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FERROMAGNETIC AND ANTIFERROMAGNETIC INTERMOLECULAR ARRANGEMENTS OF THE *N*-ALKYLPYRIDINIUM NITRONYL NITROXIDE

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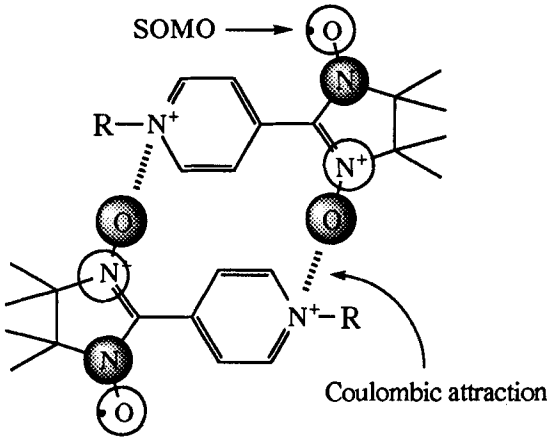
Abstract The magneto-structural correlation in some *p*-*N*-alkylpyridinium nitronyl nitroxide salts has been studied. In the iodide salts of *p*-*N*-R-pyridinium nitronyl nitroxides with R=methyl, ethyl, *n*-propyl, and *n*-butyl, the magnetic property varies from antiferromagnetic to ferromagnetic with the extension of the *N*-alkyl chain. The nearest-neighbor molecular arrangements of the nitroxides observed in the four crystals, can be classified into two groups: the radicals are connected by a intermolecular contact between the NO groups (Type I) or between the NO group and the pyridinium ring (Type II). The observed magnetic behaviors can be interpreted in terms of an antiferromagnetic intermolecular interaction for the Type I contact and a ferromagnetic for Type II. Effects of replacement of the I^- ion by Br^- or Cl^-, have been also studied in the *p*-*N*-methyl derivative.

INTRODUCTION

There is a rapid development in the field of molecular-based magnetic materials, where it is notable that experimental and theoretical reports on the ferromagnetic properties of nitronyl nitroxide radicals now appear quite frequently.[1-11] The electronic structure of the nitronyl nitroxide has been examined with an electron paramagnetic resonance,[12] an ultraviolet photoelectron spectroscopy[13] and a neutron diffraction.[14] This radical family possesses a strong spin polarization effect, mainly because of the spatial closeness between the unpaired π electron and the non-bonding electrons (n-π exchange interaction). The spin polarization effect stabilizes triplet charge transfer (CT) excited states, and the admixture of these states results in a ferromagnetic intermolecular interaction.[15]

Recently we have initiated a study of *N*-alkylpyridinium nitronyl nitroxides. They are designed to get an intermolecular arrangement for a ferromagnetic coupling. Since the oxygen atom in the NO group is equipped with a large negative charge, resulting from an electronic polarization in the NO bond, namely $N^{\delta+}O^{\delta-}$, a shorter intermolecular contact between the NO group and the pyridinium ring is expected in the

solid state, due to the Coulombic attraction force between the negative charge on the oxygen and the positive charge on the pyridinium ring (see Scheme I). The magnetic orbital (SOMO) of the nitronyl nitroxide is localized on the two NO groups, making a node on the mid α-carbon, and has little population in the aromatic substituent, while the other frontier non-magnetic orbitals are distributed on both the nitronyl nitroxide group and the substituent.[16] Therefore, a short contact between the NO groups usually means an overlap between the magnetic orbitals, which always makes the intermolecular interaction antiferromagnetic. An intermolecular contact between the NO group and, the aromatic substituent or the α-carbon, on the other hand, means an interaction between the magnetic orbital and the non-magnetic orbitals. The non-magnetic orbitals are naturally orthogonal to the magnetic orbital in the adjacent molecule. A ferromagnetic coupling can be expected through the [magnetic orbital]-[non-magnetic orbital]-[magnetic orbital] superexchange pathway.



