

## The Crystal and Molecular Structure of Two Calix[4]arenes bridged at Opposite *para* Positions

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Two macrocyclic compounds of the calix[4]arene type, in which two opposite *para* positions are connected by an additional aliphatic chain, (1) and (2) were synthesized. Single crystals were obtained from acetone without incorporation of solvent. Crystals of the methyl-substituted compound (1) are monoclinic, space group  $P2_1/c$ ,  $a = 9.269(6)$ ,  $b = 18.069(8)$ ,  $c = 38.42(2)$  Å,  $\beta = 92.66(1)^\circ$ ,  $Z = 8$ , final  $R$  value 0.065 (5 900 unique reflections). Crystals of the cyclohexyl-substituted compound (2) are orthorhombic, space group  $Pbca$ ,  $a = 10.800(4)$ ,  $b = 20.799(2)$ ,  $c = 36.492(3)$  Å,  $Z = 8$ , final  $R$  value 0.042 (4 650 unique reflections). In both cases the arrangement of the four phenolic residues corresponds to the cone conformation of calix[4]arenes, the whole molecule thus having the shape of a basket with a handle.

Calixarenes, oligonuclear compounds consisting of phenolic residues, linked by methylene groups in the *ortho* positions with respect to the hydroxy groups, have attracted appreciable interest in recent years.<sup>1</sup> The calixarenes represent an easily available class of potential guest–host molecules, as evidenced from the simple preparations of the different oligomers (mainly with 4, 6, or 8 phenolic residues in the molecule) in large quantities.<sup>2</sup> Indeed, the calixarenes as well as suitable derivatives can act as ion carriers through liquid membranes,<sup>3,4</sup> are able to form different types of inclusion complexes in the solid state,<sup>5–9</sup> and exhibit enzyme-like catalytic properties.<sup>10,11</sup>

Elucidation of their <sup>1</sup>H n.m.r. spectra has shown that the calix[4]arenes exist in the so-called cone conformation which is stabilized by a cyclic array of intramolecular hydrogen bonds involving the hydroxy groups.<sup>12,13</sup> (It was for this molecular shape that Gutsche<sup>1</sup> proposed the name 'calixarenes', which is now generally accepted for the whole class of compounds.) The same conformation was also found exclusively in the solid state for several examples.<sup>5–8</sup> Nevertheless, the structure of the calix[4]arene ring is flexible enough to permit a rapid interconversion of the two opposite cone conformations in solution at a temperature slightly above room temperature. Below 0 °C this inversion becomes slow relative to the n.m.r. time scale and the cone conformation is 'frozen'. However, no other conformations (*e.g.* partial cone, 1,2- or 1,3-alternate) can be detected for the calix[4]arenes (in contrast to some derivatives<sup>12,14,15</sup>).

Thus, the reactivity of the hydroxy groups in the calix[4]arenes is determined by a closed ring of intramolecular hydrogen bonds, which still has a certain flexibility, allowing the hydroxy groups shortly to come into closer contact. From the  $pK_1$  values it may be concluded<sup>16</sup> that even small changes in the preferred conformation, caused for instance by slightly different substituents in the phenolic residue opposite to the dissociating residue, can cause large effects. To elucidate further the reactivity of the hydroxy groups, we tried to construct more rigid molecules, in which the cone conformation of calixarenes is fixed. This seemed to be possible by connecting two opposite *para* positions by an aliphatic chain of appropriate length.<sup>17</sup> Furthermore, variation of this chain length should lead to small but definite changes of the mutual position of the hydroxy groups.

Indeed it could be seen from the temperature independence of the AB system observed for the methylene protons that the resulting molecules are rigid.<sup>17</sup> We now show by X-ray analysis

that the calixarenes really do exist in a cone-like conformation, and compare their shape with that of unbridged calixarenes.

### Experimental

**Synthesis of Bridged Calixarenes.**—**Compound (1)** (R = Me). A solution of 1,8-bis-(*p*-hydroxyphenyl)octane (1.49 g, 5 mmol), 2,6-bis(bromomethyl)-*p*-cresol (2.94 g, 10 mmol), and TiCl<sub>4</sub> (4 g, 21 mmol) in dry dioxane (500 cm<sup>3</sup>) was heated to 100 °C (bath temperature) for 30 h. The solvent was evaporated off and the dark red residue dissolved in CH<sub>2</sub>Cl<sub>2</sub>. Silica gel (50 g) was added, the mixture evaporated, and the dry powder extracted for 24 h in a soxhlet apparatus with CH<sub>2</sub>Cl<sub>2</sub>. This procedure (twice) removes most of the unidentified tarry products. The crude extract was purified by flash chromatography (silica gel E. Merck, 230–400 mesh ASTM, CH<sub>2</sub>Cl<sub>2</sub>) to give a slightly yellow solid from the first fractions, which on recrystallization from acetone gave pure (1) (565 mg, 20%), m.p. 280–282 °C (Found: C, 81.2; H, 7.4. C<sub>38</sub>H<sub>42</sub>O<sub>4</sub> requires C, 81.1; H, 7.5%;  $\nu_{\max}$  (KBr) 3 250 (OH), 3 010, 2 920, and 2 850 (CH), 1 610 (C=C), and 1 485 and 1 460 cm<sup>-1</sup> (CH);  $\delta$  (200 MHz; CDCl<sub>3</sub>; SiMe<sub>4</sub>) 0.08 (4 H, m, CH<sub>2</sub>), 0.48 (4 H, m, CH<sub>2</sub>), 1.13 (4 H, m, CH<sub>2</sub>), 2.21 (6 H, s, ArMe), 2.34 (4 H, br t, ArCH<sub>2</sub>), 3.35 (4 H, d, ArCH<sub>A</sub>H<sub>B</sub>Ar,  $J_{AB}$  13.8 Hz), 4.15 (4 H, d, ArCH<sub>A</sub>H<sub>B</sub>Ar,  $J_{AB}$  13.8 Hz), 6.61 (4 H, s, ArH), 6.88 (4 H, s, ArH), 8.99 (2 H, s, OH), and 9.10 (2 H, s, OH);  $m/z$  562 ( $M^+$ , 100%), 544 (8), and 281 (10).

