ESR of the Anion Radical of 2,6-Dithioxobenzo[1,2-*d*:4,5-*d*′]bis[1,3]dithiole-4,8-dione. Observation of the Satellites of ^{17}O, ^{13}C, and ^{33}S and the Second-Generation Satellites due to Both ^{13}C and ^{33}S in Natural Abundance

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ESR study of the anion radical produced by the reduction of the title compound (DTB-BDTD) with potassium metal in 1,2-dimethoxyethane is reported. In addition to the satellites of ^{17}O, ^{13}C, and ^{33}S, the second-generation satellite lines of extremely low intensity, arising from both ^{13}C and ^{33}S isotopes in natural abundance, have been detected. It was found that these satellites vary markedly in line width among each component of its multiplet. This line width effect was used to determine the sign of hfs constants of these magnetic nuclei, and the resulting signs agreed well with those estimated from the spin densities obtained by the McLachlan procedure and the INDO method.

ESR investigation of hf interactions with magnetic isotopes in their low natural abundance through the measurement of hfs constants (hfsc's) of these nuclei provides valuable information for consideration of the electronic structures of organic radicals. Especially, hfsc data of extremely less abundant ^{17}O are valuable.[1)] It may be generally required for the observation of such hfsc's that there are no abundant magnetic nuclei such as ^{1}H and ^{14}N in a radical or that the spin population amounts to much less on these nuclei, even though they are in a radical.

The title quinone fused with 1,3-dithiole units, **1** (Fig. 1), has strong electron affinity[2)] and its anion radical is stable enough to be fairly diluted in usual aprotic solvents. Therefore, the absence of ^{1}H and ^{14}N in **1** enables us to expect that hfsc's arising from ^{13}C, ^{33}S, or ^{17}O are observable.

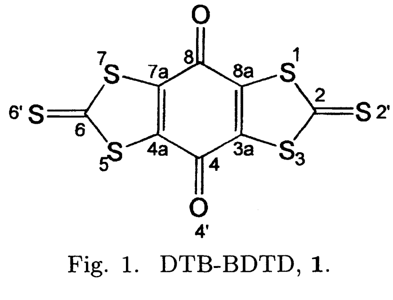

Fig. 1. DTB-BDTD, **1**.

Experimental

The anion radical of **1** was produced under high vacuum by contact with potassium metal in 1,2-dimethoxyethane. ESR spectra were observed at the range of room temperature to −90 °C with a JEOL-FE1XG (100 kHz modulation). Quinone **1** was prepared as described in the literature.[3)]

MINDO calculations of spin densities were carried out using the program MNDO of the library programs of Institute for Molecular Science with an M-680 computer at this Institute, and INDO calculations using the program UCINDO[4)] with an M-660L at Ibaraki University. The McLachlan calculations of π-spin densities were made with a personal computer using a program made on the basis of the literature.[5)]

Results and Discussion

ESR Spectra. The ESR spectra of $\mathbf{1}^{-\bullet}$ are shown in Fig. 2. Two sets of satellite lines arising from the nuclei with spin 1/2 were detected (Fig. 2b). These four lines were almost equal in intensity (about 1% relative to the main line), though the line widths vary each other. The larger hfsc (0.195 mT, absolute value) could be assigned to C_4 and the smaller (0.061 mT) to C_2 with the aid of a theoretical spin density distribution. The other two satellite lines with slightly smaller intensity than carbon satellites (Fig. 2b) were found to be the outer two lines of a quartet arising from a nucleus

