High Birefringence Liquid Crystals For Optical Communications

2007

Amanda Jane Parish
University of Central Florida

Find similar works at: https://stars.library.ucf.edu/etd

University of Central Florida Libraries http://library.ucf.edu

Part of the Electromagnetics and Photonics Commons, and the Optics Commons

STARS Citation

Parish, Amanda Jane, "High Birefringence Liquid Crystals For Optical Communications" (2007). Electronic Theses and Dissertations. 3290.
https://stars.library.ucf.edu/etd/3290

This Masters Thesis (Open Access) is brought to you for free and open access by STARS. It has been accepted for inclusion in Electronic Theses and Dissertations by an authorized administrator of STARS. For more information, please contact lee.dotson@ucf.edu.
HIGH BIREFRINGENCE LIQUID CRYSTALS FOR OPTICAL COMMUNICATIONS

by

AMANDA PARISH
B.S. Boston University, 2004

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in the College of Optics and Photonics at the University of Central Florida Orlando, Florida

Fall Term
2007
ABSTRACT

High birefringence (Δn>0.4) nematic liquid crystals are particularly attractive for infrared applications because they enable a thinner cell gap to be used for achieving fast response time and improved diffraction efficiency. In this thesis, the mesomorphic and electro-optic properties of several new fluorinated isothiocyanate (NCS) terphenyl and phenyl tolane single compounds and mixtures are reported. The single compounds demonstrated Δn~0.35-0.52 in the visible spectral region at room temperature and exhibit relatively low viscosity. It was found that lateral fluorine substitutions and short alkyl chains eliminate smectic phase and lower the melting temperature of the single compounds. However, the consequence of using highly conjugated compounds to improve electro-optic properties is that the nematic phase is exhibited at high temperatures, over 100°C, and therefore single compounds cannot be used for device applications. Therefore, several mixtures based on the terphenyl and phenyl-tolane compounds were formulated and evaluated. The purpose of mixtures is to find the optimum balance between electro-optic performance and the mesomorphic properties that determine the operating temperature range. It was found that mixture formulations greatly improved mesomorphic properties to produce nematic phase at or near room temperature and suppressed smectic phase to below 0°C or eliminating completely. The analysis presented evaluates the benefits of lowering the operating temperature versus the consequence of degrading the electro-optic properties.
To my parents, David and Kathryn,

my sisters, Alissa and Jessica,

and Steve
ACKNOWLEDGMENTS

I would like to extend my sincerest thanks to all who assisted and encouraged me during my studies at CREOL. I would especially like to thank Prof. Shin-Tson Wu for his guidance, assistance, inspiration, and for sharing his immense knowledge of both optics and life with me during this time. I would also like to express my appreciation to the members of the liquid crystal displays group have welcomed me and shared with me invaluable knowledge. I have learned much about optics and liquid crystals as well as valuable life skills in team work, research principles, and communication skills.

I would also like to thank my thesis committee members, Professors Stephen M. Kuebler and Boris Y. Zeldovich, for their assistance and invaluable suggestions during my preparations. I can only begin express the extent of my gratitude to Dr. Sebastian Gauza for his mentorship, advice, and tremendous patience in teaching me invaluable skills. Without Dr. Gauza, my research would neither have found the direction it did nor have been as successful as it has been. I would also like to recognize my colleagues who have supported me and enriched my research, including Dr. Haiqing Xianyu, Dr. Hongwen Ren, Zhibing Ge, and Qiong Song.

My research and studies were graciously funded by the Network Centric Systems division of Raytheon Co. through the Advanced Scholars Program. I am thankful to all of those at Raytheon that have believed in me and made this opportunity possible, including Dr. Terry Dorschner, Scott Whatamough, and Martin Reed.
Finally, I would like to express my love and appreciation to my parents, David and Kathryn
Parish, my sisters, Alissa and Jessica, and the love of my life Steve for their encouragement and
moral support that have made me believe in myself and made my accomplishments possible.
# TABLE OF CONTENTS

LIST OF FIGURES ................................................................................................................................. ix

LIST OF TABLES ........................................................................................................................................ xii

CHAPTER ONE: INTRODUCTION .............................................................................................................. 1

1.1. Motivation ........................................................................................................................................ 1

1.2. Overview of Laser Beam Steering .................................................................................................. 1

1.3. Thesis Overview ............................................................................................................................. 8

CHAPTER TWO: LIQUID CRYSTAL OPTICS ......................................................................................... 10

2.1. Liquid Crystal Phase ..................................................................................................................... 10

2.2. Liquid Crystal Properties ............................................................................................................... 12

2.2.1. Orientational Order Parameter ............................................................................................... 12

2.2.2. Dielectric Anisotropy ............................................................................................................... 13

2.2.3. Birefringence ........................................................................................................................... 17

2.2.4. Elastic Constants ...................................................................................................................... 25

2.2.5. Viscosity ................................................................................................................................... 26

2.2.6. Figure of Merit .......................................................................................................................... 28

2.3. Molecular Structure ...................................................................................................................... 29

CHAPTER THREE: EXPERIMENTAL CHARACTERIZATION .......................................................... 34
3.1. Experimental Method .................................................................................................... 35

3.1.1. Thermal Analysis ..................................................................................................... 35

3.1.2. Electro-optic Measurements .................................................................................... 35

3.2. Experimental Results and Discussion ........................................................................ 40

3.2.1. Terphenyl Compounds ............................................................................................ 43

3.2.2. Terphenyl Mixtures ................................................................................................. 53

3.2.3. Phenyl Tolane Compounds ..................................................................................... 58

3.2.4. Phenyl Tolane Mixtures .......................................................................................... 70

CHAPTER FOUR: CONCLUSION ......................................................................................... 74

REFERENCES .......................................................................................................................... 77
LIST OF FIGURES

Figure 1.1 (a) Phase to voltage relationship and (b) repeated ramp voltage applied to patterned electrodes ........................................................................................................................................... 2
Figure 1.2 Side view of OPA section showing spatial relationship between patterned electrodes, glass substrates, and liquid crystal material. ......................................................................................................................... 3
Figure 1.3 Illustration of 1-D beam steering device and conceptual imposed phase shift ............ 3
Figure 1.4 Illustration of 2-D beam steering device ............................................................................. 5
Figure 1.5 Angular Dependent Diffraction Efficiency ............................................................................ 6
Figure 1.6 Illustration of wide-view 2-D beam steering device ............................................................ 6
Figure 1.7 Illustration of OPA Adaptive Optic device ............................................................................ 7
Figure 2.1 Illustration of molecular arrangement in different phases .................................................. 11
Figure 2.2 Illustration of liquid crystal director (n) .................................................................................. 12
Figure 2.3 Illustration of dielectric anisotropy and birefringence .......................................................... 14
Figure 2.4 Refractive indices of a uniaxial nematic liquid crystal .............................................................. 22
Figure 2.5 Temperature dependence of indices of refraction of nematic liquid crystals .................. 22
Figure 2.6 Wavelength dependence of indices of refraction of nematic liquid crystals .................. 23
Figure 2.7 Optical density of biphenyl and terphenyl molecular structures ......................................... 24
Figure 2.8 Elastic constants of liquid crystals ......................................................................................... 26
Figure 2.9 Rotational Viscosity of liquid crystals ...................................................................................... 27
Figure 2.10 Rotational Viscosity of liquid crystals .................................................................................... 29
Figure 2.11 Basic ring structures: (a) cyclohexane and (b) phenyl .......................................................... 30
Figure 2.12 Common linking structures: (a) Alkane, (b) ether, (c) azo, (d) acetylene (e) diacetylene

Figure 3.1 Schematic diagram of experimental setup for electro-optic property measurements

Figure 3.2 Terphenyl compound phase transition temperatures

Figure 3.3 Temperature dependent birefringence ($\Delta n$) of terphenyl compounds studied

Figure 3.4 Birefringence ($\Delta n$) of terphenyl compounds versus Reduced Temperature

Figure 3.5 Temperature dependent visco-elastic coefficient ($\gamma_1/K_{11}$) of terphenyl compounds studied

Figure 3.6 Visco-elastic coefficient ($\gamma_1/K_{11}$) of terphenyl compounds versus Reduced Temperature

Figure 3.7 Temperature dependent FoM of terphenyl compounds studied

Figure 3.8 FOM of terphenyl compounds versus Reduced Temperature

Figure 3.9 Tolane guest general structure

Figure 3.10 Terphenyl guest-host mixtures phase transition temperatures

Figure 3.11 Temperature dependent birefringence ($\Delta n$) of the terphenyl guest-host mixtures studied

Figure 3.12 Temperature dependent visco-elastic coefficient ($\gamma_1/K_{11}$) of the terphenyl guest-host mixtures studied

Figure 3.13 Temperature dependent FoM of the terphenyl guest-host mixtures studied

Figure 3.14 Phase Transition Temperatures of phenyl-tolane compounds
Figure 3.15 Temperature dependent birefringence ($\Delta n$) of phenyl-tolane compounds. ........... 64

Figure 3.16 Birefringence ($\Delta n$) of phenyl-tolane compounds versus Reduced Temperature ..... 64

Figure 3.17 Temperature dependent birefringence ($\Delta n$) of tri-fluorinated phenyl-tolane compounds. ............................................................................................................................................. 65

Figure 3.18 Birefringence ($\Delta n$) of tri-fluorinated phenyl-tolanes versus Reduced Temperature 65

Figure 3.19 Temperature dependent visco-elastic coefficient ($\gamma_1/K_{11}$) of phenyl-tolane compounds. .................................................................................................................................................. 66

Figure 3.20 Visco-elastic coefficient ($\gamma_1/K_{11}$) of phenyl-tolanes versus Reduced Temperature... 66

Figure 3.21 Temperature dependent visco-elastic coefficient ($\gamma_1/K_{11}$) of phenyl-tolane compounds. .................................................................................................................................................. 67

Figure 3.22 Visco-elastic coefficient ($\gamma_1/K_{11}$) of tri-fluorinated phenyl-tolanes versus Reduced Temperature .................................................................................................................................................. 67

Figure 3.23 Temperature dependent FoM of phenyl-tolane compounds. ................................. 68

Figure 3.24 FoM of phenyl-tolane compounds versus Reduced Temperature. ............................ 68

Figure 3.25 Temperature dependent FoM of tri-fluorinated phenyl-tolane compounds............. 69

Figure 3.26 FOM of tri-fluorinated phenyl-tolane compounds versus Reduced Temperature. 69

Figure 3.27 Phase transition temperatures of phenyl-tolane mixtures ....................................... 71

Figure 3.28 Temperature dependent birefringence ($\Delta n$) of the phenyl-tolane mixtures......... 72

Figure 3.29 Temperature dependent visco-elastic coefficient ($\gamma_1/K_{11}$) of the phenyl-tolane mixtures. .................................................................................................................................................. 72

Figure 3.30 Temperature dependent FoM of the phenyl-tolane mixtures................................. 73
LIST OF TABLES

Table 3.1 Molecular structures and phase transition temperatures of terphenyl isothiocyanate compounds ................................................................. 44

Table 3.2 Molecular structures and phase transition temperatures of phenyl-tolane isothiocyanates ........................................................................ 59

Table 3.3 Phase transition temperatures and compositions of the selected doped systems. .... 71
CHAPTER ONE: INTRODUCTION

1.1. Motivation

Continuous advancements in the field of infrared applications, such as laser beam steering at \(\lambda=1.55\text{\mu m}\) [14], demand ongoing development of nematic liquid crystal (LC) materials with both high birefringence (\(\Delta n\)) and low viscosity. Phase modulation applications require a \(2\pi\) optical phase change (\(\delta=2\pi d\Delta n/\lambda\), where \(d\) denotes cell gap of the homogeneous LC cell and \(\lambda\) is wavelength), which in turn requires the optical path length (\(d\Delta n\)) to increase proportionally to the longer IR wavelengths. Another key performance parameter of infrared applications is response time, which is proportional to \(d^2\) and visco-elastic coefficient (\(\gamma_1/K_{11}\)). To meet the response time requirements, the two preferred approaches are to have low rotational viscosity (\(\gamma_1\)) LC mixtures and to reduce the cell gap [21]. However, high birefringence and low rotational viscosity are opposing LC characteristics. A highly conjugated LC compound usually exhibits a high viscosity because of its increased moment of inertia. Moreover, high birefringence LC compounds usually possess high melting temperatures. To lower the melting temperature, many LC structures need to be developed and eutectic mixtures formulated.

