The Optical and Physical Properties of a Photosensitive Nematic Liquid Crystal

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# Table of Contents

Abstract

1 Introduction

2 Theory

2.1 The Photosensitive Liquid Crystal

2.1.1 What is a Liquid Crystal?

2.1.2 Nematic Liquid Crystals

2.1.3 Photo-Isomerization of Liquid Crystal ZhK 440

2.1.4 Calculation of Photo-Isomerization Yields of Cis Isomer

2.2 Thermodynamics

2.2.1 The Clapeyron Equation

2.2.2 Phase Transitions of Impure Substances

2.2.3 Measuring the Latent Heat of Transition

2.3 Optical Measurements

2.3.1 Jones Vectors

2.3.2 Index of Refraction

2.3.3 Absorption

2.3.4 Birefringence

2.3.5 Order Parameter

Abstract 4

1 Introduction 5

2 Theory 9

2.1 The Photosensitive Liquid Crystal 9

2.1.1 What is a Liquid Crystal? 9

2.1.2 Nematic Liquid Crystals 10

2.1.3 Photo-Isomerization of Liquid Crystal ZhK 440 10

2.1.4 Calculation of Photo-Isomerization Yields of Cis Isomer 12

2.2 Thermodynamics 15

2.2.1 The Clapeyron Equation 16

2.2.2 Phase Transitions of Impure Substances 18

2.2.3 Measuring the Latent Heat of Transition 22

2.3 Optical Measurements 24

2.3.1 Jones Vectors 24

2.3.2 Index of Refraction 26

2.3.3 Absorption 28

2.3.4 Birefringence 30

2.3.5 Order Parameter 36
3 Methods and Results

3.1 Irradiation Experiments in Solution

3.1.1 Absorption

3.1.2 Irradiation Experiments

3.1.3 Calculation of Cis Isomer Yield

3.2 Optical and Physical Measurements on the Liquid Crystal Phase

3.2.1 Measuring the Indices of Refraction

3.2.2 Birefringence Experiments

3.2.3 Order Parameter Measurements

3.2.4 Determination of the Latent Heat of Transition

3.3 Irradiation Experiments in the Liquid Crystal Phase

3.3.1 Birefringence of Impure Mixtures

3.3.2 Calculation of Cis Isomer Concentration

3.3.3 Photo-excitation and De-excitation

4 Discussion

5 Conclusions

Acknowledgements

Bibliography
Abstract

Liquid crystals have been an important part of the technological revolution of the past 20 years. Studies that examine liquid crystals with unique properties, such as the photosensitivity of ZhK 440, can help initiate the development of new technologies in industries such as display manufacturing and nanotechnology. The purpose of this study was to determine the basic physical properties of ZhK 440 and more thoroughly describe its photosensitivity. This nematic liquid crystal is being studied not only because it can potentially be useful in industry, but also because a systematic investigation into the isomerization properties of azoxy liquid crystals has never been made. Optical properties, such as birefringence and the indices of refraction, were measured. The extent of cis-trans isomerization upon excitation with UV and visible light were examined both in solution and in the liquid crystal phase. Order parameter values as a function of temperature and the latent heat of transition were also determined. Finally, an estimated spectrum of the cis isomer was produced. The data suggest that this system is easily manipulable with light, and holds promise for future technological applications.
Chapter 1

Introduction

Liquid crystals, as a phase of matter, have intrigued scientists ever since their discovery by F. Reinitzer in 1888 (Collings and Hird, 1997). Since then, a plethora of substances have been documented as displaying some sort of ordered, flowing state, with properties between those of a liquid and a solid. Such materials have been extensively used in display manufacturing, non-linear optics, and nanotechnology research. Their beauty and usefulness stem in large part from the ease with which they can be manipulated by external stimuli, such as electric and magnetic fields.

The liquid crystal that is the topic of this research is one that was developed at the Institute of Cybernetics at the Georgian Academy of Sciences. It is a 1:2 mixture of two similar azoxy-benzenes and is called ZhK 440 (Figure 1.1). ZhK 440 was developed and chosen because of its wide nematic liquid crystal phase, which includes room temperature. A nematic phase is one of orientational, but not translational order, Figure 1.2. The novel advantage of a photosensitive liquid crystal system is that the temperature of the transition to the isotropic phase can be manipulated by exposing the system to various wavelengths of light. Another unique aspect of this particular system is the relatively high energy barrier between the cis and trans isomer (Figure 1.1), estimated to be $63 \pm 7$ KJ/mol in a recent undergraduate thesis (Levy, 2004).

The photosensitivity of the compounds arises from the N=N double bond (Figure 1.1). When the compounds in their most stable trans isomer conformation are bombarded with ultraviolet light at around 341nm, an excitation of the bond occurs and some percentage of the substance converts to a cis conformation. If enough molecules are converted to a cis
state, a transition from the nematic to the isotropic phase occurs because the bent molecular shape disturbs the orientational order of the sample.

While azo-benzenes have been studied for years because of their interesting property of photosensitivity, no fundamental studies on azoxybenzene compounds displaying a liquid crystal phase have been published to date. The photosensitivity of the azo-benzene liquid crystals arises for reasons analogous to the ones given above, and has been examined because of such a system’s high potential to be useful in all-optical switching devices. Lee et al. (2000) found that irradiation of azo-benzene compounds in solution with 366nm light produced a photo-stationary state with a different spectra than that of the original, implying the production of cis isomer. They also found that in the liquid crystal state irradiation induced changes in the azo-benzene doped samples that were analogous to temperature induced changes in traditionally switched systems. In a study with a similar purpose, Kurihara et al. (1998) showed that the nematic-isotropic phase transition temperature could be lowered to room temperature photo-chemically, in samples doped with an azobenzene compound.

Chanishvili et al. (2005) recently conducted a study to determine the potential usefulness of the azoxy-benzenes of ZhK 440 in a device. The photosensitivity of the compounds was exploited in a series of experiments where ZhK 440 was mixed with a cholesteric liquid crystal in order to demonstrate that the resulting mixture’s peak diffraction wavelength varied
with exposure to ultraviolet light. A cholesteric liquid crystal arises because the molecules displaying this phase are chiral. Because of this, in an aligned sample, the orientation of the preferred alignment direction (called the director) rotates along an axis perpendicular to the plane of the director. The pitch of this helix is what determines the sample’s peak diffraction wavelength. In the experiments the group describes, they were able to manipulate this pitch using the photo-activity of ZhK 440. This result is the first successful step towards using photosensitivity, in combination with an appropriate chiral dopant, to construct a new type of optical display. This display, unlike current ones, would be manipulated with ultraviolet light rather than with electric voltage. However, in order to continue with research in this vein, much more needs to be learned about the physical and optical properties of the photosensitive part of this mixture.

The photo-isomerization (transition between cis and trans states of the molecules) of ZhK 440 is what causes a shift in the peak diffraction wavelength of the ZhK 440/chiral dopant mixture. Since the entire display functions due to ZhK 440’s absorption of ultraviolet light, this property needs to be thoroughly explored. In order for the sample to be effective in a device, it must be possible to easily control isomerization of ZhK 440 with light. To this end, experiments were done to determine the optimal wavelength for excitation and de-excitation of the sample. The experiments were based on previous work done on azo-benzene compounds where distinct equilibria between cis and trans concentrations were achieved using specific irradiation wavelengths (Zimmerman et al., 1958).

The overall purpose of this work was to investigate the novel physics involved in this
intricate system using the available techniques of thermodynamics, optics, and spectroscopy. However, the applied aspects of the project were also noted when deciding which research avenues to pursue. For example, Chanishvili et al. (2005) claim that a change in the orientational order of the ZhK 440 liquid crystal is partially responsible for changes in the indices of refraction of the ZhK 440/chiral dopant mixture. Therefore, it was important to investigate the relationship between the order parameter of ZhK 440 and various factors, such as temperature and exposure to ultraviolet light. This was the motivation for measuring birefringence, parallel and perpendicular indices of refraction, and order parameter of the ZhK 440 system. Finally, it was also important to determine the effectiveness of ultraviolet light at promoting the trans to cis isomerization. To this end, Fisher’s method (Delaire et al., 1993) was used to calculate the amount of cis isomer produced in solution upon irradiation. In the liquid crystal phase, the amount of cis isomer produced was estimated using the method described by McColl (1974).
Chapter 2

Theory

2.1 The Photosensitive Liquid Crystal

2.1.1 What is a Liquid Crystal?

Liquid crystals are materials in a phase of matter that exhibits some characteristics of a liquid and some characteristics of a solid (Collings and Hird, 1997). Specifically, liquid crystals flow like liquids but on a molecular level, they are somewhat ordered, like solids. When discussing the “ordering” of molecules, we distinguish between two types: orientational and positional. Orientational ordering refers to the molecules having a preferred orientation with respect to the other molecules in the material. Positional ordering refers to molecules having a preferred position with respect to the others. The solid phase exhibits the most order of any of the other phases of matter. All the atoms or molecules in a solid, or crystal lattice, have a specific orientation and position. Atoms or molecules in a liquid, on the other hand, have neither of these types of order. The extent of the ordering in a liquid crystal phase largely depends on the type of liquid crystal phase one has in mind. Some liquid crystals exhibit a degree of order similar to a solid, having both orientational and positional order. Others have only orientational order. The extent of the ordering can even vary within a particular sample, in a particular liquid crystal phase, depending on outside conditions such as the presence of an external electromagnetic field or the temperature of the sample. Order will be discussed more thoroughly in a later section.
2.1.2 Nematic Liquid Crystals

As mentioned earlier, there are many types of materials that exhibit a somewhat ordered, yet flowing state (Collings and Hird, 1997). The type of liquid crystal of interest to us, however, is known as nematic. Nematic liquid crystals only have orientational order and no positional order. Materials that exhibit this kind of phase tend to consist of molecules that are long, and have rigid centers that do not allow rotations that result in non-linear molecular conformations. Liquid crystal ZhK 440, Figure 1.1, satisfies these general requirements by having a highly conjugated molecular center about which the molecule cannot easily bend. The molecules tend to align with their long axis, more or less parallel to each other. This preferred, unique direction is called the “director” and is depicted in Figure 2.1.

2.1.3 Photo-Isomerization of Liquid Crystal ZhK 440

The material we are concerned with in this work, displays a nematic liquid crystal phase at room temperature. As mentioned in the introduction, it consists of a 1:2 mixture of two azoxy compounds, Figure 1.1, that undergo geometric isomerization when exposed to ultraviolet light. In general, for any photochemical reaction to occur the compound must absorb light energetic enough to induce the reaction ((Lowry and Richardson, 1987) & (Carey and Sundberg, 2000)). In photochemical processes involving organic compounds, these absorptions correspond to excitations of electronic states. Usually, the electronic excitation is the promotion of an electron from the Highest Occupied Molecular Orbital (HOMO), which is
bonding, into the Lowest Unoccupied Molecular Orbital (LUMO), which is, in most cases, anti-bonding. This type of promotion is assumed to be near instantaneous, so that during its course only the electrons are reorganized and the much heavier nuclei remain in the geometry of their ground state. This is generally referred to as the Franck-Condon principle, the logical conclusion of which is that the resulting excited state has a geometry with non-minimal energy. After the excitation is complete, however, the conversion to a new minimum geometry occurs very rapidly. It is assumed that the photochemical reaction we are studying proceeds in accordance with these general principles.

A mechanism for azoxybenzene cis-trans conversions has been difficult to study experimentally and so has largely remained a matter for speculation. In a recently published paper Basch and Hoz (1997) propose a mechanism for this process by way of modeling the energies of possible conformations. The stable intermediates proposed by the group are depicted in Figure 2.2. The paper proposes that during the conversion process, the center nitrogen to nitrogen interaction has a bond order approaching unity. The compounds in liquid crystal ZhK 440 are assumed to follow a process quite similar to this one, being that the substituents on the benzenes are unlikely to impact the energetics of this isomerization beyond slightly shifting the absorption maximum.
### 2.1.4 Calculation of Photo-Isomerization Yields of Cis Isomer

We now want to consider the effects of irradiating an all trans sample at its absorption wavelength. If the extinction coefficients of the cis and trans isomers are unknown at that wavelength, then we have no direct way of determining the amount of cis isomer produced. Fischer’s method (Delaire et al., 1993) was developed to solve exactly this kind of problem.

