

Electric Field-Induced Birefringence in Liquid-Crystalline Blue Phases

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The optical behaviour of liquid-crystalline 'Blue Phases' (BP) of polar cholesterogenic compounds in electric fields up to $100 \text{ kV} \cdot \text{cm}^{-1}$ has been investigated by means of polarization microscopy. By an observation parallel to the field direction a birefringence dependent on the field strength was detected in the BP I. This result is discussed in terms of a non-linear electro-optic effect, showing that the BP I becomes optically biaxial in an electric field. In the BP II a birefringence was not observed under the same conditions probably indicating that the field induces an optical uniaxiality with the optic axis parallel to the field. The results are discussed with respect to possible cubic structures of the BPs.

1. Introduction

In cholesteric liquid crystals of small helical pitches one can observe so-called Blue Phases (BP) in a very small temperature span ($\lesssim 1 \text{ K}$) close below the clearing point [1]. These BPs are optically isotropic, i.e. they exhibit no birefringence [2, 3]. From this result a cubic BP structure has been derived [4, 5] which was evidenced by observation of Bragg-type light scattering [6, 7] and growing liquid single crystals belonging to cubic crystal classes [8, 9].

It is well known that the helical pitch of cholesteric liquid crystals can be changed by an electric field perpendicular to the helix axis [10]. Because of the optical activity [1, 11] of BPs the molecules are arranged helically in these phases too so that an electric field effect on the BP structure should be expected. Attempts to study the phase transition in BPs in the presence of an electric field are known [12–14]. The aim of this paper is to detect a distortion of the cubic BP structure by application of an electric field.

2. Experimental

Because of the high dielectric anisotropy required the following cyanobiphenyls exhibiting a large permanent dipole moment along the molecular long

axis have been used: cholesterogenic 4-cyano-4'-(2-methylbutyl)-biphenyl, **CB 15** (BDH); nematogenic 4-cyano-4'-n-hexoxy-biphenyl, **M 18** (BDH) and a nematogenic mixture of cyanobiphenyls **ZLI 1612** (Merck). Mixtures of cholesterogenics and nematogenics were prepared in cells of tin dioxide coated glass plates with $12 \mu\text{m}$ mylar spacers in a Mettler heating stage FP 52. The cell was driven by a square wave voltage source (0 to 140 Volt, 0 to 400 Hz). Rectangular voltage pulses have been used to ensure a well defined voltage level. Mostly, frequencies in the range of 170...400 Hz were used. In this range no frequency effect on the BP properties has been observed. The textures were observed parallel to the direction of the electric field by a polarizing microscope Leitz SM-Lux-Pol.

3. Results

We confine ourselves to results obtained at lower electric field strengths at which the liquid-crystalline textures behave statically. As an example we report results obtained for a mixture of CB 15/M 18 with 49.6 mol% CB 15. The behaviour of other mixtures was quite similar [15]. All mixtures used exhibit *two* Blue Phases as described previously [1] in the following order (on increasing temperature): cholesteric/BP I/BP II/isotropic.

3.1. Field-induced textures of BP II

Cooling down the isotropic liquid phase of the CB 15/M 18 mixture mentioned above close below

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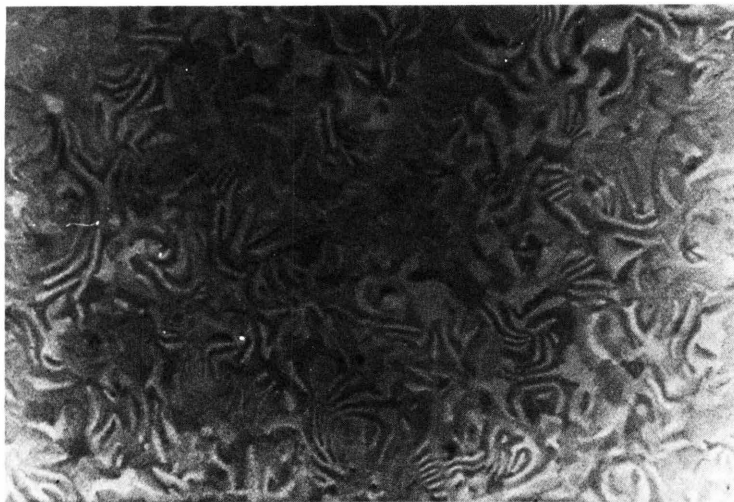


Fig. 1. BP II texture in an electric field. (In transmission; crossed polarizers; mixture M18/CB15, 49.6 mol% CB15; sample thickness 12 μm ; voltage 22.3 V.) Temperature 31.20 $^{\circ}\text{C}$.

