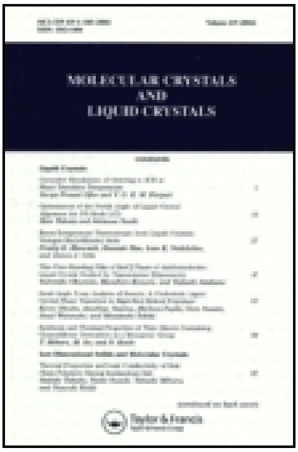

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Study of the Orientational Order and Dynamics in the Nematic and Smectic Phases of p′-Hexyloxybenzyliden-p-Fluoroaniline by Means of ^{2}H-NMR

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STUDY OF THE ORIENTATIONAL ORDER AND DYNAMICS IN THE NEMATIC AND SMECTIC PHASES OF *p*'-HEXYLOXYBENZYLIDEN-*p*-FLUOROANILINE BY MEANS OF ^{2}H-NMR

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Abstract

Measurements of orientational order parameters and spectral densities of motion in the nematic, smectic A and smectic B phases of *p*'-hexyloxybenzyliden-*p*-fluoroaniline, fully deuterated in the chain and partially deuterated in the aniline ring, are reported. The deuterium spin-lattice (T_{1Z}) and quadrupolar (T_{1Q}) relaxation times have been measured at 46.04 MHz using a broadband multiple pulse Jeener-Broekaert sequence. The orientational order of the C-D bonds and the spectral densities determined suggest that, on entering the highly ordered smectic phases, the internal motions of the first two methylene groups in the chain slow down sensibly. These effects are discussed within the framework of the models used to describe molecular and internal dynamics in mesomorphic phases.

INTRODUCTION

The orientational order of the aromatic core of the liquid-crystalline compound *p*'-hexyloxybenzyliden-*p*-fluoroaniline (FAB-OC6) partially deuterated on the aniline ring, has been recently studied throughout all its mesophases by means of ^{2}H-NMR.[1] This compound exhibits, apart from a nematic phase, both a smectic A and a smectic B phase. The results indicate that the smectic phases of FAB-OC6 are strongly oriented, the principal orientational order parameter S_{ZZ} for the aromatic core reaching a value of 0.9 in the smectic B phase. Moreover the orientational order for the aromatic core of the mesogenic molecules is extremely sensitive to temperature variations in the smectic B phase and in the nematic phase while, on the contrary, it is essentially constant in the smectic A phase.

This behaviour may indicate a strong coupling between the orientational and translational order present in the smectic phases: in the smectic A phase, as the temperature increases, the excess of thermal energy is dissipated in motions which influence essentially the translational order (for instance through the elongation of the chain which can become conformationally rigid by lowering the temperature, as confirmed by X-ray measurements[2]); in the smectic B phase, where the translational order is close to its maximum, the excess of thermal energy can be dissipated only in orientational motions.

In order to have further insight into the molecular behaviour in these phases, we have undertaken the study of the orientational order and molecular dynamics in FAB-OC6 deuterated both in the chain and in the aromatic core as shown in Fig. 1.

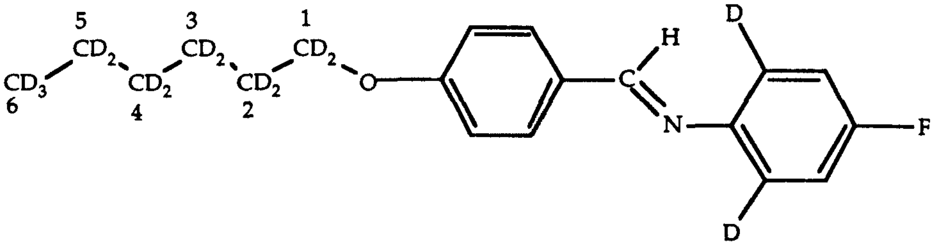

FIGURE 1 *p'*-hexyloxybenzyliden-*p*-fluoroaniline-d_{15} (FAB-OC6) with numbering of deuterium nuclei used in the text.

The study of chain dynamics in thermotropic liquid crystals is not an easy task; several ^{2}H relaxation studies on alkyl chains both in nematic and smectic phases are reported in the literature,[3-8] while we have no knowledge of dynamic studies on alkoxy chains.

The aim of this paper is not a detailed investigation of the molecular dynamics, for which a multifrequency study is in progress, but the evaluation of the possibility of inferring qualitative information on the overall and internal motions on the basis of the orientational order parameters and relaxation times, in particular in the highly ordered smectic phases where some of these motions are expected to be severely hindered.

