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Influence of the molecular tilt on the structure of smectic blue phases

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Smectic blue phases (BP$_{sm}$) are original physical systems of thermotropic liquid crystals, displaying a double geometrical frustration: the extension of chirality in the three spatial dimensions, such as classical blue phases, and the competition between smectic order and helical twist, such as twist grain boundary (TGB) phases. We report experimental evidence of the influence of the underlying TGB($_A$ or $_C$) phase on the BP$_{sm}$ structure.

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The effect of chirality on the organization of liquid crystals is presently a subject of intense interest. A spontaneous twist of the molecular orientation appears for chiral mesogens. But this local orientational order can induce frustration and therefore, complex structures sometimes occur. These include the blue phases (BP) between the cholesteric phase and the isotropic phase [1]. Two of these blue phases, BP1 and BP2, exhibit an unusual cubic symmetry in which the orientational order is periodic and long range in three dimensions. The blue phase structure involves a twist of the director (average molecular orientation) extending not only in one direction, as in the cholesteric phase, but in both directions perpendicular to the director. This is sometimes called a double twisted structure. This double twisted structure cannot extend perfectly into three-dimensional space. Geometrical models of the BP1 and BP2 blue phases consist of cubic networks of double twist cylinders separated by defect lines. Thus blue phases can also be seen as a periodic array of disclination lines. Since smectic layers cannot be continuously twisted, Renn and Lubensky predicted twist grain boundary (TGB) phases [2], which represent a second example of a frustrated chiral system. TGB phases have been experimentally found by Goodby *et al.*, in 1989, for TGB$_A$ [3] and by Nguyen *et al.*, in 1992, for TGB$_C$ [4]. They consist of blocks of pure smectic material (which can be either smectic-*A* for TGB$_A$ or smectic-*C* for TGB$_C$) separated by parallel, regularly spaced grain boundaries formed by a periodic array of screw dislocations. Such a dislocation arrangement allows helical twist. In TGB phases, as in blue phases, the frustration is relieved by the presence of defects.

Recently new chiral phases, called smectic blue phases (BP$_{sm}$), have been discovered in the following phase sequence: TGB$_A$-BP$_{sm(A)}$1-BP$_{sm}$2-BP$_{sm}$3-Iso, without any intermediate cholesteric state [5]. Contrary to classical blue phases, these phases exhibit quasi-long-range smectic order that can be studied by x-ray scattering. The smectic order is correlated with the orientational three-dimensional order and is therefore enhanced in some directions. The smectic peak positions give information on the symmetry of the BP$_{sm}$ unit cell. Note that the BP$_{sm}$ lattice parameter is in the UV range [5], preventing study by optical scattering of visible light (Kossel diagram technique) that is commonly used to find the symmetry of classical blue phases [6]. The structures of smectic blue phases have been investigated and BP$_{sm}$2 appears hexagonal [7], whereas BP$_{sm(A)}$1 exhibits a cubic symmetry [8]. These studies have been mainly carried out by x-ray scattering on BP$_{sm}$ monodomains, grown *in situ* in the heating stage. The third smectic blue phase called BP$_{sm}$3 has, like classical BP3 [9], an amorphous structure of the same macroscopic symmetry as that of the isotropic phase [10]. Up to now, all structural investigations of BP$_{sm}$ have been done on the series of compounds FH/FH/HH-*n*BTMHC [7,8]. Lately, a new molecule, named 16FHFH-BTC1M8, has been synthesized, which exhibits a new phase sequence, TGB$_C$-BP$_{sm}$-Iso, which does not show any TGB$_A$ phase. Three smectic blue phases have also been observed in 16FHFH-BTC1M8: BP$_{sm(C)}$1 between 67.3 and 68.2 °C, BP$_{sm}$2 between 68.2 and 69.0 °C, and BP$_{sm}$3 between 69.0 and 70.4 °C (upon heating) [11]. The main interest of this compound is that the molecules are tilted in the TGB$_C$ phase adjacent to BP$_{sm}$, contrary to the FH/FH/HH-nBTMHC series exhibiting a TGB$_A$-BP$_{sm}$ transition. It has been shown that the presence of smectic order disturbs the orientational order of blue phases, but what is the nature of the smectic order (smectic-*A* or smectic-*C*) in the smectic blue phases? Indeed, the nature of BP$_{sm}$ smectic order is not

