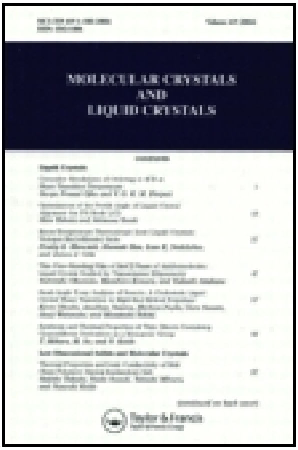


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

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

Layer Structures of Ferroelectric Smectic Liquid Crystals Formed by Bent-Core Molecules

Antal Jákli [a], Christiane Lischka [b], Wolfgang Weissflog [b], Sebastian Rauch [c] & Gerd Heppke [c]

[a] Central Research Institute for Solid State Physics and Optics, H-1525, Budapest, P.O. Box 49, Hungary

[b] Institute für Physikalishe Chemie, Martin Luther Universitat, Mühlpforte 1, 06108, Halle, Germany

[c] Iwan-N-Stranski-Institut, TU Berlin, Strasse des 17 Juni 135, 10623, Berlin, Germany

Version of record first published: 24 Sep 2006

Mol. Cryst. Liq. Cryst., 1999, Vol. 328, pp. 299-307
Reprints available directly from the publisher
Photocopying permitted by license only

Layer Structures of Ferroelectric Smectic Liquid Crystals Formed by Bent-Core Molecules

ANTAL JÁKLI[a], CHRISTIANE LISCHKA[b], WOLFGANG WEISSFLOG[b], SEBASTIAN RAUCH[c] and GERD HEPPKE[c]

[a]*Central Research Institute for Solid State Physics and Optics, H-1525 Budapest, P.O. Box 49, Hungary,* [b]*Institute für Physikalishe Chemie, Martin Luther Universitat, Mühlpforte 1, 06108 Halle, Germany and* [c]*Iwan-N-Stranski-Institut, TU Berlin, Strasse des 17 Juni 135, 10623 Berlin, Germany*

Achiral bent-shaped molecules may form chiral and polar smectic phases, due to a spontaneous tilt of the planes of the molecules. The lowest energy-state is racemic, and in the textures of the ground state usually fine fringes appear parallel to the smectic layers. Recently it was found that the formation of the fringes could be suppressed resulting in a uniform texture in the ground state. In this paper we show evidences for field induced tilted and horizontally zigzagging layer structures. We discuss properties of various layer structures and compare them to our experimental observations. Finally we give a qualitative explanation for the observed field-induced-uniform-racemic ground state.

Keywords: ferroelectric liquid crystals; chirality; smectic layers

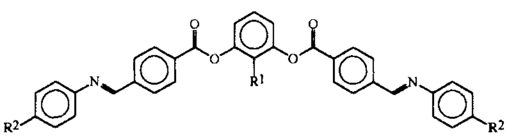
INTRODUCTION

Recently smectic phases of achiral banana shaped molecules[1],[2] received considerable interest, because it was found that they are ferroelectric[3]. Planar textures of films of these phases generally consist of fine fringes parallel to the smectic layers. Niori et al.[3] suggested that the fringes indicate a spontaneous helix formation due to a two-dimensional escape from a macroscopic polarization[4]. Link et al.[5] proposed that the fine fringes correspond to two types of domains parallel to the smectic layers. In each domain the director tilts uniformly, but changes sign at the domain boundaries. Lately it was found[6] that under extended application of moderate electric fields, the fringe pattern can be gradually suppressed, resulting in a uniform texture that shows almost no electro-optical switching. It was suggested that the suppression of the fringes and the small optical modulation could be explained supposing that the layers are tilted with respect to the film surface.

In the present paper we report additional experimental observations which support this idea, and discuss optical properties of various possible structures of planar racemic states.

EXPERIMENTAL

We carried out measurements on three different materials. Their molecular structures and phase transition temperatures are listed below.



R^1	R^2	Name	Phase sequence (in °C)
H	OC_7H_{15}	A	XB_4 156 XB_3 165 XB_2 172 I
H	OC_8H_{17}	B	XB_4 156 XB_3 161 XB_2 174 I
CH_3	OC_8H_{17}	C	Cr 155 XB_3 162 XB_2 169 I

TABLE 1 Molecular structures and phase - sequences of the studied materials. Substance *A* has been synthesised in Berlin[7], *B* and C were prepared in Halle [8],[9]. Physical studies have already been reported on substance *A*[6] and *B* [4].

We investigated *2 μm* and *6μm* clean *ITO* coated, and *10 μm* rubbed polyamide coated cells in their XB_2 phases.

