

## Ferromagnetic Spin Interaction in a Crystalline Molecular Complex Formed by Inter-heteromolecular Hydrogen Bonding: a 1 : 1 Complex of Phenyl Nitronyl Nitroxide Radical and Phenylboronic Acid

Takeyuki Akita, Yasuhiro Mazaki and Keiji Kobayashi\*

Department of Chemistry, College of Arts and Sciences, The University of Tokyo, Komaba, Meguro-ku, Tokyo 153, Japan

A crystalline molecular complex derived from phenyl nitronyl nitroxide and phenylboronic acid exhibits a ferromagnetic spin interaction ( $J = +0.65$  K) below 30 K: X-ray analysis reveals the crystal structure to be constituted of a one-dimensional array of two component molecules linked alternately by the NO...HOB hydrogen bond.

There has been growing interest in the preparation and characterization of organic radical solids which exhibit intermolecular ferromagnetic interactions.<sup>1</sup> Among those, nitronyl nitroxide radicals substituted with aromatic rings have been extensively studied.<sup>2</sup> In nitronyl nitroxide radicals the electron spins are more localized at the NO bonds and very little spin density is at the central  $sp^2$  carbon atom bridging the two NO groups, which results in insufficient spin polarization on the substituent  $\pi$ -moiety. We have envisaged that an intermolecular spin-coupler would facilitate the spin interaction between the neighbouring two nitroxide radical centres to provide an alternative path of the direct spin transmission. As such an intermolecular spin coupler we have chosen phenylboronic acid **1** and prepared a hydrogen-bonding molecular complex with phenyl nitronyl nitroxide radical **2**. In contrast to the recent reports, which have demonstrated the successful molecular and crystal designs by the use of inter-homomolecular hydrogen bonds to realize a ferromagnetic interaction in the solid state,<sup>3,4</sup> our approach is the employment of the inter-heteromolecular hydrogen bond to constitute a supramolecular structure and a spin transmission path.

Complexation with diamagnetic organic molecules such as **1** may be considered to result in the dilution of the spin concentration in the solid-state and therefore seems not to be promising, nevertheless we have observed clear intermolecular magnetic interactions which, moreover, are ferromagnetic at low temperature. The present study provides the first example of spin transmission through diamagnetic compounds *via* inter-heteromolecular hydrogen bonding.

When phenylboronic acid **1** was recrystallized from a mixture of hexane and dichloromethane with phenyl nitronyl nitroxide **2**, the complex of **1** and **2** with a 1 : 1 stoichiometric ratio was isolated as blue prisms. The crystalline complex is stable at ambient temperature but decomposes at 114 °C. The temperature dependence of the paramagnetic susceptibility of the polycrystalline sample of the complex was measured by means of a SQUID susceptometer in the temperature range 2–300 K. Fig. 1 depicts the results in the form of temperature dependence of the product of the paramagnetic susceptibility ( $\chi$ ) with the temperature. The room temperature value of  $\chi T$  is about 0.378  $\text{emu K mol}^{-1}$  in good agreement with the value expected for uncorrelated spins based on the Curie constant. As the temperature is lowered, the  $\chi T$  value increases, suggesting that ferromagnetic interaction is predominant at low temperatures. Based on the crystal structure described below the magnetic data were analysed in terms of a one-dimensional Heisenberg

model for ferromagnetically coupled linear arrays of spin 1/2.<sup>5</sup> Thus, the best fit obtained with  $g = 2.007$  gave an intrachain ferromagnetic interaction of  $J/k_B = +0.65$  K and an interchain antiferromagnetic interaction of  $J'/k_B = -0.40$  K.

