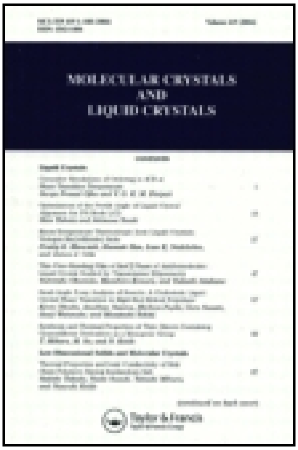

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Magic Angle Spinning ^{1}H-NMR Study of the Spin Density Distribution of Pyridyl Nitronyl Nitroxides in the Crystalline Phase

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The electron spin density distribution was investigated for *p*- and *m*-pyridyl nitronyl nitroxides (*p*-PYNN and *m*-PYNN) in the crystalline phase by the temperature dependence of the solid state high resolution ^{1}H-MAS NMR spectrum. The results were compared with that of phenyl nitronyl nitroxide (PNN) for elucidating the effect of incorporation of a nitrogen atom into the aromatic group. For *p*-PYNN, the magnitude of the negative spin density at 3 and 5 positions of the pyridyl group was suppressed by 30% in comparison with that of PNN and the positive spin density at 2 and 6 positions was slightly enhanced by 10%. On the other hand, the positive spin density at 2, 4 and 6 positions of pyridyl group of *m*-PYNN was suppressed by 30% in average and the negative one at 5 was also suppressed by 20%. The DFT calculation at UBLYP/6–31G(d, p) level suggested that the molecular geometry largely contributed to the change of the spin density in addition to the effect of incorporation of the nitrogen atom. In fact, the spin density distribution of the aromatic ring of *p*-PYNN was remarkably reduced in solution compared with that in the crystalline phase.

Keywords: organic magnetism; nitronyl nitroxide radical; ^{1}H-MAS-NMR; Fermi contact shift; electron spin density distribution; DFT calculation

INTRODUCTION

Since the discovery of the organic ferromagnet, 2-(4'-nitrophenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-1-oxyl-3-oxide (or *p*-nitrophenyl nitronyl nitroxide),[1] the magnetism of aryl nitronyl nitroxides has attracted much interest.[2] The spin density distribution of the aromatic moiety of the aryl nitronyl nitroxide is considered to be an important parameter for the intermolecular magnetic interaction in the crystalline phase[3,4]. It is desired to clarify the effect of chemical modification of a aromatic ring on rearrangement of its electron spin density distribution for producing novel organic magnetic materials.

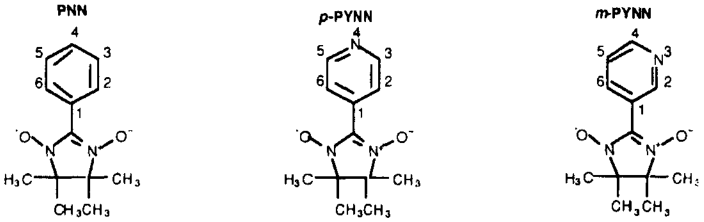

FIGURE 1 Molecular structure and numbering scheme of protons of aryl group.

In this paper, we report the hyperfine coupling constants (hfcc's) of the protons of *p*- and *m*-pyridyl nitronyl nitroxide (*p*-, *m*-PYNN) in the crystalline phase. The hfcc's were determined from the temperature dependence of the Fermi contact shifts of the protons measured by high speed (~15kHz) magic angle spinning (MAS) NMR. We also performed theoretical calculations of the hfcc's of these compounds at UBLYP/6-31G(d, p) level. The effect of the incorporation of a heteroatom into an aromatic moiety on the spin density distribution is discussed.

