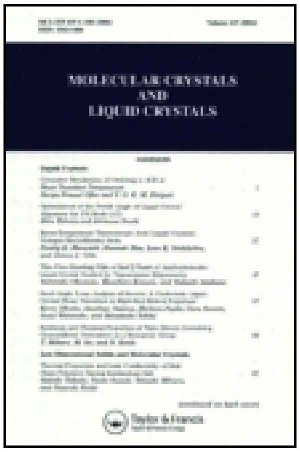

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Ferromagnetic Intermolecular Interaction of N-Protonated Pyridylphenylcarbene

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FERROMAGNETIC INTERMOLECULAR INTERACTION OF *N*-PROTONATED PYRIDYLPHENYLCARBENE

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Abstract The HCl and DCl salts of phenyl-4-pyridyldiazomethane were prepared and irradiated at 6 K to generate the carbenes. Their ESR spectra indicated presence of plural triplet carbenes with slightly-different zero-field splitting constants. Besides the triplet species, we found a quintet species whose signal intensity decreases with increasing temperature. The quintet spin state was concluded to be a ground state which was produced by an intermolecular ferromagnetic interaction of the triplet carbenes. The ferromagnetic interaction would be explained by the McConnell mechanism, judging from the crystal structure of the HCl salt of phenyl-4-pyridylketone.

INTRODUCTION

Magnetic properties of organic radical solids have been studied extensively, and the interests in organic ferromagnetism have been intensified in recent years.[1] One of the strategies to get organic ferromagnets is to construct organic radical crystals with ferromagnetic intermolecular interactions which are known to seriously depend on intermolecular arrangements. From the viewpoint of the supramolecular chemistry,[2] nitronylnitroxides are the most developed materials among the organic radicals, making use of the fact that the unpaired electron of this radical family is almost localized on the two NO groups. We designed *N*-alkylpyridinium nitronylnitroxide cations to pull apart the unpaired electrons in the nearest neighbor intermolecular arrangement by the Coulombic attraction between the positive charge on the pyridinium ring and the polarized negative charge on the NO group.[3,4] In fact, some of the cations take designed intermolecular arrangements and show ferromagnetic properties. We also found that the *N*-protonated *m*-pyridyl nitronylnitroxide shows a ferromagnetic intermolecular interaction,[5] besides which this system is quite unusual, because naked protons and unpaired electrons are coexistent. Such a situation may afford new physico-chemical properties, such as magnetic interactions through the proton, cooperative phenomena between proton dynamics and magnetism, and so on. However, the localization of the unpaired electron of the nitronylnitroxide would be disadvantageous, not only to get strong intermolecular ferromagnetic couplings but also for realizing the new properties. In this meaning, the studies on ferromagnetic interactions of delocalized unpaired electrons must be important. One can see the most delocalized unpaired electrons in carbenes. Although high spin carbenes have been studied extensively,[6] there have been a few reports on the intermolecular interactions of carbenes.[7] In this work, we studied ferromagnetic properties of a carbene with a protonated substituent, the HCl salt of phenyl-4-pyridylcarbene, by means of ESR and crystallographic analysis.

EXPERIMENTAL

Materials

The HCl salt of diazo precursor was obtained, according to the procedure in Figure 1. Phenyl-4-pyridylketone (**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. Into the CCl_4 solution of **2**, HCl gas was passed slowly, resulting in an orange precipitate of the HCl complex **3**. This was rather 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 $C_{12}H_{10}ClN_3$: C, 62.21; H, 4.35; N, 18.14; Cl, 15.30). The agreements were not so satisfactory, probably because of the decomposition. The decrease in the nitrogen percentage indicated elimination of the diazo group, but the results 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 2062.6 cm^{-1}, indicating the *N*-protonation and the diazo group, respectively. The carbene **4** was generated by irradiation to **3** with a high pressure mercury lamp and pyrex filters. The deuterated material of **4** was also prepared, using DCl gas in the second step. The HCl salt of **1**, namely **5**, was prepared by the same procedure as that for **3**. The single crystals of **5** were obtained by slow evaporation from the acetone solution.

ESR Measurement

The ESR measurements were performed on a JEOL JES-RE2X spectrometer equipped with an Air Product LTR-5500 helium flow cryostat. The spectra were recorded in the temperature range 6-100 K.

