E.S.R. Observation of the Radical Trianion and Radical Anion of Bis(1,2,5-thiadiazolo)-tetracyanoquinodimethane

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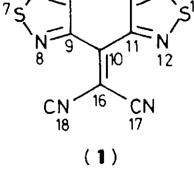
The radical trianion of bis(1,2,5-thiadiazolo)-tetracyanoquinodimethane (**1**) is formed, as well as its radical anion, by electrolysis in acetonitrile at room temperature and has been characterized by e.s.r. spectroscopy.

The radical trianions of π-conjugation systems afford valuable information on the molecular orbitals, particularly next lowest unoccupied molecular orbitals (NLUMOs), of these systems through their e.s.r. hyperfine splitting (h.f.s.) patterns. They are also of considerable interest as intermediates, so-called novel species, leading to the development of new routes in organic synthesis.[1] Tetracyanoarenoquinodimethane is one of a few groups of which trianions have already been observed.[1,2] Although the third half-wave reduction potential of tetracyanoanthraquinodimethane (TCNAQ) [$E_{1/2}{}^{(3)}$, −2.06 V *vs.* standard calomel electrode (SCE)][3] is less negative than those of several other tetracyanoarenoquinodimethanes, of which trianions have been detected,[2] the formation of the trianion of TCNAQ has not so far been confirmed. This has been attributed to thermodynamical instability of this trianion due to the non-planarity arising from steric interaction between the cyanomethylene groups and *peri*-hydrogens.[4] Recently, an unique electron acceptor forming highly conductive complexes with some electron donors, bis(1,2,5-thiadiazolo)-TCNQ (BTDA-TCNQ) (**1**), was synthesized by Yamashita *et al.*,[5] in order to improve the non-planarity of TCNAQ. This molecule was expected to form its trianion because it has considerably less negative [$E_{1/2}{}^{(3)}$, −1.5 V *vs.* SCE][5] than that of TCNAQ. We report here the formation of the trianion of (**1**), as well as its radical anion, by electrolysis.

The electrolytic reduction of (**1**) was performed in MeCN with $Bu^n{}_4NClO_4$ as supporting electrolyte at room temperature in a Pyrex cell with two platinum wire electrodes. A blue species giving the e.s.r. spectrum shown in Figure 1a was generated initially at an applied voltage of 0.35 V (appearance voltage V_a), at 2.1 V the solution turned colourless, spectrum 1a disappearing simultaneously, and at 2.65 V a light orange species occurred, a new spectrum (Figure 1b) being observed. On reducing the voltage to 0.35 V or less again, spectrum 1a gradually superseded 1b even if no separate oxidative operation was performed. This may be attributed to the oxidation of the latter species by the solvent, a small residue of the neutral precursor, or some impurities. These changes are completely reversible and allow us to consider the redox sequence in equation (1).

$$(\mathbf{1}) \underset{-e^-}{\overset{e^-}{\rightleftharpoons}} (\mathbf{1})^{\cdot -} \underset{-e^-}{\overset{e^-}{\rightleftharpoons}} (\mathbf{1})^{2-} \underset{-e^-}{\overset{e^-}{\rightleftharpoons}} (\mathbf{1})^{3\cdot -} \qquad (1)$$



(**1**)

Both spectra 1a and b can be straightforwardly analysed to give the hyperfine coupling constants for two sets of four equivalent nitrogens listed in Table 1. In spectrum 1a, one set of ^{13}C satellite lines was observed. It is known that in the e.s.r. spectra of tetracyanoarenoquinodimethane trianions the hyperfine coupling constants of the cyano nitrogens are considerably smaller than those of the corresponding radical

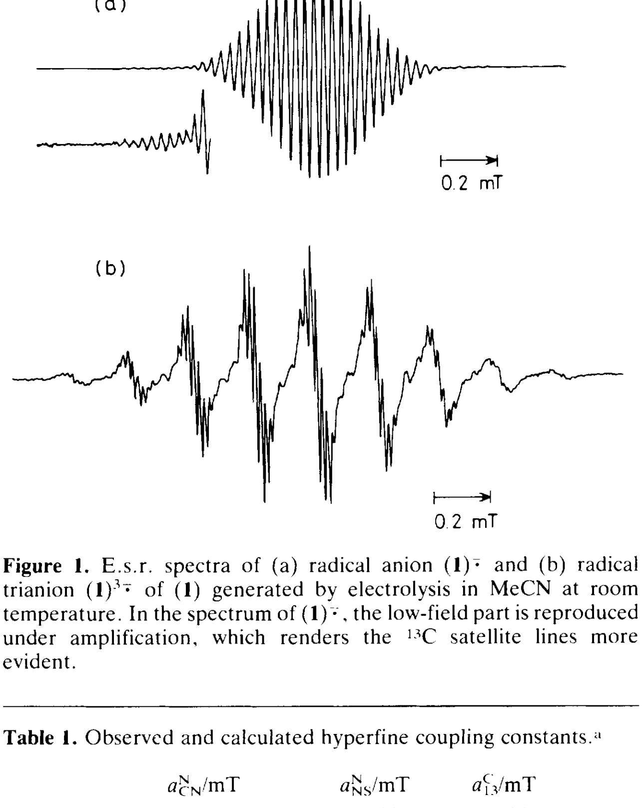


Figure 1. E.s.r. spectra of (a) radical anion $(\mathbf{1})^{\cdot -}$ and (b) radical trianion $(\mathbf{1})^{3\cdot -}$ of (**1**) generated by electrolysis in MeCN at room temperature. In the spectrum of $(\mathbf{1})^{\cdot -}$, the low-field part is reproduced under amplification, which renders the ^{13}C satellite lines more evident.