1.2. Overview of Laser Beam Steering

The primary application for which the materials presented in this thesis were developed and studied is in the field laser beam steering by means of Optical Phased Arrays (OPAs). OPAs are transmissive, single cell gap liquid crystal devices that can alter the beam path of an incident
laser with great precision. This is accomplished by applying a ramp voltage across a series of independently controllable patterned electrodes on a glass substrate. The exact voltages used are determined by the phase to voltage relationship of the liquid crystal material used to fill the device. A sample phase-voltage relationship is illustrated in Figure 1.1, where the red circles indicate equally spaced increments of phase change that an incident beam would experience if it were to pass through a device with the corresponding voltage applied. In an OPA, there are many electrode stripes on the glass substrate that are independently controlled, and the voltage applied to each stripe corresponds to the incremental voltages that produce a constant phase ramp, as illustrated in Figure 1.1 and Figure 1.2. The required dynamic range the liquid crystal materials must produce is a phase change between $0$ and $2\pi$, any additional phase change is meaningless as the net change will cycle back to $0$. Therefore, there is no need to apply constantly increasing voltage across the whole device. Instead, a repeated series of ramp voltages is used, as is demonstrated in Figure 1.1, Figure 1.2, and Figure 1.3. The net effect of

![Voltage Phase profile](image)

**Figure 1.1** (a) Phase to voltage relationship and (b) repeated ramp voltage applied to patterned electrodes
Figure 1.2 Side view of OPA section showing spatial relationship between patterned electrodes, glass substrates, and liquid crystal material.

Figure 1.3 Illustration of 1-D beam steering device and conceptual imposed phase shift
applying the repeated stair voltage profile across the device is to create a transmissive blazed grating. This is accomplished because the incremental increase in the applied voltage across the surface of the device causes the liquid crystal molecules to reorient incrementally from horizontal, aligned with rubbing direction, to vertically, aligned with applied field, and results in ramp-like nature of the effective index of refraction across the device.

One OPA device is capable of redirecting an incident laser beam along the plane perpendicular to the direction of the electrodes. Therefore, to extend the use of OPAs to two dimensional (2-D) applications, two OPA devices must be used in conjunction. By orienting the two devices perpendicularly to each other, the combined system can then control the direction of the deflected beam in both the horizontal, or azimuth, as well as the vertical, or elevation, direction, as illustrated in Figure 1.4.

The diffraction efficiency of an OPA describes the proportion of the total energy of the incident beam that is redirected along the desired output direction. As the diffraction angle is increased, the diffraction efficiency of an OPA declines, as illustrated in Figure 1.5. In this example, when the beam is deflected by ±3.39° the normalized intensity in the first diffracted order of the output beam is only about half that of the incident beam. The energy that is lost from the first diffracted order is distributed in higher diffracted orders, known as side lobes. The process that causes field intensity to be lost from the first order is cause by fringing fields
that exist inside of the liquid crystal layer. Fringing fields are caused by the difference in voltage potential of neighboring electrodes, creating a local lateral field that can slightly alter the orientation of the liquid crystal molecules from their desired positions. The fringing fields deflect increasing amounts of the incident beam into the higher orders, decreasing the amount of energy in the desired first order beam. Therefore, the field of view of a single OPA is greatly limited by this performance. To compensate for this, a series of holographic gratings is used in conjunction with two pairs of azimuth and elevation OPA devices, as illustrated in Figure 1.6. The result of this is a system that has nearly a ±45° field of view in all directions.

Figure 1.4 Illustration of 2-D beam steering device
**Figure 1.5 Angular Dependent Diffraction Efficiency**

<table>
<thead>
<tr>
<th>Angles (deg.)</th>
<th>Normalized Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>-4</td>
<td>1</td>
</tr>
<tr>
<td>-3</td>
<td>0.9</td>
</tr>
<tr>
<td>-2</td>
<td>0.8</td>
</tr>
<tr>
<td>-1</td>
<td>0.7</td>
</tr>
<tr>
<td>0</td>
<td>0.6</td>
</tr>
<tr>
<td>1</td>
<td>0.5</td>
</tr>
<tr>
<td>2</td>
<td>0.4</td>
</tr>
<tr>
<td>3</td>
<td>0.3</td>
</tr>
<tr>
<td>4</td>
<td>0.2</td>
</tr>
</tbody>
</table>

**Figure 1.6 Illustration of wide-view 2-D beam steering device**
In addition to the beam steering purpose of OPAs, an alternate implementation can be used to create Adaptive Optic (AO) devices. Compared to the striped electrode pattern of a beam steering OPA, and AO OPA has independently controllable electrode pixels, as illustrated in Figure 1.7. This structure is used to correct for phase disturbances introduced by propagation or to pre-correct a wavefront prior to propagation. This can recover or prepare a wavefront for the disturbances that can be introduced during atmospheric propagation or from thermal disturbances. An AO device can be operated in either a transmissive mode, as illustrated in Figure 1.6 or in a reflective mode, as illustrated in Figure 1.7. Transmissive devices offer the advantage of being suitable for insertion in an in-line configuration. Whereas reflective devices offer the advantage of reducing the cell gap by half, due to the beam passing through the liquid crystal layer twice and effectively doubling the cell gap, and therefore improving the switching speed.

Figure 1.7 Illustration of OPA Adaptive Optic device
Future developments and success in the field of OPAs are closely related to new and improved liquid crystal materials used in these devices. The development of LCs with improved birefringence is at the forefront of this field and is the primary motivation for the research covered in this thesis. Materials with increased birefringence will lead to devices with thinner cell gaps, as the $2\pi$ phase change necessary for phase modulation can be accomplished in a smaller propagation distance through the liquid crystal layer. Reducing the cell gap of the OPA devices will improve performance in two important aspects. The first is improved response time, as the time it takes for LC molecules to reorient is related to the square of the cell gap. Secondly, a thinner cell gap will serve to weaken the fringing fields, thereby resulting in more power being transmitted in the desired first order and less power being lost in the side lobes. An additional challenge to material development is that materials with high birefringence in the visible region usually experience a 15%-20% reduction in birefringence at IR wavelengths. Therefore, only a portion of the increased birefringence realized by materials development is exploitable for IR applications such as OPAs.

1.3. Thesis Overview

The research work covered in this thesis focuses on liquid crystal materials aimed at improving birefringence and response time for optical communication devices.

The organization of the thesis is as follows:

Chapter 2 gives an overview of liquid crystal materials and physical properties.
In Chapter 3, new high-birefringence terphenyl isothiocyanate and phenyl-tolane isothiocyanate molecules with multiple lateral fluorine substitutions are presented and characterized. Mixtures made of these materials are also presented.

Finally, Chapter 4 includes a summary of the achievements presented in this thesis.
CHAPTER TWO: LIQUID CRYSTAL OPTICS

Liquid crystals exist in a mesophase between solid and crystal, in which the fluid nature of a liquid coexists with a partially ordered crystalline structure. Liquid crystals were first observed around 1850 by Virchow, Mettenheimer, and Valentin while studying nerve fibers that demonstrated strange behaviors when viewed using polarized light, but were not formally recognized for another three decades. In 1887, Otto Lehmann was investigating phase transitions when he noted that during heating one particular substance would change from a clear liquid to a cloudy liquid before crystallizing when viewed with a polarizing microscope, but dismissed this as simply an imperfect phase transition. The next year, Friedrich Reinitzer, an Austrian botanist studying the biological function of cholesterol in plants, noted that during melting cholestreryl benzoate became a cloudy liquid at 145.5°C before becoming a clear liquid at 178.5°C. Collaboration with Lehmann and others resulted in recognition of this behavior as a new phase of mattered identified as liquid crystal phase.

2.1. Liquid Crystal Phase

It is generally accepted that matter can exist in three distinct states: solid, liquid, and gas. However, this only the most basic description, as under extreme conditions different states of matter can exist, such as plasma at extremely high temperatures and superfluid helium at extremely low temperatures. The primary difference between states of matter is the degree of order present in the material, which is directly related to the temperature and pressure conditions. For liquid crystals, the molecules exist in a partially ordered state between isotropic
liquid and crystal, and can be classified based upon the degree of orientational and positional order. Using mechanical, magnetic, or electrical force, the order of matter in liquid crystal state can be controlled such that useful properties can be employed. There are several types of liquid crystals discovered - including thermotropic, lyotropic, and polymeric - but the research covered in this thesis will cover only thermotropic liquid crystals.

In thermotropic LCs, phase changes occur as the temperature is increased: solid, liquid crystal, isotropic liquid, and finally vapor. The phases of thermotropic LCs are illustrated in Figure 2.1. The solid to liquid crystal transition occurs at the melting point (Tm) and the liquid crystal to isotropic liquid transition occurs at the clearing point (Tc). The mesophase, classified as liquid crystal, that occurs between Tm and Tc manifests itself in the matter as a milky liquid that retains certain degrees of order. This mesophase can be further described by classifying the specific degrees of order present. Nematic phase is characterized by one dimensional order and can extend from Tm to Tc or can occur after one or more smectic phases from a transitional...
temperature above Tm to Tc. Smectic liquid crystal phases can occur from Tm to Tc or can occur over temperature ranges below nematic phase. There are at least 9 distinct smectic phases, and are characterized by additional degrees of positional order.

2.2. Liquid Crystal Properties

2.2.1. Orientational Order Parameter

In rod-like liquid crystals the long molecular axis tends to align in a preferred direction. The tendency of liquid crystals to exhibit a preferred molecular orientation is essential to macroscopic properties as it serves to essentially amplify the anisotropic properties of the individual molecules. This preferred direction is identified as the director and is represented by the vector \( n \), illustrated in Figure 2.2. The order parameter, \( S \), is used to describe the degree to which liquid crystal molecules are oriented along the director and is defined as:

[Figure 2.2 Illustration of liquid crystal director \( (n) \)]
$$S = \frac{1}{2} (3\langle \cos^2 \theta \rangle - 1)$$

Equation 2.2.1

Where $$\langle \rangle$$ denotes a thermal average of the molecules and $$\theta$$ is the angle between each molecule and the director. In the absence of an electric field or surface anchoring, there is no difference in terms of system energy if the long axis is pointing up the direction of the director or down director. Therefore $$\theta$$ and $$\theta + \pi$$ are degenerate positions and are physically equivalent. In this definition, if the molecules are perfectly oriented, as they are in a crystalline state, $$\theta = 0$$ for each molecule and then $$S=1$$. In contrast, if the molecules are randomly oriented, as they are in an isotropic liquid, there is no molecular order and the thermal average results in $$S=0$$. Therefore, $$S$$ can vary between 0 and 1, with higher values corresponding to a more highly ordered state. For typical liquid crystals, the order parameter decreases as the temperature rises. The most common values of $$S$$ are between 0.3 and 0.8. It should be noted that molecular orientation occurs independent of an electric field and is not affected by the presence of a permanent dipole moment, as will be covered in the next section.

