Chapter 3

Effect of the Smectic I* Phase Temperature Range on the Nature of the Tilted Fluid to Hexatic Transition
Effect of the $I^*$ range on the nature of $C^*-I^*$ transition

### 3.1 Introduction

As discussed in the previous chapter, hexatic liquid crystalline phases possess long-range bond-orientational order (BOO) but negligible interlayer correlation. Examples include hexatic B (hex B), smectic I (Sm I), smectic F (Sm F) etc. More appropriately, the hex B phase can also be described as smectic A (Sm A) pliaic supplemented by a six-fold BOO. In a similar fashion, the Sm I and Sm F phases represent smectic C (Sm C) type of order supplemented by the six-fold BOO. Theoretically, it has been argued that in the Sm C phase, long range order in tilt always induces BOO, albeit of small amplitude. This BOO grows rapidly on transformation from Sm C to Sm I (or Sm F) phase. In other words, both Sm C and Sm I (or Sm F) have identical symmetry. Consequently, Sm C transforms to Sm I (or Sm F), either through a first order phase transition or evolves continuously from one phase to another without a phase transition.

Experimentally, Brock et al., measured BOO and in-plane positional order both in Sm C and Sm I phases of a racemic 4-(2-methylbutyl)phenyl 4'- (octyloxy)-(1,1')-biphenyl-4-carboxylate (or 8OSI) (racemic is a 1:1 mixture of the right and left handed forms). Results showed that the Fourier components of the hexatic order grow progressively on cooling from the Sm C phase to the Sm I phase. The BOO locked to the tilt grows continuously, confirming that there is no abrupt transition; rather the evolution is smooth and continuous. Further these results confirm the theoretical prediction that the field $h$ arising due to a coupling between the tilt and hexatic order parameters induces a finite liexatic
order in the Sm C phase and can destroy the Sm C-Sm I phase transition.

The situation that the Sm C-Sm I transformation can be either first order or of continuous evolution type without a phase transition, is similar to the gas-liquid transition or the paramagnetic-ferromagnetic transition in the presence of a non-zero applied field. It is well known that in these cases, the first order phase boundary terminates at a critical point followed by a continuous evolution region-usually termed as the supercritical region. But such a critical point has not been seen in Sm C-tilted hexatic (Sm F or Sm I) systems. Based on simultaneous analysis of ac-calorimetric data and the hexatic order parameter, Garland et al.,\(^3\) argued that in 8OSI the zero tilt-field transition may be a first order transition. Despite these efforts, it is not known what material parameters control the strength of this tilt field and consequently the nature of the transition. This chapter discusses experiments carried out to identify the material parameter responsible and also the search for a Sm C-Sm I critical point.

### 3.2 Experimental

Experiments have been carried out on three compounds belonging to the homologues series of 4 - n- alkoxy biphenyl - 4' - (2' - methyl butyl) benzoates (nOBMBB) series.\(^4\) These compounds exhibit Cholesteric $\rightarrow$ Sm C* $\rightarrow$ Sm I* $\rightarrow$ Sm J phase sequence on cooling from the isotropic phase. (The asterisk indicates that the phases are chiral. But in the present discussion we ignore the differences between the chiral and achiral versions. Also to be noted is that the Sm J phase is the crystalline form of the Sm I phase and hence the name Cry J).
Effect of the $l^*$ range on the nature of $C^*-I^*$ transition

The structural formula of the compounds studied are given in Table 3.1.

The experiments have been carried out using aligned samples obtained by cooling at a slow rate from the high temperature cholesteric phase in the presence of an in situ 0.8 T magnetic field. The details of the experimental set up have already been described in Chapter 2.

### 3.3 Results

Figure 3.1 shows a plot of temperature versus layer spacing $d$ for the 7th, 10th and 12th homologues of the nOBMBB series. The thermal variation of $d$ shows an increase on passing from Sm C* to the Sm I* phase. The absence of a jump in $d$ as well as the absence of a two-phase coexistence region confirms that the Sm C* phase evolves continuously into the Sm I* phase with decrease in temperature. Another feature which supports this conclusion is the thermal variation of the X-ray diffraction peak intensity across the Sm C*-Sm I* transition. The monotonic variation of intensity seen in figure 3.2 (for 12OBMBB) is characteristic of transformations of the continuous evolution type. Similar features were observed for the 7th and 10th homologues also.

