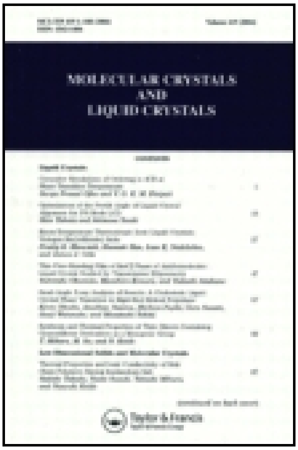

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Twisted Domains in Smectic B_2-Phase Under an External Electric Field

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A simplified model is used to approximate the energies of observed structures in smectic B_2- phase composed of bent-shaped molecules. Twisted, mixed (having alternating layers with twisted and uniform molecular structure) and anticlinic antiferroelectric structures coexist without an applied field having thus nearly the same energies. When an electric field is applied, mixed structure starts to be preferred. The first critical field compensates surface polar anchoring on e.g., upper sample surface and favorites partly unwound structure. The second critical field leads to transition to uniform synclinic ferroelectric structure. The behavior of the energies of B_2-phase structures under an electric field permits the estimation of model parameters, like e.g., anchoring energies.

Keywords: B_2-phase; bent-shaped molecules; field-induced structural transitions; twisted structures

1. INTRODUCTION

Textures observed in smectic phases composed of bent-shaped molecules are the consequence of the dipolar ordering of molecules [1–12].

Observations of twisted structures in B_2 (denoted also as Sm-CP) phase composed of molecules with bent-shaped cores are reported in Refs. [9–12]. Without an applied electric field, usually anticlinic antiferroelectric structure exists. However, when sample is cooled slowly, domains of twisted ferroelectric structure are observed together with domains of anticlinic antiferroelectric structure (SmC_AP_A) [12].

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In [12] the influence of an external electric field was documented. Twisted domains start to be unwound under an electric field. Inspired by observations [12], energies of twisted, partly unwound and uniform ferroelectric structures together with anticlinic antiferroelectric structure were investigated in the present contribution. In order to determine approximately the energy of anticlinic antiferroelectric structure of B_2 phase, we use the analogy with the method given in [13,14] for antiferroelectric smectic liquid crystals with elongated molecules. In [12] it was proposed how anticlinic antiferoelectric and synclinic ferroelectric structures can be mediated by a twist deformation.

In order to take simply in account the energy of twist deformation of B_2 phase we adopted the elasticity of biaxial nematics [15]. As for chiral term in the elastic free energy, the linear term in gradients of polarization, proposed in [16,17], is added. The linear term in polarization gradients transforms to surface term present in surface anchoring energy [18–20].

In this contribution a model of B_2 structures will be proposed based on the assumption deduced from experimental observations [12] where bulk SmC_AP_A structure is influenced by surface anchoring. This surface anchoring may lead to twisted deformation of basic SmC_AP_A structure. Model energies of possible resulting structures are studied under an external electric field. This will give us a quantitative estimation of model parameters like anchoring energies.

So this contribution is organized in the following way: After short review of experimental observations in part 2, the following model energies will be considered in part 3: interaction energy between neighbor smectic layers preferring energetically anticlinic antiferroelectric structure with respect to synclinic ferroelectric structure, elastic energy and surface anchoring energies. The twisted solution connecting synclinic ferroelectric and anticlinic antiferroelectric structures will be reviewed in part 4 together with the energies of twisted structure, partly untwisted and uniform structures under electric field. In part 5, the estimation of model parameters will be done using experimental values of critical electric fields and energies of different B_2 structures.

2. EXPERIMENTAL OBSERVATIONS

The material used in observations of B_2 phase is based on a central 1,3-phenylene unit with ester linkages and lateral methoxy groups near central benzene ring called 10WDVI in [11] and in materials having asymmetrical bent core with six phenyl rings, laterally substituted by a methoxy group denoted in [12] as **4d** (or 11BVID11). When materials are cooled very slowly from the isotropic phase, two types of domains may appear simultaneously. In one domain the optical extinction in crossed polarizers along smectic layer normal occurs. It is probably a structure composed of mesoscopic grains of SmC_AP_A of opposite handedness (chirality) [7,11]. In the second type of domain there is the rotation of polarized light plane. We can consider that this domain has a twisted structure of molecular organization within the smectic layers [7,9–12].

The observed twisted structure in [11] and [12] is the consequence of strong polar anchoring on surfaces. The polar anchoring leads to the synclinic ferroelectric order on surfaces. The preferred orientations of molecular polarizations on upper and lower surfaces are opposite as glass plates used for sample preparation are the same.

As both types of structures are observed in one sample, one can conclude that those structures have very similar energies.

Applying a dc electric field of about 0.5 V/mm (called the first critical threshold field E_1 [12] – there are some small changes of the field for different materials of [12]) the polarity of one surface is compensated and the SmC_AP_A order is restored on this surface [12]. This leads to partial unwinding of the structure as the polar anchoring on one surface is accented by a field. When field increase and reach the second critical field E_2, about $1 \div 10\,\mathrm{V/\mu m}$ depending on material, the structure is completely unwound and is uniform. However, the observations [12] show that the change of chirality during switching of structures is not probable. Thus the resulting uniform ferroelectric structure induced by field is expected to be synclinic.

Electric field also changes the domain composed of SmC_AP_A mesoscopic grains of opposite chirality. This domain transforms to uniform synclinic ferroelectric structure (SmC_SP_F) and this transformation is surely finished at the second critical field [12].

