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# Cholesteric Structure-1 Optical Properties

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# Cholesteric Structure—I Optical Properties

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## Introduction

In 1889 Reinitzer,[1] working with cholesteryl benzoate, discovered a state of matter that was later termed cholesteric liquid crystals. It is doubtful whether the discovery of liquid crystals would have been made at that time if the optical properties of the cholesteric phase were less pronounced. Like other liquid crystals, materials in this state act as birefringent fluids. However, at that point the resemblance ends. The optical properties may be summarized as follows:[2]

1. The cholesteric structure is uniaxial and optically negative while other liquid crystal structures are optically positive; thus, for the cholesteric phase, there is a single optic axis normal to the surface along which the index of refraction is a minimum.
2. The cholesteric structure is optically active with rotatory powers many times that of common optically active materials. The plane of linearly polarized light is rotated through an angle several hundred times that of the usual optically active materials, such as sucrose or optically active quartz.
3. When illuminated with white light, the cholesteric structure scatters the light to give an iridescent color, which varies with substance temperature and angle of incident beam.
4. The cholesteric structure is circularly dichroic for some wavelength region; that is, one circularly polarized component of the incident beam is transmitted without attenuation, whereas the other is scattered. Either the right or the left hand circular polarized component may be affected.

These optical properties depend on a delicately balanced molecular arrangement. A change of shape or dipole moment or any other disturbance which interferes with the weak forces between molecules results in a dramatic change. Reflection, transmission birefringence, optical rotation and color all undergo marked transformations.

## Transmission Properties

The optical properties of a representative material were studied in some detail. The material used was an equal-part mixture by weight of the following commercially available chemicals:

1 part cholesteryl benzoate
1 part cholesteryl acetate
1 part cholesteryl palmitate

Transmission measurements were made using a water-cooled cell to maintain temperature stability. An automatic recording dual-beam instrument, the Cary Model Spectrophotometer, was used to plot the optical density of a sample compared to a reference. Since the rate of scan was such that it took less than 30 sec to measure regions of interest, the effects temperature changes in the sample were small. By using materials with relatively low temperature sensitivities, the effects of temperature drift were further minimized. Samples were prepared by sandwiching the cholesteric liquid between microscope slides specially chosen for flatness.

The first property of the structure to be determined was the circular dichroism. To do this, a left circular polarizer was inserted in the sample beam and a transmittance curve obtained as shown in Fig. 1. The transmittance right circular polarized was measured in a similar manner.

The circular dichroism ($D$) of a sample is

$$D = \frac{(I_R/I_0) - (I_L/I_0)}{(I_R/I_0) + (I_L/I_0)} = \frac{I_R - I_L}{I_R + I_L}$$

where $I_R$ is the intensity of right circularly polarized light transmitted and $I_L$ is the intensity of left circularly polarized light transmitted when unpolarized light of intensity $I_0$ is incident on the sample. The circular dichroism is directly obtainable from spectrophotometric measurements. The plot of the result of these measurements is shown in Fig. 3 for a 10 micron thick film.

One of the most interesting properties of cholesteric liquids is their abnormally high optical rotatory power. If plane polarized

