

CHAPTER VIII

OPTICAL PROPERTIES OF NON-ABSORBING CHOLESTERIC

Introduction

Cholesteric liquid crystals are endowed with unique optical properties (Friedel 1922). For light propagating along the axis they exhibit optical rotatory power of the order of thousands of degrees per millimetre. When white light is incident on the surface of a cholesteric selective reflexion takes place over a small spectral range. The wavelength λ_0 of maximum reflexion varies with the angle of incidence in accordance with Bragg's law. When light is incident normally on the surface, for wavelengths of the order of λ_0 the reflected light is circularly polarised, reflexion being prominent only for a wave which is circularly polarised with the same sense as the cholesteric helix, that too over a small spectral range around λ_0 . Light circularly polarised in the opposite sense goes through unreflected. Contrary to reflexion from a dielectric mirror the reflected circular wave has the same sense of circular polarisation as that of the incident wave. In the neighbourhood

of the region of reflexion the rotatory dispersion is anomalous. The optical rotatory power ρ_p changes sign as one goes through the reflexion band, vanishing at λ_0 . On either side of λ_0 ρ_p attains high values of opposite signs.

Oseen (1933) proposed that a cholesteric could be regarded as a continuously twisted birefringent medium. The principal axes of the local index ellipsoid twist continuously as one moves along the helical axis. On the basis of this model de Vries (1951) solved the Maxwell's equations obtaining an approximate expression for ρ_p valid for wavelengths outside the reflexion band, which predicted an anomalous behaviour of ρ_p at λ_0 . Nearly four decades earlier Mauguin (1911) had worked out the rotatory power of twisted birefringent structures having large pitches compared to the wavelength, using the Poincare sphere. His results can be recovered from de Vries theory*. An exact theory of the optical properties of a semi-infinite cholesteric was given by Kats (1970) and independently by Nityananda (1973) for the Oseen model. This theory can be extended to finite sample thicknesses also (Nityananda and Kini 1975).

The optical properties of cholesterics can also be ^{explained} on the basis of the Jones calculus and the dynamical theory. This model, due to Chandrasekhar and Srinivasa Rao (1968) assumes that a cholesteric can be regarded as a helical stack of birefringent layers, each layer being a few Å thick. They were able to work out the optical properties of an infinite cholesteric. The theory was later on extended by Chandrasekhar and Shashidhara Prasad (1971) to the case of finite sample thickness and for wavelengths in the neighbourhood of the reflexion band (see also Chandrasekhar et al. 1973).

Even impurities have a profound influence on properties like pitch and optical rotation in cholesterics. In particular the optical properties of mixtures of right-handed and left-handed cholesteric liquid crystals (LR mixture) have been the subject of many detailed experimental studies. Such a mixture adopts the helical structure of a cholesteric. But the pitch of the mixture is a sensitive function of the composition of the mixture (i.e., of the relative concentrations of the ingredients) and of the temperature. Friedel (1922) observed that at any given temperature, the pitch of the mixture changes

as the composition ^{is} changed, approaching infinity at a particular composition and behaving like a nematic; the optical rotation at this composition will be zero. Friedel (1922) also discovered that as the temperature of an LR mixture of a given composition is changed, the rotatory power also changes. As the temperature approaches a particular value (called the nematic temperature T_N) the rotatory power decreases, becomes zero when the temperature equals T_N and changes sign when the temperature crosses T_N . This inversion of the rotatory power with temperature indicates that the structure changes handedness as the temperature is varied. It need hardly be said that T_N is a function of (i) the individual ingredients of the mixture, and (ii) the composition of the mixture.

Sackmann et al (1968) 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 technique. (The cholesteric can be regarded as a phase grating for light polarised normal to the helix and propagating perpendicular to the twist. This gives rise to a diffraction pattern from which the

value of the pitch can be worked out.) They showed that the inverse pitch varies almost linearly with temperature passing through zero at a temperature $T_N = 42.5^\circ\text{C}$. Baessler et al. (1969) measured the optical rotation in the OM mixture in order to investigate the change in the handedness of the helical structure with temperature and the perturbation of the structure by electric fields. But these authors assumed that the so-called Mauguin-de Vries equation holds good for all values of the pitch.

In this chapter a rigorous theory of the optical behaviour of a compensated cholesteric mixture is developed. The Mauguin-de Vries equation is shown to be valid only at temperatures far removed from the nematic temperature T_N . The theoretical predictions for the variation of the optical rotatory power of the QM mixture with temperature and with sample thickness have been found to be in conformity with the detailed experimental observations carried out recently by Suresh (1977).

Theory

There are many techniques for solving Maxwell's equations and one of the most elegant is the Jones

matrix method (Jones 1941). Any elliptic vibration can be regarded as a coherent addition of two linear vibrations at right angles to one another (example along the OX and OY directions) with appropriate amplitudes and phases. Let A_1 and A_2 be the resolved components of the electric vector along OX and OY. (A_1 and A_2 are in general complex). The intensity of the radiation is $I = |A_1|^2 + |A_2|^2$. Let ϵ_1 and ϵ_2 be the phases of A_1 and A_2 respectively. The azimuth Λ and the ellipticity w of the ellipse are given by

$$\tan 2\Lambda = \cos \delta \tan 2\alpha \quad \text{and} \quad \sin 2w = \sin \delta \sin 2\alpha \quad (1)$$

where

$$\tan \alpha = \frac{|A_1|}{|A_2|} \quad \text{and} \quad \delta = \epsilon_1 - \epsilon_2.$$

