Magnetic Properties of Phenyl Nitronyl Nitroxides

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Abstract Magnetic properties and crystal structures of several
derivatives of phenyl nitronyl nitroxide (abbreviated as PNN; 2-
phenyl-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazol-1-oxyl-3-N-
oxide) are investigated. Some of them have the intermolecular
interactions between the nitroxide group and the phenyl group,
which are suggested to be favorable to ferromagnetic coupling. As
a result of the coexistence of different types of magnetic
interactions, anomalies in the temperature dependence of
paramagnetic susceptibility are found for some compounds.

INTRODUCTION

In the search for organic ferromagnets, it is needed to improve a
rational method of designing the structure of the radical molecule and
their arrangement in the crystal. The finding of bulk ferromagnetism
in the β-phase of *p*-nitrophenyl nitronyl nitroxide (*p*-NPNN)[1,2] have
established the existence of intermolecular interactions leading to
ferromagnetic order. This urged us to study the correlation between
the ferromagnetic intermolecular interactions and the crystal
structures of the nitronyl nitroxide family. In this paper, the
magnetic properties of a series of phenyl nitronyl nitroxide
derivatives are discussed in the light of magneto-structural
correlation. The intermolecular interactions between nitroxide group
and phenyl group (abbreviated as NO⋯φ type interactions in what
follows) are commonly found for the compounds exhibiting ferromagnetic
interaction. In some compounds stationary behavior of the temperature
dependence of the product of the paramagnetic susceptibility and
temperature, $\chi_p T$, is observed at low temperatures. This is
considered as a result of the coexistence of different types of
magnetic interactions, strong and weak ones, or ferro- and
antiferromagnetic ones. Formation of clusters including more than two
spins is suggested for such cases.

EXPERIMENTAL

The compounds (1-8 in Fig. 1) were synthesized by the reported method.[3] Single crystals of them were grown in solution by evaporation of solvent. Magnetic susceptibilities (1.8-300 K) and magnetizations (up to 5.5 T) were measured by use of a Quantum Design MPMS SQUID magnetometer. X-ray intensity data were collected by a MAC Science automatized four-circle diffractometer. The program system "Crystan" by MAC Science was used in the calculations in crystal structure analysis.
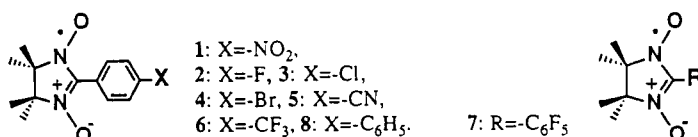
1: X=-NO$_2$,
2: X=-F, 3: X=-Cl,
4: X=-Br, 5: X=-CN,
6: X=-CF$_3$, 8: X=-C$_6$H$_5$.   7: R=-C$_6$F$_5$

FIGURE 1   The compounds picked up in this paper.

TABLE I   Crystallographic Data at Room Temperature.

	1 (δ-phase)	2	4	5	6	7
System	momo-clinic	tetra-gonal	mono-clinic	ortho-rhombic	tri-clinic	mono-clinic
Space Group	P2$_1$/c	I4$_1$/a	P2$_1$/n	Ic2a	P$\bar{1}$	Aa
a/Å	8.963	21.931	16.404	10.482	9.899	11.383
b/Å	23.804	21.931	10.955	26.615	11.289	11.638
c/Å	6.728	11.110	15.591	9.903	7.138	10.910
α/deg	90	90	90	90	94.27	90
β/deg	104.25	90	96.60	90	106.64	104.18
γ/deg	90	90	90	90	75.65	90
Z	4	16	8	8	2	4

RESULTS AND DISCUSSION

The Highest-temperature Phase of p-NPNN (1)

