LETTER TO THE EDITOR

Magnetism in the nitronyl nitroxide isomers 1-NAPNN and 2-NAPNN studied by μ^+SR

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Abstract. We report the results of muon-spin-rotation/relaxation (μ^+SR) experiments on two recently discovered nitronyl nitroxides, 1- and 2-naphthyl nitronyl nitroxide (1-NAPNN and 2-NAPNN). These two compounds are chemical isomers but, because of their slightly different molecular shapes, they have quite different crystal packing. A clear magnetic transition in the zero-field muon-spin relaxation is observed in 1-NAPNN below 100 mK while no such transition is seen in 2-NAPNN. These results support the postulate that the crystal structure strongly influences the nature of the magnetic ground states in these materials.

The nitronyl nitroxides are an interesting class of molecular crystals which show a variety of magnetic ground states depending on the precise details of their crystal structure and chemical composition [1–7]. Because they are fully organic, composed only of carbon, hydrogen, nitrogen and oxygen, the observation [1, 2] of ferromagnetism at 0.65 K in one of them, *para*-nitrophenyl nitronyl nitroxide (*p*-NPNN), was remarkable. Muon-spin-rotation/relaxation (μ^+SR) is a technique which has been successfully used to observe the ferromagnetic transition in a number of these materials [3–7]. In μ^+SR the transition to a state in which there is a local field which is quasistatic on a microsecond time-scale can often be monitored by observing the onset of coherent oscillations in the positron decay asymmetry.

There is an unpaired spin on the nitronyl nitroxide molecule which is associated with the two N–O groups. By making chemical changes to the rest of the molecule, the overlap of particular orbitals on neighbouring molecules can be altered, thereby favouring (or hindering) the ferromagnetic ordering of these spins. A series of materials which incorporate the nitronyl nitroxide group can be synthesized, enabling a systematic study to be made of the magnetism in this family of molecular crystals. Such experiments are aimed at providing an understanding of the rôle of the molecular structure in determining the intermolecular orbital overlap, the crystal structure, and hence the magnetic properties.

In this letter, we report the first μ^+SR study of two *isomeric* nitronyl nitroxides which, though having precisely the same chemical formula, exhibit contrasting magnetic properties. The samples are 1- and 2-naphthyl nitronyl nitroxide (1-NAPNN and 2-NAPNN, both $C_{17}H_{19}N_2O_2$, see figure 1) which consist of the usual nitronyl nitroxide group attached to a 'double benzene ring' (naphthalene) group in two different positions. These two compounds
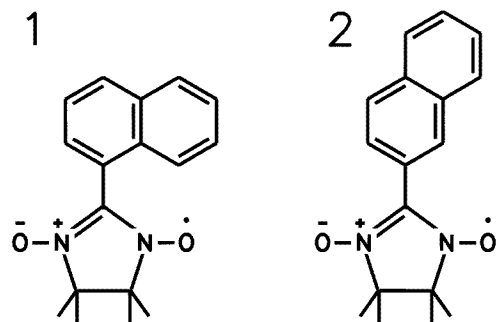
**Figure 1.** Molecular structure: **1**, 1-NAPNN; **2**, 2-NAPNN.

are chemical isomers but, because of their slightly different molecular shapes, they have quite different crystal packing. 1-NAPNN has a monoclinic structure (space group Cc—see figure 2(a)) while 2-NAPNN is orthorhombic (space group $P2_12_12_1$—see figure 2(b)) [8]. The differences in crystal structure lead to a dramatic effect on the magnetic ground states: as described below, in 1-NAPNN the orbital overlap determined by the crystal structure is favourable for ferromagnetic ordering while in 2-NAPNN it is not. This is supported by bulk magnetic susceptibility measurements, carried out to just below 2 K, which show a positive Weiss constant ($\theta = +0.2$ K) in 1-NAPNN but a negative Weiss constant ($\theta = -0.05$ K) in 2-NAPNN [9]. Our μ^+SR measurements show that a clear transition in the zero-field relaxation function occurs in 1-NAPNN just below 100 mK while no transition is observed for 2-NAPNN. These two compounds illustrate the substantial effect of molecular shape on crystal structure and hence magnetic properties.

