ESR of the Trianion and Anion Radicals of Benzo[g][1,2,5]thiadiazolo[3,4-b]quinoxaline-5,10-dione and Its Selenium Analogue

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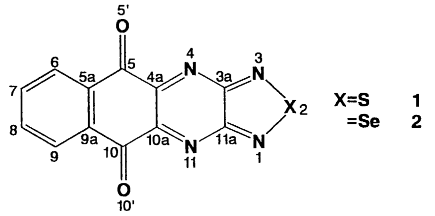
The anion and trianion radicals of title compounds were generated by electrolysis in acetonitrile at room temperature and their ESR spectra were measured, which can be identified on the basis of π-MO calculations of hfsc's.

The observation of hyperfine(hf) interactions in the ESR spectra of trianion radical has afforded the valuable data for discussing the electronic states of these molecules, since the pattern of hf splitting(hfs) reflects well the next lowest unoccupied MO(NLUMO) of such a π-type molecule.[1] It has been considered that the prerequisites for observation of the stable trianion radical in a solution are a low energy of the NLUMO and the low repulsion energy due to the excess three charges in a molecule.[2] The reduction potentials of the title compounds Benzo[g][1,2,5]thiadiazolo[3,4-b]quinoxaline-5,10-dione(BTDQD)(**1**) and Benzo[g][1,2,5]selenadiazolo[3,4-b]quinoxaline-5,10-dione(BSDQD)(**2**) measured by cyclic voltammetry in CH_3CN were -0.25(E_1), -1.18(E_2), and -1.44 V(E_3) and -0.20(E_1), -1.03(E_2), and -1.35 V(E_3) vs. SCE, respectively. These results imply that the electron affinity of the naphthoquinone fused with either a pyradine or thiadiazole ring is similar in magnitude to that of naphthoquinone, while **1** having these two rings and **2** having a selenadiazole ring instead of a thiadiazole ring have a considerably large electron affinity and further that the anion radicals of **1** and **2** are more stable than that of the naphthoquinone fused with either a pyradine or thiadiazole ring.[3] These results seem to be due to a cooperative effect of these two rings for the π-conjugation of whole molecule. On the other hand, it has been predicted from the *ab initio* calculation that on the reduction the heterocyclic rings mainly accept first two electrons and the third electron mainly occupies the dione parts.[3] In order to confirm this prediction, this paper reports on the generation and the ESR spectra of the anion and trianion radicals of **1** and **2**.



The processes of syntheses of **1** and **2** were described elsewhere.[3] The 0.01 M acetonitrile solution of **1** was electrolyzed with tetra-*n*-butyl ammonium perchlorate (0.1 M) as an electrolyte in a Pyrex-cell with two Pt-wire electrodes at room temperature. The reduction voltage was measured between two platinum electrodes. At 0.6 V, the ESR spectrum shown in Figure 1 began to appear, which can be identified as the anion radical of **1**, $\mathbf{1}^-$, from the comparison with the hfs constants(hfsc's) evaluated by the MO calculation. Elevating the voltage to 3.2 V, this spectrum disappeared and a new one appeared, which is shown in Figure 2. These changes are reversible. These two votages 0.6 and 3.2 V seem to correspond to E_1 and E_3 of **1**, respectively. From this fact together with the comparison of calculated and experimental hfsc's, the latter spectrum can be ascribed to the π-trianion radical of **1**,

