



# Crystal Structure of a Calix[4]crown Ether-Ester and Molecular Recognition of Alkyl- and Arylalkylamines

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**Abstract.** The crystal and molecular structure of **3** has been determined by X-ray analysis. The crystal data are: triclinic, space group  $P\bar{1}$ ,  $a = 12.999(2)$ ,  $b = 14.114(3)$ ,  $c = 16.132(3)$  Å,  $\alpha = 91.62(2)$ ,  $\beta = 97.71(1)$ ,  $\gamma = 91.38(2)^\circ$ ,  $V = 2930.6(9)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_m = 1.046$  g cm<sup>-3</sup>. Rotational disorder has been seen in the *t*-butyl groups which were refined isotropically. Least-squares refinement based on  $F^2$ , using 4827 observed reflections with  $I > 2\sigma(I)$  and 18 restraints, led to  $R = 0.123$ . The calix is found in a cone conformation. The crown ether part of the molecule is not in a fully extended conformation but has folds in the chain. The calix[4]crown ether-ester exhibits molecular recognition properties toward alkylamines.

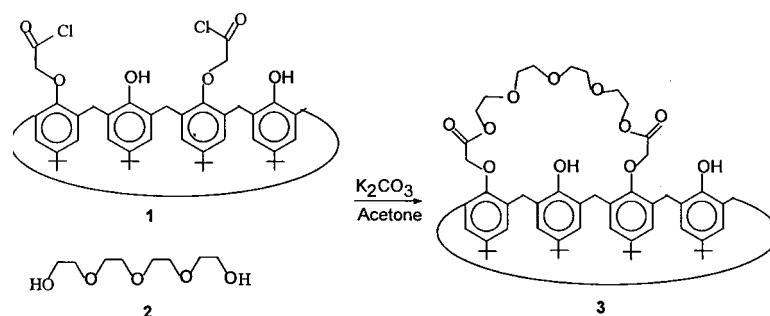
**Key words:** calix[4]arene, calixcrown, ether ester, crystal structure.

## 1. Introduction

Calixarenes, which structurally resemble spherands and natural cyclodextrins, have received much attention over the past decade [1]. These are useful building blocks for preorganized lipophilic or water soluble cation receptors and carriers [2]. In particular *p*-tert-butylcalix[4]arene which is easily accessible in large quantities is a popular building block [3] or platform for assembling more elaborate structures with ligating side arms or podands. The introduction of substituents on the phenolic OH groups of *p*-tert-butylcalix[4]arene produces derivatives with different shapes and conformational mobilities depending upon the nature and number of these substituents. Several tetra and disubstituted calix[4]arenes have been synthesized, some of which are now well established as selective receptors for metal cations [4–7]. There are examples in which two calixarenes are joined by a single bridge [8], the singly bridged calixcrowns [poly(oxyethylene)bridge] [9–11], calixspherands(*m*-teranisyl bridge) [12], and double and triple calixarenes with metallocene (ferrocene) bridges [13]. Use of various conformationally constrained spacers such as phthaloyl dichloride or biphenyl-4,4'-disulfonyl dichloride led to

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the formation of 1,2 bridged single calixarenes and bridged triple calixarenes [14, 15]. In all these examples the parent *p*-tert-butylcalix[4]arene was reacted with an activated bifunctional reagent such as a diacid dichloride, an oligoethylene glycol ditosyl ester or a bisbromomethylated teranisyl system. Calixarenes with diamide bridges spanning the 1,3-(distal) positions on the lower rim have been synthesized from the syn 1,3 diacid dichloride of *p*-tert-butylcalix[4]arene and various bifunctional amines [16]. Interestingly calixarenes with diester bridges spanning the 1,3 distal positions on the lower rim have not been synthesized either from the parent *p*-tert-butylcalix[4]arene or from the syn 1,3 diacid dichloride of *p*-tert-butylcalix[4]arene. In the present manuscript we have used the easily available syn 1,3-diacid dichloride of *p*-tert-butylcalix[4]arene and combined it with tetraethylene glycol to give a calixcrown ether ester (Scheme 1) in moderate yields (30%). A preliminary investigation of the complexing behaviour of this calix crown ether-ester towards biologically important guests such as biogenic amines is also reported. The ester moieties are known to decrease the complexing ability of the ligand but increases the decomplexation property of their complexes – a combination of both these phenomena is one of the factors responsible for the selective ionophore character of naturally occurring nactins which possess ester moieties. While this work was in progress the synthesis of this compound was reported by Zheng *et al.* [17].



