value of τ for CN-NO_2-A might be different from that for Bz-NO_2-A. We are now planning to measure the $T_n(n\pi^*)$ lifetimes using a picosecond mode-locked Nd^{3+}:YAG laser or Nd^{3+}:glass laser.

Acknowledgment. We express our sincere thanks to Dr. Hiroaki Ohya of Kyoto University for his valuable help and suggestion concerning simulation of ESR spectra and calculation of spin densitities. Thanks are also due to Professor Satoshi Hirayama of Kyoto Institute of Technology for his collaboration in the experiments on the steady-state photolysis in basic ethanol.

Registry No. CN-NO_2-A, 14789-43-6; Bz-NO_2-A, 40933-02-6; CAOH, 14789-46-9; BAOH, 75532-21-7.

Optical Activity due to Isotopic Substitution. Synthesis, Stereochemistry, and Circular Dichroism of (+)- and (−)-[2,7,12-$^2H_3$]Cyclotribenzylene

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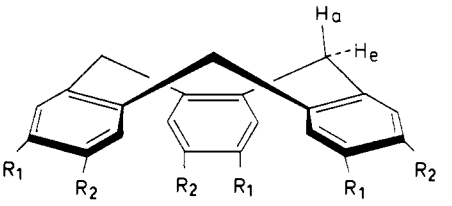
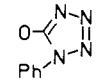
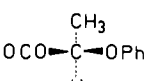
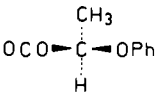
Abstract: The enantiomers of [2.7.12-$^2H_3$]cyclotribenzylene (**3**), whose chirality is due to isotopic substitution, were synthesized from cyclotriguaiacylene (**2**), and their absolute configuration was established as *M*-(−) or *P*-(+). The phenolic groups in the starting compound **2** were removed by hydrogenolysis of the corresponding tris(2-phenyl-1-tetrazolyl) ether **8**, and the resulting cyclotrianisylene (**4**) was demethylated into cyclotriphenolene (**5**). Optical resolution of **5** followed by deuteriolysis of the phenolic groups then provided the desired (+)- and (−)-**3** with a high isotopic purity. The energy barrier for crown inversion in **3** was calculated from the racemization rates to be $\Delta G^{\ddagger}$ = 112.5 kJ/mol (298 K). The circular dichroism of (*M*)-(−)-**3** consisted of a well-resolved sequence of positive and negative bands centered at 265 nm with $\Delta\epsilon$ ca. +0.01 to −0.06 from high to low energy. Interpretation in terms of vibronic rotation of the B_{2u} transition moment, induced by the deuterium atoms perturbing the breathing mode of each phenyl ring, was qualitatively consistent with the observed spectrum.

There is a continuous interest in the chiroptical properties of molecules optically active by isotopic substitution.[1] The isotope acting as an electronically neutral perturber, originates weak Cotton effects which in turn may reveal some intrinsical electronic, vibrational, or conformational properties of the substrate. So far, most of the work in this area has been concerned with the n → π* transition of ketones chiral by deuterium substitution.[2] Recently, the number of chromophores studied has, however, increased, including substrates having thioketone,[3] alkene and diene,[4] quinone,[5,6] carboxylic acid,[7] anhydride, imide, and nitrosamine structures.[6,8] On the other hand, as yet there have been very few reports dealing with the aromatic chromophore.[9-11]

In previous papers,[11,12] we described the synthesis and circular dichroism (CD) of (*M*)-(−)-[$^2H_9$]cyclotriveratrylene (**1**) in which the chirality arises from the selective replacement, on the aromatic rings, of three OCH_3 by three OCD_3 substituents. This compound exhibited a strong isotopically engendered exciton CD connected with the aromatic B_{2u} transition, the origin of which was ascribed to a difference in the rotamer populations of Ar–O–CH_3 vs. Ar–O–CD_3. Recently we have obtained the enantiomers of an analogous, simpler compound, [2,7,12-$^2H_3$]-cyclotribenzylene ((+)- and (−)-**3**), in which no such conformational changes can occur since the deuterium atoms responsible for the chirality are bound directly to the aromatic rings.[13] We now report the full synthetic details and the chiroptical properties of **3**. This compound actually displays a comparatively strong CD, which therefore can be solely ascribed to a "primary effect" of a deuterium atom on the properties of the benzene chromophore. There is only one previous example in which such a "primary effect" of an isotope was observed: (*S*)-(−)-[4-^2H]-[2.2]paracyclophane (**12**);[9] however, the CD of this compound was substantially weaker than that of **3**.



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

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[†] Collège de France.
[‡] Istituto di Scienze Chimiche.

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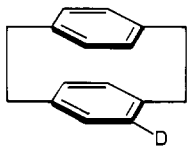


B

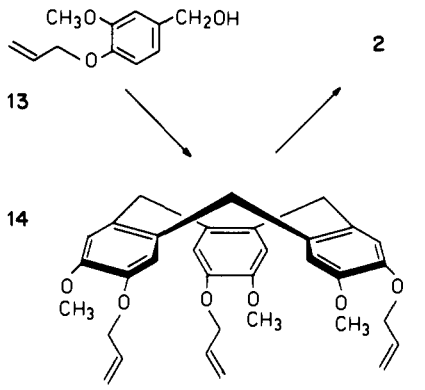
Syntheses and Absolute Configurations

There are very few C_3-functionalized cyclotriveratrylenes available in multigram quantities, allowing for subsequent multistep transformations.[14] One of these is C_3-cyclotriguaiacylene (**2**), which can be prepared easily as summarized in Scheme I. The phenolic allyl ether of vanillyl alcohol **13** actually undergoes smooth trimerization in the presence of perchloric acid,[14] affording the C_3-cyclotriveratrylene derivative **14** in 50–55% isolated yield. The allyl ethers of **14** can then be cleaved back to the phenols under mild conditions,[39] giving **2** in ca. 35% overall yield from vanillyl alcohol.

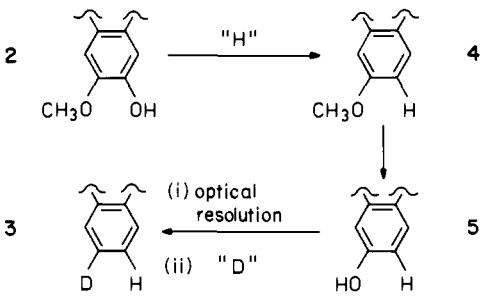
Thus, using **2** as the starting material for the synthesis of **3**, we outline the sequence depicted in Scheme II, the first step of which consists of the removal of the three phenolic groups to give the racemic C_3-tris(methyl ether) **4**. Demethylation of this compound and optical resolution of the resulting triphenol **5** followed by replacement of the three phenolic oxygens by three deuterium atoms is then expected to provide the desired enantiomers of **3**. However, as chiral cycloveratrylenes racemize on heating (via crown inversion) over a barrier of 110–115 kJ/mol, we are faced with the requirement that all the transformations of the above sequence must be performed at temperatures ≤20 °C whenever optically active material is involved.

