

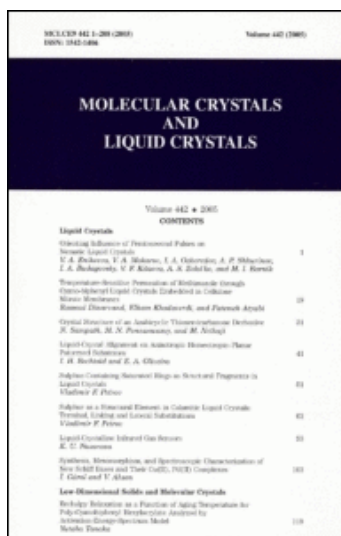
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## Molecular Crystals and Liquid Crystals

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## Theory of the Optical Properties of Non-absorbing Compensated Cholesteric Liquid Crystals

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# Theory of the Optical Properties of Non-absorbing Compensated Cholesteric Liquid Crystals

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**Abstract**—A theory is developed of the optical properties of a non-absorbing compensated cholesteric liquid crystal. It is shown that the Mauguin-de Vries equation fails when the pitch becomes very large. Theoretical curves are presented of the dependence of the rotatory power on pitch for different values of the sample thickness. The results are in agreement with the observed variation of the rotatory power of a compensated cholesteric mixture with temperature.

## 1. Introduction

The optical behavior of mixtures of right-handed and left-handed cholesteric liquid crystals has been the subject of many detailed experimental studies.<sup>(1-5)</sup> Such a mixture adopts the helical structure of a cholesteric, but the pitch is sensitive to composition and temperature. Friedel<sup>(1)</sup> observed that at a particular composition the pitch approaches infinity and the mixture exhibits the properties of a nematic. He also found that for any given composition an inversion of the rotatory power with temperature occurs, indicating that the structure changes handedness as the temperature is varied. More recently, Sackmann *et al.*<sup>(2)</sup> made a direct determination of the pitch as a function of temperature in a 1.75:1 weight mixture of cholesteryl chloride and cholesteryl myristate (CM) using laser diffraction techniques and showed that the *inverse* pitch varies almost linearly with temperature, passing through zero at  $T_N = 42.5^\circ\text{C}$ . Baessler *et al.*<sup>(4,5)</sup> measured the optical rotation in the CM mixture to investigate the change in the handedness of the helix with temperature and the perturbation of the structure by electric fields. These

authors have assumed that the Mauguin-de Vries equation<sup>(6,7)</sup> holds good for all values of the pitch.

In this paper we develop a rigorous theory of the optical behavior of a compensated cholesteric mixture neglecting the effect of absorption. (The case of absorbing systems is dealt with in a separate paper.) It is shown that the Mauguin-de Vries equation is valid only at temperatures much higher or lower than the nematic point  $T_N$ , but fails in the vicinity of  $T_N$  where the pitch is very large. Measurements are presented of the variation of the rotatory power of the CM mixture with temperature for samples of different thicknesses. The results are in agreement with the predictions of the theory.

## 2. Theory

We apply the theory of light propagation along the optic axis of a cholesteric liquid crystal developed in a previous paper.<sup>(8)</sup> The structure is regarded as a helically arranged pile of thin birefringent layers, the principal axes of the successive layers turned through a small angle  $\beta$ . The pitch  $P$  is assumed to be much greater than  $\lambda$  the wavelength of light in vacuum so that the effect of reflections is neglected completely.

We define  $2\gamma$  to be the phase retardation produced by a single layer, i.e.,

$$\gamma = \frac{\pi}{\lambda} (\Delta\mu)p$$

where  $\Delta\mu$  is the layer birefringence and  $p$  the thickness of each layer. We now apply the Jones calculus<sup>(9-11)</sup> to such a system assuming that light is incident normal to the layers, i.e., along  $OZ$ . Let the principal axes of the first layer make an angle  $\beta$  with respect to the coordinate axes  $OX$ ,  $OY$ . If the Jones retardation matrix with respect to the principal axes is

