Journal of Inclusion Phenomena and Macrocyclic Chemistry **40:** 221–224, 2001.

Large Calixarenes: Structure and Conformation of a Calix[16]arene Complexed with Neutral Molecules *

C. BAVOUX[1], R. BAUDRY[2], I. DUMAZET-BONNAMOUR[2], R. LAMARTINE[2] and M. PERRIN[1]**
Université Claude Bernard Lyon I, UMR 5078, [1]Laboratoire de Cristallographie, [2]Laboratoire de Chimie Industrielle, 43, Boulevard du 11 Novembre 1918, 69622 Villeurbanne cedex, France

(Received 20 December 2000; in final form 23 March 2001)

Key words: calix[16]arene, complexation, crystal structure, large calixarenes

Abstract

A crystal of an inclusion compound between a calix[16]arene and molecules of acetonitrile and dichloromethane, used as solvents, has been obtained and its X-ray structure studied. The cell is monoclinic, space group C2/c with $a = 38.508(8)$ Å, $b = 21.593(4)$ Å, $c = 26.625(5)$ Å and $\beta = 121.34(3)°$. The macrocycle is in the form of two superimposed celtic torcs connected by their extremities.[1] Two acetonitrile molecules are situated in the middle of this double torc, two dichloromethane molecules are encapsulated in the pseudo calix[4]arenes obtained on both extremities of the torcs by the folding of the last four phenolic rings. A disorder is observed for the other acetonitrile and dichloromethane molecules situated outside the macrocycle.

Introduction

As part of our studies dealing with large calixarenes ($n > 8$), we recently presented the synthesis [1] and the X-ray structure of calix[10]arenes complexed with neutral molecules [2] and a study of the *p-tert*-butylcalix[12]arene and its uranyl complex [3]. In making the most of the Stewart and Gutsche procedure [4] we have isolated *p-tert*-butylcalix[16]arene; single crystals have been obtained. Up to now the largest calixarene to have its structure determined is a calix[12]arene. Herein we present the X-ray structure and the conformation of this macrocycle crystallized with solvent molecules. The solid state conformation of the *p-tert*-butylcalix[16]arene is discussed and compared to those of the calix[4] and [8] parents.

Experimental

Synthesis

Calixarenes containing more than eight aryl units have been isolated from both the base-induced cyclocondensation of linear phenolic oligomers [2] and the acid-catalyzed condensation of *p-tert*-butylphenol and formaldehyde [4]. The acid-catalyzed process provides a better source of these "large" calix[n]arenes in which n = 9–20 are present in significant amount. We have now synthesized *p-tert*-butylcalix[16]arene according to the Gutsche and Stewart procedure. *p-tert*-Butylcalix[16]arene has been isolated from a mixture of calix[7] to [20]arenes by a gradient flash chromatography column (a 50 mm silica gel column was eluted with a mixture of toluene/hexane from respectively 40/60 to 100/0) affording some fractions containing mainly calix[12], [15] and [16]arenes. *p-tert*-Butylcalix[12]arene is eliminated from this mixture by a precipitation in chloroform/acetonitrile. *p-tert*-Butylcalix[15] and [16]arenes were then dissolved in ethyl acetate and after several hours, a white precipitate was filtered to give *p-tert*-butylcalix[16]arene. Pure *p-tert*-butylcalix[16]arene (0.35 g; 0.86% yield) was obtained by precipitation from chloroform/acetonitrile.

Crystal structure analysis

Colourless crystals were obtained from evaporation of a saturated solution of a mixture of acetonitrile and dichloromethane. Due to the difficulty of obtaining a suitable single crystal for the data collection, the X-ray analysis experiment was performed on the triangular shaped extremity of a large crystal mounted on a glass rod and cooled at 123 K in a stream of nitrogen. A Nonius Kappa-CCD diffractometer was used, its detector positioned at 47 mm distance from the crystal; φ scans with 1° steps during 30 s were performed to obtain the data. Unit cell parameters were determined from 10 frames and the data collection consisted of 182 frames. Using only φ scans on an extremity of the crystal allowed a maximum size less than 0.8 mm for the part of the crystal bathed by the X-rays.

---

* Supplementary Data relating to this article have been deposited with the British Library as Supplementary Publication No. SUP 82288 (31 pages).

** Author for correspondence.

[1] The celtic torc was jewellery used as a bracelet or necklace, consisting of an open ring.

