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R. T. Thompson [a] , D. W. Kydon [b c] , D. D. Lasic [b d] & H. Peemoeller [b]

[a] Department of Nuclear Medicine, Victoria Hospital, London, Ontario, Canada, N6A 4G5

[b] Guelph-Waterloo Program for Graduate Work in Physics, Waterloo Campus, University of Waterloo, Waterloo, Ontario, Canada, N2L 3G1

[c] Physics Department, University of Winnipeg, Winnipeg, Manitoba, Canada, R3B 2E9

[d] Liposome Technology, Inc., 1050 Hamilton Court, Menlo Park, California, 94025

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R. T. THOMPSON

Department of Nuclear Medicine, Victoria Hospital, London, Ontario, Canada N6A 4G5

and

D. W. KYDON,† D. D. LASIC‡ and H. PEEMOELLER

Guelph-Waterloo Program for Graduate Work in Physics, Waterloo Campus, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1

The homologues of the *p*-alkoxybenzoic acid liquid crystal series with eight, nine and fifteen CH_2 groups in their tail sections were studied by NMR in solid and liquid crystalline phases. The proton relaxation rates T_1^{-1}, T_{1X}^{-1} and T_{1D}^{-1} were measured and compared with the relaxation rates of the homologues of the same liquid crystal series with 3 to 10 carbon atoms in the alkyl tail. The analysis of the origin of proton spin relaxation is based on the assumption that, approximately, all homologues have the same order director fluctuation rate. This rate is determined experimentally for PDBA (10 CH_2 groups in tail) from T_1 dispersion and assumed equal in all other homologues. The derived molecular diffusion relaxation rate increases with increasing mass of the molecules and when temperature is lowered. This rate also displays small oscillations with number of carbon atoms in the alkyl tail similar to the even-odd alternation of the melting temperature.

INTRODUCTION

Molecules of para-alkoxybenzoic acid form nematic liquid crystalline phases if the number (n) of carbons in the alkyl chains is larger than three.[1] For $n > 6$, this homologous series has a smectic phase also.[1] A weak odd–even effect of transition temperatures [solid–smectic, smectic–nematic, and, nematic–isotropic] was observed in the interval $6 \leq n \leq 10$[2].

This homologous liquid crystalline system, which is composed of dimers rather than monomers has several interesting properties regarding its structure and dynamics. Detailed x-ray structural analyses have been published.[3] Several members of this homogolous series have been studied by NMR relaxation.[4–7] Ultrasound absorption[8,9] and dielectric loss[10] have been reported. In addition, IR,[11,12] R[1,12]

†Permanent address: Physics Department, University of Winnipeg, Winnipeg, Manitoba, Canada R3B 2E9.

‡Present address: Liposome Technology, Inc., 1050 Hamilton Court, Menlo Park, California 94025.

and DSC[11,12,13] measurements in crystalline and liquid crystalline states have been performed.

In an earlier study of the *p*-benzoic acid [BA] nematogen series, measurements of spin-lattice relaxation times were reported in both the solid phase[6] and in the nematic phase.[7] Nematogens having two to seven CH_2 groups in their molecular tails were studied. Here we report on NMR results on the liquid crystals *p*-nonyloxybenzoic acid (PNBA) and *p*-decyloxybenzoic acid (PDBA), which have eight and nine CH_2 groups in their tail sections, respectively. Both the solid and nematic phase are investigated. In addition, NMR results in the liquid crystalline phase of *p*-hexyldecyloxybenzoic acid liquid crystal (PHBA), with 15 CH_2 groups in its tail section, are presented.

The relaxation time of the proton Zeeman energy at high fields, T_1, and in the rotating frame, T_{1X}, as well as that of the proton dipolar energy, T_{1D}, are related among themselves and compared with the relaxation rates of the shorter homologues of the BA nematogen series.

The mechanics of the initial analysis[7] involved solving rate equations of T_1, T_{1X} and T_{1D} for the order director fluctuation relaxation rate R_{ODF} and a rate R_Z due to essentially white processes. Built into these equations was the assumption that in these materials, only the protons on benzene rings are relaxed by the order director fluctuations. As a consequence, the contribution to the observed rate from such fluctuations was introduced as $f_i R_{ODF}$ where f_i is a weighting factor equal to "a", the benzene protons spin weight for $i = 1$ or X, and, equal to "c", the benzene proton dipolar weight for $i = D$. This resulted in consistent solutions[7] for homologues with $n = 6$ to 10. For homologues $n = 3$ to 5, a very slow relaxation rate R_s had to be added to the T_{1D} rate equation. This slow rate was also estimated[7] from the experimentally determined difference Δ of $T_{1\rho}^{-1}$ (at r.f. field pulse amplitude $H_1 = 0$) and T_{1D}^{-1}. Although the solutions of the rate equations of T_1, T_{1X} and T_{1D} were of the right magnitude generally, several shortcomings are noted.[7] The most important are a) ($a R_{ODF}$) increases too rapidly with molecular mass (see Table I) and b) R_Z, which is to a large extent the molecular diffusion rate, has a temperature dependence opposite to that expected.

