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Pinched-cone Calix[6]arene: New Synthesis of *p*-(1,1,3,3-tetramethylbutyl)calix[6]arene. Structure of its 1 : 3 Complex with Chloroform *

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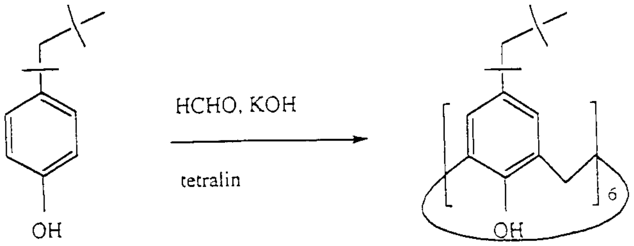
Abstract

A new method is described for the synthesis of *p*-(1,1,3,3-tetramethylbutyl)calix[6]arene isolated in a 30% yield. For the first time the crystal structure is given. The crystals are monoclinic, space group C2/c, a = 24.144(5) Å, b = 14.093(3) Å, c = 26.972(5) Å, β = 93.36(3)°, V = 9162(3) Å^3, Z = 4. The macrocycle with C2 symmetry presents the pinched-cone conformation. It crystallizes with three chloroform molecules, two of them are positioned in the cones shaped by the phenol moieties; the third chloroform is located in the cavity near the hydroxyl groups; this solvent molecule is disordered around the 2 axis. The packing of the complex is described.

Introduction

p-(1,1,3,3-Tetramethylbutyl)calix[n]arenes [1] are not well-known macrocycles. There are few publications about these macrocycles. Munch described the synthesis of *p*-(1,1,3,3-tetramethylbutyl)calix[4]arene [2], and Ungaro *et al.* [3] reported the crystal and molecular structure of this calixarene and its complex with toluene. Shinkai *et al.* [4] described the synthesis of *p*-(1,1,3,3-tetramethylbutyl)calix[6]arene, which was used for the synthesis of carboxylate derivatives. These macrocycles present good extraction abilities of rare earth metal ions.



As a part of our systematic work on the inclusion properties of calixarenes, we report in this paper the synthesis, and for the first time, the crystal and the molecular structure of *p*-(1,1,3,3-tetramethylbutyl)calix[6]arene.

Experimental

Synthesis

p-(l,1,3,3-Tetramethylbutyl)phenol (5 g, 24 mmol), 4.3 mL (57.81 mmol) of 37% formalin solution and 1.294 g (19.6 mmol) of potassium hydroxide pellets (85%) were placed in a 100 mL, three necked, round-bottomed flask equipped with a nitrogen inlet, a mechanical stirrer, a Dean-Stark trap and a condenser. Under a nitrogen atmosphere, the reaction mixture was stirred and heated to 105 °C (15 minutes). 40 mL of tetralin were also added, the solution was refluxed for 5 hours and allowed to cool to room temperature. After removing the solvent in vacuo, the residue was extracted with 100 mL of chloroform. The solution was washed once with 60 mL of 1N hydrochloric acid and three times with 100 mL of water. The chloroform layer was dried over anhydrous sodium sulphate. After removal of sodium sulphate by filtration, and evaporation of the chloroform solution, the precipitate was recrystallised in a chloroform-acetone mixture. The mixture was filtered several times to give 1.59 g (30%) of *p*-(1,1,3,3-tetramethylbutyl)calix[6]arene as a white powder. TLC (SiO_2, chloroform: heptane = 5: 5 v/v, Rf = 0.66); mp (decomp) > 267 °C; ^{1}H NMR (300 MHz, $CDCl_3$, TMS, 25 °C) δ 0.72 (54H, s, $C(CH_3)_3$), 1.29 (36H, s, $C(CH_3)_2$), 1.70 (12H, s, C—CH_2—C), 3.85 (12H, s, br, Ar—CH_2—Ar), 7.07 (12H, s, ArH), 10.27 (6H, s, OH) ; ^{13}C NMR (300 MHz, $CDCl_3$, TMS, 25 °C) δ 29.78 (Ar—$\mathit{C}H_2$—Ar), 32.0, 32.35 and 32.80 (—$\mathit{C}H_3$), 33.41 (—$\mathit{C}(CH_3)_3$), 38.29 (—$\mathit{C}(CH_3)_2$—), 57.45 (—$\mathit{C}H_2$—), 125.78, 127.06, 127.40 and 129.52 (ArC—H), 137.53 (ArC—$C(CH_3)_2$—),

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143.35 (Ar*C*— O); MS (FAB, negative mode, NBA.) m/z: calcd M= 1309, found $[M—H]^-$ = 1308.

