

A two-state model for the modulated B₇ liquid crystalline phase exhibited by bent-core molecules

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Abstract

Liquid crystals (LC) made of bent-core (BC) organic molecules have been intensively studied over the past two decades. The B₇ LC consists of smectic layers in which *tilted* molecules have an in-plane polar packing, the polarization vector (\mathbf{P}) having a *splay distortion* forming stripes of tens of nanometers in width, and undulated layers giving rise to 2D rectangular or oblique lattices. The prevailing phenomenological theory attributes this structure to a strong coupling between molecular tilt in the layers and $\text{div}\mathbf{P}$. Based on our recent studies on other phases exhibited by BC molecules, we propose a new model in which the physical origin of the stripes arises from a minority (~10%) of the BC molecules having less bent excited state (ES) conformers which can freely rotate about their long axes, and aggregate to form smectic C type walls, in which the tilt angle is relatively small. The more bent ground state (GS) conformers with polar packing in turn form the splayed structure between such walls to lower the free energy. The mismatch in the layer spacing between the domains with ES and GS conformers generates the structures in the B₇ phase described above. The model predicts a weak first order transition from B₇ to the uniform B₂ phase as the temperature is lowered, as experimentally observed in some compounds. We show that the observed slow increase of the stripe width in the LC to micrometer dimensions in free standing films can be attributed to changes in the physical parameters by chemical degradation and absorption of ions by the exposed polarized layers. We also describe different possible structures of the undulated layers, including a stacking of racemic pairs of SmC_aP_F layers within the stripes. Some possible methods of testing the model are also indicated.

Keywords: bent-core molecules, B₇ phase, layer polarization

(Some figures may appear in colour only in the online journal)

1. Introduction

The commercially important nematic (N) liquid crystals (LC) have an *apolar* orientational order of rod-like molecules. Ferroelectric polarization is observed only in the plane of the liquid layers of some types of smectic LCs. The first type was discovered in smectic C* (SmC*) LCs in which the long axes of chiral molecules tilt from the layer normal, and the polarization \mathbf{P} is orthogonal to the tilt plane [1]. Achiral bent core (BC) molecules were subsequently found to have a polar packing in smectic layers [2], and usually tilted in the plane

orthogonal to \mathbf{P} (the B₂ phases), making the layers themselves chiral [3]. In macroscopic samples of SmC* LCs, chiral interactions generate a helielectric structure. However, thin free standing films of SmC* with just a few layers exhibit an average nonzero ferroelectric polarization \mathbf{P} . As the smectic layers are liquid, $\text{div}\mathbf{P}$ is an allowed distortion, which integrates out as a surface term. Several theoretical models [4–7] were developed in which it was demonstrated that by allowing for a spatial variation in the magnitude of \mathbf{P} , the term $\mathbf{P}^2 \text{div}\mathbf{P}$ can generate periodic defect structures in the medium, close to the paraelectric to ferroelectric transition temperature. If

the elastic constants for $\text{div}\mathbf{P}$ and $\text{curl}\mathbf{P}$ distortions are equal, a stripe structure results in which regions with the favorable splay of \mathbf{P} are separated by thin walls which accommodate unfavorable splay of \mathbf{P} , with a spatially varying reduced magnitude of \mathbf{P} . It goes over to the uniform structure without the distortion in a second order transition at which the stripe width diverges [7]. If the elastic constants are unequal, an additional hexagonal structure which has a few disclinations of the \mathbf{P} field in each unit cell can also be stabilized [7]. However, such intermediate defect phases have not been found in SmC^* LCs.

Organic compounds with BC molecules exhibit a variety of LC phases [8], of which the B_7 phase is well known for the spectacular optical textures exhibited in a sample seen under a polarizing microscope. Usually the B_7 LC separates from the isotropic phase in the form of helical or double helical filaments with a variety of motifs in a strong first order transition [9, 10]. Indeed it is difficult to prepare mono-domain samples, and quantitative optical measurements have not been made on any B_7 sample. High resolution small angle x-ray scattering studies and freeze fracture electron microscopy enabled the Boulder group to elucidate the structure in 2003 [11]. The medium consists of stripes with widths in the range of a few 10s of nanometers, in which transversely polarized layers with *tilted* BC molecules exhibit $\text{div}\mathbf{P}$ distortion (figure 1). The layers are undulated (U, figure 2), with an effective layer spacing which is slightly larger (by a few %) than that of the low temperature SmC_5P_F^* (B_2) phase. The subscript 'S' in the last symbol stands for synclitic, 'F' for ferroelectric, and the asterisk signifies a chiral structure [3]. The authors of [11] proposed that the defect walls separating the stripes have a locally larger layer spacing, forcing the layers forming the stripes themselves to tilt for filling space (figures 1 and 2). The orientational distribution of \mathbf{P} is symmetric about the center of the stripe, and the spatially averaged $\langle\mathbf{P}\rangle$ points along the positive ξ -axis in a given stripe, say. The orientation of $\langle\mathbf{P}\rangle$ of the neighbouring stripe can be either ferroelectric (along $+\xi$) or anti-ferroelectric (along $-\xi$). In some cases, one of the neighbours was found to have ferroelectric and the other anti-ferroelectric orientations [11]. Further, the slopes of the tilted layers of neighbouring stripes can have the same sign, giving rise to an oblique 2D lattice, or if they have opposite signs, a rectangular 2D lattice. Treating each layer in a stripe as a block, it has been proposed that the symbol SmCPU_S be used for blocks which are polar (P), with tilted molecules in the layer (SmC) whose undulation (U) has synclitic (subscript S) tilt with its neighbor [12]. One can similarly define the symbol SmCPU_A . A further variety is caused by the chiral sense of the block. The molecules themselves are achiral, and can tilt in one of two opposite directions in a plane normal to the polar axis, defining the layer chirality. If neighbouring stripes have the same chirality, it is indicated by using [S] at the end of the symbols described above. If they have opposite chirality, the two stripes form a racemic pair, described by [A]. In most of the early studies, only the textures were used to identify the LC as B_7 , and it turns out that the textures result from any underlying 2D lattice structure. Specifically, in several cases, including that of [9], the blocks are formed by broken layers, and neighbouring blocks have a shift of half a layer

