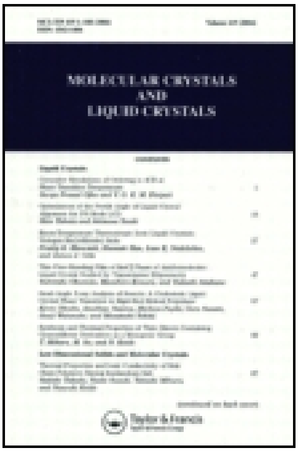

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Ferromagnetic Intermolecular Interactions and Magnetically Ordered States in Some Organic Radical Crystals

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Version of record first published: 24 Sep 2006.

To cite this article: Tadashi Sugano , Mohamedally Kurmoo , Peter Day , Francis L. Pratt , Stephen J. Blundell , William Hayes , Masayasu Ishikawa , Minoru Kinoshita & Yuji Ohashi (1995): Ferromagnetic Intermolecular Interactions and Magnetically Ordered States in Some Organic Radical Crystals, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 271:1, 107-114

To link to this article: http://dx.doi.org/10.1080/10587259508034043

Mol. Cryst. Liq. Cryst., 1995, Vol. 271, pp. 107–114
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FERROMAGNETIC INTERMOLECULAR INTERACTIONS AND MAGNETICALLY ORDERED STATES IN SOME ORGANIC RADICAL CRYSTALS

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Abstract Recent results of magnetization, susceptibility and muon spin rotation (μSR) measurements and crystal structure determinations of the organic radicals based on α-nitronyl nitroxide are described. Temperature variation of μSR and a.c. susceptibility reveals that the organic radicals, which are found to exhibit ferromagnetic intermolecular interactions, undergo magnetic phase transitions at around 0.1~ 0.7 K. The organic radicals have not only a simply ferromagnetic ordered state but also canted spin magnetic orders. Microscopic views of the magnetically ordered states in the organic radicals are discussed by taking account of the molecular arrangements in the crystals.

INTRODUCTION

A considerable number of two series of organic radicals, α-nitronyl nitroxide (2-substituted 4,4,5,5-tetramethyl-3-oxy-2-imidazolinyl-1-oxyl) and 4-(arylmethyleneamino)-TEMPO (4-(arylmethyleneamino)-2,2,6,6-tetramethylpiperidin-1-oxyl), have been found to exhibit ferromagnetic (FM) intermolecular interactions.[1] Of these radicals, the *β* modification of *p*-nitrophenyl nitronyl nitroxide (*p*-NPNN),[2] 4-benzylideneamino-TEMPO (Ref. 3) and 4-(*p*-phenylbenzylideneamino)-TEMPO (Ref. 4) have recently been found to show phase transitions to ferromagnetically ordered states.

Experimental studies that correlate the magnetically ordered state and crystal structure of the organic radicals with FM intermolecular interaction are needed to elucidate the mechanisms of FM intermolecular interaction in these organic radicals. Muon spin rotation (μSR) technique is a powerful tool to study magnetically ordered states.[5] We have therefore measured μSR of 3-quinolyl nitronyl nitroxide (3-QNNN), *p*-pyridyl nitronyl nitroxide (*p*-PYNN) and *p*-NPNN. We discuss here microscopic views of the magnetically ordered states of these organic radicals on the basis of the μSR results and crystal structures.

The quest for new organic ferromagnets is also necessary to throw light on the mechanisms of FM intermolecular interactions between organic radicals. We have therefore measured magnetization isotherms and temperature dependence of susceptibility of new derivatives of nitronyl nitroxide; naphthyl, quinolyl, pyrenyl, fluorenyl, carboxyaryl and trihydroxyphenyl nitronyl nitroxide. In this paper we present data on several nitronyl-nitroxide derivatives with FM intermolecular interactions.

EXPERIMENTAL

All the organic radicals studied here were prepared by the reported method[6] and recrystallized from benzene, chloroform and methanol solutions.

The magnetization isotherms up to 5.5 T or 7 T and the magnetic susceptibility χ of a polycrystalline sample at 0.1 ~ 0.3 T were measured by using a Quantum Design MPMS2 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. Low-temperature a.c. susceptibility of a polycrystalline sample was measured by using an induction method.

