DEVELOPMENT AND CHARACTERIZATION OF
BLUE PHASES MADE FROM BENT-CORE LIQUID CRYSTALS

A dissertation submitted
to Kent State University in partial
fulfillment of the requirements for the
degree of Doctor of Philosophy

by
Stefanie Taushanoff
May, 2011
# Table of Contents

List of Figures ........................................................................................................... vii

Acknowledgements .................................................................................................... xv

CHAPTER 1: Chirality, Bent-Core Liquid Crystals and Blue Phases ................……1

1.1 Introduction ......................................................................................................... 1

1.2 Chirality and Liquid Crystals ............................................................................ 3

1.2.1 Molecular Chirality ...................................................................................... 3

1.2.2 The Cholesteric Phase .................................................................................. 5

1.3 The Blue Phases ................................................................................................. 13

1.4 Bent-Core Liquid Crystals ................................................................................ 18

CHAPTER 2: Materials and Characterization Methods ........................................... 23

2.1 Materials Studied .............................................................................................. 23

2.2 Characterization Methods ................................................................................ 28

2.2.1 Polarizing Optical Microscopy ................................................................... 29

2.2.2 Differential Scanning Calorimetry ............................................................... 36
2.2.3 Optical Activity.................................................................36
2.2.4 Electro-Optical Behavior...................................................40
2.2.5 Kossel Diagrams.............................................................42
2.2.6 X-Ray Scattering.............................................................43

CHAPTER 3: Bent-Core Liquid Crystal Blue Phases.............................................45

3.1 Introduction..............................................................................45
3.2 The Phase Diagram...............................................................46
3.3 Texture Analysis and Differential Scanning Calorimetry.....................49
3.4 Electro-Optical Switching and Optical Activity...............................57
3.5 X-Ray Scattering and Smectic Clusters.......................................63

CHAPTER 4: Chiral Mixtures of Bent-Core and Rod-Shaped Liquid Crystals........66

4.1 Introduction..............................................................................66
4.2 Chiral Mixtures of Bent-Core and Rod-Shaped Liquid Crystals..............67
4.2.1 Sample A: Control............................................................69
4.2.2 Sample B..................................................................................71
4.2.3 Sample C..................................................................................73
4.2.4 Sample D..................................................................................75
4.2.5 Sample E..................................................................................77
4.2.6 Conclusions................................................................................79
4.3 Chiral Mixtures of Bent-Core Liquid Crystals.................................81
4.4 Other mixtures...............................................................................84
  4.4.1 Introduction................................................................................84
  4.4.2 F521 and BDH-1281.................................................................85
  4.4.3 Mixtures involving CB15 and 6O08............................................87

CHAPTER 5: Blue Phases Stabilized by Nanoparticles and Polymer Networks........90
  5.1 Introduction..................................................................................90
  5.2 Cadmium Sulfide Nanoparticles..................................................93
  5.3 Nanoparticle Stabilization of Bent-Core Blue Phases I:
    Small Nanoparticles.........................................................................98
5.4 Nanoparticle Stabilization of Bent-Core Blue Phases II:
   Large Nanoparticles.................................................................................103

5.5 Polymer Stabilization.............................................................................107

5.6 Conclusions............................................................................................111

CHAPTER 6: Summary and Future work.........................................................113

6.1 Summary..................................................................................................113

6.2 Future work.............................................................................................115

REFERENCES...............................................................................................118
List of Figures

Figure 1: A chiral molecule (A) can not be superimposed over its own mirror image, even if it is otherwise completely free to rotate. An achiral molecule (B) can be superimposed over its own mirror image after rotation.................................................................4

Figure 2: 5CB. A typical calamitic liquid crystal consists of a rigid core (A), a semi-flexible tail (B), optional polar groups or substituents (C) and has a length (L) approximately 4 or more times larger than its width (W).........................................................................................................................6

Figure 3: The isotropic phase (A) is favored at higher temperatures. The nematic phase (B) is favored at lower temperatures.................................................................................................................................7

Figure 4: The three bulk deformations of a nematic liquid crystal.........................................................8

Figure 5: Chiral molecules twist into a helix orthogonal to the plane in which the director rotates. A simplified diagram (below) shows the helix ..............................................................9

Figure 6: Simplified cross section of a double twist cylinder. The pale green caps serve as a guide to the eye for following the twist, the helical axis alternate colors in blue and lavender for visual clarity.........................................................................................................................12

Figure 7: Two different views of three double-twist cylinders meeting at a defect. Seen from one side of the unit cell, a well-defined lattice of cylinders is clearly visible (A), but it is not instantly clear that the half-pitch diameter (molecules at the edge of the cylinder form an angle of ±π/4 with respect to the cylinder’s core) allows two cylinders to meet without defects. Seen from the vantage point of looking down a disclination line (B), one can more clearly see how the cylinders fit together in a smooth and fluid manner until the defect area where three cylinders meet. .......12

Figure 8: A typical bent core molecule with some common linking groups. Recreated from Pelzl, et al. Liquid Crystals Vol. 28 (2001) pp 970. .........................................................................................................................19
Figure 9: Liquid crystal dimers used by Coles and Pivnenko to create broad-temperature range blue phases. .......................................................... 23

Figure 10: F493, the principal bent-core nematic used in this work. ......................... 25

Figure 11: F521. Note the shorter, more rigid legs and the short flexible tails. ............... 25

Figure 12: Molecular structure of F533. ............................................................... 26

Figure 13: Calamitic liquid crystal 6OO8. .............................................................. 27

Figure 14: Propagation of light through a nematic liquid crystal between crossed polarizers (A). The final intensity of light depends on the thickness of the sample (d), the birefringence (∆n = n_e - n_o), and the wavelength of the incoming light (λ). A typical nematic texture (B) formed by placing a small drop of liquid crystal on a glycerin substrate. ............................................. 30

Figure 15: Examples of different liquid crystal textures as seen between crossed polarizers. A) An isotropic-smectic transition. B) A chiral nematic oily streak texture (in reflection). C) Smectic A focal conic domains. D) Bent-core B7 phase. ................................................... 31

Figure 16: An unusually colorful platelet texture formed using F493 with 36wt% CB15. ........ 32

Figure 17: An example of a blue phase of calamitic liquid crystals. Photos courtesy of Dr. Shin-Ying Lu. .......................................................... 33

Figure 18: Polarized light entering a thick BPIII sample has ample opportunity to scatter and depolarize before emerging (A), resulting in a uniform blue texture under transmission POM (B). This works only if the lattice size is large enough to scatter visible light. .......................... 34

Figure 19: A blue phase of the calamitic liquid crystal 6OO8 (left). When the transition to N* starts, the same lighting conditions that allow for visual inspection of the BP texture over saturate the picture as cholesteric oily streaks begin to appear (right). If the material was viewed using lighting and camera settings appropriate for N*, the BP textures could be missed entirely. ....... 35
Figure 20: Rotary optical dispersion is the wavelength-dependence of the optical rotatory power. Blue phases are far more optically active at shorter wavelengths therefore it is best to use as short a wavelength as your equipment will allow (blue, near-UV or UV) in OA experiments.

Figure 21: Simplified diagram of electrostriction in the BPI and BPII phases. The electric field stretches the lattice along one axis, thereby changing the wavelength of the reflected light.

Figure 22: F493 + CB15 (36wt%) mixture: in transmission (A), reflection (B), and reflection with voltage applied (C).

Figure 23: A bent-core sample (A) rests on a heat stage and a calamtic sample (B) as it cools rapidly after being removed from the heat stage; the temperature gradient to displays the full range of reflection colors the sample is capable of.

Figure 24: Phase diagram of F493 and small concentrations of chiral dopant BDH-1281.

Figure 25: A concentration gradient cell allows a cursory inspection of a binary mixture that is efficient in both time and materials.

Figure 26: 40 micron thick concentration gradient cell, between pure F493 (right) and a maximum of 4.9wt% BDH-1281 in F493 (left) at 70.0°C.

Figure 27: A comparison of typical textures of four blue phase mixtures at temperatures just below their respective Iso-BPIII transition temperatures: A) 1.4wt% BDH-1281 in F493 at 70.6°C B) 3.2wt% at 69.0°C C) 4.9wt% at 65.0°C and D) 7.2wt% at 58.8°C.

Figure 28: DSC scans for three blue phase samples and pure F493 shows the decrease in latent heat as the chirality of the sample increases. ClPbis10BB (F493) shows a distinct peak at the isotropic-nematic transition. The peaks become less distinct (the latent heat of the transition decreases) as the chirality increases. Mixture 1 = 3.2wt% BDH-1281 in F493, Mixture 2 = 4.9wt% and Mixture 3 = 7.2wt%. 
Figure 29: A selection of pictures showing the different textures of different concentrations and alignment conditions for bent-core and calamitic nematic liquid crystals doped with BDH-1281. The phrase “unaligned” refers to the lack of alignment layer in the cell, “planar” refers to the polyimide alignment layer. ............................................................54

Figure 30: A more detailed look at the effects of similar chiral dopant concentration on the textures and temperature ranges of calamtic and bent-core liquid crystals. In column 1, the cell had no alignment layer; in column 2, “unaligned” refers to the lack of alignment layer in the cell. Column 3, “planar” refers to the polyimide alignment layer. ..........................................................55

Figure 31: Examples of streaking in Mixture 1.4 at 65.8°C (A) and 58.0°C (B), Mixture 3.2 at 60°C (C) upon cooling and the "cholesteric rivers" that appear in a sample of liquid crystal dimers and BDH-1281 after standing for several hours at room temperature (D).................................56

Figure 32: Mixture 3.2 A) Optical rotation with respect to temperature at 532 nm. B) Optical rotatory dispersion at 3°C below the Iso-BPIII transition.................................................................58

Figure 33: Switching in an IPS cell in Mixture 1.4 (A) and Mixture 4.9 (B) under an 57Vrms AC field. ..............................................................................................................................60

Figure 34: Mixture 1.4 under high field (A) and with the field removed (B) at 71.5°C...........61

Figure 35: Mixture 2 at 66.0°C. Clockwise from upper left: (A) 0V, (B) 11V, (C) 32V, (D) 43V. ..............................................................................................................................62

Figure 36: Response of blue phase to voltage at isotropic and two different temperatures in the BPIII range..........................................................63

Figure 37: X-Ray scattering shows that small smectic clusters (broad peaks) appear at temperatures as high as 89C. The broad peak and low intensity of the signal, as compared to the sharp, intense peak formed by the smectic phase (aqua peak, right axis) shows that the smectic clusters are small, only a few layers thick. ..........................................................64
Figure 38: A simplified drawing of how an amorphous lattice interspersed with smectic clusters might appear. The smectic clusters inhibit long-range lattice order, preventing the appearance of BPI or BPII.

Figure 55: Phase diagram for mixtures of F493 and 60O8, taken from reference [52].

Figure 56: Textures of sample A. A) Isotropic (90.0˚C) B) BP (71.9˚C) Note that between picture A and B no adjustments were made to either the light or the camera settings C) Transition to N* begins (66.5˚C) D) Transition continues (64.5˚C) Between pictures C and D the exposure time of the pictures was reduced by half. E) 42.0˚C F) Crystal (33.6˚C).

Figure 57: Transmission spectra for Sample A for several temperatures. The bold lines (green, aqua and grey) show temperatures where the BP reflection peaks occur.

Figure 58: Sample B textures. A) Isotropic (69.5˚C) B) Platelets are visible in this blue phase (63.0˚C) C) Transition begins (50.0˚C) D) N* (41.0˚C) E) N* (32.0˚C) F) Smectic C (27.2˚C).

Figure 59: Sample B transmission spectra. Temperatures within the blue phase region are in bold.

Figure 60: Sample C textures. A) Isotropic (80.0˚C) B) BP (45.0˚C) C) transition to smectic (38.0˚C) D) transition to smectic (37.5˚C) E) Smectic C (35.8˚C) F) smectic (32.8˚C)

Figure 61: Transmission spectra for sample C (no polarizers) shows peaks corresponding to the blue phase from between 71˚C and approximately 38-40˚C.

Figure 62: Sample D textures: A) isotropic (70.0˚C) B) Undetermined blue phase (65.7˚C) C) Platelet appears (61.8˚C) D) Blue phase (44.6˚C) E) Smectic transition begins (43.5˚C) F) Smectic C (32.4˚C) G) Smectic C* (25.4˚C) H) Transition (24.8˚C)

Figure 63: Transmission spectra for Sample D, no polarizers. The blue phase peaks extend to the visible wavelengths.
Figure 64: Transmission spectra for Sample E, no polarizers. The sample is similar to sample D in its reflected wavelengths, but spans a shorter temperature range.

Figure 65: A) BP (70.0°C) B) BP as it edges into the visible spectrum (69.1°C) C) Transition to Sm begins (52.9°C) D) Smectic C* (52.4°C) E) at 40.0°C F) at 26.5°C.

Figure 66: Rough draft of phase diagram for a 6.64wt% BDH-1281 in 6O08 mixture doped with F493: the large blue phase area may in some cases be two separate (BPI and BPII) phases, while at some concentration between 5 and 10wt% F493, the smectic phases overtake the chiral nematic and crystal phases, which is consistent with the results using non-chiral mixtures from Figure 1.

Figure 4.67: A) Iso B) BPIII (67.0°C) C) Transition to N* begins (64.5°C) D) N* (59.5°C)

Figure 68: Transmission spectra of the chiral three bent-core mixture. The blue phase scatters light strongly at the near-UV end of the visible spectrum, while the cholesteric shows a broad peak.

Figure 69: A) BP-N* transition at 102°C B) 5wt% BDH-1281 in F521 at C, with oily streaks visible in the upper portion of the picture which have been removed from the lower portion (electrode area) by an applied and removed electric field, which serves to align the cholesteric liquid crystal in a planar configuration.

Figure 70: A more detailed look at cholesteric oily streaks in a 5.9wt% BDH-1281 in F521 sample.

Figure 71: A) Platelet texture at 53.8°C B) BP-Cr transition at 38.5°C.

Figure 72: A) Blue phase platelets at 34.2°C and B) the BP-Crystal transition at 33.6°C.

Figure 73: Simplified diagram of how a lyotropic nanoreactor can influence the shape and size of nanoparticles. As the nanoparticles form in the fluid areas of the sample, the phospholipid or surfactant walls guide their shape.
Figure 74: A series of nanoparticles synthesized in Symperonic A7 under different conditions. The bright yellows (left) indicate a smaller nanoparticle than the deep golds (right). .......................... 95

Figure 75: A) Absorbance spectra for nanoparticles synthesized in DPPC at two different temperatures show a shift in the leading edge of the spectra indicating a difference in diameters. B) The relation between band-gap energy and nanoparticle diameter from reference [94] .................. 96

Figure 76 A) Spherical CdS nanoparticles synthesized in Synperonic A7 at a high rate of shear (2000 s⁻¹). B) Anisotropic CdS nanoparticles made under the same conditions as (A) except the shear rate was reduced (1600 s⁻¹). ................................................................................................. 97

Figure 77: CdS nanoparticles made in Synperonic A7 show both spherical and long nanoparticles. ........................................................................................................................................ 98

Figure 78: Aggregates of diamond nanoparticles in a bent-core blue phase. ...................... 100

Figure 79: A diffusion method for introducing nanoparticles into liquid crystal. The hydrophobic nanoparticles should readily leave the hydrophilic ethylene glycol and migrate to the liquid crystal ........................................................................................................................................ 101

Figure 80: A sample of ethylene glycol (top) and 6OO8 with BDH-1281 (bottom) displays a texture gradient 3 hours after filling (T = 67.2 °C) after 24 hours at isotropic temperatures, the gradient when cooled becomes more pronounced (T = 65.3 °C) .................................................. 101

Figure 81: 50/50 mixture of F493 and 6OO8 with 5% chiral dopant A) control sample crystallizes at 60 °C B) Held at isotropic overnight with a 0.2wt% CdS in E.G. sample reduces the transition to approximately 55 °C C) doubling the concentration of CdS in the E.G. and holding at isotropic overnight actually decreased the temperature range ........................................................................................................ 102

Figure 82: 50/50 F493 and 6OO8 (with 5wt% BDH-1281) A) no nanoparticles B) 0.005% silica nanoparticles C) 0.02% silica nanoparticles D) 0.035% silica nanoparticles. Larger amounts of
nanoparticles appear to extend the BPIII phase at the expense of the BPI or BPII phase seen at low and no-nanoparticle concentrations; the overall increase in temperature range is approximately 5°C.

