

**Chiroptical Properties and Mesophase Stability of Saturated Chiral Dopants
for High Peak Power Liquid Crystal Device Applications**

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Abstract

Liquid crystal polarizer (LCP) devices are critical optics on the OMEGA laser used to transmit circularly polarized light while also functioning to protect the system from retro reflections. The chiral dopant used in the nematic LC host mixture in the majority of OMEGA LCP's is CB-15, a compound containing delocalized π -bonded structural elements that negatively impact the laser-induced damage threshold (LIDT) of the host LC, depending on the dopant concentration. The optical absorption of the material also increases as the incident wavelength approaches the ultraviolet (UV) region of the spectrum. These two factors serve to reduce the operational lifetime of LC optics employing CB-15 and prevent them from being deployed in the UV portion of the laser system for applications such as polarization control. The LIDT's of liquid crystals (LC's) are consistently higher in *saturated* materials (molecules in which π -bonds are either completely absent or widely isolated) than in their unsaturated counterparts, such as CB-15. In this work, several different saturated chiral dopants were evaluated over a wide range of concentrations in two different nematic LC hosts with the goal of finding a replacement material for CB-15 that possesses a higher LIDT. The factors considered included helical twisting power (HTP), UV absorbance, solubility, and LC phase orientation. Evaluation of these series of properties using polarizing optical microscopy and UV-VIS-NIR spectrophotometry showed that cholesterol oleate (CO), S-811, and MLC-6247 are promising saturated chiral dopant candidates. Although CO has a low HTP when calculated in terms of weight concentration, CO shows the best results to date due to CO's low UV absorbance, good solubility, and ability to produce the desired planar LC orientation. Future research is needed to determine the laser damage resistance of these promising chiral dopants.

1. Introduction

In the OMEGA laser system at the Laboratory for Laser Energetics (LLE), liquid crystal (LC) devices are used to transmit circularly polarized laser light, while simultaneously preventing back-reflected light from causing damage to the laser system. Circular polarization is desired as it allows the laser amplifiers to operate at nearly 100% efficiency by mitigating birefringence effects [1].

Unpolarized light contains two different circularly polarized components: right-handed (RH) and left-handed (LH). LC circular polarizers (LCP's) isolate one handedness of light from the other by allowing one handedness to pass through the device, while the other handedness is reflected or scattered. This effect is called “selective reflection” [1]. An illustrative example of the selective reflection effect is shown in Fig. 1. For a right-handed LCP, the right-handed circular light passes through the LC device towards the target, while the left-handed light is reflected. When back-reflected left-handed circular light encounters the LC device, the light is reflected diffusely since it is unable to pass through the LC device.

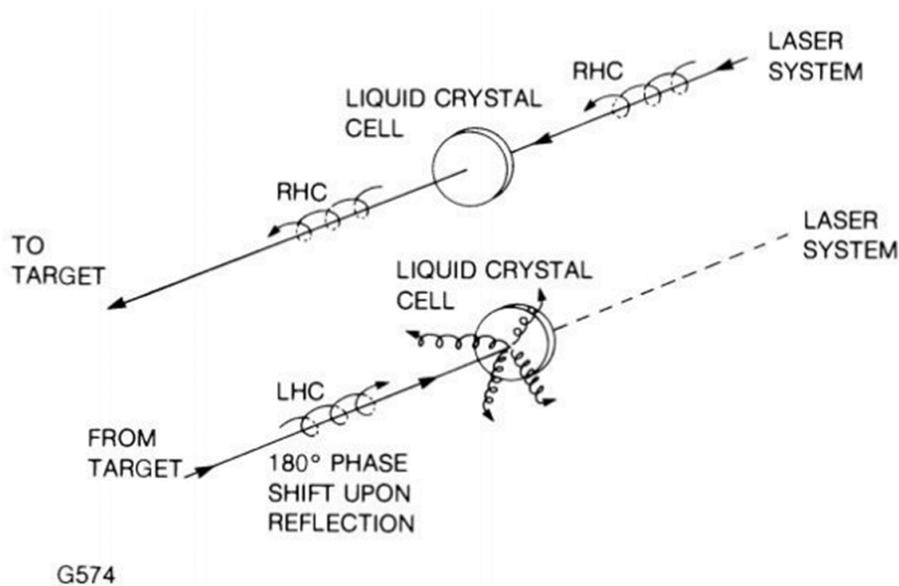


Fig. 1: Illustration of the use of LCP's to protect the laser system from back-reflected light. RHC and LHC denote the two polarizations of light [2].

