Bull. Chem. Soc. Jpn., ***69***, *1841—1848 (1996)*

Proposed Mechanism of Ferromagnetic Interaction of Organic Ferromagnets: 4-(Arylmethyleneamino)-2,2,6,6-tetramethylpiperidin-1-oxyls and Related Compounds

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(Received November 16, 1995)

A possible mechanism of ferromagnetic coupling of a series of organic radical ferromagnets is presented, based on their crystal structures and molecular-orbital calculations. The investigated radicals are 4-(arylmethyleneamino)-2,2,6,6-tetramethylpiperidin-1-oxyls (abbreviated as Ar–CH=N–TEMPO, where Ar = phenyl, 4-methylthiophenyl, 4-chlorophenyl, 4-biphenylyl, and 4-phenoxyphenyl), and 4-hydroxyimino-TEMPO. All of these radical crystals have characteristic features that oxygen atoms of N–O radical sites of TEMPO moieties always locate near methyl- and/or methylene-hydrogens at β-positions of N–O in the TEMPO moieties of adjacent molecules. A positive spin on the N–O radical induces negative spins on the β-hydrogen atoms due to an intramolecular spin-polarization, ON(↑)–C(↓)–C(↑)–H(↓), which in turn induces a positive spin on the N–O sites of the adjacent molecules. This spin-alternation mechanism of ferromagnetic coupling among N–O sites via hydrogen bridges is also applicable to the case of an organic metamagnet, bis(2,2,6,6-tetramethylpiperidin-1-oxyl-4-yl) 1,6-hexanedicarboxylate. In the case of an organic ferromagnet, 2,4,6,8-tetramethyl-1,5-diazaadamantane-1,5-dioxyl, both the spin-alternation and direct exchange mechanisms seem to be operative.

Organic radical crystals which show bulk ferromagnetic transitions have attracted much attention,[1] and, to our knowledge, eighteen kinds of ferromagnets of organic radical crystals have been discovered in the past few years.[2—7] Kinoshita discussed the origin of ferromagnetic coupling of the first organic ferromagnet, β-phase of *p*-nitrophenyl nitronyl nitroxide (β-NPNN, Chart 1), based on the crystal structure and semiempirical UHF molecular-orbital calculation.[8] He postulated that a large intramolecular spin-polarization effect, large intermolecular SOMO–HOMO and SOMO–LUMO interactions, and negligibly small intermolecular SOMO–SOMO interaction are important factors for the intermolecular ferromagnetic interaction; SOMO, HOMO, and LUMO denote singly-occupied, highest-occupied, and lowest-unoccupied molecular orbitals, respectively. One of the authors (K. Y.) and his co-workers analyzed the intermolecular magnetic interaction of β-NPNN from semiempirical and ab initio molecular-orbital calculations.[9] The results indicated that the net ferromagnetic inter-plane interaction was in accord with an extended McConnell model.[10] The ferromagnetic transition temperature (T_c) calculated by the mean-field approximation was close to the observed one. Although the ferromagnetic coupling of 2,4,6,8-tetramethyl-1,5-diazaadamantane-1,5-dioxyl (TMAO, Chart 1) was briefly discussed from the viewpoint of the intermolecular SOMO–SOMO overlap,[11] the origin of magnetic interactions of most of the other organic-radical ferromagnets have not been analyzed yet.

We have synthesized a series of 4-(arylmethyleneamino)-2,2,6,6-tetramethylpiperidin-1-oxyls (abbreviated as ArCH=N–TEMPO) and related species.[4] The magnetic measurements have clearly demonstrated the ferromagnetic phase transitions of the crystals of these species at low temperatures ($\leq$0.4 K). In order to clarify the origin of the intermolecular ferromagnetic interactions, the crystal structures have been determined by the X-ray diffraction analysis. Since radical centers are localized on the N–O sites due to the aliphatic framework of the TEMPO ring, we must focus on the arrangements of the N–O sites. The structural analyses of these crystals have revealed that the direct exchange interactions between SOMO spins on the N–O groups should be negligible because of the long intermolecular O···O distances. However, the crystal structures show that near the N–O group do exist methyl and methylene groups belonging to the adjacent molecule, suggesting the possibility of intermolecular ferromagnetic interactions via hydrogen bridges.

This paper will discuss extensively a possible mechanism of intermolecular ferromagnetic interaction of these materi-

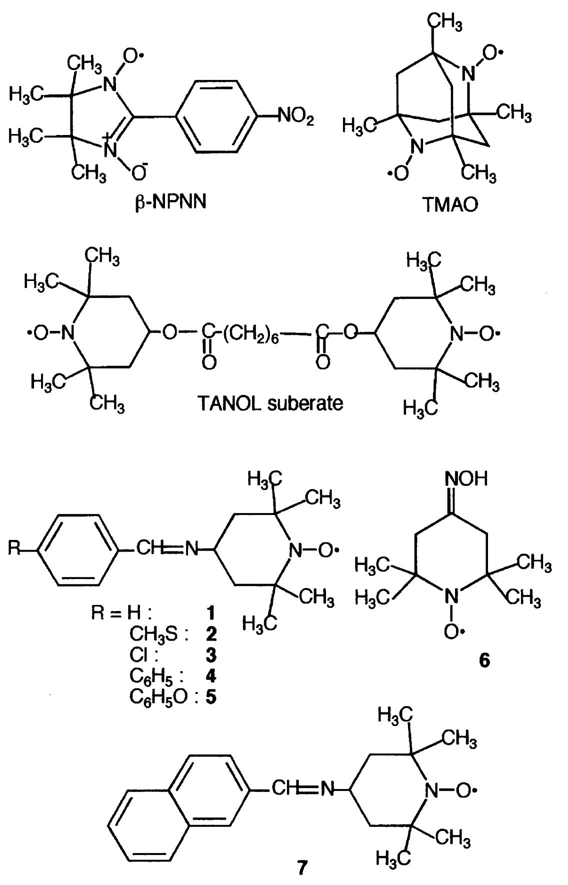

Chart 1.

