

Chapter 3

Effect of the Smectic I* Phase Temperature Range on the Nature of the Tilted Fluid to Hexatic 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 liexatic 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) phase 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. Theoretically¹ 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.,² 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 \longrightarrow Sm C* \longrightarrow Sm I* \longrightarrow 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).

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

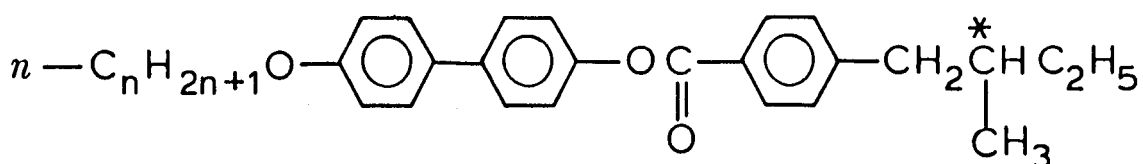
Figure 3.1 shows a plot of temperature versus layer spacing d for the 7th, 10th and 12th homologues of the nOBMBB series. The thermal variation of d shows an increase on passing from Sm C^* to the Sm I^* phase. The absence of a jump in d as well as the absence of a two-phase coexistence region confirms 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.⁵ 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 ($\sim 0.1\text{\AA}$) 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



4-n-alkoxybiphenyl 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

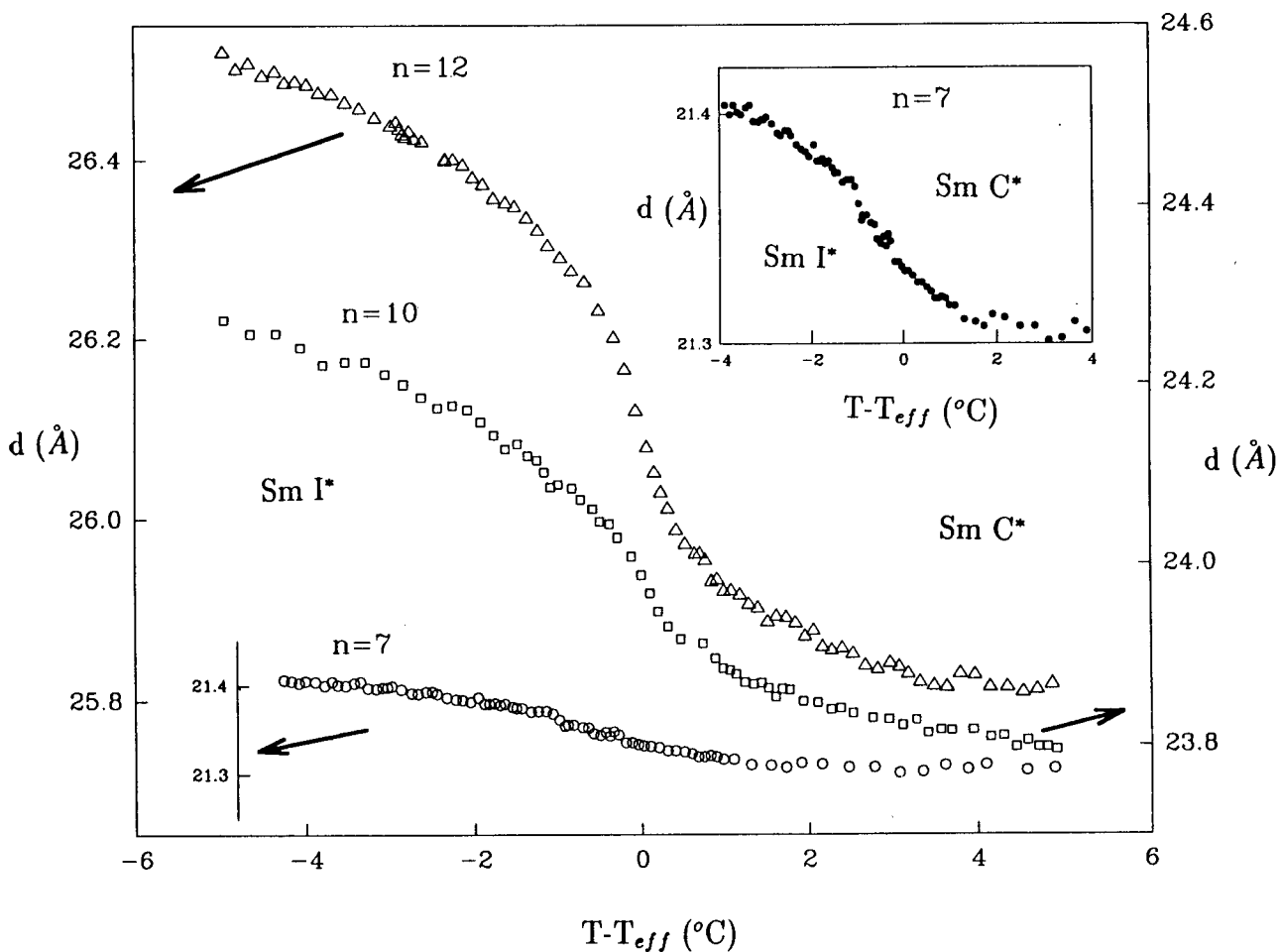


Figure 3.1: Temperature variation of the layer spacing d in the vicinity of Sm C*-Sm I* transition for the three homologues, $n=7$ (o), $n=10$ (□) & $n=12$ (Δ) of nOBMBB series. The data for $n=7$ is also shown in the inset on an enlarged scale. The continuous variation of d for all the three compounds indicates that the transition is of the continuous evolution type. Here T_{eff} , the pseudo transition temperature is identified as the inflection point on the curve. The value of T_{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