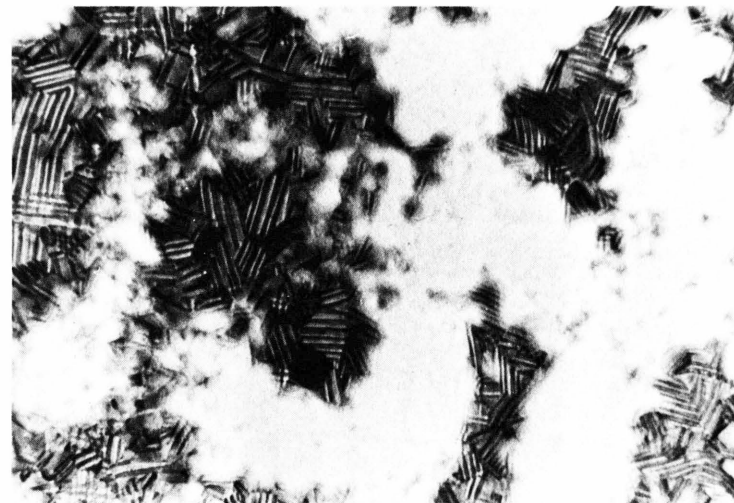


Fig. 2. Phase transition BP II \rightarrow BP I in an electric field. (Experimental conditions: cf. Figure 1.) Temperature 30.90 $^{\circ}\text{C}$.

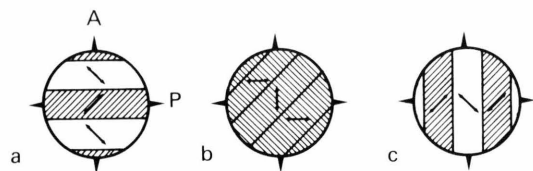


Fig. 4. Sketch of the striated BP I in an electric field: a, c diagonal positions; b extinction position. A, P vibration directions of the analyser and polarizer, respectively.



Fig. 3. BP I texture in an electric field. (Experimental conditions: cf. Figure 1.) Temperature 30.83 $^{\circ}\text{C}$.

the clearing temperature a polycrystalline texture with platelets of different colours [16] occurred. Applying an electric field at constant temperature (31.2 °C) the platelet texture was turned into a new one shown in Fig. 1 at $E = 1.8 \cdot 10^4 \text{ V} \cdot \text{cm}^{-1}$. The colour of the regions separated by diffuse dark lines was yellow to orange showing a red-shift on increasing field strength. As the dark lines move when the sample is rotated with respect to the axes of the polarizers they cannot be caused by light scattering but rather by birefringence. The birefringence, however, was so small that it could not be measured quantitatively in monochromatic light even at higher field strengths. After switching off the field the lines were preserved after standing over night. On increasing voltage at constant temperature the texture of Fig. 1 turned into the well-known cholesteric focal conic texture indicating a field-induced phase transition $\text{BP II} \rightarrow \text{cholesteric}$ which was reversible.

3.2. Field-induced textures of BP I

On cooling the BP II texture of Fig. 1 at constant field strength down to 30.9 °C a new texture began to develop (Figure 2). At 30.8 °C all the sample showed a blue striated texture (Fig. 3) with the striations, alternately light and dark, running parallel to each other within different small areas. On heating up the cholesteric phase at the same field strength the same texture also has been obtained but not so well developed. Consequently, the texture shown in Fig. 3 is due to BP I.

In the BP I texture (Fig. 3) a birefringence obviously was detected. It should be emphasized that the observation direction was parallel to the electric field. The birefringence was measured in monochromatic light using interference filters. By rotation of the stage the sample could be brought into extinction positions which were found to be the same for the dark and light striations. The extinction positions were obtained after rotation by 90° but the sample did not extinguish completely. On further rotation the dark striations became light and vice versa. An identical position, however, is only obtained after rotation by 180°. By means of a unit retardation plate (gypsum plate) the fast and slow vibration direction within the striations could be determined (cf. Figure 4). The axes of the slow vibrations are oriented by an angle of 45° to the

direction of the striations and change their position by 90° proceeding from one striation to the neighbouring one. The magnitude of the birefringence increased with field strength. The largest value which could be estimated was $\Delta n \simeq 0.02$.

On decreasing the field strength at constant sample orientation the contrast between the dark and light striations decreased to zero at a given small voltage U_0 . At still lower voltages $U < U_0$ the dark and light striations interchanged. It could be shown that Δn first decreases with decreasing field strength but increases again at $U < U_0$. At U_0 the direction of the fast vibration turned by 90°. On repeating the cycle of decreasing and increasing field strength, U_0 turned out to decrease with time. On switching off the electric field the birefringence was preserved but decreased continuously to zero in time. On increasing the field strength at constant temperature the focal conic texture of the cholesteric phase developed, indicating a field-induced phase transition $\text{BP I} \rightarrow \text{cholesteric}$.

