

NMR investigations of molecular motions in *p-n*-hexyloxybenzylidene-*p'-n*-propylaniline

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Abstract. Proton spin-lattice relaxation times, T_1 , have been measured in the smectic phases, S_G^2 , S_G^1 and S_A , and in the nematic phase of HxBPA, in the temperature range, $220\text{ K} < T < 360\text{ K}$. In the S_G^1 and S_G^2 phases, T_1 has been measured at 15 and 40 MHz. The ($S_G^1 \rightarrow S_G^2$) and ($S_G^2 \rightarrow S_G^1$) transitions are clearly seen as discontinuities in T_1 . The former transition is seen to be due to possible freezing or change of hydrocarbon chain motions of the molecule. Our data in the S_G^1 phase have been fitted to a model in which anisotropic rotational diffusion of the end hydrocarbon chains as also that of the rigid part of the molecule are considered. In the nematic phase, at 351 K, the observed behaviour of T_1 , measured in the frequency range, 5 to 40 MHz, agrees well with the theoretical predictions of Ukleja *et al* and Freed, who take into account long range collective order fluctuations and local reorientations. Using these theories, the correlation time for short range reorientations has been calculated from our results to be 4.3×10^{-10} and 1.1×10^{-9} s respectively.

Keywords. Smectic crystals; molecular motions; NMR.

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1. Introduction

The compound, *p-n*-HexyloxyBenzylidene-*p'-n*-PropylAniline or HxBPA (figure 1), exhibits (Usha Deniz *et al* 1977a) two smectic crystalline and two liquid crystalline

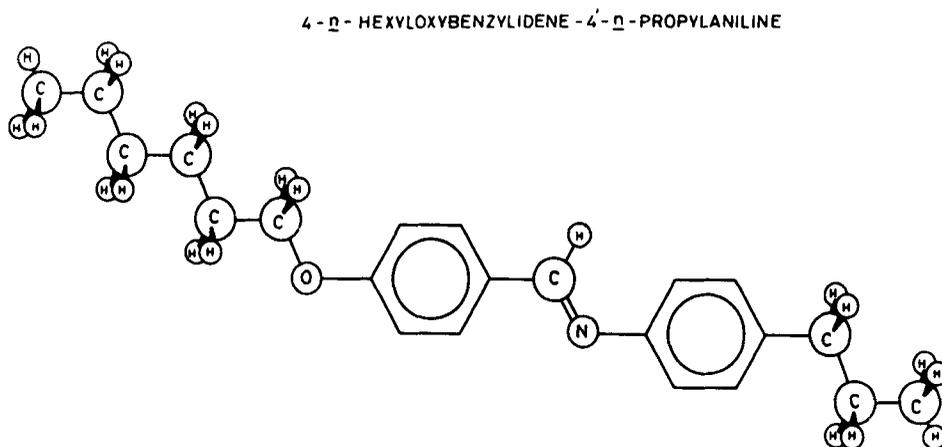
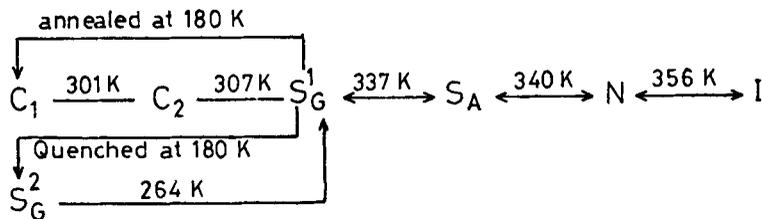


Figure 1. A model of the molecule, HxBPA.

phases, in the temperature range $180\text{ K} < T < 360\text{ K}$. Its scheme of transitions is as follows:



C: Crystal, S: Smectic, N: Nematic, I: Isotropic liquid. The earlier nomenclature used (Usha Deniz *et al* 1977a, b; Mehta 1980) for some of these phases is given below:

$$C_2 \equiv P_1; \quad S_G^{1*} \equiv S_H; \quad S_G^{2*} \equiv P_2, \quad S_m \text{ and } S_H.$$

