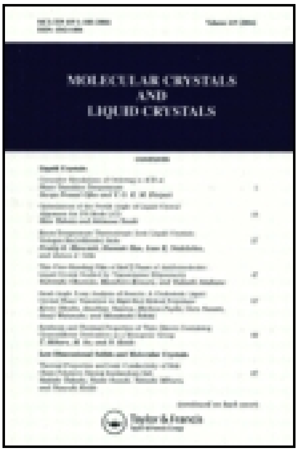

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FERRO- AND ANTIFERROMAGNETIC INTERACTIONS AND CRYSTAL STRUCTURES OF SOME ORGANIC RADICALS BASED ON NITRONYL NITROXIDE

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Abstract Our recent results of magnetization, susceptibility and electron paramagnetic resonance (EPR) measurements and crystal structure determinations for the organic radiclals based on α-nitronyl nitroxide are described. The 3-quinolyl derivative with ferromagnetic intermolecular interaction shows a considerable shift of resonance field in EPR at low temperature probably due to short-range magnetic-order formation. The *p*-diethylaminophenyl derivative is characterized as a typical one-dimensional Heisenberg antiferromagnet.

INTRODUCTION

A considerable number of the derivatives of the organic radical, α-nitronyl nitroxide (2-substituted 4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-1-oxyl-3-oxide), have recently been found to exhibit a ferromagnetic (FM) intermolecular interaction.[1-7] In order to understand possible mechanisms of the FM intermolecular interaction in the organic radicals, experimental studies of magnetic properties and crystal structures of α-nitronyl nitroxides with FM intermolecular interaction are of great interest. It is also interesting to compare the magnetic properties and crystal structures of α-nitronyl nitroxides exhibiting antiferromagnetic (AFM) intermolecular interaction with those of α-nitronyl nitroxides showing FM interactions to clarify the origin of the FM intermolecular interaction between the organic radicals. In this paper, we report magnetization isotherms at low temperature, temperature dependence of static susceptibility and electron paramagnetic resonance (EPR) spectra, and crystal structures of α-nitronyl nitroxide compounds with FM and AFM intermolecular interactions, namely 3-quinolyl nitronyl nitroxide (3-QNNN) and *p*-diethylaminophenyl nitronyl nitroxide (DEAPNN). Magnetic properties of the new α-nitronyl nitroxide compounds, *p*-N-oxypyridyl nitronyl nitroxide (*p*-NOPNN) and 2-nitro-4,5-methylenedioxophenyl nitronyl nitroxide (NMDOPNN) are also presented.

EXPERIMENTAL

3-QNNN, DEAPNN, *p*-NOPNN and NMDOPNN were prepared by the reported method[8] and recrystallized from benzene solutions.

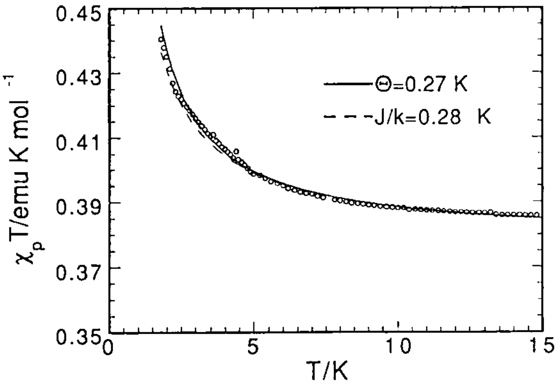
The magnetization isotherms up to 20.5 T were measured using an induction method with a multilayer pulse magnet at the Institute for Solid State Physics. The magnetic susceptibility χ was measured by a Quantum Design SQUID magnetometer. Paramagnetic susceptibility χ_p was obtained by subtracting the diamagnetic contribution, which was estimated from the χ vs. 1/T plot at high temperatures. The EPR spectra were recorded on a Varian E9 Reflection Spectrometer with an Oxford Instruments ESR900 cryostat at the Inorganic Chemistry Laboratory, University of Oxford.

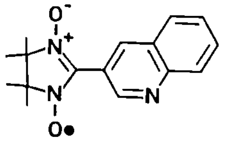
The crystal structures were solved by direct methods and refined by full-matrix least-squares fittings with anisotropic thermal parameters for non-hydrogen atoms only. $R = 0.062$ and $Rw = 0.082$ for monoclinic 3-QNNN (ref. 7) and $R = 0.053$ and $Rw = 0.048$ for tetragonal DEAPNN.

