Selective sensing of caesium ions by novel calix[4]arene bis(dibenzocrown) ethers in an aqueous environment

Jong Seung Kim,*,†,[a] Il Hwan Suh,[b] Jong Kuk Kim[c] and Moon Hwan Cho[d]

[a] *Department of Chemistry, Konyang University, Nonsan 320-711, Korea*
[b] *Department of Physics, Chungnam National University, Taejon 305-764, Korea*
[c] *Department of Chemical Engineering, Konyang University, Nonsan 320-711, Korea*
[d] *Department of Chemistry, Kangwon National University, Chuncheon 200-701, Korea*

Calix[4]arene bis(dibenzocrown) ethers **3** and **4** were successfully synthesized in the fixed 1,3-alternate conformation in over 70% yield *via* the reaction of calix[4]arene with dibenzo dimesylates **6** and **7**, respectively, in acetonitrile in the presence of caesium carbonate as base. Exhibiting typical ^{1}H NMR spectrum patterns, **3** and **4** are in the 1,3-alternate conformation, which is confirmed by X-ray analysis. Among four synthetic compounds tested, **3** shows the best selectivity and efficiency for a caesium ion complexation over other alkali metal ions using the single flux method through a bulk liquid membrane system. Enhancement of the complexation ability is attributable to the flatness and lipophilicity of the ethereal linkages caused by introducing the dibenzo groups on the calix[4]arene moiety. Two phase extraction experiments using calix[4]arene bis(crown) ethers with caesium ions are found to give a 1:1 ligand–metal complexation ratio.

Introduction

Calix[4]arenes have been of particular interest as organic hosts and selective ionophores in inclusion complexation.[1] Much attention has been paid to the conformational behavior of calix[4]arene *via* solid state, solution state, molecular mechanics and NMR experiments.[2–4] It is known that the calix[4]arenes are able to exist in the following four different conformations: cone, partial cone, 1,2-alternate and 1,3-alternate.[5,6] 1,3-Distal capping of calix[4]arene at the lower rim has been achieved with polyether linkages such as calix-crown ethers,[7] and double-calix-crowns.[8] Reinhoudt and co-workers reported that 1,3-dialkoxycalix[4]arene-crown-6 derivatives were successfully prepared and are exceptionally selective ionophores for caesium ions when they are fixed in the 1,3-alternate conformation.[9] In particular, calix-bis(crowns) in which the polyether linkages are directly connected to the upper and lower rims of calix[4]arene in the 1,3-alternative conformation compounds **1** and **2** were
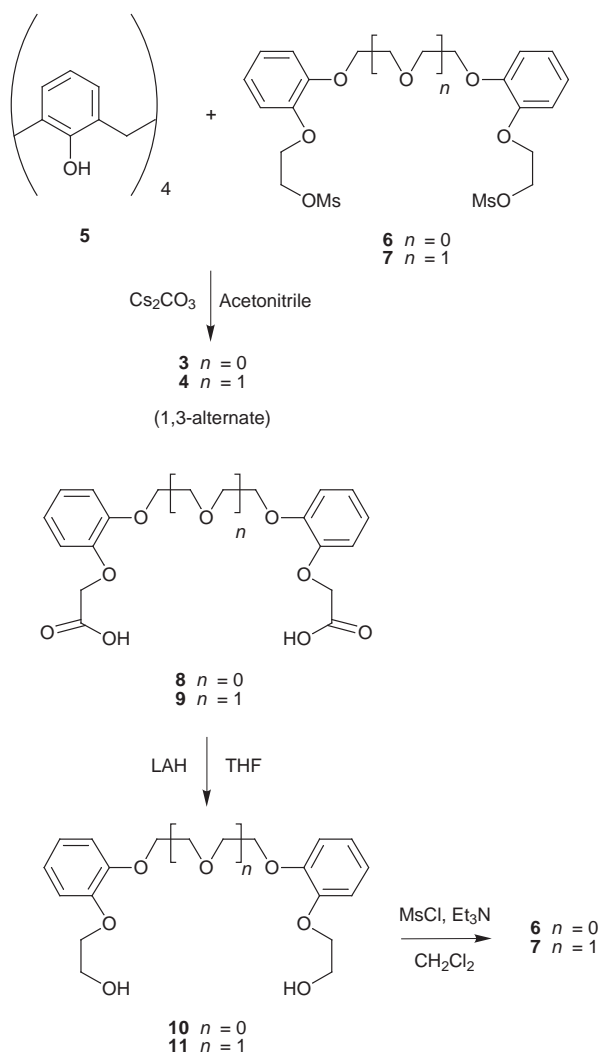