3. ENERGY CONSIDERATIONS IN B_2 MODEL STRUCTURES

In this section, different energy contributions of the total energy of the B_2 structures are outlined. After general description of molecular orientation in the part 3.1 the free energy having the anticlinic antiferroelectric B_2 phase as the basic state is proposed in the part 3.2. Then the surface anchoring energy is taken in account (part 3.3). As the other domains of anticlinic antiferroelectric structure treated in this contribution are twisted modifications of basic state, the simplified twist deformation will be introduced in the part 3.4. Interaction of B_2 structures with an external electric field is treated in part 3.5.

3.1. Molecular Orientation in Layers

The orientation of bent-shaped molecule in layers can be described by three Eulerian angles θ, ϕ and ψ [15]. Those angles are defined in the coordinate system with x and y axes parallel to the smectic layers and z-axis normal to the plane of smectic layers (Fig. 1). Angle θ describes the tilt of a long molecular axis which coincides with molecular unit director $\vec{n}$. The azimuthal angle ϕ characterizes the director rotation around z-axis. The direction of the molecular dipole moment of a bent-shaped molecule can be denoted as $\vec{p}$ perpendicular to $\vec{n}$, the angle ψ also describes the rotation of $\vec{p}$. The detailed geometrical representation of molecule is also given in Figure 1. Sample surfaces are supposed to be perpendicular to x-axis.

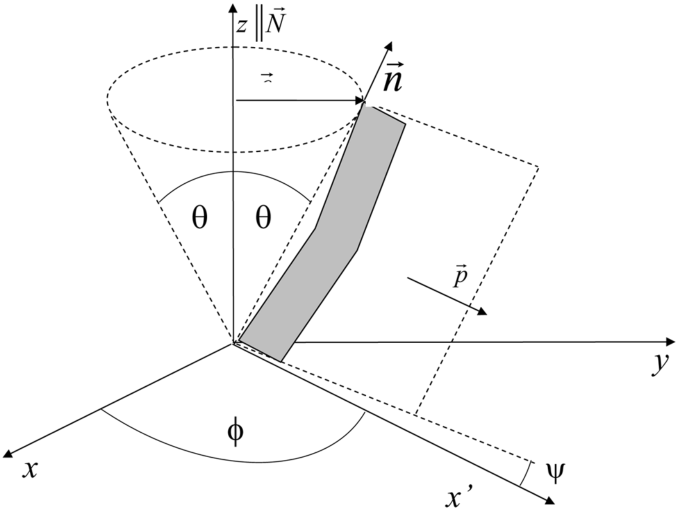

FIGURE 1 Bent-shaped molecule and the coordinate system. The plane of bent-shaped molecule (which is represented by a gray bent-shaped object) is defined by director $\vec{n}$ and vector $\vec{p}$ parallel to spontaneous polarization. The $\vec{c}$-director is the projection of $\vec{n}$ onto the layer plane the normal of which, $\vec{N}$, is parallel to z-axis. Eulerian angles are defined using the coordinate system (x, y, z): first, the plane of molecule is tilted from z-axis by an angle θ (The angle θ is the apex angle of a cone on the surface of which the director $\vec{n}$ of a bent-shaped molecule is situated). Then the tilted molecular plane is rotated around z-axis by an azimuthal angle ϕ from x-axis. This rotation transforms x-axis to x'-axis. Finally, the plane of molecule is rotated around the director $\vec{n}$ by an angle ψ from x'-axis.

When we suppose no layer deformations the molecular tilt angle is constant and the molecular orientation depends only on two variable angles ϕ and ψ. Then the molecular orientation is determined by vectors $\vec{n}$ and $\vec{p}$ expressed in [15] in the form:

$$\begin{aligned}\vec{p} &= (\cos\theta\cos\phi\cos\psi - \sin\phi\sin\psi, \cos\theta\sin\phi\cos\psi + \cos\phi\sin\psi,\\ &\qquad -\sin\theta\cos\psi), \qquad (1)\\ \vec{n} &= (\sin\theta\cos\phi, \sin\theta\sin\phi, \cos\theta).\end{aligned}$$

With the molecular tilt angle θ fixed the director $\vec{c} = (\cos\phi, \sin\phi, 0)$ which is the projection of the director $\vec{n}$ onto the plane (x, y) of smectic layers can be used to determine the molecular orientation in layers.

In order to describe geometrically an anticlinic antiferroelectric state of B$_2$ phase we use the bilayer continuous model proposed in [13,14] for antiferroelectric liquid crystals with elongated molecules. Let us suppose that the molecular orientation is characterized by angles ϕ_1 and ψ_1 in odd-numbered layers and ϕ_2 and ψ_2 in even-numbered layers. Then we can define vectors $\vec{c}_1 = (\cos\phi_1, \sin\phi_1, 0)$, $\vec{c}_2 = (\cos\phi_2, \sin\phi_2, 0)$ and $\vec{p}_1$ and $\vec{p}_2$ using expression (1) with angles ϕ_1, ψ_1 and ϕ_2, ψ_2, respectively. According to Ishibashi and Orihara [13] let us introduce vectors

$$\vec{c}_+ = (\vec{c}_1 + \vec{c}_2)/2 \quad \text{and} \quad \vec{c}_- = (\vec{c}_1 - \vec{c}_2)/2, \tag{2a}$$

and

$$\vec{p}_+ = (\vec{p}_1 + \vec{p}_2)/2 \quad \text{and} \quad \vec{p}_- = (\vec{p}_1 - \vec{p}_2)/2. \tag{2b}$$

The combination of the above noted vectors given by expressions (2) is used because it defines each of synclinic or anticlinic, ferroelectric or antiferroelectric molecular structures. Moreover we suppose smectic layers to be perpendicular to sample surfaces.

