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Tempo-Based Organic Ferromagnets and Metamagnets (Tempo = 2,2,6,6-Tetramethywiperidin-1-yloxyl)

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TEMPO-BASED ORGANIC FERROMAGNETS AND METAMAGNETS (TEMPO = 2,2,6,6-TETRAMETHYLPIPERIDIN-1-YLOXYL)

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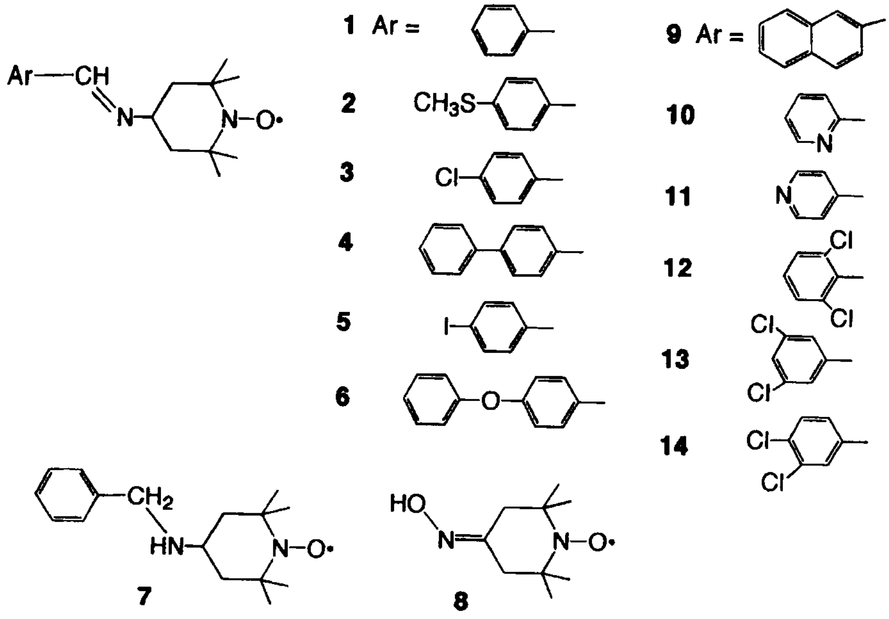
Abstract We have studied the magnetic properties of a series of 2,2,6,6-tetramethylpiperidin-1-yloxyl (TEMPO) radicals, among which eight ferromagnets and six metamagnets were found. Based on their crystal structures, a mechanism of intermolecular ferromagnetic coupling was proposed. The ferromagnetic interactions in the crystals of 4-(*p*-methylthiobenzylideneamino)-TEMPO and 4-benzylamino-TEMPO were explained by the proposed mechanism. The ferromagnetic transition of 4-(*p*-chlorobenzylideneamino)-TEMPO was confirmed by zero-field μSR measurements.

keywords: organic/molecular ferromagnet, ferromagnetic interaction, TEMPO, crystal structure, muon spin rotation/relaxation

INTRODUCTION

This paper is dedicated to Professors Fumio Ogura and Yusei Maruyama on the occasion of leaving Hiroshima University, Japan, and Institute for Molecular Science, Japan, respectively. It is our great pleasure to contribute in this special issue.

Organic radicals exhibiting bulk ferromagnetic transitions have been sought for several decades,[1] and several strategies for obtaining intermolecular ferromagnetic interactions have been presented.[2] The first organic-radical ferromagnet was discovered in 1991,[3a] and the number of organic-radical ferromagnets has amounted to 18 kinds, to our knowledge.[3] Stimulated by the strategy of organic ferromagnets using charge-transfer (CT) complexes presented by Yamaguchi et al,[2i] one of the authors (T. N.) synthesized 2,2,6,6-tetramethylpiperidin-1-yloxyl (TEMPO) substituted donor molecules and their CT complexes with acceptor molecules.[4] Although the latter CT-complexes gave paramagnetic materials, some of the former materials, 4-arylmethyleneamino-TEMPO's, showed intermolecular ferromagnetic interaction.[5] We have systematically studied the magnetic properties of a series of 4-substituted TEMPO's, and found that they have surprisingly high probability of giving materials with intermolecular ferromagnetic interaction.[6] Of 165 radicals investigated, 52 radicals exhibited intermolecular ferromagnetic interaction. This finding may be amazing in view of the fact that only six radicals with intermolecular ferromagnetic interaction were known at the time of 1991.[7] Among the ferromagnetic radicals, eight radicals (**1** - **8**) were found to show bulk ferromagnetic transitions below 0.4 K, which were confirmed by the measurements of ac magnetic susceptibilities and magnetization curves.[6,8] Very recently, the presence of spontaneous magnetization in the crystal of **3** was confirmed by means of zero-field muon spin rotation/relaxation (μSR) measurements below the Curie temperature (T_C).[9] We have also found that six radicals (**9** - **14**) exhibit metamagnetic behavior below 0.3 K with the critical fields (H_C) of spin-flip transition of less than 200 Oe.[6] Based on the X-ray crystallographic analyses of these ferromagnets and metamagnets,[10] a mechanism of intermolecular ferromagnetic interaction was proposed.[3f,8,11] We report here some organic ferromagnets whose crystal structures have been recently determined, and explain the origin of ferromagnetic interactions along with the proposed mechanism. This paper also briefly overviews the results of TEMPO-based ferromagnets and metamagnets.