LCP devices consist of a mixture of a nematic LC host and a chiral dopant. Nematic LC's are rod-shaped molecules that exhibit anisotropy, meaning the physical properties of the material are directionally dependent [3]. In the nematic phase, there is long-range orientation of the LC molecules aligned in a particular direction, along a common axis, referred to as the director. However, they are not ordered in the same way as in a solid [3]. Instead, they maintain their fluidity and mobility, similar to a liquid. LCP's employ mixtures that orient in the chiral nematic LC phase. The chiral nematic LC phase is a phase that is characterized by the presence of chirality, or handedness, in the alignment of the LC molecules (Fig. 2). In this phase, the LC molecules are aligned in a particular direction, similar to the nematic phase, but they also exhibit a helically twisted structure in which the orientation of the molecules rotates along the axis perpendicular to the director (Fig. 2) [3]. This twisting structure is referred to as the cholesteric helix and possesses a pitch length, which is the distance for one full revolution of the director, the average alignment direction of the LC molecules [3]. The operational selective reflection wavelength of an LCP is governed by the pitch length and the average refractive index of the mixture.

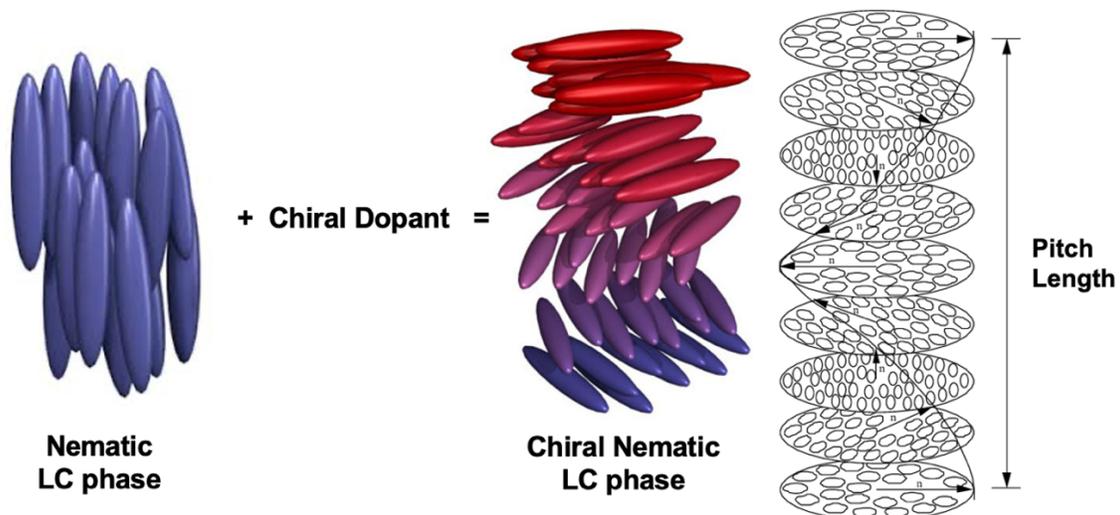


Fig. 2: Visual representation of the components in a chiral nematic LC mixture, which includes a nematic LC and a chiral dopant. The chiral nematic LC mixture has a pitch length that comprises one full rotation of the director axis.

This “selective reflection” effect occurs for specific wavelengths that satisfy the equation $\lambda_{\max} = np$, where λ_{\max} is the selective reflection peak wavelength, n is the average refractive index of the mixture, and p is the pitch length. The pitch length is dependent on the chiral dopant concentration, its helical twisting power (HTP) (Fig. 3), and the mixture temperature [1].

$$\frac{1}{P} = B_M * c$$

$P = \text{pitch length}$
 $B_M = \text{HTP}$
 $c = \text{wt\% concentration}$

Fig. 3: Equation used for the calculation of helical twisting power (HTP) of a chiral dopant. Because the value of HTP depends on the host LC composition, it must be determined separately for each host.

Molecular structures referred to as “saturated” contain almost no double bonds or π -bonded systems. In contrast, unsaturated structures contain delocalized π -bonds, typically in the form of benzene rings (Fig. 4).

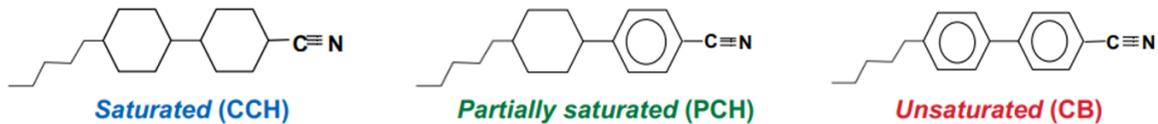


Fig. 4: Illustration of saturated, partially saturated, and unsaturated molecular structures [4].

According to previous research conducted at LLE, laser-induced damage thresholds of LC’s are much higher in saturated materials than in unsaturated materials (Fig. 5), which makes saturated structures more favorable for use in a high-peak-power laser system [5].