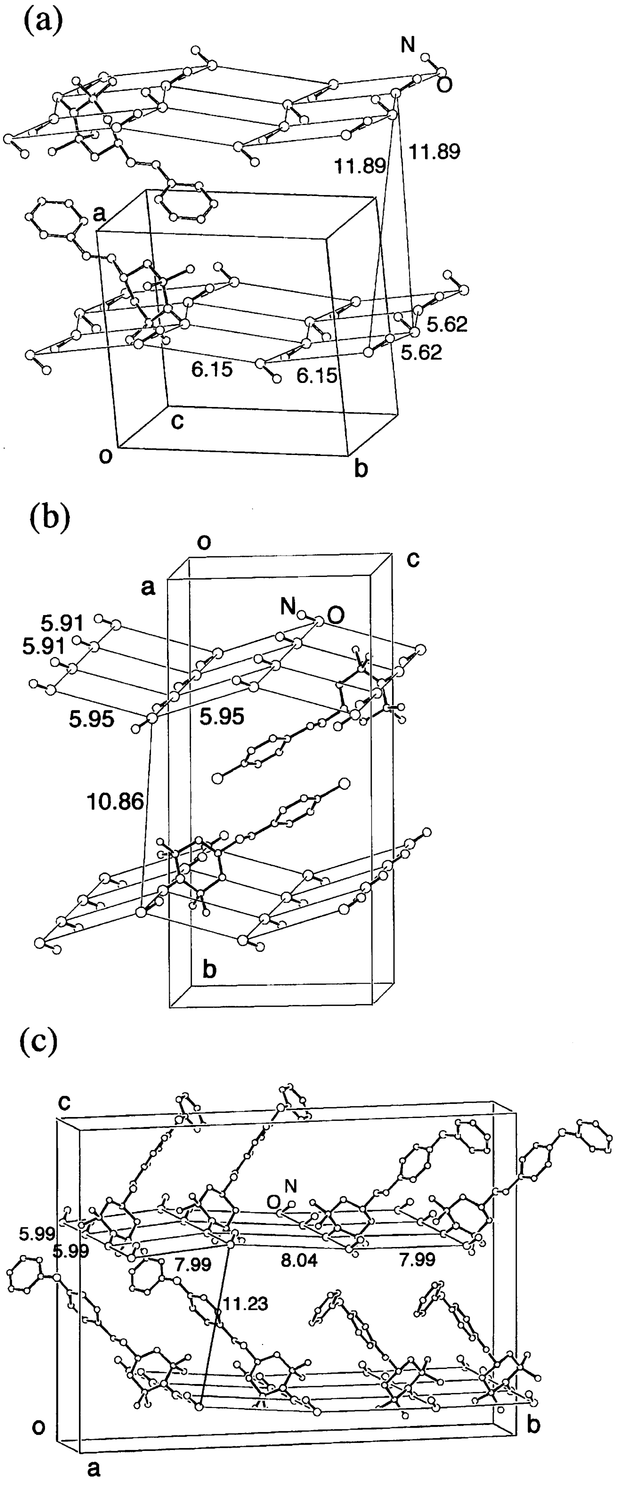

Fig. 1. Arrangements of N–O sites in the crystals of **1** (a), **3** (b), and **5** (c). Two, two, and eight molecular structures are shown for **1**, **3**, and **5**, respectively, in order to envisage molecular packings.

als based on crystal structures available, leading to a new proposal of the intermolecular ferromagnetic interaction via hydrogen bridges. The semiempirical and ab initio MO calculations will be carried out in order to confirm the proposal based on experimental grounds. The applicability of our proposal will be also discussed in relation to the experimental results by other groups: an organic metamagnet, bis(2,2,6,6-tetramethylpiperdin-1-oxyl-4-yl) 1,6-hexanedicarboxylate[12] (TANOL suberate, Chart 1) and to an organic ferromagnet, TMAO.[3]

Results and Discussion

Characteristic Features of Crystal Structures. X-Ray crystallographic analyses[4,13] were made for organic-radical ferromagnets, i.e., benzylideneamino-TEMPO (**1**), 4-(4-methylthiobenzylideneamino)-TEMPO (**2**), 4-(4-chlorobenzylideneamino)-TEMPO (**3**), 4-(4-phenylbenzylideneamino)-TEMPO (**4**), 4-(4-phenoxybenzylideneamino)-TEMPO (**5**), and 4-hydroxyimino-TEMPO (**6**)[14] (Chart 1). The materials, **1**, **2**, **3**, **4**, **5**, and **6** were found to possess T_C's of 0.3,[4a] 0.3,[4e] 0.4,[4d] 0.4,[4b] 0.2,[4e] and 0.25 K,[4e] respectively; we define the transition temperature as the temperature where the divergence of ac magnetic susceptibilities starts. Figure 1 shows the arrangements of N–O sites of **1**, **3**, and **5**. Two, two, and eight molecular structures are shown for **1**, **3**, and **5**, respectively, in order to envisage the molecular packing in crystals. The arrangements of molecules in **2** and **4** were found to be very similar to those of **1** and **3**, respectively. Two common features were found in **1**—**5** and TANOL suberate.