The notable features of figure 3.1 are

- Although the total variation of $d$ across the transition is quite small ($\sim 0.1\AA$) for the 7th homologue, the essential feature (see inset of figure 3.1) observed for the higher homologues - an increase in $d$ on going from Sm C* to Sm I* phase - remains unaltered.

- The overall variation in $d$ and its rate of variation with temperature,
Effect of the I* range on the nature of C* - I* transition

nOBMBB

\[ n \underset{C_nH_{2n+1}O-O-C-O}{\text{--}} \underset{\text{CH}_2\text{CHC}_2\text{H}_5}{\text{--}} \underset{\text{CH}_3}{\text{--}} \]

4-n-olkoxy biphenyl 4-(2'-methylbutyl) benzoate

n = 7, 10 and 12

Isotropic → Cholesteric → Sm C* → Sm I* → Cry J

Table 3.1: Structural formula of compounds belonging to nOBMBB series. Compounds used are with n=7, 10 & 12.
Effect of the P range on the nature of \( C^* - I^* \) transition

Figure 3.1: Temperature variation of the layer spacing \( d \) in the vicinity of Sm C*-Sm I* transition for the three homologues, \( n=7 \) (○), \( n=10 \) (□) & \( n=12 \) (△) of nOBMBB series. The data for \( n=7 \) is also shown in the inset on an enlarged scale. The continuous variation of \( d \) for all the three compounds indicates that the transition is of the continuous evolution type. Here \( T_{\text{eff}} \), the pseudo transition temperature is identified as the inflection point on the curve. The value of \( T_{\text{eff}} \) obtained in this manner is in very good agreement with observations of Goodby et al.\(^4\)
Effect of the $I^*$ range on the nature of $C^*-I^*$ transition

Figure 3.2: Thermal variation of peak intensity near the transition for the 12th member of nOBMBB series. Note the continuous variation in intensity on passing from Sm $C^*$ to Sm $I^*$ phase. This feature is characteristic of a continuous transformation.  

$T - T_{eff} \ (\degree C)$

peak intensity (a.u.)

Sm $I^*$

Sm $C^*$

12OBMBB
Effect of the $I^*$ range on the nature of $C^*-I^*$ transition

\[
\Delta d/\Delta T', \text{ particularly near the pseudo-transition point } T_{\text{eff}}, \text{ increase as the chain length is increased.}
\]

Notice that on increasing ‘n’ the temperature range ($R$) of the Sm $I^*$ phase increases. $R$ is 2.1°C for $n = 7$, 8.9°C for $n = 10$ and 16.2°C for $n = 12$. Presumably, this increase in $R$ is associated with the increase in the strength of the phase transformation, as reflected in the rate of variation of $d$.

It may be recalled here that a similar trend has been observed\(^6\) for the 10,13,15 and 19th members of the terephthal-bis alkyl aniline (TB$n$A) series which exhibit the Sm C-Sm I transition (see figure 3.3). In all these compounds the transition is first order accompanied by a jump in the layer spacing. The jump in $d$ across the transition increases with an increase in the temperature range of the Sm I phase. The lower members of the TB$n$A series with $n = 5$, 6, 7 and 8 exhibiting the Sm C-Sm F transition also show this type of relationship between the strength of the transition and the range of the hexatic phase, viz., the Sm F phase\(^7\) (see figure 3.4). A point that must be noted is that the higher homologues of TB$n$A series show the presence of a second hexatic phase, i.e., Sm F below Sm I. In order to see the influence of having a second hexatic phase on the nature of Sm C-Sm I transition, we undertook measurements on compounds which are structurally similar but differ in the number of hexatic phases they show.

