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Linear Antiferromagnetic Interaction in Organic Free Radicals

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The static magnetic susceptibilities from 1.8°K to 300°K, and the 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 the antiferromagnetic interaction and the broadening of the 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 of the grounds of susceptibility, the ESR, and the specific heat measurements. In addition to a short-range ordering of spins, the possibility of long-range ordering is also discussed in two radicals, BDPA-Bz and *p*-Cl-BDPA, on the basis of discontinuities in the slope of susceptibility, the rapid broadening of the ESR linewidth, and the disappearance of the ESR absorption.

Since the beginning of the history of free radical chemistry in 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. At first sight it seems that the paramagnetic susceptibility can be described by the Curie law: $\chi_c = Ng^2\beta^2S(S+1)/3kT$, which can be applied to the radical solids with N spins of $S=1/2$. For all radicals measured above 77°K, however, this simple relation does not hold; 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 an 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 the temperature is lowered, the singlet level becomes increasingly populated at the expense of the triplet level, so that the susceptibility decreases. The molar susceptibility for the singlet ground state dimers, each having a triplet state lying at an energy, Δ, above this ground state, is given as:

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

where $S=1$. In the ion-radical salts or charge-transfer complexes, the charged diamagnetic molecules may be considered to play an important role in forming dimers. For the sake of simplicity, we will 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 the hyperfine splittings of nitroxide radicals

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[1] M. Gomberg, *J. Amer. Chem. Soc.*, **22**, 757 (1900); *Ber.*, **33**, 3150 (1900).

[2] See for example, D. J. E. Ingram, "Free Radicals as Studied by ESR" Butterworths, (London) (1958); A. R. Forrester, J. M. Hay, and R. H. Thomson, "Organic Chemistry of Stable Free Radicals" Academic Press, (London) (1968).

[3] H. Nishiguchi, This Bulletin, **40**, 1587 (1967); Y. Sato, M. Kinoshita, M. Sano, and H. Akamatu, *ibid.*, **40**, 2539 (1967); **42**, 3051 (1969); D. B. Chesnut and W. D. Phillips, *J. Chem. Phys.*, **35**, 1002 (1961).

like TANOL,[4] the unpaired electron is exclusively localized on the N–O bond.[5] On the other hand, BDPA[6] has delocalized spin densities, even on the carbon atoms of biphenylene.[7,8] We studied the magnetic properties of two types of radicals in order to ascertain how the exchange interaction between the unpaired electrons would be affected by the delocalization of an unpaired electron. The stable radicals studied here are the following compounds.

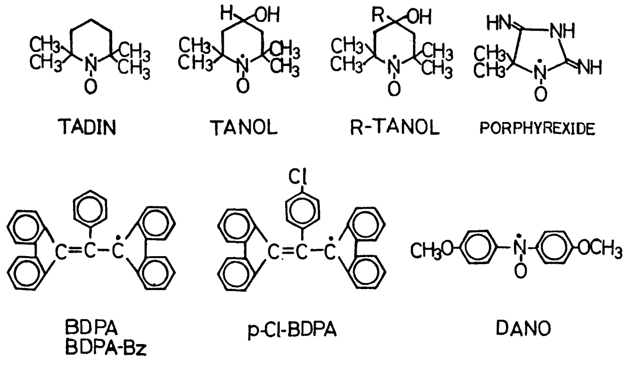

Fig. 1. Molecular structures of the radicals.

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 the ESR spectra of TANOL and found a broad maximum in the intensities near 6°K.[9] The susceptibility had previously been measured by several investigators,[10,11] and a broad maximum at 6.5°K had been found. They suggested that this behavior of the paramagnet could be well described by the Heisenberg one-dimensional model with isotropic antiferromagnetic interaction. The magnetic susceptibility of BDPA-Bz has been measured above the temperature of liquid nitrogen by Duffy[12] and in the helium region by Edelstein *et al.* and by Pake *et al.*[13] Hamilton *et al.*[14] 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 the phenomena tentatively. However, the accuracy of the measurements and the methods of analysis do not seem satisfactory.

