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Purely Organic Magnetism of Pyridyl-Substituted Stable Thioaminyl Radicals

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N-[(4-Nitrophenyl)thio]- (**1a**) and *N*-[(2,4-dichlorophenyl)thio)]-2,6-diphenyl-4-(3-pyridyl)phenylaminyl (**1b**), *N*-[(4-nitrophenyl)thio]- (**2a**) and *N*-[(2,4-dichlorophenyl)thio]-4-phenyl-2,6-di(3-pyridyl)phenylaminyl (**2b**) were generated by PbO_2 oxidation of the corresponding precursors and isolated as radical crystals. For **1b** X-ray crystallographic analysis was performed. The magnetic susceptibility measurements were carried out for the isolated radicals using a SQUID magnetometer in the temperature range 1.8 – 300 K. The susceptibilities of **1a** and **2a** were analyzed in terms of a one-dimensional (1D) antiferromagnetic (AFM) regular Heisenberg model with exchange interaction of $2J/k_B = -63.4$ and -17.8 K, respectively, and that of **1b** was interpreted in terms of a 1D AFM alternating Heisenberg model with $2J/k_B = -12.8$ K and $\alpha = 0.91$. On the other hand, that of **2b** was explained in terms of a 1D ferromagnetic regular Heisenberg model with $2J/k_B = 22.4$ K.

Keywords: Stable free radicals; Magnetism; Isolation; X-ray crystallography

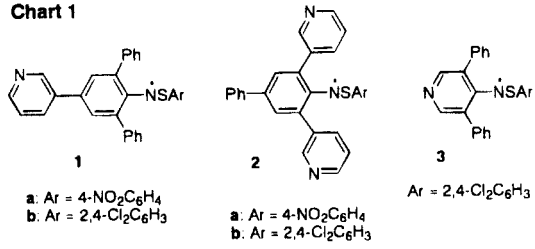
INTRODUCTION

Since the discovery of the first purely organic ferromagnet with $T_C = 0.60$ K in 1991[1], magnetism of stable free radical crystals has attracted much

attention. Since the discovery of the first organic ferromagnet, a variety of stable free radical crystals have been investigated, and 18 kinds of organic ferromagnets have been found[2-13]. However, since free radicals are inherently unstable, examples of isolable free radicals are seriously limited[14], and the free radicals whose magnetism has been investigated have been almost limited to nitroxide and nitronyl nitroxides. Therefore, the quest of a new class of stable free radicals is strongly desired for the further advances in chemistry and physics of purely organic magnetism. Standing on this background, we have made an effort to search for a new class of isolable stable free radicals[15], and it has been found that *N*-(arylthio)-2,4,6-triarylphenylaminyls and their derivatives are isolable stable free radicals[16-19]. Magnetic studies of the thioaminyl radical crystals have shown that four radicals crystals couple ferromagnetically with $2J/k_B$ = +3.6–+28.0 K[20].

In the present work five kinds of pyridyl-substituted thioaminyl radicals, **1a**, **1b**, **2a**, **2b** , and **3** (see Chart 1) were investigated. Of the five radicals investigated, the former four radicals could be isolated as radical crystals, and one of them (**1b**) was investigated by X-ray crystallography. The magnetic studies for the isolated radical crystals revealed that, although the magnetic interactions of **1a**, **1b**, and **2a** were antiferromagnetic (AFM), that of **2b** was ferromagnetic (FM). Herein we report isolation, X-ray crystallographic analysis, and magnetic characterization of **1** and **2**.

