Diastereoselective Functionalization of a Spherand-Type Calixarene

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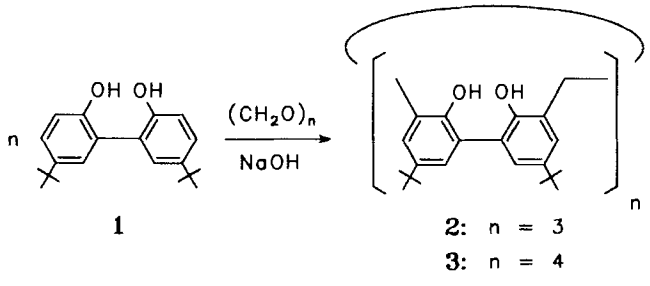
Condensation of 5,5'-di-*tert*-butyl-2,2'-dihydroxybiphenyl (**1**) with formaldehyde yields a cyclic trimer **2** (and tetramer **3**) having three (four) methylene groups less than a calix[6]-arene (calix[8]arene). Alkylation of the (flexible) trimer with *ethyl* bromoacetate gives exclusively the stereoisomer **4** with C_2 symmetry, while the isomer with D_3 symmetry is not observed. Two isomers **6a** and **6b** (C_2 and C_1 symmetry) are obtained by treatment with *tert-butyl* bromoacetate which both are converted by transesterification with methanol into the same hexamethyl ester **5** having C_2 symmetry. These results are rationalized by restricted rotation around Ar–Ar bonds for larger O-alkyl groups also around Ar–CH_2–Ar bonds. The structure of the hexaethyl ester **4** is also confirmed by single crystal X-ray analysis.

Calixarenes are macrocyclic compounds in which phenolic units are linked by methylene bridges *ortho* to the phenolic hydroxyl groups[1]. Usually, they are prepared by base-catalyzed condensation of *p-tert*-butylphenol, which – depending on the conditions – gives the calix[4]-[2], calix[6]-[3], or calix[8]arene[4] in yields of 50% or higher. Similar reaction conditions have recently successfully been applied to diphenols like 1,3-bis(5-*tert*-butyl-2-hydroxyphenyl)propane[5] and a rather rigid dihydroxy[2.5]metacyclophane[6].

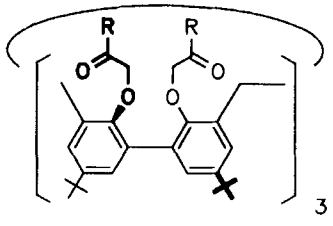


1 **2**: n = 3 **3**: n = 4

A recent publication of Yamato et al.[7] describing the condensation of 5,5'-di-*tert*-butyl-2,2'-dihydroxybiphenyl (**1**) with formaldehyde has prompted us to report on our own attempts in this field. According to Yamato et al. the cyclic trimer **2** is obtained with NaOH as a base (49% yield of pure product in our hands) in xylene, while larger cations give increasing yields of the cyclic tetramer **3**, which should be the main product in the presence of CsOH. Since our main objective was a further derivatization of these compounds we have so far concentrated on **2**. This macrocyclic molecule with three methylene bridges may be regarded as an intermediate between a calix[6]arene, posessing six methylene bridges, and a spherand[8] having all phenolic units directly connected (no bridge). The single phenol units in **2** belong to biphenyl as well as to diphenylmethane substructures.

Results and Discussion

The ^{1}H-NMR spectrum of **2** is very simple, showing at room temperature singlets for the *tert*-butyl groups (δ = 1.357), the methylene protons (δ = 4.032), and the OH protons (δ = 8.495) and a pair of doublets (δ = 7.206 and 7.404, ^4J = 2.4 Hz) for the aromatic protons. This can be understood by a fixed conformation with D_3 symmetry (see later) or more likely by a flexible molecule which has effectively D_{3h} symmetry. In fact, at lower temperature a broadening of the singlet of the methylene protons and a splitting into several broad signals occurs[7].



3

	R
4	OC_2H_5
5	OCH_3
6	$OC(CH_3)_3$
7	OH

Attachment of larger alkyl (or acyl) groups to the phenolic oxygens should lead to a situation, where the OR groups within a biphenyl unit cannot pass each other. That means the rotation around the Ar–Ar σ bond is hindered, and each biphenyl unit is fixed in a certain configuration. (According to Yamato et al. a methoxy group is already sufficiently large[7].) Two different diastereomers, both chiral, should then be expected[9]:

a) A compound in which all biphenyl units have the same configuration (*RRR* or *SSS*).

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b) A compound in which the configuration of one biphenyl unit differs from that of the other two (*RRS* or *SSR*).

As Figure 1 illustrates, the former would have D_3 symmetry and the latter C_2 symmetry[10].