RESULTS AND DISCUSSION

Mechanism of Intermolecular Ferromagnetic Interactions

During the course of our study on the magnetism of TEMPO-based materials,[5] the magnetic properties of a series of TEMPO radicals possessing various aryl groups attracted our attention from the viewpoint of structure-magnetism relationship. Modification of the aromatic moiety may results in the modification of the arrangement of the radical sites in the crystal. Actually, we have demonstrated that a slight change of intermolecular atomic distances may decide the occurrence of ferromagnetic phase transitions.[3f]

The temperature dependence of magnetic susceptibility (χ) was measured for 165 TEMPO derivatives above 1.8 K on a SQUID magnetometer. Fifty two radicals were found to show intermolecular ferromagnetic interaction,[6] which was confirmed by the increase of χT values at low temperature regions. Positive Weiss temperatures, ranging from +0.03 to +0.75 K, were found for these materials. The probability of finding ferromagnetic radicals is 32% (52/165) for these TEMPO-based materials. Therefore the general belief that organic radicals rarely show intermolecular ferromagnetic interactions must be abandoned owing to these experimental results.

The exceptionally high probability of finding ferromagnetic organic radicals in these TEMPO derivatives may be caused by the following reason. We have found that TEMPO-based organic ferromagnets[3f,8] and metamagnets[11] have a common molecular arrangement in crystals; an oxygen atom of an N-O radical site of a TEMPO moiety always locates near methyl- and/or methylene-hydrogens at β-positions of N-O in the

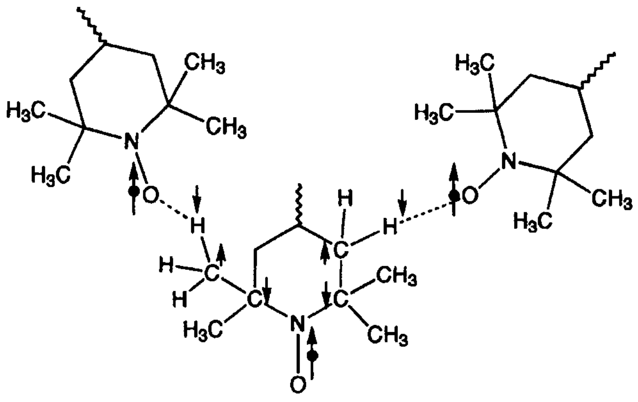


FIGURE 1 A plausible spin-polarization mechanism of intermolecular ferromagnetic interactions found for a series of TEMPO-based ferromagnets. Only TEMPO portions are drawn for the sake of simplicity.

TEMPO moieties of adjacent molecules. A positive spin on the N-O site induces negative spin density on the β-hydrogen atoms due to an intramolecular spin polarization, which in turn induces a positive spin on the N-O sites of the adjacent molecules caused by the through-space orbital overlap between 1s(H) and π^*(N-O) orbitals, $ON(\uparrow)\text{-}C_{\alpha}(\downarrow)\text{-}C_{\beta}(\uparrow)\text{-}H_{\beta}(\downarrow)\cdots(\uparrow)ON<$, thereby leading to parallel spin-alignments of N-O sites in crystals. This mechanism is illustrated in Fig. 1.

The above mechanism is plausible from all of the experimental results and molecular-orbital calculations. The negative spin densities on the β-hydrogen atoms were confirmed by the solid-state ^{1}H MAS NMR measurements.[12] The temperature dependence of the chemical shifts of β-protons in **1**, **3**, and **8** in a solid state indicated that the hyperfine splitting constants of β-protons were negative and consequently the spin densities of the β-hydrogen atoms were negative. The solution ^{1}H NMR and ENDOR measurements of related TEMPO derivatives supported the negative hyperfine splitting constants of β-protons.[13] The UHF/MNDO/PM3 calculation of **1**, **3** and **9** also indicated the negative spin densities of the β-hydrogen atoms.[3f,8,11] APUHF/4-31G and INDO calculations of dimer of **1** suggested that participation of methyl groups in **1** was important for the ferromagnetic interaction and that phenyl groups had no effect on the intermolecular magnetic interaction.[8,14]

Organic Ferromagnets

Table 1 summarizes TEMPO-based ferromagnets, their transition temperatures (T_C), and proposed dimensionalities of magnetic interactions which were obtained based on the X-ray crystallographic data (vide infra).

We studied magnetic properties of several ferromagnetic radicals in the temperature range of a ^{3}He-^{4}He dilution refrigerator, and found that **1** - **8** exhibited bulk ferromagnetic transitions below 0.4 K. Figure 2 shows the temperature dependence of the ac magnetic susceptibility (χ_{ac}, Fig. 2(a)) of **2** and its magnetization curves (Fig. 2(b)) measured at 53 and 560 mK as a typical example. The upsurge of χ_{ac} at around 0.3 K suggests a magnetic phase transition. In order to clarify this transition, isothermal magnetization was measured to give an S-shaped hysteresis curve, which is characteristic of a ferromagnet. The transition temperature was estimated at 0.3 K by the intersection of two straight lines tangent to a χ_{ac} curve at paramagnetic and upsurge regions, as shown in Fig. 2(a), because S-shaped magnetization curves were obtained at higher temperatures than that affording the χ_{ac} peak.

