Organic Radicals Exhibiting Intermolecular Ferromagnetic Interactions with High Probability: 4-Arylmethyleneamino-2,2,6,6-tetramethylpiperidin-1-yloxyls and Related Compounds

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A series of 4-arylmethyleneamino-2,2,6,6-tetramethylpiperidin-1-yloxyls (4-arylmethyleneamino-TEMPO) and related compounds were synthesized, and their magnetic susceptibilities were measured by a SQUID magnetometer in the temperature range of 1.8—100 K. Of 165 radicals investigated, 52 kinds of radicals exhibited intermolecular ferromagnetic interactions. These were confirmed by the increase of effective magnetic moments in low-temperature regions. Positive Weiss temperatures (θ), ranging from +0.03 to +0.75 K, were found for these materials. Over 100 kinds of radicals exhibited antiferromagnetic interactions with θ ranging from −0.01 to −24 K. The surprisingly high probability of finding organic radicals with intermolecular ferromagnetic interaction may be understood by the characteristic molecular arrangements in the crystals. An oxygen atom of an NO radical site of a piperidin-1-yloxyl moiety is apt to locate near methyl- and/or methylene-hydrogens of β-positions of the adjacent molecules, and the resultant spin polarization gives rise to parallel spin alignments of nearest NO sites in the crystals. 4-(4-Iodophenylmethyleneamino)-TEMPO exhibited a bulk ferromagnetic transition at 0.4 K. Six radicals exhibited metamagnetic transitions at magnetic fields lower than 200 Oe below 0.1 K.

Organic radicals exhibiting intermolecular ferromagnetic interactions have been sought for several decades in order to discover organic ferromagnets.[1] At the time of 1991, only five organic radicals were known to show intermolecular ferromagnetic interactions.[2] However, much progress has been made in these few years, and the number of organic-radical ferromagnets has now amounted to eighteen kinds,[3] to our knowledge, since the discovery of the first organic-radical ferromagnet.[3a,3b] The reason why only a few ferromagnetic organic radicals have been found over a long period of time is that antiferromagnetic interaction is more favorable for interacting radicals, due to the orbital overlap of radical centers. In spite of these facts, several strategies for obtaining ferromagnetic organic materials have been presented.[4] Stimulated by the strategy of organic ferromagnets using charge-transfer complexes presented by Yamaguchi et al.,[4j] one of the authors (T. N.)[5a] and other groups[5b—e] have attempted syntheses of organic ferromagnetic materials containing donor or acceptor molecules with a radical substituent: for example, tetrathiafulvalenylmethyleneamino-TEMPO; TEMPO stands for 2,2,6,6-tetramethylpiperidin-1-yloxyl. Soon after that, we found that the organic radical crystals of 4-(2-naphthylmethyleneamino)- and 4-benzylideneamino-TEMPO's showed intermolecular ferromagnetic interactions,[6] and have reported that several TEMPO derivatives exhibit bulk ferromagnetic transitions below 0.5 K.[3d—h] A possible mechanism of ferromagnetic interaction was presented, based on the crystallographic data of these ferromagnets.[7]

In the course of these studies, we have found that a series of 4-arylmethyleneamino-TEMPO's and related compounds have high probabilities of giving radicals with intermolecular ferromagnetic interactions. Of 165 radicals investigated, 52 kinds of radicals exhibited intermolecular ferromagnetic interactions, as confirmed by the increase of effective magnetic moments in low-temperature regions. This paper reports magnetic interactions of a variety of TEMPO derivatives, and explains why these materials exhibit intermolecular ferromagnetic interactions with surprisingly high probabilities. This paper also reports a bulk ferromagnetic transition of 4-(4-iodophenylmethyleneamino)-TEMPO and metamagnetic behavior of several 4-arylmethyleneamino-TEMPO's.

Experimental

Materials. Most of the materials for magnetic measurements in this study were synthesized as described below; as to the material numbers, see Figs. 2 and 3. The materials **8**, **31**, **38**, **59**, **61**, **75**, **76**, **79**, **89**, **131**, **140**, **143**, and **151** possess two TEMPO moieties, and

47, **50**, and **103** possess three TEMPO moieties in a molecule. All of these materials were obtained in moderate yields and characterized by means of mass spectroscopy. The samples used in magnetic measurements were recrystallized from ethanol unless otherwise stated. The purities of the samples were confirmed by melting points typically within 2 °C. Commercially available samples (**149**, **150**, **152**, **156**, **158**, **159**, **162**—**165**) were used without further purification.

Synthesis. **(a) 4-Arylmethyleneamino-TEMPO's.** All of 4-arylmethyleneamino-TEMPO's (see Figs. 2a and 3a were synthesized by the reactions of the corresponding arenecarbaldehydes with 4-amino-TEMPO by procedures described before.[6] Several materials of this type are known in the literature.[8] Most of the arenecarbaldehydes were commercially available, but some aldehydes were synthesized by reported methods.[9] 4-(Methylsulfinyl)- and 4- (methylsulfonyl)benzaldehydes were prepared by the oxidation of 4-(methylthio)benzaldehyde ethylene acetal, followed by the deprotection of ethylene acetal by hydrolysis with aqueous $HClO_4$. 4-(Methylseleno)benzaldehyde was obtained by a lithiation of 4-bromobenzaldehyde ethylene acetal, followed by successive reactions with selenium and iodomethane, and finally by the hydrolysis with aqueous $HClO_4$.

