# ARTICLES

# An Ideal One-Dimensional Antiferromagnetic Spin System Observed in Hydrogen-Bonded Naphth[2,3-d]imidazol-2-yl Nitronyl Nitroxide Crystal: The Role of the Hydrogen Bond

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A novel stable organic radical, 2-(naphth[2,3-*d*]imidazol-2-yl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-1-oxyl-3-oxide (**4**), has been designed, synthesized, and structurally characterized to examine the effects of ring extension on 2-(benzimidazol-2-yl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-1-oxyl-3-oxide (**2**). **4** forms four-centered intramolecular and intermolecular hydrogen bonds, and the hydrogen bonds are repeated along the *c*-axis to form a one-dimensional chain structure. This hydrogen-bonding motif contrasts that of **2**, which forms three-centered intramolecular and intermolecular hydrogen bonds. The magnetic susceptibility measurement of **4** reveals that an antiferromagnetic interaction is dominant between spins, and the magnetic behavior is reproduced by the Bonner-Fisher model with J = -14 cm<sup>-1</sup>. Because each hydrogen-bonded chain is well isolated, a magnetic interaction pathway was thought to exist along the chain direction. Two interaction pathways have been assumed: (i) through-space interaction between the O atoms of the nitroxide and (ii) through the NH···ON intermolecular hydrogen bond. We have concluded that pathway (i) is predominant, by considering the identical magnetic data between the NH nondeuterated and deuterated samples. The hydrogen bond mainly has a role in crystal scaffolding.

## 1. Introduction

One of the main topics of molecular magnetism is the construction of a crystal system with a controlled dimensionality of magnetic interactions, because the bulk magnetism of molecular solids is closely correlated to the crystal structures. To construct such a system, intermolecular forces such as metal coordination and hydrogen bonding have been introduced.<sup>1</sup> Focusing on purely organic radical crystals, many organic radical molecules that carry hydrogen-bonding sites have been reported and characterized.<sup>2</sup> Several quantum chemical calculations claim the capability of a hydrogen bond to propagate magnetic interaction,<sup>3</sup> as well as to control the crystal packing. The occurrence of magnetic interaction through the hydrogen bond was recently reported, and it was confirmed by solution electron spin resonance (ESR) spectra of tert-butyl nitroxide and poly-(chloro)triphenylmethyl radicals.<sup>4</sup> However, a complicated problem is still present in the existing crystalline compounds: because undesirable molecular contacts occur frequently, the question of whether the hydrogen bond itself propagates magnetic interaction or just has a role in crystal scaffolding is not always clear. As a result, a magnetic structure does not always correspond to the crystal structure controlled by a hydrogen bond. To scrutinize the relationship between a hydrogen bond and the magnetic properties of radical solids, we must systematically study the organic radical molecules

whose hydrogen-bonding sites have high extensibility and compare the similarities and/or differences in these radical crystals.



Among the organic radical molecules that carry hydrogenbonding sites, we have been focusing on the nitronyl nitroxide (NN) units that carry imidazole rings.<sup>5</sup> From the standpoint of crystal engineering, imidazole has a very interesting skeleton, because it has both a proton-donor site and a proton-acceptor site to form a hydrogen bond similar to a water molecule, and the bond is reported to form a chain structure in the crystal.<sup>6</sup> We have combined imidazole rings and NN units. As shown in Figure 1, the derivatives have one NH proton-donor site (D) and three proton-acceptor sites (one imine N atom  $(A_1)$  and two nitroxide O atoms (A<sub>2</sub>)), and their crystal structures are expected to be controlled by hydrogen bonds. In the case of imidazol-2-yl nitronyl nitroxide (1), a hydrogen bond chain of the type D···A<sub>1</sub> is observed.<sup>5a</sup> In the case of benzimidazol-2-yl nitronyl nitroxide (2), which exhibits intermolecular ferromagnetic interaction with  $J = +12 \text{ cm}^{-1}$  in the crystal, however, A<sub>2</sub> rather than A<sub>1</sub> participates in the intermolecular hydrogen bond. We have also reported the magnetic properties of 4(5)-methylimidazol-2-yl nitronyl nitroxide (3).5b Judging from its magnetic

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Spin in H-Bonded Naphth[2,3-d]imidazol-2-yl NN



Figure 1. Molecular design of imidazol-2-yl nitronyl nitroxide (NN) derivatives.

