

PROTON NMR STUDIES ON ANTIFERROMAGNETIC PHASE TRANSITION OF THE DANO CRYSTAL

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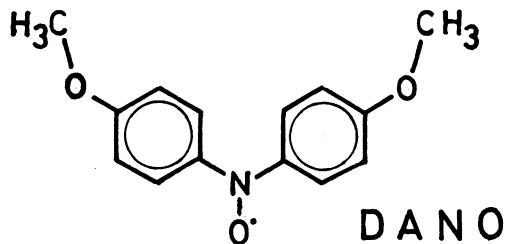
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Proton NMR spectra of di-p-anisyl nitric oxide radical (DANO) crystal have characteristics of the antiferromagnetic state at low temperatures. The transition temperature to the magnetic ordered state was determined to be $T_N = 1.67 \text{ K} \pm 0.02 \text{ K}$ from the temperature dependence of NMR line shift. The magnetic properties of the DANO crystal are discussed in terms of the magnitude of the resonance field shift.

Recently, the phenomenon of the long range magnetic ordering of unpaired electron spins in some crystals of organic free radicals has been found from measurements of several macroscopic properties such as magnetic susceptibility or specific heat.¹⁾ These measurements, however, can not give the detailed information on the magnetic ordering of the spins. On the contrary, broad line NMR enables us to determine the directions of the spin alignment in the magnetically ordered state, since this method makes it possible to detect directly the magnetic field acting on the nuclei due to the spontaneous magnetization of the electron spins.

In the NMR measurement on the powdered crystal of organic free radicals²⁾, the intensity of the unshifted NMR line was observed to decrease in the vicinity of its magnetic phase transition temperature but any shifted line characteristic to the magnetically ordered state could not be observed. We performed the measurement on a single crystal of di-p-anisyl nitric oxide (DANO) in the temperature range between 1.27 K and 4.2 K and studied the shift of NMR lines due to magnetic ordering. The NMR spectra are strongly dependent on temperature but are not so much affected by the applied resonance frequency or by the magnitude of the external magnetic field (H_0) between 2.5 kOe and 10 kOe. The spectra obtained at 4.2 K with H_0 of about 9.5 kOe parallel to the b- and a-axes of the crystal are shown in Fig.1; at this temperature the system is in the paramagnetic state. The shifted lines were observed on both sides of the free proton resonance line; high-field shifted lines and low-field ones. Temperature dependence of these shifts (δH) for H_0 parallel to the a-axis is shown in Fig. 1 and Fig. 2. The magnitude of the shift gradually decreases with a lowering of the temperature from 4.2 K to 2 K. Below



about 1.7 K, however, many resonance lines appear and the magnitudes of the shift increase abruptly. The most characteristic feature of the spectra in this temperature range is that the shifted lines observed on both low- and high-field sides are nearly symmetric about the unshifted line.

The hyperfine field acting on the i -th proton nucleus is³⁾

$$H_{hf}^i = (\tilde{A}_i/g_N\beta_N) \cdot \langle s \rangle, \quad (1)$$

where $\langle s \rangle$ is the expectation value of the electron spin of the radical molecule to which the proton belongs. g_N and β_N are the g-factor and the nuclear magneton respectively. Hyperfine interaction tensor \tilde{A}_i is composed of the isotropic Fermi contact term and the anisotropic dipolar term. Their magnitudes are related to the spin density on the carbon atom bonded to the proton. The protons in a DANO molecule are classified into three groups; ortho-, meta- and methoxy-protons. Since the spin densities⁴⁾ on the carbon atoms attached to the ortho-protons are positive,