Figure 83: Three-component bent core mixture with 1.9% BDH-1281. A) Control at 63.0°C B) Control at 49.2°C C) Control at 30.0°C D) 0.02% nanoparticles at 63.0°C E) 0.02% nanoparticles at 49.0°C F) 0.02% nanoparticles at 29.9°C G) 0.05% nanoparticles at 56.8°C H) 0.05% nanoparticles at 50.0°C I) 0.05% nanoparticles at 29.4°C.

Figure 84: The BPIII temperature range is greatly expanded through the addition of nanoparticles. Even the temperatures beneath which frustrated white streaks occur is reduced (grey dotted line).

Figure 85: The polymer stabilized blue phase shows a light blue texture at room temperatures from scattering of the lower wavelengths.
ACKNOWLEDGEMENTS

I would like to thank the following people for their support and help:

My advisor Dr. Antal Jákli and all the members of JákliLab with whom I worked during my time at the Liquid Crystal Institute, including John Harden, Christopher Bailey, Nick Diorio, Wilder Iglesias, Dierdre Manion-Fischer, and Tracy Zhang.

The faculty and staff of the LCI for making the Chemical Physics Interdisciplinary Program a second home to me from the very first classes I took here, when I was still a KSU physics undergraduate.

The National Science Foundation’s EASPI program and the JSPS Summer Institute, and especially Dr. Hideo Takezoe of the Tokyo Institute of Technology for allowing me to study in his lab, and Khoa Van Le for all of his assistance during that time.

My family for their patience and understanding through a decade of higher education, particularly the last five years.

My roommate Joshua D. Wygle, for eight years of valuable rent-splitting and moral support, and all of our mutual friends from Elementary Japanese I & II, and all of the CPIP students who helped make five years of graduate school so very enjoyable.

And finally, the members of my defense committee for their participation in the most important day of my graduate career.
Chapter 1

Chirality, Bent-Core Liquid Crystals and Blue Phases

1.1 Introduction

The blue phases of liquid crystals are a set of phases that exist between the isotropic and cholesteric phases of certain liquid crystalline materials. Until recently, no discussion about blue phases could begin without emphasizing the elusiveness of these delicate phases: the temperature range of a typical blue phase spanned 2 °C or less. From a practical standpoint, their most notable feature was their stability, or lack thereof; their limited temperature span was impractically narrow. Now, however, research on blue phase liquid crystals is undergoing a type of Renaissance due to recent innovations which greatly improve their stability and expand their potential for use in practical applications.

Blue phases were most likely first observed in 1888, part and parcel with the first observations of liquid crystals by Friedrich Reinitzer, but the bulk of experimental research into their structure would wait until almost a hundred years later as it was a task that required extraordinary precision and patience at a time when there was some controversy on whether or not blue phases were even worthy of intense scrutiny.[1]

Research into the structure of blue phases revealed a three-dimensional lattice of cylindrical liquid crystal “logs” lashed with a corresponding lattice of disclination lines.[1, 2] This idea of a three-dimensionial fluid crystal lattice was very exciting, but also frustrating – defect-mediated phase transitions tend to be fragile; the very characteristics that made the phase unique and exciting also made it so fleeting as to be useless from a
practical point of view. The list of potential applications (photonic band gap crystals, alignment layer-free displays, tunable color filters) was very attractive, but of what practical use is a laser or display with an operational temperature range of 2°C or less?

Understanding of the blue phases gradually increased and focus has turned to expanding their temperature range and stability. In the last decade, three promising avenues have been explored: polymer stabilization, nanoparticle stabilization, and use of unconventional liquid crystals. Polymer and nanoparticle stabilization operate on the same principle: filling up the space in the disclination lines should reduce the free energy costs of the defects, thereby stabilizing the phase. Unconventional liquid crystals, e.g. liquid crystalline dimers or unusually-shaped liquid crystals, have been found to easily make relatively broad-temperature blue phases, but the mechanism is less well-understood.

Recently, two publications have brought blue phases back into the limelight: in 2002, Hirotsugu Kikuchi, et al, described polymer-stabilized blue phases with broad temperature ranges and fast switching times, and in 2005 H. Coles and M. Pivnenko presented a broad-temperature blue phase that existed at room temperature using liquid crystal dimers. By 2008 Samsung was showing a blue phase liquid crystal display (BPLCD) prototype at the Society for Information Display’s annual conference; the high-end video product was slated to be available 2011. Interest in the blue phases was officially revived.

In this work we combine two methods: using bent-core liquid crystals and chiral dopants to create blue phases, and if necessary stabilizing said phases with polymer or
nanoparticles. The goal was to create broad temperature range, stable blue phases that operated as close to room temperatures as possible.

1.2 Chirality and Liquid Crystals

A short discussion on chirality as it relates to nematic liquid crystals is required to fully appreciate the blue phases.

1.2.1 Molecular Chirality

Chirality was defined by Lord Kelvin in 1894\cite{8} as an object that cannot be superimposed over its own mirror image no matter what symmetry operations are subsequently applied. The simplest example is that of a carbon centered in a tetrahedron surrounded by four different and distinct groups. In contrast, a carbon molecule bonded to only three distinct groups (for instance, if two of the bonds are both occupied by hydrogen) can be superimposed over its own mirror image after rotation (Figure 1).
Figure 1: A chiral molecule (A) can not be superimposed over its own mirror image, even if it is otherwise completely free to rotate. An achiral molecule (B) can be superimposed over its own mirror image after rotation.

The classification system for chiral molecules starts with the “chirality rule,” which is best described as follows in the text *Chirality in Liquid Crystal.*[9]

The absolute configuration of such molecules, “R” or “S”, is described by the chirality rule developed by Cahn, Ingol, and Prelog (1966). According to sequence rules, the four ligands are arranged in a priority list, e.g. A>B>D>E. Ligands of higher atomic number precede ligands of lower atomic number. If the consideration of the nearest neighbors of the chiral center does not result in an unambiguous sequence, the next sphere of ligands is to be investigated until the priority sequence is found. The molecule is then viewed from the side opposite to the ligand with lowest priority, E. If the sense of direction of the three remaining ligands in the sequence A→B→D is clockwise, the configurational descriptor is R (for Latin rectus, right), and if it is counterclockwise, it is S (for Latin sinister, left).
Next, one must take into consideration the sign of the optical activity, positive or negative. Chiral materials rotate plane polarized light. If this rotation is clockwise, the material is positive (+); counterclockwise is negative (-).

Liquid crystals can have multiple chiral centers in either handedness or configuration. A center achieves its status as R or S based on which configuration is “more represented in the molecule” as a whole. For the purposes of chiral liquid crystal phases, positive or negative optical rotation can be determined by a relatively simple experiment which is described thoroughly in Chapter 2.

A chiral molecule with a given handedness is called an enantiomer. A mixture of enantiomers can be either chiral if molecules of one handedness are more prevalent than those of the other or achiral if the mixture is racemic (containing equal amounts of both enantiomers).

1.2.2 The Cholesteric Phase

In this work we are primarily concerned with phases related to the nematic phase of ordinary thermotropic calamitic and bent-core molecules. A typical calamitic liquid crystal contains elongated molecules that consists of a stiff section (usually a chain of 2 or more benzene rings) and a flexible tail section (carbon chain). A simple example of an achiral liquid crystal is 5CB (Figure 2):
Figure 2: 5CB. A typical calamitic liquid crystal consists of a rigid core (A), a semi-flexible tail (B), optional polar groups or substituents (C) and has a length (L) approximately 4 or more times larger than its width (W).

In the isotropic phase, these molecules enjoy complete positional and orientational freedom just like in any liquid. At cooler temperatures, some liquid crystals form a nematic phase where the molecules still enjoy positional freedom but their long axis now fluctuate around an imaginary line (Figure 3) called the director (n):
Figure 3: The isotropic phase (A) is favored at higher temperatures. The nematic phase (B) is favored at lower temperatures.

The free energy of the nematic phase is described by (Eq 1.1):

$$F = \frac{1}{2} \left[ \int K_1 (\nabla \cdot \mathbf{n})^2 + K_2 (\mathbf{n} \cdot \nabla \times \mathbf{n})^2 + K_3 (\mathbf{n} \times \nabla \times \mathbf{n})^2 \right] dV$$  \hspace{1cm} (1.1)

Where \( \mathbf{n} \) is the director and \( K_1, K_2 \) and \( K_3 \) are elastic constants corresponding to splay \((K_1)\), twist \((K_2)\) and bend \((K_3)\) (see Figure 4).
Figure 4: The three bulk deformations of a nematic liquid crystal.

Now imagine that 5CB contained a chiral carbon or several. A chirality term must be added to the $K_2$ (twist) elastic term to account for natural pitch of the material ($q_0 = 2\pi/p$ where $p$ is the pitch of the cholesteric helix) (Eq. 1.2). The solution to minimizing this equation is to allow $\mathbf{n}$ to twist as one travels along a line in the sample orthogonal to the plane in which the director rotates\textsuperscript{[9]} (Figure 5).

$$F = \frac{1}{2} \left[ \int K_1 (\nabla \cdot \mathbf{n})^2 + K_2 (\mathbf{n} \cdot \nabla \times \mathbf{n} + q_0)^2 + K_3 (\mathbf{n} \times \nabla \times \mathbf{n})^2 \right] dV \quad (1.2)$$
Figure 5: Chiral molecules twist into a helix orthogonal to the plane in which the director rotates. A simplified diagram (below) shows the helix.

When a nematic liquid crystal spontaneously twists because of the molecular chirality of its components, it is known as a chiral nematic or cholesteric phase, so named because the first chiral materials studied were esters of cholesterol. This cholesteric phase has several interesting properties - such as the ability to reflect circularly polarized light in a narrow band of wavelengths - that make such materials desireable for applications such as signage or electronic books. Unfortunately for anyone who would like to exploit these properties, most naturally chiral materials are not optimized for practical applications. Fortunately, when an achiral nematic is mixed with a chiral molecule, the entire mixture can become chiral. The use of chiral dopants allows for the creation of chiral materials with specific transition temperature, helical pitches, or optical bandgaps. The above example of a chiral phase of 5CB will not happen in a pure sample
at any temperature but can be achieved through the addition of a chiral dopant.

The pitch of the cholesteric phase is the length of the helical axis along which the director rotates 360°. When the pitch is in the same range as the wavelength of visible light (short-pitch materials), the material begins to reflect one handedness of circularly polarized light at that wavelength due to Bragg diffraction.[10]

Chirality (κ) in liquid crystals is thought of in terms of inverse pitch, i.e., if two materials have the same elastic constants, the material with a shorter helical pitch has a higher chirality. The helical twisting power (HTP) (the normalized reciprocal of the pitch p⁻¹) of a molecule is complicated and depends on many factors, including but not limited to the number and position of chiral carbons in the molecule and the orientation of the chiral substituents in relation to the orientational axis of the whole molecule[11].

Macroscopically, HTP is defined as a combination of the partial differentials of the reciprocal pitch with respect to the molar fraction of each enantiomer taken in the limit as the opposite enantiomer’s concentration approaches zero:[11] (Eq. 1.3)

\[
(HTP)_e = \frac{1}{2} \left\{ \left( \frac{\partial p^{-1}}{\partial x_e} \right)_{x_{e^\dagger} = 0} - \left( \frac{\partial p^{-1}}{\partial x_{e^\dagger}} \right)_{x_e = 0} \right\}
\]

(Eq. 1.3)

Where \( e^\dagger \) is the enantiomer of \( e \) and \( x_e, x_{e^\dagger} \) are the molar fractions of \( e \) and \( e^\dagger \). We are primarily interested in mixing small amounts of chiral material into achiral liquid crystals. In which case, the HTP of the mixture should be the HTP of the guest molecules normalized for concentration; assuming relatively dilute solutions, the total HTP (Eq. 1.4)
of the mixture is the sum of all the HTP values of the component chiral additives multiplied by their respective concentrations in the sample:\textsuperscript{11}

\[ HTP = \sum_i x_i(HTP)_i \]  

(1.4)

The practical use of this is that, roughly speaking, adding more of a chiral dopant to an achiral nematic material will result in a more highly chiral mixture. The HTP of a chiral dopant can range from approximately 10 $\mu$m$^{-1}$ (ZLI811, Merck\textsuperscript{12}) to over 150$\mu$m$^{-1}$\textsuperscript{13}

If the chirality of a material is high enough, a three dimensional double twist structure becomes energetically favorable. A double twist cylinder of chiral nematic liquid crystals consists of a ring of molecules set at 45° to the helical axis that twists through the center of the cylinder (Figure 6). The cylinders can grow relatively long, but their diameter is limited to approximately half a pitch: the angle of the exterior molecule needs to be $\pi/4$ with respect to the center axis of the cylinder to eliminate the presence of defects where two cylinders meet, while bend distortion energies at larger angles prevent diameters greater than the length of a single twist from $+45^\circ$ to $-45^\circ$ from a center molecule.\textsuperscript{9} At the points where three cylinders meet there is no avoiding defects, therefore the ideal packing of a series of double twist cylinders becomes a crystalline lattice of cylinders laced with disclination lines (Figure 7).
Figure 6: Simplified cross section of a double twist cylinder. The pale green caps serve as a guide to the eye for following the twist, the helical axis alternate colors in blue and lavender for visual clarity.

Figure 7: Two different views of three double-twist cylinders meeting at a defect. Seen from one side of the unit cell, a well-defined lattice of cylinders is clearly visible (A), but
it is not instantly clear that the half-pitch diameter (molecules at the edge of the cylinder form an angle of $\pm \pi/4$ with respect to the cylinder’s core) allows two cylinders to meet without defects. Seen from the vantage point of looking down a disclination line (B), one can more clearly see how the cylinders fit together in a smooth and fluid manner until the defect area where three cylinders meet.

1.3 Blue Phases

The phases created by networks of these double-twist cylinders and their corresponding defect lines are called the blue phases – so named for the characteristic flash of blue one might see in a sample as it cools from isotropic.

Blue phases were almost certainly first noticed in 1888 by Dr. Friedrich Reinitzer, who noted a brief hazy blue color that appeared just as his clear liquid turned cloudy; or as it turned out, between the isotropic and cholesteric phases. Reinitzer’s observation makes the blue phase the first liquid crystalline phase discovered – tied only with the chiral nematic (cholesteric) phase. Yet now, almost a century and a half later, one can buy signs, thermometers, or novelty jewelry containing chiral nematic liquid crystals while the blue phase, the cholesteric’s unpopular and less-understood cousin, is just starting to see use in practical applications.

The reason for this discrepancy lies in the delicate nature of the defect-mediated double-twist cylinder structure. The conditions under which lattices of double-twist cylinders are energetically favorable occur within a very narrow temperature band close
to the isotropic transition temperature. This made them difficult to study and effectively useless for practical purposes.

“They are totally useless, I think, except for one important intellectual use, that of providing tangible examples of topological oddities, and so helping to bring topology into the public domain of science, from being the private preserve of a few abstract mathematicians and particle theorists,” Sir Charles Frank, of Frank Free Energy fame, said of blue phases in 1983. This harsh and decisive quote came at a time of intense interest in and progress towards understanding the exact nature of the phases – yet no one would be able to contradict him in his lifetime.

It was 1956 when British chemist George Gray began taking a closer look at the strange textures between the cholesteric and isotropic phases. In 1969, Alfred Saupe combined a large quantity of liquid crystal with a very good temperature controller to show that those textures belonged to a phase that was decidedly not the cholesteric. Although not above criticism, it marked the beginning of sustained interest in the research of blue phases.

Brazovskii, et al. laid the theoretical framework for understanding blue phases in the early 1970’s by using Landau theory to show when non-one dimensional cholesteric structures would be energetically favorable. Although not above criticism, it marked the beginning of sustained interest in the research of blue phases.

