# Bent Core Nematics

## Alignment and Electro-Optic Effects

Omaima. A. Elamain

**UNIVERSITY OF GOTHENBURG**

Cover: Snapshot of the texture of BC nematic ClPbis10BB filled in the cell with cell gap of 1.89 $\mu m$. The photograph is taken at 100°C at heating.

# Dedication

This dissertation is completely dedicated to the memory of my father
**Abubaker Osman**... who passed away on April 24, 2011.
I miss you every day and I hope this work makes you proud.

# Bent Core Nematics - Alignment and Electro-Optic Effects

**Omaima. A. Elamain**

Department of Physics, University of Gothenburg

**ABSTRACT**

A new class of liquid crystal materials has been recently discovered. These materials are constituting of bent core (BC) molecules. Being initially only of scientific interest, now they attract the interest not only of scientists but also of engineers because of their great potential for applications in liquid crystal displays (LCDs) and photonics devices.

The present study focused mainly on pure BC nematics and their binary mixtures (BC/RL) with a rod-like (RL) nematic related to their

*a*) anchoring properties with respect to a solid surface in contact with these materials

*b*) general behavior under an applied dc electric field, and particular electro-optic response due to the linear coupling with the applied field

*c*) polar electro-optic response due to flexoelectricity.

The conventional methods for obtaining vertical alignment (VA) of the RL nematics were unable to promote VA of the BC and their binary (BC/RL) mixtures, for the concentration less than 20wt%, instead they adopted planar alignment (PA).

In concentration higher than 20wt%, the binary mixtures adopted VA in a very narrow temperature interval below the transition to the isotropic phase; where anchoring transition from VA to PA was observed upon cooling.

Interestingly, field-induced optically isotropic state and switching of the sample optic axis between three mutually orthogonal directions were observed in BC and BC/RL, with concentration less than 40wt%. Due to the similarity in the molecular structures, the above observations were compared with the one observed in anti-ferroelectric liquid crystals (AFLC) with molecular tilt close or equal to 45°. Periodic domain pattern and helical molecular order, with helix axis parallel to the cell substrate and normal to the domains, were found to be formed under an applied dc electric field, as a result of flexoelectricity of the BC materials. Polar flexoelectric response was detected in these materials when subjected to an out-of plane or in-plane low frequency electric field.

# Papers included in this thesis

**I** ***Alignment and alignment transition of bent core nematics***
**Omaima Elamain**, Gurumurthy Hegde and Lachezar Komitov, Appl. Phys. Lett. **103**, 023301 (2013).

**II** ***Field-induced optically isotropic state in bent core nematic liquid crystals: Unambiguous proof of optical biaxility***
**Omaima Elamain**, Gurumurthy Hegde, Katalin Fodor-Csorba and Lachezar Komitov. submitted for publication to Journal of Physics D: Applied Physics, under revision.

**III** ***Optically isotropic state in bent core nematic mixtures with rod like molecules induced by dc electric field***
**Omaima Elamain**, Gurumurthy Hegde, Katalin Fodor-Csorba and Lachezar Komitov, submitted for publication to Journal of APL, under revision.

**IV** ***Periodic pattern formation in a bent core nematic liquid crystal***
**Omaima Elamain**, Gurumurthy Hegde, Katalin Fodor-Csorba and Lachezar Komitov, manuscript to be submitted for publication to Liquid Crystal.

**V** ***Polar In-Plane and Out-of-Plane Switching in Bent Core Nematics Due to Flexoelectricity***
**Omaima Elamain**, Gurumurthy Hegde and Lachezar Komitov, manuscript to be submitted for publication to Journal of Physics D: Applied Physics.

# Contribution Report

The author has made the following contributions to the papers:

**Paper I:** Main author, all experimental work and contributed to manuscript preparation.

**Paper II:** Main author, all experimental work and manuscript preparation.

**Paper III:** Main author, all experimental work and manuscript preparation.

**Paper IV:** Main author, all experimental work and manuscript preparation.

**Paper V:** Main author, all experimental work and contributed to manuscript preparation.

# Abbreviations

| | |
|---|---|
| $AC$ | Alternating current |
| $AFLCs$ | Anti-Ferroelectric liquid crystals |
| $BC$ | Bent core molecules |
| $BCLCs$ | Bent core Liquid Crystal |
| $BCN$ | Bent core nematics |
| $DC$ | Direct current |
| $DSM$ | Dynamic scattering modes |
| $EHC$ | Electro-hydrodynamic Convection |
| $FE$ | Flexolectric effect |
| $FEO$ | Flexo-electro -optics |
| $HAF$ | Horizontal anti-ferroelectric |
| $HAN$ | Hybrid aligned nematics |
| $ITO$ | Indium Tin Oxide |
| $LC$ | Liquid crystal |
| $LCDs$ | Liquid crystal displays |
| $NMR$ | Nuclear magnetic resonance |
| $PA$ | Planar Alignment |
| $PDLCs$ | Polymer disperte liquid crystal |
| $PS$ | Pattern Stripe |
| $RL$ | Rod-Like |
| $TA$ | Twisted Alignment |
| $TN$ | Tilted Alignment |
| $ULH$ | Uniform Lying Helix |
| $UV$ | Ultra Violet |
| $VA$ | Vertical alignment |
| $XRD$ | X-ray Diffraction |

# Contents

# Chapter 1

# Introduction

Conventional liquid crystals, are a well-known example of viscoelastic fluids and far from being scientific curiosity anymore. Liquid crystal state of matter and the related phenomena with this state of matter are actually common topics in academic books [1, 2, 3] and also in our daily life.

Liquid crystal (LC) phases of compounds composed of bent core (BC ) molecules, known as" banana shaped molecules", on the other hand represent a rather newly discovered class of liquid crystals. These have evoked considerable attention during the last decade, due to the influence of novel and peculiar polar switching in spite of their achiral molecules.

## 1.1 Aim

The aim of this work has been to investigate the characteristic properties of BC liquid crystals, especially those exhibiting nematic phases, and their mixtures with a calamitic, rod-like(RL) mesogen with different concentrations.

The project had a focus on the following topics:

1. Alignment of BCs and their binary mixtures with RL nematic.

It was necessary, as a first step in the experimental work performed on the BC materials, to study and understand the influence of the alignment conditions on the actual alignment of these materials, in a conventional sandwich cells usually used for preforming study on such materials.

2. Behavior of a BC nematic and BC/RL mixtures subjected to an applied dc electric field. The study performed on this topic was focus on several phenomena related to

• Electro-optic response due to the polar coupling between the dc field and the net molecular dipole moment of the BC molecules

• Periodic domain pattern formation in BC nematics

• Electro-optic response in an initially deformed nematic layer, the so called hybrid aligned nematic (HAN).

# Chapter 2

# Liquid Crystals Basics

The Austrian botanist Friedrich Reinitzer [2] was the first one who recorded the observation of the liquid crystal phase in 1888 while heating cholesteryl benzoate. This substance was called a liquid crystal because it showed phases intermediate between crystalline solid and isotropic liquid. Liquid crystal molecules are highly anisotropic in shape, like rods, disks or bananas. The molecules in liquid crystal phase exhibit long-range orientational ordering and sometimes partial positional ordering.

Liquid crystal phases brought by purely thermal processes are labeled as thermotropic [3]. However, it is worth mentioning that another type, known as lyotropic liquid crystals, exists. In this case, some amphiphilic compounds show mesomorphism as a function of concentration, when mixed with certain solvents [1, 4].

The thermotropic liquid crystals are, in their turn, classified depending on the molecular shape. The most common shape is a rod-like(RL) and the liquid crystals with such molecules are called calamitic LCs (Fig. 2.1). They have a rigid core, typically composed of benzene rings, and flexible tails. The molecular rigid
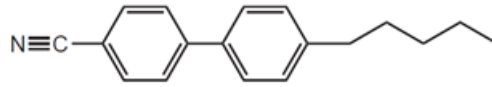
*Figure 2.1: The molecular shape of liquid crystal,5CB.*

core may have a kink (bend) thus forming a banana shaped molecule.

The simplest LC phase is called the nematic phase. The term nematic comes from the Greek word for "threads" [1, 5] and refers to the thread-like defects observed in nematics (Fig 2.2). Molecules in the nematic mesophase have a preferred direction of orientational order, known as the director $\mathbf{n}$ , but they have no positional long-range order.

For uniaxial nematics the preferred direction is characterized by a director $\mathbf{n}$ , which does not distinguish between head and tails [3, 6]. The degree of order in a
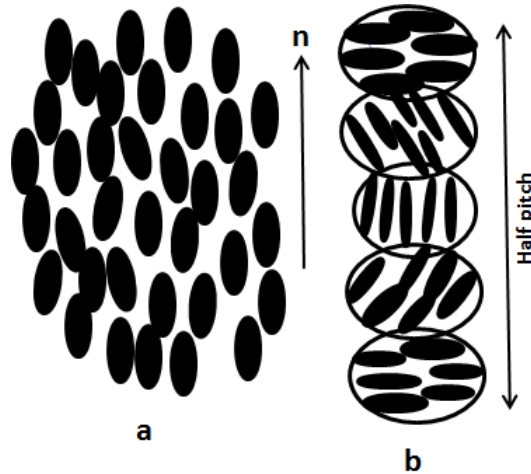


*Figure 2.2: The molecular ordering in nematic and Cholesteric phase liquid crystals.*

nematic LC is typically computed by the order parameter $\mathbf{S}$ given by (2.1)

$$\mathbf{S} \;=\; \frac{1}{2}\langle 3\cos^2\theta - 1\rangle, \tag{2.1}$$

where $\theta$ is the angle between the director and the local molecular orientation. For a perfectly ordered nematic, $\mathbf{S}$ has a value of 1, while for an isotropic sample $\mathbf{S}$ has a value of 0. The order parameter is a proper way of quantifying the degree of molecular order in the liquid crystal, and it affects the anisotropy of liquid crystal material properties, such as the birefringence (optical anisotropy) and the dielectric anisotropy [2, 5].

The smectic phases (Fig 2.3), which are found at lower temperatures than the nematic, form well-defined layers that, can slide on top of each other. The smectics exhibit positional order along one direction perpendicular to the smectic layers. In the smectic A phase, the molecules are oriented along the layer normal, while in the smectic C phase they are tilted away with respect to the smectic layer normal.
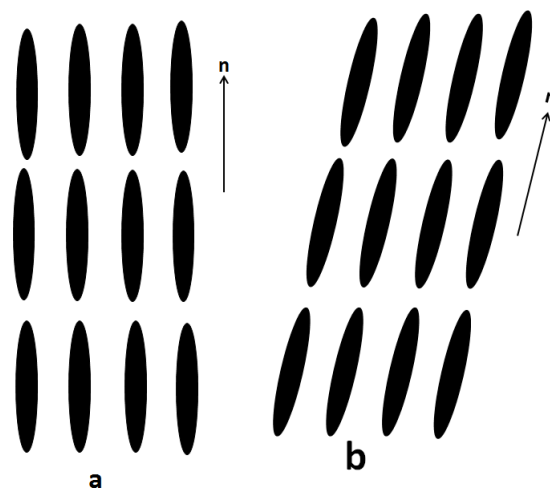


*Figure 2.3: The molecular ordering in a) smecticA phase and b) smectic C phase.*

## 2.1 Chirality

In some cases the molecules of the nematic LC phase lack mirror symmetry, since they are chiral, and such LCs are known as chiral nematic or cholesteric (Fig.2.2), where the molecules form a helical order [3, 7].