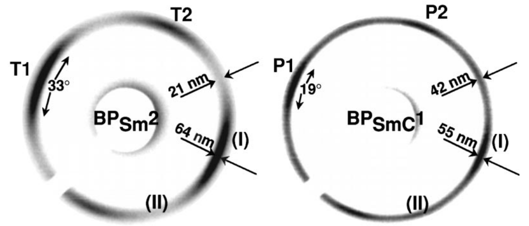

FIG. 1. Experimental x-ray scattering patterns obtained for BP$_{sm}$2 and BP$_{sm\text{-}C}$1 monodomains, respectively. These two patterns were recorded in the same orientation, corresponding roughly to the maximum intensity of the main smectic peak (T1 for BP$_{sm}$2 and P1 for BP$_{sm\text{-}C}$1). The parts of the ring with higher intensity are labeled (I) and the parts with lower intensity are marked (II). Note the decrease in the angular spread (along the ring) of smectic peaks in the BP$_{sm\text{-}C}$1 phase. Due to their angular spread the T2 and P2 peaks are also visible in these patterns.

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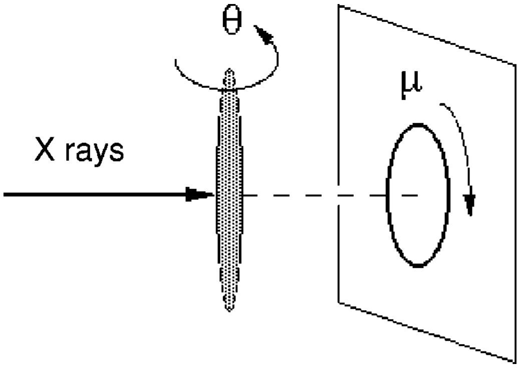

FIG. 2. Schematic representation of the x-ray scattering geometry.

yet experimentally known or even predicted. Therefore, the comparison between these two compounds should help us to determine what the influence of the local smectic order is on the BP_{sm} structure. In this Rapid Communication, we report that the structure of the first smectic blue phase, $\mathrm{BP}_{sm}1$, is affected by the nature of the smectic order of adjacent phases, in contrast with $\mathrm{BP}_{sm}2$, which remains unchanged. Indeed, we show that in the case of a TGB_C-BP_{sm} transition, the $\mathrm{BP}_{sm}1$ structure, called $\mathrm{BP}_{sm\text{-}C}1$, appears hexagonal, thus differing from the $\mathrm{BP}_{sm\text{-}A}1$ cubic symmetry exhibited in the case of a TGB_A-BP_{sm} transition.

