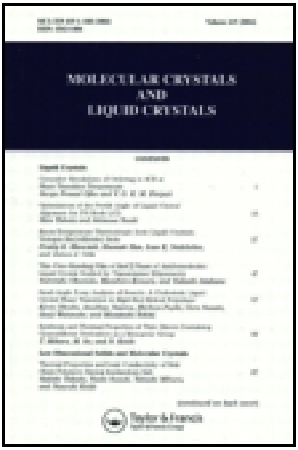


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Structures of Possible Phases of Achiral Polar Smectic Liquid Crystals formed by Bow Shaped Molecules

Mojca Čepič [a] [b] , Boštjan Žekš [a] [c] & Janez Mavri [d]

[a] J. Stefan Institute, Jamova 39, 1111, Ljubljana, Slovenia

[b] Faculty of Education, Kardeljeva pl. 16, 1113, Ljubljana, Slovenia

[c] Institute of Biophysics, Medical Faculty, Lipičeva 2, 1105, Ljubljana, Slovenia

[d] Kemijski Institut, Hajdrihova 19, 1115, Ljubljana, Slovenia

To cite this article: Mojca Čepič, Boštjan Žekš & Janez Mavri (1999): Structures of Possible Phases of Achiral Polar Smectic Liquid Crystals formed by Bow Shaped Molecules, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 328:1, 47-56

To link to this article: http://dx.doi.org/10.1080/10587259908026044

Mol. Cryst. Liq. Cryst., 1999, Vol. 328, pp. 47-56
Reprints available directly from the publisher
Photocopying permitted by license only

Structures of Possible Phases of Achiral Polar Smectic Liquid Crystals formed by Bow Shaped Molecules

MOJCA ČEPIČ[ab], BOŠTJAN ŽEKŠ[ac] and JANEZ MAVRI[d]

[a]*J. Stefan Institute, Jamova 39, 1111 Ljubljana, Slovenia,* [b]*Faculty of Education, Kardeljeva pl. 16, 1113 Ljubljana, Slovenia,* [c]*Institute of Biophysics, Medical Faculty, Lipičeva 2, 1105 Ljubljana, Slovenia and* [d]*Kemijski Institut, Hajdrihova 19, 1115 Ljubljana, Slovenia*

The state of order of achiral polar liquid crystals formed by bow shaped molecules is described by two two-dimensional order parameters, $\vec{P}$ and $\vec{\xi}$, giving the order of molecular dipoles and the tilt of the molecules, respectively. The free energy is written as an expansion in terms of both order parameters up to the sixth order and takes into account interactions between nearest neighbouring smectic layers. Three different antiferroelectric structures consistent with experimental observations are the result of the free energy minimization. An experiment to verify the suggested structures is proposed.

Keywords: achiral polar liquid crystal; bow shaped molecule

INTRODUCTION

Recent discovery of achiral polar smectic liquid crystals formed by bow shaped molecules[1] and their applicative potentials, stimulated extensive experimental studies such as optic, dielectric, x-ray and free standing films observations as well as synthesis of new compounds with similar properties. They appear in many different phases named B_N [2]. Some of the phases exhibit similar properties as some already known materials like ferroelectric liquid crystals[1]. One of the phases, frequently called 'switchable' phase, B_2 exhibits antiferroelectric hysteresis[3] and is easily polarized in an external electric field. Its polarization is ten to hundred times larger than polarization of ferroelectric liquid crystals[3]. This phase exhibits also a large dielectric response at low frequencies[1].

Phases stable at lower temperatures than the 'switchable' phase, B_3 and B_4, have smaller dielectric responses[1]. The lowest temperature phase B_4, which still has liquid crystalline properties, forms two kinds of domains, which reflect left or right handed polarized light, respectively, although molecules are achiral[4]. With the synthesis of new materials with bow shaped molecules, many new stable phases with similar or different properties have been observed.

At present, to our knowledge, none of the phases has a known, experimentally confirmed structure. Possible origin of large polarization in the "switchable" B_2 phase is due to the parallel ordering of molecular dipoles because of the steric effects[1]. Also possible types of helicoidal modulations have been discussed[5]. There are also some suggestions that molecules are tilted similarly as in the chiral ferroelectric or antiferroelectric phases[6].