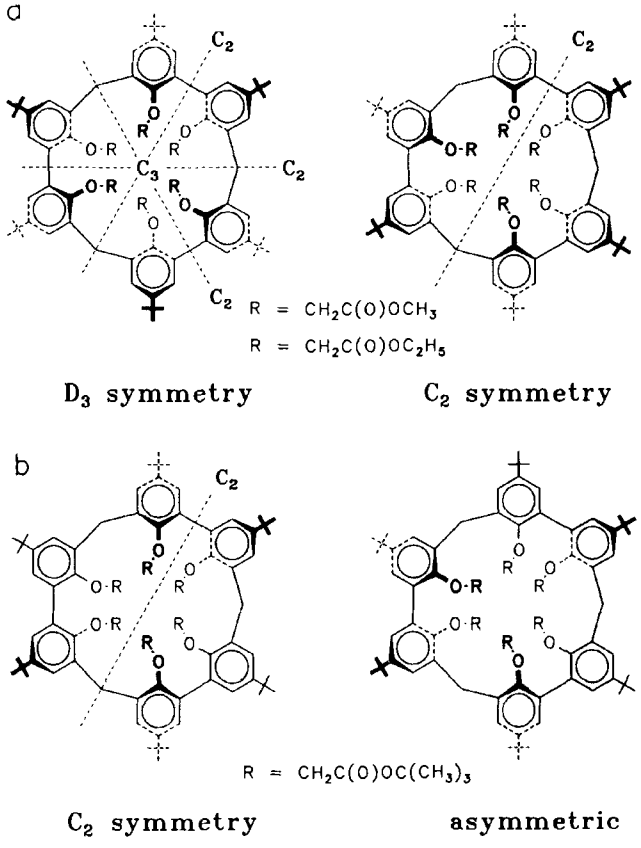

Figure 1. a) Schematic representation of hexaethers with D_3 and C_2 symmetry, assuming that by *O*-alkylation the rotation around the Ar–Ar bond is hindered. b) Schematic representation of hexaethers with C_2 and C_1 symmetry, assuming that by *O*-alkylation also the rotation around the Ar–CH_2–Ar bonds is hindered. Note that the configuration of the biphenol substructures is the same for both isomers

Alkylation of **2** with an excess of ethyl bromoacetate, a reaction frequently applied to calixarenes, led to a mixture from which only one pure product could be isolated. According to its mass spectrum it was the hexaester **4**. Three signals for *tert*-butyl protons (superimposed by the methyl triplets of the ethyl groups) and six doublets of equal intensity for the aromatic protons enabled the assignment of the C_2 isomer, although the region of the methylene protons prevented an easy interpretation. However, acid-catalyzed transesterification in boiling methanol gave in practically quantitative yield the corresponding hexamethyl ester **5**, the ^{1}H-NMR spectrum of which was somewhat easier to interpret. Here, besides three signals for the methyl groups, three pairs of doublets (ratio 2:2:2) for the diastereotopic O–CH_2–CO protons and a pair of doublets and a singlet (ratio 2:1) for the Ar–CH_2–Ar protons have to be expected. Two of these 17 signals are obviously superimposed by the three signals for the methyl groups, but all signals are discernible in the NMR spectrum of the Cs^+ complex (see below). The remainder of the spectrum was analogous to that of the hexaethyl ester, thus further confirming its conformation. The final proof was obtained by an X-ray structure analysis of the hexaethyl ester (see below).

Variation of the reaction conditions led to an optimized yield of **4** (92% with Cs_2CO_3 in acetonitrile), making it an easily available starting compound for further derivatization. However, the corresponding isomer with D_3 symmetry could not be isolated up to now. (Yamato reports on the formation of the corresponding trimethyl ether in low yield; however, "...the isolation of a pure sample was not successful".[7]) A possible explanation may be, that the D_3 arrangement allows no intramolecular hydrogen bonding within a diphenylmethane subunit which, although not any longer possible in the final alkylation product, may well be a factor to stabilize intermediates in the stepwise *O*-alkylation.

Due to the "regular up and down" of the *O*-alkyl groups in the D_3 arrangement, the introduction of bulkier residues might favor its outcome, and therefore we attempted the alkylation with *tert*-butyl bromoacetate. In fact, we obtained two isomeric hexa-*tert*-butyl esters (**6a** and **6b**, separable by chromatography, proven by mass spectrometry). One of them was the C_2 isomer, characterized by NMR evidence as described above. The second one, however, was obviously totally asymmetric. Its ^{1}H-NMR spectrum (Figure 3) showed 12 doublets of equal intensity in the aromatic region, proving the presence of 6 different aromatic units and 12 different aromatic protons. Accordingly 12 singlets for *tert*-butyl groups are expected, which superimpose to form 8 signals (3:1:1:1:1:3:1:1). Since all three Ar–CH_2–Ar and all six O–CH_2–CO groups are different, 9 pairs of doublets should be observed for these diastereotopic protons. In fact, 35 of these 36 signals are discernible.

