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Magnetic Properties of Some Iminoxyl Polyradicals. V. EPR Studies of the TEMPAD Biradical

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The EPR of pure and diluted crystals of bis(2,2,6,6-tetramethylpiperidine-4)azine-1,1′-dioxyl (the TEMPAD biradical) was studied. From the spectra of the diluted cyrstal, the intra- and inter-molecular dipole-dipole interactions were identified. The crystal-field parameters of the intra-molecular coupling determined for the EPR spectra were: $|D|/hc \simeq 0.00477\ \text{cm}^{-1}$ and $|E|/hc \simeq 0.00032\ \text{cm}^{-1}$ and two kinds of principal axes were found. As the z-axis of the intra-molecular dipole-dipole coupling is in the direction connecting two N–O bonds in a molecule, the TEMPAD molecules in a unit cell may be said to occupy two different sites. The crystal-field parameters of the inter-molecular dipole-dipole coupling were determined to be: $|D'|/hc \sim 0.012\ \text{cm}^{-1}$ and $|E'|/hc \sim 0.003\ \text{cm}^{-1}$ and the z-axis of the tensor was in the direction of the a-axis. The assumed molecular-stack model could account for the aforementioned results. The EPR spectra of the pure TEMPAD biradical are one symmetrical Lorentzian line in all the directions; the angular dependence of the peak-to-peak linewidths was explained by means of the term of the inter-molecular dipole-dipole interaction obtained from the spectra of the diluted crystal using the three-dimensional Anderson-Weiss formula. The exchange parameter for the best-fit curve was of the order of magnitude of the weak exchange interaction estimated roughly from the small Weiss constant appearing in the paramagnetic susceptibility of the diluted crystals.

There have been many investigations regarding the magnetic properties of organic, stable free-radical solids; they have been adequately discussed elsewhere.[1] In these works, some short-range ordering effects caused by the exchange interaction between unpaired electrons have been of special interest. On the other hand, the dipole-dipole interactions of organic free-radical solids have been little studied in spite of their importance for the spin correlation.

Recently, Takizawa *et al.* reported the EPR spectra of the radical pair of di-p-anisyl-nitric-oxide in the diamagnetic host, and assumed the structure of the radical pair in the host.[2] In the case of diluted biradicals, we can expect the existence of the intra- and inter-molecular radical pairs which will have an influence on the magnetic behavior of the dense system.

Previous magnetic studies of bis(2,2,6,6-tetramethylpiperidine-4)azine-1,1′-dioxyl (the TEMPAD biradical) have revealed two kinds of exchange interaction; one is the strong inter-molecular exchange interaction which produces the broad maximum in the paramagnetic susceptibility (χ_M) of the 100% case at the temperature of 16.5 K[3] and the large Weiss

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[1] A. Nakajima, H. Ohya-Nishiguchi, and Y. Deguchi, This Bulletin, **44**, 2120 (1971).

[2] O. Takizawa, J. Yamauchi, H. Ohya-Nishiguchi, and Y. Deguchi, to be published.

[3] A. Nakajima, H. Nishiguchi, and Y. Deguchi, *J. Phys. Soc. Jap.*, **24**, 1175 (1968).

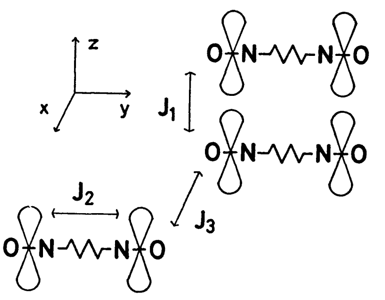

Fig. 1. Simplified molecular-stack model assumed from the χ_M-T results.

constant in the χ_M-T curves of the diluted crystals,[4] and the other is the weak intra-molecular exchange interaction which affects the hyperfine structure in the EPR spectrum in solution[5] and the small Weiss constant in the χ_M-T curves of the diluted crystals.[4] As the unpaired electron is localized around the N–O bond, the aforementioned results can be explained by the simplified molecular-stack model (shown in Fig. 1) on the basis of the localized spin treatment.[4] The EPR spectrum of the powdered TEMPAD biradical at room temperature was a symmetrical line, and new lines appeared on both sides of the central line at low temperatures. They have been explained in terms of the dipole-dipole interaction of the intra-molecular spin pair on the basis of the triplet exciton theory.[6]

In this paper, the author will report on his EPR studies of pure and diluted crystals of the TEMPAD biradical, determine the orientations of the intra- and inter-molecular radical pairs, and discuss the magnetic behavior of the dense system according to the assumed molecular-stack model.