In a μ^+SR experiment, a beam of spin-polarized positive muons is stopped in a target specimen. Each muon subsequently decays (with a mean lifetime of 2.2 μs), emitting a positron preferentially along the muon-spin direction because of the parity violation of the weak interaction [10]. The time-dependent positron emission asymmetry is described by the muon-spin-relaxation function $G_z(t)$, given by

$$G_z(t) = (N^+(t) - \alpha N^-(t))/(N^+(t) + \alpha N^-(t))$$

where $N^{\pm}(t)$ are the time histograms of positrons counted in the forward ($+$) and backward ($-$) detectors and where α is a factor which reflects the different solid angles and efficiencies of the forward and backward detectors. We used polycrystalline powder samples of 1-NAPNN and 2-NAPNN in the form of discs 25 mm in diameter and 1 mm thick. These were mounted on a high-purity silver sample holder which was in turn mounted on a dilution refrigerator in the MUSR facility at ISIS (at the Rutherford Appleton Laboratory, UK).

Longitudinal-field (LF) measurements (figure 3) have been used to measure temperature-dependent repolarization of the initial asymmetry. In the LF technique a magnetic field is applied parallel to the initial muon-spin direction. If muonium (μ^+e^-) is formed in the sample, a fraction of the muon polarization oscillates very rapidly due to the hyperfine interaction and is not observable. As the applied field is increased, this lost polarization is recovered since the amplitude of the oscillations decreases as the field 'quenches' the hyperfine interaction [11, 12]. The midpoint field of this observed recovery of polarization (monitored by the field dependence of $G_z(0)$) provides information about the strength of the hyperfine interaction. The fitted curves (figure 3) assume muonium with an isotropic hyperfine interaction and yield hyperfine constants in the range 200–400 MHz (typical of muonium in a radical state) and paramagnetic fractions of ~30% which are comparable with values obtained in other nitronyl nitroxides [4].

(*a*)