data, **3** probably forms the same pattern of hydrogen bond as **2**, although we have not succeeded in solving the crystal structure yet. From these results, we have recognized that the steric and/or electronic effects of substituents R and/or R' of the imidazole ring influence the crystal structure of the imidazol-2-yl nitronyl nitroxide derivatives, and the skeleton is appropriate for a systematic study of the effects of a hydrogen bond on the intermolecular magnetic interaction. In this paper, we describe the synthesis, crystal structure, and magnetic properties of newly designed naphth[2,3-d]imidazol-2-yl nitronyl nitroxide (**4**) to examine the effects of ring extension on the crystal packing and magnetic behavior of **2**.

# 2. Experimental Section

**2.1. General Methods.** Magnetic susceptibility measurements were performed using a Quantum Design MPMS-5 SQUID susceptometer that was working at the field strength of 0.5 T in the temperature range of 1.8–300 K. ESR spectra were recorded on a JEOL JES-RE3X X-band (9.4 GHz) spectrometer. <sup>1</sup>H NMR spectra were obtained on a Varian MVX-300 spectrometer. Mass spectra were measured on a JEOL JMS-DX302 mass spectrometer, using *m*-nitrobenzyl alcohol as a matrix.

2.2. Syntheses. 2.2.1. Naphth[2,3-d]imidazole-2-carbaldehyde diethyl acetal (5). To a solution of sodium (1.20 g, 52.2 mmol) in dry ethanol (30 mL) were added 2,3-diaminonaphthalene (4.00 g, 25.3 mmol) and ethyl diethoxyacetate (5.35 g, 30.3 mmol). The mixture was refluxed for 24 h and cooled to room temperature, and then the solvent was removed under vacuum. The residue was dissolved in water, neutralized with acetic acid, and extracted with ethyl acetate. The organic layer was separated, dried over anhydrous sodium sulfate, and evaporated to dryness. Chromatography on silica gel with chloroform/ethyl acetate (1/1) as the eluent yielded naphth[2,3d]imidazole-2-carbaldehyde diethyl acetal (5) (3.31 g, 48%), which was recrystallized as a white powder from an ethyl acetate/n-hexane (1/1) solution. Mp: 214-215 °C [196-197 °C].<sup>7</sup> <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 300 MHz): δ 8.17(s, 1H, Ar–H), 8.00(dd, 2H, Ar-H, J = 2 and 7 Hz, Ar-H), 7.94(s, 1H, Ar-H), 7.37(m, 2H, Ar-H), 5.77(s, 1H, CH), 3.70(m, 4H, 2 × CH<sub>2</sub>), 1.21(t, 6H, J = 7 Hz, 2 × CH<sub>3</sub>). Fast atom bombardment-mass spectroscopy (FAB-MS): observed 271 [M+1]+ (calculated for  $C_{16}H_{18}N_2O_2 = 270.33$ ). Elemental analysis calculated for C<sub>16</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub>: C, 71.09; H, 6.71; N, 10.36. Found: C, 70.98; H, 6.79; N, 10.38.

2.2.2. Naphth[2,3-d]imidazole-2-carbaldehyde (6). A solution of **5** (4.10 g, 15.1 mmol) in 1M sulfuric acid (100 mL) was stirred for 1 h at room temperature and then refluxed at 100 °C for 10 min. After the solution was cooled to room temperature, the pH was adjusted to ca. 10 with aqueous sodium carbonate solution. The precipitate was filtered off, washed with water, and dried under vacuum to yield naphth[2,3-d]imidazole-2-carbaldehyde (6) (2.62 g, 88%) as a yellow powder. Mp: > 300 °C. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 300 MHz at 80 °C):  $\delta$  10.07(s, 1H, CHO), 8.27(br-s, 2H, Ar–H), 8.04(br-s, 2H, Ar–H), 7.42-(br-s, 2H, Ar–H). Elemental analysis calculated for C<sub>12</sub>H<sub>8</sub>-N<sub>2</sub>O: C, 73.46; H, 4.11; N, 14.28. Found: C, 73.17; H, 4.35; N, 14.18.

