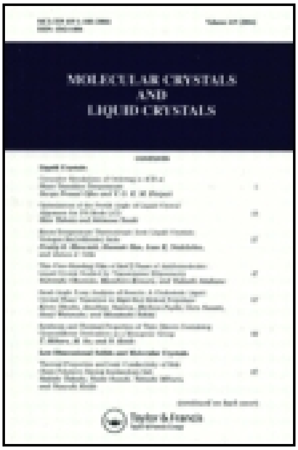

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Orientation, Structure and Dynamics in the Highly Ordered Smectic Phases of 7BEF5 by ^{2}H-NMR

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Orientation, Structure and Dynamics in the Highly Ordered Smectic Phases of 7BEF5 by ^{2}H-NMR

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^{2}H-NMR spectroscopy is employed to investigate the orientational order in the nematic and smectic A, B, and G phases formed by 4-(2-methylbutyl)phenyl-4'*n*-heptylbiphenyl-4-carboxylate (7BEF5). The dynamics of the aromatic molecular core is studied in a temperature interval including the $S_A - S_B$ transition, by the analysis of the deuterium Zeeman and Quadrupolar relaxation times with the rotational diffusion model.

Keywords: liquid crystals; deuterium NMR; relaxation times; molecular motions

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 obtaining two spectral densities of motion, $J_1(\omega_0)$ and $J_2(2\omega_0)$, which can be used to extract information on the dynamics in liquid crystalline phases. Deuterium spin relaxation has been used extensively to investigate nematic and 'disordered' smectic phases, i.e. smectic phases with a liquid-like order within the layers, while the 'ordered' crystal-like smectic phases have been studied only in a limited number of cases[2].

It seemed thus interesting to study the dynamics of **7BEF5** (see fig. 1), a chiral mesogen in racemic mixture which exhibits, in addition to a nematic and a smectic A phase, highly ordered smectic B and G phases:

7BEF5: $$I \xrightarrow{147.2^\circ C} N \xrightarrow{137^\circ C} S_A \xrightarrow{67^\circ C} S_B \xrightarrow{57^\circ C} S_G \xrightarrow{40^\circ C} C$$

The crystal G phase is characterized by a tilted arrangement, with the molecules hexagonally close packed within the layers. A decrease in layer spacing was observed by neutron scattering at the S_B-G transition[3]. The mesomorphic behaviour of 7BEF5-d_6 and 7BEF5-d_{18}, deuteriated as shown in fig. 1, is found to be quite analogous to that of 7BEF5.

The orientational order of 7BEF5-d_{18} was already studied[4] by recording ^{2}H-NMR spectra on cooling from the isotropic phase throughout its mesomorphic temperature range. The quadrupolar splittings of the biphenyl fragment were used to determine the principal order parameter of the molecular core. A preliminary dynamic study was also presented.

The dynamic behaviour of the molecules in the different phases is here reinvestigated by measuring the spin-lattice Zeeman and quadrupolar relaxation times of the aromatic deuterons in 7BEF5-d_6, which gives simpler spectra. These allow us to unequivocally assign all the splittings of 7BEF5-d_{18} and to obtain some information on the structure of this mesogen. A global target analysis of the spectral densities, moreover, gives a better description of the dynamics in the various phases.

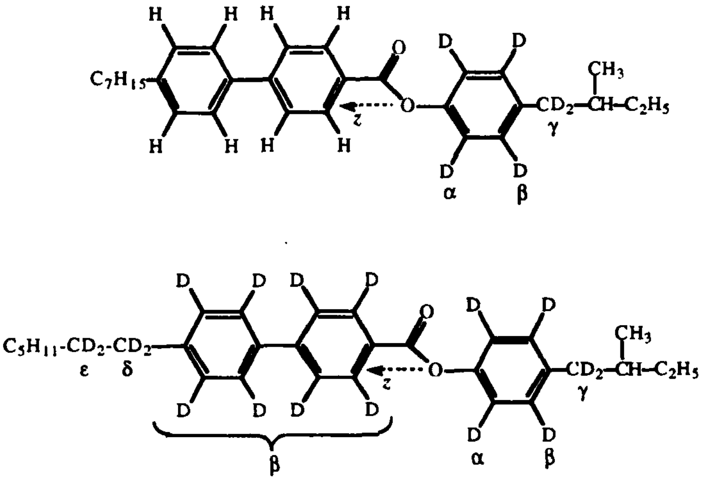

FIGURE 1 Structure and labelling of 7BEF5-d_6 and 7BEF5-d_{18}.

