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The influence of solvent of crystallization upon the solid-state conformation of calix[6]arenes'

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The X-ray structures of complexes between *p-t*-butylcalix[6]arene and DMSO (3) and calix[6]arene and benzene (2), acetone (4), and dioxane/water (5) are presented and compared to similar studies. The solid state conformation appears to be very dependent upon the crystallization solvent. Those solvents that cannot participate in hydrogen bonding with the calixarene co-crystallize with the calixarene in a pinched cone conformation in which all calixarene -OH groups hydrogen bond with each other in a cyclic array. When the solvent can disrupt the intra-calixarene hydrogen bonding, however, the macrocycle adopts some form of the 1,2,3-alternate conformation. The finer features of this conformation depend upon both the extent of the calixarene-solvent hydrogen bonding, as well as other interactions.

INTRODUCTION

Interest in calixarenes (1) as potential host compounds is increasing due to the relative ease in which they may be substituted by a large spectrum of functional groups, as well as the wide range of receptor sites of differing shape and size that may be defined by these molecules.[2] This latter feature of the calixarenes arises as a consequence of the rotation about the methylene bridges which allows the aromatic rings to adopt different relative orientations; thus cavities of varying geometries may be constructed.

The inherent problem with calixarenes is that they are not usually rigid because of this rotation about the methylene bridges. In order to synthesize a calixarene with a "preformed" cavity, therefore, the rotation must be stopped. Methods of achieving this for calix[4]arenes (1, n = 4) are well established, utilizing either sufficiently bulky substituents[3] or inter-ring bridges.[4] For the calix[6]arenes, however, the problems associated with "freezing" a particular conformation are more difficult to overcome. It is possible to eliminate the rotation by substitution with bulky groups. Unlike the calix[4]arenes, however, in which the rotation is limited to the passage of the oxygen end of an aromatic through the center of the calixarene, and *O*-substitution by any group larger than ethyl is sufficient to stop the rotation,[3] both ends of the aromatic rings of an unsubstituted calix[6] arene may pass through the center of the macrocycle, and even unsubstituted aryl R' groups[5] or *para-t*-butyl groups[6] are of insufficient bulk to completely halt conformational interchange. Thus, while judicious functionalization of calix[6]arenes may produce a molecule with a pre-formed cavity, the fact that most of the synthetic sites must be utilized for conformational control reduces the range of groups accessible for defining the electronic attributes of the cavity. A number of calix[6]arenes in which two or more aromatic subunits are linked at either the oxygen or *para*-positions have been reported, and in most cases, these calixarenes are more conformationally rigid.[5,7] Again, however, the number of sites available for further substitution is reduced by using this approach.

While it is, therefore, difficult to obtain calix[6]arenes with preformed cavities in the solution phase, many potential applications of calixarenes lie in solid state molecular recognition. Thus, it is important to gain an understanding of the factors that affect the more easily controlled crystalline conformational properties. Although it is well established that the conformations of unsubstituted calixarenes are dependent primarily upon the extent of intra-calixarene hydrogen-bonding,[8] no

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systematic study has been carried out on either the effects of disrupting these interactions or upon secondary effects due to included solvent. In this contribution, we describe the crystal structures of simple calixarenes crystallized from four different solvents (benzene, DMSO, acetone and dioxane/water), and compare the results to others reported in the literature. The aims of this work are to define similarities and differences between solid-state calix[6]arene conformations, as well as to investigate the effects of the parameter that is most easily modified when obtaining calixarenes in the solid state—the solvent of crystallization.

EXPERIMENTAL

Preparation

Calix[6]arene (**1**, R = R' = H)[9] and *p-tert*-butylcalix[6]arene[10] (**1**, R = *t*-Bu, R' = H) were synthesized according to literature procedures. Complexes **2** and **3** were recrystallized from benzene and DMSO without modification. Complexes **4** and **5** were recrystallized from acetone and dioxane solutions of the calix[6]arene·Na$^+$ salt,[11] respectively.

Crystallography

Crystal and data collection and solution details are given in Table 1. Standard procedures in our laboratory have been described previously.[12] Data were collected on an Enraf-Nonius CAD-4 diffractometer equipped with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) and corrected for Lorentz and polarization effects. The structures were solved by using direct methods (SIR[13] for **2**, **3** and **5** and MULTAN[14] for **4**) and difference Fourier syntheses and refined by using full-matrix least squares.[15] Three of the *t*-butyl groups in **3** exhibited some disorder. Relative occupancies were determined by refining the occupancy factors together with a common thermal parameter. The presence of a solvent molecule of partial occupancy was noted towards the latter stages of refinement of **3**. Refinement of a common occupancy for this, linking the thermal parameter to that of the other solvent molecules, resulted in a calculated occupancy of 0.48(8). The positional parameters and a common thermal parameter were included in further refinement cycles. An area of disorder was also noted in **5**. This was resolved into eighteen positions over a center of inversion corresponding to a molecule of dioxane in nine overlapping orientations. Each position of electron density was treated as a carbon atom of 1/3 occupancy due to the impossibility of distinguishing between oxygen and carbon contributions (no short contacts between any of the disorder positions and other atoms were present). The inclusion of anisotropic parameters was dependent upon the number of observed data. In complexes **2–4**, the calixarene oxygens, methylene carbons and full-occupancy solvent atoms were treated with anisotropic thermal parameters, while in complex **5**, only the oxygen atoms of the calixarene and full occupancy solvent molecules were refined in this fashion. For

TABLE 1 Crystal data and Experimental Details for Complexes **2–5**

Compound	**2**	**3**	**4**	**5**
Crystal habit	block	block	parallelpiped	block
Crystal size (mm^3)	0.3 × 0.35 × 0.42	0.12 × 0.22 × 0.25	0.12 × 0.15 × 0.48	0.21 × 0.23 × 0.41
Molecular formula	$C_{54}H_{48}O_6$	$C_{71}H_{99}O_{8.5}S_{2.5}$	$C_{48}H_{48}O_8$	$C_{58}H_{72}O_{16}$
Molecular mass	792.98	1168.74	752.91	1025.21
Space group	C2/c	$P\bar{1}$	$P2_1/a$	$P\bar{1}$
Unit cell:				
a (Å)	22.333(3)	15.965(2)	8.965(1)	10.5040(8)
b (Å)	10.332(2)	16.433(1)	20.648(2)	12.020(1)
c (Å)	18.922(4)	17.596(2)	11.434(1)	12.2873(9)
α (°)	90	63.751(6)	90	68.725(7)
β (°)	98.29(3)	63.184(8)	112.67(1)	66.386(6)
γ (°)	90	88.001(8)	90	83.112(8)
Volume (Å^3)	4321(1)	3616.0(9)	1953.0(4)	1324.0(2)
Z	4	2	2	1
D_{calc} (g cm^{-3})	1.224	1.073	1.280	1.286
μ_{calc} (cm^{-1})	0.73	1.31	0.81	0.87
2θ range (°)	2–44	2–36	2–44	2–40
Measured refl'ns	2890	4960	2649	3158
Unique refl'ns	2817	4960	2475	3158
R_{merg}	0.027	—	0.032	—
Obs'd refl'ns (I > 3σ(I))	1091	2588	962	1501
R	0.0712	0.0712	0.0556	0.0678
R_w	0.0703	0.1030	0.0563	0.0759
GOF	1.33	1.46	0.93	1.67
w	$[0.04F^2 + (\sigma F)^2]^{-1}$	$[0.04F^2 + (\sigma F)^2]^{-1}$	$[0.04F^2 + (\sigma F)^2]^{-1}$	$[0.04F^2 + (\sigma F)^2]^{-1}$
$(\text{shift/error})_{max}$	<0.04	<0.01	<0.01	<0.1
$(\text{Final electron density})_{max}$	0.13	0.61	0.18	0.39

complexes **2**, **4**, and **5**, all hydrogen atoms were located from difference maps and included in the model (in idealized positions, if possible, [$d_{C\text{-}H}$ = 0.95 Å, U(H) = 1.3 U_{eq}(attached atom)]) and not refined. The positions of most of the hydrogen atoms in complex **3** were not apparent from difference maps, however, so these were calculated and treated as above. Scattering factors were taken from the usual source.[16] No variation of $w(|F_0| - |F_c|)$ *vs.* $|F_0|$ or $(\sin \theta/\lambda)$ was observed. Final atomic coordinates are given in Tables 2–5 for complexes **2** to **5**, respectively. Bond lengths and angles (between atoms of highest occupancy where appropriate) are listed in Tables 6 and 7, respectively.