Organic free radicals have plate-like structure of a low symmetry and condense into a crystalline solid with a small coordination number, as may be seen from the X-ray analysis of several radicals.[15–17] Therefore, the radicals may form a magnetic chain or plane different from that of the three-dimensionally interacting spin system. Since the distance between chains or planes is presumed to be 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 the $2P_z\pi$-orbital, which has a uniaxial angular dependence. Therefore, we conjecture that organic free radicals are more likely to form a "magnetic chain" than a "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 are actually possible in some cases. The magnetic behavior has several features different from that of 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 in order to compare the observed values with the theoretically calculated ones. Later, more quantitative interpretations of the magnetic behavior will be made using the data published previously.

Experimental

The radical TANOL and its derivatives were prepared through the oxidation of the corresponding amine of 4-substituted 2,2,6,6-teramethylpiperidine following the process of Rozantsev.[18] They were purified a few times through recrystallization from ethereal alcohol. The details of the synthesis have been published elsewhere.[19] The samples of BDPA and its derivatives were prepared according to the procedures of Koelsch[20] and of Kuhn and Neugebauer.[8] After recrystallization from a benzene-benzine solutions, the melting points were found to agree well with the values in the literature. The results of the 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 such solvent molecules as benzene and acetone. BDPA with 1 mol of benzene will hereafter be 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; BDPA was thus obtained. BDPA, whose data have been published previously, is suspected to contain 1 mol of crystal benzene.

The susceptibility measurements were done, by means of a magnetic torsion balance described elsewhere,[21] on powder

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[4] 2,2,6,6-tetramethyl-4-piperidinol-1-oxyl.

[5] R. Briere, H. Lemaire, and A. Rassat, *Bull. Soc. Chim. Fr.*, **1965** 3273; E. G. Rozantsev and M. B. Neiman, *Tetrahedron*, **20**, 131 (1964).

[6] 1,3-bisdiphenylene-2-phenyl-allyl.

[7] K. H. Hausser, *Z. Naturforsch.*, **14a**, 425 (1959).

[8] R. Kuhn and F. A. Neugebauer, *Monatsh.*, **95**, 3 (1964).

[9] Yu. S. Karimov and E. G. Rozantsev, *Soviet Physics-Solid State*, **8**, 2255 (1967).

[10] J. Yamauchi, T. Fujito, E. Ando, H. Nishiguchi, and Y. Deguchi, *J. Phys. Soc. Japan*, **25**, 1558 (1968).

[11] Yu. S. Karimov, *JETP Lett.*, **8**, 145 (1968).

[12] W. Duffy, Jr., *J. Chem. Phys.*, **36**, 490 (1962).

[13] J. H. Burgess, R. S. Rhodes, M. Mandel, and A. S. Edelstein, *J. Appl. Phys.*, **33**, 1352 (1962); M. E. Anderson, R. S. Rhodes, and G. E. Pake, *J. Chem. Phys.*, **35**, 1527 (1961).

[14] W. O. Hamilton and G. E. Pake, *J. Chem. Phys.*, **39**, 2694 (1963).

[15] A. W. Hanson, *Acta Cryst.*, **6**, 32 (1953).

[16] J. Lajzerowicz-Bonneteau, *ibid.*, **B24**, 196 (1968).

[17] P. Anderson and B. Klewe, *Acta Chem. Scand.*, **21**, 2599 (1967); D. E. William, *J. Amer. Chem. Soc.*, **91**, 1243 (1969).

[18] E. G. Rozantsev, *Izv. Akad. Nauk SSSR, ser. khim.*, **12**, 2218 (1964).

[19] K. Watanabe, J. Yamauchi, H. Takaki, H. Nishiguchi, and Y. Deguchi, *Bull. Inst. Chem. Res.* (Kyoto Univ.), **48**, 88 (1970).

[20] C. F. Koelsch, *J. Amer. Chem. Soc.*, **79**, 4439 (1957).

[21] M. Mekata, *J. Phys. Soc. Japan*, **17**, 796 (1962).