TABLE 1 Curie temperatures (T_C), intra-sheet O···O distances (d), nearest inter-sheet O···O distances (d_{inter}), and proposed dimensionalities of dominant magnetic interactions for organic ferromagnets **1** - **8**.

Materials	T_C	d(O···O) / Å	d_{inter}(O···O) / Å	Dominant Magnetic Property[a)]
1	0.3	5.62, 6.15	11.89	2D
2	0.3	5.67, 6.21	13.57	2D
3	0.4	5.91, 5.95	10.86	2D
4	0.4	5.96, 6.09	13.40	2D
5	0.4	-[b)]	-[b)]	-[b)]
6	0.2	5.99, 8.00, 8.03	11.23	1D
7	0.2	5.97, 6.43	10.06	1D
8	0.25	5.33	-	1D

a) 1D = quasi-one-dimensional magnetic property; 2D = quasi-two-dimensional magnetic property. b) Not determined yet.

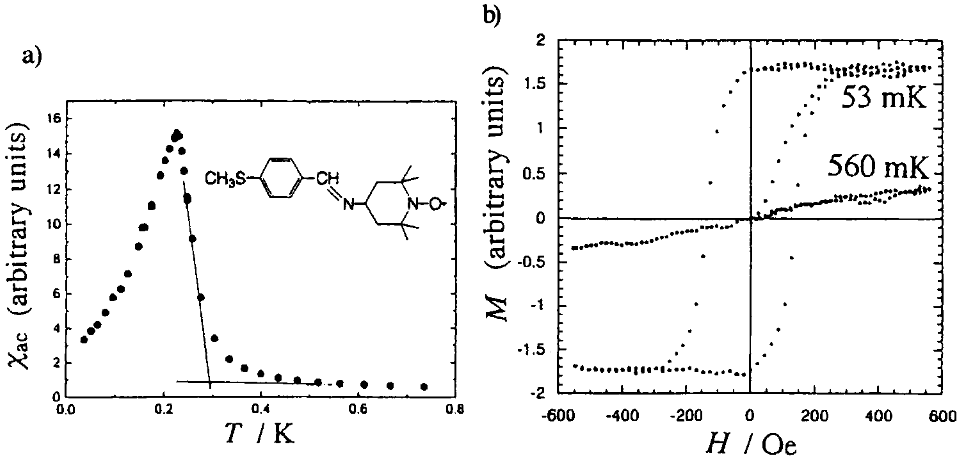


FIGURE 2 a) Temperature dependence of the ac magnetic susceptibility of **2** below 0.8 K, showing the ferromagnetic transition at about 0.3 K. b) The M-H curves of **2** measured at 53 mK (below T_C) and at 560 mK (above T_C)

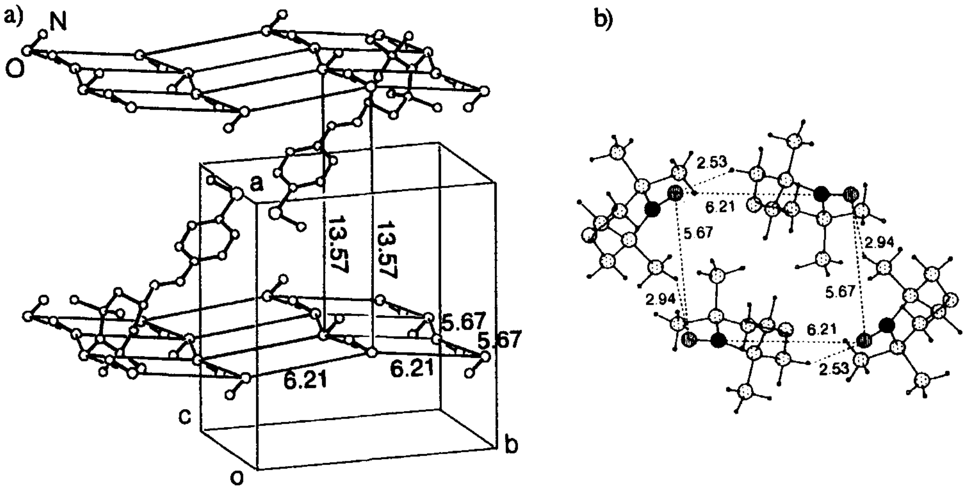


FIGURE 3 a) Arrangement of the N-O sites in the crystal of **2**. Two molecular structures are shown. Hydrogen atoms are omitted for the sake of clarity. b) Nearest four TEMPO moieties within a sheet. Selected atomic distances are shown in Å.

In all of the crystal structures of ferromagnets **1** - **4**, **6** and **7**, three characteristic features are found.[3c-g,6] (1) N-O radical sites are located on two-dimensional zigzag sheets. Intra-sheet O···O distances are about 6 Å, and inter-sheet O···O distances are longer than 10 Å. (2) Oxygen atoms of N-O radical sites are located near methyl and/or methylene hydrogens at β-positions of adjacent molecules with the intermolecular O···H distances close to the sum of the van der Waals radii (2.6 Å). (3) Aromatic rings gather together in the clearances of these zigzag sheets.

