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Electrochemistry of quaternary ammonium binaphthyl salts

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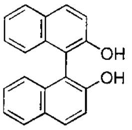
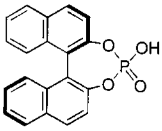
The redox behaviour of the binaphthyl unit in quaternary ammonium salts with an appended crown ether (3) is dramatically affected by the presence of metal cations and this effect can be used as an analytical tool to detect micromolar concentrations of alkali metal ions.

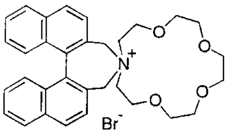
Axially chiral 2,2′-disubstituted 1,1′-binaphthyls, such as BINOL **1**,[1] have been utilised as a scaffold to construct a fascinating array of molecules, ranging from chiral ligands applied in asymmetric, metal-catalysed reactions[2,3] to complex supramolecular structures employed in molecular recognition studies.[4–6] The binaphthyl skeleton itself is normally viewed as an inert, robust block, whose activity is confined to occasional racemization; very little is known of its actual chemistry.



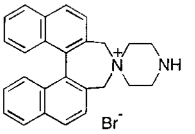
(±)-**1**



(*R*)-(–)-**2**



(±)-**3**



(±)-**4**

Shoute has recently studied the pulse radiolysis of BINOL hydrogen phosphate **2** in aqueous solutions (at pH 9.5, where **2** is dissociated).[7] Using time-resolved absorption spectroscopy, he has been able to show that the initially generated radical anion ($\mathbf{2}^- + e^- \longrightarrow {}^{-\bullet}\mathbf{2}^-$) either undergoes an acid-catalysed protonation (${}^{-\bullet}\mathbf{2}^- + H^+ \longrightarrow {}^{\bullet}H\mathbf{2}^-$) or transfers an electron to organic molecules present in the solution.[7] Since the protonation of radical anions is generally known to be slowed down by electron-withdrawing groups,[8] we became interested in the electrochemical generation of radical species from tetraalkylammonium binaphthyl salts, as a continuation of our efforts to develop new chiral ligands and electrochemical sensors.[9–11] Herein, we disclose preliminary results of the elucidation of the redox properties of novel quaternary aza-crown ether salt **3** and show how this molecule can be used in an electrochemical sensor for alkali metal cations in solution.

The quaternary ammonium aza-crown ether (±)-**3** was prepared from (±)-2,2′-bis(bromomethyl)-1,1′-binaphthyl[12] and the commercially available 1-aza-15-crown-5 (20 °C, overnight; 55%) in analogy to the published procedure.† Fig. 1 shows a cyclic voltammogram of a 2×10^{-3} mol dm^{-3} solution of **3** in MeCN containing 0.1 mol dm^{-3} $TBABF_4$ on a pyrolytic graphite (PG) electrode which gave a quasi-reversible response with ΔE_p = 129 mV. The electron transfer process was also found to be reversible on a Hg/Au amalgam electrode but was significantly less reversible on Pt, Au, Fe and Ag electrodes.

A quasi-reversible process on the PG electrode was also observed when the crown ether unit was replaced with a piperazine ring, as in (±)-**4**.[13] By contrast, reduction of (±)-**1**, carried out under the same conditions, showed an irreversible process, suggesting that the relative stability of **3** and **4** originates in the presence of the N^+ group. The addition of 20 μmol dm^{-3} of HCl (aq) to a solution of **3** in MeCN caused the current for the re-oxidation of the radical species to decrease dramatically.

The radical species generated from **3** (and from its congener **4**) must be stable in the order of minutes to allow quasi reversible responses to be observed with slow scan rate voltammograms (ν = 10 mV s^{-1}). To demonstrate the increased stability of the $ArCH_2N^+$ system, the visible spectrum of **3** was measured during a bulk electrolysis experiment. Fig. 2 shows the spectrum of **3** in the electrolyte solution described above as a function of time following the application of a constant current density of 50 μA cm^{-2} to a PG rod electrode. The growth of a peak at 410 nm is consistent with the formation of a binaphthyl radical species analogous to that observed by Shoute[7] for **2** (*vide supra*). This peak disappeared following the addition of 20 μmol dm^{-3} of HCl (aq), suggesting a chemical reaction which must clearly be an irreversible process that would account for the loss of the reverse peak in Fig. 1 following the acidification of the solution.