EXPERIMENTAL

FAB-OC6-d_{15} has been synthesised following the procedure described in the literature[9] starting from suitably deuterated compounds. Commercial *p*-F-aniline (Aldrich) was refluxed for 50 hours with DCl/D_2O. The hydrochloric acid was neutralized by potassium carbonate, *p*-F-aniline-2,6-d_2 (**I**) extracted with ether, dried and distilled. Commercial (Cambridge Isotope Laboratory) hexylbromide-d_{13} was refluxed with *p*-oxybenzaldehyde and potassium carbonate in dry acetone for 60 hours and vacuum distilled to obtain *p*-n-hexyloxy-d_{13}-benzaldehyde (**II**). **I** and **II** were refluxed with anhydrous benzene for several hours. The crude product was purified by several crystallizations from anhydrous ethanol.

Undeuterated FAB-OC6 shows a smectic B phase from 325.1K to 329.6K, a smectic A phase from 329.6K to 334.3K and a nematic phase from 334.3K to 335.8K.[2] The deuterated compound used shows slightly different transition temperatures due to an isotopic effect and the possible presence of impurities.

^{2}H-NMR spectra were recorded at different temperatures ranging from 320 to 334K (Figure 2).

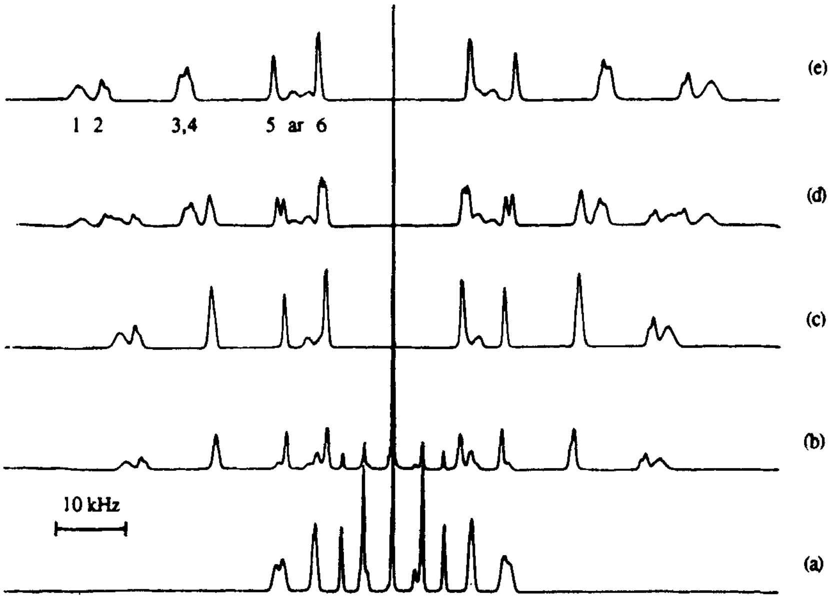

FIGURE 2 ^{2}H-NMR spectra of FAB-OC6-d_{15} at different temperatures in the different mesophases [(a) nematic (334K), (b) nematic and smectic A (332.5K), (c) smectic A (329K), (d) smectic A and smectic B (327.5K), (e) smectic B (322K)].

The spin-lattice (T_{1Z}) and quadrupolar (T_{1Q}) relaxation times have been determined by means of the Wimperis pulse sequence (90_0-$2\tau_1$-67.5_{270}-$2\tau_1$-45_{90}-τ_1-45_{90}-τ_2-α_0)[10] with τ_1 = 7.5 μsec optimized experimentally. The spin-lattice relaxation times have been also determined by means of the Aperiodic Pulse Saturation Recovery technique,[11] using fifteen 90-degree pulses spaced by delays ranging from 8.4 msec to 600 μsec for preliminary signal saturation.

All the experiments were performed on a Bruker AMX-300 working at 46.04 MHz with a 10-mm multinuclear probe. For all the experiments, except for APSR, we used a relaxation delay of 3 sec. In all cases well resolved spectra were obtained after 200 acquisitions. The 90-degree pulse was 10 μsec. Temperature control was good to 0.1°C.

