PHYSICAL REVIEW B **72**, 024435 (2005)

Magnetic ordering in a genuine organic crystal with triangular antiferromagnetic spin units

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(Received 11 March 2005; published 18 July 2005)

A typical magnetic behavior has been studied in a genuine organic radical crystal of antiferromagnetic triangular spin units, N,N,N-Tris[p-(N-oxyl-tetra-butyamino)phenyl]amine. The magnetic susceptibility measurements indicate that a ground-state doublet is achieved within a molecule when the temperature is cooled down to about 60 K from 300 K, giving the effective spin value of each molecule at lower temperatures to be $S=1/2$. Below 60 K, the magnetic susceptibility increases ferromagnetically down to 1 K, being followed by an antiferromagnetic decrease at lower temperatures. The analyses of the magnetic field dependence of heat capacity and magnetization reveals that the intermolecular ferromagnetic and antiferromagnetic interactions are working with the respective value $2z_fJ_f/k_B=6.0$ K and $2z_{\mathrm{af}}J_{\mathrm{af}}/k_B=-1.35$ K, which reasonably explains the observed value of the transition temperature $T_N(0)=0.74$ K at the field $H=0$ T: It is suggested that organic magnets order at the temperature predicted by Rushbrooke–Wood for isotropic Heisenberg spin systems, including not only the present tri-radical system, but also to the most typical genuine organic ferromagnets of mono-radical ($S=1/2$) and biradical ($S=1$). A fully mapped temperature-magnetic field phase boundary is obtained to be described by a single formula $T_N(H)=T_N(0)[1-(H/H_c)^a]^\xi$ with the values $T_N(0)=0.735$ K, $H_c=1.01\pm0.01$ T, $a=2.05\pm0.02$, and $\xi=0.48+0.01$, where $H_c=2H_{\mathrm{ex}}=2\times 2z_{\mathrm{af}}J_{\mathrm{af}}\langle S\rangle/g\mu_B$, without any trace of the existence of the bicritical point on it as seen in normal antiferromagnets with uniaxial anisotropy. It is discussed that the critical indices may be $a=2.0$ and $\xi=0.5$ for nonfrustrated antiferromagnets with infinitesimally small anisotropy.

DOI: 10.1103/PhysRevB.72.024435 PACS number(s): 75.10.Jm, 61.66.Hq, 75.50.Xx

I. INTRODUCTION

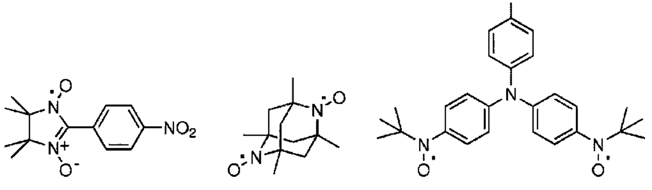
Since the first genuine organic ferromagnetic compound, β-phase *p*-NPNN,[1] was realized in 1991, there have been reported several well-defined organic ferromagnets. However, the value of the magnetic transition temperature of metal-free ferromagnets synthesized thereafter is still below liquid helium temperatures, as shown in Fig. 1 and Table I. In these compounds, the magnetic moment is originated to the singly occupied electron on molecular orbital (SOMO), mainly localized on NO groups, while the magnetic interactions are propagated via other delocalized molecular orbitals.[2]

To increase the transition temperature T_c, one must enhance intermolecular ferromagnetic interactions and the value of effective spins within a molecule as well. In Dupeyredioxyl with $T_c=1.48$ K,[3] the highest value of metal-free ferromagnets except for the C_{60}-based compound,[4] the spin value in a molecule is effectively $S=1$ which arises in the stronger intramolecular ferromagnetic coupling J_0 ($\sim$170 K), while its bulk ferromagnetism is realized by the weak intermolecular ferromagnetic interaction $J\sim1$ K, as schematized in Fig. 2.[5]

The small T_c implies the difficulty in introducing strong ferromagnetic interactions between neighboring molecules. The planar structures of organic molecules are generally apt to be piled up in crystal to bring about mostly antiferromagnetic SOMO-SOMO overlapping (of the order of 10^2 K at most). Recently, by making use of intermolecular antiferromagnetic interactions between "multispin" molecules, such as triradical spin as shown in Fig. 2(c), a strategy to realize a high T_c ferrimagnetic organic compound has started. In reality, there have been two experimental reports on this strategy, but their ordering temperatures are still below 1 K.[6,7]