EXPERIMENTAL

The synthesis and characterization of the mesophases were reported by Fodor-Csorba *et al*[3,5]. The ^{2}H-NMR spectra of 7BEF5-d_6 were recorded using a Bruker AMX300 spectrometer, operating at 46.06 MHz, in the temperature range from 146°C to 45°C, both with and without proton decoupling. The Wimperis pulse sequence[6] was employed to simultaneously measureT_{1Z} and T_{1Q} for the different deuterons, with τ_1, the relevant delay between pulses, empirically optimized to 15μs.

RESULTS AND DISCUSSION

^{2}H-NMR spectra

A selection of the ^{2}H-NMR spectra of 7BEF5-d_6 is shown in fig.s 2a and b.

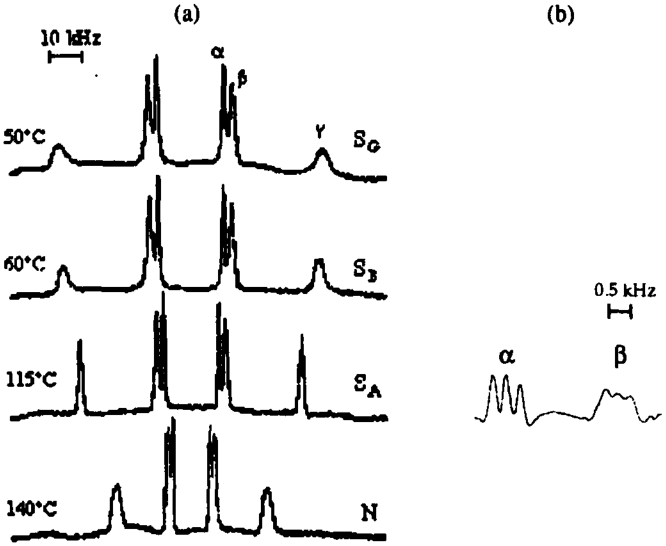

FIGURE 2 (a) ^{2}H-NMR spectra of 7BEF5-d_6; (b) right components of the α and β doublets in the {^{1}H}^{2}H-NMR spectrum at 83°C. The triplet structure is due to dipolar coupling between the α and β deuterons. The β deuterons, also coupled to the γ ones, give signals with greater linewidth.

The comparison between the ^{2}H-NMR spectra of 7BEF5-d_6 and 7BEF5-d_{18} (see ref. 4) allows the assignment of the various doublets to be made, while the dipolar coupling between the α and β phenyl deuterons can be accurately measured from the proton decoupled ^{2}H-NMR spectra of 7BEF5-d_6. The relevant quadrupolar and dipolar splittings are given in fig. 3. In fig. 4 the dipolar splittings relative to the S_A and S_B phases are shown.

The fact that the deuterons of the biphenyl fragment show the same splitting as the β deuterons of the phenyl ring most probably indicates that the *para* axes of the rings are parallel and that the C-D directions for all these deuterons form the same angle with the *para* axis. A slightly different angle between the C-D_α direction and the *para* axis can justify the difference between the α and β quadrupolar splittings.

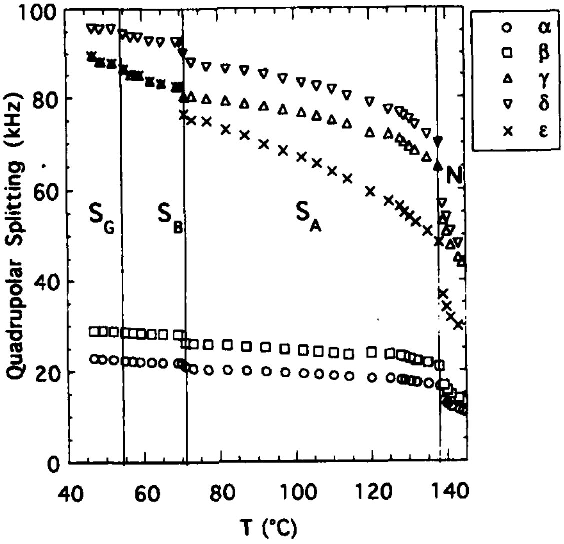

FIGURE 3 Quadrupolar splittings of 7BEF5-d_{18}. The labelling of the deuterium splittings follows that of fig. 1. The average experimental uncertainty on the splittings is less than 300 Hz.

