FREE RADICALS IN REDOX REACTIONS OF 4,4'-DI-(2,6-DIPHENYLTHIAPYRYLO)MONOMETHINECYANINE FLUOROBORATE

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ESR spectroscopic and electrochemical studies of the one-electron reduction and oxidation of 4,4'-di-(2,6-diphenylthiapyrylo)monomethinecyanine have been carried out. Relatively stable cyanine free radicals have been detected and characterized.

In the whole area of the chemistry of cyanine compounds [1] there have been virtually no reports of radicals or ion-radicals formed during redox reactions of cyanines.

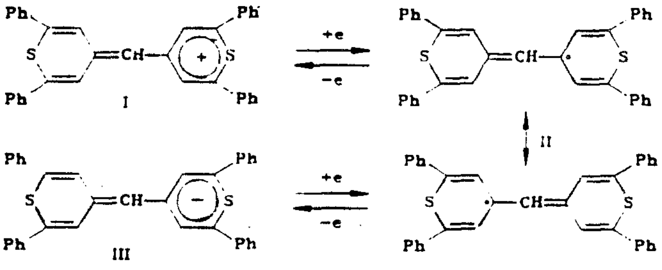
We have now used ESR and cyclic voltammetry (CVA) to examine the reduction and oxidation of 4,4'-di-(2,6-diphenylthiapyrylo)monomethinecyanine (I) in acetonitrile.

When the cyanine (I) is chemically reduced at a zinc mirror, the ESR spectra show a signal with a clearly apparent doublet structure (a_H^{CH} = 0.55 mT, Fig. 1). The high value of the splitting constant at the methine proton indicates delocalization of the unpaired electron over both of the thiapyryl moieties, while the smallest splitting constant (a_H = 0.03 mT) probably relates to the meta-protons of the phenyl substituents. In view of the multiplicity of the HSC for the meta-, ortho-, and para-protons of the benzene rings, and of the thiapyrylene ring protons, it was not possible to find the values of the other splitting cases in the present case. The appearance of the ESR spectrum showed little change as the multiplicity of the constant varied, as a result of the high ratio of the intensities of the central components to those of the lateral components.

The ESR signal for the radical (II) remained stable for several months in an evacuated system.

Electrochemical reduction of the cyanine (I) under CVA conditions at a stationary platinum electrode (Fig. 2a) takes place in two reversible one-electron stages. The first one-electron wave ($E_{1/2}$ = –0.45 V) probably arises from the formation of the free radical (II), and the second wave ($E_{1/2}$ = –1.22 V) to that of the diamagnetic anion (III).

According to the ESR and CVA findings, reduction of the cation (I) proceeds as follows:



The relatively facile reduction of the cyanine (I) was unexpected. Under DVA conditions, on oxidation of the cation (I) one partially reversible one-electron wave with $E_{1/2}$ = 1.14 V is observed (Fig. 2b).

On oxidation of the (I) cation with lead dioxide, the ESR spectra show a signal which is fundamentally different from that for the radical (II), being substantially less both in terms of the extension of the spectrum (0.4 mT as compared with 1.7) and the value of the minimum splitting constant (0.016 mT as compared with 0.03), no doublet constant being seen (Fig. 3).

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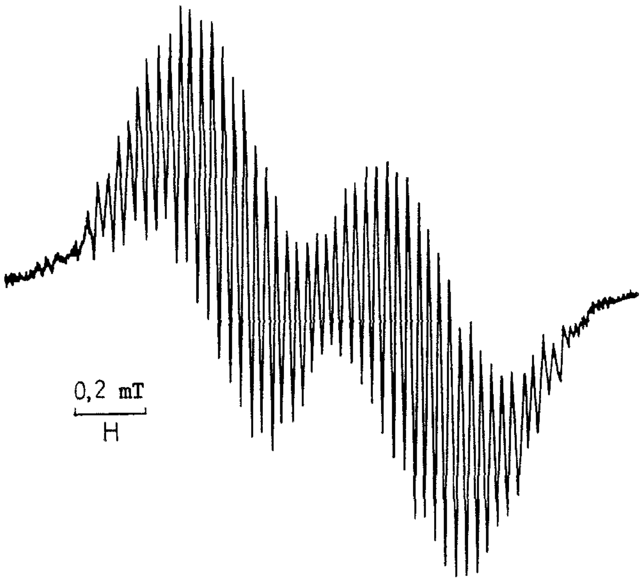


Fig. 1. ESR spectrum of the radical (II) at 25°C in acetonitrile.

