Acta Chemica Scandinavica, 1998: 52: 407–416
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ACTA
CHEMICA SCANDINAVICA
ISSN 0904-213X

Dynamic Factors in the Design of Redox-switched Calix[4]arene Cationophores

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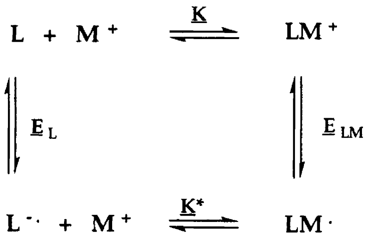
Dedicated to Professor Lennart Eberson on the occasion of his 65th birthday

Bethell, D., Dougherty, G. and Cupertino, D. C., 1998. Dynamic Factors in the Design of Redox-switched Calix[4]arene Cationophores. – Acta Chem. Scand. 52: 407–416. © Acta Chemica Scandinavica 1998.

Syntheses are described of four calix[4]arenes, each bearing a 9,10-anthraquinone moiety as a redox switch to modify cation binding. The first compound, having a triester-amide lariat-type structure, showed no experimental evidence (from cyclic voltammetry in acetonitrile solution) for enhancement of binding of alkali-metal cations, indicating negligible interaction between the binding site and the switchable group. Computer modelling showed that a large steric barrier prevents rotation of the switch into the energetically favourable position that would enhance cation binding. Compounds in which the anthraquinone formed part of a 1,3-bridging unit spanning the lower rim of the calix showed large cation-binding enhancements, the values being affected by the other, auxiliary groups on the lower rim of the calixarene. Unusual CV behaviour was observed in the case of the compound with two methoxy auxiliary donor groups in the presence of K^+, but not with Na^+. Computer modelling and NMR spectroscopic evidence indicates that this effect is attributable to a slow change of the calixarene from a cone to a partial cone conformation in binding K^+, whereas the smaller Na^+ fits easily into the available cavity of the cone conformation.

Largely as a result of pioneering work in the early 1980s,[1] especially that of Echegoyen, Gokel and coworkers[2] and more recently that of Beer and his associates,[3] there has been continuing interest in the development of redox-switching as a means of enhancing the selective binding of ions by initially electrically neutral ionophores. The driving force for this research has been mainly the development of selective ion sensors, but increasingly it is being realised that applications in the field of metal extraction might be possible. Most of the systems studied have been of the macrocyclic polyether type. Typical redox switches for cation binding are quinones or nitrobenzene units, capable of undergoing one or more single electron transfers at a suitable electrode.[4] These switching groups may be either incorporated within the macrocycle or attached to it by a short chain as in the so-called lariat ionophores. Taking the simplest case of a macrocyclic ligand L capable of binding a monocation M^+, either in its neutral state or, more strongly after one-electron reduction, the system of equilibria can be represented as in Scheme 1. Here, binding constants are represented by K for the neutral ligand and K^* for the reduced form, while E_L and E_{LM} are the reversible potentials for one-electron reduction of the ligand in its unbound and bound states. The relationship between these quantities is given by the general equation (1), where $n=1$ for the situation in Scheme 1, F is the Faraday constant, R the gas constant and T the absolute temperature. The redox potentials are often replaced by the corresponding peak potentials for reduction waves available, for example, from cyclic voltammetry. The right-hand side of eqn. (1) represents the logarithmic binding enhancement factor.[5]



Scheme 1.

$$\frac{nF}{2.3RT}(E_{LM}-E_L)=\log\frac{K^*}{K} \qquad (1)$$

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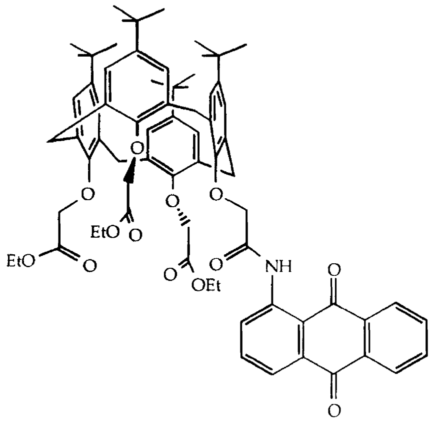
Calix[4]arenes (in the cone conformation) have been used to provide a rigid structure to which donor groups capable of cation binding could be attached, and selectivity in the binding of alkali-metal ions has been observed.[6] Redox-switchable calixarenes are an obvious extension, and when this work was started none had been described. Now such compounds are known, both of the type in which a quinone group replaces one of the phenolic groups within the calix[7] and ones in which the quinone switch is attached to the lower rim of the calix.[8] The present paper provides a detailed account of our contribution in this area, particularly regarding the design of systems to maximise alkali-metal cation binding. Our starting point was the desire to achieve large, selective binding enhancements among the group of alkali metal cations. We began by examining a calix[4]arene **1** bearing an anthraquinone switch in a lariat type arrangement, chosen for its ease of preparation; lack of success with this compound led us to undertake computer modelling of the conformational properties of the ligand, which in turn led us to the design, synthesis and characterisation of a group of calix[4]arenes bridged across the lower rim by a polyether chain containing the anthraquinone switch **2a**–**c**.

Results and dicussion

Lariat-type ionophores: synthesis. Our first ionophore design was based on the calix[4]arene tetraester **3** [R = Et] which is known to bind alkali-metal cations well,[9] the carbonyl oxygen atoms acting as the donor sites.[9c,10] Picrate extraction experiments from water into dichloromethane show some binding selectivity towards sodium ions. Selective monohydrolysis of this compound, followed by attachment of an anthraquinone unit through an ester or amide linkage, was thought a convenient route to a lariat-type switchable cationophore.

The method for the preparation of **3** [R = H] described by McKervey *et al.*,[11] in which a single ester group in the tetraester is hydrolysed by treatment with a catalytic amount of trifluoroacetic acid in chloroform solution, proved capricious in our hands. We surmised that this was a consequence of reliance on adventitious water, since the reaction has been claimed to proceed by way of a complexed hydroxonium ion. We undertook a more detailed examination of the reaction and were able to find an optimum mixture of chloroform, ethanol and water that gave reproducible monohydrolysis, although even then it was necessary to monitor the progress of the reaction by ^{1}H NMR spectroscopy. Without further purification, treatment of the acid with excess thionyl chloride afforded the acid chloride which was added to a toluene solution of 1-aminoanthraquinone containing triethylamine. Compound **1** was formed in 50% overall yield, and ^{1}H NMR spectroscopy confirmed that it had retained its cone conformation. Attempts to use the same sequence of reactions to prepare the *N*-methyl analogue of **1** failed, but the acid chloride did react successfully with 2-nitroaniline.

