



Synthesis and Ion Binding Properties of Cesium Selective Quadruply Bridged Calix[6]arenes

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Abstract

Several quadruply bridged calix[6]arenes were prepared in high yield by the reaction of various 1,4-di-O-alkylated calix[6]arenes with 1,2,4,5-tetrakis-(bromomethyl)benzene in the presence of Cs_2CO_3 . The alkali metal extraction study established that this compound shows the high selectivity toward Cs^+ among alkali metal cations. The cesium binding characteristics were investigated with ^1H NMR and UV spectroscopy.

Introduction

Cesium-137 is a nuclear fission product and constitutes a major source of heat in nuclear wastes [1, 2] along with strontium-90. Much effort has been made in the development of improved processes [3, 4] for the removal of cesium-137 from nuclear wastes. For the development of efficient cesium ionophores, several crown ethers [5–7] have been prepared and their binding properties were investigated. As a selective ionophore, calixarene showed excellent ion binding properties when a proper modification was made. Several sodium selective ionophores based on calix[4]arene ester and crown ether derivatives [8–10] were reported. But many fewer cesium selective ionophores [11, 12] are reported. Even though bis(homooxa)calix[4]arene and upper rim bridged calix[4]arene showed cesium selectivity [13], generally the calix[4]arene framework is believed to be small for the cesium ion. On the other hand the calix[6]arene framework is known to be the proper size for cesium without modification, but the parent calix[6]arene is too flexible to bind cesium selectively. In order to decrease the flexibility of calix[6]arene, Gutsche first reported the phenylene bridge calix[6]arenes [14, 15] and also calix[6]crown compounds [16, 17] were reported. The triply bridged calix[6]arene was also reported by Shinkai [18, 19] and it showed a high selectivity for cesium. But the trimethylation [20] reaction of calix[6]arene which was necessary for the triply bridging produced mixtures of several components, which required a difficult separation procedure. For the development of a simple method for cesium selective ionophores we utilized a two step reaction from calix[6]arene and obtained the quadruply bridged calix[6]arene [21] which could be the most bridged calix[6]arene so far reported. Here we report the synthesis of the various quadruply bridge calix[6]arene

derivatives and investigate their alkali metal ion binding properties by UV, ^1H NMR and solvent extraction.

Experimental

Synthesis

Unless otherwise noted, starting materials were obtained from commercial suppliers and used without further purification. Infrared (IR) spectra were determined on a FT-IR spectrometer. Nuclear magnetic resonance (NMR) spectra were recorded on a 300 MHz spectrometer. UV-absorption spectra were obtained on a HP 8453 spectrophotometer. Thin layer chromatography (TLC) analyses were carried out on silica gel plates.

Dialkylation of calix[6]arene

The compounds **1a**, **1b**, **1c**, **1e**, **2a** and **2b** were synthesized by the procedure reported [14, 22] previously.

