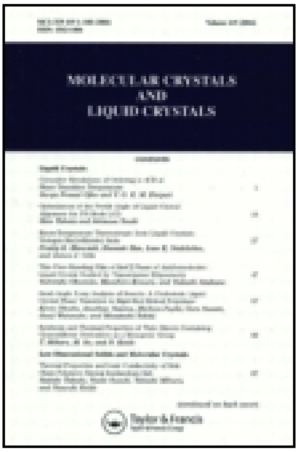

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Ferromagnetic Spin Ordering Along Intermolecular Hydrogen Bonds of a Hydroquinone Derivative Carrying a Nitronyl Nitroxide

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FERROMAGNETIC SPIN ORDERING ALONG INTERMOLECULAR HYDROGEN BONDS OF A HYDROQUINONE DERIVATIVE CARRYING A NITRONYL NITROXIDE

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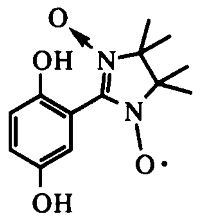
Abstract The crystal structure of an organic ferromagnet, α-HQNN, was characterized by one-dimensional chains constructed through intermolecular hydrogen bonds. Furthermore two parallel hydrogen-bonded chains are connected by bifurcated hydrogen bonds. The analysis of heat capacity data indicates the three-dimensional ferromagnetic intermolecular interaction in this crystal. The results confirm the presence of the ferromagnetic intermolecular interaction along hydrogen bond. The observed isotope effect in the α-HQNN-d_2 crystal is consistent with the above interpretation.

INTRODUCTION

Discovery of the first genuine organic ferromagnet, p-NPNN (p-nitrophenyl nitronyl nitroxide), in 1991 has stimulated the progress in the field of molecular magnetism, and thereafter several organic ferromagnets have been reported successively.[1,2,3] It is time to establish methodology of designing an organic ferromagnet. We have reported the ferromagnetic phase transition at 0.5 K of α-phase crystal of HQNN (2,5-dihydroxyphenyl nitronyl nitroxide), which is a stable organic radical carrying hydroxy groups as orientation controlling sites in crystal.[2] Recently, Veciana et al. reported the ferromagnetic phase transition (0.45K) of *o*-hydroxyphenyl nitronyl nitroxide.[3] These results suggest that the hydrogen bond is able to systematize open-shell molecules into a molecular assembly of prominent magnetic properties. Replacement of hydrogen of the hydroxy group with deuterium in such organic radicals should perturb the crystal structures and intermolecular magnetic interactions. In this respect, we have investigated the magnetic property of the α-phase crystal of HQNN-d_2 in which phenolic hydrogens are substituted with deuterium.



HQNN

RESULTS AND DISCUSSION

Crystal structure of α-HQNN

In the α-phase crystal, HQNN forms both intra- and intermolecular hydrogen bonds. The intramolecular hydrogen bond is formed between phenolic hydroxy group at the 2'-position and nitronyl nitroxide group. This hydroxy group also participates in an intermolecular hydrogen bond with the phenolic hydrogen (5'-position) of the translated molecule along the *c*-axis, constructing a one-dimensional chain. There are two parallel hydrogen-bonded chains, in which facing molecules are related with an inversion symmetry. It is to be noted that these hydrogen-bonded chains are also connected by bifurcated hydrogen bonds. Besides, the oxygen atom of the NN group is closely located to the hydrogen atom of methyl group of a vicinal molecule in the *ab*-plane. These parallel hydrogen-bonded chains are packed in a herringbone-type structure.

The dimensionality in magnetic interaction of α-HQNN

The magnetic susceptibility of α-HQNN can be interpreted by the molecular field approximation.[2] Furthermore the ratio of the critical temperature (0.42 K) of the heat capacity of α-HQNN to the Weiss temperature (0.75 K) is calculated to be 0.56.[4] This value is close to that of three-dimensional Heisenberg model.[5] When the entropy of the high temperature region than Tc and that of the lower is compared, the ratio of the high side to the lower is 0.40 to 0.60.[4] Since the ratio should increase accompanied by decrease in the dimensionality of spin-spin interaction, it is also a scale for estimating the dimensionality of the spin system. The obtained value is consistent with a three dimensional Heizenberg model (z=6 z: number of closest magnetically interacting molecules).[5] Thus it may be concluded that the magnetic interaction in α-HQNN has a three-dimensional character. The magnetic interaction along the hydrogen bonds is, therefore, comparable to those along other directions.

Plausible spin-spin exchange mechanism in α-HQNN

The spin distribution of the phenyl nitronyl nitroxide has been investigated in detail by neutron diffraction experiment: There is an alternation in the spin densities on carbon atoms of the phenyl ring.[6] It is to be noted that carbon atoms (2',5'), at which hydroxy groups are substituted, have spin densities of the different signs (-0.037 and +0.025, respectively). In the α-phase crystal, one-dimensional hydrogen-bonded chain is constructed through the intermolecular hydrogen bond between these two hydroxy groups.

