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An Inclusion Complex between Acetonitrile and *p-tert*-Butylcalix[6]arene

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Abstract. *p-tert*-Butylcalix[6]arene forms a complex with 1.5 acetonitrile molecules, that are included in the macrocycle cavity. This complex crystallizes in the monoclinic system: space group $P2_1/m$, $a = 14.043(4)$, $b = 16.916(11)$, $c = 14.199(11)$ Å, $\beta = 98.27(6)°$, $V = 3338(4)$ Å^3, $Z = 2$ (formula units). Refinement led to a final conventional R value of 0.113 for 1654 reflections. The *pinched cone* conformation of the calixarene is the same as that of the neutral and free R-calix[6]arene already described. The two acetonitrile molecules interact with some phenyl ring π-clouds, a methylene bridge and some *tert*-butyl groups of the calixarene.

Key words: *p-tert*-butylcalix[6]arene, guest-host system, crystalline structure.

1. Introduction

The ability of calixarenes to form guest–host systems with various neutral organic molecules has been the subject of intensive work in the past few years (for a review, see [1–2]). The examples of such complexes (either *endo* or *exo* complexes) are particularly numerous in the case of calix[4]arene derivatives but few cases have been reported for calix[6]arene derivatives. Two *endo* complexes of *p-tert*-butylcalix[6]arene have been structurally characterized, with toluene [3] or benzene [4] as a guest molecule. In both cases, the inclusion has no effect on the calixarene conformation, which is the same as that of free *p-tert*-butylcalix[6]arene [3], described as a *pinched cone*. Acetonitrile has previously been shown to behave as a guest molecule with the tetracarbonate of *p-tert*-butylcalix[4]arene [5] and with *p-tert*-butylcalix[4]arene and its dihomooxa analogue [6]. In this paper, we report the crystal and molecular structure of the complex in which two (one half-populated) acetonitrile molecules are included in the cavity of *p-tert*-butylcalix[6]arene.

2. Experimental

2.1. SYNTHESIS

Platelet-shaped crystals suitable for X-ray crystallography were obtained by slow evaporation of a solution of *p-tert*-butylcalix[6]arene (0.3 mmole), purchased from Fluka and used without further purification, in acetonitrile (50 mL) containing a small amount of triethylamine (1.5 mL).

2.2. CRYSTAL DATA

$(C_{66}H_{84}O_6)\cdot(NC_2H_3)_{1.5}$, formula weight = 1034.98. Monoclinic, space group $P2_1/m$ (No. 11); $a = 14.043(4)$, $b = 16.916(11)$, $c = 14.199(11)$ Å, $\beta = 98.27(6)°$, $V = 3338(4)$ Å^3, $Z = 2$ (formula units); $D_x = 1.03$ g cm^{-3}; $\mu = 0.60$ cm^{-1}.

2.3. STRUCTURE DETERMINATION

A crystal of the title compound having approximate dimensions of $0.50 \times 0.50 \times 0.3$ mm was mounted in a glass capillary. The lattice parameters were obtained from the least-squares refinement of the setting angles of 25 reflections ($8 < \theta < 12°$). Data were collected with an Enraf-Nonius CAD4 diffractometer using MoK$_\alpha$ radiation (0.71073 Å) in the range $1 < \theta < 20°$, at room temperature, in the $\omega/2\theta$ scan mode. 3392 reflections were measured, of which 3237 were unique ($R_{\text{int.}} = 0.027$). Three standard reflections, measured every 60 min, indicated an intensity variation of -1.5% that was linearly corrected. 1654 reflections with $I > 3\sigma(I)$ were used after Lorentz-polarization correction. Absorption effects were empirically corrected [7].

