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LOW ABSORPTION LIQUID CRYSTAL MATERIALS FOR MIDWAVE INFRARED

by

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

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ABSTRACT

Liquid crystal is an amazing class of soft matters with applications spanning from visible, infrared, millimeter wave, to terahertz. In addition to direct-view displays and projection displays, liquid crystal is also widely used in adaptive optics, tunable-focus lens, and laser beam steering. Although the visible region has well developed materials and mixtures for the vast variety of applications, the midwave infrared (MWIR) region of the electromagnetic spectrum invites much development as only a few materials have been developed with these applications in mind. Unlike visible region, the major challenge for mid-wave infrared liquid crystal is inherently large absorption loss. To reduce absorption, some molecular engineering approaches have been considered, such as deuteration, fluorination, and chlorination. The fluorine and chlorine not only act as the polar group to provide dipole moment but also helps shift some vibration absorption bands outside the MWIR window. Long phenyl ring compounds, fluorinated tolane materials, and chlorinated terphenyl mixtures are explored; as well as a look as the potential bromine might introduce for future development. In this thesis, we first review the current materials and their performance in the mid-wave infrared region, explain the need for higher performing liquid crystals, and then discuss the methodology of compound development and mixture formulation. Some new chlorinated liquid crystal compounds are synthesized, mixture formulated, and their properties evaluated. Finally, we will explain the future work which needs to be performed in this field.
This thesis is dedicated to God and my Lord and Savior, Jesus Christ, who has provided ample discovery opportunities in the realm of science. The more I learn, the more I come to know the scientifically creative side of God.
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CHAPTER 1: INTRODUCTION

1.1 Background

Liquid crystals (LCs) have become a vital ingredient to our daily tech-savvy lives around the world. They are utilized in the consumer market in television, computer screens, projectors, tablets, and smartphones. Many LC materials have been developed and optimized for these uses in the visible portion of the electromagnetic spectrum. Optimization efforts have shown advancements in important parameters such as viscosity, birefringence ($\Delta n$), dielectric anisotropy ($\Delta \varepsilon$), absorption coefficient ($\alpha$). These have led to device improvements in response time which allows for high frame rates, lower driving voltage leading to lower power consumption which is especially important in battery operated devices, and higher transmittance which helps improve contrast ratio. Most of these developments have been done in the visible region of light, leaving a gap for liquid crystal development for use in the infrared region.

1.2 Application Motivation

The infrared (IR) region beckons the development of high performing liquid crystal materials for its own set of applications. Some of these applications include optical waveguides, laser pulse modulation, and IR displays. Like Displays which has its own assortment of devices for different applications, laser beam steering is another important application full of varying devices and their associative applications. Some of these devices include items such as micro-electro mechanical systems (MEMs), optical
phase arrays (OPAs), electro-wetting array, and the steerable electro-evanescent optical refractors (SEEORs). An affordable high precision random laser beam steering device opens doors for use in industry such as laser target designation, missile countermeasures, satellite communication, wind profiling, and gas cloud identification.

1.2.1 Optical Phase Arrays

Optical Phase Arrays (OPAs) have become a popular method for laser beam steering since they were one of the first solutions to offer a method that did not need the mechanical mirror movements which allowed for high speed steering, and can also be compact and low power. OPAs function in the same basic way as RADAR arrays, but unlike RADAR arrays that usually generate the signal as part of the arrays, OPAs take an input beam and redirect it based on phase modulation. OPAs face more complexity than their RADAR phased array antenna counterparts due to the magnitudes of difference between wavelengths [1]. There are several ways the phase modulation can be accomplished that range in level of simplicity and efficiency, usually gaining efficiency with complexity. Similar to display applications, the OPA has an LC cell containing two substrates that sandwich a liquid crystal and its layers that the beam passes through which is shown in Figure 1. On both substrates, there are anti-reflective coatings and an alignment layer which adds a slight pre-tilt angle, ~2-3°, to the LC. On one substrate there is a common transparent electrode and on the other there are striped transparent electrodes at a designed specific size and spacing that can be powered individually for voltage control. This stripped electrode pattern allows for a
stair-step voltage, and thus a stair step index of refraction, and a phase shifted output beam from a polarized input beam.

The voltage is applied in step increments that repeat $2\pi$ phase. An example of a one dimensional OPA with the applied voltage step slope and the phase shifted output wave is shown in Figure 2 [1]. Due to the diffraction nature and fringing fields of an OPA, the intensity falls off as the angle off-axis increases due to higher order modes and it is difficult to achieve greater than $\sim 4^\circ$. The steering efficiency is governed by a relation to the number of grating steps used and by

$$\eta = \left(1 - \frac{\Lambda_F}{\Lambda}\right)^2 \quad (1)$$

where $\Lambda_F$ is called the flyback region and $\Lambda$ is the grating period between $2\pi$ phase resets. The flyback region comes from the device’s inability to instantly change its
voltage and is comprised from the device design and liquid crystal visco-elastic properties including birefringence [1]. Another important OPA parameter is the switching speed which comes from the liquid crystal material time constant. This time constant can be the relaxation time or the turn-on time depending if the device is voltage driven into the on and off state.

To address the OPA small angle intensity issue, blazed diffraction gratings, volume holograms, or birefringent prisms can be used to assist in this with angles up to 40° [2, 3]. These combined allow for rough wide angle steering as well as high precision continuous steering at narrow angles.

The ability to fabricate and power the number of electrodes needed to make a 2-D array is beyond the current technological capabilities. 2-D devices can be achieved by the use of two 1-D OPAs in series. An example of a 2-D wide angle system is shown in Figure 3; it shows the use of gratings and two OPA pairs for large and small angle steering. Reflective devices can also be used to offer faster switching as half of the LC thickness is needed since light passes through the cell twice.
OPAs have been demonstrated in the visible region as well out to the long-wave region of 10.6μm [4]. Much development of optimization has been done and patents
developed involving fabrication and device driving techniques [5, 6, 7]. The physics of
diffraction and fringing field have been studied through numerical modeling and optimal
selection and design methods have been proposed while considering LC tilt angle of the
LC director in relation to effective index of refraction, width of electrodes and cell
thickness concerning fringing field effect, surface LC alignment angle in relation to out-
of-plane twist component (leads to de-polarization of incident light). With those
considered, diffraction efficiency can be determined through voltage and cell thickness
selection [8].

1.2.2 LC Optical Waveguide

The benefits of laser pulse modulation using liquid crystals is that the phase can
be modified at a high level of precision for high speed lasers in a controlled manner
without the use of mechanical moving parts. One method of beam steering is through
the use of an optical phase array (OPA) in which separately controlled electrode strips
are mounted to glass so that a gradient of voltages can be applied to produce a
constant phase ramp between 0 and $2\pi$.

SEEORs have been developed by Vescent Photonics and offer an interesting
use for LC device employing waveguide optics and an interesting use of the cladding
layer and liquid crystals. This technology is useful in vehicle collision avoidance,
spectrometers, optical switches, optical delays, and tunable lasers. An example of one
dimensional optical waveguide SEEOR is shown in Figure 4 [9]. Two dimensional
steering has been achieved through the use of out of plane beam steering and has also been demonstrated.

Figure 4: Example of 2-D Optical Waveguides. Referenced from [9]

The one dimensional figure is sufficient in explaining the role of liquid crystal material. The input laser beam is guided through a core with air as a cladding and then enters a region with a liquid crystal cladding layer on the top; a side view breakdown can be viewed in Figure 5 [10]. The liquid crystal has a high birefringence of \(~0.2\) and has rubbed alignment layers on both top and bottom of the LC cell. Voltage can be applied to the electrode changing the index of refraction of the LC cell. This in turn changes the index of refraction of the waveguide that is seen by the laser, and although it has a smaller effect since the birefringence is only in the cladding, this can be compensated by a longer path length [9, 11]. The greater the birefringence, the more control and wider field of view (FOV) the device can achieve in less space.
This SEEOR device compensates for several of the LC parameters that can be a hindrance in other devices. Response time is addressed by allowing the beam core to be a solid material and the LC being a thin layer, and the thinner the LC gap, the quicker it can be driven. The SEEOR has been demonstrated in the visible and near infrared region thus far.

