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Experimental and Theoretical Spin Density in a Ferromagnetic Molecular Complex

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The association of phenylboronic acid (no unpaired electron) with the free radical phenyl nitronyl nitroxide (S = 1/2) constitutes an inter-heteromolecular hydrogen bonding system presenting ferromagnetic intermolecular interactions. We have investigated its spin density distribution in order to visualize the pathway of these magnetic interactions. The spin density of this complex was measured by polarized neutron diffraction. The data were treated using both direct and indirect methods. As in the **isolated** PNN, the main part of the spin density is located on the O-N-C-N-O fragment of the PNN radical. But, with the PNNB, the global spin density distribution give evidences that the phenylboronic acid constitutes a spin transmission path between PNN radicals via hydrogen bonds. The experimental results are compared to those obtained by density functional theory calculations.

Keywords: spin density; neutron diffraction; hydrogen bonds; maximum of entropy; ferromagnetic coupling

INTRODUCTION

Recently, the interest has been growing in the preparation and characterization of hydrogen-bonding ferromagnetic molecular materials based on nitroxide

radicals. Much works have been devoted to the use of inter-homomolecular hydrogen bond (IHoHB) to obtain a ferromagnetic interaction in the solid state. Another approach is the use of inter-heteromolecular hydrogen bond (IHeHB) to constitute a supramolecular structure and a spin transmission path via a diamagnetic compound. The first example[1] of this type of molecular complex presenting ferromagnetic intermolecular interaction was obtained with the phenylboronic acid (no unpaired electron, compound **1**, Figure 1) in association with the phenyl nitronyl nitroxide (PNN) (S = 1/2, compound **2**, Figure 1). We have shown, for one of the IHoHB radicals, that hydrogen bonds play a major role in the propagation of magnetic interactions[2]. We report here an investigation of the role of the hydrogen bonds in the transmission of ferromagnetic interactions in the PNNB molecular complex. This study includes the temperature dependence of the crystal structure (X-Ray diffraction), the experimental (polarized neutron diffraction) and the theoretical (*ab initio* calculations) spin density determination of the PNNB. The latter results are compared to those obtained previously for the "isolated" PNN radical[3] which is paramagnetic.

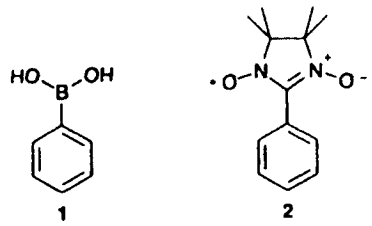

FIGURE 1 Chemical structure of the PNNB complex: (**1**) phenylboronic acid, (**2**) phenyl nitronyl nitroxide.

Neutron and X-Ray Diffraction.

Polarized neutron diffraction is a very powerful technique for spin density studies in magnetic molecular materials[4]. The measurements are usually performed in the paramagnetic state. A periodic spin density is induced in a

single crystal sample by applying a strong external magnetic field at low temperature. Using a polarized beam one measures the flipping ratios R of Bragg reflections (hkl) which are related to the magnetic structure factors F_M's (centric case) by:

$$R_{(h,k,l)} = \frac{I^{\uparrow}}{I^{\downarrow}} = \frac{F_N^2 + F_M^2 + 2F_N F_M}{F_N^2 + F_M^2 - 2F_N F_M} \qquad (1)$$

where the F_N's are the nuclear structure factors and $I^{\uparrow}$ and $I^{\downarrow}$ are the scattered intensities for 'up' and 'down' polarizations of the incident beam. The F_M's may be directly deduced from the R's if the crystal structure is known[7]. Thus, generally the experiment has to include two steps: (i) The precise structure of the crystal at low temperature (location of the hydrogen atoms and thermal parameters) is determined. (ii) Measurement of the flipping ratios is performed with polarized neutrons.

Herein, the classical procedure was started. However, during the first step it appeared that on cooling, the compound undergoes a crystallographic phase transition at T=220K. As a consequence, the large crystal which was utilized for that unpolarized neutron experiment was no more a single crystal at low temperature and the crystal structure could not be refined on this sample. A tentative experiment to pass the 220K transition on a small crystal, suitable for X-ray diffraction, happened to be successful: below this temperature the sample remained a single crystal and it was possible to perform an X-ray diffraction experiment to determine the low temperature structure of this compound.

