

A Doubly Deprotonated Form of Calix[6]arene: Crystal and Molecular Structure of (Calix[6]arene-2H)²⁻ · (HNEt₃⁺)₂

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Abstract. The doubly deprotonated form of calix[6]arene, with two protonated triethylamines as counter-ions, crystallizes in the monoclinic system: space group $P2_1/n$, $a = 8.465(4)$, $b = 17.822(8)$, $c = 15.182(6)$ Å, $\beta = 90.18(4)^\circ$, $V = 2291(2)$ Å³, $Z = 2$. Refinement led to a final conventional R value of 0.063 for 1046 reflections. The macrocycle conformation is not a *pinched cone*, usual for free R -calix[6]arene, but a distorted 1,2,3-*alternate cone*, since the molecule lies on a symmetry center. Furthermore, one of the torsion angles defined by the methylene bridges is near to zero, which is unusual in calixarene structures.

Supplementary Data relating to this article (atomic coordinates for hydrogen atoms, anisotropic displacement parameters for oxygen and nitrogen atoms, and observed and calculated structure factors) are deposited with the British Library as Supplementary Publication No. SUP 82182 (7 pages).

Key words: Calix[6]arene, calixarene conformation, crystalline structure.

1. Introduction

The high flexibility of calixarenes [1] gives rise to a large number of conformations depending primarily on the presence of bulky substituents and also on more subtle effects due to intramolecular hydrogen bonding or to the complexation of neutral molecules or ions. These conformational properties have recently been reviewed [2] and an unequivocal symbolic representation of the calixarene conformations proposed [3]. In the solid state, the structures determined so far for R -calix[6]arene with free OH groups (where R is a substituent at the *para* position on the phenolic ring) show that the molecule generally possesses a symmetry plane, resulting in the *pinched cone* conformation with oxygen atoms at the corners of a *boat* conformation hexagon and O · · O distances indicative of the presence of intramolecular cyclic hydrogen bonding [2, 4]. Some exceptions have been reported, such as the structure of *p*-sulfonatocalix[6]arene and its octaanion [5], in which the macrocycle adopts a 1,2,3-*alternate* or *double partial cone* conformation and lies around a symmetry center. The other examples of molecules with a symmetry center coinciding with

a crystallographic one are O-derivatives of *R*-calix[6]arene [2, 6] and/or metal-coordinating calix[6]arenes (see for example [7, 8]): in the first case, this has been attributed to the suppression of intramolecular cyclic hydrogen bonding and the subsequent release of the macroring [6]. We report here the crystal and molecular structure of the amine salt of the doubly deprotonated form of calix[6]arene, noted (calix[6]arene-2H)²⁻, which also adopts a *1,2,3-alternate cone* conformation.

2. Experimental

2.1. SYNTHESIS

Calix[6]arene (0.25 mmole), purchased from Janssen Chimica and used without further purification, was reacted with a large excess of triethylamine (10 mL) in acetonitrile (15 mL). A clear colourless solution resulted which, on slow evaporation, yielded platelet-shaped crystals suitable for X-ray crystallography.

2.2. CRYSTAL DATA

(C₄₂H₃₄O₆²⁻)·(NC₆H₁₆⁺)₂, formula weight = 839.2. Monoclinic, space group *P*2₁/*n* (No. 14); *a* = 8.465(4), *b* = 17.822(8), *c* = 15.182(6) Å; β = 90.18(4)°; *V* = 2291(2) Å³; *Z* = 2; *D_x* = 1.22 g cm⁻³; μ = 0.73 cm⁻¹.

2.3. STRUCTURE DETERMINATION

A crystal of the title compound having approximate dimensions of 0.50 × 0.40 × 0.15 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 < θ < 12°). Data were collected with an Enraf-Nonius CAD4 diffractometer using MoK_α radiation (0.71073 Å) in the range 1 < θ < 23°, at room temperature, in the ω/2θ scan mode. 3569 reflections were measured, of which 3141 were unique (*R*_{int.} = 0.021). Three standard reflections, measured every 60 min, indicated an intensity variation of -0.4% that was linearly corrected. 1046 reflections with *I* > 3σ(*I*) were used after Lorentz-polarization correction; absorption effects were empirically corrected [9].

