Unusually Large Magnetic Interactions Observed in Hydrogen-Bonded Nitronyl Nitroxides

Naoki Yoshioka,* Munetoshi Irisawa, Yuichiro Mochizuki, Takanari Kato, Hidenari Inoue, and Shigeru Ohba†
Department of Applied Chemistry, Faculty of Science and Technology, Keio University, Yokohama 223
†*Department of Chemistry, Faculty of Science and Technology, Keio University, Yokohama 223*

(Received December 4, 1996)

Two nitronyl nitroxide derivatives bearing imidazole and benzimidazole ring were prepared and their hydrogen-bonded structures and magnetic properties were characterized.

There has been increasing research interest in the study of molecular-based magnetism. Utilizing the intermolecular magnetic coupling in crystal, purely organic radicals with a bulk ferromagnetism have been reported.[1] Among various intermolecular interactions, hydrogen bonds are strong in energy and whose directional properties are better understood than many other types of non-bonded interactions. Intermolecular hydrogen bond is also theoretically pointed out to propagate the magnetic coupling.[2] Subsequently, introducing the hydrogen bonding site into organic radicals is an useful way of controlling magnetic interaction and/or molecular arrangement in crystal. Although various types of organic radicals and molecular complexes with OH sites have been prepared and structurally characterized,[3] few studies on the radical with a NH site have been reported except for nitronyl nitroxides bearing a methyltriazole[4] and a *N*-protonated pyridyl ring.[5] As organic radicals with a pair of proton donor (>NH) and acceptor (=N-) sites, nitronyl nitroxides with imidazole ring, 2 - (imidazole - 2 - yl) - 4, 4, 5, 5 - tetra - methylimidazoline -1 -oxyl -3- oxide) (mp 141-143 °C) and 2-(benzimidazole-2-yl) -4, 4, 5, 5- tetramethylimidazoline -1- oxyl-3-oxide) (mp 217-219 °C) (abbreviated as Im-NN and BIm-NN, respectively) were prepared according to the literature method.[6] Recrystallizations from CH_2Cl_2 / hexane gave suitable crystals for X-ray analysis.[7]

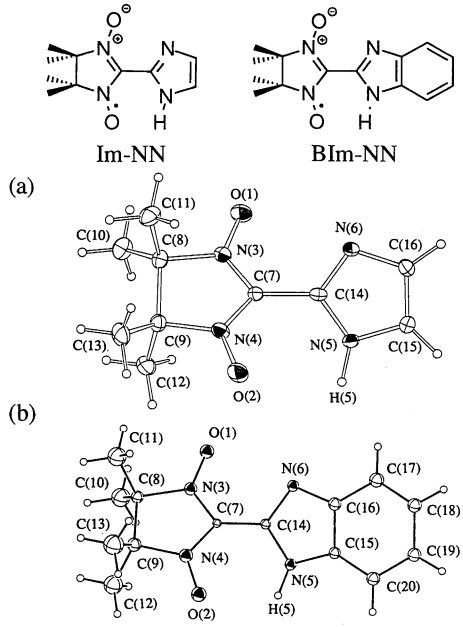

Figure 1. Atom numbering schemes and molecular conformations of (a) Im-NN and (b) BIm-NN.

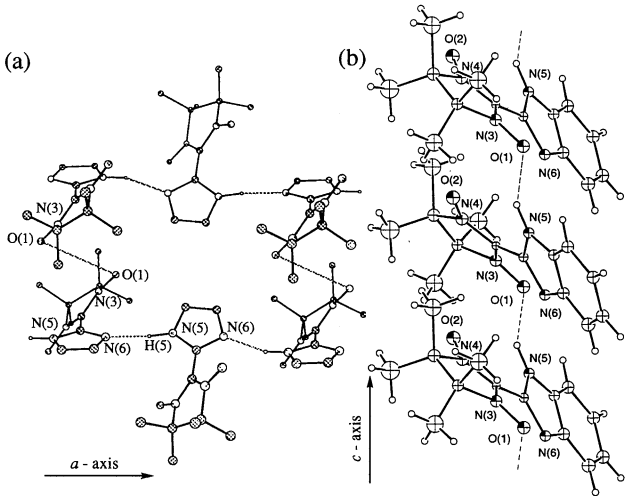

Figure 2. View of hydrogen bonded chains observed in (a) Im-NN along the *a* direction and (b) BIm-NN along the *c* direction.