The aim of this paper is to present a theoretical model which allows for various structures of phases appearing in achiral polar smectic liquid crystals. Two order parameters, which describe the molecular ordering in smectic layers, are introduced. The free energy based on intralayer as well as interlayer interactions is expressed as an expansion in terms of both order parameters. The minimization of the free energy leads to three different antiferroelectric structures which can appear in various phase sequences. Theoretically predicted properties of these phases are consistent with experimental observations.

ORDER PARAMETERS AND FREE ENERGY

To describe the orientation of a molecule in a smectic layer we imagine a bow shaped molecule and introduce two vectors - the arrow vector $\vec{a}$ and the string director $\vec{n}$, Fig.1a. Two two dimensional order parameters give two termodynamical averages related to these two vectors. The first order parameter $\vec{P}_j$ gives the average projection of arrow vectors $\vec{a}$ on the smectic layer j, Fig.1b. Since it is proportional to the layer polarization, we call this order parameter simply *polarization order parameter* of the j-th smectic layer. Its value gives the ordering of arrow directors and is nonzero always when arrows are ordered at least partially in the same direction.

$$\vec{P}_j = P_0 < \{a_{x,j}, a_{y,j}\} >= \{P_{x,j}, P_{y,j}\}, \tag{1}$$

where P_0 is the polarization of the single layer when all molecular arrow vectors are ordered in the same direction within the layer. The second order parameter describes the average projection of the string directors $\vec{n}$ i.e. directions of lines joining both bow ends, on the j-th smectic layer. Due to the up and down symmetry of the molecule, the order parameter is in the same way as the order parameter introduced in tilted smectic liquid crystals. Therefore we call it *tilt order parameter*.

$$\vec{\xi}_j = < \{n_{x,j}n_{z,j}, n_{y,j}n_{z,j}\} > = \{\xi_{x,j}, \xi_{y,j}\} \tag{2}$$

The tilt order parameter is nonzero whenever average string direction is not normal to the smectic layer i.e. molecules in the j-th layer are tilted in the average.

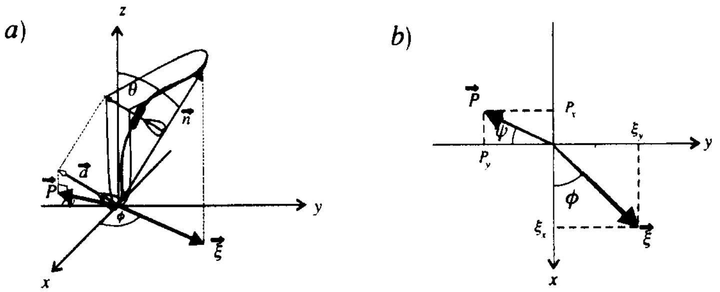


FIGURE 1 a) The orientation of a molecule in a smectic layer. On a bow shaped molecule the arrow vector and the string director are visualized. b) The polarization and the tilt order parameters for j-th smectic layer if all molecules are oriented in the same way as the molecule in a).

Free energy is expressed as the sum over all smectic layers. The analysis of the intralayer interactions, especially steric ones, leads to the assumption, because of the strong anisotropy of the molecules, that the transition from the isotropic to the smectic phase has to appear simultaneously with the appearance of the polarization order parameter $\vec{P}_j$. Smectic ordering contribution is assumed as an additional constant to the free energy and its possible variations are neglected in this paper. The free energy is therefore written only in terms of string and arrow order parameters where intralayer and interlayer interactions are taken into account explicitly similarly as for ferroelectric and antiferroelectric liquid crystals[7–9].

$$\begin{aligned} G = \sum_j \frac{1}{2}\alpha_{P,0}\,\vec{P}_j^2 + \frac{1}{4}\beta_{P,0}\,\vec{P}_j^4 + \frac{1}{6}\gamma_{P,0}\,\vec{P}_j^6 + \frac{1}{2}\alpha_{\xi,0}\,\xi_j^2 + \frac{1}{4}\beta_{\xi,0}\,\xi_j^4 + \\ \frac{1}{2}\,\Omega_0\left(\vec{\xi}_j \times \vec{P}_j\right)^2 + \frac{1}{2}\,\alpha_{P,1}\,\left(\vec{P}_j \cdot \vec{P}_{j+1}\right) + \frac{1}{2}\,\alpha_{\xi,1}\,\left(\vec{\xi}_j \cdot \vec{\xi}_{j+1}\right) + \\ \frac{1}{3}\lambda\left(\left(\vec{\xi}_j \times \vec{P}_j\right) + \left(\vec{\xi}_{j+1} \times \vec{P}_{j+1}\right)\right)\left(\vec{\xi}_j \times \vec{\xi}_{j+1}\right). \end{aligned} \tag{3}$$

