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Thiocalix[4]arenes. I. Synthesis and Structure of Ethylthiocalix[4]arene Methyl Ether and the Related Structure of Bromocalix[4]arene Methyl Ether

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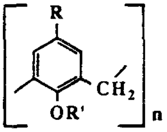
Abstract. Bromocalix[4]arene methyl ether serves as a precursor in the synthesis of the title thiocalixarene via the reagent CuSEt. Ethylthiocalix[4]arene methyl ether crystallizes in the monoclinic space group $P2_1/c$ with $a = 20.577(9)$, $b, = 10.722(5)$, $c = 20.315(9)$ Å, $\beta = 120.46(4)°$, and $D_c = 1.24$ g cm^{-3} for $Z = 4$. Refinement based on 1441 observed reflections led to $R = 0.080$. The configuration of the calixarene lies between the partial cone and the 1,3-alternate conformations. Bromocalix[4]arene methyl ether crystallizes in the triclinic space group $P\bar{1}$ with $a = 12.283(7)$, $b = 17.658(9)$, $c = 18.118(6)$ Å, $\alpha = 90.25(6)$, $\beta = 105.95(4)$, $\gamma = 105.11(6)°$, and $D_c = 1.68$ g cm^{-3} for $Z = 4$. Refinement based on 3028 observed reflections led to $R = 0.083$. The unit cell also contains four $CHCl_3$ molecules which exist pairwise enclathrated by six calixarenes. The partial cone conformation of the bromocalixarene is identical to that of ethylthiocalix[4]arene methyl ether.

Key words. Calix[4]arene, thiocalixarene, bromocalixarene, crystal structure.

Supplementary Data relating to this article are deposited with the British Library as Supplementary Publication No. SUP 82094 (34 pages).

1. Introduction

One of the most active areas of calixarene research involves the functionalization of the upper rim of the calix, R. With R = *tert*-butyl as the starting point, R = H



[1], Br [2], CN [2], CO_2R'' [3], $CH_2NR''_2$ [4], NO_2 [5], and SO_3Na [6, 7], among others have been reported. There has been one mention of R = CH_2SMe [8], but we report here the first synthesis of the thio functionality bonded directly to the aromatic ring and the corresponding crystal structure. The synthesis was effected by the use of CuSEt on the bromocalix[4]arene methyl ether.

The four known conformations of calix[4]arenes, the cone, the partial cone, the 1,2-alternate, and the 1,3-alternate, have been extensively studied [9, 10] and were recently reviewed by Gutsche [11]. The structure of the title compounds lies mid-way between the partial cone and the 1,3-alternate.

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2. Experimental

2.1. PREPARATION OF BROMOCALIX[4]ARENE METHYL ETHER, 1

To a solution of 9.17 g (19.1 mmol) calix[4]arene methyl ether [12] in 400 mL methyl ethyl ketone was added 23 g (0.13 mmol) *N*-bromosuccinimide. The yellow solution was stirred at room temperature for 24 hr. The reaction mixture was washed with 400 mL of 10% $NaHSO_4$ and water. The organic layer was dried over Na_2SO_4, filtered, and evaporated off to give 12.0 g (79%) of light yellow powder. Recrystallization from $CHCl_3$/MeOH (10 : 1) yielded 11.1 g (73%) of colorless cube-shaped crystals.

2.2. PREPARATION OF ETHYLTHIOCALIX[4]ARENE METHYL ETHER, 2

Copper(I) oxide (28.6 g, 0.20 mol), ethane thiol (24.8 g, 0.40 mol), and 500 mL diethyl ether were heated for 12 hr under a nitrogen atmosphere with refluxing and stirring. 200 mL of absolute ethanol were added 2 hr prior to completion of the reaction. The cuprous ethylmercaptide was collected by filtration, washed with methanol, and dried (50 g, 100%). Following the procedure of Adams and Ferratti for the conversion of *p*-bromomethoxybenzene to *p*-ethylthiomethoxybenzene [13], 8.75 g (0.07 mol) of cuprous ethylmercaptide was added to a solution of 8.6 g (0.10 mol) bromocalix[4]arene methyl ether in 170 mL quinoline and 10 mL pyridine. The reaction mixture was refluxed for 18 hr under a nitrogen atmosphere. The warm solution was poured into cracked ice and an excess of hydrochloric acid. After standing for an hour, the acid mixture was filtered through a sintered glass funnel, and the solid was freed as much as possible from water. The powdery solid was extracted for 2 hr in a soxhlet with chloroform as a solvent. The chloroform layer was concentrated *in vacuo* and chromatographed on silica gel (*n*-hexane : acetone 6 : 1) and then recrystallized from acetone to afford 4.0 g (47.8%) of pale yellow crystals.

2.3. X-RAY DATA COLLECTION AND STRUCTURE DETERMINATION OF 1

Single crystals were sealed in thin-walled glass capillaries. Final lattice parameters as determined from 25 high-angle reflections ($2\theta > 30°$) carefully centered on an Enraf-Nonius CAD-4 are given in Table I. Intensity data were recorded on the diffractometer in the usual manner [14]. A summary of data collection parameters is also presented in Table I.