1.2.3 Other IR Applications

IR display and applications used to characterize and test performance of IR detectors which are widely used for industry by fire fighters and in security. They are also a vital component in the defense industry for both ground and aerial applications.
1.3 Overview

Now that benefits of high performing liquid crystal mixtures in the IR region has been realized through the applications discussed, the properties and development of the materials and mixtures will be discussed. This text will cover the testing of several liquid crystal materials and their performance in the mid-wave infrared region. First, liquid crystals will be explained along with the governing equations of the physical properties which dictate the design limitations and tradeoffs. Then the methods of material selection and measurement methods will be discussed. The results will be given and explained. A discussion of future work will be included. Lastly, there will be a conclusion summing the main points.
CHAPTER 2: LIQUID CRYSTAL MATERIALS

In 1922, a scientist by the name of George Friedel in reference to these unique materials we know as liquid crystals (though he objected to this name) that had already been discovered and studied for 33 years by several people in various countries said there exists

“…a field of study that is scarcely penetrated by exploration and extraordinarily rich in surprises. At each step one can find unresolved problems. [12]”

Although it has been over 90 years since he has claimed this and much has been learned, it still holds true today as discoveries and technological advances continue to allow us to discover and develop our understanding of these materials properties and characteristics.

Liquid crystals, named as such by Otto Lehmann [13], were discovered in cholesteryl benzoate (145-178.5°C) by botanist Friedrich Reinitzer in 1888 when he achieved a white hazy liquid mixture just after the melting point before achieving a uniformly clear liquid in the isotropic phase which is now known as the clearing point [14]. This phase between the solid and liquid is known as the mesophase. Years later in 1962, a connection was found through an electric field induced over a liquid crystal (LC) material p-azoxyanisole with a melting point of 116°C that was heated to 125°C and applied 1,000 V/cm, and long parallel strips were observed [15]. Richard Williams patented this envisioning it could lead to usefulness in television which was still far off
2.1 Liquid Crystal Definition

Liquid Crystals are amorphous materials that exist in the mesophase between a crystalline solid and an isotropic liquid. They possess the fluidity of a viscous liquid while retaining some important characteristics of a crystal. Two vital characteristics of liquid crystals are their optical (birefringence) and electromagnetic anisotropy. LCs can have structures of either a discotic, disc-like, shape or a calamitic, long thin rod, shape [17]. They can occur in a specific temperature region, thermotropic, like the one discovered by F. Reinitzer, or they can occur through the introduction of a solvent, lyotropic, which are useful in the biology and biophysics. The text will focus on the thermotropic calamitic liquid crystals as they are utilized in the applications mentioned in Chapter 1, and henceforth any mention of liquid crystals unless otherwise stated assumes it is of this type.

As a liquid crystal transitions from a solid to an isotropic liquid over temperature, the properties change as would be expected. There are some sub-phases within this region that may occur, but are not required, depending on the crystal which depend on the order. The phases can be listed in order of occurrence: Solid, Smectic-C, Smectic-A, Nematic, Isotropic, shown in Figure 6 [18].
The molecules tend to point on a direction parallel to their long axis which is given by the director, \( n \), and can change based on location given as \( n(r) \).

Smectic is the LC phase just beyond the melting point. It is derived from the word soap because of its slipperiness [12]. It is viscous and most similar to a solid because they possess two dimensional order, both positional and orientation. The molecules are arranged side by side in layers, but unlike solids, these layers are free to move over each other. Although there are at least 9 smectic phases, the two main types are smectic-A and smectic-C. Smectic-A is when the long axis of the molecule, the director, is perpendicular to the layers and the tilt goes to zero [19]. Smectic-C phase transition comes from cooling smectic-A, has a lower entropy, and is notably different from Smectic-A by the director being at some nonzero angle from the layers [20, 21]. The LC can have an added component or can be intrinsically chiral, meaning that the layers direction rotates in a helical structure, or along a cone, then this would fall into a smectic-C* phase. These chiral smectic-C phases can also be ferroelectric [22, 23].

Nematic means ‘threadlike’ is the LC phase nearest the clearing point, and have become the mainstream phase of choice for the displays industry. In nematic phase, the
distinct layers seen in the smectic disappear. The molecules are all oriented in one
direction without any position orientation, meaning they can rotate and translate freely.
Nematic phase will be the phase used for materials of this discussion.

Cholesteric, also called chiral-nematic, liquid crystals are arranged in very thin
layers where each layer has the long axis of the molecules aligned in parallel to each
other. The director is rotated slightly from layer to layer with a helical structure that
causes Bragg scattering in the visible light creating a beautiful effect, decreasing with
temperature rise [24]. From a thermal perspective, the chiral phase is equivalent to the
nematic phase. This chiral phase can allow for ferroelectric behavior, which can
contribute to fast response time but was not widely adopted in display applications due
to the degraded greyscale.

2.2 Liquid Crystal Physical Properties

There are a few properties that can be defined for a specific material that will
determine its usefulness in certain applications or types of devices. Some of the main
parameters will be described in the following sections.

2.2.1 Order and Elastic Constants

It is helpful to express a mathematical representation of the direction and order in
relation to the LC structure. To describe the broader sense of direction, we use the
order parameter given by

\[ S = \frac{1}{2} \left( 3 \cos^2 \theta - 1 \right) \]  \hspace{1cm} (2)
where the average of the polar angles, $\theta$, which is the angle between the director and the longitudinal axes of the molecules. The Order is a scaled parameter between 0 and 1, with 0 as the fully chaotic state which occurs when it reaches the isotropic phase. In opposition to the Order, there are elastic deforming and restoring forces in LC molecules. These forces can be broken down into three basic parts known as the elastic moduli: splay ($K_{11}$), twist ($K_{22}$), and bend ($K_{33}$) and are shown in Figure 7.

Figure 7: Elastic moduli: Splay ($K_{11}$), Twist ($K_{22}$), and Bend ($K_{33}$).

Splay, $K_{11}$, molecules get spread out by stress (a) twist-molecules are twisted by stress, $K_{22}$ (b), and bend- molecules are bent by stress, $K_{33}$ (c) and is given by the elastic theory
\[ f_x = \frac{1}{2} [ K_{11} |\nabla \cdot n|^2 + K_{22} |n \cdot \nabla \times n|^2 + K_{33} |n \times \nabla \times n|^2 ] \]  

where \( f_x \) is the free energy \([18, 25]\). A more simplified relation between the order and the elastic constant is

\[ K_{ii} = A_0 S^2 \]  

where \( A_0 \) is the material constant \([26]\). Nematic LC tend to have an order in the range of 0.4-0.7. As far as elastic moduli are concerned, \( K_{22} < K_{11} < K_{33} \) for most nematic LCs.

### 2.2.2 Viscosity

Viscosity is more than just the ease of flow of the material; it can split into parts, and rotational viscosity is the primary one of concern for uniaxial LCs as it has to do with the resistance of the LC to rotate about the director axis. Rotational viscosity depends on molecular orientation, structure, and temperature. It can be complicated but takes some the form of

\[ \gamma_1 = f(S)g(T) \propto S \cdot \exp\left(\frac{E}{k_B T}\right) \]  

where \( f(S) \) is some function of the directional order parameter, \( g(T) \) is some exponential function of temperature, and the second equation is one of several theories where \( E \) is activation energy and \( k_B \) is Boltzmann’s constant \([27, 28]\). As seen in the equation, viscosity is exponentially affected by temperature. Since the order parameter is related to viscosity and the elastic constant, it is beneficial to use a combined term called the visco-elastic coefficient and is given by
\[
\frac{\gamma_1}{K} = \frac{A \cdot \exp\left(\frac{E}{(k_B T)}\right)}{(1 - T/T_c)^\beta}
\]

Where \(\gamma_1\) is rotational viscosity, \(K\) is elastic constant, \(E\) is the activation energy, \(k_B\) is Boltzmann constant, \(T\) is temperature, and \(T_c\) is the clearing temperature.