(*b*)
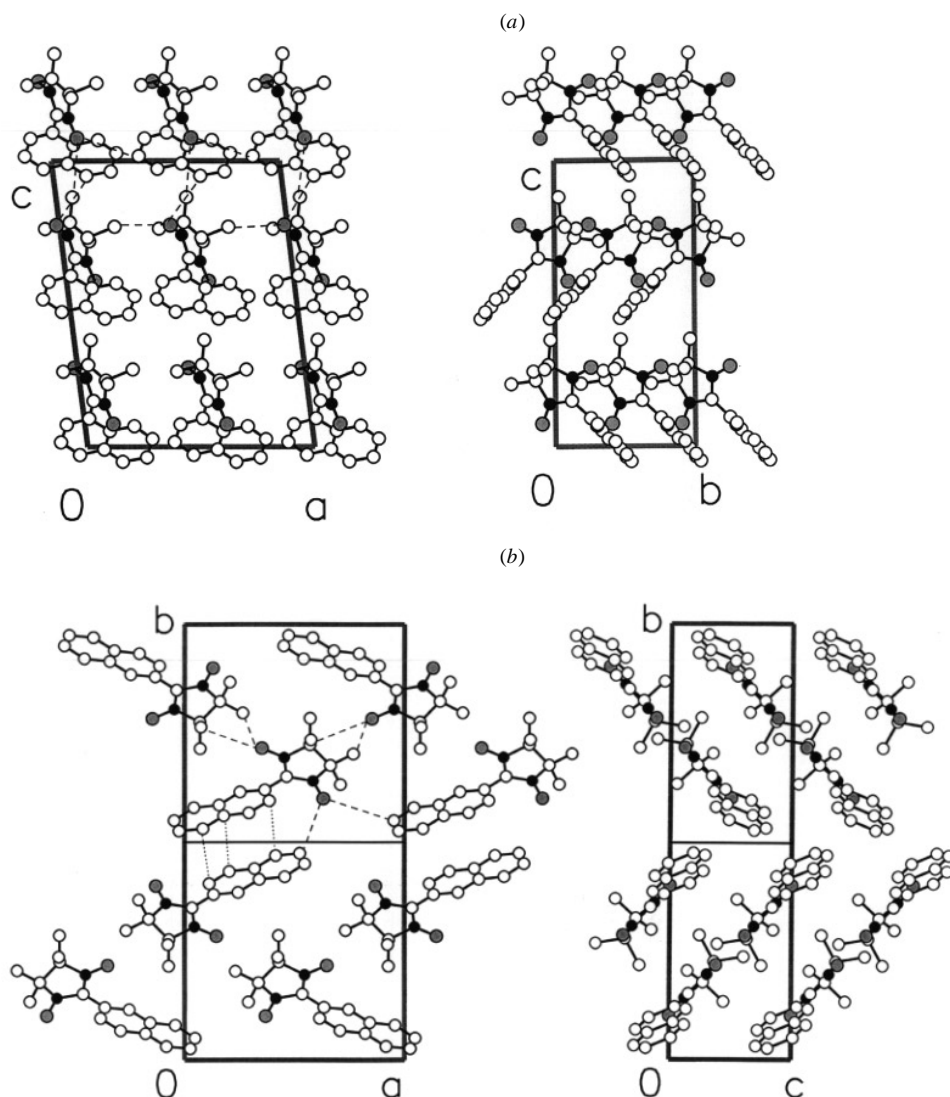
Figure 2. The crystal structure of (a) 1-NAPNN and (b) 2-NAPNN projected along different crystal axes. Nitrogen (oxygen) atoms have been drawn as filled (shaded) circles for clarity. The empty circles correspond to carbon atoms. The hydrogen atoms are not shown. Intermolecular interactions favouring ferromagnetic (antiferromagnetic) ordering are shown as dashed (dotted) lines (for details, see the text). The solid line in (b) shows the (020) plane which divides the unit cell into two parts.