On the other hand, the *g*-factor in these organic systems is nearly 2.00; 10^{-2} smaller anisotropy, than metallic ions at most. In other words, the physical picture of cooperative phenomena of genuine organic magnetic systems can be based on the Heisenberg Hamiltonian without anisotropy, except for the lowest temperatures where the dipole-dipole interactions work. Moreover, interesting low temperature excitations are also expected in the dispersion relation for isotropic $S=1/2-S=1$ alternative systems in one dimension.[8,9]

Under the circumstances, we will see an example of how the effective spin arises within each triradical crystal molecule, and what rules the bulk magnetic behavior in the crystallized state with the use of N,N,N-Tris[p-(N-oxyl-



(a) $T_C = 0.61$ K (b) $T_C = 1.48$ K (c) $T_C = 0.74$ K

FIG. 1. The prototype genuine organic mono-, bi-, and triradical molecules with ferromagnetic intermolecular interactions.

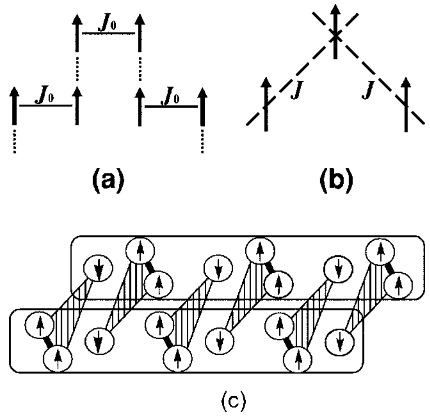


FIG. 2. The schematization of intra- and intermolecular interactions in the case of biradical Dupeyredioxyl (a) and (b); J_0 is the intramolecular ferromagnetic interaction much stronger than the intermolecular interaction J between $S=1/2$-spins (a), and (b) is a schematized intermolecular interaction J between $S=1$-spins (Ref. 5). The scheme (c) is a model of ferrimagnets composed of triradical molecules.

tetra-butyamino)phenyl]amine (hereafter abbreviated as Tris-NO).[10] The experimental results of magnetic susceptibility, heat capacity, and magnetization for the powdered sample are given here. A remarkable result will be revealed on the fully mapped temperature-magnetic field phase diagram without any trace of the bicritical point, as observed in normal antiferromagnets with metallic ions. The relation between magnetic transition temperature and intermolecular interactions will be generally discussed not only about Tris-NO but also other typical organic ferromagnets.

II. EXPERIMENTAL RESULTS AND ANALYSIS

A. The magnetic susceptibility from 300 K to 0.1 K

Tris-NO is one of the triradicals cultivated by Itoh *et al.*[10] as bridging ligands for magnetic metal ions to make hybrid-spin networks. The crystal Tris-NO itself has been expected to order ferromagnetically below 2 K. In this section, it will be helpful to review their results in the temperature region 300 K–2 K and to report our experimental results of magnetic susceptibility measurements down to 0.1 K to grasp the perspective magnetic behavior of this triradical.

TABLE I. Comparison of experiments of magnetic ordering temperature of the prototype genuine organic systems to theoretical values for the isotropic Heisenberg system. The parameters for 2,5,-DFPNN and DTDA are taken from Refs. 16 and 17, respectively.

	S	$2zJ/k_B$	T_c (theo.)	T_c (obs.)
β-phase p-NPNN	$1/2\times1$	3.6	0.60	0.61
Dupeyredioxyl	$1/2\times2$	3.6	1.7	1.48
Tris-NO	$1/2(\times3)$	4.6	0.76	0.74
2,5,-DFPNN	$1/2\times1$	2.8	0.46	0.48
DTDA	$1/2\times1$	9.0	1.5	1.30

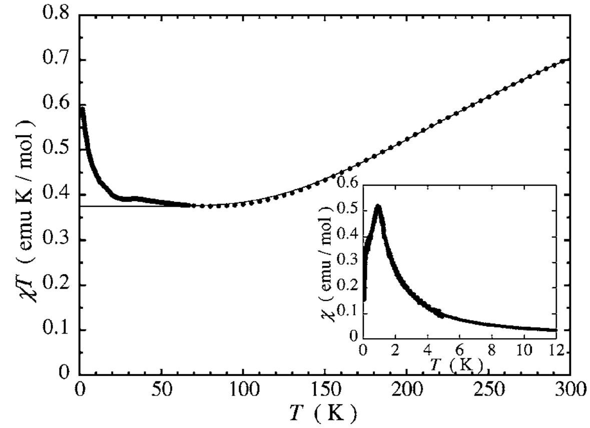


FIG. 3. The magnetic susceptibility of Tris-NO measured in the field 0.5 T, plotted χT vs T for $T>1.8$ K. The solid curve is the theoretical value for the triangular spin system for $\Delta_1=559$ K and $\Delta_2=1015$ K in Eq. (2). The inset is the low-temperature χ in the region 0.1–12 K.