2.2.3 Dielectric Anisotropy

Dipole moment, permittivity, and dielectric anisotropy are all ways to discuss a material’s electrical properties that determine how responsive it is to an induced electric field, which can be drastically effected by the polarity of the material. The bonds in the material may be polar if the electrons are not equally shared between the atoms. The polarity of the bonds within a material are directionally additive in determining the polarity of the material. The dielectric anisotropy and can be expressed by the equation:

\[
\varepsilon_\parallel = NhF \left\{ \langle \alpha_\parallel \rangle + \left( \frac{F\mu^2}{3k_B T} \right) \left[ 1 - S(1 - 3\cos^2 \theta) \right] \right\}
\]

\[
\varepsilon_\perp = NhF \left\{ \langle \alpha_\perp \rangle + \left( \frac{F\mu^2}{3k_B T} \right) \left[ 1 + \frac{S}{2} (1 - 3\cos^2 \theta) \right] \right\}
\]

\[
\Delta \varepsilon = \varepsilon_\parallel - \varepsilon_\perp = (\langle \alpha_\parallel \rangle - \langle \alpha_\perp \rangle) - \frac{\mu^2 FS}{2k_B T} (1 - 3\cos^2 \theta)
\]

where \(\varepsilon_\parallel\) is the permittivity along the axis of the director and \(\varepsilon_\perp\) is the permittivity perpendicular to the director [18, 29]. With this definition, it is possible to have both positive and negative \(\Delta \varepsilon\), which makes sense depending on the orientation of the polar bonds orientation that can cause \(\varepsilon_\perp\) to be larger than \(\varepsilon_\parallel\). To utilize the dielectric anisotropy in a device, the LC molecules are aligned in a similar direction to each other.
which is normally done through rubbing a polymer layer to create order and a small pre-tilt angle. Dielectric anisotropy is variable with frequency, decreasing as frequency increases; some materials have a crossover frequency point where $\Delta \varepsilon$ crosses zero and becomes negative. It is also variable with temperature decreasing as temperature increases and quickly approaches zero at $T_c$ when the LC reaches the isotropic phase. In bulk material, even with polar LCs, the overall charge is neutral because the LC molecules are disorganized throughout. This is an important parameter in determining the amount of voltage needed to create a large enough electric field to fully rotate the liquid crystal rod-like structure.

2.2.4 Birefringence

Birefringence is the property that caused that milky appearance cholesteryl benzoate which alluded botanist F. Reinitzer to the existence of the liquid crystal phase. Birefringence is a different index of refraction between the extraordinary axis ($n_e$), along the director, and the ordinary axis ($n_o$); this is from the uniaxial nature of the crystal in its solid form. Birefringence creates a phase shift in the light output from the device which depends on the distance the light travels within the material. Using crossed polarizers with one before the device causing the input light to be polarized and the other being rotated 90° at the output, an intensity modulator can be obtained. Birefringence can be described as

$$\Delta n = n_e - n_o$$

(10)
For a phase modulation device, a $2\pi$ phase change is needed. For intensity modulation, to achieve a fully transparent to fully opaque state, only $\pi$ phase is needed for a transmissive device and half that for a reflective device. The relation is expressed as

$$\delta = \frac{(2\pi d\Delta n)}{\lambda} \quad (11)$$

where $\delta$ is the phase, $d$ is the cell gap containing liquid crystal material, and $\lambda$ is the wavelength. If we want a phase of $2\pi$ in the mid-wave region, which has higher wavelength than the visible region, we must have a larger $\Delta n$. Since a large cell gap means more total absorption, it is advantageous to have a high $\Delta n$ [30].

### 2.2.5 Absorption

Absorption occurs when energy is transferred from light to a material via oscillation causing a decrease in the overall transmission. An absorption peak known as resonance occurs when the energy of the photons is matched with the material. This energy is transferred through the vibration of covalent bonds as depicted in Figure 8. The resonant wavelength is given by

$$\lambda \sim \frac{2\pi c}{\sqrt{\frac{\mu}{K}}} \quad (12)$$

Liquid crystal resonant wavelengths are normally in the range of 1 $\mu$m to 50 $\mu$m.
The visible region has been fortunate that absorptions have not been a major issue. In contrast, the infrared region is cluttered by molecular vibrations and their overtones. Some molecular vibrations include asymmetrical stretching, symmetrical stretching, scissoring, twisting, rocking, wagging, and plane deformation. The molecular vibration can be related to the reduced mass by

\[ \omega = \sqrt{\frac{\kappa}{\mu}} \]  

where \( \omega \) is the molecular vibration frequency, \( \kappa \) is the spring constant, and \( \mu \) is the reduced mass of the diatomic group [31]. From the equation, it can be observed that as the mass increases, so does the resonant wavelength. This approach is used as molecules of larger mass are used in an attempt to shift absorption peaks to longer wavelengths, yielding a low absorption gap in the wavelength region of interest.

Another difference between the infrared and the visible region is related to the overall absorption. As the cell gap increases, the absorption coefficient becomes exponentially more important as it contributes to the total transmission by Beer’s law.
where $\alpha$ is the absorption coefficient and $l$ is the length the light travels through the medium, or cell gap in most cases. This is a bigger concern in the infrared region because the connection to wavelength calls for an increased cell gap size in order to achieve a full phase change as given in Equation (11).

### 2.2.6 Figure of Merit

In order to be able to compare materials and mixtures that have variable performance in their properties with one being more desirable in one property and another material performing better with a different property, a figure of merit has been established. Although the true ideal material mixture will depend on the device application and its associative requirements, a general figure of merit is very useful for general material and mixture development. For display applications, the figure of merit is given by

$$
\text{FoM} = \frac{\Delta n^2}{\gamma^{1/3}} \gamma^{1/3} / K
$$

where $K$ is the elastic constant determined by molecular alignment and can be reduced to a specific moduli ($K_{11}$, $K_{22}$, or $K_{33}$) depending on the orientation of the LC in a cell [32].

For infrared applications, transmission becomes more of a significant factor and should be considered in the merit of a material. A different figure of merit is defined considering transmission and using the absorption coefficient, $T$ is determined from Beer's law as given in equation (14) where $\alpha$ is the absorption coefficient and $d$ is the
distance. The distance can be determined by equation (11) where the phase, $\delta$, for most applications is $2\pi$ modulo which would make the distance, $d=\lambda/\Delta n$. From this, the figure of merit can be written as

$$T = \exp\left(-\frac{\alpha \lambda}{\Delta n}\right) \rightarrow \text{FoM} = \frac{\Delta n}{\alpha}$$

(16)

This figure of merit is useful for the infrared region where the absorption coefficient is a prominent factor.

2.3 Liquid Crystal Molecular Structure

Not all crystals possess a mesophase, and those that produce a mesophase may only possess one of the aforementioned liquid crystal phases. Over the years there has been somewhat of a standard structure developed with several common building blocks. It is within these guidelines that new LC materials can be developed and studied. The molecular structure has a direct impact on the physical properties previously mentioned which has a lot to do with the size, weight, and type of bonds. While one parameter is being optimized, care needs to be taken that the other properties remain reasonable and that the mesophase can be maintained before a useful mixture can be realized. The basic chemical molecular structure has a rigid body or core with a tail of sorts as seen in the left part of Figure 9 where A, Z, and B are part of the body and R and X makeup the tails.
2.3.1 The Rigid Body Portion of the Crystal

Regions A and B make the ring structure portion of the liquid crystal which are a part of the rigid core. A combination of none to several of either cyclohexane or benzene rings can be used. Cyclohexane consists of all saturated bonds that are all $\sigma$-bonds. The benzene ring consists of unsaturated bonds of six $\sigma$-bonds and six $\pi$-bonds. Replacing one or several of the Hydrogens on the ring in positions 2, 3, and/or 4 as shown in the right side of Figure 9 with a polar bond using cyano (CN), fluoro (F) or chloro (Cl) will impact the dielectric anisotropy. The saturated $\sigma$-bonds of the cyclohexane rings have a transition to $\sigma^*$ in the vacuum ultraviolet (VUV) region at c.a. 125nm. The $\pi$-bonds of the unsaturated phenyl ring is slightly less symmetric than a benzene (unattached to structure) whose transitions to $\pi^*$ are at c.a. 180nm, 203nm, and 256nm. These transition wavelengths depend on the conjugation length, which can be enlarged with substitutions of Hydrogen with molecules that contribute bonds or by adding phenyl rings. For example, 5PCH, has wavelengths of c.a. 198nm, 235nm, and
265nm. These UV absorptions have an effect in the visible and IR region from their harmonics.

