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Synthesis and Cation Binding Properties of Triester Calix[4]arenes and Calix[4]quinones

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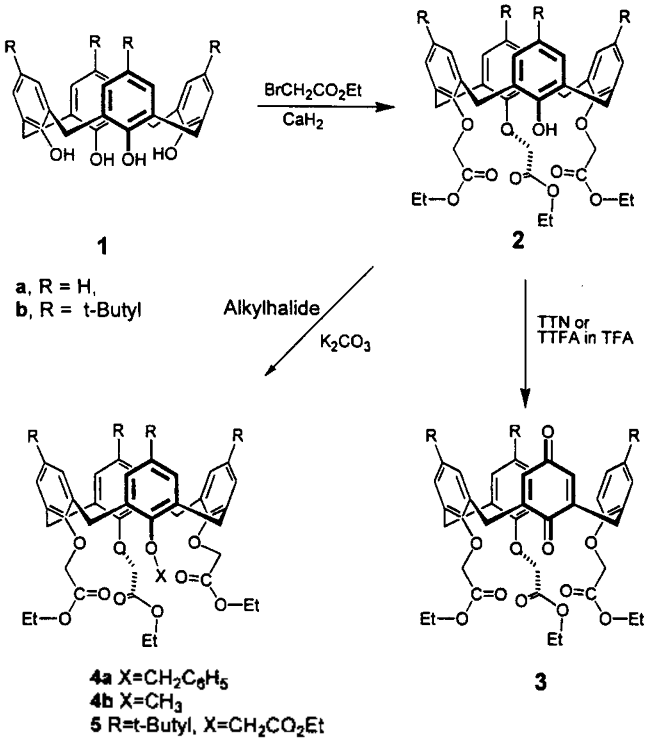
Calixarenes[1] have received much attention recently as a interesting class of cyclophanes possessing ionic and molecular binding properties.[2] Their potential as enzyme mimics has been suggested and appropriate functionalization of the phenolic units could extend this comparison to redox-switching enzyme.[3]

Calixarene esters have shown the remarkable ionophoric properties[4] toward the alkali metals. 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] and Beer *et al.*[6] reported the cation binding properties of diester calix[4]quinone. This stimulated us to design a new ester group containing calixquinone. In pursuit of redox switchable receptors we prepared a series of triester calix[4]arene and their corresponding quinone and investigated their cation binding properties.

Triester calix[4]arenes and their corresponding quinones were prepared by the selective trialkylation followed by the oxidation of free phenolic unit (Scheme). Trialkylation was carried out with ethyl bromoacetate in the presence of CaH_2 in DMF according to the reported procedure.[7] The oxidation of **2a** with thallium(III) nitrate (TTN)[8] produced the new triester calix[4]quinone **3a** as a pale yellow powder in 34% yields. On the other hand, the oxidation of **2b** was succeeded only with $Tl(OCOCF_3)$ in trifluoroacetic acid solution,[9] which produced **3b** in 40% yields. For comparison of cation binding properties among the triester calix[4]arenes, their alkyl derivatives **4a** and **4b** were prepared by the reaction of **2** with the corresponding alkyl halides in the presence of K_2CO_3. The methyl derivative **4b** was prepared by the reaction of **2b** and methyl iodide in the presence of NaH because benzylation reaction between **2b** and benzyl bromide in the presence of K_2CO_3 failed probably due to the steric factor of **2b**.

The ^1H NMR spectra of triester calix[4]quinone **3a** showed three doublets at 7.13, 6.81, and 6.20 ppm and two triplets at 6.96 and 6.48 for the nine aromatic protons and a singlet at 6.82 for the two quinone protons. The bridge methylene protons appear as two pair of doublets between 3.2 to 4.6 ppm region and a complicated multiplet at around 4.2 ppm region represents the $-OCH_2CO_2-$ and $-OCH_2-$ protons. The ^{13}C NMR spectra **3a** showed two peaks at 32.41 and 31.06 ppm for the bridge methylene carbons, indicating that **3a** exists as a cone conformation.[10,11] The stepwise addition of a solid $NaClO_4$ to CD_3CN solution of **3a** resulted in large significant downfield shifts[10] of the ligand protons corresponding to the complexed species as shown in Figure 1. Most notable down field shifts were observed for a doublet at 6.20 ppm and a triplet at 6.48 ppm which represent six aromatic



