

# Reaction of Trimethylaluminum with Calixarenes. I. Synthesis and Structure of [Calix[8]arene Methyl Ether] $[\text{AlMe}_3]_6 \cdot 2$ Toluene and of [*p*-*tert*-Butylcalix[8]arene Methyl Ether] $[\text{AlMe}_3]_6 \cdot 4$ Benzene

ANTHONY W. COLEMAN, SIMON G. BOTT, and JERRY L. ATWOOD★  
*Department of Chemistry, University of Alabama, University, AL 35486, U.S.A.*

(Received: 22 July 1986; in final form: 30 December 1986)

**Abstract.** Reaction of the methyl ether of calix[8]arene with  $\text{AlMe}_3$  yields [calix[8]arene methyl ether]  $[\text{AlMe}_3]_6 \cdot 2$  toluene, **1**, while that of *p*-*tert*-butylcalix[8]arene gives [*p*-*tert*-butylcalix[8]arene methyl ether]  $[\text{AlMe}_3]_6 \cdot 4$  benzene, **2**. Both compounds **1** and **2** fail to react with alkali metal salts, MX. In **1**, the absence of a butyl *para*-substituent affords greater flexibility than is the case for the *tert*-butyl compound **2**. Thus, all six of the  $\text{AlMe}_3$  groups are located on the outside of the macrocyclic ring (in projection) in **1**, but two  $\text{AlMe}_3$  units are found on the inside in **2**. Colorless, air-sensitive crystals of **1** belong to the triclinic space group  $P\bar{1}$  with  $a = 13.690(8)$ ,  $b = 14.317(4)$ ,  $c = 14.738(6)$  Å,  $\alpha = 76.11(3)$ ,  $\beta = 62.36(4)$ ,  $\gamma = 82.41(4)^\circ$ , and  $D_c = 1.06 \text{ g cm}^{-3}$  for  $Z = 1$ . Refinement led to  $R = 0.101$  for 1154 observed reflections. **2** crystallizes in  $P\bar{1}$  with  $a = 12.400(6)$ ,  $b = 16.229(8)$ ,  $c = 19.251(5)$  Å,  $\alpha = 96.17(3)$ ,  $\beta = 107.25(3)$ ,  $\gamma = 101.54(3)^\circ$ , and  $D_c = 1.01 \text{ g cm}^{-3}$  for  $Z = 1$ . Refinement of **2** gave  $R = 0.128$  for 4351 observed reflections. The macrocyclic array in both **1** and **2** lies about a crystallographic center of inversion.

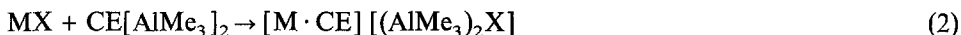
**Key words:** Calix[8]arene, crystal structure,  $\text{AlMe}_3$ , aromatic adduct.

**Supplementary Data** relating to this article are deposited with the British Library as Supplementary Publication No. SUP 82049 (48 pages).

## 1. Introduction

Reaction of  $\text{AlMe}_3$  with crown ethers has produced a number of products which have been characterized X-ray crystallographically: [12-crown-4]  $[\text{AlMe}_3]_2$  [1], [15-crown-5]  $[\text{AlMe}_3]_4$  [2], [18-crown-6]  $[\text{AlMe}_3]_4$  [3], [18-crown-6]  $[\text{AlMe}_3]_4 \cdot p$ -xylene [4], [dibenzo-18-crown-6]  $[\text{AlMe}_3]_2$  [2], and [dibenzo-18-crown-6]  $[\text{AlMe}_3]_3$  [3]. The use of such related alkyls as  $\text{AlEt}_3$  or  $\text{GaMe}_3$  has yielded a similar series [5]. Our interest in these exotic species has been two-fold. First, in the course of the investigation of the general reaction (1), we often encountered salts, MX, which for reasons of lattice energy could not be induced to react. The use of crown ether  $\cdot \text{AlMe}_3$  complexes,  $\text{CE}[\text{AlMe}_3]_2$ , on the other hand, often gave a facile reaction (2), and afforded reaction with such difficult materials as KCl [6].

★ Author for correspondence.



Thus, the crown ether  $\cdot \text{AlMe}_3$  complexes react smoothly to release the  $\text{AlMe}_3$  to attack the anion,  $\text{X}^-$ , while the crown ether associates itself to the cation,  $\text{M}^+$ .

Our second interest is in the conformation of the crown ether  $\cdot \text{AlMe}_3$  complexes themselves. Remarkable distortions have been noted, as the 15-crown-5 ring, for example, is essentially turned inside-out. In each case the driving force is the formation of strong Al—O bonds.

