SYNTHESIS AND ESI-MS ALKALI METAL ION BINDING SELECTIVITIES OF CONE, PARTIAL CONE, AND 1,3-ALTERNATE 1,3-BIS(α-PICOLYLOXY)-*p-tert*-BUTYLCALIX[4]ARENE CROWN-6 AND 1,1′-BINAPHTHALENE-2,2′-DIYL CROWN-6 CONFORMERS

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Dedicated to Professor Ivan Stibor on the occasion of his 60th birthday in recognition of his outstanding contributions to supramolecular chemistry.

The syntheses of 1,3-bis(α-picolyloxy)-*p-tert*-butylcalix[4]arene crown-6 and 1,1′-binaphthalene-2,2′-diyl crown-6 title conformers have been achieved by two complementary synthetic strategies, which differ in the order in which the polyether loop and the pendant picolyl groups are introduced. The structure and conformation of all new compounds have been firmly established by NMR spectroscopy, and further proven by X-ray analysis for the intermediate *p-tert*-butyl-25,27-(1,1′-binaphthalene-2,2′-diyl-crown-6)-26,28-dihydroxycalix[4]arene. Within each set of conformers, the nature of the polyether chain has little or no influence on the overall conformation of the calixarene platform. The alkali metal ion binding selectivities of the two series of calixarenes have been evaluated in competitive complexation experiments by electrospray ionization mass spectrometry. In the *p-tert*-butylcalix[4]arene crown-6 series, partial cone and 1,3-alternate conformers show a peak selectivity for the larger Cs^+ ions, while the cone one preferentially binds the smaller Na^+ ions. On the other hand, the cone and 1,3-alternate binaphthyl-containing analogues show a preference for Na^+ ions, the partial cone being quite unselective.

Keywords: Alkali metal ion selectivity; Calixarenes; Crown compounds; Electrospray ionization mass spectrometry; Pyridine derivatives; Biaryls; Binaphthalenes; X-ray diffraction.

During the past two decades calixarenes have played a prominent role in the development of host-guest and supramolecular chemistry[1], and the search for new strategies aimed at the non-covalent synthesis of calixarene-based multicomponent supramolecular architectures with desired functions is very active[2]. We have recently shown that 1,3-bis(α-picolyloxy)-*p-tert*-butylcalix[4]arene (**6**) and 1,2,4,5-tetrafluoro-3,6-diiodobenzene modules form non-covalent 2-D supramolecular assemblies[3], which rely on a combination of attractive π–π and halogen-bonding interactions. The former involve the outside faces of the two phenol rings of the calixarene and both faces of the perfluoroarene, while the latter – electron donor–acceptor attractions – concern the nitrogen atoms (electron donors) of the pendant picolyl groups and the iodine atoms (electron acceptors) of the perfluoroarene.

Halogen-bonding interactions[4] are currently being exploited as a further non-covalent tool to promote self-assembly processes of appropriate couples of electron-donor and electron-acceptor modules[5]. The strength of halogen bonding depends on the electron density on the donor site[6], and recent studies have demonstrated the unique electron donor ability of iodide anions in promoting the formation of multicomponent supramolecular aggregates involving electron-acceptor diiodoperfluorocarbon modules[7]. Since ion-pairing of alkali metal iodides in organic media is detrimental to the electron density on the halide, strong enhancements of the anion electron density have been achieved by resorting to "naked" anions, generated via confinement of the countercation inside the cavity of an appropriate receptor[7].

All these observations have renewed our interest in the potential offered by pyridine-calixcrown tectons in the anion-promoted[8] synthesis of multicomponent supramolecular assemblies. Calixcrowns are a class of very efficient and size-selective synthetic receptors for alkali metal ions[9]. Pyridine-containing analogues[10] combine the well known ability of calixcrowns to wrap and segregate the alkali metal cations within their ionophoric cavity with the propensity of pyridyl nitrogen atoms to act as electron-donor modules[11]. 1,3-Bridged bis(α-picolyloxy)-*p-tert*-butylcalix[4]arene crown-5 conformers are much more efficient and selective than 1,2-bridged regioisomers[12], and display a strong affinity for K^+ ions, the 1,3-alternate conformer being slightly more selective than the naturally occurring ionophore valinomycin[10].

As an extension of these studies[10], in this paper we report the synthesis, NMR characterization and conformational features of cone, partial cone and 1,3-alternate conformers of 1,3-bis(α-picolyloxy)-*p-tert*-butylcalix[4]arene

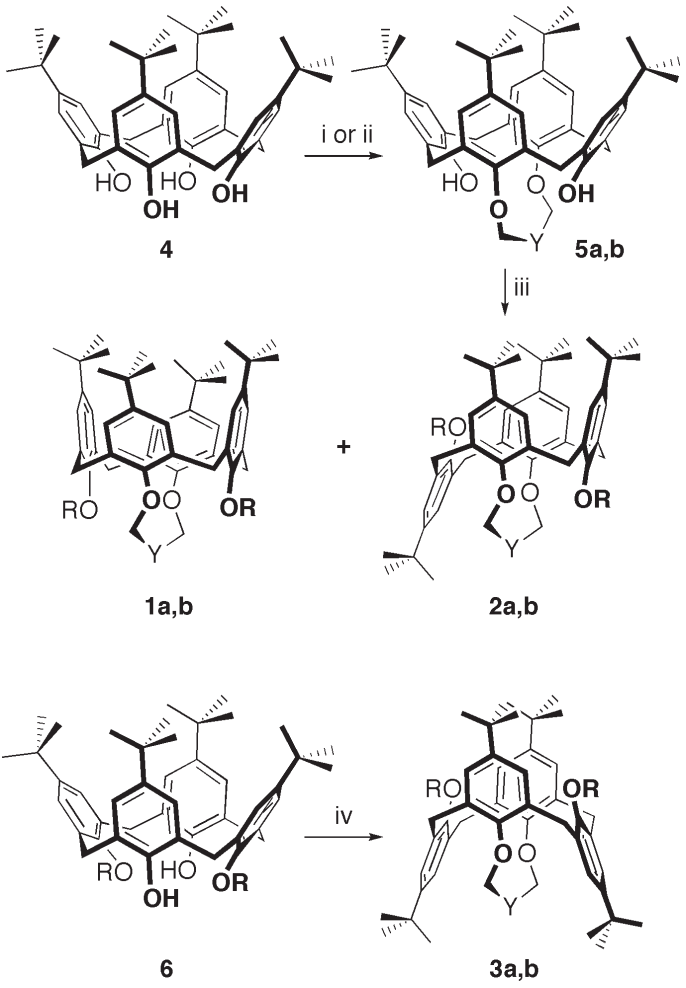
crown-6 **1a**–**3a** and their 1,1′-binaphthalene-2,2′-diyl crown-6 analogues **1b**–**3b** (vide infra, Scheme 1). In the quest for new cation segregating agents (to generate naked iodide anions), a screening of the binding selectivities of the two series of pyridine-calixcrowns toward alkali metal iodides was carried out by electrospray ionization mass spectrometry (ESI-MS).

