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Preparation and Structure of (Calix[8]arene Methyl Ether)·$2CDCl_3$

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

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Abstract. The methyl ether of calix[8]arene crystallizes from $CDCl_3$ with two molecules of the solvent per molecule of host. An X-ray structural investigation has shown that the $CDCl_3$ guests exist within the calixarene framework. The complex resides on a crystallographic center of inversion, and the cavity is roughly circular in projection as measured by the distance between centroids of aromatic rings related by the center: 14.5, 13.9, 10.1, and 11.2 Å. Six of the oxygen atoms are found on the inside and two on the outside. Crystals belong to the triclinic space group $P\bar{1}$ with $a = 11.741(9)$, $b = 11.810(9)$, $c = 12.484(8)$ Å, $\alpha = 94.74(8)$, $\beta = 104.41(8)$, $\gamma = 111.30(9)°$, and $D_c = 1.31$ g cm^{-3} for $Z = 1$. Refinement led to a final R value of 0.086 for 949 observed reflections.

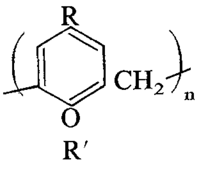
Key words: calix[8]arene, crystal structure, $CDCl_3$ guest.

Supplementary Data relating to this article are deposited with the British Library as Supplementary Publication No. SUP 82038 (10 pages).

1. Introduction

Calixarene chemistry is now an important area of macrocyclic endeavor [1]. Recent work has focused on synthesis [2–4], structure, and cation transport [5,6]. It is well-known among those involved in the synthesis that calixarenes retain solvent, often tenaciously [1]. Andreetti, Ungaro, and coworkers have shown examples of three different ways in which solvent may be included in the solid state: (1) within the calixarene cavity [7], (2) within the cavity formed by two calixarenes, 'face-to-face' [8], and (3) within channels [9] or layers [10] in the crystal, but external to the cavity. Using the classification of Weber and Josel [11], (1) and (2) are examples of cryptato-cavitate inclusion, while tubulato- refers to the channel-type and intercalato-, to the layer-type. With the suspected propensity for inclusion it is interesting to note that of the nine published calix[4]arene structures, only five show inclusion phenomena [5,7–10, 12–14]. Calix[5]arene forms an inclusion complex [15], but none of the four calix[6]arenes [5,16–18] nor the three calix[8]arenes [19–21] studied have been shown to form inclusion complexes. The possible cavities in the larger, more flexible structures are often seen to either collapse into lower energy packing modes, or become oriented such that R and R′ in the general calixarene structure, **1**, serve as barriers to the entrance of existing cavities. With this in mind, we decided to investigate the inclusion chemistry of some very simple calixarenes, R = H, R′ = Me. Here we report the first structure which shows inclusion within a calix[8]arene cavity.

★ Author for correspondence.



(1)

2. Experimental

2.1. PREPARATION OF THE METHYL ETHER OF CALIX[8]ARENE

Calix[8]arene. Following a modification of the preparation of this compound [22], t-butylcalix[8]arene (26 g, 0.02 mol) was suspended in benzene (500 ml) and $AlCl_3$ (66 g, 0.5 mol) was added in portions. The exothermic reaction leads to the formation of a two-layer system, the bottom layer being a red-orange color. The mixture is stirred at room temperature for 24 h, and is then added carefully to water (1 l). The resultant gelatinous suspension is filtered, and washed with acetone (5 × 200 ml) to remove water. The resultant insoluble pale pink solid was used without further purification.

