



## Crystal Structure of the *p*-cumylcalix[8]arene-dimethylsulfoxide 1:5 Complex \*

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### Abstract

*p*-cumylcalix[8]arene crystallizes with 5 DMSO molecules in the tetragonal space group  $P\bar{4}$ . The parameters have values:  $a = b = 17.443(3)$ ,  $c = 9.829(2)$  Å. Refinement based on 2454 observed reflections led to a final R value of 0.073. Four dimethylsulfoxide molecules are connected by hydrogen bonds to the calixarene. The macrocycle shows an alternate conformation around the  $\bar{4}$  axis. In the network, another DMSO in disordered manner is found between the calixarenes.

### Introduction

Many complexes of calixarenes with solvent molecules have been studied by X-ray diffraction methods in the solid state [1–2]. In contrast to calix[4]arenes and calix[6]arenes, few crystal structures of calix[8]arenes were studied. Furthermore, except for *p*-*t*-butylcalix[8]arene [3–5], a calix[8]arene from bisphenol [6], and another one with propoxy substituents [7], all calix[8]arenes already studied are substituted at the hydroxyl groups. We report here the X-ray crystal structure of *p*-cumylcalix[8]arene, the first calix[8]arene found with a high degree of symmetry complexed with dimethylsulfoxide in an alternate conformation.

### Experimental

#### Synthesis

The synthesis of *p*-cumylcalix[8]arene was accomplished as follows according to the modified standard Petrolite Procedure [8]. A mixture of 39 g (0.13 mole) of *p*-cumylphenol, 16.6 g (0.6 mole) of paraformaldehyde and 2 mL (0.03 mole) of 13N KOH in 150 mL of tetraline was stirred and refluxed in a 250 mL flask equipped with a Dean-Stark water collector. After 15 min all of the solid had gone into solution and a precipitate began to separate after 2 h. The beige solid precipitate was filtered and washed with diethyl ether to give 9.58 g (24.5%) of *p*-cumylcalix[8]arene.

**5,11,17,23,29,35,41,47-octa[2-Phenylisopropyl]-48,49,50,51,52,53,54,55-octahydroxycalix[8]arene.** Elemental analysis: C<sub>128</sub>H<sub>128</sub>O<sub>8</sub>; C: 85.52; H: 7.12; O: 6.92 (calc

C: 85.68, H: 7.19, O: 7.13, % total 99.56); R<sub>f</sub> = 0.72 (chloroform/hexane: 1/1); mp 333–334 °C; theoretical weight: 1794.44, 1793.9 (46.5)M<sup>+</sup>, 1792.9(42)M<sup>+</sup>-H, 1775.8(16)M<sup>+</sup>-H<sub>2</sub>O, 1121.5(14), 897(12), 681.2(19.5), 673(27), 613(100), 596.1(53), 595(80), 593(97). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25 °C): δ 1.58 (s, CH<sub>3</sub>, 48H), 3.25–4.3 (dd, ArCH<sub>2</sub>Ar, 16H), 6.28 (s, C<sub>6</sub>H<sub>2</sub>, 16H), 7.2 (s, C<sub>6</sub>H<sub>5</sub>, 40H), 9.55 (s, OH, 8H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 25 °C): δ 30.6 (C-C<sup>1</sup>H<sub>3</sub>), 31(C<sup>2</sup>H<sub>3</sub>), 32.1(ArCH<sub>2</sub>Ar), 42.2 (C-CH<sub>3</sub>), 125.6, 126.8, 127.9, 128.6, 131.4, 144.4, 146.6, 150.4 (Ar).

#### X-ray data collection, structure determination and refinement

The slow evaporation of a saturated solution of *p*-cumylcalix[8]arene in dimethylsulfoxide (DMSO) gave single crystals. One of them mounted in a Lindeman capillary was transferred to a Nonius Kappa CCD diffractometer. The intensity data were collected at –100 °C with graphite monochromatized Mo K $\alpha$  radiation. The detector was initially positioned 30 mm from the crystal; unit cell parameters were determined from 10 frames.  $\varphi$  Scans with 1.5° steps during 90 sec were performed to obtain 4404 data points. The structure was solved by direct methods using the SHELXS97 [6] program. The asymmetric unit consists of a quarter of a calixarene, one DMSO bonded to the calix and a quarter of DMSO situated out of the cavity. The refinement using full-matrix least squares was performed by SHELXL97 [9]. All hydrogen atoms were calculated at theoretical positions and kept riding on the previous atom. Anisotropic temperature factors were calculated for non-H atoms except for the disordered DMSO molecule out of the cavity. A final R factor of 0.073 was obtained. Crystal and data collection details as well as parameters of the refinement are given in Table 1.