RESULTS AND DISCUSSION

*Synthesis and Conformational Features of 1,3-Bridged Calix[4]arene Crown-6 Conformers **1–3***

The two complementary synthetic strategies leading to the three different conformers of 1,3-bis(α-picolyloxy)-*p*-*tert*-butylcalix[4]arene crown-6 (**1a**–**3a**) and their 1,1′-binaphthyl crown-6 analogues (**1b**–**3b**) are shown in Scheme 1. The pivotal crown ethers **5a** and **5b** were obtained in 35–40% yield by reacting *p*-*tert*-butylcalix[4]arene (**4**) with either pentaethylene glycol ditosylate (PGD) or 2,2′-bis{2-[(tosyloxy)ethoxy]ethoxy}-1,1′-binaphthalene (BGD) under the conditions (K_2CO_3 in refluxing CH_3CN) described by Shinkai for the synthesis of the 1,3-crown-4-*p*-H-calix[4]arene[13]. More conveniently, **5b** was obtained in 62% yield by carrying out the reaction in dry toluene at 70 °C in the presence of *t*-BuOK (2.1 equivalents). In contrast with intermediate **5a**, where an achiral crown-6 chain joins two *distal* phenol rings, the incorporation of the chiral 1,1′-binaphthalene-2,2′-diyl moiety in **5b** causes doubling of the expected NMR spectral patterns. In particular, the presence of two AX systems for the $ArCH_2Ar$ groups, with a $\Delta\delta$ separation around 1 ppm between *exo* and *endo* geminal protons, and two distinct resonances at δ 30.9 and 31.8 ppm, for the pertinent carbons, suggest that **5b** adopts a cone conformation in solution. This is further proved by single-crystal X-ray analysis.

Crystals of **5b** were grown from an acetonitrile/dichloromethane solution and the structure analysis shows that both solvent molecules are present within the calix[4]arene cup. A view of **5b** with our numbering scheme is shown in Fig. 1. The molecule adopts an open cone conformation with the values of the dihedral angles which the four aromatic rings (C11–C16, C21–C26, C31–C36, C41–C46) make with the plane of the methylene carbons which link them being 67.7(1), 49.0(1), 73.3(1) and 53.8(1)°, respectively. This conformation is stabilized by the formation of intramolecular O–H···O hydrogen bonds (O2–H···O1 2.641(2) and O4–H···O3 2.706(2) Å). The structural arrangement is very similar to that reported by Andreetti et al.[15] for the pyridine clathrate of the analogue **5a**. The binaphthyl moiety



SCHEME 1

Synthesis of 1,3-bridged calix[4]crown-6 conformers **1**–**3**

(i) PGD, K_2CO_3, CH_3CN, reflux; (ii) BGD, anhydrous toluene, *t*-BuOK, 70 °C; (iii) PicCl·HCl, Cs_2CO_3, anhydrous DMF, 60–70 °C; (iv) PGD or BGD, Cs_2CO_3, CH_3CN, reflux

has the two rings inclined at 68.5(1)° to reduce intramolecular interactions. The torsion angles of the O–C–C–O moieties in the polyether chains are in the range 55.9(2) to 77.5(2)°. On the other hand, the C–O–C–C torsion angles show more variability with four angles close to 90° (74.1(2), 89.7(2), 90.5(2) and 97.6(2)°) and four close to 180° (155.6(2), 158.5(2), 164.7(2) and 177.9(2)°).

The exhaustive alkylation of **5a** with an excess of 2-(chloromethyl)pyridine hydrochloride (PicCl·HCl) and Cs_2CO_3 in anhydrous *N*,*N*-dimethylformamide (DMF) at 60–70 °C afforded a mixture of dialkylated cone **1a** (21%) and partial cone **2a** (50%) conformers, which were separated by chromatography. Similarly, the reaction of **5b** with PicCl·HCl under the same conditions gave, after chromatography, cone **1b** (26%) and partial cone **2b** (39%). The stereochemical outcome of these reactions parallels the one observed in the alkylation of the 1,3-crown-5-*p*-*tert*-butylcalix[4]arene homologue under the same experimental conditions[10].

The remaining 1,3-alternate conformers **3a** and **3b** were obtained in 51 and 45% isolated yields by alkylation of *syn*-*distal* bis(α-picolyloxy)-*p*-*tert*-butylcalix[4]arene (**6**) with either PGD or BGD (1 equivalent) and Cs_2CO_3 (10 equivalents) in refluxing CH_3CN.

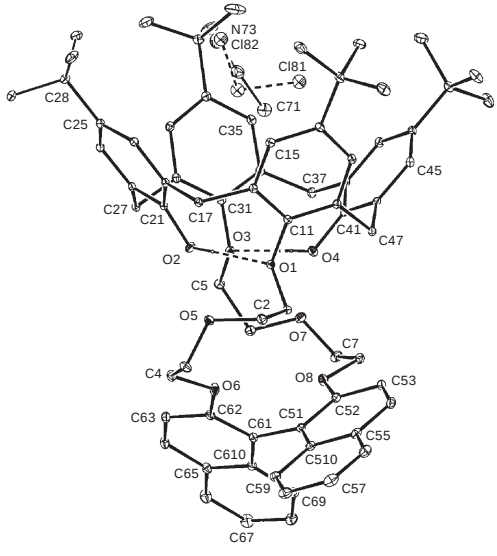


FIG. 1

A view of **5b** with our numbering scheme made with PLATON [14]. For clarity, displacement ellipsoids are drawn at the 10% probability level and the only H atoms shown are those involved in the intramolecular O–H···O hydrogen bonds. The *t*-Bu methyl groups at C28 are disordered over two sites; only the major orientation is shown

Structures and conformations of all new compounds were established by FAB (+) MS, ^{1}H and ^{13}C NMR spectroscopy. The NMR probes are especially useful for establishing calix[4]arene conformations, taking advantage of the well-documented patterns of the ^{1}H NMR resonances (particularly those arising from $ArCH_2Ar$[1] and OCH_2Py groups[16] and the position of the ^{13}C NMR resonances associated with the same groups[17].

The ^{1}H and ^{13}C NMR spectra of **1a** are almost superimposable (except for the crown ether portion) on those of the cone conformer of the smaller crown-5 analogue[10], suggesting that they adopt the same conformation in solution.