Scheme 1.

## 2. Experimental

### 2.1. GENERAL

$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were obtained using a Bruker Acc 200 MHz spectrometer using TMS as an internal standard and  $\text{CDCl}_3$  as solvent. Equimolar amounts of the host and the guest were mixed together in  $\text{CDCl}_3$  for carrying out complexation studies. FAB mass spectra were recorded on a JEOL S X 102/DA-6000 mass spectrometer using xenon (6 KV, 10 mA) as the FAB gas. The Syn 1,3-diacidchloride of *p*-tert-butylcalix[4]arene was prepared by the reported method [18]. Alkylammonium picrates were prepared by the neutralization

reaction of the appropriate amine with picric acid in methanol and purified by recrystallization from methanol [19].

## 2.2. SYNTHESIS OF COMPOUND **3**

A solution of compound **1** (2 g, 2.5 mmol) in dry dichloromethane (50 mL) and a solution of the diol **2** (0.486 g, 2.5 mmol) in dry dichloromethane (50 mL) were added simultaneously via a dropping funnel to a stirred solution of triethylamine (5 mmol) in dry dichloromethane (200 mL) at room temperature. The addition time was approximately 2 hr. When the addition was completed the solution was filtered and the solvent was removed by distillation. The solid residue was purified by flash chromatography over silica and subsequent recrystallization from hexane. The single crystals for X-ray were grown by slow evaporation of a solution of the compound in hexane. Yield 30%. m.p. 151–152°C (Hexane). Mass spectrum (FAB, NBA):  $m/z$  922( $M^+$ ).  $\nu_{\max}$ . (KBr)/ $\text{cm}^{-1}$  1750 (ester).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  7.16 (s, 2H, ArOH), 7.01 (s, 4H, ArH), 6.83 (s, 4H, ArH), 4.76 (s, 4H,  $\text{OCH}_2\text{CO}$ ), 4.39–4.46 (m, 8H,  $\text{ArCH}_2\text{Ar}$ ,  $\text{OCH}_2$ ), 3.87 (t, 4H,  $J = 6.0$ , Hz,  $\text{OCH}_2$ ), 3.72 (t, 4H,  $J = 6.0$ , Hz,  $\text{OCH}_2$ ), 3.66 (t, 4H,  $J = 5.4$  Hz,  $\text{OCH}_2$ ), 3.33 (d, 4H,  $J = 13.2$  Hz,  $\text{ArCH}_2\text{Ar}$ ), 1.25 [s, 18H,  $\text{C}(\text{CH}_3)_3$ ], 1.00 [s, 18H,  $\text{C}(\text{CH}_3)_3$ ],  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  169.18(CO), 150.55 (ArC), 150.11 (ArC), 147.23 (ArC), 141.57 (ArC), 132.59 (ArC), 127.99 (ArC), 125.78 (ArC), 125.06 (ArC), 72.39 ( $\text{PhOCH}_2$ ), 70.99 ( $\text{OCH}_2$ ), 66.85 ( $\text{OCH}_2$ ), 64.74 ( $\text{OCH}_2$ ), 33.93 [ $\text{C}(\text{CH}_3)_3$ ], 33.78 ( $\text{CH}_2$ ), 31.46 ( $\text{CH}_3$ ).