The nature of the S_G^2 and C_2 phases was not known prior to 1978, hence the change of nomenclature. It has since been confirmed by X-ray diffraction (Mehta 1980; Usha Deniz and Mehta 1982), that the S_G^1 and S_G^2 phases have similar *c*-face centred monoclinic structures with the *b*-axis as the unique axis and the molecular long axis, \hat{n} , oriented along the *c*-axis. The molecules are packed in a pseudohexagonal manner in the smectic planes, whereas they have an almost ideal hexagonal packing in a plane perpendicular to their long axes. The lattice constant *a* increases, *b* decreases and *c* remains almost constant as the temperature is decreased in both the S_G^1 and S_G^2 phases (Usha Deniz and Mehta 1982), leading to a net decrease in the area per molecule in the smectic plane, as the sample is cooled from the S_G^1 to the S_G^2 phase. Since the intermolecular distance, *b*, perpendicular to \hat{n} is smaller in the S_G^2 phase than in the S_G^1 phase, the molecular motions in these two phases could be somewhat different. Raman scattering experiments (Usha Deniz *et al* 1977b; Mehta 1980) have shown that when one goes from the S_G^2 to the S_G^1 phase, the neighbourhood of the end hydrocarbon (hc) chains of the molecule changes significantly, whereas such a change does not occur in the environment of the central rigid portion of the molecules. This change is thought to be due to chain disorder. The Raman results, however, give no clue to the nature of this disorder, which can be either static or dynamic. Neutron quasi-elastic scattering experiments (Mehta 1980; Sinha *et al* 1973) carried out at 257K (S_G^2) and 300 K (S_G^1) with HxBPA, show the presence of a rotational diffusion motion in the S_G^1 phase, which is absent in the S_G^2 phase. Form factors for neutron elastic scattering indicate that the motion in the S_G^1 phase is most probably that of the end hydrocarbon chains. These results are inconclusive since the observed change in molecular motion could be due to a simple thermal effect and need not be connected with the phase change from S_G^2 to S_G^1 .

This paper describes proton spin-lattice relaxation measurements which have been done, mainly to study the changes occurring in the molecular motions of HxBPA at the $S_G^2 \rightleftharpoons S_G^1$ transitions. We have also investigated the contribution of the orientational order fluctuations and short range molecular reorientations to the proton spin-lattice relaxation rate in the nematic phase.

2. Experimental details

The proton spin-lattice relaxation times, T_1 have been measured using Model CPS-2, Spin-Lock Ltd. NMR Instrument (Spin-Lock Ltd., Port Credit, Ontario, Canada)

*The phase S_H is now called S_G (Demus *et al* (1980) *Mol. Cryst. Liq. Cryst. Lett.* **56** 311)

and a box car signal averager (Princeton Applied Research Corporation, Model 162). The temperature of the sample was stabilized by a home-built automatic temperature controller and could be maintained to within ± 0.3 K. The accuracy in the measurement of temperature is 1 K. The temperature range investigated is $223 \text{ K} < T < 358 \text{ K}$. T_1 was determined mostly at frequencies (ν) of 15 and 40 MHz either by the $\pi/2 - \tau - \pi/2$ method or progressive saturation recovery method. Both methods have been used in some measurements and yield identical results.

The temperature dependence of T_1 in S_G^1 and S_G^2 phases was determined both while heating and cooling the sample. To avoid the presence of the crystalline phase (C_1 or C_2) in the sample and to obtain it in a polycrystalline form in the S_G phase, the sample was heated to the isotropic liquid phase and quenched in liquid nitrogen, for the heating cycle. The sample was then placed in the NMR probe maintained at 223 K, before heating it to the desired temperature. For the cooling cycle, the sample was heated to the isotropic liquid phase and cooled rapidly to room temperature (RT) to obtain it in a polycrystalline form. It was then placed in the NMR probe and (a) heated to 315 K and cooled to the required temperature for measurements above 278 K and (b) cooled directly from RT for measurements below 278 K. Thermal cycling or cooling in the magnetic field from S_A , N or I phases resulted in a multidomain sample in the S_G phase from which data would have been hard to interpret. Hence the polycrystallinity of the sample was assured by the methods indicated above. In the other two phases the measurements were carried out only while heating.

3. Results and discussion

The temperature dependence of T_1 in all phases at 15 MHz is shown in figure 2 for the heating cycle. The notable features in this figure are the discontinuity in T_1 appearing at the $S_G^2 \rightarrow S_G^1$ transition and a broad minimum in the S_G^1 phase around 277 K. The limited T_1 data in the S_A phase do not permit any detailed analysis. The results obtained in the other three liquid crystalline phases are discussed in detail below.

