Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Electric field-induced blue phases in liquid-crystalline systems of high chirality and negative dielectric anisotropy

B. Spier[a]; H. Stegemeyer[a]
[a] Institute of Physical Chemistry, University of Paderborn, Paderborn, F. R. Germany

To cite this Article Spier, B. and Stegemeyer, H.(1991) 'Electric field-induced blue phases in liquid-crystalline systems of high chirality and negative dielectric anisotropy', Liquid Crystals, 9: 1, 1 — 9

To link to this Article: DOI: 10.1080/02678299108036758

URL: http://dx.doi.org/10.1080/02678299108036758

LIQUID CRYSTALS, 1991, VOL. 9, NO. 1, 1-9

Electric field-induced blue phases in liquid-crystalline systems of high chirality and negative dielectric anisotropy

by B. SPIER and H. STEGEMEYER
Institute of Physical Chemistry, University of Paderborn, D-4790 Paderborn, F.R. Germany

(*Received 12 February 1990; accepted 9 August 1990*)

Electric field effects on liquid-crystalline blue phases (BP) of high chirality and negative dielectric anisotropy have been studied by polarizing microscopy and reflection spectrometry. Temperature-electric field phase diagrams are presented and selective reflections of different blue phases in electric fields are shown. In systems showing only BP I and BP III but lacking a zero field BP II an electric field-induced blue phase was observed in the temperature region of BP III and was identified as a BP II.

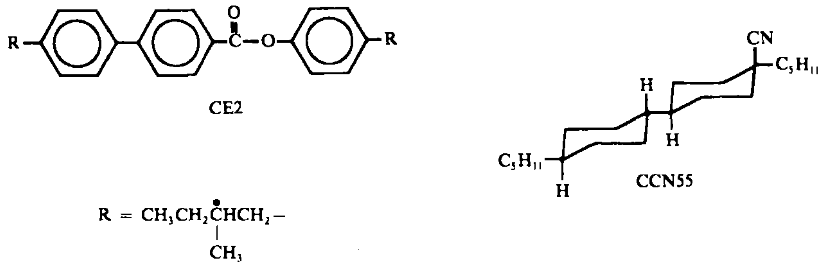
1. Introduction

Up to three liquid-crystalline blue phases can be observed in a small temperature range just below the clearing point in cholesterogenic compounds with sufficiently high chirality [1]. Cubic structures of BP I and BP II have been determined with space groups $I4_132$ (O^8) and $P4_232$ (O^2), but the structure of BP III, which exists immediately below the isotropic phase, is still unknown. The BP III appears amorphous and until now solely one weak broad selective reflection of polarized light [2] has been observed. Calorimetric measurements [3, 4] show that BP III is a thermodynamically stable phase; the transition enthalpy BP III/Iso is 50 times larger than those for BP I/BP II and BP II/BP III. This means that the BP III structure is more related to BP II than to the isotropic phase. Three models attempt to describe the properties of BP III: the quasicrystal model [5–8], the double twist model [9] and the randomized cubes model [10, 11]. All three models open the possibilities of electric field effects such as field-induced orientation and reorientation of BP III. Additionally field-induced phase transitions starting from BP III and resulting in other blue phases only stable in the field could be expected and have been observed by Yang and Crooker as well as by our group [12, 13].

In this paper we show experimentally and theoretically that even in mixtures lacking a field free BP II a field-induced phase transition BP III to BP II is observable.

2. Experiments

The mixtures investigated consisted of cholesterogenic CE2 (BDH) and nematogenic CCN55 (Merck). Because of an axial CN-group CCN55 possesses a negative dielectric anisotropy ($\Delta\varepsilon = -5$). The strong helical twisting power of CE2 allows high concentrations of the nematogenic CCN55 to keep $\Delta\varepsilon$ high enough without losing the high chirality. The samples were placed between tin oxide coated glass slides separated by 16 μm spacers. A modified Mettler hot stage FP5/52 was used to control the temperature. An electric field with square waves of 1 kHz was generated by a



Scheme 1.

function generator coupled to a high voltage amplifier. Observations were made with a polarizing microscope (Leitz Ortholux-Pol-II-BK) equipped with an illuminator for transmitted and reflected light. Selective reflection spectra of the samples were obtained by a spectrometer unit attached to the photo tube of the microscope. In all cases the field direction and the direction of observation were parallel. Because the selective reflections in BP I depend strongly on temperature, these measurements were accomplished close to the BP I/BP II or BP I/BP III phase transitions.

