Electro-optics of liquid crystals of bent-shape molecules

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1. Abstract

We consider geometrical conditions of liquid crystals of bent-shape molecules that result in optically isotropic antiferroelectric structure that can be reversibly switched to birefringent states. An example of an ester based banana-shape substance is discussed that almost fulfills the ideal conditions and provides fast electro-optical switching with or without crossed polarizers.

2. Introduction

All liquid crystal displays working today contain rod-shape molecules. Recently we showed [1] that liquid crystals of bent-shape molecules can also be used in displays with features and underlying principles that are not present in calamitic liquid crystals. They can combine the inexpensive synthesis with ferroelectric properties that lead to bistable fast switching devices which can work either without polarizers or can offer excellent contrast with perfect dark state.

Smectic layers of bent-shape molecules [2] lose the reflection symmetry, i.e. each layer becomes chiral [3] if the molecular planes are tilted. The chirality of the adjacent layers may have the same sign in micrometer ranges resulting chiral (C) domains, or it may alternate forming macroscopically racemic (R) domains. In addition, due to the close packing of the kinked molecules, the materials are antiferroelectric or ferroelectric. The antiferroelectric - racemic (AF-R) and ferrolectric - chiral (FE-C) states are synclinic (the director tilt is uniform in the adjacent layers), whereas the AF-C and FE-R states are anticlinic. The anticlinic structures are transparent, whereas - due to equivalence of the director tilt directions and of the sign of the chirality - films consisting synclinic domains scatter light. This is due to the fact that the differently tilted synclinic domains are separated by defects, which are observable even without polarizers. These features mean that during the electric field-induced AF-FE transition the textures switch from opaque to transparent in the racemic state and from transparent to opaque in the chiral state. The materials can be designed so that both the opaque racemic AF and the transparent chiral AF states be stable and interchangeable with suitable fields.[4] This implies their use in optical storage devices. For example we can envision privacy windows that consume energy only during the transformation from one state to the other. This transformation requires about the same time as needed to turn over one page in a book.

On materials with glassy state at room temperature one can freeze in both the opaque and clear states where both may have 3 different electrical states: polarization is positive, negative or zero.[5]

In addition to the differences in the light-scattering properties, anticlinic and synclinic domains also differ in their birefringences. Anticlinic domains have small birefringence ($\Delta n_a < 0.05$) [3,6] since the tilt angles are typically larger than $30°$. However, synclinic domains have large birefringences comparable to calamitic liquid crystals ($\Delta n_s > 0.1$). The first optically isotropic ($\Delta n \sim 0$) "banana phases" were reported both with spontaneously chiral domains of opposite handedness [7] and without observed chirality [8], but no electro-optical switching was observed there. Recently in an ester-based 'banana material', 1,3-phenylene-bis[4-(10-undecenyloxy)benzoyloxy] benzoate (Pbis11BB)[9] we observed that in bookshelf geometry the texture can be reversibly switched between optically isotropic and birefringent states. The observations suggested 'orthoconic' ($\sim45°$ director tilt angle)[10] anticlinic director structure in the antiferroelectric state and synclinic structure in the ferroelectric state.

In this paper we concentrate on the switching between the optically isotropic and birefringent states: we summarize the main experimental results and analyze the necessary conditions of the optical isotropy.