Low-temperature μSR measurements for polycrystalline pellet and single crystal samples were carried out at the ISIS muon facility of the Rutherford Appleton Laboratory in the U.K. and the πM3 beam line at the Paul Scherrer Institute in Switzerland. Details of the experiments and theoretical analyses are described elsewhere.[7,8]

RESULTS AND DISCUSSION

Magnetic interactions in two series of isomers of nitronyl nitroxides: quinolyl and naphthyl nitronyl nitroxides

First, we describe the magnetic properties of the three structural isomers of quinolyl nitronyl nitroxide (QNNN). Figure 1 shows the temperature dependence of the product of χ_p and temperature T for 2-quinolyl nitronyl nitroxide (2-QNNN; crosses), 3-quinolyl nitronyl nitroxide (3-QNNN; circles) and 4-quinolyl nitronyl nitroxide (4-

QNNN; triangles). The product χ_pT of 3-QNNN increases steeply on lowering temperature, while that of 4-QNNN decreases very rapidly upon lowering temperature as shown in the inset of Figure 1. In the case of 2-QNNN, χ_pT increases a little with decreasing temperature. The solid curves in Figure 1 represent 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 for 3-QNNN and $\Theta = +0.04$ K for 2-QNNN. The positive Weiss constants indicate FM intermolecular interaction in 2-QNNN and 3-QNNN. The crystal structure of 2-QNNN (not shown) is similar to that of 3-QNNN.[9] The NO groups of the neighboring 2-QNNN molecules, on which singly occupied molecular orbital (SOMO) is localized, are separated from each other as is also observed for 3-QNNN. The SOMO-SOMO overlap is therefore so small that FM intermolecular interaction is favored.[10]

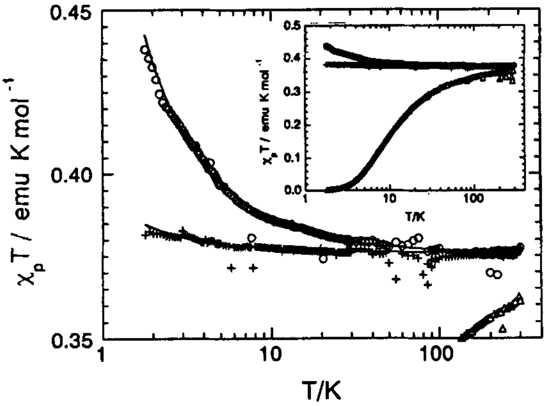

FIGURE 1 Temperature dependence of χ_pT of 2-QNNN (crosses), 3-QNNN (circles) and 4-QNNN (triangles).

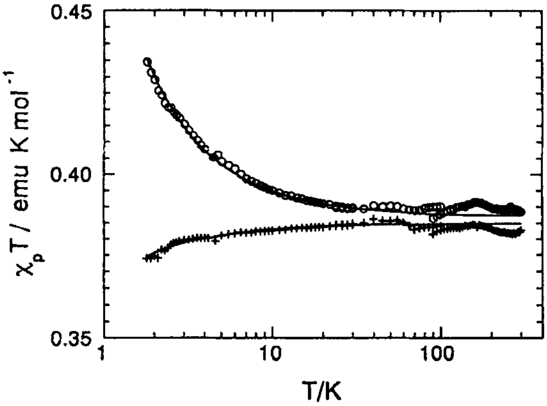

FIGURE 2 Temperature dependence of χ_pT of 1-NAPNN (circles) and 2-NAPNN (crosses).

Next, we present the magnetic properties of the two structural isomers of naphthyl nitronyl nitroxide (NAPNN). Figure 2 shows the temperature dependence of $\chi_p T$ for 1-naphthyl nitronyl nitroxide (1-NAPNN; circles) and 2-naphthyl nitronyl nitroxide (2-NAPNN; crosses). The product $\chi_p T$ of 1-NAPNN increases steeply on lowering temperature, while that of 2-NAPNN decreases slightly with decreasing temperature. The solid curves in Figure 2 represent the susceptibility calculated for the Curie-Weiss law with a Curie constant C = 0.386 emu K mol^{-1} and a Weiss constant Θ = +0.20 K for 1-NAPNN and Θ = −0.05 K for 2-NAPNN. The positive Weiss constant of 1-NAPNN indicates FM intermolecular interaction. The molecular structure of 1-NAPNN with FM interaction is similar to that of 4-QNNN with antiferromagnetic (AFM) interaction, while the molecular structure of 2-NAPNN with AFM interaction is similar to 2- and 3-QNNN with FM interaction, except for the absence of a nitrogen atom in the aromatic ring. Therefore, the molecular structure of the organic radical seems not to be predominantly responsible for the sign of the intermolecular magnetic interaction. To examine this point further, crystal structure analyses of 1- and 2-NAPNN are currently in progress.

Magnetic interactions in some carboxyaryl nitronyl nitroxides

Carboxy groups have a potential to form hydrogen-bond among molecules. Hydrogen-bonds may affect physical properties of materials. We have therefore synthesized some carboxyaryl derivatives of nitronyl nitroxide and measured temperature dependence of them in order to study the effects of hydrogen-bonds on the intermolecular magnetic interactions.

