Bull. Chem. Soc. Jpn., *71*, 2583—2587 (1998)

Ferromagnetic and Antiferromagnetic Phases of 4-(4-Iodobenzylideneamino)-2,2,6,6-tetramethylpiperidin-1-yloxyl

Takayuki Ishida,* Kensuke Togashi, Ron Imachi, Hajime Yamamoto,
Masanori Yasui, Fujiko Iwasaki, and Takashi Nogami*

Department of Applied Physics and Chemistry, The University of Electro-Communications,
Chofugaoka, Chofu, Tokyo 182-8585

(Received May 25, 1998)

Temperature dependences of d.c. magnetic susceptibilities and magnetizations were measured for two different crystallographic phases of 4-(4-iodobenzylideneamino)-2,2,6,6-tetramethylpiperidin-1-yloxyl. Intermolecular ferromagnetic (Weiss temperature $\theta = +0.71$ K) and antiferromagnetic ($\theta = -0.23$ K) interactions were found for α- and β-phases, respectively, in the magnetic measurements above 1.8 K; the former phase showed a bulk ferromagnetic transition at 0.28 K. Based on the X-ray crystallographic data, intermolecular magnetic interactions are discussed. In the α-phase crystal, NO-radical sites form two-dimensional zigzag sheets. The ferromagnetic interaction within the sheet can be interpreted in terms of a *β-hydrogen mechanism*, $\mathrm{ON}(\uparrow)\text{–}\mathrm{C}_\alpha(\downarrow)\text{–}\mathrm{C}_\beta(\uparrow)\text{–}\mathrm{H}_\beta(\downarrow)\cdots(\uparrow)\mathrm{ON}<$, in which the magnetic interaction is transmitted by β-hydrogens. A dimer structure was found in the β-phase crystal, and direct exchange and/or dipole interactions between N–O radicals seem to be the main origin of the antiferromagnetic interaction.

Studies on the organic radicals exhibiting intermolecular ferromagnetic interactions and bulk ferromagnetic transitions have progressed greatly in these few years.[1)] The number of organic radical-ferromagnets has amounted to twenty kinds, to our knowledge.[2)] Figure 1 shows TEMPO-based organic-radical ferromagnets **1**—**8** found by our group, together with their ferromagnetic transition-temperatures (T_c);[3)] TEMPO stands for 2,2,6,6-tetramethylpiperidin-1-yloxyl. Although organic radicals exhibiting intermolecular ferromagnetic interaction were few until the year of 1991,[4)] a number of organic radicals exhibiting intermolecular ferromagnetic interaction have been reported in these past few years. For example, we have reported 52 kinds of TEMPO-based organic radicals exhibiting intermolecular ferromagnetic interaction.[2h)] Here, a ferromagnetic organic radical means a radical in which the χT value increases at the low temperature range; χ denotes a magnetic susceptibility. Nowadays, the number of ferromagnetic organic radicals probably exceeds 100 kinds. Large efforts have also been made for the elucidation of the mechanism of the intermolecular ferromagnetic interaction and for the strategy of obtaining organic-radical ferromagnet.[5,6)] We explained the high probability of ferromagnetic organic radicals found in TEMPO-derivatives in terms of a *β-hydrogen mechanism.*[6)]

We have systematically studied the intermolecular magnetic interaction of 4-(4-halobenzylideneamino)-TEMPO's. Fluoro-, chloro-**3**, and bromo-derivatives exhibited intermolecular antiferromagnetic (Weiss temperature $\theta = -2.6$ K), ferromagnetic ($\theta = +0.69$ K), and ferromagnetic ($\theta = +0.32$ K) interactions, respectively.[2h)] In the case of **3**, we observed a bulk ferromagnetic transition at 0.28 K, which was confirmed by an ac magnetic susceptibility-, magnetization-,[2f)] μSR-,[7)] and heat capacity-measurements.[8)] As an extension of these studies, we have studied magnetic properties and crystal structures of iodo-derivative **6** in order to see the structure-magnetism relation. We found two crystallographically different phases which show intermolecular ferromagnetic and antiferromagnetic interactions; these two phases are denoted as α- and β-phases, respectively. The α-phase crystal exhibited a bulk ferromagnetic transition at 0.28 K.[2h)] This paper reports the magnetic properties, and we propose a mechanism of intermolecular magnetic interactions of the two phases of **6**, based on the crystal structures.

