

Guest- Host Dye Systems for Liquid Crystal

Electro- Optical Device Applications

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Nematic liquid crystals are desirable for the liquid crystal point diffraction interferometer (LCPDI) because they respond readily to electric and magnetic stimuli. Liquid crystals are used in the LCPDI to produce phase shifting, which is achieved by applying a voltage. The LCPDI device is desirable as a diagnostic tool both for testing aberrations in the optics of the OMEGA laser and for NASA experiments in microgravity fluid physics. As drive voltages for the LCPDI increase, the contrast of fringes begins to fade. In order to match the output intensities of the object beam front and reference wave front, a mixture of negative and positive dichroic dyes (the “guests”) are needed to blend with the nematic liquid crystal Merck E7 (the “host”).

Project goal

The LCPDI requires a dye with a consistently high optical density (O.D.) at 543.5 nm. Previous research has shown that negative dichroic dyes are desirable because their optical density increases with increasing voltage. However, negative dichroic dyes are not commonly available, and have to be synthesized. These dyes are needed at relatively high percentages, which creates some complications in the guest-host dye system. An ideal dye candidate for blending with Merck E7 would have (1) good solubility at high concentrations; (2) a high “order parameter” (S) in the E7 “host” (the maximum attainable value of S is 1); (3) a high dichroic ratio to maximize contrast; and (4) a high optical density at 543.5 nm.

A series of negative dichroic anthraquinone dyes were synthesized and purified for this project. These dyes were added to Merck E7 nematic liquid crystal at different percentages to determine the solubility limit. Once the solubility limit was obtained, these mixtures were used to fabricate cells for finding the order parameter and dichroic ratio of the dye. The Lambda 900 spectrophotometer was used to determine both the dye maximum wavelength (λ_{\max}) in E7 and the O. D. at different applied voltages.

The ultimate goal of this project was to create a balanced mixture of negative and positive dichroic dyes in Merck E7 for the LCPDI device that would maintain an O.D. of 2 independent of applied voltage.

Structure and Properties of Liquid Crystals

Mesogens are the molecular components that make up a liquid crystalline phase. These molecules are rigid/ rod shaped, and align along a common axis called the director.

Liquid crystals (LC) exist in a “mesophase,” an intermediate phase between a solid and isotropic liquid state, thus having a unique double melting point. A perfect crystal has an order parameter of one, while an isotropic liquid has an order parameter of zero. The order parameter S of a liquid crystalline material usually ranges from 0.3 to 0.9. Due to a common alignment direction and the unique shape of the molecules, mesogens exhibit anisotropic properties (properties that vary due to the direction of measurement). In terms of optical properties, liquid crystals exhibit multiple refractive indices (ordinary and extraordinary, n_o and n_e), which results in birefringence (defined as $\Delta n = n_e - n_o$). The observed magnitude of the LC birefringence depends on the direction of its optical axis with respect to the incident light.

Liquid crystals can be separated into three categories, depending on their degree of order. Nematic liquid crystals are the least ordered. The long axes of these mesogens align parallel to each other. Nematic liquid crystals are desirable for the LCPDI because they readily respond to electric and magnetic stimuli. Cholesteric liquid crystals align similar to nematics, but protruding side groups cause the long axes of the mesogens to stack on top of each other in a helical fashion. These structures have a high optical activity and readily rotate plane polarized light. Smectic liquid crystals are the most highly ordered. The molecules align parallel to each other, but can organize into rows, and in some cases, rows and columns that are free to slide past each other.

When pure nematic liquid crystals are placed into a cell, in the absence of external forces or effects they tend to align parallel to the substrates. If the nematic liquid crystal molecules have large dipoles parallel to the molecular axis, they will align with an electric field applied perpendicular to the glass substrates. The liquid crystal mixture

Merck E7 used in these experiments is composed of cyanobiphenyl and cyanoterphenyl compounds, as shown below in Fig. 1. The cyano (CN) group has a large dipole moment.

