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Naoki Yoshioka [a], Naoki Matsuoka [a], Munetoshi Irisawa [a], Shigeru Ohba [b] & Hidenari Inoue [a]

[a] Department of Applied Chemistry, Faculty of Science and Technology, Keio University, 3-14-1 Hiyoshi Kohoku-ku, Yokohama, 223-8522, Japan

[b] Department of Chemistry, Faculty of Science and Technology, Keio University, 3-14-1 Hiyoshi Kohoku-ku, Yokohama, 223-8522, Japan

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Magnetic Properties of Nitronyl Nitroxide Derivatives Bearing N-H Site: an Approach to Ferromagnetic Self-Assemblies Using Hydrogen Bond

NAOKI YOSHIOKA[a], NAOKI MATSUOKA[a], MUNETOSHI IRISAWA[a], SHIGERU OHBA[b] and HIDENARI INOUE[a]

[a]*Department of Applied Chemistry, Faculty of Science and Technology, Keio University, 3–14–1 Hiyoshi Kohoku-ku, Yokohama 223–8522, Japan and* [b]*Department of Chemistry, Faculty of Science and Technology, Keio University, 3–14–1 Hiyoshi Kohoku-ku, Yokohama 223–8522, Japan*

Nitronyl nitroxide derivatives bearing NH site, imidazolyl-2-nitronyl nitroxide (**Im-NN**), 4(5)-methyl-imidazolyl-2-nitronyl nitroxide (**MeIm-NN**), and benzimidazolyl-2-nitronyl nitroxide (**BIm-NN**) were synthesized, and were self-assembled by hydrogen bonding at NH site with nitrogen atom on imidazole ring or oxygen atom of nitroxide moiety. Ferromagnetic intermolecular interactions were observed in **MeIm-NN** and **BIm-NN.** The magnetic interaction can be rationally explained by McConnell model.

Keywords: organic radicals; ferromagnetic interactions; nitronyl nitroxide derivatives; molecular self-assembly; McConnell model

INTRODUCTION

Molecular compounds exhibiting ferromagnetic ordering are attracting increasing attention in recent years[1]. More than dozen of purely organic radicals with bulk ferromagnetism caused by intermolecular magnetic coupling have been realized by world wide laboratories[2]. Whereas these ferromagnetic orderings have been fortuitously discovered, methodology for designing the intermolecular coupling pathway has not been established yet. As a guiding principle of intermolecular magnetic coupling, McConnell suggested the condition for ferromagnetic interaction in stacked radical molecules which possessed both positive and negative spin densities [3].

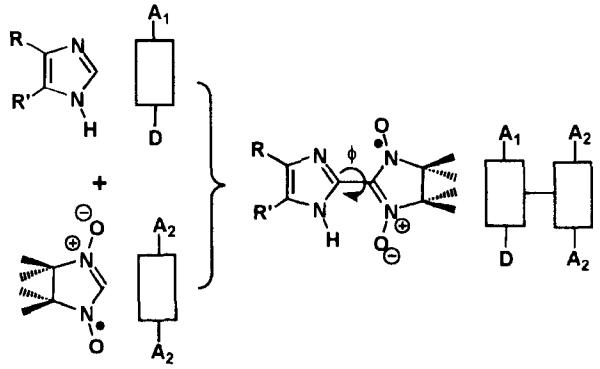

FIGURE 1 Molecular design of self-assembled nitronyl nitroxide derivatives.

According to his mechanism, the ferromagnetic interaction would be achieved when the product of the spin densities becomes negative between the interacting spin sites each belonging to the neighboring radical molecules. Organic ferromagnets so far reported have suitable arrangements to fulfill the above requirement, however, to control the arrangement of open-shell molecules in the crystal does not reach to a predictable stage. By using both molecular and supramolecular techniques, strictly programmed and controlled molecular system with magnetic cooperativity can be envisaged. Hydrogen bonds, in particular, are well suited for building molecular assemblies with specific shapes and sizes because their energies are roughly comparable to thermal energies and fairly directional. The design of molecular assemblies using hydrogen bonds to control structure in the solid state has yielded a number of potentially useful structural motifs[4]. According to the strategy, we combined imidazole rings having both pyrrole-type and pyridine-type nitrogen atoms with nitronyl nitroxide, **NN** (= 4,4,5,5-tetramethyl-1*H*-imidazoline-1-oxyl-3-oxide) whose oxygen atoms exhibited