The structure was solved by direct methods using SIR88 [8], which gave the main part of the calixarene moiety. The remaining part of the structure (*tert*-butyl groups and acetonitrile molecules) was determined from subsequent Fourier differences. The refinement was performed by full-matrix least-squares on F with anisotropic thermal parameters for the oxygen atoms, the *tert*-butyl groups of rings **1** and **3**, and one of the acetonitrile molecules [N(1)—C(1N)—C(2N)]. The other acetonitrile molecule [N(2)—C(3N)—C(4N)] was difficult to locate properly, probably because of some disorder and/or partial occupation, and has been fixed in the last refinement cycles, with an occupation factor of 0.5. The *tert*-butyl substituents of rings **2** and **4** were found to be disordered and modelled with six isotropic terminal carbon atoms. The hydrogen atoms bound to carbon atoms were located at their ideal positions (C—H 0.95 Å) and constrained to ride their parent atom. Analytical scattering factors for neutral atoms were corrected for f' and f''. The final R values were $R = 0.113$ and $R_w = 0.120$ ($w = 1$) for 236 parameters refined. The residuals on the final electron density map were $\Delta\rho_{\text{max}} = 0.66$ and $\Delta\rho_{\text{min}} = -0.83$ e Å^{-3}. All calculations were performed on a VAX 4200 computer.
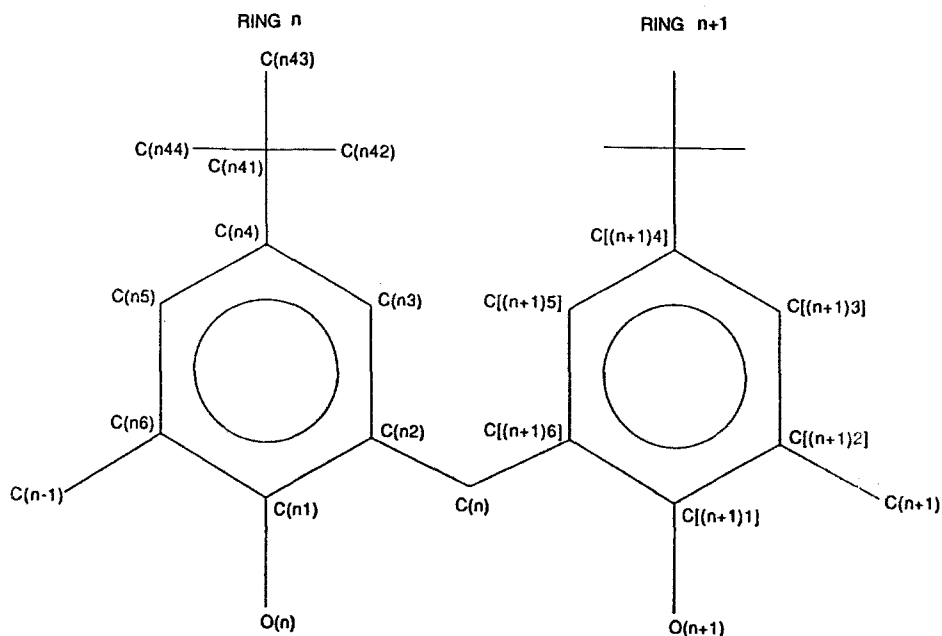
Fig. 1. Atom numbering scheme.

3. Discussion

The structure determination gives the overall formula (*p-tert*-butylcalix[6]arene)·(CH$_3$CN)$_{1.5}$. Fractional atomic coordinates and equivalent displacement parameters are given in Table I. The atom numbering scheme is given in Figure 1, and an ORTEP [9] view of the molecular assembly in Figure 2.

The molecule possesses a symmetry plane, that passes through atoms O(1), C(11), C(14), O(4), C(41) and C(44) and contains the two CH$_3$CN moieties. A pseudo-mirror plane for the calixarene skeleton crosses two methylene bridges at C(2) and C(2^i) and bisects the O(1)—O(4) line: this plane is no longer a mirror when the *tert*-butyl groups and the CH$_3$CN molecules are considered. The shape of the calixarene corresponds to the well-known *pinched cone* conformation, already observed in free *p-tert*-butylcalix[6]arene [3], the oxygen atoms being at the corners of a *boat* conformation hexagon. The O· · ·O distances (O(1)· · ·O(2) 2.64(1), O(2)· · ·O(3) 2.65(1) and O(3)· · ·O(4) 2.61(1) Å) are typical of this conformation and suggest the formation of intramolecular cyclic hydrogen bonding. The ϕ and χ torsion angles used by Ugozzoli and Andreetti [10] to define the calixarene conformation are reported in Table II: they do not differ significantly from those of the free macrocycle.

