CHEMISTRY LETTERS, pp. 67-70, 1988.

ESR of Radical Anion and Radical Trianion of [1,2,5]Thiadiazolo-tetracyanonaphthoquinodimethane

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 the title compound as well as its radical anion, formed by the electrolytic reduction in acetonitrile in the presence of nBu_4NClO_4 at room temperature, was characterized by the analysis of their ESR spectra.

The radical trianions of conjugated π-systems have recently been of considerable interest from the theoretical viewpoint that their ESR hfs patterns describe their next lowest unoccupied orbital (NLUMO) and furthermore from the expectation that they may make new routes as starting materials and intermediates in organic synthesis.$^{1)}$ For several groups of conjugated π-systems, the radical trianions have so far been formed and characterized by ESR and ENDOR spectroscopy.$^{2,3)}$ Although 11,11,12,12-tetracyanoanthraquinodimethane (**1**)(TCNAQ) exihibits the third half-wave reduction potential E_3 (-2.06 V vs. SCE)$^{4)}$ less negative than those of the other several tetracyanoarenoquinodimethanes, of which the radical trianions have already been observed by several workers,$^{3)}$ the formation of radical trianion of **1** has so far been confirmed neither by electrolytic nor alkali metal reduction. This may be attributed to the nonplanarity due to the steric interaction between cyanomethylene groups and peri hydrogens.$^{5)}$ In order to improve partially such a disadvantageous property as an electron acceptor, an unique electron acceptor [1,2,5]thiadiazolo-tetracyanonaphthoquinodimethane (**2**)(TDA-TCNNQ) was synthesized by Yamashita et al.$^{6)}$ **2** has thus been expected to form its radical trianion, because a substantially less negative E_3 (-1.5 V vs. SCE) than that of TCNAQ$^{7)}$ induces the relatively great ease of formation of $\mathbf{2}^{3-\cdot}$. We report here the generation of radical trianion of **2** as well as its radical anion by the electrolysis in acetonitrile.

A 10^{-3} mol dm^{-3} acetonitrile solution of **2** was electrolyzed with 0.1 mol dm^{-3} nBu_4NClO_4 as a supporting electrolyte using a Pyrex cell with two platinum electrodes at room temperature. At about 0.5 V (an appearance voltage, V_a) a blue species giving an ESR spectrum I occurred, at about 2.0 V it changed to a colorless species, I disappearing simultaneously, and at about 3.3 V the solution turned to yellow, a new spectrum II being observed (Fig. 1). On decreasing the voltage to

