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Observation of a new metastable liquid-crystalline phase in supercooled blue phase systems

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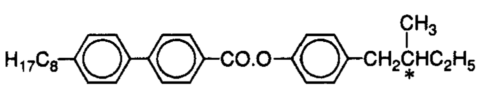
A new metastable liquid-crystalline phase BP S was observed in pure chiral compounds. The BP S is transformed reversibly from the supercooled BP I and is thermodynamically stable with respect to the BP I and metastable to the cholesteric phase. Rhombic single crystals of the BP S probably indicate a cubic lattice structure as in other BPs, but the lattice constant exhibits an anomalous temperature dependence.

In chiral liquid crystals up to three blue phases have been observed just below the clearing point, two of which exhibit a cubic lattice structure with quite definite symmetry groups (BP I–O^8, BP II–O^2) [1,2], although in theory we can find many more possibilities for the structural designations [3–5]. It has been found, that the low temperature BP I can be supercooled to a large extent with respect to the cholesteric phase [6]. In this Preliminary Communication we report the observation and properties of a new metastable liquid-crystalline phase reversibly transformed from the supercooled BPI.

We used the BDH compound CE8:



which exhibits the following liquid-crystalline phases:

S_C^* 83°C S_A 134°C Ch 139·6°C BP I 139·7°C BP II 139·85°C BP III 140°C I.

The BPs are characterized by their lattice constants, derived from the Bragg reflections of circularly polarised light, which have been measured by means of transmission and reflection spectroscopy. The transmission spectra were obtained with a 2300 Varian spectrophotometer. The reflection spectra measurements and visual observations of the morphology of the blue phases were carried out with a Leitz-Ortholux-Pol II BK microscope equipped with Jarrel Ash automatised monochromator and Vario Orthomat 2 Photocamera. The temperature of the samples was controlled with a modified Mettler F5/52 hot stage. Perfect monodomain samples of the blue phases 12 μm thick were grown with a polyimide treated and rubbed surface.

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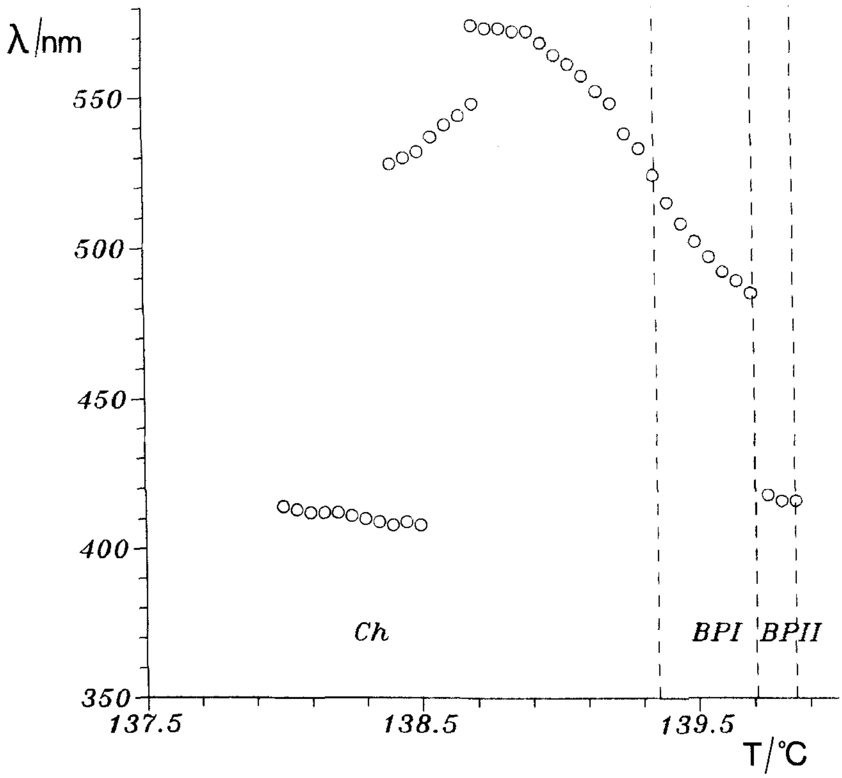

Figure 1. Temperature dependence of the lattice constant of the blue phases of CE8 for the cooling rate of 0·007°C min^{-1}.