2.2.3. 2-(Naphth[2,3-d]imidazol-2-yl)-4,4,5,5-tetramethyl-4,5*dihydro-1H-imidazolyl-1-oxyl-3-oxide* (4). To a solution of 6 (1.62 g, 8.24 mmol) in dry N-methyl-2-pyrrolidinone (NMP, 80 mL) was added 2,3-bis(hydroxyamino)-2,3-dimethylbutane<sup>8</sup> (1.80 g, 12.4 mmol). The mixture was heated at 130 °C for 10 min and then stirred at room temperature for 48 h. The solution was taken up in dichloromethane (300 mL), cooled to 0 °C, and then sodium periodide (10.6 g, 49.4 mmol) in water (300 mL) was added with stirring. The organic layer was washed with water, dried over anhydrous sodium sulfate, filtered, and evaporated to dryness. Chromatography on silica gel with chloroform as the eluent yielded 2-(naphth[2,3-d]imidazol-2yl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazolyl-1-oxyl-3oxide (4) (0.67 g, 25%), which was recrystallized in the form of dark-green needles by slow evaporation from a dichloromethane/methanol solution. Mp: 229-230 °C (decomposition). FAB-MS: observed 324  $[M+1]^+$  (calculated for  $C_{18}H_{19}N_4O_2$ = 323.37). Elemental analysis calculated for  $C_{18}H_{19}N_4O_2$ : C, 66.86; H, 5.92; N, 17.33. Found: C, 66.57; H, 6.08; N, 17.33.

2.3. X-ray Diffraction Analysis. A dark-green needlelike crystal of 4 (0.55 mm  $\times$  0.20 mm  $\times$  0.20 mm) was measured at a temperature of 297 K on a Rigaku four-circle AFC-7R diffractometer with graphite monochromated Mo Ka radiation  $(\lambda = 0.71073 \text{ Å})$ . The data were collected using the  $\theta - 2\theta$  scan technique to a maximum  $2\theta$  value of 65.0°. The structure was solved by a direct method (SIR92)<sup>9</sup> and refined by SHELXL-97<sup>10</sup> on a Silicon Graphics O<sup>2</sup> workstation with the program system teXsan.<sup>11</sup> Three standard reflections were measured every 150 reflections. Absorption correction was made by the  $\Psi$  scan method. The positions of all H atoms were introduced by difference Fourier maps. Non-H atoms were treated anisotropically, and H atoms were treated isotropically. Because the Flack parameter led to an inconclusive value, a Friedel pair was merged before the final refinement, resulting in the absolute direction of the polar axis being chosen arbitrarily.

**2.4. Computational Details.** *J* values were calculated with Gaussian 03<sup>12</sup> at the UB3LYP<sup>13a,b</sup> or UBLYP<sup>13c</sup>/6-31G\* levels for a hydrogen-bonded dimeric coordinate extracted from X-ray analysis. Spin annihilation was performed using the following equation that was developed by Yamaguchi et al.<sup>14</sup>

$$J = \frac{E^{\rm LS} - E^{\rm HS}}{\langle S^2 \rangle^{\rm HS} - \langle S^2 \rangle^{\rm LS}}$$

Tight convergence was used to discuss small energy differences  $(10^{-8} \text{ au})$ . Highest occupied molecular orbital-lowest-unoccupied molecular orbital (HOMO–LUMO) mixed initial guesses were created to estimate broken-symmetry singlet-state energies.

#### 3. Results

**3.1. Syntheses.** The synthetic route of **4** is shown in Scheme 1. **5** was synthesized by the cyclization reaction of 2,3-diaminonaphthalene with ethyl diethoxyacetate under a strong basic condition, using sodium ethoxide as described by Browne.<sup>15</sup> **5** was hydrolyzed using diluted sulfuric acid to yield the corresponding aldehyde (**6**). **6** is not soluble in most organic solvents, not even in dimethyl sulfoxide (DMSO) at room temperature, which suggests the formation of the same dimeric structure as reported for benzimidazole-2-carbaldehyde.<sup>16</sup> The condensation reaction of **6** with 2,3-bis(hydroxyamino)-2,3-dimethylbutane was performed using NMP as a solvent, with heating, followed by chemical oxidation using sodium periodide to give **4** as a dark-green solid.<sup>17</sup>