(1) The N–O radical sites are arranged in two-dimensional zigzag sheets with intermolecular O···O distances of about 6 Å, and inter-sheet distances are longer than 10 Å.

(2) The aromatic rings (aliphatic chains in the case of TANOL suberate) gather together in the clearances between zigzag sheets.

These crystal structures suggest that intra-sheet magnetic interactions are much stronger than inter-sheet ones. Therefore, we will discuss intra-sheet magnetic interactions among N–O sites in these materials. On the other hand, the crystal structures of **6**[14)] and TMAO[3)] are quite different from those of **1**—**5** and TANOL suberate. However, **6** and TMAO have molecular arrangements of TEMPO moieties in common with those of **1**—**5** and TANOL suberate, so that a mechanism of ferromagnetic coupling similar to those of **1**—**5** and TANOL suberate can be applied to these compounds (vide infra). Table 1 summarizes important intra-sheet O···O distances ($d(\mathrm{O\cdots O})$) of **1**—**6**, TANOL suberate and TMAO, and nearest inter-sheet O···O distances ($d_{\mathrm{inter}}(\mathrm{O\cdots O})$) of **1**—**5** and TANOL suberate.

Estimation of Direct Intra-Sheet Magnetic Interaction. First of all, we will discuss the magnitudes of direct magnetic interactions, exchange and dipole–dipole interactions between N–O sites. Yoshizawa and Hoffmann performed the extended Hückel calculations of TMAO, and discussed the possibility of the ferromagnetic interaction because there was no SOMO–SOMO overlap integral.[11)] One of the authors (K. Y.) and his co-workers also presented no SOMO–SOMO overlap and orientation principles for the intermolecular ferromagnetic interactions.[15,16)] They further performed ab initio and semiempirical MO calculations of direct exchange interactions between N–O radical sites, by changing mutual orientations and distances, and found that the exchange interaction is negligibly small for a radical pair with longer distances than 4.6 Å.[15)] Since the distances between N–O sites are about 6 Å in **1**, **2**, **3**, **4**, and **5**, and 5.3 Å in **6**,[14)] direct exchange interaction can not explain the T_c's, 0.25—0.4 K, of these materials.

Dipole–dipole interaction ($E_{\mathrm{d-d}}$) is another possible mechanism of ferromagnetic interaction. Suzuki and Kawamoto have discussed the possible role of the $E_{\mathrm{d-d}}$ term for the ferromagnetic interaction between N–O groups.[17)] If we approximate $E_{\mathrm{d-d}}$ as

$$E_{\mathrm{d-d}} = \mu_1\mu_2/(4\pi\mu_0 r^3),$$

$E_{\mathrm{d-d}}/k$'s are estimated to be about 5 and 3 mK at r=5 and 6 Å, respectively. Here, μ_i (i=1,2), μ_0, r, and k are interacting magnetic moments of 1/2 spins, magnetic permeability of vacuum, distance between 1/2 spins, and Boltzmann constant, respectively. The estimated values are too small to be compatible with the T_c's in these materials. Therefore, some other mechanism of ferromagnetic interaction must be considered.

Possible Mechanism of Intra-Sheet Ferromagnetic Interaction. A possible mechanism of intra-sheet ferromagnetic interaction will be presented here, based on crystal structures. As will be described in the next section, crystal structure analyses of **1**, **2**, **3**, **4**, **5**, and **6** revealed that an oxygen atom of an N–O radical site was found to locate always near methyl- and/or methylene-hydrogens at the β-positions of N–O sites in TEMPO moieties of the adjacent molecules. These intermolecular atomic O···H distances were close to the sum of van der Waals radii (2.6 Å). Therefore, we can suggest the following mechanism for the origin of ferromagnetic couplings of these materials.

A positive spin on the N–O site induces a negative spin on the methyl- and/or methylene-hydrogens connected to β-carbons, due to an intramolecular spin-polarization, $\mathrm{O{-}N}(\uparrow){-}\mathrm{C}_\alpha(\downarrow){-}\mathrm{C}_\beta(\uparrow){-}\mathrm{H}_\beta(\downarrow)$. Orbital overlap between these hydrogens and the π^*(N–O) orbital of the adjacent molecule induces a positive spin on the N–O site, thereby giving rise to a parallel spin-alignment of N–O sites depicted as $\mathrm{O{-}N}(\uparrow){-}\mathrm{C}_\alpha(\downarrow){-}\mathrm{C}_\beta(\uparrow){-}\mathrm{H}_\beta(\downarrow)\cdots(\uparrow)\mathrm{O{-}N}\langle$. Thus, we denote this situation as "spin alternation" in this paper.

As a typical example, possible spin-polarization in the case of **3** is illustrated in Fig. 2(a), based on the crystal structure; only CNOC and $(\mathrm{CH_3})_2\mathrm{CNOC}(\mathrm{CH_3})_2$ portions of TEMPO moieties are shown for the sake of simplicity. This figure shows that the polarizations of spins alternate throughout the aliphatic framework. The intramolecular spin-alternation of TEMPO derivatives were confirmed by ENDOR and NMR measurements which revealed that the signs of the ^{1}H and ^{13}C hyperfine splitting constants (hfsc's) alternated throughout the hydrocarbon framework and that negative spin was

Table 1. Intra-Sheet O···O Distances (d) of **1**—**6**, TANOL Suberate, and TMAO, Nearest Inter-Sheet O···O Distances (d_{inter}) of **1**—**5** and TANOL Suberate, and Proposed Dimensionalities of Magnetic Properties

Materials	$d(\mathrm{O\cdots O})$ / Å	$d_{\mathrm{inter}}(\mathrm{O\cdots O})$ / Å	Proposed magnetic property[a)]
1	5.62, 6.15	11.89	2D
2	5.67, 6.21	13.57	2D
3	5.91, 5.95	10.86	2D
4	5.96, 6.09	13.40	2D
5	5.99, 8.00, 8.03	11.23	1D
6	5.33	—	1D
TANOL suberate	6.04, 6.18	10.01	2D
TMAO	4.077, 4.659, 5.863	—	3D

a) 1D = quasi-one-dimensional magnetic property; 2D = quasi-two-dimensional magnetic property; 3D = three-dimensional magnetic property.