The most notable feature of this structure is the inclusion of two acetonitrile molecules (one presumably half-populated) in the calixarene cavity. One of them only [N(1)—C(1N)—C(2N)] is well resolved; the assignment of nitrogen and car-

TABLE I. Fractional atomic coordinates and equivalent isotropic displacement parameters for non-hydrogen atoms, with ESD in parentheses. Starred atoms were refined anisotropically ($B_{eq.} = (4/3) \sum_i \sum_j \beta_{ij} \mathbf{a}_i . \mathbf{a}_j$).

Atom	x/a	y/b	z/c	$B_{eq.}$
O(1)	0.6004(8)	0.25	0.5055(7)	3.0(3)*
O(2)	0.4634(6)	0.1490(5)	0.5332(5)	4.0(2)*
O(3)	0.3728(6)	0.1555(5)	0.6842(6)	4.0(2)*
O(4)	0.4169(8)	0.25	0.8288(8)	3.7(3)*
C(1)	0.5938(8)	0.0995(7)	0.4067(9)	3.4(3)
C(2)	0.2619(8)	0.1167(7)	0.5050(8)	3.4(3)
C(3)	0.332(1)	0.1012(8)	0.8630(9)	4.8(3)
C(11)	0.602(1)	0.25	0.407(1)	2.9(4)
C(12)	0.5999(8)	0.1783(7)	0.3589(8)	2.5(2)
C(13)	0.6004(8)	0.1800(8)	0.2619(8)	3.1(3)
C(14)	0.599(1)	0.25	0.210(1)	3.7(4)
C(141)	0.594(1)	0.25	0.102(1)	5.1(6)*
C(142)	0.544(2)	0.180(1)	0.057(1)	14.8(9)*
C(143)	0.689(2)	0.25	0.072(2)	15(1)
C(21)	0.4275(8)	0.0992(8)	0.4592(8)	3.3(3)
C(22)	0.3313(8)	0.0781(8)	0.4454(8)	2.9(3)
C(23)	0.2977(9)	0.0296(8)	0.3709(8)	3.6(3)
C(24)	0.3567(9)	-0.0020(8)	0.3106(9)	4.1(3)
C(25)	0.4533(9)	0.0210(8)	0.3247(9)	3.8(3)
C(26)	0.4901(8)	0.0719(7)	0.3987(8)	2.9(3)
C(241)	0.319(1)	-0.0553(9)	0.227(1)	5.4(4)
C(242)	0.219(2)	-0.066(2)	0.206(2)	10(1)
C(243)	0.353(2)	-0.024(2)	0.130(2)	9.0(9)
C(244)	0.367(2)	-0.135(1)	0.236(2)	7.1(8)
C(245)	0.254(2)	-0.015(3)	0.158(3)	12(2)
C(246)	0.392(2)	-0.096(2)	0.178(2)	10(1)
C(247)	0.264(3)	-0.126(2)	0.265(3)	11(2)
C(31)	0.3012(8)	0.0986(8)	0.6825(8)	3.4(3)
C(32)	0.2836(9)	0.0674(8)	0.7707(9)	3.8(3)
C(33)	0.2118(9)	0.0084(8)	0.765(1)	4.5(3)
C(34)	0.1614(9)	-0.0186(8)	0.6825(9)	3.8(3)
C(35)	0.1805(8)	0.0168(8)	0.5995(9)	3.6(3)
C(36)	0.2502(8)	0.0757(7)	0.5988(8)	2.8(3)

bon atoms is based on the bond distances (N(1)—C(1N) 1.12(4), C(1N)—C(2N) 1.35(4) Å) and supported by previous observations of nitrogen being directed *exo* with respect to the macrocycle cavity [5]. As already noticed [6], this assumption is in agreement with what would be expected if the guest–host interaction was a dipole–dipole one. The second acetonitrile molecule [N(2)—C(3N)—C(4N)] is

TABLE I. Continued.