The X-ray crystal structure of the complex is shown in Fig. 2.† There are two crystallographically independent molecules for both **1** and **2**. The boron atoms form planar trivalent bonds. Their phenyl substituents are almost coplanar to the plane made by the trivalent boron moieties. The twist angles are as slight as

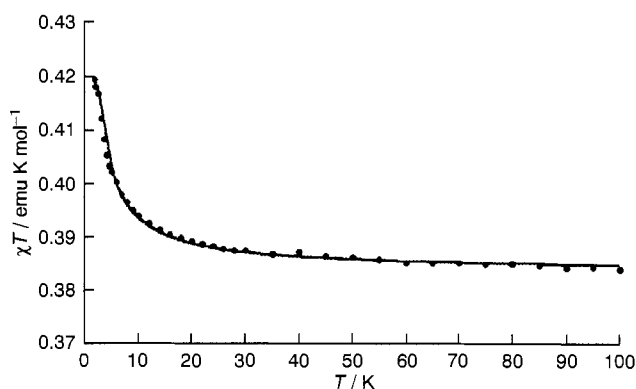


Fig. 1 Temperature dependence of products of paramagnetic susceptibility  $\chi$  and temperature  $T$  for the 1 : 1 complex of **1**·**2**. The solid line is calculated based on a 1-D chain model.

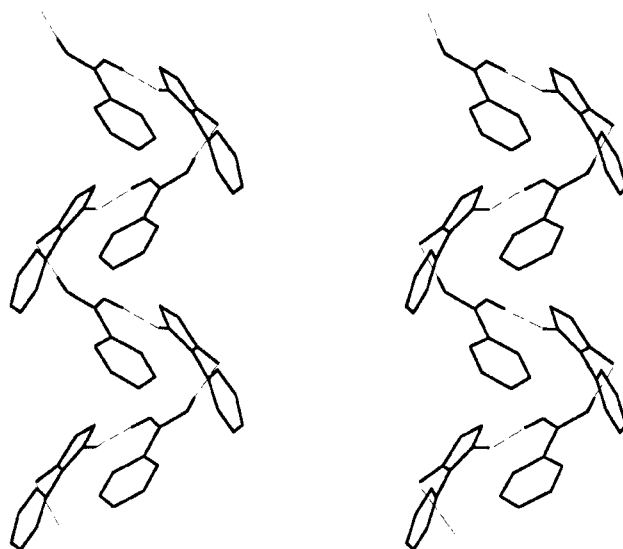
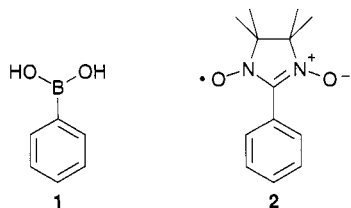


Fig. 2 Stereoscopic view of the crystal structure of the complex **1**·**2** along the  $b$  axis. The broken lines indicate the hydrogen bonds. For simplicity, the methyl groups and the hydrogen atoms, except for those of O–H, are not shown. Selected interatomic distances (Å) and angles (°): B–O: 1.356(3), 1.354(3), B–C: 1.567(3), N–O: 1.287(2), 1.278(2), C(1)–N: 1.342(2), 1.342(2), C–B–O: 117.0(2), 125.6(2), O–N–C(1): 125.6(2), 125.0(2), N–C–N: 108.2(2).



6.1° and 7.4°. The phenyl ring of **2** is not coplanar with the nitronyl nitroxide, O(1)–N(1)–C(1)–N(2)–O(2), and forms an angle of 36.7°. In the uncomplexed phenyl nitronyl nitroxide, the corresponding dihedral angle is about 30°,<sup>6,7</sup> being in good agreement.

Each of the component molecules are connected by hydrogen bonds between the NO groups of **2** and the OH groups of **1**. Thus, the radical species **2** is arranged alternately with phenylboronic acid **1** to make an infinite chain of ...**1**...**2**...**1**...**2**.... The O...O distances are 2.78 and 2.79 Å. The ON–C–NO plane intersects with the neighbouring planar O–B–O moieties with angles 14.1° and 82.0°. There are no observed short inter-heteromolecular and inter-homomolecular contacts. The shortest contact between the nitronyl nitroxide groups is an interchain one of 4.49 Å observed for the O...C(1) distance of the two nitronyl nitroxide molecules. The O...O, N...N, and N...O distances are 4.72, 4.64 and 4.50 Å, respectively. Thus, it seems unlikely that these radical pairs are responsible for ferromagnetic spin interactions through space. Furthermore, as shown in Fig. 3, these radical moieties are arranged to make a centrosymmetrically related pair with parallel overlapping of the radical centres that contribute mostly to the SOMO (singly occupied molecular orbital). Such a SOMO–SOMO pairing, if the overlapping of the molecular orbitals could be possible for this large a separation, would lead to an antiferromagnetic spin interaction. A similar dimeric arrangement in the crystal of *N*-ethylpyridinium nitronyl nitroxide has recently been described to be responsible for an antiferromagnetic contribution.<sup>7</sup>

