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Formation and Spin Density Distribution of the Radical Anion and Radical Trianion of Bis[diphenylpyradino]tetracyanoquinodimethane Studied by ESR

Masatoshi HIRAYAMA,* Akihiko SEKI, Yoshiro YAMASHITA,†
Takanori SUZUKI,† and Tsutomu MIYASHI†
Department of Chemistry, Faculty of Science,
Ibaraki University, 2-1-1 Bunkyo, Mito 310
†Department of Chemistry, Faculty of Science,
Tohoku University, Aramaki, Sendai 980

The radical trianion of title compound as well as its radical anion was formed by electrolytic reduction of its neutral precursor in acetonitrile at room temperature and characterized by their ESR and calculated spin density distributions.

The radical trianions of π-conjugated systems have recently been of great interest in viewpoint that the theoretical prediction of a next lowest unoccupied π-MO may be checked by their ESR hfs patterns.1) It has been considered that the requirements for the formation of stable trianions are (a) a considerably high third half-wave potential (E_3) in a suitable solvent, (b) possession of several strong electron-withdrawing groups, and (c) thermodynamical stability of a resulting radical trianion. The ESR observation of some tetracyanoarenoquinodimethane trianions by Gerson et al.1h) has prompted us to find the stable radical trianions of several TCNQ's fused with thiadiazole rings.2) Bis[diphenylpyradino]tetracyanoquinodimethane (BDPP-TCNQ) (**1**) synthesized recently by Yamashita et al.3) reveals a much less negative E_3 (-1.43 V vs. SCE in acetonitrile) and further is considered to have a planar structure except for the four phenyl rings twisted considerably. Thus, these characteristics have allowed us to expect the formation of stable trianion of **1**. We report here on the ESR and spin density distribution of the radical trianion of **1** as well as its radical anion.

The electrolysis of a 10^{-3} mol dm^{-3} acetonitrile solution of **1** was performed with nBu_4NClO_4 as a supporting electrolyte at room temperature using a high-vacuum Pyrex cell with two platinum-wire electrodes. At 0.15 V applied between two electrodes an yellow green species was formed giving an ESR spectrum (I) (Fig. 1b), at 1.2 V this species disappeared and further at 3.4 V the solution turned reddish-brown, a new ESR spectrum (II) (Fig. 1a) being observed. On decreasing the voltage to 0.15 V or less, II gradually changed into I, even if no separate oxidative operation was performed. This may be due to the oxidation of the reddish-brown species by a small amount of neutral precursor or some impurities. It was confirmed that these redox reactions are completely reversible. Since I has a lot of lines in the

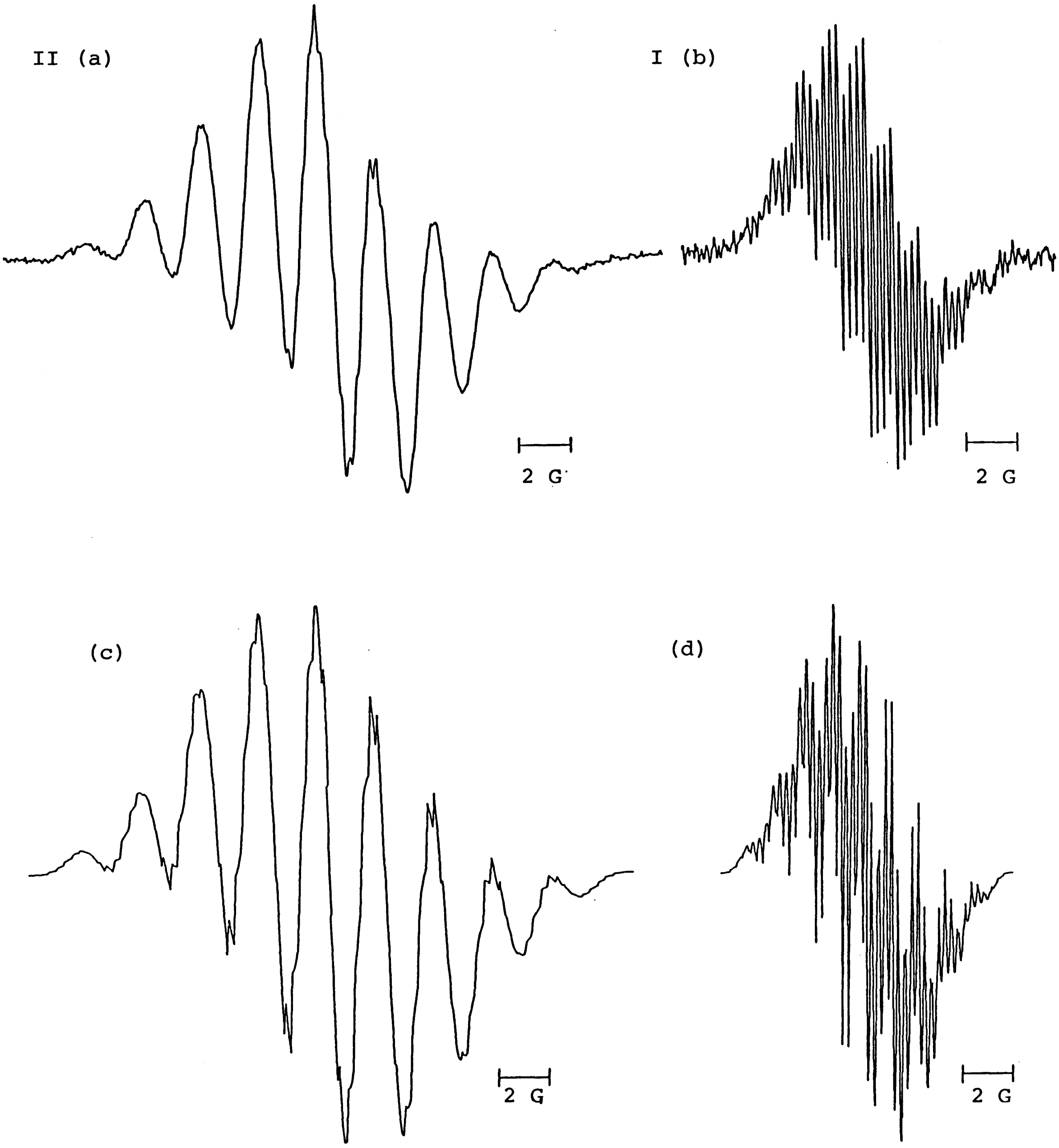
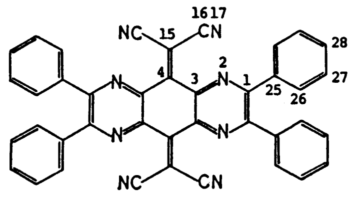