(b) 4-Arylmethylamino-TEMPO's (45, 147, 148). They were synthesized by the reductive amination of 4-oxo-TEMPO with the corresponding benzylamines in the presence of $Na[BH_3(CN)]$, according to the reported method.[10]

(c) 4-R–N=TEMPO (46, 48, 49, 51, 52, 136—144) and 4-R–NHN=TEMPO (125—135). Materials expressed as 4-R–N=TEMPO and 4-R–NHN=TEMPO were obtained by the condensation of 4-oxo-TEMPO with the corresponding hydrazines and hydroxylamines, respectively.[11] 4-Hydroxyimino-TEMPO-OD (**49**) was obtained by recrystallization of **48** from deuterated methanol. The deuterium content of **49** was 88%, as determined by means of an EI mass spectroscope.

(d) Amides and Esters of TEMPO. Materials possessing CONH and CO_2 linkages between aryl and TEMPO moieties (**50**, **146**, **151**, **153**, **161**) were obtained by the reactions of the corresponding carbonyl chlorides with 4-amino- and 4-hydroxy-TEMPO, respectively, in the presence of pyridine. A phthalimido derivative (**160**) was obtained by use of phthalic anhydride instead of chloride.[12]

(e) Miscellaneous. Material **47** was obtained from 4-amino-TEMPO and an aqueous solution of formaldehyde according to the reported method.[13] Material **154** was prepared by cyanoamination of 4-oxo-TEMPO with sodium cyanide and ammonium chloride.[14] Dicyanomethylene compound **155** was obtained by Knoevenagel reaction of 4-oxo-TEMPO and malononitrile in the presence of molpholine. 4-Methoxy-TEMPO (**157**) was obtained by methylation of 4-hydroxy-TEMPO by use of sodium hydride and methyl iodide.

Magnetic Measurements. The magnetic susceptibility in the temperature range of 1.8—100 K was measured by a SQUID magnetometer (MPMS-7, Quantum Design). The diamagnetic contribution was estimated by Pascal's atomic constants. The AC magnetic susceptibility was measured by applying a magnetic field of ca. 40 mOe (127 Hz), and magnetization curves were obtained by an integration technique in which the differences of voltages induced on pickup and reference coils by a sweeping magnetic field is integrated over time by a computer, as described elsewhere;[3b] both of them were measured down to 40 mK by using a ^3He–^4He dilution refrigerator.

Results and Discussion

Temperature Dependence of Magnetic Susceptibilities. The temperature dependence of molar magnetic susceptibilities (χ_M) of 4-arylmethyleneamino-TEMPO's and related compounds was measured in the temperature range of 1.8—100 K. The observed data were analyzed on the basis of the equation:

$$\chi_M = \frac{Ng^2\mu_B^2 S(S+1)}{3k(T-\theta)} = \frac{N\mu_B^2}{k(T-\theta)}. \qquad (1)$$

The last equation is derived by setting g=2 and S=1/2. Here, the symbols have their usual meanings. The effective magnetic moment ($\mu_{\rm eff}$) is defined by

$$\frac{\mu_{\rm eff}}{\mu_B} = \frac{1}{\mu_B}\left(\frac{3kT\chi_M}{N}\right)^{1/2} = \left(\frac{3T}{T-\theta}\right)^{1/2} \qquad (2)$$

Figure 1 shows temperature dependence of $\mu_{\rm eff}/\mu_B$ values of 4-(4-iodophenymethyleneamino)- (**4**), 4-(3,4-dichlo-