1 n = 0
2 n = 1

3 n = 0
4 n = 1
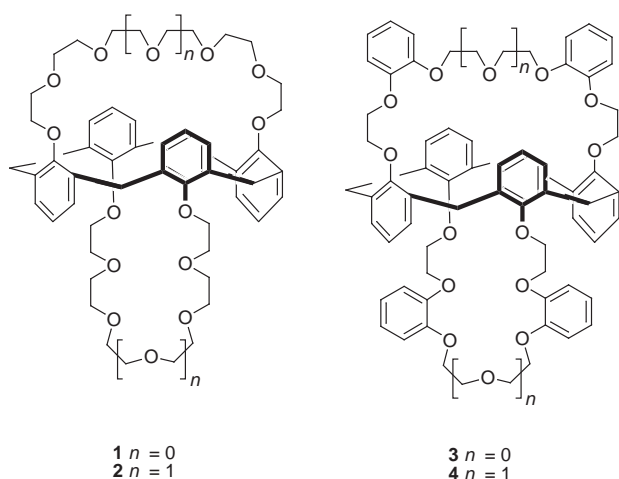
recently reported to be highly selective caesium ion carriers.[10] It has been shown that introducing aryl substituents such as phenyl or naphthyl into the polyether ring greatly enhances the

metal ion selectivity and efficiency.[11] It is also reported that introduction of a 1,2-phenylene residue in the middle of the crown of calix[4]-bis(crown)-6 favors the complexation of caesium over other alkaline metal ions because the replacement of sp³ carbons by sp² ones in the ethereal linkage leads to a flattening of the glycolic chain, the 'flattening effect'.[12] However, calix[4]arene crown ethers having two benzo moieties, and thus having the two benefits listed above, have not been studied so far. With this in mind, we have investigated the synthesis, crystal structure and complexation behavior of calix[4]arene bis-(dibenzocrown)-6-ethers. This will enable their utilization in the field of nuclear waste treatment, which is important given current environmental concerns.[13]

Results and discussion

To study the influence of the lipophilicity of the organic carrier, as well as the flattening effect of the ethereal linkage, when the calix[4]arene crown ether complexes with a specific metal ion, calix[4]arene bis(dibenzocrown) ethers **3** and **4** were prepared in the 1,3-alternate conformation. The synthetic route for the precursors and the cyclization is depicted in Scheme 1. The starting materials, acyclic polyether dicarboxylic acids **8** and **9**, can be easily prepared by reaction of the corresponding bisphenol with 2-bromoacetic acid in the presence of NaH as a base in THF.[14] Subsequently, reduction of the diacid with lithium aluminum hydride in THF gave the corresponding diol **10** in 93% yield. Mesylation of the diol with methanesulfonyl chloride in the presence of triethylamine in CH_2Cl_2 provided 1,2-bis[2-(2-methylsulfonyloxyethoxy)phenoxy]ethane **6** in 91% yield. Ditosylation of the diols using toluene-*p*-sulfonyl chloride was also attempted. However, due to difficulties in handling toluene-*p*-sulfonyl chloride and pyridine (as the base) in the laboratory, and the unpleasant smell of the reaction, we changed the leaving group to mesylate. The yield of the tosylation using the known method is *ca.* 50–70%. However, dimesylation of the dibenzo diol using methanesulfonyl chloride in the presence of triethylamine gave the dibenzo dimesylate in greater than 90% yield without any handling difficulties. Furthermore, the cyclization yield using the dimesylate with calix[4]arene in the presence of Cs_2CO_3 was much improved (over 70%) over that of the corresponding ditosylate, resulting

† E-mail: jongskim@kytis.konyang.ac.kr

Scheme 1 Synthetic route for the preparation of calix[4]arene bis(dibenzocrown) ethers

Fig. 1 Minimum-overlap view of the structure **3** showing the atom labeling scheme. The displacement ellipsoids are drawn at the 40% probability level. **A**–**G** indicate the phenyl groups.

