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Nonlinear optical director reorientation in heliconical cholesteric liquid crystals: a brief review

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Cholesteric liquid crystals, also known as chiral nematics, possess a right-angle helicoidal structure with pitch in the submicrometer and micrometer range. Although the possibility of getting optical reorientation in this kind of materials has been considered since the discovery of giant optical nonlinearity in nematic liquid crystals, a significant light-induced modulation of the helical structure has shown to be a challenging task. The recent experimental realization of a chiral phase with an oblique helicoidal structure, identified as the heliconical phase predicted by Meyer and DeGennes in 1968, offers the opportunity to observe such an optical reorientation of the optic axis. This paper is a brief review of the nonlinear optical properties of these unconventional chiral nematic liquid crystals and is aimed at showing that the world of liquid crystalline phases can still amaze with new material properties and new physics.

Introduction

The long story of the interaction between liquid crystals (LC) and light started at the beginning of 1980 when the group led by B.Ya. Zel'dovich reported a nonlinear optical response in thin samples of nematic liquid crystals [1]. The observed optical nonlinearity was about nine orders of magnitude higher than in a standard nonlinear medium like CS_2. Such a strong nonlinear response, that took the name of giant optical nonlinearity (GON), was due to a collective reorientation of the LC molecules induced by the electric field of an electromagnetic wave at optical frequency.

The work of Zel'dovich highlighted for the first time that a continuous optical wave of moderate intensity could produce strong nonlinear optical effects in liquid crystalline materials. After the first observation, many nonlinear optical phenomena were discovered and studied in liquid crystals by a rapidly increasing number of scientists in the world [2-12]. The peculiar physical properties of these materials opened a completely new branch of nonlinear optics based on the effects of their collective optical reorientation. Basically, the LC nonlinear optical response is due to the ability of the optical field to induce an optical torque on the LC molecules [13]. This leads to an intensity dependent refractive index $n = n^0 + \Delta n(I)$, where n^0 is the refractive index in the absence of light and $\Delta n(I)$ is the intensity dependent term (Δn is commonly indicated as the optically induced birefringence), which affects the propagation of the light itself giving rise to a nonlinear optical behavior. Indeed, a rigorous treatment of the effect must consider the LC elasticity, responsible for the collective response of these materials. A theory that couples the propagation of an electromagnetic wave in an anisotropic medium to the elastic properties of LCs was readily developed in the first years after the Zel'dovich paper [14,15].

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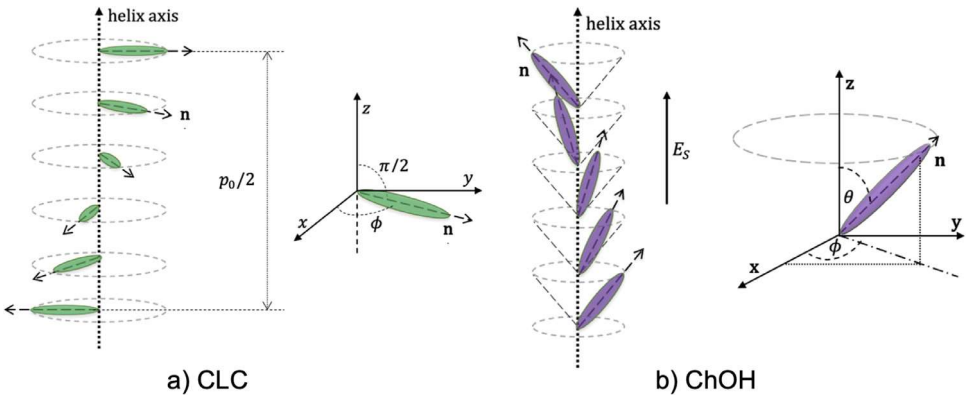


Fig. 1

Spatial arrangement of the molecular director in (a) conventional cholesteric (CLC) and (b) heliconical cholesteric liquid crystal (ChOH). a) A π rotation in planes perpendicular to the helix axis is depicted occurring along a distance $P_0/2$, where P_0 is the pitch of the helix. The director orientation is also shown; b) oblique heliconical structure sustained by a static electric field and local orientation of the director of a ChOH with helical axis along the z axis. E_S is the externally applied low frequency electric field, indicated as E in the text. Adapted with permission from ref. [52].

Thanks to their strong nonlinear response, liquid crystals may be used as sample media to study nonlinear optical effects, thereby greatly simplifying the experimental setup and the signal detection. At the same time, nonlinear optics represents a tool to study the liquid crystal phase and to get new or alternative measurements of the relevant physical parameters such as for instance elastic constants and viscosities [16]. Moreover, several applications for new optical devices have been proposed in these four decades from the discovery of GON, even if strong limitations are given by the slow response times that characterize the LC collective optical reorientation [see for example 17-20].

Although several years have passed and a remarkable amount of work has been done, nonlinear optics of liquid crystals is still a flourishing research field. This is mainly due to the large amount of different liquid crystalline materials, a part from the most used thermotropic nematic phase, exhibiting nonlinear optical response spanning from Polymer Dispersed Liquid Crystals [21] to lyotropic [12,22,23] and ionic [24] LC up to the more recent phases as the blue phase [25] and the ferroelectric nematic phase [26].