Experimental

The TEMPAD biradical and bis(2,2,6,6-tetramethylpiperidine-4)azine (the diamine), which 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. following the method described by Rassat *et al.*[5,7] The single crystals of both the pure and diluted TEMPAD in the diamine host (less than 2 mol % in concentration) were crystallized from their ether solutions. The monoradical impurity, shown in Fig. 2(c), was formed in the diamine crystal by the air-oxidation, and its EPR spectra were used for the analysis of the hyperfine structure of the biradical spectra.[8]

The EPR measurements were carried out at room temperature using an X-band spectrometer, JEOLCO JES-ME-3X, equipped with a 100 kHz-field modulation for the first derivatives and an 80 Hz-field modulation for the second derivatives. As a standard sample, peroxylamine disulfonate, $[\cdot ON(SO_3)_2]^=$ ($A_N=13.0$ gauss and $g=2.00537$), was used. The mount for holding the crystals in the microwave cavity was made of Teflon, and it had a quartz rod; the crystals were fixed to the mount with silicon grease. The error in the measurements of the angle was about 2 degrees.

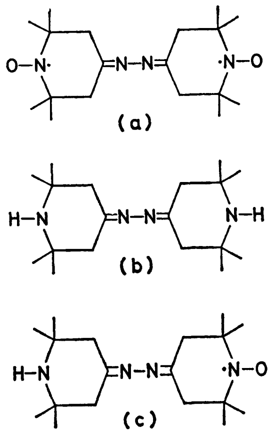

Fig. 2. Molecular structure of the TEMPAD biradical (a), the corresponding diamine (b), and the monoradical (c).

Results and Discussion

Diluted Crystal. The Hamiltonian of the biradical with a strong exchange interaction, introduced by Kurita,[9] is given by:

$$\mathcal{H} = \mathcal{H}_z + \mathcal{H}_{hf} + \mathcal{H}_{dip} + \mathcal{H}_{ex} + \mathcal{H}' \tag{1}$$

$$\mathcal{H}_z = \mu_B \sum_{ij} \bar{g}_{ij} H_i (S_{1j} + S_{2j}) \tag{2}$$

$$\mathcal{H}_{hf} = (1/2) g_0 \mu_B \sum_{ij} (A_{ij}^{I} I_j^{I} + A_{ij}^{II} I_j^{II})(S_{1i} + S_{2i}) \tag{3}$$

$$\mathcal{H}_{dip} = (4\mu_B{}^2/R^3)[(\boldsymbol{S}_1\cdot\boldsymbol{S}_2) - 3(\boldsymbol{S}_1\cdot\boldsymbol{R})(\boldsymbol{S}_2\cdot\boldsymbol{R})R^{-2}] \tag{4}$$

$$\mathcal{H}_{ex} = J(\boldsymbol{S}_1\cdot\boldsymbol{S}_2) \tag{5}$$

$\mathcal{H}'$: inter-molecular term

where μ_B is the Bohr magneton and where the other notations are all the same as in Kurita's equation except for the last inter-molecular term in Eq. (1). In the case of the orthorohmbic symmetry, the term of the intra-molecular dipole-dipole interaction (Eq. (4)) can be rewritten as follows:

$$\begin{aligned}\mathcal{H}_{dip} &= D_{xx}S_x{}^2 + D_{yy}S_y{}^2 + D_{zz}S_z{}^2 \\ &= D[S_z{}^2 - (1/3)S(S+1)] + E(S_x{}^2 - S_y{}^2)\end{aligned} \tag{6}$$

where $S_j = S_{1j} + S_{2j}$ $(j=x, y, \text{ and } z)$,

S is the eigen value of the total spin: $\boldsymbol{S}=\boldsymbol{S}_1+\boldsymbol{S}_2$,

$$D_{jj} = (1/2)g_0{}^2\mu_B{}^2\langle(R^2-3X_j{}^2)/R^5\rangle \quad (X_j = X, Y, \text{ and } Z) \tag{7}$$

$$D_{xx} = -D/3+E,\ D_{yy} = -D/3-E,\ D_{zz} = 2D/3 \tag{8}$$

where D and E are the crystal-field parameters of the biradical.

