TITLE:

Linear Antiferromagnetic Interaction in Organic Free Radicals(Dissertation_全文)

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CITATION:

Yamauchi, Jun. Linear Antiferromagnetic Interaction in Organic Free Radicals. 京都大学, 1971, 理学博士

ISSUE DATE:

1971-11-24

URL:

<https://doi.org/10.14989/doctor.r1878>

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學位申請論文

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主論文

Linear Antiferromagnetic Interaction in Organic Free Radicals

Linear Antiferromagnetic Interaction in Organic Free Radicals

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Synopsis

The static magnetic susceptibilities from 1.8°K to 300°K and ESR spectra from 1.5°K to 300°K of several organic free radicals have been measured on powder samples. The broad maxima in the susceptibility which indicate antiferromagnetic interaction and the broadening of ESR absorption lines have been observed. The data are analysed on the basis of the linear Heisenberg model and shown to be consistent with the one-dimensional magnetic chain model of isotropic exchange interaction. Discussions are made on the grounds of susceptibility, ESR, and specific heat measurements. In addition to a short range ordering of spins a possibility of long range ordering is also discussed in two radicals: BDPA-Bz and p-Cl-BDPA, on the basis of discontinuities of the slope of susceptibility, the rapid broadening of the ESR linewidth, and disappearance of the ESR absorption.

Introduction

Since the history of free radical chemistry dated from 1900 when Gomberg published his discovery of the first stable radical, triphenylmethyl,¹⁾ a number of stable radicals have been prepared and investigated by means of modern techniques.²⁾ It is now possible to detect, and even to study, extremely unstable free radicals. As it is our purpose to examine the exchange interaction between unpaired electrons, the present study is confined to the stable radicals which can be obtained in a substantial concentration. A free radical is, as is well known, an atom, molecule or complex which contains one or more unpaired electrons. In the present paper we are concerned exclusively with organic free radicals which have one unpaired electron on each molecule.

The magnetic properties of the organic free radicals have attracted much interest in recent years. Although the radical molecules constituting the solid are quite complicated, the solid itself can be simply regarded as an array of molecules each containing one unpaired electron in its highest filled orbital. The paramagnetic susceptibility is at first sight described by the Curie law: $\chi_0 = Ng^2 \beta^2 S(S+1)/3kT$, which can be applied to the radical solids with N spins of $S=1/2$. For all radicals measured in some temperature range above 77°K this simple relation does not hold and the deviation apparently can be explained by the Curie-Weiss law with negative Weiss constants which imply an antiferromagnetic exchange interaction.

between the unpaired electrons. Some of the ion radical salts and charge transfer complexes exhibit the anomalous paramagnetism which can be interpreted in terms of an exchange-coupled pair model.³⁾ This anomalous paramagnetism arises from strong exchange coupling between the unpaired electrons on adjacent molecules, each pair forming a lower singlet state and an upper triplet state. As temperature is lowered, the singlet level becomes increasingly populated at expense of the triplet level so that the susceptibility decreases. The susceptibility for singlet ground state dimers, each having a triplet state lying at an energy Δ above this ground state is given as

$$\chi = (Ng^2\beta^2 S(S+1)/3kT)[1 + (1/3)\exp(\Delta/kT)]^{-1} \quad (1)$$

where $S=1$. In the ion radical salts or charge transfer complexes the charged diamagnetic molecules may be considered to play an important role to form dimers. For simplification we limit ourselves to the radicals which are electrically neutral. The unpaired electron occupies a molecular orbital spreading over a whole molecular framework. According to the investigation of hyperfine splittings of nitroxide radicals like TANOL* the unpaired electron is exclusively localized on N-O bond.⁴⁾ On the other hand, BDPA** has the delocalized spin densities, even on the carbon atoms of biphenylene.⁵⁻⁵⁾ We studied the magnetic properties of two types of radicals in order to know how the exchange interaction between the unpaired electrons would be affected by the

*2,2,6,6-tetramethyl-4-piperidinol-1-oxyl

**1,3-bisdiphenylene-2-phenyl-allyl

delocalization of an unpaired electron. The stable radicals studied here are following compounds.

