ESR of the π-Radical Formed by Photoreduction of Bis(1,2,5-selenadiazolo)-tetracyanoquinodimethane in Methanol. Observation of a Large ^{77}Se Hfs

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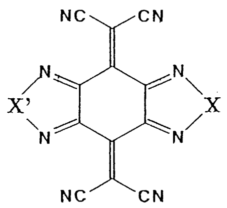
A large ^{77}Se hfs was observed in the ESR spectrum of a radical generated by photoreduction of the electron acceptor, BSDA–TCNQ(**3**), with 355 nm laser irradiation in methanol. This spectrum was identified as the anion radical of a proton adduct of **3**, which was supported by the MO calculation.

In the investigation of electronic states of heterocyclic compounds the experimental determination of ESR hfsc's arising from hetero atoms is very useful as well as the determination of those from ^{1}H and ^{13}C nuclei. The ^{33}S hfsc's in the cation radicals of several sulfur–containing heterocycles have been observed by several workers[1] and reasonably reproduced by taking 3.30 mT as a σ–π parameter Q^S in the relation of $a^S = Q^S \cdot \rho_S^\pi$. Also for ^{17}O, the value of Q^O has been evaluated using the ^{17}O hfsc's measured in a few radicals of oxygen-containing compounds and has led to the good agreements between experimental and calculated a^O's.[2] For another familiar atom in the VI group, Se, a^{Se}'s have scarecely been detected in a high–resolution ESR in solution,[3] in spite of the large value of A_0 (13468 MHz) and the relatively high natural abundance (7.58%).



X=S, X'=S **1**
X=S, X'=Se **2**
X=Se, X'=Se **3**

Therefore, no detailed discussion has been made for Q^{Se} relating a^{Se} to ρ_{Se}^π. More data of a^{Se} are thus required. The observed hfs pattern in the trianion radical of a π–accepter, bis(1,2,5–thiadiazolo)–tetracyanoquinodimethane (BTDA–TCNQ)(**1**), reflects well its NLUMO, the spin densities having a large value on sulfur atoms.[4] This allows us to expect that a trianion radical of the title compound (BSDA-TCNQ)(**3**)[5] or (1,2,5–thiadiazolo)(1,2,5–selenadiazolo)–TCNQ(TSDA–TCNQ)(**2**) may give rise to a large a^{Se}. However, an attempt to prepare a trianion radical of **3** or **2** was unsuccesful by electrochemical reduction in acetonitrile.[6]

This paper reports a large hfsc of ^{77}Se detected from the ESR spectrum obtained after UV–light irradiation to a methanol solution of **3** at room temperature in vacuo. Irradiation was made using 3000 pulses of Nd:YAG laser (355 nm, 8 ns). As shown in Figure 1, three sets of satellite spectrum with hfsc due to I=1/2 nucleus (0.320 mT, 0.230 mT, 0.960 mT) were observed in addition to the main spectrum composed of an a^N (0.160 mT) due to four equivalnet nitrogens. The intensity ratios of these satellites to the main spectrum indicate that the first satellite (0.320 mT) arises from four equivalent ^{13}C's, the second (0.230 mT) two equivalent ^{13}C's, and the third (0.960 mT) two