In this report, instead of the "shared" rate ($a R_{ODF}$), an effective rate R_{ODF}^{eff}, determined directly from T_1 dispersion results, was utilized. This more direct determination of the order director fluctuation rate has made possible the simplification of the rate equations. It is found that the above mentioned shortcomings are absent.

EXPERIMENT AND RESULTS

The *p*-alkyloxybenzoic acid liquid crystals PNBA, PDBA and PHBA are dimers (the general formula is shown in Figure 4 of Reference 7). The pure materials were obtained from Frinton Laboratories.

The temperature dependences of the relaxation times T_1 and T_{1X} were measured with a modified CP-2 Spin-Lock spectrometer and that of T_{1D} was measured with a Bruker SXP spectrometer. The T_1 dispersion was also measured with the SXP

TABLE I

Summary of Spin Thermometric Data

Compound	T (°C)	T_1^{-1} (s^{-1})	T_{1X}^{-1} High H_1 (s^{-1})	T_{1D}^{-1} (s^{-1})	T_{1X}^{-1} Low H_1 (s^{-1})	$T_{1\rho}^{-1}(0)$ (s^{-1})	Δ[a] (s^{-1})	H_L' (G)	A[b] Low H_1 (s^{-1} G^2)
PNBA									
smectic 92–101°C	120	1.4 ± 0.1	2.9 ± 0.2	6.0 ± 0.8	2.8 ± 0.3	5.5 ± 0.6		0.9 ± 0.1	—
nematic 101–143°C	140	1.2 ± 0.1	3.6 ± 0.2	5.9 ± 0.5	3.5 ± 0.3	5.8 ± 0.6		0.9 ± 0.1	—
PDBA	130	2.0 ± 0.1	4.2 ± 0.3	9.5 ± 0.9	4.3 ± 0.5	12.0 ± 2.0	2.5	0.8 ± 0.1	1.6
smectic 93–121°C									
nematic 121–151°C									
PHBA									
smectic 100–131°C	100	2.6 ± 0.2	9.1 ± 0.5	18.5 ± 1.5	9.0 ± 0.9	18.8 ± 1.5	0.3	1.0 ± 0.1	0.3
nematic 131–133°C	110	2.0 ± 0.1	6.5 ± 0.4	13.7 ± 0.9	6.3 ± 0.6	13.8 ± 1.0	0.1	1.0 ± 0.1	0.1
	120	1.7 ± 0.1	5.0 ± 0.3	10.9 ± 0.9	5.0 ± 0.5	11.3 ± 1.0	0.4	1.0 ± 0.1	0.4
	130	1.5 ± 0.1	3.7 ± 0.3	7.7 ± 0.7	3.5 ± 0.4	8.2 ± 0.8	0.5	1.0 ± 0.1	0.5

[a] $\Delta = T_{1\rho}^{-1}(0) - T_{1D}^{-1}$.

[b] The factor A is defined[7] through $T_{1\rho}^{-1}(0) = T_{1D}^{-1} - A\,H_L'^{-2}$ where H_L' is the local field in the rotating frame.

spectrometer. T_1 was obtained using a 90–90 pulse sequence, T_{1X} with the spin-locking pulse sequence, and T_{1D} with the Jeener-Broekaert sequence.

The temperature dependences of the proton T_1 and T_{1X} (H_1 = 6 G) in the solid phase at 33.8 MHz are shown in Figure 1(a) and (b) for PNBA and PDBA, respectively. The temperature dependences of T_1, T_{1X}, and T_{1D} in the nematic and smectic phases are presented in Figures 2, 3, and 4 for PNBA, PDBA, and PHBA, respectively. At a few selected temperatures the H_1 dispersion of T_{1X} at high H_1 fields and of $T_{1\rho}$ at lower H_1 fields were measured and analyzed utilizing the approach given in Reference 7. The results are summarized in Table I.

Figure 5 gives T_1 of PDBA plotted as a function of $\nu^{-1/2}$, where ν is the frequency in the range 10 to 60 MHz. The accuracy of each T_1 determination is ±5%. In addition, a small deviation is possible due to different thermal history of the sample. At the same temperature and frequency, we noted differences in T_1 of the order 10%. The reported results were obtained on a liquid crystal in its first heating cycle.