This result, surprising at first sight, may be rationalized as follows: If the residues attached to the phenolic oxygens are large enough, even the rotation around Ar–CH_2–Ar bonds may be restricted. This would not concern the D_3 case with its regular alternation of all phenolic units, but for the C_2 symmetry of the biphenyl units two different arrangements of the diphenylmethane units are possible, as shown in Figure 1. Both exhibit *the same* configuration of the biphenol units, but only one retains the C_2 symmetry. The definite proof for this interpretation was given by the fact, that both isomeric hexa-*tert*-butyl esters can be converted quantitatively by acid-catalyzed methanolysis into the same hexamethyl ester with C_2 symmetry.

The hexaethyl ester can be easily hydrolyzed to the corresponding hexaacid. In comparison with the esters this compound exhibits a ^{1}H-NMR spectrum with rather broad signals in the aromatic and methylene region. Its entire purity as such is difficult to establish; since rigorous drying could lead to anhydride structures, the presence of which cannot be entirely ruled out as indicated by the mass spectrum. Three sharp NMR singlets for the *tert*-butyl groups (ratio 1:1:1) may be taken as an indirect proof for the (ester- and anhydride-free) hexaacid with C_2 symmetry. Conversion to the hexaacid chloride (usually according to the thionyl

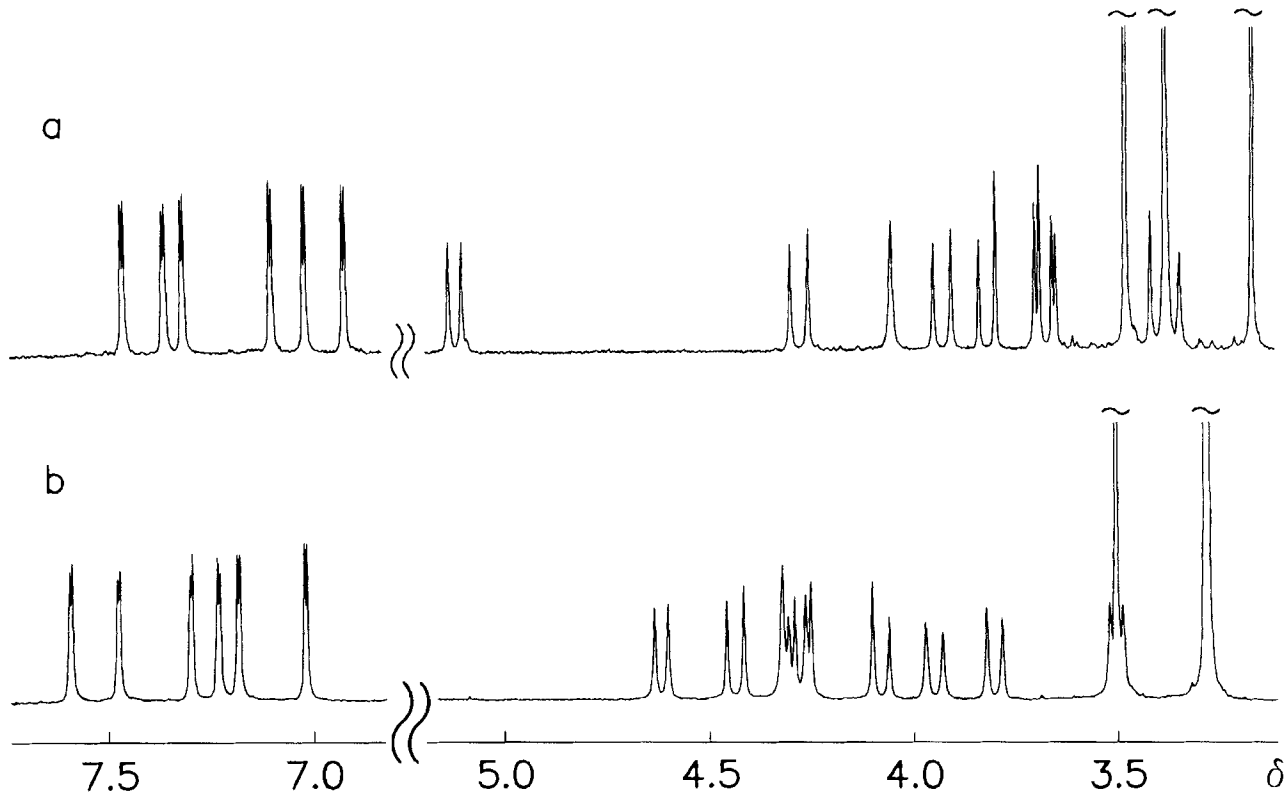

Figure 2. ^{1}H-NMR spectrum (400 MHz, CD_2Cl_2) of the hexamethyl ester **5** before (a) and after (b) shaking (ultrasonic treatment) with an excess of solid CsI

chloride method) and its subsequent methanolysis give the hexamethyl ester **5** in practically quantitative yield, and further esters should be available in a similar way. Reaction of the hexaacid chloride with diethylamine leads to hexaamides, obviously occuring as a mixture of stereoisomers for the reasons discussed above.

