BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 713—716(1972)

Magnetic Properties of Some Iminoxyl Polyradicals. III.
Exchange Interaction in Iminoxyl Biradicals

Akira NAKAJIMA, Hiroaki OHYA-NISHIGUCHI, and Yasuo DEGUCHI*
Department of Chemistry, Faculty of Science, Kyoto University, Kyoto
**College of Liberal Arts and Science, Kyoto University, Kyoto*

(Received September 11, 1971)

The EPR spectra of TEMPAD and Sulfite biradicals in a dilute solution have been reasonably interpreted in terms of the variation in the ratio of the intra-molecular exchange interaction to the ^{14}N hyperfine interaction. Comparing these spectra with the theoretical ones, the authors have estimated the intra-molecular exchange interactions as $10.0\cdot A=2\times10^{-2}k$ and $3.0\cdot A=5\times10^{-3}k$ respectively. The magnetic susceptibility of the TEMPAD biradical exhibits a broad maximum at a temperature of 16.5°K, while 50 and 75% TEMPAD diluted in corresponding diamine have no maximum in the temperature range measured. The magnetic susceptibility of the sulfite biradical also shows a broad maximum at 15.0°K, in spite of the weak intra-molecular exchange interaction. These results indicate that the origin of the short-range ordering is the inter-molecular exchange interaction between unpaired electrons in different molecules.

There have been a number of investigations with regard to the magnetic properties of organic, stable free radical solids; these investigations will be adequately introduced elsewhere.1) In these works, some short-range ordering effects caused by the exchange interaction between unpaired electrons are of special interest. The mechanism of the exchange interaction, namely, intra- or inter-molecular exchange interaction, is also an interesting subject to us.1)

Previously, the present authors reported the magnetic susceptibility of bis(2,2,6,6-tetramethylpiperidine-4) azine-1,1′-dioxyl (the TEMPAD biradical), which indicates a broad maximum at 16.5°K. In order to explain this result, we assumed a thermal equilibrium between the singlet ground state and the excited triplet

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1) A. Nakajima, H. Ohya-Nishiguchi, and Y. Deguchi, This Bulletin, to be published.

state caused by the strong exchange interaction between the two unpaired spins in a molecule. On the basis of this model, one could estimate the exchange parameter as $J=-1.14\times10^{-3}$ eV;[2] however, we could find no evidence supporting the model.

On the other hand, recent EPR studies of other iminoxyl biradicals indicate fairly weak exchange interaction in a molecule which is of the same order as the hyperfine interaction.[3–5] These results are inconsistent with our estimation.

In order to clarify this discrepancy, one should take into account the existence of an inter-molecular exchange interaction in addition to an intra-molecular one. As for the experimental study of these two exchagne mechanisms, one must apply some techniques for the elimination of either intra- or inter-molecular exchange interaction. The present authors have made a couple of experiments along those lines: one of them was the dilution of TEMPAD in a diamagnetic matrix in order to decrease the inter-molecular exchange interaction, and the other was the study of other biradicals with a weak intra-molecular exchange interaction aimed at enhancing the inter-molecular exchange interaction.

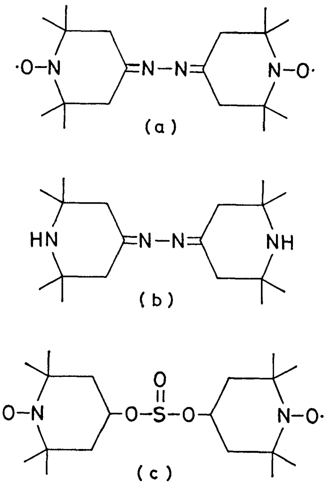

Fig. 1. Molecular structures of the TEMPAD biradical (a), the corresponding diamine (b), and the Sulfite biradical (c).

In this paper, the authors shall report the EPR spectra and the magnetic susceptibilities of the TEPMAD biradical (Fig. 1a) diluted in the corresponding diamine (Fig. 1b) and bis(2,2,6,6-tetramethylpiperidine-4)sulfite-1,1′-dioxyl (the sulfite biradical, Fig. 1c), which has a weak intra-molecular exchange interaction.[4]

Experimental

The TEMPAD biradical and the corresponding diamine were prepared from 2,2,6,6-tetramethyl-4-piperidone (triacetoneamine supplied by the Aldrich Chemicals Co.) following the method described by Rassat *et al.*[6] After purification by chromatography and recrystallization, pure diamine and TEMPAD (mp 139±0.5°C and 182±1.0°C) respectively were obtained. The sulfite biradical was prepared from the TANOL radical (2,2,6,6-tetramethyl-4-hydroxypiperidine-1-oxyl) obtained by the oxidation of the corresponding amine with hydrogen peroxide, following the process of Rozantsev *et al.*[4]