The first task was determining the phases’ structure. Based on his own experiments, Saupe had proposed a cubic structure. Both theory and experiment would come to agree with Saupe; however it would be some time before they agreed with each other. Models based on Landau free energy theory and models based on defects both described cubic lattice structures, although they tended to differ which types of lattices
would be expected. The beautiful platelet texture exhibited by the blue phase was readily broken down by experiment into two subtly different platelet textures: some theory predicted hexagonal and $O_5$, a type of body-centered cubic structure, while other theory and experiment suggested $O_8$ (a different body-centered cubic structure) and $O_2$, a simple cubic structure. Moreover, no theory really predicted the “blue fog” phase that sometimes appeared in materials of sufficiently high chirality.

The free energy density of the blue phases has some additional terms that are not always relevant in the nematic and cholesteric phases. The free energy of a cholesteric phase in its simplest geometry can be reduced to:

$$ F = \int \frac{1}{2} K_2 (\vec{n} \nabla \times \vec{n} + q_0)^2 \, dV $$

(1.5)

As there are no splay or bend terms in a planar-anchored, defect-free cholesteric. A double-twist cylinder, however, includes a bend term and also maintains the surface term:

$$ F = \int \left[ \frac{1}{2} K_2 (\vec{n} \nabla \times \vec{n} + q_0)^2 + \frac{1}{2} K_3 (\vec{n} \times \nabla \times \vec{n})^2 - K_{24} \nabla \cdot (\vec{n} \nabla \cdot \vec{n} + \vec{n} \times \nabla \times \vec{n}) \right] dV $$

(1.6)

Which in cylindrical coordinates simplifies to:

$$ F = -K_2 \left( q_0 + \frac{\sin(2q_0 R)}{R} \right) + K_3 \frac{\sin^2(q_0 R)}{R} - 2\pi K_{24} \sin^2 \Psi(R) $$

(1.7)

Where $\Psi(R)$ describes the tilt of the molecule as a function of radius, with $\Psi(R) = \ldots$
0 at the center.\textsuperscript{[21]} Assuming that $K_{24}$ is larger than zero and the radius is small, $F$ becomes negative and the double-twist geometry is energetically favorable. For reasons already described, the maximum radius of a double-twist cylinder in a liquid crystal is going to be 1/2 of its pitch. The question then becomes, do the free energy gains of a double-twist cylinder structure more than offset the cost of the unavoidable defect lines therein?

To answer this the free energy of the disclination lines must be taken into account, which includes the free energy of the material surrounding the disclination, the free energy of the core, the free energy of the surface of the disclination line, and the free energy of the interface between the disclination line and the ordered liquid crystalline sections (Eq. 1.8-1.12):\textsuperscript{[17]}

\[
F_1 = \int dV \left[ \frac{1}{2} K_1 (\nabla \cdot \vec{n})^2 + \frac{1}{2} K_2 (\nabla \times \vec{n} + q_0)^2 + \frac{1}{2} K_3 (\vec{n} \times \nabla \times \vec{n})^2 \right] \tag{1.8}
\]

\[
F_2 = \int dV \frac{1}{2} (K_2 + K_{24}) \nabla \cdot [(n \nabla) n - n (\nabla \cdot n)] \tag{1.9}
\]

\[
F_3 = \alpha (T_{iso} - T) \pi R^2 \tag{1.10}
\]

\[
F_4 = 2 \sigma \pi R \tag{1.11}
\]

\[
F = F_1 + F_2 + F_3 + F_4 \tag{1.12}
\]
Where $F_1$ is the standard free energy of a chiral nematic, $F_2$ is the commonly-neglected surface term that now must be taken into account because, $F_3$ is the energy of the defect core and $F_4$ is the free energy at the interface. $K_1$, $K_2$ and $K_3$ are the curvature elastic constants of the liquid crystal, as is $K_{24}$, the saddle-splay term. $T_{iso}$ is the clearing point of the material, $R$ is the radius of the defect core.

In their derivation, Meiboom, et. al. reduce $F_1$ to the free energy of a nematic surrounding an $S = -1/2$ defect (Eq. 1.13) and $F_2$ is integrated around the cylinder (Eq. 1.14) and the single-constant approximation is applied:

\[
F_1 = \frac{1}{4} \pi K \ln \frac{R_{\text{max}}}{R} \quad (1.13)
\]

\[
F_2 = -\pi (K_2 + K_{24}) = -\pi K \quad (1.14)
\]

This argument states that, for some temperatures $T$, the free energy of the disclinations is actually negative, and therefore the lattice structure of the blue phases becomes energetically favorable. The conditions are satisfied for any such $T$ that $F_3 < F_2$, a condition most readily satisfied when $T$ is close to $T_{iso}$.

Once BPI (body-centered cubic structure O$_8$) and BPII (simple cubic O$_2$) structures were determined, attention turned to the “blue fog” phase. The blue fog phase got its name from its texture, or more appropriately, its lack thereof. Usually a dark blue-violet, with no characteristic defect textures or birefringence colors, it was a difficult
phase to detect and even more difficult to explain. Today the generally accepted model for the BPIII (formerly, blue fog) phase is one of short-range cubic structure without long-range order, sometimes described as the “amorphous crystal.”[18]

All of this effort in forwarding a fundamental understanding of the blue phases, and still no one could argue with Sir Frank – a century of research on the blue phases and every last experiment was performed on a phase spanning 2°C or less. The highly ordered lattice structure of BPI and BPII led the imagination to plenty of highly desirable potential applications, but the vanishingly small temperature range remained a serious problem.

1.4 Bent Core Liquid Crystals

A bent core liquid crystal has bent or banana-like shaped molecules. A typical banana molecule consists of at least three[22] but usually five benzene rings connected by groups such as azomethine, ester or thioesters and commonly ending with carbon tails. The end product is a molecule shaped like a boomerang with banners on the ends, the properties of which can be adjusted through careful selection of the interconnecting groups within boomerang structure or substituents attached to remaining sites on the benzene rings,[23] or modification of the tail section: long, short, symmetrical, asymmetrical, saturated, unsaturated, etc. Interconnecting groups or substituents can determine the presence or absence of a mesophase, as well as the angle formed by the
rigid arms of the boomerang and by extension the packing behavior of the whole molecule (Figure 8).

Figure 8: A typical bent core molecule with some common linking groups. Recreated from Pelzl, et al. Liquid Crystals Vol. 28 (2001) pp 970.

Similar to the history of the blue phase, the history of bent core liquid crystals is both long and short. The very first banana molecules that show a characteristic bent-core mesophase were synthesized in the laboratory of Daniel Vorländer of Martin Luther University (Halle, Germany) in or around 1929. However, Dr. Vorländer’s four-decade stewardship of Martin Luther University’s Chemical Department included the synthesis and partial characterization of thousands of mesogens leading to too many groundbreaking liquid crystal discoveries to completely catalog in one lifetime. And so it happened that his banana molecules sat in a cigar box for seven decades until Pelzl, et al.\cite{Pelzl} rediscovered and characterized them - ten years after Matsunaga and coworkers had
synthesized the first modern bent-cores.\textsuperscript{[25]}

Polarized optical microscopy of pure bent core liquid crystals reveal several textures unique to bent core liquid crystals, initially identified as the B1 through B7 phases. Takezoe’s review of the bent core liquid crystals details the structure and complexity of these phases.\textsuperscript{[26]} The banana shape of the molecule tends to favor smectic order and the resulting textures show characteristics in common with calamitic smectics, such as focal conic domains and striated fan textures.\textsuperscript{[27]} A true nematic phase for bent core liquid crystals was not observed until 2000\textsuperscript{[28]} – and even so, bent core nematics would turn out to be not completely free of smectic order, a detail which will be explained and exploited thoroughly in Chapter 3.

In the body of literature concerning banana-shaped mesogens, three characteristics are routinely singled out as being especially interesting or important: molecular biaxiality, flexoelectricity, and perhaps most intriguingly, the appearance of chiral phases of achiral molecules.

A biaxial molecule is one that is more accurately represented by a box shape rather than a cylinder. This property caused bent-core liquid crystals to be strong contenders in the search for the ever-elusive biaxial nematic phase\textsuperscript{[29]}, but for our purposes the relevance comes from the suggestion the molecular biaxiality is one mechanism by which blue phases could be stabilized\textsuperscript{[30, 31]} by relieving some of the frustration of the defect lines.

Flexoelectricity is the result of polar alignment that happens when a sample is bent or flexed – “polarization induced by distortion.”\textsuperscript{[32]} A calamitic nematic sample in
the proper geometry can produce on the order of 10 picocoulombs per meter of electric charge when flexed.\textsuperscript{[33]} From the beginning, bent core molecules were expected to improve these results up to a hundredfold by virtue of their unique shape and optimal packing geometries. Recent experiments showed that bent core nematic liquid crystals produce nanocoulombs per meter – 1,000 times that of calamitics.\textsuperscript{[34]}

It has been suggested that molecular biaxiality\textsuperscript{[35]} and/or a large flexoelectric constant\textsuperscript{[36]} may play a role in stabilizing blue phases. What is clear is that to date, the published work on stable blue phases with larger than normal temperature ranges (excluding polymer- or nanoparticle-stabilized materials) invariably involves non-traditionally shaped mesogens and these tend to display molecular biaxiality and/or larger flexoelectric constants.\textsuperscript{[6, 37, 38]}

Achiral bent core molecules were first used to create ferroelectric smectic phases,\textsuperscript{[39]} but they also possessed a surprising affinity for spontaneously forming chiral phases,\textsuperscript{[40-43]} notably the B2, B4 and B7 phases. An achiral bent-core liquid crystal may be racemic but still sort into evenly-matched domains of opposing chirality.\textsuperscript{[26]} Many external factors can easily induce the bent-core liquid crystal to choose between an R or S configuration, including chiral dopants or symmetry breaking using chiral surfaces or polymer networks.\textsuperscript{[42]}

In their 2005 Nature article, Coles and Pivnenko used liquid crystalline dimers consisting of rigid sections connected by a flexible carbon chain to create broad-temperature blue phases.\textsuperscript{[6]} They speculate that the flexoelectric properties of their material help in stabilizing the blue phase.\textsuperscript{[36]} By using bent-core materials, we increase
all of the properties presumed to encourage the formation of blue phases (a molecular structure that at least allows a bend, leading to flexoelectricity and molecular biaxiality) in the hopes that a simple method of consistently producing stable, wide-temperature range blue phases will follow.
Chapter 2

Materials and Characterization Methods

2.1 Materials Studied

This work is primarily concerned with using bent-core nematic liquid crystals to reproduce and improve upon the room temperature blue phase materials first published by Coles and Pivnenko.\textsuperscript{[6]} Liquid crystal dimers like those used in reference [1] were synthesized and provided to us (Figure 9) by Dr. Robert Twieg (Department of Chemistry, Kent State University) and the experiments replicated.

![Figure 9: Liquid crystal dimers used by Coles and Pivnenko to create broad-temperature range blue phases](image)

The resulting highly chiral mixtures were found to be unstable and prone to phase separation between the liquid crystal dimer mixtures and the chiral dopant. The idea to
move on and use bent-core nematics in place of flexible liquid crystal dimers stemmed from the observation that many of the properties that supposedly made the dimers suitable for making blue phases could be matched or exceeded by the bent-core molecules.

We chose family of bent core liquid crystals first synthesized by Dr. Katalin Fodor-Csorba at the Research Institute for Solid State Physics and Optics, Hungarian Academy of Sciences in Budapest. These molecules consist of “five phenyl rings connected by ester moieties” [44] and long carbon chains. A great deal of effort has already gone into the thorough characterization of these molecules, [45] including viscosities and rheological properties [46, 47], electro-optical properties, [48] electric response [49], second harmonic generation [50] and flexoelectric properties [34, 51]. These materials have been studied in mixtures with calamitic liquid crystals [52], elastomers [53–55] and fibers. [56, 57]

Members of this 1,3-phylene bis[4’-{4-[4’-(alkenyloxy)benzoyloxy)]benzonate family of bent core mesogens are considered suitable materials for such a variety of projects for several reasons, not the least of which are their relatively low transition temperatures (typically isotropic at temperatures of less than 100 °C) and miscibility with other mesogens [52]. In this case, the large nematic ranges of certain variants, notably 4-Chloro-1,3-phenylene Bis{4-[4’-(9-enyloxy)-benzoyloxy)]benzonate (or, F493) was a large factor in the choice to use them for creating blue phase mixtures. Several liquid crystals were used in our effort to expand the temperature range of the blue phases, including multiple bent-core nematic liquid crystals, a calamtic liquid crystal, and two
Chiral dopants. Chiral dopants are purchased from Merck (Germany) and used as provided, while the bent-core and calamitic liquid crystals were synthesized by Jarrod Williams and Robert Twieg from the Department of Chemistry, Kent State University.

The primary bent-core material used was 4-Chloro-1,3-phenylene Bis{4-[(9-enyloxy)-benzoyloxy]} benzoate, hereinafter referred to as F493 (Figure 10).

Figure 10: F493, the principal bent-core nematic used in this work.

A second bent-core nematic used as a host material for chiral dopant was 4,6-dichloro-1,3-phenylene-bis[4’-(oct-7-enyloxy) biphenyl]-4-carboxylate, otherwise known as F521 (Figure 11).

Figure 11: F521. Note the shorter, more rigid legs and the short flexible tails.
F493 and F521 are similar bent-core nematics whose differences include the extra chlorine attached to the central benzene ring on F521, the missing ester groups between the lower benzene rings on the legs of F521 that result in a shorter, more rigid core, and the shorter flexible tail lengths of F521.

Although the nematic phase of F493 is monotropic (appears only on cooling and is only metastable), it spans from approximately 54°C to 75°C. The nematic phase of F521 is broader, spanning a range of about 50°C starting just under 100°C. For this reason we expected F521 to produce better results after the addition of chiral dopant, but (as we show later) it was F493 that resulted in the blue phase with the broadest temperature range.

A third bent-core nematic material appears only as a component in a bent-core nematic mixture with interesting properties. A 1:1.1:1.05 mixture of F493:F521:F533 (4,6- dichloro-1,3-phenylene-bis[4’ (non-8-enyloxy) biphenyl]-4-carboxylate, Figure 12) exhibits liquid crystalline phases down to room temperatures. F533 is most similar to F521, but with slightly longer flexible tails (Figure 12). Chiral materials based upon the mixture of all three bent-core nematics are explored in Chapters 4 and 5.

**Figure 12: Molecular structure of F533.**
The calamitic liquid crystal 4-n-octyloxyphenyl 4-n-hexyloxybenzoate (hereinafter referred to as 6O08) (Figure 13) was used both as a control material to compare the differences between bent-core and rod-shaped samples doped with comparable amounts of a given chiral dopant, and also as an ingredient in mixtures aimed at expanding the blue phase temperature range.

![Chemical structure of 6O08](image)

**Figure 13**: Calamitic liquid crystal 6O08.

6O08 strongly resembles the legs of our bent-core nematic mixtures, particularly F493 with its intermediary ester groups between the benzene rings. These similarities offer the opportunity to make a reasonably fair comparison between the bent-core and rod-shaped chiral mixtures as they are as similar as a bent-core and rod-shaped molecule can be. In addition, we examine chiral mixtures of the two of them together, as mixtures of this liquid crystal with the bent-core nematics used in this work are already well-studied.[52]
Chiral dopants used were BDH-1281 and CB15 (Merck). BDH-1281 is a high-HTP chiral dopant most notable for its use in the broad-temperature blue phases reported by Coles and Pivnenko in 2005. The benefit to using BDH-1281 is that it keeps the amounts of chiral additive needed to achieve highly chiral phases like blue phases very small, typically less than 5wt%.

CB15 is a commonly used chiral dopant that is fluid at room temperatures. It was used in mixtures where it could function as both a chiral dopant and a calamtic additive, with responsibilities that included reducing the transition temperatures and diluting the concentration of bent-core liquid crystals in a chiral mixture, for reasons detailed in Chapter 4.