Chart 1

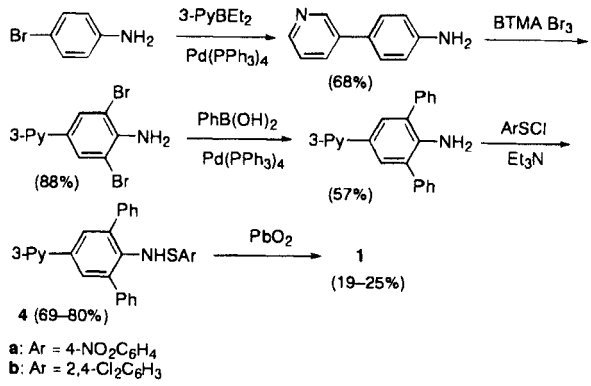


EXPERIMENTAL

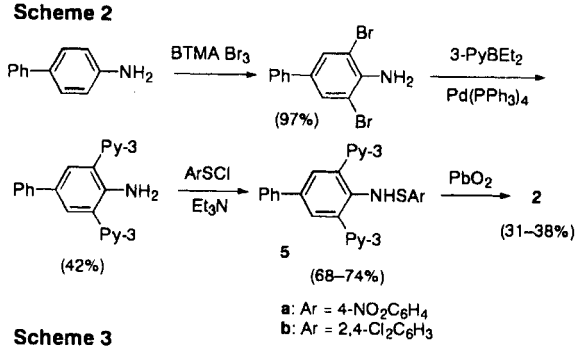
Precursors **4**, **5**, and **6** were prepared according to Schemes 1, 2, and 3, and isolation of **1** and **2** were performed as follows: a benzene solution of a

precursor was treated with PbO_2. After filtration, the benzene was removed by freeze-drying, and the residue was crystallized from EtOH or hexane–ethyl acetate to give pure radical crystals.

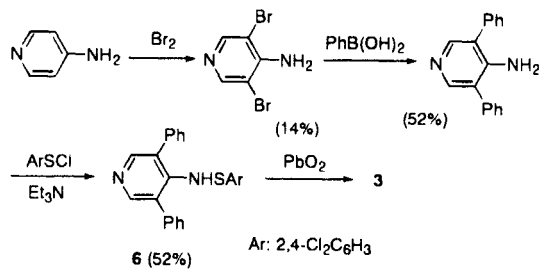
Scheme 1



Scheme 2



Scheme 3



RESULTS and DISCUSSION

Preparation of Precursors and Isolation of Radicals

Preparation of precursors **4**, **5**, and **6** are shown in Schemes 1, 2, and 3.

Oxidation of **4**, **5**, and **6** was carried out in benzene with PbO_2. When PbO_2 was added to a stirred solution of **4**, **5**, or **6**, an initially light yellow (**4a**, **5a**) or colorless solution (**4b**, **5b**, **6**) immediately turned green (**1b**, **2a**, **2b**), yellowish green (**1a**), or purple (**3**), and intense ESR signals were observed from the solutions. Although **3** was gradually decomposed in solution ($t_{1/2}$ ~ 8 h at 20 °C), **1a**, **1b**, **2a**, and **2b** were quite persistent and could be isolated radical crystals.

Isolation of **1a**, **1b**, **2a**, and **2b** were carried out as follows: the precursors were treated with PbO_2 in benzene and, after filtration, the solvent was removed by freeze-drying. The resulting dark green or blue crystalline residue was crystallized from hexane–ethyl acetate (**1a**, **1b**, and **2b**) or EtOH (**2a**) to give radical crystals in 19–38% yields. The IR spectra showed no presence of a NH group, and the elemental analyses agreed with the calculations. The magnetic susceptibility measurements carried out with a SQUID magnetometer showed >93% purity for the isolated radicals.

X-Ray Crystallographic Analysis

Although **1a**, **1b**, and **2b** crystallized to microcrystals, **1b** provided a sufficiently large single crystal for X-ray crystallography. The molecular and crystal structure of **1b** are shown in Figures 1 and 2.

The X-ray crystallographic results show that there are two conformers in the crystals of **1b**. One is a syn-form, and the other is an anti-form. In the syn-form the pyridyl nitrogen and ortho chlorine atom on the phenylthiyl benzene ring are in the same side with respect to the ring A–N–S–ring E π-framework of the radical molecule, and in the anti-form they are in the opposite side to each other. The bond lengths and bond angles are nearly identical to each other, but the torsion angles are somewhat different.