In some smectic LC, if the molecules are chiral, the existence of the layers add more restriction in forming a helical order of the molecules and the chiral nature expresses in twist across the layers. In Sm A phase the director n is parallel to layer normal.

As a consequence there is no way for forming a helix even though the molecules are chiral. Only for molecules with very strong twisting power, as in TGB phase,the $SmA^*$ phase consist of blocks of SmA layers forming a helicoidal layer structure. In the chiral smectic A phase, an electric field applied along the smectic layers induced polarization perpendicular to the layer normal.

The later result in a molecular tilt proportional to the field strength. This effect is known as electroclinic effect [8].

In chiral semectic C, the LC molecules usually possess a permanent dipole moment at some arbitrary angle with respect to the long molecular axis, and a helix can develop along an axis parallel to the smectic layer normal.

The phase is called chiral smectic C, which possesses a spontaneous polarization and therefore exhibits ferroelectric properties [8, 9]. Therefore the chiral $SmC^*s$ are called ferroelectric LCs or FLCs.

## 2.2   Anti-ferroelectrics

The anti-ferroelectric liquid crystal (AFLCs) materials are also chiral smectic liquid crystals with molecules tilted in an opposite direction in the adjacent layers ( Fig2.4), which is the so called anticlinic molecular order. The direction of the spontaneous polarization in AFLC is alternating on passing from one layer to the next and therefore the total spontaneous polarization of AFLC is zero.

Since the smectic layers of AFLC have dimension much smaller than the light
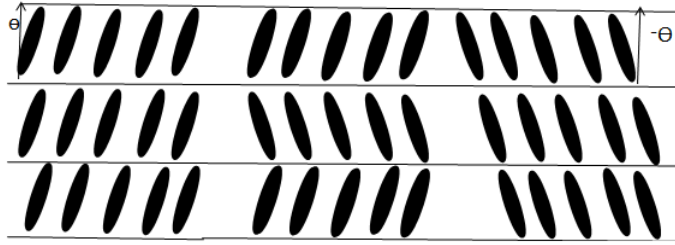


*Figure 2.4: Schematic presentation of the field induce FLC state in AFLC state.*

wavelength, the light will be not sensitive to the AFLC structure. Therefore the alternating tilt in the adjacent layers result in an effective dielectric tensor, which is the average of the dielectric tensors associated with the two types of layers alignment in AFLC [8]. These tensors represent two SmC with different molecular tilts $((+\theta)$ and $(-\theta)$, respectively). Since the smectic layers have dimension much smaller that the light wave length , the light will be not sensitive to the AFLC structure. The resulting dielectric tensor is

$$\varepsilon_{anticl} = \frac{1}{2}[\epsilon_{syncl}(+\theta) + \epsilon_{syncl}(-\theta)] = \begin{pmatrix} \varepsilon_\perp cos^2\theta + \varepsilon_\parallel sin^2\theta & 0 & 0 \\ 0 & \varepsilon_\perp & 0 \\ 0 & 0 & \varepsilon_\perp cos^2\theta + \varepsilon_\parallel sin^2\theta \end{pmatrix}.$$

$$(2.2)$$

In some AFLCs with a so-called horizontal antiferroelectric (HAF)state, when the tilt angle in the adjacent layers becomes 45°, the AFLCs material exhibits an optically zero in-plane birefringent $\Delta n = 0$. The material then appears completely dark between cross polarizers.

The optical axis of these materials switches between three mutually perpendicular directions. This was experimentally confirmed using a $\lambda$-red plate inserted between the AFLCs sample and the analyzer at 45 °.

This in turn caused either an increase or a decrease of the total phase retardation of the sample depending on the polarity of the applied electric field [10].

## 2.3   The Bent Core liquid crystals

Conventional liquid crystal molecules normally rotate freely along this symmetry axis since the rotation about the symmetry axis does not affect the order parameter, unless there is no symmetry requirement [11, 12].

From this viewpoint, molecules with shapes deviating from a rod, such as bent shape, have been thought of as "bad" molecules for forming liquid crystals. Thus, only a very few bent-core molecules have been synthesized before the discovery of their polar behavior.

Within the past two decades, great interest has been developed in the liquid crystalline properties of banana shaped mesogens. These mesogenes have the same chemical composition and basic chemical architecture of conventional calamitics, but have a sharp bend within the linkage of the core group which result in unique liquid crystal phases having no counterpart in conventional calamitic liquid crystals.

BCLCs have attracted scientific interest for their unique properties compared to conventional calamitic liquid crystals. Even though their differences, they share the same basic macroscopic phase classification (isotropic, nematic, smectic) [13, 14, 15].

### 2.3.1   Basic Thermotropic Liquid Crystal Phases of Bent Core Molecules

The Vorländer group synthesized the first bent-core liquid crystals in 1929, but the mesophases were not reported [12, 16]. The first bent-core liquid crystal compound reported in the literature was published in 1932 [12, 17].

In the early of 1990s a new wave of synthesis and research of bent-core molecules

began, and many of novel phases and interesting physical properties were discovered [18].

The phases of bent-core materials reported so far include the isotropic and nematic phases, the so called $B_1$ to $B_8$ smectic phases, a subset of which are distinctive bent-core smectic phases, and several other smectic phases with direct analogues to calamitic liquid crystals.

### 2.3.2   Smectic Phases of Bent-Core Molecules Phase

The bent-core molecular architecture favors close packing of the molecules into layers, therefore it is not so surprising that the best-characterized BCLCs are smectics exhibiting direct isotropic-smectic transitions. The tilted smectic structure is in fact the most common smectic structure in BCLCs.

BCLC smectic layers can be spontaneously polar without the usual requirement for calamitics, i.e. that the molecules possess a chiral center [19].

Niori [20] presented the first obvious example of ferroelectricity in banana shaped achiral molecules, ascribing the polar packing of the molecules. Link [21] reported on the spontaneous formation of chirality in a smectic phase of banana shaped achiral molecules, a chiral layer structure with a handedness depending on the tilted molecular direction.

Weissflog [22] published that ferroelectricity could be detected for one of the mesophases in some achiral banana-shaped molecules by varying direction of connecting groups and substituents.

### 2.3.3   The Nematic Phase of Bent-Core Molecules

The existence of nematic phase in BC liquid crystals is rather unusual, due to the fact that the bend molecular shape is not commensurate with the translational

freedom of the nematic phase. Never the less a new generation of nematic liquid crystals was recently designed based on achiral bent core molecules.

The nematic phase of these BCLCs showed unique properties such as chiral domains with opposite handedness under electric field application [23], gaint flexoelectricity[24], possibility of biaxial physical properties and a polar switching [25, 26].

The relationship between chemical structure and mesophase behavior known in calamitic liquid crystals cannot be applied to bent mesogens.

The question arises how the BC compounds have to be constructed to be able to form nematic phase. Different aspects should be taken into account: the size of the molecules, the position as well as the magnitude of the bend which should be in the range 135 ° or 140 °, the influence of substituents and linkage groups, and the length of the terminal chains [27, 28, 29].

The basic rule that a bend of the molecules is unfavorable for the formation of mesophases is also valid for banana shaped liquid crystals. Therefore, liquid crystalline properties are rarely described for strongly angled mesogens having two, three or four aromatic rings [28, 29].

# 2.4 Anisotropic physical properties of liquid crystals

The ordered structures of anisotropic molecules make the macroscopic physical properties of liquid crystals as well anisotropic.

## 2.4.1 Dielectric anisotropy

Almost all liquid crystal molecules have dipoles, and the sum of these dipoles is the polarization which is linearly proportional to the applied electric field E as

$$P = \epsilon_{\circ} \chi_e E, \tag{2.3}$$

where $\varepsilon_{\circ}$ is the permittivity of the free space and $\chi_e$ is the electric susceptibility. The electric displacement induced in the material by electric field is defined as

$$D = \epsilon E, \tag{2.4}$$

where $\epsilon$ is the dielectric permittivity of the material.

The dielectric permittivity $\epsilon$ of a material is defined as the ratio of the capacitance $C_{mat}$ of the parallel plate capacitor that contains the material to the capacitance $C_{vac}$ of the same capacitor that contains a vacuum

$$\epsilon = \frac{C_{mat}}{C_{vac}}. \tag{2.5}$$

The interaction between a liquid crystal and an electric field is dependent on the magnitude of the dielectric permittivity measured parallel $\epsilon_{\parallel}$ and perpendicular $\epsilon_{\perp}$

to the director and to the difference between them i.e., the dielectric anisotropy $\Delta\epsilon$ (See Eq 2.5). The dielectric permittivity measured along the x axis is unique, whereas the dielectric permittivities measured along the y and z axes are identical in uniaxial nematics. it can be expressed as

$$\Delta\epsilon = \epsilon_{\parallel} - \epsilon_{\perp}. \tag{2.6}$$

The dielectric constants $\epsilon_{\parallel}$ and $\epsilon_{\perp}$ are measured for vertical and planar alignment of the liquid crystal material in the capacitance $C_{mat}$ , respectively. The magnitude of the dielectric constance dependent on the temperature, (see Fig 2.5), and the frequency of the applied field up to the transition to the isotropic liquid, i.e, up to the clearing point.

Above the clearing point, the dielectric constants measured along all three axes are equal due to the isotropic nature of the liquid(isotropic) phase and, therefore, the dielectric anisotropy is zero.

The application of an electric field can easily reorient the the liquid crystal molecules due to their dielectric anisotropy.

From this interaction we obtain an additional term in the free energy density according to [7]

$$F_{diele} = -\frac{\epsilon}{8\pi}E^2 - \frac{\Delta\epsilon}{8\pi}(n \cdot E)^2. \tag{2.7}$$

The coupling between the dielectric anisotropy and the applied electric field (the dielectric coupling)is described by the second term, which is the dielectric response.
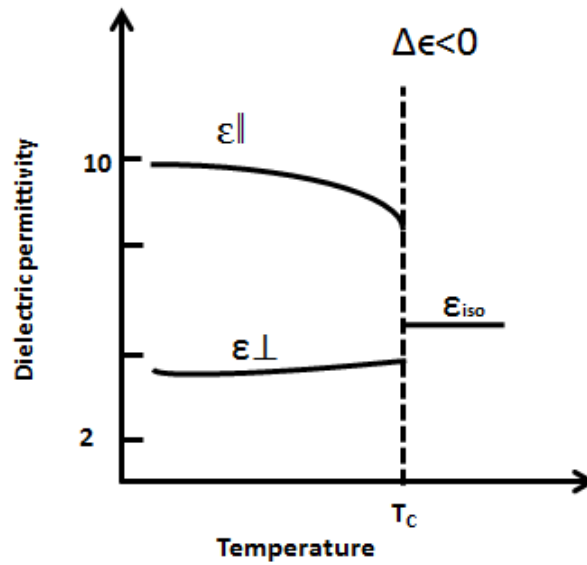
Figure 2.5: *Temperature dependence of the liquid crystal dielectric constants $\epsilon_{\parallel}$ and $\epsilon_{\perp}$*

## 2.4.2   Optical anisotropy

In uniaxially nematics and smectic liquid crystals the light traveling through a birefringent medium will take two paths depending on its polarization direction, parallel or perpendicular with respect to the optic axis of the material, corresponding to two refractive indices, ordinary $n_o$ and extraordinary $n_e$.