2.2 Characterization Methods

Identification of the blue phases can be a challenge, particularly that of the enigmatic BPIII. Of particular importance is patience: while initial characterization of liquid crystals usually involves a rate of cooling anywhere between 1°C (polarizing optical microscopy) and 10°C (differential scanning calorimetry) per minute; blue phases, even those where wide temperature ranges are expected, should be approached more cautiously. In the case of the isotropic – BPIII transition, the sample must be narrowly observed because the subtle nature of the transition can make it very difficult to detect.

Methods used in this work include: polarizing optical microscopy, differential scanning calorimetry, optical rotary dispersion measurements, electro-optic behavior, x-
ray scattering and high magnetic fields. Kossel diagrams were attempted but ultimately disregarded as a tool for characterizing these particular materials.

2.2.1 Polarizing Optical Microscopy

Textural analysis using Polarizing Optical Microscopy (POM) is traditionally the liquid crystal researcher’s weapon of choice for the initial characterization of new materials. With POM, linearly polarized light is transmitted through a sample with thickness $d$ and birefringence $\Delta n$. Light traveling through the sample will travel along two paths at different speeds, one along the ordinary and one along the extraordinary axis of the sample. The wavelength of the light, thickness of the sample and birefringence of the material determine the phase shift of the resulting light (Figure 14).

Viewing the sample between crossed polarizers allows one to see these shifts as textures composed of different colors and intensities, for example, the Schlieren texture of the nematic which results from phase retardation that occurs as the light travels through the birefringent liquid crystal (Eq 2.1).

\[
I = \frac{1}{2} I_0 \sin^2(2\varphi) \sin^2 \left( \frac{\pi d}{\lambda} \frac{n_0 n_e}{\sqrt{n_e^2 \cos^2 \theta + n_o^2 \sin^2 \theta}} - n_o \right) \quad (2.1)
\]
Where $\varphi$ is the angle between the local director and the polarization direction of the incoming light, $d$ is the sample thickness, $\theta$ is the angle formed between the director and the direction of light propagation and the $\lambda$ is the wavelength of light.

\[ I = \frac{1}{2} I_0 \sin^2(2\varphi) \sin^2\left(\frac{\pi d n}{\lambda}\right) \]

**Figure 14**: Propagation of light through a nematic liquid crystal between crossed polarizers (A). The final intensity of light depends on the thickness of the sample ($d$), the birefringence ($\Delta n = n_e - n_o$), and the wavelength of the incoming light ($\lambda$). A typical nematic texture (B) formed by placing a small drop of liquid crystal on a glycerin substrate.
Some phases, like the chiral nematic, are best viewed with a reflection microscope because the structure of the phase causes selective reflection of particular wavelengths. These textures do not need to be viewed between crossed polarizers\textsuperscript{[21]} but since they reflect circularly polarized light the presence of crossed polarizers will not prevent one from viewing them. Different phases of liquid crystals in different alignments each have their own distinct texture (Figure 15).

**Figure 15:** Examples of different liquid crystal textures as seen between crossed polarizers. A) An isotropic-smectic transition. B) A chiral nematic oily streak texture (in reflection). C) Smectic A focal conic domains. D) Bent-core B7 phase.

Blue phases, however, are optically isotropic and tend to look at least indistinct, if not entirely black, between crossed polarizers, so at first glance this is not a method that
seems particularly suited to them. Bragg reflection from crystalline domains in the platelet texture of BPI and BPII can be viewed using a reflection microscope, and indeed this sometimes results in the gorgeous textures like the one seen in Figure 16.

However, depending on the dimensions of the crystal lattice and the size of the domains, BPI or BPII are just as likely to reveal themselves as purple or dark blue flecks on black background as in Figure 17. These textures difficult to see and are easily missed, especially if they exist only over a small temperature range.

![Image](image_url)

**Figure 16:** An unusually colorful platelet texture formed using F493 with 36wt% CB15.
Figure 17: An example of a blue phase of calamitic liquid crystals.

*Photos courtesy of Dr. Shin-Ying Lu.*

For BPIII, which lacks the long-range lattice structure necessary to form even specks of purple glitter, visual inspection should be all but useless. However, we did not find this to be the case. The amorphous crystal structure of the BPIII scatters light quite well, so in a sufficiently thick sample the depolarized light serves well enough to inspect samples visually – provided that the crystalline lattice size is sufficiently large (Figure 18).
Figure 18: Polarized light entering a thick BPIII sample has ample opportunity to scatter and depolarize before emerging (A), resulting in a uniform blue texture under transmission POM (B). This works only if the lattice size is large enough to scatter visible light.

For any blue phase, thick samples are preferable for POM; a sample of several hundred microns thickness would not be unreasonable. However, with the bent-core blue phases samples of 25 or even 10 microns are frequently adequate, although they require more caution in order to properly observe the Iso-BP transition. Micrography of a blue phase, especially at the transition, has a lot in common with taking pictures at night (Figure 19). Unlike cholesteric or nematic textures, simply increasing the amount of light will not always result in brighter, clearer pictures. Optimum results require more control over the camera, including the ability to properly white balance and adjust exposure times. Because the visibility of the phase transition is a function of so many variables,
many of which have nothing to do with the material itself, POM provides at best an estimate of the Iso-BP transition temperature.

**Figure 19**: A blue phase of the calamitic liquid crystal 6008 (left). When the transition to N* starts, the same lighting conditions that allow for visual inspection of the BP texture over saturate the picture as cholesteric oily streaks begin to appear (right). If the material was viewed using lighting and camera settings appropriate for N*, the BP textures could be missed entirely.

Polarized optical microscopy for the samples presented was done primarily on an Olympus BX51 Transmission/Reflection Polarized Optical Microscope equipped with a Q-Imaging QICAM-Fast 12-bit camera with 1392x1040 resolution and textures analyzed using ImagePro 6.2 Software from Media Cybernetics.
2.2.2 Differential Scanning Calorimetry

Differential Scanning Calorimetry (DSC) is a crucial part of characterizing any new liquid crystal material, and is usually performed first to provide a guide for the other methods of characterization.

In DSC, a small amount of carefully-weighed material is heated and cooled several times along side a reference sample (usually the air in an empty, sealed sample holder). The experimental sample is kept at the same temperature as the reference sample; at phase transitions, this will require the machine to adjust the amount of heat being added or removed from the sample in comparison to the reference sample. The enthalpy of transition can be determined by the area under the resulting curve, and the shape of the curve can indicate the type of transition (e.g. glass transition or crystallization).[58]

For our pure bent-core blue phase mixtures, DSC was especially helpful in establishing the nature of the phase transition as chirality increased, which is particularly interesting in the case of the BPIII-Isotropic transition.[59] DSC of our blue phase samples was performed at the Tokyo Institute of Technology using a PerkinElmer Pyris Diamond DSC.

2.2.3 Optical Activity

Chiral substances are optically active: they will rotate plane polarized light as the light travels through the sample. Optical rotatory dispersion is the wavelength
dependence of the optical activity. Optical activity is the result of circular birefringence – when the left and right modes of circularly polarized light travel at different speeds, the result is an apparent rotation of plane polarized light.\(^{[60]}\) Bensimon, et al. provide a derivation for the optical activity of blue phases\(^{[61]}\) starting with the isotropic phase (Eq. 2.2) as:

\[
\phi = \frac{k_0^2}{2} \gamma
\]  

(2.2)

Where \(\phi\) is the angle of rotation, \(k_0\) is the optical wave number in a vacuum and \(\gamma\) is from the Laudau optical-activity tensor \(\gamma_{ijk} = \gamma e_{ijk}\), where \(e_{ijk}\) is the Levi-Civita antisymmetric third rank tensor. The result for the blue phase is more involved, even when written in the more practical form (Eq. 2.3) derived by Lacoste, Collings and Lubensky.\(^{[62]}\)

\[
\Phi = \frac{\omega^2 \kappa}{k_b T L} \frac{1}{48 \pi r^{3/2} \sqrt{\tau_1}} - \frac{\omega^4 \kappa}{15 \pi \sqrt{\tau_2} t}
\]  

(2.3)

Where \(\omega\) is the frequency of light, \(\kappa\) is the chirality (inverse pitch times correlation length), \(r = 1 + \rho/2\) where \(\rho\) is a ratio of Landau coefficients, \(\tau_1\) and \(\tau_2\) are the reduced temperatures of the first two modes of the small anisotropic local fluctuation of the electric permittivity tensor and \(t\) is reduced temperature \(t = \frac{T - T_{N*}}{T_{N} - T_{N*}}\) where \(T_{N*}\) is the limit of metastability of the isotropic phase.

While explaining the origins of the optical rotation in chiral liquid crystal phases
is a complex problem, measuring the rotation is a fairly straightforward experiment especially when the phase in question is stable over a wide temperature range. Polarized light travels through a sample, then through a rotating analyzer, while intensity is measured as a function of analyzer angle. The phase shift of that curve is also the angle of rotation of the plane polarized light. From equations 2.2 and 2.3 one important practical consideration is apparent: the optical rotatory power of a material is a function of wavelength (Figure 20).

**Figure 20:** Rotary optical dispersion is the wavelength-dependence of the optical rotatory power. Blue phases are far more optically active at shorter wavelengths therefore it is best to use as short a wavelength as your equipment will allow (blue, near-UV or UV) in OA experiments.

Once again the highly chiral nature of blue phases necessitates special consideration; since the blue phase twists light most dramatically at the lower end of the
visible spectrum,\textsuperscript{[63]} it becomes important to be able to take data at wavelengths near-UV or below. This leads to several practical problems:

1. The spectrum of most common light sources is extremely weak in the near-UV compared to the visible. Solutions include increasing the brightness of the lamp, longer spectrometer integration times, or finding a light source with a more appropriate spectrum, such as a xenon-based lamp.

2. Fused silica and plastic absorb UV, and the set-up clearly places layers of both glass and plastic between the light source and the sample. If necessary, quartz glass components can be used.

3. Tabletop mini-spectrometers, such as Ocean Optics models (such as the USB2000 or USB2000+), while extremely useful in this experimental set-up, can be subject to a dramatic decline in performance around the near-UV or near-IR. Care should be taken to ensure the proper model of spectrophotometer and fiber optic cables are being used.

For most optically active materials, a thicker sample is easier to work with than a thinner one because the optical rotation may be in the order of tens of degrees or less per millimeter (e.g, for sugars like sucrose or glucose\textsuperscript{[64]}). Blue phases rotate the polarization in the tens or hundreds of degrees per millimeter\textsuperscript{[63]}, so samples less than 100 microns are frequently sufficient to provide a (repeatable) measurable amount of rotation. In our case, 25 micron cells were thick enough to rotate the light but thin enough to not inadvertently rotate past the 360° mark.
Optical activity measurements were performed using an OceanOptics USB2000+ minispectrophotometer attached to a DT-Mini-2-GS light source. A rotating analyzer was controlled and light intensity recorded using a custom-designed LabVIEW computer program, and the resulting curve fitted using Easy Plot in order to find the minimum angle of intensity and hence the angle of rotation of the plane of polarized light.

2.2.4 Electro-optical Activity

Blue phases show decidedly different switching behavior than ordinary chiral nematics. A standard planar-aligned cholesteric cell will reflect a narrow band of wavelengths ($\Delta \lambda = P \Delta n$, where $P$ is the pitch and $\Delta n = n_e - n_o$, or birefringence) at 0V; at some threshold voltage $V_{th}$, the average alignment of the molecules is with the electric field, the helix disappears and cell no longer reflects the light. Furthermore, under some conditions the cell can be made to switch between an aligned planar or scattering focal conic state depending on the manner in which the voltage is applied and removed.\textsuperscript{[10]}

A standard cell with parallel top and bottom electrodes and the electric field perpendicular to the substrate allows us to observe an effect known as electrostriction in BPI and BPII phases. Electrostriction occurs when one edge of the cell lattice stretches in response to the applied electric field (where the applied field is less than the threshold necessary to change the phase), changing the reflected color (Figure 21).\textsuperscript{[65]} In BPIII, the effect of a field applied in this manner causes an increase in the intensity of the reflected light as well as a narrowing of the reflection bandwidth.\textsuperscript{[66]}
Figure 21: Simplified diagram of electrostriction in the BPI and BPII phases. The electric field stretches the lattice along one axis, thereby changing the wavelength of the reflected light.

All three phases will switch from a dark state to a bright state when a cell with interdigitated electrodes is used. In an In-Plane Switching (IPS) cell the electric-field-induced birefringence (Kerr effect) allows for a bright state with maximum brightness when the director is at 45° between the crossed polarizers (Figure 22). The Kerr effect and its importance to applications of blue phases are discussed in detail in Chapter 5.

Figure 22: F493 + CB15 (36wt%) mixture: in transmission (A), reflection (B), and reflection with voltage applied (C)
Switching is most interesting for application purposes – materials that can switch rapidly and at reasonably low voltages are desirable for display applications. For characterization purposes, switching is one way to determine if the material is at or near the transition temperature even if there is no visible texture. While not a definitive test for BP by any means, it can provide a hint that a BP may span a larger temperature range than a purely visual inspection would suggest.

Texture switching experiments were performed using an Olympus BX60 microscope equipped with a Melles-Griot photodetector and an Instec STC200D heat stage. The voltage was provided by a Hewlett-Packard 33120A Function Generator and amplified with an FLC F20AD 20x voltage amplifier. Photodetector signal was measured using a Hewlett-Packard 34401A Multimeter. Custom LabVIEW programs used for measuring intensity as a function of voltage, controlling the heat stage or taking pictures were written by Christopher Bailey and Péter Salamon.

2.2.5 Kossel Diagrams

The Kossel Diagram is an unusual addition to the liquid crystal characterization arsenal. Borrowed from crystallography, where it is used to study the structure of crystals, it is not normally a technique to be applied to fluids of reduced dimensionality. However, the structure of BPI and BPII can be most conclusively distinguished using this method, which can use a standard microscope equipped with a conoscope function to view Bragg reflected light on the back focal plane. The resulting pattern is a function of
the wavelength of light used and reveals the reciprocal lattice vectors of the sample \cite{67}.

The essentials of a clear Kossel diagram are a bright monochromatic light source and a large (on the order of 1 mm$^2$) monodomain crystal. The last requirement is the most difficult to obtain. One method is to cool the sample slowly until crystals form, then heating the sample very slightly until the smaller crystals melt back into isotropic. Cool again before the larger crystals melt completely, allowing them to grow larger, repeat as necessary. This is a technique that requires a precise heat stage and a good deal of experience and patience.

Kossel diagrams do not feature prominently in this work for a very simple reason: most of the samples examined – and all of the samples which had a stable, broad-temperature range blue phase – were of the BPIII variety. Kossel diagrams are excellent for showing the structure of a large monodomain crystal with good long-range order, which is precisely what a BPIII is not.

\subsection{2.2.6 X-Ray Scattering}

Small angle X-ray scattering (SAXS) measurements became necessary to see if the smectic clusters reported in the pure F493\textsuperscript{[68]} also exist in the chiral dopant – induced BPIII phase, as will be described in Chapter 3.

In SAXS a sample is bombarded with x-rays at an angle normal to the surface of the sample; diffraction is detected on a CCD camera as a function of angle $\theta$, resulting in a circular ring pattern for isotropic materials or optically isotropic materials lacking long-range order as in the BPIII phase. Analysis of the radius of the rings and their widths
provides information of the periodicity and correlation length of the layered clusters.

X-ray scattering experiments were performed at the Brookhaven National Laboratory in Upton, New York by Nick Diorio, Antal Jákli and Samuel Sprunt of Kent State University.
Chapter Three

Bent-Core Liquid Crystal Blue Phases

3.1 Introduction

Thus far, the literature of broad-temperature range blue phase materials focuses on two methods: polymer stabilization\[^3\] or nanoparticle stabilization\[^4\] of calamitic blue phase mixtures. Inspired by the success of using liquid crystal dimers to create blue phases with a very broad temperature range,\[^6\] one asks: how broad a temperature range can be achieved without filling the disclination lines?

