

Cation Recognition by New Diester- and Diamide-Calix[4]arenequinones and a Diamide-Benzo-15-Crown-5-Calix[4]arene*

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Abstract. The synthesis, metal, ammonium and alkyl ammonium cation coordination chemistry and electrochemical recognition studies of new diester- and diamide-calix[4]arenequinone receptors are described. In addition the synthesis and coordination properties of a novel diamide benzo-15-crown-5-calix[4]arene molecule is reported.

Key words: Calix[4]arenequinones, cation coordination, electrochemistry, benzo-15-crown-5-calix[4]arene.

1. Introduction

In pursuit of advancing chemical sensor technology considerable interest is being shown in the incorporation of organic and transition metal redox-active centres into various crown ether, cryptand and calixarene macrocyclic structural frameworks [1]. With the cyclic polyethers, these systems can be designed to selectively electrochemically recognise the binding of metal [2] and ammonium guest cations [3] either by through-space interactions and/or via various bond linkages between the receptor site and the redox centre. In addition, redox responsive anion receptors based on cobalticinium [4], ruthenium (II) bipyridyl derivatives [5] and functionalised calix[4]arenes [6] have also been described. Although the synthesis [7, 8] and electrochemical properties [9, 10] of calix[4]arenequinones have recently been reported, their potential use and application to amperometric sensor technology has not, to our knowledge, been exploited. We report here the first examples of such an application in which simple new lower rim diester and diamide modi-

* This paper is dedicated to the commemorative issue on the 50th anniversary of calixarenes.

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fied calix[4]arenequinones bind and electrochemically recognise Group 1 and 2, ammonium and alkyl ammonium guest cations. In addition the synthesis and coordination properties of a novel diamide benzo-15-crown-5-calix[4]arene receptor are also described.

2. Experimental

2.1. SOLVENT AND REAGENT PRETREATMENT

Where necessary solvents were purified and dried prior to use using standard procedures. Unless otherwise stated commercial grade chemicals were used without further purification.

p-tert-Butylcalix[4]arene bis ethyl ester [11], *p*-tert-butylcalix[4]arene bis diethyl amide [11], *p*-tert-butylcalix[4]arene bis acid chloride [11], and 4-aminobenzo-15-crown-5 [12] were synthesised according to literature methods.

2.2. INSTRUMENTAL METHODS

Melting points were recorded on a Gallenkamp melting point apparatus in open capillaries and are uncorrected.

NMR spectra were recorded on a Brüker AM 300 instrument. IR spectra were recorded on a Perkin Elmer 1710 IR FT spectrometer. UV spectra were recorded on a Perkin-Elmer Lambda 6 spectrometer. Electrochemical measurements were conducted on a Princeton Applied Research Potentiostat/Galvanostat Model 273. Fast atom bombardment mass spectra were performed at University College, Swansea by the S.E.R.C. mass spectrometry service. All elemental analyses were carried out by the Inorganic Chemistry Laboratory, Oxford.

2.3. SYNTHESIS

5,17-Di-tert-butyl-26,28,-bis-(carboethoxymethyl)-calix[4]-25,27-diquinone (3)

p-tert-Butylcalix[4]arene bis ethyl ester (0.82 g, 1 mmol) was stirred in 0.88 M thallium trifluoroacetate (TTFA) in trifluoroacetic acid (TFA) solution (6.8 mL, 6 mmol), for 2 h in the dark. The TFA was then removed *in vacuo* and the residue poured onto ice/water (50 mL). The product was then extracted into chloroform (100 mL), separated and the organic layer washed with water (100 mL). The organic layer was then dried over MgSO₄ and reduced *in vacuo*. The residue was purified by column chromatography on silica gel eluting with chloroform/methanol 90 : 10 (v/v). The product was collected and triturated with methanol to give a yellow powder (0.48 g, 65%).

¹H-NMR (CD₂Cl₂, 300 MHz) 1.10 (s, 18H, (CH₃)₃C), 1.28 (t, *J* = 7.1 Hz, 6H, CH₂CH₃), 1.58 (s, 2H, H₂O), 3.27 (d, *J* = 13.3Hz, 4H, ArCH₂Ar), 4.02 (d, *J* = 13.3Hz, 4H, ArCH₂Ar), 4.23 (q, *J* = 7.1Hz, 4H, CH₂CH₃), 4.39 (s, 4H, OCH₂), 6.71 (s, 4H, C=CH), 6.85 (s, 4H, ArH).

^{13}C -NMR (CD_2Cl_2 , 75.42 MHz) 14.10 (CH_3CH_2), 31.27 ($(\text{CH}_3)_3\text{C}$), 32.71 (ArCH_2Qu), 33.88 ($(\text{CH}_3)_3\text{C}$), 61.35 (CH_2O), 71.29 (CH_2O), 126.81 ($\text{CH}=\text{C}$), 128.36, 132.88 (ArH), 146.61, 147.86, 169.26 ($\text{C}=\text{O}$), 185.40 ($\text{C}=\text{O}$), 188.57 ($\text{C}=\text{O}$).

IR: 1760.0 cm^{-1} , 1733.9 cm^{-1} , 1654.8 cm^{-1} (carbonyl stretches). M.P. 235°C (dec.). Microanalysis: (3) + H_2O . *Calcd.* C, 70.0; H, 6.7. *Found:* C, 70.0; H, 6.7. FAB MS: m/z 738 ($(\text{M} + \text{H})^+$ 737).

5,17-Di-tert-butyl-26,28,-bis-(diethylcarbamoylmethoxy)-calix[4]-25,27-diquinone (4)

5,11,17,23-Tetra-tert-

butyl-25,27-bis(diethylcarbamoylmethoxy)-26,28-dihydroxycalix[4]arene (1.0 g, 1.18 mmol) was stirred in 0.88 M TTFA/TFA solution (8.1 mL, 7.1 mmol) for 2 h in the dark. The TFA was then removed *in vacuo* and the residue poured onto ice/water (50 mL). The product was then extracted with chloroform (100 mL) and then washed with 100 mL water. The organic layer was then reduced *in vacuo*. The residue was purified by column chromatography on silica gel eluting with chloroform/methanol 90 : 10. (v/v) The product was collected and reduced *in vacuo*. The solid was collected and dried *in vacuo*. The product was a yellow powder (0.12 g, 15%).

^1H -NMR (CDCl_3 , 300 MHz) 1.13 (s, 18H, $(\text{CH}_3)_3\text{C}$), 1.28 (m, 12H, NCH_2CH_3), 3.32 (d, $J = 13.3\text{Hz}$, 4H, ArCH_2Ar), 3.44 (m, 4H, NCH_2CH_3), 3.66 (d, $J = 13.3\text{Hz}$, 4H, ArCH_2Ar), 4.35 (s, 4H, OCH_2), 5.48 (CH_2Cl_2), 6.62 (s, 4H, $\text{C}=\text{CH}$), 6.96 (s, 4H, ArH).