The key steps of this synthesis are the selective replacements of the phenolic groups in **2** or **5** by hydrogen or deuterium atoms. We first expected that these transformations could be effected under mild conditions using the recent catalytic transfer hydrogenation method of Johnstone et al.[15] Accordingly, we converted the triphenol (±)-**2** into the tris(2-phenyltetrazolyl ether) (±)-**8**, which unfortunately proved to be totally inert under the specified hydrogenolysis conditions (10% palladium on charcoal in benzene–ethanol–water, with hydrazine as the H donor). This failure was presumably due to the fact that **8** was very sparingly soluble under these conditions. We therefore turned to the original procedure of Musliner and Gates[16] using molecular hydrogen, although it was reported to require prolonged reaction times at 35–40 °C under 2–3 atm of H_2. These conditions were not suitable

Scheme I



Scheme II



in our case, since they would have lead to some racemization in the resolved samples. Nevertheless we found that by using a dichloromethane–methanol ca. 2:1 mixture as the solvent instead of benzene[16] or ethanol,[17] hydrogenolysis took place smoothly at 15–20 °C under 1 atm of H_2, with 10% palladium on charcoal as the catalyst, and afforded (±)-C_3-cyclotrianisylene (**4**) in 90% isolated yield. The reaction was faster in a dichloromethane–methanol mixture than in pure dichloromethane (ca. 24 vs. 60 h), and it was faster still when conventional shaking was replaced by ultrasonic stirring, in which case hydrogenolysis went to completion over about 7–9 h. We did not use ultrasonic stirring, however, in the hydrogenolysis of optically active derivatives such as (−)-**8** and (+)- or (−)-**9** (see below), as ultrasounds are known to induce within liquids local temperature rises due to cavitation phenomena.[18] To our knowledge there is only one previous report on the use of ultrasounds in heterogeneous catalytic hydrogenation.[19] Moreover, although there are some examples of catalytic hydrogenations carried out in, or in the presence of, chloroform and in 1,1,2,2-tetrachloroethane,[20] the use of dichloromethane in such reactions does not seem to have been reported as yet; surprisingly, no or very sluggish hydrogenolysis took place when chloroform–methanol was employed instead of dichloromethane–methanol as the solvent, although the tetrazolyl ether was soluble in both cases.[21]

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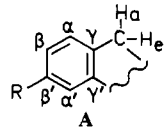
(21) Although we did not study in detail the influence of the solvent, we observed that hydrogenolysis of **8** failed completely under acidic conditions, such as in acetic acid containing $HClO_4$. Moreover, in agreement with a previous report,[20a] we found that a chloroform–methanol 2:1 mixture on shaking in the presence of Pd/C and H_2 became acidic within 30 min due to the formation of HCl. In contrast, treatment of dichloromethane–methanol mixtures under similar conditions did not gave evidence for HCl formation even after 2 h.

Table I. ^{1}H NMR Spectral Data for Compounds **3–7**[a]



A

	H_α				H_β				$H_{\alpha'}$	H_a		AX q		H_e	R
4	7.28 d	←	(8.4)	→	6.44 dd	←	(2.7)	→	6.88 d	4.76	←	(13.6)	→	3.64	3.74 s (OCH_3)
5	7.14 d	←	(8.3)	→	6.44 dd	←	(2.6)	→	6.72 d	4.70	←	(13.2)	→	3.49	ca. 4.3 (OH)
6	7.34 d	←	(8.4)	→	6.85 dd	←	(2.5)	→	7.08 d	4.82	←	(13.6)	→	3.73	2.27 s ($OCOCH_3$)
7	7.38 m				7.09 m					4.92	←	(13.3)	→	3.76	
3	7.38 d	←	(7.6)	→	7.09 d				7.38 s	4.91	←	(13.3)	→	3.76	

[a] High-field (250 or 270 MHz) spectra in $CDCl_3$, except for **5** in dioxane-d_8; δ from internal $(CH_3)_4Si$, with the coupling constants in parentheses.

Table II. ^{13}C NMR Spectral Data for Compounds **3–7**[a,b]

	α	α'	β	β'	γ	γ'	CH_2	R
4	130.65	115.02	111.75	157.94	131.20	140.80	36.15	54.77 (OCH_3)
5	132.39	117.74	115.16	157.19	132.39	143.21	37.32	(OH)
6	130.96	122.58	120.15	149.26	136.31	140.37	36.47	169.3, 21.0 ($OCOCH_3$)
7	129.93		126.84		139.35		37.06	(H)
3	129.91	129.84	126.75	*c*	139.38	139.38	37.08	(D)

[a] See Table I for carbon labeling. [b] Spectra recorded at 20 MHz, δ from internal $(CH_3)_4Si$ in $CDCl_3$ (**3**, **6**, **7**), in $CDCl_3$ + acetone-d_6 (**4**), and in dioxane-d_8 (**5**). [c] The C–D triplet was not detected.

Compound **4** on reaction with boron tribromide afforded the tris(phenol) (±)-**5** (C_3-cyclotriphenolene) as a high-melting crystalline material which was characterized as its triacetate **6**. The structures of **4–6** are consistent with the ^{1}H and ^{13}C NMR spectra (Tables I and II). The locked "crown" conformation in all these compounds is evidenced by the typical AB (or AX) quartet of the methylene bridges, in which the axial hydrogens (H_a) resonate ca. 1.2 ppm downfield with respect to their equatorial (H_e) counterparts.[22] As a further structural proof, **5** was converted into the tris(2-phenyltetrazolyl ether) (±)-**9**, which on hydrogenolysis as above gave the known hydrocarbon **7** (cyclotribenzylene) mp 278 °C (lit.[23] 274–276 °C). Incidentally, this new synthesis of **7** seems to be much more convenient than that described previously.

The optical resolution of **5** was achieved by converting this triphenol into the corresponding mixture of diastereomeric triesters with (*R*)-(+)-2-phenoxypropionic acid.[24] The esterification was effected in mild conditions and 80% isolated yield by allowing the optically pure acid to react with (±)-**5** in the presence of dicyclohexylcarbodiimide and (dimethylamino)pyridine at room temperature.[25] The diastereomers were completely resolved chromatographically, affording (−)-**10**, $[\alpha]_D$ −86° (in $CHCl_3$), mp 187 °C, and (+)-**11**, $[\alpha]_D$ +195° and mp 162 °C. Their 270-MHz ^{1}H NMR spectra (Experimental Section) showed weak differences in the chemical shifts of the α-, α'-, and β-hydrogens of the cyclotribenzylene moiety; the H_β resonances, well separated from the other aromatic peaks, differed enough (6.77 vs. 6.80 ppm) to assess that **10** and **11** were pure within the detection limit of the NMR method. A similar conclusion was drawn from analytical TLC.[26]

The diastereomers **10** and **11** were cleaved back to resolved **5** by reduction with lithium triethylborohydride in tetrahydrofuran at 0 °C. This procedure ensured better yields and less racemization risks than alkaline hydrolysis. In this way (−)-**10** and (+)-**11** afforded (−)-**5** and (+)-**5**, respectively, having virtually identical rotations, $[\alpha]_D$ 190 ± 5° (in dioxane). Our assumption that these

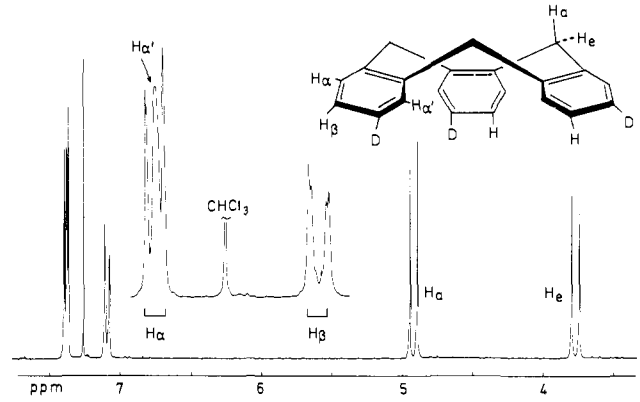


Figure 1. ^{1}H NMR spectrum (250 MHz) of (*M*)-(−)-**3** in $CDCl_3$, with the aromatic region enlarged.

compounds are close to enantiomeric purity rests on the following arguments: (i) no racemization of the resolving agent has taken place during esterification,[26] (ii) the diastereomers have been completely separated, and (iii) racemization during the cleavage step is unlikely, as indicated by the kinetic experiments discussed below.

