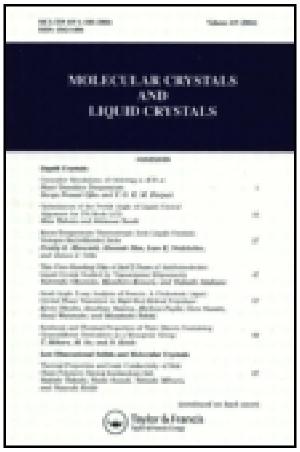

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Goro Maruta [a], Sadamu Takeda [a b], Takashi Kawakami [a], Wasuke Mori [a c], Ron Imachi [d], Takayuki Ishida [d], Takashi Nogami [d] & Kizashi Yamaguchi [a]

[a] Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka, 560, Japan

[b] Institute for Molecular Science, Myodaiji, Okazaki, 444, Japan

[c] Department of Chemistry, Faculty of Science, Kanagawa University, Hiratsuka, Kanagawa, 259-12, Japan

[d] Department of Applied Physics and Chemistry, The University of Electro-Communications, Chofu, Tokyo, 182, Japan

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SOLID STATE ^{1}H-MAS-NMR AND SPIN DENSITIES ON PROTONS OF THE ORGANIC FERROMAGNETIC TEMPO DERIVATIVES

GORO MARUTA[1], SADAMU TAKEDA[1,2], TAKASHI KAWAKAMI[1], WASUKE MORI[1,3], RON IMACHI[4], TAKAYUKI ISHIDA[4], TAKASHI NOGAMI[4] AND KIZASHI YAMAGUCHI[1]
[1]Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan; [2]Institute for Molecular Science, Myodaiji, Okazaki 444, Japan; [3]Department of Chemistry, Faculty of Science, Kanagawa University, Hiratsuka, Kanagawa 259-12, Japan; [4]Department of Applied Physics and Chemistry, The University of Electro-Communications, Chofu, Tokyo 182, Japan

Abstract Electron spin densities on hydrogen atoms of 4-(arylmethyleneamino)-2,2,6,6-tetramethylpiperidin-1-oxyls (abbreviated as Ar-CH=N-TEMPO), which show ferromagnetic behavior at low temperatures, were determined in their crystal phases from the temperature dependence of the Fermi contact shift measured by high speed magic angle spinning proton nuclear magnetic resonance. This method revealed a large negative hyperfine coupling constant for the methyl and methylene protons, A = -1.00 MHz for Ar = p-Cl-ph and A = -1.32 MHz for Ar = ph, and very small one for the aryl group protons, $|A| < 0.01$ MHz for p-Cl-ph and A = +0.04 MHz for ph. The observed negative hyperfine coupling constant (negative spin density) of methyl and methylene protons matches with spin alternation for the intermolecular spin polarization mechanism through the contact of methyl and/or methylene protons to adjacent N-O radical group. This contact potentially contributes to the intermolecular ferromagnetic interaction.

INTRODUCTION

Ferromagnetism in purely organic materials attracts a grate interest, since Kinoshita *et al.* reported a molecular ferromagnet at low temperature.[1] Most examples of organic ferromagnetic crystals, such as several Ar-CH=N-TEMPO derivatives, are based on nitroxide (N-O) radicals.[1-8] Main interest of this field is to control the intermolecular magnetic interaction between N-O radical groups in crystal to produce the ferromagnetic ordering. As a possible intermolecular ferromagnetic interaction path, a close contact of methyl and/or methylene protons to N-O radical group of adjacent molecules in crystal has been noticed from X-ray diffraction experiment.[6,9] The methyl and methylene protons are expected to be intermolecular ferromagnetic exchange coupler via spin polarization mechanism (NO(↑)-C(↓)-C(↑)-H(↓)···NO(↑)). The electron spin polarized on the proton may be a key point.

In this paper we report the experimental results of the determination of electron spin density or hyperfine coupling constant on protons of Ar-CH=N-TEMPO derivatives in their respective crystal phase to elucidate a possible ferromagnetic interaction path. The hyperfine coupling constant was determined from the temperature dependence of the Fermi contact shift which was measured by high speed magic angle spinning proton nuclear magnetic resonance (MAS-NMR).

