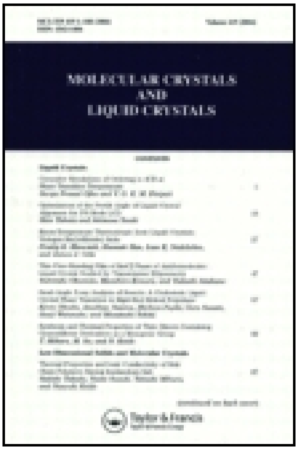

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Microscopic Organization and Tilt Angle in Smectic A and Chiral Smectic C Phases: Characterization and Orientational Order by ^2H NMR and Electric Polarization Measurements

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Microscopic Organization and Tilt Angle in Smectic A and Chiral Smectic C Phases: Characterization and Orientational Order by ^{2}H NMR and Electric Polarization Measurements

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^{2}H-NMR spectroscopy is employed to investigate the orientational order, tilt angle and layers organization of the chiral smectic liquid crystal (-)-(S)-[4-(2-methylbutyloxy carbonyl) phenyl] 4-*n*-heptyl-biphenyl carboxylate-d_8 (MBHB-d_8) in the magnetic field. The electrooptical behaviour of this material has also been investigated. The results from these two different techniques show the importance of molecular conformation for the electric and structural properties of this mesogen.

Keywords: deuterated liquid crystals; chiral smectics; ferroelectrics; ^{2}H NMR; electric polarization

INTRODUCTION

Chiral ferroelectric and antiferroelectric phases found in some liquid crystals have been recently attracting considerable attention[1]. The interest in these mesophases, and in the rich variety of chiral subphases in between, stems from the polar properties connected to spontaneous or field induced broken symmetries. Although some theoretical models have been proposed[2] in order to explain the variation of the tilt angle and layers organization of chiral phases, the theories are mainly based on continuum, modelling the mesogenic molecules as rotational ellipsoids, while a microscopic description of their molecular behaviour is still sparse or missing.

In order to study new ferroelectric/antiferroelectric liquid crystals at a molecular level, we have prepared the following mesogen, (-)-(S)-[4-(2-methyl-butyloxycarbonyl)phenyl] 4-*n*-heptyl-biphenyl carboxylate both unenriched (MBHB), and partially deuterium labelled in the biphenyl moiety of the mesogenic core (MBHB-d_8), as shown in Figure 1.

The aim of the present work was the investigation of the properties of this material both by NMR spectroscopy and by electrooptical methods. The orientational order, the organization of the smectic layers (the tilt angle) as well as the structure of the aromatic part of the mesogenic molecule can be studied by NMR: in this sample the partial labelling allows ^{2}H-NMR to be used for the biphenyl fragment, while information concerning the phenyl fragment, which appears as a relatively isolated AA'BB' spin system, can be extracted by ^{1}H-NMR. Moreover, electrooptical measurements have been performed to investigate the electric polarization, response time and tilt angle of this material.