X-ray Structural Analysis

X-ray diffraction data on **5** were collected on RIGAKU AFC-5 automatic four-circle diffractometer with graphite-monochromatized Mo K_α radiation (λ=0.71073Å). Unit cell dimensions were obtained by a least-squares refinement using 25 reflections with $20° < 2\theta < 25°$. During data collection, the intensities of three representative reflections were measured as a check on crystal stability, and no loss was shown. No absorption correction was carried out, because the influence of the absorption was negligibly small. Structures were solved by direct method (SAPI 85) and refined by block-diagonal least-squares method (UNICS III). The anisotropic thermal parameters were introduced to all non-hydrogen atoms. The position of hydrogen atoms were found by differential Fourier methods, and were refined isotropically.

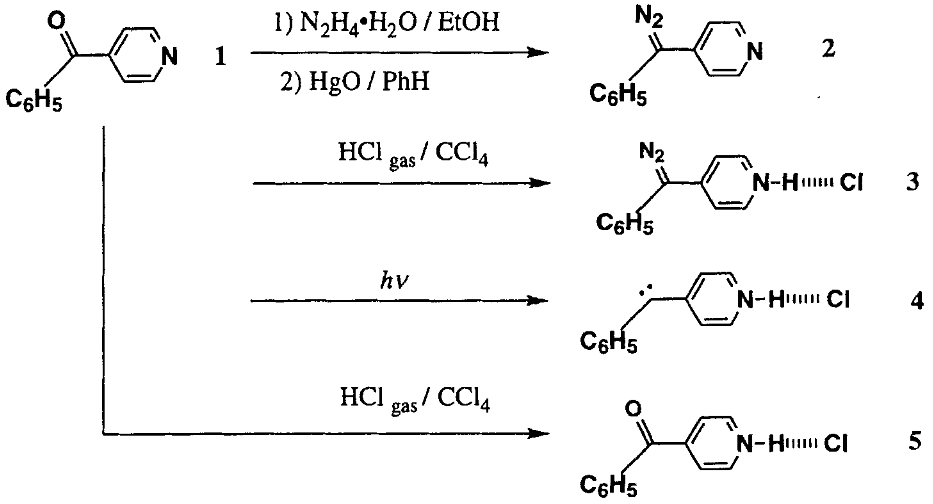

FIGURE 1 Reaction scheme of the HCl salt of phenyl-4-pyridycarbene (**4**) and the related compounds.

RESULTS AND DISCUSSION

Figure 2(a) shows the ESR spectrum of **4** generated in an ESR sample tube at 6 K. The absorption around 100 mT, 460 mT, 530 mT and 770 mT can be assigned to those of the randomly-oriented triplet carbene with two aromatic substituents. Since the complicated triplet signals are simplified after annealing at 40 K (not shown), the complication of the signals would be due to presence of plural triplet carbenes with slightly-different zero-field splitting constants in the solid. After annealing, the zfs parameters of **4** are determined to be D=0.404 cm^{-1} and E=0.0187 cm^{-1}, which are in good agreement with those of the carbenes obtained from phenyl-4-pyridylcarbene; D=0.405 cm^{-1} and E =0.0185 cm^{-1}. The open circles in Figure 3 show the temperature dependence of the reciprocal peak height I_{peak}^{-1} of the stared signal in Figure 2(a). Except the data at *ca.*63 K, the intensity of the triplet signal follows the Curie law, indicating that the triplet state is the ground state. The deviation of the highest temperature data would be caused by decomposition of the carbene. It is found that the triplet carbene is survival with the rather naked protons.