There is however a specific class of liquid crystals for which GON has been reported to be absent in conditions of strong surface anchoring [27]. This is the class of chiral nematic, or cholesteric, liquid crystals (CLC). In these materials the director **n**, i.e. the unit vector that defines the average molecular orientation, rotates around an axis in a helical fashion. The angle between **n** and the helix axis is fixed at $\pi/2$ and, if this axis coincides with the **z** axis, the director can be expressed as $\mathbf{n} = (\cos\varphi,\ \sin\varphi,\ 0)$, being φ the azimuthal angle. The distance corresponding to a 2π rotation of **n** defines the helix pitch P_0 (Fig. 1a).

The helical order imparts to CLC peculiar optical properties as the existence of a reflection band originated by Bragg diffraction of light from the periodic structure and the consequent strong rotatory power [28-30].

Indeed, a cholesteric liquid crystal cell separates the light beam traveling along the helix axis into two components of a right-handed and left-handed circular polarization. The right-handed circularly polarized wave is strongly reflected by a right-handed cholesteric helix, while the left-handed circularly polarized mode is transmitted. The opposite occurs when the cholesteric helix is left-handed. In other words, the mode rotating with the same handedness as the CLC helix undergoes Bragg diffraction because it sees the periodicity of the structure, while the mode rotating in the opposite direction is not affected. The Bragg reflection band is centered at the wavelength $\lambda_B = \bar{n}\, P_0$, being $\bar{n} = \frac{n_\parallel + n_\perp}{2}$ the average refractive index of the liquid crystal and $n_\perp$ and $n_\parallel$ the refractive indexes seen by light polarized perpendicular (ordinary wave) and parallel (extraordinary wave) to the molecular director **n**, respectively. The selective reflection is observed in a spectral range determined by the optical anisotropy $\Delta n = (n_\parallel - n_\perp)$ and by the pitch, according to the relation $\Delta\lambda = (n_\parallel - n_\perp)\, P_0$.

Because of the existence of selective Bragg reflection, a linearly polarized beam impinging on a CLC experiences strong changes, such as a large rotation of the major axis of polarization and an eventual transformation of the transmitted light into circularly polarized light. The rotation of polarization is described by the rotatory power ρ that for a light beam of wavelength λ_0 has the following expression [30]:

$$\rho = -\frac{2\pi\alpha^2}{8P_0\left(\frac{\lambda_0}{\lambda_B}\right)^2\left[1-\left(\frac{\lambda_0}{\lambda_B}\right)^2\right]} \qquad (1)$$

being $\alpha^2 = \frac{(n_\parallel^2 - n_\perp^2)^2}{n_\parallel^2 + n_\perp^2}$ and λ_B the central wavelength of the reflection band.

It is known that P_0 and thus λ_B respond to a variety of stimuli, mainly of thermal and chemical nature [31]. For example, doping a CLC with photoactive chiral dopants allowed the realization of tunable filters [32-35], and tunable mirrorless lasers in a range of some tenths of nm have been demonstrated based on dye-doped cholesterics [36,37]. However, the absence of nonlinear optical director reorientation in CLC has made the optical control of the transmitted and reflected light elusive till recently.

The possibility of inducing a nonlinear optical response in CLC was initially studied by Zel'dovich and Tabiryan [27], who found that GON cannot be obtained in these materials in conditions of strong anchoring on at least one boundary surface. At the same time, they evaluated the light-induced change of the helix pitch, which for typical material parameters is only about 0.1% of the initial pitch. Some years later the reason for the absence of GON in CLC was explained by E. Santamato and coworkers [38]. To understand this point, it is necessary to keep in mind that there exist three fundamental types of elastic deformations in liquid crystals, which correspond to basic variation of the LC director orientation: splay, twist, and bend [13]. Each of these deformations is described by a specific elastic constant that represents the energy required to induce the specific director distortion. Santamato and his group showed that the threshold for optical reorientation when pure twist is involved is several orders of magnitude higher than in processes where other deformations are induced. Since in CLC the angle the director forms with the helix axis is fixed at $\pi/2$, only twist deformation would be possible, which explains the absence of GON.

These arguments explain why the clear observation of nonlinear director reorientation in CLC driven by pure optical torque was only rarely reported and in conditions of weak surface anchoring [39].

In 1968 Meyer and DeGennes independently predicted the existence of a CLC phase with a peculiar structure [40,41]. In this unconventional cholesteric phase, LC molecules align at an angle θ lower than $\pi/2$ with the helix axis under the action of an external electric field **E** applied along the helix axis itself. In these conditions the nematic director depends also on the cone angle θ and can be expressed as: $\mathbf{n} = (\sin\theta\sin\varphi, \sin\theta\cos\varphi, \cos\theta)$, where $\varphi(z) = 2\pi z/P$ is the angle of homogeneous azimuthal rotation and P is the field dependent pitch [41]:

$$P = \frac{2\pi}{E}\sqrt{\frac{K_3}{\epsilon_0\Delta\epsilon}} \tag{2}$$

In this formula, K_3 is the bend elastic constant and $\Delta\varepsilon$ the dielectric anisotropy, i.e. the difference between the dielectric components parallel and perpendicular to the nematic director **n**. This new cholesteric phase, called oblique helicoidal cholesteric or simply heliconical cholesteric (ChOH), could be realized only if the bend elastic constant K_3 is lower than the twist elastic constant K_2, that is the condition $K_3/K_2 < 1$ must hold. Since in conventional LC the bend elasticity is typically higher than twist elasticity, heliconical cholesterics have not been experimentally observed for decades.