As samples with mole fractions $x_{CE2} > 0{\cdot}44$ show selective reflections in the UV the phase transitions could not be detected visually. In such cases the phase transitions have been detected by means of the intensity of the transmitted light, which was influenced by selective reflection and optical rotation in the various phases as described by Miller *et al.* [14]. We used 1 mm cuvettes, which fit well into the Mettler hot stage, FP52.

3. Results

Figure 1 shows the relative *x*–*T* phase diagram for CE2/CCN55 mixtures. As for the system of high chirality discussed by Collings and Crooker [14, 15] the BP II

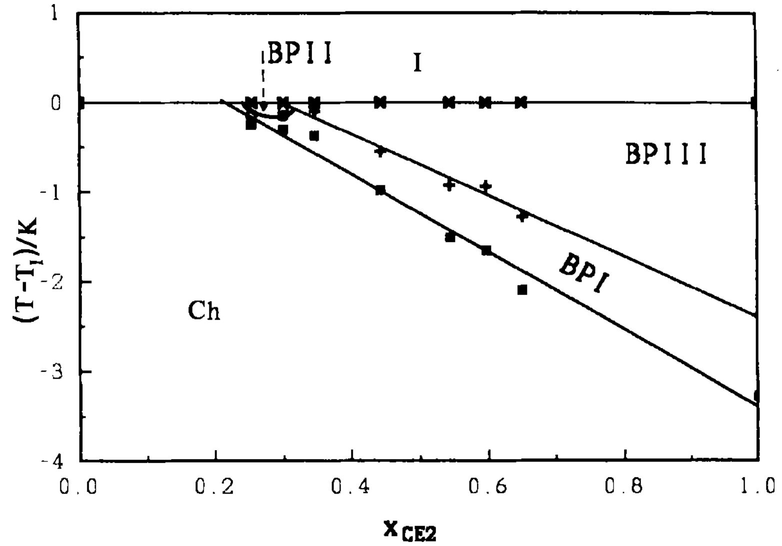


Figure 1. *x*–*T* phase diagram of the CE2/CCN55 mixed system. (Lines are guides for the eyes.)

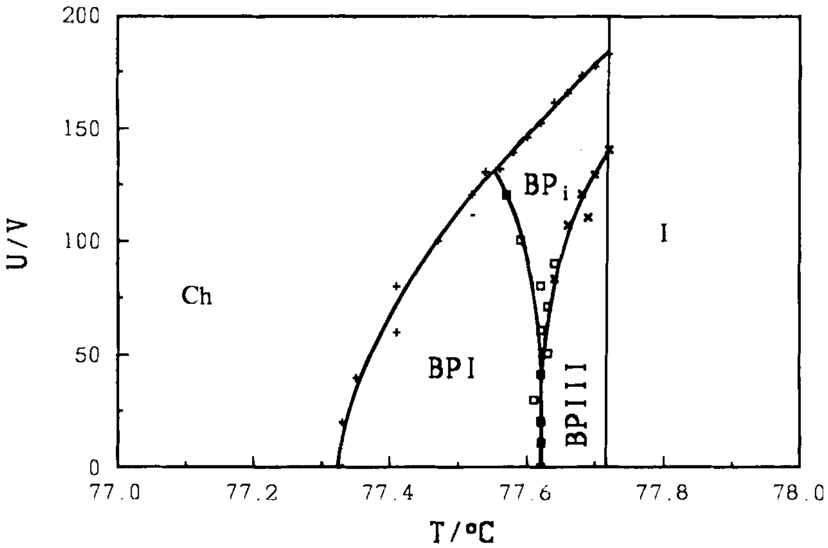


Figure 2. T–U phase diagram of a CE2/CCN55 mixture with x_{CE2} = 0·34. (Lines are guides for the eyes.)

extends only over a small concentration interval and disappears with increasing chirality (increasing mole fraction x_{CE2}). The temperature intervals of BP I and BP III increase with increasing chirality.