Table 1. Observed and calculated hyperfine coupling constants.[a]

	a^N_{CN}/mT	a^N_{NS}/mT	a^C_{13}/mT
$(\mathbf{1})^{\cdot -}$	0.100	0.033	1.100
	0.082[b]	0.064[b]	0.550[d]
	0.105[c]	0.026[c]	
$(\mathbf{1})^{3\cdot -}$	0.017	0.219	
	0.030[b]	0.227[b]	
	0.026[c]	0.265[c]	

[a] The observed values are in the first lines. MO parameters used for $C(CN)_2$ groups are those proposed by Fraenkel *et al.*: $h_N = 1.0$, $k_{CN} = 2.0$, and $k_{13,14} = 0.9$;[6] and for thiadiazole rings those proposed for a p-orbital model by Kwan *et al.*: $h_S = 1.0$, $h_N = 0.8$, $k_{CN} = 1.08$, and $k_{SN} = 0.78$.[7] [b] Calculated using spin densities obtained from HMO's. [c] Calculated using spin densities obtained by McLachlan's method. [d] Calculated from McLachlan's spin densities combined with the Karplus–Fraenkel relationship.[8]

anions, while those of the ring protons are larger, and that the h.f.s. patterns of these trianions coincide with the characteristics of their NLUMOs.[2] These differences in h.f.s. patterns are also observed between spectra 1a and b, providing evidence that spectra 1a and b arise from $(\mathbf{1})^{\cdot-}$ and $(\mathbf{1})^{3\cdot-}$, respectively. We can therefore rule out the possibility that spectrum 1b arises from another paramagnetic species produced by proton abstraction from the solvent. In Table 1, the observed nitrogen hyperfine coupling constants of $(\mathbf{1})^{\cdot-}$ and $(\mathbf{1})^{3\cdot-}$ are compared with those calculated from the spin densities obtained by the simple HMO and McLachlan's method. For the calculation of $a^{\mathrm{N}}_{\mathrm{CN}}$, the nitrogen σ–π parameters proposed by Fraenkel *et al.* were employed; *i.e.*, 2.31 and −0.68 mT ($P^{\mathrm{N}} + Q^{\mathrm{N}}_{\mathrm{NC}}$) and $Q^{\mathrm{N}}_{\mathrm{CN}}$, respectively, in $a^{\mathrm{N}} = (P^{\mathrm{N}} + Q^{\mathrm{N}}_{\mathrm{NC}})\rho^{\pi}_{\mathrm{N}} + Q^{\mathrm{N}}_{\mathrm{CN}}\rho^{\pi}_{\mathrm{C}}$,[6,8] while for $a^{\mathrm{N}}_{\mathrm{SN}}$ those proposed for a p-orbital model by Kwan *et al.* were tentatively used; *i.e.*, 2.2, 0.09, and −0.17 mT[9] as ($S^{\mathrm{N}}_{\mathrm{N}} + Q^{\mathrm{N}}_{\mathrm{NS}} + Q^{\mathrm{N}}_{\mathrm{NC}}$), $Q^{\mathrm{N}}_{\mathrm{SN}}$, and $Q^{\mathrm{N}}_{\mathrm{CN}}$, respectively, in $a^{\mathrm{N}} = (S^{\mathrm{N}}_{\mathrm{N}} + Q^{\mathrm{N}}_{\mathrm{NS}} + Q^{\mathrm{N}}_{\mathrm{NC}})\rho^{\pi}_{\mathrm{N}} + Q^{\mathrm{N}}_{\mathrm{SN}}\rho^{\pi}_{\mathrm{S}} + Q^{\mathrm{N}}_{\mathrm{NC}}\rho^{\pi}_{\mathrm{C}}$.[7] Although the observed hyperfine coupling constants do not correlate satisfactorily with the calculated ones, their correspondence may be useful enough to support the identification of spectra 1a and b with $(\mathbf{1})^{\cdot-}$ and $(\mathbf{1})^{3\cdot-}$, respectively. The ^{13}C hyperfine coupling constant could be assigned to the exocyclic carbons bearing cyano substituents (positions 13 and 16), although the value calculated from McLachlan's spin densities combined with the Karplus–Fraenkel relationship[8] is much smaller than the observed one.

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References

1 F. Gerson and W. Huber, *Acc. Chem. Res.*, 1987, **20**, 85, and references therein.

2 F. Gerson, R. Heckendorn, D. O. Cowan, A. M. Kini, and McRae Maxfield, *J. Am. Chem. Soc.*, 1983, **105**, 7017.

3 A. M. Kini, D. O. Cowan, F. Gerson, and R. Möckel, *J. Am. Chem. Soc.*, 1985, **107**, 556.

4 A. Aumüller and S. Hünig, *Liebigs Ann. Chem.*, 1984, 618; S. Yamaguchi, H. Tatemitsu, Y. Sakata, and S. Misumi, *Chem. Lett.*, 1983, 1229; B. S. Ong and B. Keoshkerian, *J. Org. Chem.*, 1984, **49**, 5002; Y. Nishizawa, T. Suzuki, Y. Yamashita, T. Miyashi, and T. Mukai, *Nippon Kagaku Kaishi*, 1985, 904.

5 Y. Yamashita, T. Suzuki, T. Mukai, and G. Saito, *J. Chem. Soc., Chem. Commun.*, 1985, 1044.

6 P. H. Rieger and G. K. Fraenkel, *J. Chem. Phys.*, 1962, **37**, 2795.

7 C. L. Kwan, M. Carmack, and J. K. Kochi, *J. Phys. Chem.*, 1976, **80**, 1786.

8 M. Karplus and G. K. Fraenkel, *J. Chem. Phys.*, 1961, **35**, 1312.

9 C. L. Talcott and R. J. Myers, *Mol. Phys.*, 1967, **12**, 549.