Table 1. Results from susceptibility measurements

	χ_d (10^{-4} emu/mol)	θ (°K)	T_m (°K)	$\chi_{\max}$ (10^{-4} emu/mol)	$\chi_{T=0}$ (10^{-4}emu/mol)	$\chi_{\max}/\chi_{T=0}$	J/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-BDPA	−2.8	−6	5.6	196	150±10	1.3	−4.4
DANO[40]	−1.4	−3.4	4	287	200	1.4	−3.1

samples of about 100—50 mg in a field of 8.8 KOe. The measurements on all the samples were carried out in the temperature region attainable by pumping of liquid helium. No ferromagnetic impurities were found in any samples by checking the field dependence of magnetization up to 12 KOe at 4.2°K. The temperatures were measured with a carbon resister and an AuCo-Cu thermocouple calibrated by measuring the magnetic susceptibility of manganese Tutton salt and the vapor pressures of liquid helium, liquid hydrogen, and liquid nitrogen.

The ESR absorption spectra were observed between 1.5°K and 77°K using a JES-S1OE-type X-band spectrometer with an 80 Hz field modulation. The cavity with the TE_{102} mode was immersed in a liquid helium bath. The temperatures were measured with a carbon resister and an AuCo-Cu thermocouple attached to the cavity wall. An aqueous solution of peroxylamine disulfonate was used as a standard for the estimation of the *g*-value at room temperature. The magnetic field was calibrated from a hyperfine splitting of Mn^{2+} in MgO.

Results

Susceptibility. The data have been corrected for diamagnetism using Pascal's constants.[22] 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 the 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, as determined from the susceptibility, was found to be nearly 100% within the limit of experimental accuracy. At lower temperatures, the molar susceptibility, however, deviates from the Curie-Weiss law and reaches a broad maximum at the T_m temperature. The values θ, T_m, and $\chi_{\max}$ (the maximum susceptibility at T_m) of each sample are summarized in Table 1. When the temperature is decreased further, the susceptibility decreases comparatively slowly towards a finite susceptibility at $T=0$°K, $\chi_{T=0}$. The values $\chi_{T=0}$ in Table 1 are roughly estimated by the extrapolation of the χ_M-T curve. Figures 2—4 show the molar susceptibilities of the radicals.

ESR. ESR measurements were carried out in powder samples. The *g*-values were practically isotropic and were close to the free electron *g*-factor in all radicals; the latter factor is used in the theoretical

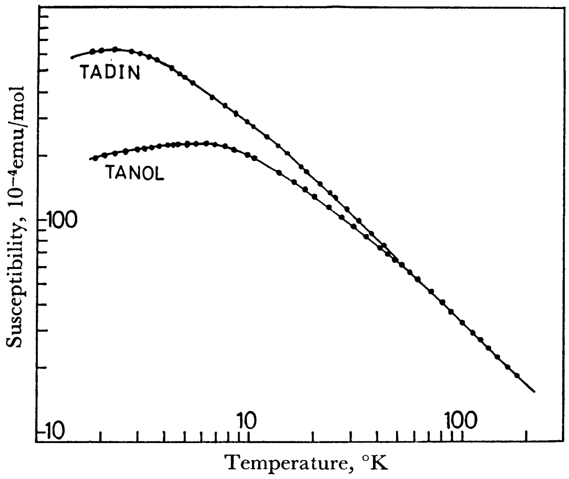

Fig. 2. Magnetic molar susceptibilities of TANOL and TADIN.

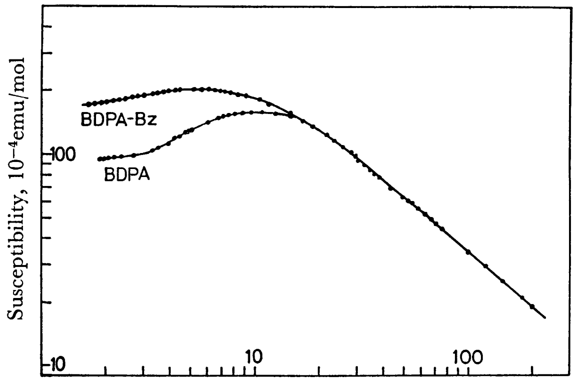

Fig. 3. Magnetic molar susceptibilities of BDPA-Bz and BDPA.

