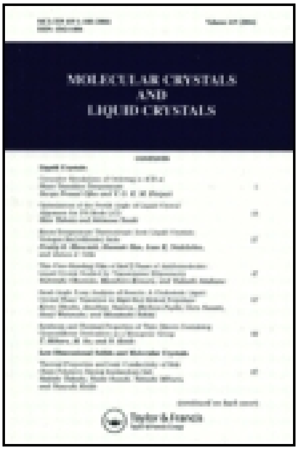

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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To cite this article: F. Moussa , J. J. Benattar & C. Williams (1983): Positional Order and Bond Orientational Order in the Liquid Crystal Smectic F Phase, Molecular Crystals and Liquid Crystals, 99:1, 145-154

To link to this article: http://dx.doi.org/10.1080/00268948308072036

Mol. Cryst. Liq. Cryst., 1983, Vol. 99, pp. 145–154
0026-8941/83/9904-0145/$18.50/0

Printed in the United States of America

Positional Order and Bond Orientational Order in the Liquid Crystal Smectic F Phase[†]

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(Received March 29, 1983)

The smectic F phase occurring in TBBA homologues has been studied by means of X-ray scattering. It was already known that this phase consists of stacked uncorrelated layers. The temperature dependence of the in-plane positional correlation length, characteristic of a short range order has been analyzed. No divergency can be observed at the transition smectic F ⇄ smectic G. The existence of a long range bond-orientational order within a layer has been established. From the X-ray measurements, a basis is provided for the discussion of the behavior of the aliphatic chains.

INTRODUCTION

The homologues of TBBA:

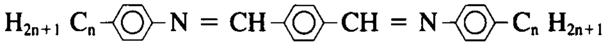

exhibit a complex polymorphism when the number n of Carbon atoms in the aliphatic chains is increased. Among the compounds with n given by $5 \leq n \leq 13$ which have a smectic F phase (Sm F), we have particularly focussed our attention on the C_5 compound (TBPA)[1,2,3,4] and the C_{10} compound (TBDA)[5,6] In this paper we present a detailed analysis of the molecular order in the C_{10} compound which gives the following transitions:

[†] Presented at the Ninth International Liquid Crystal Conference, Bangalore, December 6–10, 1982.

[‡] Laboratoire commun au CEA, CNRS.

$$\mathrm{Cr} \underset{73^\circ\mathrm{C}}{\rightleftarrows} \mathrm{Sm\,G} \underset{115^\circ\mathrm{C}}{\rightleftarrows} \mathrm{Sm\,F} \underset{149^\circ\mathrm{C}}{\rightleftarrows} \mathrm{Sm\,I} \underset{156^\circ\mathrm{C}}{\rightleftarrows}$$

$$\mathrm{Sm\,C} \underset{196^\circ\mathrm{C}}{\rightleftarrows} \mathrm{Sm\,A} \underset{198^\circ\mathrm{C}}{\rightleftarrows} \mathrm{Liq}$$

First we recall what is known of the local structure of the smectic F phase. We analyze and compare single domain and polydomain X-ray spectra, and from them the nature of the molecular ordering is deduced. Then, from their contribution to the scattering, we discuss the behavior of the aliphatic chains.

MOLECULAR ORDERING IN THE SMECTIC F PHASE

Two kinds of X-ray investigations have been performed:

1. The structural studies have been made on single domain samples. They have been obtained either by slowly melting single crystals or by cooling samples from the isotropic liquid phase to the Sm A phase in a strong magnetic field (16 kG). As the local structure of the smectic F phase is derived from the structure of the smectic G phase, let us summarize the main features of this phase: the molecules are arranged in a nearly hexagonal lattice with their long molecular axes tilted with respect to the layer normal. Though this phase has a layered structure, (*hkl*) Bragg peaks exist, such as (201), and are characteristic of a three-dimensional (3D) order, (Figure 1).

