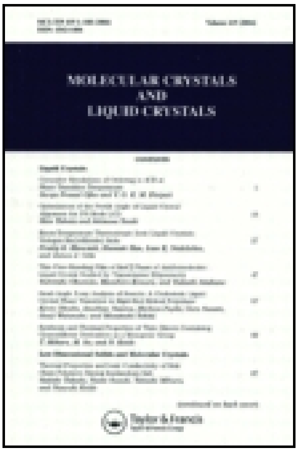

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Ferromagnetic Spin Interaction Through the Inter-Heteromolecular Hydrogen Bond: A 1:1 Crystalline Complex of Phenylboronic Acid and Phenyl Nitronyl Nitroxide

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To cite this article: Takeyuki Akita , Yasuhiro Mazaki & Keiji Kobayashi (1996): Ferromagnetic Spin Interaction Through the Inter-Heteromolecular Hydrogen Bond: A 1:1 Crystalline Complex of Phenylboronic Acid and Phenyl Nitronyl Nitroxide, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 279:1, 39-45

To link to this article: http://dx.doi.org/10.1080/10587259608042174

Mol. Cryst. Liq. Cryst., 1996, Vol. 279, pp. 39–45
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FERROMAGNETIC SPIN INTERACTION THROUGH THE INTER-HETEROMOLECULAR HYDROGEN BOND: A 1:1 CRYSTALLINE COMPLEX OF PHENYLBORONIC ACID AND PHENYL NITRONYL NITROXIDE

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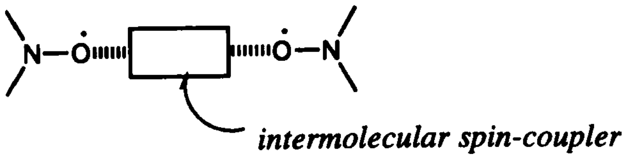
Abstract A crystalline molecular complex derived from phenyl nitronyl nitroxide (**1**) and phenyl boronic acid (**2**) exhibits a ferromagnetic spin interaction (J= +0.65 K) below 30 K: An X-ray analysis revealed the crystal structure constituted of one-dimensional array of two component molecules linked alternately by the NO--HOB hydrogen bonds. The NO--HO-B-OH---ON linkage was suggested to act as a path for ferromagnetic spin coupling. An unusual formation of nitrosonium salt (**3**) was found in the reaction of **1** and BF_3. Its molecular and crystal structures were determined.

INTRODUCTION

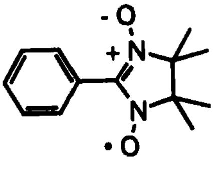
A number of stable diradical species, in which radical centers are connected through an appropriate π-conjugation, have extensively been investigated.[1] In diradicals comprised of two nitronyl nitroxide radical units, the electron spins are more localized at the NO bonds and very little spin density is at the central sp^2 carbon atom bridging the two NO groups, which results in insufficient spin polarization on the substituent π-moiety and hence in insufficient spin-transmission. We have envisaged that an *intermolecular spin-coupler* would facilitate the spin interaction between the neigboring two nitroxide radical centers to provide a path of the direct spin-transmission, not through the π–moiety attached to the nitroxide radical.



As such an intermolecular spin-coupler we have chosen boron compounds and tried to prepare the complexes with **1**. Boron compounds are anticipated to coordinate to the NO group of a nitronyl nitroxide moiety and the B-ON bond thus formed could act as a spin-transmission path as well as a building block of supramolecular structure. In the investigation on these lines, we have found a ferromagnetic 1:1 complex of **1** and phenylboronic acid (**2**) which is formed by the inter-heteromolecular hydrogen bond. We describe herein the structural and magnetic characterization of this complex. Furthermore, we demonstrate an unusual formation of 4,4,5,5-tetramethyl-1-oxo-2-phenyl-4,5-dihydroimidazolium tetrafluoroborate N(3)-oxide (**3**), a diamagnetic salt derived from **1** and BF_3 etherate.

MATERIALS

When phenylboronic acid **2** was recrystallized with phenyl nitronyl nitroxide **1** from a mixture of hexane and dichloromethane, the complex of **1** and **2** with a 1:1 stoichiometric ratio was isolated as blue needles. The crystalline complex is stable at ambient temperature but decomposes at 114 °C.



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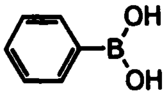

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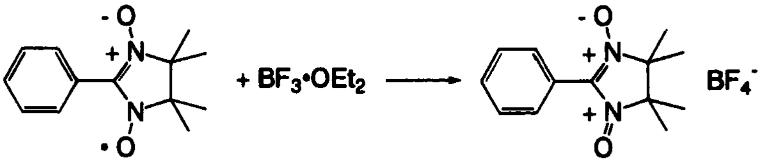
In order to prepare a complex of **1** with BF_3, we mixed **1** and BF_3 etherate in ether. Contrary to our anticipation, this led to the isolation of nitrosonium salt **3** as orange crystals of mp 174 °C. The nitrosonium perchlorate salt has been known as the oxidation product of **1** by copper (II) perchlorate.[2] The structure of tetrafluoroborate was determined by an X-ray analysis as described later.