## 2.3. X-RAY STRUCTURE DETERMINATION

A sample of **3** was recrystallized from hexane and its crystal structure was determined by X-ray diffraction (Table I). The crystal used had dimensions  $0.20 \times 0.30 \times 0.30$  mm. The diffraction data were measured at 293 K on a Siemens P4 diffractometer using graphite monochromatised  $\text{MoK}_\alpha$  ( $\lambda = 0.71069 \text{ \AA}$ ) and were refined from least squares fit of the setting angles of 25 reflections within the  $\theta$  range 15–20°. The systematic data collection in the range  $2^\circ < 2\theta < 40^\circ$  was performed with the  $\theta$ - $2\theta$  scan technique. Three standard reflections were measured after every 100 reflections. Corrections were made for Lorentz and polarization effects but none for absorption. The structure was solved by direct methods using SHELXTL-PLUS [22]. Refinement based on  $F^2$  data revealed rotational disorder in the methyl carbons of three out of four tert-butyl groups. During refinement the bond length involving these carbon atoms, which were assigned isotropic U values, was restrained to a realistic value (C-C 1.520(5) Å) and the s.o.f.'s of the carbon atoms were fixed at 0.70. After refinement, the difference Fourier maps yielded one satellite peak near each of the nine disordered C atoms. Because of the satisfactory geometry, these peaks were refined with the same restraints as above. A similar treatment with the methyl carbons attached to C(53), did not show any satellite

Table I. Crystallographic data

<b>Experimental</b>	
<i>Crystal data</i>	
$C_{56}H_{74}O_{11}$	$D_X = 1.046 \text{ Mg m}^{-3}$
$M_r = 923.15$	MoK $\alpha$ radiation
Triclinic	$\lambda = 0.71073 \text{ \AA}$
$P\bar{1}$	
$a = 12.999 (2) \text{ \AA}$	Cell parameters from 25 reflections
$b = 14.114 (3) \text{ \AA}$	$\theta = 15\text{--}20^\circ$
$c = 16.132 (3) \text{ \AA}$	$\mu = 0.071 \text{ mm}^{-1}$
$\alpha = 91.62 (2)^\circ$	$T = 293(1)\text{K}$
$\beta = 97.71(1)^\circ$	
$\gamma = 91.38(2)^\circ$	
$V = 2930.6(9) \text{ \AA}^3$	
$Z = 2$	
<i>Data Collection</i>	
Siemens single crystal	$\theta_{\text{max}} = 20.01^\circ$
Diffractometer	$h = 0 \rightarrow 11$
$\omega/2\theta$ scans	$k = -13 \rightarrow 13$
5842 Measured reflections	$l = -15 \rightarrow 15$
4827 Observed reflections	3 standard reflections after 100 reflections.
$[I > 2\sigma(I)]$	Intensity decrease – none
<i>Refinement</i>	
Refinement on $F_0^2$	H atoms treated as riding atoms
Final R = 0.12	$\Delta\rho_{\text{max}} = 1.124 \text{ e\AA}^{-3}$
wR = 0.34	$\Delta\rho_{\text{min}} = -0.443 \text{ e\AA}^{-3}$
4827 reflections	
568 parameters	
18 restraints	

peak and so this group was not treated as a disordered group. All the methyl groups in the tert-butyl groups were refined isotropically. All other atoms were refined anisotropically. H atoms were fixed geometrically, and they were made to ride on their respective C atoms.

### 3. Results and Discussion

#### 3.1. STRUCTURAL DATA

The structure of this compound has been confirmed by spectroscopic and X-ray crystallographic methods. In the  $^1\text{H}$  NMR the presence of an AB system for the benzylic protons ( $\text{ArCH}_2\text{Ar}$ ) and two singlets for the tert-butyl hydrogens at  $\delta 1.25$  and  $\delta 1.01$ , two singlets for the aromatic protons, a singlet each for the  $\text{OCH}_2\text{CO}$  protons and OH protons and a signal at  $\delta 33.78$  ppm in the  $^{13}\text{C}$  NMR respectively showed that **3** is present in the cone conformation. Mass spectrometric analysis showed that the capped calixarene was the dominant product. Double or triple calixarenes were not isolated although their formation cannot be ruled out. The final X-ray structure is shown in Figure 1. The torsion angles  $\phi$  and  $\chi$  around the  $\text{ArCH}_2$  bonds around C(19); C(26); C(33); C(40) as defined in [16, 20, 21] are  $-68.9(10)^\circ$ ,  $102.3(9)^\circ$ ,  $-99.8(9)^\circ$ ,  $59.5(10)^\circ$ ,  $-64.1(9)^\circ$ ,  $106.0(8)^\circ$ ,  $-102.0(8)^\circ$  and  $64.5(9)^\circ$ , respectively. The alternating  $+/-$  sequence is characteristic for the cone conformation [22] and the deviation from  $90^\circ$  indicates its deformation (to be compared with the values of  $88.9(4)$ ,  $-89.4(5)^\circ$  found in the *p*-tert-butylcalix[4]arene 1:1 toluene complex [23]). The aromatic ring C(27)–C(28)–C(29)–C(30)–C(31)–C(32) is almost flat with a maximum deviation of C(32) of  $0.02 \text{ \AA}$  from a least squares plane. The remaining three rings are planar. The connecting methylene C-atoms form an approximate plane where alternate C atoms lie  $0.03 \text{ \AA}$  above and below this plane (Figure 2). The interplanar angles found between this plane and the rings carrying crown are  $100.4(2)^\circ$  and  $85.3(2)^\circ$  while these are  $43.1(2)^\circ$  and  $39.8(2)^\circ$  for those carrying OH groups. Thus the presence of a crown at the phenyl rings of the calix[4]arene pushes them further away. The interplanar angles between opposite aromatic rings bearing the crown is  $15.1(2)^\circ$  and between the second pair is  $82.9(3)^\circ$ , showing that the rings in the pair having the crown are parallel while the other pair is almost perpendicular to each other as has been seen earlier in substituted *p*-tert-butylcalix[4]arenes [4].

