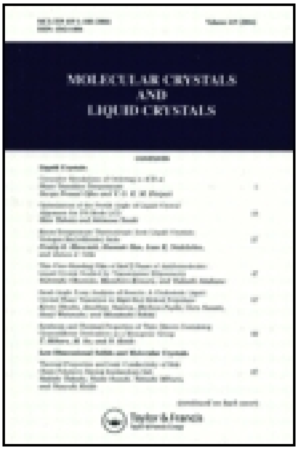

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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Version of record first published: 21 Mar 2007.

To cite this article: J. Shashidhara Prasad & M. S. Madhava (1973): Rotatory Dispersion of Cholesteric Liquid Crystals, Molecular Crystals and Liquid Crystals, 22:1-2, 165-174

To link to this article: http://dx.doi.org/10.1080/15421407308083341

Molecular Crystals and Liquid Crystals. 1973. Vol. 22, pp. 165–174

Printed in Great Britain

Rotatory Dispersion of Cholesteric Liquid Crystals†

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Received September 25, 1972; *in revised form November* 14, 1972

Abstract—Measurements of rotatory dispersion and circular dichroism of (i) a mixture of nematic *p*-methoxybenzylidene-*p'*-butylaniline (MBBA) and spectratherm (ii) a mixture of cholesteryl benzoate and nematic *p*-azoxyphenetole (PAP) and (iii) cholesteryl cinnamate for different thicknesses have been made. The experimental data on cholesteryl cinnamate are in qualitative agreement with the theoretical predictions of Dreher *et al.*,⁽¹⁾ Chandrasekhar and Shashidhara Prasad⁽²⁾ and Aihara and Inaba.⁽³⁾ Also the results of the mixtures are in qualitative agreement with the theoretical predictions, that for thick specimens the circular dichroism plotted as a function of wavelength should exhibit a flat top maximum.

An attempt has been made to fit the rotatory dispersion and circular dichroism data of cholesteryl cinnamate. It is found that the same constants can be used to explain our data as well as that due to Mathieu,⁽⁴⁾ approximately well.

1. Introduction

The optical properties such as rotatory power, reflection, circular dichroism, etc., of cholesteric liquid crystals have been theoretically discussed by a number of workers, using two different models: one based on Oseen's dielectric continuum model; and the other by using the difference equations for wave propagation in a periodic structure (as in Darwin's dynamical theory of X-ray diffraction). de Vries⁽⁵⁾ and Aihara and Inaba⁽³⁾ have used the first model to explain the optical properties at normal incidence. Taupin⁽⁶⁾, also Berreman and Scheffer⁽⁷⁾ have treated the case of oblique incidence and have calculated by numerical method the reflected and transmitted intensities. Dreher, Meier and Saupe⁽¹⁾ have solved the case

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† Presented at the Fourth International Liquid Crystal Conference, Kent State University, August 21–25, 1972.

of reflection by cholesteric liquid crystals for arbitrary angles of incidence. Chandrasekhar and Srinivasa Rao(8) and Chandrasekhar and Shashidhara Prasad(2) have discussed the optical properties for normal incidence using the second model.†

The various theoretical discussions give the following important theoretical predictions for the case of normal incidence. The theoretical results for a specimen of infinite thickness predicts a flat-topped maximum for reflection with no possibility of rotatory power measurement inside the region of reflection. But for a film of finite thickness there exists secondary maxima on either side of the principal maximum in the region of selective reflection; the wavelength separations from the central peak to the secondary peaks become larger when the thickness is reduced.

The circular dichroism phenomenon is due to the difference in the reflection coefficients between the right and left circularly polarized light waves instead of the difference in the absorption coefficients as in the case of ordinary materials exhibiting optical activity. As a consequence, the characteristics of circular dichroism are closely related to the selective reflections and show almost similar results except that the maximum value and the half width of the central maximum are slightly smaller. As regards rotatory dispersion the theory shows that the maximum value of rotatory power varies much with thickness of the specimen while the curve is almost independent of thickness, far away, on either side, of the region of selective reflection. In the light of these theoretical predictions some experiments were conducted which are discussed below.