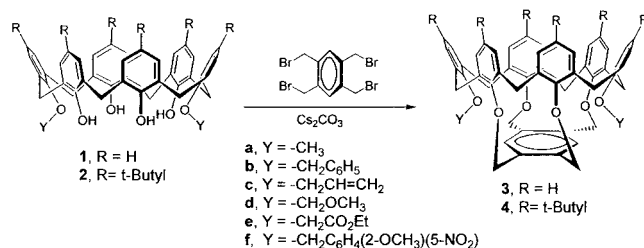
Compound **1d**

Under the similar conditions [14] described for **1a**, calix[6]arene (0.64 g, 1.0 mmol) and $\text{ClCH}_2\text{OCH}_3$ (0.36 mL, 2.4 mmol) produced 0.65 g (87%) of **1d** as a white powder. mp >256 °C dec. ^1H NMR (CDCl_3) δ 8.19 (s, 4H, OH), 7.20 (d, 6H, ArH, $J = 7.50$ Hz), 7.17 (d, 4H, ArH, $J = 6.57$ Hz), 6.89 (s, 4H, ArH), 6.80 (t, 4H, ArH, $J = 7.50$ Hz), 4.86 (s, 4H, $-\text{OCH}_2-$), 3.94 and 3.89 (two s, 12H, ArCH_2Ar), 3.24 (s, 6H, $\text{CH}_3\text{O}-$). ^{13}C NMR (CDCl_3) δ 151.89, 151.36, 133.46, 129.36, 129.26, 128.52, 127.78, 126.93, 125.40, 120.58 and 100.21 (Ar), 57.50 ($-\text{OCH}_2-$), 31.60 and 31.37 (ArCH_2Ar). IR (KBr) 3426 cm^{-1} (OH). Anal. Calcd for $\text{C}_{46}\text{H}_{44}\text{O}_8$: C, 76.22; H, 6.12. Found: C, 76.17, H, 6.10.

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Table 1. Percent extraction of alkali picrates into dichloromethane at 25 °C

Ligands	% Extraction				
	Li ⁺	Na ⁺	K ⁺	Rb ⁺	Cs ⁺
3a	0	0	0	36	96
3b	0	0	0	36	97
3c	0	0	0	35	96
3d	0	0	0	14	74
3e	0	0	0	35	98
3f	0	0	0	0	0
4a	0	0	4	37	97
4b	0	0	8	35	96
5^a	11	50	86	89	100
6^b	0	0	5	8	77

^aCited from Ref. 8.^bCited from Ref. 18.

Scheme 1.

Compound 1f

Under the similar conditions [14] described for **1a**, calix[6]arene (1.3 g, 2.0 mmol) and 2-methoxy-5-nitrobenzylbromide (1.0 g, 4.08 mmol) produced 1.6 g (83%) of **1f** as a pale yellow crystal. mp 181–183 °C. ¹H NMR (DMSO-*d*₆) δ 9.19, 8.56, 8.32 (s, d, m, 6H, nitro phenyl protons), 7.33–6.82 (m, 18H, ArH), 5.12 (s, 4H, -OCH₂Ar), 3.98 (two s, 12H, ArCH₂Ar), 3.34 (s, 6H, -OCH₃). ¹³C NMR (DMSO-*d*₆) 164.41, 156.33, 154.02, 143.36, 136.15, 132.91, 131.88, 131.37, 130.79, 129.89, 128.96, 128.11, 126.80, 126.08, 123.18 and 113.95 (Ar), 69.76 and 59.24 (-OCH₂- and -OCH₃), 33.69 and 32.78 (ArCH₂Ar). IR (KBr) 3416 cm⁻¹(OH), 1465, 1342 cm⁻¹(NO₂). Anal. Calcd for C₅₈H₅₀N₂O₁₂: C, 72.04; H, 5.21. Found: C, 72.10, H, 5.18.

Capping of dialkylcalix[6]arene

The compounds **3a**, **3b** and **3c** were synthesized by the procedure reported [21] previously. A typical reaction procedure for the capped calix[6]arene derivatives are as

Table 2. Bathochromic shifts (λ_{max}) of alkali picrates extracted into the dichloromethane phase

Ionophore	λ (nm)			
	Na ⁺	K ⁺	Rb ⁺	Cs ⁺
18-crown-6 ^a	367	369	368	369
[2,2,1]cryptand ^a	375	375	375	375
[2,2,2]cryptand ^a	375	375	375	376
6	377	378	378	378
3a	^b	^b	378	379

^aCited from Ref. 22.^bExtraction was not detected.

follows. To a solution of 1.2 g (1.8 mmol) of **1a** and 4.7 g of Cs₂CO₃ in 700 mL acetonitrile, 1.0 g of 1,2,4,5-tetrakis(bromomethyl)benzene (2.2 mmol) was added. The mixture was refluxed for 16 h, and the solvents were removed. The residue was treated with CHCl₃ and H₂O (each 250 mL), and the organic layer was separated and removed under reduced pressure. The residue was triturated with MeOH to give 1.0 g (66%) of **3a**.