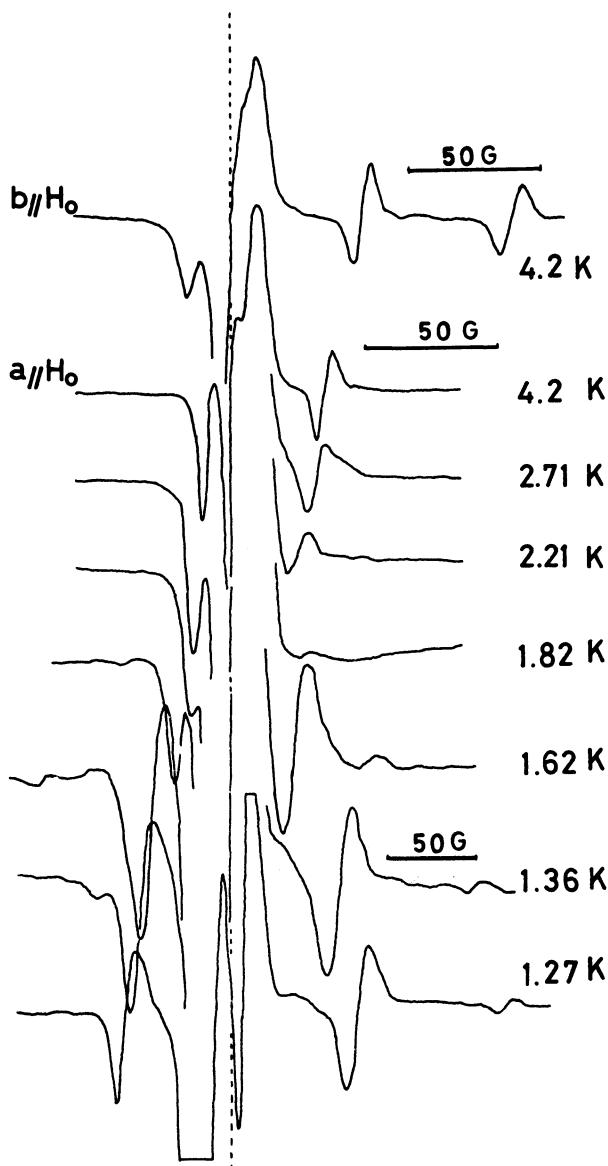
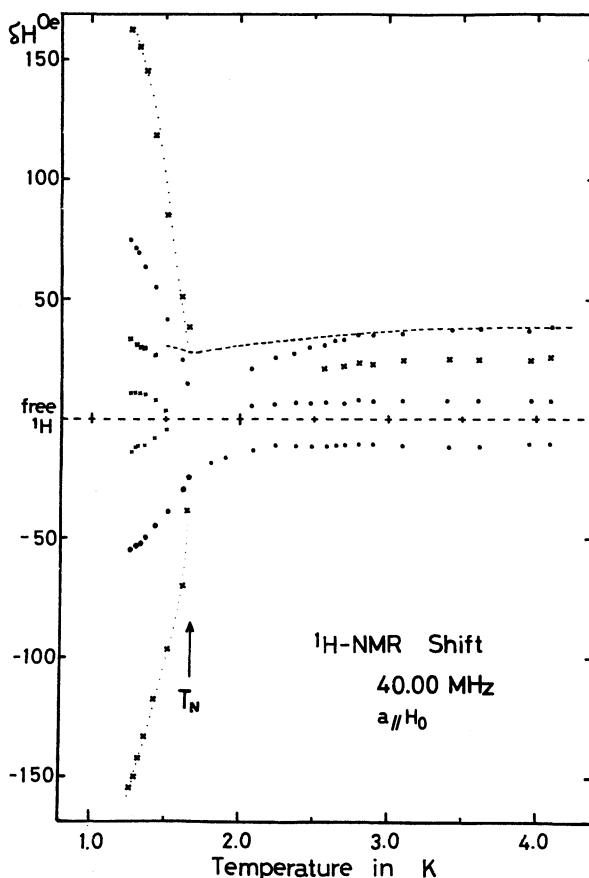


Fig.1. NMR spectra of the DANO crystal for H_0 parallel to the a- and b-axes. Dotted line shows the free proton resonance position.

Fig.2 Temperature dependence of the shift for $H_0 \parallel a$ -axis and 40.00 MHz.



the ortho-proton line must be observed on the high-field side of the free proton line, as is shown in the spectra at 4.2 K in Fig.1. The low-field line is expected to come from the meta-protons connected to the carbon atoms whose spin densities are negative. The lines from the methoxy-protons are hidden in the unresolved central line due to its small hyperfine value.

In the paramagnetic state of the crystal, $\langle \mathbf{s} \rangle$ in Eq.(1) is induced by H_0 and the direction of $\langle \mathbf{s} \rangle$ is parallel to H_0 . The resonance field shift, δH , is

$$\delta H = (A\chi H_0/N g_N \beta_N \cdot g_e \beta_e), \quad (2)$$

where g_e and β_e are the g-factor and the Bohr magneton of the electron spin respectively, and χ and N are the magnetic susceptibility and the spin number per mole. The temperature dependence of the shift calculated from Eq.(2) is shown with the dashed line in Fig.2 fitted to one of the resonance line shift at 4.2 K. The observed shift deviates from the dashed line below 2.8 K, suggesting the existence of some changes in the spin system.