Experimental

Synthesis of 6. Synthesis of **6** was made by a condensation reaction of 4-iodobenzaldehyde and 4-amino-2,2,6,6-tetramethylpiperidin-1-oxyl, by the procedures described elsewhere.[9)] It was recrystallized from ethanol. The crystals of α- and β-phases were discernible from the difference of the crystal shapes; plate (α-phase) and prism (β-phase).

Magnetic Measurements. The magnetic susceptibility in the temperature range of 1.8—100 K was measured on a SQUID magnetometer (MPMS-7, Quantum Design). The diamagnetic contribution was estimated by Pascal's atomic constants.

Results and Discussion

Magnetic Measurements. The temperature dependences of the molar magnetic susceptibilities (χ_M) of α- and β-phases of **6** were measured at the magnetic field of 5000 Oe in the temperature range of 1.8—100 K. The observed data were analysed on the basis of the equation:

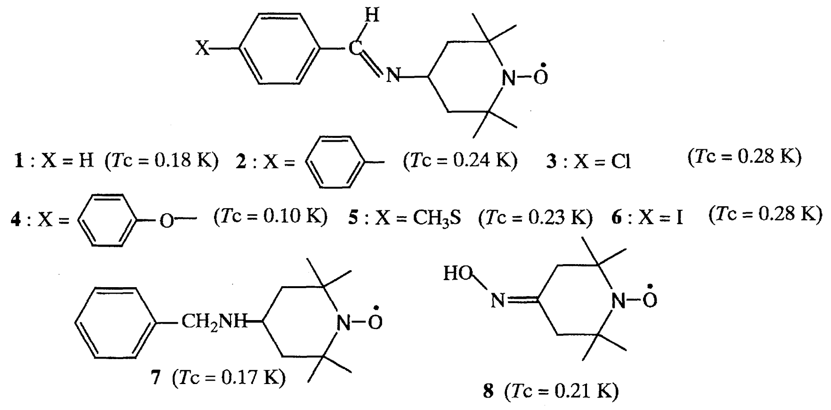

Fig. 1. TEMPO-based organic-radical ferromagnets and their ferromagnetic transition temperatures (T_c).

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

The last equation is derived by setting $g = 2$ and $S = 1/2$. Here, the symbols have their usual meanings.

Figure 2 shows the temperature dependence of $\chi_M T$ values of α- and β-phases of **6**. The above equation could reproduce quite well the observed temperature dependences. The θ-values estimated by the best-fit of the data below 20 K were +0.71 K and −0.23 K for α- and β-phases of **6**, respectively, indicating that α- and β-phases have intermolecular ferromagnetic and antiferromagnetic interactions, respectively. In order to see the magnetic behavior of the α-phase of **6** in more detail, the temperature dependence of a.c. magnetic susceptibilities and isothermal magnetizations were measured in the temperature range of a ^{3}He–^{4}He dilution refrigerator.[10] It showed a bulk ferromagnetic transition[2h] at 0.28 K, as described previously.[3] However, no detailed mechanism of the ferromagnetic interaction of **6** was described,[3] because no X-ray crystallographic datum was available at that time. Thus, this paper reports the mechanism of intermolecular magnetic interactions of α- and β-phases of **6**, based on their crystal structures.

