



## Crystal Structures of Two Calix[10]arenes Complexed with Neutral Molecules

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### Abstract

Two calix[10]arenes were synthesized: the tert-butyl calix[10]arene (*t*-Bu-C10) and the detertbutylated analogue (H-C10). Both were crystallized from saturated solutions: *t*-Bu-C10 from a mixture of toluene and tetrahydrofuran (THF), H-C10 from acetone. In each case, complexes were obtained: H-C10, acetone 1 : 2 and *t*-Bu-C10, toluene, THF 1 : 2.5 : 0.5. The crystal structures of these two complexes and the different conformations of the macrocycles are presented here. For the first, the crystals are triclinic, space group  $P\bar{1}$ ,  $a = 9.037(2)\text{Å}$ ,  $b = 11.447(2)\text{Å}$ ,  $c = 15.197(3)\text{Å}$ ,  $\alpha = 80.79(3)^\circ$ ,  $\beta = 84.96(3)^\circ$ ,  $\gamma = 88.60(3)^\circ$ ,  $V = 1545.7(5)\text{Å}^3$ ,  $Z = 1$ ; the complex with *t*-Bu-C10 is orthorhombic, space group  $Fmm2$ ,  $a = 32.211(6)\text{Å}$ ,  $b = 32.289(7)\text{Å}$ ,  $c = 12.179(2)\text{Å}$ ,  $V = 12667(4)\text{Å}^3$ ,  $Z = 4$ . The complex from H-C10 shows a pleated loop conformation with H-bonds between acetone and hydroxyl groups. The complex from *t*-Bu-C10 shows several cavities, in the cones shaped by the phenol moieties and near the hydroxyl groups. The packings are given for both crystals.

### Introduction

Numerous X-ray crystal structures of complexes of calixarenes with neutral molecules have been described in the literature [1, 2]. Only a few of these, however, deal with calixarenes containing more than 6 aryl units [3–6] and none with those containing more than 8. The present paper describes the X-ray crystal structures of two calix[10]arenes, one carrying *p*-*t*-butyl groups (designated as *t*-Bu-C10) complexed with toluene and THF and one carrying only *p*-H (designated as H-C10) complexed with acetone.

### Experimental

#### Synthesis

Calix[10]arene (H-C10) was obtained by de-*t*-butylation of *p*-*t*-butylcalix[10]arene (*t*-Bu-C10), prepared as described in the literature [7, 8]. To 0.20 g (0.12 mmol) of *t*-Bu-C10 dissolved in 20 mL of toluene was added 0.50 g (3.74 mmol; 30 eq.) of anhydrous AlCl<sub>3</sub>. The mixture was stirred for 18 h at room temperature under N<sub>2</sub>, and an additional 0.40 g of AlCl<sub>3</sub> was then added. After stirring for a total of 30 h, 1N HCl was added, the organic phase was separated and washed with H<sub>2</sub>O, dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure. Addition of Et<sub>2</sub>O produced a precipitate

which was removed by filtration, dried, and recrystallized from CHCl<sub>3</sub>/MeOH(5 : 7) to give 0.05 g (40%) of H-C10.

<sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>): 3.87 (s, 20H, ArCH<sub>2</sub>), 6.66 (t, 10H,  $J = 7.5$  Hz, *p*-ArH); 6.87 (d, 20H,  $J = 7.5$  Hz, *m*-ArH); 8.78 (bs, 10H, OH); <sup>13</sup>C NMR (DMSO *d*<sub>6</sub>): 30.44 (CH<sub>2</sub>); 119.69 (C<sub>p</sub>); 127.53 (C–CH<sub>2</sub>); 128.03 (C<sub>m</sub>); 151.79 (C–OH); ES–MS: [M–H] 1059.5 [M + Na–H] 1081.5. Anal. calcd for C<sub>70</sub>H<sub>60</sub>O<sub>10</sub>: 1.2 CHCl<sub>3</sub>: C: 70.99 H: 5.12 O: 13.28; found: C: 70.70 H: 5.48 O: 13.02.

#### Crystal structure analysis

*t*-Bu-C10 gave colorless losangic crystals on evaporation of an saturated solution of a mixture of toluene and THF while H-C10 gave needles from acetone.