2. Experimental

Circular dichroism and anomalous rotatory dispersion curves right through the reflection band have been reported by Mathieu

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† It has been shown in the paper " On the theory of propogation of light by cholesteric liquid crystals " by Rajaram Nityananda (presented at the IVth International Liquid Crystal Conference) that both the approaches are fully equivalent when the approximations made earlier by de Vries and Chandrasekhar and Shashidhara Prasad are removed. Also, the conflicting result that the rotatory power changes sign once according to de Vries and twice according to Chandrasekhar and Shashidhara Prasad has been shown to be nonexisting by the exact solution.

for cholesteryl cinnamate and by Fergason(9) for a mixture of cholesteryl benzoate, cholesteryl acetate and cholesteryl palmitate. The reflection spectra for a film of finite thickness has been reported by Dreher, Meier and Saupe for a mixture of cholesteryl nonanoate, cholestryl chloride and cholesteryl acetate and Chandrasekhar and Shashidhara Prasad have carried out measurements on circular dichroism and rotatory power for a few compounds.

Presently we have carried out some detailed measurements of rotatory dispersion and circular dichroism of (i) a mixture of nematic *p*-methoxybenzylidene-*p*′-butylaniline (MBBA) and spectratherm (ii) a mixture of cholesteryl benzoate and nematic *p*-azoxyphenetole (PAP) and (iii) cholesteryl cinnamate for different thicknesses. The measurements were made on " plane texture " preparations between microscope slides. No spacers were used for thin specimens. Spacers were used in the case of thick specimens ($25\,\mu$). The specimens were maintained in the liquid crystalline range by placing the microscope slides at the centre of an electric oven with a stabilized power supply. The temperature was determined by using a calibrated copper-constantan thermo-couple. The polarimetric arrangement consisted of a Perkin–Elmer–Hitachi (model 139) monochromator, linear polarizer and analyser and sensitive photo transistor detector. Ordinary polarizers (H-polaroids) were used as analyser and polarizer in the visible region of the spectrum and special infrared polaroids for the range 6500–10000 Å. The relative rotations were obtained by taking the extinction readings with and without the specimen and the rotation could be determined to $\pm 4'$ of arc from 4000–10000 Å. Very small areas of the film about $2 \times 2\ \mathrm{mm}^2$ were used for the experiment. The optical homogeneity of the film areas were checked by the uniformity and perfection of the extinction for wavelengths outside the region of reflection. The film thickness for cholesteryl cinnamate was measured by forming interference fringes between the glass surfaces in the air gaps. Present rotatory power data for cholesteryl cinnamate outside the region of reflection is in good agreement with the previous available data.

The circular dichroism was obtained by measuring the intensity of the transmitted light for right and left circular polarization and applying the formula

$$D = \frac{I_l - I_r}{I_l + I_r}$$

This procedure eliminates errors arising from reflections from glass surfaces, spectral variation of the source and of the sensitivity of the detector, etc. However there is certain limitation due to the fact that the quarter wave plate has to be achromatic for the measurement to be quantitatively precise. Since D involves the difference of two intensity measurements, which is quite small for the subsidiary maxima, the error in the heights of the maxima may be expected to be appreciable. No corrections have been made for this.

The circular dichroism and rotation dispersion measurements of (i) a mixture of 0.0111 gm of MBBA and 0.0075 gm of spectratherm at room temperature (24 °C) and (ii) a mixture of 0.0062 gm of cholesteryl benzoate and 0.0051 gm of PAP at 131 °C are given in Figs. 1 and 2. The specimens were thick enough in both the

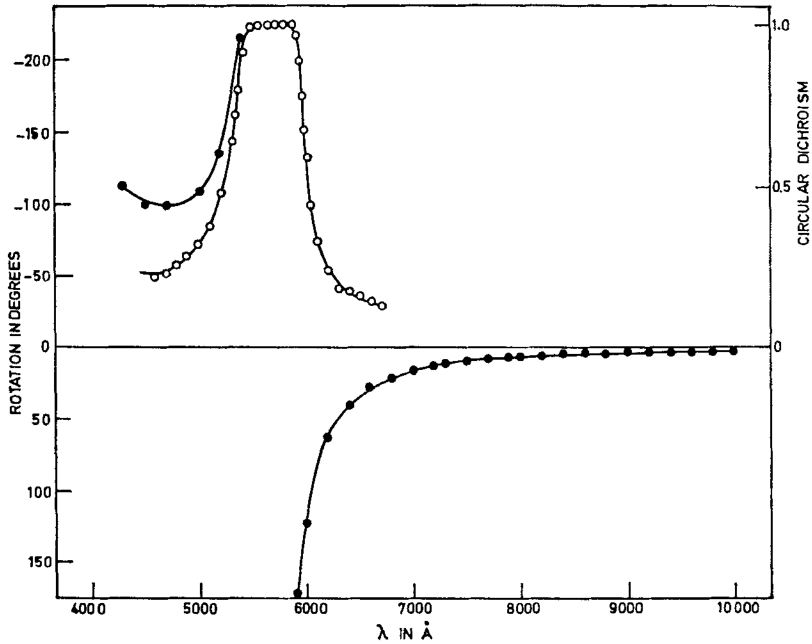

Figure 1. Rotation dispersion and circular dichroism of a thick specimen of a mixture of nematic p-methoxybenzylidene-p'-butylaniline (MBBA) and spectratherm (thickness = 25μ).

