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Intermolecular ferromagnetic interaction in the crystal of a diphenyl nitroxide derivative. The role of spin-polarized hydrogen atoms located near a neighboring N–O site

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Abstract

The crystal of 9,9-dipropyl-9,10-dihydroacridin-10-yloxyl exhibited a positive Weiss constant (+0.77 K) ascribable to a three-dimensional network of ferromagnetic interactions. The orbital orthogonality between the antibonding N–O π^* and H 1s orbitals was found in a nearly isosceles triangle geometry of neighboring H atoms and the N–O site. The following spin polarization scheme is proposed: $>N(\uparrow)-C(\downarrow)=C_o(\uparrow)-C_m(\downarrow)-H_m(\uparrow)\cdots O(\uparrow)-N<$, where *o*- and *m*-positions are defined with respect to the N–O group. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

The research on purely organic magnetic materials has greatly progressed in recent years [1]. We have reported organic ferro- and metamagnets having a 2,2,6,6-tetramethylpiperidin-1-yloxyl (TEMPO) radical group [2–4]. Although TEMPO radicals are very stable and the TEMPO-based materials are easily accessible, they have low $T_{\rm C}$ or $T_{\rm N}$ (<0.3 K); sterically bulky substituents such as four methyl groups in a TEMPO moiety pull the N–O radical centers apart, and the spin densities on aliphatic substituents are generally small. The intermolecular exchange interaction is considered to be proportional to the polarized spin densities at contacting atoms

[5]. For developing high- $T_{\rm C}$ organic magnets, we turn our attention to π -conjugated radicals, especially diphenyl nitroxides.

As reported recently [6], the magnetism of 9,9bis(*p*-tolyl)-9,10-dihydroacridin-10-yloxyl (BTAO) obeys a ground triplet-state dimer model with $2J/k_{\rm B}$ = +18 K, which is consistent with the dimeric molecular arrangement. This interaction is much stronger than those observed for TEMPO-based magnets. We have studied the magnetism of its derivatives having less bulky substituents than *p*-tolyl in order to realize stronger ferromagnetic interaction. However, antiferromagnetic interactions are dominant for DMAO, DEAO and DBAO (these formulas are shown below) as indicated by the negative Weiss temperatures (-13, -4.6 and -1.6 K, respectively) [7]. Among them a propyl derivative, DPAO (9,9-dipropyl-9,10-dihydroacridin-10-yloxyl), showed inter-

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molecular ferromagnetic interaction. We will report here the structure and magnetism of the DPAO crystal and discuss its mechanism of the interaction based on the crystal structure.



2. Experimental

The precursor 9,9-dipropyl-9,10-dihydroacridine was prepared according to the method reported by Noyori et al. [8]. The photochemical reaction of acridine and butanoic acid gave 9-propyl-9,10-dihydroacridine with loss of CO_2 . After oxidation of 9-propyl-9,10-dihydroacridine with $K_3Fe(CN)_6$, the resultant 9-propylacridine was subjected again to the photoreaction with butanoic acid, giving 9,9-dipropyl-9,10-dihydroacridine. Radical DPAO was obtained by oxidation of the amine with *m*-chloroperbenzoic acid in dichloromethane and isolated by passing through an HPLC (Jaigel 1H + 1H, Japan Analytical Industry) eluted with chloroform. The specimen was purified by repeated recrystallizations from dichloromethane-hexane (m.p. 146–148°C).

X-ray diffraction data of a single crystal of DPAO were collected on a RIGAKU AFC-5R diffractometer and analyzed by SHELXS-86 [9] and SHELXL-97 [10] program packages. The crystallographic data of DPAO were: orthorhombic, P2₁2₁2₁, *a* = 12.060(3), *b* = 12.466(3), *c* = 10.892(3) Å, *V* = 1637.6(7) Å³, *Z* = 4, $D_{calc} = 1.137$ g cm⁻³, *R* = 0.049 for 2092 observed reflections.

An X-band ESR spectrum was measured on an ESP-300E spectrometer (Bruker). A dilute benzene solution of DPAO was purged with nitrogen. Hyper-fine splitting constants were determined by computer simulation.

Magnetic properties of a polycrystalline sample of DPAO were measured on MPMS SQUID and PPMS

DC magnetometers (Quantum Design) equipped with 7 and 9 T superconducting magnets, respectively.

3. Results

3.1. Crystal structure

We initially expected pancake-type stacking of benzene rings, which is favorable for strong magnetic interaction according to McConnell's model [5]. In fact, such a stacking of acridine skeletons was found in a crystal of BTAO [6]. However, neighboring acridine skeletons were not arranged parallel in the DPAO crystal. Fig. 1a depicts the molecular structure of DPAO. The alkyl chain $(CH_3CH_2 CH_2)_2C$ has all-*trans* conformation. Fig. 1b shows the molecular arrangement of DPAO, in which the $(CH_3CH_2CH_2)_2C$ moieties are omitted for the sake of clarity.

