

Alternative Methods of Modifying the Calixarene Conformation. The Synthesis and Molecular Structures of *t*-Butylcalix[4]arene Methyl Ether Complexed with Aluminum Alkyl Species

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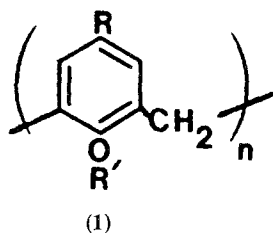
Abstract. The configurations of calix[4]arenes may be modified by the formation of donor-acceptor complexes which make use of the basicity of the oxygen atoms of the macrocycle. The complex [*t*-butylcalix[4]arene methyl ether][AlMe₃]₂, **2**, exhibits the previously unseen '1,2-alternate' geometry, while [*t*-butylcalix[4]arene methyl ether][MeAlCl₂]₂, **3**, and [*t*-butylcalix[4]arene methyl ether][EtAlCl₂]₂, **4**, show the '1,3-alternate' configuration. **2** crystallizes in the triclinic space group *P* $\bar{1}$ with $a = 11.14(1)$, $b = 11.60(1)$, $c = 12.02(1)$ Å, $\alpha = 77.32(8)$, $\beta = 67.91(8)$, and $\gamma = 69.34(8)^\circ$ with $D_c = 1.06$ g cm⁻³ for $Z = 1$. Refinement based on 1270 observed reflections led to $R = 0.106$. **3** as the benzene solvate belongs to the monoclinic space group *C2/c* with $a = 12.116(2)$, $b = 21.557(7)$, $c = 23.470(6)$ Å, and $\beta = 104.05(2)^\circ$ with $D_c = 1.13$ g cm⁻³ for $Z = 4$. Refinement based on 2335 observed reflections led to $R = 0.075$. **4** crystallizes in the monoclinic space group *C2/c* with $a = 12.062(4)$, $b = 21.175(6)$, $c = 21.596(5)$ Å, and $\beta = 100.78(4)^\circ$ with $D_c = 1.18$ g cm⁻³ for $Z = 4$. Refinement based on 2529 observed reflections gave $R = 0.082$. The Al—O lengths in all three complexes are normal for donor-acceptor interactions.

Key words: Calix[4]arene, aluminum alkyl, crystal structure.

Supplementary Data relating to this article are deposited with the British Library as Supplementary Publication No. SUP 82053 (45 pages).

1. Introduction

Of the numerous macrocyclic compounds to have received recent attention for their inclusion properties, some of the most studied are the calixarenes (**1**) [1]. There are



several reasons for this, the most important of which is the ease of variation of the cavity shape and size by judicious functionalization at the oxygen atoms (R'). In the

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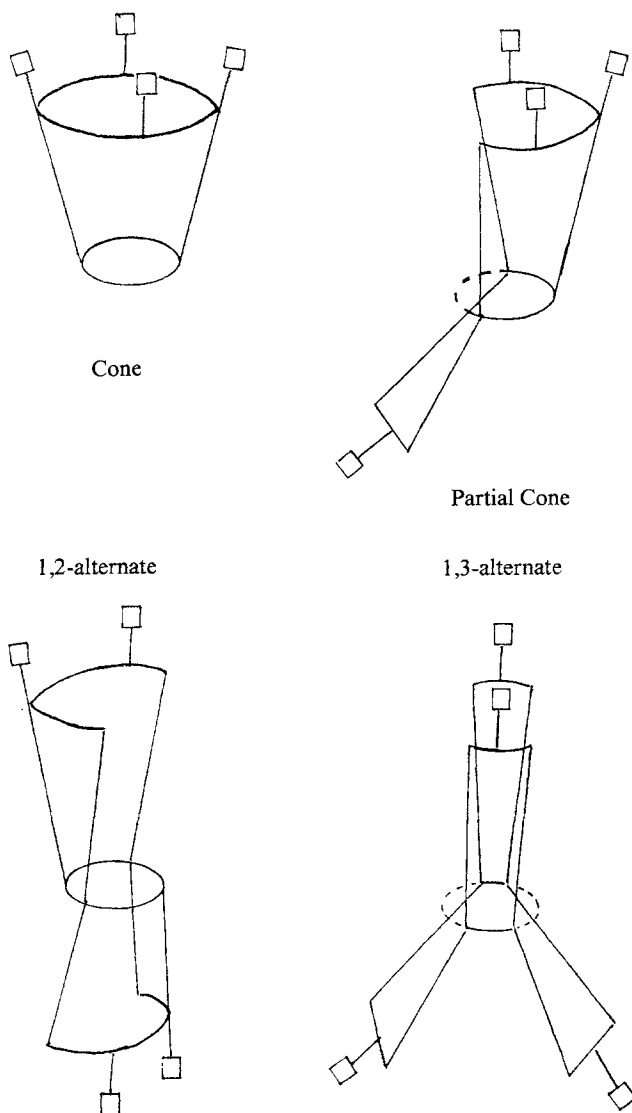