The molecular structure of Tris-NO is shown in Fig. 1(c), together with the relevant monoradical β-phase p-NPNN(a), and the biradical Dupeyredioxyl(b). Tris-NO has no three-fold axis passing through the central nitrogen atom. The three phenyl rings are tilted by 29.9°, 34.3°, and 57.3°, respectively, from the central and nearly co-planar NC3 unit. The interatomic distance between oxygen atoms is different (9.73 Å, 11.30 Å, and 11.40 Å).[10] Then, the intramolecular paths of magnetic interaction among three $S=1/2$ spins are nonsymmetrical to each other.

The paramagnetic susceptibility χ obtained by Itoh *et al.*[10] quantitatively agree with our present results which are shown as χT versus T plot in Fig. 3. The diamagnetic contribution of the value $\chi_{\text{dia}}=-329\times10^{-6}$ emu mol^{-1} for Tris-NO is taken into consideration. As they pointed out, the χT value at 300 K amounts to 0.659 emu K mol^{-1}, a value distinctly smaller than the theoretical one of 3×0.375 emu K mol^{-1} for independent three $S=1/2$ spins, implying the antiparallel coupling within the molecule around 300 K. The χT value decreases with the temperature until it reaches almost a constant value 0.375 emu K mol^{-1} in the temperature region of 100 K–60 K, a value for an isolated $S=1/2$ spin. Below 60 K, χT increases gradually indicating the existence of ferromagnetic intermolecular interaction at lower temperatures. Prior to the low-temperature behavior, we see the magnetic features within a molecule. The molecular spin states of a triradical are the eigenstates of the Hamiltonian:

$$H=-2(J_{12}\mathbf{S}_1\cdot\mathbf{S}_2+J_{23}\mathbf{S}_2\cdot\mathbf{S}_3+J_{31}\mathbf{S}_3\cdot\mathbf{S}_1), \qquad (1)$$

where J_{ij} is the interaction parameter between spin $\mathbf{S}_i$ and $\mathbf{S}_j(i,j;1,2,3)$, we get the microstates from the basis set $|S_1,S_2,S_3\rangle$, $(S_i;\pm1/2)$. The value of χT is obtained with the relative energy gaps Δ_1 and Δ_2 which are functions of J_{ij},[11]

$$\chi T=\frac{N_A g^2\mu_B^2}{4k_B}\cdot\frac{1+\exp(-\Delta_1/k_BT)+10\exp(-\Delta_2/k_BT)}{1+\exp(-\Delta_1/k_BT)+2\exp(-\Delta_2/k_BT)}. \qquad (2)$$

The experimental data above 60 K can be well reproduced with Eq. (2) for $\Delta_1=559$ K and $\Delta_2=1015$ K.[10] In other

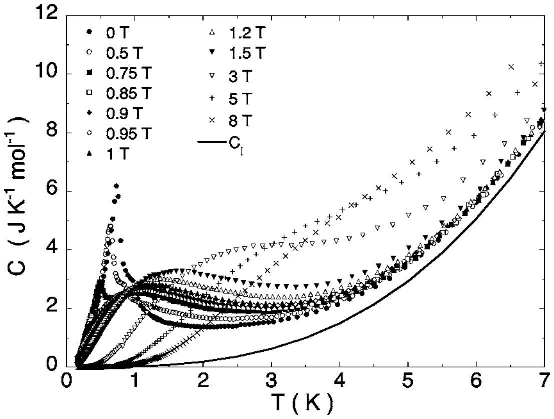


FIG. 4. The low-temperature heat capacity of Tris-NO in the fields up to 8 T. The solid line indicates the lattice contribution taken as $C_l = 0.02T^3$ (J/mol/K).