in the successful preparation of calix[4]arene bis(dibenzo-crown) ethers in the 1,3-alternate conformation. No other isomers were observed. It is well-known that the 1,3-alternate conformation of calix[4]arene derivatives can be proved *via* the splitting patterns and chemical shifts of their NMR spectra. A singlet peak at around δ 3.80 in the ^{1}H NMR spectrum for the bridging methylene carbons, as well as a single carbon peak at about δ 38 in the ^{13}C NMR spectrum, indicates that the species exists in the 1,3-alternate conformation.[9] Compounds **3** and **4** are locked in the 1,3-alternate conformation according to their ^{1}H NMR spectra (CDCl$_3$), which show singlet peaks at δ 3.75 and 3.72 for the bridging methylene hydrogens of **3** and **4**, respectively. In the ^{13}C NMR spectra, single peaks at around δ 37.6 and 37.4 for **3** and **4**, respectively, strongly imply the characteristic 1,3-alternate conformation due to the magnetic equivalence of the H$_{exo}$ and H$_{endo}$ protons on the NMR time-scale. This 1,3-alternate conformation is in full agreement with the X-ray crystal structure shown in Fig. 1. The influence of the attachment of the dibenzo moieties on the crown ether linkages mentioned previously are shown by this ORTEP structure (*vide supra*). The molecular conformation of calix[4]arene bis(dibenzocrown)-6-ether **3** is depicted in Fig. 1. It shows the calix[4]arene molecule in the 1,3-alternate conformation: two phenyl groups are up and the other two phenyl groups are down, facing each other in a 1,3-alternate fashion. Two ethereal linkages (one up and one down) involving two benzo groups are bonded to the *ortho* carbon atoms of the aromatic phenyl groups in the calix[4]arene main frame.
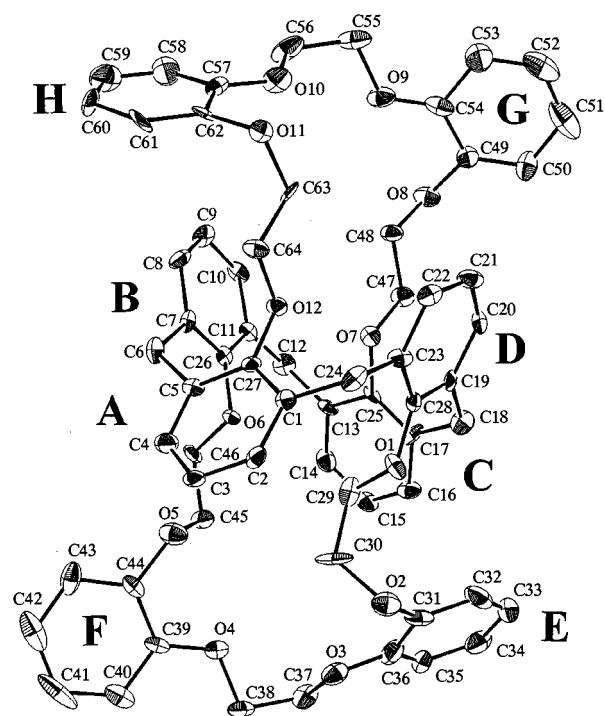
The aromatic C$_{sp2}$–C$_{sp2}$ distances in the molecule vary from 1.337(16) to 1.414(15) Å, with an average value of 1.376 Å, C$_{sp3}$–O$_{sp2}$ distances from 1.359(10) to 1.411(8) Å with a mean value of 1.381 Å, and C$_{sp3}$–C$_{sp3}$ distances from 1.478(12) to 1.521(10) Å with a mean value of 1.508 Å. Bond angles involving the bridging methylenes are C1–C24–C23 = 115.8(6), C5–C6–C7 = 120.9(6), C11–C12–C13 = 117.5(6) and C17–C18–C19 = 118.3(6)°, which are significantly larger than the tetrahedral angle. These large values might be attributable to the repulsive forces between the phenyl rings in the calix[4]arene. The relative dihedral angles between two adjacent rings in the calix[4]arene are: A–B = 84.9(3), B–C = 103.2(3), C–D = 88.4(3) and D–A = 100.3(3)°, whereas those between the pairs of facing rings are: A–C = 51.8(7) and B–D = 35.0(3)°. The two facing pairs of phenyl rings are slightly splayed out from the central axis. The dihedral angles between the two pairs of benzo groups 5–6 and 7–8 in the ethereal linkages are 54.8(4) and 89.3(5)°, respectively. Both the torsion angles O3–C37–C38–O4 = 69.7(11)° in the bottom ethereal linkage and of the corresponding O9–C55–C56–O10 = 76.1(13)° in the top ethereal linkage are *gauche*. However, O1–C29–C30–O2 = 53.5(9) and O5–C45–C46–O6 = 74.3(10)° in the bottom ethereal linkage are *gauche* while the corresponding O7–C47–C48–O8 = 178.4(15) and O11–C63–C64–O12 = 171.5(14)° in the top ethereal linkage are *anti*, the most pronounced difference in the structures of the two ethereal linkages. Oxygen–oxygen distances between the phenoxy oxygens are O2–O4 = 587(9), O3–O5 = 4.639(9), O8–O10 = 5.021(9) and O9–O11 = 4.824(10) Å and O6–C29 = 3.690(10) Å, which is the shortest distance in the ethereal linkages. So the title macrocyclic molecule contains a somewhat flexible cavity lined with twelve oxygen atoms. The closest intermolecular distance not involving an H-atom is O8–C37 (0.5 − *x*, 0.5 + *y*, 1 − *z*) = 3.243(21) Å, which indicates that the intermolecular packing is governed by van der Waals forces.