4. Discussion

4.1. Electric field effects in the BP I

Although the viscosity of BPs is much larger than that of cholesterics [18] the molecular orientation in BPs can be changed by an electric field much more easily than in solids. The electric field-induced optical anisotropy described in the previous section can be discussed in terms of a non-linear dielectric behaviour as follows:

The expansion of the permittivity ϵ in powers of the electric field strength E can be written as [19]

$$\epsilon = \epsilon^0 + \xi_1 E + \xi_2 E^2 + \dots, \quad (1)$$

where ϵ^0 is the second rank permittivity tensor whilst ξ_1 and ξ_2 are tensors of third and fourth rank, respectively. In cubic systems the representation quadric of ϵ^0 is a sphere. Consequently, the dielectric behaviour of a cubic phase is isotropic ($\epsilon = \epsilon^0$). The representation surfaces of ξ_1 and ξ_2 , however, generally may be of lower symmetry than spherical, although their symmetry at least must include the elements of the crystal point group (Neumann's principle [20]). Thus, sufficiently high fields may induce an optical anisotropy in cubic crystals via (1). This anisotropy may be uniaxial or biaxial depending on the direction of the external field

relative to the cubic crystal axes. By an electric field applied parallel to C_n axes with $n = 3, 4$ or 6 the cubic crystal will be distorted to an optically uniaxial one with its optic axis parallel to the field [21]. This effect would lead to pseudo-isotropy with the viewing direction parallel to the field. Actually, a field-induced birefringence was observed under these conditions (cf. Section 3.2). If the field direction is parallel to an axis of $n \leq 2$ one will obtain an optically biaxial crystal [21] which seems to be the case in our systems.

Because of the optical activity of BPs [1] only the enantiomorphic cubic crystal classes 23 and 432 are to be discussed.

According to the conditions given above, in 23 crystals maximum birefringence will be obtained if the field and observation directions are parallel either to the C_2 axis normal to faces of the crystallographic form $\{100\}$ or to the C_1 axis normal to faces of $\{110\}$. 432 crystals exhibit C_2 axes normal to faces of $\{110\}$ whereas the rotation axes of the other faces under discussion are of an order $n > 2$ (e.g. C_4 in the case of $\{100\}$ faces). The field-induced birefringence of BPI thus can be understood in terms of the following different situations:

- i) E normal to a $\{100\}$ face (C_2) of 23 crystals;
- ii) E normal to a $\{110\}$ face (C_1) of 23 crystals;
- iii) E normal to a $\{110\}$ face (C_2) of 432 crystals.

To try a decision between these possibilities the Bragg-type light scattering in BPI has to be taken into account [15]. Generally, in BPs circularly polarized light of wavelength λ_{hkl} is selectively reflected at different lattice planes (hkl) of a cubic structure (normal incidence) [7]:

$$\lambda_{hkl} = 2d\bar{n}(h^2 + k^2 + l^2)^{-1/2}, \quad (2)$$

where d is the lattice parameter and \bar{n} the mean refractive index. In the BPI system under discussion two selective reflection bands have been found in the visible (λ_1) and the near u.v. (λ_2) with a wavelength ratio $\lambda_1/\lambda_2 = 1.37$, which is approximately $\sqrt{2}$ [15]. This ratio can be obtained e.g. for the cases given in Table 1.

The electro-optic effects described above have been observed in the visible corresponding to the long wavelength reflection (λ_1) at $\{100\}$, $\{110\}$, or $\{200\}$, respectively. Case iv) can be cancelled because a C_3 axis is normal to $\{111\}$ faces in 23 as well as in 432 crystals. In case iii) reflection at $\{200\}$

Table 1. Selective reflection in BPI.

| | λ_1 : reflection at | λ_2 : reflection at | Possible space groups [22] |
|------|-----------------------------|-----------------------------|---|
| i) | (100) | (110) | P 23 |
| ii) | (110) | (200) | I 23; I 2 ₁ 3; I 4 ₁ 32 |
| iii) | (200) | (220) | |
| iv) | (111) | (211) | |

can only explain the experimental results if a C_2 is normal to the plane (23 crystals).

To decide between the possibilities i), ii), and iii), additionally the selection rules for Bragg scattering in BPs are to be taken into account which have been derived by Hornreich and Shtrikman [22] using a Landau theory approach.

