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A ^{2}H NMR Study of Orientational Order and Spin Relaxation in the Mesogen p-Hexyloxybenzylidene-p′-Fluoroaniline

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A ^{2}H NMR STUDY OF ORIENTATIONAL ORDER AND SPIN RELAXATION IN THE MESOGEN p-HEXYLOXYBENZYLIDENE-p'-FLUOROANILINE

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Abstract

^{2}H NMR measurements of orientational order and spectral densities in the nematic, smectic A and smectic B phases of *p*-hexyloxybenzylidene-*p*'-fluoroaniline (FAB-OC6) deuterated in the benzylidene methine group and in the aniline ring are reported. The orientational order parameters obtained indicate a high order of the aromatic core in the smectic phases. The Wimperis pulse sequence was used to measure the Zeeman and quadrupolar spin-lattice relaxation times at the frequency of 46.04 MHz. The spectral densities are discussed within rotational diffusion models for the reorientational motions, taking also into account internal rotations and collective fluctuations.

INTRODUCTION

Deuterium Nuclear Magnetic Resonance spectroscopy and nuclear spin relaxation measurements have revealed powerful means for probing structure, ordering and dynamics in liquid crystals[1]. In recent years numerous NMR studies of liquid crystals have employed the deuterium probe to measure the orientational order and to obtain information on the structure of mesogenic molecules and their organisation within the different mesophases. The deuterium Zeeman (T_{1Z}) and quadrupolar (T_{1Q}) spin-lattice relaxation times have been employed for the separation of two spectral densities of motion, $J_1(\omega)$ and $J_2(\omega)$, which can be used to obtain information on the dynamics in liquid crystalline phases[2]. Two different models have been proposed for the reorientational motions of cylindrical molecules in uniaxial phases; in both cases rotational diffusion tensors have been used to describe these motions. In the model proposed by Nordio[3] the tensor is diagonal in the molecular frame and is described by two diffusion coefficients, $D_{//}$ and $D_{\perp}$, relative to the motions about and of the long molecular axis, respectively. In the *third rate anisotropic viscosity model*[4] the diffusion tensor, diagonal in the laboratory frame, is characterised by three diffusion coefficients: D_α and D_β describe the spinning and tumbling motions of the long molecular axis, whereas D_γ is relative to the rotation of the molecule around its long axis. The internal motions, either considered as free rotations or jumps among sites, have been usually superimposed to the molecular reorientations[2]. The contribution of collective order fluctuations to relaxation, at the frequencies normally used in NMR experiments, can be safely neglected in the smectic phases[2,5], while it has been found of relevance in the nematic phase of some compounds[6].

Several studies of the dynamics in the nematic and disordered smectic phases of mesogens have been reported in the literature[1,2], while the ordered smectic phases have been studied only in a limited number of cases[7]. It seemed thus interesting to apply the above mentioned models to FAB-OC6 (see Figure 1), a compound which exhibits, in addition to a nematic and a smectic A phase, a highly ordered smectic B phase[8].

This smectogen, partially deuterated in the aniline ring and in the alkoxy chain, has been previously studied by us[9]. The trend of the C-D quadrupolar splittings with the temperature suggested that, on entering the smectic B phase, a freezing of the conformational flexibility of the two methylene groups nearest to the aromatic core occurs. Only local order parameters, however, could be obtained in the previous work, thus preventing a more detailed analysis. Moreover the presence of a single type of deuteron in the core precluded a full analysis of the overall dynamics. Therefore we decided to deuterate FAB-OC6 on the linkage group, in addition to partial deuteration of the aniline ring, in order to perform a complete study of the orientational order and relaxation behaviour of the entire molecule. In this paper the results concerning the molecular core are reported; they allow a reinvestigation of the alkoxy chain dynamics, which is currently in progress.

