Cation Effects on the Cyclic Voltammograms of Azotoluene and the Potassium Cation Selectivity of the Electrochemically Reduced Azo-cryptand 7,16-Azobis(1,3-phenylenemethylene)-1,4,10,13-tetraoxa-7,16-diazaoctadecane

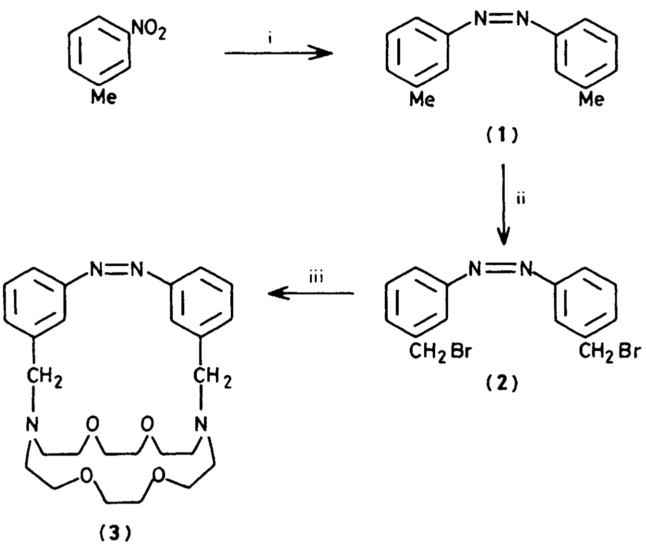
Deborah A. Gustowski,[a] Vincent J. Gatto,[a] Angel Kaifer,[b] Luis Echegoyen,*[c] Robert E. Godt,[d] and George W. Gokel*[a]

[a] *Department of Chemistry, University of Maryland, College Park, MD 20742, U.S.A.*
[b] *Department of Chemistry, University of Puerto Rico, Rio Piedras, Puerto Rico 00931*
[c] *Department of Chemistry, University of Miami, Coral Gables, FL 33124, U.S.A.*
[d] *Department of Physiology, Medical College of Georgia, Augusta, GA 30901, U.S.A.*

Azobenzenes are shown for the first time to exhibit substantial Li^+ and Na^+ cation effects on their electrochemical behaviour, and although K^+ does not interact with Ar–N=N–Ar, or its reduced form, a strong interaction is observed when K^+ is bound as a cryptate complex.

Azocryptands and crown ethers having an integral azo linkage have been of considerable recent interest as photochemically switchable cation binders. The efforts of Shinkai[1] and Ueno[2] and coworkers have been especially notable in this context.[3] Unfortunately, the azocryptands have proved to be generally poor cation binders and the switching (*cis–trans* isomerization) rate has generally proved low. Moreover, cation binding by the azocryptands has proved far more feeble than expected.[4] In light of our recent observation that electrochemical reduction leads to anion radicals having considerably enhanced binding strengths,[5] we undertook the cyclic voltammetric study of 3,3′-azotoluene (**1**) and its derivative, the title compound (**3**) which is reported here.

3,3′-Azotoluene (**1**), was obtained as an orange solid (50%,



Scheme 1. *Reagents:* i $LiAlH_4$; ii NBS–CCl_4; iii 4,13-diaza-18-crown-6, Na_2CO_3, MeCN.

Table 1. Cyclic voltammetry of azoarenes.

Compound[a]	Cation[b]	Equiv.[c]	E_p(c)	E_p(c)′	E_p(a)	E_p(a)′
(**1**)	None	—	−1.38	—	−1.23	—
(**1**)	Li^+	0.5	−1.38	−1.22	−1.24	—
(**1**)	Li^+	1.0	−1.38	−1.25	−1.25	—
(**1**)	Li^+	2.0	—	−1.26	—	—
(**1**)	Na^+	0.5	−1.39	—	−1.26	—
(**1**)	Na^+	1.0	−1.40	—	−1.26	—
(**1**)	Na^+	2.0	−1.39	—	No oxidation	
(**1**)	K^+	0—2	−1.38	—	−1.24	—
(**3**)	None	—	−1.45	—	−1.32	—
(**3**)	Li^+	0.33	−1.44	−1.23	−1.32	—
(**3**)	Li^+	0.5	−1.46	−1.27	−1.32	—
(**3**)	Li^+	1.0	−1.48	−1.30	No oxidation	
(**3**)	Li^+	2.0	—	−1.30	No oxidation	
(**3**)	Na^+	0.5	−1.46	—[d]	−1.32	—
(**3**)	Na^+	1.0	−1.42	—[d]	−1.29[e]	—
(**3**)	Na^+	2.0	−1.39	—[d]	−1.22[e]	—
(**3**)	K^+	0.33	−1.45	−1.26	−1.32	none
(**3**)	K^+	0.5	−1.46	−1.28	−1.32	none
(**3**)	K^+	1.0	−1.46	−1.29	−1.32	−1.19
(**3**)	K^+	2.0	—	−1.31	—	−1.17

[a] Solutions contain 2.8—3.0 mM of ligand and 0.1M Bu_4NClO_4 in dry MeCN. [b] Cations added as the perchlorate. [c] In equivalents of ligand. E_p(c) or E_p(c)′ reduction or cathodic potential; E_p(a) or E_p(a)′ oxidation or anodic potential, all in V. [d] Shoulder on adjacent peak. [e] These peaks were broad, making precise assignment difficult.

m.p. 49—50 °C) by $LiAlH_4$-mediated reductive dimerization of 3-nitrotoluene.[6] The toluene methyl groups were brominated (*N*-bromosuccinimide–CCl_4) to give (39%) 3,3′-bisbromomethylazobenzene, (**2**). Reaction of (**2**) with 4,13-diaza-18-crown-6 (1 mol. equiv.) and Na_2CO_3 in MeCN gave the title compound (**3**), in 31% yield as an orange solid, m.p. 131—132 °C.† The sequence is illustrated in Scheme 1.