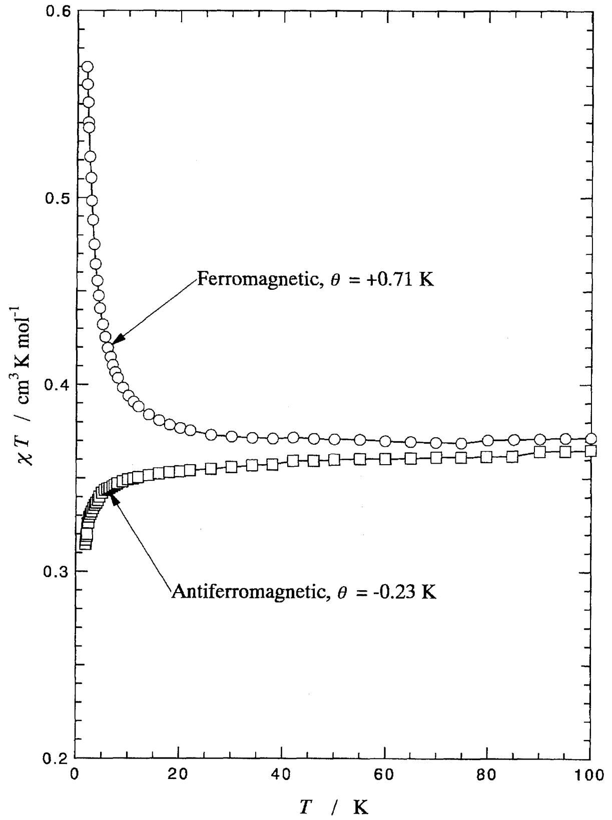

Fig. 2. Temperature dependences of $\chi_M T$ values of ferromagnetic α-phase and antiferromagnetic β-phase of **6** measured above 1.8 K.

Crystal Structures. Crystal structures of a series of 4-(4-halobenzylideneamino)-TEMPO's, including α- and β-phases of **6**, will be reported elsewhere.[11] In order to clarify the origin of the intermolecular magnetic interactions of α- and β-phases of **6**, important features of their crystal structures from the viewpoint of the magnetic interaction will be described below. Figure 3 shows the arrangement of the N–O radical-sites in the α-phase ferromagnetic crystal. Two molecular structures are drawn to envisage the molecular packing. The N–O radical-sites form two-dimensional zigzag sheets which are parallel with the *ac* plane. Intrasheet O···O distances are 5.89 and 5.91 Å along the *a*- and *c*-

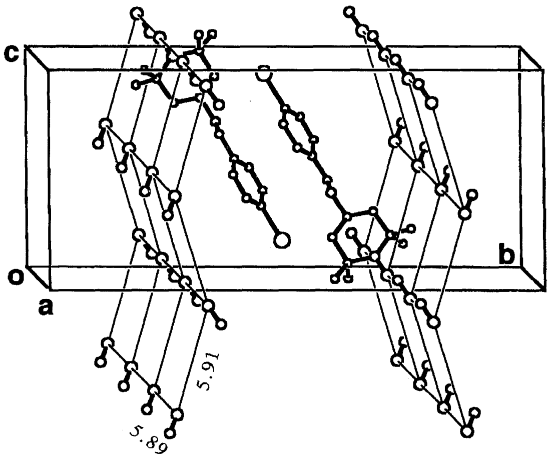

Fig. 3. Arrangements of N–O radical-sites in the α-phase crystal of **6** with intermolecular O···O distances in Å. Two molecular structures without hydrogen atoms are drawn to envisage the molecular packing.

axes respectively. Compared with these distances, the nearest intersheet O···O distance is 13.96 Å. Iodophenyl rings gather together in the clearances between zigzag sheets with weak pπ–pπ orbital interaction. These characteristic features of molecular arrangement were also found for several TEMPO-based organic ferromagnets.[2c—2h)]

Figure 4 shows the molecular arrangement of β-phase antiferromagnetic crystal viewed along the *b*-axis ($0<y<0.25$). Two sites of molecules (A- and B-sites in Fig. 4) form a dimer, and the dimers arrange toward [1 0 1] directions. The intradimer O···N, O···O, and N···N distances are 4.63, 5.47, and 5.70 Å, respectively. However, we can not find any sheet structure of N–O radical-sites in the β-phase crystal, unlike the case of the α-phase crystal. This structure (Fig. 4) suggests that the strongest magnetic interaction comes from the intradimer interactions between NO radical-sites. Other intermolecular magnetic interaction seems to be much weaker, because the next nearest O···O distance is 7.17 Å.