RESULTS AND DISCUSSION

Orientational Order

The ^{2}H-NMR spectra result from a superposition of doublets, each arising from a different type of deuterium, with splitting due to quadrupolar interaction. Given the large number of different deuterium nuclei present, a COSY spectrum was necessary for an unambiguous assignment of the peaks. In the 2D spectrum cross peaks connect two diagonal peaks relative to dipolarly interacting deuterons, thus indicating which deuterons belong to neighboring methylene groups.

The quadrupolar splittings ($\Delta\nu_q$) observed in the spectra are proportional to the local orientational order parameters (S_{CD}) being:

$$S_{CD} = \frac{2}{3}\frac{\Delta\nu_q}{q_{CD}} \qquad (1)$$

with q_{CD} the quadrupolar coupling constant (q_{CD} = 185 kHz for aromatic deuterons, q_{CD} = 165 kHz for aliphatic deuterons) and where the asymmetry parameter η is neglected. The values thus obtained are shown in Figure 3.

The aromatic deuterons have low local order parameter due to the geometry of the system: in fact the long molecular axis of the molecule lies close to the para axes of the aromatic rings and therefore the C-D bonds lie at an angle close to the magic angle with respect to the principal axis. The data are consistent with the high orientational order observed in these phases.[1] The data relative to the chain deuterons show that the local order parameter decreases along the chain going from the first methylene to the methyl group. This preliminary observation indicates that even in the quite rigid smectic B phase the alkyl chain still has a certain mobility. In fact if the chain were in a rigid all-trans configuration, all the methylene deuterons would have the same orientation with respect to the principal molecular axis and therefore should show the same quadrupolar splitting.

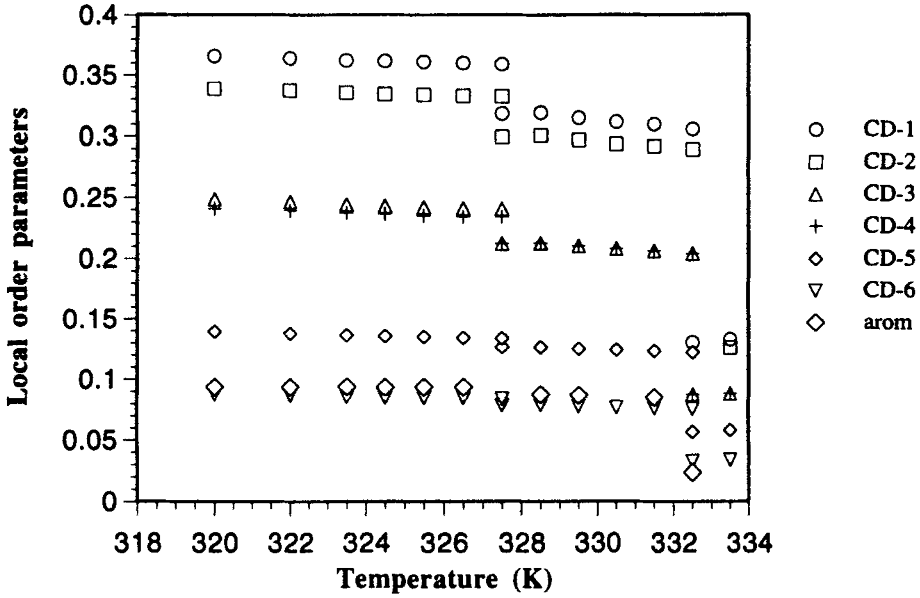

FIGURE 3 Local orientational order parameters of the different deuterium nuclei of FAB-OC6 at different temperatures.

The pairwise clustering of the methylene local order parameters going along the chain is a common feature in liquid crystalline compounds[12] and has been referred to as an "even-odd" effect arising from the conformational distribution of the chain.

The values of S_{CD} for the first two methylene groups in the chain, close to one half of the previously determined molecular principal order parameter,[1] indicates that the C-D bonds in these groups lie almost perpendicular to the principal axis of the molecule, with an angle closer to 90° for the first methylene. This is true in particular in the smectic B phase but holds also in the smectic A phase.

Whereas in the smectic B phase all local order parameters are essentially constant throughout the whole mesomorphic range, the local order in the smectic A phase is constant only in the case of the aromatic core and the two terminal groups of the chain, showing a small but visible variation for the first four methylene groups. Moreover a sharp jump is observed at the N-S_A transition for all the deuterons, while at the S_A-S_B transition the variation is relevant only for the first four methylene groups. All these observations seem to indicate that, while at the N-S_A transition there is a stiffening of the aromatic core and a slowing down of the overall motions, at the S_A-S_B transition the main feature is the blocking of the chain conformational freedom, more relevant for the first groups of the chain. Further evidence of this should come from analysis of the relaxation times.