RESULTS AND DISCUSSION

Calix[6]arenes Crystallized from Non-Hydrogen Bonding Solvents

The structure of the benzene complex of calix[6]arene (**2**) is shown in Figure 1.[17] The calixarene adopts the "pinched cone" conformation, in which all of the oxygen atoms lie on the same side of the molecule, and the aromatic fragments are arranged such that the oxygens define a boat shaped array. Thus, two opposite aromatic rings lie somewhat flatter than the remaining four, so that the methylene bridges bonded to these point towards the oxygen atoms, while the two methylene bridges that connect only the more "vertical" aromatic rings point towards the center of the calix, and away from the oxygens. The potential molecular C_{2v} symmetry is reflected in the solid state, as the molecule lies on a two-fold rotation axis that passes through the center of the calix. The intra-oxygen distances are normal for a hydrogen-bonded system, being 2.61(1), 2.68(1), and 2.63(1) Å, for the order O1a-O1b-O1c-O1a'. The hydrogen atoms were located from a difference map, and, as would be expected for a room-temperature structure determination of a "cyclic" system,[18] each of these lies virtually in between two oxygen atoms, with O-H distances of 1.27, 1.35, 1.42, 1.29, 1.37 and 1.28 Å for the bonding pattern used above.

TABLE 2 Final fractional atomic coordinates for **2**

Atom	x	y	z	B_{eq}*
O1a	−0.0269(3)	0.0795(6)	0.1307(3)	5.9(2)
O1b	0.0825(3)	0.0804(6)	0.2016(3)	5.3(2)
O1c	0.1097(3)	−0.0617(5)	0.3204(3)	5.4(2)
C1a	−0.0359(4)	0.1380(8)	0.0653(4)	4.7(2)
C1b	0.1265(4)	0.1395(8)	0.1677(4)	4.4(2)
C1c	0.1639(4)	−0.0041(9)	0.3527(5)	4.9(2)
C2a	−0.0812(4)	0.0921(8)	0.0313(4)	4.5(2)
C2b	0.1080(4)	0.2443(9)	0.1221(4)	5.0(2)
C2c	0.2068(4)	0.0253(8)	0.3115(4)	4.7(2)
C3a	−0.0884(4)	0.152(1)	−0.0532(5)	6.5(3)
C3b	0.1532(4)	0.3005(9)	0.0898(5)	5.8(2)
C3c	0.2582(4)	0.089(1)	0.3436(5)	6.0(2)
C4a	−0.0519(5)	0.254(1)	−0.0666(5)	6.9(3)
C4b	0.2103(4)	0.257(1)	0.1001(5)	6.2(2)
C4c	0.2656(4)	0.118(1)	0.4171(5)	6.1(2)
C5a	−0.0090(5)	0.302(1)	−0.0128(5)	6.1(2)
C5b	0.2274(4)	0.156(1)	0.1465(5)	6.2(2)
C5c	0.2213(4)	0.0809(9)	0.4554(5)	5.5(2)
C6a	0.0003(4)	0.2430(9)	0.0545(4)	4.9(2)
C6b	0.1837(4)	0.0977(8)	0.1808(4)	4.5(2)
C6c	0.1698(4)	0.0227(9)	0.4268(5)	4.9(2)
C7a	0.0454(5)	0.2987(9)	0.1121(4)	5.8(3)
C7b	0.2028(4)	−0.0120(9)	0.2337(5)	6.0(3)
C7c	−0.1222(4)	−0.0158(9)	0.0297(5)	5.9(3)
C1s	0.1328(5)	0.389(1)	0.3731(6)	8.3(3)
C2s	0.1262(7)	0.498(1)	0.4077(5)	11.2(4)
C3s	0.1060(6)	0.608(1)	0.3719(7)	10.8(4)
C4s	0.0896(7)	0.606(1)	0.3059(8)	13.7(5)
C5s	0.101(1)	0.499(1)	0.2658(7)	17.7(7)
C6s	0.1211(8)	0.391(1)	0.3039(7)	14.1(6)

*$B_{eq} = (4/3) *[a^2*B_{11} + b^2*B_{22} + c^2B_{33} + ab(\cos \gamma)B_{12} + ac(\cos \beta)B_{13} + bc(\cos\alpha)B_{23}]$

Two general systems of describing the calixarene conformation have been utilized in the past—the relative orientation of the aromatic planes, and the torsion angles about the methylene bridges. While the former is not a very consistent method for the larger calixarenes because of the difficulty in selecting an origin plane,[19] it does enable discussion of certain points. Three obvious choices exist for the "origin" plane—the plane (plane 1) defined by the four methylene carbons attached to the "flattened" aromatics, C7b, C7b', C7c and C7c' (which plane is virtually parallel (6°) to the plane defined by the four oxygens that make up the bottom of the boat); and the plane (plane 2) defined by the methylenes in each half of the molecule, C7a, C7b, C7c and C7a' (which plane is virtually parallel (8°) to the plane defined by the three oxygens in the "prow" of the boat). A third plane, that defined by averaging ALL of the methylene carbons which is the standard used for calix[4]arene structures, is not appropriate for calix[6]arene conformations. The values for the angles made by each aromatic ring (A, B, and C, matching the numbering scheme) with each of these origin planes are given in Table 8. Also listed in Table 8 are the angles between the planes defined by each aromatic ring. All three sets of numbers emphasize the "flattening" of ring C, and the "pinching" of rings A and B.

The torsion angles about the methylene bridges (Table 9) define the conformation as, (according to the system of Ugozzoli and Andreetti)[19] "$C_2 - + + - + - - + + - + -$", in common with other "pinched-cone" calix[6]arene structures. The flattening of ring C relative to A and B is demonstrated effectively in an analysis of these numbers, and is more apparent than in previous structures.[20,21]

Two symmetry-related molecules of benzene occupy the calixarene cavity, lying virtually perpendicular to the flattened rings (angle of 98(1)°), as shown in Figure 2. The closest interactions are those between the bottom two carbons of the benzene ring and the closest "edge" of the calix aromatics on either side of the flattened ring.

