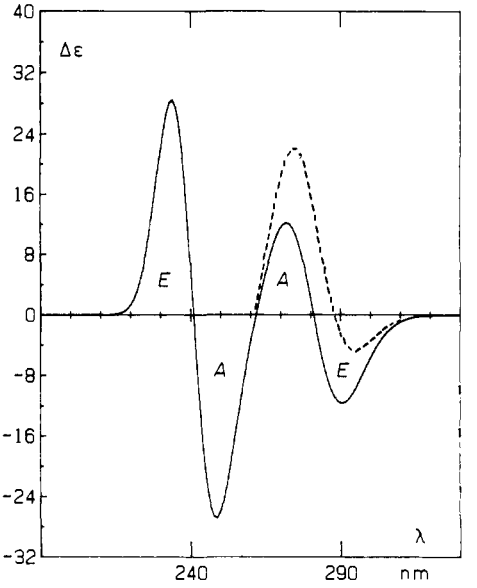


Figure 1. Theoretical sequence of exciton bands for $0 < \theta < \sim 45°$: (—) zero-order spectrum; (---) after configuration interaction. The CD curves were calculated by using the following data: $D_{mon}(B_{1u}) = 3 \times 10^{-36}$ cgsu and $D_{mon}(B_{2u}) = 2 \times 10^{-36}$ cgsu, $\theta = +25°$; these figures specifically correspond to (*P*)-(+)-**4**.

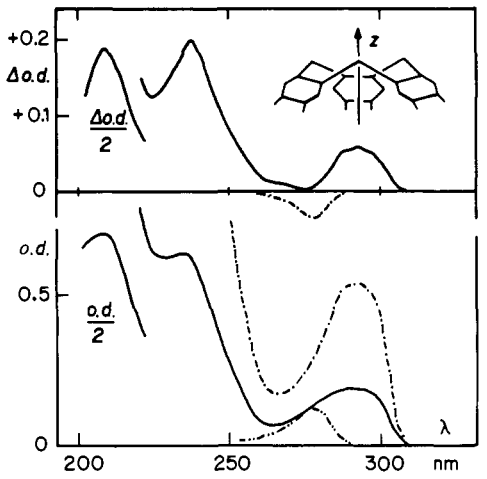


Figure 2. Lower part: (—) isotropic absorption spectrum ($E_\parallel + E_\perp/2$) of an oriented sample of **1** in the nematic phase ZLI 1167; (-·-·-) absorption components along the z axis (A_z) and (-··-··-) along the degenerate in-plane x and y axes ($A_x + A_y$) computed by the reduction method of ref 24, assuming a disk-like molecular shape. Upper part: (—) liquid crystal linear dichroism spectrum of the oriented sample ($E_\parallel - E_\perp$); (-·-·-) reduced spectrum $E_\parallel - E_\perp - (d'/2)(E_\parallel + E_\perp)$, showing the negative LD contribution of polarization along the z axis (in arbitrary units for $d' = 0.28$).

and a decrease of the negative one (Figure 1) as $R(\text{int})$ in eq VII and VIII is positive ($\mu_\alpha\cdot m_p$ (positive) > $\mu_p\cdot m_\alpha$ (negative)).

In principle, if eq VIII is valid, the interference term $R(\text{int})$ is very small for small values of θ, reaching its maximum at $\theta = 22.5°$ and returning to zero to $\theta = 45°$. However, considering the overall simplicity of the treatment, restricted to p–α interaction and, moreover, based on the point-dipole approximation which severely underestimates interaction potentials,[21] a quantitative agreement between angle θ and the magnitude of the interference term would probably be too much to be expected.

Linear Dichroism. In order to check the validity of the exciton approach in this system, we have recorded the linear dichroism (LD) spectrum of cyclotriveratrylene (**1**) dissolved in the nematic-phase ZLI 1167 (Figure 2). The LD spectrum consists of two positive bands at ca. 292 and 237 nm and of a partially cancelled negative component at ca. 277 nm, which becomes quantitatively defined in the decomposed spectrum.[24] The molecule can be considered "disk-shaped"; in this case,[25] transitions

Table II. Experimental and Calculated CD Spectra for the B_{2u} Transition

	observed			calculated				
	λ, nm	Δε	$10^{40}R$, cgsu	θ, deg	$10^{40}R_{corr}$, cgsu	λ, nm	Δε	
(−)-2	299	−5.3	−7.0	+2.8	±6.4	297	−4.2	b
	277	+3.8	+5.0			276	+4.4	
(−)-3	298	−9.8	−11	+4.5	±10.3	297	−6.4	b
	277	+8.0	+10			276	+7.2	
(−)-6	298	−0.26	−0.3	+0.15	±0.3	296	−0.23	b
	277	+0.30	+0.3			276	+0.24	
(−)-7	296	−2.8	−3.0	+1.4	±3.2	296	−2.2	b
	276	+2.5	+3.0			276	+2.3	
(−)-8	295	+8.0	+8.0	−3.9	±9.0	296	+5.9	b
	276	−9.5	−10			276	−6.1	
(−)-9	295	+5.2	+6.0	−3.0	±7.0	296	+4.5	b
	276	−7.4	−8.0			276	−4.7	
(−)-4	292	+8.0	+5.4	−25	+5.0	295	+4.7	c,d
	273	−17	−23		−28	275	−22	
(−)-5	292	+9.0	+6.0					c,d
	273	−22	−29					
(−)-10	292	+8.0	+4.9	−38	+3.7	292	+2.0	c,d
	275	−13.5	−17		−15	278	−16	

[a] Assuming a bandwidth at half-maximum of 2700 cm^{-1} for all compounds but 10 (2300 cm^{-1}). [b] Without interference term, $D_{mon}(B_{2u}) = 3 \times 10^{-36}$ cgsu. [c] With interference term, $D_{mon}(B_{2u}) = 2 \times 10^{-36}$ cgsu. [d] The R_{corr} values were obtained from the areas of the calculated CD curves.

