(+) 10E4M6: a critical A-C* and the first C*-hexatic B liquid crystal phase transitions
P. Keller, P.E. Cladis, P.L. Finn, H.R. Brand

To cite this version:

HAL Id: jpa-00210169
https://hal.archives-ouvertes.fr/jpa-00210169
Submitted on 1 Jan 1985

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
(+10E4M6: a critical A-C* and the first C*-hexatic B liquid crystal phase transitions

P. Keller
Laboratoire L. Brillouin, CEN Saclay, 91191 Gif-sur-Yvette Cedex, France

P. E. Cladis, P. L. Finn
AT & T Bell Laboratories, Murray Hill, NJ 07974, U.S.A.

and H. R. Brand (*)
Department of Physics, Kyushu University, 33, Fukuoka, 812, Japan

(Reçu le 25 septembre 1984, révisé le 12 août 1985, accepté le 21 août 1985)

Résumé. Nous avons déterminé que la phase smectique C* dans (+)10E4M6 (4'- (4-méthylhexyloxy)phényl 4-decyloxybenzoate) apparaît entre deux phases smectiques orthogonales : une phase smectique A au-dessus de 70 °C et une phase smectique B hexatique en-dessous de 31,3 °C.

La transition C*-A montre peu d'hystérésis en température et semble continue, avec une anomalie de capacité calorifique importante. Dans la phase smectique C*, la variation de l'angle θ, d'inclinaison des molécules est suivie par rayons X; elle peut être décrite par θ ~ (T_{CA} - T)^β avec β = 0,32 ± 0,08 (T_{CA} est la température de transition C*-A). Pour comparaison, un analogue non chiral de (+)10E4M6 a été étudié : (10E6) (4'-hexyloxyphényl 4-decyloxybenzoate). Il présente un saut de chaleur spécifique à la transition C-A plus faible que pour (+)10E4M6 et une variation de θ ~ (T_{CA} - T)^β avec β = 0,35 ± 0,07.

La transition C*-B hexatique est monotropicque et discontinue. Deux longueurs coexistent au voisinage de la transition, qui correspondent à une variation de l'angle d'inclinaison des molécules de 23° à 0°. Un traitement de surface produit un ancrage fort de l'orientation du directeur à la surface et oblige les plans smectiques à se reformer à la transition C*-B hexatique. Celle-ci représente la première observation non équivoque au microscope polarisant de la reformation des plans smectiques à une transition entre deux phases de genre smectique.

Abstract. We have determined that the C* phase in (+)10E4M6 (4'- (4-methylhexyloxy)phenyl 4-decyloxybenzoate) occurs between two orthogonal phases : an A phase above 70 °C and a hexatic B phase below 31.3 °C.

The C*-A transition shows very little temperature hysteresis and seems continuous with a large anomalous heat capacity. X-ray measurements of the tilt angle, θ, in the C* phase could be described by θ ~ (T_{CA} - T)^β with β = 0.32 ± 0.08, T_{CA} the C*-A transition temperature. In comparison, a non-chiral analogue of (+)10E4M6 called 10E6 (4'-hexyloxyphenyl 4-decyloxybenzoate), exhibited a much smaller specific heat jump at the C-A transition and β = 0.35 ± 0.07.

The C*-hexatic B transition is monotropic and discontinuous. Two lengths coexist in the transition region corresponding to a change in tilt angle from 23° to zero. Strong anchoring conditions of the director orientation by surface treatment forces the layers to reform at the C* to B transition. This is the first unequivocal observation in the polarizing microscope of the reformation of smectic layers at a transition between two smectic phases.

1. Introduction.
In contrast to nematic liquid crystals which only show orientational order along a particular direction called the director, n, smectic liquid crystals also have a layer structure [1]. In general they occur at lower temperatures and a typical layer spacing is 20-35 Å. Here we are concerned with the appearance of a tilted smectic phase (the director is not parallel to the layer normal) between two orthogonal smectic phases (the director is parallel to the layer normal)
of a chiral compound: (+)10E4M6 (4’-4-methylhexyloxyphenyl-4-decyloxybenzoate) [2], shown in figure 1.