3

MAGNETIC PROPERTIES

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. Figure 1 depicts the results in the form of temperature dependence of the product of the paramagnetic susceptibility (χ) with the temperature. The room temperature value of χT is about 0.38 emu Kmol^{-1} in good agreement with the value expected for uncorrelated spins based on the Curie constant. As the temperature is lowered, the χT value increases, suggesting that a ferromagnetic interaction is predominant at low temperatures. Based on the crystal structure the magnetic data were analyzed in terms of one-dimensional Heisenberg model for ferromagnetically coupled linear arrays of spin 1/2.[3] 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.

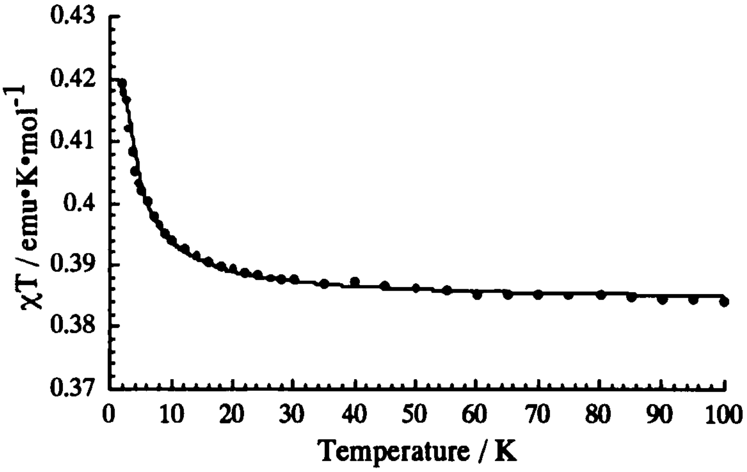


FIGURE 1 Temperature dependence of products of paramagnetic susceptibility χ and temperature T for the 1:1 complex of **1** and **2**. The solid line is calculated based on a 1-D chain model.

CRYSTAL STRUCTURE

Complex (1)(2)

The X-ray crystal structure of the complex is shown in Figure 2. Crystal data are as follows; monoclinic, space group $P2_1/n$, a=14.764(3), b=9.482(3), c=13.686(2) Å, β=90.20(1)° at room temperature. V=1915.9(7) Å^3, Z=4. Data with 4° < 2θ < 55° were collected. No. of parameter 380 for 2674 independent reflections with Fo > 3σ(Fo). R=0.039, Rw =0.045.

The boron atoms form planar trivalent bonds. Their phenyl substituents are almost coplanar to the plane made by the trivalent boron moiety. The twist angles are as slight as 6.0 ° and 7.5°. The phenyl ring of **1** molecules is not coplanar with the nitronyl nitroxide fraction 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°,[4] being in good agreement.

Each of the component molecules are connected by the hydrogen bonds between the NO groups of **1** and the OH groups of **2**. Thus, diradical species **1** is arranged alternately with phenylboronic acid **2** to make an infinite chain of --**1**--**2**--**1**--**2**--. The O---O distances are 2.78 Å and 2.79 Å. The ON-C-NO plane intersects with the neighboring 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 interchain one of 4.49 Å observed for the O---C(1) distance. The O--O, N---N, and N---O distances are 4.724 Å, 4.644 Å, and 4.504 Å, respectively. These radical units are arranged to make a centrosymmetrically related pair with parallelwise overlapping of the radical centers, as shown in Figure 3.

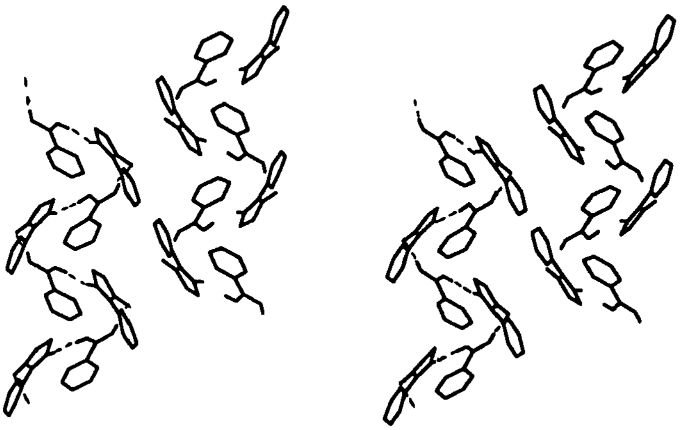


FIGURE 2 Stereoscopic view of of the crystal structure of complex (**1**)(**2**). The broken lines indicate the hydrogen bonds. For simplicity, the hydrogen atoms and methyl groups are not shown. Selected interatomic distances (Å) and angles (°): B-O; 1.356(3). B-C; 1.567(3). N-O; 1.287(2), 1.278(2). C(1)-N; 1.342(2), 1.342(2). C-B-O; 117.0(2), 125.6(2). O-N-C(1); 125.6, 125.0. N-C-N; 108.2 (2).

