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Dipolar Interaction in TEMPAD Biradical. II[1]

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The EPR of TEMPAD single crystals diluted in diamagnetic matrices was studied. The results of the 10% TEMPAD were almost the same as those of the very dilute one studied previously. In the case of the 25% TEMPAD, the spectra are composed of three parts. The central broad line, whose linewidth was analyzed in comparison with the pure TEMPAD case using the three-dimensional Anderson-Weiss formula, is the spectrum of clusters constructed by the free radicals. The side lines with the hyperfine splitting are the spectrum of the isolated TEMPAD molecule, and the outer broad lines are from the molecules coupled in pairs along the a-axis. The EPR spectra of the pure TEMPAD at very low temperature were also measured in order to have information concerning the dipolar interaction in the pure crystal. These spectra are the superposition of the spectra caused by the intra-molecular dipolar interaction and of the spectra due to impurities. All the results were explained with the suitable molecular stack model and the triplet exciton theory.

There have been a number of investigations regarding the magnetic properties of organic stable free radical solids.[2-4] In these works, the magnetic ordering effects caused by some magnetic interactions between unpaired electrons have been of special interest. When the unpaired electrons couple with each other three-dimensionally, the long-range ordering effect can occur.[2,3] On the other hand, the low-dimensionally coupled spins or clustering spins induce the short-range ordering effect.[3,4]

To clarify these magnetic ordering effects, one must study the magnetic interactions, especially the exchange interaction and the dipolar interaction between unpaired electrons. EPR spectroscopy is a powerful technique for the study of these magnetic interactions, because it gives much information about the microscopic magnetic structure and the dynamical behavior of the magnetic system.

Previous magnetic studies of 2,2,6,6-tetramethyl-4-piperidone azine 1,1′-dioxyl (TEMPAD) revealed three kinds of exchange interactions (see Fig. 1):[5-7] one of them is the stronger inter-molecular exchange interaction along the a-axis (J_1;$J_1/k=-12.8$ K) which produces the broad maximum in the magnetic susceptibility (χ_M) of the pure TEMPAD at the temperature of 16.5 K and the large Weiss constant in the χ_M-T curves of the diluted crystals.[5,7] The second kind is the weaker inter-molecular exchange interaction (J_1'; $|J_1'|/k\sim1$ K) in the inter-molecular alternating chain, and the third is the weaker intra-molecular one (J_2; $|J_2|/k\sim2\times10^{-2}$ K) which affects the hyperfine structure in the EPR spectrum in solution[6]; both contribute to the small Weiss constant in the χ_M-T curves of the diluted TEMPAD crystals.[7]

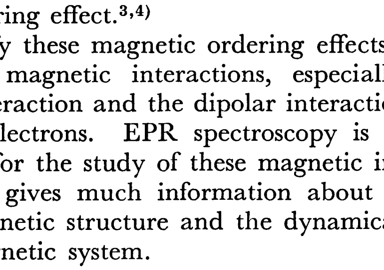

Fig. 1. Exchange interactions in TEMPAD biradical.

The EPR of the diluted TEMPAD in the diamine host was also studied and the principal values and the direction cosines of the inter- and the intra-molecular dipolar interactions were determined.[8] The angular dependence of the EPR linewidth of the pure TEMPAD could be well explained using the three-dimensional Anderson-Weiss formula, which indicates that the inter-molecular dipolar interaction and the weak exchange interactions (J'_1 and J_2) are very important for the dynamical behavior in our case.[8] The EPR spectrum of the powdered TEMPAD at room temperature shows one symmetrical line, and new lines appear on both sides of the central line at very low temperatures. They have been explained in terms of the intra-molecular dipolar interaction on the basis of the triplet exciton theory.[1]

In this paper, the authors will report on their EPR studies of the pure TEMPAD at very low temperature and of the diluted TEMPAD in the diamine host at room temperature. Some discussion is given on the inter- and intra-molecular exchange and dipolar interactions in the biradical crystal by comparison with the data published elsewhere.

Experimental

TEMPAD and 2,2,6,6-tetramethyl-4-piperidone azine (the diamine), whose molecular structures are shown in Figs. 2(a) and 2(b), respectively, were prepared from 2,2,6,6-tetramethyl-4-piperidone supplied by the Aldrich Chemicals Co. in accordance with the method described by Rassat *et al.*[9] The single crystals of the pure TEMPAD and the 25% and 10% TEMPAD in the diamine host were crystallized from their ethereal solutions.