Monodomains must be grown to determine the different BP_{sm} structures. Contrary to classical blue phases, the growth of $\mathrm{BP}_{sm\text{-}A}1$ monodomains directly from the $\mathrm{BP}_{sm}2$ phase is possible using a very low cooling rate (0.01 °C per 10 min), as previously shown [8]. We have therefore used this nucleation process to obtain a $\mathrm{BP}_{sm\text{-}C}1$ monodomain induced from a $\mathrm{BP}_{sm}2$ one. Several series of x-ray scattering experiments on $\mathrm{BP}_{sm\text{-}C}1$ monodomains have been performed. The scattering patterns obtained, either with $\mathrm{BP}_{sm\text{-}C}1$ or $\mathrm{BP}_{sm}2$ monodomains, exhibit pairs of peaks indicating that the smectic order is not isotropic, but extends in certain directions of the three-dimensional unit cell (Fig. 1). The modulation of smectic peaks, defined by $C=(I_{\mathrm{Max}}-I_{\mathrm{min}})/(I_{\mathrm{Max}}+I_{\mathrm{min}})$, is nevertheless weaker in the $\mathrm{BP}_{sm\text{-}C}1$ phase. In the following, we will characterize the peaks by the position of their maximum intensity. The 16FHFH-BTC1M8 compound is contained in a glass capillary tube (1 mm diameter) placed vertically inside a hot stage. The sample can be rotated around its main axis to explore the entire reciprocal space (Fig. 2). Once the monodomain is grown, different scattering patterns are recorded on imaging plates by rotating the capillary by steps of 10° between scans. Let us call θ this rotation angle. The intensity $I(\theta,\mu)$ along the ring has been analyzed as a function of the angle, μ, with the vertical axis (Fig. 2). Then, by combining these various profiles we can determine the directions of smectic order enhancement, i.e., where the different smectic peaks are located (Tables I and III) and then deduce the angles between these peaks (Tables II and IV). Note that these x-ray scattering studies do not give direct information on the orientational unit cell, which is at a much higher length (200 nm) than the scale (linked to the smectic order) probed in these experiments. Nevertheless, the symmetry of the smectic order certainly reflects that of the three-dimensional orientational order in each BP_{sm} phase.

TABLE I. Positions of the four smectic peaks T1, T2, T3, and T4 for a $\mathrm{BP}_{sm}2$ monodomain. μ is the angle with the vertical axis. θ is the rotation angle around this axis (see Fig. 2). The monodomain was grown with $\theta=0$ along the x-ray beam. The angles are given in degrees.

	T1	T2	T3	T4
θ	25	65	-42	-68
μ	113	28	46	100

TABLE II. Angles (in degrees) between the directions along which the smectic peaks are observed for the $\mathrm{BP}_{sm}2$ monodomain (reported in Table I).

	T1	T2	T3	T4
T1	0	91	91	89
T2	91	0	121	118
T3	91	121	0	121
T4	89	118	121	0

The results of the exploration of the reciprocal space of both $\mathrm{BP}_{sm}2$ and $\mathrm{BP}_{sm\text{-}C}1$ monodomains are reported Fig. 3. The $\mathrm{BP}_{sm}2$ monodomain exhibits four pairs of peaks (Table I) showing a hexagonal structure: T1 is perpendicular to the three others peaks (T2, T3, and T4), which are separated by angles of about 120° (Table II). Then, a temperature decrease induces the transition from $\mathrm{BP}_{sm}2$ to $\mathrm{BP}_{sm\text{-}C}1$. Only one smectic peak is common to $\mathrm{BP}_{sm}2$ and $\mathrm{BP}_{sm\text{-}C}1$: P1 $\equiv$T1. However, the three other $\mathrm{BP}_{sm\text{-}C}1$ peaks, P2, P3, and P4, have rotated by an angle of around 30°, with respect to $\mathrm{BP}_{sm}2$ peaks (Tables III and IV), and appear to have been ‘‘inserted’’ between those of $\mathrm{BP}_{sm}2$. The limited accuracy of the maximum intensity measurements is due to the weak modulation of peaks in $\mathrm{BP}_{sm\text{-}C}1$ phase (Tables IV and V). Note that this rotation proves that the slight smectic order enhancements are really associated with the $\mathrm{BP}_{sm\text{-}C}1$ phase. Thus the symmetry exhibited by the $\mathrm{BP}_{sm\text{-}C}1$ smectic peaks seems similar to that of $\mathrm{BP}_{sm}2$, even if the structures of these two phases differ in terms of smectic order. Figure 3 summarizes the evolution in the directions of smectic order enhancement, between $\mathrm{BP}_{sm}2$ and $\mathrm{BP}_{sm\text{-}C}1$ for the new 16FHFH-BTC1M8 compound (with a TGB_C-BP_{sm} transition), and between $\mathrm{BP}_{sm}2$ and $\mathrm{BP}_{sm\text{-}A}1$ [8] for the already known FH/FH/HH-nBTMHC series (with a TGB_A-BP_{sm} transition).