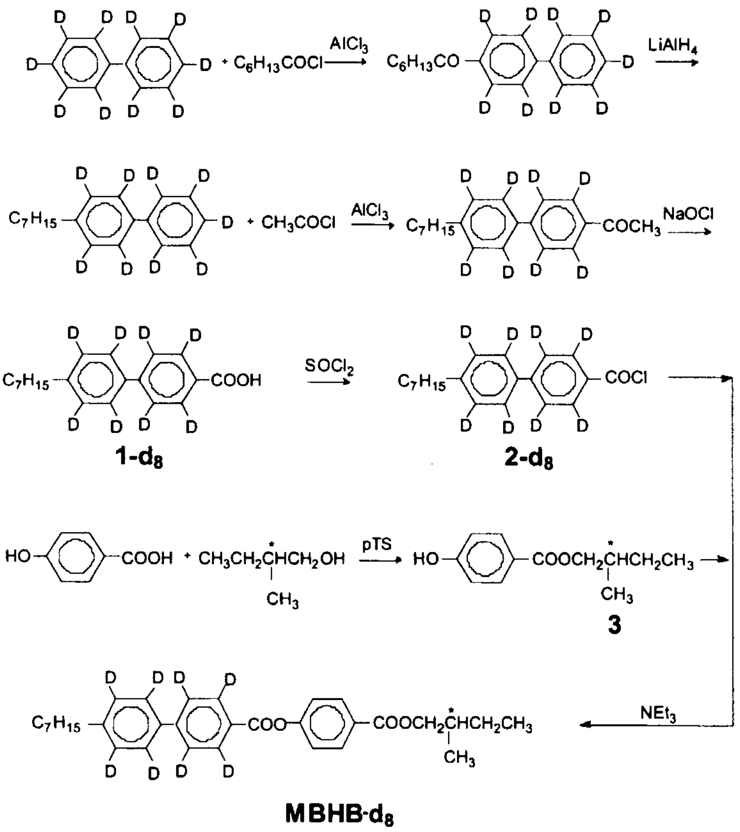

FIGURE 1 Scheme of the synthesis of MBHB-d_8.

SYNTHESIS

The yield was checked in all the synthetic steps on the non-labelled compounds.

4-*n*-heptylbiphenyl carboxylic acid-d_8 (**1-d_8**) and its non-labelled analogue (**1**) were prepared according to our method developed earlier[13].

4-*n*-heptylbiphenyl carboxylic acid chloride-d_8 (**2-d$_8$**) was prepared from 0.88 g (2.98 mmol) of **1-d$_8$** by refluxing for 3 hours in large excess of oxalyl chloride in presence of three drops of dimethyl formamide. The excess of oxalyl chloride was distilled off, and its residues were removed by sweep distillation with dichloro methane. The material **2-d$_8$** obtained was used without further purification.

(-)-(S)-4-[(2-methylbutyloxycarbonyl)phenol] (**3**) was prepared by acid catalysed direct ester formation[4].

(-)-(S)-4-[(2-methylbutyloxycarbonyl)phenyl-4-*n*-heptylbiphenyl carboxylate-d_8] (**MBHB-d$_8$**)[5]: 0.93 g (2.98 mmol) of **2-d$_8$** was reacted with 0.62 g (2.98 mmol) of **3** in dry benzene at room temperature in presence of 2 ml (excess) of triethylamine.

After 24 hours the reaction mixture was poored on cold water, washed 3x20 ml of 5% HCl, water, 5% $NaHCO_3$ and water again, dried over magnesium sulfate. The solvent was evaporated and the crude product recrystallized from ethyl and methyl alcohol several times. 0.6g (41%). The measured specific rotation was $[\alpha]^{25}_D=1.95$ (c = 1 $CHCl_3$).

MBHB: ^1H NMR ($CDCl_3$): 0.9 (d, CH_3), 0.98 (d, CH_3), 1.2-1.4 (m, CH_2), 1.78 (m, CH_2), 1.68 (m, CH), 2.66 (t, CH_2), 4.22 (t, OCH_2), 7.31 (2H), 7.33 (2H), 7.74 (2H), 7.58 (2H), 8.12 (2H), 8.24 (2H) ppm.

MBHB-d$_8$: ^1H NMR ($CDCl_3$): 0.9 (d, CH_3), 0.98 (d, CH_3), 1.2-1.4 (m, CH_2), 1.78 (m, CH_2), 1.68 (m, CH), 2.66 (t, CH_2), 4.22 (t, OCH_2) ppm.

This material was characterized by optical microscopy and differential scanning calorimetry. By these methods the following phases have been found:

Cr (53°C SmF*) 58°C SmC* 94°C SmA* 162.5 °C I

By optical microscopy the attribution of the monotropic low-temperature phase to a Smectic F is not certain; a Smectic I phase could also be possible.

ORIENTATIONAL ORDER

The ^{2}H-NMR spectra were recorded using a Varian VXR-300 spectrometer, operating at 46.06 MHz, in the temperature range from 30°C to 160°C.