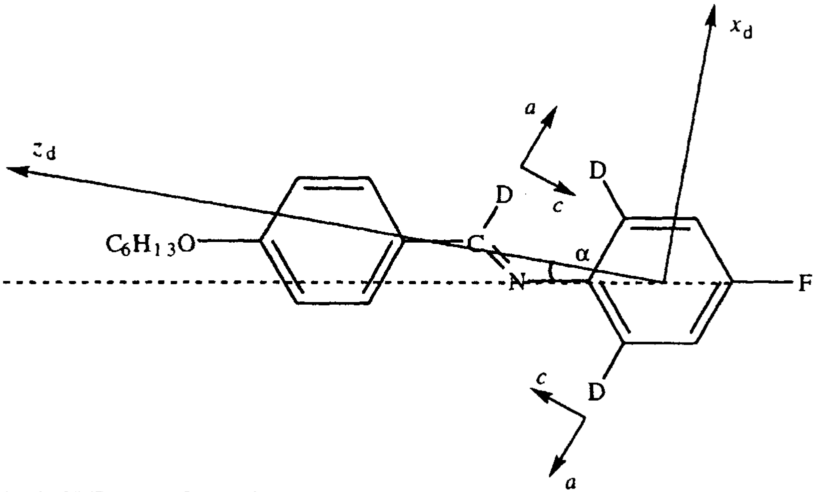

FIGURE 1 Molecular structure of FAB-OC6 and location of the local and molecular reference frames.

EXPERIMENTAL

FAB-OC6-d_3 has been synthesised following the procedure described in the literature[10] starting from suitably deuterated compounds. To a stirred suspension containing 8.7 mmol of pyridinium chlorochromate and 1.7 mmol of sodium acetate in 10 ml of anhydrous dichloromethane, 5 mmol of 4-hexyloxybenzyl-d_2-alcohol (obtained by reduction of 4-hexyloxybenzoic acid with $LiAlD_4$) were added. The mixture was stirred for 2 h and then extracted with anhydrous ether; the solvent was removed by distillation under reduced pressure, giving approximately 80% of 4-hexyloxy-d-benzaldehyde. The deuteration grade, determined by means of ^{1}H NMR, was found to be higher than 97%. The aldehyde was allowed to reflux for several hours in anhydrous benzene with 4-fluoroaniline-2,6-d_2, prepared as described in ref. 9. The crude product was purified by several recrystallizations from anhydrous ethanol.

The phase diagram of undeuterated FAB-OC6 has been reported in ref. 8. The deuterated compound under investigation shows similar transition temperatures, even if it shows appreciable biphasic regions (0.5 degrees at the N-S_A transition and 1.5 degrees at the S_A- S_B one).

^{2}H NMR experiments were performed on a Bruker AMX-300 spectrometer working at 46.04 MHz. The 90-degree pulse was 8 μs. A relaxation delay of 200 ms was used in all the experiments. The number of scans ranged between 1600 and 10000. The temperature control was good to 0.1 °C. ^{2}H NMR spectra were recorded as a function of temperature in the range 319-334 K, on cooling from the isotropic phase. ^{2}H spin-lattice Zeeman (T_{1Z}) and quadrupolar (T_{1Q}) relaxation times were measured in the same temperature range by means of the Wimperis pulse sequence $(90_0\text{-}2\tau_1\text{-}67.5_{270}\text{-}2\tau_1\text{-}45_{90}\text{-}\tau_1\text{-}45_{90}\text{-}\tau_2\text{-}45_0)$[11], with $\tau_1 = 6$ μs, experimentally optimised.

RESULTS AND DISCUSSION

Orientational order

The ^{2}H NMR spectra of FAB-OC6-d_3, recorded at different temperatures, show similar features in all the liquid crystalline phases, as can be observed in the selection reported in Figure 2. The methine deuteron gives rise to the outer doublet, with splitting due to the quadrupolar interaction, and line broadening ascribable to minor dipolar interactions with the aromatic protons and deuterons. The inner doublet of doublets is attributed to the aromatic deuterons, the larger splitting arising from the quadrupolar interaction and the smaller one from the dipolar coupling with the proton nuclei on the same ring. Both interactions are averaged by fast rotation of the phenyl ring around its *para* axis.