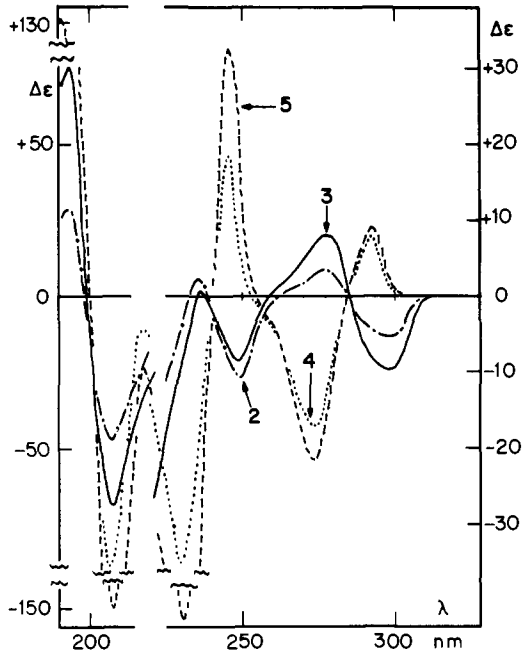


Figure 3. Circular dichroism spectra of the (−) enantiomers **2–5** in methanol.

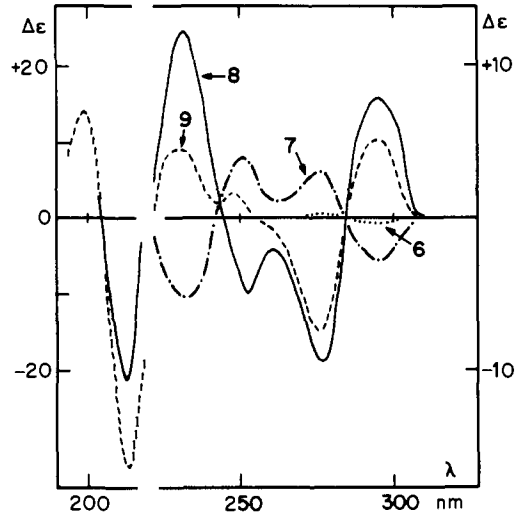


Figure 4. Circular dichroism spectra of (−)-**6** in dioxane and (−)-**7–9** in methanol.

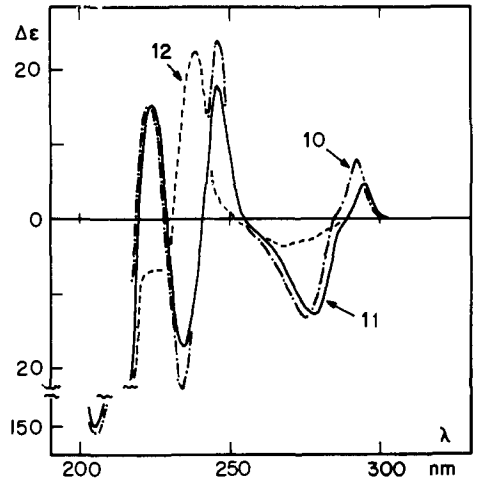


Figure 5. Circular dichroism spectra of the (−) enantiomers **10–12** in methanol.

that are polarized perpendicularly to the plane of the disk (i.e., along the C_3 axis) should give negative LD, while those polarized in the plane give positive LD. Therefore, the positive LD at 292 nm should be assigned to the E component of the B_{2u} transition, which is expected at low energy with a polarization perpendicular to the C_3 axis. The negative band at 277 nm should then correspond to the A component of the same transition, expected at higher energy and polarized along the C_3 axis. In the C_{3v} group to which derivative **1** belongs, the A component of the B_{1u} transition has A_2 symmetry and is electrically forbidden. Hence, only a positive LD band corresponding to the E component should be observed, in good agreement with the spectrum (237 nm). The exciton theory, therefore, gives a good explanation of the LD spectrum of **1**.

Moreover, the separation between the resolved components of the B_{2u} transition is ca. 1800 cm^{-1}. This value will be a useful reference in the evaluation of the intensities of the CD spectra, as the splittings calculated by using the point-dipole approximation (eq II) are always too small.

Discussion

The CD spectra of the (−) enantiomers **2–12** are reported in Figures 3–5, the corresponding rotational strengths for the B_{2u}

Table III. Ultraviolet Isotropic Absorption Spectra

				B_{1u}		B_{2u}	
		λ	ε	λ	ε	λ	ε
1	*a*	204	65 000	232	28 300	292	9 300
2	*a*	205	66 000	230	30 700	292	9 600
	b	219	150 000	241	33 500	301	15 900
3	*a*	205	63 600	230	22 900	292	9 600
4	*a*	200	69 200	227	29 400	288	7 700
7	*a*	204	88 400	231	34 400	291	10 400
8	*a*	205	71 500	231	31 600	292	9 900
10	*a*	199	54 300	230	19 400	288	4 400
28	*a*			226 sh	9 300	282	3 100
29	*c*			219	5 700	276	2 600
	a			220	7 000	276	2 800
	b			236	14 000	289	4 800

[a] In methanol, c = 0.5–0.9 g/L. [b] In methanol + CH_3ONa (0.2 M). [c] In methanol + HCl (1 drop of 12 N HCl/5 mL).

transitions in **2–10** are assembled in Table II, and relevant UV data are given in Table III.