Crystals of *t*-Bu-C10 as a 1 : 3 complex with toluene/THF and H-C10 as a 1 : 2 complex with acetone were mounted in glass capillaries and bathed in a stream of cold N<sub>2</sub> during data collection. The cell parameters were calculated from 10 frames with 10 steps, and all reflections were collected to provide the data shown in Table 1.

The structures were found by direct methods using the SHELXS97 [9] program. Due to the space groups, half a calixarene is used in the asymmetric unit for H-C10, and a quarter for *t*-Bu-C10. Both structures were refined using SHELXL97 [9] with anisotropic temperature factors for all non-H atoms. Hydrogen atoms were calculated at theoretical positions and refined riding on C atoms.

In both cases, solvent molecules were trapped: H-C10 gave a 1 : 2 complex with acetone; the two solvent molecules are situated around the center of symmetry of the macro-

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Table 1. Crystal data and structure refinement for calix[10]arenes

Identification code	Calix[10]arene	<i>t</i> -butyl Calix[10]arene
Empirical formula	C <sub>76</sub> H <sub>72</sub> O <sub>12</sub>	C <sub>122.50</sub> H <sub>164</sub> O <sub>10.50</sub>
Formula weight	1177.34	1804.54
Temperature	293(2) K	223(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system, space group	Triclinic, P-1	Orthorhombic, Fmm2
Unit cell dimensions	$a = 9.0371(18)$ Å $\alpha = 80.79(3)^\circ$ $b = 11.447(2)$ Å $\beta = 84.96(3)^\circ$ $c = 15.197(3)$ Å $\gamma = 88.60(3)^\circ$	$a = 32.211(6)$ Å $\alpha = 90^\circ$ $b = 32.289(7)$ Å $\beta = 90^\circ$ $c = 12.179(2)$ Å $\gamma = 90^\circ$
Volume	1545.7(5) Å <sup>3</sup>	12667(4) Å <sup>3</sup>
Z, Calculated density	1, 1.265 Mg/m <sup>3</sup>	4, 0.946 Mg/m <sup>3</sup>
Absorption coefficient	0.085 mm <sup>-1</sup>	0.058 mm <sup>-1</sup>
F(000)	624	3932
Theta range for data collection	2.74 to 29.55 deg.	3.16 to 28.28 deg.
Limiting indices	$0 \leq h \leq 12, -14 \leq k \leq 14, -19 \leq l \leq 19$	$0 \leq h \leq 40, 0 \leq k \leq 40, 0 \leq l \leq 16$
Reflections collected/unique	6859/6859 [R(int) = 0.0000]	4109/4109 IR(int) = 0.00001
Completeness to theta = 29.55	79.4%	96.6%
Refinement method	Full-matrix least-squares on F <sup>2</sup>	Full-matrix least-squares on F <sup>2</sup>
Data/restraints/parameters	6859/72/430	4109/1/362
Goodness-of-fit on F <sup>2</sup>	0.749	1.278
Final R indices [I > 2 sigma (I)]	R1 = 0.0500, wR2 = 0.1036	R1 = 0.0971, wR2 = 0.2732
R indices(all data)	R1 = 0.1487, wR2 = 0.1287	R1 = 0.1105, wR2 = 0.2908
Largest diff. peak and hole	0.298 and -0.275 e.Å <sup>-3</sup>	0.889 and -0.613 e.Å <sup>-3</sup>