We begin by describing a basic experiment on a material that is most stable as the trans isomer, but can be promoted into the cis conformation using light. The reverse reaction (cis to trans isomerization) can occur with the use of light or heat, but thermal relaxation is so slow that it can be neglected for experimentally relevant time scales. Now, this material has a peak absorption at some wavelength, $\lambda_{peak}$. However, isomerization can be promoted using a wavelength in the vicinity of $\lambda_{peak}$, but that is not equal to $\lambda_{peak}$. We will call this wavelength $\lambda_{irr}$, for irradiation. We now define some symbols that will be useful to us. All symbols will be defined for the trans isomer or (trans to cis isomerization), but will also be used for the cis isomer, with the subscript c (and cis to trans isomerization with the subscript ct).

- $A_{irr}$ → absorption at $\lambda_{irr}$
- $\Phi_{tc}^{irr}$ → quantum yield of trans to cis isomerization at $\lambda_{irr}$
- $\epsilon_{irr}^{t}$ → extinction coefficient of the trans isomer at $\lambda_{irr}$
- $c_{t}$ → concentration of trans isomer

Now since we have assumed that once a molecule has been promoted from the trans to the cis state, thermal reversion is slow enough to be neglected, we conclude that a sample will come to equilibrium upon irradiation at which point photo-induced isomerization will be equal in both directions. We assume this equilibrium has been reached in all irradiation experiments, or if it has not, we extrapolate the experimental values to infinite time. Now we can write down the following expression for concentrations of each isomer at equilibrium:

\[
\frac{c_{t}^{irr}}{c_{c}^{irr}} = \frac{\Phi_{tc}^{irr} \epsilon_{irr}^{t}}{\Phi_{tc}^{irr} \epsilon_{irr}^{t}} = \frac{\Phi_{tc}^{irr} A_{c}^{irr}}{\Phi_{tc}^{irr} A_{t}^{irr}}
\]  

(2.1.1)

We can now posit that were we to irradiate at two different wavelengths, near the peak, we could write down an equation for each of them like equation 2.1.1 above. Now, if we assume that the quantum yields are wavelength independent (which are good assumptions
at irradiation wavelengths close to the peak absorption), we can take the ratio of these two
equations to cancel out unknown quantities:

\[
\frac{c_{t}^{\text{irr1}} / c_{c}^{\text{irr1}}}{c_{t}^{\text{irr2}} / c_{c}^{\text{irr2}}} = \frac{A_{t}^{\text{irr1}} / A_{c}^{\text{irr1}}}{A_{t}^{\text{irr2}} / A_{c}^{\text{irr2}}}
\]  

(2.1.2)

We now define a new quantity, \( \alpha^{\text{irr}} \) as the fraction of cis isomer at the equilibrium point due
to irradiation at wavelength \( \lambda^{\text{irr}} \). We now rewrite the concentration ratios of the cis and
trans isomers, in terms of this new quantity.

\[
\frac{c_{t}^{\text{irr}}}{c_{c}^{\text{irr}}} = \frac{1 - \alpha^{\text{irr}}}{\alpha^{\text{irr}}}
\]  

(2.1.3)

Equation 2.1.2 becomes:

\[
\frac{(1 - \alpha^{\text{irr1}})/\alpha^{\text{irr1}}}{(1 - \alpha^{\text{irr2}})/\alpha^{\text{irr2}}} = \frac{A_{t}^{\text{irr1}}/A_{c}^{\text{irr1}}}{A_{t}^{\text{irr2}}/A_{c}^{\text{irr2}}}
\]  

(2.1.4)

Now we want to express the above equation in terms of experimentally obtainable data.
To do this we state that the total observed absorption of a sample at any particular wave­
length is due to the absorption at that wavelength due to the trans isomer plus the absorption
due to the cis isomer. In other words,

\[
A^{\text{irr1}} = A_{t}^{\text{irr1}} (1 - \alpha^{\text{irr1}}) + A_{c}^{\text{irr1}} \alpha^{\text{irr1}}
\]  

(2.1.5)

\[
A^{\text{irr2}} = A_{t}^{\text{irr2}} (1 - \alpha^{\text{irr2}}) + A_{c}^{\text{irr2}} \alpha^{\text{irr2}}
\]  

(2.1.6)

We now define a quantity, \( \Delta \), as the change in absorption, at a particular wavelength, due
to the creation of cis isomer:

\[
\Delta^{\text{irr1}} = A^{\text{irr1}} - A_{t}^{\text{irr1}}
\]  

(2.1.7)

\[
\Delta^{\text{irr2}} = A^{\text{irr2}} - A_{t}^{\text{irr2}}
\]  

(2.1.8)

Now we try to express the absorption due to cis isomer, \( A_{c}^{\text{irr}} \), in terms of the experimentally
measurable \( \Delta \). We do this for a general irradiation wavelength, \( \lambda^{\text{irr}} \), knowing that it will be true for both wavelength 1 and 2.

\[
A^{\text{irr}} = A_{t}^{\text{irr}} + \Delta^{\text{irr}}
\]

\[
A_{t}^{\text{irr}} - A_{t}^{\text{irr}} \alpha^{\text{irr}} + A_{c}^{\text{irr}} \alpha^{\text{irr}} = A_{t}^{\text{irr}} + \Delta^{\text{irr}}
\]

\[
A_{c}^{\text{irr}} = A_{t}^{\text{irr}} + \frac{\Delta^{\text{irr}}}{\alpha^{\text{irr}}}
\]  

(2.1.9)
Plugging this result into equation 2.1.4, we get:

\[
\frac{(1 - \alpha_{irr1})/\alpha_{irr1}}{(1 - \alpha_{irr2})/\alpha_{irr2}} = 1 + \frac{\Delta_{irr1}}{\alpha_{irr1}A_{irr1}}
\]

\[
= 1 + \frac{\Delta_{irr2}}{\alpha_{irr2}A_{irr2}}
\]

(2.1.10)

We now define a quantity called \( \delta \), which is a ratio between the change in absorption due to the creation of cis, and the absorption due to trans:

\[
\delta_{irr1} = \frac{\Delta_{irr1}}{A_{irr1}} = \frac{A_{irr1} - A_{irr1}^t}{A_{irr1}^t - A_{irr1}^t}
\]

(2.1.11)

\[
\delta_{irr2} = \frac{\Delta_{irr2}}{A_{irr2}} = \frac{A_{irr2} - A_{irr2}^t}{A_{irr2}^t - A_{irr2}^t}
\]

(2.1.12)

Note that \( \delta \) is defined as an entirely measurable quantity. We can use the above equations to write equation 2.1.10 in a simpler form:

\[
\frac{(1 - \alpha_{irr1})/\alpha_{irr1}}{(1 - \alpha_{irr2})/\alpha_{irr2}} = \frac{1 + \delta_{irr1}}{1 + \delta_{irr2}}
\]

\[
= \frac{(\alpha_{irr1} + \delta_{irr1})/\alpha_{irr1}}{(\alpha_{irr2} + \delta_{irr2})/\alpha_{irr2}}
\]

\[
1 - \alpha_{irr1}
\]

\[
= \frac{\alpha_{irr1} + \delta_{irr1}}{\alpha_{irr2} + \delta_{irr2}}
\]

\[
1 - \alpha_{irr2}
\]

(2.1.13)

Doing some more algebra on the above equation, which is omitted here, we can rearrange it to write,

\[
\alpha_{irr2} = \frac{\delta_{irr1} - \delta_{irr2}}{1 + \delta_{irr1} - \alpha_{irr1}/\alpha_{irr2} (1 + \delta_{irr2})}
\]

(2.1.14)

Now we have almost accomplished our goal of being able to calculate the amount of cis isomer created upon irradiation with a particular wavelength. The above equation tells us what fraction of our sample has been converted to cis isomer, only in terms of quantities that can be determined experimentally, except for the ratio of \( \alpha \)'s in the denominator. All we need to do is express that ratio in terms of measurable quantities, and we will have competed our task successfully. To get at this, consider the whole spectra of the material when it is at equilibrium concentrations of cis and trans isomer. We can argue that the ratio of cis isomer fractions (\( \alpha \)'s) is the same as the ratio of the changes in absorption due to the creation of cis isomer (\( \Delta \)'s). In other words,

\[
\frac{\alpha_{irr1}}{\alpha_{irr2}} = \frac{\Delta_{irr1}}{\Delta_{irr2}}
\]

(2.1.15)
For practical purposes of decreasing error, we pick the $\Delta$’s in such a place in the spectra, where the change in absorption is greatest due to the creation of cis isomer. Thus, our final equation becomes:

$$
\alpha_{irr}^{irr} = \frac{\delta_{irr1} - \delta_{irr2}}{1 + \delta_{irr1} - \frac{\Delta_{peak}^{irr1}}{\Delta_{peak}^{irr2}} (1 + \delta_{irr2})}
$$

(2.1.16)

Using the above equation, we can figure out the amount of cis isomer created, without knowing extinction coefficients or rate constants for either isomer. The only measurement we need to make is the change in the spectra due to irradiation of an all trans isomer sample by two different wavelengths.

### 2.2 Thermodynamics

When exposure to ultraviolet light leads to the isomerization of ZhK 440, as discussed in the previous section, one of the most important questions we can ask is, what amount of cis isomer does exposure produce? This is a question that is very difficult to answer spectroscopically for materials not dissolved in solution, but found in the liquid crystal phase. And so, to answer this question for the liquid crystal phase, we turn to thermodynamics. By studying the phase transition of ZhK 440 from the nematic to the liquid phase, much information can be gleaned about the basic properties of the sample at hand.

A phase transition is most commonly the transition of a substance between two states with different degrees of ordering. Specifically, states at lower temperatures exhibit more ordering than those at higher temperatures. One method of discussing the ordering of a material is by considering any symmetries it exhibits about an axis or plane. If a material has a symmetry about an axis, then rotation about that axis produces no difference in the material’s measured physical properties. Isotropic materials, such as liquids, have symmetry about all axes. More ordered materials can have symmetries about two, one, or no axes. Phase transitions from less ordered states to more ordered states often result in what is called a broken symmetry, or the loss of symmetry about one of the axes of the material. If a phase transition, induced by decreasing temperature, results in a broken symmetry and a discontinuity in its properties, then the transition is said to be first order. A transition from an isotropic phase to a nematic liquid crystal phase is one such transition. The nematic phase is one of lower symmetry, having only one symmetry axis aligned along the director. The isotropic, or liquid phase, is, as the name suggests, of higher symmetry, having an infinite
Phase transitions of pure substances are abrupt, occurring at a discrete temperature. If a substance has an impurity or is itself a mixture, there will be a range of temperatures over which the transition occurs. This range is also known as the coexistence region because the substance exists in both phases in that range. The greater the dissimilarity of the two compounds in a mixture, the greater the range of temperature over which the transition occurs. This range also increases with the amount of impurity. Due to the tremendous similarity in the structures of the two compounds in the ZhK 440 mixture, the coexistence region of the nematic to isotropic phase transition is only tenths of a degree wide. For this reason, we will from now on regard the mixture as “pure” when it is entirely in the trans-isomer conformation.

2.2.1 The Clapeyron Equation

The Clapeyron Equation, which we are about to derive, describes the slope of a coexistence line that is the boundary between two phases of a pure substance (Levine, 1995). This equation will be useful in the next section, where phase transitions will be discussed more thoroughly.
To begin the derivation we shall consider a one component, two phase system, such as the one depicted in Figure 2.3. The actual phases represented by Phase A and B are irrelevant, as this analysis applies to any one component system. Now, since we are concerned with the slope of the coexistence line, we now consider two points on this line, which are infinitesimally close together (points 1 and 2 in Figure 2.3). During coexistence, the system is in equilibrium and the molar Gibbs free energies of one component phases in equilibrium are always equal. Therefore, the following relationships must be true:

\[ G_{m,1}^A = G_{m,1}^B \]  \hspace{1cm} (2.2.17)
\[ G_{m,2}^A = G_{m,2}^B \]  \hspace{1cm} (2.2.18)

where the m subscripts signify molar quantities. But the molar Gibbs energy at point 2 can also be expressed with the addition of a tiny step to point 1:

\[ G_{m,1}^A + dG_m^A = G_{m,1}^B + dG_m^B \]  \hspace{1cm} (2.2.19)

Using equation 2.2.17 in equation 2.2.19, we can now write:

\[ dG_m^A = dG_m^B \]  \hspace{1cm} (2.2.20)

We now invoke one of the four Gibbs equations for a closed system, undergoing a reversible process, where only pressure-volume (P-V) work is being done:

\[ dG_m = V_m dP - S_m dT \]  \hspace{1cm} (2.2.21)

Combining equation 2.2.20 with equation 2.2.21, we obtain the following relationship:

\[ V_m^A dP - S_m^A dT = V_m^B dP - S_m^B dT \]  \hspace{1cm} (2.2.22)

Rewriting the above, we get:

\[ (V_m^A - V_m^B) dP = (S_m^A - S_m^B) dT \]

\[ \frac{dP}{dT}_{coexistence} = \frac{\Delta S_m}{\Delta V_m} \]  \hspace{1cm} (2.2.23)

We could stop here, having come up with a perfectly reasonable expression for the slope of the boundary between two phases. However, carrying around a change in entropy, \( \Delta S \), is not
that useful since it is almost impossible to measure directly. For that reason, we recall from basic thermodynamics the expression that applies to the change in entropy in any reversible phase change:

$$\Delta S = \frac{\Delta H}{T}$$  \hfill (2.2.24)

where $\Delta H$ is the enthalpy, or amount of energy input necessary to induce a phase transition. We now plug the above relationship into equation 2.2.23, to obtain the Clapeyron equation in its most common form:

$$\left(\frac{dP}{dT}\right)_{coex} = \frac{\Delta H}{T \Delta V}$$  \hfill (2.2.25)

### 2.2.2 Phase Transitions of Impure Substances

We now consider a sample of our liquid crystal in the trans isomer state. We introduce a small amount of impurity into this sample. This impurity can be either the same compound, but in the cis conformation, or anything else. We now assume that the resulting mixture is an *ideally-dilute solution*. In other words, the mole fraction of the liquid crystal, $X_{440}$, is much greater than that of the impurity, $X_i$. We consider the transition of such a mixture from the nematic phase to the isotropic phase.