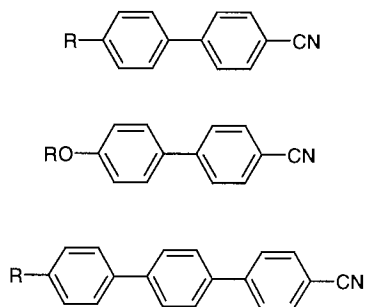


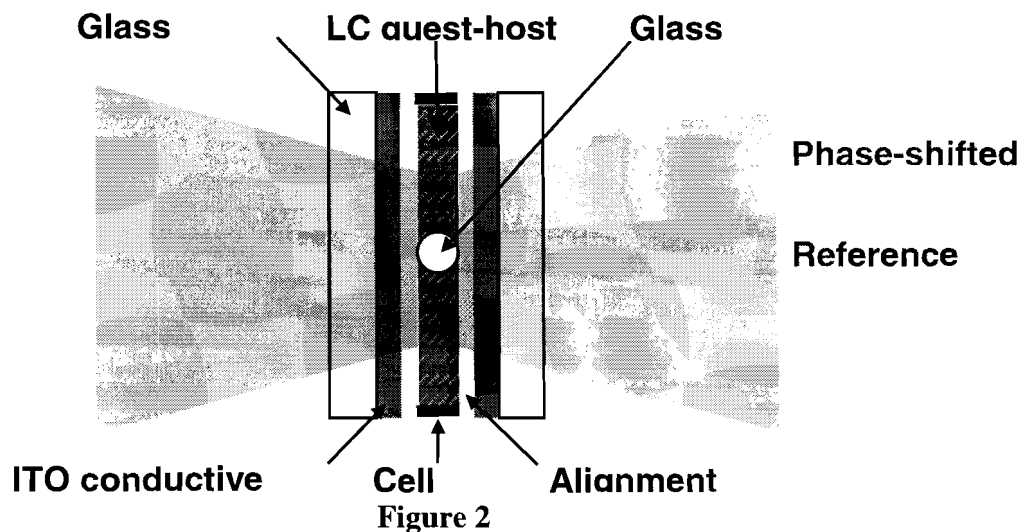
Figure 1

The LCPDI

To optimize the performance of the OMEGA laser, the hundreds of lenses and optical parts in the system must be tested for aberrations. The LCPDI is a better tool than a commercial interferometer for testing both OMEGA optics and for NASA experiments in microgravity fluid physics because it is small and compact (about the size of a quarter), insensitive to environmental factors such as air currents and vibrations, and is substantially less expensive. Figure 2 shows the configuration of the LCPDI. The main structure of the LCPDI consists of two pieces of glass that each contain an electrically conductive coating of mixed indium- and tin oxides (ITO). This coating allows voltage to go through the cell. The substrates were cleaned and spin coated with nylon polymer dissolved in formic acid. The nylon acts as an alignment layer to insure that all of the LC molecules are pointing in the same direction. After drying on a hot plate, the substrates were buffed. Buffing is essential to the fabrication of a cell. This process produces microscopic scratches in the nylon coating of the substrate. These scratches allow the LC material to align in the cell with all of the LC molecules pointing in a common direction. The cell gap was created using glass beads with a 22-micron diameter mixed in an UV –

curing epoxy mixture. The beads were placed at each of the four corners of the cell, which sets the cell gap/ path length of the cell at 22 microns. Using a microscope, a polystyrene divinyl benzene microsphere having a diameter ranging from 22- 42 microns is placed in the middle of the cell. Because the plastic microsphere in the middle of the cell is larger in diameter than the cell gap, it is compressed into a more cylindrical shape when the glass plates are bonded together. The cell is then filled with the LC fluid and sealed with epoxy to prevent fluid leakage. Wires are applied to the outside of the cell.

The LCPDI device uses a green helium neon laser. As the beam enters the cell, the plastic microsphere splits the beam into two, producing a reference wave front (the portion of the beam that went through the plastic microsphere), and an object beam front (the portion of the beam that passed through the LC matrix)*.



*C. Mercer and K. Creath, "Liquid- Crystal Point- Diffraction Interferometer for Wave- Front Measurements", Appl. Opt. 35, (10), 1996.



Figure 3

Figure 3 above compares interference fringes from an actual LCPDI device (left) to those generated by a computer simulation (right). The simulation shows the effect when there is an aberration in the object beam.