The structure was solved by direct methods using SIR88 [10] and refined by full-matrix least-squares on *F*² with anisotropic thermal parameters for oxygen and nitrogen atoms. The hydrogen atoms bonded to carbon atoms were located at their ideal positions (C—H 0.95 Å) and constrained to ride their parent carbon atom. Analytical scattering factors for neutral atoms were corrected for *f*' and *f*". The final *R* values were *R* = 0.063 and *R_w* = 0.066 (*w* = 1) for 145 parameters refined. The residuals on the final electron density map were Δρ_{max.} = 0.31 and Δρ_{min.} = -0.19 e Å⁻³. All calculations were performed on a VAX 4200 computer.

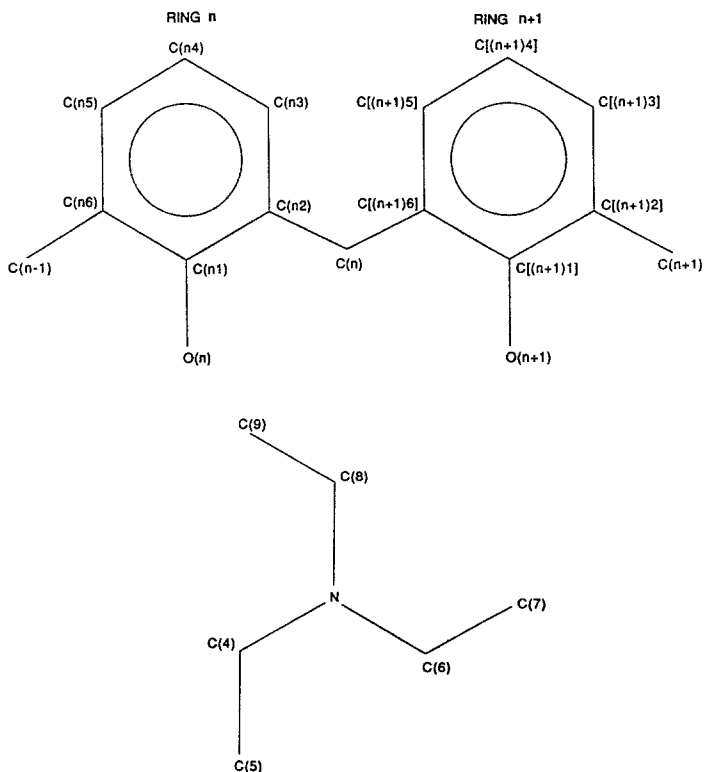


Fig. 1. Atom numbering scheme.

3. Discussion of Results

The structure determination gives the overall formula $(\text{H}_4\text{L}^{2-}) \cdot (\text{HNET}_3^+)_2$ (where L^{6-} is the six-fold deprotonated form of calix[6]arene). The asymmetric unit contains only one half of the macrocycle and one triethylamine molecule since the calixarene molecule lies on a symmetry center. Fractional atomic coordinates and equivalent thermal parameters are given in Table I and selected bond distances and angles in Table II. The atom numbering scheme is given in Figure 1, an ORTEP [11] view of the molecule and the counter-ions in Figure 2 and a stereoscopic view of the packing in Figure 3. Bond distances and angles in both the macrocycle and the triethylamine molecule do not present any abnormal features.

The existence of a 1 : 2 calixarene/triethylamine adduct in the solid state is at variance with the 1 : 1 ratio determined in benzonitrile solution by conductometric measurements; however, potentiometric measurements have shown the particular stability of the doubly deprotonated form of calix[6]arene [12].

The $\text{O}(2) \cdots \text{N}$ distance of 2.67(1) Å indicates a possible strong hydrogen bond between the deprotonated phenolic oxygen and the protonated nitrogen of triethylamine, confirmed by the presence of a peak attributable to the hydrogen

