Crystal and Molecular Structures of
p-(1,1,3,3-Tetramethylbutyl)calix[5]arene and
Its 1:1 Complex with Toluene

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Abstract. A cyclic pentamer was obtained from *p*-(1,1,3,3-tetramethylbutyl) phenol. It crystallizes from a mixture of acetone and toluene at room temperature giving a 1:1 complex with toluene (compound A), whereas at 50°C the empty form (compound B) is obtained. Crystals of A are orthorhombic, space group $Pna2_1$, $a = 20.083(2)$, $b = 12.936(6)$, $c = 28,423(1)$ Å, $Z = 4$, final R value $= 0.067$. The empty form, B, is monoclinic $P2_1/c$, $a = 18.695(2)$, $b = 11.673(5)$, $c = 35.100(4)$ Å, $\beta = 114.33(1)$, $Z = 4$, final R value $= 0.135$. The macrocycle is in the cone conformation for both compounds; the toluene molecule lies in the cone as often found for calix[4]arenes.

Key words. Calixarene, inclusion compounds, crystal structure.

1. Introduction

Calixarenes [1] form a class of synthetic macrocycles having phenolic residues in a cyclic array linked by methylene groups at positions *ortho* to the hydroxy groups. This class of macrocycles represents a large number of compounds by varying the number of phenolic units in the cyclic array and the nature of the substituents at both the R_1 and R_2 positions; we look here at calixarenes with $R_2 = H$ and the same R_1 on the phenolic units; furthermore calixarenes are able to exist as either the empty form and/or as inclusion compounds. Two types of inclusion compounds have been found with calixarenes: the guest molecules lie inside the cones forming cage-like clathrates [2, 3], or the guest molecules lie between the macrocycles [4, 5]. According to the nomenclature proposed by Weber and Josel [6] one finds cryptato-cavitate or tubulato or intercalato clathrates. Several studies have been reported concerning calix[4]arenes [2–5], as well as calixarenes with 6 or 8 phenol entities [7, 8]. Very few studies are known concerning calixarenes with an odd number of rings. However calix[5] or calix[7]arenes are known, having been synthesized by Kammerer *et al.* [9]. But X-ray studies have been reported for only one calix[5] arene, prepared from phenol [10] and one calix[7]arene [11], prepared from *p*-ethylphenol. We report here the crystal and molecular structures of the empty form of the calix[5]arene prepared from *p*(1,1,3,3-tetramethylbutyl)phenol

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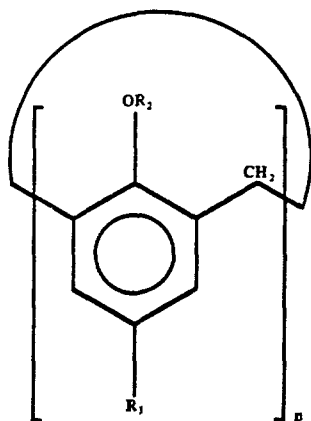
Formula

(*p*-octylphenol) and its 1 : 1 complex with toluene. The preparation of the macrocycle and its characterization will be reported elsewhere [12].

2. Experimental

2.1. CRYSTALLISATION

On the assumption that CH_3-π interactions play a role in the formation of neutral host–guest complexes we chose solvents carrying CH_3 groups. Powdered calix[5]arene is sparingly soluble in toluene. So we used a mixture of toluene and acetone and beautiful rhomboidal, transparent crystals were obtained (compound A); after some hours at 50°C, the crystals became opaque, suggesting transformation. A saturated solution in an acetone–toluene mixture was evaporated at 50°; needle-shaped crystals were obtained (compound B). Powder diagrams of A after some hours at 50°C are similar to those of B. It was thought that, at room temperature, a complexed form was obtained (compound A) whereas at 50°C the empty form (compound B) was prepared.

2.2. X-RAY STRUCTURE ANALYSIS. CALIX[5]ARENE: TOLUENE (1 : 1) CLATHRATE

A colourless crystal ($0.5 \times 0.3 \times 0.7$ mm^3) was sealed with mother liquor in a glass Lindeman capillary for the X-ray analysis. Lattice parameters were refined by least-squares fit of 25 $(\theta, \varphi, \omega, \kappa)_{hkl}$ measurements taken on a Nonius CAD4 diffractometer ($6° \leqslant \theta \leqslant 48°$).

Crystal data

C_{75} H_{110} O_5, C_7H_8, $M = 1090.7 + 92.1$, orthorhombic, $a = 20.083(2)$, $b = 12.936(6)$, $c = 28.423(1)$ Å, $V = 7384(4)$ Å^3, $Z = 4$, $D_C = 1.065$ g cm^{-3}, $F(000) = 2600$, CuK_α radiation: $\lambda = 1.5418$ Å, $\mu = 4.57$ cm^{-1}, Space group *Pnma* or *Pna2*$_1$. Space group *Pna2*$_1$ (No. 62) was confirmed by the analysis.

Intensity data were collected up to $\theta° = 73°$ by using the ω–2θ scan mode with graphite monochromatized CuK_α radiation. Three standard reflections were measured every hour to control intensity variation; Lorentz and polarisation corrections

were applied and absorption was corrected with the programs PSI and EAC of SDP [13]. 14690 reflections were measured, 9409 after merge ($R_{int} = 0.04$); 7522 were considered as observed [$I > 3\sigma(I)$].