Hence be $n_o$ is the index experienced by a light ray with its plane of vibration perpendicular to the optical axis, coinciding with the long molecular axis, while $n_e$ is observed by a linearly polarized wave with the vibration plane parallel to the optical axis.

The optical anisotropy is defined as

$$\Delta n = n_{\parallel} - n_{\perp}, \tag{2.8}$$

where $n_e$ and $n_o$ are the light refractive indices parallel and perpendicular to the optic axis, respectively [1, 3].

### 2.4.3  Uniaxial and biaxial liquid crystal

The uniaxial phase, translationally ordered LCs with a rotational symmetry axis, is the simplest one. This phase has a single director, n, describing the preferred alignment direction of the orientationally ordered molecules.

The biaxial phase lack rotational symmetry and the LC is characterized by three orthogonal directors a primary director n and two secondary directors l and m forming an ellipse.

In the biaxial mesophase, there is a partial molecular orientational order in three dimensions without translational order.
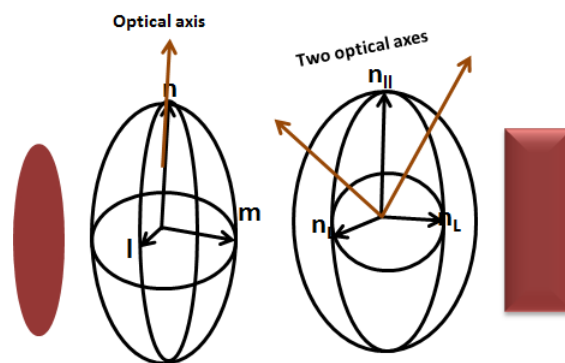


*Figure 2.6:  Uniaxial nematic (left) and biaxial nematic (right) phases and their corresponding indicatrices.*

## 2.4.4    The biaxial-uniaxial nematic transition

The nematic liquid crystals, which is known to be a uniaxial. M.J. Freiser [30] predicted theoretically the existence of the biaxial phase in nematic LCs due to the reduction of the molecular symmetry. Starting with the discovery of biaxiality in lyotropic nematic[31] a new class of materials open for study and utilization.

The biaxiality was demonstrated in thermotropic nematic phase in early 2004 in the so called bent core nematics BCNs [26, 32].

In the biaxial nematic phase, fast switching and wider viewing angles are predicted [33].

The homeotropic alignment of BCN offers a straightforward approach to discriminate between uniaxial and biaxial nematic within the nematic range by means of optical observations, since the birefringence goes to zero in the uniaxial while it does not in the biaxial case.

The optical conoscopic measurement are usually used to confirm the uniaxial or biaxial character of the LCs [34].

## 2.5 Continuum Theory

The lowest free energy state for a non-chiral nematic is one in which all the mesogens are uniformly aligned parallel to one preferred direction assigned as the director. In fact, thermal fluctuations hold off realization of this low energy state, and the molecules fluctuate around the preferred direction.

Furthermore, uniform alignment may be inconsistent with boundary conditions or external fields.

Understanding the energy of these deviations from uniform alignment is important in order to predict the equilibrium state of nematics.

This free energy can be expressed as a sum of undistorted free energy $F_0$ and distorted free energy $F_d$, which comes from the bulk elastic distortion.

$$F_r = F_0 + F_d. \tag{2.9}$$

Generally, the elastic distortion in LCs can be presented as a combination of three types of elastic distortions, namely splay, bend and twist (Fig 2.7) [1, 9].

$$F_d = K_1(\nabla \cdot n(r))^2 + K_2(n(r) \cdot \nabla \times n(r))^2 + K_3(n(r) \times \nabla \times n(r))^2. \tag{2.10}$$

Each of these deformations is associated with elastic constants K1 , K2 , and K3 , respectively, which in general are temperature dependent.

The LC elastic free energy density $F_d$ is also known as the Frank - Oseen elastic energy density and expressed in Eq(2.10).

SPLAY $k_{11}$          TWIST $k_{22}$          BEND $k_{33}$

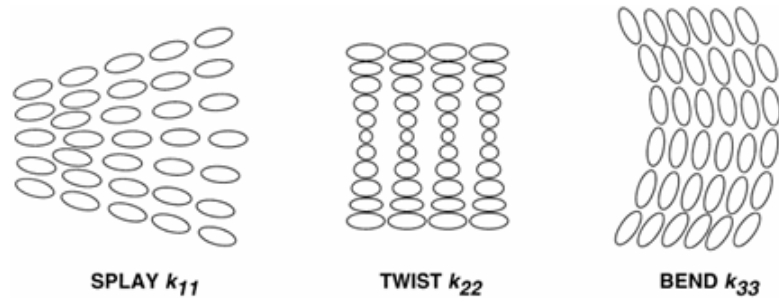*Figure 2.7: Schematic representation of the three principal types of deformation in a nematic phase.*

The description of the distorted free energy is significantly simplified if the so called one-elastic constant approximation, where K 11 = K 22 =K 33, is used. In this case the Frank-Oseen equation becomes.

$$F_d = \frac{K}{2}(\nabla \cdot n(r))^2 + (n(r) \times \nabla \times n(r))^2. \tag{2.11}$$

## 2.6    The Flexoelectricity

The flexoelectricity is a general physical property of LCs. It is the coupling between electric polarization and elastic deformations in liquid crystals. It was first predicted for a nematic liquid crystal by Meyer [35] 40 years ago [2]. Flexoelectricity has the potential to serve as the basis for a wide variety of technologies relying on electromechanical coupling. Electro-optic effects arising from the coupling between flexoelectric polarization and the applied electric field have been proved to be very attractive also for display applications [36].

### 2.6.1    The basic of flexoelectricity

The presence of the polarization P in liquid crystals (LCs) in response to elastic deformations, which appears in the case of asymmetric polar molecules (Figure 2.10), is known as the flexoelectric (FE) effect [2].
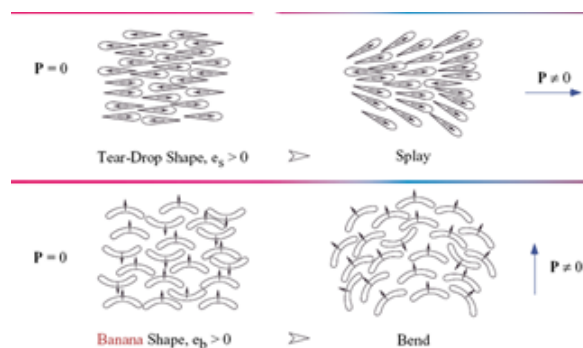


*Figure 2.8: Flexoelectric effect. Structure of an undeformed nematic liquid crystal with drop and banana shaped molecules, respectively, and the same subjected to splay and bend deformation, respectively.[37].*

In the nematic phase, splay and bend deformations give rise to polarization characterized by two independent flexoelectric (FE) coefficients splay ($e_s$) and bend ($e_b$) respectively. Their contributions to the induced polarization can be written as

$$P = e_1 n.\nabla n + e_3(n \times \nabla \times n) \tag{2.12}$$

In case of nonpolar molecules the FE effect originates from the gradient of quadrupole moment density (Fig.2.11)[2].
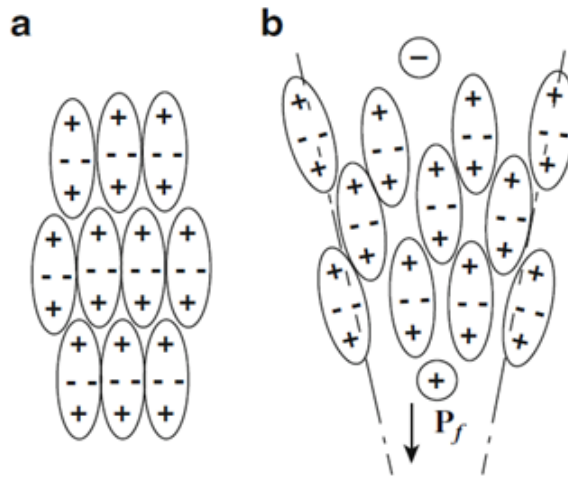


*Figure 2.9: Quadrupolar flexoelectric polarization , $P_f$. Undistorted state a), and appearance of polarization due to the splay distortion b).*

Such polarization does neither need shape asymmetries nor dipole moments in mesogenic molecules, and can easily be observed in a cell with hybrid alignment due to its intrinsic bend-splay distortion.

Flexoelectric polarization can influence electro- optical properties, defect formation and structural instability[6].

## 2.6.2 Flexoelectric effects in Cholesteric

An interesting consequence of the flexoelectric coupling is the so called chiral flexo-electro-optic (FEO) effect[37, 38], which is observed in a short pitch cholesteric aligned in uniform lying helix (ULH) texture. The ULH refers to a texture of uniformly aligned cholesteric, in which helical axis lies parallel to the glass substrates along a preferred direction.

When an electric field applied normal to the helical axis of the cholesteric liquid crystal sample, the molecules in the ULH texture will simultaneously rotate in the plane of the sample around the direction of the electric field forming a periodic splay- bend pattern and thus induced flexoelectric polarization [39].

This pattern is created by a simultaneous rotation of all molecules around the direction of the applied field. In short pitch cholesteric, however, the helical axis takes on the properties of the optical axis, and the optic axis of the sample will follow the rotation of the molecules. This rotation of the optical axis is almost linearly proportional to the applied electric field.

Where flexoelectric deformation can be seen as splay- bend [38, 40]. This polarization reduces the free energy by -P.E where P is given by Eq2.12. Hence, the molecular rotation increases until the flexoelectric torque is balanced by the electric torque. The induced deviation of the optical axis (E) is found to be

$$\Phi(E) = \arctan(\frac{e_f E p_0}{2\pi K}), \tag{2.13}$$

where $e_f$ is the avearage flexelectric coefficient $e_f = \frac{e_s + e_b}{2}$, $p_0$ the pitch and $K$ the average elastic coefficient for splay -bend deformations.

This formula simplified to

$$\Phi(E) = \frac{e_f E p_0}{2\pi K} \tag{2.14}$$

if the angle is small the simple behaviour described in Eq 2.14 is generally perturbed by the dielectric coupling which tends to unwind the cholesteric helix, limiting the linear regime of the flexoelectrocoptic effect[40].

The ULH is intrinsically unstable since it is incompatible with both planar and homeotropic alignments. However, an appropriate design of the liquid crystal (LC) molecules surface anchoring stabilizes the helix [38, 39, 40, 42]. The ULH texture could be also stabilized by creating a polymer network in the liquid crystal bulk. The case of the FEO effect is of particular interest, first of all, the response times of this effect in short pitch cholesteric materials are in the microsecond range.