TABLE III. Positions of the four smectic peaks P1, P2, P3, and P4 for the $\mathrm{BP}_{sm\text{-}C}1$ monodomain grown from the $\mathrm{BP}_{sm}2$ phase. The angles are given in degrees.

	P1	P2	P3	P4
θ	26	-13	-59	-80
μ	111	27	74	124

TABLE IV. Angles (in degrees) between the directions along which the smectic peaks are observed on the $\mathrm{BP}_{sm\text{-}C}1$ monodomain grown from $\mathrm{BP}_{sm}2$.

	P1	P2	P3	P4
P1	0	89	91	91
P2	89	0	123	111
P3	91	123	0	126
P4	91	111	126	0

TABLE V. Features of smectic order for $\mathrm{BP}_{sm}2$, $\mathrm{BP}_{sm\text{-}C}1$, and $\mathrm{BP}_{sm\text{-}A}1$ monodomains. ξ represents the correlation length (in nm) associated with the smectic order, ω is the angular spread of the peaks, and C is their modulation.

Phase	$\mathrm{BP}_{sm}2$	$\mathrm{BP}_{sm\text{-}C}1$	$\mathrm{BP}_{sm\text{-}A}1$
ξ_M (main peak)	64	55	59
ξ_b (between peaks)	21	42	28
ω (°)	33	19	33
C_M (main peak)	0.56	0.22	0.34
C_o (other peaks)	0.52	0.17	0.34

A first theoretical approach for combining smectic order with three-dimensional orientational order has been proposed by Kamien [12] with a model of smectic double twist cylinders. Our experimental results can be easily interpreted from this geometrical model by assuming that the regions where the smectic order can easily extend, corresponding to the peaks, are the smectic double twist cylinders cores. Indeed, in the annular and concentric domains wrapping around this perfect smectic core, the smectic layers are distorted by the twist (Fig. 4). A geometrical model of the structure of smectic blue phases can be sketched by packing these smectic double twist cylinders according to the observed symmetries [12,8]. If the structure of these cylinders, corresponding to the peaks in the x-ray scattering patterns, is nearly the same (in terms of angular spread and of correlation length of the smectic order) for both $\mathrm{BP}_{sm}2$ and $\mathrm{BP}_{sm\text{-}A}1$ phases, the structure is clearly different for $\mathrm{BP}_{sm\text{-}C}1$ phase (Table V). The angular spread, ω, of the peaks along the ring is proportional to the radius of smectic double twist cylinders. ω decreases from 33° to 19° at the $\mathrm{BP}_{sm}2$-$\mathrm{BP}_{sm\text{-}C}1$ transition, suggesting that the outer smectic layers of the smectic double twist cylinders vanish, and only the inner ones, close to the core, remain [Region (I) in Figs. 1 and 4]. The correlation length of the positional order ξ, defined as $\xi = 2\pi/\mathrm{FWHM}$ (full width at half maximum), has been roughly estimated to be 60 nm for the smectic peaks of all BP_{sm}. But ξ associated with the smectic background of the scattering ring increases from 21 nm in $\mathrm{BP}_{sm}2$ to 42 nm in $\mathrm{BP}_{sm\text{-}C}1$, showing that the smectic order improves *between* the cylinders [Region (II) in Figs. 1 and 4]. This last point is confirmed by the very weak modulation of smectic peaks observed in the $\mathrm{BP}_{sm\text{-}C}1$ phase (Table V).