Calix[8]Arene Methyl Ether. Calix[8]arene (21.2 g, 0.025 mol) was added to a suspension of NaH (24 g, 1 mol) in DMF (50 ml) : THF (500 ml) under N_2, and the resultant suspension refluxed for 2 h. On cooling, MeI (142 g, 1 mol) was added and the solution was again refluxed (6 h). The solvent was removed under vacuum and the solid washed carefully with water (1 l). The suspension was filtered. The solid was extracted with $CHCl_3$ (250 ml) and allowed to evaporate to a small volume (25 ml). The crystals formed were filtered to yield pure calix[8]arene methyl ether (12 g, 40%). A further crop of crystals was obtained by allowing the remaining $CHCl_3$ to evaporate to 5 ml (total yield, 20 g, 78%). ^1H NMR: 6.8 δ (s.3), 4.0 δ (s.3), 3.5 δ (s.3).

Suitable crystals for the X-ray diffraction study were grown by diffusion of Et_2O into a solution in $CDCl_3$ in a 5 mm NMR tube.

2.2. X-RAY DATA COLLECTION AND STRUCTURE SOLUTION FOR (CALIX[8]ARENE METHYL ETHER)·$2CDCl_3$

Since the title compound loses solvent very rapidly [1], single crystals were sealed with a drop of mother liquor in thin-walled glass capillaries. Lattice parameters as determined from 25 axial reflections ($2\theta > 24°$) centered on an Enraf–Nonius CAD-4 diffractometer are given in Table I (more accurate values were not obtained due to the crystal decay). Intensity data were recorded in the usual manner [23]. 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. The crystal decomposed (due to loss of solvent) isotropically during data collection down to only 20% of the original scattering power. At this point data collection was terminated, and the intensities were scaled accordingly.

Structure solution was accomplished by means of the direct methods program MULTAN [24], and the subsequent calculation of difference Fourier maps allowed the location of all nonhydrogen atoms. Because of the lack of data only the chlorine atoms were refined with anisotropic thermal parameters. The hydrogen atoms on the methylene carbon atoms were placed in calculated positions, as was the deuterium atom of the guest.

Table I. Crystal data for (calix[8]arene methyl ether)$\cdot 2CDCl_3$

Mol wt.	1202.0	Radiation	Mo$K\alpha$
Space group	$P\bar{1}$	Max cryst dimens, mm	0.3 × 0.3 × 0.4
Cell constants		Scan width, deg	$0.8 + 0.2 \tan\theta$
a, Å	11.741(9)	Std reflections	200, 030, 004
b, Å	11.810(9)	Decay of stds	80%
c, Å	12.484(8)	Refctns measd	3748
α, deg	94.74(8)		
β, deg	104.41(8)	$2(\theta)$	0–32
γ, deg	111.30(9)		
Cell vol, Å^3	2298	Obsd reflectns	949
Mol/unit cell	1	No of para. varied	112
ρ(calc), g cm^{-3}	1.31	R	0.086
μ(calc), cm^{-1}	3.32	R_w	0.082

Table II. Final fractional coordinates and equivalent isotropic thermal parameters