\* Data relating to this article are deposited at the Cambridge Crystallographic Data Centre no. CCDC179404.

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Table 1. Crystal data and refinement summary

Empirical formula:	C <sub>128</sub> H <sub>128</sub> O <sub>8</sub> · 5 C <sub>2</sub> H <sub>6</sub> OS
Formula weight:	2184.96
Temperature:	173 K
Wavelength:	0.71073 Å
Crystal system, space group:	Tetragonal, P $\bar{4}$
Unit cell dimensions:	$a = 17.443(3)$ Å $b = 17.443(3)$ Å $c = 9.829(2)$ Å
Volume:	$2990.6(9)$ Å <sup>3</sup>
Z, Calculated density:	1, 1.213 Mg/m <sup>3</sup>
Absorption coefficient:	0.159 mm <sup>-1</sup>
$F(000)$ :	1170
Crystal size:	0.23 × 0.18 × 0.07 mm
Theta range for data collection:	2.34 to 23.81 deg
Limiting indices:	$-19 \leq h \leq 19$ , $-13 \leq k \leq 14$ , $-10 \leq l \leq 11$
Reflections collected/unique:	4404/2454 [R(int) = 0.0693]
Completeness to theta:	99.8%
Absorption correction:	None
Max. and min. transmission:	0.9643 and 0.9889
Refinement method:	Full-matrix least-squares on F <sup>2</sup>
Data/restraints/parameters:	2454/0/371
Goodness of fit on F <sup>2</sup> :	1.090
Final R indices [I > 2 sigma (I)]:	R1 = 0.0731, wR2 = 0.1785
R indices (all data):	R1 = 0.0976, wR2 = 0.1955
Largest diff. peak and hole:	0.67 and -0.38 e. Å <sup>-3</sup>

Figure 1 calculated with PLATON [10] gives the numbering scheme of the asymmetric unit of the calixarene and of the solvent molecules.

The coordinates of atoms, bond lengths, bond angles and torsion angles are given as Supplementary Data.

## Results and discussion

Figure 2 shows that the macrocycle adopts an alternate conformation due to the  $\bar{4}$  symmetry. Angles at methylene groups are alternatively 113.4(6)° and 116.9(6)°. The usual inclination angles of the phenolic rings versus the mean plane of the methylene bridges are respectively 154.4(3) and 123.3(2)°. The values of the dihedral angles between planes formed by the phenolic rings and benzenic rings show that those planes are almost perpendicular at 81.4(2) and 81.5(2)°; this situation is the same as in the case of *p*-cumylphenol and *p*-cumylcalix[6]arene [11]. This conformation is found for the first time for calix[8]arenes. Indeed the *p*-tert-calix[8]arene [3] as well as the one from bisphenol moieties [6] show the pleated loop conformation. *p*-tert-Butyl-calix[8]arenes crystallized with pyridine [5] as well as octa(*p*-hydroxy) octakis (propyloxy) calix[8]arene [7] crystallized from pyridine and water show a chair conformation with a centre of inversion.

It is known that the pleated loop conformation is stabilized by the cyclic array of hydrogen bonds between the hydroxyl groups. In contrast, as illustrated in Figure 2, four dimethylsulfoxide molecules are bound to the *p*-cumylcalix[8]arene through hydrogen bonds giving a (1:4) complex. This situation is repeated along the 'c' axis. However, the DMSO molecule presents a disorder involving two