X-Ray Analysis

The structure and configuration of **4** could be confirmed by an X-ray analysis. Figure 4 shows a view of the molecule from different directions.

All bond distances and bond angles are close to usual values.

To describe the molecular conformation of the macrocycle, the plane of the three methylene carbon atoms C(01), C(12), and C(23) may be taken as an obvious reference plane. Table 1 compares the dihedral angles which the aromatic rings I to VI include with this plane and gives the positions of the phenolic oxygens of these rings with respect to this reference plane. From the signs (+−, −+, +−) of these distances follows that the configuration of the dihydroxybiphenyl unit III/IV is opposite to that of I/II and V/VI, and hence the C_2 configuration derived already from the NMR spectra in solution.

As Figure 4 demonstrates, three aromatic rings are close to coplanar with the phenolic oxygens pointing inwards (their dihedral angles are II/IV 21.5°, IV/VI 12.5°, and VI/II 14.0°) while the other three rings are pointing up or down. The conformation of the biphenyl subunits may be described by their dihedral angles which are 73.6° (I/II), 89.3° (III/IV), and 59.6° (V/VI), thus differing by 30°. The torsional angles around the aryl-methylene links can be used for the description of the conformation of the diphenylmethane subunits[11]. Their values (using the carbon carrying the phenolic oxygen) are −75.2°, 113.1° (II/III), 70.1°, −108.6° (IV/V), and 63.3°, −121.7° (VI/I).

The ether-ester chains attached to the phenolic oxygens extend in the direction given by these oxygens (that means, chains of rings I/IV/V and II/III/IV are found at different sides of the molecule and none of the chains is threaded through the annulus). Their orientation may be characterized by the torsional angles around the Ar−O and the O−CH_2 bonds. They are collected in Table 2, together with the dihedral angle between the C−(C=O)−O plane and the corresponding aromatic ring. No general rule can be derived from these values, showing that the pendant ether-ester chains just fill the crystal lattice, or that their conformation is determined by "packing effects".

The crystal lattice contains one *n*-hexane molecule which is completely disordered. There are 5 detectable maxima of electron density which can be connected by bonds resulting in unsuitable bond distances and angles. A center of symmetry is doubling these 5 peaks. This means *n*-hexane is moving over the center of symmetry.

Complexation of Alkali Ions

Alkylation of calixarenes with ethyl bromoacetate (followed by further derivatization) leads to neutral ligands for

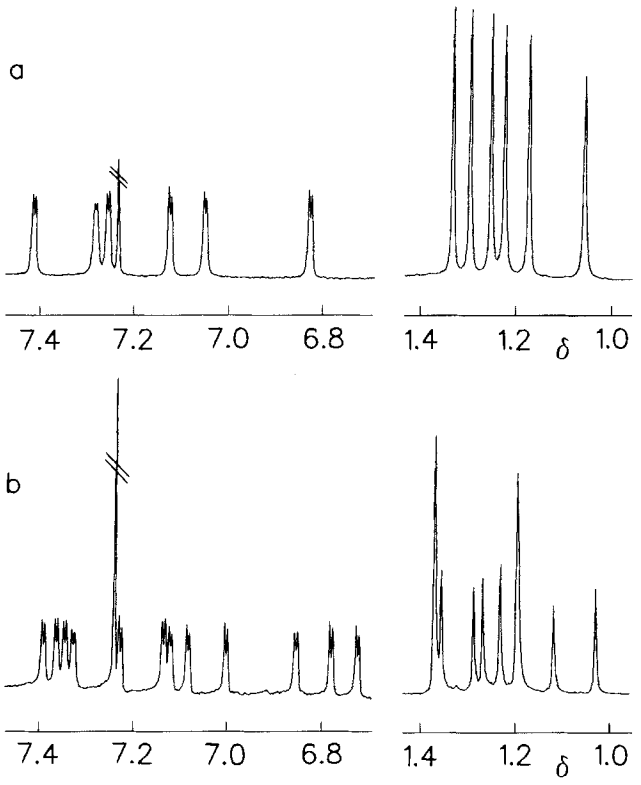

Figure 3. Comparison of the ^{1}H-NMR spectra (400 MHz, $CDCl_3$) of the two isomeric hexa-*tert*-butyl esters **6a** (a) and **6b** (b) evidencing C_2 and C_1 symmetry. Signals of *tert*-butyl groups are represented on a reduced scale. The doubly crossed signal belongs to traces of undeuterated solvent

a variety of cations[12]. Tetraester derivatives of calix[4]arenes in the cone conformation, for instance, are clearly more selective with respect to sodium than potassium, which has been used in sensor techniques by several groups[13]. Such a Na^+ complex in $CDCl_3$ is kinetically stable on the NMR time scale[14]. The corresponding derivatives of larger calixarenes prefer the complexation of larger alkali ions (although the selectivities are less pronounced) and a caesium-selective electrode was based on a hexaester[15].

