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Thermal, X-Ray and Birefringence Measurements in Hexatic Liquid Crystal Phases

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A number of experimental data on hexatic liquid crystal phases, namely the smectic I and F phases of various members of the TBnA family, are presented. They allow a better understanding of the respective structures and information of the smectic I and F phases.

Keywords: birefringence, DSC, x-ray

1. INTRODUCTION

Hexatic liquid crystal phases have been intensively studied, experimentally[1–4] and theoretically,[5–6] in recent years. The interest in these phases stems from the fact that they materialize the successive orderings between the liquid state and the three-dimensional crystalline order.

We have undertaken a systematic study of various hexatic phases in order to clarify their structural features and to understand the correlation between the different type of orders which take place in hexatic liquid crystals, i.e. bond orientational order, tilting order, and positional order.

In this paper, we briefly summarize the experimental results obtained from four members of the TBnA family from thermal, X-ray and birefringence measurements.

2. DSC MEASUREMENTS

DSC (differential scanning calorimetry) measurements were performed using a Mettler Thermosystem FP 800, on TBPA, TBDA, TB12A and TB14A. The var-

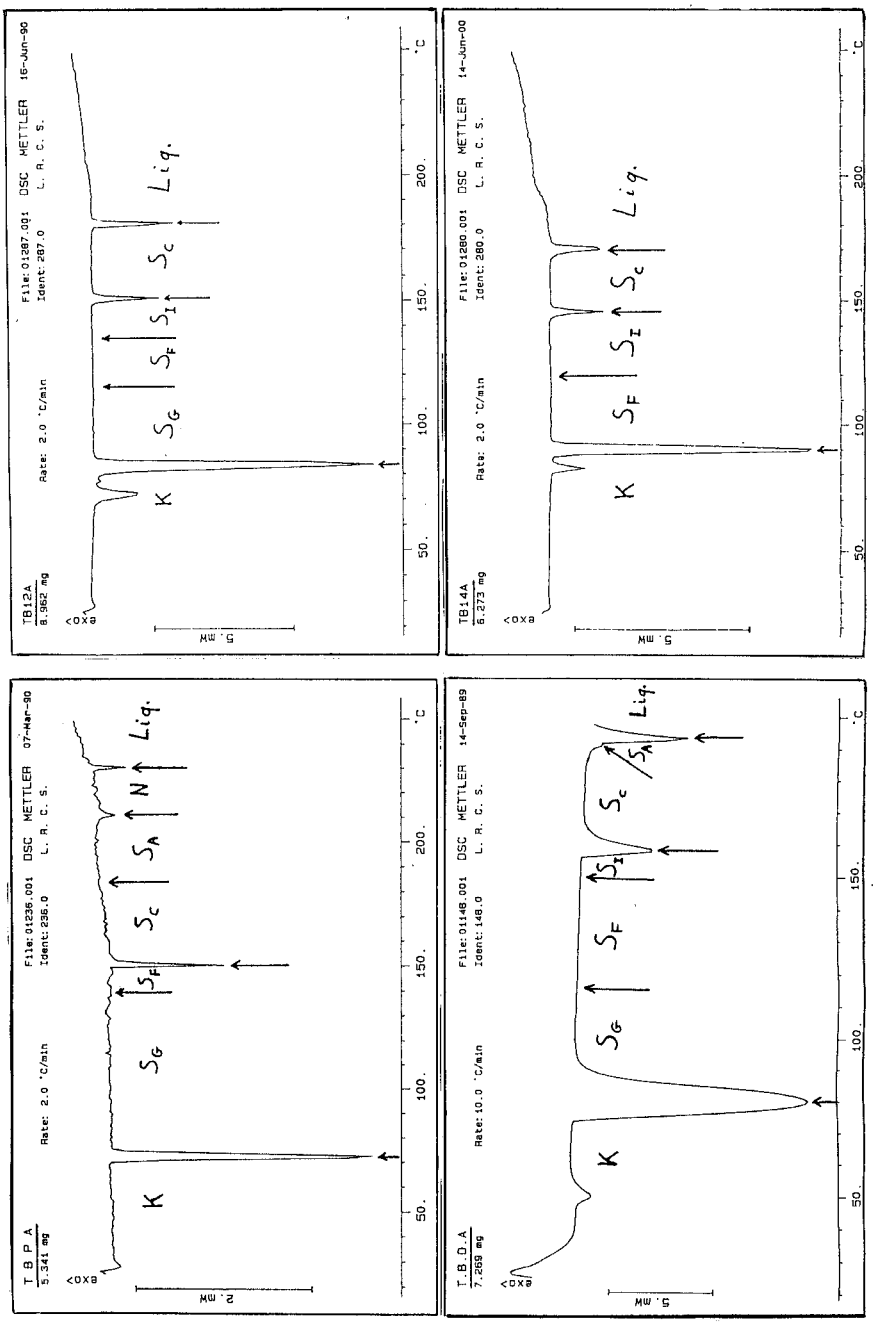


FIGURE 1 DSC measurement on TBPA, TBDA, TP12A and TB14A.

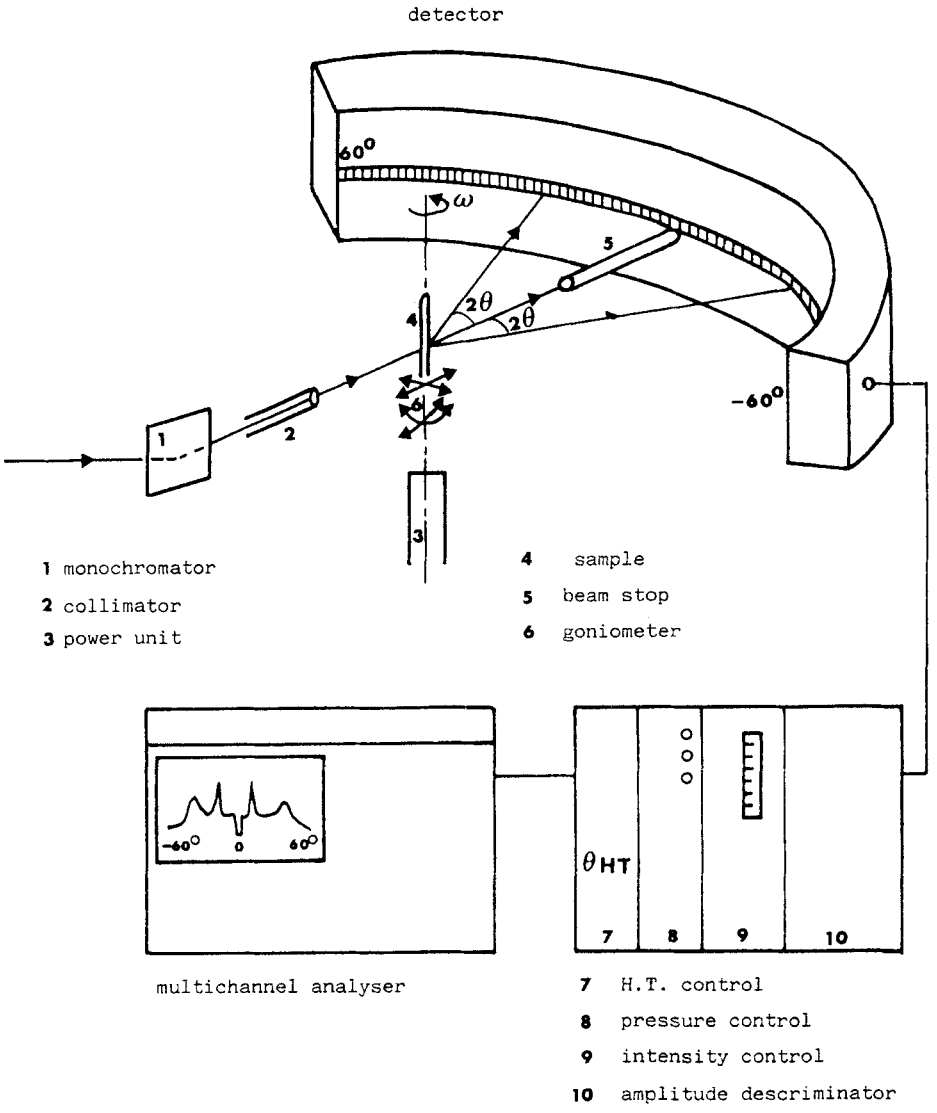
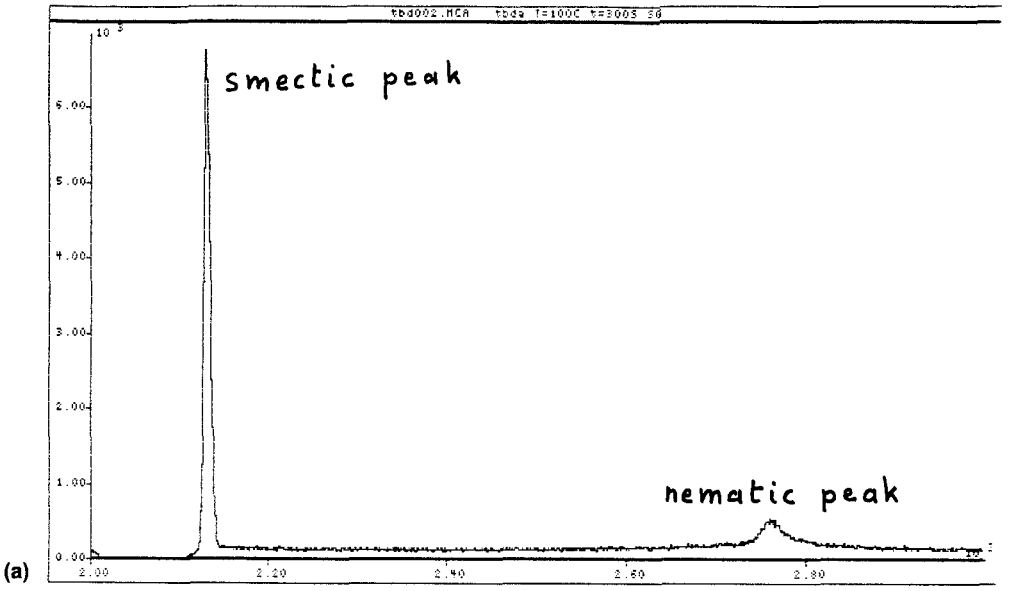