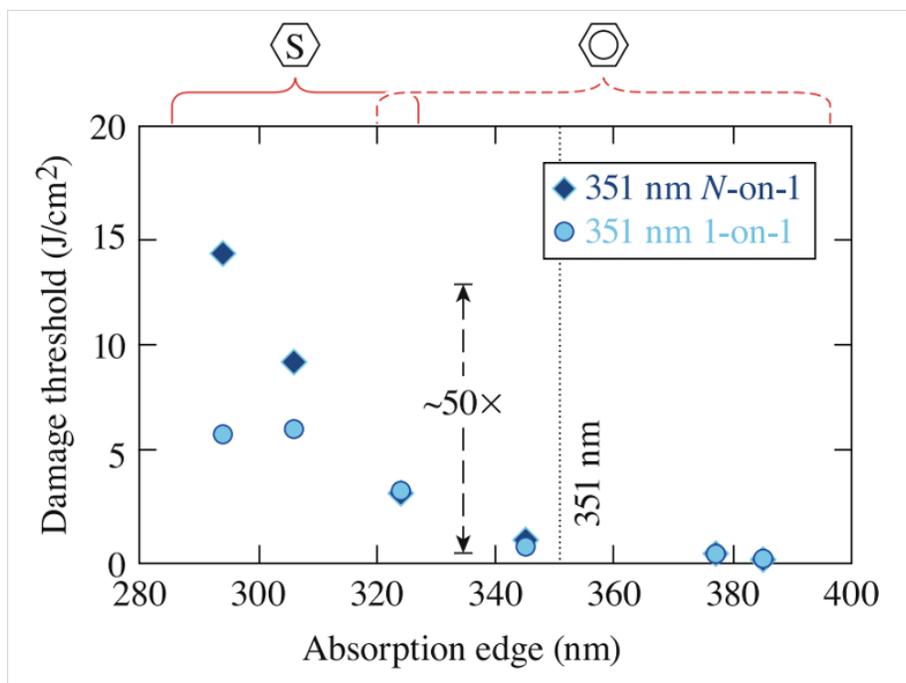


Fig. 5: Graph of damage threshold (J/cm^2) vs absorption edge (nm) of saturated (left part of graph) and unsaturated (right part of graph) LC compounds [5].

The current chiral dopant, CB-15, used in the LCP devices in the OMEGA laser system has a highly unsaturated structure. It has many double bonds, in the form of two conjugated benzene rings and a triple bond between carbon and nitrogen in the cyano group.

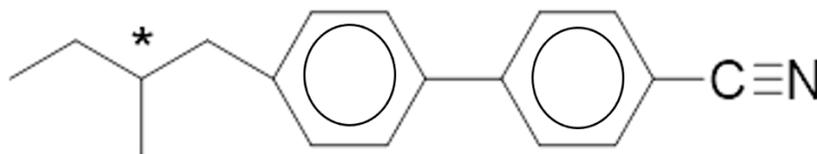


Fig. 6: The molecular structure of CB-15, the current chiral dopant used in the OMEGA LCP devices.

For this study, the goal was to find a more laser-damage-resistant, saturated chiral dopant to replace CB-15. Ten commercially available saturated chiral compounds were evaluated as dopants in the nematic host LC's ZLI-1167 and MLC-2037 (Table 1). ZLI-1167 showed better compatibility and stability with the dopants, so this study is focused mainly on this host.

Saturated Chiral Compounds	Nematic Host LC's
Cholesterol oleate (CO)	ZLI-1167
S-(-)-Perillyl alcohol	MLC-2037
L-Proline t-butyl ester	
Uridine	
2-Ethyl fenchol	
S-(-)-Limonene	
S-811	
MLC-6247	
Stigmasterol	
Androsterone C9 ester	

Table 1: Table displaying a list of 10 different saturated chiral compounds and 2 nematic host LC's studied in this work.

The saturated chiral dopants tested contain little-to-no double bonds in the structures, and they possess either mesogenic or isotropic phases in their pure state (three examples are shown in Fig. 7). Mesogenic materials are those that exhibit mesophase behavior, meaning they exhibit both liquid-like and solid-like properties, and display orientation-dependent optical properties. Isotropic materials have no preferred orientation, and their physical properties are the same regardless of the measurement direction (e.g., water) [3]. The distinction between mesogenic and isotropic is a fundamental aspect of the behavior of LC materials and has important implications for the design and functionality of LC materials and devices.