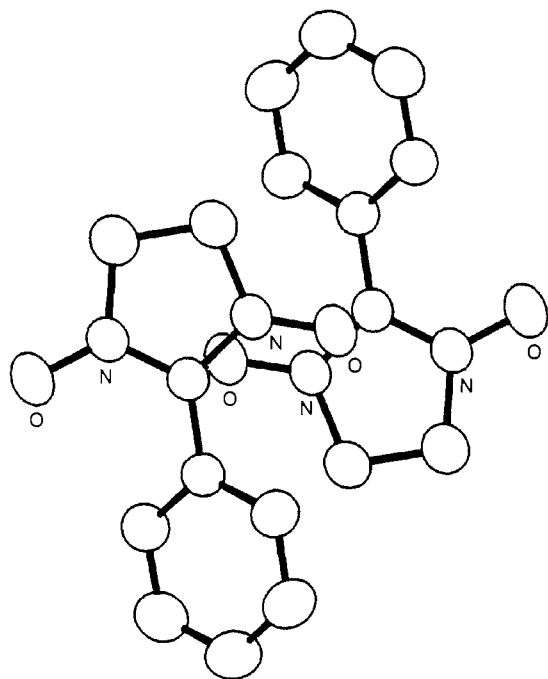


Fig. 3 Molecular overlapping of the interchain pairwise **2** molecules

Thus, the ferromagnetic spin interaction in the complex of **1** and **2** could be ascribed to one-dimensional chain linked by the NO...HO–B–OH...ON hydrogen bond rather than the through space contact of the nitronyl nitroxide molecules. Although the origin of the ferromagnetic nature can not clearly be interpreted at this stage, the importance of hydrogen bonding for generating and propagating the ferromagnetic interactions has been pointed out.<sup>8</sup> It may be important to explore the hetero-component crystals including a radical species for better understanding the magneto-structural relations, since those diversify the bulk magnetic properties of radical species depending on the constituent component.<sup>9</sup>

Financial support by the Grant-in-Aid Scientific Research on Priority Area (No. 06218209) from the Ministry of Education, Science and Culture, Japan, is gratefully acknowledged.

Received, 3rd July 1995; Com. 5/04285B

### Footnote

† Crystal data: C<sub>19</sub>H<sub>24</sub>BN<sub>2</sub>O<sub>4</sub>, *M* = 355.22, monoclinic, space group *P*2<sub>1</sub>/*n*, *a* = 14.764(3), *b* = 9.482(3), *c* = 13.686(2) Å, β = 90.20(1)° (room temp.). *V* = 1915.9(7) Å<sup>3</sup>, *Z* = 4, *D*<sub>c</sub> = 1.231 g cm<sup>-3</sup>. *F*(000) = 756.0. 4323 measured reflections, 3472 unique reflections, collected on a Rigaku AFC-5 four-circle diffractometer with monochromatic Mo-Kα radiation (0.71069 Å). No. of parameters 380 for 2674 independent reflections with *F*<sub>o</sub> > 3σ(*F*<sub>o</sub>). Solution SHELXS-86, refinement UNICS-III, C, N, B, O anisotropic, H isotropic. *R* = 0.039, *R*<sub>w</sub> = 0.045. Four methyl groups exhibit disorder due to the puckered five-membered ring. The positions of the disordered atoms were located from a differential Fourier map. The fixed occupancy factors, 0.5, were estimated from their peak heights. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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