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Proton NMR Spectra of Selectively Deuterated *p,p′*-Azoxyanisoles in the Solid State

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Selectively deuterated PAA's, PAA-d_8, and PAA-d_6 have been studied by proton NMR from 77 K to the melting point (390 K). The temperature dependences of T_1, the line width, and the second moment for these compounds are presented. It has been demonstrated that PAA is in the rigid state at 77 K on an NMR time scale, and as the temperature increases the two methyl groups begin to rotate about the C_3 axis, followed by libration about the C–O axis. There is no evidence for motions of the ring protons except self-diffusion and/or slow reorientation of the molecular axis in the higher temperature range from 286 K to the melting point.

p,p′-Azoxyanisole (PAA, 4,4′-dimethoxyazoxybenzene) is one of the most important compounds in nematic liquid crystals and has been widely studied by NMR.[1)] In the proton resonance, however, it is difficult to distinguish the two different types of protons, *i.e.*, the ring and the methyl protons, although their spin-lattice relaxation times are expected to show different dependences on temperature. Thus we have synthesized the two selectively deuterated PAA's, *i.e.*, the ring-proton-deuterated PAA (PAA-d_8) and the methyl-proton-deuterated PAA (PAA-d_6), and already reported their proton relaxation times and anisotropic molecular motions in the nematic and isotropic liquid states.[2)]

In this paper the spin-lattice relaxation times T_1, the line widths, and the second moments of the two selectively deuterated PAA's are presented from 77 K to the melting point. The internal motions of the methyl protons are distinguishable from the motion of the ring protons, and it is possible to discuss the effects of the internal reorientations of the side chains on T_1 of the benzene protons of the central part of the molecule.

Proton relaxation times T_1 and $T_{1\rho}$ have been studied in the solid state,[3)] and the molecular motions depending on temperatures were discussed. It has been suggested that there is a question about the activation of the internal rotation around the C–O axis for PAA in the solid state. It will be shown here that such hindered rotation about this axis does not exist.

Experimental

The method of synthesis and purification of the selectively deuterated PAA's have been described in a previous paper.[2)] The compounds were sealed in a 10 mm o.d. glass tube after a number of melt-solidify-pump-thaw cycles.

The proton NMR spectrum was observed by an NMR Specialities PS-60RW spectrometer operating at 55 MHz. The temperature control apparatus has been reported in the previous paper.[2)] T_1 measurements were carried out by the usual 180°-τ-90° pulse sequence. The accuracy of the semilogarithmic plot was within ±10%. To obtain the cw spectrum the FID signal was digitized by a Biomation 1010 waveform recorder and then accumulated in a FACOM F-PDT-8 microcomputer. The pulse width for 90° nutation was approximately 4.5 μs. The sampling time was 0.5 to 1 μs, data points were about 200 to 600 and the accumulation was 1 to 16 times depending on the temperature. The accumulated FID signal was punched on to paper tape and Fourier-transformed by a FACOM 270/30 computer. The second moment was also calculated by the computer from the cw spectrum obtained.

Results and Discussion

The Fourier-transformed cw spectra of PAA-d_8 are shown in Fig. 1. At 77 K the methyl protons of PAA-d_8 show a triplet, which is the typical pattern for a three-spin system in the rigid lattice. The spacing between the two outer lines is 14.8 G, which agrees well with the theoretical value of 4α, where $\alpha=(3/2)\mu_H/r^3$ and $r=1.79$ Å. As the temperature increases, each line broadens, the triplet collapeses into a broad single line at about 92 K, and then the line narrows into another triplet with small splitting. The change of the spectral patttern is due to the activation of the reorientation of the methyl group about the C_3 axis and agrees well with the theoretically calculated

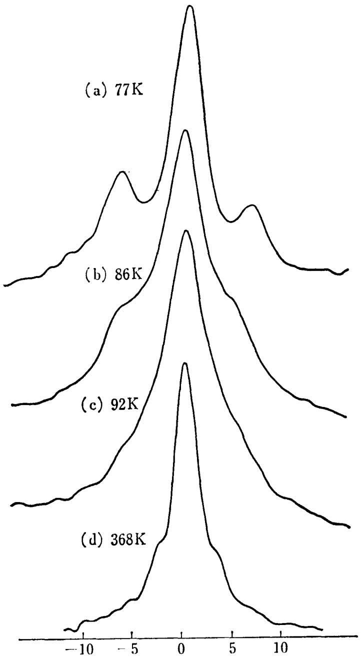

Fig. 1. Fourier transformed cw spectra of PAA-d_8 at (a) 77 K, (b) 86 K, (c) 92 K, and (d) 368 K. Throughout this paper 10^4 G = 1 T.

