



Structural Study of C-undecylcalix[4]resorcinarene Solvate with Dioxane

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Abstract. The crystal structure of the molecular complex of C-undecylcalix[4]resorcinarene with dioxane has been determined by X-ray analysis. The asymmetric unit contains one host and four guest molecules. The calix[4]resorcinarene moiety adopts a bowl conformation with C_{4v} symmetry. Four undecyl chains are axially oriented. Calix molecules are packed in a bowl-to-bowl fashion with alternating hydrophilic and hydrophobic layers. One of the 'hydrophilic' dioxane molecules is located at the rim of the calix moiety and is hydrogen bonded to the other one. There is no interaction to attract, or direct the dioxane molecule into the interior of the cavity. There is an *exo* complex formed. The dioxane molecules – located in the hydrophobic part – are highly disordered.

Key words: C-undecylcalix[4]resorcinarene, crystal structure, dioxane solvation, *exo* molecular complex

1. Introduction

Calix[4]resorcinarenes have attracted remarkable interest in recent years due to their versatile complexing properties, conformational flexibility, a great variety of ways for their further functionalization and an easy synthetic and commercial availability. The ease of forming multicomponent species involving calix[4]resorcinarenes made them interesting species for molecular recognition processes [1], transport across membranes [2], ion channels [3], self-assembling monolayers at the air-water interface [4] and metal complexation [5]. An excellent review article covering the chemistry of calix[4]resorcinarenes has appeared recently [6].

We have been interested in calix[4]resorcinarenes as molecular hosts for molecular recognition studies in solution by means of HPLC experiments, transport across liquid and supported plastic membranes, thermochemistry and NMR techniques. Generally, calixarenes form stable solvates with almost all solvents from which they are crystallized. A large number of their solvates is stable, thus this feature may have a serious impact on the molecular recognition phenomena in

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solution, since the solvent will compete with the species involved in the recognition process. It has been interesting for us to undertake a research programme aiming at the structure and thermal stabilities of a wide range of solvates. These studies would allow a rational choice of the solvents suitable for the molecular recognition studies.

Examination of the Cambridge Structural Database [7] (Release 5.15, April 1998) shows only nine crystal structures of resorcinol-based calixarene molecular complexes [8–12]. The calix[4]resorcinarene moiety has been found in the crystal structures in two different conformations: the first one with C_{4v} symmetry and a bowl conformation [8–11] and the other with C_{2v} symmetry and a chair conformation [12]. The first conformation is stabilized by bridging the hydroxy groups of adjacent aromatic rings with covalent linkages of one or more atoms and is formed when aliphatic aldehydes are used in the condensation reaction. The bowl shaped resorcinarenes are capable of forming supramolecular complexes with many different guest species which can be embedded in the crystal lattice either in the cavity formed by resorcinol units, above the cavity or in a close proximity of alkyl chains.

On the other hand, when a benzaldehyde derivative is used in the condensation reaction, the resorcinarene moiety adopts a chair conformation – only two such crystal structures have been determined so far [12] – and the guest molecules surround the host molecule forming highly solvated structures.

In this paper we present the molecular and crystal structure of the tetra(C-undecyl)-calix[4]resorcinarene complex with dioxane.

2. Experimental

The title compound was prepared according to literature [13] (all reagents were purchased from Aldrich or Merck). Dioxane was distilled over CaH_2 . The tetra(C-undecyl)calix[4]resorcinarene was crystallized from hot dioxane and left for a slow cooling. Prism-shaped and colorless crystals were obtained after one-day standing. They were stable in solution but decomposed when exposed to air. Therefore, a crystal of calix of size $1.5 \times 0.5 \times 0.4$ mm suitable for X-ray data collection was sealed in a glass capillary. Accurate unit-cell parameters were determined by a least-squares fitting of the setting angles of 32 reflections with 2θ in the range 55° – 61° . The intensity data were measured on a KUMA KM-4 diffractometer [14] using graphite-monochromatized $\text{CuK}\alpha$ radiation. The relevant crystallographic data together with structure refinement details are listed in Table 1. The 2θ – θ scan method with a variable scan speed depending on reflections intensity, was applied. Two control reflections were measured every 100 current measurements. The data were corrected for Lorenz and polarization effects, but not for absorption.

