

Synthesis, Structure and Alkali Metal Ion Binding Properties of a Podand Polyether Derived from Calix[4]arene, 5,11,17,23-tetra-*tert*-butyl-25,27-di(phenylmethoxy)-26,28-di(2'-methoxyethoxy)-calix[4]arene

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(Received: 16 April 1996; in final form: 22 October 1996)

Abstract. The ligand 5,11,17,23-tetra-*t*-butyl-25,27-di(phenylmethoxy)-26,28-di(2-methoxyethoxy)calix[4]arene, designed as an analogue of some calixcrown species in order to evaluate possible origins of their selectivity in alkali metal ion binding, has been synthesised and structurally characterised by X-ray crystallography. The crystals are monoclinic, $P2_1/n$, $a = 15.940(6)$, $b = 19.388(5)$, $c = 20.020(5)$ Å, $\beta = 109.10(2)$ deg., $Z = 4$, conventional R on $|F|$ being 0.073 for 3454 independent, 'observed' ($I > 3\sigma(I)$) reflections. $^1\text{H-NMR}$ studies in 1 : 1 $\text{CD}_3\text{CN}/\text{CDCl}_3$ solvent have shown that the ligand exerts a strong preference for the lighter alkali metal ions (Li^+ and Na^+) contrary to the binding behaviour of known calixcrowns. This may reflect interactions restricted to the lower rim donor atoms without concomitant interaction with the calixarene π -electrons, perhaps because the latter interactions are substituted by those with the benzyl group π -electrons.

Key words: Calix[4]arene, polyether, crystal structure, alkali metal ion binding.

Supplementary Data related to this article have been deposited with the British Library as Supplementary Publication SUP 82218 (28 pages).

1. Introduction

Polyethers generated through *O*-alkylation reactions of the calixarenes [1] have been shown to act as ligands of considerable versatility in forming complexes with both 'soft' and 'hard' metal ions [2,3]. 'Calixcrown' ligands [4–8] resulting from

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cyclisation reactions of calixarenes with polyethylene glycol ditosylates (and related species) provide particular examples of such ligands for which quite remarkable metal ion selectivity is found. There is some evidence that this selectivity may in part be due to the fact that metal ions enveloped by the crown ether loops in such ligands are also involved in bonding interactions with the π electrons of the calixarene phenyl groups [4–11]. It is possible, however, that this interaction is simply enforced by the binding to the ethereal oxygen donors and hence it is of interest to compare the properties of calixcrowns with those of less restricted calixarene ethers. For very simple alkyl ethers, it appears that a soft metal ion like Ag(I) may bind to both O- and π -electron donor sites [12], yet there is no evidence of π donation for hard metal ions such as Al(III) and Na(I) [13, 14]. Introduction of functionality into the ether alkyl arm, however, does seem to alter the binding site for Ag(I) [15] and hence we have been interested in studying the metal ion binding properties of calixcrown analogues which are calix[4]arene derivatives with pendant polyether arms. An appropriate group of compounds, rather readily obtained through selective 1,3 dialkylation [16, 17] of calix[4]arenes, is one which may be described as the '2 + 2' family of calix[4]arene polyethers. A particular example of a simple compound from this group is the *p*-*t*-butylcalix[4]arene derivative, a six-oxygen donor ligand, 5,11,17,23-tetra-*t*-butyl-25,27-di(phenylmethoxy)-26,28-di(2'-methoxyethoxy)calix[4]arene (**2**, see Scheme 1). The present work describes the synthesis and structural characterisation of this ligand along with an evaluation of its selectivity in binding to the alkali metal cations.

2. Experimental

Uncorrected melting points (m.p.s) were measured on a Buchi 500 apparatus in sealed capillaries under nitrogen. $^1\text{H-NMR}$ spectra recorded at the different institutions were measured on Bruker SY200 and AM 300 instruments. Spectra of complexes of the alkali metal triflates (trifluoromethanesulfonates) in 1:1 $\text{CDCl}_3/\text{CD}_3\text{CN}$ were obtained by adding the solid triflates to a solution (10^{-2} mol L^{-1}) of the ligand until the spectra remained unchanged. Similarly, to obtain spectra of complexes of the alkali metal picrates in CDCl_3 , the solid picrates were agitated under a solution of ligand (10^{-2} mol L^{-1}) until picrate resonances reached a maximum intensity. Mass spectra (FAB^+) were recorded on a VG-Analytical ZAB HF instrument. Elemental analyses were provided by the Service de Microanalyse of the Institut de Chimie de Strasbourg.