In the polyether chain the O–C–C–O torsion angles range from  $21.1(10)^\circ$  to  $-175.6(8)^\circ$  whereas the C–O–C–C torsion angles range from  $-75.1(13)^\circ$  to  $179.9(7)^\circ$  (Table II). The O–C–C–O torsion angles for the two 1,4-dioxa units at the two extreme ends are significantly different from that required for minimum energy conformation [24] (O–C–C–O  $\sim 60^\circ$  and C–O–C–C  $\sim 180^\circ$ ). These two angles are rather small for a gauche conformation. This is because of the presence of the calix[4]arene on the O atom and carbonyl O at one of the C atoms in these two 1,4-dioxa units making them a rigid unit. The remaining O–C–C–O units are close to gauche except for O(5)–C(9)–C(10)–O(6) ( $-175.6(8)^\circ$ ). Similarly all C–O–C–C units are close to anti conformation except for C(4)–O(3)–C(5)–C(6) ( $-79.6(13)^\circ$ ) and C(7)–C(8)–O(5)–C(9) ( $-75.1(1)^\circ$ ). These changes introduce folds in the crown ether part of the molecule. This folding is greater than what has been found in a similar crowned *p*-tert-butylcalix[4]arene [9].

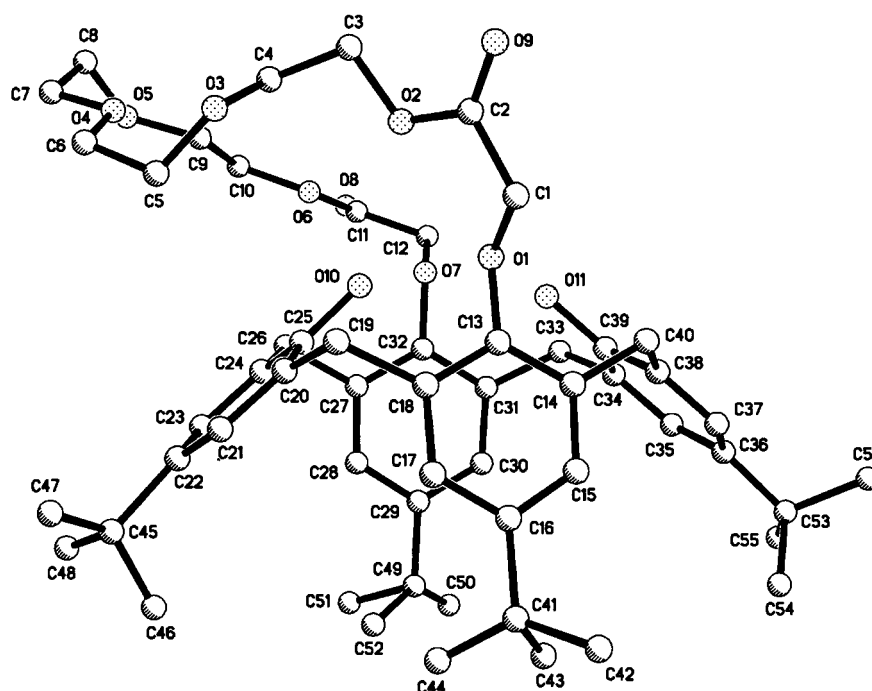


Figure 1. A view of the molecule showing the labelling scheme. Hydrogens have been omitted for the sake of clarity.