● denotes rotation, ○ circular dichroism.

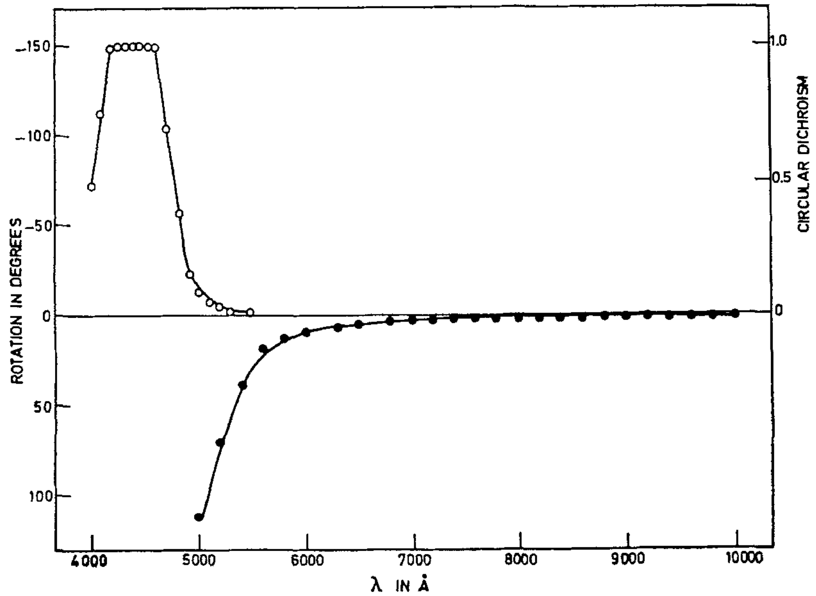

Figure 2. Rotation dispersion and circular dichroism of a thick specimen of a *mixture of cholesteryl benzoate and nematic p-azoxyphenetole* (PAP) thickness = 25μ).

● denotes rotation, ○ circular dichroism.

cases to give a flat-topped maximum with no secondary maxima as given by the theory for a film of infinite thickness. The rotation dispersion curve is anomalous round the region of reflection with sharp finite peaks at the edges of the reflection band. It has not been possible to obtain any points inside the region of reflection band because one of the circularly polarized components was totally reflected. The rotation curve beyond the region of reflection on the long wavelength side decreases asymptotically with the wavelength axis.

Figure 3 shows the reduced rotatory dispersion measurements of cholesteryl cinnamate for thicknesses 3 μ, 2 μ and 1 μ at 150 °C. The curve for 1 μ thickness is due to Mathieu.(4) The rotatory power (in degrees per millimeter) is plotted versus $\lambda - \lambda_0$. The rotatory dispersion curves are in very good agreement with that predicted for different thicknesses by Chandrasekhar and Shashidhara Prasad and Aihara and Inaba.

