

## **Circular dichroism in absorbing mixtures of right- and left-handed cholesterics**

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**Abstract.** A rigorous theory of the optical properties of absorbing mixtures of left and right handed cholesteric liquid crystals has been developed. Detailed expressions and illustrative calculations of the dependence of circular dichroism on pitch and sample thickness are presented. Experimental studies have been carried out on a 1.64:1 (by weight) mixture of cholesteryl myristate in which was dissolved 1.48% (by weight) of linearly dichroic  $\beta$ -carotene. The variation of circular dichroism with pitch exhibits anomalous behaviour, the sign of the dichroism being opposite below and above the nematic temperature. The peak value of the circular dichroism (per unit thickness) *decreases* as the sample thickness increases from 4 to 12.7  $\mu$ . These features are in qualitative agreement with the predictions of the theory.

### **Introduction**

Mixtures of right-handed and left-handed cholesteric liquid crystals adopt the helical structure of a cholesteric whose pitch is sensitive to composition and temperature<sup>1-3</sup>. At a particular composition the pitch approaches infinity and the mixture assumes a nematic structure. For any given composition the rotary power changes sign at a particular temperature—the temperature at which the structure changes handedness. A rigorous theory of the optical properties of such non-absorbing compensated cholesteric was developed recently by Chandrasekhar *et al*<sup>4</sup>. The theoretical dependence of rotatory power on pitch and on sample thickness are in agreement with the experimental variation of the rotatory power with temperature for different sample thicknesses<sup>3,4</sup>.

Recently Sackmann and Voss<sup>5</sup> 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. A theory of the optical properties of such absorbing cholesterics<sup>6</sup> lead to some interesting conclusions regarding absorbing compensated systems. In this paper we present the theory together with the experimental studies carried out on 1.64 : 1 (by weight) mixture of cholesteryl chloride and cholesteryl myristate (CM)

in which was dissolved 1.48% (by weight) of  $\beta$ -carotene. We find that the theory can account for the experimentally observed features.

### Theory

We look upon the cholesteric structure as a helical stack of very thin birefringent layers. Each layer is supposed to have uniaxial symmetry with the principal axes of the successive layers turned through a small angle  $\beta$ . This angle  $\beta$  is taken to be positive for a right handed structure and negative for a left-handed one. We can use the Jones calculus to work out the optical properties of such a medium for light travelling along the helical axis<sup>7</sup>. We are throughout interested in the regime in which the pitch  $P$  of the helix is much greater than the wavelength  $\lambda$  of light.

Let  $2\gamma$  be the phase retardation per layer, *i.e.*,

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

where  $p$  is the layer thickness and  $\Delta\mu$  the layer birefringence. Let  $k_1$  and  $k_2$  be the principal absorption coefficients of the layer. Then the Jones matrix of any layer with reference to its principal axes is

$$G_0 = \begin{bmatrix} e^{-\gamma} & 0 \\ 0 & e^{i\gamma} \end{bmatrix} \times \begin{bmatrix} e^{-k_1 p} & 0 \\ 0 & e^{i k_2 p} \end{bmatrix} = e^{-\alpha} \begin{bmatrix} e^{-i\hat{\gamma}} & 0 \\ 0 & e^{i\hat{\gamma}} \end{bmatrix}$$

where  $\alpha = \frac{k_1 + k_2}{2} p$  and  $\hat{\gamma} = \gamma - i \left( \frac{k_1 - k_2}{2} \right) p = \gamma - i\delta$  (say).

(The convention here is that the phase factor at any point  $z$  is given by  $\exp [-i (2\pi\mu z/\lambda)]$ .)

