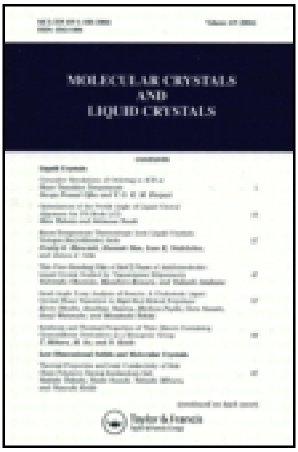

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STABLE MONO-, DI-, AND TRIRADICALS AS CONSTITUENT MOLECULES FOR ORGANIC FERRIMAGNETS

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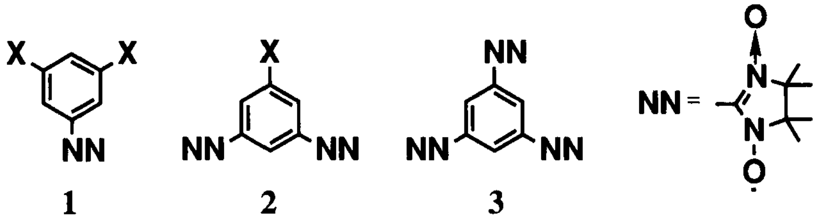
Abstract In order to realize organic ferrimagnets, we have prepared stable organic radicals, mono-, di-, trinitronyl nitroxides (**1**~**3**) with different spin multiplicities. Among them, intramolecular ferromagnetic couplings in tri- and diradicals (**3** and **2a**), which are hidden by antiferromagnetic intermolecular interaction in the neat sample, were elucidated by using mixed crystals of **3** and **2a** and trinitrobenzene (**2a**:TNB = 1:1, **3**:TNB = 1:1). An X-ray crystallographic analysis of the mixed crystals revealed that **3** or **2a** and TNB are stacked alternately in a one-dimensional column along the *c* axis. Ferromagnetic coupling in **3** was determined to be J/k_B=23 K by applying a triangular cluster model, and that for **2a** (J/k_B=23K) was consistent with the above results.

INTRODUCTION

High spin organic molecules are important building blocks for constructing organic magnetic material.1) If stable polyradicals with different spin multiplicities are stacked alternately with antiferromagnetic interaction, the mixed crystal should exhibit ferrimagnetic property. The importance of ferrimagnets can be easily understood by the practical utility of magnetite. As constituent molecules for organic ferrimagnets stable mono-, di-, and triradicals (**1**,**2**,**3**) were prepared.



a : $X = H$, b : $X = NO_2$

RESULTS & DISCUSSION

Among designed polyradicals, we are interested in an intramolecular magnetic coupling of 1,3,5-tris(4',4',5',5'-tetramethylimidazolin-2'-yl)benzene-3',3'',3'''-trioxide-1',1'',1'''-trioxyl (**3**) and 1,3-bis(4',4',5',5'-tetramethylimidazolin-2'-yl)benzene-1',1''-dioxide-3',3''-dioxyl (**2**) as reasonably stable tri- or diradical which is supposed to have a quartet or triplet spin multiplicity in the ground state, respectively, based on the spin correlation through the meta-substituted phenyl ring.[2] Recently an unusual magnetic property of powdered sample of **3** has been reported.[3] In order to re-examine magnetic property of