Figure 3 shows the temperature dependence of $\chi_p T$ of nitronyl nitroxide 2-furancarboxylic acid (2-FCANN; circles), nitronyl nitroxide *p*-phenoxyacetic acid (*p*-POANN; crosses) and nitronyl nitroxide *p*-cinnamic acid (*p*-CINANN; triangles). The temperature dependences of $\chi_p T$ of these three radicals are not totally reproduced by the Curie-Weiss law with negative (AFM) Weiss constants Θ = −2.5 K for 2-FCANN, Θ = −1.3 K for *p*-POANN and Θ = −1.2 K for *p*-CINANN, as shown by the dotted lines in Figure 3. Upon lowering temperature, the experimental data exhibit an upward shift from the theoretical values calculated by using the Curie-Weiss law. Since any AFM model predicts a downward shift from the values of the Curie-Weiss law, upward shift implies that weak FM interaction coexists with major AFM interaction. We have therefore analyzed the experimental data by assuming that there are two types of interaction, i.e., FM and AFM interactions. The solid lines represent the values calculated with Θ = −2.8 K and Θ = +0.57 K for 2-FCANN, Θ = −1.7 K and Θ = +0.3 K for *p*-POANN, and Θ = −1.6 K and Θ = +0.3 K for *p*-

ClNANN. The values obtained by this procedure give a good fit to the experimental values. However, more elaborate analyses and crystal structure determinations are indispensable to understand the magnetic interactions in these compounds.

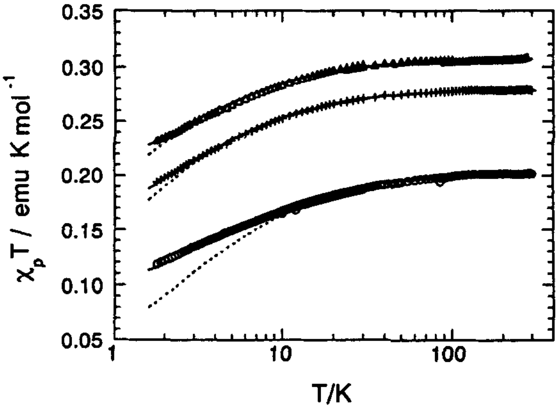

FIGURE 3 Temperature dependence of $\chi_p T$ of 2-FCANN (circles), *p*-POANN (crosses) and *p*-ClNANN (triangles). The vertical scale is shifted upward by 0.05 for *p*-POANN and 0.10 for *p*-ClNANN.

Magnetically Ordered states and μSR spectroscopy of some nitronyl nitroxides with FM intermolecular interaction

μSR of a single crystal sample is an important technique in providing evidence for the direction of spontaneous magnetization of organic radical crystals, since zero-field (ZF) measurements directly probe the local magnetic field averaged over the bulk of the sample and can be carried out down to a few tens of mK where some organic radicals are in the magnetically ordered state. We have therefore studied magnetic structures of two nitronyl nitroxide derivatives, 3-QNNN and *p*-PYNN, through the measurement of ZF-μSR.

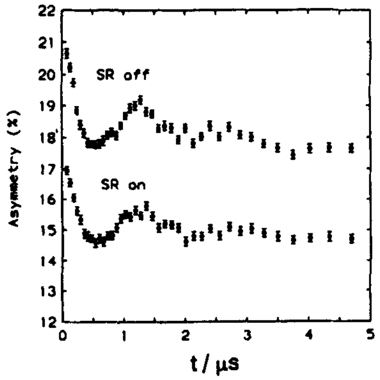

FIGURE 4 Time evolution of ZF-μSR of an aligned array of single crystals of 3-QNNN at 10 mK with a spin rotator off (upper) and on (lower).

Figure 4 shows ZF-μSR of an aligned array of single crystals of 3-QNNN at 10 mK, which is well below the transition temperature. The upper spectrum was recorded with a spin rotator switched off and the lower spectrum was observed with the spin rotator switched on. When the spin rotator is switched off, the polarization direction of the incident muon spin is parallel to the muon beam. On the other hand, when the spin rotator is switched on, the polarization direction of muon spin is rotated by 45° from the muon beam for our experimental set up. The amplitude of μSR oscillation measured with the muon spin parallel to the beam is larger than that measured with the muon spin rotated by 45°. The amplitude of μSR oscillation, induced by the internal magnetic field of a sample, is largest when the direction of internal field is perpendicular to the muon spin, while the amplitude of μSR oscillation is reduced when the internal field is parallel to the muon spin. Therefore, the direction of internal field is approximately perpendicular to the muon beam. Since the crystallographic *c* axis of the single crystals of 3-QNNN was oriented perpendicular to the muon beam, it is concluded that the internal magnetic field is nearly parallel to the *c* axis of 3-QNNN.