**3.2. Solution ESR Spectra.** Solution ESR spectra of **4** were measured at room temperature in  $5 \times 10^{-5}$ M of benzene, benzene/methanol (19/1), and benzene/methanol- $d_1$  (19/1) solutions. The spectrum of the benzene solution consists of typically five lines, as usually shown in 2-aryl nitronyl nitroxides, but the relative intensity (height of the first-derivative peaks) of ca. 1:1.7:2:1.7:1 is clearly different from the expected intensity of 1:2:3:2:1 (spectrum not shown). This is probably due to the nonequivalence of the nitrogen nuclei (I = 1) of the nitroxide unit by forming an intramolecular N(H)···O hydrogen bond. Such nonequivalence of the nitrogen nuclei has also been reported for intramolecular hydrogen-bonded 2-hydroxyphenyl nitronyl nitroxides.<sup>18</sup> When 5% methanol was added to the



**Figure 2.** (a) Experimental and (b) simulated ESR spectra of **4** in a benzene/methanol solution. Main figures correspond to the central signals ( $M_I = 0$ ).

 TABLE 1: Experimental and Calculated Hyperfine

 Coupling Constants (hfccs) of 4

	hfcc (mT)	
site	experimental <sup>a</sup>	calculated <sup>b</sup>
a <sub>N</sub>		
nitroxide N	0.739	(+)0.571, (+)0.437
naphthimidazole 1 N	0.013	(-)0.017
naphthimidazole 3 N	0.042	(-)0.081
a <sub>H</sub>		
methyl H	0.023	
naphthimidazole 1 H	0.016	(+)0.014
naphthimidazole 4 H	0.043	(+)0.052

 $^{a}$  5 × 10<sup>-5</sup>M benzene/methanol (19/1) solution at room temperature. <sup>b</sup> UB3LYP/EPR-II for experimental geometry.

solution, the nonequivalence disappeared, and the relative intensity approached the ideal values, because of the coupling of the unpaired electron with two equivalent nitrogen nuclei (Figure 2). Each line exhibits a more-complex pattern, showing the coupling of the unpaired electron with 12 hydrogen nuclei  $(I = \frac{1}{2})$  of four methyl groups and hydrogen and/or nitrogen nuclei of the naphth[2,3-d]imidazole ring. When comparing the spectra of the benzene/methanol and benzene/methanol- $d_1$ solutions, we found that each complex pattern is different (compare Figures 2 and 3). Hyperfine coupling constants (hfccs) obtained by the curve-fitting technique<sup>19</sup> are summarized in Table 1. The spectrum of the benzene/methanol- $d_1$  solution can be nicely reproduced by the same hfccs for the benzene/ methanol solution, except for one hfcc for a proton. We assigned the hfcc for the NH proton of the naphth[2,3-d]imidazole ring by considering the proton exchange reaction between the



**Figure 3.** (a) Experimental and (b) simulated ESR spectra of 4 in a benzene/methanol- $d_1$  solution. Main figures correspond to the central signals ( $M_I = 0$ ).

TABLE 2: Calculated Spin Densities of 4<sup>a</sup>

atom	spin density
01	+0.382
O2	+0.322
N3	+0.249
N4	+0.285
N5	-0.006
N6	-0.052
C7	-0.203
C14	+0.039
H5	-0.001
H17	+0.001

<sup>*a*</sup> UB3LYP/EPR-II calculation for experimental geometry. See ORTEP drawing for atom numbering.



Figure 4. ORTEP drawing and atomic numbering of the molecular structure of 4.

hydroxyl proton of methanol and the NH proton of the naphthimidazole ring. Although the spectra were not sufficiently resolved to assign hfccs for all the protons, the results showed that spin densities are induced at least on the imidazole moiety, which includes the NH proton-donor site.

Calculated hfccs (taken directly from calculated Fermi contact terms), using Gaussian 03 at the UB3LYP/EPR-II<sup>20</sup> level for the experimental geometry, are compared with experimental hfcc values in Table 1. Calculated Mulliken spin densities at the same level are also summarized in Table 2. The experimental and calculated results suggest that small spin densities are located on the methyl groups and imidazole ring, although most of the spin densities localized on the ONCNO moiety of the NN unit.