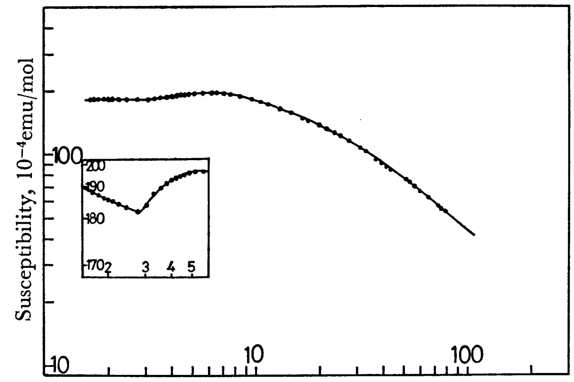

Fig. 4. Magnetic molar susceptibility of *p*-Cl-BDPA.

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[22] P. W. Selwood, "Magnetochemistry," Interscience Publisher, New York (1956).

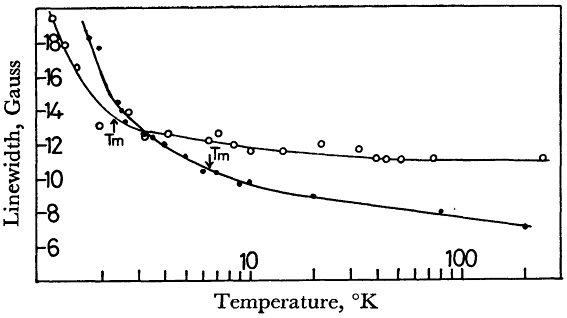

Fig. 5. Linewidths of TANOL (●) and TADIN (○).

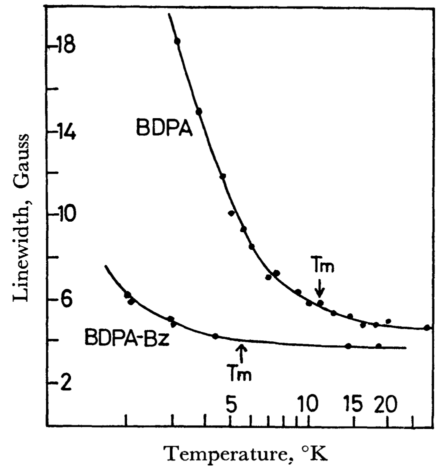

Fig. 6. Linewidth of BDPA-Bz and BDPA.

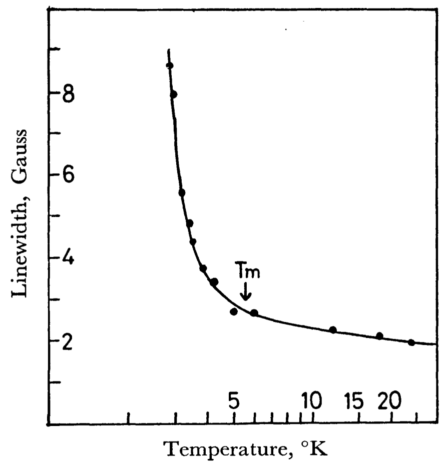

Fig. 7. Linewidth of *p*-Cl-BDPA.

calculation of susceptibility. The 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 all the radicals except *p*-Cl–BDPA[23] can be observed above the temperature of 1.8°K; the ESR line of *p*-Cl–BDPA broadens out and disappears as the temperature approaches 2.8°K from higher temperatures. Figures 5—7 show the temperature dependence of the linewidths of the radicals.

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 a comparison of the experimentally-obtained susceptibility with that of the dimer model described by Eq. (1). If one enumerates the energy separation between singlet and triplet states, Δ, of Eq. (1) from the following relation;

$$\Delta/k = 1.60T_m, \tag{2}$$

Eq. (1) will reproduce qualitatively the experimental results of susceptibility, but the magnitude of the paramagnetic susceptibility differs from the observed value. The theory predicts a much larger value, $\chi_{\max}$, at T_m than the observed one; besides the deviation of the susceptibility becomes larger as the temperature is decreased below T_m. For instance, $\chi_{\max}$ in TANOL is equal to 226×10^{-4} emu/mol; this is in contrast to the theoretical $\chi_{\max}$ value of 298×10^{-4} emu/mol calculated from Eqs. (1) and (2) using T_m=6.5°K. Therefore, it may safely be said that no pairing of electron spins in the radicals and no dimerization of molecules occur.