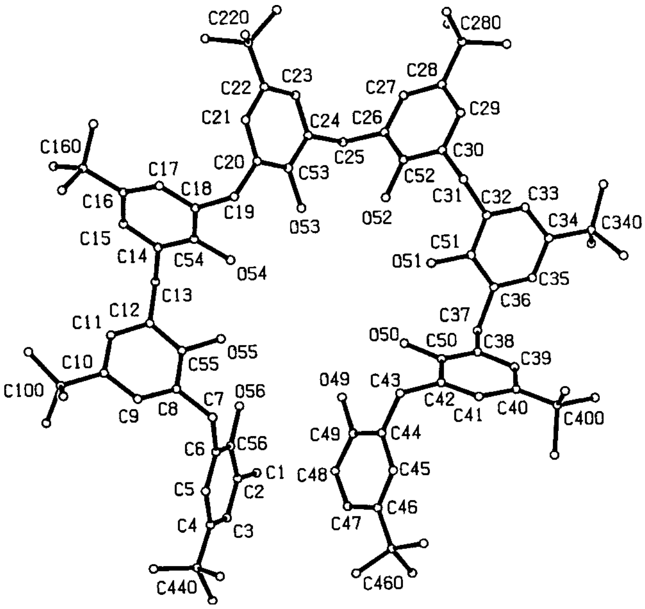

Figure 1. Numbering scheme.

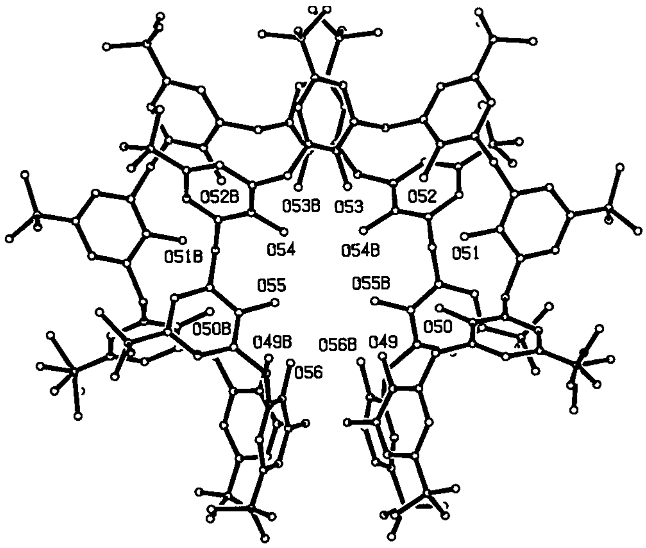

Figure 2. View of the macrocycle.

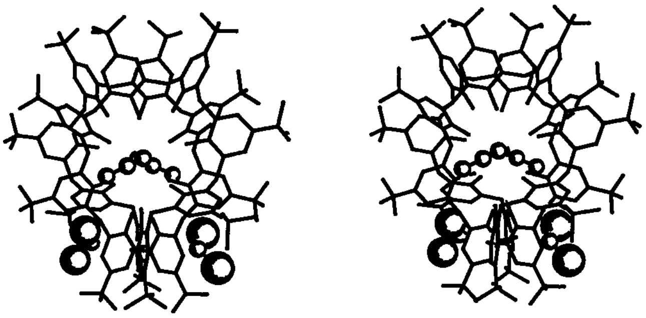

Figure 3. Stereoscopic view of the supramolecular entity.

The structure was solved by direct methods using the SHELXS97 [5] program. The asymmetric unit consists of half a 1:2:2 calixarene, dichloromethane, acetonitrile clathrate and disordered molecules of solvents situated out of the cavity: a disordered dichloromethane molecule with three possible positions, a disordered molecule of acetonitrile with two possible positions and another molecule of acetonitrile with a site occupation factor of 0.6. The refinement using full-matrix least squares was performed by SHELXL97 [6]. All hydrogen atoms were calculated at their theoretical positions and refined riding on the previous atom. Anisotropic temperature factors were calculated for non H-atoms except in two disordered solvent molecules. A final R_1 factor of 0.097 and a goodness of fit of 1.043 have been obtained.

Crystal and data collection details together with structure refinement are summarized in Table 1. Figure 1 gives the numbering scheme of the asymmetric unit of the calixarene. Coordinates of atoms, bond lengths, bond angles, torsion angles and angles between mean planes are contained in the supplementary data.

Results and discussion

Figure 2 calculated by PLATON [7] shows the conformation of the macrocycle. It can be described as two superimposed celtic torcs in which the benzene rings at each extremity of one torc are bent in order to be connected by their CH_2-group with the rings at the extremity of the other torc.