RESULTS

In all the studied samples, in absence of an external field, mainly grainy racemic textures form with some isolated homogeneous fan shaped domains (see also Ref.[5],[6]). The model of the grainy racemic texture is illustrated in Figure 1/a and 1/a'. Figure 1/a (1/a') corresponds to a domain with positive (negative) director tilt $+\theta$ ($-\theta$). Accordingly, the extinction direction makes $+\theta$ ($-\theta$) angle with the layer normal. The coexistence of the domains with positive and negative tilt directions leads to the appearance of the fine fringes parallel to the smectic layers. Each domain is antiferroelectric, i.e. the direction of the polarisation is opposite in the subsequent layers.

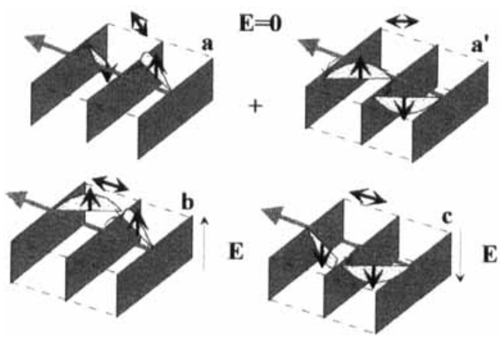


Figure 1 Model for racemic bookshelf textures with fine stripes parallel to the smectic layers. In zero electric fields (a) and (a') the structure is antiferroelectric: polarisation alternates between up-and-down, but the director tilts in the same directions. In the two type of domains (*a* and *a'*) the tilt and the extinction directions (denoted by ↔) are different. Under strong electric fields (b and c) the states become ferroelectric, but the tilt direction alternates. The extinction directions are parallel to the smectic layer normal. See color plate XIII at the back of this issue.

Above a threshold electric field the fringes disappear and, independent of the polarity of the field, the extinction directions become parallel to the layer normal (see *Figure 1/b* and *1/c*). After short-term application of electric fields the fringes reappear. However, after longer-term electric field treatment *(f~10Hz, E~3V/μm)* no fringe formation occurs in the ground state[6]. The time needed for the formation of the uniform racemic texture increases with the film thickness. Shearing the film periodically *(amplitude~50μm, f~1Hz)* simultaneously with the application of a low frequency field *(E~3V/μm, f~1Hz)* the smectic layers turn uniformly parallel to the shear direction. The extinction directions in the ground state, and under fields are practically the same: they are parallel to the layer normal. This kind of behaviour can be explained if we assume that under zero field the polarisation of the layers are parallel to the boundary plates, as it is illustrated in *Figure 2/a* and *2/a'*. (The structures under electric fields shown on *Figure 2/b* and *2/c*, and are the same as of *Figure 1/b* and *1/c*). The very weak electrooptical switching observed in uniform textures[6] indicates that the polarisation is not exactly horizontal.

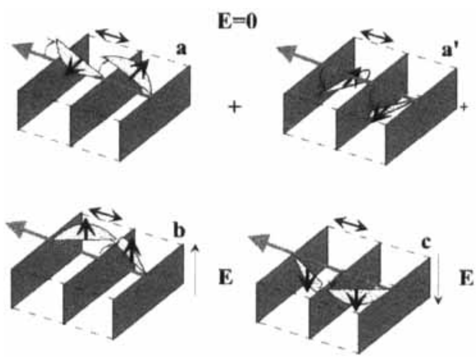


Figure 2 Model of uniform racemic bookshelf textures. In zero electric fields (a and a'), the structure is antiferroelectric, synclinic with horizontal polarisation. The extinction directions (denoted by ↔) are parallel to the layer normal in both *a* and *a'*. The structures under strong electric fields (b and c) are the same as of Figure 1/b and 1/c.

See color plate XIV at the back of this issue.

In case of structures of Figure 2, however, the surface conditions may not optimal, since the planes of the molecules are tilted with respect to the substrate. The surface energy can be minimised by a suitable tilt of the layers as depicted in *Figure 3/a and 3/a'*. For the sake of simplicity, we assume uniform tilt, but the same arguments would hold also for bent layers. For tilted layers and for planar anchoring the structure corresponding to *Figure 3/a'* becomes favoured, because there the planes of the molecules are parallel to the substrates.