Crystallization

Crystals of the named complex were obtained by evaporation of a saturated solution from chloroform at room temperature. A losange shaped crystal was used to study the crystal structure.

Data collection and structure refinement

A Nonius Kappa CCD diffractometer was used for data collection. The selected crystal was mounted on a thin glass fiber and bathed in a cold nitrogen stream for the duration of the collection. From 10 frames with 2° steps, the initial set of cell parameters was obtained. Then 266 frames were collected with 3 strategies. 17772 reflections were collected, of which 9288 unique were used for the structure determination. Table 1 summarizes the values of the different data. The structure was solved by direct methods using the SHELXS [5] program. Due to the space group, only half of the calixarene can be found, i.e., this macrocycle is symmetrical. One of the chloroform molecules is well positioned, but another one is in a disordered position. The structure was refined using SHELXL 97 [6] with anisotropic temperature factors for all non-H atoms. Hydrogen atoms were calculated at theoretical positions and refined riding on C atoms. The final R has a value 0.077 with $I > 2\sigma(I)$.

The final atomic coordinates and equivalent thermal parameters for non-H atoms as well as bond distances and bond angles are in good agreement with other calixarenes and have been deposited as supplementary data.

Results and discussion

Figure 1 shows the numbering scheme on an ORTEP drawing at 50% probability [7]. The title calixarene adopts a pinched cone conformation as do other calix[6]arenes with free OH groups. This shape (Figure 2) with C2 symmetry reveals two half cones and a cavity near the hydroxyl groups, the six oxygen atoms being at the corners of a boat conformation hexagon. The dihedral angles φ and χ as defined by Ugozzoli *et al.* [8] shows the sequence of signs characteristic of the pinched cone conformation: C2(−+, +−, +−). The same sequence is found for other calix[6]arenes already studied: *p-tert*-butylcalix[6]arene crystallized as an empty form, or as the complex with benzene [9] or acetonitrile [10], and also for *p*-isopropylcalix[6]arene [11]. However the values of φ and χ are slightly different as well as the symmetry of the macrocycles. *p-tert*-butylcalix[6]arene-acetonitrile presents a mirror while the title compound has a C2 symmetry. The *p-tert*-butylcalix[6]arene in its empty form has no symmetry. Table 2 gives the φ and χ values for calix[6]arenes and their sequences of signs.

Compounds **1**, **2**, **3** and **4** are all in pinched-cone conformation with some differences about the φ and χ angles. It seems that the volume of the substituent does not affect

Table 1. Crystal data and structure refinement for the title compound

Identification code	*p*-(tert-octyl)calix[6]arene
Empirical formula	$C_{90}H_{132}O_6.3\ CHCl_3$
Formula weight	1668.06
Temperature	123(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, C2/c
Unit cell dimensions	a = 24.144(5) Å
	b = 14.093(3) Å, β = 93.36(3)°
	c = 26.972(5) Å
Volume	9162(3) $Å^3$
Z, Calculated density	4, 1.209 Mg/m^3
Absorption coefficient	0.325 mm^{-1}
F(000)	3576
Crystal size	0.45 × 0.40 × 0.10 mm
Theta range for data collection	1.82 to 26.33 deg.
Limiting indices	$-29 \Leftarrow h \Leftarrow 30$, $-17 \Leftarrow k \Leftarrow 17$, $-33 \Leftarrow 1 \Leftarrow 33$
Reflections collected/unique	17772/9288 [R(int) = 0.0629]
Completeness to theta = 26.33	99.4%
Absorption correction	None
Max. and min. transmission	0.9682 and 0.8674
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	9288/0/511
Goodness-of-fit on F^2	1.036
Final R indices [I > 2 sigma (I)]	R1 = 0.0767, wR2 = 0.1777
R indices (all data)	R1 = 0.1402, wR2 = 0.2102
Largest diff. peak and hole	0.870 and −0.695 e. $Å^{-3}$