Atom	x/a	y/b	z/c	U_{eq}
Cl(1)	0.6599(7)	0.5465(7)	0.4784(6)	0.149
Cl(2)	0.9116(7)	0.6629(8)	0.4718(7)	0.181
Cl(3)	0.7036(9)	0.6055(9)	0.2783(6)	0.207
C(33)	0.763(2)	0.659(2)	0.426(2)	0.099
D	0.765(2)	0.747(2)	0.448(2)	0.080
O(1)	0.622(1)	0.844(1)	0.3841(9)	0.072
O(2)	0.475(1)	0.671(1)	0.0636(9)	0.070
O(3)	0.153(1)	0.309(1)	-0.064(1)	0.063
O(4)	0.314(1)	0.132(1)	0.231(1)	0.066
C(1)A	0.654(2)	0.970(2)	0.386(1)	0.051
C(2)A	0.661(2)	1.013(2)	0.285(1)	0.058
C(3)A	0.704(2)	1.138(2)	0.290(2)	0.077
C(4)A	0.734(2)	1.214(2)	0.384(2)	0.086
C5)A	0.731(2)	1.173(2)	0.487(2)	0.086
C(6)A	0.690(2)	1.048(2)	0.487(1)	0.058
C(7)A	0.685(2)	0.996(2)	0.594(1)	0.073
C(8)A	0.482(2)	0.763(2)	0.352(2)	0.075
C(1)B	0.418(2)	0.755(2)	0.060(1)	0.053
C(2)B	0.284(2)	0.704(1)	0.002(1)	0.045
C(3)B	0.222(2)	0.782(2)	-0.004(1)	0.055
C(4)B	0.286(2)	0.904(2)	0.048(1)	0.059
C(5)B	0.415(2)	0.951(2)	0.106(1)	0.050
C(6)B	0.480(2)	0.873(2)	0.109(1)	0.052
C(7)B	0.623(2)	0.924(2)	0.174(1)	0.066
C(8)B	0.544(2)	0.672(2)	-0.020(2)	0.081
C(1)C	0.150(2)	0.371(2)	0.035(1)	0.047
C(2)C	0.128(2)	0.301(2)	0.120(1)	0.059
C(3)C	0.129(2)	0.364(2)	0.220(1)	0.059
C(4)C	0.154(2)	0.489(2)	0.237(2)	0.069
C(5)C	0.180(2)	0.555(2)	0.151(1)	0.056
C(6)C	0.182(2)	0.495(2)	0.052(1)	0.052
C(7)C	0.209(2)	0.568(1)	-0.040(1)	0.065
C(8)C	0.033(2)	0.263(2)	-0.154(2)	0.083
C(1)D	0.203(2)	0.091(2)	0.262(1)	0.055
C(2)D	0.198(2)	0.030(2)	0.351(1)	0.056
C(3)D	0.090(2)	-0.009(1)	0.385(1)	0.054
C(4)D	-0.016(2)	0.010(2)	0.326(1)	0.067
C(5)D	-0.014(2)	0.064(2)	0.232(1)	0.066
C(6)D	0.096(2)	0.109(2)	0.199(1)	0.060
C(7)D	0.099(2)	0.164(1)	0.095(1)	0.064
C(8)D	0.402(2)	0.261(2)	0.286(2)	0.076

Blocked-matrix least-squared refinement ultimately resulted in

$$R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o| = 0.086 \quad \text{and} \quad R_w = \{\Sigma w(||F_o| - |F_c||)^2/ - \Sigma w(F_o)^2\}^{1/2} = 0.082\,.$$

The largest parameter shifts in the final cycle of refinement were less than 0.01 of their estimated standard deviations. Unit weights were used at all stages. Neutral atom scattering factors were taken from the usual sources [23]. The final values of the positional parameters are given in Table II.

3. Results and Discussion

The structure and atom labelling scheme are shown in Figure 1 and important bond lengths and angles are given in Table III. The complex resides on a crystallographic center of inversion, and the closest contact between the two $CDCl_3$ molecules is Cl(1)···Cl(1)′ at 3.71 Å. The fact that the guest molecules lie partially inside the host macrocycle is best seen

