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Dynamics of 4,4′-di-*n*-heptylazoxybenzene (HAB) studied using dielectric and ^{2}H NMR relaxation measurements

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Results of studies of 4,4′-di-*n*-heptylazoxybenzene (HAB) in the isotropic, nematic and smectic A phases are presented. Two experimental methods were employed: broad band dielectric spectroscopy and nuclear magnetic resonance spectroscopy. The complex dielectric permittivity, $\varepsilon^*(\omega)=\varepsilon'(\omega)-i\varepsilon''(\omega)$, was measured in the frequency range 1 kHz–4 GHz. This allowed two main relaxation processes to be separated in all the phases studied: the low frequency (l. f.) process connected with molecular reorientations around the short axes, and the high frequency (h. f.) process connected with the rotations around the long axes. The corresponding relaxation times and activation enthalpies were obtained. The l. f. relaxation time changes step-wise at the phase transitions, whereas the h. f. relaxation time passes smoothly through all the phases. The measurement of ^{2}H spin-lattice relaxation times was carried out throughout the mesophase range at 61.38 MHz. These data were analysed together with the relaxation times measured at 10.00 and 46.04 MHz, available from previous studies. Using suitable theoretical models the principal components of the diffusional tensor, $D_{\parallel}$ and $D_{\perp}$, as well as the diffusion coefficients D_R relative to the internal rotation of the phenyl rings, were determined. The results of both studies are compared and discussed.

1. Introduction

Dielectric spectroscopy (DS) is a powerful tool with which to study the stochastic reorientational motions of molecules in mesomorphic phases if the constituent molecules possess a permanent dipole moment(s). The wide frequency range available in this method (from sub-hertz up to several gigahertz) enables one to follow very slow as well as very fast rotations of molecules or of their polar segments. On the other hand, a straightforward relationship between the measured spectrum, i.e. the complex permittivity $\varepsilon^*(\omega)=\varepsilon'(\omega)-i\varepsilon''(\omega)$, and the parameters characterizing the rotating molecules (the dipole moment μ and the relaxation time τ) facilitates the molecular interpretation of observed relaxation processes.

^{2}H NMR spectroscopy has been established as a very powerful tool for studying structural, orientational and dynamic properties of liquid crystalline phases in suitably deuterium-labelled compounds [1, 2]. The ^{2}H Zeeman (T_{1Z}) and quadrupolar (T_{1Q}) spin-lattice relaxation times, in particular, are strongly dependent on molecular dynamics in the kHz to hundreds of GHz range. Their analysis in terms of complex theoretical models allows very detailed information to be obtained, not only on overall molecular spinning and tumbling motions, but also on internal motions of molecular fragments and, possibly, on collective order director fluctuations. However, it has been recently shown [3] that in some cases, for instance when experimental relaxation times arising from only one type of deuteron—and measured at only one frequency—are available, some of the motional parameters obtained from the analysis, and particularly the diffusional coefficient relative to the overall tumbling motion, may include a very large error or, in the worst cases, be substantially undetermined. To overcome this problem a larger set of NMR relaxation measurements would be necessary but, since this is not always available, the comparison between NMR and dielectric relaxation data could be very helpful in many situations.

It may also be interesting to analyse DS and NMR data together using an appropriate theoretical

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approach. In fact a relationship between the correlation times $\tau^{L}_{m,n}$, which are related to dielectric relaxation times, and the overall molecular rotational diffusional constants ($D_{\parallel}$ and $D_{\perp}$), that can be obtained from NMR relaxation data, may be derived from theoretical studies on uniaxial mesophases [4–6]. However, a quantitative comparison between DS and NMR results is possible only in the case of the experimental dielectric low frequency relaxation time ($\tau_{\text{l.f.}}$), which can be identified with the correlation time $\tau^{1}_{0,0}$ and therefore related to the diffusional coefficient $D_{\perp}$. By contrast, the experimental dielectric high frequency relaxation time ($\tau_{\text{h.f.}}$) is a combination of different relaxation components $\left(\tau^{1}_{1,0}, \tau^{1}_{1,1} \text{ and } \tau^{1}_{0,1}\right)$ and can only be qualitatively compared with the rotational diffusional constant $D_{\parallel}$. Fortunately, in the case of the compound studied in this work, the dipole group is (relatively) rigidly linked to the benzene rings constituting the rigid molecular core, and discussion of the relationships between the diffusion coefficients determined for the rings and $\tau_{\text{h.f.}}$ seems to be justified.

Recently a comparison between NMR and dielectric relaxation data has been attempted for the liquid crystal FAB-OC6 [7] for which, however, NMR relaxation data at only one Larmor frequency were available. The aim of this work is to investigate further the possibility of quantitatively comparing NMR and dielectric relaxation data in a case for which self-consistent results can be independently obtained from the two techniques.

The chemical structure of the compound studied, 4,4′-di-*n*-heptylazoxybenzene (HAB), is shown in figure 1. HAB has a single dipole group (N_2O) at the centre of the molecular core. In fact, the dipole moment is inclined from the lowest inertia moment axis (long axis) by *c*. 60° which means that the compound exhibits a small positive dielectric anisotropy, $\Delta\varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp} > 0$, in the N phase. Its static dielectric properties have been studied previously [8, 9] and revealed a change in the sign of $\Delta\varepsilon$ within the SmA phase which was attributed to increasing dipole correlations between molecules due to the formation of the smectic planes [8]. The relaxation measurements on HAB have not yet been reported. Because the dipole moment has non-zero longitudinal and transverse components, both principal molecular motions (i.e. around the short axis and around the long axis) should contribute to the dielectric relaxation spectra. The former process falls in the MHz frequency range and is called the low frequency (l. f.) relaxation process. The second is observed at thousands of MHz or even GHz frequencies and is termed the high frequency (h. f.) relaxation process. Therefore, a broad frequency band is needed to study both relaxation processes in particular phases.

