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NEW D3 AND C3h CRYPTOPHANES WITH ETHYLENIC BRIDGES

Syntheses, Structural Assignments, and Absolute Configurations and Circular Dichroism of the D3 Isomers

Jacqueline Gabard, Josette Canceill and André Collet*

Chimie des Interactions moléculaires, Collège de France, ER C.N.R.S. N° 285,
11, place Marcelin-Berthelot, 75005 Paris, France.

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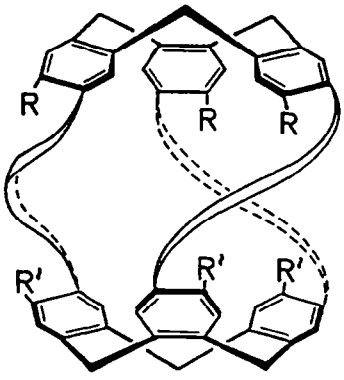
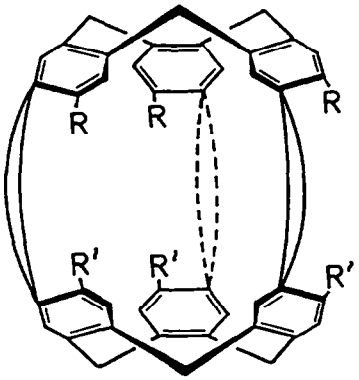
Summary. Two (D3/C3h) cryptophane pairs, (I/J) and (K/L), in which the two cyclotriveratrylene caps are linked by three trans (I/J) or cis (K/L) $OCH_2CH{=}CHCH_2O$ bridges have been synthesised, and their structures established by mass spectrometry, NMR, optical activity and circular dichroism data. The D3 cryptophanes **I** and **K** have been obtained in racemic and resolved forms, and their absolute configurations have been determined by chemical correlation with the known P-(-)-cyclotriguaiacylene. The circular dichroism spectra of **I** and **K** could be satisfactorily analyzed in the light of the exciton model, extended to the coupling of six equivalent chomophores in a D3 array.

The name "cryptophane" designates hollow molecules made of two cyclotriveratrylene units, linked to one another by three bridges.[1] These compounds possess a roughly spherical and almost rigid lipophilic cavity, and three windows allowing suitable guest molecules to go in.[2,3] In order to obtain a fine host-guest tuning, stepwise changes in the size and shape of the cavity and in the cross section of the windows can simply be achieved by varying the length and the structure of the bridges, and the way in which they are attached to the upper and lower caps. With respect to each bridge, the R and R' benzene substituents may display either a "anti" or a "syn" relationship as depicted in Scheme I. When R=R' (e.g., OCH_3), the anti cryptophanes have a D3 structure hence are chiral, while the syn ones belong to the C3h point group and are therefore achiral; both types are chiral, however, if R is different from R' (C3 group). Another important difference between anti and syn cryptophanes is conformational in nature : as viewed along the C3 axis, the upper and lower cyclotriveratrylene units are eclipsed in the syn type, whereas they are twisted away by ca 50-60° (staggered) in the anti type.[4] All these features make the cryptophanes well suited for investigating and modelling molecular recognition phenomena,[9] and justify the efforts to elaborate efficient synthetic routes to these compounds.

Scheme I



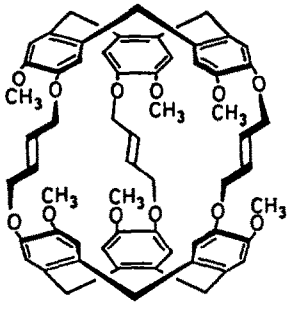
anti



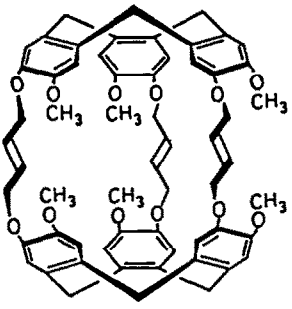
syn

Thus far, we have prepared cryptophanes with $O(CH_2)_2O$ and $O(CH_2)_3O$ bridges (e.g., cryptophanes A,[6] C and D,[1] E and F,[7] and some derivatives[8]). We have found[7,10] that several of these hosts strongly and selectively bind neutral molecules of complementary size such as the halogenomethanes and isobutane, in

