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^{13}C Spin-Lattice Relaxation Times in Liquid Crystalline *p,p'*-Azoxyanisole

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The ^{13}C spin-lattice relaxation time T_1 in the liquid crystalline compound *p,p'*-azoxyanisole; (PAA; 4,4'-dimethoxyazoxybenzene) was observed in the nematic and isotropic liquid phases. From the obtained T_1's of the ring and the methyl carbons, the anisotropic rotational diffusion constants were determined. It is concluded that the rotational reorientation around the molecular axis is faster by an order of 10^3 than the rotational motion around the axis perpendicular to the molecular axis in the nematic and isotropic liquid states.

Nuclear relaxation time in the liquid crystals is known to give important information about molecular motions and intermolecular interactions of some interesting compounds. The nematic liquid crystal *p,p-'* azoxyanisole (PAA); 4,4'-dimethoxyazoxybenzene) and its deuterated species have been studied by observing ^{1}H, ^{2}D, ^{13}C and/or ^{14}N relaxation times.[1-9)] Most of the relaxation studies were made by the ^{1}H resonance, but the ^{1}H relaxation time is affected by both intra- and intermolecular interactions. The spins of the other nucleus, however, relax predominantly by the intramolecular processes. In particular, the relaxation of ^{13}C nuclei, which is bonded by one or more protons, mainly takes place through the dipole-diploe interaction with the attached protons modulated by the molecular reorientations.

PAA contains two different types of carbons bearing protons, *i. e.*, the ring carbons and the methyl carbons. Clearly the relaxation times of the ring carbons can be expected to be affected by the motion of the nematic director. Although the motion of the methyl carbons is averaged by the internal rotation, the relaxation time will be also affected by the anisotropic motion of the elongated molecule in the nematic state. Here we would like to present the temperature dependence of ^{13}C spin-lattice relaxation times for the ring and the methyl carbons observed in the nematic liquid crystalline and in the isotropic liquid states, and to discuss the anisotropic rotation of the nematic molecule.

Experimental

PAA was purified by the zone melting method, degassed, and then sealed into a 12-mm sample tube under vacuum. The ^{13}C relaxation times were obtained by the 180°—τ—90° pulse method using a Varian XL-100-15 spectrometer operating at 25.16 MHz in the external ^{19}F lock mode with proton decoupling. The temperature range of the nematic liquid crystalline phase is 117—135 °C for PAA, and T_1's were observed both in the nematic and in the isotropic liquid states by varying the temperature from 118 to 175 °C. In the nematic phase the measurement was made without sample spinning in order to prevent the disturbance of the allignment of the nematic director along the external magnetic field.

Results and Discussion

The ^{13}C spectrum of PAA in CDCl$_3$ solution at ambient temperature consists of ten peaks arising from the 10 chemically non-equivalent carbons.[10)] In the isotropic state at higher temperature, the ^{13}C spectrum shows a similar pattern to that for the CDCl$_3$ slouion, but only 8 peaks are observed due to the overlapping of two sets of two peaks, *i. e.*, the signals from two methyl carbons and from four ring carbons meta to OCH$_3$ group. Here four peaks are obtained from the carbons bearing protons. In the isotropic state the ^{13}C chemical shifts relative to that of the methyl carbons are nearly constant throughout the temperature range studied, and agree with those in CDCl$_3$ solution within 0.8 ppm. This fact suggests that the molecular structure of PAA does not significantly change from ambient to sufficient high temperatures.

In the nematic state where the molecules are in an anisotropic condition, the ^{13}C spectral lines for PAA are rather broad, probably due to insufficient proton decoupling. The lines of the two quaternary aromatic carbons bonded to nitrogen disappear, as shown by Pines and Chang.[11)] But the change in the spectrum from the isotropic to the nematic states in the ^{13}C resonance is much smaller than that in the ^{1}H or ^{2}D resonances, so that the measurement of ^{13}C relaxation times is still possible by the usual high resolution technique.

In this paper, since the molecular motion of PAA will be discussed assuming the dipole-dipole mechanism as the relaxation process, T_1's are observed for the carbons bonded by protons, *i. e.*, three aromatic carbon peaks and one methyl carbon peak. The temperature dependences of these T_1's are shown in Fig. 1, which

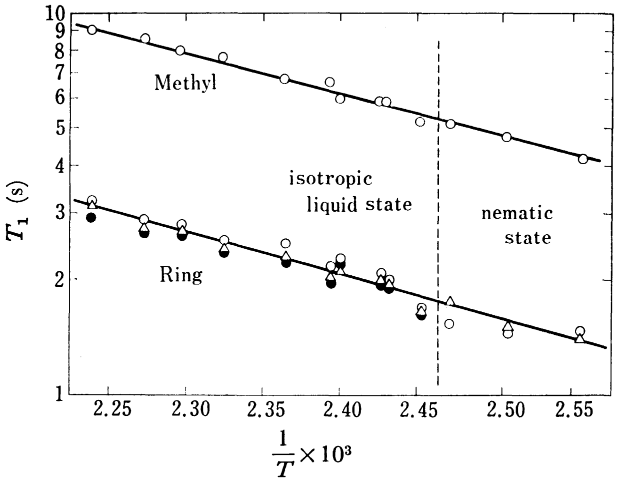

Fig. 1. The temperature dependences of ^{13}C relaxation times for PAA in the nematic and isotropic states. The ring carbons are expressed from a lower to a higher field by ○, ●, and △. In the nematic phase the two signals at the lower field collapses to a broad line which is shown by ○.