SCHEME I

FERROMAGNETIC AND ANTIFERROMAGNETIC INTERMOLECULAR ARRANGEMENTS OF *p-N*-ALKYLPYRIDINIUM NITRONYL NITROXIDES [17]

Crystal Structures and Intermolecular Arrangements

X-ray crystal analyses and magnetic measurements have been carried out on iodide salts of *p-N*-R-pyridinium α-nitronyl nitroxides with R=methyl (*p*-MPYNN$^+$), ethyl (*p*-EPYNN$^+$), *n*-propyl (*p*-PrPYNN$^+$), and *n*-butyl (*p*-BPYNN$^+$). The structure of *p*-MPYNN$^+$•I$^-$ crystallizes in the triclinic $P\bar{1}$ space group [a=11.843(7) Å, b=12.695(7) Å, c=9.532(2) Å, α=95.53(5)°, β=90.55(5)°, γ=146.89(2)°, V=768.3(8) Å^3 and Z=2], where

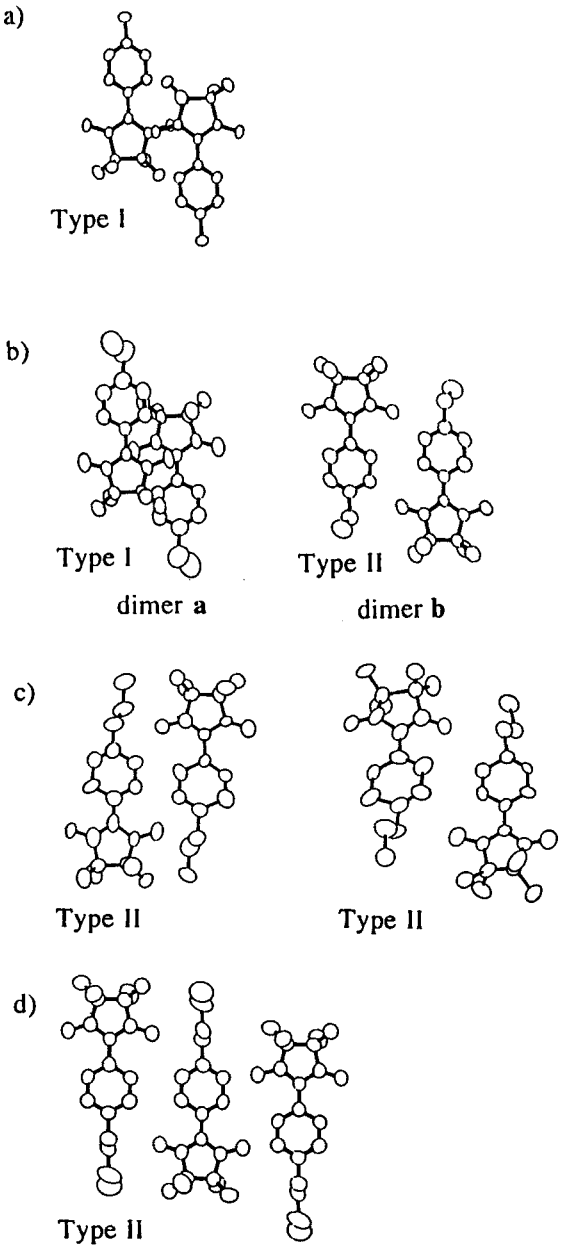


FIGURE 1 Intermolecular arrangements of the *p*-*N*-alkylpyridinium nitronyl nitroxides observed in their iodide salts; (a) *p*-MPYNN$^+$; (b) *p*-EPYNN$^+$; (c) *p*-PrPYNN$^+$; (d) *p*-BPYNN$^+$.

p-MPYNN$^+$ exists as a dimer and the iodide ion is located out of the plane on the pyridinium ring. The structure of *p*-EPYNN$^+$•I$^-$•0.5H_2O belongs to the triclinic $P\bar{1}$ space group [a=12.582(6) Å, b=13.633(8) Å, c=11.120(6) Å, α=93.31(4)°, β=115.47(2)°, γ=88.91(4)°, V=1719(2) Å^3 and Z=4]. There are two crystallographically independent molecules, each of which forms a centro-symmetric dimer. Crystal structures of *p*-PrPYNN$^+$•I$^-$ and *p*-BPYNN$^+$•I$^-$ crystallize in the triclinic $P1$ [a=13.644(3) Å, b=14.798(1) Å, c=9.873(2) Å, α=91.56(1)°, β=113.11(1)°, γ=92.23(1)°, V=1830.3(5) Å^3 and Z=4] and in the monoclinic $P2_1/n$ [a=12.311(2) Å, b=13.643(2) Å, c=11.789(2) Å, β=100.75(2)°, V=1945.3(6) Å^3 and Z=4] space group, respectively. They have a similar structure: the crystal consists of a 2-D layer which is formed by a contact between the pyridinium ring aligned parallel to the layer and the iodide ion located in the plane on the pyridinium ring. The nearest-neighbor interaction between the nitroxide molecules appears in the interlayer molecular arrangement.