Edelstein has successfully employed the linear Ising model for the qualitative interpretation of the susceptibilities of BDPA–Bz and PAC.[24] The Ising models are theories treating spatially-localized spins between which the exchange coupling is represented as $-2JS_{iz}S_{jz}$. Although Stout and Chisholm have treated the small interactions between Ising chains in $CuCl_2$ by introducing a molecular field,[25] organic free radicals have never been observed to have so large an anisotropic character. In fact, all 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;[26] the Hamiltonian is given by:

$$H = \sum_{i=1}^{N/2}\{J(1+d)S_{2i-1}S_{2i}+J(1-d)S_{2i}S_{2i+1}\}, \tag{3}$$

where $J(1+d)$ and $J(1-d)$ are the exchange constants between neighboring spins and where d is a parameter that represents the degree of alternation. Unfortunately, the theoretical susceptibility results do not agree with the more exact treatments for the limiting cases of d=1 and d=0. Recently Duffy and Barr obtained the exact eigenvalue spectrum and thermodynamic prop-

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[23] 1,3-bisdiphenylene-2-*p*-chlorophenyl-allyl.

[24] A. S. Edelstein, *J. Chem. Phys.*, **40**, 488 (1964).

[25] J. W. Stout and R. C. Chisholm, *J. Chem. Phys.*, **36**, 979 (1962).

[26] Z. G. Soos, *J. Chem. Phys.*, **43**, 1121 (1965); Z. G. Soos and H. M. McConnell, *ibid.*, **43**, 3780 (1965); Z. G. Soos, *ibid.*, **46**, 253 (1967); 4284 (1967).

erties of the same Hamiltonian as Eq. (3) and compared their results with the experimental results.[27] They fitted the 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, in an intermediate alternation, there is an excited state with an energy gap from the ground state at $T=0$°K, so the susceptibility decreases exponentially as $T \to 0$°K. These schemes fail to explain a finite susceptibility at $T=0$°K unless $d=0$.

Previous to these investigations, theoretical calculations of the thermodynamic properties of one-dimensional long chains with isotropic and anisotropic interactions were made by Griffiths[28] and by Bonner and Fisher.[29] The corresponding spin Hamiltonian is given by:

$$\boldsymbol{H} = -2J\sum_{i=1}^{N}\{S_{iz}S_{i+1z}+\gamma(S_{ix}S_{i+1x}+S_{iy}S_{i+1y})\}, \tag{4}$$

which reduces to the Ising case when $\gamma=0$ and to the Heisenberg case when $\gamma=1$. Bonner and Fisher also estimated the behavior of susceptibility and specific heat for $N \to \infty$. The susceptibility for a pure antiferromagnetic Heisenberg chain displays a round maximum, and the corresponding specific heat exhibits an anomaly of the Schottky type. One of the crystalline solids which clearly exhibit antiferromagnetic linear chain behavior is $Cu(NH_3)_4SO_4 \cdot H_2O$, whose magnetic quantities can be explained qualitatively and also quantitatively in terms of this model, since each Cu^{2+} ion couples within a -O-Cu-O-Cu-O- chain and since interactions between chains are negligible.[30]

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 has already been described in the introduction. Therefore, it is reasonable to analyse and discuss the results using the theory of the one-dimensional Heisenberg model based on Bonner and Fisher's calculations, which will be briefly summarized in the case of isotropic Heisenberg interaction with $\gamma=1$ and $N \to \infty$ in Eq. (4). The susceptibility displays a rounded maximum of height:

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

at

$$kT_m/|J| = 1.282. \tag{6}$$

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

$$C_{\max}/Nk = 0.350 \tag{7}$$

at

$$kT_{mc}/|J| = 0.962. \tag{8}$$

It is worth remarking that χ_M can approach a finite nonzero value, $\chi_{T=0}$, at $T=0$°K, as there is no energy gap between the ground state and the first excited states when $\gamma=1$ and $N \to \infty$. $\chi_{T=0}$ is given by the following relation with the parameter J:

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

One can obtain the J parameter in Eq. (4) from several relations, (5), (6), (8), and (9). Assuming the J value from the T_m value experimentally obtained with the use of the (6) relation, we can evaluate the χ_M, $\chi_{\max}$, and $\chi_{T=0}$ values, which are dependent on the manner of evaluating J. On the other hand, the $\chi_{\max}/\chi_{T=0}$ and T_m/T_{mc} ratios are independent of the J parameter and are equal to 1.45:1 and 1.33:1 respectively.