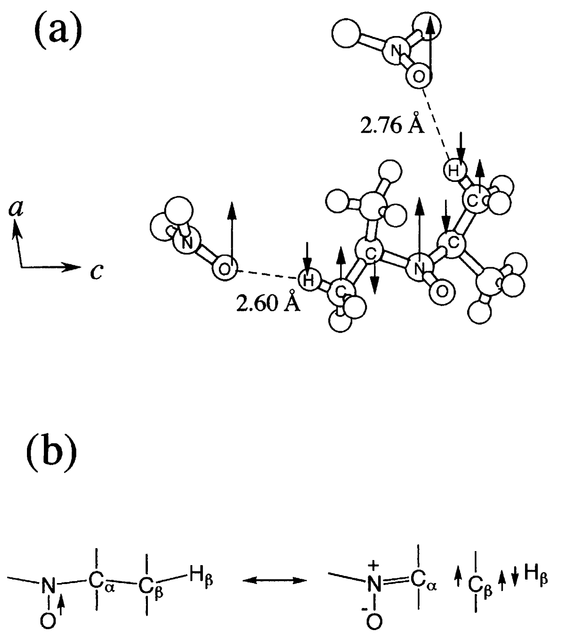

Fig. 2. (a) Possible spin-alternation in the aliphatic framework of **3**; only CNOC and $(CH_3)_2CNOC(CH_3)_2$ portions of TEMPO moieties are shown for the sake of simplicity. (b) Resonance structures giving down-spin polarization of hydrogen atoms connected to a carbon atom at the β-position of the N–O site.

induced on the β-hydrogen atoms.[18] These results are also consistent with UHF/MNDO-PM3[19] molecular orbital calculation of **1**, based on its geometry determined by the X-ray crystallography. The spin distributions on C_α, C_β, and H_β atoms in the nearest pathway along the *b* axis were calculated to be −0.017, +0.0013, and −0.0006, respectively, and those along the *c* axis to be −0.017, +0.0060, and −0.0004, respectively. A similar calculation of **3** revealed that the spin distributions on C_α, C_β, and H_β atoms in the nearest pathway along the *a* axis were −0.020, +0.024, and −0.002, respectively, and those along the *c* axis −0.021, +0.0053, and −0.001, respectively. Negative-spin polarizations of β-hydrogen atoms of several related radicals were also confirmed by ab initio UHF calculations.[20]

These facts can be interpreted in terms of a hyperconjugation shown in Fig. 2(b).[21] The absolute values of hfsc's of β-hydrogens (or β-carbons) are greater than those of α-hydrogens (or α-carbons) in general, which can reasonably be explained by hyperconjugation theory.[21b] Therefore the negative-spin polarization on β-hydrogens are compatible with the above-mentioned mechanism of intra-sheet ferromagnetic coupling.

The geometry dependence of hyperconjugation is stated briefly. The TEMPO moiety has a chair form and the nitroxide oxygen locates on an equatorial position in all of the crystals analyzed here. There are three types of β-carbons: axial methyl, equatorial methyl, and ring methylene groups. The magnitude of the hyperconjugation effect depends on the mutual geometry of radical sites and β-carbon atoms in a TEMPO ring. As to the spin distribution, the axial methyl groups may be the most preferable β-carbons and hydrogens among the three, because the dihedral angles between the p_z orbital of a nitroxide nitrogen and a C_α–C_β σ-bond are smallest, leading to the largest contribution of the canonical structure described in Fig. 2(b). The UHF/MNDO calculations[19] on the TEMPO rings supported the above consideration; the spin densities of axial C_β's (ca. +0.02) are larger than those of the equatorial C_β's (ca. +0.005) and those of the ring methylene C_β's (ca. +0.003), and the negative spin densities of H_β's are induced almost in proportion to the positive spin densities of the bonded C_β. However, spin polarization can also take place along a σ-bond pathway irrespective of dihedral angles.

In the next section, the crystallographic evidence that oxygen atoms of N–O sites always locate near methyl- and/or methylene-hydrogens at the β-positions of TEMPO moieties of adjacent molecules in **1**—**6** will be described. This will allow us to postulate the above-mentioned spin-alternation mechanism as the origin of the ferromagnetic coupling in these materials.

Intra-Sheet Molecular Arrangements of TEMPO Moieties in 1—6. In order to discuss the origin of intra-sheet ferromagnetic interaction, arrangements of $CH_2C(CH_3)_2NOC(CH_3)_2CH_2$ portions in TEMPO moieties in two-dimensional zigzag sheets of **1**, **3**, and **5** will be described in more detail.