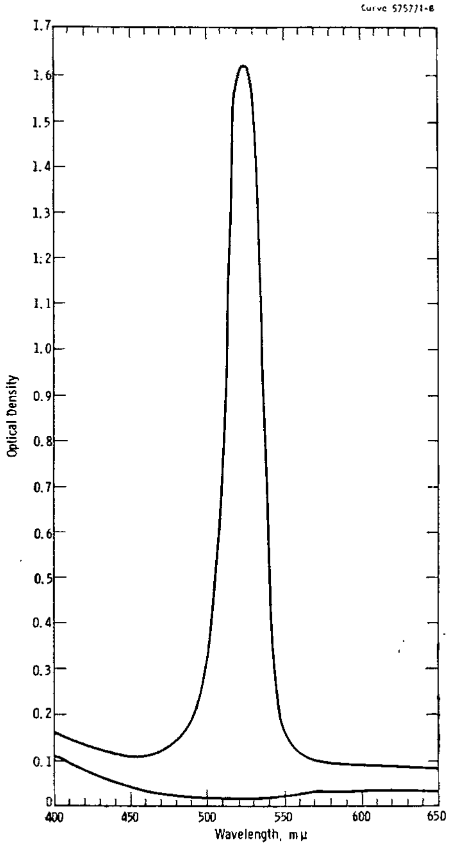

Figure 1. The transmission of left circular polarized light by the cholestric structure at 24° C as measured by the spectrophotometer. The lower line is the zero line of the instrument with circular polarizers in place. The upper curve is the density of the sample plus that of the polarizer and includes the losses due to surface reflections. The sample is 10 microns thick.

light is projected through these materials, the plane of polarization will be rotated by an amount greater than in any known compound, in certain cases, thousands of degrees rotation per millimeter of thickness traversed. The rotation was not directly measurable in the region of maximum reflectance, so it was decided to analyze the light in terms of components.

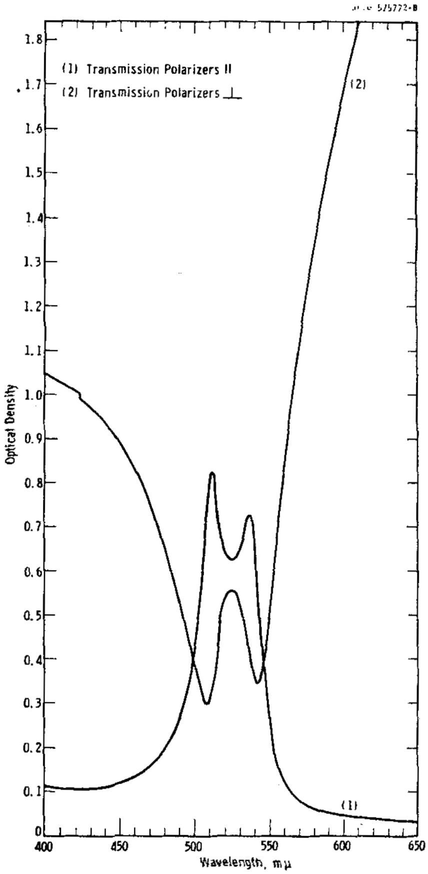

Figure 2. The transmission of the cholesteric phase with crossed linear polarizer and analyzer, and parallel polarizer and analyzer as measured by the spectrophotometer. The color as seen by the eye with crossed polarizers appears the same as the scattered light.

The state of polarization of light is completely defined by three independent parameters. Usually these are taken to be the amplitude of two linearly polarized components at right angles to each other and the phase difference between these two components. For the analysis of circular dichroism and optical activity of emergent light to be specified by the amplitude or right and left circularly polarized components and the phase difference, $\phi$, between these components.

To determine the phase difference, $\phi$, we examine the expressions for circularly polarized light in terms of the displacements in a Cartesian coordinant system. For left circular polarized light propagating in the $z$ direction, the displacements are

$$\begin{aligned} x_1 &= A_1 \sin \omega t \\ y_1 &= A_1 \cos \omega t \end{aligned}$$

and for right circular polarization the components are

$$\begin{aligned} x_2 &= -A_2 \sin (\omega t + \phi) \\ y_2 &= +A_2 \cos (\omega t + \phi) \end{aligned}$$

where $A_1$ and $A_2$ are the amplitudes and $\omega$ is $2\pi$ times the frequency.

