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Liquid Crystals

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N.M.R. study of collective molecular motions in smectogen liquid crystals

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The proton spin relaxation dispersion, $T_1(\nu)$, was studied by field-cycling techniques over a broad Larmor frequency range in the nematic and smectic phases of several liquid crystals (4,4′-bis-heptyloxyazoxybenzene, 4-cyano-4′-8-alkylbiphenyl, 4-cyano-4′-9-alkylbiphenyl, 4-cyano-4′-11-alkylbiphenyl and 4-cyano-4′-9-alkoxybiphenyl) with different sites of the nitrogen atom. The results can be explained quantitatively in terms of nematic and smectic order fluctuations ($T_1 \propto \nu^{1/2}$, $T_1 \propto \nu^1$), molecular self-diffusion, molecular rotations and up to six cross-relaxation resonances due to a nitrogen–proton coupling The order fluctuations contribution and the transition from the $\nu^{1/2}$ to the ν^1 dispersion profile occurs always at Larmor frequencies in the kilohertz range. Some additional measurements of the frequency dependence of the dipolar relaxation time $T_{1D}(\nu)$, are not in accord with existing theories.

1. Introduction

It is well known that in thermotropic liquid crystalline mesophases the longitudinal proton spin relaxation time, T_1, is determined essentially by dipolar magnetic couplings between neighbouring protons, which are modulated by three kinds of molecular reorientations: on the one hand collective motions such as order fluctuations of the director (OF), and on the other two non-collective motions such as self-diffusion (SD) and hindered molecular rotations (Rot) [1, 2]. Many recent papers on this topic discuss the relative importance of the non-collective and collective relaxation mechanisms with rather conflicting conclusions, because the theoretical details of the more recent sophisticated models are difficult to confirm experimentally [3–6]. The early relaxation model of Pincus [7] and Blinc *et al.* [8], later derived more precisely by Freed [9] and Ukleja *et al.* [10], predicts that in some favourable cases the OF contribution may be detected by a characteristic dependence of T_1 on the Larmor frequency ν. In nematic (N) liquid crystals the expected square-root law, $T_1 \propto \nu^{1/2}$, has frequently been verified experimentally by various research groups [11–14], mainly with the help of the fast field-cycling (FFC) technique [15]. However, the linear dependence [16, 17], $T_1 \propto \nu^1$, predicted for special smectic (Sm) order fluctuations (ondulation waves) have only rarely been studied by this method [18–22].

Hence, to improve the understanding of relaxation by order fluctuations, this paper presents a systematic study of the proton Larmor frequency dependence of T_1, obtained by FFC N.M.R., for a number of smectogen liquid crystals. A comparison

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of $T_1(\nu)$ in the nematic and smectic mesophases, in particular the examination where the OF modes reveal cut-off frequencies, should allow a critical test of the underlying theoretical concepts. Furthermore, since the dipolar relaxation time, T_{1D} [23, 24], is often considered and used an alternative means to T_1 field-cycling, we also performed measurements of the Larmor frequency dependence of T_{1D} to control the consistency of the two methods. Finally, we looked for effects not yet included in the relaxation analysis of liquid crystals, namely the coupling of protons with quadrupolar nuclei. It is known from recent studies [25, 26] of biological compounds that FFC methods make it possible to observe interactions between protons and not necessarily neighbouring, quickly relaxing quadrupolar nuclei such as nitrogen, because this coupling involves resonant relaxation dips through level crossings. The liquid crystals considered were selected to have one or two nitrogen atoms at different molecular sites, and thus allowed us to vary the quadrupolar coupling constant (K) and the asymmetry parameter (η) of the nitrogen quadrupole transitions, which determine the position and the shape of the dips.

2. Experimental techniques

We have studied over a broad Larmor frequency range, namely from $\nu = 100\,\mathrm{Hz}$ to 100 MHz, the dispersion of the longitudinal proton spin relaxation time T_1 in the following smectogen liquid crystals: 4,4′-bis-heptyloxyazoxybenzene (HpAB; Eastman-Kodak); 4-cyano-4′-8-alkylbiphenyl (8-CB; B.D.H.); 4-cyano-4′-9-alkylbiphenyl (9-CB; B.D.H.); 4-cyano-4′-11-alkylbiphenyl (11-CB; B.D.H.) and 4-cyano-4′-9-alkoxybiphenyl (9-OCB; B.D.H.). All compounds were sealed in glass tubes under vacuum without further purification. In addition, in one of the samples (HpAB) we also measured the proton dipolar relaxation time T_{1D} at various Larmor frequencies between 15 and 85 MHz.