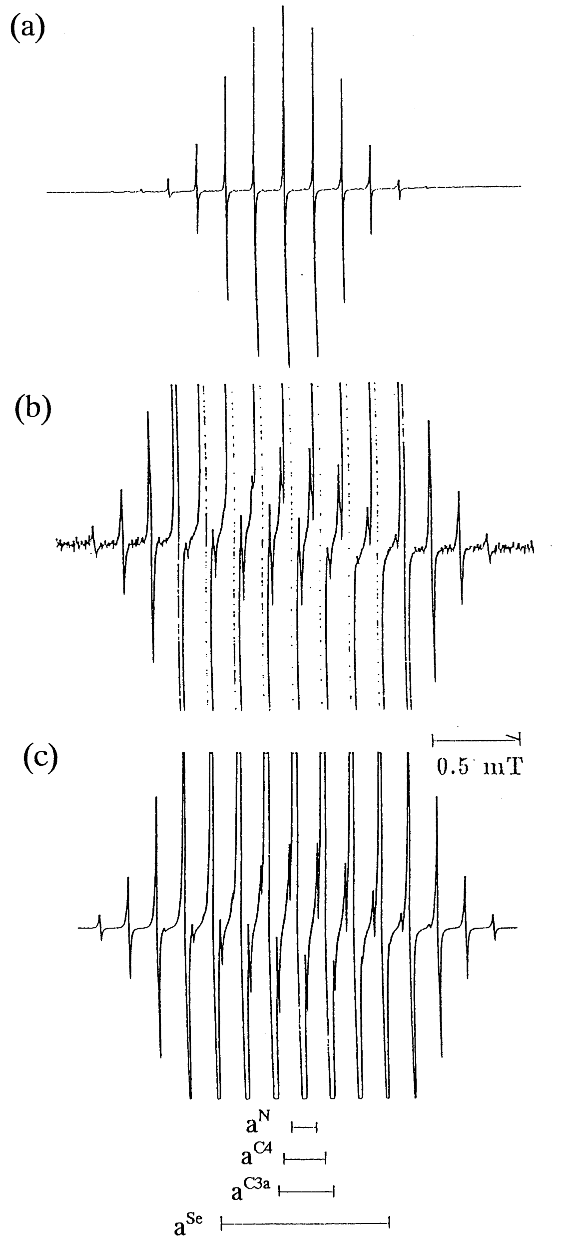
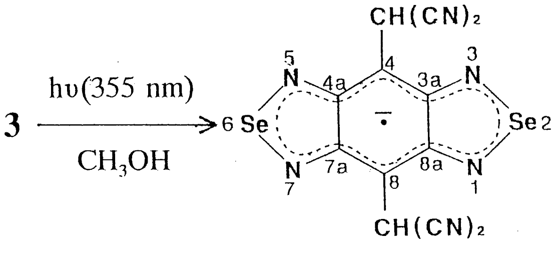


Figure 1. ESR spectrum of $(\mathbf{3}\text{-}H_2)^{\cdot-}$ (a), that at high amplification (b), and its simulation (c).

Table 1. π–Spin densities and experimental and calculated hfs constants of $(\mathbf{3}\text{–H}_2)^{\cdot-}$ (in mT)

Position	$\rho^{\pi\ a}$	$a_{cal}{}^{b}$	a_{obs}
C_4	0.1107	0.307	0.230
C_{3a}	–0.0465	–0.313	0.320
N	0.0591	0.142	0.160
Se	0.3643		0.960

[a] Calculated with h_{Se}=0.7 and k_{NSe}=0.6 and λ=1.2 in the McLachlan procedure. [b] Estimated by using ρ^{π} and the Karplus–Fraenkel equation with several Q–values.