The first observation of a heliconical cholesteric phase was reported in 2014 by the group led by professor Lavrentovich [42]. Heliconical cholesterics were realized by adding a chiral dopant to a LC dimer having a bend elastic constant K_3 one order of magnitude smaller than K_2.

The fundamental difference between ChOH and conventional CLC is the oblique helicoidal arrangement of the LC molecules, thanks to which an external electric field parallel to the heliconical axis induces both twist and bend deformations (Fig. 1b). Being the dielectric torque always nonzero in this geometry, a change of the field strength results in a change of the structural periodicity (eq. (2)), while it does not perturb the single-harmonic character of the structure. This is an important point, since an external field applied along the helix in conventional CLC has quite a different effect. For LC with positive dielectric anisotropy ($\Delta\varepsilon = \varepsilon_{||} - \varepsilon_{\perp} > 0$) it typically rotates the helix axis perpendicular to itself producing a light scattering fingerprint texture, while for LC with negative dielectric anisotropy ($\Delta\varepsilon = \varepsilon_{||} - \varepsilon_{\perp} < 0$) it would cause no realignment. In ChOH instead, the field can efficiently tune the wavelength of selectively reflected light in a broad spectral range, from ultraviolet to infrared, as shown in several papers [42-45]. Similarly to the pitch, the cone angle θ between **n** and the helix axis also depends on the external field [42] according to the following relation:

$$sin^2\theta = \frac{k}{1-k}\left(\frac{E_{NC}}{E} - 1\right) \tag{3}$$

where $k = K_3/K_2$, $E_{NC} = \frac{2\pi K_2}{P_0\sqrt{\epsilon_0\Delta\epsilon K_3}}$ is the critical field above which ChOH transforms into an unwound nematic state ($\theta = 0$) and $P_0 > P$ is the pitch in the absence of field (i.e. when $\theta = \pi/2$). Note that the heliconical structure needs an external electric field **E** applied along the helix axis, to exist. This field is the one that appears in both eq. (2) and (3), i.e. is the same field that is used to tune the structure. When the value of **E** becomes equal to E_{NC} the helix unwinds and a nematic order is established.

By using a multicomponent mixture of flexible dimers, rod-like molecules and chiral dopant, the range of operation of these materials, otherwise above 100°C, has later been extended to room temperature and below [44]. The value of the critical field is typically of the order of a few V/μm, while tuning of the ChOH pitch requires lower fields, typically in the range (0.3 – 1.5) V/μm, depending on the specific composition and temperature [44,45].

The possibility of electrically tuning the pitch and thus the reflected wavelength makes ChOH very promising for many applications that require dynamically controlled transmission and reflection of electromagnetic waves. Worthy of note, these materials are non-absorbing in a broad spectral range, including visible, and transparent everywhere except in the electrically preselected reflection band.

For a comprehensive review of ChOH electro-optics and of their applications we remind the reader to the recent paper by O. Lavrentovich [46].

As for the interaction with optical fields, the heliconical phase gives a new opportunity to observe the effect of a light beam on the helical structure since, as already outlined, the interaction with a field involves both twist and bend deformations. While light-induced twist is hard to observe due to the high intensity required [38], light-induced bend corresponds to the GON effect in nematic liquid crystals, thus the optical field is expected to produce a torque comparable to the one originated by the low-frequency field and competing with it to determine both the cone angle of the structure and its pitch.

In this article we review the recent papers dealing with the effects of light on this novel class of cholesteric LCs, with the aim of giving a comprehensive idea of both the experimental results achieved and the theoretical framework that has been developed in the few years passed from the first experimental observations of the heliconical phase.