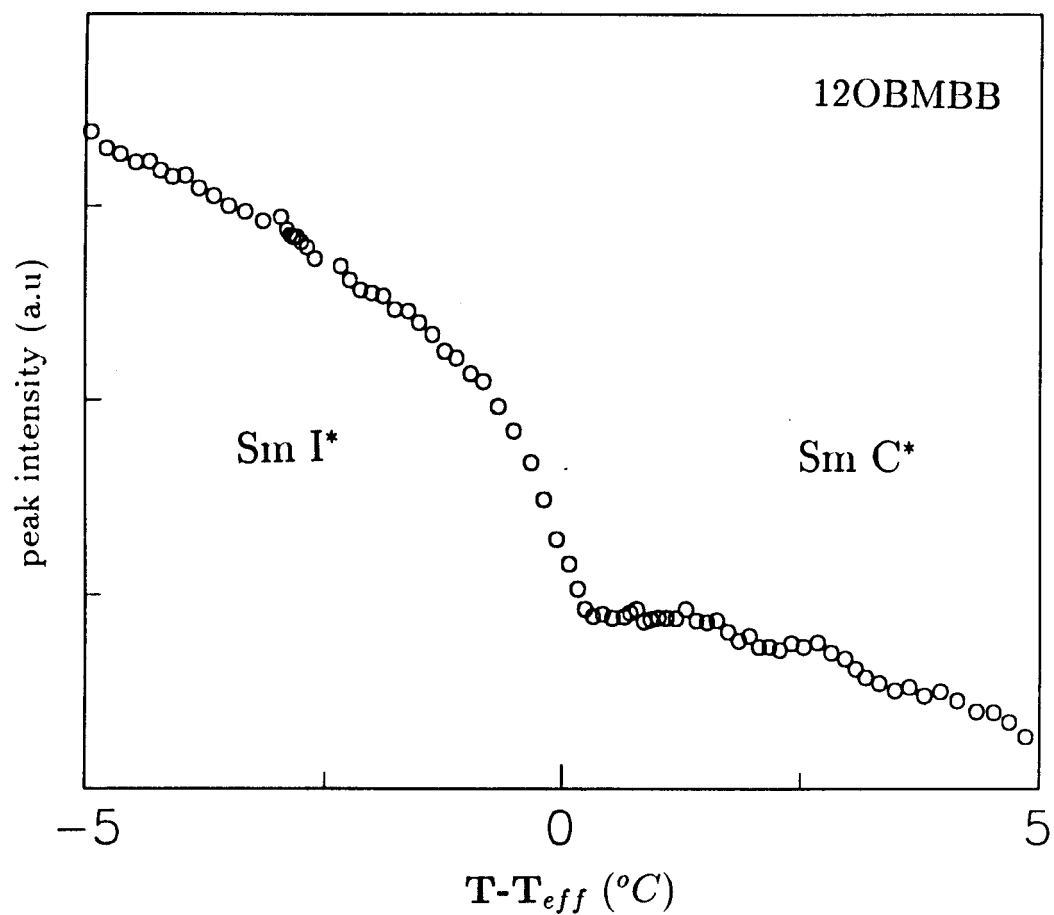


Figure 3.2: Thermal variation of peak intensity near the transition for the 12th member of nOBMBB series. Note the continuous variation in intensity on passing from Sm C* to Sm I* phase. This feature is characteristic of a continuous transformation.⁵

$\Delta d/\Delta T$, particularly near the pseudo-transition point T_{eff} , increase as the chain length is increased.

Notice that on increasing 'n' the temperature range (R) of the Sm I^* phase increases. R is $2.1^\circ C$ for $n = 7$, $8.9^\circ C$ for $n=10$ and $16.2^\circ C$ 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 observed⁶ for the 10,13,15 and 19th members of the terephthal-bis alkyl aniline (TBnA) 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 TBnA 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 phase⁷ (see figure 3.4). A point that must be noted is that the higher homologues of TBnA 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 are⁸

- I. bis-(4'-n-heptyloxybenzylidene)-1,4-phenylenediamine (TB7OA) and Terephthal-bis-decylaniline (TB10A)

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

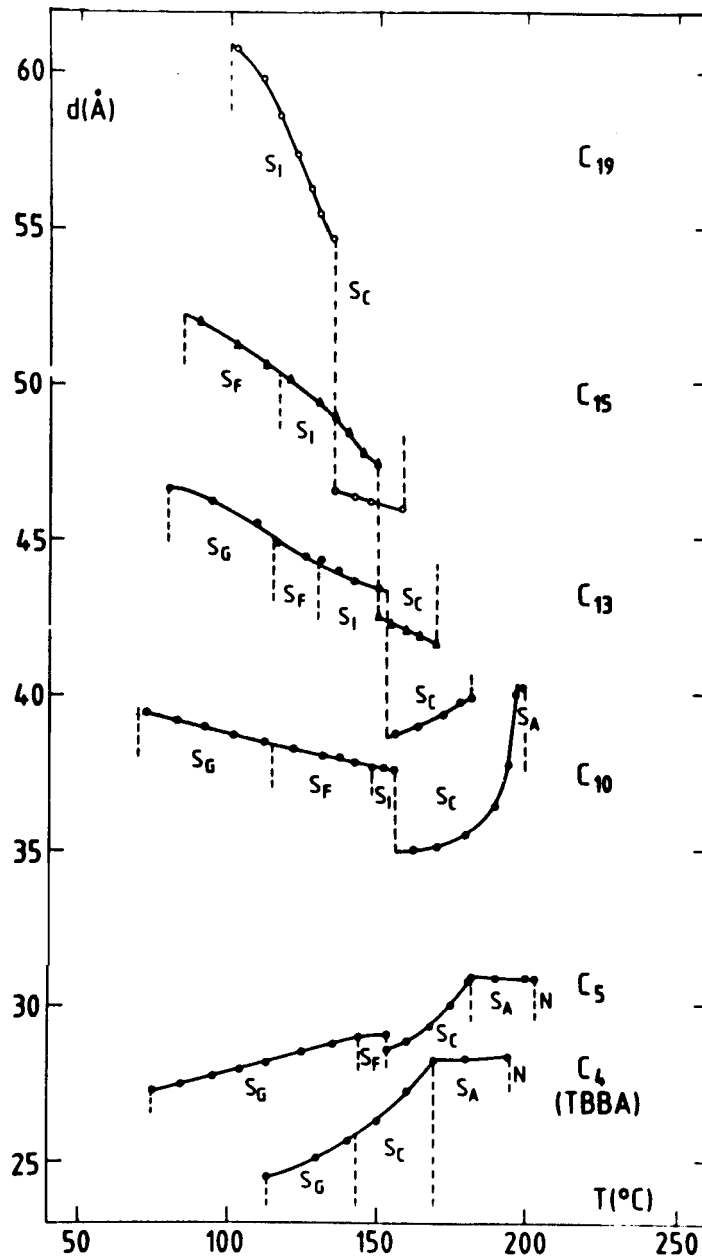


Figure 3.3: Thermal variation of d near Sm C-Sm I transition for higher members of TBnA homologous series. (adapted from Ref. 6). Notice the jump in d at the Sm C-Sm I transition, indicating a first-order change.

