

Magnetic Interactions in TEMPAD Biradical

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The magnetic interactions in nitroxyl biradical, TEMPAD, were discussed in detail using the results from magnetic susceptibility and EPR measurements on a single crystal and polycrystalline samples. Measurements were also carried out on diluted biradicals in diamagnetic matrices. With all the results reported elsewhere, exchange and dipolar interactions were studied in the TEMPAD biradical. It was clarified that for the study of magnetic interactions, especially in order to obtain magnetic interaction parameters, the susceptibility and EPR measurements must be carried out on both pure and diluted systems and both single and powder samples. Temperature variations are also effective in the EPR studies. In addition to these results it is important to check the EPR linewidth because both of the interactions are inherent in the linewidth.

INTRODUCTION

Recently the magnetic properties of many organic stable free radicals have been investigated very actively. It has been reported that many of these organic radicals exhibit some effects of the magnetic interactions between unpaired electron spins in the radical molecules. In the magnetic short-range order region many problems on low-dimensionality of the magnetic interactions or spin cluster arise and in the magnetic long-range order region problems on magnetic phase transitions or ordered phases should be required to be solved. In these phenomena the magnetic interactions between unpaired electron spins may play the most important role in the organic free radicals as well as the other magnetic materials and may become the most important clue to clarify the magnetic properties in the organic free radical solids.¹⁾

The investigations on the problems may be divided broadly into two categories. The first is to deduce the magnetic interactions from the macroscopic physical quantities and the second is to investigate them microscopically after the simplification of the problem by magnetic dilution method. As for sample materials, these two investigations concern the condensed spin systems and the diluted spin systems respectively. The discussion should be made comprehensively from these two complementary points of view. However, there have been few investigations, in this sense, on the magnetic properties of organic free radicals because of the lacking of suitable radical crystals.

We can carry out these experiments on biradical, where there are two spins which magnetically interact each other. If we dilute the biradical in a certain diamagnetic environment, the magnetic problem can be simplified to what is called "two-body problem" and we can investigate precisely the magnetic interactions in the two-body system. These may be closely relevant to those in the condensed systems. In the course of these works we tried several experiments and in this paper we will make detailed discussions generally

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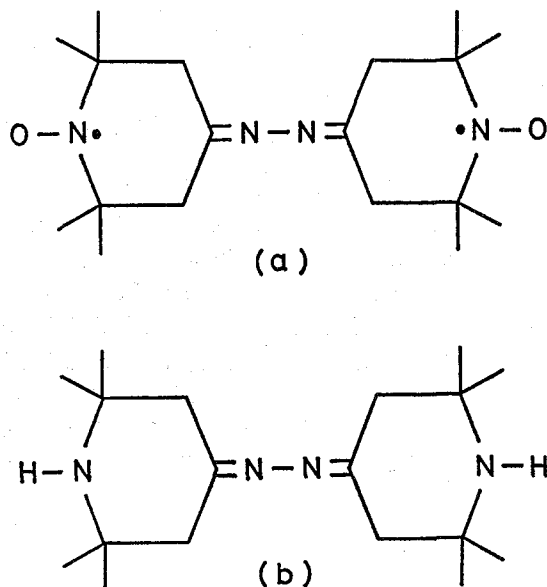


Fig. 1. Molecular structures of the TEMPAD biradical (a) and the corresponding diamine (b).

on the above-mentioned matter together with the other results published elsewhere.

The biradical TEMPAD, 2,2,6,6-tetramethyl-4-piperidone azine 1,1'-dioxyl, is very stable and has a localized spin density at nitrogen and oxygen nuclei of nitroxyl.²⁾ This can easily form two-spin system both in solution and in solid, that is, form solid-solution in a diamagnetic host molecule, 2,2,6,6-tetramethyl-4-piperidone azine (the diamine), where the biradicals are distributed homogeneously. The molecular structures of the TEMPAD biradical and the corresponding diamine are given in Fig. 1.

EXPERIMENTAL

TEMPAD and the corresponding diamine were prepared from 2,2,6,6-tetramethyl-4-piperidone supplied by the Aldrich Chemicals Co. following the method described by Rassat *et al.*³⁾ After purification by chromatography and recrystallization, pure TEMPAD and diamine were obtained. The melting points were $182 \pm 1.0^\circ\text{C}$ and $139 \pm 0.5^\circ\text{C}$ respectively. The single crystals of both the pure and the diluted TEMPAD in the diamine host were crystallized from their ethereal solutions. The diluted TEMPAD crystals of less than 2%, 10%, 25%, 50%, and 75% in concentration were obtained and their elementary analyses agreed well with the calculated values.

The EPR measurements were carried out at room temperature using X-band spectrometers, JEOLCO JES-ME-3X and JES-PE-3X equipped with a 100 kHz field modulation and, at low temperatures, JES-ME-3X equipped with an 80 Hz field modulation. In the low temperature measurements, the temperatures were determined by measuring the vapor pressures of liquid helium and also by measuring the electric resistance of carbon resistors. The magnetic field was calibrated with 0.1% Mn^{2+} in MgO (the hyperfine coupling constant between central two lines is $86.2 \times 10^{-4} T$ and

$g=2.00641$) and peroxyamine disulfonate $[\cdot\text{ON}(\text{SO}_3)_2]^2-$ ($A_N=13.0 \times 10^{-4}T$ and $g=2.00550$) as a standard sample. The mount for holding the crystals in the microwave cavity was made of Tefron, and it had a quartz rod; the crystals were fixed to the mount with silicon grease. The error in the measurements of angles was estimated to be about two degrees.

