Journal of Crystallographic and Spectroscopic Research, Vol. 21, No. 1, 1991

Structure of 5,17-dimethyl-11,23-dioctylcalix[4]arene

F. Gharnati,[1] M. Perrin,*[,1] S. Rantsordas,[1] H. Goldmann,[2] and V. Böhmer[2]

Received March 27, 1990

The title compound $C_{46}O_4H_{60}$ crystallizes in the triclinic space group, $P\bar{1}$, with $a = 11.584(2)$, $b = 16.261(2)$, $c = 11.172(1)$ Å, $\alpha = 103.15(8)$, $\beta = 95.68(1)$, $\gamma = 96.85(1)°$. The structure was solved by direct methods, and refined by weighted full-matrix least squares to $R = 0.097$. This is the second calix[4]arene with two different alkyl substituents at *para* positions of the phenolic rings. The macrocycle adopts the cone conformation. Interactions CH_3–π are established between two calixarenes related by a center of symmetry. Comparisons are made between the conformation of this molecule and that of symmetrically substituted calix[4]arenes.

Introduction

Although several crystal structures of *para*-substituted calix[4]arenes have been described following the first publication of Andreetti *et al.* (1979) of the structure of *p-tert*-butyl calix[4]arene, most of them are of molecules with identical phenolic units (Andreetti, 1983; Ungaro, 1984, 1985). A previous paper from our groups reported the crystal structure of a calix[4]arene with three different substituents in the *para*-position of the OH group (Rantsordas *et al.*, 1990). We now describe a compound with two different *para* substituents, methyl and octyl, in opposite phenolic units. It is the first example of an X-ray crystal structure of a calixarene with such long alkyl chains in *para*-position. The title compound was prepared as an open chain model for bridged calix[4]arenes (Goldmann *et al.*, 1988) and we were interested to know if this alternating substitution pattern has any influence on the molecular conformation and if the alkyl chains would be included in the cavity by a kind of "self complexation" as was observed for *tert*-octylcalix[4]arene (Andreetti, 1983).

[1] Laboratoire de Minéralogie-Cristallographie (URA 805) 43, Boulevard du 11 Novembre 1918-69622 Villeurbanne Cedex, France.
[2] Institut für Organische Chemie, Johannes Gutenberg Universität, D-6500 Mainz, Germany.

Experimental

The calixarene was prepared as described for similar examples (Böhmer *et al.*, 1987; Goldmann *et al.*, 1988) by condensation of a linear trimer, easily obtained by condensation of a 2.6-bishydroxymethyl-4-octylphenol with excess of *para*-cresol (Kämmerer *et al.*, 1975), with bisbromomethylated 4-octylphenol in dioxane in the presence of $TiCl_4$.

2.6-Bisbromomethyl-4-octylphenol

A rapid stream of gaseous HBr was passed through a suspension of 20.6 g (0.1 mol) 4-octylphenol and 6.6 g (0.22 mol) paraformaldehyde in 40 ml of glacial acetic acid for 5–10 min. During this time the temperature increased and a homogeneous (brownish) solution formed from which a crystalline product precipitated. After 20 min the reaction mixture was cooled down to complete the crystallization, 50 ml of petroleum ether (bp. 40–80°C) was added, and the product was collected by filtration. Recrystallization from cyclohexane gave 28 g (71%) of the pure product, m.p. 77–78°C [lit. m.p. 87–90°C (Bright and Cammarata, 1952)]. Calcd. for $C_{16}H_{24}Br_2O$: C 49.00, H 6.17, Br 40.75; Found: C 49.05, H 5.70, Br 40.91.

^{1}H NMR ($CDCl_3$, 90 MHz, ppm): δ 7.06 (s, 2H, ArH), 5.5–5.1 (br s, 1H, ArOH), 4.54 (s, 4H,

0277-8068/91/0200-0069$06.50/0

Ar—CH_2—Br), 2.50 (t, 2H, Ar—CH_2—), 1.77–1.26 (m, 12H, —$(CH_2)6$—), 0.87 (br t, 3H, —CH_3).

