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^{2}H NMR spectroscopy of liquid crystals: structure and orientational order of a chiral smectogen in its A, C* and J* phases

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^{2}H NMR spectroscopy is employed to investigate the orientational order, molecular structure and phase transitions of the chiral smectic liquid crystal 1-methylheptyl 4′-(4-*n*-decyloxybenzoyloxy)biphenyl-4-carboxylate (**10B1M7**), showing smectic A, C* and J phases, as well as several sub-smectic C* phases. Two optically pure, differently deuteriated isotopomers have been purposely synthesized and studied.

1. Introduction

Chiral ferroelectric (FLC) and antiferroelectric (AFLC) phases found in some liquid crystal materials have recently been attracting considerable attention [1–6]. The interest in these mesophases, and in the rich variety of chiral sub-phases in between, stems from their polar properties connected to spontaneous or field-induced broken symmetries. There is presently much effort devoted to elucidating the structure and the polar properties of such intermediate mesophases. In fact, it is certain that several sub-phases can exist between FLC and AFLC phases, but they need further characterization from both the experimental and theoretical point of view. Although many different theoretical models have been suggested [7–9], the microscopic nature of the variation of the tilt angle in adjacent smectic layers and the organization of chiral phases is still far from being well understood.

Many experimental methods have also been employed for clarifying the molecular behaviour of FLC, AFLC and phases in between [10, 11]. To this end, NMR spectroscopy, in particular ^{13}C NMR spectroscopy, has been extensively used for probing the structure, ordering and dynamics of these kinds of chiral phase [12]. ^{2}H NMR spectroscopy, even if less extensively employed in this field, has been shown to be very useful for studying the structure and the dynamics of chiral smectic mesogens [13, 14].

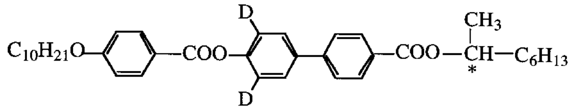
In order to study ferroelectric/antiferroelectric liquid crystals at a molecular level by ^{2}H NMR, we have prepared two differently deuteriated, optically pure samples of the mesogen 1-methylheptyl 4′-(4-*n*-decyloxybenzoyloxy)-biphenyl-4-carboxylate (**10B1M7**): one, with absolute configuration *R*, is deuterium labelled in the biphenyl moiety of the mesogenic core (**10B1M7-I**), and the other, having absolute configuration *S*, is partially deuteriated on the phenyl ring (**10B1M7-II**) (see figure 1).

The aim of the present work was the investigation of the structural properties of this material within its various mesophases by ^{2}H NMR spectroscopy. The partial deuterium labelling allows the use of ^{2}H NMR spectroscopy for obtaining the average orientational order of the two aromatic fragments with respect to the applied magnetic field, as well as information on their relative geometry and, possibly, on their tilt angle inside the smectic C* phase. Comparison with the findings of a previous study of this mesogen by ^{13}C NMR [15] will also be made.

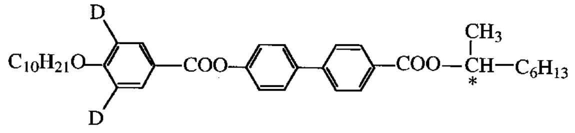
2. Experimental

2.1. *Synthesis*

The synthesis of **10B1M7** was performed following the generic route reported by Goodby *et al.* [2]. **10B1M7-II**



10B1M7-I



10B1M7-II

Figure 1. Structures of **10B1M7-I** and **10B1M70II**.

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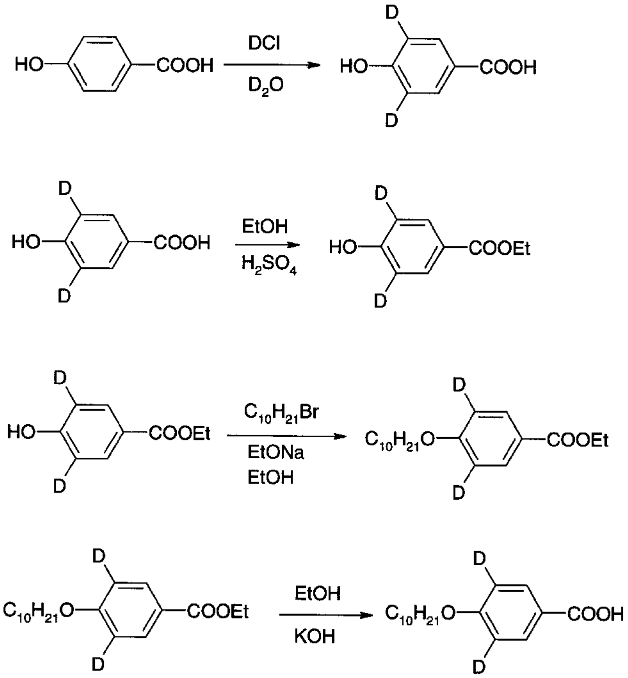
was prepared starting from 4-hydroxybenzoic acid, which had been deuteriated at positions 3 and 5 of the aromatic ring [16, 17] (scheme 1), whereas **10B1M7-I** was synthesized by deuteriating 4′-hydroxy-4-cyanobiphenyl at positions 3′ and 5′ [18] (scheme 2).