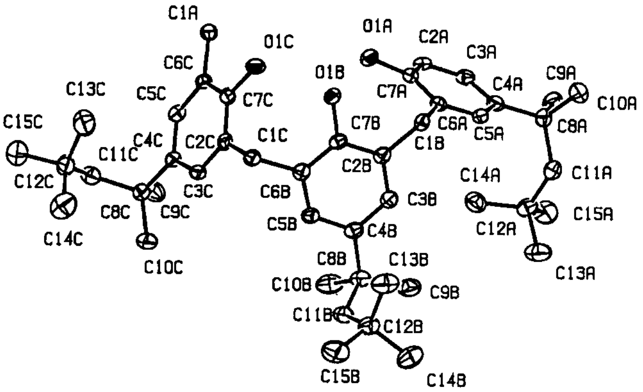

Figure 1. ORTEP drawing and numbering scheme of the asymmetric unit (half calixarene). All the atoms are represented by thermal ellipsoids at 50% probability. H atoms are omitted for clarity.

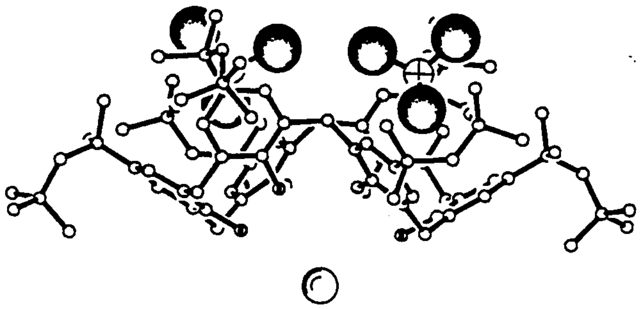

Figure 2. Inclusion complex with the chloroform molecules. The disordered one is shown as a circle.

Table 2. φ and χ angles for some calix[6]arenes

	sym.	φ	χ	φ	χ	φ	χ	φ	χ	φ	χ	φ	χ
1	none	−113.8	+109.1	+96.3	−84.7	+94.8	−109.1	−75.5	+93.0	+93.0	−85.7	+82.5	−98.1
2	none	−92.7	+91.5	+100.5	−83.4	+86.2	−92.2	−101.7	+95.6	+92.1	−84.3	+80.0	−101.5
3	m.	−89.0	+98.0	+95.0	−83.0	+78.0	−98.0						
4	2	−78.1	+117.8	+93.3	−84.9	+75.1	−110.9						
5	none	−5.3	+97.6	+107.7	−74.7	+76.4	−101.7	−97.8	+6.5	−102.3	+81.1	−80.9	+94.4
6	none	+88.5	−86.4	+87.9	−94.2	+92.8	−86.8	+89.2	−90.1				
7	4	+90.3	−90.7										
8	none	+81.5	−100.6	+98.2	−80.9	+84.3	−88.0	+83.1	−84.8	+86.1	−75.8		
9	none	+88.4	−100.1	+98.7	−83.6	+90.2	−85.0	+85.2	−87.1	+85.7	−87.4		

1* *p*-isopropylcalix[6]arene (empty form) (isomorphous with *p*-tertbutylcalix[6]arene
2* *p*-*tert*-butylcalix[6]arene–benzene
3* *p*-*tert*-butylcalix[6]arene–acetonitrile
4* *p*-octylcalix[6]arene (title compound)
5* cumylcalix[6]arene–dimethylformamide
6 *p*-octylcalix[4]arene (empty form)
7 *p*-octylcalix[4]arene–toluene
8 *p*-octylcalix[5]arene (empty form)
9 *p*-octylcalix[5]arene–toluene

*All the sequences begin at the particular CH_2 bridge inside the cavity.

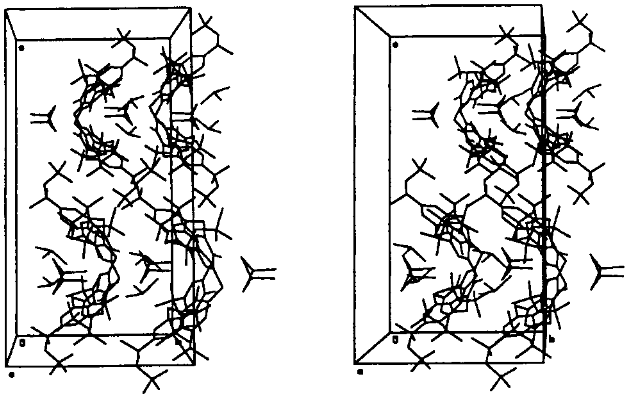

Figure 3. Stereoview of the packing along [100]. The two positions of the disordered chloroform are drawn.

