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# Ferromagnetic and antiferromagnetic intermolecular interactions of organic radicals, α-nitronyl nitroxides. II

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The temperature dependence of the magnetic susceptibilities and the magnetizations for the three kinds of α-nitronyl nitroxides, 2-R-4,4,5,5-tetramethyl-4,5-dihydro-1$H$-imidazolyl-1-oxy 3-oxide [with R = phenyl (I), 3-nitrophenyl (II), 4-nitrophenyl (III)] have been measured. It is found that the intermolecular spin interaction is ferromagnetic in the crystal of III, while it is antiferromagnetic in I or II. UV–visible absorption spectra suggests the enhancements of the π-electron delocalization and the spin polarization in III in comparison with the others. The difference in the magnetic coupling between I or II and III is interpreted based on these two effects.

## I. INTRODUCTION

Magnetic properties of organic crystals have been studied extensively and there has recently been an increasing interest in organic/molecular ferromagnetism.[1-3] While the majority of organic and organometallic radicals exhibit antiferromagnetic (AFM) intermolecular interactions, a few radicals have been confidently proved to possess ferromagnetic (FM) interactions.[4] To our knowledge, there are only three crystals of metal-free organic radicals with FM intermolecular interactions: galvinoxyl,[4-7] tanol suberate,[8-12] and bis[p-(octyloxy)phenyl]-carbene,[13] although these compounds do not fall into the three-dimensional (3D) FM ordered state even at low temperatures. On the other hand, the theoretical approaches to the FM intermolecular interaction have been initiated by McConnell[14] in the mid 1960's, and it has been recently suggested[15,16] that the enhancement of the spin polarization and the extension of the π-electron conjugation system lead to the FM coupling, based on the molecular orbital (MO) calculations.

In this point of view, α-nitronyl nitroxide which is a stable organic radical of $S = 1/2$ has a quite interesting molecular structure (see Fig. 1). Two N–O groups are bonded by a carbon atom and the unpaired electron is delocalized on the whole skeleton.[17,18] Within a one-electron approximation, the unpaired electron is distributed evenly between the two N–O groups, making a node at the α-carbon atom.[17,18] This feature is very similar to that of the allyl radical,[19] the simplest odd-alternant hydrocarbon. Furthermore, the spin–polarization effect in α-nitronyl nitroxide is much more magnified by the $n$ electrons near the unpaired electron ($n$–π exchange interaction), compared with the case of allyl radical. It should be noted here that α-nitronyl nitroxides form complexes with various metal ions, and their magnetic properties and structure have been studied in detail by the groups of Gatteschi and Rey.[20-27]

We have initiated a study of the effect of various substituents upon the electronic states and the intermolecular interactions of α-nitronyl nitroxides which can be easily modified by various chemical substitutions.[18,28] In this report, we describe the magnetic properties of three different α-nitronyl nitroxides, 2-R-4,4,5,5-tetramethyl-4,5-dihydro-1$H$-imidazolyl-1-oxy 3-oxide [with R = phenyl (I), 3-nitrophenyl (II), and 4-nitrophenyl (III), see Fig. 1]. Radical I is an α-phenyl substituted compound, while radicals II and III have a nitro group at the $m$ and $p$ position, respectively, in the phenyl ring of the parent radical I. The nitro group is usually expected to enhance the spin polarization effect. The correlation between the magnetic properties and the electronic structure is discussed.

## II. EXPERIMENTAL

The nitroxide radicals I, II, and III were prepared by the method reported in Ref. 18 and were purified by recrystallization from benzene or ether solution (I, found: C, 67.06%; H, 7.51%; N, 12.02%, calculated for $C_{13}H_{17}N_2O_2$: C, 66.93%; H, 7.34%; N, 12.01%; II, found: C, 56.13%; H, 5.86%; N, 15.13%, calculated for $C_{13}H_{16}N_3O_4$: C, 56.11%; H, 5.79%; N, 15.10%; III, found: C, 56.12%; H, 5.85%; N, 15.09%, calculated for $C_{13}H_{16}N_3O_4$: C, 56.11%; H, 5.79%; N, 15.10%). Radicals I and II were blue crystals, while III was a green one. The radical concentrations in them were estimated to be 100% within experimental error from the Curie constants.