^{13}C -NMR (CDCl_3 , 75.42 MHz) 12.61 (CH_3CH_2), 14.44 (CH_3CH_2), 31.34 ($(\text{CH}_3)_3\text{C}$), 33.18 (ArCH_2Qu), 34.04 ($(\text{CH}_3)_3\text{C}$), 40.29 (CH_3CH_2), 41.97 (CH_3CH_2), 61.35 (CH_2O), 73.57 (CH_2O), 127.21 ($\text{CH}=\text{C}$), 128.89, 132.53 (ArH), 146.62, 147.66, 167.17 ($\text{C}=\text{O}$), 185.47 ($\text{C}=\text{O}$), 188.59 ($\text{C}=\text{O}$). M.P. 195°C (dec.). Microanalysis: (4) + CH_2Cl_2 . *Calcd.* C, 67.19; H, 6.90; N, 3.20. *Found:* C, 67.33; H, 6.86, N, 3.18. FAB MS: $(\text{M} + \text{Na})^+$ @813 $(\text{M} + \text{Cs})^+$ @923. Sodium salts were used to clean the FAB spectrometer and CsI to calibrate it.

Diamide-benzo-15-crown-5-calix[4]arene (7)

A solution of 4-aminobenzo-15-crown-5 (1.20 g, 4.23 mmol) and triethylamine (0.6 g, 6.0 mmol) in dry dichloromethane (50 mL), was added to the *p*-tert-butylcalix[4]arene bis acid chloride (5) (1.54 g, 1.92 mmol). The resulting solution was stirred for 12 h, and then washed with 1 M HCl (50 mL) and then water (50 mL). The organic layer was dried (MgSO_4), filtered and the solvent removed under reduced pressure leaving a pale brown solid. Recrystallisation from dichloromethane/hexane gave the product as a white powder (1.54 g, 60%).

^1H -NMR (CDCl_3 , 300 MHz) 1.10 (s, 18H, $(\text{CH}_3)_3\text{C}$), 1.28 (s 18H, $(\text{CH}_3)_3\text{C}$), 3.52 (d, $J = 13.3\text{Hz}$, 4H, ArCH_2Ar), 3.74–3.99 (m, 32H, OCH_2), 4.21 (d, $J =$

13.3 Hz, 4H, ArCH₂Ar), 4.59 (s, 4H, ArOCH₂), 6.76 (d, $J = 8.6$ Hz, 2H, ArH), 6.84 (d, $J = 8.6, 1.8$ Hz, 2H, ArH), 6.97 (s, 4H, ArH), 7.06 (s, 4H, ArH), 7.30 (d, $J = 1.8$ Hz, 2H, ArH), 8.16 (s, 2H, OH), 10.15 (s, 2H, NH).

¹³C-NMR (CDCl₃, 75.42 MHz) 31.00, 31.62 ((CH₃)₃C); 32.37 (ArCH₂Ar); 33.98, 34.23 ((CH₃)₃C); 68.56, 69.69, 69.80, 70.60, 70.73, 71.14 (OCH₂CH₂O); 74.79 (CH₂O); 106.21, 111.27, 114.88, 125.80, 126.44 (ArH); 127.22, 132.00, 132.26, 143.61, 145.61, 148.44, 148.87, 149.23, 149.37 (Ar); 164.92 (C=O).

M.P. 155–159°C. Microanalysis: *Calcd.* C, 70.45; H, 7.62; N, 2.16. *Found:* C, 70.32; H, 7.62; N, 2.26. FAB MS (in the presence of K⁺): MK⁺ @1336.

2.4. UV/VIS SPECTRAL EXPERIMENTS FOR DETERMINING ASSOCIATION CONSTANTS

The titrations were conducted by progressively adding a cation solution (0.1 M in CH₃CN) using a 10 μL syringe, to the cuvette containing 3.0 mL of the compound solution (5 × 10⁻⁵ M in CH₂Cl₂/CH₃CN 4 : 21 (v/v) for (3) and 5 × 10⁻⁵ M in CH₃CN for (4) and (7)). The maximum addition for all the cations was less than 150 μL to minimise the change of the solution volume. The spectrum was recorded after each addition. The added equivalents of the cation were then plotted against the absorption intensity change at a certain wave length around the absorption peak of the spectrum (310–370 nm). This was repeated at three different wave lengths. A locally-written non-linear curve fitting computer program was used to fit the experimental titration curves using the equation for a 1 : 1 complex:

$$\alpha = (I - I_f^0)/(I_c^0 - I_f^0) + (I - I_f^0)/[C_f^0 K (I_c^0 - I)] \quad (1)$$

where α is the added equivalents of cations, I_f^0 , I and I_c^0 are absorption intensities of the free ligand, the ligand plus α equivalents of cations and the ligand plus large excess cation solutions. C_f^0 is the concentration of the free ligand and K is the association constant. The fitting procedure was repeated for each cation for all the three titration curves at different wave lengths and the averaged value of K is reported.

2.5. CRYSTALLOGRAPHY

Crystal data are given in Table I, together with refinement details. Data were collected with MoK_α radiation using the MAR research Image Plate System. The crystal was positioned at 70 mm from the image plate: 120 frames were measured at 2° intervals with a counting time of 5 min. Data analysis was carried out with the XDS program [13]. The structure was solved using direct methods with the SHELX86 program [14]. All non-hydrogen atoms were refined anisotropically and hydrogen atoms isotropically in calculated positions using the SHELXL program [15]. All calculations were carried out on a Silicon Graphics R4000 Workstation at the University of Reading. Positional parameters are listed in Table II, molecular dimensions in Table III.