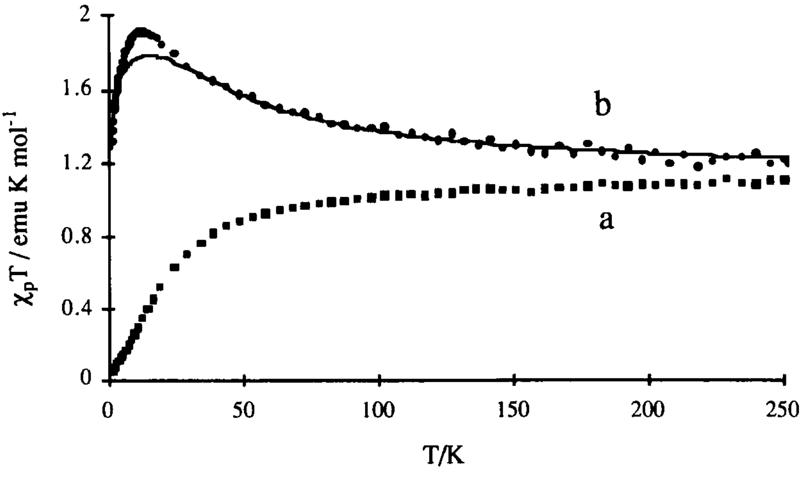


FIGURE 1 Temperature dependence of the χ_pT for the neat sample (plot a, ■) and the 1:1 mixed crystals (plot b,●) with 1,3,5-trinitrobenzene: the solid line is a theoretical curve obtained by the triangular model with $J/k_B = 23$ K, $\theta = -0.7$K.

3, we measured temperature dependence of magnetic susceptibility cautiously on a neat powdered sample. Besides we prepared mixed crystals of **3** with 1,3,5-trinitrobenzene (TNB) to obtain more detailed information on the intramolecular magnetic coupling.

When the magnetic susceptibility of a powdered sample of **3** was measured, only the antiferromagnetic interaction was observed (θ = -14K)(plot a in FIGURE 1). The result suggests that the intrinsic ferromagnetic (FM) coupling in **3** is hidden by the relatively strong intermolecular AF interaction.

In order to evaluate intramolecular magnetic coupling which is hidden in the neat sample, we prepared mixed crystals of **3** by which the intermolecular AF interaction could be suppressed. Slow evaporation of a chloroform solution of **3** and TNB afforded single crystals of a complex with an equimolar composition. An X-ray crystallographic analysis of the crystal revealed that **3** and TNB are stacked alternately in a one-dimensional column along the *c* axis as shown in FIGURE 2a.[4] These columns run in parallel each other and no appreciable intercolumnar van der Waals contacts are recognized. Since tilting of nitronylnitroxide (NN) groups to the benzene ring (32.8° and 25.5°) is not in a propeller-like manner, the molecule has not C_3 but C_2 symmetry . The shortest intermolecular distances (3.078(7) Å) are found between the oxygen atoms of NN and nitrogen atoms of the nitro groups which belong to two TNB molecules placed above and below **3** in the column. The

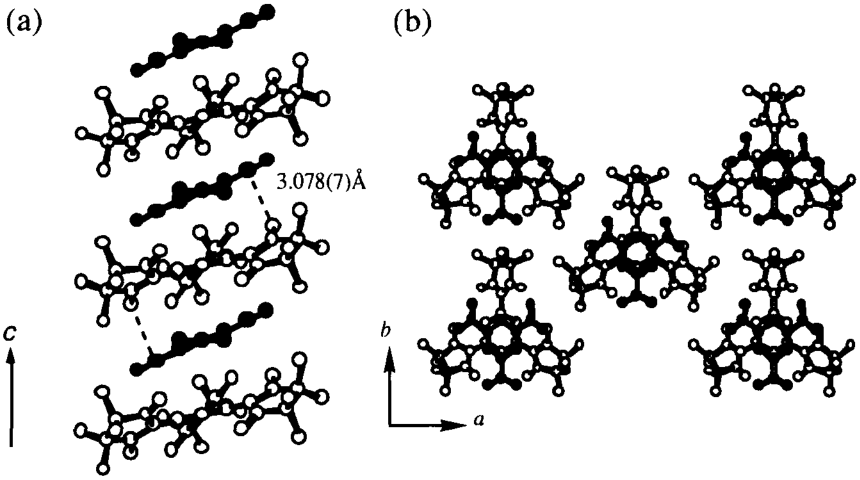


FIGURE 2 Crystal structure of **3**•TNB: (a) a stacking column along the *c* axis: dotted lines depict shortest N•••O distances; (b) a molecular overlapping scheme projected along the *c* axis.

interaction may be of a Coulombic nature between negatively charged oxygen atoms in NN groups and positively charged nitrogens in the nitro groups.[5] No appreciable CT band was observed when an absorption spectrum of the complex was recorded in a KBr pellet.