TABLE 3 Final fractional atomic coordinates for **3**

Atom	x	y	z	B_{eq}*
O1a	0.1893(5)	−0.1410(4)	0.3782(4)	4.8(2)
O1b	0.3079(5)	−0.0502(4)	0.1830(4)	4.7(2)
O1c	0.2969(5)	0.1251(5)	0.1643(4)	5.2(2)
O1d	0.3316(5)	0.1698(5)	0.4042(5)	5.8(3)
O1e	0.3197(5)	0.0755(4)	0.5815(4)	5.1(2)
O1f	0.2285(5)	−0.0688(4)	0.5896(4)	4.8(2)
C1a	0.2105(7)	−0.2145(6)	0.4394(6)	3.7(3)
C1b	0.3955(7)	−0.0760(6)	0.1751(6)	3.4(3)
C1c	0.3797(7)	0.1652(7)	0.1485(6)	3.8(3)
C1d	0.2854(7)	0.2411(7)	0.3885(6)	4.3(3)
C1e	0.2418(8)	0.0991(7)	0.6432(7)	5.2(3)
C1f	0.1524(7)	−0.1318(6)	0.6743(6)	3.6(3)
C2a	0.1785(7)	−0.2340(7)	0.5352(6)	4.4(3)
C2b	0.3976(7)	−0.1669(6)	0.2280(6)	3.3(3)
C2c	0.4691(7)	0.1551(7)	0.0923(7)	4.5(3)
C2d	0.2573(7)	0.2689(6)	0.3183(6)	3.7(3)
C2e	0.2290(7)	0.1873(7)	0.6147(7)	4.7(3)
C2f	0.1301(7)	−0.1415(7)	0.7651(6)	4.0(3)
C3a	0.2054(8)	−0.3085(7)	0.5894(7)	4.7(3)
C3b	0.4830(7)	−0.1859(7)	0.2214(6)	4.1(3)
C3c	0.5514(8)	0.1981(7)	0.0785(7)	5.2(3)
C3d	0.2083(8)	0.3422(7)	0.3032(7)	5.0(3)
C3e	0.1468(8)	0.2087(7)	0.6760(7)	5.1(3)
C3f	0.0530(7)	−0.2062(7)	0.8482(6)	4.2(3)
C4a	0.2657(8)	−0.3612(7)	0.5535(7)	5.1(3)
C4b	0.5678(7)	−0.1197(7)	0.1594(6)	4.2(3)
C4c	0.5438(8)	0.2521(7)	0.1246(7)	5.2(3)
C4d	0.1875(8)	0.3884(7)	0.3587(7)	5.2(3)
C4e	0.0800(7)	0.1397(7)	0.7663(6)	4.1(3)
C4f	−0.0016(7)	−0.2675(7)	0.8453(6)	4.2(3)
C5a	0.2946(8)	−0.3375(7)	0.4568(7)	5.2(3)
C5b	0.5656(7)	−0.0301(7)	0.1024(6)	4.0(3)
C5c	0.4520(8)	0.2599(7)	0.1823(7)	5.1(3)
C5d	0.2190(7)	0.3635(7)	0.4227(7)	4.5(3)
C5e	0.0930(7)	0.0511(7)	0.7928(7)	4.4(3)
C5f	0.0210(7)	−0.2582(7)	0.7566(7)	4.3(3)
C6a	0.2691(7)	−0.2652(6)	0.3994(6)	3.8(3)
C6b	0.4794(7)	−0.0081(7)	0.1082(6)	3.9(3)
C6c	0.3707(7)	0.2177(6)	0.1961(6)	3.8(3)
C6d	0.2687(7)	0.2939(7)	0.4400(6)	4.4(3)
C6e	0.1734(7)	0.0278(7)	0.7348(6)	3.9(3)
C6f	0.0975(7)	−0.1908(6)	0.6711(6)	3.5(3)
C7a	0.3087(8)	−0.2401(6)	0.2934(6)	4.3(4)
C7b	0.4805(8)	0.0939(7)	0.0436(6)	4.9(4)
C7c	0.2695(8)	0.2151(7)	0.2648(7)	5.1(4)
C7d	0.2986(8)	0.2666(7)	0.5162(7)	5.5(4)
C7e	0.1878(8)	−0.0709(7)	0.7686(7)	5.2(4)
C7f	0.1134(7)	−0.1783(7)	0.5762(6)	4.3(4)
C8a	0.295(1)	−0.4450(9)	0.6184(9)	8.7(4)
C8b	0.6661(9)	−0.1428(8)	0.1531(8)	6.5(4)
C8c	0.634(1)	0.2974(9)	0.1156(8)	7.9(4)
C8d	0.1197(9)	0.4657(9)	0.3489(9)	7.9(4)
C8e	−0.0035(8)	0.1669(7)	0.8306(7)	5.2(3)
C8f	−0.0811(8)	−0.3417(8)	0.9371(7)	5.8(3)
C9a	0.289(2)	−0.439(2)	0.701(1)	8.7(7)
C9b	0.721(1)	−0.064(1)	0.1483(9)	9.1(4)
C9c	0.727(1)	0.275(1)	0.055(1)	10.4(5)
C9d	0.020(1)	0.414(1)	0.423(1)	15.3(7)
C9e	0.012(2)	0.264(2)	0.808(2)	11.(1)
C9f	−0.088(1)	−0.431(1)	0.936(1)	12.9(6)
C10a	0.401(2)	−0.439(2)	0.570(2)	10.1(8)
C10b	0.729(1)	−0.135(1)	0.053(1)	10.7(5)
C10c	0.625(1)	0.268(1)	0.216(1)	12.8(6)
C10d	0.140(1)	0.533(1)	0.381(1)	13.2(6)
C10e	−0.086(2)	0.162(2)	0.822(2)	12.(1)
C10f	−0.177(2)	−0.328(2)	0.937(2)	19.0(9)
C11a	0.220(2)	−0.535(2)	0.649(2)	14.(1)
C11b	0.658(1)	−0.230(1)	0.226(1)	13.0(6)
C11c	0.649(1)	0.402(1)	0.054(1)	14.8(7)
C11d	0.094(2)	0.479(2)	0.274(2)	9.6(9)
C11e	−0.019(2)	0.120(2)	0.929(2)	10.(1)
C11f	−0.076(2)	−0.362(1)	1.024(1)	16.4(8)
S1	0.0276(2)	0.0175(2)	0.3784(2)	5.9(1)
O1s	0.1023(5)	−0.0132(4)	0.4077(4)	5.2(2)
C1s	−0.0638(8)	−0.0838(9)	0.4414(8)	7.9(5)
C2s	0.0741(8)	0.0328(8)	0.2597(7)	6.4(4)
S2	0.4603(2)	−0.0299(2)	0.4225(2)	6.8(1)
O2s	0.5675(5)	−0.0079(6)	0.3587(6)	8.1(4)
C3s	0.425(1)	−0.151(1)	0.490(1)	12.4(7)
C4s	0.4082(8)	−0.0089(9)	0.3472(7)	6.7(4)
S3	0.5024(8)	0.4308(7)	0.7893(7)	13.1(3)
O3s	0.550(2)	0.422(2)	0.723(1)	13.1(3)
C5s	0.490(3)	0.362(2)	0.881(2)	13.1(3)
C6s	0.546(3)	0.501(2)	0.784(2)	13.1(3)

$*B_{eq} = (4/3) *[a^2*B_{11} + b^2*B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$

Thus, C1s lies at distances of 3.67(1), 3.67(1), and 3.76(1) Å, from C1b, C1a', and C6a', respectively; while C6s is 3.73(1) Å from C2b.

This conformation has been observed for a number of simple calix[6]arene structures, including *p-t*-butylcalix[6]arene crystallized from benzene,[21] chloroform,[20] and tetrachloroethylene,[22] and *p-i*-propylcalix[6]arene crystallized from a carbon disulfide/benzene mixture.[21] In addition, unsolvated *p-t*-butylcalix[6]arene included in the lattice of a europium-calix[6]arene complex has the same conformation,[23] as does the 1,4-*O*-thiophosphate complex.[24] While high thermal motion of both the *p*-substituents and included solvent precluded high quality structure refinement for some of these structures, some general features may be extracted for discussion.

The most important point to appreciate is that solvent interactions may play little role in the crystal structures. The two structures crystallized from benzene alone are such that two benzene molecules are included in the cavity (Figure 2); however, the only interactions between the calixarene and tetrachloroethylene are *exo*-cavity, while poor crystal quality precluded any definite statement being made concerning the *iso*-propyl derivative. Thus, intramolecular hydrogen bonding between all six calixarene oxygens would indeed appear to be the primary factor influencing the conformation. In addition, it is interesting to note that this conformation is also found for a 1,4-*O*-substituted calixarene crystallized from hexane, despite the fact that there is not a full complement of phenolic hydrogens.

Calix[6]arenes Crystallized from Hydrogen-Bonding Solvents—1,2,3-Alternate Conformers

The remaining three structures presented herein were all crystallized from solvents that may take part in hydrogen bonding—DMSO, acetone and dioxane/water. In all

TABLE 4 Final fractional atomic coordinates for 4

Atom	x	y	z	B_{eq}*
O1a	0.4207(6)	0.5161(2)	0.2691(5)	3.7(1)
O1b	0.0488(6)	0.3720(2)	0.0101(5)	3.6(1)
O1c	−0.2645(6)	0.3706(2)	−0.1892(4)	3.4(1)
C1a	0.3294(8)	0.4823(4)	0.3222(6)	2.9(2)
C1b	0.1194(8)	0.3135(4)	0.0586(6)	2.6(1)
C1c	−0.2101(8)	0.3373(3)	−0.2698(6)	2.6(1)
C2a	0.2818(8)	0.5167(3)	0.4060(6)	2.7(1)
C2b	0.2698(8)	0.3169(4)	0.1563(6)	2.7(1)
C2c	−0.1299(8)	0.2791(4)	−0.2222(6)	2.8(2)
C3a	0.1866(9)	0.4851(4)	0.4581(7)	4.3(2)
C3b	0.3431(9)	0.2598(4)	0.2126(7)	3.7(2)
C3c	−0.0655(9)	0.2452(4)	−0.2965(7)	4.0(2)
C4a	0.1405(9)	0.4212(4)	0.4274(7)	4.3(2)
C4b	0.2705(9)	0.2009(4)	0.1704(7)	3.4(2)
C4c	−0.0868(9)	0.2667(4)	−0.4148(7)	4.8(2)
C5a	0.1920(9)	0.3888(4)	0.3443(7)	3.7(2)
C5b	0.1235(8)	0.1984(4)	0.0706(6)	3.1(2)
C5c	−0.1736(9)	0.3229(4)	−0.4621(7)	4.1(2)
C6a	0.2855(8)	0.4181(4)	0.2892(6)	2.6(1)
C6b	0.0472(7)	0.2545(3)	0.0121(6)	2.6(1)
C6c	−0.2387(8)	0.3586(4)	−0.3906(7)	3.1(2)
C7a	0.3476(9)	0.3817(4)	0.2033(7)	3.4(2)
C7b	−0.1172(8)	0.2525(4)	−0.0958(7)	3.4(2)
C7c	0.3462(8)	0.5844(4)	0.4496(7)	3.5(2)
O1s	0.1308(7)	0.0290(3)	0.1704(6)	8.2(2)
C1s	0.2303(9)	−0.0052(4)	0.1560(7)	4.3(2)
C2s	0.339(1)	0.0190(5)	0.0952(8)	6.2(3)
C3s	0.256(1)	−0.0714(5)	0.2047(9)	7.6(3)