3.2. The Free Energy of the Non-Deformed Anticlinic Antiferroelectric B$_2$ Phase

In order to express the preference of liquid crystal to organize itself into anticlinic antiferroelectric structure we use non-gradient free energy terms given in [13]:

$$w_C = \frac{\alpha_-}{2}\vec{c}_-^{\,2} + \frac{\alpha_+}{2}\vec{c}_+^{\,2} + \frac{\beta_-}{4}\vec{c}_-^{\,4} + \frac{\beta_+}{4}\vec{c}_+^{\,4} + \frac{\gamma_{c1}}{2}\vec{c}_+^{\,2}\vec{c}_-^{\,2} + \frac{\gamma_{c2}}{2}(\vec{c}_-\vec{c}_+)^2, \tag{3}$$

with $\vec{c}_+^{\,2} = \frac{1}{2}(1 + \cos(\phi_1 - \phi_2))$ and $\vec{c}_-^{\,2} = \frac{1}{2}(1 - \cos(\phi_1 - \phi_2))$.

The expression (3) is written for parameters $\vec{c}_+$ and $\vec{c}_-$ only because we suppose that the vector of spontaneous polarizations $\vec{p}_1$ is perpendicular to director $\vec{c}_1$ and $\vec{p}_2$ is perpendicular to $\vec{c}_2$ and all those vectors lie in the layer plane. This assumption reflects the experimental observations that the non-orthogonal configuration of spontaneous polarization $\vec{p}_1$ with director $\vec{c}_1$ and $\vec{p}_2$ with $\vec{c}_2$ can be achieved by an external electric field above some critical value [8]. The expression (3) is usually used to investigate phase transitions in systems with elongated molecules as e.g., coefficients α_- and α_+ in energy w_C generally depend on temperature. In this contribution we suppose the fixed temperature already at the range of the existence of the antiferroelectic state. In order to obtain simplified one constant model potential derived from (3) for fixed temperature we simplify (3) to the form [23]:

$$w_C = \frac{\beta_-}{2}\left(-1 + \frac{\vec{c}_-^{\,2}}{2}\right)\vec{c}_-^{\,2} = \frac{\beta_-}{16}(-1 + \cos(\phi_1 - \phi_2))(3 + \cos(\phi_1 - \phi_2)), \quad (4)$$

with one parameter β_- which determines the minimum of (4) for $\phi_1 = \phi_2 + \pi$ (anticlinic antiferroelectric structure, $w_C = -\beta_-/4$). The synclinic ferroelectric structure ($\phi_1 = \phi_2$) is characterized by $w_C = 0$, i.e. in higher energy as compared with anticlinic antiferroelectric structure.

3.3. Surface Anchoring Energy

Another contribution to the total energy of B_2 structure is the anchoring energy. The anchoring of bent-shaped molecules to sample surfaces was already discussed in [18]. As smectic layers are perpendicular to sample surfaces the anchoring energy W_A can be expressed using [19]:

$$W_A = -\gamma_1(\vec{N}_S \cdot \vec{p}_+)^2 + \gamma_2(\vec{N}_S \cdot \vec{p}_+) - \gamma_3(\vec{N}_S \cdot \vec{p}_-)^2 + \gamma_5(\vec{N}_S \cdot \vec{c}_+)^2 + \gamma_6(\vec{N}_S \cdot \vec{c}_-)^2. \quad (5)$$

In this expression, the external normal to sample surface is denoted as $\vec{N}_S$ (parallel or antiparallel to the x-axis) and parameters γ_1, γ_2 and γ_3 are the anchoring constants–anchoring energies per unit surface.

The first term in (5) characterizes the non-polar anchoring and it attains minimal value for $\vec{p}_+$ parallel or antiparallel to $\vec{N}_S$. The second term expresses the polar anchoring of molecules. Note that this term corresponds to the bulk term $div\,\vec{p}_+$ which can exist in polar B_2-phase [16,17]. This term can be transformed to the surface term which adds to surface anchoring energy. Let us suppose that the preferable orientation for $\vec{p}_+$ aims to the inside of the sample. Then this term has the sign (+) in (5). The third term describes the antiferroelectric interaction of molecules with surfaces.

Parameters γ_1, γ_2, and γ_3 are expected to be positive and $\gamma_1 + \gamma_2 > \gamma_3$ [23]. Thus the antiferroelectric anchoring is unfavorable as compared with ferroelectric anchoring.

As shown in [18], other anchoring terms are possible which can prefer the plane of bent-shaped molecules to be either parallel or perpendicular to the surface. Such terms can be e.g., $\gamma_4(\vec{N}_S \cdot \vec{c}_+)$, $\gamma_5(\vec{N}_S \cdot \vec{c}_+)^2$ and $\gamma_6(\vec{N}_S \cdot \vec{c}_-)^2$. When supposing smectic layers to be perpendicular to sample surfaces and when the preferred anchoring of the $\vec{c}$-directors is either synclinic or anticlinic with $\vec{c}$-directors parallel to surfaces, then $\gamma_4 = 0$, and $\gamma_5 > 0$, $\gamma_6 > 0$.

3.4. Deformation Energy of B_2 Phase

We suppose that layers of B_2 phase are not deformed so the tilt angle θ is constant. Polarizations $\vec{p}_1$ and $\vec{p}_2$ lie in smectic planes and they are perpendicular to directors $\vec{c}_1$ and $\vec{c}_2$, respectively. Then the molecular orientation in bilayer is described by directors $\vec{c}_1$ and $\vec{c}_2$ as in the case of antiferroelectric phase composed of elongated molecules. The orientation of directors in smectic layer is again determined by azimuthal angles ϕ_1 and ϕ_2. The angles ϕ_1 and ϕ_2 will depend on one variable x oriented along the sample thickness. Then in one constant approximation the elastic deformation density can be written simply [15,21]:

$$f_d = \frac{K}{4}\left[\left(\frac{\partial \phi_1}{\partial x}\right)^2 + \left(\frac{\partial \phi_2}{\partial x}\right)^2\right], \tag{6}$$

with one elastic constant K. The expression (6) is the simplest deformation which can be also obtained from the deformation free energy density of non-chiral smectic with elongated molecules with independent molecular deformations in neighbor layers. The only chiral term used in our model is the term $div\,\vec{p}_+$ already introduced into the anchoring energy (5) as the term characterized by the parameter γ_2.