The dipolar and the two quadrupolar splittings were used to determine the local order parameters on the basis of equations (1) and (2), respectively[12]:

$$\Delta D_{DH} = -2K_{DH}\frac{S_{DH}}{r_{DH}^3} \tag{1}$$

$$\Delta\nu_q^{(i)} = \frac{3}{2}\nu_q\left[S_{aa}^{(i)} + \frac{\eta}{3}\left(S_{cc}^{(i)} - S_{bb}^{(i)}\right)\right] \tag{2}$$

where $K_{DH} = \frac{\gamma_D\gamma_H h}{4\pi^2}$, r_{DH} is the internuclear D-H distance, ν_q is the quadrupolar coupling constant (185 kHz for both aromatic and methine deuterons[13]) and η is the asymmetry parameter (here assumed 0.03[14]). S_{DH} is the order parameter relative to the internuclear D-H direction, whereas $S_{aa}^{(i)}$, $S_{bb}^{(i)}$ and $S_{cc}^{(i)}$ are the order parameters in the local reference frames shown in Figure 1. The geometrical data have been taken according to the X-ray structure of benzylideneaniline[15]. In particular, the angles formed by the aromatic and methine C-D bonds with the *para* axis of the aniline ring are taken 61° and 118°, respectively, and the internuclear distance, r_{DH}, 2.46 Å. The molecular fragment formed by the fluorinated ring and the central linkage -CH=N- is assumed to be planar and rigid, with the exception of a rapid 180° flip of the ring about its *para* axis.

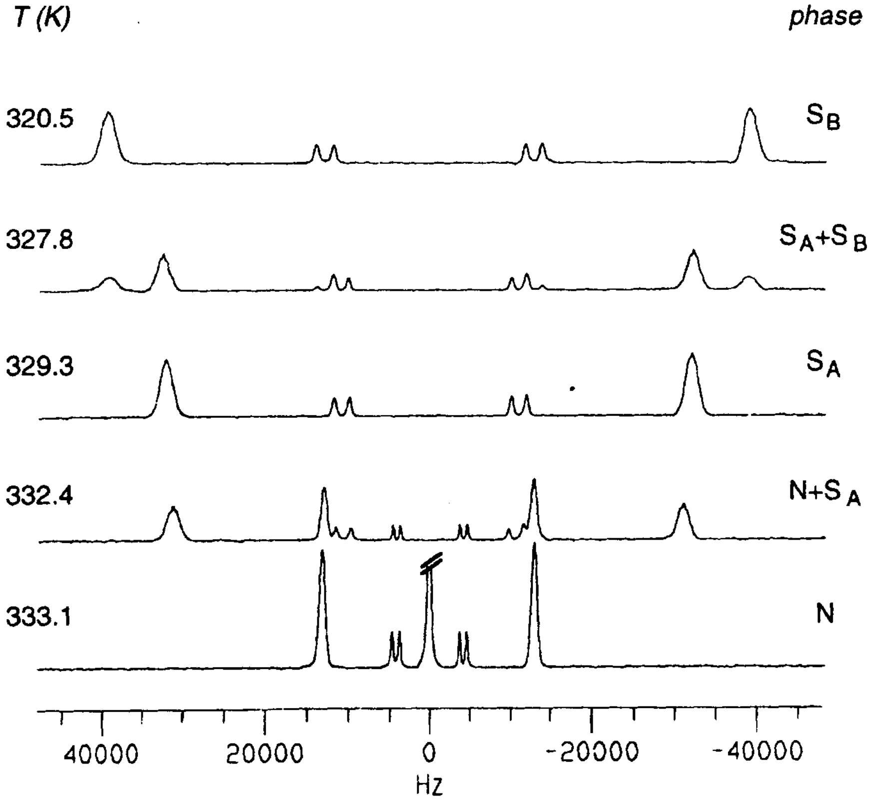

FIGURE 2 ^{2}H-NMR spectra of FAB-OC6-d$_3$ at different temperatures.

Equations (1) and (2) can be rewritten in terms of S^d_{xx}, S^d_{yy} and S^d_{zz}, the order parameters in the frame x_d, y_d, z_d, fixed on the molecular core, where the Saupe matrix of the planar fragment is diagonal[16]. In this frame, the x_d and z_d axes are in the plane of the fragment.