The EPR spectra were measured using X-band (9.5 GHz) spectrometers, JEOLCO JES-ME-3X equipped with an 80 Hz field modulation at low temperatures and JEOLCO JES-PE-3X equipped with a 100 kHz field modulation at room temperature. In the low temperature measurements, the temperature was determined by measuring the vapor

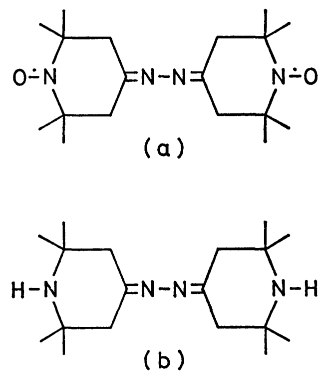

Fig. 2. Molecular structures of the TEMPAD biradical (a) and the corresponding diamine (b).

pressures of liquid helium. The magnetic field was calibrated with 0.1% Mn^{2+} in MgO (the hyperfine coupling constant between central two lines is 86.2×10^{-4} T and $g=2.00641$) and peroxylamine disulfonate, $[\cdot ON(SO_3)_2]^{2-}$ ($A_N=13.0\times10^{-4}$T and $g=2.00550$). The error in the measurements of angles was estimated to be about two degrees.

Results and Discussion

Crystal Structure. The crystal structures of the TEMPAD and the diamine crystals are the monoclinic system with the parameter β of nearly 90° (see Table 1); thus we can adopt the a, b, and c-axes as the rectangular coordinate system for the pure and the diluted single crystals (see Figs. 3(a) and 3(b)). It should be noted here that the molecular stack model presumed from the EPR results[8] indicates that the electron spins form a linear chain along the a-axis. This means that the direction of the largest exchange and dipolar interactions is along the a-axis, as is shown in Fig. 1.

TABLE 1. THE SPACE GROUPS AND THE LATTICE CONSTANTS FOR THE DIAMINE AND TEMPAD BIRADICAL

	Diamine	TEMPAD
Space group	Monoclinic C_c	Monoclinic C_c or $C_{2/c}$
a	29.0 Å	29.1 Å
b	12.6 Å	12.8 Å
c	10.4 Å	10.5 Å
β	~90°	~90°
z	8	8

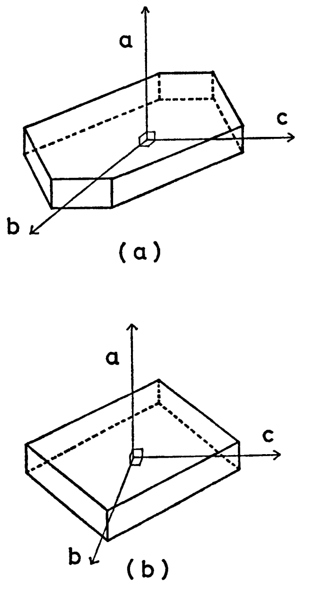

Fig. 3. Coordinate systems of the diamine host (a) and the TEMPAD crystal (b).

Exciton Density. If the electron spins form an alternate linear chain, in which the spins couple with each other through exchange interactions, a short-range ordering will occur at low temperature and then some triplet excitons will be produced. The triplet exciton plays an important role in the dynamic behavior of the unpaired electrons of the TEMPAD biradical at low temperature. The density of the triplet exciton is given by

$$\rho = 1/[1+(1/3)\exp(\delta/kT)] \qquad (1)$$

where $\delta=2|J_1|$[10]. From the χ_M-T curve, J_1/k is equal to -12.8 K for the TEMPAD biradial and the density of the triplet exciton at 4.2 K is about 0.5%. Even in a pure TEMPAD crystal, this low density of the triplet exciton makes it possible to observe the EPR spectra modified by the intra-molecular dipolar interaction at low temperature.