$$G = \begin{bmatrix} e^{i\gamma} & 0 \\ 0 & e^{-i\gamma} \end{bmatrix},$$

the retardation matrix with respect to  $OX$ ,  $OY$  is

$$J_1 = S G S'$$

where

$$S = \begin{bmatrix} \cos \beta & -\sin \beta \\ \sin \beta & \cos \beta \end{bmatrix},$$

and  $S' = S^{-1}$  is the transpose of  $S$ , so that  $SS' = S'S = E$ , the unit matrix. The retardation matrix for  $n$  layers is

$$J_n = S^n (GS')^n = \begin{bmatrix} a & b \\ c & d \end{bmatrix}, \quad \text{say.} \quad (1)$$

It can be shown that<sup>(8)</sup>

$$(GS')^n = \frac{\sin n\theta}{\sin \theta} (GS') - \frac{\sin(n-1)\theta}{\sin \theta} \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \quad (2)$$

where  $\cos \theta = \cos \beta \cos \gamma$ . Since  $\beta$  and  $\gamma$  are small,

$$\theta^2 \simeq \beta^2 + \gamma^2. \quad (3)$$

From (1) and (2),

$$a = \left[ \cos n\beta \cos n\theta + \frac{\tan \beta}{\tan \theta} \sin n\beta \sin n\theta \right] + i \left[ \frac{\sin n\theta}{\sin \theta} \sin \gamma \cos(n+1)\beta \right] \quad (4)$$

$$b = \left[ \frac{\tan \beta}{\tan \theta} \cos n\beta \sin n\theta - \sin n\beta \cos n\theta \right] + i \left[ \frac{\sin n\theta}{\sin \theta} \sin \gamma \sin(n+1)\beta \right] \quad (5)$$

$$c = -b^*, \quad d = a^*, \quad i = (-1)^{1/2}$$

where  $a^*$  and  $b^*$  are respectively the complex conjugates of  $a$  and  $b$ .

It is a standard result in optics<sup>(10,11)</sup> that such a system can be replaced by a rotator and a retarder. If  $\rho$  is the rotation produced by the system,  $2\phi$  the phase retardation and  $\psi$  the azimuth of the principal axes of the retarder,

$$J_n = \begin{bmatrix} \cos \rho & -\sin \rho \\ \sin \rho & \cos \rho \end{bmatrix} \begin{bmatrix} \cos \psi & -\sin \psi \\ \sin \psi & \cos \psi \end{bmatrix} \times \begin{bmatrix} \exp i\phi & 0 \\ 0 & \exp -i\phi \end{bmatrix} \begin{bmatrix} \cos \psi & \sin \psi \\ -\sin \psi & \cos \psi \end{bmatrix} \quad (1')$$

From (1) and (1') we get

$$a = \cos \phi \cos \rho + i \sin \phi \cos(2\psi + \rho) \quad (6)$$

$$\begin{aligned} b &= -\cos \phi \sin \rho + i \sin \phi \sin (2\psi + \rho) \\ c &= -b^* \quad \text{and} \quad d = a^*. \end{aligned} \quad (7)$$

Equating the real and imaginary parts of (4) and (6), and of (5) and (7), we obtain after simplification

$$\rho = n(\beta - \theta') \text{ radians} \quad (8)$$

$$\phi = \cos^{-1} \left[ \frac{1 + \tan^2 n\theta'}{1 + \tan^2 n\theta} \right]^{1/2} \quad (9)$$

$$\psi = \frac{1}{2}[(n+1)\beta - \rho],$$

where

$$\theta' = \frac{1}{n} \tan^{-1} \left[ \frac{\tan \beta \tan n\theta}{\tan \theta} \right]. \quad (10)$$

In these equations,  $n$  represents the total number of layers in the system, so that  $n\rho$  is the thickness of the sample.