**3.3. X-ray Analysis.** A dark-green single crystal of **4** suitable for X-ray analysis was obtained by slow evaporation from a dichloromethane/methanol solution. Crystallographic data of **4** 

**TABLE 3:** Crystal and Refinement Data of 4

parameter	value
chemical formula	$C_{18}H_{19}N_4O_2$
formula weight	323.37
crystal system	orthorhombic
space group	<i>Pca</i> 2 <sub>1</sub> (No. 29)
lattice constants	
a	13.515(3) Å
b	11.858(3) Å
С	10.593(3) Å
volume, V	1697.6(8) Å <sup>3</sup>
Ζ	4
calculated density, D <sub>calcd</sub>	1.265 g cm <sup>-3</sup>
μ	$0.085 \text{ mm}^{-1}$
total reflections collected	7114
independent reflections	3103
reflections observed $(I > 2\sigma(I))$	1407
number of parameters	293
R <sub>int</sub>	0.0453
$R(I > 2\sigma(I))$	0.041
wR (all data)	0.082
goodness of fit	0.83

are summarized in Table 3. 4 crystallizes in the noncentrosymmetric space group  $Pca2_1$ , with four molecules in a unit cell. Figure 4 shows an ORTEP drawing of 4. The dihedral angle between the best planes of the imidazole ring (N(5)-C(14)-N(6)-C(16)-C(15)) and the O(1)-N(3)-C(7)-N(4)-O(2)moiety is 12.4°; the coplanarity becomes higher when compared to the corresponding angles of 48.4° for 1 and 24.3° for 2. The crystal structure along the *a*- and *c*-axes is shown in Figure 5. Short intermolecular distances of 3.12 Å between N(5)···O(1)\* and 3.13 Å between  $N(5) \cdots N(6)^*$  are found (symmetry code: (\*)  $-x + \frac{3}{2}$ , y,  $z - \frac{1}{2}$ ), forming four-centered (trifurcated) intramolecular and intermolecular hydrogen bonds between the NH proton (D), the imine N atom  $(A_1)$ , and the nitroxide O atoms (A<sub>2</sub>) (denoted by dashed lines).<sup>21</sup> The hydrogen bonds are repeated along the c-axis to form a one-dimensional chain structure in edge-to-edge fashion. Along the hydrogen-bonded chain, close contact between the O atoms of the nitroxide is observed, and the distance of 2.99 Å between  $O(2) \cdots O(1)^*$  is slightly shorter than the sum of the van der Waals radii of the two O atoms (3.04 Å).<sup>22</sup> Judging from the distance, a strong



Figure 5. ORTEP drawings of the crystal structure of 4 along the *a*-axis (left) and along the *c*-axis (right). Dashed lines show intramolecular and intermolecular hydrogen bonds.



**Figure 6.**  $\chi_m - T$  and  $\chi_m T - T$  (inset) plots of ( $\bigcirc$ ) **4** and ( $\bigcirc$ ) **4**- $d_1$ . Solid line is calculated using the Bonner-Fisher model with J = -14 cm<sup>-1</sup>.

magnetic interaction between the O atoms, which carry a large positive spin density, is expected. On the other hand, the shortest O···O distance between hydrogen-bonded chains is 4.47 Å  $(O(1) \cdot \cdot O(2)^{**};$  symmetry code: (\*\*) -x + 2, -y,  $z + \frac{1}{2})$ . The methyl groups of the NN units intervene between the O atoms, and the large interchain orbital overlap seems to be negligibly small.

3.4. Solid-State Magnetic Properties. The magnetic susceptibility measurement of a polycrystalline sample of 4 was performed. The diamagnetic contribution was estimated using the Pacault method.<sup>23</sup> Figure 6 shows  $\chi_m$  vs T and  $\chi_m T$  vs T (inset) plots for 4, where  $\chi_m$  is the molar susceptibility and T is the absolute temperature. At 300 K,  $\chi_m T = 0.36$  emu K mol<sup>-1</sup>, which corresponds to the value expected for an isolated monoradical (0.375 emu K mol $^{-1}$ ). The value decreases slowly as the temperature decreases, which suggests that an antiferromagnetic interaction is dominant between spins. Focusing on the  $\chi_m$  vs T plot,  $\chi_m$  increases gradually as the temperature decreases and has a broad maximum at 12 K. Solution ESR spectra and density functional theory (DFT) calculations show that most of the spin densities are concentrated on the ONCNO moiety (see Tables 1 and 2), and the results are consistent with reported polarized neutron diffraction (PND) studies for other NN derivatives.<sup>24</sup> When compared to the intrachain O····O distance of 2.99 Å, even the shortest interchain O····O distance of 4.47 Å is too long to affect the magnetic character. Therefore, we consider that an ideal one-dimensional spin system is selfassembled along the hydrogen-bonded direction. The magnetic data can be nicely fit to the Heisenberg one-dimensional antiferromagnetic chain model (the Bonner-Fisher model<sup>25</sup>), using  $H = -JS_1 \cdot S_2$  and the numerical expression<sup>26</sup>