3.1 S_G^1 and S_G^2 phases

Our results obtained at 15 MHz are shown in figure 3 for the heating and cooling cycles. The values of T_1 obtained in the heating run are in good agreement with those observed while cooling, except in the vicinity of the $S_G^2 \rightleftharpoons S_G^1$ transitions, where hysteresis is observed. The observed discontinuity in T_1 at 263 K for the heating run is clearly related to the $S_G^2 \rightarrow S_G^1$ transition observed in our DSC measurements (Usha Deniz *et al* 1977a). In the light of the results of Raman (Usha Deniz *et al* 1977b; Mehta 1980) and neutron scattering (Mehta 1980; Sinha *et al* 1973) studies, one expects that (a) the dominant contribution to T_1 in the S_G^1 phase for temperatures below 328 K, is most probably from the rotational diffusion motion of the hc chains of the molecule, and (b) the discontinuity in T_1 may be due to the freezing of this chain motion in the S_G^2 phase or an abrupt change in the nature of the chain motion. The decrease of T_1 for $T > 328$ K, might be brought about by the increased rotational or translational (or both) diffusion of the HxBPA molecule in this temperature range. Evidence for increased diffusion comes from X-ray diffraction patterns (Mehta 1980) of HxBPA which show that the polycrystalline HxBPA sample at 300 K, rapidly changes into one with rather large single crystal grains on heating it to about 320 K. This would

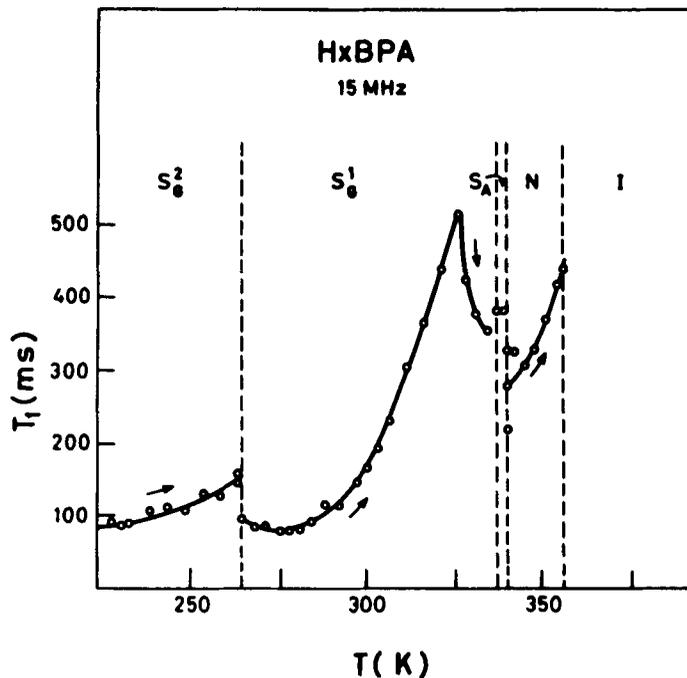


Figure 2. Temperature dependence of T_1 at 15 MHz. The lines are guides to the eye.

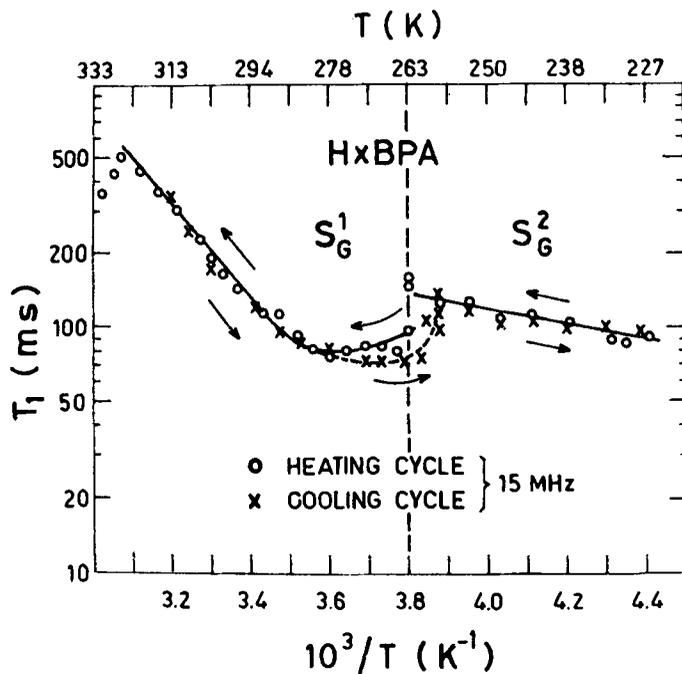


Figure 3. T_1 as a function of $10^3/T$ in the S_G^1 and S_G^2 phases for the heating and cooling cycles. The lines are guides to the eye.