One half of the molecule corresponds to the asymmetric unit and the other one is obtained by a 2 axis parallel to $\vec{b}$; Figure 2 gives the numbering scheme for the O atoms in the asymmetric unit and shows how atoms deduced by the 2 axis are called O(49B), O(50B) etc…

The four moieties bearing O(50), O(49), O(56B) and O(55B), situated at each side of the aperture of the double torc, exhibit a pseudo calix[4]arene shape in a cone conformation. The remaining parts of the macrocycle exhibits a pleated loop shape as seen in Figure 3, which represents the 1:2:2 calixarene, dichlomethane, acetonitrile clathrate. The conformation of a macrocycle can be described by the values of torsional angles ϕ and χ as proposed by Andreetti *et al.* [8] and adopted by Gutsche [9]. Table 2 gives their values and the following sequence of signs is obtained for half of the molecule:

$$-+, -+, +-, -+, +-, -+, +-, -+,$$

the four first signs correspond to the cone conformation of the extremities of the torc and the others give a sequence similar to the one found in the *p*-t-butylcalix[8]arene referenced by Gutsche and in both calix[10]arenes studied by Perrin *et al.* [2].

Steric considerations dictate that the benzene rings in the superimposed torcs are more or less parallel (angles of 16.0(6)° between rings bearing O(55) and O(51B) or O(55B) and O(51), 16.9(4)° for rings with O(54) and O(52B) or O(54B) and O(52) and angles of 4.0(7)° between rings bearing O(53) and O(53B)).

The shortest distances between one of the previous planes and the atoms of one nearly coplanar ring are 2.75(2) Å and 2.78(2) Å for carbons of rings bearing O(51) and O(55B) and their symmetric equivalents.

O· · ·O distances between the neighbouring oxygens in the macrocycle are reported in Table 3. They correspond to

Table 1. Crystal data and structure refinement

Empirical formula	$C_{176}H_{224}O_{16}$, 4(CH_2Cl_2), 5.2 (C_2H_3N)
Formula weight	3148.74
Temperature	123(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, C2/c
Unit cell dimensions	a = 38.508(8) Å, α = 90°
	b = 21.593(4) Å, β = 121.34(3)°
	c = 26.625(5) Å, γ = 90°
Volume	18910(7) Å^3
Z, calculated density	4, 1.106 mg/m^3
Absorption coefficient	0.177 mm^{-1}
F(000)	6762
Crystal size max	0.8 mm
Theta range for data collection	1.13 to 22.40 deg.
Limiting indices	$-40 \Leftarrow h < 40$, $-23 \Leftarrow k \Leftarrow 21$, $-26 \Leftarrow 1 \Leftarrow 25$
Reflections collected/unique	12959/9116 [R(int) = 0.0509]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	9115/1/1050
Goodness-of-fit on F^2	1.043
Final R indices [I > 2sigma(I)]	Rl = 0.0969, wR2 = 0.2430
R indices (all data)	R1 = 0.1648, wRI = 0.2955
Largest diff. Peak and hole	0.841 and −0.492 e. Å^{-3}

Table 2. Selected torsion angles (°)

Φ angles		χ angles	
C(47B)–C(48B)–C(1)–C(2)	−89.3(8)	C(48B)–C(1)–C(2)–C(3)	79.4(9)
C(5)–C(6)–C(7)–C(8)	−106.2(9)	C(6)–C(7)–C(8)–C(9)	82(1)
C(11)–C(12)–C(13)–C(14)	79(1)	C(12)–C(13)–C(14)–C(15)	−98.4(9)
C(17)–C(18)–C(19)–C(20)	−84.1(9)	C(18)–C(19)–C(20)–C(21)	82(1)
C(23)–C(24)–C(25)–C(26)	75(1)	C(24)–C(25)–C(26)–C(27)	−100.3(9)
C(29)–C(30)–C(31)–C(32)	−99.9(9)	C(30)–C(31)–C(32)–C(33)	78.1(9)
C(35)–C(36)–C(37)–C(38)	107.4(9)	C(36)–C(37)–C(38)–C(39)	−76.3(9)
C(41)–C(42)–C(43)–C(44)	−87(1)	C(42)–C(43)–C(44)–C(45)	85.3(9)

Table 3. Selected bond distances (Å)

O(49)···O(50)	2.687(7)	O(53)···O(54)	2.833(7)
O(50)···O(51)	2.784(7)	O(54)···O(55)	2.779(7)
O(51)···O(52)	2.744(7)	O(55)···O(56)	2.749(7)
O(52)···O(53)	2.803(7)	O(56)···O(49B)	2.786(9)

the circular H-bond network usually observed in calixarenes for non substituted OH-groups.