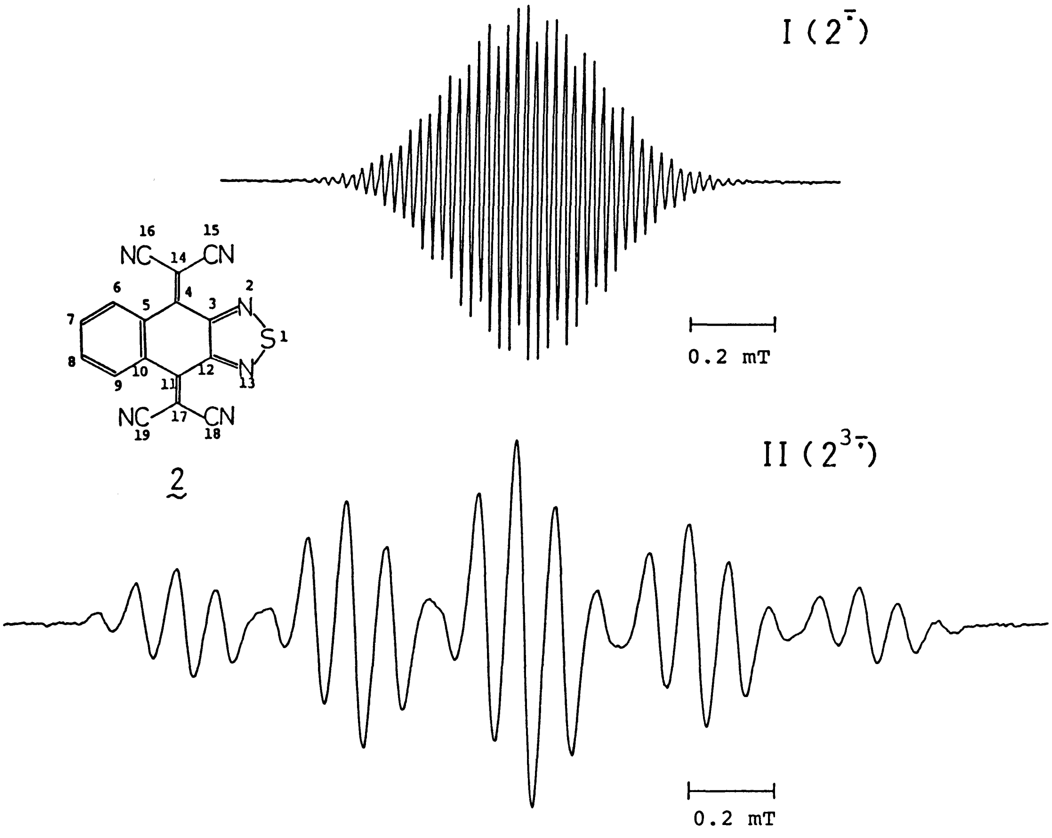

Fig. 1. ESR spectra of radical anion and radical trianion of 2 generated by the electrolysis in CH_3CN with nBu_4NClO_4 at room temperature.

0.5 V or less, I gradually superseded II. These changes were completely reversible. Such spontaneous reoxidation of the latter paramagnetic species at low potentials might be due to a small amount of neutral precursor, solvent, or some impurities. In any event, it may be plausible to consider that these results reveal the following redox sequence;

$$2 \underset{-e^-}{\overset{e^-}{\rightleftharpoons}} 2^{\cdot-} \underset{-e^-}{\overset{e^-}{\rightleftharpoons}} 2^{2-} \underset{-e^-}{\overset{e^-}{\rightleftharpoons}} 2^{3\cdot-}$$

Therefore, I and II can be expected to arise from the radical anion $2^{\cdot-}$ and the radical trianion $2^{3\cdot-}$, respectively. I was identified to $2^{\cdot-}$ on the basis of the analysis with the aid of simulation. II clearly consists of an a^N (two equivalent nitrogens) and an a^H (four equivalent hydrogens), although line widths are much broader than those of I. It has been known that in several radical trianions of tetracyanoarenoquinodimethanes the hfs constants of cyano nitrogens are considerably small and those of ring protons are generally much larger than those of corresponding $2^{\cdot-}$ and

Table 1. Comparison of observed and calculated hfs constants in mT[a]

	a^N_{CN}	a^N_{SN}	a^H_6	a^H_7
$\mathbf{2}^{\cdot-}$	0.096	0.048	0.024	0.096
	0.080[b]	0.064[b]	0.045[b]	0.071[b]
	0.104[c]	0.037[c]	0.009[c]	0.058[c]
$\mathbf{2}^{3\cdot-}$	<0.04	0.410	0.094	0.094
	0.026[b]	0.400[b]	0.083[b]	0.039[b]
	0.022[c]	0.485[c]	-0.102[c]	-0.018[c]

a) The observed values are in the upper 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 $k_{14,15}$=0.9[8] and for TDA 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.[9] a^H's were calculated taking -2.4 mT in McConnell's equation. For the calculation of a^N_{CN}, the nitrogen σ-π parameters proposed by Fraenkel et al. were employed; i.e, 2.31 and -0.68 mT as $(P^N + Q^N_{NC})$ and Q^N_{CN}, respectively, in $a^N=(P^N + Q^N_{NC})\rho^\pi_N + Q^N_{CN}\rho^\pi_C$,[8,10] while for a^N_{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[11] as $(S^N_N + Q^N_{NS} + Q^N_{NC})$, Q^N_{SN}, and Q^N_{CN}, respectively, in $a^N=(S^N_N + Q^N_{NS} + Q^N_{NC})\rho^\pi_N + Q^N_{SN}\rho^\pi_S + Q^N_{CN}\rho^\pi_C$.[9]

b) Calculated using spin densities obtained from HMO's.

c) Calculated using spin densities due to McLachlan's method.