In the smectic F phase, the (*hk*0) Bragg spots of Sm G are replaced by rods of scattering elongated along **C*** (parallel to the layer normal). There is no longer an *hkl* Bragg peak with $l \neq 0$ on a 3D positional order. The local structure can be described by a *C*-centered monoclinic cell similar to that of the Sm G phase, with $a = 9.64$ Å, $b = 5.22$ Å, $c = 41.7$ Å, $\beta = 112°$, at $T = 120°\mathrm{C}$ (Figure 2).

Figure 3 shows an X-ray pattern analyzed by an *xy* microdensitometer (the X-ray beam being nearly parallel to the long molecular axis). One can see clearly the six-fold modulation of the intensity. This indicates that: (i) there is a quasi long-range order in the orientation of the bonds in the layers, and (ii) this order extends in three dimensions. Since the direction of the reciprocal lattice basis vector **a*** is well defined, this means that there is a long-range order in the tilt molecular orientation extending in three dimensions. Moreover, the tilt orientation order must be strongly coupled with the bond orientational order; if not, instead of a six-fold modulated ring, one should observe a continuous one.

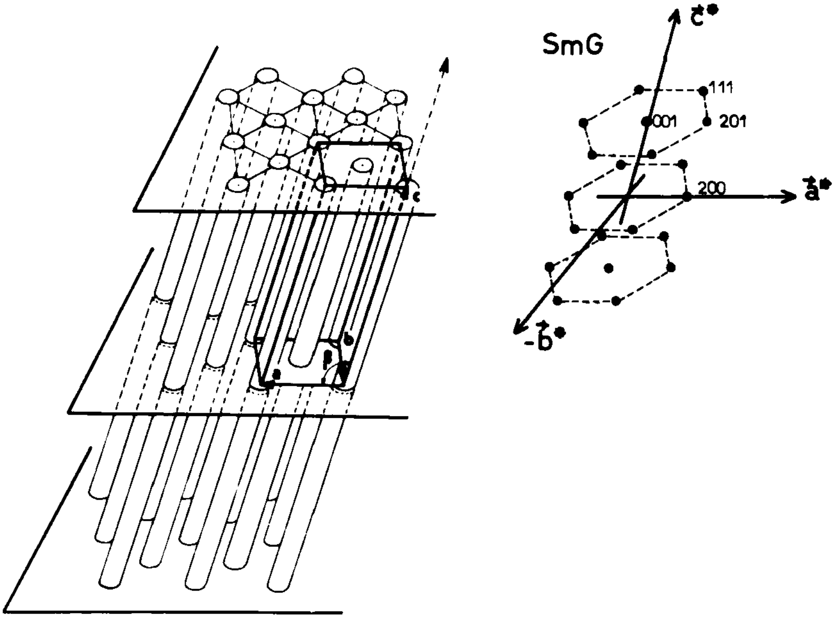

FIGURE 1 Monoclinic cell associated with the pseudohexagonal structure of the Smectic G phase and its reciprocal lattice. (For the sake of simplicity, molecules have been represented by cylinders instead of rigid cores and aliphatic chains).

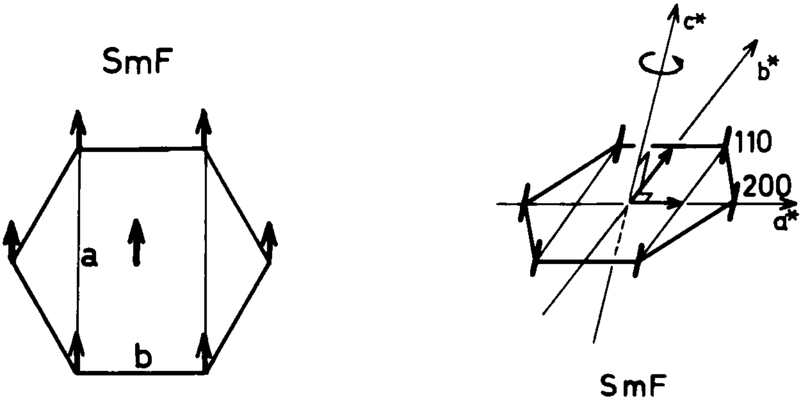

FIGURE 2 Local structure of the smectic F phase (Sm F) and a representation of the diffuse rods in reciprocal space. In the real space, the arrows represent the projection of the long molecular axis **c** on the layer plane (**a**, **b**).