The paramagnetic susceptibility measurements were performed with powder samples of about 50–100 mg over the temperature region of 1.8–273 K and in magnetic fields of $8-9 \times 10^{-1}T$, using a torsion balance which has been described elsewhere.⁴⁾ The temperature of the samples was determined by means of a AuCo-Cu thermocouple and a carbon resistor set on samples, which had been calibrated beforehand by means of a standard sample, Mn-Tutton's salt. The diamagnetic contributions of TEMPAD biradical and the diamine were calculated to be -2.37×10^{-4} and -2.33×10^{-4} emu/mol respectively. The diamagnetic contributions of the diluted crystals were estimated as the same of the aforementioned two values multiplied by each concentration.

DISCUSSIONS

Magnetic Interactions. Generally the magnetic interactions may involve exchange and dipolar interactions. The exchange interaction we mean is an isotropic exchange interaction of Heisenberg type, that is, the exchange interaction Hamiltonian $\mathcal{H}_{ex}$ is expressed as

$$\mathcal{H}_{ex} = - \sum_{\langle ij \rangle} 2J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j \quad (1)$$

where J_{ij} is an exchange interaction parameter between the unpaired electrons i and j , and the summation is taken over all the interacting ij pairs. The anisotropic contribution to the exchange interaction may be small enough to be neglected in the case of organic free radicals in which the anisotropy of g -values is estimated to be less than 0.2% in magnitude.

The dipolar interaction can be expressed by the Hamiltonian,

$$\mathcal{H}_{dip} = \sum_{\langle ij \rangle} \frac{g^2 \mu_B^2}{R_{ij}^3} \left\{ \mathbf{S}_i \cdot \mathbf{S}_j - \frac{3(\mathbf{S}_i \cdot \mathbf{R}_{ij})(\mathbf{S}_j \cdot \mathbf{R}_{ij})}{R_{ij}^2} \right\} \quad (2)$$

where g is g -value and μ_B is the Bohr magneton. In the case of orthorhombic symmetry, $\mathcal{H}_{dip}$ can be rewritten as follows,

$$\begin{aligned} \mathcal{H}_{dip} &= \sum_{\langle ij \rangle} (D_{xx}^{ij} S_x^2 + D_{yy}^{ij} S_y^2 + D_{zz}^{ij} S_z^2) \\ &= \sum_{\langle ij \rangle} \left\{ D^{ij} [S_z^2 - \frac{1}{3} S(S+1)] + E^{ij} (S_x^2 - S_y^2) \right\} \end{aligned} \quad (3)$$

where $S_l = S_{il} + S_{jl}$ ($l=x, y$, and z) and S is the eigen value of the total spin $\mathbf{S} = \mathbf{S}_i + \mathbf{S}_j$. The crystal field parameters D^{ij} and E^{ij} are related to the elements of the dipolar tensor as

$$\begin{aligned} D_{xx}^{ij} &= -\frac{1}{3} D^{ij} + E^{ij} \\ D_{yy}^{ij} &= -\frac{1}{3} D^{ij} - E^{ij} \\ D_{zz}^{ij} &= \frac{2}{3} D^{ij} \end{aligned} \quad (4)$$

where

$$D_{li}^{ij} = \frac{1}{2} g^2 \mu_B^2 \left\langle \frac{R_{ij}^2 - 3X_l^2}{R_{ij}^5} \right\rangle$$

$X_l = X, Y, \text{ and } Z$
 $l = x, y, \text{ and } z$

Besides these two interactions, the Hamiltonian of the biradical contains Zeeman and hyperfine terms, thus the total Hamiltonian is given by

$$\mathcal{H} = \mathcal{H}_z + \mathcal{H}_{hf} + \mathcal{H}_{dip} + \mathcal{H}_{ex} \quad (5)$$

here

$$\mathcal{H}_z = \sum_i \mu_B \mathbf{S}_i \tilde{\mathbf{g}}_i \mathbf{H} \text{ and } \mathcal{H}_{hf} = \sum_{i,j} \mathbf{S}_i \tilde{\mathbf{A}}_{ij} \mathbf{I}_{ij}$$

The exchange and dipolar interactions can be divided into two types of interactions, namely intra- and inter-molecular interactions depending on whether i and j spins are in the same molecule or not. It should be noted here that in the diluted systems the biradical may contain only intra-molecular interactions and that the more the concentration of TEMPAD increases, the larger the contribution of the inter-molecular interactions becomes. Moreover a significant feature is that the dipolar interactions are orientation-dependent whereas the exchange interactions have no dependence on the crystal orientation because of the isotropic Heisenberg type interactions. The magnetic interactions in TEMPAD biradicals is shown in Fig. 2 schematically with due regard to the crystal structure mentioned below.

