

## Intermolecular and Intramolecular Contributions to Proton Relaxation in Liquid Crystals\*

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The intermolecular and intramolecular spin-lattice relaxation times have been determined by isotopic dilution for the nematic and isotropic phases of *p*-azoanisole. Derived correlation times for rotational and translational motions suggest that these processes are strongly coupled in the nematic phase. Comparison of rotational correlation times with results from dielectric studies indicates that rotational reorientation occurs by large jumps (greater than 60°) in the nematic phase.

In the last three years there has been a sustained effort to carry out and interpret NMR experiments on liquid crystals.<sup>1-13</sup> A major part of this effort has been devoted to understanding the observed frequency and temperature dependence of the proton spin-lattice relaxation time  $T_1$  in the nematic mesophase. Most explanations of experimental observations attribute the unusual behavior of  $T_1$  to an intramolecular mechanism—modulation of the dipolar intramolecular energy by hydrodynamic orientational modes of motion in the liquid crystal.

This intramolecular mechanism has been criticized and alternate explanations,<sup>12</sup> including intermolecular mechanisms,<sup>9,10</sup> have been proposed to account for experimental observations. However, the relative importance of intermolecular and intramolecular contributions to spin-lattice relaxation in liquid crystals has not been specifically determined.

We report preliminary results of an isotopic dilution experiment designed to separate intermolecular and intramolecular contributions to  $T_1$  in the nematic and isotropic phases of *p*-azoanisole (PAA).

The  $T_1$  measurements were made with a Ventron Magnion PNMR-200 spectrometer using a Biomation 802 transient recorder and Fabri-Tek 1062 computer to average the data. The temperature gradient across the sample in the probe was less than 0.2°C.  $T_1$  values were determined from a saturation- $\tau$ -90° pulse sequence, averaging sixteen decays for approximately twenty  $\tau$  values. PAA-(CD<sub>3</sub>)<sub>2</sub> and perdeuterated PAA prepared in this laboratory and recrystallized PAA obtained from Eastman Kodak exhibited essentially the same melting and nematic-isotropic transitions determined from differential thermal analysis measurements. The  $T_1$  values found for pure PAA-(CD<sub>3</sub>)<sub>2</sub> are consistently higher than

that reported by Martins.<sup>3</sup> Our  $T_1$  values for pure PAA are in good agreement with those reported by Dong, Forbes, and Pintar.<sup>4</sup>

The results of the isotopic dilution study of PAA and PAA-(CD<sub>3</sub>)<sub>2</sub> in perdeuterated PAA are shown in Fig. 1. The concentration dependence of  $T_1$  was examined in the nematic (120°C) and isotropic phase just above the nematic-isotropic transition (136°C). If it is assumed that only two mechanisms contribute to the overall relaxation, i.e.,

$$T_1^{-1} = T_{1a}^{-1} + T_{1r}^{-1}, \quad (1)$$

then it is possible to experimentally determine the intramolecular ( $T_{1a}$ ) and intermolecular ( $T_{1r}$ ) contributions to spin-lattice relaxation.  $T_{1r}$  is obtained from the slopes of the linear least-squares fit of the data in Fig. 1, and the extrapolated intercept yields  $T_{1a}$ . The values of  $T_{1a}$  and  $T_{1r}$  corrected for the deuteron-proton inter-

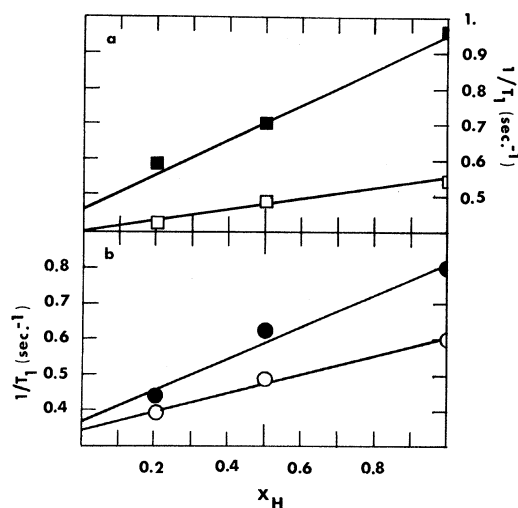


FIG. 1. Spin-lattice relaxation rate ( $T_1^{-1}$ ) versus mole fraction protonated species ( $X_H$ ) for (a) PAA-(CD<sub>3</sub>)<sub>2</sub> in PAA-*d*<sub>14</sub>, and (b) PAA in PAA-*d*<sub>14</sub>. Solid symbols, 136°C; open symbols, 120°C.

