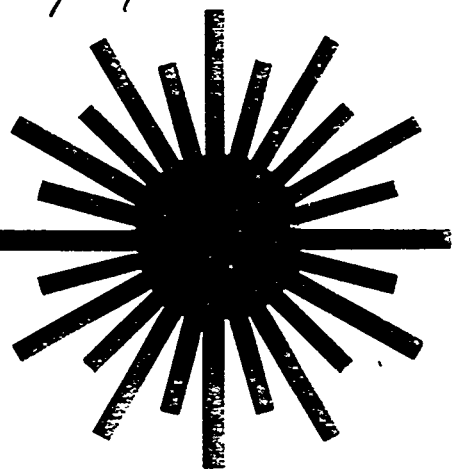
UR
LLE



1998 SUMMER RESEARCH PROGRAM FOR HIGH SCHOOL JUNIORS

AT THE

UNIVERSITY OF ROCHESTER'S

LABORATORY FOR LASER ENERGETICS

STUDENT RESEARCH REPORTS

PROJECT COORDINATOR

Dr. R. Stephen Craxton

March 1999

Laboratory Report 300

Laboratory for Laser Energetics
University of Rochester

DISCLAIMER

1998 SUMMER RESEARCH PROGRAM FOR HIGH SCHOOL JUNIORS AT THE UNIVERSITY OF ROCHESTER'S LABORATORY FOR LASER ENERGETICS

STUDENT RESEARCH REPORTS

PROGRAM COORDINATOR

Dr. R. Stephen Craxton
LABORATORY FOR LASER ENERGETICS
University of Rochester
250 East River Road
Rochester, NY 14623-1299

During the summer of 1998, 11 students from Rochester-area high schools participated in the Laboratory for Laser Energetics' Summer High School Research Program. The goal of this program is to excite a group of high school students about careers in the areas of science and technology by exposing them to research in a state-of-the-art environment. Too often, students are exposed to "research" only through classroom laboratories that have prescribed procedures and predictable results. In LLE's summer program, the students experience all of the trials, tribulations, and rewards of scientific research. By participating in research in a real environment, the students often

become more excited about careers in science and technology. In addition, LLE gains from the contributions of the many highly talented students who are attracted to the program.

The students spent most of their time working on their individual research projects with members of LLE's technical staff. The projects were related to current research activities at LLE and covered a broad range of areas of interest including optics, spectroscopy, chemistry, diagnostic development, and materials science. The students, their high schools, their LLE supervisors and their project titles are listed in the table. Their written reports are collected in this volume.

The students attended weekly seminars on technical topics associated with LLE's research. Topics this year included lasers, fusion, holography, nonlinear optics, global warming, and scientific ethics. The students also received safety training, learned how to give scientific presentations, and were introduced to LLE's resources, especially the computational facilities.

The program culminated with the High School Student Summer Research Symposium on 26 August at which the students presented the results of their research to an audience that included parents, teachers, and members of LLE. Each student spoke for approximately ten minutes and answered questions. At the symposium an Inspirational Science Teacher award was presented to Mr. David Crane, a chemistry teacher at Greece Arcadia High School. This annual award honors a teacher, nominated by alumni of the LLE program, who has inspired outstanding students in the areas of science, mathematics, and technology.

High School Students and Their Projects (1998)			
Student	**High School**	**Supervisor**	**Project**
Steven Corsello	Pittsford Mendon	K. Marshall	Computer-Aided Design and Modeling of Nickel Dithiolene Near-Infrared Dyes
Peter Grossman	Wilson Magnet	R. S. Craxton	Group Velocity Effects in Broadband Frequency Conversion on OMEGA
Joshua Hubregsen	Pittsford Sutherland	S. Jacobs	A Study of Material Removal During Magnetorheological Finishing (MRF)
Nieraj Jain	Pittsford Sutherland	M. Guardelben	Analyzing Algorithms for Nonlinear and Spatially Nonuniform Phase Shifts in the Liquid Crystal Point Diffraction Interferometer
Leslie Lai	Pittsford Mendon	M. Wittman	The Use of Design-of-Experiments Methodology to Optimize Polymer Capsule Fabrication
Irene Lippa	Byron-Bergen	K. Marshall	Synthesis and Analysis of Nickel Dithiolene Dyes in a Nematic Liquid Crystal Host
Phillip Ostromogolsky	Brighton	F. Marshall	Investigation of the X-Ray Diffraction Properties of a Synthetic Multilayer
Michael Schubmehl	The Harley School	R. Epstein	An Analysis of the Uncertainty in Temperature and Density Estimates from Fitting Model Spectra to Data
Joshua Silbermann	Penfield	P. Jannimagi	Automated CCD Camera Characterization
Abigail Stern	The Harley School	J. Knauer	Design and Testing of a Compact X-Ray Diode
Amy Turner	Churchville-Chili	R. S. Craxton	Ray Tracing Through the Liquid Crystal Point Diffraction Interferometer

A total of 91 high school students have participated in the program since it began in 1989. The students this year were selected from approximately 60 applicants. Each applicant submitted an essay describing their interests in science, a copy of their transcript, and a letter of recommendation from a science or math teacher.

LLE plans to continue this program in future years. The program is strictly for students from Rochester-area high schools who have just completed their junior year. Applications are generally mailed out in February with an application deadline near the end of March. For more information about the program or an application form, please contact Dr. R. Stephen Craxton at LLE.

This program was supported by the U.S. Department of Energy Office of Inertial Confinement Fusion under Cooperative Agreement No. DE-FC03-92SF19460.

SYNTHESIS AND ANALYSIS OF NICKEL DITHIOLENE DYES IN A NEMATIC LIQUID CRYSTAL HOST

by

IRENE LIPPA

Byron-Bergen High School

Bergen, NY

Synthesis and Analysis Of Nickel Dithiolene Dyes In A Nematic Liquid Crystal Host

Irene Lippa

Advisor: Kenneth L. Marshall

Byron-Bergen Central School

Laboratory for Laser Energetics

University of Rochester

High School Research Program

1998

The Liquid Crystal Point Diffraction Interferometer (LCPDI) can be employed to evaluate the Omega Laser system for optimum firing capabilities. This device utilizes a nickel dithiolene infrared absorbing liquid crystal dye dissolved in a liquid crystal host medium (Merck E7). Three nickel dithiolene dyes were characterized for both their solubility in the E7 host and their infrared spectral absorption.