MS: m/z 394/392/390 (M^+, 12/24/12%), 313/311 (73/73%, 295/293/291 (3/6/3%), 231 (33%), 215/213 (92/100%), 133 (93%)

IR (KBr, cm^{-1}): 3510 (ν_{OH}), 2900, 2850 (ν_{CH}), 1600 ($\nu_{C=C}$), 570 (ν_{CBr}).

5,17-Dimethyl-11,23-dioctylcalix[4]arene

A solution of 3.35 g (7.5 mmol) 2.6-bis(2-hydroxy-5-methylbenzyl)-4-octylphenol (Kämmerer *et al.*, 1975), 2.94 g (7.5 mmol) 2.6-bisbromomethyl-4-octylphenol, and 6.9 g (36 mmol) $TiCl_4$ in 500 ml of dry dioxane was heated under argon for 96 h to 100°C. The dark red solution was evaporated, the residue dissolved in CH_2Cl_2, and after addition of 50 g silica gel the solvent was removed. The silica gel was then extracted in a Soxhlet apparatus for 24 h with CH_2Cl_2. This procedure, which removes most of the oligomeric and polymeric byproducts as well as titanium complexes, was repeated. The crude product was finally purified by flash chromatography (silica gel, $CHCl_3$) to give 720 mg (14.2%) of the calixarene, which formed large, colorless crystals from acetone, mp. 162°C.

Calcd. for $C_{46}H_{60}O_4$: C 81.61, H 8.93, O 9.45; Found: C 81.71, H 8.97, O 9.59. ^1H NMR ($CDCl_3$, 200 MHz) δ 10.15 (s, 4H, ArOH), 6.84 (s, 4H, ArH), 6.81 (s, 4H, ArH), 4.20 (br d, 4H, $ArCH_AH_BAr$), 3.42 (br d, 4H, $ArCH_ACH_BAr$), 2.40 (t, 4H, $ArCH_2$—), 2.12 (s, 6H, $ArCH_3$), 1.51 (m, 4H, —CH_2—), 1.26 (m, 20H, —$(CH_2)_5$—), 0.87 (t, 6H, —CH_3).

MS: m/z 676 (M^+, 100%), 658 (5%), 338 (6%), 135 (11%), 133 (14%), 121 (14%).

IR (KBr, cm^{-1}): 3150 (ν_{OH}), 3010, 2955, 2930, 2850, (ν_{CH}), 1600 ($\nu_{C=C}$), 1475 (δ_{CH}).

Crystals suitable for X-ray determination were grown from acetone. Preliminary unit cell parameters and space group determination were obtained by photographic methods. A needle was used for data collection with an automatic Nonius CAD 4 four circle diffractometer; graphite monochromator and Cu Kα radiation were used (λ = 1.54178 Å). Lattice parameters were refined from 25 reflections $11 < \theta < 46°$.

Crystal data: $C_{46}O_4H_{60}$, Mr = 676.98 D_c = 1.11 g cm^{-3}, a = 11.584(2), b = 16.261(2), c = 11.172(1) Å, α = 103.15(8), β = 95.68(1), γ = 96.85(1)°, V = 2017.3(9) $Å^3$, Z = 2, space group $P\bar{1}$, μ = 4.65 cm^{-1}, $F(000)$ = 736, T = 293 K. $\omega - 2\theta$ scan mode was used to collect intensities of reflections with $\theta < 73°$ (h: −14 to 14, k: −20 to 20, l = −13 to 13). Three standard reflections were measured every hour to control intensity variation; Lorentz and polarization corrections were applied and absorption was corrected with program PSI and EAC of SDP (Frenz, 1985). Reflections (17132) were measured, 7222 of which were considered as observed [$I > 3\sigma(I)$] after merg (Rint. = 0.03). The structure was solved by direct methods using MULTAN (Main *et al.*, 1982) and refined on F by SHELX 76 (Sheldrick, 1976). An E map showed clearly all non-H atoms of the molecule; H positions were determined by difference Fourier syntheses or by geometrical calculations. Non-H-atoms were refined first isotropically, then anisotropically. However, some constraints were applied to the octyl chains. H-Atoms were refined isotropically with constant U, some H-atoms of octyl group being fixed at the theoretical distances of 1.08 Å. At the end of the refinement the R value, calculated with 5541 F_{hkl}, is R_w = 0.097 with goodness of fit of 1.16. Residual electron density in final difference Fourier synthesis have value 0.20 e. $Å^{-3}$. Atomic scattering factors are from SHELX.

