

Calix[4]arene Dibenzo-crown Ethers as Cesium Ionophore

Jong Seung Kim*, Moon Hwan Cho[§], Ill Yong Yu, Jin Hyun Pang, Eung Tae Kim[§],
Il Hwan Suh[†], Mi Ran Oh[†], Do Young Ra^{††}, and Nam Sook Cho^{††}

Department of Chemistry, Konyang University, Nonsan 320-800, Korea.

[§]Department of Chemistry, Kangwon National University, Chuncheon 200-701, Korea

[†]Department of Physics, Chungnam National University, Taejeon 305-764, Korea

^{††}Department of Chemistry, Chungnam National University, Taejeon 305-764, Korea

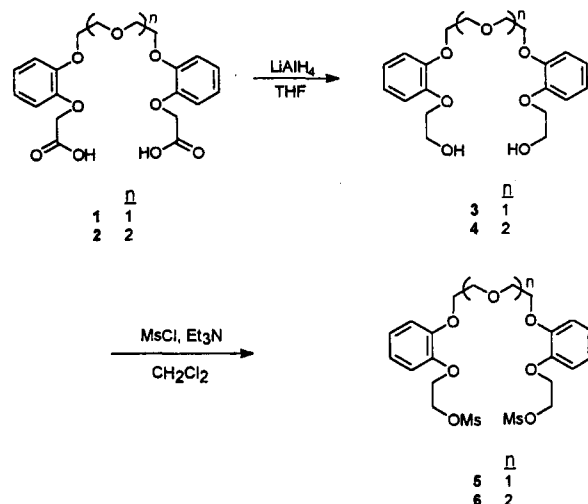
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Calix[4]arene molecule, cyclic tetramer of phenols, has been proven to be a useful three dimensional molecular building block for the synthesis of molecules with specific properties.¹ Much attention has been paid to the conformational behaviors of calix[4]arene by means of solid state, solution state, molecular mechanics, and NMR experiment.²⁻⁴ Several groups have succeeded in demonstrating that calix[4]arenes serve as an excellent receptor for the specific binding of guest atoms and molecules.⁵⁻⁷ 1,3-Distal capping of calix[4]arene at the lower rim has been achieved with polyether linkage such as calixcrown ether,⁸ calix-doubly-crowned,⁹ double-calix-crown.¹⁰ Shinkai reported that the calix[4]arene crown-4 shows very high potassium selectivity in ion-selective electrodes.¹¹ Recently, interestingly, Reinholdt and Ungaro have reported that 1,3-dialkoxycalix[4]arene-crown-6 derivatives were successfully prepared and they are exceptionally selective ionophores for cesium ion when they are fixed in the 1,3-alternate conformation.¹² It has been known that introducing aryl substituents such as phenyl or naphthyl into the polyether ring greatly enhance the metal ion selectivity and efficiency.¹³

Upon the above view points, we have paid attention to prepare calixcrown ethers as organic carrier able to selectively separate the cesium ion from MLW¹⁴ (medium level of radio active waste). Now we report that successful syntheses of 1,3-diallyloxycalix[4]arene crown ethers containing dibenzo groups as well as a conformational analysis by solid state structure and ¹H NMR measurement. Upon the use of bulk liquid membrane process, cesium selectivity toward alkali metal ions was measured with varying the size of polyether linkage attached on the lower rim of corresponding calix[4]arene.

Results and Discussion

To study an influence of polyether ring size of the organic carrier when the calix[4]arene dibenzocrown ether complexes with specific metal ion, we have attempted many reactions to prepare an acyclic polyether able to be attached on the calix[4]arene lower rim. The synthetic route for the preparation of corresponding dibenzodimesylate is described in Scheme 1. Reaction of 1,5-bis[2-(carboxymethoxy)phenoxy]-3-oxapentane (1) and 1,8-bis[2-(carboxymethoxy)phenoxy]-3,6-dioxaoctane (2) with LiAlH₄ in THF gave a corresponding diols (3, 4) with 82% and 78% yield, respectively. Mesylation of the each diol with methanesulfonyl chloride in