Effect of the I^* range on the nature of C-I' transition

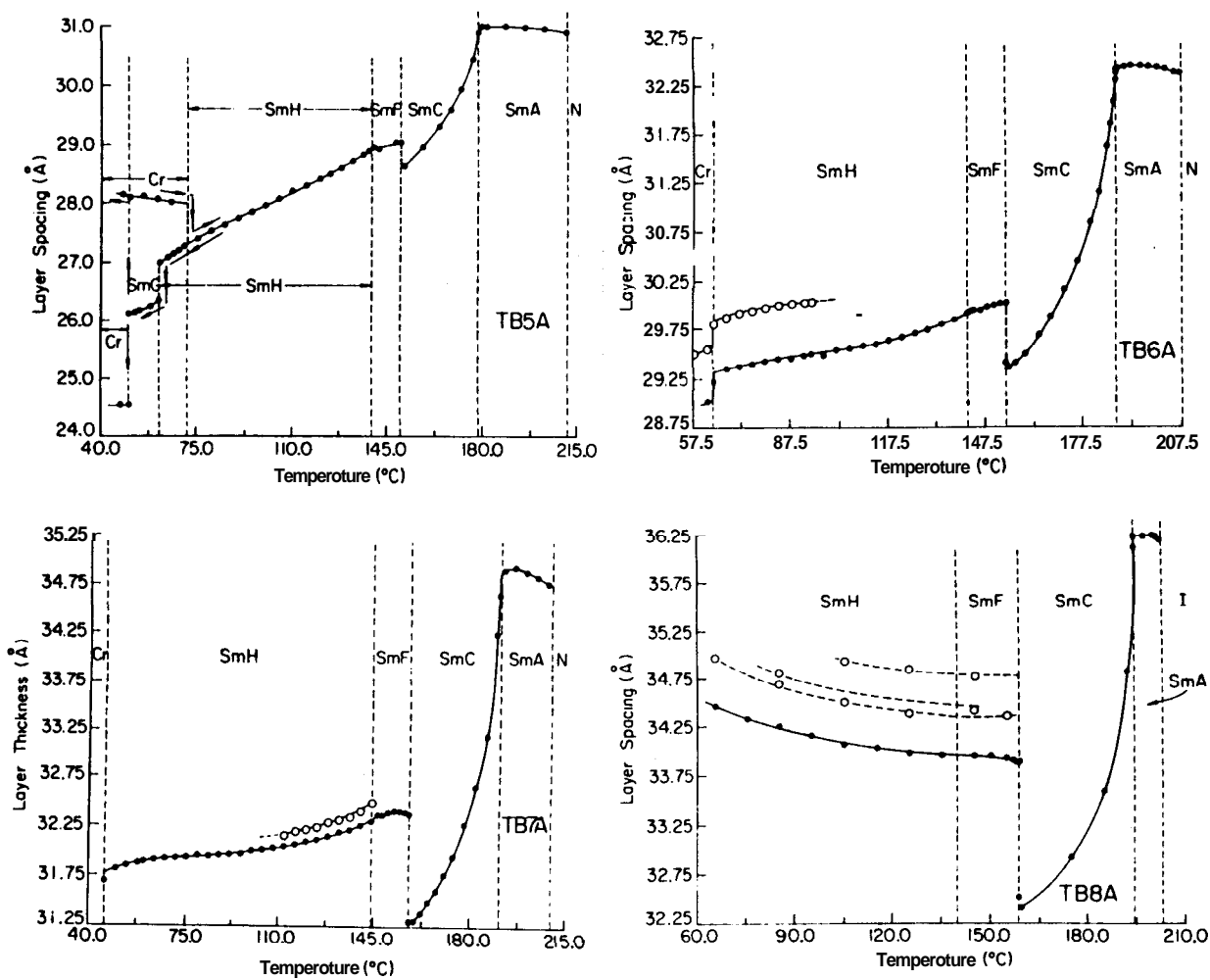


Figure 3.4: Thermal variation of d near Sm C-Sm F transition for lower members of TB_nA series. (From Ref. 7). The transition is first order for all the compounds.

2. 4-(2'-methylbutyl)phenyl 4'-n-octyloxybiphenyl-4-carboxylate (8OSI*) and 4-(2'-methylbutyl)phenyl 4'-n-octylbiphenyl-4-carboxylate (8SI*)

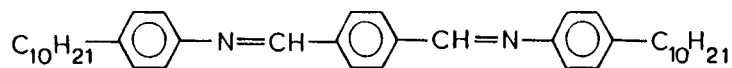
The structural formulae and the transition temperatures of these compounds are given in Table 3.2. TBIOA and TB7OA look structurally similar (see Table 3.2). Both the compounds have approximately the same temperature range of Sm I phase, e.g., $\sim 7^\circ\text{C}$ for TB7OA and $\sim 9.1^\circ\text{C}$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

Similarly the only structural difference between 8OSI* and 8SI* is that 8OSI* has an alkoxy chain while 8SI* has an alkyl one. 8OSI* 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 8OSI* (4.8°C).

Figures 3.5 and 3.6 show the thermal variation of layer spacing across Sm C-Sm I transition for TBIOA 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 TBIOA ($\approx 2\text{\AA}$) is about 16 times higher than that for TB7OA. From Table 3.2 it is seen that the hexatic temperature range is larger for TBIOA than for TB7OA.

Effect of *the I'* range on the nature of C-I' transition

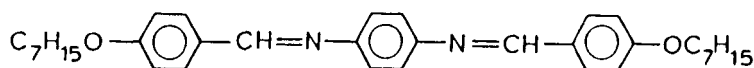
TB10A



terephthal - bis - decylaniline

Isotropic	→	Sm A	→	Sm C	→	Sm I
	191.0		189.2		154.8	
	→	Sm F	→	Cry G		
	148.7		-115			

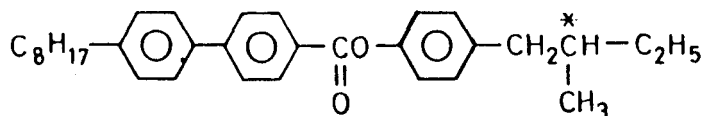
TB70A



bis - (4'-n - heptyloxybenzylidene) -1,4 - phenylenediamine

Isotropic	→	N	→	Sm C	→	Sm I	→	Cry J
	237.6		195.7		165.4		158.7	

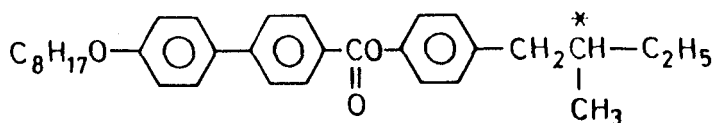
8SI*



4-(2'-methylbutyl)phenyl 4'-n-octylbiphenyl-4-carboxylate

Isotropic	→	Blue phase	→	Cholesteric	→	Sm A	→	Sm C*
	139.8		135.9		134.1		84.4	
←	Sm I*	→	Sm F*	→	Cry G			
68.3		64.3		62.3				

8OSI*



4-(2'-methylbutyl)phenyl 4'-n-octyloxybiphenyl-4-carboxylate

Isotropic	→	Cholesteric	→	Sm A	→	Sm C*
			169.4		133.8	
←	Sm I*	→	Cry J			
79.9		-75.1				

Table 3.2: Structural formulae and transition temperatures (in °C) for TB10A, TB70A, 8SI* and 8OSI*.

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

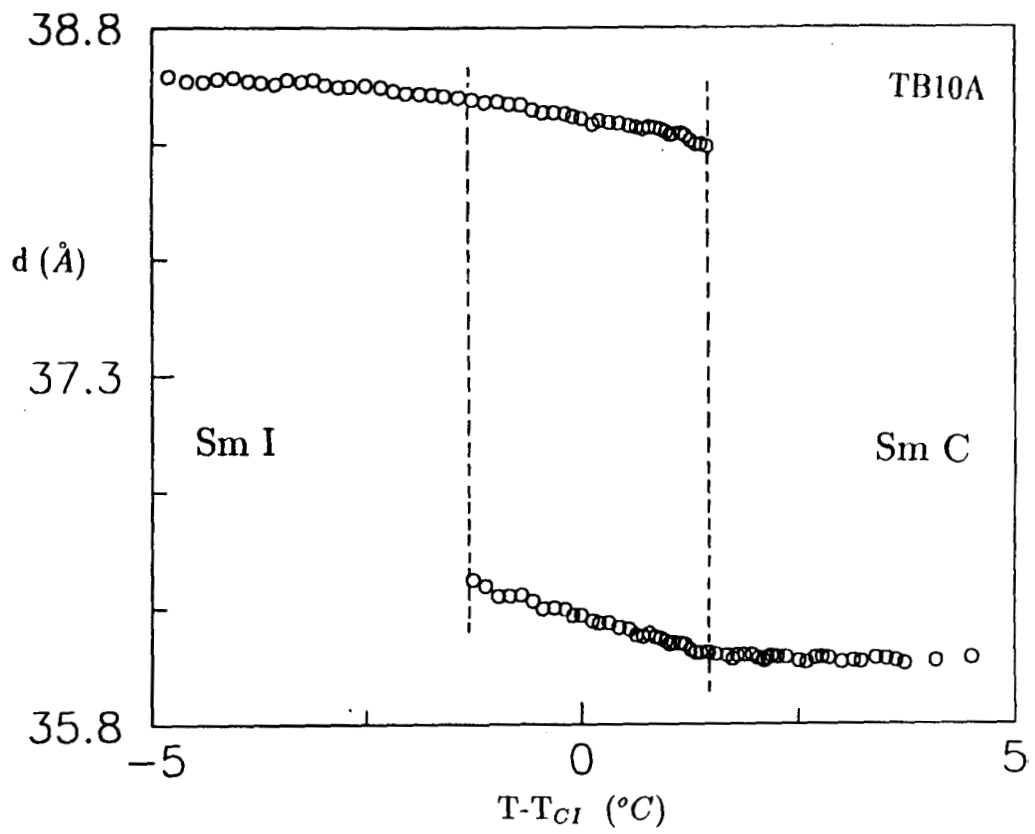


Figure 3.5: Variation of d near Sm C-Sm I transition for TB10A. T_{CI} is the Sm C-Sm I transition temperature. The dotted lines indicate the two-phase coexistence region.

