Evidence for Polymorphism within the So-called "Blue Phase" of Cholesteric Esters
IV. Temperature and Angular Dependence of Selective Reflection *

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Dedicated to Prof. Dr. E Kuss on the occasion of his 65th birthday

From selective reflection (SR) measurements as a function of temperature it has been shown that cholesteryl myristate exhibits two "blue phases" (BP) between the isotropic and the cholesteric state. The SR of the two BP shows the same angular dependence as found in the corresponding cholesteric state. From our results a model of the BP is proposed with the molecular axes inclined to the helix axis by a critical angle of 54.74° explaining the absence of birefringence as well as the cholesteric-like optical properties.

Recently, it has been shown by optical and calorimetric measurements that the phenomenon of the so-called "blue phase" (BP) of various cholesteryl esters is caused by one or even two thermodynamically stable phases just below the clearing points [1, 2].

The characteristic colours of BP leading to their trivial name [3] originate from selective reflection (SR) of circularly polarized light accompanied by an anomalous dispersion of optical rotatory power (ORD) [4] with the same sign as that in the cholesteric state: left handed for cholesteryl myristate (CM) and nonanoate (CN), right handed for cholesteryl chloride [5]. This optical behaviour indicates a helical arrangement of molecules within the BP similar to the normal cholesteric phase, but on the other hand no birefringence has been detected [4, 6]. An obvious explanation of the optical isotropy due to a globular structure of randomly oriented helical axes seems to be not compatible with the small half-width of the SR-bands of about 10 nm found in all BP [2].

In a former paper Goldberg and Schnur [7] mentioned the colour of light reflection in BP not to be dependent on the observation angle in contrast to the behaviour of the cholesteric phase [8]. As this observation is not consistent with our SR results the angular dependence of BP emission has been reinvestigated. By a simple experiment it could be shown easily that the SR of BP actually does depend on the observation angle: Cooling down CN in a thermostatted capillary tube close below the clearing point (91.5 °C) a bright green colour appears if the sampel is illuminated with white light in the viewing direction whereas the colour changes to blue with an angle of 90° between the direction of incidence and observation.

Quantitative information about the angle dependence has been obtained by measuring the spectral distribution of SR by means of a fluorescence spectrophotometer MPF 4 (Perkin-Elmer). Synchronous scanning of the excitation and emission monochromator enables SR measurements for oblique light incidence. Because of the beam geometry given by the construction of the MPF 4 photometer the sum of the angles of incidence, φ_{I}, and observation, φ_{S}, always is 90°. φ_{I}, however, could be varied indepently. For experimental reasons we chose fixed angles $\varphi_{\mathrm{I}} = 69°$ and $\varphi_{\mathrm{S}} = 21°$ (see Figure 1). The aperture at the entrance slits of both monochromators was reduced to 1°. The temperature was controlled to a stability better than 0.05 °C. The samples have been prepared between quartz plates separated by a 12 μm spacer.

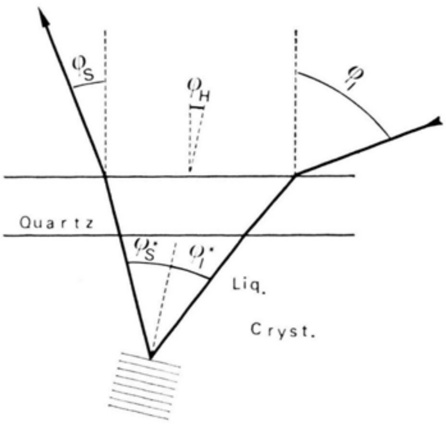

Fig. 1. Beam geometry of selective reflection for oblique incidence. φ_{I} angle of incidence, φ_{S} angle of observation; φ_I^* angle of incidence and φ_s^* angle of scattering in the mesogenic state; φ_{H} tilt angle of helical axes.

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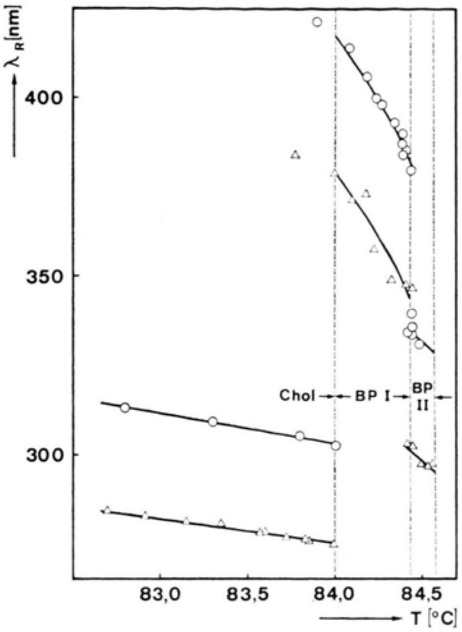

Fig. 2. Temperature dependence of the maximum wavelength λ_R of selective reflection of CM. ○: λ_R^0 for normal incidence; △: λ_R^φ for oblique incidence.

The temperature dependence of the SR bands of CM for normal incidence measured by a Cary 17 I spectrometer [2] is shown in Fig. 2 together with that for oblique incidence. In agreement with the calorimetric results [1] three stable phases are evidenced characterized by defined values of λ_R. For normal incidence CM shows the following properties: on cooling down the isotropic liquid the BP II appears in the range of 84.6 to 84.45 °C, the sharp SR band is shifted from 330 to 334 nm. At 84.45 °C a second peak related to BP I occurs at 379.5 nm; on further cooling the first peak vanishes while the second one is shifted to 417 nm at 84.0 °C. BP I may be supercooled below the phase transition temperature, the indicated shift λ_R vs. temperature is published elsewhere [4]. On heating the planar cholesteric texture checked by polarizing microscopy a value of 302.5 nm was measured at the transition temperature of 84.0 °C.