Compound **5** was assigned *P*-(−) absolute stereochemistry by chemical connection to (*P*)-(−)-**2**, whose absolute configuration is based on a previous X-ray determination.[27] A sample of (−)-**2** having >90% ee[40] was first converted into (*M*)-(−)-**8**, $[\alpha]_D$ −81° (in $CHCl_3$), which on hydrogenolysis gave (*P*)-(−)-**4**, $[\alpha]_D$ −157° (in $CHCl_3$). On the other hand, (+)-**5** on methylation afforded (+)-**4**, $[\alpha]_D$ +161°. Comparison of the rotations of **4** obtained from either route actually supports the foregoing assumption as to the enantiomeric purity of the samples of (+)- and (−)-**5** obtained by the resolution method. These reactions also furnished the absolute configurations of **10** and **11** as shown by the stereoformulas.

Finally, in order to replace the OH groups in (+)- and (−)-**5** by deuterium atoms we transformed these triphenols into the

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(26) When esterification was carried out via the acid chloride (prepared from (*R*)-(+)-2-phenoxypropionic acid and $SOCl_2$), some racemization of the resolving agent occurred, resulting in the formation of small quantities of isomers *P*(*RRS*), *P*(*RSS*), *P*(*SSS*) and of the corresponding *M*(*RRS*) etc., in addition to the desired *P*(*RRR*) and *M*(*RRR*) diastereomers **10** and **11**. This complication was entirely avoided by using the esterification method of Neises and Steglich.[25]

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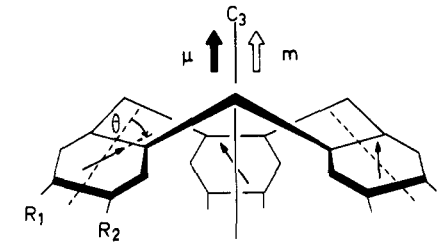
Table III. Rate Constants and Eyring Activation Parameters for Ring Inversion in **1–5**

	k (20 °C), 10^{-8} s^{-1}	$t_{1/100}$ (20 °C), h	$\Delta H^{\ddagger}$, kJ mol^{-1}	$\Delta S^{\ddagger}$, J mol^{-1} K^{-1}	$\Delta G^{\ddagger}_{298\,K}$, kJ mol^{-1}	solvent
1	11.5	12.1	108.3 (1.3)	−7.9 (6)	110.8	$CHCl_3$
2	3.46	40.3	112.9 (1.5)	−2.5 (5)	113.6	$CHCl_3$
3	5.54	25.2	110.7 (2.8)	−6.0 (9)	112.5	$CHCl_3$
4	3.51	39.8	117.5 (0.5)	+13 (2)	113.5	$CHCl_3$
5	2.91	48.0	115.0 (1.4)	+3.2 (5)	114.0	dioxane

corresponding tetrazolyl ethers (*M*)-(+)- and (*P*)-(−)-**9**, exhibiting $[\alpha]_D$ +259° and −255°, respectively (in $CHCl_3$). Deuteriolysis was achieved using 99.4% isotopically enriched deuterium gas in a CD_2Cl_2–CD_3OD 2:1 mixture, under conditions similar to those used for the conversion of **8** into **4**. We employed deuteriated solvents to avoid palladium-catalyzed hydrogen exchange between deuterium gas and solvent, which sometimes takes place in such reactions.[17] The resulting hydrocarbons **3** were isolated by TLC in order to eliminate any residual optically active starting material or incompletely transformed intermediates;[28] then they were crystallized from pentane at 20 °C. In this way, compound (+)-**8** gave (−)-**3**, mp 281 °C, whose chemical purity was assessed by TLC and by microcalorimetric examination of the melting point (DSC).[29] This compound exhibited a relatively high rotation, opposite to that of the starting material, $[\alpha]_{546}$ −2.9 ± 0.2°, $[\alpha]_{365}$ −8.9 ± 0.5° (in $CHCl_3$). Similarly, (−)-**8** gave (+)-**3**, $[\alpha]_{365}$ +8.7°. These figures are similar to those reported by Weigang et al.[9] for the paracyclophane **12**, $[\alpha]_{546}$ −4.0 ± 1.1°, and by ourselves[12] for **1**, $[\alpha]_{546}$ 3.7 ± 0.2°. Assuming that the deuterium atoms have replaced the oxygen groups regiospecifically (see below), these reactions also provide the absolute configuration of **3**, *M*-(−) or *P*-(+).

The 250-MHz ^1H NMR spectrum of (−)-**3** (Table I and Figure 1) displayed the AX quartet of the methylene bridges intact (δ 4.91 and 3.76), indicating that no detectable deuterium substitution had taken place at the benzylic positions. This result markedly contrasts with those reported in earlier work[17] involving similar deuteriation and tritiation experiments of tetraline derivatives, in which extensive labeling on the benzylic hydrogens was observed. Moreover, the aromatic part of the spectrum of **3** was consistent with the presence of one deuterium atom on each phenyl ring at the expected position. Integration gave an overall deuterium content of 0.97 D atom per phenyl ring, that is 97.6% isotopical yield (based on the 99.4% deuterium content of the gas used). On the basis of a statistical repartition[30] this would correspond to 91% of D_3 and 8% of D_2H molecules in the "trimer". This result is in agreement with mass spectroscopic measurements, which showed an intense molecular ion peak at M^+ m/z 273 corresponding to $C_{21}H_{15}D_3$; comparison of the relative intensities of the M^+ and $M^+ - 1$ peaks in **3** and in the parent nondeuteriated hydrocarbon **7** showed that the D_3/D_2H ratio was about 91:9. We are presently trying to extend the scope of this efficient deuteriation procedure to other aromatic systems, including tetralin and dihydroanthracene derivatives which, according to previous work,[17] are very sensitive to catalytic hydrogen exchange hence are difficult to label specifically.