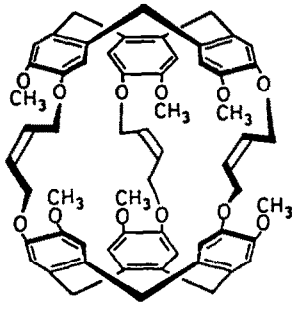
organic lipophilic solvents, where no hydrophobic effects can account for the surprizing stability of the complexes ($K_s > 10^2$ M^{-1} at 300 K). In water, where the complexes are further stabilized by hydrophobic forces, the binding constants may become as high as 10^3 - 10^4 M^{-1} for guests such as CH_2Cl_2 and $CHCl_3$.[8] In the present article, we report the synthesis of four new anti and syn cryptophanes (**I, J, K, L**) in which the two caps are linked by three trans or cis $OCH_2CH{=}CHCH_2O$ bridges. In C.P.K. models, the cavity in **I-L** is very slightly larger in size than that of the previously synthesised cryptophanes. We also expect that the double bonds in the bridges will allow subsequent transformations of these compounds into systems of greater complexity, incorporating, for instance, reactive groups within reach of the complexed guest.



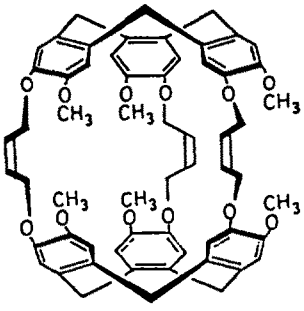
(-)-I



J



(-)-K



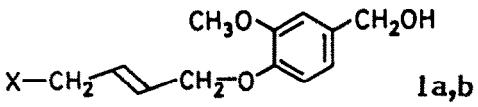
L

Syntheses and Stereochemical Assignments

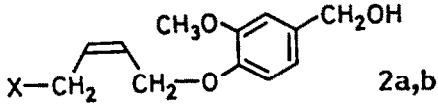
For the synthesis of cryptophanes **I-L**, we employed the same route as previously described for **A-F**.[1,6,7] The required key intermediates **4a** and **4b** were prepared from C3 cyclotriguaiacylene[11,12] **3**, and the ω-iodinated vanillyl alcohol derivatives **1** and **2**. Reaction of vanillyl alcohol with E or Z 1,4-dichloro-2-butene (K_2CO_3 in acetone) provided the ω-chlorinated compounds **1a** and **2a**, which in turn were converted to the desired iodides, by reaction with INa.

Alkylation of the phenolic groups of (±)-**3** by iodides **1b** and **2b**, to give the cryptophane precursors (±)-**4a** and (±)-**4b**, respectively, could be effected in good yield at room temperature, by using 25% aqueous NaOH as the base in DMF/HMPA. We employed the same procedure for preparing the optically active precursors (+)-**4a** and (-)-**4b**. The alkylation of P-(-)-**3** (ca. 91% ee) with **1b** gave M-(+)-**4a** showing $[\alpha]_D$ +54° ($CHCl_3$), and that of M-(+)-**3** with **2b** similarly furnished P-(-)-**4b** showing $[\alpha]_D$ -73°. The racemization of chiral cyclotriveratrylenes (via crown inversion) is very slow at room temperature,[1] hence the ee's of (+)-**4a** and (-)-**4b** (isolated by TLC) should be close to those of the samples of **3** used as starting materials.

Cyclization of the vanillyl alcohol ends of **4a** and **4b** was effected by warming (55°C) diluted solutions of these precursors in formic acid. The reaction of (±)-**4a** afforded a mixture of cryptophanes **I** and **J**, which were isolated by TLC in 34% and 4.5% yield, respectively; in a similar way, (±)-**4b** gave the cryptophanes **K** (25%) and **L** (50%). The D3 structure (anti in Scheme I) was assigned to **I** and **K**, and the C3h structure to **J** and **L**, because the same reactions, starting from (+)-**4a** and (-)-**4b**, furnished optically active **I** ($[\alpha]_D$ -154°



