

## Quasi-Complete Solvation of C-Phenylcalix[4]resorcinarene\* in the Crystalline State. Single Crystal X-ray Diffraction Study\*\*

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### Abstract

The crystal structure of C-phenylcalix[4]resorcinarene in a very solvated environment (DMSO) has been determined. The asymmetric unit contains nine molecules of DMSO and one molecule of water for each molecule of the resorcinarene. The C-phenylcalix[4]resorcinarene adopts an approximate  $C_{2v}$  symmetry (boat conformation, also known as flattened-cone conformation) in which two opposite resorcinol rings are almost parallel, while the other two are nearly coplanar.

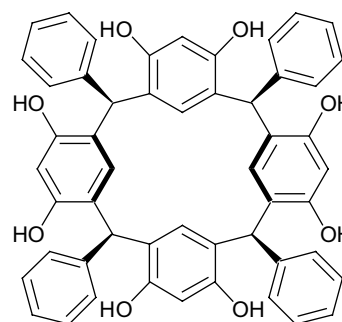
### Introduction

The study of macromolecules and, of particular interest, the study of the behavior of macromolecules in solution and in highly solvated state in the solid phase, has been of continuous and growing interest in the recent years, due to the impact that these compounds may have in the better understanding of larger species like bio-molecules. Studies in the solid state by X-ray diffraction experiments result in an interesting technique that exhibits not only the three-dimensional structure of a particular compound but also the conformation and the interactions among molecules or solvent molecules in the unit cell. This technique has been of crucial importance in the understanding of molecules such as calixresorcinarenes [1], a fact that has taken these species from mere fancy molecules to having multiple potential applications such as supports for GC columns [2], kidnapping agents for heavy metals [3], extraction of toxic and radioactive wastes [4], supports important in the developments of nano-technologies [5], vehicles for the transport of multiple substrates [6], and visual indicators for saccharides [7]. Thus, in this paper, we report our findings of the study in the solid state of the compound C-phenylcalix[4]resorcinarene in a quasi-complete solvated state.

\* 4,6,10,12,16,18,22,24-Octahydroxy-2,8,14,20-tetraphenyl-calix(4)arene.

\*\* Supplementary data related to this article are deposited with the British Library as Supplementary Publication No. 82308 (3 pages).

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(1)

*Scheme 1.*

### Experimental

#### *Materials and methods*

Unless stated otherwise, all reactions were carried out under an atmosphere of dinitrogen using conventional Schlenk glassware. Solvents were dried using established procedures and distilled under dinitrogen immediately prior to use. The  $^1\text{H}$  NMR spectra were recorded on a JEOL GX300 spectrometer. Chemical shifts are reported in ppm down field of TMS using the solvent (DMSO- $d_6$ ,  $\delta = 2.15$ ) as internal standard. Elemental analyses were determined on a Perkin-Elmer 240. Positive-ion FAB mass spectra were recorded on a JEOL JMS-SX102A mass spectrometer operated at an accelerating voltage of 10 kV. Samples were desorbed from a nitrobenzyl alcohol (NOBA) matrix using 3 KeV

xenon atoms. Mass measurements in FAB are performed at a resolution of 3000 using magnetic field scans and the matrix ions as the reference material or, alternatively, by electric field scans with the sample peak bracketed by two (polyethylene glycol or cesium iodide) reference ions. C-phenylcalix[4]resorcinarene was prepared according to the published procedure [8] (all reagents were purchased from Aldrich Chem. Co.). Dimethyl sulfoxide (DMSO) was used as received without further purification.

*Data collection and refinement for C-phenylcalix[4]resorcinarene·9DMSO·H<sub>2</sub>O (1).*

