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Ion Complexation Properties of Calix[6]Arene Derivatives: I. 1,4-Calix[6]Crown-4 Derivatives

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A series of 1,4-*p*-*tert*-butyl-calix[6]crown-4 tetraesters, tetraamides, tetraacids with defined conformation have been synthesized, and their complexation properties towards metal ions and alkyl ammonium ions were investigated systematically. It was found that 1,4-*p*-*tert*-butyl-calix[6]crown-4 tetraethylester (3a) and 1,4-*p*-*tert*-butyl-calix[6]benzocrown-4 tetramethylester (4b) show high selectivity towards Na^+, Li^+, respectively and all of them exhibit high complexation abilities towards $Et_2NH_2^+$ cation.

Keywords: calix[6]crown, synthesis, recognition, complexation, selectivity

INTRODUTION

Calixarenes have been used as versatile building blocks for artificial receptors in supramolecular chemistry enabling the design and construction of more elaborate molecules and assemblies.[1–4] In order to preorganize the host it is usually desirable to prepare the calixarenes with well-defined structural features suitable for complexation. Many calix[4]arenes derivatives including calix[4]crown derivatives with defined conformation have been synthesized and their outstanding complexation abilities have been reported.[3] Calix[6]arene possesses a ionophoric cavity larger than that of calix[4]arene, which make it the next candidate for close scrutiny. However, the attempts to apply calix[6]arenes as hosts to specific molecular recognition was unsuccessful for a long time because of their large conformational freedom. Gutsche *et al.* previously described that "*even the calix[6]arenes are rather flexible and further insight into their mode of action must await the construction of more rigid and conformationally-defined analogs*" .[5]

More recently, it was shown that the phenyl unit rotation can be suppressed by the multipoint bridging,[6,7] monobridging,[8–10] or doubly bridging[11] of the lower rim. A series of calix[6]arene derivatives with defined conformation have been synthesized. However, only a few papers concerned the ion recognition properties of them.[8,11,12] the rigid cavity of 1,3,5-tris(bromomethyl)benzene capped calix[6]arene[12] and rigid stereochemical isomers of calix[6]arene bis-crown-4[11] show very high cesium ion selectivity among alkali metal ions.

In this paper, we wish to report the selectively bridging of calix[6]arene at 1,4-positions by an improved method, the syntheses of 1,4-*p*-*tert*-butylcalix[6]crown-4 tetraesters, tetraamids and tetraacids, and a systematical investigation on their recognition properties towards alkali metal ions, ammonium and alkylammonium cati-

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* Corresponding Author.

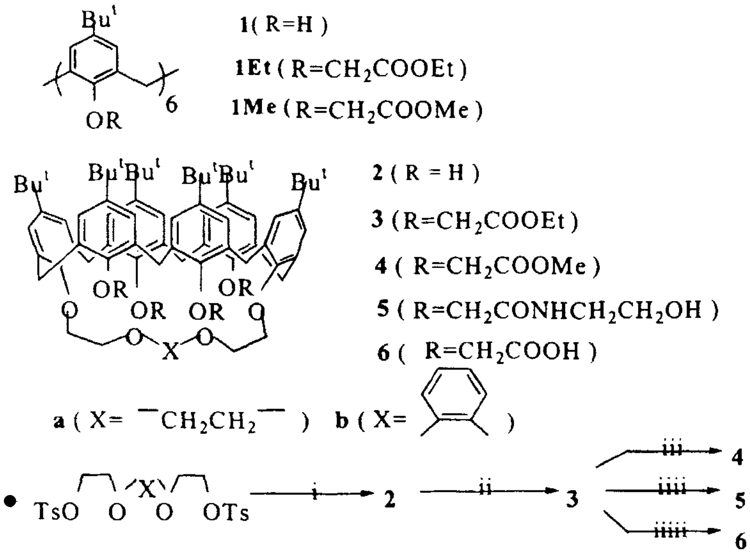
ons. It was found that 1,4-*p-tert*-butyl-calix[6] crown-4 tetraethylester (**3a**) and 1,4-*p-tert*-butyl-calix[6]benzocrown-4 tetramethylester (**4b**) show very high selectivity towards Na^+, Li^+, respectively. These phenomena were never reported for the calix[6]arene derivatives. And also, the $Et_2NH_2^+$ cation may be the most matchable ion to be included into the π-base cavity of the hosts.