3. Results

The material *Pbis11BB* has a tilted polar smectic mesophase between *71°C* and *91.5°C*. In the bookshelf alignment the texture is black between crossed polarizers. The textures then can be reversibly switched between the optically isotropic and birefringent states. The conoscopic images of the textures are also completely black and featureless at zero fields meaning negligible birefringence even for oblique light incidences. The electric field dependence of the integrated light intensity I(E) transmitted between crossed polarizers is shown in *Figure 1*.
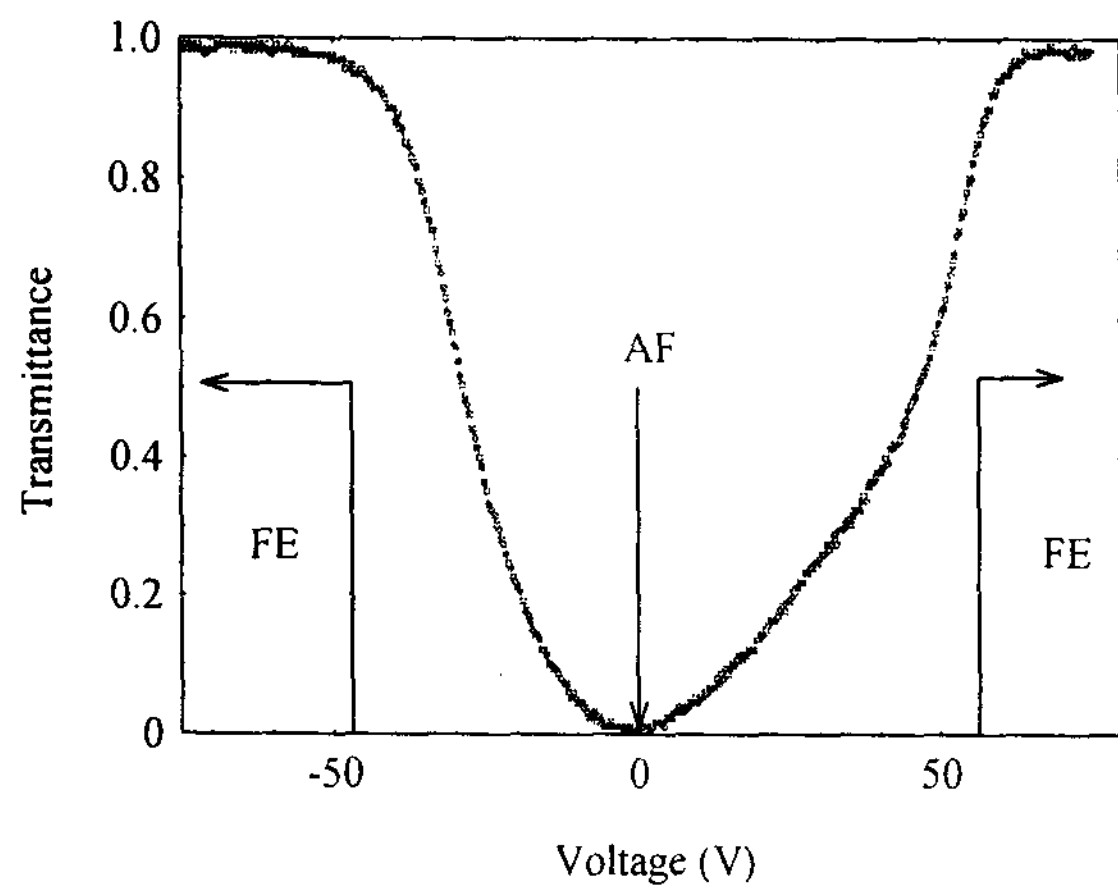

Figure 1: Voltage dependence of the transmission of a 4μm cell between crossed polarizers.

It is seen that *I(E) ~ E* (V-shape switching) if *E< 10V/μm*, then *I(E)* rises steeply in the *10V/μm < E < 12V/μm* regime, and remains constant at higher fields. The corresponding birefringence increases from *Δn=0* at *E=0* to *Δn~0.2* at *E~13V/μm*. Simultaneous observations on the polarization currents reveal an antiferroelectric ground state that is switched to the ferroelectric state in the voltage range, where the birefringence increases sharply (see *Figure 2*). Note that the value of the polarization depends strongly on how we determine the background. If we choose a straight line as background the calculated polarization