A first group of compounds, **2**, **3**, and **6–9**, in which R_1 and R_2 = OH and/or *O*-alkyl groups, shows nearly conservative CD in the B_{2u} region, centered at 235 nm (Figures 3 and 4). In these compounds, substituents R_1 and R_2 are very similar to each other, hence the value of θ should be very small and the contribution of the interference term negligible. The sign of θ for each derivative can be deduced from the sequence of signs of the B_{2u} couplet (eq III), and this in turn leads to the following sequence of spectroscopic moments of the substituents, with regard to the B_{2u} transition:

$$OH > OCD_3 > OCH_3 > OC_2H_5 > O\text{-}i\text{-}C_3H_7$$

Not only the signs but also the magnitudes of the CD bands are in agreement with this sequence (Table II). The intensity of **8** (OCH_3, O-*i*-C_3H_7) is thus greater than that of **9** (OC_2H_5, O-*i*-C_3H_7), which is greater than that of **7** (OC_2H_5, OCH_3). Likewise, the difference in the magnitude of the spectroscopic moments being larger in **3** (OC_2H_5, OH) than in **2** (OCH_3, OH), the latter has the lower intensity.

In benzene rings bearing OH or *O*-alkyl substituents, the equilibrium between planar and nonplanar conformations of the Ar–O–R bonds is governed by the balance of resonance and steric effects.[26] While in the crystal state planar conformers are generally preferred, the actual position of the equilibrium in solution is still a matter of discussion, in particular in the case of ortho-disubstituted derivatives such as *o*-dimethoxybenzene (veratrole).[26-29] The sequence of spectroscopic moments reported above seems to be connected to the inhibition of resonance,[30] due to populations of nonplanar conformers increasing on going from the smallest (OH) to the bulkiest (O-*i*-C_3H_7) group. This view is confirmed by the CD spectrum of **6**, where the OCD_3 group, effectively smaller, must be given a spectroscopic moment larger than the OCH_3 group.[10]

With regard to the B_{1u} transition, derivatives **7–9** bearing two *O*-alkyl groups do not follow the sequence of signs predicted in Figure 1 and observed for **2** and **3**. Instead **7** and **8** show a B_{1u} couplet opposite to that expected, and **9** exhibits in this region two CD bands of the same sign (Figure 4). In these compounds, the value of θ is close to zero, and the polarization θ' of the B_{1u} transition is therefore close to 90°, the angle at which inversion of the spectrum should occur if eq III is still followed. The actual inversion in **7** and **8** and the disappearance of the CD couplet in **9** could be connected to vibronic effects, affecting in a different way the two transitions (in other words, θ' seems to be slightly different from the expected value (θ + 90°) in this system).

The experimental rotatory strengths, λ_{max}, and $\Delta\epsilon$ values of the B_{2u} transition could be satisfactorily reproduced from the theoretical rotatory strengths R given by eq III, using values of $|\theta| < 5°$ and $D_{mon} = 3 \times 10^{-36}$ cgsu as suggested from the UV spectrum of 4,5-dimethylveratrole (**28**) (Table III). The values of R (eq III) were corrected for cancellation effects[8] by the relation $R_{corr} = R\Delta\tilde{\nu}/\Gamma$, in which Γ, the UV bandwidth at half maximum, was taken as 2700 cm^{-1} (from the UV spectrum of **28**). As already stated, the interaction potentials based on the point-dipole approximation are always underestimated,[21] and in the present case the exciton splitting of **1**, $\Delta\tilde{\nu} = \tilde{\nu}_A - \tilde{\nu}_E$, calculated from eq II by the relation $\Delta\tilde{\nu} = 3V/hc$, was one-third of the experimental value deduced from the LD spectrum (600 vs. 1800 cm^{-1}). We therefore systematically adopted, in the estimation of $\Delta\tilde{\nu}$ as a function of θ, values 3 times larger than those calculated by eq II. Finally, the λ_{max} and $\Delta\epsilon$ values assembled in Table II were obtained by means of a curve plotter according to Mason,[8,31] assuming that the CD spectrum consists of a sum of Gaussian bands (see Appendix section).

We wish to emphasize that the set of polarization angles θ for **2**, **3**, and **6–9** assembled in Table II is self-consistent, in the sense that it accounts for the actual sequence of signs and relative magnitude of the B_{2u} CD couplets in these compounds. It is based, however, on calculations which cannot pretend to yield more than a correct order of magnitude (even if the agreement between observed and calculated spectra is, here, fairly good). Furthermore, it should be remembered that these polarization angles depend on the spectroscopic moments of the substituents which are very sensitive to steric effects and in this case only refer to ortho-disubstituted derivatives.

A second group of derivatives (**4**, **5**, **10**, and **11**) shows two bands of different intensities in the B_{2u} region (Figures 3 and 5). In all cases the band at higher energy has the larger CD. While for the acylated compounds **4** and **5** the difference in the band areas is moderate, **10** and **11**, containing a single OH or OCH_3 substituent on each ring, exhibit a drastic reduction of the low-energy component. The sequence of signs of the B_{1u} and B_{2u} CD bands is, in all these compounds, in agreement with that predicted in Figure 1.

In derivatives **4** and **5**, acylation of the phenolic groups causes a marked decrease of their spectroscopic moment (from ca. +35 to +10 L/mol·cm),[19] and the value of θ then becomes very far from zero; however, even without taking into account the moment of the methylene bridges composing the crown, we are still far from reaching the "magic angle" region (~45°). In the case of **10** and **11**, where only one OH or OCH_3 group is present, without considering the methylene bridges, one should have $\theta > 45°$, while from the CD spectra and the known absolute configurations, it is clear that the magic angle has not been reached.

