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Communications to the Editor

Magnetically Coupled Molecular System Composed of Organic Radicals with Different Spin Multiplicities

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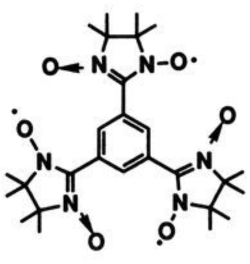
Construction of organic ferromagnets and ferrimagnets has been one of the challenging targets for organic and physical chemists since the theoretical basis of these fascinating materials was proposed.[1] While some molecular organic ferromagnets are now known,[2] organic ferrimagnets have not yet been realized.[3] Although an approach toward this goal is conceptually straightforward, there are some practical problems from the viewpoint of crystal engineering.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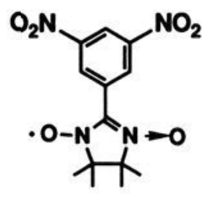
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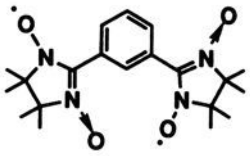
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Recently we succeeded in preparing 1:1 mixed crystals where triradical **1** and 1,3,5-trinitrobenzene (TNB) are stacked alternately, held together by electrostatic interactions between nitronyl nitroxide (NN) groups of **1** and nitro groups of TNB.[4] Since application of this strategy for preparing an organic ferrimagnetic system should be promising, monoradical **2**, carrying two nitro groups on the phenyl ring, was selected as an appropriate partner for diradical **3**, whose ground-state spin multiplicity was proved to be triplet through intramolecular ferromagnetic coupling.[5]

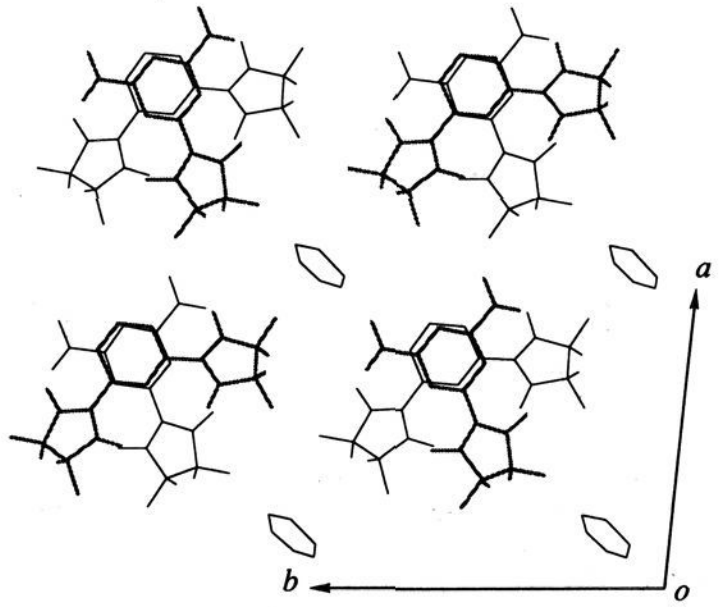

Figure 1. Crystal structure of the mixed crystal $\mathbf{2}\cdot\mathbf{3}\cdot\mathrm{C_6H_6}$ normal to the *ab* plane. Molecules drawn by thick lines are located on the same plane.