The isotopomer HAB-d_{12}, selectively deuteriated as indicated in figure 1, was previously studied by ^{2}H NMR to investigate its structural and orientational ordering behaviour [10]. ^{2}H NMR relaxation times at two different Larmor frequencies were also measured [11] and a partial analysis in terms of dynamic behaviour was performed in the smectic A phase [3]. In this paper new measurements at a third Larmor frequency and a thorough analysis of NMR relaxation times to obtain dynamic parameters for molecular, internal and collective motions in both the nematic and smectic A phases are reported.

The results obtained independently from NMR and dielectric relaxation measurements are compared and discussed.

2. Experimental

The sample had been synthesized for previous studies according to the procedure described elsewhere [12]. Its phase transition temperatures determined by DSC (heating, $5\,\mathrm{K\,min^{-1}}$) are:

Cr – 38.8°C – SmA – 58.5°C – N – 75.7°C – I.

In dielectric measurements the SmA phase could be supercooled to 26°C. The measurements of the complex dielectric permittivity, $\varepsilon^* = \varepsilon' - i\varepsilon''$, were performed with the aid of two sets of apparatus. In the frequency range 1 kHz–20 MHz an Agilent 4194A impedance analyser was used. The plane capacitor ($C_o \sim 50\,\mathrm{pF}$) has gold covered plates. In the N phase the sample was oriented by means of a magnetic field ($\mathbf{B} = 0.8\,\mathrm{T}$). The alignment was then retained in the SmA phase. To study the high frequency process, the time domain spectrometer (TDS) at Uppsala University was used to cover the frequency range 20 MHz–4 GHz. Two time windows, 10 and 50 ns, were used and then the spectra were spliced [13]. All measurements were carried out on cooling samples. During collection of the spectra the temperature was stabilized to within ±0.1 K.

^{2}H T_{1Z} and T_{1Q} measurements at the Larmor frequencies of 10.00 and 46.04 MHz were available from previous studies [11]. The measurement of ^{2}H spin-lattice relaxation times was performed over the mesophase range at 61.38 MHz on a Varian Infinity Plus 400 spectrometer using the broadband version (90_0-$2\tau_1$-67.5_{270}-$2\tau_1$-45_{90}-τ_1-45_{90}-τ_2-45_0) [14] of the Jeener–Broekaert pulse sequence [15] followed by an echo sequence (τ_e-90_0-τ_e). Temperature was controlled to within 0.1°C. The 90 degree pulse was 2.8 μs. The best value of the delay τ_1 was found experimentally to be 55 μs, while the echo delay τ_e was fixed at 40 μs. The variable delay τ_2 ranged from 10 μs to 1 s. A relaxation delay of 1 s and 200 scans were used.

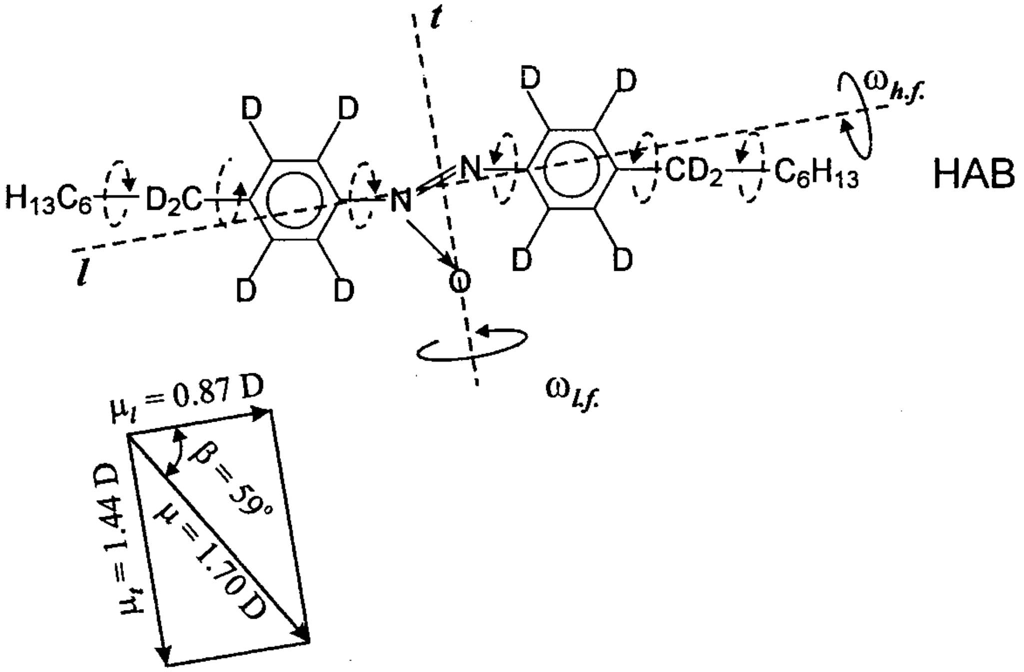

Figure 1. Structure of HAB-d_{12}. The lowest (l) and highest (t) inertia moment axes are shown with the respective whole-molecule rotations observed in the dielectric studies. The intramolecular rotations about the N–C and C–C bonds are marked by dashed lines. The angle β between the dipole moment and the molecular long axis was estimated from the dielectric increments measured in the isotropic phase (figure 2).