Region Z is called the linking group. It is part of the rigid core but can vary and will have a great contribution to the temperature transitions. Some of the common linking groups are shown in Figure 10 and consist of saturated groups and unsaturated groups with double and triple bonds.

Region R and X from Figure 9 are called the side chain and terminal group. They can be identical, different, or one may not exist. The side chain usually consists of a chain like structure with a few common ones being some length $n$ of an alkyl ($C_nH_{2n+1}$), alkoxy ($OC_nH_{2n+1}$), alkenyl ($C_nH_{2n-1}$), or alkenyloxy ($OC_nH_{2n-1}$) group. The length of the chain has a direct effect of the melting temperature and the types of mesophase observed. In general, the longer the side chain, the lower the melting point to some degree and the smectic phase being introduced with continued length [18 of book]. The terminal group can consist of the same as the side chain groups just

Figure 10: Linking Group Examples
mentioned which have weak polar bonds, but other groups can be used to help increase the dielectric anisotropy, which in turn help decrease the applied voltage needed. The other terminal groups can consist of cyano (CN), isocyanate (NCS), sulfide and halides like F, C, and CF$_3$.

2.3.3 Several Liquid Crystal Materials

To observe how the building blocks of the chemical molecular structure of an LC relate to their properties, we will look at a few example LC materials.

2.3.3.1 Twelve CB materials of varying side chain length

The side chain length and composition is one method that can be altered for parameter optimization. To understand how the side chain can contribute to the temperature transitions and the liquid crystal phase achieved, we will look at the same LC body as 5CB but alter the length of the side chain. 5CB gets its name in part because of n=5 in its alkyl side chain (C$_n$H$_{2n+1}$), and Figure 11 shows the transition temperatures of the LC phases as the side chain ranges from n=1 to 12 where K is the crystalline phase, S$_A$ is the smectic-A phase, N is nematic phase, I is the isotropic phase, and (N) denotes a monotropic nematic phase [33].
It can be observed from Figure 11 that as the chain length is increased the nematic phase is introduced and the length continues to lower the melting point for n=3 to n=7. At n=8, smectic-A phase exists introduced along with the nematic phase, and as the chain length increases more, the nematic phase is lost.

2.3.3.2 Seven materials of varying core length

Another important parameter is the length of the core in a substance. Many LC materials have been developed that consist of single phenyl rings, biphenyl, and terphenyl compounds. Several compounds with varying core size are shown in Table 1 with the name, temperature transition phases, structure, birefringence, dielectric...
anisotropy, and enthalpy [34, 35, 33, 36, 37, 38, 39]. 5PCH, 5CB, 5BCH, and 5CT all have the cyano terminal group and an R5 side chain. 5PCH (single) and 5BCH (biphenyl) have an additional saturated hexane ring, while 5CB (biphenyl) and 5CT (terphenyl) do not have one. The comparison from the single phenyl ring to the biphenyl ring, of the hexane cyano compounds, shows an increase of 66°C in the melting point and a small increase in both the birefringence and the dielectric anisotropy. Comparing the biphenyl to the terphenyl compounds, 5CB to 5CT, shows an increase in the melting point by 107°C, a slightly higher birefringence, and no significant change in the dielectric anisotropy. Within either the single phenyl or biphenyl, some observations can be seen with some structural modifications such as modifying the terminal group from cyano (5PCH) to isocyanate (3NCS) where the cyano has a wider nematic phase. Looking at the three biphenyl compounds, it can be observed that the addition of oxygen by exchanging the chain from alkyl to alkoxy increases the nematic range, birefringence, and dielectric anisotropy, but increases the melting point by as much as it increased the nematic phase. 5CDP has two phenyl rings and a tolane; this material has a birefringence comparable to the terphenyl compound but a significantly lower melting point. One additional thing to note that it is not obvious from the table, is the UV absorption shifts of $\lambda_1$ and $\lambda_2$ related to the phenyl rings. The UV absorptions for a phenyl, biphenyl, and terphenyl material just discussed is shown in Figure 12. From the figure, $\lambda_1$ remains consistent but $\lambda_2$ shifts depending on the material. Table 2 lists $\lambda_2$ and the dichroic ratio of the absorption coefficients for several compounds from Table 1 [39]. A long $\lambda_2$ resonance can cause UV stability
issues for materials in the visible region, but since the focus is on the infrared region, the UV can be filtered out and a longer $\lambda_2$ could help with the absorption and birefringence at longer wavelengths.
Table 1: Structure and Properties of varying number of phenyl rings in core

<table>
<thead>
<tr>
<th>Core Type</th>
<th>Structure</th>
<th>Name</th>
<th>Phases(°C)</th>
<th>Δn</th>
<th>Δε</th>
<th>ΔH (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclohexane-Phenyl</td>
<td><img src="image1.png" alt="Structure" /></td>
<td>5PCH</td>
<td>K 30 N 55 I</td>
<td>0.13</td>
<td>9.8</td>
<td>4.3</td>
</tr>
<tr>
<td>Cyclohexane-Phenyl</td>
<td><img src="image2.png" alt="Structure" /></td>
<td>3NCS</td>
<td>K 39 N 41.5 I</td>
<td>0.19</td>
<td>13</td>
<td>3.6</td>
</tr>
<tr>
<td>Biphenyl</td>
<td><img src="image3.png" alt="Structure" /></td>
<td>5CB</td>
<td>K 24 N 35.3 I</td>
<td>0.18</td>
<td>16.7</td>
<td>4.1</td>
</tr>
<tr>
<td>Biphenyl</td>
<td><img src="image4.png" alt="Structure" /></td>
<td>5OCB</td>
<td>K 48 N 68 I</td>
<td>0.22</td>
<td>17.9</td>
<td>6.9</td>
</tr>
<tr>
<td>Biphenyl</td>
<td><img src="image5.png" alt="Structure" /></td>
<td>5BCH</td>
<td>K 96 N 222 I</td>
<td>0.19</td>
<td>12</td>
<td>4.7</td>
</tr>
<tr>
<td>Terphenyl</td>
<td><img src="image6.png" alt="Structure" /></td>
<td>5CT</td>
<td>K 131.5 N 240 I</td>
<td>0.32</td>
<td>16.3</td>
<td>4.1</td>
</tr>
<tr>
<td>Tolane</td>
<td><img src="image7.png" alt="Structure" /></td>
<td>5CDP</td>
<td>K 55 N 70.7 I</td>
<td>0.30</td>
<td>10</td>
<td>6.9</td>
</tr>
</tbody>
</table>
Figure 12: UV absorptions of $\lambda_1$ and $\lambda_2$ for 5PCH at left, 5CB in center, and 5CT on right. Referenced from [39].