Bent-core liquid crystals had already been shown to possess several properties that suggested they would have a promising answer to the above question. For example, doping a cholesteric material made from traditional calamitic liquid crystals induces blue phases,\[^69\] showing that their greater response to the effects of the chiral dopant can be transferred to the host molecules. Bent-core molecules made chiral through the attachment of a chiral molecule displayed blue phases spanning $20^\circ$C.\[^70\] Bent-core molecules are biaxial, and molecular biaxiality can have the effect of stabilizing the blue phase, thus increasing the temperature range.\[^30\]

The drawback to exploring bent-core molecules as a path to stable, broad-temperature range blue phases has traditionally been their high transition temperatures. The blue phases formed by the chiral bent-cores of Yelamaggad, et. al. appeared at temperatures exceeding $150^\circ$C,\[^70\] far too high to consider for practical use. Many other bent-core liquid crystals exhibit liquid crystalline phases at prohibitively high
temperatures. Moreover, bent-core liquid crystals with a nematic phase are relatively new\cite{28} and so while it would make intuitive sense that a bent-core nematic would be the simplest route to a bent-core blue phase, they have not been readily available until recently.

The family of bent-core nematic liquid crystals to which F493 belongs is particularly promising: the nematic phase spans 20°C (in the case of F493; it is even larger in F521) and can be found at the comparatively low temperature range of 50°-70°C.\cite{52} Additionally F493 is known to have a twist elastic constant (\(K_{22}\)) value a tenth that of typical calamitics,\cite{71} leading us to expect the bent-core nematic to react very strongly to the addition of chiral dopant. It was the hope that a broad nematic range would lead to a broad cholesteric range, possibly even a broad-range blue phase. And in fact doping F493 with small amounts of a high-HTP chiral dopant did result in broad temperature range BPIII. That the material prefers to form BPIII over the more commonly seen BPI or BPII is thanks largely to a feature peculiar to bent-core nematics, including F493, that we did not initially consider when selecting the material for these experiments.

### 3.2 The Phase Diagram

Mixtures of F493 and chiral dopant BDH-1281 were made using concentrations of 0, 1.4, 3.2, 5.4 and 7.2wt% chiral dopant (from here referred to as Control, Mixture 1.4, Mixture 3.2, Mixture 5.4 and Mixture 7.2, respectively). The mixtures in this chapter were made by placing small amounts of bent-core nematic and chiral dopant in crystal
form in a clean vial, then adding an excess of chloroform. The vial was then capped and mixed in an ultrasonic mixer for at least 10 minutes. The chloroform was then evaporated in a vacuum oven at 58°C until gone, then above the isotropic transition temperature of the material (95-100°C) for 10-20 minutes.

For comparison, similar mixtures were made using 6008, a calamitic liquid crystal chosen for its similarity to the arms of F493.

The difference in their response to the addition of chiral dopant can be seen even without a microscope. A 3.2wt% chiral dopant mixture in F493 cools from isotropic to a hazy sky blue shade with little visible change until crystallization turns it white. The 6008 mixtures, on the other hand, showed obvious cholesteric reflection in all of the colors rainbow (Figure 23). The difference between the two became more obvious when it was attempted to measure the reflection spectra with a tabletop minispectrometer – the cholesteric sample clearly showed that the set-up was functional, but it was never able to obtain a clear spectrum for the light-scattering blue phase sample.
**Figure 23:** A bent-core sample (A) rests on a heat stage and a calamitic sample (B) as it cools rapidly after being removed from the heat stage; the temperature gradient to displays the full range of reflection colors the sample is capable of.

The phase diagram of mixtures of bent-core nematic (BCN) F493 and chiral dopant BDH-1281 show several interesting features: we see no cholesteric phase below the blue phase, the phase diagram for mixtures above 1.4wt% chiral dopant is Iso-BPIII – SmX-Cr. The addition of chiral dopant decreases the temperature range of the blue phase, steadily and slightly at first, then more dramatically after about 5wt%. A sample containing 7.2wt% chiral dopant showed no visible blue phase textures, but did show electro-optical switching behavior consistent with the other samples, and BPIII, for a small range of temperatures.

When the chiral dopant concentration was increased to 7.9% all indications of a liquid crystal phase disappeared completely and the sample transitioned from the isotropic directly to crystal. This decrease of temperature range is completely a result of a decrease of the Iso-BP transition temperature, the crystallization temperature remains largely unaffected by changes in chiral dopant concentration (Figure 24).
3.3: Texture analysis and Differential Scanning Calorimetry

Due to the limited amount of liquid crystalline material, the samples were mixing in minute amounts, sometimes barely enough to fill a 25-micron thick cell (approximately 5-10 mg). In order to determine the phase behavior of mixtures with chiral dopant concentrations of less than 1.4wt%, concentration gradient cells were constructed using samples of pure F493 and F493 + BDH1281. The purpose of this was to determine a lower boundary of chiral dopant concentration required for a blue phase to appear, and to see if N* or platelet textures (BPI or BPII) would ever appear. A cell was filled with both samples simultaneously via capillary filling by placing powder samples next to each other on the ledge of the cell and then heating the materials to isotropic. As the cell filled, the materials commingled resulting in an area of steadily increasing chiral dopant concentration (Figure 25). POM temperature sweeps are performed as soon as a sufficiently wide gradient is established.

**Figure 24:** Phase diagram of F493 and small concentrations of chiral dopant BDH-1281.
Figure 25: A concentration gradient cell allows a cursory inspection of a binary mixture that is efficient in both time and materials.

Figure 26: 40 micron thick concentration gradient cell, between pure F493 (right) and a maximum of 4.9wt% BDH-1281 in F493 (left) at 70.0°C.

Two contact cells were required before a reasonable estimation could be made of when one could expect the cholesteric (N*) phase to appear: in only a narrow band of concentrations under 0.5wt% chiral dopant. It is as yet unknown if there is a
concentration of BDH-1281 that would show an Iso-BP-N*-Cr phase sequence (Figure 26) in F493, although results using other bent-core nematics show such a phase sequence is possible (see Chapter 4).

![Images of blue phase mixtures](image)

**Figure 27:** A comparison of typical textures of four blue phase mixtures at temperatures just below their respective Iso-BPIII transition temperatures: A) 1.4wt% BDH-1281 in F493 at 70.6°C B) 3.2wt% at 69.0°C C) 4.9wt% at 65.0°C and D) 7.2wt% at 58.8°C.

Lower concentrations (≤ 3.2wt% chiral dopant) displayed uniform bright blue textures (Figure 27). Under the right camera conditions, the onset of the colored texture matched the transition temperatures obtained using DSC, especially at the lower chiral dopant concentrations where the texture changes were most pronounced. Higher concentrations viewed under the same camera and lighting conditions showed a darker, more purple-blue or black texture where the transition could not be visually matched as
well to the DSC values, until the highest chirality mixtures (>5wt%) when DSC could no longer detect the transition.

Differential scanning calorimetry was used to confirm the transition temperatures, although the method would become less helpful as the concentration of chiral dopant increased. This is because as the chirality of the mixtures increased, the latent heat of the transition decreased until by Mixtures 3 & 4 the transition was nearly undetectable (Figure 28). This is consistent with the known behavior of the isotropic-BPIII transition: as chirality increases, the phase transition approaches a critical point.\textsuperscript{59,72}

\textbf{Figure 28:} DSC scans for three blue phase samples and pure F493 shows the decrease in latent heat as the chirality of the sample increases. ClPbis10BB (F493) shows a distinct peak at the isotropic-nematic transition. The peaks become less distinct (the latent heat of the transition decreases) as the chirality increases. Mixture 1 = 3.2wt% BDH-1281 in F493, Mixture 2 = 4.9wt% and Mixture 3 = 7.2wt%. 

![Iso-BP transition detail](image-url)
The blue textures were the same regardless if the cell had a planar alignment layer or no alignment layer, which eliminates the possibility of a cholesteric phase. In contrast, there was a marked difference in textures when mixtures of 6OO8 and BDH-1281 were in cells with planar alignment layers or without (Figure 29, Figure 30). Both the uniformity of the texture and its indifference to alignment layers indicated that the observed phase was BPIII.
<table>
<thead>
<tr>
<th>Concentration</th>
<th>Temperature</th>
<th>Alignment Condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.4% BDH in F493 (unaligned)</td>
<td>72.8°C</td>
<td></td>
</tr>
<tr>
<td>3.2% BDH in F493 (unaligned)</td>
<td>69.0°C</td>
<td></td>
</tr>
<tr>
<td>4.9% BDH in F492 (unaligned)</td>
<td>65.0°C</td>
<td></td>
</tr>
<tr>
<td>7.2% BDH in F493 (unaligned)</td>
<td>58.8°C</td>
<td></td>
</tr>
<tr>
<td>1.4% BDH in 6008 (unaligned)</td>
<td>75.0°C</td>
<td></td>
</tr>
<tr>
<td>3.2% BDH in 6008 (unaligned)</td>
<td>69.5°C</td>
<td></td>
</tr>
<tr>
<td>4.8% BDH in 6008 (unaligned)</td>
<td>69.2°C</td>
<td></td>
</tr>
<tr>
<td>7.2% BDH in 6008 (unaligned)</td>
<td>63.5°C</td>
<td></td>
</tr>
<tr>
<td>1.4% BDH in 6008 (planar)</td>
<td>74.2°C</td>
<td></td>
</tr>
<tr>
<td>3.2% BDH in 6008 (planar)</td>
<td>69.4°C</td>
<td></td>
</tr>
<tr>
<td>4.8% BDH in 6008 (planar)</td>
<td>70.4°C</td>
<td></td>
</tr>
<tr>
<td>7.2% BDH in 6008 (planar)</td>
<td>59.4°C</td>
<td></td>
</tr>
</tbody>
</table>

**Figure 29:** A selection of pictures showing the different textures of different concentrations and alignment conditions for bent-core and calamitic nematic liquid crystals doped with BDH-1281. The phrase “unaligned” refers to the lack of alignment layer in the cell, “planar” refers to the polyimide alignment layer.
**Figure 30:** A more detailed look at the effects of similar chiral dopant concentration on the textures and temperature ranges of calamtic and bent-core liquid crystals. In column 1, the cell had no alignment layer; in column 2, “unaligned” refers to the lack of alignment layer in the cell. Column 3, “planar” refers to the polyimde alignment layer.
One unusual feature that appeared primarily in the lower-concentration mixtures, and particularly in Mixture 1.4, was the appearance of white streaks at temperatures near the crystallization temperature. These streaks usually originated from sample edges or spacers and slowly branched out into the sample. Earlier mixtures involving BDH-1281, especially those involving the flexible dimers described by Coles and Pivnenko,[6] suffered from phase separation in the form of streaks of cholesteric winding their way, river-like, through an optically isotropic sample.

Figure 31: Examples of streaking in Mixture 1.4 at 65.8°C (A) and 58.0°C (B), Mixture 3.2 at 60°C (C) upon cooling and the "cholesteric rivers" that appear in a sample of liquid crystal dimers and BDH-1281 after standing for several hours at room temperature (D).
The streaks in the F493–BDH1281 samples are similar to those cholesteric rivers in shape and growth pattern, but lack the distinctive coloration (Figure 31) and only appear as the sample approaches the BP-Smectic or BP-Crystal transition. In the mixtures with higher concentrations of chiral dopant (Mixture 3.2 and above) the streaks can be avoided through careful cooling of the sample, and are more likely to appear if the sample is cooled too quickly.

The streaking may be a result of phase separation, areas with slightly less chiral dopant that are attempting to transition to a chiral nematic phase as the rest of the sample transitions to smectic.

3.4 Electro-optical Switching and Optical Activity

Mixture 2 (3.2wt% BDH-1281) was selected for particular scrutiny by optical and electro-optical experiments. The reason for this was that Mixture 2 seemed to be the optimal mixture: the temperature range was still broad, but it displayed less of a tendency for streaking at the lower end of that range, and was far less prone to image sticking (an image of the electrodes that remains after the electric field is removed).

Optical activity and optical rotatory dispersion (ORD) measurements were performed at the Tokyo Institute of Technology using Chino DB1000 temperature controller, a Wavetek 75 arbitrary waveform generator and an NF Electronic Instruments 4010 amplifier, then later repeated at Kent State University using the equipment described in Chapter 2. The results of both experiments were similar to published results
for BPIII using traditional liquid crystals,[63] but over a larger temperature range (Figure 32a) and with significantly more optical rotation (Figure 32b).

![Figure 32: Mixture 3.2 A) Optical rotation with respect to temperature at 532 nm. B) Optical rotatory dispersion at 3°C below the Iso-BPIII transition.](image)

Optical rotation in isotropic fluids like corn syrup is generally on the order of a few degrees per millimeter and in fact in some materials is so weak the preferred measurement is degrees per decimeter.[64] Published values for traditional blue phases are on the order of 30-70 degrees per millimeter.[63] Our bent-core blue phases show hundreds of degrees per millimeter. Also unlike blue phases made from more traditional liquid crystals, the optical rotatory dispersion spans the entire visible range. The sheer breadth of these results was unexpected – the spectrometer used was purchased with these experiments in mind, but the focus was on providing extra sensitivity to the lower end of the visible and near-UV spectrum. It was not expected that the near-IR capabilities of the spectrometer would ever be necessary for the study of bent-core blue
phases.

The optical rotatory dispersion curve red-shifts as the pitch of the chiral material increases. The pitch is also related to the lattice size, with the dimensions of the unit cell being approximately equal to p. So we know just from the bright blue color of some of our mixtures that the pitch of some of our materials is on the order of the wavelength of blue visible light, compared to 300nm or less than traditional calamitic blue phases.  

Electro-optical switching experiments were performed with two major goals in mind: first, to see if the response of the material to electric fields was consistent with that of known BPIII materials, and second, to compare the switching behavior to that of blue phase materials that are nearly ready for use commercially, specifically the Samsung Blue Phase Liquid Crystal Display (BPLCD) which debuted at the Society for Information Display annual conference in 2008.

Initial experiments involved in-plane switching using cells with interdigitated electrodes 10 microns wide, spaced 10 microns apart, which were made by Nicholas Diorio in the Liquid Crystal Institute Cleanroom. Cells were placed between crossed polarizers with the electrodes at a 45° angle to both the polarizer and analyzer. Most pictures were taken at the edge of the electrode area, so that one can easily compare the section experiencing an applied field to a control area that does not experience the fields. Unswitched strips within the electrode area are due to missing electrodes – strips of ITO that did not make it through the lithography process intact.

All samples responded to an applied field in an IPS cell by switching to a bright
state, which notably tended to be green at higher concentrations of chiral dopant and more yellow as chirality decreased (Figure 33). Mixture 1 would only respond to the field once, at which point it was “stuck” with an image of the bright state which no combination of voltages or frequencies of applied field could erase (Figure 34). The only way to return it to the dark state was to heat to isotropic and re-cool the sample. Mixture 2 only stuck at low temperatures, and all subsequent mixtures also showed less and less inclination towards sticking.

Figure 33: Switching in an IPS cell in Mixture 1.4 (A) and Mixture 4.9 (B) under an 57V_{rms} AC field.
Figure 34: Mixture 1.4 under high field (A) and with the field removed (B) at 71.5 °C.

The response of Mixture 2 to electric fields was typical of all the mixtures, especially in terms of the high voltages required to achieve a bright state. Even at near-isotropic temperatures, 5 volts per micron were required to achieve maximum brightness (Figure 35). These voltages are comparable to many other examples in the published literature on electro-optical responses of blue phases, both for polymer-stabilized blue phases and those made using large, unusually-shaped liquid crystals.[38, 73, 74]
Figure 35: Mixture 2 at 66.0°C. Clockwise from upper left: (A) 0V, (B) 11V, (C) 32V, (D) 43V.

Switching speed of the cell was heavily temperature-dependent and at its best is more comparable to current LCD standards than the high switching speeds claimed by Samsung\cite{7} and others.\cite{3, 73} At 68 °C, Mixture 2 showed a \( \tau_{on} \) of about 6 - 7 ms when a 15 V/\( \mu \)m pulse is applied. As expected, this increases as temperature decreases. By 60 °C, a 20 ms pulse does not provide sufficient time for the cell to reach maximum brightness (Figure 36).
Figure 36: Response of blue phase to voltage at isotropic and two different temperatures in the BPIII range.