### 2.2.2. Dielectric Anisotropy

Rod-like liquid crystals are axially symmetric about the long axis of the molecule, the director, and as a result the dielectric constant along the long, or preferred, axis ($$\varepsilon_\parallel$$) and perpendicular axis ($$\varepsilon_\perp$$) are different, as illustrated in Figure 2.3. In a liquid crystal molecule, the electric polarization has two components, parallel and perpendicular to the long axis, which can be
defined as the electric dipole of the molecules per volume. In a bulk material that is aligned and anchored, the dielectric constants parallel ($\varepsilon_\parallel$) and perpendicular ($\varepsilon_\perp$) to the long axis are then defined as this electric polarization divided by the field strength. Some liquid crystal materials are neutral and therefore do not have permanent dipoles. In a neutral material, an applied electric field produces forces on atomic charges, the positive nuclei and negative electrons, and causes the positive and negative charges to be displaced. The effect of this is an induced dipole. However, many liquid crystal compounds contain atomic bonds that can cause parts of the molecule to have slightly negative or positive charges, thereby creating a permanent dipole moment with a magnitude much greater than the induced dipole moments of neutral molecules. When no electric field is present, molecules with permanent dipole moments are equally as likely to align parallel or anti-parallel to the preferred orientational direction, and therefore the net dipole of the bulk material is neutral. As a result of this, the presence of a permanent dipole moment does not affect orientational order and the molecules are not aligned in the absence of an electric field. In either the case of an induced or
permanent dipole, the molecules will tend to orient along the direction of an applied field, responding to the squared magnitude of the field and therefore independent of field polarity. If the bulk material is in the nematic phase, is aligned, and is given a pre-tilt angle, all molecules will align in the same direction under the force of an applied field. This means that if the terminal group is considered the "head" of the molecule and the side chain is the "tail" then all molecules will align head-to-tail (molecular components terminal group and side chain will be defined later in this chapter). However, if a pre-tilt is not induced, the molecules could be aligned either head-to-tail or head-to-head. In this situation, switching is not uniform and therefore is not a useful configuration.

The difference between the parallel and perpendicular dielectric constants is defined as the dielectric anisotropy, $\Delta \varepsilon$. The dielectric anisotropy is primarily determined by the molecular dipole moment ($\mu$), the angle the dipole moment with respect to the director, and the order parameter ($S$) as described by the Maier and Meier mean field theory [12]:

$$
\varepsilon_{//} = N h F \left[ \langle \alpha_{//} \rangle \right] + \left( F \mu^2 / 3 kT \right) \left[ 1 - (1 - 3 \cos^2 \theta) S \right]
$$

$$
\varepsilon_{\perp} = N h F \left[ \langle \alpha_{\perp} \rangle \right] + \left( F \mu^2 / 3 kT \right) \left[ 1 - (1 - 3 \cos^2 \theta) S / 2 \right]
$$

$$
\Delta \varepsilon = N h F \left[ \left( \langle \alpha_{//} \rangle - \langle \alpha_{\perp} \rangle \right) - \left( F \mu^2 / 2 kT \right) (1 - 3 \cos^2 \theta) S \right]
$$

Equation 2.2.2
Where $N$ is the molecular packing density, $h=3\varepsilon/(2\varepsilon+1)$ is the cavity field factor, $\varepsilon=(\varepsilon_\parallel+2\varepsilon_\perp)/3$ is the averaged dielectric constant, $F$ is the Onsager reaction field, and $<\alpha/>$ and $<\alpha \perp>$ are the principal elements of the molecular polarizability tensor.

Due to the dielectric anisotropy of rod-like liquid crystals, when an electric field is applied a torque is induced in the molecules. This causes them to rotate until the induced dipole moment of the molecule is aligned with the electric field. For most rod-like liquid crystals, the longitudinal polarizability, parallel to the molecular axis, is greater than the transverse polarizability, perpendicular to the molecular axis. Therefore, since the macroscopic dielectric constant is proportional to the molecular polarizability, rod-like molecules have a positive dielectric anisotropy ($\Delta\varepsilon>0$) even for non-polar molecules. For polar liquid crystal compounds, the permanent dipole moment has an additional contribution to the dielectric anisotropy. The nature of this contribution can be to enhance $\Delta\varepsilon$ or even to create a negative $\Delta\varepsilon$, depending on the angle between the permanent dipole moment and the molecular axis. If a liquid crystal molecule has more than one dipole group, the effective dipole moment can be found through vector addition of the individual contributing dipole moments. The larger the dielectric anisotropy value is for a liquid crystal molecule, the weaker the electric field must be to reorient the dipole moment along the field direction. The dielectric anisotropy of liquid crystals is inversely proportional to temperature, decreasing as $S/T$. As the temperature reaches the clear point ($T_c$) of a liquid crystals, the dielectric anisotropy abruptly approaches zero and the dielectric constant becomes the mean of the parallel and perpendicular components of the dielectric constant.
In summary, liquid crystal materials can have an induced or permanent dipole moment, the dipole can be parallel or perpendicular to the molecular long axis, and the presence of an electric field the larger of the two dipoles will reorient to lie along the field direction.

2.2.3. Birefringence

Similar to dielectric anisotropy, rod-like liquid crystals exhibit optical anisotropy, or birefringence ($\Delta n$). This is an essential physical property of liquid crystals and is a key element in how they are implemented in display devices and other applications. To make use of this property, liquid crystal molecules must be aligned through a treatment such as rubbing or SiO$_2$ deposition in order to force the molecules to have the same orientation. Optical anisotropy means that the propagation speed of light waves is dependent on the direction of orientation of the liquid crystal molecule and the polarization of the light. Therefore, the light wave propagating through the liquid crystals will experience different refractive indices depending on orientation and polarization. Most rod-like liquid crystals are uniaxial nematics and exhibit two principle refractive indices, the ordinary index ($n_o$, $n// $) and the extraordinary index ($n_e$, $n_\perp$), illustrated in Figure 2.3. Birefringence ($\Delta n$) is defined as the difference between $n_e$ and $n_o$: $\Delta n = n_e - n_o$. When an electric field is incident upon an aligned sample of liquid crystals, $n_o$ is experienced when the electric field vector oscillates perpendicular to the director, or optic axis, of the molecules ($n$) and $n_e$ is experienced when the oscillation is parallel to the director, illustrated in Figure 2.4. The three primary forces governing the refractive indices of uniaxial liquid crystals are molecular conjugation, wavelength of incident light, and temperature.
Molecular polarizability at optical frequencies determines the refractive indices of liquid crystals. The polarizability is primarily governed by the presence of delocalized electrons not participating in chemical bonds and \( \pi \)-electrons. Due to these factors, liquid crystal molecules composed of phenyl rings, unsaturated carbon rings, have higher birefringence than equivalent molecules composed of cyclohexane rings, saturated carbon rings. The ordinary and extraordinary refractive indices are determined by corresponding ordinary and extraordinary molecular polarizabilities \( \alpha_o \) and \( \alpha_e \). The Lorentz-Lorenz equation correlates the refractive index of an isotropic medium with molecular polarizability at optical frequencies. Vuks modified this equation [18] by assuming that the internal field in a liquid crystal is equal in all directions, and therefore produced a semi-empirical equation correlating macroscopic refractive index with microscopic molecular polarizability for anisotropic materials.

\[
\frac{n_{e,o}^2 - 1}{(n^2) + 2} = \frac{4\pi}{3} N \alpha_{e,o}
\]

**Equation 2.2.3**

In Equation 2.2.3, \( n_e \) and \( n_o \) are the extraordinary and ordinary refractive indices, \( N \) is the number of molecules per unit volume, \( \alpha_{e,o} \) is the molecular polarizability, and \( \langle n^2 \rangle \) is defined as:

\[
\langle n^2 \rangle = \frac{(n_e^2 + 2n_o^2)}{3}
\]

**Equation 2.2.4**

Based on Equation 2.2.4, equations for extraordinary and ordinary refractive indices can then be expressed as:
\[
\begin{align*}
n_e &= \left(1 + \frac{4\pi N \alpha_e}{1 - \frac{4}{3} \pi N \langle \alpha \rangle} \right)^{1/2} \\
n_o &= \left(1 + \frac{4\pi N \alpha_o}{1 - \frac{4}{3} \pi N \langle \alpha \rangle} \right)^{1/2}
\end{align*}
\]

Equation 2.2.5

Equation 2.2.6

Where \(<\alpha>\) is the average polarizability of the liquid crystal molecules as defined by [2]:

\[
\langle \alpha \rangle = \frac{\alpha_e + 2\alpha_o}{3}
\]

Equation 2.2.7

In Equations 2.2.5 and 2.2.6, the ordinary and extraordinary expressions for refractive index are still coupled to each other. To resolve this, Wu proposed the three-band model based on the UV absorption wavelengths of a liquid crystal molecule. The \(\sigma-\sigma^*\) transitions that occur in vacuum UV around 180nm are described by \(\lambda_0\). The \(\pi-\pi^*\) transitions that occur at longer UV wavelengths between 180 and 400nm are described by \(\lambda_1\) and \(\lambda_2\). The ordinary and extraordinary refractive indices can then be expressed as [9], [25], [27]:

\[
n_e \approx 1 + g_{0e} \frac{\lambda^2 \lambda_0^2}{\lambda^2 - \lambda_0^2} + g_{1e} \frac{\lambda^2 \lambda_1^2}{\lambda^2 - \lambda_1^2} + g_{2e} \frac{\lambda^2 \lambda_2^2}{\lambda^2 - \lambda_2^2}
\]

Equation 2.2.8

\[
n_o \approx 1 + g_{0o} \frac{\lambda^2 \lambda_0^2}{\lambda^2 - \lambda_0^2} + g_{1o} \frac{\lambda^2 \lambda_1^2}{\lambda^2 - \lambda_1^2} + g_{2o} \frac{\lambda^2 \lambda_2^2}{\lambda^2 - \lambda_2^2}
\]
Where $g_i \approx N Z_i f_i$ are proportionality constants, $Z_o$ is the number of responsible $\sigma$-electrons and $Z_1 = Z_2$ is the number of $\pi$-electrons in a LC compound. This model was further refined and expressed in extended Cauchy equations as [10]:

$$n_e \approx A_e + \frac{B_e}{\lambda^2} + \frac{C_e}{\lambda^4}$$

Equation 2.2.10

Where

$$A_e = 1 + g_{oe} \lambda_o^2 + g_{1e} \lambda_1^2 + g_{2e} \lambda_2^2$$

$$B_e = g_{oe} \lambda_o^4 + g_{1e} \lambda_1^4 + g_{2e} \lambda_2^4$$

$$C_e = g_{oe} \lambda_o^6 + g_{1e} \lambda_1^6 + g_{2e} \lambda_2^6$$

Equation 2.2.11

And

$$A_o = 1 + g_{oo} \lambda_o^2 + g_{1o} \lambda_1^2 + g_{2o} \lambda_2^2$$

$$B_o = g_{oo} \lambda_o^4 + g_{1o} \lambda_1^4 + g_{2o} \lambda_2^4$$

$$C_o = g_{oo} \lambda_o^6 + g_{1o} \lambda_1^6 + g_{2o} \lambda_2^6$$

Equation 2.2.12
Equation 2.2.10 is a 3-coefficient Cauchy equation derived from the three-band model and is applicable to anisotropic media. The Cauchy coefficients are related to the resonance wavelengths ($\lambda_i$) and transition intensity ($g_i$). Furthermore, the above equations can be used to describe the refractive index of a mixture composed of several components, as the coefficients simply become the superposition of those of the individual components.