For Larmor frequencies smaller than 6·8 MHz, the $T_1(\nu)$ measurements were carried out with a home-built FFC spectrometer [15, 27], whereas the T_1 and T_{1D} data at the higher frequencies were obtained by means of a conventional frequency variable N.M.R. apparatus [27] and standard pulse methods [15, 23, 24] (90° – 90° for T_1, Jeener–Broekaert for T_{1D}). In both spectrometers it is possible to adjust the temperature of the sample within ±0·5°C. The accuracy of the Larmor frequency in the FFC instrument was estimated to be better than ±1 per cent. In order to orientate the director of the liquid crystals parallel to the Zeeman field, the thermal treatment was always performed in the following way. First, the samples were heated to the isotropic phase with the high magnetic field of the spectrometer on. Then they were cooled to the desired temperature in the nematic or smectic phase.

3. Results

Figure 1 illustrates the $T_1(\nu)$ profiles in the smectic state of all five compounds. The temperatures were selected approximately in the middle of the individual phases. Obviously, the dispersion profiles are characterized by the following: (*a*) a shallow high frequency dispersion (range I, $\nu \geqslant 10^6$ Hz for HpAB and $\nu \geqslant 10^4$ Hz for the *n*-CBs and 9-OCB); (*b*) a stronger variation at medium and low frequencies, showing a $T_1 \propto \nu^1$ law (range II, $10^3 \leqslant \nu \leqslant 10^6$ Hz for HpAB and $10^3 \leqslant \nu \leqslant 10^4$ Hz for the *n*-CBs and 9-OCB); (*c*) both regimes start with a T_1 plateau on the low frequency side; (*d*) the two ranges and plateaux are superimposed by various dips, where T_1 decreases up to a factor of 2. Compounds with one nitrogen site (*n*-CBs and 9-OCB) show three resonance effects, whereas HpAB with two nitrogen atoms reveals four resolved dips.