Fig. 1

In many stable neutral radicals the susceptibility deviates from the Curie-Weiss law at low temperatures and shows a broad maximum. Rozantsev et al. have observed the temperature dependence of the intensities of ESR spectra of TAROL and found a broad maximum in the intensities near 6°K .⁷⁾ The susceptibility was measured by several investigators⁸⁻⁹⁾ and a broad maximum at 5.5°K was found. They suggested that such a behavior of the paramagnet is well described by the Heisenberg one-dimensional model with isotropic antiferromagnetic interaction. The magnetic susceptibility of BDPA-Bz has been measured above liquid nitrogen temperatures by Duffy¹⁰⁾ and in the helium region by Edelstein et al. and by Fuke et al.¹¹⁾ Hamilton et al.¹²⁾ have used the proton Knight shift to measure the susceptibility and also measured the specific heat. They obtained the maximum susceptibility at 5.7°K and explained phenomena tentatively. However, the accuracy of ~~the mea~~ the measurements and the methods of analysis do not seem satisfactory.

Organic free radicals have plate-like structure of low symmetry and condense into a crystalline solid with a small coordination number, as is seen from X-ray analysis of several radicals.¹³⁻¹⁵⁾ Therefore, the radicals may form magnetic chain

or plane different from three-dimensionally interacting spin system. Since the distance between chains or planes is presumed much greater than the distance between nearest molecules in the chain or plane, the exchange coupling between nearest-neighbor electrons in different chains or planes is much weaker than that between nearest neighbor electrons in the same chain or plane. The orbital occupied by the unpaired electrons is $2p_z$ π -orbital which has a uniaxial angular dependence. Therefore, we conjecture that organic free radicals is likely to form "magnetic chain" rather than "magnetic plane".

From the theoretical point of view, the one-dimensional model of spin interaction is of considerable interest since it admits of an exact solution under certain simplifications which may actually be possible in some cases. The magnetic behaviors have several features different from those of the usual three-dimensional spin systems.

The susceptibility and ESR measurements of several neutral stable radicals using a magnetic torsion balance and an ESR spectrometer at low temperatures were carried out in order to examine the exchange interaction and spin correlation in organic free radicals and to compare the observed values with the theoretically calculated ones. A more quantitative interpretations of the magnetic behaviors will be made together with the data published previously.

Experimental

The radicals TANOL and its derivatives were prepared through the oxidation of the corresponding amine of 4-substituted 2,2,6,6-tetramethylpiperidine following the same process as that of Momantsev.¹⁶⁾ They were purified a few times through recrystallizing from ethereal alcohol. The details of the synthesis have been published elsewhere.¹⁷⁾ The samples of BDPA and its derivatives were prepared according to the procedures of Koelsh¹³⁾ and of Kuhn and Neugebauer.⁶⁾ After recrystallization from benzene-benzine solution melting points agreed well with the values in the literatures. Elementary analysis of carbon, hydrogen and nitrogen of each sample corresponded closely to the calculated values. As reported by Kuhn et al., the radical solid BDPA complexes readily with solvent molecules such as benzene and acetone. BDPA with 1 mole benzene will be, hereafter, abbreviated as BDPA-Bz and BDPA containing no benzene molecule as BDPA. BDPA-Bz was heated in vacuo at about 90°C for several hours and then BDPA was obtained. BDPA whose data have been published previously will be suspected to contain 1 mole crystal benzene.

The susceptibility measurements were done by the magnetic torsion balance described elsewhere¹⁹⁾ on the powder samples of about 100-50 mg in field of 8.8 KOe. The measurements on all samples were carried out in the temperature region attainable by pumping on liquid helium. The ferromagnetic impurities were not found on all samples by checking the field dependence of magnetization up to 12 KOe at 4.2°K. Temperatures were measured with a

carbon resistor and an AuCo-Cu thermocouple calibrated by measuring the magnetic susceptibility of manganese Eutton salt and vapor pressures of liquid helium, liquid hydrogen and liquid ~~nitrogen~~ nitrogen, respectively.