TABLE I. Crystal data and structure refinement for (3).

| | |
|--|---|
| Empirical formula | C ₄₄ H ₄₈ O ₁₀ |
| Formula weight | 736.82 |
| Temperature | 293(2) K |
| Wave length | 0.71071 Å |
| Crystal system | orthorhombic |
| Space group | C22 ₂ 1 |
| Unit cell dimensions | $a = 14.158(10)$ Å, $b = 11.993(10)$ Å, $c = 22.029(10)$ Å |
| Volume | 3741(4) Å ³ |
| Z | 4 |
| Density (calculated) | 1.31 Mg/m ³ |
| Absorption coefficient | 0.09 mm ⁻¹ |
| $F(000)$ | 1568 |
| Crystal size | 0.3 × 0.3 × 0.2 mm |
| Theta range for data collection | 2.23–24.05 deg. |
| Index ranges | $0 \leq h \leq 16$, $-13 \leq k \leq 13$, $-23 \leq l \leq 23$ |
| Reflections collected | 4956 |
| Independent reflection | 2698 [$R(\text{int}) = 0.0441$] |
| Refinement method | Full-matrix least-squares on F^2 |
| Data/restraints/parameters | 2698/0/256 |
| Goodness-of-fit F^2 | 0.616 |
| Final R indices [$I > 2\sigma(I)$] | $R1 = 0.0693$, $wR2 = 0.2255$ |
| Largest diff. peak and hole | 0.283 and -0.223 e Å ³ |

3. Results and Discussion

3.1. SYNTHESIS AND CONFORMATIONAL STUDIES

Using the methodology of McKillop [16] which was applied to calixarenes by Gutsche and coworkers [8], the oxidation of *p-tert*-butylcalix[4]arene bis ethyl ester (1) [11] and *p-tert*-butylcalix[4]arene bis ethyl amide (2) [11] with thallium trifluoroacetate in trifluoroacetic acid for 2 h at room temperature produced the new diester- and diamide-calix[4]arenediquinones (3) and (4) as yellow powders in yields of 65% and 15% respectively (Scheme 1). The room temperature ¹H-NMR spectrum of both receptors exhibit the typical AB splitting patterns of the methylene protons consistent with a cone conformation for the calix. Low temperature ¹H-NMR spectra, however, in CD₂Cl₂, revealed the coexistence of cone and partial cone conformers. For example with (3) Figure 1 shows that on cooling the proton resonances broaden and it is noteworthy that the tertiary butyl resonances split into two resonances at low temperatures suggesting the presence of two species in solution. Casnati and coworkers [10] have recently investigated the conformational properties of alkyl calixarenediquinones and report a similar dynamic process.

TABLE II. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for (3). $U_{(eq)}$ is defined as one third of the trace of the orthogonalised U_{ij} tensor.

| | <i>x</i> | <i>y</i> | <i>z</i> | $U_{(eq)}$ |
|--------|----------|-----------|----------|------------|
| C(11) | 4325(4) | -528(4) | 4014(2) | 42(1) |
| C(12) | 3873(4) | -1147(4) | 4460(2) | 48(1) |
| C(13) | 2957(4) | -1488(4) | 4406(2) | 48(1) |
| C(14) | 2521(4) | -1265(4) | 3862(2) | 48(1) |
| C(15) | 2933(4) | -651(4) | 3406(2) | 45(1) |
| C(16) | 3810(3) | -239(4) | 3502(2) | 40(1) |
| C(17) | 2494(4) | -584(5) | 2791(2) | 49(1) |
| C(21) | 3088(3) | -1153(4) | 2328(2) | 42(1) |
| C(22) | 3323(4) | -2224(5) | 2379(3) | 49(1) |
| C(23) | 3942(4) | -2747(4) | 1958(3) | 52(1) |
| C(24) | 4394(4) | -2076(4) | 1503(3) | 51(1) |
| C(25) | 4167(3) | -1010(4) | 1421(2) | 41(1) |
| C(26) | 3450(4) | -520(4) | 1805(2) | 41(1) |
| C(27) | 5339(4) | -294(5) | 4036(2) | 51(1) |
| O(1) | 3133(3) | 386(4) | 1691(2) | 65(1) |
| O(2) | 4095(4) | -3741(3) | 1981(3) | 93(2) |
| O(30) | 4250(3) | 364(3) | 3061(2) | 47(1) |
| C(31) | 3887(4) | 1451(4) | 2970(3) | 52(1) |
| C(32) | 4473(4) | 2345(5) | 3228(3) | 56(1) |
| O(33) | 5210(4) | 2233(4) | 3443(3) | 96(2) |
| O(34) | 4086(3) | 3298(3) | 3142(3) | 82(2) |
| C(35) | 4577(7) | 4290(7) | 3312(6) | 102(3) |
| C(36) | 4321(11) | 4676(12) | 3871(7) | 177(7) |
| C(100) | 2480(5) | -2164(5) | 4893(3) | 60(2) |
| C(101) | 2860(9) | -1940(10) | 5501(4) | 132(5) |
| C(102) | 1451(8) | -1918(18) | 4911(7) | 219(10) |
| C(103) | 2530(13) | -3348(8) | 4744(6) | 182(8) |

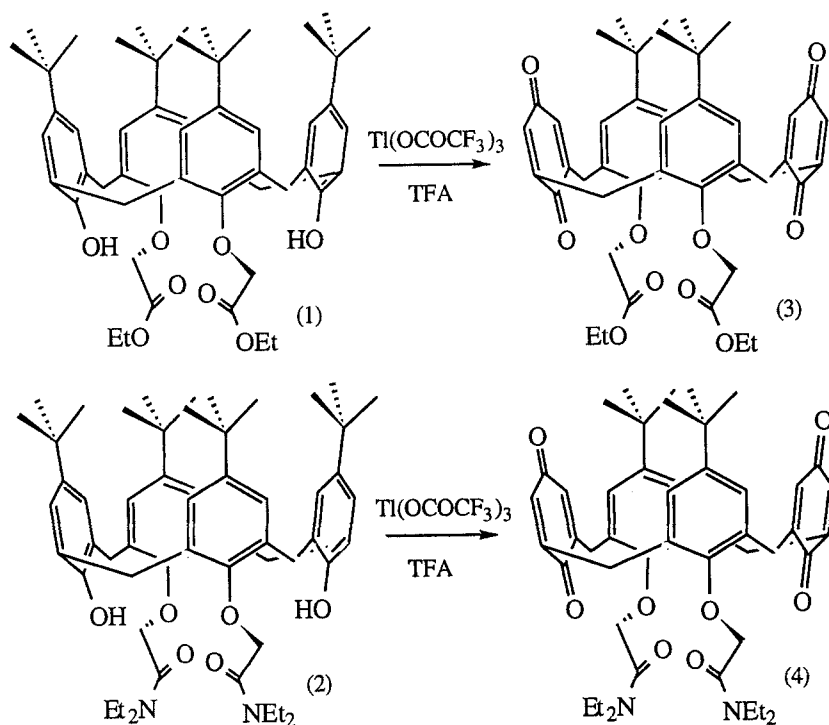
The mobility of the quinone moieties rotating through the calix cavity whilst the two aromatic rings remain fixed relative to one another is a possible explanation for the variable temperature $^1\text{H-NMR}$ results. At low temperatures this dynamic process is slowed on the NMR timescale and the quinone groups adopt fixed cone and partial cone conformations. Respective relative integrations of the methylene proton resonances suggest both (3) and (4) at low temperatures exist in CD_2Cl_2 solution at 50 : 50 mixtures of cone and partial cone conformers. The condensation of the 1,3-distally substituted chlorocarbonyl calix[4]arene (5) [11] with two moles of 4-aminobenzo-15-crown-5 (6) in the presence of triethylamine gave the new diamide-benzo-15-crown-5-calix[4]arene (7) as a white solid in 60% yield (Scheme 2). The room temperature $^1\text{H-NMR}$ spectrum suggests (7) adopts a rigid