only be possible if the translational and rotational diffusion motions were rapid for $T \geq 320$ K. In the cooling run, the temperature dependence of T_1 is smooth in the neighbourhood of the $S_G^2 \rightarrow S_G^1$ transition temperature, but changes rapidly at 257 K, indicating a change in the molecular (probably chain) motion at this temperature. In the S_G^1 phase, for $282 \text{ K} < T < 320 \text{ K}$, the T_1 values from both cycles are almost identical. The average activation energy, E_A , for this motion, obtained from our data in this temperature region, is $37.3 \pm 1.3 \text{ kJ/mol}$. The close agreement between T_1 values of the heating and cooling runs below 257 K, shows that in these runs, there is no difference in the molecular motions contributing to T_1 . This implies that while cooling, the entire sample gets converted into the S_G^2 phase at 257 K. Further, the abrupt change in the slope, dT_1/dT , at the $S_G^2 \rightleftharpoons S_G^1$ transition, both while heating and cooling, clearly indicates that at this transition there is a sudden change in the motion(s) contributing to the relaxation rate. It is interesting to note that the cooling transition was not observed in DSC, possibly because calorimetry is not sensitive to the change of molecular motions occurring at this point, in HxBPA.

The T_1 data at 15 and 40 MHz in the heating cycle is given in figure 4. As stated before, a well defined, though somewhat shallow, minimum is observed at 277 K for the 15 MHz data. If a molecular motion with a single correlation time, τ , is assumed to contribute to the relaxation rate, one obtains $\tau \approx 6 \times 10^{-8} \text{ s}$ (since $\omega\tau \sim 1$, where $\omega = 2\pi\nu$) at 277 K and the minimum in T_1 is expected to shift to 305 K for 40 MHz. Instead, a very shallow minimum which is hardly shifted with respect to the one observed at 15 MHz, is seen. It seems, therefore, that molecular motions with more

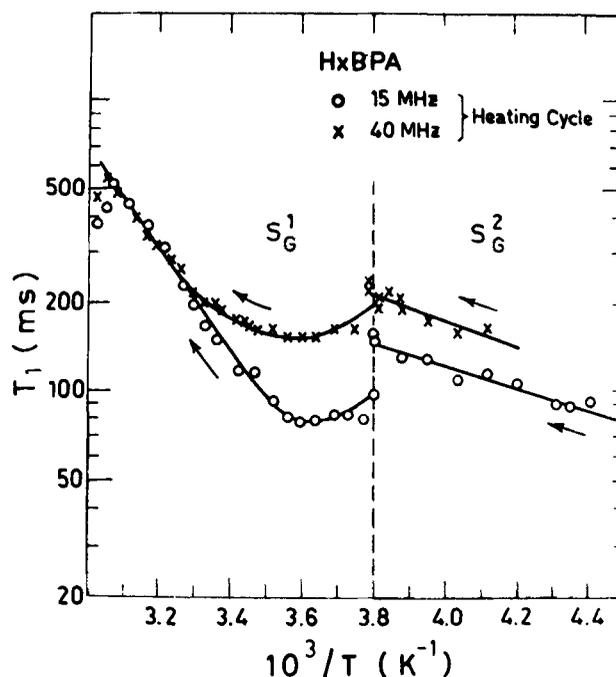


Figure 4. Temperature dependence of T_1 in the S_G^1 and S_G^2 phases, at 15 and 40 MHz, for the heating cycle. The lines are guide to the eye.

than one correlation time, are contributing to the relaxation rate. For $T > 307$ K, the relaxation rate is independent of frequency, indicating that in this temperature region, the molecular motions are very fast ($\omega\tau \ll 1$) (Noack 1971). On the other hand, in the S_G^2 phase, the frequency dependence of T_1 suggests that the molecular motion is slow.

3.2 Models for molecular motions in the S_G^1 phase ($T < 328$ K)

Various molecular motions such as the translational diffusion of molecules, collective lattice vibrational modes, undulation modes of the smectic planes and the rotational diffusion of the hc chains or of the entire molecule, might contribute to T_1 in the S_G^1 phase. Translational diffusion motion and undulation modes, if present, would be very slow due to the nearly 3-dimensional order in the S_G^1 phase, and their contribution to the relaxation rate, T_1^{-1} would be negligible. No abrupt change would be expected in the lattice vibrational modes at the $S_G^1 \rightleftharpoons S_G^2$ transitions, both while heating and cooling, since no structural change is observed (Usha Deniz and Mehta 1982) at these transitions. The fact that T_1 shows sudden changes at these transition temperatures, indicates that the main contribution to the relaxation rate is not from structural changes. The above considerations indicate that rotational diffusion motions make the dominant contribution to $1/T_1$ in the S_G^1 phase for $T < 328$ K.