TABLE I. Spin-lattice relaxation times.

Compound	Temperature	$T_{1a}$ (sec)	$T_{1r}$ (sec)
PAA	120° (nematic)	2.98 ± 0.1	3.72 ± 0.3
	136° (isotropic)	2.87 ± 0.15	2.18 ± 0.1
PAA-(CD <sub>3</sub> ) <sub>2</sub>	120° (nematic)	2.60 ± 0.1	6.29 ± 0.3
	136° (isotropic)	2.13 ± 0.1	2.08 ± 0.1

action<sup>14</sup> are given in Table I.

In principle, it is possible to derive from the experimentally determined values of  $T_{1a}$  and  $T_{1r}$  the correlation times for the tumbling motion of the molecule,  $\tau_c$ , and for translational motion,  $\tau_t$ . Considering only dipolar interactions,  $\tau_c$  is obtained from

$$T_{1a}^{-1} = \frac{3}{2} \gamma^4 \hbar^2 \tau_c \sum_j r_{ij}^{-6}. \quad (2)$$

In computing the correlation times the PAA-(CD<sub>3</sub>)<sub>2</sub> data in Table I were used in order to restrict consideration to the motion of the rigid molecular framework of the PAA molecule. Hence  $r_{ij} = 2.47 \text{ \AA}$ , the value of the nearest-neighbor internuclear distance of the ring protons. To obtain  $\tau_t$ , Harmon and Muller's<sup>15</sup> expression for determining the self-diffusion coefficient  $D$  from  $1/T_{1r}$  is used. In Eq. (31) of Ref. 15 the following constants were used: molecular diameter  $\sigma = 6 \text{ \AA}$  and  $\langle r^2 \rangle / \sigma^2 = 0.7$ , where  $\langle r^2 \rangle$  is the mean squared flight distance. The translational correlation time is derived from the expression<sup>16</sup>

$$\tau_t = \sigma^2 / 2D. \quad (3)$$

It should be noted that in evaluating  $\tau_t$  the effect of rotational molecular motion on the intermolecular relaxation rate was neglected.<sup>17</sup> The calculated values of  $\tau_c$  and  $\tau_t$  are given in Table II.

The data in Table I clearly show that both intramolecular and intermolecular mechanisms make substantial contributions to the spin-lattice relaxation rate in PAA. The derived value of  $T_{1r}$  for PAA in the nematic phase is in good agreement with an earlier value<sup>4</sup> (3.57 sec) obtained for the contribution of translational diffusion to spin-lattice relaxation by an extrapolation of  $1/T_{1r}$  to infinite Larmor frequency in a  $1/T_{1r}$  versus  $\omega_L^{-1/2}$  plot, and with a previous estimate of  $T_{1r}$ <sup>11</sup> (3.13 sec) obtained from Harmon and Muller's Eq. (31) using the experimental value of  $D$  for PAA in the nematic phase.

That  $T_{1a}$  for PAA is slightly greater than  $T_{1a}$  for PAA-(CD<sub>3</sub>)<sub>2</sub> implies that methyl group reorientation does not contribute significantly to intra-

molecular phenyl proton relaxation. When the methyl-phenyl interaction is negligible the intramolecular spin-lattice relaxation can be separated<sup>13</sup> into a contribution from the methyl protons,  $T_{1a}^M$ , and the phenyl protons,  $T_{1a}^P$ :

$$T_{1a}^{-1} = \frac{3}{7} (T_{1a}^M)^{-1} + \frac{4}{7} (T_{1a}^P)^{-1}. \quad (4)$$