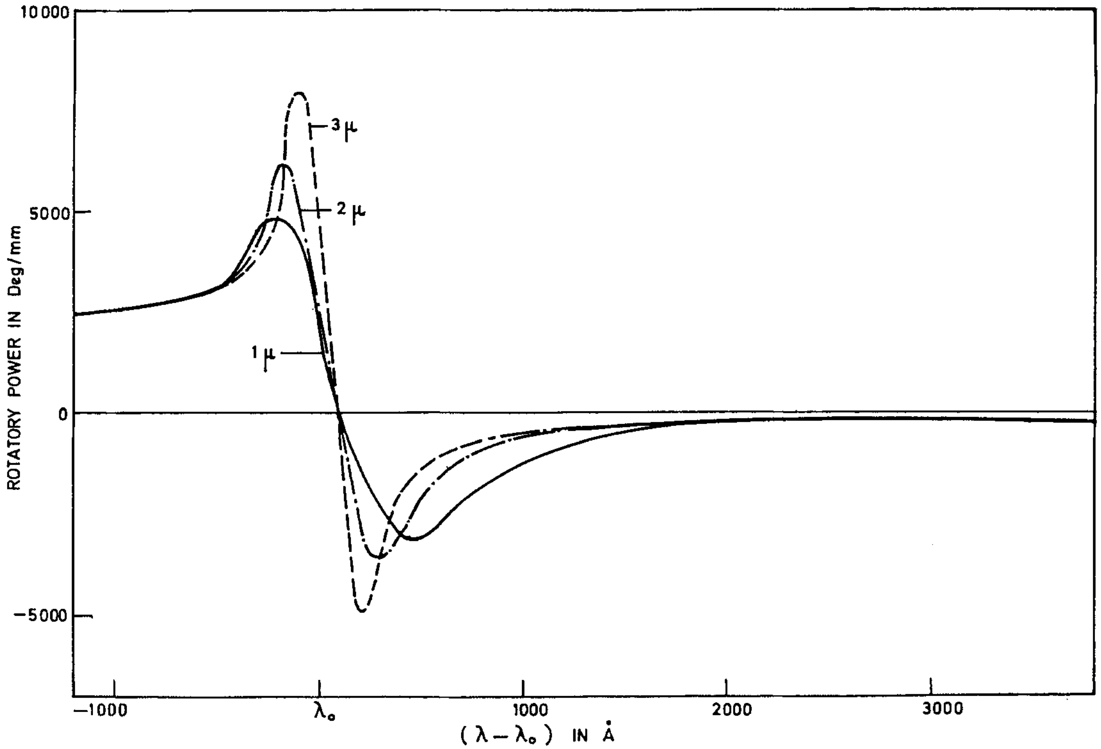

Figure 3. Reduced rotatory dispersion of cholesteryl cinnamate for different thicknesses (3μ, 2μ and 1μ). The data for 1μ thickness is due to Mathieu.(4)

3. Theoretical Fit for Cholesteryl Cinnamate

We have made an attempt to fit the rotatory dispersion and circular dichroism data of our measurements on 3 μ thick specimen and that of Mathieu for 1 μ thickness.

We have used the expression given by S. Chandrasekhar and J. Shashidhara Prasad for reflection

$$R = \frac{Q^2}{\epsilon^2 + \xi^2 \coth^2 m\xi}$$

where

$$\xi \simeq \pm (Q^2 - \epsilon^2)^{1/2}$$

$$Q^2 = Q_0^2 \left(\frac{\sin \epsilon}{\epsilon}\right)^2$$

$$\epsilon = -2\pi(\lambda - \lambda_0)/\lambda$$

m = number of planes, is given by thickness/pitch as used in the deriving the theory. The width of total reflection is given by $\Delta\lambda = 2P\Delta n/\pi = Q_0 \lambda_0/\pi$ where $Q_0 = 2\Delta n/n$. Also $n_d P = \lambda_0$, where n_d = refractive index for right circularly polarized light, λ_0, the wavelength of maximum reflection and P = pitch. The relation between the circular dichroism and reflection being $D = R/2 - R$. The expression for rotatory power is

$$\rho = \frac{-\pi(\Delta n)^2 P}{4\lambda^2} + \frac{\psi - \epsilon}{2P} \text{ radians/centimeter}$$

where Δn = layer birefringence

and $$\tan m\psi = \frac{\epsilon}{\xi \coth m\xi}.$$

Figures 4 and 5 give the theoretical fit for the case of cholesteryl cinnamate which has the wavelength of maximum reflection λ_0 = 5200 Å and $\Delta\lambda$ the width of total reflection = 280 Å. n_d is assumed to be 1.5, the order of refractive index of glass, which in turn gives the value of Δn. Δn is assumed to vary linearly from 0.15 at 4000 Å to 0.07 at 10000 Å.