The mechanism of stabilisation of the binaphthyl system in **3** by the N^+ group is intriguing. Whereas in conjugated systems the effect of an electron-withdrawing group[8] can easily be understood, in **3** the electron-withdrawing N^+ is insulated from the aromatic ring by the benzylic CH_2 group, so that direct conjugation is precluded. However, molecular modelling shows that the twisted-chair conformation of the dihydroazepine ring in **3** renders the CH_2–N^+ σ-bond almost perpendicular to the aromatic system (Fig. 3). Hence, this conformation is ideally predestined to allow a donation from the aromatic π-system to the low-lying σ^* orbital of the C–N^+ bond, so that a stabilisation (similar to that observed with the 'normally' conjugated systems) can be anticipated.

The effect of the quaternary ammonium group of **3** can, *a priori*, be modified by complexation of the crown ether moiety with a metal cation. Note that the positive charge on nitrogen in **3** can be assumed to be partly stabilised either by interaction with a lone pair of one of the oxygen atoms or, more likely, *via*

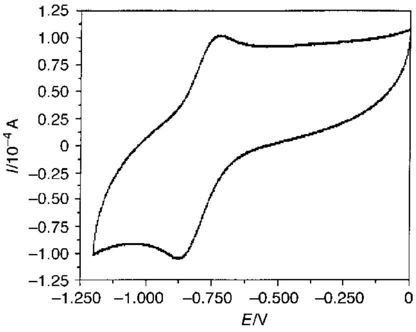


Fig. 1 Cyclic voltammogram of a 2×10^{-3} mol dm^{-3} solution of (±)-**3** in MeCN containing $TBABF_4$ (0.1 mol dm^{-3}) on a pyrolytic graphite (PG) electrode (sweep rate = 0.1 V s^{-1}). Potentials *vs.* SCE.

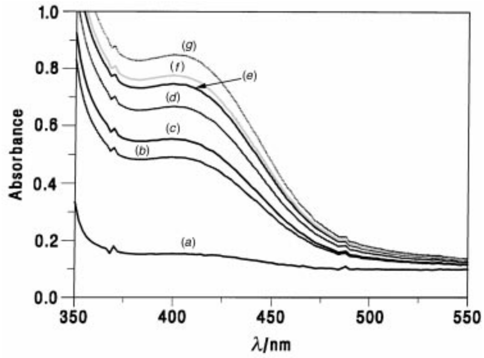


Fig. 2 Visible spectrum of (±)-**3** in the electrolyte solution described in Fig. 1 as a function of time following the application of a constant current density of 50 μA cm^{-2} to a PG rod electrode: (*a*) 0, (*b*) 1, (*c*) 2, (*d*) 3, (*e*) 4, (*f*) 5 and (*g*) 6 min.

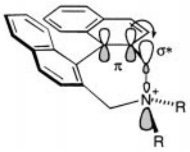
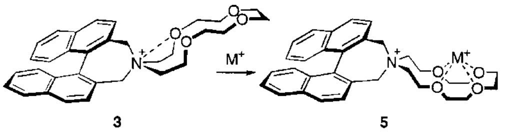


Fig. 3 Stereoelectronic effects in **3**.



Scheme 1

the Cieplak effect.[14] Complexation of **3** with the metal cation (**3** → **5**; Scheme 1) should engage the latter, Lewis basic oxygen, leaving N^+ with a higher effective charge. To address this issue, the electrochemical experiments were repeated in the presence of $LiClO_4$ and $NaClO_4$, respectively. Fig. 4 shows that the peak current for the cathodic process decreases linearly as the concentration of Li^+ increases. Since the redox potentials of both processes are unaffected by the addition of Li^+, it can be concluded that the irreversible transformation of **3** is precluded by Li^+ binding. The decrease in current must result from the effective decrease in the concentration of unbound **3**. These results appear to be in agreement with the original hypothesis of increasing stabilisation of the binaphthyl system by enhancement of the neighbouring charge.