Relaxation Times

The Jeener-Broekaert pulse sequence (90_0-τ_1-45_{90}-τ_2-α)[13] is normally used to measure the Zeeman (T_{1Z}) and Quadrupolar (T_{1Q}) relaxation times simultaneously. In fact the resulting sum and difference of the intensity of the two doublet components relative to one type of deuteron are respectively related to the τ_2 variable delay by the Equations:

$$M_+(\tau_2) = 2K\sin\alpha\left[1 - \exp(-\tau_2/T_{1Z})\right] \tag{2a}$$

$$M_-(\tau_2) = 3K\sin\alpha\cos\alpha\exp\left(-\tau_2/T_{1Q}\right) \tag{2b}$$

where α is the flip angle of the monitoring pulse, which is usually chosen around 45° in order to have a large dynamic range, thus being able to follow equally well the sum and difference magnetizations from a single set of recovery curves. The relaxation times can be thus obtained from a global non-linear least-squares fit of the data to Equations (2a) and (2b), yielding T_{1Z}, T_{1Q} and K.

This method, however, requires the adjustment of the τ_1 parameter, which is quadrupolar splitting-dependent and it is therefore necessary to perform one experiment for each type of deuteron present in the sample. The simultaneous measurement of the T_{1Z} and T_{1Q} relaxation times for all the deuterium nuclei is made possible by the Wimperis (or broadband Jeener-Broekaert) pulse sequence which is clearly less time-consuming.

A preliminary comparison between the Jeener-Broekaert and the Wimperis pulse sequences has been made in order to verify the applicability of this method for all the deuterium nuclei of FAB-OC6. This test, not reported here, indicated a very good agreement between the two techniques for all the deuterium nuclei, as also found in a previous work.[14] We thus used the broadband Jeener-Broekaert pulse sequence to determine the T_{1Z} and T_{1Q} relaxation times for all the deuterons at several temperatures in the three mesomorphic phases.

It must be pointed out, however, that the behaviour of the Jeener-Broekaert and Wimperis pulse sequences becomes far from ideal when the quadrupolar splitting of the deuterium nuclei increases. One of the principal causes of the incorrect working of these techniques arises from a period of precession of the magnetization in the x-y plane of the laboratory frame too short with respect to the pulse length: when the 90-degree pulse is not very short and when the precession rate is high, as for deuterium nuclei with large quadrupolar splittings, the evolution of the magnetization during the pulse becomes no longer negligible. In this case the trend of M_+ and M_- with τ_2 is not exactly reproduced by Equations (2a) and (2b) and the experimental data can be fitted only with a three-parameter least-squares method for T_{1Z} and a two-parameter one for T_{1Q}, in an analogous way to the data treatment used for the Inversion-Recovery technique when pulse imperfections are taken into account.[15]

All this considered, in order to verify the reliability of the relaxation times obtained with the above described methods, we also measured the T_{1Z} relaxation times for all the deuterium nuclei at several temperatures by means of the Aperiodic Pulse Saturation Recovery (APSR) technique. A comparison between the T_{1Z} values obtained (shown in Figure 4) indicates good agreement between the two sets of measurements.