The compounds used are\(^8\)

I. bis-(4′-n-heptyloxybenzylidene)-1,4-phenylenediamine (TB7OA) and Terephthal-bis-decylaniline (TB10A)
Effect of the $l^*$ range on the nature of $C^0$-$l^*$ transition

Figure 3.3: Thermal variation of $d$ near Sm C-Sm I transition for higher members of TBBnA homologous series. (adapted from Ref. 6). Notice the jump in $d$ at the Sm C-Sm I transition, indicating a first-order change.
Effect of the $I'$ range on the nature of C-$I'$ transition

Figure 3.4: Thermal variation of d near Sm C-Sm F transition for lower members of TB$n$A series. (From Ref. 7). The transition is first order for all the compounds.
2. 4-(2'-methylbutyl)phenyl 4'-n-octyloxybiphenyl-4-carboxylate (80SI*) and 4-(2'-methylbutyl)phenyl 4'-octylbiphenyl-4-carboxylate (8SI*)

The structural formulae and the transition temperatures of these compounds are given in Table 3.2. TB1OA and TB7OA look structurally similar (see Table 3.2). Both the compounds have approximately the same temperature range of Sm I phase, e.g., ~ 7°C for TB7OA and ~ 9.1°C for TB1OA. The only difference is that TB1OA shows the presence of a second hexatic phase viz., Sm F phase with a range of ~ 30°C below Sm I whereas TB7OA has only one hexatic (Sm I) phase. Thus the effective hexatic phase temperature range for TB1OA can be taken as ~ 40°C compared to ~ 9.1°C of TB7OA.

Similarly the only structural difference between 80SI* and 8SI* is that 80SI* has an alkoxy chain while 8SI* has an alkylone. 80SI* shows the presence of only one hexatic phase, viz., the Sm I* phase, but 8SI* shows two types of hexatics, Sm I* and Sm F* phases. But notice that the combined temperature range of the hexatic phases is slightly higher for 8SI* (6°C) than for 80SI* (4.8°C).

Figures 3.5 and 3.6 show the thermal variation of layer spacing across Sm C-Sm I transition for TB1OA and TB7OA. It is clear that the transition is first order for both the compounds marked by a jump in the layer spacing and also by the presence of a two-phase coexistence region. In fact, the cross-over behaviour in intensity seen across Sm C-Sm I transition (see figures 3.7 and 3.8) is also typical of a first order transition. The jump in layer spacing for TB10A (~ 2 Å) is about 16 times higher than that for TB7OA. From Table 3.2 it is seen that the hexatic temperature range is larger for TB10A than for TB7OA.
Effect of the I' range on the nature of C-I' transition

**TB10A**

\[
\begin{array}{c}
\text{C}_{10}H_{21} - N = CH - C_{10}H_{21} \\
\text{terephthal - bis - decylaniline}
\end{array}
\]

Isotropic \(\rightarrow\) Sm A \(\rightarrow\) Sm C \(\rightarrow\) Sm I

\[191.0 \rightarrow 189.2 \rightarrow 154.8\]

\(\rightarrow\) Sm F \(\rightarrow\) Cry G

\[148.7 \rightarrow -115\]

**TB7OA**

\[
\begin{array}{c}
\text{C}_7H_5O - CH = N - C_7H_5O - N = CH - OC_7H_5 \\
\text{bis - (4'-n-heptyloxybenzylidene)-1,4-phenylenediamine}
\end{array}
\]

Isotropic \(\rightarrow\) N \(\rightarrow\) Sm C \(\rightarrow\) Sm I \(\rightarrow\) Cry J

\[237.6 \rightarrow 195.7 \rightarrow 165.4 \rightarrow 158.7\]

\[8SI^{*}\]

\[
\begin{array}{c}
\text{C}_8H_{17} - CO - \text{CH}_2\text{CH} - \text{C}_2\text{H}_5 \\
4-(2'-methylbutyl)phenyl 4'-n-octylbiphenyl-4-carboxylate
\end{array}
\]

Isotropic \(\rightarrow\) Blue phase \(\rightarrow\) Cholesteric \(\rightarrow\) Sm A \(\rightarrow\) Sm C*

\[139.8 \rightarrow 135.9 \rightarrow 134.1 \rightarrow 84.4\]

\(\rightarrow\) Sm 1* \(\rightarrow\) Sm F* \(\rightarrow\) Cry G

\[68.3 \rightarrow 64.3 \rightarrow 62.3\]

\[8OSI^{*}\]

\[
\begin{array}{c}
\text{C}_8H_{17}O - CO - \text{CH}_2\text{CH} - \text{C}_2\text{H}_5 \\
4-(2'-methylbutyl)phenyl 4'-n-octyloxybiphenyl-4-carboxylate
\end{array}
\]