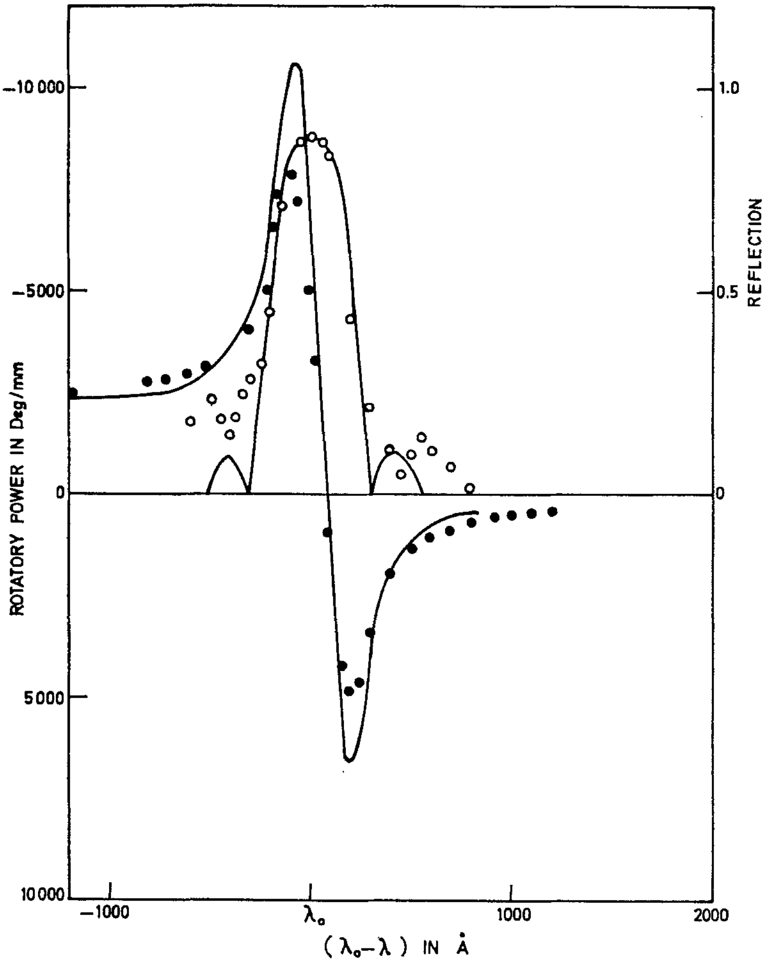

Figure 4. Computed and experimental data of rotatory dispersion and reflection for 3μ thick specimen of cholesteryl cinnamate.

——— theoretical, ● experimental points of rotatory power, ○ experimental points of reflection.

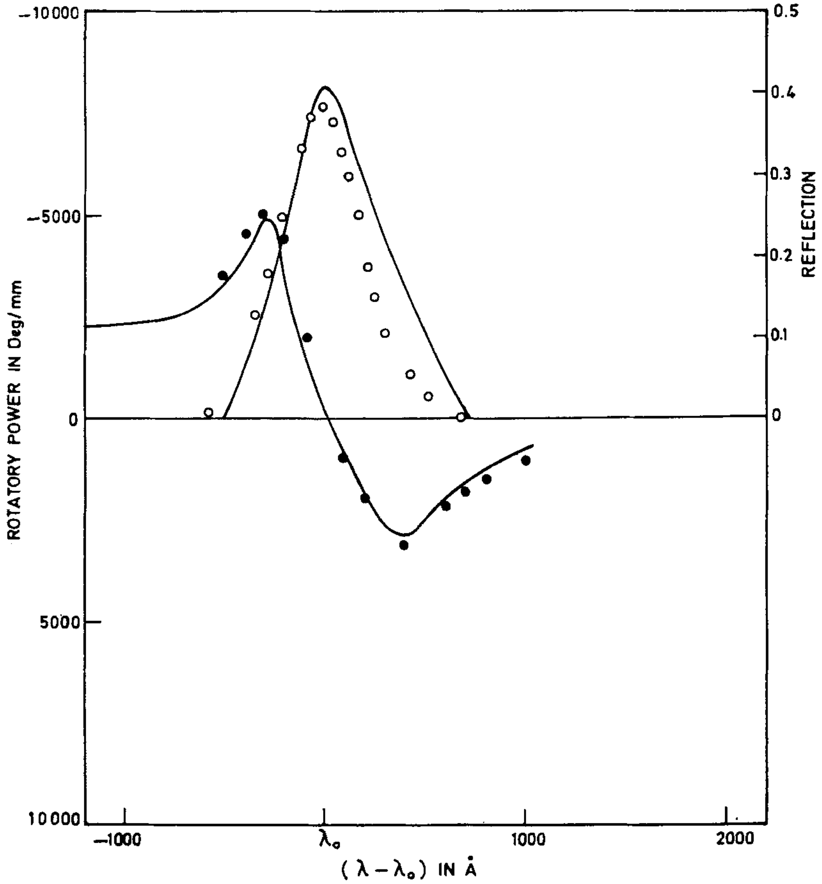

Figure 5. Computed and experimental data of rotatory dispersion and reflection for 1μ thick specimen of cholesteryl cinnamate.

——— theoretical, ● experimental points of rotatory power, ○ experimental points of reflection.

Slight deviations of the experimental data from the theoretical data, in the maximum values of the rotatory power and reflection bands and also in the position of the secondary maxima for a specimen of thickness 3 μ are probably due to the fact that the specimen was not perfectly homogeneous and uniform, as it was prepared in between ordinary microscope slides. The curves were also plotted against $\lambda - \lambda_0$ in order to elucidate the uniqueness of the theory rather than to give a perfect fit.

Acknowledgements

The authors thank the Head of the Department of Physics, University of Mysore, Mysore, for encouragement.

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