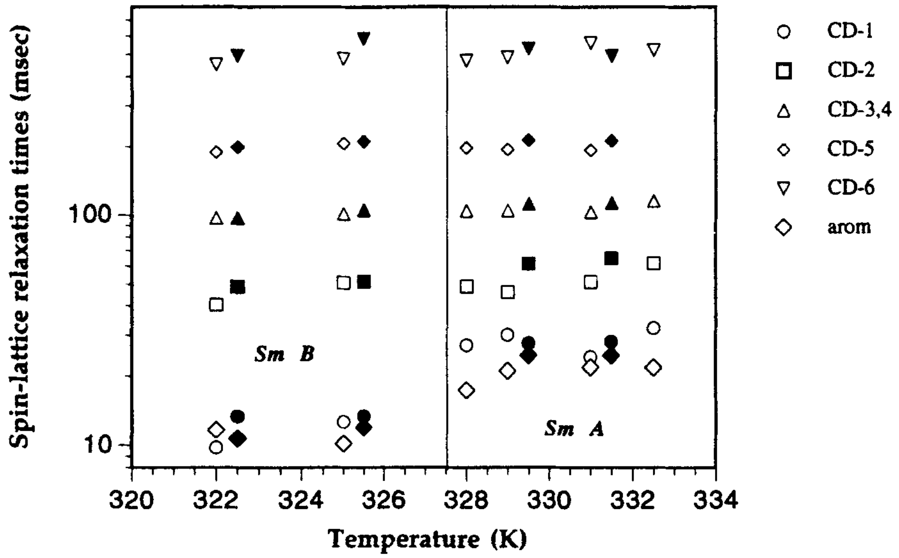

FIGURE 4 Spin-lattice relaxation times obtained for the different deuterons in the smectic A and B phases by means of the Wimperis (open symbols) and the APSR (filled symbols) sequences. Errors are within 10%.

Dynamics

A first qualitative analysis of the data can be made on the basis of the trend of the Zeeman relaxation rates ($R=1/T_{1Z}$) of the different deuterium nuclei. Beckmann et al.[16] give an approximate expression for the relaxation rate in terms of the local order parameter and an effective correlation time τ^0, which is assumed valid in the fast motion regime:

$$R_i \propto \left(1 - S^i_{CD}\right)\tau^0_i \qquad (3)$$

Equation (3) shows that two competing factors determine the temperature dependence of the relaxation rate. On lowering the temperature the higher ordering should cause a decrease in R, while the increasing correlation times should lead to more effective relaxation.

A preliminary discussion of the dynamical behaviour of FAB-OC6 in the different mesomorphic phases will be therefore made on the basis of the temperature trend of the effective correlation times. In Figure 5 the correlation times, multiplied by the proportionality constant implied by Equation (3), are reported.

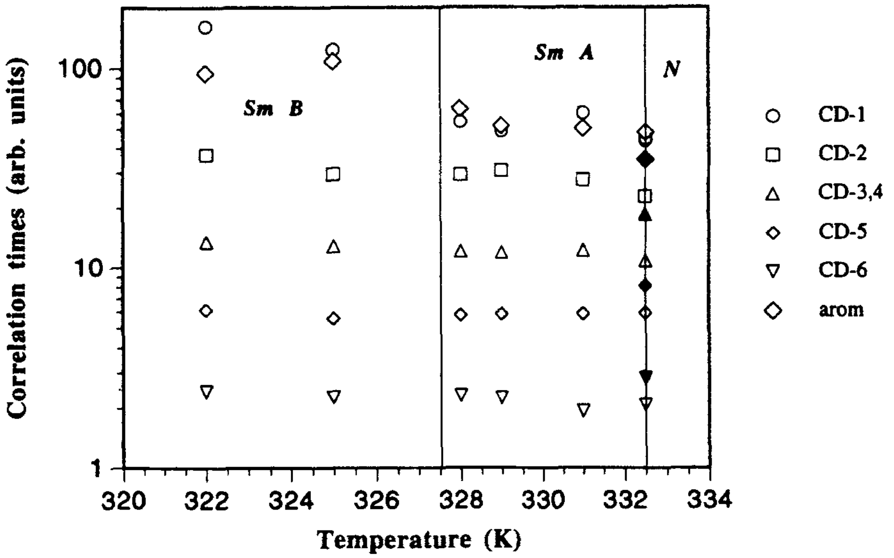

FIGURE 5 Effective correlation times at different temperatures. For clarity the data relative to the nematic phase are reported with filled symbols. Estimated errors are within 10%.

It is to be observed that the correlation times decrease going down along the chain from the aromatic core to the methyl group. This behaviour has been observed for other liquid crystals[16] and can be interpreted assuming that the internal rotations are the dominant motions as anticipated from the analysis of the orientational order.

While the aromatic and the first methylene deuterons show a strong decrease of τ on going from the smectic B to the smectic A phase, the other deuterons do not show discontinuities. Moreover, the first two groups of the chain show a small but regular decrease with increasing temperature within both smectic phases, whereas the other members of the chain show an essentially constant trend.

The values obtained for the terminal groups of the chain in the nematic phase are higher than those in the smectic A phase and therefore differ from the expected behaviour. Although similar trends have been observed in other cases,[17] it must be pointed out that for this compound the nematic range is very small and the nematic phase always cohexists with either the smectic A or the isotropic phase; pre-transitional phenomena may therefore be present.[16]

The spectral densities $J_1(\omega_0)$ e $J_2(2\omega_0)$ have been determined from the relaxation times:

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

and

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

The values obtained are reported in Figure 6a and 6b respectively.