FIGURE 2 Scheme of the X-ray measurement experiment.

iation of transition enthalpy as a function of temperature is represented in Figure 1. One can verify that the transition enthalpy within the sequence of I, F and G phases is negligible compared to the enthalpies which are associated with the smectic C-smectic I (or smectic F) transition, and the smectic G-crystal transition.



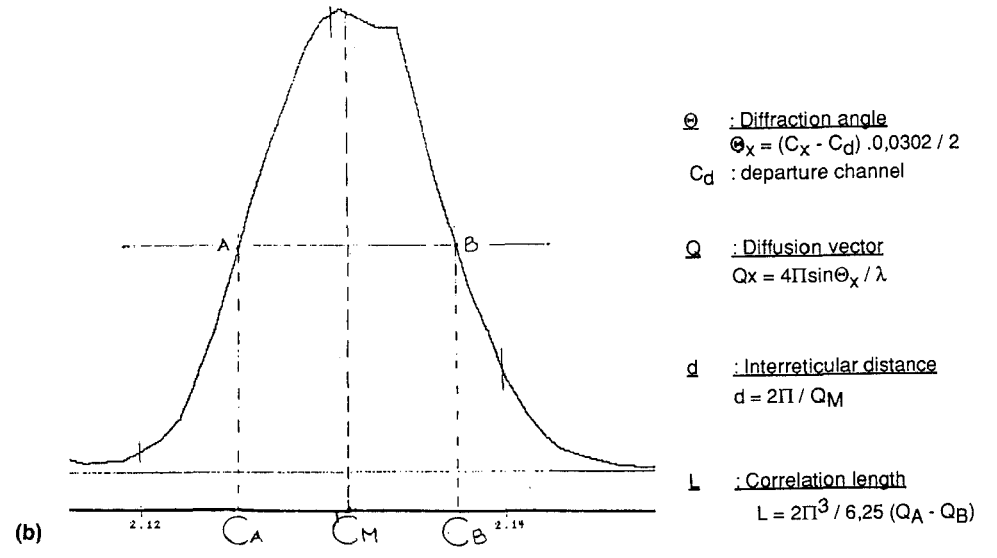


FIGURE 3 3a, Diffraction spectrum obtained for the layer ordering (smectic peak) and orientational ordering within the smectic planes (nematic peak); 3b, Characteristic physical quantities used in the diffraction analysis.

3. X-RAY MEASUREMENTS

X-ray measurements were performed using a multichannel diffractometer mounted in the laboratory in order to determine the interlayer distance in each smectic phase