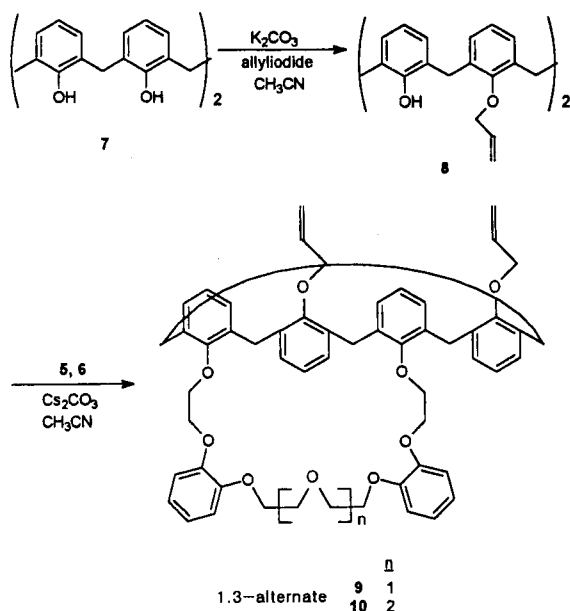


Scheme 1. Synthetic route for dibenzodimesylates (5, 6) from acyclic polyether dicarboxylic acids (1, 2).

the presence of triethylamine in CH₂Cl₂ provided 1,5-bis[2-(2-methanesulfonyloxyethoxy)phenoxy]-3-oxapentane (5) and 1,8-bis[2-(2-methanesulfonyloxyethoxy)phenoxy]-3,6-dioxaoctane (6) in 92% and 88% yield, respectively.

Synthetic route for 1,3-bis(1-allyloxy) calix[4]arene dibenzocrown ether was depicted in Scheme 2. Reaction of calix[4]arene with alkylating agents in acetonitrile in the presence of K₂CO₃ is a well established synthetic method to obtain 1,3-dialkoxycalix[4]arene in the cone form.¹² The corresponding diallyl ether of calix[4]arene (8) and its crown ether analogues are of specially interest due to synthetic utilities that its double bond affords.¹⁵ It was reported that the use of 2.5 equivalents of K₂CO₃ as a base provided the 1,3-dialkyloxy calix[4]arene with 50-65% yields.¹² Fortunately, however, we found the improved synthetic method that the use of only one equivalent of K₂CO₃ gives one spot on TLC analysis (R_f: 0.6, ethyl acetate:hexanes=1:9) and provided the product in more than 90% yield (see experimental). For 8, AB quartet splitting pattern (*J*=13 Hz, Δ*v*=378 Hz, chemical shift difference value) in ¹H NMR spectra was observed, indicating a characteristic cone conformation. Subsequently, cyclization reaction of 1,3-diallyloxy calix[4]arene with dibenzodimesylates (5, 6) in the presence of Cs₂CO₃ resulting in a successful preparation of 1,3-diallyloxy calix[4]arene dibenzocrown ethers (9, 10) in the 1,3-alternate conformation with 90% and 92% yield, respectively. No other conformational isomers were observ-

*To whom correspondence should be addressed



Scheme 2. Synthetic route for calix[4]arene dibenzocrown ethers (9 and 10).

ed. A number of attempts for cyclization with dibenzoditosylate as a cyclizing agent gave 50-70% yield. Instead, changing the cyclizing agent to the dibenzodimesylate, we obtained the 1,3-alternate calix[4]arene dibenzocrown-7 and corresponding dibenzocrown-8 with much better yield as mentioned above.

It is well documented that calix[4]arene crown ether in the 1,3-alternate conformation as inferred from the 1H NMR spectra ($CDCl_3$) shows a singlet peak of about δ 3.7 for the bridging methylene hydrogens of the calix[4]arene moiety. The ^{13}C NMR spectra with one signal around 38 ppm indicates the characteristic of 1,3-alternate conformation as well. Interestingly, however, for compound 9 small AB quartet ($J=14.8$ Hz $\Delta\nu=11.07$ Hz, chemical shift difference value) in 1H NMR spectrum was observed at δ 3.64. This 1H NMR pattern in 1,3-alternate conformation of calix[4]arene system seems to be unusual. X-ray crystallographic determination led us to strongly confirm that the compound 9 is fixed in the 1,3-alternate conformation as shown in Figure 1. AB splitting pattern in NMR experiment may indicate that the structure of 1,3-alternate 1,3-diallyloxy calix[4]arene dibenzocrown ether (9) is slightly less flexible than that of compound 10 resulting in the fact that H_{exo} and H_{endo} in methylene hydrogens between aryl units for 9 are not exactly equivalent on NMR time scale.