The structure was solved by direct methods using the program SHELXS-86 [15] and the refinement was carried out by the full-matrix least-squares method with the program SHELXL-97 [16]. All non-hydrogen atoms were refined anisotropically. Due to disorder of the terminal parts of the C-undecyl chains, some of

Table I. Crystal data and structure refinement

Empirical formula	$C_{88}H_{144}O_{16} \cdot (C_4H_8O_2)_4$	
Formula weight	1458.03	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	$a = 12.608(4) \text{ \AA}$	$\alpha = 97.31(1)^\circ$
	$b = 13.366(1) \text{ \AA}$	$\beta = 93.99(2)^\circ$
	$c = 26.726(3) \text{ \AA}$	$\gamma = 94.38(2)^\circ$
Volume	$4440(1) \text{ \AA}^3$	
Z	2	
D_x	1.091 g cm^{-3}	
Radiation	CuK_α	
μ	0.580 mm^{-1}	
θ range	1.67 to 75.17°	
hkl range	$-15 \leq h \leq 14$	
	$-16 \leq k \leq 16$	
	$0 \leq l \leq 33$	
Decay of standards	4.7%	
Reflections:		
collected	17978	
unique	17764 [R(int) = 0.0394]	
with $I > 2\sigma(I)$	9790	
Number of parameters	937	
Number of restraints	34	
Goodness of fit on F^2	1.246	
R[$I > 2\sigma(I)$]	0.0954	
$wR(F^2)[I > 2\sigma(I)]$	0.2868	

Largest diff. peak and hole 0.642 and -0.744 e\AA^{-3} .

the bond lengths and bond angles were restrained (altogether 34 parameters were restrained). The H atoms were placed in calculated positions, with the exception of the hydroxyl hydrogen atoms which were located from the difference Fourier map. Two of the four dioxane molecules in the asymmetric unit were highly disordered and their hydrogen atoms could not be located. The hydrogen atoms were refined isotropically as a 'riding model', i.e., they were restrained to move together with their carrier atoms, in order to maintain the starting geometry. The isotropic thermal parameters of hydrogen atoms were assigned as 1.2-times the equivalent thermal parameters of the appropriate carrier atom. The function $\sum w(|F_o|^2 - |F_c|^2)^2$ was minimized, with $w^{-1} = [\sigma^2(F_o)^2 + 0.4 P^2]$ where $P = (F_o^2 + 2F_c^2)/3$. The maximum value of shift/esd in the final cycle of refinement was less than 0.2. Atomic