TABLE III. Bond lengths [\AA] and angles [deg] for (3).

| | | | |
|--------------------|-----------|----------------------|-----------|
| C(11)—C(16) | 1.387(7) | C(13)—C(14)—C(15) | 123.4(5) |
| C(11)—C(12) | 1.387(8) | C(16)—C(15)—C(14) | 118.0(5) |
| C(11)—C(27) | 1.464(8) | C(16)—C(15)—C(17) | 120.3(5) |
| C(12)—C(13) | 1.365(8) | C(14)—C(15)—C(17) | 121.0(5) |
| C(13)—C(14) | 1.374(8) | C(15)—C(16)—O(30) | 120.1(4) |
| C(13)—C(100) | 1.503(8) | C(15)—C(16)—C(11) | 121.2(4) |
| C(14)—C(15) | 1.377(7) | O(30)—C(16)—C(11) | 118.2(4) |
| C(15)—C(16) | 1.353(7) | C(21)—C(17)—C(15) | 111.2(4) |
| C(15)—C(17) | 1.492(7) | C(22)—C(21)—C(17) | 121.8(5) |
| C(17)—C(21) | 1.487(7) | C(26)—C(21)—C(17) | 119.8(4) |
| C(21)—C(22) | 1.332(8) | C(21)—C(22)—C(23) | 121.7(5) |
| C(21)—C(26) | 1.472(7) | O(2)—C(23)—C(22) | 121.1(5) |
| C(22)—C(23) | 1.421(8) | O(2)—C(23)—C(24) | 120.0(5) |
| C(23)—O(2) | 1.213(7) | C(22)—C(23)—C(24) | 118.9(5) |
| C(23)—C(24) | 1.435(8) | C(25)—C(24)—C(23) | 121.7(5) |
| C(24)—C(25) | 1.332(7) | C(24)—C(25)—C(26) | 118.7(5) |
| C(25)—C(26) | 1.445(7) | C(24)—C(25)—C(27*) | 122.0(5) |
| C(26)—O(1) | 1.203(6) | C(26)—C(25)—C(27*) | 119.3(4) |
| C(27*)—C(25) | 1.496(7) | O(1)—C(26)—C(25) | 120.5(5) |
| O(30)—C(31) | 1.415(6) | O(1)—C(26)—C(21) | 120.0(5) |
| C(31)—C(32) | 1.469(9) | C(25)—C(26)—C(21) | 119.6(4) |
| C(32)—O(33) | 1.153(8) | C(11*)—C(27*)—C(25) | 109.1(4) |
| C(32)—O(34) | 1.281(7) | C(16)—O(30)—C(31) | 115.0(4) |
| O(34)—C(35) | 1.428(9) | C(16)—O(30)—C(31) | 115.0(4) |
| C(35)—C(36) | 1.36(2) | O(30)—C(31)—C(32) | 114.4(5) |
| C(100)—C(103) | 1.460(12) | O(33)—C(32)—O(34) | 123.4(6) |
| C(100)—C(101) | 1.468(10) | O(33)—C(32)—C(31) | 125.8(6) |
| C(100)—C(102) | 1.487(13) | O(34)—C(32)—C(31) | 110.7(5) |
| | | C(32)—O(34)—C(35) | 119.8(6) |
| C(16)—C(11)—C(12) | 117.9(5) | C(36)—C(35)—O(34) | 112.9(9) |
| C(16)—C(11)—C(27) | 119.6(4) | C(103)—C(100)—C(101) | 111.4(9) |
| C(12)—C(11)—C(27) | 122.1(5) | C(103)—C(100)—C(102) | 104.3(12) |
| C(13)—C(12)—C(11) | 122.5(5) | C(101)—C(100)—C(102) | 107.3(10) |
| C(12)—C(13)—C(14) | 116.3(5) | C(103)—C(100)—C(13) | 110.0(6) |
| C(12)—C(13)—C(100) | 121.8(5) | C(101)—C(100)—C(13) | 112.8(5) |
| C(14)—C(13)—C(100) | 121.6(5) | C(102)—C(100)—C(13) | 110.6(7) |

*Symmetry element $1 - x, y, 0.5 - z$.

cone conformation in solution, which in contrast to (3) and (4) does not broaden at lower temperatures.



Scheme 1. The synthesis of the calixarenequinones (3) and (4).

3.2. STRUCTURE DETERMINATION OF (3)

Crystals of (3) suitable for X-ray crystallographic determination were obtained by slow evaporation of a $CH_2Cl_2/MeOH$ solution of (3). The molecule has crystallographically imposed C_2 symmetry. The most striking feature of the structure is the difference in orientation of the rings and this is illustrated in Figures 2 and 3. The two phenyl rings are spread out considerably by comparison with the calix[4]arene structure in that they intersect at an angle of 114.2° (see Figure 2). The distance between the two oxygen atoms O(30) and O(30*) is 3.26 \AA . By contrast, the two quinone rings intersect at 31.1° , but unlike the calix[4]arene structures, the rings are oriented such that they are closer at the top of the cone than at the bottom (see Figure 3). The distance between the two oxygens at the top of the cone (O(2) and O(2*)) is 3.43 \AA and at the bottom of the cone is 6.38 \AA . This gives rise to a cramped cavity and it is perhaps not surprising that no solvent was located in the crystal.