In view of the large variety of smectic phases under current investigation, and in order to fix ideas, we first give an overview of the framework into which we believe our data fit. In smectic A (orthogonal) and C (tilted) phases, there is complete 2-dimensional fluidity in the plane of the layers. In addition, the director in the C phase of chiral compounds, generally denoted as C*, spirals around the layer normal with a uniform pitch typically 2-5 µm. Owing to its chirality and in-plane fluidity, C* is helielectric: there is a polarization, P, perpendicular to the plane spanned by n and the layer normal, which rotates in space with the same pitch as n. « Bond orientational » order characterizes the orthogonal smectic phase known as hexatic B [3, 4]. We interpret [5] this to mean that in-plane translational motions are restricted to the lines of a centred hexagonal grid.

A tilted analogue of hexatic B with the centred hexagonal in-plane grid replaced by a rectangular one, is called smectic I or F depending upon whether the tilt direction is along a short or a long side of the rectangle [6]. In crystal B phases, the in-plane translational order is discrete: molecules are localized on a 2-d hexagonal lattice but rotate freely about their long axis. The final orthogonal smectic phase we mention is smectic E. It is characterized by a rectangular 2-d in-plane lattice and hindered rotations about the long molecular axis.

On cooling, the C* phase typically transforms to another tilted smectic phase like I*, or to the crystal. Hexatic B phases frequently occur between a smectic A phase at higher temperatures and a crystal B or smectic E phase at lower temperatures [3, 4, 7]. Only one compound [7] is known to exhibit a hexatic B phase below a C phase.

(+)10E4M6 is the first pure compound we know to exhibit the C*-hexatic B transition. This makes it interesting for the study of the effect of chirality on the stability of the rich variety of liquid crystal phases in general. Up to now, this kind of study has only been made on mixtures [8] of chiral solutes and non-chiral solvents or racemates [5]. Here we compare the liquid crystal properties of (+)10E4M6 to those of a very similar non-chiral compound 10E6 (4-hexyloxyphenyl 4-decyloxybenzoate) [9] in which a simple hexyl chain replaces 4-methylhexyl of (+)10E4M6 (see Fig. 1). Since the aromatic sections of both molecules are identical it is reasonable to suppose that the inter-molecular interactions they evoke are also identical. Their hydrocarbon chains differ in that one H is replaced by CH₃ in the chiral compound making it the more chunky variant of the two. Thus, although there is a one to one correspondence between the phases of (+)10E4M6 and 10E6, the temperature regime of a given phase is generally higher in the non-chiral compound owing to its more rod-like shape.

In contrast, racemic mixtures (same aromatic core; 50% left-handed chains, 50% right-handed ones) typically exhibit the same temperature regimes as the chiral species [5]. Presumably, this is because the difference in stereo-chemistry resulting from chirality is negligible when the hydrocarbon chains are « melted » as they are believed to be in all liquid crystal phases [10]. There is, however, one known exception to this general observation [11].

2. Observations.

2.1 DSC. — From observations of (+)10E4M6 in the polarizing microscope and DSC (Fig. 2) we obtain the following sequence of transitions:

<table>
<thead>
<tr>
<th>Phase</th>
<th>Transition</th>
<th>Temperature (°C)</th>
<th>Heat of Melting (cal/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xtal</td>
<td>4.35</td>
<td>37.4</td>
<td>13.2</td>
</tr>
<tr>
<td>2.1</td>
<td>hexatic B</td>
<td>21.3</td>
<td></td>
</tr>
<tr>
<td>C*</td>
<td>70.69</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A23 chol</td>
<td>23</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Iso</td>
<td>25</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

T_{melt} = 37.4 °C and heat of melting = 13.2 cal/g.