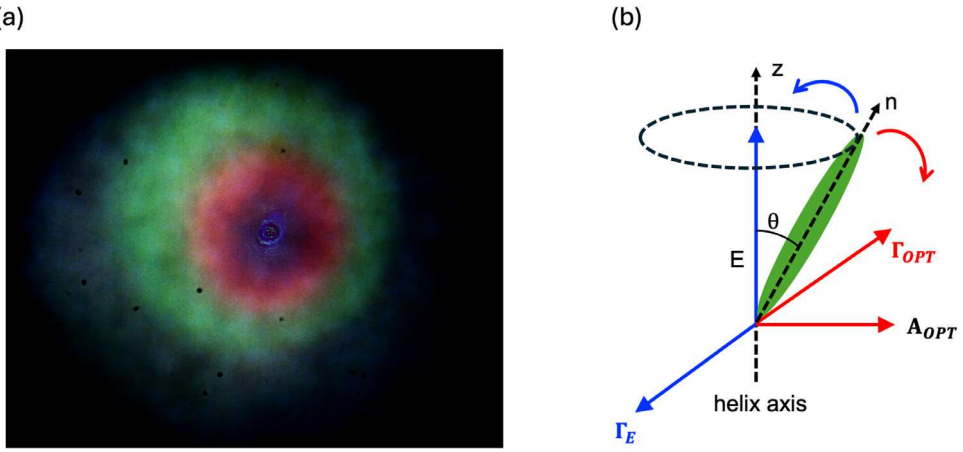


Fig. 2

a) Sample appearance in reflection mode under the combined action of light and of a low frequency electric field higher than the critical one required to unwind the helix; b) sketch of the static (E) and optical (A_{OPT}) fields and of the corresponding torques exerted on the molecular director n. Adapted with permission from ref. [47].

The first experimental observations

The first report about the effect of optical fields on the oblique heliconical cholesteric LCs was published in 2019 [47]. This paper reports a demonstration of tuning the helical pitch by means of the optical torque, orthogonal to the helical axis, exerted by a light beam of moderate intensity. The analyzed samples were 20 μm thick cells with conductive glass confining surfaces, treated to get planar anchoring of the LC molecules. The effect of light on the LC cells was investigated using a pump-probe configuration. An homemade inverted microscope apparatus was realized, where a cw frequency-doubled Nd:YAG laser (λ = 532 nm) acted as a pump beam and the white light of a super luminescent LED source, focused by the same optics, was the probe. The pump beam polarization was orthogonal to the helix axis, thus the optical field was in a plane perpendicular to the low frequency electric field necessary to stabilize the heliconical structure. The used setup allowed monitoring both the reflection spectra and the sample appearance in reflection mode.

The pitch of CLC can be affected by temperature variations [31,48], which holds for ChOH samples as well. This means that any light induced variation of the pitch might in principle be due to laser heating. Authors of ref. [47] ruled out this possibility by performing the experiments starting from a situation of totally unwound helix, obtained by increasing the external electric field above the critical value. In these conditions the nematic director is aligned in a uniaxial fashion parallel to the field, i.e. along the helix axis, and the sample appears dark when viewed between crossed polarizers; this homeotropic state was preserved as the temperature rase. Since the oblique helicoid was absent, the heating possibly induced by laser irradiation could not modify the Bragg reflection. Starting from this configuration, light irradiation with intensity of the order of 10^4 W/cm^2 restored the colored appearance of the sample originating in Bragg reflection, which proved that the optical field is indeed able to restore the heliconical structure by exerting a torque that opposes the one due to the low frequency electric field. This is shown in Fig. 2, which reports the sample appearance in reflection mode under the combined action of light and of a low frequency electric field higher than the critical one. A sketch of the low frequency (**E**) and optical ($\mathbf{A}_{OPT}$) fields and of the corresponding torques is also drawn. Noteworthy, the light intensity required to exert the optical torque that restores the heliconical structure, has values typical of GON [1]. As shown in the figure, the wavelength of the selective reflection decreased moving from the center of the beam to the periphery and to the not irradiated region where nonlocal reorientation can take place, indicating that the pitch of the heliconical structure is higher for higher intensity, i.e. light irradiation produces a red shift of the Bragg resonance. To further demonstrate the occurrence of the optical reorientation effect, authors made additional experiments. They measured the critical voltage necessary to produce the unwound nematic structure in the presence of light irradiation (Fig. 3a) and the shift in reflected wavelength induced by light for a fixed low frequency electric field as a function of the pump beam intensity (Fig. 3b). The critical voltage was determined at the occurrence of a dark texture between crossed polarizers, for different values of the pump beam intensity, holding the low frequency field E fixed at 5 V/μm, a value higher than E_{NC}. The light induced wavelength shift was instead measured for E = 2.28 V/μm, corresponding to a zero-intensity reflected wavelength $\lambda_B(0) = 427$ nm. As shown in Fig. 3, both these quantities increase with light intensity, according to the following relations [47]:

$$V'_{NC} = \sqrt{V_{NC}^2 + \frac{\Delta\epsilon_{OPT}}{\Delta\epsilon} d^2 \frac{\epsilon_r^2 I}{\epsilon_0 c n_{av}}} \tag{4.1}$$

$$\Delta\lambda = n_{av}\left[2\pi\sqrt{\frac{K_3}{\epsilon_0\Delta\epsilon\left(E^2 - \frac{\Delta\epsilon_{OPT}}{\Delta\epsilon}\frac{I}{\epsilon_0 c n_{av}}\right)}} - P(0)\right] \tag{4.2}$$

that fit quite nicely the experimental data (full red lines in Fig. 3 a and b, respectively). In these equations, $\Delta\varepsilon$ and $\Delta\varepsilon_{OPT}$ are the dielectric anisotropy at low and optical frequency, respectively and n_{av} is the average LC refractive index.