Strikingly, the resonances of the calixarene skeleton in **1b** are very close to those observed for **1a**, confirming that not only the length but also the nature of the polyether chain have no influence on the conformation of the calixarene. In **1b** the $ArCH_2Ar$ protons appear as two AX systems because of the axial chirality of the binaphthyl moiety, while the $OC\mathbf{H}_2Py$ protons are diastereotopic and give rise to an AB system. Furthermore, the four-spin system of the 2-pyridyl moieties in **1b** is shifted upfield in comparison with **1a**, because the heteroaromatic pendant groups lie under the shielding region of the juxtaposed binaphthyl units. Figure 2 shows the

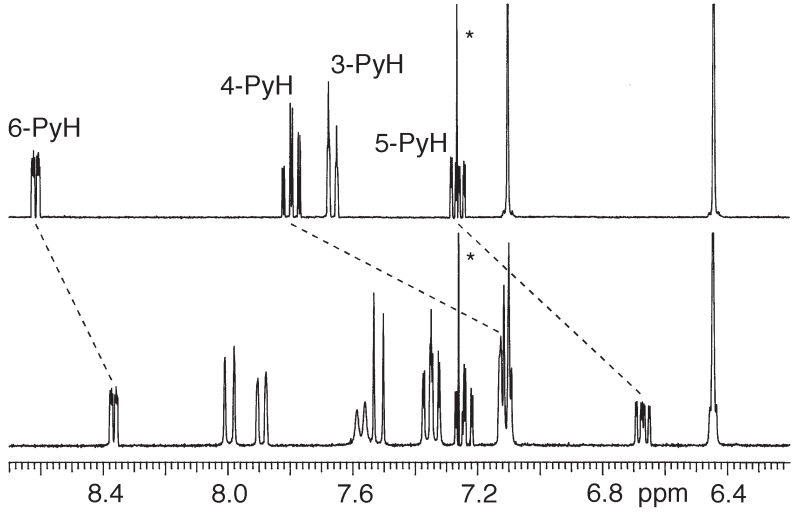


FIG. 2

The aromatic regions in the ^{1}H NMR spectra ($CDCl_3$, 300 MHz) of calix[4]arene crown-6 **1a** (upper trace) and its binaphthyl analogue **1b** (lower trace), the latter showing characteristic upfield shifts for the Py protons. The position of 4-PyH was confirmed by homodecoupling experiments; *, residual $CHCl_3$

similarities of the spectra of **1a** and **1b**, and chemical shift differences of the pyridyl side-arms, the most conspicuous shieldings pertaining to 4- and 5-PyH protons, with Δδ values of 0.68 and 0.59 ppm, respectively.

The C_s symmetry of partial cone conformer **2a** is corroborated by the presence of three singlets (ratio 2:1:1) for the *t*-Bu groups, one AX and one AB system (ratio 1:1) for the $ArCH_2Ar$ groups, two singlets (δ 4.03 and 5.12 ppm) for the $OC\mathbf{H}_2Py$ protons, and two sets of resonances for the *anti*-oriented pyridyl side-arms (henceforth the notations Py and Py′ will refer to the pyridine ring *syn* or *anti* to the crown ether moiety respectively). Previous studies have shown that calix[4]arenes in a fixed partial cone conformation very often display self-inclusion phenomena of the inverted heteroaromatic pendant group inside the calix cup generated by the three remaining aryl units[18]. This peculiarity is confirmed by the remarkable upfield shifts experienced by the Py′ protons in **2a** (with the diagnostically important 3-Py′H resonating at δ 4.73 ppm), which are suggestive of the inclusion of this group in a specific orientation (ring nitrogen *exo* to the calix cavity). In the partial cone calix[4]arene crown-5 analogue, the Py′ group is slightly more shielded (3-Py′H proton at δ 4.53 ppm)[10].

The ^{1}H NMR spectrum of the binaphthyl derivative **2b** is much more complex than that of **2a**, and was analysed with the aid of a 2D COSY spectrum (see Experimental for proton assignments). Despite the proliferation of the spectral lines arising from the chiral nature of **2b**, the whole conformation is very similar to that observed for **2a**, with the inverted Py′ group included into the cavity (doublet at δ 4.71 ppm for 3-Py′H). Also in this case, the resonances of the Py protons (*syn* to the polyether chain) are shifted upfield (Δδ in the range 0.12–0.39 ppm), relative to the pertinent protons in **2a**, by the ring current effect of the adjacent binaphthyl unit.

The 1,3-alternate conformer **3a** shows the expected AB system for the $ArCH_2Ar$ protons and a single resonance for the relevant carbons at δ 39.2 ppm. The geometry of this conformer is such that two pockets are generated by the two pairs of facing aryl rings, one above and one below the mean methylene-containing plane. Each of the two pockets is filled by the crown ether moiety on one side, and partly filled by the picolyl groups on the other side. This conformational arrangement can easily be deduced from the ^{1}H NMR spectrum of **3a**, which shows remarkable shieldings for the α-oxymethylene protons of the polyether chain (multiplet at δ 2.90–2.95 ppm) and for the 3-Py′H protons (double triplet at δ 6.49 ppm) of the pendant heteroaromatic ring (Δδ ca. 1.2 ppm relative to the pertinent protons in the cone conformer **1a**). On the other hand, as a result of the axial chirality present in **3b**, the high-field α-oxymethylene protons (4 H) are seen as

two sets of partly superimposed eight-line patterns centered at δ 2.65 and 2.75 ppm, while the $ArCH_2Ar$ protons split into two AB systems. Here again the 3-Py′H protons experience a similar upfield shift (Δδ 1.19 ppm) in comparison with the pertinent protons in the cone conformer **1b**.

Competitive Complexation Experiments by ESI-MS

Alkali metal ion (Na^+, K^+, Rb^+, and Cs^+) binding studies with the two series of calixcrowns **1a**–**3a** and **1b**–**3b** were undertaken by using the ESI-MS technique. This method, also called "supramolecular mass spectroscopy"[19], has recently been shown to provide a powerful tool for the rapid assessment of the host–guest complexes[20] and the selectivity of calixcrown systems with alkali metal ions[21]. Complexes preformed in an appropriate solution are transferred into the gas phase as charged and solvated species, and analyzed by an electrospray ionization ion trap mass spectrometer. The ions observed in the resulting mass spectra often reflect the equilibrium distribution of the complexes present in solution, so that binding affinities and selectivities can be directly estimated in competitive complexation experiments by measuring the ion intensities of relevant complexes observed after analyzing solutions containing well-defined compositions of host and guests.

Sample solutions were obtained by mixing equal volumes of stock solutions of calixcrown (10^{-3} mol/l) and alkali metal iodides (2.5×10^{-3} mol/l) in MeCN to a final 10^{-5}–10^{-6} M solution which contained calixcrown: Na^+:K^+:Rb^+:Cs^+ in a 1:2.5:2.5:2.5:2.5 ratio. The compositions of the solutions analyzed by ESI-MS are collected in Table I, while typical spectra with **3a** and **3b** are shown in Figs 3 and 4.

The mass spectrum with **3a** (Fig. 3) shows a prominent peak at *m/z* 1165.4 (relative abundance 100%) corresponding to the $[MCs]^+$ ion, along with peaks of lower intensity for fragment ions at *m/z* 1073.4 (33%), 1058.4 (16%), 981.3 (7%) and 966.4 (5%), corresponding to the sequential losses of a picolyl radical (Pic, C_6H_6N) and/or a neutral molecule of pyridine-2-carbaldehyde (Py–CHO, C_6H_5NO) from the $[MCs]^+$ ion. This fragmentation process is present in the entire series of calixcrowns under investigation (Table I). The perfect size-matching of the crown-6 loop for the Cs^+ ion is in agreement with the much lower intensities (≤3%, Table I) of molecular ion peaks corresponding to $Rb^+\subset$**3a**, $K^+\subset$**3a**, $Na^+\subset$**3a** ions (*m/z* 1117.5, 1071.5, and 1055.5, respectively). Solution-binding studies of alkali metal ions with 1,3-dialkoxycalix[4]crowns-6 have shown a strong selectivity for cesium ions[22], especially when they are fixed in the 1,3-alternate conforma-

tion, which has led to their utilization in the field of nuclear waste treatment[23]. In sharp contrast, the ESI mass spectrum of the binaphthyl-containing 1,3-alternate conformer **3b** shows a significant preference for Na^+ {$[MNa]^+$, *m/z* 1279.5 (100%)} over the larger alkali metal ions {$[MK]^+$, *m/z* 1295.4 (36%); $[MRb]^+$, *m/z* 1341.3 (17%); $[MCs]^+$, *m/z* 1389.3 (22%)} (Fig. 4).