This experiment was performed using a Siemens SMART CCD area detector three-circle diffractometer. The values of the cell parameters as function of temperature show (figure 2) that there is a phase transition around 220K: the angles α and γ increase respectively from 90° to 92° and 91°.

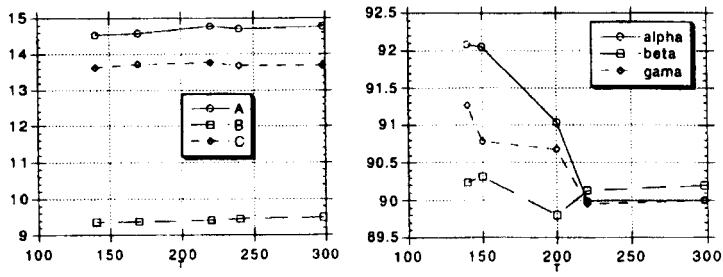

FIGURE 2 Evolution of the cell parameters in function of temperature (X-ray diffraction).

The new structure was solved at T=143K by direct method. The corresponding crystal data are given in Table 1, in comparison with those of room temperature. A view of the independent molecules is given on figure 3.

TABLE 1 Crystal data at room temperature and 143K

	room temperature	143K
Space group	$P2_1/n$	$P\bar{1}$
a	14.764 (3) Å	14.5322 (1) Å
b	9.482 (3) Å	9.3596 (2) Å
c	13.686 (2) Å	13.6398 (2) Å
α	90	92.079 (1)°
β	90.20 (1) °	90.234 (1) °
γ	90	91.263 (1)°

As described above, to calculate the F_M's from the flipping ratios measurement, detailed knowledge of the crystal structure at the temperature where the polarized neutron experiment is performed is required. A single crystal, of size 6.0x1.0x1.0 mm^3, was used for this experiment (conventional neutron diffraction, D15 lifting counter diffractometer, ILL's reactor (Grenoble, France), T=5K). The evolution of the width of several reflections in function of the temperature shows that the phase transition around 220K is accompanied by a twinning of this crystal: only the reflections of type (h0l) are untwinned.

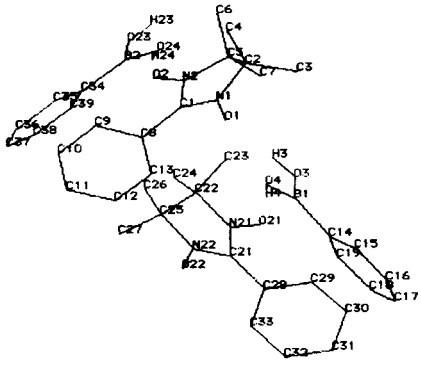

FIGURE 3 View of the four independent molecules in their crystal geometry at T=143K with the numbering scheme of the atoms.

Consequently, we have only collected reflections in the $(\vec{a}, \vec{c})$ plane. In these conditions, 346 independent Bragg intensities were measured with $\sin\theta/\lambda \leq 0.74$ Å^{-1} (λ = 1.173 Å). The cell constants at T=5K were determined to be a = 14.50(1) Å, b = not refined, c = 13.66(2) Å, α = not refined, β = 89.75(9)°, γ = not refined. The x and z atomic positions were refined, starting from the low temperature X-ray values, yielding χ^2 = 2.1 (wR-factor = 4.9%).

The polarized neutron experiment was performed on the same crystal that we used in the unpolarized neutron diffraction experiment on the D3 polarized neutron lifting counter spectrometer at the ILL reactor. Because of the twinning of the crystal, only the flipping ratios of type (h0l) were collected (T = 1.5K, H=4.6T, $\sin\theta/\lambda \leq 0.35$ Å^{-1}). 45 independent flipping ratios were measured.

Data Treatment.

The reconstruction of the spin density distribution from the magnetic structure factors $F_M(hkl)$ is a typical Inverse Fourier (IF) problem. To solve

this IF problem we have used two different methods. First, we have performed a maximum of entropy (ME) reconstruction[5]. Since we have only measured reflections of type (h0l), the ME reconstructed spin density map, Figure 4, was the projection onto the plane $(\vec{a}, \vec{c})$.

As previously observed in the **isolated** PNN[3], the majority of the spin density is located on the O-N-C-N-O fragments of each radical included in the asymmetric unit. However, compared to the isolated case, the spin density is not equally shared between the four atoms of the two NO groups of each radical. A strong unbalance is observed between the two oxygen atoms: the spin density on O2 (O21) is larger than on O1 (O22). Beside this, a positive contribution is observed on the hydrogen atoms H4 and H24.