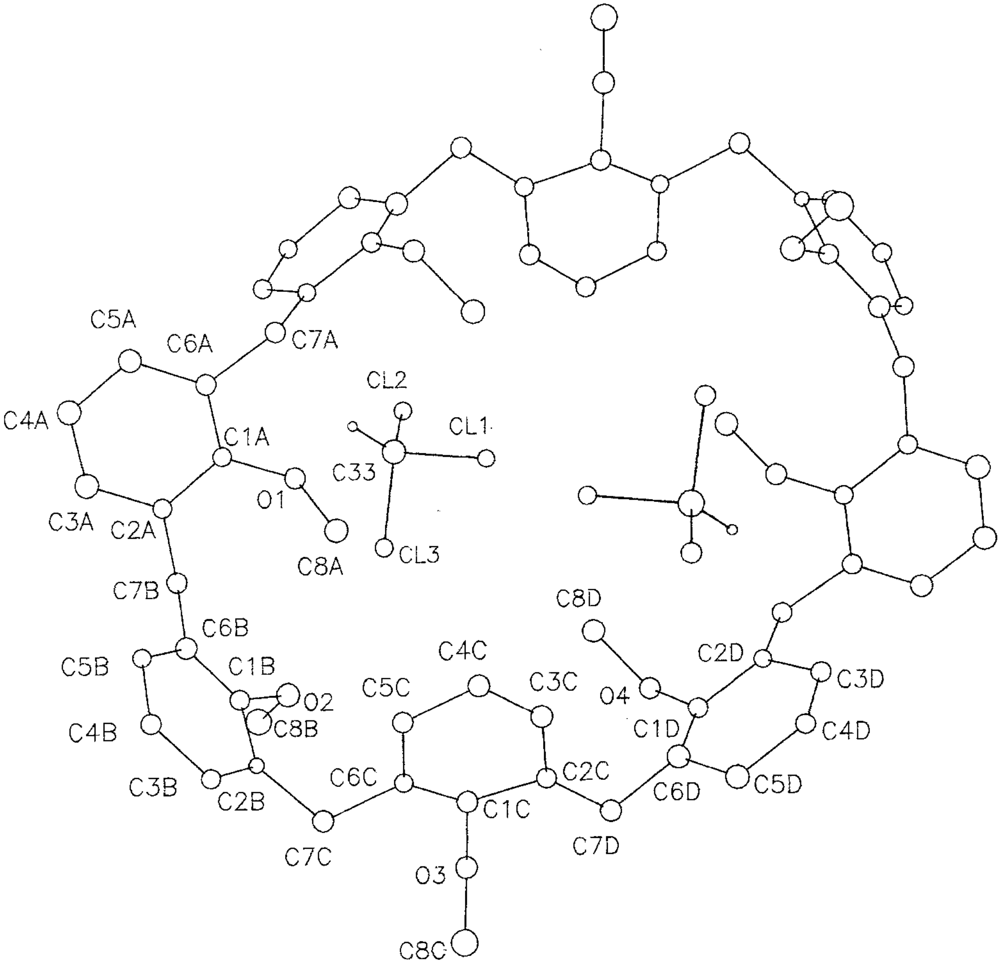


Fig. 1. Molecular structure and atom numbering scheme for (calix[8]arene methyl ether) · $2CDCl_3$. The molecule lies on a crystallographic center of inversion.

Table III. Bond lengths (Å) and angles (°)

Atoms	Distance	Atoms	Distance
O(1)—C(1)A	1.39(2)	O(1)—C(8)A	1.50(2)
O(2)—C(1)A	1.38(3)	O(2)—C(8)B	1.47(3)
O(3)—C(1)C	1.38(2)	O(3)—C(8)C	1.45(2)
O(4)—C(1)D	1.39(2)	O(4)—C(8)D	1.47(2)
C(1)A—C(2)A	1.40(3)	C(1)B—C(2)B	1.43(2)
C(1)C—C(2)C	1.42(3)	C(1)D—C(2)D	1.38(3)
C(1)A—C(6)A	1.37(2)	C(1)B—C(6)B	1.32(2)
C(1)C—C(6)A	1.36(3)	C(1)D—C(6)D	1.40(3)
C(2)A—C(3)A	1.38(3)	C(2)B—C(3)B	1.37(3)
C(2)C—C(3)C	1.39(3)	C(2)D—C(3)D	1.36(3)
C(2)A—C(7)B	1.52(2)	C(2)B—C(7)C	1.50(2)
C(2)C—C(7)D	1.51(3)	C(3)A—C(4)A	1.30(3)
C(3)B—C(4)B	1.37(2)	C(3)C—C(4)C	1.38(3)
C(3)D—C(4)D	1.39(3)	C(4)A—C(5)A	1.41(3)
C(4)B—C(5)B	1.38(2)	C(4)C—C(5)C	1.41(3)
C(4)D—C(5)D	1.39(3)	C(5)A—C(6)A	1.38(3)
C(5)B—C(6)B	1.40(3)	C(5)C—C(6)C	1.38(3)
C(5)D—C(6)D	1.39(3)	C(6)A—C(7)A	1.52(3)
C(6)B—C(7)B	1.53(2)	C(6)C—C(7)C	1.52(3)
C(6)D—C(7)D	1.50(3)	C(33)—Cl(1)	1.74(2)
C(33)—Cl(2)	1.68(3)	C(33)—Cl(3)	1.76(2)
C(33)—D	1.05(4)		