2.1. PREPARATION OF **2**

2.1.1. 5,11,17,23-tetra-*t*-butyl-25,27-dihydroxy-26,28-di(2'-methoxyethoxy)calix[4]arene, **1**

A 500 mL round-bottomed flask was equipped with a condenser and charged with acetonitrile (375 mL), *p*-*t*-butylcalix[4]arene (6.52 g; 10.0 mmol) and potassium

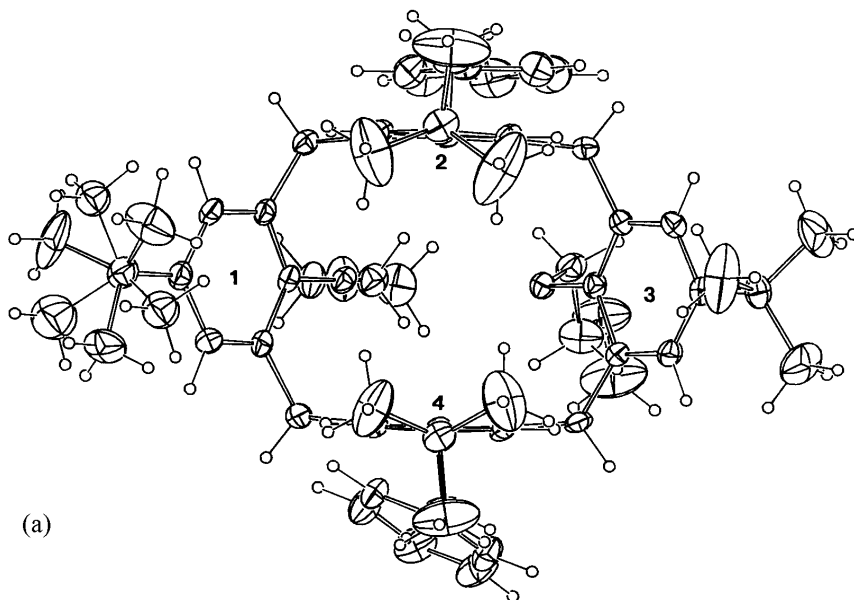


Figure 1. Views of the molecule **2** (a) down and (b) *quasi-normal* to the cone axis and (c) in a perspective showing the array of oxygen and benzyl phenyl ring donor units about the lower rim. 20% thermal ellipsoids are shown for the non-hydrogen atoms; hydrogen atoms have arbitrary radii of 0.1 Å. In (a), the alternate set of components for the disordered *t*-butyl group is shown with line bonds. Atom numbering is indicated in (b), where bonds in the nearest unit are shown bold, as is also the case in (c).

carbonate (20.02 g; 145.0 mmol). The reaction mixture was stirred under nitrogen at room temperature for 2 h. 2-Methoxyethyl tosylate (5.77 g; 25.0 mmol) was added and the contents were heated at reflux for 3 days. After cooling to room temperature, the solvents were removed in vacuo (45 °C). Dichloromethane (300 mL) was added and the suspension was neutralised with 1 mol L⁻¹ HCl. The organic layer was dried over sodium sulfate. The filtered solution was concentrated and mixed with methanol to yield pure **1** as a white solid, m.p. 175–177 °C. ¹H-NMR (200 MHz; CDCl₃, (CH₃)₄Si reference) δ 7.27 (s, 2H, ArOH), 7.05 (s, 4H, ArH *meta* calix), 6.79 (s, 4H, ArH *meta* calix), 4.37 (d, 4H, *J* = 13.0 Hz, Ar CH₂Ar), 4.15 (t, 4H, *J* = 4.7 Hz, Ar OCH₂CH₂O), 3.88 (t, 4H, *J* = 4.7 Hz, Ar OCH₂CH₂O), 3.54 (s, 6H, OCH₃), 3.29 (d, 4H, *J* = 13.0 Hz, ArCH₂Ar), 1.29 (s, 18H, *t*-C₄H₉), 0.96 (s, 18H, *t*-C₄H₉). Mass spectrum (FAB⁺): *m/z* 764.5 (Calc. 765.1). *Anal. Calcd.* for C₅₀H₆₈O₆: C 78.49; H 8.96; *Found*: C 78.3; H 8.8. Yield 74%.