In this report we focus attention on the same questions with regard to calixarenes. Here, the greater flexibility of the macrocycle should permit even greater geometrical distortions. Indeed, this expectation has been borne out.

## 2. Experimental

All experimental work was carried out under a nitrogen atmosphere in a dry box. Solvents were distilled under  $\text{N}_2$  over Na/benzophenone prior to entry into the dry box. Calix[8]arene methyl ether and *p*-*tert*-butylcalix[8]arene methyl ether were prepared as previously described [7], and included  $\text{CHCl}_3$  was removed by grinding and subsequent removal under reduced pressure at  $100^\circ\text{C}$  for 5 days.

### 2.1. PREPARATION OF [CALIX[8]ARENE METHYL ETHER] $[\text{AlMe}_3]_6 \cdot 2$ TOLUENE

To a solution of calix[8]arene methyl ether (960 mg, 1 mmol) in toluene (20 ml) was added  $\text{AlMe}_3$  (1.06 g, 8 mmol). A slight color-change to very pale yellow was observed. The solution was left for 12 h and large colorless crystals of the product [calix[8]arene methyl ether]  $[\text{AlMe}_3]_6 \cdot 2$  toluene resulted. The compound [*p*-*tert*-butylcalix[8]arene methyl ether]  $[\text{AlMe}_3]_6 \cdot 4$  benzene was prepared by an analogous method.

### 2.2. REACTION OF *p*-*tert*-BUTYLCALIX[8]ARENE METHYL ETHER WITH THE $\text{Cs}[(\text{AlMe}_3)_2\text{N}_3]$ LIQUID CLATHRATE

The liquid clathrate of  $\text{CsN}_3$  was prepared by the reaction of  $\text{CsN}_3$  (180 mg, 1 mmol) and  $\text{AlMe}_3$  (2 ml of 1 M soln in toluene) in toluene (15 ml). After 30 min a clear two-phase system was established.

To the upper layer was added a solution of *p*-*tert*-butylcalix[8]arene methyl ether (1.4 g, 1 mmol) in benzene (20 ml) and the system was stirred for 1 h. The resultant two-phase system was allowed to stand for 48 h, at which point colorless crystals were found at the interface. Single-crystal X-ray analysis showed these to be identical with [*p*-*tert*-butylcalix[8]arene methyl ether]  $[\text{AlMe}_3]_6 \cdot 4$  benzene.

### 2.3. X-RAY DATA AND STRUCTURE SOLUTION FOR [CALIX[8]ARENE METHYL ETHER] $[\text{AlMe}_3]_6 \cdot 2$ TOLUENE, **1**

Single crystals of **1** were sealed in thin-walled glass capillaries under a nitrogen atmosphere. Final lattice parameters as determined from 25 reflections ( $2\theta > 24^\circ$ ) accurately centered on an Enraf–Nonius CAD-4 are given in Table I. Intensity data were recorded in the usual manner [8]. A summary of data collection parameters is also presented in Table I.

Table I. Crystal data and summary of intensity data collection and structure refinement

Compound	1	2
mol wt	1578.2	2155.3
space group	$P\bar{1}$	$P\bar{1}$
cell constants		
<i>a</i> , Å	13.690(8)	12.400(6)
<i>b</i> , Å	14.317(4)	16.229(8)
<i>c</i> , Å	14.738(6)	19.251(5)
α, deg	76.11(3)	96.17(3)
β, deg	62.36(4)	107.25(5)
γ, deg	82.41(4)	101.54(3)
cell vol., Å <sup>3</sup>	2483	3567
molecules/unit cell	1	1
ρ(calc), g cm <sup>-3</sup>	1.06	1.01
μ(calc), cm <sup>-1</sup>	0.94	0.90
radiation	MoKα	MoKα
scan width, deg	0.8 + 0.2 tan θ	0.8 × 0.2 tan θ
study reflections	300, 030, 002	200, 020, 002
variation of studies	<3%	<4%
2(θ)range	2–40	2–40
observed reflections	1154	4351
No. of parameters varied	160	480
GOF	1.43	2.08
<i>R</i>	0.101	0.128
<i>R</i> <sub>w</sub>	0.113	0.131