Structure solution was complicated by the existence of two independent calixarene molecules (and two independent chloroform molecules), but was solved with effort using the direct methods program MULTAN [15]. Because of the rather poor diffracting ability of the crystal, only 3028 observed reflections out of 8018 measured were used. The paucity of data allowed refinement using anisotropic thermal parameters of only the bromine atoms. The hydrogen atoms were positioned in geometry-fixed positions for the methylene groups and the ring carbon atoms, and were not located for the methyl groups or the solvent molecules. The solvent molecules also exhibited disorder about the carbon atoms such that six chlorine sites were fitted for each chloroform molecule. These difficulties notwith-

Table I. Crystal data for **1** and **2**

	1	**2**
Compound	$C_{32}H_{28}O_4Br_4 \cdot CHCl_3$	$C_{40}H_{48}S_4O_4$
Mol. wt.	915.61	721.08
Space group	$P\bar{1}$	$P2_1/c$
a (Å)	12.283(7)	20.577(9)
b (Å)	17.658(9)	10.722(5)
c (A)	18.118(6)	20.315(9)
α (°)	90.25(6)	90
β (°)	105.95(3)	120.46(4)
γ (°)	105.11(6)	90
Cell vol. (Å^3)	3635	3863
Mol./unit cell	4	4
D_{calc} (g/cm^3)	1.68	1.24
μ (cm^{-1})	46.68	2.80
Radiation	MoK_α	MoK_α
Cryst. size (mm)	0.3 × 0.35 × 1.3	0.15 × 0.18 × 0.22
Scan width (°)	$0.75 + 0.2 \tan(\theta)$	$0.8 + 0.2 \tan(\theta)$
Std. reflections	200, 020, 002	400, 020, 00–4
Decay	<5%	<2%
2θ range (°)	2–40	4–42
Reflections measured	8018	3608
Reflections observed	3028	1441
No. parameters varied	417	433
R	0.083	0.080
R_w	0.083	0.082

standing, the structure refined to $R = 0.083$. The final values of the positional parameters are given in Table II. Tables of hydrogen atom positions, anisotropic thermal parameters, and structure factors are available as supplementary material.

2.4. X-RAY DATA COLLECTION AND STRUCTURE DETERMINATION OF 2

Crystal handling and data collection proceeded as for **1**. Lattice parameters and a summary of the structure determination are presented in Table I. The hydrogen atoms were placed in geometry-fixed positions but not refined. The non-hydrogen atoms were treated with anisotropic thermal parameters. No solvent molecules are found in the lattice. The final values of the positional parameters are given in Table III. Tables of hydrogen atom positions, anisotropic thermal parameters, and structure factors are available as supplementary material.

3. Results and Discussion

Although the partial cone conformation has been observed in the solid state [16], NMR results for various calix derivatives show occasional discrepancies which have been attributed to the presence of a 'flattened cone' [12]. For the title compounds the configuration is close to a flattened 1,3-alternate. The ^{1}H NMR spectra of both

Table II. Final fractional atomic coordinates for **1**

Atom	*x/a*	*y/b*	*z/c*	U_{eq}
Br(1)	0.8832(4)	−0.2267(2)	0.9333(2)	0.088
Br(2)	0.3338(3)	0.0121(2)	0.5637(2)	0.081
Br(3)	0.1113(4)	0.0173(2)	0.9227(2)	0.102
Br(4)	0.1176(4)	0.2216(3)	0.5543(2)	0.107
Br(5)	0.3612(4)	0.4914(2)	0.0820(2)	0.095
Br(6)	0.8117(3)	0.7506(3)	0.4138(3)	0.102
Br(7)	0.3059(4)	0.7191(2)	0.0517(2)	0.084
Br(8)	−0.1475(4)	0.5066(2)	0.4222(2)	0.116
O(1)	0.552(2)	−0.181(1)	0.634(1)	0.069
O(2)	0.727(2)	0.013(1)	0.848(1)	0.061
O(3)	0.478(2)	−0.1166(9)	0.8555(9)	0.047
O(4)	0.429(2)	−0.311(1)	0.840(1)	0.070
O(5)	0.189(2)	0.422(1)	0.360(1)	0.073
O(6)	0.291(2)	0.6150(9)	0.3643(9)	0.046
O(7)	0.121(2)	0.734(1)	0.324(1)	0.075
O(8)	−0.005(2)	0.520(1)	0.128(1)	0.083
C(1)A	0.629(3)	−0.190(2)	0.704(2)	0.067
C(2)A	0.601(3)	−0.262(2)	0.736(2)	0.053
C(3)A	0.673(3)	−0.273(2)	0.805(2)	0.064
C(4)A	0.778(3)	−0.211(2)	0.839(2)	0.060
C(5)A	0.799(3)	−0.139(2)	0.807(2)	0.062
C(6)A	0.725(3)	−0.129(2)	0.740(2)	0.052
C(7)A	0.742(3)	−0.049(2)	0.706(2)	0.067
C(8)A	0.579(3)	−0.199(2)	0.565(2)	0.072
C(1)B	0.639(3)	0.013(2)	0.784(1)	0.048
C(2)B	0.645(2)	−0.012(2)	0.710(1)	0.048
C(3)B	0.552(2)	−0.009(1)	0.647(2)	0.051
C(4)B	0.459(3)	0.014(2)	0.654(1)	0.053
C(5)B	0.449(2)	0.034(1)	0.726(1)	0.044
C(6)B	0.541(3)	0.034(2)	0.791(2)	0.054
C(7)B	0.528(2)	0.050(2)	0.871(1)	0.052
C(8)B	0.818(3)	0.086(2)	0.875(2)	0.072
C(1)C	0.392(3)	−0.088(2)	0.873(1)	0.045
C(2)C	0.415(3)	−0.003(2)	0.879(2)	0.058
C(3)C	0.328(2)	0.026(2)	0.895(1)	0.051
C(4)C	0.229(3)	−0.024(2)	0.902(2)	0.065
C(5)C	0.202(3)	−0.108(2)	0.893(1)	0.053
C(6)C	0.290(2)	−0.136(1)	0.875(1)	0.042
C(7)C	0.265(3)	−0.226(2)	0.860(1)	0.063
C(8)C	0.569(3)	−0.130(2)	0.921(2)	0.057
C(1)D	0.358(2)	−0.286(1)	0.774(1)	0.044
C(2)D	0.276(2)	−0.248(1)	0.783(1)	0.040
C(3)D	0.205(2)	−0.229(1)	0.715(1)	0.047
C(4)D	0.222(3)	−0.243(2)	0.645(2)	0.057
C(5)D	0.310(3)	−0.278(2)	0.640(2)	0.054
C(6)D	0.377(2)	−0.300(2)	0.705(1)	0.049
C(7)D	0.484(2)	−0.325(2)	0.702(2)	0.058
C(8)D	0.373(3)	−0.391(2)	0.859(2)	0.085
C(1)E	0.221(3)	0.436(2)	0.295(2)	0.054
C(2)E	0.152(3)	0.421(2)	0.222(2)	0.058
C(3)E	0.188(3)	0.437(2)	0.160(2)	0.056
C(4)E	0.322(3)	0.474(2)	0.173(2)	0.055