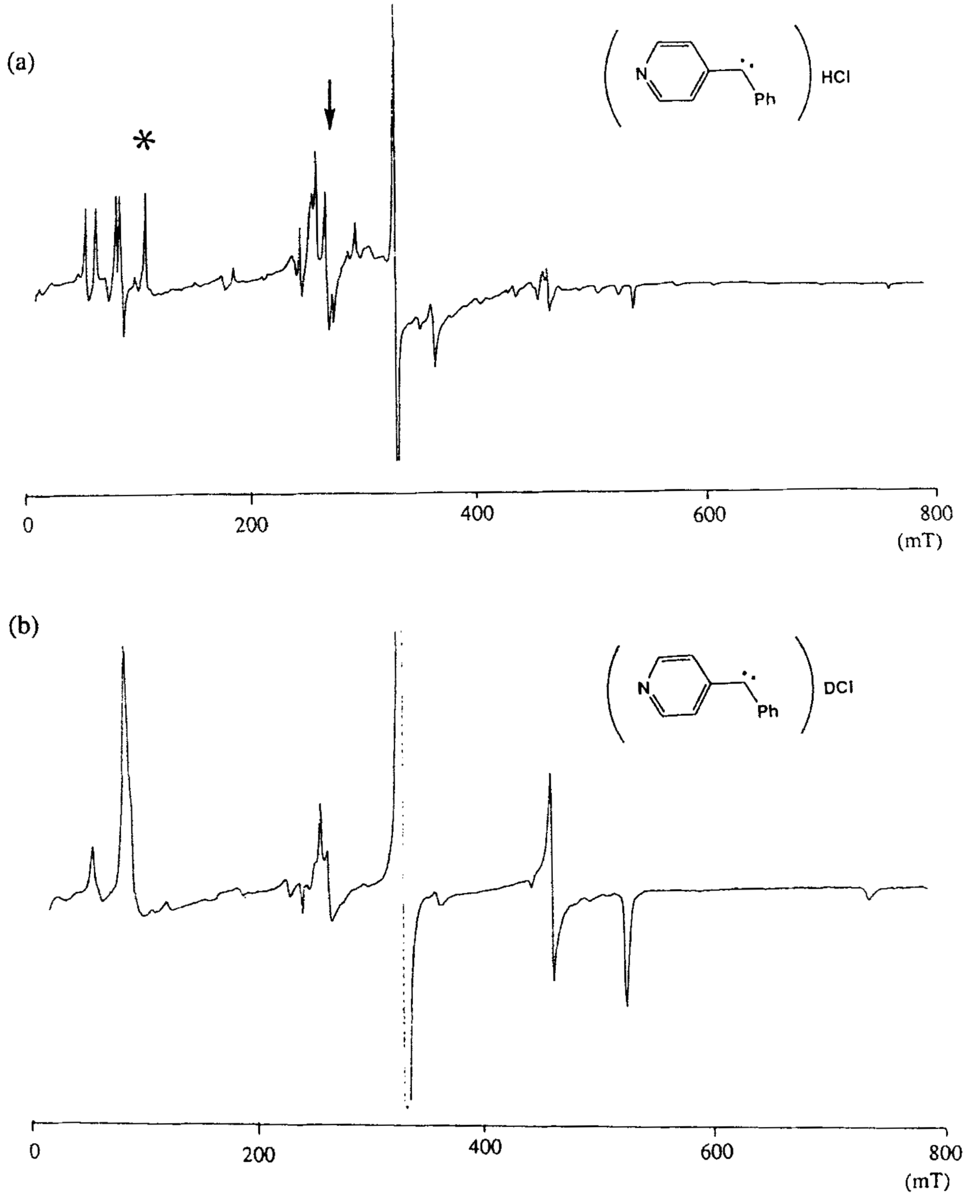

FIGURE 2 ESR spectra of **4** (a) and the corresponding deuterated material (b).

Furthermore, Figure 2(a) shows additional signals around 260 mT. They are assignable to quintet spin species which are created by an intermolecular interaction between the carbenes. The closed circles in Figure 3 show the temperature dependence of I_{peak}^{-1} of the arrow signal in Figure 2(a). As the temperature is increased, the value of I_{peak}^{-1} increases with an increase of the gradient. This behavior indicates that the quintet spin species are in a ground state and there is a thermally-accessible excited state with lower spin multiplicity. The interaction between the triplet carbenes is thought to be ferromagnetic, and the coupling intensity is expected to be not so stronger than the thermal energy of the maximum temperature in the measurement. To our knowledge, this is the third observation of the ferromagnetic intermolecular interaction between carbenes in the long history of the carbene study. Based on the zfs parameters of the triplet spin, the parameter of quintet signals are roughly estimated to D=0.135 cm^{-1} and E=0.0062 cm^{-1} by the model of weakly interacted two carbenes. However the simulated quintet signal can not reproduce the observed one, presumably due to the fact that the interaction of the carbene is rather stronger than that assumed in the theory.