RESULTS AND DISCUSSION

3-QNNN

First, we describe the magnetic properties and crystal structure of 3-QNNN exhibiting FM intermolecular interaction. Figure 1 shows the temperature dependence of the product of χ_p and temperature T for 3-QNNN below 15 K. The product $\chi_p T$ increases steeply on lowering the temperature. The solid curve in Figure 1 represents the susceptibility calculated for the Curie-Weiss law, $\chi_p = C/(T - \Theta)$, with a Curie constant $C = 0.376$ emu K mol^{-1} and a Weiss constant $\Theta = +0.27$ K. The positive Weiss constant indicates FM intermolecular interaction for 3-QNNN. Although, as shown in the broken curve in Figure 1, the temperature dependence of $\chi_p T$ is reproduced by a one-dimensional (1D) FM Heisenberg model as well as the mean-field three-dimensional (3D) model, i.e., the Curie-Weiss law, the magnetic dimension of 3-QNNN seems to be at least two as evidenced from the crystal structure.[7] The angular dependence of the EPR linewidth of 3-QNNN shows behavior characteristic of an isotropically exchange-coupled spin system.[9] Therefore, 3-QNNN seems not to be a 1D FM system.





3-QNNN

FIGURE 1 Temperature dependence of $\chi_p T$ of 3-QNNN.

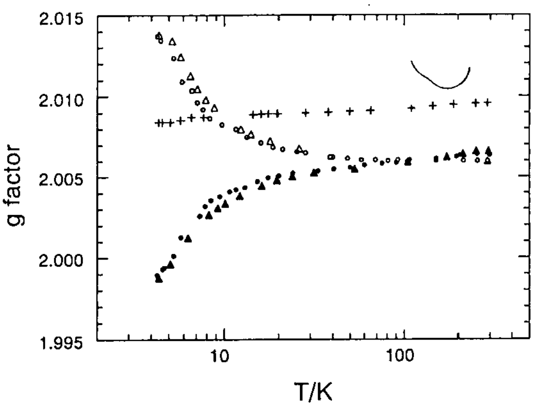


FIGURE 2 Temperature dependence of g factors of 3-QNNN. Open circles and triangles represent g_c measured with different crystal orientations in the cavity. Closed circles and triangles represent g_{a*}. Crosses represent g_b.

At low temperature, the g factors of 3-QNNN exhibit a significant shift from those at room temperature. Figure 2 shows the temperature dependence of the g factors of 3-QNNN measured with the static fields parallel to the three orthogonal axes. The g factor with the field parallel to the crystallographic c axis, g_c, increases on lowering the temperature. In contrast, the g factor with the field parallel to the a* direction, g_{a*}, decreases with the decrease of temperature. The g factor with the field parallel to the b axis, g_b, decreases only slightly on lowering temperature. Molecular displacement may cause g factor shift in the solid state. However, the values of the g factor at low temperature exceed the molecular g factors of α-nitronyl nitroxides, which are in the range between 2.002 and 2.011. Therefore, it is not persuasive to consider molecular displacement as an origin of g factor shift.

A significant g factor shift at low temperature is observed for some inorganic compounds such as $[(C_6H_{11}NH_3)CuCl_3]$ and K_2MnF_4 which are a 1D ferromagnet[10] and a 2D antiferromagnet,[11] respectively. The g factor shift results from short-range order effects.[12] Since the magnetization isotherm of 3-QNNN indicates short-range FM order formation at low temperature,[7] the g factor shift observed for 3-QNNN is probably due to the effects of short-range order. An increase of g factor (a decrease of resonance field) occurs along an easy axis while a decrease of g factor (an increase of resonance field) occurs along a hard axis.[13] Therefore, one can determine the preferential direction of spin magnetic moments in the solid by measuring the g factor shifts at low temperature.

Since the g factor of 3-QNNN increases along the c axis and decreases along the b and a axes, the easy axis of 3-QNNN appears to be the c axis. In a ferromagnet the easy axis corresponds to the preferential direction of spins. The preferred spin orientations in the 3-QNNN crystal is thus along the c axis.

To discuss the relation between the spin orientaions and molecular structure of 3-QNNN, the crystal structure projected along the a axis is shown in Figure 3. The molecular long-axis is oriented nearly perpendicular to the ac plane. The preferred spin orientations would therefore be perpendicular to the molecular long-axis of 3-QNNN. This implies that the preferred spin orientations are nearly parallel to the direction through the O-N-C-O-N bonds of nitronyl nitroxide, although more elaborate studies will be needed to confirm this.

