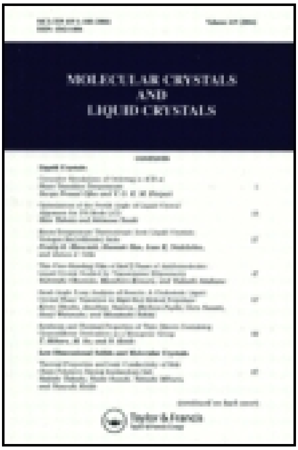

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Angular Dependence of Selective Reflection from the Blue Phase

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We have measured the angular dependence of the selective reflection in the blue phases of cholesteryl oleyl carbonate and cholesteryl myristate. We have also measured the wavelength dependence of the index of refraction in the blue and isotropic phases and the intrinsic optical absorption in the isotropic phase of both materials. The angular dependence is explained by the equation of Ferguson, which also describes the angular dependence of the selective reflection in the cholesteric phase. Using the absorption and refractive index data we are able to explain the visual appearance of the blue phase.

1 INTRODUCTION

In certain cholesteric liquid crystals, over a narrow temperature region between the isotropic and cholesteric phase, there exists a distinct, stable intermediate phase commonly called the blue phase.[1,2] Optical studies by Bergmann and Stegemeyer[3] have shown that the blue phase exhibits a selective reflection peak and rotatory power anomaly analogous to that found in the cholesteric phase.[4] Expanding on this analogy, one might expect to find in the blue phase an angular dependence of the selective reflection wavelength λ similar to that given by Ferguson[4] for cholesterics:

$$\lambda = 2dn \cos \tfrac{1}{2}\left\{\sin^{-1}\left(\frac{\sin \theta_I}{n}\right) + \sin^{-1}\left(\frac{\sin \theta_R}{n}\right)\right\} \qquad (1)$$

where θ_I and θ_R are respectively the incident and reflected angles of the light relative to the sample normal, d is half the pitch P of the cholesteric helix, and n is an average index of refraction. However Bergmann and Stegemeyer,[3] who (like Ferguson[4]) inferred the presence of the selective reflection from light transmitted through the blue phase, did not (unlike Ferguson) observe any angular dependence when their sample was rotated.[3] Later, by observing reflected instead of transmitted light, Bergmann and Stegemeyer[5] and Johnson, *et al.*[6] found that Eq. (1) was satisfied for at least one angle other than $\theta_I = \theta_R = 0°$.

Recently it has been shown from both reflection[6] and transmission[7] data that the words "blue phase" may be misleading. Wavelengths other than blue may selectively reflect, depending on the spacing of the Bragg planes of either a simple cubic or body centered cubic structure, the latter recently proposed by Hornreich and Shtrikman.[8] Whatever the structure, it is implicit in these models that Eq. (1) be satisfied. To date however, no systematic verification of the validity of Eq. (1) has been reported.

We have measured the selective reflection wavelength $\lambda(\theta)$ directly over an angular range of 100° in the blue phase of two different cholesteric liquid crystals. We have also measured separately the index of refraction and optical absorption as a function of wavelength. We find our selective reflection data is well described by Eq. (1), from which we then extract values of the pitch and refractive index. Using these and our other results, we then explain why the blue phase appears blue.

II EXPERIMENT

Cholesteryl oleyl carbonate (COC) and cholesteryl myristate (CM) were obtained from Aldrich Chemical Co. The COC was first passed through a 1000 Å filter and then degassed at 10^{-5} Torr. The CM was purified by three recrystallizations from acetone, then passed through a 2000 Å filter. Isotropic to blue phase transition temperatures were 35.53 ± .07° C for COC and 84.67 ± .07°C for CM which indicate purity was comparable with that reported elsewhere.[9,10]

The sample cells used in the angular dependence measurements consisted of a 6 mm thick ring shaped brass spacer epoxied between two glass cover slips. Once filled with liquid crystal, the cell was then sealed with a teflon plug. For the optical absorption measurements, the liquid crystal was placed between two quartz cover slips approximately 25 μ apart.

Temperature control was effected by placing the sample in a double oven, the inner stage of which was controlled to ± .01° C by a Neslab Tx–3 water bath. The outer stage consisted of a metal cylindrical enclosure resistively heated and maintained within a degree of the inner stage to minimize temperature gradients. The oven was mounted at the ends of two lens benches arranged in the shape of a "V". One arm contained a tungsten lamp and a Jarrel Ash 82–410 monochrometer; the other movable arm contained a photomultiplier detector. The output of the detector was fed to a strip chart recorder which in turn displayed the reflected intensity as a function of monochrometer wavelength. Transmission was measured by replacing the tungsten source with a deuterium lamp and swinging the movable optical bench to a position opposite the monochrometer.