A crystalline colorless prism of C-phenylcalix[4]resorcinarene·9DMSO·H<sub>2</sub>O (**1**), grown from a saturated solution of (**1**) in DMSO was glued to a glass fiber. The crystals are stable in solution but decomposed when exposed to air, very likely due to loss of solvent. Thus, to avoid loss of solvent during crystallization, the mounted crystal was covered with Paratone N<sup>®</sup>. The X-ray intensity data were measured at 293 K on a Bruker SMART APEX CCD-based X-ray diffractometer system equipped with a Mo-target X-ray tube ( $\lambda = 0.71073$  Å). The detector was placed at a distance of 4.837 cm. from the crystal. A total of 1800 frames were collected with a scan width of  $0.3^\circ$  in  $\omega$  and an exposure time of 10 s/frame. The frames were integrated with the Bruker SAINT software package [9] using a narrow-frame integration algorithm. The integration of the data using a monoclinic unit cell yielded a total of 65,760 reflections to a maximum  $2\theta$  angle of  $50.00^\circ$  ( $0.93$  Å resolution), of which 12,778 were independent. Analysis of the data showed negligible decay during data collection. The structure was solved by direct methods using SHELXS-97 program [10]. The remaining atoms were located via a few cycles of least-squares refinements and difference Fourier maps, using the space group  $P21/n$ , with  $Z = 4$ . Hydrogen atoms of the hydroxy groups in the title compound and those of the water molecules were located by difference Fourier maps; the rest of the hydrogen atoms were positioned at calculated locations. All hydrogen atoms included in the refinement of (**1**) were refined using a riding model. All nine DMSO molecules are located at definite positions; however, for at least six DMSO molecules their sulfur atoms (S4 to S9) are disordered between two sites above and below the plane formed by the oxygen and the two carbon atoms. The site occupation probabilities for the two positions could be determined for each sulfur atom. They vary between 0.52 and 0.85. Two of the sulfur atoms (S8 and S9) are 0.52 and 0.53, suggesting that there is no preference for either position. Values greater than 0.80 for S4, S5, S6 and S7 reveal an increasing preference for one site. The second components are signed with a trailer B letter (see supplementary material). Thermal parameters were refined for hydrogen atoms on the phenyl groups using a  $U_{eq} = 1.2$  Å to

Table 1. Crystal data and experimental details for C-phenylcalix[4]resorcinarene·9 DMSO·H<sub>2</sub>O (**1**)

Formula	C <sub>52</sub> H <sub>40</sub> O <sub>8</sub> ·9(C <sub>2</sub> H <sub>6</sub> OS)·H <sub>2</sub> O
Formula weight	1514.01
Crystal size, mm/colour/shape	0.284 × 0.222 × 0.218/colorless/block
Absorption coefficient, mm <sup>-1</sup>	0.311
Temperature, K	293(2)
Crystal system	Monoclinic
Space group	$P 21/n$
$a$ , Å	13.069(1)
$b$ , Å	28.057(1)
$c$ , Å	21.909(1)
$\beta$ , °	92.049(1)
$V$ , Å <sup>3</sup>	8028.4(8)
$Z$	4
Density (calculated)	1.253 mg m <sup>-3</sup>
$F(0\ 0\ 0)$	3216
Theta range for data collection	$1.18^\circ$ to $25.01^\circ$
Index ranges	$-15 \leq h \leq 15$ , $-33 \leq k \leq 33$ , $-26 \leq l \leq 26$
Reflections collected	65,760
Independent reflections	14,158 [ $R(\text{int}) = 0.1786$ ]
Absorption correction	Analytical: face-indexed
Max. and min. transmission	0.9736 and 0.9596
Refinement method	Full-matrix least-squares on $F^2$
Data/restraints/parameters	14158/0/942
Goodness-of-fit on $F^2$	1.011
Final $R$ indices [ $I > 2\sigma(I)$ ]	$R1 = 0.0947$ , $wR2 = 0.1760$
$R$ indices (all data)	$R1 = 0.2738$ , $wR2 = 0.2373$
Largest diff. peak and hole	0.498 and $-0.453$ e Å <sup>-3</sup>

precedent atom. The final cycle of refinement was carried out on all non-zero data using SHELXL-97 [10] and anisotropic thermal parameters for all non-hydrogen atoms. The details of the structure determination are given in Table 1 and hydrogen bond lengths (Å) and angles (°) are given in Table 2. The numbering of the atoms is shown in Figure 1 (ORTEP) [11].

## Results and discussion

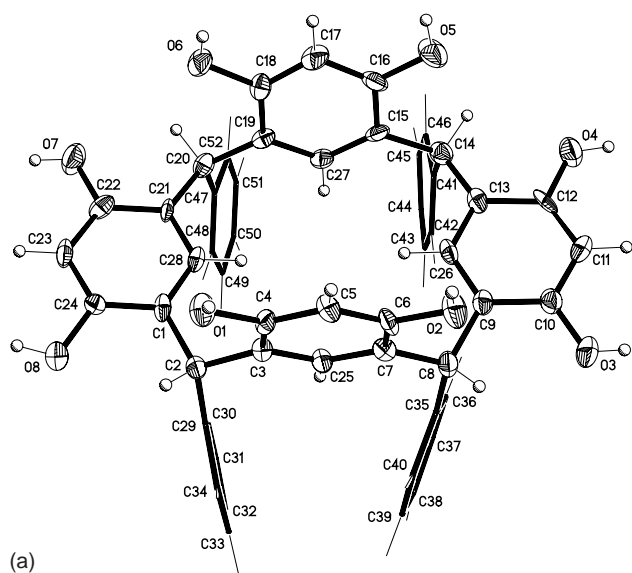
The C-phenylcalix[4]resorcinarene molecule adopts an approximate  $C_{2v}$  symmetry (boat conformation, also known as flattened-cone conformation) in which two opposite resorcinol rings are almost parallel, while the other two are nearly coplanar (Figure 1). The dihedral angles of the coplanar rings to the reference plane (C2—C8—C14—C20) are  $4.494(2)^\circ$  and  $3.991(2)^\circ$ , while analogous values for the parallel rings are  $82.036(5)^\circ$  and  $76.066(5)^\circ$ , and the phenyl rings are approximately perpendicular with the dihedral angles ranging from  $85.475(4)^\circ$  to  $87.716(4)^\circ$ .