Table II. Final positional parameters for 1

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Al(1)	0.7315(9)	0.4386(7)	0.456(1)
Al(2)	0.3827(8)	0.0460(8)	0.7374(9)
Al(3)	0.652(1)	-0.3845(8)	0.754(1)
Me(1)	0.596(3)	0.436(2)	0.591(3)
Me(2)	0.882(3)	0.401(3)	0.455(3)
Me(3)	0.726(3)	0.546(2)	0.339(3)
Me(4)	0.317(3)	-0.077(2)	0.737(3)
Me(5)	0.355(3)	0.072(2)	0.875(3)
Me(6)	0.383(3)	0.158(2)	0.627(3)
Me(7)	0.736(3)	-0.506(3)	0.766(4)
Me(8)	0.486(3)	-0.389(3)	0.847(3)
Me(9)	0.703(3)	-0.307(3)	0.609(3)
O(1)	0.712(2)	0.322(1)	0.409(1)
O(2)	0.548(2)	0.008(1)	0.671(2)
O(3)	0.694(2)	-0.302(1)	0.824(1)
O(4)	0.950(2)	-0.424(1)	0.831(2)
C(1)A	0.789(2)	0.240(2)	0.390(3)
C(2)A	0.867(3)	0.241(2)	0.292(3)
C(3)A	0.942(2)	0.161(2)	0.281(2)
C(4)A	0.933(3)	0.091(2)	0.367(3)
C(5)A	0.853(3)	0.098(3)	0.462(3)
C(6)A	0.775(3)	0.170(2)	0.482(3)

Table II (continued)

Atom	$x/a$	$y/b$	$z/c$
C(7)A	0.686(2)	0.176(2)	0.582(2)
C(8)A	0.614(3)	0.317(2)	0.394(3)
C(1)B	0.616(2)	0.017(2)	0.721(2)
C(2)B	0.684(3)	0.102(2)	0.675(3)
C(3)B	0.750(2)	0.106(2)	0.722(2)
C(4)B	0.750(2)	0.036(2)	0.801(2)
C(5)B	0.680(2)	-0.042(2)	0.847(3)
C(6)B	0.616(2)	-0.056(2)	0.800(2)
C(7)B	0.542(2)	-0.142(2)	0.841(2)
C(8)B	0.596(3)	-0.032(2)	0.578(3)
C(1)C	0.622(2)	-0.282(2)	0.926(2)
C(2)C	0.547(2)	-0.207(2)	0.929(2)
C(3)C	0.476(2)	-0.198(2)	1.026(2)
C(4)C	0.475(2)	-0.261(2)	1.120(3)
C(5)C	0.551(3)	-0.328(2)	1.108(3)
C(6)C	0.633(2)	-0.343(2)	1.014(2)
C(7)C	0.729(2)	-0.415(2)	0.996(2)
C(8)C	0.806(2)	-0.252(2)	0.761(2)
C(1)D	0.932(2)	-0.372(2)	0.908(2)
C(2)D	0.829(2)	-0.361(2)	0.986(2)
C(3)D	0.813(3)	-0.314(2)	1.068(3)
C(4)D	0.899(3)	-0.265(2)	1.056(3)
C(5)D	1.001(3)	-0.271(2)	0.971(3)
C(6)D	1.023(2)	-0.321(2)	0.893(2)
C(7)D	0.869(2)	0.318(2)	0.202(2)
C(8)D	0.970(2)	-0.524(2)	0.866(2)
T(1) <sup>a</sup>	1.026	0.098	0.800
T(2)	1.027	0.180	0.725
T(3)	0.944	0.250	0.752
T(4)	0.859	0.240	0.854
T(5)	0.858	0.158	0.929
T(6)	0.941	0.088	0.902

<sup>a</sup> T refers to a toluene ring carbon atom. They were set at C—C = 1.39 Å and treated as a rigid group. The toluene methyl group could not be located.

Structure solution was accomplished by means of the direct methods program MULTAN [9], and the subsequent calculations of difference Fourier maps allowed the location of all non-hydrogen atoms. Due to the lack of data only the AlMe<sub>3</sub> groups were refined with anisotropic thermal parameters. The hydrogen atoms of the methylene and aromatic carbon atoms were placed in calculated positions, and blocked-matrix least squares refinement ultimately resulted in  $R = \Sigma(\|F_o\| - |F_c|)/\Sigma |F_o| = 0.101$  and  $R_w = \{\Sigma w \|F_o\| - |F_c|\}^2 / \Sigma w |F_o|^2\}^{1/2} = 0.113$ . The largest parameter shifts in the final cycles of refinement were less than 0.01 of their estimated standard deviations. Neutral atom scattering factors were taken from the usual sources [8]. The final values of the positional parameters are given in Table II.