Scheme III. In-Phase Coupling of the B_{2u} Transition with $\theta > 0$, Leading to a Positive Rotatory Strength at High Energy



Conformational Stability

The "crown" is the only observable conformation of cyclotriveratrylenes which do not bear bulky substituents on the aromatic positions ortho to the nine-membered ring.[22] In the chiral derivatives involved in this study, crown inversion affords the enantiomer of the starting compound, and measurement of the racemization rates in turn provides the energy barrier, which is too high to be measured by NMR techniques. Thus, the Eyring activation parameters for the inversion process (i.e., (+) → (−) or the inverse) in compounds **1–5** are assembled in Table III. These data show very little variation on passing from the hexasubstituted compounds **1** and **2** to the nonsubstituted hydrocarbon **3**. In terms of rate constants, however, the differences are more significant: the values of $t_{1/100}$, defined as the time necessary to lose 1% of rotation at 20 °C in solution, actually vary from 12 to 48 h. In practice, all of these compounds can therefore be considered conformationally homogeneous and rigid at ambient temperature, at which the CD measurements discussed below were recorded.

Detailed force-field calculations on the mechanism of the ring inversion of the parent hydrocarbon **7** have been reported recently by Ermer.[31] It was concluded that the rate-determining step is the passage from the crown to a readily pseudorotating saddle-twist form,[22] obtained by flipping one of the methylene bridges. The computational estimation of the energy barrier ($\Delta H^{\ddagger}$ = 142 kJ/mol) is, however, ~30% larger than the experimental one (110.7 kJ/mol).[32]

Circular Dichroism

As our previous work has shown,[33,34] the CD spectra of chiral C_3 derivatives of cyclotriveratrylene can be interpreted in terms of exciton coupling between the transition moments of the three aryl chromophores (Scheme III). Accordingly, the presence of substituents R_1 and R_2 having spectroscopic moments of different magnitudes is considered to cause a rotation of the electric transition moments B_{2u} and B_{1u} of each phenyl ring from the symmetrical positions (θ = 0 or 90°), thus generating overall collinear electric and magnetic moments in the "trimer". In fact, due to the favorable geometry and relatively strong dipole strengths of the transitions in this system, even a very small deviation of θ originates intense exciton CD, which in turn provides a sensitive, differential measurement of the relative magnitudes of nearly identical spectroscopic moments (providing that the absolute configurations of the compounds involved are known). In particular compound **1** shows, in the B_{2u} region, an unequivocal exciton couplet with $\Delta\epsilon$ ±0.3.[11] It was interpreted as being due to inequality of the spectroscopic moments of the OCH_3 and OCD_3 substituents; the deuterium-substituted group was considered to have the stronger spectroscopic moment, as a consequence of its better conjugative ability due to the higher population of the planar

(28) The reaction byproduct 2-phenyltetrazolone as well as the di- and monotetrazolyl ether intermediates are highly polar, hence any residual amounts of these compounds can be readily separated chromatographically from the hydrocarbon **3**.

(29) For example, see: Draguet-Brughmans, M.; Bouché, R. *J. Therm. Anal.* **1981**, *20*, 141–146 and references therein: Brown, M. E. *J. Chem. Educ.* **1979**, *56*, 310–313. In our case the melting scan was analyzed according to the procedure developed in our laboratory by Fouquey and Leclercq.[38] We emphasize that in the case of isotopic substitution the DSC method cannot distinguish labeled from unlabeled species (e.g., D_3 vs. D_2H, etc.) nor (+) from (−) enantiomers, since all these compounds cocrystallize, forming ideal solid solutions. Accordingly, only "foreign" impurities (such as solvent residues) can be revealed in this case.

(30) Assuming an overall deuterium content of x D atom per phenyl ring ($x < 1$), the D_3, D_2H, DH_2, and H_3 "trimers" should be obtained in the statistical ratio $x^3/3x^2(1-x)/3x(1-x)^2/(1-x)^3$, respectively. With x = 0.97, we would thus obtain for the four species 0.9127/0.0847/0.0026/2.7 × 10^{-5}. More than 99.7% of the sample would therefore consist of the D_3 and D_2H molecules in a 91.5/8.5 ratio.

(31) Ermer, O. "Aspekte von Kraftfeldrechnungen"; Wolfgang Baur Verlag: Munich, 1981; pp 368–379.

(32) Ermer, O., private communication. One of the reasons for this overestimation is that the rate-determining transition states involve very large bond angle openings, the energetical description of which requires negative anharmonicity terms which as yet are improperly calibrated.

(33) Collet, A.; Gottarelli, G. *J. Am. Chem. Soc.* **1981**, *103*, 204–205.

(34) Collet, A.; Gottarelli, G. *J. Am. Chem. Soc.* **1982**, *104*, 7383–7384.

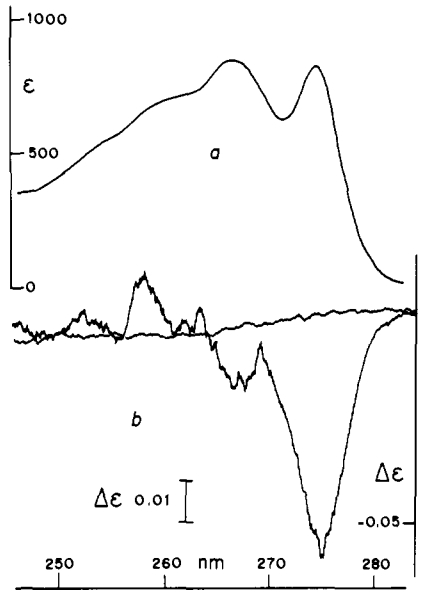


Figure 2. UV (a) and CD (b) spectra of (*M*)-(−)-**3** in acetonitrile at room temperature. The CD curve (concentration 2.1 10^{-3} M) is the average of 32 scans.[42]

conformation with respect to the slightly bulkier OCH_3 group.

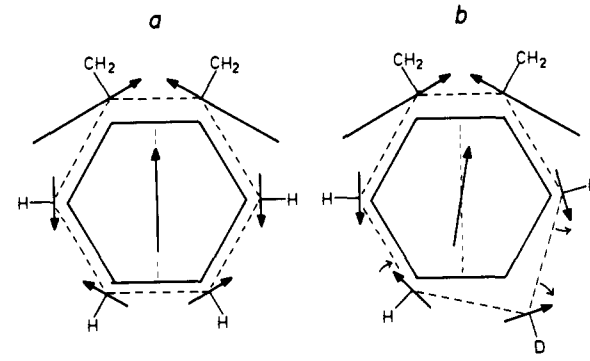
The CD spectrum of (*M*)-(−)-**3** is apparently more complex than that of **1** and consists of two well-resolved sequences of oppositely signed bands in the range 250–280 nm corresponding to the B_{2u} transition (Figure 2). The first negative band (275 nm, $\Delta\epsilon$ −0.06) is about 3 times stronger than that of the paracyclophane **12** in the same region.[9] There is correspondence between the maxima and shoulders in the absorption spectrum (Figure 2) and the maxima in the CD spectrum. In particular the weak positive CD band at 263 nm seems to correspond to the inflection in the absorption spectrum at this wavelength.