In the sense of Landau expansion, only the first coefficient $\alpha_{P,0} = \alpha(T - T_0)$ is temperature dependent and changes its sign at the temperature T_0 where an isotropic phase becomes unstable and polarized smectic layers are formed. Next two terms describe intralayer interactions and sixth order term is necessary due to the first order transition to the phase where polarization order parameter is nonzero, so $\beta_{P,0}$ is assumed negative and $\gamma_{P,0}$ positive. The two terms in tilt order parameters with coefficient $\alpha_{\xi,0}$ and $\beta_{\xi,0}$, present van der Waals attractive interactions and can induce the tilt of the molecules. The term Ω_0 resumes attractive intralayer van der Waals interactions as well packing entropy of the molecules in the layer. We expect that due to both effects the most probable direction of the tilt is perpendicular to the orientation of the polarization. The coupling constant Ω_0 is therefore assumed negative. In our notation all the coefficients describing intralayer interactions have the subscript 0.

Interactions between molecules from neighbouring layers are presented as interlayer coupling terms. The coefficients have additional subscript 1, which means interactions with first i.e. nearest neighbouring layers. The coefficient $\alpha_{P,1}$ gives electrostatic dipolar, steric interactions and van der Waals interactions between nearest layers. Electrostatic dipolar interactions are the most important, favour antiparallel alignment of dipoles in nearest layers[10] and the coefficient is always positive. Due to the small but existing partial penetration of the molecules between the layers, it is possible either, that steric interactions favouring sinclinic tilt prevail over van der Waals interactions which favour anticlinic tilt in nearest layers ($\alpha_{\xi,1} < 0$) or the opposite ($\alpha_{\xi,1} > 0$). The parameter can also change sign due to the growing tilt[8] or polarization order parameter. Last term (λ) resumes attractive van der Waals interactions between molecules from neighbouring layers. The coefficient is expected to be of the same order as the chiral coefficient in chiral ferroelectric liquid crystals i.e. ten to hundred times smaller than other coefficients attributed to interlayer interactions.

STRUCTURES AND THEIR PROPERTIES

To find the stable structures at various temperatures, we have to find the values of polarization and tilt order parameters in each smectic layer. For the simplest possible stable structures we assumed that constant amplitude aproximation is valid i.e. the magnitudes of both, polarization and tilt order parameters do not vary from layer to layer. This assumption is reasonable for bulk samples while in very thin cells or in the free standing films also the variation of magnitudes can be important. This approximation is expresed as

$$\begin{aligned} \vec{P}_j &= P(\cos\psi_j, \sin\psi_j) \\ \vec{\xi}_j &= \theta(\cos\phi_j, \sin\phi_j), \end{aligned} \tag{4}$$

where both phase angles are presented on Fig. 1b. Magnitudes of the polarization and tilt order parameters, P and θ, respectively, can vary with temperature, while phase angles ψ_j and ϕ_j can vary also from layer to layer. Rotational simmetry allows for further reduction of number of unknown variables,

$$\Phi_j = \phi_{j+1} - \phi_j \tag{5}$$

is a relative orientation of polarization order parameters in nearest layers and

$$\Psi_j = \psi_{j+1} - \psi_j \tag{6}$$

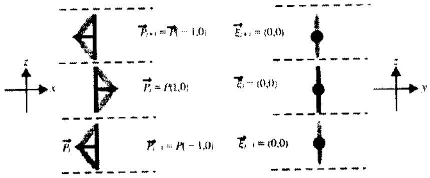
is a relative orientation of tilt order parameters in nearest layers. The relative orientation between polarization and tilt direction in the layer Δ_j is due to the strong coupling Ω_0 always $\pm\pi/2$. The simplest solutions are expected when relative orientations are also constant over the sample i.e. $\Phi_j = \Phi$ and $\Psi_j = \Psi$. The free energy is then