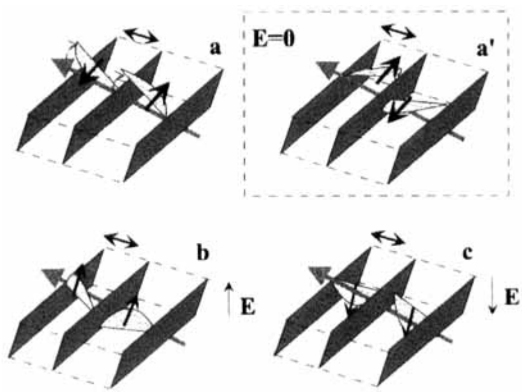


Figure 3 Model of uniform racemic textures with smectic layers tilted with respect to the film normal. In zero electric fields (a and a'), the structure is antiferroelectric (polarisation alternates horizontally), but the director tilts in the same direction. The angle between the plane of the molecules and of the substrate (pretilt) depends on the relative direction of the director - and layer tilt. In case of (a) the pretilt is $\theta+\alpha$, whereas in case of (b) it is $|\theta-\alpha|$ (θ is the director, α is the layer tilt angle). With planar anchoring a' is favourable. These structures under strong positive and negative electric fields are shown in b and c, respectively. The extinction directions are not sensitive to the electric fields.
See color plate XV at the back of this issue.

In the 6μm cell of substance *A* we indeed observed domain wall motions during the reformation from the grainy to the uniform texture, indicating the transformation of the smectic layer.

Under stronger rectangular fields *(E~4-5V/μm, f~1Hz)* a gradual formation of broad *(~0.1mm)* stripes take place in about 5 minutes. These stripes are perpendicular to the smectic layers and to the fine fringes that can be observed on virgin cells. Simultaneously, a periodic motion with the frequency of the field and speed of about *0.1mm/s* can be observed perpendicular to the smectic layers. In *Figure 4* we show the initial uniform (a) and the striped (b) textures of this cell. In the latter case the modulation of the extinction direction is $\pm 11^o$ with respect to the uniform texture.

Figure 4: Textures of a 6μm ITO coated film of substance *A* in the XB_2 phase *(T=168°C)*. a.) Uniform racemic texture emerged in 5 minutes from a fringe pattern under *U=15V, 0.6Hz* voltage treatment. b.) Striped texture formed from texture a.) under *U=25V, f=0.6Hz*.

The extinction directions do not change with field reversal and remain stable even after field removal (see *Figure 5*).

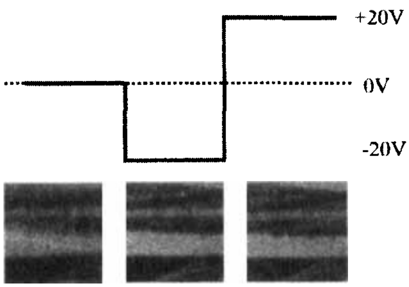


Figure 5. Behaviour of the striped texture under electric fields (*T=168 °C, d=6μm*, clean ITO coated film containing substance *A*). Area: $10^{-2}mm^2$.

The stripes disappear and the previous uniform texture (corresponding to *Figure 4/a*) reforms quickly once a shear is applied perpendicular to the stripes. These kind of observations resemble to the field induced "chevron-to-striped bookshelf" transitions of SmC* films[10], and thus confirm the observations of the previous section. For tilted or bent smectic layers vertical fields exert a torque on the smectic layers and tend to transform them to upright position (bookshelf textures). A transformation to a uniform bookshelf texture would require the formation of new layers, which can occur only by slow nucleation processes. The number of layers can be maintained with smectic layers zig-zagging along the substrate. This results in a modulation of the extinction direction and stripes appear normal to the smectic layers.

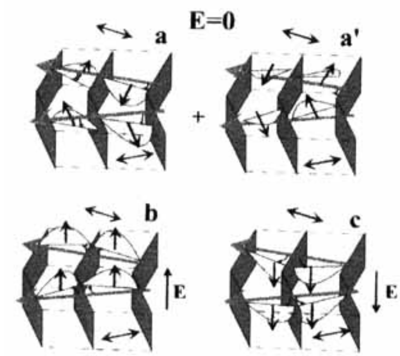


Figure 6. Model of striped bookshelf racemic textures with smectic layers zigzagging horizontally. In zero electric fields (a and a'), the structure is antiferroelectric (polarisation alternates horizontally, but the directors tilt in the same direction. Both in *a* and *a'* the extinction directions are parallel to the layer normal. The extinction directions are the same in the ground states (*a, a'*), under strong positive (b) and negative (c) electric fields.

See color plate XVI at the back of this issue.

The striped bookshelf (horizontally zigzagging layer) structure is illustrated in *Figure 6* in the ground state (a and a') and under fields of different polarity (*b, c*). It is assumed that the horizontal modulation angle is equal to the director tilt angle and the electric field is large enough to induce a transition to the ferroelectric states. In the above-idealised case the extinction direction is everywhere parallel to the layer normal, i.e. it is modulated by the zigzag angle. The experimentally observed $\pm 11^{\circ}$ modulation angle is smaller than the director tilt angle, indicating that the layers are still not vertical.