Mechanism of Intermolecular Magnetic Interactions of α- and β-Phases of 6. Based on the crystal structures of α- and β-phases described above, the origin of the intermolecular magnetic interaction will be discussed below. In the case of the α-phase crystal, intermolecular ferromagnetic interaction was observed as shown in Fig. 2(a). Characteristic molecular arrangement was found for this crystal, in which the oxygen atom of an N–O radical-site locates near the methyl- and methylene-hydrogens (β-hydrogens) of the adjacent molecule (Fig. 5(a)). Figure 5(a) shows only $CH_2C(CH_3)_2NOC(CH_3)_2CH_2$ portions of TEMPO moieties for the sake of clarity. The close interatomic O···H(methyl) distances are 2.77 and 2.52 Å along the *a*- and *c*-axes, respectively. Close intermolecular O···H(methylene) distance (2.77 Å) was also found along the *c*-axis. These distances are close to the sum of van der Waals radii (2.6 Å). Therefore, the following spin-polarization mechanism, which we term *β-hydrogen mechanism*,[6)] can explain the intermolecular ferromagnetic interaction. As illustrated in Fig. 5(b), a positive spin-density on the N–O site induces negative spin-density on the methyl- and methylene-hydrogen atoms due to an intramolecular spin-polarization, which in turn induces positive spin-density on the N–O sites of the adjacent molecules caused by the 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 the crystal. Such an intermolecular ferromagnetic interaction is operative among the N–O sites on the two-dimensional zigzag sheet shown in Fig. 3. Thus, the α-phase crystal seems to have a two-dimensional magnetic property. The origin of the intersheet ferromagnetic interaction of NO-sites is not clarified yet. Theoretical and experimental grounds for this *β-hydrogen mechanism* were described elsewhere.[6,12)] The ferromagnetic interaction of all of the TEMPO-based ferromagnets could be explained by this mechanism.[6,13)]

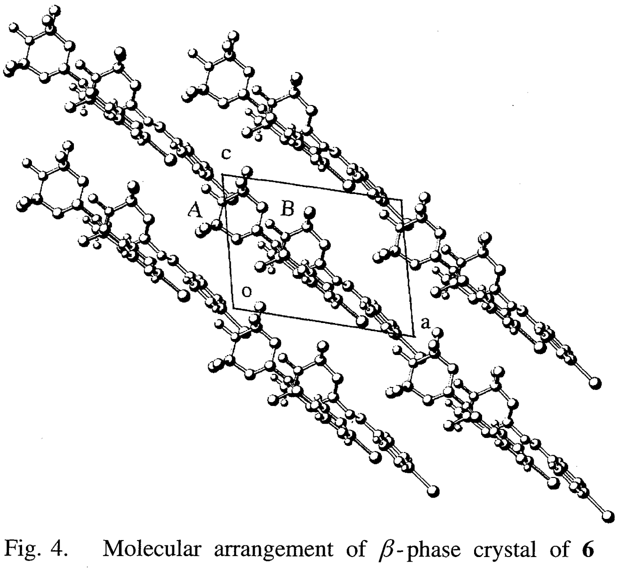

Fig. 4. Molecular arrangement of β-phase crystal of **6** viewed along the *b*-axis ($0<y<0.25$). Hydrogen atoms are omitted. A- and B-site molecules form a magnetic dimer.

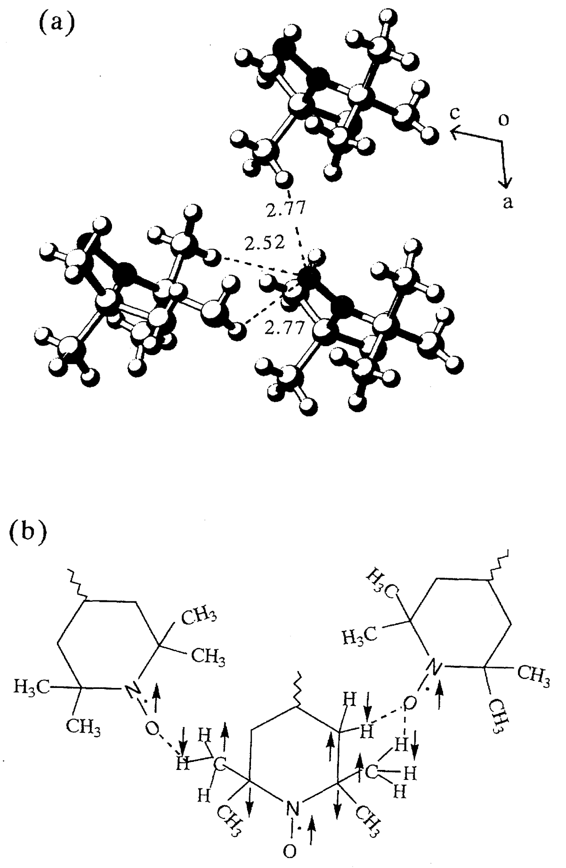

Fig. 5. (a) Close intermolecular NO···$H_\beta C$ distances (in Å) on the two-dimensional zigzag sheet which is parallel with the *ac* plane; only $CH_2C(CH_3)_2NOC(CH_3)_2CH_2$ portions of TEMPO moieties are shown for the sake of clarity, and NO-radical sites are shown by filled circles. (b) Spin-polarization mechanism (*β-hydrogen mechanism*) of the α-phase crystal of **6**.