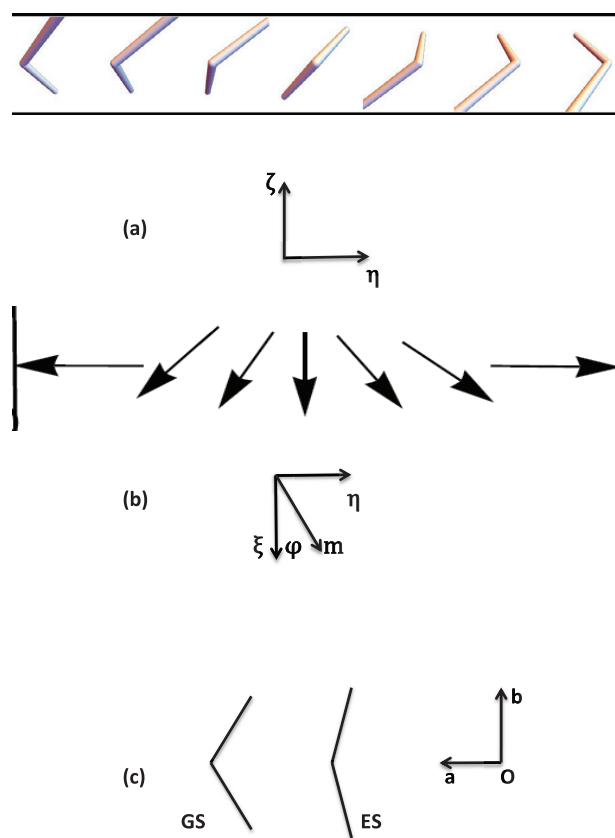


Figure 1. The splay distortion of the polar order \mathbf{m} across a stripe in the B_7 liquid crystalline phase. (a) Side view of the stripe of width w , viewed from the ξ -axis of the $\xi\eta\zeta$ coordinate system fixed to the layer made of tilted molecules. In our model, as described in the caption (c) below, the ground state conformers forming the stripe have a tilt angle θ_G . (b) View from the layer normal (ζ axis). The distortion is described by the azimuthal angle $\varphi(\eta)$ made by the polar vector \mathbf{m} with the ξ -axis. The thick vertical lines at the two ends of the stripe represent walls, separated by the width w . According to the earlier model [17], the wall is made of a narrow defect across which the splay distortion with reversed sign separates neighbouring stripes. (c) Schematic diagram of the ground state conformer with a large bend angle, which packs with a polar order in the stripes. The excited state conformer is less bent and rotates freely. In our model, the walls shown in (b) are in the smectic C state of excited state conformers. In the BC molecule- fixed frame shown on the right, \mathbf{a} is along the arrow axis, \mathbf{b} along the bow axis and \mathbf{O} along the normal to the molecular plane.

spacing along the layer normal in the wall, to geometrically fit the tilted (in some cases, upright) BC molecules at the walls between neighbouring stripes. Such structures are indicated by adding a prime at the end of the above described symbols (e.g. SmCPU'_A). They are also known as $B_{1\text{revtilt}}$ LC phases in the literature. They have usually small stripe widths, and unlike the LC phases with layer continuity across the walls between stripes, they are often not switchable by an accessible electric field. A large number of BC compounds exhibit these variants of the stripe structures [12]. (Some authors stick to the symbol B_7 for the last mentioned ($B_{1\text{rev}}$) structure, and use the symbol B'_7 for the structures with layer continuity.) Some compounds with the strongly polar cyano (CN) or nitro (NO_2) groups attached to the central phenyl ring of the BC molecules

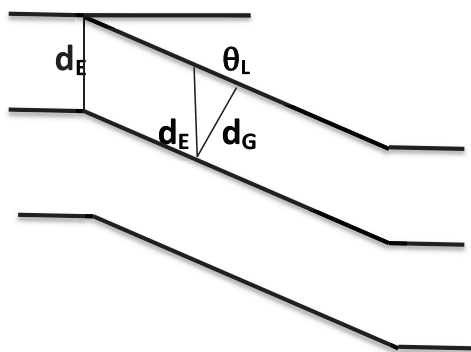


Figure 2. Schematic diagram showing the tilting of the layer with a spacing d_G made of ground state conformers, which is smaller than d_E , the layer spacing in the walls made of ES conformers with a smaller tilt angle θ_E . The layer tilt angle $\theta_L = \cos^{-1}(d_G/d_E)$. A stacking of the structure fills space [11].

have a stripe width with less than about 10 molecules [13], and probably these do not have a splay deformation of the \mathbf{P} -field. Our focus in this paper is on the stripe phases with splay distortion of the \mathbf{P} -field, and having layer continuity between the stripes (SmCPU structures). Hereafter, the symbol B_7 signifies only such structures.

As it is quite difficult to get monodomain samples of B_7 LCs, apart from the x-ray determination of lattice parameters, only a few physical studies have been reported. In a few compounds which exhibit the $SmC_5P_F^*$ phase at lower temperatures, the stripe width increases as the temperature is lowered towards the transition [11], and the transition temperature is enhanced by the application of DC electric field [11, 14]. When some compounds with poor chemical stability are maintained in the B_7 phase for a prolonged time, the stripe width increases with time [11]. Usually, because of the 2D lattice structure, B_7 LCs can only be drawn as fibers, but in some cases free standing films drawn across a hole have been obtained, changing the temperature from the lamellar phases in which they form. In such films, stripes with a width \sim micrometers form over a period of time [15, 16].

The strong first order transition from the isotropic phase to the B_7 phase with a relatively large polarization shows that the early phenomenological theories [4–7] that we referred to above are not suitable for this modulated LC. A detailed phenomenological model of the B_7 phase has been developed [17–19], including terms describing the smectic order, molecular tilt, elasticity of the nematic, smectic and polar orders. The proposed driving mechanism for splay of \mathbf{P} in the B_7 phase is a strong enough coupling between molecular tilt and $\text{div}\mathbf{P}$, which is assumed to be $\kappa(\nabla \cdot \mathbf{P})|\mathbf{n} \times \nabla \psi|^2$, \mathbf{n} being the nematic director and ψ the smectic order parameter. As the tilt angle can have spatial variations, this term will not reduce to a surface term. For a given set of other parameters of the model, the modulated structure is found to have a lower free energy compared to that of the uniform structure above a critical value of κ , which is lower when the tilt angle is larger. The stripes are separated by narrow walls in which \mathbf{P} has a splay distortion whose sign is opposite to that in the stripes. The temperature and electric field dependences of the structural parameters, and the transition between the B_7 and B_2 phases

have not been investigated using the model. The splay angle across the stripe has to be smaller than $\sim 20^\circ$ for the stripe width to be in the tens of nm range as found in experiments [19]. More importantly, it has been shown that when the tilt angle is zero, as in $SmAP_F$ phase, the coupling term is zero, and the stripe phase cannot be stabilized [18].

The Boulder group discovered in 2012 [20] a compound which exhibited a transition between the $SmAP_F$ and $SmAP_{Fmod}$ phases, in both of which the tilt angle is zero (smectic A phases). The $SmAP_{Fmod}$ phase is just the *non-tilted* variety of the B_7 phase, contradicting the prediction of the model mentioned above. Also, as aligned samples could be obtained, detailed optical studies were made on the $SmAP_{Fmod}$ LC.