### 3. Discussion

At temperatures well away from the nematic point  $T_N$ , the pitch is relatively small,  $\beta (= 2\pi p/P)$  becomes much larger than  $\gamma$ , and from (3) and (10)  $\theta' \simeq \theta$ . The total rotation produced by  $n$  layers then becomes

$$\begin{aligned} \rho &= n(\beta - \theta) = n[\beta - (\beta^2 + \gamma^2)^{1/2}] \\ &= -n\gamma^2/2\beta. \end{aligned}$$

Hence the rotatory power is  $-\pi(\Delta\mu)^2 P/4\lambda^2$  which is the Mauguin-de Vries equation.

As the temperature approaches  $T_N$ ,  $\rho$  departs from the Mauguin-de Vries equation. At  $T = T_N$ ,  $P = \infty$ ,  $\theta' = \beta = 0$ , and the rotation vanishes for all values of sample thickness, whereas the Mauguin-de Vries equation predicts infinite rotation.

As we are interested mainly in the optical rotation we shall not consider in detail the behavior of  $\phi$ , the phase retardation produced by the system, except to remark that  $\phi$  given by (9) vanishes whenever  $n\theta = m\pi$ , where  $m$  is 0, 1, 2 ... etc. Thus  $\phi$  exhibits oscillations as the pitch is varied. (The significance of this result will be discussed when considering absorbing systems.)

Some illustrative curves of the theoretical variation of the rotatory power for  $\lambda 5893 \text{ \AA}$  with temperature (and with pitch) derived from

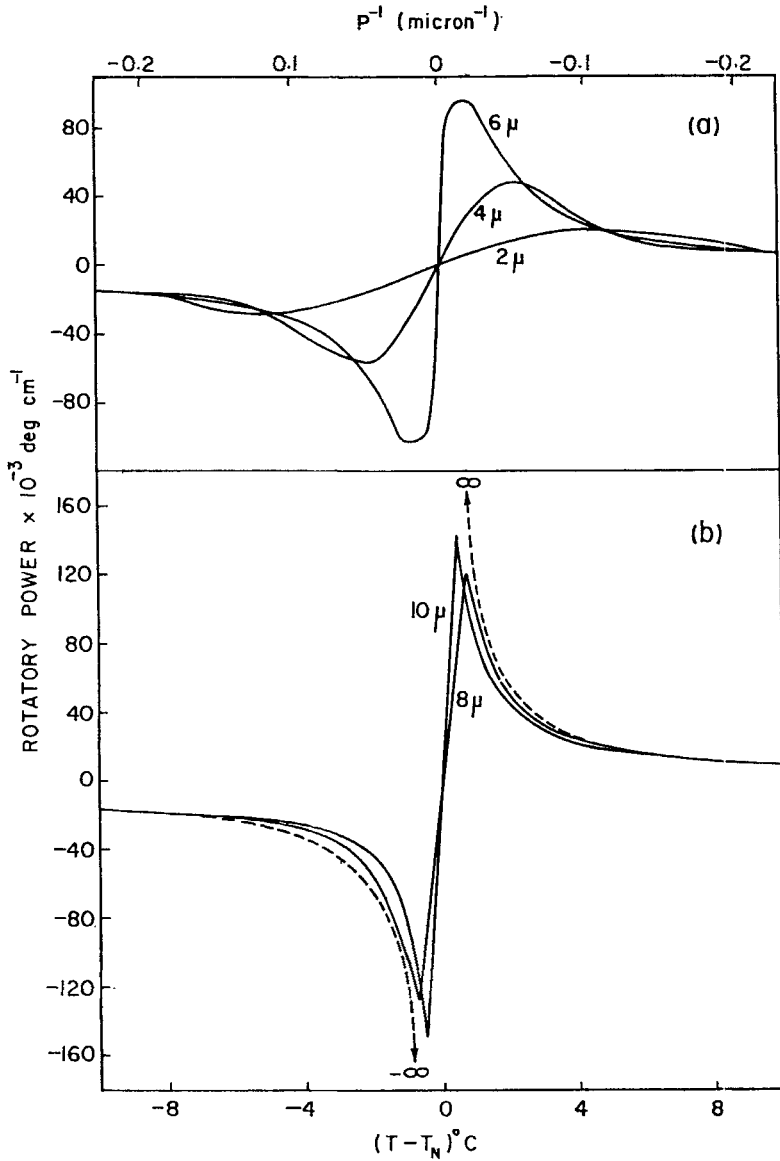


Figure 1. Theoretical variation of the rotatory power with temperature (and inverse pitch) for samples of thickness (a)  $2\mu$ ,  $4\mu$  and  $6\mu$ , (b)  $8\mu$  and  $10\mu$ . The broken curve in (b) is the rotatory power given by the Mauguin-de Vries equation.