One can use this to estimate  $T_{1a}^M$  and the correlation time for methyl group reorientation. Using for  $T_{1a}^P$  the value of  $T_{1a}$  determined for PAA-(CD<sub>3</sub>)<sub>2</sub>, Eq. (4) yields values of  $T_{1a}^M = 3.68 \pm 0.4 \text{ sec}$  for PAA in the nematic phase and  $5.36 \pm 0.4 \text{ sec}$  in the isotropic liquid at 136°C. These values of  $T_{1a}^M$  with Eq. (2) yield effective correlation times for the methyl group reorientation,  $\tau_{\text{eff}}(120^\circ) = 2.0 \times 10^{-10} \text{ sec}$ ,  $\tau_{\text{eff}}(136^\circ) = 1.37 \times 10^{-10} \text{ sec}$ , which are significantly shorter than those determined for reorientation of the phenyl group assuming the latter corresponds to the reorientational correlation time of the whole molecule ( $\tau_c$ , Table I). In molecules such as toluene in the liquid state, methyl group reorientation was found to be mixed with the rapid reorientation of the molecule as a whole, with both ring and methyl motions characterized by a single effective rotational correlation time.<sup>18</sup> The additional degree of motional freedom in PAA (reorientation about the methoxy-oxygen-ring-carbon bond) may account for the order of magnitude difference between  $\tau_{\text{eff}}$  and  $\tau_c$ .

In the nematic phase a comparison with PAA-(CD<sub>3</sub>)<sub>2</sub> shows the presence of the protonated methyl group on PAA decreases  $T_{1r}$  by about a factor of 2 (Table I). The similar values of  $\tau_c$  at 120

TABLE II. PAA-(CD<sub>3</sub>)<sub>2</sub> rotational and translational correlation times.

Temperature	$\tau_c$ (10 <sup>9</sup> sec)	$\tau_t$ (10 <sup>9</sup> sec)
120° (nematic)	4.03 ± 0.1	1.03 ± 0.1
136° (isotropic)	4.93 ± 0.1	0.34 ± 0.04

and 136°C may well reflect a high degree of similarity in the molecular motion and microscopic "structure" between the nematic phase and the isotropic liquid just above the clearing point. The correlation time for translational diffusion does decrease at the nematic-isotropic transition approaching a value comparable to that found in ordinary liquids.

In the nematic phase,  $\tau_c$  and  $\tau_t$  differ by only a factor of 4, whereas in the isotropic phase they differ by a factor of about 15. This fact suggests that rotational and translational motions may be more strongly coupled (i.e., PAA molecules execute one twisting or tumbling motion while simultaneously executing a lateral or translational jump) in the nematic state than in the isotropic state.

It is also instructive to compare the rotational correlation time determined from NMR,  $\tau_c$ , with the molecular reorientation time obtained from dielectric measurements,  $\tau_d$ . For ordinary liquids  $\tau_d/\tau_c \cong 3$  if the molecule reorients itself by small jumps ( $<15^\circ$ ), whereas for jumps larger than about  $60^\circ$ ,  $\tau_d/\tau_c \cong 1$ .<sup>19</sup> The correlation time for reorientation of the long molecular axis of PAA in the nematic phase extracted from dielectric studies is  $\tau_d = 4.3 \times 10^{-9}$  sec.<sup>20</sup> The close agreement between  $\tau_d$  and  $\tau_c$  reported here implies that molecular rotational reorientation occurs by large jumps in the nematic phase. In this comparison of  $\tau_d$  and  $\tau_c$  we have neglected the experimentally observed frequency dependence of  $T_1$  attributed to thermal oscillations of the local nematic axis. This additional mechanism of relaxation, thought to affect predominantly intramolecular relaxation, would result in frequency-dependent values of  $\tau_c$ . However, since for PAA  $T_1^{-1}(60 \text{ MHz})/T_1^{-1}(10 \text{ MHz}) = 0.7$ ,<sup>6</sup> one would expect at most a 30% change in  $\tau_c$  over this frequency range. Hence the general conclusions drawn about the reorientational jump size would appear to remain valid. It would of course be helpful to study the frequency dependence of  $T_1$  in isotopically dilute samples to determine unequivocally whether or not the frequency depen-

dent mechanism has intermolecular and/or intramolecular origins.

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