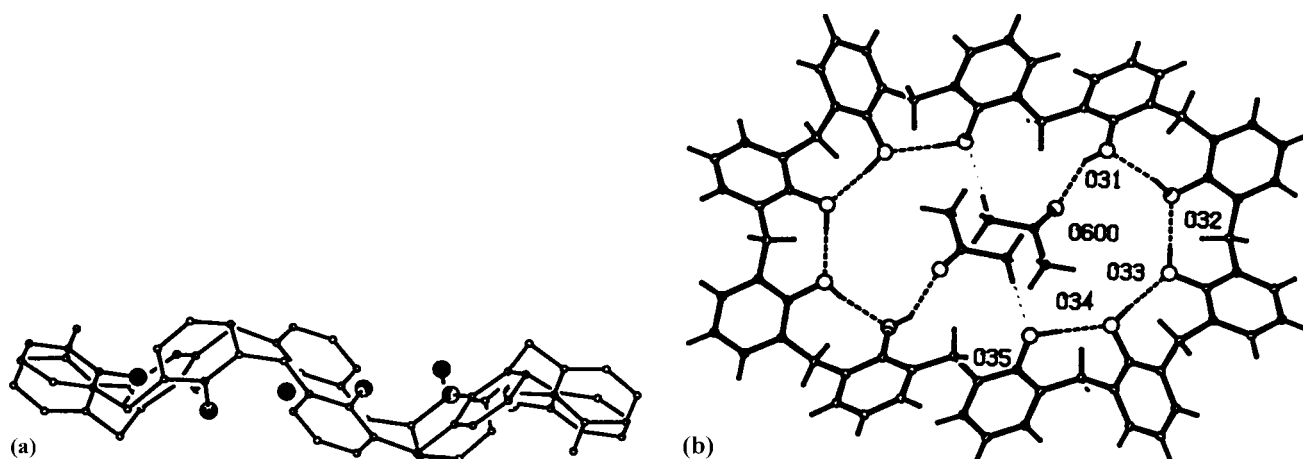


Figure 1. H-C10: (a) view showing the pleated loop conformation; (b) H-bonds and interactions between H-C10 and acetone.

Table 2. Torsion angles  $\phi$  and  $\chi$  for H-C(10) and *tert*-C(10)

$\phi$ angles		$\chi$ angles	
H-C10			
C(5)–C(6)–C(7)–C(8)	-97.6(3)	C(6)–C(7)–C(8)–C(9)	80.3
C(29) <sup>a</sup> –C(30) <sup>a</sup> –C(1)–C(2)	88.6(3)	C(30) <sup>a</sup> –C(1)–C(2)–C(3) <sup>a</sup>	-7.7(3)
C(11)–C(12)–C(13)–C(14)	86.4(2)	C(12)–C(13)–C(14)–C(15)	-90.0(3)
C(17)–C(18)–C(19)–C(20)	-87.6(3)	C(18)–C(19)–C(20)–C(21)	90.8(3)
C(23)–C(24)–C(25)–C(26)	110.9(2)	C(24)–C(25)–C(26)–C(27)	-72.5(3)
<i>t</i> -Bu-C10			
C(3) <sup>b</sup> –C(2) <sup>b</sup> –C(1)–C(2)	-85.8(5)	C(2) <sup>b</sup> –C(1)–C(2)–C(3)	85.8(5)
C(5)–C(6)–C(7)–C(8)	94.8(5)	C(6)–C(7)–C(8)–C(9)	-80.5(4)
C(11)–C(12)–C(13)–C(14)	-78.4(5)	C(12)–C(13)–C(14)–C(15)	86.3(5)

<sup>a</sup> -X + 3, Y, Z.<sup>b</sup> -X, Y, Z.

cycle. *t*-Bu-C10 gave a 1 : 3 complex with toluene and THF. Two toluenes are found symmetrically by a plane, and another site is occupied either by a THF or a toluene molecule. The R values were 0.05 and 0.097 for H-C10 and *t*-Bu-C10, respectively. The coordinates for the atoms along with bond lengths, bond angles, and torsion angles are contained in the Supplementary Data.

## Results and discussion

Figures 1 and 2, calculated with PLATON [10], show the conformation of the macrocycles for each compound. It is seen that they are very different. H-C10 presents a center of symmetry and the conformation is a pleated loop one as already found for *tert*-butyl calix[8]arene [5]. According to