ESR absorption spectra were observed between 1.5°K and 77°K using JES-S10E type X-band spectrometer with an 30 Hz field modulation. The cavity with TE₁₀₂ mode was immersed in a liquid helium bath. Temperatures were measured with a carbon resistor and an AuCo-Cu thermocouple attached to the cavity wall. An aqueous solution of peroxyamine disulfonate was used as a standard for the estimation of g-value at room temperature. Magnetic field was calibrated from a hyperfine splitting of Mn⁺⁺ in MgO.

Results

Susceptibility. The data have been corrected for diamagnetism using Pascal's constants.²⁰⁾ The calculated diamagnetic contribution is listed in Table 1. The absolute molar susceptibility, χ_M , corrected for diamagnetism, was compared with various theoretical calculations. All radicals discussed here obey the Curie-Weiss law with a negative Weiss constant, Θ , in a relatively high temperature region. The radical concentration of each sample determined from the susceptibility was found out to be nearly 100 % within the limit of the experimental accuracy.

At lower temperatures the molar susceptibility, however, deviates from the Curie-Weiss law and reaches a broad maximum at the temperature, T_m . The values θ , T_m , and χ_{max} (a maximum susceptibility at T_m) of each sample are summarized in Table 1. On decreasing the temperature further, the susceptibility decreases comparatively slowly towards a finite susceptibility at $T=0^\circ K$, $\chi_{T=0}$. The values $\chi_{T=0}$ in Table 1 are roughly estimated by extrapolation of $\chi_{T=0}$ -T curve. Figs. 2-4 show molar susceptibilities of the radicals.

ESR. ESR measurements were carried out in powder samples. The g-values were practically isotropic and close to the free electron g-factor in all radicals, which is used in the theoretical calculation of susceptibility. ESR absorption spectrum in each sample shows a single line which has an exchange-narrowed Lorentz shape. The linewidth, which was taken to be the peak-to-peak linewidth of the first derivative of the absorption spectrum, started to increase rapidly as the temperature was decreased below T_m where the susceptibility went through a broad maximum. The ESR lines of the radicals except p-cl-BDPA* can be observed above the temperature $1.8^\circ K$ but the ESR line of p-Cl-BDPA broadens out and disappears as the temperature approaches to $2.8^\circ K$ from higher temperatures. Fig^s 5-7 show the temperature dependence of the linewidths of the radicals.

*1,3-bisdiphenylene-2-p-chlorophenyl-allyl

Discussion

Susceptibility. It may be conjectured that the neutral organic free radicals unlike ion radical salts have little tendency to form dimers. This fact is confirmed by comparison of the experimentally obtained susceptibility with that of the dimer model described by Eq. (1). If one would enumerate the energy separation between singlet and triplet states, Δ , of Eq. (1) from a following relation,

$$\Delta/k = 1.60T_m, \quad (2)$$

Eq. (1) will reproduce qualitatively the experimental results of susceptibility but the magnitude of paramagnetic susceptibility differs from the observed. The theory predicts much larger value, $\chi_{\max}$, at T_m than the observed one and besides a deviation of susceptibility becomes larger as decreasing the temperature below T_m . For instance, $\chi_{\max}$ in TANOL is equal to 226×10^{-4} emu/mol in contrast to the theoretical $\chi_{\max}$ 298×10^{-4} emu/mol calculated from Eqs. (1) and (2) using $T_m = 6.5^\circ\text{K}$. Therefore, it may be safely said that a pairing of electron spins in the radicals or a dimerization of molecules does not occur.

Edelstein has employed successfully the linear Ising model for the qualitative interpretation of the susceptibilities of BDPA-Bz and PAC.²¹⁾ Ising models are theories treating spatially localized spins between which the exchange coupling is represented as $-2JS_{1z}S_{2z}$. Although Stout and Chisholm have treated the small interactions between Ising chains in CuCl_2 by introducing a molecular field,²²⁾ organic free radicals have

never been observed to have so large anisotropic character. In fact all of organic free radicals have nearly isotropic g-values, so that the linear Ising model does not explain our results quantitatively. Therefore, we presume that it is not adequate to discuss the magnetic properties of organic free radicals on the basis of Ising models.