Figure 3 shows the arrangement of N-O radical sites of **2** as a typical example. Two molecular structures are drawn in order to envisage the crystal structure. The nearest O···O distances are 5.67 and 6.21 Å, along the *c* and *b* axes respectively. The nearest $\mathrm{O\cdots H_{methylene}}$ distance is 2.53 Å and $\mathrm{O\cdots H_{methyl}}$ distance is 2.94 Å along the *b* and *c* axes respectively. The intra-sheet ferromagnetic interaction of **2** can be interpreted in terms of the mechanism through intervening methyl and methylene groups (Fig. 1).

Detailed analysis of crystal structures of TEMPO-based ferromagnets clarified that the mechanism might be valid when an O···H distance was close to 2.6 Å and consequently an O···O distance was ca. 6 Å.[8] In the case of **6**,[8,10] the N-O radical sites are located on two-dimensional zigzag sheets and the shortest intra-sheet O···O distance is about 6 Å in one direction, but the second intra-sheet O···O distance is 8 Å. No methyl or methylene hydrogen atom close to an N-O site of an adjacent molecule was found in the second direction. Therefore, this material seems to have a quasi-one-dimensional magnetic correlation. The low dimensionality may be responsible for the lower T_C (0.2 K) than those of **1** - **4**.

We have developed TEMPO-based ferromagnets containing Ar-CH=N- groups. In order to obtain information of a role of Ar-CH=N- groups on magnetic interactions, we investigated magnetic properties of a partially saturated substrate, Ph-CH_2-NH-TEMPO (**7**).

The temperature dependence of ac magnetic susceptibility of **7** (Fig. 4(a)) shows an upsurge of χ_{ac} at 0.2 - 0.3 K. Its magnetization (Fig. 4(b)) measured at 30 mK exhibited an S-shaped curve which is characteristic of a ferromagnet. Slight curvatures at crossing regions of the abscissa are probably caused by a magnetic anisotropy of the polycrystalline specimen.

Figure 5 shows the arrangement of N-O radical sites in the crystal of **7**. Two molecular structures are drawn in order to envisage the crystal structure. The nearest O···O distances are 5.97 and 6.43 Å, which are close to 6 Å, along the *c* and *a* axes respectively. The nearest O···H_{methyl} distances are 2.54 and 3.53 Å along the *c* and *a* axes respectively. The ferromagnetic interaction along the *c* axis can be interpreted in terms of the spin-polarization mechanism (Fig. 1). However, the C···H distance of 3.53 Å seems to be somewhat larger than the sum of the van der Waals radii and the mechanism through β-hydrogen atoms hardly seems to be operative along the *a* axis. Thus, the magnetic property of **7** is supposed to be quasi-one-dimensional (Table 1).

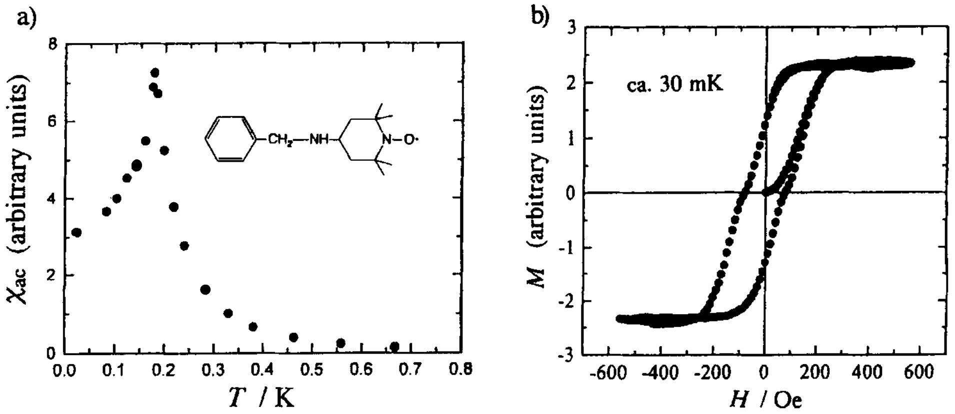


FIGURE 4 a) Temperature dependence of the ac magnetic susceptibility of **7** below 0.8 K, showing the ferromagnetic transition at about 0.3 K. b) The *M-H* curves of **7** measured at 30 mK (below T_C).

In view of the ferromagnetic transition of **7**, the presence of CH=N double bond is not a crucial factor for realization of ferromagnets, and consequently the spin distribution onto the aromatic group does not seem to contribute to the ferromagnetic interactions. This finding is consistent with the proposed mechanism (Fig. 1) in which only aliphatic groups in the TEMPO moiety work as ferromagnetic couplers. The aromatic groups can be regarded as packing-control substituents in crystals.