DETERMINATION OF HYPERFINE COUPLING CONSTANT BY MAS-NMR

Almost localized electron spin at N-O radical group induces electron spin at other atoms in a molecule by spin polarization mechanism through bonding.[10,11] Electron spin has two states, α and β. Supposing α-spin for the N-O radical group, the spin density $\rho(r)$ on proton at coordinate $r = 0$ can be expressed by,

$$\rho(0) = \sum_{Occupied} \left|\varphi^{\alpha}(0)\right|^2 - \sum_{Occupied} \left|\varphi^{\beta}(0)\right|^2, \tag{1}$$

where $\varphi^{\alpha,\beta}(r)$ designate UHF molecular orbitals and r is electron coordinate. The sign of spin density depends on the coordinate r and alternates at nuclear sites in order throughout the bonding network of hydrocarbon. The spin polarization mechanism also operates between neighboring radical molecules through intermolecular contact.[12,13]

Magnitude and sign of the electron spin density on proton in the crystal can be simultaneously determined from Fermi contact shift ($\delta_{con.}$) which appears in the isotropic shift of proton MAS-NMR spectrum,[14,15]

$$\delta_{obs.} = \delta_{dia.} + \delta_{con.}, \tag{2}$$

where

$$\delta_{con.} = \frac{g\beta \cdot S(S+1)}{\gamma_N \cdot 2\pi} \cdot \frac{A}{3kT}. \tag{3}$$

Hyperfine coupling constant A is proportional to electron spin density ($\rho(0)$) on proton at coordinate $r = 0$,

$$A = \frac{8\pi}{3} g\beta \frac{\gamma_N}{2\pi} \rho(0). \tag{4}$$

$\delta_{obs.}$ is the observed shift of proton in ppm, $\delta_{dia.}$ is the shift that the same nuclear spin would have in an equivalent diamagnetic environment, T is the absolute temperature, and the other terms have their usual meaning. $\rho(0)$ is proportional to spin density ρ_H of 1s-orbital of hydrogen atom. Hyperfine coupling constant A can be described as $A = Q_H\rho_H$, where Q_H is 1420 MHz for isolated hydrogen atom.

Dipole interaction between proton and electron spin may also contribute to the NMR shift in principle due to an anisotropy of g-value of electron spin. However, organic radical with S=1/2 spin shows only a small anisotropy of g-value[16] and the contribution of the dipole interaction to the isotropic NMR shift is negligibly small in the present case. Then we confine ourselves to the isotropic shift described in eqs. (2) and (3) and its temperature dependence for evaluating the hyperfine coupling constant A.

EXPERIMENTAL

Preparation of Ar-CH=N-TEMPO derivatives has been previously reported.[2-6] Proton high speed MAS (Magic Angle Spinning) NMR spectra were measured by a single pulse method for polycrystalline materials between 170 and 290 K at the resonance frequency of 300.13 MHz with Bruker DSX300 spectrometer and 4mm CP/MAS probe. $\pi/2$ pulse length was 1.2 μs. A conventional zirconia rotor (4mm) with boron nitride cap was used. Very broad background signal from the CP/MAS probe is much smaller in intensity than the MAS NMR signals of the samples. The samples (*ca.* 10~20 mg) were carefully packed at the center of the rotor (2~3 mm long) to achieve homogeneous temperature at the sample position and Teflon powder or zirconia powder was used as spacer. The zirconia powder, which was used only for Ar = ph, showed a little proton background signal due probably to adsorbed water and was subtracted from the raw spectrum. This procedure did not disturb the determination of the MAS NMR shifts. Rotor, cap and Teflon powder did not show any proton background signal. The thermometer of the CP/MAS NMR probe was calibrated against the contact shift of carboxyl carbon of ^{13}C-enriched (35%) $Sm(CH_3{}^*COO)_3{\cdot}4H_2O$.[17] Uncertainty of the temperature measurement was 5 K. All proton NMR shifts were measured from the external reference of tetramethylsilane dissolved in CCl_4.

RESULTS AND DISCUSSION

Before discussing the experimental results on Ar-CH=N-TEMPO derivatives, it is noted that the spin density of these compounds should be measured in their crystal phase. We observed a sensitive change of the proton MAS NMR spectrum of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) by a structural phase transition.[18] The phase transition temperature was determined to be 290.8 K by differential thermal analysis, which is in agreement with the reported one.[19] In the high temperature tetragonal phase three distinct proton signals were assigned, *i.e.* 4-(methylene): +14.5 ppm, 2(6)-methyl: -15.0 ppm, and 3(5)-(methylene): -25.6 ppm at 291 K, which are similar to those, +15.5 ppm, -14.6 ppm and -28.8 ppm in order from high to low frequency in $CDCl_3$ solution at 297 K and to reported values.[20] However those are distinctly different from +3.4 ppm (4-(methylene)) and -36.7 ppm (2(6)-methyl and 3(5)-(methylene)) in the low temperature monoclinic phase at 260 K. The signals of 2(6)-methyl and 3(5)-(methylene) protons could not be resolved due to a large line-width. The remarkable change is induced by the structural phase transition. In the higher temperature phase dynamic ring inversion of TEMPO frame-work may occur[21] as often found for saturated six-membered ring in solution and Fermi contact shift differs from the frozen framework in the lower temperature phase. This result indicates that the correct determination of the electron spin density on proton of TEMPO derivatives should be performed in their crystal phases.