The experimental T_1 values are fitted to $T_1^{-1} = B + A\,\nu^{-1/2} + C\,\nu^{-2}$ where $A\nu^{-1/2}$ is the contribution due to order director fluctuations, $C\,\nu^{-2}$ the contribution due to diffusion and B is a white relaxation rate. (Solid line in Figure 5). The fit

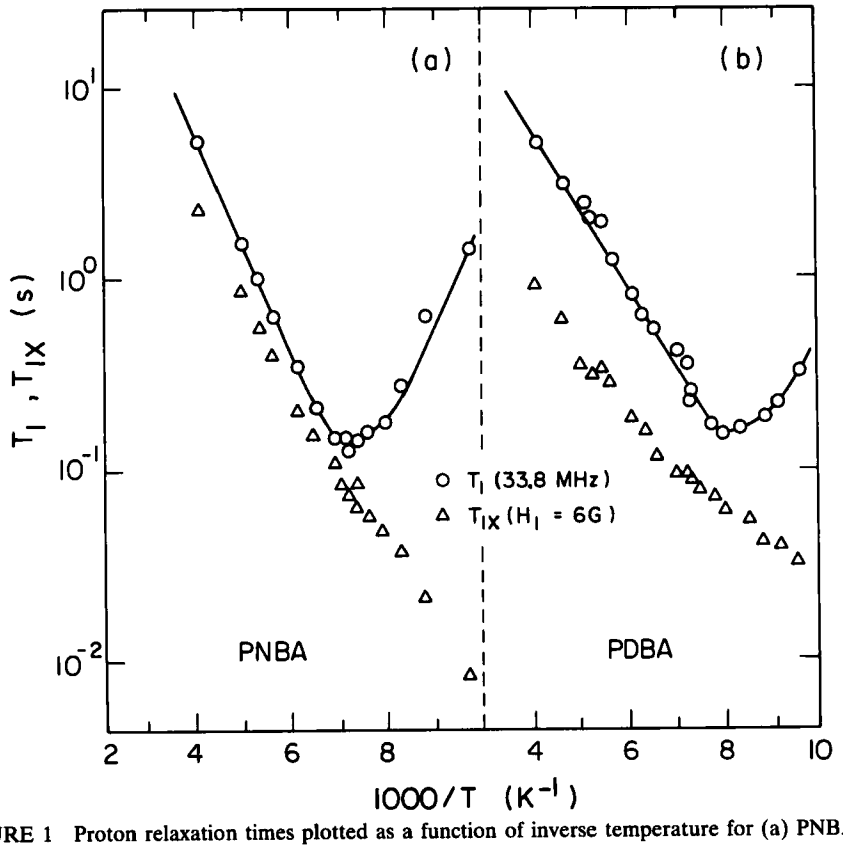

FIGURE 1 Proton relaxation times plotted as a function of inverse temperature for (a) PNBA and (b) PDBA.

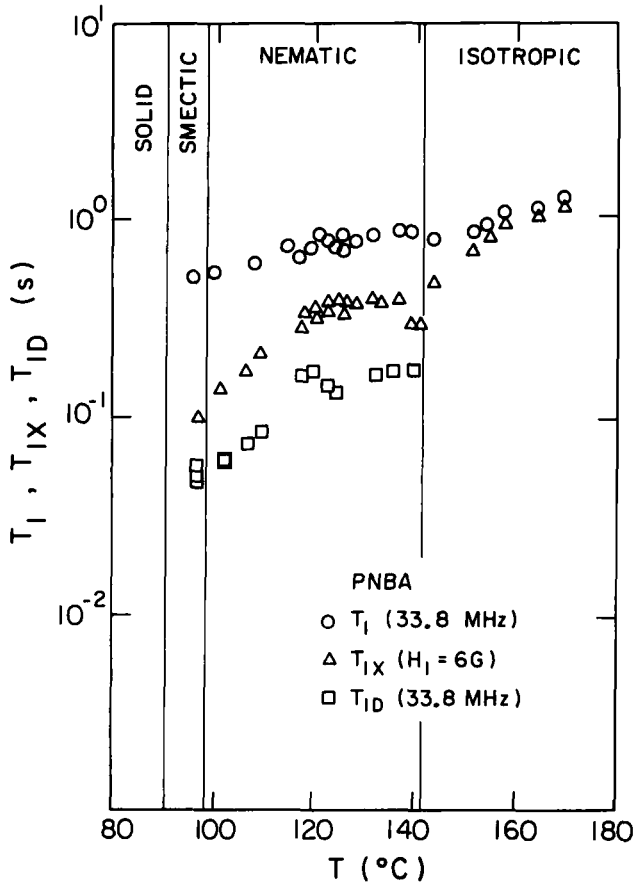

FIGURE 2 Proton relaxation times versus temperature in PNBA (*n*, the number of carbon atoms in the alkyl chain equals 9).

is good. For comparison the dispersion was also analyzed as $T_1^{-1} = B + A\,\nu^{-1/2}$. This fit was found to be reasonable also. It is important to note that the spin thermometric analysis was made at 33.8 MHz, where the difference between the two fits is quite small, see Figure 5 and Table II.

