

A supramolecular network of 2-(4,4,5,5-tetramethyl-3-oxylimidazoline-1-oxide)-5-bromopyridine built through π – π stacking and hydrogen bonding interactions

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ABSTRACT: The X-ray study of 2-(4,4,5,5-tetramethyl-3-oxylimidazoline-1-oxide)-5-bromopyridine (**PyNN**) shows an unusual 3-D supramolecular assembly formed by the combined non-covalent interactions of π – π stacking and H-bonding forces. The mean π – π stacking distance between two pyridine units is ~ 3.64 Å. The angle between the plane of the pyridine ring and the stack column axis (*c*-axis) is 7.46° . The H-bonding distance between the oxygen atom of the water and the nitronyl nitroxide (NN) oxygen [H \cdots O–N] is 1.891 Å. Two potential short N–O \cdots O–N contacts are found (N–O1 \cdots O1–N = 3.673 Å and N–O1 \cdots O2–N = 3.695 Å) along the stacked column. Four water molecules through H-bonding with four different radical oxygens form a perfect square in the *a*, *b* plane which extends as a tubular cage along the stack axis. Experimental spin densities of **PyNN** estimated from the ¹H-NMR spectroscopy and its bulk magnetic property have been correlated with the X-ray structure in an attempt to understand the possible magnetic exchange interactions. The observed low temperature antiferromagnetic interaction is analyzed on the basis of McConnell's model I (*spin polarization approach*) and this magnetic behavior is probably due to the dominant N–O \cdots O–N close contacts along the chain surpassing the stacking, H-bonding and other interactions.

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KEYWORDS: intermolecular hydrogen bonding; radicals; pi-interactions; paramagnetic NMR studies; magnetic properties; spin densities; supramolecular chemistry

INTRODUCTION

The preparation of pure organic based magnetic materials mostly depends on the construction of supramolecular entities¹ following the *crystal engineering*² approach, although most of the exciting developments in organic magnets are based on serendipity. The discovery of the first pure organic based magnet by Kinoshita and co-workers³ in 1991, i.e. the β -phase of *p*-nitrophenyl nitronyl nitroxide with $T_c = 0.65$ K, evoked the successive rapid development and discovery of other pure organic molecules based ferromagnets⁴. Many paramagnetic molecules were assembled in the solid state using H-bonding synthons

such as carboxylic, acetylene, and hydroxy groups^{1,6,7} although scarce reports are available on π – π stacking^{7c,d,j}. Magnetic ordering in these compounds is mainly driven by intermolecular interactions. In most of the known compounds¹ the magneto-structural correlations are interpreted following the McConnell's model I⁵ considering the spin polarization pathways, i.e. short intermolecular contacts (through space) between atoms carrying different sign of spin densities mediate ferromagnetic interaction. Recently Novoa *et al.*⁶ have checked the validity of this model for several nitronyl nitroxide (NN) derivatives and emphasized the importance of considering all the magnetically active short contacts. Many experimental⁷ and computational⁸ reports are available on the magnetic exchange interactions pathways of paramagnetic molecules in the solid state, aggregated via π – π stacking and hydrogen bonding forces. To our knowledge no literature is available on the 3-D solid state organization of NN derivatives through both π – π stacking and

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H-bonding interactions, where water acts as H-bond linker. In this work, we report here such an example, i.e. the molecular crystal structure of a monoradical 2-(4,4,5,5-tetramethyl-3-oxylimidazole-1-oxide)-5-bromopyridine (**PyNN**) forming π - π stacking together with the H-bonding to the tetrameric water extending the structure into 3-D. Determination of the proton hyperfine coupling constants and the spin densities deduced from the $^1\text{H-NMR}$ spectroscopy and also the bulk magnetic properties will be discussed.