Atom	x/a	y/b	z/c	$B_{eq.}$
C(341)	0.085(1)	-0.0809(9)	0.682(1)	5.1(4)*
C(342)	0.105(1)	-0.138(1)	0.758(1)	15.8(7)*
C(343)	0.069(2)	-0.128(1)	0.601(1)	20.7(9)*
C(344)	-0.005(1)	-0.044(1)	0.691(2)	22(1)*
C(41)	0.331(1)	0.25	0.869(1)	3.8(4)
C(44)	0.157(1)	0.25	0.940(1)	4.4(5)
C(45)	0.2016(9)	0.1806(9)	0.9238(9)	4.7(3)
C(46)	0.2876(9)	0.1783(8)	0.8872(8)	3.6(3)
C(441)	0.057(2)	0.25	0.979(2)	6.6(6)
C(442)	0.047(3)	0.177(2)	1.039(2)	14(2)
C(443)	-0.019(3)	0.25	0.895(3)	14(2)
C(444)	-0.005(2)	0.181(2)	0.951(2)	11(1)
C(445)	0.080(4)	0.25	1.079(3)	11(2)
N(1)	0.176(2)	0.25	0.325(2)	9.2(7)*
C(1N)	0.247(2)	0.25	0.297(2)	8.1(8)*
C(2N)	0.332(2)	0.25	0.263(2)	11(1)*
N(2)	-0.071	0.25	0.671	10.4
C(3N)	0.026	0.25	0.653	12.8
C(4N)	0.101	0.25	0.653	13.7

TABLE II. Values of the torsional angles ϕ and χ (°) defining the calixarene conformation (ϕ = C(n3)—C(n2)—C(n)—C[(n + 1)6], χ = C(n2)—C(n)—C[(n + 1)6]—C[(n + 1)5]).

Ring numbers	ϕ	χ
1–2	−83(1)	95(1)
2–3	98(1)	−89(1)
3–4	−98(2)	78(2)