Similar observations on 10E6 reveal the following sequence of phases:

<table>
<thead>
<tr>
<th>Phase</th>
<th>Transition</th>
<th>Temperature (°C)</th>
<th>Heat of Melting (cal/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xtal</td>
<td>39.3</td>
<td>58.25</td>
<td>21.48</td>
</tr>
<tr>
<td>2.6</td>
<td>hexatic B</td>
<td>22.6</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>27.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>83.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N</td>
<td>90.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Iso</td>
<td>1.3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

T_{melt} = 58.25 °C and heat of melting = 21.48 cal/g.
Comparing the phase transitions of 10E6 with (+)10E4M6, it is seen that the more bulky, chiral hexyl chain depresses the liquid crystal phase transition temperatures and the C* phase is 5 °C wider than the C phase. The temperature range of the hexatic B phase has nearly tripled from 13.5 °C to 35.8 °C since the crystallization temperature is depressed about 35 °C! Compared to 10E6, the melting point depression of (+)10E4M6 is on the order of 20 °C.

2.2 X-RAY MEASUREMENTS. — The layer spacing of (+)10E4M6 and 10E6, measured as a function of temperature using a Rigaku rotating anode and a linear detector, is given in figures 3a and 3b, respectively. In the C* phase, the layer spacing decreases continuously from 32.1 Å at 70 °C to 29.4 Å at 45 °C, i.e., 2.7 Å over a range of 25°. This corresponds to a variation of the tilt angle from 0° to ≈24° at 45 °C. At 58.8 °C, we determined by optical means that the tilt angle was ~16°. This is to be compared with the ~22° from the X-ray data. By measuring the dis-

![DSC curves in the vicinity of the isotropic transition of a) 5.05 mg (+)10E4M6 and b) 6.01 mg 10E6 showing the small heat capacity anomaly at the C-A transition and wider nematic range of 10E6 compared to the C*-A transition and cholesteric phase, respectively, of (+)10E4M6. Scan rate is 1 °C/min.](image1)

![X-ray layer spacing measured as a function of temperature. The molecular length in the stereo model is 35.5 Å. a) (+)10E4M6, b) 10E6.](image2)
stance between « pitch lines » as seen in the optical microscope in the C* phase, the pitch was found to be ~ 9 μm at 60 °C. At 63.2 °C, 10 V/14 μm was sufficient to « switch » the C* phase in a « soliton-switch » mode typical of helielectrics [12]. Below 45 °C the layer spacing again increases to about 30 Å at the transition to the hexatic B phase, which showed no response to an electric field up to 10⁶ V/cm over its entire temperature range.

At the C*-hexatic B transition, the layer spacing jumps 3.3 Å to 33.3 Å. Fully extended, (+)10E4M6 is about 35 Å. A similar jump is also observed at the C-hexatic B transition in the 3-ring ester 80.05 [7]. These jumps contrast drastically with the continuous 5 Å increase in layer spacing observed in MORA12 over a 10 °C temperature interval in a novel intermediate phase called P* [13]. We note that although the temperature range of the liquid crystal phases is different, the layer spacings in 10E6 are nearly identical to those of (+)10E4M6. As we have previously observed [5, 22] both the temperature range and the layer spacings are comparable in a racemic mixture, to those of the chiral compound in the liquid crystal phases.

The layer spacing in the hexatic B phase of (+)10E4M6 and 10E6 is 1 Å longer than in the A phase reflecting the growth of orientational order throughout the broad C* (C) range of (+)10E4M6 and 10E6. The orthogonal nature of the hexatic B phase was confirmed by observation of a thick freely suspended film in the optical microscope. In the chiral compound, the film is black between crossed polarizers for all temperatures below 70 °C to room temperature, even in the C* phase since the optic axis of the helicoidal structure is also along the layer normal. In 10E6, however, only the A and B phase are black between crossed polarizers indicating that these phases are orthogonal. We did not observe the smectic E phase previously reported by Shashidhar and Kleinhans [9] below the B phase of 10E6.