Compound 3d

Under the similar reaction conditions described for **3a**, **1d** (1.2 g, 1.5 mmol) produced 0.80 g (74%) of **2d** as a white powder. mp >220 °C dec. ¹H NMR (CDCl₃) δ 7.17–6.93 (m, 14H, ArH), 6.28 and 6.00 (t and d, 6H, *J* = 7.6 Hz), 5.21 and 4.60 (a pair of d, 8H, -OCH₂-, *J* = 11.3 Hz), 4.96, 4.56, 3.61 and 3.47 (two pairs of d, 12H, ArCH₂Ar, *J* = 17.4 Hz), 5.11 (s, 4H, -OCH₂-), 3.75 (s, 6H, -OCH₃). ¹³C NMR (CDCl₃) δ 152.97, 152.47, 135.96, 135.74, 131.95, 131.66, 130.90, 129.16, 126.31, 123.05, 122.67, and 99.35 (Ar), 68.38 and 57.84 (-OCH₂-), 33.73 and 30.78 (ArCH₂Ar). Anal. Calcd for C₅₆H₅₀O₈: C, 79.04; H, 5.92. Found: C, 79.11, H, 5.85.

Compound 3e

Under the similar reaction conditions described for **3a**, **1e** (1.2 g, 1.48 mmol) produced 0.91 g (63%) of **3e** as a white powder. mp >245 °C dec. ¹H NMR (CDCl₃) δ 7.15–6.94 (m, 14H, ArH), 6.28 and 6.01 (t and d, 6H, ArH, *J* = 7.65 Hz), 5.20 and 4.64 (a pair of d, 8H, -OCH₂-, *J* = 11.2 Hz), 5.06, 4.60, 3.55 and 3.50 (two pairs of d, 12H, ArCH₂Ar, *J* = 17.4 Hz), 4.54 (s, 4H, -OCH₂CO₂-), 4.35 (q, 4H, -OCH₂C-, *J* = 7.14 Hz), 1.36 (t, 6H, -CH₃, *J* = 7.14 Hz). ¹³C NMR (CDCl₃) δ 169.21, 153.34, 153.07, 136.03, 135.75, 132.11, 131.44, 130.88, 130.78, 129.17, 126.35, 123.20, and 122.58 (Ar), 69.58 and 68.48 (-OCH₂-), 61.19 (-OCH₂CH₃), 33.72 and 29.99 (ArCH₂Ar), 14.25 (CH₃CH₂-). IR (KBr) 1752 cm⁻¹(CO₂-). Anal. Calcd for C₆₀H₅₄O₁₀: C, 77.07; H, 5.82. Found: C, 76.95, H, 5.89.

Compound 3f

Under the similar reaction conditions described for **3a**, **1f** (0.97 g, 1.00 mmol) produced 0.60 g (54%) of **3f** as a pale yellow powder. mp 201–203 °C. ¹H NMR (CDCl₃) δ 8.75, 8.30, and 8.27 (three d, 3H, nitro phenyl protons), 7.14–6.95 (m, 16H, ArH), 5.24 and 4.70 (a pair of d, 8H, ArOCH₂-, *J* = 11.1 Hz), 5.01, 4.64, 3.56 and 3.50 (two pairs of d, 12H, ArCH₂Ar, *J* = 18.0 Hz), 5.01 (s, 4H, -OCH₂Ar), 3.98 (s, 6H, ArOCH₃). ¹³C NMR (CDCl₃) δ 163.30, 160.82, 154.87, 153.44, 153.12, 141.55, 137.37, 135.06, 134.03, 133.26, 131.88, 130.18, 129.58, 129.23, 127.94, 127.86, 127.24, 126.26, 126.09, 125.90, 124.78, 124.74, 122.76, 119.06, 110.37 and 109.36 (Ar), 71.68, 68.13 and 56.06 (-OCH₂-, -OCH₃), 31.32 and 30.45 (ArCH₂Ar). IR (KBr) 1455, 1342 cm⁻¹(NO₂). Anal. Calcd for C₆₈H₅₆N₂O₁₂: C, 74.71; H, 5.16. Found: C, 74.66, H, 5.12.