Crystal Structure. The crystal structures of the TEMPAD and the diamine crystals are the monoclinic system with the parameter β of nearly 90° . As is shown in Table I,

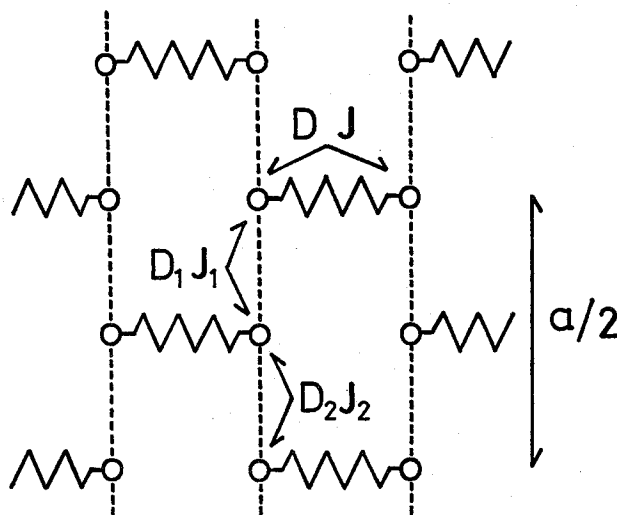


Fig. 2. Magnetic interactions in TEMPAD biradical. D and J mean intra-molecular dipolar and exchange interactions respectively. D_1 , J_1 , D_2 , and J_2 mean inter-molecular interactions. $\bigcirc$ in the figure represents N-O nitroxyl group in a molecule.

Table I. The Space Groups and the Lattice Constants for the Diamine and TEMPAD Biradical

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

the crystal parameters are almost the same with each other. This fact may promise a homogeneous mixing between the two molecules as is in fact expected in experimental results. Thus we can adopt the **a**-, **b**-, and **c**-axes as the rectangular coordinate systems for the pure and the diluted single crystals (see Fig. 3). Because of the lacking of the more definite crystallographic study, we have no information about the molecular stacking in a unit cell. However, from the EPR measurements mentioned later, we can find that the tensor of the intra-molecular dipole-dipole interaction has two principal axes (ρ and q sites). As the z -axis of the tensor of the intra-molecular dipole-dipole coupling is in the direction connecting two NO-bonds in a molecule, the TEMPAD molecule in a unit cell occupies two different sites.⁵⁾ A suitable molecular stack model is shown

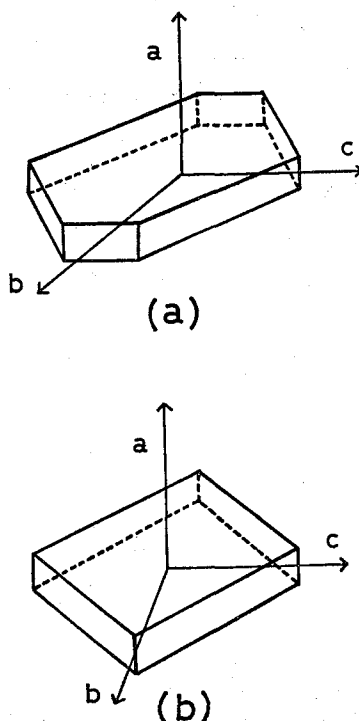


Fig. 3. Rectangular coordinate systems of the diamine host (a) and the TEMPAD crystal (b).

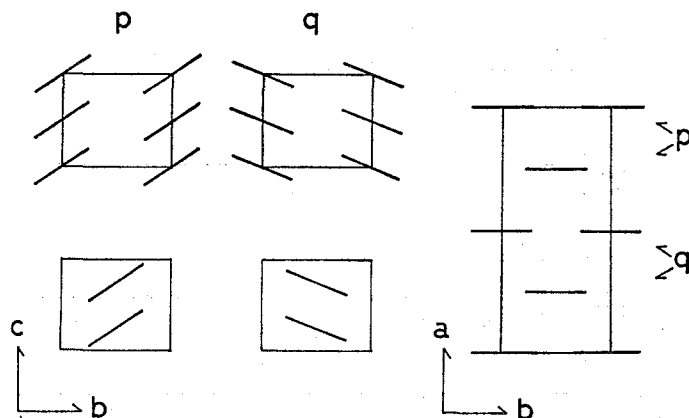


Fig. 4. Assumed stack model for the TEMPAD molecules in a unit cell. Each segment indicates the TEMPAD molecule and the angles from the **b**-axis are about 22.0° and -12.5° for the *p*- and *q*-sites, respectively.

in Fig. 4; each segment indicates the TEMPAD molecule, and the angles from the **b**-axis are about 22.0° and -12.5° for the *p*- and *q*-sites respectively. The distance between the two radicals in a molecule could be estimated from the relation $D \sim 3 \mu_B / R^3$, and then $R \sim 8.2 \text{ \AA}$. Thus, it may be reasonable that we can assume the magnetic interactions in TEMPAD biradical as is shown in Fig. 2.