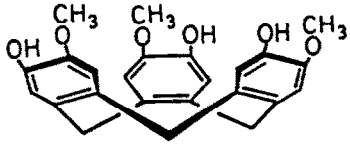
1a,b



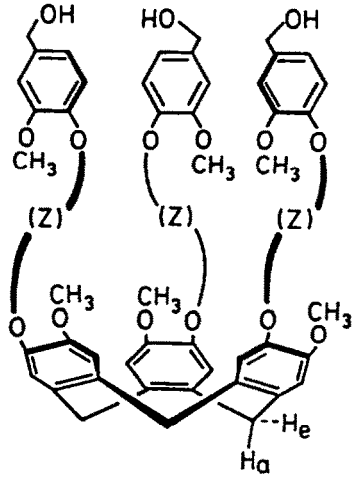
2a,b

a X = Cl

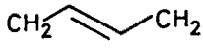
b X = I

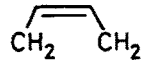


P-(-)-3



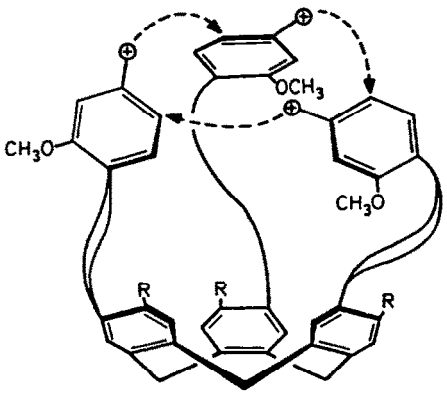
M-(+)-4a,b

a Z = 

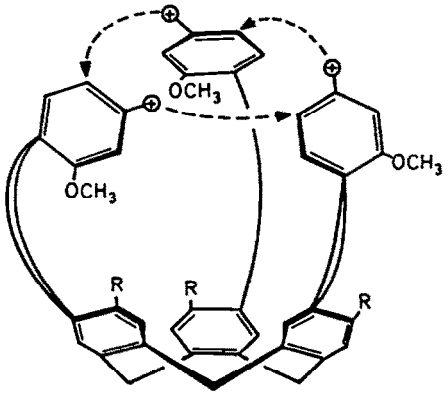
b Z = 

in $CHCl_3$) and K ($[\alpha]_D$ +71° in $CHCl_3$), and the isomers J and L for which no rotation could be detected. It is interesting that the stereochemistry of the cyclization is reversed when the double bond in the precursor bridges is changed from trans to cis. For the absolute configuration depicted in Scheme II, the results show that the cyclization of the trans precursor proceeds counterclockwise (as viewed from the template ring), leading to the anti isomer (I) preferentially; in contrast, that of the cis precursor proceeds clockwise and gives the syn isomer (L) as the major product. We have previously observed that precursors of the same type with $O(CH_2)_2O$ bridges preferentially led to the anti cryptophanes (A, C),[1,6] whereas with $O(CH_2)_3O$ bridges the syn was preferred (E).[7] The fact that the presence of a even or odd number of atoms in the bridges affects the stereochemical outcome of the reaction is not surprizing, since it certainly determines the orientation of the reactive veratryl ends with respect to the template ring. Changing a double bond from trans to cis probably has a similar effect.

Scheme II



(→Anti)



(→Syn)

The cryptophanes I-L are crystalline solids which strongly retain solvents, and melt with decomposition at ca. 240-260°C. They display expected mass (m/z M^+ 972) and NMR spectra (Table 1). The cyclotriveratrylene units in I-L exhibit the characteristic AX quadruplet of the CH_2 bridges, where the pseudo-axial hydrogens (H_a) resonate ca. 1.2 ppm downfield, with respect to their pseudo-equatorial counterparts (H_e) (a consequence of the steric congestion at the top of the crown[13]). As can be seen in Table 1, the spectra of the four cryptophanes are very similar and only differ in details.

The absolute configurations of the (-)-isomers of **I** and **K** shown on the stereoformulas are based on the known P-(-) absolute configuration of cyclotriguaiacylene.[12] The actual enantiomeric purity of the optically active cryptophanes obtained in this work is unknown (to date there is no method allowing such a determination for this class of compounds). The fact that, in similar reactions,[1] the intramolecular trimerization is fast, compared to the crown inversion rate, even at temperatures as high as 60-90°C, indicates that the ee of the present samples of (-)-**I** and (+)-**K** is probably not very different from that of the precursors (+)-**4a** and (-)-**4b**.