Isotropic \(\rightarrow\) Cholesteric \(\rightarrow\) Sm A \(\rightarrow\) Sm C*

\[169.4 \rightarrow 131.8\]

\(\rightarrow\) Sm 1* \(\rightarrow\) Cry J

\[79.9 \rightarrow -75.1\]

**Table 3.2:** Structural formulae and transition temperatures (in °C) for TB10A, TB7OA, 8SI* and 8OSI*.
Effect of the $I^*$ range on the nature of $C^*-I^*$ transition

Figure 3.5: Variation of $d$ near Sm C-Sm I transition for TB10A. $T_{CI}$ is the Sm C-Sm I transition temperature. The dotted lines indicate the two-phase coexistence region.
Effect of the $I^*$ range on the nature of $C^*-I^*$ transition

Figure 3.6: Temperature dependence of $d$ for TB70A. The data in the coexistence region are represented by filled circles.
Effect of the $\mathbf{T'}$ range on the nature of $C^*-J'$ transition

Figure 3.7: Thermal variation of peak intensity near Sm C-Sm I transition for TB10A. Filled symbols mark the data in the two phase region. The cross-over in intensity at the transition point is characteristic of a first order transition.
Effect of the $I^*$ range on the nature of $C^*-l^*$ transition

Figure 3.8: Thermal variation of peak intensity near the transition for TB70A. The data in the co-existence region are marked by filled symbols.
Figures 3.9 & 3.10 show $d$ vs. $T$ plots for $\text{8SI}^*$ and $\text{8OSI}^*$. $\text{8SI}^*$ shows a first order Sm C*-Sm I* transition characterised by a jump in layer spacing (see figure 3.9) and a crossover behaviour in intensity (Figure 3.11) confirming that it is of first order type, a feature in agreement with the observations of Dierker et al. For $\text{8OSI}^*$, the smooth variation of both $d$ (see figure 3.10) and intensity (figure 3.12) on going from Sm C* to Sm I* phase indicates that it is of continuous evolution type, in agreement with the high resolution synchrotron X-ray measurements of BOO and in-plane positional order. These features support the concept of a relationship between the range of the hexatic phase and the strength of the transition.

3.4 Discussion

Motivated by the success of the fit carried out by Wen et al., on the layer spacing variation across the Sm $A_d$-Sm $A_2$ transition, we attempted a fit of the data to the following expression

$$d = d_{eff} + A^\pm t^x + et$$

(3.1)

Where $t = (T - T_{eff})$, $et$ represents a background variation, the co-efficients $A^+$ & $A^-$ are the amplitude terms above ($T > T_{eff}$) and below ($T < T_{eff}$) the transformation respectively. As seen in figure 3.13 this expression describes the data very well for all the three materials. Table 3.3 shows the results of this computation. A remarkable result is the value of the exponent $x$ obtained for different materials. The value of $x \sim 0.5$ (we will ignore the small variation in $x$ seen as a function of chain length in $n\text{OBMBB}$ compounds) is in excellent
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Figure 3.9: $d$ as a function of reduced temperature for $8SI^*$. Notice the jump in $d$ indicative of a first order $Sm C^*-Sm I^*$ transition.
Effect of the $I^*$ range on the nature $C^*-I^*$ transition

Figure 3.10: $d$ vs. $T$ plot for 8OSI*. Absence of a jump in layer spacing suggests that the transformation is of the continuous evolution type.
Figure 3.11: Plot of peak intensity as a function of reduced temperature for 8SI*. Filled symbols mark the data in the two phase region.
Effect of the $I^*$ range on the nature of $C^*-I^*$ transition

Figure 3.12: Temperature dependence of peak intensity for 8OSI$^*$. 
Effect of the I' range on the nature of $C^*-I^*$ transition

Figure 3.13: Thermal variation of $d$ across $Sm\,C^*-Sm\,I^*$ transition for compounds belonging to $nOBMBB$ series. Solid line is a fitting to equation 3.1.
Effect of the $I^*$ range on the nature of $C^*-I^*$ transition

Table 3.3: Fit parameters for the three homologues of nOBMBB series and for 8OSI*.