Lariat-type ionophores: electrochemical behaviour. Compound **1** was well-behaved in cyclic voltammetric experiments at modest potential scan rates in acetonitrile solutions containing 0.1 M tetrabutylammonium perchlorate as the supporting electrolyte. Two quasi-reversible couples were detected with formal potentials of −779 and −1328 mV vs. a silver wire quasi-reference (see Table 1). The presence in the solution of a half or one equivalent of sodium perchlorate had only a small effect on the appearance of the cyclic voltammogram of **1**, the first current peak being shifted ca. 40 mV in the anodic direction while the second (corresponding to dianion formation) shifted some 100 mV and two waves could be just resolved in the half equivalent experiment. These effects are too small to indicate any substantial additional interaction between the ionophore and sodium ion on one-electron reduction other than a weak ion-pairing effect, greater in the dianion than in the anion



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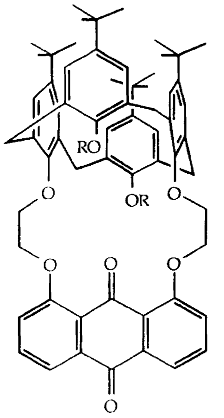

2 a: R = CH_3
b: R = $CH_2CO_2CH_2CH_3$
c: R = $CH_2CON(CH_2CH_3)_2$
d: R = H

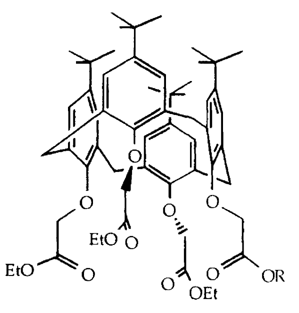

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Table 1. Peak potentials and formal reduction potentials from cyclic voltammetry of **1** and related model compounds.[a]

Compound	Cation	$-E_p^R$/mV	$-E_p^O$/mV	$-E_1^R$/mV
1	NBu_4^+	815	743	779
	Na^+	770	690	730
Aq-NHAc	NBu_4^+	831	769	800
	Na^+	815	738	777
Aq-NMeAc	NBu_4^+	850	734	792
	Na^+	800	715	758

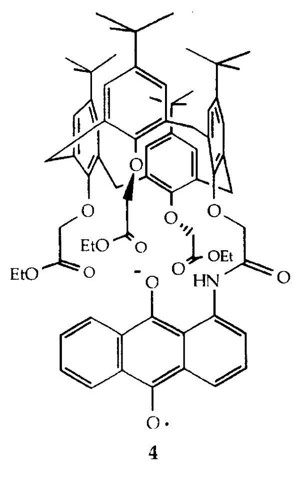
[a] Cyclic voltammetry in acetonitrile containing 0.1 M tetrabutylammonium perchlorate at room temperature: substrate concentration 2.5 mM; potential scan rate 100 mV s^{-1}. In experiments with added sodium perchlorate the sodium ion concentration was 2.5 mM.

radical. This was confirmed by cyclic voltammetry on 1-acetamidoanthraquinone (AQ-NHAc) and its *N*-methyl analogue (AQ-NMeAc), both of which showed very similar effects on the first reversible reduction wave when sodium ions were present.[12] The conclusion seemed inescapable, namely that reduction of the anthraquinone moiety does not lead to cooperative binding of sodium ions in this calixarene.

There are several possible explanations of the behaviour of **1**.

(1) Hydrogen bonding between the quinone carbonyl group and the adjacent amide proton is so strong that it cannot be broken to allow the negatively charged oxygen in the reduced form to act as a donor towards the metal cation.

(2) Rotation of the reduced quinone unit about the C(1)–N bond, as shown in **4**, so that it occupies a position above the calixarene cavity and so contributes to the binding of the sodium ion therein cannot take place. This hindrance could arise as a result of hydrogen bonding as indicated above, but might alternatively result from a steric barrier to rotation in the congested environment around the lower rim.



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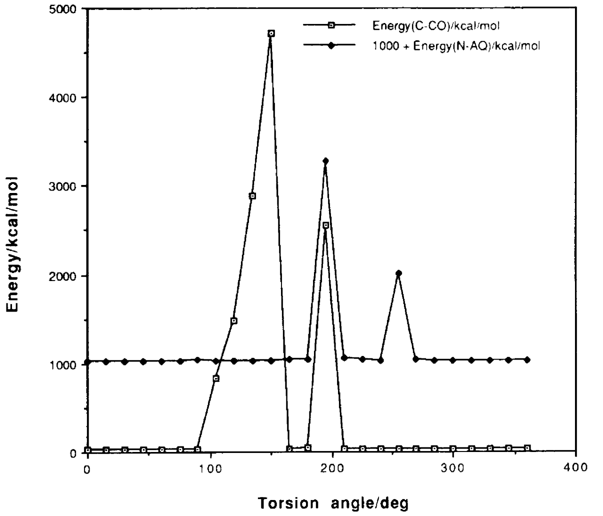

Fig. 1. Calculated energies for **1** as a function of the torsion angle about the amide C–CO bond (-□-) and about the N–anthraquinone bond (-◆-). The zero of the torsion angle scale is that of the minimum energy conformation, which is approximately that shown in structural formula **1**.

Hydrogen-bonding as an important influence seems to be excluded by the similarity in behaviour of 1-acetamidoanthraquinone and its *N*-methyl analogue. We therefore sought evidence for a steric barrier to cooperative binding of sodium ions by **1** by computer modelling. The effects on the total energy of the molecule of rotation of the anthraquinone moiety relative to the calix in **1** was examined using the Sybyl program (Tripos Associates) on a Silicon Graphics Indigo workstation. Two rotations were investigated, that about the OCH_2–CONH bond, which carries the anthraquinone over the cavity as in **4**, and, for comparison, that about the NH–anthraquinone bond which would give structures in which cooperative binding of metal cations would be less favourable because the calix and quinone would, at best, be much further apart.

Initially the structure **1** was energy minimised. A gridsearch was then carried out, rotating the OCH_2–CONH bond through 360° in steps of 15° and calculating the minimised energy after each step. The energies of the conformations so generated are displayed in Fig. 1, together with the values for rotation about the NH-anthraquinone bond. In both cases a double barrier to rotation is generated. The calculations are quite unsophisticated since the program attempted to minimise the energies only with respect to other simple motions in the intermediate conformations, but without any bond disconnection – atomic repositioning – bond reconnection cycles. This procedure greatly exaggerates the barriers to rotation because, as the rotation of the OCH_2–CONH bond is driven, the anthraquinone group is forced into contact with the lower rim substituents and, using the retricted minimisation routine, this leads to distortion of the quinone nucleus. It is emphasised that the results in Fig. 1, especially the very high absolute values of the energy barriers, are indicative only. Nevertheless we believe it to be legitimate to draw two conclusions: firstly that a conformation exists close in energy to the starting conformation depicted in **1** but with the quinone lying directly above the calix cavity, as shown for the radical anion in **4**; secondly that the barrier to rotation of the anthraquinone unit into this position from which it could enhance sodium cation binding by the ester groups on the lower rim of the calix is likely to be so large as to prohibit such motion on the timescale of the electrochemical measurements.

Anthraquinone-bridged calix[4]arenes: synthesis. The low energy calculated for **1** when the anthraquinone had been rotated over the calix cavity encouraged us to believe that compounds of type **2** could be synthesised. Moreover, modelling of **2a** suggested that the cavity could easily contain a sodium ion, and was just large enough to accommodate a potassium ion, suggesting the possibility of discrimination between the two ions.