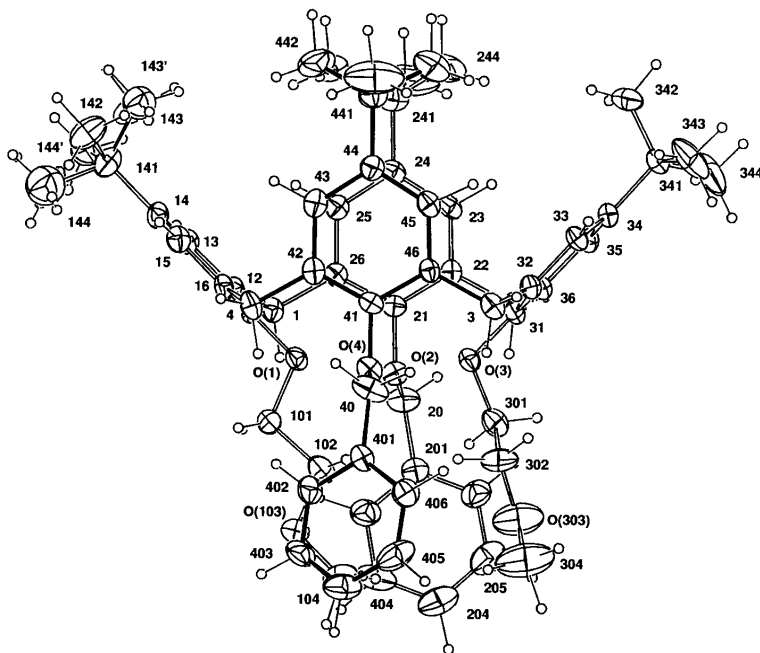


Figure 1b. See caption to Figure 1(a).

2.1.2. 5,11,17,23-tetra-*t*-butyl-25,27-di(2-methoxyethoxy)-26,28-di(phenylmethoxy)-calix[4]arene, **2**

A 250 mL round bottomed flask was equipped with a condenser and charged with acetonitrile (120 mL), calixarene **1** (3.0 g; 4.0 mmol), potassium carbonate (5.40 g; 40.0 mmol) and benzyl bromide (6.73 g; 40.0 mmol). The contents were heated at reflux for 36 h. The work-up was carried out as previously described for **1** to provide a white solid, m.p. 189–192 °C. ¹H-NMR (300 MHz; CDCl₃, (CH₃)₄Si reference), δ 7.48–7.31 (m, 10H, C₆H₅), 7.02 (s, 4H, ArH *meta* calix), 6.49 (s, 4H, ArH *meta* calix), 4.72 (s, 4H, CH₂C₆H₅), 4.34 (d, 4H, *J* = 12.4 Hz, Ar CH₂Ar), 3.98 (t, 4H, *J* = 7.6 Hz, Ar OCH₂CH₂O), 3.58 (t 4H, *J* = 7.6 Hz, Ar OCH₂CH₂O), 3.06 (d, 4H, *J* = 12.4 Hz, ArCH₂Ar), 3.03 (s, 6H, OCH₃), 1.27 (s, 18H, *t*-C₄H₉), 0.85 (s, 18H, *t*-C₄H₉). *Anal. Calcd.* for C₆₄H₈₀O₆: C 81.32 ; H 8.13; *Found*: C 81.4; H 8.1. Mass spectrum (FAB⁺): *m/z* 967.6 (Calc. **2** + Na⁺ 968.1). Yield 78%.

2.2. CRYSTALLOGRAPHY

Crystals of **2** suitable for the X-ray work were obtained by slow evaporation at 298 K of a methanol solution.