RESULTS AND DISCUSSION

Synthesis and conformation

The synthetic route was depicted in scheme 1. The *p-tert*-butylcalix[6]-1,4-crown-4s have been synthesized in 1999 by our group by reacting *p-tert*-butylcalix[6]arene **1** with triethylene glycol ditosylates in K_2CO_3 / CH_3CN.[5] The reaction product was difficult to be separated and the yields of calix[6]-1,4-crown-4 **2a** and calix[6]-1,3-crown-4were (19%) and (20%), respectively.. However, we found that by using toluene as the solvent instead of MeCN, **2a** was obtained as the main product in satisfactory yield (40%) and the work up was simplified in comparison with the original method. By the same method, **2b** was also obtained in satisfactory yield (55%).

Further treatment of **2** with ethyl bromoacetate in the presence of NaH as a base in dioxane gave **3a** and **3b** in high yields of 85%, 83%, respectively. They were further converted to **4a(b)**, **5a(b)** and **6a(b)** via ester exchange, aminolysis and hydrolysis, respectively. The yields were almost quantitative.The structures and conformations of **3**, **4**, **5** and **6** as shown in Scheme 1 were confirmed by ^{1}HNMR, FAB-MS and elemental analysis. The ^{1}HNMR spectra of these compounds show two singlets in a ratio of 1:2 for *tert*-butyl, which indicates that they are 1,4-bridged calix[6]arene tetrasubstituted products. Two pairs of doublets (ratio 1:2) with an AB pattern for the methylene protons in calix[6]arene skeleton and AB system for the protons of the OCH_2CO, reveal that they adopt cone conformations.[8,10] The stable cone conformation of these derivatives can attribute to the intramolecular bridging of calix[6]arene in comparison with that *p-tert*-butylcalix[6]arene hexaacetates possesses no defined conformation.



SCHEME 1 i. K_2CO_3, toluene. ii. NaH, dioxane. iii. Toluene, methanol iv. $H_2NC_2H_4OH$. V. NaOH, EtOH

Extraction Studies

Examination of the CPK molecular models revealed that these compounds were highly pre-organized for binding cations. The percentage extractions of hosts **2**, **3**, **4**, **5** and **6** towards a series of alkylammonium cations as well as Li^+, Na^+, K^+, and NH_4^+ from water into CH_2Cl_2 at 20°C were summarized in Table I.

From the Table I, it can be seen that the derivatives **3**, **4**, **5** and **6** with more stable cone conformations showed outstanding affinity towards testing cations with a few interesting abnormal as comparing with their conformational mobile precursor **2**. The ionophore **1**-ethylester and **1**-methylester exhibit high extraction capabilities for alkali metal cations with increasing ion radius, but low extraction capabilities for lithium ion. As mentioned above, the rigid cavity of 1,3,5-tris(bromomethyl)benzene capped calix[6]arene[12] and rigid stereochemical isomers of calix[6]arene bis-crown-4[11] show very high cesium ion selectivity among alkali metal ions also. However, the contrary phenomena were observed for these calix[6]-1,4-crown-4 derivatives which showed the larger ion radius, the lower extraction capability. And moreover, **3a** and **4b** which show outstanding selectivity toward Na^+, Li^+ respectively. To the best of our knowledge, **4b** is the first example with high lithium ion selectivity, and also, **3a** is an outstanding selective ionophore for sodium ion, especially, in calix[6]arene chemistry. The increase of complexation ability towards alkali metal cations could be attributed to the combination of the triethylene glycol spacer reducing the flexibility of conformation, the newly created not so rigid small cavity in the calix[6]crown-4's and the favorable influence of esters groups on the complexation of alkali metal cations. The high selectivity may be due to the cooperation of the appropriate structure of the polyoxyethylene spacer and the appropriate alkyl chain in the ester moiety that can create an appropriate size of cavity and thus improve complexation selectivity. It is difficulty to explain no such selectivity has been observed but large complexation ability for **3b**, **4a**, **6a** and **6b**. However, it can be concluded that the complexation ability towards alkali metal ions are very sensitive to the structures of the hosts, and the ester groups are the most favorable group among the substituted groups used to create selective ionphores.

