

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

I. Calorimetric and Microscopic Measurements

K. Bergmann and H. Stegemeyer

Lehrstuhl für Physikalische Chemie, Gesamthochschule Paderborn

Z. Naturforsch. **34a**, 251–252 (1979);
received December 19, 1978

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 \rightarrow BP (ΔH_{CB}) and BP \rightarrow isotropic (ΔH_{BI}) phase transitions have been re-investigated 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 \rightarrow 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 \rightarrow BP II. This suggestion is supported by the spectroscopic results given in [10].

Reprint requests to Prof. Dr. H. Stegemeyer, Lehrstuhl für Physikalische Chemie, Gesamthochschule Paderborn, Postfach 1621, D-4790 Paderborn.

0340-4811 / 79 / 0200-0251 \$ 01.00/0

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 \rightarrow 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.

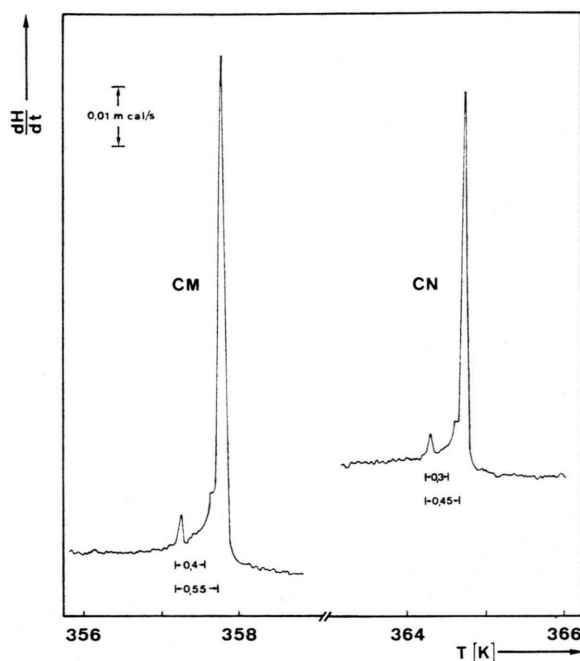


Fig. 1. DSC traces of CM (2.756 mg) and CN (2.919 mg) heating from cholesteric to isotropic state. Heating rate 0.625°/min.

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



Dieses Werk wurde im Jahr 2013 vom Verlag Zeitschrift für Naturforschung in Zusammenarbeit mit der Max-Planck-Gesellschaft zur Förderung der Wissenschaften e.V. digitalisiert und unter folgender Lizenz veröffentlicht: Creative Commons Namensnennung-Keine Bearbeitung 3.0 Deutschland Lizenz.

Zum 01.01.2015 ist eine Anpassung der Lizenzbedingungen (Entfall der Creative Commons Lizenzbedingung „Keine Bearbeitung“) beabsichtigt, um eine Nachnutzung auch im Rahmen zukünftiger wissenschaftlicher Nutzungsformen zu ermöglichen.

This work has been digitalized and published in 2013 by Verlag Zeitschrift für Naturforschung in cooperation with the Max Planck Society for the Advancement of Science under a Creative Commons Attribution-NoDerivs 3.0 Germany License.

On 01.01.2015 it is planned to change the License Conditions (the removal of the Creative Commons License condition "no derivative works"). This is to allow reuse in the area of future scientific usage.

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

	Cholesteric		BP I	BP II	Isotropic
$\theta/^\circ\text{C}$	96.00		96.25	96.25	96.60
Heating	planar (blue)		"planar" (green \rightarrow blue)	platelet ^a (green/blue)	
Heating	focal-conic		platelet (green/yellow/red)	platelet (green/blue)	
Cooling	focal-conic	super-cooled \leftarrow	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.

The support of this work by the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

- [1] O. Lehmann, Z. phys. Chem. **56**, 750 (1906).
- [2] G. W. Gray, J. Chem. Soc. **1956**, 3733.
- [3] F. P. Price and J. H. Wendorff, J. Phys. Chem. **75**, 2839 (1971).
- [4] L. S. Goldberg and J. M. Schur, Radio Electron. Eng. **39**, 279 (1970).
- [5] S. A. Jabarin and R. S. Stein, J. phys. Chem. **77**, 399 (1973).
- [6] H. Arnold and P. Roediger, Z. phys. Chem. **283**, 239 (1968).
- [7] D. Armitage and F. P. Price, J. Phys. (Paris) Colloq. **36**, C 1, 133 (1975).
- [8] D. Armitage and F. P. Price, J. Appl. Phys. **47**, 2735 (1976).
- [9] K. Bergmann and H. Stegemeyer, Ber. Bunsenges. Phys. Chem. **82**, 1309 (1978).
- [10] K. Bergmann, P. Pollmann, G. Scherer, and H. Stegemeyer, Z. Naturforsch. **34a**, 253 (1979).
- [11] K. Bergmann and H. Stegemeyer, to be published.
- [12] D. Demus and L. Richter, Textures of Liquid Crystals, Weinheim, New York 1978.
- [13] P. Pollmann and G. Scherer, Z. Naturforsch. **34a**, 255 (1979).