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

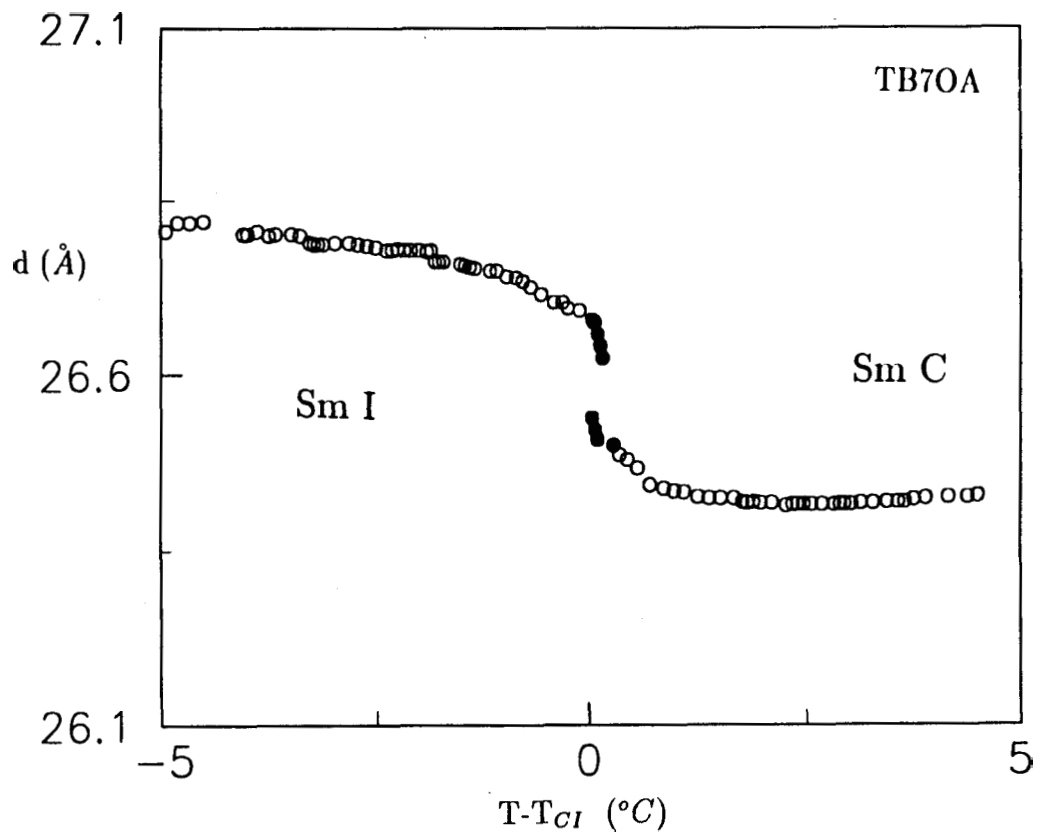


Figure 3.6: Temperature dependence of d for TB70A. The data in the coexistence region are represented by filled circles.

Effect of the Γ range on the nature of C^*-I^* transition

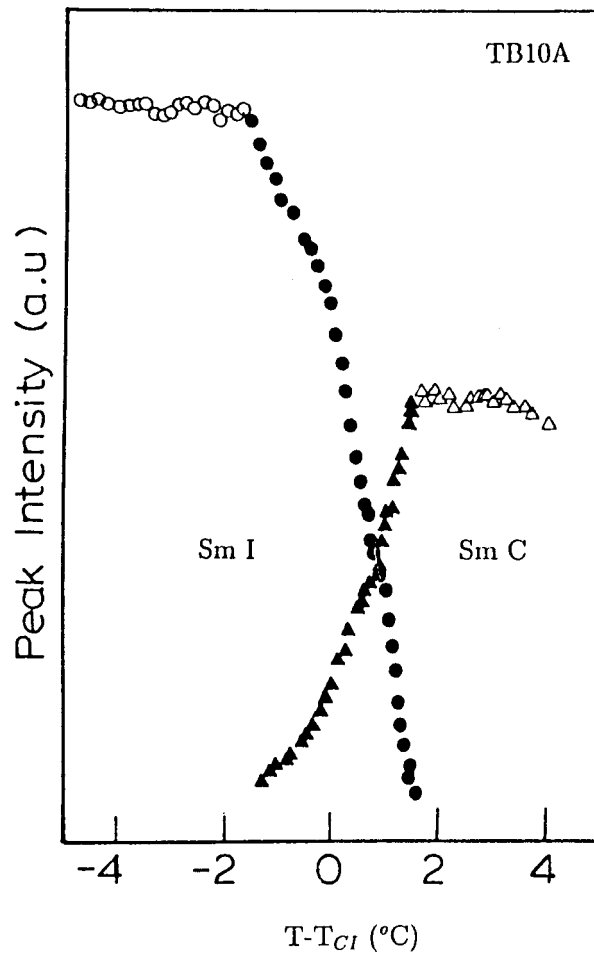


Figure 3.7: Thermal variation of peak intensity near Sm C-Sm I transition for TB10A. Filled symbols mark the data in the two phase region. The cross-over in intensity at the transition point is characteristic of a first order transition.