Fig. 1. Four configurations of calix[4]arenes [3].

parent calixarenes ($R' = H$), rotation about the methylene bridges gives rise to numerous conformations which can be 'frozen out' by substitution of larger groups [2]. For example, calix[4]arene theoretically can adopt four geometries (Figure 1) [3]. When $R = H$, small alkyl groups as the oxygen substituents (e.g. $-Me$, $-Et$) lead to the 'partial cone' configuration being favored. Changing R' to $-COMe$ results in a conformational change to the '1,3-alternate' configuration and very large groups such as $-CH_2Ph$ or $-SiMe_4$ tend to hold the calix in the 'cone' geometry [4].

Utilization of the basicity of the oxygen atoms allows additional binding sites which may be varied to adjust the conformation. We have recently reported the sen-

sitivity of the calix[8]arene geometry to adduct formation with trimethylaluminum [5] and in this contribution we discuss the similar complexes of calix[4]arene: [*t*-butylcalix[4]arene methyl ether][RAIX₂]₂, where X = R = Me (compound 2); R = Me, X = Cl (compound 3) and R = Et, X = Cl (compound 4).

2. Experimental

All manipulations were carried out under N₂ in an inert atmosphere box. Benzene was dried over Na/benzophenone. Trimethylaluminum was obtained from Texas Alkyls Corporation and was used without further purification. The starting compounds for the calixarene syntheses were purchased from Aldrich Chemicals.

2.1. PREPARATION OF [*t*-BUTYLCALIX[4]ARENE METHYL ETHER][AlMe₃]₂, 2

To a suspension of *t*-butylcalix[4]arene methyl ether [6] (1.4 g, 2 mmol) in benzene (25 ml) was added trimethylaluminum (2 ml of a 2 M solution in toluene, 4 mmol). The macrocycle dissolved to yield a pale yellow solution. Overnight, colorless crystals of 2 grew from the solution.

Table I. Crystal data and summary of intensity data collection and structure refinement for compounds 2, 3, and 4

Compounds	2	3 + Benzene	4
Mol. Wt.	849.3	1009.1	958.8
Space group	<i>P</i> $\bar{1}$	<i>C2/c</i>	<i>C2/c</i>
Cell constants			
<i>a</i> , Å	11.14(1)	12.116(2)	12.062(4)
<i>b</i> , Å	11.60(1)	21.577(7)	21.175(6)
<i>c</i> , Å	12.02(1)	23.470(6)	21.596(5)
<i>α</i> , deg	77.32(8)	90	90
<i>β</i> , deg	67.91(8)	104.05(2)	100.78(4)
<i>γ</i> , deg	69.34(8)	90	90
Cell vol, Å ³	1338	5951	5419
Molecules/unit cell	1	4	4
<i>ρ</i> (calc), g cm ⁻³	1.06	1.13	1.18
<i>μ</i> (calc), cm ⁻¹	0.90	2.67	2.92
Radiation	MoK α	MoK α	MoK α
Max crystal dims. (mm)	0.08 × 0.12 × 0.12	0.9 × 0.9 × 0.2	0.8 × 0.3 × 0.3
Scan width, deg	0.8 + 0.2 tan θ	0.8 + 0.2 tan θ	0.8 + 0.2 tan θ
Standard refl'ns	050,200	800,0140,0016	200,020,002
Decay of stds.	<2%	<1%	<5%
Refl'ns measured	2699	3141	4615
2 θ range, deg	2–40	1–40	2–44
Refl'ns considered			
observed (<i>I</i> > 3 σ (<i>I</i>))	1270	2335	2529
No. of params. varied	133	298	221
GOF	1.1	1.84	1.12
<i>R</i>	0.106	0.075	0.082
<i>R</i> _w	0.103	0.081	0.087

2.2. PREPARATION OF [*t*-BUTYLALIX[4]ARENE METHYL ETHER][MeAlCl₂]₂, **3**

Complex **3** was prepared as for **2**, except that the source of the aluminum species was a 1 M solution of methylaluminum sesquichloride in toluene [7].