The χ_pT vs. T plot of the complex **3**•TNB is also shown by the plot b in FIGURE 1. The result shows a sharp contrast to the case of the neat sample of **3**. Although the Curie constant of the complex has a limit value of 1.13 emu K mol^{-1} ($3 \times S = 1/2$) at the high temperature side as in the case of the powdered sample, the χ_pT value increases gradually with lowering temperature. The experimental value approaches to 1.88 emu K mol^{-1} at T = 10 K, which corresponds to S = 3/2. Thereafter the χ_pT plot exhibits a convex curve at lower temperatures than 10 K due to intermolecular AF interaction. The result may be interpreted that three spins of **3** behave independently to give S = 1/2 at the high temperature limit and that these spins interact ferromagnetically at low temperatures to give S = 3/2 species. The experimental data can be reproduced by a triangular model with $J/k_B = 23$ K, $\theta = -0.7$K (FIGURE 1) using the following equation (1). Compared with the result on the neat sample, the intramolecular FM coupling becomes observable by inserting

$$\chi_pT = \frac{Ng^2\mu_B^2}{4k_B}\frac{5+\exp(-3J/k_BT)}{1+\exp(-3J/k_BT)}\frac{T}{T-\theta} \text{ ---------------- } (1)$$

spacers of TNB between **3**. The weak intermolecular AF interaction detected in the complex seems to be originated from a superexchange type interaction through TNB.

The same methodology was applied to determine the ferromagnetic coupling of **2a**.[6] The mixed crystals of **2a** and TNB was prepared. Two kinds of crystals with the different composition was formed (**2a**:TNB = 1:1, **2a**:TNB = 1:2). The χ_pT vs. T plot of the complex **2a**•TNB (1:1) was reasonably reproduced by $J/k_B = 23$K, $\theta = -2.0$K using the following equation (2). The degree of ferromagnetic coupling is consistent with the previous case.

$$\chi_pT = \frac{Ng^2\mu_B^2}{k_B}\frac{1}{3+\exp(-2J/k_BT)}\frac{T}{T-\theta} \text{ ------------- } (2)$$

Although crystal structure of the complex of **2a**•TNB(1:1) has not been determined yet, that of 1:2 complex was elucidated. As shown in FIGURE 4, diradical **2a** was sandwiched by two TNB molecules above and below[7]. The NN groups of **2a** are twisted to the same direction. Oxygen atoms of NN groups are close to the nitrogen

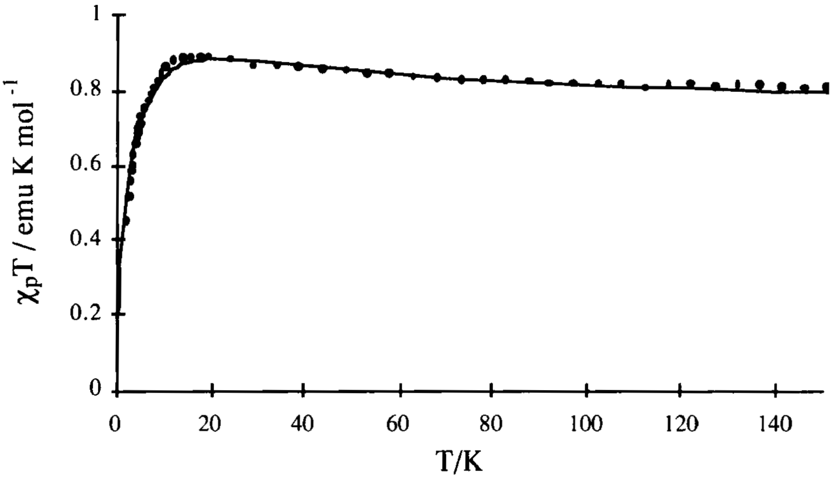


FIGURE 3 Temperature dependence of the χ_pT for the 1:1 mixed crystals (●) with 1,3,5-trinitrobenzene: the solid line is a theoretical curve obtained by equation (2) with J/k_B = 23 K, θ = -2.0K.