TABLE I
ESI mass spectra of dipyridylcalixcrown-6 **1a**–**3a** and **1b**–**3b** after competitive complexation experiments with mixtures of sodium, potassium, rubidium and cesium iodides (2.5 equivalents of each salt) in acetonitrile[a,b]

Ion assignment	**1a**	**2a**	**3a**	**1b**	**2b**	**3b**
$[MCs]^+$	1165(3)	1165(53)	1165(100)	1389(3)	1389(59)	1389(22)
$[MCs–Pic]^+$		1073(100)[c]	1073(33)[c]		1297(100)	
$[MCs–PyCHO]^+$		1058(27)				
$[MCs–2Pic]^+$		981(16)	981(7)			
$[MRb]^+$	1117(10)	1117(19)	1117(3)	1341(8)	1341(48)	1341(17)
$[MRb–Pic]^{+\bullet}$	1025(4)	1025(36)		1249(8)	1249(61)	1249(8)
$[MRb–PyCHO]^+$		1010(8)			1234(9)	
$[MRb–2Pic]^+$		933(4)			1157(8)	
$[MK]^+$	1071(21)	1071(8)	1071(2)	1295(21)	1295(64)	1295(36)
$[MK–Pic]^{+\bullet}$	979(10)	979(11)		1203(19)	1203(76)	1203(13)
$[MK–2Pic]^+$				1111(17)	1111(19)	
$[MNa]^+$	1055(100)	1055(1)	1055(2)	1279(100)	1279(49)	1279(100)
$[MNa–Pic]^{+\bullet}$	963(29)			1187(67)[c]	1187(30)[c]	1187(46)[c]
$[MNa–PyCHO]^+$				1172(5)	1172(6)	1172(13)
$[MNa–2Pic]^+$	871(4)			1095(80)	1095(11)	1095(12)
$[MH]^+$	1033(23)	1033(2)	1033(<<1)	1257(28)	1257(61)	1257(13)
$[MH–Pic]^+$				1165(9)	1165(6)	

[a] Masses for relevant ions are reported to the closest integer with peak intensities in parentheses. [b] Only unequivocally assigned fragment ions having intensities ≥ 3% are listed. [c] The loss of a neutral molecule of pyridine-2-carbaldehyde (C_6H_5NO, 107 a.m.u.) from the $[MCs – Pic]^+$ or $[MNa – Pic]^+$ ions may account for the formation of additional fragment ions at *m/z* 966 (9% with **2a** and 5% with **3a**) or *m/z* 1080 (15% with **1b**, and 3% with both **2b** and **3b**).

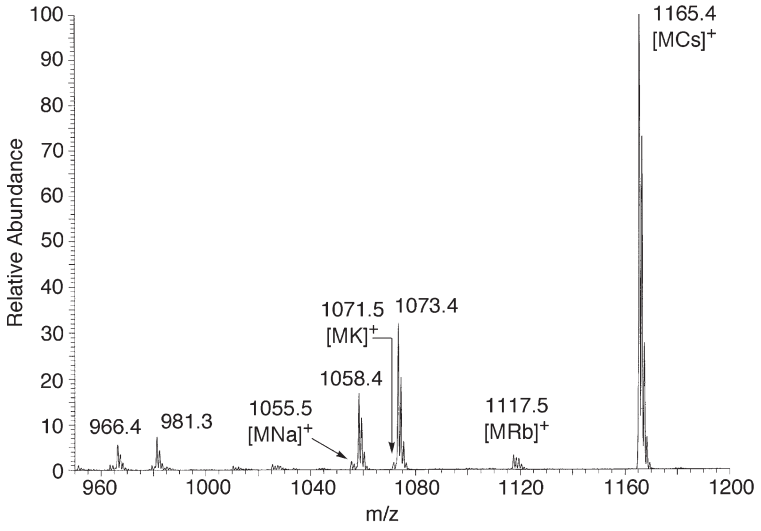


FIG. 3

ESI-MS of an acetonitrile solution of dipyridylcalix[4]arene crown-6 **3a** with Na^+, K^+, Rb^+, Cs^+ iodides (1:2.5:2.5:2.5:2.5)

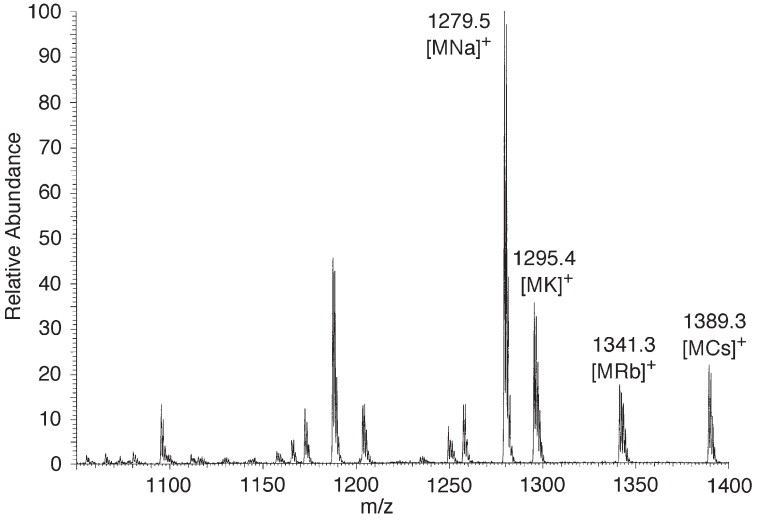


FIG. 4

ESI-MS of an acetonitrile solution of dipyridylcalix[4]arene crown-6 **3b** with Na^+, K^+, Rb^+, Cs^+ iodides (1:2.5:2.5:2.5:2.5). See Table I for peak assignment of fragments at masses lower than $[MNa]^+$ ion

The selectivity of a calixcrown for a given couple of metal ions can be estimated from the ratio of the ESI-MS distribution percentages of the relevant complexes listed in Table II [21]. Thus, the Cs^+/Na^+ selectivity for **2a** and **3a** is ca. 54 and 49, respectively. On the other hand, calixcrowns **1a**, **1b** and **3b** show a reverse Na^+/Cs^+ selectivity (about 33 for **1a**, **1b** and 4 for **3b**), while **2b** is rather unselective and shows a slight preference for K^+.

The unexpected Na^+ selectivity shown by **1b** and **3b** over the larger alkali metal ions may be rationalized in terms of steric hindrance of the crown cavity by the bulky binaphthyl subunit of the crown-6 strap as well as the α-picolyl pendant groups in the cone conformer **1b** or the upper-rim *t*-Bu substituents in the 1,3-alternate conformer **3b**. Although this explanation does not hold with cone **1a**, which lacks the binaphthyl residue, the present results are in agreement with recent ESI-MS studies by Dozol et al.[24], who have shown that the Cs^+ selective 1,3-dialkoxycalix[4]crowns-6 display an affinity for Na^+ ions, which is weak in solution, but surprisingly stronger in the gas phase.