2.3. PREPARATION OF [*t*-BUTYLALIX[4]ARENE METHYL ETHER][EtAlCl₂]₂, **4**

Complex **4** was prepared as for **2**, except that the source of the aluminum species was a 2 M solution of ethylaluminum dichloride in hexane.

2.4. X-RAY DATA COLLECTION AND STRUCTURE DETERMINATION FOR **2**

Single crystals were sealed in thin-walled glass capillaries. Final lattice parameters as determined from 25 high-angle reflections ($2\theta > 25^\circ$) carefully centered on an Enraf-Nonius CAD-4 are given in Table I. Intensity data were recorded on the diffractometer in the usual manner [8]. A summary of data collection parameters is also presented in Table I. The intensities were corrected for Lorentz and polarization effects, but not for absorption.

Table II. Final fractional coordinates for **2**

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Al	0.6289(6)	0.2592(4)	0.6652(5)
O(1)	0.603(1)	0.1368(8)	0.5908(2)
O(2)	0.265(1)	0.1715(9)	0.5939(9)
C(1)a	0.624(2)	0.010(1)	0.639(1)
C(2)	0.747(2)	-0.075(1)	0.594(1)
C(3)a	0.771(2)	-0.195(1)	0.650(2)
C(4)a	0.671(2)	-0.234(1)	0.745(1)
C(5)a	0.546(2)	-0.147(1)	0.787(1)
C(6)a	0.520(2)	-0.022(1)	0.733(1)
C(7)a	0.694(2)	-0.367(1)	0.808(2)
C(8)a	0.593(2)	-0.419(2)	0.791(2)
C(9)a	0.668(2)	-0.367(2)	0.937(2)
C(10)a	0.838(2)	-0.448(2)	0.747(2)
C(11)a	0.862(2)	-0.0474(9)	0.4931(9)
C(12)a	0.552(2)	0.1790(9)	0.4840(9)
C(13)a	0.4424(8)	0.3802(6)	0.7059(7)
C(14)a	0.7699(8)	0.3213(6)	0.5300(7)
C(15)a	0.6798(8)	0.1571(6)	0.8041(7)
C(1)b	0.226(2)	0.073(1)	0.666(2)
C(2)b	0.265(2)	0.023(1)	0.769(2)
C(3)b	0.220(2)	-0.067(1)	0.846(2)
C(4)b	0.137(2)	-0.122(1)	0.825(2)
C(5)b	0.116(2)	-0.080(1)	0.716(2)
C(6)b	0.159(1)	0.012(1)	0.634(1)
C(7)b	0.077(2)	-0.220(1)	0.910(2)
C(8)b	-0.078(2)	-0.180(2)	0.935(2)
C(9)b	0.147(2)	-0.343(1)	0.849(2)
C(10)b	0.098(2)	-0.237(2)	1.035(2)
C(11)b	0.379(1)	0.066(1)	0.786(1)
C(12)b	0.162(2)	0.291(1)	0.626(1)

Structure solution was accomplished by means of the direct methods program MULTAN [9] and the subsequent calculation of a difference Fourier map using the SHELX system of computer programs [10] allowed the location of all non-hydrogen atoms. Refinement with isotropic thermal parameters led to a reliability index of $R = \sum(|F_o| - |F_c|) / \sum|F_o| = 0.140$. Conversion to anisotropic thermal parameters and further refinement with blocked least-squares matrices gave $R = 0.110$. Inclusion of hydrogen atoms at calculated positions and further refinement led to final values of $R = 0.106$, $R_w = \{\sum w(|F_o| - |F_c|)^2 / \sum w(F_o)^2\}^{1/2} = 0.103$. The largest parameter shifts in the final cycles of refinement were less than 0.02 of their estimated deviations. The largest residual peaks on a final difference map were less than $0.3 e/\text{\AA}^3$ and were located around the *t*-butyl groups.