Results and discussion

Atomic parameters with esd's in parentheses are given in Table 1 with the numbering scheme given in Fig. 1. Usual calculations for description of the conformation and the packing were computed with PARST (Nardelli, 1983). Selected bond lengths and angles as well as torsion angles are listed in Tables 2 and 3. The aromatic C—C bonds are normal and vary from 1.423(9) to 1.370(8) Å; C—O bonds have values 1.406(5), 1.396(6), 1.383(7), and 1.398(5) Å. In the benzene rings internal angles at the substituted *para* positions have successive values 119.5(5), 117.8(5), 117.9(7), and 118.8(6)° from rings A to D. These angles are smaller than 120° as stated by Domenicano *et al.* (1975).

As with all parent calix[4]arenes the molecule is found in the cone conformation, which is determined by a cyclic array of intramolecular hydrogen bonds between adjacent hydroxyl groups. Thus all O—O distances are nearly equal.

O(25) · · · O(26): 2.664(5) Å

O(26) · · · O(27): 2.662(5) Å

O(27) · · · O(28): 2.671(5) Å

O(28) · · · O(25): 2.658(5) Å

Peaks due to H atoms of the hydroxyl group are found near the middle between the oxygen atoms probably due to the "flip-flop" type usually found for calix[4]arenes. These positions of the H atoms were introduced in the refinement at fixed positions.

Table 1. Final atomic coordinates with esd's in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
O(25)	0.3788(2)	0.5151(2)	0.4729(3)	C(22)	0.1196(4)	0.6226(3)	0.5205(4)
O(26)	0.4433(3)	0.5136(2)	0.7079(3)	C(23)	0.0445(3)	0.5812(3)	0.4132(4)
O(27)	0.4492(3)	0.3464(2)	0.6423(3)	C(24)	0.0797(4)	0.5162(3)	0.3294(4)
O(28)	0.3828(2)	0.3479(2)	0.4071(3)	C(25)	0.2651(3)	0.5360(3)	0.4545(4)
C(1)	0.1919(3)	0.4920(3)	0.3483(4)	C(26)	0.3582(4)	0.5351(3)	0.7850(4)
C(2)	0.2254(4)	0.4190(3)	0.2548(4)	C(27)	0.3624(4)	0.3027(4)	0.6903(5)
C(3)	0.1958(4)	0.3332(3)	0.2836(4)	C(28)	0.2720(4)	0.3005(3)	0.3616(5)
C(4)	0.0853(4)	0.2837(4)	0.2374(5)	C(51)	−0.0691(5)	0.1561(4)	0.2167(6)
C(5)	0.0522(4)	0.2074(4)	0.2669(5)	C(52)	−0.0839(5)	0.1127(4)	0.0846(6)
C(6)	0.1307(5)	0.1783(4)	0.3451(5)	C(53)	−0.2036(5)	0.0594(4)	0.0381(6)
C(7)	0.2412(4)	0.2242(3)	0.3923(5)	C(54)	−0.2207(6)	0.0117(6)	−0.0926(7)
C(8)	0.3216(5)	0.1929(4)	0.4837(6)	C(55)	−0.3373(7)	−0.0408(6)	−0.1416(8)
C(9)	0.3020(5)	0.2270(4)	0.6154(5)	C(56)	−0.3523(9)	−0.1131(8)	−0.077(1)
C(10)	0.2142(5)	0.1826(4)	0.6674(7)	C(57)	−0.463(1)	−0.1737(8)	−0.119(1)
C(11)	0.1897(5)	0.2123(5)	0.7868(7)	C(58)	−0.498(1)	−0.2266(9)	−0.034(1)
C(12)	0.2524(6)	0.2880(5)	0.8559(6)	C(111)	0.0957(6)	0.1595(5)	0.8362(7)
C(13)	0.3397(5)	0.3343(4)	0.8105(5)	C(171)	0.1123(5)	0.6124(5)	1.0360(6)
C(14)	0.4025(5)	0.4172(4)	0.8905(6)	C(172)	0.1564(8)	0.6924(6)	1.1279(8)
C(15)	0.3407(4)	0.4921(4)	0.8760(5)	C(173)	0.2673(9)	0.6975(6)	1.2032(9)
C(16)	0.2588(5)	0.5187(4)	0.9555(5)	C(174)	0.3248(9)	0.7848(6)	1.285(1)
C(17)	0.1956(4)	0.5843(4)	0.9436(5)	C(175)	0.263(1)	0.8181(7)	1.390(1)
C(18)	0.2135(4)	0.6226(4)	0.8484(5)	C(176)	0.322(1)	0.9064(7)	1.4694(9)
C(19)	0.2951(4)	0.6003(3)	0.7665(4)	C(177)	0.322(2)	0.9242(8)	1.5984(9)
C(20)	0.3105(4)	0.6449(3)	0.6628(4)	C(178)	0.381(1)	1.0093(6)	1.6803(9)
C(21)	0.2326(3)	0.6005(3)	0.5434(4)	C(231)	−0.0765(4)	0.6083(4)	0.3899(5)