Table 2: UV resonant wavelengths and absorption coefficient ratio of 5 different compounds

<table>
<thead>
<tr>
<th>Name</th>
<th>$\lambda_2$ (nm)</th>
<th>$\alpha_{//}/\alpha_{\perp}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5PCH</td>
<td>235</td>
<td>5.6</td>
</tr>
<tr>
<td>3NCS</td>
<td>272</td>
<td>6.5</td>
</tr>
<tr>
<td>5CB</td>
<td>282</td>
<td>5.6</td>
</tr>
<tr>
<td>5OCB</td>
<td>298</td>
<td>6.2</td>
</tr>
<tr>
<td>5CT</td>
<td>306</td>
<td>8.8</td>
</tr>
</tbody>
</table>

2.3.3.3 5CB, 4-Cyano-4'-pentylbiphenyl and D5CB

LC 4-Cyano-4'-pentylbiphenyl, also known as 5CB, has become somewhat of a standard in the industry. 5CB was first synthesized in 1972, is about 20 Å long, and has nematic phase at room temperature. Its three-dimensional chemical structure is shown in Figure 13. The shape ratio and bonds in 5CB cause it to be in nematic LC phase at room temperature with a range of c.a. 10°C. It has low absorption in the visible region,
and the UV absorption is shown in Figure 14 and the $\lambda_1$ and $\lambda_2$ absorptions can be observed, which change slightly depending on the method of measurement.

Figure 13: 3D Model of 5CB where blue is N, grey is carbon, and pink is hydrogen

Figure 14: Absorption of 5CB in the UV range using four different methods of measurement. Referenced from [33]
Figure 15: Transmission of 5CB into the infrared region with a cell gap of 8 μm at room temperature. Referenced from [40]

5CB has some obvious absorption issues when looking at the absorption in the infrared region due to molecular stretching, deformations, and vibrations. The known absorption bands are CN at 4.45 μm and CH bonds of the alkyl chain from 3.4 μm to 3.6 μm range. To address the absorptions from the CH bonds, carbon-deuteron was substituted in 5CB to make a perdeuterated 4'-pentyl-4-cyanobiphenyl, D5CB [40]. The thought was that since deuterium (D) has larger mass, it will shift the vibration absorptions to longer wavelengths by the vibration absorption relation of Equation (13). The transmission through the full infrared region is shown in Figure 16 and the absorption coefficient to 3.2 μm in Figure 17 [40]. The deuterium did shift a lot of the vibrations in the 3.5 μm range to just past the CN vibrations. Although this shows
improvement of overtones effecting the telecommunication wavelength of 1.55 μm, the deuterium shift is not long enough to push the vibrations out of the MWIR region.

Figure 16: Transmission of 5CB in black and D5CB in gold from 2.5 to 22 μm in a cell gap of 8 μm at room temperature. Redrawn from [40]

Figure 17: Absorption of 5CB in the light line and D5CB in the dark line. Referenced from [40]
CHAPTER 3: EXPERIENTAL DATA FOR LOW ABSORPTION LIQUID CRYSTALS

In looking for a low absorption liquid crystal on the MWIR region, several new compounds are investigated. For a useful liquid crystal mixture in the MWIR region, it is desirable to have a birefringence of 0.2 at 4 μm, dielectric anisotropy of c.a. 5, wide nematic range, and an absorption coefficient of less than 5cm⁻¹ in the 4 to 5 μm range. The primary focus will be on the low absorption coefficient. The MWIR region is 3 to 5 μm with a focus on the 4 to 5 μm region. Long-wave infrared is in the 8 to 12 μm region. Since previous success have been found in the long terphenyl compounds with chloro substitutions, chloro substitutions will be investigated on longer core materials with additional phenyl rings, specifically four and five rings. Also, terphenyl tolane compounds with fluoro substitutions will also be investigated.

3.1 Fluorinated Compounds

Another approach for low absorption MWIR liquid crystals is to use fluoro substitutions. The fluoro polar bond can provide benefits to the liquid crystal viscoelastic properties, lower melting point, and has shown some transmission benefits. Tolane as a linking group is known to exhibit high birefringence, low viscosity, and a wide nematic range [41]. We will specifically look at the absorption coefficients of several tolane and terphenyl core structures with two different terminal groups. The triple bond in tolane material can have UV instability, but this is not a concern for the infrared region as the UV input light can be filtered. The first set of materials, group A,
has a trifluoromethoxy terminal group and the second set, group B, has a difluoromethoxy terminal group with a double carbon bond. The tolane materials’ structure and temperature phase transitions of group A are listed in Table 3 that were measured by Minggang Hu who also measured the transmission using $5 \times 10^{-5} \text{ mol/mL}$ CCl$_4$ solution [41]. A1 and A4 are identical except on the second phenyl ring has a fluorine bonded to position 3 of A1 and position 2 of A4. A2 is the same as A1, except a fluorine bond is added on the last phenyl ring in position 3. A5 is the same as A4 except a fluorine bond is added on the last phenyl ring in position 5.

Table 3: Group A Fluorinated Tolane Liquid Crystal Materials

<table>
<thead>
<tr>
<th>Name</th>
<th>Compound</th>
<th>Temperature Phases (°C)</th>
<th>Δn</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>F$_3$CO-[(-\text{CH}_2\text{CH}-\text{CH}_2\text{CH}-\text{CH}_2\text{CH}-\text{CH}-\text{CH}-\text{CH}_2\text{CH}-\text{CH}_2\text{CH}-\text{CH}-\text{CH}]-F</td>
<td>Cr 95.3 N 137.4 I</td>
<td>0.2875</td>
</tr>
<tr>
<td>A2</td>
<td>F$_3$CO-[(-\text{CH}_2\text{CH}-\text{CH}-\text{CH}-\text{CH}-\text{CH}-\text{CH}-\text{CH}-\text{CH}]-F</td>
<td>Cr 66.5 N 87.3 I</td>
<td>0.2735</td>
</tr>
<tr>
<td>A4</td>
<td>F$_3$CO-[(-\text{CH}_2\text{CH}-\text{CH}-\text{CH}-\text{CH}-\text{CH}-\text{CH}-\text{CH}-\text{CH}_2\text{CH}-\text{CH}_2\text{CH}-\text{CH}-\text{CH}-\text{CH}]-F</td>
<td>Cr 62.5 S 69.2 N 151.0 I</td>
<td>0.2965</td>
</tr>
<tr>
<td>A5</td>
<td>F$_3$CO-[(-\text{CH}_2\text{CH}-\text{CH}-\text{CH}-\text{CH}-\text{CH}-\text{CH}-\text{CH}-\text{CH}_2\text{CH}-\text{CH}_2\text{CH}-\text{CH}-\text{CH}-\text{CH}-\text{CH}-\text{CH}-\text{CH}_2\text{CH}-\text{CH}_2\text{CH}-\text{CH}-\text{CH}-\text{CH}]-F</td>
<td>Cr 79.9 N 103.1 I</td>
<td>0.2785</td>
</tr>
</tbody>
</table>

The Group A materials were measured on the Perkin Elmer Spectrum One FT-IR Spectrometer using 100% of material in the isotropic phase by heating the cell to about
20°C above the clearing point. The absorption for A1 and A2 are shown in Figure 18, and the absorption for A4 and A5 are shown in Figure 19. A2 with the additional fluoro to position 3 on the last phenyl ring has a lower absorption of A1. The same observation is not true for the A5 comparison with A4. In fact, they are quite similar; the additional fluoro in position 4 on the last phenyl ring made no distinguishable difference in absorption. Overall, the smallest absorption coefficient is still above 10 cm\(^{-1}\) which indicates these materials are not suitable for low absorption applications.