METHOD

The static proton NMR spectrum of paramagnetic polycrystalline specimen exhibits a large width due to the anisotropic dipole interaction between the nuclear spin and electron spins[5]. Magic angle spinning (MAS) technique averages the interaction in principle and provides the isotropic shift of the NMR absorption line. The observed isotropic shift in ppm consists of the paramagnetic term and the temperature independent diamagnetic term. The Fermi contact term and the anisotropy of the g-value contribute to the paramagnetic term.

$$\delta_{\mathrm{iso}} = \delta_{\mathrm{para}} + \delta_{\mathrm{dia}}, \tag{1}$$

$$\delta_{\mathrm{para}} = \frac{g\mu_{\mathrm{B}}S(S+1)}{3k_{\mathrm{B}}T} \cdot \frac{A_{\mathrm{H}}}{\gamma_{\mathrm{H}}/2\pi}, \tag{2}$$

$$A_{\mathrm{H}} = A_{\mathrm{Fermi}} + A_{\mathrm{pseudo}}, \tag{3}$$

where A_{Fermi} and A_{pseudo} are respectively the Fermi and the pseudo contact coupling constant of the proton in Hz, T is the absolute temperature, and the other terms have their usual meanings.[6,7] The symbol g in Eq. 2 represents the isotropic value $g = (g_{xx}+g_{yy}+g_{zz})/3$. The anisotropy of g-tensor is very small for typical organic radical crystals, *e.g.* the principal values of the g-tensor of PNN radical fall in the range 2.00620±0.0040.[8] Thus in our case, the contribution of the pseudo contact term is estimated to be less than 0.01 MHz and can be neglected in Eqs. 2 and 3. The paramagnetic NMR shift as a function of inverse temperature gives the hfcc A_{H} which is related with the electron spin density $r(R_{\mathrm{H}})$ at the proton position R_{H} as follows[9],

$$A_{\mathrm{H}} \cong A_{\mathrm{Fermi}} = \frac{8\pi}{3} g\mu_{\mathrm{B}} \frac{\gamma_{\mathrm{H}}}{2\pi} \rho(R_{\mathrm{H}}). \tag{4}$$

EXPERIMENTAL

Preparation of PYNN's has been previously reported[10]. High speed ^{1}H-MAS NMR spectra were measured by a single pulse method for polycrystalline samples between 190K and 300K at the resonance frequency of 300.13 MHz with a Bruker DSX300 spectrometer and a 4mm CP/MAS probe. The $\pi/2$ pulse length was 1.2 μs and a conventional zirconia rotor with boron nitride cap was used. The specimen (*ca.* 35-40 mg) was carefully packed at the center of the rotor (4-5 mm long) to achieve homogeneous temperature over the sample area and Teflon powder was used as spacer. Dry N_2 gas evaporated from the liquid N_2 container was utilized for the high speed magic angle spinning (9-15 kHz).

The thermometer of the MAS probe was calibrated against the isotropic chemical shift of the ^{207}Pb-MAS NMR spectrum of $Pb(NO_3)_2$[11] and the solid-solid phase transition temperatures of cyclooctanone ($C_8H_{14}O$, T_t=227 K) and diazabicyclooctane ($(C_2H_4)_3N_2$, T_t=350 K) which were detected by ^{1}H-MAS NMR at the spinning rate of 3.5 kHz and 10 kHz. These brittle-plastic phase transition temperatures[12] of orientationally disordered crystals were determined by differential thermal analysis. Temperature raise of the sample as the spinning speed increased was also examined and calibrated. Uncertainty of the temperature measurement after the calibration was 4 K and temperature fluctuation during accumulation was within 2 K. An error of reading the ^{1}H-MAS NMR shift was ± 1-2 ppm.

Proton NMR spectrum of *p*-PYNN was also measured for almost saturated concentration in acetone-d_6 solution between 225 and 290 K. All proton NMR shifts were measured from the tetramethylsilane dissolved in CCl_4.

THEORETICAL CALCULATIONS

Electron spin density at the coordinate R can be computed as the difference between electron density of α spin and that of β spin,[13]

$$\rho(R)=\sum_i^{\text{occ}}\left|\psi_i^{\alpha}(R)\right|^2-\sum_i^{\text{occ}}\left|\psi_i^{\beta}(R)\right|^2, \tag{5}$$

where ψ_i^{α} is an unrestricted molecular orbital for the α spin electron, and each summation runs over the occupied orbitals.

Using the GAUSSIAN 94 program package[14], we performed UBLYP/6-31G(d, p) calculations for *p*-PYNN, *m*-PYNN and PNN molecules. To investigate the chemical effect of incorporation of the nitrogen atom without geometry modification, the set of atomic coordinates of *p*-PYNN determined by X-ray diffraction[15] was used for three molecules in common. Coordinates of the hydrogen atoms were optimized by PM3[16]. The UB3LYP/6-31G(d, p) calculations were also performed but the spin contamination was too large to accept the results: $\langle s^2\rangle \sim 0.82$. The hfcc's A_{H} were obtained by Eqs 4 and 5.