*$B_{eq} = (4/3) * [a^2 * B_{11} + b^2 * B_{22} + c^2 B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$

TABLE 5 Final fractional atomic coordinates for 5

Atom	x	y	z	B_{eq}*
O1a	1.3958(5)	0.3776(5)	0.2537(5)	4.1(2)
O1b	1.1781(5)	0.6506(5)	0.3725(5)	3.8(2)
O1c	0.7985(5)	0.7943(5)	0.5927(5)	4.2(2)
C1a	1.3605(8)	0.4658(7)	0.1628(7)	3.4(2)
C1b	1.2579(8)	0.7530(7)	0.3064(7)	3.0(2)
C1c	0.9018(8)	0.7875(7)	0.6365(7)	3.1(2)
C2a	1.2999(8)	0.4297(7)	0.1006(7)	3.3(2)
C2b	1.3939(8)	0.7436(6)	0.2282(6)	2.9(2)
C2c	1.0341(8)	0.8247(7)	0.5462(7)	3.0(2)
C3a	1.2629(9)	0.5156(7)	0.0075(7)	4.1(2)
C3b	1.4794(8)	0.8452(7)	0.1615(7)	4.0(2)
C3c	1.1381(9)	0.8247(8)	0.5862(8)	4.4(2)
C4a	1.2857(9)	0.6360(8)	−0.0203(8)	4.8(2)
C4b	1.4290(9)	0.9541(8)	0.1730(8)	4.3(2)
C4c	1.113(1)	0.7874(8)	0.7141(8)	5.0(2)
C5a	1.3444(9)	0.6698(7)	0.0449(7)	4.0(2)
C5b	1.2941(9)	0.9605(8)	0.2507(7)	4.2(2)
C5c	0.9810(9)	0.7482(8)	0.8011(8)	4.4(2)
C6a	1.3812(8)	0.5869(7)	0.1396(7)	3.1(2)
C6b	1.2043(8)	0.8606(7)	0.3210(7)	3.2(2)
C6c	0.8726(8)	0.7451(7)	0.7670(7)	3.5(2)
C7a	1.4432(8)	0.6256(7)	0.2131(7)	3.8(2)
C7b	1.0573(8)	0.8703(7)	0.4072(7)	3.7(2)
C7c	1.2707(9)	0.2970(7)	0.1338(7)	4.3(2)
O1w	0.4419(6)	0.6238(6)	0.6283(6)	6.4(2)
O1s	1.0676(6)	0.3676(5)	0.6469(5)	4.9(2)
O4s	1.2386(6)	0.4394(6)	0.7364(6)	6.3(2)
C2s	1.215(1)	0.3692(9)	0.5856(9)	5.5(2)
C3s	1.280(1)	0.3532(9)	0.6756(9)	5.9(3)
C5s	1.090(1)	0.4391(9)	0.7961(9)	6.2(3)
C6s	1.027(1)	0.4573(8)	0.7038(8)	5.3(2)
O7s	0.5178(7)	0.1242(5)	0.4573(6)	6.5(2)
C8s	0.430(1)	0.060(1)	0.584(1)	7.1(3)
C9s	0.520(1)	0.0657(9)	0.3751(9)	6.5(3)
C10s	0.070(3)	0.921(2)	0.066(2)	4.7(7)
C11s	−0.031(3)	0.982(3)	0.128(3)	6.1(8)
C12s	0.103(4)	0.932(3)	−0.052(3)	9(1)
C13s	−0.103(2)	0.906(2)	0.071(2)	3.1(5)
C14s	0.088(3)	1.016(2)	0.048(2)	5.1(7)
C15s	−0.007(3)	0.923(3)	0.116(3)	5.9(8)
C16s	−0.024(3)	0.887(2)	0.016(2)	4.8(7)
C17s	−0.130(3)	0.965(3)	0.095(3)	6.2(8)
C18s	0.146(3)	0.981(2)	−0.002(2)	4.8(7)

*$B_{eq} = (4/3) * [a^2 * B_{11} + b^2 * B_{22} + c^2 B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$

three cases, the conformation of the calix[6]arene may be loosely described as 1,2,3-alternate, in which three adjacent oxygen atoms lie on one side, and the other three on the other side of the molecule. The relative orientations of the aromatic rings in each complex, however, differ dramatically, due to interactions with solvent molecules. Views of the conformations of each complex are shown in Figures 3 through 5 for **3**–**5**, respectively. Each of these Figures is drawn so that the aromatic rings for which the oxygen lies on the top half of the molecule are on the right-hand side of the picture. "Side-on" views of each complex are presented in Figures 6 through 8, for **3** to **5**, respectively. In each case, these are drawn to show the entire interaction of one calixarene molecule with solvent (thus the contents of each Figure do not match the actual stoichiometry of the complex).

Complex **3**, shown in Figures 3 and 6, may readily be described as two mutually inverted trimeric subunits (consisting of rings A–C and D–F), and so matches the general description of a 1,2,3-alternate conformation. The two "halves", however, are rather dissimilar. A demonstration of these differences may be found in the angle of inclination of the aromatic rings relative to the average plane of the molecule (plane 1, drawn through C7A, C7B, C7D and C7E), as shown in Table 10. Thus, ring B is oriented in a virtually perpendicular fashion with respect to the average plane, ring C adopts a less perpendicular geometry, while the remaining rings are more "flattened", with angles of between 35 and 54°. The hydrogen bonding between the phenolic moieties is still intact within the trimeric units, however, so that the O...O distances are 2.72(1), 2.76(1), 2.72(1) and 2.74(1) Å, for O1A...O1B, O1B...O1C, O1D...O1E, and O1E...O1F, respectively. Although the hydrogens were not located in this structure, the intra-calixarene hydrogen bonding scheme may be inferred from the location of the solvent molecules (*vide infra*). Thus, the O...H-O pattern in one trimeric subunit is sequential, such that the hydrogen attached to O1C interacts with O1B, and the hydrogen attached to O1B interacts with O1A; while the other subunit consists of the hydrogens attached to both O1D and O1F interacting with O1E.

An examination of the torsion angles about the methylene bridges (Table 11) allows a description of the conformation as $C_1 - + - + - + + - + - - +$.[19] *It is in-*