The shortest distance between neighboring hydroxy groups is 3.70 Å; this shows that no intramolecular hydrogen bonding exists; however, all potential donors are involved in intermolecular hydrogen bonds with solvent and water molecules. Each molecule of (**1**) forms eight intermolecular hydrogen bonds to solvent mole-

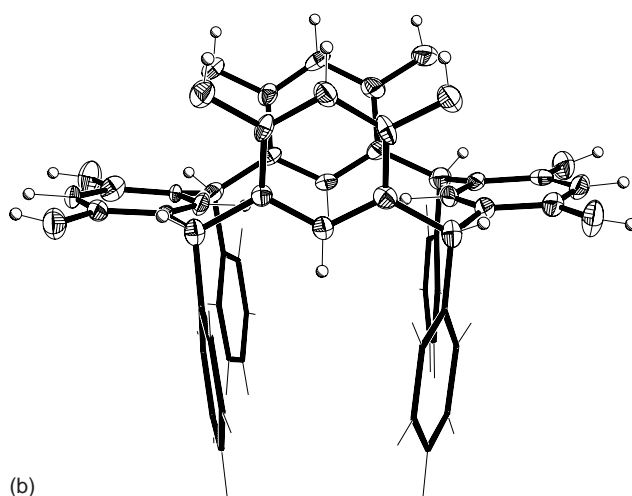
Table 2. Hydrogen bonds for C-phenylcalix[4]resorcinarene · 9DMSO · H<sub>2</sub>O (1) [Å and °]

D—H...A	<i>d</i> (D—H)	<i>d</i> (H...A)	<i>d</i> (D...A)	<(DHA) <sup>o</sup>
O(1)—H(1)...O(11)	0.82	1.97	2.713(7)	150.1
O(2)—H(2)...O(12) <sup>I</sup>	0.82	1.92	2.715(8)	164.1
O(3)—H(3)...O(16) <sup>II</sup>	0.82	1.87	2.668(8)	165.4
O(4)—H(4)...O(13) <sup>III</sup>	0.82	1.88	2.688(8)	167.0
O(5)—H(5)...O(17) <sup>I</sup>	0.82	1.83	2.639(9)	171.7
O(6)—H(6)...O(18) <sup>IV</sup>	0.82	1.89	2.712(7)	177.8
O(7)—H(7)...O(10) <sup>IV</sup>	0.82	1.82	2.615(8)	162.3
O(8)—H(8)...O(9)	0.82	1.90	2.718(7)	173.0
O(18)—H(18A)...O(14) <sup>V</sup>	0.82	2.05	2.659(9)	130.8
O(18)—H(18B)...O(15) <sup>V</sup>	0.85	1.89	2.721(12)	165.9

Symmetry transformations used to generate equivalent atoms: <sup>I</sup>*x* + 1/2, −*y* + 3/2, *z* + 1/2; <sup>II</sup>*x*, *y* + 1, *z*; <sup>III</sup>−*x* + 3/2, *y* + 1/2, −*z* + 3/2; <sup>IV</sup>−*x*−1/2, −*y* + 3/2, *z* + 1/2; <sup>V</sup>*x* + 1, *y*, *z*.



(a)



(b)

Figure 1. (a) The molecular structure of (1) indicating the numbering of the atoms. For clarity the atoms in the phenyl rings are not represented by thermal ellipsoids. The thermal ellipsoids have been drawn at 50% probability. (b) Side view showing the flattened-cone conformation.