Table III. Final positional parameters for **2**

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Al(1)	0.9544(4)	0.1885(2)	0.5267(2)
Al(2)	1.5142(4)	0.1885(2)	0.4932(2)
Al(3)	1.3074(4)	0.0460(3)	0.1236(2)
O(1)	1.1027(7)	0.2264(4)	0.6124(4)
O(2)	1.3433(7)	0.1659(4)	0.4459(4)
O(3)	1.2525(7)	0.0092(4)	0.2055(4)
O(4)	1.1053(6)	-0.2165(5)	0.2525(4)
C(1)A	1.177(1)	0.3113(7)	0.6327(6)
C(2)A	1.1525(9)	0.3685(7)	0.6810(6)
C(3)A	1.223(1)	0.4516(7)	0.6996(6)
C(4)A	1.314(1)	0.4753(7)	0.6723(6)
C(5)A	1.333(1)	0.4150(7)	0.6251(6)
C(6)A	1.263(1)	0.3314(7)	0.6044(6)
C(7)A	1.387(1)	0.5704(8)	0.6946(8)
C(8)A	1.440(2)	0.590(1)	0.7778(9)
C(9)A	1.487(2)	0.581(1)	0.660(1)
C(10)A	1.309(2)	0.628(1)	0.665(1)
C(11)A	1.057(1)	0.3460(7)	0.7135(5)
C(12)A	1.146(1)	0.1656(7)	0.6597(7)
C(13)A	0.996(1)	0.1112(9)	0.4573(8)
C(14)A	0.848(1)	0.126(1)	0.5740(9)
C(15)A	0.928(1)	0.2971(9)	0.4984(8)
C(1)B	1.2795(9)	0.2271(7)	0.4212(6)
C(2)B	1.2612(9)	0.2831(7)	0.4723(6)
C(3)B	1.2076(9)	0.3462(7)	0.4485(6)
C(4)B	1.178(1)	0.3568(7)	0.3742(6)
C(5)B	1.1975(9)	0.2978(7)	0.3255(6)
C(6)B	1.2483(9)	0.2321(7)	0.3450(6)
C(7)B	1.124(1)	0.4294(7)	0.3478(7)
C(8)B	1.003(1)	0.3904(9)	0.2937(9)
C(9)B	1.199(2)	0.481(1)	0.308(1)
C(10)B	1.115(2)	0.489(1)	0.4119(9)
C(11)B	1.289(1)	0.2685(7)	0.5521(6)
C(12)B	1.269(1)	0.0778(6)	0.4381(7)
C(13)B	1.568(1)	0.3154(8)	0.5263(8)
C(14)B	1.563(1)	0.1431(9)	0.4096(7)
C(15)B	1.523(1)	0.1216(9)	0.5741(8)
C(1)C	1.146(1)	0.0201(7)	0.2108(6)
C(2)C	1.141(1)	0.0954(7)	0.2518(6)
C(3)C	1.038(1)	0.1070(7)	0.2505(6)
C(4)C	0.932(1)	0.0452(7)	0.2174(6)
C(5)C	0.943(1)	-0.0299(7)	0.1810(6)
C(6)C	1.043(1)	-0.0461(7)	0.1779(6)
C(7)C	0.814(1)	0.0594(8)	0.2129(7)
C(8)C	0.752(1)	-0.0068(9)	0.2514(9)
C(9)C	0.820(1)	0.1494(8)	0.2538(8)
C(10)C	0.738(1)	0.048(1)	0.1308(8)
C(11)C	1.2569(9)	0.1654(6)	0.2883(6)
C(12)C	1.320(1)	-0.0347(7)	0.2591(6)
C(13)C	1.452(1)	0.136(1)	0.1758(9)
C(14)C	1.174(1)	0.083(1)	0.0654(9)
C(15)C	1.335(2)	-0.060(1)	0.0795(9)
C(1)D	0.993(1)	-0.2434(7)	0.2040(6)
C(2)D	0.965(1)	-0.2045(7)	0.1420(6)

Table III (continued)