Thus the elliptic vibration can be uniquely represented by the column vector

$$\vec{D} = \begin{bmatrix} A_1 \\ A_2 \end{bmatrix} \quad (2)$$

Let the vibration be incident on a linearly birefringent

plate which has principal axes parallel to OX and OY (principal refractive indices n_1 and n_2). Let φ_1 and φ_2 be the phase retardation of the vibrations A_1 and A_2 . Then the outcoming light will be

$$\vec{D'} = \begin{bmatrix} A_1 \exp(-i\varphi_1) \\ A_2 \exp(-i\varphi_2) \end{bmatrix} \quad (3)$$

We can write $D' = J D$ where J is the 2×2 matrix

$$\begin{bmatrix} \exp(-i\varphi_1) & 0 \\ 0 & \exp(-i\varphi_2) \end{bmatrix} \quad (4)$$

This can be written as

$$\exp(-i\varphi) \begin{bmatrix} \exp(-i\gamma) & 0 \\ 0 & \exp(i\gamma) \end{bmatrix} \quad (5)$$

where

$$\varphi = \frac{\varphi_1 + \varphi_2}{2}$$

$$\gamma = \frac{\varphi_1 - \varphi_2}{2}$$

J is called the Jones matrix for the birefringent

plate. If the principal axes are inclined at angles β and $\beta + \frac{\pi}{2}$ to OX the Jones matrix is obviously given by

$$J(\beta) = \exp(-i\varphi) S(\beta) J S(-\beta) \quad (6)$$

where $S(\beta)$ is the rotation matrix

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

If a system rotates the plane of polarisation by an angle ρ the Jones matrix for the system is given by

$$J = \exp(-i\varphi) S(\rho) \quad (7)$$

If an optical system consists of a number of subsystems the total Jones matrix of the system is obtained as a product of the Jones matrices of the individual subsystems taken in the proper order.

In the model used by Chandrasekhar and Srinivasa Rao the cholesteric is regarded as a helically arranged pile of n birefringent plates, each of thickness p , such that the principal axes of the successive layers is turned through a constant

angle of β . The sample thickness is obviously np . By convention $\beta > 0$ for RH cholesterics and $\beta < 0$ for left handed cholesterics.

If $\Delta \mu$ is the birefringence of each plate and λ the wavelength of light which travels perpendicular to the principal axes the phase retardation produced by a single plate is

$$\frac{2\pi}{\lambda}(\Delta \mu)p = 2\gamma \text{ say} \quad (9)$$

It is assumed that the light is incident normally on the cholesteric (i.e., along OZ) and that the pitch P of the structure is much larger than the wavelength. Let the principal axis of the first layer make an angle β with OX. Then the Jones matrix for the layer with respect to OX and OY is

$$G_1 = S G S' \quad (10)$$

where

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

$$G = \begin{bmatrix} \exp(-i\gamma) & 0 \\ 0 & \exp(i\gamma) \end{bmatrix},$$

S' is the transpose of S and since S is orthogonal $S^t \equiv S^{-1}$.

The phase factor in the matrix G can be ignored for non-absorbing systems* The Jones matrix for the second layer with respect to the principal axes of the first layer is SGS' . But with respect to OX and OY this becomes

$$G_2 = S(SGS')S' = S^2 G (S')^2$$

Similarly the Jones matrix of the n^{th} layer with respect to OX and OY is

$$G_n = S^n G (S')^n \quad (11)$$

Hence the net Jones matrix for the entire system is

$$\begin{aligned} J &= G_n G_{n-1} \dots G_2 G_1 \\ &= S^n G (S')^n \cdot S^{n-1} G (S')^{n-1} \dots S^2 G (S')^2 S G S' \\ &= S^n (GS')^n \end{aligned} \quad (12)$$

A simple calculation (see Appendix) shows that

$$(GS')^n = \frac{\sin n\theta}{\sin \theta} (GS') - \frac{\sin (n-1)\theta}{\sin \theta} \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \quad (13)$$

where $\cos \theta = \cos \beta \cos \gamma$.

Since β and γ are small we can write $\theta^2 \approx \beta^2 + \gamma^2$.

Substituting we can write

$$J = \begin{bmatrix} a & b \\ c & d \end{bmatrix} \quad (14)$$

where

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

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

$$c = -b^* \quad \text{and} \quad d = a^*,$$

the asterisk represents complex conjugates.

It has been shown by Hurwitz and Jones (1941) that for light of a given wavelength an optical system consisting of any number of retardation plates is optically equivalent to a system containing a retardation plate and a rotator. Let the OM mixture be equated to a rotator producing a rotation ρ and a retardation plate, having a phase retardation of 2ϕ , whose principal axes have an azimuth of ψ . The

Jones matrix for this system is

$$\begin{aligned}
 & \begin{bmatrix} \cos \rho & -\sin \rho \\ \sin \rho & \cos \rho \end{bmatrix} \begin{bmatrix} \cos \psi & -\sin \psi \\ \sin \psi & \cos \psi \end{bmatrix} \\
 & \times \begin{bmatrix} \exp(-i\phi) & 0 \\ 0 & \exp(i\phi) \end{bmatrix} \begin{bmatrix} \cos \psi & \sin \psi \\ -\sin \psi & \cos \psi \end{bmatrix} \\
 & = \begin{bmatrix} a' & b' \\ c' & d' \end{bmatrix} \quad (15)
 \end{aligned}$$

where

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

Putting $a = a'$ and $b = b'$ and solving for ρ , ϕ and ψ one obtains

$$\rho = n(\beta - \theta') \quad (16)$$

$$\phi = \cos^{-1} \left[\frac{1 + \tan^2 n\theta'}{1 + \tan^2 n\theta} \right]^{\frac{1}{2}} \quad (17)$$