In addition, the FEO can show a small temperature dependence, since both the average flexoelectric coefficients $e_f$ and the average elastic constant K are scaled quadratically with the nematic order parameter S [42].

By choosing chiral LC mixtures with a temperature compensated pitch, it is possible to obtain an electro-optic characteristics which are temperature independent[39, 41].

This makes the FEO effect potentially attractive and useful for applications such as wide viewing angle displays, due to the in-plane switching and grey scale capability as well as the sub-millisecond light shutters.

## 2.7 Fredricks transition

The combination of an external magnetic or electric fields, and a confined surface can distort the director field. A nematic liquid crystal cell has two plates treated in a way which leads to surface interactions that impose a specified orientation on the liquid crystal.

Fig2.10 shows a nematic liquid crystal slab, confined between parallel plates, with strong planar anchoring. When an external field is applied to the cell, it is found
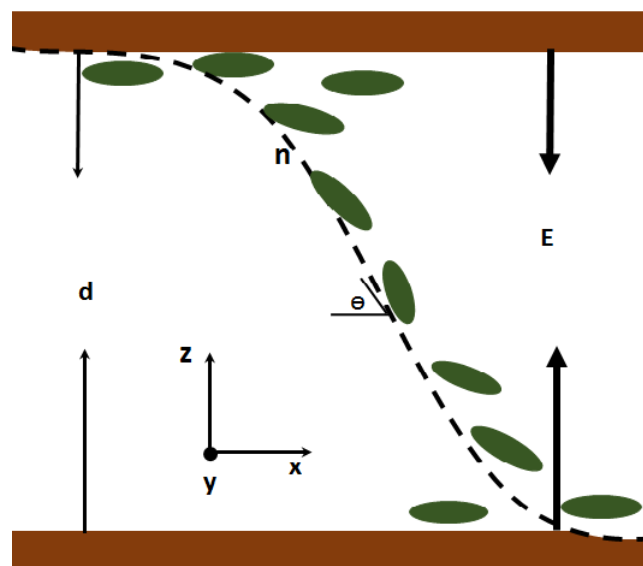


*Figure 2.10: Deformation of the director profile above the threshold field in planar oriented nematic liquid crystal sample.*

that a critical field exists below which no distortion occurs.

The bifurcation defined by the lowest critical field is conventionally called a Fredericks transition.

At a sufficiently high field, the dielectric torque forces the molecules into the field

direction if $\Delta\varepsilon > 0$, and this field is defined by

$$V_c = (\frac{\pi K_{ii}}{\Delta\varepsilon\varepsilon_0})^{\frac{1}{2}}, \tag{2.15}$$

If the elastic deformation is splay or bent then $K_{ii}$ consider to by $K_{11}$ and $K_{33}$ [1, 2, 3, 6]. This Fredericks transition give rise to quadratic electro-optic effect. The applied electric field disturbs the director orientation, a process which is governed by the generation of the bent /splay deformations. The equation of motion of the director is for the case of infinite anchoring energy and it will be balanced by the torque due to elastic and viscosity forces. This can be expressed by

$$k\frac{d^2\phi}{dz^2} + E^2\Delta\varepsilon\sin(\phi)\cos(\phi) = \gamma\frac{\partial\phi}{\partial t}, \tag{2.16}$$

In the limit of a small angle $\phi$ the above equation reduced to linear form

$$k\frac{d^2\phi}{dz^2} + E^2\Delta\varepsilon\phi) = \gamma\frac{\partial\phi}{\partial t}. \tag{2.17}$$

Solving this equation we find

$$\phi = \phi_0 exp(\frac{t}{\tau}).sin(\pi z), \tag{2.18}$$

from which the rise time $\tau_r$ can be calculated as

$$\tau_r = \frac{\gamma d^2}{\Delta\varepsilon V^2 - k\pi^2}. \tag{2.19}$$

At zero field the decay time expressed as

$$\tau_d = \frac{\gamma d^2}{k\pi^2}. \tag{2.20}$$

## 2.8   The Electro- Optic Effects in Liquid Crystal

As introduced in the previous sections, the anisotropic behaviour of liquid crystals is unique which lead, when combined with interaction with an external fields, to the most important application of liquid crystals the one in, namely, liquid crystal displays ( LCDs). Thier operation is based on electro-optic effects in liquid crystals generated by external applied electric field.

Consider the case where a liquid crystal sample is placed between crossed polarizers whose transmission axes are aligned at some angle $\theta$ between the optical axis and the transmission direction of the polarizer. The output intensity then becomes

$$I_{out} = E_{out}^2 = E_o^2 \sin^2(2\theta) \cdot \sin^2(\frac{(2\pi \Delta n L)}{\lambda}) = I_o \sin^2(2\theta) \cdot \sin^2(\frac{(2\pi \Delta n L)}{\lambda}), \quad (2.21)$$

where $L$ is the sample thickness, $I$ is the intensity passed through the sample and $\lambda$ is the light wavelength. The term $(2\pi \cdot \Delta n \cdot L/\lambda)$ represents the phase difference $\delta$ and the equation can be rewritten as

$$I_{out} = I_o \sin^2(2\theta) \cdot \sin^2(\frac{\delta}{\lambda}). \quad (2.22)$$

This equation is the important one in all liquid crystal device applications based on "field controlled light transmission", for a cell inserted between two crossed polarizers.

The first term represents the changes of the transmitted light through the cell due to switching of the cell optic axis in the plane of the cell. This is the case of the electro-optic response due to electro-clinic effect in the smectic $A^*$[43], the ferroelectric switching in ferroelectric LCs [44] and flexoelectric effect in short pitch cholesterics aligned in ULH texture [45].

The second term of Eq 2.22 represents the transmitted light changes due to the out-of-plane switching of the cell optic axis.

Electro-optic effects arising from the out-of-plane switching of the optic axis are electrically controlled birefringence, twisted nematics (TN), etc.

It is worth mentioning that another type of controlling the liquid crystals, known as field controlled scattering, is used in polymer dispersed liquid crystals PDLCs [46].

Generally, there are two conventional ways of applying an electric field in the LCDs namely, across the cell gap (out-of plane) or along the confining substrates (in-plane).

The generated electro-optic response by the electric field could be quadratic or linear.

Depending on the coupling of the electric field with the liquid crystal properties and the way the electric field is applied to the liquid crystal cell.

## 2.8.1   Quadratic Electro-Optic Effects

The coupling between the dielectric anisotropy of the LC material and the applied electric field give rise to a quadratic term in the free energy. Thus the electro-optic response due to this coupling does not depend on the polarity of the field, i.e. is non polar.

For example of such electro-optic response due to dielectric coupling is the one generated by the Fredricks transition and the field induced unwinding of the helix in cholesteric liquid crystal.

## 2.8.2 Linear Electro-Optic Effects

The coupling between an applied electric field and the polarization, spontaneous or induced, which the liquid crystal molecules may possess, add an additional linear term to the free energy defined by

$$F_e = -PE. \tag{2.23}$$

Thus the linear coupling between the applied electric field and the spontaneous or induced polarization of the LC results in an electro-optic response which depends not only on the magnitude of the applied field but also on the polarity of the field. The linear electro-optic effect are attractive for application in LCDs.

Among the linear electro-optic effects the most attractive are those taking place in para-, ferro and antiferoelectric LCs as well the one found in cholesterics aligned in ULH textue.

### 2.8.2.1 Electro-clinic effect

The electro-clinic effect is a special effect allowed by the symmetry in chiral smectics A. It is a field-induced tilt in the director relative to the layer normal in the application of E field along the smectic layers of a chiral smectic A aligned in a bookshelf geometry. The induced tilt $\theta$ of the sample optic axis is in the plane of the sample and depends linearly on the applied electric filed. This is defined as

$$\theta_{ind} = eE = \frac{\mu E}{(\alpha(T - T_c))}, \tag{2.24}$$

where $\theta$ is the induced tilt, $\mu$ and $\alpha$ are thermodynamic and structural coefficients respectively, associated with the response time

$$\tau = \frac{\gamma_\theta}{(\alpha(T - T_c))}.$$                          (2.25)

The response times of the electroclinic effect are in microsecond range and both rise and fall time are equal. A major disadvantages of this effect is the strong temperature dependence of the field induced tilt of the sample optic axis.

## 2.9   Liquid crystals alignment

The alignment of liquid crystals is of vital importance for their study and device applications such as LCDs, for instance. A variety of methods have been developed and used for achieving LC alignment. There are three basic categories liquid crystal alignment - vertical (homeotropic)(VA), planar (PA) and intermediate (tilted). The alignment promoted by the sample substrate surface may be different. Thus, hybrid and twisted alignment could be realized.

### 2.9.1   Vertical (homeotropic) alignment (VA)

The liquid crystal molecules are oriented perpendicular to the confining substrates. The VA is obtained by coating the substrates surface in contact with the liquid crystal by a thin layer made from polyimide like the one produced by Nissan (SE 1211), they contain long alkyl chains sticking out almost perpendicular from the alignment layer surface [47, 48].

### 2.9.2   Planar (homogeneous) alignment (PA)

The liquid crystal molecules are preferably oriented parallel to the surface of the substrates confining the LC slab. Polyimides have been used for the homogeneous alignment layers because of high stability. The unidirectionally buffed polyimide alignment layer orients the liquid crystal molecules parallel to substrate with the long molecular axis of the molecules in the rubbing direction [48]. Mechanical treatment of the alignment layer is a conventional method enabling the achievement of uniform PA. This method is widely used in the LCD industry.

### 2.9.3   Tilted alignment (TA)

The liquid crystal molecules are tilted at a certain angle with respect to the substrates. It can be achieved by oblique evaporation technique [49] or by hard rubbing of specially designed alignment materials. Different LCD modes required different pretilt of the LC molecules anchored to the substrate.
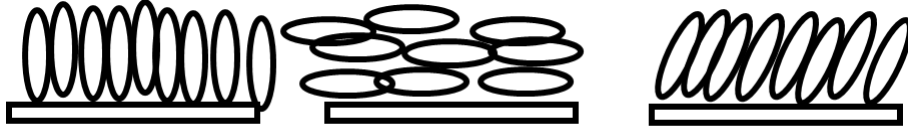


*Figure 2.11: Types of molecular surface alignments.*

Occasional change in the alignment direction, also known as an alignment transition, may occur due to changes in the surface-solid surface interactions. The alignment transition could be induced by temperature or by light [34]. It might be of second or of first order.