**Compound (2)** (R = cyclohexyl). A solution of 1,8-bis-(*p*-hydroxyphenyl)octane (1.49 g, 5 mmol), 2,6-bis(bromomethyl)-4-cyclohexylphenol (3.62 g, 10 mmol), and TiCl<sub>4</sub> (4.56 g, 24 mmol) was heated in dry dioxane (500 cm<sup>3</sup>) for 96 h at 100 °C. Isolation and purification procedures were as described for (1) to give pure (2) (140 mg, 4%), m.p. 266–268 °C (Found: C 82.7; H 8.3. C<sub>48</sub>H<sub>58</sub>O<sub>4</sub> requires C, 82.5; H 8.4%;  $\nu_{\max}$  (KBr) 3 240 (OH), 3 010, 2 920, and 2 850 (CH), 1 610 (C=C), and 1 480 and 1 460 cm<sup>-1</sup> (CH);  $\delta$  (200 MHz; CDCl<sub>3</sub>; SiMe<sub>4</sub>) 0.01 (4 H, m, CH<sub>2</sub>), 0.44 (4 H, m, CH<sub>2</sub>), 1.11 (4 H, m, CH<sub>2</sub>), 1.33 (10 H, m, cyclohexyl), 1.76 (10 H, m, cyclohexyl), 2.34 (4 H + 2 H, m, ArCH<sub>2</sub> + ArCH), 3.37 (4 H, d, ArCH<sub>A</sub>H<sub>B</sub>Ar,  $J_{AB}$  13.8 Hz), 4.16 (4 H, d, ArCH<sub>A</sub>H<sub>B</sub>Ar,  $J_{AB}$  13.8 Hz), 6.62 (4 H, s, ArH), 6.90 (4 H, s, ArH), 9.04 (2 H, s, OH), and 9.14 (2 H, s, OH);  $m/z$  698 ( $M^+$ , 100%), 680 (5), 615 (20), and 533 (2).

**X-Ray Structure Analysis.**—The conditions for the X-ray analysis of compounds (1) and (2) were essentially the same. The latter set of data in the discussion below is for compound (2).

**Table 1.** Atomic co-ordinates of the methyl-compound (1)\*

Compound (1a)				Compound (1b)			
Atom	x	y	z	Atom	x	y	z
O(1)	0.324 4(8)	0.459 5(4)	-0.169 6(2)	O(1)	0.873 0(7)	0.684 3(3)	0.997 5(2)
O(2)	0.171 3(7)	0.476 1(4)	-0.228 5(2)	O(2)	0.974 1(8)	0.728 9(4)	0.938 4(2)
O(3)	0.288 6(8)	0.365 7(4)	-0.264 8(2)	O(3)	0.860 0(8)	0.616 1(4)	0.901 1(2)
O(4)	0.411 5(7)	0.336 3(3)	-0.200 5(2)	O(4)	0.739 9(7)	0.580 0(4)	0.960 8(2)
C(1)	-0.063 1(12)	0.219 1(6)	-0.265 8(2)	C(1)	0.513 5(13)	0.720 7(7)	0.845 8(3)
C(2)	0.077 5(11)	0.194 7(5)	-0.257 2(2)	C(2)	0.501 2(13)	0.651 5(6)	0.862 1(2)
C(3)	0.195 7(11)	0.244 7(6)	-0.257 6(2)	C(3)	0.614 0(13)	0.616 0(6)	0.879 4(2)
C(4)	0.338 9(11)	0.213 1(5)	-0.245 5(2)	C(4)	0.578 2(13)	0.543 6(5)	0.897 0(2)
C(5)	0.356 4(12)	0.206 1(5)	-0.206 4(2)	C(5)	0.507 6(14)	0.555 6(6)	0.932 5(3)
C(6)	0.324 9(12)	0.136 9(6)	-0.189 5(3)	C(6)	0.361 9(12)	0.550 4(6)	0.934 7(3)
C(7)	0.327 1(14)	0.131 7(6)	-0.153 7(3)	C(7)	0.287 3(11)	0.566 9(5)	0.964 4(3)
C(8)	0.350 7(12)	0.194 5(6)	-0.134 2(3)	C(8)	0.378 3(10)	0.591 9(5)	0.992 5(2)
C(9)	0.381 3(10)	0.265 2(6)	-0.149 2(3)	C(9)	0.523 5(10)	0.598 3(5)	0.992 8(3)
C(10)	0.403 7(12)	0.331 8(5)	-0.125 4(2)	C(10)	0.610 3(12)	0.625 5(5)	1.024 0(2)
C(11)	0.259 1(12)	0.377 2(5)	-0.122 8(2)	C(11)	0.640 1(12)	0.708 3(6)	1.022 3(2)
C(12)	0.156 4(13)	0.355 4(6)	-0.098 9(3)	C(12)	0.543 8(11)	0.760 5(5)	1.033 4(2)
C(13)	0.028 4(12)	0.392 7(5)	-0.096 0(3)	C(13)	0.569 2(12)	0.837 1(5)	1.030 5(2)
C(14)	-0.002 9(10)	0.450 6(5)	-0.118 1(2)	C(14)	0.697 7(10)	0.859 0(6)	1.017 6(2)
C(15)	0.096 4(12)	0.474 5(5)	-0.142 9(3)	C(15)	0.799 3(12)	0.810 0(6)	1.006 5(2)
C(16)	0.055 2(12)	0.539 3(5)	-0.167 6(2)	C(16)	0.940 4(11)	0.841 2(6)	0.991 5(3)
C(17)	-0.037 1(12)	0.516 8(6)	-0.199 2(3)	C(17)	0.931 8(12)	0.856 0(6)	0.953 0(3)
C(18)	-0.183 8(11)	0.527 1(5)	-0.199 0(3)	C(18)	0.899 4(13)	0.928 1(6)	0.940 8(3)
C(19)	-0.278 8(12)	0.504 9(6)	-0.226 5(3)	C(19)	0.889 0(16)	0.946 4(6)	0.905 5(3)
C(20)	-0.216 1(12)	0.471 5(6)	-0.255 9(3)	C(20)	0.893 0(14)	0.890 0(7)	0.880 8(3)
C(21)	-0.070 4(13)	0.463 4(6)	-0.255 9(3)	C(21)	0.922 6(13)	0.816 0(6)	0.890 3(3)
C(22)	-0.000 3(11)	0.421 1(5)	-0.285 8(2)	C(22)	0.919 4(11)	0.751 9(6)	0.865 9(2)
C(23)	0.039 8(11)	0.341 1(6)	-0.276 4(2)	C(23)	0.769 6(12)	0.714 3(6)	0.863 2(2)
C(24)	-0.080 2(13)	0.293 6(6)	-0.274 8(2)	C(24)	0.651 6(12)	0.749 7(6)	0.846 6(2)
C(25)	-0.187 9(12)	0.168 5(6)	-0.258 9(3)	C(25)	0.386 2(13)	0.767 7(6)	0.832 5(3)
C(26)	-0.247 5(15)	0.178 5(10)	-0.224 2(3)	C(26)	0.363 2(12)	0.833 0(6)	0.857 9(2)
C(27)	-0.176 6(15)	0.202 7(8)	-0.194 6(3)	C(27)	0.349 5(13)	0.808 0(6)	0.896 6(3)
C(28)	-0.231 7(14)	0.213 6(8)	-0.160 2(3)	C(28)	0.332 5(13)	0.872 7(6)	0.921 9(2)
C(29)	-0.153 7(17)	0.251 6(9)	-0.131 7(3)	C(29)	0.337 4(13)	0.848 2(6)	0.959 6(3)
C(30)	-0.214 6(14)	0.263 9(7)	-0.099 2(3)	C(30)	0.316 2(15)	0.913 1(6)	0.984 3(3)
C(31)	-0.151 6(23)	0.307 7(11)	-0.073 2(4)	C(31)	0.313 8(11)	0.888 6(6)	1.023 4(3)
C(32)	-0.079 2(11)	0.371 5(6)	-0.068 5(2)	C(32)	0.461 2(11)	0.890 8(5)	1.043 8(3)
C(33)	0.227 4(11)	0.436 3(5)	-0.145 3(3)	C(33)	0.766 1(11)	0.732 6(5)	1.008 0(2)
C(34)	0.023 5(12)	0.484 6(5)	-0.228 2(3)	C(34)	0.941 0(12)	0.799 8(6)	0.926 9(3)
C(35)	0.170 7(12)	0.316 1(6)	-0.266 7(2)	C(35)	0.750 3(13)	0.647 8(6)	0.881 5(3)
C(36)	0.380 6(12)	0.269 3(6)	-0.185 6(3)	C(36)	0.592 1(11)	0.579 3(5)	0.961 3(3)
C(37)	0.304 4(17)	0.055 7(6)	-0.136 9(3)	C(37)	0.125 3(11)	0.556 1(7)	0.966 5(3)
C(38)	-0.441 6(12)	0.512 4(6)	-0.227 2(3)	C(38)	0.861 9(21)	1.025 6(6)	0.893 0(4)

