

Dideoxygenated calix[4]arene crown-6 ethers enhanced selectivity for caesium over potassium and rubidium

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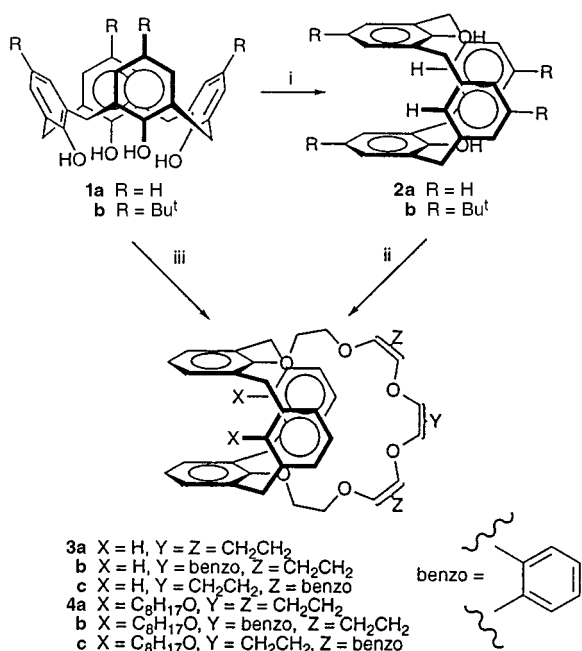
Received (in Columbia, MO, USA) 2nd December 1998, Revised 6th July 1999, Accepted 6th July 1999

Calix[4]arene crown-6 ethers derived from dideoxygenated calix[4]arene exhibit enhanced extraction selectivity for caesium over potassium; the crystal structure of the uncomplexed calix[4]arene monobenzocrown-6 ether exists in the 1,3-alt conformation in the solid state.

Calixarenes¹ have been taking on an increasingly important role in host-guest chemistry, in large part because they can provide a well-organized platform for the attachment of pendant functional groups.^{2,3} The incorporation of a calix[4]arene (**1** in Scheme 1) moiety into crown ethers⁴ has been used to develop powerful, highly selective ionophores for alkali metal cations,^{5,6} the properties of which are often dependent on the conformation adopted by the calixarene. Whereas diethoxycalix[4]arene crown-4 ether in the cone conformation exhibits high sodium selectivity,⁷ diethoxycalix[4]arene crown-5 ether in the 1,3-alternate conformation exhibits selectivity for K⁺ over Na⁺ exceeding that of Valinomycin.⁸ Furthermore, 1,3-alt calix[4]arene crown-6 ethers exhibit high caesium binding^{9,10} with selectivities for Cs⁺/Na⁺ of ca. 10⁴–10⁵,^{9–11} a property which has led to their study for the selective removal of caesium from nuclear fuel reprocessing wastes.^{12,13} However, Cs/K selectivities are only ca. 80–600, which is of concern since the wastes may contain as much as 1 M K⁺ in a typical matrix containing 5–7 M Na⁺, but only 10^{–6}–10^{–3} M Cs.¹⁴ Having undertaken an effort to develop extractants with improved Cs/K selectivity, we have synthesized three new calix[4]arene crown-6-ethers (**3a–c** in Scheme 1)[†] derived from di-dehydroxylated

calix[4]arene **2a**,¹⁵ which exhibit Cs⁺/Rb⁺ and Cs⁺/K⁺ selectivities significantly greater than that of comparable 1,3-dialkoxycalix[4]arene crown-6-ethers **4a–c**.