### 2.9.4   Hybrid alignment

The hybrid alignment is a combination of the VA at the one confining surface and PA at the other surface. This results in a splay-bend deformation in the liquid crystal layer, (Fig 2.12)[6]. Such is the case of hybrid aligned nematic, known in the literature using the abbreviation HAN. An in-plane electric field applied normal to the deformation plane, i.e parallel to the substrate (the in-plane), will couple to the flexoelectric polarization and induce a twist deformation of this plane. From the twist angle $\phi$ one can calculate the flexoelectric coefficient [50] according to

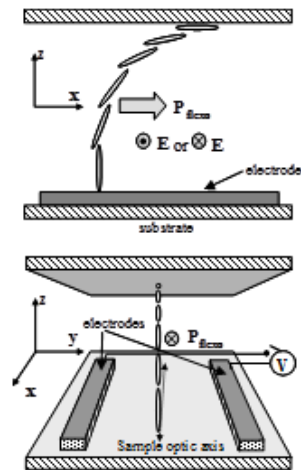$$\phi = -\frac{e^\star E d}{\pi \lambda},\tag{2.26}$$

*Figure 2.12: Schematic presentation of a HAN cell showing the field-induced twist angle ,θ.*

where $\phi$ is the twist angle, E is the electric field, d is the cell thickness, K is the elastic constant and $e$ the average flexoelectric coefficient, e is given by $e = \frac{e_s - e_b}{2}$ and the magnitude $e^\star = \frac{e}{K}$ is a normalized flexoelectric coefficient, which is represent the probational constant between applied field and induced tilt $\phi$.

## 2.10   Electrohydrodynamic Instabilities

Series of effects can be observed in nematic liquid crystals when an applied electric field rises above the Frederics transition, known as Electrohydrodynamic Convection (EHC). It appears as periodic pattern formation in nematic liquid crystal materials driven away from equilibrium.

The character of EHC depends on the anisotropy of the LC material parameters, such as dielectric constant and conductivity, as well as on the cell thickness and frequency of the applied field [6].

The driving force for EHC is the electric volume force acting on space charges that are generated by initial director distortions together with positive conductivity anisotropy.

This mechanism was suggested by Carr[51] and incorporated into a one- dimensional model by Helfrich Helfrich [52]. The first experiments of Williams and Kapustin, who obtained formation of periodic domain pattern [4] were interpreted to show the origin of the normal rolls formation i.e., the roll with axis perpendicular to the equilibrium alignment of the director. Later on, formation of oblique rolls were observed [53].

At higher electric field, the rolls are destroyed and the turbulence regime started. In general, turbulence occurs when a sufficient strong external field is applied to the liquid crystal material [54]. In nematic liquid crystals the turbulent states are called dynamic scattering modes (DSMs)[55].

### 2.10.1   The Instabilities in Bent Core Liquid Crystals

Up to now, very little work has been done on EC in bent-core nematics (BCN). So far several authors have reported on EC in BC nematic liquid crystals forming

spatially non-standard electrohydrodynamic instabilities under application of an electric field with different frequencies.

The bent shape, electrical conductivity changing sign with the frequency of the applied field and the flexoelectricity of the BC nematic material were considered as the mechanisms behind the formation of different periodic domain patterns. They were classified as a) with domains parallel to the director at low frequencies (parallel stripes, PS) as well as b) the regime prewavy 1 and c) prewavy2 , taking place at different threshold voltage and frequencies, with more complicated domain patterns [56].

## 2.10.2 Flexoelectric domains

In some planar nematic liquid crystal cells, the distortions of the director under an applied low frequency electric field appears at certain voltage as a spatially periodic stripes running along the direction of the undisturbed initial director (longitudinal domains).

These stripes, known as flexoelectric domains, are observable by polarizing microscope when a DC or very low frequency AC driving voltages are applied to the sample. A simplified model explaining their flexolectric nature was presented by Bobylev and Pikin [57].

# Experimental Work

Electro-optical methods are the most commonly used techniques in liquid crystals research. The basic idea is simple, but a carefully carried out electro-optical investigations could actually be all that is needed to identify many liquid crystal materials, using other techniques only for confirmation.

## 3.1 The materials

The investigated substances are a single compounds with the common structure shown in 3.1:
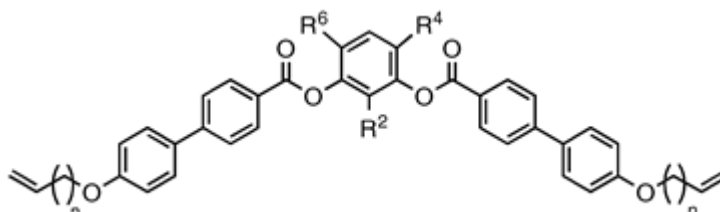


*Figure 3.1: The Chemical Structure of banana shaped liquid crystals used in this work.*

Two compounds with one chlorine substituents in $R^4$ position and different ter-

minal group length $(CH)_{n+1}$ or $(CH)_{n-1}$ were used in the study performed in this Thesis. The phase transition of the these two is shown in Table.3.1 The char-

*Table 3.1: The phase transition and the chemical substitution in the central ring for the two BC liquid crystal materials used in this work*

| ClPbis10BB labeled as F493 | $n = 8$ | heating Cr.76-77 N 81Iso | $R^4 = Cl$ | $R^6 = H$ |
|---|---|---|---|---|
| | | cooling Iso 81N 67 Cr | | |
| ClPbis10BB labeled as M1118 | $n = 8$ | Cr1.71.2 Cr2 78.9N 102 Iso | $R^4 = Cl$ | $R^6 = H$ |

acterization of these BC liquid crystal materials were carried out by polarizing microscope, XRD, NMR and quantum mechanical calculations and the results are reported in [28, 29]. The compounds were synthesized by K.Fodor-Csrba [27].

*Table 3.2: The nematic phase interval of BC( F493) and its mixture as a function of concentration.*

| Concentration (%) | 0 | 7 | 20 | 30 | 40 |
|---|---|---|---|---|---|
| Temp. interval ° C | 11 | 22 | 34 | 40 | 47 |

The most detailed set of experiments was done with (ClPbis10BB, labeled as F493). These compounds were chosen because

1. They are well-aligned and uniformly oriented in field-off state as well as in the presence of the external field.

2. The nematic phase is assumed to be uniaxial in field-off state.

The conventional nematic liquid crystals used as a guest compounds in the binary mixture with the BC nematic, is MLC6608 with negative dielectric constant,

produced by Merck industry Co. Germany, dissolved in the BC nematic host in different concentrations Table. 3.2.

## 3.2   Experimental Cells

For the purpose of the optical and electro-optical study, conventional sandwich cells, with gap filled with the liquid crystal materials under study, were prepared. Most of the cells used in our investigations were homemade.

Experimental cells of conventional sandwich type (EHC, Japan), with a cell gap of about 2 $\mu m$, were also used.

The homemade cells were made with glass substrates which inner surface was pre-coated with transparent ITO electrodes, After passing a thoroughly cleaning procedure on top of of the ITO film a polyimide alignment layer was deposited by spin coating.

The alignment layer was made from polyimide material promoting planar alignment (PA) and vertical (homeotropic) alignment (VA), respectively. In order to obtain uniform alignment of the liquid crystal in field-off as well as in field-on state, the alignment layer was unidirectionally rubbed.

The substrates were assembled in a sandwich cell with the rubbing directions of the substrates being anti-parallel.

The cell gap between the parallel substrates was controlled by spacers mixed in the glue, fixing the position of the substrates in the sandwich cell.

## 3.3    Thickness measurement

The cell gap were measured using a Shimadzu UV 3100 spectrophotometer,which work is based on Fabry-Perot effect[58], in this effect the interference of the light between two plates are at a distance d from each other.
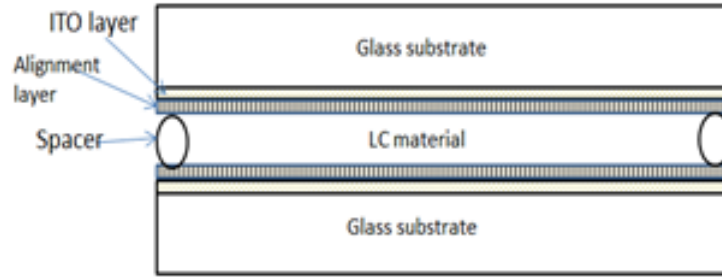


*Figure 3.2: Simplified LCs cell.*

The thickness of the cell is given by

$$\frac{1}{2}d = \frac{\triangle\lambda}{\lambda_1.\lambda_2} \tag{3.1}$$

where $\lambda$ is the light wavelength, $\lambda_1$ is the light wavelength in the first interference, $\lambda_2$ is the light wavelength in the second interference and $\Delta\lambda$ is the difference between the two wavelengths.

## 3.4    Cell inspection

The pure BC nematic liquid crystal as well as its mixtures with RL mesogens were filled into the experimental cells in the isotropic phase by means of capillary forces (Fig 3.2). The quality of the PA/VA of the cells was inspected by polarizing

microscope (Zeiss, Germany, SIP 040003729) with crossed polarizers.

The position of the cell slow optic axis, i.e. the sample optic axis was detected by inserting a $\lambda$ -red optical plate between the sample and the analyzer of the polarizing microscope at 45° with respect to the transmission direction of the analyzer.

## 3.5 Electro-Optical Measurements

The electro-optical measurements, depicted in Fig 3.3) was used in the electro-optic measurements in addition to the polarizing microscope.
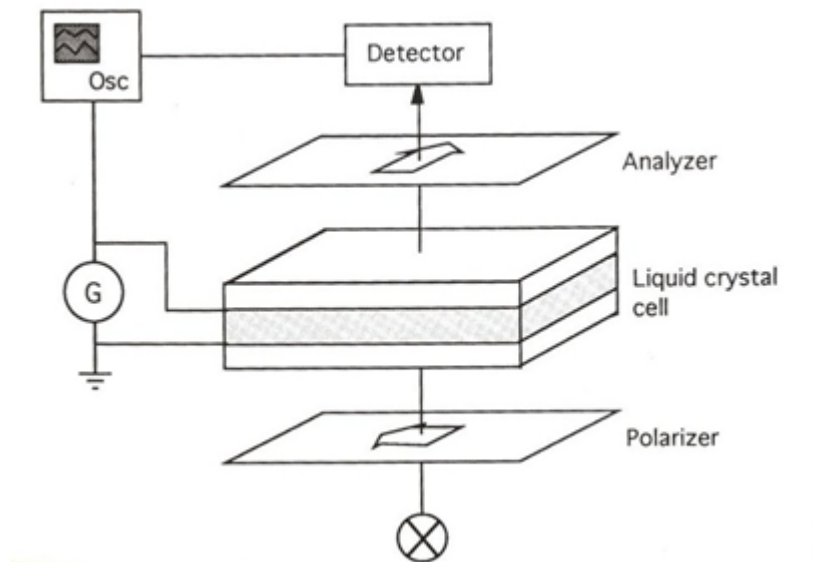


*Figure 3.3: The electro-optic experimental set up.*

It is consists of containing an optical detector, a function generator with an amplifier connected to the cell through resistance box, and a photodiode connected to a Tektronix TDS 540 digital storage oscilloscope.

# Chapter 4

# Summary of the Results

Electro- optic measurements have been performed on benzene derivative bimesogen nematic bent core liquid crystals and their binary mixtures with rod like conventional nematic liquid crystals.

The results are presented in details in the attached papers 1-5. In this chapter a summary of the obtained results is presented in a comprehensive way.

## 4.1 Alignment and alignment transition of bent core nematics

The alignment of a pure BC nematic material and their binary mixture with rod like nematics MLC6608 and MLC6873-100, in concentration 5, 10 and 20 wt% was studied in presence of planar and vertical anchoring conditions, respectively.