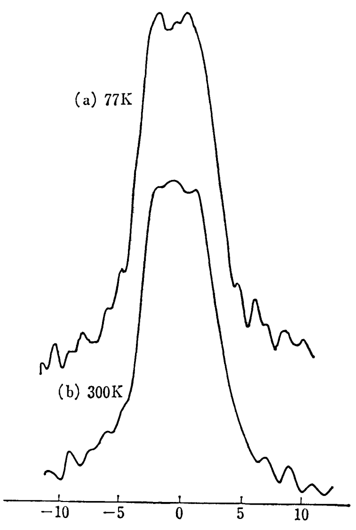

Fig. 2. Fourier transformed cw spectra of PAA-d_6 at (a) 77 K and (b) 300 K.

spectra for an isolated methyl group reported by Cobb and Johnson.[4] The spectral pattern for PAA-d_8 does not change significantly from 103 K to the melting point at 390 K (117.5 °C). The temperature dependences of the outer spacing of the triplet, the half line width of the central line, and the second moment of PAA-d_8 are shown in Fig. 3 (a), (b), and (c) respectively. Since the second moment was calculated from the Fourier-transformed spectrum, where it was difficult to draw a definite base line in the technique employed in this paper, the error was rather large, about 10 to 15% of the obtained value. This error comes directly from the uncertainty of the base line position.

The proton cw spectra of PAA-d_6 are shown in Fig. 2. As may be seen, the spectral pattern is almost unchanged from 77 K to the melting point. The line width is also constant from 77 to 285 K, and a little line narrowing is observed below the melting point, as shown in Fig. 4. The second moment of PAA-d_6 in Fig. 4 also shows a similar behavior to the line width with the change of the temperature.

In discussing the molecular motions of PAA in the solid state, interesting points are the methyl reorientation around the C_3 axis and the C–O axis, the libration of the benzene rings about the C–N axis, the molecular overall reorientation, and the self-diffusion. It has been suggested from the study of proton T_1 and $T_{1\rho}$ of PAA,[3] that the reorientation of the methyl groups about the C_3 axis is the predominant relaxation mechanism between 77 and 167 K, and that the internal rotation about the C–O axis is activated between 167 and 238 K, and in this temperature range there is also proton cross relaxation to the nitrogen. Then as the temperature increases the fast random molecular reorientation and slow self-diffusion take place. In the same paper,[3] however, it was written that as an opinion of other researchers, there is a question on the rotation about the C–O axis in the solid state.

In this study, the second moment of PAA-d_8 decreases from 22.6 to 6.0 G^2 at about 103 K, which corresponds to the change from the methyl group which is isolated in the rigid lattice to the methyl group freely rotating about the C_3 axis. If the rotation of the methyl group around the C–O axis were further activated in higher temperatures, the second moment should become about 0.56 G^2, since the second moment will decrease by a factor of $\left(\frac{3\cos^2\theta-1}{2}\right)^2$ by the additional rotation.[6] The angles COC (θ) have been determined as 118.7 and 118.1° from X-ray analysis.[5] However, at temperatures just below the melting point, the second moment is still 3.8±0.5 G^2. Thus it is concluded that the methyl groups do not rotate around the C–O axis in the solid state.

The second moment of the ring protons of PAA-d_6 is almost constant from 77 K to about 200 K, and a little narrowing is observed near below the melting point, as shown in Fig. 4. The second moment of the

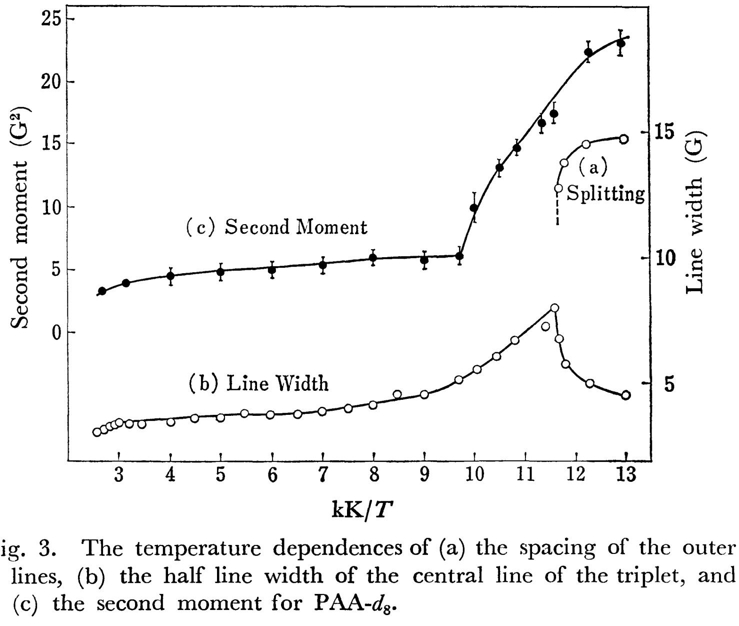

Fig. 3. The temperature dependences of (a) the spacing of the outer lines, (b) the half line width of the central line of the triplet, and (c) the second moment for PAA-d_8.