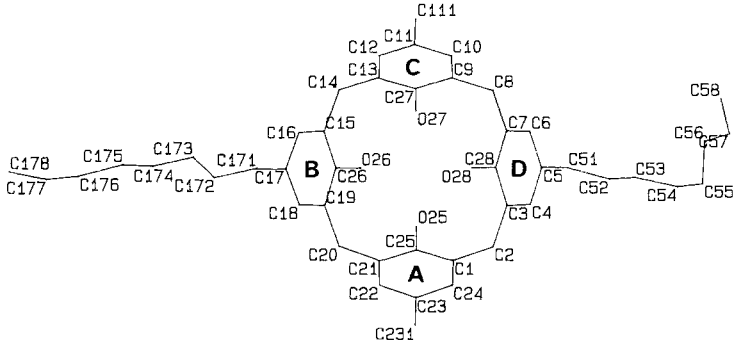

Fig. 1. Conformation and numbering scheme of the molecule studied.

Table 2. Bond distances (Å) with esd's in parentheses

O(25)−C(25)	1.405(5)	C(9)−C(27)	1.383(7)	C(21)−C(25)	1.387(6)
O(26)−C(26)	1.396(6)	C(10)−C(11)	1.38(1)	C(22)−C(23)	1.390(6)
O(27)−C(27)	1.383(7)	C(11)−C(12)	1.372(9)	C(23)−C(24)	1.373(6)
O(28)−C(28)	1.397(5)	C(11)−C(111)	1.53(1)	C(23)−C(231)	1.534(6)
C(1)−C(2)	1.509(6)	C(12)−C(13)	1.393(9)	C(51)−C(52)	1.467(9)
C(1)−C(24)	1.411(6)	C(13)−C(14)	1.495(8)	C(52)−C(53)	1.519(8)
C(1)−C(25)	1.381(5)	C(13)−C(27)	1.387(8)	C(53)−C(54)	1.47(1)
C(2)−C(3)	1.510(8)	C(14)−C(15)	1.514(9)	C(54)−C(55)	1.49(1)
C(3)−C(4)	1.408(6)	C(15)−C(16)	1.403(8)	C(55)−C(56)	1.52(2)
C(3)−C(28)	1.410(7)	C(15)−C(26)	1.376(8)	C(56)−C(57)	1.49(1)
C(4)−C(5)	1.375(8)	C(16)−C(17)	1.386(9)	C(57)−C(58)	1.47(2)
C(5)−C(6)	1.394(8)	C(17)−C(18)	1.369(8)	C(171)−C(172)	1.46(1)
C(5)−C(51)	1.528(7)	C(17)−C(171)	1.515(8)	C(172)−C(173)	1.45(1)
C(6)−C(7)	1.390(7)	C(18)−C(19)	1.401(7)	C(173)−C(174)	1.53(1)
C(7)−C(8)	1.524(9)	C(19)−C(20)	1.513(8)	C(174)−C(175)	1.47(2)
C(7)−C(28)	1.378(8)	C(19)−C(26)	1.399(7)	C(175)−C(176)	1.54(1)
C(8)−C(9)	1.500(8)	C(20)−C(21)	1.510(6)	C(176)−C(177)	1.40(1)
C(9)−C(10)	1.423(9)	C(21)−C(22)	1.411(6)	C(177)−C(178)	1.52(1)