the weak Lewis base character(Fig. 1)[5]. The most of spin densities are equally distributed over a pair of NO groups, whereas a large negative spin density exists over the carbon atom between the two NO bonds. The charge density distribution in **Im-NN**[6] implies that -NH proton is a good proton donor (D) and -N= and -O atom are good proton acceptors (named A_1 and A_2, respectively). These characteristics are suitable for controlling the molecular arrangement using hydrogen bond. From the point of hydrogen-bond pattern, **Im-NN** derivatives are expected to have four basic motifs due to the competition between the formation of $A_1 \cdots D$ versus $A_2 \cdots D$: a monomer (intramolecular $D \cdots A_2$ bond), a dimer (a pair of intermolecular $D \cdots A_2$ bonds), and polymers (a pair of intermolecular $D \cdots A_2$ or $D \cdots A_1$ bond). Though imidazole derivatives without additional proton acceptor group exhibit a strong hydrogen bond corresponding to a polymeric $\cdots D\text{–}A_1 \cdots D\text{–}A_1 \cdots$ in the solid state, the motif might be changed by using the steric effect of substituents **R** and/or **R'** of imidazole ring. According to the synthetic strategy, we have prepared various **NN** derivatives with NH site as shown in Fig 2.

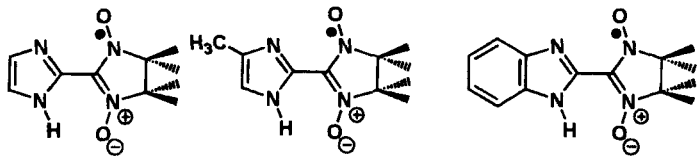

FIGURE 2 Chemical structure of nitronyl nitroxide derivatives with imidazole rings.

EXPERIMENTAL

Im-NN[5] (m.p.141 - 143 °C) was prepared by the condensation between commercially available imidazole-2-carboxaldehyde (Aldrich) and 2,3-bis(hydroxylamino)-2,3-dimethylbutane[7] in methanol, followed by $NaIO_4$ oxidation. **MeIm-NN** (m.p. 121- 122 °C) was obtained by the similar route

using 4(5)-methyl imidazole[8]. **BIm-NN**[5] (m.p. 217 - 219 °C) could not be prepared by the above method due to the poor solvent solubility of dimerized aldehyde. It was synthesized by the condensation between benzimidazole-2-aldehyde diethyl acetal[9] and bishydroxylamine monosulphate salt[7] in an acidic solution.

The magnetic susceptibility measurements have been carried out with a SQUID magnetometer (Quantum Design MPMS-5) in the temperature range 1.8- 300 K under the magnetic field of 0.5 T. Magnetization experiments were carried out up to 5.5 T.

RESULTS AND DISCUSSION

Suitable crystals for X-ray analysis were obtained for **Im-NN** and **BIm-NN** from CH_2Cl_2 / hexane. Only powdery sample was obtained for **MeIm-NN**. Crystal structures of **Im-NN** and **BIm-NN** are shown in Fig. 3. While hydrogen bonding motif of **Im-NN** is ···D–A···D–A··· type similar to that of

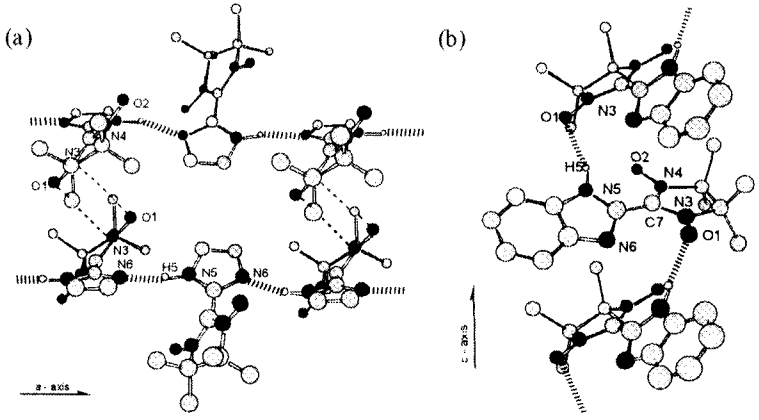

FIGURE 3 Views of hydrogen-bonded chains observed in **Im-NN** (a) and **BIm-NN** (b). Dotted lines (||||) and dashed lines (----) indicate the intermolecular hydrogen bonds and the close contact between NO moieties within chains, respectively.