Soos et al. have analysed the temperature dependence of the magnetic susceptibility by treating the system as an alternating one-dimensional chain of Heisenberg spins;²³⁾ the Hamiltonian is given by

$$H = \sum \{ J(1+d)S_{2i-1}S_{2i} + J(1-d)S_{2i}S_{2i+1} \}, \quad (3)$$

where $J(1+d)$ and $J(1-d)$ are the exchange constants between neighboring spins and d is a parameter that represents a degree of alternation. The theoretical susceptibility results do not agree unfortunately with the more exact treatments for limiting cases of $d=1$ and $d=0$. Recently Duffy et al. obtained the exact eigenvalue spectrum and thermodynamic properties of the same Hamiltonian as Eq. (3) and made comparison with experiments.²⁴⁾ They fitted susceptibility data with success in ion radical salts, charge transfer complexes and only PAC and doubly nitrated DPPH among neutral radicals. When $d \neq 0$, that is, an intermediate alternation, there is an excited state with an energy gap from the ground state at $T=0^\circ\text{K}$ so that susceptibility decreases exponentially as $T \rightarrow 0^\circ\text{K}$. These schemes fail to explain a finite susceptibility at $T=0^\circ\text{K}$ unless $d=0$.

Previous to these works, theoretical calculations of the thermodynamic properties of one-dimensional long chains with

isotropic and anisotropic interactions have been done by Griffiths²⁵ and Bonner and Fisher.²⁶⁾ The corresponding spin Hamiltonian is given by

$$H = \sum \{ JS_{iz}S_{i+1z} + r(S_{ix}S_{i+1x} + S_{iy}S_{i+1y}) \}, \quad (4)$$

which reduces to the Ising case when $r=0$ and the Heisenberg case when $r=1$. Bonner and Fisher also estimated the behaviors of susceptibility and specific heat for $N \rightarrow \infty$. The susceptibility for pure antiferromagnetic Heisenberg chain displays a round maximum and corresponding specific heat exhibits the anomaly of Schottky type. One of the crystalline solids which clearly exhibit antiferromagnetic linear chain behaviors is $\text{Cu}(\text{NH}_3)_4\text{SO}_4 \cdot \text{H}_2\text{O}$, whose magnetic quantities can be explained qualitatively and also quantitatively in terms of this model since each Cu^{++} ion couples within a $-\text{O}-\text{Cu}-\text{O}-\text{Cu}-\text{O}-$ chain and interaction between chains are negligible.²⁷⁾

Organic free radicals have a plate-like structure of low symmetry with a small coordination number. Thus the radicals may be expected to form magnetic chains as is already described in the introduction. Therefore, it is reasonable to analyse and discuss the results using the theory of one-dimensional Heisenberg model based on Bonner and Fisher's calculations, which will be briefly summarized in the case of isotropic Heisenberg interaction with $r=1$ and $N \rightarrow \infty$ in Eq. (4). The susceptibility displays a rounded maximum of height

$$\chi_{\text{max}} / (g^2 \beta^2 / |J|) = 0.07346 \quad (5)$$

at $kT_m / |J| = 1.282. \quad (6)$

The corresponding specific heat shows a Schottky type anomaly associated with the broad susceptibility maximum and goes through the maximum of height

$$C_{\max}/Nk=0.350 \quad (7)$$

at $kT_{mc}/|J|=0.962. \quad (8)$

It is worth remarking that χ_M can approach a finite nonzero value $\chi_{T=0}$ at $T=0^\circ K$ as there is no energy gap between the ground state and the first excited states when $r=1$ and $N \rightarrow \infty$.

$\chi_{T=0}$ is given by the following relation with the parameter J ,

$$\chi_{T=0}/(g^2\beta^2/|J|)=0.05066. \quad (9)$$

One can obtain the parameter J in Eq. (4) from several relations (5), (6), (8) and (9). Assuming the value J from the experimentally obtained T_m with use of the relation (6), we evaluate the values χ_M , $\chi_{\max}$, and $\chi_{T=0}$, which are dependent on a manner of evaluation of J . On the other hand, ratios $\chi_{\max}/\chi_{T=0}$ and T_m/T_{mc} are independent of the parameter J and equal to 1.45 and 1.33, respectively.