Figure 18: Absorption of A1 and A2 materials
In the group B materials having a 2,2-difluorovinyloxy group, all the C-F bonds are unsaturated and the C-O bond and C-F bonds are linked to a different carbon atom. The difference between B2 and B4 is that on the second phenyl ring, B2 has the fluoro in position 3 and B4 has it in position 2. The temperature transition phases and structure are given in Table 4. Group B materials were measured in the same way as group A materials to get the absorption coefficients, shown in Figure 20.
Table 4: Group B Fluorinated Tolane Liquid Crystal Materials

<table>
<thead>
<tr>
<th>Name</th>
<th>Compounds</th>
<th>Temperature Phases (°C)</th>
<th>Nematic range (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B2</td>
<td><img src="image" alt="B2 Compound Structure" /></td>
<td>C 66.1 N 126.2 I</td>
<td>60.1</td>
</tr>
<tr>
<td>B4</td>
<td><img src="image" alt="B4 Compound Structure" /></td>
<td>C 67.7 N 106.2 I</td>
<td>38.5</td>
</tr>
</tbody>
</table>

Figure 20: Absorption of B2 and B4 materials
There is minimal differences in the absorption coefficient between B2 and B4. The B2 measurement is noisy in the 2.5 to 3 μm wavelength range, but both materials are quite similar in the 3 to 5 μm MWIR range. Figure 21 shows a comparison between group A, group B, and 5CB. The C-H absorptions of 5CB from 3.3 to 3.5 μm is much improved in the group A and B materials since there is no alkyl chain. The same is also true for the 5CB cyano absorption at about 4.5 μm, however there is still an absorption peak from the carbon triple bond of the tolane. Group A and group B have higher absorption than 5CB due to the CF bonds. These materials could be useful in the 3 μm region, but not in the 4 to 5 μm region.
3.2 Chlorinated Compounds

3.2.1 Four and Five phenyl ring with chloro

In evaluating new LC candidates for use in the mid-wave region, the initial primary focus will be on their nematic phase temperature range and their spectral transmittance or absorption. The temperature range and enthalpy of the liquid crystals were measured using a Differential Scanning Calorimetry (DSC, TA Instruments).
Q2000). The first set of new materials include four and five phenyl ring core structures with chloro substitutions and no side chain. The side chains were eliminated as a response to minimize the -CH₂ and -CH₃ bond absorptions present even though it can be an aid in lowering melting point and widening the nematic range. The DSC measurement is shown in Figure 22 and Figure 23 for the two four phenyl ring compounds with one having chloro substitutions of on (1,3) and (2,4) positions and the other on (1,2) and (3,4) positions on the outermost phenyl rings. Both SD-05-071 and SD-05-036 contain a nematic phase with a melting temperature of nearly 200°C or higher, however SD-05-071 is monotropic. These temperatures are high as expected since the core structure was extended past the common terphenyl length and the side chain was eliminated which can aid in lowering the melting point. Since these chemicals do have a nematic phase, they can be utilized in eutectic mixtures if they possess other desirable qualities such as high transmission.
Figure 22: DSC measurement for SD-05-071 with structure Cl-P(1,3Cl)PPP(2,4Cl).

Figure 23: DSC measurement for SD-05-036 with structure Cl-P(1,2)PPP(3,4Cl).
A material with five phenyl rings and only one chloro in position 2 of the second ring was also measured, SD-05-047. The measured DSC result is shown in Figure 24. With the fifth phenyl ring, the melting point is increased to 236°C, but the material still possesses a liquid crystal phase with a range of 65°C. The melting point is very high, but this compound could be useful in a mixture if it possessed other desirable optical properties. The phase transition temperatures for the three compounds studied along with their structures is displayed in Table 5.

Figure 24: DSC measurement of SD-05-047 with structure Cl-PPP(2Cl)P.
<table>
<thead>
<tr>
<th>LC</th>
<th>Structure</th>
<th>Temperature (°C)</th>
<th>Enthalpy (Cal/mol)</th>
<th>Weight (mg/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SD-05-071</td>
<td><img src="image" alt="Structure SD-05-071" /></td>
<td>K 226 N (177.98) I</td>
<td>9556.66</td>
<td>444.18</td>
</tr>
<tr>
<td>SD-05-036</td>
<td><img src="image" alt="Structure SD-05-036" /></td>
<td>K 198.19 N 218.75 I</td>
<td>8076.77</td>
<td>444.18</td>
</tr>
<tr>
<td>SD-05-047</td>
<td><img src="image" alt="Structure SD-05-047" /></td>
<td>K 236.29 N 301.73 I</td>
<td>8984.75</td>
<td>416.95</td>
</tr>
</tbody>
</table>
| Mixture | SD-05-071: 21.91%  
SD-05-047: 33.12%  
SD-05-036: 44.96% | K 162 N 252 I | | |

Since all three compounds contained a liquid crystal phase with high melting points, a eutectic mixture was formed with these three compounds of concentrations: SD-05-071: 21.91%, SD-05-047: 33.12%, and SD-05-036: 44.96%. This mixture brought the melting point down to 162°C with a clearing point of 252°C giving a widened LC phase range of c.a. 90°C.

The temperature information showed a nematic phase for the new materials, and now the transmission can be measured for the material. The absorption coefficient is then calculated and used as the comparison of materials since it is easier to decipher.
between similar performing materials on a logarithmic scale than merely using transmission. To determine the absorption coefficient, the spectral transmission was measured on the Perkin Elmer Spectrum One FT-IR Spectrometer. Since the clearing point is so high, it is too difficult to measure the transmission in the isotropic phase. The materials were dissolved in carbon tetrachloride, CCl₄, solution and measured at room temperature. Although it is common to use 5x10⁻⁵ mol/mL concentration material in carbon tetrachloride for a 50 µm thick cell, due to the poor solubility of the compounds in the solution, a 5x10⁻⁶ mol/mL solution was used for these compounds. To compensate for the lower concentration and ensure enough material was utilized, a wider cell gap of 100um was used for a longer path length. A barium fluoride (BaF₂) cell was used because it has uniform high transmittance through the infrared region. The cell gap was determined by measuring the transmission using an empty cell and using the interference of the peaks with the Fabry-Perot effect formula

$$kd = m\pi \frac{2\pi}{\lambda} \Rightarrow d = \frac{1}{2(m_2 - m_1)}$$

(17)

where $$m_1$$ and $$m_2$$ are the wavenumbers at two peak transmission points.

Once the cell gap is measured, the cell is filled with the solution, and the transmission is measured. The transmission is normalized using a single piece of glass of BaF₂ with the assumption that the reflectance between the solution and the substrate is negligible. To go from normalized transmission to absorption coefficient, Beer's law is applied. Beer's law from equation (11) is

$$\alpha = -\ln(T)/d$$

(18)

where d is the cell gap.
The standard used for comparison to the results will be 5CB with the absorption coefficient as shown in Figure 25. This data was determined by measuring the transmission of two different known cell gaps, and calculating the difference between them to determine the absorption. This helps to eliminate errors from only using one cell, but requires more material. In this figure, you can also see the known contributions to the absorption peaks of 5CB.

Figure 25: Absorption of 5CB where str. is stretching and def. is deformation
The chlorinated long phenyl ring materials were measured and results are shown in Figure 26 and the contributing absorption mechanisms are given in Table 6 and are color coded on sections A-F identified in the figure [42]. The primary frequency and the first overtones will have the greatest effect with some second overtones playing a role. The third, fourth, and fifth overtones should be significantly weaker.

Figure 26: Absorption of chlorinated materials and 5CB
Table 6: Absorption bonds contributing to resonances color coordinated with regions displayed in corresponding figure.