words, Tris-NO molecules are in the ground doublet state below 60 K. It is reconfirmed here that the crystal at low temperatures behaves as a system of interacting $S=1/2$ spins. It should be noted here that the increase of χ at lower temperatures down to 2 K is pointed out to obey the Curie–Weiss law with the positive Curie–Weiss temperature $\theta = 0.75+0.02$ K.[10]

In order to investigate the lower-temperature behavior of Tri-NO, we carried out the ac magnetic susceptibility, heat capacity, and magnetization measurements. The results of ac susceptibility $[H_{\mathrm{rf}}(\nu)=1.0\ \mathrm{Oe}, \nu=15.9\ \mathrm{Hz}]$ are shown in the region of 0.1 K–5 K in Fig. 3. The ferromagnetic increase of χ is preserved down to 1 K, and makes a peak just below 1 K. In the lower temperatures, χ decreases rather sharply as the temperature decreases down to around 0.2 K, and then accelerates toward zero. These facts on the susceptibility imply that below 60 K, the ferromagnetic interactions $z_f J_f$ become dominant among the molecules down to 1 K, where second dominant antiferromagnetic interactions $z_{\mathrm{af}} J_{\mathrm{af}}$ begin to work through the different exchange pathways than the ferromagnetic ones, to result in a antiferromagnetic ordered phase at lower temperatures. Hereafter, z_f, z_{af}, and z stand for the coordination numbers for the respective ferro-, antiferro-, and averaged magnetic interactions J_f, J_{af}, and J. Next, we take a detailed look into the ordering behavior by heat capacity and magnetization measurements under magnetic fields.

B. Dependence of heat capacity on external magnetic fields

The adiabatic heat capacity measurements give reliable information about the transition temperature. Figures 4, 6, and 7 show the temperature dependence of the heat capacities of the Tris-NO compound observed in the external magnetic fields. In zero field $H=0$, a distinct peak is located at $T_N(0)=0.74$ K, which is comparable to the Curie–Weiss temperature $\theta=0.75$ K.[10] As the field increases, a broad heat capacity hump shifts to the higher temperatures with increasing field.

For the detailed analysis, we subtract the lattice contribution to the heat capacity, paying attention to the fact that the absolute values of C_p around 7 K slightly depend on the field for $H<1.5$ T. We can set the lattice part $C_l = 0.020T^3$ (J/mol/K) as indicated with the solid curve in Fig. 4 without a serious error for the present discussion. Then, by the subtraction of the lattice contribution, the field dependence of magnetic entropy is obtained as depicted in Fig. 5. It is noted that more than 95% of the magnetic entropy $R \ln 2$ for $S=1/2$ is consumed up until 7 K in the fields $H<1.5$ T, indicating more evidence of the ground-state doublet within a molecule. The magnetic entropy at $T_N(0)$ is about one-half of $R \ln 2$, which implies a quasi-two-dimensional character of the system, rather than three dimensional.[12]

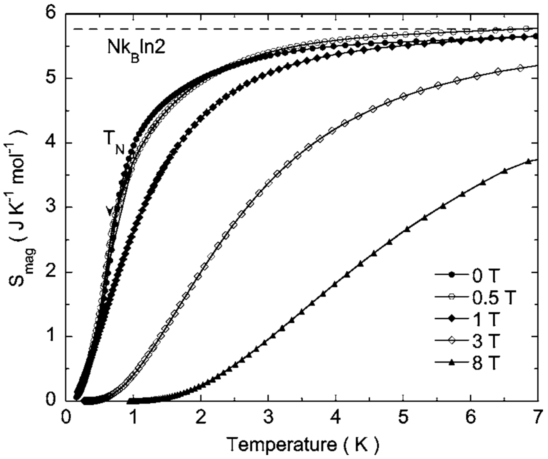


FIG. 5. The temperature dependence of the magnetic entropy of Tris-NO at various external magnetic fields in the temperature region below 7 K.