Structure analysis and refinement

The structure was solved by MULTAN [14] and refined by the SHELX [15] system of programs in the non-centrosymmetric space group *Pna2_1*. Indeed the distribution of *E* factors was dubious and closer to the centrosymmetrical theoretical model, but an attempt with *Pnma* was not satisfactory. The *E* map computed with the most consistent set of signs revealed the positions of a large number of the nonhydrogen atoms, except some of the octyl chains. A Fourier map computed with this first set of atoms revealed all the nonhydrogen atoms. Several cycles of full-matrix least squares calculations with isotropic factors led to a difference Fourier map which revealed a large number of hydrogen atoms of the host molecule. These, and the others calculated at theoretical positions, were introduced into the refinement with constant *U*. The final *R* value was 0.067 with unit weights. The final difference electron density map showed the highest residual peak of ca. $0.15\,e\,\text{Å}^{-3}$. Scattering factors for nonhydrogen atoms were taken from the *International Tables for X-Ray Crystallography* [16]; for H atoms the scattering factors tables of Stewart, Davidson and Simpson [17] were used. Atomic fractional co-ordinates are listed in Table I with the numbering scheme shown in Figure 1.
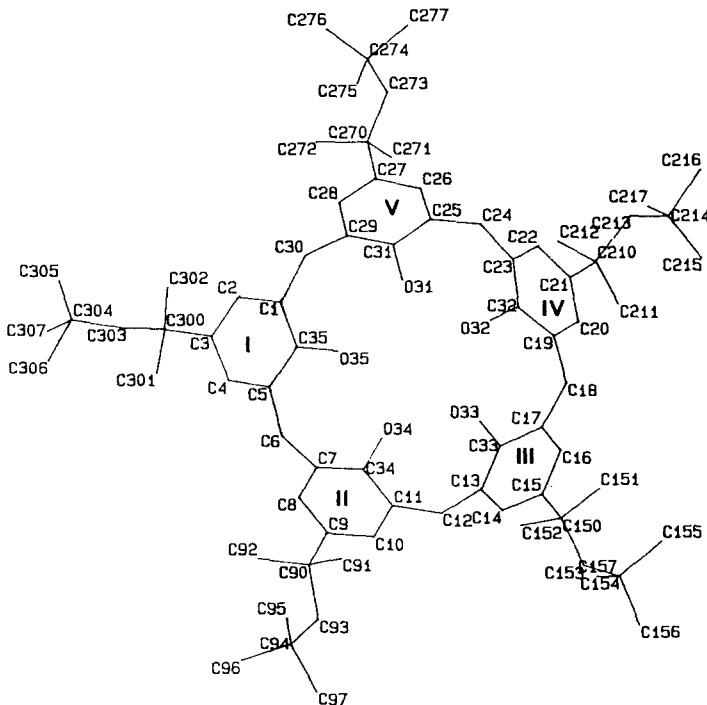

Fig. 1. Numbering scheme.

Table I. Positional parameters and their estimated standard deviations.

COMPOUND A

Atom	x	y	z	Atom	x	y	z
O(35)	0.3704(2)	0.1983(3)	0.7610(3)	O(32)	0.1647(2)	0.2426(3)	0.7110(1)
C(1)	0.4502(4)	0.0979(7)	0.7189(3)	C(19)	0.0639(2)	0.1411(4)	0.7157(2)
C(2)	0.5038(4)	0.0300(7)	0.7193(3)	C(20)	0.0244(2)	0.0642(4)	0.6966(2)
C(3)	0.5315(2)	−0.0081(3)	0.7605(4)	C(21)	0.0399(3)	0.0145(5)	0.6548(2)
C(4)	0.5026(4)	0.0305(8)	0.8026(3)	C(22)	0.0942(2)	0.0548(4)	0.6296(2)
C(5)	0.4507(4)	0.0974(6)	0.8043(3)	C(23)	0.1343(2)	0.1314(4)	0.6472(2)
C(35)	0.4221(2)	0.1294(3)	0.7612(4)	C(32)	0.1213(2)	0.1733(4)	0.6923(2)
C(300)	0.5920(2)	−0.0791(4)	0.7596(4)	C(210)	−0.0025(3)	−0.0702(5)	0.6345(2)
C(301)	0.5883(7)	−0.158(1)	0.8029(4)	C(211)	−0.0475(4)	−0.1230(7)	0.6715(3)
C(302)	0.5887(6)	−0.1494(8)	0.7179(4)	C(212)	0.0463(4)	−0.1618(6)	0.6188(3)
C(303)	0.6528(3)	−0.0077(4)	0.7637(6)	C(213)	−0.0391(3)	−0.0394(6)	0.5862(2)
C(304)	0.7269(3)	−0.0414(4)	0.7629(6)	C(214)	−0.0829(3)	−0.0544(5)	0.5826(2)