Table II. (continued)

Atom	*x/a*	*y/b*	*z/c*	U_{eq}
C(5)E	0.378(3)	0.491(2)	0.243(2)	0.059
C(6)E	0.347(2)	0.476(2)	0.306(1)	0.049
C(7)E	0.429(3)	0.506(2)	0.386(2)	0.073
C(8)E	0.196(3)	0.345(2)	0.392(2)	0.101
C(1)F	0.410(2)	0.643(1)	0.378(1)	0.039
C(2)F	0.486(3)	0.596(2)	0.391(1)	0.053
C(3)F	0.606(3)	0.629(2)	0.402(1)	0.056
C(4)F	0.651(3)	0.706(2)	0.400(2)	0.069
C(5)F	0.577(3)	0.753(2)	0.385(1)	0.062
C(6)F	0.454(3)	0.726(2)	0.372(1)	0.050
C(7)F	0.369(3)	0.777(2)	0.351(2)	0.063
C(8)F	0.252(3)	0.609(2)	0.433(2)	0.062
C(1)G	0.160(3)	0.730(2)	0.259(2)	0.051
C(2)G	0.290(2)	0.753(1)	0.274(1)	0.045
C(3)G	0.323(2)	0.745(1)	0.209(1)	0.035
C(4)G	0.265(3)	0.722(2)	0.142(2)	0.058
C(5)G	0.131(2)	0.694(1)	0.127(2)	0.050
C(6)G	0.088(3)	0.695(2)	0.191(2)	0.048
C(7)G	−0.040(3)	0.660(2)	0.185(2)	0.072
C(8)G	0.108(3)	0.813(2)	0.340(2)	0.083
C(1)H	−0.030(3)	0.518(2)	0.200(2)	0.070
C(2)H	−0.061(3)	0.585(2)	0.225(2)	0.063
C(3)H	−0.091(3)	0.582(2)	0.294(2)	0.071
C(4)H	−0.104(3)	0.511(2)	0.332(2)	0.086
C(5)H	−0.061(2)	0.450(2)	0.307(2)	0.058
C(6)H	−0.033(2)	0.449(2)	0.240(1)	0.051
C(7)H	0.020(2)	0.391(2)	0.214(2)	0.060
C(8)H	−0.111(3)	0.490(2)	0.064(2)	0.102

bromo- and ethylthiocalixarene display a very complicated pattern which affords the interpretation of a rather rigid structure in solution, presumably the one found in the solid state.

One of the two independent molecules of the bromocalix[4]arene (**1**) is shown in Figure 1 and bond lengths and angles are given in Table IV. The ‘flattened’ aromatic can act as a shelf for a guest, which would be held by interaction from the ‘B’ and ‘D’ rings and O(1). With the correct choice of substituents, it should be possible to construct a molecule of this geometry which has the ability to firmly hold a substrate such that a specific area can be exposed for further reaction.

This is demonstrated in Figure 2 for one of the chloroform molecules contained within the lattice. The major interactions holding the guest in position are Cl ··· Cπ, Br ··· Cl and H ··· O, none of which are particularly strong (3.65, 3.72 and 2.60 Å, respectively) but together combine to produce an interesting form of guest complexation.

The packing in the unit cell is shown in Figure 3. The dominant feature is the manner in which each chloroform molecule is surrounded by a second chloroform and six calixarenes in the manner of a typical hexagonal clathrate [17]. The major interactions involved in the formation of this arrangement are between both the