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
C(3)D	0.853(1)	-0.2324(7)	0.0928(6)
C(4)D	0.768(1)	-0.2980(7)	0.1021(6)
C(5)D	0.7991(9)	-0.3312(7)	0.1665(6)
C(6)D	0.9104(9)	-0.3065(7)	0.2160(6)
C(7)D	0.646(1)	-0.3264(9)	0.0436(7)
C(8)D	0.593(1)	-0.247(1)	0.031(1)
C(9)D	0.661(2)	-0.370(1)	-0.0287(3)
C(10)D	0.564(1)	-0.3948(9)	0.0683(8)
C(11)D	1.050(1)	-0.1288(6)	0.1332(6)
C(12)D	1.181(1)	-0.2715(9)	0.2476(9)
X(1) <sup>a</sup>	0.844(3)	0.295(1)	0.081(1)
X(2)	0.787(3)	0.358(1)	0.095(1)
X(3)	0.838(3)	0.444(1)	0.099(1)
X(4)	0.946(3)	0.467(1)	0.089(1)
X(5)	1.003(3)	0.404(1)	0.075(1)
X(6)	0.952(3)	0.318(1)	0.071(1)
T(7)	1.477(3)	0.713(1)	0.244(1)
T(8)	1.452(3)	0.764(1)	0.189(1)
T(9)	1.354(3)	0.718(1)	0.121(1)
T(10)	1.295(3)	0.634(1)	0.111(1)
T(11)	1.322(3)	0.584(1)	0.169(1)
T(12)	1.417(3)	0.629(1)	0.235(1)

<sup>a</sup> X and T refer to the benzene carbon atoms.

#### 2.4. X-RAY DATA COLLECTION AND STRUCTURE SOLUTION FOR

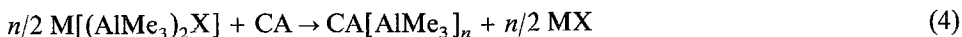
[*p*-*tert*-BUTYLCALIX[8]ARENE METHYL ETHER] [AlMe<sub>3</sub>]<sub>6</sub> · 4 BENZENE, 2

The compound was manipulated and data collected in the same manner as for **1**. Final full-matrix least squares refinement converged at  $R = 0.128$ ,  $R_w = 0.131$ . Final positional parameters are listed in Table III.

### 3. Results and Discussion

Reaction of the calixarenes, CA, with AlMe<sub>3</sub> proceeds rapidly with the evolution of heat. In dealing with AlMe<sub>3</sub> we choose to work with ethers (O–R) rather than with the parent calixarenes (O–H) because the reaction with the latter is often violent.

Preliminary experiments indicate that the [calix[8]arene methyl ether] [AlMe<sub>3</sub>]<sub>6</sub> complexes do not undergo reaction (3).



In fact, there is an indication that the addition of a methyl ether of calix[8]arene actually causes the displacement of the anion in an existing liquid clathrate [10], and favors instead a Lewis acid–base complex with AlMe<sub>3</sub>. The failure of reaction (3) is not unexpected in view of the reduced ability of calixarenes to transport alkali metal ions in comparison to that of crown ethers [11, 12]. Further evidence for the difficulty of causing a strong interaction of a