DISCUSSION

Solid Phase

The apparent activation energy E_a for the CH_3-group C_3 reorientation, which is roughly a measure for the hindering of the molecular tails, is similar in all BA homologues. It varies between (2.9 ± 0.3) kcal/mole (n = 3) and (1.9 ± 0.2) kcal/mole (n = 10) [Reference 6 and the present Figure 1]. The activation energy for the slow reorientation of each molecule around its long axis, which contributes

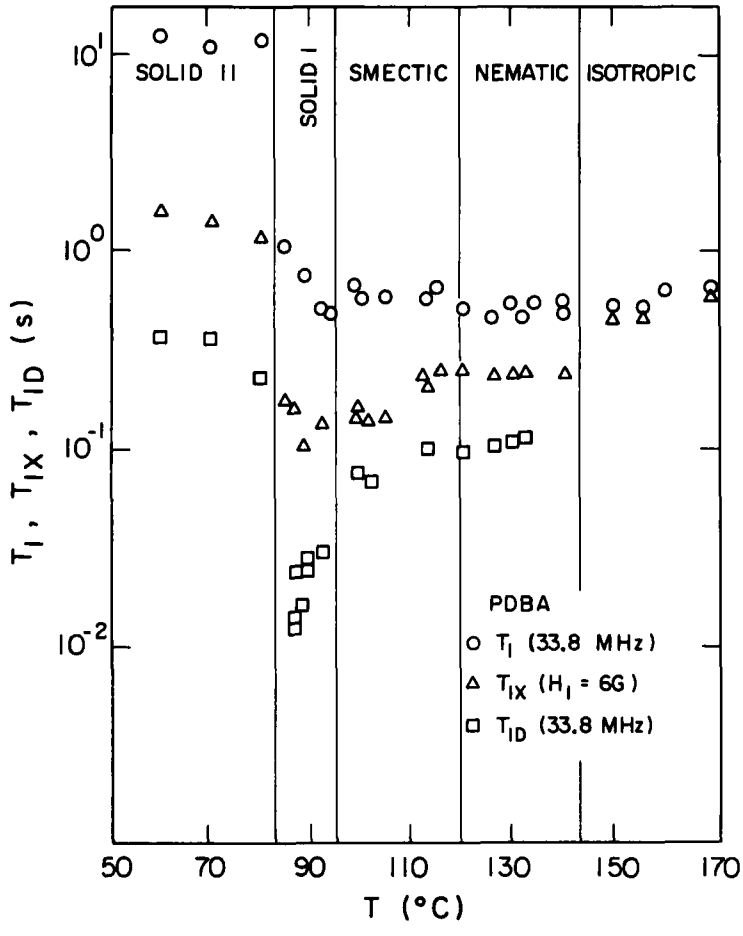

FIGURE 3 Proton relaxation times versus temperature in PDBA (n = 10).

significantly to the relaxation in the rotating frame, is also systematically decreasing: from (4.5 ± 1.0) kcal/mole (n = 5) to (1.8 ± 0.5) kcal/mole (n = 10) [Reference 6 and the present Figure 1].

By comparing Figure 1(a) and 1(b) with the temperature dependence of T_1 and $T_{1\rho}$ of other BA nematics in Reference 6 it is concluded that the two materials, although structurally similar, differ significantly in both of the above mentioned reorientations. In PNBA and PDBA the apparent E_a's for the C_3 reorientation of the CH_3 group are (2.6 ± 0.2) and (1.9 ± 0.2) kcal/mole, respectively. Using the Arrhenius relation $\tau = \tau_0 \exp(E_a/kT)$ the corresponding τ_o's are 1.5×10^{-13} s and 1.1×10^{-12} s.

We can calculate T_1 (C_3 min) assuming a spin temperature and using the BPP expression[14] for $1/T_1$ modified for this case where rapid rotation proceeds around the 3-fold axis of symmetry of the CH_3 group.

This way it is found that the C_3 reorientation of the CH_3 group generates, at 33.8 MHz, a T_1 (C_3 min) in PNBA and PDBA of 131 and 144 ms, respectively.

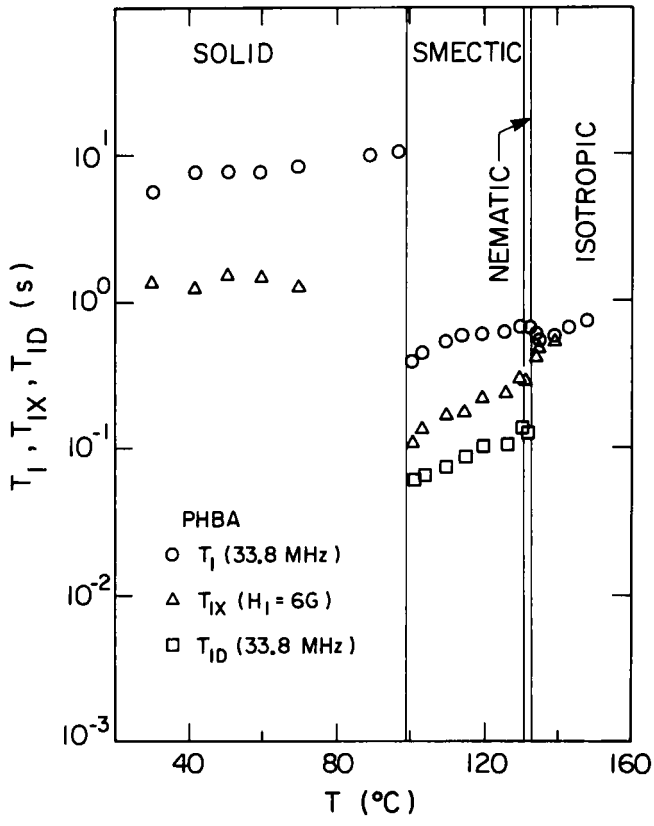

FIGURE 4 Proton relaxation times versus temperature in PHBA (n = 16).