The nearest intermolecular $O \cdots O$ distances are 6.161(2) Å. There seems to be no direct magnetic interaction among the N–O sites, because model calculations indicate that the through-space exchange and dipole interactions between two nitroxide radicals are negligible when the $O \cdots O$ distance is > 5 Å [2,11]. Rather short atomic distances are found between the N–O sites and the aromatic hydrogen atoms of a neighboring molecule. Three shortest $O \cdots H$ distances are 2.67(4), 2.93(4) and 2.96(4) Å, which we call contacts A, B and C, respectively, as shown with broken lines in Fig. 1b.

Contacts A, B and C run along the *b*, *c* and *a* axes, respectively, in a zigzag manner with 2_1 symmetry operation. All of these relations are repeated uniformly and infinitely. The DPAO crystal seems to have a three-dimensional network of magnetic interactions. In view of the intermolecular atomic distances and the direction of the N–O π^* orbital lobe (see below), contacts A and B may play a main role of magnetic coupling. A closer inspection of the molecular arrangement shows that only contacts A and B can form a three-dimensional network.

Fig. 1c shows the detailed geometries around these contacts, where intermolecular atomic distances of $N \cdots H$ and $O \cdots H$ are indicated. The N–O bond length is 1.291(4) Å. The Cartesian coordinates of selected atoms are listed in Table 1. For

Table 1



Cartesian coordinates of selected atoms neighboring an N-O site ^a				
Atom	x (Å)	у (Å)	z (Å)	
N	0	0	0	
0	1.29	0	0	
C1	-0.67	-1.26	0	
C2	-0.68	1.21	0.03	
H–C moie	ety in contact A ^b :			
Н	1.22	0.87	-2.52	
С	1.27	1.30	-3.52	
H–C moie	ety in contact B^{c} :			
Н	0.44	-0.22	2.79	
С	0.42	-0.52	3.77	
H–C moie	ety in contact C^d :			
Н	3.54	-1.88	0.45	
С	4.28	-2.42	-0.09	
-				

^aFor contacts A–C, see Fig. 1.

^bSymmetry operation is -x + 1, y + 1/2, -z + 1/2. ^cSymmetry operation is -x + 3/2, -y + 1, z - 1/2.

^dSymmetry operation is x - 1/2, -y + 3/2, -z.

both contacts A and B, the hydrogen atoms are located just above the nitroxide group, and three atoms H, O and N approximately form an isosceles triangle. The hydrogen atoms correspond to m-H atoms in both cases, where the o-, m- and p-positions are defined with respect to the nitroxide group. On the other hand, for contact C the hydrogen atom is located almost on the nitroxide >N-O plane. This hydrogen atom also corresponds to another *m*-H atom. Therefore, we have to pay attention to the role of the contacting *m*-H atoms for clarifying the mechanism of ferromagnetic interaction.

Fig. 1. (a) Molecular structure of DPAO. Thermal elipsoids of C, N and O atoms are shown at the 50% probability level. (b) Molecular arrangement in the crystal of DPAO. (CH₃CH₂CH₂)₂C moieties are omitted for clarity. Dotted lines indicate relatively short distances between nitroxide O and aromatic H atoms. (c) Detailed geometries of contacts A, B and C. N · · · H and O · · · H distances are shown with dotted lines. Standard deviations of the atomic distances are 0.04 Å.

3.2. ESR spectrum

In order to determine the spin densities on the *m*-H atoms, we measured an ESR spectrum of DPAO. The solution ESR spectrum (benzene, room temperature) indicated g = 2.0050, $a_{\rm N} = 8.82$, $a_{o-{\rm H}} = a_{p-{\rm H}} = 2.37$ and $a_{m-{\rm H}} = a_{m'-{\rm H}} = 0.77$ G, which are comparable to those of typical diphenyl nitroxides [6,12–14]. The sign of the hyperfine splitting constants or of the spin densities could not be determined by the ESR data alone. McConnell's equation with $Q_{\rm C} = -22.5$ G [15,16] gave the spin densities (ρ 's) of the carbon atoms: $|\rho_{o-{\rm C}}| = |\rho_{p-{\rm C}}| = 0.105$ and $|\rho_{m-{\rm C}}| = 0.034$.