Unit weights were used at all stages; no systematic variation of $w(|F_o| - |F_c|)$ vs. $|F_o|$ or $(\sin\theta/\lambda)$ was noted. The function $w(|F_o| - |F_c|)^2$ was minimized [10]. Neutral atom scattering factors were taken from the compilations of Cromer and Waber [11] for Al, O, and C. Scattering factors for H were from [12]. The final values of the positional parameters are given in Table II. Tables of hydrogen atom positions,

Table III. Final fractional coordinates for 3

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Al	0.1248(3)	0.0582(2)	0.1155(1)
Cl(1)	0.2180(3)	0.0011(2)	0.0699(2)
Cl(2)	0.2398(3)	0.1193(2)	0.1722(1)
O(1)	0.0817(5)	0.0021(3)	0.1698(3)
O(2)	-0.1322(5)	-0.1552(9)	0.1849(3)
C(1)	-0.0133(9)	0.0943(5)	0.0669(5)
C(1)a	-0.0365(7)	0.0014(4)	0.1686(3)
C(2)a	-0.1081(8)	-0.0371(4)	0.1288(4)
C(3)a	-0.2237(8)	-0.0278(5)	0.1202(3)
C(4)a	-0.2704(8)	0.0190(4)	0.1495(4)
C(5)a	-0.1933(6)	0.0532(3)	0.1903(4)
C(6)a	-0.0765(6)	0.0449(3)	0.2027(4)
C(7)a	-0.3996(7)	0.0276(4)	0.1354(3)
C(8)a	-0.4277(9)	0.0851(6)	0.1696(6)
C(9)a	-0.444(1)	0.0377(8)	0.0701(9)
C(10)a	-0.4469(9)	-0.0286(7)	0.158(1)
C(11)a	0.0000	0.0827(4)	0.2500
C(12)a	0.1588(6)	-0.0428(3)	0.2072(3)
C(1)b	-0.0323(7)	-0.1723(3)	0.1710(4)
C(2)b	0.0022(7)	-0.1403(4)	0.1258(3)
C(3)b	0.1037(8)	-0.1571(4)	0.1125(4)
C(4)b	0.1745(8)	-0.2030(4)	0.1439(4)
C(5)b	0.1362(8)	-0.2325(4)	0.1890(4)
C(6)b	0.0350(7)	-0.2181(4)	0.2028(3)
C(7)b	0.2889(9)	-0.2183(4)	0.1301(6)
C(8)b	-0.309(1)	-0.180(1)	0.0772(9)
C(9)b	0.378(1)	-0.186(1)	0.173(1)
C(10)b	0.360(1)	-0.272(1)	0.172(1)
C(11)b	-0.0669(6)	-0.0868(3)	0.0908(3)
C(12)b	-0.2317(8)	-0.1888(5)	0.1540(5)
C(11)c	0.0000	-0.2549(5)	0.2500

anisotropic thermal parameters, and structure factors are available as supplementary material.

2.5. X-RAY DATA COLLECTION AND STRUCTURE DETERMINATION FOR THE BENZENE SOLVATE OF 3

Data were collected and manipulated in the same manner as for **2**. After all calixarene atoms had been located and treated with anisotropic thermal parameters, peaks appeared in the area of a crystallographic center of inversion. These were subsequently modeled as a disordered molecule of benzene. Refinement converged at $R = 0.075$ and $R_w = 0.081$. Data collection and structure solution parameters are given in Table I. Final fractional atomic coordinates are listed in Table III.

2.6. X-RAY DATA COLLECTION AND STRUCTURE DETERMINATION FOR 4

Data were collected and manipulated as for **2**. Refinement converged at $R = 0.082$ and $R_w = 0.087$. Final atomic coordinates are listed in Table IV.