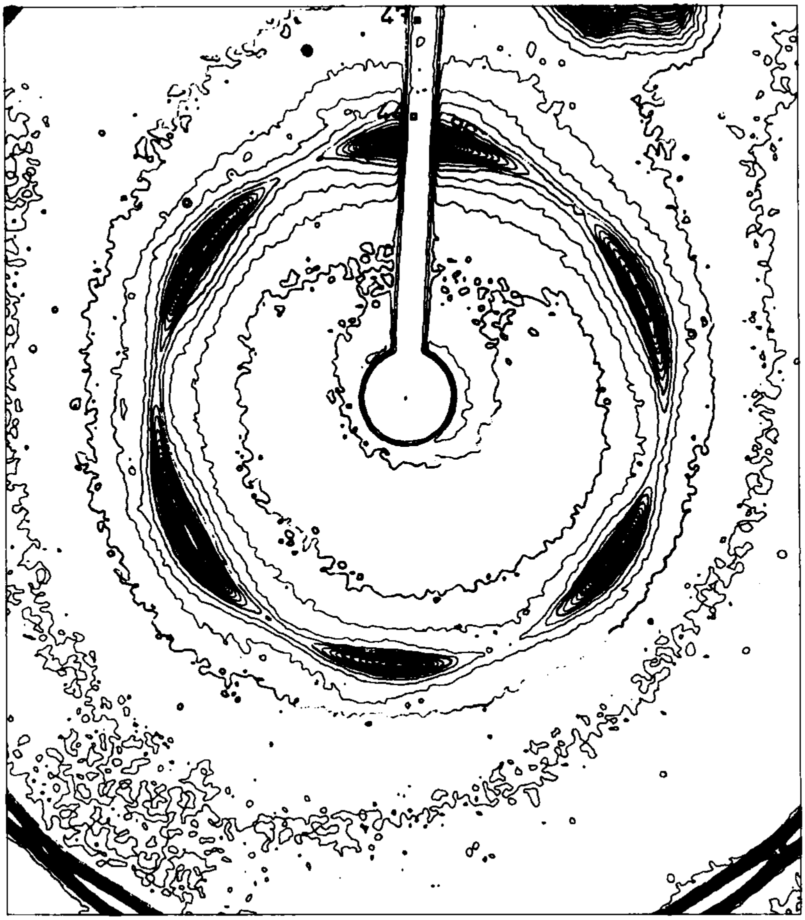

FIGURE 3 X-ray intensity map in the ($a^*, \vec{b}^*$) plane in the smectic F phase of the C_{10} compound. Note the sixfold modulation at the (±200), (±1, ±1, 0), (±1, ±1, 0) points.

From a q_r-scan through one of the six spots ($\mathbf{q}_r \| \mathbf{G}_{200}$ for instance), one can deduce the nature of the positional order of the molecules in a layer. As the scattered intensity follows a Lorentzian law with q_r, it can be concluded that a short-range order exists.

A 2D short-range-positional order within the layers, as well as a long-range order in both bond and tilt orientation therefore characterize the smectic F phase, and these are the main features of a stacked, locked, tilted hexatic phase predicted by the Halperin-Nelson (HN) theory.[7] The mosaic effects both in the layers and perpendicular to the layers prevent a quantitative analysis of the single domain spectra. One cannot check whether the bond orientational correlation function follows a power law:

$$\left\langle \exp\{i6[\theta(\mathbf{0}) - \theta(\mathbf{r})]\} \sim \frac{1}{r\eta_6} \qquad \text{with} \qquad \eta_6 < 0.25 \right\rangle$$

as described in the HN theory. On the other hand, the mosaic spread of the layer normal broadens the profile of the q_r-scan and the correlation length of the positional correlation function $\exp(-r/\xi_{\|})$ cannot be deduced from such a scan, since the mosaic distribution is unknown and varies with temperature.

Detailed analysis of the molecular positional correlations in the layers has therefore been made using powder samples.