All the samples, containing alignment layer made from SE 7992, were found, likewise calamitic (RL) nematics, to possess uniform PA with optic axis oriented parallel to the rubbing direction.

However, a substantial difference in the alignment behavior of the BC nematic

with respect to RL nematics was observed when the alignment layer in the cell was chosen to be the one promoting VA of RL nematics.

The alignment layer made from SE 1112, which was used in this work, is known to promote excellent VA of the rod like nematics, such as MLC6608 and MLC6873-100. However, it was found that this alignment layer is promoting only PA of the pure bent core nematic material instead of VA (see Fig 4.1)
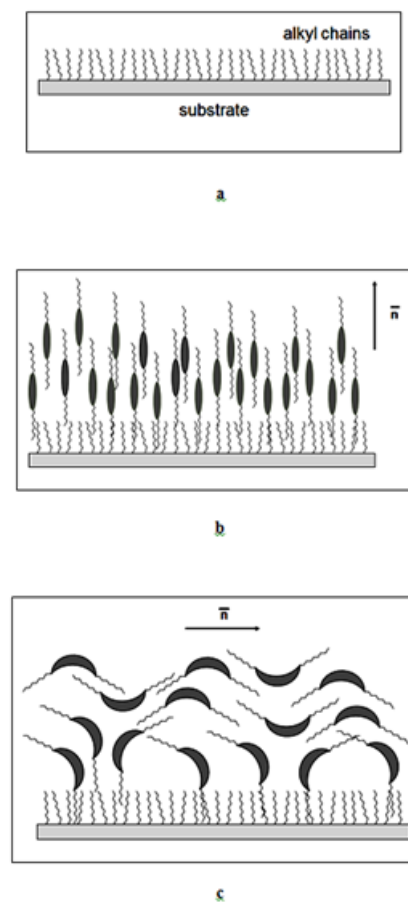


*Figure 4.1: Alignment of RL molecules and BC molecules, respectively, by polyimide alignment layer for promoting vertical alignment (VA) of RL nematic materials.*

This difference is attributed to the specific molecular shape of the BC molecules. Once they are anchored at the solid surface with vertical anchoring condition, the BC molecules screen the effect of this condition from the rest of liquid crystal molecules in the bulk.

The conventional methods for obtaining VA of the RL nematics were unable to promote VA of their binary mixtures with RL, for the concentration of the RL mesogen less than 20wt%. Instead of VA, these materials adopted planar alignment (PA).

However, for concentration of the RL mesogen higher than 20wt%, the binary mixtures adopted VA only in a very narrow temperature interval just below the transition to the isotropic phase. Anchoring transition from VA to PA was observed to take place for higher RL concentration than 20wt% upon cooling from the isotropic phase. The results obtained in this study are presented in PAPER I.

## 4.2 Field induced optically isotropic state in bent core nematic liquid crystals: Unambiguos proof of optical biaxiality

The optically isotropic state of a sample containing pure bent core nematic was observed under application of low dc electric fields.

The quality of the dark state, when the sample was inserted between two crossed polarizers was found to be excellent. Fig 4.2, is demonstrating this peculiar result.



*Figure 4.2: Photograph of a cell with cell gap of 1.8 μm containing BC nematic material at 90 C . The cell is inserted between crossed polarizers with optic axis at 45 (left) and (right) 0 with respect to the direction, of the polarizer. Dc electric field of 2V/μm is applied to the cell. As seen, the dark state of the pixel a) is excellent, and b) it does not change when the cell is rotated at 45 .*

A simple model for explaining the appearance of the optically isotropic state under dc applied electric field is proposed.

The model assumes that the position of the molecules of the BC liquid crystal material with $\Delta \varepsilon < 0$, switches from a planar to a tilted position with respect to the substrate plane, due to the polar coupling between the molecular net dipole moment and the applied dc electric field.

This coupling was considered as the origin of the out-of-plane switching of the BC molecules resulting in switching from the field-off bright state to the field-on dark state (c.f.Fig 4.3).
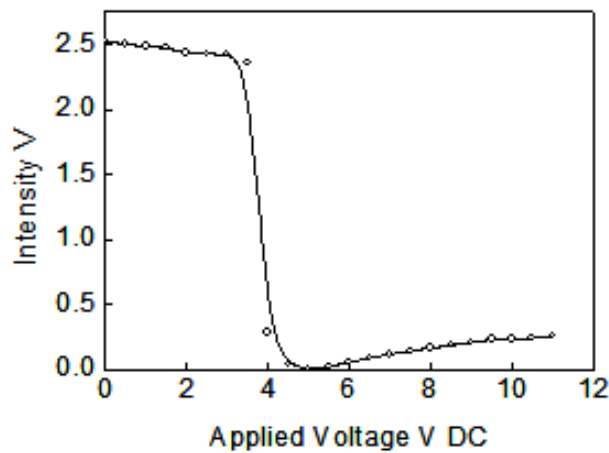


*Figure 4.3: The light transmitted intensity versus the applied voltage for the sample at 92 C. The minimum intensity of the transmitted light was achieved at field of about 2V/µm at which the cell exhibited isotropic optical properties. With the further increase of the field the isotropic optical state was transformed to a slightly birefringent (grayish) state.*

Due to similarity in the molecular structure, a comparison is made between the BC nematic liquid crystal under an applied dc field, and the bi-mesogenic siloxane AFLC with 45 ) molecular tilt.

From this comparison we concluded that BC nematic liquid crystal exhibits the same biaxial optical properties as the AFLC(45).

It should be noted that during the switching process under the applied dc field, the BC nematic liquid crystal sample optic axis changed its position between three mutually perpendicular positions: a) parallel to the substrate plane and along the rubbing direction, b) perpendicular to the substrate and c) parallel to the substrate and perpendicular to the rubbing direction likewise in the AFLC(45 ).

These results are well explained by the model made for describing the optical behavior AFLC (45) as a function of temperature, which is matching well our experimental observations reported in PAPER II.

# 4.3 Optically isotropic state in bent core nematic mixtures with rod-like molecules induced by dc electric field

Most of the BC nematics have usually high temperature nematic phase and/or a narrow temperature interval of existence. Moreover, their rotational viscosity is very high.

It is well known also that by mixing liquid crystal compounds their properties could be properly tailored. Therefore, we studied to what extend a BC nematic could be mixed with rod like nematic so that:

• the temperature interval will be enlarged at the same time as the temperature for transition to the high ordered phase, crystal or smectic, will be lowered.

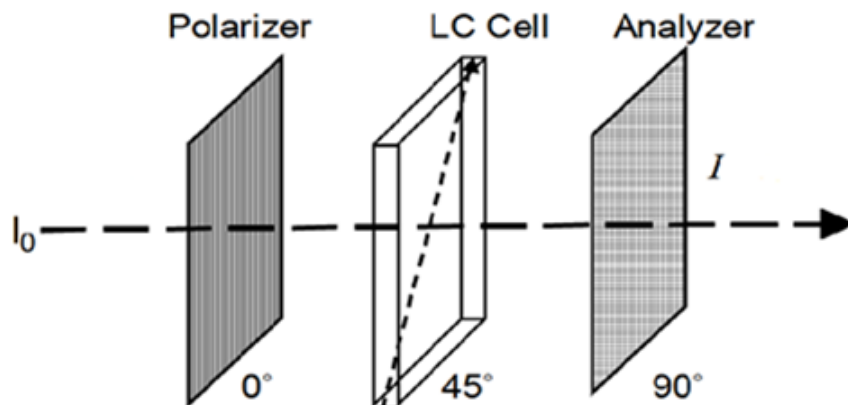• it keeps fast time to exhibit a field-induced optically isotropic state.



*Figure 4.4: The experimental arrangement for the intensity measurement.*

The study of the changes in the light transmitted intensity and the position of the sample optic axis, when a dc field is applied across the cell gap, was performed with the set-up schematically presented in Fig.4.4.

Here we investigated the temperature range of the nematic phase of the BC nematic mixed with RL nematic MLC6608 (Merck, Germany) as a function of the RL guest concentration varying this concentration in the interval 5 to 50 wt%.

It was found that the nematic phase temperature interval is broaden about $36°C$ compared to the pure material. The optically isotropic state was observed in the BC/RL binary nematic mixtures up to 40 wt% concentration of the RL mesogen (Fig4.5).
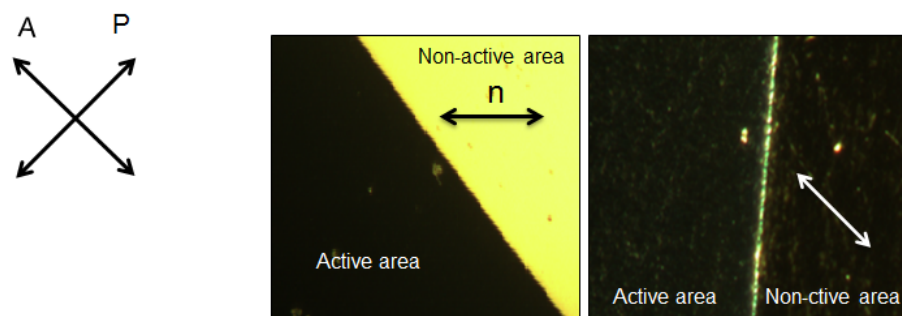


Figure 4.5: The contrast between dark state in conducting and non-conducting area for 40% MLC6608 inF493, VA cell, 1.37μm and at 80 ° C.

Fig4.6 shows the light transmitted intensity as a function of the applied monopolar voltage.

As seen, with an increase concentration of the RL mesogen the contrast of the dark(optically isotropic) state increases, at the price of slight increase of the voltage required to generated this state.

Moreover, it was found that due to the mixing of BC nematic with RL mesogen the rotational viscosity of the binary mixture decreased.

This, in turn resulted in a reduction of the response times of about 4-5 times. The mixtures with concentration of RL mesogen up to 40wt% were behave similarly like the pure BC nematic,in a switching of the sample optic axis between three mutually orthogonal directions with the applied dc electric field and a field-induced optically isotropic state.
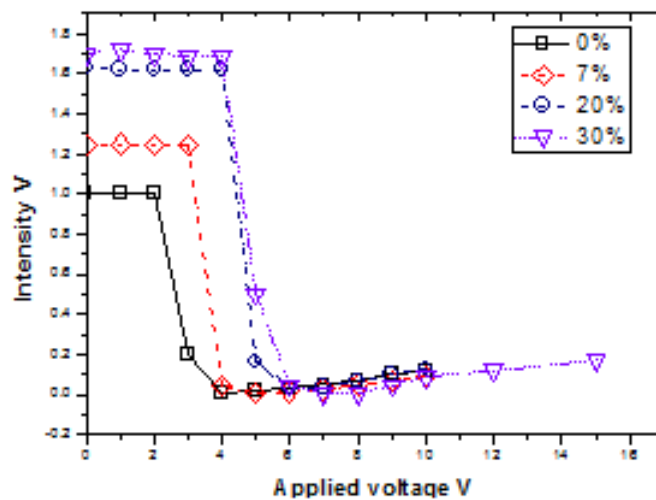


*Figure 4.6: Transmission light intensity versus the applied voltage for the cells containing pure BC nematic material and its mixtures with RL mesogenic guest at different concentrations.*

The observations made in this study indicated that the dynamical characteristics of the BC/RL nematic mixtures could be tailored by a proper choice of their components and relative concentrations so that BC/RL binary nematic liquid crystal mixtures with desired characteristics could be prepared.