$$\psi = \frac{1}{2}[(n+1)\beta - \rho] \quad (18)$$

where

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

Discussion

At temperatures well away from the nematic point T_N the pitch P is relatively small so that $\beta (=2\pi p/P)$ is much larger than γ . Hence $\theta \simeq \beta$ and therefore $\theta' \simeq \theta$. The total rotation produced by n layers is

$$\rho \simeq n(\beta - \theta) = n[\beta - (\beta^2 + \gamma^2)^{\frac{1}{2}}] \simeq n\gamma^2/2\beta$$

$$= - \frac{n \cdot \pi^2 (\Delta \mu)^2 p^2 \cdot P}{2\lambda^2 \cdot 2\pi p} = - \frac{\pi (\Delta \mu)^2 P}{4\lambda^2}$$

This is the Mauguin-de Vries equation.

As the temperature approaches T_N ρ departs from the value predicted by the Mauguin-de Vries equation. At $T = T_N$ $P = \infty$ $\beta = 0$ $\theta' = 0$. Hence

$\rho = 0$. The rotation vanishes for all sample thicknesses. But the Mauguin-de Vries equation predicts infinite rotation. In passing one may remark that the phase retardation ϕ vanishes whenever $n\theta = m\pi$, m being 0, ± 1 , ± 2 ... Thus ϕ should exhibit oscillations when the pitch (or equivalently the temperature) of the CM mixture is varied.

Some illustrative curves of the theoretical variation of the rotatory power for the sodium yellow light ($\lambda = 5893 \text{ \AA}$) with temperature (or equivalently with the pitch) derived from (16) are shown. The layer thickness p was assumed to be $10 \text{ \AA}$. The dependence of pitch on temperature was taken from the data of Sackmann et al. for the CM mixture. By inserting the values of rotatory power, observed by Baessler et al., at 20°C and 55°C (far away from T_N) into the Mauguin-de Vries equation $\Delta \mu$ at these temperatures was determined. $\Delta \mu$ at intermediate temperatures was obtained by interpolation. As the sample thickness increases the positive and negative peaks in the rotatory power curve increase in height and also get closer to T_N , so that for sufficiently thick samples the reversal in sign of the rotatory

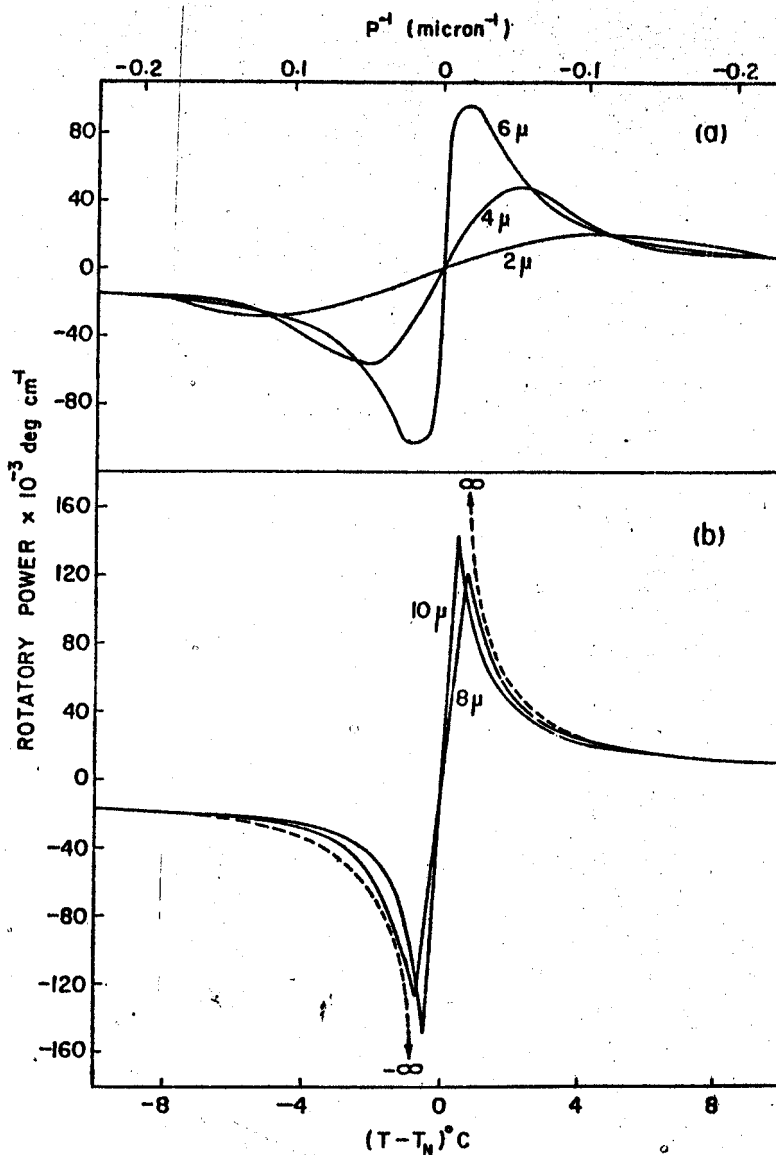


Figure 1: Theoretical variation of the rotatory power with temperature (and inverse pitch) for sample thicknesses (a) 2 μ , 4 μ and 6 μ , (b) 8 μ and 10 μ . The broken curve in (b) is the rotatory power given by the Mauguin-de Vries equation.

power takes place fairly abruptly. The trends exhibited by the curves are in close agreement with experimental observation. Denoting $\rho_{\max}(+)$ and $\rho_{\max}(-)$ as the positive and negative peaks of rotatory power and $T_{\max}(+)$ and $T_{\max}(-)$ as the temperatures at which they occur the theoretical results for samples of different thicknesses are summarised in Table 1. There is one more aspect of these equations which is explored now.

