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Intermolecular Ferromagnetic Interaction of 4-Benzylideneamino-2,2,6,6-tetramethylpiperidin-1-oxyl

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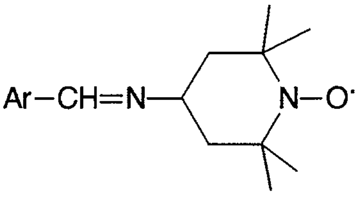
The magnetic properties of a polycrystalline sample of the title compound were studied on a SQUID magnetometer. The intermolecular ferromagnetic interaction was indicated by the upward deviation of the magnetization curves from a Brillouin function with S=1/2 below 16 K and by the increasing effective moment with decreasing temperature. The Weiss constant was + 0.7 K. The radicals possessing a 9-anthryl or 3-perylenyl group in place of the phenyl group showed anitiferromagnetic interaçtion.

Ferromagnetic interactions in crystals of stable organic radicals have been much investigated in connection with organic ferromagnets.[1)] The first purely organic ferromagnet, *p*-nitrophenyl nitronyl nitroxide (T_C = 0.65 K), was reported in 1991.[2)] Organic ferromagnets with higher T_C are now much desired. The charge-transfer complex C_{60}-tetrakis(dimethylamino)ethylene was reported to have T_C = 16.1 K.[3)] There have been a few examples of stable organic radicals showing ferromagnetic behavior with well-defined crystal structures.[4-6)] Recently, intermolecular ferromagnetic interaction of crystalline and single-component organic radicals has been reported by use of nitroxide radicals as spin sources.[6-9)] We have reported that 4-(2-naphthylmethyleneamino)-TEMPO (**1**, TEMPO = 2,2,6,6-tetramethylpiperidin-1-oxyl) involves intermolecular ferromagnetic interaction.[9)] We report here that 4-benzylideneamino-TEMPO (**2**) exhibited stronger ferromagnetic interaction than **1**.

The magnetic susceptibility was measured on a Quantum Design SQUID magnetometer at 0.5 T from 4.5 to 300 K. The magnetization curves were obtained at up to 1 T. The diamagnetic contribution was estimated from Pascal's constants. The TEMPO derivatives investigated here were synthesized from 4-amino-TEMPO and the corresponding aromatic aldehydes by the method described before.[9,10)] The products were purified by repeated recrystallizations to give polycrystalline samples.[11)]



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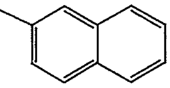

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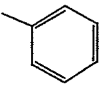

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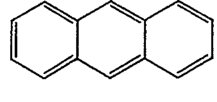

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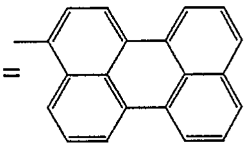

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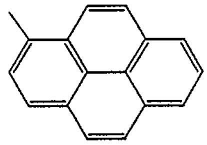


The magnetization curves of **2** measured at 4.5, 8.0 and 16 K are shown in Fig. 1. Theoretical curves of S = 1/2 - 2 with g = 2 are also drawn here. Experimental curves are deviated upward from the theoretical one given by a Brillouin function with S=1/2. The experimental magnetizations are more deviated from the S=1/2 curve at lower temperatures. Figure 2 shows that the plot of the reciprocal susceptibility against temperature for **2** gave a positive Weiss constant (θ). The extrapolation of this plot in the temperature region of 4.5-10 K gave the θ value of + 0.7 K. The Curie constant was determined to be 0.381 emu K mol^{-1}, which confirms the purity of the radical within an experimental error. The effective magnetic moment (μ_{eff}) was almost constant (about 1.76 μ_B) at a high temperature region, but below 40 K it increased with decreasing temperature and reached to 1.92 μ_B at 4.5 K.