C(305)	0.7448(8)	−0.121(2)	0.7241(5)	C(215)	−0.1350(5)	0.080(1)	0.6188(4)
C(306)	0.7471(8)	−0.096(3)	0.8044(6)	C(216)	−0.1202(4)	0.049(1)	0.5336(3)
C(307)	0.7682(4)	0.0528(8)	0.7796(5)	C(217)	−0.0416(4)	0.1568(8)	0.5764(3)
O(34)	0.2945(2)	0.2206(3)	0.8402(2)	O(31)	−0.2946(2)	0.2215(3)	0.6834(1)
C(7)	0.3692(2)	0.1042(5)	0.8765(2)	C(25)	0.2563(2)	0.1169(4)	0.6194(2)
C(8)	0.3800(3)	0.0216(5)	0.9073(2)	C(26)	0.2681(3)	0.0358(5)	0.5892(2)
C(9)	0.3301(3)	−0.0161(5)	0.9376(2)	C(27)	0.3287(3)	−0.0140(4)	0.5860(2)
C(10)	0.2691(3)	0.0356(4)	0.9355(2)	C(28)	0.3790(3)	0.0205(4)	0.6147(2)
C(11)	0.2558(2)	0.1168(4)	0.9036(2)	C(29)	0.3703(2)	0.1012(4)	0.6469(2)
C(34)	0.3075(2)	0.1453(4)	0.8725(2)	C(31)	0.3061(2)	0.1438(4)	0.6499(2)
C(90)	0.3401(3)	−0.1052(5)	0.9706(2)	C(270)	0.3388(3)	−0.1061(5)	0.5499(2)
C(91)	0.2880(4)	−0.1907(7)	0.9580(3)	C(271)	0.2924(7)	−0.1895(8)	0.5621(4)
C(92)	0.4101(4)	−0.1503(6)	0.9696(3)	C(272)	0.4049(5)	−0.1568(8)	0.5559(4)
C(93)	0.3207(3)	−0.0758(6)	1.0229(2)	C(273)	0.3223(3)	−0.0704(6)	0.4992(2)
C(94)	0.3628(3)	0.0041(6)	1.0518(2)	C(274)	0.3641(3)	0.0068(7)	0.4702(2)
C(95)	0.3825(6)	0.1022(9)	1.0271(3)	C(275)	0.3847(4)	0.1007(7)	0.4973(3)
C(96)	0.4243(5)	−0.048(1)	1.0739(3)	C(276)	0.4228(5)	−0.046(1)	0.4459(3)
C(97)	0.3191(6)	0.039(1)	1.0951(3)	C(277)	0.3177(5)	0.037(1)	0.4313(3)
O(33)	0.1618(2)	0.2445(3)	0.8103(2)				
C(13)	0.1355(2)	0.1329(4)	0.8759(2)	C(6)	0.4285(4)	0.1516(7)	0.8501(3)
C(14)	0.0941(3)	0.0554(5)	0.8924(2)	C(12)	0.1919(4)	0.1757(7)	0.9057(3)
C(15)	0.0387(3)	0.0182(4)	0.8697(2)	C(18)	0.0427(2)	0.1949(4)	0.7605(3)
C(16)	0.0251(3)	0.0646(5)	0.8254(2)	C(24)	0.1904(4)	0.1741(7)	0.6179(3)
C(17)	0.0640(2)	0.1428(4)	0.8064(2)	C(30)	0.4292(4)	0.1462(4)	0.6728(3)
C(33)	0.1210(2)	0.1713(4)	0.8312(2)				
C(150)	−0.0019(3)	−0.0737(5)	0.8901(2)	C(601)	0.8099(4)	−0.3766(7)	0.765(1)
C(151)	−0.0528(4)	−0.1143(7)	0.8542(3)	C(602)	0.770(2)	−0.401(1)	0.8016(9)
C(152)	0.0445(4)	−0.1604(6)	0.9020(3)	C(603)	0.695(1)	−0.434(1)	0.7882(8)
C(153)	−0.0398(3)	−0.0419(6)	0.9335(2)	C(604)	0.689(1)	−0.438(2)	0.7407(9)
C(154)	−0.0819(3)	0.0592(7)	0.9406(2)	C(605)	0.737(1)	−0.415(2)	0.7124(7)
C(155)	−0.1331(3)	0.0686(7)	0.9003(3)	C(606)	0.787(1)	−0.386(2)	0.7203(7)
C(156)	−0.1218(4)	0.0362(8)	0.9854(3)	C(607)	0.879(1)	−0.341(2)	0.775(1)
C(157)	−0.0416(4)	0.1518(7)	0.9447(3)				