In order to get insight into the antiferromagnetic interaction of the β-phase crystal, local arrangements of four neighboring molecules are shown in Fig. 6 with several interatomic distances. In view of the relatively short N···O

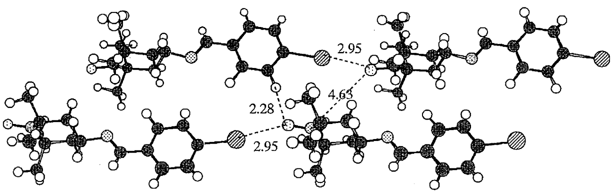

Fig. 6. Local arrangements of neighboring four molecules in the β-phase crystal of **6** with several interatomic distances in Å.

distance (4.63 Å),[14] direct exchange and/or dipole interactions between NO-radicals of A- and B-sites seem to cause the antiferromagnetic interaction, although we can not clarify the detailed mechanism. Other indirect spin-polarization pathways like $>\mathrm{NO}(\uparrow)\cdots(\downarrow)\mathrm{H}\text{–}\mathrm{C}_3(\uparrow)\text{–}\mathrm{C}_4(\downarrow)\text{–}\mathrm{I}(\downarrow)\cdots(\uparrow)\mathrm{ON}<$ (ferromagnetic interaction)[15] and $>\mathrm{NO}\cdots\mathrm{I}\cdots\mathrm{ON}<$ seem to be much weaker than the above direct antiferromagnetic interaction, because their interaction paths are longer than that of the direct interaction.

Summary. Two crystallographic phases (α- and β-phases) were found for 4-(4-iodobenzylideneamino)-TEMPO (**6**). The α-phase crystal showed a bulk ferromagnetic transition ($T_c = 0.28$ K), and the β-phase crystal was an antiferromagnet. Based on the data of the X-ray crystallography, ferromagnetic interaction of the α-phase crystal could be explained by the *β-hydrogen mechanism*. The antiferromagnetic interaction of the β-phase crystal arises from the direct exchange and/or dipole interactions of nearest NO radical sites.

This work was supported by a Grant-in-Aid for Scientific Research No. 08454218 from the Ministry of Education, Science, Sports and Culture.

References

1) For reviews, see: a) J. S. Miller and A. J. Epstein, *Angew. Chem., Int. Ed. Engl.*, **33**, 385 (1994); b) D. Gatteschi, *Adv. Mater.*, **6**, 635 (1994); c) M. Kinoshita, *Jpn. J. Appl. Phys.*, **33**, 5718 (1994); d) O. Kahn, "Molecular Magnetism," VCH Publishers, Inc., New York, Weinheim, and Cambridge (1993); e) "Molecular Magnetism: From Molecular Assemblies to the Devices," ed by E. Coronado, P. Delhaes, D. Gatteschi, and J. S. Miller, Kluwer Acad. Publ., Dordrecht, Boston, and London (1995); f) Proceedings of the International Conference on Molecule-Based Magnets, *Mol. Cryst. Liq. Cryst.*, **305—306** (1997).