EXPERIMENTAL SECTION

Compounds 2-(4,4,5,5-tetramethyl-3-oxylimidazole-1-oxide)-6-bromopyridine¹¹ and 2-(4,4,5,5-tetramethyl-3-oxylimidazole-1-oxide)-pyridine^{10a} were synthesized according to the reported procedures. Temperature-dependent static susceptibilities of randomly oriented crystalline samples were recorded using MPMS-5S (Quantum Design) SQUID magnetometer over a temperature range of 3.5–300 K at 5000 Oe applied DC field. The diamagnetic corrections of the molar magnetic susceptibilities were applied using well-known Pascal's constants. $^1\text{H-NMR}$ spectra of the radicals were recorded on Bruker DPX 300 spectrometer with solvent proton as internal standard. Chemical shifts are given in ppm relative to the signal of CDCl_3 which was taken as $\delta = 7.26$ (for ^1H). A single crystal of **PyNN** suitable for the X-ray diffraction study was obtained by slow evaporation from mixed solvents of dichloromethane:hexane (1:1 ratio). X-ray data collection was performed on a STOE IPDS II diffractometer with a graphite monochromated $\text{Mo K}\alpha$ radiation at 200 K. The structures were solved by direct methods (SHELX-97). Refinement was done with anisotropic temperature factors for all non-hydrogen atoms. The H atoms were refined with fixed isotropic temperature factors in the riding mode. Crystal data of **PyNN**: $\text{C}_{12}\text{H}_{15}\text{O}_2\text{N}_3\text{Br}$; Tetragonal; Space group: $P-42_1c$; $a = 19.655(3)$; $b = 19.655(3)$; $c = 7.3317(15)$; α, β, γ ($^\circ$) = 90; $Z = 8$; $V(\text{\AA}^3) = 2832.3(8)$; Crystal size (mm) = $0.44 \times 0.18 \times 0.11$; Index ranges = $-23 \leq h \leq 8, -22 \leq k \leq 24, -8 \leq l \leq 9$; Theta range for data collection ($^\circ$) = 2.07 – 26.19 ; D_{obsd} (mg/m^3) = 1.553 ; μ (mm^{-1}) = 2.911 ; $F(000) = 1352$; Reflections collected/unique = $5696/2744$ [$R(\text{int}) = 0.0492$]; Final R indices [$I > 2\sigma(I)$] $R1 = 0.0377$, $wR2 = 0.0769$; R indices (all data) $R1 = 0.0805$, $wR2 = 0.0949$; Largest diff. peak and hole = 0.383 and -0.387 \AA^{-3} ; GOF on $F^2 = 1.018$; $T = 200 \text{ K}$.

CCDC-287112 contains the supplementary crystallographic data of **PyNN** for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

RESULTS AND DISCUSSIONS

Synthesis and crystal structure

The synthesis of the doublet monoradical **PyNN** has been described earlier⁹. Re-crystallization of **PyNN** from the mixed solvents of dichloromethane:hexane (1:1) yielded blue needle-shaped single crystals. X-ray analysis revealed the tetragonal space group $P-42_1c$ of **PyNN** together with a co-crystallized water molecule. Per unit cell eight molecules of **PyNN** together with eight water molecules are found. The ORTEP diagram of **PyNN** is presented in Figure 1. The pyridine rings are superimposed each other by forming π - π stacks in a columnar fashion along the crystallographic c -axis. The angle between the plane of the pyridine ring and the c -axis is 7.46° (Fig. 3c). The mean interpyridine vertical stacking distance (d) between the two molecules is $\sim 3.64 \text{ \AA}$. One molecule is stacked on top of another molecule with a glide plane c running through each stack (see Fig. 2b). Besides that, two water molecules bridge two molecules of **PyNN** by forming hydrogen bonds with the NN oxygen. The H-bonding distance between the oxygen atom of the water and the NN oxygen (H3A...O2-N3) is 1.89 \AA . The four water molecules form a perfect square parallel to the a, b plane and extend as a tube along the c -axis (Fig. 3b and 4b). Each water square is hydrogen bonded with four different NN oxygens. Over all, the observed 3-D network is a combined interplay between the stacking and hydrogen bonded interactions (Fig. 3). Earlier we have reported^{9a} by AM1 calculation that the ferromagnetic coupling through space depends on the