Table IV. Final fractional coordinates for **4**

Atom	x/a	y/b	z/c
Al	0.1557(2)	0.1232(1)	0.6116(1)
Cl(1)	0.2546(1)	0.0624(1)	0.5653(1)
Cl(2)	0.2648(2)	0.1833(1)	0.6738(1)
O(1)	0.0987(3)	0.0677(2)	0.6664(2)
O(2)	-0.1217(4)	-0.0934(2)	0.6758(2)
C(1)	0.0300(5)	0.1627(3)	0.5562(3)
C(2)	0.066(1)	0.2118(5)	0.5123(6)
C(1)a	-0.0214(4)	0.0661(3)	0.6620(3)
C(2)a	-0.0679(5)	0.1096(3)	0.6975(3)
C(3)a	-0.1858(5)	0.1171(3)	0.6829(3)
C(4)a	-0.2514(5)	0.0803(3)	0.6366(3)
C(5)a	-0.2008(5)	0.0355(3)	0.6067(3)
C(6)a	-0.0838(5)	0.0265(3)	0.6181(3)
C(7)a	-0.3822(5)	0.0894(3)	0.6231(3)
C(8)a	-0.4296(6)	0.0579(7)	0.6734(5)
C(9)a	-0.4325(7)	0.0579(8)	0.5602(5)
C(10)a	-0.4104(7)	0.1586(5)	0.6180(8)
C(11)a	0.0000	0.1477(4)	0.7500
C(12)a	0.1694(5)	0.0203(3)	0.7070(3)
C(1)b	-0.0162(5)	-0.1103(3)	0.6640(3)
C(2)b	0.0261(5)	-0.0776(3)	0.6179(3)
C(3)b	0.1318(5)	-0.0960(3)	0.6063(3)
C(4)b	0.1953(5)	-0.1424(3)	0.6403(3)
C(5)b	0.1515(5)	-0.1716(3)	0.6880(3)
C(6)b	0.0442(5)	-0.1568(3)	0.7004(3)
C(7)b	0.3130(6)	-0.1591(3)	0.6269(4)
C(8)b	0.3685(8)	-0.2098(5)	0.6708(6)
C(9)b	0.3859(8)	-0.1011(5)	0.6353(8)
C(10)b	0.2969(9)	-0.1873(7)	0.5616(5)
C(11)b	-0.0346(5)	-0.0230(3)	0.5815(3)
C(12)b	-0.2127(6)	-0.1281(4)	0.6402(5)
C(1)c	0.0000	-0.1932(4)	0.7500

3. Results and Discussion

Of the four available donor sites on the calix[4]arene, only two are occupied by acceptor molecules. A similar situation was found for crown ether complexes of aluminum alkyls [13], and it may be understood in terms of the steric demands of the acceptors and the geometrical distortion required of the 'host' molecule. Clearly the oxygen atoms must be arranged so as to allow formation of a strong Al—O bond. In calix[4]arene, this distortion causes the macrocycle to adopt the 'alternate' geometries, so that two aluminum moieties bind to oxygen atoms on opposite 'faces' of the ring. When the peralkylated aluminum species is used, giving compound **2**, the previously unseen '1,2-alternate' geometry is formed (Figure 2). When two of the organic groups are replaced by chlorines, however, the geometry changes to the '1,3-alternate' [14] for both compounds **3** and **4** (Figures 3 and 4, respectively). Thus in the latter two complexes, the aluminum moieties are attached to adjacent methyl ether groups, while in **1** and **2** they are bonded to alternate methyl ether residues.

The fact that both types of aluminum species produced simple adducts with the calixarenes is in direct contrast to the behavior seen with the crown ethers, which could stabilize the AlCl_2^+ cation produced by asymmetric dissociation of halide bridged dimers [15]. This is undoubtedly due to the relative flexibility of the crowns compared to calix[4]arene, as ion-pair formation was observed for the analogous reactions of calix[6]- and calix[8]arenes [16], as evidenced by the formation of two-layer liquid clathrate systems [17]. A second difference between the adducts of crowns and calixes is the 'non-reaction' of the latter with alkali metal salts. Complexes of