Exchange Interactions in Biradical. The intra-molecular exchange interactions in biradical have connection closely with the EPR experiments in solutions. The spin Hamiltonian applied to nitroxide biradicals is

$$\mathcal{H} = g\mu_B H S_z + A(S_{1z} I_{1z} + S_{2z} I_{2z}) + 2|J|(S_1 \cdot S_2) \quad (6)$$

which is easily reduced from the general Hamiltonian Eq. (5), namely we can consider sufficiently the Zeeman, hyperfine, and intra-molecular exchange terms. The electron spin operators, S_i and S_{iz} , refer to an electron spin at the *i*-th side of the biradical; I_{iz} is the corresponding ^{14}N nuclear spin operator, then one can easily show the eigen values of Eq. (6) as

$$\begin{aligned} E_{+1}(m_1 m_2) &= g\mu_B H + |J|/2 + A(m_1 + m_2)/2 \\ E_{\pm 0}(m_1 m_2) &= -|J|/2 \pm |G|/2 \\ E_{-1}(m_1 m_2) &= -g\mu_B H + |J|/2 - A(m_1 + m_2)/2 \\ G^2 &= 4|J|^2 + A^2(m_1 - m_2)^2 \end{aligned} \quad (7)$$

and the theoretical EPR absorption energies and the relative intensities as

$$\begin{aligned} \text{(i) } m_1 \neq m_2 \\ W_{1\pm}(m_1 m_2) &= g\mu_B H + |J| + A(m_1 + m_2)/2 \mp |G|/2 \\ W_{2\pm}(m_1 m_2) &= g\mu_B H - |J| + A(m_1 + m_2)/2 \mp |G|/2 \\ \text{(relative intensity)} &= A^2(m_1 - m_2)^2 / (G^2 + 4|J||G|) \end{aligned} \quad (8)$$

$$\begin{aligned} \text{(ii) } m_1 = m_2 \\ W_3(m_1 m_2) &= g\mu_B H + A(m_1 + m_2) \\ \text{(relative intensity)} &= 1 \end{aligned} \quad (9)$$

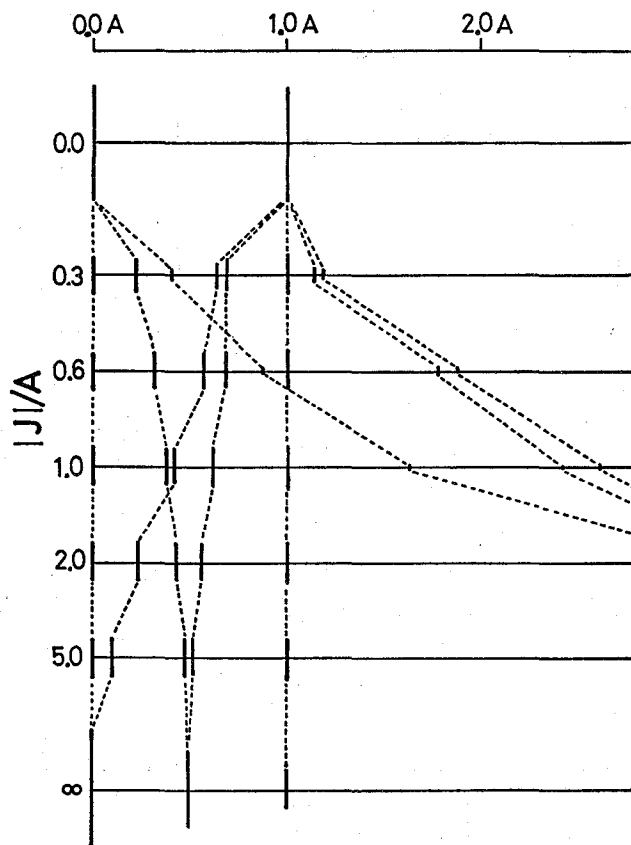


Fig. 5. The theoretical EPR absorption lines for the different values of $|J|/A$.

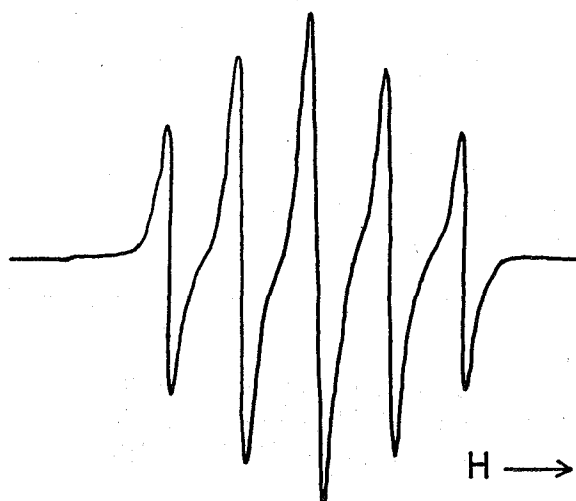


Fig. 6. The EPR spectrum of the TEMPAD biradical in THF solution.

The theoretical EPR absorption lines for various values $|J|/A$ are shown in Fig. 5.