2. *The powder patterns* have been obtained either with synchrotron radiation ($\lambda = 1.8$ Å, Lure-Orsay, France) or with a high resolution Guinier camera, ($C_0\ K_{\alpha_1}$, 1.789 Å, Physique des Solides, Orsay, France). They exhibit a diffuse ring at large angles composed of four reflexions of (110) type and two reflexions of (200) type; both types of reflexion do not have exactly the same scattering angle because of a slight distortion (1%) from a regular hexagon.

In previous papers,[4,5,8] it has been shown that the positional order of the molecules in a smectic layer can be analyzed using powder diagrams. As all orientations of the sample are statistically present, the intensity measured at constant $|\mathbf{Q}|$ value is:

$$\mathrm{I_G}(|\mathbf{Q}|) = \int d^3k S_G(\mathbf{k}) R(|\mathbf{k}| - |\mathbf{Q}|)$$

Of course, this method does not allow us to analyze orientational order. $R(|\mathbf{k}| - |\mathbf{Q}|)$ is the resolution function of the spectrometer. $S_G(\mathbf{k})$ is the structure factor of the scattering near the reciprocal lattice vector $\mathbf{G}$ (200 or 110) (Figure 2); it can be written as:

$$S_G(\mathbf{k}) = f_G(q_{\|}) \cdot g(q_{\perp})$$

with $\mathbf{k} = \mathbf{G} + \mathbf{q}$, $q_{\|}$ is the in-plane projection of $\mathbf{q}$, and $q_{\perp}$ is the projection perpendicular to the layer, (Figure 4). The in-plane structure factor $f_G(q_{\|})$ has been chosen as a Lorentzian,

$$f_G(q_{\|}) \sim [\xi_{\|}^2 q_{\|}^2 + 1]^{-1}$$

and $g(q_{\perp})$ is the square form factor of the molecule along the layer normal.

Figure 5 shows the variations of the fitting parameter $\xi_{\|}$ with temperature, for the C_{10} compound. The correlation length $\xi_{\|}$ varies from 250 Å to 150 Å over the whole range of existence of the Sm F phase; it does not

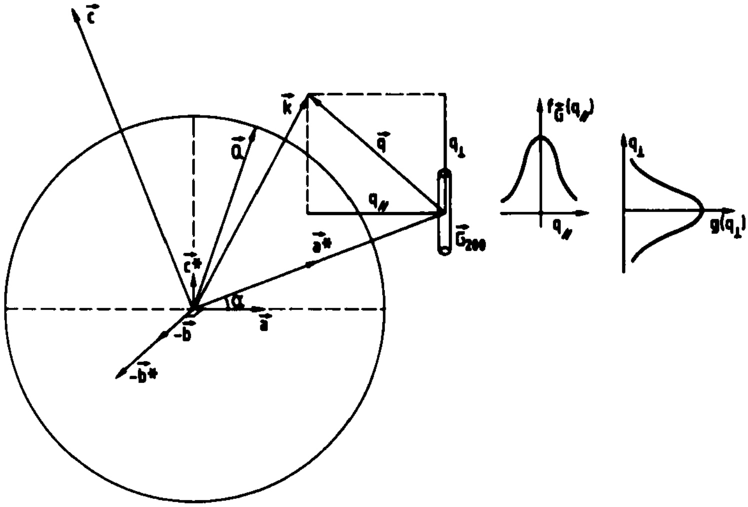

FIGURE 4 Scattering geometry: **k** = $\mathbf{G}_{200}$ + **q**; $q_\perp$ and $q_\parallel$ are respectively the **q** components perpendicular and parallel to the layer: $f_G(q_\parallel)$ is the in-plane structure factor and $g(q_\perp)$ is the form factor of the molecule.