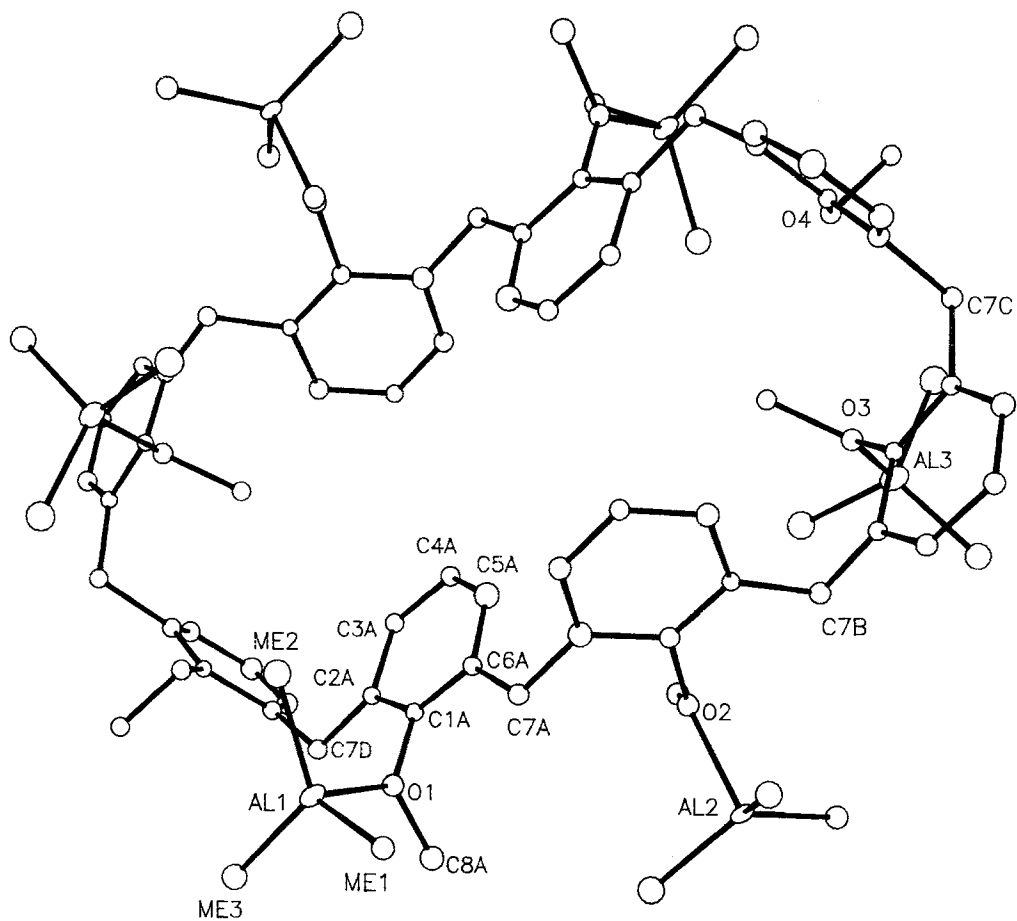


Fig. 1. View of [calix[8]arene methyl ether] · [AlMe<sub>3</sub>]<sub>6</sub>, **1**, showing the numbering scheme. The molecule resides on a crystallographic center of inversion.

Table IV. Selected bond lengths (Å) and angles (deg) for **1**

Atoms	Distance	Atoms	Distance
Al(1)—O(1)	2.04(3)	Al(2)—O(2)	2.06(2)
Al(3)—O(3)	2.03(3)		
Atoms	Angle	Atoms	Angle
Al(1)—O(1)—C(1A)	125(2)	Al(2)—O(2)—C(1B)	120(2)
Al(1)—O(1)—C(8A)	120(2)	Al(2)—O(2)—C(8B)	120(2)
C(1A)—O(1)—C(8A)	115(3)	C(1B)—O(2)—C(8B)	120(2)
Al(3)—O(3)—C(1C)	123(2)	C(1C)—O(3)—C(8C)	118(2)
Al(3)—O(3)—C(8C)	118(2)	C(1D)—O(4)—C(8D)	110(2)