The experimental EPR spectrum of the TEMPAD biradical in a tetrahydrofuran (THF) solution at room temperature⁹⁾ shown in Fig. 6 consists of five lines with an intensity ratio of 1 : 2 : 3 : 2 : 1. This result implies that the spectrum corresponds to the case of $|J| \gg A$. The linewidth of the center line, however, is considerably broader than that of the four side lines. This is caused by the incomplete superposition of the $W_{1\pm}(\pm 1, \mp 1)$, $W_{2\pm}(\pm 1, \mp 1)$, and $W_3(0, 0)$ lines. From the linewidth of the center line, we can estimate the exchange interaction parameter as $|J| \sim 10.0A$, that is, $|J|/k \sim 2 \times 10^{-3}K$ using $A = 15.0 \times 10^{-4}T$.

Next we can examine magnetic susceptibility measurements, which was first observed by Nakajima *et al.*⁷⁾ From 273 to 77 K the molar magnetic susceptibility, χ_M , obeys the Curie-Weiss law with the Weiss constant of -15 ± 2 K. Lowering the temperature furthermore, χ_M gradually deviates from the Curie-Weiss law and reaches a broad maximum, at the temperature $T_m = 16.5 \pm 0.5$ K. Then it rapidly decreases below T_m . This behavior can be explained on the basis of magnetic exchange interaction between unpaired electrons. Because the magnetic intra-molecular exchange interaction is less than 1 K, this interaction may be inter-molecular one, thus $J_1/k = -13.4$ K can be obtained by comparing χ_M with that of a Heisenberg-type pair cluster. The inter-molecular exchange interaction parameter may be also evaluated from the other model, the isotropic linear chain model,¹⁾ if we can assume the exchange interaction parameters J_1 and J_2 are nearly equal in the Fig. 2. Then $J_1/k = -12.9$ K or 15 K can be obtained from the experimental values T_m and the Weiss constant respectively. Here we can have no information about the intra-molecular exchange interaction J even though the temperature is lowered further.

In order to obtain some information about the intra-molecular exchange interaction, the magnetic susceptibilities were measured on the diluted samples,⁸⁾ then it shows two kinds of Weiss constant in the higher and lower temperature regions, which is shown

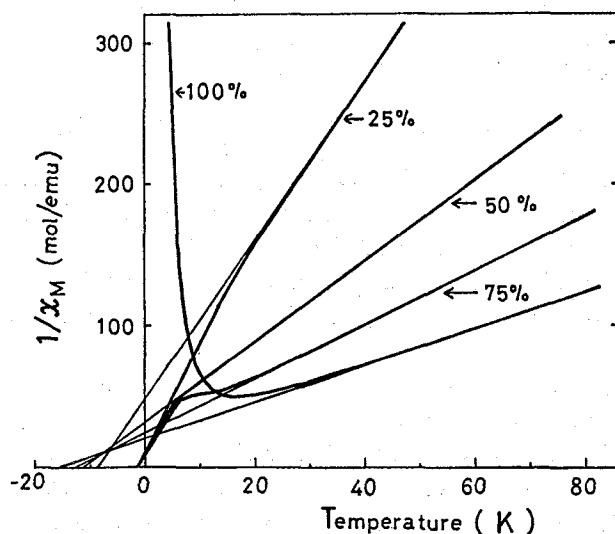


Fig. 7. Temperature dependence of the inverse paramagnetic susceptibilities of the diluted and pure crystals of TEMPAD.

Table II. The Experimental and the Theoretical Magnetic Constants for Each Concentration. The Latters are in the Case of $J_1/k = -12.8$ K and $|J|/|J_1| = 1/20$

n (%)	experimental				calculation	
	C_L	C_H	θ_L	θ_H	C_H	θ_H
25	0.131	0.181	-1.0	-8.5	0.189	-3.20
50	0.158	0.368	-1.0	-11.0	0.378	-5.25
75	0.146	0.537	-1.1	-12.5	0.574	-7.95
100	—	0.770	—	-15.0	0.772	-10.8

C_H and C_L : the paramagnetic Curie constants in the higher and lower temperature regions.

θ_H and θ_L : the Weiss constants in the higher and lower temperature regions.

in Fig. 7 and Table II. It should be noted that the diluted crystals less than 75% in concentration exhibit no maximum in the susceptibility, which may confirm that the magnetic exchange interaction which leads to a broad maximum in the susceptibility is the inter-molecular one, so that the absolute values of the Weiss constants become small as the radical concentrations decrease since the Weiss constant indicates the magnitude of the averaged exchange interaction among the coupled magnetic spins.

On the other hand, the Weiss constant θ_L at lower temperature region is of the order of magnitude of -1 K and roughly constant. In the diluted crystals of the TEMPAD biradical, we can assume that the biradicals are distributed randomly in the matrix of the diamine and that they form two portions magnetically different in microscopical scale; one is the isolated portion in which the weak intra-molecular exchange interaction exists alone, and the other is the clustering portion coupled by the strong inter-molecular exchange interaction besides the intra-molecular one. Then the paramagnetic susceptibility of the diluted crystals may be considered to be the superposition of the contributions from these two portions. If we adopt the pair model for the clustering portion and apply the Weiss molecular field approximation for the weak intra-molecular exchange interaction, the theoretical susceptibility can be calculated on the assumption of the following random distribution;

$$|J_1|\chi_M/N_0g^2\mu_B^2 = 2[n^2x/(3+e^{2x}) + n(1-n)x/4]/(1+|J|x/|J_1|) \quad (10)$$

where $x = |J_1|/kT$, N_0 the Avogadro number, and n the mole concentration of the biradical. The first term is the susceptibility of the pair model (the clustering portion) and the second term is that of the isolated portion. If we assume $J_1/k = -12.8$ K and $|J|/|J_1| = 1/20$, a good qualitative agreement with the experimental results can be obtained. Thus $J/k \sim 0.6$ K. The exchange interaction parameters are summarized in Table III.