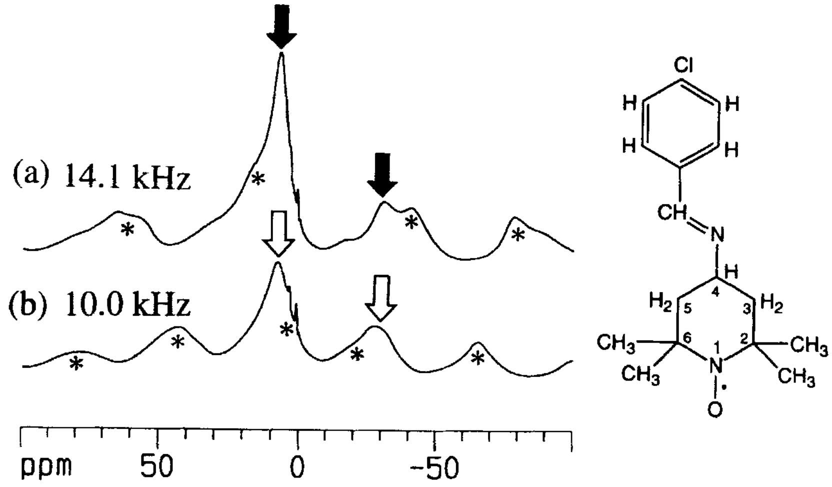

FIGURE 1 Proton MAS NMR spectra of *p*-Cl-ph-CH=N-TEMPO at 289 K; (a) measured at the spinning rate of 14.1 kHz and (b) at 10.0 kHz. Arrows indicate the isotropic shifts and asterisks indicate spinning side bands.

p-Cl-ph-CH=N-TEMPO has been recently found to show bulk ferromagnetic behavior at low temperature (T_C = 0.4 K).[5] High speed proton MAS NMR spectra of this compound measured with different spinning rates at 289 K are shown in Fig. 1, in which two isotropically shifted signals were clearly identified and distinguished from the spinning side bands. Two signals were assigned respectively to phenyl protons (7.7±0.5 ppm) and to unresolved peak of methyl and methylene protons (-30.4±1.0 ppm) from the dependence of the intensity of the peak around 8 ppm on the species of Ar-group and from similarity of the peak near -30 ppm to TEMPO described above. MAS NMR spectrum of other Ar-CH=N-TEMPO derivatives will be discussed later.

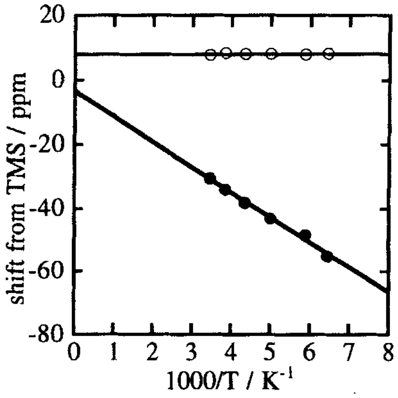

FIGURE 2 Temperature dependence of the isotropic NMR shifts of *p*-Cl-ph-CH=N-TEMPO crystal, ●: 2(6)-methyl-H (3(5)-methylene-H) and ○: ph-H. Solid lines are the result of least-squares fitting.

To obtain the hyperfine coupling constant A in eq. (3), the temperature dependence of the NMR shift of the two assigned signals was measured down to 170 K and is shown in Fig. 2. Unresolved peak of 2-methyl and 3-(methylene) protons (●) depends linearly on inverse temperature as predicted by eqs. (2) and (3). The large negative slope revealed the large negative hyperfine coupling constant (A = -1.00±0.04 MHz) and negative electron spin density ρ_H for 2(6)-methyl and 3(5)-(methylene) protons. The opposite sign of 2(6)-methyl and 3(5)-(methylene) protons from the spin of N-O radical group is in-phase with the spin alternation along the intermolecular interaction paths through the close contacts of 2(6)-methyl and/or 3(5)-(methylene) protons with adjacent N-O radicals (NO(↑)-C(↓)-C(↑)-H(↓)···NO(↑)). This type of intermolecular interaction potentially stabilizes the high spin state and contributes to the intermolecular ferromagnetic interaction. This situation is built in the crystal of *p*-Cl-ph-CH=N-TEMPO.[5,9] The NMR shift of the phenyl proton is almost independent of temperature as shown in Fig. 2 (○). The spin density on the phenyl protons is small and intermolecular magnetic interaction via phenyl contact is very weak.