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

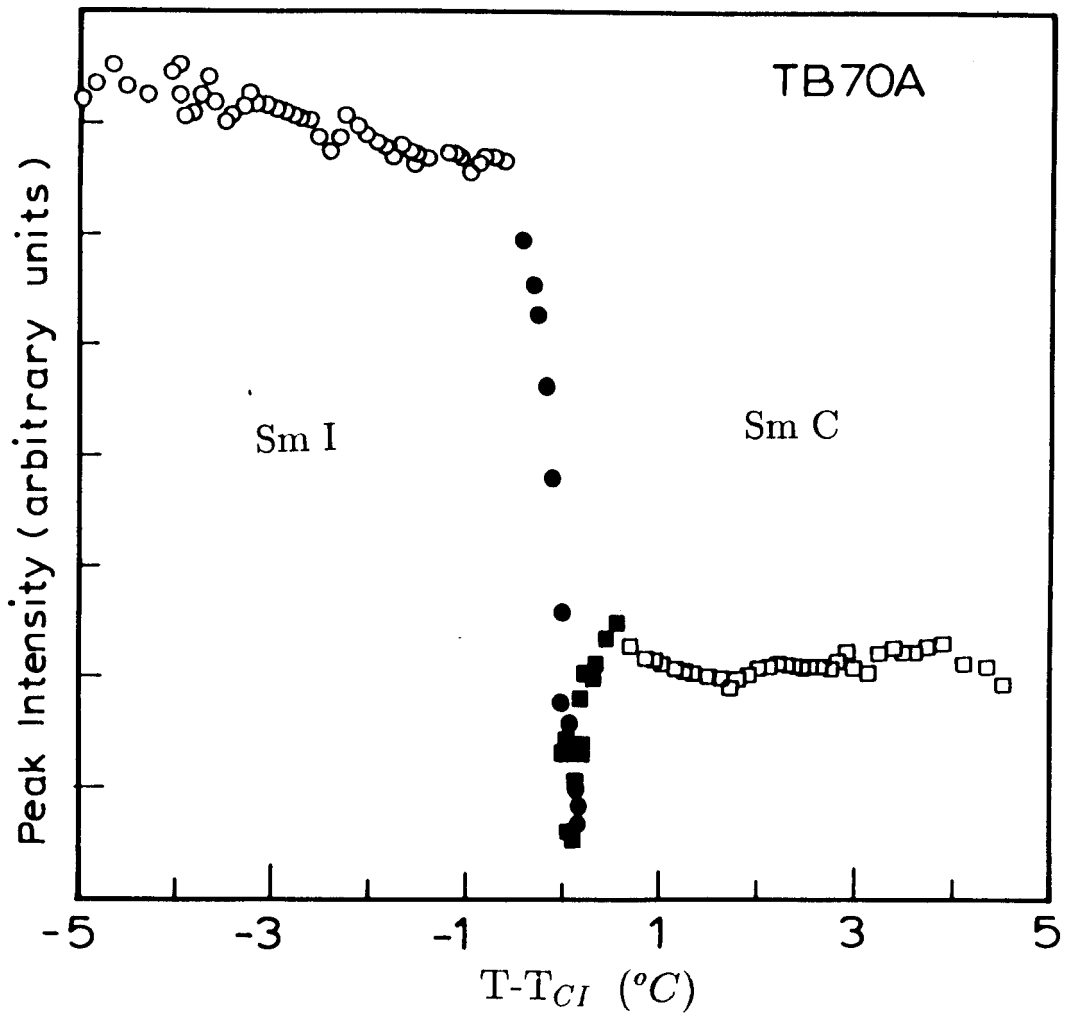


Figure 3.8: Thermal variation of peak intensity near the transition for TB70A. The data in the co-existence region are marked by filled symbols.

Figures 3.9 & 3.10 show d vs. T plots for $8SI^*$ and $8OSI^*$. $8SI^*$ 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.⁹ For $8OSI^*$, 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.² 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.,¹⁰ 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

$$d = d_{eff} + A^{\pm}t^x + et \quad (3.1)$$

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 $nOBMBB$ compounds) is in excellent

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

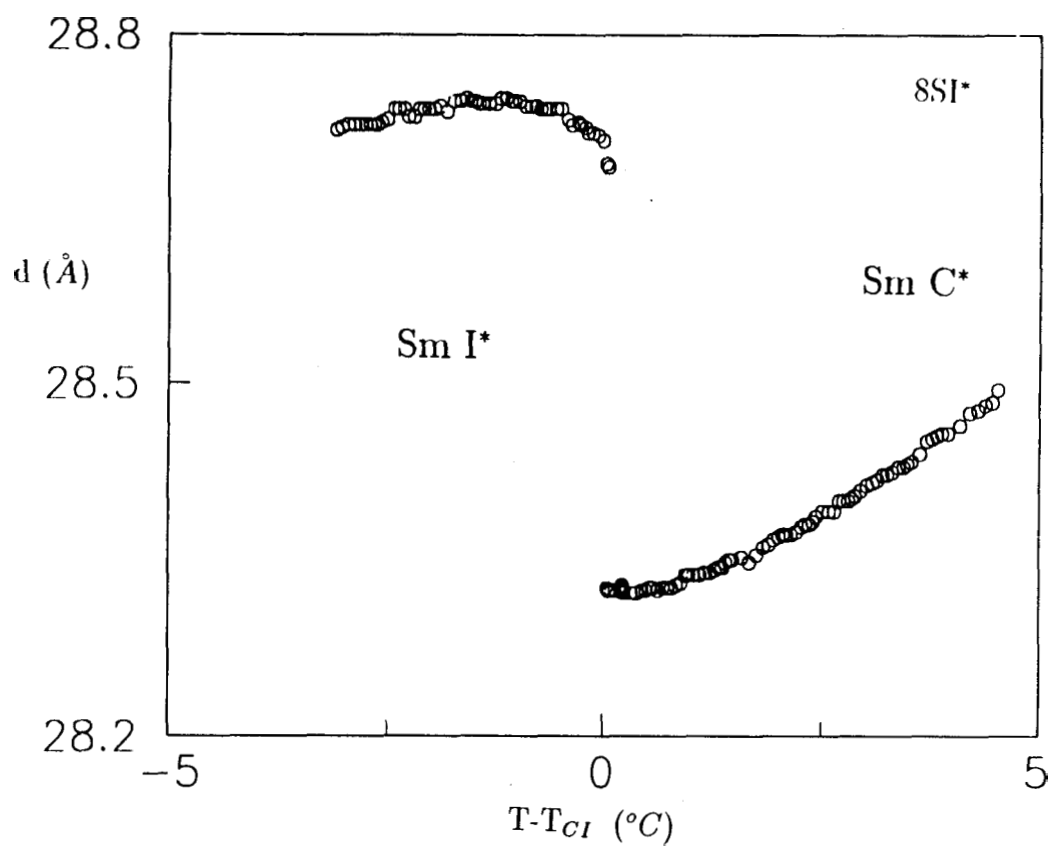


Figure 3.9: d as a function of reduced temperature for 8SI*. Notice the jump in d indicative of a first order Sm C*-Sm I* transition.

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

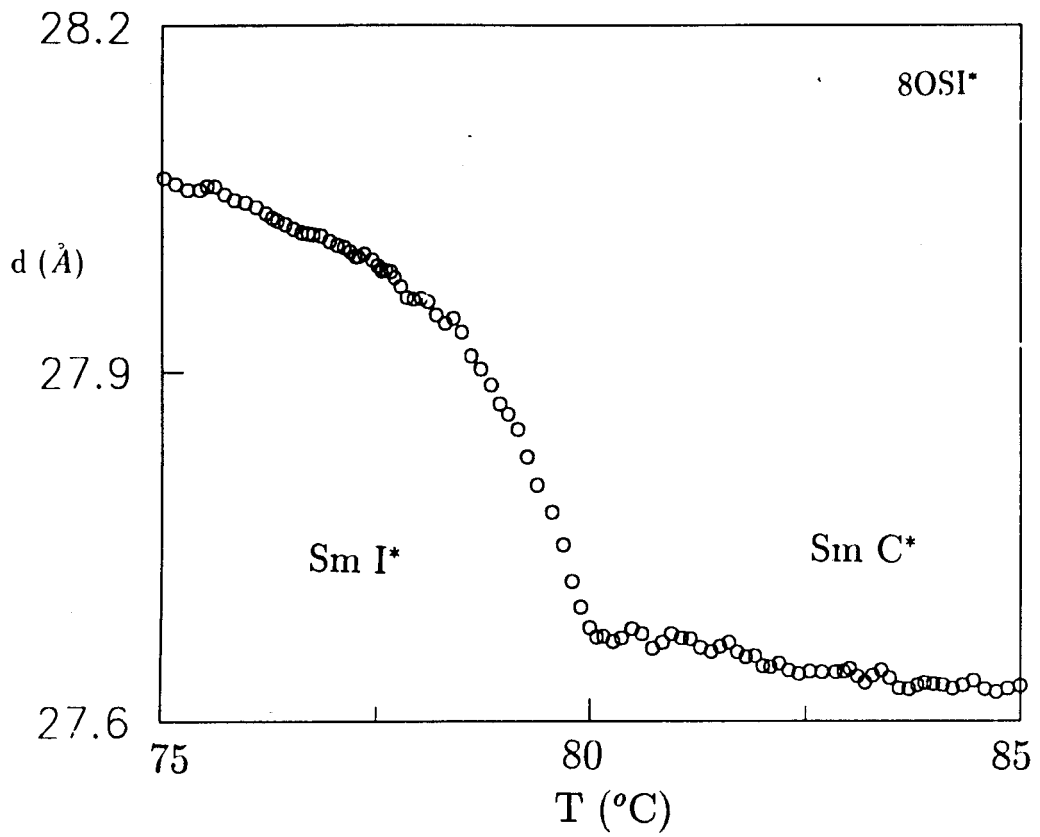


Figure 3.10: d vs. T plot for 80SI*. Absence of a jump in layer spacing suggests that the transformation is of the continuous evolution type.