The application of the external field makes the magnetic ordering temperature $T_N(H)$ shift to the lower temperatures—as can be seen in the heat capacity peaks in Fig. 6(a). It is remarkable that $T_N(H)$ can be expressed with a single curve $T_N(H)=T_N(0)[1-(H/H_c)^a]^{\xi}$, as shown in Fig. 6(b) for $H=0$, 0.5, 0.75, 0.85, 0.90, 0.95, and 1.0 T, with the values $T_N(0)=0.735$ K, $H_c=1.01\pm0.01$ T, $a=2.05\pm0.02$, and $\xi=0.48\pm0.01$. For $H>H_c$, no peak is seen, and Schottky-type heat capacities remain in the higher-temperature region as shown in Fig. 7, whose maximum becomes nearly equal to the two-level Schottky maximum $C_{\mathrm{Sho}}=3.64$ Joule/mol/K for $S=1/2$ in the respective fields. This kind of field dependence of $T_N(H)$ is a feature of antiferromagnets.[13] The phase boundary $T_N(H)$ separates the spinflopped phase and the paramagnetic phase without such a bicritical point on it as in normal antiferromagnets with a uniaxial anisotropy: We suggest that this is a general character of antiferromagnets of genuine organic compounds. That is, the bicritical point will be located in the field which depends on the anisotropy. In the case of organic compounds, anisotropy originates from the dipole-dipole interaction of 10^1-10^2 Oe. With a big single crystal of Tris-NO, although it is not available now, the existence of the bicritical point should be detected at the lowest temperatures in a low magnetic field.

Moreover, from the critical field H_c, the averaged value of the antiferromagnetic interaction is derived to be $2z_{\mathrm{af}}J_{\mathrm{af}}/k_B = -1.35$ K from the relation between H_c and the antiferro-

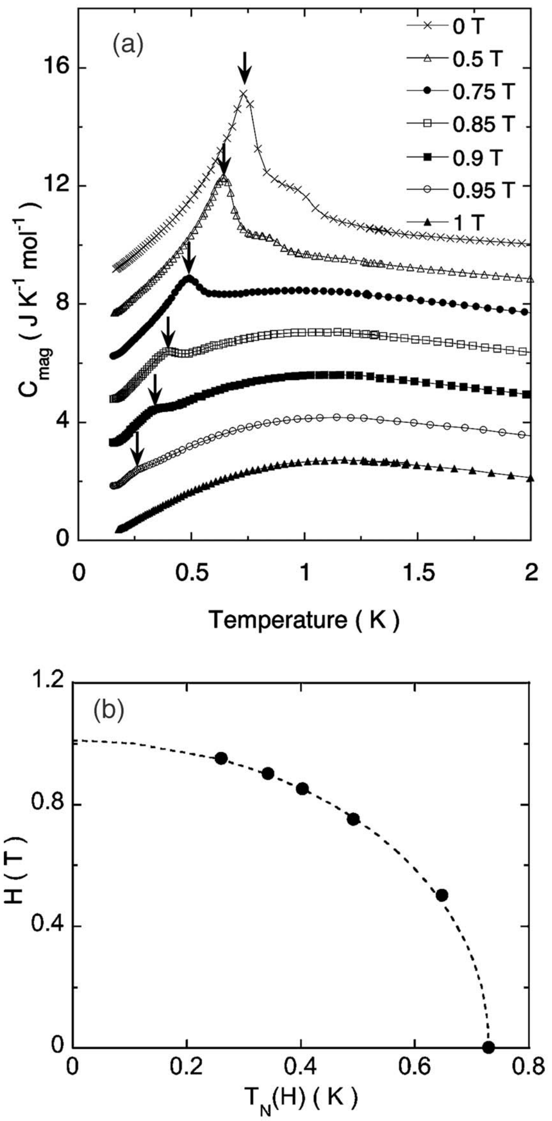


FIG. 6. (a)The field dependence of low-temperature magnetic heat capacity of Tris-NO below 2 K, for the field less than the critical field $H < H_c = 1.01$ T. The absolute values are shifted for the eye. (b) The fully mapped *T-H* phase diagram. The solid curve corresponds $T_N(H) = T_N(0)[1-(H/H_c)^a]^{\xi}$, with the values $T_c(0) = 0.735$ K, $H_c = 1.01 \pm 0.01$ T, $a = 2.05 \pm 0.02$, and $\xi = 0.48 + 0.01$.

magnetic exchange fields; $H_c = 2H_{\mathrm{ex}} = 2 \times 2z_{\mathrm{ab}}J_{\mathrm{ab}}\langle S\rangle / g\mu_B$. This corresponds to less than one-fourth of the dominant ferromagnetic interaction, as will be given later. In other words, the stronger ferromagnetic interaction works gradually below 60 K to make a ferromagnetic short-range ordering as in some low-dimensional systems, and eventually an antiferromagnetic long-range ordering is triggered by $z_{\mathrm{af}}J_{\mathrm{af}}$ at $T_N(0) = 0.74$ K.