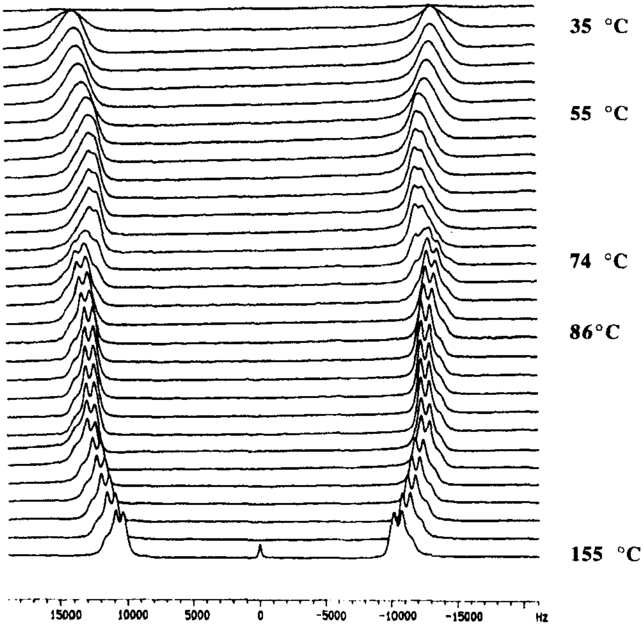

FIGURE 2 ^{2}H-NMR spectra of MBHB-d_8 recorded at variable temperature in the range 30 - 155 °C.

The temperature was stable within 0.1 °C. A series of non decoupled spectra is shown in Figure 2 as a function of temperature.

The lineshape has been considered arising from dipolar couplings among deuterons having the same quadrupolar splitting ($\Delta\nu_q$). This has been determined as difference between the weighted frequency averages of the two symmetrical signals of the quadrupolar doublet.

The principal order parameter S_{zz} relative to the biphenyl fragment has been calculated from the quadrupolar splitting by using the equation:

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

where uniaxial symmetry for the biphenyl moiety order matrix is assumed and the *z* axis is taken along the biphenyl *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.

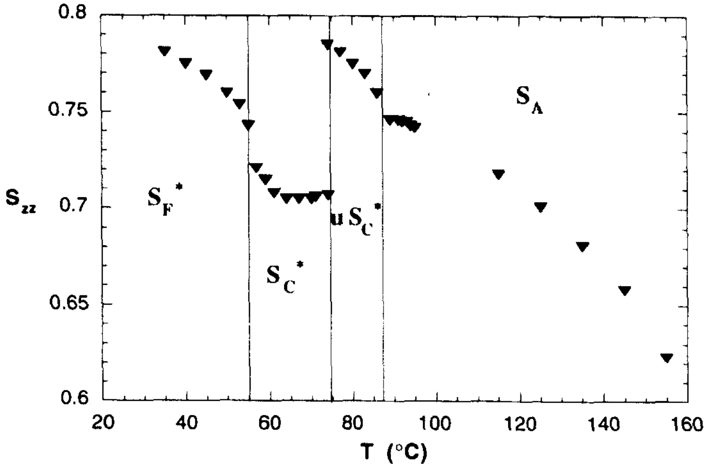

FIGURE 3 Principal order parameter of the biphenyl fragment of MBHB-d_8.

From the behaviour of S_{zz} of the biphenyl molecular fragment versus temperature shown in Figure 3, we can see that, different from behaviour of similar ferroelectric mesogens[6], the molecules of our optically pure mesogen do increase their orientational order by entering the smectic C phase, indicating that the smectic layer normals, rather than the molecule long axes, tilt with respect to the magnetic field. This would mean that the presence of the magnetic field does not allow the helix to be wound and hence an unwound SmC* (uSmC*) phase, rather a SmC* one, is formed. The NMR measurements, moreover, show a phase transition not revealed by calorimetric and microscopic methods at a temperature of 74°C, where a dramatic decrease of the order parameter takes place.

This is indicative of a transition between an uSmC* phase and a phase where the molecules tilt with respect to the magnetic field. The smectic layers normal should be now in the direction of the magnetic field, as shown in Figure 4, and the phase should be a SmC* one.

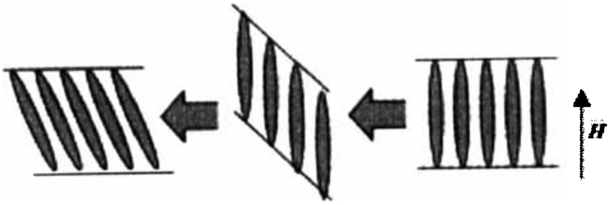

FIGURE 4 The transition between SmA (right), uSmC* (center) and SmC* (left) phases in strong magnetic field.