For the selective reflection experiment, θ_I was fixed at 50° and θ_R could be varied (to within ± 0.5°) from −40° to +60°. $\theta_R = 50°$ was excluded due to the presence of specular reflection from the cell face. The available wavelength range was from 300 nm to 650 nm (175 nm to 360 nm for transmission) and selective reflection peaks could be located to within ± 2 nm.

In order to measure the refractive indices, an equilateral aluminum prism was constructed with a hole parallel to one edge and the base. The hole was then filled with sample material and the refractive indices were found using the minimum angle of deviation method and known wavelengths from a mercury arc lamp source.

Temperature control for the index of refraction measurements was accomplished with a hot stage mounted between the prism and the spectrometer. Runs were made in the blue phase and in the isotropic phase, which could be visually distinguished from each other.

III RESULTS

We found the blue phase of COC to be stable over a temperature range of $33.8 \le T \le 35.5$°C, while the corresponding range in CM was $83.9 \le T \le 84.6$°C. In CM we observed two blue phases (BPI and BPII) as previously reported by Bergmann and Stegemeyer.[11] In COC however, only one blue phase was observed, possibly because the selective reflection of the other blue phase was below our accessible wavelength region. This point needs further investigation.

We noted that at the high temperature side of the blue phase region, the reflected peaks became very narrow, with a full width at half maximum as small as 5 nm, while on the lower temperature side they became as broad as 60 nm. In both COC and CM, on cooling, the selective reflection became red shifted.

Figure 1 shows the selective reflection peak λ_R as a function of angle. In COC, a higher temperature in the blue phase was chosen ($T = 35.30 \pm .01$°C) in order to obtain narrow peaks and smaller wavelength uncertainty. In CM, the lower temperature blue phase (BPI) was chosen ($T = 84.40 \pm .01$°C) because of its stability over a wider temperature range.

By varying n and $2dn$ we were able to obtain a least squares fit of our data to Eq. (1), with fitting parameters given by

	n	$2dn$(nm)
COC	1.53	402
CM	1.48	396

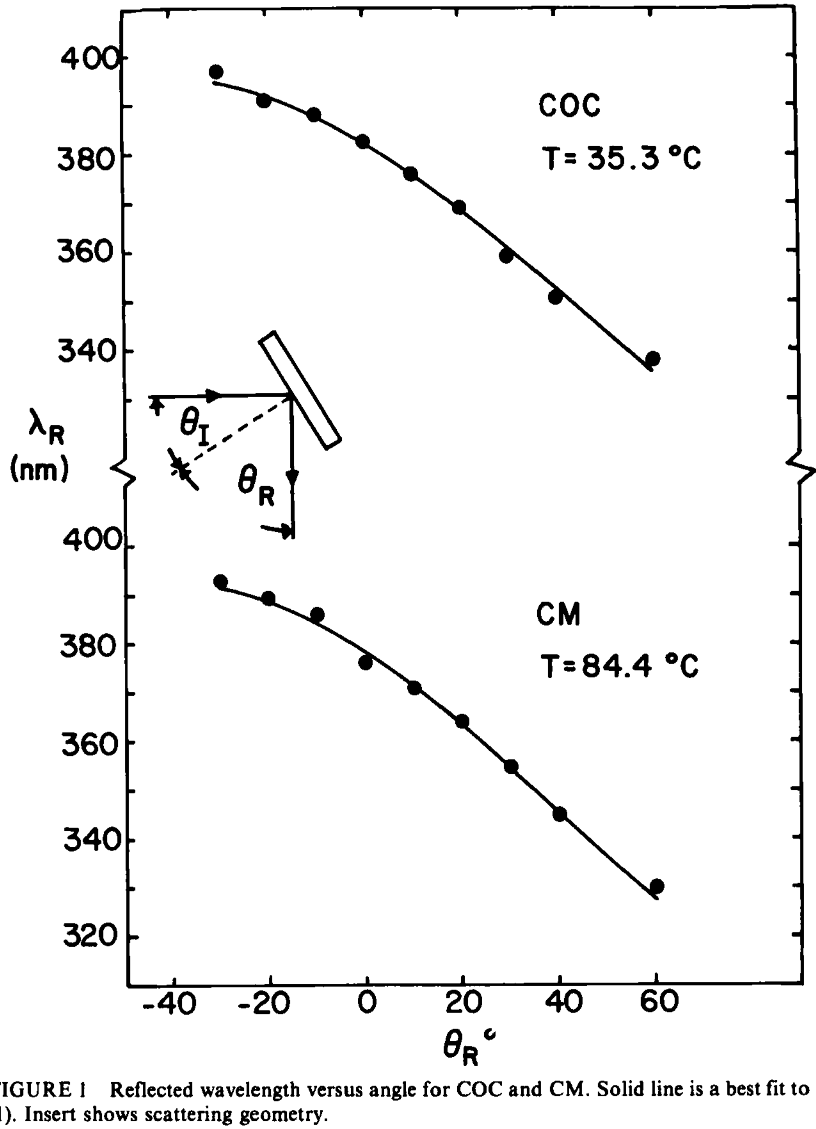

FIGURE 1 Reflected wavelength versus angle for COC and CM. Solid line is a best fit to Eq. (1). Insert shows scattering geometry.