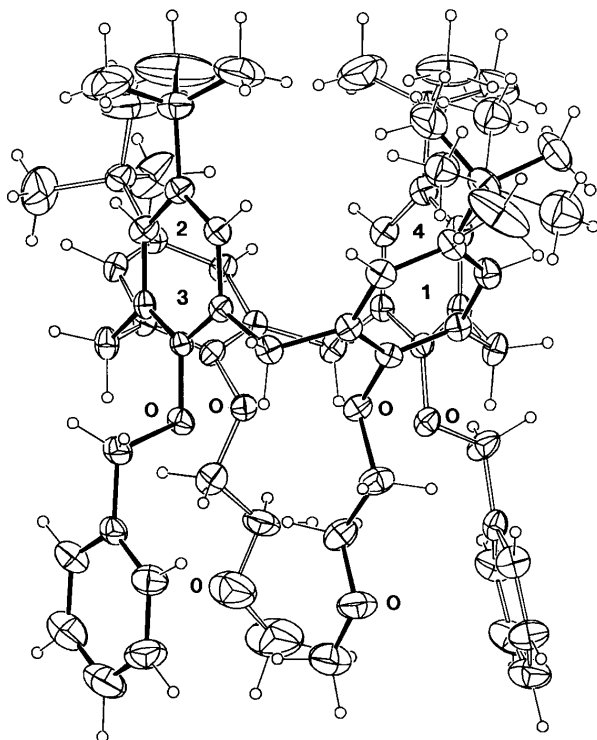


Figure 1c. See caption to Figure 1(a).

2.2.1. Structure Determination

A unique diffractometer data set (Enraf-Nonius CAD-4; $2\theta_{\max}$ 44° , $2\theta/\theta$ scan mode, monochromatic $\text{MoK}\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$) was measured at 293(2) K, yielding 6910 independent reflections, 3454 of these with $I > 3\sigma(I)$ being considered 'observed' and used in the full-matrix least-squares refinement without absorption correction. Anisotropic thermal parameters were refined for the non-hydrogen atoms; $(x, y, z, U_{\text{iso}})_\text{H}$ were included constrained at estimated values. Conventional residuals R , R' on $|F|$ were 0.073, 0.077, statistical weights derivative of $\sigma^2(I) = \sigma^2(I_{\text{diff}}) + 0.0004\sigma^4(I_{\text{diff}})$ being used. Neutral-atom complex scattering factors were employed, computation using the XTAL 3.2 program system [18] implemented by S.R. Hall. Pertinent results are given in Figure 1 and Table I. Full molecular geometries are deposited with the Cambridge Crystallographic Data Base.

2.2.2. Crystal/Refinement Data

2, $\text{C}_{64}\text{H}_{80}\text{O}_6$, $M = 945.3$, monoclinic, space group $P2_1/n$ (C_{2h}^5 , No.14 (variant)), $a = 15.940(6)$, $b = 19.388(5)$, $c = 20.020(5) \text{ \AA}$, $\beta = 109.10(2)^\circ$, $V = 5846(3) \text{ \AA}^3$,

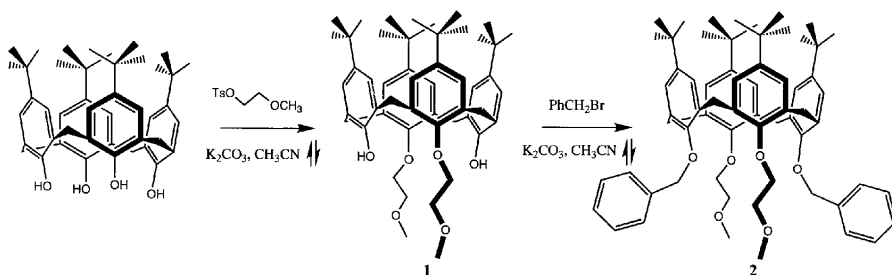


Figure 2. Stepwise synthesis of 5,11,17,23-tetra-*t*-butyl-25,27-di(phenylmethoxy)-26,28-di(2'-methoxyethoxy)calix[4]arene (**2**).

D_c ($Z = 4$) = 1.074 g cm⁻³, $F(000) = 2048$, $\mu_{\text{Mo}} = 0.7$ cm⁻¹, specimen 0.15 × 0.25 × 0.65 mm. $|\rho|_{\text{max}} 0.26e \text{ \AA}^{-3}$.

Abnormal features/variations in procedure. *t*-Butyl group C(14n) was modelled as disordered over a pair of rotationally related sites, site occupancies refining to x , $1 - x$, $x = 0.75(1)$, isotropic thermal parameter forms being refined for the smaller component.