The corresponding experimental values are 140 and 160 ms, respectively. The corresponding values agree sufficiently well to exclude the existence of nonequivalent CH_3 groups in these two materials. The slightly longer T_1 (min) may indicate that the C_3 axis itself is oscillating with a small amplitude, thus slightly reducing the dipolar interaction which causes T_1 (C_3 min) to increase.

The effect of molecular reorientation around its long axis on T_{1X} has been discussed in Reference 6. In PDBA this reorientation generates a T_{1X} (min) in the region of inverse temperature (1000/T) = 7 with an approximate value of 140 ms. The same process in PNBA is seen to occur at about the same temperature and strength, but is less apparent in the temperature region studied because of the relaxation by C_3 reorientations. Namely, in PNBA the C_3 reorientation of the CH_3 group is considerably slower and its effect is superimposed on the relaxation rate caused by the long axis reorientation. The apparent E_a for the reorientation around the long axis is (2.2 ± 0.5) kcal/mole in PNBA and (1.8 ± 0.5) kcal/mole in PDBA.

Nematic Phase

The relaxation times-temperature plots Figures 2, 3 and 4, for PNBA, PDBA and PHBA, respectively, display weak temperature dependences. All BA homologues

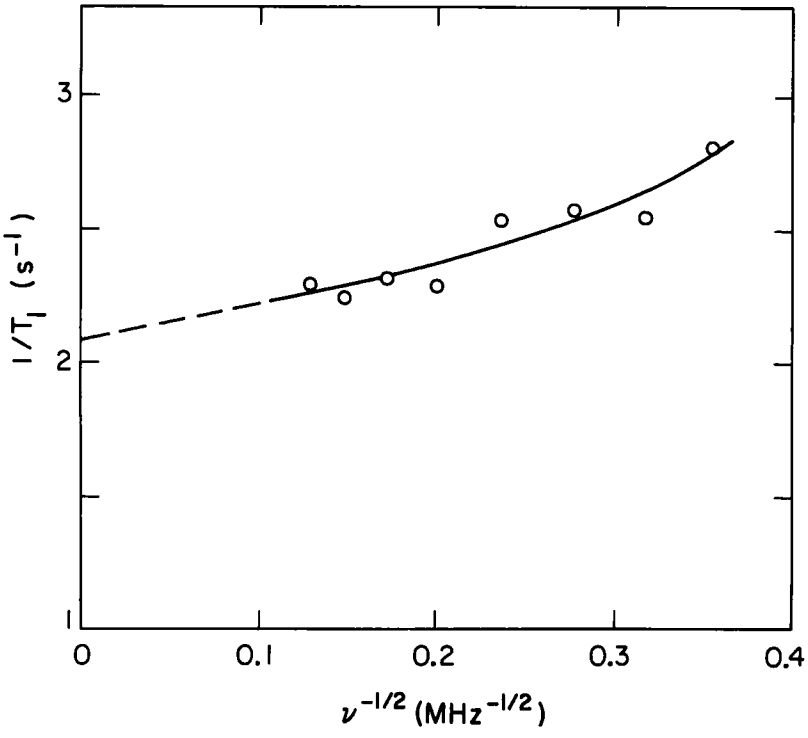

FIGURE 5 Proton spin-lattice relaxation rate versus Larmor frequency to the power (− 1/2) of PDBA (n = 10) at 130°C.

have similar temperature dependences for T_1, almost independent of temperature, while T_{1X} and T_{1D} decrease at the lower temperature end. In PNBA (Figure 2) this decrease is quite pronounced. In PDBA (Figure 3), which has a narrow nematic temperature range, this decrease occurs in the smectic phase. PHBA, which has a much longer tail and is used for comparison only, shows a temperature dependence (Figure 4) very similar to the shorter homologues.

At a few selected temperatures the dispersion of T_ρ^{-1} was obtained. The results are summarized in Table I (which is set as in Reference 7).