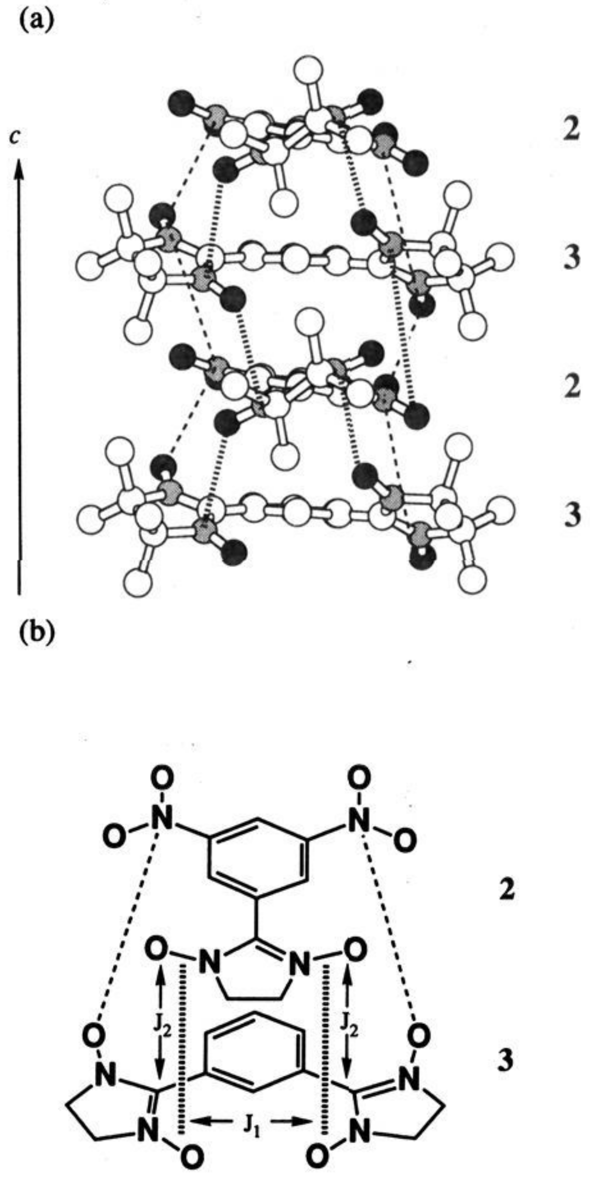

Figure 2. (a) Column structure of $\mathbf{2}\cdot\mathbf{3}\cdot\mathrm{C_6H_6}$. The broken lines (- - -) represent electrostatic interactions between the nitro group of **2** and the nitroxide moiety of **3**, and the dotted lines (···) represent electrostatic and magnetic interactions between the NN groups of **2** and **3**. (b) Schematic structure of the overlapping mode of monoradical **2** and diradical **3**; intramolecular ferromagnetic coupling J_1 and intermolecular antiferromagnetic coupling J_2 are also shown. Methyl groups are omitted for clarity.

Mixed-stack crystals of monoradical **2** and diradical **3** were obtained as black rods ($\mathbf{2}\cdot\mathbf{3}\cdot\mathrm{C_6H_6}$) from a benzene solution by slow evaporation of the solvent. The crystal structure of the mixed crystal viewed normal to the *ab* plane is shown in Figure

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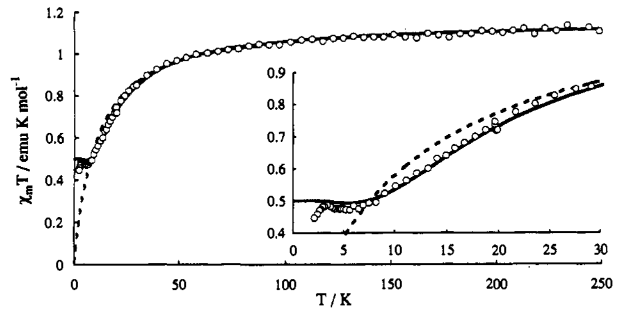

Figure 3. χT vs T plot of $2{\cdot}3{\cdot}C_6H_6$. The experimental data are represented by open circles. Calculated curves based on Curie–Weiss law ($\theta = -10$ K) and on a Heisenberg Hamiltonian are also shown by a broken line and a solid line, respectively. The inset is an expansion of the data at temperatures lower than 30 K.