Both the phenolic O atoms are involved in intramolecular hydrogen bonding with the oxygens of the substituted phenol groups. O(10) forms a H-bond with O(1) having  $O(10)\cdots O(1) = 2.89(1)$  Å,  $H(10A)\cdots O(1) = 2.14(1)$  Å, angle  $O(10)-H(10A)\cdots O(1) = 152.3(7)^\circ$  and O(11) forms another H bond with O(7) having  $O(11)\cdots O(7) = 3.00(1)$  Å,  $H(11A)\cdots O(7) = 2.23(7)$  Å, angle  $O(11)-H(11A)\cdots O(7) = 156.9(6)^\circ$ . These intramolecular hydrogen bonds are mainly responsible for the cone conformation of the calixarene. The  $O\cdots O$  contacts of the adjacent oxygens of the calix[4]arene moiety (including those forming H-bond) range from  $2.89(1)^\circ$  to  $3.12(1)$  Å with a lengthening of about 0.3 Å with respect to those observed in *p*-tert-butylcalix[4]arene [23]. The same effect has been seen previously in the crowned *p*-tert-butylcalix[4]arene [9] where there was no H-bonding due to the reciprocal orientation of the phenyl rings. This seems to be a common behaviour for 1,3-diether derivatives of *p*-tert-butylcalix[4]arene. The  $O\cdots O$  distance between the opposite phenolic oxygens  $O(1)\cdots O(7)$  is  $4.93(1)$  Å and  $O(10)\cdots O(11)$  is  $3.27(1)$  Å whereas the nonbonding distances between the *p*-carbons of the phenolic groups which are bearing the tert-butyl groups are  $C(16)\cdots C(29) = 6.12(1)$  and  $C(22)\cdots C(36) = 9.47(1)$  Å respectively. Thus the substitution of the crown ether chain at the opposite oxygens pushes them away and the other two phenolic oxygens are brought closer whereas this effect is reversed

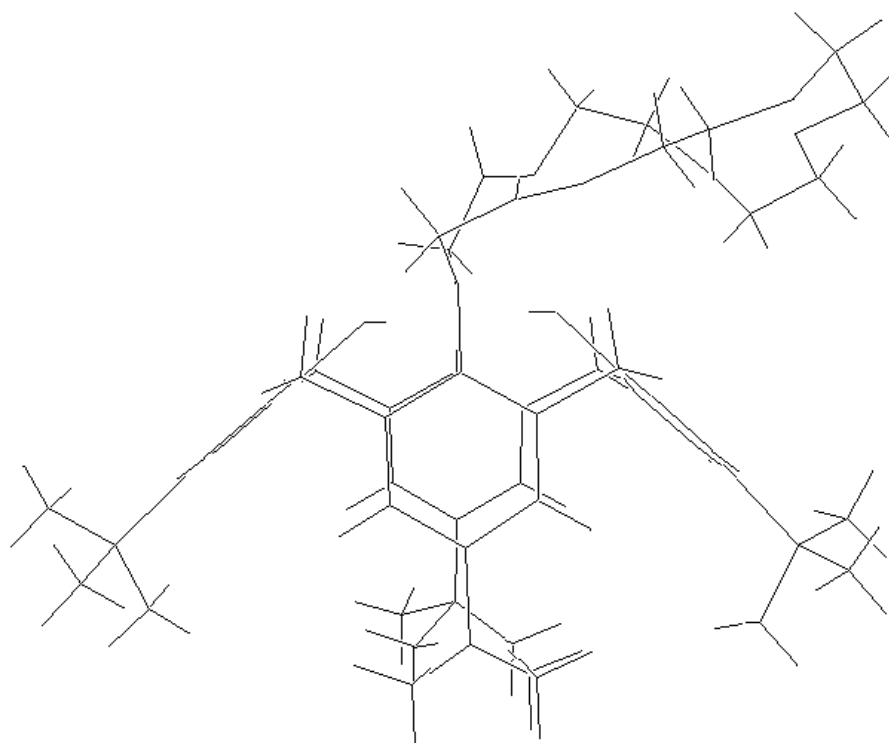


Figure 2. The orientation of the molecule from a best plane constituted of the four bridging methylene groups.