If a solution of **4** or **5** in CD_2Cl_2 (or $CDCl_3$) is shaken (ultrasound) with an excess of CsI, a completely different ^{1}H-NMR spectrum with sharp lines is obtained (Figure 2) in which the signals for the aromatic protons are slightly shifted downfield, while the methylene protons (Ar–CH_2–Ar, O–CH_2–CO) of **5** are localized now between δ = 3.5 und 4.7 in comparison with those in the free **5**, which appear in the range δ = 3.3–5.1. Shaking of **5** with various amounts of CsI clearly demonstrates (Figure 5) that a 1:1 complex is formed which is stable on the NMR time scale under these conditions. (Changes in the NMR spectrum are also observed after shaking a solution of **4** or **5** with NaI and KI, but here the signals in the spectrum are broad and unresolved, indicating incomplete complex formation and exchange of the metal ions between ligand molecules.)

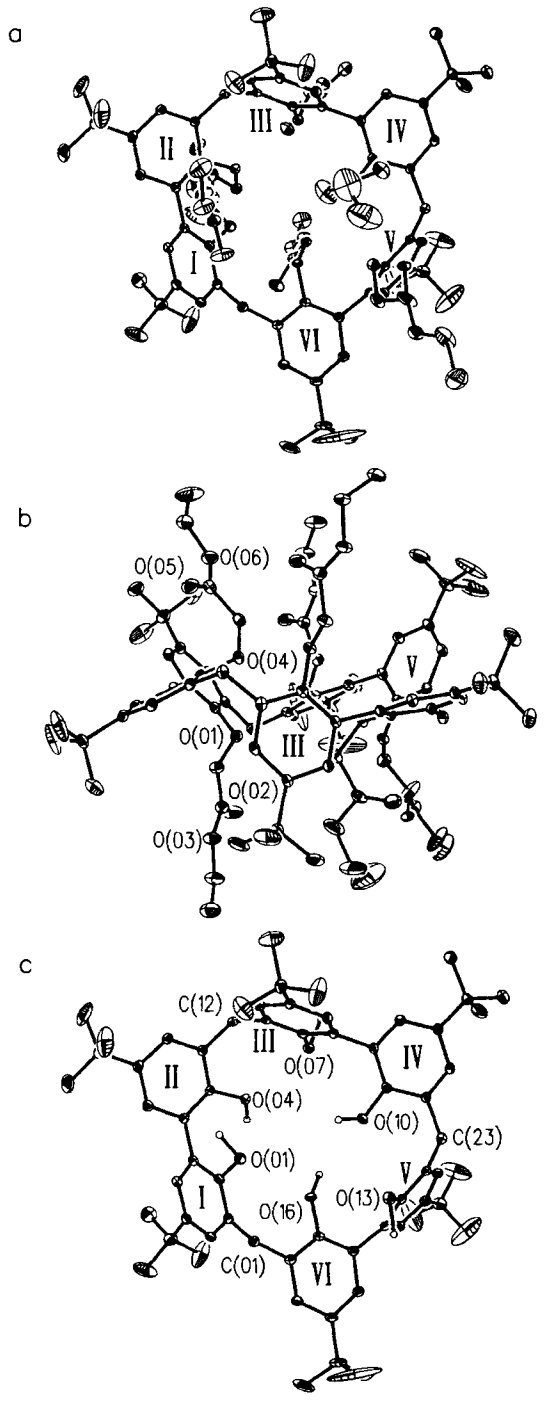

Figure 4. Molecular conformation of **4**, seen from different directions. The numbering pattern of the oxygen atoms is shown for two ether-ester chains in b. For clarity, the pendant chains are omitted in c. The "reference plane" is defined by the three marked carbon atoms C(01), C(12), and C(23)

Regarding the configuration (and conformation) of **4** and **5** (see also the X-ray structure) it is difficult to establish the structure of this complex. From the multiplicity of signals it follows that it must have C_2 symmetry (like the free ligand molecule), and hence the Cs^+ ion must be situated on the twofold axis, either in an energy minimum or in a time-averaged way. Lowering the temperature to −70°C leads to

Table 1. Orientation of the aromatic rings in **4** with respect to the reference plane {C(01)–C(12)–C(23)} of the Ar–CH_2–Ar methylene carbons

Ring	Dihedral angle	Oxygen atom	Distance from the plane (Å)
I	53.1	O(01)	+0.862
II	35.2	O(04)	−1.129
III	90.0	O(07)	−1.082
IV	14.5	O(10)	+0.411
V	81.7	O(13)	+0.358
VI	26.8	O(16)	−0.955