2) a) M. Kinoshita, P. Turek, M. Tamura, Y. Nozawa, D. Shiomi, Y. Nakazawa, M. Ishikawa, M. Takahashi, K. Awaga, T. Inabe, and Y. Maruyama, *Chem. Lett.*, **1991**, 1225; b) R. Chiarelli, M. A. Novak, R. Rassat, and J. L. Tholence, *Nature*, **363**, 147 (1993); c) T. Nogami, K. Tomioka, T. Ishida, H. Yoshikawa, M. Yasui, F. Iwasaki, H. Iwamura, N. Takeda, and M. Ishikawa, *Chem. Lett.*, **1994**, 29; d) T. Ishida, H. Tsuboi, T. Nogami, H. Yoshikawa, M. Yasui, F. Iwasaki, H. Iwamura, N. Takeda, and M. Ishikawa, *Chem. Lett.*, **1994**, 919; e) T. Nogami, T. Ishida, H. Yoshikawa, M. Yasui, F. Iwasaki, H. Iwamura, N. Takeda, and M. Ishikawa, *Synth. Met.*, **71**, 1813 (1995); f) T. Nogami, T. Ishida, H. Tsuboi, H. Yoshikawa, H. Yamamoto, M. Yasui, F. Iwasaki, H. Iwamura, N. Takeda, and M. Ishikawa, *Chem. Lett.*, **1995**, 635; g) T. Nogami, T. Ishida, M. Yasui, F. Iwasaki, H. Iwamura, N. Takeda, and M. Ishikawa, *Mol. Cryst. Liq. Cryst.*, **279**, 97 (1996); h) K. Togashi, R. Imachi, K. Tomioka, H. Tsuboi, T. Ishida, T. Nogami, N. Takeda, and M. Ishikawa, *Bull. Chem. Soc. Jpn.*, **69**, 2821 (1996); i) T. Sugawara, M. M. Matsushita, A. Izuoka, N. Wada, N. Takeda, and M. Ishikawa, *J. Chem. Soc., Chem. Commun.*, **1994**, 1723; j) J. Cirujeda, M. Mas, E. Molins, F. L. Panthou, J. Laugier, J. K. Park, C. Paulsen, P. Rey, C. Rovira, and J. Veciana, *J. Chem. Soc., Chem. Commun.*, **1995**, 709; k) A. Caneschi, F. Farraro, D. Gatteschi, A. Lirzin, M. A. Novak, E. Rentschler, and R. Sessoli, *Adv. Mater.*, **7**, 476 (1995); l) K. Mukai, K. Konishi, K. Nedachi, and N. Takeda, *J. Phys. Chem.*, **100**, 9658 (1996); m) K. Takeda, T. Hamano, T. Kawae, M. Hidaka, M. Takahashi, S. Kawasaki, and K. Mukai, *J. Phys. Soc. Jpn.*, **64**, 2343 (1995); n) T. Sugimoto, M. Tsuji, T. Suga, N. Hosoito, M. Ishikawa, and N. Takeda, *Mol. Cryst. Liq. Cryst.*, **272**, 183 (1995); o) F. M. Romero, R. Ziessel, M. Drillon, J. -L. Tholence, C. Paulsen, N. Kyritsakas, and J. Fisher, *Adv. Mater.*, **8**, 826 (1996).

3) We defined the ferromagnetic transition-temperature (T_c) from the intersection point of two straight lines tangent to a χ_{ac} curve at paramagnetic and upsurge regions (see Ref. 2c—2h). However, we have found that the temperature affording χ_{ac} peak is more appropriate for the definition of T_c, because this temperature is close to the T_c determined precisely by μSR- and heat capacity-measurements of **3**. Therefore, the revised T_c's are shown in Fig. 1.

4) a) K. Mukai, H. Nishiguchi, and Y. Deguchi, *J. Phys. Soc. Jpn.*, **23**, 125 (1967); b) A. Benoit, J. Flouquet, B. Gillon, and J. Schweizer, *J. Magn. Magn. Mater.*, **31—34**, 1155 (1983); c) T. Sugawara, S. Murata, K. Kimura, H. Iwamura, Y. Sugawara, and H. Iwasaki, *J. Am. Chem. Soc.*, **107**, 5293 (1985); d) K. Awaga and Y. Maruyama, *Chem. Phys. Lett.*, **158**, 556 (1989); e) M. Kamachi, M. Tamaki, Y. Morishima, S. Nozakura, W. Mori, and M. Kishita, *Polym. J.*, **12**, 362 (1982); f) P. -M. Allemand, G. Srdanov, and F. Wudl, *J. Am. Chem. Soc.*, **112**, 9391 (1990).

5) a) H. M. McConnell, *J. Chem. Phys.*, **39**, 1910 (1963); b) N. Mataga, *Theor. Chim. Acta*, **10**, 372 (1968); c) A. L. Buchachenko, *Dokl. Akad. Nauk SSSR*, **224**, 1146 (1979); d) R. Breslow, B. Jaun, R. Klutz, and C. -Z. Xia, *Tetrahedron*, **38**, 863 (1982); e) T. P. Radhakrishnan, Z. G. Soos, H. Endres, and L. J. Azevedo, *J. Chem. Phys.*, **85**, 1126 (1986); f) J. B. Torrance, S. Oostra, and A. Nazzal, *Synth. Met.*, **19**, 709 (1986); g) E. Dormann, M. J. Nowak, K. A. Williams, R. O. Angus, and F. Wudl, *J. Am. Chem. Soc.*, **109**, 2594 (1987); h) T. J. Lepage and R. Breslow, *J. Am. Chem. Soc.*, **109**, 6412 (1987); i) K. Awaga, T. Sugano, and M. Kinoshita, *Chem. Phys. Lett.*, **141**, 540 (1987); j) K. Yamaguchi, N. Namimoto, T. Fueno, T. Nogami, and Y. Shirota, *Chem. Phys. Lett.*, **166**, 408 (1990); k) O. Kahn, H. Stumpf, Y. Yu Pei, and J. Sletten, *Mol. Cryst. Liq. Cryst.*, **233**, 231 (1993); l) C. Kollman and O. Kahn, *J. Chem. Phys.*, **98**, 453 (1993).