Suppose we have a helix for which $\beta \ll \gamma$. (This can happen in the case of a twisted nematic since for nematics the birefringence is much larger than in the case of cholesterics.) Then $\Theta \approx [\beta^2 + \gamma^2]^{\frac{1}{2}} \approx \gamma$ and since $\beta \ll \gamma$, $\Theta' \approx 0$ so that $\rho \approx n\beta$, $\varphi = n\gamma$ and $\psi = 0$. Thus if a linearly polarised wave is incident on the medium along one of its principal axes it undergoes as much twist as the structure. In other words the plane of polarisation of light rotates with the principal area of the layers. Also for a wave which is linearly polarised at an arbitrary angle the medium also behaves as a retardation plate with a retardation given by the untwisted structure. This phenomenon is utilized in constructing 'twisted nematic display devices'.

TABLE 1

Present Theory	Thickness in microns	$\max(+)$ $\times 10^{-3} \text{ deg/cm}$	$T_{\max(+)} - T_H$ $^{\circ}\text{C}$	$\max(-)$ $\times 10^{-3} \text{ deg/cm}$	$T_H - T_{\max(-)}$ $^{\circ}\text{C}$
	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	∞	0	- ∞	0

Appendix

Consider the matrix

$$GS' = \begin{bmatrix} \exp(-i\gamma)\cos \beta & \exp(-i\gamma)\sin \beta \\ -\exp(i\gamma)\sin \beta & \exp(i\gamma)\cos \beta \end{bmatrix} = \begin{bmatrix} a & b \\ c & d \end{bmatrix}$$

It is required to evaluate $(GS')^n$. We do this by reducing GS' to diagonal form, The characteristic equation for GS' is

$$\begin{bmatrix} a - 1 & b \\ c & d - 1 \end{bmatrix} = 0$$

or

$$\lambda^2 - \lambda(a + d) + (ad - bc) = 0.$$

Observe that $ad - bc = 1$ and that

$$\frac{a + d}{2} = \cos \beta \cos \gamma = \cos \theta \text{ say}$$

The eigenvalues come out to be $\exp(\pm i\theta)$ $\lambda_{1,2}$ say.

The eigenvectors belonging to these eigenvalues may be taken to be

$$\begin{bmatrix} -b \\ a - l_1 \end{bmatrix} \quad \text{and} \quad \begin{bmatrix} -b \\ a - l_2 \end{bmatrix}$$

The 2×2 matrix T , which has these eigenvectors as columns can be used for diagonalising GS' , i.e.,

$$T^{-1}(GS')T = \Psi = \begin{bmatrix} l_1 & 0 \\ 0 & l_2 \end{bmatrix}$$

where

$$T = \begin{bmatrix} -b & , & -b \\ a - l_1 & , & a - l_2 \end{bmatrix}$$

$$(GS') = T \Psi T^{-1}$$

$$\begin{aligned} (GS')^n &= (T \Psi T^{-1})(T \Psi T^{-1}) \dots\dots (T \Psi T^{-1}) \\ &\quad \leftarrow \text{n times} \rightarrow \\ &= T \Psi^n T^{-1} \end{aligned}$$

$$T^{-1} = \begin{bmatrix} \frac{a - l_2}{\Delta} & \frac{b}{\Delta} \\ -\frac{a - l_1}{\Delta} & -\frac{b}{\Delta} \end{bmatrix}$$

where $\Delta = \det T = 2ib \sin \theta$

$$(GS')^n = \frac{l_1^n - l_2^n}{l_1 - l_2} (GS') - l_1 l_2 \frac{(l_1^{n-1} - l_2^{n-1})}{l_1 - l_2} E$$

Thus

$$(GS')^n = \frac{1}{\sin \theta} \begin{bmatrix} a \sin n\theta - \sin(n-1)\theta & b \sin n\theta \\ -\frac{\sin n\theta(a^2 - 2a \cos \theta + 1)}{b} & \sin(n+1)\theta - a \sin n\theta \end{bmatrix}$$

Making use of the fact that $ad - bc = 1$ and that

$\frac{a+d}{2} = \cos \theta$ we obtain the final expression for $(GS')^n$

viz.,

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

$$\begin{bmatrix} -b \\ a - l_1 \end{bmatrix} \quad \text{and} \quad \begin{bmatrix} -b \\ a - l_2 \end{bmatrix}$$

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where

$$T = \begin{bmatrix} -b & , & -b \\ a - l_1 & , & a - l_2 \end{bmatrix}$$

$$(GS') = T\Psi T^{-1}$$

$$(GS')^n = (T\Psi T^{-1})(T\Psi T^{-1}) \dots\dots (T\Psi T^{-1})$$

←----- n times -----→

$$= T\Psi^n T^{-1}$$

$$T^{-1} = \begin{bmatrix} \frac{a - l_2}{\Delta} & \frac{b}{\Delta} \\ -\frac{a - l_1}{\Delta} & -\frac{b}{\Delta} \end{bmatrix}$$

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CHAPTER IX

OPTICAL PROPERTIES OF ABSORBING CHOLESTERIC

Introduction

In the previous Chapter the optical properties of non-absorbing compensated mixtures of cholesterics were considered. In this Chapter the optical properties of absorbing cholesteric mixtures will be dealt with. Sackmann and Voss (1972) demonstrated experimentally that when linearly dichroic molecules are dissolved in a cholesteric liquid crystal the medium exhibits circular dichroism in the region of the absorption band of the dye molecule. They used the de Vries equation to interpret this circular dichroism. This problem was also independently dealt with by Ranganath (1973). One consequence of this model (which holds for $\frac{\lambda}{\Delta\mu} > P > \lambda$) is that the dichroic power should be independent of sample thickness, that it should become infinite for infinite pitch and that the sign of the circular dichroism should change when either the linear dichroism or the linear birefringence changes sign or when the handedness of the cholesteric changes.