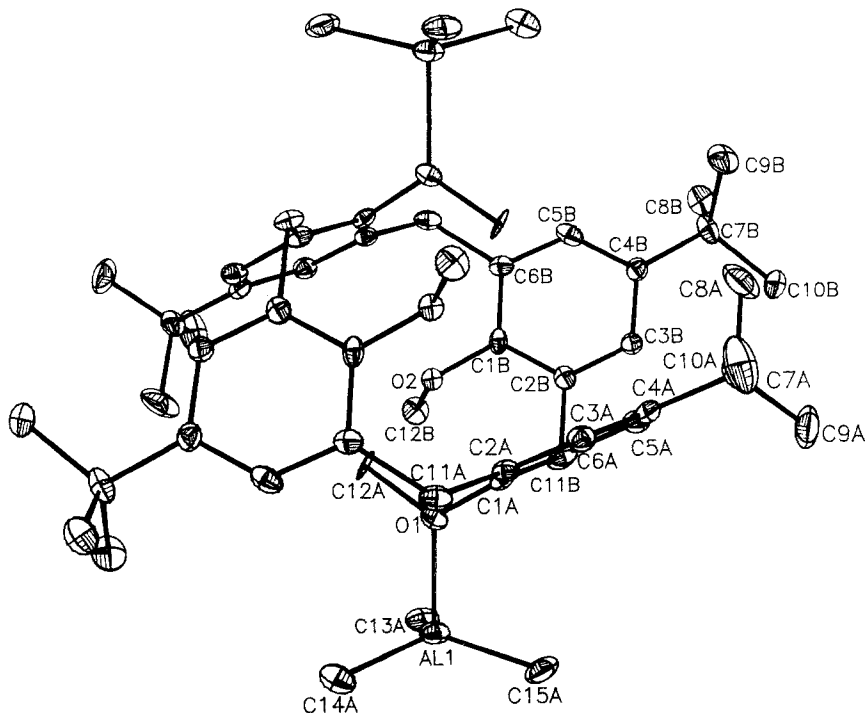


Fig. 2. The 1,2-alternate geometry exhibited by **2**.

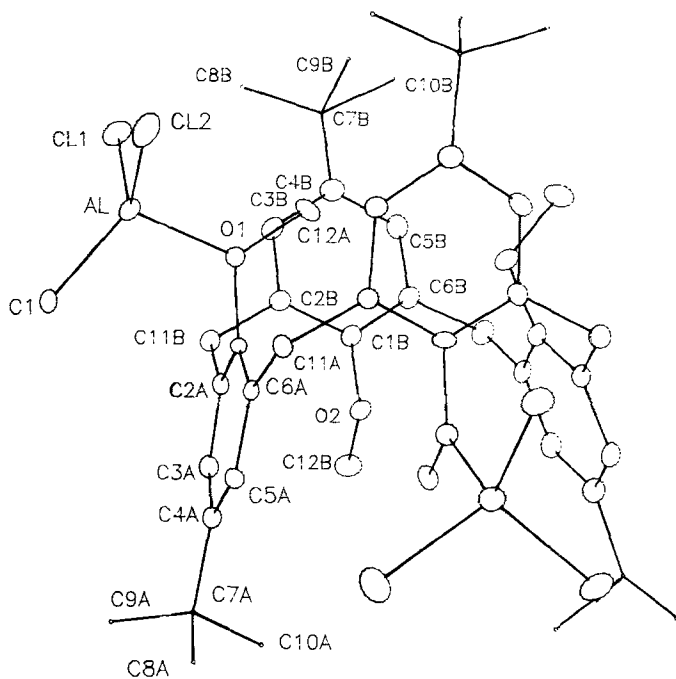


Fig. 3. The 1,3-alternate geometry of **3**.