Magnetic Characterization for Isolated Radicals

The magnetic properties of **1a**, **1b**, **2a**, and **2b** were investigated using polycrystalline samples in the temperature range 1.8–300 K on a SQUID magnetometer. The diamagnetic components were estimated using Pascal's constants. The radical purities of **1** and **2** were determined to be 98.5 (**1a**), 95.0 (**1b**), 93.0 (**2a**), and 99.0% (**2b**) from the magnetic susceptibility

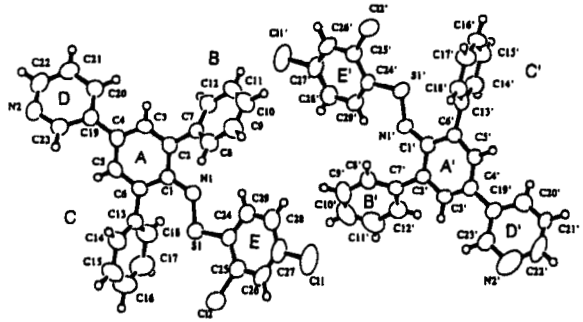


FIGURE 1. Molecular structure of **1b**.

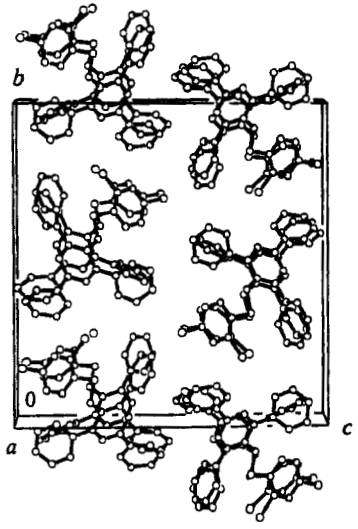


FIGURE 2. Crystal structure of **1b**.

measurements.

Figure 3 shows the temperature dependence of $\chi_{mol}T$ for **2b**. The $\chi_{mol}T$ value are nearly constant in the temperature region above 50 K, and below this temperature it increases drastically with decreasing temperature. This profile indicates that the intermolecular magnetic interaction is FM, and the $\chi_{mol}T$ vs T plots have been well analyzed using a one-dimensional (1D) regular Heisenberg model (eq 1)[21] with interchain interaction of $2J/k_B$ = 22.4 K, as shown in Figure 3.

$$\mathcal{H} = -2J \Sigma S_i \cdot S_j \qquad (1)$$

The temperature dependence of χ_{mol} for **1b** is shown in Figure 4. As found in the figure, χ_{mol} increases gradually and reaches a maximum at 10 K with decreasing temperature. Then, it decreases with decreasing temperature. This profile indicates that the interaction between the neighboring spins is AFM. The χ_{mol} vs T plots were analyzed with an alternating linear-chain model (eq 2, where α is an alternation parameter)[22], and the best fit with the experiment gave $2J/k_B = -12.8$ K and $\alpha = 0.91$.

$$\mathcal{H} = -2J \Sigma(S_{2i-1} \cdot S_{2i} + \alpha S_{2i} \cdot S_{2i+1}) \qquad (2)$$

As found in Figure 2, the radical molecules are stacked alternately with the syn and anti-froms along the crystallographic *a* axis. The SOMO-SOMO overlap between the neighboring molecules is observed along this direction, and this leads to antiferromagnetic exchange interaction between the unpaired electron spins.

The temperature dependence of χ_{mol} for **1a** are shown in Figures 5. χ_{mol} increases gradually and reaches a broad maximum at 40 K with decreasing temperature. Then, χ_{mol} decreases gradually with decreasing temperature, and below 20 K it again increases. This increase in χ_{mol} is probably due to the presence of isolated monoradicals which are randomly located in the lattice defects/or broken-chain edges. The contribution (x) of the

monoradical impurity (curve b) is estimated to be ca. 3.0% and the estimated Weiss constant (θ) is –2.0 K. The superposition of the theoretical curve (curve a) drawn by a 1D AFM regular Heisenberg model and curve b based on eq 3, where C is the Curie constant, gives curve c.

$$\mathcal{H} = -(1 - x)2J \Sigma S_i \cdot S_j + x\, C/(T - \theta) \qquad (3)$$

The best-fit with the experiment gave $2J/k_B = -63.4$ K ($\alpha = 1$). A similar magnetic behavior was observed for **2a**, and the best fit with the experiment using a 1D AFM regular Heisenberg model gave $2J/k_B = -17.8$ K. In this case paramagnetic impurity was nearly zero. Therefore, an increase in χ_{mol} in the low temperature region was not observed.