The order parameter, $S$, is temperature dependent and describes the transition of liquid crystals between crystal and isotropic liquid states. According to Haller's approximation, the temperature dependence of the order parameter can be approximated as:

$$ S = (1 - T/T_c)^\beta $$

Equation 2.2.13

Where $T_c$ is the clearing point of the material under study and $\beta$ is a material constant. The temperature dependent birefringence of a liquid crystal can then be expressed as:

$$ \Delta n(T) = (\Delta n)_0(1 - T/T_c)^\beta $$

Equation 2.2.14

Where $(\Delta n)_0$ the LC birefringence of the crystalline state at absolute zero ($T = 0$ K). At visible wavelengths, the ordinary refractive index, $n_o$, is typically between 1.50 and 1.57 and is not particularly sensitive to the molecular structure but is dependent on the incident wavelength ($\lambda$). As the wavelength is increased through the visible region, $n_o$ decreases and then saturates in the near-IR region. Additionally, $n_o$ is temperature dependent, increasing slightly over the nematic range and then rapidly increases as the temperature nears the phase transition, shown
in Figure 2.5. Conversely, the extraordinary refractive index, $n_e$, is particularly dependent on the molecular structure and can vary in the visible region from 1.5 for saturated compounds up to 1.9 for highly conjugated compounds. Similar to $n_o$, $n_e$ decreases as the wavelength of the incident field increases. However, unlike $n_o$, $n_e$ decreases slightly over the nematic range and rapidly decreases as the temperature nears the phase transition. At temperatures above the clearing point, $T_c$, liquid crystals become isotropic liquids and birefringence goes to zero as $n_e$ and $n_o$ coincide at their mean.

![Figure 2.4 Refractive indices of a uniaxial nematic liquid crystal](image)

![Figure 2.5 Temperature dependence of indices of refraction of nematic liquid crystals](image)
For IR applications, one major challenge is that birefringence decreases with longer wavelengths, as illustrated in Figure 2.6. Electronic transitions of the $\sigma$-electrons happen at 125nm, in the UV, whereas electronics transitions of $\pi$-electrons happen at 180nm and longer UV wavelengths near 200nm and 250nm. The result is that molecules with many $\pi$-electrons have strong peaks in optical density at longer wavelengths than equivalent molecules with fewer $\pi$-electrons, illustrated in Figure 2.7 where biphenyl and terphenyl cyano compounds are compared. All molecules demonstrate a reduction of birefringence with wavelength, as illustrated in Figure 2.6, where there is a region of sharp decline closer to the UV and a plateau far from resonance as wavelengths approach visible and IR. In Figure 2.6, $\lambda^*$ is the mean resonance wavelength [20], and it can be seen that the curve with the sharper decline at shorter wavelengths and overall larger birefringence corresponds to the system with resonance at a longer wavelength. Therefore, peaks of optical density at longer UV wavelengths correspond to higher birefringence at visible wavelengths, as visible wavelengths are closer to resonance and the sharp decline in birefringence occurs at longer wavelengths. The result of this behavior is
that molecules with fewer \( \pi \)-electrons exhibit the sharp reduction in birefringence at UV wavelengths but then remain relatively constant through visible and IR wavelengths, as the birefringence has reached a plateau. This behavior is preferable for display applications, where dispersion over the visible wavelengths must be kept to a minimum. Conversely, highly conjugated molecules with many \( \pi \)-electrons, such as those presented in this thesis, exhibit strong peaks in optical density at longer UV wavelengths close to resonance resulting in the sharp decline of birefringence to extend beyond UV wavelengths, meaning birefringence measured at visible wavelengths benefit from the plateau region being pushed to longer wavelengths. However, this behavior is not eliminated and the birefringence will decrease at longer wavelengths. Therefore, unlike molecules that exhibit a fairly constant birefringence over visible and IR wavelengths, highly conjugated molecules will demonstrate a reduction of birefringence between 15% and 20% as wavelength is increased from visible to IR.

![Molecular structures](image)

**Figure 2.7** Optical density of biphenyl and terphenyl molecular structures
2.2.4. Elastic Constants

Liquid crystal molecules exhibit an elastic restoring force, an important mechanical property. The effect of this force is that when a system experiences an external force that perturbs it from an equilibrium position a restoring torque returns the system to its initial form. This property is described by elastic constants of proportionality between deforming and restoring forces. Depending on the molecular alignment, three basic elastic constants describe the electro-optic effects of the restoring forces: splay ($K_{11}$), twist ($K_{22}$), and bend ($K_{33}$), illustrated in Figure 2.8. The two major application factors that are affected by the elastic constants are threshold voltage and response time. Threshold voltage for a homogeneous liquid crystal cell, the most common configuration, can be expressed as:

$$V_{th} = \pi \sqrt{\frac{K_{11}}{\varepsilon_0 \Delta \varepsilon}}$$

Equation 2.2.15

From this expression, it can be seen that a smaller elastic constant would result in a lower threshold voltage. However, since response time is inversely related to the elastic constant, a smaller value would result in a system that takes a longer amount of time to return to its equilibrium state. As a result, the proper balance between response time and driving voltage must be found for each system and its particular application. For most liquid crystal compounds, the three elastic constants have the following relationship: $K_{33} > K_{11} > K_{22}$ with typical values ranging from 3-25 pico-Newton ($pN$). Similar to many other physical properties of liquid
crystals, the elastic constant is strongly temperature dependent is proportional to the square of the order parameter ($S^2$).

![Figure 2.8 Elastic constants of liquid crystals](image)

**2.2.5. Viscosity**

Viscosity is defined as the resistance of a fluid to deform under the force of a shear stress.

Rotational viscosity ($\gamma_3$) describes a liquid crystal molecule's resistance to being rotated about the center of its long axis, as illustrated in Figure 2.9, and has an immense impact on device response time. The rotational viscosity of liquid crystal molecules is a function of molecular shape, moment of inertia, activation energy, and temperature, with the latter two being of the
most importance. A general form of the temperature-dependent rotational viscosity can be expressed as [9]:

\[ \gamma_1 = bS \cdot \exp \left( \frac{E}{kT} \right) \]

Equation 2.2.16

Where \( b \) is a proportionality constant describing molecular shape, dimension, and moment of inertia, \( S \) is the order parameter, \( E \) is the activation energy of molecular rotation, \( k \) is the Boltzmann constant, and \( T \) is the operating temperature. As the temperature is increased, rotational viscosity decreases exponentially. As a result, the response time of a liquid crystal device can be considered linearly proportional to the rotational viscosity. Additionally, since rotational viscosity and the elastic constants are dependent on the order parameter, \( S \), a new parameter is defined as the visco-elastic coefficient:

\[ \frac{\gamma_1}{K} \propto \exp \left( \frac{E}{kT} \right) \frac{1}{(1 - T/T_c)^\beta} \]

Equation 2.2.17

This new parameter describes the temperature dependent joint effect of viscosity and elastic restoring force on the response of liquid crystals molecules to applied fields.

Figure 2.9 Rotational Viscosity of liquid crystals
2.2.6. Figure of Merit

In order to compare the performance of liquid crystal molecules, two factors must be accounted for: temperature and cell gap. Each of the previously discussed parameters - dielectric anisotropy, birefringence, elastic constant, and viscosity - are temperature dependent and primarily governed by the melting and clearing points of an individual liquid crystal. Additionally, the response time of a device is determined by the cell gap, or the distance between the two electrodes. The best response time is achieved when the cell gap is exactly matched to produce the needed phase retardance for a particular application (e.g. $1\pi$ for displays or $2\pi$ for optical phased arrays) which is determined by the temperature dependent birefringence of the liquid crystal material and the wavelength of the application. As a result of these variable factors, it is difficult to compare the merits of two or more liquid crystal molecules without first leveling the field. Therefore, a Figure-of-Merit (FoM) that takes the phase retardation and visco-elastic coefficient into account for the purpose of comparison is defined as [22]:

$$FoM = \frac{K_{11}(\Delta n)^2}{\gamma_1}$$

Equation 2.2.18

where $\gamma_1/K_{11}$ is the visco-elastic coefficient and $\Delta n$ is the birefringence, as defined previously. From the previous sections, it is known that birefringence has a plateau region and then diminishes sharply as the clearing point ($T_c$) is approached while the visco-elastic coefficient is very high near the melting point ($T_m$) and then rapidly decreases to a region of little change. In
this definition of FoM, a peak will be observed in the temperature range that finds the optimum balance of the birefringence plateau and the minimum visco-elastic coefficient value. Also, since each of the component parameters is temperature depended, the FoM is as well and it allows the relative performance of liquid crystal molecules to be compared as a function of temperature.

2.3. Molecular Structure

The molecular structure of liquid crystals have an essential impact on many important properties, including which phases are exhibited, phase transition temperatures, and electro-optic properties. In general, it is theoreticised that compounds that have an elongated shape and are flexible are more likely to exhibit the mesophases characteristic of liquid crystals. This elongated shape is generally rod-like sharing basic components, illustrated in Figure 2.10, including a side change group (R), aromatic ring structures (A and B), a linking group (Z), and a terminal group (X).

![Molecular Structure Diagram](image)

Figure 2.10 Rotational Viscosity of liquid crystals
There are three commonly employed side chain groups (R): an alkyl group \( (C_{n}H_{2n+1}) \), an alkoxy group \( (C_{n}H_{2n+1}O) \), or an alkenyl \( (C_{n}H_{2n-1}) \), or an alkyl group with a carbon-carbon double bond. The length of the chain has a significant impact on the flexibility and phase transition temperatures of the liquid crystal compound and affects the elastic constant. Molecules with short side chains, containing only one or two carbon atoms, are usually not very flexible and therefore do not exhibit any liquid crystal phases. Medium length side chains, with between three and eight carbon atoms, are most common among molecules exhibiting nematic phase. As the side chain length is increased, it is commonly found that a smectic phase becomes evident and as the length is extended the nematic phase is eventually eliminated. It is also commonly found that as the side chain is increased the melting point decreases.

![Figure 2.11 Basic ring structures: (a) cyclohexane and (b) phenyl](image)

The aromatic rings (A and B) that form the core of the basic liquid crystal molecular structure can be saturated cyclohexane, unsaturated phenyl rings, or a combination of both, illustrated in Figure 2.11. Additionally, the structure is not limited to having just two aromatic rings, as in the case of a terphenyl core having three ring structures, but will always have at least one aromatic ring. In general, the melting point of the molecule will increase as the central ring structure becomes longer. Due to the fully saturated nature of the cyclohexane bonds, only \( \sigma \) electrons exist in this type of ring. Conversely, since the bonds of the benzene rings are not completely
saturated, more mobile π-electrons are present in addition to σ electrons. The ring structures of a liquid crystal molecule have an intrinsic effect on the dielectric anisotropy, birefringence, elastic constant, viscosity, and absorption. The latter property has much to do with stability, as the σ- σ* electronic transition occur at vacuum UV (λ<180nm) where as the π- π* electronic transitions occur in the UV (203nm and 256nm) and therefore are more susceptible to damage from broad-spectrum light sources.

It is possible that the basic cyclohexane and phenyl rings that form the core of a liquid crystal molecule can have other polar groups substituted in place of a hydrogen atom. The result of this type of substitution is to significantly alter the dielectric anisotropy (Δε = ε// - ε⊥).