TABLE 1. NOE OF PAA IN THE ISOTROPIC LIQUID STATE

Temperature	Methyl	Ring		
137 °C	2.1	3.0	2.8	2.7
160 °C	2.3	2.6	2.7	2.6

have been observed both in the nematic and the isotropic liquid state. In order to estimate the contribution of the dipole-dipole relaxation mechanism to the observed ^{13}C relaxation times, NOE was determined in the isotropic state, as shown in Table 1. If we consider the experimental uncertainty, the observed NOE's are not very temperature dependent. Table 1 shows that the contribution of the dipole-dipole mechanism is a little larger in the ring carbons than in the methyl carbons, probably because the spin-rotation mechanism from the internal rotation may be effective in the ^{13}C relaxation of the methyl carbons. The dipole-diploe relaxation time T_{1d} can be calculated from the observed T_1 as follows12):

$$1/T_{1d} = \frac{\mathrm{NOE}-1}{1.988} \times 1/T_1.$$

A theoretical expression of nuclear magnetic relaxation in molecules with multiple internal rotations was first derived by Wallach.13) In this derivation the molecular motion was treated as isotropic. It was shown that each internal rotation which is much faster than the overall molecular motion contributes a single factor $((3\cos^2\theta-1)/2)^2$ to the relaxation rate, where θ is the angle from the internal rotational axis of interest to the next internal rotational axis, or for the last internal rotational axis to the label axis of interset. Then Levine and his coworkers14) have extended the theory to the dipolar relaxation for the case where the molecular motion is anisotropic, and presented the numerical results of the ^{13}C relaxation times in a hydrocarbon chain attached to an axially symmetric molecule.

The methyl groups of PAA are a dual rotation system which has internal rotations around the C–O bond and the three-fold axis. Possible mechanisms which are effective in the ^{13}C dipolar relaxation process for the methyl groups of PAA are molecular overall reorientation and the internal rotations. Since these dual internal rotations are reported to be activated in solid state,19) it may be assumed that the methyl groups rotate freely around both bonds at higher temperatures in the nematic and isotropic states. We also assume that PAA is a symmetric rotor having two rotational diffusion constants, $D_{/\!/}$ and $D_\perp$, where $D_{/\!/}$ is the rotational diffusion constant for the motion about the molecular symmetry axis and $D_\perp$ is for the motion about an axis perpendicular to the molecular axis. According to the theory developed by Wallach and Levine *et al.*, and using the spectral density function for the internal rotation system attached to the molecule undergoing anisotropic molecular motion, the dipolar relaxation rate $1/T_{1d}$ for the methyl carbons of PAA can be derived as

$$\left(\frac{1}{T_{1d}}\right)_{\mathrm{Me}} = \frac{3\gamma^2\gamma'^2\hbar^2}{2r^6} \times 3\left[\frac{1}{6D_\perp}\left(\frac{3\cos^2\theta-1}{2}\right)^2 + \frac{1}{2D_\perp+4D_{\|}}\sin^4\theta\right] \times \left(\frac{3\cos^2\theta'-1}{2}\right)^2\left(\frac{3\cos^2\theta''-1}{2}\right)^2, \tag{1}$$

where θ is the angle between the molecular axis and the C–O axis, θ' is ∠COC, and θ'' is ∠OCH. The factor 3 corresponds to the three protons of the methyl groups. When $\theta=0°$, $D_{/\!/}$ does not contribute to the relaxation rate of the methyl carbons. Even if θ is assumed to be 10°,14) the contribution of $D_{/\!/}$ will be negligibly small because of the term $\sin^4\theta$. In other words, the rotation around the molecular axis of PAA has little effect on the relaxation rate of the methyl carbons, and $(1/T_{1d})_{\mathrm{Me}}$ may be assumed to be only a function of $D_\perp$. The angle ∠COC, θ' was determined to be 118° by the X-ray analysis.16) Since the geometric factor $((3\cos^2\theta'-1)/2)^2$ is very sensitive to even small changes of this angle, the $D_\perp$ calculated using Eq. 1 contains some error due to the ambiguity of θ' in the nematic and isotropic states, in addition to the experimental error of $(1/T_{1d})_{\mathrm{Me}}$.