Orientational order

The principal order parameter S_{ZZ} relative to the biphenyl fragment has been calculated from the β deuterons splitting using the equation:

$$\Delta\nu_q = \frac{3}{4}\nu_q S_{zz}\left(3\cos^2\theta - 1 + \eta\sin^2\theta\right) \tag{1}$$

where uniaxial simmetry for the biphenyl moiety order matrix is assumed and the biphenyl z axis is taken along the *para* axis. In the calculations θ, the angle between the z axis and the CD bond, is fixed to 60°, η=0.04 and ν_q=185 kHz. Using the S_{ZZ} value so obtained, a value of θ=59° is required to fit the α quadrupolar splitting.

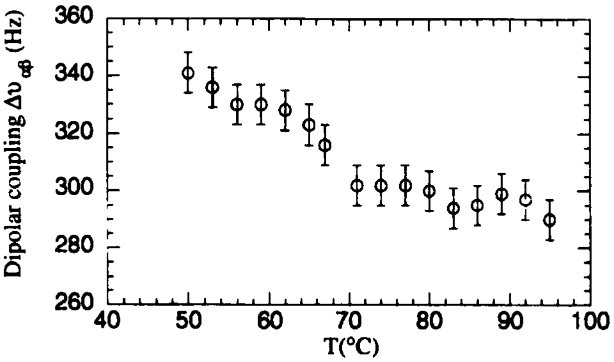

FIGURE 4 Dipolar splittings of 7BEF5-d_6 *vs* temperature in the S_A and S_B phases.

The order parameter $S_{\alpha\beta}$ relative to the $\alpha-\beta$ direction, which is substantially parallel to the *para* axis of the phenyl ring, can be obtained from the $D\alpha$-$D\beta$ splittings using eq. (2)

$$\Delta\nu_{\alpha\beta} = -4K_{ij}\frac{S_{\alpha\beta}}{r^3_{\alpha\beta}} \tag{2}$$

where $K_{ij} = \gamma_D^2 h / 4\pi^2$ and $r_{\alpha\beta}$ is the distance between the interacting nuclei, here fixed to 2.5Å. The $S_{\alpha\beta}$ values thus computed are practically coincident with the S_{zz} values obtained from the biphenyl deuterium quadrupolar splittings. Therefore, the *para* axes of the biphenyl and phenyl fragments are confirmed to be parallel and the assumption of cylindrical symmetry for the ordering matrix of the molecular core is compatible with the experimental data in the wide range of temperature and in the different mesophases explored. The trend of the order parameter S_{zz} *vs* temperature is shown in fig. 5.

The increase in S_{zz} with decreasing temperature in the S_G phase indicates that the local phase director inside the layers aligns along the magnetic field.

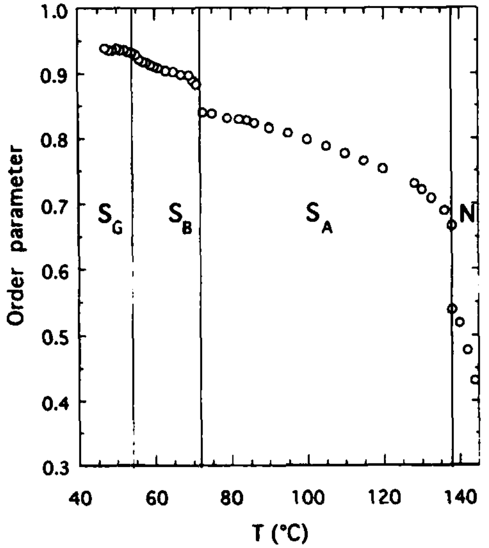

FIGURE 5 Principal order parameter of the core of 7BEF5-d_6

Molecular dynamics

In the Wimperis experiment, performed to measure T_{1Z} and T_{1Q}, the sum and difference of the intensities of a quadrupolar doublet components obey the following equations, respectively:

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

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

T_{1Z} and T_{1Q} were obtained, for each deuteron of 7BEF5-d_6 at various temperatures, by fitting the values of M_+ and M_- measured as a function of τ_2, a variable delay in the pulse sequence. Then, the spectral densities $J_1(\omega_0)$ and $J_2(2\omega_0)$ were computed using equations (4) and (5):

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

$$\frac{1}{T_{1Q}} = 3J_1(\omega_0) \tag{5}$$

The trends of the spectral densities with the temperature are plotted in fig. 6.