RESULTS AND DISCUSSION

Assignment of the NMR Signals

Figure 2 shows the ^{1}H-MAS NMR spectrum of *p*-PYNN measured at 294K. Three isotropic signals were distinguished from the spinning side bands by using different spinning speeds. The largest peak around −18 ppm was assigned to twelve unresolved methyl protons, and the other two peaks (−2 ppm and +47 ppm) were assigned to two distinct positions of the pyridyl protons. The two isotropic signals appear different in intensity. This is due to the different static line shapes of the two signals. Taking into account the distribution of the intensity over the spinning side bands, the two signals are comparable in intensity. Two sharp peaks indicated by vertical lines without spinning side band are very small amount of solvent. The temperature behavior of these isotropic shifts are depicted in Fig. 3 (a). It is evident from the figure and Eqs. 1 and 2 that the hfcc of one of the pyridyl protons exhibits positive sign and hfcc's of methyl and the other pyridyl protons show negative one. Comparing the experiment with the UBLYP/6-31G(d,p) calculation shown in Table I, we assigned the peak at + 47 ppm in Fig. 2 to the crystallographically equivalent 2 and 6 positions[15] of the pyridyl group (numbering scheme is defined in Fig. 1) and the peak at – 2 ppm to the crystallographically equivalent 3 and 5 positions.

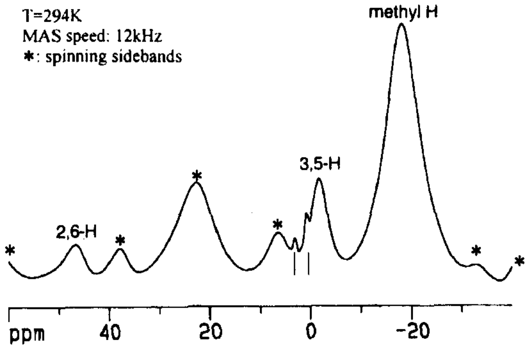

FIGURE 2 ^{1}H-MAS-NMR spectrum of polycrystalline *p*-PYNN measured at 294 K and at 12 kHz of the spinning speed.

The spectrum of *m*-PYNN is rather complex probably due to lower symmetry of the molecule in the crystalline phase compared with *p*-PYNN. Five different isotropic proton signals were resolved and assigned to the positions indicated in Fig. 3 (b) from the relative intensity among the signals and DFT calculation. A set of three signals of the pyridyl group exhibiting positive hfcc's were assigned to 2, 4 and 6 positions, although one-to-one assignment was difficult.

The values of the hfcc's were determined from the linear fitting of the isotropic NMR shifts as a function of the inverse temperature to Eq. 1 and 2. The results are listed in Table I. Intersection at infinite temperature means the diamagnetic shift.

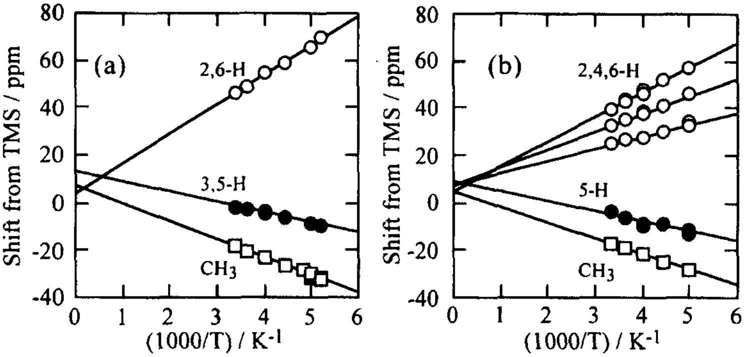

FIGURE 3 Temperature dependence of the isotropic ^{1}H-NMR shifts in the crystalline phase. (a) *p*-PYNN, ○: 2 and 6 positions, ●: 3, 5-positions, □: methyl protons. (b) *m*-PYNN, ○: 2, 4 and 6 positions, ●: 5-position, □: methyl protons. Solid lines are the results of least-squares fitting.

