Nitronyl Nitroxide Substituted Aniline *o*-APNN with a Three-dimensional Hydrogen Bond Network Showing Ferromagnetic Interaction

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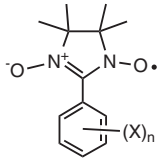
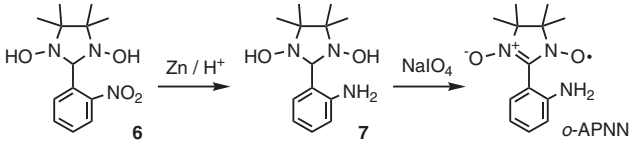
o-Aminophenyl nitronyl nitroxide (*o*-APNN) was prepared as the first aniline-substituted nitronyl nitroxide. X-Ray crystallographic analysis reveals a 3-D hydrogen bonded network due to the branching nature of $-NH_2$. Magnetic measurements indicate the presence of ferromagnetic interaction.

Hydrogen bonds play an important role in crystal engineering[1] and have been much argued in connection with the ability of propagating ferromagnetic interaction in organic magnetic materials.[2] Phenols **1**–**5** (for the chemical formulas, see below) carrying the nitronyl nitroxide group (abbreviated as NN hereafter) have been reported to exhibit intermolecular ferromagnetic interaction.[3–8] Among them, **2** and **3** which possess a hydroxyl group at the *ortho* position become genuine organic ferromagnets below ca. 0.5 K.[4,5] On the other hand, there is no report on the corresponding anilines carrying NN because undesired side-reactions take place according to a conventional synthetic procedure exploited by Ullman.[9] Namely, the amino group can not coexist with precursory aromatic aldehydes because of formation of imines.[10] Furthermore, the anilines are supposed to be oxidation-sensitive and accordingly unstable like the catechol-substituted nitronyl nitroxide.[7] We report here the preparation and magnetic properties of the first NN-substituted aniline, *o*-APNN.



$(X)_n$ = 4-OH (**1**)
2,5-$(OH)_2$ (**2**)
2-OH (**3**)
3,5-$(OH)_2$ (**4**)
3,4-$(OH)_2$ (**5**)
2-NH_2 (*o*-APNN)

The amino group was introduced after the diazaacetal cyclization of the aldehyde group (Scheme 1). Precursor **6** was prepared from *o*-nitrobenzaldehyde according to Ullman's method.[9,11] A methanol solution (65 ml) containing **6** (1.50 g; 5.30 mmol) and an aqueous solution (10 ml) of NH_4Cl (1.68 g; 31.8 mmol) were combined, and zinc (5.50 g; 84.6 mmol) was added to the mixture in small portions at room temperature for 3 h. After the mixture was stirred for 2 d, the solid was removed by filtration. Concentration of the filtrate gave a yellow solid (1.31 g) containing **7** which was used without purification. The above product (1.31 g) was suspended to 500 ml of water, an aqueous solution (ca. 10 ml) of $NaIO_4$ (1.12 g; 5.30 mmol) was added dropwise, and the resultant brown mixture was stirred at room temperature for 30 min. The organic compounds were extracted with chloroform and separated by passing a short column of silica gel with 1/1 ethyl acetate–hexane as an eluent. A purple fraction was collected and concentrated under reduced pressure. Recrystallization from CH_2Cl_2–CH_3OH gave blue blocks of *o*-APNN (271 mg; 1.08 mmol) in 20% yield from **6**, mp. 160–162 °C. Fortunately, *o*-APNN can be handled under air in the crystalline form and in solutions. The ESR spectrum (X-band, benzene, room temperature) of *o*-APNN showed a 1:2:3:2:1 quintet with $a_N = 7.5$ G at $g = 2.0065$, which is typical of NN radicals.



Scheme 1. Synthetic route to *o*-APNN.

X-Ray diffraction data of *o*-APNN were collected at 100 K.[12] Figure 1(a) shows the molecular structure of *o*-APNN. The dihedral angle between the benzene ring and O–N–C–N–O fragment is 47.88(5)°. Some hydrogen atoms are located very close to the NN oxygen atoms with the O···H distances of 2.1–2.5 Å. An intramolecular hydrogen bond is found in N1-H1···O1 with the N1···O1 distance of 2.895(2) Å. Figure 1(b) shows the molecular packing in the crystal of *o*-APNN. Owing to the geometry of $-NH_2$ group, branched intermolecular hydrogen bonds are found between the amino protons and neighboring NN oxygen atoms. H1 intervenes between N1 and $O2^{\#}$ which are separated by 3.171(2) Å. Accordingly, O1 and $O2^{\#}$ can interact through the bending O1···H1···$O2^{\#}$ system. H2 also participates in a hydrogen bond N1–H2···O1* which is nearly linear with the N1···O1* distance of 2.989(2) Å. Two superexchange-like interactions can be proposed along O1···H1–N1–H2···O1* and $O2^{\#}$···H1–N1–H2···O1*, and intramolecular spin-polarization effect along O1–N2–C7–C6–C1–N1–H1 and –H2 should be taken into consideration. These hydrogen bonds successively repeat along the cell axes with 2_1 screw symmetries due to the space group $P2_12_12_1$. Thus, the crystal has a chiral three-dimensional hydrogen bonded network. Relatively short O···H_{methyl} distances are also found between O2 and $H11^{\#}$ (2.54(3) Å) and between O1 and $H8^{\ddagger}$ (2.96(3) Å).[13]