Investigation of a mixture with 0·34 mole fraction CE2 in an electric field leads to the T–U phase diagram given in figure 2. Below 50 V the phase transitions Ch/BP I, BP I/BP III and BP III/Iso are observed by isopotentially rising the temperature. But at higher voltages an additional phase BP$_i$ (i = induced) is inserted between BP I and BP III. With increasing voltages the BP$_i$ range increases more and more at the expense of the BP I and BP III. Above 130 V a phase transition Ch/BP$_i$ occurs without any BP I phase region in between. The phase transitions Ch/BP I, Ch/BP$_i$ and BP$_i$/BP III are shifted to higher temperatures by increasing electric fields but the reverse situation was found for the transition BP I/BP$_i$. The field-induced phase BP$_i$ exhibits a strong field dependent selective reflection of circulary polarized light (see figure 3). Platelets

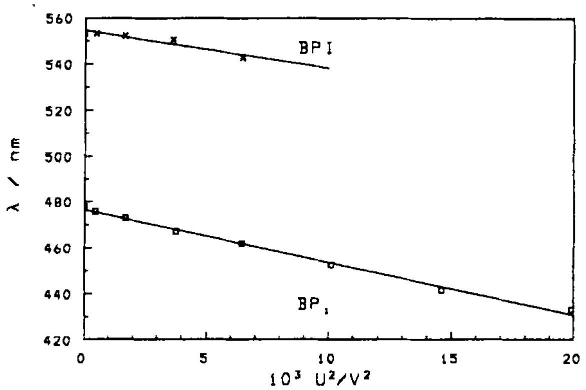


Figure 3. Selective reflection of circulary polarized light as function of U^2 for CE2/CCN55 with x_{CE2} = 0·34.

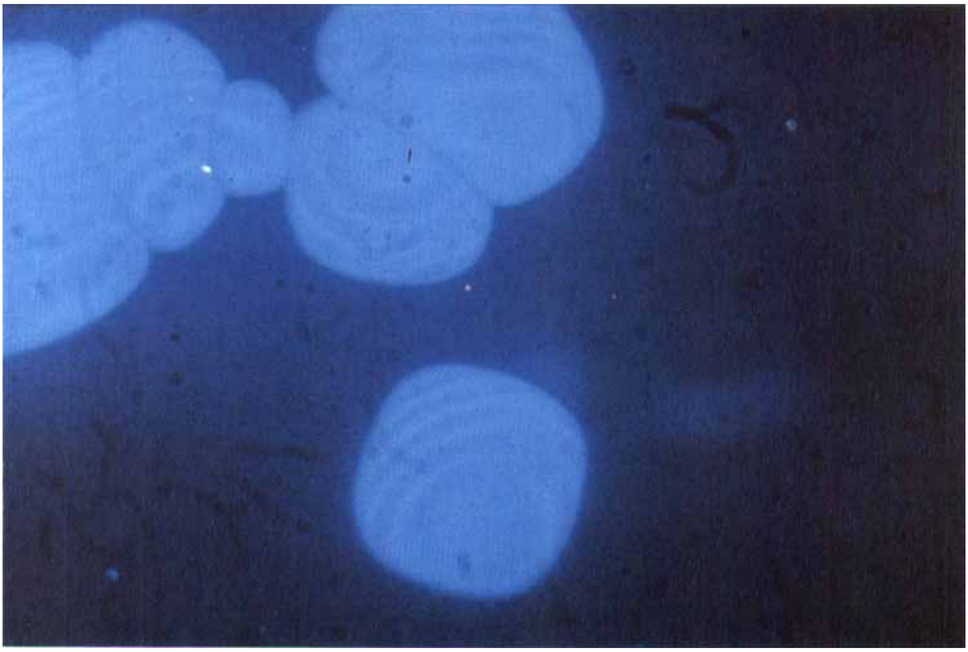


Figure 4. Quadratic single crystals of BP_i grown in an electric field.

with quadratic habit can be obtained from the BP III with increasing field strength (see figure 4). After turning off the field the BP_i platelets are slowly dissolved in the surrounding BP III. As the platelets only disappear very slowly the selective reflections of the BP_i could be measured down to 0 V (see figure 3).