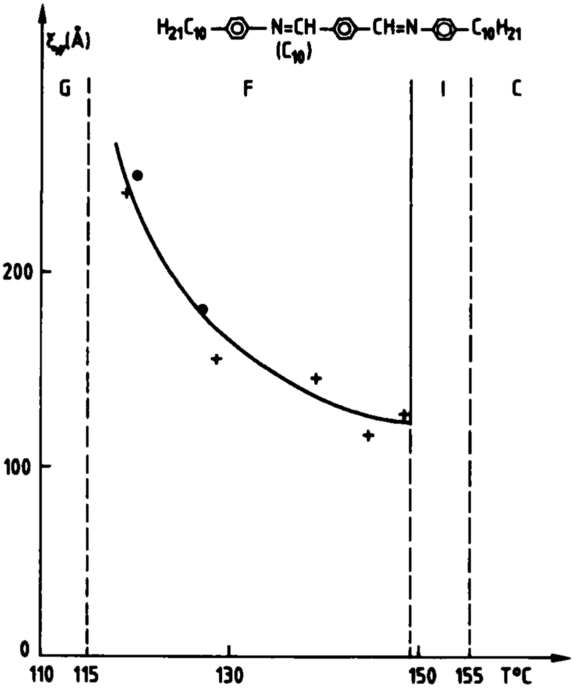

FIGURE 5 Temperature dependence of the in-plane positional correlation length $\xi_\parallel$: + fit of synchrotron radiation spectra, ● fit of Guinier camera patterns. The full line is a guide for the eye.

diverge near the transition Sm G ⇄ Sm F, although this transition is nearly second order. Nevertheless, the smectic F phase appears to have the main features of the tilted, stacked, hexatic phase of the HN theory.

A more direct method to analyze hexatic phases has been set up by Pindak and Moncton,[9] using a free standing film technique. To check whether the analysis of the powder line-shapes gives the same results, we have studied the same compound (65OBC) as that in Ref. 9.

This compound exhibits the following polymorphism

$$\underset{}{\text{Cr}} \underset{60^\circ\text{C}}{\rightleftarrows} \text{Sm B}_{\text{hex}} \underset{68^\circ\text{C}}{\rightleftarrows} \text{Sm A} \underset{85^\circ\text{C}}{\rightleftarrows} \text{Liq}$$

Pindak and Moncton identified the B phase as a hexatic phase, and measured the temperature dependence of the in-plane positional correlation length $\xi_{\parallel}$. Now we have studied the same phase with the powder technique.

Both results are reported in Figure 6. Though one does not find exactly the same values for the in-plane positional correlation length ξ, its order of magnitude is the same by both techniques. In conclusion, the behavior of the correlation length is the same for both compounds (650 BC and TBDA), and the properties of the smectic F phase and of the smectic B hexatic are quite similar. Both phases are therefore examples of hexatic phases.

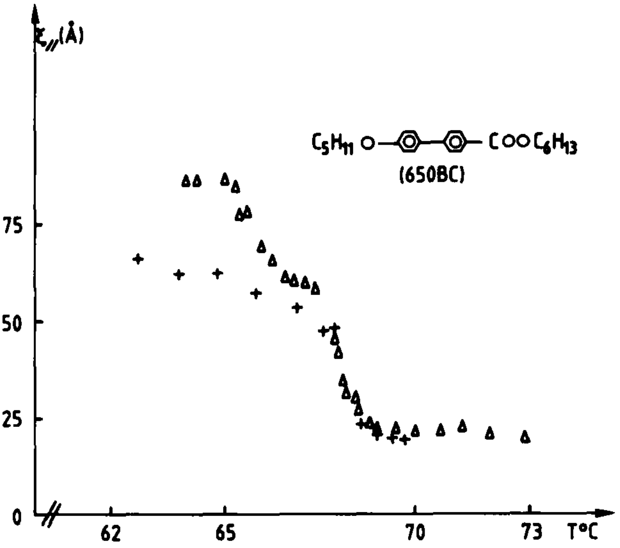

FIGURE 6 Comparison between the in-plane positional correlation length calculated from free standing film techniques by Pindak and Moncton[9] (symbol Δ) and the same fitting parameter calculated from powder measurements made on the same compound 65OBC (symbol +).