In conclusion, we have synthesized two new series of 1,3-bis(α-picolyloxy)calix[4]crown-6 derivatives and screened their binding selectivities for alkali metal iodides by ESI-MS. The potential of these new classes of cation-segregating agents in the non-covalent synthesis of multicomponent supramolecular assemblies in combination with perfluorocarbon anion receptors is currently under study.

TABLE II
Binding selectivities of dipyridylcalixcrown-6 **1a**,**b**–**3a**,**b** for alkali metal iodides in acetonitrile[a]

Calixcrown	$[MNa]^+$	$[MK]^+$	$[MRb]^+$	$[MCs]^+$
1a	74.6	15.7	7.5	2.2
2a	1.2	9.9	23.5	65.4
3a	1.9	1.9	2.8	93.4
1b	75.7	15.9	6.1	2.3
2b	22.3	29.1	21.8	26.8
3b	57.1	20.6	9.7	12.6

[a] Experimental values expressed as per cent of [M + alkali metal cation] present in a 1:2.5:2.5:2.5:2.5 solution, calculated as the peak intensity of [M + alkali metal cation] divided by the sum of the peak intensities of each complex present.

EXPERIMENTAL

Melting points were determined on a Kofler or "Electrothermal" melting point apparatus and are uncorrected. Unless otherwise stated, the ^{1}H (300 MHz) and ^{13}C (75 MHz) NMR spectra (δ, ppm; *J*, Hz) were obtained in $CDCl_3$ with tetramethylsilane as the internal standard at room temperature. The multiplicity of the ^{13}C signals was determined by means of the APT technique. FAB (+) mass spectra were obtained on a Finnigan MAT 90 spectrometer using 3-nitrobenzyl alcohol as the matrix. ESI mass spectra were recorded on a Finnigan LCQDECA ThermoQuest mass spectrometer with the following main settings: source voltage, 5 V; capillary voltage, 40 V; capillary temperature, 225 °C; standard calibration. Sample solutions were introduced into the mass spectrometer source with a syringe pump at a flow-rate of 5 μl/min. The final spectrum is the sum of several scans. All chemicals were reagent grade and were used without further purification. Pentaethylene glycol ditosylate[25], 2,2′-bis{2-[(tosyloxy)ethoxy]ethoxy}-1,1′-binaphthalene[26], and calixarenes **4** [27], **5a** and **6** [28] were prepared according to reported procedures or slight modifications thereof. All reactions were carried out under nitrogen atmosphere.

5,11,17,23-Tetra-*tert*-butyl-25,27-(1,1′-binaphthalene-2,2′-diyl-crown-6)-26,28-dihydroxycalix[4]arene (**5b**)[29]

A stirred mixture of **4** (toluene 1:1 complex, 1.0 g, 1.35 mmol) and *t*-BuOK (0.16 g, 1.42 mmol) in anhydrous toluene (40 ml) was heated at 70 °C for 0.5 h. A solution of BGD (1.1 g, 1.43 mmol) in anhydrous toluene (30 ml) was then added over 2 h. After 24 h at 70 °C, a second portion of *t*-BuOK (0.16 g, 1.42 mmol) was added, and the mixture was then kept at the same temperature for an additional 24 h. After cooling, the mixture was acidified with 1 M HCl, and extracted with Et_2O (2 × 50 ml). The combined organic extracts were washed with water and dried ($MgSO_4$). Evaporation of the solvent left a residue, which was column-chromatographed (SiO_2, hexanes–AcOEt, 5:1) to give the crown-6 derivative **5b** (0.9 g, 62%): white crystals, m.p. 332–333 °C (MeCN–CH_2Cl_2). For $C_{72}H_{82}O_8$ (1074.6) calculated: 80.41% C, 7.69% H; found: 80.27% C, 7.82% H. ^{1}H NMR: 1.03, 1.28 s, 18 H each (*t*-Bu); 3.20 dt, 2 H, *J* = 11.9, 2.4 (OCH_2CH_2O); 3.29 d, 2 H, *J* = 12.2 (equatorial-$ArCH_2Ar$); 3.30 d, 2 H, *J* = 13.2 (equatorial-$ArCH_2Ar$); 3.61 ddd, 2 H, *J* = 11.5, 7.8, 3.5 (OCH_2CH_2O); 3.72–3.89 m, 8 H (OCH_2CH_2O); 4.22 ddd, 2 H, *J* = 10.3, 6.2, 4.9 (OCH_2CH_2O); 4.30 d, 2 H, *J* = 13.2 (axial-$ArCH_2Ar$); 4.37 d, 2 H, *J* = 12.2 (axial-$ArCH_2Ar$); 4.46 ddd, 2 H, *J* = 10.3, 6.2, 4.9 (OCH_2CH_2O); 6.85, 6.94, 7.01, 7.12 d, 2 H each, *J* = 2.4 (ArH); 7.18 m, 2 H (8,8′-binaph); 7.22 ddd, 2 H, *J* = 8.5, 6.2, 1.3 (7,7′-binaph); 7.31 ddd, 2 H, *J* = 8.1, 6.2, 1.8 (6,6′-binaph); 7.48 d, 2 H, *J* = 9.0 (3,3′-binaph); 7.66 s, 2 H (OH); 7.85 dt, 2 H, *J* = 8.0, 0.8 (5,5′-binaph); 7.94 d, 2 H, *J* = 9.0 (4,4′-binaph). ^{13}C NMR: 30.9, 31.8 t ($ArCH_2Ar$); 31.0, 31.7 q (*t*-Bu); 33.8, 34.0 s (*t*-Bu); 69.9, 70.1, 70.5, 75.9 t (OCH_2); 115.3 d; 120.5 s; 123.6, 124.9, 125.08, 125.11, 125.5, 125.8, 126.3 d; 127.1 s; 127.8 d; 128.3, 129.28 s; 129.31 d; 132.8, 133.4, 134.2, 141.5, 147.2, 149.6, 150.5, 154.3 s. FAB (+) MS, *m/z* 1075 [MH^+].

Alkylation of **5a** with 2-(Chloromethyl)pyridine Hydrochloride

A stirred mixture of **5a** (0.62 g, 0.73 mmol), PicCl·HCl (0.49 g, 3 mmol) and Cs_2CO_3 (2.44 g, 7.5 mmol) in dry DMF (20 ml) was heated at 60–70 °C for 20 h. Evaporation of the solvent gave a solid, which was treated with water (20 ml) and stirred for 10 min. The solid was collected by filtration, dissolved in CH_2Cl_2, and dried ($MgSO_4$). Removal of the solvent gave a

residue, which was purified by column chromatography (neutral Al_2O_3, *n*-hexane–AcOEt, 75:25 to 0:100), to afford two fractions.