Table 3. Bond and torsion angles (°) with esd's in parentheses

C(2)−C(1)−C(24)	119.3(3)	C(18)−C(19)−C(26)	116.7(5)
C(2)−C(1)−C(25)	123.2(4)	C(20)−C(19)−C(26)	122.9(4)
C(24)−C(1)−C(25)	117.5(4)	C(19)−C(20)−C(21)	113.3(4)
C(1)−C(2)−C(3)	113.6(4)	C(20)−C(21)−C(22)	119.7(4)
C(2)−C(3)−C(4)	120.1(5)	C(20)−C(21)−C(25)	123.0(4)
C(2)−C(3)−C(28)	123.0(4)	C(22)−C(21)−C(25)	117.2(3)
C(4)−C(3)−C(28)	116.7(5)	C(21)−C(22)−C(23)	121.1(4)
C(3)−C(4)−C(5)	122.1(5)	C(22)−C(23)−C(24)	119.5(4)
C(4)−C(5)−C(6)	118.8(4)	C(22)−C(23)−C(231)	119.7(4)
C(4)−C(5)−C(51)	120.7(5)	C(24)−C(23)−C(231)	120.8(4)
C(6)−C(5)−C(51)	120.5(5)	C(1)−C(24)−C(23)	121.4(4)
C(5)−C(6)−C(7)	121.5(6)	O(25)−C(25)−C(1)	118.4(4)
C(6)−C(7)−C(8)	119.9(5)	O(25)−C(25)−C(21)	118.3(3)
C(6)−C(7)−C(28)	118.5(5)	C(1)−C(25)−C(21)	123.3(4)
C(8)−C(7)−C(28)	121.4(4)	O(26)−C(26)−C(15)	119.0(5)
C(7)−C(8)−C(9)	112.1(5)	O(26)−C(26)−C(19)	118.1(5)
C(8)−C(9)−C(10)	119.9(5)	C(15)−C(26)−C(19)	122.9(4)
C(8)−C(9)−C(27)	123.3(5)	O(27)−C(27)−C(9)	117.5(5)
C(10)−C(9)−C(27)	116.7(5)	O(27)−C(27)−C(13)	120.1(4)
C(9)−C(10)−C(11)	122.4(5)	C(9)−C(27)−C(13)	122.2(5)
C(10)−C(11)−C(12)	117.9(6)	O(28)−C(28)−C(3)	117.7(5)
C(10)−C(11)−C(111)	119.0(6)	O(28)−C(28)−C(7)	119.7(4)
C(12)−C(11)−C(111)	123.2(6)	C(3)−C(28)−C(7)	122.3(4)
C(11)−C(12)−C(13)	122.4(6)	C(5)−C(51)−C(52)	114.6(5)
C(12)−C(13)−C(14)	119.3(5)	C(51)−C(52)−C(53)	113.6(5)
C(12)−C(13)−C(27)	118.3(5)	C(52)−C(53)−C(54)	115.6(6)
C(14)−C(13)−C(27)	122.4(5)	C(53)−C(54)−C(55)	117.1(7)
C(13)−C(14)−C(15)	112.4(5)	C(54)−C(55)−C(56)	108.6(8)
C(14)−C(15)−C(16)	119.7(5)	C(55)−C(56)−C(57)	115.3(9)
C(14)−C(15)−C(26)	123.1(5)	C(56)−C(57)−C(58)	116.0(1)
C(16)−C(15)−C(26)	117.1(5)	C(17)−C(171)−C(172)	114.5(6)
C(15)−C(16)−C(17)	122.5(6)	C(171)−C(172)−C(173)	117.6(8)
C(16)−C(17)−C(18)	117.8(5)	C(172)−C(173)−C(174)	118.4(9)
C(16)−C(17)−C(171)	119.8(6)	C(173)−C(174)−C(175)	114.6(9)
C(18)−C(17)−C(171)	122.5(6)	C(174)−C(175)−C(176)	114.0(1)
C(17)−C(18)−C(19)	122.9(5)	C(175)−C(176)−C(177)	119.1(2)
C(18)−C(19)−C(20)	120.4(5)	C(176)−C(177)−C(178)	121.0(1)