If $A_1 = A_2$ (i.e., if there were no circular dichroism), the emergent light is linearly polarized in a plane at an angle of $\phi/2$ to the $y$ axis. On the other hand, if $A_1$ and $A_2$ are not equal the emergent light is elliptically polarized. The intensities of the $x$- and $y$-polarized components are

$$\begin{aligned} I_x &= A_1^2 + A_2^2 - 2A_1 A_2 \cos \phi \\ I_y &= A_1^2 + A_2^2 + 2A_1 A_2 \cos \phi \end{aligned}$$

It follows that

$$I_x + I_y = 2(A_1^2 + A_2^2)$$

and

$$\phi = \cos^{-1}\left(\frac{I_y - I_x}{4A_1 A_2}\right)$$

For linearly polarized incident light $A_2^2/A_1^2 = I_{\mathrm{R}}/I_{\mathrm{L}}$, and the expression for circular dichroism $D$ may be employed to obtain $A_1$ and $A_2$ in terms of $I_x$ and $I_y$

$$\begin{aligned} A_1 &= \tfrac{1}{2}\sqrt{(I_x + I_y)(1 - D)} \\ A_2 &= \tfrac{1}{2}\sqrt{(I_x + I_y)(1 + D)} \end{aligned}$$

With these the phase difference may be written

$$\phi = \cos^{-1}\left[\frac{I_y - I_x}{(I_y + I_x)(1 - D^2)}\right]$$

$I_x$ and $I_y$ can be directly measured as the intensities of transmitted light when light is linearly polarized and passed through a sample and the analyzer is placed parallel to the polarizer for $I_y$ and perpendicular to the polarizer for $I_x$ (Fig. 2). The phase shift can be calculated and the results for a 0.01 mm sample are shown in Fig. 3. The direction of the phase shift (i.e., the shift of $\phi$) was determined by polarizing microscope observations. (At wavelengths for which $D$ is small, the emergent light is essentially linearly polarized, rotated through an angle of $\phi/2$).

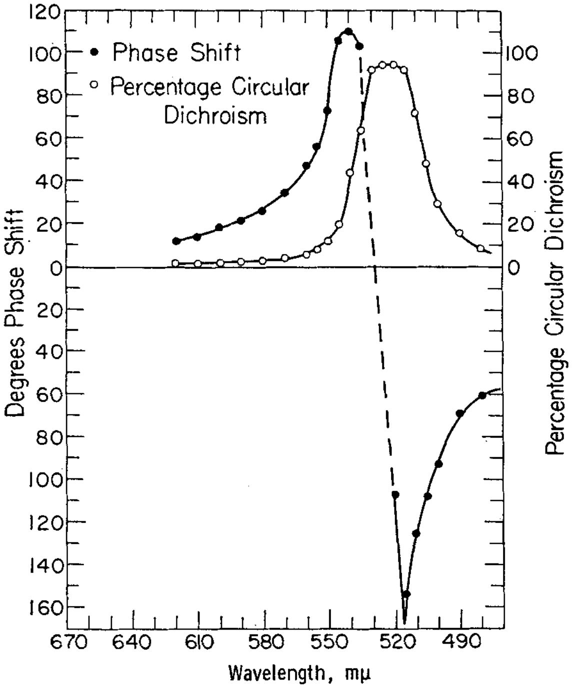

Figure 3. The circular dicroism and phase shift between right and left circular light plotted as a function of wavelength. Derived from calculations based on Figs. 1 and 2.

## Scattering Properties

Measurements were made at different angles of incidence with both polarized and unpolarized light. Figure 4 shows the transmission of unpolarized light versus the wavelength for several angles of incidence. At normal incidence, the 50% transmission (optical density 0.3) is a direct result of the near 100% circular dichroism shown in Fig. 3. As the angle of incidence increases, the selective attenuation becomes much less pronounced, until at large angles of incidence the material can no longer be considered circularly dichroic. The wavelength maximums in Fig. 4 were compared with the first order transmittance of a number of Bragg