The MacLachlan calculation of a diphenyl nitroxide portion by use of $\lambda = 1.2$ [17,18] indicated $\rho_{o-C} = +0.104$, $\rho_{p-C} = +0.097$ and $\rho_{m-C} = -0.041$. They are converted by McConnell's equation to be $a_{o-H} = -2.34$, $a_{p-H} = -2.18$ and $a_{m-H} = +0.92$ G. These absolute values agree with the observed ones. The calculation suggests that the *m*-C and *m*-H atoms have negative and positive spin densities, respectively. Furthermore, the spin polarization is well known to take place from a radical center throughout the conjugated benzene rings, giving an alternating spin density [19]. We can safely assume that the contacting H atoms, i.e. *m*-H atoms in neighboring molecules, have a positive spin density.

3.3. Magnetic properties

Static magnetic susceptibility (χ_{mol}) was measured on a SQUID magnetometer down to 1.8 K at 0.5 T. Fig. 2a shows that the product $\chi_{mol}T$ of DPAO monotonically increases with decreasing temperature and reaches 0.59 cm³ K mol⁻¹ at 1.8 K. A plot of reciprocal magnetic susceptibility against temperature gives a positive Weiss temperature (θ) of +0.77 K. The $\chi_{mol}T$ value larger than 0.5 cm³ K mol⁻¹ at 1.8 K means that more than two molecules are ferromagnetically correlated.

The magnetization curves were measured at 2.0 and 4.5 K with an applied field up to 9 T. Fig. 2b shows the data points as well as calculated Brillouin functions. The data measured at 4.5 K fall between the S = 1/2 and 1 Brillouin functions. The data exceed the S = 1 function at 2.0 K, in accordance with the result of the product $\chi_{mol}T$.



Fig. 2. (a) Temperature dependence of $\chi_{mol}T$ and χ_{mol}^{-1} of DPAO. (b) M-H curves of DPAO measured at 2.0 and 4.5 K. Solid lines are calculated Brillouin functions.

These findings clearly indicate the presence of intermolecular ferromagnetic interaction in the DPAO crystal. Since intermolecular contacts A, B and C in Fig. 1b form an infinite three-dimensional network, the magnetic dimensionality can be defined by J_A , J_B and J_C . However, we cannot determine these values separately. Although all of J_A , J_B and J_C should not be ferromagnetic for $\theta > 0$, the molecular arrangement suggests that intermolecular antiferromagnetic interaction, if any, will be small, as discussed below.

4. Discussion

The exchange interaction J is generally expressed as the sum of a positive contribution J_F , stabilizing the triplet state, and a negative contribution J_{AF} , stabilizing the singlet state (Eq. (1)) [20]. The J_F term originates in the exchange integral K. The J_{AF} term approximately increases in proportion to the product of the overlap integral S and resonance integral β .

$$J = J_{\rm F} + J_{\rm AF} \approx K + 2\,\beta S\,.\tag{1}$$

Fig. 3 shows the SOMO (singly occupied molecular orbital) surface of a DPAO molecule calculated by a semiempirical UHF/PM3 MO method [21] based on the determined molecular structure. The SOMO has antibonding π^* character at the NO site; the coefficients of 2p(O) and 2p(N) being + 0.41 and -0.59, respectively. This figure also confirms the presence of SOMO coefficients at every other carbons on the phenyl rings. These types of molecules are known to have negative spin densities on the carbons possessing no SOMO coefficients. Negatively polarized spin densities are suggested on the *m*-C atoms, and consequently the *m*-H atoms have a positive spin density.

In the following discussion of SOMO-SOMO overlaps of DPAO we have to focus on atomic



Fig. 3. SOMO surface of a DPAO molecule calculated by a UHF/PM3 method using the X-ray crystal data.

orbital overlaps among the contacting atoms shown in Fig. 1c, because a few nearest atomic orbital overlaps mainly contribute to the total molecular orbital overlap. The SOMO of DPAO has a coefficient at *m*-H atoms, indicated by the positive spin density at the *m*-H atoms, and also supported by the semiempirical UHF/PM3 MO calculation. In all cases of contacts A, B and C, therefore, the hydrogen 1s orbitals located nearest an N–O site and the N–O π^* orbital are selected on behalf of the SO-MOs of neighboring molecules.

When a hydrogen atom approaches a nitroxide on the nodal plane which bisects the N-O bond at the center, the hydrogen 1s and nitroxide π^* orbitals cannot have any appreciable net overlap due to orthogonality: the $H \cdots N$ and $H \cdots O$ atomic orbital overlaps are almost cancelled (contacts A and B). In contact A the $H \cdots O$ distance is somewhat shorter than the $H \cdots N$ one, but the overlap cancellation is rationalized in view of the larger coefficient of the N atom than that of the O atom. When a hydrogen atom approaches a nitroxide on another nodal plane defined by the >N-O plane, the hydrogen 1s and nitroxide π^* orbitals have no orbital overlap also by symmetry (contact C). In the DPAO crystal, therefore, the second term J_{AF} in Eq. (1) is negligible and the ferromagnetic term $J_{\rm F}$ survives in $J_{\rm A}$, $J_{\rm B}$ and $J_{\rm C}$. The polarized spin density at the m-H atom is positive, and the spin density at the N-O site in a neighboring molecule should also be positive by through-space ferromagnetic coupling. For contacts A and B the spin polarization scheme is shown in Fig. 4. A similar scheme can be drawn for contact C. In our previous paper on BTAO [6], the *m*-H contact was reported to cause antiferromagnetic interaction, such as $N(\uparrow)-C(\downarrow)=C_o(\uparrow)-C_m(\downarrow)-C_m(\downarrow)$ $H_m(\uparrow) \cdots O(\downarrow) - N \le A$ crucial difference is that the intermolecular SOMO-SOMO overlap is present at the contact of m-H · · · O in the previous case.