Although the resolution is far from allowing vibrational analysis, we observe that the separation between the first positive and negative bands is ca. 1800 cm^{-1}, i.e., roughly the value measured for the exciton splitting in the CD spectrum of **2** (2300 cm^{-1})[33] or in the linear dichroism spectrum of cyclotriveratrylene itself (1800 cm^{-1}).[35] The separation between bands of the same sign is instead 850–1000 cm^{-1}. Weigang and co-workers[9] in their discussion of the CD spectrum of (*S*)-(−)-**12** concluded that the observed exciton spectrum in the region of the B_{2u} transition was caused by a "vibronic rotation" of the transition dipole of the benzene ring containing the deuterium atom, "completely analogous to the electronically induced rotation" in chemically 4-substituted [2.2]paracyclophanes. The spectrum of (*M*)-(−)-**3** can apparently be explained in a similar way. Assuming the ring breathing mode as the important vibration,[9,36] the reorientation of the B_{2u} spectroscopic moment vectors on passing from the achiral hydrocarbon **7** to the deuterium-substituted **3** causes a rotation of the resulting transition moment of each benzene ring (Scheme IV). The value of θ for the *M* absolute configuration depicted is positive, thus leading to a positive rotational strength for the high energy, in-phase component, of the exciton couplet,[33] as observed (see Scheme III). An alternative approach based on the higher polarizability of the C–H vs. the C–D bond[37] gives a CD sequence opposite to that actually observed.

Experimental Section

High-field ^1H nuclear magnetic resonance spectra were recorded at 250 or 270 MHz on Brucker WM250 or 270 instruments, and routine spectra on a Perkin-Elmer R32 spectrometer (^1H, 90 MHz) and on a Varian FT80 spectrometer (^{13}C, 20 MHz). Melting points were measured by differential scanning calorimetry by using a Perkin-Elmer DSC2 instrument connected to a Hewlett-Packard HP86 calculator for data acquisition and processing (purity determination). Routine infrared spectra were recorded in Nujol suspension on a Perkin-Elmer 297 spectrometer. Rotations were measured on a Perkin-Elmer 241 spectropolarimeter using 1-dm length quartz cells, in spectrometric grade chloroform (stabilized with ethanol) or dioxane. Ultraviolet spectra were recorded on Perkin-Elmer 554 or Jasco Uvidec 510 instruments, and circular dichroism spectra on a Jasco J500A instrument equipped with a DP500 data processor. Mass spectra were obtained at 70 eV on a Thomson THN208 spectrometer. Combustion analyses were performed by the Service Central de Microanalyse du C.N.R.S. Column chromatographic separations (including filtrations) were carried out over Merck silica gel 60 (0.040–0.063 mm); analytical and preparative thin-layer chromatography were performed on Merck TLC plates silica gel F254.

Scheme IV. Sketch of the Orientation of the Spectroscopic Moment Vectors in the Breathing Mode of the Aromatic Rings or 7 (a) and **3** (b)[b]



[a] In b, the reorientation of the vectors (curved arrows) causes a rotation of the overall B_{2u} transition moment (the CH_2 bridges are considered to have the largest spectroscopic moments, and the rotations are obviously exaggerated for clarity).

Racemization Kinetics. The racemization of compounds **1–5** was followed polarimetrically in chloroform or dioxane solution, using a 1-dm thermostated cell; rotations α vs. time *t* were measured at 365 nm. Five–six temperatures in the range ca. 33–61 °C were studied for each compound (only three for **1**). The temperatures were measured with a calibrated thermocouple immersed in the circulation fluid close to the cell and were considered accurate ±0.05 K. The first-order rate constants *k* corresponding to the crown inversion process, i.e., (+) → (−) or (−) → (+), were derived from linear regressions of $\alpha(t) = \exp(-2kt)$, and, finally, regressions of $k = (RT/(\mathcal{N}h)) \exp(\Delta H^{\ddagger}/(RT) - \Delta S^{\ddagger}/R)$ afforded the Eyring activation parameters assembled in Table III with the corresponding standard deviations in parentheses. The values of $t_{1/100}$ in the table refer to (0.5/*k*) ln (100/99), in which *k* is the calculated rate constant for inversion at 20 °C (also given in the table).

3-Methoxy-4-(2-propenyloxy)benzenemethanol (13). A mixture of vanillyl alcohol (100 g, 0.65 mol), allyl bromide (63 mL, 0.73 mol), and potassium carbonate (90 g, 0.65 mol) in 150 mL of acetone was refluxed for 4 h with magnetic stirring. Then, after most of the solvent was stripped off, water was added and the organic material was extracted with dichloromethane, yielding 125 g (99%) of crude **13**. This product was recrystallized from 250 mL of diisopropyl ether, affording 100 g (80%) of pure **13**, mp 69 °C (the melting point reported in ref 14 (86 °C) is erroneous and should read 68 °C). Anal. Calcd for $C_{11}H_{14}O_3$: C, 68.02; H, 7.27. Found: C, 67.8; H, 7.4. ^1H NMR spectrum (90 Mz) δ (from internal Me_4Si in $CDCl_3$) 2.1 (s, OH), 3.82 (s, OCH_3), 4.55 (s + m, CH_2OH and OCH_2CH=), 5.1–5.5 (m, CH_2=), 5.8–6.3 (m, CH=), 6.80 (s, 2) and 6.87 (s, Ar H 2, 5, and 6, respectively); ^{13}C NMR (20 Mz) δ (from internal Me_4Si in $CDCl_3$) 55.6 (OCH_3), 64.6 (CH_2OH), 69.7 (CH_2—CH=), 117.5 (CH_2=), 133.1 (CH=); 137.9, 110.7, 149.3, 147.1, 113.2, 118.9 (Ar C_1 to C_6, respectively).

(±)-2,7,12-Trimethoxy-3,8,13-tris(2-propenyloxy)-10,15-dihydro-5*H*-tribenzo[*a*,*d*,*g*]cyclononene (14). To a solution of the above phenol-protected vanillyl alcohol **13** (100 g, 0.52 mol) in methanol (600 mL), cooled in an ice bath and magnetically stirred, was added dropwise 300 mL of 65% perchloric acid, and the resulting pink solution was stirred under nitrogen at room temperature for 18 h (crystallization of **14** began after ca. 2–3 h). Isolation of the product was best accomplished as follows: first, the precipitate was redissolved by addition of dichloromethane (ca. 1 L), and the organic phase was thoroughly washed with

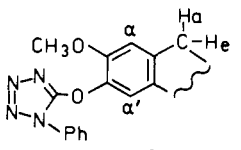
(35) Canceill, J.; Collet, A.; Gabard, J.; Gottarelli, G.; Spada, G. P. *J. Am. Chem. Soc.*, submitted for publication.
(36) Murrell, J. N. "The Theory of the Electronic Spectra of Organic Molecules"; Methuen: London, 1963; pp 121–132.
(37) Halevi, E. A. *Prog. Phys. Org. Chem.* **1963**, *1*, 109–221.
(38) Fouquey, C.; Leclercq, M. *Tetrahedron* **1970**, *26*, 5637–5651. Jacques, J.; Collet, A.; Wilen, S. H. "Enantiomers, Racemates and Resolutions"; Wiley: New York, 1981; pp 151–159.

water until neutral (CAUTION! all of the perchloric acid must be removed at this step). The dichloromethane solution was dried over sodium sulfate and evaporated under vacuum, affording a crystalline residue, which was purified by digestion in 200 mL of ether overnight and finally isolated by suction filtration, yield 48 g of **14** (53%), mp 175 °C. Anal. Calcd for $C_{33}H_{36}O_6$: C, 74.97; H, 6.86. Found: C, 75.1; H, 6.9. ^{1}H NMR spectrum (90 Mz), δ (from internal Me_4Si in $CDCl_3$) 3.74 (d) and 4.71 (d) (J = 14 Hz, H_e and H_a, respectively), 3.80 (s, OCH_3), 6.77 (s) and 6.82 (s) (Ar H), 4.55 (m, OCH_2), 5.12–5.50 (m, CH_2=), 5.72–6.30 (m, CH=); ^{13}C NMR spectrum (20 Mz) δ (from internal Me_4Si in $CDCl_3$) 36.3 (CH_2 bridges), 55.9 (OCH_3), 70.0 (OCH_2), 113.5 and 115.5 (Ar CH), 117.2 (CH_2=), 131.6 and 132.2 (Ar CCH_2); 133.6 (C=), 146.6 and 148.1 (Ar CO).