Project goal

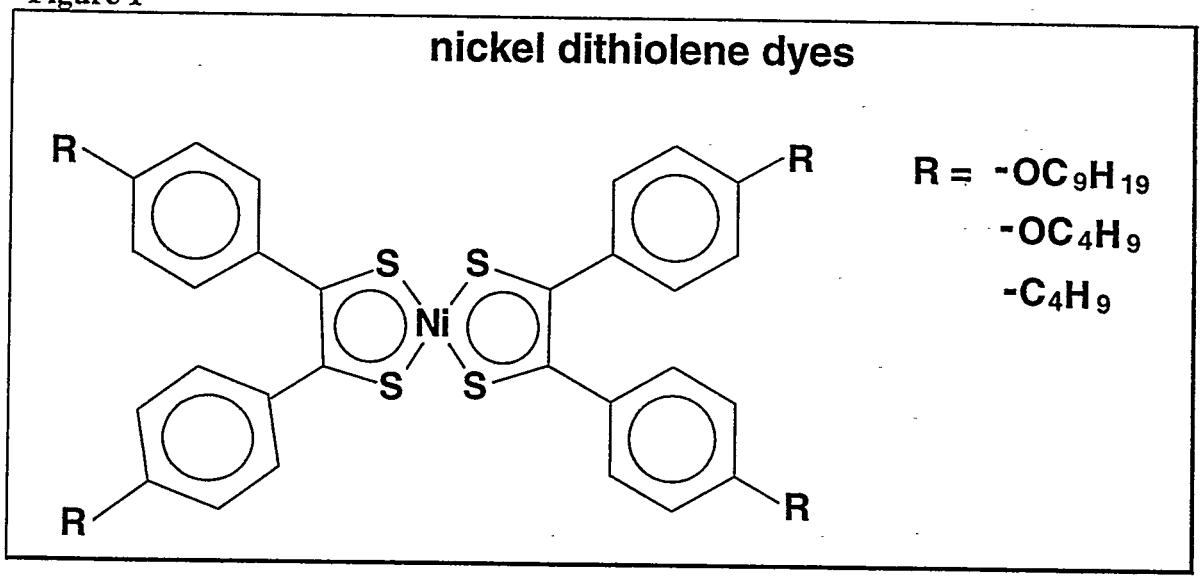
A family of infrared absorbing dyes for use in the LCPDI was synthesized and characterized. The LCPDI device assists with the diagnostics of the laser beam uniformity. The ideal dye for the LPDI should have (1) high optical absorbance at the desirable wavelength of the laser (λ_{max} 1054 nanometers); (2) high thermal stability to minimize loss of the dye chromophore to thermal degradation by the laser; (3) high solubility in the liquid crystal host to increase both dye loading and infrared optical density of the dye-host medium; and (4) a low impact on the degree of order (order parameter) of the host medium.

Previous work has shown the nickel dithiolene dye as a desirable candidate for the LCPDI. The nickel dithiolene has a unique aromatic ring structure, which imparts a relatively high infrared absorption and a high thermal and photochemical stability. With 2 alkoxyphenyl substitutions onto the nickel dithiolene core, these complexes possess optical absorbance bands at the desirable wavelength of the laser. However, these alkoxyphenyl substituted compounds have demonstrated limited solubility in the host liquid crystal medium. The potential of an alkyl-phenyl substituents to increase the solubility of the dithiolene dye in the host liquid crystal medium was the primary topic of this investigation.

In this project, p-butoxy-phenyl and p-nonoxy-phenyl substituted ($-pC_6H_4-OC_9H_{19}$ and $-pC_6H_4-OC_4H_9$) dithiolene dyes were purified and characterized along with the total synthesis, characterization and purification of a novel p-butyl-phenyl ($-pC_6H_4-C_4H_9$) substituted dithiolene dye. The solubility of these three dyes was determined in the

LCPDI liquid crystal host medium, and the absorption spectra were determined. The structure of the dithiolene dyes is shown in Figure 1.

Figure 1



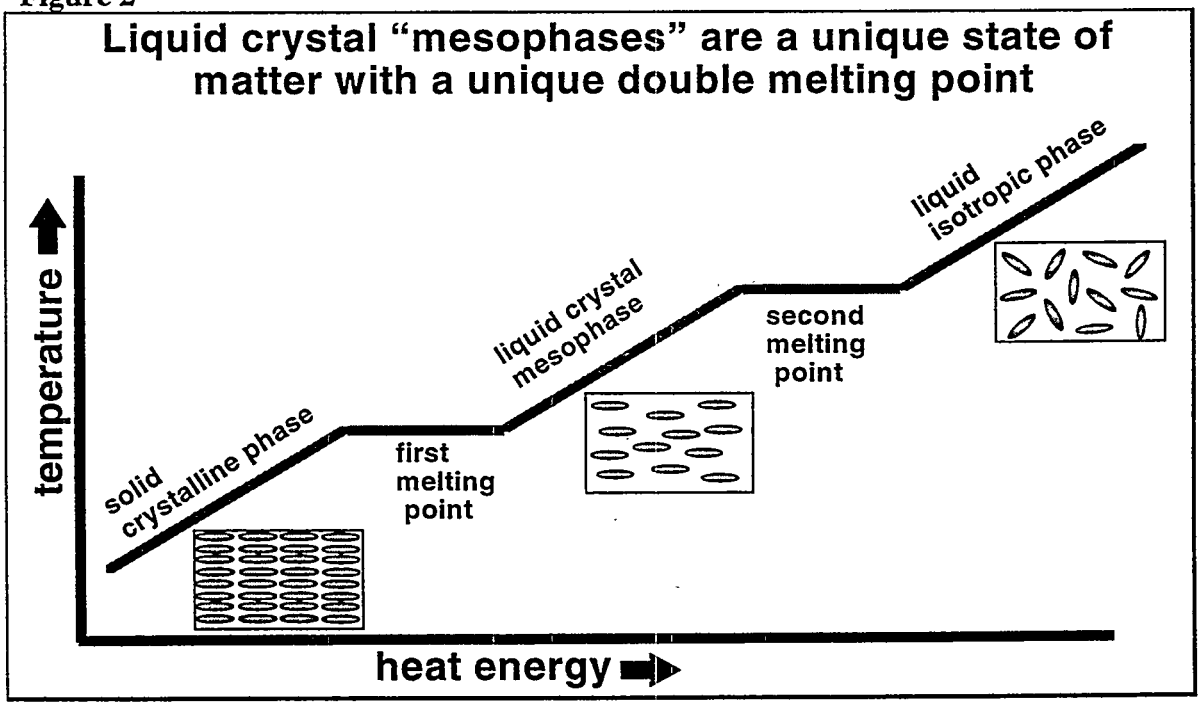
Liquid Crystals: background

Liquid crystals are compounds that can exist in a intermediate mesophase between the solid and liquid phase.

