

# Liquid Single Crystals of Cholesteric Blue Phases

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Liquid single crystals of cholesteric “Blue Phases” (BP) have been prepared and observed by polarizing microscopy. They exhibit a quadratic size without any exception. At the phase transition BP II  $\rightarrow$  BP I a cross-hatching occurs, diagonal to the square sides, indicating a four-fold crystal symmetry. The observed habitus of the BP single crystals clearly evidences a cubic structure of the molecular arrangement. Possible space groups are discussed.

In cholesterogenic liquid crystals with rather small helical pitches there exist two polymorphic chiral phases close below the clearing point which are thermodynamically stable between the states of the isotropic liquid and the cholesteric phase. Because of the scattering of visible light these phases are called “Blue Phases” (BP). For a review cf. [1]. It has been pointed out that several optical properties of BPs are quite cholesteric-like, e. g. selective reflection of circularly polarized light [2] and anomalous dispersion of optical rotatory power [3]. However, BPs are non-birefringent ( $\Delta n = 0$ ) in contrast to cholesterics ( $\Delta n < 0$ ). Two different proposals have been made regarding the molecular arrangement within BPs taking into account their optical isotropy as well as their cholesteric-like properties: i) a body-centered cubic model [4], ii) a uniaxial tilted helical structure [5]. From the experimental results referred in [1] a decision between the two models is not possible.

It is well known that BPs form a platelet texture with mosaic-like areas of different colours [6] caused by selective reflection at different wavelengths  $\lambda_R$ . Crooker [7] found out that the values of  $\lambda_R$  obtained from different platelets have the ratio  $\sqrt{1} : \sqrt{2} : \sqrt{3} : \sqrt{4}$ . This result can be interpreted in terms of a Bragg scattering at different planes ( $hkl$ ) of a cubic lattice [7]:

$$\lambda_R^{hkl} = 2 \bar{n} p \sin \theta / (h^2 + k^2 + l^2)^{1/2} \quad (1)$$

with the Bragg angle  $\theta$ , the helical pitch  $p$ , the mean refractive index  $\bar{n}$ , and the Miller indices  $h, k, l$ .

A decision between a simple cubic (sc) and a body-centered cubic (bcc) structure is not possible.

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However, as it can be seen from Eq. (1) the experimental results also can be understood if one assumes that the tilt angle of the helical axis with respect to the substrate plane is different in different platelets. This situation seems plausible in a tilted helical structure as described by model ii) [8].

From the well-known polycrystalline platelet texture [6] of BPs any information of the internal structure scarcely can be obtained. In this paper we first describe the preparation of liquid single crystals of BPs. Observations have been carried out by means of a Leitz Ortholux polarizing microscope with Mettler FP 52 heating stage. The single crystals were obtained in the case of cholesteryl nonanoate (CN) in the following way (cf. Fig. 1): Cooling down a sample of CN very slowly from the isotropic state close below the clearing point an unstructured blue texture (blue “fog”) occurs. By annealing the sample in the temperature region of BP II squares begin to grow rather quickly which will intersect with time. The quadratic single crystals can be preserved by cooling down slowly into the temperature region of BP I. Now the quadratic forms do not grow any longer, the boundaries are stable. Thus we were only able to obtain microphotographs of the BP I single crystals which are shown in Figure 1.

During the phase transition BP II  $\rightarrow$  BP I a cross-hatching within the squares occurs. From the quadratic single crystals of cholesteryl decanoate shown in Fig. 2 it can be seen that the cross-hatching runs diagonally to the sides of the squares. Such a diagonal striation has been found in the BP I of all cholesteryl esters under investigation. The striations broaden slowly with time when annealing the sample for several hours. This is shown in Fig. 3 for the BP I of cholesteryl myristate. The quadratic BP I single crystals can be supercooled with respect to the

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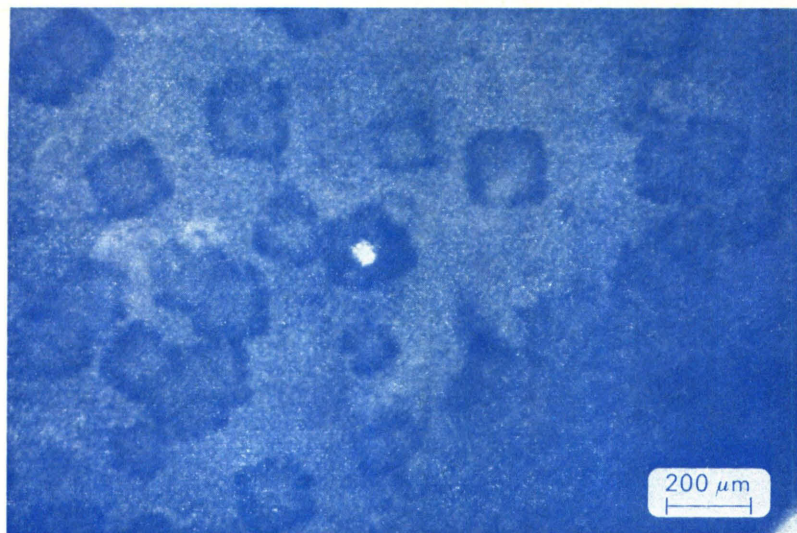


Fig. 1. Liquid single crystals of cholesteryl nonanoate in the BP I state (in transmission, crossed polarizers), 90.30 °C, uncovered sample.