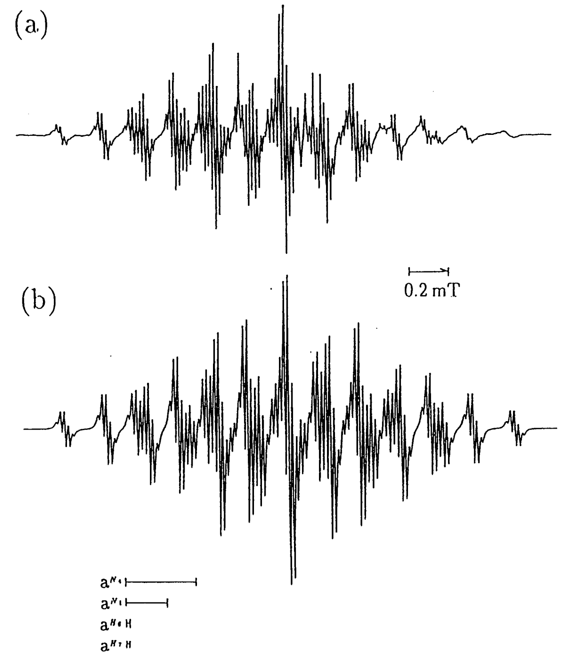


Figure 1. ESR spectrum of $\mathbf{1}^-$ formed by electrolysis in CH_3CN (a) and its simulation (b).

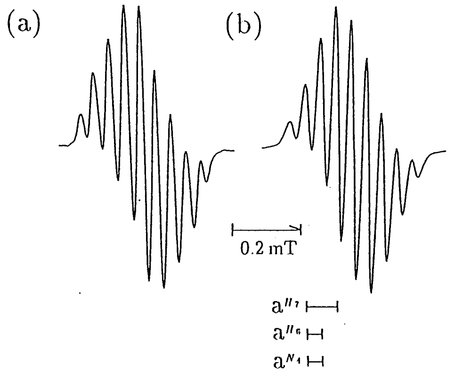


Figure 2. ESR spectrum of $\mathbf{1}^{3-}$ formed by electrolysis in CH_3CN (a) and its simulation (b).

Table 1. Observed and calculated hfs constants (in mT)

	1^-		1^{3-}		2^-		2^{3-}	
Position	a_{obs}	a_{cal}^{a}	a_{obs}	a_{cal}^{a}	a_{obs}	a_{cal}^{b}	a_{obs}	a_{cal}^{b}
N_1	0.218	0.271	<0.02	-0.011	0.319	0.363	<0.02	-0.013
N_4	0.372	0.457	0.043	0.077	0.319	0.405	0.045	0.064
H_6	0.021	-0.010	0.043	-0.059	<0.05	-0.006	0.045	-0.030
H_7	0.021	-0.006	0.086	-0.111	<0.05	-0.005	0.090	-0.105
g-value	2.0055		2.0048		2.0110		2.0046	

a) The MO parameters used were as follows: For the carbonyl group,[4] h_o=1.2 k_{co}=1.5; for the pyrazine ring,[5] h_N=0.8, k_{CN}=1.1; for the thiadiazole ring,[5] h_N=0.8, k_{NS}=0.8, h_S=1.0, and k_{NC}=1.1. The hfsc of nitrogen of thiadiazole ring was estimated by the relation $a^N=2.20\rho^N+0.09\rho^S-0.17\rho^C$ and that of the pyrazine ring by the relation $a^N=2.40\rho^N$.[6] b) h_{Se}=1.1 and k_{NSe}=0.7 were used for the selenadiazole ring and the Q values used were those for BTDQD.