Even the nematic phase exhibited by BC molecules with a relatively small bending angle ($<40^\circ$) is found to have unusual properties, even though it has the same uniaxial apolar symmetry as in the case of nematics made of unbent rod like molecules. The medium consists of *clusters* of ~ 100 molecules which usually have a local smectic C type of layered short range order [8]. We argued in an earlier study [21] that practically all BC molecules have the ester (COO) linkage groups between phenyl rings, thus making the bent aromatic core of the molecule somewhat flexible. Using the Spartan 4 (molecular mechanics) package, we found that the ester group can easily flip about the single bond linking the CO-to say a phenyl ring, giving rise to conformational variety of the core. While most of the molecules have the ground state (GS) conformations, about 10 to 20 % of the molecules occur in *excited state (ES) less bent* conformations (Figure 1). In nematics the BC molecules freely rotate about the long axes, and the ES conformers with a lower moment of inertia can approach each other more closely than the GS conformers. The increased attractive interaction of the ES conformers leads to the formation of the layered clusters, which have been directly studied using several experimental techniques [21]. We have recently argued [22]¹ that the conformational flexibility of the cores of BC molecules is also the *physical origin* of the $SmAP_{Fmod}$ phase. The lean ES conformers can rotate freely about their long axes, unlike the nonrotating strongly bent GS conformers which pack with a polar order. The ES conformers can gain rotational entropy by congregating, thus forming an interface between nonpolar SmA domains of ES conformers and the polarized domains of GS conformers. The \mathbf{P} vector of the latter points orthogonally to the interface which costs positive self-energy, that can be reduced by the allowed $\text{div}\mathbf{P}$ distortion. Based on this physical picture, we have developed a phenomenological theory of the $SmAP_F$ to $SmAP_{Fmod}$ transition, which qualitatively accounts for all the experimental observations [22]¹. Whereas up to now only one example of the transition between uniform and stripe phases with non-tilted BC molecules has been found, since a careful molecular engineering is needed to prevent the tilting, as we mentioned earlier, a large number of BC compounds exhibit the striped B_7 phase. In this paper we will argue that the physical origin

¹ There is an inadvertent error in eq.1 of this paper: $(\mathbf{m} \times \text{curl } \mathbf{m})^2$ should be replaced by $(\text{curl } \mathbf{m})^2$.

of the B₇ phase is also the conformational variety of the BC molecules, rather than a strong coupling between tilt and $\text{div}\mathbf{P}$ assumed in the earlier model [17–19].

2. Theoretical model

The model is essentially the same as the one proposed for the SmAP_F to SmAP_{Fmod} transition [22]¹. However, the molecular tilt in the layers can give rise to several different structures, some basic features of which were already described in [11, 12]. In most of the cases, the compounds exhibit a direct first order transition from the isotropic to the B₇ phase, the latter exhibiting complex optical textures as it separates from the isotropic phase. The tilt angle is usually quite large, ~30° to 40°, and hardly varies with temperature, as is often the case even with the B₂ phases with a simple layer structure [8]. The B₇ mesogens typically have long hydrocarbon chains at both ends of the molecules, and the resulting strong biphelicity ensures that the smectic layering order is also saturated [23]. On the other hand, as many compounds exhibit the B₇ to SmCP_F transition as the temperature is lowered, the polar order itself can be expected to vary with temperature. These considerations allow us to make the following assumptions to simplify the model.

- (a) The compound undergoes a (hypothetical) second order transition at a temperature T^* from nonpolar smectic C phase in which the tilted (GS and ES) molecules rotate freely, to one in which the rotation of GS conformers is no longer free and a polar order \mathbf{m} oriented orthogonal to the tilt plane, sets in. The average molecular dipole moment of a BC mesogen can be assumed to be along the arrow axis \mathbf{a} (figure 1), and shifted from the axis of lowest moment of inertia of the molecule. Even when the molecule freely rotates about that axis in the layer, the average dipolar interaction between neighbouring molecules in a layer is repulsive, which can be reduced by the molecular tilt to form the smectic C phase [24, 25]. In the polarized layer, the molecules which are packed along the \mathbf{a} axis have an attractive dipolar interaction, whereas neighbours along the orthogonal to the molecular plane (\mathbf{O} -axis, figure 1) have a repulsive energy, which is reduced by the large tilting of the molecules in the plane perpendicular to \mathbf{m} [26]. The magnitude of the order parameter $m = \langle \cos\theta \rangle$, θ being the angle made by a molecular dipole with \mathbf{m} . In view of the assumed temperature independent tilt and layering order parameters, the angular fluctuation θ is mainly confined to the \mathbf{aO} plane of the molecule.
- (b) As discussed earlier, the minority (~10%–20%) ES conformers are lean enough to rotate freely about their long (bow) axes, thus not making any contribution to the polar order. They can gain rotational entropy by congregating together in pockets in which local fluctuations with several ES conformers have formed. The two types of domains can be expected to be in dynamic equilibrium, any change in the conformation of a given molecule pushing it away across the interface to lower its free energy. As we have discussed in a recent paper, even the *clusters* of ES molecules in BC nematic liquid crystals are *long lived*, and form a quasiperiodic structure on the cell walls resulting in a self-decoration of the director field [27]. The layered smectic phases can be expected to support segregation of the two types of domains even more effectively. In general, the ES conformers also can be assumed to have a tilt order, i.e. to be in the smectic C phase, the tilt angle being smaller than that of the polarized domain of GS conformers.
- (c) The different symmetries of the domains with GS and ES conformers means that they are separated by an interface which costs a surface energy Γ per unit area. The interface is by definition *polar*: for example the dielectric constant jumps to a lower value as it is crossed from the domain with polar order to that without the polar order. As such, the polar \mathbf{m} vector *prefers* to align normal to the interface, Γ having the lowest value for that alignment. A homeotropically aligned sample of SmAP_{Fmod} LC exhibits a very low biaxiality δn for a light beam travelling along the layer normal [20], which has been attributed to splay distortion of -90° to $+90^\circ$ across the stripe [20]. In an aged free standing film of a B₇ sample with tilted molecules, the stripe width was found to increase to μm dimensions, and the \mathbf{c} -vector profile across a stripe could be traced optically [16]. The \mathbf{c} -vector was found to be anchored *parallel* to the walls of the stripe, with a bend distortion in between. As \mathbf{m} is orthogonal to \mathbf{c} , this again shows that \mathbf{m} is anchored normal to the walls. Both these experimental results on the anchoring condition at the boundary are consistent with the argument based on the vectorial nature of \mathbf{m} and the normal to the interface given above.
- (d) The resulting interfacial interruption of the polarization $\mathbf{P} = p\mathbf{m}$, where p is the magnitude of \mathbf{P} for perfect polar order, costs a positive self-energy which can be reduced by the allowed $\text{div}\mathbf{m}$ distortion of the polar field in the GS domain. It has been suggested that different cross-sections of the aromatic and aliphatic parts of the BC molecules may give rise to the $\text{div}\mathbf{m}$ distortion [17]. As we shall see below, this distortion leads to the formation of stripes of the B₇ phase.
- (e) The different tilt angles of the ES and GS domains now introduces a new physical feature, which is not significant in smectic A type LCs. The layer spacing $d_i = l \cos\theta_i$, where l is the molecular length, and θ_i the tilt angle in the given type of domain i . The larger θ_i in the polar domains of GS conformers leads to a correspondingly smaller layer spacing compared to that in the ES domains. It was argued in [11] that the walls between stripes would have a defect region with a reduced tilt, and the resulting mismatch in the layer spacings between the walls and stripes would lead to a tilting of the layers in the stripes to fill space, and the layer undulations as observed in the experiments. Our two-state model provides a concrete physical basis for this argument (figure 2). The layer undulations and the 2D periodicity of the stripe structure of the B₇ phase

in turn produces the complex textures exhibited by the B₇ samples [11].

