

## Cesium Selective Calix[6]arene Bisbridged Receptor

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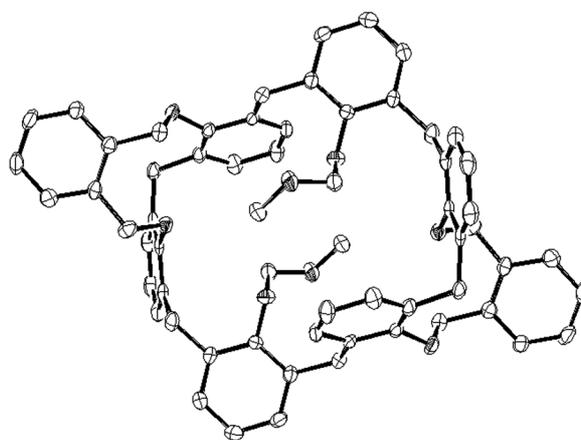
Calixcrowns are macromolecular hybrid structures composed of calix[*n*]arenes and crown ethers which have been demonstrated to be very effective complexing agents for alkali and other metal ions.<sup>1-3</sup> In particular, calix[4]arene crown-6 hosts have been extensively investigated in the sequestration and removal of radioactive Cs<sup>137</sup> ions from aqueous waste mixtures.<sup>4,5</sup> Cesium-137 is a relatively abundant nuclear fission product and constitutes a major source of heat in nuclear waters<sup>6,7</sup> along with strontium-90. Much effort has been made to the development of improved processes<sup>8,9</sup> for the removal of cesium-137 from nuclear wastes. For the efficient removal of cesium, several crown ethers have been prepared and their binding properties were investigated. Calixcrowns have been constructed from all four conformational isomers of calix[4]arenes (cone, partial cone, 1,2-, and 1,3-alternate) and structure-property correlations have been developed to a level where application of these molecules has become common.<sup>10,11</sup> Also the bis-bridged calix[4]crowns has been developed since the introduction of a second bridging unit generally increases the rigidity of the calix[4]arene framework.<sup>12</sup> For the development of a selective ligand for cesium ion, calix[6]arenes have been utilized as a receptor.<sup>13</sup> But, selectivity over potassium and rubidium is not quite high. The lack of selectivity has been attributed into the flexibility of the parent calix[6]arene moieties. The most effective approach to make them immobile is to build a bridge at the lower. Since Gutsche's lower rim-bridged calix[6]arene<sup>14</sup> in 1993, several lower rim-multibridged calix[6]arenes and their ion binding properties were reported.<sup>15-19</sup>

For the purpose of developing cesium selective ion receptors, we prepared three new calix[6]arene bisbridged receptor and investigated their structural and alkali metal ion binding properties by UV, <sup>1</sup>H NMR and solvent extraction.

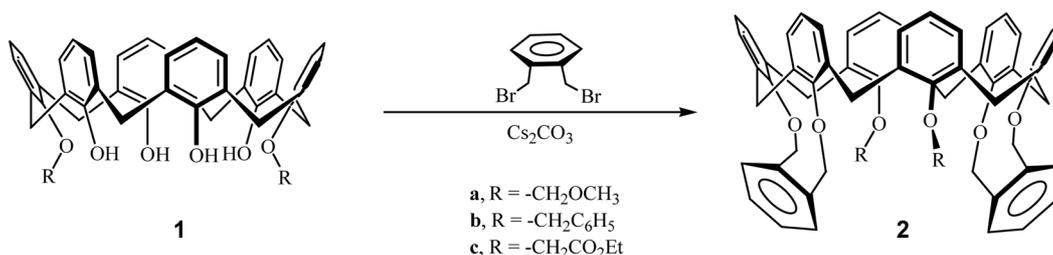
The bridging of the calix[6]arene was accomplished by the reaction of 1,4-dialkyl ethers **1**<sup>20</sup> and 1,2-bis(bromomethyl)-benzene in the presence of Cs<sub>2</sub>CO<sub>3</sub> in dilute solution as shown in Scheme 1. <sup>1</sup>H NMR spectrum of **2c** showed two pairs of doublets at  $\delta$  4.4-3.0 for the bridged methylene protons and a pair of doublets of eight diastereotopic bridged methylene protons (ArCH<sub>2</sub>O-) at  $\delta$  5.0-4.4. But, <sup>1</sup>H NMR spectrum of **2a** and **2b** did not show clear two pairs of doublets for the bridged methylene protons. The 1,2-bridged calix[6]arene ligands **1,2,3** could be defined as cone or 1,2,3-alternate conformer based on <sup>1</sup>H NMR.