Substitutions can be any polar group, and fluorine (F), cyano (CN), and chlorine (Cl) are some of the most popular. The result of the polar group substitution is to introduce an additional dipole moment that can either enhance the existing dipole moment along the long axis of the molecule or with multiple substitutions can cause the dipole moment along the short axis to become larger than that along the long axis, thereby creating a negative dielectric anisotropic (Δε < 0) liquid crystal. The presence of lateral substitutions can also serve as a method to lower the melting point of liquid crystals, useful in highly conjugated core structures such as terphenyls. One disadvantage to lateral substitutions is increased viscosity due to a larger moment of inertia which can potentially cause a slower response time.
The linking group (Z) serves to connect the two ring groups and impacts the phase transition temperature, physical properties, as well as the stability of the liquid crystal. Some of the most commonly used linking groups are summarized in Figure 2.12. The linking group can influence the linearity of the molecular structure, will increase the overall length, and affects the polarizability anisotropy. Inclusion of a linking group will often widen the temperature range of liquid crystal phase by reducing the melting point. If the linking group consists of a saturated group, such as ester or ethylene, the electron clouds of the two ring systems will not overlap. The result of this is that electronic transitions are not altered, and the absorption characteristics are similar to a single phenyl ring. However, if the linking group consists of an unsaturated group, such as acetylene or diacetylene, the π-electrons of the linking group are contributed to the core. The result of this is that the overall conjugation length is increased and the electronic transitions take place at longer wavelengths and become susceptible to damage from broad-spectrum light sources. Additionally, if the linking group tends to tilt away from the principal molecular axis, it can causes the dichroic ratio, the difference in absorption along the molecular
axis and absorption perpendicular to the molecular axis ($\alpha_{//}/\alpha_{\perp}$), to be decreased, which will lower the birefringence of the compound.

The terminal group (X) can be a neutral or a polar group or it can be a long flexible chain, similar to the side chain (R), as is used in negative dielectric anisotropic materials. The dielectric anisotropy is primarily determined by the terminal group, which therefore strongly influences the threshold voltage of the system. Several weakly polar groups are commonly used, including alkyl, alkoxy, and sulfide, resulting in liquid crystal molecules with small dielectric anisotropies. Conversely, several highly polar groups are also used to enhance the molecular dielectric anisotropy, including cyano (CN), isocyanate (NCS), and halides such as F, Cl, CF₃, and OCF₃. Additionally, the polar groups cyano and isocyanate contain several $\pi$-electrons and will therefore contribute to the conjugation of the molecule. The effect of this will be to enhance properties such as birefringence but will also produce electronic transitions at longer wavelengths which can lead to photo-instability. In contrast, a polar terminal group of fluorine (F) exhibits a strong electronegativity and will cause the electronic transitions to shift towards shorter wavelengths. Additionally, the polar group serves an important role in alignment, as in the presence of a rubbed polyimide (PI) layer the polar group of the monolayer (LC layer closest to PI) tends to face into the rubbing and the side chain end tilts out of the alignment layer. This sets the alignment orientation for the bulk material due to molecule-to-molecule interactions of upper layers.
CHAPTER THREE: EXPERIMENTAL CHARACTERIZATION

The most effective method of increasing birefringence is to elongate the π-electron conjugation of the LC compounds [1],[3],[5],[16],[26]. Conjugation length can be extended by either multiple bonds or unsaturated (phenyl) rings in the rigid core structure. However, the following problems are associated with highly conjugated LC compounds: high melting temperature, increased viscosity, reduced UV stability, and relative low resistivity due to ion trapping near the polyimide (PI) alignment interfaces [17]. The high melting temperature can be combated through the lateral fluorination of the rigid core and use of eutectic mixtures. The increased viscosity is inherent to all the highly conjugated compounds but can be mitigated by choice of polar group. UV stability can be improved by forming the rigid core of unsaturated rings instead of multiple bonds, as double and triple bonds are more susceptible to UV absorption [11],[23],[26]. Finally, it was recently shown that by using a multi-step purification process even a highly polar mixture can achieve resistivity at the level of $10^{-13}$ ohm/cm [4],[8]. For the purpose of elongating molecular conjugation, common rigid cores are phenyl-tolane and terphenyl structures and common polar groups are cyano (CN) and isothiocyanato (NCS). Due to relatively low visco-elastic coefficients and improved photo-stability, NCS terphenyl and phenyl-tolane compounds are preferable to cyano (CN) terphenyl compounds. Although the linear structure of cyano compounds creates a larger permanent dipole moment ($\mu = 4.1$D) than NCS compounds ($\mu = 3.7$D), the strong polarization of the carbon-nitrogen triple bond creates large, highly localized Huckel charges. Consequently, dimers are formed by strong molecular interactions between the nitrile groups and a significant increase in viscosity is observed. In
contrast, NCS compounds do not form dimers, and therefore rotational viscosity is significantly lower than analogous CN compounds [13]. Based on the above reasoning, several isothiocyanate terphenyl and phenyl-tolane compounds with different lateral fluorine substitutions were synthesized and studied. Furthermore, since none of the single compounds presented exhibit nematic phase at room temperature, several mixtures were formulated to improve mesomorphic properties. In this chapter molecular structures, mesomorphic properties, and electro-optic properties of six multiple fluorinated isothiocyanatoterphenyl single compounds, ten multiple fluorinated phenyl-tolane, and several mixture formulations are reported.

### 3.1. Experimental Method

**3.1.1. Thermal Analysis**

All the thermal analyses were performed using a high-sensitivity differential scanning calorimeter (DSC, TA Instrument Model Q-100). Phase transition temperatures were measured at a scanning rate of 2°C/min. Phase transition temperatures could be determined accurately to the second decimal place and melting heat enthalpy could be determined accurately to the first decimal place. Sample sizes were approximately 3mg.

**3.1.2. Electro-optic Measurements**

Several measurement techniques were utilized in characterizing the physical properties – including birefringence, visco-elastic coefficient, and Figure of Merit – of single LC compounds
in our laboratory. Measuring birefringence greater than 0.3 (at $\lambda = 633\text{nm}$) required electro-optic measurements, as the extraordinary refractive index of the LC under study exceeded the upper limit ($n_e > 1.80$) of the Abbe refractometer used in the classic refractometric method.

For the electro-optic method, homogenous cells with cell gaps of 5$\mu$m $\pm$ 0.30$\mu$m were filled at elevated temperatures above the melting point of the LC under study. The optical setup, illustrated in Figure 3.1, included a linearly polarized He-Ne laser ($\lambda = 632.8\text{ nm}$) as the light source, a linear polarizer oriented at 45° with respect to the LC cell rubbing direction, and an analyzer oriented perpendicular to the polarizer. The light transmittance was measured by a photodiode detector (New Focus Model 2031) and recorded digitally by a LabVIEW data acquisition system (DAQ, PCI 6110). Experimental driving parameters were a 1kHz square-wave
AC signal with peak to peak amplitude ramped from 0 V to 5 V that was applied to indium-tin-oxide (ITO) electrodes coated on the inner surfaces of the LC cell. The cell substrates were coated with a thin layer of polyimide alignment film, deposited on top of the ITO electrodes, and buffed to induce a 2°-3° pretilt angle. The cell was mounted in a Linkam LTS 350 Large Area Heating/Freezing Stage controlled by a Linkam TMS94 Temperature Programmer which could stabilize the cell temperature to within 0.2°C. The phase retardation (δ) of the homogeneous cells were then measured by the LabVIEW system by capturing the voltage-dependent transmittance (V-T) curve. The V-T curve was then used to determine the normalized transmittance of the LC cell between crossed polarizers, which can subsequently be expressed as [19]:

\[
T = \sin^2 \left( \frac{\delta}{2} \right).
\]

**Equation 3.1.1**

The LC birefringence (Δn) at wavelength λ and temperature T was obtained from the phase retardation (δ) measurements for a given cell gap d using the following equation [19],[26]:

\[
\delta(V, T, \lambda) = \frac{2\pi d \Delta n(V, T, \lambda)}{\lambda}.
\]

**Equation 3.1.2**

Both phase retardation (δ) and birefringence (Δn) are dependent on voltage, temperature, and wavelength. By measuring the free relaxation (decay) time for a controlled phase change, we were able calculate the visco-elastic coefficient (γ2/K11) according to the following equations [19]:

37
\[ \delta(t) = \delta_0 \exp \left( \frac{-2t}{\tau_0} \right) \]

Equation 3.1.3

and

\[ \tau_0 = \frac{\gamma_1 d^2}{K_{11} \pi^2}. \]

Equation 3.1.4

where \( \delta_0 \) is the total phase change, \( \gamma_1 \) is rotational viscosity, \( d \) is cell gap, and \( K_{11} \) is the splay elastic constant.

Figure-of-Merit (FoM) was used for comparison of compound switching speed. Birefringence and visco-elastic coefficient can be compared directly, but response time can only be compared if each compound is studied utilizing a cell gap that exactly matches its birefringence in order to result in the best possible response time. FoM eliminates the necessity of matching cell gap to birefringence, as the parameter is independent of cell gap and allows side-by-side comparison of the different compounds. To compare the performance of LC mixtures, FoM takes the phase retardation and visco-elastic coefficient into account and was defined as [22]:

\[ FoM = \frac{K_{11} (\Delta n)^2}{\gamma_1}. \]

Equation 3.1.5
Each of the three physical properties – Δn, γ1/κ_{11}, and FoM – is known to be temperature dependent. Therefore, the heating/freezing stage was used to control the environmental conditions such that experimental data could be collected at approximately 5°C intervals over the entire nematic range of the LC material under study. Since LC performance and response time is determined by several temperature dependent factors, FoM allows ideal operating temperature to be determined. Also, if an operating temperature is specified – e.g. room temperature – the best compound can be easily determined by the experimental data fitting according to the following equation [7]:

\[
\text{FoM} = \left( \frac{a_1}{b} \right) (\Delta n)^2 \left( 1 - \frac{T}{T_C} \right)^{3\beta} \exp \left( \frac{-E}{kT} \right)
\]

Equation 3.1.6

where \( a \) is a fitting parameter. Since the single LC compounds under study had nematic phases at high temperatures (above 100°C), the fitting parameters were used to extrapolate the physical properties at room temperature.
3.2. Experimental Results and Discussion

The experiments in this chapter focused on the thermotropic, rod-like molecular systems with a polar isothiocyanate (NCS) terminal group. Several variations of lateral fluorine substitutions were studied for both terphenyl and phenyl-tolane rigid core structures, with the goal of achieving the highest $\Delta n$ value as possible while retaining a relatively low viscosity and appealing mesomorphic properties. In the following sections, the structures and experimental characteristics will be examined and comparisons will be made. Additionally, mixtures will be made of the individual compounds presented and selected other compounds in either the form of host or guest materials. Mixtures will be characterized and analyzed for potential applications.

