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An Organic Ferromagnet with a T_c of 0.4 K.
4-(*p*-Phenylbenzylideneamino)-2,2,6,6-tetramethylpiperidin-1-oxyl

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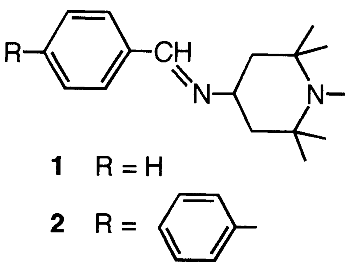
The polycrystalline sample of the title radical has a positive Weiss constant of 0.63 K. The ac susceptibility measurements indicated a ferromagnetic phase transition at about 0.4 K. The magnetization measured at 80 mK (below T_c) showed a characteristic curve of a ferromagnet with a small hysteresis. The X-ray crystal structure analysis at room temperature revealed a two-dimensional network of the N-O sites (O···O distances are 5.96 and 6.09 Å) with an inter-sheet distance of 14.2 Å.

Ferromagnetism in organic materials is of current interest.[1)] There are quite a few examples of organic ferromagnets with well-defined crystal structures in the literature.[2-5)] We have very recently reported a purely organic ferromagnet, 4-benzylideneamino-TEMPO (**1**) with a T_c of 0.18 K[5)] (TEMPO = 2,2,6,6-tetramethylpiperidin-1-oxyl). In the course of our study on the magnetic properties of the derivatives substituted by various aromatic rings in place of the phenyl group in **1**, we have found a new organic ferromagnet, 4-(*p*-phenylbenzylideneamino)-TEMPO (**2**) with a T_c of about 0.4 K. Its molecular and crystal structures were determined by X-ray crystallographic analysis.



The polycrystalline sample of **2** was prepared and purified according to the method reported previously.[6,7)] The static magnetic behavior at 0.5 T down to 1.8 K was examined by a Quantum Design SQUID magnetometer. The effective magnetic moment appeared in 1.7-1.8 μ_B due to S = 1/2 species in a higher temperature region (Fig. 1). With decreasing temperature the moment monotonously increased and reached 2.16 μ_B at 1.8 K. The plot of the reciprocal susceptibility against temperature gave a positive Weiss temperature of 0.63 K from the data below 10 K. The result indicates the presence of intermolecular ferromagnetic interaction in this system.

We extended our investigation to lower temperatures by a ^{3}He-^{4}He dilution refrigerator. The ac susceptibility, χ_{ac}, was measured down to about 70 mK at an ac magnetic field of about 5.0 nT (127 Hz). The result is plotted as a function of temperature in Fig. 2, which shows that a very sharp divergence starts at about 0.4 K and reaches a maximum at 0.27 K. We here define the transition temperature as the temperature where the divergence of χ_{ac} starts rather than χ_{ac} reaches the maximum.[8,9)] A sharp decrease of χ_{ac} signal with

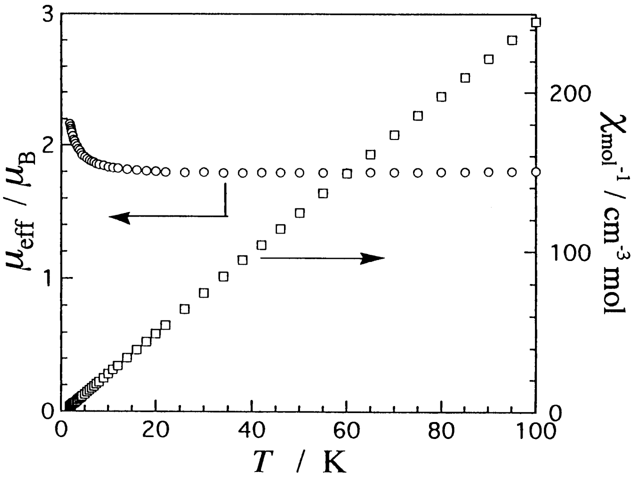


Fig. 1. Temperature dependence of the effective magnetic moment and reciprocal static magnetic susceptibility of **2**.