COMPOUND B

Atom	x	y	z	Atom	x	y	z
O(35)	0.6517(4)	−0.0732(5)	0.5489(2)	O(32)	0.8510(4)	−0.2904(6)	0.6334(2)
C(1)	0.5628(5)	0.0163(7)	0.5726(3)	C(19)	0.9839(5)	−0.2539(7)	0.6808(3)

Table I. (continued)

COMPOUND B

Atom	x	y	z	Atom	x	y	z
C(2)	0.5164(5)	0.1115(8)	0.5727(3)	C(20)	1.0364(6)	−0.2228(7)	0.7212(3)
C(3)	0.5116(5)	0.2069(8)	0.5482(3)	C(21)	1.0140(6)	−0.2081(7)	0.7535(3)
C(4)	0.5522(5)	0.2060(8)	0.5228(3)	C(22)	0.9355(6)	−0.2329(7)	0.7454(3)
C(5)	0.5993(5)	0.1123(8)	0.5223(3)	C(23)	0.8812(5)	−0.2641(7)	0.7056(3)
C(35)	0.6051(5)	0.0174(8)	0.5489(3)	C(32)	0.9064(5)	−0.2675(6)	0.6732(3)
C(300)	0.458(2)	0.313(2)	0.5468(8)	C(210)	1.0721(6)	−0.1655(7)	0.7971(3)
C(301)	0.392(2)	0.273(2)	0.5573(8)	C(211)	1.1382(9)	−0.101(1)	0.7950(4)
C(302)	0.429(1)	0.372(2)	0.5084(8)	C(212)	1.0284(9)	−0.081(1)	0.8137(4)
C(303)	0.488(2)	0.378(3)	0.577(1)	C(213)	1.098(1)	−0.257(1)	0.8297(4)
C(304)	0.568(2)	0.423(2)	0.6109(8)	C(214)	1.1282(7)	−0.3706(8)	0.8338(3)
C(305)	0.564(2)	0.553(3)	0.6051(9)	C(215)	1.100(1)	−0.438(1)	0.7954(4)
C(306)	0.637(2)	0.401(3)	0.6052(8)	C(216)	1.216(11)	−0.368(2)	0.8557(8)
C(307)	0.582(2)	0.449(3)	0.6538(9)	C(217)	1.123(2)	−0.436(2)	0.8664(7)
O(34)	0.7639(4)	−0.0551(5)	0.5174(2)	O(31)	0.6968(4)	−0.2252(6)	0.6154(2)
C(7)	0.7219(5)	0.1424(8)	0.5087(3)	C(25)	0.7403(5)	−0.1976(8)	0.6899(3)
C(8)	0.7419(5)	0.2597(8)	0.5123(3)	C(26)	0.7360(6)	−0.1334(9)	0.7225(3)
C(9)	0.8193(6)	0.2951(8)	0.5235(3)	C(27)	0.6797(6)	−0.0475(8)	0.7147(3)
C(10)	0.8755(6)	0.2122(9)	0.5281(3)	C(28)	0.6243(6)	−0.0353(8)	0.6745(3)
C(11)'	0.8573(5)	0.0944(9)	0.5249(3)	C(29)	0.6270(5)	−0.0984(8)	0.6410(3)
C(34)	0.7815(5)	0.0633(8)	0.5173(3)	C(31)	0.6890(5)	−0.1735(7)	0.6491(3)
C(90)	0.8410(7)	0.425(1)	0.5299(4)	C(270)	0.6798(9)	0.025(1)	0.7522(4)
C(91)	0.798(1)	0.479(1)	0.5561(6)	C(271)	0.759(1)	0.057(2)	0.7818(7)
C(92)	0.9236(7)	0.443(1)	0.5568(5)	C(272)	0.639(1)	0.136(2)	0.7390(7)
C(93)	0.792(1)	0.501(2)	0.4909(7)	C(273)	0.656(2)	−0.050(3)	0.7834(8)
C(94)	0.822(1)	0.496(2)	0.4550(8)	C(274)	0.578(1)	−0.113(2)	0.7701(5)
C(95)	0.858(2)	0.411(3)	0.4447(9)	C(275)	0.570(1)	−0.205(2)	0.7388(7)
C(96)	0.889(1)	0.590(2)	0.4685(7)	C(276)	0.502(1)	−0.054(2)	0.7592(7)
C(97)	0.763(1)	0.559(3)	0.4197(9)	C(277)	0.599(1)	−0.160(3)	0.8130(7)
O(33)	0.8932(4)	−0.1824(5)	0.5717(2)				
C(13)	0.9780(5)	−0.0296(8)	0.5686(3)	C(6)	0.6361(5)	0.1095(8)	0.4919(3)
C(14)	1.0493(6)	0.0298(9)	0.5885(3)	C(12)	0.9208(5)	0.0073(9)	0.5258(3)
C(15)	1.1049(6)	−0.0027(9)	0.6263(3)	C(18)	1.0133(5)	−0.2742(7)	0.6473(3)
C(16)	1.0925(6)	−0.1034(9)	0.6444(3)	C(24)	0.8002(5)	−0.2958(7)	0.6996(3)
C(17)	1.0230(5)	−0.1645(8)	0.6256(3)	C(30)	0.5598(5)	−0.0895(8)	0.5979(3)
C(33)	0.9647(5)	−0.1265(8)	0.5893(3)				
C(150)	1.1801(7)	0.068(1)	0.6499(4)				
C(151)	1.192(1)	0.086(2)	0.6932(6)				
C(152)	1.177(2)	0.175(2)	0.6294(8)				
C(153)	1.253(1)	0.002(3)	0.6540(7)				
C(154)	1.2748(9)	−0.044(2)	0.6221(5)				
C(155)	1.2146(9)	−0.101(2)	0.5866(5)				
C(156)	1.330(1)	0.019(2)	0.6104(7)				
C(157)	1.335(2)	−0.142(3)	0.6459(9)				

2.3. CALIX[5]ARENE: EMPTY FORM

A needle obtained at 50°C approximately $0.1 \times 0.3 \times 0.5$ mm³ was sealed in a glass capillary and studied at room temperature. Lattice parameters were refined by least-squares fit of 25 $(\theta, \varphi, \omega, \kappa)_{hkl}$ measurements taken on the same diffractometer $(7 \leqslant \theta \leqslant 48°)$.

Crystal data

$C_{75}H_{110}O_5$, $M = 1091.7$, monoclinic, $a = 18.695(2)$ $b = 11.673(5)$ $c = 35.100(4)$ Å, $\beta = 114.33(1)°$, $V = 6979(3)$ Å^3, $Z = 4$, $D_C = 1.039$ g cm^{-3}, $F(000) = 2400$, CuK_α radiation, $\lambda = 1.5418$ Å, $\mu = 4.50$ cm^{-1}. Space group: $P2_1/c$(No. 14).

Intensity data were collected in the same way with three standard reflections; the same corrections were applied; 27869 reflections were measured, 13941 after merge ($R_{int} = 0.04$), 11937 were considered as observed.

Structure analysis and refinement

The structure was solved by MULTAN [14] and refined by SHELX [15]. The E-map computed with the best set of signs revealed all carbon atoms of the calix[5]arene except some atoms of octyl groups; these atoms were found on a Fourier map calculated during the refinement as well as some hydrogen atoms on difference maps. The other hydrogen atoms were calculated at theoretical positions and were introduced into the refinement with constant U. The final R was 0.135 with unit weights. The final electron density map showed the highest residual peak of ca. 0.5 e Å^{-3} near the octyl chain. The difficulty during this refinement was the high values of U for carbon atoms of the octyl chains especially with the one which lies near a pseudo-symmetry plane of the molecule as discussed later. A similar situation was found with p-octylcalix[4] for which the authors have refined the structure with an average position on the plane of symmetry. Atomic fractional coordinates are listed on Table I with the same numbering scheme as for compound A.

3. Results and Discussion

3.1. MOLECULAR GEOMETRY

Some characteristic molecular geometry parameters (bond lengths, bond angles and torsion angles) are reported in Table II.