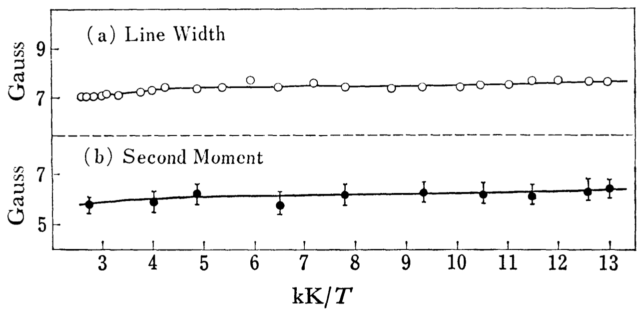

Fig. 4. The temperature dependences of (a) the half line width and (b) the second moment for PAA-d_6.

ring protons calculated for the rigid lattice is 1.67 from the protons on the same benzene ring, 0.07 from the protons of another benzene ring in the same molecule, 1.14 from the intermolecular ring protons, and 0.03 from the inter- and intramolecular CD_3 groups in the G^2 unit. The sum, 2.91 G^2 is expected for the second moment of PAA-d_6 in the rigid lattice with random orientation. However, the observed second moment is 6.2 G^2 at 77 K and 5.8 G^2 just below the melting point, both of which are larger than the calculated value. The sample used in this work was heated to melt in the nematic state for the purpose of degassing. After the rapid or slow cooling from the nematic to the solid states inside or outside the magnetic field, the second moment of PAA-d_6 observed at room temperature was almost the same value within experimental error. One possible interpretation for this disagreement between the observed and calculated second moments is that some orientation in the nematic state may still remain in the solid state. Another interpretation is the polymorphism of PAA in the solid state obtained by cooling from the nematic state as suggested by a recent study.[7)] In PAA-d_8 the methyl group may be regarded as an isolated system, so that the effects of the remaining orderness or polymorphism are probably very small on the second moment of PAA-d_8.

In the calculated second moment of PAA-d_6, the intermolecular contribution is about 40%. When the molecular motion, which causes the change of the intermolecular proton-proton distance, were activated, a decreasing of the second moment should occur. Since the second moment of PAA-d_6 does not change significantly, libration about the C–N axis or the fast molecular reorientation suggested before,[3)] both of which bring changes in the intermolecular ring proton distances, can not be assumed to take place below 250 K in the solid state.

The above discussion concerning the molecular motion of PAA can be applied to the T_1 behavior of PAA-d_8, PAA-d_6, and PAA. As shown in Fig. 5, the plots of T_1 *vs.* $1/T$ have minimum values at similar temperatures. This fact suggests that the motion, which gives the T_1 minimum, belongs to the same mode of molecular motion for all compounds. Considering the spectral patterns and the second moments, this motion is clearly the reorientation of the methyl groups about the C_3 axis.

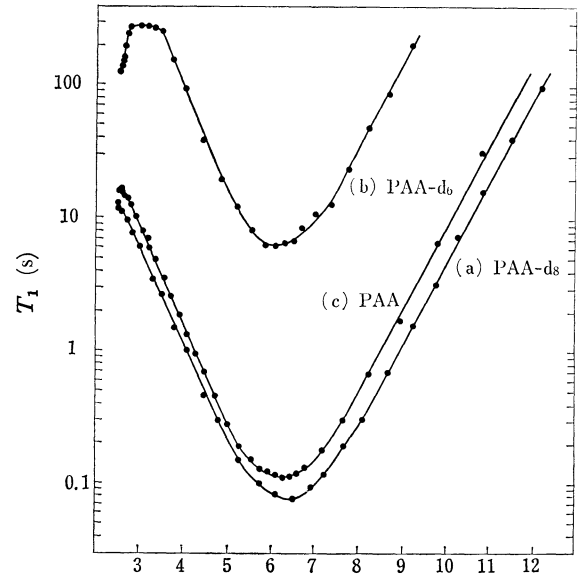

Fig. 5. The temperature dependent spin-lattice relaxations for (a) PAA-d_8, (b) PAA-d_6, and (c) PAA in the solid state observed at 55 MHz.