badly resolved and its direction has been assumed to be identical to that of the first molecule (nitrogen *exo*). The orientation of the CH_3CN axis with respect to the calixarene is different for the two molecules, probably in relation with the asymmetry observed between the *tert*-butyl groups of rings 1 and 4. The shortest intermolecular host–guest distances are found between N(1) and C(2) (3.49(3) Å) and between N(2) and C(443) (3.17(7) Å); many other contacts below 3.9 Å exist between both guest molecules and the methylene carbon atom C(2), the aromatic carbon atoms of rings 1, 2 and 3, and the *tert*-butyl groups of rings 2 and 4. Some contacts are also observed with the neighbouring calixarene moieties along the c-axis (N(1)—C(445) 3.56(6), N(2)—C(247) 3.64(4) Å). Those distances compare well with the 3.80 (between the methyl C and an aromatic C) and
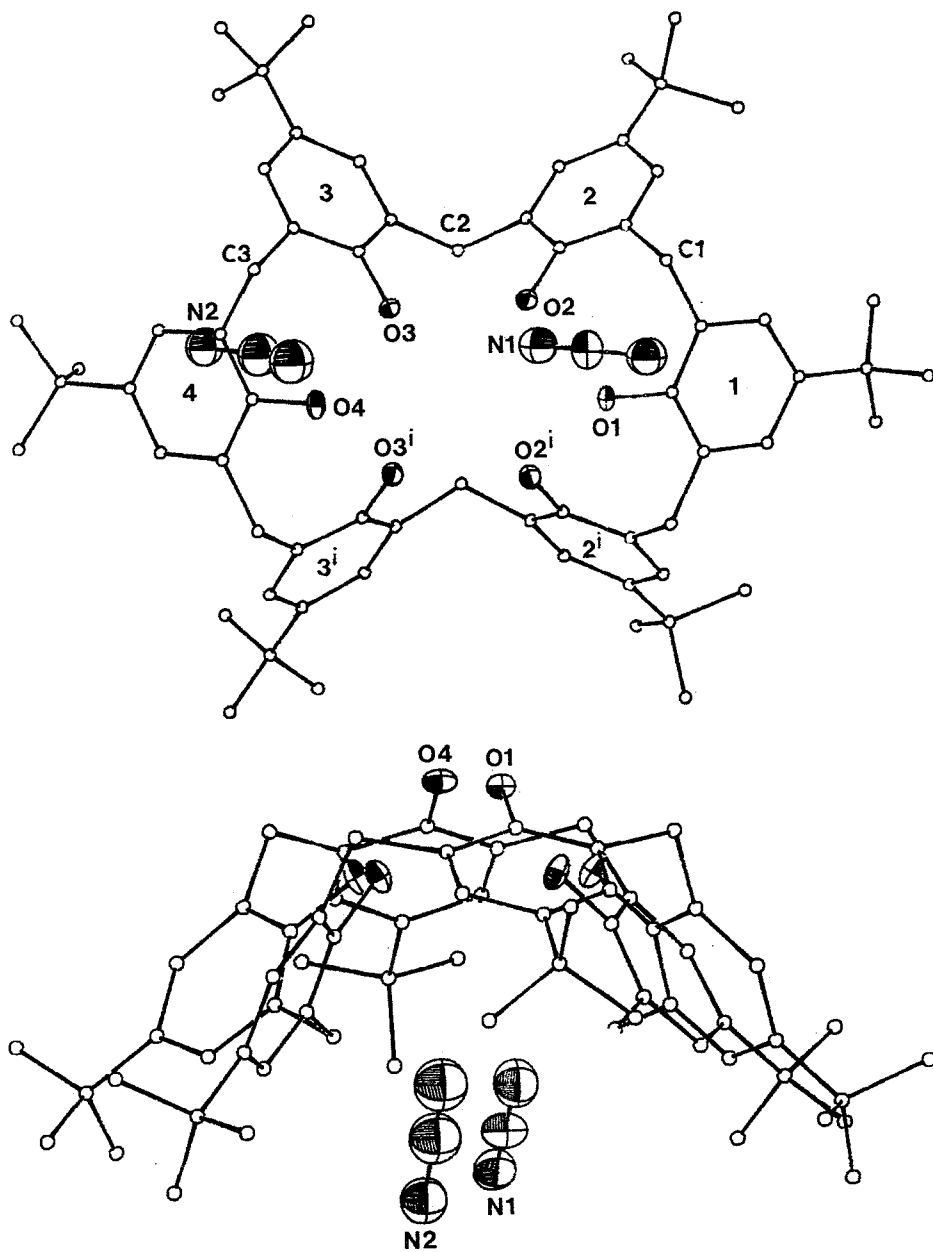
Fig. 2. Two views of (p-tert-butylcalix[6]arene)·(CH₃CN)₁.₅. $i = x, 1/2 - y, z$. For clarity, the carbon atoms of the calixarene moiety are drawn as small spheres of arbitrary radius.

3.96 Å (between N and a tert-butyl C) distances found in (p-tert-butylcalix[4]arene tetracarbonate)·(CH₃CN) [5]. They are indicative of interactions between methyl

groups and both the aromatic π-clouds and the alkyl groups (methylene bridges and *tert*-butyl substituents).

The only examples of guest–host systems based on calix[6]arene derivatives reported up to now involve aromatic guest molecules [3,4]. On the other hand, the ability of *p-tert*-butylcalix[4]arene derivatives to include acetonitrile is well known [5,6]. In this last case, the presence of the *tert*-butyl substituents has been shown to play a prominent role and to be necessary for the inclusion to take place: an *exo* complex only is formed with calix[4]arene [6]. The included acetonitrile molecule is generally located on the fourfold axis of the *p-tert*-butylcalix[4]arene derivative, but, in the case of the less-symmetrical dihomooxa derivative, it adopts a tilted and off-center position [6] comparable to that observed in our case for each CH_3CN moiety: the cavity of calix[6]arene derivatives being larger than that of calix[4]arene derivatives, the included CH_3CN molecule cannot interact equally with each phenolic unit, hence it adopts an off-center position and tilts with respect to the cone axis. The inclusion of two solvent molecules in a calixarene cavity has already been observed, either in the larger cavity of calix[8]arene octamethyl ether with $CDCl_3$ as a guest [11], or in the smaller one of dihomooxa-*p-tert*-butylcalix[4]arene, in which both one DMSO and one acetone molecules can penetrate [12]. This ability to bring two molecular species close together can be considered as indicative of the interest of calixarenes as 'enzyme mimics' [12].

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