Let the principal axes of the first layer be inclined at an angle  $\beta$  with respect to this OX and OY. Then the Jones matrix of the  $n^{\text{th}}$  layer with respect to this coordinate system is

$$G_n = S^n G_0 S^{-n}$$

where

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

and  $S^n$  is the inverse of  $S^{-n}$  (*i.e.*,  $S^n S^{-n} = E$  the unit matrix). For  $n$  layers the net Jones matrix is given by

$$\begin{aligned} J_n &= G_n \cdot G_{n-1} \cdot G_{n-2} \dots G_2 \cdot G_1 \\ &= S^n G_0 S^{-n} S^{-(n-1)} G_0 S^{-(n-1)} \dots S G_0 S^{-1} \end{aligned}$$

But  $S^m S^n = S^{m+n}$

Hence

$$J_n = S_n (G_o S^{-1})^n \tag{3}$$

If  $\lambda_1$  and  $\lambda_2$  are the eigenvalues of  $(G_o S^{-1})$  then we can show that (Appendix A)

$$(G_o S^{-1})^n = \frac{\lambda_1^n - \lambda_2^n}{\lambda_1 - \lambda_2} (G_o S^{-1}) - \lambda_1 \lambda_2 \frac{\lambda_1^{n-1} - \lambda_2^{n-1}}{\lambda_1 - \lambda_2} E$$

where  $\lambda_1$  and  $\lambda_2$  are given by

$$\lambda_1 = e^{-\alpha} e^{i\hat{\theta}} \text{ and } \lambda_2 = e^{-\alpha} e^{-i\hat{\theta}}$$

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

Therefore

$$\begin{aligned} (G_o S^{-1})^n &= e^{-n\alpha} \frac{\sin n\hat{\theta}}{\sin \hat{\theta}} (G_o S^{-1}) - e^{-(n+1)\alpha} \frac{\sin (n-1)\hat{\theta}}{\sin \hat{\theta}} E \\ &\approx e^{-n\alpha} \left[ \frac{\sin n\hat{\theta}}{\sin \hat{\theta}} (G_o S^{-1}) - \frac{\sin (n-1)\hat{\theta}}{\sin \hat{\theta}} E \right] \end{aligned} \tag{4}$$

as  $n$  is very large compared to unity.

Using (3) and (4) we can completely work out the net Jones matrix  $J_n$  in terms of  $\beta, \gamma, k_1, k_2$  and  $n$ .

The matrix  $J_n$  can be uniquely resolved into a rotator, a retarder, a circularly dichroic plate and a linearly dichroic plate. The unique matrix resolution is given by (Appendix B)

$$J_n = e^{-\chi} \Psi R \Sigma \Phi K \Sigma \Psi^{-1} \tag{5}$$

where

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

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

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

$$\Phi = \begin{bmatrix} e^{-i\varphi} & 0 \\ 0 & e^{-i\varphi} \end{bmatrix} \quad K = \begin{bmatrix} e^{-k} & 0 \\ 0 & e^k \end{bmatrix}$$

where  $\rho$  is the rotation,  $\sigma$  the circular dichroism,  $2\varphi$  the linear phase retardation,  $2k$  the linear dichroism and  $\chi$  the attenuation coefficient. From (3), (4) and (5) we get

$$\begin{aligned}\rho - i\sigma &= n(\beta - \hat{\theta}') \\ \varphi - ik &= \cos^{-1} \left[ \frac{\sec^2 n\hat{\theta}'}{\sec^2 n\hat{\theta}} \right]^{\frac{1}{2}} \\ \psi &= \frac{1}{2} [(n+1)\beta - \rho] \\ \chi &= n\alpha\end{aligned}\tag{6}$$

with

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

We shall consider two cases of special interest.

(a)  $\beta$  is very large :

In this case

$$\varphi = k = \psi = 0$$

$$\text{and } \hat{\rho} = \rho - i\sigma \approx -\frac{n\hat{\gamma}^2}{2\beta}$$

Hence

$$\rho = -\frac{n(\gamma^2 - \delta^2)}{2\beta}$$

$$\sigma = -\frac{n\gamma\delta}{\beta}$$

Therefore the linear dichroism of the layers not only results in circular dichroism but also makes a contribution to optical rotation which is opposite in sign to that due to linear birefringence. However this contribution is usually very small.