- (f) As the GS layers with a smaller layer spacing tilt with respect to the walls with thicker layers made of ES conformers to fill space efficiently (figure 2), \mathbf{m} is no longer orthogonal to the interface, but tilted away. This increases the interfacial energy, and as we shall see later, there are a few different possible alignments between the two parts of the structure, and in any given material, the one with the lowest energy is chosen.
- (g) The above considerations lead to a physical picture in which the tilted layers with polar order \mathbf{m} span between two walls made of the nonpolar ES conformers. The \mathbf{m} field will have a splay-bend distortion defined by the azimuthal angle φ . The distortion can be expected to be symmetric about the center of the layers in each stripe (figure 1), φ varying from $-\pi/2$ at one end of the stripe to $+\pi/2$ at the other end.

Using the above physical arguments, we can write the free energy density of the splay-bend distorted \mathbf{m} -field in the layers of a stripe. In view of the assumed temperature independence of the tilt angle, the expression is essentially the same as that proposed for the non-tilted case [22]¹. With reference to the cartesian coordinate system $\xi\eta\zeta$ fixed to the layer (figure 1), the free energy density is given by

$$F(\eta) = \frac{a}{2}(T - T^*)m^2 + \frac{b}{4}m^4 - \alpha(m_s^2 - m^2)\text{div}\mathbf{m} + \frac{\beta}{2}((\text{div}\mathbf{m})^2 + (\text{curl}\mathbf{m})^2) + \frac{(pm_\eta)^2}{2\varepsilon_0\varepsilon} \quad (1)$$

where m , the magnitude of \mathbf{m} , is assumed to have no spatial dependence. The first two terms describe the standard Landau theory of the hypothetical second order paraelectric SmC to ferroelectric transition at T^* mentioned in point (a) above. Most of the BC compounds exhibit a direct first order transition between the isotropic phase and the B₇ phase with polarized layers. Consequently the tilt angle is quite large and essentially temperature independent in the B₇ phase. T^* can be expected to lie well above this transition temperature. The interruption of the \mathbf{P} field by the interface between the GS and ES domains costs polarization self-energy (see point (d) above), given by the last term in equation (1), pm_η being the projected value of \mathbf{P} along the η -axis, ε_0 the vacuum dielectric constant and ε the dielectric constant of the medium without the contribution from polarization. The allowed splay distortion *lowers* this energy, as described in point (d) above, and for notational convenience we chose the relevant coefficient to be $-\alpha m_s^2$, favouring a positive sign of $\text{div}\mathbf{m}$. As we have discussed in [22]¹, the $\text{div}\mathbf{P}$ distortion generates polarization charge densities whose mutual interaction is necessarily *repulsive*. This contributes to the *positive* coefficient α of the $m^2 \text{div}\mathbf{m}$ term allowed by the polar symmetry of the medium, restricting the distortion. The latter term was introduced in [4–7], with a *spatially varying* \mathbf{m} as the driving mechanism for a possible stripe phase close to T^* . The temperature regime

in which the B₇ phase is stable is obviously very different. Further, as m increases, the BC molecules are more tightly packed, and the distortion becomes more difficult. To avoid the possibility of the $\text{div}\mathbf{m}$ term changing sign for $m > m_s$, we assume $m_s = 1$. Lastly, we use the one elastic constant ($=\beta$) approximation for both splay and bend distortions of the \mathbf{m} -field. It is convenient to describe the orientation of \mathbf{m} across the stripe by the azimuthal angle $\varphi(\eta)$ that \mathbf{m} makes with the ξ -axis (figure 1). As shown in [22]¹, using φ in equation (1), the Euler–Lagrange equation with respect to φ gives the following relation for the stripe width w :

$$w = 2\lambda \int_0^{\pi/2} \frac{d\varphi}{\sqrt{C_0 + \sin^2\varphi}} \quad (2)$$

where C_0 is the integration constant, and $\lambda = (\beta\varepsilon_0\varepsilon)^{0.5}/p$ is the length over which the \mathbf{m} -distortion relaxes the positive self-energy due to polarization. We have assumed a *strong anchoring* of \mathbf{m} at the interface, and the α -term which depends linearly on $\text{div}\mathbf{m}$ does not figure either in the φ -profile or in the stripe width w . By the Gauss' theorem, this term is just a surface term as seen below, and does contribute to the free energy, as the magnitude m depends on α . The free energy density averaged over the stripe width w takes the form

$$\bar{F} = \frac{a}{2}(T - T^*)m^2 + \frac{b}{4}m^4 - \frac{2}{w}\alpha(m_s^2 - m^2)m + \frac{2\gamma m^2}{w} + \frac{\beta m^2}{\lambda} \left(\frac{C_0}{2\lambda} + \frac{2}{w} \int_0^{\pi/2} \frac{\sin^2\varphi d\varphi}{\sqrt{C_0 + \sin^2\varphi}} \right) \quad (3)$$

where the interfacial energy has been taken into account using the mean field result that $\Gamma = \Upsilon m^2$. A comparison between the α and Υ terms in the above equation shows clearly that the former effectively generates a *negative* interfacial energy, as expected. At a given relative temperature ($T^* - T$) the averaged free energy can be minimized with respect to both the stripe width w by varying C_0 , and the order parameter m . The minimized free energy can be compared with that of the uniform phase, in which only the first two terms of equation (3) are relevant. Using a suitable set of the five parameters viz., a, b, α, β and Υ , we have shown [22]¹ that the above model predicts a weak first order transition from the uniform SmAP_F phase to the stripe SmAP_{Fmod} phase with a small jump in m . The stripe width w which is ~ 10 s of nm, decreases as the temperature is increased in the SmAP_{Fmod} phase, as seen in the experiment [20]. We have also explored the effect of an external electric field on the transition temperature, the threshold field for polarization reversal etc, which are in broad agreement with experimental results. It is clear from the above arguments that the tilt angle does not play an essential role in stabilizing the stripe phase. As such, the above model describes the splay distortion of the \mathbf{m} -field in B₇ LC as well. The tilt however plays a role in generating the detailed 2D structures, and also influences the interfacial energy due the layer tilting. The molecular tilting can also be expected to enhance the elastic coefficient β as the distortion in the \mathbf{m} -field