Our initial synthetic approach involved 1,3-dialkylation of *p-tert*-butylcalix[4]arene using allyl bromide with subsequent transformation, by ozonolysis with reductive work-up, into the calixarene di-β-hydroxyethyl ether after methylation of the remaining phenolic hydroxy groups. Treatment of this compound with sodium hydride in the presence of 1,8-dichloroanthraquinone afforded **2a** in very low yield, a result not unexpected in the light of a recent publication of Gokel and co-workers.[13]

Our preferred route to compounds of type **2** was by preparation of 1,8-bis(β-bromoethoxy)anthraquinone and use of this for 1,3-dialkylation of *p-tert*-butylcalix[4]arene to form **2d** using butyronitrile as the solvent containing sodium carbonate and sodium iodide. The product isolated in 36% yield afforded NMR and mass spectrometric data consistent with the expected structure, but yielded a CH analysis that indicated that the product was largely a Na^+ complex. The low yield of this material was a result of a difficult separation from the starting calixarene and by-products; these latter compounds appeared from FAB MS to be multiply bridged bis-calixarenes containing calixarene to anthraquinone ratios of 2:2 ($m/z = 1882.4$) and 2:3 ($m/z = 2174.7$). Crystals of compound **2d** apparently of X-ray quality were obtained, but a crystal structure could not be derived owing to the low number of reflections observed. The unit cell dimensions were found to be: $a = 13.346$ Å; $b = 21.188$ Å; $c = 22.194$ Å; $\alpha = 90°$; $\beta = 101.79°$; $\gamma = 90°$; space group $P2_1/a$; monoclinic. Attempts to use potassium rather than sodium salts in the preparation of **2** in the hope of achieving better templating in the bridging reaction were less successful; the yield of **2d** was lower, that of bis-calixarenes higher, and a small amount of a doubly 1,2-bridged calixarene ($m/z = 1232.5$) appeared. Finally, the phenolic hydroxy groups of **2d** were alkylated in tetrahydrofuran solution containing sodium hydride using dimethyl sulfate to generate **2a** in 50% yield, ethyl bromoacetate to generate **2b** in 71% yield, and using *N,N*-diethylchloracetamide, giving **2c** in 25% yield. For **2a** and **2c**, the elemental analysis again suggested contamination by the Na^+-complex, and this could be detected by small pre-peaks in cyclic voltammograms of the compounds in acetonitrile containing tetrabutylammonium perchlorate as the supporting electrolyte. Repeated recrystallisations failed to remove the contamination.

The non-bridging groups on the lower rim of the calixarene were chosen because they provide a range of donor capabilities ($OCH_2H < OCH_2{-}CO_2Et < OCH_2{-}CONEt_2$), enabling the effect of this on the electrochemical response to be evaluated. All three compounds were found to exist in solution as cone conformations; in each case the signals in the ^1H NMR spectra assigned to the protons of the methylene groups separating the aromatic units appeared as a characteristic single pair of doublets. These compounds were then used for redox-switching/cation binding studies as follows.

Anthraquinone-bridged calix[4]arenes: redox-switched cation binding. Cyclic voltammetry was again employed to evaluate the binding enhancements towards alkali-metal cations on one-electron reduction of the ionophores using relationship (1). Experiments were conducted in acetonitrile solution at 25 °C using tetrabutylammonium perchlorate as the supporting electrolyte. Potential scan rates were in the range 50 to 5000 $mV\ s^{-1}$, a range of values being used so as to establish that peak shifts were independent of scan rate. Compounds **2a**–**d** gave similar behaviour in the absence of alkali-metal cations; all gave well-defined one-electron reduction waves for the addition of the first electron, accompanied by a small pre-peak that is attributable to traces of sodium ions in the system. The second one-electron step was much less clearly defined, perhaps as a consequence of traces of water or weakly acidic protons in the substrate/electrolyte system. Added alkali-metal perchlorates with concentration ratios $[M^+]/[\text{ligand}]$ of 0, 0.5 and 1.0 had a dramatic effect on the appearance of the cyclic voltammograms. In all cases, the presence of the alkali-metal cation (0.5 equiv.) led to the appearance of additional peaks corresponding to the first and second reduction step of the ligand/metal ion complex at potentials shifted considerably in the anodic direction compared with values for the corresponding reduction of the free ligand. With one equivalent of the added alkali-metal salt and at potential scan rates below 1000 $mV\ s^{-1}$, only the first and second reduction and reoxidation waves for the complex could be detected and the second wave became clearly defined. Values of the observed peak and formal potentials relative to a Ag/AgCl reference electrode at a scan rate of 200 $mV\ s^{-1}$ are in Table 2, in which the reproducibility of the measurements on fresh solutions is indicated. Binding enhancement factors based on the first one-electron

Table 2. Peak potentials and formal potentials from cyclic voltammetry of (**2a–c**) in acetonitrile at 25 °C.[a]

Compound[b]	Cation	$-E_p^{R1}$/mV	$-E_p^{O1}$/mV	$-E_1^{R}$/mV[c]	$-E_p^{R2}$/mV	$-E_p^{O2}$/mV
2a	NBu_4^+	1154	1064	1109	1991	ca. 1600
		1151	1075	1113		
		1132	1066	1099		
		1142	1067	1105		
		1133	1066	1100		
		1133	1054	1094		
	Li^+	739	665	702	1312	1224
	Na^+	829	759	794	1443	1336
	K^+	968	866	917	ca. 1600	ca. 1400
	Rb^+	1123	902	1011	nd	nd
	Cs^+	1133	1054	1094	nd	nd
2b	NBu_4^+	1014	908	961	1689	1484
	Li^+	598	598	598	1206	1098
	Na^+	812	705	759	1560	1200
	K^+	895	801	848	nd	nd
2c	NBu_4^+	1065	975	1020	1951	ca. 1600
	Li^+	754	688	721	1474	1232
	Na^+	918	855	759	1425	1349
	K^+	979	903	941	1672	1412

[a] Potentials relative to Ag/AgCl measured at a potential scan rate of 200 mV s^{-1}. Alkali-metal cations were present at a concentration of 1.5 mM. [b] Concentration: 1.5 mM. [c] Formal potential.

reduction. are shown as a function of ionic radius in Fig. 2.

The pattern of results in Fig. 2 shows interesting features. In particular, the binding enhancements for **2a** are among the highest observed for Na^+ and K^+ using redox switchable ligands. The binding enhancement factors on one-electron reduction are highest for **2a**, the compound having, as auxiliary binding sites, OCH_3 groups that are least likely to promote strong cation binding to the neutral ligand compared with the amide and ester groups in **2c** and **2b**, respectively. Broadly speaking, the enhancements for **2a–c** are inversely proportional to the basicity of the auxiliary groups. Intuitively this seems reasonable since, other things being equal, if the the cationic charge is appreciably dissipated by these auxiliary groups, the additional electrostatic stabilisation resulting from reduction of the switch would be expected to be less significant than with the positive charge localised on the metal ion. It should also be noted that **2a** shows binding enhancements that decrease much more slowly with increasing cation radius than the other two calixarenes and when compared with similar observations on anthraquinone-switched crown ethers.[2,14]

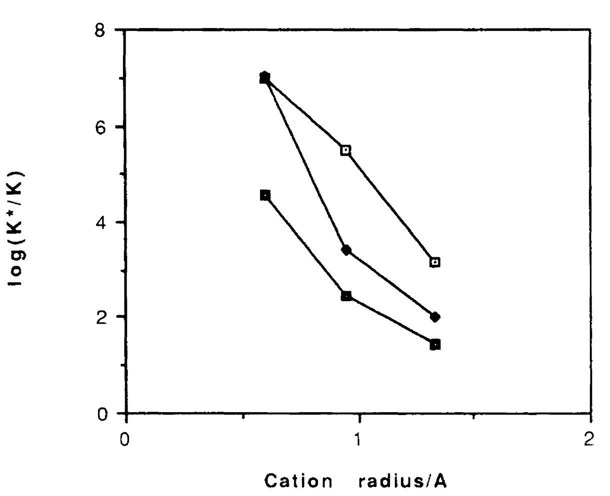

Fig. 2. Binding enhancements (K^*/K) on one-electron reduction of compounds **2** in acetonitrile solution at 20 °C: **2a**, -□-; **2b**, -◆-; **2c**, -■-.