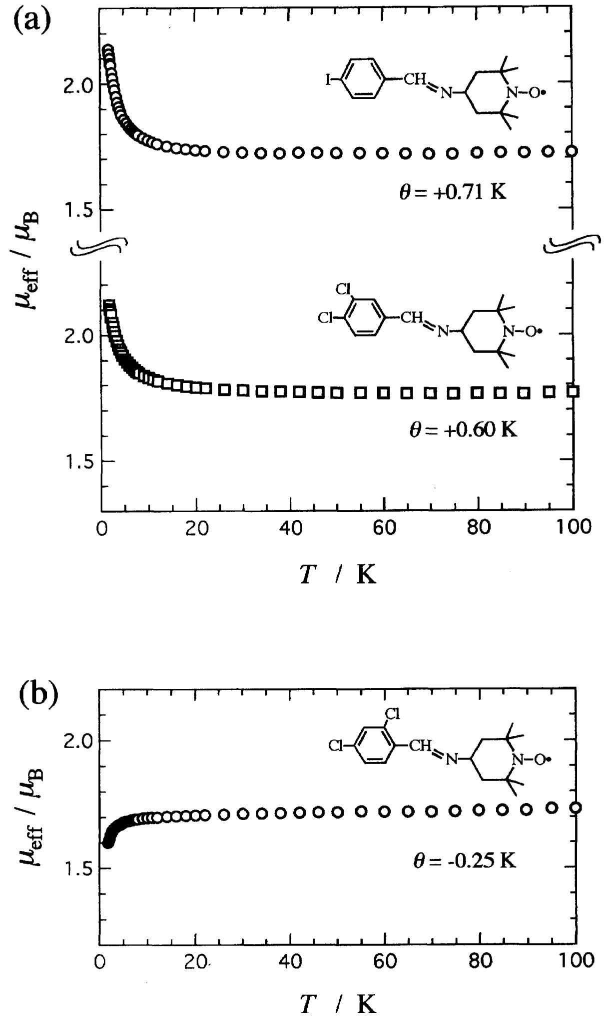
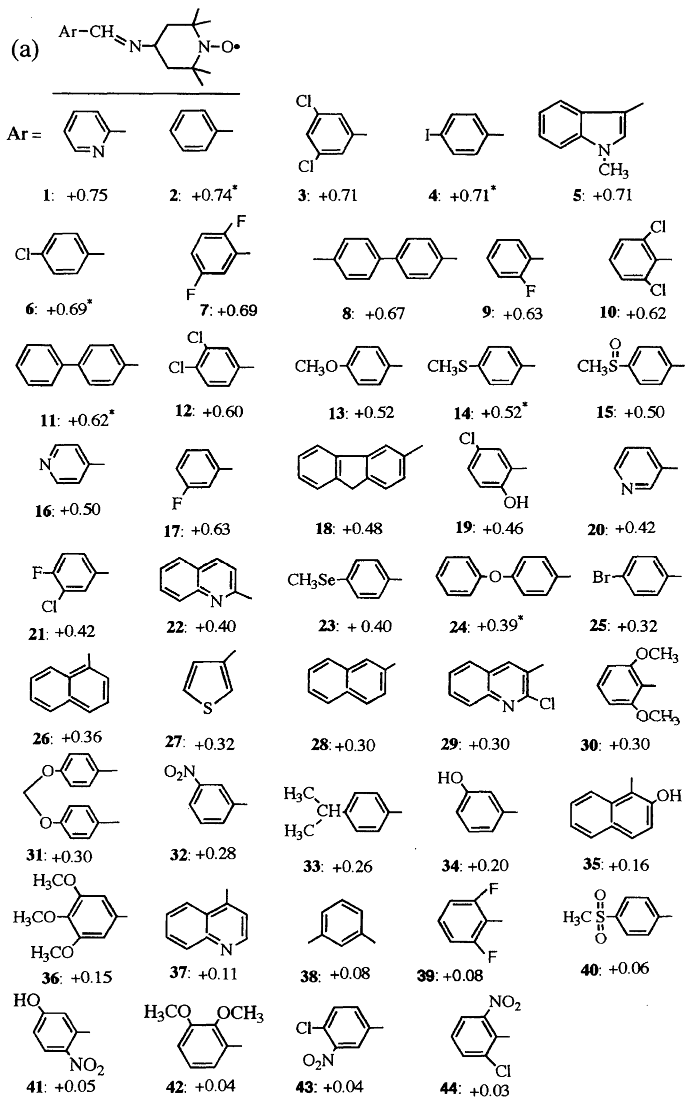


Fig. 1. Temperature dependence of effective magnetic moments. (a) 4-(4-Iodobenzylideneamino)- and 4-(3,4-dichlorobenzylideneamino)-TEMPO's (**4** and **12**). (b) 4-(2,4-Dichlorobenzylideneamino)-TEMPO (**72**).



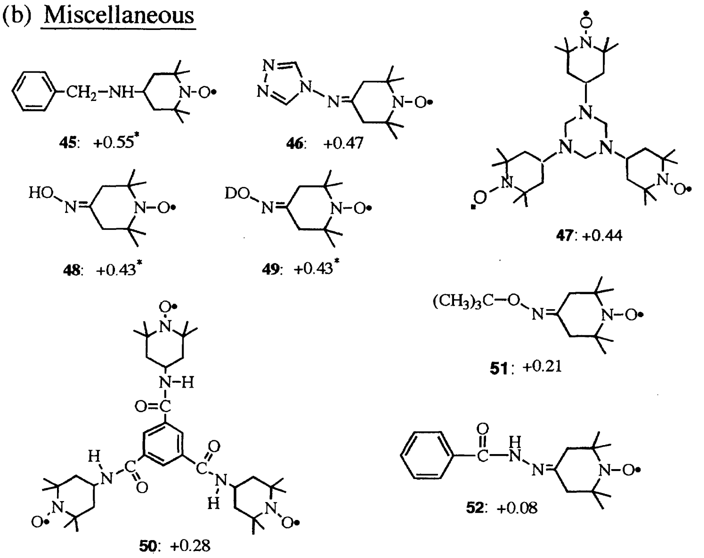
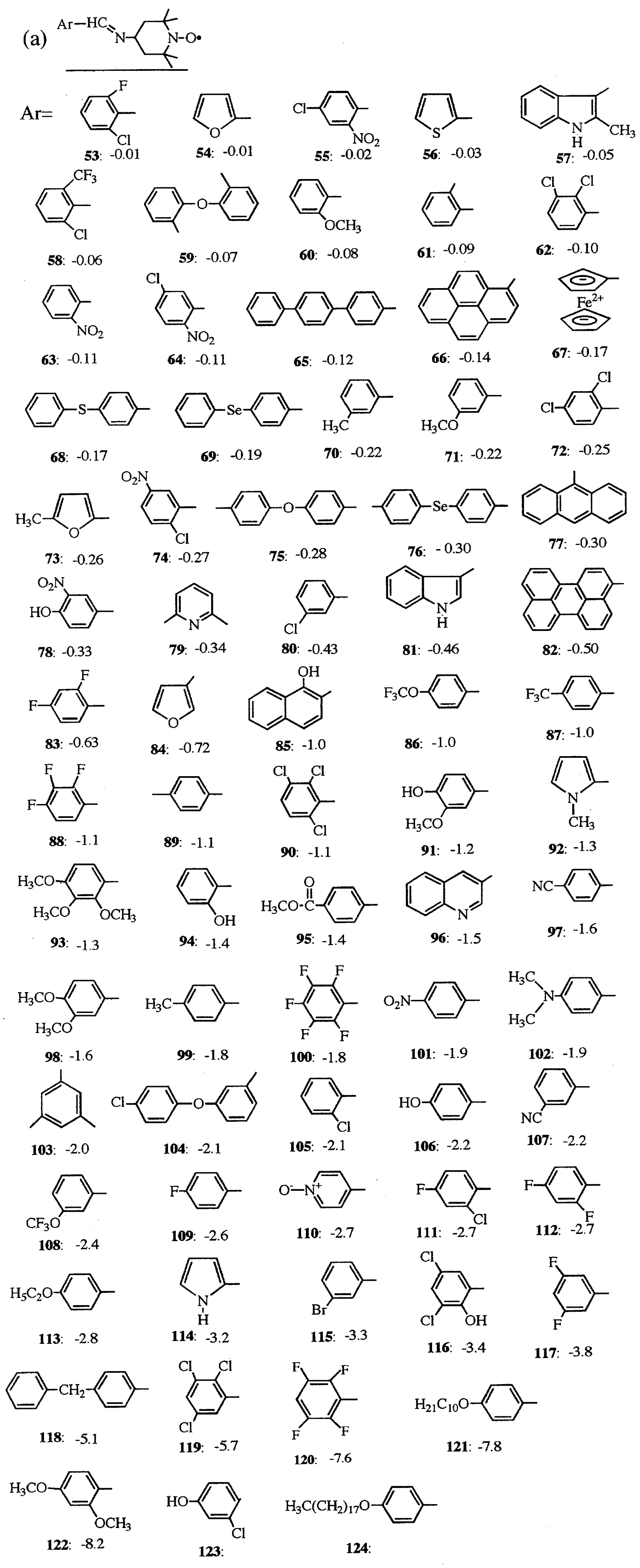