T_1 of the reorientating methyl protons may be described by

$$\left(\frac{1}{T_1}\right)_{\text{Methyl}}=\frac{9}{20}\frac{\gamma_H^4\hbar^2}{r^6}\left(\frac{\tau_c}{1+\omega_H^2\tau_c^2}+\frac{4\tau_c}{1+4\omega_H^2\tau_c^2}\right),\tag{1}$$

where r is the distance betweeen the protons within the methyl group, and $\omega_H=2\pi\nu_H$, ν_H being the resonance frequency of the protons (55 MHz). The condition for the T_1 minimum is $\omega_H\tau_c=0.616$. In the case of the ring protons, T_1 is very long and the contribution from the rotating CD_3 becomes important. Assuming that the ^{2}H relaxation of the CD_3 groups takes place mainly by the quadrupolar mechanism and that the correlation time for the reorientation of CD_3 is the same as that for CH_3 of PAA-d_8 at the same temperature, then the magnetic relaxation of the deutrons of the CD_3 is much faster than that of the ring protons by about 10^4 in the vicinity of the T_1 minimum. Theoretically, the non-resonant spins contribute to the relaxation of the resonant spins.[8)] In this case, however, the relaxation rate of the non-resonant deuterons of CD_3 is so large that it may be assumed that the effect of the magnetization of CD_3 on the dipolar relaxation time T_1 of the ring protons may be neglected. This dipolar relaxation time T_1 directly arising from the rotating CD_3 in the weak collision limit, may be written as[8,9)]

$$\left(\frac{1}{T_1}\right)_{\text{Ring}}=\frac{4}{15}\gamma_H^2\gamma_D^2\hbar^2 I_D(I_D+1)\frac{1}{N_i}\sum_{ij}\frac{1}{r_{ij}^6}\times\left(\frac{1}{2}\frac{\tau_c}{1+(\omega_H-\omega_D)^2\tau_c^2}+\frac{3}{2}\frac{\tau_c}{1+\omega_H^2\tau_c^2}+\frac{3\tau_c}{1+(\omega_H+\omega_D)^2\tau_c^2}\right),\tag{2}$$

where $\omega_D=2\pi\nu_D$ and ν_D is the ^{2}H resonance frequency, γ_D and I_D are the gyromagnetic ratio and the spin quantum number of deuteron, and r_{ij} is the distance between the ring proton i and the deuteron j of the intra- and intermolecular CD_3 groups, and N_i is the number of the ring protons. In Eq. 2, the condition of the minimum T_1 is $\tau_c=2.7\times10^{-9}$ s ($\nu_H=55.0$ MHz). Using the proton-proton distances for PAA obtained from X-ray analysis, Eq. 2 gives $(T_{1\,\mathrm{min}})_{\mathrm{Ring}}=3.8$ s, and the observed value is 6.4 s, approximately 60% of the theoretical value. On the other hand, the calculated $(T_{1\,\mathrm{min}})_{\mathrm{Methyl}}=31$ ms, compared to the observed value of 76 ms, about 40% of the theoretical value. In both cases the observed $T_{1\,\mathrm{min}}$ is longer than the calculated one. As described later, the agreement is considered satisfactory, and it can be said that the $T_{1\,\mathrm{min}}$ of the ring protons is interpreted by the rotation of the neighboring CD_3 groups.

The discrepancy between the observed and the calculated $T_{1\,\mathrm{min}}$ has already been reported for the hindered rotation of the methyl group in an isolated system, and interpreted by Johnson[10] as the following: oscillations of the methyl group, occuring in the reorientation through large angles, partially average the dipolar Hamiltonian and the efficiency of the nuclear relaxation is reduced, leading to a longer T_1 than given by the theory. Furthermore, it has been also shown that if there is cross-correlation, the relaxation is not a simple exponential decay and T_1 obtained by the half-recovery method becomes longer. In our experiments, non-exponential decay for the relaxation of all the compounds studied was not observed, but the discrepancy was a little larger, compared with the simple methyl compounds studied by Johnson. This is attributed to the coupling of the internal rotation of the methyl group about the C_3 axis with another molecular motion. In point of fact, the second moment of PAA-d_8 is smaller than the value of the isolated rotating methyl protons at this temperature.