In order to determine more accurately the polarization angles in these compounds, we made an estimation of the spectroscopic moments of the methylene bridges by comparing the B_{2u} absorption band of cyclotriveratrylene (**1**) with that of the model 4,5-dimethylveratrole (Table III). A rough estimation of the vibrational intensity was obtained by subtracting from the experimental intensity of the model the theoretical intensity, calculated from the spectroscopic moments of the OCH_3 and CH_3 groups (we used the most recent values reported by Sagiv[19]). This vibrational intensity was then subtracted from one-third the intensity of **1**, and, assuming a value of +32.5 (average of the data of Sagiv) for the spectroscopic moment of OCH_3, that of the methylene bridges was finally evaluated as ca. +19 L/mol·cm. Considering that the mean moment of CH_3 is +7.6 and that of

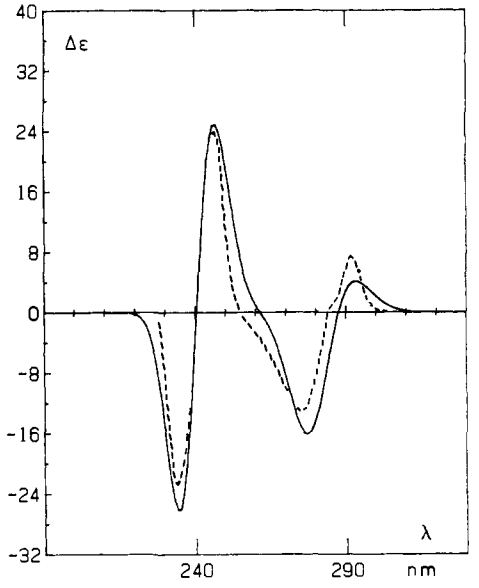


Figure 6. Calculated (—) and experimental (---) circular dichroism spectra of (*P*)-(−)-**10** in the B_{1u}–B_{2u} region. The calculated spectrum was obtained with the following data: $\theta = -38°$, $D_{mon}(B_{1u}) = 3.6 \times 10^{-36}$ cgsu and $D_{mon}(B_{2u}) = 2 \times 10^{-36}$ cgsu.

$(CH_2)_4$ is +13, this value may seem realistic, on account of the hyperconjugation occurring in **1**. Using this value, the polarization angles of the B_{2u} transition in **4** and **5** should be ca. −25° and in **10** and **11** ca. −38°, confirming that even in the second case the magic angle is far from being reached.

The qualitative shape and correct order of magnitude of the CD spectra of **4** and **10** could be satisfactorily reproduced (Figures 1 and 6), using the curve-plotting function given in the Appendix section. The value of $D_{mon}(B_{2u})$ was reduced to 2×10^{-36} cgsu, on account of the smaller intensity of the absorption in these compounds with respect to those of the first group (see Table III), and the interference term (eq VIII) was taken into account (again, the potential term contained in eqn (VIII) was multiplied by 3).

On the contrary, the CD spectrum of the acetoxy derivative **12**, in which θ should be ~−20°, completely lacks the low-energy component of the B_{2u} couplet (Figure 5), and this feature could not be reproduced even qualitatively by curve plotting when "normal" values of the dipole strengths were used. The experimental spectrum displays a very strong negative band nearly overlapping the B_{1u} couplet, and interaction of the B_{2u} transition with this band could perhaps be responsible for this nonzero order behavior.

Effect of Ionization. In order to reach the region of the magic angle θ_m, substituents R_1 and R_2 should have spectroscopic moments of very different magnitude. We expected that such a situation could be obtained in the case of **2**[20] and **11**, after ionization of the phenolic groups, and we therefore recorded the CD spectra of these compounds in 0.2 N sodium methoxide/methanol solution. Both compounds exhibited the same behavior (Figure 7 and ref 20), consisting of an apparent inversion of all CD bands. This inversion, however, is not real and very likely originates from the disappearance of the low-energy component of the B_{2u} couplet and the red shift of all transitions clearly visible in the UV spectra (Table III).

As was discussed previously, ionization of the OH groups increases considerably the absorption intensity, and this can be interpreted in terms of an enhanced spectroscopic moment. This effect causes a rotation of the resultant transition vector toward the component vector of group O^-; angle θ should therefore increase and approach the region of the magic angle. Experimental evidence shows, however, that the magic angle region is possibly reached, but not crossed. Considering the relatively large contribution of the methylene bridges (see above), the theoretical increase of the absorption intensity, necessary to reach $\theta_m \sim 45°$, critically depends on the addition law used for the calculation of the polarization angle. When the "quadratic law"[18] is used, ϵ_{max}

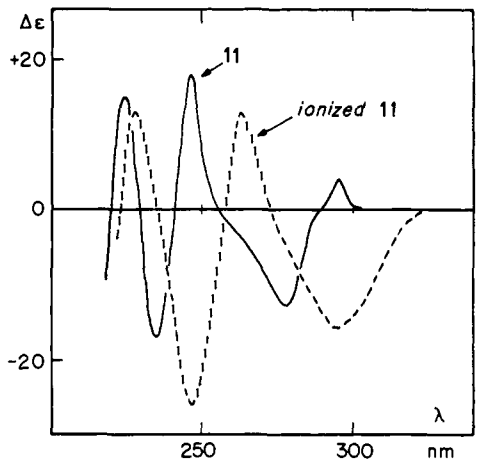


Figure 7. Circular dichroism spectra of (−)-**11** (—) in methanol and (---) in 0.2 N sodium methoxide/methanol.

should increase about twice after ionization, as observed[36] (see Table III). However, in several examples, different exceptions[32] have been observed, and data concerning the O^- substituent are not available.

Considering the above results, the only possibility of crossing the magic angle in these compounds would perhaps consist of introducing a substituent having a *negative* spectroscopic moment ortho to the OH group (e.g., $R_1 = C{\equiv}N$, $R_2 = OH$). The synthesis and optical resolution of such derivatives is not an easy task, however.

Finally, the disappearance of the low-energy component in ionized **2** and **11** is again in the trend observed above due to the dependence of the interference term with θ and seems to confirm that the interaction potential, which increases from $\theta = 0$ up to a maximum at 45°, gives a very strong contribution to this term.