$$\chi_{\rm m} = \frac{N_{\rm A}g^2 \mu_{\rm B}^2}{k_{\rm B}T} \left( \frac{0.25 + 0.074975x + 0.075235x^2}{1.0 + 0.9931x + 0.172135x^2 + 0.757825x^3} \right)$$

where  $x = |J|/(k_BT)$ . The best-fit parameter is  $J = -14 \text{ cm}^{-1}$ .

#### 4. Discussion

2 2

**4.1. Effects of Ring Extension on Molecular Structure and Crystal Structure.** The dihedral angles between the best planes of the imidazole rings and the ONCNO moieties of **1**, **2**, and **4** are  $48.4^{\circ}$ ,  $24.3^{\circ}$ , and  $12.4^{\circ}$ , respectively. These dihedral angles are determined by the balance of two electrostatic forces: an intramolecular hydrogen bond between the NH proton (D) and the O atom of the nitroxide (A<sub>2</sub>), which retains high coplanarity, and electrostatic repulsion between the lone pairs of the N atom of the imine (A<sub>1</sub>) and the O atom of the nitroxide (A<sub>2</sub>), which





Figure 7. Schematic drawing of intramolecular hydrogen bond (left) and electrostatic repulsion (right).



Figure 8. Explanation drawing of the nature as an acid of imidazole (top) and as an acid of the conjugated base (bottom).

twists the angles (Figure 7). Experimental  $pK_a$  values of parent heterocycles have been used to evaluate the electric charges of D and A<sub>1</sub>, because  $pK_a$  values are strongly affected by the atomic charge distribution within the molecules. The  $pK_a$  values of these heterocycles, as an acid (Figure 8), are 14.2, 13.2, and 12.52 for imidazole, benzimidazole, and naphth[2,3-d]imidazole, respectively,27 showing that the proton-donating character of the NH protons increases in the following order: imidazole < benzimidazole < naphth[2,3-d]imidazole. On the other hand, the  $pK_a$  values of conjugate acids of the parent heterocycles, which correspond to the proton affinity of the A1 sites (Figure 8), are 6.95, 5.53, and 5.24 for imidazole, benzimidazole, and naphth[2,3-d]imidazole, respectively, showing that the negative charge of the N atom of the imine decreases in the following order: imidazole > benzimidazole > naphth[2,3-d]imidazole. In the case of 4, we considered that the hydrogen bond between D and A<sub>2</sub> is the strongest and that the electrostatic repulsion between A1 and A2 is the weakest, resulting in the smallest dihedral angle. The electronic effect of ring extension is due to the fusion of the imidazole ring at the  $\beta$ -positions of the naphthalene ring at which the electric charge densities are rather lower than those at the  $\alpha$ -positions. In addition to the former two electrostatic forces,  $\pi$ -conjugation between the  $2p_z$  orbitals of the naphthimidazole ring and the ONCNO moiety also contribute to the planarity.

A schematic drawing of the hydrogen-bonded chain of 2 and 4 is shown in Figure 9. In the crystal of 2, D attracts two  $A_2$ sites to form three-centered (bifurcated) intramolecular and intermolecular hydrogen bonds. The A2 site that does not participate in the intermolecular hydrogen bond but does in the intramolecular hydrogen bond approaches the sp<sup>2</sup> C-atom of the neighboring molecule. The  $\sigma$ -type orbital overlap between the  $\alpha$ -spin-carrying O atom and the  $\beta$ -spin-carrying sp<sup>2</sup> C atom enables the neighboring spins to couple ferromagnetically, based on the McConnell I mechanism.<sup>28</sup> A1 does not participate in the intermolecular hydrogen bond. In the crystal of 4, on the other hand, A1 does participate in the intermolecular hydrogen bond to form four-centered (trifurcated) intramolecular and intermolecular hydrogen bonds between D, A<sub>1</sub>, and A<sub>2</sub>. The hydrogen bonds lead to an edge-to-edge molecular arrangement, and the O····C contact favorable to the occurrence of ferromagnetic interaction is collapsed.