The T–U phase diagram shown in figure 5 was obtained from a mixture containing 0·32 mole fraction CE2. As derived from the x–T phase diagram (see figure 1) in this

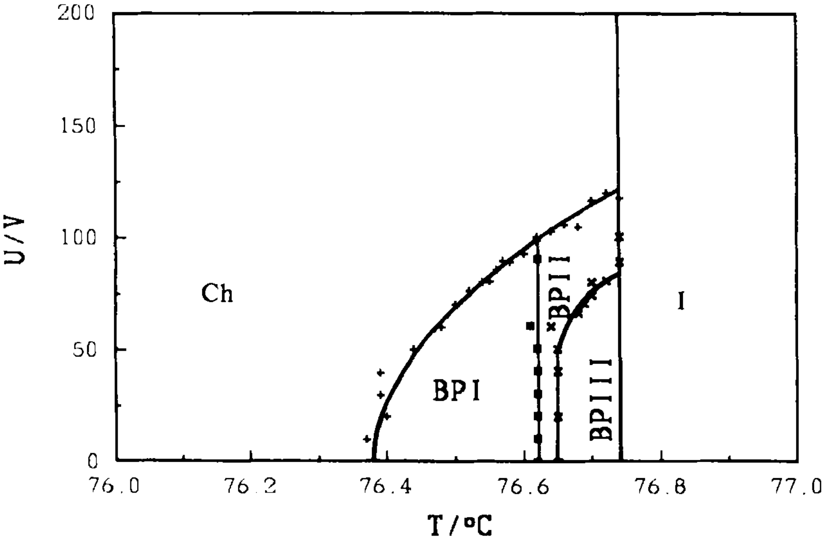


Figure 5. T–U phase diagram of a CE2/CCN55 mixture with $x_{CE2} = 0{\cdot}32$. (Lines are guides for the eyes.)

mixture a BP II also exists between the BP I and BP III. At low field strength the transition temperature BP II/BP III is field independent. But at higher fields the BP II/BP III transition temperature becomes field dependent and the BP II substitutes the BP III in the phase diagram. An electric field-induced hexagonal BP (BPH) as found by Heppke *et al.* [16] in another system with negative dielectric anisotropy was not observed in any mixtures of the examined. The reasons for the absence of BPH may be the high chirality and the different material we have used for our investigations.

4. Discussion

The question about the nature of the field-induced BP_i arises: Is the BP_i composed of the BP III building blocks (e.g. double twist cylinders [9] or cubes [10, 11]) which are oriented by the electric field or is the BP_i a field reinduced (and field distorted) BP II? The latter possibility is rather probable because the two mixtures under investigation (with and without a zero field BP II) are close together in the x–T phase diagram (see figure 1). Additionally the following results give evidence for an identity of the BP_i and BP II:

(i) quadratic shaped single crystals of the BP_i as in BP II (see figure 4),
(ii) similar phase behaviour of BP_i and BP II: both phases grow at the expense of the BP III in the T–U phase diagrams on increasing voltage.

The quadratic shapes of BP_i single crystals and the strong selective reflections are also compatible with a tetragonal phase as BP X [17]. This would mean a field-induced BP X starting from BP III.

Additional experiments were done to measure the selective reflections of BP I, BP II and BP_i as a function of field strength with the microscope spectrometer in corresponding mixtures. The different phases were always measured in their field stable orientations. Figures 4 and 6 show the wavelengths as functions of the square voltage. Using the values extrapolated to zero field to calculate the ratios of the selective reflection wavelengths $\lambda_{BP\,I}/\lambda_{BP\,II}$ and $\lambda_{BP\,I}/\lambda_{BP\,i}$ we obtain

$$(a)\ \frac{\lambda_{BP\,I}}{\lambda_{BP\,II}} = \frac{589\,\mathrm{nm}}{506\,\mathrm{nm}} = 1{\cdot}164$$

and

$$(b)\ \frac{\lambda_{BP\,I}}{\lambda_{BP\,i}} = \frac{554\,\mathrm{nm}}{476\,\mathrm{nm}} = 1{\cdot}164.$$

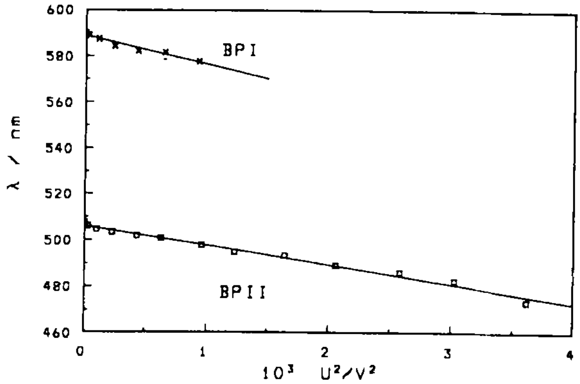


Figure 6. Selective reflection of circulary polarized light as function of U^2 for CE2/CCN55 with $x_{CE2} = 0{\cdot}32$.