Previously Reinhoudt and coworkers have reported the carrier-mediated transport of alkali metals through bulk liquid membrane and supported liquid membrane.^{12,16} In this study, we used the bulk liquid membrane to measure transport amounts of metal ions. The measured flux values from single transport experiment in bulk liquid membrane were described in Table 1. The flux values of alkali metal ions were found to increase as the size of metal ion increases when compound 9 was used while even decreasing values for cesium ion was observed using compound 10. No transport of lithium ion was observed. High cesium ion selectivity of compound 9 in this single ion transport in-

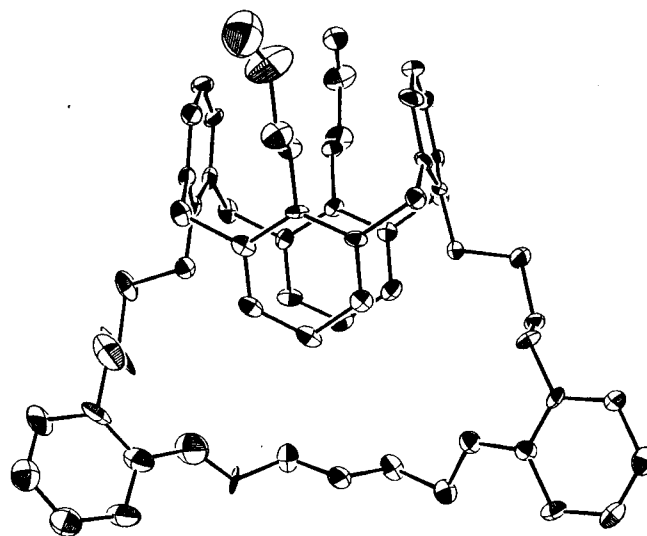


Figure 1. X-ray crystallographic structure of calix[4]arene dibenzocrown ether (9).

Table 1. Single ion transport values of alkali metal ions through bulk liquid membrane using 1,3-diallyloxy calix[4]arene dibenzocrown ethers (9, 10)^a

	Flux (10^{-8} mole s^{-1} m $^{-2}$) ^b				
	Li ⁺	Na ⁺	K ⁺	Rb ⁺	Cs ⁺
9	0.00	0.57	0.68	1.51	8.11
10	0.00	0.24	1.65	1.82	1.08

^a Transport conditions: source phase (aqueous solution of nitrate, 0.8 mL), $M(NO_3)=0.1$ 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%.

icates that ring size of dibenzocrown ether linkage containing calix[4]arene network is in a good agreement with a diameter of cesium ion. We could understand that elongation of ether linkage to three ethylene glycol unit in calix[4]arene lower rim makes it too large to adopt a cesium ion showing a low flux value. In this study, although no evidence was obtained for the π -interaction between p-orbital on benzene ring in calixarene framework and cesium ion, we assume a similar mechanistic fashion for the metal ion complexation from Reinhoudt's concept¹² which the complexed ion interacts not only with the crown ether moiety but also with the two rotated aromatic nuclei (cation/ π -interaction) of the 1,3-alternate conformation. In addition to this π -complexation concept, enhancement of the lipophilicity of crown ether framework by dibenzo group might play an important role in the selective complexation as well.

In conclusion, syntheses of 1,3-diallyloxy calix[4]arene dibenzocrown ether in the 1,3-alternate conformation from the reaction of 1,3-diallyloxy calix[4]arene with dibenzodimesylate in the presence of cesium carbonate in acetonitrile were succeeded with an over 90% yields which are better than the use of corresponding ditosylate. The evidence for 1,3-al-

ternate conformation was strongly supported by solid state structure and NMR measurement. From single ion transport of alkali metal ion through bulk liquid membrane, higher flux value of ligand **9** compared with that of **10** indicates that compound **9** goes with cesium ion with respect to the size correspondence. To optimize the selectivity and efficiency for cesium ion transport, the syntheses of 1,3-dialkyloxy calix[4]arene dibenzocrown ether which are much more lipophilic are planned and will be reported.

Experimental

Melting points were taken by the use of a Mel-Temp of Fisher-Johns melting point apparatus without any correction. IR spectra were obtained with a Perkin-Elmer 1600 Series FT-IR on potassium bromide pellet and on deposited KBr window in the case of solid product and oil, respectively, are recorded in reciprocal centimeters. ^1H and ^{13}C NMR spectra were recorded with a 400 MHz (Bruker ARX-400) and an 100 MHz spectrometer, respectively, the chemical shifts (δ) reported downfield from the internal standard, tetramethylsilane. Elemental analysis was performed by Vario EL of Elemental Analyzer in Korea Basic Science Institute in Seoul, Korea. FAB⁺ mass spectra was obtained from JEOL-JMS-HX 110A/110A High Resolution Tandem Mass Spectrometry in Korea Basic Science Institute in Taejeon, Korea.