3.5 X-Ray Scattering and Smectic Clusters

As stated before, F493 is an already well-characterized bent-core nematic liquid crystal. It has been suggested, based on dynamic light scattering,\textsuperscript{75} C\textsuperscript{13}-NMR \textsuperscript{76}, and X-ray scattering experiments\textsuperscript{77} that the nematic and even the isotropic phases of bent-core liquid crystals contain smectic clusters. These small clusters are found in the whole nematic range and up to 20°C above T\textsubscript{NI}.\textsuperscript{68, 78, 79}
Figure 37: X-Ray scattering shows that small smectic clusters (broad peaks) appear at temperatures as high as 89°C. The broad peak and low intensity of the signal, as compared to the sharp, intense peak formed by the smectic phase (aqua peak, right axis) shows that the smectic clusters are small, only a few layers thick.

X-ray scattering studies performed at Brookhaven National Laboratory in Upton, New York show the presence of smectic clusters in a 1.9wt% BDH-1281 in F493 sample, similar to results in pure F493 or certain mixtures of F493 and 6OO8. The clusters appear well above the T_{BP-I} transition temperature and persist until a smectic phase appears at 54°C (Figure 37).

These clusters would explain why a broad-temperature range BPIII is favored so completely, while BPI and BPII do not seem to appear at all. Long-range
Lattice structures would be inhibited by the presence of these clusters, which would form walls preventing the lattices from correlating orientationally over long ranges (Figure 38). Smectic blue phases, or blue phase where the core of the double-twist cylinder is a smectic section surrounded by a twist-grain-boundary-like sheath, are known to exist\cite{81,82}, but nano-sized smectic clusters would not easily form 3D twisted structures and more likely they serve to randomize and disrupt the formation of ordered crystalline monodomains.

**Figure 38:** A simplified drawing of how an amorphous lattice interspersed with smectic clusters might appear. The smectic clusters inhibit long-range lattice order, preventing the appearance of BPI or BPII.
Chapter 4

Chiral Mixtures of Bent-Core and Rod-Shaped Liquid Crystals

4.1 Introduction

Using mixtures of bent-core or of bent-core and calamitic liquid crystals served two purposes: first, to explore the possibility of using combinations of liquid crystals to lower the isotropic-blue phase transition temperature without decreasing the total temperature range of the blue phase, and second to compare the results of using bent-core liquid crystals under different circumstances thereby increasing our understanding of exactly how they serve to create stable broad-temperature blue phases.

Three broad categories of mixtures were experimented with: bent-core liquid crystals with achiral calamitcs and small amounts (less than 10% total weight) chiral dopant, mixtures of different bent-core liquid crystals with small amounts of chiral dopant, and mixtures of bent-cores and chiral and achiral calamtics, where the chiral calamtic liquid crystals make up a substantial (greater than 15wt%) fraction of the total mixture.

It is known that adding small amounts of bent-core liquid crystals to a chiral calamtic material can induce blue phases where none were apparent before. Achiral Banana shaped molecules are known to form chiral smectic phases and the intrinsic chirality of bent-core liquid crystals can be used to decrease the pitch of a chiral nematic liquid crystal material. So while mixtures of bent-core and chiral nematic materials are not unheard of, this work is the first opportunity that we are aware of where a bent-
core stabilized calamitic blue phase can be compared to blue phases comprised of that same bent-core without the rod-shaped liquid crystals.

There is at least one mixture of bent-core liquid crystals that results in a material with a near-room temperature nematic phase. Chiral dopant was added to this mixture in order to determine if such a mixture could create a room-temperature blue phase without sacrificing the total temperature range of the phase.

Finally, a short period of time was dedicated to using the chiral dopant itself as a calamtic additive, with mixed results. Certainly adding a significant amount of liquid crystalline material that is fluid at room temperatures decreased the transition temperatures. However, the results were not consistently better than those obtained with other mixtures, and when they were it seemed to come at the cost of reducing the blue phase temperature range.

4.2 Experimental Results

The family of bent-core liquid crystals to which F493 belongs offers a unique opportunity to explore the advantages and disadvantages of using bent-core liquid crystals as a chirality enhancer. Few bent-core molecules come with a companion calamitic molecule like 6008: essentially one arm of the bent-core molecules, 6008 was designed for miscibility and mixtures with F493 are already well-studied\cite{52} (Figure 39).
Figure 39: Phase diagram for mixtures of F493 and 6008, taken from reference [52].

In this study five mixtures are compared consisting of a base mixture of 6.6% BDH-1281 in 6008 and adding successively more bent-core (Table 1):

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>F493 (wt%)</td>
<td>0</td>
<td>5</td>
<td>10</td>
<td>20</td>
<td>40</td>
</tr>
</tbody>
</table>

Table 1: Concentration of bent-core nematic added to a chiral calamitic mixture.

The samples were then analyzed using polarizing optical microscopy and optical spectroscopy. As expected, adding bent-core molecules to the chiral nematic mixture induced blue phases.
4.2.1 Sample A: The Control

We know from previous experiments (see Chapter 3, Figure 2) that concentrations greater than 5% BDH-1281 in 6008 should result in a blue phase, either BPI or BPII (platelet-textured). A planar-aligned cell was filled with sample A. On cooling, it showed a subtle texture change without much color (in transmission) starting at 75.1 °C with a transition to cholesteric phase at 65.5 +/-0.1 °C (Figure 40). While difficult to see in transmission and not visible in reflection, the phase change is clearly visible to a spectrometer (Figure 41). Spectrometer measurements also suggest the reason why platelets are not easily visible using transmission or reflection – the lattice size of the blue phase is hovering at or beneath the edge of the visible spectrum. The blue phase appears to span from approximately 75 °C to 66.5 °C – a range of 8 or 9 degrees.
**Figure 40**: Textures of sample A.  
A) Isotropic (90.0°C)  
B) BP (71.9°C)  
Note that between picture A and B no adjustments were made to either the light or the camera settings.  
C) Transition to N* begins (66.5°C)  
D) Transition continues (64.5°C) Between pictures C and D the exposure time of the pictures was reduced by half.  
E) 42.0°C  
F) Crystal (33.6°C)
Figure 41: Transmission spectra for Sample A for several temperatures. The bold lines (green, aqua and grey) show temperatures where the BP reflection peaks occur.

4.2.2 Sample B

Adding 5wt% F493 extends the blue phase and creates larger, more visible platelets (Figure 42). POM and spectrometer measurements show a depressed Iso-BP transition temperature (67.0 +/- 1 °C now instead of 75 °C) but a doubled BP temperature range (17 °C instead of 8.6 °C) (Figure 43). POM shows that aside from the changes in the transition temperatures, the behavior of the materials is largely the same as Sample A until the lower temperatures, where a smectic phase appears rather than the crystal phase.
**Figure 42:** Sample B textures. A) Isotropic (69.5°C) B) Platelets are visible in this blue phase (63.0°C) C) Transition begins (50.0°C) D) N* (41.0°C) E) N* (32.0°C) F) Smectic C (27.2°C)
Figure 43: Sample B transmission spectra. Temperatures within the blue phase region are in bold.

4.2.3 Sample C

Sample C, at 10wt% bent-core, begins to behave more like a pure bent-core chiral sample, principally by losing any sign of a chiral nematic phase. A broad (spanning ~34°C) blue phase transitions directly to SmC, with no indication of a chiral nematic phase. At this point, the blue phase textures become difficult to see under the microscope (Figure 44), although the spectrometer still detects a clear peak at near-UV wavelengths (Figure 45).
Figure 44: Sample C textures. A) Isotropic (80.0°C) B) BP (45.0°C) C) transition to smectic (38.0°C) D) transition to smectic (37.5°C) E) Smectic A* (35.8°C) F) smectic (32.8°C)
Figure 45: Transmission spectra for sample C (no polarizers) shows peaks corresponding to the blue phase from between 71°C and approximately 38-40°C.

4.2.4 Sample D

Sample D contains 20% bent-core molecule, approximately 5% chiral dopant and 75% 6O8. The temperature range of the blue phase contracts from that of Sample C, with two possible reasons: first, the chiral dopant is becoming more dilute (reduced from 6.64wt%) or second, we are past the point where the bent-core additive merely stabilize the mixture and now the bent-core/chiral dopant interaction begins to dominate. The lack of a cholesteric phase suggests the latter reason. We can suspect BPI or BPII for at least some of blue phase temperature range because of one lonely platelet that appears at the lower end of the temperature range (Figure 46d). At 43.5°C, SmA* begins to appear in the form of batonettes, and SmC* appears around 25°C (Figure 46, Figure 47).
Figure 46: Sample D textures: A) isotropic (70.0°C) B) Undetermined blue phase (65.7°C) C) Platelet appears (61.8°C) D) Blue phase (44.6°C) E) Smectic transition begins (43.5°C) F) Smectic C (32.4°C) G) Smectic A* (25.4°C) H) Transition (24.8°C)
Figure 47: Transmission spectra for Sample D, no polarizers. The blue phase peaks extend to the visible wavelengths.

4.2.5 Sample E

Sample E shows a blue phase spanning from 71.3° to 53.0°C – spanning approximately 18°C, it is comparable in range to a blue phase made of pure bent-core materials using a similar amount of chiral dopant (sample E is approximately 4wt% BDH-1281; its temperature range and transition temperatures are similar to the 1.4-3.2wt% BDH-1281 in F493 mixtures). The blue phase, although its texture was not readily visible to the eye (Figure 49), was easily picked up by the spectrometer; the sharply defined peak suggests the phase is still BPI or BPII (Figure 48).
Figure 48: Transmission spectra for Sample E, no polarizers. The sample is similar to sample D in its reflected wavelengths, but spans a shorter temperature range.
Figure 49: A) BP (70.0°C) B) BP as it edges into the visible spectrum (69.1°C) C) Transition to Sm begins (52.9°C) D) Smectic A* (52.4°C) E) at 40.0°C F) at 26.5°C

4.2.6 Conclusions

It is clear from these results that adding bent-core molecules to a chiral nematic
material can induce or expand blue phases, and that the span of the blue phase temperature range results from a balance between concentration of chiral dopant and bent-core molecules. A rough phase diagram for these materials is shown (Figure 50).

**Figure 50:** Rough draft of phase diagram for a 6.64wt% BDH-1281 in 6O08 mixture doped with F493: the large blue phase area may in some cases be two separate (BPI and BPII) phases, while at some concentration between 5 and 10wt% F493, the smectic phases (SmA* at higher temperatures and SmC* at lower) overtake the chiral nematic and crystal phases, which is consistent with the results using non-chiral mixtures from Figure 39.

That the temperature range of the blue phases of a material can be as much as doubled using as little as 5% bent-core leads to interesting implications for using bent-cores as an additive and stabilizer for more traditional blue-phase materials, a result that
has immediate research applications and potential for practical applications. Unexpectedly, a bent-core stabilized blue phase can have a greater temperature range than a pure bent-core blue phase – in this case, the optimal concentration of bent-core molecules is approximately 10%.

In comparison with the bent-core blue phase material presented in Chapter 3, it is interesting to note that the platelet texture does appear when calamitics are the main component in the mixture. The smectic clusters present in F493’s nematic phase disappear when mixed with 6008, provided that the concentration of 6008 is at or greater than 50%,[80] as is the case with all of our mixtures. The absence of smectic clusters would allow for the formation of BPI or BPII, and indeed we see platelet textures in these mixtures, with no sample featuring a stable BPIII that overwhelms any other chiral phase as in the pure bent-core blue phase mixtures. It is then possible to use bent-core nematic liquid crystals to achieve a broad-temperature range material in blue phases, both with and without a long-range lattice structure.

4.3 Chiral mixtures of bent-core liquid crystals

While F493 mixed with nothing but small amounts of chiral dopant does create a stable, broad-temperature range blue phase, the original goal was to achieve a stable, broad-temperature range blue phase that included room temperatures. Mixtures of F493 showed that the addition of chiral dopant had a large effect on the isotropic transition temperature but the crystallization temperature remained constant. The most obvious
solution to this problem is to find a bent-core nematic that has a broad nematic temperature range down to below room temperatures and hope to replicate the success of F493, where a 22° C nematic phase range can be turned into an 18° C BPIII range.

No single bent-core nematic material is known form a stable nematic phase at room temperature. Many bent-core materials exhibit liquid crystalline phases at temperatures near or over 100° C. The F493 family of liquid crystals show liquid crystalline phases in the relatively convenient range of 30° – 100° C, although the nematic phase may only be some portion of that. A 1.05:1:1.1 mixture of three bent-core liquid crystals, F533:F493:F521 has a broad nematic phase that approaches room temperature. The phases and transition temperatures of this mixture are as follows: Iso – 87.7° C – N – 25.0° C – Cr. A sample of this material was mixed with BDH-1281 (2.03wt%) in chloroform and dried in a vacuum oven according to the procedure previously described.

The mixture shows a BPIII-like texture for approximately 10° C range between approximately 73° -75° C and 64° C, followed by an cholesteric phase that extends to below 30° C (Figure 4.51, Figure 52). The extremely limited amount of sample prevented the compilation of a complete phase diagram. Decreasing the amount of chiral dopant would perhaps have gained the BPIII a few more degrees near the isotropic transition temperature, but that would not be helpful in this case. It is possible that increasing the amount of chiral dopant would extend the BPIII range at the BP-N* transition; typical phase diagrams for highly chiral calamitic liquid crystals show that increasing chirality increases the BPIII temperature range, although usually by decreasing
the BPIII-BPI transition temperature \cite{85}. It is entirely possible that the BPIII-N* transition could behave in a similar manner, however in all likelihood this would be offset by a decrease in the iso-BPIII transition as in the phase diagram of pure F493 and BDH-1281.

**Figure 4.51**: A) Iso B) BPIII (67.0°C) C) Transition to N* begins (64.5°C) D) N* (59.5°C)
**Figure 52:** Transmission spectra of the chiral three bent-core mixture. The blue phase scatters light strongly at the near-UV end of the visible spectrum, while the cholesteric shows a broad peak.

In contrast to the results found using F493, the three-component mixture drives home the point that the width of the nematic temperature range may not be a very good indication of whether or not the resulting blue phase will have a wide temperature range.

### 4.4 Other Mixtures

#### 4.4.1 Introduction

In the search for a stable, broad-temperature range, room temperature blue phase many different types of mixtures were considered, most of which were completely unsuccessful. Partially successful mixtures – i.e. mixtures resulting in blue phases at too
high temperatures or with far too narrow a range – were also found. Time did not permit a return to these mixtures, but combined with what we now know about polymer and nanoparticle stabilization (Chapter 5), they may some day warrant closer inspection. What follows are the preliminary results of several different types of blue phase mixtures, including different types of bent-core molecules, calamtics, and different chiral dopants.

4.4.2 F521 and BDH-1281

4,6-dichloro-1,3-phenylene-bis[4’-(9-decen-1-yloxy)-1,1’-biphyenyl]4-carboxylate (F521) is a bent-core nematic material similar in composition to F493, differing in that it has two chlorine substitutions in the central benzene ring rather than one, along with biphenyl groups in the legs which make them a more rigid compared to F493. \(^{[52]}\) Initial mixtures of BDH-1281 and a bent-core were comprised of this material which was chosen over F493 for its larger nematic temperature range.\(^{[86]}\) As was already mentioned, a larger nematic range is no guarantee of large blue phase, and the material was ultimately put aside as a potential material for broad, room-temperature range blue phases for its narrow blue phase ranges combined with high transition temperatures, especially the >100 °C BP-N*.

The most striking difference between F521 and its cousin F493 is that F521 forms a cholesteric phase even at relatively high concentrations of chiral dopant (Figure 53, Figure 54). The \(K_{22}\) value of F521 is larger than that of its cousin F493, which would account for why the chiral dopant has less of an effect on F521.
Figure 53: A) BP-N* transition at 102°C  B) 5wt% BDH-1281 in F521 at C, with oily streaks visible in the upper portion of the picture which have been removed from the lower portion (electrode area) by an applied and removed electric field, which serves to align the cholesteric liquid crystal in a planar configuration.