TABLE 6 Bond Lengths (Å) for Complexes **2–5**

Atoms	**2**	3	4	5
O1a–C1a	1.37(1)	1.37(1)	1.38(1)	1.373(9)
O1b–C1b	1.39(1)	1.41(1)	1.376(8)	1.361(9)
O1c–C1c	1.41(1)	1.35(1)	1.38(1)	1.38(1)
O1d–C1d		1.35(1)		
O1e–C1e		1.41(1)		
O1f–C1f		1.363(8)		
C1a–C2a	1.39(1)	1.40(2)	1.39(1)	1.37(1)
C1b–C2b	1.41(1)	1.38(1)	1.382(8)	1.384(9)
C1c–C2c	1.35(1)	1.38(1)	1.40(1)	1.384(9)
C1d–C2d		1.39(2)		
C1e–C2e		1.35(2)		
C1f–C2f		1.40(2)		
C1a–C6a	1.39(1)	1.39(2)	1.39(1)	1.40(1)
C1b–C6b	1.34(1)	1.39(1)	1.39(1)	1.39(1)
C1c–C6c	1.42(1)	1.41(2)	1.38(1)	1.41(1)
C1d–C6d		1.45(2)		
C1e–C6e		1.41(1)		
C1f–C6f		1.37(2)		
C2a–C3a	1.39(1)	1.38(2)	1.38(1)	1.39(1)
C2b–C3b	1.38(1)	1.35(2)	1.38(1)	1.38(1)
C2c–C3c	1.39(1)	1.38(2)	1.39(1)	1.37(1)
C2d–C3d		1.40(2)		
C2e–C3e		1.43(2)		
C2f–C3f		1.37(1)		
C2a–C7c	1.50(1)		1.52(1)	1.53(1)
C2a–C7f		1.51(2)		
C2b–C7a	1.49(1)	1.49(1)	1.51(1)	1.50(1)
C2c–C7b	1.51(1)	1.54(2)	1.51(1)	1.52(1)
C2d–C7c		1.51(2)		
C2e–C7d		1.52(1)		
C2f–C7e		1.55(2)		
C3a–C4a	1.38(1)	1.40(2)	1.39(1)	1.39(1)
C3b–C4b	1.34(1)	1.39(1)	1.38(1)	1.39(1)
C3c–C4c	1.41(1)	1.41(2)	1.37(1)	1.39(1)
C3d–C4d		1.41(2)		
C3e–C4e		1.38(1)		
C3f–C4f		1.39(2)		
C4a–C5a	1.38(1)	1.41(2)	1.38(1)	1.37(1)
C4b–C5b	1.38(1)	1.38(1)	1.372(8)	1.37(1)
C4c–C5c	1.36(1)	1.40(1)	1.39(1)	1.37(1)
C4d–C5d		1.33(2)		
C4e–C5e		1.36(1)		
C4f–C5f		1.37(2)		
C4a–C8a		1.57(2)		
C4b–C8b		1.57(2)		
C4c–C8c		1.56(2)		
C4d–C8d		1.64(2)		
C4e–C8e		1.52(2)		
C4f–C8f		1.49(1)		
C5a–C6a	1.40(1)	1.37(2)	1.37(1)	1.39(1)
C5b–C6b	1.39(1)	1.38(2)	1.381(9)	1.39(1)
C5c–C6c	1.34(1)	1.36(2)	1.39(1)	1.37(1)
C5d–C6d		1.37(2)		
C5e–C6e		1.40(1)		
C5f–C6f		1.39(1)		
C6a–C7a	1.49(1)	1.53(1)	1.50(1)	1.52(1)
C6b–C7b	1.53(1)	1.55(1)	1.515(8)	1.50(1)
C6c–C7c		1.51(1)		
C6c–C7c'	1.49(1)		1.506(8)	1.50(1)
C6d–C7d		1.50(2)		
C6e–C7e		1.51(2)		
C6f–C7f		1.49(2)		
C8a–C9a		1.47(4)		
C8b–C9b		1.53(2)		
C8c–C9c		1.53(2)		
C8d–C9d		1.49(2)		
C8e–C9e		1.47(4)		
C8f–C9f		1.48(3)		
C8a–C10a		1.50(3)		
C8b–C10b		1.53(2)		
C8c–C10c		1.49(3)		
C8d–C10d		1.55(3)		
C8e–C10e		1.41(5)		
C8f–C10f		1.54(3)		
C8a–C11a		1.65(4)		
C8b–C11b		1.39(2)		
C8c–C11c		1.53(2)		
C8d–C11d		1.48(4)		
C8e–C11e		1.45(4)		
C8f–C11f		1.44(3)		
S1–O1s		1.491(9)		
S1–C1s		1.79(1)		
S1–C2s		1.77(1)		
S2–O2s		1.506(7)		
S2–C3s		1.76(1)		
S2–C4s		1.77(2)		
O1s–C1s			1.20(1)	
O1s–C2s				1.42(1)
O1s–C6s				1.42(1)
O4s–C3s				1.42(1)
O4s–C5s				1.43(1)
O7s–C8s				1.42(1)
O7s–C9s				1.42(2)
C1s–C2s	1.33(2)		1.48(1)	
C1s–C3s			1.46(1)	
C1s–C6s	1.30(2)			
C2s–C3s	1.37(2)			1.47(2)
C3s–C4s	1.25(2)			
C4s–C5s	1.38(2)			
C5s–C6s	1.37(2)			1.47(2)
C8s–C9s"				1.51(2)

Numbers in parentheses are estimated standard deviations in the least significant digits ' for **2**, represents (x,y,z) → (−x,y,0.5−z); for **4**, represents (x,y,z) → (−x,1−y,−z); for **5**, represents (x,y,z) → (2−x,1−y,1−z); " for **5**, represents (x,y,z) → (1−x,−y,1−z)

teresting to note that, due to the increased flexibility of calix[6]arene, the rule of thumb concerning the torsion angles for calix[4]arene does not necessarily apply for calix[6]arene; namely that if adjacent rings are oriented in the same direction the signs of the torsion angles about the connecting methylene will be different, while if the methylene connects two rings that point in opposite directions, the signs of the torsion angles will be the same. Thus, the torsion angles that comprise the pair of angles associated with each methylene are of different signs. It should be noted that the pairs associated with the two methylene groups that join oppositely-oriented aromatic rings (C7C and C7F) comprise one very small angle and one that is close to 90°, although, again the asymmetric nature of the conformation is exhibited when comparing the values of these angles for each methylene bridge.

The distorted geometry of the calixarene may be explained to a certain extent by a consideration of its interactions with solvent. The primary interaction is, as expected, rather strong hydrogen bonding between the calixarene and two acceptor DMSO oxygens. These

TABLE 7 Bond Angles (°) for Complexes **2–5**

Atoms			**2**	3	4	5
O1a	C1a	C2a	119.3(8)	122(1)	116.0(6)	116.8(7)
O1b	C1b	C2b	117.1(7)	120.3(8)	115.8(6)	117.0(7)
O1c	C1c	C2c	118.8(7)	124(1)	115.4(6)	116.7(7)
O1d	C1d	C2d		120(1)		
O1e	C1e	C2e		121.5(7)		
O1f	C1f	C2f		123(1)		
O1a	C1a	C6a	117.9(7)	116.1(9)	121.0(7)	120.9(9)
O1b	C1b	C6b	119.5(7)	118.0(8)	122.9(5)	120.6(6)
O1c	C1c	C6c	117.6(8)	116.1(9)	122.3(6)	120.9(6)
O1d	C1d	C6d		122(1)		
O1e	C1e	C6e		118.9(9)		
O1f	C1f	C6f		118(1)		
C2a	C1a	C6a	122.8(8)	122(1)	123.0(7)	122.3(7)
C2b	C1b	C6b	123.3(8)	122(1)	121.3(6)	122.4(7)
C2c	C1c	C6c	123.6(8)	120(1)	122.3(7)	122.4(9)
C2d	C1d	C6d		118(1)		
C2e	C1e	C6e		120(1)		
C2f	C1f	C6f		118.4(7)		
C1a	C2a	C3a	117.9(8)	116(1)	117.6(7)	118.9(8)
C1b	C2b	C3b	115.2(8)	117.2(8)	118.3(6)	118.8(7)
C1c	C2c	C3c	117.7(8)	121(1)	117.9(7)	118.4(7)
C1d	C2d	C3d		120(1)		
C1e	C2e	C3e		120.5(7)		
C1f	C2f	C3f		121(1)		
C1a	C2a	C7c	120.5(7)		121.2(7)	121.0(7)
C1a	C2a	C7f		120.5(9)		
C1b	C2b	C7a	123.6(8)	121(1)	120.3(6)	119.6(7)
C1c	C2c	C7b	123.8(8)	121(1)	121.6(7)	119.3(8)
C1d	C2d	C7c		121(1)		
C1e	C2e	C7d		122.0(6)		
C1f	C2f	C7e		118.5(7)		
C3a	C2a	C7c	121.6(7)		120.9(7)	120.0(9)
C3a	C2a	C7f		123(1)		
C3b	C2b	C7a	121.1(8)	121.5(8)	121.3(5)	121.6(6)
C3c	C2c	C7b	118.4(8)	118(1)	120.5(6)	122.2(6)
C3d	C2d	C7c		119(1)		
C3e	C2e	C7d		117.4(9)		
C3f	C2f	C7e		120(1)		
C2a	C3a	C4a	120.8(8)	124(1)	120.9(8)	120(1)
C2b	C3b	C4b	122.2(9)	123.0(9)	121.0(6)	120.3(7)
C2c	C3c	C4c	120.3(9)	119(1)	120.7(7)	121.1(7)
C2d	C3d	C4d		121(1)		
C2e	C3e	C4e		120(1)		
C2f	C3f	C4f		121(1)		
C3a	C4a	C5a	120.4(9)	116(1)	119.4(9)	119.7(8)
C3b	C4b	C5b	121(1)	119(1)	119.8(7)	119.5(8)
C3c	C4c	C5c	118.4(8)	118(1)	120.1(9)	119(1)
C3d	C4d	C5d		118(1)		
C3e	C4e	C5e		118.1(9)		
C3f	C4f	C5f		118.0(8)		
C3a	C4a	C8a		122(1)		
C3b	C4b	C8b		122.3(9)		
C3c	C4c	C8c		121(1)		
C3d	C4d	C8d		120(1)		
C3e	C4e	C8e		118.3(9)		
C3f	C4f	C8f		120(1)		
C5a	C4a	C8a		122(1)		
C5b	C4b	C8b		118.6(8)		
C5c	C4c	C8c		121(1)		
C5d	C4d	C8d		122(1)		
C5e	C4e	C8e		123.6(7)		
C5f	C4f	C8f		122(1)		
C4a	C5a	C6a	120.5(9)	123(1)	121.9(7)	121.9(8)
C4b	C5b	C6b	118.5(9)	119.5(8)	120.6(6)	122.4(8)
C4c	C5c	C6c	123.8(8)	123(1)	121.1(8)	122.8(9)
C4d	C5d	C6d		124(1)		
C4e	C5e	C6e		122.9(7)		
C4f	C5f	C6f		122(1)		
C1a	C6a	C5a	117.6(8)	118(1)	117.1(7)	116.9(9)
C1b	C6b	C5b	119.3(8)	119.3(9)	118.8(5)	116.5(6)
C1c	C6c	C5c	116.1(8)	118.5(9)	117.7(7)	116.4(6)
C1d	C6d	C5d		119(1)		
C1e	C6e	C5e		118.5(9)		
C1f	C6f	C5f		120(1)		
C1a	C6a	C7a	122.9(8)	122.1(9)	121.0(7)	121.7(7)
C1b	C6b	C7b	122.0(8)	123(1)	120.0(6)	122.4(7)
C1c	C6c	C7c'	122.4(8)	115(1)	122.5(7)	122.8(6)
C1d	C6d	C7d		120(1)		
C1e	C6e	C7e		120.1(9)		
C1f	C6f	C7f		120.3(7)		
C5a	C6a	C7a	119.5(8)	119(1)	121.8(7)	121.4(8)
C5b	C6b	C7b	118.6(8)	117.5(8)	121.1(6)	121.1(7)
C5c	C6c	C7c'	121.6(8)	126(1)	119.6(7)	120.7(6)
C5d	C6d	C7d		121(1)		
C5e	C6e	C7e		121.4(7)		
C5f	C6f	C7f		120(1)		
C2b	C7a	C6a	118.0(8)	112(1)	116.0(7)	114.0(7)
C2c	C7b	C6b	114.7(8)	112.8(9)	117.4(7)	113.9(7)
C2a	C7c	C6c'	115.0(8)		118.4(7)	112.9(7)
C2d	C7c	C6c		117(1)		
C2e	C7d	C6d		115(1)		
C2f	C7e	C6e		120(1)		
C2a	C7f	C6f		117(1)		
C4a	C8a	C9a		113(2)		
C4b	C8b	C9b		109(1)		
C4c	C8c	C9c		113(1)		
C4d	C8d	C9d		106(1)		
C4e	C8e	C9e		115(1)		
C4f	C8f	C9f		113(1)		
C4a	C8a	C10a		112(1)		
C4b	C8b	C10b		107(1)		
C4c	C8c	C10c		112(1)		
C4d	C8d	C10d		110(1)		
C4e	C8e	C10e		114(2)		
C4f	C8f	C10f		110(1)		
C4a	C8a	C11a		120(2)		
C4b	C8b	C11b		114(1)		
C4c	C8c	C11c		106(1)		
C4d	C8d	C11d		111(2)		
C4e	C8e	C11e		110(2)		
C4f	C8f	C11f		115(2)		
C9a	C8a	C10a		96(2)		
C9b	C8b	C10b		102(1)		
C9c	C8c	C10c		108(1)		
C9d	C8d	C10d		105(1)		
C9e	C8e	C10e		100(2)		
C9f	C8f	C10f		92(2)		
C9a	C8a	C11a		114(2)		
C9b	C8b	C11b		113(2)		
C9c	C8c	C11c		103(1)		
C9d	C8d	C11d		88(2)		
C9e	C8e	C11e		100(2)		
C9f	C8f	C11f		106(1)		
C10a	C8a	C11a		121(2)		
C10b	C8b	C11b		111(1)		
C10c	C8c	C11c		115(2)		
C10d	C8d	C11d		132(2)		
C10e	C8e	C11e		115(2)		
C10f	C8f	C11f		119(1)		
O1s	S1	C1s		106.1(5)		
O1s	S1	C1s		106.5(5)		
C1s	S1	C2s		98.4(7)		
O2s	S2	C3s		106.6(6)		
O2s	S2	C4s		107.1(5)		
C3s	S2	C4s		99.3(9)		
C2s	O1s	C6s				110.0(8)
C3s	O4s	C5s				110.6(8)
C8s	O7s	C9s				110.3(8)