5,11,17,23-Tetra-tert-butyl-25,27-crown-6-26,28-bis(2-pyridylmethoxy)calix[4]arene, partial cone conformer (**2a**) *(fraction A)*: 0.38 g, 50% yield, m.p. 258–259 °C (MeOH–CH_2Cl_2). For $C_{66}H_{84}N_2O_8$ (1032.6) calculated: 76.71% C, 8.19% H, 2.71% N; found: 76.87% C, 8.39% H, 2.66% N. ^{1}H NMR: 0.88, 1.17, 1.43 s, ratio 2:1:1, 36 H (*t*-Bu); 3.03 d, 2 H, *J* = 12.1 (equatorial-ArCH_2Ar); 3.31–3.38 m, 2 H (OCH_2CH_2O); 3.54–3.92 m, 18 H (OCH_2CH_2O); 3.84 d, 2 H, *J* = 16.8 (equatorial-ArCH_2Ar); 3.91 d, 2 H, *J* = 16.8 (axial-ArCH_2Ar); 4.03 s, 2 H (OC**H**$_2$Py′); 4.31 d, 2 H, *J* = 12.1 (axial-ArCH_2Ar); 4.73 d, 1 H, *J* = 7.6 (3-Py′H); 5.12 s, 2 H (OC**H**$_2$Py); 6.62 td, 1 H, *J* = 7.6, 1.9 (4-Py′H); 6.64 d, 2 H, *J* = 2.4 (ArH); 6.71 ddd, 1 H, *J* = 7.6, 4.9, 1.2 (5-Py′H); 6.97 d, 2 H, *J* = 2.4 (ArH); 7.00, 7.17 s, 2 H each (ArH); 7.18 ddd, 1 H, *J* = 7.6, 4.9, 1.2 (5-PyH); 7.34 dt, 1 H, *J* = 7.6, 1.2 (3-PyH); 7.62 td, 1 H, *J* = 7.6, 1.8 (4-PyH); 8.16 ddd, 1 H, *J* = 4.9, 1.9, 0.9 (6-Py′H); 8.50 ddd, 1 H, *J* = 4.9, 1.8, 0.9 (6-PyH). ^{13}C NMR: 31.0 t (ArCH_2Ar); 31.1, 31.4, 31.7 q (*t*-Bu); 33.6, 34.0, 34.1 s (*t*-Bu); 38.9 t (ArCH_2Ar); 69.8 t (OCH_2CH_2O); 69.9 t (OCH_2Py′); 70.3, 70.79, 70.83, 70.9 t (OCH_2CH_2O); 78.3 t (OCH_2Py); 120.5, 122.5, 124.37, 124.38, 124.41, 125.0, 125.3, 125.8 d (3,5-Py′, 3,5-Py, and Ar); 132.2, 132.8, 134.0, 135.1 s (bridgehead-C); 136.0, 136.1 d (4-Py′ and 4-Py); 144.7, 145.14, 145.15 s (C_{sp2}–*t*-Bu); 147.3, 148.8 d (6-Py′ and 6-Py); 152.0, 153.3, 153.9 s (C_{sp2}–O); 157.5, 157.9 s (2-Py′ and 2-Py). FAB (+) MS, *m/z* 1033 [MH^+].

5,11,17,23-Tetra-tert-butyl-25,27-crown-6-26,28-bis(2-pyridylmethoxy)calix[4]arene, cone conformer (**1a**) *(fraction B)*: 0.16 g, 21% yield, m.p. 195–197 °C (MeOH–CH_2Cl_2). For $C_{66}H_{84}N_2O_8$ (1032.6) calculated: 76.71% C, 8.19% H, 2.71% N; found: 76.47% C, 8.40% H, 2.77% N. ^{1}H NMR: 0.82, 1.33 s, 18 H each (*t*-Bu); 3.10 d, 4 H, *J* = 12.6 (ArCH_2Ar); 3.43–3.63 m, 8 H (OCH_2CH_2O); 3.62 s, 4 H (OCH_2CH_2O); 3.90–4.16 m, 8 H (OCH_2CH_2O); 4.38 d, 4 H, *J* = 12.6 (ArCH_2Ar); 4.89 s, 4 H (OCH_2Py); 6.44, 7.10 s, 4 H each (ArH); 7.26 ddd, 2 H, *J* = 7.6, 4.9, 1.2 (5-PyH); 7.67 dt, 2 H, *J* = 7.6, 1.2 (3-PyH); 7.79 td, 2 H, *J* = 7.6, 1.8 (4-PyH); 8.61 ddd, 2 H, *J* = 4.9, 1.8, 0.9 (6-PyH). ^{13}C NMR: 31.0 t (ArCH_2Ar); 31.1, 31.7 q (*t*-Bu); 33.6, 34.1 s (*t*-Bu); 69.5, 70.5, 70.6, 71.1, 72.1 t (OCH_2CH_2O); 78.8 t (OCH_2Py); 122.8, 123.4 d (3,5-Py); 124.6, 125.6 d (Ar); 131.7, 135.4 s (bridgehead-C); 136.8 d (4-Py); 144.5, 145.1 s (C_{sp2}–*t*-Bu); 149.2 d (6-Py); 152.0, 154.4 s (C_{sp2}–O); 157.6 s (2-Py). FAB (+) MS, *m/z* 1033 [MH^+].

Alkylation of **5b** with 2-(Chloromethyl)pyridine Hydrochloride

A stirred mixture of **8b** (0.418 g, 0.39 mmol), PicCl·HCl (0.256 g, 1.56 mmol) and Cs_2CO_3 (1.27 g, 3.9 mmol) in dry DMF (20 ml) was heated at 60–70 °C for 24 h. Usual workup, followed by column chromatography (SiO_2, CH_2Cl_2–AcOEt, 15:1 to 3:1) afforded two main fractions.

5,11,17,23-Tetra-tert-butyl-25,27-(1,1′-binaphthalene-2,2′-diyl-crown-6)-26,28-bis(2-pyridylmethoxy)calix[4]arene, cone conformer (**1b**) *(fraction A)*: 127 mg, 26% yield, white crystals, m.p. 276–277 °C (MeOH–CH_2Cl_2). For $C_{84}H_{92}N_2O_8$ (1256.7) calculated: 80.22% C, 7.37% H, 2.23% N; found: 80.35% C, 7.62% H, 2.21% N. ^{1}H NMR: 0.82, 1.34 s, 18 H each (*t*-Bu); 3.11 d, 2 H, *J* = 12.5 (equatorial-ArCH_2Ar); 3.17 d, 2 H, *J* = 12.7 (equatorial-ArCH_2Ar); 3.18 t, 4 H, *J* = 6.1 (OCH_2CH_2O); 3.63 ddd, 2 H, *J* = 10.5, 8.7, 5.8 (OCH_2CH_2O); 3.74 ddd, 2 H, *J* = 10.3, 8.5, 4.9 (OCH_2CH_2O); 3.83–3.96 m, 4 H (OCH_2CH_2O); 4.07–4.16 m, 2 H (OCH_2CH_2O); 4.22–4.30 m, 2 H (OCH_2CH_2O); 4.31 d, 2 H, *J* = 12.5 (axial-ArCH_2Ar); 4.43 d, 2 H, *J* = 12.7 (axial-ArCH_2Ar); 4.71, 4.82 d, 2 H each, *J* = 11.2 (OC**H**$_2$Py); 6.44 pseudo-s, 4 H (ArH);