To discuss the relation between the spin orientations and molecular arrangement of 3-QNNN, the crystal structure projected along the *a* axis is shown in Figure 5(a). The μSR results suggest that the internal field is nearly parallel to the *c* axis. As shown by arrows in Figure 5(a), the spin magnetic moments on the neighboring molecules are likely to be canted from the c axis so as to leave a net magnetic moment parallel to the c axis. This picture is consistent with the previous calculation of internal magnetic field based on the canted spin structure of 3-QNNN.[7]

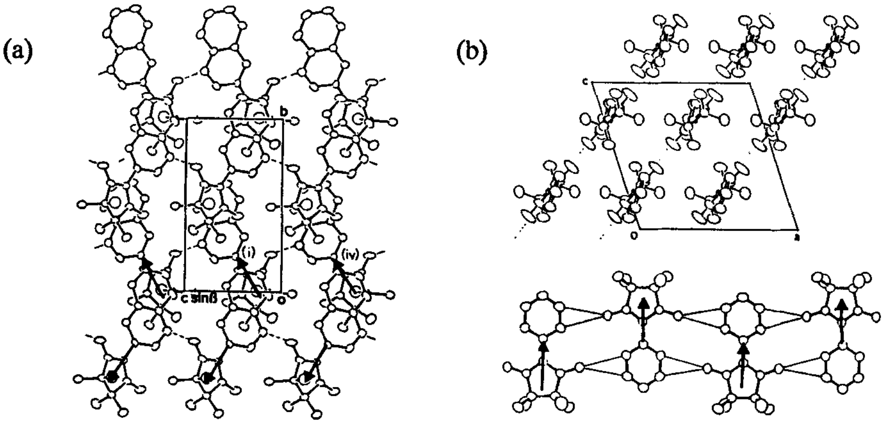

FIGURE 5 (a) A possible spin structure of 3-QNNN. (b) A possible spin structure of *p*-PYNN. The arrows represent the directions of spin magneic moments on each molecule (see text).

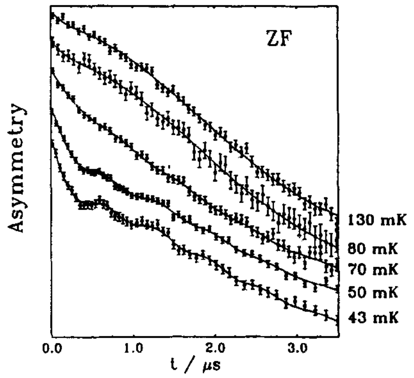

FIGURE 6 Time evolution of ZF-μSR of a polycrystalline sample of *p*-PYNN as a function of temperature.

Figure 6 shows ZF-μSR of a polycrystalline sample of *p*-PYNN. A weak oscillation is observed superimposed onto a damping background of muon polarization due to random orientations of individual magnetic moments. The oscillation frequency of ZF-μSR in *p*-PYNN is higher than that of 3-QNNN. From the temperature dependence of the frequency, the internal magnetic field of *p*-PYNN is estimated to be 12.0±0.4 mT,[8,11] twice as large as that of 3-QNNN, 6.0±0.4 mT.[7] The internal field is rather similar in size to that observed in the β modification of *p*-NPNN which is a ferromagnet, although the a.c. susceptibility of *p*-PYNN below the transition temperature is considerably smaller than that of *p*-NPNN.

To discuss the relation between the spin orientation and molecular arrangement of *p*-PYNN, the crystal structures[12] projected onto the *ac* plane (upper) and the $(10\bar{1})$ plane (lower) are shown in Figure 5(b). There are one-dimensional chains along the [101] direction. The FM intermolecular intraction in *p*-PYNN is predicted to be one-dimensional from the temperature dependence of d.c. susceptibility above 3 K.[12] The magnetic transition could therefore originate from the intrachain long-range FM ordering as represented by the arrows in Figure 5(b). Interchain disorder due to weak interchain interaction could result in incomplete three-dimensional long-range order of *p*-PYNN, because the a.c. susceptibility of *p*-PYNN below transition temperature is not so large as a ferromagnet. To confirm this picture, especially the magnetic easy axis, we are planning to measure μSR of the single crystals of *p*-PYNN.

ACKNOWLEDGEMENTS

This work was supported by the Grant-in-Aid for Scientific Research and the Grant-in-Aid for Scientific Research on Priority Area "Molecular Magnetism" (Area No.

228) from the Ministry of Education, Science and Culture (Japan), and by the EPSRC and the Royal Society (UK).

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