Scheme

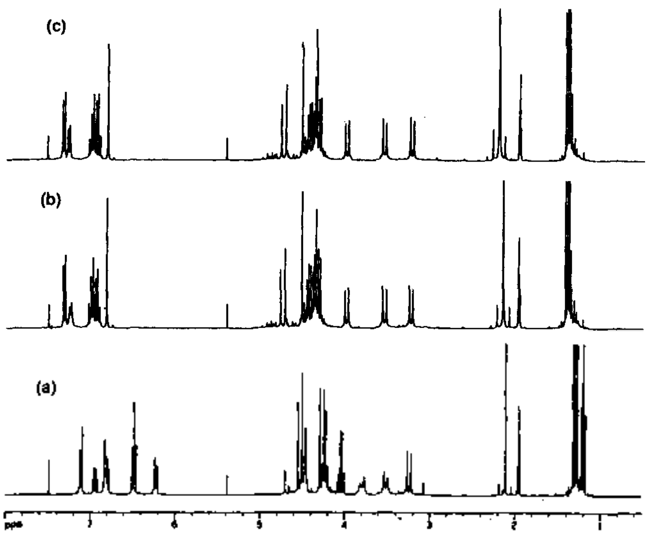


Figure 1. ^{1}H NMR spectra of **3a** (a) without cation. (b) 1 equivalent of $NaClO_4$. (c) 2 equivalents of $NaClO_4$ in CD_3CN.

protons adjacent to quinone ring. But, a singlet at 6.82 ppm which represents two quinone protons was shifted only 0.2 ppm upfield upon addition of $NaClO_4$. This observation may be attributed to the sodium ion locking the calixarene into a cone conformation by complexing strongly with the ester carbonyl oxygen donors, but not strongly interacting with the quinone carbonyl moieties. Any further significant change was not observed after one equivalent of $NaClO_4$, suggesting that **3a** complexed with sodium ion 1 : 1 solution stoichiometry. A quite similar behavior was observed when **3b** treated with $NaClO_4$, indicating that the complexing mode with metal cation is not much influenced regardless of the substituents at the para position. The ion binding properties of triester calix[4]arenes and their corresponding calix[4]quinones were investigated with usual extraction experiments[5a] of metal picrate salt into CH_2Cl_2 and the results are summarized in Table 1. For comparison, the results[5a] of closely related tetraester **5** are also listed. The most effective extraction was observed with calixarene **4b** and sodium ion. Triester ligands **2a-4b** generally resemble the discrimination behavior of the tetraester **5**[5a] with somewhat reduced extraction efficiency and a similar selectivity. That is, in general, $Na^+ \gg K^+ > Rb^+ \approx Cs^+ > Li^+$. But the effects of the structural changes in ligands such as removing the para substituents as well as alkylating or making quinone formation with OH group are remarkable for the cation extraction. By removing *t*-butyl groups at the para position decreased the sodium extraction significantly, that is, 67.1% to 19.1% going from **4b** to **4a**, suggesting that the *t*-butyl groups at the para position direct the metal binding ester groups close enough for the effective binding. Alkyl substitution on OH group increase the extraction ability three to four times and also oxidation of the OH group to quinone increase the extraction ability in about twice, suggesting that the OH proton competes with cation for binding with ester groups.

In pursuit of redox switchable receptors we prepared a series of triester calix[4]arene and their corresponding quinone and investigated their cation binding properties. Triester methyl derivative **4b** showed the highest extraction for sodium ion and complexed with sodium ion 1 : 1 solution stoichiometry. Redox properties of calix[4]quinones in the presence of cations are currently in progress.

Table 1. Extraction of Metal Picrates by Triester Calix[4]arene Derivatives

Ligands	% Extraction				
	Li^+	Na^+	K^+	Rb^+	Cs^+
2a	0.5	4.4	1.3	2.0	0.1
2b	0.5	16.9	3.7	2.1	3.0
3a	0.8	10.7	1.8	1.2	0.6
3b	0.2	21.3	5.0	2.3	1.2
4a	0.1	19.1	2.3	0.1	0.2
4b	1.7	67.1	16.6	6.9	8.7
5[5a]	15.0	94.6	49.1	23.6	48.9

Organic phase: [Ligand]=2.5×10^{-4}, (CH_2Cl_2, 5 mL). Aqueous phase: 2.5×10^{-4} M picric acid in 0.1 M aqueous MOH (5 mL). Measurements are made triplicate at room temperature.