On the other hand, since the ring carbons constitute the skeleton of the PAA molecule, the most important mechanism for the ^{13}C dipolar relaxation of the ring carbons bearing protons will be the molecular overall rotation. Huntress17) has derived a theoretical expression for the relaxation rate of a nuclear spin in a molecule undergoing anisotropic diffusional rotation, which may be applied to the dipolar relaxation rate of the ring carbons of PAA. Then

$$\left(\frac{1}{T_{1d}}\right)_{\mathrm{Ring}} = \frac{3}{2}\frac{\gamma^2\gamma'^2\hbar^2}{r^6}\frac{1}{6D_\perp}\left[1+\frac{3(D_\perp-D_{/\!/}}{5D_\perp+D_{/\!/}} \times \sin^2\alpha\left(1+\frac{3(D_\perp-D_{/\!/})}{2(D_\perp+2D_{/\!/})}\sin^2\alpha\right)\right], \tag{2}$$

where α is the angle between the molecular axis and the label axis of interest. For the dipole-dipole relaxation rate for the ring protons, $\alpha=58.7°$ (an average for two C–H bonds),20) since the rotation around the molecular axis is expected. From Eq. 2, $D_{/\!/}$ can be calculated using the $D_\perp$ value obtained from the relaxation time of the methyl carbons and Eq. 1. In Table 2 the calculated values of $D_{/\!/}$ and $D_\perp$ are listed, together with those for D_{iso}, which are calculated from the assumption of isotropic motion.

TABLE 2. ROTATIONAL DIFFUSION CONSTANTS OF PAA

Temperature	$D_\perp$	$D_{/\!/}$	D_{iso}	
			methyl	ring
137 °C	4.1×10^8	0.86×10^{11}	1.7×10^{11}	1.2×10^{10}
160 °C	4.8×10^8	1.7×10^{11}	2.0×10^{11}	1.8×10^{10}

Although Eqs. 1 and 2 are approximate equations for describing the internal and the anisotropic molecular rotations for an aligned molecule such as PAA in the nematic phase and in the isotropic phase near the transition point, where the short range order remains, they may be safely applied to the ^{13}C dipolar relaxation rate of PAA molecules at higher temperature in the isotropic state. The obtained rotational diffusion constants describe the molecular motion of PAA molecule in the isotropic state. The rotation around the long molecular axis is much faster by an order of 10^3, than the rotation around the axis perpendicular to the molecular axis. Since the observed T_1 is continuous at the transition point from the nematic to the isotropic liquid states, as shown in Fig. 1, the same picture for the molecular motion of the PAA molecule will be almost true in the nematic state. The rotational motion expressed by the diffusion constant $D_\perp$ obtained from the ^{13}C relaxation time may be compared with the thermal fluctuation of the nematic director in the nematic state, which contributes to the ^{1}H relaxation rate as a frequency dependent phenomenon[1,2,9]. The order fluctuation of the director is shown to remain in the isotropic state,[5–7] and this is consistent with the fact that $D_\perp$ obtained in the isotropic state is still very small compared with the obtained $D_{//}$. Otherwise, in the usual isotropic liquid, $D_\perp$ and $D_{//}$ would have the values of the same order for a molecule about 18 Å in length and 6 Å in diameter, the approximate size of PAA.[16]

The measurement of ^{2}D relaxation time has been made by Orwoll *et al.*[8] for PAA-d_8 (ring positions are deuterated) in the nematic and isotropic liquid states. Although the relaxation mechanism is different for the ^{13}C and ^{2}D resonances, the direction of the interaction vector for the ^{2}D resonance in PAA-d_8 is the same as that for the ^{13}C resonance in the ring carbons of PAA. The correlation times calculated based on the assumption of the isotropic motion in the ^{2}D resonance are a little longer, by several percents, than thoes in the ^{13}C resonance at every temperature. Orwoll *et al.* also observed no frequency dependence of the ^{2}D relaxation time in the nematic and isotropic states. Since the correlation times and the observing frequencies are in a similar order for the ^{13}C and the ^{2}D resonances, it can be assumed that the ^{13}C relaxation time for the ring carbons is also frequency independent, and then the extreme narrowing condition will hold in the ^{13}C relaxation time when Eq. 2 is applied. From our measurement of ^{2}D relaxation times of PAA-d_6 (the methyl protons are deuterated) in the isotropic state[18], there is also the same trend in the correlation times of the methyl groups. The temperature dependences of the ^{13}C relaxation times in the ring and the methyl carbons shown in Fig. 1 are similar to those of the ^{2}D relaxation times in the ring position[8] and the methyl groups,[18] except that at the transition point there was observed the discontinuity in the T_1 of the ^{2}D resonance, while the T_1's of the ^{13}C resonance are continuous. Arrhenius plots of the ^{13}C relaxation times give the activation energies of 5.6 and 5.0 kcal/mol for the ring and the methyl carbons, respectively. The activation energy obtained for PAA-d_8 in the isotropic state is 5.5 kcal/mol,[8] and the agreement is good. Schwartz *et al.*[4] obtained the activation energy of 6.5 kcal/mol for the ^{13}C relaxation time for the ring carbons of PAA in a similar temperature region, and interpreted it by activation of the internal rotation about the C–N bond. But as discussed above and as also pointed out by Orwoll *et al.* from the results of the ^{2}D resonance, the main activation process which affects the temperature dependent ^{13}C and/or ^{2}D relaxation times from the nematic to the isotropic liquid phases may be concluded to be the anisotropic molecular rotational process.

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