TABLE I Percentage extraction (%E) of picrate salts from water into $CHCl_3$ at 20 °C.[a] Arithmetic mean of several experiments-standard deviation on the mean: $\sigma_{N-1} \leq 1$

Host	*%E*							
	Li^+	Na^+	K^+	Cs^+	NH_4^+	$Me_2NH_2^+$	$Et_2NH_2^+$	$n\text{-}PrNH_3^+$
3a	1.4	35.9	<1	<1	23.5	37.2	65.4	17.2
3b	44.7	32.4	14.6	8.6	28.6	40.0	67.8	19.3
4a	53.1	46.0	27.4	12.3	25.7	38.9	69.3	16.8
4b	34.5	1.3	<1	<1	30.9	36.7	70.5	18.8
5a	36.7	34.5	3.4	/	34.8	39.8	72.9	20.4
5b	23.6	17.9	8.7	/	38.5	43.6	73.3	18.9
6a	47.0	38.9	21.2	/	43.6	45.7	68.6	21.1
6b	33.7	23.9	15.5	/	39.4	43.5	66.5	19.7
[b]**2a**	2.6	6.5	4.5	/	3.6	3.7	5.3	2.5
[b]**2b**	1.2	3.9	4.1	/	4.0	3.8	5.6	2.9
[c]**1Et**	11.4	50.1	85.9	/	/	/	/	/
[c]**1Me**	1.7	10.3	29.1	/	/	/	/	/

[a] 1.00ml of 0.005 mol dm^{-3} receptor solution in $CHCl_3$ was shaken (20 min) with 1.00ml of 0.005 mol dm^{-3} picrate salt solution in triple distilled H_2O and the percentage extraction was measured from the resulting absorbance at 380 nm. Control experiments showed that no picrate extraction occurred in the absence of the calixarene derivative.

[b,c] These data quoted from Ref. 10 and 13, respectively.

On the other hand, the extraction experiments of these hosts towards alkylammonium cations showed other interesting results. It had been reported by S. Shinkai et al that the π -base cavity of calix play crucial role in binding alkylammonium cations and concluded that the cone-shape cavity is preferable,[14,15] for example, C_3-symmetrically upper rim capped calix[6]arene is favorable for inclusion of trimethylammonium ion in π -base cavity than hexamethoxycalix[6]arene.[16] In this experiment, all of the eight calix[6]crown-4s derivatives adopt the stable cone conformation which should be favorable for inclusion of alkylammonium cations. Moreover, due to the almost same length of bridging, it is reasonable to assume that the hosts **3a(b), 4a(b), 5a(b)** and **6a(b)** have almost same size of the π -base cavity which had been supported by the examination of the CPK molecular models. These characteristics mean that these derivatives should have excellent and analogous extraction abilities towards alkylammonium cations. This deduction was proved by extraction experiment. From Table I, it can be seen that the complexation abilities of these hosts in binding alkylammonium cations showed the analogous change, $Et_2NH_2^+ > Me_2NH_2^+ >$ n-$PrNH_3^+$. The phenomenon can be explained as then π-base cavity of calix but not the polar region groups plays the crucial role in interaction with alkylammonium cations although the influences of the polar region groups which changed the extraction percentage a little can not be neglected completely. Also, it can be seen that all of these calix[6]arene derivatives exhibited $Et_2NH_2^+$ selectivity which may indicated that $Et_2NH_2^+$ was the most matchable one of the test cations to the π -cavity of calix[6]-1,4-crown-4s.

EXPERIMENTAL

Melting points are uncorrected. ^{1}HNMR spectra were recorded on Bruker-ARX 300 instruments at ambient temperature. TMS was used as an internal standard. FAB-MS spectra was obtained from a Kratos MS80RF mass spectrometer. UV-VIS measurements were recorded on Shimadzu-240 Uv-vis spectrophotometer equipped with two thermostat cell compartments. Elemental analyses were performs by the Analytical Laboratory of the department of chemistry. All solvents were purified by standard procedures. *p-tert*-butylcalix[6]arene, triethylene glycol ditosylates and 1,2-bistosyloxyethoxybenzene were prepared according to the published procedure.