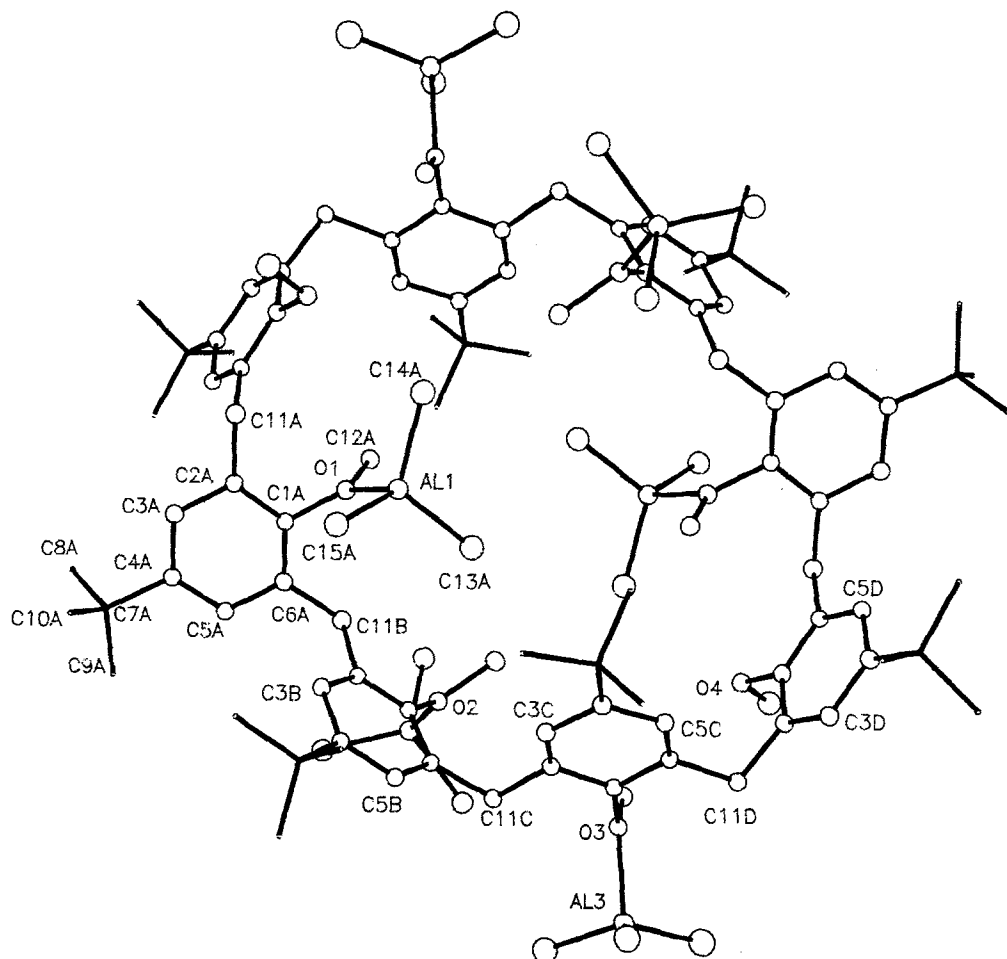


Fig. 2. View of  $[t\text{-butylcalix[8]arene methyl ether}] \cdot [\text{AlMe}_3]_6$ , **2**, showing the numbering scheme. The molecule resides on a center of inversion.

Table V. Selected bond lengths (Å) and angles (deg) for **2**

Atoms	Distance	Atoms	Distance
Al(1)—O(1)	2.003(7)	Al(2)—O(2)	1.997(9)
Al(3)—O(3)	1.99(1)		
Atoms	Angle	Atoms	Angle
Al(1)—O(1)—C(1A)	125(1)	Al(2)—O(2)—C(1B)	126(1)
Al(1)—O(1)—C(12A)	121(1)	Al(2)—O(2)—C(12B)	120(1)
C(1A)—O(1)—C(12A)	114(1)	C(1B)—O(2)—C(12B)	114(1)
Al(3)—O(3)—C(1C)	121(1)	C(1C)—O(3)—C(12C)	118(1)
Al(3)—O(3)—C(12C)	120(1)	C(1D)—O(4)—C(12D)	116(1)



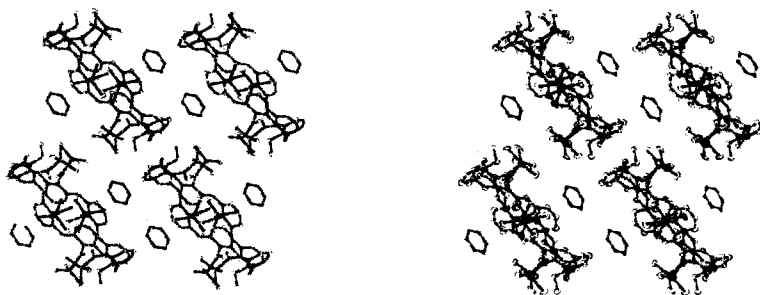


Fig. 3. Molecular packing of **1** viewed along the 100 axis. The toluene methyl groups were not located.

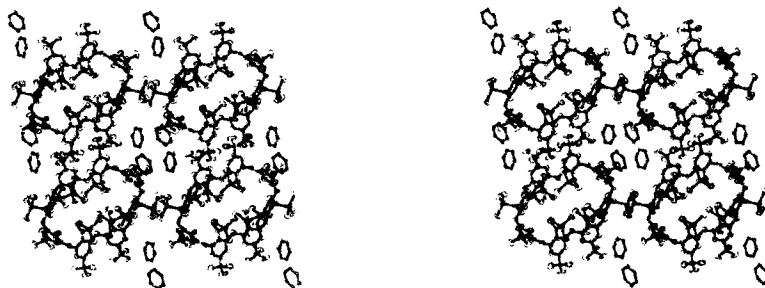


Fig. 4. Molecular packing of **2** viewed along the 010 axis.

calixarene with a cation is the fact that only one such complex, [*p*-*tert*-butylcalix[4]arene methyl ether · Na]<sup>+</sup>, has been structurally characterized [13].

The observation of reaction (4) would seem to mean that the Al—O bonds are stronger in the title complexes than in the crown ether · AlMe<sub>3</sub> adducts. The argument also seems reasonable in view of the expected lower energy requirement to position the oxygen donors of the calixarene for coordination to the aluminum atoms. Unfortunately, this is not reflected in the Al—O bond lengths. The value in [12-crown-4] [AlMe<sub>3</sub>]<sub>2</sub> is 1.977(3) Å, compared to 2.03(3)–2.06(2) Å in **1** and 1.99(1)–2.003(7) Å in **2**. (Note that the estimated standard deviations are lower for **2** because a much larger data set was obtained: 4351 observed reflections for **2** as against 1152 for **1**.)