In the coexistence region of this transition, Figure 2.4, the amount of impurity in the nematic and isotropic phases is not the same. In other words

$$X_i^N \neq X_i^I$$  \hfill (2.2.26)
We now define a vapor pressure, $P$, above such a solution. In the coexistence region, the vapor pressure of the isotropic phase, $P^I$, must be equal to the vapor pressure of the nematic phase, $P^N$. We can now use a property called Raoult’s Law, which states that the contribution of a substance to the actual vapor pressure of a mixture, is the vapor pressure of that substance in its pure state, times the fractional amount of it in the mixture (Levine, 1995). Thus, if $P^{N_0}$ is the vapor pressure of pure liquid crystal in the nematic phase, then according to Raoult’s Law,

$$P^N = P^{N_0} X_{440}^N$$  \hspace{1cm} (2.2.27)

We can also rewrite this in terms of the mole fraction of the impurity:

$$P^N = P^{N_0} (1 - X_{440}^N)$$  \hspace{1cm} (2.2.28)

By following an identical argument for the isotropic phase of the liquid crystal, we write the following relationship:

$$P^I = P^{I_0} (1 - X_{440}^I)$$  \hspace{1cm} (2.2.29)

We can now set the vapor pressure of the nematic and isotropic phases equal to each other, for reasons mentioned above.

$$P^{I_0} (1 - X_{440}^I) = P^{N_0} (1 - X_{440}^N)$$  \hspace{1cm} (2.2.30)

We keep in mind, however, that this is only true for temperatures around the coexistence region.

We now want to relate the vapor pressures of the liquid crystal in the pure nematic and pure isotropic states, $P^{N_0}$ and $P^{I_0}$, to temperature in general. Consider the phase diagram of a pure liquid crystal depicted in Figure 2.5. We begin at some temperature, $T$, and pressure, $P$, in the nematic phase and introduce energy in the form of heat. To a first approximation, the temperature of the sample rises linearly with heating. Thus, the following relationship between pressure and temperature, in the nematic phase, can be assumed:

$$P^{N_0}(T) = P_c + \left(\frac{dP}{dT}\right)^{N_0} (T - T_c)$$  \hspace{1cm} (2.2.31)

where $P_c$ and $T_c$ are the pressure and temperature, respectively, of the transition into the isotropic phase. Once the sample has undergone the phase transition we can continue to heat linearly in the isotropic phase, thus writing down a similar relationship for the temperature
Figure 2.5: An example of a phase Temperature-Pressure phase diagram showing the nematic and isotropic phases. The curved line represents the phase boundary. The line with the arrows is an example of linear heating of a sample through a transition and pressure, but noting that the rate of change of one with respect to the other will not be equal to that in the nematic phase:

\[ P^{I_0}(T) = P_c + \left( \frac{dP}{dT} \right)^{I_0} (T - T_c) \]  

(2.2.32)

We now return to our sample, where we once again set the vapor pressure of the nematic and isotropic phases equal to each other at the phase transition, and approximately equal to each other in the temperature region around the phase transition:

\[ P^{N_0}(T) (1 - X_i^N) = P^{I_0}(T) (1 - X_i^I) \]

\[ \left[ P_c + \left( \frac{dP}{dT} \right)^{N_0} (T - T_c) \right] (1 - X_i^N) = \left[ P_c + \left( \frac{dP}{dT} \right)^{I_0} (T - T_c) \right] (1 - X_i^I) \]  

(2.2.33)

Omitting the algebra, we can obtain the following result for \( (T - T_c) \):

\[ (T - T_c) = \frac{P_c (X_i^N - X_i^I)}{\left( \frac{dP}{dT} \right)^{N_0} (1 - X_i^N) - \left( \frac{dP}{dT} \right)^{I_0} (1 - X_i^I)} \]  

(2.2.34)

We can simplify the denominator a bit if we remember that we are dealing with an ideally dilute solution. This means that the vapor pressure of the mixture is due almost entirely to
the liquid crystal, and not the impurity. In other words, $X^N_i, X^I_i \ll 1$:

$$ (T - T_c) = \frac{P_c (X^N_i - X^I_i)}{(\frac{dP}{dT})^N_{o} - (\frac{dP}{dT})^I_{o}} $$  \hfill (2.2.35)

Now in order to rewrite the derivatives in the denominator as something more manageable, we recall the Clapeyron equation derived in the previous section, equation 2.2.25. We apply it as two equations: one describing the transition from the isotropic phase into the gas phase, and the other from the nematic phase into the gas phase:

$$ \left( \frac{dP}{dT} \right)^{N_o} = \frac{\Delta H_{N\rightarrow Gas}}{T_c \Delta V} $$  \hfill (2.2.36)

$$ \left( \frac{dP}{dT} \right)^{I_o} = \frac{\Delta H_{I\rightarrow Gas}}{T_c \Delta V} $$  \hfill (2.2.37)

Now if we take the difference of equations 2.2.36 and 2.2.25, we get:

$$ \left( \frac{dP}{dT} \right)^{N_o} - \left( \frac{dP}{dT} \right)^{I_o} = \frac{\Delta H_{N\rightarrow Gas} - \Delta H_{I\rightarrow Gas}}{T_c V_{gas}} $$  \hfill (2.2.38)

We now note that the difference in the change in enthalpy between the nematic - gas phases and the isotropic - gas phases is the change in enthalpy between the nematic - isotropic phases.

We can use equation 2.2.38, despite the fact that it is for a one component system and we are analyzing a mixture, because the derivatives in equation 2.2.35 apply to the nematic and isotropic states of the pure liquid crystal, as indicated by the superscripts. So, plugging equation 2.2.38 into equation 2.2.35, we get:

$$ (T - T_c) = \frac{P_c T_c V_{gas} (X^N_i - X^I_i)}{\Delta H_{N\rightarrow I}} $$  \hfill (2.2.39)

We now remember that the two Clapeyron equations, as we defined them, were for transitions into the gas phase. And so, we can apply the ideal gas law to simplify the numerator and, finally obtain:

$$ (T - T_c) = \frac{RT^2 c (X^N_i - X^I_i)}{\Delta H_{N\rightarrow I}} $$  \hfill (2.2.40)
2.2.3 Measuring the Latent Heat of Transition

We now remember that the motivation for deriving the equations in the above sections was to be able to determine the amount of impurity in a given sample. In order to do that, we would want to measure the properties of several samples with known amounts of impurities so that we may relate those to a sample with an unknown amount of impurity. To this end, we make up several samples with known small quantities of impurity, so that we remain within the confines of ideally-dilute solutions, and we measure the transition temperature depression and the spread of the coexistence region. We plot this data in a graph similar to Figure 2.6.

We now want to rewrite equation 2.2.40 in such a way that we could use the temperature and impurity data to find the latent heat of transition, or $\Delta H_{N-I}$. Once we have found the latent heat for samples with a known amount of impurity, we can then use the latent heat to determine the amount of impurity in another sample by simply measuring its transition and coexistence temperatures.
To relate the data we can obtain from the figure to the derived equation 2.2.40 we begin by trying to express the amounts of impurity in either phase to the temperature. We can immediately write equations for the slopes of the two lines bounding the coexistence region.

\[ T = T_c + \alpha_N X \]  
\[ T = T_c + \alpha_I X \]  

(2.2.41)  
(2.2.42)

where \( \alpha_N \) and \( \alpha_I \) are the slopes of the nematic and isotropic bounding lines, respectively.

Now, by examining Figure 2.6 we notice that these slopes can also be written in terms of the changes in impurity mole fraction.

\[ \frac{\delta T}{a_{II}} = X_I - X_N \]  
\[ \frac{\delta T}{a_{NI}} = X_I - X_N \]  

(2.2.43)  
(2.2.44)

If we solve the above equations for the mole fractions, we can obtain the negative of the \( \Delta X \) in equation 2.2.40 and represent it as follows.

\[ X_i^N - X_i^I = -\frac{\delta T}{2} \left( \frac{1}{|\alpha_I|} + \frac{1}{|\alpha_N|} \right) \]  

(2.2.45)

We now notice, with another inspection of Figure 2.6, that the slopes of the bounding lines can be represented in terms of the changes in transition temperature.

\[ |\alpha_I| = \left( \Delta T - \frac{\delta T}{2} \right) \frac{1}{X} \]  
\[ |\alpha_N| = \left( \Delta T + \frac{\delta T}{2} \right) \frac{1}{X} \]  

(2.2.46)  
(2.2.47)

We now plug the above equations into equation 2.2.45 and rearrange the sum to obtain:

\[ X_i^N - X_i^I = -\frac{\delta T}{\Delta T^2 - \frac{\delta T^2}{4}} \]  

(2.2.48)

We can now plug this result into equation 2.2.40 which we have rearranged to solve for the latent heat.

\[ \Delta H_{N-I} = \frac{RT_e \delta T X}{\Delta T^2 - \frac{\delta T^2}{4}} \]  

(2.2.49)

Now we have obtained an equation that only depends on temperature, the latent heat of
transition, and the mole fraction of impurity. Armed with this we can measure the latent heat using a known amount of impurity and then determine the amount of impurity in another sample by measuring the drop in transition temperature and the spread of the coexistence region.

2.3 Optical Measurements

2.3.1 Jones Vectors

In order to conveniently represent the action of various optical components on a ray of light, matrix representation is used. To understand this, we must first consider the vector representation of a ray of light (Pedrotti and Pedrotti, 1993). Figure 2.7 depicts the propagation of electric and magnetic fields created by such a ray traveling in the z direction. The light depicted in this figure is y-polarized for representational convenience. However, let us now consider the general case of a ray of light of unknown polarization. To characterize the propagation of the light wave in vector form, we need only consider either the electric or magnetic component of the wave, since exact knowledge of one provides sufficient information for the characteristics of the other. To that end, and honoring convention, we express the electric field component, $\mathbf{E}$, of a light ray, as follows:

$$\mathbf{E} = \hat{i}E_x + \hat{j}E_y$$

where, $\hat{i}$ and $\hat{j}$ represent unit vectors in the Cartesian directions, $x$ and $y$, respectively. In this equation, the amplitude of the spatial components, $E_x$ and $E_y$, can be represented as follows:

$$E_x = E_{0x}e^{i[kz-\omega t+\epsilon_x]}$$

$$E_y = E_{0y}e^{i[kz-\omega t+\epsilon_y]}$$

where $\omega$ refers to the frequency of the wave and $k$ to the propagation constant. This propagation constant, also known as the wavenumber, is inversely proportional to the speed of light in vacuum, $c$, and directly proportional to $\omega$ in the following way:

$$k = \frac{\omega}{c}$$
Magnetic Field Vectors
propagating through space

Electric Field Vectors
propagating through space

Figure 2.7: Propagating Electromagnetic Wave

Since the only spatial dependence of the wave in equation 2.3.51 is with \( z \), this is a plane wave.