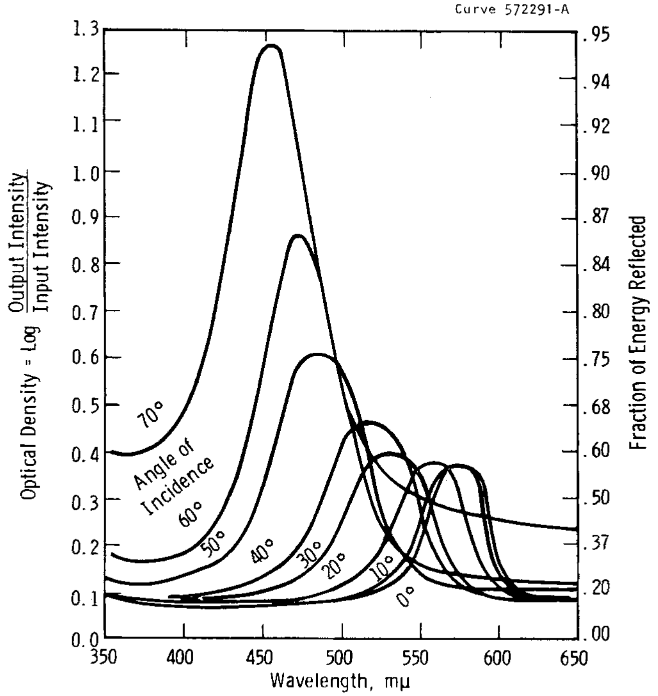

Figure 4. The transmission as a function of wavelength for unpolarized light measured for a number of angle of incidence.

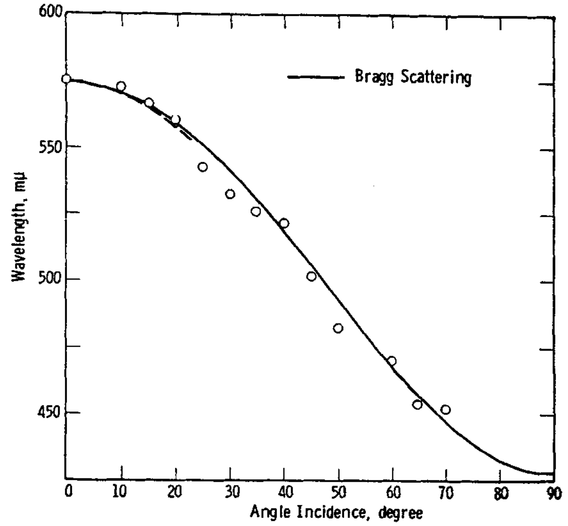

Figure 5. The wavelength of minimum transmittance as a function of angle as determined from Fig. 4 compared to Bragg scattering.

scattering planes placed in a media of index of refraction of 1.5. The results of this comparison are shown in Fig. 5.

To supplement the transmission measurements, reflectance measurements of the cholesteric structure were made with specially

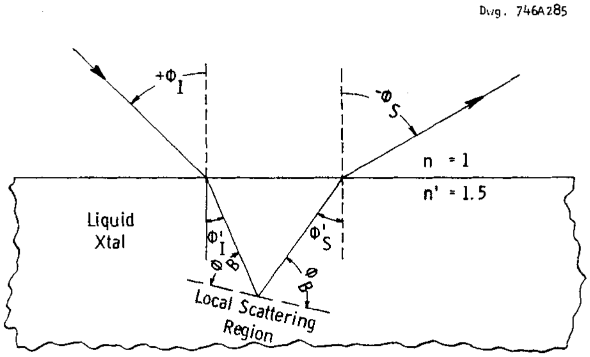

Figure 6. The angles which are involved in the scattering of light from the cholesteric structure.

constructed equipment. By using integrating attachments for the Cary Spectrophotometer, it was possible to show that the cholesteric structure absorbed no measurable radiation (within $\pm 1\%$) in the visible portion of the spectrum.