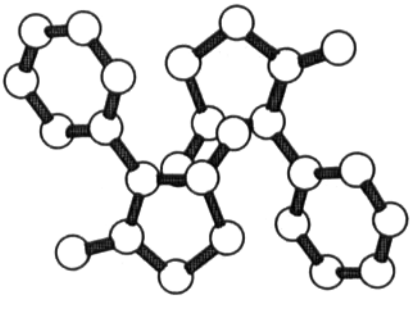


FIGURE 3 Molecular overlapping mode of the interchaine pairwise **1** molecules.

Nitrosonium salt 3

The molecular structure and molecular packing of nitrosonium salt **3** are shown in Figure 4. The crystal data are as follows; monoclinic, space group $P2_1/n$, a=15.380(4), b=12.931(3), c=7.651(3) Å, β=99.47(3)° at room temperature. V=1500.8(7) Å^3, Z=4, Data with 5° < 2θ < 55° were collected. No. of parameter 268 for 2191 independent reflections with Fo > 3σ(Fo). R=0.080, Rw =0.086.

The ON-C-NO fragment is nearly planar. On the other hand, the five-membered heterocyclic ring is twisted. The phenyl plane makes an angle of 30° with ON-C-NO plane, being in good agreement with the perchlorate salt (39°).[2] The NO bond lengths (1.218, 1.230 Å) are smaller than the one found in the complex (**1**)(**2**). The smaller distance is consistent with a high bond order in the oxidized ionic species and with the presence of unpaired electron in an antibonding orbital in the free radical. Two fluorine atoms of the tetrafluoroborate anion are oriented closely to the nitrogen atoms of the counter cation, which bear partial positive charge. The N---F distances are 3.152 and 3.092 Å.

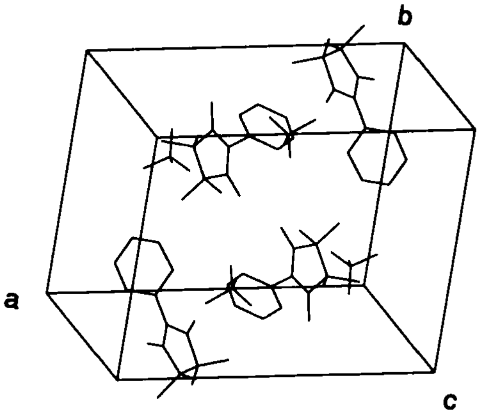
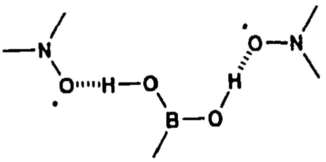


FIGURE 4 Molecular and crystal structure of nitrosonium ion **3**. Selected interatomic distances (Å) and angles (°): B-F; 1.303(9), 1.314(7), 1.317(8), 1.337(8). N-O; 1.218(5), 1.230(5). C(1)-N; 1.347(5), 1.349(5). C-N-O; 124.1(3), 124.2(3). N-C-N; 106.3(3). F-B-F; 100.6(6), 107.6(6), 109.1(6), 110.4(5), 113.7(5), 114.5(5).

DISCUSSION

The ferromagnetic spin interaction observed in complex (**1**)(**2**) could be ascribed to the intermolecular interactions through the NO---HO-B-OH---ON hydrogen bond system. Although there are relatively short contacts between two interchain molecules of **1**, these radical pairs are not conceivable to be responsible for ferromagnetic spin interactions, since these are arranged to make a centrosymmetrically related pair with parallelwise overlapping, as seen in Figure 3. Such a SOMO-SOMO pairing, if the overlapping of the molecular orbitals could be posssible for this far separation, would cause an antiferromagnetic spin interaction.

A quite similar dimeric arrangement as observed in the present work has recently been reported to be responsible for an antiferromagnetic contribution in the crystal of N-ethylpyridinium nitronyl nitroxide.[5] Thus, the ferromagnetic spin interaction in complex (**1**)(**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 nironyl nitroxide molecules. Although the origin of the ferromagnetic nature in this type of the hydrogen bond can not clearly be interpreted at this stage, the importance of hydrogen bonding for generating and propagating the ferromagnetic interactions has been pointed out.[6] Complexation with diamagnetic organic molecule such as **2** may generally be considered to result in the dilution of the spin concentration in the solid-state and therefore seems to be not promissing. Nevertheless we have observed the distinct intermolecular magnetic interaction, even better ferromagnetic one. The present study provides the first example of the spin-transmission through diamagnetic compounds via inter-heteromoleculer hydrogen bonding. In contrast to the recent reports, which have demonstrated succesful molecur and crystal designs by the use of inter-homomolecular hydrogen bond to realize a ferromagnetic interaction in the solid state,[7] our approach is the employment of the inter-heteromolecular hydrogen bond to constitute a supramolecular structure.



One may expect better results if boronic acid itself is used as an inter-heteromolecular spin-coupler. Despite of all efforts we could not obtaine molecular complexes of boronic acid with **1**. 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.[8]

ACKNOWLEDGEMENT

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.

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