

## Structure of *p*-Phenylcalix[5]arene Dichloroform Solvate

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The conformational characteristics and complexation properties of calix[5]arenes have been extensively investigated by diffraction,<sup>1-5</sup> organic synthesis<sup>6-10</sup> and computation methods.<sup>11-13</sup>

The calix[5]arenes may possess a greater propensity to completely include small organic molecules than analogous calix[4]arenes due to their larger cavity size. Furthermore, the *p*-phenylcalix[*n*]arenes are specially attractive because not only do the phenyl groups increase the size of the cavity by considerable amount but they also provide potential sites at the 4' positions for the addition of functional groups.

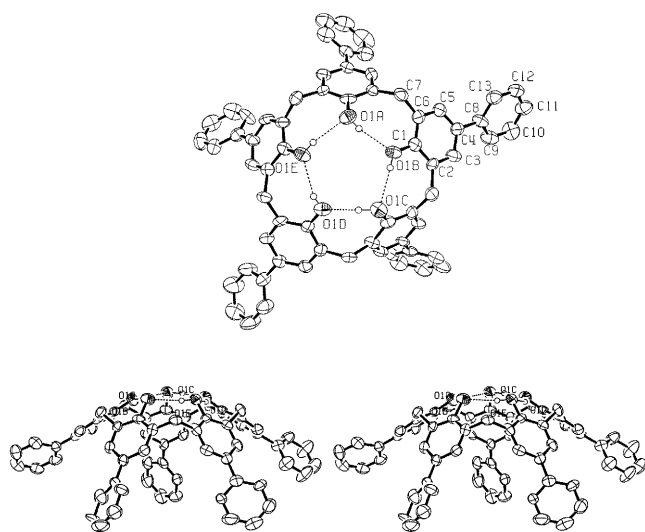
As a part of our ongoing research<sup>14-19</sup> in calixarene chemistry, we have synthesized the deep cavity *p*-phenylcalix[5]arene.<sup>6</sup> Herein we reported the crystal structure of *p*-phenylcalix[5]arene dichloroform solvate and described the molecular geometry of *p*-phenylcalix[5]arene.

The conformation of the molecule, shown in Figure 1, is mainly determined by the remarkable O-H...O intramolecular hydrogen bonding involving all five aromatic hydroxyl groups; the O...O separations are in the range 2.696-2.846 Å. The calix[5]arene shows that it adopts a distorted cone conformation. The conformation of this molecule is best described by the angles that the aromatic rings (A-E) make with the mean plane of the five macrocyclic ring methylene groups, *viz.* 125.5° (A), 147.9° (B), 122.7° (C), 146.5° (D)

and 126.1° (E). Inspection of these tilting angles reveals that B and D rings are inclined outward markedly. The relative dihedral angles between two adjacent rings are; A-B=126.2, B-C=128.8, C-D=126.9, D-E=127.2 and E-A=124.8°. Five outer rim phenyl groups are twisted away from the plane of their adjoining inner phenyl ring at dihedral angles of 30.1 (A), 34.6 (B), 43.7 (C), 42.8 (D) and 32.5° (E), respectively. The cone conformation can be described in terms of pentagon geometry shown in Table 2. The pentagons including five hydroxyl O1, methylene C7 and inner phenyl C1 atoms are close to the regular pentagons while outer phenyl C8 and C11 atoms make the distorted pentagons.

Two chloroform molecules are present within crystal lattice, but there are no short intermolecular contacts and are located outside the calix[5]arene cavity as shown in Figure 2.

A search of the 2003 release of the Cambridge Structural Database<sup>20</sup> shows that there have been structural reports on 50 calix[5]arenes out of 1342 calixarene crystal structures. Among them, 3 crystal structures of *p*-phenylcalix[5]arenes have been reported, namely: *p*-phenylcalix[5]arene<sup>1</sup> (disordered one outer phenyl group, 1.75 disordered toluene



**Figure 1.** View of the molecule with our numbering scheme (Top); A stereo view of the molecule (Bottom). Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for the sake of clarity.

**Table 1.** Intramolecular Hydrogen Bonds in *p*-Phenylcalix[5]arene

D H A	D-H	D...A	D-H...A
O1A-H...O1B	0.77 Å	2.793 Å	165°
O1B-H...O1C	0.77	2.846	169
O1C-H...O1D	0.98	2.696	171
O1D-H...O1E	0.76	2.792	150
O1E-H...O1A	0.77	2.818	168

**Table 2.** The Shape and Size of the Calix[5]arene in Terms of Pentagons

	O1	C1	C7	C8	C11
A-B	2.793 Å	3.921 Å	5.061 Å	7.689 Å	10.468 Å
B-C	2.846	4.008	5.059	7.685	10.226
C-D	2.696	3.916	5.058	7.740	10.370
D-E	2.792	3.932	5.038	7.481	9.993
E-A	2.818	3.917	5.021	6.980	8.734
A-B-C	112.6°	105.4°	105.4°	89.1°	82.8°
B-C-D	103.3	111.3	109.9	122.1	123.7
C-D-E	110.7	104.0	106.9	89.3	84.1
D-E-A	109.4	111.3	107.9	116.6	118.5
E-A-B	102.4	107.8	109.6	114.3	116.4