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

Atom	x/a	y/b	z/c	$B_{eq.}$
O(1)	0.2419(7)	-0.0583(3)	0.1736(4)	3.9(2)*
O(2)	0.2501(6)	0.0801(3)	0.2104(4)	3.3(1)*
O(3)	0.0898(7)	0.1303(3)	0.0700(4)	4.3(2)*
C(1)	0.132(1)	-0.0181(5)	0.3462(6)	3.9(2)
C(2)	0.196(1)	0.2380(5)	0.2045(5)	3.5(2)
C(3)	-0.119(1)	0.1655(5)	-0.0662(6)	4.1(2)
C(11)	0.107(1)	-0.0916(5)	0.2049(5)	3.0(2)
C(12)	0.046(1)	-0.0723(5)	0.2874(6)	3.3(2)
C(13)	-0.091(1)	-0.1101(5)	0.3143(6)	4.0(2)
C(14)	-0.164(1)	-0.1610(6)	0.2623(6)	4.3(2)
C(15)	-0.099(1)	-0.1814(5)	0.1806(6)	3.6(2)
C(16)	0.037(1)	-0.1465(5)	0.1513(5)	2.8(2)
C(21)	0.154(1)	0.1096(5)	0.2740(6)	3.2(2)
C(22)	0.121(1)	0.1867(5)	0.2710(6)	3.3(2)
C(23)	0.017(1)	0.2155(6)	0.3339(6)	4.0(2)
C(24)	-0.051(1)	0.1713(5)	0.3980(6)	4.3(2)
C(25)	-0.011(1)	0.0967(6)	0.4000(6)	4.2(2)
C(26)	0.090(1)	0.0641(5)	0.3396(6)	3.2(2)
C(31)	0.048(1)	0.2047(5)	0.0636(6)	3.1(2)
C(32)	-0.049(1)	0.2244(5)	-0.0068(6)	3.2(2)
C(33)	-0.094(1)	0.2984(5)	-0.0170(6)	4.3(2)
C(34)	-0.040(1)	0.3530(6)	0.0416(6)	4.7(2)
C(35)	0.051(1)	0.3323(5)	0.1113(6)	3.9(2)
C(36)	0.100(1)	0.2588(5)	0.1255(6)	3.1(2)
N	0.5613(8)	0.0870(5)	0.1820(5)	3.9(2)*
C(4)	0.648(1)	0.0953(7)	0.2664(7)	6.8(3)
C(5)	0.592(1)	0.0461(6)	0.3364(7)	6.9(3)
C(6)	0.588(1)	0.0143(6)	0.1354(7)	5.2(3)
C(7)	0.754(1)	-0.0001(7)	0.1049(7)	6.6(3)
C(8)	0.602(1)	0.1544(6)	0.1247(7)	5.8(3)
C(9)	0.512(1)	0.1532(7)	0.0403(7)	7.3(3)

atom on the final electron density map, with an approximately correct geometry. Such hydrogen bonds between protonated triethylamine molecules and calixarene oxygen atoms have already been observed in some other compounds, with $\text{N} \cdots \text{O}$ distances of 2.90(1) Å [13], 2.65(1) Å [14] and 2.78(4) Å [15]. Other nitrogen-containing species give hydrogen bonds with phenolic oxygen atoms, such as pyridine with *p*-*tert*-butylcalix[7]arene ($\text{O} \cdots \text{N}$ 2.632(8) Å) [16] or *p*-*tert*-butylcalix[8]arene ($\text{O} \cdots \text{N}$ 2.708(6) Å) [17]. In the structure reported here; the

TABLE II. Selected bond distances (Å) and angles (°), with ESD in parentheses. Symmetry code: $i = -x, -y, -z$.