**4.2. Spin Density Induced on the NH Proton Donor Site.** Spin-density distribution within a molecule is significantly important when intermolecular magnetic interaction is examined by applying the McConnell I mechanism for close contact between the molecules. We are especially interested in the sign



Figure 9. Schematic drawing of the hydrogen-bonding motifs of 2 (left) and 4 (right). Dashed lines show intramolecular and intermolecular hydrogen bonds.

 TABLE 4: Calculated Spin Densities on Each Basis

 Function and Fermi Contact at the NH Proton (H5) of  $4^a$ 

	spin density
1s	0.00000
28	0.00001
38	0.00010
4s	-0.00080
5px	-0.00002
5py	-0.00001
5pz	-0.00007
total Mulliken spin density	-0.00078
Fermi contact term	(+)0.01378 mT

<sup>a</sup> UB3LYP/EPR-II calculation for experimental geometry.

and magnitude of the spin density on the NH proton of 4, because the hydrogen bond could become a magnetic interaction pathway. Solution ESR spectra clearly showed that spin densities are induced on the NH proton donor site, although we could not determine the sign. To support this result, we used the calculated hfccs and spin densities of 4 (see Tables 1 and 2). Interestingly, the UB3LYP/EPR-II single point calculation for the X-ray analysis structure shows that the Mulliken spin density of the NH proton is negative and that the Fermi contact term of the proton is positive: the signs are opposite. In the case of 2-tert-butylaminoxylbenzimidazole,29 the same signs of spin density and the Fermi contact term were calculated for the corresponding NH proton (-0.00195 and -0.612 G at a UBLYP/cc-pVDZ level, respectively). Therefore, the conflict observed in 4 may not be due to the electronic structure of the imidazole skeleton itself. The spin densities of each of the basis sets of 4 summarized in Table 4 show that positive spin densities are induced on the inner shells (1s, 2s, 3s) and that negative spin densities are induced on the outer shells (4s, 5p). This result could be interpreted as follows: spin densities on inner shells are induced through a covalent bond and those on outer shells are induced through an intramolecular hydrogen bond, as shown in Figure 10.30 In summary, small negative spin densities were calculated on the NH proton-donor site. This suggests that the Fermi contact terms, which reflect only the spin densities on





Through covalent bond

Through intramolecular hydrogen bond



Figure 10. Schematic drawing of spin polarization mechanism of 4.



Figure 11. Plausible magnetic coupling mechanism of 4 along the hydrogen-bonded direction.

the nuclei, are not always a good representation of the spin densities on the entire atoms.  $^{18}\,$ 

4.3. Magnetic Interaction Pathway. It is quite natural for 4 to assume a magnetic interaction pathway along the hydrogenbonded chain direction by taking into account the magnetic character that is reproducible by the one-dimensional chain model. We have assumed two plausible interaction pathways along the chain direction, as described in Figure 11: (i) throughspace interaction between the O atoms of the nitroxide, which causes antiferromagnetic interaction; (ii) through the NH···ON intermolecular hydrogen bond, which causes ferromagnetic interaction. Experimental results showed that the antiferromagnetic interaction is dominant between spins and that pathway (i) must be the main mechanism of the interaction. To examine the contribution of pathway (ii), we prepared  $4-d_1$ , in which the NH hydrogen was replaced by deuterium. If pathway (ii) contributes greatly to the magnetic interaction, a noticeable change would be expected, as shown in the crystal of RSNN that was reported by Sugawara et al.<sup>2e</sup> **4**- $d_1$  was prepared by recrystallization from dichloromethane/methanol- $d_1$  solution. The ND stretching appears at 2432 cm<sup>-1</sup>, as expected, by applying Hooke's law to the NH stretching of 3253 cm<sup>-1</sup> for 4, and the percentage of deuteration was estimated to be ca. 50%, based on the intensities of the solid-state IR spectra. The  $\chi_{\rm m}$  vs T and  $\chi_{\rm m}T$  vs T plots of 4-d<sub>1</sub> are shown in Figure 6, with the result for 4 for comparison. The maximum  $\chi_m$  values of 4and 4- $d_1$  are both 0.0109 emu mol<sup>-1</sup> at 12 K, which suggests



Figure 12. Schematic drawing of a canted orbital overlap of 4.