An exact theory *for* the optical properties of an absorbing compensated cholesteric mixture (which holds for all values of $P > \lambda$) is developed in this Chapter. Expressions are derived for circular dichroism, optical rotation, etc. as functions of pitch (or equivalently temperature). The theory has been found to be in conformity with the detailed experimental studies carried out recently by Suresh (1977).

Theory

As in the previous Chapter one can again consider the cholesteric to be a helical stack of n birefringent layers, each of thickness p , but with this difference that each layer is linearly dichroic due to the dissolved linearly dichroic molecules. Thus each plate has two principal absorption coefficients k_1 and k_2 and two refractive indices n_1 and n_2 . The principal axes of the absorptive and index ellipsoid are assumed to coincide. The sample thickness is clearly $d = np$. Let the pitch P be such that $P \gg \lambda$ the wavelength of light so that effects of reflexions between layers can be ignored*. Light is assumed to be transmitted along the Oz direction which coincides with the axis

of the cholesteric.

The Jones matrix of any layer with respect to its principal axes is

$$\begin{aligned}
 G &= \begin{bmatrix} \exp(-i\gamma) & 0 \\ 0 & \exp(i\gamma) \end{bmatrix} \begin{bmatrix} \exp(-k_1 p) & 0 \\ 0 & \exp(-k_2 p) \end{bmatrix} \\
 &= \exp(-\alpha) \begin{bmatrix} \exp(-i\hat{\gamma}) & 0 \\ 0 & \exp(i\hat{\gamma}) \end{bmatrix} \quad (1)
 \end{aligned}$$

where $\gamma = \frac{\pi}{\lambda}(A\mu)p$ is half the phase retardation per layer,

$$\alpha = \frac{(k_1 + k_2)}{2} p \quad \text{and}$$

$$\hat{\gamma} = \gamma - i\left(\frac{k_1 - k_2}{2}\right)p \equiv \gamma - i\delta \text{ (say)} .$$

If the first layer is assumed to make an angle β with Ox and Oy we find the Jones matrix for n layers to be

$$J = S^n (GS')^n \quad (\text{see Chapter VIII}) \quad (2)$$

It can be shown (Appendix of Chapter VIII) that

$$(GS')^n = \frac{l_1^n - l_2^n}{l_1 - l_2} (GS') - l_1 l_2 \frac{l_1^{n-1} - l_2^{n-1}}{l_1 - l_2} E$$

where $l_1 = \exp(-a + i\hat{\theta})$,

$$l_2 = \exp(-a - i\hat{\theta}) ; \text{ and}$$

$$\cos \hat{\theta} = \cos \beta \cos \hat{\gamma}$$

Then

$$\begin{aligned} (GS')^n &= \exp(-n\alpha) \frac{\sin n\hat{\theta}}{\sin \hat{\theta}} (GS') - \exp \{-(n+1)\alpha\} \frac{\sin(n-1)\hat{\theta}}{\sin \hat{\theta}} E \\ &\approx \exp(-n\alpha) \left[\frac{\sin n\hat{\theta}}{\sin \hat{\theta}} (GS') - \frac{\sin(n-1)\hat{\theta}}{\sin \hat{\theta}} E \right] \quad (3) \end{aligned}$$

if (as It is in practical asses) n is assumed to be $\gg 1$.

The matrix J can be uniquely resolved into a rotator, a retarder a circularly dichroic plate and a linearly dichroic plate in the form

$$J = \exp(-\chi) \Psi R \Sigma \Phi K \Sigma \Psi^{-1} \quad (4)$$

where

$$\Psi = \begin{bmatrix} \cos \psi & -\sin \psi \\ \sin \psi & \cos \psi \end{bmatrix},$$

$$R = \begin{bmatrix} \cos \rho & -\sin \rho \\ \sin \rho & \cos \rho \end{bmatrix},$$

$$\Sigma = \begin{bmatrix} \cosh \sigma/2 & -\sinh \sigma/2 \\ \sinh \sigma/2 & \cosh \sigma/2 \end{bmatrix},$$

$$\Phi = \begin{bmatrix} \exp(-i\varphi) & 0 \\ 0 & \exp(i\varphi) \end{bmatrix},$$

$$\text{and } K = \begin{bmatrix} \exp(-k) & 0 \\ 0 & \exp(k) \end{bmatrix}$$

ρ is the rotation, σ the circular dichroism, 2φ the linear phase retardation, $2k$ the linear dichroism and χ the attenuation coefficient (see Appendix).