The C–O distances vary from 1.359(6) to 1.403(6) Å for compound A, from 1.37(1) to 1.42(1) Å for compound B similar to those found for a calix[4]arene from p-(1,1,3,3-tetra methylbutylphenol) (p-octylphenol) [4] 1.386(5) to 1.409(6) Å in the empty form and 1.380(14) to 1.413(11) Å in the complex with toluene. A characteristic feature concerns the octyl groups at *para* positions. Their bond distances and angles are given in Table II. The angles at C(93), C(153), C(213), C(273) and C(303) have values larger than 109°C, as has often been observed; the mean values are 124.3° (compound A) and 130° (compound B). The same distortion from the theoretical value of 109° is found for p-octylcalix[4] arene with values from 115.6(6) to 137.1(9) in the empty form and 120.7(1) to 142.9(3) in the complex with toluene. This fact is probably due to the steric effect with the neighbouring substituents. The same distortion is found for p-octylphenol complexed with 18-crown-6 [18] with values near 124°. For the two calix[5]arenes, four of the octyl chains extend outside the cavity, leaving the cavity accessible for a guest. The relative positions versus their benzene rings are similar. The fifth octyl chain extends outside the cavity for compound A and inside for compound B. It

seems that the toluene molecule pushes the octyl chain outside the macrocycle. In the p-octylcalix[4]arenes[4] the orientation of the octyl chains are similar in the two structures. Two of them point inside and the other two extend outside the cavity. So in both cases, the cavity is partly filled by the octyl chains and it is not possible to have an inclusion compound with the guest inside the cavity. Indeed this complex is classed as a tubulato cavitate clathrate.

For calix[4]arenes the mean plane of the bridging methylene groups is taken as the reference plane and the orientations of the phenyl rings with respect to this mean plane are given. The same comparison is made here; the dihedral angles have respective values: 145.4(1), 132.9(1), 130.7(1), 130.3(1) and 137.5(1)° from I to V for compound A and 145.4(2), 122.7(2), 132.6(2), 129.0(2) and 123.9(2)° from I to V for compound B. The corresponding values in the 25, 26, 27, 28, 29-pentahydroxy-calix[5]arene—acetone (1:2) clathrate[10] (compound C) are 126.5(8), 138.2(7), 128.3(8), 126.8(7) and 139.4(6)°. These values are larger than those found for a great number of calix[4]arenes (values around 123°). However the methylene groups deviate from the mean plane: 0.031(10), −0.034(9), 0.007(5), −0.010(10) and −0.009(8) [compound A]; −0.000(9), −0.14(1), 0.179(9), −0.172(9) and 0.117(9) [compound B] respectively for C(6), C(12), C(18), C(24) and C(30). Another important feature is the length of the O···O intramolecular contacts:

	A	B	C
O(35)–O(34)	2.736(8)	2.750(11)	2.828(9)
O(34)–O(33)	2.814(6)	2.809(8)	2.841(10)
O(33)–O(31)	2.822(6)	2.881(11)	2.856(10)
O(32)–O(31)	2.738(5)	2.791(10)	2.848(9)
O(31)–O(35)	2.696(8)	2.774(9)	2.832(10)

These values are longer than those in the range $2.65 \rightarrow 2.67$ Å found in several calix[4]arenes, but in agreement with those established in calix[7]arene[11] or calix[8]arene [19]. However the shape of this macrocycle seems like a chalice but more opened than the cone found with calix[4]arenes.

In each case the molecule has a pseudo symmetry plane passing through C(3), C(35), O(35) and C(18); the equations of such planes are:

$$0.002X + 0.008Y - 1.0Z = -21.59 \quad \text{plane (001)} \qquad \text{compound A}$$

$$0.592X + 0.468Y - 0.656Z = -9.41 \quad \text{plane } (\overline{2}\overline{1}4) \qquad \text{compound B}$$

$$0.03X + 0.04Y - 0.999Z = -2.8 \quad \text{plane (001)} \qquad \text{compound C} \\ \text{(Calculated from Andreetti [10].)}$$

Table III gives for A and B the distances of the atoms from the pseudo symmetry planes both for the skeleton of the macrocycle and for the octyl groups; the results show that the symmetry is better for compound A.

No constraints were given to the toluene molecule during the refinement; so the geometry is not perfect as often found for these sorts of complexes. The C—C bonds vary from 1.11(4) to 1.60(4) Å (1.30(11) to 1.62(9) Å in the p-octylcalix[4]arene complex [4]). The bond angles have values from 109 to 130° with an average of 119.8°.

Table II. Bond distances (Å), bond angles (°) with standard deviations (Non-H atoms).

COMPOUND A

Bond	Å	Bond	Å	Bond	Å	Bond	Å	Bond	Å
C(35)–O(35)	1,368(5)	C(34)–O(34)	1.362(7)	C(33)–O(33)	1.387(6)	C(32)–O(32)	1.359(6)	C(31)–O(31)	1.403(6)
C(3)–C(300)	1.522(6)	C(9)–C(90)	1.500(8)	C(15)–C(150)	1.554(8)	C(21)–C(210)	1.502(8)	C(27)–C(270)	1.586(8)
C(300)–C(301)	1.60(2)	C(90)–C(91)	1.56(1)	C(150)–C(151)	1.54(1)	C(210)–C(211)	1.55(1)	C(270)–C(271)	1.47(1)
C(300)–C(302)	1.49(1)	C(90)–C(92)	1.523(9)	C(150)–C(152)	1.50(1)	C(210)–C(212)	1.60(1)	C(270)–C(272)	1.49(1)
C(300)–C(303)	1.535(7)	C(90)–C(93)	1.582(9)	C(150)–C(153)	1.507(9)	C(210)–C(213)	1.608(8)	C(270)–C(273)	1.549(9)
C(303)–C(304)	1.551(7)	C(93)–C(94)	1.57(1)	C(153)–C(154)	1.57(1)	C(213)–C(214)	1.50(1)	C(273)–C(274)	1.54(1)