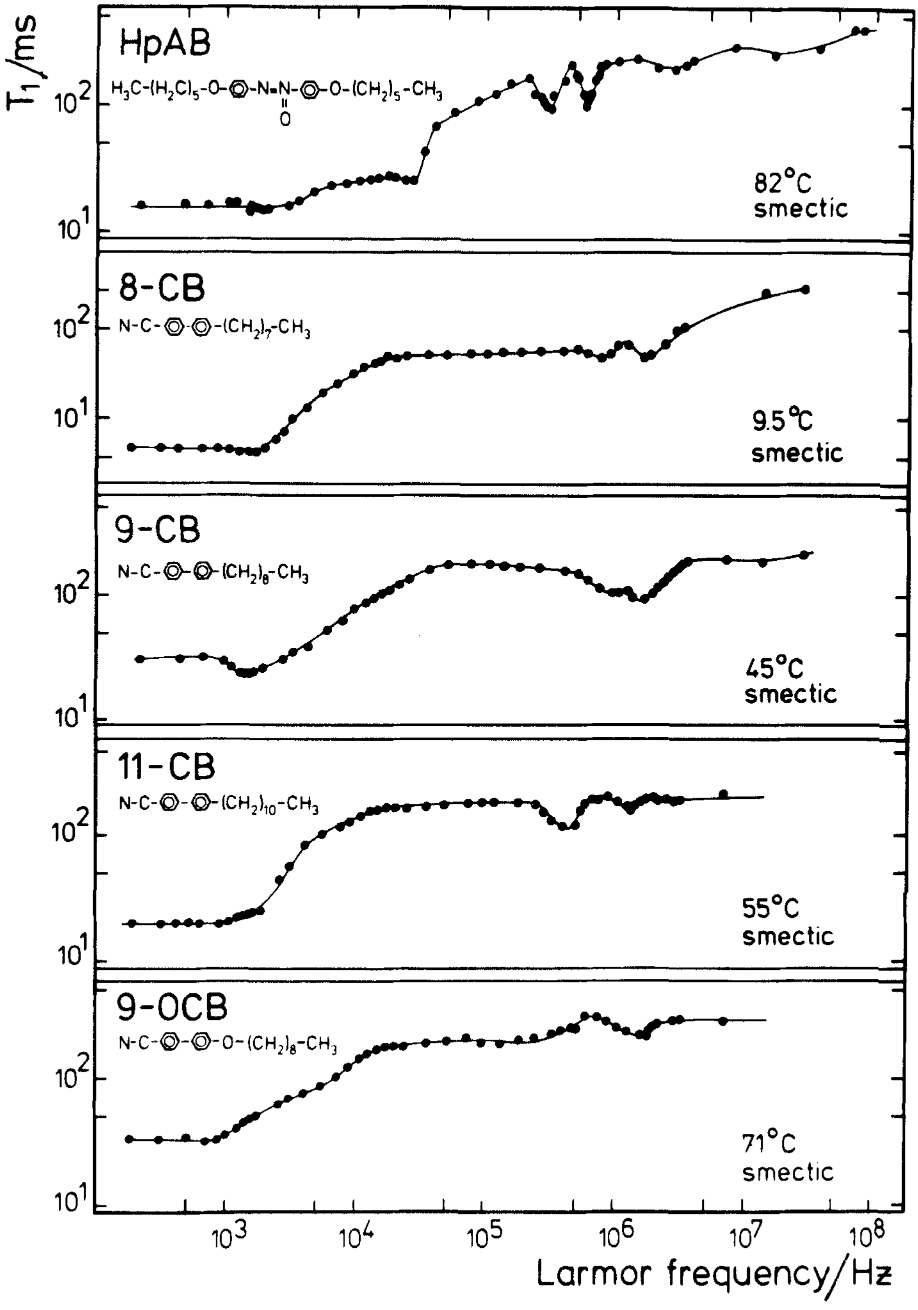

Figure 1. Experimental proton T_1 relaxation dispersion of five smectogen liquid crystals: one azoxybenzene (HpAB), three cyanobiphenyls (8-CB, 9-CB and 11-CB) and one oxycyanobiphenyl (9-OCB) at temperatures in the middle of the smectic mesophases.

Figure 2 compares the measurements performed on 8-CB at temperatures with different molecular ordering, i.e. in the isotropic, nematic and smectic phases. At medium frequencies ($10^3 \leq \nu \leq 10^6$) one clearly sees the transition from the ν^0 dispersion for the isotropic state (40°C) to the $\nu^{1/2}$ dispersion for the nematic state (32