Compound 4a

Under the similar reaction conditions described for **3a**, **2a** (0.18 g, 0.18 mmol) produced 0.10 g (52%) of **4a** as a

white powder. mp >197 °C dec. ^1H NMR (CDCl_3) δ 7.4, 7.2, 6.9, and 6.3 (four s, 14H, ArH), 5.4–3.5 (m, 26H, ArCH_2Ar , $-\text{OCH}_2-$ and $-\text{OCH}_3$), 1.55–0.96 (m, 54H, *t*-butyl protons). ^{13}C NMR (CDCl_3) δ 152.40, 145.76, 145.49, 145.09, 135.93, 135.72, 134.93, 133.89, 132.65, 128.18 and 126.04 (Ar), 69.72 ($-\text{OCH}_2-$), 61.20 ($-\text{OCH}_3$), 34.23 and 31.44 (ArCH_2Ar). Anal. Calcd for $\text{C}_{78}\text{H}_{94}\text{O}_6$: C, 83.08; H, 8.40. Found: C, 82.82, H, 8.25.

Compound 4b

Under the similar reaction conditions described for **3a**, **2b** (0.21 g, 0.18 mmol) produced 0.13 g (50%) of **4b** as a white powder. mp >216 °C dec. ^1H NMR (CDCl_3) δ 8.4–6.3 (m, 24H, ArH), 5.2–3.4 (m, 24H, ArCH_2Ar , $-\text{OCH}_2-$), 1.6–0.8 (m, 54H, *t*-butyl protons). ^{13}C NMR (CDCl_3) δ 151.27, 145.73, 135.94, 133.18, 132.07, 131.17, 128.57, 128.48, 127.64, 127.43, 127.28, 125.87 and 122.87 (Ar), 77.22 and 74.02 ($-\text{OCH}_2-$), 34.32 and 31.53 (ArCH_2Ar). Anal. Calcd for $\text{C}_{90}\text{H}_{102}\text{O}_6$: C, 84.47; H, 8.03. Found: C, 83.95, H, 7.92.

Extraction

Extraction experiments were performed by stirring a mixture of 5 mL of a 1.0×10^{-4} M solution of metal picrate and 5 mL of 1.0×10^{-3} M solution of ligand in CH_2Cl_2 for 15 h at room temperature. The extraction yield (%) was determined by measuring the amount of the metal ion in the aqueous layer before and after extraction

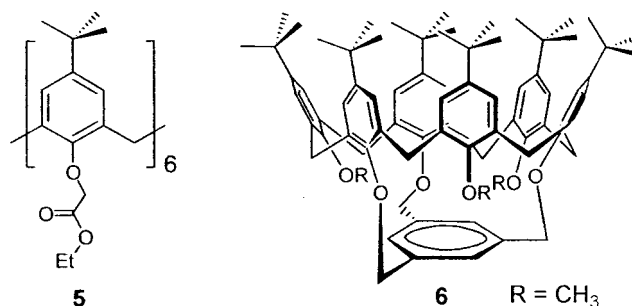
Results and discussion

Synthesis

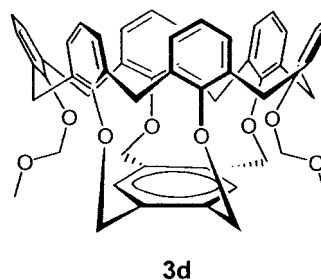
The bridging of the calix[6]arene was accomplished by first converting it to a 1,4-dialkyl ether which was then treated with 1,2,4,5-tetrakis(bromomethyl) benzene in the presence of Cs_2CO_3 in dilute solution as shown in Scheme 1 [21]. The quadruply bridging reaction was successful only when 1,4-dialkylated calix[6]arenes **1** and **2** were treated with 1,2,4,5-tetrakis(bromomethyl)benzene. Selective 1,4-dialkylation of calix[6]arene was carried out by treating calix[6]arene with the corresponding alkyl halides in the presence of $(\text{CH}_3)_3\text{SiOK}$ and a pure compound was obtained in high yield without a further additional purification procedure. In order to investigate the substituent effect for the metal binding six quadruply bridged calix[6]arenes **3a**, **3b**, **3c**, **3d**, **3e** and **3f** were synthesized from calix[6]arene **1**. Also two quadruply bridged *t*-butylcalix[6]arenes **4a** and **4b** were prepared from *t*-butylcalix[6]arene derivatives of **2a** and **2b**. The bridging reaction of di-O-alkylated *t*-butylcalix[6]arene **2** with tetakisbromomethylbenzene proceeded smoothly, but the reaction yield (about 50%) was somewhat lower than that of **1** (about 60%) and more side products were formed. It is well known [8] that calixarene ester derivatives show the metal selectivity dependent on the calixarene ring size: that is, calix[4]arene derivatives show very high Na^+ selectivity, on the other hand calix[6]arene derivative **5** in Table 1 shows a broad alkali metal selectivity with K^+ , Rb^+ , and