Fig. 2. Summary of TEMPO derivatives exhibiting intermolecular ferromagnetic interactions, and their Weiss temperatures in K. (a) 4-Arylmethyleneamino-TEMPO's. (b) Miscellaneous compounds. Only aryl portions of materials are shown for the sake of simplicity in (a). Asterisks are attached to Weiss temperatures of TEMPO-based materials which exhibit bulk ferromagnetic transitions.



53: -0.01 **54**: -0.01 **55**: -0.02 **56**: -0.03 **57**: -0.05

58: -0.06 **59**: -0.07 **60**: -0.08 **61**: -0.09 **62**: -0.10

63: -0.11 **64**: -0.11 **65**: -0.12 **66**: -0.14 **67**: -0.17

68: -0.17 **69**: -0.19 **70**: -0.22 **71**: -0.22 **72**: -0.25

73: -0.26 **74**: -0.27 **75**: -0.28 **76**: - 0.30 **77**: -0.30

78: -0.33 **79**: -0.34 **80**: -0.43 **81**: -0.46 **82**: -0.50

83: -0.63 **84**: -0.72 **85**: -1.0 **86**: -1.0 **87**: -1.0

88: -1.1 **89**: -1.1 **90**: -1.1 **91**: -1.2 **92**: -1.3

93: -1.3 **94**: -1.4 **95**: -1.4 **96**: -1.5 **97**: -1.6

98: -1.6 **99**: -1.8 **100**: -1.8 **101**: -1.9 **102**: -1.9

103: -2.0 **104**: -2.1 **105**: -2.1 **106**: -2.2 **107**: -2.2

108: -2.4 **109**: -2.6 **110**: -2.7 **111**: -2.7 **112**: -2.7

113: -2.8 **114**: -3.2 **115**: -3.3 **116**: -3.4 **117**: -3.8

118: -5.1 **119**: -5.7 **120**: -7.6 **121**: -7.8

122: -8.2 **123**: **124**:
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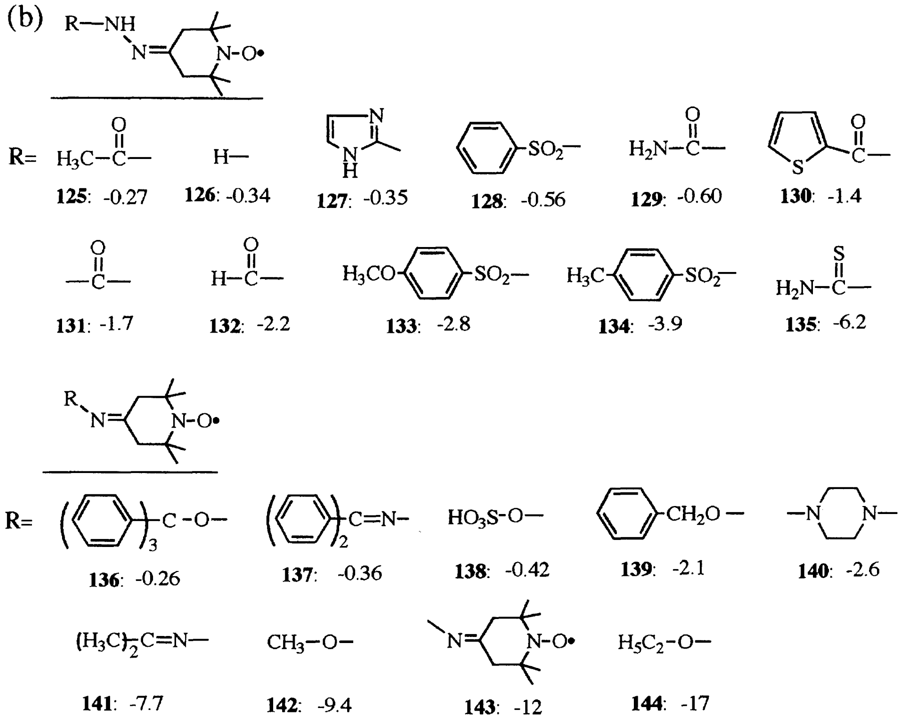