Previously Reinhoudt and co-workers reported the carrier-mediated transport of alkali metals through bulk liquid membranes and supported-liquid membranes.[9] A bulk liquid membrane system was adapted in this study to quantify the transport of metal ions. The source and receiving phases consisted of 0.8 ml of 0.1 M alkali metal nitrate and 5.0 ml of

Table 1 Single ion transport values of alkali metal ions through a bulk liquid membrane using calix[4]arene biscrown ethers **1–4**[a]

| Compound | Flux[b]/10⁻⁸ mol s⁻¹ m⁻² | | | | |
	Li^+	Na^+	K^+	Rb^+	Cs^+
1	0.00	1.92	2.10	22.25	88.75
2	0.00	0.60	1.04	6.37	10.35
3	0.00	0.00	0.00	53.53	121.51
4	0.00	0.57	2.20	7.30	12.53

[a] Transport conditions: source phase (aqueous solution of nitrate, 0.8 ml), $MNO_3 = 0.1$ M; membrane phase (CH_2Cl_2, 3.0 ml), [carrier] = 1.0 mM; i.d. of glass vial = 18 mm, stirred by 13 mm Teflon-coated magnetic stirring bar driven by a Hurst Synchronous motor; receiving phase (deionized water, 5.0 ml). [b] The average value of three independent determinations. The experimental values deviate from the reported values by an average of 10%.

deionized water, respectively. The organic medium was composed of 3.0 ml of 1.0 mM calix[4]arene dibenzocrown ether in dichloromethane. The measured flux values for single ion transport experiments in the bulk liquid membrane are described in Table 1. For **1** and **3**, stirring for 24 h at room temperature gave excellent flux values for caesium ion. No transport of lithium ion was observed. This caesium ion selectivity in this single ion transport experiment indicates that the ring size of the crown ether linkage-containing calix[4]arene network corresponds to the diameter of caesium ion compared to **2** and **4**, in which the cavity size is somewhat larger than that of compounds **1** and **3**. 1,3-Alternate calix[4]arene bis(dibenzocrown)-6-ether **3** having two benzo groups on the ethereal linkages shows better complexation behavior than that without the dibenzo unit (**1**). For **3** compared with **1**, this efficiency for caesium ions among the other alkali metal ions may be ascribed not only to the lipophilicity of the benzo moieties enhancing the solubility of the complex in organic media, but also to the rigidity and flatness of the crown ether framework, which corresponds well to previous reports that replacement of sp³ carbons by sp² ones in ethereal linkages provides a flattening of the glycolic chain.[12] So, from the X-ray crystal structure (Fig. 1), the dihedral angles O2–C31–C36–O3, O4–C39–C44–O5, O8–C49–C54–O9 and O11–C57–C62–O11 are all observed to be almost 0°, which means that the crown ether cavities are preorganized to complex the caesium ion.

To rationalize the complex ratio for compound **3** and caesium ion using caesium picrate, the extraction equilibrium and extraction constant K_{ex} are expressed as in eqns. (1) and (2):

$$[M^+]_a + [Pic^-]_a + q[H]_o \xrightleftharpoons{K_{ex}} [M^+Pic^-q[H]]_o \qquad (1)$$
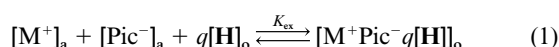
$$K_{ex} = \frac{[M^+Pic^-q[H]]_o}{[M^+]_a[Pic^-]_a[[H]_o]^q} \qquad (2)$$

where the subscripts a and o denote the aqueous and organic phases, respectively, and **H** and Pic⁻ denote the host molecule **3** and picrate anion, respectively. The calix[4]arene bis(dibenzocrown) ether and the complex $[M^+Pic^-q[H]]_o$ are highly lipophilic and should not dissolve appreciably in the aqueous phase. Therefore, the concentration of the complex in the organic phase is equal to the picrate concentration extracted from the aqueous phase into organic phase.

The distribution ratio (D_M) is expressed in eqn. (3).

$$D_M = \frac{[M^+Pic^-q[H]]_o}{[M^+]_a} \qquad (3)$$

Expressed in logarithmic form, eqns. (2) and (3) give eqn. (4).

$$\log D_M/[Pic^-]_a = \log K_{ex} + q \log [H]_o \qquad (4)$$
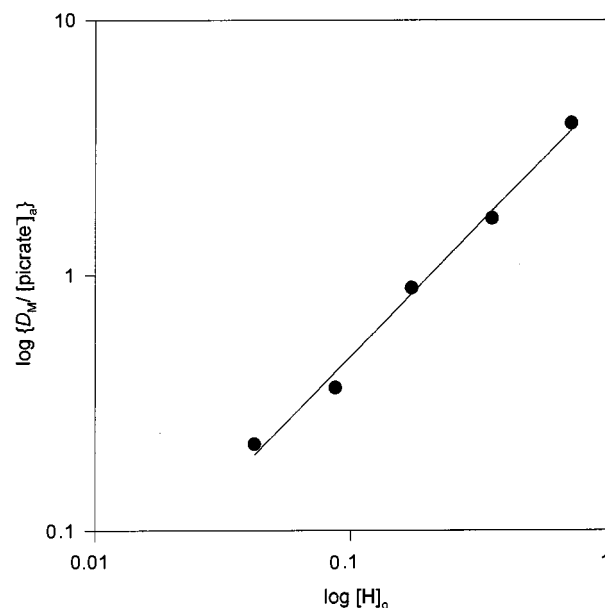
Fig. 2 Plot of log $\{D_M/[Pic^-]_a\}$ *vs.* log $[H]_o$ for extraction of caesium picrate using compound **3**

For **3**, the stoichiometric coefficient (q) and extraction constant (K_{ex}) could be found from a plot of log $D_M/[Pic^-]_a$ against log $[H]_o$, as presented in Fig. 2. The plot gives a straight line with a slope of unity (q), which strongly indicates that the calix[4]arene biscrown ether **3** complexes with the metal ion in a 1:1 ligand–metal complex ratio. The calculated extraction constant (log K_{ex}^{Cs}) was estimated to be 6.71.