<table>
<thead>
<tr>
<th>Hydrogens</th>
<th>Absorption mechanism</th>
<th>Frequency (cm⁻¹)</th>
<th>2nd overtone</th>
<th>3rd overtone</th>
<th>4th overtone</th>
<th>5th overtone</th>
<th>Wavelength (um)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetra or penta- substituted benzene containing 1 free H. C-H def.</td>
<td>900-860</td>
<td>1800-1720</td>
<td>2700-2580</td>
<td>3600-3440</td>
<td>4500-4300</td>
<td>11.11-11.63</td>
<td>m.</td>
</tr>
<tr>
<td>1,2,4-trisubstituted benzene, another peak at 852-805 C-H def.</td>
<td>885-870</td>
<td>1770-1740</td>
<td>2655-2610</td>
<td>3540-3480</td>
<td>4425-4350</td>
<td>11.30-11.50</td>
<td>m.</td>
</tr>
<tr>
<td>Benzene ring containing two adjacent H atoms C-H def.</td>
<td>870-880</td>
<td>1740-1760</td>
<td>2610-2640</td>
<td>3480-3520</td>
<td>4350-4400</td>
<td>11.50-12.50</td>
<td>v.</td>
</tr>
</tbody>
</table>

1:4 Disubstituted (two adjacent hydrogen atoms) C=H str (multiple bands)

<table>
<thead>
<tr>
<th>Hydrogens</th>
<th>Absorption mechanism</th>
<th>Frequency (cm⁻¹)</th>
<th>2nd overtone</th>
<th>3rd overtone</th>
<th>4th overtone</th>
<th>5th overtone</th>
<th>Wavelength (um)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-H i.p. def.</td>
<td>N/A</td>
<td>3212+/-12</td>
<td>4818+/-18</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1175+/-</td>
<td>2516+/-22</td>
<td>3774+/-33</td>
<td></td>
<td></td>
<td></td>
<td>7.88-8.02</td>
<td>w</td>
</tr>
<tr>
<td>6(2,5vs3,6)</td>
<td>2350+/-12</td>
<td>3525+/-18</td>
<td></td>
<td></td>
<td></td>
<td>8.47-8.56</td>
<td>w</td>
</tr>
<tr>
<td>1117+/-</td>
<td>2234+/-14</td>
<td>3351+/-21</td>
<td>4468+/-28</td>
<td></td>
<td></td>
<td>8.90-9.01</td>
<td>w</td>
</tr>
<tr>
<td>5(2,3vs5,6)</td>
<td>2026+/-10</td>
<td>3039+/-15</td>
<td>4052+/-20</td>
<td></td>
<td></td>
<td>9.82-9.92</td>
<td>w</td>
</tr>
</tbody>
</table>

1:2,4 Trisubstituted =C-H str (multiple bands)

<table>
<thead>
<tr>
<th>Hydrogens</th>
<th>Absorption mechanism</th>
<th>Frequency (cm⁻¹)</th>
<th>2nd overtone</th>
<th>3rd overtone</th>
<th>4th overtone</th>
<th>5th overtone</th>
<th>Wavelength (um)</th>
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<tbody>
<tr>
<td>C-H o-o-p def.</td>
<td>3080-3030</td>
<td>N/A</td>
<td>3.24-3.33</td>
<td>w-m</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>1606+/-6</td>
<td>3212+/-12</td>
<td>4818+/-18</td>
<td></td>
<td></td>
<td></td>
<td>6.20-6.25</td>
<td>v</td>
</tr>
<tr>
<td>1258+/-11(all clockwise)</td>
<td>2516+/-22</td>
<td>3774+/-33</td>
<td></td>
<td></td>
<td></td>
<td>7.88-8.02</td>
<td>w</td>
</tr>
<tr>
<td>6(2,5vs3,6)</td>
<td>2350+/-12</td>
<td>3525+/-18</td>
<td></td>
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<td></td>
<td>8.47-8.56</td>
<td>w</td>
</tr>
<tr>
<td>1117+/-14</td>
<td>2234+/-14</td>
<td>3351+/-21</td>
<td>4468+/-28</td>
<td></td>
<td></td>
<td>8.90-9.01</td>
<td>w</td>
</tr>
<tr>
<td>5(2,3vs5,6)</td>
<td>2026+/-10</td>
<td>3039+/-15</td>
<td>4052+/-20</td>
<td></td>
<td></td>
<td>9.82-9.92</td>
<td>w</td>
</tr>
</tbody>
</table>

Chlorine

<table>
<thead>
<tr>
<th>Hydrogens</th>
<th>Absorption mechanism</th>
<th>Frequency (cm⁻¹)</th>
<th>2nd overtone</th>
<th>3rd overtone</th>
<th>4th overtone</th>
<th>5th overtone</th>
<th>Wavelength (um)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polychlorinated C-Cl str.</td>
<td>800-700</td>
<td>1600-1440</td>
<td>2400-2100</td>
<td>3200-2800</td>
<td>4000-3500</td>
<td>12.5-14.3</td>
<td>v-s.</td>
</tr>
<tr>
<td>C-Cl equatorial, other C-Cl str.</td>
<td>780-730</td>
<td>1560-1550</td>
<td>2340-2250</td>
<td>3120-3000</td>
<td>3900-3750</td>
<td>12.4-13.3</td>
<td>s.</td>
</tr>
<tr>
<td>C-Cl axial, other monochlorinated C-Cl str.</td>
<td>Ca. 650</td>
<td>1300</td>
<td>1950</td>
<td>2600</td>
<td>3250 Ca. 15.4</td>
<td>s.</td>
<td></td>
</tr>
</tbody>
</table>

The two four-phenyl ring compounds show similar overall absorption to 5CB with a few exceptions. The data shows the absorptions from cyano at 4.5μm from 5CB is not present in the new materials. Although the absorption is lower in the E group around 3.3 μm to 3.5 μm for all three materials compared to 5CB, there is still evidence of an alkyl chain. Based on the chemical compound structures not having the alkyl chain of
CH$_2$ and CH$_3$ bonds, this observed absorption does not meet expectations; that region should show very low absorption. These absorptions connected to the alkyl chain stretching is a well-known relation, which indicates that the materials developed have impurities. Although there is more noise in SD-05-47, this five-phenyl ring compound shows an overall lower absorption in the wavelength regions shown except for region C and E. In region E, SD-05-047 has the highest absorption at c.a. 3.5 μm which makes sense since this is from the CH bonds in the phenyl rings, and it has an additional phenyl ring compared to SD-05-036 and SD-05-047, which have two more phenyl rings than 5CB. These materials show a flatter response than 5CB due to the absence of the cyano absorption, but are very similar to the average absorption in this region.

3.2.2 Eutectic Mixtures

The most success thus far in achieving low absorption liquid crystal materials have been through the use of chloro substituted terphenyl compounds. Little is known of the mesogenic phase relation to chloro substitutions, and cannot be determined a priori. Although the alkyl CH bonds have absorptions in the 3.3 to 3.5 μm range, a small tail may be tolerated in order to safeguard the existence of a nematic phase. The absorption of CH bonds in the phenyl rings are additive when adjacent, so suitable substitutions of chloro can help cause separation between the CH bonds and help reduce these absorptions. Figure 7 shows five terphenyl compounds structure and phase transition temperatures. Mixture 2 was formed with 3PP(3Cl)P-Cl and 5PP(3Cl)P-Cl with 42.67% to 57.33% weight respectively; the absorption coefficient of
Mixture 2 is shown in Figure 27. Mixture 2 has a nematic range of about 20°C with a melting point of 48.3°C with a clearing point of 69.2°C. The birefringence in the infrared region is c.a. 0.19, a dielectric coefficient of c.a. 4, and a visco-elastic coefficient of c.a. 140 ms/μm² at room temperature [43]. Since a small alkyl chain is present in both compounds, there are still absorption peaks from 3.3 to 3.5 μm as expected. Mixture 2 shows good absorption as low as 4cm⁻¹ in the 2.5 to 3.2 μm region. More notably as has not been achievable with fluoro compounds, the mixture shows a relatively uniform low absorption in 3.6 to 5.2 μm region. The absence of cyano, isocyanate, and fluoro polar groups, and instead only using chloro substitutions, clears this region. Since the chloro vibrations are out at 12.5 μm, which places them and their overtones clear of the 3-5 μm band.
Table 7: Chlorinated terphenyl compound structures and temperature phase transitions

<table>
<thead>
<tr>
<th>Structure</th>
<th>Temperature Phase Range</th>
<th>dH</th>
</tr>
</thead>
<tbody>
<tr>
<td>3PP(3Cl)P-Cl</td>
<td>K 95.01 N (70.1) I</td>
<td>6421.3</td>
</tr>
<tr>
<td>5PP(3Cl)P-Cl</td>
<td>K 71.4 N (67.1) I</td>
<td>5848</td>
</tr>
<tr>
<td>2PP(3Cl)P-Cl</td>
<td>K 106.29 N 70.6 I</td>
<td>5776.5</td>
</tr>
<tr>
<td>4PP(3Cl)P-Cl</td>
<td>K 78.3 N (45) I</td>
<td>4618.9</td>
</tr>
<tr>
<td>3PP5</td>
<td>K -18 S 47.8 I</td>
<td></td>
</tr>
<tr>
<td>3PP(3Cl)P(3Cl)-Cl</td>
<td>I at room temperature</td>
<td></td>
</tr>
</tbody>
</table>
Figure 27: Absorption coefficient of Mixture 2 with 5CB as reference.