Figure 3 shows the arrangements of $CH_2C(CH_3)_2NOC(CH_3)_2CH_2$ portions along the *b* and *c* axes in the crystal of **1**; two-dimensional zigzag sheets in **1** are parallel with the *bc* plane. An oxygen atom on N–O sites locates near methyl- and methylene-hydrogens at β-positions along the *b* axis with the distances of 2.77 and 2.48 Å, respectively. Along the *c* axis, a relatively short O···H(methyl) distance is found (2.86 Å). Thus, **1** seems to have a quasi-two-dimensional magnetic property. The molecular arrangement of **2** was found to be very similar to that of **1**. This is consistent with the experimental results that **1** and **2** have almost the same

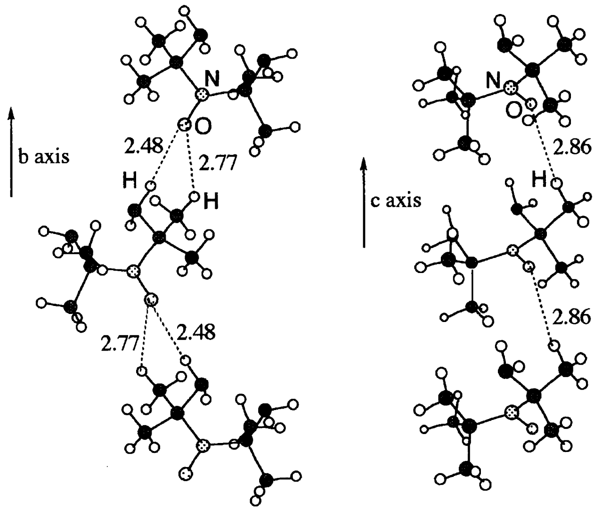

Fig. 3. Arrangements of $(CH_3)_2CNOC(CH_3)_2$ portions along the *b* and *c* axes in a two-dimensional zigzag sheet of **1**. Intermolecular O···H distances which are close to the sum of van der Waals radii are shown in Å unit.

T_c (0.3 K).[4)]

Figure 4 shows the arrangements of $CH_2C(CH_3)_2NOC(CH_3)_2CH_2$ portions of **3** in a zigzag sheet which is parallel with the *ac* plane. An oxygen atom of N–O sites locates near two methyl-hydrogens of the adjacent molecule with the distances of 2.76 and 2.78 Å along the *a* axis. Short intermolecular O···H distances can also be seen at O···H-(methyl) and O···H(methylene) along the *c* axis with the distances of 2.60 and 2.66 Å, respectively. Thus, **3** seems to have a quasi-two-dimensional magnetic property. The molecular arrangement of **4** was found to be very similar to that of **3**. This is consistent with the experimental results that **3** and **4** have almost the same T_c (0.4 K).[4)]

Figure 5 shows the arrangements of $CH_2C(CH_3)_2NOC(CH_3)_2CH_2$ portions of **5** in a zigzag sheet which is parallel with the *ab* plane. Two kinds of molecular arrangements are found. Intermolecular O···H(methyl) distances along the *a* axis in one arrangement are 2.85 and 2.87 Å, and they are 2.72 and 2.97 Å in another arrangement. However, no intermolecular O···H contact close to the sum of van der Waals radii was found along the *b* axis. Thus, **5** seems to have a quasi-one-dimensional magnetic property, which is responsible for the low T_c (0.2 K).[4)]

Figure 6 shows molecular arrangements of **6** in the crystal, which were drawn based on the reported crystallographic data.[14)] Intermolecular hydrogen bond was found at =N–OH···ON$\langle$ with a distance of 2.05 Å. This material also has intermolecular O···H(methyl) contacts (2.68 Å), which may cause ferromagnetic coupling among N–O radical sites. Intermolecular magnetic interaction through the former hydrogen bond is assumed to be much weaker than that through the latter O···H contact, because N–O radical sites are separated by six intervening atoms in the former path, and by three intervening atoms in the latter path. Thus, **6** seems to have a quasi-one-dimensional magnetic property. Although **6** has molecular arrangements quite different from those of **1**—**5**, similar mechanism of ferromagnetic coupling seems to be operative in **6**.

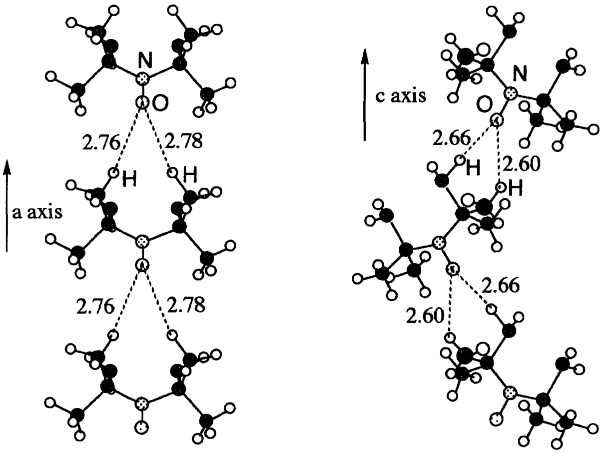

Fig. 4. Arrangements of $(CH_3)_2CNOC(CH_3)_2$ portions along the *a* and *c* axes in a two-dimensional zigzag sheet of **3**. Intermolecular O···H distances which are close to the sum of van der Waals radii are shown in Å unit.