<table>
<thead>
<tr>
<th>Compound</th>
<th>R (in °C)</th>
<th>$x$</th>
<th>$A^-$</th>
<th>$A^+$</th>
<th>$A^-/A^+$</th>
<th>$d_{eff}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C7</td>
<td>7</td>
<td>0.56 ± 0.02</td>
<td>8.5×10$^{-4}$</td>
<td>-1.5×10$^{-3}$</td>
<td>-0.6</td>
<td>21.35</td>
</tr>
<tr>
<td>C10</td>
<td>8.9</td>
<td>0.53 ± 0.01</td>
<td>3.8×10$^{-3}$</td>
<td>-4.8×10$^{-3}$</td>
<td>-0.8</td>
<td>23.99</td>
</tr>
<tr>
<td>C12</td>
<td>16.2</td>
<td>0.44 ± 0.01</td>
<td>6.9×10$^{-3}$</td>
<td>-7.1×10$^{-3}$</td>
<td>-0.9</td>
<td>26.1</td>
</tr>
<tr>
<td>8OSI*</td>
<td>4.8</td>
<td>0.44 ± 0.01</td>
<td>8.2×10$^{-3}$</td>
<td>-3.3×10$^{-6}$</td>
<td>-</td>
<td>27.68</td>
</tr>
</tbody>
</table>

Note: The error in the determination of the amplitudes $A^+$ & $A^-$ is better than 10%. However, in the case of 8OSI* the values are determined with much less accuracy, as the variation is comparable to that of the background. (Similar problem was encountered by authors of Ref.11). For this reason the ratios $A^+/A^-$ is not given for 8OSI*. 
agreement with the specific heat exponent $\alpha=0.52$ (Ref. 11) and $\alpha=0.47$ (Ref. 3) obtained for 80SI, the racernate of 80SI*. This is significant for two reasons.

1. It is known, at least in 80SI, that there is an appreciable change
   ($\sim 3$ orders of magnitude) in the in-plane density across the Sm C-Sm I transformation. In contrast, the layer thickness varies by only a few percent. Despite this small change, the temperature dependence is controlled by the same value of the exponent as in the specific heat data which reflects the total volume change.

2. The value of $x$ being $\sim 0.5$ for all these compounds is in conformity with the value obtained for a number of materials exhibiting Sm A-hex B transitions or Sm C-Sm I transitions. This feature supports the argument that the Sm C-Sm I critical point may belong to a new universality class which includes the Sm $A_d$-Sm $A_2$ critical point. In fact, the exponent obtained for the layer spacing variation near the Sm $A_d$-Sm $A_2$ critical point is also very close to 0.5. Note that all these experimental values are in close agreement with recent theoretical predictions, which places the Sm $A_d$-Sm $A_2$ and Sm C-Sm I critical points in the same but new universality class. Furthermore, the ratio of $A-/A+$ obtained for the compound belonging to nOBMBB series show a strong change on varying the chain length from $n=7$ to 12. The increase in the values of the amplitudes themselves is perhaps indicative of the approach to the critical point. This is apparent when the temperature derivative of the layer spacing is plotted (see figure 3.14). It is interesting that the plots mimic the
Effect of the $I^*$ range on the nature of $C^*-I^*$ transition

Figure 3.14: Plot of $\frac{d}{dT}(d)$ as a function of reduced temperature $T-T_{peak}$ for $n=7, 10 \& 12$th member of nOBMBB series. The data lying within $0.5^\circ$C of $T_{peak}$ are shown here.

Figure 3.15: Thermal variation of heat capacity near the Sm C-Sm I transition for 8OSI (from Ref. 11).
Effect of the $I^*$ range on the nature of C-I' transition

$C_p$ (specific heat at constant pressure) variation across the Sm C*-Sm I* transition in 8OSI\textsuperscript{11} (see figure 3.15). In fact such an agreement between the in-plane density variation and the specific heat plot across Sm A-hex B transition, were recently reported by Stoebe et al.\textsuperscript{14} In view of these results it would be interesting to study the in-plane correlation length (which can only be done with very high resolution synchroton X-ray measurements) and $C_p$ variation in nOBM3B materials to understand the nature of the Sm C*-Sm I* transformation and its approach to the critical point.