Mixture 2 low absorption coefficient from 3.6 to 5.2 μm is great news, and although a melting point of 48.3°C is significantly better than the individual chlorinated compounds, the next step would be to develop a mixture that brings the nematic phase to within room temperature. To do this, a four compound mixture was made with the first four compounds in Table 7 of concentrations of 14.1% for 2PP(3Cl)P-Cl, 36.35% for 4PP(3Cl)P-Cl, 15.45% for 3PP(3Cl)P-Cl, 34.1% for 5PP(3Cl)P-Cl. It was difficult to determine the melting point of this mixture because there were two distinct melting point peaks at 42.6°C and 51.6°C observed indicating some of the compounds might not mix.
well together as displayed in Figure 28. This is an indication that either the percentages of the components need to be adjusted to reach the eutectic point or that they do not mix well. Due to the similarity of the compounds, the latter is more likely the case.

Figure 28: DSC of 4 chlorinated terphenyl compound mixture showing two melting points

Another approach is to dope a small percentage of Mixture 2 with other another compound. It is similar to how diluters are used for lowering viscosity, except the intention in this case is to lower the melting point. The reason to use a small percentage as opposed to calculating a eutectic melting for all three compounds is that the third compound may not have the desired low absorption coefficient for MWIR or not
possess a well-defined mesophase. Mixture 2 was made and then a small percentage of third compound is added; this was done for two different compounds.

Mixture 2 with an addition of 5.03% of 3PP5 was made and tested. 3PP5 has a clearing point of c.a. -20°C and with this percentage should only bring the clearing point down a small amount to about 56°C but have a greater impact on bringing the melting point closer to room temperature [44]. The DSC result is displayed in Figure 29. This mixture only brought the clearing point down c.a. 5°C, but unfortunately did not improve the melting point. It seems that it disturbed the eutectic mixture as the melting point went up and there is a small change around 20°C. The materials for Mixture 2 were depleted, but with more materials it might be possible that the percentage of 3PP5 could be adjusted to achieve a mixture that could bring these peaks together.
Another combination of Mixture 2 plus a small percentage of a third compound was made and tested. The last compound in Table 7, 3PP(3Cl)P(3Cl)-Cl, was selected because it has a clearing point below room temperature. The mixture 2 plus with 10% 3PP(3Cl)P(3Cl)-Cl was measured in the DSC and the result is shown in Figure 30. This data was found to be repeatable. The peak at 55°C represents the clearing point of the mixture and it is in nematic phase at room temperature due to super cooling effect. The melting point is 44.2°C. This brought the melting point of Mixture 2 down 4°C.
Figure 30: DSC results for Mixture 2 with 10% diluter

3.3 Brominated Compounds

With fluorine molecular absorptions in the infrared region, chlorine is the most promising tool in terms of low absorption. But chlorine, comes with lower performance in other areas, like very high melting points. Eutectic mixtures can help with this, which means the more low absorption materials available, the better opportunity to form a good eutectic mixture with more desirable melting point and nematic phase range. One option that has yet to be explored is the use of bromine. It is in the fluoro group of the periodic table, and should possess similar bonding characteristics to fluorine and chlorine. It most likely has not been investigated as it would not be very useful in the
visible region. It has twice the molar weight as chlorine which could cause some issues with melting point and achieving a liquid crystal phase. The first step is to determine if bromine substitutions have low absorption similar to chlorine or if it shows molecular vibrations in the MWIR region like fluorine. To do this, since transmission is measured in the isotropic phase, it is not necessary to have a nematic phase. A readily available compound called 1-Bromo-4-Ethylbenzene was obtained and tested; the structure is illustrated in Figure 31.

![Bromine structure](image)

Figure 31: Bromine structure in 3-D ball and stick form on left and 2-D drawing on right

The compound has a melting point of -43°C and was measured at room temperature with 100% mixture in a 50 μm thick cell on the Perkin Elmer Spectrum One FT-IR Spectrometer. The absorption was calculated and is shown in Figure 32.
The absorption is lower than 5CB in the 3.5 μm to 5 μm region. There are absorptions in the 3.3 to 3.5 μm region from the short alkyl chain. This data shows that bromine substitutions could achieve a low absorption material for lateral bonding in the phenyl core structure if a nematic phase can be achieved.
CHAPTER 4: CONCLUSION

Three fluorine group substitutions and their effects have been examined for low absorption liquid crystal applications in the MWIR band. Fluoro compounds with their polar bonds have been desirable for their lower melting point properties and high birefringence, and compounds have been synthesized with strategically placed fluoro substitutions to help mitigate some of the 3 μm to 4.5 μm vibration absorptions. Although the fluoro compounds do not show low enough absorption coefficient in the MWIR band. However A2 could be used in the 2.5 to 3.0 μm region. For an application that had a relatively broadband light source, A2 could also be used from 3.3 to 3.8 μm.

Chlorine is the clear winner in terms of lowest absorption coefficient for the MWIR band. Chlorine is a larger molecule, which is most like the cause of its success in terms of transmission due to the vibration absorption frequency relation to reduced mass, and it is also the cause in making a more rigid crystal that has a larger melting point and a smaller nematic phase. This dictates the need for materials with the sole use of chlorine over fluorine, and the need for hydrogen to be minimized which will diminish the C-H bond molecular absorptions. Up till now, mainly terphenyl compounds have studied with chloro substitutions.

Two different four phenyl ring compounds and one five phenyl ring compounds have been investigated. With the lengthening of the core by adding phenyl rings, the melting point of 200+°C was quite high as expected, but a mesophase was found for all three compounds tested with only one being monotropic and two being enantiotropic. Although the evidence of an alkyl chain indicates impurities which can call results into
question, the five phenyl ring compound had a low absorption coefficient in parts of the MWIR region, with the lowest from 4.5 to 5 μm. Care needs to be taken to prevent impurities within the new materials, as this can have a devastating effect on the resonant frequencies, undoing the intended benefits to the absorption coefficient. Eutectic mixtures will offer expansion of the nematic phase and lowering of the melting temperature. A mixture of all three chloro 4-5 phenyl ring compounds was made and had a lower melting point of c.a. 150°C. Once a sufficient number of low absorption materials are developed, mixtures can be developed.

Mixtures of terphenyl compounds were examined and found to be a promising solution for low absorption in the MWIR region. Three mixtures were made and tested: a four compound mixture and two variations of Mixture 2 doped with 5-10% of a third compound treated like diluters for the melting point. Mixture 2 is a known mixture of two chloro terphenyl compounds that has very low absorption coefficient and a melting point of 48.3°C and a clearing point of 69.2°C. Without the use of other readily available low absorption compounds to be included in the eutectic mixture calculation, this proved to be effective in forming a mixture of low absorption using chloro substitutions to achieve nematic phase with a lower melting point. More tweaking could be done in future work to bring the melting point below room temperature. This low absorption low melting point nematic phase compound could help to open a door for applications developed in the visible or near-IR to be extended to the MWIR region.

New materials could also be synthesized using bromine. If nematic phase can be achieved, these materials could prove quite useful in eutectic mixtures in
combination with chloro terphenyl mixtures. Single and biphenyl mixtures with fluoro and chloro terminal groups do not possess a nematic phase, but the terphenyl materials have shown nematic phases for both so it is possible that terphenyl mixture with bromine substitutions will also contain a nematic phase.
LIST OF REFERENCES


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