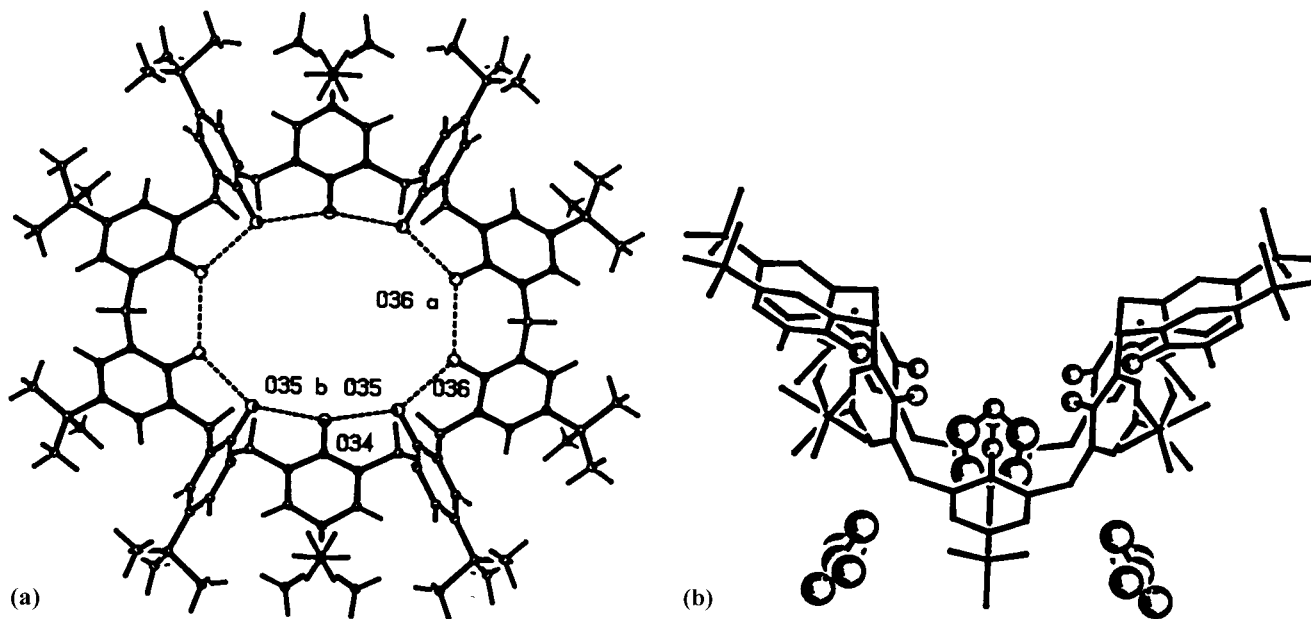


Figure 2. t-Bu-C10: (a) circular H-bonds; (b) view showing the pinched-cone conformation and the guest molecules.