TANOL system: The temperature dependence of the magnetic susceptibilities of TANOL and TADIN* have been reported by several investigators.^{2-9),23)} In the case of TANOL the exchange parameter was obtained as $|J|/k=5.0^\circ K$, which agrees well with the one from the relation $\theta = 2zJS(S+1)/3k$ with a nearest neighbor parameter $z=2$, $S=1/2$ and Weiss constant $\theta = -6.0^\circ K$. $\chi_{\max}$, 218×10^{-4} emu/mol, thus obtained from Eq. (5) is in good agreement with the

*2,2,5,6-tetramethylpiperidine-1-oxyl

experimental value, $\chi_{\max} = 226 \times 10^{-4}$ emu/mol. $\chi_{T=0}$ was then evaluated to be 130×10^{-4} emu/mol by extrapolation, while the same value is also expected from Eq. (9). The Heisenberg linear chain for $N \rightarrow \infty$ and $r=1$ predicts the theoretical ratio of $\chi_{\max}/\chi_{T=0} = 1.45$. On the other hand, the observed ratio, $\chi_{\max}/\chi_{T=0}$, is equal to 1.3 (Table 1), which is quite well in accord with the theory. It may be said, therefore, that spins in TANOL interact one-dimensionally with each other and the interaction is isotropic in the sense of Heisenberg exchange interaction. A precise determination of the crystallographic structure of TANOL is monoclinic: $a=7.052 \pm 0.010$ Å, $b=14.081 \pm 0.018$ Å, $c=5.730 \pm 0.010$ Å, and $\beta=118^\circ 40' \pm 10'$. The molecules are aggregated by the hydrogen bond and form chains parallel to a-axis.¹⁴⁾ However, it is difficult to conclude whether the direction of linear exchange interaction is along the direction of hydrogen bonding or along c-axis where the lattice constant is the shortest. We engage in clarifying this point in question.

The susceptibility of TADIN shows a broad maximum at $T_m = 2.3^\circ\text{K}$, after which χ_M decreases slowly towards constant susceptibility. $J/k = -1.8^\circ\text{K}$, which is obtained by following the same procedure mentioned above, reproduces well the experimental susceptibility χ_M , $\chi_{\max}$, and $\chi_{T=0}$. The ratio $\chi_{\max}/\chi_{T=0} = 1.3$ is also in good accord with the theory. Therefore, TADIN is considered to be one of the one-dimensional Heisenberg antiferromagnets.

The susceptibilities of TANOL derivatives (R=methyl, ethyl, phenyl, and cyclohexyl) in Fig. 1 exhibit no broad maxima in the temperature range as low as 1.3°K but deviate slightly from the Curie-Weiss law below 4°K. The Weiss constants were found to be about 0°K (methyl and ethyl derivatives), -1°K (phenyl derivative), and -2.5°K (cyclohexyl derivative). The bulkier substituent the radical has, the larger the Weiss constant becomes, but the exchange interaction are less than 1.5°K. The fact that TANOL has such a large exchange interaction as compared with those of TANOL derivatives may be ascribed to either the difference on lattice distance of the crystal axis along which the magnetic chains are formed or the difference in the strength of the hydrogen bond which was found out by infrared absorption spectra in nujol. The details of this ascription will be published elsewhere.²⁹⁾

BDPA system: The molar susceptibility of BDPA-Bz, shown in Fig. 3, exhibits a broad maximum at $T_m = 5.6^\circ\text{K}$. χ_{max} and $\chi_{T=0}$ are obtained to be 199 and 150×10^{-4} emu/mol, respectively. Considering $\chi_{\text{max}}/\chi_{T=0} = 1.3$ and the temperature dependence of the susceptibility at especially low temperature region, the data are also well explained in terms of the Hamiltonian ($N \rightarrow \infty$ and $r=1$) described above. Then we obtain $J/k = -4.4^\circ\text{K}$. If one excludes benzene molecules from BDPA-Bz by heating, the exchange interaction becomes larger from -4.4°K to -8.5°K . This radical, BDPA, also shows susceptibility decreasing towards a finite susceptibility at $T=0^\circ\text{K}$ after $T_m = 10.9^\circ\text{K}$. But ratio $\chi_{\text{max}}/\chi_{T=0} = 1.7$ is larger

than the theoretical one, since $\chi_{\max} = 153 \times 10^{-4}$ emu/mol is a little larger than the theoretical $\chi_{\max} = 130 \times 10^{-4}$ emu/mol. Thus BDPA has also the one-dimensional Heisenberg interaction like BDPA-Bz. This fact is understood by assuming that the removal of benzene molecules does not affect the spin structure in BDPA-Bz but causes the stronger exchange interaction.