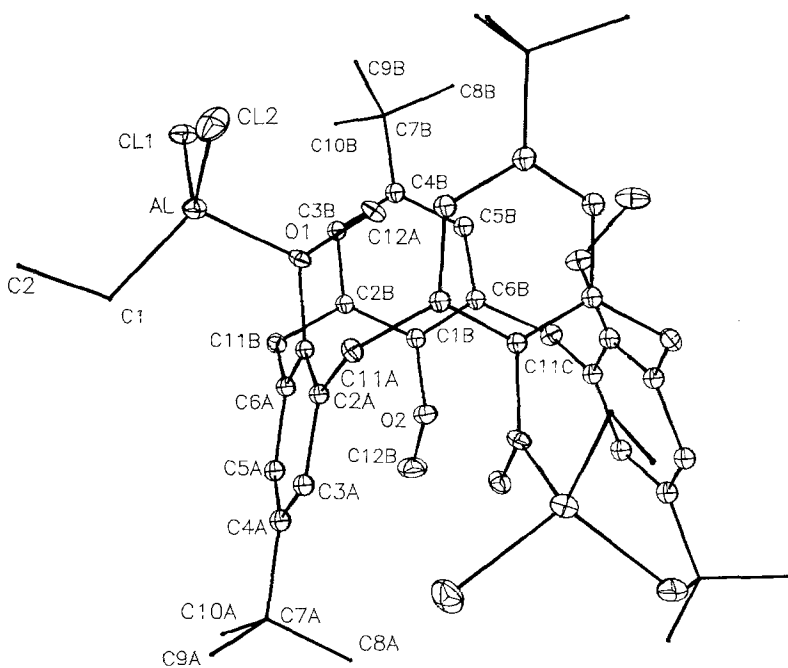


Fig. 4. The 1,3-alternate geometry of **4**.

Table V. Bond lengths (Å) and angles (°) for compounds 2-4

Atoms	(2) X = Me, R = Me	(3) X = Cl, R = Me	(4) X = Cl, R = Et
Al—X(1)	2.000(8)	2.121(5)	2.128(3)
Al—X(2)	1.997(9)	2.131(4)	2.120(3)
Al—R	1.97(1)	1.94(1)	1.937(6)
Al—O(1)	1.99(1)	1.913(7)	1.886(5)
O(1)—C(1)a	1.42(2)	1.42(1)	1.435(6)
O(1)—C(12)a	1.51(2)	1.474(9)	1.491(7)
O(2)—C(1)b	1.37(1)	1.38(1)	1.390(7)
O(2)—C(12)b	1.47(2)	1.44(1)	1.422(8)
X(1)—Al—X(2)	114.6(4)	108.9(2)	109.0(1)
X(1)—Al—R	115.3(4)	115.1(4)	114.4(2)
X(2)—Al—R	118.3(4)	117.1(4)	116.9(3)
X(1)—Al—O(1)	100.4(5)	103.6(3)	102.7(2)
X(2)—Al—O(1)	102.6(4)	102.6(2)	103.5(2)
R—Al—O(1)	101.8(4)	107.9(4)	108.8(2)
Al—O(1)—C(1)a	122(1)	115.3(5)	117.1(3)
Al—O(1)—C(12)a	119.7(7)	124.8(5)	123.6(3)
C(1)a—O(1)—C(12)a	118(1)	119.6(6)	118.2(5)
C(1)b—O(2)—C(12)b	112.5(9)	115.0(7)	114.1(8)

crowns and aluminum alkyls were found to dissociate readily to form liquid clathrates [18], although the Al—O bond in the calixarene complexes (Table V) appear to be no stronger than those formed to crown oxygen atoms (as evidenced by the average Al—O length of 1.96 Å), there was no indication of this type of behavior, the compounds appearing to be inert to all of the classic liquid clathrate-forming salts (e.g., KN₃).

The unit cells of **3** and **4** are almost identical, the only difference lying in the presence of the benzene molecules in that of **3**. In both (Figures 5 and 6 for **3** and **4**, respectively) the calix molecules are arranged in chains along the *y* axis. In **4**, these are related to each other by a direct translation parallel to both *a* and *c*, whereas in **3**, there is a slight slippage along *b*. This leads to an increase in cell volume that is slightly larger than one might expect for the effective replacement of a benzene for two methylene groups (observed change = 532 Å³, calculated change = 508 Å³ [19]) since the packing is not as efficient.

Now that structural characterizations exist for all of the possible calix[4]arene conformations, it is of interest to compare their important geometrical parameters (Table VI). Of particular note are those that define the dimensions of the space enclosed by the phenolic residues, i.e., the angles and distances between the aromatic planes and the O...O separations. Thus it can be seen that the cone and partial cone include 'cavities' in the shape of a truncated cone, while that of the 1,3-alternate configuration is cylindrical and the 1,2-alternate configuration envelops a parallelepiped-shaped region. The distance between the binding sites is always greater than that found in the crown ethers (which ranges from 2.5 to 2.8 Å in the typical coronand geometry) and may account for the reluctance of the calixarenes to complex alkali metals [20]. A final point of interest is the torsion angles around the methylene bridges. These vary a great deal between conformations, but are remarkably