TABLE 7 (Continued) Bond Angles (°) for Complexes 2–5

Atoms			2	3	4	5
O1s	C1s	C2s			121.6(8)	
O1s	C1s	C3s			121.0(9)	
C2s	C1s	C3s			117.3(9)	
C2s	C1s	C6s	118(1)			
O1s	C2s	C3s				110.5(7)
O4s	C3s	C2s				112.5(8)
O4s	C5s	C6s				110.4(8)
O1s	C6s	C5s				111.0(8)
C1s	C2s	C3s	121(1)			
C2s	C3s	C4s	120(1)			
C3s	C4s	C5s	121(1)			
C4s	C5s	C6s	116(1)			
C1s	C6s	C5s	123(1)			
O7s	C8s	C9s'				109.9(9)
O7s	C9s	C8s'				110.0(9)

Numbers in parentheses are estimated standard deviations in the least significant digits ' and ", see Table 6.

interactions are again, however, not symmetric, involving the "terminal" phenolic oxygen (O1A...O1S) of one trimeric subunit, and the "middle" oxygen (O1E...O2S') of the second, with respective O...O separations of 2.59(1) and 2.47(1) Å. The importance of these interactions in determining the conformation of the calixarene may be seen by examining the angles made by rings A and E with the mean plane of the molecule (Table 10 and *vide supra*), which are essentially the same. A second form of interaction occurs between each DMSO molecule and a symmetry related calixarene, in which a methyl group resides in the cavity. This is depicted in Figure 6 for two symmetry-transformed DMSO molecules. Thus, C4S lies above ring C, with distances to C1C, C2C, and C6C of 3.62(3), 3.73(2), and 3.72(3) Å, respectively; while C1S' lies more asymmetrically, being 3.52(3) and 3.76 Å from C1D and C2D, respectively. The angles of the two affected rings, C and D, with the mean plane of the molecule are 67 and 54°, respectively, implying that the methyl...π interaction at the bottom of each ring is sufficient to distort the conformation to a certain extent. In this vein, it should be mentioned that the two aromatic units that have no meaningful short contacts to the solvent are those that lie the most parallel (ring F, 35°) and most perpendicular (ring B, 86°) to the mean plane of the molecule.

While the calixarene in complex 3 is somewhat distorted, there is little doubt that the gross conformation corresponds to the 1,2,3-alternate, and the alternative phrase, "double partial cone"[25] is also applicable. As may be seen from Figures 4 and 5, however, the calixarene conformation in both the acetone complex, **4**, and the dioxane/water complex, **5**, is grossly distorted from the ideal. Both conformations possess a crystallographically imposed center of inversion so that, unlike compound 3, the trimeric subunits are identical. These subunits, however, contain one ring that is virtually flat (Ring B), and two others that lie closer to the perpendicular (rings A and C). Thus, although the conformation may be described as 1,2,3-alternate, a better description would be "up-up-out-down-down-out",[7b] and the cavity defined by the aromatic rings is more of a channel than two cup-shaped volumes. As shown in Table 12, this conformation may be expressed as $C_i + - - + - + - + + - + -$,[19] although the numerical values of the torsion angles differ to a certain extent.

TABLE 8 Interplane Angles (°) for 2

	Plane A	Plane B	Plane C
Plane 1	129.7(2)	131.0(2)	152.3(3)
Plane 2	142.1(2)	141.1(2)	112.5(3)
Plane A'	77.6(2)		
Plane B	55.3(3)		
Plane B'	103.5(2)	79.7(2)	
Plane C	142.5(4)	112.2(3)	
Plane C'	71.5(2)	40.7(3)	124.9(2)

TABLE 9 Methylene Bridge Torsion Angles (°) for 2

Atoms	Angle	Atoms	Angle
C5A C6A C7A C2B	−95(1)	C5A' C6A' C7A' C2B'	−95(1)
C6A C7A C2B C3B	94(1)	C6A' C7A' C2B' C3B'	94(1)
C5B C6B C7B C2C	104(1)	C5B' C6B' C7B' C2C'	104(1)
C6B C7B C2C C3C	−81(1)	C6B' C7B' C2C' C3C'	−81(1)
C5C' C6C' C7C C2A	80.2(7)	C5C C6C C7C' C2A'	80.2(7)
C6C' C7C C2A C3A	−102.0(9)	C6C C7C' C2A' C3A'	−102.0(9)

Quantitative analysis of the conformation is more complicated than the previous two structures, as there is no meaningful reference plane defined by the methylene bridges. The "best" indication of both the similarities and differences between the two structures may be obtained by examining the dihedral angles between the aromatic rings and the plane defined by C4b-C1b-O1b-O1b'-C1b'-C4b'. These are listed in Table 13. Thus, in both structures, ring A is oriented in an almost perpendicular fashion and ring B is nearly flat, although "pivoted" by 17° in complex **4**. The orientation of ring C, however,

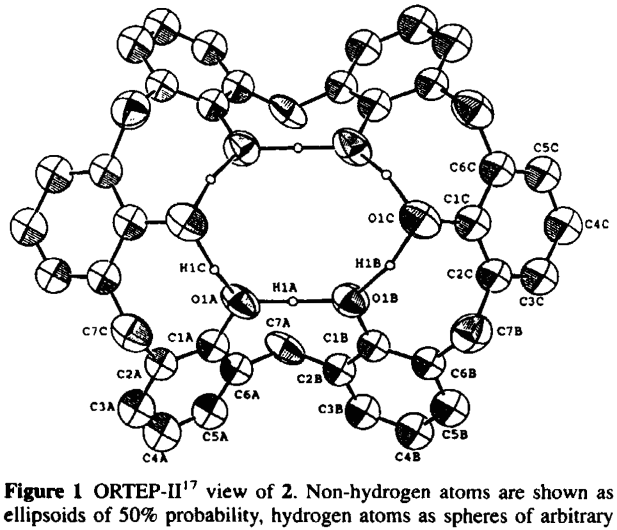

Figure 1 ORTEP-II[17] view of **2**. Non-hydrogen atoms are shown as ellipsoids of 50% probability, hydrogen atoms as spheres of arbitrary radius.