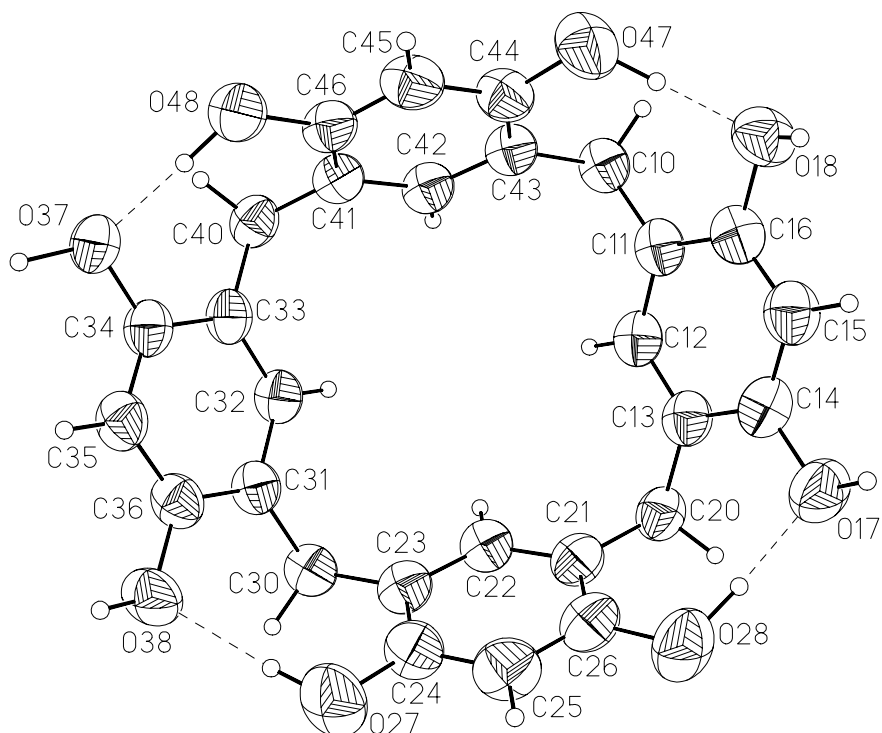


Figure 1. Calix[4]resorcinarene molecule with the C_{4v} symmetry. The C-undecyl chains are removed for clarity.

scattering factors used were those incorporated in SHELXL-97 [16]. Final atomic coordinates are given in Supplementary Materials.

3. Discussion

The crystals of C-undecylcalix[4]resorcinarene dioxane solvate crystallize with one host molecule and four dioxane molecules in the asymmetric unit. Thermal ellipsoids of atoms in the host molecule drawn at the 50% probability level as well as the numbering scheme are shown in Figure 1.

The aromatic rings of the resorcinarene moiety are arranged in all-*cis* structure with their hydroxy groups in close proximity. They are all involved in the intramolecular hydrogen bonds (Table 2) which extend the collar of the cavity. The calix moiety adopts a bowl conformation with C_{4v} symmetry and the C...C diagonal distances are: C10...C30 7.207(5) Å, C20...C40 7.216(4) Å, C12...C32 5.229(4) Å and C22...C42 5.207(4) Å.

The calix bowl “rests” on four “feet” consisting of C-undecyl chains whose axial orientation is shown in Figure 2.

Table II. Intra- and intermolecular hydrogen bonds

D–H ... A	d(D–H) Å	d(H ... A) Å	d(D ... A) Å	<(DHA) ^o
O(27)–H(27A) ... O(38)	1.00	1.87	2.840(4)	161.8
O(28)–H(28A) ... O(17)	1.13	1.69	2.803(4)	167.7
O(47)–H(47A) ... O(18)	1.06	1.67	2.733(4)	178.0
O(48)–H(48A) ... O(37)	1.03	1.68	2.704(3)	174.2
O(17)–H(17A) ... O(64) ⁱ	0.98	1.76	2.707(4)	162.5
O(18)–H(18A) ... O(61) ⁱⁱ	0.89	1.88	2.728(3)	159.3
O(37)–H(37A) ... O(51) ⁱⁱⁱ	1.07	1.53	2.582(3)	166.2
O(38)–H(38A) ... O(48) ⁱⁱⁱ	0.90	2.05	2.862(3)	149.8

Symmetry codes: (i) $x, y+1, z$; (ii) $-x+1, -y+1, -z+1$; (iii) $-x+2, -y+1, z+1$.

The calix molecules are packed in the crystal structure in a bowl-to-bowl fashion with alternating hydrophilic and hydrophobic layers (Figure 3). Out of the four dioxane guest molecules, two are located in the hydrophilic region and the other two in the hydrophobic one.

One of the “hydrophilic” dioxane molecules is located at the rim of the calix and is simultaneously hydrogen bonded to another calix moiety which is related by an inversion center with the first one. This hydrogen bond (Table 2, Figure 4) with the acceptor ... donor distance O51 ... O37ⁱⁱⁱ equal to 2.582(3) Å seems to be strong. No interactions of the type C–H(guest) ... π -electrons (host) have been found. This means that there is no interaction to direct the dioxane molecule into the interior of the cavity and the *exo* complex is formed.