The EPR measurements were carried out using X-band spectrometers, JEOLCO's JES-3BX and JES-P-10, equipped with a 100-kHz field modulation. As a standard sample, peroxylamine disulfonate $[\cdot\mathrm{ON(SO_3)_2}]^{=}$ ($A_N=13.0$ gauss, $g=2.00537$) was used. In all the EPR measurements, the samples were degassed and sealed in glass tubes *in vacuo.*

The static magnetic susceptibility measurements were performed with powder samples of about 50—100 mg over the temperature range of 1.8—273 °K and in magnetic fields of 8—9 kOe, using a torsion balance which has been described elsewhere.[7] The temperature of the samples was determined by means of a Au·Co-Cu thermocouple and a carbon resister set on samples which had been calibrated by means of a standard sample, Mn-Tutton's salt. All the data were corrected for the diamagnetic contributions calculated by the Pascal method, *i.e.* $\chi_{\mathrm{dia}}=-2.37\times10^{-4}$ emu/mol for TEMPAD and $\chi_{\mathrm{dia}}=-2.62\times10^{-4}$ emu/mol for the sulfite biradical.

Results and Discussion

EPR Spectra. The spin Hamiltonian applied by Lemaire and his co-workers to nitroxide biradicals is:[5,6]

$$\mathscr{H}=g\beta H\cdot S_z+A(S_{1z}I_{1z}+S_{2z}I_{2z})+2|J|(S_1\cdot S_2). \qquad (1)$$

The Hamiltonian is expressed in units of h, and the three righthand terms correspond to the Zeeman, hyperfine, and exchange energies. The electron spin operators, $\boldsymbol{S}_i$ and $\boldsymbol{S}_{iz}$, refer to an electron spin wavefunction at the *i*-th side of the biradical; I_{iz} is the corresponding ^{14}N nuclaer spin operator, and $\boldsymbol{S}$ is the total electron spin operator. One can then show the eigen values of Eq. (1) as:

$$\begin{aligned}
E_{+1}(m_1m_2) &= g\beta H+|J|/2+(A/2)(m_1+m_2)\\
E_{\pm0}(m_1m_2) &= -|J|/2\pm(1/2)D\\
E_{-1}(m_1m_2) &= -g\beta H+|J|/2-(A/2)(m_1+m_2)\\
D^2 &= 4|J|^2+A^2(m_1-m_2)^2 \qquad (D>0) \qquad (2)
\end{aligned}$$

and the theoretical EPR absorption energies and the relative intensities as:

i) $m_1 \neq m_2$

$$\begin{aligned}
W_{1\pm}(m_1m_2) &= g\beta H+|J|+(A/2)(m_1+m_2)\mp(1/2)D\\
W_{2\pm}(m_1m_2) &= g\beta H-|J|+(A/2)(m_1+m_2)\pm(1/2)D\\
I_{i\pm} &= A^2(m_1-m_2)^2/(D^2+4|J|\cdot D) \qquad (3)
\end{aligned}$$

ii) $m_1 = m_2$

$$\begin{aligned}
W_3(m_1m_2) &= g\beta H+(A/2)(m_1+m_2) \qquad (4)\\
I &= 1
\end{aligned}$$

The theoretical EPR absorption lines for different values $|J|/A$ are of shown in Fig. 2.

The experimental EPR spectrum of the TEMPAD

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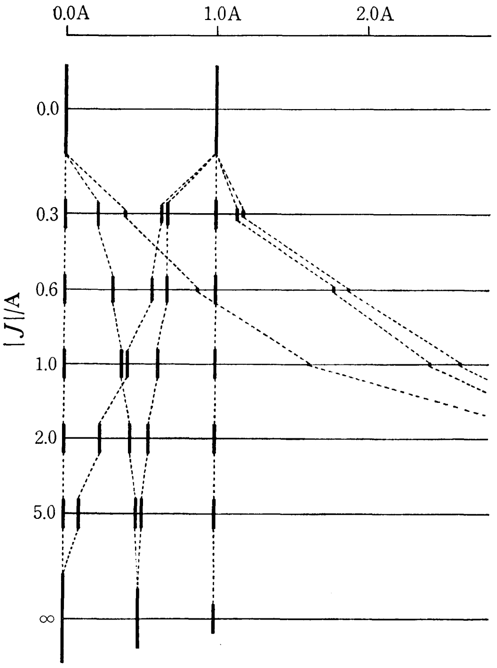

Fig. 2. The theroretical EPR absorption lines for the different values of $|J|/A$.