The wavelength of maximum scattering in the cholesteric liquid crystal is affected by the angle from which it is illuminated and the angle from which it is observed. To properly use a cholesteric liquid system the angle dependence should be understood. In many ways the cholesteric liquid behaves like a multiple layer inteference filter. However, because of the internal structure, the higher orders are suppressed. At any temperature the predominant wavelength depends on the angle of incidence and the angle of scattering. The scattering behaves in a manner analogous to X-ray scattering from powder samples. The scattering in the cholesteric liquid behaves as if it were coming from a number of regularly spaced or ordered planes existing in a medium having a refractive index of about 1.5; see Fig. 6. The wavelength of maximum reflection as a function of angle for constant temperature is given by

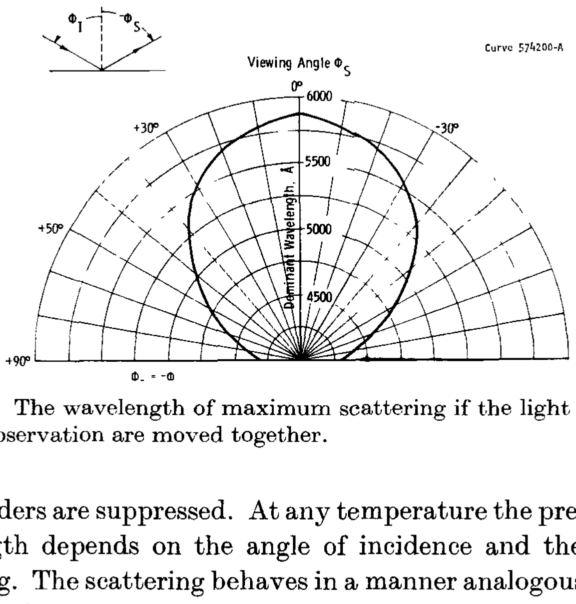

Figure 7a. The wavelength of maximum scattering if the light source and angle of observation are moved together.

$$\lambda = \lambda_n\left[\cos\tfrac{1}{2}\left\{\sin^{-1}\left(\frac{1}{1.5}\sin\phi_I\right)+\sin^{-1}\left(\frac{1}{1.5}\sin\phi_S\right)\right\}\right]$$

where

$\lambda$ = wavelength of maximum scattering
$\lambda_n$ = wavelength of maximum scattering for normal incidence and observation
$\phi_I$ = the angle of incidence
$\phi_s$ = the scattering or viewing angle

This function is shown in a polar plot for two conditions of illumination in Figs. 7a and b.

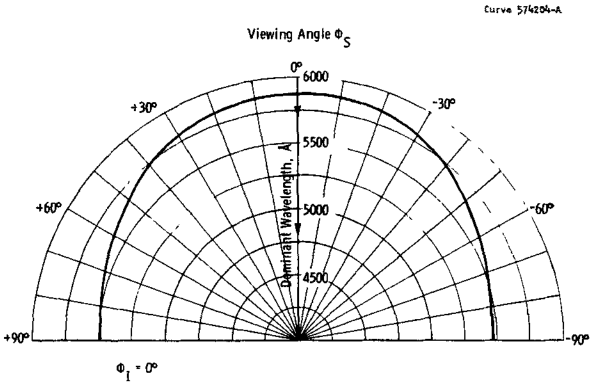

Figure 7b. The wavelength of maximum scattering if the angle of observation varies and the film is illuminated normal to the surface.

## Optical Model

An attempt to explain all of the optical properties of the oriented cholesteric phase in terms of molecular organization is not complete at present.

The following discussion is based on the observation that the circularly polarized light which is scattered from a cholesteric phase is not changed in sense while metallic reflection results in change of sense. Hence, a right circularly polarized wave is scattered from a cholesteric liquid as a right circularly polarized wave.