Diluted Crystal. The interactions between biradicals in a diamagnetic host crystal may be divided into three types of interaction; that is, an isolated biradical, a dimer, and a cluster which contains three or more interacting biradical molecules. These are shown in Fig. 4. Type I contains only intra-molecular exchange and dipolar interactions; in Type II there are inter-molecular exchange and dipolar interactions in addition to the intra-molecular interactions. "Cluster" has a very complicated interaction mechanism and may exhibit rather exchange-narrowed EPR absorptions.

The EPR results of the 10% TEMPAD single crystal are the same as those of the very diluted case (2% in concentration)[8] except for showing EPR spectra of a low resolution at some orientations. The spectra consist of two parts of the absorption lines, the one due to the intra-molecular interactions (Type I) and

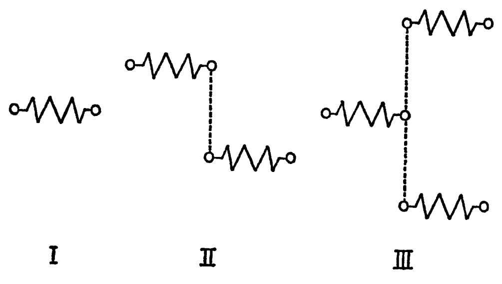

Fig. 4. TEMPAD biradicals in a diamine host crystal. Type I represents an isolated TEMPAD biradical surrounded by diamagnetic host molecules. Type II represents a pair interaction scheme. Type III represents one of the interaction schemes in which three or more TEMPAD molecules interact each other. Type III is called "cluster".

the other due to the inter-molecular interactions (Type II). The former has a doublet splitting due to intra-molecular dipole-dipole interaction and each of the doublet absorptions shows hyperfine splittings attributable to exchange-coupled nitrogen nuclei. It is the exchange interaction, J_2 in Fig. 1, that couples two nitrogen nuclei in the same molecule. The latter spectrum, which is outside of the former spectrum and has an apparently broad linewidth, comes from the inter-molecular dipole-dipole interaction. The angular dependence of these spectra can be obtained and then the principal values of the intra-molecular dipole-dipole interaction tensor and their direction cosines can be determined. These results are quite the same as in the case of the 2% TEMPAD crystal within the accuracy of the experimental error. The results of the direction cosines show that in the 10% TEMPAD crystal the biradical molecules in a unit cell occupy two different sites, the p- and q-sites, as reported in Ref. 8. The principal values and the crystal field parameters are listed in Table 2 and the splitting constants of the spectra at some orientations are summarized in Table 3. The EPR spectra of the 25% and 100% TEMPAD crystals can be analyzed on the basis of these values. The good agreement between the results of 10% and 2% TEMPAD crystals may indicate that the biradical concentration of 10% TEMPAD is not high enough to affect the EPR spectra through the inter-molecular interaction. In other words, there are in the EPR spectra mainly contributions from Types I and II and no appreciable contributions from the cluster in Fig. 4.

The results of the 25% TEMPAD are quite different from those of the 10% or 2% TEMPAD crystals. This fact indicates that an exchange narrowing effect becomes large in the 25% TEMPAD crystals. The EPR spectra of the 25% TEMPAD single crystal at some orientations are shown in Fig. 5. These spectra are composed of three kinds of spectral lines; one of them is a central broad line (X), the second is the side lines with the hyperfine splitting (Y), and the last is the broad side lines (Z). From comparing these spectra with those of the 10% or 2% TEMPAD case it follows that the contributions from Types I and II are rather decreased and that the contribution from Type III is much more increased. The central broad line can be considered to be the spectrum of the inter-molecular clusters (Type III in Fig. 4). The angular dependence of the linewidth of X is shown in Fig. 6 in comparison with that of the pure TEMPAD. The linewidth of X in the 25% TEMPAD is broader than that of the pure TEMPAD for all orientations of the crystal in the magnetic field H except for the orientation where the linewidth takes a minimum value, and the spectra of X splits into three lines for the case of $H//$a-axis. For the comparison with the pure TEMPAD