As given in Table 1, the activation energies obtained from the slopes of log T_1 *vs.* $1/T$ plots are similar for PAA, PAA-d_8, and PAA-d_6 in both the low and high temperature sides. This is another reason why the same mode of the molecular motion affects T_1's of the ring protons as well as the methyl protons. The correlation time τ_0 was obtained from τ according to the equation $\tau=\tau_0\exp(E_a/RT)$. The values of τ_0 for PAA, PAA-d_8, and PAA-d_6 in Table 1 are reasonable for the rotation of the methyl group about the C_3 axis.[11,12] The small deviation of τ_0 for PAA-d_6 is probably due to the assumption contained in Eqs. 1 and 2.

In order to explain the value of $T_{1\,\mathrm{min}}$ and the slight narrowing of the second moment of PAA-d_8 from about 100 K to the melting point, some additional process of molecular motion is necessary besides the reorientation of the methyl group about the C_3 axis. From the study of T_1 and $T_{1\rho}$ of PAA, it has been suggested that in the temperature region between 167 and 238 K, the slow rotation of the methyl group about the C–O axis is activated. However, there is not a clear change in the second moment of the methyl protons of PAA-d_8, corresponding to the dual reorientation of the methyl group. The second moment of PAA-d_8 decreases gradually from 6.0 to 3.8 G^2 in the temperature region betweeen 100 K and the melting point. Thus, the slow libration about the C–O axis may be considered, after the reorientation of the methyl group about the C_3 axis is activated. The effect of the libration on the second moment of the ring protons of PAA-d_6 is estimated as being negligible, although the second moment decreases from 6.2 to 5.8 G^2 near the melting point. Thus some other molecular motions are necessary to understand the narrowing.

Above 286 K ($1/T=3.5\times10^{-3}$), a large change appears in the T_1 of PAA-d_6. When the temperature increases, T_1 is nearly constant until 364 K, and then T_1 decreases sharply until the melting point. In this temperature range, however, the second moment and the line width decrease only to a small extent, and the spectral pattern does not change at all. Such change is not apparent in T_1 for the rotating methyl protons of PAA-d_8, but the line width and the second moment of this compound decrease to nearly the same extent as those of PAA-d_6. These facts suggest that motion of the whole molecule takes place at these temperatures. For such motion, the self-diffusion and the reorientation of the molecular axis have been assigned from the study of T_1 and $T_{1\rho}$ of PAA.[3] It should be noted that the motion of the whole molecule begins at temperatures about 105 K below the melting point. This wide temperature region for the self-diffusion and the molecular reorientation, even in the solid state, characterises the nematic liquid crystalline compound PAA.

Assuming that the relaxation mechanism for T_1 of PAA, PAA-d_8, and PAA-d_6 is the dipole-dipole interaction,

$$\left(\frac{1}{T_1}\right)_{\mathrm{PAA}}=\frac{8}{14}\left(\frac{1}{T_1}\right)_{\mathrm{PAA}\text{-}d_6}+\frac{6}{14}\left(\frac{1}{T_1}\right)_{\mathrm{PAA}\text{-}d_8}+\left(\frac{1}{T_1'}\right) \tag{3}$$

then, $1/T_1'$ is the relaxation rate mainly due to interactions between the ring and the methyl protons and a small contribution from the interactions of the protons with deuterons. On the low temperature side of the T_1 minimum, $1/T_1'$ is negeligibly small within experimental error, while on the high temperature side, $1/T_1'$ has a value larger than the relaxation rate of PAA-d_6 at all temperatures. The gradient of the log T_1' *vs.* $1/T$ plot has almost the same as that of log T_1 *vs.* $1/T$ for PAA, PAA-d_6, and PAA-d_8 which are shown in Table 1. Then the molecular motion

TABLE 1.

Compound	$T_{1\,\mathrm{min}}$(s)	Temp(K)	$\tau_0(10^{-13}$ s)	Activation energy(kJ/mol)	
				Low temp	High temp
PAA	0.11	159	1.9	12.1(±0.7)	14.3(±0.4)
PAA-d_8	0.076	154	1.7	11.5(±1.5)	15.0(±1.9)
PAA-d_6	6.3	165	6.4	11.8(±0.2)	13.6(±0.6)

which governs the temperature dependence of the interaction between the methyl and the ring protons in PAA is the same as that for the ring protons of PAA-d_6, which is considered to be the reorientation of the methyl groups and the motion of the whole molecule.

In conclusion, at 77 K PAA is in a rigid lattice in an NMR time scale, and as the temperature increases, the methyl groups begins to rotate around the C_3 axis, followed by slow libration about the C–O axis. The other motions which change the relative position of the ring protons do not occur until the molecular overall motions, which may be self-diffusion and slow reorientation of the molecular axis, start to take place at 286 K.

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