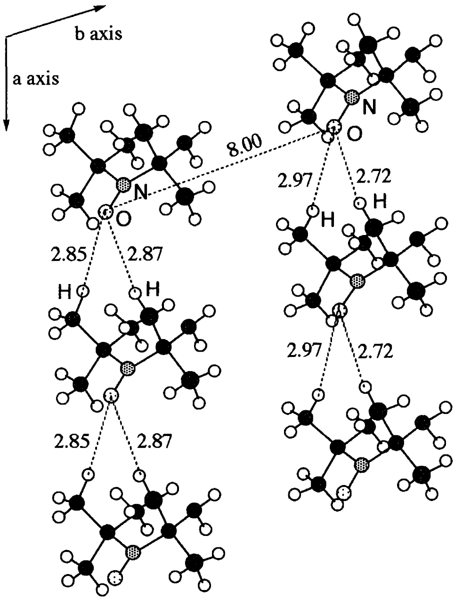

Fig. 5. Arrangements of $(CH_3)_2CNOC(CH_3)_2$ portions along the *a* and *b* axes in a two-dimensional zigzag sheet of **5**. Intermolecular O···H distances which are close to the sum of van der Waals radii are shown in Å unit.

We have found that 4-(2-naphthylmethyleneamino)-TEMPO (**7**, Chart 1) has ferromagnetic interaction among nearest N–O sites, and that metamagnetic transition occurs at 40 mK at a magnetic field of ca. 200 Oe.[22)] This material also has the molecular arrangement that an oxygen atom of the N–O site locates near methyl-hydrogens of the adjacent molecules with the distances of 2.79 and 2.72 Å along the *b* axis.[22)] Therefore, **7** seems to have a one-dimensional ferromagnetic chain along the *b* axis and antiferromagnetic interaction among chains.

Application of Spin-Alternation Mechanism to Other Organic Radical Crystals. As described above, the mechanism of ferromagnetic coupling among N–O radical sites of **1**—**6** may be caused by the characteristic arrangements of TEMPO moieties. This mechanism may be generalized to the other organic nitroxide radicals which have been reported to possess intermolecular ferromagnetic coupling. Thus, we will analyze the intermolecular ferromagnetic interaction of TANOL suberate[12)] and TMAO,[3)] from the viewpoint of the above-mentioned mechanism, based on their crystal structures.

Figure 7 shows the arrangements of N–O radical sites in TANOL suberate.[23)] One molecule was drawn to envisage the crystal structure. The N–O sites locate on two-dimensional zigzag sheets which are parallel with the ac plane. This crystallographic feature is similar to the cases of **1**—**5**. Neutron diffraction study of TANOL suberate revealed that intra-sheet N–O sites couple ferromagnetically, and inter-sheet N–O sites couple antiferromagnetically.[12)] Figures 8(a) and 8(b) show the arrangements of $CH_2C(CH_3)_2NOC(CH_3)_2CH_2$ portions along the *a* and *c* axes, respectively. A relatively short intermolecular O···H(methyl) distance (2.89 Å) along the *a*

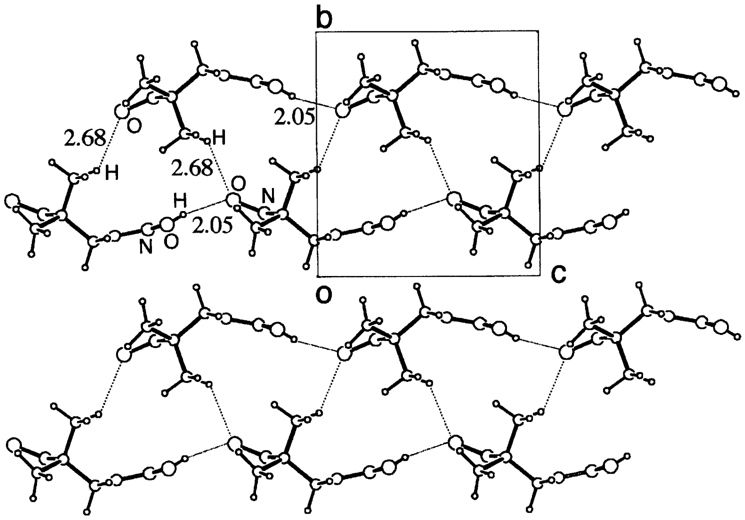

Fig. 6. Molecular arrangements of **6** in the crystal. Intermolecular O···H distances which are close to the sum of van der Waals radii, and hydrogen bonds are shown in Å unit.

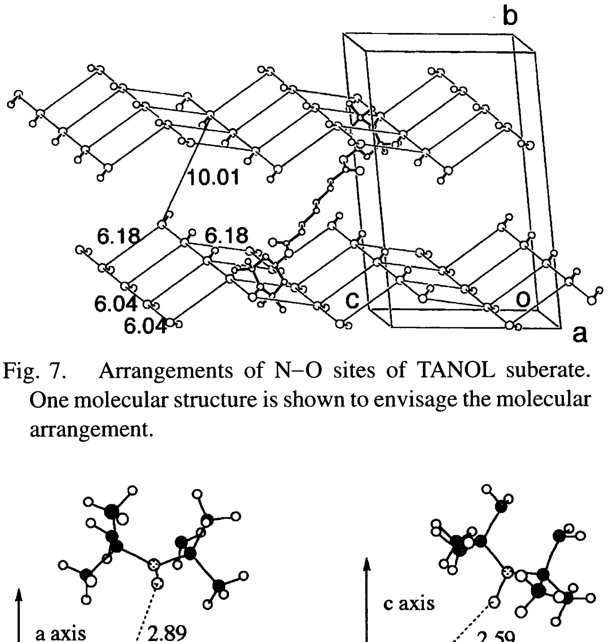

Fig. 7. Arrangements of N–O sites of TANOL suberate. One molecular structure is shown to envisage the molecular arrangement.