TANOL System: The temperature dependence of the magnetic susceptibilities of TANOL and TADIN[31] have been reported by several investigators.[10,11,32] In the case of TANOL, the exchange parameter was obtained as $|J|/k=5.0$°K; this agrees well with that obtained from the $\theta=2zJS(S+1)/3k$ relation with a nearest-neighbor parameter of $z=2$, with $S=1/2$, and with the Weiss constant $\theta=-6.0$°K. The $\chi_{\max}$ value, 218×10^{-4} emu/mol, thus obtained from Eq. (5) is in good agreement with the experimental value, $\chi_{\max}=226\times10^{-3}$ emu/mol. $\chi_{T=0}$ was then evaluated to be 180×10^{-4} emu/mol by extrapolation, while the same value can also be expected from Eq. (9). The Heisenberg linear chain for $N \to \infty$ and $\gamma=1$ 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); this is in quite good accord with the theory. It may be said, therefore, that the spins in TANOL interact one-dimensionally with each other and that the interaction is isotropic in the sense of Heisenberg exchange interaction. A precise determination of the crystallographic structure of TANOL is monoclinic: $a=7.052\pm0.010$ Å, $b=14.081\pm0.018$ Å, $c=5.780\pm0.010$ Å, and $\beta=118°40'\pm10'$. The molecules are aggregated by the hydrogen bond and form chains parallel to the a-axis.[16] However, it is difficult to conclude whether the direction of linear exchange interaction is along the direction of hydrogen bonding or along the c-axis, where the lattice constant is the shortest. We are now engaged in clarifying this point.

The susceptibility of TADIN shows a broad maximum at $T_m=2.3$°K, after which χ_M decreases slowly towards a constant susceptibility. $J/k=-1.8$°K, which is obtained by following the same procedure as has been described above, reproduces well the experimental susceptibilities, χ_M, $\chi_{\max}$, and $\chi_{T=0}$. The $\chi_{\max}/\chi_{T=0}$ ratio, 1.3:1, is also in good accord with the theory. Therefore, TADIN is considered to be a one-dimensional Heisenberg antiferromagnet.

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 1.8°K, but deviate slightly from the Curie-Weiss law below about 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 a substituent a radical has, the larger the Weiss constant becomes, but the exchange interactions 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 either to the difference in the lattice distance of the crystal

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27) W. Duffy, Jr., and K. P. Barr, *Phys. Rev.*, **165**, 647 (1968).

28) R. B. Griffiths, preprint, Stanford Univ. Carifornia

29) J. C. Bonner and M. E. Fisher, *Phys. Rev.*, **135**, A640 (1964).

30) R. B. Griffiths, *Phys. Rev.*, **135** A659 (1964); S. Saito, *J. Phys. Soc. Japan*, **26**, 1388 (1969).

31) 2,2,6,6-tetramethylpiperidine-1-oxyl.

32) J. Yamauchi, T. Fujito, H. Nishiguchi, and Y. Deguchi, Proceedings of 12th Inter. Conf. Low Temp. Phys., Kyoto (1970).

axis along which the magnetic chains are formed or to the difference in the strength of the hydrogen bond, which was found out by studying the infrared absorption spectra in Nujol. The details of this ascription will be published elsewhere.[33]