6.67 ddd, 2 H, *J* = 7.6, 4.9, 1.2 (5-PyH); 7.11 m, 6 H (ArH and 4-PyH); 7.24 ddd, 2 H, *J* = 8.4, 6.8, 1.4 (6,6′(7,7′)-binaph); 7.34 ddd, 2 H, *J* = 8.2, 6.7, 1.4 (7,7′(6,6′)-binaph); 7.35 d, 2 H, *J* = 7.9 (8,8′-binaph); 7.52 d, 2 H, *J* = 9.0 (3,3′-binaph); 7.57 d, 2 H, *J* = 7.6 (3-PyH); 7.89 br d, 2 H, *J* = 7.9 (5,5′-binaph); 7.99 d, 2 H, *J* = 9.0 (4,4′-binaph); 8.36 ddd, 2 H, *J* = 4.9, 1.8, 0.9 (6-PyH). ^{13}C NMR: 30.9 ($ArCH_2Ar$); 31.1, 31.7 (*t*-Bu); 33.6, 34.1 (*t*-Bu); 67.7, 69.1, 69.3, 71.8 (OCH_2CH_2O); 79.1 (OCH_2Py); 115.2, 120.2, 122.8, 123.2, 123.6, 124.6, 124.7, 125.4, 125.5, 125.7, 126.4, 127.8, 129.2, 129.3, 131.6, 131.7, 134.2, 135.31, 135.33, 136.6 (4-Py); 144.6, 145.2 (C_{sp2}–*t*-Bu); 149.2 (6-Py); 151.9, 154.0, 154.4 (C_{sp2}–O); 157.2 (2-Py). FAB (+) MS, *m/z* 1257 [MH^+].

5,11,17,23-Tetra-tert-butyl-25,27-(1,1′-binaphthalene-2,2′-diyl-crown-6)-26,28-bis(2-pyridylmethoxy)calix[4]arene, partial cone conformer (**2b**) *(fraction B)*: 191 mg, 39% yield, white crystals, m.p. 188–189 °C ($MeOH–CH_2Cl_2$). For $C_{84}H_{92}N_2O_8$ (1256.7) calculated: 80.22% C, 7.37% H, 2.23% N; found: 80.55% C, 7.63% H, 2.18% N. ^{1}H NMR: 0.88, 0.91, 1.15, 1.38 s, 9 H each (*t*-Bu); 2.94–4.45 m, 22 H (overlapping OCH_2CH_2O, $ArCH_2Ar$, and OCH_2Py'); 3.00 d, 1 H, *J* = 12.4 (equatorial-$ArCH_2Ar$); 3.24 d, 1 H, *J* = 13.1 (equatorial-$ArCH_2Ar$); 4.18 d, 1 H, *J* = 12.4 (axial-$ArCH_2Ar$); 4.50 d, 1 H, *J* = 13.1 (axial-$ArCH_2Ar$); 4.71 d, 1 H, *J* = 7.6 (3-Py′H); 4.77, 5.11 d, 1 H each, *J* = 11.7 (OCH_2Py); 6.58 d, 1 H, *J* = 2.5 (ArH); 6.64 td, 1 H, *J* = 7.6, 1.8 (4-Py′H); 6.68–6.74 m, 2 H (5-Py′ and ArH); 6.79 ddd, 1 H, *J* = 7.6, 4.9, 1.2 (5-PyH); 6.95, 6.97, 7.03 d, 1 H each, *J* = 2.5 (ArH); 7.05–7.14 m, 5 H (ArH and 8,8′-binaph); 7.17–7.21 m, 2 H (7,7′-binaph); 7.22 dt, 1 H, *J* = 7.6, 1.2 (3-PyH); 7.29 ddd, 1 H, *J* = 8.1, 6.7, 1.4 (6(6′)-binaph); 7.33 ddd, 1 H, *J* = 8.1, 6.7, 1.4 (6′(6)-binaph); 7.34 td, 1 H, *J* = 7.6, 1.8 (4-PyH); 7.42 d, 1 H, *J* = 9.1 (3(3′)-binaph); 7.46 d, 1 H, *J* = 9.0 (3′(3)-binaph); 7.79 dd, 1 H, *J* = 8.5, 0.9 (5(5′)-binaph); 7.84 d, 1 H, *J* = 9.1 (4(4′)-binaph); 7.89 d, 1 H, *J* = 8.1 (5′(5)-binaph); 7.99 d, 1 H, *J* = 9.0 (4′(4)-binaph); 8.16 ddd, 1 H, *J* = 4.9, 1.8, 0.9 (6-Py′H); 8.36 ddd, 1 H, *J* = 4.9, 1.8, 0.9 (6-PyH). ^{13}C NMR: 30.8, 30.9, 38.4, 39.2 t ($ArCH_2Ar$); 31.1, 31.2, 31.4, 31.7 q (*t*-Bu); 33.6, 33.7, 34.0, 34.1 s (*t*-Bu); 67.6, 67.7, 69.1, 69.3, 69.5, 69.9, 70.1, 70.3, 70.8, 79.0 t (OCH_2CH_2O and OCH_2Py); 115.1, 115.3, 119.8 d; 120.1, 120.3 s; 120.5, 122.6, 123.5, 123.8, 124.2, 125.0, 125.1, 125.2, 125.36, 125.42, 125.46, 125.58, 125.60, 125.7, 126.27, 126.29, 127.84, 127.87, 129.1, 129.21 d; 129.24 s; 129.28 d; 129.30, 132.1, 132.3, 132.80, 132.84, 133.5, 133.6, 134.2, 135.0, 135.4 s; 136.0, 136.1d (4-Py′ and 4-Py); 144.6, 145.0, 145.3 s (C_{sp2}–*t*-Bu); 147.4, 149.1 d (6-Py′ and 6-Py); 152.7, 153.2, 153.3, 153.86, 153.89, 154.0 s (C_{sp2}–O); 157.3, 157.9 s (2-Py and 2-Py′). FAB (+) MS, *m/z* 1257 [MH^+].

5,11,17,23-Tetra-*tert*-butyl-25,27-crown-6-26,28-bis(2-pyridylmethoxy)calix[4]arene, 1,3-Alternate Conformer (**3a**)

A stirred mixture of **6** (0.5 g, 0.6 mmol), PGD (0.34 g, 0.63 mmol) and Cs_2CO_3 (1.97 g, 6 mmol) in CH_3CN (70 ml) was refluxed for 24 h. After cooling, the solvent was evaporated, and the residue was partitioned between water and CH_2Cl_2. The organic layer was dried over $MgSO_4$ and concentrated. The crude product was purified by column chromatography (neutral Al_2O_3, cyclohexane–AcOEt, 5:1) to afford colorless crystals of **3a** (0.316 g, 51% yield), m.p. 146–148 °C (MeOH). For $C_{66}H_{84}N_2O_8$ (1032.6) calculated: 76.71% C, 8.19% H, 2.71% N; found: 76.43% C, 8.40% H, 2.67% N. ^{1}H NMR: 0.81, 1.38 s, 18 H each (*t*-Bu); 2.90–2.95 m, 4 H (OCH_2CH_2O); 3.27–3.32 m, 4 H (OCH_2CH_2O); 3.54 dd, 8 H, *J* = 4.3, 2.7 (OCH_2CH_2O); 3.57 s, 4 H (OCH_2CH_2O); 3.66, 3.83 d, 4 H each, *J* = 16.7 ($ArCH_2Ar$); 4.71 s, 4 H (OCH_2Py'); 6.49 dt, 2 H, *J* = 7.6, 1.2 (3-Py′H); 6.69, 7.07 s, 4 H each (ArH); 7.12 ddd, 2 H, *J* = 7.6, 4.9,