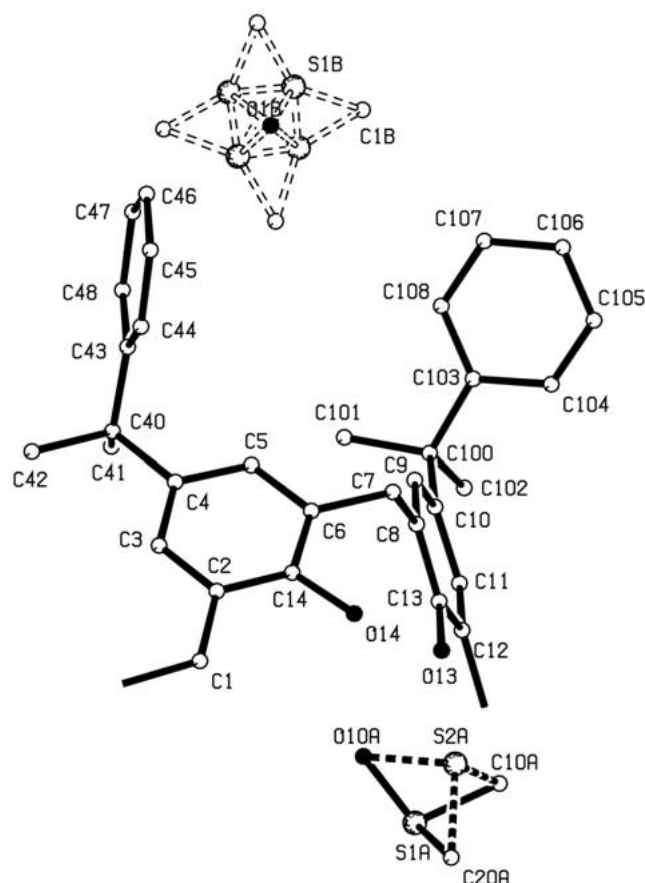


Figure 1. Numbering scheme of the asymmetric unit of the calixarene and of the solvents.

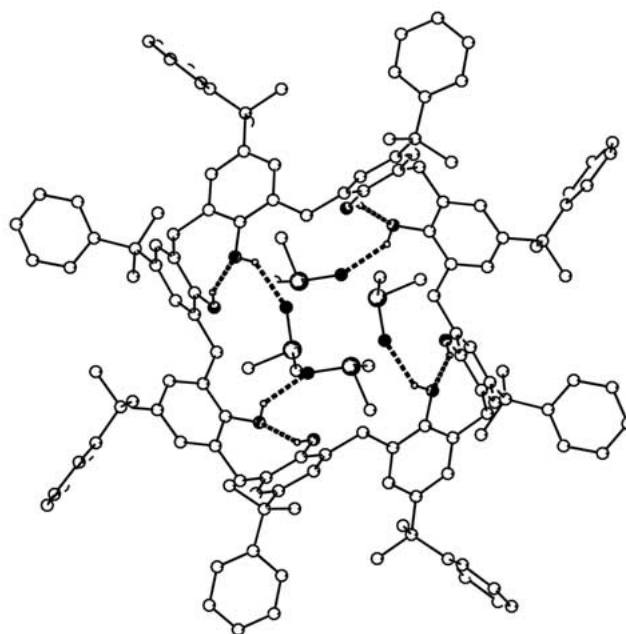


Figure 2. Conformation of the macrocycle with the solvent molecules hydrogen bonded (only the H atoms which participate to these bonds are shown).

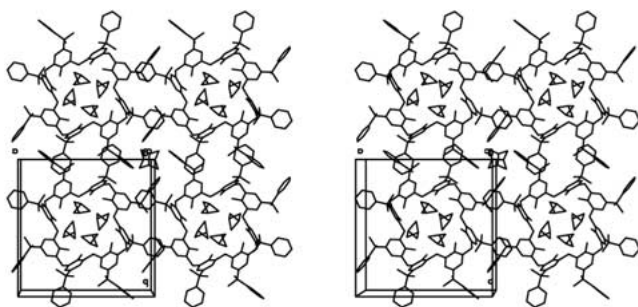


Figure 3. Stereoview of the packing of the title compound down *c* axis.

positions for the sulphur, with occupancies of 0.605 and 0.395.

An intra molecular hydrogen bond is found between O13 and O14: O13–H13 ... O14: 0.84 1.92 2.692 Å, 152°. Furthermore an intermolecular H-bond exists between O14 and the oxygen O10 A; O14–H14 ... O10 A: 0.84 1.93 2.597 Å, 135°. The present structure seems also to corroborate the conclusion of Gutsche *et al.* [8] as to the possible role of the solvent in breaking up the hydrogen bond ring between the phenolic –OH groups which are assumed to stabilize a cone conformation. The same situation was found for *p*-tert-butylcalix[8]arene with pyridine [5] and with the calixarene substituted by the propyloxy groups [7]: hydrogen bonds with the nitrogen of the solvents destroyed the pleated loop conformation.

In the packing a supplementary DMSO molecule is found between the macrocycles in the channels along the *c* axis. There are no interactions between the phenyl groups of the cumyl (C103–C108) and this DMSO. Due to the 4 symmetry the solvent is disordered with occupation 0.25 for the sulfur and oxygen atoms and 0.5 for the carbon. The oxygen atom is situated on the  $\bar{4}$  axis.

Figure 3 shows the packing of the title compound.

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