ESR Studies of Spin-Spin Dipolar Interaction in Pure and Diluted Phenoxyl Radical Solids

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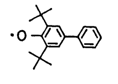
(Received August 26, 1983)

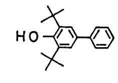
Synopsis. ESR studies have been carried out on powder samples of pure phenoxyl (2,6-di-*t*-butyl-4-phenylphenoxyl) and 3% phenoxyl diluted in its diamagnetic corresponding phenol matrix. The dipolar splittings due to the spin pairs in closest approach have been observed for both the pure and 3% phenoxyl.

Recently, many investigations have been performed for the magnetic properties of some organic stable neutral radicals, including phenoxyl radicals. The magnetic susceptibility of these radicals deviates from the Curie-Weiss law at low temperatures and shows a broad maximum. This behavior of the paramagnet could be well described by the Heisenberg one-dimensional model or singlet-triplet equilibrium model with isotropic antiferromagnetic exchange interaction: The value of the spin-spin exchange interaction (J) between neighboring radical molecules in these radical solids has been determined, by comparing experimental curve of susceptibility with theoretical one.[1] However, the examples that the property of the spin-spin dipolar interaction (D) in these radical solids has been clarified are very limited.[2,3] Recently, ESR studies have been carried out on powder samples of pure galvinoxyl and 1% galvinoxyl doped in its diamagnetic corresponding phenol matrix, which has the same crystal structure with that of galvinoxyl at 293 K. The existence of radical pairs in both the pure galvinoxyl and 1% galvinoxyl has been confirmed by the observation of the ESR zero-field splittings at 77 K, and, thus, by comparing the observed zero-field splittings, the mechanism of a first-order phase transition from paramagnetic to diamagnetic (or weak paramagnetic) reported previously for galvinoxyl at 85 K has been discussed.[4,5]



Phenoxyl Radical

(1)



Corresponding Phenol

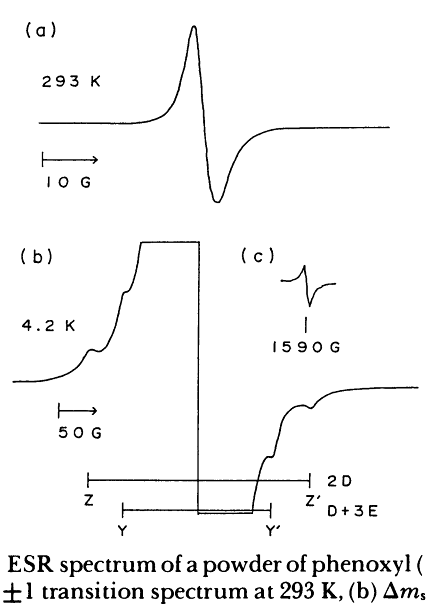


Fig. 1. ESR spectrum of a powder of phenoxyl (**1**); (a) $\Delta m_s = \pm 1$ transition spectrum at 293 K, (b) $\Delta m_s = \pm 1$ transition spectrum at 4.2 K, and (c) $\Delta m_s = \pm 2$ transition spectrum at 4.2 K.

In the present work, in order to clarify the property of the spin-spin dipolar interaction in organic radical solids, we have measured the ESR spectra of powder samples of pure 2,6-di-*t*-butyl-4-phenylphenoxyl[6] (**1**) (abbreviated to phenoxyl hereafter) (see Fig. 1) and 3% phenoxyl diluted in its diamagnetic corresponding phenol matrix in the temperature range 293—77 K and 4.2 K.

Experimental

Radical concentration of **1** was obtained from the results of the paramagnetic susceptibility measurements at 20 °C, after correcting for the diamagnetic contribution ($\chi_{\text{dia}} = -0.204 \times 10^{-3}$ emu/mol) calculated by the Pascal's method. The value was 99% for **1**, assuming the Curie law. The powder sample of 3% phenoxyl diluted in its diamagnetic corresponding phenol matrix was prepared according to the procedure used for diluted galvinoxyl.[4]

Results and Discussion

The ESR spectrum of powder sample of the phenoxyl (**1**) at 293 K shows an exchange-narrowed, Lorentz-type absorption with a width of 4.5 G (1 G $=10^{-4}$ T) located at $g=2.0047$, as shown in Fig. 1(a). When the temperature is lowered, the linewidth starts to increase gradually, and becomes 6.5 G at 77 K. In addition to the strong central singlet, two pairs of weak, broad side peaks were observed with the same order of intensity at 4.2 K, as shown in Fig. 1(b). The two pairs of absorption lines will be due to zero-field splittings arising from the intermolecular spin-spin dipolar interaction of two electrons in a triplet state.[7] In fact, the forbidden transition ($\Delta m_s = \pm 2$) was observed at about 1590 G, as shown in Fig. 1(c). The zero-field splitting parameters and g-tensor values were evaluated as $|D| = 148.2 \pm 0.4$ G and $|E| = 17.0 \pm 0.4$ G and $g_{zz} = 2.0027 \pm 0.0003$ (Z,Z′) and $g_{yy} = 2.0044 \pm 0.0003$ (Y,Y′), respectively. This phenomenon will be considered to be similar to the cases of some TCNQ salts and bisgalvinoxyl biradical, which also exhibit ESR zero-field splittings at low temperatures.[3,8] The magnetic susceptibilities of the above TCNQ salts and the bisgalvinoxyl biradical were well explained by singlet-triplet equilibrium model with lower singlet