The improved procedure for syntheses of p-tert-butylcalix[6]crown-4 2a and 2b

A mixture of *p-tert*-butylcalix[6]arene **1** (5mmol), triethylene glycol ditosylates (5.5 mmol) or 1,2-bistosyloxyethoxybenzene (5.5 mmol), anhydrous K_2CO_3 (40 mmol) in toluene (500 ml) was refluxed for 30 h under N_2. After the solvent was removed under reduced pressure, the residue was treated with HCl (10%, W/V) and extracted with $CHCl_3$. The organic layer was separated, dried by $MgSO_4$, and then filtered, concentrated. The crude products were subjected to recrystallization from $CHCl_3$ and petroleum ether(60–90°C) to afford products **2a** or **2b** in yields of 40% or 55%. The characteristics of them were in accordance with reference 10.

The procedure for syntheses of p-tert-butylcalix[6]-1,4-crown-4 tetraesters 3a and 3b

A mixture of **2**(1 mmol) with ethyl bromoacetate (5 mmol) in the presence of NaH (8 mmol) as a base in dioxane (50 ml) were stirred at 70° C for 10 h and the excess of NaH eliminated by addition of a minimal quantity of methanol (**CAUTION!**). Then the solvent was removed under reduced pressure, the residue was neutralized with HCl (10%, W/V) and extracted with $CHCl_3$. The organic layer was separated and evaporated to dryness. After recrystallized from $CHCl_3$/MeOH, **3a** and **3b** were obtained in high yields of 85%, 83%, respectively. **3a**: m. p 260–2 °C. ^{1}HNMR (300 MHz, CDCl$_3$). 1.13(s, 36 H, ArC(CH$_3$)$_3$); 1.30(t, 12 H, *J* =7.8 Hz, CH$_3$); 1.35(s, 18 H, ArC(CH$_3$)$_3$); 2.79(bs, 4 H, OCH$_2$), 3.01(bs, 4 H, OCH$_2$); 3.37(d, 2 H, *J* =15.0 Hz, ArCH$_2$Ar); 3.95 (s, 4 H, OCH$_2$); 4.25–4.37(m, 16 H, COOCH$_2$ and OCH$_2$CO); 4.37(d, 4 H, *J* =15.3 Hz, ArCH$_2$Ar); 4.43(d, 4 H, *J* =15.3 Hz, ArCH$_2$Ar); 4.59(d, 2 H, *J* =15.0 Hz, ArCH$_2$Ar); 6.98, 7.24, 7.65 (s each, 4 H each, ArH). MS (FAB): m/z=1431(MH$^+$). Anal. calcd for C$_{88}$H$_{118}$O$_{16}$: C, 73.82; H, 8.31. Found: C, 73.80; H, 8.35. **3b**: m. p 254–6 °C. δ_H: 0.90(s, 36 H, ArC(CH$_3$)$_3$); 1.10(t, 12 H, *J* =7.5 Hz, CH$_3$); 1.37(s, 18 H, ArC(CH$_3$)$_3$); 3.15 (bs, 4 H, OCH$_2$); 3.33(d, 2 H, *J* =15.3 Hz, ArCH$_2$Ar); 3.56(m, 4 H, OCH$_2$); 4.08(bs, 8 H, OCOCH$_2$); 4.42(d, 4 H, *J* =13.3 Hz, OCH$_2$CO); 4.49(d, 4 H, *J* =13.3 Hz, OCH$_2$CO); 4.52(d, 4 H, *J*= 15.6 Hz, ArCH$_2$Ar); 4.71(d, 4 H, *J* = 15.6 Hz, ArCH$_2$Ar); 4.78(d, 2 H, *J* = 15.3 Hz, ArCH$_2$Ar); 6.61(s, 4 H, ArH); 6.88(s, 8 H, ArH); 7.30 (s, 4 H, ArH), MS (FAB) m/z=1480(M+2H$^+$). Anal. calcd for C$_{92}$H$_{118}$O$_{16}$: C, 74.67; H, 8.04. Found: C, 74.72; H, 7.95.