<i>Bond distances (Å)</i>			
O(1)—C(11)	1.37(1)	O(2)—C(21)	1.37(2)
O(3)—C(31)	1.38(1)	C(1)—C(12)	1.50(1)
C(1)—C(26)	1.51(1)	C(2)—C(22)	1.50(2)
C(2)—C(36)	1.49(1)	C(3)—C(32)	1.51(2)
C(3)—C(16 ⁱ)	1.51(2)	C(11)—C(12)	1.40(1)
C(12)—C(13)	1.41(2)	C(13)—C(14)	1.35(2)
C(14)—C(15)	1.40(1)	C(15)—C(16)	1.38(1)
C(16)—C(11)	1.41(1)	C(21)—C(22)	1.40(1)
C(22)—C(23)	1.40(1)	C(23)—C(24)	1.38(1)
C(24)—C(25)	1.37(1)	C(25)—C(26)	1.38(1)
C(26)—C(21)	1.39(2)	C(31)—C(32)	1.39(1)
C(32)—C(33)	1.38(1)	C(33)—C(34)	1.40(1)
C(34)—C(35)	1.36(1)	C(35)—C(36)	1.39(1)
C(36)—C(31)	1.42(1)		
N—C(4)	1.49(2)	N—C(6)	1.49(2)
N—C(8)	1.52(2)	C(4)—C(5)	1.46(2)
C(6)—C(7)	1.50(2)	C(8)—C(9)	1.49(1)
<i>Bond angles (°)</i>			
O(1)—C(11)—C(12)	120.9(9)	O(1)—C(11)—C(16)	116.9(9)
C(11)—C(12)—C(13)	116.7(9)	C(12)—C(13)—C(14)	121.7(9)
C(13)—C(14)—C(15)	121(1)	C(14)—C(15)—C(16)	119.4(9)
C(15)—C(16)—C(11)	118.6(9)	C(16)—C(11)—C(12)	122.2(8)
C(11)—C(12)—C(1)	120.6(8)	C(13)—C(12)—C(1)	122.5(9)
C(12)—C(1)—C(26)	118.0(8)	C(1)—C(26)—C(21)	121.3(9)
C(1)—C(26)—C(25)	120.6(9)	O(2)—C(21)—C(22)	118(1)
O(2)—C(21)—C(26)	121(1)	C(21)—C(22)—C(23)	118(1)
C(22)—C(23)—C(24)	122(1)	C(23)—C(24)—C(25)	118(1)
C(24)—C(25)—C(26)	123(1)	C(25)—C(26)—C(21)	118.0(9)
C(26)—C(21)—C(22)	121(1)	C(21)—C(22)—C(2)	122(1)
C(23)—C(22)—C(2)	120(1)	C(22)—C(2)—C(36)	117.6(8)
C(2)—C(36)—C(31)	122.2(6)	C(2)—C(36)—C(35)	121.4(4)
O(3)—C(31)—C(32)	117(1)	O(3)—C(31)—C(36)	122(1)
C(31)—C(32)—C(33)	119(1)	C(32)—C(33)—C(34)	120.1(8)
C(33)—C(34)—C(35)	119.6(4)	C(34)—C(35)—C(36)	123(1)
C(35)—C(36)—C(31)	116.4(5)	C(36)—C(31)—C(32)	121(1)
C(31)—C(32)—C(3)	121(1)	C(33)—C(32)—C(3)	119(1)
C(32)—C(3)—C(16 ⁱ)	119(1)	C(3)—C(16 ⁱ)—C(11 ⁱ)	117.2(9)
C(3)—C(16 ⁱ)—C(15 ⁱ)	124(1)		
C(4)—N—C(6)	114.8(9)	C(4)—N—C(8)	107.7(8)
C(6)—N—C(8)	112(1)	N—C(4)—C(5)	114(1)
N—C(6)—C(7)	115.9(9)	N—C(8)—C(9)	111(1)

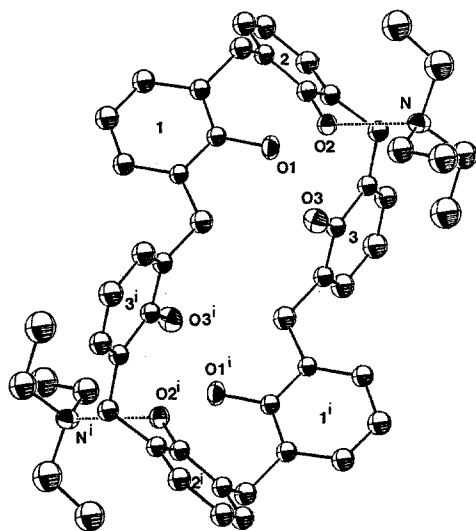


Fig. 2. View of $(\text{Calix}[6]\text{arene-2H})^{2-} \cdot (\text{HNEt}_3^+)_2$. Intermolecular hydrogen bonds are indicated by dashed lines. Symmetry code: $i = -x, -y, -z$.

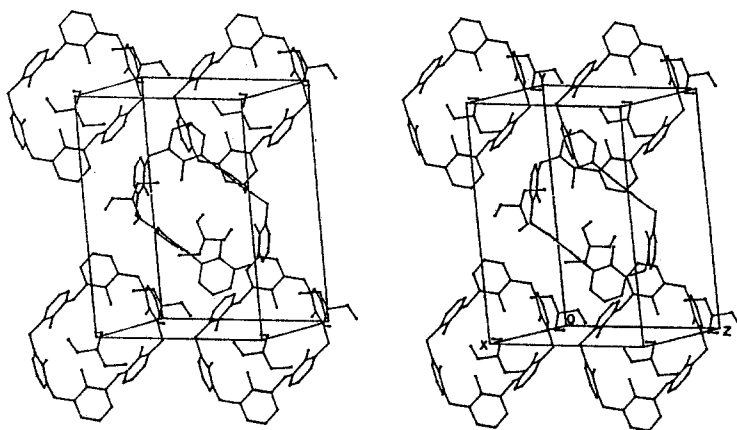


Fig. 3. Stereoscopic view of the crystal packing.

triethylamine molecules are outside the macrocycle cavity: this situation is quite different from the one observed in the structure of the complex between NMe_4^+ and $(p\text{-tert-butylcalix}[6]\text{arene-2H})^{2-}$, proposed on the basis of NMR experiments [18], in which one cation is enclosed by three phenyl groups and the other is free. The difference may be due to the fact that the location of HNEt_3^+ in our case is essentially determined by the strong $\text{O}(2) \cdots \text{N}$ hydrogen bond while such a situation is impossible in the second case.