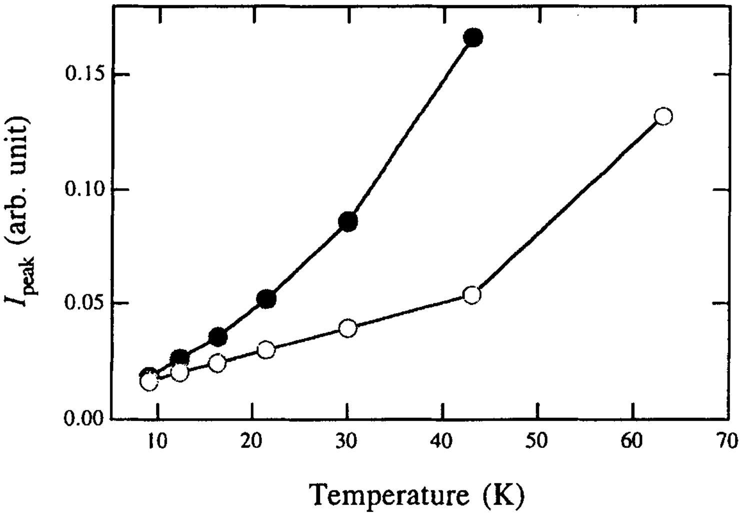

FIGURE 3 Temperature dependence of the reciprocal intensities of the triplet (open circles) and quartet (closed circles) signals.

Figure 2(b) shows the ESR spectrum of the deuterated **4**, namely the DCl salt of **3**, at 6 K. The spectrum also shows presence of the both triplet and quintet spin species, but is simpler than that of the HCl salt in Figure 2(a). There are two possible reasons for the difference between the two: one is the hyperfine coupling of the proton bonded to the nitrogen atom on the pyridyl ring and the other is the difference in the crystal field around the carbene. The former possibility would be excluded by the following facts: (a) there is no hyperfine coupling of the nitrogen atom on the pyridine ring, and (b) the complicated triplet signals in the spectrum of the HCl salt are simplified after annealing. The difference in the crystal environment could be caused by that in the hydrogen bond strength between the proton and deuteron.

To understand the mechanism of the ferromagnetic coupling of **4**, the crystal structure of the related material **5** was examined, instead of **3**, because **3** was too unstable for the crystallographic analysis. The crystal data are follows; $C_{12}H_{10}NOCl$, MW=219.67, triclinic, space group $P\bar{1}$, a =11.264(4) Å, b =12.138(4) Å, c =6.101(3) Å, α=94.59(5)°, β=98.67(5)°, γ =136.55(2)°, V=544.6(5) $Å^3$, Z=2, R=0.058, and R_w=0.060. The crystal is found to consist of an alternating molecular stack. Figure 4(a) shows the nearest neighbor intermolecular arrangement in the stack. The distance between C(6), the carbon atom of the ketone group which becomes the carbene center, and C(7), the tertiary carbon atom of the phenyl ring, is 3.825(8) Å. It is well known that the SOMO (=singly occupied molecular orbital) of the carbene has populations alternately on the atoms in the skeleton, and negative spin densities appear at the nodes of the SOMO. The starred atoms in the figure represent the atoms with negative spin densities. In the nearest neighbor arrangement, one can see encounters between the starred and non-starred atoms, namely between positive spin densities and negative spin densities. In such an arrangement, a ferromagnetic coupling has been predicted by McConnell.[8] From the viewpoint of MO theory, the arrangement means an orthogonal relation between the SOMOs. If the intermolecular arrangement is also realized in the crystal of 3, which is the parent of the carbene **4**, the generated carbenes would also have an ferromagnetic intermolecular interaction.

Figure 4(b) shows the second-nearest intermolecular arrangement, in which the pyridine rings have an overlap. The starred atoms make contact to the non-starred atoms, suggesting a ferromagnetic interaction in the corresponding carbene, as well as the nearest neighbor arrangement. The distance between C(6) and N(1) (symmetry operation; 2-x, 1-y, 1-z) is 3.419(9) Å. Even though the distance is shorter than that in the dimer, the magnetic interaction in this arrangement could be weaker than that in the dimer in Figure 4(a), because the overlap appears small. The structure of **5** suggests a possibility of an alternate ferromagnetic chain in **4**. The signals around 360 mT in Figures 2(a) and (b) could originate in higher spin species.

