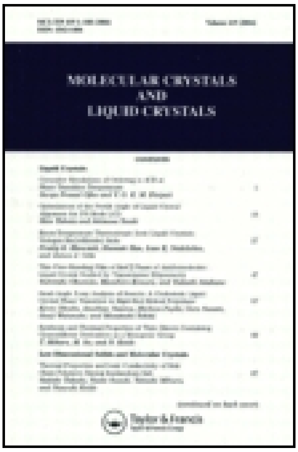

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[NHN]+ Hydrogen Bond in Organic Radical Solid

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[NHN]$^+$ HYDROGEN BOND IN ORGANIC RADICAL SOLID

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Abstract Reaction of *m*- or *p*-pyridyl nitronyl nitroxide (*m*- or *p*-PYNN) with HBr gas gave a 2:1 complex between them. The IR spectra of (*m*- and *p*-PYNN)$_2$HBr indicates an intermolecular [NHN]$^+$ hydrogen bond between two pyridyl rings. (*m*-PYNN)$_2$HBr shows ferromagnetic properties, while the *p*-isomer does antiferromagnetic properties. Furthermore, the HCl salt of phenyl-4-pyridylcarbene was generated by irradiation of the diazo precursor. The ESR spectrum shows signals of triplet and quintet spin species, latter of which indicates a ferromagnetic interaction between the triplet carbenes.

INTRODUCTION

Magnetic properties of organic radical solids have been studied extensively, and now reports on organic ferromagnetism appear quite frequently.[1] In this field, intermolecular hydrogen bonds are attractive with respect to control of the intermolecular arrangements between organic radicals,[2,3] magnetic interactions through the hydrogen bond, and cooperative phenomena between proton dynamics and magnetism. In this report , we describe (1) the magnetic properties of the HBr complexes of pyridyl nitronyl nitroxides and (2) the ESR spectrum of *N*-protonated phenyl-4-pyridylcarbene.

MAGNETIC PROPERTIES OF *N*-PROTONATED PYNN [ref.4]

An organic radical family, nitronyl nitroxide, has attracted much interest, because of potential ferromagnetic interactions. 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 (or, *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 on the *N*-protonation.

The HBr salts of *m*- and *p*-PYNN were obtained 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. Recrystallization from the CH_2Cl_2 solution resulted in polycrystalline needles, but growth of the single crystal, suitable for X-ray crystal analyses, was unsuccessful. The results of their elemental analyses were found to be 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].

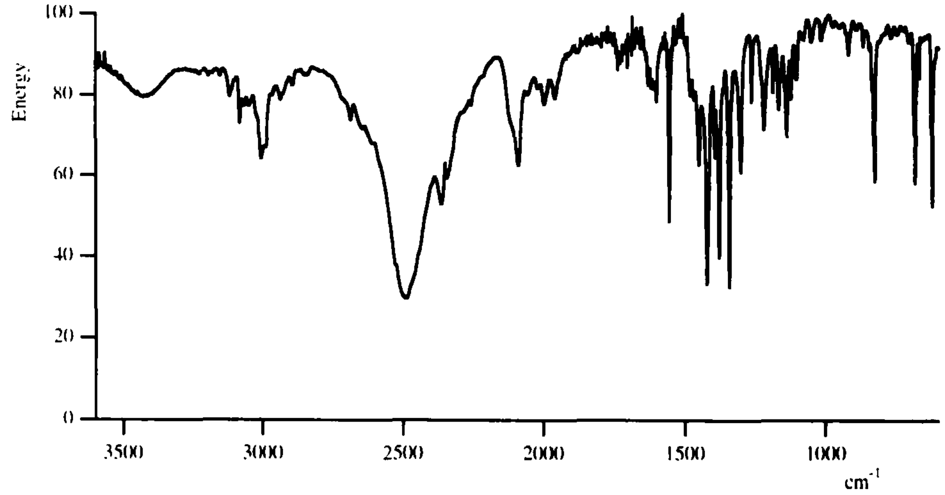
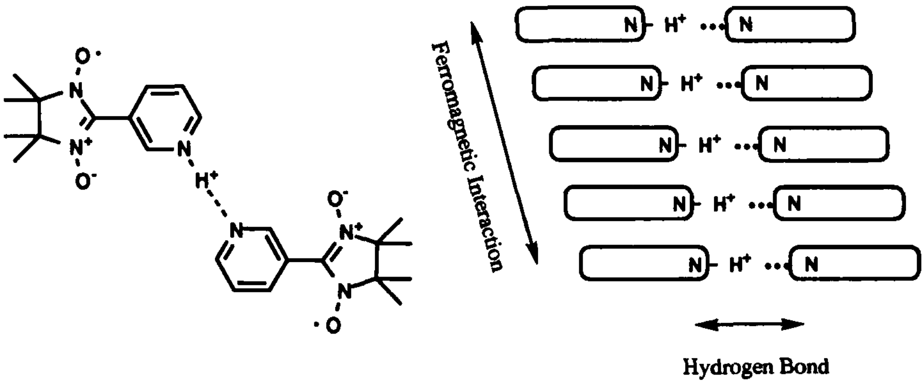


FIGURE 1 IR spectrum of $(m\text{-PYNN})_2HBr$ at room temperature.