on the corresponding *p*-carbons of the phenol rings bearing tert-butyl groups. Thus capping of *p*-tert-butylcalix [4] gives rise to an elliptical lower rim to be compared with a circular one in *p*-tert-butylcalix [4]arene. The tert-butyl groups bonded to C(16), C(22) and C(29) are disordered. Only the tert-butyl groups with the highest occupancy are shown. All the tert-butyl groups are extended outside the calixarene cavity.

### 3.2. SPECTROSCOPIC STUDY OF THE BINDING MODE

To elucidate the binding mode of host **3** complexed with ammonium, alkylammonium or arylalkylammonium picrates under solid-liquid extraction conditions the  $^1\text{H}$  (200 MHz) and  $^{13}\text{C}$  (50 MHz) NMR spectra of the complexes were recorded (Tables III and IV). Table III shows that the complexation of host **3** with alkylammonium picrates showed different chemical shifts, which indicates that conformational changes take place upon complexation with different guests. The chemical shifts of the protons in the upper part of the crown moiety moved upfield in general except in the case of ammonium, tert-butylammonium or 3,4-dimethoxyphenethylammonium picrate where these protons moved downfield. The

Table II. Important bond lengths (Å), angles and torsion angles (°)

O(1)-C(13)	1.398(9)	O(1)-C(1)	1.410(9)
O(2)-C(2)	1.308(10)	O(2)-C(3)	1.440(11)
O(3)-C(5)	1.44(2)	O(3)-C(4)	1.416(13)
O(4)-C(6)	1.420(13)	O(4)-C(7)	1.409(13)
O(5)-C(8)	1.443(14)	O(5)-C(9)	1.415(12)
O(6)-C(10)	1.455(11)	O(6)-C(11)	1.345(12)
O(7)-C(12)	1.431(10)	O(7)-C(32)	1.396(9)
O(9)-C(2)	1.192(10)	O(8)-C(11)	1.196(11)
C(3)-C(4)	1.502(15)	C(1)-C(2)	1.494(12)
C(7)-C(8)	1.45(2)	C(5)-C(6)	1.44(2)
C(11)-C(12)	1.482(13)	C(9)-C(10)	1.490(15)
C(13)-O(1)-C(1)	115.2(5)	C(2)-O(2)-C(3)	118.2(7)
C(4)-O(3)-C(5)	114.8(10)	C(7)-O(4)-C(6)	113.5(9)
C(9)-O(5)-C(8)	115.3(9)	C(11)-O(6)-C(10)	117.5(7)
C(32)-O(7)-C(12)	115.2(6)	O(1)-C(1)-C(2)	111.5(7)
O(9)-C(2)-C(1)	122.7(8)	O(9)-C(2)-O(2)	124.5(8)
O(2)-C(3)-C(4)	107.5(8)	O(2)-C(2)-C(1)	112.7(7)
O(3)-C(4)-C(3)	107.6(9)	C(6)-C(5)-O(3)	115.2(11)
O(4)-C(6)-C(5)	109.6(10)	O(4)-C(7)-C(8)	109.7(10)
O(5)-C(8)-C(7)	115.4(10)	O(5)-C(9)-C(10)	106.5(9)
O(6)-C(10)-C(9)	103.3(8)	O(8)-C(11)-O(6)	124.2(9)
O(8)-C(11)-C(12)	122.8(10)	O(6)-C(11)-C(12)	112.8(9)
O(7)-C(12)-C(11)	114.6(8)		
C(13)-O(1)-C(1)-C(2)	-153.5(7)	C(3)-O(2)-C(2)-C(1)	175.6(8)
C(4)-O(3)-C(5)-C(6)	-79.6(13)	C(2)-O(2)-C(3)-C(4)	-167.1(8)
C(5)-O(3)-C(4)-C(3)	-152.9(9)	C(7)-O(4)-C(6)-C(5)	170.9(11)
C(6)-O(4)-C(7)-C(8)	179.1(10)	C(9)-O(5)-C(8)-C(7)	-75.1(13)
C(8)-O(5)-C(9)-C(10)	-159.0(10)	C(10)-O(6)-C(11)-C(12)	179.9(7)
C(11)-O(6)-C(10)-C(9)	-172.7(8)	C(32)-O(7)-C(12)-C(11)	97.0(9)
O(1)-C(1)-C(2)-O(2)	21.1(10)	O(2)-C(3)-C(4)-O(3)	77.8(10)
O(3)-C(5)-C(6)-O(4)	68.1(15)	O(4)-C(7)-C(8)-O(5)	70.8(13)
O(5)-C(9)-C(10)-O(6)	-175.6(8)	O(6)-C(11)-C(12)-O(7)	30.7(10)