$$\begin{aligned} G = & \sum_j \frac{1}{2}\,\alpha_{P,0}\,P^2 + \frac{1}{4}\,\beta_{P,0}\,P^4 + \frac{1}{6}\,\gamma_{P,0}\,P^6 + \frac{1}{2}\,\alpha_{\xi,0}\,\theta^2 + \\ & \frac{1}{4}\,\beta_{\xi,0}\,\theta^4 + \frac{1}{2}\,\Omega_0\,\theta^2 P^2 + \frac{1}{2}\,\alpha_{P,1}\,P^2\cos\Psi + \frac{1}{2}\,\alpha_{\xi,1}\,\theta^2\cos\Phi + \\ & \frac{1}{3}\,\lambda\,\theta^3 P\,(\sin\Delta_j + \sin\Delta_{j+1})\sin\Phi, \end{aligned} \tag{7}$$

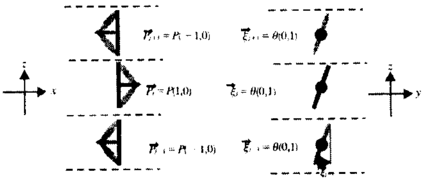
The free energy Eq.7 is minimized with respect to four variables: P, θ, Ψ, Φ. We obtained besides the trivial solution where P and θ are equal to zero, which represents a disordered structure, three different stable antiferroelectric structures:

nontilted antiferroelectric structure - Sm A P$_A$ [1], where molecules are not tilted, $\vec{\xi} = 0$, arrows are ordered, $\vec{P} \neq 0$, and have the opposite directions in neighbouring layers $\Psi = \pi$. The structure is stable when $\alpha_{P,0} < 0$ and $\alpha_{\xi,0} + \Omega_0 P^2 > 0$, Fig. 2 a. The structure is due to the opposite directions of polarization order parameters in neighbouring layers, antiferroelectric.

a) Nontilted antiferroelectric structure Sm A PA



b) Sinclinic tilted antiferroelectric structure Sm Cs PA



c) Helicoidal anticlinic tilted antiferroelectric structure Sm CA PA

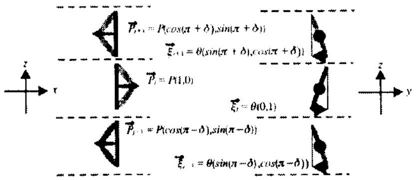


FIGURE 2 Structures of the a) nontilted antiferroelectric structure Sm A P$_A$, b) sinclinic tilted antiferroelectric structure Sm C$_S$P$_A$ and c) modulated anticlinic tilted antiferroelectric structure Sm C$_A$P$_A$ for three smectic layers.

The rotation of the molecules around the normal to the smectic lay-

---

[1] Names of three phases follow the nomenclature proposed by Link et al[6]. The Sm A and Sm C are used for nontilted and tilted smectic phase, respectively. Letter P is used for polar. Subscripts S and A are used for sinclinic and anticlinic tilt, respectively, and subscript A is also used for antiferroelectric polarization.

ers is hindered mostly by electrostatic dipole interactions between neighbouring layers, therefore relatively small external electric field can rotate arrow order parameter in each layer in the field direction and polarize the sample.

sinclinic tilted antiferroelectric phase - Sm $\mathbf{C}_S$ $\mathbf{P}_A$, where molecules are tilted $\vec{\xi} \neq 0$ in the same direction in all layers, $\Phi = 0$, the tilt order parameter is perpendicular to the polarization order parameter $\Delta = \pm\pi/2$. Also in this structure the polarization order parameters have the opposite directions in neighbouring layers $\Phi = \pi$ and therefore $\Delta_j = -\Delta_{j+1}$. The structure is stable when $\alpha_{P,0} < 0$ and $\alpha_{\xi,0} + \Omega_0 P^2 < 0$ and $\alpha_{\xi,1} < 0$, which means that steric interlayer interactions are more important than van der Waals interlayer interactions, Fig. 2 b.