(c) Miscellaneous

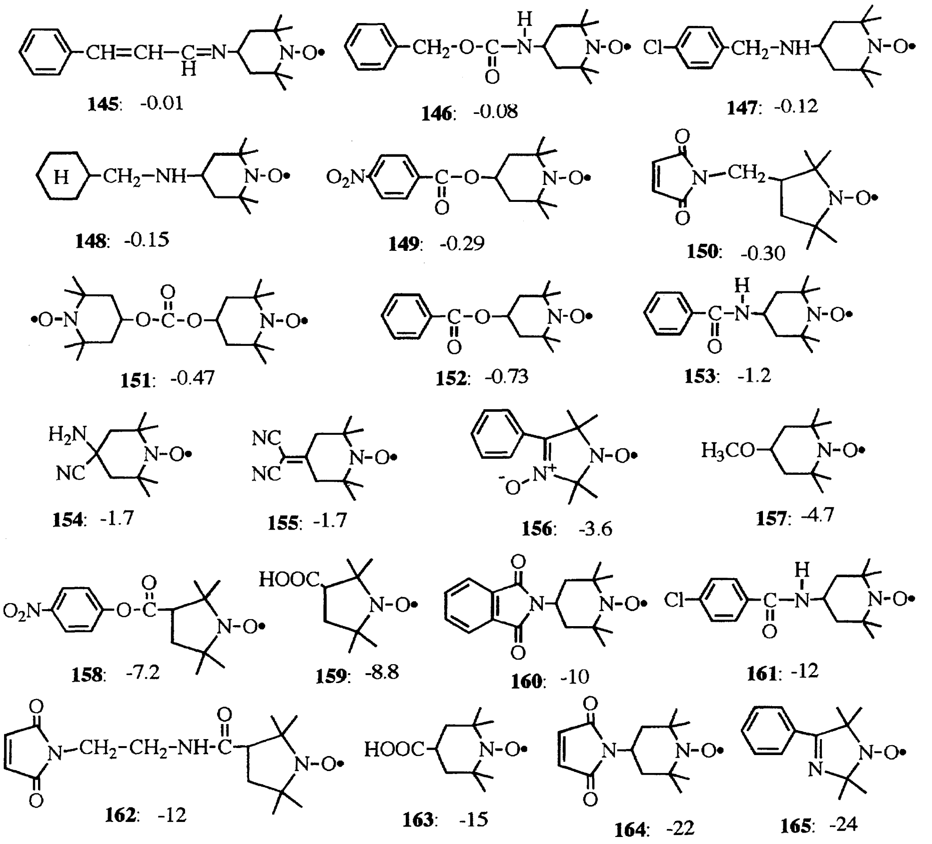


Fig. 3. Summary of TEMPO derivatives exhibiting intermolecular antiferromagnetic interactions, and their Weiss temperatures in K. (a) 4-Arylmethyleneamino-TEMPO's. (b) Compounds expressed as 4-RNHN=and 4-RN=TEMPO's. (c) Miscellaneous compounds. Only Aryl and R portions of materials are shown in (a) and (b), respectively, for the sake of simplicity.

robenzylideneamino)- (**12**), and 4-(2,4-dichlorobenzylideneamino)-TEMPO (**72**) as typical examples. Equation 2 could reproduce fairly well the observed temperature dependence. The θ-values estimated by the best fit of the data below 20 K were +0.71 and +0.60 K for **4** and **12**, respectively, indicating that **4** and **12** have intermolecular ferromagnetic interactions. On the other hand, the θ-value of **72** was calculated to be −0.25 K, indicating the presence of the intermolecular antiferromagnetic interaction. The magnetic behavior of **12** and **72** indicates that the difference of substituent positions at a phenyl group sometimes induces a profound effect on the intermolecular magnetic interactions. The estimated θ-values of 4-arylmethyleneamino-TEMPO's and related compounds are summarized in Figs. 2 and 3; only aryl portions of the materials in the cases of 4-arylmethyleneamino-TEMPO's are shown for the sake of simplicity, and 4-arylmethyleneamino-TEMPO's and other types of TEMPO derivatives are shown separately in these figures. For the materials expressed as 4-RNHN=TEMPO (**125—135**) and 4-RN=TEMPO (**136—144**), only R portions are shown in Fig. 3. Figures 2 and 3 summarize materials possessing ferromagnetic and antiferromagnetic interactions, respectively. Asterisks are attached to Weiss temperatures of TEMPO derivatives (**2**, **4**, **6**, **11**, **14**, **24**, **45**, **48**, and **49**) which exhibit bulk ferromagnetic transitions in Fig. 2.

Figure 2 shows materials possessing ferromagnetic interactions with θ ranging from +0.03 to +0.75 K, and Fig. 3 shows those possessing antiferromagnetic interactions with θ from −0.01 to −24 K, for the TEMPO-based materials. It should be noted that the number of materials possessing ferromagnetic interaction amounts to 52, which is a surprisingly large number for organic radicals. Therefore, the general belief that organic radicals rarely show intermolecular ferromagnetic interactions must be abandoned due to these experimental results.