In explaining the results of synchrotron X-ray experiments\textsuperscript{2} on 8OSI, Aharony et al\textsuperscript{15} came up with a generic phase diagram for these systems. By considering the coupling of BOO with the crystalline order parameter, they suggested a phase diagram for the Sm A-hex 13-Cry B system (see figure 3.16). Two important features of this diagram are the existence of a tricritical point (TCP) on the Sm A-hex B phase boundary\textsuperscript{16} and a triple point where the Sm A, hex B and Cry B phases meet. Neglecting the effect of induced BOO (in other words assuming the tilt field $h$ to be negligible), Aharony et al\textsuperscript{15} further argued that a similar phase diagram should exist for the tilted versions also, i.e., involving Sm C, Sm I and Cry J phases.

But due to the presence of induced BOO, Sm C and Sm I phases become isosymmetric, a factor which precludes a second order phase transition between the two phases. This situation is similar to the paramagnetic-ferromagnetic transition in the presence of a non-zero applied field, which turns the TCP into
Effect of the $I'$ range on the nature of $C^* - I'$ transition

Figure 3.16: Generic temperature-concentration phase diagram near the Sm A-hex B-Cry B triple point. The broken (full) lines indicate second-(first-) order transitions. (From Ref. 15). Note the existence of a tricritical point on the Sm A-hex B line.

Figure 3.17: Proposed phase diagram involving Sm C-Sm I-Cry J phases. CP denotes a critical point.
*Effect of the I* range on the nature of C*-I* transition*

a critical point CP. From our X-ray studies on compounds belonging to nOBMBBB series it is clear that although d evolves continuously across the Sm C*-Sm I* transformation its strength increases with an increase in the temperature range of the Sm I* phase. It may be safe to presume that with further increase in the temperature range of the Sm I* phase, a critical point followed by a region where the transition would be first order can be observed. Data on compounds belonging to other series also appear to support this idea. Further, studies on compounds TB70A and TB10A showed that the jump in d across the Sm C-Sm I transition is more for TB10A, which has a larger temperature range of hexatic phase (see figures 3.5 and 3.6). Similarly the Sm C*-Sm I* transition is continuous in 8OSI* (see figure 3.10) with slightly smaller temperature range of the hexatic phase than 8SI*, which shows a weakly first order Sm C*-Sm I* transition (see figure 3.9).

Since the temperature range of the hexatic phase has been observed to play a decisive role in controlling the nature of the Sm C-Sm I transition, we propose a tentative phase diagram (see figure 3.17) for Sm C-Sm I-Cry J systems. Notice that the Sm C-Sm I transition is first order up to a certain concentration and gets terminated at a critical point, beyond which there will be just a continuous evolution from one phase to another. Although the materials of the nOBMBBB series we have studied show only a continuous evolution, the strength of such an evolution itself increases on increasing the chain length, indicating the approach to the critical point. Thus the chain length plays the role of the parameter X in the proposed phase diagram. However, in view of the results obtained on
other compounds mentioned in this chapter, perhaps a better and more general candidate for this parameter could be the range of the hexatic phase. More experiments are needed in this direction to generalise these results.

In the light of these observations, it is interesting to note that in a recent theoretical analysis of more general phase diagrams in smectics, Deforitaines arid Prost\textsuperscript{13} also proposed topologies involving the Sm C-Sm I critical point which have been reproduced in figure 3.18.
Effect of the $l^*$ range on the nature of $C^-l^*$ transition

Figure 3.18: Phase diagrams involving Sm C, Sm I(or Sm F), Sm $B_{hex}$ (or hex B) and Sm A phases in a $(\mu, T')$ plane. Solid lines represent first-order and dotted lines second-order transitions. a) Case involving Sm C-Sm I critical point C. E; is a critical end point and P, $P'$ are tricritical points. b) Case involving Sm C-Smi I critical point C, triple point T, and three tricritical points P, $P'$, $P''$. c) Alternative topologies involving critical end point E, triple point T and tricritical point P. (From Ref. 13)
References


[8] The compound TBOA was kindly provided to us by Prof.M.E.Neubert. 8SI* & 8OSI* were given as free samples by BDH(Poole) Ltd.
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