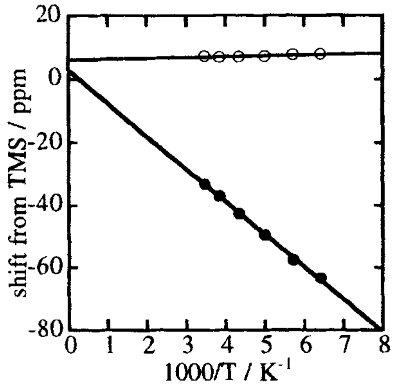

FIGURE 3 Temperature dependence of the isotropic NMR shifts of ph-CH=N-TEMPO crystal, ●: 2(6)-methyl-H (3(5)-methylene-H) and ○: ph-H. Solid lines are the result of least-squares fitting.

Temperature dependence of proton MAS NMR spectrum of ph-CH=N-TEMPO is shown in Fig. 3 which is similar to that of *p*-Cl-ph-CH=N-TEMPO. The hyperfine coupling constants are listed in Table I. The close contacts of methyl and/or methylene protons to adjacent N-O radical groups are also built in this crystal in a slightly different manner[2,9] and intermolecular ferromagnetic interaction through spin polarization mechanism is potentially operative.

TABLE I Hyperfine coupling constant A and diamagnetic shift $\delta_{dia.}$ of protons1)

material	magnetism2)	site	A / MHz	$\delta_{dia.}$ / ppm
p-Cl-ph-CH=N-TEMPO	ferro	2(6)-methyl-H (3(5)-(methylene)-H)	-1.00 (±0.04)	-3.4 (±1.6)
		aryl-H	$\lvert A\rvert$< 0.01 (±0.01)	+7.9 (±0.5)
ph-CH=N-TEMPO	ferro	2(6)-methyl-H (3(5)-(methylene)-H)	-1.32 (±0.03)	+2.7 (±1.1)
		aryl-H	+0.04 (±0.01)	+6.0 (±0.4)
TEMPO (low temperature phase)	antiferro3)	2(6)-methyl-H (3(5)-(methylene)-H)	-0.98 (±0.02)	-6.9 (±0.6)
		4-(methylene)-H	+0.06 (±0.01)	+1.8 (±0.5)

1) Values in parentheses are estimated errors.

2) Bulk magnetism at low temperature.

3) Reference 22.

Isotropic shifts of proton NMR in other Ar-CH=N-TEMPO crystals measured by high speed MAS NMR at 290 K are listed in Table II. The shifts are similar to those for Ar = p-Cl-ph and ph. These materials show ferromagnetic behavior at low temperature.[6]

TABLE II NMR shift$^{1)}$ in ppm of proton of Ar-CH=N-TEMPO in crystal at 290 K

Ar	Ar-H (±0.5)	2(6)-methyl-H (3(5)-(methylene)-H) (±1.0)	bulk magnetism at low temperature
p-CH_3-S-ph$^{2)}$	+7.4	-32.5	ferro
p-Cl-ph	+7.7	-30.4	ferro
p-ph-ph	+8.4	-34.1	ferro
p-ph-O-ph	+7.2	-34.0	ferro
ph	+8.1	-33.6	ferro
4-pyridyl	+8.6	-33.0	meta

1) Measured from TMS. Values in parentheses are estimated errors.
2) Shift of *p*-CH_3-S- is 2.1±0.2 ppm.

For the detailed discussion of the magnitude of the intermolecular ferromagnetic interaction through the contacts of methyl and/or methylene protons to adjacent N-O radical groups, it will be required to measure the hyperfine coupling constant (spin density) that the same radical molecule would have in an equivalent environment without intermolecular magnetic interactions. Here we note the result of theoretical calculation of the effective exchange integrals (J) for the dimer of ph-CH=N-TEMPO in which the methyl proton of one molecule contacts to the other N-O radical group.[9] The value of J calculated by the approximately spin projected UHF(APUHF) method by the use of 4-31G basis set and INDO method is 0.236 and 0.014 K, respectively, showing the intermolecular ferromagnetic interaction. The J values become -0.117(APUHF/4-31G) and -0.0052 K(INDO), respectively, when the methyl group contacting with the N-O radical group is replaced by the hydrogen atom. This indicates that the conversion from ferromagnetic to antiferromagnetic interaction is induced by the replacement of methyl group to hydrogen atom, suggesting a significant role of the methyl group for the intermolecular ferromagnetic interaction.[23]

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