BDPA System: The molar susceptibility of BDPA-Bz, shown in Fig. 3, exhibits a broad maximum at $T_m=5.6$°K. $\chi_{\max}$ and $\chi_{T=0}$ are obtained as 199 and 150×10^{-4} emu/mol respectively. Considering $\chi_{\max}/\chi_{T=0}=1.3$ and the temperature dependence of the susceptibility in the especially low temperature region, the data can also be well explained in terms of the Hamiltonian ($N\rightarrow\infty$ and $\gamma=1$) described above. Thus, we obtain $J/k=-4.4$°K. If one excludes benzene molecules from BDPA-Bz by heating, the exchange interaction becomes larger, going from -4.4°K to -8.5°K. This radical, BDPA, also shows a susceptibility decreasing towards a finite susceptibility at $T=0$°K after $T_m=10.9$°K. However, the $\chi_{\max}/\chi_{T=0}$ ratio, 1.7:1, is larger than the theoretical one, since $\chi_{\max}=153\times10^{-4}$emu/mol is a little larger than the theoretical $\chi_{\max}=130\times10^{-4}$ emu/mol. Thus, BDPA also has a one-dimensional Heisenberg interaction like BDPA-Bz. This fact can be understood by assuming that the removal of benzene molecules does not affect the spin structure in BDPA-Bz, but causes a stronger exchange interaction.

The data of *p*-Cl-BDPA are similar to those of BDPA-Bz, as is 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 rise in the susceptibility has also been found in the neighborhood of 1.7°K in BDPA-Bz.[13] Such a discontinuity in *p*-Cl-BDPA indicates that there may be a phase transition into an antiferromagnetic state. This will be discussed below, together with the data of ESR measurements.

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 value. At first sight, the radical concentration seems to become lower as the temperature is lowered. 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 a low concentration, the amount of the deviation of susceptibility is constant at all temperatures, 2) the radical concentrations of BDPA-Bz and *p*-Cl-BDPA are equal to above 100% if we estimate them from the susceptibility about 77°K, and 3) BDPA after the heat treatment of BDPA-Bz has about a 100% radical concentration in all temperature ranges. Although this effect is not completely accountable for at present, it may be associated with the electronic properties of allyl radicals, which behave as semiconductors,[34] as has been pointed out by Fedders and Kommandeur.[35]

ESR. The distinct character of linear magnetic chains is the development of short-range magnetic ordering without a definite transition to long-range ordering at low temperatures. The short-range magnetic ordering developed remarkably near T_m can be observed in the increase in the ESR linewidth below T_m. The data are illustrated in Figs. 5—7. The linewidth of each sample increases with the lowering of the temperature below T_m. Recently, the temperature dependence of the exchange-narrowed ESR linewidth of linear antiferromagnetic chains with the anisotropic exchange coupling was calculated by Kawasaki, using the double-time Green function method.[36] She found the following relation:

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

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

$$\Delta H = \alpha\exp(\beta T_m/T) \tag{11}$$

where α and β are constant and where α may imply ΔH_∞. The α and β values of each sample are summarized in Table 2. We cannot fit the data with the relation (10) over 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 the linewidth of the paramagnetic resonance provides additional support for the present interpretation made from the susceptibility data.

TABLE 2. PARAMETERS OF TEMPERATURE DEPENDENT LINEWIDTH: $\Delta H=\alpha\exp(\beta T_m/T)$

	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

In *p*-Cl-BDPA the relation (11) holds above 4°K. The intensities of the ESR spectra decrease immediately below 4°K, and simultaneously the ESR linewidths broaden out. The disappearance and the broadening of the lines may be attributed to the coupling between neighboring chains, which induces a spontaneous magnetization. This phenomenon may imply the onset of long-range ordering, as it may be considered that the subsequent rapid increase in linewidth is the result of 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 observe an absorption at about 1.6°K. This fact is probably related to the specific heat anomaly at 1.78°K[14]

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Specific Heat. According to the specific heat measurements of TANOL[37] and BDPA-Bz,[14] 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 from Heisenberg chains rather than from Ising chains, although in BDPA-Bz it is much smaller. This discrepancy in magnitude might be explained by assuming some type of electronic band structure.[35] The ratio of T_m to T_{mc} is unconnected with the exchange integral, J, and is equal to 1.3 for Heisenberg chains and to 2.4 for Ising chains. The observed T_m/T_{mc} ratios 1.6:1(TANOL) and 1.7:1(BDPA-Bz), deviate a little from the theoretically predicted ratio. The agreement with the theory is not so bad, however, if one takes into account of the accuracy of T_{mc}. Thus, the results of the 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 will be discussed briefly below.