When cyclic voltammetric measurements were carried out on **2a** in the presence of one equivalent of potassium perchlorate, the response changed from the clean pattern of reversible one-electron reduction to the more complex pattern illustrated in Fig. 3. The single reversible wave observed for the first electron transfer at low scan rates at −968 mV became resolved into two at the highest scan rates, the peak potentials being −968 and −1154 mV. These values are in close agreement with the values in Table 2 for the free ligand and the potassium complex. This pattern of behaviour was not observed in the reduction of **2a** in the presence of Li^+ or Na^+, nor was it found in the reduction of **2b** and **2c** in the presence lithium, sodium or potassium cations. We propose that this behaviour arises because, at the low concentrations (1.5 mM) used in the voltammetric experiments, binding of K^+ to **2a** in its neutral state is incomplete and that the binding process, after one electron transfer to the anthraquinone switch, is slow enough on the CV time-scale that it can be outrun at the high potential scan rates. At a scan rate of 200 mV s^{-1}, however, binding of potassium to uncomplexed **2a** is sufficiently rapid that essentially all the ligand is reduced at the less negative potential. The current response when the two waves are

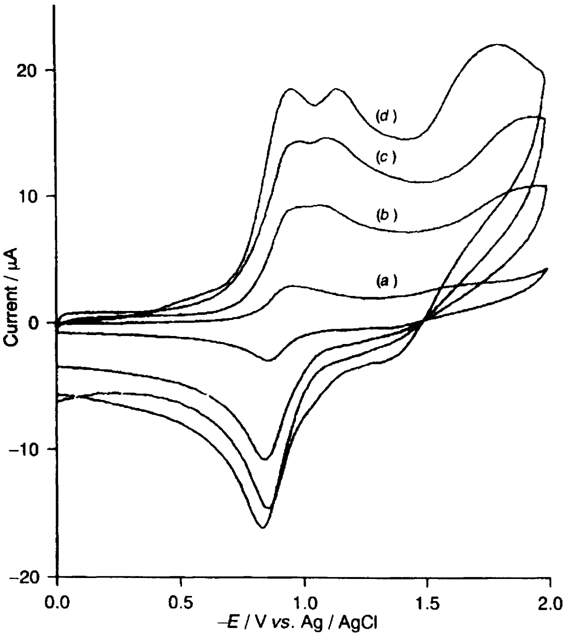

Fig. 3. Sweep rate dependence of cyclic voltammograms for the **2a**-$KClO_4$ interaction: (a) 200 mV s^{-1}; (b) 1 V s^{-1}; (c) 4 V s^{-1}; (d) 5 V s^{-1}.

fully resolved thus reflects the position of the binding equilibrium prior to reduction; from a crude estimate of the equality of the current response in the two reduction waves, we estimate a binding constant of approximately 1300 M^{-1}, and, from the potential scan rate required to resolve the current response in the presence of K^+, that the half life of the binding process is of the order of 100 ms. We estimate the binding constant of the reduced ligand to be ca. $2 \times 10^6 M^{-1}$. Clearly the effect is restricted to potassium, and this suggests that it is related to the size of the cation and the ease with which it can enter the binding site of the calixarene.

The slow rate of the K^+ binding process for **2a** (Gibbs energy barrier: ca. 16 kcal mol^{-1}) is in a range that might correspond to a conformational change in a calixarene ligand. We believe that this change is from the cone conformation of the free ligand in solution to a partial cone conformation in the potassium complex, a conformational change already described in non-switchable calix[4]arenes and calixspherands.[7b,15] The barrier to such a conformational change can be estimated, for example, from NMR results on the tetramethyl ether of *p-tert*-butylcalix[4]arene[16] as about 14 kcal mol^{-1}. Evidence in support of this interpretation is as follows.

(i) At concentrations tenfold higher than in the CV experiments, The ^1H NMR spectrum of a 0.015 M solution of **2a** in CD_3CN solution containing one molar equivalent of $KClO_4$ is quite different from the spectrum in the absence of the added salt (see Table 3). It is essentially the spectrum of the K^+ complex and shows two singlets (intensity ratio 1 : 1) for the methoxy protons in two different environments, three singlets (intensity ratio 1 : 1 : 2) for the *tert*-butyl groups and four pairs of doublets indicative of two different bridging methylene groups in the calixarene as required for the partial cone conformation. For comparison, the free ligand shows only one singlet for the two methoxy-group protons, one pair of doublets for the calixarene methylene protons, characteristic of the cone conformation, and two singlets for the *tert*-butyl protons (intensity ratio 2 : 2). The Na^+-complex also has a spectrum indicating the cone conformation, since it shows only one methoxy signal, one pair of doublets in the bridging methylene region and a singlet at high field integrating for four *tert*-butyl groups, presumably as a consequence of accidental coincidence of the signals of from *tert*-butyl groups on the bridged and unbridged aromatic rings.

(ii) Molecular modelling of the K^+/**2a** complex using both the PC Model and Sybyl programs indicates that the minimised energy of the cone conformation is less than 1 kcal mol^{-1} lower than that of a distorted partial cone conformation, shown in Fig. 4. This geometry allows the methoxy oxygen atom of the inverted methoxyphenyl moiety to coordinate to the under side of the metal cation held in close proximity to the redox switch and the remaining donor atoms. Similar calculations on the Na^+-complex yields an energy for the cone conformation more than 3 kcal mol^{-1} below that of the partial cone. While we do not wish to attach significance to the absolute values of the energies,we take these results to indicate that the partial cone conformation is relatively more accessible thermodynamically in the K^+ complex than in the Na^+ complex. However, the interpretation of the CV behaviour is, we believe, entirely a consequence of kinetic control in the binding process; because of size considerations, entry of K^+ into the calix cavity of the uncomplexed ligand (cone) forces rotation of a methoxyphenyl group about its methylene bridges, leaving the K^+ ion interacting with the oxygen atoms of the quinone bridge and the non-rotating methyl ether group, with the other, rotated methoxy-group providing solvation from the upper side. For Na^+ the smaller size presumably allows entry without methoxyphenyl-group rotation. It seems unlikely that there is a pathway for conformational change in any of the complexes; only decomplexation is possible. It should be noted that the auxiliary groups in **2b** and **2c** are too large to allow a similar conversion into a partial cone conformation, even if stronger binding of the cation would be achieved thereby.