Another hydrophilic host – guest interaction is extended over the two crystallographically different dioxane molecules with symmetry codes (i) and (ii). These are intermolecular hydrogen bonds with the donor ... acceptor distances: O(17) ... O(64)ⁱ of 2.707(4) Å and O(18) ... O(61)ⁱⁱ of 2.728(3) Å (Table 2). Finally, the two centrosymmetrically related calix moieties are hydrogen bonded by two intermolecular hydrogen bonds: O(38) ... O(48)ⁱⁱⁱ and O(48) ... O(38)ⁱⁱⁱ with the donor ... acceptor distance of 2.862(3) Å (Figure 4, Table 2). The dimer which is formed in this way encapsulates only two dioxane molecules which are located at the rims of each calix bowl.

The hydrophobic part of the crystal structure is formed by the C-undecyl side chains that interdigitate with those of the adjacent calix[4]resorcinarene and the remaining two dioxane molecules fill the voids between two such aggregates (Figure 3). The dioxane molecules are built into the crystal structure only by weak van der Waals interactions and due to that are highly disordered. It is thought that it is the loss of these by evaporation which causes the crystals to become cloudy in air.

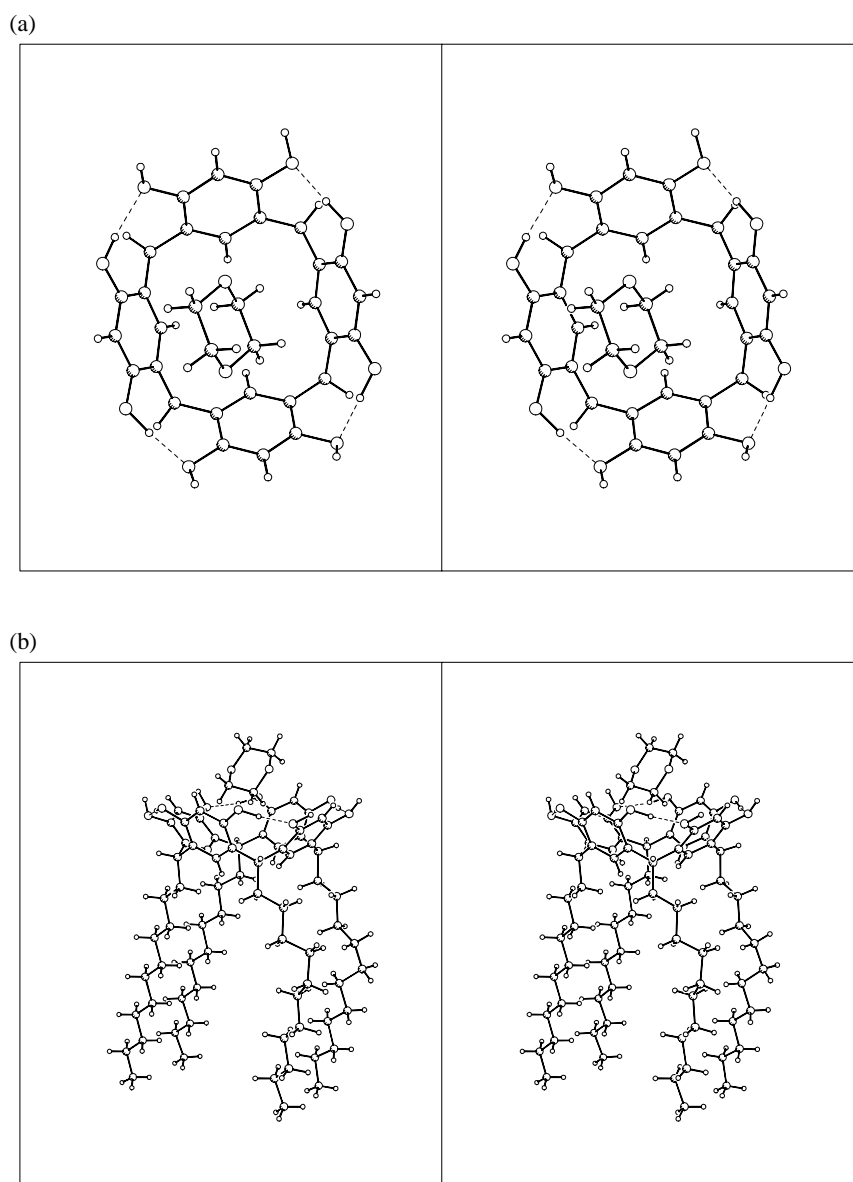


Figure 2. The stereo-diagrams of the face (a) and side (b) views of the calix[4]resorcinarene molecule. The C-undecyl chains are removed for clarity in the face view.