Conclusions

Syntheses of calix[4]arene bis(dibenzocrown) ethers in the 1,3-alternate conformation from the reaction of calix[4]arene with dibenzo dimesylates in the presence of a caesium carbonate in acetonitrile proceeded in over 70% yield, which is better than the yield obtained using the dibenzo ditosylate. Single ion transport of alkali metal ions through a bulk liquid membrane was conducted, and showed excellent caesium ion selectivity. So far, we have found that compound **3**, in which two dibenzo crown ethers are cyclized with a calix[4]arene framework, shows the best selectivity and efficiency for caesium ion complexation over other alkali metal ions because the flatness and lipophilicity of the ethereal linkage of **3** enhance the complexation ability. The flatness of the crown ethereal linkages was proven *via* a solid state structure analysis. Two phase extractions using the calix[4]arene bis(crown) ether with caesium ion are found to give a 1:1 ligand–metal complexation ratio.

Experimental

Melting points were obtained using a Fisher-Johns Mel-Temp melting point apparatus without correction. IR spectra were obtained using a Perkin-Elmer 1600 Series FT-IR apparatus as potassium bromide pellets or deposited on KBr plates for solid products and oils, respectively. ¹H and ¹³C NMR spectra were recorded on a Bruker ARX-400 spectrometer at 400 and 100 MHz, respectively. Chemical shifts (δ) are reported downfield from tetramethylsilane as internal standard. *J* Values are given in Hz. Elemental analyses were performed using a Vario EL Elemental Analyzer at the Korea Basic Science Institute in Seoul, Korea. Unless otherwise specified, reagent grade reactants and solvents were obtained from chemical suppliers and used as received. Dry solvents were prepared as follows: dichloromethane was freshly distilled from lithium aluminum hydride. Acetonitrile was pre-dried over molecular sieves (3 Å)

and distilled over P_2O_5. Compounds **1** and **2**,[9] and **5**, **7**, **8**, **9** and **11**[15] were prepared as described in the literature.

General procedure for the syntheses of calix[4]arene bis(dibenzocrown) ethers 3 and 4

A mixture of calix[4]arene **5** (2.0 mmol), Cs_2CO_3 (1.62 g, 5.0 mmol) and dimesylate (2.1 mmol) in dry acetonitrile (100 cm³) was refluxed for three days under nitrogen. Dimesylate (2.0 mmol) and Cs_2CO_3 (5.0 mmol) were added and the mixture refluxed for an additional 3 days. Acetonitrile was removed *in vacuo* and the residue extracted with dichloromethane (100 cm³) and 10% aqueous HCl (50 cm³). The organic layer was separated and washed twice with water. The organic layer was separated and dried over anhydrous magnesium sulfate, followed by removal of the solvent *in vacuo* to give a brownish oil. By TLC analysis, the two compounds **3** and **4** show up as single spots with $R_f = 0.4$ and 0.5, respectively, with ethyl acetate–hexane (1:4) as eluent. Filtration column chromatography with ethyl acetate–hexane (1:6) as eluent provided the pure 1,3-alternate calix[4]arene bis(dibenzocrown) ethers as a white solid in over 70% yield.

Calix[4]arene bis(dibenzocrown)-6-ether, 1,3-alternate (3). Recrystallized from the oil residue with diethyl ether: 72% yield, mp 228–230 °C (Found: C, 75.28; H, 5.85. $C_{64}H_{60}O_{12}$ requires C, 75.29; H, 5.88%); ν_{max}(KBr)/cm^{-1} 3068 (Ar-H), 1501, 1451, 1254, 1196; δ_H(400 MHz; CDCl₃) 3.54–3.45 (16 H, m), 3.75 (8 H, s, Ar-CH_2-Ar), 4.33 (8 H, s), 7.12–6.57 (28 H, m); δ_C(100 MHz; CDCl₃) 38.6, 54.1, 67.8, 68.7, 70.7, 115.2, 115.6, 122.0, 122.4, 122.9, 123.3, 124.0, 124.7, 125.1, 129.6, 130.0, 134.7, 149.4, 152.0, 156.5.