(b)  $\beta$  is very small :

In this case we find

$$J_n \approx e^{-n\alpha} \begin{bmatrix} \cos n\beta & -\sin n\beta \\ \sin n\beta & \cos n\beta \end{bmatrix} \begin{bmatrix} e^{-i\hat{\gamma}n} & 0 \\ 0 & e^{i\hat{\gamma}n} \end{bmatrix}$$

From this we conclude that at any point in the medium we have two linear vibrations polarized along the local principal axes of the layer.

As we move along the axis of the helix in the direction of light propagation we find that these two vibrations rotate with the principal axes. The phase retardations and amplitude reductions undergone by these two vibrations are the same as in an untwisted nematic. This is the property which is made use of in the so-called twisted nematic devices.

However at intermediate values of  $\beta$  we have to use the complete expressions (6). The parameter  $\sigma$  exhibits a marked dependence on pitch and on sample thickness<sup>6</sup>. Since in actual practice  $\sigma$  is not usually measured directly, we shall present the theoretical results in a manner that enables direct comparison with experiment. The procedure generally consists of measuring the transmitted intensities  $I_r$  and  $I_l$  for right and left circular light (of equal intensity) incident on the medium and then evaluating the parameter  $D_0$  given by :

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

To calculate  $D_0$  theoretically we use the following relations (which describe the nature of the emergent light when a right or a left circularly polarized beam is incident on the specimen) :

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

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

Then

$$I_r = |A_1|^2 + |A_2|^2$$

$$I_l = |B_1|^2 + |B_2|^2$$

In figure 1 we give the theoretical variation of the dichroic power  $D$  (*i.e.*,  $D_0/t$ ,  $t$  being the sample thickness) with inverse pitch/temperature. The theoretical values are calculated for a 1.75:1 CM mixture of  $6\mu$  thickness containing dye molecules. The dependence of pitch on temperature was taken from Sackman *et al*<sup>2</sup>. The layer birefringence  $\Delta\mu$  at 20°C and 50°C were estimated by fitting the observed rotatory power<sup>3</sup> with the de Vries equation<sup>7</sup>.  $\Delta\mu$  at intermediate temperatures were obtained by linear interpolation. This is a valid procedure as at these temperatures the de Vries equation holds good. The linear dichroism was taken to be  $0.10 \times 10^{-3}$  at  $\beta = 3 \times 10^{-3}$  on the lower temperature side of the nematic point. Further we assumed that the layer birefringence and the layer dichroism decrease at the same rate with increase of temperature. We find that  $D$  exhibits anomalous behaviour, the sign of the dichroism being opposite above and below the nematic point. The curve exhibits

some weak oscillations as the pitch/temperature is varied. The theory also leads to an interesting dependence of the dichroic power  $D$  on sample thickness. In table 1 we have given the negative peak value of  $D$  for various sample thicknesses.

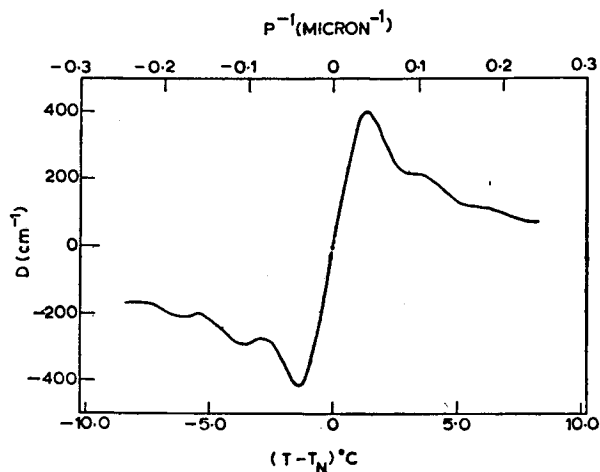


Figure 1 Theoretical dependence of dichroic power on temperature and inverse pitch

It will be seen that as the sample thickness is increased,  $D$  increases initially, reaches a maximum and decreases thereafter. In this respect the medium behaves quite differently from normal optically active substances in which the dichroic power is independent of thickness.