3.5. Interaction with an External Electric Field

The interaction energy of bent-shaped molecules in two neighbor layers with an external electric field oriented along sample thickness (x-axis) can be written as [20]:

$$\begin{aligned} w_E &= -P_s E(p_{1x} + p_{2x})/2 \\ &= -P_s E[\cos\theta(\cos\phi_1 \cos\psi_1 + \cos\phi_2 \cos\psi_2) \\ &\quad - (\sin\phi_1 \sin\psi_1 + \sin\phi_2 \sin\psi_2)]/2. \end{aligned} \tag{7}$$

In (7) the parameters E and P_s are the values of an electric field and spontaneous polarization, respectively. In the following $P_sE > 0$ will be supposed.

The expression (7) gives the interaction of the electric field with the molecular orientation. As we suppose that the field is not so strong to lead to independent rotation of polarization around the director $\vec{n}$, we put $\psi_1 = \psi_2 = \pi/2$. Then the energy density (7) transforms to $w_E = P_sE(\sin\phi_1 + \sin\phi_2)/2$. Thus the field has the tendency to orient molecules to $\phi_1 = \phi_2 = -\pi/2$ giving the energy density $-P_sE$. So the configuration $\phi_1 = \phi_2 = -\pi/2$ is minimal in an external field.

However, the real structure is given by equilibrium between the field influence and torques imposed by surface anchoring. Such an equilibrium equation is generally non-linear and can be solved usually only numerically. In this contribution, we will combine numerical calculations with simple analytical estimations.

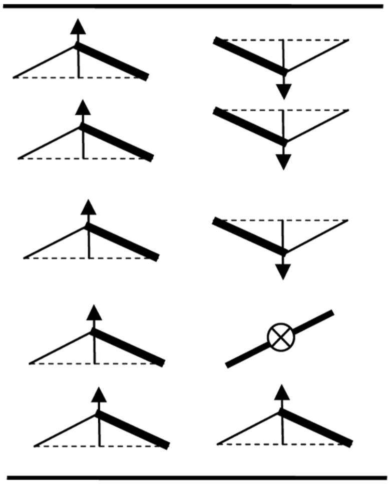

FIGURE 2 Mixed structure in B_2-phase. Smectic layers perpendicular to sample surfaces are observed from a side. Molecular orientation in neighboring layers is represented by triangles where thicker line corresponds to that arm of bent-shaped molecule inclined toward the observer. The molecular $\vec{n}$-director is situated on the surface of a cone as in Figure 1, dashed lines indicate positions of the director on the cone projected to the plane of the figure. Molecular spontaneous polarizations are depicted by arrows the length and orientations of which corresponds to the projection of polarization onto the plane of figure. One layer has twisted molecular structure while the neighbor one is uniform. Twisted deformation is concentrated near lower surface and uniform SmC_AP_A structure is realized in the sample bulk and near upper surface.

4. TWIST DEFORMATION OF B$_2$ STRUCTURE IN A FINITE SAMPLE UNDER ELECTRIC FIELD

In this part of the present contribution we will consider twisted structure of bent-shaped molecules organized in smectic layers perpendicular to sample surfaces. If sample surfaces are perpendicular to the x-axis, we obtain a thickness profile of twisted structure in the sample.

Twisted structures were already observed in [9–21]. In these references and also in [21] models of twisted structures were proposed. Anticlinic antiferroelectric structure in neighbor layers of the sample bulk is mediated by twist deformation independently in each layer with synclinic ferroelectric structures at surfaces [21]. In the following part an analytic approximate description of the twisted structure without a field will be summarized [23].

4.1. Twisted and Anticlinic Antiferroelectric Structures of B$_2$ Phase

Variation with respect to angles ϕ_1 and ϕ_2 [22] of the energy $\int_{-\frac{d}{2}}^{+\frac{d}{2}}(f_d + w_c)dx$, where d is the sample thickness, gives two non-linear equilibrium equations. Those equations can be solved approximately in an analytical form separately in lower and upper parts of the sample. In the lower part of the sample, $x \in (-d/2, 0)$ solutions can be summarized as:

$$\phi_1(x) = 2\,\mathrm{arc\ tan}\left(\frac{\mathrm{Q_d}}{-1+\mathrm{Q_d}}\right), \quad \text{and} \quad \phi_2(\mathrm{x}) = -\frac{\pi}{2}, \tag{8a}$$

with $Q_d = \frac{1}{2}\left(-\frac{x}{\zeta} - \frac{d}{2\zeta} + \frac{2\tan\frac{c_d}{2}}{-1+\tan\frac{c_d}{2}}\right)$.

In the upper part of the sample, $x \in (0, d/2)$ solutions are in the form:

$$\phi_1(x) = \frac{\pi}{2}, \quad \text{and} \quad \phi_2(x) = 2\,\mathrm{arc\,tan}\left(\frac{-\mathrm{Q_h}}{\mathrm{Q_h}-1}\right), \tag{8b}$$

with $Q_h = \frac{1}{2}\left(\frac{x}{\zeta} - \frac{d}{2\zeta} + \frac{2\tan\frac{c_h}{2}}{1+\tan\frac{c_h}{2}}\right)$.