The different J values between the results from the diluted EPR and the diluted susceptibility is slightly larger. This is possibly explained by whether or not we are observing intra-molecular exchange interaction itself or by the distinction of the molecular conformation between the solid and the dissolved states. The first reason is as follows. The magnitude of the Weiss constant θ_L comes collectively from the many kinds of weak exchange interactions, which take place by the diamagnetic dilution, but the contribution from the intra-molecular exchange interaction J must be contained and constant in

Table III. Intra- and Inter-Molecular Exchange Interaction Parameters

method of determination	$J/k(K)$	$J_1/k(K)$
EPR		
hyperfine	0.02	—
linewidth { Diluted	0.3 (25%)	—
Condensed	0.6 (100%)	—
Susceptibility		
T_m { pair model	—	—13.4
linear chain model	—	—12.9
θ_H { pair model	—	—30
linear chain model	—	—15
θ_L	0.6 (25%)	—12.8

magnitude. In the diluted limit we could have no contribution except the intra-molecular exchange interaction J . Thus we can assume averaged weak exchange interaction, which we observe in the susceptibility measurements of the diluted crystals. Considering the second reason, it is appropriate that the exchange parameters from the EPR measurements may be smaller because the exchange interactions in solution become weaker than in solid by the violent molecular motions. In the later section the EPR linewidth of the single crystal will be discussed, there we will obtain the weak exchange interaction J from the exchange field, which is also correlated to θ_L in the susceptibility, so again the above-mentioned discussions on the exchange interactions are applicable. It should be remarked here that the exchange interaction parameter obtained from the EPR linewidth in the nearly diluted limit (less than 2%) is smaller than that from the Weiss constant θ_L , whereas in the concentrated region above 25% the averaged exchange interaction is consistent in both experimental results. All things considered, we conclude discussions on the exchange interaction in TEMPAD biradical as to be $J_1/k = -13$ K, $J/k = 0.3$ K (in solid), and 0.02 K (in solution).

Dipolar Interactions in Biradical. In TEMPAD biradical the effect of dipolar interaction does not arise in susceptibility since the dipolar interaction is much smaller than the exchange interaction. EPR method is the most appropriate to observe the effect. In the usual EPR method, however, the dipolar splitting can not be observed because of the exchange interactions much larger than the dipolar interactions, so that there may be two methods for observing the dipolar interactions. The exchange effect in EPR can be reduced by diamagnetic dilution or lowering the triplet exciton density, namely lowering the temperature. Both of the method were performed.^{5,9)} On the intra-molecular dipole-dipole interactions, D , we can examine the EPR dipolar splitting in the very diluted case,⁵⁾ which is exhibited in Fig. 8. The principal values and the direction cosines of the intra-molecular dipolar interactions with regard to the **abc**-system is listed in Table IV. Here two groups of direction cosines were obtained, so that the TEMPAD molecules can have two sites in the crystals, that is, p - and q -sites.

Recently the present authors and others have a very detailed discussion on the dipolar interactions in TEMPAD¹⁰⁾ and obtained the several parameters, which is listed in Tables V and VI, where the maximum dipolar interaction can be obtained in the direction of **a**-axis,

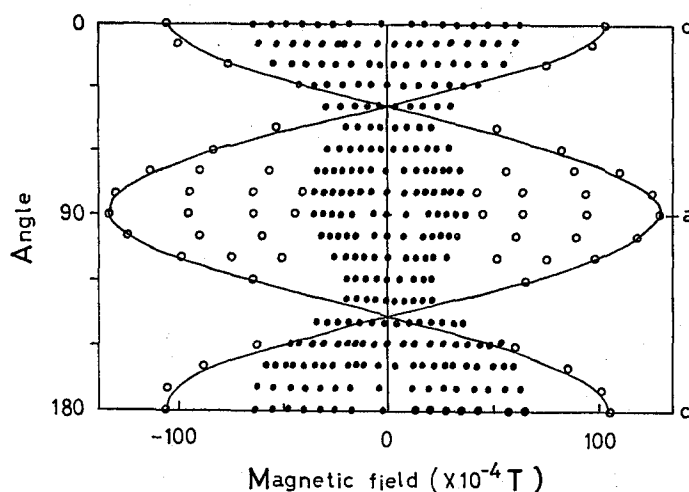


Fig. 8. Observed positions of EPR spectra in the **ca**-plane; ●: intra-molecular part, ○: inter-molecular part. The solid curves are the calculated angular variations for the inter-molecular dipolar interaction.

