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A New Organic Ferromagnet: 4-Benzylideneamino-2,2,6,6-tetramethylpiperidin-1-oxyl

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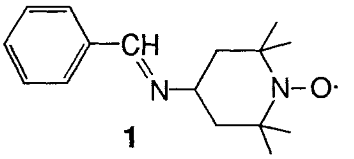
An organic radical crystal of 4-benzylideneamino-2,2,6,6-tetramethylpiperidin-1-oxyl was found to be a bulk ferromagnet, as indicated by the divergence of the ac susceptibility at 0.18 K and by the magnetic hysteresis below this temperature. The X-ray crystal structure analysis at room temperature revealed that the crystal consisted of an almost two-dimensional network of the N-O sites.

Ferromagnetism in organic radicals is currently attracting much attention.1) There have so far been three purely organic ferromagnets with well defined chemical and/or crystal structures: *p*-nitrophenyl nitronyl nitroxide (T_C = 0.60 K),2) 1,3,5,7-tetramethyl-2,6-diazaadamantane *N,N'*-dioxyl (T_C = 1.48 K),3) and the C_{60}-based charge-transfer complex (T_C = 16.1 K).4) Although several organic radicals have recently been reported to exhibit intermolecular ferromagnetic interaction,5) none of them except for the above three examples exhibits a ferromagnetic transition; two TEMPO derivatives with positive Weiss constants were proved to be organic metamagnets6,7) (TEMPO = 2,2,6,6-tetramethylpiperidin-1-oxyl). We have found the ferromagnetic interaction of the stable radical crystals of 4-(arylmethyleneamino)-TEMPO [aryl = phenyl (**1**, the title compound),8) 2-naphthyl,9) *p*-biphenylyl,10) and *p*-bromophenyl10)]. We report here that **1** exhibits ferromagnetic ordering below 0.18 K. The molecular and crystal structures of **1** were determined by X-ray diffraction analysis.



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The polycrystalline sample of **1** was prepared and purified according to the reported method.8,11) The static magnetic behavior down to 4.5 K for **1** was previously described.8) This behavior was re-examined on an Oxford Instruments Faraday balance at up to 7 T in a temperature range down to 1.7 K. The plot of the reciprocal susceptibility (χ_{dc}^{-1}) against temperature for **1** gave a positive Weiss constant (θ = 0.7 K), and the product $\chi_{dc}T$ continued to increase with decreasing temperature down to 1.7 K. As Fig. 1 shows, the magnetizations deviated upward from the Brillouin function with S = 1/2 and saturated more evidently at lower temperatures. The magnetization at 1.7 K coincided nearly with the Brillouin function with S = 3/2. The saturated magnetization value of $(5.6\pm0.1)\times10^3$ erg $Oe^{-1}mol^{-1}$ is consistent with the S = 1/2 entity and assures the purity of the sample; no ferromagnetic impurity was detected.

These results indicate the presence of intermolecular ferromagnetic coupling in this system. We extended our investigation to lower temperatures than 1.7 K, and found a ferromagnetic phase transition at

0.18 K. The ac susceptibility, χ_{ac}, was measured down to about 40 mK in a ^{3}He-^{4}He dilution refrigerator at the ac magnetic field of about 4 nT (127 Hz). The result is plotted as a function of temperature in Fig. 2, which shows a sharp peak at 0.18 K. In order to elucidate the nature of the magnetic phase transition at 0.18 K, we measured *M-H* curves below and above this temperature. The *M-H* curves were recorded by an integration technique in which the difference of the voltages induced on pickup and reference coils by sweeping the magnetic field is integrated over time by a computer, as described elsewhere.[12] The result is shown in Fig. 3. A typical ferromagnetic hysteresis curve was observed below T_C (0.18 K). The initial susceptibility came to be nearly null. This behavior is characteristic of a ferromagnet with a magnetic domain structure and not of a metamagnet,[13] and it partly explains the decrease of χ_{ac} just below the T_C.

It should be noted that the coercive force of this substance is relatively large (106 Oe), compared with that of the first organic ferromagnet, β *p*-NPNN (8 Oe).[12] The saturation magnetization M_S is estimated to be at most 0.5 μ_B per molecule, as in the case of β *p*-NPNN.[12] Because of the irregular shape of the pieces of **1**, we could not make a precise estimation of M_S.