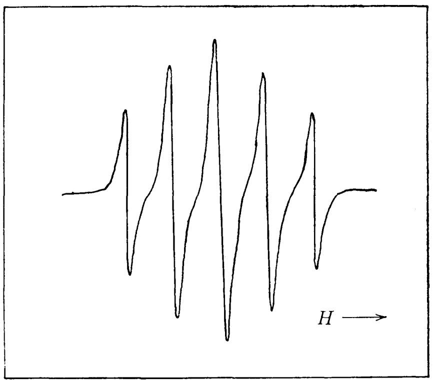

Fig. 3. The EPR spectrum of the TEMPAD biradical in THF solution.

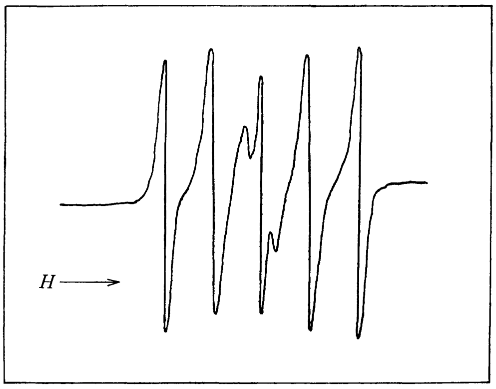

Fig. 4. The EPR spectrum of the Sulfite biradical in THF solution.

Table 1. Magnitude of the intra-molecular exchange interaction of some iminoxyl biradicals in the unit of the hyperfine energy, A.

Biradical	Solvent	Temperature	Magnitude	Reference
TEMPAD	THF	room temp.	10.0	our result
Sulfite	THF	room temp.	3.0	our result
	THF	20°C	2.8	4
Dimethyl-silicate	THF	20°C	1.7	4
Diphenyl-silicate	THF	20°C	6.0	4
Diallyl-silicate	THF	20°C	6.2	4
Carbonate	DMF	0°C	0.92	3
	DMF	−60°C	1.0	3
	n-Hexane	0°C	0.8	5
	CS_2	−100°C	1.1	5
Oxalate	CS_2	−60°C	0.15	5

biradical in a tetrahydrofurane (THF) solution at room temperature, as shown in Fig. 3, 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 line-width 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 line-width of the center line, one can estimate the exchange parameter as $|J| \simeq 10.0 \cdot A = 2 \times 10^{-2} k$ ($A =$ 15.0 gauss).

In the case of the sulfite biradical (see Fig. 4), the EPR spectrum consists seven lines, with an integrated intensity ratio of 1 : 2 : 1 : 1 : 2 : 1. This spectrum corresponds to the case of $|J| \sim A$; thus, the exchange energy can be estimated as $|J| \simeq 3.0 \cdot A = 5 \times 10^{-3} k$ ($A =$ 15.6 gauss).

The magnitudes of the intra-molecular exchange interaction estimated from the EPR spectra are listed in Table 1 in units of the hyperfine energy, A. From this table, one can understand that the $|J|$ magnitudes of these biradicals range from 10^{-4} to $10^{-2} k$, that is, that their intra-molecular exchange interactions are fairly weak compared with those estimated from the susceptibility measurements.

Magnetic Susceptibility. The magnetic susceptibility of the 100% TEMPAD biradical *versus* the temperature[1)] is shown in Fig. 5. From 273 to 77°K,

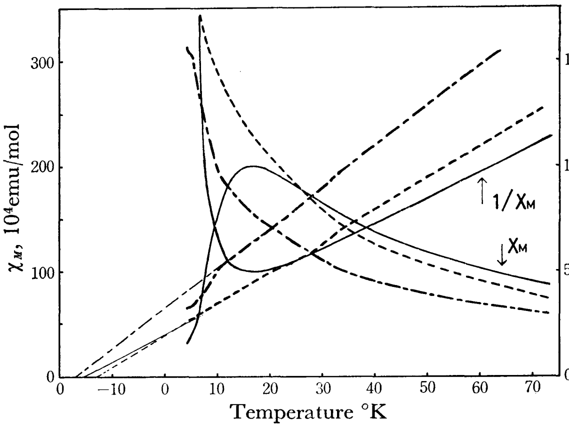

Fig. 5. Temperature dependence of the magnetic susceptibilities (χ_M) and their inverse ($1/\chi_M$) of the diluted TEMPAD biradical;
——: 100%, ----: 75%, and -—-: 50% TEMPAD.