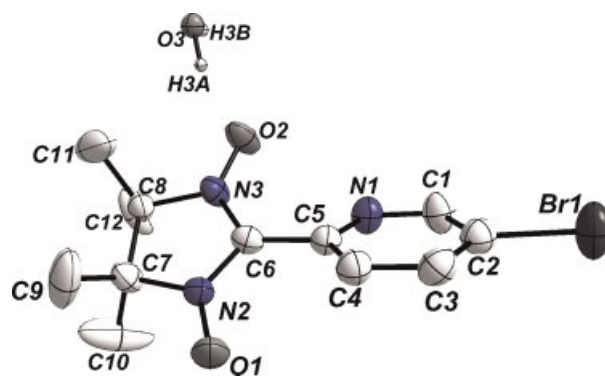


Figure 1. ORTEP plot (50% probability ellipsoids) of **PyNN** together with a co-crystallized water molecule. Hydrogen atoms are omitted for clarity in **PyNN**. Selected bond lengths [\AA]: O1–N2 (1.286(5)), O2–N3 (1.293(5)), C6–N3 (1.344(5)), C5–N1 (1.348(6)), C6–C5 (1.482(6)), N1–C1 (1.352(6)), C1–C2 (1.381(6)), C2–C3 (1.380(7)), C3–C4 (1.380(7)), C4–C5 (1.375(6)), C2–Br1 (1.898(5)), H3A–O2 (1.891). Selected bond angles [$^\circ$]: O(1)–N(2)–C(6) (126.2(4)), O(1)–N(2)–C(7) (120.5(3)), C(6)–N(2)–C(7) (113.3(4)), O(2)–N(3)–C(6) (125.4(3)), O(2)–N(3)–C(8) (121.4(3)). Selected torsional angles [$^\circ$]: N1–C5–C6–N3 (38.18), N2–C6–C5–C4 (35.41). [This figure is available in colour online at www.interscience.wiley.com]

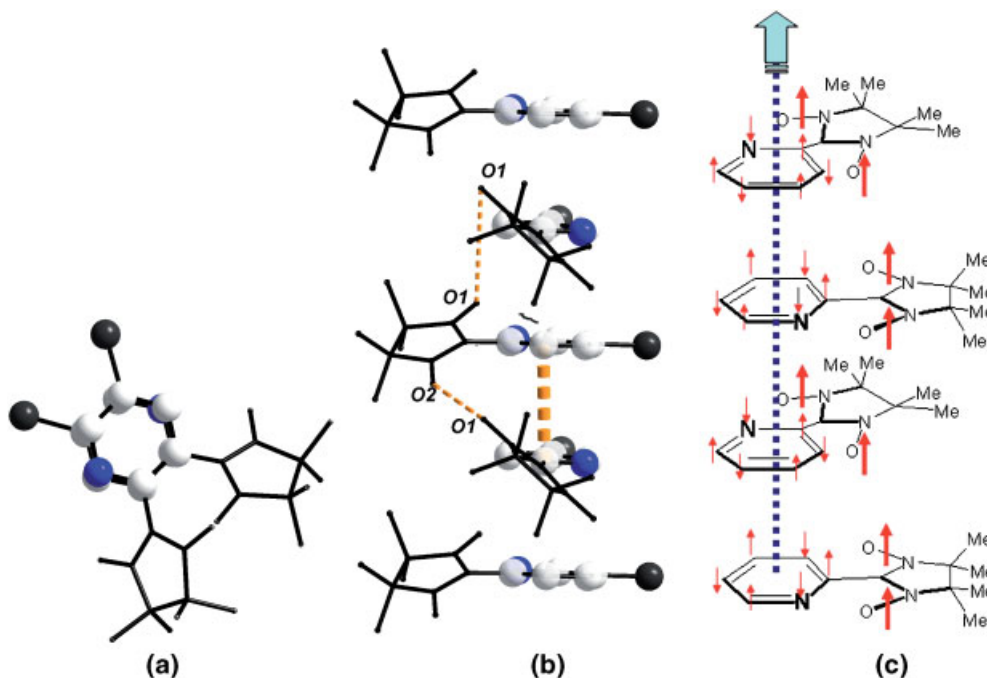


Figure 2. a,b: π - π stacking of **PyNN** along the crystallographic c -axis (water molecules and H atoms are omitted for clarity). c: Spin polarization model for **PyNN**, the arrows show the spin densities, up-positive; down-negative (Br and H atoms are omitted for clarity)

intermolecular vertical distance (d) and the alignment [rotational angle θ] of the dimeric radical stack. Larger triplet stabilization $\Delta E_{S,T}$ was observed when $\theta = 60^\circ$ and 180° . In our present case, the rotational angle θ of each pyridine and water mediated H-bonding interactions fulfills the requirements for the ferromagnetic interaction (Fig. 2c and 4b). Due to this rotational angle atoms of different sign of spin densities are aligned in such a way that the polarized spins can interact ferromagnetically through π - π stacked column. Thus, the determination of spin densities of **PyNN** becomes important, in order to consider the intermolecular contacts in the solid state.