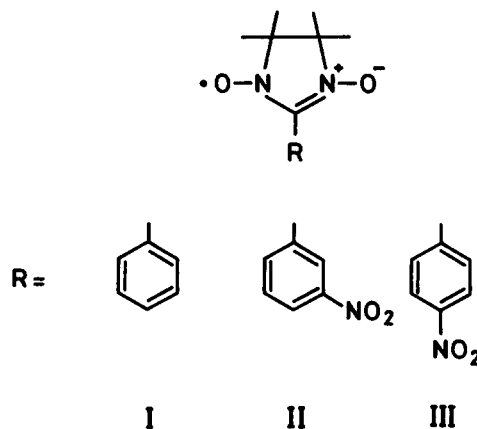The static magnetic susceptibility and the magnetiza-



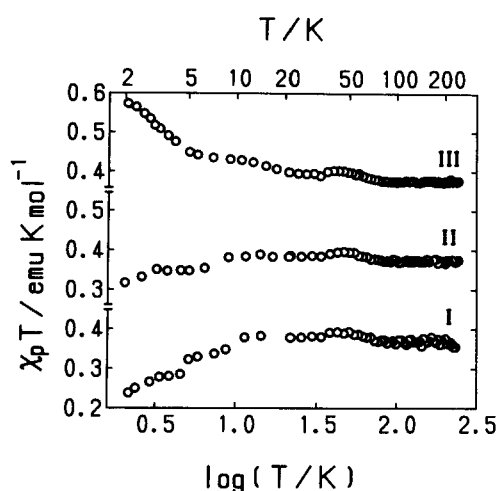FIG. 1. The molecular structures of α-nitronyl nitroxides.

FIG. 2. The temperature dependence of the product $\chi_p T$ for I, II, and III.

tion were measured by using a Faraday balance. The susceptibility measurement was carried out under the field of 1 T and the correction for the saturation effect at low temperatures was made by assuming the saturation of the $S = 1/2$ spin entity.[29] The magnetization measurement was done under the field up to 5 T. The diamagnetic corrections were made by using the diamagnetic susceptibilities determined experimentally.

The UV–VIS spectra were measured by using Hitachi U-3400 Spectrophotometer.

## III. MAGNETIC PROPERTIES

The temperature $T$ dependence of the paramagnetic susceptibilities $\chi_p$ of I, II, and III were measured over the range from 2 to 250 K. $\chi_p$ of them are found to follow the Curie–Weiss law in this temperature range. The results are shown in Fig. 2, where $\chi_p T$ is plotted as a function of logarithms of $T$. Radical I and II exhibit similar dependence on temperature. $\chi_p T$ of them in Fig. 2 are almost constant in the high-temperature range and decrease monotonically below about 10 K, indicating the presence of a week AFM intermolecular interactions. On the other hand, the temperature dependence of $\chi_p$ of III is quite different from the others. $\chi_p T$ of III increases gradually with decreasing temperature, indicating the FM coupling. There is a FM intermolecular interaction in the $p$-nitro compound III. The small humps commonly observed near 50 K should be due to the adsorbed oxygen, while its amounts are very small.

The intensity of the magnetic coupling could be estimat-

ed from the Weiss constant $\theta$ of I, II, and III were determined from the reciprocal $\chi_p$ vs $T$ plots (not shown). The obtained values are listed in Table I. As a matter of course, $\theta$ of III becomes positive in contrast to the negative ones of I and II. $\theta = +0.9$ K for III is comparable to that of the tanol suberate[10] and is much smaller than those of the complexes[20,21] between nitroxide radicals and $Cu^{+2}$. The absolute value of $\theta$ for I is larger than that in II, indicating that the AFM coupling in I is stronger than that in II.