C(24)−C(1)−C(2)−C(3)	−90.49 (0.51)	C(52)−C(53)−C(54)−C(55)	−179.60 (0.69)
C(25)−C(1)−C(2)−C(3)	87.96 (0.53)	C(53)−C(54)−C(55)−C(56)	−66.62 (1.00)
C(6)−C(7)−C(8)−C(9)	−88.33 (0.65)	C(54)−C(55)−C(56)−C(57)	−177.87 (0.86)
C(28)−C(7)−C(8)−C(9)	86.96 (0.63)	C(55)−C(56)−C(57)−C(58)	−161.13 (1.01)
C(27)−C(13)−C(14)−C(15)	89.57 (0.65)	C(17)−C(171)−C(172)−C(173)	−56.66 (0.98)
C(12)−C(13)−C(14)−C(15)	−88.22 (0.68)	C(171)−C(172)−C(173)−C(174)	170.04 (0.81)
C(18)−C(19)−C(20)−C(21)	−91.09 (0.54)	C(172)−C(173)−C(174)−C(175)	69.70 (1.23)
C(26)−C(19)−C(20)−C(21)	87.85 (0.52)	C(173)−C(174)−C(175)−C(176)	−179.21 (0.95)
C(5)−C(51)−C(52)−C(53)	177.85 (0.52)	C(174)−C(175)−C(176)−C(177)	143.32 (1.39)
C(51)−C(52)−C(53)−C(54)	−177.44 (0.61)	C(175)−C(176)−C(177)−C(178)	178.16 (1.28)

The angles at methylene bridges are of the same order than those found for symmetrical calix[4]arenes: C(1)−C(2)−C(3): 113.6(5), C(7)−C(8)−C(9): 112.1(6), C(13)−C(14)−C(15): 112.4(6) and C(19)−C(20)−C(21): 113.3(5)°.

With regard to the inclination of the four phenol entities A → D, the values of the angles between the least squares planes defined by the four bridging methylene groups and the least squares planes of the phenolic entities are: 124.6(2), 126.0(1), 121.5(2), and 123.7(1)°. The dihedral angles between ring planes of adjacent phenolic units are from A to D: 109.7(2), 107.7(2), 106.6(2), and 108.6(2)°.