The data of p-Cl-BDPA are similar to those of BDPA-Bz as shown in Fig. 4 and summarized in Table 1. Therefore, the magnetic properties of p-Cl-BDPA are similar to those of BDPA-Bz. However, a discontinuity in the slope of susceptibility was found at about 2.8°K, after which the susceptibility rises again. This rising in the susceptibility have also been found in the neighborhood of 1.7°K in BDPA-Bz.¹¹⁾ Such a discontinuity in p-Cl-BDPA indicates that there may be a phase transition into an antiferromagnetic state. This will be discussed together with the data of ESR measurement at a later part of the discussion.

In the magnetic properties of BDPA-Bz and p-Cl-BDPA there is a slight but significant difference between experiment and theory, that is, $\chi_{\max}$ is lower than the theoretically predicted one. At first sight, the radical concentration seems to become lower as lowering the temperature. At T_m an assumed concentration decreases to 80 % in both radicals. However, this is not due to a poor radical concentration as one can understand from the facts that 1) if the radical has low concentration, the amount of the deviation of susceptibility is constant in all temperature, 2) the radical concentrations of BDPA-Bz and p-Cl-BDPA are equal to about 100 % if we estimate from the susceptibility

above 77°K, 3) BDPA after heat treatment of BDPA-Bz has about 100 % radical concentration in all temperature ranges. Although this effect is not completely accountable at present, it may be associated with the electronic properties of allyl radicals which behave as semiconductors,³⁰⁾ as pointed out by Fedders and Kommandeur.³¹⁾

ESR. A distinct character of linear magnetic chains is the development of short range magnetic ordering without a definite transition to long range ordering at low temperature. The short range magnetic ordering developed remarkably near T_m can be observed in the increase of ESR linewidth below T_m . The data are illustrated in Figs. 5-7. The linewidth of each sample increases with lowering the temperature below T_m . Recently, temperature dependence of exchange narrowed ESR linewidth of linear anti-ferromagnetic chains with the anisotropic exchange coupling was calculated by Kawasaki, using double-time Green function method.³²⁾ She found a following relation,

$$\Delta H / \Delta H_{\infty} = AT^{-1/4} \quad (10)$$

in the vicinity of 0°K where ΔH_{∞} is the linewidth at infinite temperature and A is a constant. The observed linewidth versus temperature below 77°K can be fitted to a following empirical relation,

$$\Delta H = \alpha \exp(\beta T_m / T) \quad (11)$$

where α and β are constant and α may infer ΔH_{∞} . The values α and β of each sample are summarized in Table 2. We cannot fit the data with the relation (10) in a wide temperature region, even

when the other exponents are applied. The broadening of the resonance may be attributed to an increase in the correlation time of the exchange motion because of magnetic ordering below the temperature of the susceptibility maximum. This pronounced increase in linewidth of paramagnetic resonance provides an additional support for the present interpretation made from the susceptibility data.

In p-Cl-BDPA the relation (11) holds above 4°K . Intensities of ESR spectra decrease immediately below 4°K and simultaneously ESR linewidths broaden out. The disappearance and broadening of the lines may be attributed to the coupling between neighboring chains, which induces a spontaneous magnetization. This phenomenon may infer the onset of long range ordering, as it may be considered that the subsequent rapid increase of linewidth is due to the critical fluctuation of electron spins in the neighborhood of the transition temperature.