Figure 1 shows the nearest-neighbor molecular arrangements observed in the four crystals. They can be classified into the following two groups. The arrangements of *p*-MPYNN$^+$ and *p*-EPYNN$^+$ (dimer **a**) are formed by a contact between the NO groups (Type I), while those of *p*-EPYNN$^+$ (dimer **b**), *p*-PrPYNN$^+$ and *p*-BPYNN$^+$ are formed by a contact between the NO group and the pyridinium ring (Type II). It is the Type II contact that we expected in the crystal of the *N*-alkylpyridinium nitronyl nitroxide. There is an interesting relation that the nitronyl nitroxide with an 'out of plane' iodide ion has a Type I nearest-neighbor arrangement, while that with an 'in-plane' iodide ion does a Type II arrangement. The 'out of plane' iodide ion is thought to block the positive nitrogen on the pyridinium ring from the approach of the neighboring molecule. That could be why the 'out of plane' iodide ion makes the intermolecular arrangement Type I rather than Type II.

Magnetic Properties

Figure 2(a) shows the temperature dependence of the paramagnetic susceptibilities, χ_p, of the four pyridinium nitronyl nitroxide crystals, where χ_pT is plotted as a function of temperature. Figure 2(b) shows the low temperature behaviors of *p*-PrPYNN$^+$•I$^-$ and *p*-BPYNN$^+$•I$^-$ in an enlarged scale. χ_pT of *p*-MPYNN$^+$•I$^-$ and *p*-EPYNN$^+$•I$^-$ decrease with decreasing temperature, indicating antiferromagnetic intermolecular interactions in them, although the antiferromagnetic interaction in *p*-EPYNN$^+$•I$^-$ is much weaker than that in *p*-MPYNN$^+$•I$^-$. χ_pT of *p*-PrPYNN$^+$•I$^-$ shows an increase with decreasing temperature down to ca. 10 K, but it shows a quick decrease after passing through a maximum. This behavior indicates coexistence of a stronger