T_{1Z} and T_{1Q} were obtained from the trend *vs.* τ_2 of the sum and difference of the integrals of each component of a quadrupolar doublet using the equations [16]:

$$M_+(\tau_2) = A[1 - B\exp(-\tau_2/T_{1Z})] \quad (1)$$

$$M_-(\tau_2) = C + D\exp(-\tau_2/T_{1Q}) \quad (2)$$

which differ from those predicted theoretically [17], since they take into account possible experimental imperfections.

Distinct relaxation times could be measured for deuterons belonging to the two phenyl rings α (far from the N–O group) and β (close to the N–O group) since the two groups of deuterons correspond to separate quadrupolar doublets in the ^{2}H spectrum.

3. Results

3.1. *Dielectric measurements*

Typical relaxation spectra collected for particular phases of HAB are presented in figures 2–4 in the form of Cole–Cole diagrams resulting from the well known

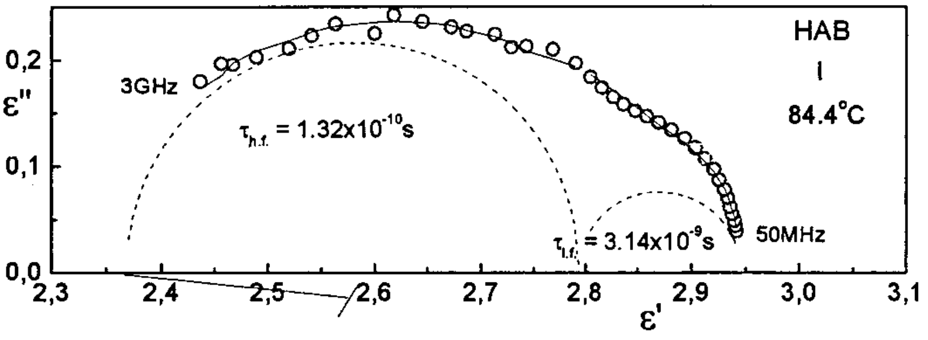

Figure 2. Cole–Cole plot for the isotropic phase of HAB. The spectra were obtained by the TDS method. Two relaxation processes were separated according to equation (4) with the relaxation times shown in the figure. The l. f. process was assumed to be a Debye process ($\alpha_1 = 0$); for the h. f. process $\alpha_2 \approx 0.06$.

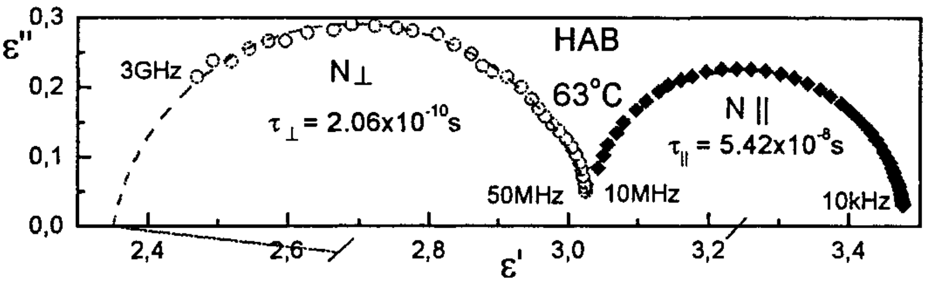

Figure 3. Cole–Cole plots for the nematic phase of HAB. The l. f. process is excellently described by the Debye equation (3) with $\alpha=0$. The h. f. process exhibits a distribution of relaxation times characterized by $\alpha \approx 0.05$. As can be seen, the static permittivities give a positive dielectric anisotropy: $\Delta\varepsilon=\varepsilon_{s\|}-\varepsilon_{s\perp}\approx+0.45$.

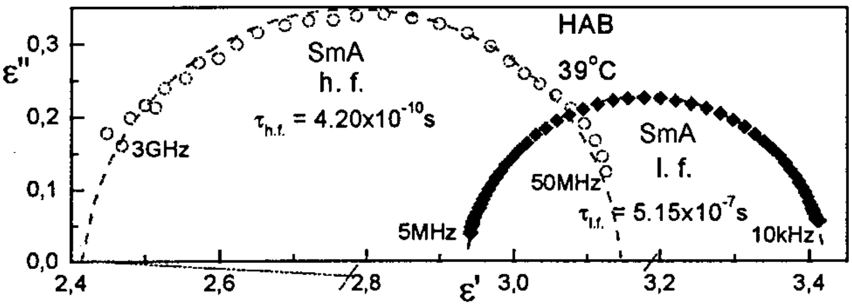

Figure 4. Cole–Cole plots for the smectic A phase of HAB. The l. f. process is well described by the Debye equation (3) with $\alpha=0$. The h. f. process exhibits a distribution of relaxation times characterized by $\alpha \approx 0.03$. Because the sample alignment in the SmA phase was not perfect (this especially concerns the TDS measurements) the circles overlap, in contrast to the behaviour seen in the N phase case, see figure 3.

equation

$$\frac{\varepsilon^*-\varepsilon_\infty}{\varepsilon_s-\varepsilon_\infty}=\frac{1}{1+(i\omega\tau)^{1-\alpha}} \tag{3}$$

where ε_s and ε_∞ are the static and high frequency permittivities, respectively, and α characterizes a distribution of the relaxation times τ. Open symbols indicate the spectra obtained with the aid of the TDS set-up, whereas filled symbols correspond to the data from the impedance analyser.