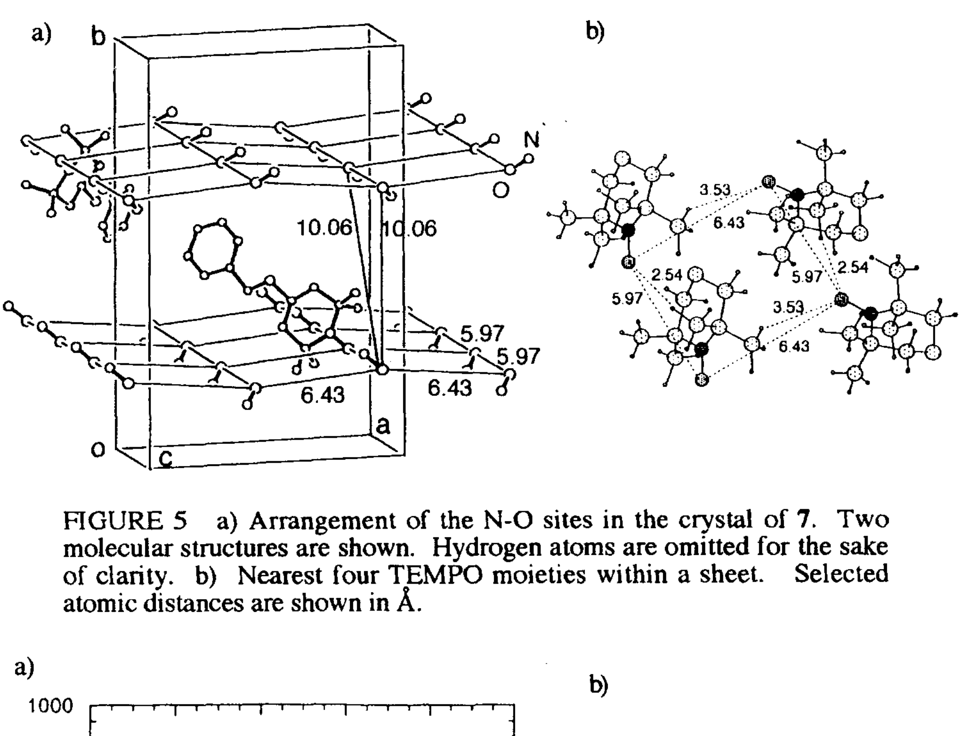


FIGURE 5 a) Arrangement of the N-O sites in the crystal of **7**. Two molecular structures are shown. Hydrogen atoms are omitted for the sake of clarity. b) Nearest four TEMPO moieties within a sheet. Selected atomic distances are shown in Å.

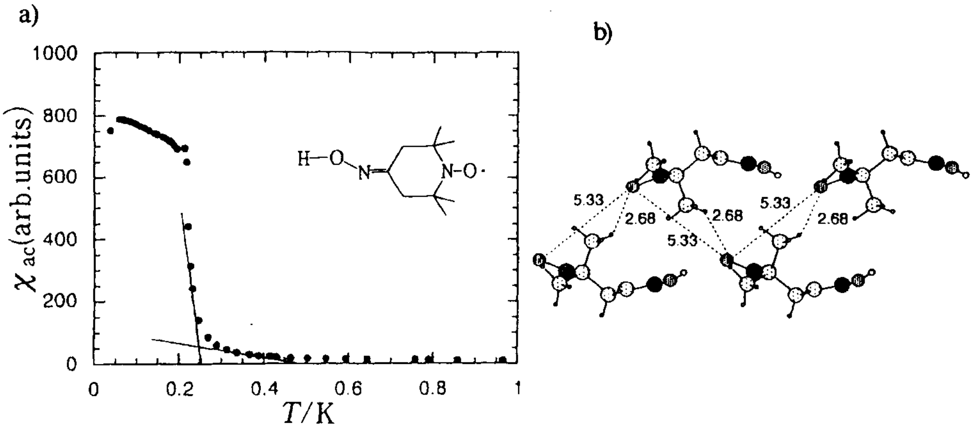
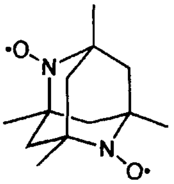


FIGURE 6 a) Temperature dependence of the ac magnetic susceptibility of **8**. b) Crystal structure of **8**.

Oxime **8** is an organic ferromagnet[3g,8] which does not possess aromatic group but hydroxyl group instead. The ferromagnetic transition was clearly observed in the measurements of ac magnetic susceptibility (Fig. 6(a)). Although **8**[15] has structural features different from those of **1** - **4**, **6**, and **7**, the mechanism (Fig. 1) also holds for **8** along one direction in the crystal because the crystal of **8** possesses a rather short intermolecular $H_{methyl}\cdots O$ distance as shown in Fig. 6(b).

The intra-chain and/or intra-sheet ferromagnetic interactions (Fig. 1) are dominant in total magnetism in TEMPO-based ferromagnets because they are strongest interactions through the nearest pathway between the N-O spin centers. Ferromagnetic phase transition requires that the inter-chain and/or inter-sheet interactions must also be ferromagnetic, probably due to dipole-dipole interactions. However, details have not been clarified yet. The proposed magnetic dimensionality based on the mechanism (Fig. 1) seems to be correlated with T_C: T_C is higher when the higher-dimensional magnetic network is constructed. The organic ferromagnet which enjoys the highest T_C (1.48 K) is tetramethyldiazaadamantane-*N*,*N*'-dioxyl (**15**).[3b] The crystal of **15** is revealed to have a three-dimensional magnetic network according to our proposed mechanism.[8]



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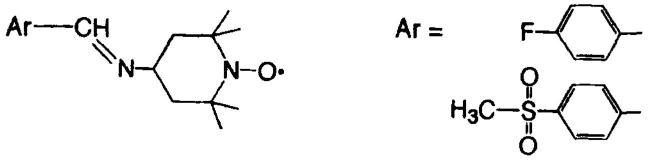
The crystal structures of antiferro- and paramagnetic radicals should be noted. The presence of dominant antiferromagnetic interactions in the crystal of **16** was indicated by the negative Weiss temperature (θ) of -2.6 K.[10] The nearest intermolecular O···O distance was found to be 5.47 Å,[10] which is relatively short in the TEMPO-based materials; the typical O···O distances are 5.6 - 6.2 Å for ferromagnetic TEMPO-based materials.[8,10] The antiferromagnetic interaction in the crystal of **16** may be explained in terms of a direct SOMO-SOMO overlap due to the short O···O distance. Although the β-hydrogen mechanism (Fig. 1) also seems to work in this crystal, the antiferromagnetic interaction should be dominant.