Table 1. 200.13 MHz ^1H NMR spectra of cryptophanes **I-L** in $CDCl_3$.

	arom. H's (s)		OCH_3 (s)	H_a	[J (Hz)] (AX q)	H_e	CH=CH	CH_2 [Jgem (Hz)]		
I	6.62	6.58	3.75	4.54	[13.8]	3.33	5.69[a]	4.57	[13.3]	4.44[b]
J	6.70	6.60	3.64	4.56	[13.7]	3.36	5.78[a]	4.61	[12.2]	4.28[b]
K	6.82	6.68	3.74	4.64	[13.7]	3.45	6.11[c]	4.37	[--]	4.17[d]
L	6.87	6.77	3.75	4.61	[13.7]	3.42	5.90[e]	5.90	[13.0]	4.40[f]

a) Broad s (almost degenerate t); b) broad AB q; c) t, J=3.6 Hz; d) m; e) t, J=3 Hz; f) splitted AB q, J=3 Hz.

Circular Dichrolsm of the D3 Cryptophanes I and K

As a further structural proof, the circular dichroism (CD) of **I** and **K** was examined and could be satisfactorily analyzed in the light of the exciton mechanism.[14] The CD curves shown in Figure 1 specifically correspond to the (-) enantiomers, which in fact have the same handedness (see the stereoformulas). The two CD spectra display essentially similar features, and closely resemble those of the other previously investigated D3 cryptophanes.[15] In these compounds, the chromophoric unit is a 1,2,4,5-tetrasubstituted benzene, in which the two lowest transitions, occurring at ca. 290 nm (B_{2u}) and ca. 240 nm (B_{1u}), are polarized along the short (a) and long (b) axes, respectively, as sketched in the insert of Figure 1. In fact, the presence of two different substituents (OCH_3 and $OCH_2CH=$) breaks the symmetry of the chromophore, and causes a weak rotation of the polarization direction of the two transitions, which in turn makes the D3 array of the transition dipoles chiral. According to the model we have proposed for the interaction of six equivalent oscillators in a D3 arrangement,[15] the coupling of the electric transition dipoles generates, for each band system, three optically active components, one (A_2 symmetry) being polarized along the C3 axis of the molecule, and two (E symmetry) in the equatorial plane. The two E levels have opposite signs and different intensities, the stronger having sign opposite to the A_2 component. Furthermore, for a staggered conformation of the cryptophanes, the splitting of the E components is predicted to be very small, compared to the energy difference between the A_2 and E levels.

Using the rules previously established for C3 cyclotriveratrylenes, the polarization directions of the B_{2u} and B_{1u} dipoles in (-)-**I** and (-)-**K** were tentatively set as shown in the insert of Figure 1, where the angles are obviously exaggerated for clarity. The calculated[16] CD components for each band system are also indicated in Figure 1, and a pictorial representation of the origin of the negative A_2 component of the B_{1u} system is depicted in Scheme II. The experimental CD spectra can be interpreted in the following

way : (i) for the B_{1u} system, the observed negative CD at 253-255 nm corresponds to the calculated A_2 component, and the positive CD at 237-239 nm represents the sum of almost degenerate E components, where the positive one prevails; (ii) the negative band at 288 nm matches the predicted A_2 component of the B_{2u} system, and the residual, poorly defined negative band in the 300 nm region probably results from the extensive overlap and mutual cancellation of the nearly degenerate E levels. These features are similar in all respects to those previously observed for D3 cryptophanes,[15] and provide further evidence for a preferred staggered conformation of these compounds in solution.[17]