CORRELATIONS BETWEEN ALIPHATIC CHAINS

Another feature of the Sm F phase appears in some powder spectra, when the counting time is large enough to allow one to detect it. Figure 7 shows a spectrum measured with the C_{15} compound (the longer the aliphatic chains, the stronger the effect). One observes a little bump near $|\mathbf{Q}| = 1.34$ Å^{-1}, and this is characteristic of pair correlations between carbon atoms belonging to different chains in a quasi liquid state. Therefore, the two parts which constitute the molecule behave quite differently: (i) the core (with the three phenyl rings and the mainly *trans*-conformation of the —CH=N— linkages) which rotates rapidly around the long axis, and (ii) the aliphatic chains which are molten, but, nevertheless, remain stretched on average. This is imposed by the value of the layer thickness which is quite near the value for the completely stretched molecule times the cosine of the tilt angle. However, the chains perform disordered motions which give rise to liquid-type correlations between them. This picture is corroborated by the analysis of the $q_\perp$-scan shown in Figure 8. This scan is perpendicular to the layers. We have compared the experimental scattered intensity with the square structure factor of the molecule calculated following different hypotheses. The best agreement is obtained with the assumption of an electron density localized in a cylinder whose length is that of the aromatic core and not the length of the whole molecule. Because

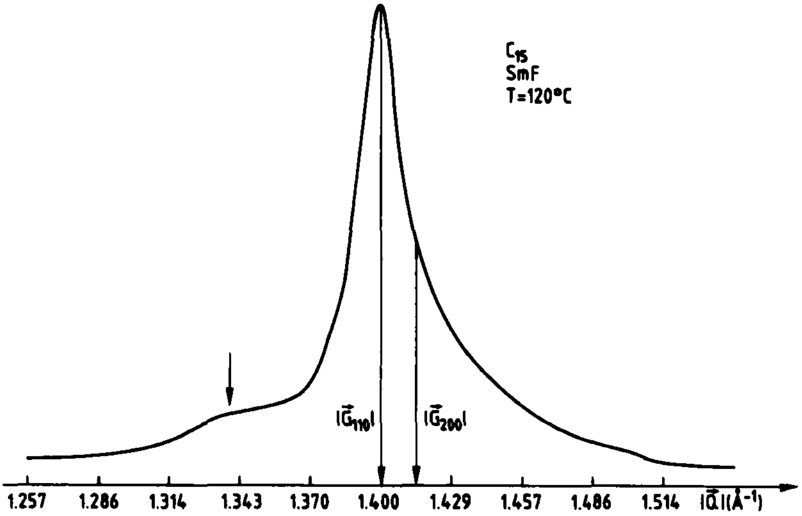

FIGURE 7 A powder spectrum of the smectic F phase of the C_{15} compound showing the additional scattering at $|\mathbf{Q}| = 1.34$ Å^{-1} due to the chains.

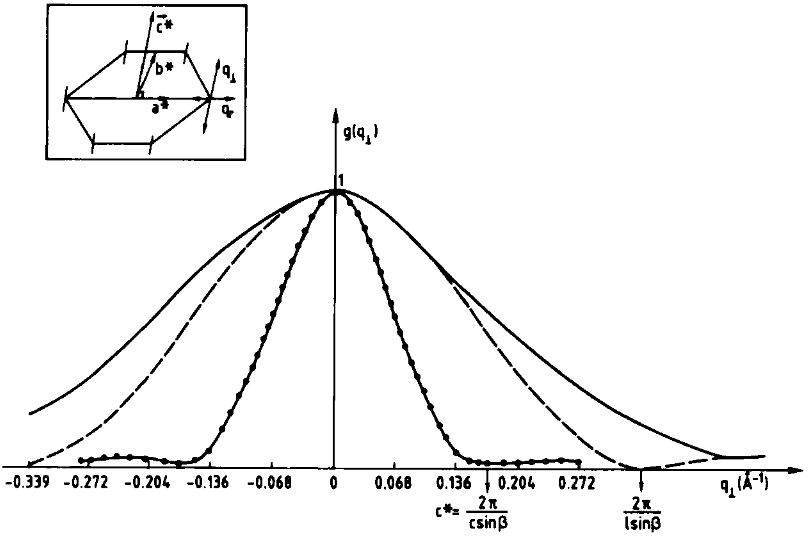

FIGURE 8 Measured intensity of the diffuse rod centered at (200) in a $q_\perp$-scan (full line). The inset describes the scan direction. The dotted line is the calculation of:

$$\left[\sin\left(q_\perp\frac{c\sin\beta}{2}\right)\Big/q_\perp\frac{c\sin\beta}{2}\right]^2$$