(±)-2,7,12-Trihydroxy-3,8,13-trimethoxy-10,15-dihydro-5*H*-tribenzo[*a*,*d*,*g*]cyclononene (2, C_3-Cyclotriguaiacylene). The tris(allyl ether) **14** (50 g, 95 mmol) was dissolved in 250 mL of hot dioxane, and to this solution were added 450 mL of ethanol, 10 g of 10% palladium on charcoal, and (dropwise) 10 mL of 65% perchloric acid.[39] This mixture was stirred under nitrogen at 55–60 °C (oil bath) for 20 h. The catalyst was filtered off and washed with some dioxane then with ca. 500 mL of dichloromethane. The organic filtrate was thoroughly washed with water, dried over sodium sulfate, and concentrated to ca. 150 mL. The desired triphenol, which was allowed to crystallize overnight, was finally collected by suction filtration, yield 31 g (80%) of **2** as nice white needles, mp ca. 309 °C dec. Combustion analysis was consistent with a monohydrate. Calcd for $C_{24}H_{26}O_6 \cdot H_2O$: C, 67.59; H, 6.15. Found: C, 67.6; H, 6.14. The ^{1}H and ^{13}C NMR spectra are identical with those previously reported for the enantiomers of **2**.[12]

(±)- and (*M*)-(−)-2,7,12-Trimethoxy-3,8,13-tris[(2-phenyltetrazolyl)oxy]-10,15-dihydro-5*H*-tribenzo[*a*,*d*,*g*]cyclononene (8). To a solution of racemic tris(phenol) **2** (2.04 g, 5 mmol) in 60 mL of anhydrous dimethylformamide was added 1.85 g (16.5 mmol) of potassium *tert*-butoxide, and the resulting suspension was stirred magnetically for 10 min under nitrogen. Then 2.71 g (15 mmol) of 1-chloro-2-phenyltetrazole (from Aldrich Chemical Co.) was added, and the mixture was stirred for 1 h and finally poured onto crushed ice, giving a crystalline product, which was collected by suction filtration, washed with water, and dried in air, yield 3.8 g (90%), mp ca. 245–250 °C dec. This product did not need further purification for the hydrogenolysis step. An analytical sample was obtained as a hemihydrate by recrystallization from benzene–dichloromethane, mp ca. 255 °C dec. Anal. Calcd for $C_{45}H_{36}O_6N_{12} \cdot {}^1/_2H_2O$: C, 63.60; H, 4.63; N, 19.78. Found: C, 63.3; H, 4.3; N, 19.5.

Optically active (*M*)-(−)-**8** was similarly obtained from a sample of (*P*)-(−)-**2** having $[\alpha]^{25}_D$ −260° ($CHCl_3$, *c* 2), i.e., >90% ee;[40] (*M*)-(−)-**8** exhibited $[\alpha]^{25}_D$ −81° ($CHCl_3$, *c* 2) and mp ca. 265 °C dec. Racemic



8

C

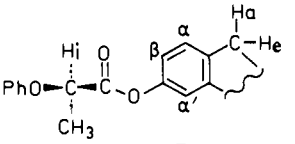
and (−)-**8** had the following ^{1}H NMR spectra (90 MHz) δ (from internal Me_4Si in $CDCl_3$) 3.66 (d, H_e) and 4.78 (d, H_a) (J = 14 Hz), 3.80 (s, OCH_3), 6.98 (s, H_α), 7.60 (s, $H_{\alpha'}$), 7.4–7.6 (m) and 7.7–7.9 (m) (Ph).

Hydrogenolysis of (±)- and (*M*)-(−)-8. (±)- and (*P*)-(−)-2,7,12-Trimethoxy-10,15-dihydro-5*H*-tribenzo[*a*,*d*,*g*]cyclononene (4, Cyclotrianisylene). A solution of (±)-**8** (1.87 g) in a mixture of dichloromethane (150 mL) and methanol (75 mL), in the presence of 1.87 g of 10% palladium on charcoal[43] as the catalyst, was stirred under H_2 (1.1 atm) by immersing the flask in the water bath of an ultrasonic cleaner (Sonoclean S2500/C, 35–40 kHz); the bath temperature was maintained at 15–20 °C by means of a refrigerating coil. In these conditions, hydrogen absorption was essentially complete after about 9 h, whereas under conventional stirring (shaking) the reaction required a longer time (ca. 24 h). The catalyst was removed by filtration, and the filtrate was washed with 1 N sodium hydroxide then water until a clear, neutral organic layer was obtained. Evaporation of the solvent under vacuum afforded 800 mg (100%) of crude **4**, which was purified by filtration over a short column of silica gel (dichloromethane as the eluant), followed by recrystallization from acetone–methanol 1:1 (v/v), yield 725 mg (90%), mp 235 °C. Anal. Calcd for $C_{24}H_{24}O_3$: C, 79.97; H, 6.71. Found: C, 79.8; H, 6.9. For ^{1}H and ^{13}C NMR spectra, see Tables I and II.

Similarly, (*M*)-(−)-**8** was submitted to hydrogenolysis as above except that conventional shaking was employed instead of ultrasonic stirring, for the reason given in the text. Ultrasonic stirring actually afforded samples of (*P*)-(−)-**4** having rotations slightly lower (5–10%) than those obtained by shaking, which exhibited $[\alpha]^{25}_D$ −157 ± 3° ($CHCl_3$, *c* 0.25).

(±)-2,7,12-Trihydroxy-10,15-dihydro-5*H*-tribenzo[*a*,*d*,*g*]cyclononene (5, Cyclotriphenolene). To a solution of cyclotrianisylene ((±)-**4**) (1.3 g, 3.6 mmol) in dry dichloromethane (25 mL), stirred under nitrogen at −78 °C, was added 1 mL (11 mmol) of boron tribromide. Stirring was continued for 10 min at −78 °C then the mixture was allowed to warm to room temperature over 1 h. Finally, it was poured onto ice and the solid was collected by suction filtration, yielding 1.1 g (100%) of **5** as a whitish powder, which decomposed without melting above 300 °C. A sample of **5** on reaction with acetyl chloride in pyridine gave the triacetate (±)-**6**, which was recrystallized from ethanol–ether, mp 218–222 °C. Anal. Calcd for $C_{27}H_{24}O_6$: C, 72.96; H, 5.44. Found: C, 72.9; H, 5.4. For ^{1}H and ^{13}C NMR spectra, see Tables I and II.