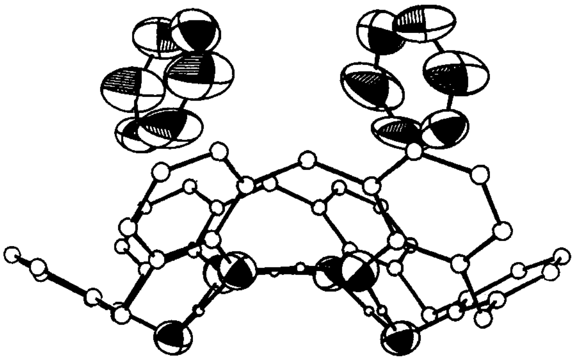

Figure 2 ORTEP-II[17] view of 2 and solvent. Non-hydrogen atoms are shown as ellipsoids of 50% probability, hydrogen atoms as spheres of arbitrary radius. Calixarene oxygens and solvent atoms are shaded.

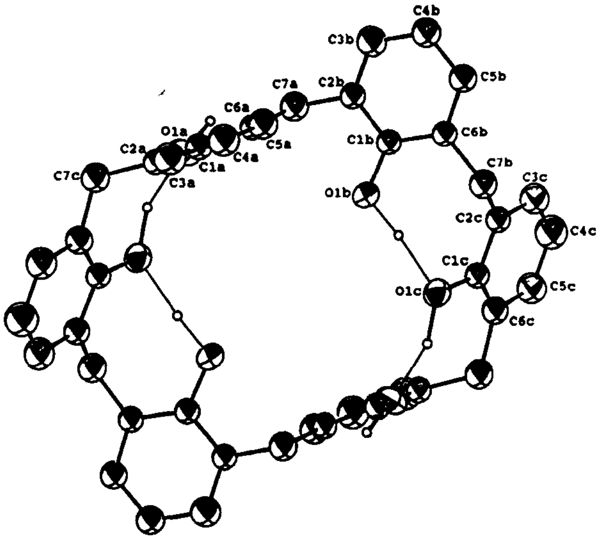

Figure 4 ORTEP-II[17] view of 4. Non-hydrogen atoms are shown as ellipsoids of 50% probability, hydrogen atoms as spheres of arbitrary radius.

differs drastically in the two complexes, being almost perpendicular in complex 5, but inclined at an angle of 55° in complex 4. Thus, the calixarene in complex 4 is better described as "up-up and out-out-down-down and out-out",[7b] while that in complex 5 is a true "up-up-out-down-down-out."[7b] This effect is also apparent from the torsion angles around the methylenes—where there is a sharp change from flat to perpendicular, one of the angles is small (Table 12). The overall result of both the pivoting of ring B and inclination of ring C in complex 4 is that the calixarene appears somewhat elongated. The reason for the difference in orientation of ring C may be ascertained by an examination of the intra-calix hydrogen bonding. In both complexes, O1a interacts with the hydrogen from O1c such that the O...O distances are 2.70(1) and 2.66(1) Å and the O-H...O angles are 158 and 171°, respectively. In complex 4, however, O1c also interacts with the hydrogen from O1b at an O...O distance of 2.86(1) Å and an angle at hydrogen of 170°, thus ring C must adopt an orientation mid-way between that of rings A and B, in order to achieve both of these interactions.

As in complex 3, the complete intra-calixarene hydrogen bonding is disrupted by interaction with solvent molecules. Thus, as shown in Figures 7 and 8, O1a hydrogen bonds through its hydrogen to a molecule of acetone (in complex 4) or water (in complex 5), with O...O contacts of 2.71(1) and 2.64(1) Å, and O-H...O angles of 143 and 150°, respectively. In complex 5, however, the presence of a second hydrogen-bond accep-

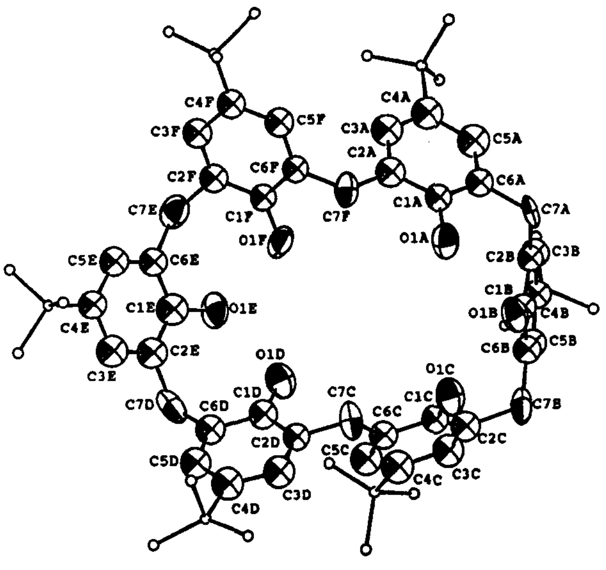

Figure 3 ORTEP-II[17] view of 3. Non-hydrogen atoms are shown as ellipsoids of 50% probability.

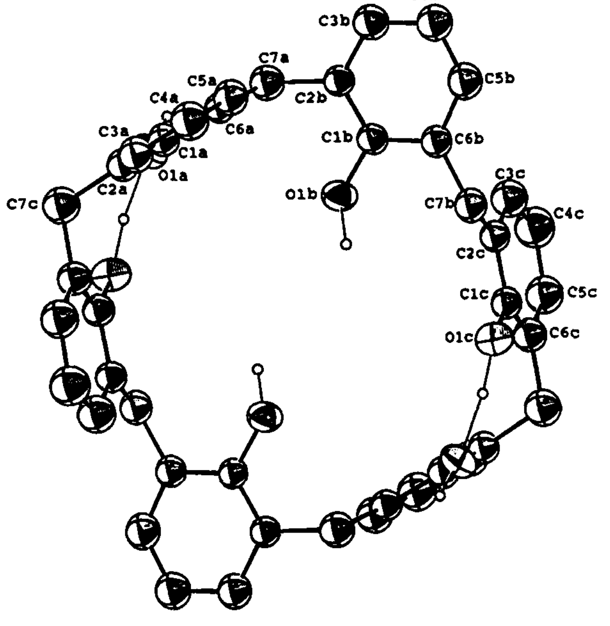

Figure 5 ORTEP-II[17] view of 5. Non-hydrogen atoms are shown as ellipsoids of 50% probability, hydrogen atoms as spheres of arbitrary radius.

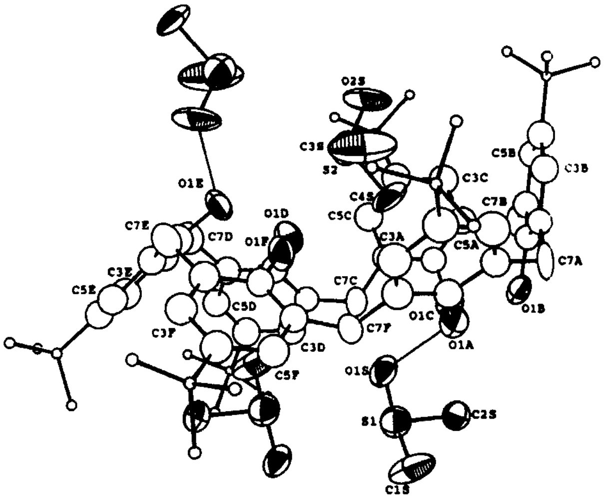

Figure 6 ORTEP-II[17] view of **3** and solvent. Non-hydrogen atoms are shown as ellipsoids of 50% probability. Calixarene oxygens and solvent atoms are shaded.

tor solvent (dioxane) enables further disruption of the intramolecular calixarene hydrogen bonding—O1b interacts with O1s at an O...O distance of 2.73(1) Å and an O-H...O angle of 154°.