A true crystalline solid has atoms or molecules fixed in position with no translational movement. These species are ordered in a regular repeating fashion in all three dimensions. A liquid has atoms or molecules with translational movement in all directions, with no dimensional order. When the disorder of a liquid extends in all three dimensions, then this true liquid is the isotropic phase. The phase transition from crystalline solid to liquid occurs at a sharp, distinct melting point. As melting occurs, all three dimensions of crystalline order are lost and the material enters the three dimensional disorder of the liquid phase.

Liquid crystals exist as a phase between the solid and liquid phase, showing a unique "double melting point". The liquid crystal can maintain partial order in one or two dimensions at an initial melting point. At this first melting point, one (or two) dimension(s) of order are lost, and the remaining dimensions of crystalline order are maintained. A second "melting" point occurs when the liquid crystal enters into the complete three dimensional disorder of a liquid. This "liquid crystalline" order that exists between the two melting points is called the mesomophic phase. The mesomorphic phase exhibits *anisotropic* properties; i.e. different physical properties (optical and electrical) in different directions. These anisotropic properties are what make liquid crystals of such value for applications. The double melting point of a liquid crystal is shown in Figure 2.

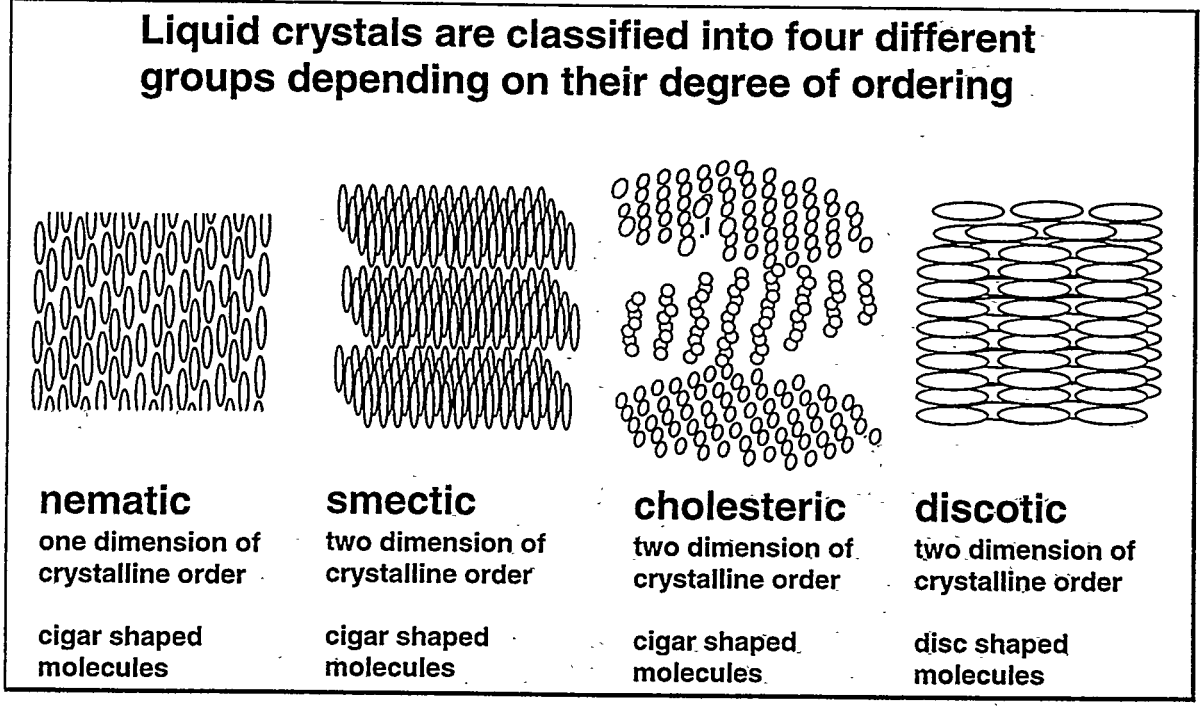
Figure 2



Liquid crystals are classified into four different groups according to the degree of ordering within the mesophase. The four groups from least to most highly ordered are

nematic, cholesteric, smectic, and discotic. Nematic liquid crystals maintain order in one dimension; here molecules are aligned with their long axes in a common direction in a one dimensional stacking pattern. Cholesteric, smectic and discotic liquid crystals maintain crystalline order in two (or more) dimensions; molecules are aligned in a common direction and in parallel planes (that can slip past each other) in a second dimension. The nematic, cholesteric and smectic liquid crystals are composed of linear (cigar-shaped) molecules. The discotic liquid crystal is composed of planar (disc shaped) molecules arranged both face to face and end to end. The different liquid crystal structures are shown in Figure 3.