We have then refined the atomic molecular orbital (AMO). In the particular case of the PNNB complex, only the ONCNO and HOBOH atoms of each pair were included in the refinement. The corresponding spin populations are displayed in Table 2.

TABLE 2 Spin populations obtained using the AMO refinement.

Atoms	Spin populations (μ_B)	Atoms	Spin populations (μ_B)
H3	0.024 (35)	H23	0.014(22)
O3	-0.020 (24)	O23	-0.051 (34)
B1	-0.067 (45)	B2	-0.037 (25)
O4	-0.034 (26)	O24	0.005 (26)
H4	0.043 (22)	H24	0.055 (25)
O21	0.284 (24)	O2	0.322 (25)
N21	0.234 (24)	N2	0.242 (25)
C21	-0.040 (23)	C1	-0.025 (20)
N22	0.301 (22)	N1	0.301 (25)
O22	0.210 (22)	O1	0.223 (25)

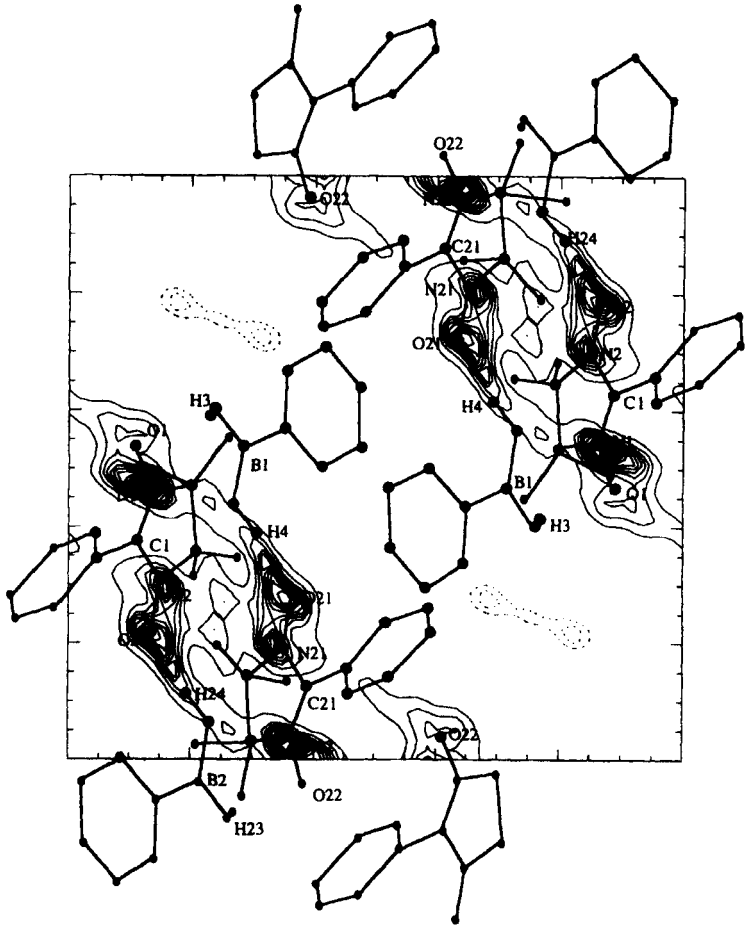

FIGURE 4 Projection of the ME reconstructed spin density of the PNNB onto the $(\vec{a}, \vec{c})$ plane. Negative contours are dashed, contour step 0.03 $\mu_B/Å^2$.

As expected from the ME results, the strongest spin populations are carried by the two NO groups of each radical. As in the other nitronyl nitroxide radicals, but not detected with ME reconstruction, the bridging sp^2 carbon atoms carry a negative spin density. However, compared to the **isolated** case,

some differences exit. On the one hand, the O:N/N:O spin partitioning, which is approximately 1:1/1:1 for the isolated PNN, is 22:30/24:32 and 21:30/23:28 respectively for O1:N1/N2:O2 and O22:N22/N21:O21; a large unbalance is found between the two oxygen atoms of each radical. On the other hand, a positive contribution is found on the hydrogen atoms H3, H4, H23 and H24.

Discussion and Ab Initio Spin density Calculations.