3. Results and Discussion

3.1. SYNTHESIS

The synthesis of **2** is illustrated in Figure 2. Initially, *p*-*t*-butylcalix[4]arene was treated with 2-methoxyethyl tosylate (2.5 eq.) and potassium carbonate (14.5 eq.) in boiling acetonitrile under nitrogen for 3 days to yield (74%) 1,3-dialkylated **1**. Selective 1,3-dialkylation of the reactant and a cone conformation for **1** were deduced from the presence of two singlets at δ 0.96 and 1.29 for the *t*-butyl groups and AB quartet resonances at δ 3.29 and 4.37 with $J = 13.0$ Hz for the ArCH₂Ar methylene protons of the calix macroring in the ¹H-NMR spectrum of **1**, though the 1,3-alternate conformation cannot be excluded on this basis alone [16, 17]. Compound **1** was further treated with benzyl bromide (10 eq.) and potassium carbonate (10 eq.) in boiling acetonitrile under nitrogen for 36 h to provide 5,11,17,23-tetra-*t*-butyl-25,27-di(phenylmethoxy)-26,28-di(2'-methoxyethoxy)calix[4]arene, **2**, in 78% yield. The cone conformation of and 2 + 2' functional group disposition in **2** were established from the crystal structure determination (see below) and these features are consistent with the presence of an AB system (δ 3.06 and 4.34 with $J = 12.4$ Hz) for the ArCH₂Ar protons and two singlets (δ 0.85 and 1.27) for the *t*-butyl groups in the chloroform solution ¹H-NMR spectrum.

3.2. CRYSTALLOGRAPHY

Crystals suitable for X-ray diffraction were obtained by slow evaporation of a methanol solution of **2** at ~298 K. The structure solution (Figure 1), with one molecule comprising the asymmetric unit, showed the calixarene moiety to be

Table I. Non-hydrogen positional and isotropic displacement parameters for compound **2**.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{(eq)}/\text{\AA}^2$
O(1)	0.3067(3)	0.6557(2)	0.7060(2)	0.056(2)
C(11)	0.3818(5)	0.6330(4)	0.6939(4)	0.050(4)
C(12)	0.4636(5)	0.6594(4)	0.7342(4)	0.053(3)
C(13)	0.5384(5)	0.6357(4)	0.7212(4)	0.059(4)
C(14)	0.5358(5)	0.5880(4)	0.6680(4)	0.063(4)
C(141)	0.6196(6)	0.5646(6)	0.6547(5)	0.084(5)
C(142)*	0.6027(9)	0.5219(9)	0.5886(8)	0.119(9)
C(143)*	0.672(1)	0.628(1)	0.647(1)	0.15(1)
C(144)*	0.676(1)	0.524(2)	0.7152(9)	0.19(1)
C(142')*	0.622(4)	0.484(3)	0.658(4)	0.16(3)
C(143')*	0.608(3)	0.592(3)	0.579(2)	0.11(2)
C(144')*	0.703(3)	0.586(3)	0.710(3)	0.10(2)
C(15)	0.4509(6)	0.5659(4)	0.6273(4)	0.064(4)
C(16)	0.3747(5)	0.5873(4)	0.6388(4)	0.055(4)
C(1)	0.4672(4)	0.7178(4)	0.7851(3)	0.058(3)
C(101)	0.2839(5)	0.6122(4)	0.7557(4)	0.078(4)
C(102)	0.2042(6)	0.6402(4)	0.7673(4)	0.082(4)
O(103)	0.1823(4)	0.5992(3)	0.8164(3)	0.104(4)
C(104)	0.1039(7)	0.6190(5)	0.8256(5)	0.124(6)
O(2)	0.3188(3)	0.8017(2)	0.7858(2)	0.056(2)
C(21)	0.3694(5)	0.8231(4)	0.7435(4)	0.048(3)
C(22)	0.3434(5)	0.8799(4)	0.7000(4)	0.049(3)
C(23)	0.3948(5)	0.9013(4)	0.6618(4)	0.059(4)
C(24)	0.4730(5)	0.8677(4)	0.6636(4)	0.058(4)
C(241)	0.5317(6)	0.8939(5)	0.6232(5)	0.084(5)
C(242)	0.5873(9)	0.8389(6)	0.6058(7)	0.20(1)
C(243)	0.591(1)	0.9480(8)	0.6631(7)	0.24(1)
C(244)	0.4800(9)	0.9239(9)	0.5541(7)	0.25(1)
C(25)	0.4949(5)	0.8099(4)	0.7055(4)	0.058(4)
C(26)	0.4434(5)	0.7852(4)	0.7451(4)	0.050(3)
C(2)	0.2570(5)	0.9181(4)	0.6931(4)	0.064(4)
C(20)	0.3475(5)	0.8356(4)	0.8543(4)	0.073(4)
C(201)	0.2824(6)	0.8198(5)	0.8906(4)	0.063(4)
C(202)	0.2909(6)	0.7633(5)	0.9325(5)	0.088(5)
C(203)	0.2309(9)	0.7489(6)	0.9663(6)	0.122(7)
C(204)	0.1595(9)	0.7917(9)	0.9581(7)	0.133(8)
C(205)	0.1505(8)	0.8493(7)	0.9160(7)	0.125(7)
C(206)	0.2118(7)	0.8629(5)	0.8833(5)	0.093(5)
O(3)	0.1531(3)	0.7964(2)	0.6417(2)	0.056(2)
C(31)	0.1489(5)	0.8503(4)	0.5956(4)	0.053(4)
C(32)	0.1021(4)	0.8383(4)	0.5224(4)	0.052(3)
C(33)	0.0989(5)	0.8929(4)	0.4764(4)	0.058(4)
C(34)	0.1360(5)	0.9563(4)	0.4968(4)	0.058(4)
C(341)	0.1322(6)	1.0147(4)	0.4454(4)	0.071(4)