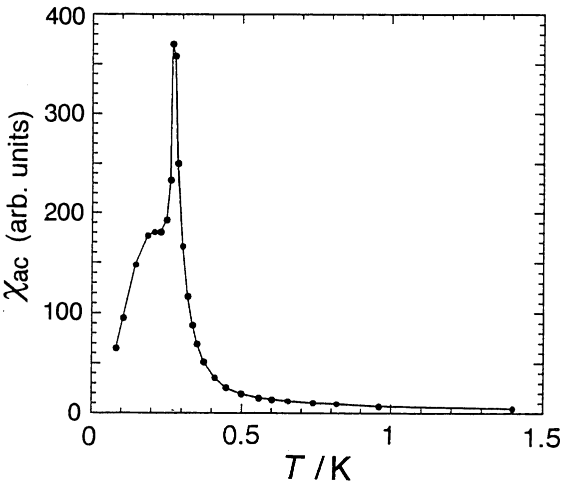


Fig. 2. Temperature dependence of the ac susceptibility of **2** below 1.4 K, showing a ferromagnetic transition at about 0.4 K.

peaking below T_C has been observed in some organic ferromagnets.[3,5] This might simply mean that once aligned moments are unable to follow such a weak ac field.

In order to elucidate the nature of the magnetic phase transition of **2** at 0.4 K, we measured *M-H* curves below and above this temperature. They were recorded by an integration technique, as described elsewhere.[10] As Fig. 3 shows, a typical S-shaped ferromagnetic curve with a small hysteresis was observed below T_C (80 mK). On the other hand, a linear paramagnetic feature was obtained above T_C (583 mK), and a transient curve between the two was observed at near T_C (388 mK). The *M-H* curve at 80 mK proves that the specimen maintains ferromagnetism down to temperatures where χ_{ac} greatly decreases.[11]

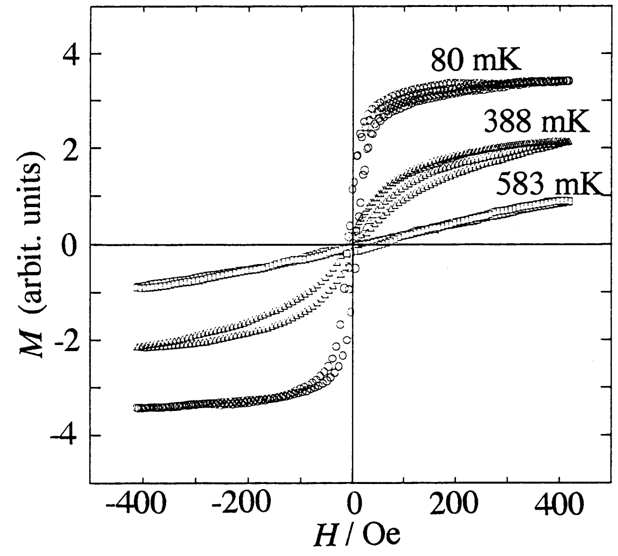


Fig. 3. *M-H* curves of **2** at 80 mK (below T_C), 388 mK (near T_C), and 583 mK (above T_C).