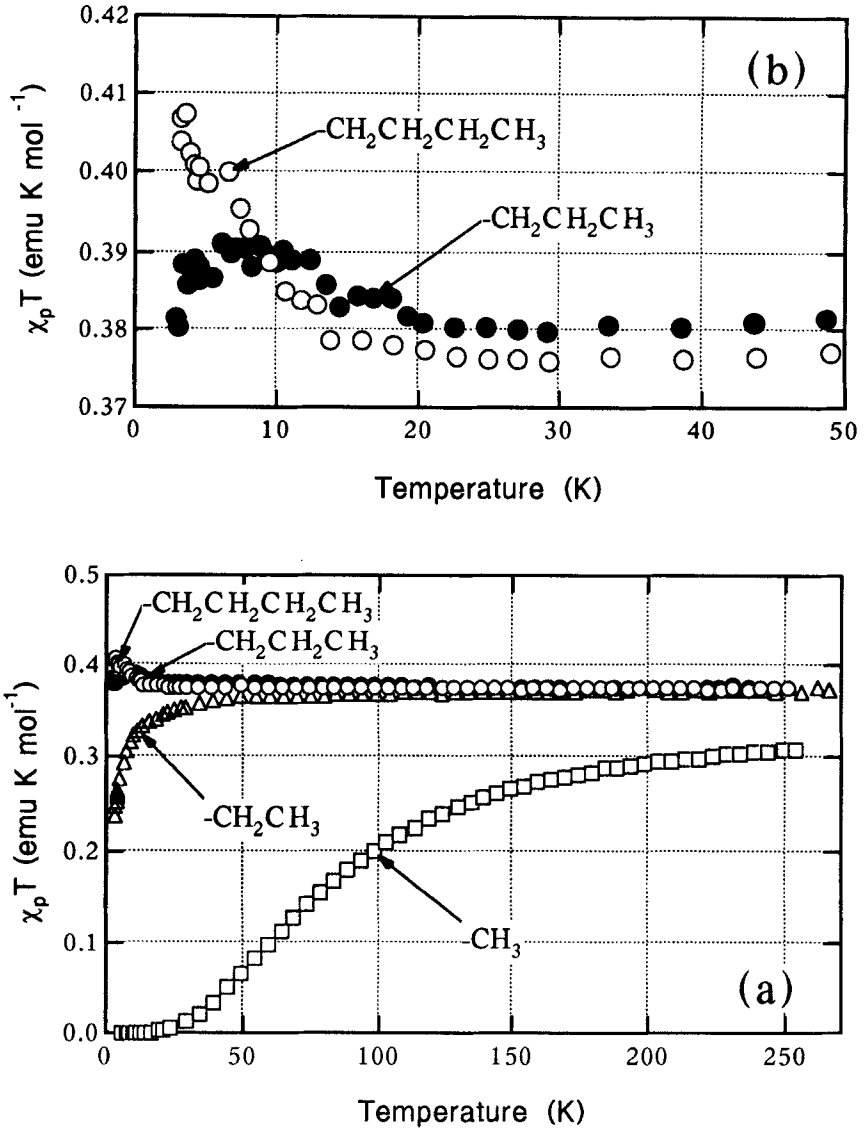


FIGURE 2 (a) Temperature dependence of the paramagnetic susceptibility of the iodide salts of *p*-MPYNN$^+$, *p*-EPYNN$^+$, *p*-PrPYNN$^+$ and *p*-BPYNN$^+$. (b) Low temperature behaviors of *p*-PrPYNN$^+$•I$^-$ and *p*-BPYNN$^+$•I$^-$ in an enlarged scale.

ferromagnetic interaction and a weaker antiferromagnetic coupling between the ferromagnetic units. χ_pT of *p*-BPYNN$^+$•I$^-$ increases with decreasing temperature in the whole range of 3-250 K. The observed magnetic behaviors can be interpreted in terms

of an antiferromagnetic intermolecular interaction caused by an overlap between SOMOs in the Type I contact and a ferromagnetic interaction caused by an overlap between SOMO and the other frontier orbitals in the Type II contact.

CRYSTAL STRUCTURES AND MAGNETIC PROPERTIES OF *p*-MPYNN$^+$•X$^-$ with X=Cl, Br and I

Effects of replacement of the I^- ion by Br^- or Cl^-, have been studied in the *p*-MPYNN$^+$•X$^-$ system. *p*-MPYNN$^+$•Br^- crystallizes into the in the triclinic $P\bar{1}$ space group [a=11.624(2) Å, b=14.576(2) Å, c=9.309(2) Å, α=95.11(1)°, β=90.15(2)°, γ=152.05(3)°, V=725.1(2) Å^3 and Z=2]. It is isostructural to *p*-MPYNN$^+$•I^-, although the unit cell volume of the Br^- salt slightly shrinks, compared with that of the I^- salt.