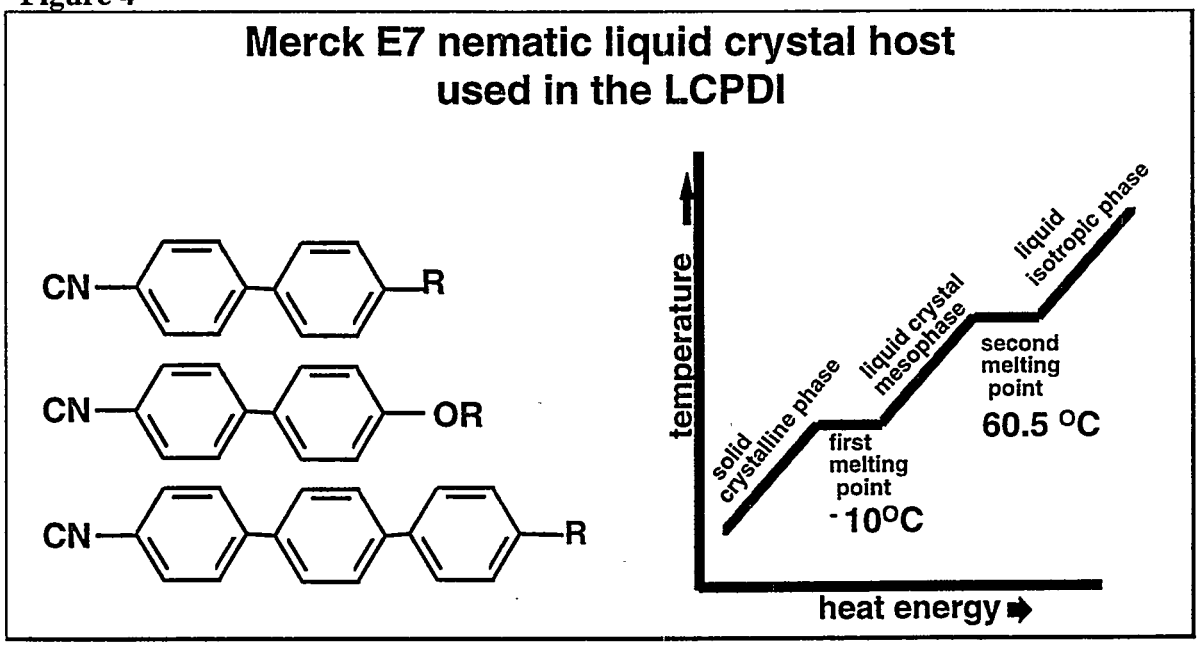
Figure 3.



Merck E7™ is the liquid crystal host used in the LCPDI device. E7 is a nematic liquid crystal mixture with a mesophase between -10 °C and 60.5 °C. The R-group substituents on the nickel dithiolene dye need to be selected for maximum solubility in

the E7 host without compromising other important properties (absorption wavelength, optical density or thermal stability). Merck E7 is a room temperature eutectic mixture of cyanobiphenyl and cyanoterphenyl liquid crystal compounds; its components are shown in Figure 4.

Figure 4



The substituted nickel dithiolene dyes are discotic liquid crystals dissolved in the E7 nematic host. There are two molecular "components" to the nickel dithiolene dye; the nickel bis (dithiolene) core and the substituted R groups. The nickel bis (ditholene) core is a unique conjugated transition metal aromatic complex which absorbs near infra-red radiation.

This group has a characteristically flat 'disk' shape, which is responsible for the discotic liquid crystal phase. The nickel bis (dithiolene) core has high thermal and photochemical stability. The substituted R groups impart the solubility in nonpolar solvents. Also, if the R groups are sufficiently long, they can form a nematic liquid crystal, as shown in Figure 5 and 6.

Figure 5

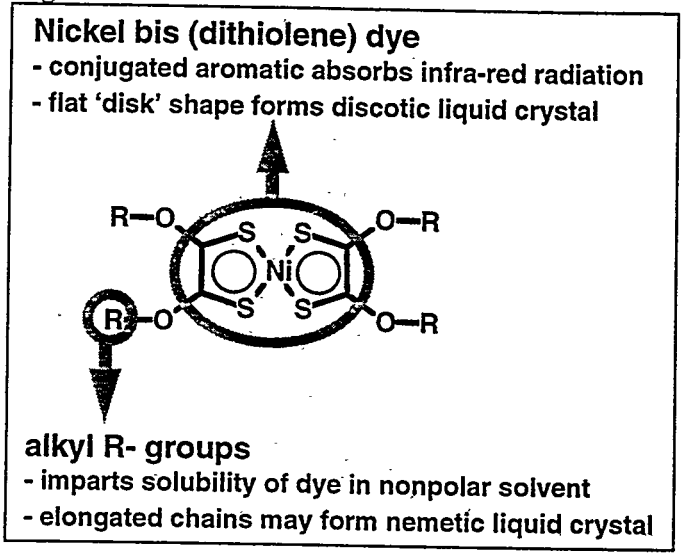
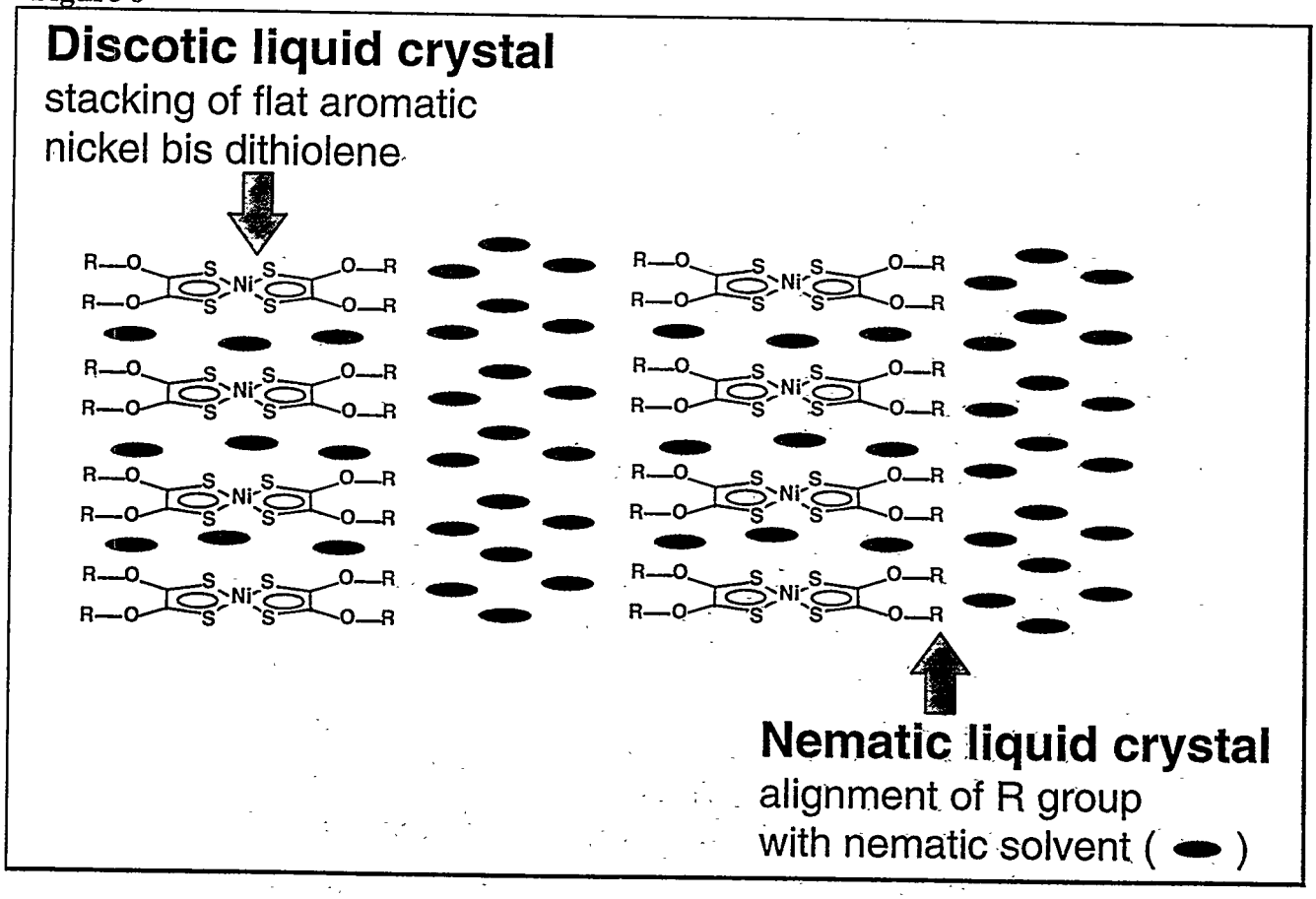
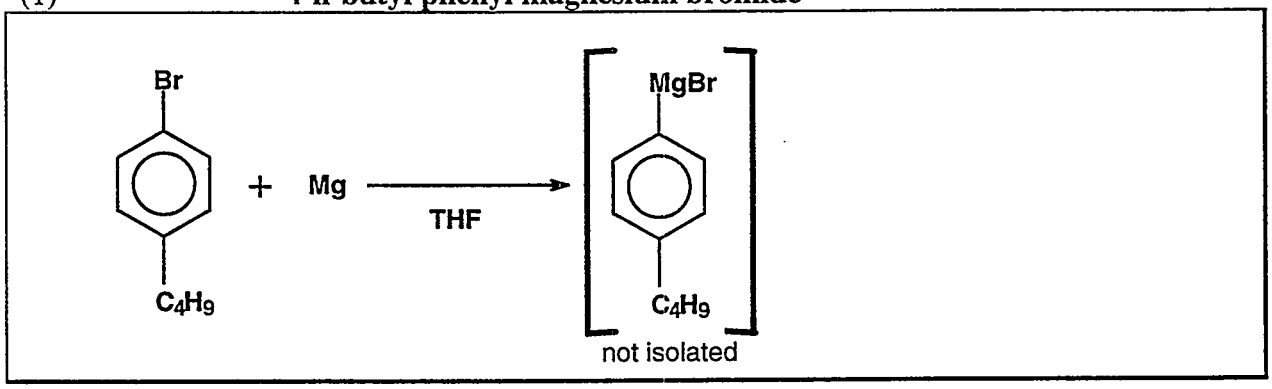