The signs of the splittings cannot be inferred directly from the spectra, but reasonable assumptions can be made on the basis of the molecular structure. The dipolar couplings are certainly negative, since the related D-H internuclear directions must lie nearly parallel to this axis, as generally found for calamitic mesogens. However, nothing can be said about the signs of the quadrupolar splittings, since the location of the long molecular axis is not known *a priori*, and it is therefore not known whether the C-D bonds under investigation form angles larger or smaller than 54.7° with respect to the molecular axis. All the four possible combinations of signs have therefore been considered for the two quadrupolar splittings and a computation of the principal order parameter, S^d_{zz}, and of the biaxiality, $S^d_{xx} - S^d_{yy}$, has been performed for each combination at each temperature. Only the case where the two quadrupolar splittings were negative gave physically acceptable results, reported in Figure 3.

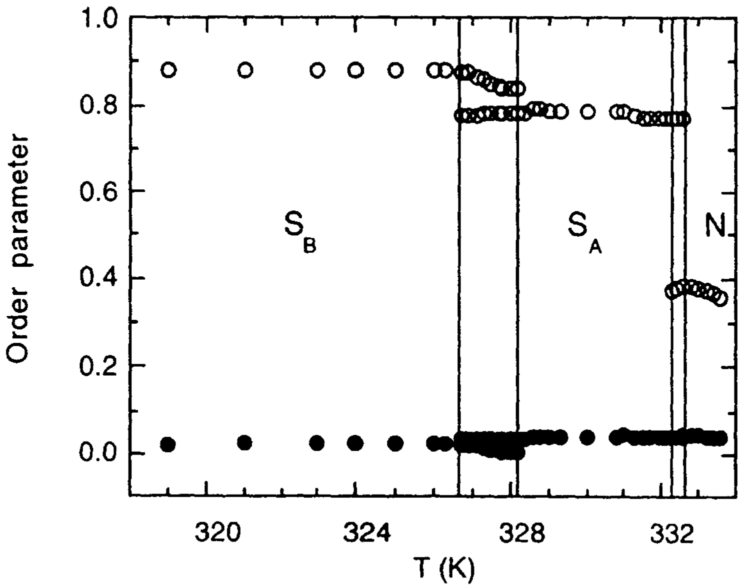

FIGURE 3 Principal order parameter S^d_{zz} (open circles) and biaxiality $S^d_{xx} - S^d_{yy}$ (filled circles) of the aromatic core of FAB-OC6 as a function of temperature.

The molecular frame was found to be located with its z_d axis forming with the *para* axis of the aniline ring an angle α of 7.3°, 8.3° and 9.3° in the nematic, smectic A and smectic B phases, respectively (see Figure 1).

The order parameter S_{zz}^d increases by lowering the temperature in the nematic phase, shows a jump at both the N-S_A and S_A-S_B phase transitions, but remains almost constant within the single smectic phases, where it presents remarkably high values, also observed for homologous compounds[17]. The biaxiality $S_{xx}^d - S_{yy}^d$ shows an almost constant value of 0.04 in both the nematic and the smectic A phase, and of 0.02 in the smectic B one. In the two biphasic regions a peculiar behaviour of both S_{zz}^d and $S_{xx}^d - S_{yy}^d$ is observed, which has not been fully understood so far.

Dynamics

The Wimperis pulse sequence[11] allowed us to contemporaneously determine the Zeeman (T_{1Z}) and quadrupolar (T_{1Q}) spin-lattice relaxation times for both the methine and the aromatic deuterons. In this experiment the sum and difference of the intensity of each component of a doublet, split by the quadrupolar interaction, obey the following equations:

$$M_+(\tau_2) = \sqrt{2}K[1 - exp(-\tau_2/T_{1Z})] \tag{3a}$$

$$M_-(\tau_2) = \frac{3}{2}K exp(-\tau_2/T_{1Q}) \tag{3b}$$

The values of the relaxation times thus obtained were used to calculate the spectral densities $J_1(\omega_0)$ and $J_2(2\omega_0)$, being:

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

$$\frac{1}{T_{1Q}} = 3J_1(\omega_0) \tag{4b}$$

where ω_0 is the Larmor frequency.