Probably, multi-component nematic mixtures containing a BC nematic component might be a promising approach in searching nematic mixtures exhibiting field-induced optically isotropic state with short switching times and ability to generate switching of the sample optic axis between three mutually orthogonal positions.

The obtained in this study results are explained by the same model described in PAPER II and are presented in PAPER III.

## 4.4 Periodic pattern formation in a bent core nematic liquid crystal

At low dc applied electric field, the samples containing a BC nematic liquid crystal showed formation of a periodic domain pattern consisting of equidistant stripes oriented along the rubbing direction, this could easily be observed in the polarizing
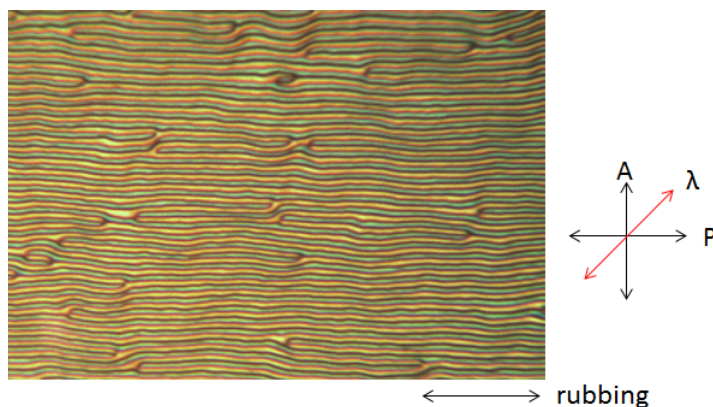


Figure 4.7: Photograph of the cell with cell gap of about $3\mu m$ under low $(1V/\mu m)$ dc applied field. The stripes are oriented along the rubbing direction. The photograph is taken with $\lambda-$ red optical plate inserted between the sample and the analyzer.

microscope between crossed polarizers. This periodic domain structure is depicted in Fig4.7.

The periodicity of the domain pattern was found to be about the size of the cell gap and decreased with the applied voltage.

When red optical $\lambda$ plate is inserted between the cell and the analyzer then it was found that the color of the single domain periodically changed, as illustrated in Fig4.7.
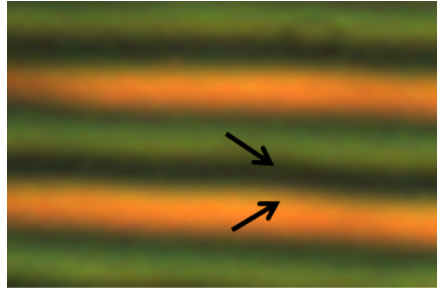
*Figure 4.8: The optical axis inclination in the stripes of the periodic pattern generated in the sample BNLC by dc electric field of $(1.5V/\mu m)$ applied across the cell.*

This observation indicates that the direction of the director in each single stripe is:

*a*) oriented obliquely with respect to the domain

*b*) the direction of the director inverts periodically when passing from one domain to another.

The inclination of the optic axis in the single stripe was found to be at $1V/\mu m$ about 22° (Fig4.8).

 This periodical inversion of the director direction along the normal to the stripes was explain on the basis of the flexoelectricity of the BC nematic and induced bent twist deformation in the BC nematic when subjected to a dc electric field.

By using a cell with twist configuration, it was proven that the domains of the periodic pattern were formed at one of the substrate surface first.

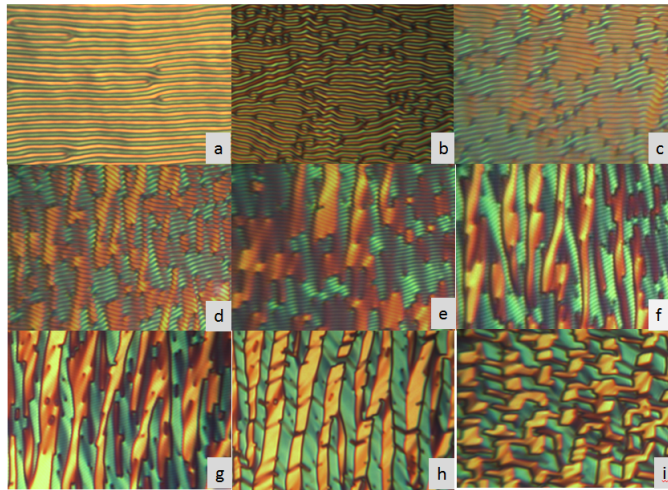At which substrate the formation of the periodic pattern will take place was found to depend on the field polarity.

*Figure 4.9: The stripe domains shrinking with application of a dc field across a vertical cell of 2μm thickness filled with BC nematic M1118, at 91 C and at different applied dc voltages; a=3 V, b=3.7 V, c= 4.6 V , d= 5.6 V, e =6.7 V, f =7.9 V, g=9 V, h=11.6 V and i= 17.8 V. The similarity between these textures and the ones of cholesterics can be noticed.*

With increasing the electric field, the periodic domains pattern underwent several transformations.

The sample texture started to look like the texture of the short pitch cholesteric Fig 4.9 and the orientation of the optic axis in the stripes went from position inclined to position almost perpendicular to the stripes.

By creating a polymer network in the BC nematic, filled in the cell gap, and thus stabilizing the periodic stripe pattern (Fig4.10), a linear electro-optic response
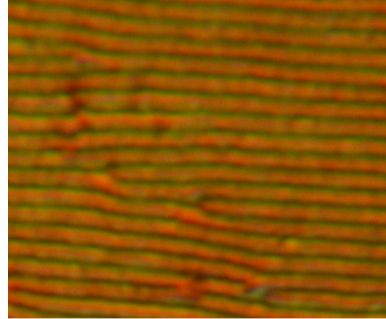


*Figure 4.10: Polymer stabilized periodic domain pattern in a PA cell with gap of $3\mu m$ , filled with BC nematic F667, without applied field. The temperature at which the photograph is taken is 90 C.*

was detected (Fig4.11).

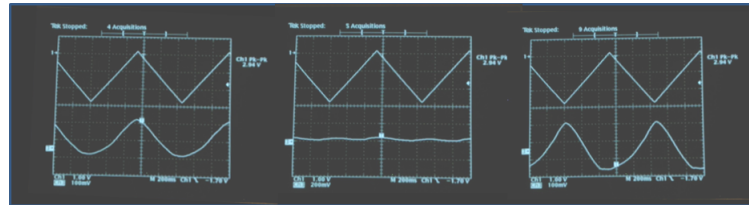This supported the assumption of a helical molecular order along the normal to the stripes.



*Figure 4.11: TElectro-optic response of PA cell with gap of $3\mu m$, filed with F669. The applied dc voltage is 3 V. The pictures are taken at 90 C for different position of the cell optic axis between crossed polarizers corresponding to: +22.5 , 0 and -22 , respectively cell gap.*

This result were more explained in PAPER IV.

## 4.5 Polar In-Plane and Out-of-Plane Switching in Bent Core Nematics Due to Flexoelectricity

The electro-optic response of nematic and its mixture with RL mesogen subjected to in-plane and out-of plane applied dc electric field, respectively, were studied. Pronounced linear electro-optic response, due to the flexoelectricity, was demonstrated to take place in cells with initially deformed liquid crystal alignment, the so called hybrid alignment nematic (HAN) Fig4.12.

For generating an in-plane electric field, an in-plane switching (IPS) electrode structure was used whereas for generating of an out-of plane electric field, the conventional electrode structure, with electrodes deposited on inner substrates surface surface, was employed.
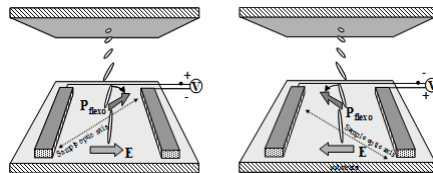


*Figure 4.12: Schematic presentation of the switching process of HAN configuration at different polarity of an in-plane dc electric field generated by the planar (interdigital) electrode structure.*

In the cell with IPS electrode structure, the top of the IPS electrode was covered with polyimide alignment layer promoting PA.

Two sets of substrates were prepared, with unidirectional rubbing normal and parallel to the generated in-plane electric field, respectively.

The inner surface of the substrate without electrode was covered with polyimide

promoting VA. The condition for deposition of the VA layer was such that alignment material was wetting the substrate surface only partially so that the VA layer had rather big holes with bare glass surface uncovered with VA material.

Hence, two kinds of domains were formed, in the cell containing IPS electrode structure with HAN and PA alignment, respectively.

The domains with HAN configuration were found to exhibit distinct polar electro-optical response due to flexoelectric polarization.

The switching of the BC/RL depicted in Fig4.13 took place in the plane of the
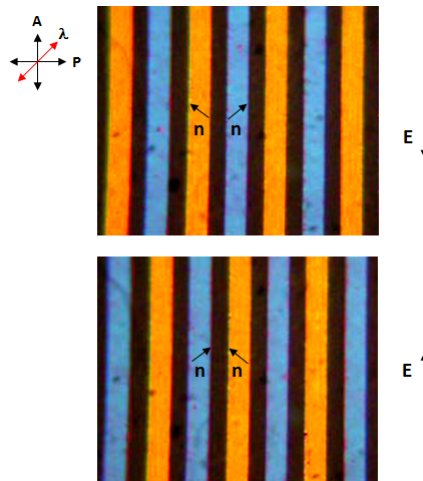


*Figure 4.13: The response of BC/RL mixture containing 10%MLC6606 in F493, 1.86 $\mu mat 95°C, \lambda - red$ optical plate is inserted between the cell and analyzer, Low frequency (0.1Hz) voltage~6 Vp-p. The direction of the director in between the IPS electrodes is depicted at different field polarity.*

substrates (in-plane switching) and the director direction at different polarity of the field is depicted as arrows.

Where the rubbing of the PA layer is made along the in-plane applied field it was observed that the switching also had a polar character being in-plane switching at one polarity of the applied field and out-of plane at the other one.

This observation is important for certain device applications.

A polar response out-of plane was found in the cells with conventional electrode structure, with electrodes on both substrates, where HAN configuration was created in a similar way as described above.

The observation made in this kind of study is described in PAPER V.

# Chapter 5

# Conclusions

The major goal of this work was to study two types of bent core liquid crystals (BCLCs) and their binary mixture with conventional nematics (rod-like, RL). Both liquid crystal materials exhibiting a nematic phase. They were found to show a variety of peculiar properties. The study was focused mainly on the experimental investigations of the BC nematic and its binary mixtures when subjected to an external electric field with the aim to understand as much as possible about their features and behavior. The out-come of the performed experiments was several important findings:

- the peculiar alignment ability of the BC nematic and BC/RL binary nematic mixtures in presence of VA conditions
- a field-induced optically isotropic state served as an ambiguous proof of the field-induced optical biaxilality
- pronounced polar in-plane and out-of-plane switching in cell with HAN configuration.