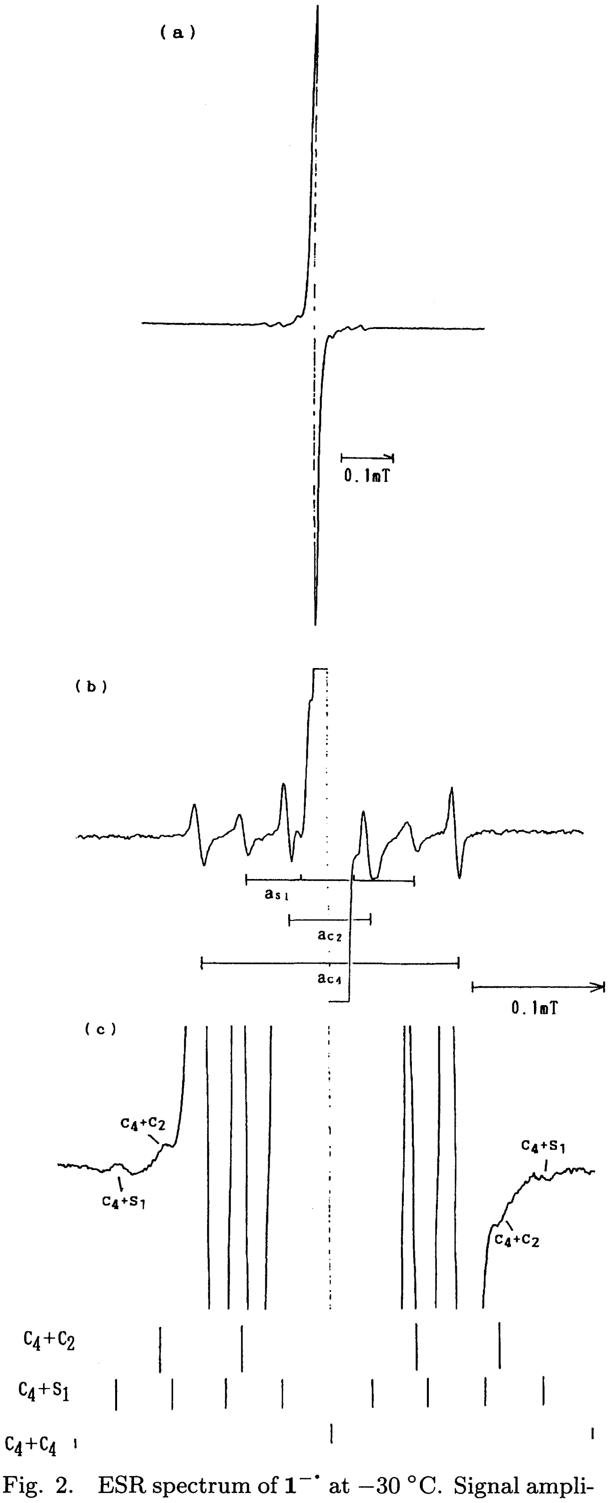

Fig. 2. ESR spectrum of $\mathbf{1}^{-\bullet}$ at −30 °C. Signal amplification increases on going from (a) to (c). Below the spectrum (c) are stick diagrams for the observable ones of second-generation satellites. The lines due to the anion radical with two ^{13}C isotopes, C_4+C_4, were not discernible.

with spin 3/2, which were assigned to S_1, on the basis of their intensities (about 0.8% relative to the main line) and the comparison of experimental hfsc (0.043 mT) with the calculated one. These lines were broader with higher field. The simulation of the main signal resulted in detection of a small doublet (0.03 mT), which was assigned to C_{3a}. At a further high gain spectrum (Fig. 2c), four lines with extremely low intensity could be detected, which appear symmetrically at both sides of the main spectrum. These lines were confirmed to be the satellite lines of the second generation on the basis of their intensities and the magnitudes of hfsc: The inner set arises from the anion radical with two ^{13}C isotopes, C_4 and C_2, and the outer one arises from one ^{13}C and one ^{33}S isotopes, C_4 and S_1. The analysis of the hyperfine pattern due to the second-generation satellites is illustrated by the stick diagrams in Fig. 2c and constructed with the use of the following hfsc's: $|a^{C4}|=0.195$ mT, $|a^{C2}|=0.061$ mT, $|a^{S1}|=0.043$ mT. Furthermore, when the modulation amplitude was substantially increased, the six lines of weak intensity appearing symmetrically about the main spectrum were found (Fig. 3), which could be ascribed to the sextet arising from ^{17}O. The value of $|a^{O}|$ was 0.861 mT, which is well reproduced by an MO calculation using the McLachlan method. Such observation of hfsc from ^{17}O isotopes in natural abundance is unique and valuable.[1] The intensities of these lines agreed well with the theoretical ones (0.012% relative to the main line) and their line widths became broader with higher field.

MO Calculation of Spin Densities and Hfs Constants. In order to estimate hfsc's of magnetic nuclei, the spin densities on s-orbital (ρ^{S}) were calculated by the MINDO method using the X-ray crystal data of the lithium salt of $\mathbf{1}^{-\bullet}$.[2] The values of isotropic hfs constants (A_0) used are as follows: ^{17}O; −4628 MHz, ^{13}C; 3110 MHz, ^{33}S; 2715 MHz. The calculation results are listed in Table 1, which correspond fairly well to experimental ones, except for a^{O}. McLachlan-type π-spin densities were also calculated to predict the signs of hfsc's, where the generally accepted values were used for MO parameters.[6] As seen from Table 1, it seems likely that hfsc's predicted by using the Karplus–Fraenkel equation[7] agree well with the experimental values rather than those by INDO. However, the two theoretical procedures gave the opposite sign for C_{3a}. The polarization parameters used here were

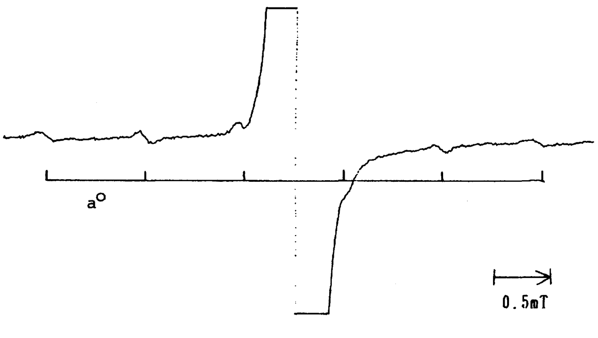

Fig. 3. ESR spectrum of $\mathbf{1}^{-\bullet}$ at high amplification and large modulation amplitude.