In HxBPA, anisotropic rotational diffusion motions of the end hc chains, of the entire molecule or of just the central rigid portions, are possible. Several CH_2 groups are present in the end hc chains of HxBPA and hence several rotational diffusion modes of these chains could be present, leading to as many values of the correlation time, τ . Various theories (Rouse 1953; Agreen 1972; Kimmich and Peters 1975) have considered such modes in chain-like molecules (polymers and lipids). It is doubtful whether these theories which have been formulated for long chains, would be applicable to the case of HxBPA which has two short end chains, having six and three segments. However, one can expect the chain motion in HxBPA to consist of more than one diffusive mode of an anisotropic nature. Since the chain axis is not parallel to the long axis of the molecule, the rotational diffusion motion of the entire molecule would lead to a somewhat loose-packed structure which would be incompatible with the observed high packing density of the S_G phase. Hence, the rotational diffusion motions of the end hc chains and of the central rigid part, rather than that of the entire molecule, would be more likely to occur.

To explain our results for $T < 328$ K, we have considered the following simple model for the motions of the HxBPA molecule. The hc chains as also the central rigid portion of the molecule undergo anisotropic rotational diffusion motion. Each of these two parts is assumed to be an ellipsoid with the rotational diffusion occurring about the three principal axes of the ellipsoid. In both cases, one of the principal axes is a symmetry axis and the motions about the other two axes are equal, that is, the correlation times for these two motions are the same. For the end chains, the symmetry axis is the chain axis and for the central rigid part, it is the long axis of the molecule. The correlation times for the motions of the two end chains are assumed to be the same. Using this model for molecular motions, the relaxation time, T_1 , is calculated from Woessner's theory (Woessner 1962).

In a two-spin system of like spins, with random uncorrelated motion, the relaxation rate turns out to be (Woessner 1962; Abragam 1961),

$$T_1^{-1} = \frac{3\gamma^4\hbar^2}{2b^6} I(I+1) \{J^{(1)}(\omega) + J^{(2)}(2\omega)\} \quad (1)$$

where γ = magnetogyric ratio, b is the internuclear separation, I = nuclear spin which is $1/2$ for protons and $J^{(i)}(\omega)$ is the i th spectral density. For our model, in which the motion is an anisotropic rotational diffusion motion which is equal about two of the principal axes, Woessner's theory gives,

$$J^{(i)}(\omega) = 2F_i \left\{ A \left[\frac{\tau_A}{1 + \omega^2 \tau_A^2} \right] + B \left[\frac{\tau_B}{1 + \omega^2 \tau_B^2} \right] + C \left[\frac{\tau_C}{1 + \omega^2 \tau_C^2} \right] \right\} \quad (2)$$

where, $F_1 = 2/15$ and $F_2 = 8/15$ and

$$A = \frac{1}{4}(3l^2 - 1)^2, \quad B = 3l^2(1 - l^2), \quad C = \frac{3}{4}(l^2 - 1)^2 \quad (3)$$

where l is the direction cosine of the internuclear vector with respect to the symmetry axis of the ellipsoid. τ_A , τ_B and τ_C are correlation times, related to the diffusion coefficients, D_1 , D_2 and D_3 , for rotation about the three principal axes. Because the ellipsoid possesses a symmetry axis, $D_2 = D_3$, and

$$1/\tau_A = 6D_2, \quad 1/\tau_B = D_1 + 5D_2, \quad 1/\tau_C = 4D_1 + 2D_2 \quad (4)$$

For the end chains of HxBPA, since the internuclear vector for the chain protons are perpendicular to the chain axis, $A = 1/4$, $B = 0$ and $C = 3/4$. The relaxation rate due to chain motion is then,

$$\begin{aligned} T_1^{-1} &= \frac{3}{40} \frac{\gamma^4 \hbar^2}{b_c^6} \left\{ \left[\frac{\tau_A(c)}{1 + \omega^2 \tau_A(c)^2} + \frac{4\tau_A(c)}{1 + 4\omega^2 \tau_A(c)^2} \right] \right. \\ &\quad \left. + 3 \left[\frac{\tau_C(c)}{1 + \omega^2 \tau_C(c)^2} + \frac{4\tau_C(c)}{1 + 4\omega^2 \tau_C(c)^2} \right] \right\} \\ &= \frac{3}{40} \frac{\gamma^4 \hbar^2}{b_c^6} F_c[\omega, \tau_A(c), \tau_C(c)], \end{aligned} \quad (5)$$

where b_c = magnitude of the internuclear vector for chain protons, and $\tau_A(c)$ and $\tau_C(c)$ are the correlation times for the chain motion.