\* Atomic co-ordinates are given in units of lattice constants. The e.s.d.s are in parentheses.

Crystals of the dimensions of  $0.3 \times 0.2 \times 0.08 \text{ mm}^3$  and  $0.5 \times 0.4 \times 0.1 \text{ mm}^3$  were sealed in Lindemann-glass capillaries; 25 reflections with  $2\theta > 8$  and  $16^\circ$  were used for cell refinement, one standard reflection, variation 4 and 1.4%; 6 689 of 11 307 and 4 650 of 5 157 unique reflections had  $I > \sigma(I)$  and were used for structure analysis; Nicolet R3 computer-controlled diffractometer,  $2\theta/\theta$  scan,  $2\theta_{\text{max.}} = 56^\circ$  [ $\lambda(\text{Mo-K}\alpha) = 0.7107 \text{ \AA}$ ,  $T = 143 \text{ K}$ ] and  $110^\circ$  [ $\lambda(\text{Cu-K}\alpha) = 1.5418 \text{ \AA}$ ,  $T = 295 \text{ K}$ ],  $3^\circ \text{ min}^{-1}$ ; no corrections for absorption or extinction. Solution of the phase problem was quite difficult for compound (1), and this could only be achieved by the random-start multisolution program SHELXS<sup>18</sup>, whereas compound (2) involved routine analysis for SHELXTL.<sup>19</sup> One of the

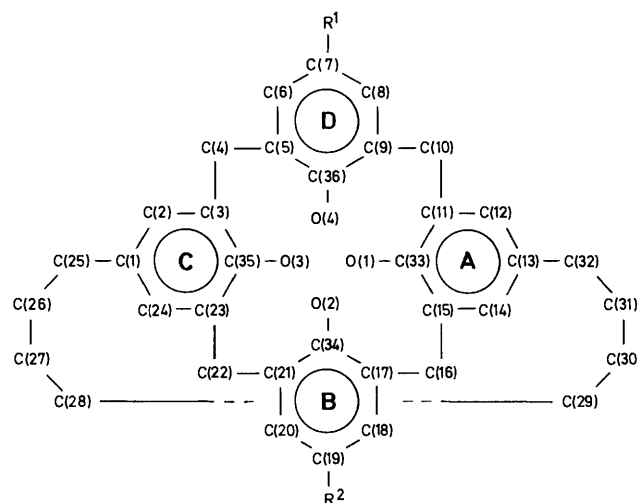
reasons for such difficulties is that the crystal lattice of (1) contains two molecules in an asymmetric unit. The difference electron density synthesis only for (2) showed the positions of hydrogens at three oxygens (Figures 1 and 2); all the other hydrogen atoms could not be found.

In the final refinement for all hydrogen atoms attached to carbon atoms a model was used with idealized geometry (C-H 0.96 Å) and temperature factors fixed at values 1.2 times that of the equivalent isotropic values for the carbon atoms, to which they were attached. The oxygen and carbon atoms were refined anisotropically, least-squares refinement of  $F$  with 5 900 [ $> 1.5\sigma(I)$ ] and 4 650 [ $> 1\sigma(I)$ ] data and 769 and 481 parameters,  $w = 1/\sigma^2(F)$ ,  $R_1 = 0.221$  and  $0.104$ ,  $R_2 = R_w = 0.065$  and  $0.042$ .\* The  $R_1$  value of (1) is especially high, because there is disorder in one of the two molecules in the asymmetric unit, and because there are relatively few large structure factors [ $2 862 > 4\sigma(I)$ ]. Since the weighting scheme is according to the counting statistics,  $R_w$  is much more significant. The 10 largest peaks in the final difference electron density synthesis were between 0.79 and 0.20, and 0.94 and  $0.27 \text{ e \AA}^{-3}$ ;  $\Delta_{\text{max.}}/\sigma = 0.1$ .

\* Lists of structure factors, anisotropic temperature factors, and hydrogen atom co-ordinates have been deposited at the Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen 2. They are available upon request, which should be accompanied by the full literature citation of this publication and the code number CSD-52380.