The S_{zz} values just before and after the transition can be compared in order to determine θ, the tilt angle of the smectic C phase, on the basis of the following equation:

$$S_{zz}^{<74^\circ} = S_{zz}^{>74^\circ} \frac{\left(3\cos^2\theta - 1\right)}{2} \tag{2}$$

obtaining a value of about 15 °.

By lowering the temperature below 74 °C a gradual increase of the molecular order can be observed up to 55 °C, where a remarkable jump of the order parameter indicates the transition between a SmC* phase and a more ordered smectic phase (tentatively classified as a Smectic F phase). The fact that the order parameter below 55 °C is however lower than in the uSmC* phase allows us to confirm that this smectic phase is still tilted, as revealed by optical microscopy.

Another interesting aspect emerging from the deuterium spectra of Figure 2 is the abrupt linewidth increase associated to the uSmC*-SmC* transition at 74°C. Such broadening originates in the helical structure of the tilted chiral phases: for instance a marked line broadening of the ^{13}C NMR signals of the mesogenic core was already observed for a chiral liquid crystal at a SmA-SmC* phase transition[7]. This broadening was ascribed to the cooperative slow fluctuations of the long axis around the cone taking place in the SmC* phases (Goldstone mode)[8]. Although a suitable theory for these line broadening effects has not yet been devised, other broadening mechanisms can be envisaged in addition to the Goldstone mode, such as the soft mode[8], the diffusion of molecules throughout the smectic layers, or a possible deformation of the molecular directors in the helix induced by the magnetic field.

The ^{1}H-NMR spectra can be utilized to obtain the ^{1}H-^{1}H dipolar splitting of the ortho protons of the phenyl ring; from this splitting the principal order parameter of the phenyl fragment can be extracted. The ^{1}H-^{1}H splitting measured at 90 °C, for instance, was 21 kHz giving a S_{zz} (Phenyl) = 0.91; considering that at the same temperature a S_{zz} (Biphenyl) = 0.75 was found from quadrupolar deuterium splittings, we conclude that the *para* axes of the two core fragments form an angle of about 20 °.

ELECTRIC POLARIZATION MEASUREMENT

Electric polarization measurements have been performed on the non-deuteriated material. We used 2 μm thick cells coated by rubbed polyimide in their inner surfaces. With fields up to 10V/μm ferroelectric-type switching was found between 55 °C and 94.5 °C. The electric polarization involved in the switching process is small. It is about 4 nC/cm^2 at 93 °C and practically zero at 75 °C. At lower temperatures it increases again up to 15 nC/cm^2 at 55 °C. This kind of behavior indicates that the polarization changes sign at around 75 °C. This anomaly at 75 °C is also shown in the voltage dependence of the switching time. It is represented together with the switching at 90 °C in the Figure 5.

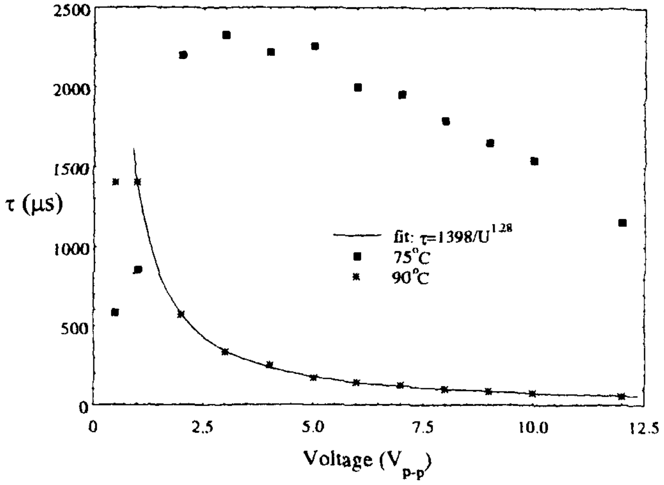

FIGURE 5 Voltage dependence of the switching time at 90 °C and 75 °C.

At 90 °C the switching time follows almost classical behaviour, and at 75 °C, however, it is quite different due to the vanishing permanent polarization.