Dichroic dyes

Because the cross-sectional area of the portion of the laser beam passing through the glass reference bead in the LCPDI is substantially smaller than that passing through the LC fluid, the intensity of the two beams is mismatched and the fringe contrast is poor. To solve this problem, a “guest” dye is added to the LC “host” to equalize the intensity in the two beams. Currently, the LCPDI utilizes Oil Red O (Fig. 4), an oil-soluble dye with an elongated molecular structure that has *positive absorption dichroism* (absorbance decreases with applied electric field).

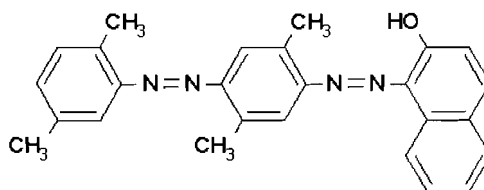


Figure 4

This effect is observed because the π -electron cloud responsible for the absorption in these molecules is distributed *along* the molecular axis. Positive dichroic dyes have been used up to now because of they are readily available and highly soluble in the liquid crystal host. However, this voltage-induced change in fringe contrast is very undesirable and limits the capabilities of the LCPDI device. One way to solve this problem that has been demonstrated in previous research is to add dyes with *negative absorption*

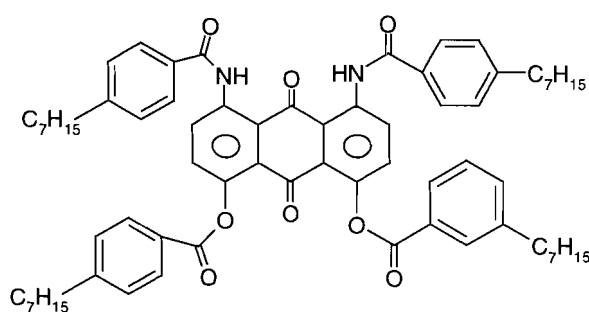


Figure 5

dichroism, (e.g., anthraquinone dyes, Fig.5) in which the optical density *increases* with increasing voltage, to guest-host mixtures containing positive dichroism dyes to reduce or eliminate the voltage dependence of the contrast. Unlike positive dichroic dyes, negative dichroic dyes such as anthraquinones have a π electron distribution cloud that extend *out and away* from the long molecular axis.

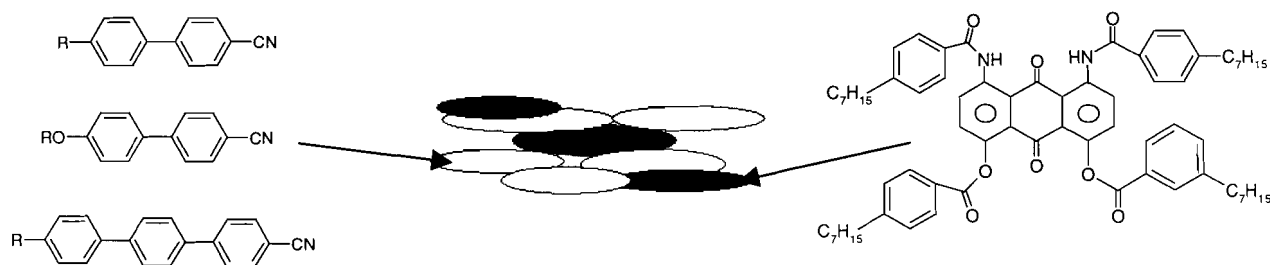


Figure 6

Guest- host dye systems are composed of mixtures of dye molecules, the “guest,” introduced into a nematic liquid crystal “host” (Figure 6). In the experiments reported

here, negative dichroic dyes based on anthraquinone were used as the “guest” and the host was Merck E7. The magnitude of absorption depends strongly on molecular structure. These anthraquinone based dichroic dyes are fairly easy to synthesize, however, purification of these dyes is very difficult.