**Table 2.** Atomic co-ordinates of the cyclohexyl compound (2)

Atom	x	y	z
O(1)	0.523 0(2)	0.860 7(1)	0.190 3(1)
O(2)	0.428 5(2)	0.883 2(1)	0.123 5(1)
O(3)	0.389 3(2)	1.014 3(1)	0.132 6(1)
O(4)	0.514 9(2)	0.990 6(1)	0.196 1(1)
C(1)	0.668 3(4)	1.085 5(1)	0.066 0(1)
C(2)	0.649 3(4)	1.108 8(2)	0.100 6(1)
C(3)	0.556 8(3)	1.087 0(2)	0.123 5(1)
C(4)	0.548 4(3)	1.112 9(2)	0.162 4(1)
C(5)	0.646 8(3)	1.080 5(1)	0.186 7(1)
C(6)	0.759 7(3)	1.110 9(2)	0.192 3(1)
C(7)	0.853 1(3)	1.082 2(1)	0.212 7(1)
C(8)	0.828 4(3)	1.021 9(1)	0.227 8(1)
C(9)	0.718 0(3)	0.989 8(2)	0.222 8(1)
C(10)	0.702 0(4)	0.923 1(1)	0.237 2(1)
C(11)	0.734 9(3)	0.873 7(2)	0.207 5(1)
C(12)	0.856 2(4)	0.860 1(1)	0.201 3(1)
C(13)	0.894 7(3)	0.820 8(2)	0.173 1(1)
C(14)	0.808 0(4)	0.793 3(1)	0.150 8(1)
C(15)	0.683 6(4)	0.804 5(2)	0.156 3(1)
C(16)	0.588 5(4)	0.773 1(2)	0.131 0(1)
C(17)	0.571 6(3)	0.809 8(1)	0.095 1(1)
C(18)	0.634 8(4)	0.791 3(2)	0.064 1(1)
C(19)	0.623 1(4)	0.823 4(2)	0.031 0(1)
C(20)	0.545 1(3)	0.876 3(2)	0.030 3(1)
C(21)	0.481 0(3)	0.898 1(2)	0.061 2(1)
C(22)	0.410 0(3)	0.960 9(1)	0.060 6(1)
C(23)	0.491 2(4)	1.015 7(2)	0.075 0(1)
C(24)	0.586 7(4)	1.039 4(2)	0.053 8(1)
C(25)	0.779 1(4)	1.105 0(2)	0.043 1(1)
C(26)	0.869 9(5)	1.050 2(2)	0.038 2(1)
C(27)	0.915 2(4)	1.021 2(2)	0.072 9(1)
C(28)	1.017 8(6)	0.975 0(3)	0.065 6(2)
C(29)	1.077 5(6)	0.948 5(3)	0.099 5(2)
C(30)	1.020 3(5)	0.899 1(3)	0.119 3(1)
C(31)	1.089 9(4)	0.867 7(3)	0.152 3(1)
C(32)	1.027 1(4)	0.809 0(2)	0.165 4(2)
C(33)	0.647 0(4)	0.845 5(2)	0.184 6(1)
C(34)	0.495 3(3)	0.862 4(2)	0.092 9(1)
C(35)	0.479 6(3)	1.039 5(2)	0.110 2(1)
C(36)	0.629 0(3)	1.020 7(2)	0.201 9(1)
C(37)	0.979 5(3)	1.113 1(2)	0.217 5(1)
C(38)	0.975 6(3)	1.183 5(1)	0.228 0(1)
C(39)	1.104 4(3)	1.212 4(2)	0.232 3(1)
C(40)	1.182 0(4)	1.203 1(2)	0.198 5(1)
C(41)	1.186 4(4)	1.133 8(2)	0.188 1(1)
C(42)	1.056 9(3)	1.104 0(2)	0.182 9(1)
C(43)	0.692 7(4)	0.800 2(2)	-0.002 8(1)
C(44)	0.609 7(5)	0.770 4(3)	-0.029 4(1)
C(45)	0.684 0(6)	0.744 3(3)	-0.062 0(1)
C(46)	0.754 8(6)	0.793 9(3)	-0.079 5(1)
C(47)	0.841 8(6)	0.821 7(3)	-0.053 1(2)
C(48)	0.769 1(5)	0.848 5(2)	-0.020 0(1)

**Scheme.** Illustrates the numbering convention employed

36.492(3) Å,  $V = 8197.2 \text{ \AA}^3$ ,  $Z = 8$ ,  $D_x = 1.133$ ,  $D_m = 1.13 \text{ g cm}^{-3}$  (295 K, in aqueous solution of  $\text{K}_2\text{HgI}_4$ ).

Fractional atomic co-ordinates for both compounds are listed in Tables 1 and 2. Carbon atoms are numbered closely following the systematic names\* as indicated in the Scheme. Thus, corresponding atoms in both compounds have the same number, and bond distances (Table 3), bond angles (Table 4), and torsion angles (Table 5) can be compared immediately. The chain of eight methylene groups connects the *para* positions of phenolic residues A and C behind a plane with the oxygens O(1)—O(4) (phenolic units A—D) arranged in a clockwise order.

Compound (1) crystallizes as two molecules (1a, b) in an asymmetric unit, each having different atomic co-ordinates and slightly different conformations [see Figure 1(a)]. However, all conformations [(1a and b) as well as (2)] generally correspond to the cone conformation of calix[4]arenes, the oxygen atoms nearly forming a plane at one side of the molecule, opposite to the octamethylene chain. Thus the whole molecule has a basket-like shape which can be best seen from Figure 1(b).

The O—O distances (in Å) are 2.630, 2.692, 2.723, and 2.665 for (1a), 2.624, 2.681, 2.679, and 2.627 for (1b), and 2.683, 2.779, 2.732, and 2.711 for (2) [always in the order O(1)—O(2)—O(3)—O(4)—O(1)]. This is in accordance with intramolecular hydrogen bonds between hydroxy groups and still quite comparable with the distance of 2.670 found for instance for *t*-butylcalix[4]arene,<sup>5</sup> and distances between 2.587 and 2.753 Å found for similar linear oligomers.<sup>21</sup>

The angles between straight lines connecting adjacent oxygen atoms are always smaller than  $90^\circ$  for O(1) and O(3) ( $80.6$ — $86.2^\circ$ ) and larger than  $90^\circ$  for O(2) and O(4) ( $94.7$ — $98.4^\circ$ ). This already shows that the ideal 'four fold' cone conformation is distorted.

This distortion becomes yet clearer by the dihedral angles between the best plane through the four methylene carbons C(4), C(10), C(16), and C(22), and the phenyl rings A—D which are as follows:

- (1a): 117.4 134.7 106.2 129.8  
 (1b): 121.0 132.2 107.2 133.0  
 (2): 114.2 131.0 108.0 128.4

The calculation and drawings were performed with a Nova 3/12 computer and SHELXTL.<sup>19</sup> Scattering factors were taken from International Tables for X-Ray Crystallography.<sup>20</sup>

## Results and Discussion

**Crystal data compound (1).**  $\text{C}_{38}\text{H}_{42}\text{O}_4$ ,  $M = 562.75$ . Monoclinic, space group  $P2_1/c$ ,  $a = 9.269(6)$ ,  $b = 18.069(8)$ ,  $c = 38.42(2)$  Å,  $\beta = 92.66(1)^\circ$ ,  $V = 6427.7 \text{ \AA}^3$ ,  $Z = 8$ ,  $D_x = 1.163$ ,  $D_m = 1.12 \text{ g cm}^{-3}$  (295 K, in aqueous solution of  $\text{K}_2\text{HgI}_4$ ).