For oblique incidence in the MPF 4 equipment just an analogous behaviour has been found at the same temperatures but with SR bands shifted to shorter wavelengths (Figure 2). The results have to be discussed in terms of the de Vries theory of cholesterics [8]: For an ideally oriented cholesteric structure selective reflection occurs under the condition $\varphi_I = \varphi_S$ with a Bragg-like angular dependence of SR [8]:

$$\lambda_R^\varphi = \lambda_R^0 \cos \varphi \,. \tag{1}$$

If a uniformly oriented structure is not achieved totally, SR will be observed too under the condition $\varphi_I \neq \varphi_S$ [9, 10]. Based on a model of local scattering regions acting as Bragg sites (cf. Figure 1). Fergason [11] derived the relation

$$\lambda_R^\varphi = \lambda_R^0 \cdot \cos \frac{1}{2} \left[\arc \sin \left(\frac{\sin \varphi_I}{\bar{n}} \right) + \arc \sin \left(\frac{\sin \varphi_S}{\bar{n}} \right) \right] \tag{2}$$

with $\bar{n}$ denoting the mean refractive index of the cholesteric liquid crystalline phase.

The wavelengths λ_R^φ obtained under the angular condition mentioned above are listed in Table 1. It should be emphasized that the quotient of the SR wavelengths for normal (λ_R^0) and oblique incidence (λ_R^φ) is the same in the BP I and BP II as well as in the cholesteric phase indicating clearly that the three polymorphic states obey the same Bragg-like reflection law.

The observed SR can be understood in terms of Fergason's model if fluctuations of the helix orientation of the scattering sites exist up to approximately $\varphi_H = 12°$ with respect to the normal. Then, the reflection condition $\varphi_I^* = \varphi_S^*$ is fulfilled. The SR wavelengths λ_R^φ calculated by means of the Fergason equation (2) for our experimental conditions $\varphi_I = 69°$ and $\varphi_S = 21°$, taking $\bar{n} = 1.5$, are up to 5 nm smaller than measured in the MPF 4 equipment. This deviation probably follows from the uncertainty of extrapolation of the $\bar{n}$ values given in [6] to shorter wavelengths.

As the half-width of the SR bands of about 10 nm observed for normal as well as for oblique incidence is somewhat larger than calculated for an ideally ordered cholesteric sample (2 to 3 nm, cf. Ref.

Table 1

	Chol	BP I	BP I	BP II
ϑ (°C)	84	84	84.45	84.45
λ_R^0 (nm)	302.5	417	379.5	334.5
λ_R^φ (nm)	275	379	346	302.5
$\lambda_R^0/\lambda_R^\varphi$	1.100	1.100	1.097	1.106

Maximum SR wavelengths λ_R for normal and oblique incidence at the transition temperatures of CM.

[11]) a fluctuation of helix orientation seems to be realistic to a certain extent according to the Fergason model. By no means the observed half-widths are compatible with the assumption of a random helix distribution [12, 13]. From our results of the optical properties of the BP state:

1. selective reflection of circularly polarized light,
2. small half-width of SR bands,
3. the same angular dependence of SR as in the cholesteric state,
4. ORD spectra,

the lack of birefringence does not seem to be due to helically structured molecular assemblies of random orientation [12, 13].

The question arises if a structure model of BP can be given explaining the cholesteric-like optical properties as well as the lack of double refraction. Strictly speaking, the molecular arrangement in the BP must be helical as in cholesterics but should give a refraction indicatrix of spherical shape ($\Delta n = 0$). Following an idea of Kuczynski [14] it can be shown that the negative indicatrix [15] of the well-known de Vries model of cholesterics [8] changes to a positive one of prolate shape by decreasing the angle Θ between the helical axis and the local nematic director (cf. Figure 3). At a critical angle of $\Theta_c = 54.74^\circ$ the indicatrix becomes spherical, which explains the experimental result of $\Delta n = 0$ although the molecules are not arranged isotropically but helically. The proposed model is sketched in Figure 3. In his theoretical treatment of the cholesteric phase Schröder [16] obtained the result that the angle Θ must not necessarily be 90°. As birefringence is proportional to $\langle P_2(\cos\Theta) \rangle$ with P_2 denoting the second-order Legendre polynomal one obtains $\Delta n = 0$ for $\cos\Theta_c = \pm 1/\sqrt{3}$, where P_2 vanishes. This is just the critical angle of the molecular long axis inclination against the pitch axis resulting for a spherical indicatrix [14].

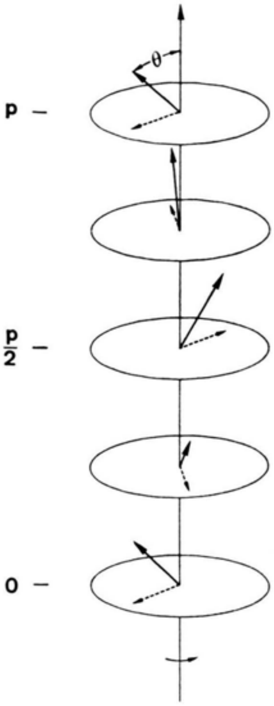

Fig. 3. A proposed helical structure for the Blue Phase resulting in a spherical indicatrix. P helical pitch, Θ angle of inclination between the molecular long axes and the helical axis.

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