The anthraquinone dyes used in this work were synthesized at LLE and contained either two or four reactive sites. As an end product, mixtures of mono- and multiple-substitution products were generally obtained (Fig. 7). Complexities arose in creating higher concentrations of dye in the guest- host dye systems that would maintain solubility

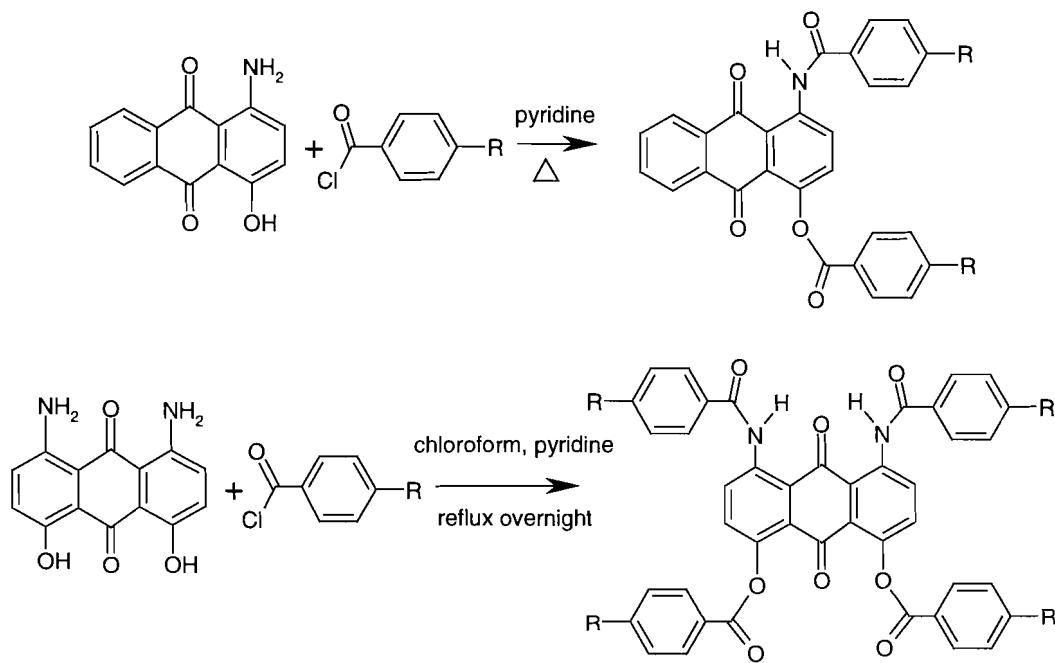


Figure 7

in Merck E7. Before inserting the guest- host mixture into a cell, the solubility limit was obtained. Dye solubility limits in the LC host were determined using a simple “sedimentation” experiment*. Samples of each dye were weighed and added to 1 gram of

*Irene Lippa, “Synthesis of Nickel Dithiolene Dyes and Analysis of Solubilities in a Nematic Liquid Crystal Host”, LLE Summer High School Research Program, 1998

Merck E7. Concentrations of dye ranged from 0.1% - 5%. The mixture was stirred and heated to 80° C (well above the liquid crystal clearing point of 65° C) for two hours. After the mixtures cooled, they were filtered through a 0.45-micron Teflon membrane filter. Slides were then prepared, and were observed every 24 hours both visually and by microscopic inspection for signs of precipitation, as shown in Fig. 8 for a 0.5 wt% mixture of 9 heptylbenzoyl dye in E7.

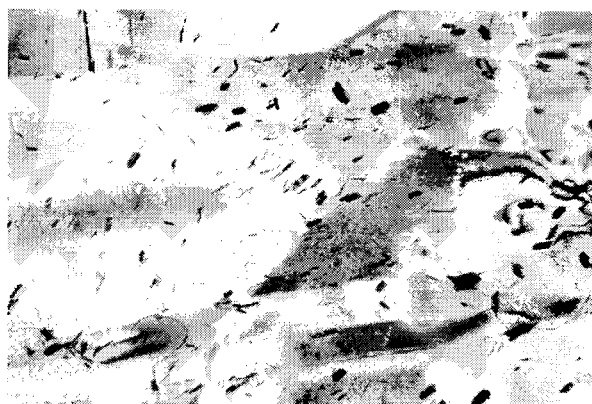


Figure 8

After the solubility limit had been found, the guest- host dye mixture was injected into a cell. The Lambda 900 spectrophotometer was used to find the absorbance of the dyes at different voltages. Voltages applied to the cell ranged from 0.1- 10 V at 1 kHz sine wave. After collecting data on the absorbance of each cell, the dichroic ratio and order parameter were determined. The dichroic (contrast) ratio is the absorbance of the dye molecule in the perpendicular orientation divided by the absorbance of the dye molecule in the parallel orientation. Ideally, the dichroic ratio should be as high as possible.