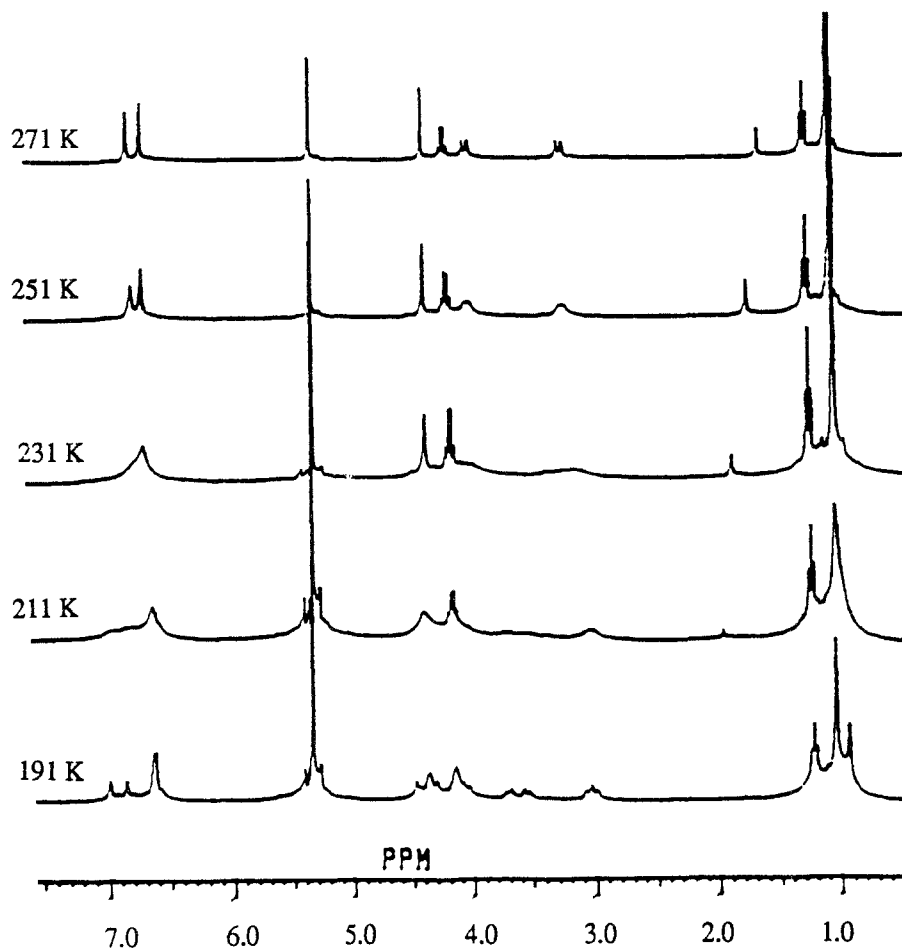


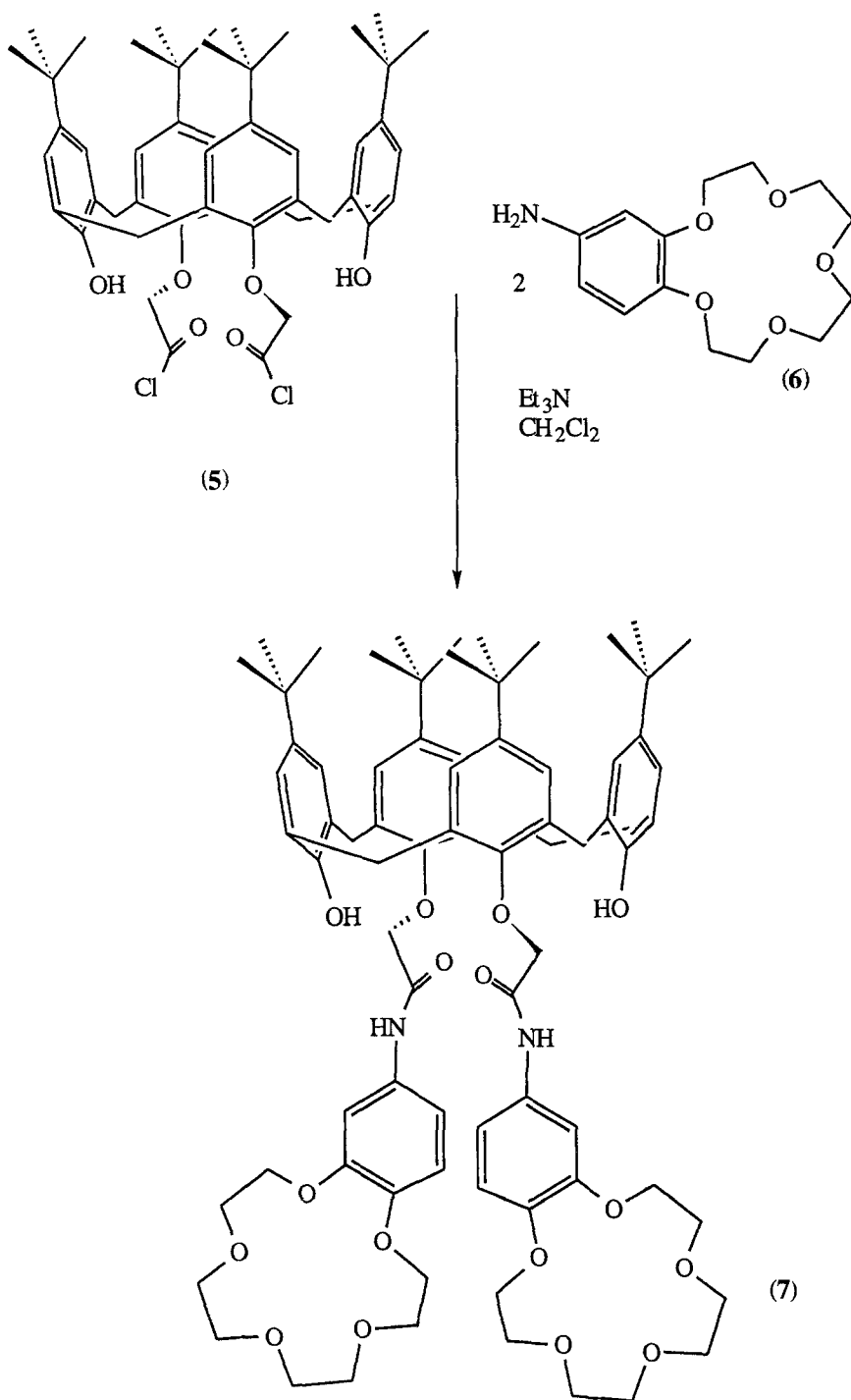
Fig. 1. The NMR spectrum of (3) from 271–191 K.

3.3. COORDINATION STUDIES

3.3.1. ^1H -NMR Titrations of (3) and (4) with Cationic Guest Species

Proton NMR solution complexation investigations of Group 1 and 2 metal cations, ammonium and butyl ammonium cations were carried out with (3) and (4), and for comparison purposes with the recently reported dimethylether calix[4]arenediquinone (8) (Figure 4).

In a typical titration experiment the stepwise addition of a concentrated solution of a cation salt in 40 : 60 (v/v) deuterated chloroform/acetonitrile to a dilute solution of (3) in the same deuterated solvent mixture of 100% deuterated acetonitrile for ligand (4) resulted in either significant downfield shifts of the receptor protons or the evolution of a new set of resonances corresponding to a solution complexed species. This most notably occurred with Ba^{2+} with (3), and Na^+ with (4). In all



Scheme 2. Synthesis of diamide-benzo-15-crown-5-calix[4]arene.