The field $H$ dependence of the magnetization $M$ was measured at 2, 3, and 4.5 K in order to confirm the magnetic couplings in I, II, and III. The results are shown in Fig. 3,







## TABLE I. The Weiss constants.

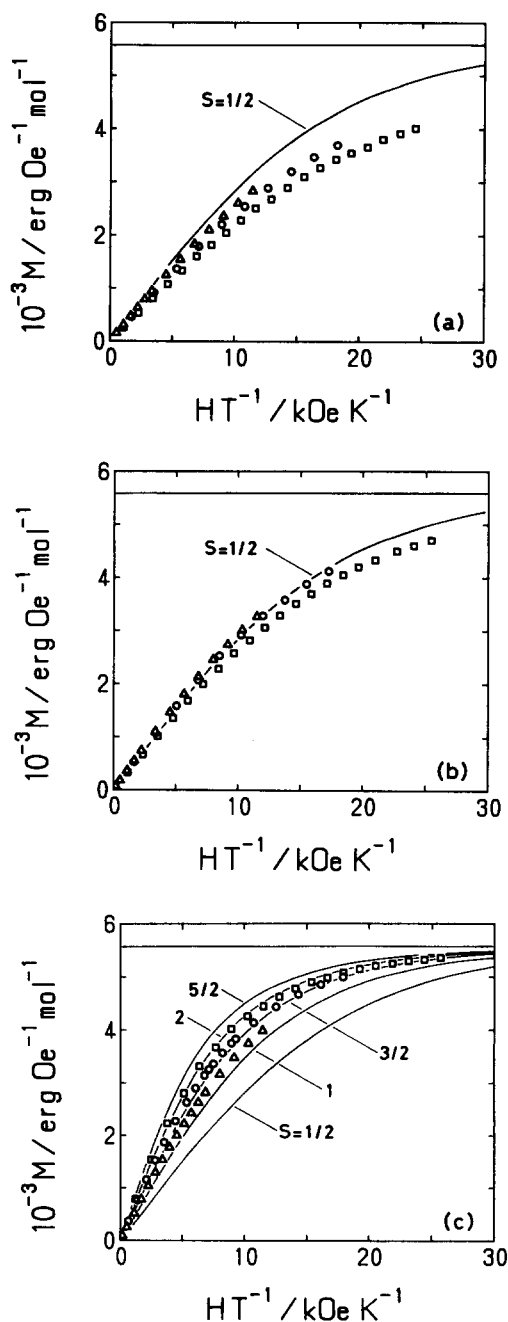|     | $\theta$/K |
| --- | --- |
| I   | $-1.4$ |
| II  | $-0.5$ |
| III | $+0.9$ |

FIG. 3. The magnetization curves of I (a), II (b), and III (c), measured at 4.5 (triangles), 3 (circles), and 2 K (squares). The solid curves are theoretical ones for various paramagnetic spin entities (Ref. 30).

where $M$ is plotted as a function of $H/T$. $M$ of the paramagnetic entities are given theoretically as[30]

$$M = M_s B_J(x) \qquad (1)$$

with

$$x = Jg\mu_B H/k_B T,$$

where $M_s$ is the saturation magnetization, $J$ is the quantum number of the total angular momentum, $g$ is Lande $g$ factor, $\mu_B$ is the Bohr magneton, $B_J(x)$ is the Brillouin function for $J$, and $k_B$ is the Boltzmann constant. In our case, $g = 2.006$[18] and $J = S$ are good approximations. The solid curves in Fig. 3 are the theoretical ones for the various spin entities. They are drawn so as to reach the saturation magnetization of $M_s$ $= 5.60 \times 10^3$ erg $Oe^{-1}$ $mol^{-1}$ which corresponds to the observed Curie constants. Figure 3(a) shows the magnetization curves of $I$ at three different temperatures. $M$ saturates more slowly than the $S = 1/2$ spin entity, which could be due to its AFM interaction. Furthermore, it is clearly shown that the magnetization comes to saturation more slowly at lower temperatures. This indicates that the intensity of the AFM coupling is comparable to the thermal energies in this temperature region (2–4 K). The magnetization curves of II are shown in Fig. 3(b). The three curves almost agree with that of the theoretical one of $S = 1/2$ and show a similar dependence on temperature as was observed in I. These results are consistent to the very week AFM interaction in II observed in the $\chi_p$ measurements.