The coercive force (H_C) of ferromagnet **2** is small (about 10 Oe at 80 mK), as reported previously on the organic ferromagnets, β-phase *p*-NPNN (8 Oe),[10] 1,3,5,7-tetramethyl-2,6-diazaadamantane *N,N'*-dioxyl (< 0.1 Oe),[3] and C_{60}-tetrakis(dimethylamino)ethylene (< 2 Oe).[4] Furthermore, the molecular-based ferromagnet PM[VO(hfac)$_2$]$_2$ also shows a small H_C (< 5 Oe).[8] The small H_C and hysteresis seem to be common features of these molecular-based ferromagnets.[12]

The X-ray diffraction data of **2** at room temperature were recorded on a RIGAKU AFC-5R four-circle diffractometer using MoK_α radiation. Figure 4 shows the crystal structure of **2** viewed along the *a* axis.[13] The imino group and two phenyl groups are almost coplanar. The averaged piperidine plane defined by the carbons at 2,3,5, and 6-positions is twisted relative to the biphenyl group by an angle of 68°. Attention must be paid to the arrangement of the nitroxide sites because of the highly localized spin density. The nearest neighbor nitroxides are related by a translation along the *a* axis, and the second nearest nitroxides are arranged along the *c* axis in a zigzag manner. They construct a two-dimensional network parallel to the *ac* plane, as illustrated in Fig. 5. Their intra-sheet O···O distances are 5.96 and 6.09 Å along the *a* and *c* axes respectively, and the nearest O···O separation between the sheets is 13.40 Å. The sheets are 14.24 Å apart on the average. The bulky biphenyl groups gather in clearances between the sheets. They are arranged in face-to-face pairs and the distance between their planes is 3.8 Å, indicating the presence of π-orbital-π-orbital interaction.

The sheet structure of the N-O sites in the crystal of **2** is similar to the case of **1** (O···O distances: intra-sheet, 5.62 and 6.15 Å; inter-sheet, 11.89 Å).5) However, the angles between the neighboring N-O bonds are quite different; those of **2** are smaller (0° and 48° between the neighbors along the *a* and *c* axes respectively) than those of **1** (98 and 82°).5) The dihedral angles between the C-O-C planes surrounding the radical nitrogen in **2** are 0 and 51°. The relationship between the geometry of the N-O sites and the ferromagnetic exchange interaction is not clear so far. However, it is noteworthy that superexchange interaction may be operative through intervening methyl groups or hydrogen atoms; the intermolecular atomic distances are 3.82 Å for O···C(methyl) and 2.82 Å for O···H(methyl).

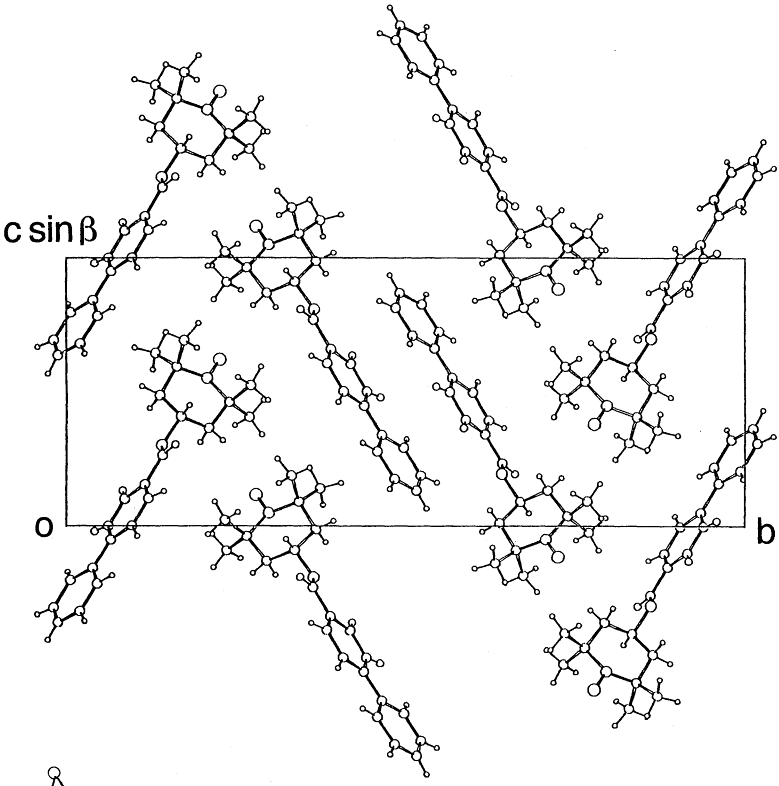


Fig. 4. Crystal structure of **2** viewed along the *a* axis.