Figure 6



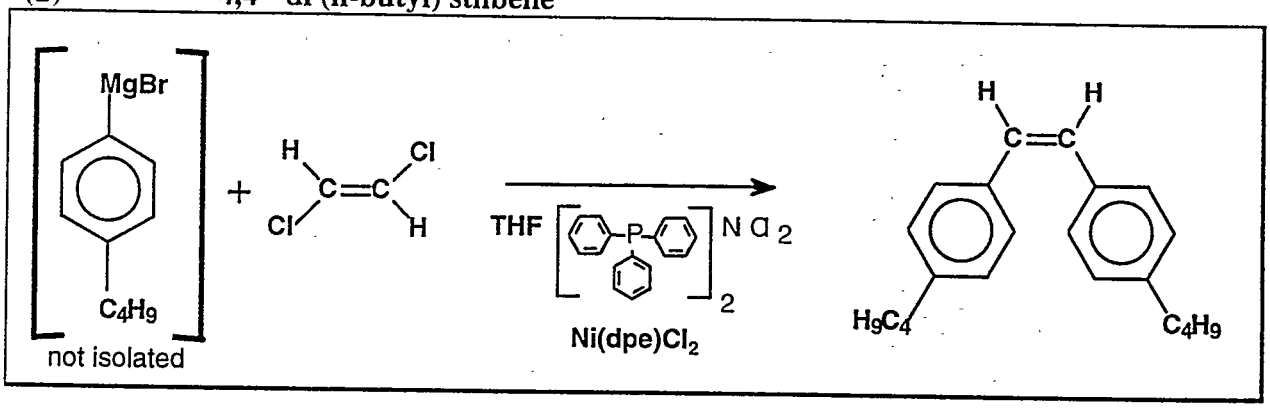
Synthesis of bis [1,2 di (4-n-butyl phenyl) ethane 1,2 dithione] nickel (0)

(1) **4-n-butyl phenyl magnesium bromide**



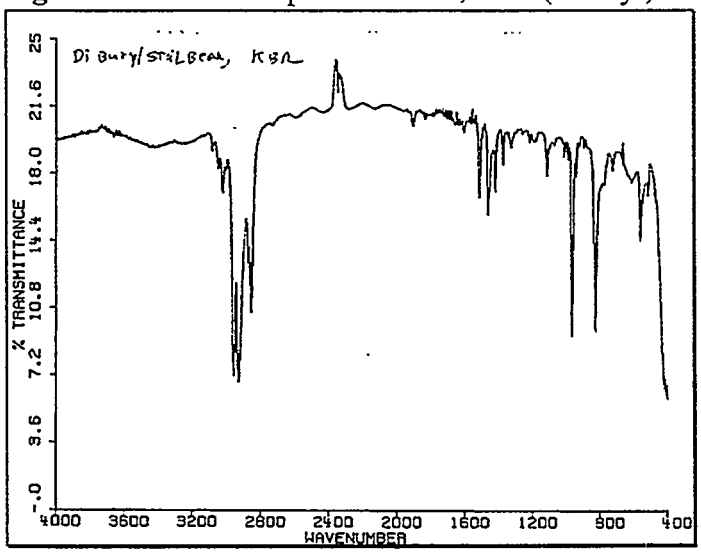
A three neck round bottomed flask was equipped with a dropping funnel, water cooled condenser, argon purge, electric heating mantle and magnetic stirrer. Sufficient tetrahydrofuran (THF) was dried over anhydrous $MgSO_4$. The flask was charged with magnesium turnings and dry THF (20 ml) was added to the bottom of the three-neck round bottomed flask. 4-butyl-bromobenzene (18 g, 84 mmol) was added to the reaction dropwise and allowed to reflux for 12 hours. The resultant product was used in the next step without isolation or purification.