Fig. 2. Liquid single crystals of cholesteryl decanoate (90.45 °C) showing the cross-hatching of BP I. Sample thickness 12 μm (in transmission).

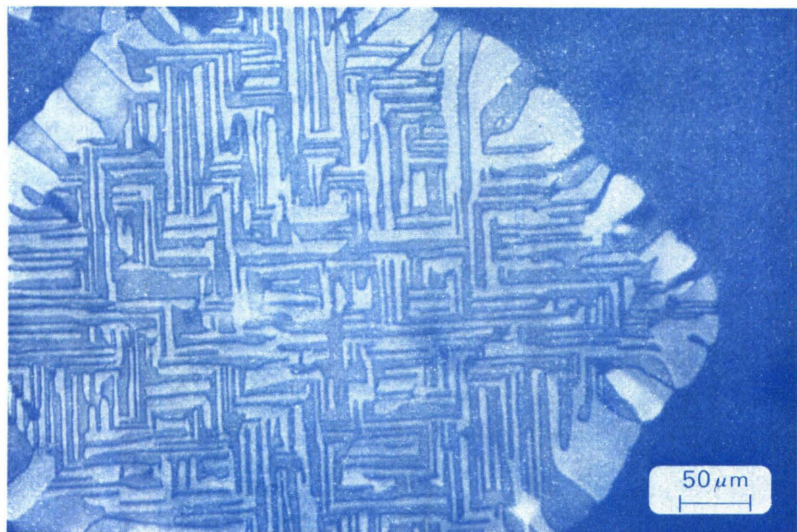


Fig. 3. Diagonal striations in a BP I single crystal of cholesteryl myristate (80.65 °C), ~ 6 μm (in reflection).

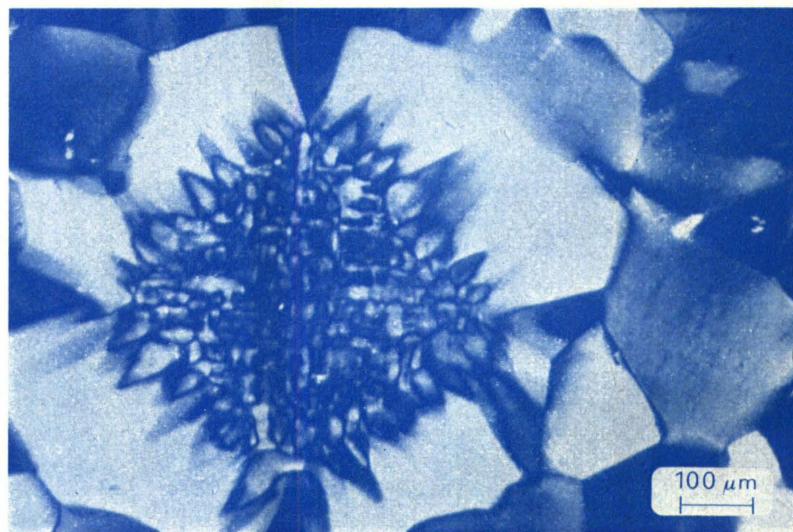


Fig. 4. Dendrites grown from a BP I single crystal of cholesteryl pentadecanoate (80.80 °C), 12 μm (in transmission).

cholesteric phase as it is known for the BP I generally. In some cases dendrites grow from the single crystals as demonstrated by Fig. 4 in the case of cholesteryl pentadecanoate. The dendrites clearly exhibit a four-fold symmetry.

Our microscopic observations of BP liquid single crystals can be summarized as follows: 1. In both BP states we are able to obtain liquid single crystals always of quadratic form. Without any exception only angles of 90 degrees have been observed between the crystals faces. 2. All squares of a given BP sample are of unique colour in contrast to the platelets which possess different colours. 3. A cross-hatching running diagonal to the sides of the squares occurs at the phase transition BP II  $\rightarrow$  BP I. 4. The diagonal striation within a square indicates a four-fold symmetry as well as the dendritic growth observed in several cases.

In BP systems with rather large pitches the growth of quadratic single crystals never could be observed from the "fog" texture within the temperature region of BP II. In these cases (e. g. mixtures of cholesteryl chloride with CN) a cross-hatching with perpendicular striations occurred over large areas of the sample directly at the phase transition BP II  $\rightarrow$  BP I without any formation of quadratic boundaries in the BP I. The growth of squares seems to be restricted to BPs with small pitches.

In solid single crystals close relationships exist between crystal habit and internal structure. Con-

sequently, the observed interfacial angles would reveal the true symmetry of the structure. As the habit of the BP liquid single crystals was always quadratic without any exception it follows strictly that BPs must belong to cubic space groups. The observed quadratic growth is expected to be caused by the forms {100} or {200}. Thus (100) or (200) must be the slowest-growing planes. Bearing in mind the observed four-fold symmetry P 432, I 432 or I 4<sub>1</sub>32 seem to be possible space groups of BPs explaining also the optical results [2, 3, 7].

(100) is the lowest-index plane in sc crystals whereas (110) is in bcc. (110), however, would lead to rhombic faces which never have been observed. Thus one can argue that the growth of the quadratic single crystals first occurring in the BP II state is determined by (100) indicating a sc structure of BP II. In the BP I state the internal structure may change to bcc preserving the quadratic habit by pseudomorphosis.

The diagonal striations observed in BP I may be discussed in terms of dislocations. As the pitch enhances during the phase transition BP II  $\rightarrow$  BP I [1] some mechanical stress will be induced within the BP I structure plausibly leading to dislocations.

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