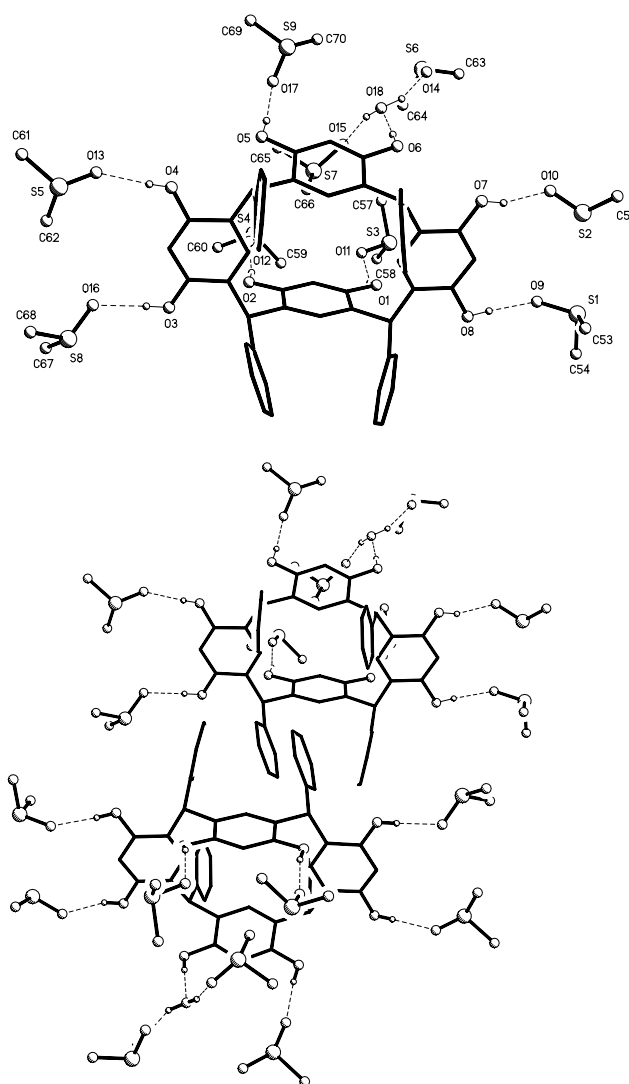


Figure 2. Hydrogen bonding scheme for (1) showing the complete solvated molecule (top) and their arrangement into 'dimers' (bottom).

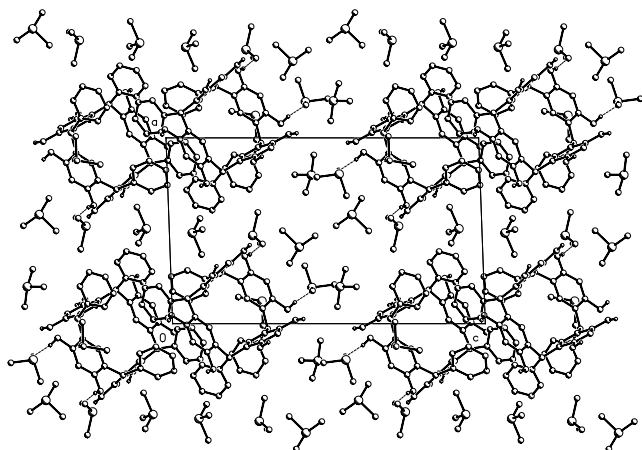


Figure 3. Crystal packing of (1) viewed down the **b** axis. Only hydroxy and water hydrogen atoms are shown.

cules, including one bridged by the water molecule. The hydrogen bonding scheme is completed by an extra solvent molecule hydrogen bonded to the water molecule (Table 2, Figure 2, top).

The fully solvated molecules of  $1 \cdot 9\text{DMSO} \cdot \text{H}_2\text{O}$  organize into centrosymmetric ‘dimers’ with one of the phenyl rings — C35 to C40 — (e.g. distance of the centroid C37 and C37 related by symmetry of 4.014) pointing to the center of the rim formed by the phenyl rings of the symmetry related molecule (Figure 2, bottom). The packing of  $1 \cdot 9\text{DMSO} \cdot \text{H}_2\text{O}$  can be deduced from Figure 3. Each packet of ‘dimers’ is completely separated from each other by layers of DMSO solvent molecules, thus preventing any direct intermolecular contacts. Only the C51—H51 bond protrudes out of this ‘solvent box’ and forms an extremely weak C51—H51 $\cdots$ O<sub>2</sub>( $x-1, y, z$ ) interaction (H $\cdots$ O distance: 2.93 Å). Sheets parallel to the ( $-1\ 0\ 1$ ) plane are built up by the bilayer arrangement of the molecules.

### Supplementary material

Supplementary data for complex **1** have been deposited at the Cambridge Crystallographic Data Centre. Copies of this information are available free of charge on request from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, U.K. (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www>.

ccdc.cam.ac.uk) quoting the deposition number CCDC 223105.

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