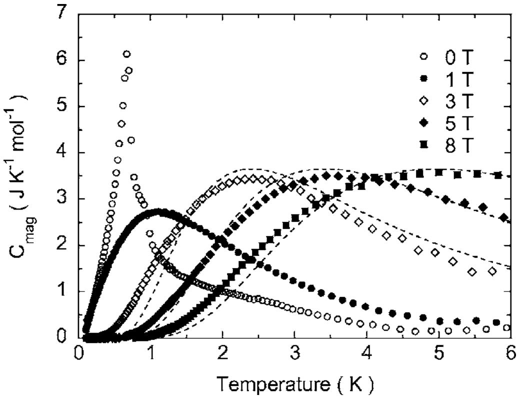


FIG. 7. The field dependence of the magnetic heat capacity of Tris-NO for the field $H < 8$ T. The dotted curves correspond to the Schottky type heat capacities in the fields $H = 3$, 5, and 8 T.

C. Temperature dependence of the magnetization and the average value of the intermolecular interactions

From the results of magnetization *M* of Tris-NO, we deduce the averaged value of the exchange interactions among molecules, including the ferro- and the antiferromagnetic interactions. Figure 8 shows the results of magnetization measured at several constant temperatures. The saturation value for $T = 1.9$ K gives a nearly equal value for $S = 1/2$. When we plot *M* against the $g\mu_B H_0/k_B T$, the data points are expected to fall on the universal Brillouin function for $S = 1/2$, where H_0 is the effective field at individual spins given by

$$H_0 = H + \lambda M. \tag{3}$$

The second term is the field coming from the neighboring spins via exchange interactions. Here λ and *M* are given as

$$\lambda = (2z_f J_f + 2z_{\mathrm{af}}J_{\mathrm{af}})/N_A(g\mu_B)^2 = 2zJ/N_A(g\mu_B)^2$$

$$M = N_A g\mu_B \langle S\rangle. \tag{4}$$

The correction for diamagnetic contribution $-NM'$ is negligible here since the magnetization M' converted in units of emu/cm^3 is small as is expected from the dilute moments in organic compounds (*N*: Demagnetization factor); the correction is less than 1% in the case of β-phase *p*-NPNN.[14] With the value $\lambda = 3.1 \pm 0.02$ (or, $2zJ/k_B = 4.6$ K) in the Brillouin function, we have the best agreement with the experimental results as can be seen in Fig. 9, except for the data near at 1.9 K where the critical fluctuation works. Putting the anti-

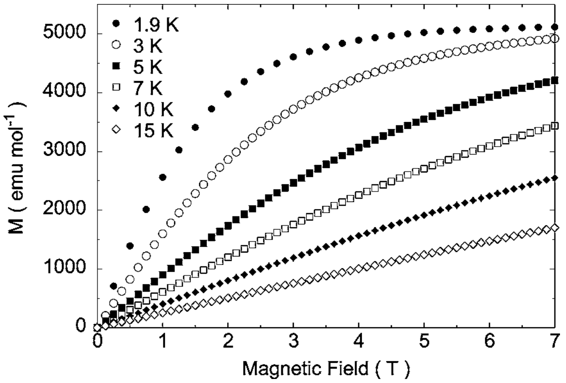


FIG. 8. The field dependence of the magnetization of Tris-NO at constant temperatures.

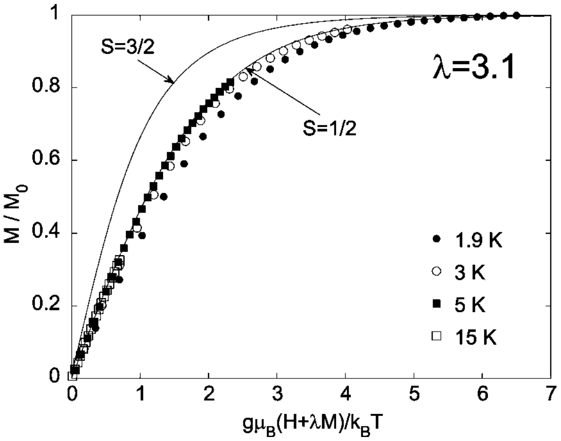


FIG. 9. The magnetization of Tris-NO divided by the saturation value for $S=1/2$ plotted against $g\mu_B H_0/k_BT$. The solid curve is the Brillouin function for $S=1/2$ with the value $\lambda=3.1(2zJ/k_B=4.6$ K), and the dotted curve is for $S=3/2$.

ferromagnetic contribution $2z_{\rm af}J_{\rm af}/k_B=-1.35$ K in Eq. (4), we have the ferromagnetic interaction to be $2z_fJ_f/k_B=6.0$ K, about four times larger than the antiferromagnetic interactions.