In Fig. 3, Weiss temperatures are not shown for **123** and **124**, because their magnetic behavior can not be analyzed by Eq.2 or a dimer model;15) they showed intermolecular antiferromagnetic interactions in view of the decrease of μ_{eff} in the low temperature regions. All of the pyrrolidin-1-yloxyl and 2,5-dihydroimidazol-1-yloxyl derivatives (**150**, **156**, **158**, **159**, **162**, and **165**) showed intermolecular antiferromagnetic interactions. UHF/MINDO calculations revealed that an intramolecular spin-polarization does not transmit to phenyl ring in **2**.7) Morover, exchange and dipole–dipole interactions between NO radical-sites are estimated to be lower than 0.01 K for the radical pair locating at a longer distance than 4.6 Å.7) Therefore, the ferromagnetic ($\theta > +0.1$ K) and antiferromagnetic ($\theta < -0.1$ K) interactions of **8**, **31**, **47**, **50**, **59**, **75**, **76**, **79**, **89**, **103**, **131**, **140**, **143**, and **151** are assumed to be caused not by intramolecular interactions but by intermolecular ones; all of these materials possess two or three TEMPO moieties in molecules, and intramolecular distances between radical sites are longer than 4.6 Å. However, we can not conclude whether such a weak antiferromagnetic interaction as **61** (θ=−0.09 K) should be attributed to an intramolecular interaction or to an intermolecular one. In view of the intermolecular antiferromagnetic interaction of **103** (θ=−2.0 K) possessing TEMPO moieties at 1-, 3-, and 5-positions of phenyl ring, the weak ferromagnetic interaction of **38** (θ=+0.08 K) possessing TEMPO moieties at *meta*-positions of phenyl ring seems to be caused by an intermolecular interaction, not by an intramolecular one.

Comments Concerning High Probability of Intermolecular Ferromagnetic Interactions. We described above that many 4-arylmethyleneamino-TEMPO's show intermolecular ferromagnetic interactions, some of which lead to bulk ferromagnetic transitions.3d—h,5—7) The surprisingly high probability of finding ferromagnetic organic radicals in these TEMPO derivatives may be caused by a common reason. We have reported that organic ferromagnets of several TEMPO derivatives have a common molecular arrangement in crystals;3d—h,7,16) an oxygen atom of an NO-radical site of a TEMPO moiety always locates near methyl- and/or methylene-hydrogens at β-positions of NO in the TEMPO moieties of adjacent molecules. A similar geometrical situation was also found in one direction in the crystal of organic metamagnet **28**.17) A positive spin density on the NO-site induces negative spin density on the β-hydrogen atoms due to an intramolecular spin-polarization, which in turn induces positive spin densities on the NO sites of the adjacent molecules caused by the orbital overlap between 1s(H) and π^*(N–O) orbitals, $\mathrm{ON}(\uparrow)\text{–}\mathrm{C}_{\alpha}(\downarrow)\text{–}\mathrm{C}_{\beta}(\uparrow)\text{–}\mathrm{H}_{\beta}(\downarrow)\cdots(\uparrow)\mathrm{O}\text{-}\mathrm{N}\langle$, thereby leading to parallel spin-alignments of NO sites in crystals. This mechanism of ferromagnetic interaction is illustrated schematically in Fig. 4. We believe that TEMPO derivatives tend to form these characteristic molecular arrangements in crystals and this is the reason for the high probability of finding ferromagnetic radicals in TEMPO derivatives. Similar ferromagnetic interaction via a CH···ON and an OH···ON bridges was also reported by the Veciana group.3j,18)

It is clear from Fig. 2 that the azomethine linkage (–CH=N–) between aryl and TEMPO moieties is not necessarily a decisive factor for the realization of intermolecular ferromagnetic interactions, because several materials pos-

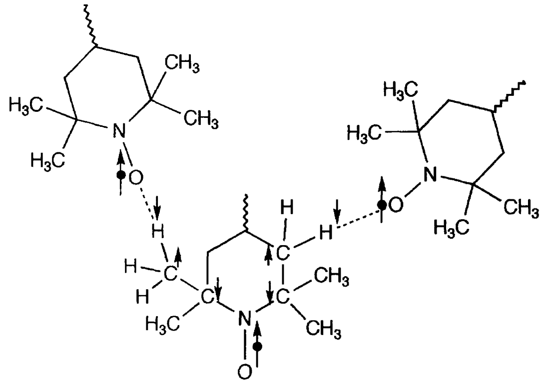
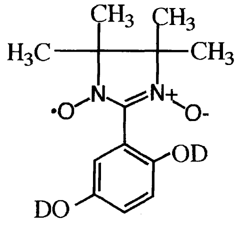


Fig. 4. A possible spin-polarization mechanism illustrating intermolecular ferromagnetic interactions found for a series of TEMPO-based ferromagnets. Only TEMPO portions are drawn for the sake of simplicity.

sessing other linkages (**45**—**52**) also exhibit ferromagnetic interactions. The probability of finding ferromagnetic radicals investigated here was 32% (52/165). However, the probability becomes higher (39%; 45/116) for 4-arylmethyleneamino-TEMPO type radicals. The arylmethyleneamino groups are supposed to be crystal-controlling substituents, favoring intermolecular ferromgnetic interactions. The tendencies that aromatic moieties gather together in the crystal and so do aliphatic moieties were found in this type of ferromagnets.[3d—h] The location of NO radical centers near methyl and methylene groups of neighboring molecules causes ferromagnetic interactions with high probabilities.

As can be seen in Fig. 2, it is noteworthy that TEMPO derivatives possessing similar structures in aromatic moieties have intermolecular ferromagnetic interactions in common, as evidenced by the results of *p*-halo- and chalcogeno-substituted derivatives (**4**, **6**, **13**, **14**, **15**, **23**, **25**, and **40**) and also by those of aza-analogues of phenyl and naphthyl groups (**1**, **2**, **16**, **20**, **22**, **26**, **28**, **29**, **35**, and **37**). Similar structures in aromatic moieties may give similar arrangements of TEMPO moieties in crystals, thus leading to intermolecular ferromagnetic interactions in a series of these materials.