If we consider the calix[4]arene without *para* sub-

Table 4. Pseudo symmetry planes and atom deviations (Å) from them

Plane I	$-0.017\,X - 0.5039\,Y - 0.8636\,Z = -8.001$				
O(27)*	0.006(5)	C(27)*	−0.004(7)	C(11)*	−0.003(8)
O(25)*	−0.002(4)	C(25)*	−0.003(5)	C(23)*	0.004(6)
C(9)	1.216(7)	C(13)	−1.210(7)		
C(10)	1.181(8)	C(12)	−1.178(7)		
C(24)	1.188(6)	C(22)	−1.199(6)		
C(28)	1.874(5)	O(26)	−1.869(5)		
C(28)	2.641(6)	C(26)	−2.638(6)		
C(8)	2.533(7)	C(14)	−2.530(7)		
C(7)	3.022(6)	C(15)	−3.008(6)		
C(6)	3.791(7)	C(16)	−3.839(6)		
C(4)	3.801(6)	C(18)	−3.821(6)		
C(3)	3.011(6)	C(19)	−3.007(6)		
C(2)	2.539(6)	C(20)	−2.547(6)		
C(5)	4.191(6)	C(17)	−4.263(6)		
C(111)	0.051(9)	C(231)	−0.007(6)		
Plane II	$-0.249\,X + 0.8396\,Y - 0.4829\,Z = 0.842$				
O(28)*	0.010(6)	C(28)	−0.009(7)	C(5)	−0.001(7)
O(26)*	−0.002(6)	C(26)	−0.010(7)	C(17)*	0.009(8)
C(7)	−1.213(7)	C(3)	1.231(7)		
C(6)	−1.198(7)	C(4)	1.187(7)		
C(8)	−2.540(8)	C(2)	2.558(7)		
C(15)	−1.218(7)	C(19)	1.221(7)		
C(16)	−1.181(8)	C(18)	1.870(7)		
C(14)	−2.551(8)	C(20)	2.547(7)		
C(13)	−2.959(8)	C(21)	3.008(7)		
C(12)	−3.684(9)	C(22)	3.808(7)		
C(11)	−4.069(9)	C(23)	4.215(7)		
C(10)	−3.698(8)	C(24)	3.805(7)		
C(9)	−2.953(8)	C(1)	3.007(7)		
O(27)	−1.895(6)	O(25)	1.895(6)		
C(27)	−2.604(8)	C(25)	2.649(7)		

Plane I—Plane II: 90.10(6)°

stituents we note that two pseudo symmetry planes are found, one formed by C(5)—C(28)—O(28)—O(26)—C(26)—C(17) and the second by C(11)—C(27)—O(27)—O(25)—C(25)—C(23). These two planes make a dihedral angle of 90.10(6)°. Table 4 gives distances of pseudo symmetrical positions of atoms versus the plane. It was very difficult to obtain good positions of the atoms for the octyl chain C(171) → C(178). The best results were obtained by fixing some bond lengths and bond angles. Because of this, B factors became largest at the end of the chains (from 7 to 25 $Å^2$ approximately). The two chains do not have the same position relative to the mean plane of the benzene ring to which they are bonded. A line connecting C(171)—C(178) is very near to the plane of benzene ring B (angle: 154.8(2)°), whereas the line C(51)—C(58) is almost perpendicular to ring D (angle: 76.3(2)°). The two chains, one "straight," the other "bent," extend outside the cavity, so it is sterically possible to have inclusion of a guest inside the macrocycle, though this is not observed.

As Fig. 2 shows, two calixarenes are related by a center of symmetry (0, 1/2, 1/2) with a CH_3 group of one of them in the cavity of the second: C(231) ($-x$, 1 $-$ y, 1 $-$ z) lies at distances of 3.726(4), 3.750(3), 3.739(4), and 3.801(2) Å from each benzene ring. Similar CH_3-π interactions between two macrocycles were already found with another calix[4]arene (Rantsordas *et al.*, 1990). In the latter case the interaction was between a methyl of the *tert*-butyl group and a benzene ring with a distance of 3.69 Å. Some attempts were made by Andreetti *et al.*, (1988) to demonstrate the necessity of the $CH_3 \cdots \pi$ interactions to explain the existence of a solid-state complex. With these relative positions of the two macrocycles it is not possible to have a guest molecule inside the cone. Furthermore there are short interactions O(25) $\cdots$ O(25):2.937(4) Å between molecules at x, y, z and $-x + 1$, $-y + 1$, $-z + 1$. Figure 3 shows the packing down "a" axis.

The structure can be described as successive columns of calixarene cones separated by layers of octyl chains, the latter being able to oscillate around their positions.

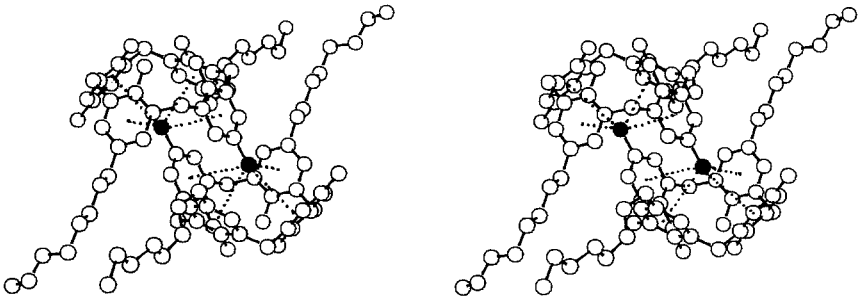

Fig. 2. Interactions $CH_3 \cdots \pi$ between two calixarenes.