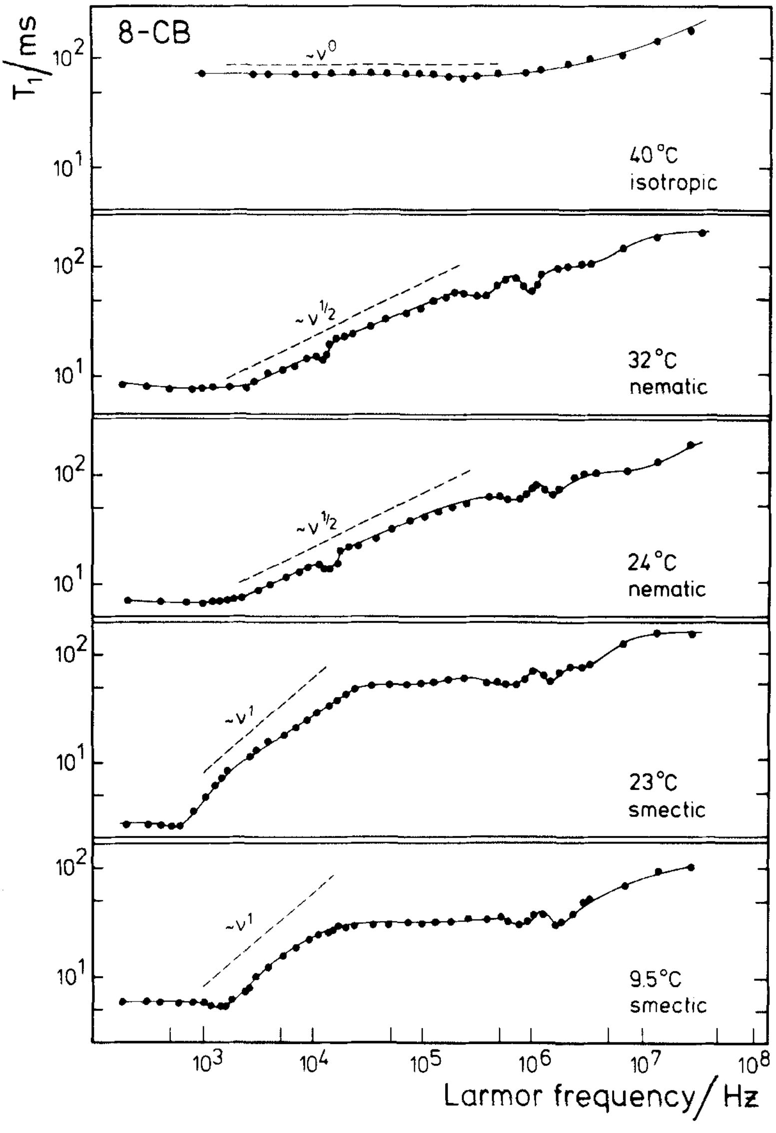

Figure 2. Proton T_1 relaxation dispersion of 8-CB, showing the different importance of order fluctuations for different molecular ordering: a negligible contribution in the isotropic phase ($T_1 \propto \nu^0$), a $T_1 \propto \nu^{1/2}$ profile for the nematic and a $T_1 \propto \nu^1$ profile for the smectic order.

and 24°C), and then to the ν^1 dispersion for the smectic state (23 and 9·5°C). Note that the last step occurs within a very narrow temperature interval, near the Sm–N phase transition at 23·5°C. Whereas the frequencies of the dips in both the nematic and smectic phases are shifted to lower values if the temperature is increased, at the Sm–N phase transition a dramatic jump takes place in the opposite direction.

Figure 3 presents a similar study carried out on 9-CB. The general behaviour is similar to that in the preceding example, in particular the sudden increase of the low dip frequency at the Sm–N phase transition. However, the details differ, for instance

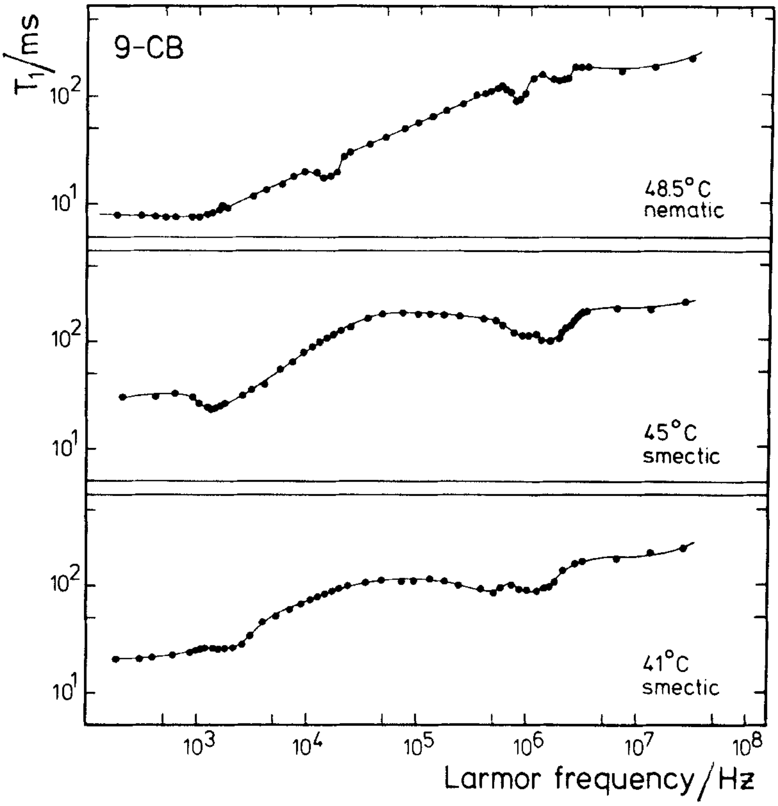

Figure 3. Proton T_1 relaxation dispersion of 9-OCB in the nematic and smectic phase.

the temperature shift of the dips in the smectic phase is smaller than in the case of 8-CB.