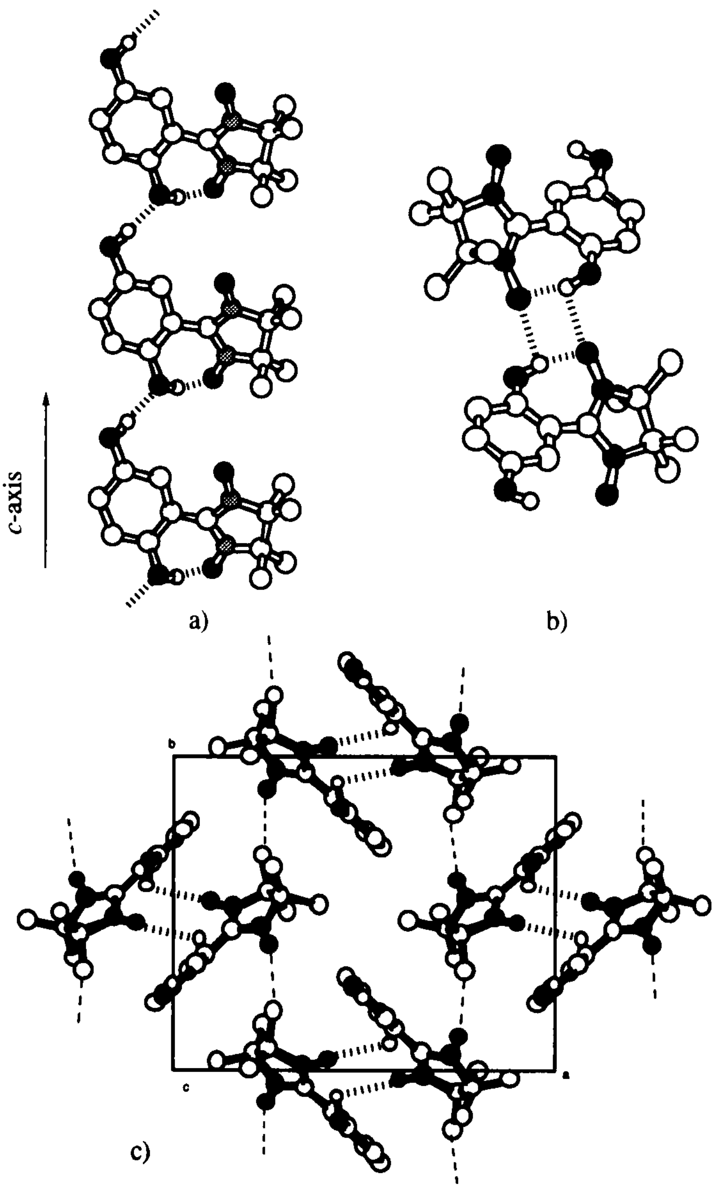


FIGURE 1 Crystal structure of α-HQNN: a) Hydrogen-bonded array along the c-axis. b) The facing two molecules connected by bifurcated hydrogen bond. c) A projected drawing along the *c*-axis. The dashed line shows the N-O•••H-C contact within the *ab*-plane.

Since the induced spin densities including signs on carbon atoms at the foot of these hydroxy groups are different, the spin polarization should be transmitted properly in accord with the condition of ferromagnetic coupling of McConnell's mechanism.[7] Besides, two nitronyl nitroxide groups are closely located with the O•••O distance of 3.159(2)Å at the interchain hydrogen-bonding site (FIG 1b). Although such a close location usually causes antiferromagnetic interaction, the antiferromagnetic intermolecular interaction is not observed in this crystal. Thus the ferromagnetic interaction in this crystal can be interpreted in relation to the hydrogen bonds as well.

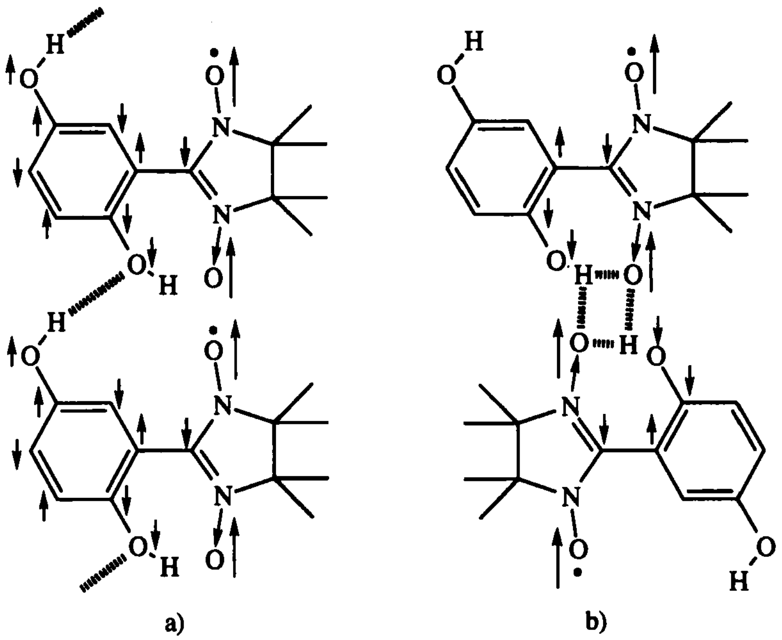


FIGURE 2 The signs of spin densities of HQNN: a) Hydrogn-bonded chain along the *c*-axis. b) The Two facing molecules connected by the bifurcated hydrogen bond.