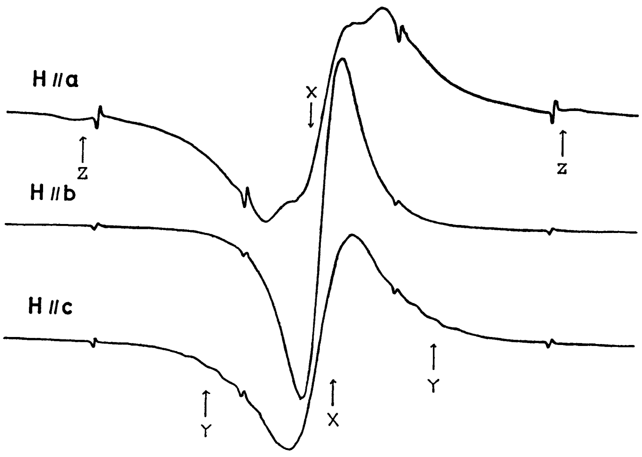

Fig. 5. Typical EPR spectra of the 25% TEMPAD crystal with the static magnetic field parallel to a, b, and c-axes. Small sharp peaks are the spectra of Mn^{2+} in MgO.

Table 2. The principal values of the tensors of the intra-molecular and inter-molecular dipole-dipole interactions with regard to the abc-system and the crystal field parameters

Principal values	Crystal field parameters
Intra-molecular dipole-dipole interaction	
D_{XX} $\pm(18.7\pm0.5)\times10^{-4}$T D_{YY} $\pm(15.3\pm0.4)$ D_{ZZ} $\mp(34.0\pm1.0)$	$\lvert D\rvert/g\mu_B$ $51.0\pm1.5\times10^{-4}$T $\lvert E\rvert/g\mu_B$ 3.4 ± 0.9
Inter-molecular dipole-dipole interaction	
D'_{XX} $\pm13\times10^{-4}$T D'_{YY} ±73 D'_{ZZ} ∓86	$\lvert D'\rvert/g\mu_B$ 130×10^{-4}T $\lvert E'\rvert/g\mu_B$ 30

Table 3. Dipolar interactions in TEMPAD biradical as the splitting of the spectrum at each orientation

Axis $(//H)$		a	b	c
2% 10%	D'	264×10^{-4}T	172×10^{-4}T	208×10^{-4}T
	D	55	40	106
25%	D'	263	—	—
	D	—	—	106
100%	D (4.2 K)	—	—	60
	D (1.7 K)	—	65	73

D': Inter-molecular dipolar coupling
D : Intra-molecular dipolar coupling

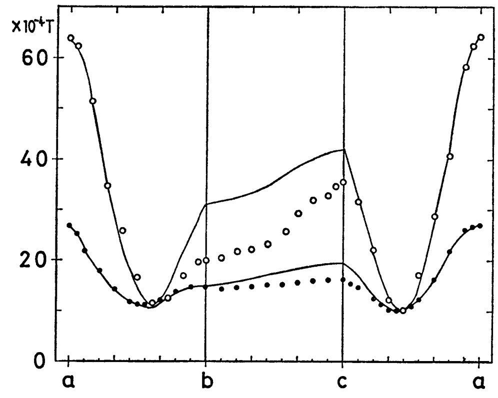

Fig. 6. Peak-to-peak linewidths of the 25% and the pure TEMPAD spectra. The solid curves are the calculated results using the three-dimensional Anderson-Weiss model. ●: Pure TEMPAD, ○: center line X of 25% TEMPAD.

case, we can consider the three-dimensional Anderson-Weiss formula for a Lorenzian line:[11]

$$\Delta H_{\mathrm{pp}} = \Delta H_{\mathrm{d}}^2/\sqrt{3}H_{\mathrm{ex}} + C \tag{2}$$

where ΔH_{pp} is the peak-to-peak linewidth, ΔH_{d}^2 the second moment of the dipolar interaction, H_{ex} an effective exchange field, and C the residual linewidth. The secular part of the second moment ΔH_{d}^2 was calculated using the term of the inter-molecular dipolar interaction (D') obtained from the 10% or 2% TEMPAD crystal. Thus H_{ex} and C were estimated to be $\sim$0.2 T ($\sim$2000 G or 0.3 K) and $\sim10^{-3}$ T ($\sim$10 G), respectively. These values reproduce quite well the angular dependence of the linewidth. If we take into account $H_{\mathrm{ex}}=0.43$ T (4300 G) and $C=9.5\times 10^{-4}$ T (9.5 G) in the pure TEMPAD crystal, the averaged inter-molecular exchange interaction in the cluster is weaker than that in the pure TEMPAD and the residual linewidth C is nearly equal to that of the pure TEMPAD. It may be reasonable that the effect of the exchange narrowing in the cluster is reduced by a diamagnetic dilution and that there is no noticeable change in the residual linewidth C because it represents the broadening mechanisms which come mainly from the nuclear hyperfine interaction and the non-secular part of the inter-molecular dipole-dipole interaction.