Unless specified otherwise, reagent grade reactants and solvents were obtained from chemical suppliers and used as received. Dry solvents were prepared as follows: tetrahydrofuran was freshly distilled from sodium metal ribbon or chunks; benzene and pentane were stored over sodium ribbon, respectively; dichloromethane was freshly distilled from lithium aluminum hydride. Acetonitrile was pre-dried from molecular sieves (3 Å) and distilled over diphosphorous pentoxide. Compounds **1**¹⁷ is known. Compound **2** was prepared by adaptation of procedure for compound **1**.

Synthesis.

1,5-Bis[2-(2-hydroxyethyloxy)phenoxy]-3-oxapentane (3). Under nitrogen, to a suspension of LiAlH_4 (2.8 g, 73.9 mmole) in 150 mL of THF was added dropwise a solution of 1,5-bis[2-(carboxymethyloxy)phenoxy]-3-oxapentane (**1**) (6.67 g, 16.4 mmole) dissolved in 50 mL of THF during a period of 30 min at 0 °C. Upon the complete addition, reaction mixture was refluxed for 20 h under nitrogen atmosphere. After cooling down to 0 °C with ice-bath, 10 mL of ethyl acetate and 10 mL of 10% NaOH aqueous solution were added dropwise to destroy the unreacted LiAlH_4 . The reaction mixture was allowed to stir for an additional 1 h at room temperature. White solid was filtered and washed with 100 mL of THF. After the organic solvent of filtrate was removed *in vacuo*, the residue was poured into a separatory funnel with 100 mL of CH_2Cl_2 . The organic layer was separated and washed with 10% HCl solution followed by washing with 100 mL of brine and dried over anhydrous MgSO_4 . The solvent was removed *in vacuo* to give a colorless oil. Recrystallization from 100 mL of diethyl ether provided 5.11 g (82%) of a white solid. mp 89-90 °C: IR (KBr pellet, cm^{-1}) 3400 (O-H), 1115 (C-O); ^1H NMR (CDCl_3) δ 6.91 (s, 8 H, Ar-H), 4.72 (br s, 2H, $-\text{CH}_2\text{CH}_2\text{OH}$), 4.25-4.19 (m, 4H, $-\text{CH}_2\text{CH}_2\text{O}-$), 4.09-4.05 (m,

4H, $-\text{CH}_2\text{CH}_2\text{O}-$), 3.99-3.84 (m, 8H, $-\text{CH}_2\text{CH}_2\text{OH}$, and $-\text{CH}_2\text{CH}_2\text{O}-$), FAB MS m/z (M^+) calcd 378.21, found 378.20. Anal. Calcd for $\text{C}_{20}\text{H}_{26}\text{O}_7$: C, 63.49; H, 6.87. Found: C, 63.21; H, 6.90.

1,8-Bis[2-(2-hydroxyethyloxy)phenoxy]-3,6-dioxaoctane (4). The synthetic procedure is same as that for compound **3**. Yield : 78%. mp 94-95 °C: IR (KBr pellet, cm^{-1}) 3400 (O-H), 1114 (C-O); ^1H NMR (CDCl_3) δ 6.91 (s, 8H, Ar-H), 4.17-4.16 (m, 4H, $-\text{CH}_2\text{CH}_2\text{O}-$), 4.10-4.00 (m, 4H, $-\text{CH}_2\text{CH}_2\text{O}-$), 4.09-4.05 (m, 4H, $-\text{CH}_2\text{CH}_2\text{O}-$), 3.99-3.84 (m, 8H, $-\text{CH}_2\text{CH}_2\text{OH}$, and $-\text{CH}_2\text{CH}_2\text{O}-$). Anal. Calcd for $\text{C}_{22}\text{H}_{30}\text{O}_8$: C, 62.55; H, 7.16. Found: C, 62.40; H, 7.04.