The values of the spectral densities calculated for the methine and aromatic deuterons at different temperatures are reported in Figure 4. Within the single phases an increase, particularly evident in the smectic B one, is observed on lowering the temperature. On going from the nematic to the smectic A phase, J_1 of the aromatic deuterons increases as expected, while J_1 of the methine deuteron shows an evident decrease. It must be considered that the J_2 values, which show irregular variations near the transition in both phases, are more affected by experimental errors. At the S$_A$-S$_B$ transition all the spectral densities increase discontinuously, as previously observed for transitions between disordered and ordered smectic phases[18]. The jump is clearly bigger for the J_2's, which in the smectic B phase become closer to the J_1's. In the case of the methine deuteron, the J_1/J_2 ratio, which is between 1.3 and 2.0 in the nematic and smectic A phases, is confined in a very narrow range (1.0-1.2) in the smectic B one.

The dynamics of FAB-OC6-d$_3$ in the biphasic regions is under investigation and will be reported in a future work.

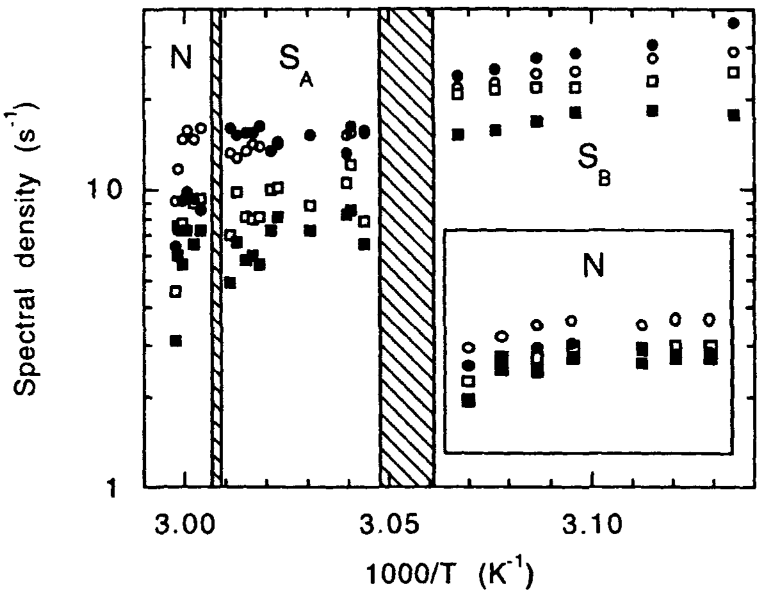

FIGURE 4 Spectral densities $J_1(\omega_0)$ (circles) and $J_2(2\omega_0)$ (squares) of FAB-OC6-d$_3$ in the different mesomorphic phases. Open and filled symbols refer to methine and aromatic deuterons, respectively. The dashed areas correspond to the biphasic regions.

The spectral densities $J_{m_L}(m_L\omega)$ can be calculated from the autocorrelation functions $G_{m_L}(t)$ through Fourier transformation:

$$J_{m_L}(m_L\omega) = \frac{3\pi^2}{2}(\nu_q)^2 \int_0^\infty G_{m_L}(t)\cos(m_L\omega t)dt \tag{5}$$

The autocorrelation functions are generally expressed by a sum of decreasing exponentials[3]. The spectral densities of the methine and aromatic deuterons can thus be expressed by equations (6) and (7), respectively:

$$J^{met}_{m_L}(m_L\omega_0) = \frac{3\pi^2}{2}(\nu_q)^2 \sum_{m_M=-2}^{2} c_{m_L m_M}[d^2_{m_M 0}(\beta_{M,Q_0})]^2 \times \sum_j a^{(j)}_{m_L m_M} \frac{(\tau^{(j)}_{m_L m_M})^{-1}}{(m_L\omega_0)^2 + (\tau^{(j)}_{m_L m_M})^{-2}} \tag{6}$$