Cs^+ . The broad selectivity of calix[6]arene is related to the flexibility of the calix[6]arene ring framework. When a quadruple bridge was made at the lower rim of calix[6]arene, a much more rigid calix[6]arene was expected. A high temperature ^1H NMR spectrum was studied and showed no change of spectrum up to 100 °C, indicating that **3** and **4** are considerably rigid and could show a high metal selectivity.

Alkali metal extraction



Two phase solvent extraction of alkali metal cations with picrate ion into dichloromethane was performed and the extraction values are compared with those of conformationally mobile calix[6]arene ester **5** [8] and Shinaki's triply bridged calix[6]arene **6** [19]. Table 1 indicates that quadruply bridged calix[6]arenes **3a**, **3b**, **3c**, **3e**, **4a** and **4b** show more than 96% extraction toward cesium ion, but almost no extraction was observed with lithium, sodium and potassium ions and 35–37% extraction was shown with rubidium ion. The cesium extraction percentage was decreased to 74% for **3d**, where the two alkyl groups were methoxymethyl. On the other hand **3f** which has two bulky 2-methoxy-5-nitrobenzyl substituents shows no extraction with alkali metal ions. Obviously *t*-butyl groups at the upper rim of calix[6]arene do not give any influence for the cesium binding, but two relatively bulky 2-methoxy-5-nitrobenzyl groups at the lower rim interrupt cesium binding completely, suggesting that cesium may enter the calix[6]arene cavity through the open side at the lower rim. The cesium extraction percentage falls from 96% for **3a** to 74% for **3d**. We do not have a reasonable explanation for this difference at this moment, but two methoxymethyl groups somehow disrupt cesium binding at the certain degree. Shinaki's triply bridged calix[6]arene **6** shows the highest selectivity toward cesium, but it extracts cesium (77%) less than quadruply bridged calix[6]arenes under the same condition.