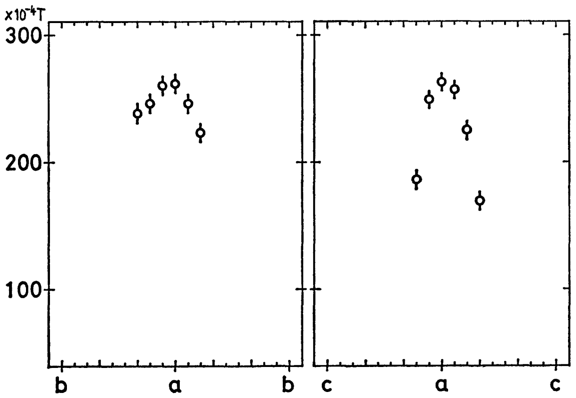

Fig. 7. Dipolar splitting of the line Z of the 25% TEMPAD crystal.

The side doublet line Y with a hyperfine structure can easily be assigned to the line of the isolated TEMPAD biradical (Type I) and corresponds to the intra-molecular dipolar interaction (D), because this spectrum has a hyperfine structure and a maximum separation 106×10^{-4} T at the $H//$c-axis. The angular dependence of the line separation of the side line Z is shown in Fig. 7. These lines, whose maximum separation is about 264×10^{-4} T at the $H//$a-axis, are caused by the pair (Type II) and correspond to the inter-molecular dipolar interaction (D') in the 10% or 2% diluted system (see Tables 2 and 3). The angular dependence of Fig. 7 is also in good agreement with that of D'. As the last two groups, Y and Z, are very much weaker than the central line X, the TEMPAD molecules are distributed homogeneously in the diamine host.

Pure Crystal. In the pure crystal, the exchange narrowing effect is so large that we can not obtain much information about any dipolar interactions in the TEMPAD biradical at room temperature. In order to reduce its effect we measured EPR spectra in the liquid helium temperature region, where the triplet exciton density becomes small enough for us to observe the dipolar splitting in EPR spectra. The EPR spectra of the pure TEMPAD single crystal at very low temperature are shown in Fig. 8. These spectra are the superposition of one central line and two side lines. The angular dependence of the two side lines are shown in Fig. 9. These lines have a maximum splitting at an orientation of the $H//$c-axis with its magnitude of about 60×10^{-4} T. The dipolar splittings of the 2%, 10%, and 25% TEMPAD crystals at room temperature and the pure TEMPAD at low temperature are listed in Table 3. From these results, the two side lines can be determined to be due to the intra-molecular dipolar interaction, which is also consistent with the powder results of 100% TEMPAD.[1] The fact that there is no hyperfine splitting may be caused by the weak inter-molecular exchange inter-

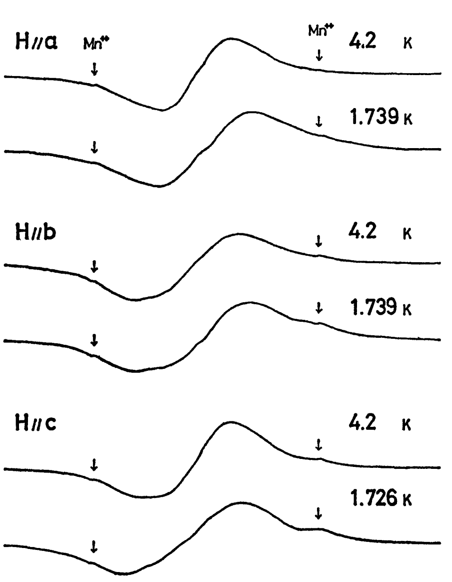

Fig. 8. Low temperature EPR spectra of the pure TEMPAD crystal at some orientations.