6) T. Nogami, T. Ishida, M. Yasui, F. Iwasaki, N. Takeda, and M. Ishikawa, *Bull. Chem. Soc. Jpn.*, **69**, 1841 (1997).

7) R. Imachi, T. Ishida, T. Nogami, S. Ohira, K. Nishiyama, and K. Nagamine, *Chem. Lett.*, **1997**, 233.

8) T. Matsumoto, Y. Miyazaki, T. Ishida, T. Nogami, and M. Sorai, "Abstract of Symposium of Molecular Structure," Nagoya, 1997, p. 735.

9) a) K. Tomioka, T. Ishida, T. Nogami, and H. Iwamura, *Chem. Lett.*, **1993**, 625; b) K. Tomioka, S. -i. Mitsubori, T. Ishida, T. Nogami, and H. Iwamura, *Chem. Lett.*, **1993**, 1239.

10) Y. Nakayama, M. Tamura, N. Shirakawa, D. Shiomi, M. Takahashi, M. Kinoshita, and M. Ishikawa, *Phys. Rev. B*, **B46**, 8906 (1992).

11) F. Iwasaki, H. Yoshikawa, H. Yamamoto, E. Kannnari, K. Takeda, M. Yasui, T. Ishida, and T. Nogami, *Acta Crystallogr.*, *Sect. B*, submitted; α-phase of **6**: monoclinic, $P2_1/c$, $a = 5.889(2)$, $b = 25.841(4)$, $c = 11.326(4)$ Å, $\beta = 105.30(5)^\circ$, $Z = 4$, $D_{\text{calc}} = 1.539$ g cm^{-3}, $R = 0.038$ for 2225 observed reflections. β-phase of **6**: monoclinic, $P2_1/c$, $a = 10.980(4)$, $b = 38.914(4)$, $c = 8.358(4)$ Å, $\beta = 103.88(3)^\circ$, $Z = 8$, $D_{\text{calc}} = 1.476$ g cm^{-3}, $R = 0.037$ for 4902 observed reflections.

12) a) Y. Kotake and K. Kuwata, *Chem. Lett.*, **1984**, 83; b) G. F. Hatch and R. W. Kreilick, *J. Chem. Phys.*, **57**, 3696 (1972); c) E. G. Jansen, U. M. Oehler, D. L. Haire, and Y. Kotake, *J. Am. Chem. Soc.*, **108**, 6858 (1986); d) T. Ishida, K. Tomioka, T. Nogami, H. Yoshikawa, M. Yasui, and F. Iwasaki, *Chem. Phys. Lett.*, **247**, 7 (1995); e) T. Kawakami, A. Oda, S. Takeda, W. Mori, T. Ishida, T. Nogami, and K. Yamaguchi, *Mol. Cryst. Liq. Cryst.*, **306**, 141 (1997); f) G. Murata, S. Takeda, T. Kawakami, W. Mori, R. Imachi, T. Ishida, T. Nogami, and K. Yamaguchi, *Mol. Cryst. Liq. Cryst.*, **306**, 307 (1997).

13) For the review of TEMPO-based radical ferromagnets and metamagnets, see: T. Nogami and T. Ishida, *Mol. Cryst. Liq. Cryst.*, **296**, 305 (1997).

14) In the crystals of TEMPO-based ferromagnets, intermolecular $O\cdots O$ distance of NO-radical sites is about 6 Å, which is much longer than the $N\cdots O$ distance (4.63 Å) of the β-phase crystal of **6**.

15) The spin-polarization on iodine is derived from the following resonance contributions. $-C(\downarrow)-I(\uparrow\downarrow) \longleftrightarrow C(\uparrow\downarrow)^- -I(\downarrow)^+$