In the isotropic phase (figure 2) the l. f. and h. f. processes merge, giving one broad relaxation spectrum. The corresponding relaxation times can be calculated by fitting the spectrum to a model function assuming two relaxation processes

$$\varepsilon^*-\varepsilon_\times=\frac{\delta_1}{1+(i\omega\tau_1)^{1-\alpha_1}}+\frac{\delta_2}{1+(i\omega\tau_2)^{1-\alpha_2}} \tag{4}$$

where $\delta_1=\varepsilon_s-\varepsilon_{s2}$ and $\delta_2=\varepsilon_{s2}-\varepsilon_\infty$ are the strengths (increments) of the two relaxation processes and depend upon the dipole moments responsible for a given relaxation process ($\delta \sim \mu^2$). τ-values corresponding to both processes observed differ by a factor of *c*. 25 in the I phase, by ~300 in the N phase and by ~1 300 in the SmA phase (figure 5).

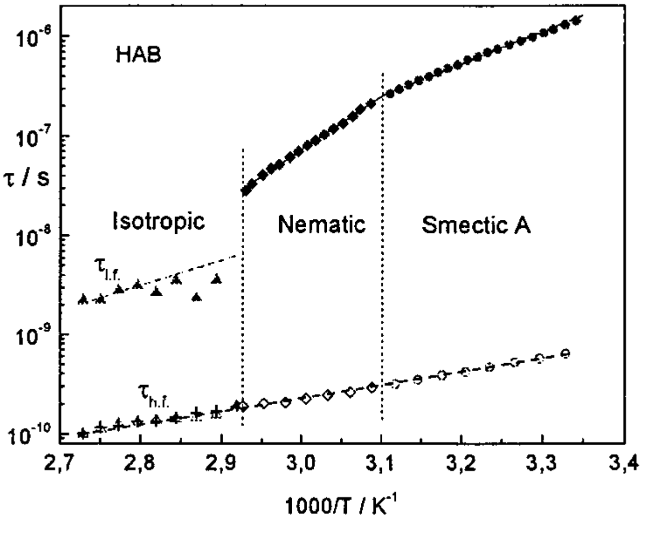

Figure 5. The relaxation times determined from the analysis of the dielectric relaxation spectra in different phases of HAB. In the isotropic phase two sets of points are shown: the triangles were obtained from the analysis of the TDS spectra measured with a 10 ns time window (compare figure 2); the crosses from the spectra collected with a 5 ns time window in which the contribution from the l. f. process can be neglected. However, only for four high temperature points was the separation of both relaxation processes reliable.

Table 1. The pre-exponential factor τ_0 (in s) and the activation enthalpy ΔH (in kJ mol^{-1}) according to the Arrhenius equation, $\tau = \tau_0 \exp(\Delta H/RT)$, for the relaxation processes in the isotropic and LC phases of HAB as determined from the dielectric relaxation studies.

	Isotropic		Nematic		Smectic A	
Process	τ_0	ΔH	τ_0	ΔH	τ_0	ΔH
l. f.	$10^{-13.341}$	46.7 ± 5	$10^{-23.038}$	101.5 ± 3	$10^{-16.194}$	59.3 ± 2
h. f.	$10^{-13.513}$	25 ± 3	$10^{-13.513}$	25 ± 3	$10^{-13.513}$	25 ± 3

The calculated relaxation times are shown in figure 5 as Arrhenius plots. The slopes of the lines give the activation enthalpy $\Delta H = R(\partial \ln\tau / \partial T^{-1})$ (R = gas constant). The values of ΔH are listed in table 1.

3.2. *NMR studies*

^{2}H T_{1Q} and T_{1Z} spin-lattice relaxation times are linked to the spectral densities $J_1(\omega_0)$ and $J_2(2\omega_0)$ through the relationships:

$$\frac{1}{T_{1Z}} = J_1(\omega_0) + 4J_2(2\omega_0) \tag{5}$$

$$\frac{1}{T_{1Q}} = 3J_1(\omega_0) \tag{6}$$

where ω_0 is the Larmor frequency. The spectral densities, which can also be obtained from the autocorrelation functions of the motions using Fourier transforms, contain all the dynamic information, but their extraction is not straightforward and requires the use of appropriate theoretical models. Moreover the dynamics of liquid crystals are complex, being characterized by the superposition of different types of motions, such as molecular reorientations, internal isomerizations and collective fluctuations. The theoretical models proposed to describe these motions lead to expressions of the autocorrelation functions containing parameters specific to the different dynamic contributions.

Several models can be used to describe the overall molecular reorientation of cylindrical molecules in uniaxial phases: the most important ones are those proposed by Nordio *et al* [18, 19], Polnaszek and Freed [20] (anisotropic viscosity), and Vold and Vold [21] (third rate anisotropic viscosity), all of them considering these motions as a small step diffusional rotation in a Maier–Saupe mean field potential. Internal motions can be considered to be decoupled from the overall molecular reorientation, and are usually described by the small step diffusion [22, 23] or the strong collision model [24]. On the basis of these models the spectral densities J_{m_L} $(m_L\omega_0)$ can be calculated as a function of the diffusional coefficients which describe both overall molecular and internal motions. Collective motions and, in particular, order director fluctuations (ODF), can be considered not to be coupled to the overall molecular motions due to the very different dynamic range experienced: their contribution to the spectral densities can therefore be considered additive and evaluated using theories proposed by Pincus [25] and Blinc *et al.* [26]. These models predict a null contribution to $J_2(2\omega_0)$, and a typical $\omega_0{}^{-1/2}$ frequency dependence for $J_1(\omega_0)$:

$$J_1^{\mathrm{DF}}(\omega_0) = \frac{3\pi^2}{2}(\nu_{\mathrm{q}})^2 \left[d^2_{00}(\beta_{i,Q_i})\right]^2 \left[d^2_{00}(\beta_{M,i})\right]^2 \times (S_{ZZ})^2 T \frac{a_{\mathrm{DF}}}{\sqrt{\omega_0}} \tag{7}$$

where ν_{q} is the quadrupolar coupling constant, $d^2_{00}(\beta)$ are the reduced Wigner matrices, β_{i,Q_i} is the angle between the C–D bond and the axis about which the internal rotation takes place, $\beta_{\mathrm{M},i}$ is the angle between this axis and the molecular long axis, S_{ZZ} is the principal order parameter and a_{DF} depends on macroscopic parameters such as the average Frank elastic constant, the viscosity coefficient and the autodiffusion translational constant.

The autocorrelation functions $g_{m_{\mathrm{L}}m_{\mathrm{M}}}(t)$, relative to the overall molecular motions, can be expressed, following Vold and Vold [21], as a sum of decreasing exponential functions:

$$g_{m_{\mathrm{L}}m_{\mathrm{M}}}(t) = c_{m_{\mathrm{L}}m_{\mathrm{M}}} \sum_j a^j_{m_{\mathrm{L}}m_{\mathrm{M}}} \exp\left(-t \middle/ \tau^j_{m_{\mathrm{L}}m_{\mathrm{M}}}\right) \tag{8}$$

For a deuteron belonging to a molecular fragment which also experiences an internal motional process, the following expression for the spectral density $J_{m_{\mathrm{L}}}(m_{\mathrm{L}}\omega_0)$ can be derived [1]:

$$J_{m_{\mathrm{L}}}(m_{\mathrm{L}}\omega_0) = \frac{3\pi^2}{2}(\nu_{\mathrm{q}})^2 \sum_{m_{\mathrm{M}}=-2}^{m_{\mathrm{M}}=2} \sum_{m_{\mathrm{R}}=-2}^{m_{\mathrm{R}}=2} c_{m_{\mathrm{L}}m_{\mathrm{M}}} \left[d^2_{m_{\mathrm{R}}0}(\beta_{i,Q_i})\right]^2 \left[d^2_{m_{\mathrm{M}}m_{\mathrm{R}}}(\beta_{\mathrm{M},i})\right]^2 \sum_j a^{(j)}_{m_{\mathrm{L}}m_{\mathrm{M}}} \frac{\left(\tau^{(j)}_{m_{\mathrm{L}}m_{\mathrm{M}}}\right)^{-1} + (1-\delta_{m_{\mathrm{R}}})D_{\mathrm{R}}}{(m_{\mathrm{L}}\omega_0)^2 + \left[\left(\tau^{(j)}_{m_{\mathrm{L}}m_{\mathrm{M}}}\right)^{-1} + (1-\delta_{m_{\mathrm{R}}})D_{\mathrm{R}}\right]^2} \tag{9}$$

where D_{R} is the diffusion coefficient for the internal motion, which is described by the strong collision model. The correlation times $\tau^{(j)}_{m_L m_M}$ can be expressed in terms of diffusional coefficients of overall molecular motions on the basis of the Nordio model:

$$\frac{1}{\tau^{(j)}_{m_L m_M}} = \frac{6D_\perp}{b^{(j)}_{m_L m_M}} + m_M^2\left(D_\parallel - D_\perp\right). \qquad (10)$$

The coefficients $a^{(j)}_{m_L m_M}$, $b^{(j)}_{m_L m_M}$ and $c_{m_L m_M}$ are tabulated in ref. [21] as a function of the principal order parameter. $D_\parallel$ and $D_\perp$ are the principal components of the diffusional tensor, diagonalized in a molecular frame, and describe the spinning and tumbling of the molecular long axis, respectively.

In our case the internal motions to consider are relative to the rotation of the phenyl rings α and β about their *para*-axis. The angles β_{i,Q_i} have been fixed to 60° while the angle between the two *para*-axes has been fixed to the value of 17°, previously determined from a ^{2}H NMR study [10].

At each Larmor frequency the trend of relaxation times, which regularly increase with increasing temperature, indicates a motional narrowing regime ($\omega_0\tau_c \approx 1$), in agreement with what is usually found for low molecular mass liquid crystals [27, 28].

In this work we have analysed all relaxation data, at the three Larmor frequencies, using a Global Target approach by assuming an Arrhenius behaviour for the diffusional coefficients within each mesophase. This global analysis was performed by means of the 'CAGE' software [3] and is based on a non-linear least squares minimization procedure. The presence of a principal minimum, giving very good agreement between experimental and calculated spectral densities (see figure 6), corresponding to a well-defined set of 'best values' for the diffusional coefficients, was revealed.

The diffusional constants of the motions found from the fitting procedure are shown in table 2; the 'a_{DF}' constant for the collective motion is 3.3×10^{-9} and $1.0\times10^{-9}\,K^{-1}\,s^{1/2} rad^{-3/2}$, for the nematic and smectic A phases respectively, indicating a very small contribution of the director fluctuation to the spectral densities $J_1(\omega_0)$ of the aromatic deuterons, in agreement with previous results [3, 11].

The diffusional coefficients obtained for the spinning and tumbling molecular motions, as well as for the internal motions of the α and β rings, are shown in figure 7.