Conclusions

The present investigation has highlighted the role that dynamic factors can play in the enhancement of binding by redox-switched ionophores. It is clear that, for there to be effective interaction between the selective binding site, in the vicinity of the lower rim of the calix[4]arene cone in the present context, the switched group must be capable of achieving the optimal conformation for binding enhancement in a time that is short in relation to the rate of potential change. This is of the order of 10 ms or

Table 3. Selected ^{1}H NMR data for **2a** and its complexes with Na^+ and K^+ in CD_3CN solution.[a]

Group	**2a**	**2a**·Na^+	**2a**·K^+
δ(MeO)	4.00 (s, 6 H)	3.85 (s, 6 H)	3.03 (s, 3 H) 3.23 (s, 3 H)
$\delta(\mathrm{Me_3C})$	0.81 (s, 18 H) 1.29 (s, 18 H)	1.22 (s, 36 H)	1.19 (s, 18 H) 1.27 (s, 9 H) 1.42 (s, 9 H)
δ(Bridging $-\mathrm{CH_2}-$), J	3.13 (d, 4 H, 12.0 Hz) 4.23 (d, 4 H, 12.0 Hz)	3.57 (d, 4 H, 12.6 Hz) 4.40 (d, 4 H, 12.6 Hz)	3.37 (d, 2 H, 12.6 Hz) 4.00 (d, 2 H, 12.6 Hz) 4.13 (d, 2 H, 12.1 Hz) 4.27 (d, 2H, 12.1 Hz)

[a] Field 200 MHz.

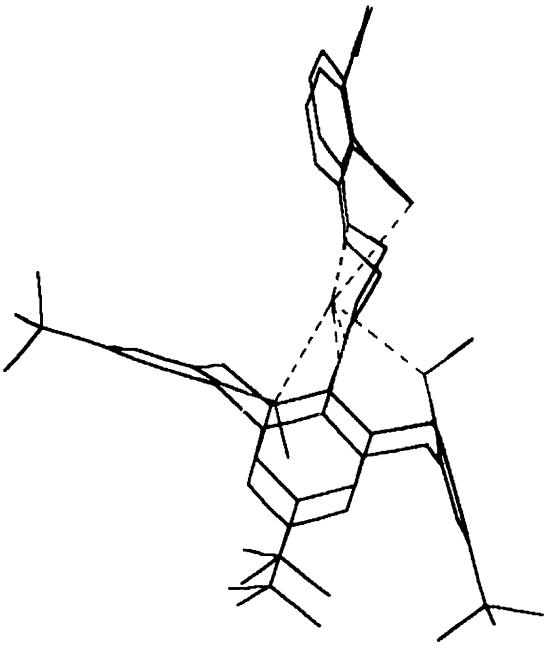

Fig. 4. Minimum energy conformation of the **2a**–K^+ complex calculated using the modelling program PC Model (v. 4.0; Serena Software, Bloomington, IN, USA). The broken lines indicate the interaction between donor O-atoms and K^+.

less under typical conditions of electrochemical measurements, but could be quite different in practical applications of selective cation binding. The findings with **2a** indicate that the design of calix[4]arene ionophores requires very careful consideration since the behaviour appears to be a very sensitive function of the radius of the target cation and of auxiliary donor groups. It needs to be emphasised, however, that absolute values of the binding constants of redox-switched ligands will be necessary before practical applications of them can be undertaken.

Experimental

*5,11,17,23-Tetra-*tert*-butyl-25, 26, 27-tris(ethoxycarbonylmethoxy)-28-(carboxymethoxy)calix[4]arene* (**3**; R = H). *p-tert*-Butylcalix[4]arene tetraester **3** (R = Et)[9c] (5.00 g, 5.034 mmol) was dissolved in chloroform (100 ml) containing 5% v/v ethanol and 1% v/v water. To this mixture was added trifluoroacetic acid (0.5 ml). The mixture was stirred at room temperature for between 3 and 5 days. The reaction was followed by monitoring the disappearance of the ArH peak for the starting material at 6.77 ppm. The mixture was then washed with water (2 x 100 ml), dried over magnesium sulfate, filtered and the solvent removed *in vacuo* to yield **3** (R = H) as an off-white solid (4.86 g). Conversion was estimated at 96% by comparison of the intergrals for the ArH peaks in the NMR spectrum. The compound was used without further purification: m.p. 160 °C (lit. 166–168 °C);[113] IR (Nujol) (C=O). ^{1}H NMR: δ 0.82 [s, 18 H, $\mathrm{C(CH_3)_3}$], 1.29 (t, 3H $\mathrm{CH_2C}H_3$), 1.30 (t, 6 H, $\mathrm{CH_2C}H_3$) 1.31 [s, 9 H, $\mathrm{C(CH_3)_3}$], 1.32 [s, 9 H, $\mathrm{C(CH_3)_3}$], 3.19 (d, 2 H, $\mathrm{ArC}H_2\mathrm{Ar}$), 3.25 (d, 2 H, $\mathrm{ArC}H_2\mathrm{Ar}$), 4.21 (q, 4 H, $\mathrm{CH_2C}H_3$), 4.25 (q, 4 H, $\mathrm{C}H_2\mathrm{CH_3}$), 4.35 (s, 2 H, $\mathrm{OC}H_2\mathrm{CO_2Et}$), 4.57 (s, 2 H, $\mathrm{OC}H_2\mathrm{CO_2Et}$), 4.59 (d, 2 H, $\mathrm{ArC}H_2\mathrm{Ar}$), 4.86 (s, 2 H, $\mathrm{OC}H_2\mathrm{CO_2Et}$), 4.94 (s, 2 H, $\mathrm{OC}H_2\mathrm{CO_2Et}$), 4.96 (d, 2 H, $\mathrm{ArC}H_2\mathrm{Ar}$), 6.53 (d, 2 H, ArH), 6.62 (d, 2 H, ArH), 7.13 (s, 2 H, ArH), 7.14 (s, 2 H, ArH). MS (FAB, 3-NOBA): $[M+\mathrm{H}]^+$, 965.46, $[M]^+$, 964.45 (requires 964.534). Analysis: Found C, 72.40; H, 7.96. Calc. for $C_{58}H_{76}O_{12}$: C, 72.17; H, 7.94%.

*5,11,17,23-tetra-*tert*-butyl-25,26,27-tris(ethoxycarbonylmethoxy)-28-(1-anthraquinonyl-carbamoylmethoxy)-calix[4]arene* (**1**). Triester, monoacid **3** (R = H) (0.5 g, 0.518 mmol) was dissolved in thionyl chloride (25 ml) and the mixture refluxed for 24 h under nitrogen. The excess thionyl chloride was distilled off under reduced pressure to yield a yellow oil. This was taken up in dry toluene (25 ml) and added to a solution of 1-aminoanthraquinone (0.127 g, 0.570 mmol) in dry toluene (25 ml). This mixture was refluxed for 16 h, whereafter it had changed colour from red to yellow. The solvent was removed *in vacuo* and the residue taken up in dichloromethane (40 ml). This solution was washed with water (3 x 25 ml), dried over magnesium sulphate and the solvent removed *in vacuo* to yield a yellow solid. This was purified by chromatography on silica (eluent CH_2Cl_2–Et_2O, 0–50%) to yield **1** as a yellow solid. This was further purified by recrystallisation from methanol at −18 °C to give yellow needles (0.250 g, 41%).