Calix[4]arene bis(dibenzocrown)-7-ether, 1,3-alternate (4). Recrystallized from the oil residue with diethyl ether: 70% yield, mp 208–210 °C (Found: C, 77.54; H, 6.49. $C_{68}H_{68}O_{14}$ requires C, 77.56; H, 6.46%); ν_{max}(KBr)/cm^{-1} 3068 (Ar-H), 1500, 1452, 1254, 1195; δ_H(400 MHz; CDCl₃) 3.70 (8 H, t), 3.72 (8 H, s, Ar-CH_2-Ar), 3.85 (8 H, t), 4.08 (8 H, t), 4.20 (8 H, t), 7.02–6.73 (28 H, m); δ_C(100 MHz; CDCl₃) 31.5, 38.4, 69.9, 70.7, 71.1, 116.2, 118.5, 122.4, 123.2, 123.3, 130.7, 134.4, 149.8, 150.8, 156.9.

1,2-Bis[2-(2-hydroxyethoxy)phenoxy]ethane (10)

Under nitrogen, to a suspension of LiAlH₄ (2.8 g, 73.9 mmol) in THF (150 cm³) was added dropwise a solution of 1,2-bis[2-(carboxymethoxy)phenoxy]ethane (**8**) (5.93 g, 16.4 mmol) dissolved in THF (50 cm³) over a period of 30 min at 0 °C. Upon complete addition, the reaction mixture was refluxed for 20 h under a nitrogen atmosphere. After cooling down to 0 °C with an ice-bath, ethyl acetate (10 cm³) and 10% aqueous NaOH (10 cm³) were added dropwise to destroy the unreacted LiAlH₄. The reaction mixture was allowed to stir for an additional 1 h at room temperature. The white solid formed was filtered off and washed with THF (100 cm³). The organic solvents were removed *in vacuo*, and the aqueous residue was poured into a separatory funnel with CH_2Cl_2 (100 cm³). The organic layer was separated and washed with 10% HCl followed by washing with brine (100 cm³), and dried over anhydrous MgSO₄. The solvent was removed *in vacuo* to give a colorless oil. Recrystallization from diethyl ether (100 cm³) provided **10** (5.11 g, 93%) as a white solid, mp 96–98 °C (Found: C, 64.75; H, 6.60. $C_{18}H_{22}O_6$ requires C, 64.73; H, 6.63%); ν_{max}(KBr)/cm^{-1} 3400 (O-H), 1115 (C-O); δ_H(400 MHz; CDCl₃) 3.99–3.84 (8 H, m, -CH$_2$CH_2OH and -CH$_2$CH_2O-), 4.05 (4 H, s, ArOCH_2CH_2OAr), 4.72 (2 H, br s, -CH$_2$CH$_2$OH), 6.91 (8 H, s, Ar-H).

1,2-Bis[2-(2-methylsulfonyloxyethoxy)phenoxy]ethane (6)

Under nitrogen, to a solution of **10** (4.1 g, 13.2 mmol) and triethylamine (2.94 g, 29.0 mmol) in dry CH_2Cl_2 (100 cm³) was added dropwise methanesulfonyl chloride (3.33 g, 29.0 mmol) over a period of 30 min at 0 °C. Upon complete addition, the reaction mixture was stirred for 5 h at 0 °C. The reaction

temperature was slowly raised to room temperature and the mixture was stirred for an additional 10 h. 10% Aqueous sodium hydrogen carbonate (50 cm³) was added and the CH_2Cl_2 layer was separated. The organic layer was washed with water (2 × 20 cm³) and brine (2 × 20 cm³), followed by drying over anhydrous magnesium sulfate. Removal of CH_2Cl_2 *in vacuo* provided a colorless oil which was recrystallized from diethyl ether (100 cm³) to give the desired product **6** (5.88 g, 91%), mp 158–160 °C (Found: C, 48.95; H, 5.29. $C_{20}H_{26}O_{10}S_2$ requires C, 48.97; H, 5.31%); ν_{max}(KBr)/cm^{-1} 1590, 1513, 1343 (SO₂), 1173 (SO₂); δ_H(400 MHz; CDCl₃) 3.07 (6 H, s, CH_3SO₂OCH₂CH₂-), 4.25 (4 H, t, MsO-CH₂CH_2O-), 4.32 (4 H, s, Ar-OCH_2CH_2O-Ar), 4.55 (4 H, t, MsO-CH_2CH₂O-), 7.01–6.90 (8 H, m, Ar-H).