Optical Resolution of 5. Diastereomeric (*P*)-(−)- and (*M*)-(+)-2,7,12-Tris[((*R*)-2-phenoxypropanoyl)oxy]-10,15-dihydro-5*H*-tribenzo[*a*,*d*,*g*]cyclononene ((−)-10 and (+)-11). To a solution of (*R*)-(+)-2-phenoxypropionic acid[20] (750 mg, 4.5 mmol) in 5 mL of anhydrous dimethylformamide was added 50 mg (0.46 mmol) of (dimethylamino)pyridine and 318 mg (1 mmol) of racemic **5**. The solution was cooled to 0 °C under nitrogen, and 1.03 g (5 mmol) of dicyclohexylcarbodiimide was added. The resulting mixture was stirred for 5 min at 0 °C then 3 h at 20 °C. The precipitate was removed by filtration and washed with 5 mL of dichloromethane. Water was added to the filtrate and the organic material was extracted with dichloromethane and washed with 1 N hydrochloric acid, aqueous sodium hydrogencarbonate, and then water until neutral. The solvent was stripped off under vacuum, and the product was purified by filtration through a short silica gel column (dichloromethane as the eluant), yielding 610 mg (80%) of the 1:1 mixture of diastereomers **10** and **11**. The resolution was effected by column chromatography over 120 g of silica gel with dichloromethane as the eluant, and the combined fractions of (−)-**10** (first eluted) and (+)-**11** were finally recrystallized from diethyl ether (without heating). In this way, 195 mg of (−)-**10**, $[\alpha]^{25}_D$ −86.5° ($CHCl_3$, *c* 1), mp 187 °C, and 235 mg of (+)-**11**, $[\alpha]^{25}_D$ +195°, mp 162 °C, were obtained. Anal. Calcd for $C_{48}H_{42}O_9$: C, 75.57; H, 5.55. Found for (−)-**10**: C, 75.4; H, 5.5. For (+)-**11**: C, 75.35; H, 5.5. ^{1}H NMR spectra (270 MHz) δ (from



10, 11

D

internal Me_4Si in $CDCl_3$) (−)-**10** 1.76 (d, CH_3) and 4.94 (q, H_i) (J = 6.8 Hz), 3.66 (d, H_e) and 4.76 (d, H_a) (J = 13.7 Hz), 6.77 (dd, H_β, J = 8.4, 2.5 Hz), ca. 6.97 ($H_{\alpha'}$) overlapped, and 7.24d (H_α) partial overlapped, 6.93–7.03 (m) and 7.27–7.34 (m) (Ph); (+)-**11** 1.75 (d, CH_3) and 4.95 (q, H_i) (J = 6.8 Hz), 3.65 (d, H_e) and 4.76 (d, H_a) (J = 13.6 Hz), 6.80 (dd, H_β, J = 8.4, 2.5 Hz), 6.93 (d, $H_{\alpha'}$, J = 2.5 Hz), 7.22 (d, H_α, J = 8.5 Hz, 6.94–7.05 (m) and 7.27–7.35 (m) (Ph).

Cleavage of Diastereomers (−)-10 and (+)-11: (−)- and (+)-Cyclotriphenolene (5). A solution of (+)-**11** (680 mg, 0.89 mmol) in 20 mL of dry tetrahydrofuran was treated dropwise with 7 mL of 1 N lithium triethylborohydride in tetrahydrofuran (Aldrich Chemical Co.) at 0 °C under argon. After the solution was stirred at 0 °C for $2^1/_2$ h it was hydrolyzed with 1 N hydrochloric acid and extracted with ether. The organic layer was washed with water, dried over sodium sulfate, and

(39) Boss, R.; Scheffold, R. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 558–559.

(40) The synthesis of (+)- and (−)-**2** was originally reported in ref 41. We have since developed a new method[35] involving resolution of (±)-**2** by formation of the diasteromeric triesters with (−)-ω-camphanic acid and subsequent column chromatographic separation over silica gel using chloroform–methanol 97:3 or dichloromethane–ether 95:5 mixtures (v/v) as eluants. Final purifications can either be effected by TLC or by crystallization, yielding diastereomers A (first eluted) $[\alpha]_D$ +47° and B $[\alpha]_D$ −52° ($CHCl_3$). Reductive cleavage of A and B ($LiAlH_4$, 0 °C) gives (+)- and (−)-**2**, respectively. Several preparations using either the original[41] or the new[35] method afforded samples of resolved **2** having similar rotations, $[\alpha]_D$ 273° (±4%); moreover, recrystallization of partially resolved samples (e.g., $[\alpha]_D$ 210°) also raised the rotation to this value, which therefore should represent the maximum rotation (±4%) of **2**.

(41) Collet, A.; Jacques, J. *Tetrahedron Lett.* **1978**, 1265–1268.

(42) The vibrational structure could possibly be enhanced at lower temperature. Unfortunately, **3** is very sparingly soluble in solvents available for such measurements.

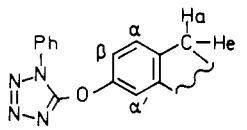
(43) The catalyst (10% Pd/C Type 3230/D) was purchased from Engelhard. Other brands (e.g., Fluka 75990) gave similar results but sometimes slightly longer reaction times (if necessary, the reaction can be monitored by TLC).

evaporated to dryness under vacuum without heating. The product was purified by filtration through 50 g of silica gel with ether as the eluant and was finally crystallized from this solvent by concentrating the solution without heating, yield 210 mg (70%) of (+)-**5**, $[\alpha]^{25}_D$ +190° (dioxane, *c* 0.25). This product on reaction with acetyl chloride in pyridine afforded the triacetate (+)-**6**, $[\alpha]^{25}_D$ +190° ($CHCl_3$ *c* 0.5), mp 222–224 °C, whose ^1H NMR spectrum was identical with that of (±)-**6** (Table I).

In the same way, diastereomer (−)-**10** gave the triphenol (−)-**5**, $[\alpha]^{25}_D$ −195° (dioxane, *c* 0.25), in 65% yield.

Stereochemical Correlation of (+)-Cyclotriphenolene (5) to (+)-Cyclotrianisylene (4). To a solution of the above triphenol (+)-**5** (10 mg) in 0.5 mL of hexamethylphosphoramide was added 2 drops of 25% aqueous sodium hydroxide, and the mixture was stirred for 10 min at room temperature under nitrogen. This was followed by the addition of methyl iodide (3 drops), and the reaction was allowed to proceed for 30 min; then, water was added, and the resulting crystalline precipitate was collected by suction filtration and dried under vacuum at room temperature, yielding 10 mg of (+)-**4**, $[\alpha]^{25}_D$ +161° ($CHCl_3$, *c* 0.25).