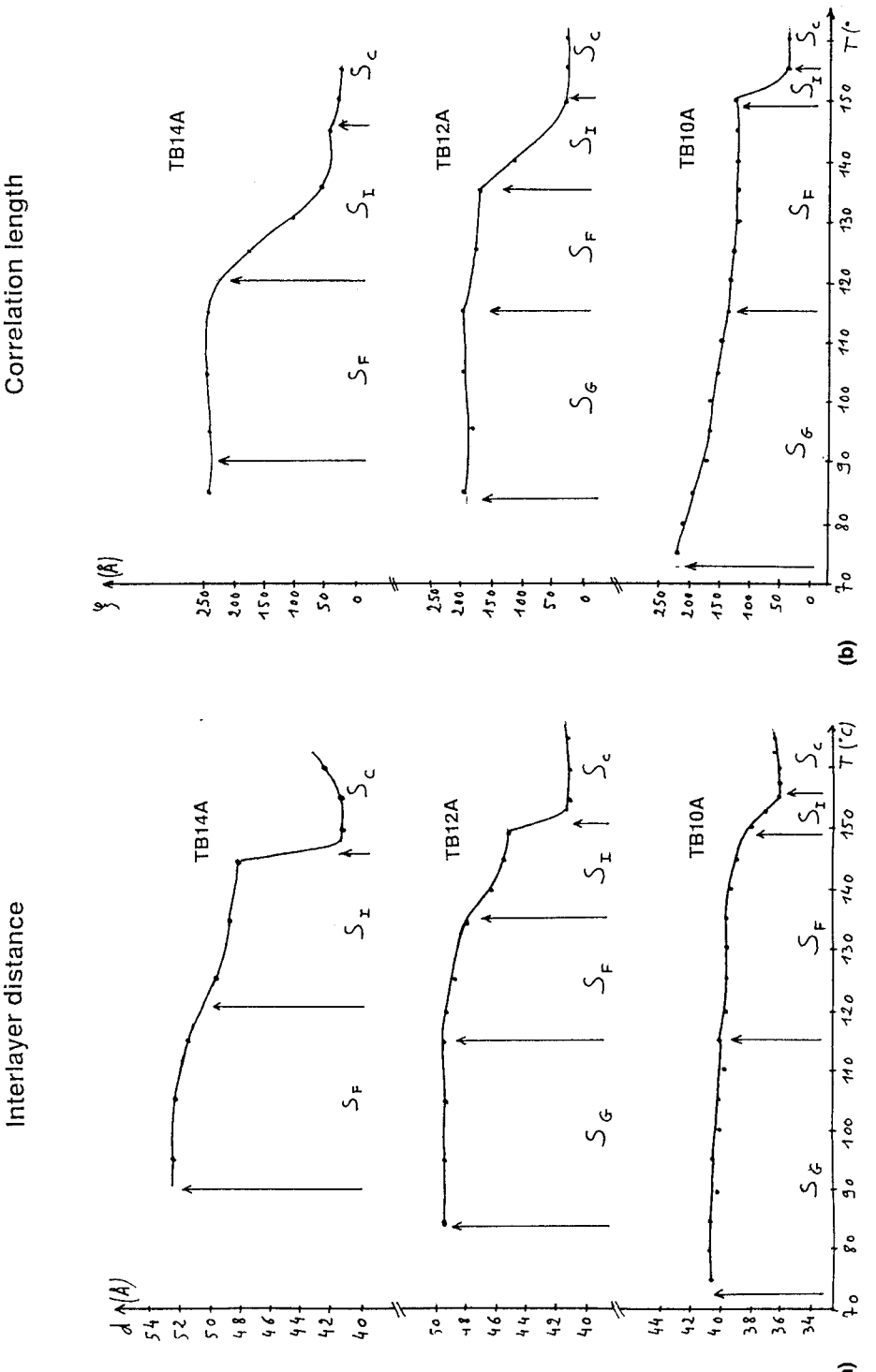


FIGURE 4 Interlayer distance (Figure 4a) and correlation length (Figure 4b) for three samples of the TBnA family.