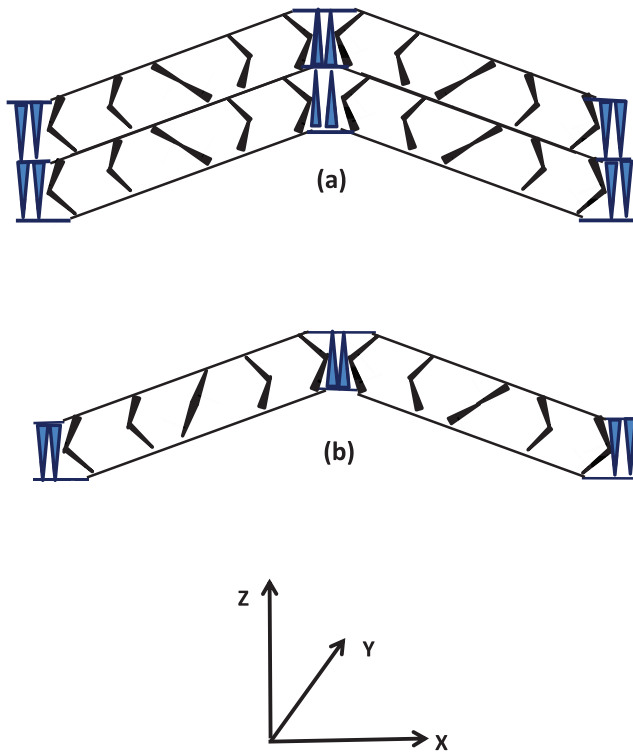


Figure 3. Schematic diagrams of possible structures when the ES conformers and layers made of GS conformers tilt in orthogonal planes, and neighbouring layers made of GS molecules tilt with opposite slopes. In both of them, the ES molecules in the central wall and the GS conformers in contact with them tilt with the lower half oriented towards the viewer, as indicated by a thicker projection on the page. In (a), the stacking of two layers is illustrated. In (a) neighbouring stripes have ferroelectric order, with the average \mathbf{m} pointing into the page. The structure (b) has anti-ferroelectric order. The optical anisotropy measured in the XYZ system shown at the bottom is higher in the anti-ferroelectric structure (b) than in the ferrostructure (a). In both structures the neighbouring layers have *opposite* chiral senses, and belong to the $\text{SmCPU}_A[\text{A}]$ class in the notation of [12]. Both ES and GS conformers are in liquid states within their respective layers, which can be expected to join smoothly at the boundaries. This probably leads to a splaying of the ES conformer orientation in the walls. The associated curvature elastic energy cost is rather low as the wall has a small width.

necessarily leads to a distortion of the \mathbf{c} -field, \mathbf{c} being the projection of the nematic director \mathbf{n} on the layer ($\xi\eta$ -) plane, and lies perpendicular to \mathbf{m} [3].

The approach taken in the earlier model [17–19] of the B_7 LC is to assume that $\text{div}\mathbf{P}$ which by itself would be just a surface term, would contribute to the free energy of the medium if it has a strong coupling with the molecular tilt in the layers of the B_7 LC, the tilt angle itself varying in space. While this description is valid if the BC molecules have an ideal, fixed shape, in reality the aromatic cores of the molecules have flexibility, and can take a variety of conformations. In nematics made of BC molecules, the leaner (ES) and fatter (GS) conformers can segregate to generate a heterogeneous structure in the medium which is visualized experimentally. By extending this argument to layered systems, we have shown that the polar anchoring of \mathbf{P} at the interface between the two types of domains leads to the allowed $\text{div}\mathbf{P}$ distortion so that the effective interfacial tension becomes negative. The stripe structure

is the final consequence. It is clear that the tilting of the molecules in the layers does not play any essential role in this mechanism, and LCs with upright molecules can also exhibit the stripe phase [20, 22]¹.

3. Some possible structures of the B_7 liquid crystal

As noted in point (e) above, the tilting of molecules does have an effect on the detailed geometrical structure of B_7 LCs, as the layers with the distorted \mathbf{m} field tilt to fill space. In view of our model of the wall with ES conformers with a relatively smaller tilt angle θ_E , we can expect in general to have two types of geometrical structures:

- (i) The ES conformers and the layers made of GS conformers tilt in *orthogonal* planes

We consider a wall with the ES conformers with the bottom half of their rotating molecules tilted with respect to the Z-axis at an angle θ_E out of the page and towards the viewer (figure 3). The layer spacing in the wall region $d_E = l_E \cos\theta_E$, l_E being the length of an ES conformer. The layer spacing of the polarized layer with GS conformers is $d_G = l_G \cos\theta_G < d_E$. Let the GS layer orientation, projecting out of the ES layer on the left side as in figure 3, be tilted downwards in the XZ plane. For filling space, the GS layer normal has to tilt by an angle θ_L from the Z-axis such that $\cos\theta_L = d_G/d_E$ (figure 2). Further, the molecule facing the wall, also prefers to tilt in the GS layer such that its bottom arm points towards the reader so that the dispersion interaction between the two types of molecules across interface is enhanced, lowering the relevant tension Γ . The \mathbf{m} vector of the GS molecule at the interface makes an angle θ_L with its normal, with an interfacial tension which can be expected to be larger than the value corresponding to $\theta_L = 0$. If the \mathbf{m} -field distortion in the GS layer is such that the central molecule points away from the viewer, the molecule tilts away from the Z-axis, and at the other end of the stripe the top half of the molecule points towards the viewer, forcing the wall at that end to have similarly tilted molecules (figure 3). The GS layer at the other side of the central wall can tilt in two possible directions in the XZ plane as well [12].

(iA) The slopes of the two layers have opposite signs (Fig 3). Again there are two possibilities: (a) the \mathbf{m} -profile is such that the average $\langle\mathbf{m}\rangle$ of the two stripes point in the same direction, i.e. the medium is ferroelectric (figure 3(a)). The chiral signs are however opposite, and the structure is $\text{SmCPU}_A[\text{A}]$ in the notation of [12]. The neighbouring GS layers can also have \mathbf{m} -profiles which are anti-ferroelectric (figure 3(b)). If the motif of the pair of layers forms the lattice, it will be rectangular. It is clear that the two structures have very different optical anisotropies, and the ferroelectric structure will be SHG active. The energy differences between the two structures cannot be large, and some combinations of both structures which will have larger lattice spacings along the X-axis are also possible [11].