Figure 4 shows the experimental results for HpAB. This diagram does not clearly demonstrate the transition from the $\nu^{1/2}$ dispersion to the ν^1 dispersion, because of the superposition with numerous dips. However, the main distinction from all of the preceding examples is that its number is clearly greater than three. In the nematic state five resolved dips are observed; the smectic state reveals four. Since some of the resonances are extremely broad (the high field dip at 110°C, as well as the high and low field dips at 82 and 75°C), they possibly reflect a combination of unresolved pairs, which gives a total number of six in any case. All of the frequencies are more strongly dependent on temperature than in the other liquid crystals studied, even stronger than for 8-CB. The figure also includes some data on the frequency dependence of T_{1D}. This T_{1D} dispersion is stronger than that of T_1 and almost identical in both mesophases, so that the ratio T_1/T_{1D} decreases between 15 and 50 MHz from about 4 to 2. One should note that although $T_1(\nu) > T_{1D}(\nu)$, the dipolar relaxation time remains larger than T_1 in the zero-frequency limit.

4. Discussion

As a first approach we tried a quantitative interpretation of the experimental $T_1(\nu)$ relaxation dispersions in terms of the models developed for nematic mesophases

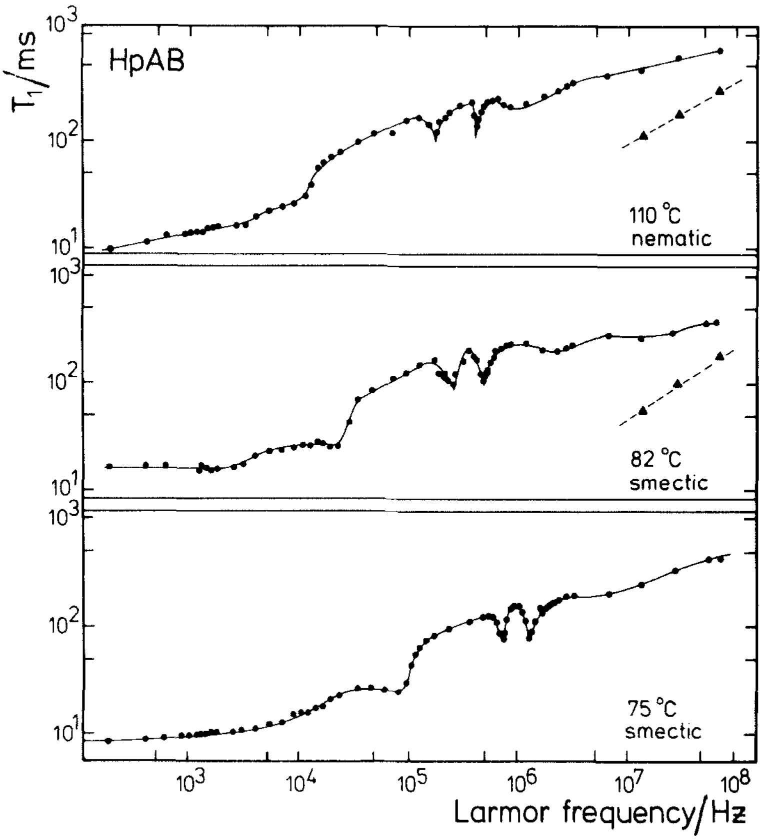

Figure 4. Proton T_1 (●) and T_{1D} (▲) relaxation dispersion of HpAB in the nematic and smectic phase, showing the anomalous T_1/T_{1D} behaviour.

[1, 2, 14, 15] with appropriate modifications for the smectic state, i.e. by a superposition of contributions originating from nematic or smectic order fluctuations (OF(N) and OF(Sm)), molecular self-diffusion (SD) and molecular rotations (Rot) combined with three or six quadrupolar dips (QD):

$$\frac{1}{T_1} = \frac{1}{T_{1\mathrm{OF}}} + \frac{1}{T_{1\mathrm{SD}}} + \frac{1}{T_{1\mathrm{Rot}}} + \sum_i \frac{1}{T_{1\mathrm{QD},i}}. \tag{1}$$

