

Synthesis, Redox, and Cation Binding Properties of Tetraester Calix[6]arenes and Calix[6]quinones

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Received December 9, 1997

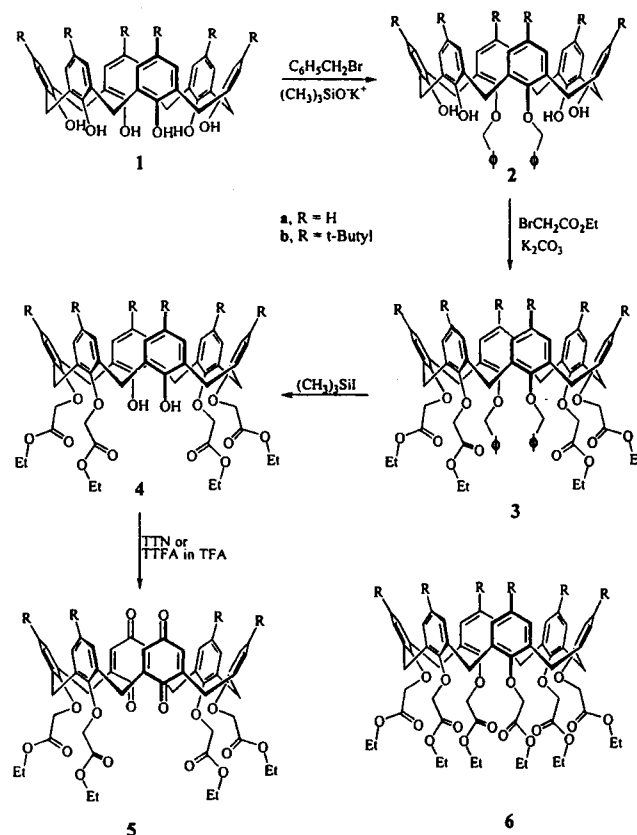
Calixarenes¹ have received much attention recently as an interesting class of cyclophanes possessing ionic and molecular binding properties.² Their potential as enzyme mimics has been suggested and appropriate functionalization of the phenolic units could extend this comparison to redox-switching enzyme.³ Calixarene esters particularly have shown remarkable ionophoric properties toward the alkali metals.⁴ For example, the tetramer ester display selectivity for the sodium ion, on the other hand the hexamer ester display selectivity for the potassium, rubidium and cesium over sodium ion.⁵ Various calix[4]arene ionophores were synthesized and their binding properties were investigated in detail, but calix[6]arene ionophores are still relatively rare. This stimulated us to design a new calix[6]arene containing tetraester group. In pursuit of redox switchable receptors we prepared a series of tetraester calix[6]arenes and their corresponding quinones and investigated their cation binding properties.

Tetraester calix[6]arenes and their corresponding quinones were prepared by the selective 1,4-dibenzoylation, exhaustive alkylation with ethyl bromoacetate, debenzoylation with $(\text{CH}_3)_3\text{SiI}$, and finally the oxidation of free phenolic unit (Scheme). Dibenzoylation was carried out by treating **1** with benzyl bromide in the presence of $(\text{CH}_3)_3\text{SiO}^- \text{K}^+$ according to the reported procedure (yield: 61-83%).^{6,7} The tetraester derivatives **3a** and **3b** were prepared by exhaustive alkylation⁸ of the dibenzyl compounds **2a** and **2b** with an excess of ethyl bromoacetate in refluxing acetone (yield: 68-73%). Subsequent removal of benzyl ether moiety by treatment with trimethylsilyl iodide⁹ yielded diphenol-tetraester **4** (yield 64-67%). Finally, the oxidation of **4a** with thallium(III) nitrate (TTN)¹⁰ produced the new tetraester calix[6]quinone **5a** as a pale yellow powder in 65% yield. On the other hand, the oxidation of **4b** was succeeded only with $\text{Ti}(\text{OCOFCF}_3)_3$ (TTFA) in trifluoroacetic acid solution,¹¹ which produced **5b** in 62% yields.

The ¹H NMR spectra of tetraester calix[6]arenes and their quinone derivatives showed two different types of spectral features depending on the *para* substituents. In the compounds containing no *para* substituent such as **3a**, **4a**, and **5a**, the ¹H NMR spectra show a well resolved spectral pattern, indicating that they exist in flexible conformations. On the other hand, in the compounds containing *p-t*-butyl group such as **3b**, **4b**, and **5b**, the ¹H NMR spectra are in general featureless showing several broad humps, which is characteristic of many conformationally flexible derivatives of calix[6]arenes. However, the stepwise addition of a solution of KSCN to CD_3CN solution of **3b** resulted in significant changes of the ligand protons corresponding to the complexed species as shown in Figure 1. The ¹H NMR spectra