For the rigid portion of HxBPA, the internuclear vector for the orthoprotons of the aromatic rings, is parallel to the long axis of the molecule. Hence, $A = 1$, $B = 0$ and $C = 0$. The relaxation rate due to the motion of the ring proton is then,

$$\begin{aligned} T_1^{-1} &= \frac{3}{10} \frac{\gamma^4 \hbar^2}{b_r^6} \left[\frac{\tau_A(r)}{1 + \omega^2 \tau_A(r)^2} + \frac{4\tau_A(r)}{1 + 4\omega^2 \tau_A(r)^2} \right] \\ &= \frac{3}{10} \frac{\gamma^4 \hbar^2}{b_r^6} F_r[\omega, \tau_A(r)] \end{aligned} \quad (6)$$

where b_r = magnitude of the internuclear vector for the orthoprotons and $\tau_A(r)$ is the correlation time for the motion of the rigid portion. One would have obtained the same expression as (6), if it were assumed that the rigid part had an isotropic rotational diffusion motion with a single correlation time, $\tau_A(r)$.

The relaxation rate due to both contributions is therefore,

$$T_1^{-1} = L \{ F_c[\omega, \tau_A(c), \tau_C(c)] + R F_r[\omega, \tau_A(r)] \} \quad (7)$$

where,

$$L = \frac{3}{40} \frac{\gamma^4 \hbar^2}{b_c^6} \quad \text{and} \quad R = 4 \frac{f_r b_c^6}{f_c b_r^6} \quad (8)$$

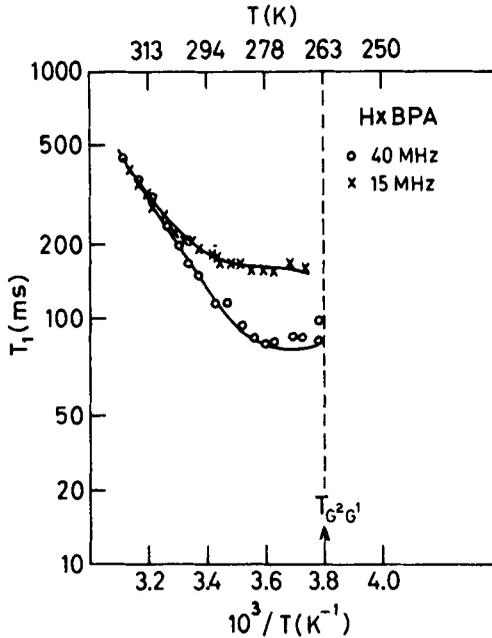


Figure 5. T_1 versus $10^3/T$ in the S_G^1 phase at 15 and 40 MHz. The lines represent best fits of our model (eq. (7)) to the experimental data.

and,

$$f_c = \frac{n_c}{n_c + n_r} \quad \text{and} \quad f_r = \frac{n_r}{n_c + n_r}$$

n_c and n_r are the number of chain and ring protons respectively. Since we have considered the diffusion motion to be thermally activated, the following expressions have been used for the temperature dependences of the correlation times:

$$(6D_2)^{-1} = \tau_A = \tau_2 = \tau_2^0 \exp(E_{A2}/k_B T) \quad (9a)$$

$$(6D_1)^{-1} = \tau_1 = \tau_1^0 \exp(E_{A1}/k_B T). \quad (9b)$$

Equation (7) was fitted to our data using L , $\tau_1^0(c)$, $\tau_2^0(c)$, $\tau_2^0(r)$, $E_{A1}(c)$, $E_{A2}(c)$, and $E_{A2}(r)$ as fitting parameters. The value of b_r was taken to be 2.46 \AA . The curve calculated, using the best fit parameters is given in figure 5 and it is found that there is good agreement between our results and the calculations. The best fit parameters are given in table 1. The value of b_c , calculated from the constant L , is also given in table 1. Its value, 1.92 \AA , agrees fairly well with that of 1.78 \AA , the distance between the methylene protons. An attempt to fit (7) with a fixed value of L (taking $b_c = 1.78 \text{ \AA}$), did not lead to such a good agreement. Models assuming chain motions alone (eq. (5)) and motion of the rigid portions alone (eq. (6)) were also fitted to the data. The model considering chain motions alone (eq. 5) gives a reasonably good fit to our data, whereas that with the motion of the rigid portions alone fails to do so. However, neither of these models gives as good an agreement with our results as does (7). In the temperature region where $\omega\tau \ll 1$, it can be seen from (1) and (2) that $T_1^{-1} \sim \exp(E_A/k_B T)$, if one assumes a single correlation time, τ , to exist. We have calculated E_A from our data at 15 and 40 MHz in such a temperature region

Table 1. Correlation times and activation energies for molecular motions in the S_G^1 phase.