Table IV. The Principal Values and the Direction Cosines of the Tensor of the Intra-Molecular Dipole-Dipole Interaction with Regard to the **abc**-System

Principal Values		Direction Cosines		
		a	b	c
D_{xx}	$\pm(18.7 \pm 0.5) \times 10^{-4} \text{T}$	(<i>p</i>) 0.938	0.335	-0.094
		(<i>q</i>) 0.910	0.396	0.118
D_{yy}	$\pm(15.3 \pm 0.4)$	(<i>p</i>) -0.346	0.866	-0.361
		(<i>q</i>) -0.412	0.892	0.183
D_{zz}	$\mp(34.0 \pm 1.0)$	(<i>p</i>) -0.040	0.371	0.928
		(<i>q</i>) -0.033	-0.216	0.976
Crystal Field Parameters				
	$ D /g\mu_B$	$51.0 \pm 1.5 \times 10^{-4} \text{T}$		
	$ E /g\mu_B$	3.4 ± 0.9		

Table V. The Principal Values of the Tensor of the Inter-Molecular Dipole-Dipole Interaction with Regard to the **abc**-System and the Crystal Field Parameters

Principal Values		Crystal Field Parameters	
D_1^{xx}	$\pm 13 \times 10^{-4} \text{T}$	$ D_1 /g\mu_B$	$130 \times 10^{-4} \text{T}$
D_1^{yy}	± 73	$ E_1 /g\mu_B$	30
D_1^{zz}	∓ 86		

Magnetic Interactions in TEMPAD Biradical

Table VI. Dipolar Interactions in TEMPAD Biradical as the Splitting of the Spectrum at Each Orientation

Axis ($\parallel H$)	a	b	c
2% D_1	$264 \times 10^{-4} \text{T}$	$172 \times 10^{-4} \text{T}$	$208 \times 10^{-4} \text{T}$
D	55	40	106
25% D_1	263	—	—
D	—	—	106
100% D (4.2K)	—	—	60
D (1.7K)	—	65	73

D_1 : Inter-molecular dipolar coupling

D : Intra-molecular dipolar coupling

Table VII. Intra- and Inter-Molecular Dipolar Interaction Parameters

method of determination	D	D_1
EPR diluted (2%)	$51 \times 10^{-4} \text{T}$	$130 \times 10^{-4} \text{T}$
(25%)	51	130
linewidth (100%)	—	(130)
low temperature EPR		
single (1.7 K)	$37 \times 10^{-4} \text{T}$	—
powder (2.8 K)	38	—

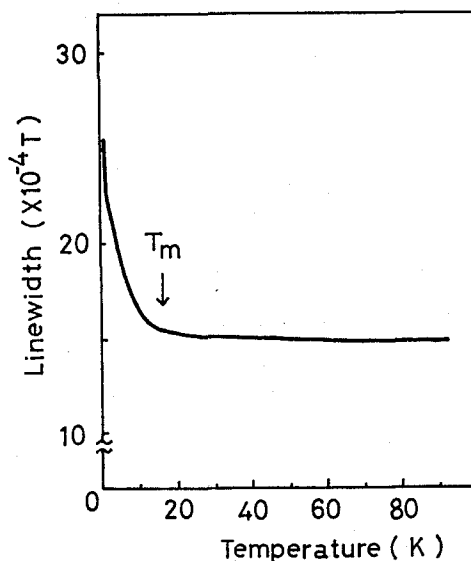


Fig. 9. Linewidth of the low temperature EPR of the TEMPAD biradical.
 T_m indicates the temperature where the susceptibility exhibits maximum.

corresponding to the maximum inter-molecular exchange interaction. Details should be referred to the literature. These values are classified as Table VII together with the results of low temperature EPR method. Until now, the inter-molecular dipolar interactions can not be obtained in the low temperature EPR method. As for the intra-

molecular dipolar interaction, there seems to be a slight discrepancy between the two methods. This may be attributed to the fact that the zero field splitting in the low temperature is not completely separated in the available temperature region on account of a very small amount of the triplet excitons present even in such a low temperature. This fact is also reasonable if we consider the temperature dependent D splitting along c -axis, namely $60 \times 10^{-4}T$ at 4.2 K and $73 \times 10^{-4}T$ at 1.7 K. In this sense the diluted EPR method is of great advantage over the low temperature EPR method, but it is true that the latter can give a strong supporting evidence.

EPR Linewidth. Both of the effects of the exchange and dipolar interactions appear in the EPR linewidth results. In the temperature dependence of the linewidth, the short range order by the exchange interaction J_1 first appears near the temperature T_m . The linewidths become large below T_m , and as the temperature is lowered further, it goes larger and larger, which may be due to the long time-correlation of the electron spins.¹⁾ The result of the