All these results seem to indicate that the *smectic order develops with an isotropic distribution between locations in which the smectic order is enhanced*. The slight observed birefringence (Δn estimated to be lower than 0.001) is consistent with the suggested structure. Indeed, the $\mathrm{BP}_{sm\text{-}C}1$ phase, examined by polarizing microscopy, shows a blue ''platelet'' texture [11]. The blue color originates from the optical activity of $\mathrm{BP}_{sm\text{-}C}1$, that can only be seen in the absence of high birefringence. Therefore, the $\mathrm{BP}_{sm\text{-}C}1$ symmetry, given by the smectic order enhancements, seems similar to the $\mathrm{BP}_{sm}2$ one, but the structural anisotropy is

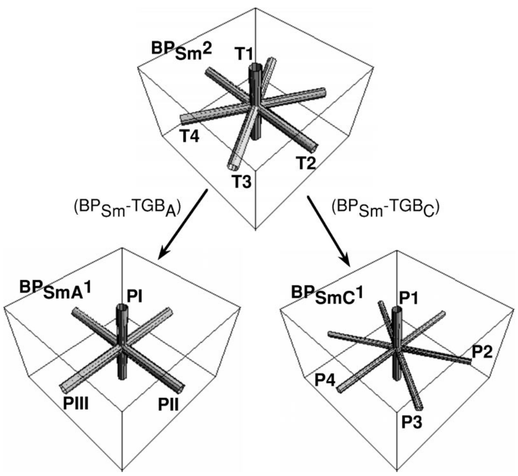

FIG. 3. Geometrical views indicating the directions of smectic order enhancement, corresponding to the smectic peaks for $\mathrm{BP}_{sm}2$, $\mathrm{BP}_{sm\text{-}A}1$, and $\mathrm{BP}_{sm\text{-}C}1$ monodomains. If the $\mathrm{BP}_{sm\text{-}A}1$ third peak, labeled PIII, is the merging of T3 and T4 found in $\mathrm{BP}_{sm}2$ [8], the three peaks P2, P3, and P4 of $\mathrm{BP}_{sm\text{-}C}1$ phase seem rotated by about 30° and are ''inserted'' between those of $\mathrm{BP}_{sm}2$.

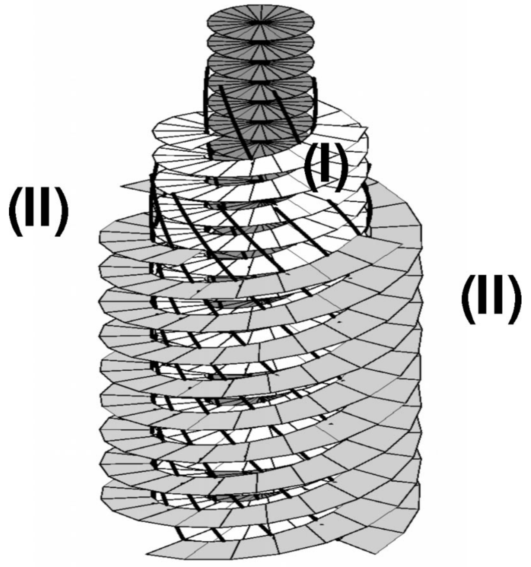

FIG. 4. Model of a smectic double twist cylinder giving rise to the experimental smectic peaks [called region (I)]. These cylinders can be packed together according to the observed symmetry (hexagonal or cubic). However, the smectic order persists between cylinders and gives rise to the continuous smectic ring [region labeled (II) in Figs. 1 and 4]. (Courtesy of Kamien.)

much lower than in BP$_{sm}$2. Indeed, the regions between smectic peaks are more extended and therefore play an important role in the BP$_{sm\text{-}C}$1 phase. This is consistent with the fact that twist can occur easily in these regions of Sm-C-like order (with for instance the Sm-C^* structure), whereas defects must be introduced in regions of smectic-A order to create twist.

Thus, we have shown that the symmetry of the first smectic blue phase depends on whether or not the molecules are tilted in the smectic layers : hexagonal BP$_{sm\text{-}C}$1 for tilted molecules and cubic BP$_{sm\text{-}A}$1 in the absence of tilt. This work should then stimulate theoretical investigations to find geometrical models of these new phases. The structural data reported in this paper concerning the influence of the local smectic order on the structure of smectic blue phases should inspire the elaboration of models describing these original phases with a double geometrical frustration: twist and smectic order in three-dimensional space.

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