

High-Temperature Magnetic Ordering in a New Organic Magnet

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Magnetization, heat capacity, and neutron diffraction experiments on the β -phase of the dithiadiazolyl radical, p -NC.C₆F₄.CNSSN[•], provide conclusive evidence that this system exhibits noncollinear antiferromagnetism at 35.5 K, an unprecedented temperature for an organic radical. On the basis of magnetization and powder neutron diffraction results, coupled with theoretical calculations of the spin distribution within the molecule, a magnetic structure for this compound is proposed in which the interactions propagate through S...N contacts. [S0031-9007(97)04066-0]

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Since the realization, in 1991, of ferromagnetism in a purely organic material, e.g., the β -phase of the p -nitrophenylnitronyl nitroxide radical [1] there has been considerable interest in developing extended molecular assemblies of organic radicals which exhibit a spontaneous magnetic moment. One of the major challenges has been to raise the magnetic ordering temperature T_c from 0.48 K observed for this first derivative. Since then several new organic magnets have been reported, most of them based on nitroxide radicals [2–4]. The highest T_c reported to date for this class of compounds is 1.48 K [2]. Weak ferromagnetism due to noncollinear antiferromagnetic ordering has also been found in organic compounds where a Néel temperature T_N of 1.7 K has been reported for the verdazyl derivative TPV [5]. The fullerene-based charge-transfer salt C₆₀.TDAE has been described as a ferromagnet below 16.1 K [6], but also as a spin-glass [7] and a superparamagnet [8]. Some of us have recently reported the synthesis of the dithiadiazolyl radical p -NC.C₆F₄.CNSSN[•], **1**, which is polymorphic [9,10]. The α -phase orders antiferromagnetically at 8 K [9], whereas preliminary magnetic measurements of the β -phase, **1** β , indicate the onset of a spontaneous magnetic moment below 36 K [10], an exceptionally high temperature for a purely organic free radical.

The conditions required not only to stabilize an organic free radical in the solid state but also to control its molecular packing in order to produce magnetic order at a finite temperature are difficult to fulfill. Indeed the contamination of a sample with small amounts of ferromagnetic impurity has been thus far at the origin of every claim for high temperature organic ferromagnetism [11,12]. Therefore any report of a new organic magnet, particularly one ordering at high temperature, requires full physical characterization using complimentary techniques which provide evidence for the intrinsic nature of the magnetic behavior. In this paper we describe detailed

magnetic, specific heat, and neutron diffraction studies on the β -phase of **1** which unambiguously illustrate the intrinsic nature of the phase transition at 36 K in **1** β and which also provide a detailed understanding of the magnetic behavior of this compound.

The magnetic measurements were made on a Quantum Design SQUID magnetometer equipped with an ac susceptibility attachment using polycrystalline samples of **1** β . Above 36 K, the magnetic susceptibility is consistent with a paramagnetic compound which exhibits strong antiferromagnetic exchange interactions [10]. Below 36 K an out-of-phase component is observed in the ac susceptibility at 1 Hz, indicative of the presence of net magnetic moments in the sample (Fig. 1). Measurements made at 10, 100, and 1000 Hz show no frequency dependence and would appear to exclude superparamagnetism and other frequency-dependent phenomena due to the presence of small magnetic particles. Isothermal magnetization curves (Fig. 2) as a function of the

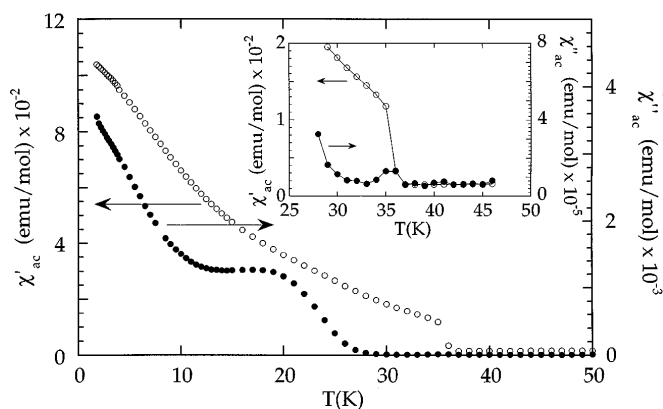


FIG. 1. Temperature dependence of the in-phase, χ' (open dots), and out-of-phase, χ'' (full dots), components of the ac susceptibility of **1** β . The inset shows in detail the region close to the transition.