Powder X-ray diffraction and differential thermal analysis technique has revealed that the β-phase of p-NPNN undergoes two structural changes on heating followed by decomposition above 150 °C.[2] The first one around 100 °C is the transition into γ-phase. The second one at about 130 °C is that from γ-phase into another phase, which is probably the same one as that reported as β$_h$-phase (high-temperature phase of β-phase) by Allemand et al.[4] Thin plate-like single crystals of this phase were readily obtained from solutions kept above 120 °C.[2] Here

let us call this phase as δ-phase, because it is not directly related to β-phase by the thermal property or the crystal structure.   The δ-phase is less stable than γ-phase toward the change into β-phase by cooling.
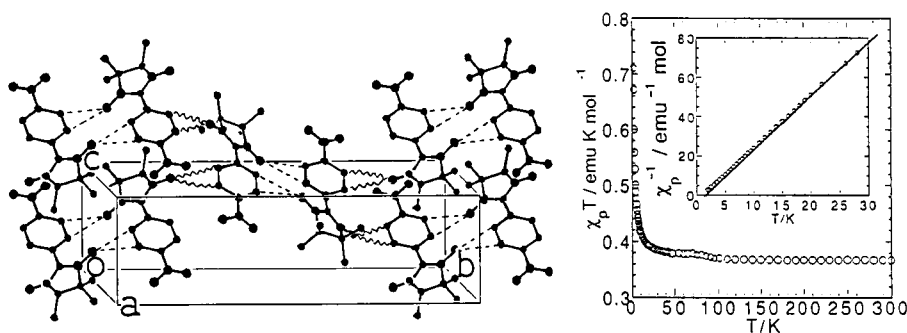

FIGURE 2   Left: Crystal structure of the δ-phase of p-NPNN. Broken and wavy lines indicates the intra- and inter-dimer NO···φ interactions, respectively.   Right: $\chi_p T$ vs. T plot for the δ-phase of p-NPNN.   The inset shows χ_p^{-1} vs. T plot and the Curie-Weiss fit (solid line).

The crystal structure of the δ-phase is shown in Fig. 2.   There are dimers of p-NPNN on the inversion centers.   The molecular arrangement in the dimer is similar to that along the [011] direction in γ-phase.[5]   Both of them has NO···φ type packing.   Between the dimers, another kind of NO···φ interaction is found.   From these features it is suggested that the intermolecular interactions form a two-dimensional (2D) network.

Paramagnetic susceptibility was measured down to 1.8 K (Fig. 2). To check the effect of β-phase created during the measurement, we examined the powder X-ray patterns just after each measurement.   The contamination of β-phase was estimated to be less than a few percent. A Curie-Weiss fit yields Weiss constant, θ, of about 2 K.   The positive value indicates that ferromagnetic interactions are dominant in the crystal.   Deviation from the Curie-Weiss law becomes appreciable below about 20 K, suggesting the low-dimensional character of this crystal.

Ferromagnetic Interactions in para-Substituted PNN's
Figure 3 shows the crystal structure of the p-fluoro-derivative **2**. The molecules are piled to form four-fold screw packing along the c-

axis. A layer of dimers spreads over the *ab*-plane. The dimer is formed by NO···ϕ interactions.

Paramagnetic susceptibility data indicate that triplet states are dominant in the crystal below about 10 K. Taking account of the dimeric structure, the NO···ϕ interactions is considered to be relevant to this ferromagnetic coupling. Moreover, below about 4 K the susceptibility slightly overshoots the value expected for a pure triplet system (Fig. 3). This involves that the interdimer extra-interactions are also ferromagnetic. We fitted the overall temperature dependence of the susceptibility to the expression,

$$\chi = \frac{C}{T-\theta} \cdot \frac{3}{[3+\exp(-2J_1/k_BT)]} \,, \tag{1}$$

where J_1 denotes the intradimer exchange coupling and other symbols have their usual meanings. The Weiss constant θ is related to the interdimer interaction J_2 by the equation, $J_2=3k_B\theta/16$, according to the mean-field theory. J_1/k_B and J_2/k_B thus estimated are 5.0 K and 0.02 K, respectively.
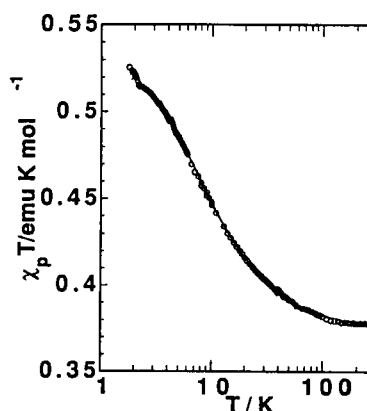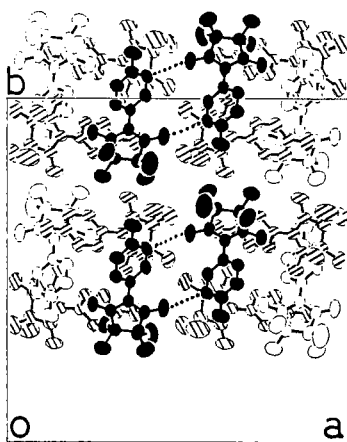