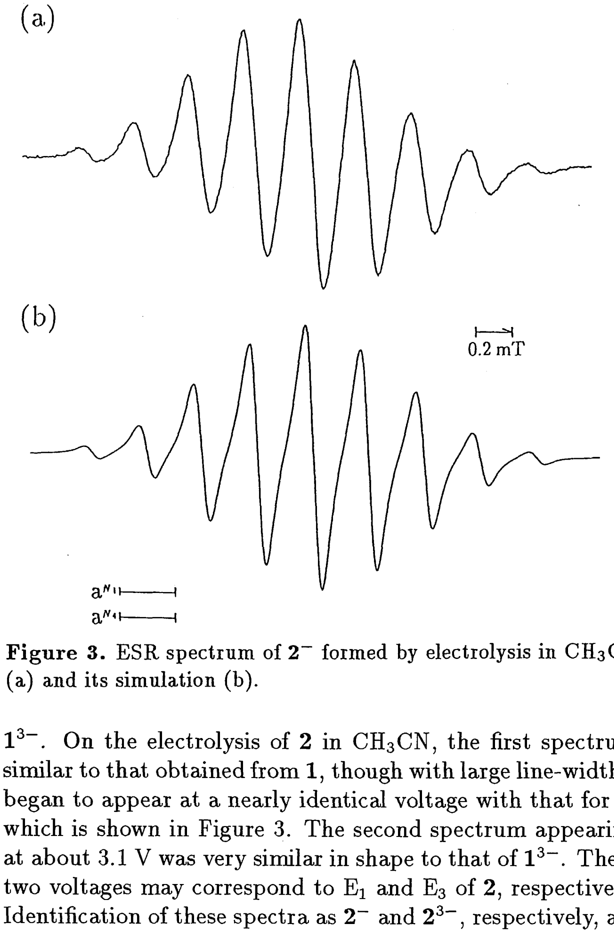


Figure 3. ESR spectrum of **2**$^-$ formed by electrolysis in CH_3CN (a) and its simulation (b).

1^{3-}. On the electrolysis of **2** in CH_3CN, the first spectrum similar to that obtained from **1**, though with large line-widths, began to appear at a nearly identical voltage with that for **1**, which is shown in Figure 3. The second spectrum appearing at about 3.1 V was very similar in shape to that of **1**$^{3-}$. These two voltages may correspond to E_1 and E_3 of **2**, respectively. Identification of these spectra as **2**$^-$ and **2**$^{3-}$, respectively, are straightforward from the similar situation to the case for **1**.

The spin densities were calculated by the McLachlan's method, because this has been generally considered to reproduce relatively well an experimental hfs pattern for such a planar π-radical, for its simplicity. The MO parameters used here are those from the literatures (see Table 1) and the values of h_{Se} and k_{SeN} for **2** were determined, considering the difference of properties of S and Se. Table 1 implies that the calculated hfs patterns of the anion and trianions may correspond relatively well to the experimental ones, respectively, for both **1** and **2**. The lowest unoccupied MO(LUMO) and NLUMO of **1** shown in Figure 4 are similar in form to those predicted from the *ab initio* calculation of the neutral molecule, respectively.[3]

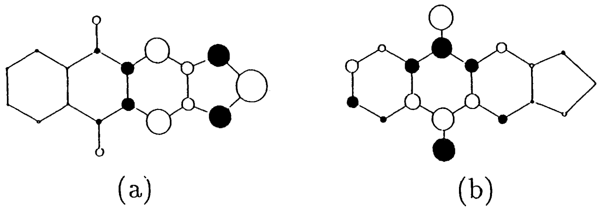

(a) (b)

Figure 4. LUMO(a) and NLUMO(b) of **1**. The area of the circle is proportional to the π-spin density. Blank and filled circles symbolize the different signs of atomic π-orbital coefficients.

As seen from Table 1, the g-value of **2**$^-$ is particularly large in those of these four radicals. It is responsible for these results that the ζ-value of Se(1688cm^{-1}) is considerably larger than that of S(382cm^{-1}) and further that the π-spin density on Se(S) of **2**$^-$(**1**$^-$) is considerably larger than that on Se(S) of **2**$^{3-}$(**1**$^{3-}$), as seen from Figure 4.

References and Notes

1 F. Gerson, R. Heckendorn, D. O. Cowan, A. M. Kini, and M. Maxfield, *J. Am. Chem. Soc.*, **105**, 7017 (1983); M. Hirayama, A. Seki, Y. Yamashita, T. Suzuki, and T. Miyashi, *J. Chem. Soc., Chem. Commun.*, **1988**, 409; M. Hirayama, A. Seki, Y. Yamashita, T. Suzuki, and T. Miyashi, *Chem. Lett.*, **1988**, 67; M. Hirayama, A. Seki, Y. Yamashita, T. Suzuki, and T. Miyashi, *Chem. Lett.*, **1988**, 769.

2 F. Gerson and W. Huber, *Acc. Chem. Res.*, **20**, 85 (1987).

3 Y. Yamashita, Y. Tsubata, T. Suzuki, T. Miyashi, T. Mukai, and S. Tanaka, *Chem. Lett.*, **1990**, 445.

4 M. Broze, Z. Luz, and B. L. Silver, *J. Chem. Phys.*, **46**, 4891 (1967).

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

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