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Electrochemical Formation of 1,3,5-Trinaphthylbenzene Tri- and Tetraanions

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Synopsis. Each of the cyclic voltammograms of tri(1-naphthyl)benzene and tri(2-naphthyl)benzene in 1,2-dimethoxyethane at −50 °C exhibits four reversible one-electron reduction steps; this may be evidence for the successive formation of the mono-, di-, tri-, and tetraanions of these hydrocarbons. The degeneracy of their π^*-orbitals can account for the formation of the tri- and tetraanions.

We reported recently a well-defined cyclic voltammogram for the reduction of decacyclene in 1,2-dimethoxyethane (DME).[1] It exhibited four reversible one-electron steps, showing a successive formation of the mono-, di-, tri-, and tetraanions of considerable stability. The formation of the tetraanion was ascribed to the lowest π^*-orbitals of decacyclene degenerating two-fold due to the molecular symmetry of C_{3h}. The only hydrocarbon tetraanions ever reported except decacyclene^{4-} have been bicyclooctatetraene^{4-} [2] and benzo[1,2: 4,5]dicyclooctane^{4-}.[3] This note deals with the voltammograms of trianphthylbenzenes, which provide further examples of hydrocarbon tetraanions.

1,3,5-Tri(1-naphthyl)benzene (I) and 1,3,5-tri(2-naphthyl)benzene (II) were prepared by the trimerization of acetylnaphthalene[4] and identified on the basis of the melting point and IR spectrum.

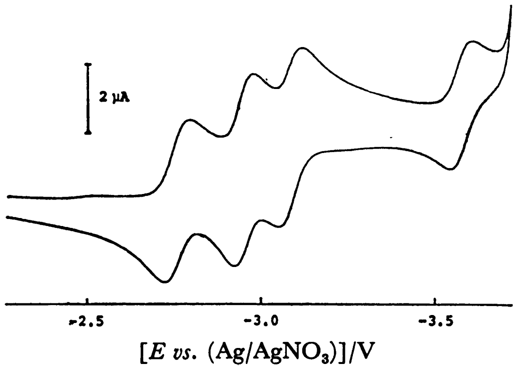

Fig. 1. Cyclic voltammogram of 0.5 mmol dm^{-3} 1,3,5-tri(β-naphthyl)benzene in 0.2 mol dm^{-1} TBAP–DME at −50 °C. Scan rate 0.1 V s^{-1}.

Figure 1 shows a cyclic voltammogram for 0.5 mmol dm^{-3} of II in 0.2 mol dm^{-3} tetrabutylammonium perchlorate (TBAP)–DME obtained with a scan rate of 0.1 V s^{-1} at −50 °C. It exhibits four reduction steps. They were all reversible one-electron transfer steps, according to the reversibility criteria of the peak separation and the peak current ratio. The ultimate current rise overlapped the reversal peak of the fourth step at −40 °C and 0.1 V s^{-1}; this step was not observed at all at room temperature and 0.1 V s^{-1}, while the first three steps remained reversible. Similar voltammograms were obtained for I. Table 1 lists the reversible half-wave potentials and the peak separations for these compounds, together with the first reduction half-wave potential for naphthalene obtained under the same experimental conditions. The residual resistance of the solution between the reference electrode and the working electrode due to incomplete compensation of the ohmic resistance may account for the peak separations greater than the theoretical separation, 43 mV at −50 °C.

A SCF MO calculation of the π-orbital energies of these substances was made by assuming that the angle between the molecular planes of naphthalene and benzene was 26° for I and 20° for II.[5] Thus the lowest π^*-orbital is two-fold degenerate and the next higher orbital differs from it by only 0.2 eV in II and 0.1 eV in I; a similar situation exists in tris(2,2′-bipyridine) complexes of transition metals[6] of D_{3d} molecular symmetry. If these orbitals are three-fold degenerate, the appearance of the voltammograms for the trinaphthylbenzenes would be very similar to that for tris(bipyridine) complexes. Comparison may better be made with the voltammogram of tris(4,7-diphenyl-1,10-phenanthroline)iron(II),[7] which exhibits two sets of three neighbouring reduction steps; these results lead to the supposition that the penta- and hexaanions of the trinaphthylbenzenes may be formed at potentials between −3.7 and −4 V *vs.* Ag/AgNO$_3$, though such highly negative potentials could not be realized.

The half-wave potentials of the first steps of tri-

Table 1. Cyclic voltammetric data for the reduction of 1,3,5-trinaphthylbenzenes and naphthalene in 0.2 mol dm^{-3} TBAP–DME at −50 °C
Scan rate 0.1 V s^{-1}.

Substance		Reduction step			
		1st	2nd	3rd	4th
1,3,5-Tri(1-naphthyl)benzene	A[a]	−2.81	−3.02	−3.15	−3.64
	B[b]	65	65	65	70
1,3,5-Tri(2-naphthyl)benzene	A	−2.76	−2.95	−3.08	−3.58
	B	60	65	70	70
Naphthalene	A	−3.09			

a) A: Reversible half-wave [potential *vs.* (Ag/AgNO$_3$)]/V. b) B: Peak separation/mV(±5 mV).

naphthylbenzenes are more positive by about 0.3 V than the half-wave potential of naphthalene, which means that the lowest π^*-orbital of each trinaphthylbenzene is more stabilized than that of naphthalene.

References

1) T. Saji and S. Aoyagui, *J. Electroanal. Chem.*, **102**, 139 (1979).

2) L. A. Paquette, G. D. Ewing, and S. G. Traynor, *J. Am. Chem. Soc.*, **98**, 279 (1976).

3) L. A. Paquette, G. D. Ewing, S. G. Traynor, and J. M. Gardlik, *J. Am. Chem. Soc.*, **99**, 6115 (1977).

4) D. B. Clapp and A. A. Morton, *J. Am. Chem. Soc.*, **58**, 2172 (1936).

5) R. J. W. Le Fevre, A. Sundaram, and K. M. S. Sundaram, *J. Chem. Soc.*, **1963**, 3180.

6) T. Saji and S. Aoyagui, *J. Electroanal. Chem.*, **108**, 223 (1980).

7) T. Saji, T. Fukai, and S. Aoyagui, *J. Electroanal. Chem.*, **66**, 81 (1975).