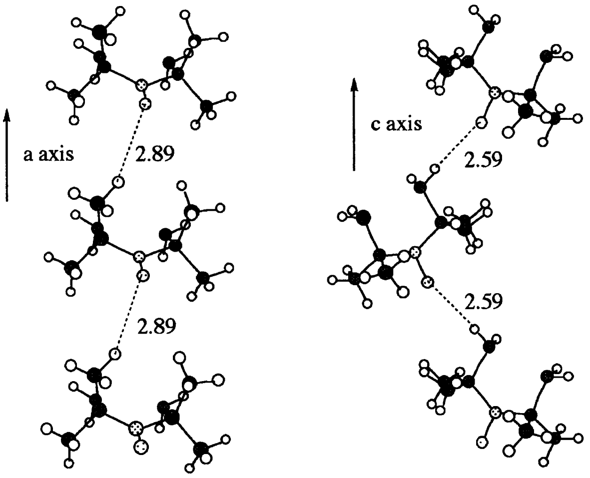

Fig. 8. Arrangements of $(CH_3)_2CNOC(CH_3)_2$ portions of TANOL suberate in a two-dimensional zigzag sheet parallel with the ac plane; (a) along the *a* axis, (b) along the *c* axis. Intermolecular O···H distances which are close to the sum of van der Waals radii are shown in Å unit.

axis and O···H(methylene) distance (2.59 Å) along the *c* axis are found. Thus, the spin-alternation mechanism described above is also applicable to TANOL suberate. This material seems to have a quasi-two-dimensional magnetic property.

TMAO has been reported to be organic radical ferromagnet with the highest T_c (1.48 K) ever reported.[3] The N–O radical sites are arranged in an anti-stacking mode in a crystal; N–O bonds of adjacent molecules point in opposite directions to one another with the intermolecular N···O distances of 4.322, 4.341, and 5.153 Å. Intramolecular N···N distance is 3.352 Å.[3] Although these distances are shorter than intermolecular O···O distances in **1**—**6** and TANOL suberate, dipole–dipole interaction is estimated to be about 10 and 5 mK for inter-radical distances of 4 and 5 Å, respectively. Thus, E_{d-d} is too small to explain the transition temperature. Recent MO calculations[15,16] showed a theoretical possibility that the anti-stacking mode of N–O sites gives essentially zero kinetic exchange integral because of the almost zero SOMO–SOMO overlap integral, whereas the ferromagnetic potential exchange term via the Coulombic interaction still remains even in a longer intermolecular region. However, in view of the intramolecular N···N distance and intermolecular N···O distances, both direct exchange mechanism and above-mentioned spin-alternation mechanism must be considered in TMAO.

In order to clarify whether or not the latter spin-alternation mechanism is applicable to TMAO, intermolecular O···H distances were analyzed, based on the crystal-structure data.[3] Since positions of hydrogen atoms in TMAO were not reported in the literature, they were estimated by a geometrical calculation. In Fig. 9, we can find intermolecular O···H contacts with distances of 2.47, 2.58, 2.66, 2.69, and 2.83 Å which are close to the sum of van der Waals radii. Furthermore, all of the hydrogen atoms involved in these O···H contacts are connected with carbon atoms at β-positions of N–O sites. Thus, intermolecular ferromagnetic coupling may be partly understood in terms of the spin-alternation mechanism. Intramolecular spin-alternation also gives rise to the parallel spin-alignment of two N–O portions, because they are separated by three carbon atoms with a possible

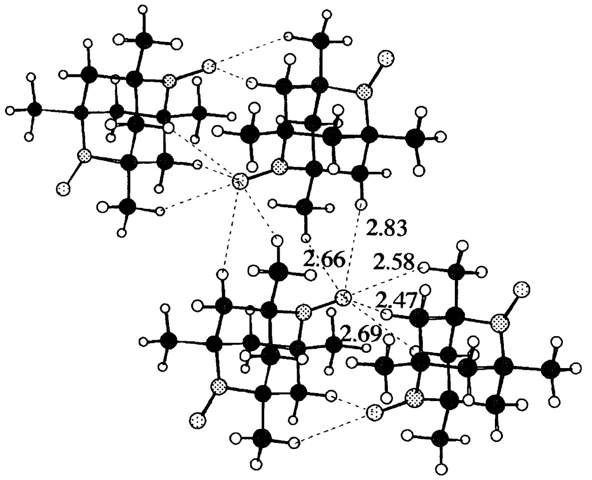

Fig. 9. Intermolecular O···H distances in TMAO which are close to the sum of van der Waals radii. O···H distances are shown in Å unit.

spin-alternation of ON(↑)–C(↓)–C(↑)–C(↓)–(↑)NO. In fact, intramolecular spin-alternation of TMAO has recently been confirmed by a neutron diffraction study.[24] Figure 10 shows positions of oxygen atoms in TMAO crystal connected by the intra- and inter-molecular ferromagnetic interactions due to the spin-alternation mechanism. The three-dimensional ferromagnetic network is drawn in this figure. The N–O radical sites may also couple through three-dimensional direct exchange interaction. This three-dimensional magnetic nature of TMAO, unlike the cases of **1**—**6** and TANOL suberate, may be the reason of its highest transition temperature in organic-radical ferromagnets. However, more detailed theoretical calculation is needed to clarify which of the two mechanisms, direct exchange and spin-alternation mechanisms, is the main origin of the ferromagnetic interaction of TMAO.