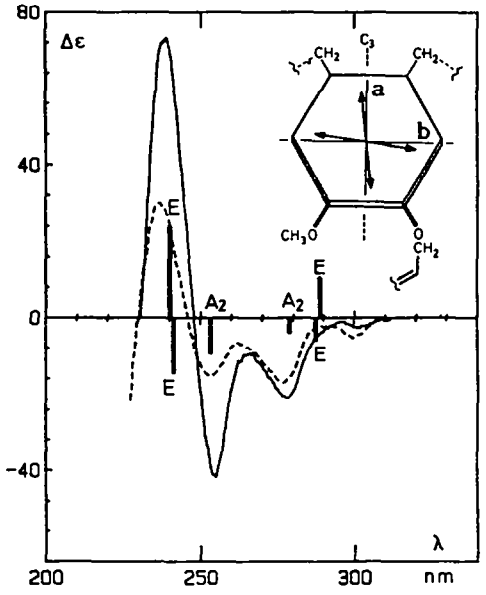
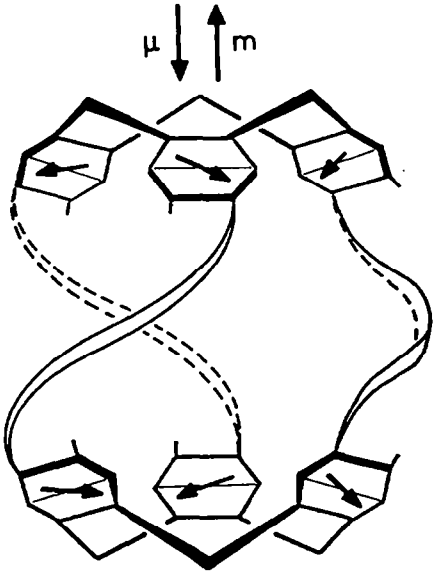


Figure 1. Circular dichroism spectra of (-)-I (solid line) in dioxane/chloroform 3:2, and of (-)-K (dotted line) in dioxane (recorded on the (+)-isomer. The bars represent the calculated CD components and the insert shows the polarization directions of the B2u (a) and B1u (b) transitions.



Scheme II. Sketch of the A2 coupling of the individual transition dipoles, which generates antiparallel electric (μ) and magnetic (m) moments along the C3 axis, hence a negative rotational strength at lower energy for the B1u system.

Acknowledgement. We are grateful to Dr. Rolando (Ecole Normale Supérieure, Paris) for the mass spectra.

Experimental Section

Melting points were measured on a Kofler hotbench or on a Perkin-Elmer DSC2 microcalorimeter equipped with a HP86 calculator for data acquisition and processing (purity evaluation). Rotations were measured on a Perkin-Elmer 241 micropolarimeter, in thermostated 1-dm quartz cells (25°C). Circular dichroïsm spectra were recorded at room temperature on a Jobin-Yvon Dichrograph V instrument, in 0.1 and 0.2-cm quartz cells. Ultraviolet spectra were obtained on a Perkin-Elmer 554 spectrometer, with the same cells and solutions as for the CD measurements. Spectrometric grade chloroform and dioxane were used for all optical measurements. ^{1}H NMR spectra were recorded at 200.13 MHz on a Brucker AM200SY instrument, equipped with a Aspect 3000 computer. Mass spectra were taken on a Nermag R10-10 spectrometer, using chemical ionization techniques.

Column chromatographic separations were carried out on Merck silica gel 60, or equivalent in other brands. Analytical and preparative thin layer chromatography (TLC) were performed over commercially available fluorescent (254 nm) silica gel plates (Merck, Whatman, and Mackerey-Nagel).

E-1,4-Dichloro-2-butene was secured by careful distillation with a spinning band column of the technical grade product, purchased from Aldrich, and containing ca. 15% of the Z-isomer; Eb_{32} 65°C. Z-1,4-Dichloro-2-butene was distilled (vigreux column) before use; Eb(760) 149-150°C. Vanillyl alcohol was

purchased from Aldrich and was used as received.

4-(4-Chloro-2-E-butenoxy)-3-methoxybenzenemethanol 1a. A mixture of vanillyl alcohol (1.92 g, 12.5 mmol), E-1,4-dichloro-2-butene (2.6 ml, 25 mmol) and potassium carbonate (1.7 g, 12.5 mmol) in acetone (25 ml) was refluxed under nitrogen for 15 h. The solvent was stripped off and the residual oil was taken up in a mixture of water and ether, which resulted in the crystallization of the di-alkylated by-product 1,4-bis(4-hydroxymethyl-2-methoxy)-2-E-butene (0.32 g, mp 135°C). The ether layer was washed with 1 N NaOH and water, yielding after evaporation of the solvent 2.3 g of crude, crystalline material, which was purified by column chromatography (dichloromethane-ether 8:2 as the eluant). Yield 1.5 g (50%) of **1a**, mp 61°C. Calcd for $C_{12}H_{15}O_3Cl$ (%) C 59.32, H 6.23; Found C 59.6, H 6.1. ^1H NMR (δ from internal TMS in $CDCl_3$): 1.6 (s, OH), 3.89 (s, OCH_3), 4.08 (pseudo-d, CH_2Cl), 4.60-4.62 (m, CH_2OH and OCH_2), 6.0-6.04 (m, CH=CH, J(CH=CH)=15 Hz), 6.85, 6.86, 6.94 (arom. H's).

