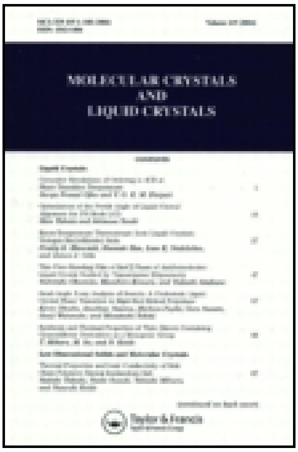

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Intermolecular Ferromagnetic Interaction of 4-(1-Pyrenylmethyleneamino)-2,2,6,6-Tetra Methylpiperidin-1-Oxyl

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INTERMOLECULAR FERROMAGNETIC INTERACTION OF 4-(1-PYRENYLMETHYLENEAMINO)-2,2,6,6-TETRAMETHYLPIPERIDIN-1-OXYL

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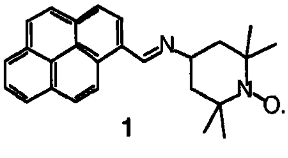
Abstract The magnetic properties of a microcrystalline sample of the title free radical were measured. This magnetic behavior can be interpreted in terms of ferromagnetic interaction inside chains or sheets accompanied by antiferromagnetic coupling between them. Other organic TEMPO derivatives containing donor or acceptor sites were synthesized.

INTRODUCTION

Ferromagnetic interactions of organic molecules have been much investigated in connection with exploring materials of organic ferromagnets.[1] A possible mechanism was proposed using a parallel spin alignment on the radical substituent adjacent to a donor or acceptor molecule in charge-transfer complexes.[2,3] When a donor or acceptor molecule carrying a radical substituent is used as a component in CT complexes, the spins on the radical substituents might be aligned in parallel, irrespective of the ferromagnetic or antiferromagnetic couplings between the radical and donor radical cation (or acceptor radical anion) sites. In the course of experimental studies based on this strategy, we have found that 4-(1-pyrenylmethyleneamino)-2,2,6,6-tetramethylpiperidin-1-oxyl (**1**) exhibited ferromagnetic interactions by itself, whereas the complexes with F_4TCNQ[3] or DDQ were paramagnetic materials.



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RESULTS AND DISCUSSION

Condensation between 1-pyrenecarboxaldehyde and 4-amino-2,2,6,6-tetramethyl-piperidin-1-oxyl in benzene at 60 °C for 6 h under nitrogen followed by cooling and filtration gave crude orange bricks of **1** (62%). The sample used for magnetic measurements was purified by repeated recrystallization from ethanol-dichloromethane to give fine needles (mp 185-187 °C). The magnetic susceptibility of **1** was obtained on an Oxford Instruments Faraday-type magnetic balance. The temperature dependence of the susceptibility was measured in a field of 1 T with a field gradient of 5 T/m over a temperature range of 1.6 to 300 K. The diamagnetic contribution was estimated from that of 4-(1-pyrenylmethyleneamino)-2,2,6,6-tetramethylpiperidine synthesized and measured separately under similar conditions and was subtracted from the observed susceptibility of **1**.

The extrapolation of the plot of the reciprocal susceptibility above 10 K against temperature (Figure 1) for **1** gave a positive Weiss constant (0.9 K), indicating ferromagnetic interactions of **1**. With decreasing temperature, the effective moment increased and reached a maximum of 1.80 μ_B at about 10 K and then decreased to 1.76 μ_B at 5.6 K. This suggests that antiferromagnetic interactions occur among the spin clusters within which the spins are already ferromagnetically coupled. In spite of the lack of structural information, an exchange parameter of the ferromagnetic coupling was estimated[4] to be 4.4 K on

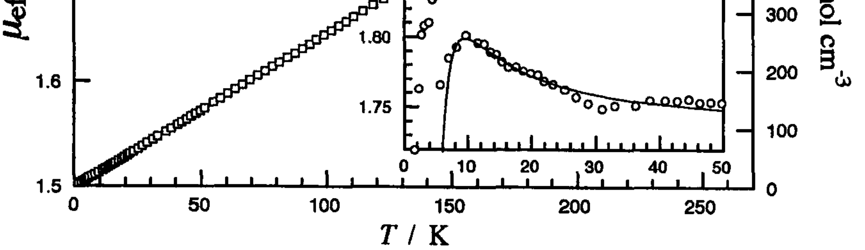


FIGURE 1 The temperature dependence of the reciprocal magnetic susceptibility and the effective moment of **1**. Inset: the experimental data (circle) and the theoretical curve of the moment (solid line, see text and ref [4]) in a low temperature region.

the assumption that the clusters had the structure of a one-dimensional Heisenberg chain[5] and the averaged interchain coupling was attributed to a single Weiss constant (-3.7 K). Chouteau[6] and Benoid[7] reported that TANOL suberate was an organic metamagnet and involved an antiferromagnetic coupling between sheets which consisted of ferromagnetically coupled 1/2-spins. Our case may also be explained by a sheet structure similar to theirs. The ferromagnetic interaction of 4-methacryloyloxy-2,2,6,6-tetramethylpiperidin-1-oxyl has been reported recently.[8] Therefore, more attention should be paid to TEMPO derivatives from the viewpoint of organic ferromagnetism.