FIGURE 3   Left: Crystal structure of **2** viewed along the *c*-axis. Broken lines indicate the intradimer NO···ϕ interactions. Right: $\chi_p T$ vs. T plot for **2**. The solid line is the fit to Eq.(1).
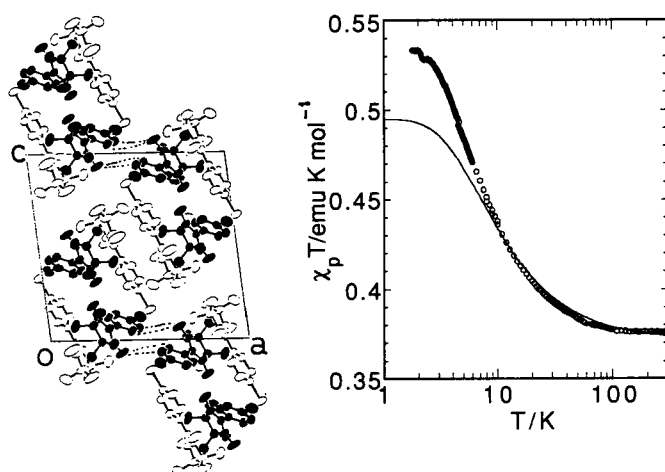
FIGURE 4   Left: Crystal structure of **4** viewed along *b*-axis.
Right: $\chi_{\mathrm{p}}T$ vs. *T* plot for **4**.   The solid line stands for the
behavior of the simple singlet-triplet gap system with *J*=4.3 K.

The temperature dependence of paramagnetic susceptibility of the
p-bromo-derivative **4** is similar to that of **2**, indicating that the
dominant intermolecular interactions are ferromagnetic.   However, the
product $\chi_{\mathrm{p}}T$ of **4** seems to saturate below 3 K (Fig. 4).   This suggests
the competition between different types of weak interactions; at least
one of them should be ferromagnetic.   The crystal structure of **4** can
be regarded   as   a considerably distorted one   of **2** (Fig. 4).   Again
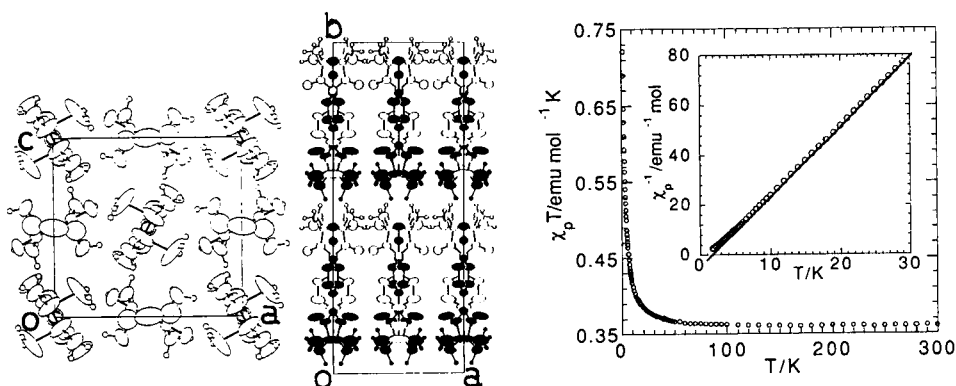

FIGURE 5   Left: Crystal structure of **5**.   Right: $\chi_{\mathrm{p}}T$ vs. *T* plot
for **5**.   The inset shows χ_{p}^{-1} vs. *T* plot and the Curie Weiss fit
(solid line).

there is a dimeric structure having NO···φ interactions.