The structure of **1** is given in Figure 1, and that of **2** in Figure 2. In the way of a general comparison, note that the absence of the *tert*-butyl groups permits more flexibility of the macrocycle. All six of the AlMe<sub>3</sub> units are on the outside in **1**, while in **2**, two AlMe<sub>3</sub> groups must move to within the boundary of the macroring (in projection). Final bond lengths and angles for **1** are given in Table IV, and for **2** in Table V.

The difference between the two molecules becomes more pronounced in the crystal packing, as shown in Figures 3 and 4 for **1** and **2**, respectively. Compound **1** accommodates two molecules of toluene per unit cell, which lie between sheets of calixarenes forming an intercalate system [14]. The major non-bonding contact is that between the methyl group of the non-aluminum-bonded oxygen and the corresponding benzene of the adjacent calixarene (C(8)*d* ··· C(5)*d*' = 3.43 Å, C(8)*d* ··· C(4)*d*' = 3.53 Å), no other contact being less than 3.70 Å. The solvent molecules are held in the layer through normal van der Waals contacts with one of the calix aromatics. The situation for compound **2** is quite the reverse, as the predominant

interactions are those between the calixarene and the four guest benzene molecules within the unit cell. Only four calix···calix contacts are smaller than 4.00 Å, all of which involve the methyl carbon atoms of the bulky groups. As can be seen from Figure 4, the guests fit in a tubulate fashion into tunnels formed by groups of four calixarene molecules. Of the two independent benzenes, one is held rather tightly within this tunnel by an interaction with the uncomplexed methoxymethyl (C(12)*d*···benzene = 3.70 Å on average) and the other fits rather more loosely (as reflected in the ease of refinement), held in place only by 'close' contact (3.85 Å on average) with a *tert*-butyl methyl (C(8)*b*).

A variation of this type of inclusion property has been reported only once before for calixarenes. Andreetti *et al.* noted that replacement of the *p*-*tert*-butyl by 1,1,3,3-tetramethylbutyl led to a change from intramolecular to tubulate type inclusion for calix[4]arene, although the molecular structure remained unchanged [15].

## Acknowledgement

We are grateful to the National Science Foundation for support of this work.

## References

1. G. H. Robinson, S. G. Bott, H. Elgamil, W. E. Hunter, and J. L. Atwood: *J. Incl. Phenom.* **3**, 65 (1985).
2. J. L. Atwood, D. C. Hrcir, R. Shakir, M. S. Dalton, R. D. Priester, and R. D. Rogers: *Organometallics* **1**, 1021 (1982).
3. J. L. Atwood, R. D. Priester, R. D. Rogers, and L. G. Canada: *J. Incl. Phenom.* **1**, 61 (1983).
4. H. Zhang, N. C. Means, C. M. Means, and J. L. Atwood: *J. Cryst. Spec. Res.* **15**, 445 (1985).
5. G. H. Robinson, W. E. Hunter, S. G. Bott, and J. L. Atwood: *J. Organometal. Chem.*, in press.
6. J. L. Atwood, D. C. Hrcir, and R. D. Rogers: *J. Incl. Phenom.* **1**, 199 (1983).
7. A. W. Coleman, S. G. Bott, and J. L. Atwood: *J. Incl. Phenom.* **4**, 247 (1986).
8. J. Holton, M. F. Lappert, D. G. H. Ballard, R. Pearce, J. L. Atwood, and W. E. Hunter: *J. Chem. Soc., Dalton Trans.* **45** (1979).
9. G. Germain, P. Main, and M. M. Woolfson: *Acta Crystallogr.* **A27**, 368 (1971).
10. J. L. Atwood in *Inclusion Compounds*, Vol. 1, J. L. Atwood, J. E. D. Davies, and D. D. MacNicol (eds.), Academic Press, London, 1984.
11. M. A. McKervey, E. M. Sowards, G. Ferguson, B. Ruhl, and S. J. Harris: *J. Chem. Soc., Chem. Commun.*, 388 (1985).
12. S. R. Izatt, R. T. Hawkins, J. J. Christensen, and R. M. Izatt: *J. Am. Chem. Soc.* **107**, 63 (1985).
13. S. G. Bott, A. W. Coleman, and J. L. Atwood: *J. Am. Chem. Soc.* **108**, 1709 (1986).
14. E. Weber and H.-P. Josel: *J. Incl. Phenom.* **1**, 79 (1983).
15. G. D. Andreetti, A. Pochini, and R. Ungaro: *J. Chem. Soc., Perkin Trans. 2*, 1773 (1983).