Atoms	Angle	Atoms	Angle
C(1)A—O(1)—C(8)A	117(1)	C(1)B(2)—O(2)—C(8)B	115(1)
C(1)C—O(3)—C(8)C	114(2)	C(1)D—O(4)—C(8)D	114(1)
O(1)—C(1)A—C(2)A	118(2)	O(2)—C(1)B—C(2)B	115(1)
O(3)—C(1)C—C(2)C	117(2)	O(4)—C(1)D—C(2)D	119(2)
O(1)—C(1)A—C(6)A	119(2)	C(2)A—C(1)A—C(6)A	123(2)
O(2)—C(1)B—C(6)B	123(2)	C(2)B—C(1)B—C(6)B	122(2)
O(3)—C(1)C—C(6)C	120(2)	C(2)C—C(1)C—C(6)C	122(2)
O(4)—C(1)D—C(6)D	119(2)	C(2)D—C(1)D—C(6)D	121(2)
C(1)A—C(2)A—C(3)A	118(2)	C(1)B—C(2)B—C(3)B	118(1)
C(1)C—C(2)C—C(3)C	116(2)	C(1)D—C(2)D—C(3)D	121(2)
C(1)A—C(2)A—C(7)B	122(2)	C(3)A—C(2)A—C(7)B	121(2)
C(1)B—C(2)B—C(7)C	122(2)	C(3)B—C(2)B—C(7)C	120(1)
C(1)C—C(2)C—C(7)D	119(2)	C(3)C—C(2)C—C(7)D	125(2)
C(2)A—C(3)A—C(4)A	121(2)	C(2)B—C(3)B—C(4)B	121(2)
C(2)C—C(3)C—C(4)C	122(2)	C(2)D—C(3)D—C(4)D	120(2)
C(3)A—C(4)A—C(5)A	122(2)	C(3)B—C(4)B—C(5)B	121(2)
C(3)C—C(4)C—C(5)C	120(2)	C(3)D—C(4)D—C(5)D	119(2)
C(4)A—C(5)A—C(6)A	120(2)	C(4)B—C(5)B—C(6)B	119(2)
C(4)C—C(5)C—C(6)C	119(2)	C(4)D—C(5)D—C(6)D	122(2)
C(1)A—C(6)A—C(5)A	117(2)	C(1)B—C(6)B—C(5)B	120(2)
C(1)C—C(6)C—C(5)C	120(2)	C(1)D—C(6)D—C(5)D	117(2)
C(1)A—C(6)A—C(7)A	120(2)	C(5)A—C(6)A—C(7)A	123(2)
C(1)B—C(6)B—C(7)B	121(2)	C(5)B—C(6)B—C(7)B	119(1)
C(1)C—C(6)C—C(7)C	121(2)	C(5)C—C(6)C—C(7)C	119(2)
C(1)D—C(6)D—C(7)D	120(2)	C(5)D—C(6)D—C(7)D	122(2)
C(2)A—C(7)B—C(6)B	114(2)	C(2)B—C(7)C—C(6)C	115(1)
C(2)C—C(7)D—C(6)D	111(1)	Cl(1)—C(33)—Cl(2)	110(1)
Cl(1)—C(33)—Cl(3)	104(1)	Cl(2)—C(33)—Cl(3)	109(2)
Cl(1)—C(33)—D	113(2)	Cl(2)—C(33)—D	109(2)
Cl(3)—C(33)—D	112(2)		