$$J^{ar}_{m_L}(m_L\omega_0) = \frac{3\pi^2}{2}(\nu_q)^2 \sum_{m_M, m_R=-2}^{2} c_{m_L m_M}[d^2_{m_R 0}(\beta_{R,Q_R})]^2 [d^2_{m_M m_R}(\beta_{M,R})]^2 \times \sum_j a^{(j)}_{m_L m_M} \frac{(\tau^{(j)}_{m_L m_M})^{-1} + (1-\delta_{m_R 0})D_R}{(m_L\omega_0)^2 + [(\tau^{(j)}_{m_L m_M})^{-1} + (1-\delta_{m_R 0})D_R]^2} \tag{7}$$

where D_R is the rate constant relative to the motion of the aniline ring about its *para* axis, for which a superimposed free rotation model[19] has been assumed; $c_{m_L m_M}$ are the mean squares of the Wigner rotation matrices, d^2_{rs} are the reduced Wigner matrices and $a^{(j)}_{m_L m_M}$ represent normalised relative weights of each exponential function with time constant $\tau^{(j)}_{m_L m_M}$. β_{R,Q_R} is the angle between the aromatic C-D bond and the *para* axis of the aniline ring (61°) and $\beta_{M,R}$ is the angle between this axis and the molecular axis z_d, indicated as α in Figure 1; β_{M,Q_0}, assumed to be $(118-\alpha)°$, is the angle between the methine C-D bond and z_d;

In the *small step rotational diffusion* model proposed by Nordio[3], the correlation times $\tau^{(j)}_{m_L m_M}$ are expressed by:

$$\frac{1}{\tau^{(j)}_{m_L m_M}} = \frac{6D_\perp + m_M^2(D_{//} - D_\perp)}{b^{(j)}_{m_L m_M}} \tag{8}$$

where $D_{//}$ and $D_{\perp}$ are the diffusion rate constants relative to the molecular spinning and tumbling motions, respectively. The coefficients $a^{(j)}_{m_L m_M}$, $b^{(j)}_{m_L m_M}$ and $c_{m_L m_M}$ depend on the order parameter S^d_{zz} and are tabulated in ref. 4 for a Maier-Saupe potential. A non linear least squares fitting procedure was employed to determine at each temperature three unknowns ($D_{//}$, $D_{\perp}$ and D_R) from the four experimental values of spectral densities. The diffusion coefficients obtained are reported in Figure 5. In the nematic phase $D_{//}$ and D_R are very similar, whereas $D_{\perp}$ is sensibly smaller.

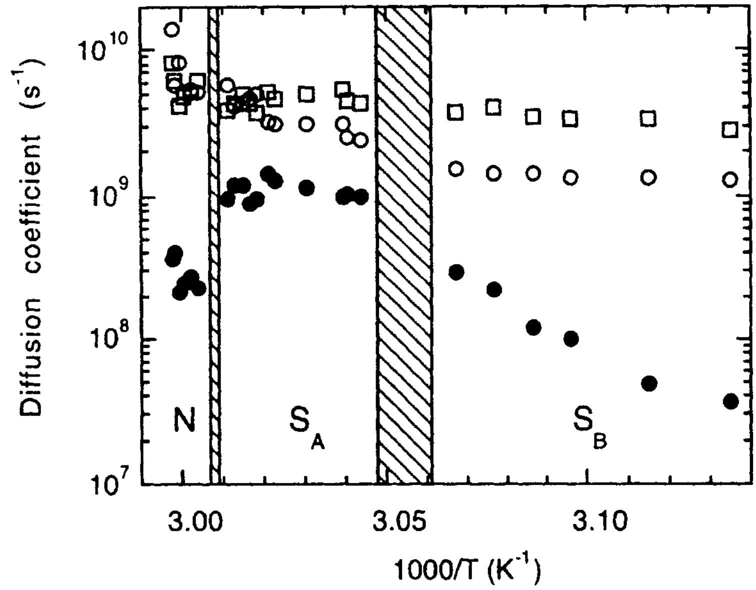

FIGURE 5 Diffusion coefficients $D_{//}$ (open circles), $D_{\perp}$ (filled circles) and D_R (open squares) of FAB-OC6 in the different mesomorphic phases.