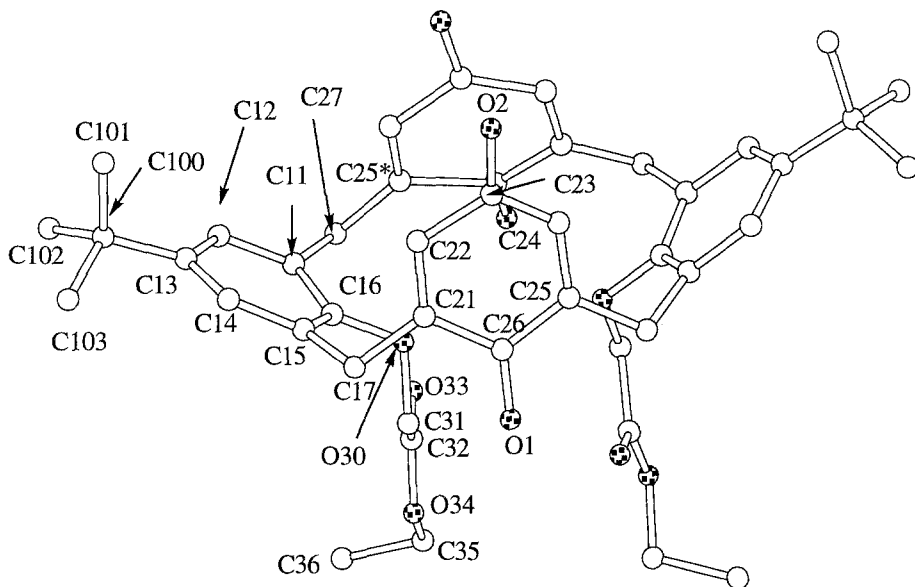


Fig. 2. The crystal structure of (3).

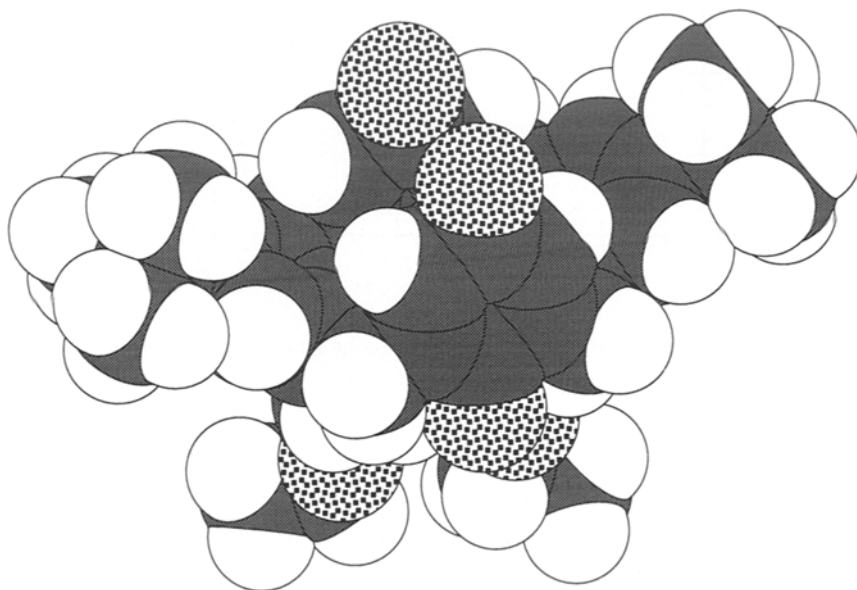


Fig. 3. A space filling representation of (3) illustrating the close proximity of the upper rim oxygens.

cases the resulting titration curves of $\Delta\delta$ ppm proton chemical shift perturbation of respective ligand versus equivalents of metal cation suggested 1 : 1 solution complex stoichiometries (Figure 5) in which the metal cationic guests are bound via favourable electrostatic interactions with the ester or amide carbonyl oxygen donor

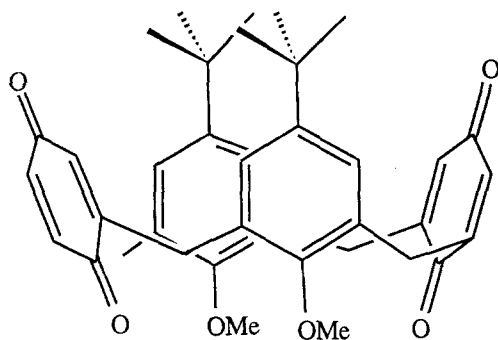


Fig. 4. The dimethylether calix[4]arenequinone (**8**).

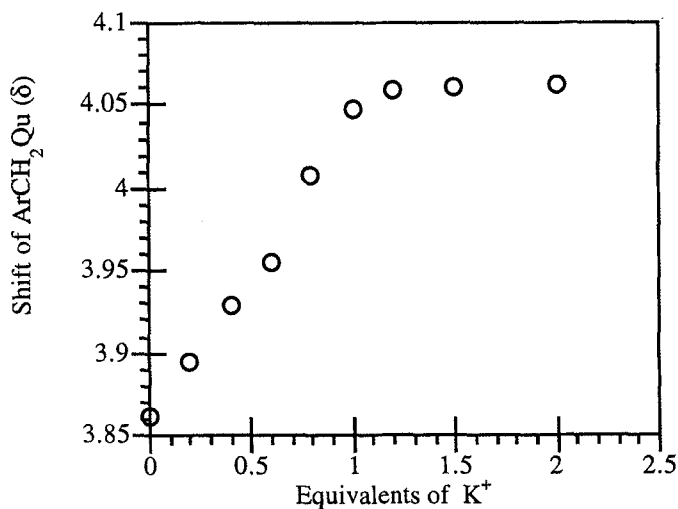


Fig. 5. Shift of one ArCH₂Qu proton (**3**) upon addition of potassium cations.

atoms and the quinone carbonyl moieties. This mode of metal cation coordination would have the effect of inhibiting the quinone calix-ring inversion process and consequently rigidifying the receptor into a cone conformation. In support of this hypothesis a low temperature ¹H-NMR spectrum (**3**) in the presence of Ba²⁺ exhibited exclusively one pair of doublets for the methylene protons.

Interestingly, the ammonium and alkyl ammonium cations also formed 1 : 1 stoichiometric complexes with (**3**) and (**4**) but did not bind to (**8**) highlighting the importance of additional favourable hydrogen bonding interactions with the respective ester or amide carbonyl moieties of these receptors.

Analogous ¹H-NMR titration experiments with (**7**) in deuterated acetonitrile gave the titration curves suggesting 1 : 1 stoichiometries with K⁺ (Figure 6), NH₄⁺, Ba²⁺, and a 2 : 1 metal-to-ligand stoichiometry with Na⁺.