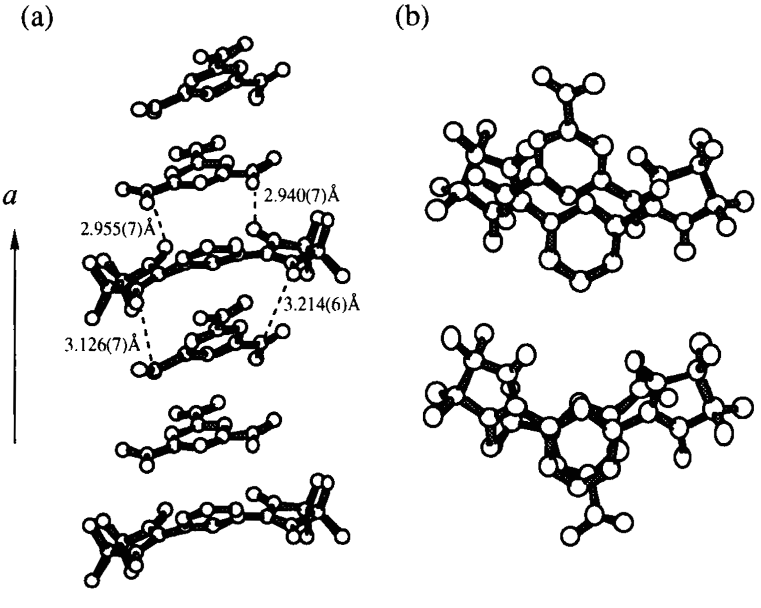


FIGURE 4 Crystal structure of **2a**•$(TNB)_2$: (a) a stacking column along the *a* axis: dotted lines depict N•••O distances; (b) a molecular overlapping scheme projected along the *a* axis.

atoms of two nitro groups of the above TNB and the other two oxygens of NN groups are close to the two nitrogen atoms of TNB located below.

In summary intramolecular ferromagnetic coupling in **3** and **2a** was first determined by using such mixed crystals of **3** or **2a** and TNB. The information is extremely important in constructing ferrimagnets using stable radicals with different spin multiplicities. Preparation of mixed crystals using stable mono-, di-, and triradicals are in progress.

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4) Crystal data for **1**•TNB: $C_{33}H_{42}N_9O_{12}$, M = 756.75, monoclinic, space group C_2, a = 21.158(3)Å, b = 12.374(2)Å, c = 7.285(1)Å, β = 104.79(1)°, V = 1844.0(5)Å^3, Z = 2, D_C = 1.362 g•cm^{-3}. The final R value is 6.0% for 1725 reflections with $|F_O| > 3\sigma|F_O|$. Anal. Found: C 52.25; H 5.61; N 16.72%. Calcd for $C_{33}H_{42}N_9O_{12}$: C 52.38; H 5.59; N 16.66%.

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7) Crystal data for **2a**•$(TNB)_2$: $C_{32}H_{34}N_{10}O_{16}$, M = 814.68, monoclinic, space group $P2_1/n$, a = 11.757(2)Å, b = 43.462(7)Å, c = 7.380(1)Å, β = 97.24(1)°, V = 3741(1)Å^3, Z = 4, D_C = 1.445 g•cm^{-3}. The final R value is 7.6% for 3330 reflections with $|F_O| > 3\sigma|F_O|$.