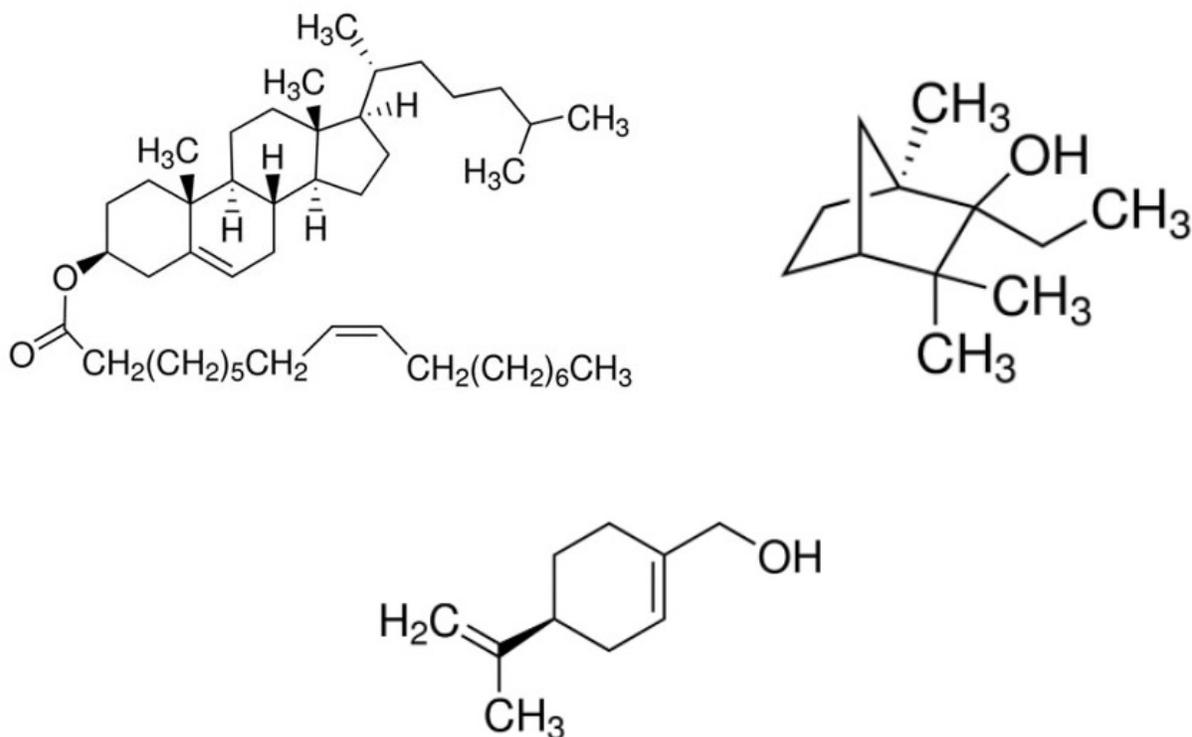


Fig. 7: The molecular structures of some of the chiral dopants studied in this work: CO (mesogenic) (top-left), 2-ethyl fenchol (isotropic) (top-right), and S-(-)-perillyl alcohol (isotropic) (bottom).

2. Experimental Procedures

2.1 UV Transmittance of chiral dopants

Evaluating the UV absorbance of the chiral dopant candidates was the preliminary screening method. To do so, the dopants were dissolved in cyclohexane at 0.235 molal concentration (molal = moles of solute per kilogram of solvent). The transmittance of the chiral dopants in cyclohexane was measured using UV-VIS-NIR spectrophotometry on a Lambda 900 (Perkin Elmer) spectrophotometer using quartz cuvettes (Starna) with 1 cm path lengths. Cyclohexane is a UV-transparent solvent that does not interfere with this analysis. This method was used since some of the chiral dopants are in the solid phase at room temperature, and they

must be in a liquid form for the UV-VIS-NIR analysis. High UV transparency is typical of saturated structures and an indicator that the compounds may possess high laser damage thresholds.

2.2 Preparation of LC Mixtures

LC mixtures were prepared by combining a saturated chiral dopant and a nematic host in a glass vial that had been cleaned with isopropyl alcohol and spectral grade methanol. Depending on the phase the chiral dopants and nematic hosts are in at room temperature, a metal spatula or a syringe was used accordingly to help measure and transfer the materials from their original containers to the cleaned glass vial. The quantities of dopants and nematic hosts were measured in milligrams using a top-loading balance, which measured to the hundredths place. The mixtures were then heated on a hot plate for 30 minutes with stirring until the mixture became homogenous. The mixtures were typically heated to 100°C unless a chiral dopant was evaluated with a boiling point below this value. In that case the mixture was heated to 50°C.

2.3 LC Phase Analysis: Polarizing Optical Microscopy

Test samples for polarizing optical microscopy were prepared by placing a small amount of the LC mixture between a microscope slide and coverslip. The slides were then placed under the polarizing optical microscope (POM) in a hot stage. The different phases of the samples were observed under the microscope at 100X magnification. Two heating cycles were run on the sample: 7°C/min followed by 2°C/min. The 7°C/min heating cycle was used to even out the mixture and make it more homogenous. The 2°C/min heating cycle was used to determine the phase behavior of the mixture. The temperatures at which the sample went through a phase transition and the orientation of the sample (planar, fingerprint, focal conic, or homeotropic, diagrammed in Fig. 8) were recorded. The heat cycle would be stopped once the mixture became completely isotropic,

which is when the LC material becomes completely transparent, and the LC molecules are randomly oriented with no long-range orientation or ordered structure. The temperatures at which the LC mixture changed phases and the orientation of the mixture were recorded again as the LC mixture cooled from its clearing point back down to room temperature. If the LC mixture had a fingerprint orientation (cholesteric helix axes parallel to the substrates), its pitch length in micrometers was determined using the POM (without the hot stage) to focus on the fingerprint pattern using a 50X objective (500X total magnification). The distance between two successive light-dark sequences in the texture in micrometers was measured in several areas of the sample, and the distances were averaged to determine the pitch length.