Wide angle X-ray diffraction as shown in figure 4 gives qualitative information about the degree of order associated with the in-plane structure. In order to obtain these data, the linear detector was rotated on an arc so that it spanned between 7 Å⁻¹ and 4 Å⁻¹ in reciprocal space. Once the experimental geometry had been set up and calibrated, the samples in figure 4 were placed in the beam path one after the other, to obtain the comparison under identical experimental conditions. 40.8 is well known to have a crystal B [3] and this is evidenced by the sharp peak displayed in the X-ray powder pattern of its in-plane structure (Fig. 4). The sharpness of the peak shown is limited by the instrumental resolution. Although other hexatic B phases have been identified on the basis of qualitative features associated with the X-ray powder pattern [14], as we are doing here, 650BC and 460BC are the only compounds which have been confirmed on the basis of single crystalline line shape, as being hexatic B, i.e. there is bond orienta-

![Figure 4](image-url)
tional order (BOO) but no long range positional order associated with the in-plane molecular structure. This lack of positional order is translated into a relatively broad in-plane powder pattern compared to the instrumental resolution, i.e., compared to the sharpness of the peak for 40.8. Comparing the data for 10E4M6 to these two «canonical» cases, we note that its wide angle pattern is not instrumentally limited and is qualitatively more like 65OBC. Thus, we conclude that the B phase of 10E4M6 is of the hexatic variety. Since 10E4M6 is an ester, this result falls in with the trend noted by Goodby [15] on the basis of observations in the polarizing microscope, that esters tend to form hexatic B phases whereas Schiff bases tend to form crystal B phases.

P* is a new phase observed [13] in MORA12 (also shown in Fig. 4). It is characterized by a large temperature dependence of its layer spacing so that in a small temperature interval its layering reaches nearly a molecular length and it is only very slightly tilted. In the P* phase, there is a helicoidal structure and a local polarization which couples linearly to an external electric field. The B phases do not exhibit this property. As is clear, on the basis of the in-plane powder patterns or observations of freely suspended thin films, we cannot exclude the possibility that the phase we have identified as hexatic B is P*. In order to do this, we checked its electric field response and found none even in fields as large as 500 V/12 μm. This observation not only rules out P* but also F* and I*. Thus, we conclude that the phase is indeed an orthogonal one and not one of the more exotic helielectric phases.

2.3 CRITICAL BEHAVIOUR AT THE A-C AND A-C* TRANSITION. — Figures 5a and b show double logarithmic plots of the tilt angle θ in the vicinity of the C*-A and C-A transition as a function of temperature. θ was determined from the measurements of the X-ray layer spacing and by assuming cos θ was the ratio of the length in the C* phase at a given temperature to the length in the A phase at TCA. This relation was first proposed as a measure of θ by Guillon and Skoulios [16] and proved to be valid with high accuracy by Safinya et al. [17]. Figure 5a shows the best fit for (+)10E4M6 and figure 5b for 10E6 for one run. Varying both TCA and the smectic A layer spacing at TCA, a least squares fit of the data in the vicinity of the A phase at TCA. This relation was first proposed as a measure of θ by Guillon and Skoulios [16] and proved to be valid with high accuracy by Safinya et al. [17]. Figure 5a shows the best fit for (+)10E4M6 and figure 5b for 10E6 for one run. Varying both TCA and the smectic A layer spacing at TCA, a least squares fit of the data in the vicinity of the A phase at TCA.

Our final average of four such runs for each compound is \( \beta = 0.32 \pm 0.08 \) for (+)10E4M6 and \( \beta = 0.35 \pm 0.07 \) for 10E6. These results are consistent with de Gennes' prediction [1] and in agreement with earlier light scattering results of Delaye [18] on a similar ester compound (4-nonyloxybenzoate 4'-butyloxyphenyl)-9E4 in our acronym, as well as optical measurements on other compounds [19, 20]. Mean field results have been reported at the C-A transition in still other compounds for which the critical region is very narrow [21] and the temperature range of the A phase is relatively broad. In 10E6M6 as in 9E4 and 10E6, the narrow temperature range of the A phase could be responsible for the large fluctuations at the A to C transition in these compounds.
2.4 Surface pinning of the director in a thin sample. — Recently, a novel electro-optic device has been proposed [23] for helielectric liquid crystals, like C*, in which the director re-orients rapidly in electric fields (in µseconds or less) but which are not bistable [24]. The idea is to construct a sample so thin that boundary effects dominate the electro-optic behaviour. The natural helical structure is unwound and the director orientation induced by the electric field is locked-in by surface forces once the field is removed. These surface interactions must be such as to orient the director in the plane parallel to the bounding plates, but in this plane, the director must also be free to re-orient [23]. The remarkable aspect of this device is the unusual properties of the bounding surfaces. As far as we know, such a simultaneously:

1. strong: the director is constrained to a unique direction once the field is turned off;
2. weak: the director slips freely from one orientation to another by rotating in the plane of this surface;

anchoring condition has not yet been discovered. Furthermore, reference [23] does not specify how to obtain it so, one might assume, that no particular precaution is required.

Another aspect of these remarkable boundary conditions is that constraining the director to lie in a plane but allowing it to rotate freely in that plane, implies that the layers also slip freely in that plane. If the layers are pinned, then as the director rotates, they will be subjected to severe dilation forces as the tilt angle changes from its old equilibrium value through zero to its new equilibrium value. This contradicts the freely rotating hypothesis.

As a point of reference, we note that strong anchoring is the most common condition. Once surface forces align the director along a preferred direction it does not change even upon cycling through the isotropic transition or re-orienting by electric, magnetic or flow fields.

Compounds like +10E4M6 with a hexatic B to C* phase transition offer a unique opportunity to build our intuition about the postulated plasticity [23] of surface forces of liquid-crystal-glass interfaces. On going from C* to B, the layer spacing undergoes a 3 Å (Fig. 3) change or a ~ 10% dilation. The question one poses is: does the director remain fixed at the glass-liquid crystal interface during this transition forcing the layers to reform or, are the layers fixed and the director free to rotate?

In order to explore this question, we prepared a thin (~ 3 µm) oriented sample of (+)10E4M6 prepared between a rubbed (no surfactant) cover-slip and microscope slide with no spacers. We found that the director was so strongly pinned by the boundary conditions that, at the C*-hexatic B transition, the layers were forced to reform. The director did not rotate as envisaged by reference [23].

In figure 6, the polarizer and analyser are crossed parallel to the edges of the photograph. Since the oriented regions are black we infer that the director is also parallel to one of the edges of the photograph. At the transition to the hexatic B phase, these regions remain black and additional lines appear at an angle of approximately 25° to the edge of the photograph. We infer these to be strain lines created as the layers reform. Since the contrast did not change through the transition, the director orientation is unchanged. In view of this result, we conclude that our boundary conditions are of the, common, strong anchoring variety.
3. Conclusion.

In conclusion, we have proposed that the generally higher temperatures of the liquid crystal phases of 10E6 compared to +10E4M6 is due to its more rod-like configuration. We found that the helicoidal structure does not affect the exponent $\beta$ at the C*-A/C-A transitions. A least square fit to the temperature dependence of the tilt angle in the vicinity of the C*-A and C-A transition as derived from X-ray measurements of the layer spacing yielded $\beta = 0.32 \pm 0.08$ and $\beta = 0.35 \pm 0.07$ respectively in agreement with results previously obtained [18] on a similar compound (9E4) and the $d = 3$, $n = 2$ helium analogy for this transition [1]. The observable A-C critical region in these compounds may be correlated to the narrow temperature range of the A phase.

In addition, on the basis of

1) observations in the polarizing microscope, particularly of thick freely suspended films,
2) the absence of a linear electrooptic response 3) and qualitative evidence from in-plane X-ray diffraction,

we identified the phase below C* to be hexatic B. To completely nail down this conclusion and to rule out the possibility it is perhaps a reentrant smectic A phase, high resolution X-ray scattering along the lines of reference [4] must be made.

The C*-hexatic B transition revealed that surface effects can indeed pin the director orientation sufficiently strongly that layers are obliged to reform at a first order transition between a tilted and an orthogonal phase.

Acknowledgments.

We thank J. W. Goodby for providing us with 10E6 and M. A. Marcus for his contributions to the nonlinear least square fitting routines used by us. One of us (H.R.B.) wishes to thank the Japan Society for the Promotion of Science for support.

References