Table 2. Orientation of the ether-ester chains in **4** with respect to the corresponding aromatic rings

Ring	Torsion angle C_{Ar}–C_{Ar}–O–C	Torsion angle C_{Ar}–O–C–C(O)	Dihedral angle Aryl/C–C(O)–O
I	−130.0	111.7	41.0
II	61.3	47.8	84.3
III	92.2	−163.3	113.5
IV	−57.0	−55.3	97.7
V	−127.5	112.6	110.8
VI	45.9	49.4	102.9

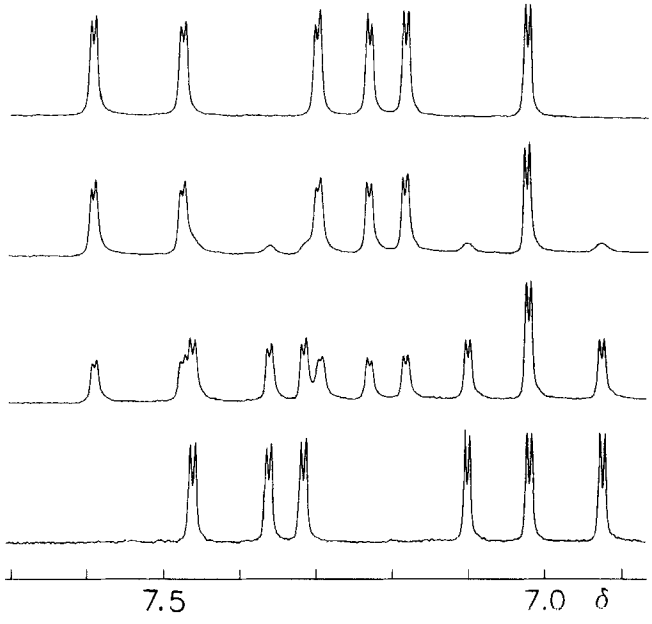

Figure 5. ^{1}H-NMR titration of the hexamethyl ester **5** with CsI. From the top to the bottom 2, 1, 0.5, and 0 equivalents of solid CsI are applied. Solvent: CD_2Cl_2

minor shifts and to some broadening of signals. However, no clear evidence for an asymmetric complex with the Cs^+ ion above or below the mean plane and an intramolecular hopping[16] between these two positions could be found.

Conclusion

Condensation of 2,2′-dihydroxy-5,5′-di-*tert*-butylbiphenyl (**1**) with formaldehyde leads to macrocyclic molecules which – as regards their size – are inbetween calixarenes and spherands. Alkylation of the trimer with alkyl bromoacetates gives ionophores with promising complexation properties and an interesting stereochemistry. While up to date only isomers with C_2 and C_1 symmetry were obtained, we hope that variation of the alkylation conditions will lead also to a derivative with D_3 symmetry, representing an interesting building block for larger host molecules and also to stereospecific derivatization of the cyclic tetramer.

Experimental

All melting points are uncorrected. – NMR: Bruker AC 200 or AM 400 in $CDCl_3$ or CD_2Cl_2, TMS as reference. – MS: Finnigan MAT 8230. – Melting points: Dr. Tottoli's melting point apparatus (Büchi). – Elemental analyses: Microanalytical Laboratory of our institute.

5,5′-Di-tert-butyl-2,2′-dihydroxybiphenyl (**1**) was prepared according to literature procedures[7,17,18].

Cyclic Trimer **2** was prepared similar to Yamato's method[7]; only benzene used as eluent in flash chromatography was replaced by the less toxic toluene, which allows a more convenient separation from the tetramer. After recrystallization from hexane we obtained 49% of **2** as a colourless solid, mp 252–254°C (ref.[7] 253–256°C). – ^{1}H-NMR and MS data are in accordance with the data in ref.[7] – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 147.47 ($C_{Ar}OH$), 144.36 [$C_{Ar}C(CH_3)_3$], 127.58, 127.51 ($C_{Ar}H$), 126.43, 125.69 ($C_{Ar}C_{Ar}$, $C_{Ar}CH_2$), 34.22 (CH_2), 32.42 [$C(CH_3)_3$], 31.56 [$C(CH_3)_3$].

Cyclic Tetramer **3** was prepared in the same manner by using CsOH instead of NaOH, according Yamato's procedure[7]. – ^{1}H-NMR and MS data are in accordance with the data in ref.[7] – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 147.11 ($C_{Ar}OH$), 144.49 [$C_{Ar}C(CH_3)_3$], 127.44, 127.15 ($C_{Ar}H$), 126.44 ($C_{Ar}C_{Ar}$, $C_{Ar}CH_2$), 34.14 (CH_2), 32.16 [$C(CH_3)_3$], 31.47 [$C(CH_3)_3$].