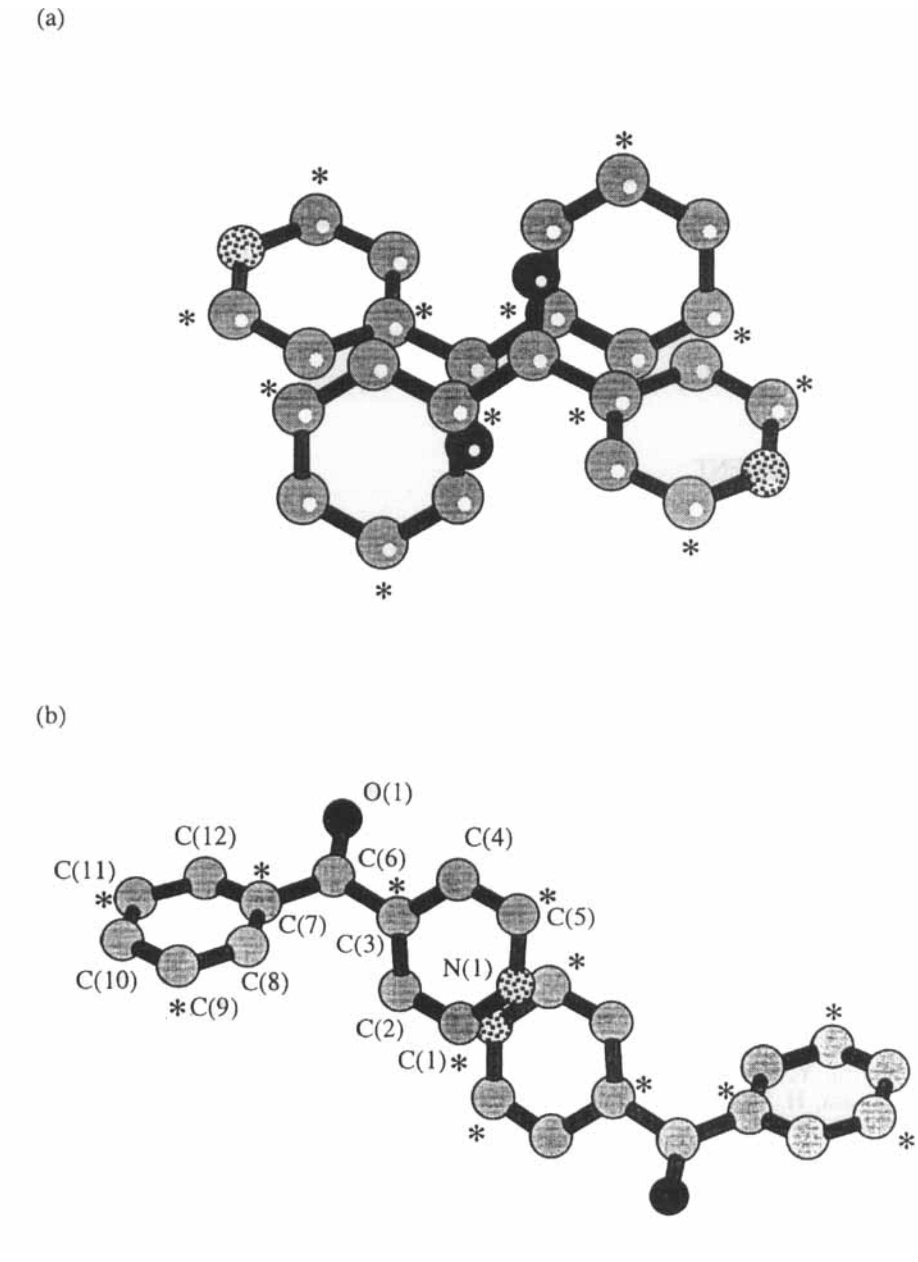

FIGURE 4 Crystal structure of **5**. (a) the nearest neighbor intermolecular arrangement. (b) the second-nearest intermolecular arrangement.

SUMMARY

The HCl and DCl salts of phenyl-4-pyridyldiazomethane were prepared. The corresponding carbenes were generated by irradiation at low temperature. ESR spectra of both salts showed the presence of quintet spin species in addition to the usual triplet species. The temperature dependence of the intensity of the quintet signals indicates that the quintet species is in a ground state formed by an intermolecular ferromagnetic interaction between the triplet carbenes. The ferromagnetic interaction is suggested to be explained in terms of the McConnell model (or an orthogonal relation between the SOMOs) by the crystallographic analysis of HCl salt of phenyl-4-pyridylketone.

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