Magnetic properties

Nuclear magnetic resonance techniques have been widely used earlier by Kreilick *et al.* and further developed by Köhler *et al.* to determine both the sign and magnitude of proton hyperfine splitting constants and spin density distribution of several NN derivatives as an alternative tool to electron nuclear double resonance (ENDOR) technique¹⁰. In concentrated solutions in which the spin exchange is very rapid, one observes a shift in the resonance line. These lines are broadened by the relaxation of proton spin in the presence of electron spin. The large chemical shift is due to local magnetic

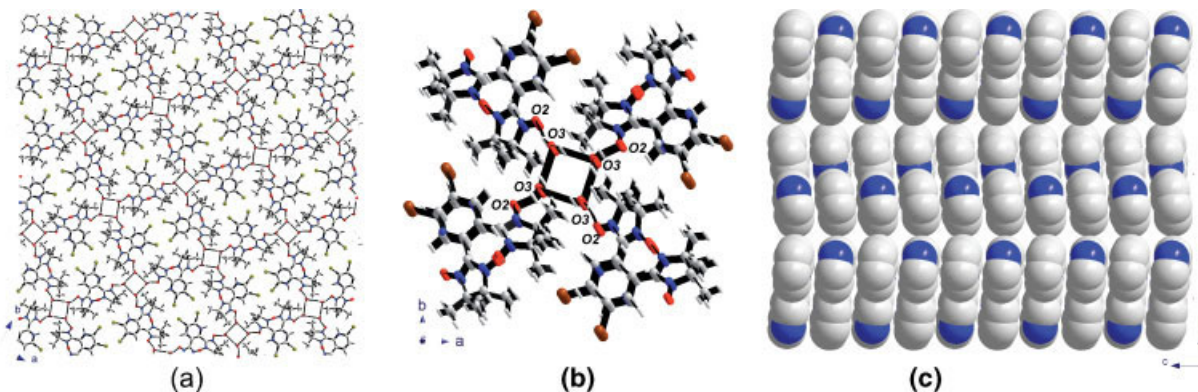


Figure 3. a: Projection of the 3-D network having π - π stacking (c -axis) and hydrogen bonding (a , b -axis) interactions. b: A closer view of the water-radical connectivity in the crystal lattice, O2 and O3 stand for radical and water oxygens, respectively. c: View along the crystallographic b -axis

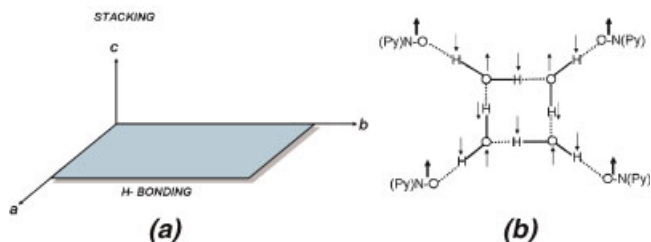


Figure 4. a: Schematic diagram of the intermolecular interaction directions along the crystallographic coordinates. b: Spin polarization model for the radical-water interaction, arrows show the spin densities

fields generated by the hyperfine interaction. The shift of a given line (ΔH) is related to the hyperfine interaction (A) by the following Eqn 1,

$$\Delta H = -A(\gamma_e/\gamma_N)(g\beta H/4kT) \quad (1)$$

Nuclei carrying positive spin shift the line to down field and the nuclei having negative spin shift the line to up field. The $^1\text{H-NMR}$ spectra was recorded for the concentrated solution of **PyNN** in CDCl_3 at room temperature. For the identification of the meta protons the spectra of compounds 2-(4,4,5,5-tetramethyl-3-oxylimidazoline-1-oxide)-6-bromopyridine¹¹ and 2-(4,4,5,5-tetramethyl-3-oxylimidazoline-1-oxide)-pyridine^{10b} were also recorded in the same conditions (See Fig. 5). The spectrum of **PyNN** shows a single down field shifted line for the ortho protons (2) due to the presence of positive spin densities. The peak from the meta protons is split into a doublet due to the different environments, and shifted high-field indicating nonequivalent negative spin densities at the meta protons (3/4). The methyl protons showed a single strong peak (1) which is shifted high-field due to the negative spin densities and the single peak is due to the averaged structures in solutions. The line shift values ($\Delta H = H_{\text{exp}} - H_{\text{dia}}$) of **PyNN** were calculated from its diamagnetic precursor⁹ chemical shift values. The calculated proton hyperfine coupling constant values using Eqn 1 and also the calculated spin densities of the aromatic ring using McConnell's equation ($A = Q\rho_c^\pi$; assuming $Q = -22.5 \text{ G}$) are as follows, for the pyridine ortho proton (2) $A_{H2} = +0.405 \text{ G}$ ($\rho_c^\pi = -0.0180$), for the two meta protons (3 and 4) $A_{H3} = -0.156 \text{ G}$ ($\rho_c^\pi = +0.0069$) and $A_{H4} \approx -0.125 \text{ G}$ ($\rho_c^\pi \approx +0.0056$), respectively, and methyl protons (1) $A_{H1} = -0.189 \text{ G}$. These values in comparison with benzene derivatives show that the two meta protons in the pyridine have different magnitude of spin densities^{10b} due to the presence of pyridyl nitrogen.