2.2. *DSC and optical microscopy*

This material was previously characterized by optical microscopy and differential scanning calorimetry by Goodby *et al.* [2], who found the following phase transitions:

$$\mathrm{I} \xrightleftharpoons{124.5^\circ\mathrm{C}} \mathrm{SmA} \xrightleftharpoons{105.4^\circ\mathrm{C}} \mathrm{ferro\ (SmC^*)} \xrightleftharpoons{75.9^\circ\mathrm{C}}$$

$$\mathrm{ferri} \xrightleftharpoons{69^\circ\mathrm{C}} \mathrm{antiferro} \xrightleftharpoons{47.8^\circ\mathrm{C}} \mathrm{J^*}$$



Scheme 1.

In our case DSC and optical microscopy gave the isotropic–smectic A, smectic A–smectic C*, as well as the smectic C*–J* transitions at slightly lower temperatures.

2.3. *NMR spectra*

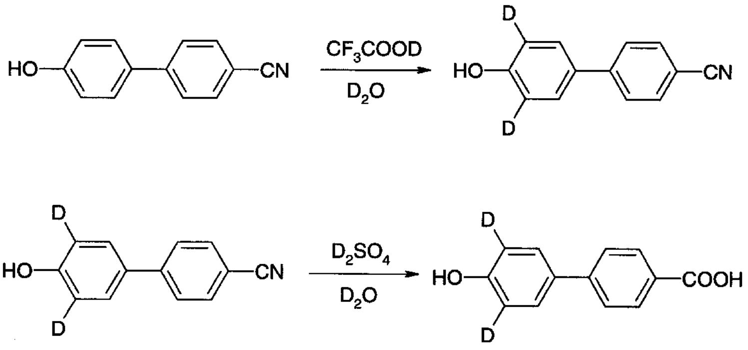
The ^{2}H NMR spectra were recorded using a Varian VXR-300 spectrometer, working at 46.04 MHz for deuterium. The samples were macroscopically aligned within the magnetic field by slow cooling from the isotropic liquid into the smectic A phase; the spectra were recorded every two degrees allowing 10 min for thermal equilibration. The temperature was stable within 0.1°C. Series of spectra of **I** and **II** are shown as a function of temperature in figures 2 and 3, respectively.

3. Results and discussion

The deuterium spectra of both **10B1M7-I** and **10B1M7-II** show a typical structure arising from a large deuterium quadrupolar splitting and a smaller deuterium–proton dipolar splitting (*ortho–meta*-interaction), as confirmed by the ^{1}H-decoupled spectra. Given the peak superposition clearly present to different extents in all the spectra, a spectral fitting procedure was applied in order to determine the correct values of the quadrupolar and dipolar splittings, as well as of the individual linewidths, using the ‘SPORT-NMR’ software [19]. As an example, the experimental and computed spectra of **I** and **II** at 94°C in the smectic C* phase, are shown in figure 4. A good fitting of all the spectra of **II** requires the assumption of a gaussian lineshape, while a satisfactory reproduction of most spectra of **I** can be obtained only by imposing a lorentzian lineshape. Since this is a suitable assumption for all the spectra of **I**, it was applied to the whole series.

The absolute value of the best-fit dipolar ($\Delta\nu_{\mathrm{dip}}$) and quadrupolar ($\Delta\nu_{\mathrm{q}}$) splittings of both phenyl and biphenyl deuterons are plotted against temperature in figures 5 and 6, respectively.

For both the deuteriated fragments the principal order parameter (S_{zz}) and the order biaxiality ($\Delta = S_{xx} - S_{yy}$)



Scheme 2.