The crystal structure of antiferromagnetic phase of **5** (θ = -0.23 K) was determined.[16,17] The nearest intermolecular O···O distance was 5.47 Å, which is relatively short. The antiferromagnetic interaction of the nearest neighboring molecules can be interpreted similarly to that of **16**.

The crystal of **17** was found to be almost paramagnetic, indicated by the Weiss constant of +0.06 K.[6] The crystal structure analysis of **17** revealed the absence of bridging β-hydrogen atoms; the shortest intermolecular O···H distance was 3.83 Å.[17] The shortest O···O distance was 6.20 Å. We could find no significant pathway for ferromagnetic or antiferromagnetic interaction. Thus, the paramagnetic feature of **17** is rationalized by the crystal structure.



(16)

(17)

Zero-Field μSR of 4-(p-$ClC_6H_4CH=N$)-TEMPO (3)

In order to obtain a decisive evidence for spontaneous magnetization below T_C, we measured zero-field μSR of the crystals of **3**. The μSR technique was successfully used for the characterization of the ferromagnetic phase of β-p-NPNN.[18] However, there is no report on μSR of TEMPO-based magnetic materials at very low temperatures, while those of organic radicals containing the nitronyl nitroxide group have widely been investigated.[19] The μSR measurements were performed at KEK, Meson Science Laboratory, The University of Tokyo. The μ^+ beam was injected perpendicular to the a axis of the aligned single crystals of **3**.[3f]

Figure 7 shows several typical μSR time spectra. Above the T_C, the slowly relaxing signal without oscillation was obtained, which corresponds to a paramagnetic phase. Near the T_C (275 and 260 mK), the signal consists of the superimposition of slowly and fast relaxing signals. Below the T_C, the appearance of oscillation clearly indicates the presence of an appreciable internal magnetic field due to a spontaneous magnetization. With decreasing temperature the oscillation frequency increased, indicating that the spontaneous magnetization increased. However, the oscillation became ambiguous at lower temperatures (30 mK).

In the presence of an internal magnetic field (B_{int}), the muon spin undergoes Larmor precession with a frequency $\nu_\mu = (\gamma_\mu/2\pi)B_{int}$, where $\gamma_\mu/2\pi$ is the muon gyromagnetic ratio. The internal magnetic field was deduced from the oscillation frequency by the relation that 1 MHz corresponds to an internal magnetic field of 75 G. The feature of the temperature dependence of the internal magnetic field (Fig. 8) is similar to those of ferromagnets and cant-magnets containing a nitronyl nitroxide group,[17,18] although B_{int} in **3** is somewhat larger than those in the latter materials. The

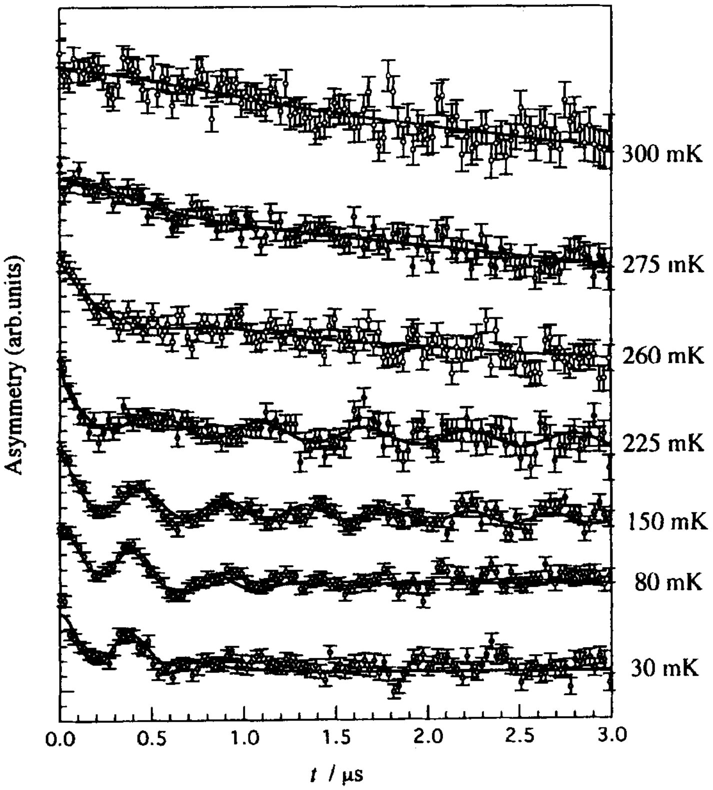


FIGURE 7 Zero-field muon spin rotation of **3**.