is *1160nC/cm²*. However if we connect the current values at *t=-T/2*, 0 and *+T/2*, where *T* is the period of the triangular wave form), we get a kinked line (dashed line in *Figure 2*).
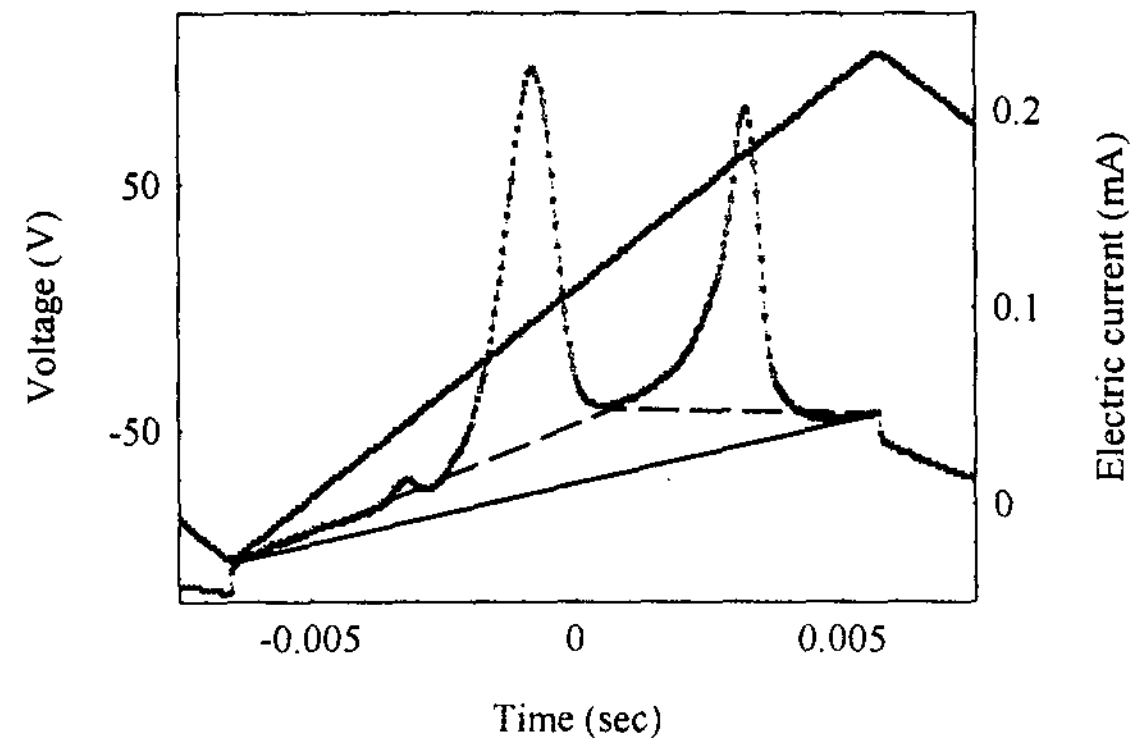

Figure 2: Time dependence of the polarization current under triangular voltage excitation. The value of polarization determined by the area above the straight line is 1160 nC/cm².

Detailed physical studies [11] indicate that the antiferroelectric state has an anticlinic director structure with a tilt angle of 49°. This is close to the orthoconic situation, but it should result in observable birefringence if the layer polarizations were normal to the substrates. The negligible birefringence and the V-shape form of the switching below the transition to the ferroelectric state indicate that the polarization is parallel to the substrates in the relaxed transformed state. This is also corroborated with the observed kinked background of the polarization current curve (dashed line in *Figure 2*), which can be explained as follows. At zero fields the polarization is horizontal and is basically normal to the fields well below the threshold for switching to the ferroelectric state. For small increasing fields therefore the torque acting on the polarization is proportional to the field, leading to a linear increase of the polarization component parallel to the electric field. In addition, the effective dielectric constant of the material is varying linearly with the voltage *V*. As $V \propto t$ the time dependence of the relevant dielectric constant (and hence the cell

capacitance) can be written as: $\varepsilon(t) = \varepsilon(0) + \varepsilon_a^{\pm} \dfrac{2t}{T}$,