In the antiferromagnetic state, the direction of $\langle \mathbf{s} \rangle$ is determined by both H_0 and the spontaneous magnetization of the electron spin. The spin system in the antiferromagnetic state forms the two sublattices with antiparallel spin directions with each other. Thus, $\langle \mathbf{s} \rangle$ of one sublattice has opposite sign with that of the other and this causes both high- and low-field shifts of the resonance lines provided the sign of A is common. In this case, the shift of the resonance field is expressed approximately as

$$\begin{aligned} \delta H &\propto (A/N g_N \beta_N \cdot g_e \beta_e) M(T) \\ &= (AM_0/N g_N \beta_N \cdot g_e \beta_e) M(T)/M_0 \end{aligned} \quad (3)$$

Here $M(T)$ is the sublattice magnetization at the temperature T and it reaches its saturation value M_0 at 0 K. The temperature dependence of $M(T)/M_0$ can be calculated by the molecular field approximation with an adjustable parameter T_N at which temperature $M(T)$ vanishes. The shift of one resonance line was fitted to Eq.(3) assuming the Brillouin function with $S=1/2$, $T_N=1.67$ K and $\delta H=210$ Oe at 0 K (Fig.3). The observed value of T_N , the phase transition temperature, had no dependence on the external magnetic field between 2.5 kOe and 10 kOe within the error of 0.02 K and is consistent with the results of the magnetic susceptibility measurements⁵⁾. The slight change of the magnitude of the shift in the temperature

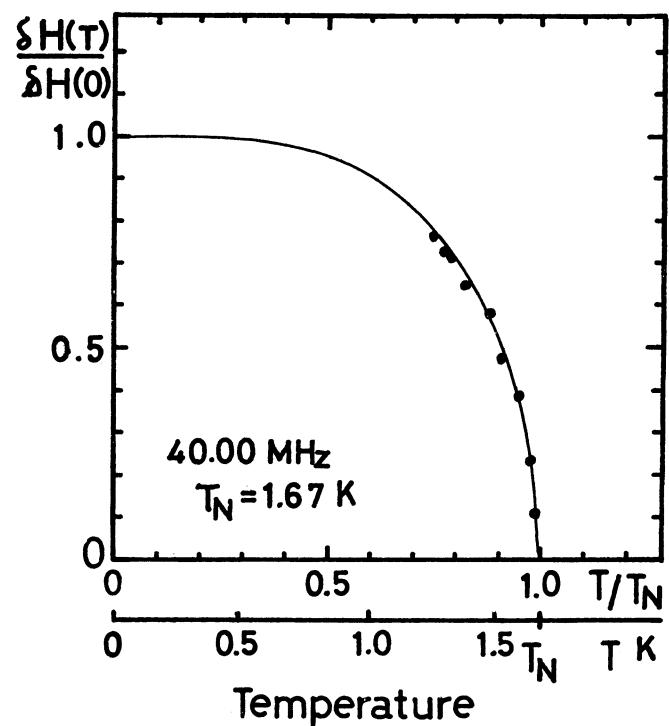


Fig.3. Temperature dependence of the shift of a high field line fitted to Eq.(3).

range between 1.67 K and 2.5 K can be attributed to the effect of the short range magnetic ordering in this crystal.

The saturation value of the shift $\delta H = 210$ Oe, extrapolated to 0 K under $H_0 = 9.4$ kOe, is compared to the magnitude of the hyperfine field calculated by Eq.(1), using the A-value determined from the shift in the paramagnetic region. The maximum shift so far obtained in this system under 9.4 kOe at 4.2 K is 130 Oe⁶⁾. This yields the maximum value of A to be 7.3×10^{-4} cm⁻¹, and hence the hyperfine field at 0 K to be about 3 kOe from Eqs.(1) and (3) putting $\chi = 300 \times 10^{-4}$ emu/mol at 4.2 K⁴⁾. As the local fields acting on the nucleus are H_{hf} and H_0 , the magnitude of the total magnetic field acting on the nucleus is greatly affected by the angle between H_{hf} and H_0 . The shift at 0 K is much smaller than that of H_{hf} , suggesting that the direction of the magnetic moment is likely to be nearly perpendicular to the external magnetic field. This is consistent to the results of the measurements on magnetic susceptibility and antiferromagnetic resonance; the spin system is in the spin-flopped state under the external magnetic field.⁵⁾

We are continuing the NMR experiment to determine the direction of the magnetic moment in the ordered state of the DANO crystal.

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