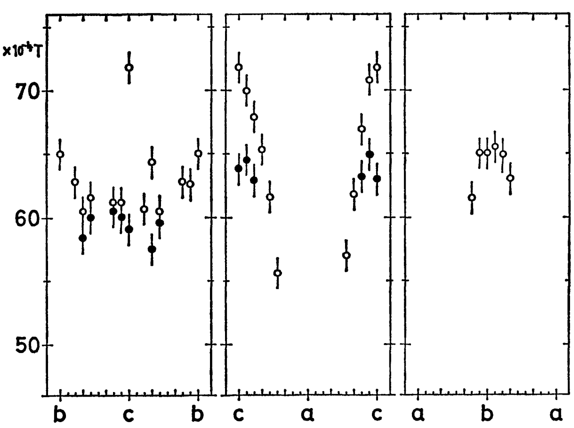

Fig. 9. Dipolar splitting of the outer peak of the pure TEMPAD spectra at low temperature. ●: 4.2 K, ○: 1.73 K.

action.

For the central line there are four possible interpretations; one of them is that it is attributable to the spectrum of the triplet exciton along the a-axis narrowed by the exciton motion, the second is that it is the spectrum of the isolated cluster, the third is due to that of the non-interacting TEMPAD molecule, and the last is that of the monoradicals derived from the TEMPAD biradical by decomposition. As the density of the triplet exciton at 4.2 K is about 0.5%, the EPR spectrum of the triplet exciton at 4.2 K must be very weak and should have a well-resolved fine structure. The spectrum of the non-interacting TEMPAD molecule shows the hyperfine splitting, as we can see in the 25% TEMPAD spectrum. Zvarykina *et al.* showed the typical spectra of a non-interacting adipate biradical at the temperature of the short-range ordering region,[12] but in our case we cannot observe the hyperfine splitting in all the directions. The g-value of the central line is slightly different from that of the two side lines; thus the central line may possibly correspond to the last case. This is also ascertained by the angular dependence of the linewidth of the central line, which is shown in Fig. 10. The dotted line(······) shows the angular dependence of 100% TEMPAD at room temperature. This angular dependence is well explained on the basis of the three-dimensional Anderson-Weiss model, as was already discussed, that is, it depends exclusively on the angular variation of the inter-molecular dipole-dipole interaction parameter, D'. The angular dependence of the linewidth clearly changes as the temperature is lowered, and at 1.73 K it can neither be explained in terms of the inter-molecular dipole-dipole interaction (D') nor the intra-molecular dipole-dipole interaction (D). Thus, we presume that the central line is due to the monoradicals. However, we do not have any reasonable explanation for the broadening mechanism of the linewidth.

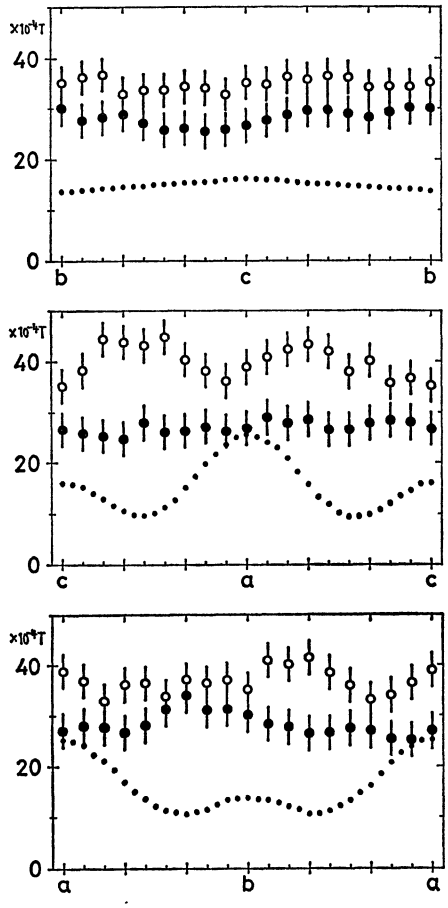

Fig. 10. Peak-to-peak linewidths of the TEMPAD spectra. ●: center line at 4.2 K, ○: center line at 1.74 K, •: at room temperature.

As for the dipolar interaction between molecules which have exchange interaction J_1 in Fig. 1, we tried to find some absorptions in a wider magnetic field region, but could not obtain any information, possibly because of the low triplet exciton density.

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