**Crystal data compound (2).**  $\text{C}_{48}\text{H}_{58}\text{O}_4$ ,  $M = 699.00$ . Orthorhombic, space group  $Pbca$ ,  $a = 10.800(4)$ ,  $b = 20.799(2)$ ,  $c =$

\* The systematic name of (1) is 7,19-dimethylhexacyclo[11.11.8.1<sup>3,23</sup>.-1<sup>5,9</sup>.1<sup>11,15</sup>.1<sup>17,21</sup>]hexatriaconta-1(24),2,5(36),6,8,11(33),12,14,17(34),-18,20,23(35)-dodecaene-33,34,35,36-tetraol

**Table 3.** Bond distances (Å) of the non-hydrogen atoms in compounds (1) and (2)

	(1a)	(1b)	(2)
O(1)–C(33)	1.391(12)	1.393(12)	1.391(5)
O(2)–C(34)	1.379(13)	1.386(13)	1.400(4)
O(3)–C(35)	1.413(13)	1.362(13)	1.375(4)
O(4)–C(36)	1.375(12)	1.371(12)	1.399(4)
C(3)–C(4)	1.499(14)	1.517(14)	1.521(4)
C(4)–C(5)	1.510(12)	1.556(15)	1.538(4)
C(9)–C(10)	1.520(14)	1.495(13)	1.494(6)
C(10)–C(11)	1.577(15)	1.524(14)	1.534(4)
C(15)–C(16)	1.544(13)	1.559(15)	1.529(5)
C(16)–C(17)	1.507(14)	1.500(14)	1.524(4)
C(21)–C(22)	1.548(14)	1.490(15)	1.515(4)
C(22)–C(23)	1.531(12)	1.545(15)	1.531(5)
C(35)–C(23)	1.332(14)	1.407(15)	1.383(5)
C(23)–C(24)	1.408(15)	1.395(15)	1.382(5)
C(24)–C(1)	1.398(15)	1.382(16)	1.377(5)
C(1)–C(2)	1.401(15)	1.405(16)	1.368(4)
C(2)–C(3)	1.421(14)	1.371(15)	1.380(5)
C(3)–C(35)	1.353(14)	1.386(16)	1.382(5)
C(36)–C(5)	1.406(14)	1.391(15)	1.375(4)
C(5)–C(6)	1.445(14)	1.361(17)	1.389(5)
C(6)–C(7)	1.379(14)	1.392(16)	1.389(4)
C(7)–C(8)	1.371(16)	1.412(13)	1.395(4)
C(8)–C(9)	1.435(16)	1.351(14)	1.378(4)
C(9)–C(36)	1.402(14)	1.434(15)	1.385(4)
C(33)–C(11)	1.397(13)	1.386(15)	1.393(5)
C(11)–C(12)	1.410(15)	1.379(15)	1.359(5)
C(12)–C(13)	1.374(15)	1.410(13)	1.378(5)
C(13)–C(14)	1.371(13)	1.369(15)	1.367(5)
C(14)–C(15)	1.422(14)	1.376(14)	1.379(5)
C(15)–C(33)	1.404(15)	1.434(14)	1.397(5)
C(34)–C(17)	1.396(14)	1.433(15)	1.372(5)
C(17)–C(18)	1.373(15)	1.413(15)	1.376(4)
C(18)–C(19)	1.400(14)	1.395(16)	1.387(4)
C(19)–C(20)	1.430(15)	1.393(17)	1.387(5)
C(20)–C(21)	1.358(17)	1.409(16)	1.396(4)
C(21)–C(34)	1.397(14)	1.437(15)	1.383(4)
C(1)–C(25)	1.507(15)	1.522(16)	1.516(6)
C(25)–C(26)	1.475(17)	1.551(15)	1.514(6)
C(26)–C(27)	1.360(18)	1.565(14)	1.485(6)
C(27)–C(28)	1.453(16)	1.535(14)	1.491(8)
C(28)–C(29)	1.455(18)	1.511(13)	1.498(9)
C(29)–C(30)	1.413(18)	1.529(15)	1.399(9)
C(30)–C(31)	1.382(22)	1.566(14)	1.564(7)
C(31)–C(32)	1.343(23)	1.543(17)	1.477(7)
C(32)–C(13)	1.533(14)	1.499(14)	1.478(6)
C(7)–C(37)	1.535(16)	1.520(15)	1.519(4)
C(19)–C(38)	1.514(16)	1.527(16)	1.515(4)
C(37)–C(38)			1.523(5)
C(38)–C(39)			1.504(6)
C(39)–C(40)			1.489(6)
C(40)–C(41)			1.524(5)
C(41)–C(42)			1.524(5)
C(42)–C(37)			1.522(5)
C(19)–C(43)			1.458(6)
C(43)–C(44)			1.535(7)
C(44)–C(45)			1.435(8)
C(45)–C(46)			1.466(8)
C(46)–C(47)			1.543(8)
C(47)–C(48)			1.443(6)
C(48)–C(43)			

They should be compared with the value of 123° which was found for *t*-butylcalix[4]arene.<sup>5</sup> The strongest deviation of this four-fold symmetry was observed for the unsubstituted calix[4]-arene-acetone (3:1) clathrate<sup>7</sup> with dihedral angles of 115.3 to 137.2°. Obviously the aliphatic chain (the handle of the basket) forces the phenolic units A and C together, the orientation of C