In porphyrexide the magnetic properties can be explained by the Ising model rather than by the linear Heisenberg model.[38] This is probably because the radical has a very small amount of anisotropy, which reduces the Heisenberg-type magnetic properties to Ising-type ones. The effect of this anisotropy was found in the temperature dependence of the ESR linewidth.[39]

The susceptibility data of DANO (di-*p*-anisylnitroxide) were shown by Duffy *et al*[40] to be consistent with the nearest-neighbor antiferromagnetic Heisenberg exchange of a quadratic layer lattice, because the radical is a magnetically layered crystal, as may be infered from the X-ray crystallographic study of Hanson.[15] However, as is shown in Table 1, $\chi_{\max}/\chi_{T=0}$ and T_m/T_{mc} (T_{mc}=3°K) are in good agreement with the linear Heisenberg model. This radical presumably has a one-dimensional interaction, for it is possible that the radical forms a magnetic chain instead of a magnetic quadratic layer. This may be understood by taking into account the fact that the molecular orbitals of the unpaired electrons have a 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 in several directions so that magnetic planes can be formed. On the other hand, in organic free radicals the wave functions are described by $p_z\pi$-orbitals which have a 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 is shown in Fig. 8. Therefore, it may be understood that the neutral organic free radicals are one-dimensional antiferromagnets.

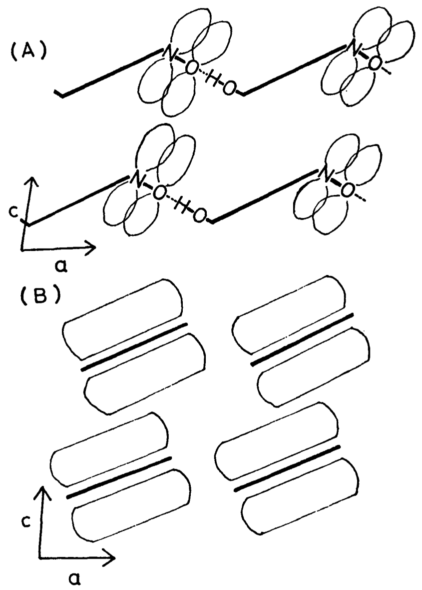

Fig. 8. Presumed exchange interaction mechanism between the unpaired electrons localized on N–O bonds (A) and between the delocalized unpaired electrons (B).
——: radical molecule, (▭): π electron cloud.

Possible Existence of Long-range Ordering. It is well known theoretically[41] that the isolated magnetic linear chains do not have any magnetic phase transition but a broad maximum susceptibility, and that, in the presence of a small interaction between chains there occurs a 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 has never been observed, although phase transitions associated with crystal deformation have been found.[42] 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 on BDPA-Bz and *p*-Cl-BDPA are considered to imply a long-range order at the Néel temperature of 1.78°K and 2.8°K respectively, because of : 1) the discontinuities of dχ_M/dT found at 1.7°K in BDPA-Bz[13] and 2.8°K in *p*-Cl-BDPA, 2) the rapid broadening and subsequent disappearance of the ESR absorption lines, and 3) the specific heat anomaly at 1.78°K in BDPA-Bz.[14] The long-range order in other radicals would be found if experiments were performed at lower temperatures.

Conclusion

The magnetic properties of neutral organic free radicals have been discussed qualitatively and quantitatively

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on the basis of a linear Heisenberg model and on the basis of the following data: 1) the qualitative behavior of χ_{M}, 2) $\chi_{\max}$ at T_m, 3) finite $\chi_{T=0}$, 4) $\chi_{\max}/\chi_{T=0}$, 5) the Schottky-type anomaly of specific heat, 6) T_m/T_{mc}, and 7) the ESR linewidth. Although the interpretations may be tentative, except in the cases of TANOL and BDPA-Bz, for lack of data from crystal-structure and/or specific-heat measurements, the data on 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 exchange interaction in a chain, the magnetic interaction between the chains is estimated to be very weak; thus, the neutral organic free radicals may be considered to be suitable crystals for studying the short-range order effect of the magnetic transition process.

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