The equality of these ratios, which are similar to that obtained by Onusseit [18] (BP I/BP II ≈ 1·15) give further evidence for the identity of BP_i and BP II. The calculated selective reflection ratios also allow a field-induced BP X to be ruled out. According to Pieranski and Cladis [17] the BP II/BP X phase transition is characterized by a jump of the selective reflection to longer wavelengths. As we have shown at the phase transition BP I/BP II a jump to shorter selective reflection wavelengths occurs. That means that the ratio $\lambda_{BP\,I}/\lambda_{BP_i}$ should be smaller than the ratio $\lambda_{BP\,I}/\lambda_{BP\,II}$, because $\lambda_{BP\,X}$ should be longer than $\lambda_{BP\,II}$. Even the mixture with a zero field BP II does not show a field-induced BP X, because there is no jump or change of slope in the selective reflection with increasing field strength (see figure 6).

If BP_i is really identical with BP II, then on cooling BP I crystals should be obtained with the typical cross-hatching from BP_i as in the field free case [19]. Indeed, if we cooled BP_i single crystals at constant voltage BP I crystals are developed which exhibit cross-hatching.

5. Thermodynamic considerations

An approach to understand the reinduction of the BP II by an electric field can be achieved by means of a thermodynamic consideration [20, 21]. In contrast to other authors [22, 23] who treated field induced orientation, birefringence and biaxiality of BPs theoretically but excluded field-induced phase transitions we are only interested in the latter case. Thus it is the purpose of this section to show that non-linear dielectric effects of higher order are a possible explanation for the reinduction of BP II (BP_i) by an electric field.

The following conditions are fulfilled for two phases α and β at equilibrium: equality of temperature, pressure and electric fields in both phases, and also the chemical potentials of the components i are equal: $\mu_i^\alpha = \mu_i^\beta$. Treating the pressure p as a constant (all experiments were performed isobarically) we need the temperature (T) and field (E) dependences of the chemical potentials which are

$$\left(\frac{\partial \mu_i}{\partial T}\right)_{p,E} = -\bar{S}_i, \tag{1}$$

$$\left(\frac{\partial \mu_i}{\partial E}\right)_{T,p} = -\bar{P}_i. \tag{2}$$

Here $\bar{S}_i$ means the partial molar entropy and $\bar{P}_i$ is the partial molar polarization for the component i. In any way the chemical potential is decreased by an increase of temperature or electric field. Additionally the partial molar polarization $\bar{P}_i$ is a function of the electric field

$$\bar{P}_i = \bar{\chi}_{0i} E, \tag{3}$$

where $\bar{\chi}_{0i}$ is the partial molar dielectric susceptibility of component i.

At constant temperature the chemical potential of component i is given as a function of the electric field strength E by

$$\mu_i = \mu_{i0} - \tfrac{1}{2}\varepsilon_0 \bar{\chi}_i E^2. \tag{4}$$

In this equation μ_{i0} represents the chemical potential without an electric field and ε_0 is the permittivity of a vacuum. Equation (4) is valid for weak electric fields acting on isotropic materials. For anisotropic materials, such as crystals, the partial dielectric

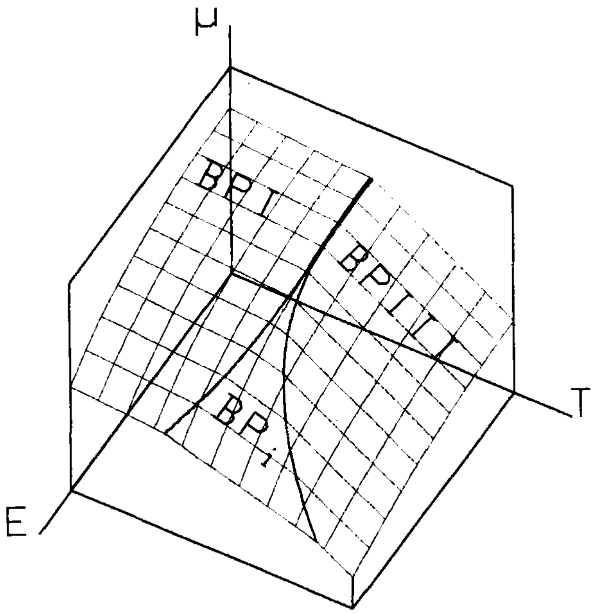


Figure 7. T–E–μ phase diagram for BP I, BP$_i$ and BP III.