Detailed information on both molecular and internal motions can be obtained from the spectral densities using suitable models. The analysis of the data by means of the more recent models for the dynamics of the alkyl chains,[8,18] superimposed to a diffusion model for the overall reorientational motions, is in progress. Some considerations can however be made already on the basis of the temperature trends of $J_1(\omega_0)$, $J_2(2\omega_0)$ and $J_1(\omega_0)/J_2(2\omega_0)$ for the different deuterons. A first evident feature is a sensible jump in $J_2(2\omega_0)$ at the S_A-S_B transition for the first methylene group and in both $J_1(\omega_0)$ and $J_2(2\omega_0)$ for the aromatic deuterons, thus revealing a relevant variation in the dynamics of these groups, already put in evidence by the effective correlation times. Another relevant feature, evident in Figure 7, where the ratio between the spectral densities is reported, is that $J_2(2\omega_0) > J_1(\omega_0)$ both in the smectic A and the smectic B phase for the first methylene group, the difference being larger in the lower temperature phase. This effect is also present, even if to a

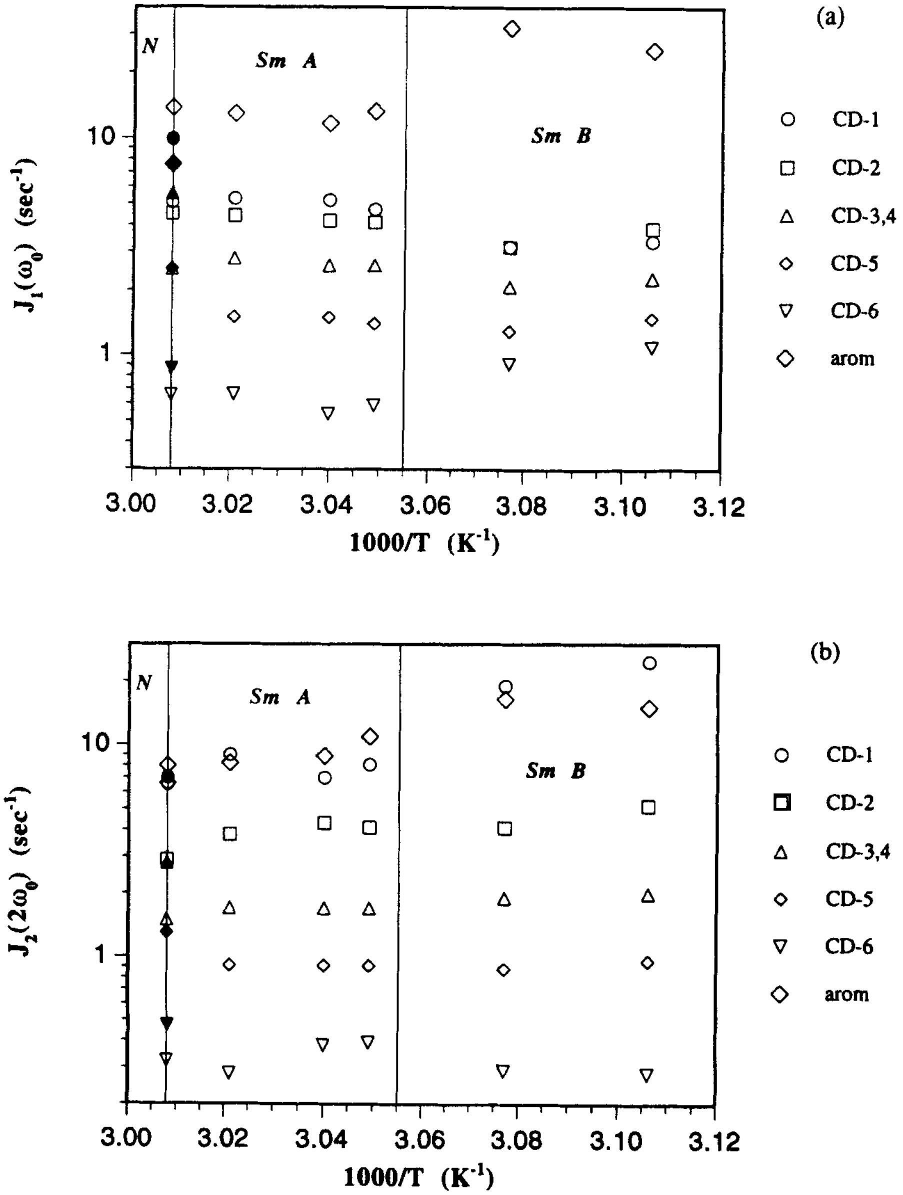

FIGURE 6 Spectral densities $J_1(\omega_0)$ (a) and $J_2(2\omega_0)$ (b) in the different mesomorphic phases. Maximum errors are around 10%.