protons adjacent to the phenolic ether and carbonyl group do undergo an upfield shift upon complexation. From these observations it appears that the guests interact more strongly with the inner part ether oxygen than with the phenolic ether oxygen. The aromatic protons were also affected, although the shift is less pronounced. The higher field one ( $\delta$  6.83) due to the aromatic protons of the intact phenol moiety shifted upfield ( $\Delta\delta = -0.09$ ) compared to the downfield shift ( $\Delta\delta = -0.06$ ) of



Table III.  $^1\text{H}$  NMR (200 MHz) induced shifts ( $\Delta\delta$  in ppm) of calix crown ester **3** complexed with alkylammonium picrates

Protons of host	$\text{NH}_4^+$	Me	$\text{Pr}^i$	Bu	$\text{Bu}^i$	$\text{Bu}^s$	$\text{Bu}^t$	Bn	MeBn	3,4-dimethoxyphenethyl
$\text{C}(\text{CH}_3)_3$	-0.02	-0.01	-0.05	-0.13	-0.02	0.0	-0.01	-0.02	-0.08	-0.03
$\text{C}(\text{CH}_3)_3$	0.02	0.0	0.03	0.03	0.00	0.02	0.01	-0.02	0.01	0.01
$\text{ArCH}_2\text{Ar}$ (eq)	0.02	0.01	0.03	0.03	0.00	0.02	0.03	0.0	0.00	0.0
$\text{OCH}_2$	0.01	0.0	-0.03	-0.07	-0.02	-0.03	0.06	-0.05	-0.05	0.07
$\text{OCH}_2$	0.02	0.01	0.0	-0.02	0.0	-0.02	0.01	-	-0.06	0.05
$\text{OCH}_2$	-0.01	-0.02	-0.01	0.0	-0.02	-0.02	0.0	-	-0.04	0.0
$\text{ArCH}_2\text{Ar}$ (ax)	0.03	0.0	-0.07	-0.09	-0.02	-0.03	-0.01	-0.08	-0.14	-0.03
$\text{OCH}_2$	0.04	0.03	0.05	0.05	0.0	0.02	0.01	0.0	0.03	0.01
$\text{ArOCH}_2$	0.01	0.0	-0.03	-0.04	-0.02	-0.02	0.01	-0.03	0.0	-0.03
ArH	-0.03	-0.02	-0.06	-0.09	-0.03	-0.04	0.0	-0.04	-0.11	-0.03
ArH	0.02	0.01	0.04	0.06	0.0	0.02	0.03	0.01	0.0	0.01
OH	-0.12	-0.05	-0.32	-0.15	-0.10	-0.19	-0.08	-	-	-0.01

Bu = isomeric butyl amines; Bn = Benzylamine; MeBn = Methylbenzylamine;  $\Delta\delta = \delta_{\text{Complexed}} - \delta_{\text{free}}$ .