susceptibility $\bar{\chi}_i$ is replaced by a second rank tensor

$$\mu_i = \mu_{i0} - \tfrac{1}{2}\varepsilon_0[\bar{\chi}_{i,kl}]E_k E_l. \tag{5}$$

(N.b. i is the index for the component i of the mixture; k and l are indices of the second rank tensor.) Higher field strengths induce additional non-linear effects and this equation has to be extended to the third and the fourth rank susceptibility tensors

$$\mu_i = \mu_{i0} - \tfrac{1}{2}\varepsilon_0[\bar{\chi}_{i,kl}]E_k E_l - \tfrac{1}{3}\varepsilon_0[\bar{\chi}_{i,klm}]E_k E_l E_m - \tfrac{1}{4}\varepsilon_0[\bar{\chi}_{i,klmn}]E_k E_l E_m E_n. \tag{6}$$

Because these tensors represent properties of crystals, they have to possess at least the same kind and number of symmetry elements as the crystal itself (principle of Neumann [24]) which is reflected in the tensor coefficients. For cubic crystals of point group 432 to which BP I and BP II belong the tensor of third rank vanishes and equation (6) becomes

$$\mu_i = \mu_{i0} - \tfrac{1}{2}\varepsilon_0[\bar{\chi}_{i,kl}]E_k E_l - \tfrac{1}{4}\varepsilon_0[\bar{\chi}_{i,klmn}]E_k E_l E_m E_n. \tag{7}$$

From this equation it is seen that non-linear electric field effects on BP I and BP II may be represented by a tensor of fourth rank and then depend on the fourth power of E. It is now possible to calculate a three dimensional T–E–μ phase diagram which describes the induction of BP$_i$ and its phase boundaries in a qualitatively correct manner. The following assumptions are made to obtain the phase diagram (see figure 7).

(*a*) In mixtures of high chirality, which exhibit only BP I and BP III in the field-off state, the chemical potential μ of BP$_i$ has to be higher than those of BP I and BP III in the field free case. This means: BP$_i$ and BP III are stable and visible, BP$_i$ is unstable and not recognized.

(*b*) To induce BP$_i$ the chemical potential of BP$_i$ has to be lowered more by the electric field than those of BP I and BP III. This is achieved by the assumption

> that the non-linear effects in the dielectric susceptibilities, which are approximated by a tensor of fourth rank, for BP_i are stronger than for BP I and BP III. The susceptibilities represented by a tensor of second rank are the same in all three phases.

In figure 7 it is seen that at zero field BP_i does not exist in the phase diagram because the chemical potential of BP_i is higher than those of BP I and BP III for all temperatures. An increase of the field strength causes a decrease of the three chemical potentials; that of BP_i is decreased the most and the BP_i is inserted between the BP I and BP III. Before induction of BP_i the phase transition point BP I/BP III is shifted to higher temperatures because the non-linear dielectric effects of the susceptibility of BP I is larger than the susceptibility of BP III. But this effect is small for small differences in susceptibility and for low fields.

After induction of BP_i the transition point BP I/BP_i is shifted to lower temperatures but the phase transition BP_i/BP III is moved to higher temperatures by an increase of the electric field because the induced susceptibility of BP_i is larger then for BP I and BP III.

Comparing the phase boundaries of BP_i in figures 2 and 7 shows good topological agreement though solely the fourth rank susceptibility tensor was used to calculate the chemical potentials of the different phases. Therefore the field-induced reinduction of BP II (BP_i) can be understood and described to a good approximation by non-linear dielectric effects.

6. Conclusion

In mixtures of CE2/CCN55 with negative dielectric anisotropy and sufficiently high chirality which do not exhibit a BP II at zero field an additional phase, BP_i, is induced by an electric field starting from the BP III. From the following results it has been suggested that the BP_i is identical with a field-distorted BP II:

(i) formation of quadratic shaped single crystals of the BP_i;
(ii) similar phase behaviour of BP_i and BP II in the *T–U* phase diagrams (both substitute the BP III on increasing voltage);
(iii) equal ratios of Bragg reflection wavelengths $\lambda_{BP\,I}/\lambda_{BP\,II}$ and $\lambda_{BP\,I}/\lambda_{BPi}$;
(iv) occurrence of a cross-hatching in BP I single crystals formed on cooling the BP_i at constant field.