4-(4-Iodo-2-E-butenoxy)-3-methoxybenzenemethanol 1b. The above chloride **1a** (200 mg, 0.8 mmol) and INa (250 mg, 1.6 mmol) were refluxed in acetone (5 ml) for 1 h 30. The solvent was evaporated off, water was added and the resulting crystalline precipitate was collected by suction filtration; yield 220 mg (80%) of iodide **1b**, mp 87°C (from aqueous methanol); this iodide is unstable and is preferably used immediately, or stored in the dark at -20°C. Calcd. for $C_{12}H_{15}O_3I$ (%) C 43.13, H 4.52; Found C 43.25, H 4.35. ^1H NMR ($\delta$from internal TMS in $CDCl_3$): 1.6 (s, OH), 3.89 (s, OCH_3), 3.89 (d, CH_2I, J(CH_2-CH=)=7.2 Hz), 4.57-4.65 (m, CH_2OH and OCH_2), 5.9-6.2 (m, CH=CH, J(CH=CH)=15 Hz), 6.84, 6.85, 6.94 (m, arom. H's).

4-(4-Chloro-2-Z-butenoxy)-3-methoxybenzenemethanol 2a. A mixture of vanillyl alcohol (3.5 g, 22.7 mmol), Z-1,4-dichloro-2-butene (4.8 ml, 45 mmol) and potassium carbonate (3.15 g, 22.8 mmol) in acetone (50 ml) was refluxed under nitrogen for 15 h. After the solvent had been stripped off, the product was taken up in water, and extracted with ether. The organic layer was washed with 1 N NaOH, then water, and was evaporated to dryness, affording crude **2a** as an oil which was purified by column chromatography as for **1a** above. In this way, 3 g of **2a** were obtained, which, after crystallization from ether gave 1.75 g (32%) of pure product, mp 41°C. Calcd for $C_{12}H_{15}O_3Cl$ (%) C 59.32, H 6.23; Found C 59.3, H 6.2. ^1H NMR (δ from internal TMS in $CDCl_3$): 1.68 (broad t, OH), 3.89 (s, OCH_3), 4.17 (d, CH_2Cl, J(CH_2-CH=)=4.7 Hz), 5.8-6.0 (m, CH=CH, J(CH=CH)=11 Hz), 6.86, 6.94 (arom. H's).

4-(4-Iodo-2-Z-butenoxy)-3-methoxybenzenemethanol 2b. The above chloride **2a** (350 mg, 1.44 mmol) and INa (435 mg, 2.88 mmol) were stirred in acetone (10 ml) at room temperature for 1 h. The solvent was evaporated under vacuum, and the residual oil was crystallized by addition of water. Recrystallization from 1 ml of isopropyl alcohol gave 340 mg (70%) of **2b**, mp 83°C (this compound is unstable and should be immediately used, or stored in the dark at -20°C). ^1H NMR (δ from internal TMS in $CDCl_3$): 1.7 (t, OH) and 4.64 (d, CH_2OH, J(CH_2-OH)=5.7 Hz), 3.90 (s, OCH_3), 3.96 (d, CH_2I, J(CH_2-CH=)=8.7 Hz), 4.71 (d, OCH_2, J(CH_2-CH=)=5.9 Hz), 5.76 and 5.96 (m, CH=CH, J(CH=CH)=11 Hz, 6.88 and 6.95 (arom. H's).