Model	$\tau_1^0(c) \times 10^{13}$ (s)	$\tau_2^0(c) \times 10^{14}$ (s)	$\tau_2^0(r) \times 10^{15}$ (s)	$E_{A1}(c)$ (kJ/mol)	$E_{A2}(c)$ (kJ/mol)	$E_{A1}(r)$ (kJ/mol)	$L \times 10^5$ (s^{-2})	b_c (Å)
Directly calculated*	15.04 ± 0.27	0.444 ± 0.005	34.54 ± 10.4	22.4 ± 0.04	42.6 ± 0.04	20.3 ± 0.6	6.34 ± 0.03	1.92 ± 0.04
		0.590			37.3 ± 1.3			

*See text

($307\text{ K} \leq T < 328\text{ K}$) and its value is given in table 1, in the row labelled 'Directly Calculated'. This value of E_A agrees fairly well with that of E_{A1} obtained from our fit (see table 1). Similar agreement can be noticed from this table in the case of the corresponding correlation times. Thus, the dominant contribution to T_1 in this temperature range, seems to be from the chain motion. The fact that a really good fit to our results could not be obtained when the value of b_c and hence of L in (7) was fixed, could be due to the assumption that the two end chains of HxBPA have the same correlation times.

3.2 Nematic phase

It can be seen from figure 2 that at 15 MHz, T_1 has a strong temperature dependence in the nematic phase of HxBPA and it increases with increasing temperature. The frequency dependence of T_1 at 351 K is shown in figure 6.

3.2.1. *Molecular motions in the nematic phase:* The reorientations of the molecule as a whole can be thought of as due to (a) collective long range orientational (nematic) order fluctuations i.e. fluctuations of a local preferred direction of orientation, $\hat{n}(\mathbf{r}, t)$ of the molecular long axis about the nematic director \hat{n}_0 , and (b) short range reorientations of the molecular long axis about $\hat{n}(\mathbf{r}, t)$ which are quite rapid (correlation time $\sim 10^{-10}$ s).

In molecules such as HxBPA, the orthoprotons of the aromatic rings would be sensitive to molecular reorientations. Several theories (Doane and Johnson 1970; Doane *et al* 1974; Blinc 1976) have considered such a two spin system in which the spin-lattice relaxation is due to molecular reorientations but with the short range (local) reorientations being neglected. Both types of molecular reorientational motions have been taken into account in some of them (Sung 1971; Ukleja *et al* 1976; Freed 1977). We consider here the theories of Ukleja *et al* (UPD) (Ukleja *et al* 1976) and Freed (Freed 1977). Both UPD and Freed make the one elastic constant approximation. UPD assume statistical independence of the two molecular motions but Freed does not do so. They both obtain,

$$T_1^{-1} = (T_1^{-1})_a + (T_1^{-1})_b + (T_1^{-1})_c \quad (10)$$

where $(T_1^{-1})_a$, $(T_1^{-1})_b$ and $(T_1^{-1})_c$ are contributions due to long range collective fluctuations, local reorientations and the cross term between the two, respectively.

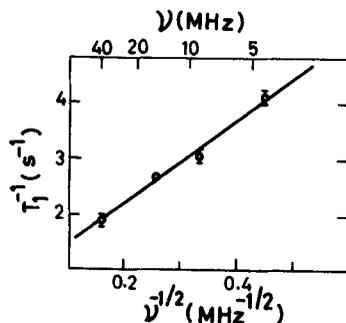


Figure 6. Frequency dependence of T_1^{-1} at 351 K in the nematic phase, fitted to eq. (13).