M.p. 130 °C. IR (Nujol) 1750 (EtOC=O), 1740 cm^{-1} (RNHC=O). ^{1}H NMR: δ 0.94 [s, 9 H, C(CH$_3$)$_3$], 0.96 (t, 6 H, OCH$_2$CH_3), 1.04 [s, 9 H, C(CH$_3$)$_3$], 1.18 [s, 18 H, C(CH$_3$)$_3$], 3.22 (d, 2 H, ArCH$_2$Ar), 3.27 (d, 2 H, ArCH$_2$Ar), 3.84 (m, 4 H, OCH_2CH$_3$), 4.21 (q, 2 H, OCH_2CH$_3$), 4.72 (s, 2 H, ArOCH_2), 4.84 (s, 2 H, ArOCH_2), 4.85 (d, 2 H, ArCH$_2$Ar), 5.04 (s, 2 H, ArOCH_2), 5.06 (d, 2 H, ArCH$_2$Ar), 5.13 (s, 2 H, ArOCH_2), 6.6 (s, 2 H, ArH), 6.73 (s, 2 H, ArH), 6.93 (s, 4 H, ArH), 7.83 (m, 2 H, AqH), 8.13 (m, 2 H, AqH), 8.31 (m, 1 H, AqH), 8.45 (m, 1 H, AqH), 9.22 (m, 1 H, AqH), 12.4 (s, 1 H, NH). MS (FAB, 3-NOBA): $[M+\mathrm{Na}]^+$ 1192.52, $[M+\mathrm{H}]^+$ 1170.56 (requires 1170.586). Analysis: Found C, 73.68; H, 7.10; N, 1.26. Calc. for $C_{72}H_{83}NO_{13}$: C, 73.88; H, 7.15, N 1.28%.

*5,11,17,23-Tetra-*tert*-butyl-25, 26, 27-tris(ethoxycarbonylmethoxy)-28-(2-nitro-phenylcarbamoylmethoxy) calix[4]arene.* Triester, monoacid **3** (R = H) (0.71 g, 0.734 mmol) was dissolved in thionyl chloride (25 ml) and the mixture refluxed for 2 h, under nitrogen. The excess thionyl chloride was distilled off under reduced pressure to leave a yellow oil. This was taken up in dry toluene (25 ml) and added to a solution of 2-nitroaniline (0.1067 g, 0.772 mmol) in dry toluene (25 ml). This mixture was refluxed for 16 h, whereafter it changed colour from orange to dark yellow. The solvent was removed *in vacuo* and the residue taken up in dichloromethane (40 ml). This solution was washed with water (3 × 25 ml), dried over magnesium sulfate and the solvent removed *in vacuo* to yield a yellow solid. This was purified by chromatography on silica (eluent CH_2Cl_2–Et_2O 0–50%) to yield the product as a dull yellow solid. This was further purified by being dissolving in methanol and stored at −18 °C for 1 week, wherupon a resinous precipitate formed. The mother liquors were decanted from this and water added to give a pale yellow precipitate (0.480 g, 60%). M.p. 96–98 °C. IR (Nujol) 1770 (EtOC=O), 1760 cm^{-1} (RNHC=O). ^{1}H NMR: δ 0.85 [s, 9 H, C(CH$_3$)$_3$], 1.05 [s, 27 H, C(CH$_3$)$_3$], 3.22 (d, 2 H, ArCH_2Ar), 3.27 (d, 2 H, ArCH_2Ar), 3.98 (m, 4 H, OCH_2CH$_3$), 4.24 (q, 2 H, OCH_2CH$_3$), 4.73 (s, 2 H, ArOCH_2), 4.75 (s, 2 H, ArOCH_2), 4.76 (d, 2 H, ArCH_2Ar), 4.90 (s, 4 H, ArOCH_2), 4.95 (d, 2 H, ArCH_2Ar), 6.72 (s, 2 H, ArH), 6.80 (s, 2 H, ArH), 6.82 (s, 4 H, ArH), 7.24 (t, 1 H, ArH), 7.66 (t, 1 H, ArH), 8.18 (d, 1 H, ArH), 8.48 (d, 1 H, ArH), 10.08 (s, 1 H, NH). MS (FAB, 3-NOBA): $[M+\mathrm{Na}]^+$ 1107.56, $[M+\mathrm{H}]^+$ 1085.58 (requires 1085.573). Analysis: Found C, 70.33; H, 7.47; N, 2.10. Calc. for $C_{64}H_{80}N_2O_{13}$: C, 70.83; H, 7.43; N 2.58%.

*25,28-[Anthraquinone-1,8-diyldioxydi(ethyleneoxy)]-5,11,17,23-tetra-*tert*-butyl-26,28-dihydroxycalixarene* (**2d**). 1,8-bis(2-bromoethoxy)anthraquinone[13d] (3.04 g, 6.694 mmol; prepared from 1,8-dihydroxyanthraquinone by treatment with 1,2-dibromoethane in dimethylformamide containing caesium carbonate at 80 °C), *p-tert*-butylcalix[4]arene (4.344 g, 6.694 mmol), sodium carbonate (5.676 g, 53.5 mmol) and sodium iodide (8.03 g, 53.5 mmol) were suspended in butyronitrile (200 ml) and heated to reflux for 18 h. The solvent was removed *in vacuo* and the residue partitioned between dichloromethane (100 ml) and HCl (100 ml, 2 M) and filtered. The organic layer was separated and washed with water (2 × 100 ml), dried over magnesium sulfate, filtered and the volume of solvent reduced to ca. 50 ml. This solution was filtered again to remove unchanged starting material (0.447 g) and the volume of solvent removed *in vacuo*. The residue was recrystallised from dichloromethane–petrol (b.p. 40–60 °C) yielding a crop of crystals (1.53 g). The solvent was removed from the mother liquors *in vacuo* and the residue was recrystallised from chloroform–methanol and the mother liquors retained. The solids thus obtained contained materials, which from FAB mass spectrometric examination contained compounds having $m/z = 1882.4$ and 2174.7 along with some **2d**. The solvent was removed from the mother liquors *in vacuo* and the residue recrystallised from dichloromethane–petrol (b.p. 40–60 °C) yielding a second crop of crystalline **2d** (0.4842 g). This was combined with the first crop to give **2d** (2.0142 g, 36% based on recovered calixarene starting material: m.p. 303–304 °C (decomp.). IR 1680 (AqC=O), 1590 cm^{-1} (AqC=O). ^{1}H NMR: δ 1.09 [s, 18 H, C(CH$_3$)$_3$], 1.19 [s, 18 H, C(CH$_3$)$_3$], 3.24 (d, 4 H, ArCH$_2$Ar), 4.23 (d, 4 H, ArCH$_2$Ar), 4.48 (m, 4 H, ArOCH$_2$) 4.68 (m, 4 H, AqOCH$_2$), 6.93 (s, 4 H, ArH), 6.96 (s, 4 H, ArH), 7.24 (d, 2 H, Ar H-2 and H-7), 7.58 (t, 2 H, Ar H-3, H-6), 7.81 (d, 2 H, Ar H-4, H-5), 8.13 (s, 2 H, ArOH). MS (FAB, 3-NOBA): $[M+\mathrm{H}]^+$ 941.41, $[M]^+$ 940.40 (requires 940.4914). Analysis: Found C, 75.64, H, 6.97. Calc. for $C_{62}H_{68}O_8$, C, 79.12, H, 7.28. Calc. for $C_{62}H_{68}ClNaO_8$: C, 74.49 H, 6.86%.