2,7,12-Tris[4-(4-hydroxymethyl-2-methoxyphenoxy)-2-E-butenoxy]-3,8,13-trimethoxy-10,15-dihydro-5H-tribenzo[a,d,g]cyclononene Rac- and M-(+)-4a. Racemic cyclotriguaiacylene **3**[11] (102 mg, 0.25 mmol) was dissolved in a mixture of DMF (3 ml) and HMPA (2 ml), and 0.12 ml of 25% aqueous NaOH (0.75 mmol) was added. The mixture was stirred under nitrogen for 10 min, then it was allowed to react for 1 h at room temperature with 250 mg (0.75 mmol) of the E-iodide **1b**; further amounts of NaOH (0.06 ml) and **1b** (125 mg) were added, and the reaction was allowed to proceed for 1 more h. Water was added and the product was extracted with ethyl acetate. The organic layer was washed with 1N HCl, water, 1N NaOH and water until neutral, dried over Na_2SO_4 and evaporated to dryness. The resulting oil (347 mg) was purified by TLC (ethyl acetate-acetone 85:15 as the eluant), yielding 175 mg (68%) of ($\pm$)-**4a**, mp 70-71°C (from dichloromethane). Calcd. for $C_{60}H_{66}O_{15}$, 0.5 CH_2Cl_2 (%) C 68.29, H 6.24; Found C 68.4, H 6.45. ^1H NMR (δ from internal TMS in $CDCl_3$): 3.50 (d, H_e) and 4.70 (d, H_a, J=14.3 Hz), 3.79 (s, OCH_3), 3.86 (s, OCH_3), 4.58 (m, CH_2OH and 2 x OCH_2C=), 6.07 (broad s, CH=CH), 6.78, 6.82, 6.92 (arom. H's).

The optically active precursor M-(+)-**4a** was similarly prepared from (-)-**3** ($[\alpha]_D$ -249° in $CHCl_3$, 91% ee), care being taken not to heat the solutions during the isolation process, in order to avoid racemization. The

product showed $[\alpha]_D$ +54° (c 0.3 in $CHCl_3$), and had the same NMR spectrum and TLC behaviour as the racemate.

2,7,12-Tris[4-(4-hydroxymethyl-2-methoxyphenoxy)-2-Z-butenoxy]-3,8,13-trimethoxy-10,15-dihydro-5H-tribenzo[a,d,g]cyclononene Rac- and P-(-)-4b. Racemic **4b** was prepared from 82 mg of (±)-**3** and the Z-iodide **2b**, by using the same procedure as described above for **4a**, except for the isolation of the product: the ethyl acetate extract was evaporated to dryness and the product was crystallized in the presence of methanol. Yield 125 mg (60%), mp 109-111°C. Calcd for $C_{60}H_{66}O_{15}$ (%) C 70.16, H 6.48; Found C 70.0, H 6.6. ^1H NMR (δ from internal TMS in $CDCl_3$): 3.52 (d, H_e) and ca. 4.7 (overlapped d, H_a, J=14.1 Hz), 3.72 (s, OCH_3), 3.80 (s, OCH_3), 4.58, 4.71, 4.73 (CH_2OH and 2 x OCH_2C=), 5.90 (m, CH=CH), 6.79, 6.86, 6.90 (arom. H's).

The optically active precursor P-(-)-**4b** was similarly prepared from M-(+)-**3** ($[\alpha]_D$ +252° in $CHCl_3$, 92% ee), and the final purification was effected by TLC (dichloromethane-methanol 95:5). **4b** showed $[\alpha]_D$ -73° (c 0.3 in $CHCl_3$).