However, a polycrystalline red brick sample purified by recrystallization from toluene-dichloromethane showed only paramagnetic behavior down to 4.5

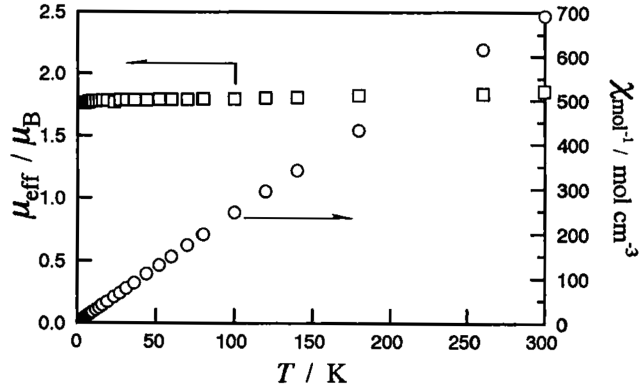


FIGURE 2 The temperature dependence of the reciprocal magnetic susceptibility and the effective moment of a different batch of **1**.

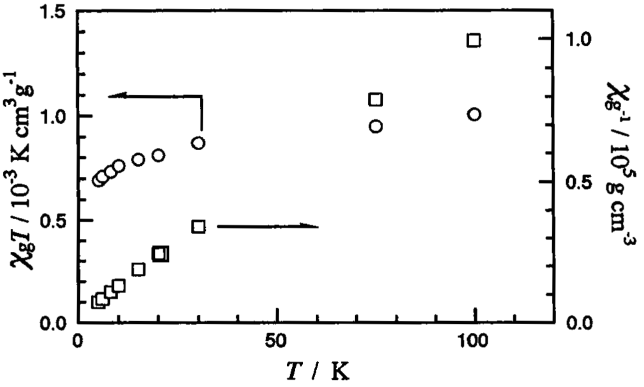
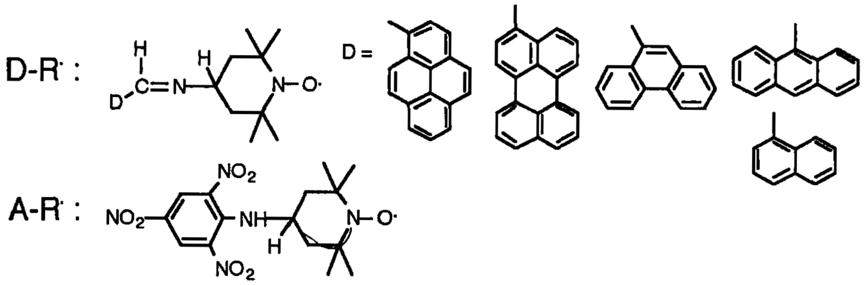


FIGURE 3 The temperature dependence of the reciprocal magnetic susceptibility and the effective moment of the complex of **1** with DDQ.

K when measured on a Quantum Design MPMS SQUID susceptometer at 0.5 T over a temperature range of 4.5 to 300 K (Figure 2). We are currently investigating the reproducibility of this magnetic behavior and the dependence of the crystalline forms.

The complexes of 1 with $TCNQF_4$[3] or DDQ exhibited paramagnetic or slightly antiferromagnetic behavior (Figure 3). We also synthesized TEMPO derivatives containing a 2,4,6-trinitrophenyl group as an acceptor site as well as a perylenyl, anthracenyl, or naphtyl group as a donor site. Some magnetic properties were measured. They are all paramagnetic materials by themselves.



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4) The fitting equation is deviated by a Weiss factor $T/(T-\theta)$ from Padé series expansion[5] as follows:

$$\chi = \frac{Ng^2\mu_B{}^2}{4\,k(T-\theta)}\,\frac{1+5.80x+16.90x^2+29.38x^3+29.83x^4+14.04x^5}{1+2.80x+7.01x^2+8.65x^3+4.57x^4} \quad \text{where}\, x = \exp(-J/2kT).$$

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