Equations (4) have been deduced starting from the free energy density written for ChOH, including the contribution of the

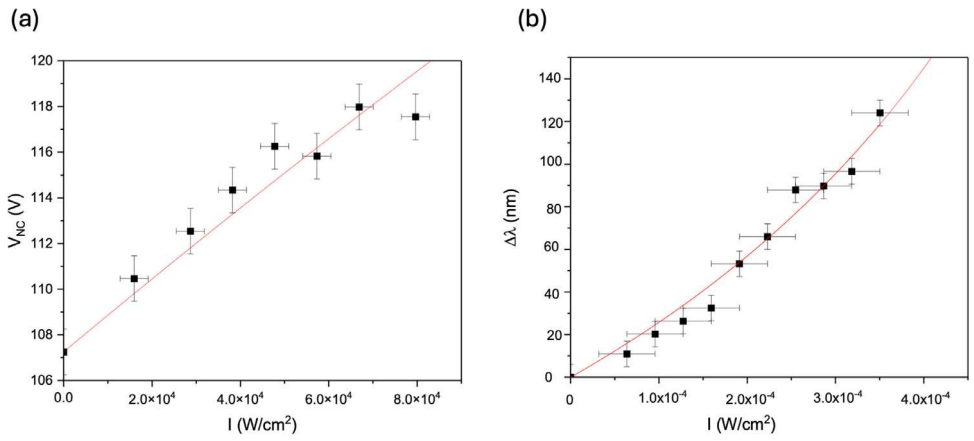


Fig. 3

a) Critical voltage necessary to unwind the heliconical structure versus pump light intensity. Continuous line is a best fit with Eq. (5.1); b) reflected wavelength variation $\Delta\lambda$ versus pump light intensity and best fit with Eq. (5.2) (continuous red line). The external low frequency electric field is 5 V/μm in a) and 2.28 V/μm in b). Adapted with permission from ref. [47].

optical field [47]:

$$f = \frac{1}{2}K_1(\nabla\cdot\mathbf{n})^2 + \frac{1}{2}K_2(\boldsymbol{n}\cdot\nabla\times\boldsymbol{n} - q_0)^2 + \frac{1}{2}K_3(\boldsymbol{n}\times\nabla\times\boldsymbol{n})^2 - \frac{1}{2}\epsilon_0\Delta\epsilon(\boldsymbol{n}\cdot\boldsymbol{E})^2 - \frac{1}{4}\epsilon_0\Delta\epsilon_{OPT}(\boldsymbol{n}\cdot\boldsymbol{E}_{OPT})^2 \quad (5)$$

calculated by considering: i) the molecular director oriented along the oblique helicoid, $\mathbf{n} = (\sin\theta\ \cos\varphi,\ \sin\theta\ \sin\varphi,\ \cos\theta)$, with the cone angle $\theta < \pi/2$; ii) the low-frequency field along the helix axis direction ($\mathbf{E} = E\mathbf{z}$); iii) the optical field in a plane orthogonal to the helix axis ($\mathbf{E}_{OPT} = E_x\mathbf{x} + E_y\mathbf{y}$). In eq. (5) K_1 is the splay elastic constant, $q_0 = 2\pi/P_0$ and P_0 is the pitch of the unperturbed cholesteric. Neglecting any light-induced twist and considering only bend deformations, the equilibrium cone angle satisfies the following equation [47]:

$$\frac{\epsilon_0\Delta\epsilon E^2 - \frac{1}{2}\epsilon_0\Delta\epsilon_{OPT}A^2_{OPT}}{K_2^2q_0^2}\left[(K_2-K_3)^2sin^4\theta + 2K_3(K_2-K_3)sin^2\theta + K_3^2\right] - K_3 = 0 \quad (6)$$

where A^2_{OPT} is the square modulus of the optical field. The condition $\sin\theta = 0$ gives the critical field for complete unwinding from which eq. (4.1) is easily derived. As for the second equation, the shift of the reflected wavelength is determined by the pitch variation $\Delta\lambda = n_{av}[P(I) - P(0)]$ where the intensity dependent pitch is given by:

$$P = 2\pi\sqrt{\frac{K_3}{\epsilon_0\Delta\epsilon\left(E^2 - \frac{\Delta\epsilon_{OPT}}{\Delta\epsilon}\frac{I}{\epsilon_0 c n_{av}}\right)}} \quad (7)$$

Substituting this expression in the one for $\Delta\lambda$ gives eq. (4.2).

According to these equations light increases the voltage needed to unwind the structure, because the torques of the low frequency and optical fields oppose each other; moreover, light affects the reflected wavelength in a way that depends on its intensity.

Theory formalization

Later, the theory of light propagation through ChOH cells in conditions of light induced director reorientation, has been formalized in three papers [49-51], and several intriguing phenomena have been foreseen. Reference [49] is particularly interesting, since it shows that light propagation through a ChOH cell in conditions of normal incidence can be described starting from the well-established theory of light propagation through conventional CLC cells, making a few simple changes in the mathematical description. Specifically, all the results of the calculations concerning light propagation in CLC can be applied to ChOH provided that the following substitution is made [49]:

$$\epsilon_p \rightarrow \epsilon_{eff} = \frac{\epsilon_p\epsilon_o}{\epsilon_p - (\epsilon_p - \epsilon_o)sin^2\theta} \quad (8)$$

being ε_p and ε_o the dielectric constant at optical frequencies parallel and perpendicular to $\mathbf{n}$, respectively. With this replacement, that considers the existence of the cone angle θ, all the relevant quantities become dependent on θ and, thus, on the intensity of the impinging light. This gives rise to a nonlinear optical response not observable in conventional cholesterics.