Measurements with zero applied magnetic field are presented in figure 4. A clear transition is observed via changes in the relaxation function $G_z(t)$ in 1-NAPNN at temperatures below 100 mK (figure 4(a)). The observed relaxation of asymmetry below this transition temperature is well fitted by two terms, one fast-decaying oscillatory term (with frequency $\sim$1 MHz and relaxation rate $\sim$3–4 μs^{-1}) which dominates the initial relaxation and a second slowly relaxing exponential (with relaxation rate, $\lambda \sim 0.3$ μs^{-1}) which dominates the long-time behaviour. Above the transition the asymmetry can be described
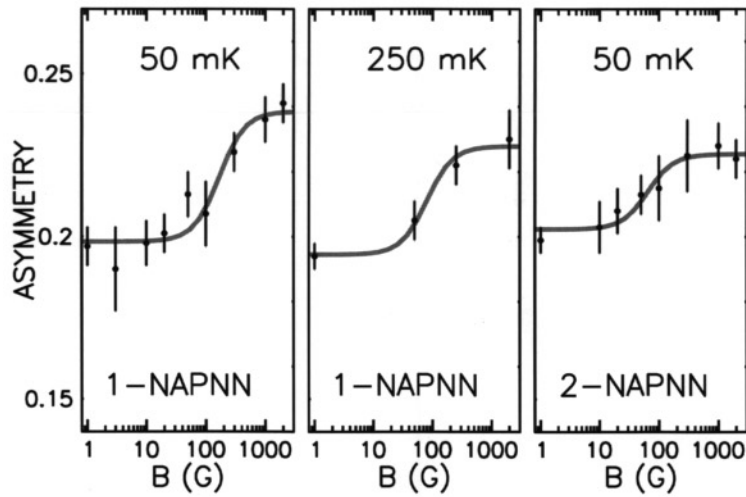
Figure 3. Repolarization of the initial asymmetry in 1-NAPNN and 2-NAPNN at the temperatures shown. The solid lines are fits assuming that the repolarization can be ascribed to isotropic muonium.
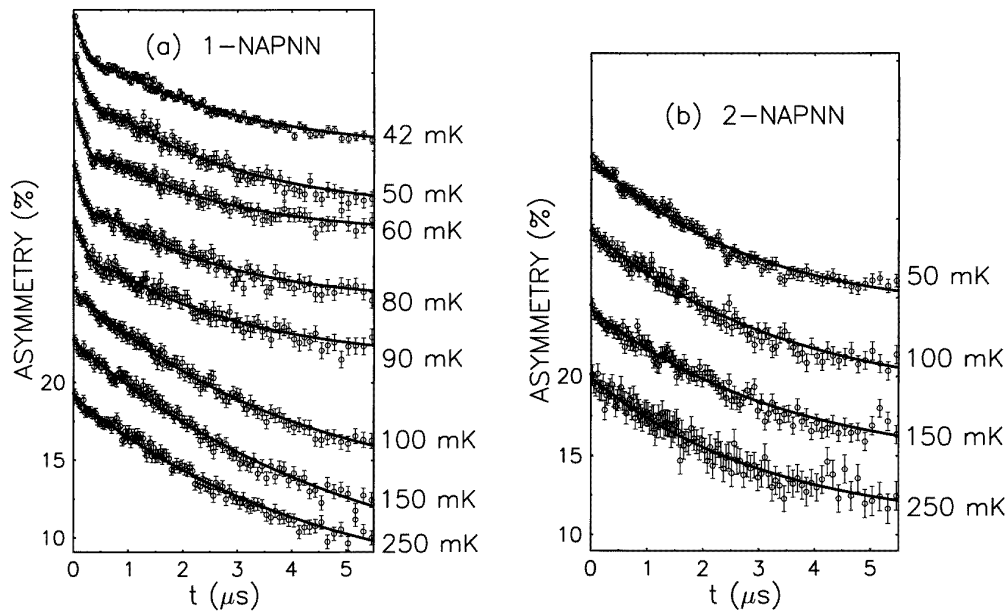
Figure 4. Zero-field μ^+SR data on (a) 1-NAPNN and (b) 2-NAPNN. The ordinate scale refers to the lowest trace in each case. The other traces are all vertically offset for clarity, but the scale factor applied to each trace of both samples is identical. Data are fitted as described in the text.

by a single-exponential decay ($\lambda \sim 0.2 \ \mu s^{-1}$). $G_z(t)$ is largely independent of temperature in 2-NAPNN and is also well described by a single slow exponential ($\lambda \sim 0.3 \ \mu s^{-1}$).

The fitted repolarization in 1-NAPNN is very similar above and below the transition (figure 3) indicating that there are no high-frequency oscillations associated with the low-

temperature state which are too fast to observe with muons from a pulsed source. Also, it is reasonable to assume that the observed relaxation in both materials is due primarily to diamagnetic muon states because the paramagnetic muon fraction deduced from the repolarization measurement is too small to account for the amplitude of the relaxing fraction. This assumption is consistent with the observation of a significant diamagnetic fraction in all other nitronyl nitroxides which have been studied with μ^+SR [4, 5].

The 1 MHz precession frequency corresponds to a local field of $\sim$75 G, comparable with values obtained for other nitronyl nitroxides [5]. The zero-field relaxation in 1-NAPNN is quenched in modest longitudinal fields, the slow relaxation disappearing at $\sim$20 G, and the fast relaxation quenching only in a field of a few hundred Gauss (not shown). These values are consistent with typical electronic dipole fields calculated for these systems, but the precise origin of the two relaxations is not clear at present. We suspect that a distribution of magnetically inequivalent muon sites leads to the observed complicated relaxation function and our fitted curves are merely parametrizations of the data. However, the form of the relaxation in 1-NAPNN is very similar to that seen in *p*-PYNN in which, below the magnetic transition temperature, very weak, but discernible, oscillations were observed on a fast-relaxing background [5]. It may be that in 1-NAPNN we are observing similar weak oscillations which are even more strongly damped, to a point where they are almost beyond resolution. However, the exponential character of the relaxation is also strongly suggestive of electron-spin dynamics, perhaps connected with two or more muon sites which become equivalent or nearly equivalent above the transition (there is also a nuclear dipolar contribution to the relaxation). That several muon sites may be energetically favourable in nitronyl nitroxides is supported by recent calculations [13].

