Evidence for Polymorphism within the So-called "Blue Phase" of Cholesteric Esters.

II. Selective Reflection and Optical Rotatory Dispersion

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In cholesteryl nonanoate the existence of two polymorphic forms of the so-called "blue phase" has been evidenced by selective reflection and optical rotatory dispersion measurements. The spectroscopic results indicate a discontinuous transition between the two phases.

Recently, we have reported [1] that the blue colour of the so-called "blue phase" (BP) of some cholesteryl esters originates from a selective reflection of circularly polarized light (SR) as described for the plane texture of cholesteric phases [2]. Additionally, within the wavelength region of SR an anomalous dispersion of optical rotatory power (ORD) has been found in the BP state [1]. According to the deVries theory of optical properties of cholesterics [2], the SR as well as the ORD results indicate that the BP state implies in some way a helical arrangement of the mesogenic molecules.

As described in Part I [3] the existence of two polymorphic BP states has been derived from calorimetric measurements. The aim of this paper is to investigate if the two different phases BP I and BP II give rise to different SR and ORD spectra. The SR spectra were measured in a Cary 17 I spectrophotometer with a Mettler FP 5 heating stage; the ORD spectra were scanned in a Jasco J 20 spectropolarimeter between quartz plates, sample thickness 25 or 12 μm, respectively. As an example, we describe the results obtained in the case of cholesteryl nonanoate (CN):

On cooling the isotropic liquid state of CN, at 91.50 °C a sharp SR band occurs at $\lambda_{II} = 404$ nm, which is shifted to 407 nm on further cooling down to 91.35 °C. At this temperature additionally a second SR band was observed at $\lambda_I = 461$ nm (cf. Figure 1). On decreasing the temperature the first SR peak at 407 nm vanishes whereas the second one remains and is shifted on further cooling to 494 nm at 91.05 °C. The ORD spectrum of CN exhibits an anomalous dispersion in the wavelength region of about 405 nm at temperatures $91.50 > \vartheta > 91.35$ °C, whereas the region of anomalous ORD at $\vartheta \lesssim 91.35$ °C is discontinuously shifted to about 465 nm (see Figure 1).

As the cholesteric state of CN has been found to exhibit a SR band at 352 nm [1] the two reflection peaks described above are to be attributed to two different BP states of CN. At the transition temperature $\vartheta = 91.35$ °C the polymorphic states BP I and BP II coexist as can be seen from the simultaneous occurrence of two SR bands (see Figure 1). From the SR measurements the following phase transition temperatures (in °C) could be derived for CN and correspond with the DSC results (see Part I [3]):

chol-91.05°-BP I-91.35°-BP II-91.50°-isotr

The relative accuracy of the temperature measurements is better than 0.05 °C.

At temperatures below 91.05 °C the BP I state can be supercooled, which is accompanied by a bathochromic shift of λ_I up to 540 nm. As mentioned before [1], in the supercooled state λ_I is dependend on the experimental conditions (e.g. cooling rates). Starting from a focal-conic texture of the CN

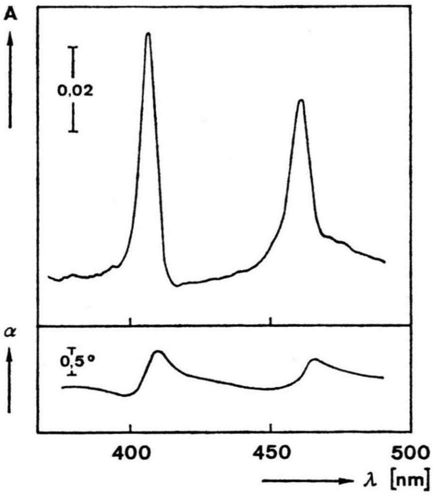

Fig. 1. Selective light reflection A(λ) and optical rotatory dispersion α(λ) of CN at the transition temperature BP I ⇄ BP II $\vartheta = 91.35$ °C. Sample thickness: 25 μm (SR); 12 μm (ORD).

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cholesteric state, on increasing the temperature the SR bands λ_I and λ_{II} appear at the same transition temperatures as mentioned above. As the reflected light within the SR bands is found to be left-circularly polarized in the BP I as well as in the BP II state, the screw sense of the molecular helical arrangement is left-handed as in the corresponding cholesteric state of CN [1].

In cholesteryl myristate also two different SR bands could be detected indicating two polymorphic BP states in agreement with the similar behaviour to CN found by calorimetric measurements [3]. These results will be published elsewhere.

Our spectrophotometric results confirm the existence of two polymorphic BP states which are thermodynamically stable in a very small temperature range. The discontinuous shift of the SR band at 91.35 °C indicates a first order phase transition BP I $\rightleftarrows$ BP II in agreement with finite values of the transition enthalpy (cf. Part I [3]). The selective reflection of circularly polarized light as well as the anomalous dispersion of optical rotatory power support the suggestion of some chiral molecular arrangement within these two BP phases.

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