Light is circularly polarized when the electric field ($E$) rotates in a uniform manner in both time and space with a constant amplitude

($A$). The vector electric field may be expressed in cylindrical coordinates $(r, \theta, z)$ with the direction of propagation in the $z$ direction and $r = 0$ as

$$\vec{E} = A\vec{r} \pm \frac{2\pi}{\lambda}(z-ct)\,\vec{\theta}$$

$\vec{r}$ = a unit vector in the $r$ direction
$\vec{\theta}$ = a unit vector in the $\theta$ direction
$\lambda$ = wavelength
$c$ = speed of light
$t$ = time
$A$ = the amplitude of the wave

The sign of the $\theta$ term determined the direction of rotation of the circularly polarized wave; clockwise or dextro being positive and counterclockwise or levo being negative.

A standing wave with unique properties occurs when two coherent circularly polarized waves of the same sense and of opposite direction of propagation interfere. The $E$ vector in terms of cylindrical coordinates propagated in the $z$ direction for levo circular polarization is

$$\vec{E} = \vec{r}A + \vec{\theta}\frac{2\pi}{\lambda}(z-ct)$$

and in the minus $z$ direction is

$$\vec{E} = \vec{r}A + \vec{\theta}\frac{2\pi}{\lambda}(z+ct)$$

The vector sum of these two waves is

$$\vec{E} = \vec{r}2A\cos\left(\frac{2\pi ct}{\lambda}\right) + \vec{\theta}\,\frac{2\pi z}{\lambda}$$

Thus, the electric vector orientation is independent of time and the magnitude is independent of spacial position.

An interesting question is how the orientation of the $E$ vector is related to the optical character of the cholesteric phase. If we assume the orientation of the structure to be that suggested by

Oseen[3] (shown in Fig. 8), then the index of refraction $n$ for light propagated parallel to the optic axis may be represented in cyclindrical coordinates as

$$n = \bar{n} + \frac{\Delta n}{2}\sin 2\left(\theta + \frac{z}{p}\right)$$

$$\bar{n} = \frac{n_x + n_y}{2}$$

$$\Delta n = n_x - n_y$$

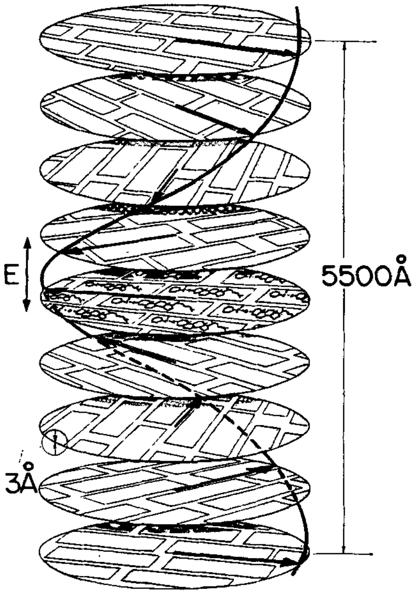

Figure 8. Probable organization of the cholesteric phase. Note that the molecules are not precisely arranged in layers. The 3 Å refers to the molecular thickness from X-ray measurement.

where $n_x$ is the maximum index of refraction in the $(\theta, r)$ plane, $n_y$ is the minimum index of refraction in the $(\theta, r)$ plane, $p$ is the pitch of the structure.

The condition for the standing wave in this structure can be satisfied when

$$p = \frac{\lambda}{n} = \text{the pitch of the helix in Fig. 8}$$

$$\lambda = \left(\bar{n} + \Delta n \tfrac{1}{2} \sin 2\left(\theta + \frac{z}{p}\right)\right) p$$

$$\theta = \tfrac{1}{2} \sin^{-1}\left[\frac{(\lambda - 2p\bar{n})}{p \Delta n}\right] - \frac{z}{p}$$