Now we can plug equation 2.3.51 into equation 2.3.50, and factor out the phase difference:

\[
\mathbf{E} = [iE_{0x} e^{(ix)} + jE_{0y} e^{(iy)}] e^{i(kz-\omega t)} = \mathbf{E}_0 e^{i(kz-\omega t)}
\]  

(2.3.53)

The vector \( \mathbf{E}_0 \) is called the *Jones vector*, and defined as follows

\[
\mathbf{E}_0 = \begin{bmatrix}
\hat{E}_{0x} \\
\hat{E}_{0y}
\end{bmatrix} = \begin{bmatrix}
E_{0x} e^{ix} \\
E_{0y} e^{iy}
\end{bmatrix}
\]  

(2.3.54)

We see that the electromagnetic wave can be written as the product of the Jones vector with a factor, varying sinusoidally in space and time:

\[
\mathbf{E} = \begin{bmatrix}
\hat{E}_{0x} \\
\hat{E}_{0y}
\end{bmatrix} e^{i(kz-\omega t)}
\]  

(2.3.55)

Note that the Jones vector describes the attributes of the propagating electric field with the amplitude and relative phases of its \( x \) and \( y \) components. For convenience, we now define
this relative phase as $\phi$:
\[
\phi = \epsilon_x - \epsilon_y
\]  \hspace{1cm} (2.3.56)

We now see that various types of light can be described easily using Jones vectors. The properties of some common and useful Jones vectors are described below:

- **Linearly Polarized Light**  \hspace{1cm} $\phi = 0^\circ \text{or} 180^\circ$  \hspace{1cm} $E_{0x}, E_{0y} \in \mathbb{R}$
- **Circularly Polarized Light**  \hspace{1cm} $\phi = 90^\circ$  \hspace{1cm} $E_{0x} = E_{0y}$  \hspace{1cm} (2.3.57)
- **Elliptically Polarized Light**  \hspace{1cm} $\phi \neq 0^\circ \text{or} 180^\circ$  \hspace{1cm} $E_{0x} \neq E_{0y}$

The convenience of Jones vectors becomes clear when they allow us to fulfill our original goal: to describe the action of various optical components on an electromagnetic wave. We can see that the action of any optical device will simply be the action of a matrix on the Jones vector, representing the incident light.

### 2.3.2 Index of Refraction

The index of refraction of a material, conventionally represented by the letter $n$, is defined as a ratio between the speed of light in vacuum, $c$, and the speed of light in that particular material, $v$ (Pedrotti and Pedrotti, 1993). This ratio, can also be related to the wavenumber, $k$, introduced in the previous section:

\[
n = \frac{c}{v} = \frac{ck}{\omega}
\]  \hspace{1cm} (2.3.58)

where $\omega$ is the angular frequency of the light. Based on this definition, it seems as though this would be a rather difficult quantity to measure, but this is not the case. The measurement can be done by using geometric optics.

Consider a wedge cell, such as the one represented in Figure 2.8. A monochromatic ray of light, produced by a laser, is sent through the liquid sample in the cell whose index of refraction we wish to know. We assume that the glass walls of the cell are thin enough so as not to significantly shift the path of the ray. We can now write down Snell’s Law to relate some of the angles in the figure:

\[
\sin \theta_1 = n \sin \theta_1'
\]  \hspace{1cm} (2.3.59)
Figure 2.8: The path of a ray of monochromatic light through a wedge cell, under the condition of minimum deviation of the light ray from its original path.

\[ n \sin \theta_2' = \sin \theta_2 \]  \hspace{1cm} (2.3.60)

where we assume that the index of refraction of air is 1. From geometry, we can be certain of the following relationships:

\[ \delta_1 = \theta_1 - \theta'_1 \]  \hspace{1cm} (2.3.61)
\[ \delta_2 = \theta_2 - \theta'_2 \]  \hspace{1cm} (2.3.62)
\[ \delta = \delta_1 + \delta_2 \]  \hspace{1cm} (2.3.63)
\[ \alpha = \theta'_1 + \theta'_2 \]  \hspace{1cm} (2.3.64)

where we have introduced the angle \( \delta \) (Figure 2.8), which is known as the deviation because it demonstrates the amount by which the presence of the wedge causes the path of the light ray to deviate from its original path. We can argue that when the angle \( \delta \) is minimized, the ray passes symmetrically through the prism (this is the special case that is depicted in Figure 2.8). The argument for why this must be true goes as follows. Suppose that the minimum deviation occurred when the incidence angle \( \theta_1 \) didn’t equal the exit angle \( \theta_2 \). By the principle of reversibility of light rays, if light were shined at the wedge at an angle equal to \( \theta_2 \), it would exit the wedge at an angle of \( \theta_1 \). In this case, the total deviation would be still be the same, and we would have to conclude that there are two angles which produce the same minimum deviation. This, however, is not true experimentally. Therefore, we must conclude that the minimum deviation occurs only when the incident angle equals the exit angle. This simplifies the above equations quite a bit, so that we have

\[ \alpha = 2\theta' \]  \hspace{1cm} (2.3.65)
Solving both of the above equations for $\theta'$ and $\theta$, respectively, we can plug the result into our version of Snell’s law, equation 2.3.59, and solve for $n$:

$$n = \frac{\sin \left( \frac{\theta + \delta}{2} \right)}{\sin \left( \frac{\theta}{2} \right)}$$

Thus, if the angle of the wedge cell is known, the index of refraction of the liquid sample can be obtained by measuring the minimum deviation angle of a monochromatic beam of light passing through it.

### 2.3.3 Absorption

A material is said to be transparent to a particular wavelength of electromagnetic radiation if radiation of that wavelength can pass through the material with little attenuation (Saleh and Teich, 1991). A material is said to be absorbing at a particular wavelength if an electromagnetic wave of that wavelength interacts with the material’s molecules or atoms in a way that decreases its intensity. A dielectric material that absorbs light in a particular range of the spectrum is said to have a complex electric susceptibility:

$$\chi = \chi_r + i\chi_i$$

The wavenumber, $k$, introduced in the previous section, can in general be represented in terms of this susceptibility, $\chi$:

$$k = \frac{\omega}{c} \sqrt{1 + \chi} = \frac{\omega}{c} \sqrt{1 + \chi_r + i\chi_i}$$

where $\omega$ is the frequency of the electromagnetic wave, and $c$ is the speed of light in vacuum. It is also useful to rewrite $k$ in terms of a real and imaginary part, where $a, b \in \mathbb{R}$, which we will for convenience define as follows:

$$k = b + i\frac{a}{2}$$
To do this we assume that the material is weakly absorbing, and so $\chi_i, \chi_r \ll 1$, and use the binomial approximation:

$$k = b + i \frac{a}{2} = \frac{\omega}{c} \left(1 + \frac{\chi_r}{2} + i \frac{\chi_i}{2}\right)$$

$$\therefore \ a = \frac{\omega \chi_i}{c}$$

(2.3.71) \hspace{1cm} (2.3.72)

Now, we see that we can rewrite the general equation for the propagation of an electromagnetic wave (equation 2.3.50) in these terms:

$$E = E_0 e^{ikz} = E_0 e^{-ibz} e^{-\frac{1}{2}a z}$$

(2.3.73)

where we have assumed a linearly polarized wave for simplicity. We now note that the intensity of an electromagnetic wave is equal to its magnitude in the following way:

$$I = |E|^2 = e^{-az}$$

(2.3.74)

From this we can see that the intensity of the light decreases as it propagates through this medium by the exponential factor given in equation 2.3.74. For this reason $a$, given by equation 2.3.72, represents an absorption coefficient. We can also rewrite $a$ in terms of the index of refraction, $n$, if we remember equation 2.3.58:

$$a = \frac{\chi_i k}{n}$$

(2.3.75)

When absorption is measured experimentally, however, what is actually recorded is the intensity of light that passes through a sample. In order to ensure that what one is calculating is actually the absorption of the sample and not the container or any of the optics, a ratio of is taken of the intensity of the light coming through the sample and that of light coming through an identical set up with a non absorbing material. We can thus define this measured absorption, $A$, as the logarithm of the intensity ratios, and relate it to the coefficient described above.

$$A = \log \frac{I_{reference}}{I_{sample}}$$

(2.3.76)

Now, plugging in the expressions for intensity from equation 2.3.74, we get:

$$A = \log \frac{1}{e^{-al}} = \frac{al}{2.3}$$

(2.3.77)
where \( l \) is the path length through the sample and the intensity of the light coming through the reference suffers no attenuation.

### 2.3.4 Birefringence

Birefringence is a property exhibited by an ordered material, whose index of refraction for light polarized along one of its axes is different from the index of refraction for light polarized along the axis perpendicular to it. For a uniaxial material, such as a nematic liquid crystal, this quantity is generally expressed as the difference between the two indices of refraction:

\[
\Delta n = n_\parallel - n_\perp
\]  

(2.3.78)

where \( n_\parallel \) is the index of refraction for light polarized parallel to the director, and \( n_\perp \) is the index of refraction for light polarized perpendicular to the director. Reasons why it is useful to measure this quantity will be discussed in a later section. However, it is important to note here that it is much easier to measure this quantity, \( \Delta n \) directly, rather than measuring the parallel and perpendicular indices of refraction separately.

Information about the birefringence, \( \Delta n \), can be obtained by measuring the change in the phase factors, \( \phi \), caused by passing light through a birefringent material. For example, let us imagine that a plate, of thickness \( d \), is placed in the \( x - y \) plane. Light, of wavelength \( \lambda_0 \), passes through this material, and obtains a phase factor, \( \epsilon \), based on the index of refraction of the material, \( n \):

\[
\epsilon = \frac{2\pi nd}{\lambda_0}
\]  

(2.3.79)

From this it is easy to see that, were a material to have two different indices of refraction, depending on the polarization of the incident light, a difference between these two might be calculated as follows:

\[
\epsilon_x - \epsilon_y = \frac{2\pi n_x d}{\lambda_0} - \frac{2\pi n_y d}{\lambda_0}
\]

\[
= \left( \frac{2\pi d}{\lambda_0} \right) (n_x - n_y)
\]

\[
= \frac{2\pi d}{\lambda_0} \Delta n
\]  

(2.3.80)
We now recall that we defined this very quantity, the phase difference \( \phi \), in equation 2.3.56

\[
\phi = \epsilon_x - \epsilon_y
\]

Now, plugging equation 2.3.56 into equation 2.3.80, we can solve for the birefringence in terms of the phase difference, as originally intended:

\[
\Delta n = \frac{\lambda_0 \phi}{2\pi d}
\]  (2.3.81)

Before we can enter into a discussion as to how to measure the phase difference \( \phi \), we must first consider a particular optical device discussed in the section below.

**Liquid Crystal as a Phase Retarder**

For the purposes of measuring birefringence, \( \Delta n \), it was assumed that a thin sample of liquid crystal acts entirely like an optical component called a *phase retarder*. A phase retarder is a device made of a substance that has different indices of refraction for light polarized in different orientations (parallel to one axis of the material vs. perpendicular to it). As a result, light that enters such a material without a phase difference between say the \( E_x \) and \( E_y \) components of the wave, will leave the material with some phase difference, \( \phi \). From this definition of a phase retarder, it is clear that a liquid crystal sample, which exhibits birefringence, will act as one.