The two theories give identical expressions for $(T_1^{-1})_a$ whereas $(T_1^{-1})_b$ and $(T_1^{-1})_c$ given by them are quite different. For the intramolecular case where (1) the internuclear vector is parallel to \hat{n}_0 , (2) $\omega \ll \omega_c$, where ω_c is a cut-off frequency for the order fluctuation modes, and (3) \hat{n}_0 is parallel to \mathbf{H} (these conditions hold good in our experiments), these theories give,

$$\begin{aligned} (T_1^{-1})_a^{\text{UPD}} &= (T_1^{-1})_a^{\text{Freed}} = \frac{9}{8} \frac{\gamma^4 \hbar^2}{\sqrt{2\pi}} \frac{k_B T}{b_r^6} \frac{S^2}{(K/\eta)^{1/2} K} \omega^{-1/2} \\ &= A(T) \omega^{-1/2} \end{aligned} \quad (11)$$

$S = \frac{1}{2} \langle 3 \cos^2 \theta - 1 \rangle$, where θ is the angle between the nematic director and the long axis of the molecule and $\langle \dots \rangle$ signifies thermal average. K is the elastic deformation constant of the nematic and η is its viscosity. Since S^2/K and $k_B T (K/\eta)^{-1/2}$ vary little with temperature, $A(T)$ is a slowly varying function of temperature.

For $\omega \tau \ll 1$, where τ is the correlation time for molecular reorientation, which is a condition that is valid in many cases,

$$(T_1^{-1})_b^{\text{UPD}} = \frac{3}{2} \frac{\gamma^4 \hbar^2}{b_r^6} (1 - S) \tau = B(T)^{\text{UPD}} \quad (12a)$$

whereas,

$$(T_1^{-1})_b^{\text{Freed}} = \frac{3}{5} \frac{\gamma^4 \hbar^2}{b_r^6} (1 - S) \tau = B(T)^{\text{Freed}}. \quad (12b)$$

It should be noted that while writing (12b), we have used the approximation, $\langle \cos^4 \theta \rangle \approx \frac{1}{3} (4S + 1)$, made by UPD. Neglecting the cross term $(T_1^{-1})_c$ which is very different in the two cases, when conditions (1) to (3) hold good and when $\omega \tau \ll 1$, both theories give,

$$T_1^{-1} = A(T) \omega^{-1/2} + B(T). \quad (13)$$

Since $B(T) \propto \tau$ in both theories and the reorientational motion is thermally activated, one would expect $B(T)$ to be exponential in T . Expressions similar to (13) are obtained in the intermolecular case, but we shall not consider them here.

Equation (13) has been fitted to the T_1 data at 351 K, using A and B as adjustable parameters. The line shown in figure 6 is calculated from (13) using the parameters obtained for the best fit which are given below

$$A(T) = (1.87 \pm 0.08) \times 10^4 \text{ s}^{-3/2}$$

$$B(T) = (0.72 \pm 0.07) \text{ s}^{-1}.$$

It is seen that agreement between our data and (13) is very good, showing that at 351 K, the major contribution to the spin-lattice relaxation is from the nematic order fluctuations and local molecular reorientations with $\omega \ll \omega_c$. Using the above value of $B(T)$ in the expression of UPD (eq. (12a)), we obtain a correlation time,

$$\tau = (4.3 \pm 0.4) \times 10^{-10} \text{ s},$$

whereas using it in Freed's theory (eq. (12b)), we obtain,

$$\tau = (1.1 \pm 0.1) \times 10^{-9} \text{ s}.$$

4. Conclusions

The proton spin-lattice relaxation times, measured in HxBPA, reveal the following interesting features:

- (a) The $S_G^1 \rightleftharpoons S_G^2$ transitions are well-defined ones, as far as molecular motions are concerned. However, thermal studies do not indicate the presence of $S_G^1 \rightarrow S_G^2$ transition. From the behaviour of T_1 , we have deduced that this transition is related to the freezing or change of some molecular motions, most probably the chain motions.
- (b) In the S_G^1 phase, the T_1 data at 15 and 40 MHz can be fitted fairly well by a model considering anisotropic rotational diffusion motion of the rigid portion of the molecule and the hydrocarbon chains. However, the value obtained for b_c from this model, is slightly higher than the actual value for the methylene protons. This may be due to the reason that our model for molecular motion assumes decoupling of the chain motions and that of the central rigid portion of the molecule.
- (c) In the nematic phase, the frequency dependence of T_1 at 351 K is very well explained by considering the nematic order fluctuations and short range molecular reorientations as the main mechanisms for spin-lattice relaxation. The correlation time for short range reorientations is calculated to be $\sim 10^{-10}$ s using UPD's theory whereas with Freed's theory it is $\sim 10^{-9}$ s.

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