Angle	°	Angle	°	Angle	°
C(5)–C(6)–C(7)	117.01(7)	C(11)–C(12)–C(13)	115.7(6)	C(17)–C(18)–C(19)	115.9(4)
C(1)–C(35)–O(35)	119.7(8)	C(7)–C(34)–O(34)	121.0(5)	C(13)–C(33)–O(33)	120.7(4)
C(5)–C(35)–O(35)	120.2(8)	C(11)–C(34)–O(34)	117.8(4)	C(17)–C(33)–O(33)	116.7(4)
C(3)–C(300)–C(303)	105.7(4)	C(9)–C(90)–C(93)	111.7(6)	C(15)–C(150)–C(153)	111.2(5)
C(300)–C(303)–C(304)	126.4(5)	C(90)–C(93)–C(94)	121.2(5)	C(150)–C(153)–C(154)	127.2(6]

Angle	°	Angle	°
C(23)–C(24)–C(25)	117.3(6)	C(29)–C(30)–C(1)	118.7(6)
C(19)–C(32)–O(32)	122.8(4)	(25)–C(31)–O(31)	119.4(4)
C(23)–C(32)–O(32)	119.3(4)	C(29)–C(31)–O(31)	118.3(4)
C(21)–C(210)–C(213)	114.0(5)	C(27)–C(270)–C(273)	110.5(5)
C(210)–C(213)–C(214)	121.8(5)	C(270)–C(273)–C(274)	125.0(5)

Torsion	°	Torsion	°
C(35)–C(1)–C(30)–C(29)	−87.6(9)	C(2)–C(3)–C(300)–C(303)	92.0(9)
C(34)–C(7)–C(6)–C(5)	−100.5(7)	C(8)–C(9)–C(90)–C(93)	126.5(6)
C(33)–C(13)–C(12)–C(11)	−97.2(7)	C(14)–C(15)–C(150)–C(153)	71.2(7)
C(32)–C(19)–C(18)–C(17)	−96.6(6)	C(20)–C(21)–C(210)–C(213)	112.5(6)
C(31)–C(25)–C(24)–C(23)	−93.4(7)	C(26)–C(27)–C(270)–C(273)	56.6(7)

COMPOUND B

C(35)–O(35)	1.37(1)	C(34)–O(34)	1.42(1)	C(33)–O(33)	1.38(1)	C(32)–O(32)	1.381(9)	C(31)–O(31)	1.39(1)
C(3)–C(300)	1.57(3)	C(9)–C(90)	1.56(1)	C(15)–C(150)	1.55(1)	C(21)–C(210)	1.55(1)	C(27)–C(270)	1.56(2)
C(300)–C(301)	1.51(5)	C(90)–C(91)	1.59(3)	C(150)–C(151)	1.46(3)	C(210)–C(211)	1.47(2)	C(270)–C(271)	1.46(2)
C(300)–C(302)	1.41(4)	C(90)–C(92)	1.46(2)	C(150)–C(152)	1.43(3)	C(210)–C(212)	1.54(2)	C(270)–C(272)	1.48(3)
C(300)–C(303)	1.24(4)	C(90)–C(93)	1.57(2)	C(150)–C(153)	1.52(3)	C(210)–C(213)	1.49(2)	C(270)–C(273)	1.61(4)
C(303)–C(304)	1.58(4)	C(93)–C(94)	1.58(4)	C(153)–C(154)	1.44(3)	C(213)–C(214)	1.43(2)	C(273)–C(274)	1.62(4)

C(5)–C(6)–C(7)	116.4(7)	C(11)–C(12)–C(13)	115.5(8)	C(17)–C(18)–C(19)	114.2(8)
C(1)–C(35)–O(35)	121.4(9)	C(7)–C(34)–O(34)	119.0(8)	C(13)–C(33)–O(33)	119.3(7)
C(5)–C(35)–O(35)	118.5(9)	C(11)–C(34)–O(34)	118.4(8)	C(17)–C(33)–O(33)	120.0(9)
C(3)–C(300)–C(303)	114.(2)	C(9)–C(90)–C(93)	113.(1)	C(15)–C(150)–C(153)	111.(1)
C(300)–C(303)–C(304)	144.(4)	C(90)–C(93)–C(94)	114.(2)	C(150)–C(153)–C(154)	130.(1)

C(23)–C(24)–C(25)	116.9(8)	C(29)–C(30)–C(1)	114.7(7)
C(19)–C(32)–O(32)	121.(1)	C(25)–C(31)–O(31)	121.4(8)
C(23)–C(32)–O(32)	117.7(9)	C(29)–C(31)–O(31)	118.2(7)
C(21)–C(210)–C(213)	113.7(8)	C(27)–C(270)–C(273)	112.(1)
C(210)–C(213)–C(214)	137.(2)	C(270)–C(273)–C(274)	124.(2)

C(35)–C(1)–C(30)–C(29)	85.(1)	C(2)–C(3)–C(300)–C(303)	80.(3)
C(34)–C(7)–C(6)–C(5)	104.(1)	C(8)–C(9)–C(90)–C(93)	124.(2)
C(33)–C(13)–C(12)–C(11)	90.(1)	C(14)–C(15)–C(150)–C(153)	65.(2)
C(32)–C(19)–C(18)–C(17)	97.(1)	C(20)–C(21)–C(210)–C(213)	–106.(1)
C(31)–C(25)–C(24)–C(23)	97.(1)	C(26)–C(27)–C(270)–C(273)	–68.(2)

Table III. Pseudosymmetry plane: $M1X + H2Y + M3Z = D$. Atoms marked with an asterisk are those used for the calculation of the equation of the mean plane.