Of all the negative dichroic dyes tested, the tetrasubstituted 1,8-bis-(heptylbenzoylamino)-4,5-bis-(heptylbenzoyloxy)anthraquinone (Fig 9) at 1 wt % in E7 was found to be the most promising for the LCPDI. Unfortunately, higher percentages of

this dye are needed, but cannot currently be achieved due to solubility issues. Overall, this tetra- substituted heptyl derivative had the best combination of solubility, order parameter, and dichroic ratio. The λ_{max} in chloroform was 526 nm, but in E7 the λ_{max} underwent a bathochromic (red) shift to 537nm.

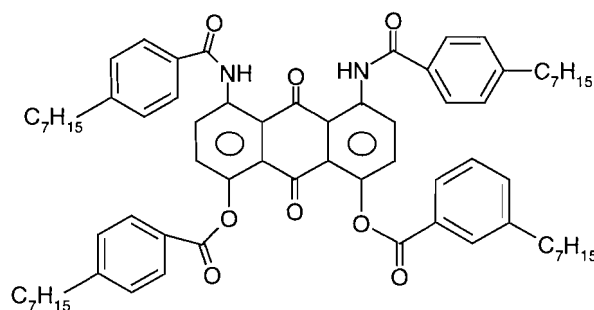
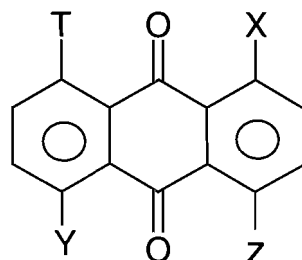


Figure 9

The same shift was also observed in “heptylbenzoyl”, which also contained heptyl groups substituted at the positions T and X (Fig 10). Heptylbenzoyl (a purple dye), had a



Functional Group:				Solubility limit	λ_{max} (CHCl ₃)	λ_{max} (E7)	D (543nm)	S
T	X	Y	Z					
H ₁₅ C ₇ PhC=ONH	H ₁₅ C ₇ PhC=ONH	H ₁₅ C ₇ PhC=OO	H ₁₅ C ₇ PhC=OO	1%	526 nm	537 nm	4.3	0.435
H ₉ C ₄ PhC=ONH	H ₁₅ C ₇ PhC=ONH	H ₉ C ₄ PhC=OO	H ₉ C ₄ PhC=OO	<0.1%	521 nm	-	-	-
H	H ₁₅ C ₇ PhC=ONH	H	H ₁₅ C ₇ PhC=OO	>3%	427 nm	410 nm	1.4	0.223
H	H ₁₇ C ₈ PhC=ONH	H	H ₁₇ C ₈ PhC=OO	>5%	427 nm	403 nm	1.6	0.274
H ₁₅ C ₇ PhC=ONH*	H ₁₅ C ₇ PhC=ONH	OH	OH	0.125%	550 nm	552 nm	12.8	0.480

Figure 10

dichroic ratio of 12.8:1. A hypsochromic (blue) shift on changing the host from chloroform to E7 was observed in heptylbenzoylamino and octylbenzoyl, which both had groups substituted at positions X and Y. Both of these dyes also exhibited high solubility in E7, (octylbenzoyl at >5%, and heptylbenzoylamino at >3%). From the data collected, it can be determined that the λ_{\max} depended on both the host composition and dye structure.