(iS) The neighbouring GS layers tilt with the same sign of the slope (figure 4). The two can have ferroelectric (figure 4(a)) or anti-ferroelectric (figures 4(b) and (c)) order, with the

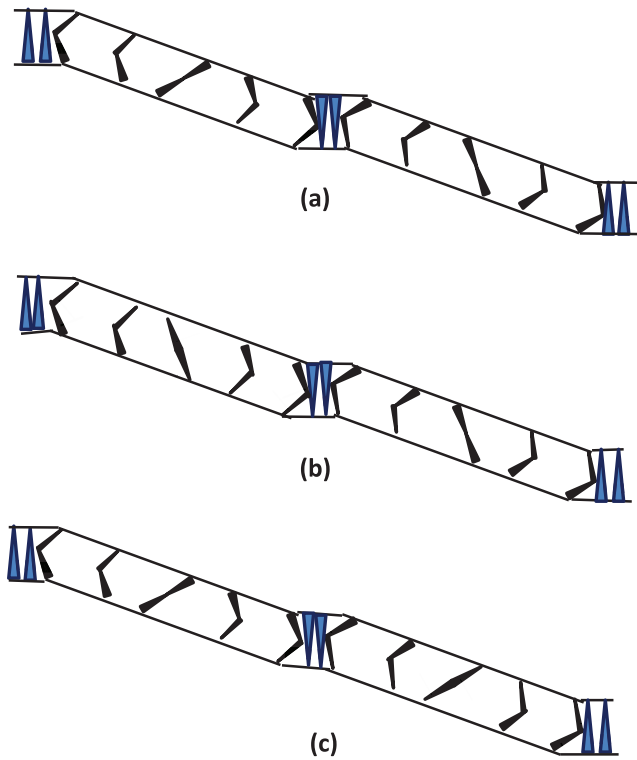


Figure 4. Schematic diagrams of possible structures when ES conformers and layers made of GS conformers tilt in orthogonal planes as in figure 3, but the neighbouring layers with GS conformers tilt in the same direction. We have illustrated the structures with the upper halves of ES molecules of the central wall tilted towards the viewer, indicated by a thicker projection on the page. Only the structure (a) is ferroelectric (with average \mathbf{m} pointed into the page), (b) and (c) being anti-ferroelectric, and all are racemic. They belong to the class $\text{SmCPU}_S[\text{A}]$ in the notation of [12]. As mentioned in the caption of figure 3, the ES conformers can splay out, for a smooth continuity between the two types of layers.

chiral signs being opposite in all cases. These structures give rise to oblique lattices ($\text{SmCPU}_S[\text{A}]$).

- (ii) *Tilt planes* of the ES conformers and the layers made of GS conformers are *parallel*

The main advantage of this geometrical structure is that the \mathbf{m} vector makes a relatively small angle $|\theta_L - \theta_E|$ from the normal at the interface (figure 5), which can be expected to have a low interfacial tension. Only oblique lattices in which all GS layers have the same slope can exploit this feature. As shown in figure 5, there are four possible structures, two being ferroelectric (homochiral or racemic neighbouring GS layers) and two anti-ferroelectric (again with two possible chiral senses). Some B_7 liquid crystals are known to exhibit *chiral domains* [11]. Further, the electron density maps of some compounds which exhibit oblique lattices appear to show *tilted walls* [19, 28]. Both of these features can be understood from the structures shown in figure 5.

Interestingly, it is possible to stack *pairs* of SmC_aP_F layers, with ferroelectrically oriented, but anticlinically tilted layers

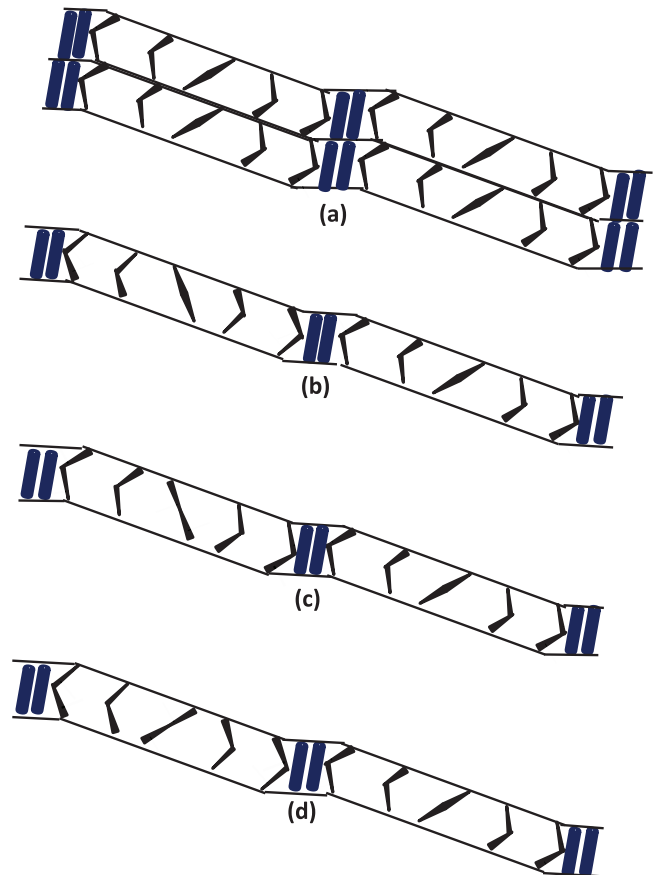


Figure 5. Schematic diagram of possible structures when ES conformers and the layers of GS conformers tilt in parallel planes. Neighbouring layers with GS conformers preferentially tilt in the same direction as the ES molecules to lower the interfacial tension. Further, as illustrated in (a), the wall itself tilts across the stacked layers, unlike in the structures of figures 3 and 4, in which it is vertical. Structure (a) is ferroelectric (with the average \mathbf{m} pointed towards the reader) with homochiral adjacent layers ($\text{SmCP}_F\text{U}_S[\text{S}]$). Structure (b) is ferroelectric (with \mathbf{m} pointed towards the reader) and racemic $\text{SmCP}_F\text{U}_S[\text{A}]$. Structure (c) is anti-ferroelectric (AF) and homochiral ($\text{SmCP}_A\text{U}_S[\text{S}]$), while (d) is AF and racemic ($\text{SmCP}_A\text{U}_S[\text{A}]$).

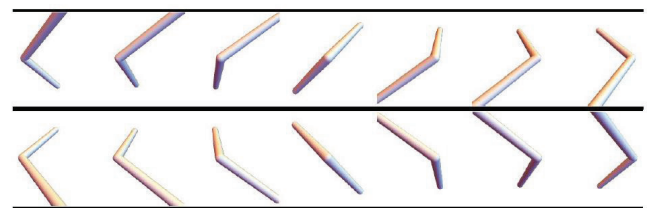


Figure 6. It is possible to have polarization splay stripes even when stacked layers have SmC_aP_F mutual orientation of the BC molecules, in which neighbouring layers have an anticlinic tilt, but ferroelectric orientation of the molecules, as shown in the figure. Such a stacking is racemic, and the SmC_aP_F mutual alignment is maintained in all parts of the stripe. The stripes with such pairs of layers can adopt structures like those in figures 3 and 4, if the ES molecules also have anticlinic tilts in successive layers. If the stripes adopt structures as shown in figure 5, the ES conformers have synclinal tilts in successive layers.

within a stripe (figure 6). The structure is clearly racemic. If the geometrical arrangements of the stacked pairs correspond to those shown in figures 3 or 4, the ES conformers in the walls also should have an anticlinic tilt to lower the energy. On the other hand, if the structures correspond to those shown in figure 5, the ES conformers can have synclinic tilt in the walls. Stripe structures with stacked SmC_aP_F pairs have been identified experimentally in some B_7 LCs by the low value of birefringence, and the response of optical textures to electric fields [29]. As was noted already in [11], the SmC_aP_F pairs cannot form stripes if the walls are made of defects with reversed $\text{div}\mathbf{P}$ distortion as the elastic cost is prohibitive. Thus, the observation of the stripe phase with SmC_aP_F pairs cannot be understood by the earlier model of B_7 [17–19].