Only the simplest theories about the four kinds of relaxation mechanisms were considered, namely Blinc's results for $T_{1\mathrm{OF}}$ in both the nematic and smectic state [1, 2, 8, 16, 28] (including the low frequency cut-off, ν_c), the Abragam–Pfeifer result for $T_{1\mathrm{SD}}$ (isotropic small-step approximation) [29, 30], the BPP model for $T_{1\mathrm{Rot}}$ modified by Woessner (anisotropic motions) [30, 31], and a Lorentzian form for $T_{1\mathrm{QD},i}$ [15, 25, 26]. With these approximations the individual contributions can be written more explicitly [32] (showing all model parameters) as

$$1/T_{1\mathrm{OF(N)}} = A_{\mathrm{N}}\nu^{-1/2} f_{\mathrm{OF(N)}}(\nu/\nu_c), \tag{2a}$$

$$1/T_{1\mathrm{OF(Sm)}} = A_{\mathrm{Sm}}\nu^{-1} f_{\mathrm{OF(Sm)}}(\nu/\nu_c), \tag{2b}$$

$$1/T_{1\mathrm{SD}} = B\tau_{\mathrm{SD}} f_{\mathrm{SD}}(\nu, \tau_{\mathrm{SD}}), \tag{2c}$$

$$1/T_{1\mathrm{Rot}} = C\tau_{\mathrm{Rot}} f_{\mathrm{Rot}}(\nu, \tau_{\mathrm{Rot}}) \tag{2d}$$

and

$$1/T_{1\mathrm{QD},i} = E_i\tau_{\mathrm{QD},i}/\{1 + [2\pi(\nu - \nu_{\mathrm{QD},i})\tau_{\mathrm{QD},i}]^2\}, \tag{2e}$$

where the amplitudes A_{N}, A_{Sm}, B, C and E_i denote parameters characteristic of the interactions, $f_{\mathrm{OF(N)}}$, $f_{\mathrm{OF(Sm)}}$, f_{SD} and f_{Rot} are spectral functions typical for the reorientations, $1/\nu_{\mathrm{c}}$, τ_{SD}, τ_{Rot} and $\tau_{\mathrm{QD},i}$ are the involved motional time constants, and $\nu_{\mathrm{QD},i}$ the observed dip frequencies. Further details are explained in the original literature [1, 2, 8, 16, 28–32].

Expressions for $T_{1\mathrm{D}}(\nu)$ are only known for some special conditions [33, 34]. Work on liquid crystals frequently make use of the relationship [35–38].

$$T_1 = 3T_{1\mathrm{D}}, \tag{3}$$

which in the case of dipolar interactions should be correct for correlated motions [34]; however, it has never been examined experimentally over a sufficiently large frequency range.

Figure 5 illustrates the complete fit for HpAB at two temperatures, one in the *nematic* and the other in the *smectic*† phase. Excellent curve fits were obtained by