(8) are shown in Fig. 1. Here the layer thickness  $p$  was assumed to be  $10 \text{ \AA}$ , and the dependence of pitch on temperature was taken from the data of Sackmann *et al.*<sup>(2)</sup> for the CM mixture. The layer birefringence  $\Delta\mu$  at  $20^\circ\text{C}$  and  $55^\circ\text{C}$  was estimated by inserting the observed values<sup>(4)</sup> of the rotatory power of CM at these temperatures into the Mauguin-de Vries equation;  $\Delta\mu$  at intermediate temperatures was obtained by interpolating linearly between  $20^\circ\text{C}$  and  $55^\circ\text{C}$ . This is a valid procedure since the Mauguin-de Vries equation holds good to a high accuracy at temperatures much higher or lower than  $T_N$ . With increasing sample thickness, the positive and negative peaks in the rotatory power curve increase in height and also get closer to  $T_N$ , so that for thick films the reversal in the sign of rotation takes place fairly abruptly. The trends exhibited by the curves are in close agreement with experimental observations.<sup>(4)</sup> Denoting  $\rho_{\max}(+)$  and  $\rho_{\max}(-)$  as the positive and negative peak values of the rotatory power and  $T_{\max}(+)$  and  $T_{\max}(-)$  as the temperatures at which they occur, the theoretical results for samples of different thicknesses are summarized in Table 1.

Baessler *et al.*<sup>(4)</sup> found that in the nematic state of CM the sample was not uniformly oriented but was composed of domains, the preferred direction in the different domains assuming different orientations in a plane parallel to the supporting surfaces. They observed a considerable increase in the transmitted intensity at this temperature even though the polarizing and analysing nicols were set in extinction positions. They concluded that the emergent beam is circularly polarized, supposedly in conformity with the de Vries theory. Circular polarization is not to be expected from theoretical considerations. To evaluate approximately the state of polarization of the light transmitted by such a multidomain sample, we use the formalism of the Stokes parameters and the Mueller matrix.<sup>(11)</sup>

A light beam having an intensity  $I$ , ellipticity  $\omega$  ( $= \tan^{-1} b/a$ ) with the major axis of the ellipse at an azimuth  $\lambda$  is analytically given by the four component Stokes vector

$$\sigma = \begin{bmatrix} I \\ M \\ C \\ S \end{bmatrix}$$

TABLE I

Present Theory	Thickness in microns	$\rho_{\max}(+)$ $\times 10^{-3}$ deg/cm	$T_{\max}(+) - T_N$ $^{\circ}\text{C}$	$\rho_{\max}(-)$ $\times 10^{-3}$ deg/cm	$T_N - T_{\max}(-)$ $^{\circ}\text{C}$
	1	7.7	9.00	-15.7	12.50
	2	19.0	4.50	-27.0	5.50
	3	30.0	3.00	-38.0	3.50
	4	46.0	2.00	-54.0	2.50
	5	64.0	1.15	-72.0	1.30
	6	94.9	0.90	-102.0	1.10
	7	104.0	0.85	-110.0	1.05
	8	120.0	0.70	-126.0	0.75
	9	130.0	0.55	-136.0	0.60
	10	142.0	0.50	-148.0	0.55
Mauguin-de Vries equation	Independent of sample thickness	$\infty$	0	$-\infty$	0



$$\begin{aligned}
 \text{where} \quad I &= \text{Intensity} \\
 M &= I \cos 2\lambda \cos 2\omega \\
 C &= I \sin 2\lambda \cos 2\omega \\
 S &= I \sin 2\omega.
 \end{aligned}$$