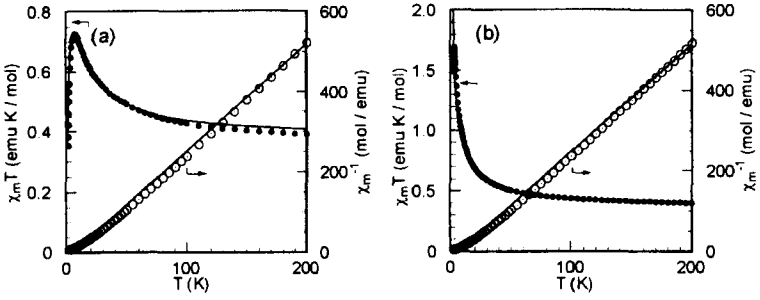

FIGURE 4 χ_m^{-1}-T (O) and $\chi_m T$-T (•) plots of **MeIm-NN** (a) and **BIm-NN** (b). Solid lines of χ_m^{-1}-T and $\chi_m T$-T plots are calculated by Curie-Weiss law and non-linear curve fit, respectively.

imidazole itself, that of **BIm-NN** belongs to $\cdots D\text{–}A_2\cdots D\text{–}A_2\cdots$ type between benzimidazole ring and NN moiety. These two types of motif exhibit quite different IR spectral patterns in ν(N-H) region: the former have very broad absorption due to the coupling of ν(N-H···N) vibrations with γ(NH···N) overtones[10], the latter showed relatively narrow absorption. **MeIm-NN** showed a narrow absorption at the region, indicating the absence of $\cdots D\text{–}A_1\cdots D\text{–}A_1\cdots$ motif.

The magnetic data for **MeIm-NN** and **BIm-NN** as the thermal variation of reciprocal molar susceptibility, χ_m^{-1}, and $\chi_m T$ product, are shown in Fig. 3. The magnetic data for **MeIm-NN** and **BIm-NN** are well described by the Curie-Weiss law with and θ = + 6.2 and +8.2 K, respectively. The positive θ values for these radicals indicate the presence of ferromagnetic interactions between the radical molecules. $\chi_m T$ of **MeIm-NN** and **BIm-NN** are equal to 0.372 and 0.376 emu K/mol at room temperature, respectively, and increase rapidly as temperature is lowered from ca. 200 K. $\chi_m T$ of **MeIm-NN** and **BIm-NN** reach maxima of 0.72 emu K/mol at 7.0 K, 1.68 emu K/mol at 3.2 K, respectively, and decrease as temperature lowered further. These behaviors are explained by the presence of dominant ferromagnetic interactions, on which weak antiferromagnetic interactions are superimposed, and are quite in contrast to that of **Im-NN** which could be analyzed by the dimer model.

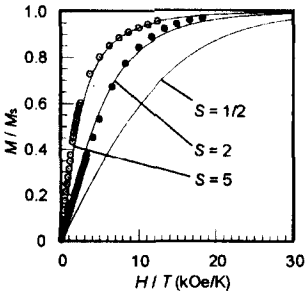

FIGURE 5 Magnetization isotherms of **BIm-NN** at 4.0 K (O) and **MeIm-NN** at 3.0 K(●). Solid lines are calculated using the Brillouin function for S = 1/2, 2 and 5, respectively.

In order to clarify the intermolecular coupling field dependence of the magnetization were measured (Fig. 5). Magnetization curves of **MeIm-NN** and **BIm-NN** exceed that of the Brillouin function with S = 1/2. The magnetization curves of **MeIm-NN** and **BIm-NN** nearly coincided with that of S = 2 and 5, respectively.