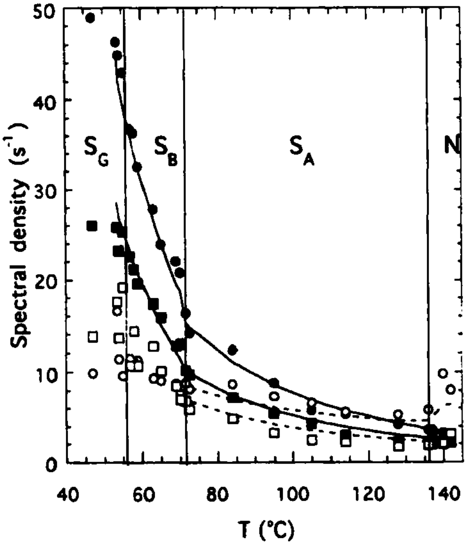

FIGURE 6 Spectral densities: $J_1(\omega_0)$ (circles) and $J_2(2\omega_0)$ (squares). The filled symbols and solid line refer to aromatic deuterons; the open symbols and dashed lines to methylenic deuterons.

At the S_A-S_B phase transition the spectral densities of the aromatic deuterons clearly show a discontinuity, but the J_1/J_2 ratio remains constant throughout the temperature range examined. On the contrary, the J_1/J_2 ratio of the methylenic deuterons reduces from about 2 to approximately 1 at the S_A-S_B phase transition and further decreases in the S_B and S_G phases.

The experimental spectral densities were interpreted using the model proposed by Nordio[7], which describes the molecular reorientation as small step rotational diffusion in the anisotropic environment given by a Maier-Saupe mean field potential. The parameters characterizing the motion, $D_{//}$ and $D_{\perp}$, are the two principal components of an axially symmetric diffusion tensor fixed in the molecular frame. $D_{//}$ and $D_{\perp}$ represent the diffusion constants relative to the spinning and tumbling motion of the molecular long axis, respectively.

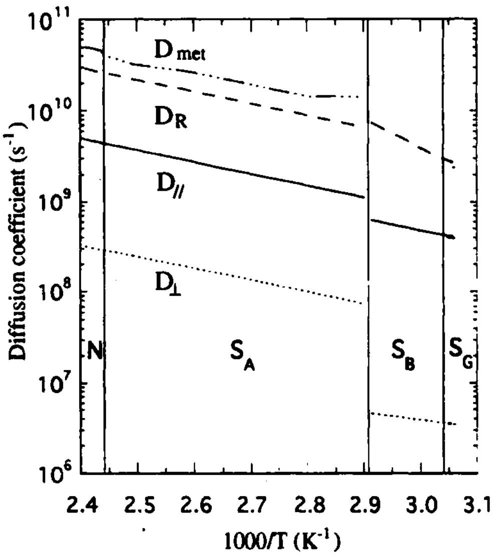

FIGURE 7 Diffusion coefficients in the various phases.

The internal motion of the aromatic rings has been considered as a free rotation around their *para* axes, with diffusion constant D_R, and has been superimposed to the molecular motions in the spectral densities analysis[8].

A global non linear least squares fitting procedure has been applied to all experimental spectral densities in each mesophase assuming an Arrhenius relationship for the temperature dependence of the diffusion constants.

A dramatic variation of the diffusion coefficients is observed at the S_A-S_B phase transition, where the larger decrease is found for $D_\perp$.

The spectral densities of the methylene deuterons could be well fitted assuming free rotation in the N and S_A phase; the same model could not fit the low J_1/J_2 ratio in the S_B and S_G phases.

CONCLUSIONS

7BEF5 shows a S_G phase with the director aligned along the external magnetic field, confirming the observation that, when a phase sequence includes both S_B and S_G phases, the smectic planes are tilted relatively to the magnetic field[9].

The Nordio model could be used to fit the data together with superimposed free rotation for the aromatic rings, thus yielding diffusion constants relative to the spinning and tumbling motion of the molecule as well as internal rotation diffusion constants.

The discontinuity in the spectral densities at the S_A-S_B phase transition can be mainly related to a strong decrease in $D_\perp$, thus indicating that at this transition the tumbling motion becomes strongly hindered and rotation about the long axis remains the only molecular motion of relevance. These results are in agreement with the hexagonal packing of the molecules inside the S_B layers, which does not exist in the S_A layers. Also the methylene rotation changes dramatically at the S_A-S_B phase transition; in fact a free rotation model cannot account for the data relative to the methylene deuterons in the highly ordered phases.

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