Yoshizawa and Hoffmann discussed the magnetic coupling of stacking dimer models of nitroxide radicals [22]. An *anti-stacking* mode favors ferromagnetic coupling because the $N \cdots N$ interactions are of opposite sign to the $N \cdots O$ interactions. Their discussion holds for the present system; the H atoms in place of the N atom approach an N–O site. To our knowledge, the DPAO crystal is the first example possessing ferromagnetic interaction due to the lack



Fig. 4. Schematic drawing of a possible mechanism of intermolecular ferromagnetic interaction between the neighboring DPAO molecules.

of SOMO–SOMO overlap in an $H \cdots N$ –O triangular geometry.

Gatteschi and co-workers reported a successful application of orbital orthogonality to the transition metal complexes in which the nitroxide O atom was coordinated to the metal center [23]. For example, the TEMPOL-Cu(hfac)₂ complex has $2J/k_{\rm B} = 19$ \pm 7 K between S = 1/2 spins of a d_{x²-y²} orbital of the copper(II) ion and the axially coordinated nitroxide [24]. In the present study, the interaction J is estimated to be as much as $\theta = 0.77$ K, which is smaller than that of the TEMPOL-Cu(hfac)₂ complex, probably because the exchange occurs in a non-covalent manner and because the polarized spin density at the H atom is small. As described in Section 1, the intermolecular exchange interaction is considered to be proportional to the product of polarized spin densities at contacting atoms (Eq. (2)) [5]. In the DPAO crystal the contacting H atoms has a spin density of 1.52×10^{-3} , as estimated by Mc-Connell's equation with $Q_{\rm H} = 508$ G. The weak ferromagnetic interaction arises from a small spin density on the *m*-H atoms.

$$H^{\rm AB} = -S^{\rm A} \cdot S^{\rm B} \sum J_{ij}^{\rm AB} \rho_i^{\rm A} \rho_j^{\rm B} \,. \tag{2}$$

The NHOMO (or a lower doubly-occupied MO) of DPAO has bonding π character at the N–O site. We can point out from the isosceles triangular geom-

etry of $H \cdots N-O$ that there is a considerable orbital overlap between the hydrogen 1s and N-O π orbitals in the case of contacts A and B. For contact C the oxygen lone-pair orbitals are located on the >N-O plane and accordingly an orbital overlap between the hydrogen 1s and oxygen lone-pair is also possible. The situation where SOMO-SOMO interaction is absent and, at the same time, appreciable SOMO-NHOMO interaction is present may favor ferromagnetic coupling in view of CT configurations among the radicals. Namely, a β -spin transfer from NHOMO to SOMO of a neighboring molecule stabilizes a triplet state within a dimer.

A spin-unrestricted picture may give an insight into CT interactions bringing about intermolecular ferromagnetic interaction. Awaga et al. suggested that large orbital overlaps between NHOMO(β) and SOMO(β) and between SOMO(α) and NLUMO(α) were responsible for the ferromagnetic coupling of the galvinoxyl radical on which they made a spin-unrestricted MO calculation [25]. The intermolecular orbital overlaps between SOMO and NHOMO and between SOMO and NLUMO seem to be necessary for ferromagnetic interaction. In the present case, the latter contribution has not yet been clarified. A more detailed theoretical calculation of orbital overlaps is needed for further discussion.

5. Summary

The DPAO crystal exhibited intermolecular ferromagnetic interaction. The positively spin-polarized hydrogen atoms located near a neighboring N–O site play an important role in the ferromagnetic exchange mechanism. Orbital orthogonality was found in the $H \cdots N$ –O geometry.

Singly occupied molecular orbitals extended on π -conjugated radicals are likely to overlap in crystal packing to give rise to intermolecular antiferromagnetic interactions [26,27]. The present work provides an example of ferromagnetic interaction in π -conjugated nitroxide radicals, in addition to those on three other ferromagnetic crystals of π -conjugated radicals are not exceptional; a search for more strongly ferromagnetic materials is now underway.

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