The magnetic susceptibility data can be analyzed using the Heisenberg model with the exchange interaction between the neighboring molecules on a chain.

$$H = -J\sum_{i=1}^{n-1} S_i \cdot S_{i+1} \qquad (1)$$

where J is the nearest-neighbor exchange integrals. The variation of magnetic susceptibility with temperature can be fitted to the empirical function[11] taking into account a mean-field correction. Then, Eq.(1) could be described as follows[12]:

$$\chi_m = \frac{N_A g^2 \beta^2 F(J,T)}{kT - zJ' F(J,T)} \qquad (2)$$

with

$$F(J,T) = \frac{1}{4}[(1 + 5.7979916x + 16.902653x^2 + 29.376885x^3 + 29.832959x^4 + 14.036918x^5)/(1 + 2.7979916x + 7.0086780x^2 + 8.6538644x^3 + 4.5743114x^4)]^{2/3}$$

$$x = \frac{J}{2kT}$$

J' is the interaction parameter, z the number of nearest neighbors of a radical belonging to adjacent chains. Magnetic parameters are summarized in Table I. Higher spin multiplicity of **BIm-NN** at low temperature can be explained by

TABLE I Magnetic parameters of **Im-NN** derivatives

Radical	J (cm^{-1})	zJ' (cm^{-1})	$\chi_m T_{max}$ (emu K/mol)	Interaction	ν_{NH}[a] (cm^{-1})
Im-NN	-123	—	—	dimer	2200-3200[b]
MeIm-NN	+12.8	-3.4	0.76 (7.0K)	1-D ferro.	3155
BIm-NN	+13	c	1.68 (3.2K)	1-D ferro.	3160

a; KBr method, b;broad complex band, c; negative but too small to be fit well.

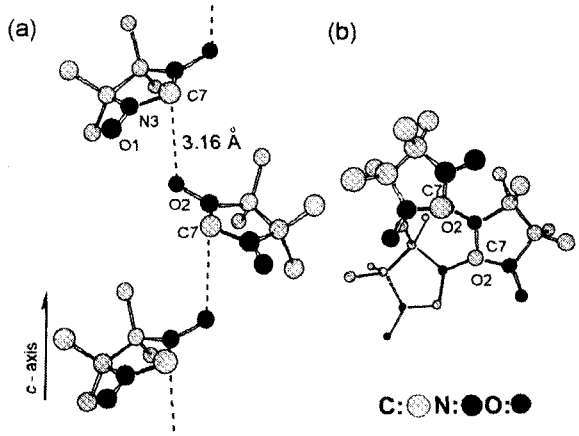

FIGURE 6 Molecular arrangement in the hydrogen bonded **BIm-NN** chain: side view of triad **NN** groups along c direction (a) and its top view (b).

the reduced interchain magnetic interaction, as J parameter of **MeIm-NN** and **BIm-NN** are almost identical. Mechanistic consideration of strong magnetic coupling observed in **BIm-NN** crystal is (i) the orthogonality of SOMO's on the adjacent molecules (contact between O2 and N'3), (ii) intermolecular coupling followed by McConnell model (contact between O2 and C'7) (iii) the spin polarization effect through hydrogen bond. Considering the structural parameters, we noticed that ferromagnetic interactions due to the orthogonality of two NO groups can be excluded due to the reduced overlap of magnetic orbitals. Fig. 6 shows the spatial arrangement of **NN** groups in **BIm-NN** chain along c-axis. Close contact between the central carbon (negative spin site) and the oxygen atom (positive spin site) of non-hydrogen bonded NO group favors the ferromagnetic array according to McConnell model. Although the spin density distribution on the benzimidazole ring is experimentally not clear, negative spin density is polarized on (N)-H atom, leading to the intermolecular ferromagnetic coupling.

We could switch the hydrogen-bond motif by using the steric effect of **R**- or **R'**- groups, taking advantage of directionality of hydrogen bond. Hydrogen bond motif could be roughly estimated by IR spectra using stretching mode of N-H site.

The present finding of strong magnetic coupling in self-assembled nitronyl nitroxides bearing NH site will enable us to design further new family of self-assembled radicals linked by hydrogen bond.

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