Finally, if the GS conformers have a small tilt angle ($\theta_G \leq 20^\circ$, say) the ES conformers can be upright ($\theta_E = 0$) and neighbouring GS layers can have all possible combinations, with the same or opposite slopes, homochiral or racemic, and ferro- or anti-ferroelectric structures.

The actual structure that a given compound adopts depends on detailed molecular features, like the flexibility of the core, the location and orientation of dipolar groups, etc. It seems that a fairly large fraction of the B_7 LCs formed by BC compounds exhibit oblique lattices [12, 28, 30–32], as the number of possible ways of generating such structures is larger.

4. Results and discussion

Most of the compounds exhibiting the B_7 LC have a relatively large ($\sim 40^\circ$) temperature independent tilt angle, and equations (1)–(3) developed above are adequate to describe the medium. The main difference compared to the nontilted version is an enhanced interfacial tension caused by the tilting of layers. We illustrate the results using the following parameter set in MKS units: $a = 10^4 \text{ J K m}^{-3}$, $b = 14 \cdot 10^5 \text{ J m}^{-3}$, $\alpha = 5.5 \cdot 10^{-4} \text{ J m}^{-2}$, $\beta = 2.5 \cdot 10^{-12} \text{ J m}^{-1}$, $\Upsilon = 2 \cdot 10^{-5} \text{ J m}^{-2}$, $p = 3.5 \cdot 10^{-3} \text{ C m}^{-2}$, and $\varepsilon\varepsilon_0 = 40 \cdot 10^{-11}$. These parameters of the phenomenological model correspond to $aT^* \sim b \sim k_B T^*/\text{molecular volume}$, β the curvature elastic constant $\sim k_B T/\text{molecular dimension}$, p leads to a typical polarization \mathbf{P} measured in B_7 liquid crystals [11], Υ is a typical liquid crystal-isotropic interfacial tension [33], and α can be expected to be an order of magnitude larger. The only difference between the above set compared to the parameters used in [22]¹ is the doubling of the interfacial tension. The free energy density is lower for the uniform (B_2) phase up to $T^* - T = 83.85 \text{ K}$, when m reaches a value of 0.7739. At that temperature, a thermodynamically very weak first order transition takes place to the B_7 phase, in which the order parameter $m = 0.7551$. The corresponding heat of transition is $\sim 5.8 \cdot 10^4 \text{ J m}^{-3}$. The main effect of the enhanced interfacial tension is an increase of $\sim 1.5 \text{ K}$ in the transition temperature, compared to that with a lower Υ [22]¹. Above the transition temperature, the stripe phase has a lower energy. The polarization of the stripe is $pm \langle \cos\varphi \rangle$, averaged over the stripe width. Even if neighbouring stripes have a ferroelectric orientation, the polarization (\mathbf{P}) in the stripe phase is

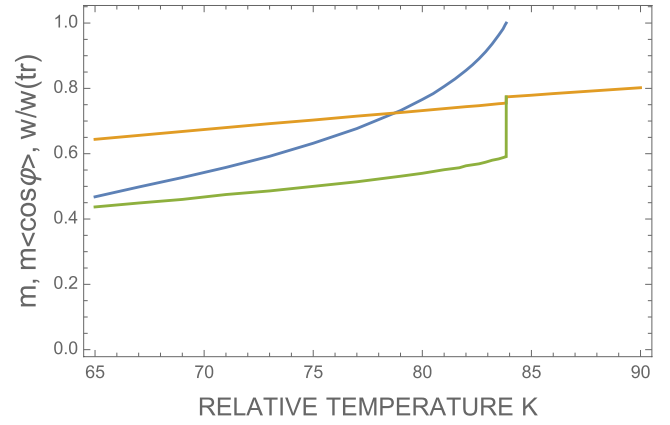


Figure 7. Variations of the order parameter m (middle curve near relative temperature $T^* - T = 83 \text{ K}$), reduced polarization $\langle m\cos\varphi \rangle$ (bottom curve) in the B_7 and B_2 phases across the transition temperature, using parameters appropriate for a fresh enclosed sample as described in the text. The top curve shows the reduced stripe width $w/w(\text{tr})$ in the B_7 LC with $w(\text{tr}) = 55.58 \text{ nm}$ at the transition temperature.

significantly smaller than in the uniform phase in view of the splay deformation of the \mathbf{m} field. The stripe width w which is 55.6 nm at the transition temperature decreases as the temperature is increased. The temperature variations of all these parameters are shown in Fig 7. They are very similar to those in the $\text{AmAP}_{\text{Fmod}}$ phase [22]¹. Both the magnitudes and the temperature dependences of these parameters are also similar to those measured in B_7 LC samples [11, 29]. Other observations on the B_7 LC, like DC electric field induced enhancement in the B_2 to B_7 transition temperature [14], polarization switching at a *threshold field* at a low enough frequency of an applied triangular electric field [11, 29], etc, are very similar to those found in the untilted $\text{SmAP}_{\text{Fmod}}$ LC [20], and we have shown that all these phenomena can be understood on the basis of our model [22]¹.

The tilting of the layers (figures 3–5) in the B_7 LC prevents monodomain samples to be prepared, and mainly x-ray and other structural studies have been conducted. Free standing films have been formed only in some rare cases, and apparently in these cases the layer tilting is easily suppressed [11, 16]. A very interesting observation in these cases is that over a long period of time (a few days), the stripe width increases to micrometer range, and becomes *visible* under a polarizing microscope. We can understand the reason for this evolution as follows. The B_7 LC typically occurs above $\sim 100^\circ \text{C}$ and the chemical compound slowly decomposes [11], the degradation products obviously preferring to drift to the less ordered walls between the stripes. More importantly, the open film which has ferroelectric polarization attracts ionic impurities from the surroundings, increasing its conductivity, and reducing the screening length. A naïve method of taking into account the better screening is to increase the *effective* dielectric constant ε of the LC. The degradation products collected in the walls will be chemically dissimilar from the BC molecules in the polarized stripes, and the interfacial tension across the wall can be expected to be enhanced. The increase in Υ