COMPOUND A

| M1 = 0.00237(0.00173) | M3 = −0.99997(0.00000) | C(3)* | 0.003(11) | C(35)* | −0.008(10) |
| M2 = 0.00801(0.00577) | D = −21.59304(0.02118) | O(35)* | 0.003(8) | C(18)* | 0.000(10) |

C(2)	1.75(8)	C(4)	−1.192(7)	C(1)	1.193(8)	C(5)	−1.236(7)
C(30)	2.507(8)	C(6)	−2.531(7)	C(29)	3.234(4)	C(7)	−3.290(5)
C(28)	4.143(5)	C(8)	−4.175(5)	C(27)	4.951(5)	C(9)	−5.041(5)
C(26)	4.864(5)	C(10)	−4.979(5)	C(25)	4.014(5)	C(11)	−4.066(5)
C(24)	4.060(8)	C(12)	−4.120(7)	C(23)	3.218(5)	C(13)	−3.280(5)
C(22)	3.710(5)	C(14)	−3.762(5)	C(21)	2.985(5)	C(15)	−3.123(5)
C(20)	1.803(5)	C(16)	−1.858(5)	C(19)	1.270(5)	C(17)	−1.310(5)
O(31)	2.208(4)	O(34)	−2.251(4)	O(32)	1.417(3)	O(33)	−1.405(4)

C(300)	0.023(11)		
C(301)	−1.214(12)	C(302)	1.200(11)
C(303)	−0.082(16)		
C(304)	−0.061(16)		
C(305)	1.034(15)	C(306)	−1.244(17)	C(307)	−0.522(15)

C(270)	5.969(6)	C(90)	−5.989(6)	C(210)	3.552(6)	C(150)	−3.714(6)
C(271)	5.610(11)	C(91)	−5.641(9)	C(211)	2.492(8)	C(151)	−2.699(7)
C(272)	5.795(11)	C(92)	−5.962(8)	C(212)	3.990(9)	C(152)	−4.059(9)
C(273)	7.413(6)	C(93)	−7.472(7)	C(213)	4.927(6)	C(153)	−4.946(6)
C(274)	8.248(6)	C(94)	−8.284(6)	C(214)	5.036(6)	C(154)	−5.139(7)
C(275)	7.489(8)	C(95)	−7.570(8)	C(215)	4.008(12)	C(155)	−3.996(7)
C(276)	8.935(10)	C(96)	−8.913(10)	C(216)	6.426(9)	C(156)	−5.245(9)
C(277)	9.352(9)	C(97)	−9.512(9)	C(217)	5.224(10)	C(157)	−6.415(7)

COMPOUND B

| M1 = 0.592(1) | M3 = −0.656(4) | C(3)* | 0.006(10) | C(35)* | −0.015(9) |
| M2 = 0.468(4) | D = −9.41(8) | O(35)* | 0.006(7) | C(18)* | 0.000(10) |

C(2)	−1.187(9)	C(4)	1.198(10)	C(1)	−1.192(9)	C(5)	1.225(9)
C(30)	−2.550(9)	C(6)	2.516(9)	C(29)	−3.129(10)	C(7)	3.148(9)
C(28)	−3.801(10)	C(8)	3.902(9)	C(27)	−4.445(11)	C(9)	4.621(10)
C(26)	−4.519(11)	C(10)	4.654(10)	C(25)	−3.861(10)	C(11)	3.903(10)
C(24)	−4.021(9)	C(12)	4.103(10)	C(23)	−3.128(9)	C(13)	3.270(10)
C(22)	−3.532(9)	C(14)	3.796(10)	C(21)	−2.768(10)	C(15)	3.118(11)
C(20)	−1.647(10)	C(16)	1.895(10)	C(19)	−1.204(9)	C(17)	1.346(10)
O(31)	−2.293(7)	O(34)	2.274(2)	O(32)	−1.474(7)	O(33)	1.405(7)

C(300)	0.03(3)		
C(301)	−1.23(3)	C(302)	1.16(3)
C(303)	−0.17(4)		
C(304)	−0.04(3)		
C(305)	−0.80(3)	C(306)	0.77(3)	C(307)	−1.02(3)

C(270)	−5.15(1)	C(90)	5.38(1)	C(210)	−3.18(1)	C(150)	3.64(1)
C(271)	−4.98(2)	C(91)	4.43(1)	C(211)	−2.04(2)	C(151)	2.58(2)
C(272)	−4.61(3)	C(92)	5.60(1)	C(212)	−3.69(1)	C(152)	4.80(3)
C(273)	−6.75(3)	C(93)	6.41(2)	C(213)	−4.36(2)	C(153)	4.96(2)
C(274)	−7.56(2)	C(94)	7.77(3)	C(214)	−4.77(1)	C(154)	4.90(2)
C(275)	−7.24(2)	C(95)	8.02(3)	C(215)	−4.32(2)	C(155)	4.97(2)
C(276)	−7.76(2)	C(96)	8.63(3)	C(216)	−4.42(3)	C(156)	6.19(2)
C(277)	−8.86(3)	C(97)	9.51(3)	C(217)	−6.14(3)	C(157)	4.32(3)

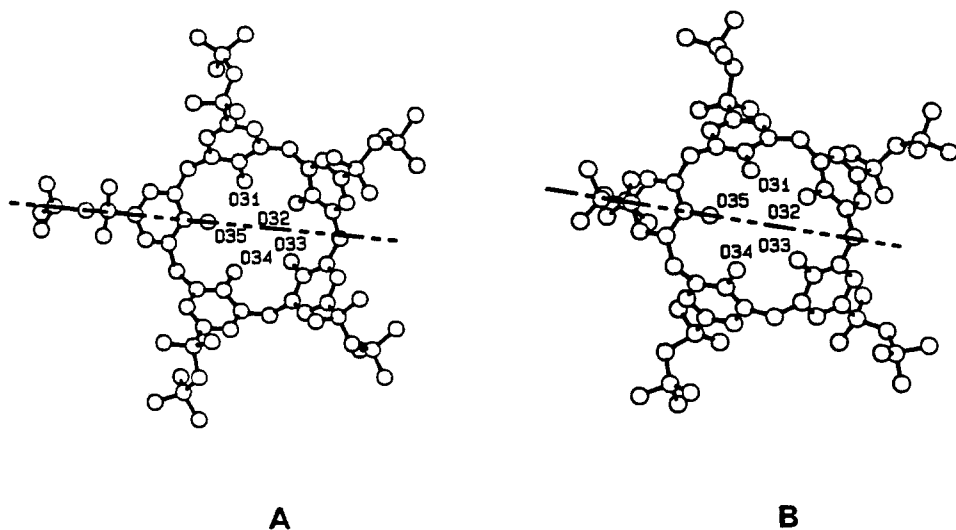A   B

Fig. 2. Conformation of both macrocycles: views perpendicular to the plane O(32), O(33) and O(35).