The procedure for syntheses of p-tert-butylcalix[6]-1,4-crown-4 esters 4a and 4b

Calix[6]-1,4-crown-4 tetraesters **3a(b)** (1 mmol) were refluxed in toluene-methanol (1:1) mixture (80 ml) for 10 h. The solvent was removed under reduced pressure and the residue was treated with water to give crude products, following by crystallized from CHCl$_3$ /MeOH, **4a(b)** was obtained as white crystal in almost quantitative yields. **4a**: m. p 226–8 °C. δ_H 0.85(s, 36 H, ArC(CH$_3$)$_3$); 1.38(s, 18 H, ArC(CH$_3$)$_3$); 2.92(bs, 4 H, OCH$_2$); 3.18(bs, 4 H, OCH$_2$); 3.34(d, 2 H, *J* =15.0 Hz, ArCH$_2$Ar); 3.43(d, 4 H, *J* =15.6 Hz, ArCH$_2$Ar); 3.67(bs, 4 H, OCH$_2$); 3.79(s, 12 H, OCH$_3$); 4.51(d, 4 H, *J* =15.6 Hz, ArCH$_2$Ar); 4.62(d, 4 H, *J* =13.6 Hz, OCH$_2$CO); 4.72(d, 4 H, *J* =13.6 Hz, OCH$_2$CO); 4.84(d, 2 H, *J* =15.0 Hz, ArCH$_2$Ar); 6.63, 6.95, 7.27(s each, 4 H each, ArH). MS (FAB) m/Z=1375(MH$^+$). Anal. calcd for C$_{84}$H$_{110}$O$_{16}$: C, 73.33; H, 8.06. Found: C, 73.40; H, 8.01. **4b**: m. p 234–6 °C. δ_H 0.86(s, 36 H, ArC(CH$_3$)$_3$); 1.38(s, 18 H, ArC(CH$_3$)$_3$); 3.17(bs, 4 H, OCH$_2$); 3.32(d, 2 H, *J* =15.3 Hz, ArCH$_2$Ar); 3.51(bs, 12 H, OCH$_3$); 3.56(s, 4 H, OCH$_2$); 4.44–4.54(m, 12 H, OCH$_2$CO and ArCH$_2$Ar); 4.67(d, 4 H, *J* =15.0 Hz, ArCH$_2$Ar); 4.72 (d, 2 H, *J* =15.3 Hz, ArCH$_2$Ar); 6.62(s, 4 H, ArH); 6.94(s, 8 H, ArH); 7.30(s, 4 H, ArH). MS (FAB) m/z=1423(MH$^+$). Anal. calcd for C$_{88}$H$_{110}$O$_{16}$: C, 74.23; H, 7.79. Found: C, 73.27; H, 7.72.

The procedure for syntheses of p-tert-butylcalix[6]-1,4-crown-4 tetraamides 5a and 5b