(a) (b)

SCHEME I

There are some precedents for such 2:1 ratio between nitrogen-containing base and proton, where it is known that the two base molecules are connected by an intermolecular [NHN]$^+$ hydrogen bond without exception.[9] The bond has been interested in, with respect to homoconjugation, proton dynamics, and so on. Figure 1 shows the IR spectrum of (m-PYNN)$_2$HBr at room temperature. The spectrum shows an intense NH stretching band at *ca.* 2500 cm^{-1}, implying the protonation of the pyridyl ring, and there is no band which is ascribed to the parent compound, m-PYNN. The presence of the protonation and the absence of m-PYNN indicate proton-sharing by the two pyridyl rings in the [(PYNN)$_2$H]$^+$ unit (see Scheme I(a)). The IR spectrum of the p-isomer (not shown) also indicated the intermolecular [NHN]$^+$ hydrogen bond.

Temperature dependence of the paramagnetic susceptibilities of (m- and p-PYNN)$_2$HBr are shown in Figure 2, where χ_pT is plotted as a function of logarithm of T and where (PYNN)•0.5(HBr) is taken as the molar unit. As the temperature is decreased, 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 behavior 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 to the upper limit of 0.501 emu K mol^{-1} (g=2) at the absolute zero temperature, the ferromagnetic interaction in (m-PYNN)$_2$HBr is concluded to cover more than three molecules. In fact, the observed temperature dependence can be quantitatively interpreted in terms of a 1-D ferromagnetic chain with a weak antiferromagnetic interchain coupling.[10] The solid curve going through the plots for (m-PYNN)$_2$HBr in Figure 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 [NHN]$^+$ hydrogen bond suggested by the infrared spectrum, cannot be ascribed to be a pathway of the ferromagnetic coupling, because it would be limited in the dimer. Therefore, the ferromagnetic interaction is expected to extend across the [NHN]$^+$ dimers, as is shown in Scheme I(b). This situation may open the possibility of a cooperative phenomenon. If m-PYNN and m-PYNN•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.

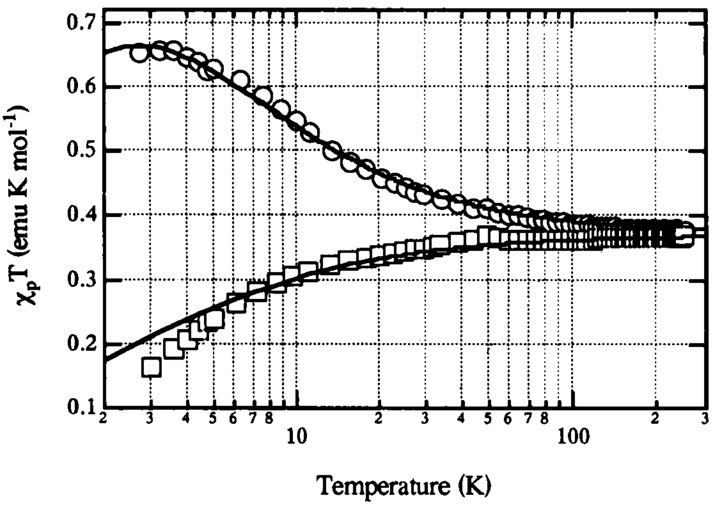


FIGURE 2 Temperature dependence of the paramagnetic susceptibilities of (*m*-PYNN)$_2$HBr (circle) and (*p*-PYNN)$_2$(HBr) (square). The solid curves are theoretical - see the text.

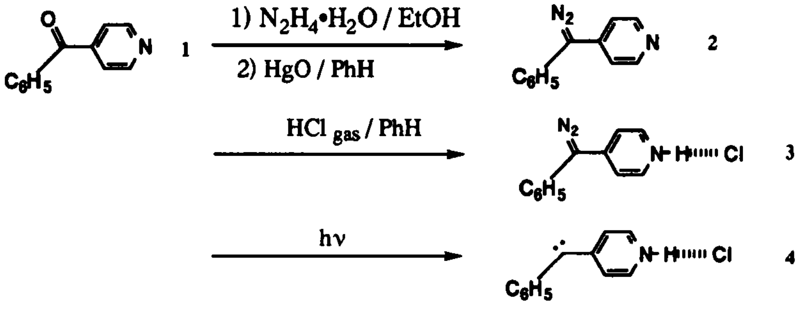
$\chi_p T$ of (*p*-PYNN)$_2$HBr decreases with decreasing temperature, suggesting an antiferromagnetic intermolecular interaction. The behavior can be understood with the Curie-Weiss law. The best fit curve in Figure 2 is obtained with the Curie and Weiss constants of C=0.371 emu K mol^{-1} and θ=-2.3 K, respectively. The intermolecular magnetic interaction depends seriously on the isomers.