Figure 3(c) shows the magnetization curves of III. The three curves exhibit more rapid saturation than that of the $S = 1/2$ spin entity, which supports the presence of the FM intermolecular interaction in III. Further, the magnetization curves of III clearly show an opposite dependence on temperature to that of I or II; $M$ in III saturates more rapidly with decreasing temperature. The FM coupling in III could be comparable to a thermal energy of 2–4 K. A similar dependence of the magnetization curve on temperature was reported in Ref. 13. It is hard to estimate the number of ferromagnetically coupled radicals from the magnetization curve, as was done in Ref. 6. However, the magnetization curve at 2 K, the lower limit of the temperature measurements, almost corresponds to the theoretical one for $S = 2$, and, therefore, it is certain that the FM interaction in III could cover more than four radicals. Through these magnetic measurements, anyhow, it is convinced that the magnetic coupling in these nitroxide radicals changes from AFM to FM depending on the substituents, and consequently that the nitroxide radical III exhibits the FM intermolecular interaction in contrast to the AFM interactions in I and II.

## IV. FM AND AFM INTERMOLECULAR INTERACTIONS

The crucial difference in the electronic states among these three compounds is that only III can resonate with a quinoid structure such as drawn in Fig. 4 and could have a larger delocalization of the unpaired electron on the nitro group. In order to confirm it experimentally, the UV–VIS absorption spectra of I, II, and III in acetonitrile were measured. The results are compared in Fig. 5, where the molar absorption coefficients below 20 000 $cm^{-1}$ are given in mag-
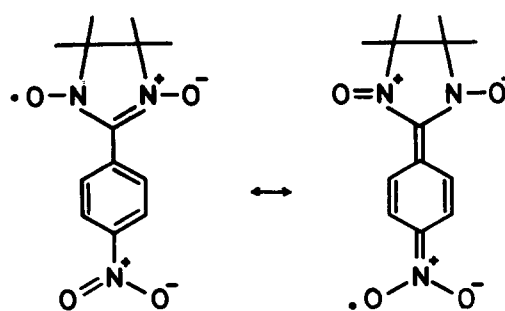


FIG. 4. A possible resonance structure of III.

nified scale indicated. The spectra of I and II are very similar except for the peak heights at 38 000 $cm^{-1}$. The nitro group introduced at $m$ position does not significantly change the electronic structure of the parent molecule I. The absorptions at 17 000 and 28 000 $cm^{-1}$ of I or II were assigned to the $n$–$\pi^*$ and $\pi$–$\pi^*$ transitions, respectively, by Ullman et al.[18] They measured the UV–VIS absorption spectra of various $\alpha$-substituted nitronyl nitroxides and found the low-energy shift of the $\pi$–$\pi^*$ transition by introducing a substituent which allows the intramolecular charge–transfer (CT) interaction between nitroxide and itself, such as $R = -CH_2I$, $-CH = CHCH_3$, $-C_6H_5$ (I), and so on.[18] In addition, the appearance of a strong absorption around 40 000 $cm^{-1}$ was commonly observed in these compounds.[18] The transitions at 28 000 and 38 000 $cm^{-1}$ of I and II have somewhat a intramolecular CT character.

The spectrum of III in Fig. 5 is quite different from the others, suggesting a drastic change in the electronic structure of III. A broad band around 25 000 $cm^{-1}$ and a strong absorption band at 31 000 $cm^{-1}$ appear, which correspond to those at 28 000 and 38 000 $cm^{-1}$ of I and II, respectively.
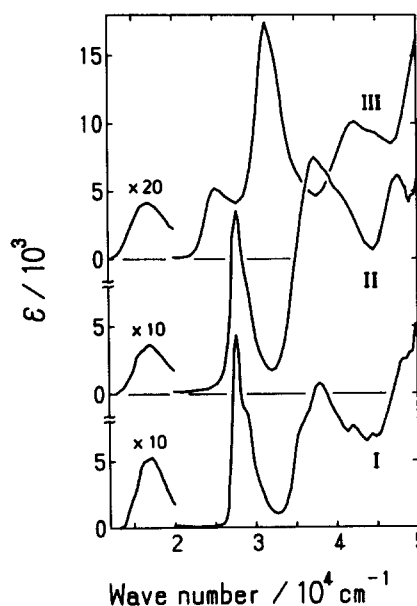


FIG. 5. UV–VIS absorption spectra of I, II, and III in acetornitrile.