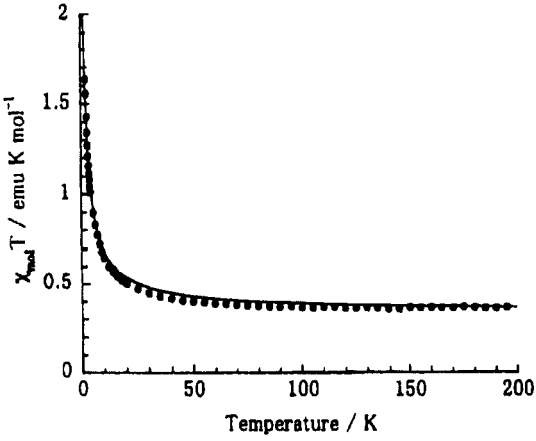


FIGURE 3. $\chi_{mol}T$ vs$T$ plots for **2b**. The solid curve represents theoretical susceptibilities calculated with a 1D regular Heisenberg model with $2J/k_B = +22.4$ K.

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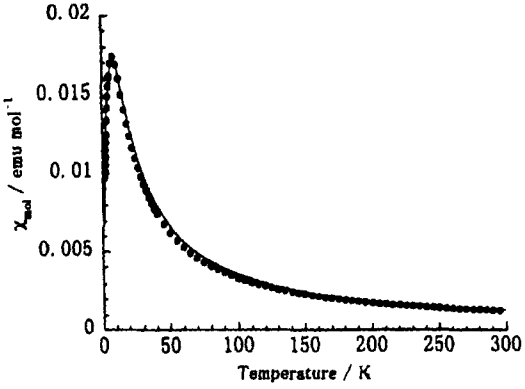

FIGURE 4. χ_{mol} vs T plots for **1b**. The solid curve represents theoretical susceptibilities calculated with a 1D alternating Heisenberg model with $2J/k_B = -12.8$ K and $\alpha = 0.91$.

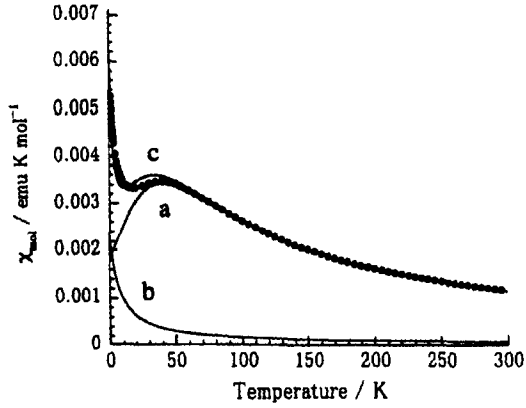

FIGURE 5. χ_{mol} vs$T$ plots for **1a**. Solid curve a represents theoretical susceptibilities calculated with 1D AFM regular Heisenberg model with $2J/k_B = -63.4$ K, and curve b is calculated for 3.0% of a monoradical impurity following the Curie-Weiss law with $\theta = -2.0$ K. Curve c is a superposition of curves a and b.

CONCLUSION

Five kinds of pyridyl-substituted thioaminyl radicals, **1a**, **1b**, **2a**, **2b**, and **3** have been generated, and the former four radicals could be isolated as radical crystals. The X-ray crystallographic analysis of **1b** has been performed and a large SOMO–SOMO overlap between the neighboring radicals was observed. The magnetic susceptibility measurements for the isolated radicals have showed that, although the intermolecular magnetic interactions of **1a** ($2J/k_B$ = −63.4 K, a = 1.0), **1b** (12.8 K, 0.91), and **2a** (−17.8 K, 1.0) are antiferromagnetic, that of **2b** is ferromagnetic, and analysis of the susceptibility data with a 1D ferromagnetic regular Heisenberg model gave $2J/k_B$ = +22.4 K.

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