Using (2), (3) and (4) it can be shown that

$$\hat{\rho} = \rho - i\sigma = n(\beta - \hat{\theta}')$$

$$\hat{\varphi} = \varphi - ik = \cos^{-1}\left(\frac{\cos n\hat{\theta}}{\cos n\hat{\theta}'}\right)$$

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

$$\chi = n\alpha$$

with

$$\hat{\theta}' = \frac{1}{n}\tan^{-1}\left[\frac{\tan \beta}{\tan \hat{\theta}} \tan n\hat{\theta}\right].$$

It is needless to say that these equations reduce to the equations (16), (17) and (18) of Chapter VIII when absorption is equated to zero.

Results

We consider two extreme cases.

Case (i) $\beta \gg |\hat{\gamma}|$

In this case $\hat{\theta}' \approx \hat{\theta}$ and $\varphi - ik \approx \cos^{-1}(1) = 0$. Therefore $\varphi = k = 0$. Therefore $\hat{\phi}$ and K are unit matrices. As has been shown in the Appendix, we can write

$$J = \exp(-\chi) \begin{bmatrix} \cos \hat{\psi} & -\sin \hat{\psi} \\ \sin \hat{\psi} & \cos \hat{\psi} \end{bmatrix} \begin{bmatrix} \cos \hat{\rho} & -\sin \hat{\rho} \\ \sin \hat{\rho} & \cos \hat{\rho} \end{bmatrix} \\ \times \begin{bmatrix} \exp(-i\hat{\phi}) & 0 \\ 0 & \exp(i\hat{\phi}) \end{bmatrix} \begin{bmatrix} \cos \hat{\psi} & \sin \hat{\psi} \\ -\sin \hat{\psi} & \cos \hat{\psi} \end{bmatrix}$$

The first and second matrices commute and the third is now a unit matrix* Thus the azimuth $\hat{\psi} = \rho + i\sigma/2$ does not come into the picture at all. We also obtain

$$\hat{\rho} = \rho - i\sigma = n(\beta - \hat{\theta}') \simeq n(\beta - \hat{\theta}) \\ \simeq n(\beta - (\beta^2 + \hat{\gamma}^2)^{\frac{1}{2}}) \simeq -\frac{n\hat{\gamma}^2}{2\beta}$$

Equating the real and imaginary parts we obtain

$$\rho = n(\gamma^2 - \delta^2)/2\beta \\ \sigma = -n\gamma\delta/\beta \quad (6)$$

Thus the linear dichroism of layers results in in circular dichroism and also makes a small

contribution to optical rotation which is opposite in sign to that due to linear birefringence. An interesting consequence of equation (6) is that σ changes sign whenever β , γ or $\Delta k = k_1 - k_2$ changes sign. This accounts for the observation of Sackmann and Voss who found that the circular dichroism at 2630 Å and 3950 Å were of opposite in sign for pyrene-2-carboxylic methyl ester dissolved in a cholesteric. This is due to the linear dichroism of the dye molecules being of opposite signs at the two wavelengths.

When the system becomes strongly dichroic the theory predicts very high rotatory power $\sim 360^\circ$ per pitch, the sign of rotation being opposite to that exhibited by transparent or weakly absorbing cholesterics. Such a situation, which corresponds to each layer becoming almost a polaroid is not likely to be encountered in practice.

$$\underline{\beta \ll |\hat{\gamma}|}$$

In this case

$$(GS')^n \approx G^n = \begin{bmatrix} \exp(-in\hat{\gamma}) & 0 \\ 0 & \exp(in\hat{\gamma}) \end{bmatrix}$$

and

$$J \approx \begin{bmatrix} \cos n\beta, & -\sin n\beta \\ \sin n\beta, & \cos n\beta \end{bmatrix} \begin{bmatrix} \exp(-in\gamma) & 0 \\ 0 & \exp(in\gamma) \end{bmatrix} \exp(-na)$$

.. (7)

Thus at any point in the medium there are two linear vibrations polarised along the local principal axes of the layer. And the two vibrations rotate with the principal axes as one goes down the helical axis. The phase retardation and amplitude reductions undergone by these two vibrations are the same as in an untwisted nematic.

Intermediate values of β : In this case the complete expression (5) should be used for calculating ρ and σ . Figure 1 illustrates the theoretical dependence of circular dichroism on temperature (or equivalently pitch) in a CM mixture sample of thickness 6μ . (Data for β and γ are the same as in Chapter I). At $\beta = 3 \times 10^{-3}$ radian on the low temperature side of T_H , $\frac{(k_1 - k_2)}{2}p$ is assumed to be 4×10^{-5} . The layer birefringence (or equivalently γ) and the layer dichroism are assumed to decrease