Such large shifts to lower-energy should result from the strong contribution of the resonance with the quinoid structures in III, on account of the CT characters of these two bands. The delocalization of the unpaired electron is considered to be much developed in the $p$-substituted compound III.

Based on schematic considerations of the molecular orbitals deduced from the absorption spectra, the difference in the magnetic couplings among I, II, and III can be qualitatively interpreted by following the method in Ref. 16. Let us consider the magnetic coupling between two neighboring radicals, $R_1$ and $R_2$, coupled by the intermolecular CT interaction. For simplicity, we assume the CT interaction from $R_1$ to $R_2$ and take account only of SOMO and NHOMO in $R_1$ and SOMO in $R_2$. Strictly speaking, disproportionation processes should be taken in our case. Two kinds of the ground-state electronic configurations are shown in Figs. 6(a) and 6(b), where there is a difference in the electronic state in $R_1$. They are drawn in a spin-unrestricted picture. The intramolecular exchange interaction or the spin–polarization effect make an energy difference between the corresponding $\alpha$ and $\beta$ orbitals. $\alpha$ is defined as a spin-direction parallel to that of the unpaired electron. In case (a), $R_1$ has a weak spin–polarization effect and a large energy separation between SOMO and NHOMO. In this case, the CT occurs from SOMO-$\alpha$ in $R_1$ to SOMO-$\beta$ in $R_2$. It is worth noting that the resonance with the virtual CT state keeps the total spin multiplicity. Namely, the electron transfers without changing its spin direction. Therefore, the CT interaction results in the AFM coupling between the unpaired electrons. This is usually the reason for an AFM coupling in the most of the organic radicals and could be the reason for the AFM interactions in I and II.

In case (b), $R_1$ has a much enhanced spin–polarization effect and a small energy separation between the two frontier orbitals. In this case, the CT takes place from NHOMO-$\beta$ in $R_1$ to SOMO-$\beta$ in $R_2$ because of the energetical advantage.
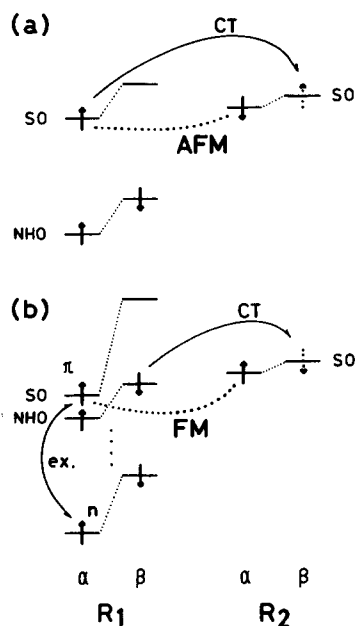


FIG. 6. AFM (a) and FM (b) intermolecular interactions.

The CT resonance occurs without losing the intramolecular exchange energies. This resonance results in the FM intermolecular interaction, as is shown in Fig. 6(b). The FM radical, galvinoxyl, has also been demonstrated to meet the conditions imposed on $R_1$ to be the case (b) by intermediate neglect of differential overlap (INDO) calculation,[16] and the radical III probably meets conditions. The delocalization of the $\pi$ electrons are much developed in III, compared with that in I or II. This suggests the smaller energy separation between the frontier orbitals in III. Furthermore, III could have a large distribution of the unpair electron on the oxygen atoms in the nitro group, as is shown in Fig. 4. The spin–polarization effect in III is also developed by the $n$–$\pi$ exchange interaction on the oxygen atoms. The spin polarization of $\pi$ electron is usually enhanced by the exchange interaction with $n$ electrons, because $n$ and $\pi$ electrons can exist close to each other. When the unpaired $\pi$ electron has a large distribution on the atoms with $n$ electrons, we can expect a large spin polarization effect. Radical II is considered to have a small distribution of the unpaired electron on the nitro group. Therefore, the spin–polarization effect in II could not be so enhanced in comparison with I. The difference in the magnetic coupling among the radicals I or II, and III, agrees well with the theoretical predictions[15,16] that the enhancement of the spin–polarization effect and the extension of a conjugation system should result in the FM coupling.

## ACKNOWLEDGMENT

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