The relation of the BP III and the field-induced BP II in the *T–E* phase diagrams given in this paper possibly allows some suggestions concerning the still unknown structure of the BP III. One of several possibilities to describe the BP III structure [25] is the cubic domain model first proposed by Collings [11]. It is assumed that the BP III consists of randomly oriented fluctuating domains of an area a few pitch lengths in size in which the molecules are arranged in a BP II simple cubic structure. The cubic domains are dynamic entities separated from each other by structural defects. An electric field orients these domains with respect to each other forming a bulk BP II structure with far fewer defects. The *T–E* phase diagrams presented here give some indications that such a coalescence of BP II domains may take place in the field. It is well known that the BP III behaves like a fluid which is nothing but a molten BP II crystal with a large number of defects partially vanishing by the influence of an electric field.

This work has been supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. The authors wish to thank E. Merck, Darmstadt (Germany), and BDH, Poole (England), for providing them with liquid crystals.

References

[1] STEGEMEYER, H., BLÜMEL, TH., HILTROP, K., ONUSSEIT, H., and PORSCH, F., 1986, *Liq. Crystals*, **1**, 3.
[2] DEMIKHOV, E. I., DOLGANOV, V. K., and KRYLOVA, S. P., 1985, *Pis'ma Zh. éksp. teor. Fiz.*, **42**, 15 [1985, *JETP Lett.*, **42**, 16].
[3] KLEIMAN, R. N., BISHOP, D. J., PINDAK, R., and TABOREK, P., 1984, *Phys. Rev. Lett.*, **53**, 2137.
[4] THOEN, J., 1988, *Phys. Rev.* A, **37**, 1754.
[5] HORNREICH, R. M., and SHTRIKMAN, S., 1986, *Phys. Rev. Lett.*, **56**, 1723.
[6] HORNREICH, R. M., and SHTRIKMAN, S., 1986, *Phys. Lett.* A, **115**, 451.
[7] ROKHSAR, D. S., and SETHNA, J. P., 1986, *Phys. Rev. Lett.*, **56**, 1727.
[8] FILEV, V. M., 1986, *Pis'ma Zh. éksp. teor. Fiz.*, **43**, 523 [1986, *JETP Lett.*, **43**, 677].
[9] HORNREICH, R. M., KUGLER, M., and SHTRIKMAN, S., 1982, *Phys. Rev. Lett.*, **48**, 1404.
[10] BELYAKOW, V. A., DEMIKHOV, E. I., DMITRIENKO, V. E., and KRYLOVA, V. K., 1985, *Zh. éksp. teor. Fiz.*, **89**, 2035 [1985, *Sov. Phys. JETP*, **62**, 1173].
[11] COLLINGS, P. J., 1984, *Phys. Rev.* A, **30**, 1990.
[12] YANG, D. K., and CROOKER, P. P., 1988, *Phys. Rev.* A, **37**, 4001.
[13] SPIER, B., and STEGEMEYER, H., 1988, *Twelfth International Liquid Crystal Conference*, Freiburg, Poster CH13.
[14] MILLER, J. D., BATTLE, P. R., COLLINGS, P. J., YANG, D. K., and CROOKER, P. P., 1987, *Phys. Rev.* A, **35**, 3959.
[15] YANG, D. K., and CROOKER, P. P., 1987, *Phys. Rev.* A, **35**, 4419.
[16] HEPPKE, G., JÉROME, B., KITZEROW, H.-S., and PIERANSKI, P., 1989, *Liq. Crystals*, **5**, 813.
[17] PIERANSKI, P., and CLADIS, P. E., 1989, *Phys. Rev.* A, **35**, 355.
[18] ONUSSEIT, H., 1983, Thesis, Paderborn, p. 25.
[19] ONUSSEIT, H., and STEGEMEYER, H., 1981, *Z. Naturf.* (*a*), **36**, 1083.
[20] KIRKWOOD, J. G., and OPPENHEIM, I., 1961, *Chemical Thermodynamics* (McGraw-Hill), p. 231.
[21] VAN HECKE, G. R., 1976, *J. chem. Educ.*, **53**, 161.
[22] LUBIN, D., and HORNREICH, R. M., 1987, *Phys. Rev.* A, **36**, 849.
[23] DMITRIENKO, V. E., 1989, *Liq. Crystals*, **5**, 847.
[24] NYE, J. F., 1985, *Physical Properties of Crystals* (Oxford University Press), p. 20.
[25] CROOKER, P. P., 1989, *Liq. Crystals*, **5**, 751.