(2) **4,4′- di (n-butyl) stilbene**

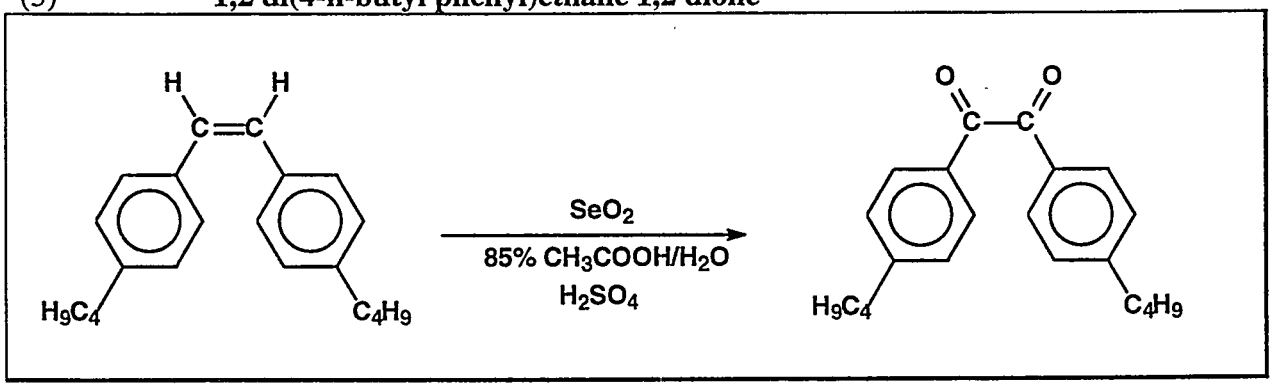


The flask containing the 4-n-butylphenyl magnesium bromide from step 1 was cooled in an ice water bath, and 0.14 g (0.25 mmol) of dichloroethylene was added dropwise. The mixture was refluxed for 20 hours. The flask was cooled to room temperature and dilute aqueous HCl (10%) is added. The resulting solid was collected, extracted with ethyl ether and dried over anhydrous $NaSO_4$. The solvent was removed under vacuum using a rotary evaporator to give a crude mixture of cis and trans isomers of 4,4'-di (n-butyl) stilbene (16.4%). Recrystallization from ethyl acetate gave a slightly yellow crystalline solid in the trans form and a white crystalline solid in the cis form (1.3 g trans, 2.23g cis) for an average 16.4% yield of 12.2 g theoretical. The IR spectrum of the cis-product is shown in Figure 7.

Figure 7 FTIR spectrum of 4,4′- di (n-butyl) stilbene



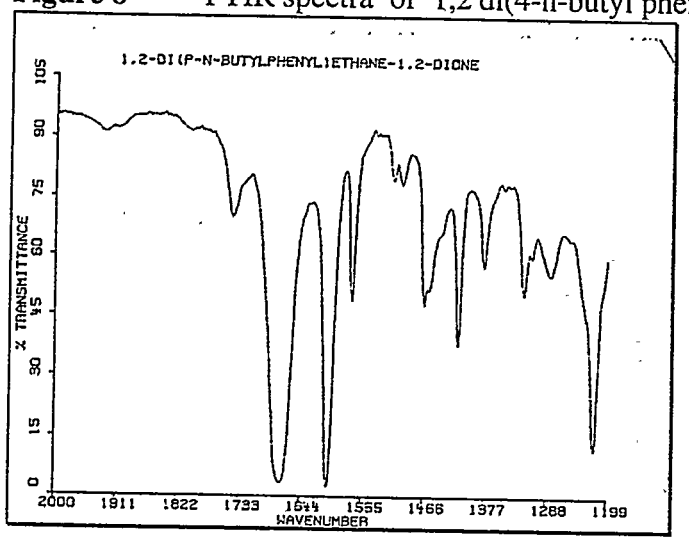
(3) **1,2 di(4-n-butyl phenyl)ethane 1,2 dione**



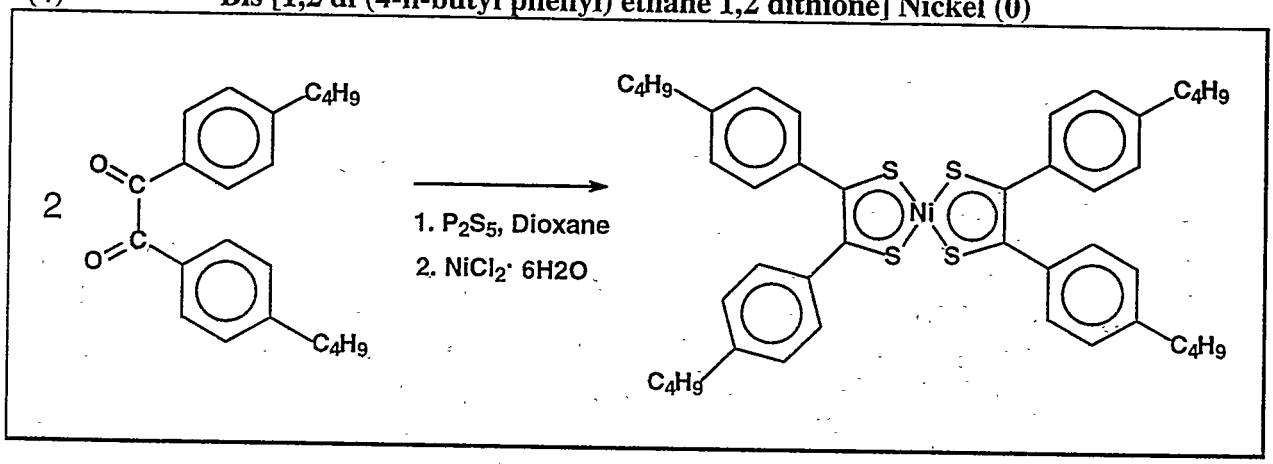
A three neck round bottomed flask was equipped with a dropping funnel, water cooled condenser, argon purge, electric heating mantle and magnetic stirrer. The flask was charged with selenium dioxide (SeO_2, 1.67 g, .01508 mmol), 4,4′- di (n-butyl) stilbene (2.0g, 7mmol), a mixture of 80% HOAc : 20% H_2O (150 ml) and concentrated H_2SO_4 (1.5ml). The reaction mixture was heated to reflux for 17 hours, insoluble solids were filtered, and the filtrate was extracted with ethyl ether. The ethyl ether extract was washed with saturated $NaHCO_3$ solution until it was neutral. The extract was dried over $MgSO_4$ and the solvent removed under vacuum to leave an oil in 80 % yield. The IR

spectrum of the product, showing the characteristic C=O stretching at ~1700 cm^{-1} , is given in Figure 8.