*25,27-[Anthraquinone-1,8-diyldioxydi(ethyleneoxy)]-5,11,17,23-tetra-*tert*-butyl-26,28-dimethoxycalixarene* (**2a**). Compound **2d** (0.5 g, 0.53 mmol), sodium hydride (0.1 g, 80% oil suspension 3.18 mmol) and dimethyl sulphate (0.234 g, 2.22 mmol) were dissolved in dry THF (50 ml). The mixture was heated to reflux for 16 h. The reaction mixture was allowed to cool and hydrochloric acid (5 ml, 2M) added to quench excess sodium hydride. The mixture was partitioned between dichloromethane (75 ml) and water (75 ml). The organic layer was separated and washed with water (2 × 30 ml), dried over magnesium sulfate, filtered and the solvent removed *in vacuo*. The residue was recrystallised from dichloromethane–methanol to yield **2a** as a yellow powder (0.2565 g, 50%). M.p. 180–183 °C (decomp.). IR: 1700 (AqC=O), 1610 cm^{-1}(AqC=O). ^{1}H NMR: δ 0.81 [s, 18 H, C(CH$_3$)$_3$], 1.29 [s, 18 H, C(CH$_3$)$_3$], 3.13 (d, 4 H, ArCH$_2$Ar), 4.00 (s, 6 H, ArOMe), 4.23 (d, 4 H, ArCH$_2$Ar), 4.41 (m, 4 H, ArOCH$_2$), 4.79 (m, 4 H, AqOCH$_2$), 6.51 (s, 4 H, ArH), 7.08 (s, 4 H, ArH), 7.32 (d, 2 H, Ar H-2, H-7), 7.62 (t, 2 H, Ar H-3, H-6), 7.78 (d, 2 H, Ar H-4 H-5). MS (FAB, 3-NOBA), $[M+\mathrm{H}]^+$

969.34, $[M]^+$ 968.33 (requires 968.5227). Analysis: Found C, 78.82, H, 7.69. Calc. for $C_{64}H_{72}O_8$: C, 79.31, H, 7.49%.

25, 27 - [Anthraquinone - 1, 8 - diyldioxydi(ethyleneoxy)] - 5, 11, 17, 23 - tetra - tert *- butyl - 26, 28 - di(ethoxycarbonylmethoxy) calixarene* (**2b**). This was prepared from **2d** in an analogous fashion to **2a**. Compound **2d** (0.5 g, 0.53 mmol), sodium hydride (0.1 g, 80% oil suspension 3.18 mmol) and ethyl bromoacetate (0.3448 g, 2.22 mmol) were dissolved in dry THF (50 ml) and refluxed for 16 h. Work-up as before and recrystallisation from dichloromethane–methanol yielded **2b** as yellow needles (0.4206 g, 71%). M.p. 306–307 °C (decomp.). IR: 1780 (COOEt), 1690 (AqC=O), 1610 cm^{-1} (AqC=O). ^{1}H NMR: δ 0.83 [s, 18 H, $C(CH_3)_3$], 1.06 (t, 6 H, OCH_2CH_3), 1.31 [s, 18 H, $C(CH_3)_3$], 3.16 (d, 4 H, $ArCH_2Ar$), 3.86 (q, 4 H, OCH_2CH_3), 4.33 (s, 4 H, $ArOCH_2CO_2Et$), 4.42 (d, 4 H, $ArCH_2Ar$), 4.57 (m, 4 H, $ArOCH_2$) 4.71 (m, 4 H, $AqOCH_2$), 6.48 (s, 4 H, ArH), 7.10 (s, 4 H, ArH), 7.34 (d, 2 H, Ar H-2, H-7), 7.60 (t, 2 H, Ar H-3, H-6), 8.00 (d, 2 H, Ar H-4 H-5). MS (FAB, 3-NOBA): $[M+H]^+$ 1113.45, $[M]^+$ 1112.44 (requires 1112.5650). Analysis: Found C, 75.30, H, 7.22. Calc. for $C_{70}H_{80}O_{12}$: C, 75.51, H, 7.24%.

25, 27 - [Anthraquinone - 1, 8 - diyldioxydi(ethyleneoxy)] - 5,11,17,23 - tetra - tert *- butyl - 26,28 - diethylcarbamoylmethoxycalixarene* (**2c**). Compound **2d** (0.5 g, 0.53 mmol), sodium hydride (0.1 g, 80% oil suspension, 3.18 mmol), sodium iodide (0.2389 g, 1.59 mmol) and *N,N*-diethyl-2-chloroacetamide (0.3179 g, 2.22 mmol) were dissolved in dry THF (50 ml). After refluxing for 16 h, the reaction mixture was worked up as before. The crude product was chromatographed on 10% w/w NaCl loaded silica (eluent: 1, dichloromethane; 2, ethyl acetate; 3, ethanol). The last fraction was recrystallised from ethanol, with activated charcoal treatment, to yield **2d** as a yellow powder (0.1536 g, 25%). M.p. 170–172 °C. IR: 1700 ($CONEt_2$), 1690 (AqC=O), 1610 cm^{-1} (AqC=O). ^{1}H NMR: δ 0.81 [s, 18 H, $C(CH_3)_3$], 1.08 (t, 12 H, NCH_2CH_3), 1.36 [s, 18 H, $C(CH_3)_3$], 2.98 (q, 4 H, NCH_2CH_3), 3.17 (d, 4 H, $ArCH_2Ar$), 3.42 (q, 4 H, NCH_2CH_3), 4.32 (s, 4 H, $ArOCH_2CONEt_2$), 4.35 (d, 4 H, $ArCH_2Ar$), 4.54 (m, 4 H, $ArOCH_2$) 4.84 (m, 4 H, $AqOCH_2$), 6.44 (s, 4 H, ArH), 7.16 (s, 4 H, ArH), 7.32 (d, 2 H, Ar H-2, H-7), 7.56 (t, 2 H, Ar H-3, H-6), 8.03 (d, 2 H, Ar H-4, H-5). MS (FAB, 3-NOBA): $[M+Na]^+$ 1189.61, (requires 1189.64927), $[M+H]^+$ 1167.59 (requires 1167.66733). Analysis: Found C, 74.50, H, 7.71, N, 2.27. Calc. for $C_{74}H_{90}N_2O_{10}$: C, 76.13, H, 7.77, N, 2.40% ($C_{74}H_{90}ClN_2NaO_{10}$ requires C 72.50, H 7.40, N 2.29%).