Table 1. π-Spin Densities ρ^{π}'s and Observed and Calculated Hfsc's, a's (in mT)

Isotope	Position	ρ^{π}	a_{calcd}(I)[a]	a_{calcd}(II)[b]	a_{obsd}
^{13}C	2	−0.0095	−0.057	−0.020	−0.061
	3a	0.0723	−0.090	0.087	(0.03)[c]
	4	0.1370	−0.190	−0.142	−0.195
^{33}S	1	0.0267	0.088	0.029	0.043
	2′	−0.0092	−0.030	−0.010	—[d]
^{17}O	4′	0.1837	−0.872	−1.420	−0.861

a) Estimated using the Karplus–Fraenkel relation and ρ^{π}. b) Estimated using the relation $a=\rho^{\mathrm{S}}\cdot A_{\mathrm{O}}$ with ρ^{S} calculated by MINDO method. See Text. c) The sign could not be determined. d) Not observable.

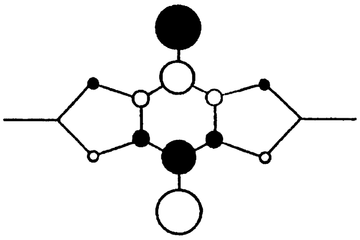

Fig. 4. LUMO of **1**. The area of the circle is proportional to the spin density. Filled and blank circles symbolize different signs of LCAO coefficients.

those in the literatures.[8] The spin distribution of $\mathbf{1}^{-\bullet}$ seems to be similar to that of p-benzosemiquinone,[8a] though a slight amount of spin is delocalized to the dithiole rings. LUMO of **1** is antisymmetric (Fig. 4) and therefore the π-spin densities of C_2 and $\mathrm{S}_{2'}$ on the nodal plane are very small in amount and minus in sign. The order of magnitude of experimental $|a^{\mathrm{O}}|$ is as follows: benzosemiquinone (−0.953 mT)>$\mathbf{1}^{-\bullet}$>1,4-naphthosemiquinone (−0.858 mT)[8a] >anthrasemiquinone (−0.753 mT).[8a] This order seems to correspond to the amount of spin delocalizing from the semiquinone moiety into neighboring rings.

Determination of the Signs of Hfsc's Using the Line Width Effect. As seen in Figs. 2 and 3, the detailed observation of satellite lines reveals marked variation in the line width among those in a multiplet. This effect can be interpreted in terms of the equation[9] $\Delta H=A+BM_{\mathrm{I}}+CM_{\mathrm{I}}{}^2$, where ΔH is the contribution of g and hyperfine anisotropies to the line width and M_{I} is the nuclear quantum number of a nucleus with hf interaction. This relation means that the variation in line width (ΔH) within one multiplet is accounted for by the dependence of the quantum numbers M_{I}. The term BM_{I} leads to different anisotropic effects in the low- and high-field regions of the spectrum of $\mathbf{1}^{-\bullet}$. Therefore, if the sign of B is known, this line width effect enables us to determine the sign of hfsc of the magnetic nucleus. The sign of B is found to be represented by the relation, sign B=sign Δg·sign μ_{X}·sign ρ_{X},[9] where μ_{X} is the magnetic moment of nucleus X, ρ_{X} is the π-spin density on X, and $\Delta g=2g_{\mathrm{ZZ}}-(g_{\mathrm{XX}}+g_{\mathrm{YY}})$. In this sort of planar π-radical, the sign of Δg may be generally regarded as minus. Therefore the sign of B can be determined from that of calculated π-spin density, and finally the sign of hfsc can be concluded from the comparison of line widths of corresponding high- and low-field lines (ΔH_{H}, ΔH_{L}). The signs of all hfsc's, except those of $\mathrm{C}_{3\mathrm{a}}$ and $\mathrm{S}_{2'}$, were determined by this procedure: The sign of a^{C2} was evaluated to be minus from $B>0$ and $\Delta H_{\mathrm{L}}<\Delta H_{\mathrm{H}}$, the sign of a^{C4} minus from $B<0$ and $\Delta H_{\mathrm{L}}>\Delta H_{\mathrm{H}}$, the sign of a^{S1} plus from $B<0$ and $\Delta H_{\mathrm{L}}<\Delta H_{\mathrm{H}}$, and the sign of a^{O} minus from $B>0$ and $\Delta H_{\mathrm{L}}<\Delta H_{\mathrm{H}}$.

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