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

III. The Circular Dichroism of the Blue Phase at High Pressures

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The pressure dependence of the circular dichroism (CD) of a blue phase could be observed for the first time. Corresponding to measurements at normal pressure two phases (BP I, BP II) can be distinguished under high pressures too. Contrary to measurements at normal pressure it was possible to observe the CD of BP II as a function of a variable of state within the very narrow region of this phase.

Cholesterogens like cholesteryl n-alkanoates can exhibit a so-called blue phase (BP) [1, 5]. Recent studies even show that two thermodynamically stable blue phases can be distinguished [2]. Both phases reveal a circular dichroism (CD) existing in a reflection of circularly polarized light within a narrow region of wavelengths [3] as is well known in the case of the Grandjean texture of cholesterics. This light reflection can be characterized by the wavelength of maximum intensity λ_R. In this paper the pressure dependence of λ_R of a blue phase could be observed for the first time.

The optical measurements were carried out using a spectrophotometer Cary 17 DH in the sample compartment of which a high pressure optical cell has been installed. The spectra were taken as a function of pressure p at constant temperature ϑ (here $\vartheta = 102\,°\mathrm{C} \pm 0.005\,°\mathrm{C}$). The investigations were done on cholesteryl nonanoate.

In the lower part of Fig. 1 the measured quantities (p/λ_R) are plotted for decreasing pressure ($\leftarrow p$).

Starting from the cholesteric phase (CH) in the Grandjean texture the CD-band of this phase vanishes at 245.0 bar within a pressure change of 0.25 bar. At the same time a new CD-band appears at somewhat longer wavelengths which probably must be attributed to the blue phase (see later). This band itself vanishes when the isotropic liquid phase (I) is reached at 236.5 bar.

In the upper part of Fig. 1 the quantities (p/λ_R) are plotted for increasing pressure ($\rightarrow p$). Starting point is now the isotropic liquid phase (I). Within a change of 0.25 bar one observes the appearing of a CD-band at 236.5 bar. This transition pressure exactly corresponds with that obtained with decreasing pressure; it must be pointed out, however, that the CD-band having been found now lies at by far longer wavelengths (see lower part of Figure 1). — Further increase o fpressure leads at 239.3 bar to a disappearing of the latter band and to an appearing of a new one at still longer wavelengths. A comparison of these results with those obtained at normal pressure shows that this shifting of λ_R must be ascribed to the transition of BP II to BP I. This phase transition BP II/BP I is enantiotropic as the transition I/BP II. Contrary to this the BP I can be supercooled up to 100 bars relative to the cholesteric phase in the focalconic texture which finally is formed when the pressure is raised furthermore. The phase transition BP I/CH can only be seen when starting from the cholesteric phase.

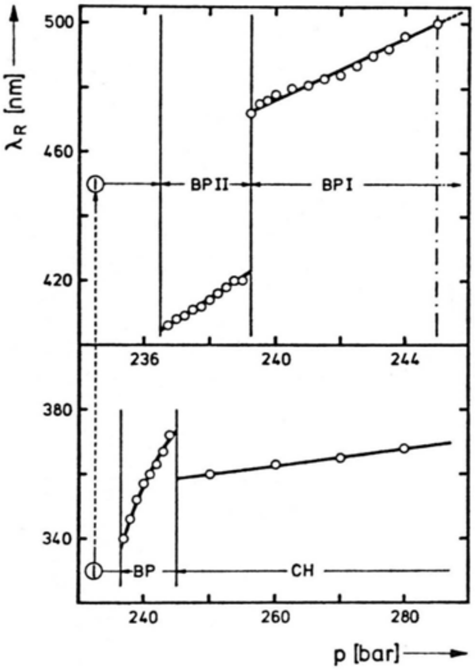

Fig. 1. The pressure (p) dependence of the reflection wavelength of maximum light intensity (λ_R) at constant temperature ($\vartheta = 102\,°\mathrm{C}$) for cholesteryl nonanoate
I = isotropic phase, BP = blue phase, CH = cholesteric phase.

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Observations with decreasing pressure, however, carried out in the described manner, allow only the determination of the total region of the BP; the transition BP I/BP II is not indicated.

Because a Δp of 0.2 bar is equivalent to a ΔT of 0.01 K (according to a $\mathrm{d}p/\mathrm{d}T$ of about 20 bar/K near an equilibrium state with a blue phase [4]) the state of a blue phase can be influenced more sensitively by varying the pressure at constant temperature than vice versa. Thus — contrary to measurements at normal pressure — it was possible to observe λ_R of BP II as a function of a variable of state within the very narrow region of this phase.

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