The X-ray diffraction data of **1** at room temperature were recorded on a RIGAKU AFC-5R four-circle diffractometer using Mo K_α radiation. As Fig. 4 shows,[14] the phenyl ring and imino group are almost coplanar,

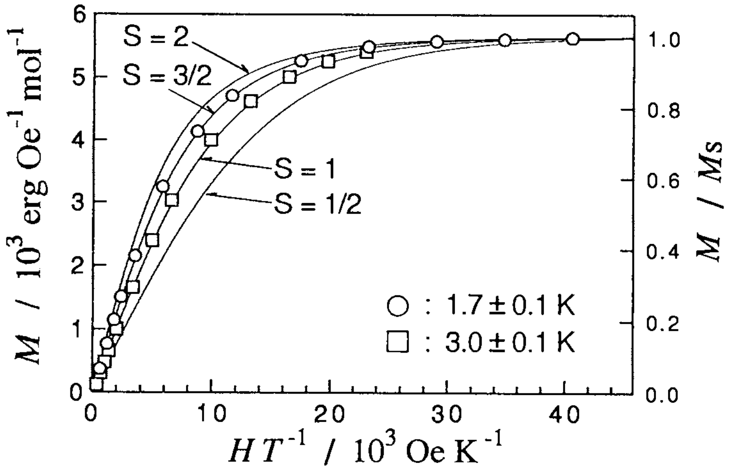

Fig. 1. Magnetization curves of **1** at 1.7±0.1 and 3.0±0.1 K. The lines are the theoretical curves given by the Brillouin functions with S = 1/2-2.

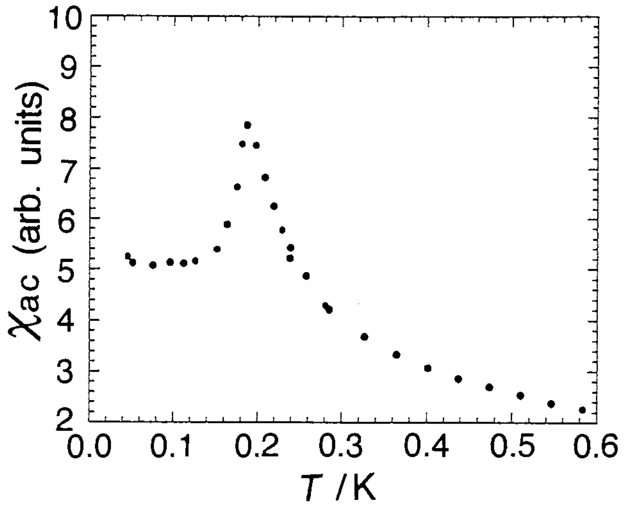

Fig. 2. Ac susceptibility of **1** below 0.6 K, showing the ferromagnetic transition at 0.18 K.

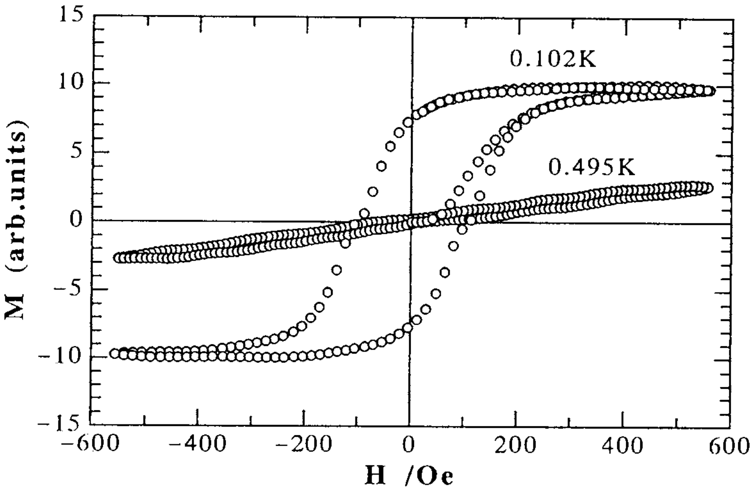

Fig. 3. Isothermal magnetization curves of **1** at 0.102 K (<T_C) and 0.495 K (>T_C).

and the averaged piperidine plane is twisted relative to the benzylideneamino moiety by an angle of 82°. The phenyl rings stack to the *b* and *c* directions and consequently the TEMPO moieties gather to construct a two-dimensional N-O network parallel to the *bc* plane (Fig. 5). The nearest neighbor nitroxides are arranged along the *c* axis with the O···O distance of 5.62 Å. The angle between the nearest N-O bonds is 98°, and that between the C-O-C planes surrounding the radical nitrogen 54°. The second nearest neighbors are arranged along the *b* axis with the O···O distance of 6.15 Å, with the angle between the N-O bonds 82° and that between the C-O-C planes 54°. The neighboring radical centers are placed to be nearly perpendicular with each other, leading to the negligibly small overlap of the SOMO's. This fact may result in a ferromagnetic coupling between the radical spins within the sheet. Since direct magnetic interaction between neighboring N-O sites[15)] is considered to be very small in view of their large distances, superexchange interaction may also be operative between them through an intervening methyl group or hydrogen atom [intermolecular atomic distances: O···C (methyl), 3.74 Å; O···H(methyl), 2.87 Å].