Now, if the liquid crystal sample is oriented with the director parallel to the \( x \) or \( y \) axis, then it’s action as a phase retarder could be represented as the following matrix, acting on the Jones vector corresponding to this light:

\[
Pr = \begin{bmatrix}
\epsilon_x e^{i\epsilon_x} & 0 \\
0 & \epsilon_y e^{i\epsilon_y}
\end{bmatrix}
\]  (2.3.82)

where \( Pr \) is the phase retardation matrix, and \( \epsilon_x \) and \( \epsilon_y \) represent the phase factors added to the respective axis of the propagating wave. Another way to express this is in terms of the phase difference, \( \phi \), so that now, the phase retarding matrix becomes:

\[
Pr = e^{i\epsilon_x} \begin{bmatrix}
1 & 0 \\
0 & e^{-i\phi}
\end{bmatrix}
\]  (2.3.83)
However we will see shortly that it is important to consider what would happen to light incident on a sample whose director is at some angle, $\theta$, to the polarization of the light. To learn how this so called phase retarder plate would affect the incident light, we perform a change of basis to equation 2.3.83. We do so by applying a rotation matrix, $R$, to it:

$$R = \begin{bmatrix} \cos \theta & -\sin \theta \\ \sin \theta & \cos \theta \end{bmatrix} \quad (2.3.84)$$

The transformation of the phase retarding matrix becomes:

$$Pr(\theta) = \begin{bmatrix} \cos (\theta) & \sin (\theta) \\ -\sin (\theta) & \cos (\theta) \end{bmatrix} e^{i\kappa x} \begin{bmatrix} 1 & 0 \\ 0 & e^{-i\phi} \end{bmatrix} \begin{bmatrix} \cos (\theta) & -\sin (\theta) \\ \sin (\theta) & \cos (\theta) \end{bmatrix}$$

$$= e^{-i\kappa x} \begin{bmatrix} \cos^2 \theta + \sin^2 \theta e^{-i\phi} & \sin \theta \cos \theta - \sin \theta \cos \theta e^{-i\phi} \\ \sin \theta \cos \theta - \sin \theta \cos \theta e^{-i\phi} & \cos^2 \theta + \sin^2 \theta e^{-i\phi} \end{bmatrix} \quad (2.3.85)$$

Now, let us specifically consider a sample whose director is oriented at $45^\circ$ with respect to the $x$ axis. In the case that we are analyzing, this makes $\theta = 45^\circ$. Plugging into equation 2.3.85, and simplifying, we get

$$Pr(45^\circ) = e^{-i\kappa x} e^{-i\frac{\phi}{2}} \begin{bmatrix} \cos \left(\frac{\phi}{2}\right) & i \sin \left(\frac{\phi}{2}\right) \\ i \sin \left(\frac{\phi}{2}\right) & \cos \left(\frac{\phi}{2}\right) \end{bmatrix} \quad (2.3.86)$$

This equation predicts action of a phase retarding plate, oriented at $45^\circ$, on incident light. These concepts were used in designing experiments to measure the birefringence of a liquid crystal sample. The theoretical aspects of two such methods are described below.

**Microscope**

The optics used in the experimental set up discussed here were all part of a microscope arrangement and are depicted in Figure 2.9. The theory behind this measurement is as follows. Monochromatic light polarized along the $x$ axis is directed at a thin liquid crystal sample ($5-10 \mu m$ thick). The sample is oriented in such a way that the director of the liquid crystal is at a $45^\circ$ angle with respect to the incident light, in the $x-y$ plane. The sample now acts as a phase retarder on the incident light. Mathematically this can be represented
as the matrix derived in equation 2.3.86 acting on horizontally polarized light, characterized by a vector. The appropriate vector for horizontally polarized light is:

\[
E = \begin{bmatrix} 1 \\ 0 \end{bmatrix} \quad (2.3.87)
\]

This light, after it passes through the sample, will have been changed into:

\[
E = e^{-i\phi_E} e^{-i\phi} \begin{bmatrix} \cos \left( \frac{\phi}{2} \right) & i \sin \left( \frac{\phi}{2} \right) \\ i \sin \left( \frac{\phi}{2} \right) & \cos \left( \frac{\phi}{2} \right) \end{bmatrix} \begin{bmatrix} 1 \\ 0 \end{bmatrix} = e^{-i\phi_E} e^{-i\phi} \begin{bmatrix} \cos \left( \frac{\phi}{2} \right) \\ i \sin \left( \frac{\phi}{2} \right) \end{bmatrix} \quad (2.3.88)
\]

This light is then passed through a standard phase retarder, called a quarter wave plate, which adds a phase difference of $90^\circ$ between the $E_x$ and $E_y$ components of the light. The quarter wave plate is oriented in such a way that the axis along which light travels faster is aligned along the $x$ axis, parallel to the original polarizer. The action of such a phase
retarder on an incident wave can be expresses as follows:

\[ Pr(90°) = e^{-\frac{\pi}{4}} \begin{bmatrix} 1 & 0 \\ 0 & i \end{bmatrix} \]  
(2.3.89)

So the light incident on this optical piece has the properties described by equation 2.3.88, whereas the light coming out of the quarter wave plate has been affected as follows:

\[ E = e^{-i\xi_x} e^{-i\frac{\phi}{2} e^{-\frac{i\pi}{4}}} \begin{bmatrix} 1 & 0 \\ 0 & i \end{bmatrix} \begin{bmatrix} \cos \left( \frac{\phi}{2} \right) \\ i \sin \left( \frac{\phi}{2} \right) \end{bmatrix} = e^{-i\xi_x} e^{-i\frac{\phi}{2} e^{-\frac{i\pi}{4}}} \begin{bmatrix} \cos \left( \frac{\phi}{2} \right) \\ -\sin \left( \frac{\phi}{2} \right) \end{bmatrix} \]  
(2.3.90)

Now, we notice that the \( x \) and \( y \) components of the light wave coming out of the apparatus have the same phase. We also note that, since we began with polarized light and have done nothing to the amplitude since, that the amplitude of the \( x \) and \( y \) components of the wave are equal. Looking back to the guidelines for characterizing light set up in equation 2.3.57, we see that the result is linearly polarized light at an angle equal to \( \frac{\phi}{2} \). This angle can be easily found by measuring the angle at which a polarizer extinguishes this light. Having found \( \phi \), we simply plug it into equation 2.3.81, and we have measured birefringence.

**Optical Table**

The second method for measuring birefringence utilizes a set-up constructed on an optical table. The placement of each of the pieces is depicted in Figure 2.10. Once again, in this method we begin with light polarized in the \( x \) direction:

\[ E = \begin{bmatrix} 1 \\ 0 \end{bmatrix} \]  
(2.3.91)

This light is then incident upon a thin liquid crystal sample, as before. The difference comes in the fact that the sample now rotates through various orientation angles, \( \theta \), from \( 0° \) to \( 180° \). Now the light coming out from this sample will have been acted upon by the matrix
Figure 2.10: Pictorial representation of the optical components of the optical table set up in equation 2.3.85:

\[
E = e^{-i\phi} \begin{bmatrix}
\cos^2 \theta + \sin^2 \theta e^{-i\phi} & \sin \theta \cos \theta - \sin \theta \cos \theta e^{-i\phi} \\
\sin \theta \cos \theta - \sin \theta \cos \theta e^{-i\phi} & \cos^2 \theta + \sin^2 \theta e^{-i\phi}
\end{bmatrix} \begin{bmatrix} 1 \\
0
\end{bmatrix}
\]

(2.3.92)

This light is then sent through a horizontal polarizer, which has the following matrix representation:

\[
\text{H-Pol.} = \begin{bmatrix} 1 & 0 \\
0 & 0 \end{bmatrix}
\]

(2.3.93)

Applying this matrix to the vector representing the incident light, we get:

\[
E = e^{-i\phi} \begin{bmatrix} 1 & 0 \\
0 & 0 \end{bmatrix} \begin{bmatrix} \cos^2 \theta + \sin^2 \theta e^{-i\phi} \\
\sin \theta \cos \theta(1 - e^{-i\phi}) \end{bmatrix}
\]
Equation 2.3.94 gives us all of the information about the light coming out of this apparatus. From this information, we can easily figure out what the intensity of this light should be:

\[
I(\theta) = |E_x|^2 + |E_y|^2
\]

\[
= \cos^4 \theta + \sin^4 \theta + 2 \sin^2 \theta \cos^2 \theta \cos \phi
\]

Thus, if we want to calculate the phase difference, \(\phi\), in order to find the birefringence, all we have to do is measure the intensity of the light exiting the set up, as a function of \(\theta\), and fit it to equation 2.3.95, with \(\phi\) as one of the parameters. Then, as with the microscope experiments, we can plug the value for \(\phi\) into equation 2.3.81 to obtain the birefringence of the sample.

### 2.3.5 Order Parameter

#### Derivation of an Expression for Order Parameter

The order parameter is a measure of orientational order in a substance (Collings and Hird, 1997). For example, when all of the molecules in a substance are perfectly aligned, such as in a solid, the order parameter should be 1. Likewise, in a liquid, where molecules tend to be randomly oriented with respect to each other, the order parameter should be 0. In a liquid crystal, where the molecules tend to align along an axis, the parameter should be somewhere in between these two extremes. It is easy to imagine that the macroscopic anisotropy of a substance can originate with the molecular anisotropy. We can think about relating the macroscopic anisotropy with the molecular anisotropy by considering how the molecular contributions add together. For example, a molecule may have a larger induced magnetic moment if the magnetic field is aligned along certain bonds of the molecule rather than perpendicular to them. So if most of the molecules in a bulk sample are aligned with the magnetic field, the sample’s interaction with the field will be different than if there is little tendency for the molecules to align. To asses this further and more mathematically, imagine a coordinate system that is attached to a molecule. Now, if we choose a molecular...
tensor property $T$, such as the induced electric or magnetic dipole moment, we can also choose a coordinate system in which this tensor is diagonal:

$$
T = \begin{bmatrix}
T_{xx} & 0 & 0 \\
0 & T_{yy} & 0 \\
0 & 0 & T_{zz}
\end{bmatrix}
$$

Let us imagine that the $z$ axis is along the long axis of the molecule (Figure 2.11). We consider the general case where the molecule is not aligned perfectly with the director, which we will say points in the $\hat{n}$ direction. The relationship between the $z$ axis of the molecule and the director is rotation by an angle $\theta$. Let us also define a coordinate system for the director (the $\hat{n}$ direction being the $z'$ axis). To keep things completely general, we rotate the other axes of the director coordinate system by an angle $\phi$ from the molecule coordinate system and call them $x'$ and $y'$ (Figure 2.11).

With these definitions we can now see how this one molecule contributes to the bulk tensor property of the material. We do so by performing a coordinate transformation from the tensor $T$ into the $T'$ basis. This is done as in the previous section, by performing two
rotations: one about the $z$ axis by an angle $\phi$, and the other about the $y$ axis by angle $\theta$.

$$\mathbf{T}' = R_y(\theta) \left[ R_z(\phi) \mathbf{T} R_z^t(\phi) \right] R_y^t(\theta)$$  \hspace{2cm} (2.3.97)

Where $R_z(\phi)$ is the rotation about the $z$ axis by angle $\phi$ given by

$$R_z(\phi) = \begin{bmatrix} \cos(\phi) & \sin(\phi) & 0 \\ -\sin(\phi) & \cos(\phi) & 0 \\ 0 & 0 & 1 \end{bmatrix}$$ \hspace{2cm} (2.3.98)

and $R_z^t(\phi)$ is it’s transpose. Likewise the rotation about the $y$ axis is given by:

$$R_y(\theta) = \begin{bmatrix} \cos(\theta) & 0 & -\sin(\theta) \\ 0 & 1 & 0 \\ \sin(\theta) & 0 & \cos(\theta) \end{bmatrix}$$ \hspace{2cm} (2.3.99)

Performing this operation on $\mathbf{T}$ produces 9 very lengthy matrix elements, all of which will be omitted here except for the diagonal entries, summarized in the equation bellow:

$$T_{x'x'} = T_{xx} \cos^2(\theta) \cos^2(\phi) + T_{yy} \cos^2(\theta) \sin^2(\phi) + T_{zz} \sin^2(\theta)$$

$$T_{y'y'} = T_{xx} \sin^2(\phi) T_{yy} \cos^2(\phi)$$ \hspace{2cm} (2.3.100)

$$T_{z'z'} = T_{xx} \sin^2(\theta) \cos^2(\phi) + T_{yy} \sin^2(\theta) \sin^2(\phi) + T_{zz} \cos^2(\phi)$$

If we sum up these components of the diagonal and obtain the trace of the tensor, we see that it was invariant under rotation. In other words

$$Tr(\mathbf{T}) = Tr(\mathbf{T}') = T_{xx} + T_{yy} + T_{zz}$$

Now anisotropy on the macroscopic level is defined as:

$$\Delta T' = T'_{z'z'} - \frac{1}{2} (T'_{x'x'} + T'_{y'y'})$$ \hspace{2cm} (2.3.101)

The definition implies that anisotropy is the difference in properties between one axis and the average of the properties along the other two axes. We can then rewrite the above equation
in terms of the trace of $T'$ by simply adding and subtracting $\frac{1}{2}T'_{z'z'}$:

$$\Delta T' = \frac{3}{2}T'_{z'z'} - \frac{1}{2}\text{trace}(T')$$  \hspace{1cm} (2.3.102)

We now express the macroscopic anisotropy (equation 2.3.102) in terms of the microscopic components. The trace of the tensors in the two bases is the same and we get the $T'_{x'x'}$ component from equation 2.3.100. The anisotropy can now be written as:

$$\Delta T' = \left(\frac{3}{2}\sin^2 \theta \cos^2 \phi - \frac{1}{2}\right)T_{xx} + \left(\frac{3}{2}\sin^2 \theta \sin^2 \phi - \frac{1}{2}\right)T_{yy} + \left(\frac{3}{2}\cos^2 \theta - \frac{1}{2}\right)T_{zz}$$  \hspace{1cm} (2.3.103)

Now we are almost ready to write an expression for the order parameter. First, we must notice that since we have a uniaxial liquid crystal, it should only have one unique axis by definition. Therefore $T'_{xx} = T'_{yy}$. Also, since molecules are always moving around, we are more interested in the average anisotropy rather than that of one molecule. By convention, the average of a quantity is denoted by angular brackets. We define two order parameters, $S$ and $D$, and rewrite the anisotropy in terms of them:

$$S = \left\langle\frac{3}{2}\cos^2 \theta - \frac{1}{2}\right\rangle$$  \hspace{1cm} (2.3.104)

$$D = \left\langle\frac{3}{2}\sin^2 \theta \sin^2 \phi - \frac{1}{2}\right\rangle - \left\langle\frac{3}{2}\sin^2 \theta \cos^2 \phi - \frac{1}{2}\right\rangle$$  \hspace{1cm} (2.3.105)

$$\langle\Delta T\rangle = \left[T_{zz} - \frac{1}{2}(T_{xx} + T_{yy})\right]S + \frac{1}{2}(T_{yy} - T_{xx})D$$  \hspace{1cm} (2.3.106)

For many molecules, $(T_{yy} - T_{xx})$ is quite small, especially compared to $[T_{zz} - \frac{1}{2}(T_{xx} + T_{yy})]$. Also, it has been shown experimentally that $D \ll S$, and so from now we concern ourselves only with the order parameter, $S$, defined in equation 2.3.104.