where $\varepsilon_a^{-} = \varepsilon_{FE} - \varepsilon_{AF}$ for *t<0*, during relaxation from the *FE* toward the *AF* structure, and $\varepsilon_a^{+} = \varepsilon_{AF} - \varepsilon_{FE}$ for *t>0*, when switching from the *AF*

to the *FE* state. This gives a contribution to the capacitive current as $\frac{A}{L}\varepsilon_o \cdot \varepsilon_a \cdot \frac{dV}{dt} \cdot \frac{2t}{T}$, where $A = 2.5\,10^{-5}m^2$ is the electrode area, $L=4\mu m$ is the sample thickness and $\varepsilon_o=8.95\,10^{-12}\,AsV^{-1}m^{-1}$, and $T=0.01$ is the time period of the applied voltage. With $\varepsilon_a^- > 0$ the slope is positive for $t<0$, and is negative $t>0$ just as seen by the dashed lines in *Figure 2*. From the slopes of the dashed lines and of the voltage form we get that $|\varepsilon_a|\sim 10$. This value is in reasonable agreement with the direct dielectric measurements [11], and makes us confident that the polarization is parallel to the substrates at zero fields.

Such a structure is illustrated in Figure 3/a. When the material is switched to the ferroelectric state the structure becomes synclinic with electric polarizations along the field (normal to the substrates). In this case the optical axis is determined by the tilt angle $\theta=49°$, which results in a small rotation of the extinction crosses of circular domains under field reversal as observed experimentally. [9] The director and layer structures of the ferroelectric states in positive and negative fields are sketched in Figure 3/b and c.