Incorporation of the effective rate R_{ODF}^{eff} into the rate equations for T_1, T_{1X} and T_{1D} (Equations 7–9 of Reference 7) yields the following

$$T_1^{-1} = R_{ODF}^{eff} + R_z \tag{1}$$

$$T_{1X}^{-1} = 2.5\, R_{ODF}^{eff} + \delta R_x + R_z \tag{2}$$

$$T_{1D}^{-1} = 3\, R_{ODF}^{eff} + \delta R_D + 2R_z. \tag{3}$$

In these equations $R_{ODF}^{eff} = R_{ring} + R_{chain}$ is the effective ODF relaxation which should satisfy the ratios $T_1/T_{1X} = 5/2$ and $T_1/T_{1D} = 3$, Reference 15. It is realized also that the molecular tails are not ideally aligned and thus there will be some

TABLE II

T_1^{-1} dispersion of PDBA at 130°C.

3-parameter fit shown on Figure 5: $T_1^{-1} = B + A\,\nu^{-1/2} + C\,\nu^{-2}$
$T_1^{-1} = (2.07 \pm 0.19) + (1.36 \pm 0.56) \times 10^3\,\nu^{-1/2} + (1.41 \pm 0.85) \times 10^{13}\,\nu^{-2}$

ν (MHz)	B	$A\,\nu^{-1/2}$	$C\,\nu^{-2}$	$T_1^{-1}(s^{-1})$
8	2.07	0.48	0.22	2.77
10	2.07	0.43	0.14	2.64
13	2.07	0.38	0.08	2.53
18	2.07	0.32	0.04	2.37
25	2.07	0.26	0.02	2.35
33.8	2.07	0.23	0.01	2.32
45	2.07	0.20	0.01	2.28
60	2.07	0.18	0.00	2.25
∞	2.07	Nil	Nil	2.07

2-parameter fit: $T_1^{-1} = B + A\,\nu^{-1/2}$
$T_1^{-1} = (1.93 \pm 0.09) + (2.25 \pm 0.37) \times 10^3\,\nu^{-1/2}$

ν (MHz)	B	$A\,\nu^{-1/2}$	T^{-1} (s^{-1})
8	1.93	0.80	2.73
10	1.93	0.71	2.64
13	1.93	0.62	2.55
18	1.93	0.53	2.46
25	1.93	0.45	2.38
33.8	1.93	0.39	2.32
45	1.93	0.34	2.27
60	1.93	0.29	2.22
∞	1.93	Nil	1.93

additional ODF rate contributing. For example in T_{1X}^{-1} the effect of J (ω_1) should be noticed. The rate resulting from J (ω_1) is labeled δR_x. On the other hand, the dipolar energy may be sensitive to a slow molecular mode which is represented, together with the ODF deviations, as δR_D. In addition, recall that the "white" relaxation rate R_z is the total contribution of all molecular motions other than ODF. That this rate is essentially white in the laboratory frame is supported by the frequency dependence of T_1 of the homologue $n = 10$, Figure 5 and Table II.

At the frequency of 33.8 MHz (at which T_{1X} and T_{1D} were determined) the experimental order director fluctuation rate was determined in PDBA to be the average of $A\,\nu^{-1/2} = 0.23$ and $0.39\ s^{-1}$ (see Table II). For the purpose of the present discussion we take $R_{ODF}^{eff} = 0.3\ s^{-1}$ at 33.8 MHz. Using this value of R_{ODF}^{eff} and the experimentally determined rates T_1^{-1}, T_{1X}^{-1} and T_{1D}^{-1}, equations (1)–(3) were solved for R_Z, δR_x and δR_D for several BA homologues in the nematic phase. Results in the middle of the nematic phase are shown in Table III. For purposes of comparison, results of the analysis according to Equations (7)–(9) of Reference 7 are also shown in Table III for the same homologues.

For each homologue considered R_Z obtained from the above analysis decreases with increasing temperature with an apparent activation energy in the interval 7.3 to 9.1 kcal/mole. In addition R_Z, in the middle of the nematic phase, increases with mass of the molecule (Table III).

TABLE III

Proton relaxation rates of BA homologues in the middle of their nematic phase. For n = 6 to 16, T is 130°C, for n = 3, T = 147°C, fo
= 4, T = 153°C and for n = 5, T = 133°C. The symbols used are given in equations (1) to (3). The experimental accuracy is ±7%.

Homologue	n	Mol. Wt.	Experimental Rates			Analysis: Equations (7) to (9) of Reference 7		Analysis: Equations (1) to (3)							
			T_1^{-1}	T_{1x}^{-1}	T_{1D}^{-1}	$a\,R_{ODF}$	R_Z	R_{ODF}^{eff}	R_Z	$2.5\,R_{ODF}^{eff}$	δR_x	$3\,R_{ODF}^{eff}$	δR_D	$D_\perp^a(10^{-6}\ cm^2\ s^{-1})$	$(T_1^{-1}$
PBA	3	360	0.6	2.3	2.5	0.5	0.1	0.3	0.3	.75	1.3	0.9	1.0	4.6	0.1
BBA	4	388	0.6	1.4	2.5	0.5	0.1	0.3	0.3	.75	0.4	0.9	1.0	3.9	0.2
PeBA	5	408	1.0	1.7	2.7	0.6	0.4	0.3	0.7	.75	0.3	0.9	0.4	3.1	0.3
HexBA	6	444	1.0	2.1	4.2	0.8	0.2	0.3	0.7	.75	0.7	0.9	1.9	2.6	0.3
HepBA	7	472	1.3	2.5	5.0	0.8	0.5	0.3	1.0	.75	0.8	0.9	2.1	2.4	0.4
OBA	8	500	1.0	2.3	4.3	0.9	0.1	0.3	0.7	.75	0.9	0.9	2.0	2.4	0.4
NBA	9	528	1.4	2.9	6.0	1.1	0.3	0.3	1.1	.75	1.1	0.9	2.9		
DBA	10	556	2.3	4.2	9.5	1.7	0.6	0.3	2.0	.75	1.5	0.9	4.6		
HBA	16	724	1.5	3.7	7.7	—	—	0.3	1.2	.75	1.8	0.9	4.4		