Conclusion

Analysis of the chiroptical properties of cyclotriveratrylenes in light of the exciton theory can provide relatively accurate information on the conformational, vibrational,[12] and electronic consequences of comparatively small chemical modifications of the benzene ring substituents.

The following points seem to be relevant: (i) The simple exciton approach is able to explain correctly the conservative CD spectra of C_3-cyclotriveratrylenes. (ii) In the case of nonconservative couplets, and also when a single CD band is present, a simple interaction of configuration treatment is able to explain the trend observed and to avoid wrong configurational assignments. (iii) From this analysis, an accurate scale of magnitude of the spectroscopic moments is given for ortho-disubstituted OH and *O*-alkyl groups. Namely, the spectroscopic moments of alkoxy groups decrease with the increasing of the alkyl chain dimensions, indicating that, in solution, the equilibria between planar and nonplanar conformers are influenced by steric effects. A quantitative translation of the spectroscopic moments scale into actual rotamer populations does not seem straightforward, however; (iv) Finally, linear dichroism measurements can be used as an independent method in order to confirm the correctness of the exciton interpretation. We feel that, owing to its technical and interpretative simplicity, this technique should be used more often in connection with CD research.

Experimental Section

Melting points were measured on a Perkin-Elmer DSC2 microcalorimeter equipped with an HP86 calculator for data acquisition and processing (purity assessment). Rotations were measured on a Perkin-Elmer 241 micropolarimeter, in thermostated 1-dm quartz cells and spectrometric grade solvents (usually Merck Uvasol chloroform stabilized with ca. 0.5% ethanol). Circular dichroism spectra were recorded at room temperature on Jouan Dichrograph II or Jasco J500A instruments, the latter equipped with a DP500 data processor. Absorption spectra (UV) were obtained on a Perkin-Elmer 554 or Jasco Uvidec 510 spectrometer. Routine ^1H and ^{13}C NMR spectra were recorded on Perkin-Elmer R32

(90 MHz) and Varian FT80A (20 MHz) instruments, respectively. Some ^1H spectra (analysis of diastereomer mixtures) were also recorded at 250 MHz on a Brucker WM250 spectrometer. Combustion analyses were performed by the Service Central de Microanalyse du C.N.R.S.

Column chromatographic separations and filtrations were carried out over Merck silica gel 60 (0.040–0.063 mm); analytical and preparative thin-layer chromatography (TLC) were performed on Merck silica gel TLC plates F254.

The syntheses of the following optically active compounds have already been reported: **2**,[3] **4**,[3] **3**,[5] **5**,[5] **7**,[5] **9**,[5] and **10–13**.[12] The preparations of (+)-**8** and (±)-**3**, as well as improved procedures for optically active **2–4**, are given in this section. Cyclotriveratrylene[34] (**1**) and 4,5-dimethylveratrole[35] (**28**) were prepared as described.

Optical Resolution of C_3-Cyclotriguaiacylene (2). Preparation and Separation of Diastereomers (*M*)-(−)-24 and (*P*)-(+)-25. Racemic **2** was obtained as described previously.[12] The resolving agent (−)-ω-camphanic acid (**17**) (6.53 g, 33 mmol) was first converted into acid chloride by 1-h refluxing with $SOCl_2$ (25 mL) in benzene (25 mL) followed by removal of the solvent and excess reagent by distillation under vacuum. To this acid chloride in 40 mL of pyridine was then added 4.08 g (10 mmol) of (±)-**2**, and the mixture was stirred at 20 °C for 2 h. Then, dropwise addition of 400 mL of cold water (stirring) resulted in the precipitation of the solid diastereomers, which were collected by suction filtration, washed with water, and dried in air (9.2 g, 97%). This crude 1:1 mixture of **24** and **25** was filtered over 150 g of silica gel, using a chloroform–methanol (98:2) (v/v) mixture as the eluant; in this way it was roughly separated into two fractions, A_1 (first eluted) (5.2 g, $[\alpha]^{25}_D$ ca. +5°) and B_1 (3.9 g, $[\alpha]^{25}_D$ ca. −13° (*c* 1, $CHCl_3$)).

Each fraction was then chromatographed over 1 kg of silica gel by using dichloromethane–ether (95:5) (v/v) as the eluant, with recycling unresolved fractions on the same column. The purest fractions were combined according to their rotations, and in this way, 3.4 g of a crop A_2 ($[\alpha]^{25}_D$ +31°) and 4.8 g of B_2 ($[\alpha]^{25}_D$ −25° (CHCl)3)) were obtained, in addition to 0.5 g of poorly resolved mixture. In order to obtain reference samples of the pure diastereomers, the latter mixture was separated by preparative TLC with the same eluant as above, giving **25** (first eluted) ($[\alpha]^{25}_D$ +47°) and **24** ($[\alpha]^{25}_D$ −52° (*c* 1, $CHCl_3$)). Final purification of crops A_2 and B_2 was best accomplished by crystallization. Thus, A_2 was dissolved in dichloromethane (30 mL) *without heating*, and the same volume of ethanol was added; crystallization occurred by concentration of the solution under vacuum, yielding 2.15 g of **25** with the same rotation as the reference sample above. Similarly, B_2 was dissolved in tetrahydrofuran (20 mL), and seeding with the reference sample followed by crystallization at 0 °C afforded 2.25 g of pure **24**. No m.p. could be recorded by DSC for these two compounds (ca. 270–300 °C dec).