The parameter $\zeta = \sqrt{4K/\beta\_}$ characterizes the length near surfaces where most of twist deformation is concentrated. Details concerning of the construction of solutions (8) of equilibrium equations will be given in [23].

Solution over the whole sample thickness is composed of solutions (8) in lower and upper half of the sample. While the first derivatives of solutions are continuous at the sample centre, solutions are continuous in limit, i.e., $\phi_1(x=0) \to \pi/2$ and $\phi_2(x=0) \to -\pi/2$ when $d \gg 2\zeta$. In this sense our solutions are approximate. Boundary conditions of solutions (8) are in the form: $\phi_1(-d/2) = c_d$, $\phi_2(-d/2) = -\pi/2$ on the lower surface and $\phi_1(d/2) = \pi/2$ and $\phi_2(d/2) = c_h$ on

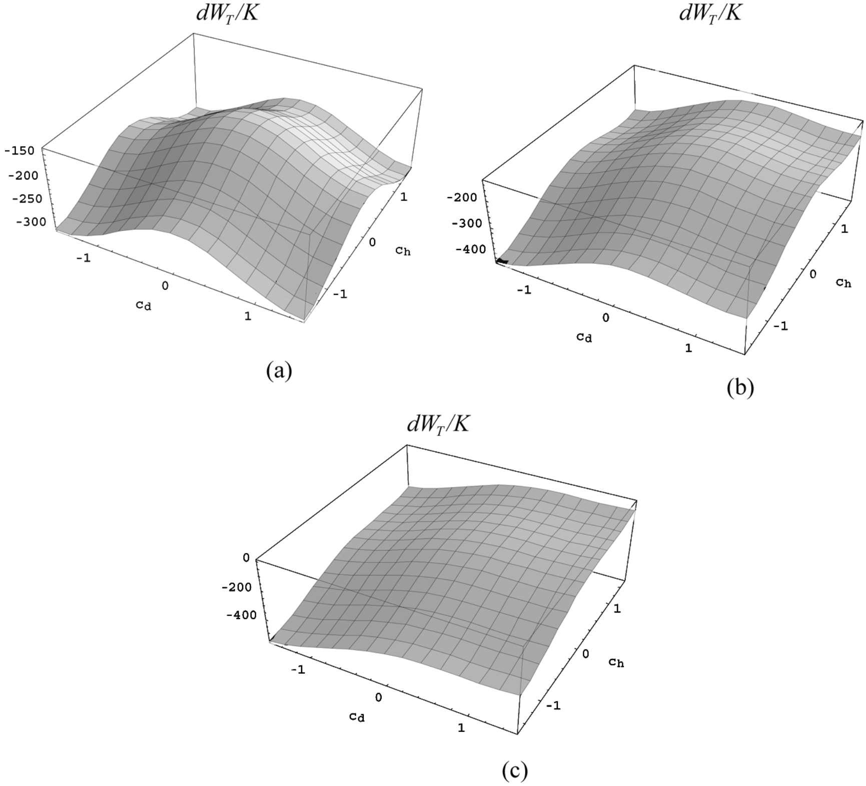

FIGURE 3 3D schematic plots of the energy dW_T/K as a function of surface $\vec{c}$-director orientations c_d and c_h on the lower and upper sample surfaces, respectively. The model parameters used to numerical calculations are enlisted in the part 5. (a) Energy for zero electric field. Energy minima are situated very closely to $c_d = \pm\pi/2$ and $c_h = \pm\pi/2$. Structures corresponding to minima are: uniform anticlinic antiferroelectric structure ($c_d = +\pi/2$, $c_h = -\pi/2$), twisted structure ($c_d = -\pi/2$, $c_h = +\pi/2$) and mixed structures ($c_d = -\pi/2$, $c_h = -\pi/2$ and $c_d = +\pi/2$, $c_h = +\pi/2$); (b) Energy surface for the electric field equal to the half of the critical field $E_1 \approx 0.5\,\mathrm{V}/\mu\mathrm{m}$. The energy surface is deformed, one of mixed structure having molecules anchored at lower surface in synclinic ferroelectric order with dipole moments parallel to field starts to be energetically favored; (c) Electric field reaches the critical value E_1. Energy surface has only one minimum for parameters $c_d = -\pi/2$, $c_h = -\pi/2$ corresponding to mixed structure schematically depicted in Figure 2.

the upper surface. The parameters c_d and c_h are principally situated at intervals $(-\pi/2, \pi/2)$ and their combination can give twisted, uniform anticlinic antiferroelectric, mixed (Fig. 3a) or intermediate solutions.

The elastic energy W_{el}^T (per unit surface of (*y,z*)-plane) stored in the B_2-structure can be evaluated as $W_{el}^T = \int_{-\frac{d}{2}}^{+\frac{d}{2}} (f_d + w_c)dx$. In order to work with non-dimensional expressions, the energy W_{el}^T will be multiplied by d/K. Using solutions (8) the expression $W_{el}^T d/K$ will take the form:

$$\begin{aligned}\frac{W_{el}^T d}{K} = 2t\Bigg(&\arctan\left(\frac{1-\tan\frac{\mathrm{c_d}}{2}}{1+\tan\frac{\mathrm{c_d}}{2}}\right) - \arctan\frac{1-\tan\frac{\mathrm{c_d}}{2}}{(1+\mathrm{t})-(\mathrm{t}-1)\tan\frac{\mathrm{c_d}}{2}}\\ &+ \frac{t\left(-t^2-1-\cos^2 c_d + \frac{t}{2}\cos c_d(-5+\sin c_d) + (t^2-1)\sin c_d\right)}{t^2+2+2t\cos c_d - t^2\sin c_d}\Bigg)\\ &- 2t\Bigg(\arctan\left(\frac{1+\tan\frac{\mathrm{c_h}}{2}}{-1+\tan\frac{\mathrm{c_h}}{2}}\right) + \arctan\frac{1+\tan\frac{\mathrm{c_h}}{2}}{(1+\mathrm{t})+(\mathrm{t}-1)\tan\frac{\mathrm{c_h}}{2}}\\ &+ \frac{t\left(t^2+1+\cos^2 c_h + \frac{t}{2}\cos c_h(5+\sin c_h) + (t^2-1)\sin c_h\right)}{t^2+2+2t\cos c_h + t^2\sin c_h}\Bigg). \qquad (9)\end{aligned}$$

The parameter t is defined as $t = d/2\zeta$.