Table I. Continued.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{(eq)}/\text{\AA}^2$
C(342)	0.2136(8)	1.0157(6)	0.4269(7)	0.188(9)
C(343)	0.0514(8)	1.0077(5)	0.3784(5)	0.154(7)
C(344)	0.1204(8)	1.0829(5)	0.4772(6)	0.158(8)
C(35)	0.1859(5)	0.9641(4)	0.5689(4)	0.061(4)
C(36)	0.1922(5)	0.9111(4)	0.6170(4)	0.054(3)
C(3)	0.0700(5)	0.7673(4)	0.4981(3)	0.059(3)
C(301)	0.0988(6)	0.8065(4)	0.6858(4)	0.076(4)
C(302)	0.0157(7)	0.7647(5)	0.6569(5)	0.103(5)
O(303)	-0.0287(6)	0.7708(5)	0.7026(4)	0.168(5)
C(304)	-0.1103(8)	0.7337(8)	0.6812(7)	0.22(1)
O(4)	0.1198(3)	0.6382(2)	0.5728(2)	0.057(2)
C(41)	0.1718(5)	0.6639(4)	0.5342(3)	0.048(3)
C(42)	0.2475(5)	0.6277(4)	0.5368(4)	0.058(4)
C(43)	0.2948(5)	0.6505(4)	0.4929(4)	0.064(4)
C(44)	0.2690(5)	0.7074(4)	0.4481(4)	0.061(4)
C(441)	0.3169(6)	0.7280(5)	0.3969(5)	0.082(5)
C(442)	0.4100(6)	0.7049(7)	0.4181(6)	0.163(7)
C(443)	0.3140(9)	0.8035(6)	0.3846(7)	0.185(9)
C(444)	0.2675(8)	0.6954(8)	0.3259(5)	0.202(9)
C(45)	0.1948(5)	0.7429(4)	0.4512(4)	0.059(4)
C(46)	0.1462(5)	0.7227(4)	0.4936(4)	0.050(3)
C(4)	0.2833(5)	0.5689(4)	0.5877(4)	0.065(4)
C(40)	0.0492(6)	0.5968(4)	0.5305(4)	0.085(4)
C(401)	-0.0009(6)	0.5636(4)	0.5708(4)	0.058(4)
C(402)	0.0379(5)	0.5208(5)	0.6266(5)	0.075(4)
C(403)	-0.0102(7)	0.4862(5)	0.6605(4)	0.090(5)
C(404)	-0.0996(8)	0.4914(6)	0.6383(6)	0.112(6)
C(405)	-0.1403(6)	0.5342(7)	0.5823(6)	0.119(6)
C(406)	-0.0919(7)	0.5700(5)	0.5500(4)	0.085(5)

*Site occupancy factors: O(142)/C(144) 0.75(2) O(142')/C(144') 1-0.75(2)

present in a cone conformation *quasi-mm* symmetry, with two of the phenyl rings (those with attached benzyl substituents) lying near-parallel (interplanar dihedral 2.9(3)°) and hence closely perpendicular to the mean plane of the methylene bridges (interplanar dihedrals 87.5(2), 89.6(2)°). The other two opposed phenyl rings, with 2-methoxyethyl substituents, have dihedral angles of 46.1(2), 45.8(2)° to this plane, the macrocycle structure thereby being closely similar to that in the simple analogue of **2**, 1,3-*bis*(cyanomethoxy)-*p*-*t*-butylcalix[4]arene [17]. Considered as a polyether for metal ion complexation, **2** is not 'preorganised' in that neither O(103) nor O(303) can be considered oriented towards some central site defined by the other four oxygen atoms. The phenyl groups of the benzyl substituents, however,

are oriented so as to form the walls of a cavity in which a metal ion could be held to interact both with them and several oxygen atoms, so that the ability observed for several calixcrowns to act as aromatic π -electron and oxygen lone pair donor ligands [4–11] could be retained in a subtly different way in **2**.