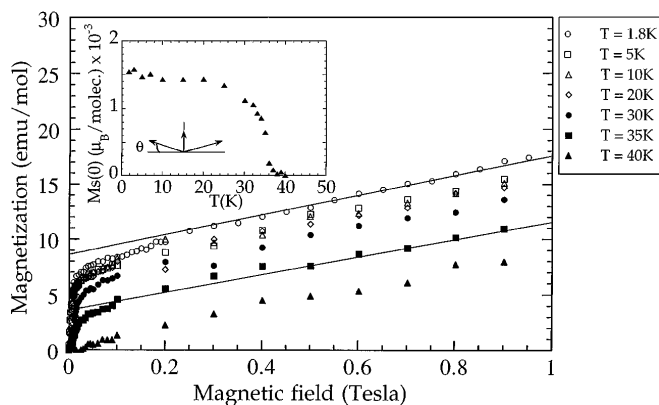


FIG. 2. Magnetization isotherms of 1β ; solid lines represent for two selected temperatures the linear component of the magnetization (see text). The inset shows the temperature dependence of the spontaneous magnetization of 1β .

magnetic field were made in the range between 1.8 and 40 K in order to determine the magnitude of the spontaneous magnetization. Below 36 K the sample magnetization can be interpreted as the contribution of two terms: $M(H, T) = M_s(T) + \chi(T) * H$, where $M_s(T)$ is the spontaneous magnetization arising from a ferromagnetic component and χ is the magnetic susceptibility of the sample at a temperature T . The spontaneous magnetization saturates in fields below 100 Oe and the curves become linear above a few kOe. The curve (Fig. 2 inset) illustrates the temperature dependence of $M_s(T)$ in the region 1.8 to 40 K. The value of $M_s(T)$ tends to $[1.5(\pm 0.1) \times 10^{-3}] \mu_B/\text{mole}$ at 0 K and drops to zero at T approaches 36 K. The calculated $M_s(0)$ is considerably smaller than the expected value for the saturated magnetization of one spin per molecule ($1 \mu_B/\text{mole}$) and is characteristic of a noncollinear antiferromagnetic (spin-canted) structure.

The symmetry requirements for the spin-canting phenomenon exclude the presence of an inversion center between interacting magnetic molecules. This is precisely a characteristic of the β -phase of 1 which crystallizes in the noncentrosymmetric polar space group $Fdd2$ [10]. The magnitude of the spontaneous magnetic moment is dependent on the canting angle. Antisymmetric exchange, also called the Dzyaloshinskii-Moriya (DM) interaction, is the most likely mechanism to cause canting of the magnetic moments [13]. However, since structurally inequivalent molecules are canted with respect to each other, very weak local anisotropy may also contribute to the canting of the moment. The DM interaction is described by the Hamiltonian

$$\mathcal{H}_{\text{DM}} = -2 \sum_{\langle i, j \rangle} \mathbf{d} \cdot (\mathbf{S}_i \times \mathbf{S}_j).$$

The order of magnitude of the Dzyaloshinskii-Moriya vector \mathbf{d} can be estimated using the relation $|\mathbf{d}/J| = (g - g_e)/g$. Using the EPR experimental value for the g factor one obtains $|\mathbf{d}/J| = 0.005 \pm 0.001$ [10]. Assum-

ing that the magnetic moments are not delocalized and using purely geometric arguments, the value of the canting angle can be estimated as $\theta = (\frac{1}{2}) \arctan(|\mathbf{d}/J|) = 0.14(3)^\circ$. Given the crude approximations made, this value agrees well with that obtained from magnetization measurements, $[\theta = 0.26(2)^\circ]$, assuming there is no preferred orientation in the sample.