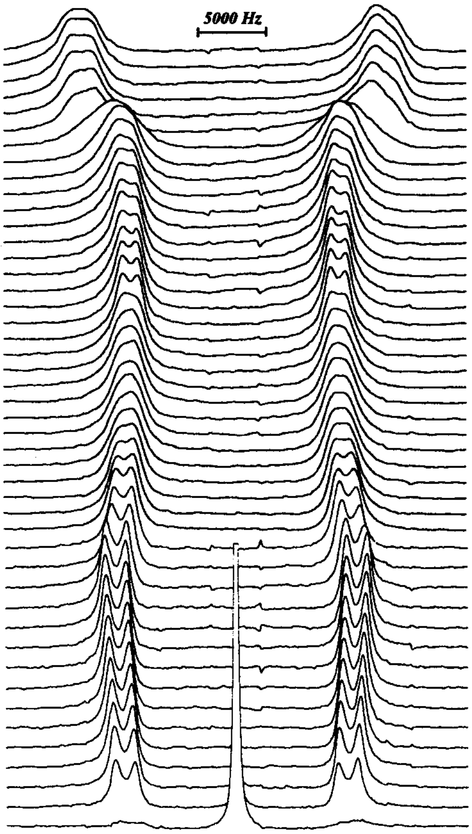


Figure 2. ^{2}H NMR spectra of **10B1M7-I** recorded at variable temperature in the range 122–32°C.

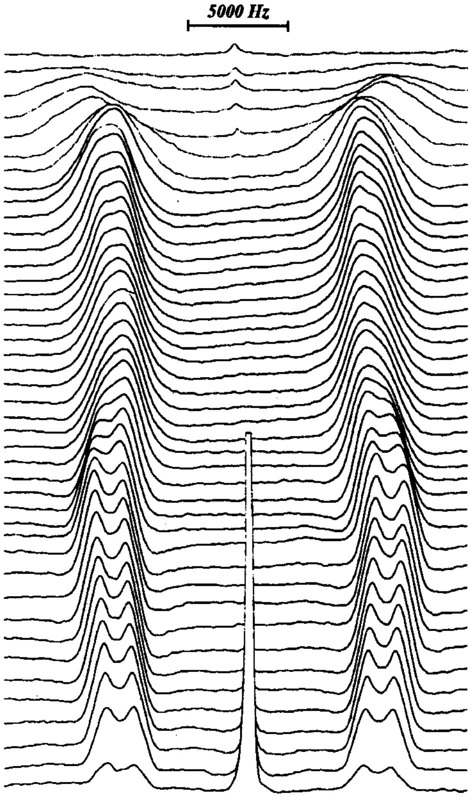


Figure 3. ^{2}H NMR spectra of **10B1M7-II** recorded at variable temperature in the range 120–40°C.

have been obtained at each temperature from the corresponding quadrupolar and dipolar splittings by using the following equations [20]:

$$\Delta\nu_{\mathrm{q}} = \frac{3}{2}q_{aa}\left[S_{zz}\left(c^2 - \frac{1}{2}s^2 - \frac{1}{6}\eta c^2 + \frac{1}{3}\eta s^2 + \frac{1}{6}\eta\right) + \Delta\left(\frac{1}{2}s^2 + \frac{1}{6}\eta c^2 + \frac{1}{6}\eta\right)\right] \quad (1)$$

$$\Delta\nu_{\mathrm{dip}} = -2K_{\mathrm{DH}}\frac{S_{zz}}{r_{\mathrm{DH}}^3} \quad (2)$$

where $K_{\mathrm{DH}} = 18434.38\,\mathrm{Hz\,\AA^3}$, $r_{\mathrm{DH}} = 2.5\,\mathrm{\AA}$, $\eta = 0.04$, $q_{aa} = 185\,\mathrm{kHz}$, $c = \cos\theta$ and $s = \sin\theta$. θ is the angle between the z axis, taken either along the biphenyl or phenyl *para*-axis, and the C–D bond, assumed to be 60° for both fragments. The y axis is taken perpendicular to the aromatic rings.

The sign of the splittings cannot be inferred directly from the spectra, but acceptable values of the order parameters can be obtained only when all the splittings are considered negative.