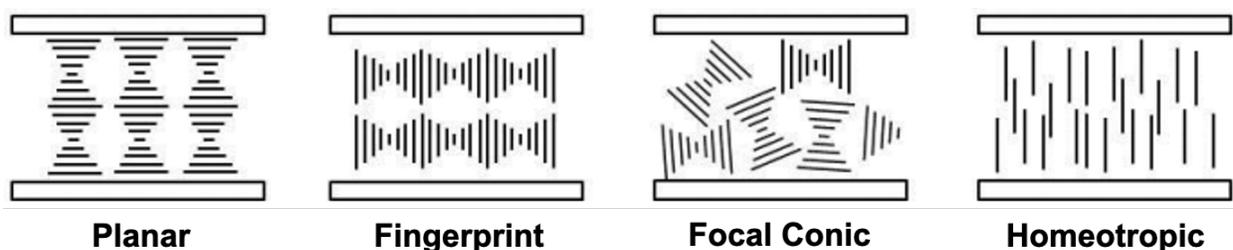


Fig. 8: Illustrations of the different types of possible chiral nematic LC orientations between two substrates.

2.4 LC Mixture Pitch Length and HTP Analysis: UV-VIS-NIR Spectrophotometry

The UV-VIS-NIR spectrophotometer (UV-VIS-NIR) was used to determine the test mixtures' selective reflection peak wavelengths (λ_{\max}). This instrument determines the transmittance of the mixture by scanning different wavelengths of light through the mixture. Initial scans of new mixtures were conducted over a wide range of wavelengths from 3000 nm to 300 nm. The selective reflection peak wavelength was determined by a 50% loss in transmission of the sample. The 50% loss in transmission is due to half of the light from the UV-VIS-NIR being reflected or scattered by the chiral nematic fluid. The minima of the percent transmission are used to determine pitch lengths, which are then used to calculate the HTP's. Pitch length vs.

concentration dilution curves were created to calculate the weight percent of chiral dopant that was needed in the nematic host to hit the 1054 nm pitch length.

2.5 LC Mixture Device Fabrication

The LC test devices were constructed in a Class 10000 clean room environment. They were created by buffing nylon alignment layers on glass substrates and depositing spacers consisting of 22-micron microspheres mixed in epoxy between the substrates applied in four places near the edges. The empty devices were placed on a hot plate and heated to 70°C, then filled with the LC mixture using a syringe and allowing the LC fluid to flow into the cell gap. In the device, the orientation of the mixture is determined using the POM and the λ_{max} is determined using the UV-VIS-NIR.

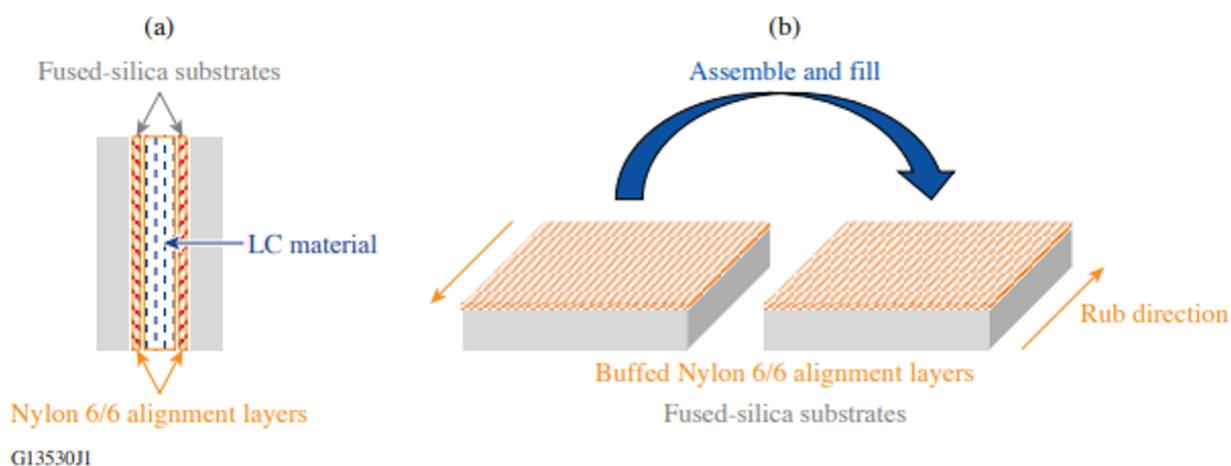


Fig. 9: Illustration showing a side view of the process of fabricating an LC device; (a) LC material is sandwiched between two fused silica substrates; (b) two fused silica substrates are coated with nylon and buffed to create alignment layers, assembled and filled.

3. Results and Discussion

The POM analysis conducted on the chiral nematic mixtures revealed that many of the chiral dopants demonstrated good phase behavior with the LC hosts. Figure 10 shows

photomicrographs of the fingerprint (left) and focal conic (right) textures observed for two chiral nematic mixtures under polarized light. The focal conic orientation is more desirable as it indicates the mixture is likely to form a planar orientation in a device. A planar orientation is necessary for a circular polarizer to function. For mixtures that displayed the fingerprint texture, the pitch length was determined by measuring the distance across the length of two successive light-dark bands. The pitch length of focal conic mixtures was obtained from their selective reflection peak wavelength determined by UV-VIS-NIR spectrophotometry.