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

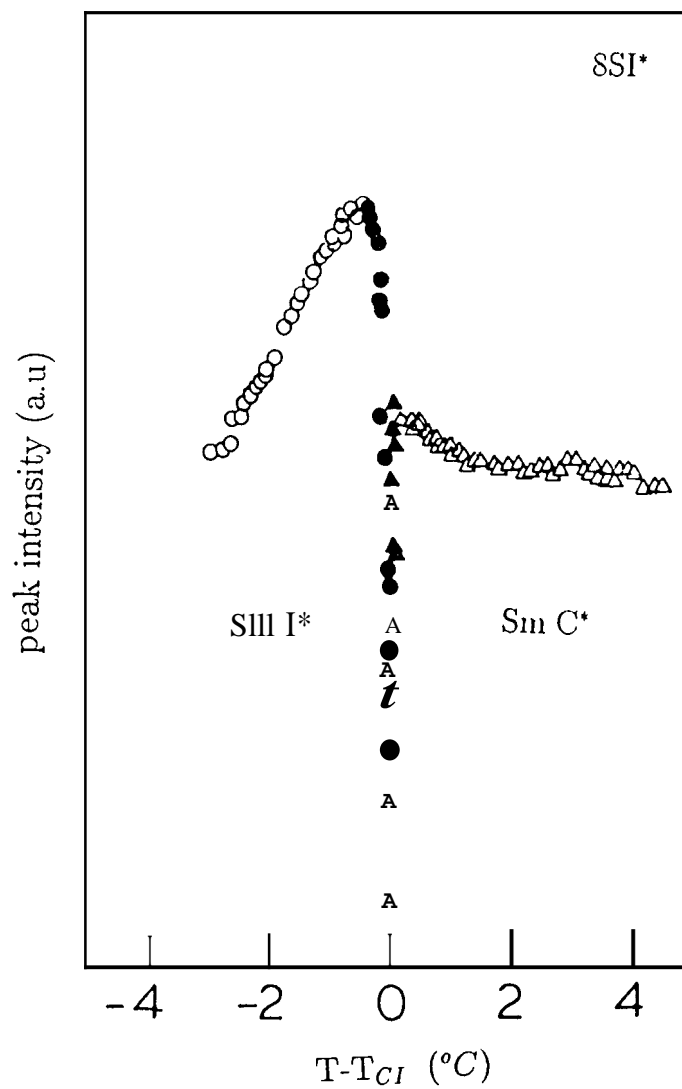


Figure 3.11: Plot of peak intensity as a function of reduced temperature for 8SI*. Filled symbols mark the data in the two phase region.

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

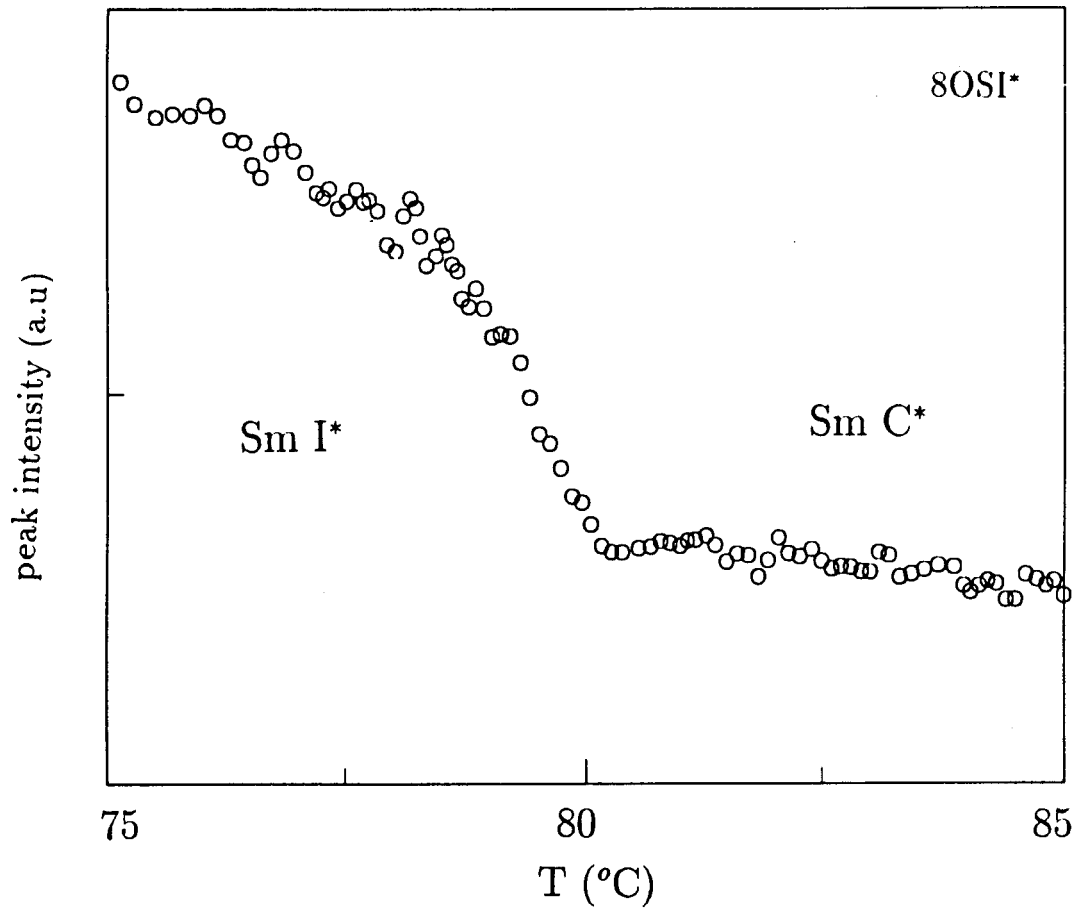


Figure 3.12: Temperature dependence of peak intensity for 80SI*.