C,H analysis and ^1H NMR suggest that both **24** and **25** crystallize as monohydrates. Anal. Calcd for $C_{54}H_{60}O_{15}$, H_2O: C, 67.07; H, 6.46. Found for **24**: C, 67.0; H, 6.7. Found for **25**: C, 67.1; H, 6.5. ^1H NMR (internal TMS in $CDCl_3$) δ (**24**) 6.91 and 7.06 (s (aromatic H's), 3.63 and 4.78 d, *J* = 13.7 Hz, H_e and H_a), 3.83 (s, OCH_3), 1.12, 1.14, and 1.17 (s, camphanyl group), 1.6–2.8 (m, camphanyl group), (**25**) 6.89 and 7.07 (s), 3.62 and 4.77 (d, *J* = 13.2 Hz), 3.82 (s); 1.09, 1.12, and 1.15 (s), and 1.6–2.8 (m).

Diastereomers (−)-**24** and (+)-**25** have nearly mirror image CD spectra (0.12 g/L in dioxane): (**24**) 293 nm (Δε +14.2) 274 (−21.2), 247 (+10.1), 232 (−51.0), (**25**) 292 (−16.8), 274 (+22.2), 247 (−12.0), 233 (+43.5).

Cleavage of Diastereomers 25 and 24. (*M*)-(+)- and (*P*)-(−)-2,7,12-Trihydroxy-3,8,13-trimethoxy-10,15-dihydro-5*H*-tribenzo[*adg*]cyclononene ((+)- and (−)-C_3-Cyclotriguaiacylene (2)). The crystalline diastereomer (+)-**25** (500 mg, 0.53 mmol) was added by portions to a stirred suspension of lithium aluminum hydride (250 mg) in 10 mL of tetrahydrofuran at 0 °C, and the mixture was stirred for 1 h at this temperature. Then the excess reagent was destroyed by dropwise addition of ethyl acetate, and the precipitated alumina was dissolved by adding 10% aqueous H_2SO_4 (ice bath). Extraction with ethyl acetate followed by evaporation of the solvent under vacuum *without heating* afforded 400 mg of crude material, from which the desired triphenol was isolated by column chromatography over 40 g of silica gel with dichloromethane–ether (9:1) (v/v) as the eluant; the yield was 213 mg (99%) which after digestion in ether (5 mL) at room temperature finally gave 186 mg (86%) of (+)-**2**, $[\alpha]^{25}_D$ +271° (*c* 0.28, $CHCl_3$), mp 304–308 °C. Recrystallization from chloroform did not raise the rotation.

Similarly, 500 mg of (−)-**24** afforded 140 mg (65%) of (−)-**2**, $[\alpha]^{25}_D$ −270° (*c* 0.3, $CHCl_3$). A partially resolved mixture of camphanates (100 mg) gave by the same treatment 32 mg of **2**, $[\alpha]^{25}_D$ +205°; two recrystallizations from chloroform afforded 11 mg, $[\alpha]^{25}_D$ +264°.

The ^1H and ^{13}C NMR spectra of (+)- and (−)-**2** have previously been reported;[4] C,H analysis of both enantiomers was consistent with the formation of monohydrates (this feature was also observed for the racemate[12]). Anal. Calcd for $C_{24}H_{24}O_6$, H_2O: C, 67.59; H, 6.15. Found for (+)-**2**: C, 67.7; H, 6.0. Found for (−)-**2**: C, 67.8; H, 6.0.

(*M*)-(−)-2,7,12-Triacetoxy-3,8,13-trimethoxy-10,15-dihydro-5*H*-tribenzo[*adg*]cyclononene (4). Triphenol (−)-**2** (15 mg) was allowed to react with acetic anhydride (0.5 mL) in pyridine (1 mL) for 1 h at 0 °C. Dilution with cold water afforded a solid which was purified by TLC on silica gel (dichloromethane–ether (9:1) (v/v) as the eluant), and the crystalline material so isolated was digested in ether: yield, 11 mg; mp 273 °C, $[\alpha]^{25}_D$ −169° (*c* 0.3, $CHCl_3$). Anal. Calcd for $C_{30}H_{30}O_9$: C, 67.40; H, 5.66. Found: C, 67.3; H, 5.55.

^1H NMR (internal TMS in $CDCl_3$) δ 2.16 (s, CH_3CO), 3.79 (s, OCH_3), 3.58 and 4.72 (d, *J* = 13.7 Hz, H_e and H_a), 6.84 and 7.00 (s, aromatic H's); ^{13}C NMR (internal TMS in $CDCl_3$) δ 20.7 and 169.1 ($CH_3C{=}O$), 36.4 (CH_2 bridges), 55.2 (OCH_3), 114.1 and 124.0 (aromatic CH's), 131.4 and 137.9 (aromatic CCH_2's), 138.4 and 149.8 (aromatic CO's).

(*P*)-(+)-2,7,12-Triisopropoxy-3,8,13-trimethoxy-10,15-dihydro-5*H*-tribenzo[*adg*]cyclononene (8). To the triphenol (+)-**2**, having $[\alpha]^{25}_D$ +271° (100 mg, 0.25 mmol), dissolved in 2 mL of HMPA (hexamethylphosphoramide) was added 0.48 mL of 25% aqueous NaOH (4-fold excess), and the resulting suspension was stirred for 15 min at room temperature. Then 0.3 mL (3 mmol) of isopropyl iodide was added, and the reaction was allowed to proceed for 4 h.[33] Dilute HCl was added, and the product was extracted with ether. The organic layer was washed with water, dried over sodium sulfate, and evaporated to dryness in vacuum (*no heating*!); the crude product was filtrated over a short column of silica gel with dichloromethane as the eluant, and the resulting solid material (120 mg) was recrystallized from ether at 20 °C, yielding 87 mg (67%) of pure **8**, $[\alpha]^{25}_D$ +14.2° (*c* 0.7, $CHCl_3$). This compound is polymorphic, mp 146, then 154, and finally 160 °C, as observed by DSC (heating rate 5 K/min from 140 °C). Anal. Calcd for $C_{33}H_{42}O_6$: C, 74.13; H, 7.92. Found: C, 74.1; H, 8.1.