3.3. METAL ION COMPLEXATION

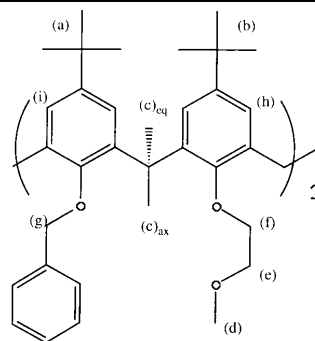
The suitability of **2** as a ligand for hard cations such as those of the alkali metals was demonstrated by the use of $^1\text{H-NMR}$ spectroscopy to study their complexation reactions. Preliminary measurements in which solid alkali metal picrates were added to chloroform solutions of **2** demonstrated (from dissolution of the solids) that complexation occurred in all cases but again exposed the phenomenon we have commented upon elsewhere [7] for some related systems that two picrate ^1H resonances could be observed even when all other aspects of the spectra were consistent with the presence of a single ligand species, so that the actual equilibria involved could not be fully characterised by $^1\text{H-NMR}$ spectroscopy. More complete but still rather complicated data were obtained by study of the influence of the addition of alkali metal ions (Li, Na, K, Rb and Cs) as their triflate salts on the spectrum of the ligand in the homogeneous medium provided by 1 : 1 $\text{CDCl}_3/\text{CD}_3\text{CN}$. The more significant aspects of these results are:

1. While the changes observed on titration of **2** with LiCF_3SO_3 , NaCF_3SO_3 , KCF_3SO_3 , and RbCF_3SO_3 were qualitatively similar right up to the point of addition of a large excess of the metal salt, those for CsCF_3SO_3 were quite different. For the four lighter alkali metals, both signal shifts and broadening (for KCF_3SO_3 , very largely the latter only) occurred on initial additions but a well-resolved limiting spectrum consistent with the presence of a single complex was eventually obtained. For CsCF_3SO_3 , little signal broadening was observed but the complexity of the spectrum increased greatly and, even with a very large excess of the salt present, it appeared that at least two complex species were present. Table II provides a summary of some of the effects observed.

2. For addition of both LiCF_3SO_3 and NaCF_3SO_3 , signal shifts were negligible beyond a M : L ratio of 1 : 1, indicating complex formation to be essentially complete at this point. For KCF_3SO_3 , shifting effects were so slight that complex formation could not be monitored in this way but for RbCF_3SO_3 , shifts were almost linear in $[\text{Rb}^+]$ even up to a M : L ratio of 5 : 1, indicating that complexation became much less effective with increasing size of the cation.

3. Both the pairs of *t*-butyl (a) and (b) (δ 1.01 and 1.19) and *meta* aromatic (h) and (i) (δ 6.81 and 7.05) proton resonances, which clearly demonstrate the no more than twofold symmetry of the free ligand, collapsed to near coincidence in the presence of a large excess of the metal cations $\text{Li}^+ - \text{Rb}^+$ (Table II). This suggests that,

Table III. $^1\text{H-NMR}$ shifts (δ) and coupling constants (Hz) for compound **2** in the presence of alkali metal triflates in 1 : 1 CDCl_3 : CD_3CN .



Inequivalent proton locations in ligand **2**

Metal (M)	M:2	H(a)	H(b)	H(c) _{eq}	H(c) _{ax}	H(d)	H(e)	H(f)	H(g)	H(h)	H(i)
None		1.01	1.19	3.06 12.1 ^a	4.33 12.1 ^a	3.07	3.47 6.3 ^a	3.86 6.3 ^a	4.84	6.81	7.05
Li	5:1	1.10	1.11	3.02 12.4 ^a	3.90 12.4 ^a	3.70	3.88 <i>broad</i>	4.30 <i>broad</i>	5.19	7.06	7.08
Na	5:1	1.12	1.15	3.06 12.5 ^a	3.96 12.5 ^a	3.84	4.03 4.9 ^a	4.05 4.9 ^a	5.11	7.12	7.14
K	5:1	1.13	1.13	3.08 12.7 ^a	4.12 12.7 ^a	3.50	3.57 <i>broad</i>	3.91 <i>broad</i>	4.86	7.10	7.11
Rb	5:1	1.11	1.14	3.06 12.5 ^a	4.17 12.5 ^a	3.44	3.56 <i>broad</i>	3.89 <i>broad</i>	4.85	7.03	7.11
Cs	0.5:1 ^b	1.00	1.19	~3.06 ^c	4.32 12.2 ^a	3.09	3.49 6.1 ^a	3.87 6.1 ^a	4.82	6.80	7.04

^a Coupling constant.