**Table 4.** Selected bond angles (°) between the non-hydrogen atoms in compounds (1) and (2)

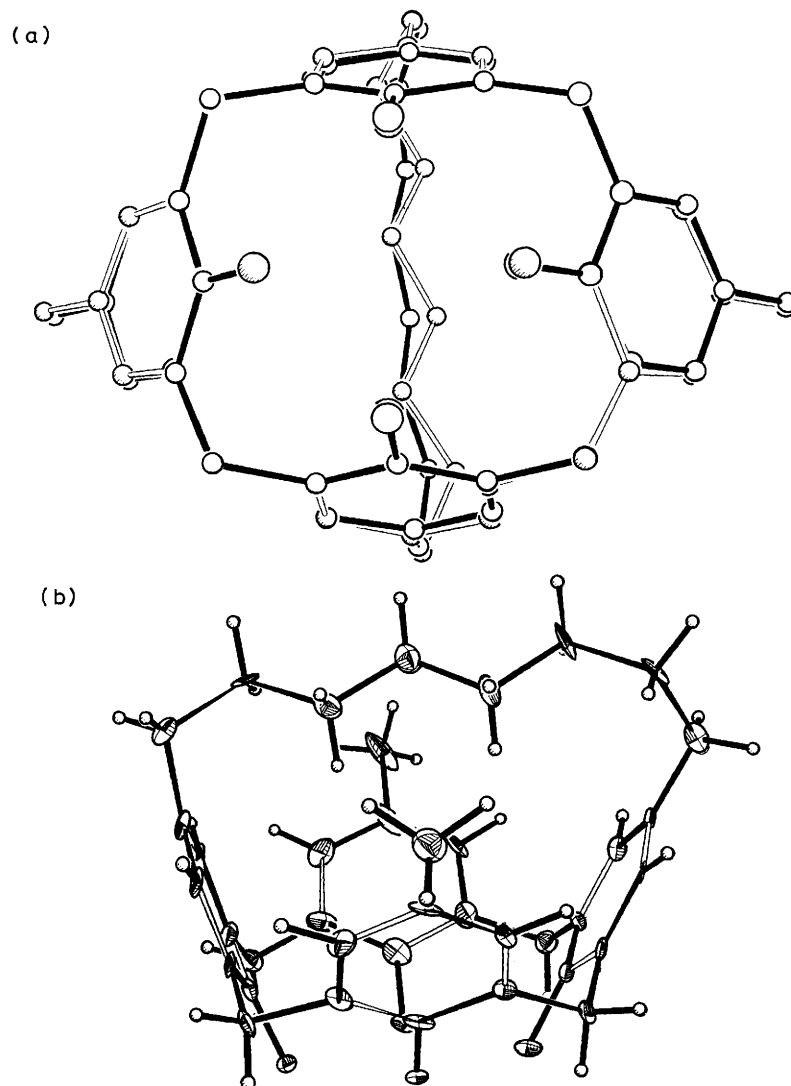
	(1a)	(1b)	(2)
O(1)–C(33)–C(11)	121.4(9)	122.7(9)	118.2(3)
O(1)–C(33)–C(15)	119.0(8)	116.3(9)	121.4(3)
O(2)–C(34)–C(17)	119.3(9)	116.8(9)	120.5(3)
O(2)–C(34)–C(21)	123.2(9)	121.0(9)	116.4(3)
O(3)–C(35)–C(23)	119.5(9)	121.7(10)	118.7(3)
O(3)–C(35)–C(3)	118.0(9)	120.9(9)	119.4(3)
O(4)–C(36)–C(5)	120.7(9)	121.2(10)	117.9(3)
O(4)–C(36)–C(9)	118.1(9)	119.4(9)	119.1(3)
C(2)–C(3)–C(4)	115.1(9)	116.2(10)	119.6(3)
C(35)–C(3)–C(4)	125.6(9)	123.3(10)	123.0(3)
C(3)–C(4)–C(5)	113.1(8)	112.3(8)	109.9(3)
C(4)–C(5)–C(36)	120.4(8)	119.7(11)	122.1(3)
C(4)–C(5)–C(6)	120.3(8)	120.2(10)	119.5(3)
C(8)–C(9)–C(10)	119.3(9)	122.3(9)	120.2(3)
C(36)–C(9)–C(10)	123.6(9)	120.8(9)	122.9(3)
C(9)–C(10)–C(11)	110.8(8)	112.4(7)	110.3(2)
C(10)–C(11)–C(33)	121.0(9)	119.0(9)	123.1(3)
C(10)–C(11)–C(12)	119.7(8)	122.5(10)	118.7(3)
C(14)–C(15)–C(16)	119.5(9)	118.7(9)	119.6(3)
C(33)–C(15)–C(16)	121.4(9)	123.5(9)	121.2(3)
C(15)–C(16)–C(17)	114.0(8)	114.9(8)	112.8(3)
C(16)–C(17)–C(34)	121.3(10)	124.2(9)	121.5(3)
C(16)–C(17)–C(18)	119.0(9)	119.5(9)	120.4(3)
C(20)–C(21)–C(22)	120.2(9)	125.3(10)	121.4(3)
C(34)–C(21)–C(22)	115.7(10)	117.0(9)	122.1(3)
C(21)–C(22)–C(23)	113.4(7)	112.1(9)	110.3(3)
C(22)–C(23)–C(35)	126.5(9)	118.5(9)	122.2(3)
C(22)–C(23)–C(24)	113.7(9)	120.8(9)	120.0(3)
C(2)–C(1)–C(25)	118.8(9)	124.6(11)	122.2(3)
C(24)–C(1)–C(25)	123.3(10)	119.9(10)	120.9(3)
C(1)–C(25)–C(26)	114.0(10)	110.0(8)	111.9(3)
C(25)–C(26)–C(27)	127.4(13)	115.3(9)	114.8(4)
C(26)–C(27)–C(28)	129.0(13)	113.5(8)	110.8(3)
C(27)–C(28)–C(29)	124.3(12)	112.6(9)	114.2(5)
C(28)–C(29)–C(30)	122.3(13)	111.8(9)	120.3(6)
C(29)–C(30)–C(31)	123.8(14)	112.7(9)	119.5(5)
C(30)–C(31)–C(32)	141.3(15)	115.3(9)	112.0(4)
C(31)–C(32)–C(13)	117.3(11)	113.6(8)	111.6(4)
C(32)–C(13)–C(12)	121.7(9)	119.5(9)	122.3(4)
C(32)–C(13)–C(14)	119.4(9)	122.8(9)	118.6(3)

always being significantly steeper (relative to the bottom of the basket) than that of A.

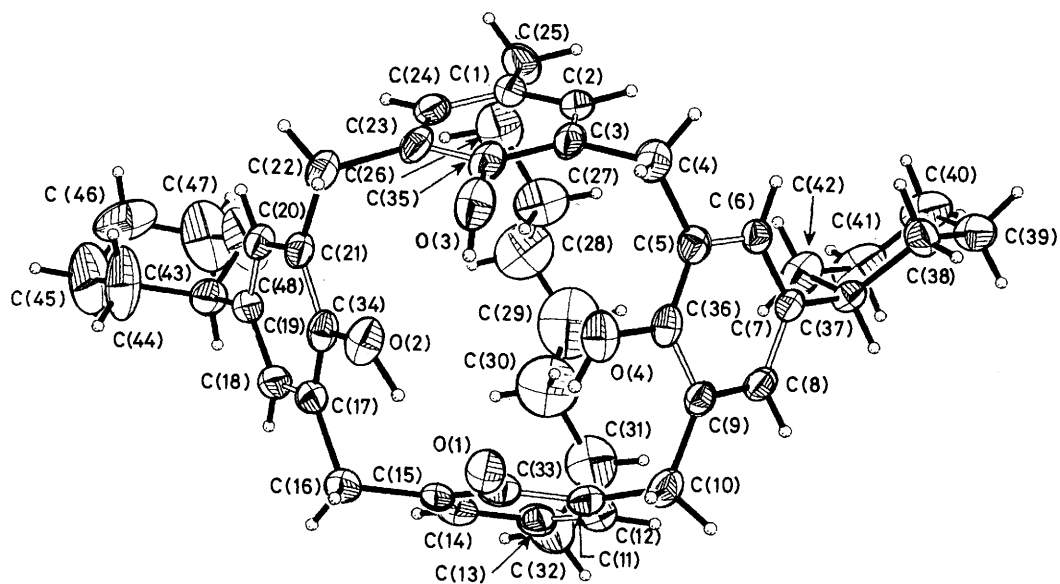
This difference in inclination can also be seen from the position of the central bond of the basket-handle, which fails to lie in a central position relative to the rest of the molecule. It is always closer to one of the aromatic rings connected by the aliphatic chain and must result from steric hindrance. The distances of atoms C(28) and C(29) from the central plane C(7), C(36), O(4), O(2), C(34), C(19) are 0.067 and 1.389 Å for (1a), 0.139 and 1.380 Å for (1b), and 0.399 and 0.891 Å for (2). A similar situation is found for compounds with a hexamethylene chain.<sup>22</sup> Compounds with odd-numbered chains are under investigation.

