

ELECTROCHEMICAL FORMATION OF 1,3,5-TRI(p-BIPHENYL)BENZENE PENTAANION

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The cyclic voltammogram of 1,3,5-tri(p-biphenyl)benzene in 0.2 M ($M = \text{mol dm}^{-3}$) TBAP-DMeE at -50°C exhibits five reversible one-electron steps. This may be evidence for the electrochemical formation of mono-, di-, tri-, tetra- and pentaanions of this hydrocarbon. The formation of the pentaanion can be ascribed to the lower three π^* -orbitals which are actually three-fold degenerate.

Cyclic voltammograms of 1,3,5-tri(1-naphthyl)benzene and the 2-isomer in 1,2-dimethoxyethane (DMeE) were reported in our recent paper.¹⁾ Each of them exhibited four one-electron steps, showing the successive formation of the mono-, di-, tri- and tetraanions of the parent compound. The similarity in appearance of the voltammograms for trinaphthylbenzenes and tris(4,7-diphenyl-1,10-phenanthroline)iron(II)²⁾ led us to the supposition that the penta- and hexaanions of trinaphthylbenzenes would have been observed if sufficiently negative potentials had been covered. This communication deals with the formation of a hydrocarbon pentaanion which has never been reported.

1,3,5-Tri(p-biphenyl)benzene (I) was prepared by the trimerization of p-acetylbiphenyl³⁾ and identified on the basis of the melting point and the IR spectrum. The test solutions contained either 0.1 or 0.5 mM of I and 0.2 M of tetrabutylammonium perchlorate (TBAP) in DMeE. Cyclic voltammograms were obtained with a potentiostat and a three-electrode cell whose working electrode and the reference electrode were respectively a platinum wire and silver one.⁴⁾ The half-wave potential of the redox system perylene/perylene¹⁻ was used as the internal reference potential. The potential of the reference system was measured in advance against a reference electrode Ag/AgNO₃(sat.). A pair of cyclic voltammograms were recorded with a test solution before and after the addition of an appropriate amount of perylene and then compared with each other.

Figure 1 shows a cyclic voltammogram for a solution containing 0.5 mM of I obtained at -50°C with a scan rate of 0.2 V s^{-1} . It exhibits five reduction steps. Table 1 lists the separation

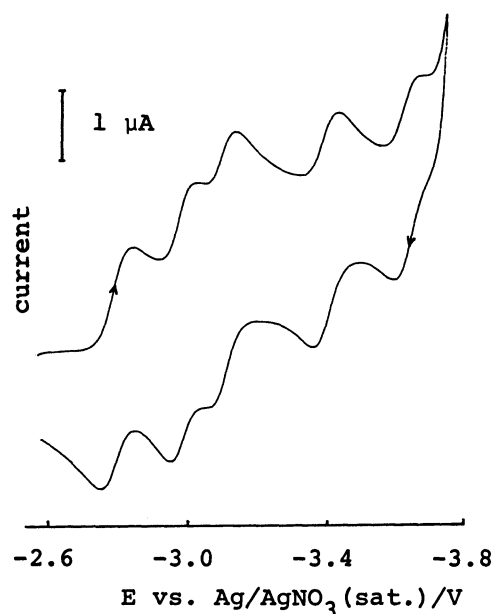


Fig.1 Cyclic voltammogram of 0.5 mM 1,3,5-tri(p-biphenyl)benzene in 0.2 M TBAP-DMeE obtained at -50°C with a scan rate 0.2 V s^{-1} .

(ΔE_p) and the midpoint potential ($E_{1/2}$) between the cathodic peak potential and the anodic one for each step obtained with a 0.1 mM solution of I. The midpoint potential can be identified with the polarographic half-wave potential. When recorded under the same experimental conditions, the peak separation of the first step for perylene was (55 ± 5) mV and the ratio of the anodic peak current to the cathodic one was 1.0. The uncompensated ohmic drop between the reference and the working electrodes may account for the peak separations which were greater than the theoretical value for the nernstian one-electron process, 43 mV. Although the proximity of the current peaks in Fig. 1 makes it difficult to evaluate the peak current ratios, it is evident that the reduction product of each step is considerably stable. Consequently, it will be safe to conclude that the half-wave potentials in Table 1 are the reversible half-wave potentials for one-electron processes. At -30°C and 0.2 V s^{-1} the ultimate current rise overlapped the fifth step.

The formation of the the pentaanion may be ascribable to the proximity of the lower three π^* -orbitals. An SCF-MO calculation of the π -orbital energies of I was made with various values for the angle θ between the benzene molecular planes. Figure 2 shows the energy levels of the lower five π^* -orbitals vs. θ . The energy of the second lowest orbital differs by only 0.3 eV from that of the lowermost two-fold degenerate ones, when θ is taken as 23° by considering the value for biphenyl.⁵⁾ Consequently, these orbitals can be regarded to be actually three-fold degenerate, in agreement with the above prediction. Very likely the possible sixth step is located beyond the negative break of the voltammogram.

References

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Table 1. Cyclic voltammetric data for the reduction of 0.1 mM 1,3,5-tri(p-biphenyl) benzene in 0.2 M TBAP-DMeE obtained at -50°C with a scan rate 0.2 V s^{-1} .

	Reduction step				
	1st	2nd	3rd	4th	5th
$E_{1/2}$	-2.80	-2.99	-3.11	-3.41	-3.62
ΔE_p	55	50	55	55	55

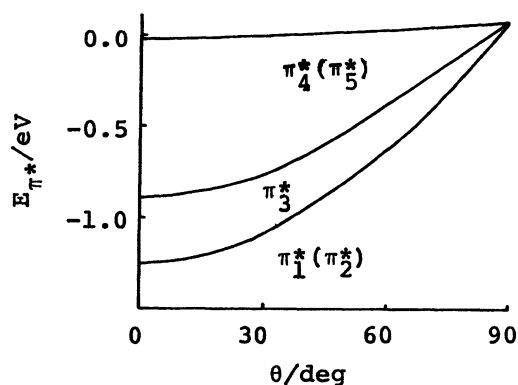


Fig. 2 Energy levels of the lower five π^* -orbitals of 1,3,5-tri(p-biphenyl) benzene (E_{π^*}) calculated with varying the twisting angle between benzene molecular planes (θ).

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