We now check if the expression we derived for the order parameter, $S$ makes sense. Specifically, if all the molecules in a sample are perfectly aligned, then the average angle by which they are rotated from the director is 0, giving $\cos \theta = 1$, and overall $S = 1$. This is exactly the result that we stated, $a$ priori, at the beginning of this section. So what do we get for $S$ if there is perfect disorder? To figure this out, we need to average all the random molecular orientations over all solid angle. So we integrate the distribution function, denoted as $\text{Dis}($θ$)$, times our expression for S. The distribution function, however, is constant over $\theta$
because all molecular orientations are considered. So now our integral becomes:

$$\langle S \rangle = Dis \int_0^\pi \left( \frac{3}{2} \cos^2 \theta - \frac{1}{2} \right) \sin \theta \, d\theta \int_0^{2\pi} d\phi$$  \hspace{1cm} (2.3.107)

This, in fact, does integrate to 0. Once again we obtain the result we desire, which is that the order parameter of a completely disordered system is 0.

**Measurement of Order Parameter**

The order parameter, $S$, can in theory be obtained through measurement of any macroscopic property that displays an anisotropy in the liquid crystal (Collings et al., 2003). In this work, $S$ is measured by comparing the absorption of light polarized along the director and perpendicular to it. In order to do this we consider a set-up where the general tensor, $T$, is now the absorption portion of the electric susceptibility tensor, $\chi_i$ (as derived with equation 2.3.72). When considering this special case, we begin by making several assumptions. First of all, we assume that the only absorbing bonds in the liquid crystal molecules are those that are along its long axis, or the $z$ axis. Thus, in the molecular coordinate basis:

$$T_{yy} = T_{xx} = 0$$  \hspace{1cm} (2.3.108)

This means that equation 2.3.106 now becomes:

$$\langle \Delta T' \rangle = T_{zz} S$$  \hspace{1cm} (2.3.109)

Setting this equal to the definition of anisotropy, given by equation 2.3.101, we get:

$$\langle \Delta T' \rangle = T_{zz} S = T_{zz}' - \frac{1}{2}(T_{xx}' + T_{yy}')$$  \hspace{1cm} (2.3.110)

The above assumption also implies that the trace of the tensor in the molecule’s basis is simply equal to $T_{zz}$, and since the trace is invariant under rotation, the following relationship is obtained:

$$Tr(T) = Tr(T') = T_{zz}$$  \hspace{1cm} (2.3.111)

Now we make another assumption, namely that since this liquid crystal is uniaxial, in
the macroscopic basis, the two directions perpendicular to the director are equivalent:

\[ T''_{yy} = T''_{xx} \]  

(2.3.112)

Putting this all together we can now write two equations:

\[ T''_{zz} - T''_{xx} = T_{zz} S \]  

(2.3.113)

\[ T''_{zz} + 2T''_{xx} = T_{zz} \]  

(2.3.114)

By adding and subtracting these equations we get the following expressions:

\[ T''_{zz} = \frac{(1 + 2S)}{3} T_{zz} \]  

(2.3.115)

\[ T''_{xx} = T''_{yy} = \frac{(1 - 2S)}{3} T_{zz} \]  

(2.3.116)

We can now arrange these in matrix form:

\[
\begin{bmatrix}
  \frac{(1-S)}{3} & 0 & 0 \\
  0 & \frac{(1-S)}{3} & 0 \\
  0 & 0 & \frac{(1+2S)}{3}
\end{bmatrix}
T_{zz}
\]  

(2.3.117)

Now, since we had originally set out to describe the absorption of light, we rewrite this in terms of the absorption tensor:

\[
\begin{bmatrix}
  \frac{(1-S)}{3} & 0 & 0 \\
  0 & \frac{(1-S)}{3} & 0 \\
  0 & 0 & \frac{(1+2S)}{3}
\end{bmatrix}
\chi_i
\]  

(2.3.118)

Using this matrix, we can now derive an expression for the order parameter, S, in terms of the electric susceptibility of the molecule. We write a set of equations similar to equations 2.3.113 and 2.3.114:

\[ \chi'_{i,zz} - \chi'_{i,xx} = \left( \frac{1 + 2S}{3} - \frac{1 - S}{3} \right) \chi_i \]  

(2.3.119)

\[ \chi'_{i,zz} + 2\chi'_{i,xx} = \left( \frac{1 + 2S}{3} + \frac{2 - 2S}{3} \right) \chi_i \]  

(2.3.120)
These can then be simplified into the following forms:

\[ \chi'_{i,zz} - \chi'_{i,xx} = S \chi_i \]  \hspace{1cm} (2.3.121)\\

\[ \chi'_{i,zz} + 2\chi'_{i,xx} = \chi_i \]  \hspace{1cm} (2.3.122)

Now dividing equation 2.3.121 by equation 2.3.122, we get an expression for \( S \) that is completely in terms of the bulk properties of the sample:

\[ S = \frac{\chi'_{i,zz} - \chi'_{i,xx}}{\chi'_{i,zz} + 2\chi'_{i,xx}} \]  \hspace{1cm} (2.3.123)

However, the above expression is in terms of the imaginary part of the electric susceptibility, not an easy quantity to measure. But, if we rewrite it in terms of the absorption coefficient, according to equation 2.3.75, we get:

\[ S = \frac{a_{zz} n_{zz} - a_{xx} n_{xx}}{a_{zz} n_{zz} + 2a_{xx} n_{xx}} \]  \hspace{1cm} (2.3.124)

We now note that, based on the way our axes are defined (Figure 2.11), we can call the \( zz \) component one that is parallel to the director and the \( xx \) component one that is perpendicular to it, rewriting the above equation as follows:

\[ S = \frac{a_{||} n_{||} - a_{\perp} n_{\perp}}{a_{||} n_{||} + 2a_{\perp} n_{\perp}} \]  \hspace{1cm} (2.3.125)

Finally, looking back at equation 2.3.77 we see that we can rewrite equation 2.3.125 in terms of absorption that can be measured.

\[ S = \frac{A_{||} n_{||} - A_{\perp} n_{\perp}}{A_{||} n_{||} + 2A_{\perp} n_{\perp}} \]  \hspace{1cm} (2.3.126)

where we have assumed that the path lengths for all the measurements are identical. Thus we conclude that the order parameter can be measured quite simply by knowing the absorption of the sample for light polarized along the director axis and for light polarized perpendicular to the director, provided that the two corresponding indices of refraction are also known.
Chapter 3

Methods and Results

3.1 Irradiation Experiments in Solution

As discussed in Section 2.1.3, the liquid crystal ZhK 440 undergoes a conformational change when exposed to light of a wavelength that it absorbs. In order to better study this property, a series of experiments were carried out in solution in order to isolate this specific effect from the complexities of the liquid crystal phase. To this end, a solution of 0.3104mM ZhK 440 in methanol was made. All of the experiments described in this section were carried out on samples obtained from this stock solution.

3.1.1 Absorption

The first step in studying this material was to obtain a spectra of the sample in solution. This solution was then kept in the dark overnight to ensure maximum concentration of the trans isomer. A spectrum was then recorded on this sample, in a quartz cuvette, using a Jastro 500 UV-Vis spectrophotometer. The resultant spectrum over relevant wavelengths is displayed in Figure 3.1. The peak absorption was measured to be at 341nm, and the second, smaller peak at 238nm. It was also noted that the sample has some absorption in the visible and near visible part of the spectrum. Therefore, care was taken from then on to maintain the sample in complete darkness at all times to ensure maximization of the trans isomer. Likewise, all subsequent experiments were carried out entirely in the dark.
Figure 3.1: Absorption spectra of a 0.3104mM solution of liquid crystal ZhK 440 in methanol, in a 1cm path length cuvette.

Figure 3.2: Absorption at 341nm of a 0.3104mM solution of liquid crystal ZhK 440 in methanol, taken over the course of 10,000 seconds.
Table 3.1: Relative intensities, at various wavelengths and distances, of the Hg lamp used in irradiation experiments.

<table>
<thead>
<tr>
<th>Wavelengths (nm)</th>
<th>313</th>
<th>335</th>
<th>366</th>
<th>405</th>
<th>436</th>
</tr>
</thead>
<tbody>
<tr>
<td>Distance from Lamp</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10cm</td>
<td>0.783</td>
<td>0.562</td>
<td>4.540</td>
<td>2.339</td>
<td>4.274</td>
</tr>
<tr>
<td>15cm</td>
<td>0.562</td>
<td>0.807</td>
<td>3.870</td>
<td>1.841</td>
<td>3.460</td>
</tr>
</tbody>
</table>

At this point it was necessary to determine whether the light source in the UV-Vis spectrophotometer was powerful enough to induce conformational change during measurement. To establish this, the ZhK 440 sample in methanol was placed into the spectrophotometer and an absorption measurement was taken at the peak wavelength of 341nm for 10,000 seconds (2 hours 46 min 40 sec), Figure 3.2. As the curve fit demonstrates, the slope of the line over this time period is very small, $-9.209 \times 10^{-8}$ Abs sec$^{-1}$. Thus, while the effect of the spectrophotometer light source is real and measurable, it was ignored for the remainder of the experiments with confidence since all subsequent measurement times were much shorter.

### 3.1.2 Irradiation Experiments

A series of experiments was carried out in order to determine the sensitivity of the trans-cis isomerization to various wavelengths that could be obtained from a mercury lamp light source. The mercury lamp light output was measured with a spectrophotometer and the relative intensities at the various wavelengths are recorded in Table 3.1. As a reference, the lamp was also placed in front of an optical photometer (Newport, model 835) to determine the actual intensity of the light for the wavelengths in the visible range. The 405nm line, at a distance of 10cm, had an intensity of 3.33 mW/cm$^2$ and the 436nm line, at a distance of 10cm had an intensity of 7.24 mW/cm$^2$. When the actual experiments were carried out, a filter was placed in front of the UV lamp so that only the light of the desired wavelength passed to the sample. The filters for 335nm, 366nm, 405nm, and 436nm light passed 41%, 34%, 44%, and 51% of the light respectively.

The irradiation experiments were conducted by placing the same solution of 0.3104mM ZhK 440 in methanol, in a quartz cuvette. A spectrum of the solution was recorded and
the absorption intensity at the maximum noted. The cuvette was then placed 10cm away from the mercury lamp. Between the mercury lamp and sample, was a filter of the desired wavelength. The sample was thus irradiated for 30 seconds. At that time it was quickly placed in the spectrophotometer, and another spectrum was recorded in order to monitor any conformational change that might have taken place. This procedure was then repeated until the spectra remained unchanged as a result of further irradiation. Figure 3.3 depicts the spectrum of the original, maximally trans isomer, superimposed with the spectrum of the maximal cis isomer that could be obtained using this method. The figure demonstrates a significant decrease in absorption at the peak wavelength of 341nm, and an increase in absorption at the secondary peak of 238nm in the cis spectra. Thus the relative amounts of cis created due to irradiation could be monitored by noting the intensity of the main absorption peak at 341nm.