Considering most device applications operate at room temperature (~23°C), the physical properties of these compounds at room temperature is of interest. Since all of the compounds exhibit nematic phase at high temperatures, close to or greater than 100°C, two methods are commonly employed to extrapolate the electro-optical properties of these single compounds at room temperature: 1) guest-host system, and 2) fitting extrapolation from elevated temperature results. In the first method, about 10 wt% of the guest compound to be investigated is dissolved in a room temperature LC host mixture. By knowing the birefringence of the host mixture, the $\Delta n$ of the guest compound at room temperature can be estimated according to the following equation:
\[(\Delta n)_{gh} = x(\Delta n)_g + (1 - x)(\Delta n)_h,\]

Equation 3.2.1

where \(gh\), \(g\), and \(h\) denote the birefringence of the guest-host system, guest compound, and host mixture, respectively. Accuracy of guest-host mixtures greatly depends on the appropriate choice of host mixtures in order to ensure proper solubility of the guest. If the guest is too similar to the host, the guest characteristics blended in with the host performance and the results may not be accurately extrapolated. Ideally, the structure of the guest should be significantly different from that of the host compounds in order to ensure there are no interactions between the compounds. However, for these compounds it was difficult to ensure proper solubility which can cause experimental error to be amplified tenfold and skew any meaningful results. In the second method, we measure the properties of the compound at several temperatures in its nematic phase using a heated mounting stage, fit the experimental data with models, and finally extrapolate the results to room temperature. In this study, we focused on the birefringence \((\Delta n)\), visco-elastic coefficient \((\gamma_1/K_{11})\) and Figure-of-Merit which is defined as [22]:

\[
FoM = K_{11} \Delta n^2 / \gamma_1
\]

Equation 3.2.2

where \(K_{11}\) is the elastic constant and \(\gamma_1\) the rotational viscosity. The temperature dependent birefringence of an LC can be described as follows:
\[ \Delta n = \Delta n_0 (1 - T / T_c)^\beta, \]

**Equation 3.2.3**

where the fitting parameters are \( \Delta n_0 \), the birefringence at \( T=0 \) K, and \( \beta \) a material constant, and \( T_c \) is the clearing temperature of the LC. By fitting the experimental data using Equation 3.2.3, we can obtain \( \Delta n_0 \) and \( \beta \). Once these two parameters are determined, the birefringence of the LC at room temperature can be extrapolated. Similarly we fit FoM with following equation [22]:

\[ FoM = a(\Delta n)^2 \left(1 - \frac{T}{T_c}\right)^{3\beta} \exp\left(-\frac{E}{kT}\right), \]

**Equation 3.2.4**

where \( a \) is a fitting parameter. The extrapolated visco-elastic coefficient at room temperature can be calculated from Equation 3.2.2.

When characterizing the individual compounds in the following experiments, it was determined that single compound testing would produce the most accurate and meaningful results instead of formulating guest-host mixtures. While the nematic ranges of the individual compounds presented are rather high, most over 100°C, the temperatures are within experimental capabilities using a heated mounting stage. Therefore, in this study we chose to use the fitting and extrapolation method instead of guest-host method to determine compound properties at room temperature.
3.2.1. Terphenyl Compounds

The first rigid core structure of the LC compounds under study was aromatic terphenyl (benzene) rings, as the unsaturated residues are rich in π-electrons. These rings are particularly desirable to elongate the π-electron conjugation along the rod-like molecule by increasing the polarizability along the principal molecular axis. At the same time photochemical stability should not be jeopardized because multiple bonds in the linking group are avoided. Based on previous experience [6] with highly conjugated linear molecular structures, three different configurations of laterally fluorinated terphenyl isothiocyanates were investigated, with two homologues of each structure.

Table 3.1 lists the compound structures and their mesomorphsic properties. For comparison, Figure 3.2 illustrates phase transition temperatures with respect to the different lateral fluorine substitutions. The clearing points of the double fluorinated structures were found to be the highest (Compounds 5 and 6). Compound 2 showed the highest melting point temperature and lowest clearing point temperature among investigated group of structures. Moreover, heat enthalpy of the melting point of Compound 2 exceeded 7 kcal/mole. Such properties suggest that a two carbon chain was too short for long and rigid terphenyl molecular core to provide attractive mesomorphic properties by means of low melting point temperature and wide temperature range of the nematic phase, even if the rigid core was extensively fluorinated. For the melting point temperature comparison, pentyl homologues were chosen. Surprisingly, lateral substitution of four fluorines did not lower the melting point temperature further than triple fluorination. From the mesomorphic properties view point, double fluorination at the
Table 3.1 Molecular structures and phase transition temperatures of terphenyl isothiocyanate compounds

<table>
<thead>
<tr>
<th>ID No.</th>
<th>Structure</th>
<th>PTT [°C]</th>
<th>DH (Cr-N) [cal/mole]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C5PP(23F)P(35F)NCS</td>
<td>Cr 90.71 Sm(A) 137.93 N 172.98 Iso</td>
<td>4089</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Iso 171.92 N 136.4 Sm(A) 86.49 Cr</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>C2PP(23F)P(35F)NCS</td>
<td>Cr 121.96 N 152 Iso</td>
<td>7040</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Iso 151.1 N 103.02 Cr</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>C5PP(23F)P(3F)NCS</td>
<td>Cr 73.17 Sm(A) 112.22 N 174.62 Iso</td>
<td>4622</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Iso 173.38 N 109.98 Sm(A) 62.97 Cr</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>C4PP(23F)P(3F)NCS</td>
<td>Cr 90.09 Sm(A) 104.53 N 163.32 Iso</td>
<td>4693</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Iso 162.2 N 101.58 Sm(A) 79.5 Cr</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>C3PPP(35F)NCS</td>
<td>Cr 106.88 N 202.61 Iso</td>
<td>3359</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Iso 201.0 N 100.47 Cr</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>C5PPP(35F)NCS</td>
<td>Cr 96.85 Sm(A) 112.37 N 188.59 Iso</td>
<td>2174</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Iso 187.72 N 171.3 Sm(A) 94.1 Cr</td>
<td></td>
</tr>
</tbody>
</table>
Figure 3.2 Terphenyl compound phase transition temperatures

phenyl ring with NCS terminal group was the most favorable. The melting point temperatures of the pentyl homologues with different degrees of lateral fluorination follow the order shown below:

**Compound 3 < Compound 1 < Compound 6**

As is common with highly conjugated linear structures, smectic phase was observed in four of the six compounds under study. The number of fluorine substitutions had no obvious affect on suppressing the smectic transition. However, a shorter alkyl chain did suppress the smectic phase in both the double and four- fluorinated structures (Compound 2 and 5). If the smectic to nematic transition was considered, double and triple fluorinated compounds showed similar transition temperatures. Clearing temperature was significantly higher for the double fluorinated compound (Compound 6):
Compound 1 ≈ Compound 3 < Compound 6

Shorter chain homologues of double and triple fluorinated terphenyls did not show smectic phase in the phase transitions sequence. We were not successful in obtaining less than a four carbon chain homologue of the triple fluorinated isothiocyanato terphenyl with sufficient chemical purity, thus data was not included in this comparison. Further synthesis must be conducted in order to specifically prove whether absence of a smectic phase was an effect of double substitution at 3”,5” positions of the phenyl ring with polar terminal group or if the length of flexible alkyl chain was the determining factor in suppressing the smectic phase.

Melting heat enthalpy was determined using DSC analysis, and found the double fluorinated compounds to have the lowest ΔH values (< 3400 cal/mole), the three-fluorinated compounds to have mid-range ΔH values around 4600 cal/mole, and the four-fluorinated compounds to have mid-range (4089 cal/mole for Compound 1) and high (7040 cal/mole for Compound 2) ΔH values. As Figure 3.2 illustrates, Compounds 5 and 6 are promising candidates for eutectic mixture formulation as they exhibited the best mesomorphic properties: widest nematic range, relatively low melting points, the highest clearing points, low melting heat enthalpy, and no evidence of a smectic phase for Compound 5.

High birefringence (Δn) values were expected for the compounds in question, as the unsaturated rings of the terphenyl structure elongate the π-electron conjugation thru entire rigid core of the molecules. Laterally unsubstituted terphenyl compounds have been known to exhibit very high melting point temperatures. To lower the melting point temperature and
diminish the tendency of terphenyl compounds to form a smectic phase, multiple lateral fluorine substitutions were made. However, this lowers the birefringence of the compound, as laterally substituted fluorine atoms trap π-electrons and pull them away from the conjugation along the main molecular axis.

The experimental data and fitting results for birefringence of the six compounds are illustrated in Figure 3.3, and show birefringence values greater than 0.36 for all structures when extrapolated to room temperature (25°C). Figure 3.4 illustrates the fitted curves plotted against reduced temperature (T/Tc) in order to account for the different clearing temperature so that the structural effects can be compared. Of the three differently fluorinated systems studied, homologues C3PPP(3,5F)-NCS and C5PPP(3,5F)-NCS (Compounds 5 and 6) exhibited highest birefringence, 0.4430 and 0.4153, respectively, when extrapolated to room temperature. This fluorination structure exhibited particularly desirable performance parameters due to the fluorine positions being adjacent to the polar NCS group, as an electron potential is created at one end of the molecule and thereby increases the polarizability of the molecule at the microscopic scale. This, combined with high clearing point temperatures, increases the total birefringence while maintaining the suppression of the smectic phase in Compound 5. Introducing a third lateral fluorine and reconfiguring the position of the other two fluorine to 2′,3′,3″ positions of the terphenyl rigid core (4-alkyl-2′,3′,3″-trifluoro-4″-isothiocyanato-[1,1′;4′,1″]terphenyl, Compound 3 and 4) decreases birefringence significantly as shown in Figure 3.3. When the reduced temperature is used to offset the effect of clearing
Figure 3.3 Temperature dependent birefringence ($\Delta n$) of terphenyl compounds studied.

Figure 3.4 Birefringence ($\Delta n$) of terphenyl compounds versus Reduced Temperature
point temperature, loss of birefringence due to additional third fluorine and lateral substituent reconfiguration is more evident over the entire temperature range of the nematic phase.

Among investigated compounds, tetra fluorinated terphenyls demonstrate the lowest birefringence with respect to the alkyl chain length which further decreases $\Delta n$ as the structure is elongated. The visco-elastic coefficient ($\gamma_2/K_{11}$) is calculated from the free-relaxation time and characterized the amount of time and energy required to rotate the LC molecules. Figure 3.5 summarizes both experimental data and fitting results for the six compounds under study and Figure 3.6 illustrates the fitted curves plotted against reduced temperature ($T/T_c$). From Figure 3.6, it is evident that the structures with more fluorine substitutions have higher visco-elastic coefficients over the entire nematic range. This is anticipated, as the structures with more fluorine substitutions have higher molecular weight with slightly larger cross-section, and may be subject to stronger molecular interactions with neighboring molecules due to additional slightly negative charges on the surface. Considering all the above, it can be surmised that additional fluorine substitutions will negatively affect the visco-elastic coefficient. This can be easily analyzed on the basis of Figure 3.5 and Figure 3.6.

Figure-of-Merit (FoM), as defined in the previous section, was used for comparison of compound switching speed. Experimental data and appropriate fitting results of the six investigated isothiocyanato terphenyls are summarized in Figure 3.7 and fitted curves plotted versus reduced temperature are summarized in Figure 3.8. It is evident that the double fluorinated terphenyl homologues (Compounds 5 and 6) are superior to trifluorinated or tetrafluorinated compounds, with almost 200% higher FoM if C3PPP(35F)NCS compound is
Figure 3.5 Temperature dependent visco-elastic coefficient ($\gamma_{1}/K_{11}$) of terphenyl compounds studied.

Figure 3.6 Visco-elastic coefficient ($\gamma_{1}/K_{11}$) of terphenyl compounds versus Reduced Temperature.
Figure 3.7 Temperature dependent FoM of terphenyl compounds studied.

Figure 3.8 FOM of terphenyl compounds versus Reduced Temperature.
compared with the others at the optimum operating temperature. The fitted curves show that ideal operating temperature is in the range of 130-160°C (FoM of 118 and 82 for Compound 5 and 6 respectively), but that even at an operating temperature of 60°C FoM values remain relatively high (55 and 35 for 5 and 6 respectively). The significantly higher FoM observed of the double fluorinated compounds is due to both higher birefringence and lower visco-elastic coefficient values compared to the structures with more fluorine substitutions. As expected, compounds with higher numbers of laterally substituted fluorine atoms and longer terminal alkyl chain demonstrate lower FoM performance and therefore are expected to be less effective in multi-component compositions intended to reduce response time to applied electric field.