a

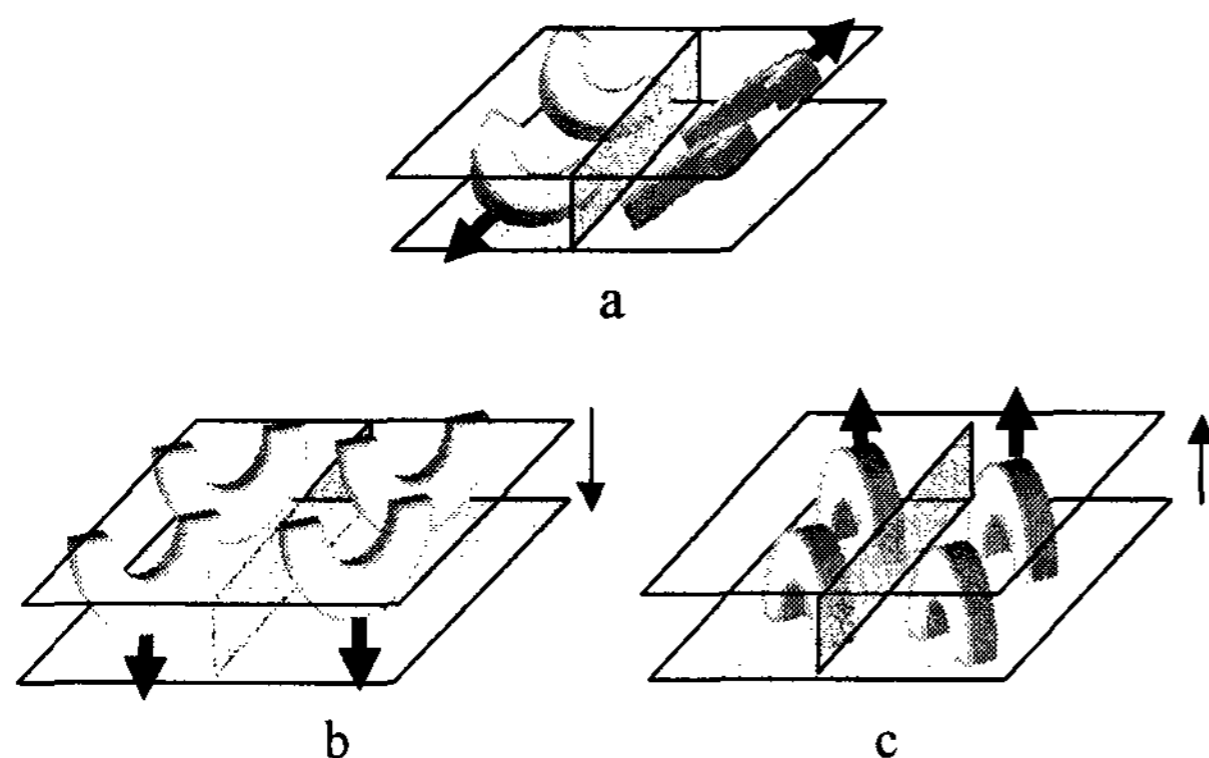
b   c

Figure 3: Director and layer structures of the polar smectic C (SmCP) phase in the bookshelf texture. (a) Antiferroelectric state; (b) Ferroelectric state with polarization pointing Up; (c) Ferroelectric state with polarization pointing Down.

The birefringence of the structures can be estimated from the anisotropy of the electronic polarizability normal to the light propagating through the sample. The electronic polarizability is mainly coming from the conjugated phenyl rings situated in the arms of the bent-shape molecules. We consider kinked molecules with opening angle Φ. We choose the orthogonal

local coordinate axes X', Y', Z' so that the king direction is along X', and the director (along the end-to-end distance of the averaged molecules) is along Z'.
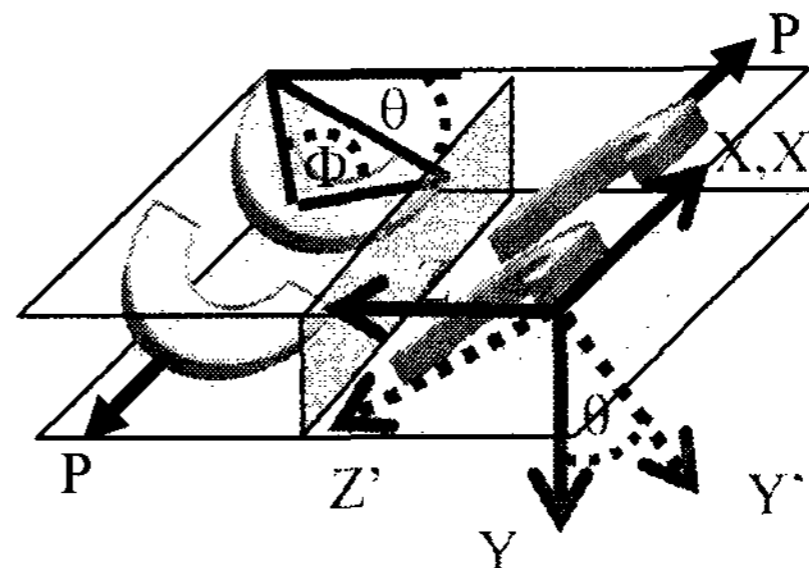

Figure 4: Parameters and coordinate system in the optically isotropic antiferroelectric state.

In the $X'Y'Z'$ frame fixed to the molecular coordinate system the dielectric constant ε_m can be written as the average of the contributions of the arms.

$$\varepsilon_m = \frac{\varepsilon(\Phi/2)+\varepsilon(-\Phi/2)}{2} = \begin{pmatrix} \tilde{\varepsilon}_1 & 0 & 0 \\ 0 & \varepsilon_2 & 0 \\ 0 & 0 & \tilde{\varepsilon}_3 \end{pmatrix}$$

where

$$\tilde{\varepsilon}_1 = \varepsilon_1 \sin^2\frac{\Phi}{2} + \varepsilon_3 \cos^2\frac{\Phi}{2}$$

$$\tilde{\varepsilon}_3 = \varepsilon_1 \cos^2\frac{\Phi}{2} + \varepsilon_3 \sin^2\frac{\Phi}{2}$$

(1)