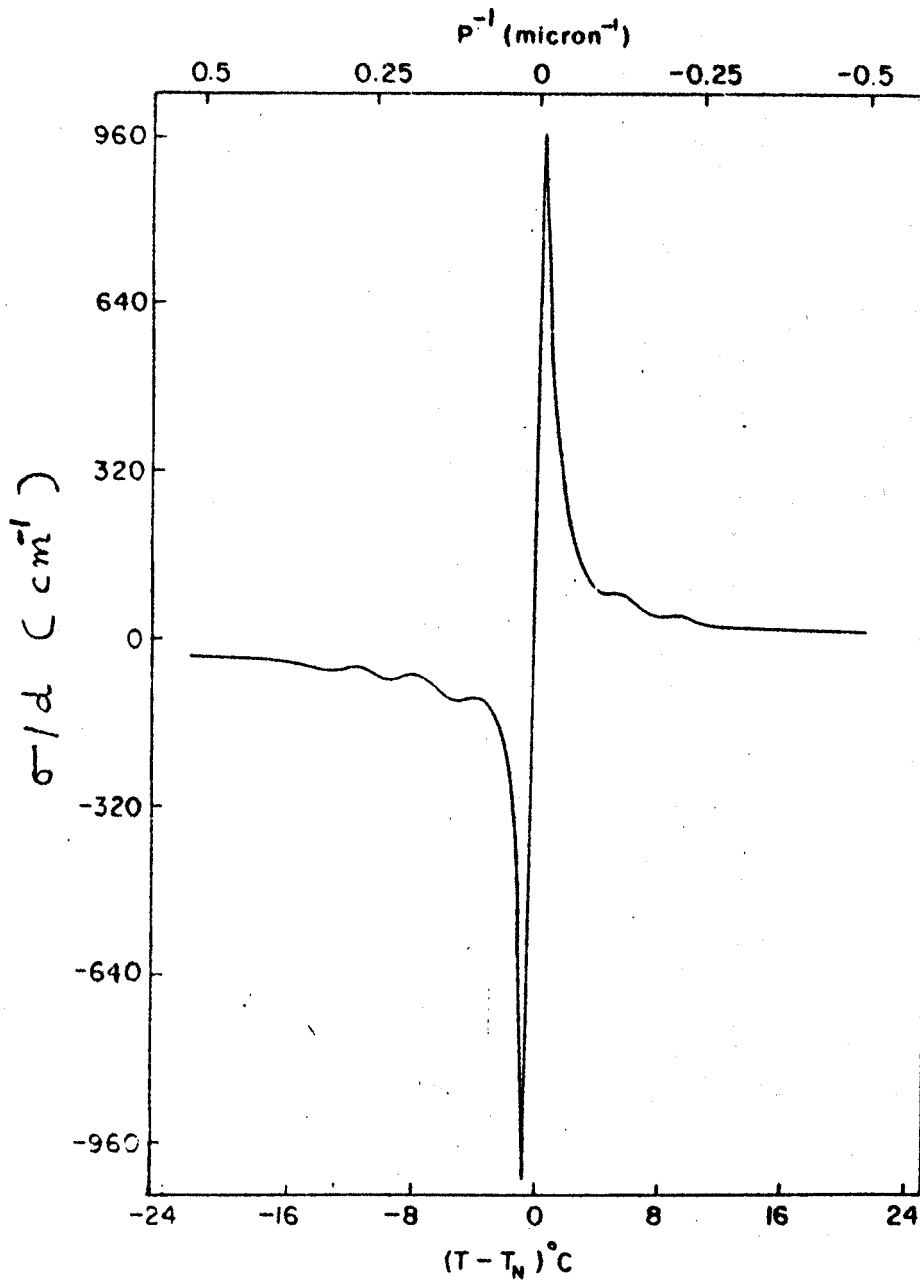


Figure 1

Theoretical dependence of circular
dichroic power σ/d ON temperature and
inverse pitch.

at the same rate with temperature increase. The curve for σ/d shows peaks at two values of temperature, one on either side of T_N and exhibits weak oscillations as temperature is changed. The peak value of σ/d and the temperature at which it occurs depend on the sample thickness. Figure 2 shows the theoretical variation of circular dichroism with sample thickness for $\beta = 0.6 \times 10^{-3}$ rad. σ exhibits pronounced oscillation as the thickness is varied.

In actual practice σ is not measured directly. In an experiment generally the transmitted intensities I_R and I_L , for right- and left-circular light (of equal intensity) incident on the medium, are measured and the circular dichroism D_0 , defined as

$$D_0 = \frac{(I_R)^{\frac{1}{2}} - (I_L)^{\frac{1}{2}}}{(I_R)^{\frac{1}{2}} + (I_L)^{\frac{1}{2}}} \quad (8)$$

is evaluated.

To calculate D_0 theoretically, we use the Jones matrix J of the pile of plates and obtain for the emergent light vector

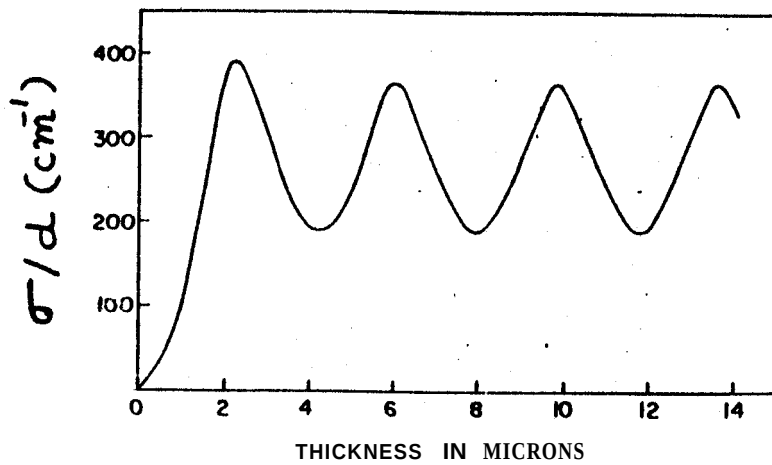


Figure 2

**Theoretical dependence of circular
dichroic power σ/d with sample
thickness.**

$$\begin{bmatrix} A_1 \\ A_2 \end{bmatrix} = \frac{1}{(2)^{\frac{1}{2}}} J \begin{bmatrix} 1 \\ +1 \end{bmatrix} \text{ for right circular light} \quad (9)$$

$$\begin{bmatrix} B_1 \\ B_2 \end{bmatrix} = \frac{1}{(2)^{\frac{1}{2}}} J \begin{bmatrix} 1 \\ -1 \end{bmatrix} \text{ for left circular light}$$

$$\text{Then } I_R = |A_1|^2 + |A_2|^2 \quad \text{and}$$

$$I_L = |B_1|^2 + |B_2|^2 .$$

The dichroic power D is the circular dichroism per unit sample thickness. Figure 3 is a plot of D as a function of temperature (inverse pitch) for the CM mixture. Theoretical values are calculated for the CM mixture of 6μ sample thickness. The data for β and γ is the same as that which has been used for calculating σ ; the linear dichroism is taken to be 10^{-4} at $\beta = 3 \times 10^{-3}$ radians on the lower temperature side of T_N . Layer birefringence and layer dichroism are assumed to decrease at the same rate with increasing temperature. D changes sign at the nematic point T_N . Also D exhibits weak oscillations as the pitch or temperature is varied and pronounced oscillations at a given temperature as sample thickness is varied. (see Table 1).