We have also measured the temperature dependence of the tilt angle (see Figure 6). Unlike the switching time and the polarization it does not show any anomaly. The tilt angle increases from zero to about 16 ° monotonously. We emphasize here the substantial agreement of this value of the tilt angle with that measured by NMR (15 °), although the tilt angles given by these two methods do not need necessarily to be identical.

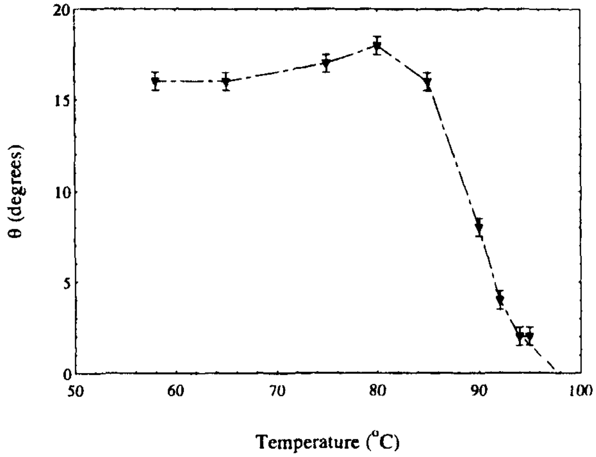

FIGURE 6 Temperature dependence of the tilt angle.

DISCUSSION

The anomaly observed at 74 °C by NMR should be in connection with the observed sign reversal of the polarization. We do not think, however, that it indicates an antiferroelectric transition. First of all, the polarization value is too small for antiferroelectricity. Secondly, there is no threshold for switching even below 75 °C.

The polarization is primarily dependent on a coupling between the local dipoles at, or in the proximity of, the asymmetric centers of the molecules in the ferroelectric mesophase. In most cases the central core is more tilted than the overall molecular structure. However, molecules are undergoing rapid reorientational motion about their long axes and many internal rotations around various bonds are also taking place at the same time. Accordingly, the spontaneous polarization depends on a time-dependent alignment of the dipoles in the system. For molecules that pack with their cores closer than the long molecular axes to the layers normal, an inversion of the polarization can happen as previously suggested by Photinos and Samulski[9] (see Figure 7).

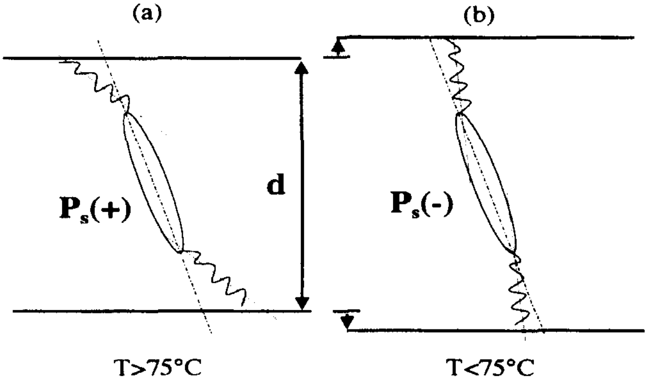

FIGURE 7 Conformational model for the polarization inversion at 75 °C.

In the literature there are materials where the polarization changes sign at some temperature (e.g. (S)-2-methylbutyl 4-*n*-octanoyloxybiphenyl-4'-

carboxylate, or (S)-2-methoxy-4-methylpentyl 4-*n*-octanoyloxybiphenyl-4'-carboxylate)[10].

The inversion is likely due to changes in the concentration of the various conformational species of the material as the temperature falls. If these species have opposite sign of their dipoles, then at a particular concentration of certain conformers the polarization becomes zero. This could happen, for instance, if the two carboxyls of the two ester groups in the mesogenic molecule reach a trans conformation. The fact the sign of the polarization changes is a good evidence for the postulation that the polarization direction is linked to conformational structure.

Above 75 °C the average conformation is like in Figure 7(a), whereas below 75 °C it is more similar to Figure 7(b). As the optical axis (it is determined by the central part of the molecule) is found to be constant during this transition, the smectic layer spacing (as could be determined by X-ray) could also change at 75 °C.

If this interpretation is correct, we can conclude that the conformational change produces a gradual change of the properties of the liquid crystalline material until the magnetic field, as the temperature lowers, is no longer above the critical field for the unwinding of the helical ferroelectric structure.

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