#### Measurements on cholesteryl chloride and cholesteryl myristate mixture

We have measured the dichroic power of a CM mixture (of composition 1.64:1 by weight) as a function of temperature for samples of various thicknesses. The CM mixture was mixed with 1.48% by weight of  $\beta$ -carotene and the combination was heated to 64°C at which temperature a homogeneous melt was formed. As the melt was cooled it adopted a cholesteric structure. The pitch of the cholesteric structure continuously increases with decrease of temperature reaching an infinite value around 51°C. When the system is cooled further it changes its handedness and the pitch gradually decreases. Above 51°C the specimen is right-handed and below this temperature it is left-handed. The dye  $\beta$ -carotene has an absorption band around 4800 Å with strong linear dichroism<sup>8</sup> ( $k_{\parallel} \approx 2.5 k_{\perp}$ ). 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 using Dupont mylar spacers of thickness 0.50 and 0.25 mils respectively. Mica spacers were used for samples of thickness 4, 8 and 9.5  $\mu$  (the uniformity in the thickness of the spacer was tested

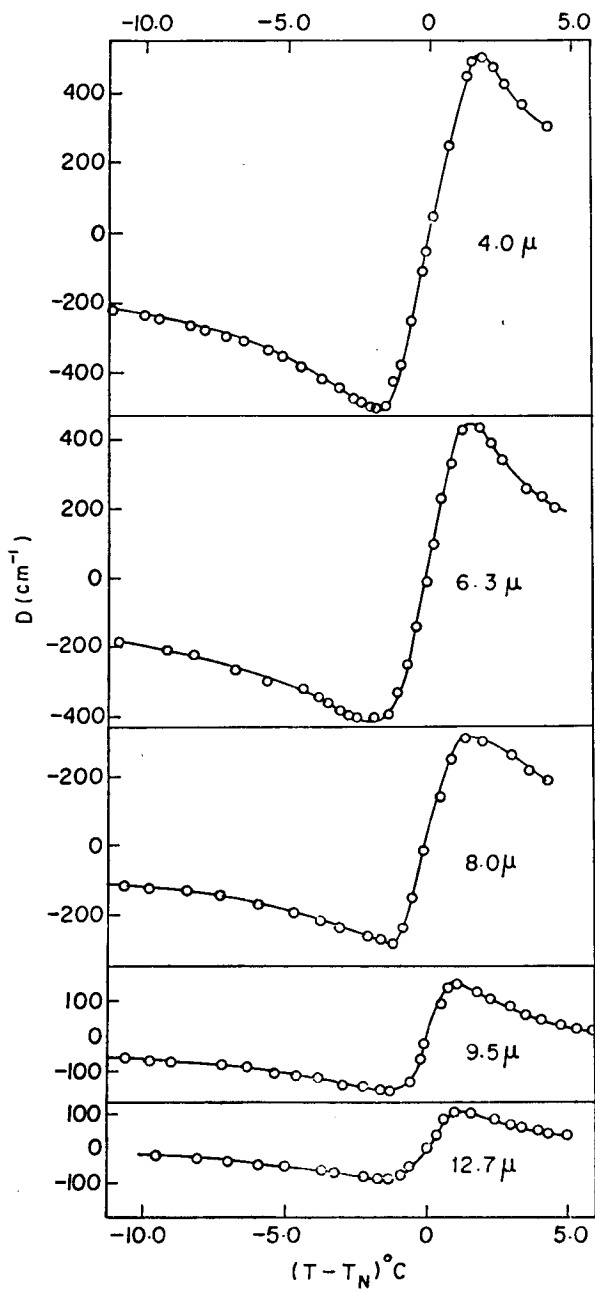
Table 1

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

with a dial gauge, model M1/100B Carl Zeiss Zena). The sample temperature was controlled by inserting the specimen in a suitably constructed heater. The temperature could be read upto  $\pm 0.1^\circ \text{C}$  on a previously calibrated thermocouple.

A tungsten filament lamp run on a stabilized power supply was used as the source. The light beam was mechanically chopped at 321 c/s. Using the Mekee Pederson reflection grating monochromater (model MP 108) experiments were carried out at 5000 Å. The intensity was sensed by a photomultiplier (model M10 FQS 29 Carl Zeiss Zena) and measured by means of a lock-in amplifier. The error in the intensity measurement was less than 2%.

