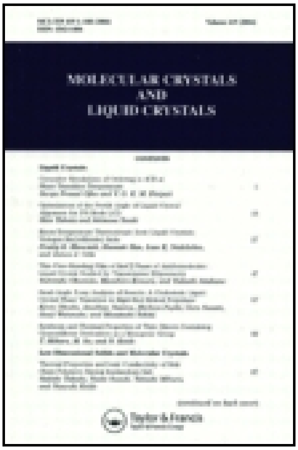

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E. T. Samulski [a] [b] , C. R. Dybowski [a] & Chas G. Wade [a]

[a] Department of Chemistry, University of Texas, Austin, Texas, 78712
[b] Department of Chemistry, University of Connecticut, Storrs, Connecticut

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Intermolecular and Intramolecular Contributions to Proton Relaxation in Liquid Crystals. II†‡

E. T. SAMULSKI,§ C. R. DYBOWSKI|| and CHAS. G. WADE

Department of Chemistry
University of Texas
Austin, Texas 78712

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Abstract—The relative importance of intermolecular (T_{1r}) and intramolecular (T_{1a}) contributions to nuclear spin relaxation in liquid crystals is discussed with particular emphasis on *p*-azoxyanisole (PAA). Previously published data on T_{1r} and T_{1a} in PAA, obtained by isotopic dilution studies, are reinterpreted in view of recent advances. Derived correlation times for rotation and translation at 120 °C (nematic phase) and at 136 °C (isotropic phase) calculated for different mechanisms are compared.

1. Introduction

A major portion of the NMR relaxation studies in liquid crystals$^{(1-15)}$ has been devoted to understanding the unusual frequency and temperature dependence of the proton spin-lattice relaxation time, T_1. This work has focused on three contributions to T_1, all of which modulate nuclear dipolar interactions: " molecular tumbling ", molecular diffusion and collective mode fluctuations. The first two effects, common to all fluids, are intramolecular and intermolecular, respectively. The third mechanism, unique to liquid crystals, arises from thermal fluctuations of the orientational order in the mesophase; as treated theoretically, it is an intramolecular

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§ Robert A. Welch Foundation Postdoctoral Fellow, 1971–72. Present address: Department of Chemistry, University of Connecticut, Storrs, Connecticut.

|| Robert A. Welch Predoctoral Fellow.

contribution. The relative importance of these has not been completely determined for any compound although evidence exists$^{(15)}$ that the dominant contribution may be different for different liquid crystals.

In order to obtain a better estimate of the relative importance of the intermolecular (T_{1r}) and intramolecular (T_{1a}) contributions to T_1, we have studied relaxation in the nematic and isotropic phases of 4,4′-azoxydianisole (PAA) and in PAA$(CD_3)_2$ (the latter a molecule with CD_3 replacing the CH_3 groups in PAA) as a function of dilution in perdeutero PAA. Such techniques$^{(16)}$ yield T_{1r} and T_{1a}. The results and techniques were published previously$^{(11)}$; it should be noted, however, that a calculation error resulted in values for rotational correlation times, τ_c, given in Table 1B of Ref. 11 which were too large by a factor of $(2\pi)^2$ and some interpretations presented in that paper must be changed accordingly. The present paper reinterprets those results and incorporates recent findings of other investigators, especially those presented at the Fourth International Liquid Crystal Conference (1972).

2. Results

In Table 1A are presented the values of T_{1a} and T_{1r} obtained$^{(11)}$ at 30 MHz and corrected for the deuteron–proton interaction.$^{(16)}$ The nematic range of all samples was approximately 118–135 °C.

To derive the correlation times from the data in Table 1A, the PAA$(CD_3)_2$ data are particularly useful as the proton interaction is largely that of dipole pairs, the essence of all theoretical models.

We have used two methods to estimate the translational correlation time, τ_t; both ultimately use Eq. (1):

$$\tau_t = \sigma^2/(2D) \qquad (1)$$

where σ is the molecular diameter and D is the self diffusion coefficient. Harmon and Muller$^{(17)}$ have derived a frequency dependent expression for T_{1r} in terms of D. Assuming T_{1r} is completely diffusion controlled, we can calculate D from this relationship. In Eq. (31) of Ref. 17, the following constants were used: σ is assumed to be 6 Å, and $\langle r^2 \rangle/\sigma^2 = 0.7$ where $\langle r^2 \rangle$ is the mean squared flight distance. This procedure yields the values labelled " calc.