The dihedral angle of Im-NN(Figure 1 (a)) between the plane of O(1)-N(3)-C(7)-N(4)-O(2) and the imidazole ring is equal to 48.4 deg. The shortest intermolecular distance is found between N(5)···N'(6) equal to 2.873(5) Å, corresponding to the hydrogen bond between the imidazole rings (Figure 2(a)). The large dihedral angle may be ascribed to the effect of the intermolecular hydrogen bonding. Between the hydrogen bonded chains, there is an intermolecular short contact between O(1)···O'(1) equal to 3.483(5) Å within the molecules related by inversion center. BIm-NN crystallizes in the space group *Pbca*. The dihedral angle between the plane of O(1)-N(3)-C(7)-N(4)-O(2) and the benzimidazole ring is 24.3 deg (Figure 1 (b)). The molecules assemble within the lattice in linear chains running along the *c* direction (Figure 2(b)). Along the chain direction, the molecules are hydrogen bonded through N(5)-H(5)···O'(1) between the benzimidazole ring and the NN group with an intermolecular N(5)-O'(1) separations equal to 2.86(3) Å. At the non-hydrogen bonding site of NN moiety, a close contact between O(2)···C'(7) equal to 3.17(3) Å is also observed.

The magnetic susceptibility of Im-NN showed a maximum at 110 K and a minimum at 20 K. A maximum in the susceptibility curve and a room temperature $\chi_M T$ value (0.31 cm^3 K mol^{-1}) lower than that expected for isolated monoradical is the signature of predominant antiferromagnetic interaction (Figure 3). The magnetic data were fit to a Bleaney-Bowers expression taking account of the presence of uncoupled isolated radical (0.6 %) with a large singlet-triplet gap of $2J$ = -123 cm^{-1}. The $\chi_M T$ value of BIm-NN at a room temperature was 0.38 cm^3 K mol^{-1} which is corresponding to an isolated monoradical. This value steeply increases with a lowering temperature and reaches a maximum

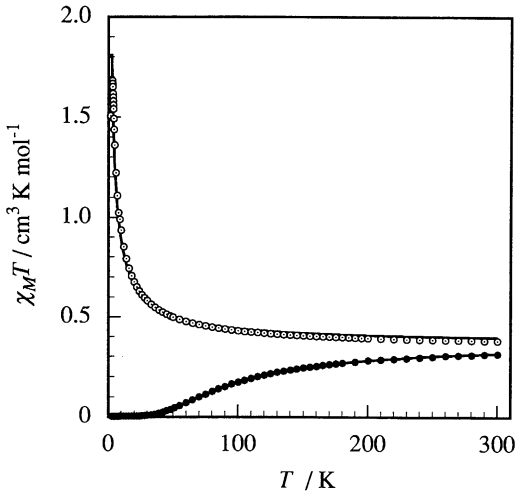

Figure 3. $\chi_M T$ versus T plots for Im-NN (●) and BIm-NN(○). Solid lines correspond to their calculated curves (see text).

value of 1.68 cm^3 K mol^{-1} at 3.2 K. As the temperature is lowered further, the $\chi_M T$ value decreases to 1.49 cm^3 K mol^{-1} at 1.8 K. The magnetic data above 4 K fit with the Curie-Weiss law $\chi_M = C/(T - \theta)$ with a Curie constant 0.376 cm^3 K mol^{-1} and a Weiss constant θ = + 8.2 K. The temperature dependence of $\chi_M T$ was quantitatively interpreted in terms of an 1D Heisenberg ferromagnetic chain,[8] $\chi_M T = N_A g^2 \mu_B^2$ [(1 + 5.7979916 K + 16.902653K^2+ 29.376885 K^3+ 29.832959K^4+ 14.036918K^5) / (1 +2.7979916K+ 7.0086780 K^2+ 8.6538644K^3+ 4.5743114 K^4)]$^{2/3}$ with $K = J / 2k_B T$. A good fit is obtained for a coupling constant J of + 12 cm^{-1} corresponding to the solid line in Figure 3. To confirm the presence of dominant ferromagnetic interaction, magnetization isotherms were measured at 2.8 and 4.0 K. At both temperatures, the magnetization curve is much above the Brillouin function for S = 1/2 spins, as shown in Figure 4.

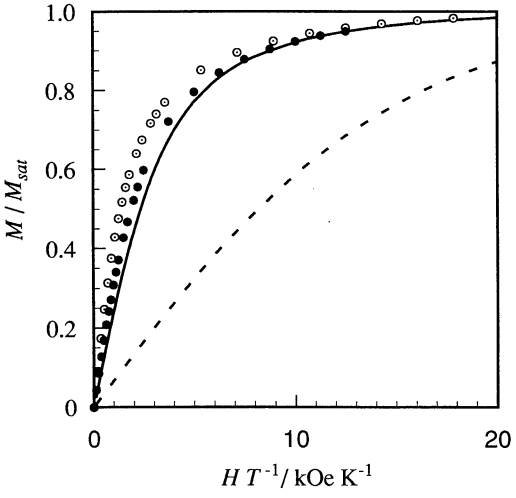

Figure 4. Magnetization isotherms of BIm-NN at 2.8 K (○) and 4.0 K (●). Broken and solid curves are calculated using the Brillouin function for S = 1/2 and 9/2, respectively.