In figure 2 is shown the experimental dependence of the dichroic power  $D$  on temperature for various sample thicknesses. We observe, firstly, that for any given thickness of the sample the temperature variation of power  $D$  follows the theoretically predicted behaviour (figure 1). The weak oscillations on the theoretical curve were not detected, presumably because of slight variations in the sample thickness. Secondly, we note that the peak dichroic power (per unit sample thickness) decreases as the sample thickness is increased from 4 to 12.7  $\mu$ , which again is in qualitative agreement with the theory.



**Figure 2** Experimental values of dichroic power versus temperature for different thicknesses of the sample in a 1.64 : 1 by weight mixture of cholesteryl chloride and cholesteryl myristate containing 1.48% by weight of  $\beta$ -carotene.



### Acknowledgements

Our thanks are due to Professor S Chandrasekhar and Professor S Ramaseshan for their helpful suggestions and support throughout this work.

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### Appendix A

Let

$$M = (G_0 S^{-1}) = e^{-\alpha} \begin{bmatrix} e^{-i\hat{\gamma}} \cos \beta & e^{-i\hat{\gamma}} \sin \beta \\ -e^{i\hat{\gamma}} \sin \beta & e^{i\hat{\gamma}} \cos \beta \end{bmatrix} = \begin{bmatrix} a_1 & a_2 \\ a_3 & a_4 \end{bmatrix} \text{ say}$$

Then the eigen values of  $M$  are given by

$$M - \lambda E = 0$$

Hence

$$\lambda_1, \lambda_2 = \frac{a_1 + a_4}{2} \pm \left[ \left( \frac{a_1 + a_4}{2} \right)^2 - \Delta \right]^{\frac{1}{2}}$$

with  $\Delta = a_1 a_4 - a_2 a_3$ .

If we select a matrix  $T$  such that

$$T = \begin{bmatrix} -a_2 & -a_2 \\ a_1 - \lambda_1 & a_1 - \lambda_2 \end{bmatrix}$$

then

$$T^{-1} M T = \begin{bmatrix} \lambda_1 & 0 \\ 0 & \lambda_2 \end{bmatrix}$$

Hence

$$M = T \lambda T^{-1}$$

$$M^n = T \lambda^n T^{-1}$$

which can be simplified to give

$$M^n = \frac{\lambda_1^n - \lambda_2^n}{\lambda_1 - \lambda_2} M - \lambda_1 \lambda_2 \frac{\lambda_1^{n-1} - \lambda_2^{n-1}}{\lambda_1 - \lambda_2} E$$

$$\text{Also } a_1 + a_4 = 2e^{-\alpha} \cos \beta \cos \hat{\gamma}; \Delta = e^{-2\alpha}$$

$$\text{Hence } \lambda_1 = e^{-\alpha} e^{i\hat{\theta}}; \lambda_2 = e^{-\alpha} e^{-i\hat{\theta}}; \hat{\theta} = \cos^{-1} (\cos \beta \cos \hat{\gamma})$$

### Appendix B

Equation (5) can be rewritten as

$$J_n = e^{-\lambda} \begin{bmatrix} \cos \hat{\psi} & -\sin \hat{\psi} \\ \sin \hat{\psi} & \cos \hat{\psi} \end{bmatrix} \begin{bmatrix} \cos \hat{\rho} & -\sin \hat{\rho} \\ \sin \hat{\rho} & \cos \hat{\rho} \end{bmatrix} \begin{bmatrix} e^{-i\hat{\varphi}} & 0 \\ 0 & e^{i\hat{\varphi}} \end{bmatrix} \\ \times \begin{bmatrix} \cos \hat{\psi} & \sin \hat{\psi} \\ -\sin \hat{\psi} & \cos \hat{\psi} \end{bmatrix}$$

$$\text{where } \hat{\psi} = \rho + i\sigma/2$$

$$\hat{\rho} = \rho - i\sigma$$

$$\hat{\varphi} = \varphi - ik$$

Using (3), (4) and the above expression we get

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

These equations can be solved to get

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

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

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

which can be simplified to yield equations (6).