In the case of BDPA-Bz the ESR signal is so feeble that we cannot also observe an absorption at about 1.6°K . This fact is probably related with the specific heat anomaly at 1.78°K .¹²⁾ Specific heat. According to the specific heat measurements of TANOL³³⁾ and BDPA-Bz,¹²⁾ Schottky type anomalies associated with the broad maximum susceptibility have been obtained at 4°K and 3°K , respectively. The anomalies are predicted by the one-dimensional Heisenberg model. The maximum specific heat in TANOL is nearly what is expected by Heisenberg chains rather than Ising chains although in BDPA-Bz it is much smaller. The discrepancy in magnitude might be explained by assuming some type of elect-

ronic band structure.³¹⁾ The ratio of T_m to T_{mc} is unconnected with the exchange integral J and equal to 1.3 for Heisenberg chains and 2.4 for Ising chains. The observed $T_m/T_{mc}=1.6$ (TANOL) and 1.7(BDPA-Bz) deviate a little from the theoretically predicted one. The agreement with the theory is not so bad if one takes into account of the accuracy of T_{mc} . Thus, the results of specific heat measurements of TANOL and BDPA-Bz are not contradictory to the interpretation from the susceptibility measurements.

Other radicals. The magnetic properties of other radicals are briefly discussed below.

In porphyraxide the magnetic properties can be explained by the Ising model rather than the linear Heisenberg model.³⁴⁾ It is probably because the radical has a very small amount of anisotropy, which reduces the Heisenberg type magnetic properties to the Ising type ones. The effect of this anisotropy was found in the temperature dependence of ESR linewidth.³⁵⁾

The susceptibility data of DANO(di-p-anisyl-nitroxide) were shown by Duffy et al.³⁶⁾ to be consistent with the nearest neighbor antiferromagnetic Heisenberg exchange of a quadratic layer lattice because the radical is a magnetically layered crystal, as inferred from the X-ray crystallographic study of Hanson.¹³⁾ But as shown in Table 1, $\chi_{max}/\chi_{T=0}$ and T_m/T_{mc} ($T_{mc}=3^\circ\text{K}$) are in a completely good agreement with the linear Heisenberg model. This radical presumably has an one-dimensional interaction owing to the possibility for the radical to form

a magnetic chain instead of a magnetic quadratic layer. This may be understandable from taking into account that the molecular orbitals of the unpaired electrons have uniaxial angular dependence.

Exchange interaction mechanism. The exchange interaction originates from an overlap of the wave functions of the unpaired electrons. In compounds of transition ions, d-orbitals spread spatially towards a few directions so that magnetic planes can be formed. On the other hand, in organic free radicals the wave functions are described by p_z π -orbitals which have uniaxial angular dependence. The exchange mechanism may be such that the interaction between unpaired electrons takes place through the overlap of the π -orbitals as shown in Fig. 8. Therefore, it may be understood that the neutral organic free radicals are one-dimensional antiferromagnets.

Possible existence of long range ordering. It is well known from the theoretical point of view³⁷⁾ that the isolated magnetic linear chains have not any magnetic phase transition but the broad maximum susceptibility and that under the existence of the small interaction between chains there occurs the magnetic transition from the short range ordered state to the long range ordered state in the lower temperature region. A sharp cooperative transition in organic free radicals have never been observed, although phase transitions associated with crystal deformation were found.³⁸⁾ There is a possibility for neutral organic free radicals to go into a long range ordered state since the interaction between chains cannot always be neglected. The data

of BDPA-Bz and p-Cl-BDPA are considered to imply long range order at Néel temperatures 1.78°K and 2.8°K , respectively, because of 1) the discontinuities of $d\chi_M/dT$ found at 1.7°K in BDPA-Bz¹¹⁾ and 2.8°K in p-Cl-BDPA, 2) the rapid broadening and disappearance of ESR absorption lines, and 3) the specific heat anomaly at 1.78°K in BDPA-Bz.¹²⁾ The long range order in other radicals would be found if the experiments at lower temperatures were performed.

Conclusion

The magnetic properties of neutral organic free radicals were discussed qualitatively and quantitatively on the basis of the linear Heisenberg model from the followings: 1) qualitative behavior of χ_M , 2) χ_{max} at T_m , 3) finite $\chi_{T=0}$, 4) $\chi_{\text{max}}/\chi_{T=0}$, 5) Schottky type anomaly of specific heat, 6) T_m/T_{mc} , and 7) ESR linewidth. Although the interpretations may be tentative, except the cases of TANOL and BDPA-Bz, for lack of data from crystal structure and/or specific heat measurements, the data of magnetic susceptibility, ESR linewidth, and specific heat are consistent with the linear Heisenberg antiferromagnetic exchange model in neutral organic free radicals. In comparison with a strong at exchange interaction in a chain, the magnetic interaction between the chains is estimated to be very weak and so the neutral organic free radicals may be considered as one of the suitable crystals for studying the short range order effect of the magnetic transition process.