The experiment described above was carried out multiple times, once for each of the wavelengths listed in Table 3.1. This was done in order to determine which wavelengths of light were most efficient at promoting the trans-cis isomerization. However, the data for irradiation with 313nm light had to be omitted since it seems that light that energetic was decomposing the sample, as was evidenced by significant and irreversible spectral changes.
Figure 3.4: Summary of irradiation experiments conducted at different wavelengths. The decaying exponentials (lines drawn in to assist the eye) represent excitations of trans to cis. The growing exponentials represent de-excitations of cis to trans.

upon irradiation with it. The absorption at 341nm, resulting from excitations with different wavelengths, were plotted vs. time (Figure 3.4). From this plot it is evident that the two excitation wavelengths that were closest to the main absorption peak, 366nm and 335nm, were the best at promoting the trans to cis isomerization. On the other hand, the two excitation wavelengths that were quite far from the main peak, at 405nm and 436nm, promoted practically no conversion to the cis isomer.

Next, the reverse process, de-excitation from cis to trans isomer, was attempted. In order to do this, the sample of ZhK 440 in methanol was subjected to several minutes of irradiation at 366nm, since that was the most effective wavelength at promoting trans to cis isomerization. A spectrum was then recorded to ensure that the sample had reached maximal conversion. Once this was established, the filter on the lamp was changed to one of the three wavelengths to be used in de-excitation, 335nm, 405nm, or 436nm. The experiments were then carried out in the same fashion as those described earlier for the forward direction. A summary of the absorption intensities at the peak absorption of 341nm is depicted in
Table 3.2: Raw data used to calculate the fraction of sample converted to cis isomer upon irradiation with a particular wavelength.

<table>
<thead>
<tr>
<th>$\lambda$ (nm)</th>
<th>$A_t^{\text{irr}}$</th>
<th>$A_{\text{infinity}}^{\text{irr}}$</th>
<th>$A_t^{\text{peak}}$</th>
<th>$A_{\text{infinity}}^{\text{peak}}$</th>
<th>$\delta$</th>
<th>$\Delta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>335</td>
<td>0.672 ± .001</td>
<td>0.501 ± .009</td>
<td>0.703 ± .001</td>
<td>0.512 ± .009</td>
<td>-0.2545 ± .0004</td>
<td>-0.191 ± .009</td>
</tr>
<tr>
<td>366</td>
<td>0.524 ± .001</td>
<td>0.394 ± .002</td>
<td>0.691 ± .001</td>
<td>0.483 ± .001</td>
<td>-0.2481 ± .0005</td>
<td>-0.208 ± .001</td>
</tr>
<tr>
<td>405</td>
<td>0.030 ± .001</td>
<td>0.041 ± .002</td>
<td>0.695 ± .001</td>
<td>0.681 ± .001</td>
<td>0.37 ± .01</td>
<td>-0.014 ± .005</td>
</tr>
</tbody>
</table>

Table 3.3: Result of calculation of the fraction of the sample converted to cis isomer upon irradiation with a particular wavelength (irr2).

<table>
<thead>
<tr>
<th>$\alpha_{\text{irr1}=405}$ $\text{irr2}=335$</th>
<th>$\alpha_{\text{irr1}=405}$ $\text{irr2}=366$</th>
<th>$\alpha_{\text{irr1}=335}$ $\text{irr2}=405$</th>
<th>$\alpha_{\text{irr1}=366}$ $\text{irr2}=405$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.47 ± .02</td>
<td>0.47 ± .01</td>
<td>0.03 ± .01</td>
<td>0.03 ± .01</td>
</tr>
</tbody>
</table>

Figure 3.4. From this figure it is evident that the less energetic wavelengths could be used to revert the sample to higher concentrations of trans isomer. However, it does not seem that either 405nm or 436nm light brings the sample to the same concentration of trans/cis isomer, regardless of direction of excitation. One can also notice that the 335nm and 366nm light bring the sample to such a similar state, that distinguishing between the concentrations that these two wavelengths promote might not be possible with the techniques employed.

3.1.3 Calculation of Cis Isomer Yield

Since a spectrum like the one displayed in Figure 3.3 was recorded after each 30 second interval of irradiation at each wavelength, the calculations described in Section 2.1.4 could be carried out in order to determine the yield of cis isomer upon irradiation. The final equation derived in that section, equation 2.1.16, calls for absorptions at photo-stationary states. These values were obtained by exponentially curve-fitting absorptions as functions of time in a way similar to Figure 3.4. These data are displayed in Table 3.2.

The fraction of the sample converted to cis isomer upon irradiation with 405nm light was calculated using both 335nm and 366nm as reference wavelengths. However, 335nm was
Table 3.4: Indices of refraction data for different wavelengths.

<table>
<thead>
<tr>
<th>Laser Wavelength</th>
<th>633nm</th>
<th>543nm</th>
<th>488nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n_\parallel$</td>
<td>1.78 ± 0.03</td>
<td>1.88 ± 0.03</td>
<td>1.95 ± 0.03</td>
</tr>
<tr>
<td>$n_\perp$</td>
<td>1.52 ± 0.02</td>
<td>1.62 ± 0.03</td>
<td>1.67 ± 0.03</td>
</tr>
</tbody>
</table>

not used as a reference wavelength for 366nm because the data obtained for irradiation with these two wavelengths are too similar to be useful. Likewise, 366nm data were not used to calculate the fraction converted to cis upon irradiation with 334nm light for the same reason. The final result of the calculations is displayed in Table 3.3.

3.2 Optical and Physical Measurements on the Liquid Crystal Phase

3.2.1 Measuring the Indices of Refraction

Section 2.3.2 describes a process for measuring the index of refraction of a sample in a wedge cell. Just such a cell was made to measure the parallel and perpendicular indices of refraction of ZhK 440 in the liquid crystal phase. The wedge cell was constructed by gluing two square pieces of glass at one end, and spacing them with a microscope cover before gluing, at the other end. The glass for the cell was thoroughly rubbed with felt prior to being glued,
in order to ensure alignment of the liquid crystal within the cell. However, before the cell could be filled and the measurement made, the angle of the wedge had to be determined. This was done by shining a laser at the cell and recording the difference in the light reflected off both surfaces of the wedge (Figure 3.5). The cell was then filled with the liquid crystal ZhK 440 sample and heated past the phase transition in order to increase sample alignment. The measurement was made after the sample cooled to room temperature and it had been established that it was sufficiently aligned by observing it under the microscope. Laser light was then used to find the angle of minimum deviation for two light polarizations and both the parallel and perpendicular indices of refraction were calculated, according to the method described in Section 2.3.2.

The measurements were done using laser light of three different wavelengths, Table 3.4. These wavelengths were chosen because the sample does not absorb light in that region, and so would not isomerize during the data collection. Data at multiple wavelengths were needed because the indices of refraction used to calculate order parameter, were needed at different wavelengths. Thus the indices of refraction at multiple wavelengths could be used to determine the dependence of the indices of refraction on wavelength, so that they could be extrapolated to the wavelength which was used to measure order parameter. The data obtained are displayed in Table 3.4. The small error, lack of overlap, and the relative sizes of these two numbers (i.e. the parallel index of refraction is greater than the perpendicular index) are good indications that they are trustworthy.

### 3.2.2 Birefringence Experiments

As mentioned in Section 2.3.4, two different experiments were carried out to study the birefringence - one using a modified microscope and the other one using an optical table. Using these two methods, birefringence was measured over a range of temperatures, starting at 25°C to the isotropic phase at roughly 71°C. This was done by placing the sample on a heating stage that allowed for constant and precise temperature monitoring. Both experiments were run on a liquid crystal ZhK 440 sample that was between two surfactant-treated, glass plates that ensured alignment in the nematic phase. The plates formed a cell that was approximately 5μm thick, the exact width of which was measured optically. The calculations of the birefringence were carried out according to the methods specified in Section 2.3.4. In the microscope experiments, the light source was simply a white light lamp, with a 633nm filter placed over it. On the optical table, a He-Ne 633nm laser was employed. The data
from the two measurements were then compared and plotted, Figure 3.6. Due to significant overlap of the data displayed, it can be safely concluded that both experimental techniques are valid, and that the data are reliable.

### 3.2.3 Order Parameter Measurements

The order parameter was measured for the liquid crystal ZhK 440 over the same temperature range as the birefringence, using a temperature controlled stage for the sample. The calculation was conducted according to equation 2.3.126, derived in section 2.3.5. This formula calls for two types of information: indices of refraction and absorption. The indices of refraction were measured as described earlier, and extrapolated to the appropriate wavelength. Then, the birefringence measured as a function of temperature in the previous section was used to determine the temperature dependence of these indices of refraction. The absorption measurements were carried out an a microscope adapted for that purpose. The sample was placed in a cell of appropriate thickness, and onto a carefully monitored heating stage. In order to measure absorption of monochromatic light, a filter of the desired
wavelength was placed over the white light source of the microscope. The light was then sent through a polarizer so that a distinction could be made between absorption of light parallel to the director versus that of light perpendicular to the director. The microscope was then brought into focus, and the cell was aligned such that its director was either parallel or perpendicular to the polarizer, as desired. The final adjustment to the microscope was the placement of an optical power meter (Newport, Model 1815-C) over one of the eye pieces. This power meter measured the intensity of light transmitted. The light intensity was then converted to absorption using the relationship for absorption, obtained in equation 2.3.76:

\[ A = \log \left( \frac{I_{\text{reference}}}{I_{\text{sample}}} \right) \]  

(3.2.1)

where A is absorption, \( I_{\text{sample}} \) is the intensity of light passed by the sample, and \( I_{\text{reference}} \) is the intensity of light passed by a non-absorbing reference sample in an identical cell. This was the general method for obtaining all of the necessary data to measure order parameter.

The order parameter measurements were conducted in two ways, to ensure reliability of the data. The first of the two types of experiments, absorption was measured directly on the sample. A 25\( \mu \)m, surfactant-treated glass cell was filled with the liquid crystal ZhK 440.
The white light of the microscope lamp was covered with a 436nm filter. This wavelength was selected because this light has enough energy to be weakly absorbed by the ZhK 440, but not enough to induce conformational change in a significant number of the molecules. In order to increase absorption by the sample, and thus decrease percent error, the thicker cell was picked for these measurements. The reference chosen for these measurements was a non-absorbing liquid crystal known as 5CB.

The second method employed to measure the order parameter involved using a mixture of the dye Disperse Red 1 with the sample of ZhK 440 (where the dye concentration by weight was <5%). The presence of the dye was small enough, and it itself was similar enough in structure to the sample (Figure 3.8) that it was assumed it did not disturb the packing of the liquid crystal. It was also assumed that the dye reflected the alignment tendency of the liquid crystal sample. Its absorbance maximum was at 488nm, well out of the absorption spectra of ZhK 440. Since this dye was much more absorbing in the visible than the ZhK 440 liquid crystal, the measurements could be carried out on a 5μm cell. A pure sample of ZhK 440 was used as the reference for these experiments.

The absorption data were then plugged into equation 2.3.126 and the order parameter, S, was also plotted for easier comparison of the two methods (Figure 3.7). The agreement between these two experimental methods was not as exact as expected. It is interesting to note, however, that the agreement between the two values increases with temperature. This will be discussed later in greater detail.

### 3.2.4 Determination of the Latent Heat of Transition

As discussed in Section 2.2.3, it is possible to measure the latent heat of transition by learning how the transition temperature responds to impurities within the sample. According to equation 2.2.49 in that section, the information necessary for this type of calculation is the drop of the average transition temperature, \( \Delta T \), and the spread of the coexistence region, \( \delta T \), due to impurities present in a sample. To this end, three mixtures were created, with
trace but different amounts of impurity in order to find exactly this kind of information. The impurity used was a compound called triphenylene (Figure 3.9), with molecular weight of 228.29 g/mol, which is comparable to that of the two compounds in ZhK 440. The boundaries of the coexistence regions were found by placing the sample in a 5μm cell. The cell was then placed on a very precise heating stage, in a microscope, and heated to several degrees below the expected lower bound of the transition temperature. Subsequently, the temperature was ramped, very slowly (0.03°C/min to 0.05°C/min). The sample was constantly observed and the temperature noted at the first sign of coexistence and its last remnant. The sample was then heated to several degrees above the coexistence region, and the procedure was conducted in reverse, by slowly cooling and noting the temperature boundaries of the coexistence region this way. This was done to account for any lag between the heating stage thermometer and sample. The values obtained in heating and cooling were averaged to give each boundary of the coexistence region.