III. DISCUSSION AND SUMMARY

First, we consider the relation between the transition temperature and magnetic interactions in the organic magnets. There has been a lot of theoretical work concerning this relation on various lattice models with different spin symmetry (such as Ising, *XY*, and/or isotropic Heisenberg spins) of different quantum numbers. Of these theoretical works, the relation obtained by Rushbrooke–Wood is valid for the three types of lattices, simple cubic ($z=6$), body centered ($z=8$), and face centered ($z=12$) lattices, with a unique formula

$$k_BT_c = 5/95(z-1)J[11S(S+1)-1], \qquad (5)$$

which is derived from the high-temperature series expansion method up to six coefficients.[15] Looking back to the present compound, as will be commented on below, we cannot identify its magnetic lattice structure. However, the averaged value of the magnetic interactions $2zJ/k_B=4.6$ K is estimated in the previous section. Now, we have noticed that Eq. (5) can be so expressed as to explicitly involve the averaged exchange interactions over the difference of the lattice structure:

$$T_c = A2zJS(S+1)/k_B, \qquad (6)$$

with the value $A=0.22\pm0.01$ for $S=1/2$, 0.24 ± 0.01 for $S=1$, and so on. It is recalled that in the mean field theory, the value of A is 1/3. It should be taken here that $2zJ/k_B$ in Eq. (6) can be interpreted as the averaged exchange interaction for any lattice of three. Putting the experimental value $2zJ/k_B$ in Eq. (6) for Tris-NO, we get $T_c=0.76$ K, in agreement with the experiment.

Then, we check whether this relation discussed just above generally holds in other genuine organic ferromagnets: In the case of the biradical Dupeyredioxyl [Fig. 1(b)], for instance, the two $S=1/2$ spins are ferromagnetically coupled within a molecule to construct an effective $S=1$ spin below 100 K. Figures 2(a) and 2(b) show a model of this schematization in two dimensions, although the real interactions are three dimensional. Our magnetization measurements on this biradical system gave $2zJ/k_B=3.6$ K and $S=1$, for which Eq. (6) gives $T_c=1.7$ K in agreement with the experimental value.[5] The same analysis employed here is applied to other typical organic ferromagnets, including β-phase *p*-NPNN, and the results are summarized in Table I.[16,17]

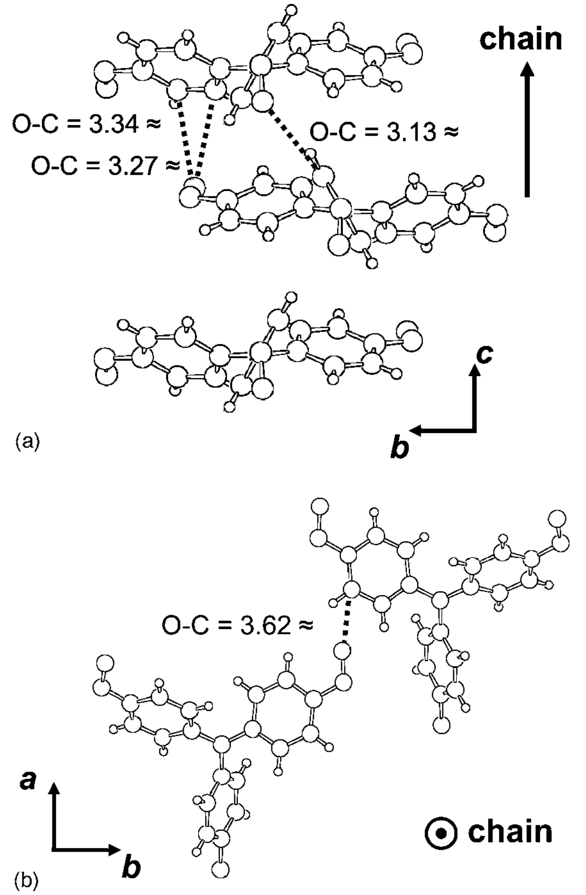


FIG. 10. Molecular arrangement along the *c* axis(a) and their projection on the *a*-*b* plane(b) (Refs. 10 and 18).