The remaining intermolecular contacts also differ substantially between complexes **4** and **5**. In **4**, the only remaining short contact is that between the acetone methyl that points towards the center of the calixarene and O1b, at a distance of 3.31(2) Å. In **5**, on the other hand, there is an extensive non-calixarene hydrogen bonding network. The two protons of the water molecule interact with the remaining oxygen of the bound dioxane (O4s) as well as the unique oxygen of a second dioxane molecule that lies over a center of inversion (O7s) with O...O contacts of 2.82(1) and 2.85(1) Å and O-H...O angles of 153 and 124°, respectively.

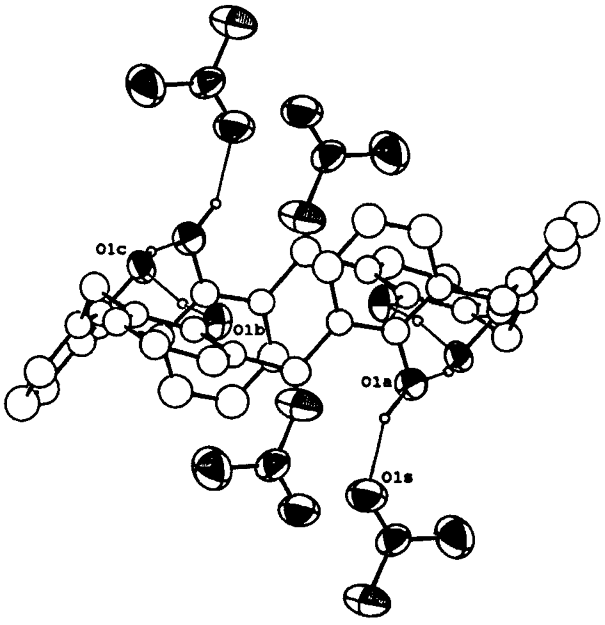

Figure 7 ORTEP-II[17] view of **4** and solvent. Non-hydrogen atoms are shown as ellipsoids of 50% probability, hydrogen atoms as spheres of arbitrary radius. Calixarene oxygens and solvent atoms are shaded.

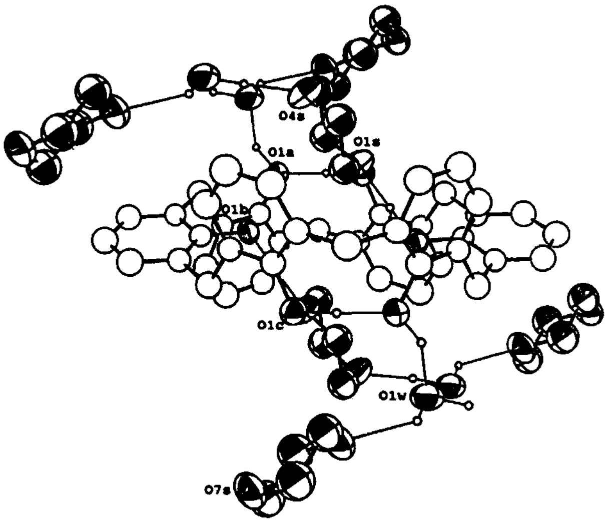

Figure 8 ORTEP-II[17] view of **5** and solvent. Non-hydrogen atoms are shown as ellipsoids of 50% probability, hydrogen atoms as spheres of arbitrary radius. Calixarene oxygens and solvent atoms are shaded.

Three distinct different versions of the "1,2,3-alternate" conformation have been crystallized from hydrogen-bonding solvents, therefore, and the particular version depends upon the nature of the interactions between the calixarene and the solvent. These may be compared to other examples of 1,2,3-alternate calix[6]arenes in the literature. Complex **3** is very similar to a europium complex of *p*-*t*-butylcalix[6]arene[23] that was crystallized from DMF, in which the calixarene acts as a monodentate ligand for the metal ion through the equivalent of O1b in **3**. In addition, the DMF complex of *p*-*t*-butylcalix[6]arene is virtually identical to **3**.[26] Most of the other simple examples of "1,2,3-alternate" complexes are highly distorted from the ideal, containing two "flattened" rings on opposite sides of the molecule and two almost perpendicular rings, with the remaining two rings adopting orientations between the two extremes. Thus, a complex in which all of the oxygens of each trimeric subunit bind to a titanium ion possesses a conformation identical to that of complex **4** (in which the three oxygens also interact with each other),[27] while three hexasubstituted calix[6]arenes in which the calix-

TABLE 10 Interplane Angles (°) for **3**

	Plane A	Plane B	Plane C	Plane D	Plane E	Plane F
Plane 1*	46.3(3)	84.0(3)	66.8(3)	54.4(3)	43.7(3)	34.5(4)
Plane B	109.6(4)					
Plane C	77.0(4)	69.2(3)				
Plane D	27.7(7)	82.9(3)	59.2(3)			
Plane E	137.1(4)	40.7(5)	64.2(4)	110.8(3)		
Plane F	99.4(3)	100.7(3)	48.2(5)	98.0(3)	68.2(3)	

*Values given as either α or 180-α, such that the angle is less than 90°.

TABLE 11 Methylene Bridge Torsion Angles (°) for **3**

Atoms	Angle	Atoms	Angle
C5A C6A C7A C2B	−93(1)	C5D C6D C7D C2E	94(1)
C6A C7A C2B C3B	76(1)	C6D C7D C2E C3E	−80(1)
C5B C6B C7B C2C	−87(1)	C5E C6E C7E C2F	77(1)
C6B C7B C2C C3C	89(1)	C6E C7E C2F C3F	−103(1)
C5C C6C C7C C2D	−4(2)	C5F C6F C7F C2A	−91(1)
C6C C7C C2D C3D	118(1)	C6F C7F C2A C3A	15(2)

arene cavity is "filled" by *O*-substituents (R' = CH_2CO_2Et,[28] CH_2CH_2OMe,[29] or CH_2CONEt_2[20]) all possess conformations virtually identical to that of **5** in which the cavity is occupied by "non-interacting" solvent. The only simple "1,2,3-alternate" calix[6]arenes observed in the solid-state that do not fit into one of these three categories are the structures of the *p*-sulfonatocalix[6]arene and its sodium salt. These complexes, that were crystallized from water, adopt conformations in which all three rings in a subunit lie at approximately 45° angles to the mean plane of the macrocycle.

CONCLUSIONS

The conformation of simple calix[6]arenes in the solid state are dependent upon the solvent of crystallization. Unless other factors intrude, such as those due to bridging or extremely bulky substituents, the general rule of thumb appears to be that the pinched-cone conformation will predominate when solvents that cannot take part in hydrogen bonding are used, and that some form of the 1,2,3-alternate conformation may result when the solvent possesses hydrogen bonding capability. Within this latter category, four different modifications may be observed. Although insufficient examples exist to draw concrete conclusions, it would appear that the presence of solvents that are bulky compared to water causes a distortion of the expected conformation, so that some rings rotate to be more perpendicular and/or parallel with respect to the mean plane of the ring. The environment of the most "flattened" ring appears to be highly important in determining the final conformation. Should the oxygen of this ring interact with adjacent calixarene oxygens (either by hydrogen bonding or bridging species) the inclination of at least some of the other aromatic rings is less distorted from the ideal. On the other hand, should this oxygen be "substituted" by either a functional group or a hydrogen-bonding solvent, the remaining calixarene rings will adopt a virtually perpendicular orientation.

TABLE 13 Interplane Angles (°) for Complexes **4** (*and* **5**)

	Plane A	Plane B	Plane C
Plane 1	82(1) *80(1)*	17(1) *3(1)*	55(1) *93(1)*
Plane B	87.8(2) *83.5(2)*		
Plane C	55.5(3) *111.2(3)*	108.2(2) *90.2(3)*	

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TABLE 12 Methylene Bridge Torsion Angles (°) for Complexes **4** (*and* **5**)

Atoms	Angle	Atoms	Angle
C5a C6a C7a C2b	14(1) *31(1)*	C5a' C6a' C7a' C2b'	-14(1) *-31(1)*
C6a C7a C2b C3b	-99.3(8) *-107.2(9)*	C6a' C7a' C2b' C3b'	99.3(8) *107.2(9)*
C5b C6b C7b C2c	-119.3(8) *-103.1(9)*	C5b' C6b' C7b' C2c'	119.3(8) *103.1(9)*
C6b C7b C2c C3c	72.9(9) *27(1)*	C6b' C7b' C2c' C3c'	-72.9(9) *-27(1)*
C5c C6c C7c' C2a'	-109.4(8) *-95(1)*	C5c' C6c' C7c' C2a	109.4(9) *95(1)*
C6c C7c' C2a' C3a'	84.1(9) *87.3 (9)*	C6c' C7c C2a C3a	-84.1(9) *-87.3(9)*

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