From these selection rules (Tables III and IV in [22]) we will find out the following: *case iii)* A long-wavelength reflection at $\{200\}$ is only allowed in the chiral body-centered cubic space groups I 23, I 2₁3, and I 4₁32 assuming that the longest-wavelength reflection at $\{110\}$ is in the near infrared and was not observed. Reflection at $\{200\}$ is the visible band λ_1 whereas that at $\{220\}$ could be the u.v. band λ_2 . In between, however, there must occur an allowed reflection at $\{211\}$ which has not been found experimentally. Consequently, *case iii)* is not probable. *Case ii)* is in agreement with allowed reflections at the lowest-indexed planes $\{110\}$ and $\{200\}$ with no other reflections in between or at longer wavelengths for the bcc space groups I 23, I 2₁3, and I 4₁32. In *case i)* reflections are allowed at the lowest-indexed planes $\{100\}$ and $\{110\}$ for the simple cubic space groups P 23 and P 4₂32 but the latter one must be ruled out because the C_4 axis is normal to $\{100\}$. The space groups which are in agreement with the experimental results are given in Table 1. Three of them belong to the 23 class, one to the 432 class.

Concerning nonlinear effects in these two classes an essential difference must be stated: As the tensor ξ_1 in (1) exhibits the symmetry of the piezo-electric tensor, it vanishes in all centro-symmetric classes and in 432 [23]. Thus, in (1) all terms with odd powers of E vanish for 432 because a reversion of the field direction has to result in a reversion of polarisation.

A decision between the classes 23 and 432 would be possible by an experimental test if the observed electro-optic effect is of second or third order. This

is not possible hitherto. In solid crystals the second and still more the third order susceptibilities are rather small. In liquid systems where only a third order effect occurs (Kerr effect), the susceptibility strongly increases with the molecular polarity because the molecules will be oriented by the electric field (e.g. nitrobenzene). The same holds in the case of form-anisotropic liquid-crystalline compounds which exhibit a large Kerr effect just above the clearing point [24]. Thus, the rather high field-induced birefringence of the systems under discussion seems to be plausible.

Generally, by the influence of an electric field a crystal will be mechanically distorted. Thus an elasto-optic effect is superimposed upon the electro-optic one also changing the refractive index. In piezo-electric crystals as those of class 23 the strain depends linearly on E . In crystals which are not piezo-electric (class 432) the field produces an electrostriction resulting from a quadratic dependence of the strain on E [19]. A similar situation seems to occur in the BPI: The preservation but slow decrease of birefringence with time after switching off the field can be explained by a residual elasto-optic effect. The decrease of Δn with decreasing voltage U and its increase at $U < U_0$ as well as the 90° switch of the fast vibration direction at U_0 may be also caused by a superposition of electro-optic and elasto-optic effects as U_0 decreases with time depending on the history of the sample.

4.2. Electric field effects in the BP II

The birefringence observed in the BP II texture with a viewing direction parallel to the field (cf. Fig. 1) was extremely weak and could not be measured quantitatively. Further, the BP II birefringence was not oriented uniquely within the platelets and did not exhibit a dependence on field strength. Thus, the weak birefringence is interpreted to be caused by a mechanical strain built up within the BP II platelets by any response of the phase to the applied field. The strain remained for some time after switching off the field. The question arises why in contrast to the BPI a birefringence with its typical field strength dependence did not

occur in the BP II although it also possesses a cubic structure [8, 22]. According to the considerations given in the previous section it seems to be plausible that the field and observation directions must be parallel to a rotation axis of the BP II crystals of an order higher than two. In this case a uniaxial birefringence with the optic axis parallel to the field and thus to the observation direction is induced which could not be observed.

The Bragg scattering measurements of the BP II [15] also resulted in two reflection bands at longer and shorter wavelengths of a ratio 1.37 which is approximately $\sqrt{2}$ as found for the BPI. The optical effect observed in the polarizing microscope is due to the long wavelength reflection in the visible, which can occur either at (110) or (200) planes because of the Bragg equation (2) as shown above for BPI. As the absence of a field-induced biaxial birefringence in the BP II indicates a lattice plane with a C_n -axis of $n > 2$, (110) planes can be cancelled because their rotation axes are of order $n \leq 2$ in all cubic crystal classes. Within the enantiomorphic cubic classes (200) planes exhibit a two-fold rotational axis in 23 but a four-fold one in 432. Provided this symmetry also holds for the tensor ξ_1 of (1) only the class 432 is valid for the BP II.

During the phase transition BP II \rightarrow BPI caused by decreasing the temperature at constant field strength (cf. Fig. 2) obviously the four-fold rotational axis parallel to the field will be transformed into a C_1 or C_2 axis enabling a biaxial birefringence. Within the different striations (light and dark) the main axes of the indicatrix are oriented perpendicularly with respect to each other (cf. Figure 4). As only a rotation of 180° produces an identical position, another symmetry element additional to those of the indicatrix must exist which may originate from the chirality of the BPI structure.

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