D" in Table 1B. Alternately we can estimate τ_t by using Eq. (1) with the experimental value of D(18); these values are presented as "exp. D". It should be noted that both evaluations neglect the effects of rotational molecular motion and "wagging" end chain interactions(15) on the intermolecular rate. These effects are presumably of less importance for PAA$(CD_3)_2$ than for liquid crystal molecules with more protons and/or longer end chains.(15) Both evaluations assume an isotropic fluid.

TABLE 1

A. Spin-Lattice Relaxation Times[a]

Compound	Temperature	T_{1a}(sec)	T_{1r}(sec)
PAA	120 ° (nematic)	2.98 ± 0.10	3.72 ± 0.30
	136 ° (isotropic)	2.87 ± 0.15	2.18 ± 0.10
PAA-$(CD_3)_2$	120 ° (nematic)	2.60 ± 0.10	6.29 ± 0.30
	136 ° (isotropic)	2.13 ± 0.10	2.08 ± 0.10

B. PAA-$(CD_3)_2$ Rotational and Translational Correlation Times

Temperature	$\tau_c \times 10^{10}$ (sec)	$\tau_t \times 10^{10}$ (sec) Calc. D	$\tau_t \times 10^{10}$ (sec) Exp. D
120 ° (nematic)	1.02 ± 0.1	10.3 ± 1.0	5.45
136 ° (isotropic)	1.25 ± 0.1	3.4 ± 0.4	4.60

[a] Ref. 11.

Calculation of the correlation time (or times) for T_{1a} presents difficulties. Two approaches may be used. In Ref. 11, we assumed this could be approximated by the well-known formula(19) for the modulation of dipolar interactions of protons on a sphere tumbling in an (isotropic) fluid:

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

where γ is the magnetogyric ratio and $r_{ij} = 2.47$ Å. Equation (2) was used to obtain τ_c in Table 1B. This was not done on the assumption that the molecular tumbling contribution was dominant for T_{1a}, but for a variety of other reasons: Eq. (3), the correlation time for collective modes, has practical difficulties associated with its evaluation; various other estimates of the correlation time (see below) indicate that they are not greatly different from ordinary liquids. Thus, application of Eq. (2) is done under the assumption that it is presently the best approximation to the molecular motion of PAA$(CD_3)_2$; one assumes the actual motion has both " tumbling " and collective mode effects. For the collective mode mechanism, τ_c has the form(1,7)

$$\tau_c = \frac{3S^2kT}{2\sqrt{2}\pi K(K\eta^{-1}+D)^{1/2}\omega^{1/2}} \tag{3}$$

where S is the order parameter, K is an " average " Frank elastic constant, η is the viscosity, D the diffusion, and ω is the frequency (radians). One can estimate τ_c from this by using $S = 0.73$, $D = 3.2 \times 10^{-6}$ cm²/sec,(23) and $\omega = 2\pi \times 30$ MHz. The definition of η(13) and the variety of Frank constants(1) impose difficulties, but we use $\eta = 2.5 \times 10^{-2}$ dyne sec/cm²(23) and $K = 5.64 \times 10^{-7}$ dyne (an average value). This gives $\tau_c^{\text{thermal fluctuations}} \approx 2.5 \times 10^{-10}$ sec at 120 °C which is only a factor of 2 larger than that calculated using Eq. (2).