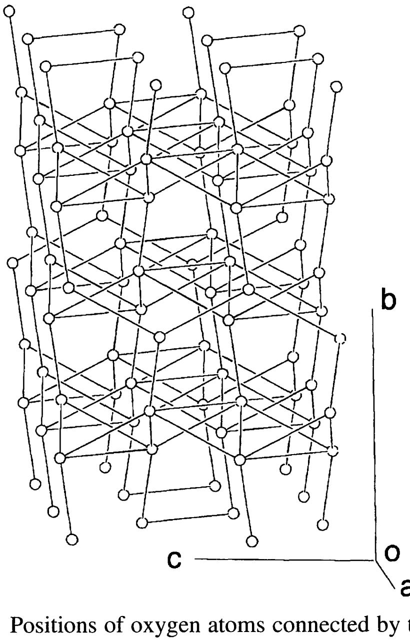

Fig. 10. Positions of oxygen atoms connected by the intra- and inter-molecular ferromagnetic interactions due to the spin-alternation mechanism in the crystal of TMAO.

Besides intermolecular O···O distances and inter-sheet O···O distances, Table 1 also summarizes proposed dimensionalities of magnetic properties of the materials discussed in this paper.

MO-Theoretical Calculations. In order to confirm the above explanations of ferromagnetic interactions between nitroxide species in the crystals of **1**—**7**, we have carried out ab initio and semiempirical calculations of the dimer of parent compound **1**, assuming the experimental packing structure determined by the X-ray diffraction method. The computational methods employed here were described previously.[9,10,15,16] Here, we show typical calculated results for the dimer of **1** along the *c* axis in Figs. 1a and 3.

The following conclusions are drawn:

(1) The effective exchange integrals (*J*) calculated by the approximately spin projected UHF (APUHF) method by the use of the 4-31G basis set and INDO parametrization[9,16] are 0.236 and 0.014 K, respectively, showing the intermolecular ferromagnetic interaction.

(2) The *J* values become −0.117 and −0.0052 K, respectively, by APUHF/4-31G and INDO, when the methyl group contacting with the N–O group of the nearest neighbor in Fig. 3 is replaced by the hydrogen atom. This indicates that the conversion from ferromagnetic to antiferromagnetic interaction is induced by the replacement of CH_3 with H.

(3) The *J* values are 0.245 and 0.014 K by APUHF/4-31G and INDO, respectively, even if the phenyl group of **1** is replaced by the hydrogen atom. This indicates that the ferromagnetic interaction along the *c* axis is independent of the phenyl group.

(4) The *J* values for the H_2NO dimer with the experimentally-determined NO positions are only 0.001 and 0.000 K, respectively, by APUHF/4-31G and INDO. Apparently, the direct exchange interaction between the N–O groups are essentially zero.

These computational results clearly show that the methyl group contacting intermolecularly with the N–O group plays an important role for ferromagnetic interaction, thus supporting the present proposal based on the crystal structures. Probably the situations should be similar in other cases discussed in this paper. A number of computational results will be shown elsewhere.

Summary. Ferromagnetic interactions in two-dimensional zigzag sheets of **1**—**5** and TANOL suberate and one-dimensional ferromagnetic interaction of **6** can be understood by a spin-alternation mechanism, which arises from the fact that an oxygen atom of an N–O radical site always locates near methyl- and/or methylene-hydrogens at β-positions of adjacent molecules. Both the spin-alternation and direct exchange mechanisms may be operative in TMAO. Four methyl groups in TEMPO moiety were originally introduced to protect the unstable N–O radical site. However, we now postulate that these methyl groups also play an important role for the realization of intermolecular ferromagnetic coupling. Although several strategies and theoretical analyses of organic ferromagnets have been reported,[1] all of them were focused on the conjugated systems of π-electrons. On the other hand, the spin-alternation mechanism of the present paper deals with the ferromagnetic coupling through the framework of the aliphatic hydrocarbon. Inter-sheet magnetic interactions of **1**—**5** and TANOL suberate are assumed to be much weaker than those of intra-sheet magnetic interaction, because of the large inter-sheet distances (> 10 Å). Therefore, we could not discuss the inter-sheet magnetic interactions of these materials in detail. The proposed dimensionalities of magnetic properties must be checked by specific heat measurements of these materials.

This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas "Molecular Magnetism" (228/04 242 208), from the Ministry of Education, Science, Sports and Culture. One of the authors (T. I.) is grateful for a financial support from The Nishida Research Fund for Fundamental Organic Chemistry.

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13) Crystallographic data. **1**: monoclinic, $P2_1/c$, a=12.684(7), b=11.740(2), c=11.624(3) Å, β=111.40(4)°, V=1528.3(1) Å^3, Z=4, D_c=1.127 g cm^{-3}, R=0.056 for 2245 observed reflections. **2**: monoclinic, $P2_1/c$, a=13.574(2), b=11.880(2), c=11.163(2) Å, β=98.76(1)°, V=1779.0(8) Å^3, Z=4, D_c=1.140 g cm^{-3}, R=0.048 for 2935 observed reflections. **3**: monoclinic, $P2_1/c$, a=5.906(2), b=24.475(5), c=11.421(4) Å, β=103.84(3)°, V=1604(1) Å^3, Z=4, D_c=1.217 g cm^{-3}, R=0.085 for 1734 observed reflections. **4**: monoclinic, $P2_1/c$, a=5.955(1), b=28.486(5), c=11.795(2) Å, β=106.72(2)°, V=1916.4(7) Å^3, Z=4, D_c=1.163 g cm^{-3}, R=0.068 for 2661 observed reflections. **5**: orthorhombic, $Pbc2_1$, a=5.993(1), b=30.565(9), c=22.032(5) Å, V=4035(2) Å^3, Z=8, D_c=1.157 g cm^{-3}, R=0.061 for 2696 observed reflections. Detailed crystallographic data of these materials will be published elsewhere.

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