Tetraesters **3a,b** (1 mmol) and ethanolamine (10 mmol) were refluxed in toluene-methanol (1:1) mixture (80 ml) for 10 h. The solvent was removed under reduced pressure and the residue was treated with water to give crude products, following by crystallized from CH$_2$Cl$_2$ / MeOH, **5a,b** was obtained as white crystal in almost quantitative yields. **5a**: m.p 273–5 °C. δ_H.0.87(s, 36 H, C(CH$_3$)$_3$); 1.42(s, 18 H, C(CH$_3$)$_3$); 3.15(s, 8H, OCH$_2$); 3.42(d, 4 H, J=15.0 Hz, ArCH$_2$Ar); 3.49(s, 4 H, OCH$_2$); 3.56(m, 10 H, NCH$_2$ and ArCH$_2$Ar); 3.80(bs, 8 H, CH$_2$OH); 4.25(d, 4 H, J=15.0 Hz, OCH$_2$CO); 4.32(d, 4 H, J=15.0 Hz, OCH$_2$CO); 4.42(d, 2 H, J=15.0 Hz,, ArCH$_2$Ar); 4.51(d, 4H, J=15.0 Hz, ArCH$_2$Ar); 6.69, 6.93, 7.35 (s, each, 4H, each, ArH); 7.85(bs, 4H, NHCO). MS(FAB): 1492(MH$_2$$^+$). Anal. calcd for C$_{88}H_{122}O_{16}N_4$: C, 70.86; H, 8.24; N, 3.75; Found: C, 70.84; H, 8.28; N, 3.73%; 5b: m. p 240–2°C δ_H. 0.84(s, 36 H, C(CH$_3$)$_3$); 1.39(s, 18 H, C(CH$_3$)$_3$); 3.27(bs, 8 H, OCH$_2$); 3.39(d, 4 H, J=14.7 Hz, ArCH$_2$Ar); 3.47(m, 10 H, NCH$_2$ and ArCH$_2$Ar); 3.65(bs, 8 H, CH$_2$OH); 4.20(d, 4H, J=15.0 Hz, OCH$_2$CO); 4.29(d, 4H, J=15.0 Hz, OCH$_2$CO); 4.43(d, 2H, J=15.0 Hz, ArCH$_2$Ar); 4.56(d, 4H, J=14.7 Hz, ArCH$_2$Ar); 6.62(s, 4 H ArH), 6.94(s, 8 H, ArH), 7.31(s, 4 H, ArH); 7.68(bs, 4 H, NHCO). MS(FAB): 1540(MH$_2$$^+$). Anal. calcd. for C$_{92}H_{122}O_{16}N_4$: C, 71.75; H, 7,99; N, 3.64; Found: C, 71.72; H, 8.04; N, 3.63%;

The procedure for syntheses of p-tert-butylcalix[6]-1,4-crown-4 tetraacetic acids 6a and 6b

Tetraesters **3a,b** (1mmol) were refluxed in ethanol (40ml)- NaOH water solvent (50%, 10ml) for 10 h. The solvent was removed under reduced pressure and the residue was neutralized with HCl (10%, W/V) and extracted with $CHCl_3$. The organic layer was separated and evaporated to dryness. **6a,b** was obtained as white crystal after crystallization from CH_2Cl_2 / MeOH, in almost quantitative yields. **6a**: m.p 296–8 °C. δ_H 1.20(s, 36 H, $ArC(CH_3)_3$); 1.33(s, 18 H, $ArC(CH_3)_3$); 2.88(bs, 4 H, $J = 7.8$ Hz, OCH_2); 3.25 (d, 4 H, $J = 15.0$ Hz, $ArCH_2Ar$); 3.37–3.49(m, 10 H, OCH_2 and $ArCH_2Ar$); 3.80(bs, 4 H, OCH_2CO); 4.01(bs, 4 H, OCH_2CO); 4.22(d, 2 H, $J = 14.7$ Hz, $ArCH_2Ar$); 4.38(d, 4 H, $J = 15.0$ Hz, $ArCH_2Ar$); 6.90, 7.01, 7.12(s each, 4 H each, ArH). MS (FAB) m/Z=1319(MH^+). Anal. calcd for $C_{80}H_{102}O_{16}$: C, 72.81; H, 7.79. Found: C, 72.80; H, 7.83%. **6b**: m. p 284–6 °C. δ_H 1.21(s, 36 H, $ArC(CH_3)_3$); 1.34(s, 18 H, $ArC(CH_3)_3$); 3.06(bs, 4 H, OCH_2); 3.29(d, 4 H, $J = 15.3$ Hz, $ArCH_2Ar$); 3.45(m, 6 H OCH_2 and $ArCH_2Ar$); 3.89(d, 4 H, $J = 14.1$ Hz, OCH_2CO); 4.12(d, 4 H, $J = 14.7$ Hz, OCH_2CO);4.16(d, 2 H, $J = 15.0$ Hz, $ArCH_2Ar$); 4.20(d, 4 H, $J = 15.3$ Hz, $ArCH_2Ar$); 7.01(s, 4 H, ArH); 7.16(bs, 8 H, ArH); 7.20(s, 4 H, ArH). MS (FAB) m/z=1367(MH^+). Anal. calcd for $C_{84}H_{102}O_{16}$: C, 73.77; H, 7.52. Found: C, 73.74; H, 7.57%.

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