Figure 1 shows the temperature dependence of the BP lattice constants of CE8. The temperature interval of the BP I can be divided into two regions. In the temperature region from 139·7°C to 139·35°C the lattice constant does not depend upon the cooling rate. In the supercooled state from 139·35°C down to the end of the BP I temperature interval a strong dependence of the BP I lattice constant on the cooling rate was observed. A saturation effect of the lattice constant takes place in this interval. On cooling the supercooled BP I further another jump in the lattice constant was observed, which indicates the occurrence of a new phase, which we call BP S (S from supercooled). The lattice constant of the BP S decreases with decreasing temperature. For cooling rates smaller than 0·007°C min^{-1} homogeneous samples of BP S were obtained. For this case the BP S does not change its lattice constant for about 1 hour at constant temperature. For larger cooling rates after the BP I a biphasic region, cholesteric + BP S, was observed. The BP S and cholesteric phases exhibit different colours in the polarising microscope. After complete transformation of the BP S to the cholesteric and subsequent heating the phase transition Ch–BP I was observed at 139·35°C.

The temperature dependence of the lattice constant of the BP I on decreasing temperature down to the phase transition to the BP S is shown in figure 2 for two different cooling rates. The larger the cooling rate the smaller the maximal values of the BP I lattice constant obtained. After the transformation of the supercooled BP I to the BP S the sample was again heated. For this subsequent heating the values of the BP S

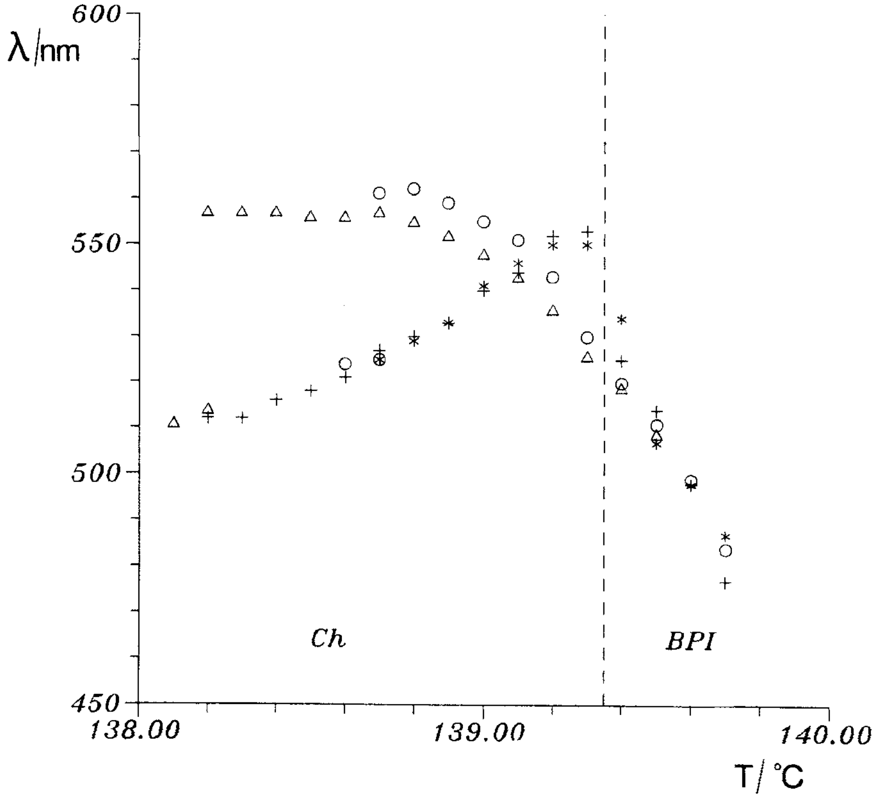

Figure 2. Temperature dependence of the lattice constant of BP I of CE8 on cooling and of BP S on subsequent heating: ○, BP I 0·02°C min^{-1}, cooling; * BP S 0·03°C min^{-1}, heating; △, BP I 0·05°C min^{-1}, cooling; + BP S 0·03°C min^{-1}, heating.

lattice constant exhibit an identical temperature dependence for the two experimental conditions. The phase transition to BP S/BP I occurs at 139·35°C. This shows that the BP S is stable with respect to the BP I at temperatures not higher than 139·35°C but is metastable with respect to the cholesteric phase. The measurements of reflection spectra of polydomain samples of the blue phases in CE8 have also indicated the occurrence of the BP S and agree with the measurements of the transmission spectra. This means, that the BP S is not a reorientational form of the monodomains of the BP I in the supercooled region.