In a monoclinic crystal, some couples of sites exist in a unit cell and can be superposed upon each other by a symmetry transform of the crystal. When $\beta \simeq 90°$ in the case of the diamine host (see Table 1), we can adopt the *a*-, *b*-, and *c*-axes as the rectangular coordinate system (Fig. 3). Some typical EPR spectra with the static magnetic field at several orientations of the *ab*- and *ca*-planes are shown in Fig. 4. The observed positions of the EPR spectra in the *ca*-plane shown in Fig. 5 have two parts of the angular depend-

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[4] A. Nakajima, This Bulletin, **46**, 779 (1973).

[5] A. Nakajima, H. Ohya-Nishiguchi, and Y. Deguchi, This Bulletin, **45**, 712 (1972).

[6] J. Yamauchi, T. Fujito, A. Nakajima, H. Ohya-Nishiguchi, and Y. Deguchi, *ibid.*, **44**, 2263 (1971).

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[8] A. Nakajima, unpublished work.

Table 1. The space groups and the lattice constants for the diamine and the TEMPAD biradical

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

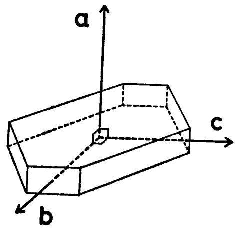

Fig. 3. System of the coordinates of the diamine host.

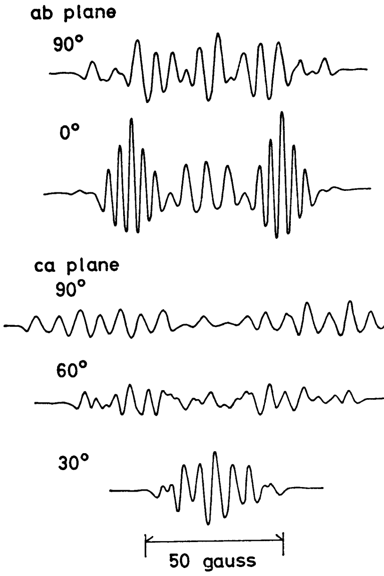

Fig. 4. Typical EPR spectra with the static magnetic field at some orientations in the *ab*- and *ca*-planes.

ence, namely, the intra- and the inter-molecular parts.

Intra-molecular Part: The g-value of the biradical is the mean-value, $\bar{g}_{ij}$, of the two radicals in a molecule.[9] As the angular dependence of the g-value is almost isotropic for the TEMPAD biradical, $\bar{g}_{ij}$ can be replaced by the $g_0=2.0060$ obtained from the EPR spectrum in solution. Although the principal axes of the tensor of the intra-molecular dipole-dipole interaction are nearly equal to those of the hyperfine tensor, it is difficult to analyze the spectra because of the complexity caused by the unequivalent molecules in a unit cell.

To solve this problem, the author chose the half-value of the hyperfine tensor of the monoradical formed

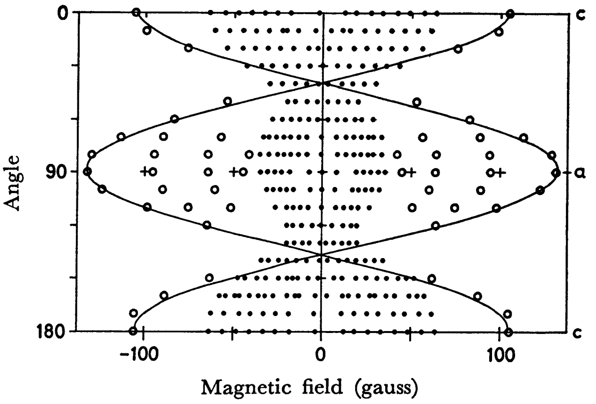

Fig. 5. Observed positions of the EPR spectra in the *ca*-plane; ●: intra-molecular part, ○: inter-molecular part. The solid curve is the calculated angular variation for the inter-molecular dipole-dipole interaction.