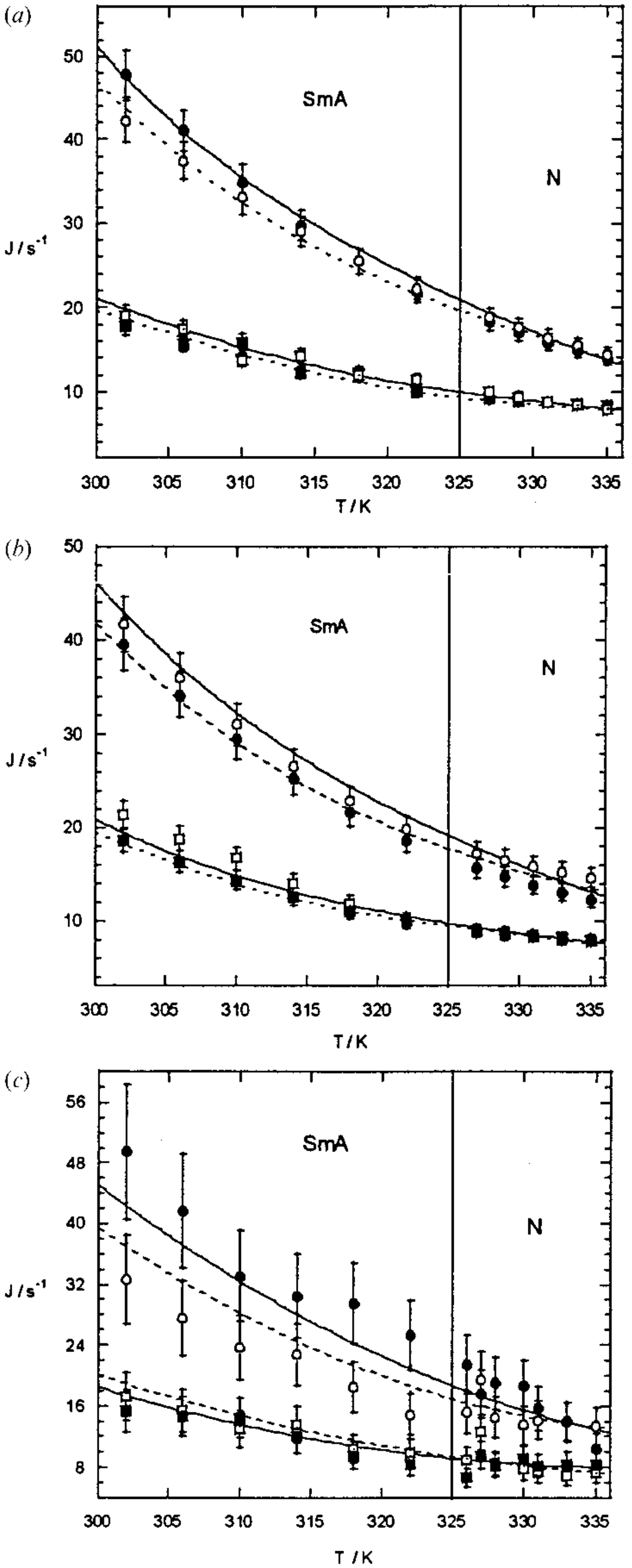

Figure 6. Experimental and calculated spectral densities vs temperature for HAB-d$_{12}$ in the nematic and smectic A phases. $J_1(\omega_0)$ and $J_2(2\omega_0)$ are indicated by circles and squares, respectively. Filled symbols refer to the α ring and empty symbols to the β ring. Solid and dotted curves refer to the fitted spectral densities of the α and β rings, respectively. The deuterium Larmor frequency is (*a*) 10 MHz, (*b*) 46.04 MHz and (*c*) 61.38 MHz.

Table 2. The pre-exponential factor D^{∞} (in s^{-1}) and the activation energy ΔH (in $kJ\,mol^{-1}$) according to the Arrhenius equation, $D = D^{\infty}\exp(-\Delta H/RT)$, for the molecular motions in the nematic and smectic A phases of HAB as determined from deuterium NMR studies.

	Nematic		Smectic A	
Motion	D^{∞}	ΔH	D^{∞}	ΔH
Tumbling	$10^{16.21}$	53.7	$10^{13.71}$	39.2
Spinning	$10^{14.55}$	32.0	$10^{13.55}$	25.5
Internal motion (α)	$10^{14.34}$	30.0	$10^{15.09}$	35.0
Internal motion (β)	$10^{13.60}$	25.0	$10^{15.25}$	35.0

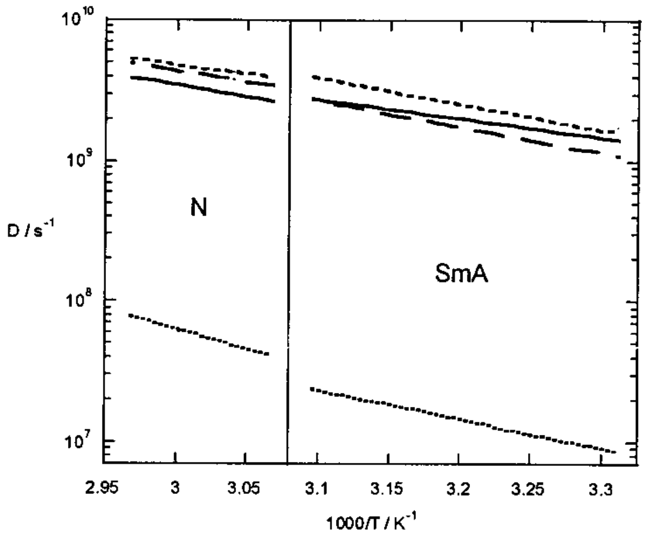

Figure 7. Diffusional coefficients $D_{\parallel}$ (solid line), $D_{\perp}$ (dotted line), $D_{R\alpha}$ (long-dashed line), $D_{R\beta}$ (short-dashed line) vs 1000/T, in the nematic and SmA phases.