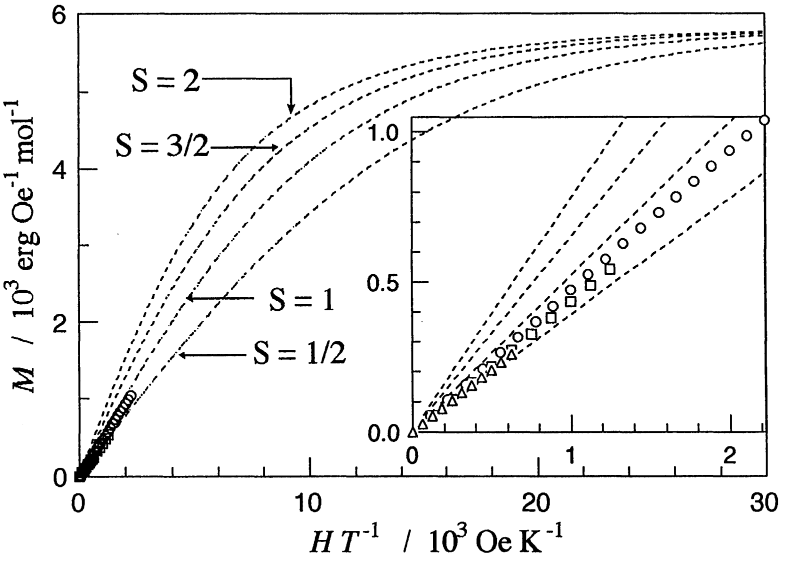


Fig. 1. Magnetization of **2** measured at 4.5 K (circles), 8.0 K (squares), and 16 K (triangles). The dashed lines are given from Brillouin functions with S=1/2, 1, 3/2, and 2. Inset shows the magnification of the plot.

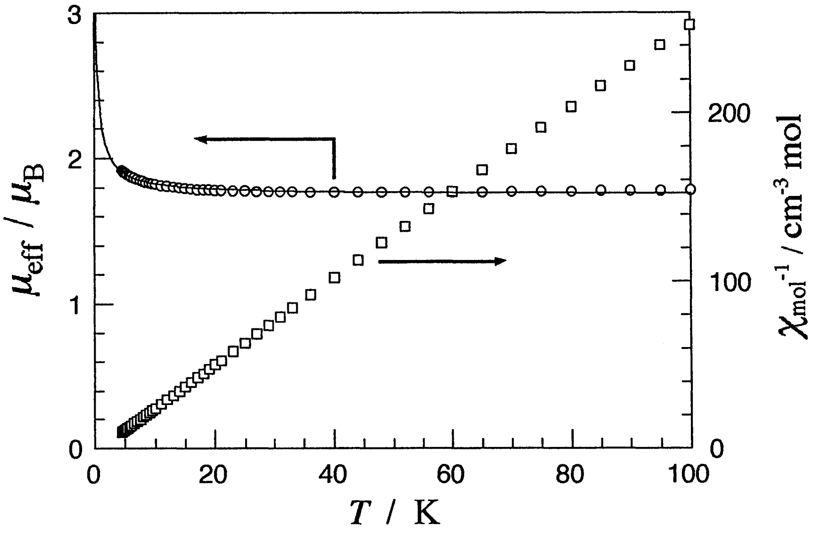


Fig. 2. Temperature dependence of the reciprocal molar magnetic susceptibility (χ_{mol}^{-1}) and the effective magnetic moment (μ_{eff}) of **2**. The solid line is a calculated μ_{eff} curve based on the Heisenberg linear chain model with $J / k_B = 0.87$ K.

These results indicate the presence of intermolecular ferromagnetic coupling in this system. Because of the lack of any structural information, an intermolecular exchange parameter J / k_B of **2** was estimated by both the Heisenberg linear chain model and singlet-triplet model. The former model gave 0.87 K by use of a Padé series expansion (Eq. 1).[12] The latter model gave 2.2 K according to the Bleaney-Bowers equation (Eq. 2).[13] The solid line in Fig. 2 is the calculated curve from the former model.

$$\chi = \frac{Ng^2\mu_B^2}{4k_B T}\left(\frac{1+5.80x+16.90x^2+29.38x^3+29.83x^4+14.04x^5}{1+2.80x+7.01x^2+8.65x^3+4.57x^4}\right)^{2/3} \quad \text{with } x = \exp(-J/2k_B T) \qquad (1)$$

$$\chi = \frac{2Ng^2\mu_B^2}{k_B T}\frac{1}{3+\exp(-2J/k_B T)} \qquad (2)$$

The ferromagnetic interaction of **2** is larger than that of **1**[9] as indicated by the larger values of the Weiss constant and the exchange parameter J. The magnetic properties of the other TEMPO derivatives possessing various aryl groups in place of the phenyl or 2-naphthyl group are also of interest. The magnetic susceptibilities of **3**, **4**, and **5** were measured in a similar manner described above. Figure 3 shows antiferromagnetic behavior of **4** as a typical example. The effective moment of **4** decreased with decreasing temperature. The temperature dependence of the reciprocal susceptibility for **4** gave a negative Weiss constant. These constants were determined to be -0.2, -1.8, and -0.1 K for **3**, **4**, and **5** respectively. Table 1 summarizes the Weiss constants of a series of the TEMPO derivatives.[14] From these findings, less sterically bulky substituents seem to be preferable for ferromagnetic interaction.