As described above, the PNNB complex undergoes a crystallographic phase transition around 220K. The space group changes from $P2_1/n$ (room temperature) to $P\bar{1}$ (below 220K). Consequently the asymmetric unit includes, below 220K, two different pairs (**1+2**) and (**1'+2'**) instead of one at room temperature[1]. But the global arrangement of the molecules in the cell is only slightly different from the room temperature one[1], the radicals are still arranged alternately with phenylboronic acid to make an infinite chain of **•••1•••2•••1'•••2'•••** along **b**-axis via hydrogen bonds NO•••HOB. The corresponding hydrogen bond distances, which were almost equivalent at room temperature[1] are now quite different: 1.96 Å, 1.84 Å, 1.96 Å and 1.91 Å respectively for H24•••O2, H3•••O1, H4•••O21 and H23•••O22.

As far as the spin density is concerned, both ME and AMO refinement converge and show that the spin density distribution is quite similar for the two pairs (**1 + 2**) and (**1' + 2'**): most of it is concentrated on the nitronyl fragment and is located on the nitrogen and oxygen atoms. This contribution may be attributed to the unpaired electron residing on the singly occupied molecular orbital (SOMO) constructed on the |2p> atomic orbital of the O and N atoms. But, Compared to the isolated PNN radical, the spin populations is not symetrically distributed between the two oxygen atoms of the nitronyl fragment: one of the two oxygen atoms is depleted in favour of the other. We have shown that this depletion is more effective on the oxygen atom involved in the shorter hydrogen bonds: the spin density on O1 (O22)- corresponding to an hydrogen bond length of 1.84 Å (1.91 Å)- is much less than on O2 (O21)- corresponding to an hydrogen bond length of 1.96 Å (1.96 Å). Beside this, the hydrogen atoms

involved in the hydrogen bonds carry a spin density of same sign that those carried by the NO groups. The stronger 'transfer' of spin density corresponds to the larger hydrogen bonds: spin density on H4 (H24) is much less than on H3 (H23).

In order to better understand the effect of the hydrogen bonds on the spin density distribution, several ab initio calculations (density functional theory (DFT)) were performed. We have compared the calculations for an isolated PNN radical and for a PNN radical connected to two phenyl boronic acids (geometry determined with X-ray). We have chosen for that the pair where the difference between the two hydrogen bond lengths is the higher: H23-OBO-H24•••O2-NCN-O1•••H3-OBO-H4. The corresponding spin populations are displayed in table 3, together with experimental values scaled to 1 μ_B/PNN radical. First of all, one can note that in the isolated case the DFT calculations give a similar spin populations for the two NO groups with a equivalent population on the two oxygen atoms. Beside this, compared to the isolated case, when the molecules are in interactions the **two oxygen** atoms O1 and O2 are **depleted** and this effect is more pronounced on the O1 atomic site: O1 move from 0.290 μ_B to 0.253 μ_B and O2 move from 0.285 μ_B to 0.268 μ_B.

TABLE 3 DFT spin populations of one of the two radical connected to two phenyl boronic acids in comparison with experimental values.

	Isolated PNN	Connected molecules	Experiment
H3	-	-0.001	0.024 (36)
O1	0.290	0.253	0.227 (25)
N1	0.220	0.233	0.307 (25)
C1	-0.089	-0.101	-0.025 (20)
N2	0.224	0.252	0.246 (25)
O2	0.285	0.268	0.328 (25)
H24	-	0.002	0.056 (25)

Thus, as experimentally observed, the stronger reduction is obtained on the oxygen atom involved in the shorter hydrogen bond. Furthermore, in the 'interacting' case, a positive but very small spin population is obtained on the H24 hydrogen atom- hydrogen atom for which the experimental results give a strong and a significant positive spin population.

In conclusion to these ab initio spin density calculations, one can say that on the whole the experimental effects are reproduced by DFT calculations. But, if there is a good qualitative agreement, in the quantitative point of view the DFT results are still very far from the experimental ones. The calculated unbalance between the two oxygen atoms represent 6% of the average of the spin populations of the O1, N1, N2 and O2 atoms, instead of 36% experimentally, and the calculated 'transfer' of spin density to the H24 atom is at least one order of magnitude less than the experimental one.

We have here direct evidences of the active role played by the hydrogen bonds in the intermolecular ferromagnetic coupling. We have shown that the intermolecular exchange pathway between the SOMO of each radical involved a diamagnetic compound, and is obtained through hydrogen bonds.

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