Table III. Final fractional atomic coordinates for **2**

Atom	*x*/*a*	*y*/*b*	*z*/*c*
S(1)	0.1577(2)	0.0366(4)	0.2371(3)
S(2)	0.0770(3)	−0.6851(5)	0.4919(3)
S(3)	0.3574(3)	−0.3556(6)	0.2377(3)
S(4)	0.5215(3)	0.0585(6)	0.6036(3)
O(1)	0.1213(6)	−0.227(1)	0.4725(7)
O(2)	0.1095(6)	−0.410(1)	0.2596(8)
O(3)	0.3049(6)	−0.593(1)	0.4690(7)
O(4)	0.2837(6)	−0.327(1)	0.5028(6)
C(1)A	0.133(1)	−0.166(2)	0.419(1)
C(2)A	0.1944(8)	−0.083(2)	0.438(1)
C(3)A	0.1991(9)	−0.027(2)	0.380(1)
C(4)A	0.146(1)	−0.050(1)	0.3050(9)
C(5)A	0.0887(8)	−0.137(2)	0.289(1)
C(6)A	0.082(1)	−0.194(2)	0.345(1)
C(7)A	0.0237(9)	−0.300(2)	0.3187(9)
C(8)A	0.078(1)	−0.157(2)	0.495(1)
C(9)A	0.1440(9)	−0.080(2)	0.1703(9)
C(10)A	0.197(1)	−0.184(2)	0.198(1)
C(1)B	0.104(1)	−0.475(3)	0.315(1)
C(2)B	0.060(1)	−0.427(2)	0.345(2)
C(3)B	0.0561(9)	−0.491(3)	0.399(1)
C(4)B	0.091(1)	−0.608(3)	0.4226(8)
C(5)B	0.134(1)	−0.651(2)	0.394(1)
C(6)B	0.142(1)	−0.587(3)	0.342(1)
C(7)B	0.1944(9)	−0.633(2)	0.315(1)
C(8)B	0.055(1)	−0.437(2)	0.184(1)
C(9)B	0.147(1)	−0.782(2)	0.551(2)
C(10)B	0.219(1)	−0.740(2)	0.602(2)
C(1)C	0.315(1)	−0.531(2)	0.415(1)
C(2)C	0.2631(9)	−0.549(2)	0.338(1)
C(3)C	0.278(1)	−0.493(2)	0.285(1)
C(4)C	0.340(1)	−0.417(2)	0.309(1)
C(5)C	0.386(1)	−0.393(2)	0.385(1)
C(6)C	0.373(1)	−0.448(2)	0.440(1)
C(7)C	0.4232(8)	−0.409(2)	0.5239(9)
C(8)C	0.348(1)	−0.708(2)	0.496(1)
C(9)C	0.4469(9)	−0.410(2)	0.264(1)
C(10)C	0.453(1)	−0.547(2)	0.267(1)
C(1)D	0.342(1)	−0.244(2)	0.5285(8)
C(2)D	0.412(1)	−0.275(2)	0.5377(8)
C(3)D	0.4676(9)	−0.187(2)	0.5629(8)
C(4)D	0.456(1)	−0.065(2)	0.5724(8)
C(5)D	0.386(1)	−0.033(2)	0.5636(9)
C(6)D	0.328(1)	−0.115(2)	0.5378(8)
C(7)D	0.2514(9)	−0.073(1)	0.5227(8)
C(8)D	0.2772(9)	−0.385(2)	0.563(1)
C(9)D	0.603(1)	−0.016(2)	0.636(1)
C(10)D	0.631(1)	−0.081(2)	0.711(1)

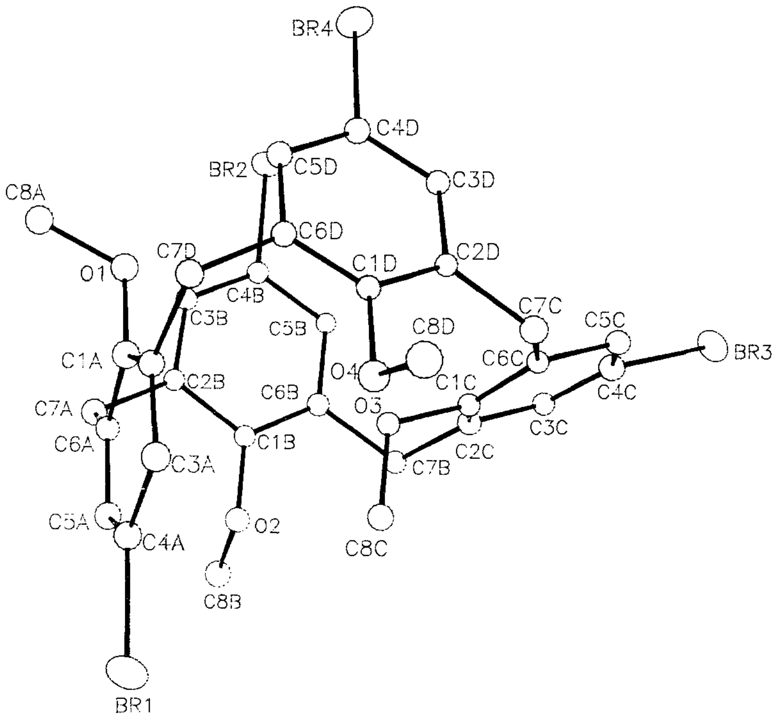

Fig. 1. Atomic numbering scheme for one of the independent molecules of **1**.

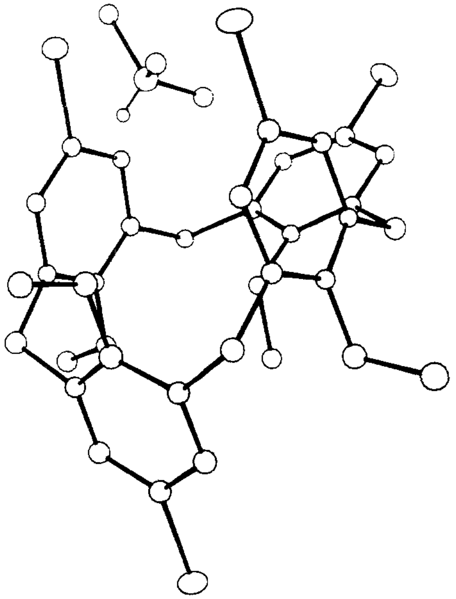

Fig. 2. View of compound **1** including the chloroform guest.