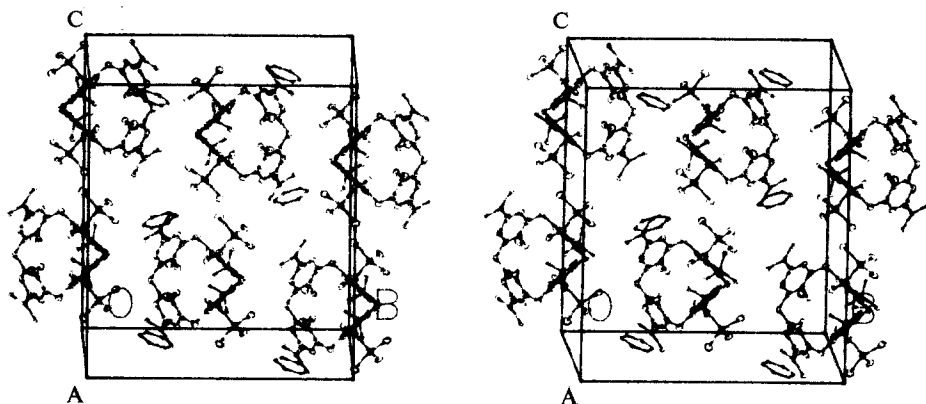


Fig. 5. Stereoview of the unit cell packing for 3.

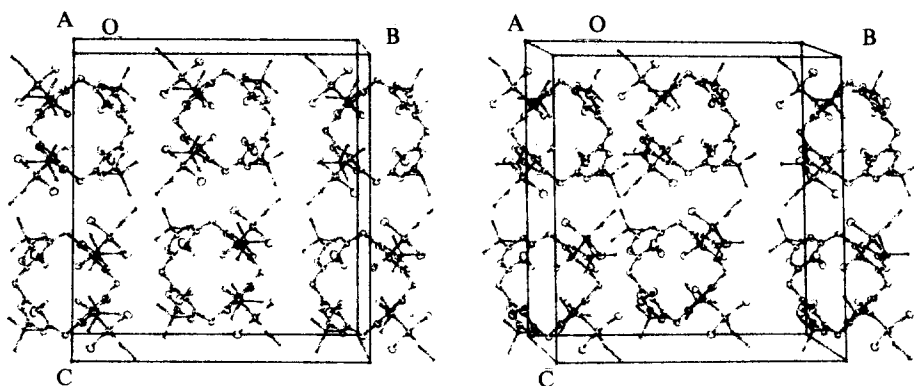


Fig. 6. Stereoview of the unit cell packing for 4.

similar between examples of the same geometry. Thus the original statement of Cornforth that only the four configurations are possible would seem to be correct [3].

It is evident that the donor sites can be used to effect the modification of calixarene configurations. This feature should enhance the prospects of the eventual use of calixarenes as 'active site' mimics.

Acknowledgement

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Table VI. Observed geometrical parameters for the conformations of calix[4]arene

Geometry	O ... O	Distance (Å)	Ce ... Ce ^a	Distance (Å)
	Adj.	Opp.	Adj.	Opp.
Cone ^b	3.16	4.44	4.59	6.22
	3.23	4.60	4.64	6.80
Partial Cone ^c	3.32	4.55	4.62	5.04
	3.34	5.90	4.67	6.77
	4.76		4.72	
	4.77		4.78	
1,2-alternate	3.63	5.35	4.64	6.28
	3.88	5.66	4.68	6.21
1,3-alternate	4.33	3.85	4.87	5.92
	4.65	4.73	5.01	5.92

Geometry	Plane Angles (°)		Torsion Angles (°)	
	Adj.	Opp.	C(5)—C(6)—M—C(2) ^b	C(6)—M—C(2)—C(3) ^d
Cone	79.7	61.1	69	83
	99.1	141.7		
Partial Cone	82	71	50	-60
	84	167	103	-105
	91		-111	108
	92		124	-121
1,2-alternate	80	0	-63	81
	100	0	140	140
1,3-alternate	84	31	-119	-132
	94		123	

^a Ce = ring centroids.^b Reference [21].^c Reference [22].^d M = methylene carbon atom.

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