^1H NMR (internal TMS in $CDCl_3$) δ 1.30 (d, *J* = 6 Hz, isopropyl group), 1.34 (d, *J* = 6.1 Hz, isopropyl groups), 4.43 (m, isopropyl groups), 3.50 and 4.74 (d, *J* = 13.6 Hz, H_e and H_a), 3.79 (s, OCH_3), 6.80 and 6.85 (s (aromatic H's); ^{13}C NMR (internal TMS in $CDCl_3$) δ 22.1 and 22.4 ($(CH_3)_2CH$), 36.6 (CH_2 bridges), 56.2 (OCH_3), 71.9 (OCH), 114.4, 118.6, 132.1, 132.9, 146.5, 149.4 (aromatic C's).

4-Ethoxy-3-methoxybenzenemethanol (30). This compound was prepared by reaction of vanillyl alcohol (20 g, 130 mmol) with ethyl iodide (17 mL, 210 mmol) and potassium carbonate (20 g, 145 mmol) in 60 mL of acetone at reflux overnight under nitrogen. After the solvent and excess reagent were evaporated off, the residue was taken up with water and extracted with ethyl acetate. The organic layer was washed with aqueous NaOH, dried over sodium sulfate, and evaporated to dryness: yield 17.9 g (76%). Recrystallization from diisopropyl oxide (50 mL) at 4 °C afforded 14.1 g of pure **30**, mp 45 and then 50 °C (polymorphic). Anal. Calcd for $C_{10}H_{14}O_3$: C, 65.91; H, 7.74. Found: C, 65.6; H, 7.8. ^1H NMR (internal TMS in $CDCl_3$) δ 1.42 (t, *J* = 5 Hz, C_2H_5O), 4.06 (q, *J* = 5 Hz, C_2H_5O), 1.7 (s, OH), 3.83 (s, OCH_3), 4.57 (s, CH_2OH), 6.82–6.89 (m, aromatic H's).

(±)-2,7,12-Triethoxy-3,8,13-trimethoxy-10,15-dihydro-5*H*-tribenzo[*adg*]cyclononene (7). To a solution of **30** (15 g, 82 mmol) in 150 mL of methanol stirred and cooled to 10–15 °C (ice bath) was added dropwise 75 mL of 65% perchloric acid. The resulting solution was kept in a refrigerator (4 °C) for 48 h (a precipitate was formed). Water (150 mL) was added dropwise with shaking, and the organic material was extracted with dichloromethane. The organic layer was thoroughly washed with aqueous NaOH (**Caution**: all the perchloric acid must be removed at this step) and then with water and dried over sodium sulfate. Evaporation to dryness gave 13.4 g of a solid from which 8.45 g of crude **7** was isolated by filtration over 100 g of silica gel (CH_2Cl_2 as the eluant). Digestion in 100 mL of refluxing diisopropyl oxide finally afforded 6.92 g (51%) of pure **7**, mp 172 °C. Anal. Calcd for $C_{30}H_{36}O_6$: C, 73.14; H, 7.37. Found: C, 73.2; H, 7.5. The ^1H NMR spectrum was identical with that of (−)-**7**.[4]

(±)-2,7,12-Triethoxy-3,8,13-trihydroxy-10,15-dihydro-5*H*-tribenzo[*adg*]cyclononene (3). A solution of lithium diphenylphosphide in tetrahydrofuran (0.7 M) was prepared from chlorodiphenylphosphine and lithium as described;[14b] 50 mL of this deep red-colored solution (35 mmol of reagent) was added to 4 g of (±)-**7** (8.1 mmol, 24.4 mequiv), and the reaction was allowed to proceed at 20 °C with stirring under nitrogen for 6 h. Then the mixture (still red-colored) was hydrolyzed with cold 6 N HCl and extracted with dichloromethane. The phenolic material was extracted with 3 × 100 mL of 1 N NaOH, and the aqueous phase was washed with dichloromethane. Upon acidification (12 N HCl) a white precipitate was obtained; after 1 h of standing, it was collected by suction filtration and dried in air to yield 3.7 g of crude **3**, which was purified by chromatography over 100 g of silica gel (dichloromethane–ether

(95:5) (v/v) as the eluant) to give 2.84 g (78%) of the desired product, mp 229-232 °C. Anal. Calcd for $C_{27}H_{30}O_6$: C, 71.98; H, 6.71. Found: C, 71.9; H, 7.1. The ^1H NMR spectrum was identical with that of (-)-**3**.[4] Recrystallization of this compound from ethyl acetate (in which it is very sparingly soluble) slowly afforded small platelets (mp 234 °C) of a monohydrate. Anal. Calcd for $C_{27}H_{30}O_6$, H_2O: C, 67.90; H, 6.96. Found: C, 67.8; H, 6.9.