[a] Estimated as discussed in text using D_{is} and activation energies given in Reference 19.

[b] Values of m needed in calculating $(T_1^{-1})_{trans}$ were determined using the known molecular structure of each liquid crystal and assumi
ensity of 1 gm/cm³. (For example alkyl-cyano-biphenyl liquid crystals in the nematic phase, for alkyl chains containing 5–9 carbons, l
ensities[20] within 4% of 1 gm/cm³.

In part, the rate R_Z is due to translational diffusion of the liquid crystal molecules. The resulting intermolecular longitudinal spin relaxation in the nematic phase has been investigated theoretically and is given by[16]

$$(T_1^{-1})_{trans} = \frac{9}{8}\gamma^4 h^2 \frac{m}{4dD_\perp} Q\left(\omega\tau, \frac{\langle r_\perp^2\rangle}{d^2}, \frac{D_\parallel}{D_\perp}\right) \quad (4)$$

where m is the number of spins per unit volume and the definitions of remaining parameters are as in Reference 16. This rate can be estimated as discussed below.

For a reasonable set of parameters, if we let $\tau = 10^{-10}$ s, Q changes by only ~10% if we let the Larmor frequency vary from 0 to 30 MHz.[17] We set $\omega\tau = 0$. For a similar set of parameters Q changes by no more than ~35% if $\langle r_\perp^2\rangle/d^2$ is varied from 1 to 0.01 and a value of 1 is assumed.[17] The ratio $D_\parallel/D_\perp$ is not expected to differ appreciably from one liquid crystal in the nematic phase to another and a representative ratio 1.5 is justified.[17,18] With these parameters Q = 5.3.[17] The diffusion constant $D_\perp$ can be estimated by projecting D_{is}, the diffusion constant in the isotropic phase, into the nematic phase using Arrhenius activation law and setting $D_\perp = D_{is}$.

D_{is} at the clearing point and activation energies for diffusion in the isotropic phase have been measured in a number of *p*-alkoxybenzoic acid liquid crystals.[19] Using values of $D_\perp$ estimated in this way (Table III) as well as parameters discussed above, we calculate $(T_1^{-1})_{trans}$ for $n = 3$ to 8 (Table III). In these calculations we have used $d = 4.3$ Å, which is the distance between two hydrogen atoms in the meta or ortho position on the benzene ring. Comparing the magnitudes and variations with mass of these calculated rates (last column of Table III) to R_Z (column 10 of Table III) suggests that the proton relaxation due to translational diffusion contributes significantly to R_Z. This is strongly supported by the fact that the apparent activation energies for R_Z (column 10 of Table III) are in the same range as those for diffusion in the isotropic phase (see Reference 19).

The rate δR_x decreases with increasing temperature. Its apparent activation of (13 ± 1) kcal/mole is essentially the same for $n = 6$, 7 and 8 homologues and less for $n = 16$ homologue (10.9 kcal/mole). The rate δR_D also decreases with increasing temperature. Its apparent activation energies for homologues $n = 6$, 7, 8 and 16 are within the interval (8.8 ± 1) to (9.9 ± 1) kcal/mole. The implication of these temperature dependences is that molecular diffusion is effective in δR_D while the rate δR_x is generated by a strongly temperature dependent mechanism.

The rate R_Z, in the subset $n = 6$ through $n = 9$, exhibits a small even–odd effect (column 10 of Table III). In liquid crystals, an even–odd effect has been observed in such parameters as the nematic–isotropic transition temperature,[1,21,22] the dielectric anisotropy,[22] the molecular optical anisotropy,[23] the nematic to isotropic transitional volume change,[20] alkyl chain carbon-13 chemical shifts[24] and alkyl chain deuteron quadrupolar splittings.[25] Theoretical treatments of the even–odd effect have also been presented.[2,26] This effect results from the alternation of the alkyl chain ordering[2] which is influenced by the presence of gauche isomers for homologues with $n > 5$.[23] Although, based on the present results, the above effect in R_Z cannot be pursued quantitatively at this time, its behavior with changing

n = 6 to 9 is qualitatively correct. It is known that homologues with even n exhibit more molecular order than those with odd n[2]. As a consequence the diffusive motion of the molecule with even n would be expected to proceed more rapidly than the molecule with odd n. Then, since R_Z is essentially a white rate, largely due to diffusion, means that the observed smaller R_Z for even n and larger R_Z for odd n (n = 6 to 9) (see Table III) are as expected.