Figure 8 FTIR spectra of 1,2 di(4-n-butyl phenyl)ethane 1,2 dione



(4) **Bis [1,2 di (4-n-butyl phenyl) ethane 1,2 dithione] Nickel (0)**



A three neck round bottomed flask was equipped with a dropping funnel, water cooled condenser, argon purge, electric heating mantle and magnetic stirrer. The flask was charged with 1,2 di (p-n-butylphenyl)ethane 1,2 dione(1.8 g, 3.6 mmol), phosphorous pentasulfide (1.2 g 5.,5 mmol) and 30 ml of dioxane. The mixture was refluxed for 5 hours. The reaction mixture was filtered hot to remove the unreacted

phosphorous pentasulfide and the residue was washed with hot dioxane several times. The filtrate was returned to the cleaned round bottom flask, and nickel (II)chloride•hexahydrate (0.48 g, 2.0 mmol) in 10 ml of water was added. The reaction was refluxed for 2 hours, and then cooled in a ice water bath. The product, a crystalline black powder, was collected by filtration to give 1 g of the crude complex at 51 % yield.

The product was purified by liquid column chromatography, using a 1:1 mixture of hexane and toluene as the eluent and a stationary phase of 5μm porosity silica gel. The crude solids were dissolved into an aliquot of the solvent and added to the column. The eluting solvent was kept running through the column until all of the material had run through. Fractional cuts of the eluent were collected and assayed using a Hitachi High Performance Liquid Chromatograph (HPLC) with a UV-Vis detector. A 20 μl injection volume on a analytical silica gel column was used for the analysis. Similar fractions of the product were combined, the solvent was removed under vacuum, and the residue was recrystallized from ethyl acetate. The purified crystalline dye solids were collected by vacuum filtration and air dried.

Fourier Transform Infra-Red (FTIR) Spectroscopy was used to detect functional groups as well as to identify the degree of substitution.

Purification of bis [1,2 di (4-n-butyoxy phenyl) ethane 1,2 dithione] nickel (0) and bis [1,2 di (4-n-nonoxy phenyl) ethane 1,2 dithione]- nickel (0)

Crude samples of bis [1,2 di (4-n-butyoxy phenyl) ethane 1,2 dithione]-nickel (0)and bis [1,2 di (4-n-nonoxy phenyl) ethane 1,2 dithione] nickel (0) synthesized previously were purified by column chromatography and assayed by HPLC. These samples were chromatographed in the same manner as described in the previous section. The products obtained were recrystallized from ethyl acatate and dried in air overnight. Table 1 compares the purity of the crude and purified samples, respectively. The nonyloxy sample shows the most dramatic improvement in purity.

Table 1

R-group name	R-group structure	Crude HPLC assay (area %)	Purified HPLC assay (area %)
p-nonoxy- phenyl	$-OC_9H_{19}$	46.0	90.0
p-butoxy-phenyl	$-OC_4H_9$	83.0	94.0
p-butyl-phenyl	$-C_4H_9$	98.5	99.4

Hot stage polarizing microscopy

Phase transitions were characterized using a polarizing microscope with a hot stage attachment. The isotropic melting points are shown in Table 2.

Table 2

R-group name	R-group structure	second melting point (°C)
p-nonoxy- phenyl	$-OC_9H_{19}$	184.3-189.1
p-butoxy-phenyl	$-OC_4H_9$	246.3-248.7
p-butyl-phenyl	$-C_4H_9$	228.3-230.6

Spectroscopy

UV-Vis-near IR spectroscopy was used to find the location and strength of the electronic absorption maxima (λ_{max}). The point of interest for the LCPDI is 1054 nm, and the absorbance of all three dyes are in this vicinity. The absorbance characteristics of the C_4 and OC_4 dyes in the liquid crystal host over the 800-1600 nm region are shown in Figure 8. The λ_{max} for all three dyes is given in Table 3.

Figure 8

The enhanced solubility of the C_4 metal complex is compromised by the hypsochromic shift of its peak absorbance

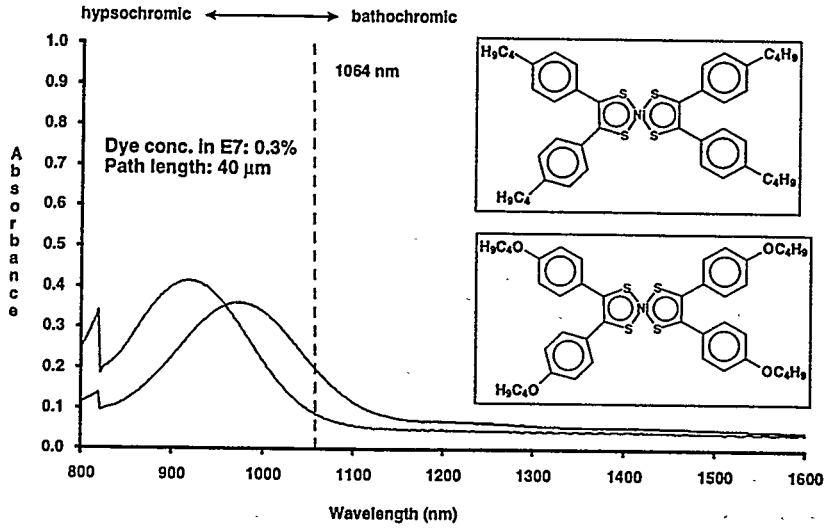


Table 3

R-group name	R-group structure	λ_{max} cyclohexane (nm)
p-nonoxy- phenyl	$-OC_9H_{19}$	912
p-butoxy-phenyl	$-OC_4H_9$	910
p-butyl-phenyl	$-C_4H_9$	870