1,5-Bis[2-(2-methanesulfonyloxyethyloxy)phenoxy]-3-oxapentane (5). Under nitrogen, to a solution of 5.0 g (13.2 mmole) of **3** and 4.08 mL (2.94 g, 29.0 mmole) of triethylamine in 100 mL of dry CH_2Cl_2 was added dropwise 2.14 mL (3.33 g, 29.0 mmole) of methanesulfonyl chloride during a period of 30 min at 0 °C. Upon the complete addition, reaction mixture was stirred for 5 h at 0 °C. Reaction temperature was slowly raised upto room temperature and stirred for additional 10 h. 50 mL of 10% aqueous sodium bicarbonate solution was added and CH_2Cl_2 layer was separated. The organic layer was washed with water (2×20 mL) and brine (2×20 mL) followed by drying over anhydrous magnesium sulfate. Removal of CH_2Cl_2 *in vacuo* provided a colorless oil which was recrystallized from 100 mL of diethyl ether to give 6.20 g (92%) of desired product. mp 98-99 °C: IR (KBr pellet, cm^{-1}) 1597, 1516, 1350 (SO_2), 1181 (SO_2); ^1H NMR ($\text{DMSO}-d_6$) δ 7.00-6.88 (m, 8H, Ar-H), 4.57-4.45 (m, 4H, $-\text{CH}_2\text{CH}_2\text{O}-$), 4.26-4.05 (m, 8H, $-\text{CH}_2\text{CH}_2\text{O}-$), 3.85-3.75 (m, 4H), 3.23 (s, 6H, $\text{CH}_3\text{SO}_2\text{OCH}_2\text{CH}_2-$); FAB MS m/z (M^+) calcd 534.12, found 534.20. Anal. Calcd for $\text{C}_{22}\text{H}_{30}\text{O}_{11}\text{S}_2$: C, 49.43; H, 5.61. Found: C, 49.21; H, 5.78.

1,8-Bis[2-(2-methanesulfonyloxyethyloxy)phenoxy]-3,6-dioxaoctane (6). The synthetic procedure is same as that for compound **5**. Yield 88%. mp 103-105 °C: IR (KBr pellet, cm^{-1}) 1597, 1516, 1348 (SO_2), 1180 (SO_2); ^1H NMR (CDCl_3) δ 6.92-6.90 (m, 8H, Ar-H), 4.55-4.50 (m, 4H, $-\text{CH}_2\text{CH}_2\text{O}-$), 4.54-4.12 (m, 8H, $-\text{CH}_2\text{CH}_2\text{O}-$), 3.85-3.82 (m, 4H), 3.72 (s, 4H, $-\text{CH}_2\text{CH}_2\text{O}-$), 3.17 (s, 6 H, $\text{CH}_3\text{SO}_2\text{OCH}_2\text{CH}_2-$). Anal. Calcd for $\text{C}_{24}\text{H}_{34}\text{O}_{12}\text{S}_2$: C, 49.82; H, 5.92. Found: C, 49.86; H, 5.81.

Synthetic method for 1,3-diallyloxy calix[4]arene (**8**) is same as that in reported literature¹² except the amount of K_2CO_3 added and recrystallization process. To a suspension of calix[4]arene **7** (5.0 g, 11.8 mmole) in 150 mL acetonitrile were added allyl iodide (4.14 g, 24.7 mmole) and K_2CO_3 (1.63 g, 11.8 mmole). The reaction mixture refluxed for 24 h under nitrogen atmosphere. The solvent was removed *in vacuo* and 50 mL of 10% aqueous HCl solution and 50 mL of CH_2Cl_2 were added. The organic layer was separated and washed with water (2×50 mL). Organic phase was dried over anhydrous MgSO_4 and the CH_2Cl_2 was removed *in vacuo* to give a colorless oil. Recrystallization from 100 mL of co-solvents (diethyl ether/hexanes: 7/3) gave 4.90 g (90%) of the desired product. Physical properties and spectral data of conformational analysis are same as that in literature.

25,27-Bis(1-allyloxy)calix[4]arene dibenzocrown-7, 1,3-alternate (9). 25, 27-diallyloxy calix[4]arene **8** (0.93 g, 2.0 mmole) was dissolved in 50 mL of acetonitrile