Here, we comment that there have been many theoretical expressions between T_c and J other than Eqs. (5) and (6), such as,

$$3k_BT_c/zJS = B(S), \qquad (7)$$

which gives nearly the same quantitative values to each other for a designated lattice.[18] Here, we used the Rushbrooke–Wood relation for the reason that it covers three types of lattices and the general value of quantum spin with one formula.

Here, we consider the probable exchange pathways considering the crystal structure of Tris-NO (space group Cc) and the spin density distribution,[10,19] although it is complicated to look at each of them in detail. The most dominant ferromagnetic interaction between the neighboring molecules may arise through three contacts O—C (3.13 Å, 3.27 Å, and 3.34 Å) along the *c* axis as indicated in Fig. 10(a), while the secondary dominant antiferromagnetic interaction is probable through C—O contact (3.62 Å) almost along the *a* axis on the *a*-*b* projection as in Fig. 10(b). Then, it looks to be a two-dimensional magnetic network on the *a*-*c* plane. In the previous section, the magnetic entropy analysis suggests a two-dimensional character. However, it is theoretically impossible for the two-dimensional Heisenberg spin system to make a magnetic ordering, and therefore other exchange pathways have to exist in Tris-NO, including smaller interaction along the other direction. In Figs. 6 and 7, we notice a small cusp on the heat capacity curve just above $T_N(0)$ which disappears with the increasing magnetic field. Just below 0.2 K in the inset of Fig. 3, on the other hand, there appears an abrupt decrease of the magnetic susceptibility which is not explained. These may be relevant to the complexity of the other inherent magnetic interactions. Nevertheless, the overall ordering behavior has been described with two dominant averaged interactions J_f and J_{af} as mentioned just above.

It is found that the $T_N(H)$ of Tris-NO is expressed as $T_N(H)=T_N(0)[1-(H/H_c)^a]^{\xi}$, with $a=2.05\pm0.02$ and $\xi=0.48\pm0.2$, which separates spin-flopped phase and paramagnetic phase for the present external fields. The inorganic antiferromagnets with uniaxial anisotropy generally preserve the antiferromagnetic phase for the fields $H<H_{\mathrm{sf}}(T)$ (spin-flopping field) applied along the anisotropy axis, and the spin-flopped phase for $H>H_{\mathrm{sf}}$, and finally the paramagnetic phase is induced for the higher field $H>H_c(T)$. In the normal antiferromagnets, the bicritical point appears on the *T*-*H* diagram at which these three phases meet, and $T_N(H)$ changes its behavior when crossing over the point. It should be stressed here that the organic radical spin is so isotropic that the uniaxial anisotropy is of the order of Oe, at most, originating from the dipole-dipole interaction. This is the reason why $T_N(H)$ of Tris-NO looks like having a unique formula as mentioned above. Quite recently, we observed $T_N(H)$ of other organic antiferromagnet composed of mono- and biradicals, $C_{33}H_{44}N_7O_8$, which gives quite a same formula as in Tris-NO with the critical indices nearly equal to $a=2$ and $\xi=1/2$. We suggest these may be the universal values for the three-dimensional organic antiferromagnets with infinitesimally small anisotropy. The detailed results will be reported elsewhere.[20]

Lastly, we comment on the probability of the $S=1/2-S=1$ alternating ferrimagnetic chain in the present system, from the theoretical interest which predicts the characteristic dispersion relation at the lowest temperatures: The critical indices of the heat capacity and magnetic susceptibility are the same as those for a $S=1/2$ ferromagnetic Heisenberg chain, $\alpha=1/2$ and $\gamma=2$, respectively.[21] The broad maximum of the heat capacity of the ferromagnetic chain grows in the field,[8,9] of the order $H\sim0.5$ J/gμ_B, for example, more than twice of the corresponding zero-field value.[21–23] In Fig. 7, however, we cannot see the sensitive field dependence of the heat capacity of Tris-NO. While, entropy analysis of this compound shows a two-dimensional character. Therefore, this is not the case for the present system.

We thank Mr. K. Kinoshita for the low-temperature susceptibility measurements.

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