In a mixture of CE8 with 10 mol % of the smectogenic 4,4′-di-*n*-decylazoxybenzene (C10) a BP S has also been observed in addition to the well-known BPs. The temperature dependence of the lattice constants of the BP I and BP S in this mixture is quite similar to that of pure CE8, as given in figure 1. In this mixture, however, we obtained the growth of well-shaped single crystals of the BP S. In figure 3 a yellowish-green rhombic-like shaped single crystal is shown which grew from the surrounding red BP I. The habit of this BP S single crystal is similar to the three dimensional orthorhombic BP I single crystals of the cubic form {110}, which we found earlier (see figures 16, 19, and 21 in [1]). Thus, it is possible, that the BP S exhibits a cubic lattice structure.

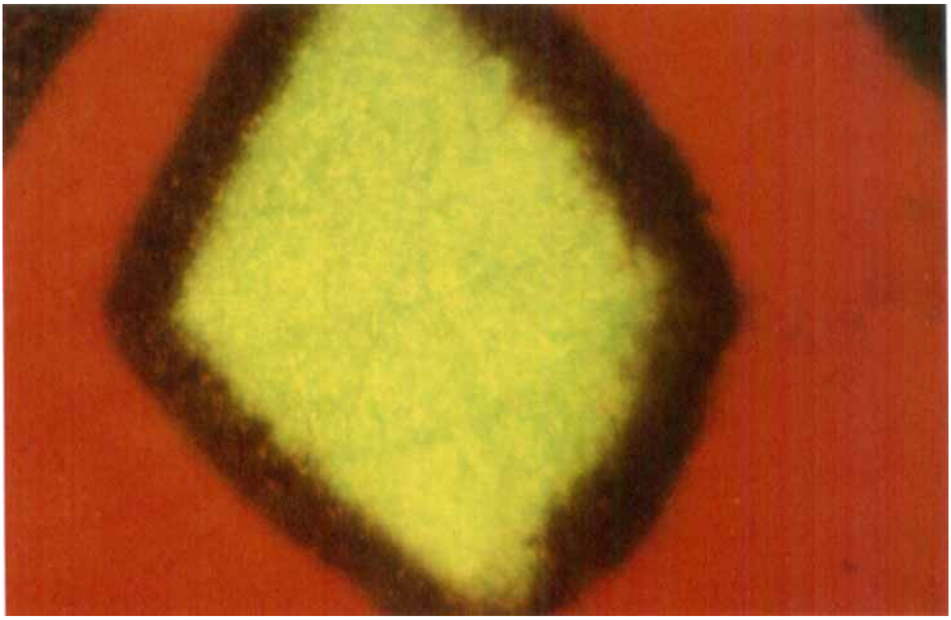

Figure 3 Rhombic BP S single crystal grown from BPI monodomain matrix. Mixture 90 mol % CE8: 10 mol, % C10; cooling rate 0·2°C min^{-1} after thermostatting the sample in the BP I at 130·6°C for 30 min.

It should be mentioned briefly, that we have found the supercooled BP S also in other pure chiral liquid crystals, for example, cholesteryl myristate. These results will be published later in more detail. In chiral liquid crystals, which do not exhibit an S_A phase besides the cholesteric and the blue phases, a BP S could not be detected. It should be emphasized, that the BP S lattice constant in contrast to that of the BP I increases with increasing temperature. Such an anomalous behaviour has been described for a BP I in a mixed system [7] under experimental conditions, which, however, cannot be compared with our system. The occurrence of the BP S can explain percularities of the temperature dependence of the lattice constant observed in the supercooled region in [8, 9]. The phase structure of the BP S is still unknown. Two principle possibilities must be taken into account: (i) as the BP S obviously occurs only in systems with an S_A phase below the cholesteric phase a new analogue to the Abrikosov dislocation lattice phase should be considered [10, 11] and (ii) because of the orthorhombic habit of the BP S single crystals (see figure 3) the possibility of another blue phase with a cubic lattice must be taken into account. The anomalous temperature dependence of the lattice constant, however, contradicts the predictions of the Landau theory of BPs [3–5].

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