and added to an excess of Cs_2CO_3 (1.62 g, 5.0 mmole) and 1,5-bis[2-(2'-mesyloxyethoxy)phenoxy]-3-oxapentane (1.12 g, 2.1 mmole) under nitrogen atmosphere. The reaction mixture was refluxed for 24 h. Then the acetonitrile was removed *in vacuo* and the residue extracted with 100 mL of methylene chloride and 50 mL of 10% aqueous HCl solution. The organic layer was separated and washed twice with water. After the organic layer was separated and dried over anhydrous magnesium sulfate followed by removing the solvent *in vacuo* to give a brownish oil. With TLC analysis, compound **9** is found to show an only one spot ($R_f=0.4$). Filtration column chromatography with ethyl acetate:hexane=1:6 as eluents provided pure 1,3-alternate calix[4]arene dibenzocrown ether. Recrystallized from the oil residue with 5/1 diethyl ether-hexanes:90% yield; mp 166-168 °C; IR (KBr pellet, cm^{-1}) 3010, 1501, 1455, 1258, 1200; ^1H NMR (CDCl_3) δ 7.02-6.93 (m, 16 H), 6.77-6.67 (m, 4H), 5.83-5.74 (m, 2H, $\text{OCH}_2\text{CH}=\text{CH}_2$), 5.11-5.00 (m, 4H, $\text{OCH}_2\text{CH}=\text{CH}_2$), 4.20 (t, $J=5.1$ Hz, 4H, $-\text{OCH}_2\text{CH}_2\text{O}-$), 4.08-4.03 (m, 4H, $-\text{OCH}_2\text{CH}_2\text{O}-$, $\text{OCH}_2\text{CH}=\text{CH}_2$), 3.84 (t, $J=5.1$ Hz, 4H, $-\text{OCH}_2\text{CH}_2\text{O}-$), 3.63 (AB quartet, $J=14.8$ Hz $\Delta v=11.07$ Hz, 8H, ArCH_2Ar); ^{13}C NMR (CDCl_3): ppm 156.8, 156.7, 150.9, 150.1, 134.6, 134.5, 134.2, 131.8, 130.9, 123.3, 123.3, 122.7, 122.6, 118.3, 117.0, 116.6, 71.3, 71.4, 71.1, 70.7, 70.3, 38.1; FAB MS m/z (M^+) calcd 846.30, found 846.41. Anal. Calcd for $\text{C}_{54}\text{H}_{54}\text{O}_9$: C, 76.57; H, 6.38. Found: C, 76.60; H, 6.41.

25,27-Bis(1-allyloxy)calix[4]arene dibenzocrown-8, 1,3-alternate (10). The synthetic procedure is same as that for **9**. Yield:92%. mp 163-165 °C; IR (KBr pellet, cm^{-1}) 3011, 1501, 1445, 1252, 1201; ^1H NMR (CDCl_3) δ 7.09-6.55 (m, 20H), 6.03-5.94 (m, 2H, $\text{OCH}_2\text{CH}=\text{CH}_2$), 5.30-5.18 (m, 4H, $\text{OCH}_2\text{CH}=\text{CH}_2$), 4.19-4.02 (m, 16H, $-\text{OCH}_2\text{CH}_2\text{O}-$, $\text{OCH}_2\text{CH}=\text{CH}_2$), 3.89 (t, 4H, $-\text{OCH}_2\text{CH}_2\text{O}-$), 3.64-3.48 (m, 4H, $-\text{OCH}_2\text{CH}_2\text{O}-$), 3.58 (s, 8H, ArCH_2Ar); ^{13}C NMR (CDCl_3): ppm 156.26, 156.22, 149.8, 149.4, 134.9, 134.2, 134.0, 131.4, 131.1, 123.0, 122.3, 122.1, 121.9, 116.6, 114.9, 114.7, 72.9, 71.4, 71.0, 70.3, 69.1, 68.7, 36.5; FAB MS m/z (M^+) calcd 890.57, found 891.10. Anal. Calcd for $\text{C}_{56}\text{H}_{58}\text{O}_{10}$: C, 75.49; H, 6.51. Found: C, 75.35; H, 6.48.

X-ray Crystal Structure. The structure was determined by application of direct methods using SHELX86 and refined by full-matrix least-squares on F using NRCVAX with anisotropic displacement factors for all non-H atoms. In the final refinement cycles a unit weight was employed. Refinement converged with R (R_w)=0.0578 (0.058) and (Δ/σ) $_{\text{max}}$ was 0.000. The $\Delta\rho_{\text{max}}$ and $\Delta\rho_{\text{min}}$ are 0.28 and -0.19 e \AA^{-3} , respectively.

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.¹⁶ Two separated water phase (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 is filled with the source phase which is a 0.8 mL of solution of 0.1 M lithium, sodium, potassium, rubidium, and cesium nitrate, respectively, using a single flux method. The outer cylinder is filled with 5.0 mL of deionized water as a 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 thermostated to 25±1

°C then 3 mL of the receiving phase was taken. The flux values (moles transported/sec m^2) for corresponding metal ion concentration were determined by the use of a Perkin-Elmer 2380 atomic absorption spectrophotometer. Blank experiments for which no calix[4]arene dibenzocrown ether is present were performed to determine a membrane leakage.

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