Competitive extractions of alkali metal nitrates by the six calix[4]arenes **3a–3c** and **4a–c** were performed essentially as described previously,¹⁴ with the organic phase consisting of 0.025 M of calixarene crown ether in 1,2-dichloroethane and the aqueous phase consisting of a mixture of alkali metal nitrates: 1.00 M LiNO₃, 1.00 M NaNO₃, 0.100 M KNO₃, 0.0020 M RbNO₃ and 0.0011 M CsNO₃. Metal ion concentrations were determined for both phases, from which distribution ratios $D_M = [M^+]_{\text{organic}}/[M^+]_{\text{aqueous}}$ were calculated directly. Caesium was analyzed by γ spectrometry, while lithium, sodium, potassium and rubidium were analyzed, subsequent to stripping of the organic phase with 1.0 mM HNO₃, by inductively coupled plasma atomic emission spectroscopy. From the data given in Table 1, it can be seen that in each case where the calixarene is changed from diethoxycalix[4]arene **4a–c** to the dihydrocalix[4]arene **3a–c** the extraction strength for caesium, expressed in terms of D_{Cs} , decreases by roughly an order of magnitude. However, an even larger decrease is observed for the extraction of the other alkali metals, to the point for K⁺ and Rb⁺ where no extraction was measured. This is despite the fact that the aqueous phase used in these experiments contained significantly higher concentrations of Li⁺, Na⁺, K⁺ and Rb⁺ than Cs⁺. As a consequence, selectivity for extraction of caesium (as expressed by $S_{\text{Cs}/M} = D_{\text{Cs}}/D_M$) increases. Since only upper limits are available for the extraction of Rb⁺ and K⁺ by calix[4]arene crown ethers **3a–c**, the magnitude of the selectivity increase as compared to **4a–d** can only be assigned a lower limit. Even so, the observed trends provide evidence that improved extraction selectivity for Cs⁺ can be obtained by appropriate modification of the calixarene portion of calix[4]arene crown-6 ethers.



Scheme 1 Reagents and conditions: i, (EtO)₂PHO, CCl₄, Et₃N, toluene, 0 °C, then K, NH₃ (liquid); ii, (TsOCH₂CH₂O-Z-O)₂Y, Cs₂CO₃, MeCN; iii, C₈H₁₇I, K₂CO₃, MeCN, then (TsOCH₂CH₂O-Z-O)₂Y, Cs₂CO₃, MeCN.

Table 1 Calix[4]arene crown-6 ethers used in this study, their distribution ratios (D_M) for the extraction of alkali metal nitrates from water to 1,2-dichloroethane at 25 °C, and the corresponding selectivities (S) for Cs⁺ ions over Li⁺, Na⁺, K⁺ and Rb⁺ ions^a

Extractant	D_{Cs}	D_{Rb} ($S_{\text{Cs/Rb}}$)	D_{K} ($S_{\text{Cs/K}}$)	$D_{\text{Na}}/10^{-5}$ ($S_{\text{Cs/Na}}$)	$D_{\text{Li}}/10^{-5}$ ($S_{\text{Cs/Li}}$)
3a	0.403	— ^b (> 58)	— ^b (> 4200)	2.17 (23000)	1.90 (32000)
3b	0.383	— ^b (> 54)	— ^b (> 4000)	— ^b (> 150000)	— ^b (> 660000)
3c	0.116	— ^b (> 17)	— ^b (> 1200)	— ^b (> 47000)	— ^b (> 200000)
4a	3.65	0.180 (20)	0.0152 (240)	22.0 (17000)	2.98 (120000)
4b	4.04	0.214 (19)	0.0141 (290)	3.9 (100000)	0.99 (> 450000)
4c	1.61	0.178 (9.0)	0.0125 (130)	— ^b (> 640000)	0.97 (170000)

^a All values are the average of two determinations. ^b Lower limits on measurement of distribution ratios: $D_{\text{Li}} = 5.8 \times 10^{-7}$, $D_{\text{Na}} = 2.5 \times 10^{-6}$, $D_{\text{K}} = 9.6 \times 10^{-5}$, $D_{\text{Rb}} = 0.0070$.

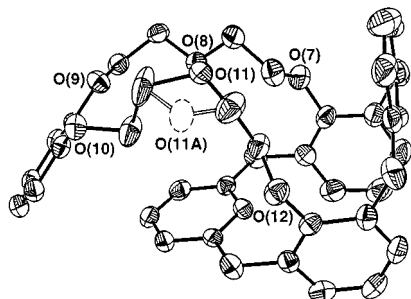


Fig. 1 ORTEP drawing (50% probability ellipsoids) of **5b**. For clarity only one molecule from the asymmetric unit is displayed, hydrogen atoms are omitted, and only oxygen atoms are labeled. The minor disorder component (O11A) is represented with a dashed boundary ellipsoid.