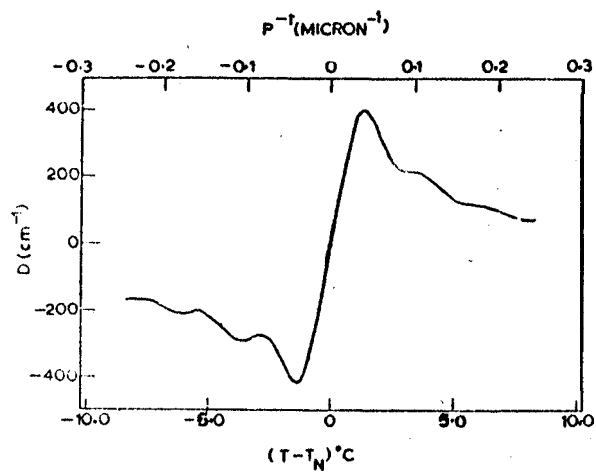


Figure 3

**Theoretical dependence of
circular dichroic power D
on temperature and inverse
pitch.**

Table 1

Sample thickness (in microns)	Negative peak value of D
2	299.8
3	382.5
4	430.2
5	441.3
7	366.5
9	348.6
11	341.0
13	305.9
15	298.5
17	272.8
19	253.6

Appendix

Equation (4) can be written as

$$J = \exp(-\chi) \begin{bmatrix} \cos \hat{\psi} & -\sin \hat{\psi} \\ \sin \hat{\psi} & \cos \hat{\psi} \end{bmatrix} \begin{bmatrix} \cos \hat{\rho} & -\sin \hat{\rho} \\ \sin \hat{\rho} & \cos \hat{\rho} \end{bmatrix} \\ \times \begin{bmatrix} \exp(-i\hat{\varphi}) & 0 \\ 0 & \exp(i\hat{\varphi}) \end{bmatrix} \begin{bmatrix} \cos \hat{\psi} & \sin \hat{\psi} \\ -\sin \hat{\psi} & \cos \hat{\psi} \end{bmatrix}$$

(See for example equation (15) of Chapter VIII, where $\exp(-\chi)$ is of course absent since in that case a transparent cholesteric is investigated. Also since an absorbing cholesteric is under investigation in the present chapter all the quantities have been made complex including even the azimuth.)

where

$$\begin{aligned} \hat{\rho} &= \rho - i\sigma \\ \hat{\varphi} &= \varphi - ik \\ \text{and } \hat{\psi} &= \psi + i\sigma/2. \end{aligned}$$

(Even if an assumption is made to the effect that $\psi = \psi' + i\psi''$ it can be shown that $\psi' = \sigma/2$ is

demanded by consistency. Hence to save labour we make this assumption in the beginning itself.)

Now calculate $J = S^n(GS')^n$ using equations 2 and 3 equating it element by element to the matrix J given above and obtain the set of equations

$$\begin{aligned} \cos \hat{\varphi} \cos \hat{\rho} \pm 1 \sin \hat{\varphi} \cos(2\hat{\psi} + \hat{\rho}) \\ = \cos n\beta \cos n\hat{\theta} + \frac{\tan \beta}{\tan \hat{\theta}} \sin n\beta \sin n\hat{\theta} \\ \pm 1 \frac{\sin n\hat{\theta}}{\sin \hat{\theta}} \sin \hat{\gamma} \cos(n+1)\beta \end{aligned}$$

and

$$\begin{aligned} \pm \cos \hat{\varphi} \sin \hat{\rho} + 1 \sin \hat{\varphi} \sin(2\hat{\psi} + \hat{\rho}) \\ = \pm \frac{\beta}{\tan \hat{\theta}} \cos n\beta \sin n\hat{\theta} \mp \sin n\beta \cos n\hat{\theta} \\ + 1 \frac{\sin n\hat{\theta}}{\sin \hat{\theta}} \sin \hat{\gamma} \sin(n+1)\beta \end{aligned}$$

These equations can be solved to obtain

$$\tan \hat{\rho} = \frac{\tan n\beta - \frac{\tan \beta}{\tan \hat{\theta}} \tan n\hat{\theta}}{1 + \frac{\tan \beta}{\tan \hat{\theta}} \tan n\beta \tan n\hat{\theta}},$$

$$2\psi + \rho = (n + 1)\beta$$

and

$$\cos^2 \hat{\varphi} = \frac{1 + \frac{\tan^2 \beta}{\tan^2 \hat{\theta}} \tan^2 n\hat{\theta}}{1 + \tan^2 n\hat{\theta}}$$

Defining

$$\tan n\hat{\theta}' = \frac{\tan \beta}{\tan \hat{\theta}} \tan n\hat{\theta}$$

one obtains the equations (5).

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