Hexaethyl Ester **4**: 1.50 g (1.61 mmol) of the trimer **2** and 3.46 g (10.6 mmol) of caesium carbonate were heated at reflux in 100 ml of dry acetonitrile; then 3.20 ml (4.84 g, 29.0 mmol) of ethyl bromoacetate was added. After refluxing under argon for 15 h, the reaction mixture was concentrated in vacuo and the residue partioned between 50 ml of CH_2Cl_2 and 50 ml of water. The organic layer was separated and the aqueous one extracted again with 50 ml of CH_2Cl_2. The combined organic extracts were dried with $MgSO_4$ and concentrated under reduced pressure to give an orange oil. This was purified by flash chromatography on silica gel (removal of excess ethyl bromoacetate with CH_2Cl_2, elution of the product with ethyl acetate/hexane, 3:7 v/v). Concentration of the fraction containing the product gave 2.15 g (92%) of **4** as a white foam. This could be further purified by recrystallization from a concentrated hexane solution. Mp 122–123°C. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.414, 7.314, 7.284, 7.096, 6.978, 6.862 (6 d, J = 2.5 Hz, each 2H, ArH), 5.207 (d, J = 13.1 Hz, 2H, $ArCH_2Ar$), 4.26–3.26 (28H, overlapped signals due to $ArCH_2Ar$, OCH_2CO, or OCH_2CH_3), 1.309, 1.275, 1.249 [3 s, each 18H, $C(CH_3)_3$], 1.064, 0.979, 0.789 (3 t, J = 7.1 Hz, each 6H, OCH_2CH_3). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 170.04, 169.95, 169.31 (CO_2R), 153.03, 152.82, 151.19 ($C_{Ar}OCH_2$), 145.95, 144.46, 144.16, 134.92, 134.55, 132.82, 130.68, 129.04, 128.43, 127.71, 126.95, 126.57, 125.24, 125.10 (other C_{Ar}), 69.44, 67.60, 66.57 (OCH_2CO), 60.10, 59.78, 59.39 (OCH_2CH_3), 34.16, 34.12, 34.06 ($ArCH_2Ar$), 31.61, 31.46, 31.38 [$C(CH_3)_3$; $C(CH_3)_3$ covered by noise], 13.99, 13.85, 13.60 (OCH_2CH_3). – FD MS, *m/z*: 1448.1 [M^+]. – $C_{87}H_{114}O_{18}$ (1447.9): calcd. C 72.17, H 7.94; found C 72.33, H 8.16.

Hexamethyl Ester **5**: 500 mg (0.345 mmol) of hexaethyl ester **4** was refluxed together with a catalytic amount of *p*-toluenesulfonic acid in 250 ml of dry methanol for 8d. The mixture was cooled to room temp. concentrated in vacuo, the residue dissolved in dichloromethane (100 ml) and the solution shaken with a saturated aqueous solution of $NaHCO_3$ (50 ml). Separation of the organic layer, drying with $MgSO_4$ and evaporation of the solvent under reduced pressure yielded 445 mg (94%) of crude product, which was purified by recrystallization from methanol to give white crystals, mp 232–234°C. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.425, 7.336, 7.286, 7.075, 6.989, 6.926 (6 d, *J* = 2.5 Hz, each 2H, ArH), 5.183 (d, *J* = 13.0 Hz, 2H, $ArCH_2Ar$), 4.291 (d, *J* = 17.1 Hz, 2H, OCH_2CO), 4.057–3.360 (14H, overlapped signals due to $ArCH_2Ar$ and OCH_2CO), 3.473, 3.382, 3.103 (3 s, each 6H, OCH_3), 1.305, 1.281, 1.248 [3 s, each 18H, $C(CH_3)_3$]. – FD MS, *m/z*: 1363.8 [M^+]. – $C_{81}H_{102}O_{18}$ (1363.7): calcd. C 71.34 H 7.54; found C 71.16, H 7.58.