4. Discussion

The dipole structure of the molecule, see figure 1, indicates that the DS method detects whole molecular motions around the principal inertia axes. Taking into account the ratio of the dielectric increments, $\delta\varepsilon = \varepsilon_s - \varepsilon_{\infty}$, observed in the isotropic phase: $\delta_{h.f.}/\delta_{l.f} \approx (\mu_t/\mu_l)^2 = \tan^2\beta$ one obtains $\beta \approx 59°$ for the angle between the dipole moment of the azoxy group (1.7 *D*) and the molecular long axis, which is markedly smaller than earlier postulated (70° [29]) and results in a positive dielectric anisotropy, $\Delta\varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp} > 0$ (compare figure 3).

Figure 5 shows that the low frequency relaxation time exhibits a jump at the I–N transition and passes smoothly at the N–SmA transition. The high frequency relaxation time passes smoothly through all phases. The activation barriers hindering both molecular motions differ considerably even in the isotropic phase (table 1). It is characteristic behaviour that the activation enthalpy for the l. f. process in the N phase is markedly larger than in the SmA phase, similar behaviour being observed for other compounds (e.g. [30]). Madhusudana *et al.* [31] have suggested that the lowering of the activation barrier is due to an anisotropic packing effect: the volume expansion mainly causes an expansion within the smectic layer whereas the layer spacing hardly varies with temperature and this favours a lowering of the activation energy in the smectic A phase. The dipole correlations in the SmA phase postulated by de Jeu *et al.* [8] show no influence on the h. f. relaxation process—the relaxation time $\tau_{h.f.}$ changes continuously with temperature through all phases (figure 5).

The experimental spectral densities, shown in figure 6, decrease regularly with increasing temperature, without discontinuities at the nematic–smectic A phase transition, indicating a motional narrowing regime for the dynamic processes mainly contributing to the deuterium relaxation. From the fitting analysis we obtain values largely typical of diffusional coefficients, in agreement with those found for low-molar mass liquid crystals [27, 28, 32]. As shown in figure 7 the diffusional coefficients for the internal reorientations of the two phenyl rings (D_{α} and D_{β}) are of the same order of magnitude as the diffusional coefficient for the spinning motion ($D_{\parallel}$), in both mesophases, while the tumbling motion is slower than the other reorientations by about 1.5–2 order of magnitude.

The contribution of director fluctuations to the spectral densities $J_1(\omega_0)$ of the aromatic deuterons, is very small, as indicated by the value of 'a_{DF}' obtained from the fitting. This is in agreement with previous results [3, 11] and is due either to the high Larmor frequency or to the critical angle between the C–D bond and the *para*-axis, which is close to the 'magic angle'.

As mentioned previously, the determination of the diffusional coefficient $D_{\perp}$ generally depends strongly on the number of ^{2}H NMR relaxation measurements, which means that more than one Larmor frequency and/or measurements at different angles between the local director and the magnetic field must be performed. In our case the diffusional constant for the tumbling motion is obtained unambiguously, in both mesophases, by combining ^{2}H NMR relaxation data performed at three different Larmor frequencies. Using the Arrhenius equation the activation energies for individual motional processes were calculated and listed in table 2.

In this context, the comparison between ^{2}H NMR and DS results, which are both self-consistent, is an important test of the validity of the theoretical models. Moreover, the theory, developed for the N phase, has been extended to the SmA phase.

According to Kozak *et al.* [33], the l. f. relaxation time is solely connected with $\tau^1_{0,0}$ in Wigner matrices notation because the h. f. process observed at parallel geometry is shifted to the GHz range and thus does not influence the spectra measured in the MHz range. Therefore, we may use the formula derived by Zakharov and Dong [5, 6]:

$$\tau_{\mathrm{l.f.}} = \left[D_{\perp} \frac{2-2S}{1+2S} \right]^{-1} = \tau^1_{0,0} \qquad (11)$$

where $\tau_{\mathrm{l.f.}}$ is the experimental dielectric low frequency time, shown in figure 5, and S is the nematic orientational order parameter S_{zz}. S_{zz} determined from ^{2}H NMR measurements is shown in figure 8. In figures 9 and 10 a comparison between the experimental dielectric relaxation times and those calculated from NMR results are shown.

An excellent agreement between the relaxation times obtained using the two spectroscopic methods can be observed in spite of the fact that both methods yield essentially different relaxation times which arise from different rank values of the Wigner matrices: $L=1$ for dielectric and $L=2$ for NMR relaxations. According to [5], in the nematic phase of 8OCB the ratio $\tau^1_{0,0}/\tau^2_{0,0} \geqslant 10$. Additionally, DS yields the (macroscopic) relaxation times, whereas NMR results lead to the (molecular) correlation times that may be different.