$(\mathbf{3}\text{–H}_2)^{\cdot-}$

equivalent ^{77}Se's. On the other hand, the laser irradiation of the methanol solution of **1** in vacuo gave rise to the anion radical $\mathbf{1}^{\cdot-}$, which did not further change with time. In contrast, by the irradiation of **2** the anion radical $\mathbf{2}^{\cdot-}$ was formed and gradually changed to a new radical after turning light off. This radical was identified as an asymmetrical neutral radical formed by the hydrogen abstraction of one dicyano methylene group from methanol.[7] Judging from such differences in photochemical reactivities among these three homologs and from the result of analysis of the present spectra, it may be concluded that the radical anion $\mathbf{3}^{\cdot-}$ is generated by photoreduction of **3**, followed by its proton abstraction from methanol, the disproportionation of resulting **3**–H to **3**–H$_2$, and the reduction of **3**–H$_2$ to $(\mathbf{3}\text{–H}_2)^{\cdot-}$. Then, the π–spin density distribution of $(\mathbf{3}\text{–H}_2)^{\cdot-}$ was calculated by the McLachlan's method by taking a planar framework except two CH(CN)$_2$ groups for the radical molecule. The MO parameters for Se were varied in the ranges of $0.5 < h_{Se} < 1.1$ and $0.5 < k_{NSe} < 0.9$, considering its electronegativity and bond length Se–N.[5] The values of h_N and k_{NC} were taken to be 1.0 and 1.1, respectively. Q^{C}_{CN} and Q^{C}_{NC} were taken tentatively to be equal to $Q^{C}_{CC'}$ and $Q^{C}_{C'C}$,[8] respectively, while Q^N=2.40 mT was used in the relation of $a^N=Q^N\cdot\rho^{\pi}_{N}$.[9] The calculated hfs pattern fits relatively well to the experimental one, when 0.7 and 0.6 are taken for h_{Se} and k_{NSe}, respectrively, as seen in Table 1. It may be interpreted that the C–H bond is fixed in the molecular plane to avoid the steric hindrance between the cyano group and the selenadiazole ring. Consequently, the hfs of the C–H proton must be so small as to be unobservable. Thus, the MO calculation supports well the identification of the spectrum as $(\mathbf{3}\text{–H}_2)^{\cdot-}$. The LUMO(sym) of **3**–H$_2$ is similar to NLUMO(sym) of **3**, showing contrast to LUMO(antisym) of **3**, and thus a fairly large amount of spin exists on Se in the radical anion $(\mathbf{3}\text{–H}_2)^{\cdot-}$ (Figure 2). Although a relatively large value is expected for Q^{Se}, more data of a^{Se} are desired for estimation of this value.

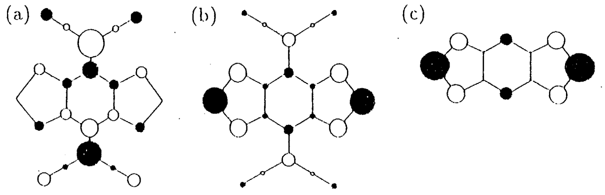


Figure 2. LUMO of **3** (a), NLUMO of **3** (b), and LUMO of **3**–H$_2$ (c). The areas of circles are proportional to the π–spin densities. Blank and filled circles symbolize the different signs of atomic π–orbital coefficients.

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References and Notes

1 F. Gerson, Ch. Wydler, and F. Kluge, *J. Magn. Reson.*, **26**, 271 (1977); C. L. Kwan, M. Carmack, and J. K. Kochi, *J. Phys. Chem.*, **80**, 1786 (1976); F. B. Bramwell, R. C. Haddon, F. Wudl, M. L. Kaplan, and J. H. Marshall, *J. Am. Chem. Soc.*, **100**, 4612 (1978); H. Bock, G. Brahler, U. Henkel, R. Schlecker, and D. Seebach, *Chem. Ber.*, **113**, 289 (1980); L. Cavara, F. Gerson, D. O. Cowan, and K. Lerstrup, *Helv. Chim. Acta*, **69**, 141 (1986).
2 P. D. Sullivan, J. R. Bolton, and W. E. Geiger, Jr., *J. Am. Chem. Soc.*, **92**, 4176 (1970).
3 M. L. Kaplan, R. C. Haddon, F. B. Bramwell, F. Wudl, J. H. Marshall, D. O. Cowan, and S. Gronowitz, *J. Phys. Chem.*, **84**, 427 (1980).
4 M. Hirayama, A. Seki, Y. Yamashita, T. Suzuki, and T. Miyashi, *J. Chem. Soc., Chem. Commun.*, **1988**, 490.
5 T. Suzuki, C. Kabuto, Y. Yamashita, G. Saito, T. Mukai, and T. Miyashi, *Chem. Lett.*, **1987**, 2285.
6 The electrolysis of **3** in CH$_3$CN gave only an uninterpretable spectrum composed of two sets of two equivalent a^N, while the electrolysis of **2** in CH$_3$CN gave $\mathbf{2}^{\cdot-}$, but at higher voltage resulted in an unanalyzable spectrum, which seems to be a superposition of two spectra.
7 To be published.
8 M. Karplus and G. K. Fraenkel, *J. Chem. Phys.*, **35**, 1312 (1961).
9 J. H. Freed and G. K. Fraenkel, *J. Chem. Phys.*, **40**, 1815 (1964).