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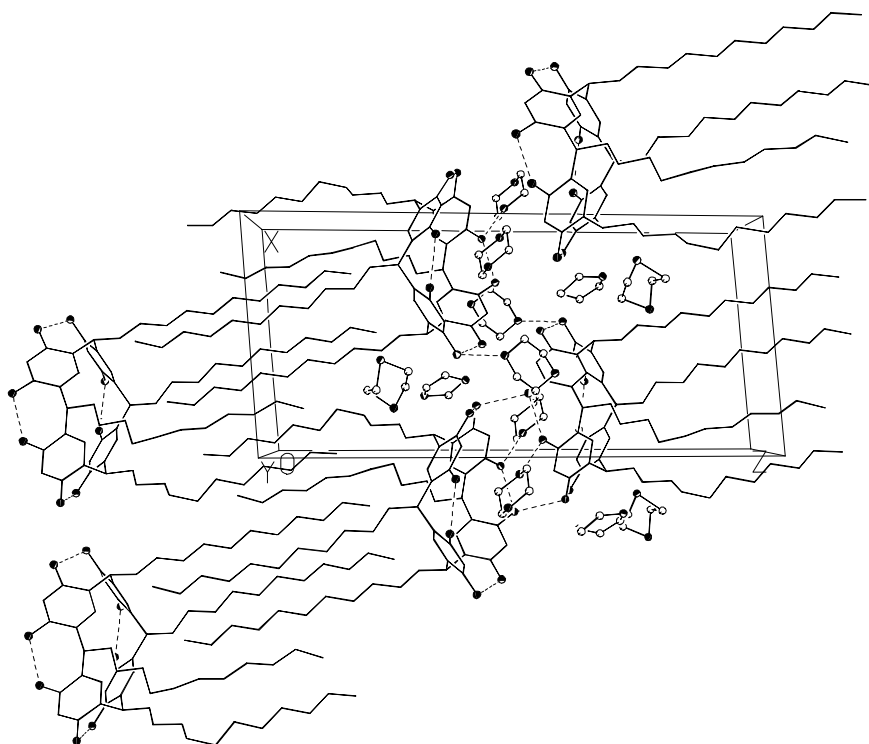


Figure 3. Crystal structure arrangement of the C-undecylcalix[4]resorcinarene solvate with dioxane molecules.

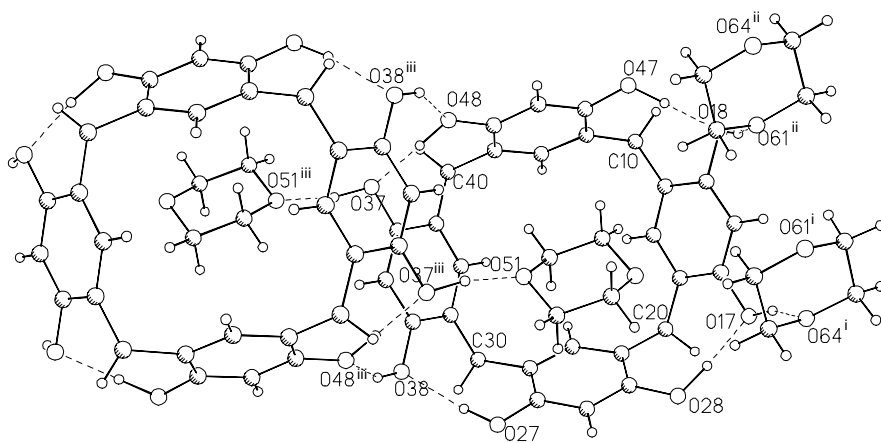


Figure 4. Intra- and intermolecular hydrogen bonds. The calix[4]resorcinarene moieties form a centrosymmetrical dimer connected by two intermolecular hydrogen bonds: $O(38) - H \cdots O(48)^{iii}$ and $O(48) \cdots H - O(38)^{iii}$.

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