The data from these experiments are summarized in Table 3.5 and plotted in Figure 3.10. The average latent heat is 5.1±.2 cal/mol. As shown, only very small amounts of impurity were used, in order to ensure the validity of the ideally-dilute solution approximation. However, the small quantities used and the difficulty of measuring them properly were in part responsible for the large error.
Figure 3.10: Plot of impurity (triphenylene) mole fraction vs. the nematic-isotropic transition temperature (°C) for ZhK 440. (Error bars are obscured by the size of points).
3.3 Irradiation Experiments in the Liquid Crystal Phase

The final endeavor of this project was to demonstrate the effect of irradiation on the sample in the liquid crystal phase. To this end, several experiments were conducted, using the tools developed for the previous experiments and the data obtained therein.

3.3.1 Birefringence of Impure Mixtures

Initially, the birefringence of the mixtures with triphenylene impurity were measured for comparison purposes. This was done on the assumption that the birefringence was affected by a non liquid crystalline impurity in general, with the decrease not specific to the nature of that impurity. Thus it was hoped that the amount of cis isomer created in a pure sample upon irradiation could be determined by comparing it to the birefringences of the triphenylene impurity mixtures. The mixtures used were the same as those documented in Table 3.5. The birefringence of these samples was measured according to the method described in Section 3.2.2. The results are displayed in Figure 3.11.

The next experiment attempted was irradiating a 5μm sample of ZhK 440 with 366nm light and measuring the birefringence. The experiment was set up on the optical table, but the birefringence measurement was taken with optics that corresponded to the microscope.
set up described in Section 2.3.4. The UV lamp was set up 15cm away from the sample and the appropriate filter was placed in front of it. Unfortunately, no quartz sample cells were available and so the cell was not entirely transparent to the irradiation at this wavelength. For this reason, the irradiation had to be carried out for longer periods of time to make up for the lack of light intensity. The irradiation time periods were 30 seconds each. After each irradiation interval, the birefringence was measured. Figure 3.11 displays a plot of the results obtained. From the figure one can see that the data from the triphenylene impurity mixtures were insufficient to fully determine the amount of cis isomer created upon irradiation. As a first guess using the two sets of data, however, it appears that about 20% cis isomer is necessary to depress the transition to room temperature. Likewise, it is interesting to note, that the nematic-isotropic phase transition temperature of the ZhK 440 sample (usually at about 71°C) can be depressed to room temperature simply by irradiation.

3.3.2 Calculation of Cis Isomer Concentration

At this point it was interesting to determine if a better estimate of how much cis was actually created when the sample was near its transition into the isotropic phase at room temperature. To attempt this, the sample at 25°C was irradiated until its birefringence was 0.119, which was close to the transition, but definitely before it had reached room temperature. The sample was then placed in the microscope and slowly heated to determine the temperature range of the coexistence region. This was the best way to estimate the values for $\Delta T$ and $\delta T$, which could be plugged into equation 2.2.49, along with the value established for $\Delta H$ in Section 3.2.4, in order to determine the mole fraction of cis isomer produced. The resultant phase transition occurred between 31.91±.50°C and 49.77±.50°C and the mole fraction was calculated to be $X_{\text{cis}} = 0.076±.009$. The large error in this number is due to both the large error in the calculated value for $\Delta H$ and to the large uncertainty in the temperatures and the coexistence region boundaries. The large uncertainty in the temperatures is due to the fact that the temperature of the sample had to be ramped quickly in order to minimize thermal relaxation during the measurement process. This thermal relaxation might also be a partial explanation for the fact that this estimate is lower than the estimate from the birefringence data of the previous section.
3.3.3 Photo-excitation and De-excitation

At this time, we attempted to demonstrate that, like in the solution experiments, the liquid crystal sample could be brought back to close to its original state with light of lower energy. To this end, the same sample cell was irradiated with 366nm light until a birefringence just above the phase transition was achieved. Then the filter in front of the lamp was switched to 436nm and the irradiation, along with birefringence measurements, was repeated. Figure 3.12 displays the results of these experiments.

In order to compare these results with those obtained for the experiments in solution, another experiment was done in order to determine to what birefringence the sample could be brought down if irradiated from the all trans isomer state with the 436nm light. The same sample in the 5μm cell was irradiated with 436nm, light until no change could be observed in the birefringence. This photo-stationary state was then compared to the one obtained in the previous experiment. This data is plotted on one graph for ease of comparison, Figure 3.13. From this figure one can see that the system approaches, but does not quite reach, the same cis/trans isomer equilibrium state, when irradiated with 436nm light, starting from
Figure 3.13: Plot of birefringence vs. time for excitation and de-excitation of ZhK 440 in the liquid crystal phase, using 436nm light

different initial states. The fact that the two lines never converge is in agreement with the data obtained for the sample in solution, where the same phenomenon was observed.
Chapter 4

Discussion

The irradiation experiments conducted in solution demonstrated the possibility of manipulating the system quite successfully with ultraviolet light. Figure 3.4 especially demonstrates the ease with which a desired isomer could be promoted by simply switching the wavelength of irradiation. The calculations done according to Fischer’s method (Delaire et al., 1993), discussed in Section 3.1.3, clearly show that quite a bit of cis isomer can be produced if the system is irradiated with a wavelength of light that falls close to the maximum trans absorption at 341nm. From Table 3.3 it is clear that the difference in the amount of cis isomer produced upon irradiation with 366nm light and 335nm light was insignificant. The calculations also point to the fact that although 405nm light can be used to promote higher concentrations of trans isomer (Figure 3.4) even light of this wavelength is energetic enough to promote the production of some cis isomer (Table 3.3).

At this point it was thought useful to be able to estimate the spectrum of the pure cis isomer. This could be done, for all relevant wavelengths, using equations 2.1.5 and 2.1.6. The general method is as follows. We would like to calculate the pure cis isomer spectrum for each of the three irradiation wavelengths, to ensure the validity of the method. However, those equations assume that a photo-stationary state has been reached, which is only the case for irradiation with 366nm light, Figure 3.4. To account for this, we use the $\alpha$ calculated for irradiation at a particular wavelength to determine $A^\text{irr}_c$, by way of equation 2.1.5. Then, we use the last spectra obtained in a given irradiation experiment to obtain the value for $\alpha$ that was attained in that particular experiment, using that same equation. Now, since equation 2.1.5, is valid at all wavelengths, we can use the $\alpha$ that corresponds to the actual amount of cis isomer produced for a given spectrum (not the $\alpha$’s determined for the photo-stationary
states), to determine $A_e$ for all wavelengths. This was done for each of the irradiating wavelengths. The three calculated spectra were then averaged and are displayed in Figure 4.1. In this figure, although it is only an estimate, it is clear that the spectra of the cis and trans isomers overlap significantly. This is very different from the spectra of azo-benzenes reported by Zimmerman et al. (1958). In their work, they report that spectra of the cis and trans isomers of azobenzenes have different peaks in the ultraviolet and visible ranges. The significant overlap of the spectra helps to explain why it was impossible to convert the entire system to cis isomer by way of irradiation, since the overlap implies that irradiation with any wavelength will promote some of both isomers.

At this point, it is interesting to note that irradiation with a particular wavelength of light did not seem to bring the sample to exactly the same absorption level, regardless of whether the sample started out as all trans isomer or not (Figure 3.4). It was expected that irradiation with a given wavelength would always produce the same photo-stationary state, independent of starting point, as reported by Zimmerman et al. (1958) from their experiments on azo-benzenes. This difference in the spectral shifts from trans to cis isomer between the azo-benzenes and azoxy-benzenes might be a clue as to why they were able to reach the same photo-stationary states from both directions with irradiation. For example, azoxy-benzenes might have different intermediate states that make excitation and de-excitation not entirely symmetric processes. However, in the thermal limit, regardless of irradiation history, all the isomer converts to trans isomer if not exposed to light for a sufficient amount of time.

In the liquid crystal phase, the birefringence measurements proved to be a highly useful tool for future experiments. As the microscope and optical table data overlapped entirely both methods were used, depending on convenience, as analytical techniques. The index of refraction measurements were also successful, demonstrating a sufficient degree of accuracy to be used in the calculation of the order parameter. The order parameter data proved to be somewhat less reliable than the birefringence data, especially since the two measurement methods did not overlap satisfactorily at lower temperatures (Figure 3.7). The lack of agreement in this data is possibly due to isomerization of the sample as a result of irradiation with 436nm light during the direct measurement. This explanation is supported by the fact that Figure 3.13 demonstrates a slight lowering of the birefringence upon exposure to 436nm light. The appearance of agreement in the order parameter measurements at higher temperatures is probably a manifestation of the greater importance of thermal effects over photo-induced processes at higher temperatures. However, the agreement between the general shapes of the curves of order parameter vs. temperature and birefringence vs.
temperature justifies the assumption that birefringence could be used to establish degree of orientational order in a sample.

The measurements of the latent heat of transition demonstrated a fair degree of uncertainty in the final value. This might be because, in such dilute mixtures, measurements of mole fraction are highly prone to error. However, the precise nature of the numbers obtained leads to a degree of confidence in the experiment. Also, the usefulness of the numbers in estimating the amount of cis isomer in the liquid crystal phase should be noted.

The irradiation experiments in the liquid crystal phase were in agreement with those in the solution phase in most aspects. Excitation and de-excitation of the sample were demonstrated to good satisfaction, a possible sign for a mixture potentially to be used in a device. The low amount of cis isomer calculated to have been produced when the phase transition is depressed by about 30°C is somewhat surprising (Section 3.3.2). Yet the amount of cis isomer calculated is only as good as the assumptions that were made in the derivation of equation 2.2.49, which was used to calculate both the latent heat of transition and the amount of cis isomer. Since all mole fractions seem to be bellow 0.1, the assumptions of ideally-dilute solutions should be warrented. Regardless, the induced melting of the sample
at room temperature by way of irradiation is a testimony to the incredible sensitivity of the liquid crystal phase to minor disturbances in orientational order by way of impurities. Finally, the irradiation experiments done in the liquid crystal phase are consistent with those done in solution. Specifically, as Figure 3.13 demonstrates, irradiation with the same wavelength of light does not seem to bring the sample to the same exact ratio of cis to trans isomer, independent of the starting point of the sample. This agreement in the irradiation data, supports the idea that the observed phenomenon is indicative of something fundamental about the energetics of excitation and de-excitation of the azoxy-benzene compound. In addition, irradiation with 436nm light reduces the birefringence about a quarter as much as when the 7.6% cis isomer measurement was made. This implies about 2% cis isomer, which is consistent with the solution measurements, in that irradiation with 405nm light produced 3% cis isomer and 436nm light produced less cis isomer than that.

Much work remains to be done on this system if it is to be thoroughly understood. Future studies would have to include irradiation experiments in a solution of a non-polar solvent, since solvent effects often determine the exact position of an absorption peak (Lowry and Richardson, 1987). Such a study would further the understanding of the energetics of this isomerization, assisting in more precise manipulation of the system. Conducting the irradiation experiments in a non-polar solvent might also allow for use of lower wavelengths, such as ones even lower than 313nm (the data that had to be discarded in this study). One possible explanation for the decomposition of ZhK 440 upon irradiation with 313nm light is the occurrence of the photo-Wallach rearrangement, a reaction that only takes place in polar solvents (Patai, 1997). Irradiating at lower wavelengths might be a way of driving the system to higher concentrations of cis isomer more efficiently since the trans isomer is much less absorbent there (Figure 4.1). Also, more precise irradiation studies in the liquid crystal phase should be conducted in order to establish the plausibility of building a device using this system. Finally, much of the data in this document could be improved were it to be obtained with a light source of uniform intensity at all wavelengths, with more irradiation wavelengths accessible.
Chapter 5

Conclusions

The studies described in this work are the most extensive studies done on an azoxy-benzene liquid crystalline system to date. While significant work has been done on the azo-benzene liquid crystalline system, as described in the introduction, the data obtained here convinces one that this system is sufficiently different to warrant investigation in its own right. This study, which was largely preliminary, has provided a wealth of basic physical and chemical information about this unique and delicate system. We conclude that there is direct correspondence between absorption experiments done in solution and those done in the liquid crystal phase. We now also have a relatively reliable way of determining cis isomer concentrations in solution, by measuring absorption peak height, and in the liquid crystal phase, by measuring the birefringence. We also conclude that the liquid crystal phase is quite easily manipulated with relatively small intensities of ultraviolet light. Furthermore, the estimated cis isomer spectra provides future experimenters with a starting point for irradiation studies in the liquid crystal phase. These findings, combined with the estimated energetics of isomerization (Levy, 2004), are a good point from which to continue technological applications.
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Bibliography


66