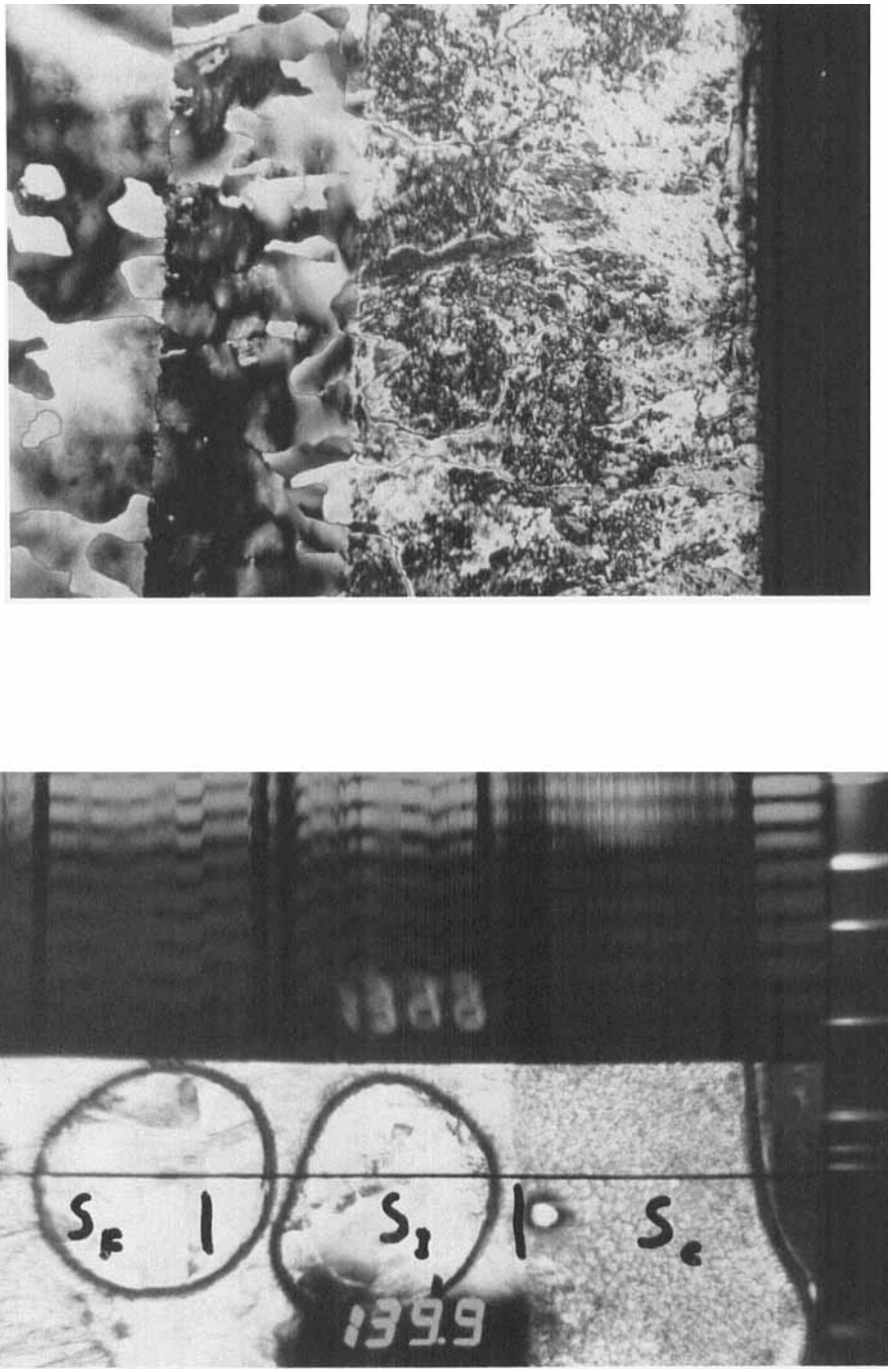


FIGURE 5 Polarizing optical micrograph (Figure 5a) and channeled spectrum for the sequence of SmF-SmI-SmC phases. See Color Plate II.

and to investigate the correlation length between the molecular units within the smectic planes. The experimental setup is schematized in Figure 2. It allows measurement for each temperature of two distinct peaks respectively differing in their intensities, which represents the position of the planes in the smectic phases and the orientational order within the smectic planes (Figure 3a). From these data one can deduce (as shown in Figure 3b) the interlayer distance and the correlation length, which are represented in Figure 4a and Figure 4b, respectively. The results shown in Figure 4a reveal that the interlayer distance within the smectic F and G phases remain practically constant, slightly decreasing in the SmI phase and undergoing a sharp discontinuity at the SmI-SmC transition.

The correlation length between the molecules is also approximately constant in the smectic F and the smectic G planes. By contrast, a sharp decrease of the correlation length occurs within the smectic I phase and reaches a plateau at the smectic C phase (Figure 4b).

4. BIREFRINGENCE MEASUREMENTS

Figure 5a shows a polarizing micrograph of the sequence of SmF-SmI-SmG phases in TBDA, using a hot stage with a 1°C mm^{-1} temperature gradient. The thermograph shows that the three phases are separated by a clearcut phase front which is indicative of a first order transition line. Figure 5b represents the local birefringence measurement in each of the preceding phases, for which we have used a channeled spectrometer made in our laboratory.[7] The variation of local birefringence allows an interpretation of the local molecular orientation in each phase.[7] Figure 5b clearly shows that the molecular orientation exhibits a jump at the two SmF-SmI and SmI-SmC transitions. Besides it appears as largely disordered in the smectic C phase in comparison with the smectic I and F phases which are more orientationally ordered.

5. SUMMARY AND DISCUSSION

We have shown that the sequence of SmC-SmI-SmF-SmG phases are separated by first order transitions. The first order nature of the transitions clearly appears in the polarizing optical micrograph (Figure 5a), and the jump of birefringence (Figure 5b). These transitions must be very close to second order, as they are not associated with strong thermal effects (Figure 1) or (for the transitions between hexatic phases) in the interlayer distance (Figure 4a) or correlation lengths (Figure 4b).

A second interesting result is that the smectic I phase appears as an intermediate ordering state between the SmG and SmF phases. A more extended investigation of the hexatic order within the planes, and of the phase diagram, is necessary before drawing definite conclusions.

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