lesser extent, for the second methylene group in the smectic B phase only. $J_1(\omega_0)/J_2(2\omega_0)$ values less than one have been found only in discotic mesogens,[19] in small molecules dissolved in liquid crystals[20-22] and in angle dependent relaxation measurements.[3]

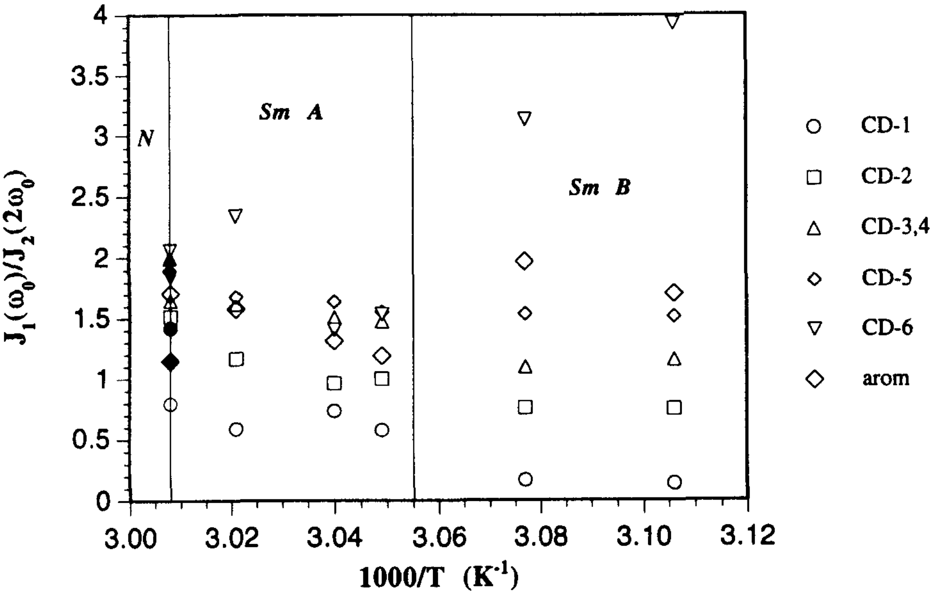

FIGURE 7 Spectral density ratio in the different mesomorphic phases.

The spectral density ratio is indicative of the validity of the various models for molecular reorientation in thermotropic liquid crystals.[23] In particular the values obtained for the aromatic deuterons in several mesogens are quite lower [cfr. 23 and references therein] than those predicted by the small-step rotational diffusion model. In such model[24] the molecular reorientational motion is described in terms of rotational diffusion of the long molecular axis, the diffusion tensor being assumed diagonal in a molecule fixed frame, with principal components $D_{//}$, the spinning rotation diffusion constant, and $D_{\perp}$, the tumbling rotation diffusion constant.

Vold and Vold[23] have proposed an alternative model ("third rate anisotropic viscosity" model) which, assuming a diffusion tensor diagonal in the laboratory fixed frame, introduces a third rate constant D_γ relative to the molecular motion around its principal axis, in addition to the two principal diffusion rate constants (D_α for rotation around the director and D_β for that toward the director) with γ motion assumed uncorrelated with α and β motions. The correlation function for the overall molecular motion can therefore be written in terms of the product of the correlation functions of the two distinct motions:

$$C_M(t) = \sum_{K=-2}^{2} \sum_{K'=-2}^{2} d_{0K}(\beta')d_{0K'}(\beta')\Gamma_{KK'}(t)G_{MKK'}(t) \tag{5}$$

where $d_{0K}(\beta')$ are the reduced Wigner rotation matrix elements with β' the angle between the molecular symmetry axis and the principal axis of the molecule fixed electric field gradient tensor for the deuteron under investigation, usually taken along the corresponding C-D bond. $\Gamma_{KK'}(t)$ are the correlation functions for motion about the molecular axis and $G_{MKK'}(t)$ are correlation functions for motion of this axis. The assumption made greatly simplifies the problem and is justifiable only if the two types of motion have different time scales, i.e. motion about the long molecular axis is much faster than motion of this axis, as is usually found in many nematogens.