Magnetic susceptibility of *o*-APNN was measured on a SQUID magnetometer in a temperature range 1.8–100 K. As Fig. 2 shows, the magnetic susceptibility of *o*-APNN obeyed the Curie-Weiss law ($\chi_{mol} = C/(T - \theta)$) with $C = 0.375\ cm^3\ K\ mol^{-1}$ and $\theta = +0.74$ K. The *M*-*H* curve measured at 1.8 K exhibited paramagnetic behavior, and the data fell close to the theoretical Brillouin function of $S = 3/2$. These findings indicate that the ferromagnetic interaction is operative in the crystal of *o*-APNN.

From the previous reports on phenols **2**[4] and **3**,[5] the hydroxyl group at the *ortho* position seems to be crucial in crystal packing and structural dimensionality, and the mechanistic investigation on the exchange interaction in **2** led to the spin po-

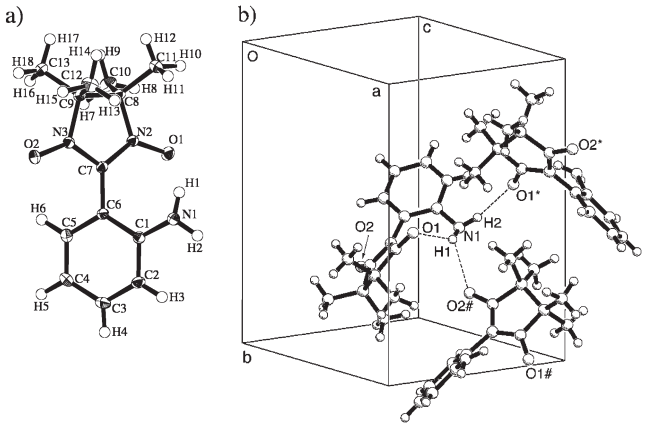


Figure 1. (a) Ortep drawing of *o*-APNN with thermal ellipsoids at the 50% level. The size of hydrogen atoms is arbitrary. (b) Molecular arrangement in the crystal of *o*-APNN. Hydrogen bonds are denoted with dotted lines. Symmetry operation codes for # and * are $1/2 + x$, $1/2 - y$, $2 - z$ and $1/2 - x$, $-y$, $1/2 + z$, respectively.

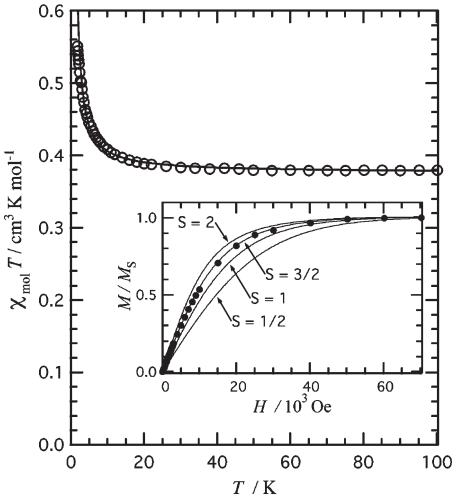


Figure 2. Temperature dependence of $\chi_{mol}T$ and $\chi_{mol}{}^{-1}$ for *o*-APNN. The solid line represents the Curie-Weiss analysis. Inset shows the *M*-*H* curve measured at 1.8 K. The solid lines correspond to the Brillouin functions of $S = 1/2 - 2$.

larization scheme through the hydrogen bonds described as $O_{NN}(\uparrow)\cdots H(\downarrow)\cdots O_{NN}(\uparrow)$.[4] Furthermore, the solid-state ^{1}H and ^{2}H NMR results on **3** revealed the negative spin density on the hydroxyl hydrogen atom.[8] In the present study, although we have no experimental evidence of the spin density on the amino hydrogen atoms, we can propose that H1 is negatively spin polarized in the same way as **2**, and that the intermolecular ferromagnetic interaction can be explained as $O1(\uparrow)\cdots H1(\downarrow)\cdots O2^{\#}(\uparrow)$ owing to the O–H bonding nature. Intramolecular spin polarization also gives negative spin density on H1 and H2, assuming that the nitrogen in *o*-APNN works similarly to the oxygen in **3**.[8] Thus, the hydrogen bonds between $O1\cdots O1^*$ and $O2^{\#}\cdots O1^*$ through the amino group can promote ferromagnetic exchange interactions. However, their interactions may be weaker than that of $O1\cdots H1\cdots O2^{\#}$ because of the longer distances. The present discussion does not exclude other possible ferromagnetic exchange pathways such as the β-hydrogen mechanism.[2b]

In summary, we have synthesized *o*-APNN as an NN-substituted aniline for the first time and constructed the three-dimensional hydrogen bond network due to the branching character of $-NH_2$, where the hydrogen bonds provide ferromagnetic exchange pathways. The *ortho* position has a geometrical advantage for the hydrogen bonds, and this work may afford a clue to crystal and molecular designs for organic ferromagnetic crystals.