By increasing the number of laterally substituted fluorine, we noted that birefringence gradually decreased with a maximum of 25% loss if 4-propyl-3″,5″-difluoro-4″-isothiocyanato-[1,1′;4″,1′′]terphenyl (Compound 5) was compared with 4-pentyl-2′,3′,3″,5″-tetrafluoro-4″-isothiocyanato-[1,1′;4″,1′′]terphenyl (Compound 1) at the temperature 25°C. The visco-elastic coefficient was also significantly affected by increasing the number of lateral substituents. Using the same compounds for comparison (1 and 5), the γ₁/K₁₁ coefficient showed a difference of almost 500% at 25°C. Therefore, the performance parameter, which is considered as a figure-of-merit, was substantially different for presented compounds. Detailed DSC analysis does not show a significantly lower melting point temperature when the number of fluorine substitutions was increased from two to four. These results led to the conclusion that for the case of rigid terphenyl-NCS core, further fluorination does not affect mesomorphic properties
to the same extent as fluorine substitutions in the positions closest to the polar group. The difluorinated NCS terphenyl structure showed the best overall performance of the three fluorinated structures studied. These two compounds will yield faster response times, as the higher birefringence value will allow for a thinner cell gap and the lower viscosity will allow the molecules to be rotated faster. The mesomorphic properties (wide nematic range, suppressed smectic phase) and relatively low melting heat enthalpy makes the double-fluorinated NCS terphenyl structure an ideal candidate for eutectic mixtures and potentially an all-isothiocyanato terphenyl based mixture.

3.2.2. Terphenyl Mixtures

Based on the single compound results, a mixture comprised of Terphenyl Compounds 1, 2, 4, 5, and 6 was formulated (UCF-Base). The mesomorphic properties of this multi-fluorinated NCS terphenyl mixture exhibited the melting point at 37.4°C, the clearing point at 183.6°C, and a smectic phase extending from the melting point to 114.9°C. The melting point of the mixture was 30 to 80 degrees lower than its constituents and its clearing point remained comparable. The smectic phase of the mixture was unsurprising, as most of the compounds it is comprised of also demonstrated smectic phases. The electro-optic properties UCF-Base demonstrate a very high birefringence, $\Delta n=0.4$ when extrapolated to 25°C (Figure 3.11), and a Figure of Merit of nearly 70 at the ideal operating temperature of 125°C (Figure 3.13). However, due to the wide temperature range of a smectic phase this mixture is ill-suited for devices operating at room temperature. Therefore, dopants must be introduced in order to suppress the smectic phase and lower the melting point of the mixture. In order to maintain the high birefringence
of the mixture as well as lower the melting point, fluorinated NCS tolanes of the following structure were used:

![Figure 3.9 Tolane guest general structure](image)

These compounds were chosen as dopants because they exhibit high birefringence and show no evidence of a smectic phase. Two mixtures were designed using the fluorinated NCS terphenyl mixture (UCF-Base) as the host and fluorinated NCS tolanes as the guest, one containing 20% of the guest mixture (UCF-A) and the other containing 40% (UCF-B). The mesomorphic properties (Figure 3.10) of the guest-host systems were significantly improved compared to the host mixture. For the 20% guest system (UCF-A) the melting point was reduced to 2°C, the clearing point was 147°C, and the smectic to nematic transition was lowered by 46°C to 69°C. The 40% guest system (UCF-B) shows further improvement, exhibiting a melting point of -4°C, a clearing point of 119°C, and the smectic to nematic transition was reduced by nearly 84 degrees. It is clearly evident that the addition of the guest mixture significantly lowered both melting and clearing points, thereby appreciably reducing the operating temperature of the mixture. The electro-optic properties of the 20% guest-host system demonstrate a birefringence of 0.38 at 25°C. Increasing the percentage of the guest mixture causes the birefringence to drop slightly to 0.37 at 25°C. The lower birefringence of
the guest-host systems were primarily due to the lower clearing points of the systems, not because the phenyl-tolane dopants have a birefringence less than the host mixture [3]. The visco-elastic coefficient of the 20% guest-host system exhibited very little change compared to the UCF-Base host alone. Further doping the system with 40% of the guest showed a significant increase in the visco-elastic coefficient (Figure 3.12). However, compared to the single terphenyl compounds, the mixtures retained the positive characteristics of the best performing compounds exhibiting visco-elastic coefficient values comparable to the difluorinated compounds and significantly less than compounds with four fluorine substitutions. Despite retaining relatively high birefringence, the Figure of Merit at optimal temperature demonstrated by the guest-host systems was lower than the terphenyl host mixture (UCF-Base) due to lower clearing temperatures and higher visco-elastic coefficients. However, even the lower Figure of Merit demonstrated by UCF-B is higher than the commercially available liquid crystals [7].
The presented results of the multi-fluorinated NCS terphenyl base mixture and subsequent guest-host mixtures demonstrate potential usefulness in liquid crystal devices, such as optical phased arrays. Further investigation of such systems will lead to improved eutectic mixture formulations with lower melting temperatures and will diminish or eliminate smectic phase. The goal for these mixtures will be to obtain nematic phase at room temperature and to suppress smectic phase to below 0°C or to eliminate smectic phase completely. The choice of dopant compounds will be the critical factor in designing mixtures with higher birefringence and improved operating temperatures. As demonstrated in the presented results, increasing the concentration of the guest mixture improves mesomorphic properties but adversely affects the electro-optic properties due primarily to the lower clearing temperature.

Figure 3.11 Temperature dependent birefringence (Δn) of the terphenyl guest-host mixtures studied.
Figure 3.12 Temperature dependent visco-elastic coefficient ($\gamma_1/K_{11}$) of the terphenyl guest-host mixtures studied.

Figure 3.13 Temperature dependent FoM of the terphenyl guest-host mixtures studied.
3.2.3. Phenyl Tolane Compounds

The second group of compounds studied contained rigid core structures consisting of phenyl-tolane with isothiocyanate (NCS) polar groups. In these molecules, two saturated phenyl rings were linked to a third phenyl ring by a carbon-carbon triple bond, as illustrated in the molecular structures shown in Table 3.2. Both the saturated phenyl rings and the triple bond contributed π-electrons to the molecular conjugation and enhanced the birefringence of the molecules by increasing the molecular polarizability. In general, UV stability of the tolane linking group would be of concern, but for IR applications filters can be used to eliminate this risk. Table 3.2 lists the compound structures and Figure 3.14 illustrates the mesomorphic properties of the eight isothiocyanato phenyl-tolane LCs investigated. Despite multiple lateral substitutions, the melting temperatures of these compounds were relatively high. The di-fluorinated isothiocyanato-tolane compounds, 7 and 8, exhibited a wide nematic range with clearing point temperatures over 200 °C. The propyl homologue (Compound 7) exhibited a melting transition at 122 °C which was relatively high. The pentyl homologue (Compound 8) showed a much lower melting transition at 55 °C, but exhibited a smectic phase up to 119 °C. The melting point heat fusion enthalpy (ΔH) was significantly different for the homologue pair of Compounds 9 and 11. Compound 7, which had a short alkyl chain of three carbons, showed a ΔH value of approximately 6.3 kcal/mol that was about twice that of Compound 8, which had an alkyl chain length of five carbons. A different lateral fluorination scheme was utilized for the second homologue series (Compounds 9, 10, and 11) that was investigated. This triple fluorination scheme had a fluorine substitution in both the second and third positions of the middle phenyl
<table>
<thead>
<tr>
<th>ID No.</th>
<th>Structures</th>
<th>Phase Transition Temperatures [°C]</th>
<th>ΔH (Cr-N) [cal/mole]</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>C₃H₇F₅NCS</td>
<td>Cr 122.0 N 233.6 Iso</td>
<td>6263</td>
</tr>
<tr>
<td>8</td>
<td>C₅H₁₁F₅NCS</td>
<td>Cr 55.0 S 119.0 N 208.5</td>
<td>3770</td>
</tr>
<tr>
<td>9</td>
<td>C₂H₅F₅NCS</td>
<td>Cr 73.7 N 223.3 Iso</td>
<td>5452</td>
</tr>
<tr>
<td>10</td>
<td>C₃H₇F₅NCS</td>
<td>Cr 82.2 S 89.2 N 240.5 Iso</td>
<td>5814</td>
</tr>
<tr>
<td>11</td>
<td>C₅H₁₁F₅NCS</td>
<td>Cr 53.5 S 135.0 N 218.0 Iso</td>
<td>3359</td>
</tr>
<tr>
<td>12</td>
<td>C₃H₇F₅NCS</td>
<td>Cr 110.6 N 204.1 Iso</td>
<td>7738</td>
</tr>
<tr>
<td>13</td>
<td>C₃H₇F₅NCS</td>
<td>Cr 124.0 N 225.9 Iso</td>
<td>7234</td>
</tr>
<tr>
<td>14</td>
<td>C₅H₁₁F₅NCS</td>
<td>Cr 75.0 S 152 N 233 Iso</td>
<td>6550</td>
</tr>
</tbody>
</table>
ring and the last phenyl ring had a single fluorine substitution in the position adjacent to the NCS terminal group. The measured melting point transition temperature for these compounds was significantly lower than that observed for di-fluorinated Compounds 7 and 8, but only the ethyl homologue did not exhibit a smectic phase. The pentyl homologue in this series showed an exceptionally low heat fusion enthalpy ($\Delta H$) of about 3.4 kcal/mol. Although the melting temperatures for Compounds 9, 10, and 11 were relatively low, the smectic phase present in the propyl and pentyl homologues decreased their usefulness. The positions of the laterally substituted fluorine in Compound 12 were different from the tri-fluorinated phenyl-tolanes already discussed. The middle phenyl ring had a fluorine group at the second position and the last phenyl ring adjacent to the terminal NCS group was fluorinated in the 3 and 5 positions, similar to Compounds 7 and 8. Comparing the propyl homologues (Compounds 7 and 12) showed that an additional fluorine substitution at the middle ring slightly decreased melting temperature. Comparing the melting temperatures of Compounds 7 and 13 as well as 8 and 14
showed that fluorination of the phenyl ring adjacent to the NCS group results in the best mesomorphic properties of the di-fluorinated series considered.

High birefringence ($\Delta n$) values were expected from the phenyl-tolane series of compounds as the three saturated phenyl rings and the carbon-carbon triple bond contribute many $\pi$-electrons the molecular conjugation. The experimental data and fitting results for the temperature dependent birefringence of selected di- and tri-fluorinated phenyl-tolanes are illustrated in Figure 3.15. Among presented compounds, di-fluorinated Compound 7 had the highest birefringence, whereas the least appealing was Compound 12 based on this comparison. From the equation used to extrapolate the FoM, Equation 3.2.4, it is evident that the birefringence of an LC strongly depends on the clearing point temperature. Therefore, to make unbiased comparisons we evaluated the birefringence of each set of the components at a reduced temperature defined as $T/T_c$, with results shown in Figure 3.16. If compounds of equal alkyl chain length are compared, it is evident that fewer lateral fluorine substitutions have higher birefringence. This is not surprising, as fluorine substitutions trap electrons and decrease the number of $\pi$-electrons able to contribute to the electron conjugation that enhances birefringence. Another aspect of molecular structure that affects birefringence is that a longer alkyl chain slightly decreases the birefringence because of the molecular packing density is lowered. If the homologue series of Compounds 9, 10, and 11 are compared, this effect can be seen in Figure 3.17 and Figure 3.18. Comparing the two tri-fluorinated compounds from Figure 3.15 and Figure 3.16, Compound 12 has a slightly higher birefringence.
than Compound 10 which demonstrates that fluorine substitutions adjacent to the polar group is preferable to substitutions in the middle ring.