χ_M increases paramagnetically with a decrease in the temperature and obeys the Curie-Weiss law: the Weiss constant is found to be about −15±2°K. When the temperature is lowered further, the χ_M-T curve gradually deviates from the Curie-Weiss law and shows a broad maximum at the temperature of 16.5±0.5°K. χ_M drops rapidly below that temperature. This behavior apparently suggests that a short-range ordering occurs as a result of the negative exchange interaction between unpaired electrons.

If one may apply some practical models, one can calculate the exchange interaction from three experimental values, *i.e.*, the temperature at the broad maximum, the value of χ_M at the broad maximum, and the Weiss constant. These values and the corresponding exchange parameters for the pair and the Ising linear-chain models are listed in Table 2.

The magnetic susceptibilities of 50 and 75% TEMPAD solid solutions diluted with the corresponding diamine, which are shown in Fig. 6, have been corrected for the diamagnetic contributions of the same value as that of the TEMPAD biradical. It should be noted that they show no maximum in the presently adopted temperature range and that their Weiss constants are nearly the same as that of 100% TEMPAD (−13°K for 75% and −16°K for 50%).

TABLE 2. SOME MAGNETIC CONSTANTS OF 100% TEMPAD BIRADICAL AND CORRESPONDING EXCHANGE PARAMETERS FOR THE PAIR AND THE ISING LINEAR-CHAIN MODELS

	Experimental results	Exchange parameter J (°K)	
		Pair	Ising L-C
T (χ_{max})	16.5±0.5°K	−13.4	−16.8
χ_{max}	200±10×10^{-4} emu	−15	−14
θ	−15±2°K	−30	−15

θ: the Weiss constant

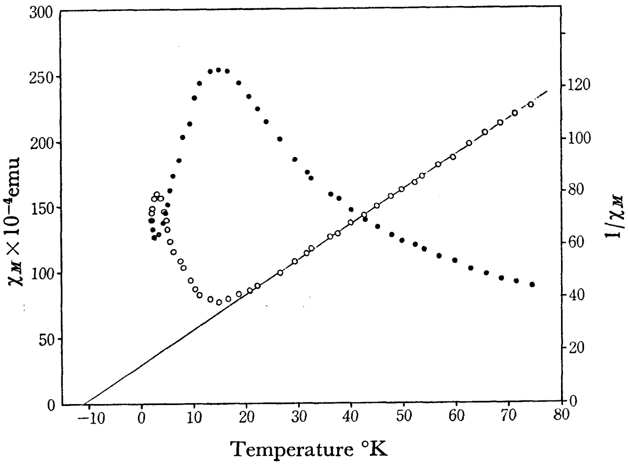

Fig. 6. Temperature dependence of the magnetic susceptibility of the Sulfite biradical;
●: χ_M, ○: $1/\chi_M$.

The diluted TEMPAD system, we can assume, will consist of two parts; inter-molecular dimers and isolated molecules. On this assumption, the paramagnetic susceptibility can be described as the superposition of these two parts; then, the Weiss constant obtained from the high-temperature region of the $1/\chi_M$-T curve may be to be contributed mainly by the intermolecular dimers. In the low-temperature region, these dimers almost entirely fall into the singlet ground state and the Curie constant is contributed to by only the isolated part. Our experimental results indicate these inclinations. The full details will be given in the following work.

TABLE 3. SOME MAGNETIC CONSTANTS OF SULFITE BIRADICAL AND CORRESPONDING EXCHANGE PARAMETERS FOR THE PAIR AND THE ISING LINEAR-CHAIN MODELS

	Experimental results	Exchange parameter J (°K)	
		Pair	Ising L-C
T (χ_{max})	15±1°K	−13	−15
χ_{max}	254±10×10^{-4} emu	−19	−18
θ	−11±2°K	−22	−11

θ: the Weiss constant

The magnetic susceptibility of the sulfite biradical shows nearly the same behavior as that of 100% TEMPAD except for the rapid increase below 3°K. In order to explain this behavior, the pair model and the Ising linear-chain model can be applied. The exchange parameters of the models estimated from a comparison with the experimental results are listed in Table 3. Scince the intra-molecular exchange interaction of the sulfite biradical is fairly weak ($5\times10^{-3}k$), the large exchange interaction appearing in the magnetic susceptibility must be attributed to the inter-molecular exchange interaction.

The authors are very much indebted to Professor Hideo Takaki for his continuing guidance and encouragement through this work. They also wish to thank Professor Mamoru Mekata, Dr. Jun Yamauchi, and their collaborators for their helpful advice and discussions.