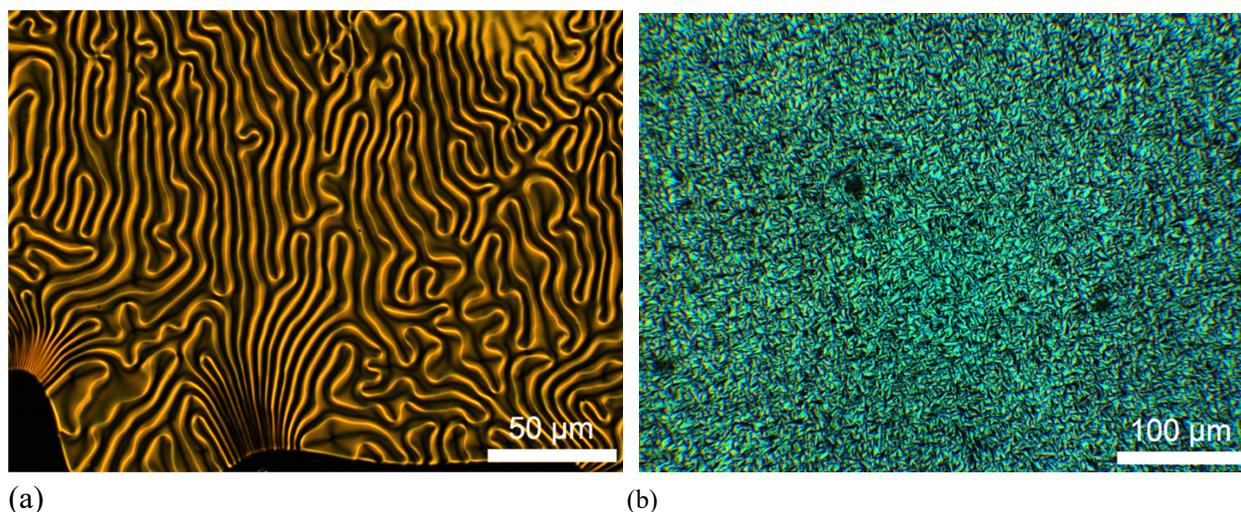


Fig. 10: Photographs taken using POM of (a) 15 wt% S-(-)-perillyl alcohol in ZLI-1167 “fingerprint texture” and (b) 39.17 wt% CO in ZLI-1167 “focal conic” texture; these photographs differ from the side-view diagrams in Fig. 8 in that they are captured from the direction of incident light propagation.

Pitch length and helical twisting power (HTP) are inversely related in the equation shown in Fig. 3. The HTP for a single dopant may also be different depending on which nematic host it is dissolved in. The chemistry of both the host and dopant are important to the HTP.

The UV absorbance values of the pure chiral dopants in cyclohexane were determined by UV-VIS-NIR spectrophotometry. With the exception of S-(-)-perillyl alcohol, all of the dopants tested demonstrated a lower UV absorbance than CB-15 (Fig. 11), which indicates that these

compounds may be more resistant to laser-induced damage. The CB-15 solution absorbs a significant amount of UV light and is completely absorbing by 325 nm.

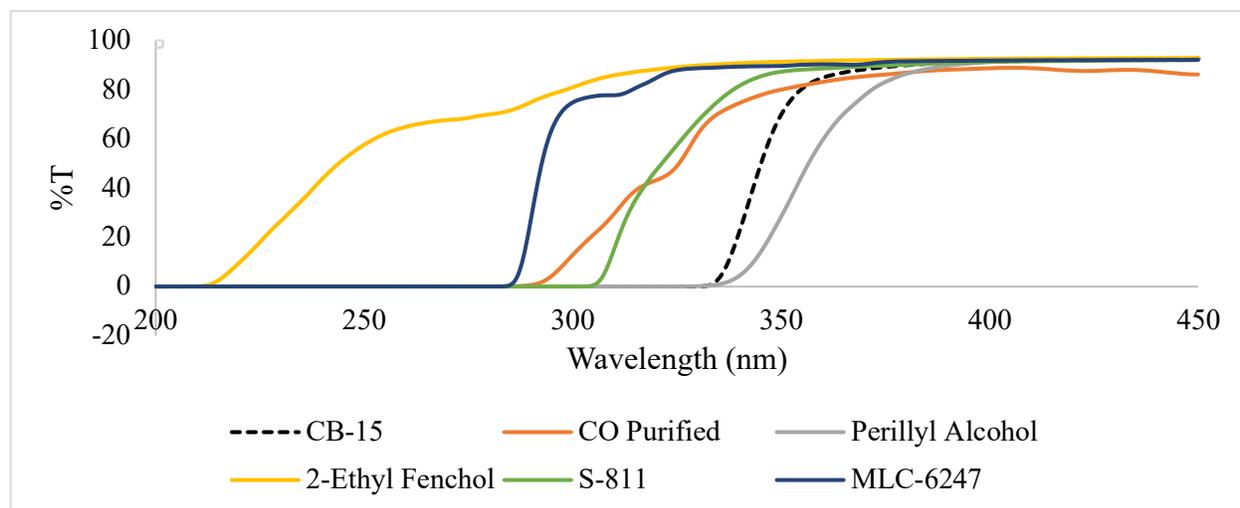


Fig. 11: Graph of the UV-Vis absorption spectrum of pure chiral dopants dissolved in cyclohexane. The spectrum of CB-15 in cyclohexane is shown in the dashed line and exhibits a sharp UV absorption cutoff below 350 nm.