The total energy of the structure will be obtained by adding to the above bulk energy (9) the surface anchoring energy (again as a non-dimensional expression) at upper and lower surfaces:

$$\begin{aligned}\frac{W_A d}{K} = &-\frac{g_1}{4}\left[(1-\sin c_d)^2 + (1+\sin c_h)^2\right] - \frac{g_2}{2}\left[2 - \sin c_d + \sin c_h\right]\\ &-\frac{g_3}{4}\left[(1+\sin c_d)^2 + (1-\sin c_h)^2\right] + \frac{(g_5+g_6)}{4}\left[\cos^2 c_d + \cos^2 c_h\right], \qquad (10)\end{aligned}$$

with $g_i = \gamma_i\, d/K, (i = 1,2,3,5,6)$. The parameters g_i, namely g_5 and g_6, could be adjusted in such a way that minima of the function $(W_{el}^T + W_A)d/K$ are situated near $c_d = \pm\pi/2$ and $c_h = \pm\pi/2$. When the anchoring is not so strong the energy minima are shifted from those limit values of c_d and c_h in order to relax the twist deformation energy.

Note that twisted structure with the rotation of molecules by the angle π in each layer is realized for $c_d = -\pi/2$ and $c_h = \pi/2$ with the energy (in K/d units):

$$\frac{W^T d}{K} = -2(g_1+g_2) - 4t\left[t\left(1 - \frac{1}{1+t^2}\right) - \arctan\mathrm{t}\right]. \qquad (11)$$

The uniform anticlinic antiferroelectric structure in the whole sample described by $c_d = \pi/2$ and $c_h = -\pi/2$ has the energy $W^{AA}d/K$:

$$\frac{W^{AA} d}{K} = -2g_3 - \frac{\beta\_d^2}{4K} = -2g_3 - 4t^2. \qquad (12)$$

Finally, the mixed structure twisted near one surface and anticlinic antiferroelectric near the other surface is also possible. At boundaries this structure is characterized by parameters $c_d = -\pi/2$, $c_h = -\pi/2$ and by the energy $W^{AT}d/K$ in the form:

$$\frac{W^{AT}d}{K} = -2t\left[t\left(1 - \frac{1}{1+t^2}\right) - \arctan t\right] - (g_1 + g_2 + g_3) - 2t^2. \quad (13)$$

Based on observations of [12], energies of above mentioned structures are the same, i.e., it is $W^T \approx W^{AA} \approx W^{AT}$ without an external electric field what gives the relation:

$$(g_1 + g_2 - g_3) \approx 2t\left[\frac{t}{1+t^2} + \arctan t\right]. \quad (14)$$

The behavior of those structures under an electric field will be treated in the following part.

4.2. Structures Stabilized by a Field

An application of an electric field on the twisted B$_2$ structure leads to its deformation. The structure is not fixed at surfaces but it could change with parameters c_d and c_h what are molecular orientations at lower and upper surfaces, respectively. Let us suppose for simplicity that the principal deformation of solutions (8) under an external electric field is connected with the change of parameters c_d and c_h. In order to evaluate the energy contribution W_E due to an applied electric field we calculate $\frac{W_E d}{K} = \frac{d}{K}\int_{-\frac{Kd}{2}}^{\frac{d}{2}} w_E dx = \frac{dP_sE}{2K}\int_{-\frac{d}{2}}^{\frac{d}{2}}(\sin\phi_1 + \sin\phi_2)dx$ (in non-dimensional units) using solutions (8). Then

$$\begin{aligned}\frac{W_E d}{K} = &-\varepsilon\left(\arctan\frac{\cos\frac{\mathrm{c_d}}{2} - \sin\frac{\mathrm{c_d}}{2}}{\cos\frac{\mathrm{c_d}}{2} + \sin\frac{\mathrm{c_d}}{2}} - \arctan\frac{\cos\frac{\mathrm{c_d}}{2} - \sin\frac{\mathrm{c_d}}{2}}{(1+\mathrm{t})\cos\frac{\mathrm{c_d}}{2} - (\mathrm{t}-1)\sin\frac{\mathrm{c_d}}{2}}\right)\\ &+\varepsilon\left(\arctan\frac{\cos\frac{\mathrm{c_h}}{2} + \sin\frac{\mathrm{c_h}}{2}}{\cos\frac{\mathrm{c_h}}{2} - \sin\frac{\mathrm{c_h}}{2}} - \arctan\frac{\cos\frac{\mathrm{c_h}}{2} + \sin\frac{\mathrm{c_h}}{2}}{(1+\mathrm{t})\cos\frac{\mathrm{c_h}}{2} + (\mathrm{t}-1)\sin\frac{\mathrm{c_h}}{2}}\right). \quad (15)\end{aligned}$$

Again $t = d/2\zeta$. The non-dimensional parameter ε is defined as $\varepsilon = \frac{P_sEd\zeta}{K} = \frac{P_sEd^2}{K}\frac{1}{2t}$. In our model the solution describing the structure is modified by field through boundary coefficients c_d and c_h which change with the electric field.