of **3b** turned into a well resolved spectral pattern when complexed with potassium ion. That is, the aromatic region consists of five lines (δ 7.39, 7.34, 7.19, 7.13, and 7.05 ppm with a intensity of 1:5:2:1:2) while the bridging methylene region displays several doublets and multiplets. The resonances of *t*-butyl groups consist of three singlets at δ 1.33, 1.28, and 1.53 ppm with an intensity of 1:1:1 and methyl protons show two triplets at δ 1.22 and 0.67 ppm. This observation could be attributed to the conformational changes of **3b**, that is, potassium ion locking the calixarene into a distorted cone conformation by complexing strongly with the ester carbonyl oxygen donors and benzyl ether oxygen donors. Any further significant change was not observed after one equivalent of KSCN, suggesting that **3b** complexed with potassium ion 1:1 solution stoichiometry.

The cation binding properties of tetraester calix[6]arenes and their corresponding calix[6]quinones were investigated with usual extraction experiments^{5a} of metal picrate salt into



Scheme

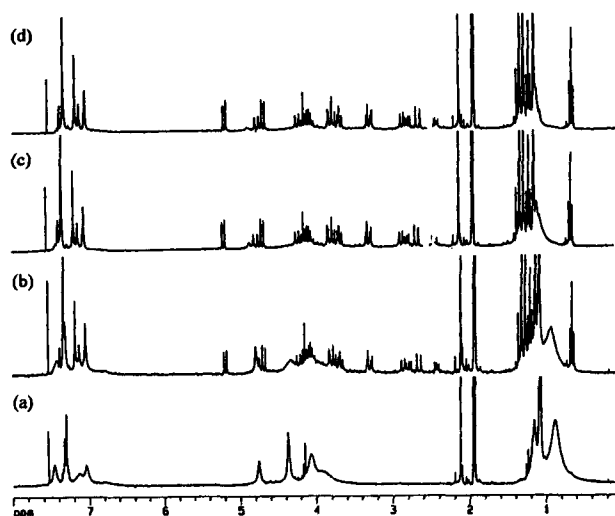


Figure 1. ^1H NMR spectra of **3b** (a) without cation, (b) with 0.5 equivalent of KSCN, (c) with 1 equivalent of KSCN, and (d) with 2 equivalents of KSCN in CD_3CN .

CH_2Cl_2 and the results are summarized in Table 1. For comparison, the results^{5a} of closely related hexaester **6** are also listed. Tetraester ligands **3a-5b** generally resemble the discrimination behavior of the hexaester **6** with reduced extraction efficiency, but similar selectivity. That is, in general, $\text{Cs}^+ > \text{Rb}^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+$. But the effects of the structural changes in ligands such as removing the *para* substituents as well as alkylating or making quinone group are remarkable for the cation extraction. Removal of *t*-butyl groups at the *para* position generally decreased the cation extraction significantly, for example, potassium extraction decreased dramatically, that is, 56.9% to 10.2% going from **3b** to **3a**, suggesting that the *t*-butyl groups at the *para* position direct the metal binding ester groups close enough for the effective binding. But one exception was observed when cesium was extracted with **3a**. Cesium extraction increased 7.4% when *t*-butyl group was removed. Increase in the cesium extraction with **3a** might be explained by the fact that cesium is the largest alkali metal cation and **3a** might be easier to bind with cesium than **3b**. Alkyl substitution on OH group increase the extraction ability three to four times, but oxidation of the OH group to quinone decrease the extraction ability toward cesium and rubidium cation.

Table 1. Extraction of Metal Picrates by Tetraester Calix[6]arene Derivatives

| Ligands | % Extraction | | | | |
|-------------------------|---------------|---------------|--------------|---------------|---------------|
| | Li^+ | Na^+ | K^+ | Rb^+ | Cs^+ |
| 3a | 0.3 | 0.8 | 10.2 | 27.8 | 70.7 |
| 3b | 1.4 | 8.7 | 56.9 | 59.8 | 63.3 |
| 4a | 0.9 | 1.0 | 2.2 | 8.8 | 13.2 |
| 4b | 0.8 | 0.5 | 11.3 | 14.9 | 19.0 |
| 5a | 1.1 | 0.8 | 4.8 | 4.2 | 6.8 |
| 5b | 0.8 | 0.5 | 2.8 | 1.1 | 4.1 |
| 6b ^{4a} | 6.7 | 15.6 | 66.2 | 60.5 | 88.9 |

Organic phase: [Ligand] = 2.5×10^{-4} M, (CH_2Cl_2 , 5 mL). Aqueous phase: [M^+Pic] = 2.5×10^{-4} M, (5 mL). Measurements are made triplicate at room temperature.