anticlinic tilted antiferroelectric structure - Sm $\mathbf{C}_A$ $\mathbf{P}_A$, where molecules are tilted $\vec{\xi} \neq 0$ in nearly opposite directions $\Phi = \pi \pm \delta$ in neighbouring layers, where δ is small. Van der Waals interactions prevail over steric interactions. Due to the special shape of the molecules the attractive van der Waals interlayer interactions induce the rotation of the molecules and cause the helicoidal modulation of the structure with the pitch extending over $2\pi d/\delta$, where d is the thickness of the smectic layer. Only in this structure is the last term in Eq. 7 is different from zero. Since its effective sign depends on the mutual orientations of the average string and arrow order parameters in the layer (the sign of the vector product), domains of left and right handed helicoidal modulated structures are formed. The structure is stable when $\alpha_{P,0} < 0$ and $\alpha_{\xi,0} + \Omega_0 P^2 < 0$ and $\alpha_{\xi,1} > 0$, which means that van der Waals interlayer interactions are more important than steric interlayer interactions, Fig. 2 c.

The proposed signs of model parameters allow for the phase sequence where the nontilted Sm A P_A phase is stable directly below the isotropic phase. With lowering temperature, the polarization order parameter increases and intralayer van der Waals interactions becomes significant inducing the tilt of the molecules. Below the Sm A P_A phase therefore either the sinclinic tilted Sm $\mathrm{C}_S\mathrm{P}_A$ phase or the anticlinic tilted Sm $\mathrm{C}_A\mathrm{P}_A$ phase depending on the nature of prevailing interlayer interactions, is stable. It is natural to expect that also interlayer interactions are influenced by the magnitude of the polarization or tilt order parameters and that similarly as in antiferroelectric liquid crystals[8,9] with lowering temperature steric interlayer interactions decrease and van der Waals interactions inducing anticlinic tilt prevail. In this case the anticlinic tilted Sm C_AP_A phase become stable below the sinclinic tilted Sm C_SP_A phase. Theoretical prediction allows also for a direct first order transition from the isotropic to the sinclinic Sm C_SP_A or anticlinic tilted Sm C_AP_A phase. Shortly, all three phases appear always at the same sequence with lowering temperature: I $\leftrightarrow$Sm A $P_A \leftrightarrow$Sm $C_SP_A \leftrightarrow$Sm $C_AP_A \leftrightarrow$Cr. In various samples some of the phases are not stable, but tilted phases are always stable at lower temperatures than the nontilted one and the anticlinic tilted phase is always stable below the sinclinic tilted one.

COMPARISON WITH EXPERIMENTAL RESULTS AND CONCLUSIONS

Let us briefly resume the present state of experimental knowledge about achiral polar liquid crystals formed by bow shaped molecules and compare them with the theoretical predictions of the model. This liquid crystals exhibit various phase sequences. The homologuous series studies have shown, that phases with liquid crystalline properties exist in at least four different stable phases named B_1, B_2, B_3 and B_4 [2].

The B_1 phase is stable in homologues with shorter chain lengths. Its appearance through polarizing microscope is similar to the Sm A phase of rodlike liquid crystals. In the present state of the phenomenological model there is no structure with similar properties. Including into the free energy also the terms which acount for dipolar interactions between next nearest layers can lead to the similar structures as the Sm C_α^* phase in antiferroelectric liquid crystals. Such a structure should appear through polarizing microscope like the Sm A phase.

The B_2 phase has antiferroelectric properties, i.e. exhibit two polarization peaks within a half period when applying triangular voltage. The state at high voltage has extremely large polarization (up to 1000 nAs/cm^2) indicating large ordering of molecular dipoles. In the model the structure with antiferroelectric properties which can be the most easily polarized is the Sm A P_A phase.

The present state of experimental evidence of the B_3 phase is that it appears through polarizing microscope as the Sm C^* phase.

The lowest temperature B_4 phase have domains, which reflect right or left handed polarized light, respectively, indicating coexistence of left and right handed helicoidally modulated domains. In the present model the structure of the Sm C_AP_A phase has such properties providing the coefficient λ is ten times smaller than other coefficients. In this case the two helicoidally modulated domains exist since the mutual polarization and tilt direction is doubly degenerated due to the degeneracy of $\Delta = \pm\pi/2$.