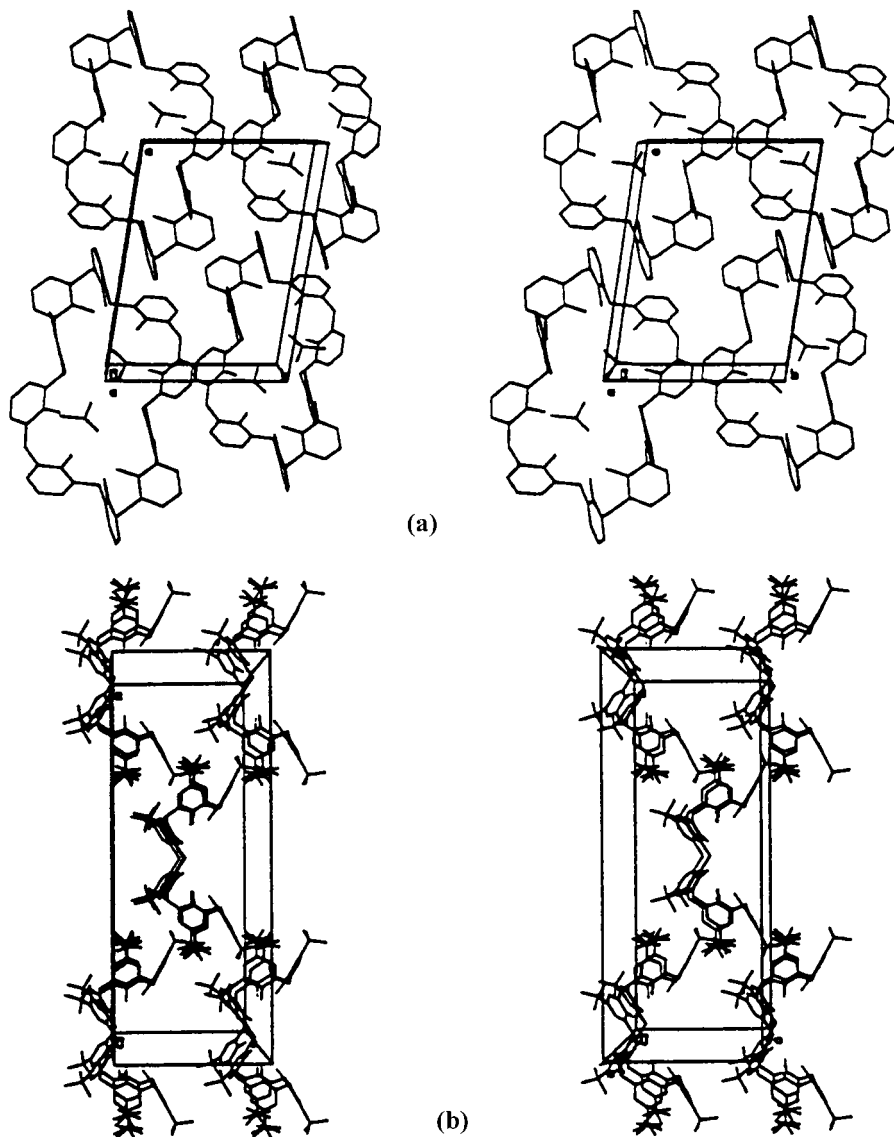


Figure 3. Stereoview of the packing: (a) H-C10 viewed down the [100] direction; (b) t-Bu-C10 with a limited number of molecules for clarity.

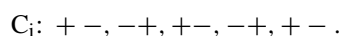
Table 3. Hydrogen bonds for H-C10

	H...A	D...A	D-H...A
O(35)-H(35) ... O(34)	1.956(2)	2.757(2)	165.3(1)
O(34)-H(34) ... O(33)	1.842(2)	2.659(2)	174.1(1)
O(33)-H(33) ... O(32)	1.853(2)	2.671(2)	174.8(1)
O(32)-H(32) ... O(31)	2.032(2)	2.819(2)	160.7(1)
O(31)-H(31) ... O(600)*	1.959(2)	2.650(9)	141.5(3)
O(31)-H(31) ... O(700)*	2.03(1)	2.79(2)	153.2(4)

D...H all at 0.82 Å.

\* O(600) and O(700): two disorder positions of acetone oxygen.

Andreotti *et al.* [12] the conformation can be described with the values of torsional angles  $\varphi$  and  $\chi$ . Table 2 gives their values for both compounds. It is seen that H-C10 can be represented by the sequence:



H-C10 crystallizes as a 1 : 2 complex with acetone. The two guest molecules are situated inside the macrocycle around the center of symmetry. Furthermore the acetone presents a disorder around the carbon atom C(600) of the carbonyl group. So there are two positions for the oxygen viz. O(600) and O(700) and two positions for each of the methyl groups.

Circular H-bonds are usually found for free calixarenes (not substituted at OH groups). In the case of the H-C10 the ring is interrupted at the O(31) ... O(35)<sup>a</sup> bond (4.902(3)Å), due to the solvent trapped. Indeed a hydrogen bond is found between the oxygen atom of the acetone molecule and the oxygen O(31) of the calixarene. Table 3 gives the characteristics of these bonds. Furthermore a short interaction exists between O(35) and one of the hydrogens of one of the methyl groups of the acetone molecule. This situation has already been found with calix[6]arenes: solvents such as acetone, DMSO etc. can disrupt the intramolecular H-bonds; in this case calix[6]arene assumes a distorted 1,2,3-alternate conformation instead of the pinched cone one [13].

In *t*-Bu-C10, the macrocycle has two symmetry planes. Its shape is very similar to that found for calix[6]arene [11]: two cavities are formed by the phenolic moieties and another one is seen near the hydroxyl groups. This is a pinched-cone

conformation.  $\varphi$  and  $\chi$  angles are given on Table II and the sequence is: C<sub>2v</sub>: +, + -, - +.

Circular H-bonds between the hydroxyl groups are found. The O...O distances are: O(34) ... O(35): 2.959(5), O(35) ... O(36): 2.761(4), O(36)<sup>a</sup> ... O36b: 2.753(4)Å. Due to the symmetry of the macrocycle, hydroxyl H atoms are not easily positioned; probably the circular bonds can be clockwise or counter clockwise.

*t*-Bu-C10 trapped neutral molecules in the solid state. First, toluene molecules are situated between macrocycles in such a way that there are two toluenes for one calix[10]arene. Furthermore in the cavity near the OH groups, either a toluene, or a THF molecule are trapped. The refinement with this situation has given the better results, particularly the B factors are reasonable values.

Stereoviews of the packing are given in Figures 3a and 3b.

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