Figure 54: A more detailed look at cholesteric oily streaks in a 5.9wt% BDH-1281 in F521 sample.
It seems clear that these differences affect the intrinsic chirality of the bent-core molecules which has a dramatic effect on their response to the chiral dopant. The exact effects different substituents have on the intrinsic chirality of the molecules, and how this in turn affects the properties of chiral mixtures made with these molecules, should be the subject of further studies.

4.4.3 Mixtures involving CB15 and 6O08

CB15 is a commonly used chiral dopant whose most important feature is that it is fluid at room temperature. It was hoped that by adding CB15 to a mixture, the phase temperature ranges could be lowered. Using a chiral dopant as a calamitic additive would hopefully reduce the transition temperatures without making it necessary to substantially increase the amount of BDH-1281. This turned out to be partially successful: the transition temperatures were lowered, and in fact resulted in some of the lowest-temperature blue phases in the entire project. The platelet textures formed by some of these mixtures are strikingly beautiful and came in all the colors of the rainbow. However greatest success in terms of lowering the crystallization temperature came at the cost of the temperature range.

A mixture containing 36wt% CB15, 44.5wt% 6O08 and 1.4wt% BDH-1281 in F493 formed platelet textures indicating BPI or BPII from approximately 56°C to 38.5°C – a range of about 17.5°C. The platelets went from green at higher
temperatures to red at lower temperatures, and then transitioned directly to the crystal phase (Figure 55).

![Image of platelet texture](image)

**Figure 55:** A) Platelet texture at 53.8°C B) BP-Cr transition at 38.5°C

A mixture of 25.7wt% CB15, 13.6wt% 6O08 and 60.7wt% F493 resulted in typical blue phase textures at temperatures as low as 34.0°C, however total temperature range seemed very small, less than 5°C (Figure 56).

![Image of blue phase platelets](image)

**Figure 56:** A) Blue phase platelets at 34.2°C and B) the BP-Crystal transition at 33.6°C.
4.5 Conclusions

Mixtures of different bent-core or bent-core and rod-shaped liquid crystal offer infinite possibilities for blue phase materials. The smectic clusters which prevented the formation of BPI and BPII in pure bent-core mixtures can be eliminated by adding calamitic liquid crystals with no detriment to the temperature range of the resulting blue phase. Similarly, mixtures of different bent-core liquid crystals can be devised in an effort to modify the temperature range of the phase.
Chapter 5

Blue Phases Stabilized by Nanoparticles and Polymer Networks

5.1: Introduction

Blue phases are defect-mediated phases, meaning that the defects play an integral role in stabilizing the phase. Another common example of defect-mediated phases include the twist-grain boundary phase (TGB). In each case, the defects serve as break points that relieve the system of the stress caused by the conflicting forces governing the phase behavior. The TGBA* phase, for example, appears between the cholesteric and smectic A* phases. Constant layer spacing requirement of the smectic phase is in direct conflict with the twisting of the helical axis which is perpendicular to the director – there is no way to twist the director within the plane of the layers while keeping a constant layer spacing. Screw dislocations appear at intervals to relieve this tension.[9, 87] Like blue phases, TGBA* phases often occur in narrow temperature ranges.

Defects occur when the sample is frustrated in some manner, be it from the conflicting demands in transitioning from one phase to another, as in the case of defect-mediated phases, or if the boundaries of a sample require conditions that are incongruent with the behavior of the bulk, such as the Grandjean steps in a cholesteric wedge cell.[88] When possible, a system will attempt to minimize the presence of defects: in the nematic phase line defects of equal but opposite charge will annihilate each other in order to decrease the system’s total free energy,[89] in cholesterics, oily streaks will prefer to form
networks with no free ends which will slowly coarsen over time.\textsuperscript{[90]} For blue phases, the presence of the defect is necessary in order for the lattice structure to exist, and for a narrow range of temperatures the energy cost of the defects is low enough to stabilize the entire phase.\textsuperscript{[9]} The free energy per unit length of a blue phase disclination line can be described as (Eq. 5.1)

$$F_{\text{discl}} = F_{\text{el}} + F_{\text{surf}} + F_{\text{core}} + F_{\text{int}}$$

Where $F_{\text{discl}}$ is the total free energy per unit length of the disclination, comprised of the elastic energy associated with the defect ($F_{\text{el}}$), the elastic energy at the disclination surface ($F_{\text{surf}}$), the energy of the core ($F_{\text{core}}$) and the energy associated with melting of the order area to the isotropic core ($F_{\text{int}}$).\textsuperscript{[30]} Mieboom, et. al.’s free energy calculations for blue phase double-twist cylinder lattices\textsuperscript{[17]} have $F_{\text{core}}$ as the only explicitly temperature-dependent term (Eq. 5.2):

$$F_{\text{core}} = \alpha(T_{\text{iso}} - T)\pi R_0^2$$

Where $T_{\text{iso}}$ is the isotropic transition temperature, $R_0$ is the cutoff radius size ($\approx$ molecular length), and $\alpha(T_{\text{iso}} - T)$ (enthalpy) represents the difference in free energies of the isotropic and ordered phases at temperature $T$.

$F_{\text{surf}}$ is normally dropped in elastic free energy calculations because it can be transformed into a surface integral and neglected because surface terms do not scale competitively with the bulk terms and are thus negligible – in this case, however, the
interior surface of the disclination must be taken into consideration and the solution becomes the energy per unit length of the disclination line\textsuperscript{[17]} (Eq. 5.3):

$$F_{\text{surf}} = -\pi(K_{22} + K_{24}) = -\pi K$$  \hspace{1cm} (5.3)

$F_{\text{surf}}$ can cause the total free energy, $F_{\text{discl}}$, to be less than zero provided that $F_{\text{core}}$ does not overwhelm it. This condition is satisfied most easily at temperatures near the isotropic clearing temperature, where defects tend to cost less in terms of free energy.\textsuperscript{[17]}

In order to increase the temperature range of the blue phase, one must reduce the energy cost of the disclination lines. Isotropic particles, like nanoparticles or monomers, are assumed to migrate to isotropic areas of a liquid crystalline sample when the opportunity is available because there they will serve to decrease the core energy. Adding nanoparticles or monomers to an isotropic sample and cooling to the blue phase will result in the isotropic particles concentrating in the defect lines, where they will serve to disrupt any tendency towards orientational order within the core as temperatures decrease thereby relieving the thermal energy term from being solely responsible for stabilizing the blue phase.\textsuperscript{[3]} The greater the reduction of $F_{\text{core}}$, the greater the stability of the blue phases over larger temperature ranges.

In this chapter we explore expanding the temperature range of bent-core blue phases utilizing both nanoparticle and polymer stabilization. Nanoparticle stabilization is particularly interesting because of the potential for nanoparticle additives to not only provide extra stabilization but also to improve some of the qualities, like threshold
voltage, that have yet to be optimized not only in our bent-core blue phases, but most broad-temperature range blue phases reported to date.\textsuperscript{[38, 73]}

5.2: Cadmium Sulfide Nanoparticles

Our initial attempts at nanoparticle stabilization utilized cadmium sulfide nanoparticles. Cadmium sulfide nanoparticles were chosen in the hopes that their semiconducting properties could help improve the electrooptical properties of the samples and also because of a concurrent series of experiments that had us optimistic that we would be able to synthesize our own CdS nanoparticles efficiently and conveniently using a method developed with Bota et al using lyotropic materials to influence the shape and size of nanoparticles as they are grown.\textsuperscript{[91]}

Cadmium sulfide nanoparticles can be formed using lyotropic phases of surfactants or phospholipids as nanoreaction chambers. In this method, the size and shape of the water-rich areas of a lyotropic material influences the final size and shape of the nanoparticle (Figure 57). Similar methods have been reported to synthesize BiOCl nanoparticles\textsuperscript{[92]} and silver.\textsuperscript{[93]}

The advantages of this method include cost, simplicity and safety. While phospholipids can be as expensive as liquid crystals (up to $200/gram when purchased in small amounts) the remaining materials are far more cost effective and readily available from suppliers such as Sigma Aldrich. The reaction itself requires few steps and is quickly accomplished. The most hazardous consumable is the cadmium nitrate
tetrahydrate; special care should be taken to avoid direct contact or any kind of ingestion of cadmium-based materials.

![Diagram of lyotropic nanoreactor](image)

**Figure 57**: Simplified diagram of how a lyotropic nanoreactor can influence the shape and size of nanoparticles. As the nanoparticles form in the fluid areas of the sample, the phospholipid or surfactant walls guide their shape.

A 10mmol solution of cadmium nitrate tetrahydrate (Cd(NO₃)₂ · 4H₂O) in deionized water is added to a lyotropic substance; the amount of which is determined by the desired phase. Initial experiments used phospholipids 1,2-Dipalmitoyl-sn-Glycero-3-Phosphocholine (DPPC) and 1,2-Dilauroyl-sn-Glycero-3-Phosphocholine (DLPC) (Avanti Polar Lipids, Alabaster, AL) in the inverted hexagonal phase as the lyotropic nanoreactors. Later, lamellar phases of the commercial surfactant Synperonic A7 (Conservation Resources International, LLC, Springfield, VA) were substituted. Synperonic A7 had the advantage of being significantly less costly and was used as a
potential method for increasing the amount of nanoparticles that could be made at one time.

Once the material in the proper phase has been prepared, a 120% molar excess of ammonium sulfide (NH$_4$)$_2$S is added drop-wise and mixed in thoroughly. The entire reaction is complete within minutes and the mixing can be stopped as soon as the sample turns a uniform shade of yellow (Figure 58). The size of the nanoparticles is roughly correlated to the final yellow color of the sample. The resulting nanoparticles were examined using transmission electron microscopy (TEM) and spectroscopy.

![Figure 58](image)

**Figure 58:** A series of nanoparticles synthesized in Symperonic A7 under different conditions. The bright yellows (left) indicate a smaller nanoparticle than the deep golds (right).

Transmission electron microscopy was the preferred method for examining a sample as it allowed us to directly measure the size and anisotropy of the particles; however a TEM was not always instantly available. Absorbance curves allowed for a
more convenient estimation of nanoparticle size. As described by Lippens and Lannoo,\textsuperscript{[94]} the absorbance curves of light through a solution of CdS particles can be used to determine the bandgap energy of the particles, which is related to their size\textsuperscript{[95]} (Figure 59).

**Figure 59:** A) Absorbance spectra for nanoparticles synthesized in DPPC at two different temperatures show a shift in the leading edge of the spectra indicating a difference in diameters. B) The relation between band-gap energy and nanoparticle diameter from reference [94].

Nanoparticles made using this method ranged from \(\approx10\text{nm}\) to over \(100\text{nm}\) in size, from spherical or rod-shaped with up to 10:1 aspect ratios. Phospholipid lyotropic nanoreactors generally made the best anisotropic particles, while Synperonic A7 nanoreactors combined with high shear rates (up to \(2000\text{s}^{-1}\)) could create relatively monodisperse spherical nanoparticles. In either case it was found to be better to add the ammonium sulfate drop-wise in relatively low concentration of solution, than to add one
small, highly concentrated drop, otherwise the results would not be uniform. Nanoparticle shape and size was a function of the size and shape of the lyotropic nanoreactors as determined by choice of lyotropic material, concentration, and temperature and shear rate (Figure 60). Surfactant-based nanoparticles tended to be large (tens or hundreds of nanometers) while phospholipid-based nanoparticles were smaller (less than 10 nanometers).

Figure 60 A) Spherical CdS nanoparticles synthesized in Synperonic A7 at a high rate of shear (2000s$^{-1}$). B) Anisotropic CdS nanoparticles made under the same conditions as (A) except the shear rate was reduced (1600s$^{-1}$).

Synthesizing and characterizing the nanoparticles was a simple, straightforward set of procedures. Preparing the samples for practical use was another problem. Synperonic A7 proved difficult to remove from the sample entirely, and our methods of washing and rewashing samples were inefficient. In addition, we never devised or acquired a method to weed undesirable nanoparticles out of a given sample which would
have been crucial since not every sample was monodisperse (Figure 61). For the purposes of increasing the temperature range of bent-core blue phases we purchased commercially available CdS nanoparticles even as we were synthesizing our own.

![Image of CdS nanoparticles](image)

**Figure 61:** CdS nanoparticles made in Synperonic A7 show both spherical and long nanoparticles.

Commercially produced nanoparticles were obtained from NN-Labs of Fayetteville, AK. Spherical nanoparticles with diameters of 4-5nm came suspended in toluene and used as provided.

### 5.3: Nanoparticle Stabilization of the Bent-Core Blue Phase I: Small Nanoparticles

For nanoparticle-stabilized blue phases reported thus far, successful attempts to add nanoparticles have in the past been limited mostly to gold.\[^{4}\] Gold nanoparticles have been added to blue phases using a sputtering method, which like our diffusion method provides no way to be exactly certain of the concentration of nanoparticles introduced into the sample.\[^{4}\] Yoshida, et al report a drastic increase of blue phase
temperature range along with a depression of the isotropic-blue phase transition temperature\textsuperscript{[4]} – two results we strive to emulate. More recently, cadmium selenide nanoparticles have been used to extend the temperature range of blue phases, particularly BPIII, in calamitic blue phase mixtures\textsuperscript{[96, 97]}

Two methods were used in an attempt to introduce cadmium sulfide nanoparticles into liquid crystal. The first method involved adding 0.02-0.1wt\% nanoparticles (4-5 nm in diameter) in either toluene or chloroform to a mixture of liquid crystals and solvent, then slowly evaporating the solvent until the material crystallized. At that point, the material was heated to isotropic under a vacuum to remove the remaining solvent, and then mixed using an ultrasonic bath.

This method did not result in uniform blue phases with the desired characteristics. No broadening of the blue phase temperature ranges were observed, in fact, it often seemed like nanoparticles were causing the opposite to occur. Higher concentrations of nanoparticles predictably resulted in archipelago-like aggregates forming. The procedure was repeated using 4-5nm diamond nanoparticles obtained from Skyspring Nanomaterials (Huston, TX), with the same results (Figure 62).
Figure 62: Aggregates of diamond nanoparticles in a bent-core blue phase.

A second method suggested by Paul Luchette of the Liquid Crystal Institute was to allow the nanoparticles to diffuse into the liquid crystal. Nanoparticles were mixed into ethylene glycol in concentrations ranging from 0.1 to 0.4wt% using an ultrasonic mixer. Immediately after mixing, a 100-400 micron capillary tube was filled partway with this mixture, followed by the target liquid crystal mixture. The tube was then left at temperatures above the liquid crystal’s isotropic temperature for times ranging from two to twenty-four hours before a temperature sweep was performed. The hope was that the hydrophobic nanoparticles would prefer to migrate from the hydrophilic ethylene glycol into the liquid crystal (Figure 63).
Figure 63: A diffusion method for introducing nanoparticles into liquid crystal. The hydrophobic nanoparticles should readily leave the hydrophilic ethylene glycol and migrate to the liquid crystal.

Figure 64: A sample of ethylene glycol (top) and 6008 with BDH-1281 (bottom) displays a texture gradient 3 hours after filling (T = 67.2 °C) after 24 hours at isotropic temperatures, the gradient when cooled becomes more pronounced (T = 65.3 °C).
This method initially seemed more successful than the first attempts in the sense that we saw none of the aggregation problems that plagued the previous samples, but still observed no consistently expanded temperature ranges (Figure 65). Any changes in phase temperature ranges and transitions that did occur were not consistent and could be a result of ethylene glycol contamination within the sample (Figure 64). In addition, we did not find a way to remove the sample from the capillary tube, or to use this method to fill a cell appropriate for electro-optical measurements. Finally, this method destroyed our ability to precisely measure the concentration of nanoparticles that potentially migrated to the liquid crystal, and introduced the possibility that the sample was contaminated by ethylene glycol. These shortcomings opened the door for many questions about what exactly was responsible for any observed effects and if the results could even be made stable in a more practical cell configuration.