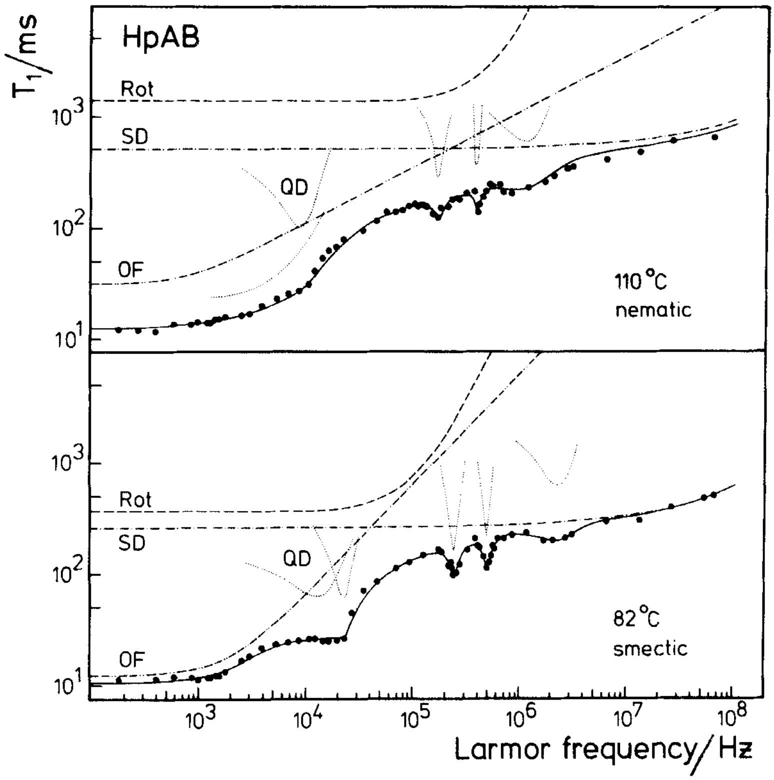

Figure 5. Curve fit of equations (1) and (2) to the experimental relaxation dispersion of HpAB in the nematic and smectic phase. In both cases the high field QD contribution is an unresolved doublet.

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† Since for HpAB the transition from the $\nu^{1/2}$ to the ν^1 dispersion is only weakly developed, both diagrams can be interpreted with nematic-type order fluctuations. Such a possibility was published in 1987 by Vilfan *et al.* (*J. chem. Phys.*, **86**, 1055).

Table 1. Model-fitting parameters of equations (1) and (2) for HpAB.

OF, SD, Rot

Temp./°C	$A_N/10^5\,s^{-3/2}$ $A_{Sm}/10^5\,s^{-2}$	ν_c/kHz	$B/10^9\,s^{-1}$	τ_{SD}/ns	$C/10^5\,s^{-1}$	$\tau_{Rot}/\mu s$
82	1·6	10	2·9	52	6	9
110	90	4	4·2	19	0·08	18

QD

	Dip number					
	1	2	3	4	5	6
T = 82°C						
$E_i/10^5\,s^{-1}$	3·5	2	3	4·5	18	18
$\nu_{QD,i}$/kHz	13	23	250	510	2300	2600
$\tau_{QD,i}/\mu s$	9	16	4	2	0·12	0·12
T = 110°C						
$E_i/10^5\,s^{-1}$	6	0·85	1·2	1·4	2·0	2·0
$\nu_{QD,i}$/kHz	0·4	9	180	420	1100	1300
$\tau_{QD,i}/\mu s$	14	22	50	40	16	16

including six T_1 dips and using the parameters A, B, C, D, E_i, ν_c, τ_{SD}, τ_{Rot}, $\tau_{QD,i}$ and $\nu_{QD,i}$ summarized in table 1. The consistency of these data with related physical quantities was checked as far as possible. For instance, consider the smectic results. Taking values of the self-diffusion constant D_{SD} of azoxybenzenes extrapolated from the literature [39] and our fitted τ_{SD}s, the effective distances of closest approach between the spins of two neighbouring molecules were calculated to vary between 4×10^{-10} and 6×10^{-10} m; this is in satisfactory accord with the diameter of the HpAB molecule of about $6{\cdot}5 \times 10^{-10}$ m. The activation energy of self-diffusion was calculated to be 138 kJ mol^{-1}, which is comparable with results for other smectic liquid cyrstals [40]. The coherence length ξ of the collective motions, estimated from the cut-off frequency ν_c by means of [1, 2, 28]

$$\xi = (2\pi L/\eta\nu_c), \tag{4}$$

the effective elastic constant L, and the effective viscosity η [41, 42], has a value of $7{\cdot}5 \times 10^{-9}$ m at 82°C, which corresponds to approximately two molecular lengths. For the nematic state at 110°C the same estimation gives approximately 46 molecular lengths, due to the smaller viscosity. A similar number is obtained by evaluating the T_{1OF} contribution [16] with an estimated splay elastic constant of 4×10^{-11} N. The activation energy for the order fluctuation term is 71 kJ mol^{-1}, i.e. about half the diffusion barrier as often observed in nematics [1]. Finally, τ_{Rot} is comparable with the megahertz dielectric absorption regime [42, 43] of azoxybenzenes. A more quantitative discussion will be presented elsewhere.

The frequency range where the OF term in smectic HpAB dominates the total relaxation is similar to the range known for TBBA [18, 20]. In contrast, as seen from figure 1, the $T_1 \propto \nu^1$ regime for the n-CBs and 9-OCB is much shorter, although the amplitude A_{Sm} does not differ significantly. So the distinctions do not indicate basic differences, they are essentially a consequence of the increased τ_{SD}s, or reduced diffusion constants, of the SD contribution at the lower temperatures. This is also supported by the observation that the cut-off frequencies ν_c are similar for all of the smectogens.