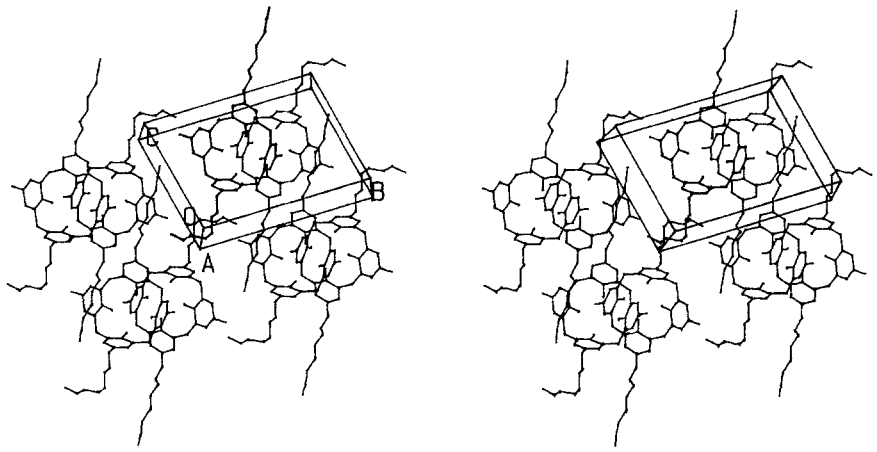

Fig. 3. Packing down "a" axis.

References

Andreetti, G. D., Pochini, A., and Ungaro, R. (1983) *J. Chem. Soc. Perkin Trans II*, 1773.

Andreetti, G. D., Ungaro, R., and Pochini, A. (1979) *J. Chem. Soc. Chem. Comm.* 1005.

Andreetti, G. D., Ori, O., Ugozzoli, F., Alfieri, C., Pochini, A., and Ungaro, R. (1988) *J. Incl. Phenom.* **6,** 523.

Böhmer, V., Marschollek, F., and Zetta, L. (1987) *J. Org. Chem.* **52,** 3200.

Bright, W. M., and Cammarata, P. (1952) *J. Am. Chem. Soc.* **74,** 3690.

Domenicano, A., Vaciago, A., and Coulson, C. A. (1975) *Acta Crystallogr.* **B31,** 221-234.

Frenz, B. A. (1985) *Enraf-Nonius Structure Determination Package* (College Station, Tex.).

Goldmann, H., Vogt, W., Paulus, E., and Böhmer V. (1988) *J. Am. Chem. Soc.* **110,** 6811.

Kämmerer, H., Eberle, K., Böhmer, V., and Grossmann, M. (1975) *Makromol. Chem.* **176,** 3295.

Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J. P., and Woolfson, M. M. (1982) *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-Ray Diffraction Data* (Univ. of York, England and Louvain, Belgium).

Nardeli, M. (1983) *Comput. Chem.* **7,** 95.

Rantsordas, S., Perrin, M., Gharnati, F., Lecocq, S., Vogt, W., Fey, T., and Böhmer, V. (1990) *J. Incl. Phenom.* (in press).

Sheldrick, C. M. (1976), SHELX. *Program for Crystal Structure Determination* (Univ. of Cambridge, England).

Ungaro, R., Pochini, A., Andreetti, G. D., and Sangermano, V. (1984) *J. Chem. Soc. Perkin Trans II*, 1979.

Ungaro, R., Pochini, A., Andreetti, G. D., and Domiano, P. (1985) *J. Chem. Soc. Perkin Trans II*, 197.

Structure factor data have been deposited with the British Library, Boston Spa, Wetherby, West Yorkshire, UK, as supplementary publication No. 63130. (34 pages).