The phase transition in 1β at 36 K from paramagnetism to a magnetically ordered phase and its bulk character has been studied by means of heat capacity measurements, performed in a commercial low temperature (4–300 K) ac calorimeter (Sinku-Riko, model ACC1-VL). The sample was a pressed pellet ($2 \times 1 \times 0.2$ mm) of polycrystalline powder with a weight of approximately 1 mg. The resulting relative values of the heat capacity were scaled to absolute values with DSC (differential scanning calorimeter) measurements around room temperature. The experimental heat capacity measurements are presented in Fig. 3. A small peak is observed at $T_N = 35.5$ K, indicative of the bulk nature of the transition and of the establishment of long range magnetic order.

In order to estimate the magnetic heat capacity, all the nonmagnetic (e.g., lattice and electronic) contributions must be subtracted from the experimental data. Usually data from an isostructural nonmagnetic compound are used for this purpose. In this case no such analog was available and an estimation using an interpolation method has been applied. The lattice contribution has been taken from a smooth interpolation between the experimental values above 80 K and below 20 K and has been carried out on a curve of effective Debye temperatures which have a smaller temperature variation than the heat capacity curve. Although the 80 K limit is clearly indicated by a trend change in the experimental curve, the 20 K limit is somewhat arbitrary. It has been adjusted to give a transition entropy $\Delta S = 0.7R$ corresponding to the ordering of an $S = \frac{1}{2}$ system. This is represented in Fig. 3 as a solid line. The magnetic heat capacity (Fig. 3 inset) has been

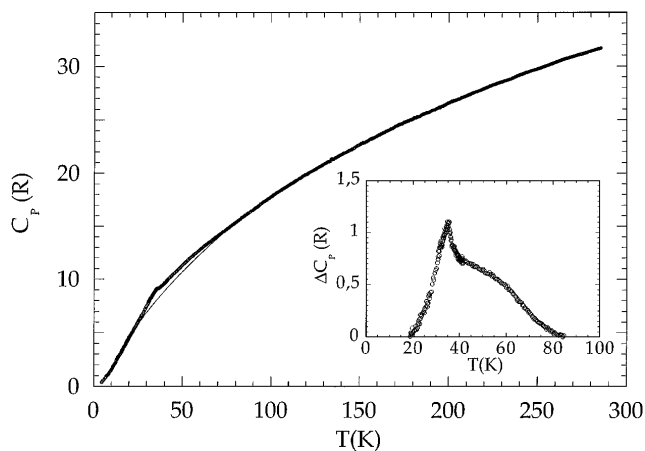


FIG. 3. Heat capacity of 1β . The solid line is the estimation for the lattice and the inset shows the estimated magnetic heat capacity.

obtained by subtraction of this estimated lattice contribution from the experimental data. The result does not depend appreciably on the details of the lattice estimation apart from the high and low temperature tails. The critical entropy $S(T_c)$ is only $0.26R$ (38% of the total entropy) and is small compared to the typical values (ca. $0.4-0.5R$) observed for three-dimensional Heisenberg systems of localized spins. The broad heat capacity shoulder observed above the peak, together with the small value of the critical entropy strongly supports the importance of short range order effects in this compound.

The cooperative character of the magnetic anomaly observed in the heat capacity measurements has been confirmed in neutron diffraction experiments. Although this technique is not sensitive enough to detect the small canting angle observed in the magnetic studies, it allows us to infer the average antiferromagnetic structure of this compound. The experiments were performed at the high-flux neutron powder diffractometer D1B ($\lambda = 2.52 \text{ \AA}$) at the Institut Laue Langevin in Grenoble. The high resolution of this instrument at small angles makes it very suitable for monitoring the thermal evolution of the magnetic reflections. Diffraction patterns were also collected at room temperature, 50 and 1.5 K in the high-resolution diffractometer D2B to confirm the absence of any structural phase transition in the temperature range studied.