^b At low ratios, changes appeared less marked than with the other metals but at 5 : 1 the spectrum was very much more complex and indicative of the presence of at least two species (see text).

^c Overlap of one component of the doublet with the more intense methoxyl signal (d) made estimation of the mean doublet shift and the coupling constant (seemingly ~ 15 Hz) difficult so that results for the axial proton should be considered more reliable.

for these cations, the complexed ligand **2** must adopt a conformation in which the upper portion of the cone is more symmetrical than in the free. In the presence of a 5 : 1 molar ratio of CsCF_3SO_3 , there are at least six signals for the t-butyl groups of **2**, though one is considerably more intense than the others.

4. The lower field doublet component of the calixarene methylene bridge proton resonances, which is presumed to be that due to the 'axial' (c) proton [19] (having a similar orientation relative to the macrocyclic ring plane as do the benzyl and

methoxyethyl substituents), undergoes the larger shifts on addition of any of the metal ions and, for Li–Rb, can be observed to be significantly broader than its higher field doublet pair at intermediate ($\sim 2-3 : 1$) $M : 2$ ratios. Again for Li–Rb, both broadening and shifting effects were observed for the protons (d), (e), (f), (g), (h) and (i). Although these broadening effects may merely reflect relatively slow exchange of the metal cations between their solvated forms and complexes with **2** (as is known to occur in some related systems [20, 21]), the large magnitude of the shifts for protons in groups adjacent to oxygen donors is explicable in terms of cation binding to those donors producing marked conformational and electronic changes, and hence may justify the conclusion that Li^+ , Na^+ , K^+ and Rb^+ , at least, must bind to the lower rim substituents of the calixarene. Such interpretation of the shifts must nonetheless be considered very tentative, since the effects are similar in nature to those observed for alkali metal ion binding to a *p*-octylcalix[4]arene tetraketone [22, 23], where a crystal structure determination [22] has indeed shown lower rim binding for Na^+ , yet at least in regard to aromatic protons, the shifts are of similar sign and magnitude to those for Ag^+ bonding to calix[4]arene tetraethers, where crystallography [24] has shown attachment to the aromatic π electrons. Further uncertainty is generated by the fact that Ag^+ binding to the tetraketone causes similar shifts to that of Na^+ [23].

5. The complex multiplet associated with the aromatic protons of the benzyl groups is significantly affected by all cations, though again marked broadening effects are only observed for Li–Rb at intermediate ratios and Cs provides the most complicated ultimate spectrum. This is perhaps the clearest evidence that Cs^+ may interact with the lower rim substituents and of course it also carries the implication that all the cations may be involved in polyhapto donor interactions with the benzyl π electrons. Significantly, however, all the alkali metal cations produced upfield shifts for the benzyl aromatic proton resonances, whereas presumed (in solution) polyhapto binding of Ag^+ to calixarene phenyl groups causes downfield shifts of their protons [24].

Evidence that in the gas phase the stability of the complexes was similar to that in solution was the fact that in the FAB^+ mass spectra, $(2 + M)^+$ peaks could be detected in all cases (Li: m/z 951; Na: m/z 967; K, m/z 983; Rb: m/z 1029; Cs: m/z 1077) but only for Cs was a peak for 2^+ (m/z 944) also detectable. The different solution behaviour of Cs^+ relative to that of the other metals may conceivably be associated with the formation of an ML_2 species in addition to ML and the former might well dissociate in the gas phase to give ML and L. The ability of the complexes to dissociate readily in solution led to the frustration of many efforts to obtain crystals (with both picrates and triflates of the alkali metals) for structure determination, since only the free ligand crystallised out in all cases. Hence, although it is clear that **2** displays quite different selectivity to

known calixcrowns and plausible reasons for this can be advanced, the exact form of coordination to the alkali metal cations remains to be established.

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