Effect of the Γ range on the nature of C^*-I^* transition

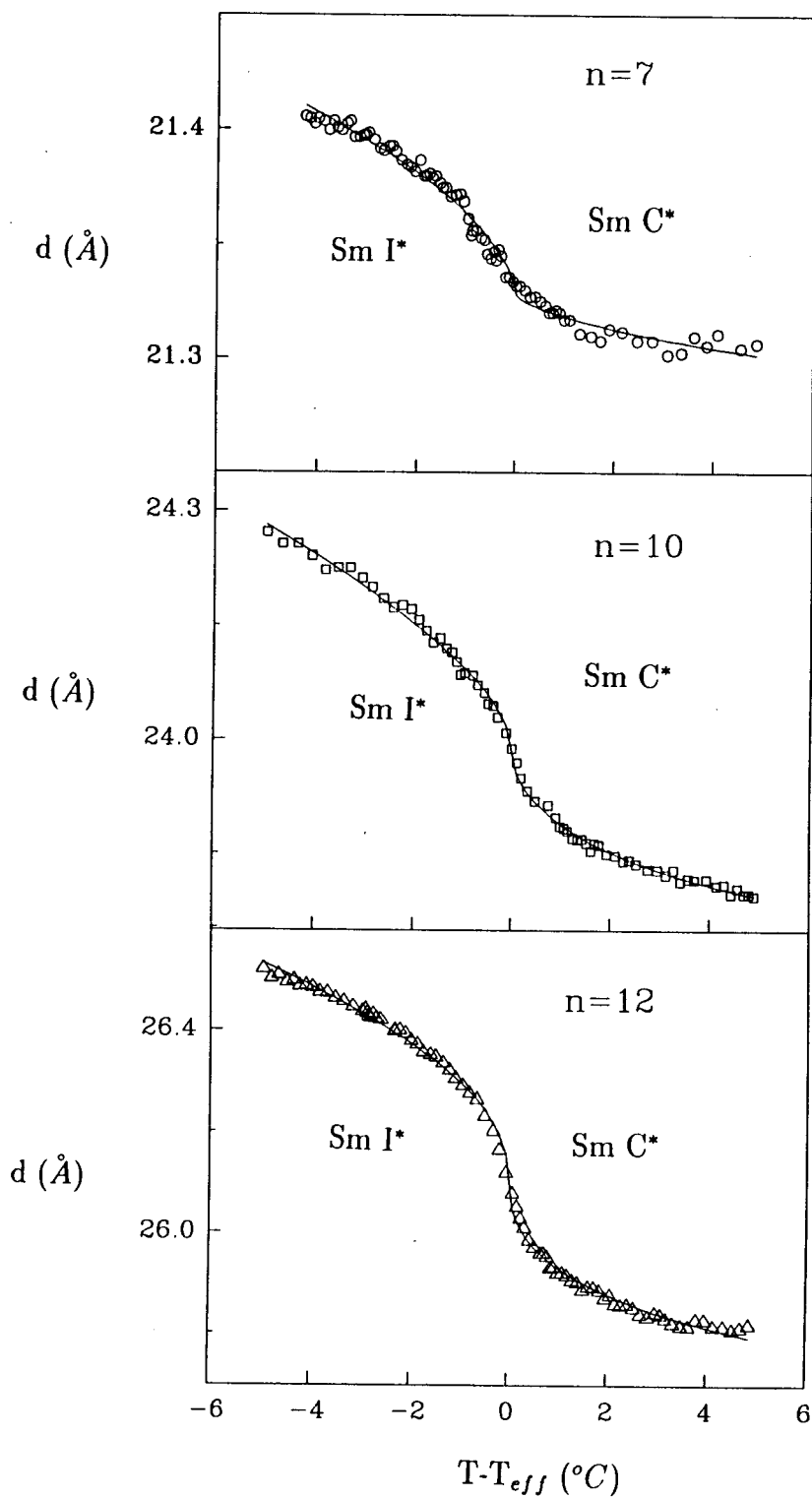


Figure 3.13: Thermal variation of d across $Sm C^*-Sm I^*$ transition for compounds belonging to n OBMBB series. Solid line is a fitting to equation 3.1.

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*.

Compound	R (in °C)	x	A^-	A^+	A^-/A^+	d_{eff}
C7	7	$0.56 \pm .02$	8.5×10^{-4}	-1.5×10^{-3}	-0.6	21.35
C10	8.9	$0.53 \pm .01$	3.8×10^{-3}	-4.8×10^{-3}	-0.8	23.99
C12	16.2	$0.44 \pm .01$	6.9×10^{-3}	-7.1×10^{-3}	-0.9	26.1
8OSI*	4.8	$0.44 \pm .01$	8.2×10^{-3}	-3.3×10^{-6}	-	27.68

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 8OSI, the racemate of 8OSI*. This is significant for two reasons.

1. It is known, at least in 8OSI, that there is an appreciable change (~ 3 orders of magnitude) in the in-plane density across the Sm C-Sm I transformation.² In contrast, the layer thickness varies by only a few per cent. 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 ~ 0.5 for all these compounds is in conformity with the value obtained for a number of materials exhibiting Sm A-hex B transitions¹² or Sm C-Sm I transitions.^{11,3} 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.¹³ 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 0.5.¹⁰ Note that all these experimental values are in close agreement with recent theoretical predictions,¹³ 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

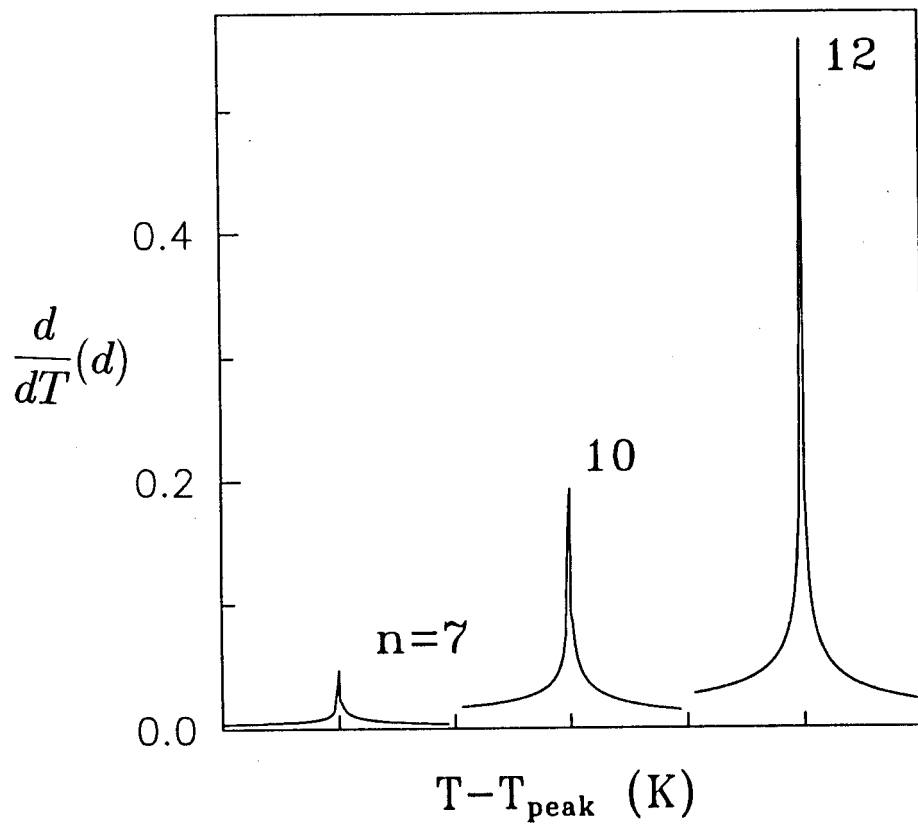


Figure 3.14: Plot of $\frac{d}{dT}(d)$ as a function of reduced temperature $T - T_{peak}$ for $n=7, 10$ & 12th member of $nOBMBB$ series. The data lying within 0.5°C of T_{peak} are shown here.

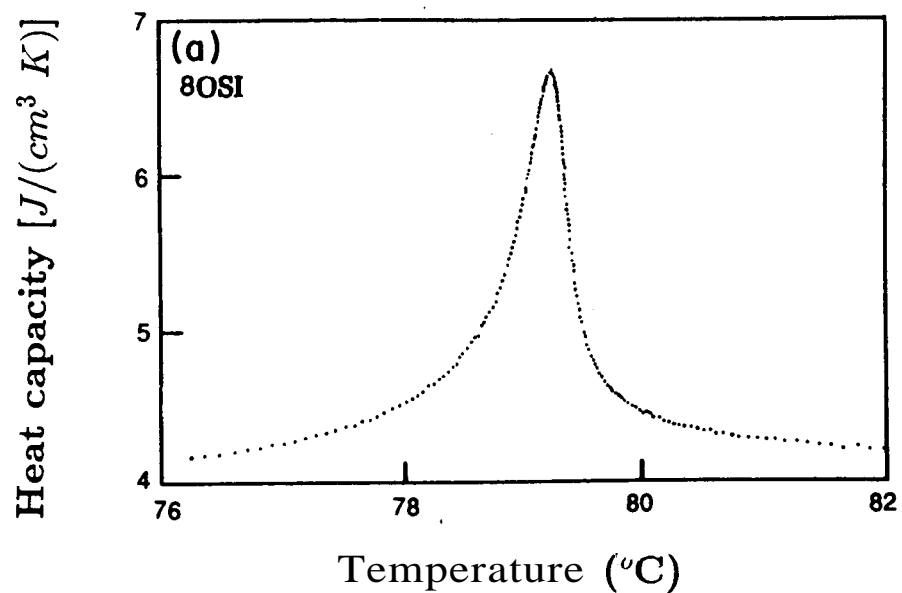


Figure 3.15: Thermal variation of heat capacity near the Sm C-Sm I transition for 80SI (from Ref. 11).