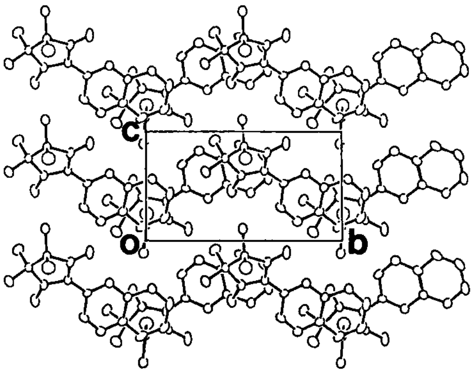
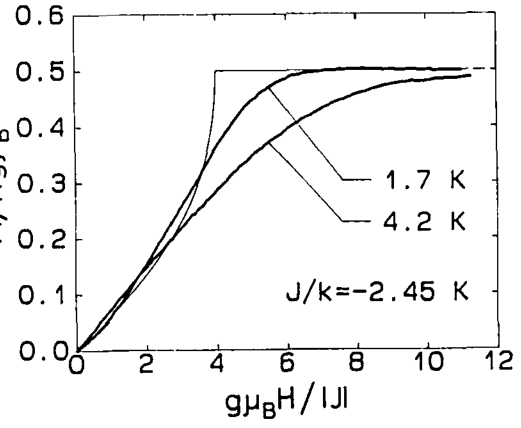
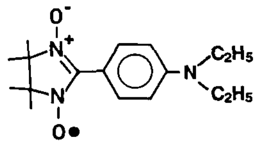


FIGURE 3 The crystal structure of 3-QNNN.

DEAPNN

Secondly, we show the magnetic properties and crystal structure of DEAPNN, which is a typical 1D AFM Heisenberg system. The thick solid lines in Figure 4 show the magnetization isotherms of DEAPNN at 1.7 and 4.2 K in the magnetic fields up to 20.5 T. The magnetization M is normalized by dividing $Ng\mu_B$ where N is Avogadro's constant. In this scale, the saturation magnetization is 0.5 for the $S = 1/2$ system.[14] The magnetic field H is shown by the reduced field $g\mu_B H/|J|$ with an exchange coupling constant $J/k = -2.45$ K, which is determined from the temperature dependence of χ_p.[15] The magnetization isotherm at 1.7 K does not follow the Brillouin function with $S = 1/2$ unlike conventional organic materials. The magnetization isotherm shows upward curvature at reduced field lower than $g\mu_B H/|J| \cong 3$, saturating rapidly around the field $g\mu_B H/|J| \cong 6$, and finally becomes constant at $g\mu_B H/|J| > 7$. The magnetization isotherm at 4.2 K shows rather monotonous field dependence. Saturation of magnetization at high reduced fields, however, still appears rapid compared with that predicted by the Brillouin function with $S = 1/2$.





DEAPNN

FIGURE 4 Magnetization isotherms of DEAPNN at 1.7 and 4.2 K are shown by thick solid lines. Thin solid line represents the zero-temperature isotherm (see text).

The behavior of the magnetization isotherms of DEAPNN at low temperatures is well interpreted in terms of the spin-flop phenomenon in the 1D regular isotropic AFM Heisenberg model. The zero-temperature isotherm, calculated by Bonner and Fisher,[14] is drawn by the thin solid line in Figure 4. At low reduced fields, $M/Ng\mu_B$ at 1.7 K follows approximately the zero-temperature isotherm. However, the singularity at $g\mu_B H/|J| = 4$ is not observed. Instead of the singularity, the magnetization isotherm exhibits rapid saturation around $g\mu_B H/|J| \cong 6$. The absence of a clear singularity in the magnetization isotherm at finite temperature has already been predicted by Bonner and Fisher[14] and the magnetization isotherms observed are well reproduced with the exchange coupling constant $J/k = -2.45$ K.[15] It is worth noting that, to the best of our knowledge, this is the first time that the spin-flop phenomenon in a 1D regular Heisenberg antiferromagnet has been observed in a purely organic material.[15]

To discuss magnetic dimension of DEAPNN further, the crystal structure is shown in Figure 5. The DEAPNN molecules form side-by-side stacks along the c axis and the neighboring molecules are arranged in a head-to-tail manner. The DEAPNN molecules in the neighboring stacks are oriented so that the molecular long axes are perpendicular to each other. Then the exchange coupling between the molecules in the neighboring stacks would not be strong and the coupling would be restricted to the neighboring molecules within the stacks. This situation is consistent with the 1D antiferromagnetic behavior of DEAPNN.