As an obvious consequence of equation (2), the behaviour of the S_{zz} order parameter exactly reproduces that of the dipolar splitting. Therefore, the trend against temperature of S_{zz} for the two deuteriated fragments can be seen in figure 5, using the suitable scale on the right of the graph. Note that it has been previously observed that the S_{zz} values of the phenyl rings in phenyl benzoate dissolved in a liquid crystal are different, and this was attributed to the motion about the C–O bond in the COO group [21].

In our case, the phenyl order parameter is always greater than that for the biphenyl, thus indicating that the phenyl *para*-axis is more aligned to the magnetic field. We would have obtained the opposite result if S_{zz} had been computed from equation (1), neglecting the biaxiality term, since $|\Delta\nu_{\mathrm{q}}|$ is always greater for the deuteria on the biphenyl group. On the other hand, such a procedure should necessarily have been applied if, as often happens in this kind of study, the quadrupolar splittings were the only available order-dependent experimental data.

In the smectic A phase, the order parameters increase regularly with decreasing temperature. Below the smectic A–smectic C* transition temperature at about 100°C, a gradual decrease of the S_{zz} values of both the biphenyl and the phenyl fragments takes place,

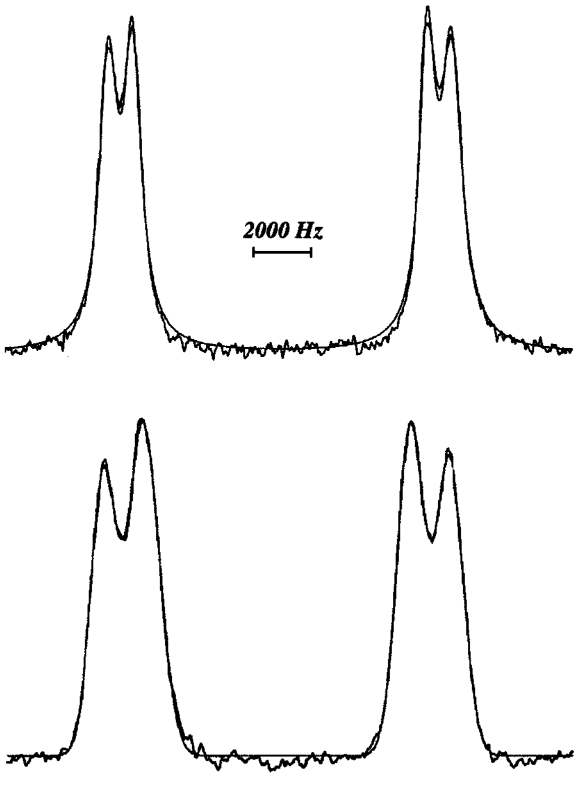


Figure 4. Experimental and fitted ^{2}H NMR spectra of **I** (top) and **II** (bottom) at 94°C.

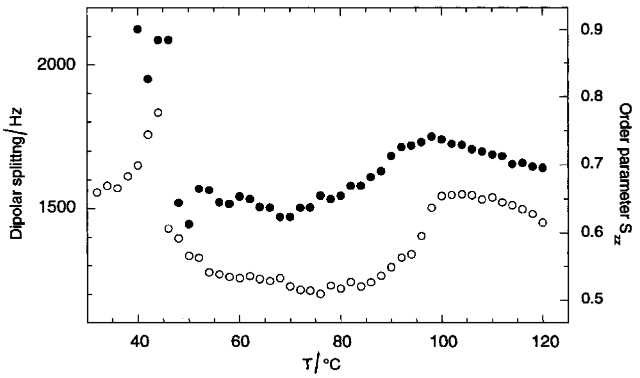


Figure 5. Measured deuterium dipolar splittings $\Delta\nu_{\mathrm{dip}}$ (scale on the left) and principal order parameter values S_{zz} (scale on the right) of the phenyl (filled circles) and biphenyl (open circles) fragments of **10B1M7** as a function of temperature.

indicating that the local directors increasingly tilt with respect to the magnetic field. A very similar behaviour is reported, for instance, for a mixture 40.8-d_4/HOAB [22], while a different behaviour has been recently observed for 4-(2-methylbutyloxycarbonyl)phenyl 4′-*n*-heptylbiphenyl-4-carboxylate-d_8 (MBHB-d_8) [14]. In the latter case the layers, rather than the local director inside them, tilt at the smectic A–smectic C* phase transition; that is the presence of the magnetic field prevents the winding of the helix formed by the local director in the smectic C* phase.