The magnetic measurement of polycrystalline sample of **PyNN** was performed using a Quantum Design SQUID magnetometer at an applied field of 0.5 T in the temperature range of 3.5–300 K. The temperature dependence of the χT value of **PyNN is shown in Fig. 6. The χT value of**

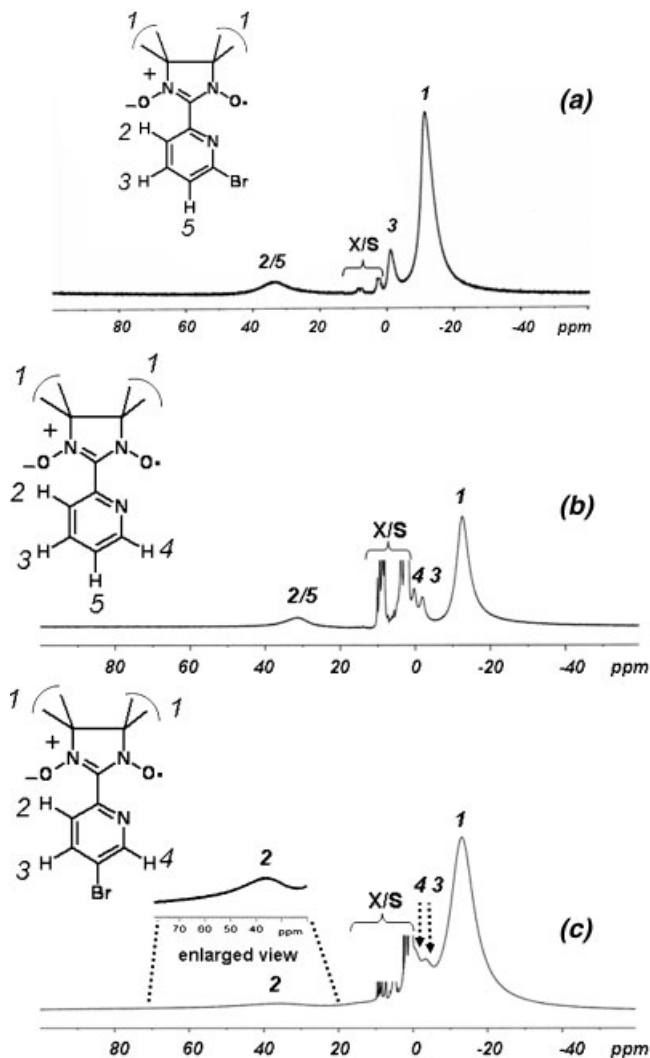


Figure 5. $^1\text{H-NMR}$ (300 MHz) spectra of (a) 2-(4,4,5,5-tetramethyl-3-oxylimidazoline-1-oxide)-6-bromopyridine¹¹, (b) 2-(4,4,5,5-tetramethyl-3-oxylimidazoline-1-oxide)-pyridine^{10b}, and (c) **PyNN** measured in CDCl_3 solvent at room temperature. S = solvent, X = diamagnetic impurities

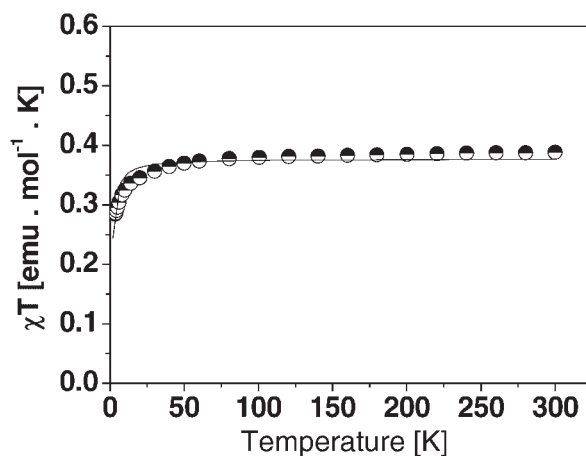


Figure 6. Magnetic behavior of **PyNN** together with a water molecule (Dotted line and the solid line show the experiment curve and fit, respectively.)