Clearly, such details cannot be resolved from the $T_{1\mathrm{D}}$ dispersion. In view of the unexpected $T_1(\nu)/T_{1\mathrm{D}}(\nu)$ decrease by a factor of 2, even the dominating relaxation mechanism is not evident. From the $T_1 \propto \nu^1$ profile it could be argued that smectic order fluctuations are dominating, but the high field T_1 dispersion excludes such an interpretation. It should also be noted that $T_{1\mathrm{D}}(\nu)$ shows almost no difference between the two mesophases. *Qualitatively*, the decrease in $T_1/T_{1\mathrm{D}}$ demonstrates that the underlying process changes from a slower one at low ν to a faster one at high ν [34], and in this way supports the T_1 analysis. However, none of the available $T_{1\mathrm{D}}$ calculations describes the experimental data *quantitatively*, in particular not the transition from $T_{1\mathrm{D}}(\nu)$ to T_1 in the zerofield ($\nu \to 0$), where both time constants have the same meaning. Hence previous works relying on equation (3) need to be re-examined!.

Taking into account that HpAB has two chemically inequivalent nitrogen sites, the number and position of quadrupolar dips in figure 5 can be understood quantitatively, using standard relationships between ν_{QD}, the quadrupolar coupling constant $K = e^2qQ/h$, and the electric field gradient asymmetry parameter η [44], namely

$$\nu_{\mathrm{QD}\pm} = \tfrac{3}{4}(e^2qQ/h)(1 \pm \eta), \qquad \nu_{\mathrm{QD}0} = \tfrac{1}{2}(e^2qQ/h)\eta. \tag{5}$$

Since $\eta \ll 1$, $\nu_{\mathrm{QD}\pm}$ are two high frequency lines and $\nu_{\mathrm{QD}0}$ is one low frequency line of the triplet. Note that two dip positions, number (1, 2) and (5, 6) as listed in table 1, are not resolved resonances, hence the total number is $2 \times 3 = 6$. Table 2 shows data for all the compounds. As expected from equation (5), molecules with only one

Table 2. Quadrupolar coupling constants and asymmetry parameters obtained from the quadrupolar dip analysis.

			K/kHz		η/%	
Compound	Temp./°C	Phase	Dip numbers (1, 5, 6)	Dip numbers (2, 3, 4)	Dip numbers (1, 5, 6)	Dip numbers (2, 3, 4)
HpAB	110	N	400	1600	0·6	0·02
	93	S	50	2100	8	0·07
	89	S	110	2400	7	0·2
	82	S	500	3260	4·6	0·4
	75	S	1270	4800	11	0·6
			Dip No (1, 2, 3)			
8-CB	32	N	900		3·5	
	24	N	1530		2	
	23	S	1400		0·3	
	9·5	S	1660		0·9	
9-CB	48·5	N	1930		1·2	
	45	S	1310		0·8	
	41	S	1330		0·8	
11-CB	55	S	1130		0·3	
9-OCB	41	S	1100		0·4	

nitrogen exhibit three resonances, whereas HpAB shows six. In the case of HpAB the two high dip frequency pairs, (3, 4) and (5, 6), are related to the low frequency dips 1 and 2, respectively, to give a triplet. We assign the nitrogen bonded to the oxygen atom to the larger η and the smaller K. This is reasonable because of the high asymmetry produced by the oxygen charge distribution. In this way the two quadrupolar triplets for HpAB can be assigned to the dips combinations (1, 5, 6) and (2, 3, 4), respectively. Our results clearly show that even in the nematic phase the molecular rotations, especially those about the longitudinal axis, are insufficient to average the perpendicular EFG component to an undetectable low magnitude. Surprisingly, in the two examples 8-CB and 9-CB, the unaveraged EFG is much greater in the nematic than in the smectic phase. Another interesting point is the unusually strong temperature dependence of the quadrupolar parameters observed by the HpAB and 8-CB relaxation dips (two compounds with similar nematic and smectic mesophases); this point is a matter of our actual study [45]. In solids the strong temperature effect has been discussed in terms of changes in the EFG averaging due to changes in the intramolecular dynamics [46–48].

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