Coexistence of Intermolecular Ferromagnetic Interaction and $[NHN]^+$ Hydrogen Bond in *N*-Protonated *m*-Pyridyl Nitronyl Nitroxide

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Reaction of 2-(3-pyridyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-1-oxyl 3-*N*-oxide (*m*-PYNN) and HBr gas gives rise to the complex $(m\text{-PYNN})_2HBr$, in which the coexistence of an intermolecular ferromagnetic interaction and an $[NHN]^+$ hydrogen bond is found.

There has been much recent interest in molecular-based magnetic materials.[1,2] One of the advantages of such materials is the realization of cooperative phenomena between magnetism and other physical properties,[3] which is interesting from the viewpoints of both application and basic science.

An organic radical family, nitronyl nitroxide, has attracted much interest in this field, because of potential ferromagnetic interactions.[4] We have embarked upon a systematic study of 2-(3- and 4-pyridyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-1-oxyl 3-*N*-oxide [*m*- and *p*-pyridyl nitronyl nitroxide (PYNN), respectively] derivatives, making characteristic chemical modifications such as *N*-alkylation, *N*-oxidation and *N*-protonation. We have already reported the magneto–structural correlation in the parent compounds, *m*- and *p*-PYNN,[5,6] and those in the *N*-alkylated materials.[7,8] Here we report the results of the *N*-protonation.

The *N*-protonation of *m*- and *p*-PYNN was carried out by the following procedure: flowing HBr gas into the dry benzene solution of *m*- or *p*-PYNN resulted in precipitation of the complex between PYNN and HBr. The reaction was completed within 2 h. The microcrystalline powder obtained was washed several times with the solvent. Recrystallization from CH_2Cl_2 solution resulted in polycrystalline needles, but growth of a single crystal suitable for X-ray crystal analysis, was unsuccessful. The HBr complexes of the two isomers were sensitive to moisture, but were stable for a few weeks in a dry refrigerator. The results of their elemental analyses were found to agree with those of the 2 : 1 complex between PYNN and HBr [found for the *m*-PYNN complex: C, 52.30; H, 6.31; N, 15.25, found for the *p*-PYNN complex: C, 52.88; H, 6.18; N, 15.31; calc. for $(PYNN)_2HBr$: C, 52.46; H, 6.05; N, 15.29]. The corresponding HCl complexes were also obtained by the same procedure using HCl gas, but were found to be slightly unstable. In this report, we focus on the more stable HBr complexes.

There are some precedents for such a 2 : 1 ratio between nitrogen-containing base and protons, where it is known that the two base molecules are connected by an intermolecular $[NHN]^+$ hydrogen bond without exception.[9] This bond has given rise to much interest, with respect to homoconjugation, proton dynamics, and so on. In fact, the infrared spectra suggest that (*m*- and *p*-PYNN)$_2$HBr also involve an intermolecular $[NHN]^+$ hydrogen bond, such as is shown in Fig. 1(*a*). Their spectra show an intense NH stretching band at *ca.* 2500 cm^{-1}, implying the protonation of the pyridyl rings, and there is no band which is ascribable to *m*- or *p*-PYNN. The presence of the protonation and the absence of the parent PYNN can be understood in terms of proton-sharing by the two pyridyl rings in the $[(PYNN)_2H]^+$ unit. To our knowledge, this is the first example of an intermolecular $[NHN]^+$ hydrogen bond to be found in organic radical solids.

The temperature dependence of the paramagnetic susceptibilities of (*m*- and *p*-PYNN)$_2$HBr are shown in Fig. 2, where χ_pT is plotted as a function of log *T* and where (PYNN)·0.5(HBr) is taken as the molar unit. As the temperature decreases, χ_pT of the *m*-isomer increases to a maximum of *ca.* 0.65 emu K mol^{-1} at 3.5 K, but, after passing through the maximum, it shows a slight decrease. This behaviour indicates a stronger ferromagnetic interaction and a weaker antiferromagnetic interaction between the ferromagnetic units. Since, if the ferromagnetic coupling is limited in a dimer, the value of χ_pT should approach the upper limit of 0.501 emu K mol^{-1} (g = 2) at absolute zero, the ferromagnetic interaction in $(m\text{-PYNN})_2HBr$ is concluded to cover more than three molecules. In fact, the observed