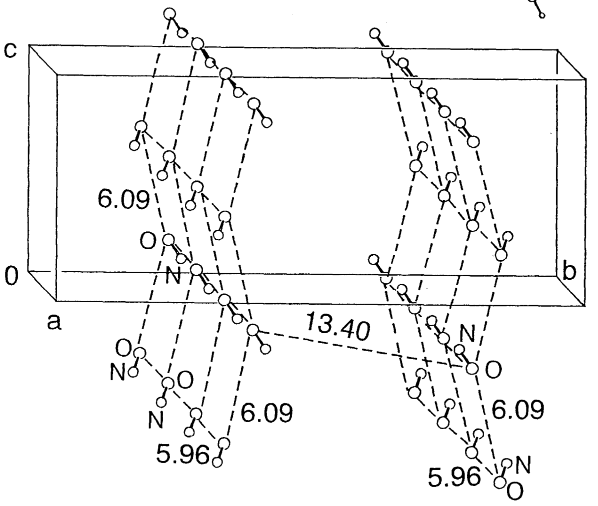


Fig. 5. Arrangement of the N-O sites in the crystal of **2**. Selected O···O distances are shown (in Å) with dotted lines.

The distance between the sheets of **2** (14.24 Å) is longer than that of **1** (10.8 Å) owing to the bulkyness of the additional phenyl group in **2**. Theoretical calculations suggested that exchange interaction decreases like an exponential function with an increase of the distance among spins.14) Assuming that the transition temperature of **2** is not lower than that of **1**9) in spite of the difference of the inter-sheet distances, the ferromagnetisms of **1** and **2** may be interpreted as two-dimensional ordering of the radical spins. The intermolecular ferromagnetic interactions and the difference of the transition temperatures of **1** and **2** must be clarified theoretically in connection with their crystal structures.

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7) The condensation of *p*-phenylbenzaldehyde and 4-amino-TEMPO gave the product **2** as orange needles, mp 129-131 °C (from hexane-dichloromethane).
8) S.-i. Mitsubori, T. Ishida, T. Nogami, H. Iwamura, N. Takeda, and M. Ishikawa, *Chem. Lett.*, **1994**, 685.
9) We reported that the T_c of **1** was 0.18 K as defined by a maximum of χ_{ac}.5) Since the divergence of χ_{ac} starts at a higher temperature than 0.18 K, this value seems to be rather underestimated.
10) Y. Nakazawa, M. Tamura, N. Shirakawa, D. Shiomi, M. Takahashi, M. Kinoshita, and M. Ishikawa, *Phys. Rev.*, **B46**, 8906 (1992).
11) This fact also proves that the shoulder of the χ_{ac} curve at about 0.2 K as shown in Fig. 2 is not essential to the determination of the magnetic ordering in this temperature region.
12) A subsequent *M-H* measurement on a single crystal of **1** also showed a small H_c (about 10 Oe at 65 mK). More details will be published elsewhere.
13) The crystallographic data: $C_{22}H_{27}N_2O$, monoclinic, $P2_1/c$, $a = 5.955(1)$, $b = 28.486(5)$, $c = 11.795(2)$ Å, $\beta = 106.72(2)°$, $V = 1916.4(7)$ Å^3, $Z = 4$, $D_c = 1.163$ g cm^{-3}, $R = 0.068$, $R_w = 0.087$ for 2661 observed reflections.
14) For example, see K. Yamaguchi, M. Okumura, J. Maki, T. Noro, H. Namimoto, M. Nakano, T. Fueno, and K. Nakasuji, *Chem. Phys. Lett.*, **190**, 353 (1992).

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