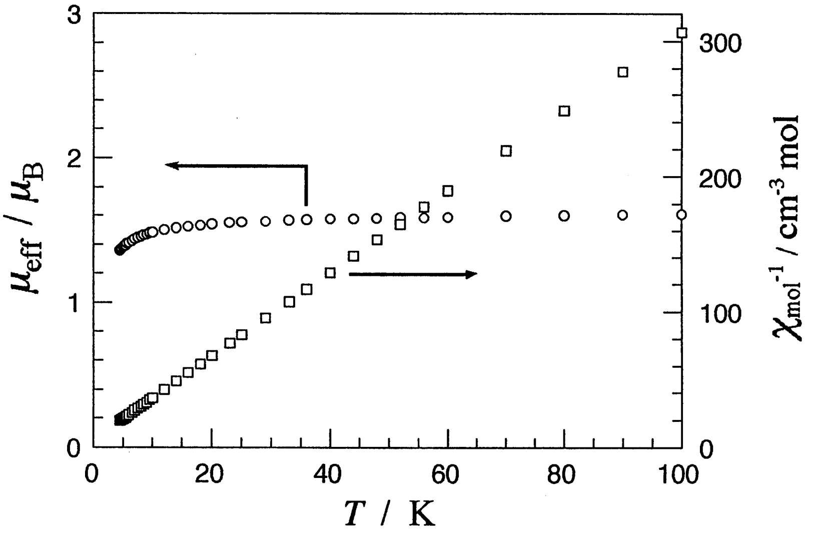
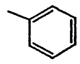
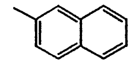
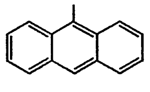
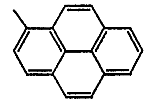
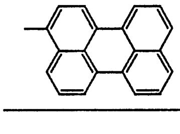


Fig. 3. Temperature dependence of the reciprocal molar magnetic susceptibility (χ_{mol}^{-1}) and the effective magnetic moment (μ_{eff}) of **4**.

Table 1. Weiss constants of the polycrystalline samples of 4-arylmethyleneamino-TEMPO

Ar	Weiss constant, θ / K	Ref.
	0.7	this work
	0.5	9
	-0.2	this work
	-0.1 0.9	this work, 10 10
	-1.8	this work

Since the Ar-CH=N- π-system and the nitroxide radical center are separated by three

sp^3 carbons, the spin polarization mechanism$^{15)}$ on the aromatic groups does not seem to work effectively for magnetic interaction. We are now examining the crystal structures of **1** and **2** to reveal whether their magnetisms depend on exchange or superexchange interaction between the radical centers directly or through the aromatic π-electrons. The TEMPO radicals seem to have delicate magnetic structures, as suggested by the fact that 4-methacryloyloxy-TEMPO was proved to be a metamagnet, while 4-acryloyloxy-TEMPO showed antiferromagnetic coupling.$^{7)}$ A few successful crystal designs such as a sliding molecular stack of triphenyl verdazyl derivatives$^{5)}$ were reported. The introduction of the packing-control substituent to stable organic radicals will be of great interest.

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11) The mass and IR spectra of the new compounds satisfied the presented structures. The melting points (recrystallization solvents) of the compounds are as follows: **2**, 118-120 °C (ethanol); **3**, 171-173 °C (benzene-hexane); **5**, >224 °C, decomp (dichloromethane-ethanol). 1-Naphthyl and 9-phenanthryl derivatives were synthesized only to give oily products.

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14) The material **5** has been reported to have both a positive Weiss constant and very weak antiferromagnetic coupling.$^{10)}$ We are now examining the presence of polymorphism in the crystal of **5**.

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