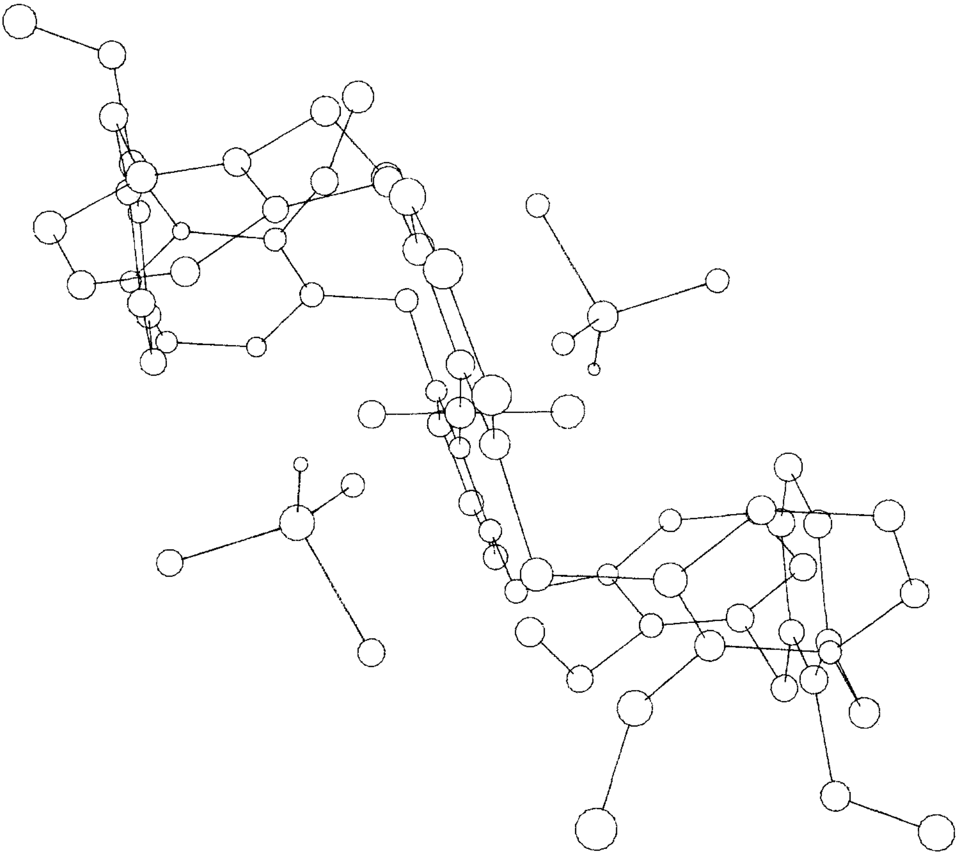


Fig. 2. Rotation of 90° from Figure 1.

in Figure 2. The views in Figures 1 and 2 are 90° to one another.

The shape of the cavity seen from the perspective of Figure 1 is rather circular. This is illustrated by a comparison of the distances between centroids of the aromatic rings related across the center of inversion: C(A)···C(A)′ = 13.9 Å, C(B)···C(B)′ = 14.5 Å, C(C)···C(C)′ = 10.1 Å, and C(D)···C(D)′ = 11.2 Å.

Another general aspect of the host is that six of the oxygen atoms are oriented towards the inside of the cavity while two are on the outside. This may be compared with a 4-in/4-out arrangement for R = octyl, R′ = CH_2CH_2OMe [21], 6-in/2-out for R = tert-butyl, R′ = COMe [19], and all-in for R = tert-butyl, R′ = H [20].

For a guest such as $CDCl_3$ and a host such as a calix[8]arene, the position of the guest is determined by the interplay of rather weak forces. Since there exists substantial torsional freedom within the calixarene [25], the cavity may be either hydrophillic or lipophillic in nature. Thus in the absence of a strong interaction between guest and host, the guest often seems to be a normal molecule of solvation and our classifications may appear as formalisms with vague borders separating one type from another.

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