References and Notes

1 M. C. Etter, *Acc. Chem. Res.*, **23**, 120 (1990); J.-M. Lehn, M. Mascal, A. DeCian, and J. Fischer, *J. Chem. Soc., Perkin Trans. 2*, **1992**, 461; G. R. Desiraju, *Acc. Chem. Res.*, **35**, 565 (2002).

2 a) G. Maruta, S. Takeda, R. Imachi, T. Ishida, T. Nogami, and K. Yamaguchi, *J. Am. Chem. Soc.*, **121**, 424 (1999). b) T. Nogami, T. Ishida, M. Yasui, F. Iwasaki, N. Takeda, M. Ishikawa, T. Kawakami, and K. Yamaguchi, *Bull. Chem. Soc. Jpn.*, **69**, 1841 (1996). c) N. Yoshioka, M. Irisawa, Y. Mochizuki, T. Kato, H. Inoue, and S. Ohba, *Chem. Lett.*, **1997**, 251. d) D. Papoutsakis, J. P. Kirby, J. E. Jackson, and D. G. Nocera, *Chem.—Eur. J.*, **5**, 1474 (1999). e) Y. Pontillon, T. Akita, A. Grand, K. Kobayashi, E. Lelievre-Berna, J. Pecaut, E. Ressouche, and J. Schweizer, *J. Am. Chem. Soc.*, **121**, 10126 (1999). f) J. R. Ferrer, P. M. Lahti, C. George, P. Oliete, M. Julier, and F. Palacio, *Chem. Mater.*, **13**, 2447 (2001).

3 E. Hernandez, M. Mas, M. E. Molis, C. Rovira, and J. Veciana, *Angew. Chem., Int. Ed. Engl.*, **32**, 882 (1993).

4 T. Sugawara, M. M. Matsushita, A. Izuoka, N. Wada, N. Takeda, and M. Ishikawa, *J. Chem. Soc., Chem. Commun.*, **1994**, 1723; M. M. Matsushita, A. Izuoka, T. Sugawara, T. Kobayashi, N. Wada, N. Takeda, and M. Ishikawa, *J. Am. Chem. Soc.*, **119**, 4369 (1997).

5 J. Cirujeda, M. Mas, E. Molins, F. L. Panthou, J. Laugier, J. G. Park, C. Paulsen, P. Rey, C. Rovira, and J. Veciana, *J. Chem. Soc., Chem. Commun.*, **1995**, 709.

6 J. L. Garcia-Munoz, J. Cirujeda, J. Veciana, and S. F. J. Cox, *Chem. Phys. Lett.*, **293**, 160 (1998).

7 J. Cirujeda, L. E. Ochando, J. M. Amigo, C. Rovira, J. Rius, and J. Veciana, *Angew. Chem., Int. Ed. Engl.*, **34**, 55 (1995).

8 H. Heise, F. H. Kölen, F. Mota, J. J. Novoa, and J. Veciana, *J. Am. Chem. Soc.*, **121**, 9659 (1999).

9 E. F. Ullman, J. H. Osiecki, and R. Darcy, *J. Am. Chem. Soc.*, **94**, 7049 (1972).

10 L. A. Bigelow and H. Eatough, *Org. Synth.*, Coll. Vol. **I**, 80 (1941).

11 O. Shimomura, K. Abe, and M. Hirota, *J. Chem. Soc., Parkin Trans. 2*, **1988**, 795.

12 Crystallographic data for *o*-APNN: $C_{13}H_{18}N_3O_2$, orthorhombic, $P2_12_12_1$, $a = 10.7178(4)$, $b = 12.9588(4)$, $c = 9.0698(4)$ Å, $V = 1259.7(1)$ Å^3, $Z = 4$, $D_{calcd} = 1.309\,g\,cm^{-3}$, $\mu(Mo\,K\alpha) = 0.09\,mm^{-1}$, $R = 0.042$ ($I > 2.0\sigma(I)$), $R_w = 0.104$ (all data) for 2107 unique reflections. All of the hydrogen atoms could be found in difference Fourier maps, and their coordinates and isotropic temperature factors were included in the refinement.

13 The symmetry operation code of ‡ is $1/2 - x$, $-y$, $-1/2 + z$.

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