The difference in inclination of the phenolic residues is also reflected by the torsion angles for the arylmethylene bonds in the calixarene entity. These values are higher (absolute values from 88.3–102.1°) for ring A and C than for the rings B and D (absolute values between 73.6–84.1°). Again there is no remarkable difference between molecules (1a) and (1b), as well as between compounds (1) and (2).

Such a difference also appears in the conformation of the aliphatic chain. For (1a) some short bond distances and some unusual bond angles are the result of disorder which can also be seen from the temperature coefficients. For (1b) all distances



**Figure 1.** (a) Molecules (**1a**) and (**1b**) (seen from the bottom of the basket). (b) Molecular structure of molecule (**1b**), showing 30% probability thermal ellipsoids for the non-hydrogen atoms



**Figure 2.** Molecular structure of compound (**2**) (seen from the bottom of the basket), showing 30% probability thermal ellipsoids for the non hydrogen atoms. [The hydrogen atom of O(1) could not be found experimentally]

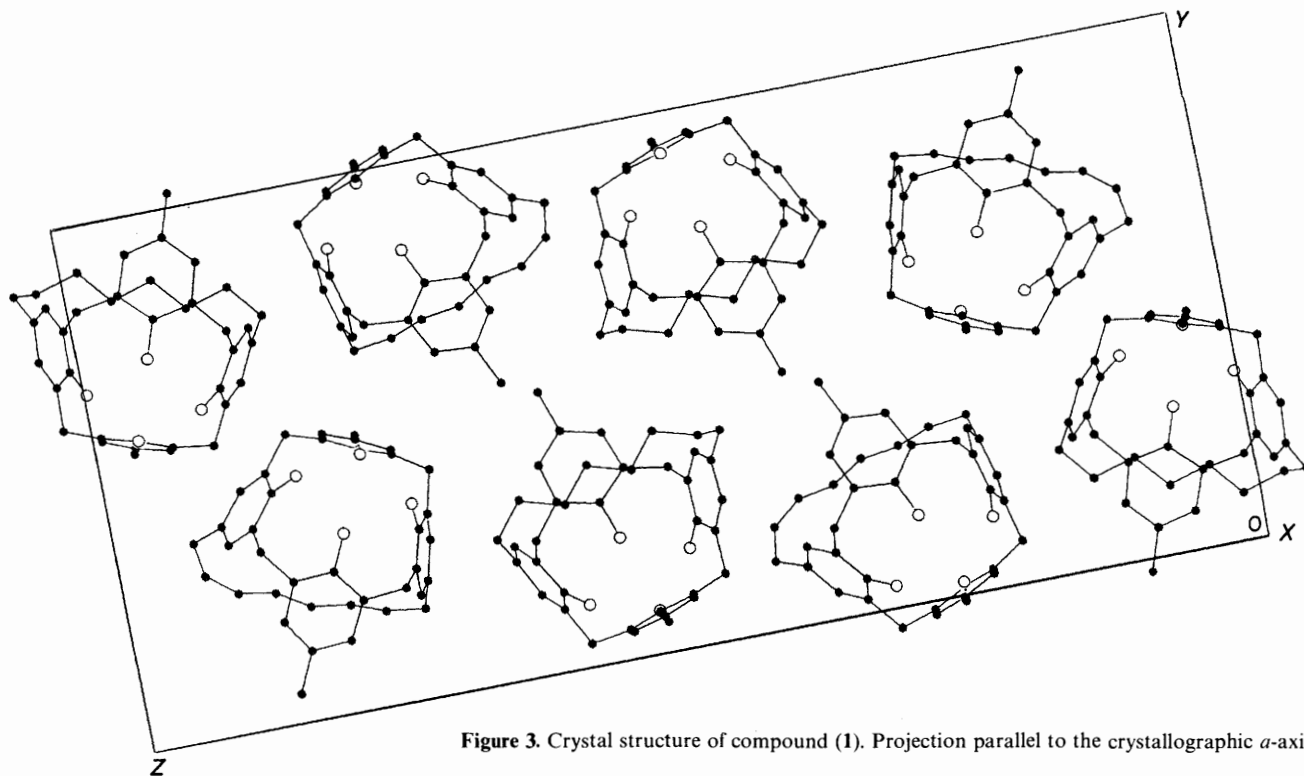


Figure 3. Crystal structure of compound (1). Projection parallel to the crystallographic *a*-axis