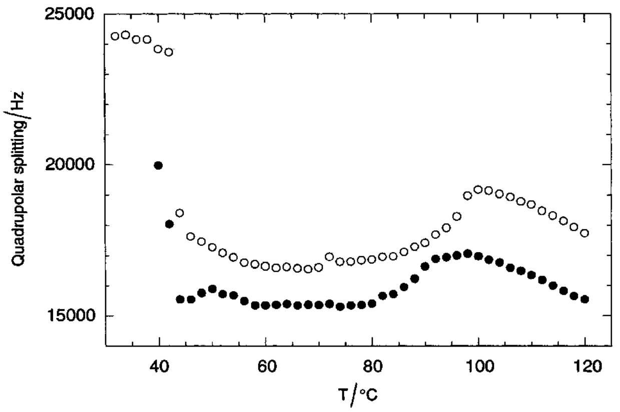


Figure 6. Measured deuterium quadrupolar splittings $\Delta\nu_{q}$ of the phenyl (filled circles) and biphenyl (open circles) fragments of **10B1M7** as a function of temperature.

In agreement with the findings of a previous ^{13}C NMR study [15], no intra-smectic C* phase transitions can be revealed from the trend of the order parameters of the phenyl fragment, and the fluctuations observed can rather be ascribed to the non-negligible error affecting the dipolar splitting measurements. On the other hand, at about 70°C, where a smectic C* ferri–antiferro transition has been found by Goodby *et al.* [2] and by Kilian *et al.* [23], a discontinuity in the trend of S_{zz} of the biphenyl fragment, followed by a slight increase, can be revealed. The reliability of this observation will be confirmed later, when discussing the biaxiality trend.

Finally, with decreasing temperature, a substantial jump of the S_{zz} parameter of both fragments is observed at the onset of the crystal J* phase. Here the S_{zz} values reach a maximum not far from the limiting value of 1. Then, below the transition, these order parameters, or at least that of the biphenyl group which is better determined, rapidly decrease. The crystal J* phase is known to be highly ordered and tilted, and therefore for our compound it seems that, when such a phase forms in the magnetic field, the *para*-axes of the two fragments tend to align along the field; then they begin to increase their tilt angle.

The order biaxiality of the two fragments, reported in figure 7, shows remarkably different behaviour with varying temperature. The phenyl biaxiality has a substantially constant trend, with a value of about 0.05 in the smectic A phase, and a slight decrease in the smectic C* phase where it assumes the value of about 0.04 below 70°C. Finally, this parameter increases in the J* phase where, on the other hand, it is very poorly determined. The biphenyl biaxiality is always much smaller and nearly constant inside each phase, with

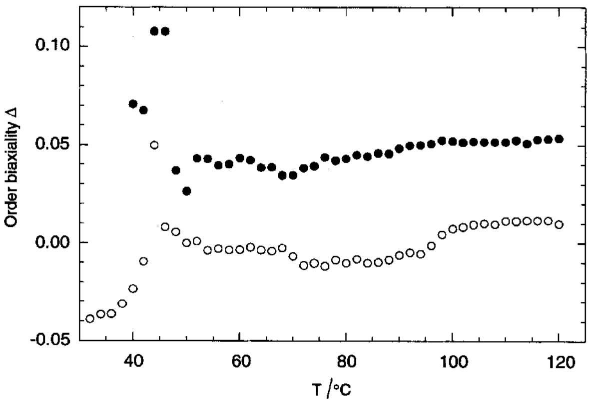


Figure 7. Order biaxiality Δ of the phenyl (filled circles) and biphenyl (open circles) fragments of **10B1M7** as a function of temperature.

the exception of the J* phase, but presents well defined discontinuities at the various phase transitions. The most interesting of these is found at 70°C, where the smectic C* ferri–antiferro transition is expected. This discontinuity is the combined result of the discontinuities in the experimental parameters $\Delta\nu_{\text{dip}}$, reflected into the S_{zz} trend, as already pointed out, and $\Delta\nu_{\text{q}}$. The latter parameter (see figure 6) is particularly well determined, with a quite smooth trend and a small but evident jump at 70°C; this has also been confirmed by recording a variable temperature series of proton-decoupled ^{2}H NMR spectra.

As far as the difference in biaxiality between the phenyl and biphenyl fragments is concerned, we must recall that a regular molecular geometry (for instance angles of 60° between C–D bonds and *para*-axes) has been assumed in the calculations, but the experimental data can likewise be well reproduced also in the presence of small distortions of the geometry, obtaining different values for the biaxiality.