3. Discussion

The data in Table 1A clearly show that both intramolecular and intermolecular mechanisms make substantial contributions to the spin-lattice relaxation rate in PAA. The experimentally derived value of T_{1r} for PAA in the nematic phase is in good agreement with an earlier value(4) (3.57 sec) obtained for the contribution of translational diffusion to spin-lattice relaxation by an extrapolation of a $1/T_1$ vs. $\omega^{-1/2}$ plot to infinite Larmor frequency, and with a previous estimate of T_{1r}(12) (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$(CD_3)_2$ implies that methyl group reorientation does not contribute significantly to *intramolecular* phenyl proton relaxation. When the methyl–phenyl interaction is negligible the intramolecular spin-lattice relaxation can be separated(14) into a contribution from the methyl protons, T_{1a}^{M}, and the phenyl protons, T_{1a}^{P}.

$$T_{1a}^{-1} = (3/7)(T_{1a}^{M})^{-1} + (4/7)(T_{1a}^{P})^{-1} \tag{4}$$

One can use this equation 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$(CD_3)_2$, Eq. (4) yields values of $T_{1a}^{M} = 3.68 \pm 0.4$ sec for PAA in the nematic phase and 5.36 ± 0.4 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, $\tau_{\text{eff}} = 5.1 \times 10^{-12}$ sec (120 °C); $\tau_{\text{eff}} = 3.5 \times 10^{-12}$ sec (136 °C), which are significantly shorter than those determined for reorientation of the phenyl group protons, assuming the latter corresponds to the reorientational correlation time of the whole molecule (τ_C, Table 1B). 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.(21) 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 τ_{eff} and τ_C.

In the nematic phase, a comparison with PAA$(CD_3)_2$ shows the presence of the protonated methyl group on PAA decreases T_{1r} by about a factor of two (Table 1A). This change emphasizes the fact that the interaction of chain protons with phenyl protons is predominantly *intermolecular*. Doane and co-workers(15) have emphasized that this may be due in part to what they term end chain " wagging " effects, that is, internal motions of the end chain about the mean orientation of the carbon structure. This motion has the effect of modulating the dipolar interactions between spins on two adjacent molecules and could yield an intermolecular contribution even when the molecular centers of mass were fixed. Concurrent with this effect is the more conventional molecular diffusion process, which causes modulation of the same intermolecular interaction. Thus, the actual intermolecular end chain–phenyl process is rather complex, probably being characterized by a composite correlation time: when diffusion is slow, the correlation time for the end chain internal motion dominates, but as diffusion increases, it may also contribute. The theory of the end chain reorientation intermolecular contribution has not been derived, so an exact quantitative separation is not possible. It is known(15,22) that the presence of long end chains on the homologs of PAA tends to decrease T_1 (the overall relaxation time), the value reaching a lower plateau of about 0.1 sec for the 5 and 7 carbon homologs.

It should be emphasized that the frequency dependence of T_1^{-1} may arise from intramolecular (Eq. 3) or intermolecular (diffusion) effects; the former gives an $\omega^{-1/2}$ frequency term, the latter an $\omega^{+1/2}$ dependence. Both have been observed for different liquid crystals⁽¹⁵⁾: PAA exhibits $\omega^{-1/2}$ and MBBA exhibits $\omega^{+1/2}$. Thus in principle one can separate the two effects, the wagging contribution, of course, may give a different dependence and tend to obscure the results. It is interesting to note that the size of D seems to determine whether the intermolecular or intramolecular mechanism is observed. For the few compounds where K and η are known, $K/\eta \sim 10^{-5}$ cm^2/sec. Thus from Eq. 3, D has little effect on the intramolecular term until $D \lesssim 10^{-5}$. On the other hand, as D *decreases*, the diffusion contribution to T_1 is favored. For molecules of this size, a D of 10^{-7} cm^2/sec is necessary for easily observed intermolecular effects. For PAA, $D \approx 3.2 \times 10^{-6}$ cm^2/sec (120 °C) which is in the middle of the above range.

The fact that both Eqs. 2 and 3 yield similar correlation times at 120 °C may be fortuitous given the approximations present in both cases. No simple means of distinguishing between the two exists although frequency dependence studies might be of value. The similar values of τ_c at 120 °C and 136 °C may well reflect a high degree of similarity in the molecular motion and microscopic " structure " in the nematic phase and in the liquid just above the clearing point. It is known⁽⁶⁾ that some order persists for a few degrees above the clearing point. A firm conclusion on possible differences in translational motion at 120 °C and 136 °C is not possible; there is some evidence from the τ_t data that translation increases slightly but one would expect this as T increases.

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