The author is much obliged to Professor H. Takaki and Professor Y. Deguchi for a continuous encouragement throughout this work and also indebted to Dr. H.O. Nishiguchi, Dr. M. Mekata and members of the laboratory for illuminating discussions. Thanks are also due to Mr. T. Fujito for a hearty cooperation in experiments.

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Figure Captions

Fig. 1 Molecular structures of the radicals.

Fig. 2 Magnetic molar susceptibilities of TANOL and TADIN.

Fig. 3 Magnetic molar susceptibilities of BDPA-Bz and BDPA.

Fig. 4 Magnetic molar susceptibility of p-Cl-BDPA.

Fig. 5 Linewidths of TANOL (•) and TADIN (o).

Fig. 6 Linewidths of BDPA-Bz and BDPA.

Fig. 7 Linewidth of p-Cl-BDPA.

Fig. 8 Presumed exchange interaction mechanism between the unpaired electrons localized on N-O bonds (A) and between the delocalized unpaired electrons (B).
— : radical molecule, : π electron cloud.

Table 1, Results from susceptibility measurements.

	χ_d (10^{-4} emu/mol)	θ (°K)	T_m (°K)	χ_{max} (10^{-4} emu/mol)	$\chi_{T=0}$ (10^{-4} emu/mol)	$\frac{\chi_{max}}{\chi_{T=0}}$	T, K (°K)
TANOL	-1.1	-6	6.5	226	180 ± 10	1.3	-5.0
TADIN	-1.1	-1	2.3	660	500 ± 50	1.3	-1.8
cyclohexyl TANOL	-1.8	-2.5	(1.5)	-	-	-	(-1)
BDPA-Bz	-3.2	-8	5.6	199	150 ± 10	1.3	-4.4
BDPA	-2.6	-8	10.9	153	90 ± 10	1.7	-8.5
p-Cl-BDFA	-2.8	-6	5.6	196	150 ± 10	1.3	-4.4
DANO ^{Ref. 36)}	-1.4	-3.4	4	287	200	1.4	-3.1

Table 2, Parameters of temperature dependent
 linewidth: $H = \alpha \exp(\beta T_m / T)$.

	T_m (°K)	α (Gauss)	β
TANOL	6.5	8.4	0.20
TADIN	2.3	8.2	0.48
BDPA-Bz	5.6	2.8	0.28
BDPA	10.9	3.5	0.49
p-Cl-BDPA	5.6	1.6	0.51

TADIN

TANOL

R-TANOL

PORPHYREXIDE

BDPA
BDPA-Bz

p-Cl-BDPA

DANO

Fig 1. 小内 導. 縮尺 $\frac{1}{2}$

Fig. 2 小分子 磁 鉄 $\frac{1}{2}$

Fig.3. 山内湾 磁化率

Fig. 4. 山内 淳 総 5/2

Fig.5. 山内 導 線 1/2

Fig.6 山内 導 線 Ⅱ

Fig. 7 山内 淳 紙 1

Fig. 8

參考論文

- 1 Magnetic Properties of Organic Stable Radicals 1.
2,2,6,6-tetramethyl-4-hydroxypiperidine-1-oxyl
- 2 Magnetic Properties of Organic Stable Radicals 2.
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- 3 Magnetic Properties of Organic Stable Radicals 3.
diphenyl nitric oxide
- 4 Electron Spin Resonance Studies of Diphenyl Nitric
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- 5 ESR Studies of Stable Free Radicals: 2,2,6,6-tetra-
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- 7 Dipolar Interaction in TEMPAD Biradical
- 8 Synthesis of Stable Free Radicals: 2,2,6,6-tetra-
methyl-4-hydroxypiperidine-1-oxyl-4-derivatives