For linear polarization,  $\omega = 0$ . When the light beam passes through an optical system  $\sigma$  changes to  $\sigma'$ , i.e.,

$$\sigma' = [\mathbf{m}]\sigma.$$

Here  $[\mathbf{m}]$  is a  $4 \times 4$  matrix called the Mueller matrix. For a phase retarder having a retardation  $2\phi$  having its principal plane at an azimuth  $\psi$ , we have

$$[\mathbf{m}] = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & a_1 & a_2 & a_3 \\ 0 & b_1 & b_2 & b_3 \\ 0 & c_1 & c_2 & c_3 \end{bmatrix}$$

where

$$\begin{aligned}
 a_1 &= 1 + (\cos 2\phi - 1) \sin^2 2\psi, & a_2 &= \left( \frac{1 - \cos 2\phi}{2} \right) \sin 4\psi, \\
 & & a_3 &= -\sin 2\phi \sin 2\psi \\
 b_1 &= \left( \frac{1 - \cos 2\phi}{2} \right) \sin 4\psi, & b_2 &= 1 + (\cos 2\phi - 1) \cos^2 2\psi, \\
 & & b_3 &= \sin 2\phi \cos 2\psi \\
 c_1 &= \sin 2\phi \sin 2\psi, & c_2 &= -\sin 2\phi \cos 2\psi, & c_3 &= \cos 2\phi.
 \end{aligned}$$

Assuming that the domains are of equal dimension and that  $\psi$  can assume all possible values,  $[\mathbf{m}]$  becomes

$$\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & \frac{1}{2}(1 + \cos 2\phi) & 0 & 0 \\ 0 & 0 & \frac{1}{2}(1 + \cos 2\phi) & 0 \\ 0 & 0 & 0 & \cos 2\phi \end{bmatrix}$$

which is the Mueller matrix for the multidomain sample. In such a case it is clear that

$$\begin{aligned}
 I' &= I \\
 M' &= M \left( \frac{1 + \cos 2\phi}{2} \right)
 \end{aligned}$$

$$C' = C \left( \frac{1 + \cos 2\phi}{2} \right)$$

$$S' = S(\cos 2\phi).$$

The intensity of the completely polarized part of  $I'$  is given by  $I_p = (M'^2 + C'^2 + S'^2)^{1/2}$  which is evidently less than  $I'$ . Substituting the value of the birefringence of the CM mixture, and assuming the incident light to be linearly polarized ( $\omega = 0$ ),  $I_p$  turns out to be zero for a sample thickness of about  $6\mu$ ; in other words, the emergent beam is completely *unpolarized*. Thus, in general, there will be considerable depolarization of the transmitted beam which will explain the observations of Baessler *et al.*

In the above calculation, the beams emerging from the different domains are assumed to be incoherent, but in reality there may be a certain degree of coherence. In the extreme case when the beams are completely coherent it is easily shown that the incident linearly polarized light will emerge without any change in the state of polarization. Since this result does not agree with observations, we may conclude that the former assumption is probably the more realistic one.

#### 4. Measurements on cholesteryl chloride-cholesteryl myristate mixture

We have measured the rotatory power of a CM mixture (of composition 1.6 : 1 by weight) as a function of temperature for samples of thickness 12.7, 6.4 and  $3\mu$ . The polarimetric arrangement was of the standard type (Model No. 103071 manufactured by Winkel-Zeiss, Gottingen) and the light source was a sodium lamp ( $\lambda 5893 \text{ \AA}$ ). Plane texture films of the mixture were prepared between two glass slides whose surfaces were optically flat. Samples of thickness 12.7 and  $6.4\mu$  were obtained by using Dupont mylar spacers of thickness 0.50 and 0.25 mils respectively. For the thinner sample, no spacer was used and the thickness was measured by forming interference fringes in the air spaces around the specimen. Since the plates could not be held perfectly parallel without a spacer, the thickness measurement of the  $3\mu$  sample is estimated to be uncertain to  $\pm 20$ -25 %. The sample temperature could be controlled by a suitably constructed

heater and could be read to  $\pm 0.1^\circ\text{C}$  by a previously calibrated thermocouple.