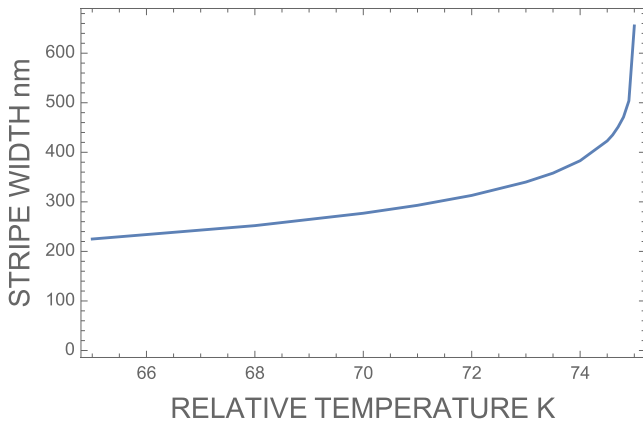


Figure 8. Temperature variation of the stripe width in the B_7 phase, with parameters appropriate for an aged and exposed sample as described in the text. The transition temperature has increased by $\sim 10^\circ$ K compared to the fresh sample (figure 7), and the enlarged stripe width becomes visible under a polarizing microscope.

increases the stripe width w to lower the average free energy density of the stripe. As w increases, the effective elastic constant for splay deformation also increases, as is known from earlier studies on the dependence of β on the deformation length in SmC^* LCs [34, 35]. In short, the parameters describing an aged, exposed B_7 sample will be quite different from those corresponding to a fresh enclosed one, such that the length λ , and hence the stripe width w (see equation (2)) are enhanced. Our calculations show that as the stripe width increases say with an increase in Υ , the uniform to stripe phase transition temperature also increases. In order to illustrate the influence of the parameters, we have used the following set: $\varepsilon\varepsilon_0 = 200 \cdot 10^{-11}$, $\alpha = 3.72 \cdot 10^{-4} \text{ J m}^{-2}$, $\Upsilon = 6 \cdot 10^{-5} \text{ J m}^{-2}$, $\beta = 10 \cdot 10^{-12} \text{ J m}^{-1}$, $p = 2.5 \cdot 10^{-3} \text{ C m}^{-2}$, the other parameters being the same as before. The altered parameters are within a factor of five of those assumed for the fresh sample. The transition temperature shifts to $T^* - T = 75 \text{ K}$, and further, at that temperature, the stripe width $w = 660 \text{ nm}$, which is much larger than the value (55.6 nm) found at the transition temperature using the parameter set used earlier, relevant for a fresh enclosed sample. The stripe width decreases rapidly as the temperature is increased (figure 8), as has been found in free standing films [16]. The structure of B_7 LC is quite delicate, and sensitively depends on the purity of the sample. In particular, ionic impurities attracted by the polarized stripes play a significant role in changing the structural parameters.

5. Conclusions

In conclusion, we have argued that a model that was recently proposed by us [22]¹ to describe the modulated ferroelectric phase exhibited by a BC compound with upright molecules in layers ($SmAP_{Fmod}$) and its transition to the uniform $SmAP_F$ ferroelectric phase [20] is applicable to the B_7 phase exhibited by a large number of BC compounds. The latter LC is made of modulated ferroelectric layers with *tilted* molecules, and occurs with either rectangular or oblique 2D lattice structures

[11, 12]. The prevailing theory is based on the assumption that a strong coupling between molecular tilt and splay distortion of the polarization field gives rise to the modulation, the splay stripes being separated by narrow defect regions with the opposite sign of splay distortion [17–19]. This model predicts that the experimentally observed stripe widths of tens of nanometers require that the splay angle across a stripe is *restricted* to $\leq 20^\circ$. It also implies that the observation of stripe widths $\sim 100 \text{ nm}$ to a few micrometers found in the free standing films of some B_7 samples [11, 16] cannot be predicted by the model. Further, the model is not applicable to the $SmAP_{Fmod}$ phase [20] mentioned above. It cannot also account for the stripe phase found in materials which have the SmC_aP_F stacking of layers.

Our model is based on our earlier proposal that the conformational variety of BC molecules leads to the heterogeneous structure [21] of the clustered nematic phase exhibited by several BC compounds [8]. A small fraction ($\sim 10\%$ – 20%) of the BC molecules are in a less bent excited state (ES), and interact better to form SmC type clusters in the nematic phase. We have earlier argued that in the case of ferroelectric LCs, the ES molecules can rotate relatively freely in the layers and aggregate to form domains and interfaces with the regions made of polarized layers of the ground state (GS) conformers with a relatively large bend angle [22]¹. The \mathbf{P} vector of the latter naturally prefers to align with polar anchoring perpendicular to the interface, which costs an electrostatic self-energy which is in turn reduced by the allowed splay distortion of \mathbf{P} , but with an additional cost mainly due to the coulomb interaction of the polarization charges associated with the distortion. If the favourable coefficient is large enough, the effective interfacial energy can become negative, leading to the formation of the modulated structure. As molecular tilt plays no role in this mechanism, it can describe both the $SmAP_{Fmod}$ and B_7 phases. Indeed the stripe width (\sim a few tens of nm), the thermodynamically weak transition to a lower temperature uniform ferroelectric phase, and the electric field induced enhancement of that transition temperature are experimentally found to be similar in both the tilted and nontilted versions [11, 20]. Our model provides a common description of both. In a few cases in which free standing films could be formed, the stripe width of B_7 LC was found to increase with time to the micrometer range [11, 16]. We have argued that the exposed polarized layers attract ions, reducing the screening length, which in turn increases the effective dielectric constant. Further, the chemical degradation products and the absorbed ions (of one sign) which are collected in the wall region also increase the interfacial tension. These changes in the physical parameters in turn increase the stripe width, though to enlarge it to tens of micrometers a more detailed analysis of ionic screening is needed. However, both the experimental observations and our analysis bring out the possibility that the B_7 liquid crystal may not be observed if the sample is not sufficiently pure. If the stripe width increases to tens of μm , the wall formation may depend on the *local* impurity content and the stripes may become irregular. Consequently, it is possible that in

some potential B₇-forming compounds, high impurity levels might have erased the usual characteristic features of the B₇ LC. One way of testing our model is to deliberately add ionic and other impurities to fresh samples exhibiting the B₇ phase, and look for both enhancements of the stripe width at a given temperature and the transition temperature from the B₇ to B₂ phases. Further, by doping rod-like molecules with roughly similar dimensions of the core and chain moieties in a BC compound exhibiting only the SmC_sP_F or SmC_aP_F phase, it may be even possible to *induce* the B₇ phase in the mixtures, as freely rotating rods can form walls. Our model also provides a natural basis for the argument that the lower tilt angle in the ‘defect regions’ between the splay distorted stripes, and the resulting mismatch in the layer spacing with that in the splayed stripes generates the layer undulated structures of the B₇ LC [11]. The proposed model does not have the deficiencies of the earlier one which were mentioned in the previous paragraph. Further, our model leads to several possible structures with rectangular and oblique lattices, the particular one chosen in a given compound depending on the detailed molecular structure. In short, the conformational variety of BC molecules is the root cause of the *heterogeneous* structures exhibited by the nematic, SmAP_{Fmod} and B₇ LCs made of such molecules.

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