***(M)*-(+)-, *(P)*-(−)-, and (±)-2,7,12-Tris[(2-phenyl-1-tetrazolyl)-oxy]-10,15-dihydro-5*H*-tribenzo[*a*,*d*,*g*]cyclononene (9).** To a solution of (+)-cyclotriphenolene (**5**) (300 mg, 0.94 mmol) in 10 mL of dry dimethylformamide at 0 °C was added 362 mg (10% excess) of potassium *tert*-butoxide, and the suspension was stirred for 10 min. Then 530 mg (2.93 mmol) of 1-chloro-2-phenyltetrazole was added, and the mixture was stirred for $1^1/_2$ h while allowing the temperature to rise to 20 °C. Finally, the suspension was poured onto ice and the solid was collected and dried in air, affording 650 mg of crude (+)-**9**. This was recrystallized by dissolution in 15 mL of cold dichloromethane, to which 10 mL of ethanol was subsequently added; the solution was concentrated under vacuum without heating, until crystallization occurred. In this way 540 mg (77%) of pure (+)-**9** was obtained, having $[\alpha]^{25}_D$ +259° ($CHCl_3$



9

E

c 0.25), mp ca. 270–275 °C dec. Anal. Calcd for $C_{42}H_{30}N_{12}O_3$: C, 67.19; H, 4.03; N, 22.39. Found: C, 67.2; H, 3.8; N, 22.4. ^1H NMR spectrum (270 MHz) δ (from internal Me_4Si in $CDCl_3$) 3.83 (d, H_e) and 4.90 (d, H_a) (J = 13.7 Hz), 7.18 (dd, H_β, J = 8.5, 2.7 Hz), 7.44 (d, H_α, J = 8.5 Hz), 7.46 (d, $H_{\alpha'}$, J = 2.7 Hz), 7.50–7.60 (m, Ph, H meta/para), 7.74–7.79 (m, Ph, H ortho).

Similarly, (−)-**5** afforded (−)-**9**, which exhibited $[\alpha]^{25}_D$ −255° ($CHCl_3$, *c* 0.25), and (±)-**5** gave (±)-**9**, mp ca. 255 °C dec.

10,15-Dihydro-5*H*-tribenzo[*a*,*d*,*g*]cyclononene (7, Cyclotribenzylene). To a solution of the tetrazolyl ether (±)-**9** (70 mg) in a mixture of dichloromethane (5 mL) and methanol (3 mL) was added 70 mg of 10% palladium on charcoal as the catalyst.[43] This mixture was stirred for 7 h under 1.1 atm of H_2, by immersing the flask in the water bath of an ultrasonic cleaner whose temperature was maintained at 15–20 °C by cooling (see the hydrogenolysis of (±)-**8** above). The catalyst was filtered off and the filtrate, to which some dichloromethane was added, was washed with 1 N sodium hydroxide then water until a clear organic layer was obtained. The solvent was evaporated to dryness, and the crude hydrocarbon was purified by filtration through a short column of silica gel (dichloromethane as the eluant), followed by crystallization from benzene, yielding 20 mg (80%) of white crystals of **7**: mp 278 °C (lit.[19] 274–276 °C); mass spectrum, m/z M^+ 270 (100%), $M^+ - 1$ 269 (13.1%); ^1H and ^{13}C NMR spectra, Tables I and II.

***(M)*-(−)- and *(P)*-(+)-[2,7,12-$^2H_3$]-10,15-Dihydro-5*H*-tribenzo[*a*,*d*,*g*]cyclononene (3).** The tetrazolyl ether (+)-**9** (250 mg, $[\alpha]^{25}_D$ +259° in $CHCl_3$) was dissolved in a mixture of CD_2Cl_2 (15 mL) and CD_3OD (10 mL) and was shaked for 1 h with 250 mg of 10% palladium on charcoal[43] under 1.1 atm of deuterium (99.4% isotopically pure). Then an additional amount of the catalyst (250 mg) was added, and the deuteriolysis was allowed to proceed for 18 h at room temperature with vigorous mechanical shaking. The catalyst was filtered off and washed with dichloromethane, and the filtrate was washed with 1 N sodium hydroxide then water until a clear organic solution was obtained. Evaporation of the solvent under vacuum without heating afforded 90 mg (99%) of the crude hydrocarbon, which was isolated by TLC on silica gel (dichloromethane–hexane 30/70 v:v as the eluant) and then crystallized from pentane (without heating), affording 55 mg of white crystals of (−)-**3**: $[\alpha]^{25}_D$ −2.3 ± 0.2°, $[\alpha]^{25}_{578}$ −2.6 ± 0.2°, $[\alpha]^{25}_{546}$ −2.9 ± 0.2°, $[\alpha]^{25}_{436}$ −5.2 ± 0.3°, $[\alpha]^{25}_{365}$ −8.9 ± 0.5° ($CHCl_3$, *c* 2.6); mass spectrum, m/z M^+ 273 (100%), $M^+ - 1$ 272 (22.5%); ^1H and ^{13}C NMR spectra, Tables I and II; UV spectrum (3.2×10^{-4} M in acetonitrile) λ (ε) 274.5 nm (830), 266.5 (850), 259 (sh 680), 253 (sh 510); CD spectrum (2.1×10^{-3} M in acetonitrile), λ (Δε) 275 nm (−0.060), 267 (−0.012), 263 (+0.007), 257.8 (+0.015), 252.2 (+0.006).

This compound was submitted to the DSC method for purity assessment;[29] 1.197 mg was thus heated at 1.25 K/min from 520 K, and the melting peak was analyzed in the range 548–555 K: mp 554.1 ± 0.2 K (281 °C), enthalpy of fusion 37.9 kJ/mol, molar purity x = 0.996 (irrespective of the isotopic or optical purity).[29] The racemate, which was obtained by heating the sample of (−)-**3** above the melting point (at ca. 285 °C) for 2 min then cooling until recrystallization had occurred, exhibited the same melting point as the enantiomer (280.5 °C).

In a similar way, the enantiomer (+)-**3** was obtained by deuteriolysis of (−)-**9** as above and had $[\alpha]^{25}_D$ +2.1°, $[\alpha^{25}_{578}$ +2.3°, $[\alpha]^{25}_{546}$ +2.6°, $[\alpha]^{25}_{436}$ +5.2°, and $[\alpha]^{25}_{365}$ +8.7° ($CHCl_3$, *c* 1.6).

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Registry No. M-(−)-**1**, 75399-70-1; P-(−)-**2**, 68182-93-4; (±)-**2**, 81370-49-2; P-(+)-**3**, 89255-59-4; M-(−)-**3**, 89209-37-0; (±)-**4**, 89209-33-6; (+)-**4**, 89255-57-2; P-(−)-**4**, 89255-56-1; (±)-**5**, 89209-34-7; (+)-**5**, 89255-54-9; P-(−)-**5**, 89255-53-8; (±)-**6**, 91797-49-8; (+)-**6**, 91712-56-0; **7**, 38059-10-8; (±)-**8**, 89209-32-5; M-(−)-**8**, 89255-58-3; M-(+)-**9**, 89209-36-9; P-(−)-**9**, 89255-55-0; (±)-**9**, 91796-58-6; P-(−)-**10**, 91712-57-1; M-(+)-**11**, 89255-52-7; **13**, 86534-11-4; (±)-**14**, 91741-78-5; vanillyl alcohol, 498-00-0; allyl bromide, 106-95-6; 1-chloro-2-phenyltetrazole, 14210-25-4; (*R*)-(+)-2-phenoxypropionic acid, 1129-46-0.