An estimate of the angle ϕ between the *para*-axes of the phenyl and biphenyl fragments can be obtained by relating their order parameters through the relationship:

$$S_{zz}^{\text{biphenyl}} \approx S_{zz}^{\text{phenyl}} \frac{3\cos^2\phi - 1}{2}. \tag{3}$$

Substantially constant trends of ϕ, with average values of 14.5°, 22° and 19.5° were found within the 120–100°C, 95–75°C and 70–50°C ranges, respectively, with intermediate values around the phase transitions. These results can be compared with what has been reported for phenyl benzoate dissolved in a nematic solvent [21]. In this case, conformations where the *para*-axes of the rings are not parallel, due to rotation about the C–O bond in the COO group, are substantially populated. An average angle of 12° can be roughly estimated from the ring S_{zz} values given by equation (3). On the other hand, crystallographic data for phenyl benzoate indicate that the COO group and the bonds formed with the phenyl rings are coplanar and that the *para*-axes of the rings form an angle of 6° [24].

As already mentioned, the spectral fitting procedure yields individual linewidths, and their average values at the various temperatures are reported in figure 8. The remarkable changes in the linewidth throughout the temperature range investigated, which can be qualitatively observed from the spectra reported in figures 2 and 3, are related to the phase transitions. The linewidth increases very slowly on cooling within the smectic A phase; after the smectic A–smectic C* transition it increases much faster, even though the trends are somewhat different for the two fragments as the transition at 70°C is approached. In both cases, however, a decrease can be clearly revealed below this transition, followed by a sharp maximum at about 45°C, where the smectic C*–J* transition occurs. This complex behaviour of the linewidth cannot be interpreted here in detail, but it is clear that it reflects the presence of different dynamic situations in the different smectic phases, which deserve further investigation. In particular, the line broadening occurring on cooling at the onset of the smectic C* phase has been previously observed [15] and it is probably ascribable to motional processes, involving the molecular axes, taking place when the directors originate the helical structure [14].

In order to evaluate the tilt angle in the smectic C* phase, we could adopt a procedure already used for tilt angle measurements from birefringence data by Skarabot *et al.* [25]: the temperature dependence of the principal order parameter in the smectic A region could be fitted to a power law in order to describe mathematically the increase of the orientational order. This curve could then be extended to the smectic C* phase, ascribing the differences in the measured order parameters to the tilt

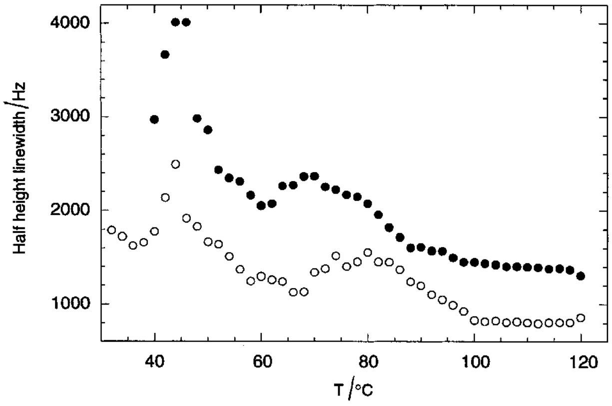


Figure 8. Half height linewidth of the ^{2}H NMR resonances of the phenyl (filled circles) and biphenyl (open circles) fragments of **10B1M7** as a function of temperature.

angle. In this procedure, however, a continuous trend of the molecular orientational order at the smectic A–smectic C* transition is assumed, but is not fully justified given the variety of behaviour reported in the literature [26, 27].

From the trend of the principal order parameters we can directly try to draw some conclusions concerning the tilt angle: this must regularly increase within the smectic C* phase, at least up to about 70°C, given the smooth decrease of S_{zz} from 100 to 70°C. However, since the tilt angle of **10B1M7** has been previously determined by Goodby *et al.* [2] by means of optical microscopy measurements, we tried to use these data to correct quantitatively our order parameters for the effect of the tilt angle. Unfortunately, neither of the two slightly different sets of data reported in [2] was in close agreement with our findings, probably due to the different experimental conditions, and therefore we only made use of the asymptotic value of about 27° for the tilt angle to estimate the correction of the principal order parameters in the smectic C* phase below 70°C. The S_{zz} values so calculated, now ascribable to the molecular orientational order only, range from 0.90 to 0.95 for the more oriented phenyl fragment.