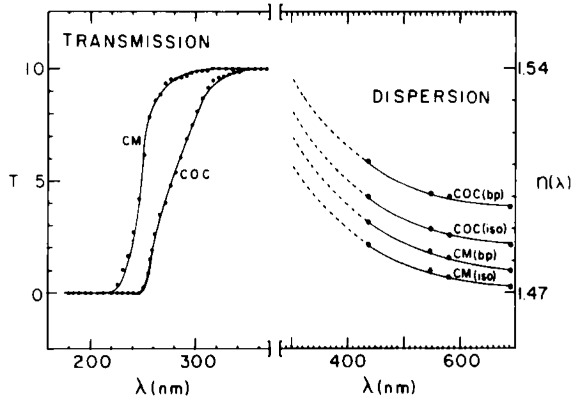

FIGURE 2 Optical transmission T vs. wavelength λ in the isotropic phase and refractive index n in both the isotropic and blue phase. The solid line in the transmission data is a guide to the eye. Solid lines in the dispersion data are a fit to the arbitrary function $n = a\lambda^{1/4} + b\lambda^{-1/4}$. The dashed lines show the extrapolation to lower wavelength.

This fit corresponds to the solid lines in Figure 1.

The index of refraction in Figure 2 was found in both the isotropic and blue phases using four of the most intense mercury lines. These data were then fitted to the arbitrary function $n(\lambda) = a\lambda^{1/4} + b\lambda^{-1/4}$ with a and b adjustable; the solid line is the resulting fitted dispersion curve. We then extrapolated this curve (dashed line) down to shorter wavelengths to compare this index to that found from our selective reflection data. Choosing the average wavelength over the selective reflection wavelength region to be 360 nm, we obtained for COC and CM in the blue phase, refractive indices of 1.52 and 1.50 respectively.

Figure 2 shows the optical transmission in the isotropic phase of both CM and COC. Below 247 nm for COC and 221 nm for CM no light was transmitted, indicating strong intrinsic absorption below these wavelengths. Note that any higher order Bragg lines would appear in this absorption region.

IV DISCUSSION

As the fitted curve in Figure 1 indicates, the angular dependence of selective reflections in the blue phase is well described by the Ferguson equation Eq. (1). Further evidence of the validity of Eq. (1) lies in the comparison of the fitted indices of refraction to those extrapolated from the actual measurement in Figure 2. The agreement is within 1%.

In the light of recent experiments[6,7] showing that the blue phase exhibits a number of Bragg reflections compatible with either simple cubic or body centered cubic structure, Eq. (1) must be written in the form

$$\lambda_{hkl} = \frac{2d_o n \cos \frac{1}{2}\left[\sin^{-1}\left(\frac{\sin \theta_I}{n}\right) + \sin^{-1}\left(\frac{\sin \theta_R}{n}\right)\right]}{\sqrt{h^2 + k^2 + l^2}} \tag{2}$$

Here d_o is now the edge length of the cubic unit cell and h, k, l are the Miller indices corresponding to the structure and the particular Bragg line.

We can now explain the visual appearance of the blue phase. At high temperature, above the isotropic-blue phase transition, the isotropic phase appears clear in transmission (since the only absorption is in the UV) and also on reflection (since there are no selective reflections). As the temperature is lowered, the isotropic-blue phase transition occurs, and a set of Bragg peaks occur. The longest wavelength peak, which occurs on back reflection ($\theta_I = \theta_R = 0$ in Eq. 2), is still below the visible threshold. The liquid crystal thus appears visually clear, and this transition is easily missed by microscopists. Lowering the temperature further, the peak moves to longer wavelengths and the blue phase begins to appear visually violet on back reflection. At other viewing angles (see Eq. 2) the peak is still below the visual threshold. In transmission, the liquid crystal begins to appear faintly yellow since the violet has been selectively reflected.

Note that the blue appearance of the blue phase is a coincidence of the small unit cell size. For longer pitch cholesterics several Bragg peaks may be in the visible region and the blue phase is not blue.[6]

V Acknowledgement

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