Hexa-tert-butyl Ester **6** was prepared like the hexaethyl ester **4** by using potassium carbonate and *tert*-butyl bromoacetate (same molar ratio) in 94% yield. The two isomers could be separated by preparative TLC on silica gel (plate size 20×20 cm) with hexane/ethyl acetate (37:3, v/v) as eluent; the C_2 isomer **6a**, mp ca. 285°C (dec.), showed a higher R_f value than the C_1 isomer **6b**, mp ca. 145°C (after softening). – ^{1}H NMR (400 MHz, $CDCl_3$): C_2 isomer **6a**: δ = 7.419, 7.286, 7.260, 7.129, 7.055, 6.813 (6 d, *J* = 2.3 Hz, each 2H, ArH), 5.165 (d, *J* = 13.1 Hz, 2H, $ArCH_2Ar$), 4.099 (d, *J* = 17.3 Hz, 2H, OCH_2CO), 4.078 (d, *J* = 13.1 Hz, 2H, $ArCH_2Ar$), 4.059 (d, *J* = 15.5 Hz, 2H, OCH_2CO), 3.609 (d, *J* = 15.8 Hz, 2H, OCH_2CO), 3.498 (d, *J* = 17.3 Hz, 2H, OCH_2CO), 3.443 (d, *J* = 15.9 Hz, 2H, OCH_2CO), 3.325 (d, *J* = 13.2 Hz, 2H, $ArCH_2Ar$), 3.141 (d, *J* = 17.6 Hz, 2H, OCH_2CO), 1.332, 1.296, 1.252, 1.224, 1.174, 1.057 [6 s, each 18H, $C(CH_3)_3$]. – C_1 isomer **6b**: δ = 7.390, 7.361, 7.343, 7.326, 7.226, 7.135, 7.120, 7.082, 7.001, 6.852, 6.778, 6.772 (12 d, *J* = 2.4 Hz, each 1H, ArH), 5.040 {13.6}, 4.886 {15.4}, 4.867 {13.4}, 4.750 {13.8}, 4.313 {16.1}, 4.249 {15.7}, 4.190 {15.8}, 3.993 {15.4}, 3.848 {17.3} (9 d, *J* [Hz] in { }, each 1H, $ArCH_2Ar$ or OCH_2CO), 3.566–3.356 (br. m, 7H, $ArCH_2Ar$ or OCH_2CO), 2.939 (d, *J* = 14.9 Hz, 1H, $ArCH_2Ar$), 2.865 (d, *J* = 18.2 Hz, 1H, $ArCH_2Ar$), 1.367 [s, 27H, $C(CH_3)_3$], 1.354, 1.286, 1.267, 1.231 [4 s, each 9H, $C(CH_3)_3$], 1.195 [s, 27H, $C(CH_3)_3$], 1.117 [s, 9H, $C(CH_3)_3$], 1.029 [s, 9H, $C(CH_3)_3$]. – FD MS: **6a**, *m/z*: 1616.5 [M^+]; **6b**, *m/z*: 1616.7 [M^+]. $C_{99}H_{138}O_{18}$ (1616.2).

Hexaacid **7**: 1.20 g (0.83 mmol) of the hexaethyl ester **4** and 1.40 g (35.0 mmol) of NaOH (dissolved in 50 ml of water) were refluxed overnight under argon in 100 ml of ethanol. After cooling, the mixture was acidified with conc. H_2SO_4 to pH 1. A further addition of 100 ml of water, storage overnight at 5°C, filtration by suction and recrystallization from water/ethanol yielded 1.40 g of a white solid which obviously contained the monosodium salt. The free acid was obtained after a second recrystallization from formic acid as white needles, mp ca. 290°C (dec.). – ^{1}H NMR (200 MHz, CD_2Cl_2): δ = 7.553, 7.318, 7.265, 7.185 (4 br. d, *J* = 2 Hz, each 2H, ArH), 7.142 (br. s, 4H, ArH), 5.047 (d, *J* = 13.7 Hz, 2H, $ArCH_2Ar$), 5.0–3.0 (br. m, 20H, $ArCH_2Ar$, OCH_2CO), 1.372, 1.287, 1.157 [3 s, each 18H, $C(CH_3)_3$]. – FD MS, *m/z*: 1263.6 [$(M - H_2O)^+$], 1304.1 [$(M + Na)^+$]. – $C_{75}H_{90}O_{18}$ (1279.55): calcd. C 70.40, H 7.09; found C 68.24, H 7.22.

X-Ray Structure Analysis: Single crystals of **4** were grown from *n*-hexane; monoclinic, space group *C2/c*, *a* = 37.069(4), *b* = 16.186(4), *c* = 30.442(4) Å, β = 105.62(1)°, *V* = 17591(5) Å^3, *Z* = 8. A crystal of 0.5 × 0.5 × 0.3 mm was sealed in a Lindemann glass capillary. 25 reflections with Θ > 5° were used to determine the cell constants. All reflections ($-44 < h < 42$, $0 < k < 19$, $0 < l < 36$, 15559 reflections measured, 15548 out of 15566 unique reflections) were used for the structure analysis with a computer-controlled diffractometer (Siemens), Mo-K_α radiation, μ = 0.712 mm^{-1}, *T* = 193 K. The phase problem was solved by direct methods[19], and the structure parameters were refined by least-squares methods [minimization of $(F_o^2 - F_c^2)^2$, weighting scheme: $w = 1/\sigma^2(F)$ according to the counting statistics, 1012 parameters, coordinates of the H atoms calculated, for $|F| > 4\sigma$ (7831 reflections): *S* = 1.04, *R* = 0.067, R_w = 0.176, 10 largest peaks in the difference map: 0.43···0.29 electrons/Å^3]. All calculations were performed by a DEC 3000 AXP Mod. 400 [Alpha Technology) with the SHELXS and SHELXL programs[19,20]. Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository number CSD-57841, the names of the authors and the journal citation.

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[311/93]