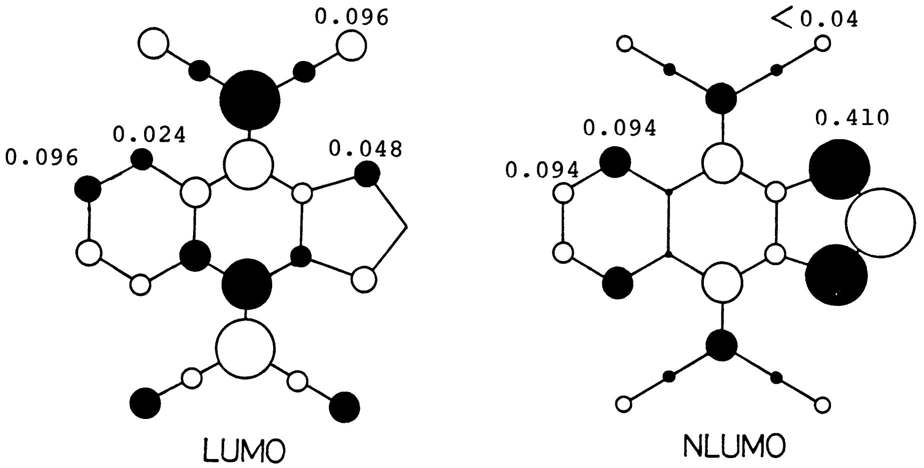

Fig. 2. Comparisons of the observed hfs constants (in mT) and MO's. The areas of the circles are proportional to the squares of the LCAO coefficients (spin densities). Blank and filled circles symbolize different signs of these coefficients. These comparisons are based on all the calculated hfs constants (a^H and a^N's) approximately proportional to the π-spin densities of respective carbon or nitrogen with a similar value of σ-π parameter (|Q|=2.2—2.4 mT).

that their hfs patterns well exhibit the characteristics of their NLUMO's.$^{3)}$ As shown in Table 1, the hfs pattern of II relative to that of I is just characteristic of this sort of trianion. Thus, the redox sequence between the neutral precursor and the trianion is supported also by the structural information due to hfs data. The line broadening observed for $\mathbf{2}^{3-\cdot}$ may be presumably both homogeneous and inhomogeneous in origin. The former, which must be particularly effective, arises most likely from an electron exchange between $\mathbf{2}^{3-\cdot}$ and the respective dianion $\mathbf{2}^{2-}$ still present in the solution, while the latter is caused by the unresolved ^{14}N hfs's due to cyano nitrogens. The LUMO and NLUMO described using the simple HMO's were actually compared with the observed hfs constants of $\mathbf{2}^{-\cdot}$ and $\mathbf{2}^{3-\cdot}$, respectively. As seen from Fig. 2, these hfs patterns are well reflected in these MO's, respectively. Table 1 shows the comparisons between observed and calculated hfs constants, which reveal good correlation.

References

1) F. Gerson and W. Huber, Acc. Chem. Res., 20, 85 (1987).
2) W. Huber, Tetrahedron Lett., 1983, 3595; W. Huber, Helv. Chim. Acta, 66, 2582 (1983); W. Huber, ibid., 68, 1140 (1985); W. Huber, K. Müllen, C. Schnieders, M. Iyoda, and M. Nakagawa, ibid., 69, 949 (1986); W. Huber, H. Unterberg, and K. Müllen, Angew. Chem., 95, 239 (1983); F. Gerson, R. Heckendorn, R. Möckel, and F. Vögtle, Helv. Chim. Acta, 68, 1923 (1985).
3) F. Gerson, R. Heckendorn, D. O. Cowan, A. M. Kini, and M. Maxfield, J. Am. Chem. Soc., 105, 7017 (1983).
4) A. M. Kini, D. O. Cowan, F. Gerson, and R. Möckel, J. Am. Chem. Soc., 107, 556 (1985).
5) 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., 49, 5002 (1984); Y. Nishizawa, T. Suzuki, Y. Yamashita, T. Miyashi, and T. Mukai, Nippon Kagaku Kaishi, 1985, 904.
6) Y. Yamashita, T. Suzuki, T. Mukai, and G. Saito, J. Chem. Soc., Chem. Commun., 1985, 1044.
7) T. Suzuki, C. Kabuto, Y. Yamashita, and T. Mukai, Chem. Lett., 1987, 1129.
8) P. H. Rieger and G. K. Fraenkel, J. Chem. Phys., 37, 2795 (1962).
9) C. L. Kwan, M. Carmack, and J. K. Kochi, J. Phys. Chem., 80, 1786 (1976).
10) M. Karplus and G. K. Fraenkel, J. Chem. Phys., 35, 1312 (1961).
11) C. L. Talcott and R. J. Myers, Mol. Phys., 12, 549 (1967).

(Received October 7, 1987)