Fig. 1. ESR spectra of $\mathbf{1}^{3\cdot-}$ (a) and $\mathbf{1}^{\cdot-}$ (b) and their simulations (c and d).

very narrow total width, considerable dilution was made for separation of lines at the expense of S/N. I can thus be identified as the radical anion of **1** with the help of a simulation (Fig. 1d). The hfs constants are shown in Table 1. II can be, though very broad in line width, straightforwardly analyzed to a hfs constant due

Table 1. The spin densities and the observed and calculated hfs constants in gauss



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	Anion			Trianion		
	ρ^{π} a)	a(calcd) b)	a(obsd)	ρ^{π} a)	a(calcd) b)	a(obsd)
1	0.0049			0.0463		
2	-0.0056	-0.134	0.24	0.1112	2.670	2.22
3	0.0428			-0.0095		
4	0.0378			0.0577		
15	0.2652			0.0659		
16	0.0038			0.0017		
17	0.0513	1.160	1.04	0.0134	0.300	0.3
25	-0.0010			-0.0014		
26	0.0015	-0.036 c)	<0.1	0.0111	-0.260 c)	<0.3
27	-0.0012	0.028 c)	<0.1	-0.0044	0.100 c)	<0.3
28	0.0016	0.038 c)	<0.1	0.0128	-0.300 c)	<0.3
	g=2.0031			g=2.0034		

a) Spin densities obtained by the McLachlan's method. MO parameters used were; h_N=1.0, k_{NC}=2.0, and k_{15-16}=0.9 for dicyanomethylene groups,[4] h_N=0.8 and $k_{1-2}=k_{2-3}$=1.1 for pyradine rings,[6] and k_{1-25}=0.8 corresponding to a twisting angle between pyradine and phenyl rings.

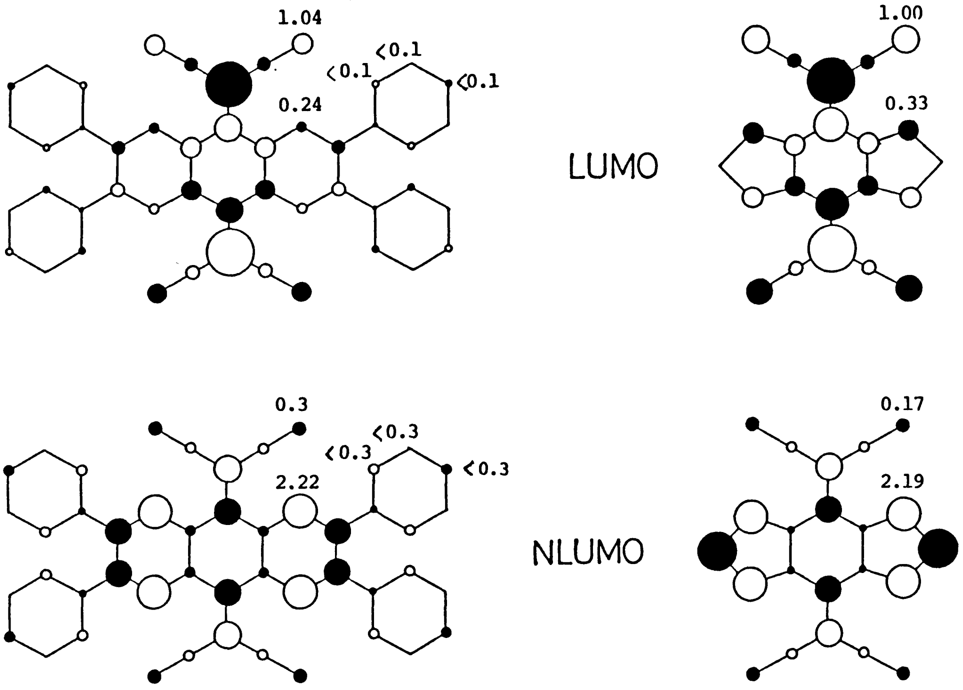
b) See Text for σ-π parameters.