For reasons discussed in the previous section, measurements of the rotatory power are comparatively difficult in the neighborhood of the nematic point. This is particularly so for thick specimens because the rotatory power changes from a large positive value to a large

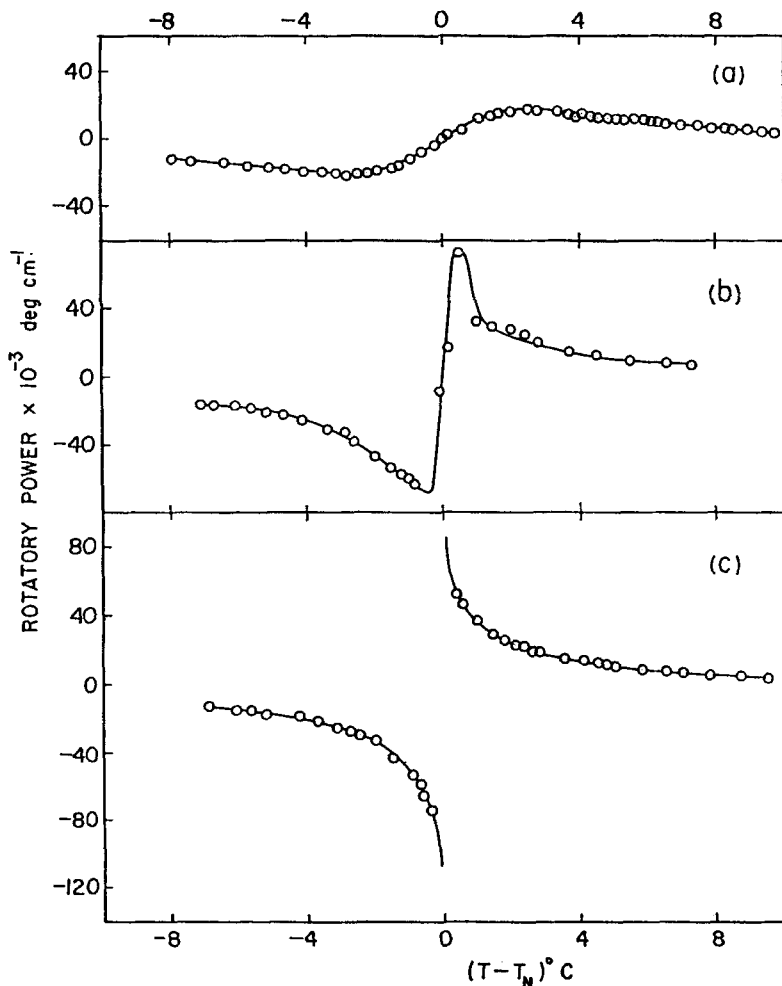


Figure 2. Experimental rotatory power as a function of temperature for a 1.6:1 by weight mixture of cholesteryl chloride and cholesteryl myristate. Sample thickness (a)  $3 \pm 0.75\mu$  (b)  $6.4\mu$  (c)  $12.7\mu$ .

negative value in a very small temperature interval around  $T_N$ , so that unless the temperature is kept truly constant measurements become practically impossible. We were able to determine the rotatory power in the region between the positive and negative peaks for the  $3\mu$  sample and to a lesser degree of accuracy for the  $6.4\mu$  sample, but not for the  $12.7\mu$  sample. Nevertheless, it is clear from Fig. 2 that the trends in the observed data are in close agreement with the theoretical curves in Fig. 1. Baessler *et al.*<sup>(4)</sup> have also reported measurements on the CM mixture for  $10\mu$  and  $3\mu$  samples which show exactly the same features. However, it is found both in our data and in those of Baessler *et al.* that the observed peak values of the rotatory power for the thinner samples are less than the theoretical values even after allowing for errors in the thickness measurements. This discrepancy may be due to the presence of inhomogeneities in the plane texture preparation and also due to wall effects.

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