The broken line represents:

$$\left[\sin\left(q_\perp\frac{l\sin\beta}{2}\right)\Big/q_\perp\frac{l\sin\beta}{2}\right]^2.$$

c is the length of the molecule, l that of the core, and $\beta = (\mathbf{a}, \mathbf{c}) = 112°$.

of the motions of the aliphatic chains, the scattering is mainly due to the rigid part of the molecules. A square wave is, of course, a rough way to describe the true electron density of the molecule, and this is why, finally, a Lorentzian law $\propto [1 + (\xi_\perp q_\perp)^2]^{-1}$ has been chosen. From the profile shown in Figure 8, ($\xi_\perp \approx 10$ Å) for the $g(q_\perp)$ function (Eq. 1). A possible explanation for this discrepancy is that in the single domain $q_\perp$-scan (Figure 8), the interlayer mosaic widens the profile and the true $\xi_\perp$ should certainly be larger than 6 Å.

But in both cases, it is clear that the part of the molecules which contributes to the scattering at the ($hk0$) points concerns essentially the aromatic core and not the entire molecule. A similar conclusion is established[10] concerning the smectic B phase. In this paper the authors emphasize that the aromatic cores and the aliphatic chains form two distinct sublayers: the interactions between the cores are considered responsible for the molecular order, while interchain interactions are not thought to contribute in this way.

In conclusion, we point out that both X-ray techniques, on single domain and on poly-domain samples, are complementary. The former has permitted us to observe the 3D long-range bond orientational order of the smectic F phase, and the latter to make a detailed study of the positional order. Moreover, they have allowed a better understanding of the behavior of the aliphatic chains which play an important role in the smectic F phase.

Acknowledgments

The authors are very grateful to C. Germain who synthesized the compounds, and they have benefited from many discussions with Professor M. Lambert. They also thank G. Jannink for a critical reading of the manuscript.

References

1. D. Demus, S. Diele, M. Klapperstück, V. Link and H. Zaschke, *Mol. Cryst. Liq. Cryst.*, **15**, 161 (1971).
2. J. J. Benattar, J. Doucet and M. Lambert, *Phys. Rev.*, **A20**, 2505 (1979).
3. A. J. Leadbetter, J. P. Gaughan, B. Kelly, G. W. Gray and J. W. Goodby, *J. Phys. (Paris)*, **40**, 178 (1979).
4. J. J. Benattar, F. Moussa and M. Lambert, *J. Phys. (Paris)*, **41**, 1371 (1980).
5. J. J. Benattar, F. Moussa and M. Lambert, *J. Phys. (Paris) Lett.*, **42**, L67 (1981).
6. P. A. C. Gane, A. J. Leadbetter and P. G. Wrighton, *Mol. Cryst. Liq. Cryst.*, **66**, 247 (1981).
7. B. I. Halperin and D. R. Nelson, *Phys. Rev. Lett.*, **41**, 121 (1978); D. R. Nelson and B. I. Halperin, *Phys. Rev.*, **B19**, 2457 (1979); D. R. Nelson and B. I. Halperin, *Phys. Rev.*, **B21**, 5312 (1980); S. Ostlund and B. I. Halperin, *Phys. Rev.*, **B23**, 335 (1981).
8. J. J. Benattar, F. Moussa and M. Lambert to be published in a special issue of the *Journal de Chimie Physique*, Paris, article entitled "Polymorphism in Liquid Crystals."
9. R. Pindak, D. E. Moncton, S. C. Davey and J. W. Goodby, *Phys. Rev. Lett.*, **46**, 1135 (1981).
10. F. Barbarin, J. P. Chausse, C. Fabre, J. P. Germain, B. Deloche and J. Charvolin, *J. Phys.*, **44**, 45 (1983).