The conformations of the two calix[5]arene molecules are given in Figure 2 where both drawings are taken perpendicular to the O(32), O(33) and O(35) plane.

3.2. PACKING

The results obtained show that the macrocycle has the 'cone' conformation both in the empty form and in the complex with toluene. Previous observations have shown that the complexes do not always have an intramolecular host–guest character. The clathrate can be of the channel type with the solvent between the macrocycles and the intermolecular van der Waals contacts between both calixarenes and solvent molecules. Only the crystal structure is able to show where the solvent molecules are located in the solid. Looking at compound A, we can see that the toluene is inside the macrocycle, giving a supramolecule with contacts as described here: the carbon of the methyl group has contacts with atoms C(1) → C(5) of ring I with distances between 3.58 and 3.95 Å. This is in agreement with the existence of CH_3-π interaction which determines the inclusion ability of calixarenes towards aromatic molecules [20]. We note the unusual position of the toluene molecule inside the macrocycle with the plane of the benzene ring almost parallel to the plane O(31) → O(35) (dihedral angle 10.3°). The solvent molecule usually has its ring plane almost perpendicular to the plane of the oxygen atoms.

In the crystals, for both compounds, the different macrocycles are bound by van der Waals contacts as shown in Figure 3.

For compound A, the arrangement looks like slices of macrocycles with the aperture of the cones alternatively in one direction, then in the other direction. For compound B, each slice is formed with cones alternatively pointing up and down.
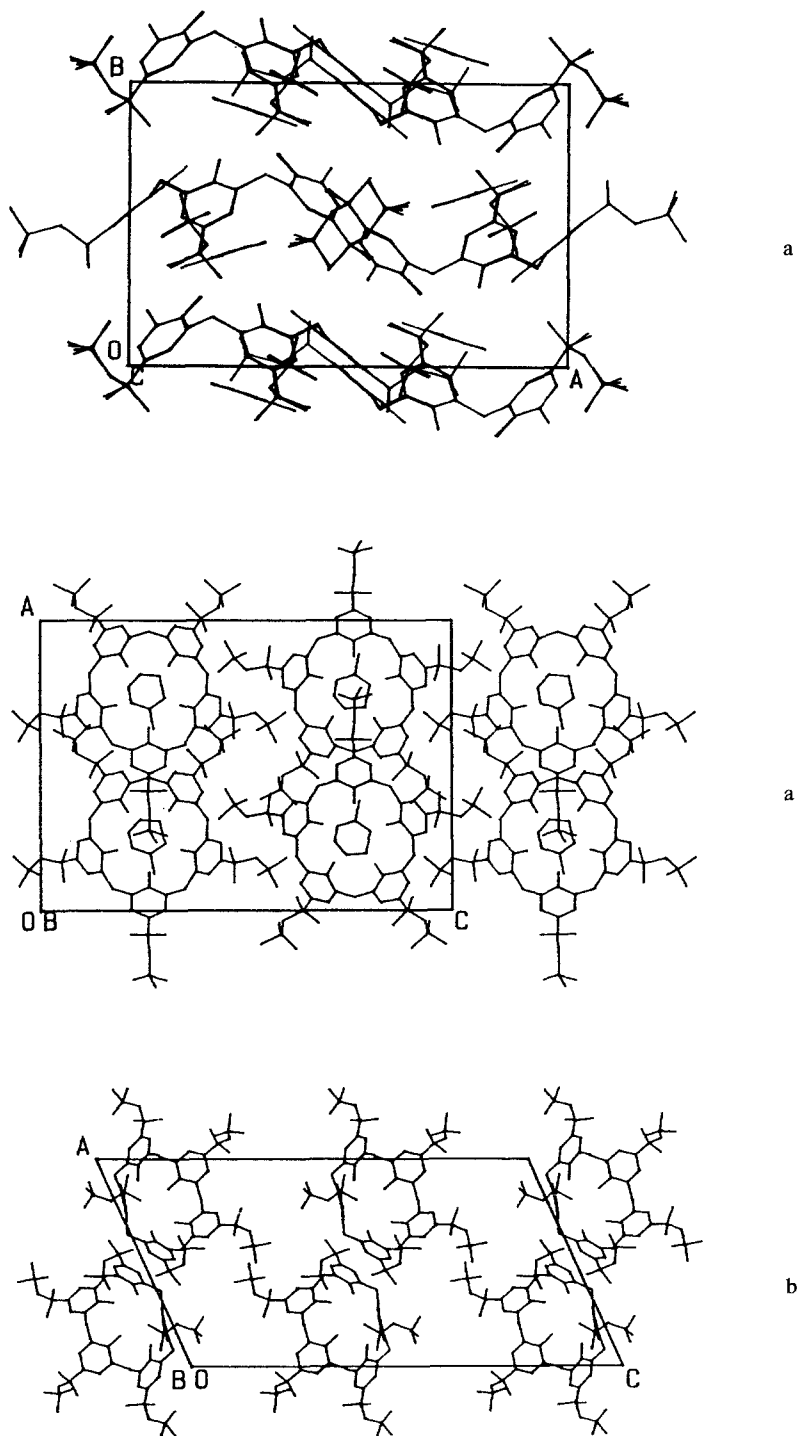
Fig. 3. Packing for both compounds: (a) compound A: view along [001] and [010]; (b) compound B: view along [010].

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