1.2 (5-Py′H); 7.57 td, 2 H, *J* = 7.6, 1.8 (4-Py′H); 8.47 ddd, 2 H, *J* = 4.9, 1.8, 0.9 (6-Py′H). ^{13}C NMR: 31.0, 31.7 q (*t*-Bu); 33.5, 34.0 s (*t*-Bu); 39.2 t ($ArCH_2Ar$); 67.8, 70.0, 70.8, 71.1, 71.4, 72.8 t (OCH_2CH_2O and OCH_2Py'); 122.0, 122.5 d (3,5-Py′); 125.6, 125.9 d (Ar); 132.8, 133.2 s (bridgehead-C); 136.8 d (4-Py′); 144.5, 145.0 s (C_{sp2}–*t*-Bu); 148.1 d (6-Py′); 153.9, 154.1 s (C_{sp2}–O); 158.0 s (2-Py′). FAB (+) MS, *m/z* 1033 [MH^+].

5,11,17,23-Tetra-*tert*-butyl-25,27-(1,1′-binaphthalene-2,2′-diyl-crown-6)-26,28-bis(2-pyridylmethoxy)calix[4]arene, 1,3-Alternate Conformer (**3b**)

A stirred mixture of **6** (0.442 g, 0.53 mmol), BGD (0.408 g, 0.53 mmol) and Cs_2CO_3 (1.73 g, 5.3 mmol) in CH_3CN (70 ml) was refluxed for 24 h. Usual workup, followed by column chromatography (SiO_2, CH_2Cl_2–Et_2O, 95:5) afforded **3b** (0.3 g, 45% yield) as colorless crystals, m.p. 265–266 °C (MeOH). For $C_{84}H_{92}N_2O_8$ (1256.7) calculated: 80.22% C, 7.37% H, 2.23% N; found: 80.12% C, 7.53% H, 2.31% N. ^{1}H NMR: 0.81, 1.25 s, 18 H each (*t*-Bu); 2.65, 2.75, 3.24 ddd, 2 H each, *J* = 10.2, 8.6, 5.9 (OCH_2CH_2O); 3.36–3.48 m, 6 H (OCH_2CH_2O); 3.65, 3.66, 3.76, 3.81 d, 2 H each, *J* = 16.7 ($ArCH_2Ar$); 3.90, 4.19 ddd, 2 H each, *J* = 10.2, 8.6, 5.9 (OCH_2CH_2O); 4.68 s, 4 H (OCH_2Py'); 6.48 dt, 2 H, *J* = 7.6, 1.2 (3-Py′H); 6.68 s, 4 H (ArH); 6.96, 7.05 d, 2 H each, *J* = 2.4 (ArH); 7.08 br d, 2 H, *J* = 8.0 (8,8′-binaph); 7.09 ddd, 2 H, *J* = 7.6, 4.8, 1.2 (5-Py′H); 7.21 ddd, 2 H, *J* = 8.2, 6.8, 1.4 (7,7′-binaph); 7.33 ddd, 2 H, *J* = 8.2, 6.8, 1.4 (6,6′-binaph); 7.43 d, 2 H, *J* = 9.0 (3,3′-binaph); 7.54 td, 2 H, *J* = 7.6, 1.8 (4-Py′H); 7.89 br d, 2 H, *J* = 8.0 (5,5′-binaph); 7.97 d, 2 H, *J* = 9.0 (4,4′-binaph); 8.45 ddd, 2 H, *J* = 4.8, 1.8, 0.9 (6-Py′H). ^{13}C NMR: 31.1, 31.8 (*t*-Bu); 33.5, 34.0 (*t*-Bu); 39.1 ($ArCH_2Ar$); 66.9, 67.1, 69.2, 69.5 (OCH_2CH_2O); 72.7 (OCH_2Py'); 115.4, 120.4, 122.0, 122.3, 123.6, 125.3, 125.41 (×2), 125.43 (×2), 126.3, 127.8, 129.3, 129.4, 132.49, 132.51, 132.90, 132.92, 134.1, 136.8 (4-Py′); 144.6, 144.8 (C_{sp2}–*t*-Bu); 148.1 (6-Py′); 153.58, 153.60, 154.1 (C_{sp2}–O); 158.0 (2-Py′). FAB (+) MS, *m/z* 1257 [MH^+].

X-ray Crystallographic Study

Crystals of **5b**, $C_{72}H_{82}O_8 \cdot 0.90(C_2H_3N) \cdot 0.10(CH_2Cl_2)$, MW = 1120.9, triclinic, space group $P\bar{1}$, *a* = 10.8999(2) Å, *b* = 16.0960(3) Å, *c* = 19.2399(2) Å, α = 71.7230(8)°, β = 87.8078(8)°, γ = 73.7639(8)°, *V* = 3072.89(9) Å^3, *Z* = 2, d_x = 1.211 g/cm^3, μ = 0.09 mm^{-1}, *F*(000) = 1204. Data were collected using a Nonius KappaCCD diffractometer at 150 K with θ in the range 2.5–26.3°. In all, some 24 138 reflections were measured and these reduced to 12 433 unique measurement (R_{int} 0.0176) of which 9291 had $I > 2\sigma(I)$. The structure was solved by direct methods using SHELXS97 [30] and refined using SHELXL97 [31] via full-matrix least-squares calculations using all 12 433 measured F^2 data. All H atoms were treated as riding atoms. The calixarene cup includes a mixture of acetonitrile and dichloromethane (0.90/0.10 as the relative occupancies). The orientation of these molecules is as usually found, with the acetonitrile methyl and dichloromethane methylene groups directed to the base of the calixarene cup. No intra-cup calixarene–solvent distances are less than the sum of the relevant van der Waals radii. Inter-calixarene contacts are also of the van der Waals variety and there are no solvent-accessible voids in the crystal lattice.

The methyl groups of one of the calixarene *t*-Bu substituents were disordered over two orientations, one major and one minor. With the exception of the *t*-Bu carbons present in the minor orientation, all calixarene- and acetonitrile-of-solvation non-H atoms were allowed anisotropic displacement parameters during the refinement. An overall isotropic vibration parameter was refined for the atoms of the 0.10 occupancy dichloromethane mole-

cule. The final refinement cycles had 798 variables and maximum shift/error = 0.008. The final difference map was featureless with maximum and minimum density values of 0.416 and –0.225 e/Å^3. Final R values are 0.0414 (for the 9291 observed reflections) with $R_w(F^2)$ = 0.1225 for all 12 433 measured reflections. Full details are in the archived crystallographic CIF file. CCDC 121654 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

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