Four molecules of solvent form with a calixarene a supramolecular entity represented in Figure 3 which could be classified as a cavitato clathrate. Two molecules of acetonitrile (with the N(1) atoms) fit the cavity of the macrocycle, each one being in the center of one torc. The shortest distances between this solvent molecule and the macrocycle are 3.00(1) Å and 3.10(1) Å between the nitrogen of acetonitrile and oxygen atoms O(50) and O(53) respectively. Two molecules of dichloromethane with the Cl(30) and Cl(31) atoms are encapsulated in the two pseudo calix[4]arenes situated at each extremity of the open ring. Their planes are nearly perpendicular (83.5(8)°) to the benzene ring bearing the O(55) and O(55B) atoms respectively. Shortest distances between these molecules and the macrocycle are 3.960(9) Å and 3.84(1) Å respectively for the carbon in the para position in the ring bearing O(55) and the carbon of the *p-tert*-butyl group connected to it.

Other molecules of solvent are situated in the interhost space and they all exhibit disorder. A molecule of dichloromethane has three possible positions with occupation factors of 0.4 for the molecule containing Cl(60) and Cl(61), 0.3 for the one containing Cl(50) and Cl(51) and 0.3 for the molecule with Cl(70) and Cl(71). Molecules of acetonitrile are present in the interhost space. One of them exhibits a disorder with two possible positions with site occupation factors of 0.72 and 0.28. Another one occupies the site at a 60% ratio.

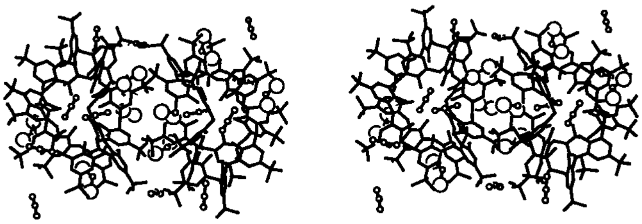

Figure 4. View of the compound.

Figure 4 shows the endo-calix compound with its acetonitrile and dichloromethane molecules trapped in the macrocycle and the two other solvent molecules situated between two clathrates.

Conclusion

In the paper cited previously [4] Gutsche wrote that "calixarenes incorporate as many cone-like and/or pleated loop-like conformational segments as possible" because "the cone and the pleated loop provide the best conformation-stabilizing structures in the calixarene family".

This postulate is especially well-verified in the title compound for which the sixteen moieties are organized in such a way that they form two pleated loops, each one with five moieties, and two pseudo calix[4]arenes in cone conformations. The moieties bearing O(55) and O(55B) take part in the pleated loop and in the cone, allowing the formation of both conformations in the same molecule.

The shape of this molecule induces the formation of different cavities: the middle of the torcs is edged by hydroxyl groups and the cavities in the pseudo calix[4]arenes exhibiting π electrons in their phenolic rings. This variety in the shape and function of the cavities may be correlated with the fact that they are occupied by different solvents: the middle of one torc is occupied by an acetonitrile molecule whereas the pseudo calix[4]arenes retain dichloromethane molecules. In a recent paper [10] an acetonitrile molecule was observed occupying the cavity of a calix[4]arene with its nitrogen atom oriented exo with respect with the macrocycle. In the title compound the shortest distances with the macrocycle concern the nitrogen atoms, and the acetonitrile does not fit the cavity of the pseudo calix[4]arene. This study confirms the ability for one macrocycle to host various small molecules and for a small molecule to be accommodated by the different sorts of cavities exhibited by large calixarenes.

References

1. I. Dumazet, J-B. Regnouf-de-Vains, and R. Lamartine: *Syn. Commun.* **27**, 2547 (1997).
2. M. Perrin, N. Ehlinger, L. Viola-Motta, S. Lecocq, I. Dumazet, S. Bouoit-Montesinos, and R. Lamartine: *J. Incl. Phenom.* in press.
3. P. Leverd, I. Dumazet, R. Lamartine, and M. Nier1ich, *J. Chem. Soc. Chem. Commun.* 493 (2000).
4. D.R. Stewart and C.D. Gutsche: *J Am. Chem. Soc.* **121**, 4136 (1999).
5. G.M. Sheldrick: SHELXS97, *Program for Crystal Structure Solution*, University of Göttingen, Germany (1997).
6. G.M. Sheldrick: SHE LXL97, *Program for Crystal Structure*, University of Göttingen, Germany (1997).
7. A.L. Spek: PLATON, *A Multipurpose Crystallographic Tool*, Utrecht University, Utrecht, The Netherlands (1999).
8. F. Ugozzoli and G.D. Andreetti: *J. Incl. Phenom. Mol. Recognit. Chem.* **13**, 337 (1992).
9. C.D. Gutsche: 'Calixarenes Revisited', in J.F. Stoddart (ed.), *Monographs in Supramolecular Chemistry*, Royal Society of Chemistry, Cambridge (1998).
10. A.F. Danil de Namor, E.E. Custellano, L.E. Pulcha Salazar, O.E. Pino, and O. Dafou: *Phys. Chem. Chem. Phys.* **1**, 285(1999).