The crystal structure confirms that **2a** exists as the 1,2,3-alternate conformation as shown in Figure 1. Two methoxy-methyl substituents were tilted inward to fill the empty calixarene cavity. Table 1 shows the detail data for X-ray structure refinement for **2a**.

The alkali metal binding properties were investigated from



**Figure 1.** Crystal structure of **2a**. Solvent molecule (molecule of chloroform) and hydrogen atoms have been omitted for clarity.



**Scheme 1.** Synthesis of 1,2-bridged calix[6]arene.

**Table 1.** Crystal data and structure refinement for **2a**

Empirical formula	C32 H29 Cl3 O4
Formula weight	583.90
Crystal system	Monoclinic
Space group	P2(1)/c
Unit cell dimensions	a = 8.2317(6) Å $\alpha = 90^\circ$ . b = 19.8039(14) Å $\beta = 94.3230(10)^\circ$ . c = 17.1879(13) Å $\gamma = 90^\circ$ .
Goodness-of-fit on F2	1.221
Final R indices [I > 2 $\sigma$ (I)]	R1 = 0.0956, wR2 = 0.1670
R indices (all data)	R1 = 0.1278, wR2 = 0.1781
Largest diff. peak and hole	0.342 and -0.417 e.Å <sup>-3</sup>

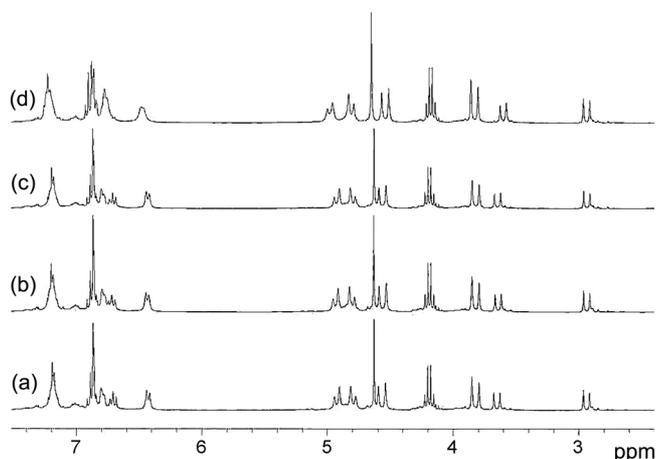
**Table 2.** Percentage extraction (%) of alkali picrates from water into CH<sub>2</sub>Cl<sub>2</sub> at 25 °C<sup>a</sup>

Ligands	%E				
	Li <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Rb <sup>+</sup>	Cs <sup>+</sup>
<b>2a</b>	0	0	0	0	0
<b>2b</b>	0	0	0	0	0
<b>2c</b>	0	0	0	0	12

<sup>a</sup>1 × 10<sup>-3</sup> M receptor solution in CH<sub>2</sub>Cl<sub>2</sub> was shaken (15 hrs) with 1 × 10<sup>-4</sup> M picrate salt solution in H<sub>2</sub>O.

two phases extraction experiment where aqueous solutions of the picrate salts are shaken with methylene chloride solutions of ligands. The amount of metal ion was determined from picrate absorption in the UV spectrum. Table 2 showed the percent extraction of metal picrate salts by **2a**, **2b** and **2c**. **2a** and **2b** showed no extraction with alkali metal ions and only **2c** showed 12% of cesium extraction. Two aromatic rings at the lower rim of calix[6]arene do not give any influence for the cesium binding. But, a weak binding of cesium with **2c** can be explained from the effect of two ester groups at 1,4-position.

The cation binding properties of **2c** were examined by <sup>1</sup>H NMR experiment in CD<sub>3</sub>CN. The addition of excess CsClO<sub>4</sub> caused a slight downfield shift of bridged methylene protons

**Figure 2.** <sup>1</sup>H NMR spectra of **2c** (a) without cation (b) with 100 eq. of KClO<sub>4</sub> (c) with 100 eq. of RbClO<sub>4</sub> (d) with 100 eq. of CsClO<sub>4</sub> in CD<sub>3</sub>CN.

at  $\delta$  4.85 and methylene protons adjacent ester group at  $\delta$  4.60. However, the addition of other alkali metal ions was not changed the spectrum at all as shown in Figure 2.

In summary, three calix[6]arene bisbridged ligands were synthesized by the bridge reaction of 1,4-dialkylcalix[6]arene with 1,3-bis(bromomethyl)benzene in the presence of cesium carbonate. X-ray structure analysis provide the 1,2,3-alternate conformation of ligand **3a**. Only ligand **3c** binds cesium ions weakly, presumably due to the 1,2,3-alternate conformation.