By measuring the free relaxation time of a homogeneous cell, we are able to calculate the visco-elastic coefficient of the LC compounds [24]. Results are illustrated in Figure 3.19 and Figure 3.21. We found that Compounds 12 and 13 demonstrated the highest visco-elastic coefficient among the investigated phenyl-tolane structures. Compound 10, tri-fluorinated at different positions of the rigid core phenyl rings, exhibited a moderate visco-elastic coefficient. Surprisingly, the lowest value of $\gamma_2/K_{11}$ measured was the double fluorinated Compound 14.

Despite having a long, five carbons alkyl chain, Compound 14 exhibited a slightly lower visco-elastic coefficient than Compound 7. If the difluorinated compounds with different lateral fluorination positions were compared, we observed the following sequence of $\gamma_2/K_{11}$ values:

$$
\text{Compound 14} < \text{Compound 7} < \text{Compound 13}
$$

Using the reduced temperature scale illustrated in Figure 3.20, we observed the same sequence. When the $\gamma_2/K_{11}$ coefficient was compared for the homologue series of Compounds 9, 10, and 11, the pentyl homologue (Compound 11) exhibited the lowest value. This result was similar to the comparison of di-fluorinated compounds, for which the pentyl homologue (Compound 14) also demonstrated the lowest $\gamma_2/K_{11}$ value. Surprisingly the ethyl homologue (Compound 9) exhibited a slightly higher visco-elastic coefficient than the other two homologues with shorter alkyl chain lengths, as illustrated in Figure 3.21 and Figure 3.22.
Figure-of-Merit (FoM) was used for comparison of compound switching speed, and is the most important comparison. Figure 3.23 shows the temperature dependent FoM of di- and tri-fluorinated phenyl-tolanes. Among all the compounds investigated, the difluorinated compound (7) showed the highest FoM of 180 μm²/s at 160-170 °C. Conversely, the trifluorinated compound (12) exhibits the lowest FoM as it barely reached 100 μm²/s at its optimal temperature due to its lowest birefringence and highest visco-elastic coefficient. As illustrated in Table 3.2, Compound 10 is different from Compound 12 only in the positions of the lateral fluorine substitutions, but their mesomorphic properties and electro-optical performance are quite different. Compound 12, with two fluorine substitutions adjacent to the NCS polar group, had a high melting point and low clearing point and therefore had a much narrower nematic range when compared to Compound 10. The low Tc of Compound 12 negatively affected its birefringence and additionally its visco-elastic coefficient was relatively high. As a result of these to parameters, the FoM of Compound 12 was low. In contrast, Compound 10 demonstrated a respectable FoM of 140 μm²/s at the optimal temperature, which was slightly higher than that of the di-fluorinated Compounds 13 and 14. For the tri-fluorinated Compounds 10, 12, 13, and 14, we found that there was no significant difference between the di- and tri-fluoro substitutions. Instead, the critical issue was the position at which the fluorine was substituted. The two compounds (12 and 13) with a single fluorination in the middle phenyl ring showed a severe increase in visco-elastic coefficient which made them less appealing from the perspective of achieving a fast response time.
Figure 3.15 Temperature dependent birefringence ($\Delta n$) of phenyl-tolane compounds.

Figure 3.16 Birefringence ($\Delta n$) of phenyl-tolane compounds versus Reduced Temperature
Figure 3.17 Temperature dependent birefringence ($\Delta n$) of tri-fluorinated phenyl-tolane compounds.

Figure 3.18 Birefringence ($\Delta n$) of tri-fluorinated phenyl-tolanes versus Reduced Temperature
Figure 3.19 Temperature dependent visco-elastic coefficient ($\gamma_1/K_{111}$) of phenyl-tolane compounds.

Figure 3.20 Visco-elastic coefficient ($\gamma_1/K_{111}$) of phenyl-tolanes versus Reduced Temperature
Figure 3.21 Temperature dependent visco-elastic coefficient ($\gamma_1/K_{11}$) of phenyl-tolane compounds.

Figure 3.22 Visco-elastic coefficient ($\gamma_1/K_{11}$) of tri-fluorinated phenyl-tolanes versus Reduced Temperature
Figure 3.23 Temperature dependent FoM of phenyl-tolane compounds.

Figure 3.24 FOM of phenyl-tolane compounds versus Reduced Temperature.
Figure 3.25 Temperature dependent FoM of tri-fluorinated phenyl-tolane compounds.

Figure 3.26 FOM of tri-fluorinated phenyl-tolane compounds versus Reduced Temperature.
3.2.4. Phenyl Tolane Mixtures

Based on the single compound results in the previous section, several mixtures were composed using different concentration of fluorinated phenyl tolane isothiocyanates. Like the terphenyl base mixture previously discussed, a formulation based solely on the available phenyl tolane isothiocyanate compounds, possesses a high melting point and extended smectic temperature range. Therefore, its results are not included here. Instead, to lower the melting point we prepared a base mixture containing highly conjugated isothiocyanato tolanes, cyclohexyl tolanes, and terphenyls. The purpose was to accommodate as high a concentration of phenyl tolane isothiocyanates as possible while not compromising the electro-optical performance of the final composition.

The phase transition temperatures, as determined by DSC analysis, and concentration values of selected sample mixtures are listed in Table 3.3 and illustrated in Figure 3.27. The nematic range of the mixtures was very wide, spanning about 100°C. The D10 mixture exhibited no smectic phase, and more importantly was nematic at room temperature. As expected, as the concentration of phenyl tolane dopant was increased the melting point of the mixtures and more importantly caused the smectic to nematic transition to appear. The base mixture used for our experiment showed birefringence of 0.37 at room temperature. As the degree of dilution by high birefringence phenyl tolanes was increased in the base mixture, the birefringence of the UCF-Ds mixtures increased as shown in Figure 3.28. The relaxation time of the diluted mixtures also increased slightly with increased amounts of base mixture. The visco-elastic coefficient of the four investigated mixtures of different degrees of dilution is illustrated
in Figure 3.29. The temperature dependent figure-of-merit for the mixtures is illustrated in Figure 3.30. Due to the lower birefringence and slightly increased viscoelastic coefficient, UCF-D10 exhibits a 30% lower FoM than UCF-D50.

Table 3.3 Phase transition temperatures and compositions of the selected doped systems.

<table>
<thead>
<tr>
<th>Doped System</th>
<th>Wt % ratio (host:guest)</th>
<th>Phase Transition Temperatures [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>UCF-D10</td>
<td>90 : 10</td>
<td>Cr 8.9 N 124.7 Iso</td>
</tr>
<tr>
<td>UCF-D20</td>
<td>80 : 20</td>
<td>Cr 7.3 S 25.6 N 128.8 Iso</td>
</tr>
<tr>
<td>UCF-D30</td>
<td>70 : 30</td>
<td>Cr 12.7 S 32.4 N 137.6 Iso</td>
</tr>
<tr>
<td>UCF-D50</td>
<td>50 :50</td>
<td>Cr 29.1 S 62.7 N 160.1 Iso</td>
</tr>
</tbody>
</table>

Figure 3.27 Phase transition temperatures of phenyl-tolane mixtures
Figure 3.28 Temperature dependent birefringence ($\Delta n$) of the phenyl-tolane mixtures.

Figure 3.29 Temperature dependent visco-elastic coefficient ($\gamma_1/K_{11}$) of the phenyl-tolane mixtures.
Figure 3.30 Temperature dependent FoM of the phenyl-tolane mixtures.
CHAPTER FOUR: CONCLUSION

The first set of compounds that were developed, characterized, and analyzed were three homologue series of laterally fluorinated terphenyl rigid core structures with isothiocyanate (NCS) polar groups. It was noted that by increasing the number of laterally substituted fluorine the birefringence gradually decreased with a maximum of 25% loss if 4-propyl-3”,5”-difluoro-4”-isothiocyanato-[1,1’;4’,1’’]terphenyl (Compound 5) was compared with 4-pentyl-2’,3’,3”,5”-tetrafluoro-4”-isothiocyanato-[1,1’;4’,1’’]terphenyl (Compound 1) at a temperature of 25°C. The visco-elastic coefficient was also significantly affected by increasing the number of lateral substituents. Using the same compounds for comparison (1 and 5), the $\gamma_1/K_{11}$ coefficient showed a difference of almost 500% at 25°C. As a result, the Figure of Merit (FoM) that was used as a performance parameter was substantially different for presented compounds. Detailed DSC analysis did not show a significantly lower melting point temperature when the number of fluorine substitutions was increased from two to four. These results led to the conclusion that for the case of rigid terphenyl-NCS core, further fluorination does not affect mesomorphic properties to the same extent as fluorine substitutions in the positions adjacent to the polar group. The difluorinated NCS terphenyl structure (Compounds 5 and 6) showed the best overall performance of the three fluorinated structures studied. These two compounds will yield faster response times, as the higher birefringence value will allow for a thinner cell gap and the lower viscosity will allow the molecules to be rotated faster. The mesomorphic properties (wide nematic range, suppressed smectic phase) and relatively low melting heat enthalpy makes these double-fluorinated NCS terphenyl structure an ideal
candidate for eutectic mixtures and potentially an all-isothiocyanatoterphenyl based mixture. However, since none of the single terphenyl compounds studied, even the best performing, were nematic at room temperature, mixtures must be formulated to lower the operating temperature to room temperature such that they can be usable in device applications.

Designing a multi-fluorinated NCS terphenyl host mixture and doping with fluorinated NCS tolanes produced high birefringence mixtures with operating temperatures well below those obtained for single compounds. Additionally, the visco-elastic coefficient exhibited by the base mixture and tolane-doped mixtures retained the low values of the best performing single compounds so that switching speed of future applications can be improved. Future work should concentrate on designing guest mixtures that achieve the best balance between improving mesomorphic properties and retaining the advantageous electro-optic properties of the all-terphenyl base mixture.

The second set of compounds that were developed, characterized, and analyzed were a series of eight laterally fluorinated phenyl-tolane rigid core structures with isothiocyanate (NCS) polar groups. In general, UV stability of the tolane linking group would be of concern, but for IR applications filters can be used to eliminate this risk. Multiple fluorinations were seen to lower the melting temperature, but also increase the viscosity. Therefore a compromise needed to be made between high Figure of Merit (FoM) and low melting temperature of the compounds. It was observed that having the middle phenyl ring difluorinated, without additional fluorine substitutions of the phenyl ring linked with terminal NCS group decreases visco-elastic coefficient. At present it is still unclear whether this situation is similar to the one observed for
the laterally fluorinated dialkyl terphenyl compounds [15]. Further synthesis needs to be performed in order to make a more detailed comparison. Additionally, it was seen that using the high-birefringence phenyl-tolane compounds as dopants in a base mixture consisting of isothiocyanato tolanes, cyclohexyl tolanes, and terphenyls, the nematic range could be lowered to room temperature and that the smectic phase evident in the single compounds could be eliminated or suppressed to below 0°C. Future formulations of these mixtures could improve birefringence while maintaining the mesomorphic properties obtained in the low-concentration mixtures. The presented fluorinated phenyl-tolane isothiocyanates show high FoM and are particularly appealing for long wavelength applications, such as laser beam steering.

ACKNOWLEDGEMENTS

This work is supported by DARPA Bio-Optics Synthetic Systems program under Contract No. W911NF04C0048, and NATO Programme Security Through Science, Collaborative Linkage Grant No. CBP.EAP.CLG 981323.
REFERENCES