In the crystal of the p-cyano-derivative **5**, molecular layers spread over the ac-plane, affording a typical 2D structure (Fig. 5). The molecules are arranged to form a nearly-square-lattice in the layer. The nearest-neighbor interactions in the layer correspond NO···φ and/or NO···cyano interactions. A Curie-Weiss fit of the temperature dependence of the paramagnetic susceptibility of **5** yields the Weiss constant, θ=1.5 K, indicating the ferromagnetic interactions within the layer.

In contrast to these three compounds, p-chloro-derivative **3** exhibits antiferromagnetic intermolecular interactions. The paramagnetic susceptibility of **3** follows the usual singlet-triplet model,

$$\chi = \frac{C}{T} \cdot \frac{3}{[3+\exp(-2J/k_BT)]} \qquad (2)$$

with J/k_B=-0.9 K.

Antiferromagnetic Heisenberg Systems

The temperature dependence of the paramagnetic susceptibility of the p-trifluoromethyl- and pentafluoro-derivatives (**6** and **7**, respectively) can be analyzed in terms of the alternating antiferromagnetic Heisenberg chain model,

$$H = -2J \sum_i (S_{2i-1} \cdot S_{2i} + \alpha S_{2i} \cdot S_{2i+1}). \qquad (3)$$

We obtained J/k_B=-10.4 K and α=0.2 for **6**, and J/k_B=-2.8 K and α=0.4 for **7**. The crystal structure of **6** contains molecular chains along the a-axis (Fig. 6). Within the chain, neighboring molecules
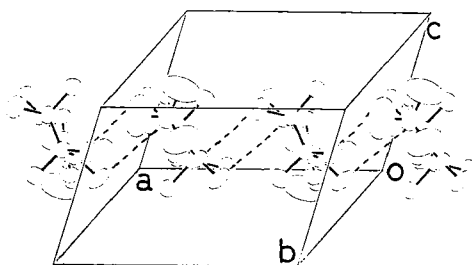

FIGURE 6   Crystal structure of **6**.

the two NO groups which form a parallelogram as a consequence of inversion symmetry. This exemplifies the antiferromagnetic nature of are associated with each other by relatively short distances between such kind of direct interactions between nitroxide groups.

In Fig. 7, $\chi_p T$ of biphenyl compound **8** is plotted against T. The decrease in $\chi_p T$ as T lowers indicates the antiferromagnetic intermolecular interactions in the crystal. Below about 5 K, $\chi_p T$ seems to approach a constant value, about 1/2 of the room temperature value. This stationary behavior implies the coexistence of different types of magnetic interactions. Another example is the case of p-bromo compound **4** below 3 K. For such cases formation of finite size cluster of spins is expected. For example, a four-spin cluster model,

$$H = -2J_1(\boldsymbol{S}_1 \cdot \boldsymbol{S}_2 + \boldsymbol{S}_3 \cdot \boldsymbol{S}_4) - 2J_2 \boldsymbol{S}_2 \cdot \boldsymbol{S}_3 , \qquad (4)$$

well reproduces the observed temperature dependence of $\chi_p T$ when $J_1/k_B = -1.5$ K and $J_2/k_B = -6.6$ K are employed.
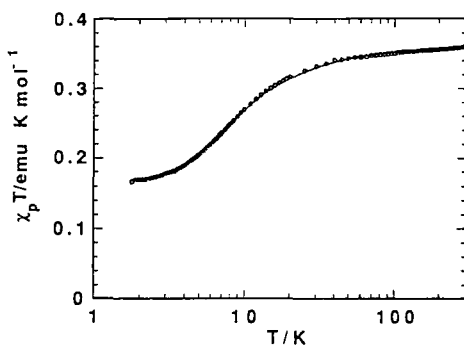

FIGURE 7 $\chi_p T$ vs. T plot for **8**. Solid line indicates the values calculated on the basis of Eq. (4).

<u>SUMMARY</u>

Ferromagnetic intermolecular interactions are found for the crystals of **1**, **2**, **4** and **5**. Nitroxide-phenyl (NO···φ) interactions are the common structural feature of these compound. The crystals of **3**, **6**, **7** and **8** have antiferromagnetic interactions. Formation of spin clusters is

suggested for the case of **4** and **8**.

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