In bookshelf geometry of the anticlinic antiferroelectric state the molecular planes are tilted with respect to the XZ plane of the substrate by angle θ, and the ratio of the X and Z components of the electronic polarizability will depend on Φ and θ. The dielectric tensor of the laboratory system is obtained via rotation of the coordinate system around X' by the tilt angle θ.

$$\hat{\varepsilon}_l = \begin{pmatrix} \tilde{\varepsilon}_1 & 0 & 0 \\ 0 & \varepsilon_2\cos^2\theta + \tilde{\varepsilon}_3\sin^2\theta & \sin\theta\cdot\cos\theta(\tilde{\varepsilon}_3 - \varepsilon_2) \\ 0 & \sin\theta\cdot\cos\theta(\tilde{\varepsilon}_3 - \varepsilon_2) & \varepsilon_2\sin^2\theta + \tilde{\varepsilon}_3\cos^2\theta \end{pmatrix}$$ (2)

The projection of the dielectric tensor to the X,Y,Z axes then expressed as

$$\begin{pmatrix} \varepsilon_x \\ \varepsilon_y \\ \varepsilon_z \end{pmatrix} = \begin{pmatrix} \tilde{\varepsilon}_1 \vec{X}' \\ \left(\varepsilon_2 \cos^2 \theta + \tilde{\varepsilon}_1 \sin^2 \theta \right) \vec{Y}' + \sin \theta \cos \theta \left(\tilde{\varepsilon}_1 - \varepsilon_2 \right) \vec{Z}' \\ \sin \theta \cos \theta \left(\tilde{\varepsilon}_1 - \varepsilon_2 \right) \vec{Y}' + \left(\varepsilon_2 \sin^2 \theta + \tilde{\varepsilon}_1 \cos^2 \theta \right) \vec{Z}' \end{pmatrix} \quad (3)$$

The material is optically isotropic if the conditions $|\varepsilon_X| = |\varepsilon_Y| = |\varepsilon_Z|$ are fulfilled. The condition $|\varepsilon_X| = |\varepsilon_Z|$ means that the film is homeotropic for light normally incident for a material with bookshelf geometry. Assuming uniaxial arms ($\varepsilon_1 = \varepsilon_2$) Eq.(3) gives that

$$\Phi = 2 \tan^{-1} \left(1 / \cos \theta \right) \quad (4)$$

The isotropic condition for the light normally incident to the YZ plane (viewing the film along the smectic layers parallel to the substrates) is fulfilled for

$$\theta = 45° \quad (5)$$

or if $\varepsilon_2 = \varepsilon_3$ (which would be true only for disc-like arms). Finally the optically isotropic condition for the light incident normal to the XY plane requires that

$$\Phi = 2 \tan^{-1} \left(1 / \sin \theta \right) \quad (6)$$

In these approximations a completely optically isotropic condition can be obtained by combining Eq.(4)-(6). These give that the ideal parameters for optically isotropic state are:

$$\theta = 45° \ and \ \Phi = 109.5° \quad (7)$$

In a number of banana-shaped liquid crystals the observed tilt and opening angles are very close to these 'ideal' values. Note that for the experimentally studied *Pbis11BB* the angles are $\theta=49°$ and $\Phi\sim114°$ [11], which obeys the homeotropic condition of Eq. (4) and also near the conditions of Eqs. (5) and (6) explaining the negligible birefringences for oblique incidences.

In the ferroelectric transformed state (*Figure 3*/b and c) the birefringence is comparable to rod-shape liquid crystals, since the molecular planes are along the light beam.

Finally we emphasize that an antiferroelectric anticlinic bent-core liquid crystal with the above calculated 'ideal' parameters can be used in displays which provides sub-millisecond switching and very wide viewing angle without the need of precise uniform alignment control. These features offer both scattering type (without polarizers) and electrically controllable birefringent (with polarizers) displays. The feature that the birefringence continuously varies

without the change of the optic axis may find application in beam-steering devices, too.

4. Acknowledgement

5. References

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