S-811 and MLC-6247 both had favorable UV transmission, but no further research was done pursuing these chiral dopants due to time constraints. A more detailed study of these promising chiral dopants will be performed in future studies. Due to a combination of promising properties such as good solubility, low UV absorbance, and promising LC orientation, the λ_{\max} for the CO mixture in ZLI-1167 was fine-tuned to the operating wavelength of the OMEGA circular polarizers (1054 nm). This process involved preparing a series of concentrations ranging from 30% to 50% CO in 5% increments and measuring the selective reflection band on the UV-VIS-NIR. A plot of the λ_{\max} vs wt% CO was constructed (Fig. 12) from this data. Based on this plot, 41.5% CO in ZLI-1167 was determined to be the concentration necessary for generating a λ_{\max} at 1054 nm. Using the UV-VIS-NIR, the 41.5% CO in ZLI-1167 mixture was determined to have a λ_{\max} of 1049 nm, which is within the specification tolerances for OMEGA (1054 +/- 13 nm).

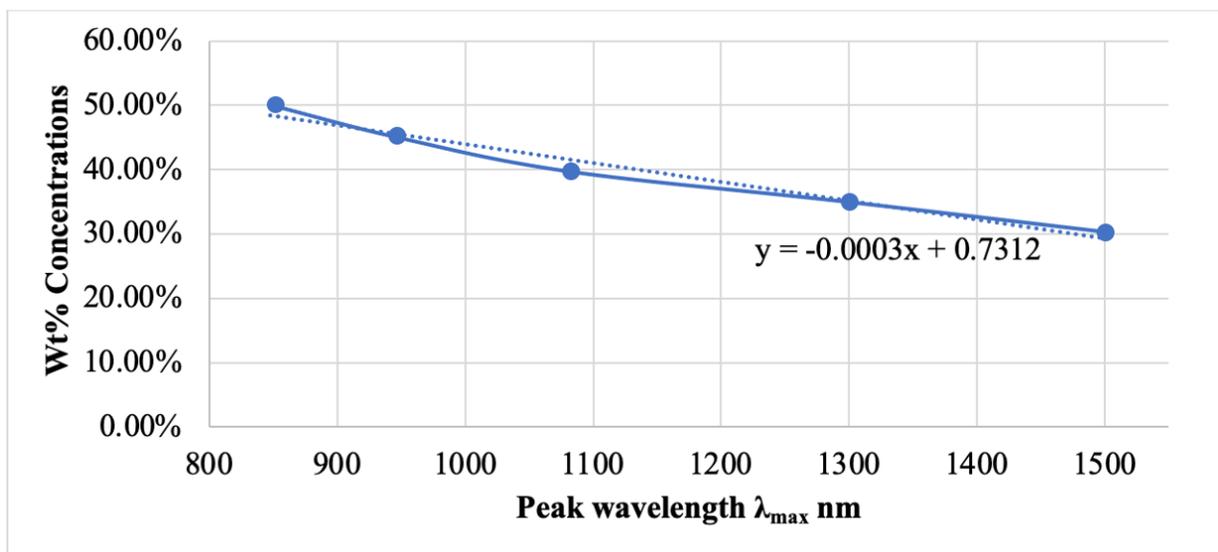


Fig. 12: A dotted best-fit linear graph of the wt% concentration vs. λ_{\max} was created using data from the % transmittance of 5 dilutions of CO in ZLI-1167 mixture at different wavelengths represented by the points on the solid line.

The mixtures 19.43 wt% CB-15 in ZLI-1167 and 41.13 wt% CO in ZLI-1167 both represent a wt% concentration of chiral dopant that generates λ_{\max} near 1054 nm. The enantiomeric purity of both dopants is assumed to be 100%. The equation shown in Fig. 3 was used to determine the HTP of both mixtures. The 19.43 wt% CB-15 in ZLI-1167 mixture had an HTP of $4.83 \mu\text{m}^{-1}$, and the 41.13 wt% CO in ZLI-1167 mixture had an HTP of $2.28 \mu\text{m}^{-1}$. Although CO has a smaller HTP than CB-15, its improved UV transparency makes it promising.

Using the 41.13% CO in ZLI-1167 mixture as the reference, an LC device was then fabricated using 41.5% CO in ZLI-1167 following the procedures described in Section 2.2 and Fig. 9. The purpose of the device was to see if the focal conic chiral nematic mixture was able to align in the desired planar orientation when placed between two fused silica substrates with alignment layers. This phase alignment is critical for an LCP to function properly, so any new LC candidate mixture must demonstrate the ability to align in this orientation. Analysis by POM showed that the

CO-in-ZLI-1167 LC device displayed a planar orientation (Figure 13), demonstrating that CO is a viable candidate to replace CB-15.