Cryptophanes I and J. In a 1-liter rotavapor flask containing a solution of (±)-**4a** (150 mg) in DMF (1.5 ml) was added 300 ml of formic acid. The flask was fitted to the rotavapor and heated in the water bath (55°C) for 3 h. Formic acid was stripped off under vacuum, and the crude cryptophane mixture was roughly separated by TLC (chloroform-acetone 9:1 as the eluant), into a faster moving fraction (R_f 0.62, impure **I**, 70 mg), and a slower moving fraction (R_f 0.39, impure **J**, 20 mg). Each fraction was further purified by TLC (same eluant) and the cryptophanes were eventually crystallized from acetone. Yield 48 mg (34%) of cryptophane **I**, and 6.5 mg (4.5%) of cryptophane **J**. NMR: see Table 1. Mass spectra (chemical ionization (CH_4)); (**I**) m/e 972 (M^+, 56%), 942 (17%), 920 (10%), 780 (4%), 565 (13%), 513 (25%), 461 (62%), 409 (100%); (**J**) m/e 972 (M^+, 46%), 942 (17%), 920 (13%), 783 (4%), 565 (8%), 513 (29%), 461 (69%), 409 (100%). Cryptophanes **I** and **J** were found by NMR in $C_2D_2Cl_2$ to contain acetone and water; satisfactory C, H combustion analyses were obtained for the following compositions: (**I**) [$C_{60}H_{60}O_{12}$, C_3H_6O, 0.25 H_2O] Calcd. (%) C 72.8, H 6.74; Found C 73.0, H 6.4; (**J**) [$C_{60}H_{60}O_{12}$, 0.5 C_3H_6O, 1.5 H_2O] Calcd. (%) C 71.77, H 6.46; Found C 71.8, H 6.3.

The same reaction, starting from M-(+)-**4a**, afforded cryptophane **I** having $[\alpha]_D$ -154°, $[\alpha]_{578}$ -162°, $[\alpha]_{546}$ -185°, (c 0.25 in $CHCl_3$), and cryptophane **J**, for which no rotation was observed.

Cryptophanes K and L. The precursor (±)-**4b** (150 mg in 1.5 ml of DMF) was cyclized to cryptophanes **K** and **L** by heating at 55°C in 300 ml of formic acid as described above. After the solvent had been evaporated off, 5 ml of $CHCl_3$ were added and the sparingly soluble cryptophane **L** which crystallized was separated (67 mg). The mother liquors were chromatographed (TLC), with chloroform-acetone 93:7 as the eluant; 45 mg of the faster moving cryptophane **K** (R_f 0.57) were obtained and were recrystallized from acetone, yield 35 mg (25%). A further amount (5 mg) of the slower moving cryptophane **L** (R_f 0.46) was also recovered; the total yield of **L** was thus 72 mg (50%). NMR spectra see Table 1. Mass spectra (Chemical ionization (CH_4)): (**K**) m/e 972 (M^+, 71%), 783 (6%), 565 (60%), 513 (46%), 461 (46%), 409 (100%); (**L**) m/e 972 (M^+, 100%), 942 (14%), 920 (14%), 783 (4%), 560 (17%), 513 (33%), 461 (56%), 409 (100%). Cryptophane **K** was found by NMR in $C_2D_2Cl_2$ to contain acetone and water, and cryptophane **L** was found to contain chloroform and water. Satisfactory C, H analyses were obtained for the following compositions: (**K**) [$C_{60}H_{60}O_{12}$, C_3H_6O, 3 H_2O] Calcd. (%) C 69.73, H 6.69; Found C 69.2, H 6.2; (**L**) [$C_{60}H_{60}O_{12}$, $CHCl_3$, 2 H_2O] Calcd. (%) C 64.92, H 5.81; Found C 64.6, H 5.7.

The same cyclization procedure from P-(-)-**4b** furnished cryptophane **K**, which showed $[\alpha]_D$ +83°, $[\alpha]_{578}$ +88°, $[\alpha]_{546}$ +112° (c 0.175 in $CHCl_3$), and cryptophane **L**, which was optically inactive.

References and Notes

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[4] This description is based on the X-ray crystal structure of cryptophane C (anti),[2] D (syn),[3] and E (anti),[5] and on examination of space-filling models.

[5] In cryptophane E, the two cyclotriveratrylene units are twisted away by 58°. We are indebted to M. Cesario, J. Guilhem and C. Pascard for this determination (work to be published).

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[16] For the calculation of the CD spectra of (-)-I and (-)-K, the polarization angles (see insert in Figure 1) were taken to be -2° and +2° for the B_{2u} and B_{1u} transitions, respectively, and the dipole strengths of these transitions were estimated from the UV spectra of suitable monomer models. All necessary details for these calculations are given in references 12 and 15.

[17] The CD calculation show that a decrease of the twist angle of the two caps, on going from a staggered (60°) to an eclipsed (0°) conformation, increases the splitting of the E levels to such an extent that the separation of the components would become observable in the experimental CD spectra, in the B_{1u} region.