The possibility of optically tuning the pitch leads to an intensity dependence of the spectral location of the Bragg resonance, as experimentally demonstrated in [47], which means that a monochromatic wave of the helical structure can either enter or exit from the Bragg resonance by increasing the intensity depending on the initial spectral location. In other words, the light-induced shift of the Bragg resonance affects the propagation of the light itself if the wavelength is close to or inside the resonance. This gives rise to a remarkable nonlinear optical response on the transmission of a light beam circularly polarized with the same handedness of the heliconical structure [49,52]. The dependence of the transmitted intensity I_T on the incident light intensity as calculated in [49,52] starting from the CLC theory and using eq. (9), is shown in Fig. 4 for different values of the low frequency electric field necessary to stabilize the ChOH structure. One interesting consequence of the intensity dependent transmission is the possibility of observing self-transparency. Indeed, if for a certain intensity I, the wavelength is inside the Bragg reflection band and no transmission is possible, increasing

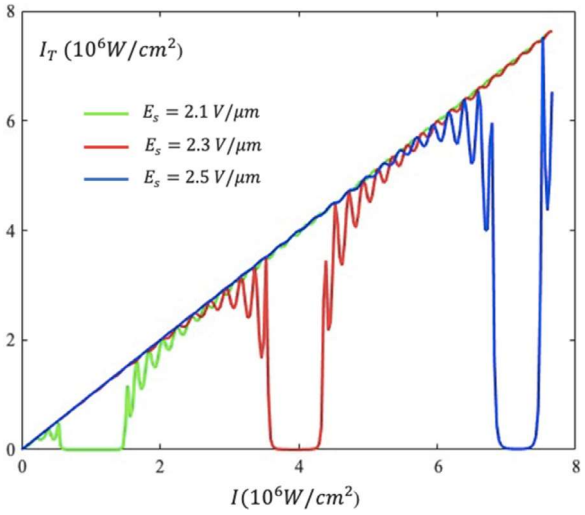


Fig. 4

Transmitted intensity I_T vs impinging intensity I of a ChOH sample for a circularly polarized beam with the same handedness of the helix and $\lambda = 514$ nm. The sample thickness is $d = 20\ \mu$m. The transmitted intensity is plotted for different values of the applied low frequency field E. Adapted with permission from ref. [52].

I leads to a shift of the band and to a sudden increase of light transmission. The effect on the refractive index of the resonant mode was also analyzed [49] and a large variation of this parameter was calculated with a positive nonlinearity on the two edges of the resonance and negative nonlinearity when crossing the resonance. Noteworthy, as indicated by eq. (8) the ChOH pitch also depends on the low frequency electric field, which can thus be used as an additional degree of freedom.

The results reported in [49] were obtained under the approximation of constant light intensity through the ChOH cell, which, to be strict, is good whenever the beam that induces the director reorientation (pump) is not the same beam which transmission is monitored (probe). When the effect is self-induced, the intensity of the light beam travelling through the cell is affected by the change in transmittivity induced by the beam itself, which makes things more complex. It has been shown that near the Bragg resonance the distribution of the optical field inside the LC layer is inhomogeneous and the nature of the inhomogeneity is different for different wavelengths of the propagating beam [52]. With the aim of describing in a more rigorous way the propagation of a single beam traveling in the medium with an intensity high enough to induce significant optical reorientation and wavelength close to the Bragg resonance, a multi-layer approach has been proposed [50,51]. The approach is based on the Ambartsumian's layer addition modified method [53]. This method considers the cell as a stratified material and the optical field is recalculated after traveling through each layer, allowing a more careful determination of the effects of light on the structure and thus on the propagation of the light itself. Ref. [50] showed that this treatment leads to additional effects with respect to those obtained in [49]. Specifically, while a red shift of the Bragg resonance is observable at very low intensities, instabilities in the optical transmission come soon into play. This effect depends again on light intensity and corresponds to the onset of a non-uniform distribution of both the cone angle and the pitch. Authors also showed the existence of a critical intensity that depends on the material parameters, for the onset of an oscillating behavior in the optical transmission for wavelengths close to the edge of the Bragg resonance.

In a following paper [51], the instabilities of the optical transmissions were considered in more details and the time evolution of the transmission spectrum was analyzed for increasing values of the incident light intensity. The onset of damped oscillations, followed by stable oscillations and by chaotic behavior at higher intensity, were reported. These self-induced effects are strongly asymmetric at the opposite side of the Bragg resonance, which was explained in the following way: since the light induced red shift of the Bragg resonance leads to a decrease in transmittivity, this results in a decrease of the intensity I of the light propagating through the cell. This has the consequence of increasing the torque exerted by the low frequency electric field, which is opposite to the optical torque, with consequent blueshift of the resonance. This in turn leads to an increase in transmittivity and light intensity inducing again a redshift of the resonance able to restart the process. At high intensity the Bragg resonance disappears, and transmission becomes unstable for any wavelength.