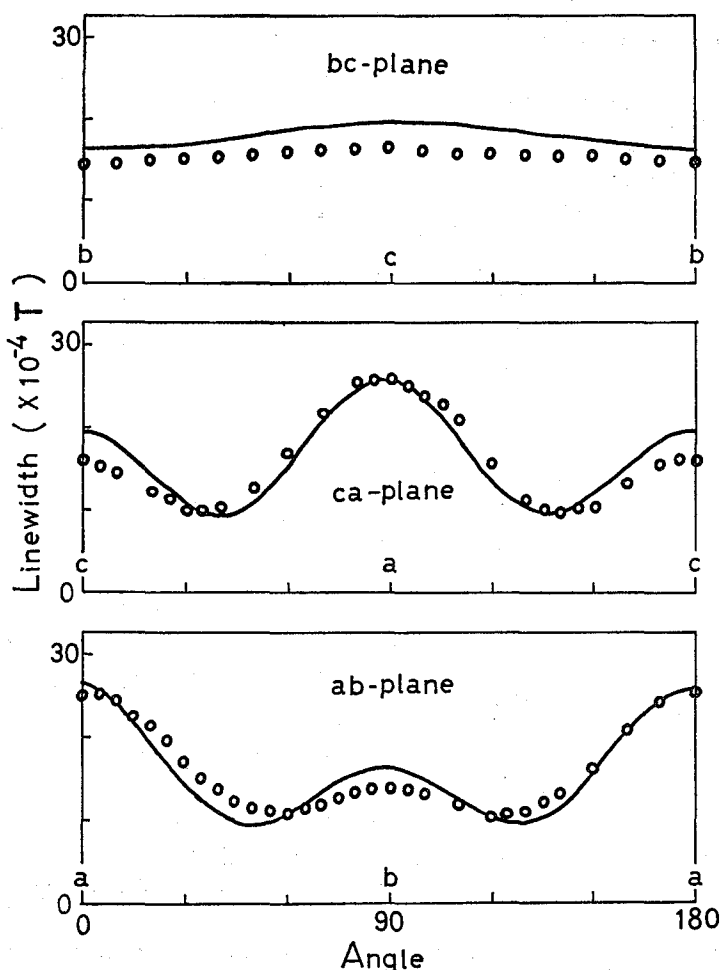


Fig. 10. The angular dependence of the EPR linewidth of the TEMPAD biradical. The solid curves are the calculated results using the three-dimensional Anderson-Weiss formula.

TEMPAD biradical is shown in Fig. 9. In the single crystal measurements the linewidth is expressed by three-dimensional Anderson-Weiss formula,¹¹⁾ that is,

$$\Delta H_{pp} = \Delta H_d^2 / \sqrt{3} H_{ex} + C \quad (11)$$

where ΔH_{pp} is the peak-to-peak linewidth, ΔH_d^2 , the second moment of the sum of the dipole-dipole interactions, H_{ex} , an effective exchange field, and C , a residual linewidth. As the angular dependence of the linewidth is smallest in the **bc**-plane, the inter-molecular dipole-dipole interaction along the **a**-axis is dominantly effective to the second moment. Therefore the secular part of the second moment was calculated using the term of the inter-molecular dipole-dipole interaction obtained from the spectra of the diluted crystal. On the above assumption on the dipolar term, we can explain the angular dependence quite well, as is shown in Fig. 10 by solid lines, with two adjustable parameters $H_{ex} = 4300 \times 10^{-4} \text{T}$ and $C = 9.5 \times 10^{-4} \text{T}$. H_{ex} can be related to the exchange interaction parameter J/k , which is estimated to be 0.6 K. This experiment can be also carried out in the 2% crystal. In this case J/k can be obtained to be 0.3 K. These values are also listed in Table III. Here we have concentration-dependent average J values such that J becomes small as the concentration decreases.

In conclusion we can say that for the study of magnetic interactions, especially in order to obtain magnetic interaction parameters, the susceptibility and EPR measurements must be carried out on both pure and diluted systems and both single and powder samples. Temperature variations are also effective in the EPR studies. In addition to these results, it is important to check the EPR linewidth because both of the interactions are inherent in the linewidth.

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REFERENCES

- (1) J. Yamauchi, *Bull. Chem. Soc. Japan*, **44**, 2301 (1971).
- (2) E. G. Rozantsev, "Free Nitroxyl Radicals", Plenum Press (1970).
- (3) R. Briere, R. M. Dupeyre, H. Lemaire, C. Morat, A. Rassat, and P. Rey, *Bull. Soc. Chim. Fr.*, **1965**, 3290.
- (4) M. Mekata, *J. Phys. Soc. Japan*, **17**, 796 (1962).
- (5) A. Nakajima, *Bull. Chem. Soc. Japan*, **46**, 1129 (1973).
- (6) A. Nakajima, H. O. Nishiguchi, and Y. Deguchi, *ibid.*, **45**, 713 (1972).
- (7) A. Nakajima, H. Nishiguchi, and Y. Deguchi, *J. Phys. Soc. Japan*, **24**, 1175 (1968).
- (8) A. Nakajima, *Bull. Chem. Soc. Japan*, **46**, 779 (1973).
- (9) J. Yamauchi, T. Fujito, A. Nakajima, H. O. Nishiguchi, and Y. Deguchi, *ibid.*, **44**, 2263 (1971).
- (10) A. Nakajima, J. Yamauchi, H. O. Nishiguchi, and Y. Deguchi, *ibid.*, **49**, 886 (1976).
- (11) T. Z. Huang, R. P. Tayler, and Z. G. Soos, *Phys. Rev. Letters*, **28**, 1054 (1972), P. W. Anderson and P. R. Weiss, *Rev. Mod. Phys.*, **25**, 269 (1953).