Table 2. 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}	$\pm(18.7\pm0.5)$	(p)	0.938	0.335	−0.094
	gauss	(q)	0.910	0.396	0.118
D_{yy}	$\pm(15.3\pm0.4)$	(p)	−0.346	0.866	−0.361
		(q)	−0.412	0.892	0.183
D_{zz}	$\mp(34.0\pm1.0)$	(p)	−0.040	0.371	0.928
		(q)	−0.033	−0.216	0.976
Crystal field parameter					
$\lvert D\rvert/g_0\mu_B$	51.0 ± 1.5 gauss				
$\lvert E\rvert/g_0\mu_B$	3.4 ± 0.9 gauss				

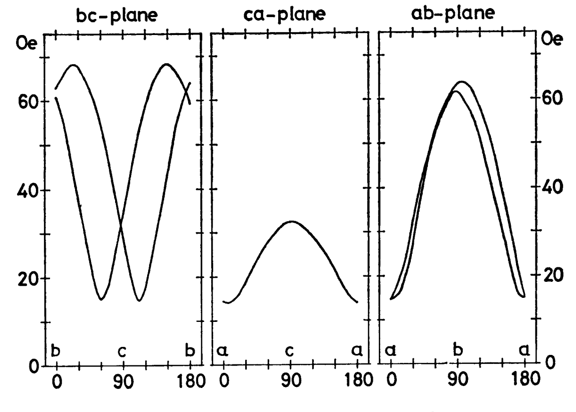

Fig. 6. Angular dependence of the hyperfine structure of the monoradical with regard to the abc-system.

in the diamine, as that of the biradical. The angular dependence of the hyperfine structure of the monoradical with regard to the *abc*-system is shown in Fig. 6.[8] Then, the principal values and the direction cosines of the tensor of the intra-molecular dipole-dipole interaction with regard to the *abc*-system, which are summarized in Table 2, could be determined. The calculated angular dependence on the *ca*-plane is shown in Fig. 7 in comparison with the experimental

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[9] Y. Kurita, *Nippon Kagaku Zasshi*, **85**, 833 (1964).

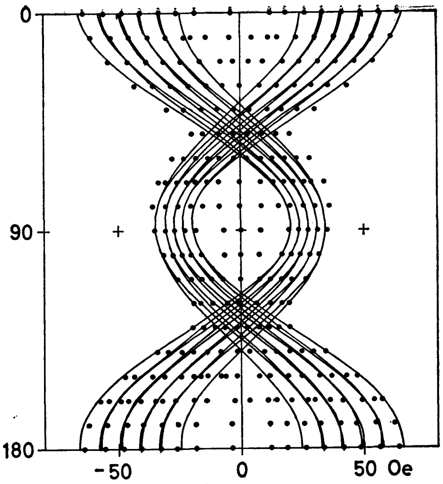
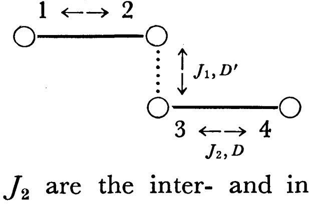


Fig. 7. Calculated angular dependence of the EPR spectra for the intra-molecular dipole-dipole interaction compared with the experimental results.

results. From Table 2 we can find that the tensor of the intra-molecular dipole-dipole interaction has two principal axes (p and q). As the z-axis of the tensor of the intra-molecular dipole-dipole coupling is in the direction connecting two N–O bonds in a molecule, the TEMPAD molecule in a unit cell occupies two different sites. A suitable molecular-stack model is shown in Fig. 8; each segment indicates the TEMPAD molecules, 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 equation: $|D| \sim 3\mu_B/R^3$, and then $R \sim 8.2$ Å.

Inter-molecular Part: Outside of the intra-molecular spectra broad lines appeared, apparently under the large field-modulation width (2—10 gauss). The angular dependence of the broad lines shown in Fig. 5 can be explained as a result of the inter-molecular dipole-dipole interaction between biradical molecules. According to the aforementioned molecular-stack model, the system of the coupled two biradicals can be shown as:



where J_1 and J_2 are the inter- and intra-molecular exchange interactions, and where D' and D are the inter- and intra-molecular dipole-dipole interactions. In the case of the TEMPAD biradical, $|J_1| \gg g_0\beta H_0 > |J_2| \simeq |D'| > |D|$; then, the spin Hamiltonian can be briefly given by:

$$\mathcal{H} \simeq g_0\beta \boldsymbol{H}_0\cdot(\boldsymbol{S}_0+\boldsymbol{S}_1+\boldsymbol{S}_4) + \boldsymbol{S}_0\cdot\boldsymbol{D}'\cdot\boldsymbol{S}_0 + \boldsymbol{S}_0\cdot\boldsymbol{D}\cdot(\boldsymbol{S}_1+\boldsymbol{S}_4) \tag{9}$$