Solid state structure

Compound **3** was crystallized from methylene chloride by slow evaporation. A crystal of size $0.33 \times 0.4 \times 0.13$ mm was mounted on an Enraf-Nonius CAD4 diffractometer with graphite monochromated Mo-Ka radiation, and accurate cell parameters and an orientation matrix were determined from the least-squares fit of 25 accurately centered reflections with a θ range of 10.41 to 13.47°. The intensity data were collected in the $\omega - 2\theta$ scan mode to a maximum 2θ of 23°. Three standard reflections (13 2 0, 14 0 -1, 14 0 -2) were measured every 240 min, and the intensities of the standards remained constant within 0.82% throughout data collection. Of the 7353 unique reflections measured, 1804 were considered to be observed $[F_o > 3\sigma(F)]$ and used in the subsequent structural analysis. The program used to solve the structure was SHELX86.[16] The program used to refine the structure and to prepare material for publication was NRCVAX.[17] ORTEPII was used for molecular graphics.[18] Data were corrected for Lorentz and polarization effects. No absorption correction was applied. The structure was solved by direct methods. All remaining non-hydrogen atoms were found by iterative cycles of full-matrix least-squares refinement and difference-Fourier synthesis. All non-hydrogen atoms were refined anisotropically except for three atoms (C49, C53 and C58). All hydrogen atoms were included at calculated positions (dc-H = 1.08 Å) and their parameters fixed during the refinement. Refinement converged with $R(R_w) = 0.056$ (0.060) and $(\Delta/\sigma)_{max}$ was 0.000. Detailed crystal data are described in Table 2.

Full crystallographic details, excluding structure factor tables, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc.*, *Perkin Trans. 1*, available *via* the RSC Web page (http://www.rsc.org/authors). Any request to the CCDC for this material should quote the full literature citation and the reference number 207/232.

Transport of alkali metal ions in a bulk liquid membrane system

Liquid membrane transport experiments were carried out as reported earlier using a bulk liquid membrane apparatus.[19] Two water phases (one containing the salt to be transported) were separated by a dichloromethane phase which constituted the membrane. The interior of the tube above the organic media was filled with the source phase (0.8 cm³ of 0.1 M lithium, sodium, potassium, rubidium or caesium nitrate) using a single flux method. The outer cylinder was filled with deionized water (5.0 cm³) and acted as the receiving phase. The details of the transport conditions are summarized in the footnotes of Table 1. Each experiment was repeated three times in a room thermostatted to 25 ± 1 °C, and 3 cm³ of receiving phase was taken. The flux values (moles transported s^{-1} m^{-2}) for each metal ion concentration were determined using a Perkin-Elmer 2380 atomic absorption spectrophotometer. Blank experiments, for which no calix[4]arene bis(dibenzocrown) ether was present, were performed to determine the background membrane leakage.

Table 2 Experimental data for the X-ray diffraction studies on compound **3**

formula	$C_{64}H_{60}O_{12}$
M	1021.172
crystal system	monoclinic
space group	$P2_1/a$
$a/\text{Å}$	26.0714(27)
$b/\text{Å}$	12.9484(14)
$c/\text{Å}$	15.8652(51)
$a(°)$	90.0
$\beta(°)$	99.022(19)
$\gamma(°)$	90.0
$V/\text{Å}^3$	5289.5(19)
Z	4
$F(000)$	2160
calculated density/g cm^{-3}	1.282
radiation/Å (Mo-Ka)	0.71 069
number of reflections	25
2θ range (°)	20.82–26.94
μ/mm^{-1}	0.082
T/k	288
crystal size/mm	$0.33 \times 0.4 \times 0.13$
color	colorless
diffractometer	Enraf-Nonius CAD-4
data collection method	$\omega/2\theta$
scan width	$0.8 + 0.34 \tan\theta$
absorption correction	none
no. of unique reflections	7353
reflections observed [$F_o \geqslant 3\sigma[F_o]$]	1804
θ_{max}	23.0°
hkl range	0 28; 0 14; -17 17
interval/min	240
standard reflections	13 2 0, 14 0 -1, 14 0 -2
orientation check reflection	13 2 0
intensity variation (%)	less than 0.82
R	0.016
parameters	670
R_f, R_w	0.056, 0.060
GOF	0.55
$(\Delta/\sigma)_{max}$	0.000
$(\Delta\rho)_{max}$/e Å^{-3}	0.49
$(\Delta\rho)_{min}$/e Å^{-3}	-1.47
extinction correction	none

Extraction equilibrium

The alkali metal concentrations in the aqueous layer were analyzed with a UV–VIS spectrometer. The amount of caesium picrate complex in the organic solution was calculated from the mass balance of caesium and the stoichiometric coefficient between extractant and caesium picrate.

Caesium picrate was prepared by reaction of picric acid and potassium carbonate.[20] To obtain the various properties of the extraction equilibrium, such as the distribution ratio of caesium picrate (D_M), the extraction equilibrium constant (K_{ex}) and the stoichiometric coefficient between extractant and caesium picrate, an aqueous solution (20.0 cm^3) containing 0.20 mM caesium picrate and a chloroform solution of the same volume with an extractant concentration of 0.05–0.08 mM were mixed and equilibrated by shaking at 25 °C. Concentrations of picrate anion extracted from the aqueous phase into the organic layer were determined by UV spectrophotometry ($\lambda_{max} = 368$ nm).