Instrumental methods. (a) Infrared (IR) spectra were recorded in the range 4000–600 cm^{-1} on a Perkin–Elmer 1320 or Perkin–Elmer 1720 FT infrared spectrometers. Spectra of solid samples were recorded as nujol mulls or KBr discs.

(b) Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker WM 200 (200 MHz) spectrometer. Deuteriochloroform, with tetramethylsilane as an internal standard, was used as the solvent, unless otherwise stated. Spectra were recorded on the δ scale and signals are quoted in the form: chemical shift (multiplicity, number of protons, assignment), measured in ppm.

(c) Cyclic voltammetry. In the early stages of the investigation, cyclic voltammograms were recorded using an EG&G model 173 potentiostat fitted with a 276 interface. The potential sweep was generated by an Apple II microcomputer which also served to collect the data. Voltammograms were recorded without IR compensation on an XY plotter. In later experiments a Princeton Applied Research Model 263A potentiostat/galvanostat was used, controlled from a PC using Model 270/250 software. This allowed direct reading of peak potentials. Compensation for ohmic loss was applied in these experiments.

Acetonitrile for electrochemical experiments was taken from a freshly opened bottle of the highest available purity and was dried by passage through a column of alumina N super I (ICN Biochemicals). The inorganic salts were of analytical reagent quality and were dried overnight at 100 °C before use.

References

1. Sugihara, K., Kamiya, H., Yamaguchi, M., Kaneda, T. and Misumi, S. *Tetrahedron Lett. 22* (1981) 1619; Wolf, R. E. and Cooper, S. R. *J. Am. Chem. Soc. 106* (1984) 4646; see also Delgado, M., Wolf, R. E., Hartmann, J. A. R., McCafferty, G., Yagbasan, R., Rawle, S. C., Watkin, D. J. and Cooper, S. R. *ibid. 114* (1992) 8983.
2. For a review, see Gokel, G. W. In: Stoddart, J. F., Ed., *Crown Ethers and Cryptands*, Monographs in Supramolecular Chemistry, Royal Society of Chemistry, Cambridge 1991, p. 145 *et seq.*
3. Beer, P. D., Gayle, H. A. and Chen, Z. *Adv. Phys. Org. Chem. 31* (1997). *In press.*
4. Examples: nitroaromatic-switched crowns, Kaifer, A., Echegoyen, L., Gustowski, D. A., Goli, D. M. and Gokel, G. W. *J. Am. Chem. Soc. 105* (1983) 7168; switchable lariat crowns, Echegoyen, L., Gustowski, D. A., Gatto, V. J. and Gokel, G. W. *J. Chem. Soc., Chem. Commun.* (1986) 220; anthraquinone-containing crowns, Delgado. M., Gustowski, D., Yoo, H., Gatto, V. J., Gokel, G. W. and Echegoyen, L. *J. Am. Chem. Soc. 112* (1988) 119; anthraquinone-containing cryptands, Chen, Z., Schall, O. F., Icalá, M., Li, Y., Gokel, G. W. and Echegoyen, L. *ibid. 114* (1992) 444.
5. Togo, H., Hashimoto, K., Morihashi, K. and Kikuchi, O. *Bull. Chem. Soc. Jpn. 61* (1988) 3026.
6. For a review of early work, see Gutsche, C. D. In: Stoddart, J. F., Ed., *Calixarenes*, Monographs in Supramolecular Chemistry, Royal Society of Chemistry, Cambridge 1989.
7. (a) Gomez-Kaifer, M., Reddy, P. A., Gutsche, C. D. and Echegoyen, L. *J. Am. Chem. Soc. 116* (1994) 3580; (b) Beer, P. D., Chen, Z., Drew, M. G. B. and Gale, P. A. *J. Chem. Soc., Chem. Commun.* (1994) 2207.
8. A preliminary account of the present work is in Bethell,

D., Dougherty, G. and Cupertino, D. C. *J. Chem. Soc., Chem. Commun.* (1995) 675.

9. (a) Chang, S. K. and Cho, I. *Chem. Lett.* (1984) 477; Chang, S. K. and Cho, I. *J. Chem. Soc., Perkin Trans. 1* (1986) 211; Chang, S. K., Kwon, S. K. and Cho, I. *Chem. Lett.* (1987) 947; (b) Arduini, A., Pochini, A., Reverberi, S. and Ungaro, T. *Tetrahedron 42* (1986) 2089; (c) Arnaud-Neu, F., Collins, E. M., Deasy, M., Ferguson, G., Harris, S. J., Kaitner, B., Lough, A. J., McKervey, M. A., Marques, E. M., Ruhl, B. L., Schwing-Weill, M. J. and Seward, E. M. *J. Am. Chem. Soc. 111* (1989) 8681.
10. Arduini, A., Ghidini, E., Pochini, A., Ungaro, R., Andretti, G. D., Calestani, G. and Ugozzoli, F. *J. Inclusion Phenom. 6* (1988) 119.
11. Barrett, G., Bohmer, V., Ferguson, G., Gallagher, J. F., Harris, S. J., Leonard, R. G., McKervey, M. A., Owens, M., Tabatabai, M., Vierengel, A. and Vogt, W. *J. Chem. Soc., Perkin Trans. 2* (1992) 1595.
12. In the presence of sodium ions, the second reduction waves, particularly of the *N*-methyl compound, were markedly affected by adsorption, and stripping peaks appeared on the anodic part of the cycle. A similar effect has been reported in the cyclic voltammetry of crown ethers incorporating anthraquinone units in the macrocycle.
13. (a) Lu, T., Kim Yoo, H., Zhang, H., Bott, S., Atwood, J. L., Echegoyen, L. and Gokel, G. W. *J. Org. Chem. 55* (1990) 2269; (b) Fang, J., Lu, T., Kim, H., Delgado, I., Geoffroy, P., Atwood, J. L. and Gokel, G. W. *ibid. 56* (1991) 7079; (c) Kim Yoo, H., Davis, D. M., Chen, Z., Echegoyen, L. and Gokel, G. W. *Tetrahedron Lett. 31* (1990) 55; (d) Kim, H., Schall, O. F., Fang, J., Trafton, J. E., Lu, T., Atwood, J. L. and Gokel, G. W. *J. Phys. Org. Chem. 5* (1992) 482.
14. Caridade Costa, J. M., Jeyashri, B. and Bethell, D. *J. Electroanal. Chem. 351* (1993) 259.
15. (a) Ghidini, E., Ugozzoli, F., Ungaro, R., Harkema, S., El-Fadl, A. A. and Reinhoudt, D. N. *J. Am. Chem. Soc. 112* (1990) 6979; (b) Bakker, W. I. I., Haas, M., Khoo-Beattie, C., Ostaszewski, R., Franken, S. M., den Hertog, H. J., Verboom, W., de Zeeuw, D., Harkema, S. and Reinhoudt, D. N. *ibid. 116* (1994) 123.
16. Groenen, L. C., van Loon, J.-D., Verboom, W., Harkema, S., Casnati, A., Ungaro, R., Pochini, A., Ugozzoli, F. and Reinhoudt, D. N. *J. Am. Chem. Soc. 113* (1991) 2385.

Received April 30, 1997.