Since in the model three different antiferroelectric phases are stable, we suggest as the possible structure for the B_3 phase the Sm C_SP_A phase, which can appear below the Sm A P_A phase. The free standing films experimental studies have shown the existence of the antiferroelectric films formed from bow shaped molecules where strong indications that the molecules are tilted exist[6]. Additional order present in all restricted systems can influence the phase sequence and therefore the first stable phase can already be tilted.

Proposed structures have to be tested experimentally. In order to suggest the experiment which can give the hint to the structure, we modeled the molecular shape by the molecular orbital calculations[11]. The resulting molecular polarizability tensor is significantly biaxial having the largest polarizability along the string direction and the smallest one perpendicular to the arrow and string direction. Their ratio is approximately 3:2:1 and therefore in the analysis of optical measurements biaxiality of the polarizability tensor has to be taken strictly into account. To test the proposed structures we suggest the conoscopic studies of relatively thick films in the small external field applied along smectic layers. Films with even number of layers orient with polarization along the electric field[6]. Optical properties of films with the Sm A P_A structure, should have three different average refractive indices, the largest one for a light polarized perpendicularly to the smectic layers and the smallest one for a light polarized in the direction within a smectic layer perpendicular to the electric field. All three values should differ significantly. The angle between the normal to the smectic plane and the optical axes should therefore be of the order ten degrees or more degrees and can be seen on conoscopic figure.

The films with the Sm C_SP_A structure will also have three different refractive indices, but the tilt of the molecules would tilt also the plane with both optical axes. This tilt should give information about the magnitude of the average molecular tilt.

Thick films with domains of left and right handed helicoidally modulated Sm C_AP_A structure should behave almost uniaxially due to the averaging of optical properties over the part of the existing helix. The largest refractive index should be smaller than the largest one in the Sm A P_A or the Sm C_SP_A phase and the second one sholud be similar by the magnitude to the intermediate refractive index. Due to the possible noncompleteness of the helix, the optical axes can be slightly tilted with respect to layer normal in the direction perpendicular to the electric field.

The presented model takes into account only interactions between nearest layers and assumes very strong coupling between the polarization and tilt order parameter within one layer. If this is not the case i.e. interactions up to more layers are significant and/or the polarization tilt coupling is weaker, large variety of structures can become stable.

Acknowledgement

We would like to thank Barbara Rovšek, Igor Muševič and Marta Klanjšek Gunde for stimulating discussions. The financial support of the Ministry of Science and the University of Ljubljana is acknowledged.

References

[1] T. Niori, T. Sekine, J. Watanabe, T. Furukawa, H. Takezoe, *J. Mater. Chem.*, **6,** 1231, (1996).
[2] Here we are following the nomenclature suggested at the Workshop on Banana Liquid Crystals held in Berlin, December 1997 (unpublished). The phases of achiral polar liquid crystals are named as B_N, wher N is the subscript 1,2,.. etc.
[3] G. Heppke, S. Rauch, N.K. Sharma, to be published in the Proceedings of FLC'97, Brest, France.
[4] P. Collings, G. Heppke, D. Krüerke, C. Löhnig, J. Rabe, W. Stocker, presented at the Workshop on Banana Liquid Crystals held in Berlin, December 1997 (unpublished).
[5] T. Sekine, T. Niori, J. Watanabe, T. Furukawa, S. W. Choi, H. Takezoe, *J. Mater. Chem.*, **7**, 1307, (1997).
[6] D. R. Link, G. Natale, R. Shao, J.E. Maclennan, N.A. Clark, E. Körblova, D.M. Walba, *Science*, **278**, 1924, (1997).
[7] M. Čepič, B. Žekš, Mol. *Cryst. Liq. Cryst.*, **263**, 61, (1995).
[8] B. Žekš, M. Čepič, *Liquid Crystals: Physics, Technology and Applications, Proceedings of SPIE(ECLC97)*, **3318,** 68 (1998).
[9] M. Škarabot et al., Phys.Rev.E., **58,** 575, (1998).
[10] M. Čepič, B. Žekš, *Mol. Cryst. Liq. Cryst.*, **301,** 221, (1997).
[11] M.J. Frisch et al, *Gaussian 94,* Revision B.3, Inc., Pittsburgh PA, (1995).