Table IV.  $^{13}\text{C}$  NMR (50 MHz) induced shifts ( $\Delta\delta$  in ppm) of calix crown ester **3** complexed with alkylammonium or arylalkylammonium picrates

Carbons of host	Me	Bu <sup>n</sup>	Bu <sup>i</sup>	Bu <sup>s</sup>	Bu <sup>t</sup>	Bn	MeBn	3,4-dimethoxyphenethyl
CH <sub>3</sub>	0.0	0.48	0.00	-0.03	0.0	-0.01	-0.08	-0.02
CH <sub>2</sub>	0.0	0.01	0.03	0.23	0.03	0.02	0.01	0.01
-C-	0.02	0.09	0.15	0.14	0.02	0.04	0.11	0.03
OCH <sub>2</sub>	-0.06	-0.39	-0.09	-0.22	-0.07	-0.10	-0.37	-0.11
OCH <sub>2</sub>	0.08	0.24	0.08	0.12	0.07	0.05	0.10	-0.14
OCH <sub>2</sub>	-0.04	-0.41	-0.10	-0.22	0.10	-0.09	-0.40	-0.12
OCH <sub>2</sub>	0.03	0.22	0.07	0.11	0.06	0.07	0.12	0.06
C-5(Ar)	-0.04	0.21	0.08	0.15	0.08	-0.07	-0.08	
C-3(Ar)	0.01	0.10	0.05	0.10	0.05	0.05	0.49	0.05
C-6(Ar)	0.02	0.09	0.06	0.14	0.07	0.05	0.10	0.05
C-2(Ar)	-0.11	-0.53	-0.05	-	-0.12	-0.10	-0.44	-0.12
C-4(Ar)	-	0.73	0.02	-	0.23	-	-	0.23
C-4'(Ar)	0.07	0.40	0.10	-	0.12	-	0.38	0.13
C-1(Ar)	-0.07	-0.30	-0.07	-	-0.07	-0.05	-0.04	-0.07
C-1'(Ar)	-	-0.24	-0.06	-	-0.09	-0.07	-0.34	
C=O	0.07	0.18	0.03	0.22	0.32	0.10	0.26	

Bu = isomeric butylamines; Bn = Benzylamine; MeBn = Methylbenzylamine;  $\Delta\delta = \delta_{\text{Complexed}} - \delta_{\text{free}}$ .

the lower field one ( $\delta = 7.01$ ) containing the crown moiety. Furthermore, the tert-butyl protons also moved towards the opposite direction upon complexation ( $\Delta\delta = -0.13$  and  $0.03$ ) for butylammonium guest. Another point to note are the changes in chemical shift of the bridging methylene protons upon complexation. In the case of the butylammonium guest, for example, the higher field resonance ascribable to the equatorial protons of the host [25] shifted to a downfield position ( $\Delta\delta = 0.03$ ). The lower field one ascribable to the axial protons, moved to a higher field position ( $\Delta\delta = -0.09$ ). The difference in the chemical shifts of the bridging methylene protons is generally decreased ( $0.98-1.08$ ) compared with the value of the free host ( $1.10$ ). This might be due to the endo-rotation of the calix-crown, forming a somewhat flattened calixarene framework upon complex formation. The difference in chemical shifts of the bridging methylene protons is known to decrease with a minor increase in the flatness of the calix[4]arene backbone [26]. These observations indicate that the central part of the crown periphery is the primary binding site and the conformation of the calixarene moiety changes into a somewhat flattened cone form upon complexation with these ammonium guests. Other guests employed such as ammonia, methyl, isopropyl, isobutyl, sec. butyl, tert-butyl-, benzyl,

methyl, methylbenzyl, and 3,4-dimethoxyphenyl-ammonium picrates also exhibit similar behaviour but the changes are somewhat less pronounced.

Table IV shows the  $^{13}\text{C}$ NMR induced shifts of host **3** complexed with picrate salts of different alkylammonium and arylalkylammonium salts. The chemical shift of the bridging methylene carbons of the free host at 33.8 ppm indicates that the free calix-crown host preferentially adopts the cone conformation in chloroform solution [27]. Upon complexation with 1.00 equivalent of *n*-butylammonium picrate, there is no significant change in this bridging carbon signal, which might indicate that the complexed host mainly adopts the somewhat flattened, cone shaped conformation, rather similar to the host in solution. In this cone conformation, the underivatized phenol rings protrude outward relative to the mean plane of the crown moiety thus forcing the guest to interact with the phenyl and *p*-tert-butyl moiety. In general, the better the guest the larger the shift induced in the host, this clearly implies guest-induced conformational changes in the host.

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