c) -23.7 gauss is taken as Q^{H}_{CN} in the McConnell's equation.

to four equivalent nitrogens and a partially-resolved small hfs due to another set of four equivalent nitrogens (Fig. 1c). These results strongly indicates a possibility that $1^{\cdot-}$ is further reduced into $\mathbf{1}^{3\cdot-}$ via $\mathbf{1}^{2-}$.

Then, the hfs constants of hydrogens and nitrogens were estimated from McLachlan-type spin densities, where the σ-π parameters used for the cyano groups were ones proposed for a series of aromatic nitrile anion radicals by Fraenkel et al.;[4] i.e, 23.1 and -6.8 G as $(P^N + Q^N_{NC})$ and Q^N_{CN}, respectively, in $a^N=(P^N + Q^N_{NC})\rho^{\pi}_N + Q^N_{CN}\rho^{\pi}_C$, while Q^N used for nitrogens of pyradine rings was a standard value for pyridine-type radical anions, 24.0 G.[5] As seen from Table 1, the result for **1** supports the above identification of I as $\mathbf{1}^{\cdot-}$, while the calculated hfs pattern for a presumed radical trianion of **1**, $\mathbf{1}^{3\cdot-}$, corresponds well to that of II. From these results combined with the reversible redox-reaction it may be concluded that II arises from $\mathbf{1}^{3\cdot-}$ and then a possible formation of a secondary paramagnetic product can be ruled out.

The LUMO and NLUMO described using simple HMO's of **1** are compared with the observed hfs patterns of $\mathbf{1}^{\cdot-}$ and $\mathbf{1}^{3\cdot-}$, respectively, in Fig. 2. It is seen from these comparisons that the observed hfs patterns are well reflected in the respective MO. These MO's are very similar to those of bis[thiadiazolo]TCNQ (BTDA-TCNQ) (**2**),[2b] respectively, as shown in Fig. 2 (LUMO is antisymmetry and NLUMO symmetry). The substitution of a diphenylethylene group for a sulfur atom scarcely affects the π-framework of **2**.



1 2

Fig. 2. Comparisons of the hfs patterns (in gauss) and MO's for 1 and 2. The areas of the circles are proportional to the squares of the LCAO coefficients. Blank and filled circles denote different signs of these coefficients.

References

1) a) F. Gerson, R. Heckendorn, D. O. Cowan, A. M. Kini, and M. Maxfield, J. Am. Chem. Soc., 105, 7071 (1983); b) W. Huber, Tetrahedron Lett., 1983, 3595; c) W. Huber, Helv. Chim. Acta, 66, 2582 (1983); d) W. Huber, H. Unterberg, and K. Müllen, Angew. Chem., 95, 239 (1983); e) F. Gerson, R. Heckendorn, R. Möckel, and F. Vögtle, Helv. Chim. Acta, 68, 1923 (1985); f) W. Huber, ibid., 68, 1140 (1985); g) W. Huber, K. Müllen, C. Schnieders, M. Iyoda, and M. Nakagawa, ibid., 69, 949 (1986); g) F. Gerson and W. Huber, Acc. Chem. Res., 20, 85 (1987).

2) a) M. Hirayama, A. Seki, Y. Yamashita, T. Suzuki, and T. Miyashi, Chem. Lett., 1988, 67; b) M. Hirayama, A. Seki, Y. Yamashita, T. Suzuki, and T. Miyashi, J. Chem. Soc., Chem. Commun., submitted.

3) Y. Yamashita, T. Suzuki, G. Saito, and T. Mukai, Chem. Lett., 1986, 715.

4) P. H. Rieger and G. K. Fraenkel, J. Chem. Phys., 37, 2795 (1962).

5) J. H. Freed and G. K. Fraenkel, J. Chem. Phys., 40, 1815 (1964).

6) C. L. Kwan, M. Carmack, and J. K. Kochi, J. Phys. Chem., 80, 1786 (1976).

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