where $\boldsymbol{S}_0 = \boldsymbol{S}_2 + \boldsymbol{S}_3$ and where $\boldsymbol{D}$ and $\boldsymbol{D}'$ are the tensors of the intra- and inter-molecular dipole-dipole interactions respectively. When $|D'| \gg |D|$, the system can be treated as one with one spin-pair (S_2 and S_3) and two monomers (S_1 and S_4). On this assumption, the principal values which are listed in Table 3 were roughly calculated: the z-axis of the tensor, $\boldsymbol{D}'$ was found to be in the direction of the a-axis. The calculated angular dependence, which is shown in Fig. 5, agreed with the experimental results except for the case of the ab-plane. The slight lack of agreement in the case of the ab-plane can be reduced by disregarding the $\boldsymbol{D}$-tensor. The distance between the radicals along the a-axis can be estimated from the value of D' at 6.0 Å, which agrees with the separation between the nearest neighbors in the direction of the a-axis, $a/4 = 7.2$ Å (Table 1).

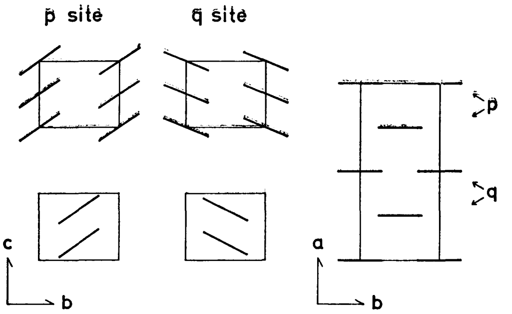


Fig. 8. Assumed stack model for the TEMPAD molecules in a unit cell. Each segment indicates the TEMPAD molecule and the angles from the b-axis are about 22.0° and $-12.0°$ for the p- and q- sites, respectively.

TABLE 3. 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'_{xx}	± 13 gauss	$\lvert D'\rvert/g_0\mu_B$	130 gauss
D'_{yy}	± 73	$\lvert E'\rvert/g_0\mu_B$	30
D'_{zz}	∓ 86		

The EPR spectra with the static magnetic field around the a-axis showed three other kinds of weak broad lines, which can be explained as dipole-dipole interactions among the next nearest and further neighbors. The distances of these couplings were roughly estimated to be 6.6, 7.5, and 8.5 Å respectively.

The obtained crystal-field parameters of the intra- and inter-molecular dipole-dipole interactions are summarized in Table 4 in comparison with those of other triplet states. The order of magnitude of our results was in the class of the thermally-excited triplets or of the radical pair.

Pure Crystal. As the crystal structure of the TEMPAD biradical is nearly equal to that of the diamine (see Table 1),[4] we can adopt the same a-, b-, and c-axes as the rectangular coordinate system as in the case of the diamine (Fig. 9). The EPR spectra of the TEMPAD biradical have one absorption line in all the directions, and the angular dependence of the g-value is almost the same isotropically as in the diluted crystal. The absorption lines are all symmetrical Lorentzian, and the peak-to-peak linewidths, shown in Fig. 10, varied with the static magnetic field in the bc-,

Table 4. The crystal field parameters of the intra- and the inter-molecular dipole-dipole itneractions of the TEMPAD compared with other triplet states

Triplet states	D/hc(cm^{-1})	E/hc(cm^{-1})	Ref.
((Biradical))			
TEMPAD (Intra)	± 0.00477	± 0.00032	This
(Inter)	± 0.012	± 0.003	Work
((Optically excited triplets))			
Naphthalene (Durene)	$+0.10119$	-0.01411	10
Quinoxaline (Durene)	± 0.1007	∓ 0.0182	11
((Ground state triplets))			
Diphenylmethylene (Benzophenone)	± 0.40505	∓ 0.01918	12
Fluorenilidene (Diazofluorene)	± 0.40923	∓ 0.02828	12
((Thermally excited triplets))			
$(\phi_3XCH_3)^+(TCNQ)_2^-$	0.0062	0.00098	13
$Cs_2^+(TCNQ)_3^{-2}$	± 0.00936	± 0.00151	14
[Morpholinium]$^+\cdot$ (TCNQ)$^-$	± 0.0148	± 0.00191	15
$(TMPD^+)_2\cdot$ $[Ni(nmt)_2]^{2-}$	± 0.0204	± 0.00266	16
((Radical pair))			
Dimethylglyoxime	0.0290	0.0	17

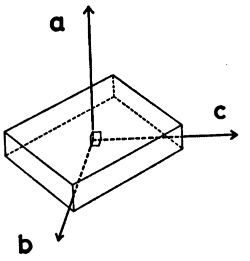


Fig. 9. System of the coordinates of the TEMPAD biradical same as the diamine host.

ca-, and *ab*-planes.