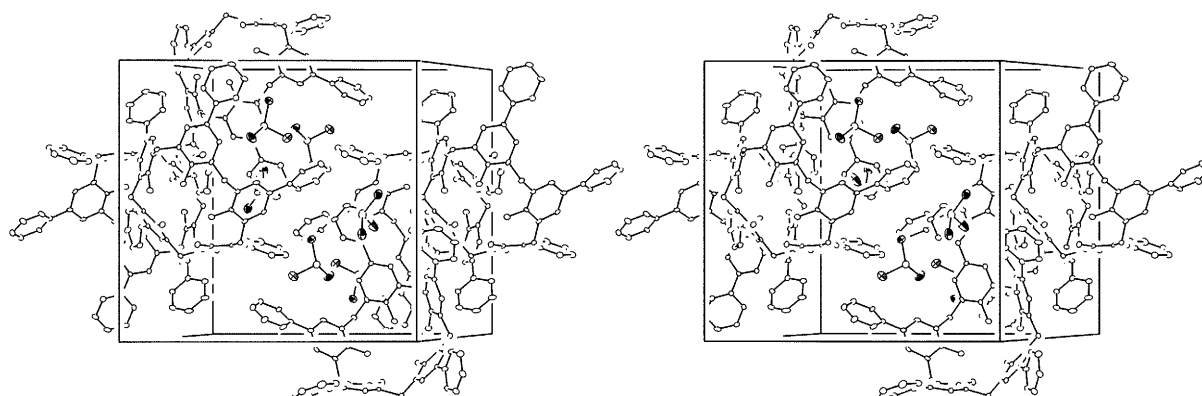


Figure 2. A stereoview of the crystal structure of *p*-phenylcalix[5]arene dichloroform solvate in view down the *c* axis.

Table 3. Summary of the O...O and C...C separations and pentagon angles for the reported *p*-phenylcalix[5]arenes

	I	II	III	IV
O1...O1	2.70-2.85 Å	2.74-2.79 Å	2.68-2.75 Å	2.70-2.73 Å
	102-113°	103-108°	106-110°	105-110°
C7...C7	5.02-5.06	5.03-5.07	5.05-5.09	5.06-5.08
	105-110	106-109	107-109	108-109
C11...C11	8.73-10.47	9.09-10.53	9.19-10.54	9.68-10.39
	83-124	83-119	103-112	102-105

I: chloroform solvate (this work), II: toluene solvate, III: fullerene complex 1, IV: fullerene complex 2.

solvate complex); *p*-phenylcalix[5]arene-fullerene<sup>1</sup> (2/1 inclusion and 1.5 toluene solvate complex). All three calix[5]arenes are in unsymmetrical cone conformation with intramolecular hydrogen bonding. The geometry of the pentagones, involving range of O...O, C...C separations and angles, are summarized in Table 3 for the *p*-phenylcalix[5]arene structure determination. The O...O separations are similar in all four determinations and in the range 2.7-2.9 Å. Two calix[5]arene molecules of fullerene complex have a more symmetric cone conformation than in dichloroform solvate (this work) and toluene solvate forms.

The results of this study suggest that the distortion of a cone conformation is not sufficient to ensure the intramolecularly since other factors, for instance crystallization solvent or crystal packing effects, could become predominant.

### Experimental Section

The crystals of title compound were obtained by recrystallization from chloroform and methanol at room temperature.

X-ray data were collected using a Nonius CAD-4 diffractometer with MoK $\alpha$  graphite monochromated radiation up to  $\theta_{\max}$  of 20°. Space Group is monoclinic, P2<sub>1</sub>/c. The  $\omega/2\theta$  scan width was (0.9 + 0.35tan $\theta$ )°.

Refinement was by full-matrix least-squares methods. All H atoms of hydroxyl groups were located in successive difference Fourier maps, and all other H atoms were located in geometrically calculated positions and refined isotropically.

Table 4. Crystal Data of *p*-Phenylcalix[5]arene

Formula	C <sub>65</sub> H <sub>50</sub> O <sub>5</sub> ·2CHCl <sub>3</sub>
Mw,amu	1149.79
Crystal system	monoclinic
Space group	P2 <sub>1</sub> /c
<i>a</i> , Å	18.981(4)
<i>b</i> , Å	18.043(3)
<i>c</i> , Å	17.488(4)
$\beta$ , °	109.95(2)
Z	4
V, Å <sup>3</sup>	5630(2)
$\mu$ (Mo-K $\alpha$ ), cm <sup>-1</sup>	3.6
Density, gcm <sup>-3</sup>	1.36 (calc.)
Diffractometer	Enraf-Nonius CAD-4
Radiation	Mo-K $\alpha$ ( $\lambda$ = 0.7107 Å) graphite monochromator
Crystal size, mm	0.5 × 0.6 × 0.45
$\theta_{\text{limits}}$ , °	20
Scan type	$\omega/2\theta$
Scan range, °	0.9 + 0.35tan $\theta$
No. of observed reflections	2656  F <sub>o</sub>   > 4 $\sigma$  F <sub>o</sub>
R	0.088

ly. The following programs are used: Data collection: CAD-4-PC software,<sup>21</sup> Cell refinement: SET4<sup>21</sup> and CELDIM,<sup>21</sup> Data reduction: WinGX,<sup>22</sup> Program(s) used to solve structure: SHELXS-97,<sup>23</sup> Program(s) used to refine structure: SHELXL-97,<sup>23</sup> Molecular graphics: ORTEP3.<sup>24</sup> The crystal data and refinements were summarized in Table 4.

**Supporting Information Materials.** Crystallographic data for *p*-phenylcalix[5]arene have been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition numbers CCDC 254185.

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