Diffraction patterns were measured in D1B at 1.5 K, where the sublattice magnetization should be practically saturated, and at 50 K where the temperature is clearly in the paramagnetic regime although still close to T_N . This choice of temperatures, imposed by the magnetic characteristics of the sample, produces a rather large temperature difference for the two data sets and the associated lattice contraction induces noticeable shifts in the positions of the Bragg reflections. Since the magnetic moment ($S = \frac{1}{2}$) is partially delocalized (see below), the intensities of the magnetic Bragg reflections were very weak, but sufficient to allow differences between the paramagnetic and the antiferromagnetic regimes to be observed. A difference diagram (Fig. 4) where the nuclear contribution (pattern at 50 K) has been subtracted from the nuclear and magnetic one (pattern at 1.5 K) emphasizes the magnetic contributions arising in the magnetic Bragg reflections (111) and (220). The negative peaks are due to the displacement of nuclear reflections, arising through lattice contraction on cooling. Nevertheless, the difference in the (220) reflection between negative and positive peaks gives a net positive contribution, corresponding to a magnetic reflection. The situation is different for the (311) reflection where negative and positive peaks are equal and no magnetic contribution can be observed. In another set of experiments we followed the temperature dependence of the magnetic reflections (111) and (220). Both show a discontinuity at the transition temperature.

A structural requirement for weak ferromagnets is that the magnetic and nuclear lattices must be equal, since the

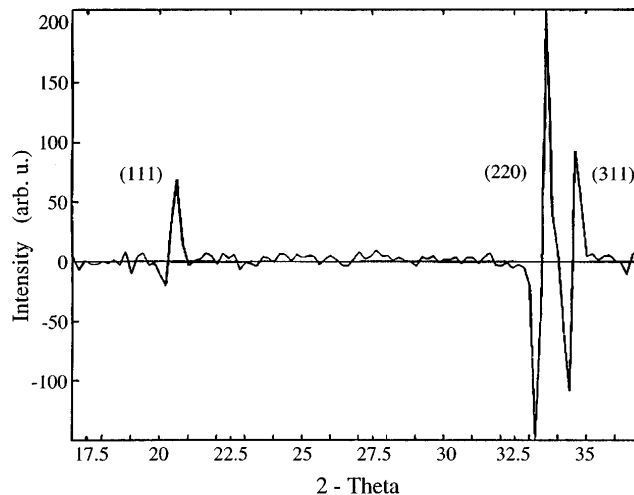


FIG. 4. Difference diagram of neutron powder diffraction patterns of 1β measured at 1.5 K (nuclear and magnetic lattice) and 50 K (nuclear lattice).

lack of colinearity of the spins cannot change the magnetic symmetry of the crystal [13]. Figure 4 also illustrates that no extra reflections are present in the low temperature diffraction pattern, indicative of a propagation vector $\mathbf{k} = 0$ and in good agreement with the noncollinear character of the magnetic structure.

In order to analyze the magnetic structure we require a knowledge of the spin distribution within the molecule. This can be made by computing the atomic spin population on each of its constituent atoms following the well-established Mulliken population analysis. Previous computations on nitronyl nitroxide radicals [14] have shown that if a Mulliken population analysis is carried out on a density functional wave function [15], both the sign and the magnitude of the atomic spin populations are in excellent agreement with the experimental values obtained from neutron analysis. Consequently we have carried out a density functional computation using the nonlocal exchange functional of Becke [16] and the nonlocal Lee-Yang-Parr correlation functional [17]. The computation employed the cc-pVDZ basis set [18]. This is a Gaussian contracted basis set of double "zeta" quality, member of the newly developed correlation-consistent family which is known to give exceptional results.