An initial test cell containing 0.8206g of 1 wt % tetraheptylbenzoyl in Merck E7 and 0.0106g of 2 wt. % Oil Red O in E7 was assembled and evaluated (Fig 11). This guest- host dye mixture was prepared by blending two stock mixtures of positive and negative dichroic dyes. No miscibility or conductivity problems were observed. At 543.5 nm, the O.D. was 3 over a range of 0 -1 volts, but the O.D. dropped at higher voltages (Fig. 12). From this analysis, it was concluded that larger concentrations of negative dichroic dyes will be needed to produce voltage- independent contrast.

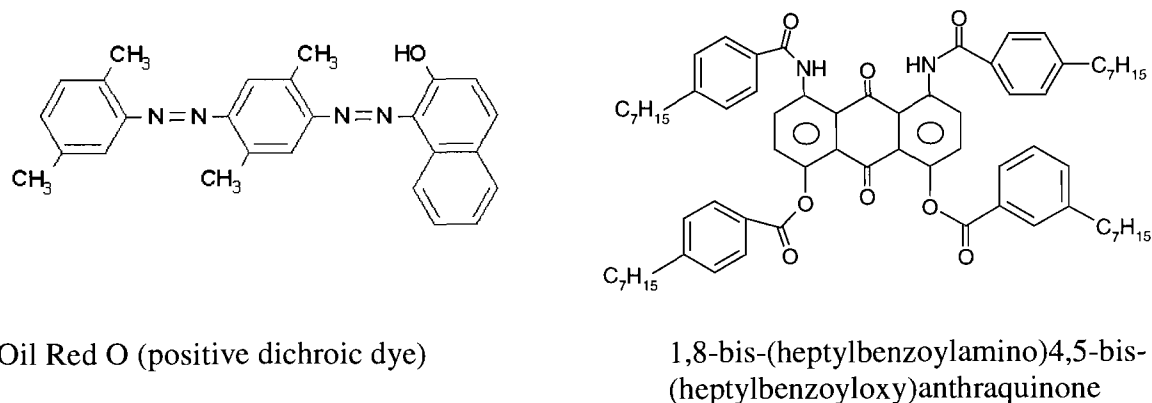


Figure 11

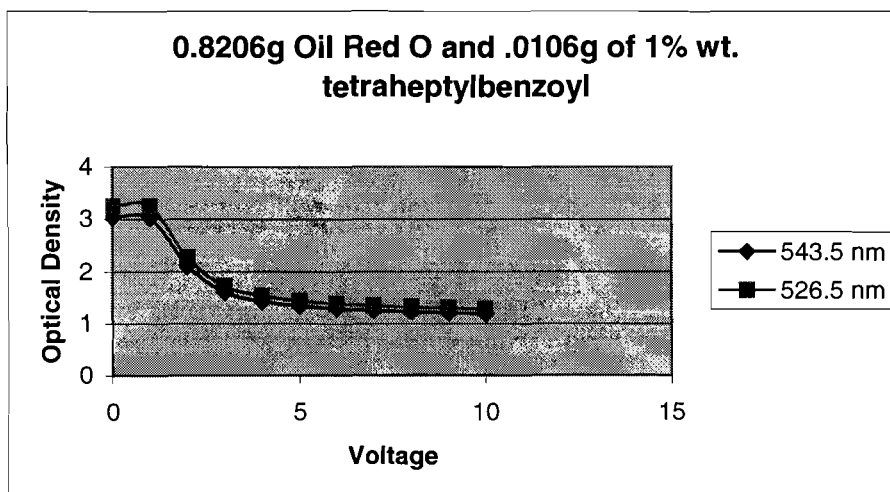


Figure 12

Summary

Negative dichroic dyes are expected to enhance the performance of the liquid crystal point diffraction interferometer. The LCPDI is desirable as a diagnostic tool for testing aberrations in the lenses of the OMEGA laser and for NASA experiments in microgravity fluid physics. Due to the unique structure and properties of negative dichroic dyes, the optical density increases with an increase in voltage. The λ_{\max} of anthraquinone-based negative dichroic dyes shift either to longer or shorter wavelengths (depending on molecular structure) when dissolved in a nematic LC host. Select anthraquinone dyes displayed outstanding solubility characteristics in nematic LC. In the future, mixtures of Oil Red O and negative dichroic dyes are expected to improve the contrast of fringes in current LCPDI devices.

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