Recently, we found that *m*- and *p*-PYNN made 1:1 complexes with HCl. They were prepared by the same procedure for (*m*- and *p*-PYNN)$_2$HBr. Unexpectedly, the elemental analyses indicated the 1:1 ratio between PYNN and HCl [found for the *m*-PYNN complex: C; 52.89, H; 6.29, N; 15.53, Cl; 13.23, found for the *p*-PYNN complex: C; 52.87, H; 5.97, N; 15.29, Cl; 13.17, calc. for PYNN•HCl: C; 53.24, H; 6.33, N; 15.52, Cl; 13.10]. The reaction of PYNN with HBr and HCl gases resulted in formation of the 2:1 and 1:1 complexes, respectively. We speculate that the 1:1 ratio is caused by the smaller acidity of HCl than that of HBr and the larger electron negativity of Cl than that of Br, both of which are expected to stabilize the $NH^+{\cdots}Cl^-$ hydrogen bond rather than the $[NHN]^+$ bond. The IR spectra of the HCl complexes indicated the *N*-protonation, as well as the HBr salts described before. We are working on their magnetic measurements.

CARBENE WITH *N*-PROTONATED PYRIDYL RING

The unpaired electron in the nitronyl nitroxide is known to be almost localized on the two NO groups. This could be disadvantageous for the direct coupling between the unpaired electron and the proton, and the intermolecular magnetic interaction through the proton. For these we have also embarked upon the protonation of pyridylcarbenes which contain a delocalized unpaired electron. In this section we report the ESR spectrum of the HCl salt of phenyl-4-pyridylcarbene.

The carbene was obtained, according to the procedure shown in Scheme II. 4-Benzoylpyridine 1 was condensed with hydrazine hydrate in ethanol to afford the hydrazone derivative. The diazo compound 2 was obtained by oxidation of the hydrazone with HgO in a basic condition. It was dissolved in CCl_4 and exposed to HCl gas, resulting in an orange precipitate of the HCl complex 3. This was quite unstable to light and moisture, and decomposed gradually. The results of the elemental analyses of 3 were follows; C, 62.91; H, 5.09; N, 14.56; Cl, 14.99 [calc. for 3: C, 62.21; H, 4.35; N, 18.14; Cl, 15.30]. The agreement was not so satisfactory, because of the decomposition which was clearly indicated by the decrease in the nitrogen percentage caused by elimination of the diazo group, but suggested a 1:1 ratio between 2 and HCl. The IR spectrum of 3 showed ν(N-H) at 2830.7 cm^{-1} and $\nu(N_2)$ at 2062.6cm^{-1}, indicating the *N*-protonation and the diazo group, respectively.



SCHEME II

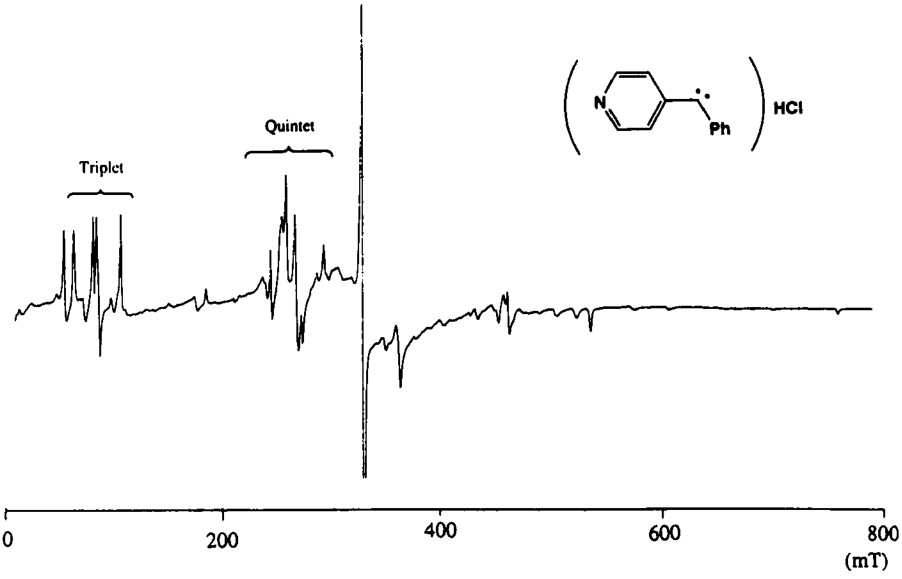


FIGURE 3 ESR spectrum of 4.

The carbene 4 was generated in an ESR sample tube by irradiation at 6 K with a high pressure Mercury lamp. Figure 3 shows the ESR spectrum of 4. The complicated signals around 80 mT are thought to be due to triplet species. A possible explanation for the splitting is difference in the crystal field around the triplet carbene caused by the *N*-protonation. The signals around 260 mT are assignable to those of quintet spin species, which are suggested to be ground states by temperature dependence of the signal intensity. There could be a ferromagnetic interaction between the triplet carbenes. To our knowledge, this is the second case[11] that the quintet signals are observed owing to an intermolecular ferromagnetic interaction between two mono carbenes.

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