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Intermolecular Ferromagnetic Interaction of 4-(2-Naphthylmethyleneamino)-2,2,6,6-tetramethylpiperidin-1-oxyl

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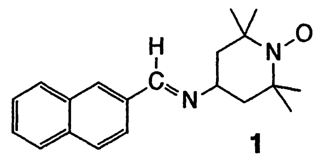
The magnetic susceptibility and magnetization of a polycrystalline sample of the title compound were measured on a Faraday balance and a SQUID susceptometer. The intermolecular ferromagnetic interaction was indicated by the facts that the $\chi_{\mathrm{mol}}T$ value increased with decreasing temperature and that the magnetization measured at 1.7 and 4.2 K saturated more rapidly than that of a Brillouin function with S = 1/2.

Ferromagnetic interactions of organic molecules have been much investigated in connection with exploring organic ferromagnets.[1] Among them the first purely organic ferromagnet was reported for *p*-nitrophenyl nitronyl nitroxide.[2] A possible mechanism was proposed about a parallel spin alignment on the radical substituent adjacent to a donor or acceptor molecule in charge-transfer complexes.[3] In the course of experimental studies based on this strategy,[4] we have found that 4-(2-naphthylmethyleneamino)-2,2,6,6-tetramethylpiperidin-1-oxyl (**1**)[5] involves intermolecular ferromagnetic interaction.



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The magnetic susceptibility was measured on a Faraday balance at 2 T from 2 to 280 K and on a SQUID susceptometer at 0.5 T from 4.5 to 300 K. The data obtained at low temperatures on the balance were corrected for the saturation effect. The magnetization curves were obtained on the balance at up to 7 T. The diamagnetic contribution was estimated from Pascal's constants.

The plot of the reciprocal susceptibility against temperature for **1** (Fig. 1) gave a positive Weiss constant (0.5 K) from the data obtained on the Faraday balance. The product $\chi_{\mathrm{mol}}T$ increased with decreasing temperature down to 2 K. Reproducibility of the increasing tendency of $\chi_{\mathrm{mol}}T$ was confirmed by the SQUID measurements as shown in the inset of Fig. 1.

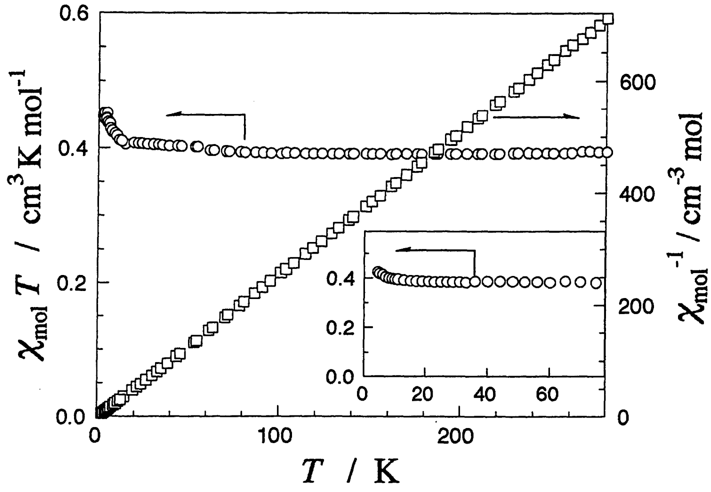

Fig. 1. Temperature dependence of the reciprocal magnetic susceptibility (χ_{mol}^{-1}) and the product $\chi_{\mathrm{mol}}T$ for **1** measured on a Faraday balance. Inset: temperature dependence of $\chi_{\mathrm{mol}}T$ measured on a SQUID susceptometer.

The magnetization curves for **1** measured at 1.7 and 4.2 K are shown in Fig. 2. Theoretical curves for various spin values are superimposed here. Experimental curves exhibit more rapid saturation than that of the theoretical one for S=1/2 and the magnetization saturates more rapidly at lower temperature.

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 1 was estimated by both the Heisenberg linear chain model[6] and singlet-triplet model.[7] On the assumption of the former model the value was obtained to be 0.2 K. The latter model gave the value of 1.2 K.

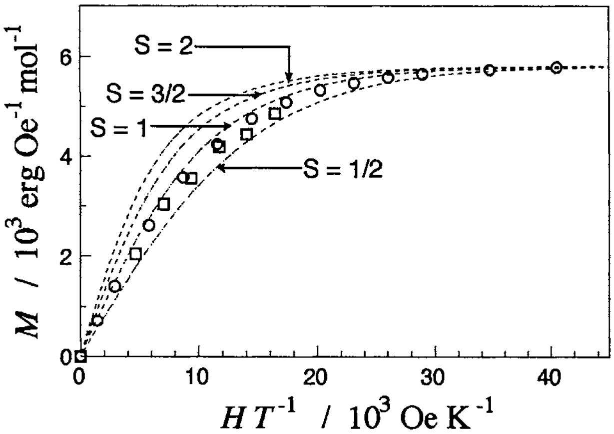

Fig. 2. Magnetization for 1 measured at 1.7±0.1 K (circles) and 4.2±0.1 K (squares). The dashed lines are based on Brillouin functions with S=1/2, 1, 3/2, and 2.

4-Methacryloyloxy-2,2,6,6-tetramethylpiperidin-1-oxyl has been recently proved to be a metamagnet, while its acryloyloxy derivative showed antiferromagnetic coupling.[8] Antiferromagnetic coupling between ferromagnetic sheets in TANOL suberate was reported.[9] These TEMPO radicals seem to have delicate magnetic structures. We are now investigating the magnetism below 1.7 K and the crystal structure for 1.

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