C_p (specific heat at constant pressure) variation across the Sm C*-Sm I* transition in 8OSI¹¹ (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.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 synchrotron X-ray measurements) and C_p variation in nOBMBB 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 experiments² on 8OSI, Aharony et al¹⁵ 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 boundary¹⁶ 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 al¹⁵ 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

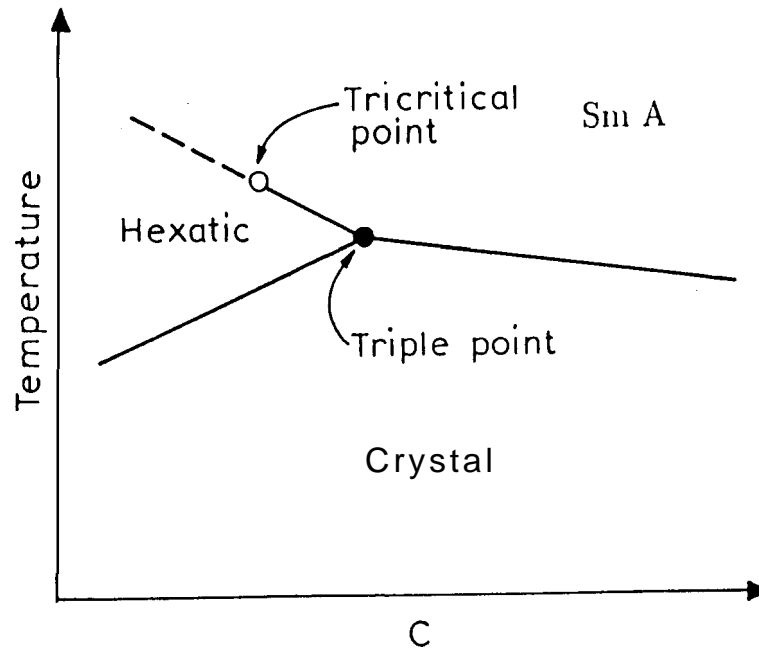


Figure 3.16: Generic temperature-concentration phase diagram near the Sm A-hex B-Cry B triple point. The broken(full) lines indicate second-(first-) order transitions. (From Ref. 15). Note the existence of a tricritical point on the Sm A-hex B line.

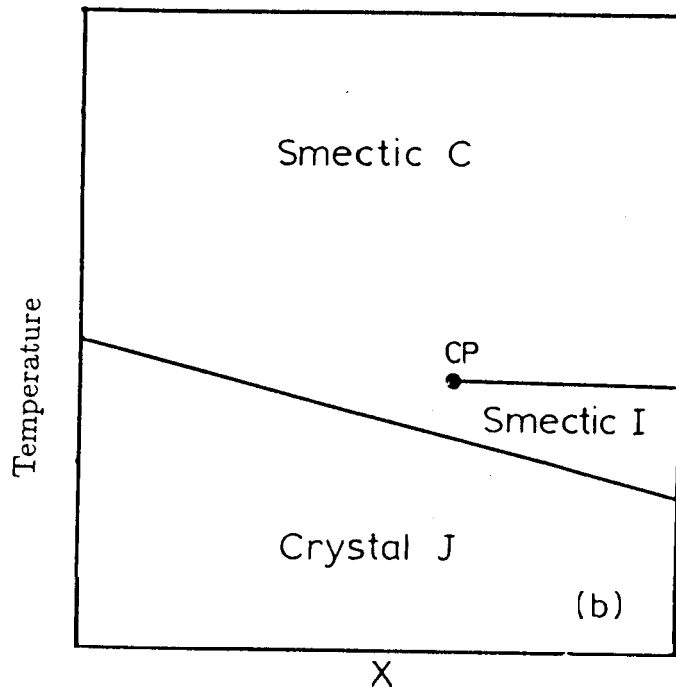


Figure 3.17: Proposed phase diagram involving Sm C-Sm I-Cry J phases. CP- denotes a critical point.

a critical point CP. From our X-ray studies on compounds belonging to nOBMBB 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.⁶⁻⁷ Further, studies on compounds TB7OA 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 nOBMBB 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, Deforaines and Prost¹³ also proposed topologies involving the Sm C-Sm I critical point which have been reproduced in figure 3.18.

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

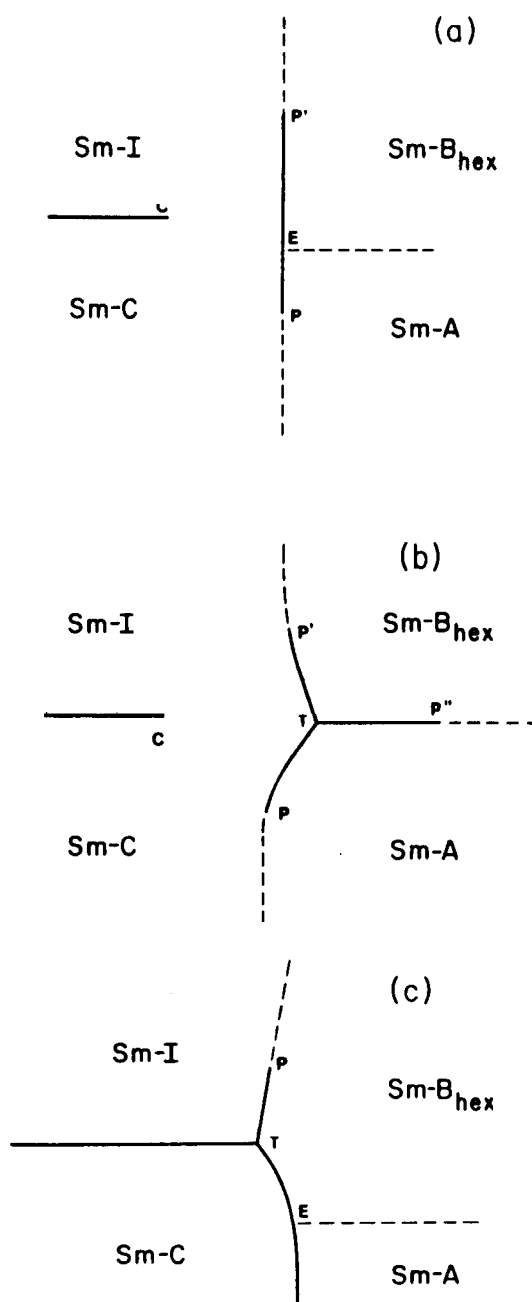


Figure 3.18: Phase diagrams involving Sm C, Sm I(or Sm F), Sm B_{hex}(or hex B) and Sm A phases in a (μ, T) plane. Solid lines represent first-order and dotted lines second-order transitions. a) Case involving Sm C-Sm I critical point C. E: is a critical end point and P, P' are tricritical points. b) Case involving Sm C-Sm 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)

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