## Experimental Section

**37,40-Dimethoxymethoxy-38,39,-41,42-bis(*o*-xylyleneoxy)calix[6]arene (2a).** To a solution of 0.5 g (0.69 mmol) of 1,4-methoxymethyl calix[6]arene (**1a**) and 1.8 g (5.5 mmol) of Cs<sub>2</sub>CO<sub>3</sub> in 400 mL of CH<sub>3</sub>CN was added 0.4 g (1.5 mmol) of 1,2-bis(bromomethyl)benzene. The mixture was refluxed for 24 h under an atmosphere of N<sub>2</sub>, and the solvents were removed. The residue was treated with CHCl<sub>3</sub>-H<sub>2</sub>O, and the organic layer was separated and removed under reduced pressure. The residue was triturated with MeOH, and the resulting white precipitate was removed by filtration and purified from column chromatography of the residue afforded 0.3 g (47%) of **2a**. mp 264-267 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.31 (s, 2H, ArH), 7.16 (s, 6H, ArH), 6.92 (d, 8H, ArH,  $J = 4.77$  Hz), 6.84 (m, 3H, ArH), 6.75 (m, 2H, ArH), 6.57 (m, 2H, ArH), 6.40 (m, 3H, ArH), 4.83 (br s, 8H, -OCH<sub>2</sub>-), 4.62 (br s, 4H, -OCH<sub>2</sub>-), 4.54 (d, 4H, ArCH<sub>2</sub>Ar,  $J = 16.95$  Hz), 3.87-3.80 (m, 6H, ArCH<sub>2</sub>Ar), 3.25 (br s, 6H, -OCH<sub>3</sub>), 3.03 (d, 2H, ArCH<sub>2</sub>Ar,  $J = 14.19$  Hz).

**37,40-Dibenzoyloxy-38,39,-41,42-bis(*o*-xylyleneoxy)calix[6]arene (2b).** Following the same procedure described for **2a**, 0.24 g (39%) of **2b** was obtained after column chromatography (eluent; chloroform). mp > 227 °C dec; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.37-7.23 (m, 12H, ArH), 7.02-6.40 (m, 24H, ArH), 4.41 (m, 6H, -OCH<sub>2</sub>-), 4.11 (m, 6H, -OCH<sub>2</sub>-), 3.86 (d, 4H, ArCH<sub>2</sub>Ar,  $J = 16.86$  Hz) 3.49 (d, 2H, ArCH<sub>2</sub>Ar,  $J = 14.61$  Hz) 2.92 (d, 2H, ArCH<sub>2</sub>Ar,  $J = 14.73$  Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  155.68, 154.00, 138.16, 135.15, 134.37, 133.28, 130.70, 129.53, 128.40, 127.67, 127.33, 126.17, 123.81 and 123.21 (Ar), 73.60, 71.47 and 70.68 (-OCH<sub>2</sub>-), 30.87 and 27.14 (ArCH<sub>2</sub>Ar).

**37,40-Di(ethyloxycarbonyl)methoxy-38,39,-41,42-bis(*o*-xylyleneoxy)calix[6]arene (2c).** Following the same procedure described for **2a**, 0.2 g (32%) of **2c** was obtained after column chromatography (eluent; chloroform). mp > 261 °C dec; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.06-6.94 (m, 12H, ArH), 6.57 (t, 2H, ArH,  $J = 7.38$  Hz), 6.39 (d, 4H, ArH,  $J = 6.39$  Hz), 4.58 (t, 8H, ArOCH<sub>2</sub>- with *o*-xylene and ArCH<sub>2</sub>Ar,  $J = 16.7$  Hz), 4.37 (d of broad, 8H, ArOCH<sub>2</sub>- with *o*-xylene and -OCH<sub>2</sub>COO-), 4.26 (q, 4H, -CO<sub>2</sub>CH<sub>2</sub>-), 3.95 (d, 2H, ArCH<sub>2</sub>Ar,  $J = 13.74$  Hz), 3.82 (d, 4H, ArCH<sub>2</sub>Ar,  $J = 17.01$  Hz), 3.03 (d, 2H, ArCH<sub>2</sub>Ar,  $J = 13.86$  Hz), 1.29 (t, 6H, -CH<sub>3</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  168.93 (CO<sub>2</sub>), 156.10, 155.99, 153.96, 136.28, 136.11, 132.36, 131.83, 130.46, 129.88, 129.33, 128.96, 128.79, 128.47, 128.00, 127.45, 123.92 and 123.48 (Ar),

77.20, 73.64, 69.33 and 61.14 (-OCH<sub>2</sub>-), 32.12 and 31.59 (ArCH<sub>2</sub>Ar), 14.23 (CH<sub>3</sub>).

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