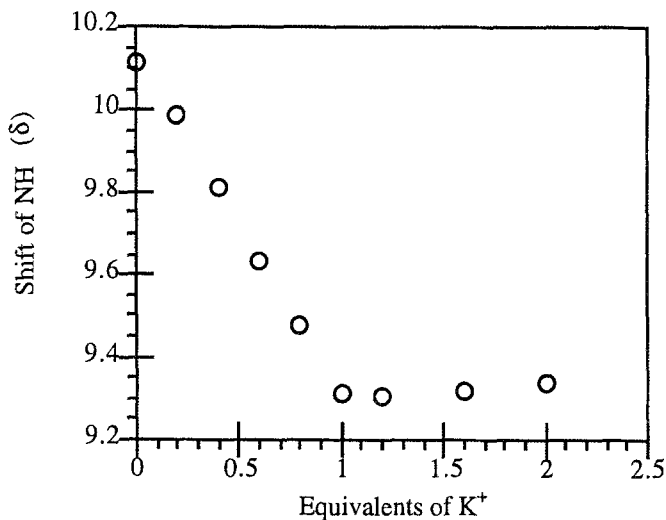


Fig. 6. Shift of the NH proton (7) upon addition of potassium cations.

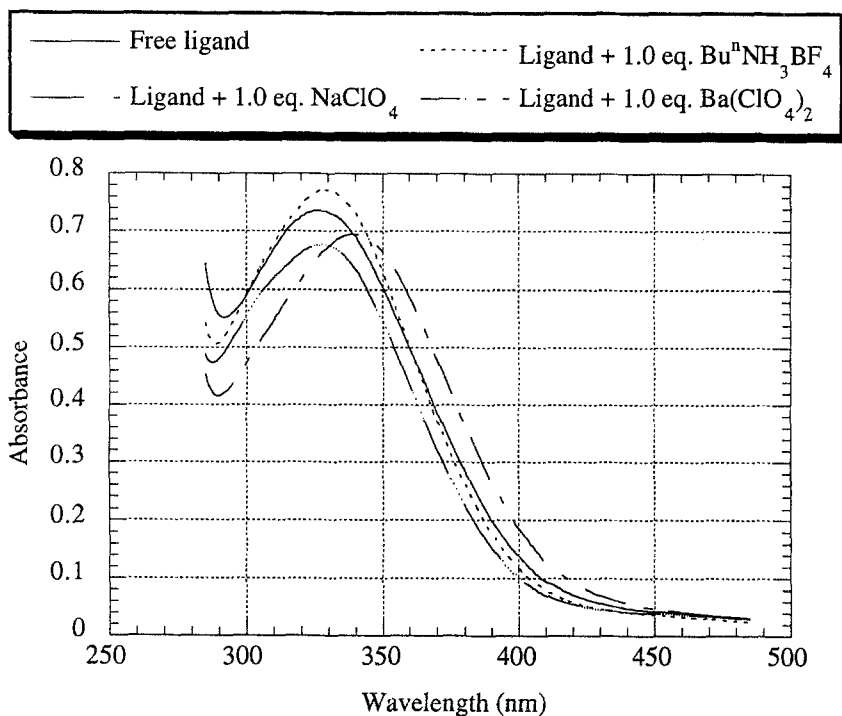


Fig. 7. The UV/vis spectrum of ligand (4) in acetonitrile (2.7×10^{-4} M) in the absence and presence of guest cations.

3.3.2. UV/Vis Spectroscopic Investigations – Association Constant Determinations

For the calix[4]arene-diquinone receptors the respective electronic absorption spectrum exhibits an absorbance ca. 330 nm corresponding to the n to π^* transition of

TABLE IV. Association-constants calculated for (3), (4) and (8) (maximum error $\pm 15\%$).

| Cation | (3) | (4) | (8) |
|--|-------------------|--------------------|-------------------|
| Na ⁺ | ^a | 1.58×10^5 | ^b |
| K ⁺ | 7.2×10^4 | 4.9×10^4 | 1.9×10^4 |
| Ba ²⁺ | 4.8×10^5 | 1.8×10^5 | 5.3×10^4 |
| NH ₄ ⁺ | 1.1×10^4 | 1.2×10^3 | ^b |
| Bu ⁿ NH ₃ ⁺ | 6.6×10^3 | 1.0×10^4 | ^b |

^a Association constant too large to be reliably calculated using curve fitting method.

^b No evidence of binding was seen.

the quinone groups. The addition of cationic guests to acetonitrile solutions of, for example (4) (Figure 7), resulted in significant red shifts and intensity perturbations of this absorption band. Association constant data for (3), (4) and (8) with various guest cations were determined using a non-linear curve fitting computer program (see Experimental) and the results are presented in Table IV.

For both (3) and (4) Na⁺ and Ba²⁺ cations form very stable complexes. It is noteworthy that the diamide calix[4]arene-diquinone (4) exhibits a larger association constant for BuⁿNH₃⁺ than for NH₄⁺ whereas with the diester derivative (3) the reverse trend is observed. Preliminary electronic absorption titration data of (7) with K⁺ and Ba²⁺ cations gave association constants of 5×10^4 and 3×10^3 respectively. Interestingly, this K⁺ over Ba²⁺ selectivity preference is similar to that exhibited by the dimethyl ether calix[4]diquinone ligand (8) but is the reverse shown by (3) and (4).

3.3.3. Electrochemical Studies

The electrochemical properties of (3), (4) and (8) were investigated using cyclic and square wave voltammetries. The redox behaviour of all these ligands were very similar. For example the cyclic and square wave voltammograms of (4) are shown in Figure 8. Potentials refer to a Ag/Ag⁺ (1.0 mM AgNO₃ in CH₃CN) reference electrode whose potential is 330 ± 10 mV versus SCE. Both of the cyclic and square wave voltammograms of the free receptor (4) exhibit reversible/quasi-reversible wave couples (1/1' and 2/2'), a broad irreversible wave (3) and prewaves (4 and 5). Except for the prewaves, the multiwave feature has also been observed by others [9, 10]. Detailed studies [9, 10] have revealed that waves 1 and 2 correspond to the consecutive one-electron transfer to each of the quinone moieties, leading to the formation of a diradical structure. The addition of one or more equivalents of NaClO₄ or KPF₆ to electrochemical solutions of (4) resulted in the disappearance of waves 1 and 2 and the evolution of reversible new wave couples at more anodic potentials. Anodic potential perturbations were generally observed with (3), (4), (8) and all cationic guests, and the results are summarised in Table V. Interestingly

TABLE V. A summary of voltammetric properties of (3), (4) and (8) in acetonitrile, supporting electrolyte: 0.10 M TBABF₄.