In 10 μm films of substances *B* and *C* no stripes form perpendicular to the layers in fields above a threshold of $E_{th} \sim 4V/\mu m$. Instead, the birefringence decreases considerably and, switching off the field, fine stripes appear parallel to the layers. These stripes, however, are not visible after switching off smaller fields ($<3V/\mu m$). We think that in these films both the vertical (Figure 1) and horizontal (Figure 2) polarisations are stable at zero field. $E_{th} \sim 4V/\mu m$ might correspond to the threshold for the anchoring transition from the horizontal to the vertical polarisation directions. Removing strong fields ($E > E_{th}$) two types of domain form (Figure 1/a and 1/a'). Moderate AC fields, however induce horizontal polarisation directions (Figure 2), which do not lead to stripe formation.

For a qualitative explanation of the moderate AC field induced horizontal polarisation we compare the free energies when the polarisation alternates between up and down (Figure 1/a), and when they are parallel to the substrates (Figure 2/a). For a vertical polarisation no torque acts, and the ferroelectric coupling has zero contribution to the free energy (we can neglect the electro-clinic effect, since the polarization does not couple to the director tilt). When the polarization is perpendicular to the electric field, there is a torque in each layer. This deforms the pure antiferroelectric structure, so that the polarization has a small vertical component: $\sim P_o\delta$. If the polarisation can follow the electric field, than $\Delta F = -\int P(z)E dz \cong -P_o E\delta$ and the free energy is smaller than for Figure 1/a. Accordingly, the horizontal polarization becomes favoured, and a static torque drives the polarisation perpendicular to the electric field. The driving mechanism is not yet clear. It maybe connected to the flow that occurs under AC fields (electromechanical effects). The flow becomes larger as the angle between the polarisation and the electric field increases[11], thus facilitating the drifting process. When the layers tilt by an angle α (as observed in the thin films) the electric energy gain decreases by $P_o E_o \delta (1-\cos\alpha)$. Consequently, the layer tilt occurs only under low fields, and only if the surface energy were dominating. This simple model explains the main features of the field-induced alignment.

Acknowledgement

The work was supported in part by a VW Stiftung between I.-N.- Stranski Institute and the Research Institute for Solid State Physics and Optics; by the Copernicus Grant IC15-CT96-0744, and by the Hungarian National Science Research Fund OTKA T-023102. One of the author (A.J.) acknowledges useful comments from Prof. Alfred Saupe and Dr. István Jánossy.

References

[1] Y. Matsunaga and S. Miyamoto, *Mol. Cryst. Liq. Cryst.*, **237**, 311 (1994).

[2] T. Akutagawa, Y. Matsunaga and K. Yashuhara, *Liq.Cryst.*, **17**, 659 (1994).

[3] T. Niori, T. Sekine, J. Watanabe, T. Furukawa and H. Takezoe, *J. Mater. Chem.* **6**(7), 1231 (1996).

[4] T. Sekine, T. Niori, M. Sone, J. Watanabe, S.W. Choi. Y. Takanishi and H. Takezoe, *Jpn. J. Appl. Phys.*, **36,** 6455 (1997).

[5] D.R. Link, G. Natale, R. Shao, J.E. Maclennan, N.A. Clark, E. Körblova, D.M. Walba, *Science,* **278,** 1924 (1997).

[6] A. Jákli, S. Rauch, D. Lötzsch, G. Heppke, *Phys.Rev. E,* **57**, 6737 (1998).

[7] G. Heppke, A. Jákli, D. Krüerke, C. Löhning, D. Lötzsch, S. Paus, S. Rauch and K. Sharma, Abstracts, European Conference on Liquid Crystals, Zakopane, Poland, ISBN# 83–911181–8–1 (1997), p. 34.

[8] W. Weissflog, Ch. Lischka, I. Benne, T. Scharf, G. Plezl, S. Diele, H. Kurth, Proc. SPIE 3319, 14 (1998).

[9] S. Diele, S. Grande, H. Krth, Ch. Lischka, G. Pelzl, W. Weissflog, I. Wirth, *Ferroelectric,* in press.

[10] see for example: L. Lejcek, S. Pirl, Liq. Cryst., **8**, 871 (1990) and J. Funfschilling, M. Schadt, *Jpn. J. Appl. Phys.*, **30,** 741 (1991).

[11] A. Jákli and A Saupe, *Mol. Cryst. Liq. Cryst.*, **237**, 389 (1993).