4.2.1. The First Critical Field

The behavior of different structures outlined in part 4.1 under an electric field can be studied by the numerical investigation of the total energy given as the sum of (9), (10) and (15) in units K/d, what is the expression $W_T d/K = (W_{el}^T + W_A + W_E)d/K$. We suppose $P_s E > 0$ so the ferroelectric order of molecules anchored at lower surface is preferred. Therefore at lower fields namely the twisted structure near the upper surface will be deformed as the field acts against the ferroelectric anchoring on the upper glass plate. Then the surface $W_T d/K$ will be deformed and one of minima starts to be favored. The favored minimum which is pronounced by field corresponds to mixed structure having synclinic ferroelectric order at lower surface and anticlinic antiferroelectric order at the upper surface. The field is not yet so strong to perturb the anticlinic antiferroelectric order. All considered structures change to one structure at such an electric field when the surface $W_T d/K$ will have only one minimum. Such a field will be called the first critical field E_1 and it can be found from conditions

$$\frac{\partial}{\partial c_d}\left(\frac{W_T d}{K}\right) \geq 0 \quad \text{and} \quad \frac{\partial}{\partial c_h}\left(\frac{W_T d}{K}\right) \geq 0 \tag{16}$$

which should be valid at intervals $c_d \in (-\pi/2, \pi/2)$ and $c_h \in (-\pi/2, \pi/2)$.

The simultaneous validity of above conditions can be examined only numerically using [22].

The elimination of twisted deformation near the upper sample surface is then driven by the tendency of material to reach minimum $\mathrm{SmC_AP_A}$ structure when the influence of surface anchoring is eliminated.

At the first critical field E_1 the energy of so called mixed structure in the electric field E_1(in K/d), denoted as $W_{E_1}^{AT}$, is simply:

$$\frac{W_{E_1}^{AT} d}{K} = \frac{W^{AT} d}{K} - \varepsilon_1 \arctan t. \tag{17}$$

The last term in (17) can be obtained from (15) taking $\varepsilon_1 = P_s E_1 d\zeta/K$ and $c_d = c_h = -\pi/2$.

The development of the energy of B_2 structure with field is demonstrated in Figure 3.

The expression (17) together with Figure 3 clearly shows that the electric field E_1 decreases the energy of mixed structure as compared with the energies of structures without field. Basically, the structure is still mostly in antiferroelectric anticlinic state with imposed twist which is deformed by the field.

4.2.2. The Second Critical Field

Further increase of an external electric field can completely unwind twist of mixed structure and transforms existing anticlinic antiferroelectric structure to synclinic ferroelectric structure. We expect the electric field being still lower than the field necessary to change a chirality of layers as discussed in [8]. Then the transformation of structures is realized simultaneously by rotation of molecules on the surface of cone shown in Figure 1 and by rotation of molecules on the upper surface. Note that at the lower surface molecules are already in synclinic ferroelectric state. This synclinic ferroelectric structure at the lower surface serves as a nucleus of ferroelectric phase in sample bulk. Then the increase of the field necessary for transition to the uniform synclinic ferroelectric structure, $d^2P_s(E_2 - E_1)/K$, should be equal to the difference of the bulk energy between uniform synclinic ferroelectric and anticlinic antiferoelectric structures, equal to $4t^2$ (see (4)), and the energy barrier in the anchoring energy at the upper surface. This energy barrier can be determined from the expression (5) as the difference of W_Ad/K at $\phi_1 = -\pi/2$, $\phi_2 = 0$ and at $\phi_1 = -\pi/2$, $\phi_2 = -\pi/2$:

$$\left[\left.\frac{W_Ad}{K}\right|_{\phi_2=0} - \left.\frac{W_Ad}{K}\right|_{\phi_2=-\pi/2}\right]_{\phi_1=-\pi/2} = \frac{1}{4}(3g_1 - 2g_2 - g_3 + g_5 + g_6).$$

Thus the second critical field can be roughly estimated as:

$$\frac{d^2(P_sE_2)}{K} = \frac{d^2(P_sE_1)}{K} + 4t^2 + \frac{1}{4}(3g_1 - 2g_2 - g_3 + g_5 + g_6). \tag{18}$$

5. ESTIMATION OF PARAMETERS IN THE MODEL OF B$_2$ STRUCTURE

In this part, the changes of model energy of twisted B$_2$ structure with an external electric field will be shown and used to estimate the order of anchoring energies and the coupling constant β_- of the anticlinic antiferroelectric order.

In [12] the first and the second critical fields were determined as $E_1 \approx 0.5$V/μm and $E_2 \approx (1 \div 10)$V/μm. The first critical field is that one which compensates polar anchoring of the upper surface [12] and leads to the mixed structure described in previous part. Spontaneous polarization P_s is $P_s \approx 500\,\mathrm{nC/cm^2}$ and the sample thickness for which observations were done is about $d \approx 4\,\mu$m.

As we have in our model more parameters then experimental data given in [12] permit to determine we will do some simplifications. Supposing the polar anchoring energy to be the dominant term as compared with non-polar and antiferroelectric anchoring terms we chose simply $\gamma_1 \approx \gamma_3 \approx 0$. As for value of parameters γ_5 and γ_6 we suppose $\gamma_5 \approx \gamma_6$ for simplicity.

In following estimations of model parameters we will use the value of the elastic constant K taken as for nematic phase of rod-like molecules, i.e., $K \approx 10^{-11}$ J/m [20]. The parameter ζ which characterizes the length on which the principal part of twist deformation realizes is principally determined by β_- with K fixed. We expect this length should not be too small as compared with visible wave-lengths in order to obtain observable optical effects.