1.[6] Two kinds of radical molecules, **2** and **3**, are stacked alternately to form a columnar structure along the *c* axis as presented in Figure 2. In examining the overlap between **2** and **3** more closely, one finds short intermolecular distances (3.04–3.40 Å) between the nitro groups of **2** and the NN groups of **3** on the rear side, presumably derived from electrostatic interactions between the positively charged nitrogen atom of the nitro group and the negatively charged oxygen atom of the NN group. As a result of electrostatic interactions, the NN groups of **3** on the front side are located in proximity to that of **2**, stacked above and below. Although the distances between NN groups of **2** and **3** are not equal, they are in the range of 3.18–3.38 Å. These geometrical features should cause the antiferromagnetic interaction to be of reasonable strength (Figure 2). On the other hand, any intercolumnar magnetic interaction is expected to be very weak, because the NN groups of **2** and **3** in the column are separated from those in adjacent columns by methyl groups and by included benzene molecules (Figure 1). Therefore, the structure of the mixed crystal can be regarded as a pseudo-one-dimensional magnetic system.

Magnetic susceptibility of the mixed crystal was measured by a Faraday-type magnetic balance at temperatures between 2.2 and 250 K. The χT vs T plot is shown in Figure 3, where the molar χ value is evaluated for the repeating unit of $2{\cdot}3{\cdot}C_6H_6$. Judging from the χT value (1.13 emu K/mol) at 250 K, all spins behave paramagnetically at higher temperatures, while the value becomes gradually smaller with decreasing temperature until 10 K due to the presence of intermolecular antiferromagnetic interaction between **2** and **3**. The temperature dependence of the magnetic susceptibility obeys Curie–Weiss law with $\theta = -10$ K (Figure 3). In the temperature range of 4–6 K (refer to the inset of Figure 3), the χT value becomes nearly constant (0.48 emu K/mol). This value is larger than 0.375 emu K/mol expected for one paramagnetic spin ($S = {}^1/_2$) which remains as a result of the antiferromagnetic coupling among three spins in the repeating unit. Thus the magnetic behavior suggests that a short-range magnetic spin coupling starts to appear at temperatures lower than 10 K (Figure 3). The saturation value of $M_s = 1.0$ $\mu_B/2{\cdot}3{\cdot}C_6H_6$ at 30 kOe/K suggests that one-third of the total spins contribute to the magnetization. In addition, the average spin multiplicity of the sample at 2.2 K is found to be about 1.1 by curve fitting using a Brillouin function.

The spin system of the mixed crystal consists of an intramolecular ferromagnetic coupling (J_1) of **3** and intermolecular antiferromagnetic couplings (J_2) between **2** and **3**. Judging from the intermolecular distances between the NN groups of **2** and **3**, the antiferromagnetic interactions between the NN groups of **3** and that of **2** above and below are not distinctly different, and they are approximated to be equal. Thus the spin system can be theoretically analyzed using a Heisenberg Hamiltonian, with parameters of J_1 and J_2 as shown in Figure 2b. A theoretical value of χT was evaluated by diagonalization of the Heisenberg Hamiltonian for a six-spin configuration with a periodic boundary condition. The experimental values in the χT vs T plot were well reproduced by $J_1/k_B = +20$ K and $J_2/k_B = -30$ K, although the decrease in the χT value at temperatures below 3 K shows the existence of an additional antiferromagnetic interaction between the units.

In summary, a magnetically coupled organic molecular system composed of different spin multiplicities was first constructed using monoradical **2** and diradical **3**. The spin system is unique from the aspect of the competing magnetic interaction between intramolecular ferromagnetic and intermolecular antiferromagnetic couplings, although ferrimagnetic spin ordering has not been achieved. This sharply contrasts with one-dimensional metal–metal or metal–radical ferrimagnetic systems, where an extremely large ferromagnetic interaction is guaranteed by electron spins in d orbitals of metal ions.

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(6) Crystal data: $C_{33}H_{43}N_8O_{10}{\cdot}C_6H_6$, $M = 789.87$, triclinic, space group $P1$, $a = 11.526(3)$, $b = 13.260(2)$, and $c = 7.288(2)$ Å, $\alpha = 106.57(2)°$, $\beta = 106.34(3)°$, $\gamma = 90.38(2)°$, $V = 1020.0(5)$ Å^3, $Z = 1$, $D_c = 1.286$ g cm^{-3}. $R = 0.059$ for 2807 independent reflections $[|F_0| \geq 3\sigma(|F_0|)]$ and 711 parameters.