Since the molecular shapes of the all-trans isomer and trans-gauche isomer are quite different, resulting in different degrees of molecular ordering in the nematic phase, it might be expected that each of the relaxation rates (Equations 1–3) should be affected by the trans-gauche alternation. Our present analysis precludes the observation of this effect in R_{ODF}^{eff}. Although a rather weak even–odd effect can be noticed in δR_D (n = 6 to 9), it is not pronounced in δR_D or δR_X because either these rates are insensitive to the trans-gauche alternation or the analysis (Equations 1–3) does not provide sufficient resolution. Additional information about the odd–even effect in proton relaxation could be obtained by making independent determinations of R_{ODF}^{eff} for other members of the homologous series under investigation.

CONCLUSION

The proton spin-lattice relaxation results in the *p*-alkoxybenzoic acids with n = 8 and 9 have been presented and analyzed using a thermometric approach. For comparison purposes, the results of similar analysis for homologues with n = 3 to 7 and n = 10 and 16 have also been included. The present analysis yields the correct dependence of the molecular diffusion rate on temperature and molecular mass. In addition, the same rate exhibits a trans-gauche alternation for n = 6 to 9. It is found that the sense of this alternation (smaller R_Z for even n) is in keeping with the conclusion that R_Z is a white relaxation rate.

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References

1. Von B. Eternberg, W. Pilz, P. Reich and H. D. Koswig, *Z. Phys. Chemie*, **264**, 499 (1983).
2. S. Marčelja, *J. Chem. Phys.*, **60**, 3599 (1974).
3. R. F. Bryan, P. Hartley, R. W. Miller and M.-S. Shen, *Mol. Cryst. Liq. Cryst.*, **62**, 281 (1980) and references therein.
4. B. Deloche and B. Cabane, *Mol. Cryst. Liq. Cryst.*, **19**, 25 (1972).
5. R. T. Thompson, Ph.D. Thesis, University of Waterloo (1975).
6. R. T. Thompson and M. M. Pintar, *J. Chem. Phys.*, **65**, 1787 (1976).
7. R. T. Thompson, D. W. Kydon and M. M. Pintar, *J. Chem. Phys.*, **67**, 5914 (1977).
8. A. P. Kapustin and N. T. Bykova, *Sov. Phys. Cryst.*, **13**, 281 (1968).
9. L. S. Chou and S. V. Letcher, *J. Physique*, Colloque C5, 587 (1981).
10. L. S. Chou and E. F. Carr, *Phys. Rev. A*, **7**, 1639 (1973).

11. M. Ikeda and T. Hatakeyama, *Mol. Cryst. Liq. Cryst.*, **39**, 109 (1977).
12. N. Kirov, M. P. Fontana, F. Cavatorta and H. Ratajczak, *Mol. Cryst. Liq. Cryst.*, **75**, 303 (1981).
13. T. Hatakeyama and M. Ikeda, *Mol. Cryst. Liq. Cryst.*, **45**, 275 (1978).
14. A. Abragam, The Principles of Nuclear Magnetism, Clarendon, Oxford, 1972, Chapter 8.
15. R. G. C. McElroy, R. T. Thompson and M. M. Pintar, *Phys. Rev. A*, **10**, 403 (1974).
16. S. Žumer and M. Vilfan, *Phys. Rev. A*, **17**, 424 (1978).
17. M. Vilfan, Private communication.
18. V. Breternitz and H. Kresse, *Phys. Lett.*, **54A**, 148 (1975).
19. L. A. Miljkovic, R. T. Thompson, M. M. Pintar, R. Blinc and I. Zupančič, *Chem. Phys. Lett.*, **38**, 15 (1976).
20. D. A. Dunmur and W. H. Miller, *J. Physique*, Colloque C3, 141 (1979).
21. W. H. de Jeu, J. van der Veen and W. J. A. Goossens, *Solid State Commun.*, **12**, 405 (1973) and references therein.
22. G. Nimtz, M. Schifferdecker, I. Shih and S. Mishra, *Solid State Commun.*, **29**, 287 (1979).
23. J. R. Lalanne, B. Lemaire, J. Rouch, C. Vaucamps and A. Proutiere, *J. Chem. Phys.*, **73**, 1927 (1980).
24. A. Pines, D. J. Ruben and S. Allison, *Phys. Rev. Lett.*, **33**, 1002 (1974).
25. B. Deloche, J. Charvolin, L. Liebert and L. Strzelecki, *J. Physique*, Colloque C1, 21 (1975).
26. D. A. Pink, *J. Chem. Phys.*, **63**, 2533 (1975).