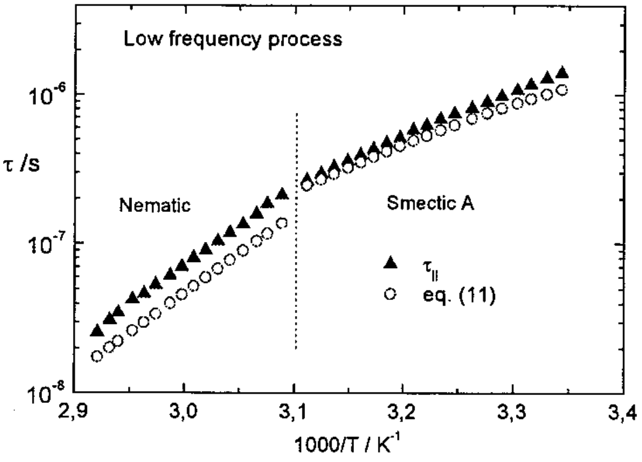

Figure 9. Comparison of the low frequency relaxation times determined from DS studies and calculated from the NMR diffusion coefficient $D_{\perp}$ using equation (11). The order parameter S was obtained from the NMR data.

For the l. f. relaxation time, the relationship (11) that was developed for the N phase gives, in our case, an even better agreement between dielectric and NMR results in the SmA phase. This result could in principle be fortuitous, and we believe more experimental data are needed to verify the possibility of extending equation (11) to smectic A phases; nevertheless, this result is very encouraging since in the case shown here, the tumbling motion was independently and reliably characterized by both experiments.

The h. f. relaxation time measured in the perpendicular geometry in the N phase may consist of two components: $\tau^1_{1,0}$ and $\tau^1_{1,1}$ ([33, 34]). The ratio of amplitudes (increments) for both processes is $(1-S)\mu_l^2/(1-S/2)\mu_t^2 \sim 1$ for the present case which

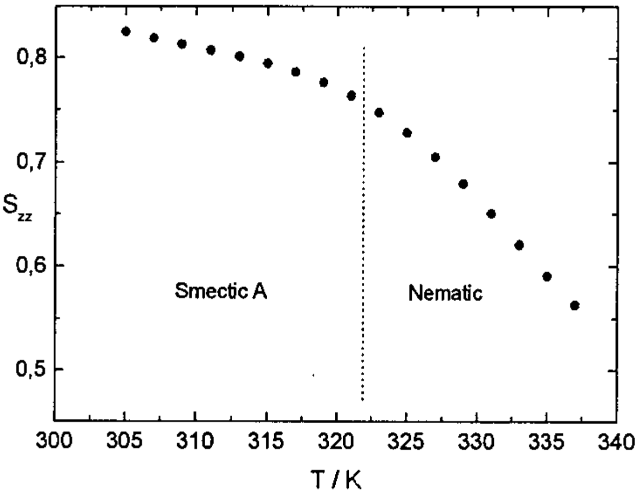

Figure 8. The orientational order parameter determined from NMR measurements in the N and SmA phases of HAB.

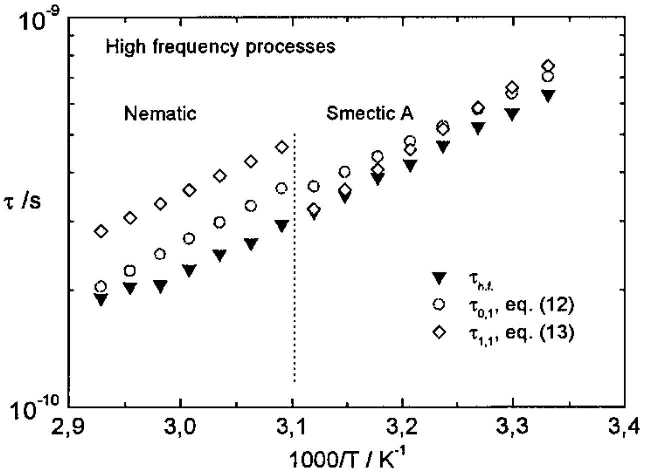

Figure 10. Comparison of the high frequency relaxation times obtained from the DS measurement and calculated using equations (12) and (13) from the NMR data as described in the text.

means that $\tau_{\text{h.f}}$ is dominated by $\tau_{1,1}^{1}$. From dielectric studies of other nematics it is known [35, 36] that both relaxation times, $\tau_{0,1}^{1}$ and $\tau_{1,1}^{1}$, are similar and depend slightly on temperature. Taking this into consideration we can approximately compare the DS and NMR results using the formula [5, 6]

$$\tau_{0,1}^{1} = \left(D_{\parallel} + D_{\perp}\frac{1+2S}{1-S}\right)^{-1} \approx \tau_{\text{h.f.}}. \qquad (12)$$

On the other hand, Coffey and Kalmykov [34] derived the expression,

$$\tau_{1,1}^{1} = \tau_{\text{D}}\frac{2+S}{2+(2+S)\Delta - S/2}, \qquad (13)$$

where τ_{D} can be assumed as the extrapolation of the l. f. relaxation time from the isotropic to LC phases, and $\Delta = (D_{\parallel}/D_{\perp}\text{-}1)/2$.

Figure 10 presents the comparison of $\tau_{\text{h.f}}$ and the correlation times calculated using equations (12) and (13) with diffusion coefficients and order parameters derived by NMR results. Even in this case a very good agreement can be observed, not only in the nematic phase, but also in the smectic A phase, notwithstanding the many assumptions and approximations used for the data analysis.

In conclusion, fully consistent relaxation times have been obtained using both the spectroscopic methods employed to study the molecular dynamics in the nematic and smectic A phases of HAB. Further work is in progress in order to verify the possibility of extending this conclusion to other thermotropic liquid crystals.

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