Cyclic voltammograms (c.v.s) were obtained as previously reported.[5] Azobenzenes are known to undergo reversible redox behaviour in which the radical anion's excess of electron density is localized in the N=N bond system.[7] Our previous efforts with C-[5a] and N-pivot[5b] lariat ethers have shown that, upon electrochemical reduction, enhanced binding is in the order $Li^+ > Na^+ > K^+$. This contrasts with the binding behaviour usually observed for neutral crown ether complexes in which the stability constants decrease in the order $K^+ > Na^+ > Li^+$.[8] Indeed, the product of stability constant times enhancement is similar in magnitude for each cation.[5,9] This indicates that for lariat ethers, electrochemical reduction leads to enhanced cation binding, but very poor cation selectivity. We therefore expected Li^+ and perhaps Na^+ to affect the cyclic voltammograms of (**1**) and (**3**) much more than K^+. Indeed, the electrochemical behaviour of (**3**) in the presence of 0—2 equiv. of either Li^+ or Na^+ closely paralleled that observed for (**1**). The results are summarized in Table 1.

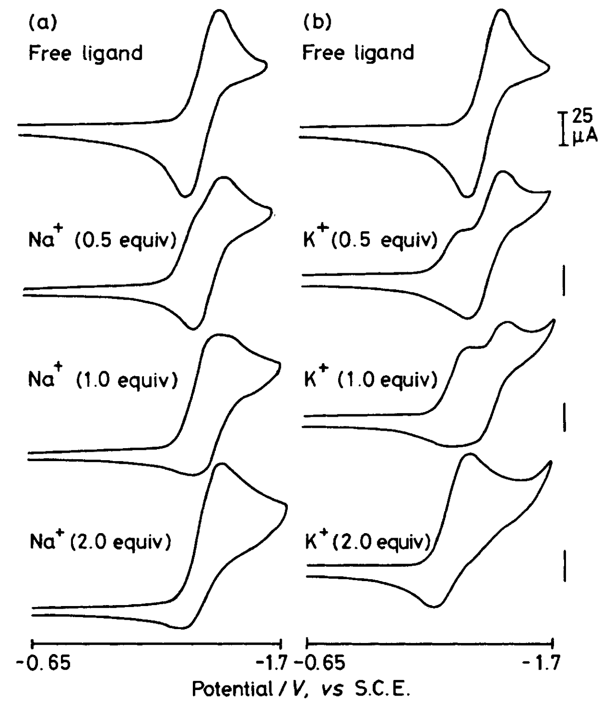


Figure 1. Cyclic voltammograms for (**3**) with (a) sodium or (b) potassium cation added. (S.C.E. = standard calomel electrode.)

As expected, the electrochemistry of (**1**) was largely indifferent to the presence of K^+. Remarkably different behaviour for (**3**) is observed during incremental addition of K^+. When 0.33 equiv. of K^+ is added, a new reduction peak is observed at −1.26 V. When 1 equiv. of K^+ is added a small, second oxidation peak also appears at more positive potential. The new reduction peak intensifies when 0.5 equiv. of K^+ is added. The reduction potentials at −1.29 V and −1.46 V are of nearly equal intensity when 1 equiv. of K^+ has been added. Calculated by the method previously reported,[5] the binding enhancement for reduced (**3**) with K^+ is a factor of 230. When 2 equiv. of K^+ have been added, only the new redox couple (−1.31, −1.17 V) is observed. The excess of K^+ is probably required for kinetic reasons.

An examination of Corey–Pauling–Koltun molecular models suggests that the hole size of cryptand (**3**) is nearly identical to the cation size of K^+. The cations Li^+ and Na^+ can associate with the N=N bond from above or can enter the cryptand with relative ease. The c.v.s of (**1**) and (**3**) are therefore similar in the presence or absence of these cations. When K^+ is present, it is held inside the macrobicyclic structure and interacts strongly with the azo linkage. This is

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† Satisfactory elemental analyses were obtained. ^{1}H n.m.r. ($CDCl_3$): δ 2.73 (t, 8H), 3.27—4.19 (m, 20H), 7.13—7.73 (m, 6H), and 8.65 (s, 2H).

the first example of K^+ (over Na^+ or Li^+) selectivity and binding strength enhancement upon electrochemical reduction of a neutral macrocyclic or macrobicyclic species. This demonstrates for the first time that K^+ selectivity can be attained in an electrochemically reduced system when K^+ is held in a three-dimensional and structurally rigid cage.

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