As can be seen from this expression, the structure should give rise to standing waves in the region where

$$p\left(\bar{n} - \frac{\Delta n}{2}\right) > \lambda > p\left(\bar{n} + \frac{\Delta n}{2}\right)$$

or $$\Delta\lambda = p\Delta n \qquad \frac{\Delta\lambda}{\lambda_{\max}} = \frac{\Delta n}{\bar{n}}$$

where $$\Delta\lambda = \lambda_1 - \lambda_2$$

$$\lambda_1 = p\left(\bar{n} + \frac{\Delta n}{2}\right)$$

$$\lambda_2 = p\left(\bar{n} - \frac{\Delta n}{2}\right)$$

and $$\lambda_{\max} = \frac{p}{2\bar{n}}$$

In this region the standing wave will occur in a region of constant index of refraction. From Fig. 3

$$\frac{\Delta n}{n} = \frac{\Delta\lambda}{\lambda_{\max}} = 0.0286$$

thus if $\bar{n} = 1.5$, $\Delta n = 0.043$, a value which is of the same order as the birefringence measured for many of these materials in the crystalline phase or smectic phase. A further result of the structure is to introduce a phase shift in the circular polarized light that interacts with the structure. The wavelength of any light scattered within the material will be equal to the pitch of the helix. The other sense of circular polarized light will be transmitted with a wavelength of $\lambda/\bar{n}$. Thus a phase change $\phi$ will be introduced which can be expressed as optical activity. The phase shift will be

$$\phi = 2\pi d\left(\frac{1}{p}-\frac{2\bar{n}}{\lambda}\right).$$

Since

$$\frac{1}{p} = \frac{\bar{n}}{\lambda_{\text{max}}}$$

then

$$\phi = 2\pi d\frac{1}{\lambda_{\text{max}}}-\frac{1}{\lambda}.$$

Solving for the thickness $d$ of the sample from Fig. 3 we find

$$d \approx 10.3\ \mu$$

This is well within the accuracy of the physical measurement.

## Changes in Optical Properties

The wavelength of maximum scattering ($\lambda_{\text{max}}$) of a thin film of the material will change from UV scattering to IR scattering simply by changing the temperature or the environment. The mechanism for this change is readily explained by a change in pitch in the twisted model, if we assume that the angle between planes changes with temperature (see Fig. 8). The wave number of maximum scattering will also change, since the distance between two aligned axes is

$$p = \frac{d}{\psi}\times 180^\circ = \frac{\lambda}{2}$$

where $p$ is distance of alignment or pitch, $\lambda$ is wavelength of scattered light, $d$ is plane spacing, and $\psi$ is angle between adjacent planes in degrees.

If we assume the spacing of the planes in the model to be on the order of 3 Å (a figure obtained from X-ray diffraction studies of crystals for the thickness of a cholesterol molecule), then the entire range of visible colors can be traversed with an angular shift of 7 min, the difference between 9 and 16 min.

## Summary

The optical effects which occur in various cholesteric materials are all very similar. The wavelength of maximum scattering is directly proportional to the pitch of the structure. The wavelength of maximum scattering, as a function of angle of incidence, is directly related to the index in the $(\theta, r)$ plane. The peak width appears to have a direct relation to the birefringence of the $(\theta, r)$ plane. The thickness can be inferred independent of index of refraction from the optical activity in the region of the scattering peak. These relations appear to hold for all materials that do not have an adsorption band in the scattering region.

This paper has dealt only with conditions where the cholesteric phase is well aligned and the optical axis is unidirectional over regions large compared to the wavelength of light. One area which lacks explanation in terms of the model is the presence of higher orders. Although of very low intensity and very broad peaks, they are easily found when observing thick films.

A further area which has not been treated is the nonbirefringent condition which appears when a cholesteric material is cooled from the isotropic phase. In this case, the material is transparent over long path lengths with what appears to be a slight Rayleigh scattering and a very high flow-birefringence. The transition from this structure to the colored structure has some of the characteristics of a phase change. This structure will be discussed at length in a later paper.

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