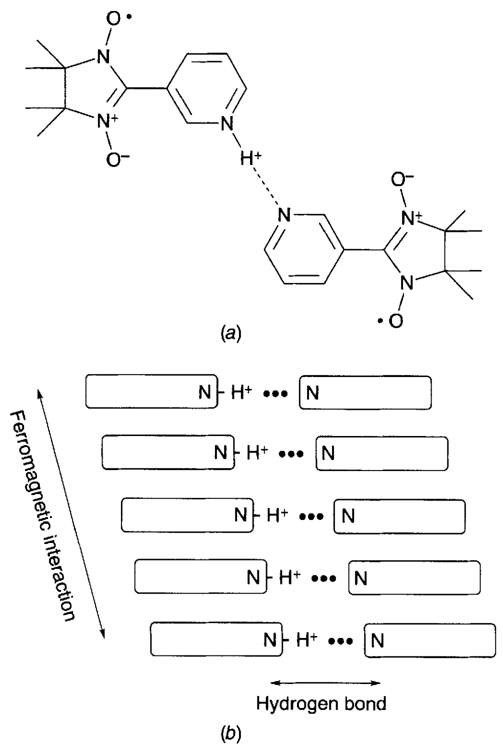

Fig. 1 Intermolecular hydrogen-bonding interactions in $(m\text{-PYNN})_2HBr$: (*a*) connection of two base molecules by an $[NHN]^+$ hydrogen bond; (*b*) ferromagnetic interaction across the $[NHN]^+$ dimers

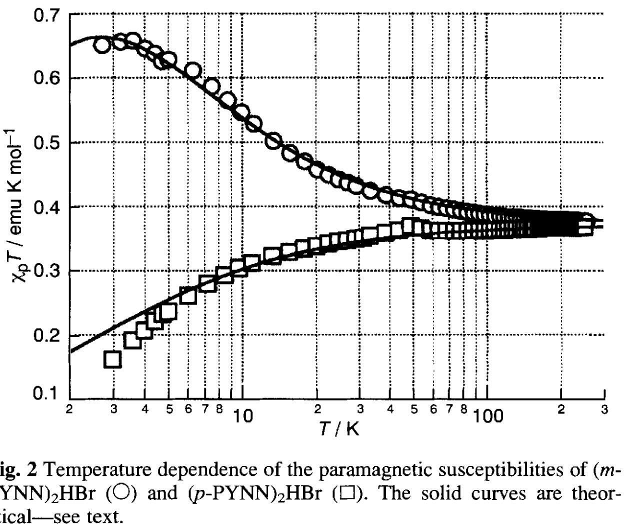

Fig. 2 Temperature dependence of the paramagnetic susceptibilities of (*m*-PYNN)$_2$HBr (○) and (*p*-PYNN)$_2$HBr (☐). The solid curves are theoretical—see text.

temperature dependence can be quantitatively interpreted in terms of a 1-dimensional ferromagnetic chain with a weak antiferromagnetic interchain coupling.[10] The solid curve going through the plots for $(m\text{-PYNN})_2\text{HBr}$ in Fig. 2 is the best fit obtained with $g = 2$ (fixed), an intrachain ferromagnetic interaction of $J/k_B = 5.7$ K and an interchain antiferromagnetic interaction of $J'/k_B = -0.24$ K.

The intermolecular $[\text{NHN}]^+$ hydrogen bond suggested by the IR measurements cannot be ascribed to a pathway of the ferromagnetic coupling, because it would be limited in the dimer. Generally speaking, the magnetic interaction of the nitronyl nitroxide, either ferromagnetic or antiferromagnetic, is not governed by the intermolecular contact between the substituents at the α-position (namely, the pyridyl groups in this case), on which there is little unpaired electron density, but originates in the intermolecular contacts of the NO groups, upon which the unpaired electron is localized.[8] Therefore, the ferromagnetic interaction is expected to extend across the $[\text{NHN}]^+$ dimers, as indicated in Fig. 1(*b*). This situation may open the possibility of a cooperative phenomenon. If *m*-PYNN and $m\text{-PYNN}\cdot\text{H}^+$ prefer different intermolecular magnetic couplings, the position of the proton would critically affect the intermolecular magnetic interaction, and in its turn the bulk magnetism. We are looking for cooperative phenomena between the proton dynamics and the magnetism.

The value of χ_pT of $(p\text{-PYNN})_2\text{HBr}$ decreases with decreasing temperature, suggesting an antiferromagnetic intermolecular interaction. This behaviour can be understood with the Curie–Weiss law. The best fit curve in Fig. 2 is obtained with the Curie and Weiss constants of $C = 0.371$ emu K mol^{-1} and $\theta = -2.3$ K, respectively. The intermolecular magnetic interaction depends on the isomer.

We have carried out the *N*-protonation of *m*- and *p*-pyridyl nitronyl nitroxides, which are attracting interest in the field of molecular-based magnetic materials. The material obtained (*m*-isomer) is found to be ferromagnetic, and also to include an intermolecular $[\text{NHN}]^+$ hydrogen bond, which will attract much interest with respect to proton dynamics, homoconjugation and so on. Coexistence of the two unusual features may lead to cooperative phenomena between them in future.

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