Noteworthy, the existence of a photonic band gap was also analyzed in a precedent paper [54] where the photonic properties of ChOH – including tunable band gap and optical modes – for light propagating along the helical axis in the regime of heliconical pitch comparable to the wavelength of light, were studied using numerical simulations. In this case however, no optical nonlinear interaction between light and sample was considered. Interestingly, authors predicted the existence of a component of the optical field along the light propagation direction, which results in the Poynting vector $\mathbf{S} = \mathbf{E} \times \mathbf{H}$ rotating about the same direction.

A longitudinal component of the optical field was also theoretically predicted in 1997 by Drevensek-Olenik and Copic [55] in the case of phase matched Second Harmonic Generation in Smectic C*. Smectics (Sm) are a class of liquid crystals in which molecules are arranged within parallel planes thus exhibiting a certain amount of positional order, besides being orientationally ordered as in nematics. There exist several kinds of smectic liquid crystals, among them the SmC* phase is characterized by a helical spatial modulation of the molecular tilt and by a nonvanishing spontaneous electrical polarization. The direction of the modulation is normal to the smectic layers. The period of the helix is usually of the same order of magnitude as the wavelengths of the visible light. As authors of ref [55] point out, the longitudinal field term is a consequence of the tilt angle formed with the helical axis and vanishes in the case of the conventional cholesteric phase.

Since SmC* show an oblique helicoidal structure similar to that of ChOH, an optical tuning as the one reported in [47] could in principle be expected also in these materials. However, the periodic molecular-scale density modulation of SmC* (which is absent in ChOH) makes any changes of the pitch and conical tilt angle difficult since it requires to change the thickness of

molecular layers and the introduction of multiple defects such as dislocations with a molecular-scale Burgers vectors. On the contrary, in the density uniform ChOH, the pitch change could produce only dislocations of a large Burgers vector equal to the pitch; these dislocations could be avoided or expelled if the cell is sufficiently thick, or if it is treated for a weak planar [42] or perpendicular director anchoring [43].

Possible applications

The existence of a nonlinear optical reorientation of the nematic director in ChOH, opens the door to the use of these materials for the optical control of the light properties.

The possibility of using the nonlinear optical response of heliconical cholesterics to control the polarization of the light propagating through a ChOH cell, was experimentally demonstrated in [56] by optically tuning the Bragg resonance of the structure. According to eq. (8), the existence of the cone angle that characterizes the ChOH phase, leads to an effective refractive index that depends on θ through the expression:

$$n_{eff}^2 = \frac{\left(n_{\parallel}^2 n_{\perp}^2\right)}{n_{\parallel}^2 - \left(n_{\parallel}^2 - n_{\perp}^2\right) sin^2\theta} \tag{9}$$

If $n_{\parallel}^2$ is replaced by n_{eff}^2 in the expression of the CLC rotatory power, eq. (1) becomes valid for ChOH also. This means that tuning of the Bragg wavelength λ_B by an optical field, would produce a strong variation of the polarization state of a light beam of wavelength λ close to λ_B. Therefore, one may expect that such an optical field is able to modify the polarization state of a second, weak, beam travelling through a ChOH cell when the intensity dependent (I) approaches λ. To experimentally demonstrate this hypothesis, authors performed pump-probe experiments using a cw frequency-doubled Nd:YAG laser ($\lambda = 532$ nm) as a pump and a low power monochromatic beam from a laser diode ($\lambda = 405nm$) as a probe. The pump beam was linearly polarized orthogonal to the heliconical axis, collinear to the probe and of intensity in the range $(10 \div 16)x10^3 W/cm^2$. It was used to reestablish the ChOH structure in the presence of a low frequency electric field higher than E_{NC}, and tune the pitch, as described in [47]. The wavelength of the probe beam corresponded to a short pitch that was easily restored by the pump beam starting from the unwound configuration. The polarization of the probe beam was varied among linear horizontal, linear vertical, circular righthanded and circular lefthanded. The polarization of the probe light transmitted by the ChOH cell was analyzed by a rotating quarter waveplate, a fixed Glan-laser polarizer and a photodiode. The transmitted probe light intensity I_P was detected as a function of the angle a that the axis of the rotating quarter waveplate forms with that of the Glan laser polarizer, for different values of the intensity of the pump beam. The obtained set of curves, one set for each polarization of the probe beam incident on the LC cell, were fitted by the function [57]:

$$I_P(\alpha) = \frac{1}{2}[A - Bsin(2\alpha) + Ccos(4\alpha) + Dsin(4\alpha)] \tag{10}$$

Here, the fitting parameters A, B, C, and D are related to the Stokes parameters describing the output probe polarization state through simple relations dependent on the phase delay introduced by the quarter wave plate [57]. Once the Stokes parameters were retrieved, they were used to determine the polarimetric curves for all the cases analyzed and to reconstruct the polarization ellipses.