| | No. of redox couples | E_{pc} (V) of each redox couple |
|--|----------------------|--|
| Free (3) | 4 | -0.75 (s); -0.85 (r); -1.10 (r); -1.24 (s) |
| (3) + Na ⁺ | 2 | -0.70 (r); -0.80 (s) |
| (3) + K ⁺ | 3 | -0.75 (s); -0.85 (r); -0.93 (r) |
| (3) + Ba ²⁺ | 1 | -0.52 (ec, a) |
| (3) + NH ₄ ⁺ | 1 | -0.67 (ec) |
| (3) + Bu ⁿ NH ₃ ⁺ | 1 | -0.68 (ec) |
| Free (4) | 4 | -0.81 (r); -0.91 (r); -1.11 (r); -1.26 (q) |
| (4) + Na ⁺ | 2 | -0.81 (r); -0.89 (r) |
| (4) + K ⁺ | 2 | -0.83 (r); -0.92 (r) |
| (4) + Ba ²⁺ | 1 | -0.64 (ec, a) |
| (4) + NH ₄ ⁺ | 1 | -0.69 (ec) |
| (4) + Bu ⁿ NH ₃ ⁺ | 1 | -0.78 (ec) |
| Free (8) | 2 | -1.05 (r); -1.09 (r) |
| (8) + Na ⁺ | 2 | -0.90 (r); -0.99 (s) |
| (8) + K ⁺ | 2 | -1.02 (r); -1.09 (r) |
| (8) + Ba ²⁺ | 1 | -0.52 (ec, a) |
| (8) + NH ₄ ⁺ | 1 | -0.85 (ec) |
| (8) + Bu ⁿ NH ₃ ⁺ | 1 | -0.94 (ec) |

E_{pc} The potential of the reduction current peak; r: reversible; q: quasi-reversible; s: single reduction peak without corresponding reoxidation peak; ec: electron transfer followed by a chemical reaction; ec, a: electron transfer followed by a chemical reaction with insoluble product which adsorbs onto the electrode surface.

addition of one or more equivalents of NH₄PF₆ or BuⁿNH₃BF₄ to electrochemical solutions of (4) resulted in EC mechanistic behaviour (Figure 8) which was not affected by subsequent addition of equivalent amounts of Na⁺ or K⁺ cations. This finding is contrary to the respective association constant data calculated from UV/vis titration results in which the ammonium association constants are comparatively smaller in magnitude to those of the alkali metal cations. The relatively strong interactions of these ammonium cations with the radical anions formed by the reduction of the respective quinone moieties of (4) may be responsible for this electrochemical observation and EC mechanistic behaviour. In the presence of more than one equivalents of Ba(ClO₄)₂, both of the cyclic and square wave voltammograms of (4) showed typical adsorption characteristics.

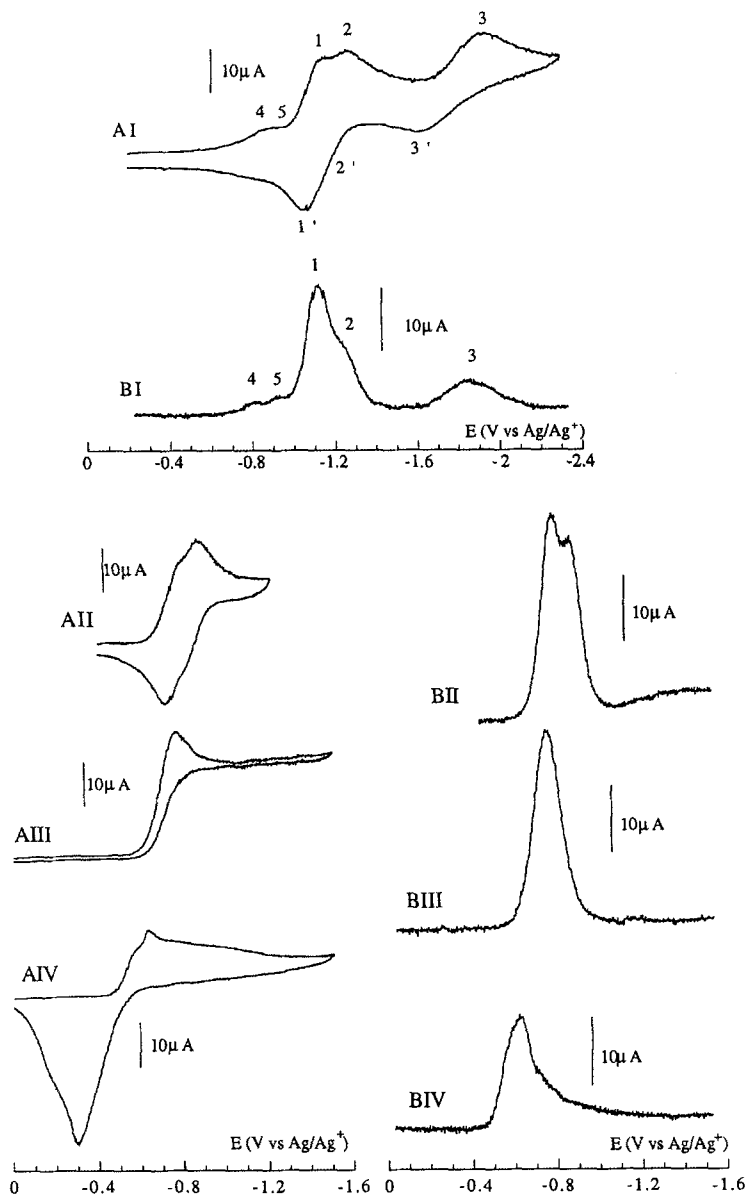


Fig. 8. Cyclic (A, scan rate: 100 mV s^{-1}) and square wave (B, frequency: 10 Hz for BI and 60 Hz for the others) voltammograms of ligand (4) ($5 \times 10^{-4} \text{ M}$) in acetonitrile in the absence (I) and presence of two equivalents of NaClO_4 (II), $\text{Bu}^n\text{NH}_3\text{BF}_4$ (III) and $\text{Ba}(\text{ClO}_4)_2$ (IV). The units of current (vertical) and potential (horizontal) are Ampère and Volt (vs. Ag/Ag^+), respectively.

4. Conclusions

New diester/diamide-calix[4]arenequinones and a diamide-benzo-15-crown-5-calix[4]arene receptor molecule have been prepared and shown to complex Group 1 and 2 metal, ammonium and alkylammonium cations with association constants up to 4.8×10^5 with Ba^{2+} and **(3)** in acetonitrile solution. The redox-active quinone containing receptors electrochemically recognise these cationic guest species, including for the first time, the amperometric detection of an alkyl ammonium cationic guest species by a redox-active ionophore.

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