Table IV. Bond lengths (Å) and angles (°) for 1

Atoms	Distance	Atoms	Distance
Br(1)—C(4)A	1.91(3)	Br(2)—C(4)B	1.90(3)
Br(3)—C(4)C	1.94(4)	Br(4)—C(4)D	1.90(3)
Br(5)—C(4)E	1.85(3)	Br(6)—C(4)F	1.87(3)
Br(7)—C(4)G	1.84(3)	Br(8)—C(4)H	1.85(4)
O(1)—C(1)A	1.39(3)	O(1)—C(8)A	1.45(4)
O(2)—C(1)B	1.35(3)	O(2)—C(8)B	1.46(3)
O(3)—C(1)C	1.39(4)	O(3)—C(8)C	1.45(3)
O(4)—C(1)D	1.42(3)	O(4)—C(8)D	1.49(4)
O(5)—C(1)E	1.35(4)	O(5)—C(8)E	1.49(4)
O(6)—C(1)F	1.37(3)	O(6)—C(8)F	1.44(4)
O(7)—C(1)G	1.41(4)	O(7)—C(8)G	1.49(4)
O(8)—C(1)H	1.41(4)	O(8)—C(8)H	1.46(4)
C(1)A—C(2)A	1.40(4)	C(1)B—C(2)B	1.44(4)
C(1)C—C(2)C	1.45(4)	C(1)D—C(2)D	1.39(5)
C(1)E—C(2)E	1.34(4)	C(1)F—C(2)F	1.37(5)
C(1)G—C(2)G	1.48(4)	C(1)H—C(2)H	1.43(5)
C(1)A—C(6)A	1.38(4)	C(1)B—C(6)B	1.38(5)
C(1)C—C(6)C	1.33(4)	C(1)D—C(6)D	1.36(4)
C(1)E—C(6)E	1.48(4)	C(1)F—C(6)F	1.45(4)
C(1)G—C(6)G	1.33(3)	C(1)H—C(2)H	1.42(4)
C(2)A—C(3)A	1.36(4)	C(2)B—C(3)B	1.39(4)
C(2)C—C(3)C	1.39(5)	C(2)D—C(3)D	1.39(3)
C(2)E—C(3)E	1.32(5)	C(2)F—C(3)F	1.39(4)
C(2)G—C(3)G	1.37(4)	C(2)H—C(3)H	1.39(5)
C(2)A—C(7)D	1.54(3)	C(2)B—C(7)A	1.52(5)
C(2)C—C(7)B	1.50(4)	C(2)D—C(7)C	1.51(4)
C(2)E—C(7)H	1.54(4)	C(2)F—C(7)E	1.56(4)
C(2)G—C(7)F	1.45(3)	C(2)H—C(7)G	1.52(4)
C(3)A—C(4)A	1.44(4)	C(3)B—C(4)B	1.34(5)
C(3)C—C(4)C	1.35(3)	C(3)D—C(4)D	1.37(4)
C(3)E—C(4)E	1.54(4)	C(3)F—C(4)F	1.33(4)
C(3)G—C(4)G	1.24(3)	C(3)H—C(4)H	1.42(5)
C(4)A—C(5)A	1.39(4)	C(4)B—C(5)B	1.40(4)
C(4)C—C(5)C	1.42(4)	C(4)D—C(5)D	1.40(5)
C(4)E—C(5)E	1.26(4)	C(4)F—C(5)F	1.35(5)
C(4)G—C(5)G	1.53(4)	C(4)H—C(5)H	1.44(5)
C(5)A—C(6)A	1.35(4)	C(5)B—C(6)B	1.38(4)
C(5)C—C(6)C	1.41(5)	C(5)D—C(6)D	1.36(4)
C(5)E—C(6)E	1.31(4)	C(5)F—C(6)F	1.42(4)
C(5)G—C(6)G	1.39(4)	C(5)H—C(6)H	1.35(4)
C(6)A—C(7)A	1.52(4)	C(6)B—C(7)B	1.54(4)
C(6)C—C(7)C	1.55(4)	C(6)D—C(7)D	1.51(5)
C(6)E—C(7)E	1.52(3)	C(6)F—C(7)F	1.52(5)
C(6)G—C(7)G	1.51(4)	C(6)H—C(7)H	1.49(5)

Atoms	Angle	Atoms	Angle
C(1)A—O(1)—C(8)A	118(3)	C(1)B—O(2)—C(8)B	117(2)
C(1)C—O(3)—C(8)C	116(2)	C(1)D—O(4)—C(8)D	113(2)
C(1)E—O(5)—C(8)E	117(3)	C(1)F—O(6)—C(8)F	114(2)
C(1)G—O(7)—C(8)G	112(2)	C(1)H—O(8)—C(8)H	112(3)
O(1)—C(1)A—C(2)A	117(2)	O(2)—C(1)B—C(2)B	119(3)
O(3)—C(1)C—C(2)C	116(2)	O(4)—C(1)D—C(2)D	119(2)
O(5)—C(1)E—C(2)E	128(3)	O(6)—C(1)F—C(2)F	125(2)
O(7)—C(1)G—C(2)G	114(2)	O(8)—C(1)H—C(2)H	117(3)