BC nematic and their binary mixture with RL nematics showed unexpected sensitivity to the alignment conditions. This study showed that these liquid crystal

materials promoted alignment by planar anchoring condition in a similar way as the RL nematics. Moreover, a substantial difference in the alignment behavior " of the BC nematics and BC/RL nematic mixtures " was observed in the presence of homeotropic anchoring conditions, until the concentration of the RL molecules exceeded certain value.

Important step in understanding the field-induced optically isotropic state in a pure BC nematic and the switching of the position of the sample optic axis in between three mutually orthogonal directions was the comparison made between the BC nematic, under an applied dc electric field, and AFLC with molecular tilt of 45 being a function of the temperature.

This comparison proved that BC nematic adopt biaxial optical properties under an applied dc electric field.

The studies on the specific behavior of the BC nematics and the BC/RL binary mixtures showed a very important issue of the correlation between the alignment behavior of the BC/RL mixtures as a function of the concentration of the RL nematic component, as well as, the appearance of field-induced isotropic optical state and switching of the sample optic axis by the applied dc field.

The role of the flexoelectricity in BC nematic materials was confirmed by the study performed on the formation of periodic domain (stripe) pattern taking place under an applied dc electric field.

Helical molecular order in the periodic pattern was confirmed by stabilizing it by means of polymeric network created in the liquid crystal layer.

The pronounced flexoelectric polarization in the BC nematics and in the binary BC/RL nematic mixtures were demonstrated in cells containing two different electrodes sets, for generating in -plane and out-of-plane electric field, respectively.

The liquid crystal layer in the cells containing these materials, in HAN configu-

ration, were found to exhibit a pronounced low voltage polar in-plane and out-of-plane electro-optic response, due to flexoelectricity, showing a potential for different device applications including LCDs.

What has been reported in this Thesis is a good start for further work on the multi-component mixtures of BC and RL nematics for tailoring the properties of these mixtures so that the optically isotropic state will be obtained at even lower voltages as well as to reduce substantially the response time.

Further study on the enhancement of flexoelectric polarization in nematics as well as in short pitch cholesterics by addition of BC mesogens will be a good continuation of the work presented in this thesis.

# Acknowledgments

I would like to express my gratitude to my supervisor Prof. Lachezar Komitov for introducing me to the world of liquid crystals and having confidence in me. None of my research in liquid crystals would have been possible without his constant support and guidance. Thanks are also extended to Dr. Omer Nour at Linköping University for initiating the contact with my supervisor.

I also owe a lot to Prof. Katalin Fador-Csbor for collaboration in preparing materials.

I further want to give special thanks to my examiner Prof. Dag Hanstorp for his valuable advices during all my work, and for his constructive criticism.

A big thank is due to LC group at Göteborg University: Gurumurthy, Gunnar, Ingolf and Andiry for sharing their experiences, help with many facilities and company.

I deeply thanks the administrators at Physics Department.

I would like to acknowledge the financial support of the Khartoum University.

I wish to thank my colleague Rasha Mohamed for many fruitful discussions and company.

Finally, but most importantly, I am indebted to my family, mam, siblings, loving husband and son for being my endless inspiration, my perpetual motivation and support. Their poise, intelligence and patient make every day of mine worthwhile!

# Bibliography

[1] Peter J. Collings and Michael Hird, *Introduction to Liquid Crystals chemistry and Physics*, Taylor and Francis, USA and UK, 1997.

[2] D. Demus, J. Goodby, G. W Gray, H. W Spiess and V. Vill, *Handbook of Liquid Crystals*, Wiley-VCH, USA and UK, 1998,1979.

[3] V. G Chigrinov, *Liquid Crystals Devices physics and Applications*, Artech House, Boston and London, 1999.

[4] L.M. Blinov and V. G Chigrinov, *Electrooptic Effects in Liquid Crystals*, Springer USA and France, 1996..

[5] Deng-Ke Yang and Shin-Tson Wu, *Fundamentals of Liquid Crystal Devices*, John Wiley and Sons England, 2006..

[6] Lev M. Blinov, *Structure and Properties of Liquid Crystals*, Springer Dordrecht Heidelberg London New York, 2011.

[7] Heinz- Siegfried Kitzerow and Christian Bahr, *Chirality in Liquid Crystals*,Springer Vew York, 2001 .

[8] Sven T. Lagerwall, *Ferroelectric and Antiferroelectric Liquid Crystals*, Wiley-VCH, Germany, 1999.

[9] E. B. priestley, Peter J. Wojtowicz and Ping Sheng, *Introduction to Liquid Crystals*, Plenum Press, New Jersey November 1979..

[10] Olsson. N, Andersson. G, Helgee. B and Komitov. L, *J. Liquid Crystals*, **32**, No. 9, 1125 (2005).

[11] Ayyalusamy Ramamoorthy, *Thermotropic Liquid Crystals: Recent Advances*, springer 2007.

[12] R. A. Reddy and C. Tschierske, *J. Mater.Chem.*, **16**, 907(2006).

[13] Hideo Takezoe, and Yoichi Takanishi, *Jap. J. Appl. Phys.*, **45**, 2(2006).

[14] Katalin Fodor-Csorba, Aniko Vajda, Giancarlo Galli, Antal Jakli, Dietrich Demus, Sandor Holly, Eszter Gacs-Baitz, *Macromol. Chem. Phys.*, **203**, 1556-1563(2002).

[15] A. Jakli, M. Chambers, J. Harden, M. Madhabi, J. Kim, Q. Li, G. Nair, N. Ebler, K. Fodor-Csorba, J. Gleeson and S. Sprunt, **63**, 2831(1929).

[16] Vorlnder, D. Ber,*SPIE* **6911**, 691105-1(2008).

[17] Vorlnder.D, and A.Apel ,*Ber. Dtsch.Chem.Ges*,**65**, 5(1932).

[18] T. C. Lubensky, and L. Radzihovsky, *Phys. Rev. E.*, **66**, 031704(2002).

[19] P. Lagerwall, F. Giesselmann, M. D. Wand and D. M. Walba, *J. Chem. Phys.*, **16**, 3606(2004).

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

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

[22] W. Weissflog, H.N. Shreenivasa, Siegmar Diele and G. Pelzl, *Phil. Trans. R. Soc. A.* , **364**, 2657 (2006).

[23] G. pelzl, S.Diele, A. Eremin, H. Kresse and . W. Weissflog, *J. Mater. Chem.* , **12**, 2591-2593 (2002).

[24] J. Harden, B. Mbanga, N. ber, K. Fodor-Csorba, S. Sprunt, J. T. Gleeson, and A. Jkli, *App. Phys. Lett.*, **96**, 102907(2010).

[25] Yun Jang, Vitaly P. Panov, Antoni Kocot, J. K. Vij, A. Lehmann, and C. Tschierske, *App. Phys. Lett.*, **97**, 183304(2009).

[26] C. Tschierske and D.J. Photinos, *J. Mater.Chem.*, **20**, 4263(2010).

[27] K. Fodor-Csorba, A. Vajda, A. Jakli, C.Slugovc, G. Trimmel, D. Demus, E.Gacs-Baitz, S. Holly and G. Galli. , *J. Mater. Chem.*, **14**, 2499(2004).

[28] Valentina Domenici, *ChemPhysChem.*, **8**, 2321(2007).

[29] Valentina Domenici, *Pure Appl. Chem.*, **79**, 1(2007).

[30] M. J. Freiser, *J.Phys. Rev. Lett.*, **24**, 1041(1970).

[31] J. Yu, A. Saupe, *Phys. Rev. Lett.*, **45**, 1000(1980).

[32] L. A. Madsen, T. J. Dingemans, M. Nakata and E. T. Samulski, *Phys. Rev. Lett.*, **92**, 145505(2004).

[33] Ji-Hoon Lee , Tong-Kun Lim , Won-Taeck Kim and Jung-Il Jin, *J. Appl. Phys.* **101** ,034105, (2007).

[34] B. Senyuk, H. Wonderly, M. Mathews, Q. Li, S. V. SHIYANOVSKII, and O. D. LAVRENTOVICH, *Phys. Rev. E.*, **82**, 041711(2010).

[35] Meyer, R. B, *Phys. Rev.Lett.*, **22**, 918(1969).

[36] J. S. Patel and R. B. Meyer, *Phys. Rev.Lett.*, **58**, 1538 (1987).

[37] L. Komitov , *liquid crystals lecture notes*, unpublished 2009.

[38] Rudquist. P., Komitov. L., and Lagerwall. S. T., *Phys. Rev. E.*, **50**, 4735(1994).

[39] Rudquist. P., Komitov. L., and Lagerwall. S. T., *Ferroelectrics.*, **213**, 447(1998).

[40] G. Hedge and L. Komitov, *Appl .Phys. Lett.*, **96**, 113503(2010).

[41] Rudquist. P., Komitov. L., and Lagerwall. S. T. , *Liq. Cryst.*, **24**, 329(1998).

[42] Rudquist. P., Buivydas. M., Komitov. L. and Lagerwall. S. T. , *J. Appl. Phys. *, **76**, 7778(1994).

[43] S. Garoff, Meyer, R. B., *Journal of Phys. Rev.Lett.*, **28**, 848(1977).

[44] P.J. Collings, *Journal of the Franklin Institute.*, **342**, 599(2005).

[45] G. Carbone, P. Salter, S. J. Elston, P. Raynes, L. D. Sio, S. Ferjani, G. Strangi, C. Umeton, and R. Bartolino,*Appl. Phys. Lett.*, **95**, 011102, (2009).

[46] Henning Molsen and H. S. Kitzerow, *J. Appl. Phys.*, **75**, (1994).

[47] H. Jayathilake, M. Zhu, C. Rosenblatt, N, Andrey, C. Weeraman and A. Benderskii, *J. Chem. Phys.*, **125**, 064706(2006).

[48] Johann Georg Meier, Ralf Ruhmann, and Joachim Stumpe, *Macromolecules.*, **33**, 843(2000).

[49] Shoichi Ishihara, *IEEE/ OSA J. Display Tech.*, **1**, No. 1 September (2005).

[50] I. Dozov, Ph. Martinot-Lagarde and G. Durand,*J. Physque letters.*, **44**, L-817 (1983).

[51] E. F. Carr, *Liq. Cryst.*, **7**, 253(1969).

[52] W. Helfrich,, *Chem. Phys.*, **51**, 4092(1969).

[53] A. M. L. NIP and J. A. TLJSZYkXJ, *Phy.s. ChvmSnliL* , **58**, 9(1997).

[54] S.Kai , M. Andoh and S. Yamaguchi, *Phys. Rev. A.*, **46**, 12(1992).

[55] S.Kai M. Andoh S. Yamaguchi and N. Chizumi, *Phys. Rev.Lett.*, **64**, 10(1990).

[56] D.Wiant, J.T.Gleeson, N.bert, K.Fodor-Csorba, A.Jkli and T.Tth-Katona, *Electronic- Liquid Crystal Communications.*, **7**, 12(2005).

[57] Yu.P. Bobylev, S.A. Pikin, Zh. Eksp. Teor. Fiz, *Sov. Phys. JETP* ., **72**, 369(1977).

[58] Yang. K. H *J. Appl. Phys.* , **9**, 64(1988).