We could not detect a deuterium isotope effect in the crystal of 4-hydroxyimino-TEMPO-OD (**49**) compared with those of nondeuterated material **48**, suggesting that the hydroxy hydrogen atom does not participate in the pathway of intermolecular magnetic interaction.[3h,7] Very recently, Sugawara et al. have reported that the crystal of 2-(2,5-dideuteroxyphenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-1-yloxyl 3-oxide (abbreviated as DTI-$(OD)_2$) showed a smaller Weiss temperature than that of the nondeuterated one (Chart 1).[19] Their result was interpreted in terms of spin-polarization along the intermolecular hydrogen bonds.[19] However, **48** have a pathway of magnetic interaction through the aliphatic hydrogen atoms (β-hydrogen atoms), not through the hydroxyl hydrogen.[7] Our experimental result obtained here is consistent with the mechanism described above. The magnetic studies of methyl- and methylene-deuterated TEMPO derivatives are now underway.



DTI-$(OD)_2$

Chart 1.

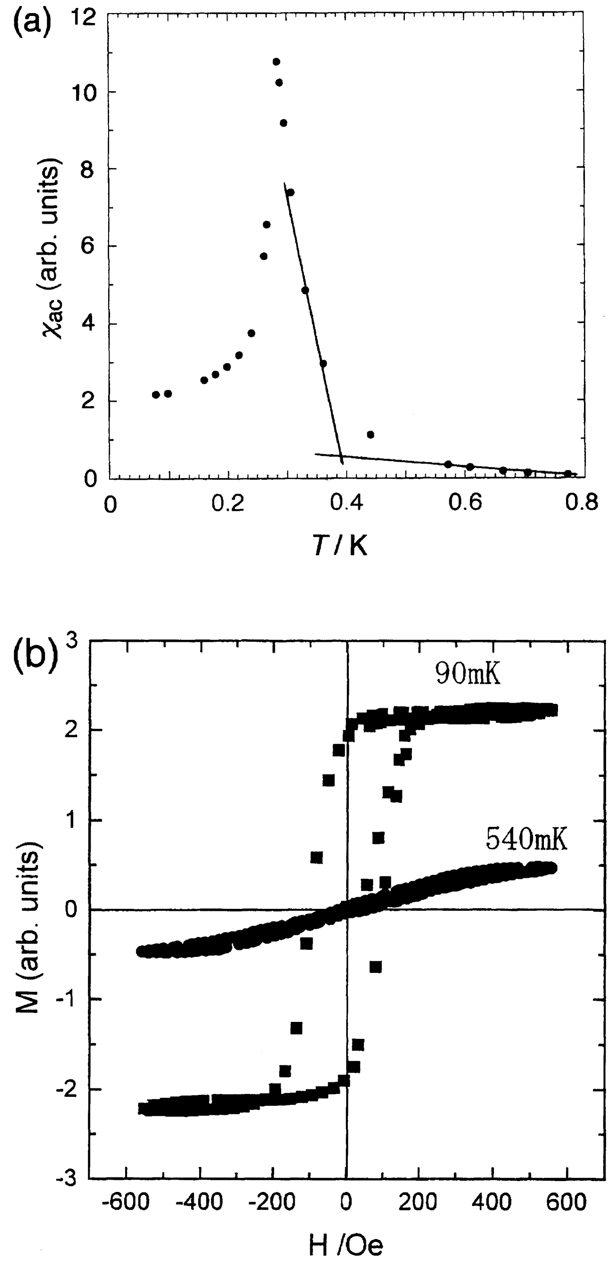


Fig. 5. (a) Temperature dependence of AC magnetic susceptibility of 4-(4-iodobenzylideneamino)-TEMPO (**4**). Ferromagnetic transition temperature (T_c) was estimated to be 0.4 K by the intersection between two straight lines tangent to χ_{ac} curve at upsurge and paramagnetic regions. (b) Isothermal magnetization curves of **4** measured at 90 and 540 mK.

Ferro- and Meta-magnetic Transitions of Several 4-Arylmethyleneamino-TEMPO's. We have newly found 4-(4-iodobenzylideneneamino)-TEMPO (**4**) to exhibit bulk ferromagnetic transition after we reported seven kinds of organic-radical ferromagnets.[3d—h] Figure 5a shows the temperature dependence of AC magnetic susceptibilities (χ_{ac}) of **4**. The upsurge of χ_{ac} around at 0.4 K suggests a magnetic phase transition from a paramagnetic phase. In order to elucidate this phenomenon, isothermal magnetizations were measured at 90 and 540 mK (Fig. 5b). That at 90 mK gave an S-shaped hysteresis curve which is characteristic of a ferromagnet. The transition temperature (T_c) was estimated to be 0.4 K by the intersection of two straight lines tangent to a χ_{ac} curve at paramagnetic and upsurge regions, as shown in Fig. 5a.[20] The paramagnetic linear magnetizations were observed at 540 mK (above T_c) as shown in Fig. 5b.