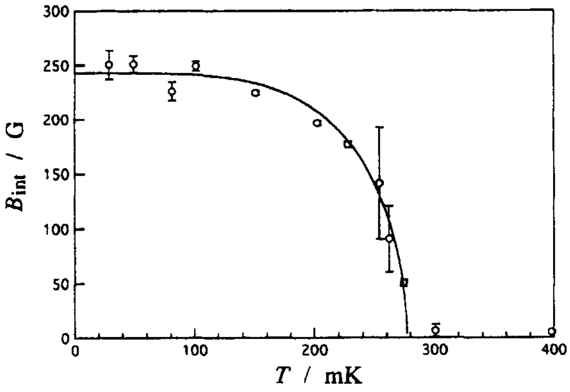


FIGURE 8 Temperature dependence of the internal magnetic field of **3**.

data were fit to the solid curve of $M(T) \propto [1 - (T/T_C)^{\alpha}]^{\beta}$ with $\alpha = 3.2$ (± 1.3) and $\beta =$ 0.46 (± 0.15). The theoretical Ising 2- and 3-dimensional models gave $\beta = 0.125$ and 0.325 or 0.313, respectively, and Heisenberg 3-dimensional model gave $\beta = 0.364$ or 0.38.[20] Therefore, the experimental results are consistent with bulk ferromagnetism due to 3-dimensional ordering within the experimental errors.

A field of 10 Oe was applied along the *a* axis of the crystal of **3**, *i.e.* perpendicular to the direction of the initial muon polarization, with lowering the temperature from 400 to 200 mK, and it was then removed. The presence of the remnant magnetization was confirmed by μSR measurements; B_{int} was ca. 200 G at 200 mK. The remnant magnetization decreased on heating the sample, and completely disappeared at 280 mK. A similar analysis of the temperature dependence of the oscillation frequency gave almost the same results as above.

The transition temperature (T_C) was determined to be 0.28 K from the μSR experiments, which is somewhat lower than that determined by the χ_{ac} measurements (Table 1). One of possible explanations of this difference in T_C is as follows. The divergence of χ_{ac} may be attributed to the two-dimensional magnetic ordering within a sheet structure of the N-O arrangement.[3f] On the other hand, the N-O spins are three-dimensionally ordered below T_C which is defined by the appearance of B_{int} evidenced by the μSR measurements.

Organic Metamagnets

Although intermolecular ferromagnetic interaction was confirmed by the SQUID measurements above 1.8 K, the magnetic measurements below 1.8 K clarified that at least six materials exhibited antiferromagnetic transitions, and that metamagnetic behavior was observed for them by applying relatively weak magnetic fields.[6] These facts show that the strongest intermolecular magnetic interaction is ferromagnetic, but ferromagnetically coupled spins antiferromagnetically interact in these materials. Table 2 summarizes TEMPO derivatives exhibiting metamagnetic behavior, Néel temperatures (T_N) defined by the temperature affording χ_{ac} peak, magnetic fields of spin-flip transitions (H_C), and temperatures measured for spin-flip transitions (T).

As a typical example of the metamagnetic behavior, Fig. 9(a) shows the temperature dependence of the ac magnetic susceptibility (χ_{ac}) of **13**. The χ_{ac} measurements revealed that some magnetic phase transition occurred at ca. 0.1 K, as evidenced by the upsurge and peak of χ_{ac}. The decrease of the χ_{ac} below 0.1 K can be understood by either of three origins: demagnetization effects of a ferromagnet, formation of magnetic domain structures, or an antiferromagnetic transition.

TABLE 2 4-Arylmethyleneamino-TEMPO derivatives exhibiting metamagnetic transitions.

Aryl group	T_N a) / K	H_C b) / Oe	T c) / K
2-naphthyl (**9**)	0.12	180	0.04
2-pyridyl (**10**)	0.26	10 - 20	0.05
4-pyridyl (**11**)	0.12	110	0.09
2,6-dichlorophenyl (**12**)	0.20	20	0.04
3,5-dichlorophenyl (**13**)	0.12	20	0.05
3,4-dichlorophenyl (**14**)	0.10	20	0.04

a) Néel temperatures. b) Critical magnetic fields inducing spin-flip transitions. c) Temperatures for the measurements of spin-flip transitions.

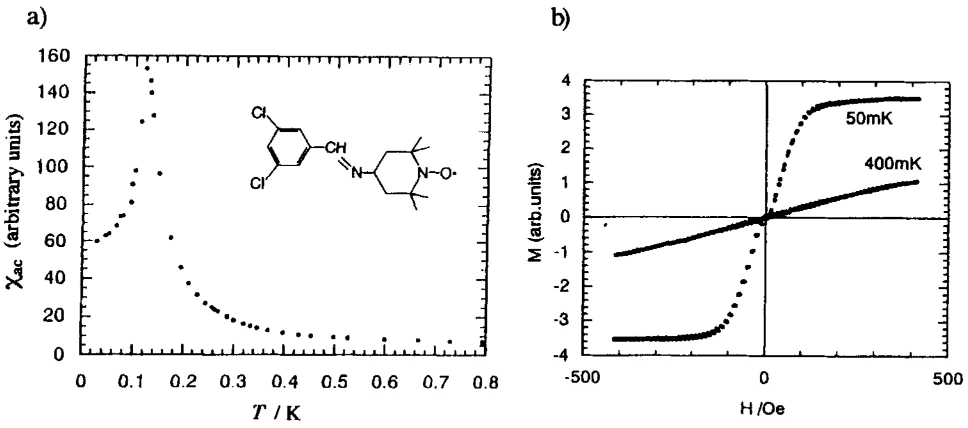


FIGURE 9 a) Temperature dependence of the ac magnetic susceptibility of **13**. b) *M-H* curves of **13** measured at 50 mK (below T_N) and at 400 mK (above T_N).