**Figure 65:** 50/50 mixture of F493 and 60O8 with 5% chiral dopant A) control sample crystallizes at 60°C B) Held at isotropic overnight with a 0.2wt% CdS in E.G. sample reduces the transition to approximately 55°C C) doubling the concentration of CdS in the E.G. and holding at isotropic overnight actually decreased the temperature range.
Yoshida, et al[4] report that the addition of nanoparticles elongated the pitch of their blue phase samples which, if replicated in our CdS-doped samples, would cause them to shift towards the green wavelengths. We do not see any indication of that; rather in samples where there was an isotropic-looking phase down to crystallization, the black texture probably indicates a complete destruction of liquid crystalline order rather than a near-UV scattering phase.

The failure of CdS to have any affect on the blue phase is perplexing considering that semiconducting CdSe nanoparticles of 3.5nm diameter have been shown to increase the temperature range of BPIII liquid crystalline materials.[97] Consider that perhaps the difference stems from the differences in the host materials: lower concentrations of CdS nanoparticles may have showed no results because they were too small to have a significant effect on the disclination lines. Bent-core liquid crystals are larger (5-6 nm along the long axis where calamitics are 2-3nm) and take up more space than most calamitics and could pack such that the disclination lines were also a bit larger, so perhaps a larger nanoparticle would produce more desirable results.

5.4: Nanoparticle Stabilization of Bent-Core Blue Phases II: Large Nanoparticles

The previous poor results with CdS and diamond nanoparticles of less than 5nm diameter prompted us to try a with the larger silica particles. To test the idea that larger nanoparticles might succeed in bent-core blue phases where 4-5nm nanoparticles failed, hydrophobic silica nanoparticles (R 812, Degussa, Germany) of 7nm diameter were used,
as they are already known to disperse uniformly in liquid crystals, having been used to study memory effects in smectic \cite{98} and nematic \cite{99} liquid crystals.

Silica nanoparticles were added to a 50/50 mixture of F493 and 6OO8 with 5wt% chiral dopant using the solvent-evaporating method described in the previous section. Three different concentrations of silica nanoparticles were studied: 0.005wt%, 0.02wt% and 0.035wt%. Nanoparticles were measured out by mixing a larger amount of nanoparticle powder with chloroform, covering, and placing in a sonic bath. A microliter syringe was used to measure out the nanoparticles to each sample, while the chloroform-nanoparticle mixture is constantly weighed to maintain accuracy. Chloroform is very volatile so it is imperative to keep the sample well covered and take care to account for any evaporation. Homogeneity is also an issue, so the samples were measured out as quickly as possible after sonicating.

For the two samples with the highest concentrations of nanoparticles, the presence of nanoparticles depressed the BP-Crystal transition temperature by 5-8°C (Figure 66). The lowest-concentration sample reduced the BP-Cr transition temperature by about 1°C while leaving the visible Iso-BP transition unaffected at approximately 75°C. The higher concentration samples saw a significant decrease in the visible Iso-BP transition (~66.5°C) and a decrease in the BP-Cr transition to 51-53°C. All samples remained stable for 24 or more hours.
Figure 66: 50/50 F493 and 6008 (with 5wt% BDH-1281) A) no nanoparticles B) 0.005% silica nanoparticles C) 0.02% silica nanoparticles D) 0.035% silica nanoparticles. Larger amounts of nanoparticles appear to extend the BPIII phase at the expense of the BPI or BPII phase seen at low and no-nanoparticle concentrations; the overall increase in temperature range is approximately 5°C.

Using the three-component bent-core mixture described in chapter 4, 0.02wt% and 0.05wt% silica nanoparticles were added by the solvent-evaporating method as previously described. In stark contrast to the previous attempts, positive results were acquired with both experiments almost instantly. The temperature range of these blue
phases extended to near room temperatures: control samples transitioned to cholesteric at approximately 63°C, while nanoparticle-added samples maintained a BPIII-like texture down to below 25°C. The Iso-BP transition temperature saw no great changes from the control sample. No aggregates large enough to affect the texture were detected (Figure 67) and the white streak defects appeared only at the lower end of the temperature range (Figure 68).

**Figure 67:** Three-component bent core mixture with 1.9% BDH-1281. A) Control at 63.0°C B) Control at 49.2°C C) Control at 30.0°C D) 0.02% nanoparticles at 63.0°C E) 0.02% nanoparticles at 49.0°C F) 0.02% nanoparticles at 29.9°C G) 0.05%
nanoparticles at 56.8°C H) 0.05% nanoparticles at 50.0°C I) 0.05% nanoparticles at 29.4°C.

**Figure 68:** The BPIII temperature range is greatly expanded through the addition of nanoparticles. Even the temperatures beneath which frustrated white streaks occur is reduced (grey dotted line).

### 5.5 Polymer Stabilization

Polymer stabilization of liquid crystals has been used in display applications since the 1980’s, notably the polymer dispersed liquid crystal devices (e.g., privacy windows) and polymer-stabilized cholesteric liquid crystal devices (e.g., reflective displays).[100] Polymer stabilization is the use of a polymer network within the defect areas of the blue phase unit cell to reduce the frustration of the defect cores thereby stabilizing the phase.
It was one of the first methods used to create blue phases stable enough to use for practical applications.\textsuperscript{[3, 7]} Polymer-stabilized blue phases can be used for transmissive\textsuperscript{[7]} or reflective displays.\textsuperscript{[101]}

Blue phases were first polymer stabilized in 2002 by Kikuchi, et. al. Kikuchi and team were able to expand the temperature range of the blue phase from 1.1 °C to over 60 °C while keeping properties like fast switching intact. The switching time of blue phases – reported in the submillisecond range \textsuperscript{[3, 74]} – is very important since microsecond switching (i.e., 80-90Hz/frame times three subframes: red, green and blue) allows for color-sequential displays \textsuperscript{[102]}. Add to this advantage the fact that blue phases do not require alignment layers and that the transmittance is not dependent on cell gap after a certain thickness \textsuperscript{[73, 74, 103]} and blue phase displays become very desirable from a manufacturing perspective: no color filters over pixels required for color-sequential displays, no alignment layer, and less stringent cell gap requirements all add up to a simpler device that is cheaper to manufacture.

The drawback to a polymer-stabilized calamitic blue phase display is its high switching voltage. An in-plane switching cell can have an on-state voltage of more than 50 V\textsubscript{rms}.\textsuperscript{[3, 73, 74]} far too high for most applications. Blue phases made by unusually-shaped liquid crystals tend to have high switching voltages even without a polymer network \textsuperscript{[38, 104]} and therefore start at a disadvantage.

A monomer and photoinitiator are mixed with a liquid crystalline material in the isotropic state. As it cools into the blue phase, the monomer and photoinitiator will phase separate out, concentrating in the still-isotropic disclination lines. UV irradiation
polymerizes the monomers into a permanent network.

To study the effect of polymer networks on our bent-core BPIII materials we made polymer-stabilized mixtures using the monomer 4,4’ bisacryloyloxybiphenyl (BABB-6) with benzoin methyl ether (BME) as a photoinitiator. These were mixed with one of three chiral bent-core materials using chloroform and dried according to procedures already described. IPS cells were filled in a darkened room and the sample cooled slowly before being exposed to UV light from a 300W Black Ray Model B Ultraviolet Lamp for 1-2 hours to polymerize the network.

Several chiral bent-core mixtures were tried with various concentrations (1.5 – 6wt%) of polymer. Initial mixtures using polymers in chiral mixtures of F493 or F493 + 6OO8 were particularly unsuccessful. The addition of polymer erased any trace of blue phase textures. The cause of this could have been a too-high concentration of monomer (3 or 6wt%) or an excess of photoinitiator, which would provide a polymer of small molecular weight.

Reducing the amount of monomer in the sample produced better results. A mixture of 1.5wt% polymer with 0.15% BME added to a sample comprised of 1.9% BDH-1281 in F493/F521/F533 was mixed and a cell filled. The sample was cooled at a rate of 0.5C/minute and exposed to UV light for 1 hour. The results were not immediately apparent, however the cell showed a distinctive light blue color at room temperatures after sitting several hours (Figure 69).

The sample proved to be very difficult to characterize. It could take an hour or longer to reach equilibrium after a temperature change, no matter how slowly performed.
This made determining an isotropic – blue phase transition temperature, either visually or via electrooptical measurements, difficult and impractical at best. The cells could not be switched to a bright state using voltages less than 150V, which was the limit of our standard electro-optical experimental set-up.

Figure 69: The polymer stabilized blue phase shows a light blue texture at room temperatures from scattering of the lower wavelengths.

Polymer stabilization is obviously an important method for creating blue phase materials robust enough to use in practical applications, but it may be less suited for bent-core blue phase materials. We know from the body of literature published on polymer-stabilized calamitic blue phase mixtures that the single largest problem facing the
BPLCD is the high switching voltages. Without a polymer network, our own bent-core blue phase mixtures started switching around $30V_{\text{rms}}$ and had a bright-state voltage closer to $75V_{\text{rms}}$. Adding a polymer network would not improve these numbers. It is highly likely that our concentration of polymer is still too high, but highly unlikely that any concentration of polymers that could stabilize a blue phase could do so without negatively impacting the threshold voltages.

The literature on polymer-stabilized blue phases does not focus on fine-tuning the polymer network as a viable way to significantly improve the performance of BPLCDs, rather it focuses on the importance of increasing the Kerr constant of the materials [73, 103, 105] used or improving display performance with clever electrode design. Bent-core blue phases would probably benefit from following this example: bent-cores already stabilize or form large temperature range blue phases and any improvement in their performance is probably better served synthesizing molecules optimized for such a task, rather than fine-tuning a polymer network that may do more harm than good.

5.6 Conclusions

We found that widening and fine tuning bent-core blue phase materials by adding nanoparticles and/or polymer networks possible just as on calamitic blue phase materials, with some adjustments to account for the differences between bent-core and rod-shaped liquid crystals. One example is that the studied bent-core materials are larger than their typical calamitic counterparts, suggesting that the defect cores of the bent-core blue phase
are also larger requiring larger nanoparticles. This indeed was found experimentally, where 7nm silica nanoparticles were found to successfully increase the bent-core blue phase where smaller CdS nanoparticles had no effect.

Similar to calamitic blue phases, our bent-core blue phases could be stabilized by polymer networks. The price of such a network is the increased driving voltage for a given cell thickness. Methods used to reduce the driving voltages of calamitic blue phase displays, such as new electrode design, could be equally well applied to bent-core blue phases.
Chapter 6

Summary and Future Work

6.1 Summary

We showed that bent-core nematic liquid crystals are suitable for creating liquid crystalline blue phases and inducing or expanding the temperature range of blue phases in chiral calamitic liquid crystalline materials. The low twist elastic constant ($K_{22}$) and molecular biaxiality of bent-core nematics allowed them to easily make stable blue phases with large temperature ranges simply by adding chiral dopant.

When small amounts of chiral dopant were used, the smectic clusters that occur in bent-core nematics favors the appearance of BPIII, the amorphous crystal phase. BPI and BPII are prevented from forming by the smectic clusters, which break up and randomize the lattice structure. In F493, the BPIII can span as much as 18° C, which is the largest temperature range for a BPIII material that we are aware of. Bent-core blue phases made with F493 exhibit electro-optic switching at voltages comparable to polymer-stabilized calamitic blue phases, but lacks the sub-millisecond switching speeds that make the blue phases desirable for color-sequential displays.

If the bent-core nematic was sufficiently diluted, either by the addition of a companion calamitic material or through the addition of a significant amount of chiral dopant, the smectic clusters no longer prevented the formation of BPI or BPII and these phases began to appear in lieu of BPIII. Even small amounts of bent-core liquid crystal
added to a chiral calamitic mixture can expand the temperature range of blue phases that are already present. We achieved a blue phase (BPI or BPII) that spanned 33°C by adding a small amount (10wt%) of F493 to a chiral mixture of 6008.

Polymer and nanoparticle stabilization both worked to expand the temperature range of the bent-core blue phases. Polymer stabilization resulted in a stable, room-temperature BPIII. The polymer network unfortunately inhibited the electro-optical response of the material. An optimized polymer network would not destroy the switching abilities of the liquid crystal and may actually improve some qualities, such as switching speed.

Small nanoparticles (5nm diameter or less) had no effect or a detrimental effect on the blue phases, depending on the concentration of nanoparticles added to the sample. Cadmium sulfide (CdS) nanoparticles were introduced to bent-core blue phase samples in several concentrations using two different methods, with no positive results. Diamond nanoparticles of a similar size also did nothing to increase the temperature ranges of the bent core blue phases.

Silica nanoparticles (7nm diameter) met with greater success when added to bent-core blue phase materials. A 0.05wt% concentration of silica nanoparticles expanded the temperature range of a bent-core blue phase from 5°C to over 40°C. The silica nanoparticles could be added to the liquid crystal easily by mixing in an excess of solvent and slowly drying under a vacuum. Mixtures involving silica nanoparticles were stable at higher temperatures but tended to display streaky white defect areas at lower temperatures, a problem they shared in common with several non-particle-added bent-
core blue phase samples.

In conclusion, bent-core nematic liquid crystals have been shown to form a stable BPIII phase when doped with an appropriate chiral dopant. The same liquid crystals can stabilize the BPI or BPII phases of chiral calamitic mixtures. Nanoparticle and polymer stabilization are both viable methods of expanding the temperature range of bent-core blue phases, just as in calamitic blue phases. Nanoparticle stabilization could additionally help decrease the threshold switching voltage of the bent-core blue phase materials, while an optimal polymer network could improve switching speed which is a particular problem in bent-core blue phases as compared to their calamitic counterparts.

6.2 Future Work

The experiments described in this work covered quite a bit of breadth at the expense of depth. Future work would focus on refining some of the conclusions drawn in these pages. In particular, more bent-core nematic materials should be used to create blue phases so that we may begin to better understand which qualities of the bent-core liquid crystals are important to optimizing their response to chiral dopant.

In addition to the blue phases, adding chiral dopant to bent-core or mixtures of bent-core and rod-shaped liquid crystals generated phases whose properties, while interesting, were outside the scope of the project. The bent-core rod-shaped mixtures formed chiral smectic phases down to room temperatures which were only cursorily addressed in this work. A thorough characterizing of the smectic regions of the phase
The diagram should include ferroelectric measurements and x-ray diffraction studies, at several concentrations of chiral dopant. The N* phase of F521 was not examined in any kind of detail, leaving the cholesteric bent-core phase open for further studies.

The bent-core/rod-shaped mixtures require Kossel diagrams, which were not performed because of time constraints (the Kossel diagram itself is a straightforward process, preparing a sample with properly sized monodomains in order to obtain a clear diagram can be a time-consuming, delicate process). Kossel diagrams would allow us to complete the phase diagram by assigning BPI or BPII to the platelet textures observed by POM. In addition, further mixtures should be made and characterized: the experiments in chapter 4 could be repeated for several concentrations of chiral dopant and compared to a series of experiments in which the chiral dopant concentration is constant for all mixtures. Because the bent-core and rod-shaped mixtures offered the largest temperature ranges, down to the lowest temperatures, continuing work along this path is likely the most expedient route to finding bent-core stabilized blue phases that are appropriate for use in practical applications.

We have shown that 7nm silica nanoparticles can expand the temperature range of the blue phase of bent-core liquid crystals. Limitations in both time and materials prevented a complete examination of the effects of silica nanoparticles, or larger CdS nanoparticles. Now that we can reasonably suspect that larger nanoparticles can produce the desired effect where smaller nanoparticles fail, the process should be repeated to find the optimal results for several types of nanoparticles, including silica, cadmium sulfide, and gold. In terms of applications, bent-core blue phases share the same drawback as
polymer-stabilized calamitic blue phases: the voltages required for switching are too high. Nanoparticle stabilization with gold or CdS could then serve twofold purpose: first, stabilization, and second, reduction of the threshold voltages.

Finally, smaller bent-core materials, consisting of three benzene rings where typical bent-core liquid crystals contain five, should be explored both as an additive to stabilize blue phases made of smaller calamitic materials (e.g., 5CB or E7, two commonly used nematic liquid crystals) and to continue to examine the relationship between molecular size and effective use of nanoparticles in stabilizing blue phases.
REFERENCES

1. J. Cohen. The Blue Phase of Cholesteric Liquid Crystals.


78. A. Jáıklı. New Methods to Study the Biaxiality of Nematic Liquid Crystals: The Case of Bent-Core Materials. 2009