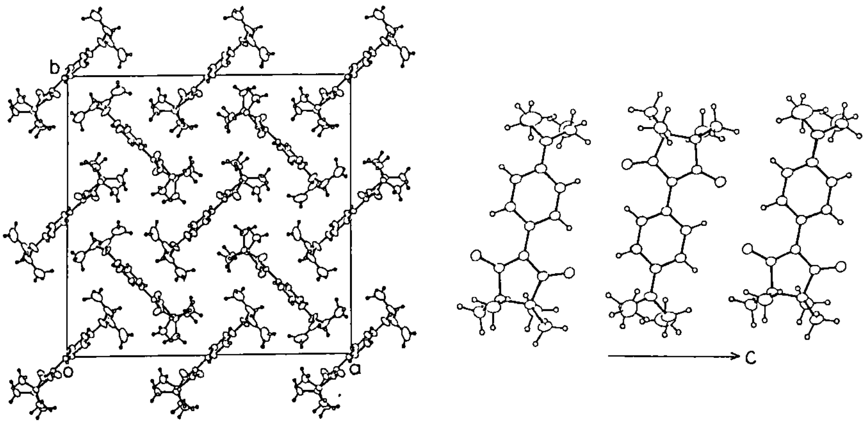
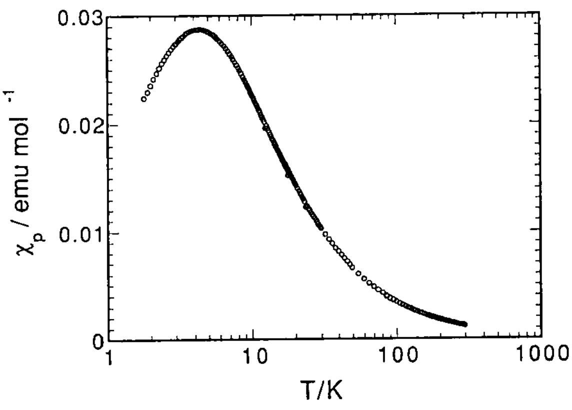


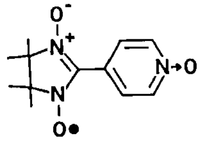
FIGURE 5 The crystal structure of DEAPNN.

The 1D antiferromagnetic behavior is further observed in the angular dependence of the EPR linewidth of DEAPNN. The linewidth shows a maximum at the field parallel to the c axis (the stacking direction) while it shows minima at the fields along the direction tilted from the c axis by 54.7°, i.e., the magic angle. In contrast, the linewidth is constant in the ab plane, which is perpendicular to the stacking direction. Such behavior is characteristic of 1D exchange coupled spin systems.

p-NOPNN and NMDOPNN

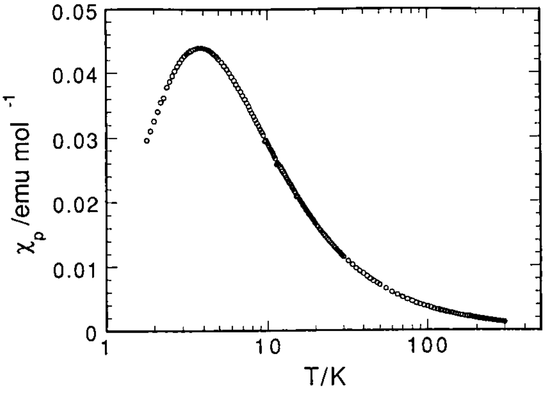
These two nitronyl nitroxide compounds were synthesized to obtain more effective intermolecular interaction by modifying the molecular structure of *p*-nitrophenyl nitronyl nitroxide (*p*-NPNN), the first organic ferromagnet.[4] The *p*-NOPNN molecule has an N-oxide group instead of the nitro group of the *p*-NPNN molecule to make a more planar substituent with the nitronyl nitroxide moiety. The NMDOPNN molecule has a methyldioxo group at the periphery of the *o*-nitrophenyl substituent. If the substituent moieties are located near the NO group(s) of the nitronyl nitroxide moieties of neighboring molecules, as observed for the *p*-NPNN crystal, it could result in FM intermolecular interaction because large magnitude of SOMO-NHOMO (NLUMO) overlaps, which favor FM intermolecular interaction,[16] are expected.

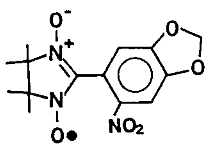




p-NOPNN

FIGURE 6 Temperature dependence of χ_p of *p*-NOPNN.





NMDOPNN

FIGURE 7 Temperature dependence of χ_p of NMDOPNN.

Figure 6 shows the temperature dependence of χ_p of *p*-NOPNN. A broad maximum of χ_p is observed around 4.5 K. This behavior indicates AFM intermolecular interaction in *p*-NOPNN. Figure 7 shows the temperature dependence of χ_p of NMDOPNN. A broad maximum of χ_p is observed around 4 K. This result suggests AFM intermolecular interaction in NMDOPNN. Thus both the two nitronyl nitroxide derivatives, *p*-NOPNN and NMDOPNN, exhibit weak AFM intermolecular interaction contrary to the expectation mentioned above. To discuss their magnetic properties further, it will be necessary to determine their crystal structures.

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