Table IV (continued)

Atoms	Angle	Atoms	Angle
O(1)—C(1)A—C(6)A	120(3)	C(2)A—C(1)A—C(6)A	123(3)
O(2)—C(1)B—C(6)B	121(3)	C(2)B—C(1)B—C(6)B	120(2)
O(3)—C(1)C—C(6)C	121(2)	C(2)C—C(1)C—C(6)C	122(3)
O(4)—C(1)D—C(6)D	117(3)	C(2)D—C(1)D—C(6)D	124(2)
O(5)—C(1)E—C(6)E	115(2)	C(2)E—C(1)E—C(6)E	116(3)
O(6)—C(1)F—C(6)F	116(3)	C(2)F—C(1)F—C(6)F	119(3)
O(7)—C(1)G—C(6)G	123(3)	C(2)G—C(1)G—C(6)G	122(3)
O(8)—C(1)H—C(6)H	119(3)	C(2)H—C(1)H—C(6)H	123(3)
C(1)A—C(2)A—C(3)A	119(2)	C(1)B—C(2)B—C(3)B	116(3)
C(1)C—C(2)C—C(3)C	116(3)	C(1)D—C(2)D—C(3)D	116(3)
C(1)E—C(2)E—C(3)E	126(3)	C(1)F—C(2)F—C(3)F	121(3)
C(1)G—C(2)G—C(3)G	112(2)	C(1)H—C(2)H—C(3)H	117(3)
C(1)A—C(2)A—C(7)D	122(2)	C(3)A—C(2)A—C(7)D	119(2)
C(1)B—C(2)B—C(7)A	119(2)	C(3)B—C(2)B—C(7)A	124(3)
C(1)C—C(2)C—C(7)B	121(3)	C(3)C—C(2)C—C(7)B	123(3)
C(1)D—C(2)D—C(7)C	123(2)	C(3)D—C(2)D—C(7)C	120(3)
C(1)E—C(2)E—C(7)H	114(3)	C(3)E—C(2)E—C(7)H	120(2)
C(1)F—C(2)F—C(7)E	116(3)	C(3)F—C(2)F—C(7)E	123(3)
C(1)G—C(2)G—C(7)F	122(3)	C(3)G—C(2)G—C(7)F	126(3)
C(1)H—C(2)H—C(7)G	120(3)	C(3)H—C(2)H—C(7)G	122(3)
C(2)A—C(3)A—C(4)A	118(3)	C(2)B—C(3)B—C(4)B	123(3)
C(2)C—C(3)C—C(4)C	120(3)	C(2)D—C(3)D—C(4)D	121(3)
C(2)E—C(3)E—C(4)E	117(2)	C(2)F—C(3)F—C(4)F	122(3)
C(2)G—C(3)G—C(4)G	132(3)	C(2)H—C(3)H—C(4)H	120(3)
Br(1)—C(4)A—C(3)A	118(2)	Br(2)—C(4)B—C(3)B	119(2)
Br(3)—C(4)C—C(3)C	119(2)	Br(4)—C(4)D—C(3)D	119(2)
Br(5)—C(4)E—C(3)E	113(2)	Br(6)—C(4)F—C(3)F	122(3)
Br(7)—C(4)G—C(3)G	133(3)	Br(8)—C(4)H—C(3)H	120(3)
Br(1)—C(4)A—C(5)A	120(2)	C(3)A—C(4)A—C(5)A	121(3)
Br(2)—C(4)B—C(5)B	120(2)	C(3)B—C(4)B—C(5)B	121(2)
Br(3)—C(4)C—C(5)C	116(2)	C(3)C—C(4)C—C(5)C	125(3)
Br(4)—C(4)D—C(5)D	120(2)	C(3)D—C(4)D—C(5)D	121(3)
Br(5)—C(4)E—C(5)E	133(3)	C(3)E—C(4)E—C(5)E	114(3)
Br(6)—C(4)F—C(5)F	119(2)	C(3)F—C(4)F—C(5)F	118(3)
Br(7)—C(4)G—C(5)G	112(2)	C(3)G—C(4)G—C(5)G	116(3)
Br(8)—C(4)H—C(5)H	121(2)	C(3)H—C(4)H—C(5)H	118(3)
C(4)A—C(5)A—C(6)A	120(2)	C(4)B—C(5)B—C(6)B	118(3)
C(4)C—C(5)C—C(6)C	114(3)	C(4)D—C(5)D—C(6)D	119(3)
C(4)E—C(5)E—C(6)E	131(3)	C(4)F—C(5)F—C(6)F	125(3)
C(4)G—C(5)G—C(6)G	117(2)	C(4)H—C(5)H—C(6)H	122(3)
C(1)A—C(6)A—C(5)A	119(3)	C(1)B—C(6)B—C(5)B	121(3)
C(1)C—C(6)C—C(5)C	122(3)	C(1)D—C(6)D—C(5)D	119(3)
C(1)E—C(6)E—C(5)E	116(2)	C(1)F—C(6)F—C(5)F	114(3)
C(1)G—C(6)G—C(5)G	120(3)	C(1)H—C(6)H—C(5)H	117(3)
C(1)A—C(6)A—C(7)A	120(2)	C(5)A—C(6)A—C(7)A	121(2)
C(1)B—C(6)B—C(7)B	119(2)	C(5)B—C(6)B—C(7)B	119(3)
C(1)C—C(6)C—C(7)C	121(3)	C(5)C—C(6)C—C(7)C	117(2)
C(1)D—C(6)D—C(7)D	121(2)	C(5)D—C(6)D—C(7)D	120(3)
C(1)E—C(6)E—C(7)E	121(3)	C(5)E—C(6)E—C(7)E	123(3)
C(1)F—C(6)F—C(7)F	120(2)	C(5)F—C(6)F—C(7)F	126(2)
C(1)G—C(6)G—C(7)G	118(3)	C(5)G—C(6)G—C(7)G	122(2)
C(1)H—C(6)H—C(7)H	116(3)	C(5)H—C(6)H—C(7)H	125(3)
C(2)B—C(7)A—C(6)A	111(3)	C(2)C—C(7)B—C(6)B	110(2)
C(2)D—C(7)C—C(6)C	112(2)	C(2)A—C(7)D—C(6)D	114(2)
C(2)F—C(7)E—C(6)E	111(2)	C(2)G—C(7)F—C(6)F	111(2)
C(2)H—C(7)G—C(6)G	112(3)	C(2)E—C(7)H—C(6)H	115(2)