0.388 emu mol⁻¹ K at room temperature is close to the value for a pure $S = \frac{1}{2}$ species. The value decreases gradually down to ~ 75 K then further decreases sharply down to 3.5 K to the value of 0.284 emu mol⁻¹ K. This behavior indicates antiferromagnetic interaction.

The obtained magnetic behavior of **PyNN** is surprising at first glance, since one may anticipate ferromagnetic interactions along the stack (*c*-axis) and also *via* H-bonded connection along the *a*, *b* plane. Here the role of the pyridine stack for the magnetic exchange interaction cannot be ignored since the presence of spin densities and their signs are clearly deduced from the ¹H-NMR spectroscopy. One can question the role of water as a magnetic exchange linker, but a recent bulk magnetic study shows the function of a single water molecule as a ferromagnetic chemical linker between two NN radicals (N—O...H—O—H...O—N) in a biradical¹². However, from the obtained result it is clear that even if there is magnetic interaction, presumably it should be weak due to the long through bond contact distance of 8.521 Å (N—O2...H3A—O3—H3B...O3—H3A...O2—N) between the two NN radical units bridged by two water molecules (see Fig. 4b). The intermolecule contacts between the **PyNN** moieties are given in Table 1. The shortest intermolecular contacts involving N—O group are (i) two N—O...O—N intermolecular contacts (N—O1...O1—N = 3.673 Å and N—O1...O2—N = 3.695 Å) along the stacked column, which is comparable to the mean stack distance of ~ 3.65 Å, (ii) two N—O1...C4 and N—O1...C6 interactions between the N—O group and the pyridine carbons. But considering the magnitude of spin densities, the N—O...O—N interaction should be the dominant one due to the presence of large spin densities on the NO units. The interaction between pyridine units within the stacks should be much less important since the spin densities distribution is significantly lower. The possible ferromagnetic exchange interactions between the N—O group and the pyridine carbons (C4 and C6) and also N—O and methyl hydrogen (H12C) are probably moderate due to the contact between atoms carrying high spin densities and those with low spin densities. The

plausible antiferromagnetic interactions between the methyl hydrogen (H11B) and water hydrogen (H3A), and also pyridine meta hydrogen (H1) and methyl hydrogen cannot be ignored since both contacts are comparatively short even though these contacts carry small spin densities. So, the observed antiferromagnetic interaction most probably arises due to the close N—O...O—N contacts between the molecules along the chain. Assuming negligible interaction through water molecules (*a*, *b* plane) and strong interaction along the stack column (*c*-axis) the magnetic plot was found to be fitted using Bonner–Fischer's model¹³ for an isotropic 1-D Heisenberg chains of $S = \frac{1}{2}$ spin carriers along the stack column with the value of $J/2k = -0.53 (\pm 0.01)$ K.

CONCLUSIONS

In this paper we have shown the 3-D solid state organization of **PyNN** radical derivative through both π – π stacking and water mediated H-bonding interactions. The distribution of spin densities in the stacked pyridine and the NN was demonstrated from the ¹H-NMR spectroscopy. The observed antiferromagnetic behavior of the bulk crystalline sample was correlated with the solid state exchange interaction pathways through π – π stacking and H-bonding according to McConnell's model I. In the above analysis all potential close contacts between the atoms in the crystal lattice were considered and the absence of ferromagnetic interaction in the present compound may probably be due to the two strong potential N—O...O—N interactions which overshadows the stacking, H-bonding and other interactions.

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Table 1. Intermolecular interatomic contacts, distances and sign of interaction of **PyNN**

Interatomic contacts	Distance (Å)	Sign of interaction
π – π stack (pyridine ... pyridine)	~ 3.65 (mean)	+ ... –
H3A ... O2	1.89	– ... +
N—O1 ... O1—N	3.673	+ ... +
N—O1 ... O2—N	3.695	+ ... +
N—O1 ... C4	3.172	+ ... –
N—O1 ... C6	2.909	+ ... –
N—O2 ... H12C(methyl)	2.516	+ ... –
Br ... H9A(methyl)	3.018	+ ... –
(water)H3A ... H11B(methyl)	2.175	– ... –
H1 ... H9C (methyl)	2.328	– ... –

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