In another perhaps less rigorous way of treating the problem, the data for the principal order parameter in the SmA phase of our chiral mesogen, relative to the phenyl ring, were superimposed on the S_{zz} trend in the SmA phase of a different smectogen showing a SmA phase of nearly the same temperature range, and a subsequent SmC phase where the molecules align along the magnetic field [28]. From these results we evaluated the tilt angle q_0 in the SmC* phase of **10B1M7**, supposing that the nematic order inside the smectic layers of the two smectogens had similar trends. The trend of the tilt angle so obtained, shown in figure 9, in agreement with what was obtained by Goodby *et al.*, with an asymptotic value of 27° [2], and can be fitted by the Landau equation:

$$q_0 = q_0^*[(T_c - T)/T_c]^\beta \qquad (4)$$

with $30° < q_0^* < 70°$ and $0.06 < \beta < 0.36$, where the parameter values increase with increasing temperature.

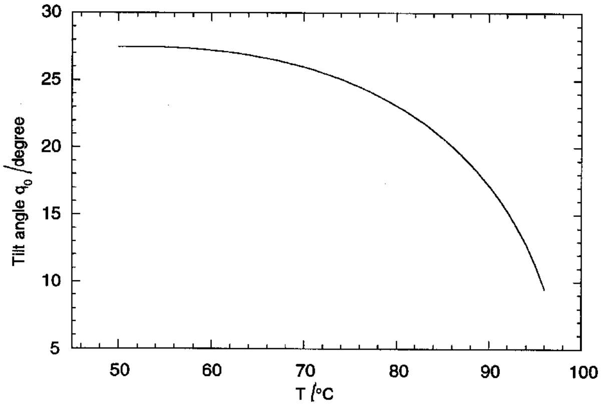


Figure 9. Temperature dependence of the molecular tilt angle q_0.

4. Conclusions

The results obtained confirm that deuterium NMR is a very useful and powerful technique for getting information about molecular geometry and phase structure of chiral liquid crystals. Of course deuteriation in more than one site is required to obtain information on different molecular fragments, and the cost and work required for this purpose are non-negligible drawbacks. The deuteriation at both phenyl and biphenyl moieties allowed us to find larger principal order parameters and biaxiality for the phenyl fragment with respect to the biphenyl fragment. These results, which are at first unexpected, can perhaps be rationalized by considering that the perturbing chiral centre is near the biphenyl moiety. In fact, recent ^{2}H NMR findings for a similar liquid crystal showed that the chiral chain lies obliquely with respect to the core axis [13], thus suggesting that the part of the core nearest to the chiral centre (the biphenyl group) could also be tilted with respect to the best-ordered core fragment (the phenyl ring). We have also found that the molecular core of our smectogen is remarkably bent, the two *para*-axes forming an angle ranging from 14.5° to 22° in the different mesophases. This seems a general structural result for the class of mesogens having an ester bridge in the core; they therefore show a semi-banana-like structure [14]. Moreover, straightforward information has been obtained on the tilt angle characterizing the SmC* phase, even though angular-dependent measurements which will be performed in the near future, would be more informative [29]. The currently available data, however, show that the angles formed between the *para*-axes of the aromatic fragments and the magnetic field progressively increase on cooling as the smectic C* phase is entered; they then reach a constant value and abruptly decrease at the smectic C*–J* transition, increasing again within the J* phase.

The use of spectral fitting procedures produced more reliable values for the dipolar and quadrupolar splittings, as well as for the linewidths. Therefore, in addition to the more evident smectic A–smectic C* and smectic C*–J* transitions, a slight but clear discontinuity in the trend of most experimental parameters at 70°C, particularly evident for the biphenyl deuterons, has been revealed. Such behaviour can be associated with the ferri–antiferro transition. At the moment it is difficult to discuss these tiny effects in terms of molecular behaviour, but our results suggest that ^{2}H NMR can play an important role also in clarifying the nature of intra-smectic C* transitions. In particular, the linewidth trend against temperature and the different lineshapes found for phenyl and biphenyl deuteria highlight the presence of complex dynamic processes. The line broadening occurring as the helix formed by the local directors winds within the smectic C* phase, for instance, can probably be explained in terms of cooperative fluctuations of the molecular long axes [30], even though additional experimental studies and suitable theoretical models are needed.

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