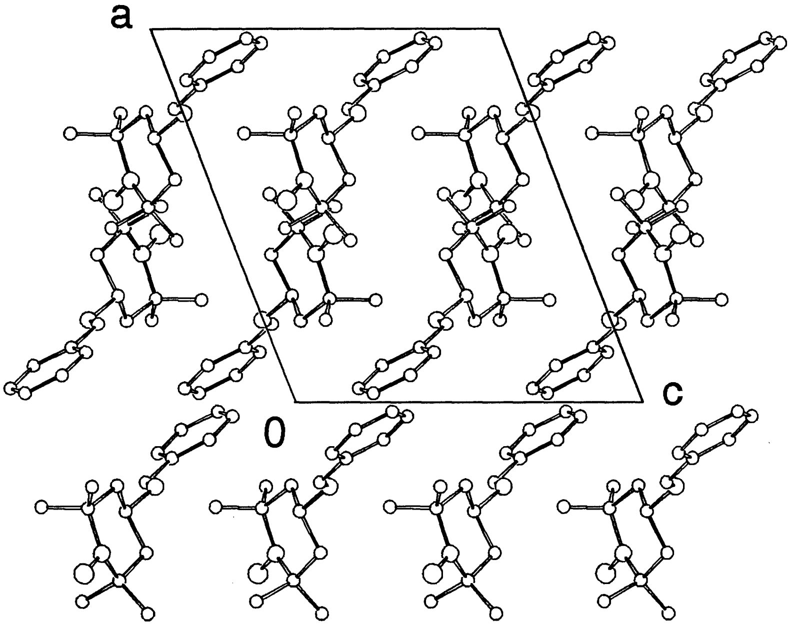

Fig. 4. Crystal structure of **1** viewed along the *b* axis. Hydrogen atoms are omitted for clarity.

The bulk ferromagnetism needs the ferromagnetic interaction between the sheets which are 10.8 Å apart on the average. Although the nearest O···O distance in the neighboring sheets is rather long (11.89 Å), the angle between the N-O bonds is 98° and that between the C-O-C planes 54°. The explanation of the ferromagnetic coupling in the sheets in terms of the orthogonality of the N-O sites may also hold for the ferromagnetic coupling among neighboring sheets. The low T_C results from the weak ferromagnetic couplings due to the long distances among the N-O sites.

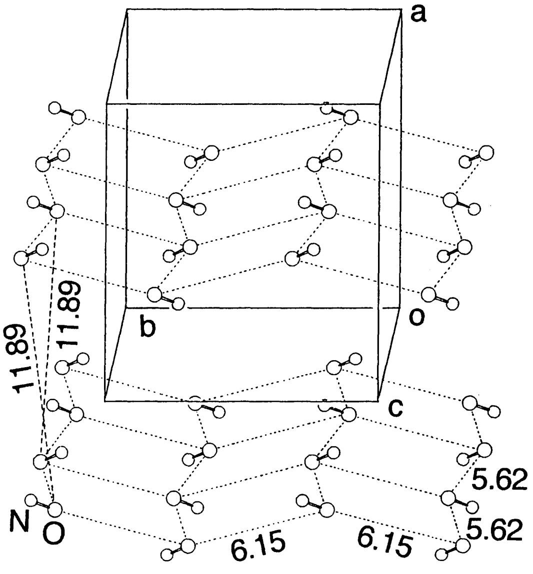

Fig. 5. Arrangement of the N-O sites in the crystal of **1**. Selected intermolecular O···O distances are shown (in Å) with dotted lines.

In conclusion, **1** is a bulk ferromagnet below 0.18 K. In spite of the low T_C, the ferromagnet composed of only light elements is still of great interest. The crystal structure of **1** may provide a simple model for studies on the magneto-structure correlation because of the highly localized spin density on the N-O groups. Theoretical study on the origin of the ferromagnetism is underway.

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14) The crystallographic data: monoclinic, $P2_1/c$, $a=12.684(7)$, $b=11.740(2)$, $c=11.024(3)$ Å, $\beta = 111.40(4)°$, $V = 1528.3(1)$ Å^3, $Z = 4$, $D_C = 1.127$ g cm^{-3}, $R = 0.056$, $R_W = 0.066$ for 2245 observed reflections.

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