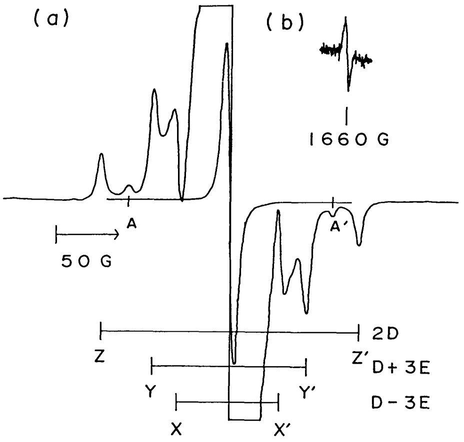


Fig. 2. ESR spectrum of a powder of 3% phenoxyl (**1**) at 293 K; (a) $\Delta m_s = \pm 1$ transition spectrum and (b) $\Delta m_s = \pm 2$ transition spectrum.

and upper triplet states. Therefore, our ESR data of the phenoxyl (**1**) indicate that this radical is a ground singlet with a thermally accessible triplet state.

The ESR spectrum of 3% phenoxyl at 293 K shows three pairs of absorption lines (Z,Z'; Y,Y'; and X,X') with the same order of intensity, as shown in Fig. 2(a). The three pairs of absorption lines apparently represent zero-field splittings arising from the intermolecular dipolar interaction of two electrons in a triplet state; thus, the zero-field splitting parameters and g-tensor values were evaluated as $|D| = 101.3 \pm 0.4$ G and $|E| = 6.9 \pm 0.4$ G and $g_{zz} = 2.0043 \pm 0.0003$ (Z,Z'), $g_{yy} = 2.0042 \pm 0.0003$ (Y,Y'), and $g_{xx} = 2.0045 \pm 0.0003$ (X,X'), respectively. In addition, the other weak $\Delta m_s = \pm 1$ absorptions (A,A') with a separation of about 161 G were observed in the ESR spectra, as shown in Fig. 2(a). The weak absorptions may be due to a radical triad.[9]

Careful measurements of the positions of the resonance lines show that this zero-field splitting is linearly temperature-dependent with $\mathrm{d}|D|/\mathrm{d}T = -(28 \pm 2) \times 10^{-3}$ G K^{-1}. In the same way the $|E|$ thermal dependence is estimated to be about $\mathrm{d}|E|/\mathrm{d}T = -(4 \pm 2) \times 10^{-3}$ G K^{-1}. This result may be interpreted as arising from the thermal expansion of the crystal lattice. The zero-field splitting parameters observed at 4.2 K are $|D| = 109.3 \pm 0.4$ G and $|E| = 7.9 \pm 0.4$ G. Here, the calculated average interelectronic distances, using a model of two point dipoles, are 6.50 Å at 293 K and 6.34 Å at 4.2 K for 3% phenoxyl. The spectrum at 4.2 K is similar to those above 77 K, and at 4.2 K, no deviation from linear temperature-dependency has been observed in D and E values.

In the present experiments, we observed the dipolar splittings due to the spin-pairs in closest approach for both the pure and 3% phenoxyl (**1**) at 4.2 K.[4] If the crystal structure of the phenol precursor of **1** is the same as that of phenoxyl (**1**), the value of the dipolar splitting observed for the diluted phenoxyl crystals will be considered to be the same as that of the neat phenoxyl crystal. However, the D and E parameters ($|D| = 148.2$ G and $|E| = 17.0$ G) obtained for pure phenoxyl are very different from those ($|D| = 109.3$ G and $|E| = 7.9$ G) obtained for 3% phenoxyl (**1**) at 4.2 K. Therefore, at first, we expected that the pure phenoxyl may show a first-order phase transition at low temperature, as observed for galvinoxyl,[5] and measured the Debye-Scherrer X-ray diffraction patterns at 293 K. However, the diffraction patterns observed for the pure phenoxyl and the corresponding phenol did not agree with each other in their diffraction angles and intensities at 293 K, contrary to our expectations. Both the phenoxyl radical (**1**) and the corresponding phenol may be considered to be biphenyl derivatives; the molecule of biphenyl is planar or nearly so in both the solid and triplet state, but twisted 30—40° around the central single bond in the vapor and in solution. Thus, the degree of twisting of biphenyl molecule is clearly due to a delicate balance of non-bonded repulsion and conjugation. In a previous paper,[10] it is reported that the phenoxyl radical (**1**) has planar character, because the inter-ring bond acquires some double-bond character in the phenoxyl radical in view of a valence-bond. On the other hand, the corresponding phenol does not acquire such double bond character, showing different crystal structure with that of the pure phenoxyl.

As described above, we observed the zero-field splittings due to the spin-pairs in closest approach for the pure phenoxyl at 4.2 K; the result indicates that this radical is a ground singlet with a thermally accessible triplet state. However, usually, the powder sample of the radical solids shows an "exchange-narrowed" single ESR absorption line, because of strong spin-spin exchange interaction operating between neighboring radical molecules. Consequently, the examples that the property of the spin-spin dipolar interaction (D) in the radical solids has been clarified are very limited.[2,3] Therefore, the observation of the dipolar splittings in phenoxyls diluted in their diamagnetic corresponding phenol matrices may be of significance.

The authors are much obliged to Professor Noboru Hirota of Kyoto University for the ESR measurements at 4.2 K.

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