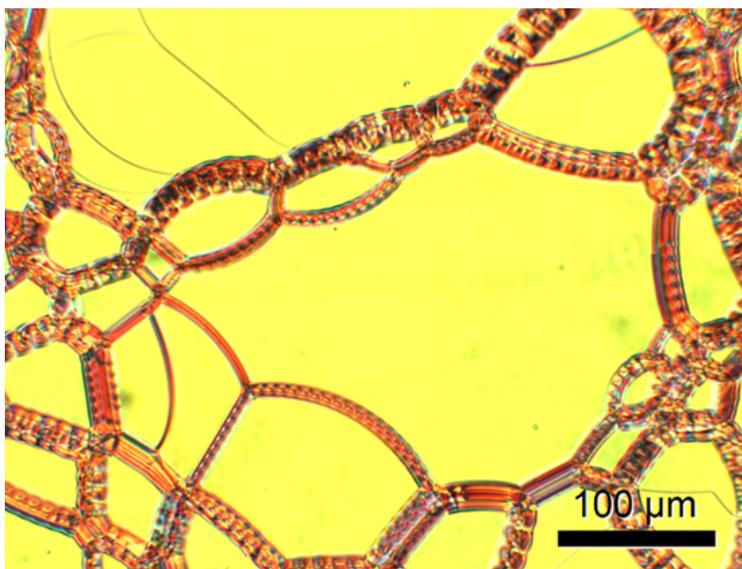


Fig. 13: POM micrograph of a mixture of 41.5% CO in ZLI-1167 in an LC device. The homogenous yellow background with sporadic disclination lines (brown), often termed as the “oily streaks” texture, indicates that a planar orientation has been achieved.

Overall, CO was found to be the most promising chiral dopant since it has a balance of important properties such as high HTP, low UV absorbance, good solubility, and a planar chiral nematic orientation in the ZLI-1167 nematic host. While S-811 and MLC-6247 showed promising UV absorbance, further research needs to be done to evaluate these dopants. The other chiral dopants were not evaluated further due to them displaying a fingerprint texture or insolubility in the nematic host ZLI-1167. A summary of these properties and behavior including physical state, solubility, wt.% concentration, pitch length, texture, twist sense, and HTP in ZLI-1167 is shown in Table 2.

Dopant	Physical state (25°C)	Soluble in ZLI-1167	Dopant concentration Wt. %	Pitch length (μm)	Texture	Twist sense	HTP in ZLI-1167 (μm ⁻¹)
CB-15	Isotropic liquid	Y	19.43%	1.066	Planar	RH	4.83
Cholesteryl oleate	Solid	Y	41.13%	1.067	“Oily streaks”	LH	2.28
S-811 (R-811)	Solid	Y	13.35%	1.064	Planar	LH (RH)	7.04
MLC-6247	Solid	Y	14.06%	1.055	Planar	LH	6.74
S-(-)-Perillyl alcohol	Isotropic liquid	Y	15%	2.15	Fingerprint	LH (RH)	3.10
2-Ethyl fenchol	Isotropic liquid	Y	15%	5.02	Fingerprint	LH (RH)	1.33
S-(-)-Limonene	Isotropic liquid	Y	10%	2.62	Fingerprint	LH (RH)	3.54
L-Proline, t-butyl ester	Isotropic liquid	Y	15%	11.07	Fingerprint	LH (RH)	0.602
Uridine	Solid	N	--	--	--	LH	--
Stigmasterol	Solid	N	--	--	--	LH	--
Androsterone C9 ester	Solid	N	--	--	--	--	--

Table 2: Table displaying a list of 11 different saturated chiral compounds and their properties studied in ZLI-1167.

4. Conclusions

Ten different saturated chiral dopants were tested in two different nematic hosts (Table 1) as alternatives to CB-15. Using POM and UV-VIS-NIR, the solubility, UV absorbance, HTP, and orientation of the mixtures and pure dopants were determined. Most of the chiral dopants were not evaluated in further detail, due to either their fingerprint texture observed by the POM or their insolubility in the ZLI-1167 nematic host (Table 2). A few of the mixtures that showed good results were then filled into devices. The devices were tested for planar orientation using the POM, which

is essential for circular polarizers to work, and for the selective reflectance peak using the UV-VIS-NIR to determine that the λ_{\max} was maintained. After testing a range of different saturated chiral dopants, CO was determined to be a very promising dopant candidate for LCP's. However, CO cannot be used as a direct replacement for CB-15, as it transmits left-handed circularly polarized light while CB-15 passes right-handed circularly polarized light. Some dopants under consideration are available in both left-handed and right-handed forms, such as S-811, which is left-handed and R-811, the right-handed form of S-811. As a result, they can be considered as replacements for CB-15 in right-handed LCP's. Future research will be focused on determining the laser damage threshold of chiral nematic mixtures employing CO and other promising dopants such as S-811 and MLC-6247.

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6. References

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