The strong inter-molecular exchange interaction (J_1 in Fig. 1), which determines the energy levels of the magnetic system, will never affect the linewidth. On the other hand the weak intra-molecular exchange interaction (J_2) will cause a narrowing of the linewidth. In the case of a narrowing, we can apply the usual three-dimensional Anderson-Weiss formula for a Lorentzian line:[18]

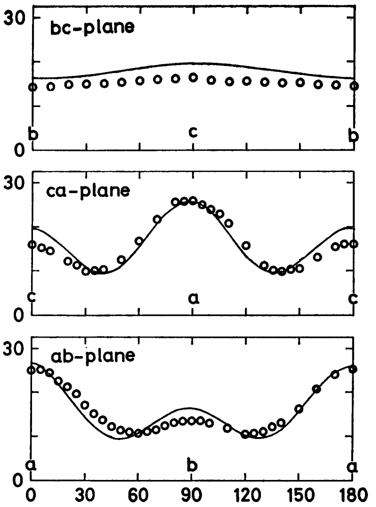


Fig. 10. The angular dependence of the EPR linewidths of the TEMPAD biradical. The solid curves are the calculated results using the three-dimensional Anderson-Weiss formula.

$$\Delta H_{pp} = \Delta H_d^2/\sqrt{3}H_{ex} + C, \qquad (10)$$

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 dominant in 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. In Eq. (10), two adjustable parameters, H_{ex} and C, were estimated to be 4300 and 9.5 gauss respectively. The calculated curves are also shown in Fig. 10. The value of H_{ex} ($\sim$0.6 K) was of about the same order of magnitude as the weak intra-molecular interaction, 1 K, estimated from the $\chi_M - T$ curve of the diluted TEMPAD biradical.[4] The residual linewidth, C, represents all the broadening mechanisms besides the secular part of the inter-molecular dipole-dipole interaction: (1) the non-secular part of the inter-molecular dipole-dipole coupling, (2) the residual nuclear hyperfine broadening, and (3) the intra-molecular or long-range dipole-dipole couplings.

Summary

The EPR of the diluted and pure crystals of the TEMPAD biradical was studied at room temperature. From the spectra of the diluted crystal, the intra- and inter-molecular dipole-dipole interactions were identified. The crystal-field parameters of the dipole-dipole couplings were obtained as:

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16) M. J. Hove, B. M. Hoffman, and J. A. Ibers, *ibid.*, **56**, 3490 (1972).

17) Y. Kurita, *ibid.*, **41**, 3926 (1964).

18) T. Z. Huang, R. P. Taylor, and Z. G. Soos, *Phys. Rev. Lett.*, **28**, 1054 (1972). See also the following paper as the original work; P. W. Anderson and P. R. Weiss, *Rev. Mod. Phys.*, **25**, 269 (1953).

a) Intra-molecular couplings:

$|D|/hc \simeq 0.00477\ \mathrm{cm}^{-1}$ and $|E|/hc \simeq 0.00032\ \mathrm{cm}^{-1}$,

b) Inter-molecular coupling:

$|D'|/hc \sim 0.012\ \mathrm{cm}^{-1}$ and $|E'|/hc \sim 0.003\ \mathrm{cm}^{-1}$.

In the assumed molecular-stack model, the TEMPAD molecules in a unit cell occupy two different sites (*p*- and *q*-sites), and the inter-molecular coupling is in the direction of the *a*-axis. The linewidth variation in the EPR spectra of the pure TEMPAD biradical could be explained in terms of the inter-molecular dipole-dipole interaction, using the three-dimensional Anderson-Weiss formula. The obtained exchange parameter was of the order of magnitude of the weak intra-molecular interaction estimated from the $\chi_M - T$ of the diluted TEMPAD biradical.

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