Solubility

Solubility limits of each dye were determined in both cyclohexane and Merck E7 liquid crystal. Samples of each dye were mixed in a series of weight percents (0.3 wt % to 1 wt %) in E7 to make a total volume of 2 ml. The dyes were dissolved in the LC host by heating the host to 100°C and stirring for several hours. Upon cooling, each

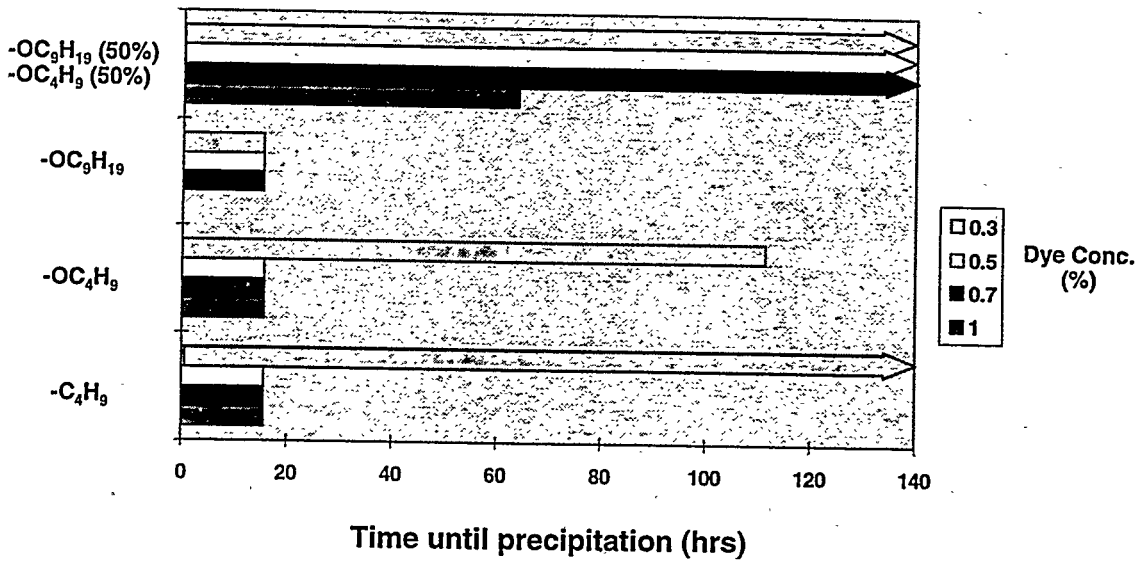
sample was filtered through a 0.5 μm Teflon membrane filter to remove undissolved dye and insoluble particles. An additional set of samples containing a 1:1 ratio of the OC_4 and OC_9 dyes was also prepared over the same range of concentrations.

All samples were checked periodically both visually and by microscopic inspection for signs of dye precipitation. The solubility results in E7 are given in Table 4 and Figure 9.

Table 4

R-group name	**R-group structure**	**solubility limit cyclohexane (wt%)**	**solubility limit Merck E7™ (wt%)**
p-nonoxy- phenyl	$-OC_9H_{19}$	0.025	<0.3%
p-butoxy-phenyl	$-OC_4H_9$	< 0.001	0.3% (110 hours until precipitation)
1:1 mixture p-nonoxy- phenyl & p-butoxy-phenyl	$-OC_9H_{19}$ & $-OC_4H_9$	NA	>1.000 (solution after 140 hours)
p-butyl-phenyl	$-C_4H_9$	0.050	0.3% (solution after 140 hours)

Figure 9



At the time of this writing, the lower concentration of 1:1 OC_4/OC_9 dye mixture in E7 was still in solution and its solubility limit was larger than the rest of the dyes; however, an actual number of hours until precipitation has yet to be determined. The 0.3% , 0.5%, and 0.7% weight percent dye mixtures had not precipitated after 140 hours. The $-C_4H_9$/E7 mixture was also stable at 0.3%. This shows us the high solubility rate of the $-C_4H_9$ as well as the important discovery that the mixing of dyes with similar structures can increase the solubility limit.

Summary

A new alkyl phenyl-substituted nickel dithiolene was successfully synthesized and its solubility was evaluated in a nematic LC host. The solubility of this dye in the same host was benchmarked against existing alkoxy-substituted analogs. Both the solubility and the spectral properties of nickel dithiolenes are affected by relatively minor changes in terminal functional groups. Although the only differences between the $-OC_4$, $-C_4$, and $-OC_9$ were different length chains and lack of oxygen present, there was a dramatic effect on both the solubility limits and the λ_{max} absorption. The new $-C_4$ nickel dithiolene shows enhanced solubility in liquid crystal, but a hypsochromic shift of its peak absorbance compromises its efficiency at 1054 nm. Substantial improvements in dye solubility can be made by using mixtures of dyes with similar structures. The net gain in solubility limit of mixed dyes in E7 has made a substantial improvement over the solubility limits of either dye by itself.

In the future, more computer modeling should be performed prior to synthesis in order to give additional guidance into what structural aspects would favor desirable characteristics. The long term stability of both the $-C_4$ and the mixed-dye systems also needs to be further evaluated. Further dye development needs to be done in order to completely satisfy the LCPDI device requirements.

Acknowledgments:

I gratefully acknowledge the Laboratory for LaserEnergetics, my Project Advisor, Kenneth L. Marshall, the Summer Research Program Supervisor, Dr. R. Stephen Craxton, as well as the Optical Materials Lab staff and students, Nathan Bickel, Joann Starowitz, and Adam Smith.

References:

Mueller-Westerhoff, U. The Synthesis of Dithiolene Dyes With Strong Near-IR Absorption. *Tetrahedron,* Vol.47, No6. pp909-932, 1991, Pergamon Press plc.

Ohta, K. Discotic Liquid Crystals of Transition Metal Complexes, 4:1 Novel Discotic Liquid Crystals Obtained from Substituted Bis(dithiolene)nickel Complexes by a New Method. Mol. Cryst. Liq. Cryst.,1987 Gordon and Breach Science Publishers S.A., Vol 147, pp15-24.