The magnetic property of Im-NN can be explained by the intermolecular short contact of two NO bonds between hydrogen bonded chains. The close contact makes up the direct overlap of magnetic orbitals causing a strong antiferromagnetic interaction. The intermolecular distance between the N(3)-O(1) bonds equal to 3.38 Å is the shortest among those reported for nitronyl nitroxides.[9]

A preliminary mechanistic consideration of strong magnetic coupling observed in BIm-NN crystal is (i) the spin polarization effect through hydrogen bond and (ii) the orthogonality of SOMO's on the adjacent molecules. If the positive spin density is polarized on C(14), the former implies that the negative spin density is polarized on H(5) due to the presence of a lone pair of electrons on N(5), leading to the intermolecular ferromagnetic coupling. A through space interaction between O(2) with a positive spin density and C'(7) with negative one also causes a ferromagnetic spin alignment based on McConnell's theory.[10] Similar magnetic interaction has been reported for nitronyl nitroxide derivatives with lithium benzoate[11] and pyrimidyl group.[12] The decisive mechanism will be discussed elsewhere. A maximum value of $\chi_M T$ of BIm-NN is larger than other ferromagnetically coupled nitronyl nitroxides described so far.

The present finding of strong ferro- and antiferromagnetic interaction reveals that the introduction of NH site into organic radicals has potentiality for constructing magnetically coupled molecular systems.

References and Notes

1 M. Kinoshita, *Jpn. J. Appl. Phys.*, **33**, 5718 (1994) and references therein.
2 a) K. Yamaguchi, M. Okumura, J. Maki, T. Noro, H. Namimoto, M. Nakano, and T. Fueno, and K. Nakasuji, *Chem. Phys. Lett.*, **190**, 353 (1992), b) T. Kawakami, S. Takeda, W. Mori, and K. Yamaguchi, *Chem. Phys. Lett.*, **261**, 129 (1996).
3 a) T. Sugawara, M. Matsushita, A. Izuoka, N. Wada, N. Takeda, and M. Ishikawa, *J. Chem. Soc., Chem. Commun.*, **1994**, 1723, b) J. Cirujeda, M. Mas, E. Molins, F. Lanfranc de Panthou, J. Laugier, J. G. Park, C. Paulsen, P. Rey, C. Rovira, and J. Veciana, *J. Chem. Soc., Chem. Commun.*, **1995**, 709, c) T. Akita, Y. Mazaki, and K. Kobayashi, *J. Chem. Soc., Chem. Commun.*, **1995**, 1861.
4 a) Y. Pei, O. Kahn, M. A. Aebersold, L. Ouahab, F. LeBerre, L. Pardi, and J. L. Tholence, *Adv. Mater.*, **6**, 681 (1994), b) A. Lang, Y. Pei, L. Ouahab, and O. Kahn, *Adv. Mater.*, **8**, 60 (1996).
5 T. Okuno, T. Otsuka, and K. Awaga, *J. Chem. Soc., Chem. Commun.*, **1995**, 827.
6 E. F. Ullman, J. H. Osiecki, D. G. B. Boocok, and R. Darcy, *J. Am. Chem. Soc.*, **94**, 7049 (1972).
7 Crystal data of Im-NN: $C_{10}H_{15}N_4O_2$, M = 223.26, monoclinic, space group $P\,2_1/a$, a = 9.983(2) Å, b = 11.993(2) Å, c = 10.856(2) Å, β = 117.18(1)°, V = 1156.2(3) Å^3, Z = 4, Dx = 1.282 g/cm^3; Mo $K\alpha$ radiation, final conventional R factor 9.6% for 1715 independent reflections. Crystal data of BIm-NN: $C_{14}H_{17}N_4O_2$, M = 273.31, orthorhombic, space group $Pbca$, a = 15.545(4) Å, b= 20.107(3) Å, c= 8.742(3) Å, V = 2732.4(12) Å^3, Z = 8, Dx = 1.329 g/cm^3 Mo $K\alpha$ radiation, final conventional R factor 9.5% for 484 independent reflections.
8 D. D. Swank, C. P. Landee, and R. D. Willet, *Phys. Rev. B*, **20**, 2154 (1979).
9 a) J. Laugier, P. Rey, C. Benelli, D. Gatteschi, and C. Zanchini, *J. Am. Chem. Soc.*, **108**, 6931 (1986), b) A. Caneschi, D. Gatteschi, J. Laugier, P. Rey, and R. Sessoli, *Inorg. Chem.*, **27**, 1553 (1988), c) A. Caneschi, F. Ferraro, D. Gatteschi, P. Rey, and R. Sessoli, *Inorg. Chem.*, **29**, 1756 (1990), d) A. Yamaguchi, K. Awaga, T. Inabe, T. Nakamura, M. Matsumoto, and Y. Maruyama, *Chem. Lett.*, **1993**, 1443.
10 H. M. McConnell, *J. Chem. Phys.*, **39**, 1910 (1963).
11 K. Inoue and H. Iwamura, *Chem. Phys. Lett.*, **207**, 551 (1993).
12 F. Lanfranc de Panthou, D. Luneau, J. Laugier, and P. Rey, *J. Am. Chem. Soc.*, **115**, 9095 (1993).