Table 3. Main interactions between chloroform and calixarene (Å)

– chloroform and hydroxyl groups:					
$Cl_4 \cdots O_1B$	3.501	$Cl_4 \cdots O_1C$	3.616	$Cl_4 \cdots O_1A^a$	3.576
– chloroform and phenolic moieties:					
$Cl_1 \cdots O_1A$	3.440	$Cl_1 \cdots C_7A$	3.586		
$Cl_1 \cdots C_2A$	3.508	$Cl_1 \cdots C_7A$	3.360		
$Cl_1 \cdots C_2B$	3.706	$Cl_1 \cdots C_3B$	3.648		
$Cl_1 \cdots$centroïd B	3.502				
– chloroform–chloroform					
$Cl_5 \cdots Cl_3$	3.818				
$Cl_3 \cdots Cl_3^a$	3.251				
a: $1 - X, Y\frac{1}{2} - Z$					

this shape. The cone is destroyed in compound **5**, as already described [12]; this is due to the solvent trapped by the calixarene. Indeed when the solvent does not engage in H-bonds with the OH groups, the cyclic array of intramolecular H-bonds is not disrupted and the cone conformation exists. In contrast, when there are some H-bonds with the solvent, an alternate conformation is seen

Concerning the *p*-(1,1,3,3-tetramethylbutyl) group, several calixarenes (with 4 or 5 moieties) were studied with this substituent [3, 13]; in each case the empty form and the complex with toluene are known. φ and χ angles are also reported in Table 2; it can be seen that the range of values are larger when the number of moieties is increased (86.4 → 94.2 for calix[4], 75.8 → 100.6 for calix[5], and 75.1 → 117.8 for calix[6] (the title compound).

Concerning the octyl chains, the angles at C(11)(A, B or C) have values larger that 109° (123.7, 123.1 and 124.8) as already observed for calix[4]arenes [3] and calix[5]arenes [13]. Four *p*-(1,1,3,3-tetramethyl)chains (for B and C and their symmetric counterparts related by the 2 axis) extended outside the macrocycle. This situation can be compared with that found in calix[4] and calix[5]arenes with the same substituent. With calix[4]arene, the two structures (empty form and complex with toluene) show two octyl chains outside and two inside the macrocycle. In both cases the cavity is empty, the complex with toluene being a tubulato cavitate clathrate. In the case of calix[5]arene, the empty form consists of a macrocycle with four chains outside and one chain inside while the complex shows the toluene molecule inside the cavity and all the 5 octyl chains extended outside.

For the title compound the angles between lines C(4)–C(12) and the aromatic ring have been calculated for the three moieties A, B and C. The values are 139.3, 140.5 and 150.5°. The angles between the phenyl rings and the mean plane defined by the methylene bridges are respectively 142.2(1), 119.64(8) and 130.6(1)° in good agreement with those found for other calix[6]arenes [8, 9, 10]. Intramolecular O···O distances show strong H bonds (2.749, 2.658, 2.747 Å).

The macrocycle crystallizes with 3 $CHCl_3$ molecules; two of them are symmetrically positioned in the half cones. The third is in the cavity found near the hydroxyl groups. This last is in a disordered position around the axis of symmetry with two common chlorine atoms. This molecule is drawn as a circle in Figure 2.

A stereoview of the packing is given in Figure 3. In the 'b' direction, the calixarenes are organized with the three chloroforms between two macrocycles. The disordered chloroform has small interactions with the oxygen atoms of hydroxyl groups; the two chlorine atoms of the molecules, Cl_4 and Cl_4^a, interacts with the six oxygens of the hydroxy groups: Cl_4 with O_1B, O_1C and O_1A^a and Cl_4^a with the others. This situation probably stabilises the conformation of the macrocycles. However, the H-bonds array is not disturbed and the pinched-cone conformation remains. The two other chloroforms lie in the cavity of the calixarene; the chlorine atom Cl(1) interacts with the rings A and B, while Cl(2) points outside the cavity. The third chlorine Cl(3) lies at a distance of 3.818 Å from chlorine Cl(5) of the disordered solvent molecule. These main interactions between chlorine atoms of the chloroform molecules and the macrocycle are given in Table 3.

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