Fig. 4 also shows the effect of Na^+ on the cathodic current for the reduction of **3**. It can be seen that the current decreases more rapidly upon addition of Na^+ to the solution. This effect presumably results from the greater binding constant for Na^+ over Li^+ with the 1-aza-15-crown-5 unit.[15] However, because the reduction current has fallen to effectively zero with the addition of 0.5 equiv. of Na^+, it is likely that the Na^+ ion complexes with two crown ether molecules. Complementary results were obtained with 1-aza-12-crown-4, a lower homologue of **3** which exhibited higher affinity to Li^+.

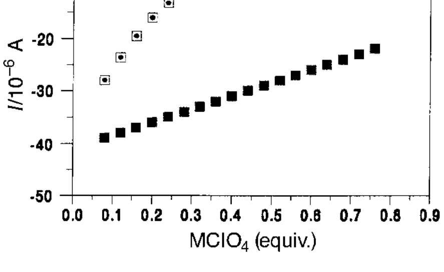


Fig. 4 Peak current for the reduction of (±)-**3** (5×10^{-3} mol dm^{-3}) in MeCN following the addition of $NaClO_4$ and $LiClO_4$ to the solution: (■) M = Li and ⊡ M = Na.

The observed response to the presence of Li^+ or Na^+ suggests that these systems can be potentially utilised as sensors for detecting alkali metal cations and, perhaps, of other cationic species. While there are numerous electrochemical, alkali metal sensors based on crown ethers,[16–18] most of them are potentiometric, relying on a change in energy of the electroactive moiety which tends to limit their sensitivity. As Fig. 4 clearly shows, a solution of **3** can detect the concentrations of Na^+ below 10 μmol dm^{-3}. Presumably, further tailoring the aza-crown ether cavity could generate molecules specific for other cations.

In conclusion, we have demonstrated for the first time that the radical species, generated electrochemically from a quaternary ammonium binaphthyl salt such as **3**, is relatively stable in non-acidic media. Since binding a cation to the appended crown ether moiety dramatically affects the redox behaviour of the binaphthyl unit, this novel class of binaphthyl crown ethers may be developed into very sensitive electrochemical sensors specific to alkali metal cations at micromolar concentrations which are beyond reach of the crown ether-based devices currently available.

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Notes and references

† *Synthesis* of (±)-**3**. A solution of (±)-2,2′-di(bromomethyl)-1,1′-binaphthyl[12] (500 mg, 1.14 mmol) and 1-aza-15-crown-5 (523 mg, 2.38 mmol) in benzene (5 ml) was left at ambient temperature overnight. The precipitate was filtered off and washed with benzene and the crude product was recrystallized from boiling distilled water (44 ml). The crystalline product was collected by suction and dried in a desiccator to afford pure (±)-**3** (359 mg, 55%): mp 268–271 °C (decomp.); ν_{max}(KBr)/cm^{-1} 2995, 2981, 2956, 2887, 2854, 1130, 1123, 1112, 1092; δ_H(200 MHz, DMSO-d_6) 3.52–3.72 (m, CH_2O, 16 H), 3.78–4.19 (m, CH_2N^+, 4 H), 3.92 (d, *J* 13.0, 2 H, ArCH_2), 4.85 (d, *J* 13.0, 2 H, ArCH_2), 7.27–8.35 (m, 12 H, arom); *m*/*z* (FAB MS) (3 : 1 thioglycerol–glycerol matrix) 498 (M − Br)$^+$, 470, 322, 308, 281, 279, 266, 265, 252 (Calc. for $C_{32}H_{36}BrNO_4$: C, 66.43; H, 6.27; N, 2.49. Found: C, 66.22; H, 6.27; N, 2.29%).

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