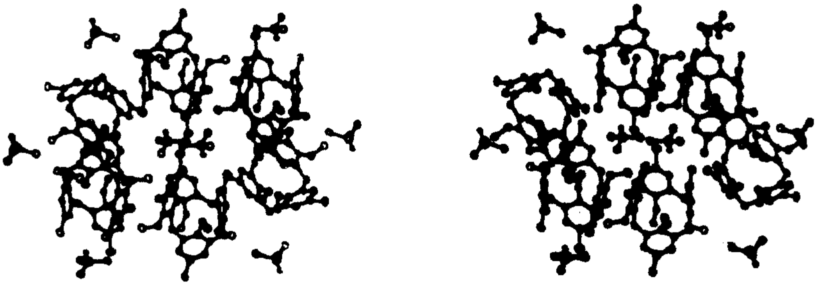

Fig. 3. A stereoview of the crystal packing of **1**.

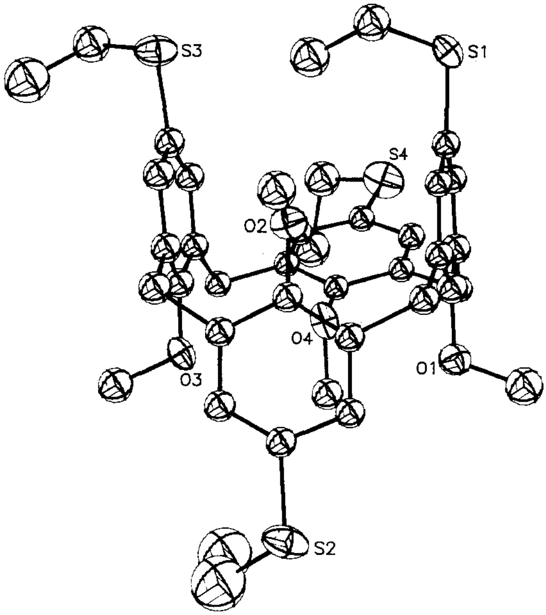

Fig. 4. A view of compound **2**.

calixarene and chloroform (primarily Cl···Cπ, the shortest of which is 3.33 Å) and calix and calix ($C_{sp^3}\cdots C\pi$, the shortest of which is 3.36 Å, and $Br\cdots C_{sp^3}$, which range from 3.54 to 3.80 Å). The shortest contact between solvent molecules, which is found at the center of the calixarene aggregate, is 3.69 Å.

The structure of the thiocalix[4]arene (**2**) is given in Figure 4 and bond lengths and angles in Table V. There is little difference in the overall calixarene geometry – a feature which is to be expected as it is the functionality at the phenolic oxygen which determines the calixarene conformation. Indeed, a comparison of the structure found in the bromo- and thiocalix[4]arenes (in which R′ = Me) with the partial cone found for R = —$OCOCH_3$ reveals that the 'flattened' aromatic is more so in the former than the latter (the angle between the plane of the methylene carbons and the aromatic plane is 25° for R′ = Me (in **1** and in **2**), compared to 39.3° for