We now discuss the effect of the crystal structure on the magnetic properties observed by μ^+SR. The crystal structures projected onto the *ac* and *bc* planes of 1-NAPNN (figure 2(a)) demonstrate that the noncentrosymmetric 1-NAPNN molecules are oriented in the same direction along the *c*-axis as found for 3-quinolyl nitronyl nitroxide (3-QNNN) which exhibits ferromagnetic interactions [14]. There are several intermolecular interatomic distances between neighbouring molecules in 1-NAPNN which are comparable with those found for 3-QNNN, as shown by the dashed lines in figure 2(a). Of these interatomic contacts which form a three-dimensional (3D) molecular network, the contacts between the oxygen atoms of the NO groups and the carbon atoms on the naphthyl ring, as well as the contacts between the oxygen atoms of the NO groups and the methyl carbon atoms, are of particular relevance in the ferromagnetic intermolecular interaction. The former contacts may result in SOMO–NHOMO (singly occupied molecular orbital–next highest occupied MO) and/or SOMO–NLUMO (next lowest unoccupied MO) overlaps which favour ferromagnetic intermolecular interaction [15], while the latter contacts could also yield a ferromagnetic intermolecular interaction via the hydrogen bonds between NO and methyl groups [16]. The magnetic transition in 1-NAPNN therefore probably arises from the 3D network structure with ferromagnetic interactions. Although our μ^+SR experiments have demonstrated a magnetic transition at about 100 mK in this material, we cannot determine whether this is antiferromagnetic or ferromagnetic. However, the latter interpretation is supported by susceptibility measurements (see above) [9].

The crystal structure of 2-NAPNN projected on to the *ab* and *ac* planes (figure 2(b)) is, as noted above, very different from that for 1-NAPNN. The molecular arrangement of 2-NAPNN in the half of the unit cell divided at the (020) plane (the solid line in figure 2(b)) is very similar to that found for 3-QNNN [14] which shows ferromagnetic interactions [6, 7, 14] and has a molecular structure which is almost identical to that of 2-NAPNN. Although this kind of molecular arrangement, and hence the dashed lines

in figure 2(a), appear to therefore yield a ferromagnetic intermolecular interaction, the molecular arrangement of 2-NAPNN in the other half of the unit cell gives rise to an antiferromagnetic ground state of the crystal as a whole. This is because there are several intermolecular interatomic contacts between the carbon atoms on the naphthyl rings standing opposite to each other across the (020) plane as shown by the dotted lines in figure 2(b) which increase the SOMO–SOMO overlap [15], thereby favouring an antiferromagnetic interaction between the two halves of the unit cell. This result is especially surprising when one considers the similarity in molecular shapes of 2-NAPNN and 3-QNNN; they differ by only one atomic position (a carbon–hydrogen group in the first benzene ring in 2-NAPNN is replaced by a nitrogen atom in 3-QNNN) but this difference is sufficient to lead to differing crystal structures which in turn result in 2-NAPNN being dominated by antiferromagnetic interactions (and hence the negative Weiss constant observed in susceptibility experiments [9]) while 3-QNNN is a ferromagnet with $T_C \sim 270$ mK [6, 7].

In conclusion, we have presented ZF μ^+SR data for the isomeric nitronyl nitroxides 1-NAPNN and 2-NAPNN. These compounds have identical chemical formulae but very different crystal structures. We have observed a repolarization of the initial asymmetry confirming the existence of a fraction of paramagnetic muon states in both materials. A clear magnetic transition is observed in the zero-field muon-spin relaxation in 1-NAPNN just below 100 mK which may be due to the onset of ferromagnetism, an interpretation which is supported by susceptibility measurements; no transition is seen in 2-NAPNN down to 50 mK.

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