Since previous studies have shown that the 1,3-alternate conformation is preferred for high caesium binding and selectivity⁹ and that calixarenes bearing substituents smaller than ethoxy are conformationally mobile,¹⁶ we considered the conformational preferences of these new compounds. The crystal structure of **3b** (Fig. 1)[‡] reveals that this compound crystallizes with two molecules in the crystallographic asymmetric unit, with the calix[4]arene portions of both molecules clearly in the 1,3-alt conformation. The calix[4]arene crown-6-ethers **3a–c** exhibit room temperature ¹H NMR (CDCl₃) where the Ar-CH₂-Ar resonances of the calixarene appear as a pair of doublets at $\delta \sim 4.2$ and ~ 3.7 with a coupling constant of ~ 15.5 Hz, while the intraannular proton on the deoxygenated aromatic ring is found upfield at $\delta \sim 6.0$. Grynszpan and Biali¹⁷ interpreted the upfield shift of the corresponding proton in **2b** in terms of shielding by the two phenolic rings in the 1,3-alt conformation, whereas the positions and coupling constants of the calixarene methylenes are more consistent with the report by Ting *et al.*¹⁵ where the ‘unsubstituted phenyl rings can rotate freely’. The calixarene methylene carbon of **3b** was observed at δ 35.3, similar to the values reported to be observed for the 1,3-alternate conformers in conformationally immobile calix[4]arenes.¹⁸ We performed VT-NMR on **3b** in CDCl₃ and observed a decrease in the separation between the pair of doublets assigned to the calixarene methylene resonances, from 216 to 187 Hz ($\Delta\delta = 29$ Hz), when the temperature was decreased from 340–220 K, consistent with rapid conformational interconversion which shows upon lowering the temperature. Conversely, in toluene-*d*₈, the separation between this pair of doublets decreased, from 340 to 298 Hz ($\Delta\delta = 42$ Hz), when the temperature was increased from 170 to 370 K, suggesting a slow conformational interconversion which speeds up with increasing temperature. However, coalescence was not achieved even when a solution of **3b** was heated to 500 K in nitrobenzene-*d*₅. In (CD₂Cl)₂, $\Delta\delta \approx 0$ over the temperature range 240–340 K. Consequently, the solution conformation cannot be assigned to the calixarene portion of **3b** based on these results.

The results reported here have significant ramifications, not only in the effort to develop more highly selective extractants, but also in understanding the conformational and electronic factors which contribute to the remarkable ionophoric properties of calixarenes and calix[4]arene crown ethers. Efforts in this area are the subject of ongoing investigations.

This research was sponsored by the Environmental Management Science Program, Offices of Energy Research and

Environmental Management, U.S. Department of Energy, under contract DE-AC05-96OR22464 with Oak Ridge National Laboratory, managed by Lockheed Martin Energy Research Corporation.

Notes and references

[†] ¹H NMR and ¹³C NMR data were consistent with the assigned structures for all new compounds.

[‡] Crystal data for **5b**: C₄₂H₄₂O₆, 642.8 g mol⁻¹, triclinic, $a = 10.634(3)$, $b = 17.432(4)$, $c = 19.578(4)$ Å, $\alpha = 70.959(17)$, $\beta = 89.846(17)$, $\gamma = 77.52(2)^\circ$, $V = 3340.6(13)$ Å³, $T = 173(2)$ K, $P\bar{1}$, $Z = 4$, $\mu = 0.084$ mm⁻¹, refinement of F^2 , final $wR2 = 0.117$, on all 8182 independent reflections. CCDC 182/1353. See <http://www.rsc.org/suppdata/cc/1999/1751> for crystallographic data in .cif format.

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Communication 9/05682C