These reconstructions, which represent the main results of ref. [56], are reported in Fig. 5 for the different states of polarization of the probe beam. Fig. 5 shows that the incoming linearly polarized probe light undergoes a rotation of the polarization direction up to becoming almost circularly polarized in the neighborhood of a specific value of the pump intensity. On the contrary, circularly polarized light is strongly reflected, as shown by the small ellipses, if the handedness has the same sign of that of the cell and stays unaffected in the opposite case. Noteworthy, the maximum effect on the probe polarization is observed by varying the pump intensity in a neighborhood of the value $I_B = 12.7 \times 10^3 W/cm^2$ that was therefore identified as the intensity corresponding to the resonant wavelength, i.e. $\lambda_B(I_B) = 405$nm. The low pump intensity values, which correspond to those of GON [1], also assure an efficient pitch tuning without affecting the symmetry of the single harmonic heliconical structure.

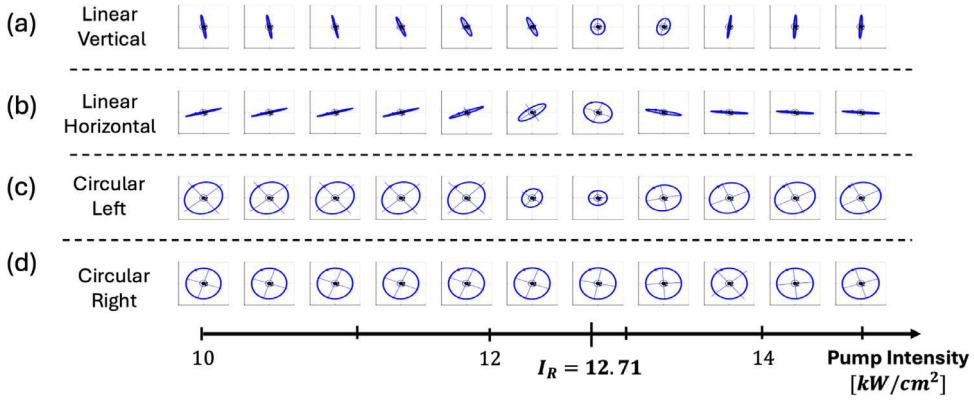


Fig. 5

Plots of the polarization state of the probe beam at the exit of the ChOH sample. Figures (a-d) show the changes in the probe light polarization obtained with a fixed value of the low frequency field$E = 5V/\mu m$, higher than E_{NC}, while varying the pump intensity. Adapted with permission from ref. [56] © Optical Society of America.

Besides confirming the previously reported phenomenon of optical tuning of the heliconical cholesterics [41], this result may open the door for the development of simple and efficient polarization modulators optically controlled. Indeed, the results described in [56] demonstrated two important things: i) thanks to the efficient optical tuning of the heliconical pitch, the polarization state of light with any wavelength from UV to near IR could be easily controlled using a single sample and ii) the resonance wavelength can be tuned gradually by slowly varying the intensity of the pump beam thus imposing in principle a fine control on the polarization state of monochromatic light. The amount of optical rotation of the axis of a linearly polarized beam can be tailored by choosing the appropriate value of the pump intensity (closer or farther to the resonance intensity I_R). In the same way the transmittivity and reflectivity of a circularly polarized light can be finely controlled.

As a final remark, we point out that the values of the light intensity used in the described experiments [47,56] are lower than those used in the theoretical papers [49-52]. Unfortunately, we do not have a clear explanation for this at the moment and further study is necessary to address this discrepancy.

Conclusions

Contrary to conventional right angle CLC, the heliconical cholesteric phase is capable of bend deformations, which offers new opportunity of observing light induced reorientation of the molecular director. In this paper we reviewed the results obtained up to now about the optically induced director reorientation and about the consequent nonlinear optical behavior of these peculiar liquid crystal structures. Notably, optical nonlinearity is observed for moderate intensity values, comparable to those typical of the Giant Optical Nonlinearity of nematic liquid crystals. This, combined to the ability of ChOH of preserving the single-harmonic character of the helicoidal structure and to the simplicity of the liquid crystal cells, will most probably open the gate to both the observation of unexpected phenomena and to the realization of devices for the optical control of light of very simple architecture. Indeed, it is remarkable that a simple ChOH cell is itself a device capable of efficient and wide optical and electrical tunability.

The interest behind these materials is also demonstrated by the increasing number of recent papers aimed at improving the stability of ChOH mixtures [58-60] or at suggesting novel applications as for example heliconical cholesteric-based elastomers [61], optical filters [62], ferroelectric nematic heliconical cholesterics [63] and many other possible uses [64,65]. A very recent work [66] shows that the electrically tunable reflectivity of ChOH can be increased from 50 to 100% in conditions of oblique incidence. In this case, the band of total reflection is associated to the entire pitch P and there exist satellite reflection bands correspondent to fractions of P. This observation, which is not new for conventional cholesterics [67] and SmC* [68], represents a novelty for heliconical cholesteric liquid crystals and will certainly enlarge the number of possible applications of these materials.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

CRediT authorship contribution statement

Liana Lucchetti: Writing – review & editing, Writing – original draft, Validation, Supervision, Methodology, Conceptualization. **Giovanni Nava:** Investigation, Formal analysis, Data curation, Conceptualization.

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