With this simplification, it is possible to use different models to describe the two types of motion. While the α and β motions are usually treated within the small step rotational diffusion model, a simple model has been proposed[23] for the γ motion which assumes a single exponential decay for the first and second order correlation functions with different decay rates k_1 and k_2 related by an adjustable parameter p:

$$k_2 = (3p+1)k_1 \tag{6}$$

This model encompasses both the strong collision and small-step diffusion models. If the parameter p is equal to 0 we are in the strong collision limit, while p takes the value of 1 in the small step diffusion model.

The spectral densities $J_1(\omega_0)$ and $J_2(2\omega_0)$ obtained from ^2H-relaxation measurements are related to the individual first and second order correlation functions and are dependent on the β' angle defined above, being:

$$J_M(\omega) = \int_0^\infty C_M(t)e^{-i\omega t}dt \tag{7}$$

If only the α and β motions are considered, the calculated $J_1(\omega_0)/J_2(2\omega_0)$ ratio can never be as low as the values usually found. On the other hand, assuming a dominant γ motion, and in the extreme narrowing limit, the ratio of the spectral densities can be approximated to:

$$\frac{J_1(\omega_0)}{J_2(2\omega_0)} = \frac{4}{\tan^2\beta'}\frac{k_2}{k_1} \tag{8}$$

In the case of small-step rotational diffusion $k_2/k_1 = 4$ while it is 1 in the strong collision model. It is evident from Equation (8) that the angular factor assumes particular relevance for the predicted value of $J_1(\omega_0)/J_2(2\omega_0)$. In the case of aromatic deuterons, where β' is normally close to 60°, the calculated spectral density ratio can range from 16/3 to 4/3 according to the p value, and the experimental data relative to these deuterons can thus be used to monitor which model is more likely. In our case the $J_1(\omega_0)/J_2(2\omega_0)$ values are close to those predicted by the strong collision model as it is usually found in rod-like mesogens.

Another important feature of Equation (8) is that, within the limits of validity of the assumptions made, a range of β' values may exist for which $J_2(2\omega_0)$ may become greater than $J_1(\omega_0)$. Thus, in the assumption of a blocked conformation for the first methylene group of the FAB-OC6 chain, which is probably reasonable in the smectic B phase, on the basis of the previous observations relative to the orientational order and the effective correlation time, and taking into account that the angle ϕ-O-CH_2 for similar compounds[12] ranges between 115° and 125°, we can estimate an angle β' in the range 101.2°-106.6°. The low values of $J_1(\omega_0)/J_2(2\omega_0)$ determined experimentally for this CD_2 group are consistent with the lower estimated value of β' and assuming the same p value obtained from the data relative to the aromatic deuterons. This remains qualitatively true for the next methylene in the chain even if for these deuterons we could expect that rotation around the additional C-C bond, even if partially frozen, gives rise to a mean angle farther from 90° and consequently a larger $J_1(\omega_0)/J_2(2\omega_0)$ value. As we proceed along the chain, of course, the conformational disorder increases and, moreover, the internal rotations become more and more relevant with respect to the overall motions and therefore these arguments are no longer valid.

CONCLUSIONS

The above results all indicate that on passing from the smectic A phase to the even more ordered smectic B phase, the molecular α and β motions slow down sensibly and the γ motion remains practically the only molecular motion effective for relaxation in the smectic B phase. As far as the internal chain motions of the chain are concerned, while the terminal groups essentially do not show a sensible variation throughout the whole temperature range studied, thus revealing that for these groups the main motion is in fact the internal rotation about the C-C bonds, the first methylene groups of the chain, besides being strongly influenced from the overall molecular motions, have internal rotations sensibly slowed down in the smectic A phase and almost frozen in the smectic B phase.

Little can be said about the nematic phase being its range of existence too low to allow the onset of typical nematic character only.

It is evident that for a more complete understanding of the dynamics in these mesophases it is necessary to well characterize the dynamical behaviour of the aromatic core, which is possible only using the mesogenic compound fully deuterated only on the rigid core. Moreover, in order to put in evidence other possible motions which may contribute to relaxation, such as order director fluctuations, which have been observed for other mesogens,[14] a multifrequency study is essential.

The results obtained in this work however show that even a relaxation study at one frequency can yield useful information on the dynamical behaviour in highly ordered phases.

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