that the effect of deuteration on the magnetic interaction is negligible and that pathway (i) is predominant. The hydrogen bond mainly has a role in crystal scaffolding. Even though a small spin density is induced on the NH proton and pathway (ii) might exist in the crystal, the magnitude is much smaller than that of pathway (i), and the observed magnetic interaction of  $-14 \text{ cm}^{-1}$  is mainly propagated by pathway (i).<sup>31</sup>

As mentioned previously, the O···O distance of the nitroxide units along the hydrogen-bonded chain direction is 2.99 Å. Judging from the O···O distance and the spin densities carried by the O atoms of the nitroxide, the experimental J value of  $-14 \text{ cm}^{-1}$  is much smaller than that which is expected. This can be explained by the canted overlap between the  $p_z$  orbitals (Figure 12). Spin densities are located in the  $p_z$  orbitals perpendicular to the ONCNO mean planes, and a strong antiferromagnetic interaction is expected when a perfect antiparallel orbital overlap is realized, as shown in crystals such as 1 or 4-azaindol-2-yl nitronyl nitroxides.<sup>32</sup> In the case of 4, however, the dihedral angle between the best planes of neighboring ONCNO moieties along the hydrogen-bonded chain is 68.3°, and the overlap between the  $p_z$  orbitals is incomplete, resulting in a weaker antiferromagnetic interaction than expected.

*J* values calculated for the coordinate of a hydrogen-bonded dimer at the UB3LYP/6-31G\* and UBLYP/6-31G\* levels are -1.0 and -17.7 cm<sup>-1</sup>, respectively, qualitatively reproducing the experimentally obtained *J* value of -14 cm<sup>-1</sup>. The strong functional dependency might due to limitations of the density functional calculation in the present case.

# 5. Summary

The one-dimensional hydrogen-bonded chain observed in the crystal of 2-(naphth[2,3-*d*]imidazol-2-yl)-4,4,5,5-tetramethyl-4,5dihydro-1*H*-imidazolyl-1-oxyl-3-oxide (4) can be recognized as an ideal one-dimensional spin system because each chain is wellisolated by the steric effects of the naphth[2,3-*d*]imidazole ring and four methyl groups. Although two magnetic interaction pathways ((i) through-space interaction between the O atoms of the nitroxide and (ii) through the NH···ON intermolecular hydrogen bond) have been assumed, we have concluded that pathway (i) is predominant and that the hydrogen bond mainly has a role in crystal scaffolding.

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**Supporting Information Available:** Variation of Fermi contact terms and Mulliken spin densities of H atoms, as a function of the dihedral angle between the aryl rings and the ONCNO moeities (Figure 1S); angular dependence of calculated *J* values for rotation of the naphthimidazole ring (Figure 2S) and the NN unit (Figure 3S). (PDF and CIF data.) This material is available free of charge via the Internet at http://pubs.acs.org.

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(30) We calculated spin densities and Fermi contact terms of **2** and phenyl nitronyl nitroxide at the UB3LYP/6-31G\*//AM1 level, by changing the dihedral angle between the aryl rings and the ONCNO moieties from  $0^{\circ}$  to  $90^{\circ}$ . Calculations for **2** show that the sign of the spin densities at the NH proton changes while changing the angle, although that of Fermi contacts is always positive. On the other hand, the sign of both the spin densities and Fermi contact terms of the *ortho*-proton of phenyl nitronyl nitroxide is always positive. In the case of **2**, the magnitude of spin density induced through a covalent bond seems smaller than that induced through an intramolecular hydrogen bond. Therefore, we consider that the explanation is reasonable for imidazol-2-yl nitronyl nitroxide derivatives. See Supporting Information (Figure 1S) for more details.

(31) We investigated the angular dependence of the calculated J values for a hydrogen-bonded dimeric coordinate of 4 by rotating the naphthimidazole ring or NN unit around the C-C bond, from  $-30^{\circ}$  to  $+30^{\circ}$  (0° corresponds to the experimental geometry). The rotation of the naphthimidazole ring does not affect the J values very much, whereas rotation of the NN unit does affect the J values significantly, showing that the close contact between the nitroxide O atoms induced by the intermolecular hydrogen bond, rather than the intermolecular NH···ON hydrogen bond, is responsible for the antiferromagnetic character. In Figure 2S in the Supporting Information, the maximum J value appears at 0°, which implies that the NH···ON hydrogen bond is a ferromagnetic interaction pathway. See Supporting Information (Figures 2S and 3S) for more details.

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