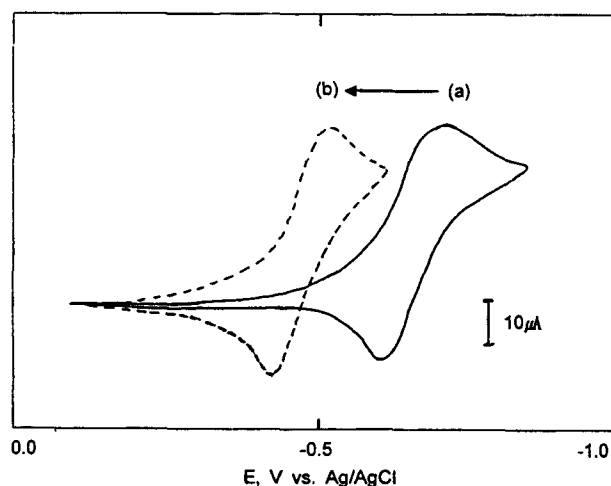


Figure 2. Cyclic voltammograms of **5b** (3 mM) (a) without cation, and (b) with 1 equivalent of CsNO_3 in CH_3CN containing 0.1 M TBAP at glassy carbon electrode (scan rate: 50 mV/sec).

Tetraesters of calix[6]arenequinones contain two quinone groups as ring member. Electrochemical reduction of calix[6]arenequinone (**5b**) shows two peaks of which the first wave is reversible process of one-electron transfer at +0.73 V vs Ag/AgCl, and the second is quasi-reversible wave of one-electron transfer at +1.15 V. The number of electrons corresponding to each peak was confirmed by coulometry. Figure 2 shows the cyclic voltammograms for calix[6]arenequinone (**5b**) in the absence of any cation and in the presence of Cs^+ in MeCN containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAP) at glassy carbon electrode. With addition of 1 equivalent of Cs^+ , the cyclic voltammetry for **5b** displayed a new wave at a far positive potential than that of the free calixarene, and further addition of Cs^+ makes no change. Table 2 shows the value of potential shift due to the presence of cations. The shift magnitude of reduction potential depends on the size of metal cations and the complexation strength between reduced semiquinonecalix[6]arenes and cations. The larger the size of alkali metal ion, the larger the value of ΔE . This result exhibits a reverse trend to that obtained from calix[4]arenequinones.¹² The ligating sites of calix[6]arenequinones may be six carbonyl oxygens which are four esters and two quinones. The cavity of six carbonyl oxygens

Table 2. Electrochemical Data*

| Ligand | Cation | $E^{\circ\text{N}}$ | $\Delta E^{\circ\text{N}}$ |
|-----------|------------------|---------------------|----------------------------|
| 5a | none | 0.73 | — |
| | Na^+ | 0.63 | 0.10 |
| | K^+ | 0.65 | 0.08 |
| | Cs^+ | 0.56 | 0.17 |
| 5b | Ba^{2+} | 0.73 | 0.00 |
| | none | 0.73 | — |
| | Na^+ | 0.62 | 0.11 |
| | K^+ | 0.65 | 0.08 |
| | Cs^+ | 0.50 | 0.23 |
| | Ba^{2+} | 0.67 | 0.06 |

*Obtained in MeCN solution containing 0.1 M NBu_4PF_6 as supporting electrolyte.

in calix[6]arenequinones seems to be larger than that of four carbonyl oxygens in calix[4]arenequinones. The size of semiquinonecalix[6]arenes is comparable to the size of Cs⁺ and their relatively strong complexation results in larger positive potential shift. The complexation of calix[6]arenequinones with Cs⁺ is found to more stable complex than with Ba²⁺.

In pursuit of redox switchable receptors we prepared a series of tetraester calix[6]arenes and their corresponding quinones and investigated their cation binding properties. Tetraester benzyl derivative **3b** showed high extraction for potassium, rubidium, and cesium ion and complexed with potassium ion in 1:1 solution stoichiometry. The magnitude of shift in reduction potential depends on the size of metal cations and the complexation strength between reduced semiquinonecalix[6]arenes and cations. Generally, the larger the size of alkali metal ion, the larger the value of ΔE .

Acknowledgment. We are indebted to the Basic Science Research Institute Program, Ministry of Education of Korea (BSRI 97-3429 and BSRI 97-3450) for generous support of this work.

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Chemical Vapor Deposition of MgO Films Using a New Single Source

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Received December 13, 1997

The MgO single crystal is a preferred substrate for growing various thin film materials. The oxygen lattice of MgO crystal matches well with those of perovskite oxide crystals as well as those of Si and GaAs crystals. MgO buffer layers were employed to grow high T_c superconductors¹⁻⁴ and fer-

roelectrics⁵⁻¹⁰ as well as a nitride.¹¹ Growing high quality superconductor films on GaAs using the MgO buffer layer received great attention for RF and microwave applications.^{2,12,13}

There were several reports on chemical vapor deposition (CVD) of MgO although MgO films were more frequently prepared by physical vapor deposition methods such as electron beam evaporation,¹² pulsed laser deposition,^{7,9-11} and

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