The measurement of isothermal magnetization below 0.1 K gave double S-shaped curves (50 mK, Fig. 9(b)). With increasing the magnetic fields from zero to ca. 20 Oe at 50 mK, the magnetization increased only slightly. However, it increased abruptly at ca. 20 Oe, and was saturated around at ca. 100 Oe. These experimental results verify the spin-flip transition from an antiferromagnetic phase to a ferromagnetic phase by applying the magnetic field of ca. 20 Oe at 50 mK. Therefore, the χ_{ac} peak at 0.1 K can be interpreted as the antiferromagnetic transition.

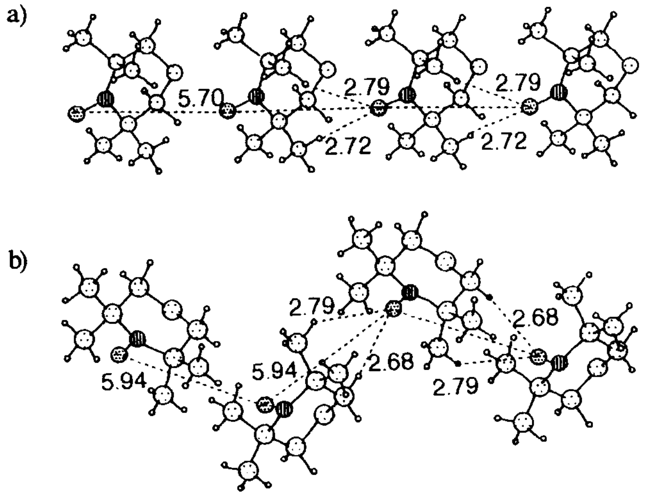
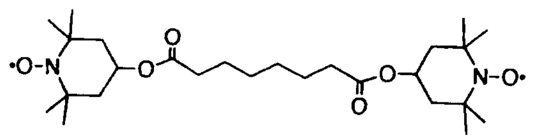


FIGURE 10 Nearest neighboring TEMPO moieties of **9** (a) and **13** (b). Selected atomic distances are shown in Å.

Similar metamagnetic behavior was also observed for the materials summarized in Table 2. The relatively weak H_C values (lower than 200 Oe) can be understood as the weak antiferromagnetic interactions of these TEMPO-based materials. Similar metamagnetic behavior has also been reported for other TEMPO-based materials.[21,22]

The positive Weiss constants of **9** - **14**, obtained by the SQUID measurements above 1.8 K, indicated that ferromagnetic interactions were dominant in these materials. In the crystal of **9**, the ferromagnetic pathway through β-hydrogen atoms in one direction is shown in Fig. 10(a).[9] The crystal structures of **13**[10] similarly possessed the ferromagnetic channel through β-hydrogen atoms in one direction as shown in Fig. 10(b). Therefore, the weak antiferromagnetic interaction may be attributed to the other directions in the crystals of **9** and **13**. The ferromagnetic pathway of a metamagnet, bis(2,2,6,6-tetramethylpiperidin-1-yloxyl-4-yl) 1,6-hexanedicarboxylate (**18**)[23] can also be analyzed by our proposed mechanism.[8]



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SUMMARY

SQUID measurements revealed that 52 radicals exhibited intermolecular ferromagnetic interactions in a series of TEMPO-based materials. Among them, eight TEMPO-based ferromagnets are reported. The ferromagnetic transition of **3** was confirmed by μSR measurements. Metamagnetic behavior was observed for six radicals.

On the basis of the crystal structures of the TEMPO-based ferro- and metamagnets, a mechanism of intermolecular ferromagnetic coupling was proposed. The proposed mechanism can be applied to the nearest neighbor TEMPO moieties in all of the ferromagnets and metamagnets investigated here as well as those exploited by other groups. They have dominant ferromagnetic interactions through β-hydrogen atoms, accompanied by secondary weak magnetic interactions along other directions which is responsible for deciding whether the material is a ferromagnet or metamagnet.

Generally, there are many interactive pathways in organic magnetic materials. It is very difficult to discern between the pathway of ferromagnetic coupling and that of antiferromagnetic coupling. In most organic radical materials, ferromagnetic interaction is buried in strong antiferromagnetic interactions caused by, for example, SOMO-SOMO overlaps. The ferromagnetic interaction can be observed only when other antiferromagnetic coupling is negligibly small, as often found in TEMPO and aliphatic nitroxide radicals. We can suggest that β-hydrogen mechanism always causes ferromagnetic interaction under such suitable conditions that the intermolecular orbital overlaps between $1s(H_\beta)$ and $\pi^*(NO)$ orbitals are present.

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