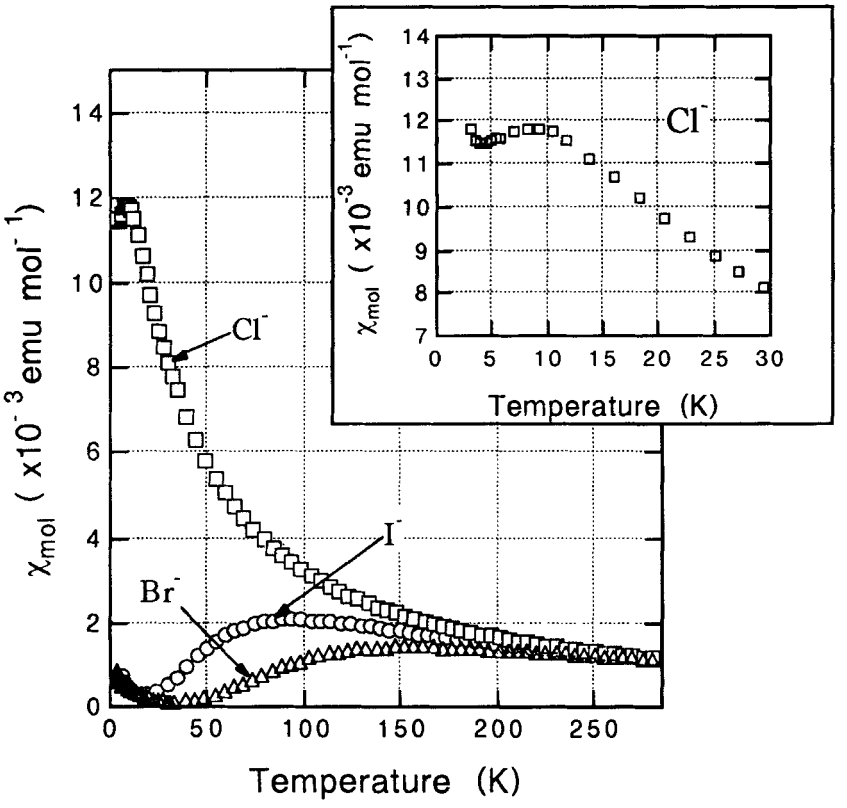


FIGURE 3 Temperature dependence of the molar magnetic susceptibility of the three halogenide salts of *p*-MPYNN$^+$.

Each Br^- ion is surrounded by four pyridinium rings. The *p*-$MPYNN^+$ molecules take a Type I dimerized structure, such as that in Figure 1(a). On the other hand, *p*-$MPYNN^+ \bullet Cl^- \bullet 0.5H_2O$ crystallizes into the orthorhombic *Pbca* space group [a=10.694(2) Å, b=23.672(5) Å, c=11.939(3) Å, V=3022(1) $Å^3$ and Z=8]. The Cl^- ion is surrounded by three pyridinium rings, presumably because of the smaller ion radius. Further, there is no dominant dimerized structure of the organic radical in the crystal, and intermolecular orbital overlaps between the NO groups appear to be much smaller than those in the I^- and Br^- salts.

Figure 3 shows the temperature dependence of molar magnetic susceptibility of the three *p*-$MPYNN^+$ salts. The inset shows the low-temperature behavior of the Cl^- salt. The isostructural I^- and Br^- salts show similar temperature dependence: χ_p makes a maximum in the intermediate temperature range and shows a slight increase below 25 K because of lattice defects. The temperature of the maximum χ_p of the Br^- salt is higher than that of the I^- salt, indicating a stronger antiferromagnetic coupling in the former. This would be due to the shrink of the structure of *p*-$MPYNN^+ \bullet Br^-$. *p*-$MPYNN^+ \bullet Cl^-$ shows a small maximum of χ_p at much lower temperature (*ca.* 9 K), followed by a small increase below 4 K. The magnetic interaction in the Cl^- salt is thought to be much weaker than those in the other two, reflecting the smaller intermolecular overlap between the NO groups. Quantitative analyses are in progress.

EXPERIMENTAL SECTION

Materials

The nitronyl nitroxide cation radicals were prepared by *N*-alkylation of *p*-pyridyl nitronyl nitroxide, as reported in ref. 18: the iodide salts were precipitated in the corresponding alkyl iodide solutions of *p*-pyridyl nitronyl nitroxide. The replacement of the I^- ion was carried out, according to the following procedure:

$$2p\text{-R-PYNN}^+ \bullet I^- + Ag_2SO_4 \rightarrow (p\text{-R-PYNN}^+)_2SO_4^{2-} + 2AgI$$
$$(p\text{-R-PYNN}^+)_2SO_4^{2-} + BaX_2 \rightarrow 2p\text{-R-PYNN}^+ \bullet X^- + BaSO_4$$

X-ray Structure Determination

X-ray diffraction data were collected on a RIGAKU AFC-5 or an ENRAF NONIUS CAD4 automatic four-circle diffractometer with graphite monochromatized Mo-K_α radiation at room temperature. Unit cell dimensions were obtained by a least-squares refinement using 25 reflections with $20° < 2\theta < 25°$. During data collection, the

intensities of three representative reflections were measured as a check on crystal stability, and no loss was shown.

Magnetic Measurements

Static magnetic susceptibility and magnetization were measured with a Faraday balance whose details were described previously.[19] Temperature dependence of magnetic susceptibility was examined in the range of 3-250 K in a field of 1 T. Corrections for the diamagnetic contribution were carried out, using diamagnetic susceptibilities evaluated by assuming that paramagnetic susceptibilities follow the Curie law at high temperatures.

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