Supposing e.g., $\zeta \approx 0.2\,\mu\text{m}$ we obtain $t \approx 8.75$ with corresponding parameter $\beta_- \approx 10^3 \text{J/m}^3$.

Using (14) with $\gamma_1 \approx \gamma_3 \approx 0$ the model parameter γ_2 can be determined as $\gamma_2 \approx 10^{-4} \text{J/m}^2$. For the first critical field $E_1 \approx 0.5\,\text{V}/\mu\text{m}$ (i.e. $\varepsilon_1 = P_S E_1 d\zeta/K \approx 175$) the fit (16) gives $\gamma_5 \approx \gamma_6 \approx 0.5 \times 10^{-3}\,\text{J/m}^2$. This relatively strong anchoring characterized by parameters γ_5 and γ_6 assures the synclinic or anticlinic surface order of molecules with $\vec{c}$-directors parallel to surfaces. Without a field the energy dW_T/K has four minima at $c_d = \pm\pi/2$ and $c_h = \pm\pi/2$ separated by the barrier determined principally by parameters g_5 and g_6.

The application of the electric field favors one of mixed structures. At the critical field $E_1 \approx 0.5\,\text{V}/\mu\text{m}$ there is only one minimum for parameters $c_d = -\pi/2$, $c_h = -\pi/2$. It means that the conditions (16) are valid at that field.

Using the above mentioned parameters the plot of the energy dW_T/K as a function of surface $\vec{c}$-director orientations c_d and c_h can be calculated and energy plot visualized using methods of [22] is seen in Figure 3.

When increasing the parameter β_- for an order, i.e. taking $\beta_- \approx 10^4\,\text{J/m}^3$ with K fixed, the length ζ decreases to $\zeta \approx 0.06\,\mu\text{m}$. Then $t \approx 28$ and we estimate $\gamma_2 \approx 0.22 \times 10^{-3}\,\text{J/m}^2$ what corresponds to relatively strong anchoring [20]. The value of the anchoring energy (i.e., polar anchoring energy in our model) should increase with the decrease of the length ζ what can be expected from the expression (14) because surface anchoring should balance increasing twist energy.

As the critical field $E_1 \approx 0.5\text{V}/\mu\text{m}$ is kept unchanged, there is again $\gamma_5 \approx \gamma_6 \approx 0.5 \times 10^{-3}\,\text{J/m}^2$. The numerical investigation of $W_T d/K$ shows that the first critical field is determined by anchoring parameters γ_5 and γ_6.

Second critical fields estimated using (18) are systematically lower as compared with experimentally obtained data. It means that barriers in (18) are probably underestimated in the present model.

6. CONCLUSIONS

In the present contribution we have studied the influence of an electric field on twisted structures in the sample with the liquid crystal of bent-shaped molecules. We suppose that the uniform $\mathrm{SmC_AP_A}$ structure corresponds to the minimum of the bulk energy. However, the thickness of our sample is such that the competition between bulk and surface energies cannot be neglected. Therefore anchoring conditions impose a twist deformation on $\mathrm{SmC_AP_A}$ structure.

Without an applied external electric field twisted structure and domains of uniform chiral anticlinic antiferroelectric structures $\mathrm{SmC_AP_A}$ are observed [12]. The twist deformation occurs in a part of one layer close to one surface while the neighbour layer is uniform near this surface. The twist deformation permits to connect bulk $\mathrm{SmC_AP_A}$ structure with synclinic ferroelectric $\mathrm{SmC_SP_F}$ structure at surface. The twisted structure in the sense of the present contribution is the structure mediating synclinic ferroelectric $\mathrm{SmC_SP_F}$ structures at both surfaces with bulk $\mathrm{SmC_AP_A}$ structure.

The present model shows that together with twisted and $\mathrm{SmC_AP_A}$ structures so called mixed structures can exist. Mixed structures are bulk $\mathrm{SmC_AP_A}$ structures twisted near one sample surface to the surface $\mathrm{SmC_SP_F}$ structure and uniformly continuing to the second surface.

As the mentioned structures are observed as domains coexisting in the same sample for particular sample thickness we have expected that their energies may be comparable.

When an external electric field is applied to the sample, the rearrangement of the structure occurs by the rotation of molecules on the surface of cone with spontaneous polarization tangent to cone surface. This molecular rotation is possible when external electric field is smaller than electric field leading to simultaneous rotation on the cone and rotation around the molecular $\vec{n}$-director axis [8]. The chirality of smectic layers is unchanged by such a transition.

Under an increasing external electric field twisted structure starts to transform. At the first critical field E_1 (15) the ferroelectric anchoring energy is compensated on one surface. Near that surface the structure is spontaneously untwisted to anticlinic antiferroelectric $\mathrm{SmC_AP_A}$ structure. On the other surface, where the ferroelectric anchoring is not perturbed by an electric field, the structure rests in twisted order. Therefore E_1 supports the mixed structure whose energy is thus lower as compared with energies of structures without field. Moreover, the value of the first critical field permits to fit parameters of anchoring energies which are responsible for the preferred anchoring of the $\vec{c}$-directors parallel to surfaces with synclinic or anticlinic order.

In conclusion, in this contribution models of $\mathrm{B_2}$ structures observed in [12] were proposed. Observations of [12] documented the combination of particular sample thickness and the material choice which lead to coexisting twisted and uniform anticlinic antiferroelectric structures. Behavior of those structures in electric field was treated approximately and some model parameters were estimated. Anchoring energies seem to have an order of values of strong anchoring known from nematics.

So the present model of the twisted B_2 structure can describe qualitatively its transformation to mixed structure at electric fields up to the first critical field.

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