Figure 2 shows that many TEMPO radicals exhibit intermolecular ferromagnetic interactions which were verified by the SQUID measurements above 1.8 K. However, magnetic measurements below 1.8 K clarified that at least six materials exhibited antiferromagnetic transitions, and that metamagnetic behavior could be observed for them by applying relatively weak magnetic fields. These facts show that the strongest intermolecular magnetic interaction is a ferromagnetic one, but ferromagnetically coupled spins interact antiferromagnetically in these materials. Table 1 summarizes TEMPO derivatives exhibiting metamagnetic behavior, magnetic fields of spin-flip transitions (H_c), temperatures for the measurements of spin-flip transitions (T_{sf}), and Néel temperatures (T_N). As a typical example of the metamagnetic behavior, Fig. 6 shows the temperature dependence of AC magnetic susceptibilities (χ_{ac}) of 4-(3,4-dichlorobenzylideneamino)-TEMPO (**12**) (Fig. 6a), and its isothermal magnetization curve measured at 40 mK (Fig. 6b). The AC susceptibility measurements revealed that some magnetic phase transition occurred at ca. 0.1 K, as evidenced by the susceptibility peak. The decrease of the χ_{ac} below 0.1 K can be understood by either of three origins; the formation of ferromagnetic domains, the demagnetization effect of ferromagnet, and the antiferromagnetic transition. Measurements of isothermal magnetizations below 0.1 K gave double S-shaped curves. On increasing the magnetic fields from zero to ca. 20 Oe, the magnetization increased only slightly. However, it increased abruptly at ca. 20 Oe, and was saturated around at 400 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 40 mK. Therefore, the χ_{ac} peak at 0.1 K can be understood by the antiferromagnetic transition. Similar metamagnetic behavior was also observed for the materials summarized in Table 1. We define Néel temperatures of these materials from the peaks of AC magnetic susceptibilities in Table 1. The relatively weak H_c values (lower than 200 Oe) can be understood by the weak antiferromagnetic interactions of these TEMPO-based materials. Similar metamagnetic behavior has also been reported for other TEMPO-based materials.[17,21,22]

Table 1. 4- Arylmethyleneamino- TEMPO's Exhibiting Metamagnetic Transitions

Aryl group	H_c[a)]	T_{sf}[b)]	T_N[c)]
	Oe	K	K
2-Pyridyl (**1**)[d)]	10—20	0.05	0.26
3,5-Dichlorophenyl (**3**)	20	0.05	0.12
2,6-Dichlorophenyl (**10**)	20	0.04	0.20
3,4-Dichlorophenyl (**12**)	20	0.04	0.10
4-Pyridyl (**16**)[d)]	110	0.09	0.12
2-Naphthyl (**28**)[e)]	180	0.04	0.12

a) Cirtical magnetic fields inducing spin-flip transitions. b) Temperatures for the measurements of spin-flip transitions. c) Néel temperatures. d) See Ref. 3h. e) See Ref. 17.

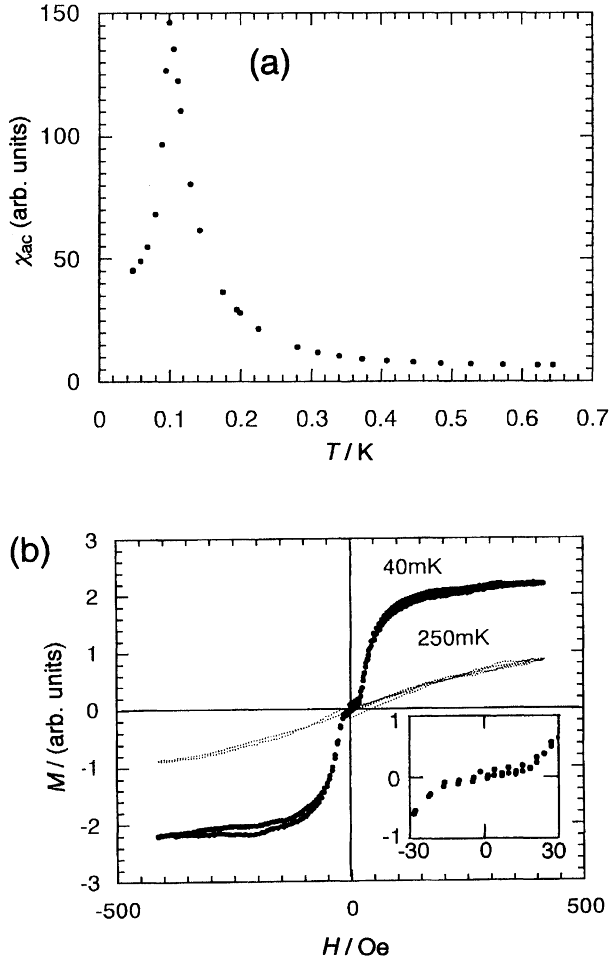


Fig. 6. (a) Temperature dependence of AC magnetic susceptibility of 4-(3,4-dichlorobenzylideneamino)-TEMPO (**12**). (b) Isothermal magnetization curve of **12** measured at 40 mK. Inset shows the magnification of the curve in the region of low magnetic fields.

Although we have discussed the origin of intermolecular ferromagnetic interactions of TEMPO derivatives,[3g,3h,7)] the origins of the intermolecular antiferromagnetic interactions have not been clarified yet. The X-ray crystallographic studies of TEMPO derivatives showing antiferromagnetic interactions and theoretical studies based on the crystal structures are needed for the full understanding of intermolecular magnetic interactions of TEMPO-based materials.

Summary. We have found that 52 kinds of 4-arylmethyleneamino-TEMPO's and related compounds show intermolecular ferromagnetic interactions. The surprisingly high probability of finding ferromagnetic organic radicals may be caused by the characteristic molecular arrangements in crystals of these materials. 4-(4-Iodophenylmethyleneamino)-TEMPO showed bulk ferromagnetic transition with a T_c of 0.4 K. Six TEMPO derivatives showed metamagnetic transitions below 0.1 K at magnetic fields lower than 200 Oe.

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