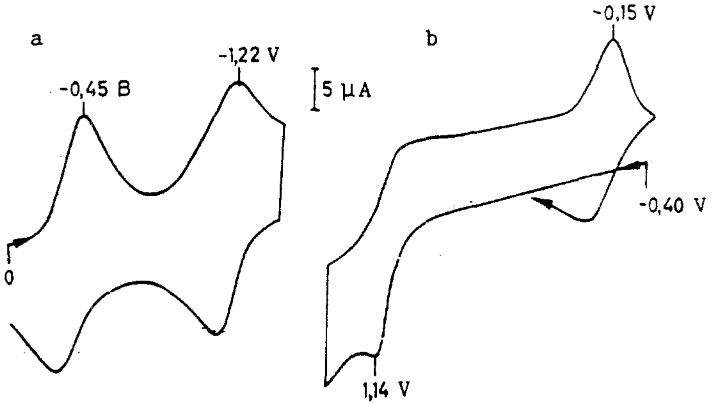


Fig. 2. Cyclic voltammograms for the monomethinecyanine fluoroborate (I) ($c = 5 \cdot 10^{-3}$ moles/liter): a) reduction; b) oxidation.

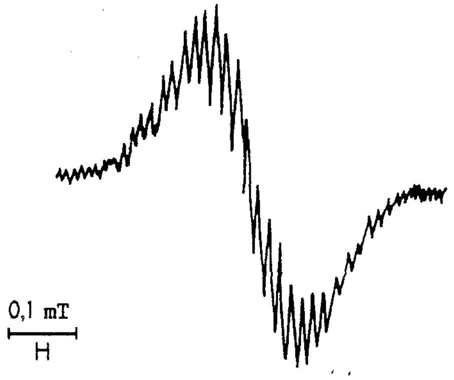
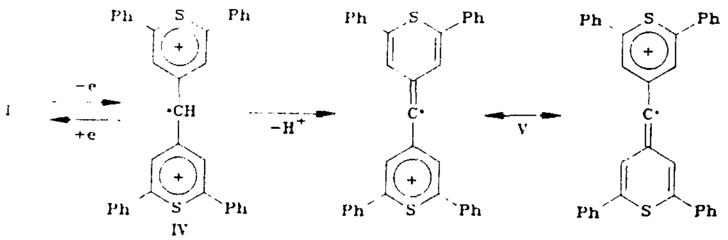


Fig. 3. ESR spectrum of the cation-radical (V) at 25°C in acetonitrile.

The ESR signal seen on oxidation of the cyanine (I) is apparently attributable to the cation-radical (V), formed by fragmentation of the dication-radical (IV) which is unstable under the experimental conditions.



This is confirmed by the presence of a proton wave on the cathode branch of the cyclic voltammogram (–0.14 V), identified by addition of perchloric acid. The partially reversible one-electron wave at $E_{1/2} = 1.14$ V thus corresponds to the formation of the dication-radical (IV).

The stability of the ESR signal for the cation-radical (V) in vacuo was comparable with that of the radical (II).

EXPERIMENTAL

ESR spectra were recorded on a Radiopan SE/X-2543 radiospectrometer in vacuo (10^{-3} mm).

Cyclic voltammograms were obtained on a P-5827M potentiostat with an additional source of triangular pulses [3]. The operating frequency of the suppressive pulses was 0.1 Hz. Voltammograms were obtained in the three-electron mode. The working electrode was a platinum needle ($l = 3$ mm, $d = 0.5$ mm), auxiliary electrode a platinum spiral, and the reference electrode a saturated calomel electrode with a water-impermeable diaphragm. The base electrolyte was tetrabutylammonium perchlorate. Acetonitrile was kept for 1 week over 4-Å molecular sieves, then redistilled over calcium hydride and phosphoric anhydride. The number of electrons involved in reduction was determined by comparison with the authentic one-electron reduction of triphenylpyrylium perchlorate and, in oxidation, with ferrocene.

The starting cyanine (I) was obtained by a method reported previously [2].

LITERATURE CITED

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