The mean plane formed by the methylene carbon atoms is generally chosen as a reference plane for the molecule. In our case, the maximum deviation of

TABLE III. Values of the torsional angles ϕ and χ (°) defining the calixarene conformation ($\phi = \text{C}(n3) - \text{C}(n2) - \text{C}(n) - \text{C}[(n+1)6]$, $\chi = \text{C}(n2) - \text{C}(n) - \text{C}[(n+1)6] - \text{C}[(n+1)5]$).

Ring numbers	ϕ	χ
1-2	-93 (1)	99 (1)
2-3	-81 (1)	114 (1)
3-1 ⁱ	91 (1)	-2 (1)

± 0.77 Å of the methylene carbon atoms from their mean plane is so large that the plane does not make a useful reference. On the other hand, the six oxygen atoms are in a plane with a maximum deviation of ± 0.09 Å; the three planes defined by the phenolic rings **1**, **2** and **3** have dihedral angles with this mean plane of 99.4(2), 106.5(2) and 7(1)° respectively: the plane of rings **3** and **3ⁱ** (where $i = -x, -y, -z$) is nearly parallel to the mean plane, the oxygen atoms O(3) and O(3ⁱ) pointing towards the interior of the macrocycle. Despite the departure of the six methylene carbon atoms from a plane, the conformation of the macrocycle can be described in the notation proposed by Kanamathareddy and Gutsche [19] as (*u, u, o, d, d, o*) with the methylene carbon atoms mean plane as a reference.

The conformation of calixarenes can also be described, using the symbolic representation proposed by Ugozzoli and Andreotti [3], by the Schoenflies symbol of the point group symmetry of the molecule and the sequence of the signs of the ϕ and χ torsion angles defined by the methylene bridges around the molecule. The values of the six angles necessary to describe the conformation of the title molecule are given in Table III. It may be noticed that one of these angles is near to zero (C(32)—C(3)—C(16ⁱ)—C(15ⁱ)—2(1)°). The resulting conformation corresponds to $C_i + -, +-, -0$. The sequence $+-, +-$ indicates a *cone* arrangement for the three rings on one half of the molecule, the conformation of the whole being a *1,2,3-alternate cone* or *hinged, three up, three down*, as the one already observed in the octaanion of *p*-sulfonatocalix[6]arene [5] or in the Eu³⁺ complex of (*p*-*tert*-butylcalix[6]arene-2H)²⁻ [8]; the same conformation has also been proposed for the inclusion complex of NMe₄⁺ with (*p*-*tert*-butylcalix[6]arene-2H)²⁻ [18]. This is one of the possible conformations for *p*-*tert*-butylcalix[6]arene in solution [20]. The occurrence of this conformation in the solid state in our case can be ascribed to the fact that the situation in which both triethylamine molecules would lie on the same side of the macrocycle would be energetically unfavourable owing to electrostatic repulsion between charged species. Another similarity with the Eu³⁺ complex is the occurrence of a very low value for one torsion angle, nearly zero in our case, or 3–6° in the complexing molecule of reference [8] (174–177° with the convention used by the authors).

The O...O distances (O(1)—O(2) 2.53(1), O(2)—O(3) 2.68(1), O(1)—O(3) 3.93(1), O(3)—O(1ⁱ) 4.82(1) Å) indicate possible intramolecular hydrogen bonding in each *half-cone* groups (between O(2) and O(1) or O(3)); this hydrogen bonding array is disrupted between rings **3** and **1ⁱ** as a consequence of the upside-down reversal of the *cone* shape. On the final electron density map, some residual density peaks actually appear, which may be due to the hydrogen atoms located between O(1) or O(3) and O(2). An analogous situation occurs in the octaanion of *p*-sulfonatocalix[6]arene [5] (in which two phenolic oxygen atoms are deprotonated). It has been suggested that the formation of strong hydrogen bonds between the deprotonated oxygen atoms and their two protonated neighbours could account for the low acidity of the remaining protons [5, 12].

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