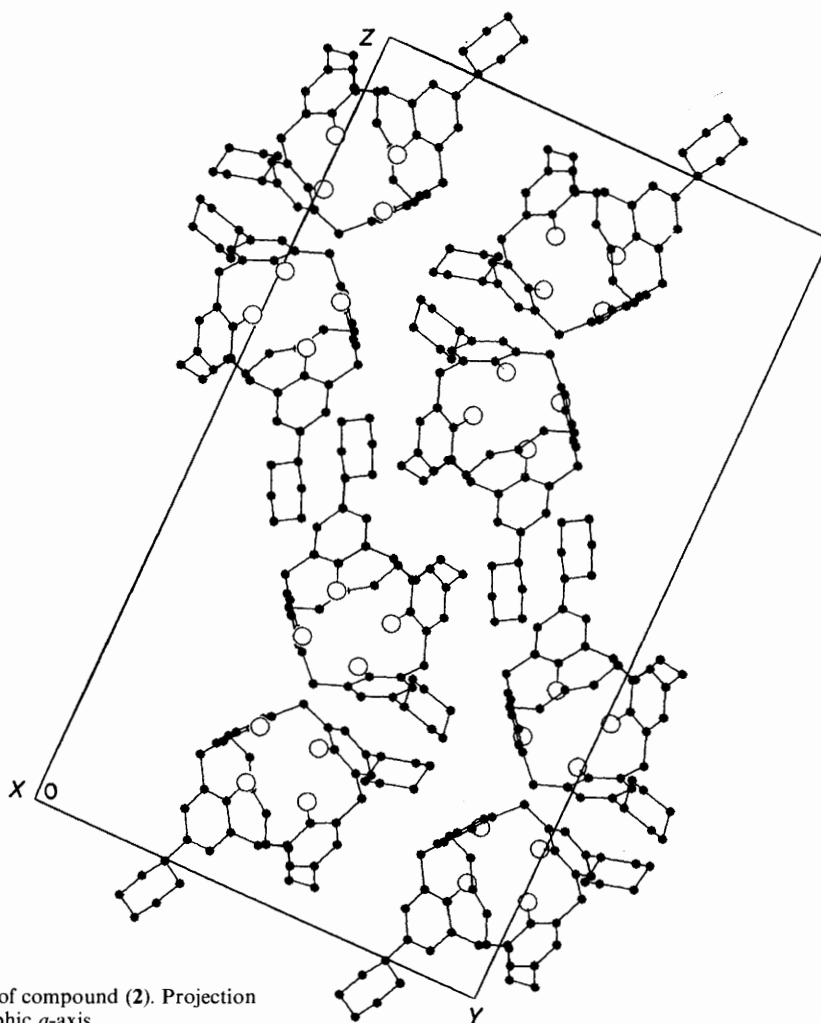


Figure 4. Crystal structure of compound (2). Projection parallel to the crystallographic *a*-axis

**Table 5.** Selected torsion angles ( $^{\circ}$ ) for compounds (1) and (2)

	(1a)	(1b)	(2)
O(1)–C(33)–C(11)–C(10)	–3.0(14)	–5.5(13)	–3.2(5)
O(1)–C(33)–C(15)–C(16)	2.8(14)	4.7(13)	–1.6(5)
O(2)–C(34)–C(17)–C(16)	–2.9(14)	–6.6(16)	–1.4(5)
O(2)–C(34)–C(21)–C(22)	6.7(14)	8.7(15)	7.4(5)
O(3)–C(35)–C(23)–C(22)	–1.0(14)	–0.5(15)	–2.2(5)
O(3)–C(35)–C(3)–C(4)	0.2(14)	–2.6(15)	1.0(5)
O(4)–C(36)–C(5)–C(4)	–10.4(15)	–11.5(14)	–3.0(4)
O(4)–C(36)–C(9)–C(10)	4.5(15)	5.6(13)	5.2(4)
C(35)–C(3)–C(4)–C(5)	98.8(11)	97.5(12)	98.7(4)
C(3)–C(4)–C(5)–C(36)	–74.1(12)	–73.6(12)	–81.7(4)
C(36)–C(9)–C(10)–C(11)	80.6(12)	84.1(11)	82.2(4)
C(9)–C(10)–C(11)–C(33)	–92.3(11)	–92.2(11)	–95.1(4)
C(33)–C(15)–C(16)–C(17)	94.5(12)	88.3(12)	96.9(4)
C(15)–C(16)–C(17)–C(34)	–80.1(12)	–78.0(13)	–82.4(4)
C(34)–C(21)–C(22)–C(23)	74.0(11)	81.0(12)	80.2(4)
C(21)–C(22)–C(23)–C(35)	–100.1(12)	–102.1(11)	–101.4(4)
C(23)–C(24)–C(1)–C(25)	171.3(9)	170.0(9)	173.9(3)
C(3)–C(2)–C(1)–C(25)	–169.2(8)	–167.9(10)	–173.0(3)
C(24)–C(1)–C(25)–C(26)	–77.9(13)	–66.9(12)	–64.8(5)
C(2)–C(1)–C(25)–C(26)	90.9(12)	104.0(12)	110.4(4)
C(1)–C(25)–C(26)–C(27)	–28.0(21)	–53.0(12)	–55.6(5)
C(25)–C(26)–C(27)–C(28)	179.6(14)	177.8(9)	–171.3(4)
C(26)–C(27)–C(28)–C(29)	–168.9(16)	–173.2(9)	174.1(5)
C(27)–C(28)–C(29)–C(30)	176.9(14)	–178.5(10)	78.7(8)
C(28)–C(29)–C(30)–C(31)	–171.5(16)	177.4(10)	174.2(5)
C(29)–C(30)–C(31)–C(32)	40.0(35)	92.3(12)	–169.1(5)
C(30)–C(31)–C(32)–C(13)	–36.6(30)	–64.9(11)	–52.5(6)
C(31)–C(32)–C(13)–C(12)	–71.0(15)	–65.6(11)	–67.0(5)
C(31)–C(32)–C(13)–C(14)	109.4(14)	118.9(10)	111.0(4)
C(32)–C(13)–C(12)–C(11)	–176.5(9)	–178.8(8)	176.7(3)
C(32)–C(13)–C(14)–C(15)	177.0(9)	177.8(9)	–178.1(3)

and angles are compatible with carbon–carbon single bonds. Here the aliphatic chain contains four subsequent *anti* conformations (closer to ring C than to A), while in (2) a *gauche* conformation in the middle is followed by two *anti* conformations at both sides. Steric effects may explain the adoption of this particular conformation, in which closer contact between C(28) and C(29) and the cyclohexyl residues is avoided.

The planes of the cyclohexyl groups form angles of  $76.4^{\circ}$  and  $82.5^{\circ}$  with the adjacent phenolic rings B and D. The orientation of the best plane through the methylene carbons connecting the carbon atoms C(1) and C(13) (the handle of the basket) is not perpendicular to the plane through the four oxygens (the bottom of the basket). It forms an angle of  $80.8^{\circ}$  for (1a),  $81.9^{\circ}$  for (1b), and  $85.4^{\circ}$  for (2). All these data show the absence of mirror planes through O(1)/O(3) or O(2)/O(4) in both compounds, which will, however, hold for the average conformation in solution.

Both compounds form a pure molecular lattice; the packing is shown in Figures 3 and 4. No intermolecular hydrogen bonds are found in either structure which suggests that the conformation in solution cannot be entirely different from the conformation in the crystalline phase.

In conclusion we can state that the cone conformation of the calixarenes is 'fixed', if two opposite phenolic residues (A and C)

are connected by an aliphatic chain of appropriate length, regardless of the substituents in the *para* position of the other phenolic residues (B and D). Therefore, a different reactivity of the hydroxy groups, which is observed for instance in photo-CIDNP experiments in comparison with unbridged calixarenes,<sup>2,3</sup> cannot be explained by a different conformation (e.g. the fixed 1,3-alternate conformation<sup>1</sup>). The reason must be in the degree of flexibility in the rigid structure of the bridged compounds.

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