Table V. Bond lengths (Å) and angles (°) for **2**

Atoms	Distance	Atoms	Distance
S(1)—C(4)A	1.77(2)	S(1)—C(9)A	1.76(2)
S(2)—C(4)B	1.77(3)	S(2)—C(9)B	1.69(2)
S(3)—C(4)C	1.79(3)	S(3)—C(9)C	1.73(2)
S(4)—C(4)D	1.76(2)	S(4)—C(9)D	1.66(2)
O(1)—C(1)A	1.39(3)	O(1)—C(8)A	1.39(3)
O(2)—C(1)B	1.38(3)	O(2)—C(8)B	1.39(2)
O(3)—C(1)C	1.38(3)	O(3)—C(8)C	1.46(2)
O(4)—C(1)D	1.37(3)	O(4)—C(8)D	1.43(3)
C(1)A—C(2)A	1.44(3)	C(1)B—C(2)B	1.41(4)
C(1)C—C(2)C	1.38(3)	C(1)D—C(2)D	1.40(4)
C(1)A—C(6)A	1.36(3)	C(1)B—C(6)B	1.38(4)
C(1)C—C(6)C	1.37(3)	C(1)D—C(6)D	1.45(3)
C(2)A—C(3)A	1.36(3)	C(2)B—C(3)B	1.34(4)
C(2)C—C(3)C	1.40(4)	C(2)D—C(3)D	1.36(3)
C(2)A—C(7)D	1.52(2)	C(2)B—C(7)A	1.51(3)
C(2)C—C(7)B	1.53(2)	C(2)D—C(7)C	1.50(3)
C(3)A—C(4)A	1.38(2)	C(3)B—C(4)B	1.40(4)
C(3)C—C(4)C	1.38(3)	C(3)D—C(4)D	1.37(3)
C(4)A—C(5)A	1.41(2)	C(4)B—C(5)B	1.37(4)
C(5)C—C(5)C	1.36(3)	C(4)D—C(5)D	1.40(4)
C(5)A—C(6)A	1.36(4)	C(5)D—C(6)B	1.33(4)
C(5)C—C(6)C	1.40(4)	C(5)D—C(6)D	1.35(3)
C(6)A—C(7)A	1.54(3)	C(6)B—C(7)B	1.53(4)
C(6)C—C(7)C	1.55(2)	C(6)D—C(7)D	1.51(3)
C(9)A—C(10)A	1.46(2)	C(9)B—C(10)B	1.38(3)
C(9)C—C(10)C	1.48(3)	C(9)D—C(10)D	1.50(3)

Atoms	Angle	Atoms	Angle
C(4)A—S(1)—C(9)A	101.2(9)	C(4)B—S(2)—C(9)B	115(1)
C(4)C—S(3)—C(9)C	104(1)	C(4)D—S(4)—C(9)D	103(1)
C(1)A—O(1)—C(8)A	113(2)	C(1)B—O(2)—C(8)B	116(2)
C(1)C—O(3)—C(8)C	113(2)	C(1)D—O(4)—C(8)D	114(1)
O(1)—C(1)A—C(2)A	124(2)	O(2)—C(1)B—C(2)B	120(2)
O(3)—C(1)C—C(2)C	120(2)	O(4)—C(1)D—C(2)D	123(2)
O(1)—C(1)A—C(6)A	115(2)	C(2)A—C(1)A—C(6)A	120(2)
O(2)—C(1)B—C(6)B	120(3)	C(2)B—C(1)B—C(6)B	120(3)
O(3)—C(1)C—C(6)C	118(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	118(2)
C(1)A—C(2)A—C(3)A	119(2)	C(1)B—C(2)B—C(3)B	119(2)
C(1)C—C(2)C—C(3)C	118(2)	C(1)D—C(2)D—C(3)D	120(2)
C(1)A—C(2)A—C(7)D	114(2)	C(3)A—C(2)A—C(7)D	127(2)
C(1)B—C(2)B—C(7)A	119(2)	C(3)B—C(2)B—C(7)A	121(3)
C(1)C—C(2)C—C(7)B	119(2)	C(3)C—C(2)C—C(7)B	123(2)
C(1)D—C(2)D—C(7)C	116(2)	C(3)D—C(2)D—C(7)C	124(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	120(2)	C(2)D—C(3)D—C(4)D	123(2)
S(1)—C(4)A—C(3)A	115(1)	S(2)—C(4)B—C(3)B	116(2)
S(3)—C(4)C—C(3)C	117(2)	S(4)—C(4)D—C(3)D	128(2)
S(1)—C(4)A—C(5)A	126(1)	C(3)A—C(4)A—C(5)A	119(2)
S(2)—C(4)B—C(5)B	125(2)	C(3)B—C(4)B—C(5)B	119(2)
S(3)—C(4)C—C(5)C	123(2)	C(3)C—C(4)C—C(5)C	120(3)

Table V. (continued)

Atoms	Angle	Atoms	Angle
S(4)—C(4)D—C(5)D	115(2)	C(3)D—C(4)D—C(5)D	117(2)
C(4)A—C(5)A—C(6)A	122(2)	C(4)B—C(5)B—C(6)B	121(2)
C(4)C—C(5)C—C(6)C	121(2)	C(4)D—C(5)D—C(6)D	123(2)
C(1)A—C(6)A—C(5)A	119(2)	C(1)B—C(6)B—C(5)B	120(3)
C(1)C—C(6)C—C(5)C	118(2)	C(1)D—C(6)D—C(5)D	118(2)
C(1)A—C(6)A—C(7)A	125(2)	C(5)A—C(6)A—C(7)A	116(2)
C(1)B—C(6)B—C(7)B	120(2)	C(5)B—C(6)B—C(7)B	120(2)
C(1)C—C(6)C—C(7)C	124(2)	C(5)C—C(6)C—C(7)C	118(2)
C(1)D—C(6)D—C(7)D	121(2)	C(5)D—C(6)D—C(7)D	121(2)
C(2)B—C(7)A—C(6)A	112(1)	C(2)C—C(7)B—C(6)B	114(2)
C(2)D—C(7)C—C(6)C	113(1)	C(2)A—C(7)D—C(6)D	110(2)
S(1)—C(9)A—C(10)A	117(1)	S(2)—C(9)B—C(10)B	122(2)
S(3)—C(9)C—C(10)C	113(2)	S(4)—C(9)D—C(10)D	114(2)

R′ = —OCOCH$_3$ [16]). The chloroform molecule which is 'held' on the 'shelf' for the bromo derivative is replaced in the thiocalix[4]arene by an ethyl group from a phenolic residue adjacent to the 'flattened' aromatic, producing a form of intramolecular inclusion. In the thiocalixarene the packing is typical for an organic molecule.

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