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

I. Calorimetric and Microscopic Measurements

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Calorimetric measurements as well as microscopic observations confirm the existence of two thermodynamically stable polymorphic forms of the so-called "blue phase" of cholesteryl nonanoate and myristate.

It is well known for a long time that various cholesteryl esters show violet-blue colours just below their clearing points, a phenomenon which usually is called "The Blue Phase" (BP) [1, 2]. Recently, the BP has been demonstrated by thermodynamic and optical measurements to be a *stable* phase in a very narrow temperature range of about 0.5 degrees [3–9].

The cholesteric → BP (ΔH_{CB}) and BP → isotropic (ΔH_{BI}) phase transitions have been reinvestigated by means of differential scanning calorimetry (Perkin-Elmer DSC-2) for highly purified cholesteryl myristate (CM) and nonanoate (CN). To improve the resolution we used gold pans instead of aluminum pans.

From the thermograms (Fig. 1) transition-enthalpies ΔH_{BI} of 1.1 kJ mole^{-1} for CM and 0.53 kJ mole^{-1} for CN have been measured, whereas the respective values of ΔH_{CB} were found to be much smaller: within the range of accuracy 34 J mole^{-1} for CM and 17 J mole^{-1} for CN.

As a new result we have observed a third peak, almost hidden in the BP → isotropic peak in highly resolved thermograms, which is well reproducible although not completely separated. In both cases this effect has been found just 0.15 K below the clearing point. The change of enthalpy is estimated to be of the same order of magnitude as for ΔH_{CB}. We attribute this additional enthalpy to a phase transition between two polymorphic "blue phase" states BP I → BP II. This suggestion is supported by the spectroscopic results given in [10].

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Additional evidence for two polymorphic "BP" states originates from visual observations by means of polarizing microscopy. As in CM the selective reflection band λ_R [9] causing the well-known blue colour is positioned at the end of the visible wavelength region the transition BP I → BP II of the pure CM could not be observed by eye. Adding a nematogenic compound (p-pentylphenyl-2-chloro-4-(p-pentylbenzoyloxy)-benzoate, PCPB) λ_R is shifted to longer wavelengths [11]. In mixtures of CM with PCPB we have detected *three* phase transitions near the clearing point (Leitz Ortholux-Pol with Mettler heating stage FP 5). The resulting textures are summarized in Table 1.

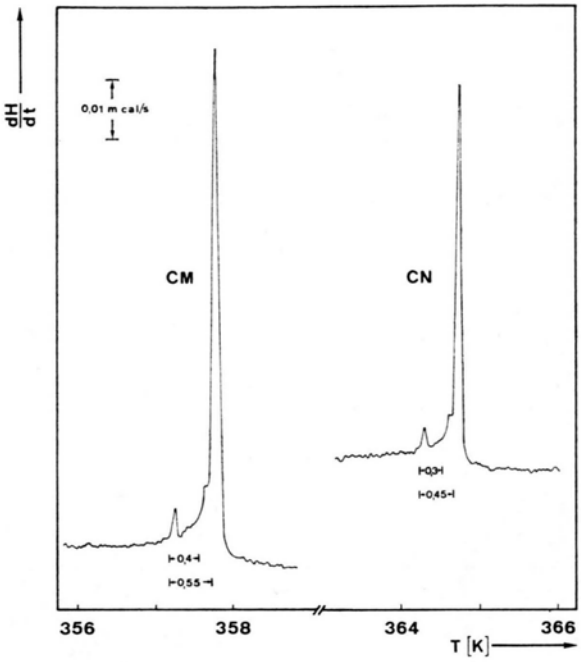

Fig. 1. DSC traces of CM (2.756 mg) and CN (2.919 mg) heating from cholesteric to isotropic state. Heating rate 0.625°/min.

BP II reveals a green/blue platelet texture, reversible on heating as well as on cooling. The green/yellow/red platelets of BP I occur on cooling; only this phase can be supercooled. On heating, this BP I texture only occurs on starting from the cholesteric focal-conic texture. On heating a cholesteric planar texture the phase transition at 96.00 °C is indicated by a sharp colour jump from blue to green but the planar texture seems to

Table 1. Phase transitions and textures of CM/PCPЬ, 42.37 mole-% CM.

	Cholesteric	BP I	BP II	Isotropic
ϑ/°C		96.00	96.25	96.60
Heating	planar (blue)	"planar" (green → blue)	platelet[a] (green/blue)	
Heating	focal-conic	platelet (green/yellow/red)	platelet (green/blue)	
Cooling	focal-conic	supercooled ← platelet (green/yellow/red)	platelet (green/blue)	

[a] The platelet texture is of the same form as shown by Demus [12], Figure 158.

remain. This observation is of interest with respect to the results presented in [13].

Thus it has been demonstrated that BP I and BP II are thermodynamically stable phases with finite changes of enthalpy at defined transition temperatures; only the texture is influenced by the experimental conditions.

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