The other magnetic interaction may exist between an oxygen atom of the nitronyl nitroxide group and a hydrogen of a methyl group of the vicinal molecule, because the methyl protons are spin polarized due to the through-bond mechanism.

Magnetic property in deuterated α-HQNN

Since the distance of the intermolecular hydrogen bonds is supposed to be elongated by deuteration, the intermolecular spin-spin exchange interaction along this direction should be decreased. Deuterated α-HQNN (α-HQNN-d_2) was prepared by recrystallization of

HQNN from ethyl acetate containing 5 % of ethanol-d_1(99.5%). The α-phase crystals with a size of ca. 0.3 × 0.3 × 0.4 mm were obtained by using small amount of seed crystals.

IR spectra of the crystal shows peaks at 2434 and 1030 cm^{-1} which are assignable to the O-D stretching and the bending modes, respectively. Besides, there is a broad peak at 1800-2100 cm^{-1} assignable to the O-D stretching of the intramolecular hydrogen bond. These results suggest the hydrogen atoms of both intra- and intermolecular hydrogen bonds are deuterated. The percentage of deuteration of the sample was estimated to more than 60 % based on the intensities of IR absorption peaks.

The magnetic susceptibility was measured at the temperature range of 2.5 and 250 K with a Faraday-type magnetic balance (main field 5 kOe, gradient 200 Oe cm^{-1}). A Curie constant of 0.383 emu•K•mol^{-1} at an ambient temperature assures the purity of the sample. The χT value increases at temperatures lower than 20 K. This result suggests the ferromagnetic intermolecular interaction also exists in deuterated α-HQNN. The plot was well reproduced by the Curie-Weiss equation with a Weiss temperature of +0.60 ± 0.05 K. This value is smaller than that of non-deuterated α-HQNN (0.75 ± 0.05 K). The result is consistent with the interpretation that the spin-spin interaction exists along the intermolecular hydrogen bond.

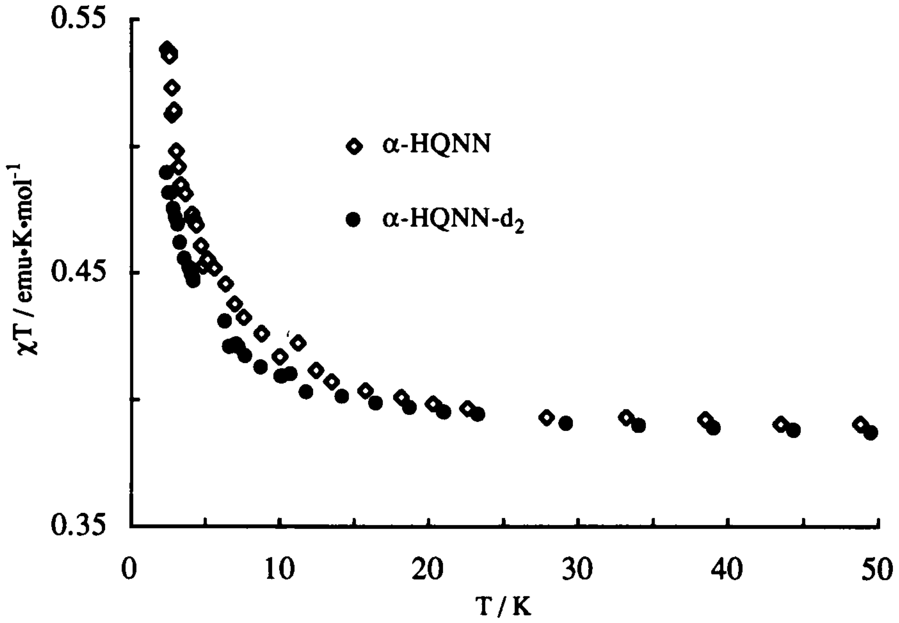


FIGURE 3 Temperature dependence of the magnetic susceptibility of the deuterated and the non-deuterated α-HQNN.

CONCLUSIONS

The intermolecular hydrogen bond turned out to be effective in constructing organized molecular assemblies[8] which exhibit the ferromagnetic property. Although it is crucial to induce significant spin densities on hydrogen-bonding sites, hydrogen bonds may play an important role in designing molecular ferromagnets as a "ferromagnetic coupler".

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