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Synthesis of Sila-Macrocycles, New Type of Metal Ligands

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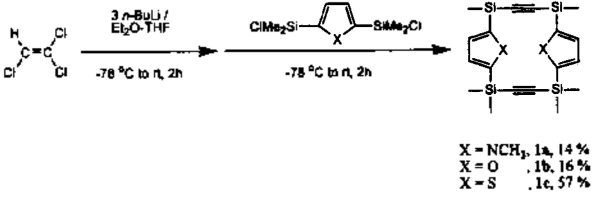
Cyclic species with alternating silicon and acetylenic units have been studied by many groups due to their unusual orbital interactions and potential coordination capabilities.[1] Sila-calixarenes were also synthesized to investigate the binding properties towards metal ions.[2] Carbon is commonly used as the bridging element in macrocycles such as porphyrins or calixarenes. Introduction of silicon as a bridge instead of carbon can give new binding properties absent in the carbon analogues.[3] Since the C-Si bond lengths are longer than C-C bonds, smaller rings become less strained when silicon is introduced. Many groups have studied macrocycles because the pocket size and shape can be adjusted easily for the inclusion processes. We report the synthesis of new sila-macrocycles containing both C≡C bonds and heteroaromatics, and the metal complexation behavior of these compounds.

As shown in Scheme 1, dilithioacetylene was generated from trichloroethylene quantitatively according to the literature procedure.[4] Slow addition of the corresponding 2,5-bis(chlorodimethylsilyl)heteroaromatics[5] gave readily the macrocycles which have rigid structures and will stack easily. The C≡C bond was inserted to give new coordination site. If we can bind both of the C≡C bond in a single molecule with some metal, the product would be either a metal complex or a ladder polymer with defined nanostructure. The X-ray structure analysis of **1c** (Figure 1) reveals that the overall structure is similar to the tetrathiasila-calix[4]arene.[2] It has C_2 axis of symmetry and thiophene ring is twisted from the plane composed of four silicon atoms to relieve steric crowdness of the two sulfur atoms.



Scheme 1. Syntheses of macrocycles **1a**, **1b** and **1c**.

Corriu *et al.*[7] reported the synthesis of linear polymer having the same repeat unit as the thiophene derivative **1c** using 2,5-dilithiothiophene and bis(chlorodimethylsilyl)-acetylene. The difference can be explained by the fact that the reactivity of the dianions towards chlorosilane reagents differ. The less reactive dilithioacetylene allowed time for intramolecular α-ω elimination of LiCl rather than reacting with another molecule to give linear polymer.

To further enhance the binding possibility by control of the ring size, a diacetylene unit was introduced as shown in Scheme 2. Dilithiobutadiyne was generated from hexachlorobutadiene by Barton's method,[6] and subsequent reaction with 2,5-bis(chlorodimethylsilyl)heteroaromatics gave the cyclization products. As a whole, product yields are poor because

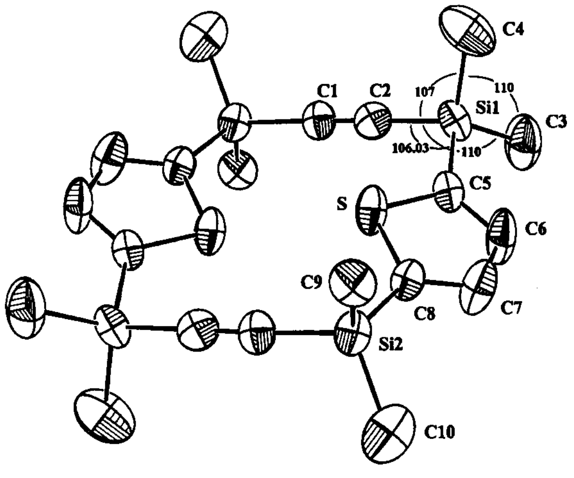


Figure 1. ORTEP view of $[C_{20}H_{28}S_2Si_4]$ with selected bond lengths (Å) and angles (°): Si(1)-C(2) 1.853(4), Si(1)-C(5) 1.860(6), C(1)-C(2) 1.201(6), C(5)-C(6) 1.364(6), C(6)-C(7) 1.422(10), C(5)-S 1.708(6); C(2)C(1)Si(2) 175.0(5), C(2)Si(1)C(5) 106.0(3), C(2)Si(1)C(3) 110.4(2), C(2)Si(1)C(4) 107.6(2), C(3)Si(1)C(4) 110.8(4), Si(1)C(5)S 122.7(2), Si(1)C(5)C(6) 128.1(5), C(5)C(6)C(7) 112.9(6). Selected dihedral angles (°): C(2)Si(1)C(5)S −36.84, C(2)Si(1)C(5)C(6) 146.56, C(5)Si(1)C(2)C(1) 52.63, C(8)SC(5)Si(1) −177.05.