Optical Resolution of (±)-3; Preparation and Separation of Diastereomers 26 and 27. Triphenol (±)-**3** (500 mg, 1.1 mmol, 3.3 mequiv) and (*R*)-(+)-2-phenoxypropionic acid[15] (810 mg, 4.9 mmol) were allowed to react in 5 mL of dimethylformamide in the presence of dicyclohexylcarbodiimide (1.03 g, 5 mmol) and 4-(dimethylamino)pyridine (60 mg, 0.2 mmol);[38] after the solution was stirred for 3 h at 20 °C under nitrogen, the precipitate (dicyclohexylurea) was removed by filtration and washed with 50 mL of dichloromethane. The filtrate was washed with 1 N HCl, water, and 5% aqueous $NaHCO_3$, dried over sodium sulfate, and evaporated to dryness. The solid residue (1.4 g) was taken up with 20 mL of ether and collected by suction filtration, affording 1 g (100%) of the 1:1 mixture of **26** and **27**. These diastereomers were separated over silica gel, using dichloromethane-ether (99:1) as the eluant; the 1:1 mixture was first chromatographed on a column (200 g of adsorbent), giving four partially resolved fractions which then were submitted to preparative TLC. In this way, 345 mg of **27** (first eluted) was obtained as a white amorphous powder having $[\alpha]^{25}_D$ +99° (*c* 0.5, $CHCl_3$), and 335 mg of **26** was isolated after crystallization from ether, $[\alpha]^{25}_D$ +37° (*c* 0.5, $CHCl_3$) (**26** very likely forms a crystalline complex with ether, as suggested from ^1H NMR). Both diastereomers were pure, as judged from TLC and from their 250-MHz ^1H NMR spectra: ^1H NMR (internal TMS in $CDCl_3$) δ (**27**) 1.33 (t, *J* = 6.9 Hz, C_2H_5O), 3.99 (q, *J* = 6.9 Hz, C_2H_5O), 1.78 (d, *J* = 6.8 Hz, CH_3CH), 4.79 (q, *J* = 6.8 Hz, CH_3CH), 3.53 and 4.67 (d, *J* = 13.8 Hz, H_e and H_a), 6.80 and 6.90 (s, aromatic H's of the cyclotriveratrylene cap), 6.99-7.02 and 7.26-7.32 (m, aromatic H's of the phenoxypropionate residue), (**26**) 1.26 (t), 3.77-4.00 (m), 1.77 (d), 4.95 (q), 3.49 and 4.65 (d), 6.72 and 6.80 (s), 6.95-7.02 and 7.27-7.33 (m).

Cleavage of Diastereomers 27 and 26 to (+)- and (-)-3. Diastereomer **27** (278 mg, 0.31 mmol) was added by portion to a stirred suspension of lithium aluminum hydride (150 mg) in 5 mL of tetrahydrofuran at -5 °C under nitrogen. The mixture was stirred for 15 min at this temperature and then 1 h at 20 °C. Hydrolysis was carried out at 0 °C (internal temperature) by adding successively several drops of ethyl acetate, ether (nonanhydrous), water, and finally 1 N sulfuric acid in order to dissolve precipitated alumina. Extraction with ether (100 mL) followed by evaporation to dryness under vacuum (*no heating*!) afforded a mixture of the desired triphenol and 2-phenoxypropanol, which was separated by chromatography over 40 g of silica gel (dichloromethane-ether (99:1)). The purest fractions on evaporation (20 °C) afforded a glass (130 mg, 93%), which on standing in the presence of ether became crystalline; 110 mg (79%) of pure (+)-**3** was thus collected: mp 250 °C; $[\alpha]^{25}_D$ +293° (*c* 0.34, $CHCl_3$). Anal. Calcd for $C_{27}H_{30}O_6$: C, 71.98; H, 6.71. Found: C, 71.5; H, 6.8.

In a similar way, cleavage of **26** afforded (-)-**3**, having $[\alpha]^{25}_D$ -293° (*c* 0.30, $CHCl_3$).

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Appendix

Spectra Calculations and Curve Plotting. The A and E components of each CD couplet were assigned wavenumbers $\tilde{\nu}_A = \tilde{\nu}_0 + {}^2/_3\Delta\tilde{\nu}$ and $\tilde{\nu}_E = \tilde{\nu}_0 - {}^1/_3\Delta\tilde{\nu}$, respectively, where $\tilde{\nu}_0$ is the wavenumber of the "monomer"; as discussed in the text, $\Delta\tilde{\nu}$, the exciton splitting, was considered to be 3 times the value calculated with the point-dipole approximation (eq II); i.e., $\Delta\tilde{\nu} = 3(3V/hc)$. Then, each component was given the corresponding rotatory strength from eq III, without configuration interaction, or from eq III + IV, with interaction, and, assuming that the CD spectrum is the sum of these *i* Gaussian bands, the theoretical spectrum was plotted by using function IX,[8] where $A = 4N(2\pi)^{5/2}/3hc10^3 \ln 10 = 18.8 \times 10^{37}$ cgsu.

$$\Delta\epsilon(\tilde{\nu}) = A\sum_i \left(\frac{R_i\tilde{\nu}_i}{\sigma_i}\right) \exp\left(\frac{-(\tilde{\nu}-\tilde{\nu}_i)^2}{2\sigma_i^2}\right) \qquad \text{(IX)}$$

The standard deviation of a band, $\sigma_i = \Gamma_i/2.354$, was considered to be a function of the wavenumber,[31] $\sigma_i = P(\tilde{\nu}_i)^{1/2}$, and the curve plotting function IX accordingly becomes (X).

$$\Delta\epsilon(\tilde{\nu}) = ((18.8 \times 10^{37})/P)\sum_i (R_i(\tilde{\nu}_i)^{1/2}) \exp\left(\frac{-(\tilde{\nu}-\tilde{\nu}_i)^2}{4P^2\tilde{\nu}_i}\right) \qquad \text{(X)}$$

Parameter *P* was usually taken to be 6.123, corresponding to $\Gamma = 2700$ cm^{-1} at 285 nm.

Stereoelectronic Effects in the Cationic Rearrangements of [4.3.2]Propellanes

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Abstract: The preparation and cationic rearrangement of some 15 [4.3.2]propellane derivatives are described. The resulting products are summarized in Tables I-III. The rearrangements were found to be under strict stereoelectronic control, wherein the central or peripheral σ-bond of the cyclobutane ring best aligned with the leaving group (π-system in the case of olefins) undergoes initial migration. Product assignments were based either on single-crystal X-ray analysis or chemical correlation with known compounds.

In 1978 Ranieri and Calton published the isolation and characterization of quadrone (**1**), a biologically active sesquiterpene with a unique carbon skeleton.[2,3] The years since this discovery have witnessed significant activity directed toward the synthesis of **1**; to date seven syntheses of *racemic* quadrone have been reported.[4a-g] Our own interest in the quadrone structure[5] led us

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