Effect of Incorporation of A Nitrogen Atom on the Electron Spin Density Distribution of Aromatic Ring

Since the π-spin density ρ_π at an aromatic carbon site is proportional to the hfcc A_H of the corresponding proton bonded to the carbon through McConnell's relationship[17] $A_H = Q\rho_\pi$ (Q = – 63.2 MHz)[18], we can estimate the rearrangement of the π-spin density in the aromatic ring by incorporation of the nitrogen atom and its position from the experimentally determined hfcc's of the protons. The experimental values are listed in the left hand side of Table I. The hfcc's of the protons of phenyl nitronyl nitroxide (PNN) determined by ENDOR experiment in solution has been reported by Takui *et al*[18]. The numbering scheme of the protons is common for the three compounds and defined in Fig. 1. The absolute values of the hfcc's at 3-H and 5-H positions of *p*-PYNN are remarkably reduced by 30% compared with PNN and those at 2-H and 6-H are slightly enhanced by 10%. On the other hand, the hfcc's of 2-H, 4-H and 6-H positions of *m*-PYNN are significantly suppressed by 30% on the average and the hfcc at 5-H is also suppressed by 20%. The enhancement and suppression of the hfcc of the individual proton correspond to those of the π-spin density ρ_π at the aromatic carbon site. Suppression of the electron spin density of the aromatic ring by incorporation of the nitrogen atom into the phenyl group appears significant for *p*-PYNN and *m*-PYNN molecules in each crystalline phase. It is mentioned that the absolute values of the hfcc's of methyl protons are remarkably larger for *p*-PYNN and *m*-PYNN compared with PNN.

Although the employed calculation method gave underestimate of the electron spin density, we can discuss a pure chemical effect of the incorporation of the nitrogen atom into the aromatic ring without geometry modification on the spin density distribution. Result of the calculation is listed in the right hand side of Table I. In comparison with PNN, a trend of enhancement or suppression of each calculated absolute value of the hfcc of aromatic ring is in agreement with the experiment for *p*-PYNN, although the change of the calculated hfcc on incorporating the nitrogen atom is not large. On the other hand, all of the calculated absolute values of hfcc of the aromatic ring are enhanced for *m*-PYNN. The observed suppression of the electron spin density of the aromatic ring of *m*-PYNN in its crystalline phase is probably induced by a non-trivial modification of the molecular geometry. The molecular geometry contributes to the change of the spin density distribution in addition to the effect of incorporation of the nitrogen atom into the aromatic ring. In fact, the temperature behavior of the ^{1}H-NMR spectrum of *p*-PYNN in acetone-d_6 solution gave remarkably small hfcc's compared with those found in the crystalline phase: – 0.33 ± 0.04 MHz for 3- and 5-H, + 1.1 ± 0.3 MHz for 2- and 6-H, and – 0.68 ± 0.02 MHz for methyl-H. The magnetic susceptibility measurements of *p*-PYNN gave small exchange interaction $J = 0.27$ K[10,15]. This result is consistent with the linear relation of the observed isotropic NMR shifts as a function of the inverse temperature in the high temperature region above 190 K. The intermolecular magnetic interaction is too small to interpret the observed change of the spin density distribution of *p*-PYNN between the two phases.

TABLE I Observed (A_H) and calculated (A_{calc}) hfcc's.

	A_H / MHz			A_{calc} / MHz		
site	PNN[18]	*p*-PYNN	*m*-PYNN	PNN	*p*-PYNN	*m*-PYNN
2-H	1.454	1.59 ± 0.06	1.33 ± 0.04	0.98	1.01	1.03
4-H	1.310	------	0.97 ± 0.02	0.68	------	0.77
6-H	1.454	1.59 ± 0.06	0.66 ± 0.05	0.98	1.01	1.02
3-H	− 0.82	− 0.56 ± 0.02	------	− 0.28	− 0.23	------
5-H	− 0.82	− 0.56 ± 0.02	− 0.55 ± 0.09	− 0.28	− 0.23	− 0.34
CH_3	− 0.58	− 0.96 ± 0.03	− 0.85 ± 0.01	− 0.44	− 0.45	− 0.45
				− 0.57	− 0.57	− 0.57

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