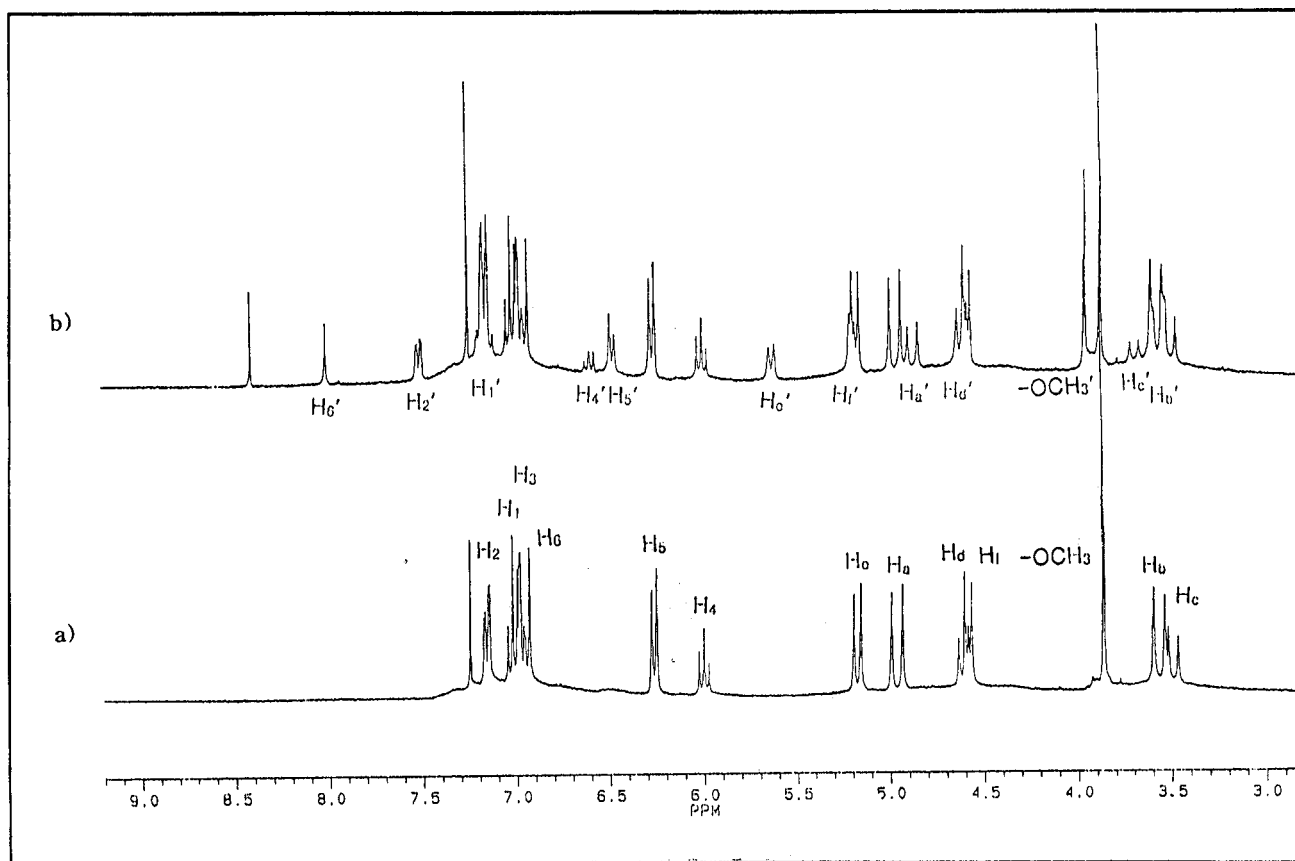
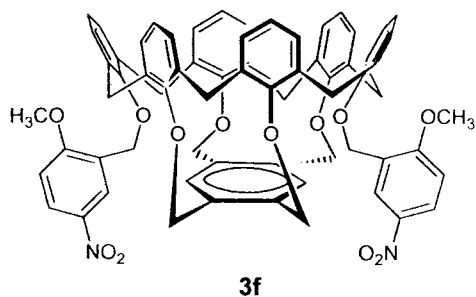


Figure 1. Partial ^1H NMR spectra of **3a** and **3a**- Cs^+ complex in CDCl_3 . Prime peaks correspond to the ^1H NMR spectra of the **3a**- Cs^+ complex.



UV-visible and ^1H NMR characteristics

Inoue found [23] that the ion pair tightness in solution could be evaluated by the bathochromic shift of the absorption band of the picrate anion extracted into the organic phase with a macrocyclic ligand from aqueous metal picrate solution. We investigated the absorption spectra of alkali picrate in the dichloromethane phase after two-phase solvent extraction and found a large bathochromic shift of picrate anion in the presence of **3a**. As shown in Table 2, the λ_{max} of cesium picrate shifted from 354 nm to 379 nm in the presence of **3a**. The 25 nm bathochromic shift is larger than those induced by 15 nm of 18-crown-6, 21 nm of [2,2,1]cryptand, and 22 nm of [2,2,2] cryptand and comparable with the 24 nm shift of **6**, indicating that the metal picrate ion pair is highly separated. Cesium ion could be surrounded by the calixarene aromatic rings and a quadruply bridged durenyl ring, but the picrate anion is located outside the calixarene. Therefore, the

picrate anion of the **3a**- M^+Pic^- complex could behave as a highly solvent separated anion which was observed by the large bathochromic shift.