The results from these calculations indicate that most of the unpaired density is concentrated on the sulfur-nitrogen ring, in which the unpaired spin densities at S, N, and C atoms are $+0.284$, $+0.250$, and -0.063 atomic units (a.u.), respectively. The populations on the six-membered ring are orders of magnitude smaller and, in all cases, are less than 0.005 a.u. These results have been confirmed by performing a limited multiconfiguration computation, using the multiconfigurational self-consistent field (MCSCF) method on a reduced multiconfigurational space. Therefore superexchange pathways propagating parallel to the c axis should be negligible since they would connect two

magnetic heterocyclic rings through a nonmagnetic six-membered one.

Since the spin densities are mainly localized in the S and N atoms of the five-membered ring, magnetic interactions propagate through four nearest neighbor rings which are not in the same ab crystallographic plane. This permits the propagation of the magnetic interaction throughout the three dimensions of the lattice. According to the classification of magnetic space groups [19], the nuclear space group $Fdd2$ allows two ferromagnetic space groups $*Fd'd'2'$ and $*Fd'd'2$, which are compatible with the existence of a resultant magnetic moment. However, $*Fd'd'2$ does not allow a canting of the magnetic moments since they are fixed along the direction of the c axis and we can therefore conclude that the magnetic space group is $*Fd'd'2'$, in which the spins are fixed in the ab plane and the resulting magnetic moment is oriented parallel to either the a or the b axis.

The orientation of the spins was determined by finding the best agreement between the experimental diffraction pattern and those calculated at different orientations. Since the magnetic form factor for this molecule is not known, we have approximated the radical to five magnetic ions placed in the same nuclear positions as the C, N, and S atoms in the five-membered ring and with the appropriate calculated magnetic densities. This permits the reproduction of the extinctions but not the ratio of the integrated intensities of magnetic Bragg peaks in the experimental diffraction pattern. The spin structure is represented in Fig. 5, where the orientation of the molecular moments is parallel to the b axis. The small canting cannot be observed in the neutron diffraction experiments; however, the most plausible orientation of the resultant magnetization observed in the magnetic experiments runs parallel to the a axis.

In summary, we have presented an extensive characterization of the magnetic properties of the beta-phase of the dithiadiazolyl radical, $\text{NC}_6\text{F}_4\text{CNSSN}^\cdot$. We have provided conclusive evidence that this compound orders as a weak ferromagnet at 35.5 K, a temperature that is at least 1 order of magnitude higher than that of any other purely organic free-radical compound. Density functional calculations indicate that spin densities are mainly concentrated on the S and N atoms of the heterocyclic ring and we have proposed a magnetic structure for this compound in which the interactions propagate through intermolecular S...N contacts. The fact that the ordering temperature has been raised by more than an order of magnitude with respect to systems based on N...O interactions opens up exciting possibilities in organic magnetism.

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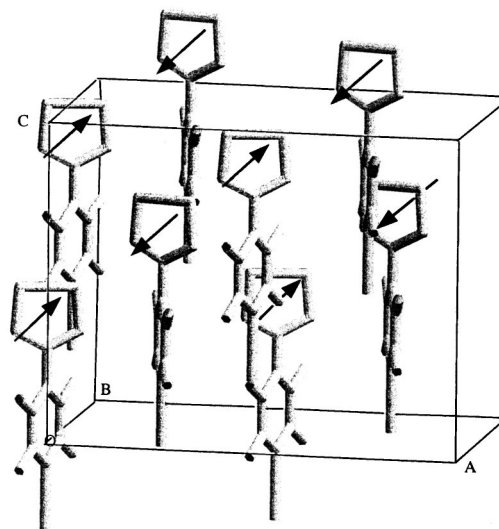


FIG. 5. Magnetic structure of 1β . The molecular magnetic moments are denoted by arrows placed in the five-membered ring.

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