All three coefficients decrease with decreasing temperature and tend to a constant value on approaching the N-S$_A$ phase transition. The low values of $D_{\perp}$ are not surprising; the anomalous behaviour is the increase of this coefficient entering the smectic A phase, which, to the best of our knowledge, has been observed only for two mesogens[18]. On the contrary, at the N-S$_A$ phase transition $D_{//}$ and D_R do not show any appreciable discontinuity. Within the smectic A phase both D_R and $D_{\perp}$ are almost independent of temperature, with values of about $5 \cdot 10^9$ s^{-1} and $1 \cdot 10^9$ s^{-1}, respectively, while $D_{//}$ shows a clear decreasing trend with decreasing temperature. At the S_A-S_B phase transition all the motions slow down, but only $D_\perp$ presents a well-defined jump and, in the S_B phase, the three diffusion constants decrease with an Arrhenius dependence, the tumbling motion being by far the most strongly activated. In this phase the calculated activation energies are 36±11 kJ/mol for D_R, 25±6 kJ/mol for $D_{//}$ and 312±32 kJ/mol for $D_\perp$. The latter value seems exceptionally high if compared with those reported for other mesogens in the smectic B phase[18]. It seems however reasonable that the tumbling motion becomes strongly hindered in this highly ordered phase, due to the hexagonal packing within the layers[20].

The increase of $D_\perp$ at the N-S_A transition deserves further discussion: it must be considered that $D_\perp$ is the coefficient most affected by small errors in the experimental data, which, in this case, could be larger than usual since the nematic phase is present in a very small temperature range and always coexists with a relevant amount of isotropic phase. However, given the unexpectedly high values of the methine J_1 in the nematic phase with respect to those in the smectic A phase, also an effect due to nematic order director fluctuations could be present. It is theoretically predicted that order director fluctuations in the nematic phase contribute to J_1 through the terms expressed in equations (9a) and (9b) for the methine and aromatic deuterons, respectively[21]:

$$J_1^{met(DF)}(\omega_0) = (v_q)^2 A_{DF}[d_{00}^2(\cos\beta_{M,Q_0})]^2 \omega_0^{-\frac{1}{2}} \tag{9a}$$

$$J_1^{ar(DF)}(\omega_0) = (v_q)^2 A_{DF}[d_{00}^2(\cos\beta_{R,Q_R})]^2 [d_{00}^2(\cos\beta_{M,R})]^2 \omega_0^{-\frac{1}{2}} \tag{9b}$$

where:

$$A_{DF} = \left(\frac{3\pi^2}{2}\right)\frac{3kT(S_{zz}^d)^2}{4\pi\sqrt{2}K(D+K/\eta)^{\frac{1}{2}}} = K_{DF}T(S_{zz}^d)^2 \tag{10}$$

with K the average Frank elastic constant, D the average autodiffusion translational constant and η the average viscosity coefficient of the liquid crystal phase. From equations (9a) and (9b) it results that $J_1^{ar(DF)}$ is negligible due to the value of β_{R,Q_R}, close to the magic angle, while contributions of 10-20% to J_1 are expected for the methine deuteron using for K_{DF} values reported in the literature[22]. Subtraction of $J_l^{(DF)}$ from the experimental J_l values has the effect of increasing $D_\perp$ and decreasing $D_{//}$. In order to reach for $D_\perp$ in the nematic phase the same values found in the smectic A phase, a contribution of $J_l^{met(DF)}$ of at least 30% to J_l^{met} has to be assumed. However, the corresponding decrease in $D_{//}$ is too high and physically unreasonable. Therefore order director fluctuations alone cannot account for the anomalous behaviour of $D_\perp$ in the nematic phase.

The experimental spectral densities were also interpreted using the *third rate anisotropic viscosity* model[4]. The correlation times $\tau^{(j)}_{m_L m_M}$ in equations (6) and (7) are here expressed as:

$$\frac{1}{\tau^{(j)}_{m_L m_M}} = k_{m_M} + \frac{6D_\beta + m_L^2(D_\alpha - D_\beta)}{b^{(j)}_{m_L m_M}} \tag{11}$$

where k_{m_M} reflects the γ-motion and, in the strong collision limit, is given by:

$$k_{m_M} = (1 - \delta_{m_M 0})D_\gamma \tag{12}$$

In this case, the four experimental values of $J_{m_L}(m_L\omega_0)$ were used to calculate the four diffusion constants D_α, D_β, D_γ and D_R from equations (6) and (7) by means of Newton's method[23]. In the nematic phase, the computation gave values ranging from $5\cdot10^8$ to $1.5\cdot10^9$ s^{-1} for D_α, $7\cdot10^7$ to $1.6\cdot10^8$ s^{-1} for D_β, $8\cdot10^9$ to $1.2\cdot10^{10}$ s^{-1} for D_γ and $3\cdot10^8$ to $2\cdot10^9$ s^{-1} for D_R, with no clear trend with the temperature. The method failed to converge to physically acceptable values of the D's in the two smectic phases. A critical study was made in order to investigate the incidence of experimental errors and geometrical assumptions on the solution of equations (6) and (7) when the *third rate* model is assumed. It was found that, in the nematic phase, a variation of ±10% in T_{1Z} and T_{1Q} of the aromatic deuterons strongly influences the resulting diffusion constants; in fact, differences up to one order of magnitude for D_R were observed. Errors on the relaxation times of the methine deuteron have minor effects. Since the dipolar splittings were determined with an error of 50 Hz, S^d_{zz} was calculated with an uncertainty of 6 %, which results in an estimated error on D_β up to 50%. Among the geometrical parameters, the angle β_{M,Q_0} exerts a considerable influence on the values determined for the *D*'s; in particular, a variation of this angle from -3° to +3° with respect to the assumed value gave a D_β value 6 times smaller, whereas D_α and D_R changed of about 50%, and D_γ of only 10%. In the smectic A phase, Newton's method gave negative values for D_β and/or D_R. A convergence to positive values for all the unknowns could be obtained by varying both T_1's of the aromatic deuterons by +10%; in this case, however, the condition $D_\gamma >> D_\alpha, D_\beta$, which guarantees that the motion about the long molecular axis is not correlated with motions of this axis, condition required in the *third rate* model, was no longer sustained. Moreover, the results are quite critical and minor modifications of geometrical parameters yielded negative D_β values. No variation of molecular structure and experimental data in the ranges above mentioned gave acceptable, i.e. all positive, diffusion constants in the smectic B phase.

CONCLUSIONS

FAB-OC6 shows highly ordered smectic A and B phases. The Saupe order matrix obtained in this work for the aromatic core, together with the local order parameters determined for the alkoxy chain in a previous work[9], indicates that the overall reorientational motions as well as internal rotations of the methylene groups slow down on going from the nematic to the smectic B phase. The molecule, apart from the terminal part of the chain, tends to stiffen in the smectic A and smectic B phases. The low biaxiality observed indicates that the rotation of the molecule about its long axis is sufficiently fast to give an average cylindrical shape to the core, even in the smectic B phase.

It was possible to interpret the relaxation data only in the small step rotational diffusion model proposed by Nordio, thus obtaining, besides the diffusion constant relative to the internal rotation of the aniline ring, the diffusion constants $D_{//}$ and $D_\perp$, relative to the motions about and of the long molecular axis, respectively. Order director fluctuation modes are probably of relevance in the nematic phase of this mesogen but do not influence much the resulting trends of the diffusion coefficients. While ring rotation does not change appreciably, as indicated by D_R, which is nearly constant throughout the different phases, molecular motions are subject to variations going from the nematic to the smectic B phase. In particular $D_{//}$ shows small jumps at the phase transitions, slightly decreasing with decreasing temperature; on the other hand, $D_{\perp}$ presents a sizeable jump at the S_A-S_B transition and strongly decreases within the smectic B phase becoming more than one order of magnitude less than in the smectic A phase. This confirms what inferred from the orientational order findings: in the highly ordered smectic B phase, which has hexagonal packing of the molecules within the smectic layers, the tumbling motion becomes strongly hindered and rotation about the long axis is the only molecular motion of relevance. Ring rotations, which do not influence much the molecular shape, are still active, while internal rotations involving the first methylene groups of the chain become impeded because of steric hindrance. All this is consistent with the picture given for highly ordered smectic B phases on the basis of other techniques[20].

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