To obtain further insights into the cesium binding site we investigated the complexation properties by ^1H NMR spectroscopy. The ^1H NMR spectra of **3a** and **3a**- Cs^+Pic^- are shown in Figure 1. The peaks corresponding to the **3a**- Cs^+ complex appear separately from those corresponding to free **3a** at room temperature. The results indicate that the association-dissociation is slower than the NMR time-scale. The chemical shift difference between **3a** and the **3a**- Cs^+ complex is summarized in Figure 2 and reveals that a significant down-field shift is observed for the durenyl ArH (H6), anisole ArH protons (H4) and two $-\text{OCH}_2$ protons (He and Hf) ($\Delta\delta = +1.08, +0.60, +0.61$ and $+0.45$, respectively). On the other hand the methoxy and bridge methylene protons (Ha, Hb, Hc and Hd) are little affected ($\Delta\delta = +0.08, +0.19$ and -0.09 , respectively). It is well known that the cation- π interaction operates in the metal binding and the chemical shifts of ArH protons in such complexes mostly move to lower magnetic field [22]. Therefore, the results indicate that the major driving force for Cs^+ inclusion is the Cs^+ -oxygen interaction with the durenyl linked four oxygens as well as the Cs^+ - π interaction of durenyl and the anisole aromatic rings whereas the two methoxy oxygens in the anisole scarcely participate to the Cs^+ binding.

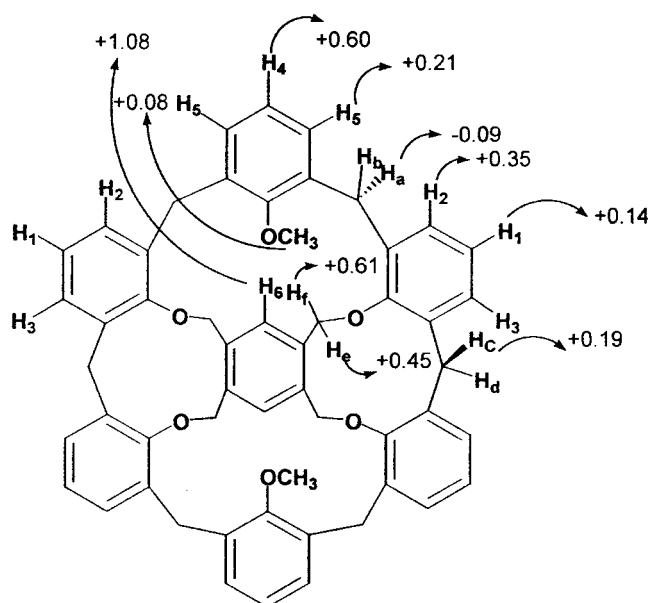


Figure 2. Chemical shift difference between free **3a** and the **3a**-Cs⁺ complex. A plus sign (+) denotes a shift to lower magnetic field and a minus sign (−) denotes a shift to higher magnetic field.

Conclusion

By the reaction of 1,4-O-dialkylcalix[6]arenes with 1,2,4,5-tetrakis(bromomethyl)benzene several quadruply bridged calix[6]arenes were synthesized in high yield. The alkali metal extraction study established that these compounds show high selectivity toward Cs⁺ among alkali metal cations. The absorption spectra of alkali picrate in the dichloromethane phase after two-phase solvent extraction showed a large bathochromic shift (25 nm) of picrate anion in the presence of **3a**, indicating that the metal picrate ion pair is highly separated. The significant down-field shifts of ¹H NMR spectra between **3a** and the **3a**-Cs⁺ complex were observed for the durenyl ArH, anisole ArH protons and two -OCH₂ protons ($\Delta\delta$ +1.08, +0.60, +0.61 and +0.45, respectively), but much smaller changes were observed for methoxy and bridge methylene protons ($\Delta\delta$ = +0.08, +0.19 and -0.09, respectively). These results strongly suggest that the major driving force for Cs⁺ inclusion is the Cs⁺-oxygen interaction with durenyl linked four oxygens as well as the Cs⁺- π interaction of durenyl and anisole aromatic rings whereas the two methoxy oxygens in the anisole scarcely participate in the Cs⁺ binding.

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