References

1 C. D. Gutsche, *Calixarenes*, The Royal Society of Chemistry, Cambridge, 1989; C. D. Gutsche, in *Synthesis of Macrocycles*: *Design of Selective Complexing Agents*, ed. R. M. Izatt and J. J. Christensen, Wiley, New York, 1987, p. 93.
2 C. D. Gutsche, B. Dhawan, J. A. Levine, K. H. No and L. J. Bauer, *Tetrahedron*, 1983, **39**, 409.
3 P. D. J. Grootenhuis, P. A. Kollman, L. C. Groenen, D. N. Reinhoudt, G. J. van Hummel, F. Ugozzoli and G. D. Andreetti, *J. Am. Chem. Soc.*, 1990, **112**, 4165.
4 J. Royer, F. Bayard and C. Decoret, *J. Chim. Phys.*, 1990, **87**, 1695.
5 R. Ungaro and A. Pochini, in *Frontiers in Supramolecular Organic Chemistry and Photochemistry*, ed. H.-J. Schneider, VCH, Weinheim, Germany, 1991, pp. 57–81.
6 G. D. Andreetti, F. Ugozzoli, R. Ungaro and A. Pochini, in *Inclusion Compounds*, ed. J. L. Atwood, J. E. D. Davies and D. D. MacNicol, Oxford University Press, New York, 1991, vol. 4, pp. 64–125.
7 W. F. Nijenhuis, E. G. Buitenhuis, F. de Jong, E. J. R. Sudhölter and D. N. Reinhoudt, *J. Am. Chem. Soc.*, 1991, **113**, 7963.
8 Z. Asfari, R. Abidi, F. Arnaud and J. Vicens, *J. Inclusion Phenom. Mol. Recognit. Chem.*, 1992, **13**, 163; Z. Asfari, J. Weiss, S. Pappalardo and J. Vicens, *Pure Appl. Chem.*, 1993, **65**, 585.
9 A. Casnati, A. Pochini, R. Ungaro, F. Ugozzoli, F.Arnaud, S. Fanni, M.-J. Schwing, R. J. M. Egberink, F. de Jong and D. N. Reinhoudt, *J. Am. Chem. Soc.*, 1995, **117**, 2767; R. Ungaro, A. Casnati, F. Ugozzoli, A. Pochini, J.-F. Dozol, C. Hill and H. Rouquette, *Angew. Chem.*, *Int. Ed. Engl.*, 1994, **33**, 1506.
10 E. Ghidini, F. Ugozzoli, S. Harkema, A. Abu E-Fald and D. N. Reinhoudt, *J. Am. Chem. Soc.*, 1990, **112**, 6979.
11 C. Hill, J.-F. Dozol, V. Lamare, H. Rouquette, S. Eymard, B. Tournois, J. Vicens, Z. Asfari, C. Bressot, R. Ungaro and A. Casnati, *J. Inclusion Phenom. Mol. Recognit. Chem.*, 1994, **19**, 399.
12 Z. Asfari, C. Bressot, J. Vicens, C. Hill, Z.-F. Dozol, H. Rouquette, S. Eymard, V. Lamare and B. Tournois, *Anal. Chem.*, 1995, **67**, 3133.
13 *Radioactive Waste Management and Disposal*, ed. L. Cecille, Elsevier, London, New York, 1991.
14 J. S. Kim, M. H. Cho, S. C. Lee, Y.-I. Lee, W. Sim and N. S. Cho, *Microchem. J.*, 1997, **55**, 115; J. S. Kim, A. Ohki, N. S. Cho, I. Y. Yu, T. Hayashta and S. Maeda, *Bull. Korean Chem. Soc.*, 1996, **17**, 953.
15 J. S. Kim, A. Ohki, M. H. Cho, J. K. Kim, D. Y. Ra, N. S. Cho, R. A. Bartsch, K. W. Lee and W.-Z. Oh, *Bull. Korean Chem. Soc.*, 1997, **18**, 1014.
16 G. M. Sheldrick, *Acta Crystallogr.*, *Sect. A*, 1990, **46**, 467.
17 E. J. Gabe, Y. Le Page, J. P. Charland, F. L. Lee and P. S. White, *J. Appl. Crystallogr.*, 1989, **22**, 384.
18 C. K. Johnson, *ORTEP-A Fortran Thermal Ellipsoid Plot Program, Technical Report ORNL-5138*, Oak Ridge National Lab., U.S.A., 1976.
19 G. Gokel, in *Crown Ethers & Cryptands*, ed. J. F. Stoddart, The Royal Society of Chemistry, London, UK, 1991, p. 81; S. S. Lee, J. H. Jung, S. H. Yu and M. H. Cho, *Thermochim. Acta*, 1995, **259**, 133; M. H. Cho, K. W. Seon-Woo, M. Y. Hea, I. C. Lee, C. J. Yoon and S. J. Kim, *Bull. Korean Chem. Soc.*, 1988, **9**, 5.
20 C. J. Pedersen, *Fed. Proc.*, 1968, **27**, 1305.