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

Blue phase mixtures exhibiting low fractions of a chiral compound experimental observation of some unusual properties

G. Heppke[a]; H. -S. Kitzerow[a]; D. Lötzsch[a]; Ch. Papenfuß[a]
[a] Iwan-N.-Stranski-Institut, Technische Universität Berlin, Berlin 12, F.R. Germany

To cite this Article Heppke, G. , Kitzerow, H. -S. , Lötzsch, D. and Papenfuß, Ch.(1990) 'Blue phase mixtures exhibiting low fractions of a chiral compound experimental observation of some unusual properties', Liquid Crystals, 8: 3, 407 — 418
To link to this Article: DOI: 10.1080/02678299008047356
URL: http://dx.doi.org/10.1080/02678299008047356

LIQUID CRYSTALS, 1990, VOL. 8, NO. 3, 407–418

Blue phase mixtures exhibiting low fractions of a chiral compound

Experimental observation of some unusual properties†

by G. HEPPKE, H.-S. KITZEROW, D. LÖTZSCH and Ch. PAPENFUß
Iwan-N.-Stranski-Institut, Technische Universität Berlin, Sekr. ER 11,
Strasse des 17. Juni 135, D-1000 Berlin 12, F.R. Germany

(*Received 15 February 1990; accepted 16 April 1990*)

We have used chiral compounds with very high helical twisting power as components in induced-cholesteric mixtures in order to obtain new blue phase systems. In one of these mixtures an *unusual large blue phase temperature range* of more than 10 K was observed. The lattice constant of the BPI in this system *increases* strongly with increasing temperature, a behaviour observed for the first time. The threshold voltage for the field-induced BP/cholesteric phase transition in this mixture *decreases* with increasing temperature. Thus the *reentrant* phase sequence cholesteric phase–blue phase–cholesteric phase–isotropic phase can be observed with increasing temperature if an electric field is applied to the sample.

1. Introduction

During the past few years the blue phases (BP) occurring in chiral liquid crystal systems have been studied extensively [1]. As far as their structural aspects are concerned, the observations reveal a chiral cubic lattice for the modifications BP I and BP II and an amorphous or quasi-crystalline structure for BP III (or blue fog). One of the spectacular properties of blue phases is Bragg reflection in the visible wavelength range due to the size of the lattice constants (several hundreds of nanometres). Very brilliant electro-optic effects [2] can be observed in BP systems due to electrostriction [3, 4] and due to field-induced phase transitions [5].

In most systems studied the temperature range for the existence of blue phases is very small (typically of the order 0·1 K in pure compounds and of the order 1 K for the BP–isotropic two phase region in mixtures). Only in a few mixtures have larger temperature ranges been found [6, 7], either due to phase separation in mixtures containing many compounds, or due to the fact that BP I can be supercooled with respect to the cholesteric phase.

Although the first observation of a blue phase was made more than one hundred years ago, the development of blue phase materials is still in progress. Only in the past 15 years has the investigation of blue phases been extended to substances different from the derivatives of cholesterol [8] and more recently it has been shown that blue phases can occur also in induced-cholesteric mixtures containing a nematogenic compound and a non-mesogenic chiral dopant [7]. Because of the requirement of high chirality, blue phases have so far been observed only in pure chiral substances or in mixtures containing large fractions of chiral compounds.

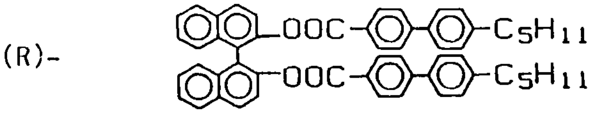
---

† The experimental results of this paper were presented at the *5th European Winter Liquid Crystal Conference 1987*, Borovets, Bulgaria.

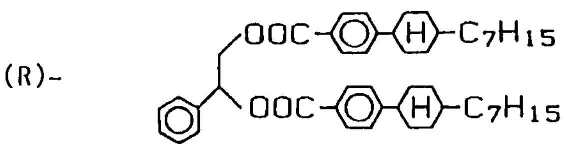
In this paper, we present investigations on new induced-cholesteric blue phase systems which contain only a very small fraction of the chiral dopant. Recently, mesogenic chiral esters of 1,1′-bi-2-naphthol, 1-phenyl-1,2-ethandiol and 1,2-diphenyl-1,2-ethandiol have been synthesized [9] which exhibit unusually high values of the helical twisting power (HTP = $(pc)^{-1}$, where c is the concentration of the chiral dopant in a nematic solvent and p is the resulting pitch. Usually the twisting power is constant over a wide range of concentration.) From the extremely high HTP values reported in [9], blue phases were expected to occur in induced-cholesteric mixtures with less than 10 wt % concentration of the chiral dopant. Some of these new chiral dopants exhibit very high absolute values of the HTP temperature coefficients, in contrast to the systems studied so far. For the systems investigated earlier, the BP lattice constants were found to decrease with temperature in BP I and to be nearly constant in BP II [1]. An additional aspect of the investigations reported here was to study the influence of the temperature dependence of the cholesteric pitch on the temperature dependence of the lattice constants of the blue phases occurring in the mixture. In the second part of the paper, investigations on electric field effects are reported for one of the new mixtures exhibiting a positive dielectric anisotropy. This mixture attracted our interest due to the very large temperature range of its blue phases. It is found that this mixture exhibits unusual behaviour under the influence of an electric field, namely a new example of reentrancy.

2. Experiment

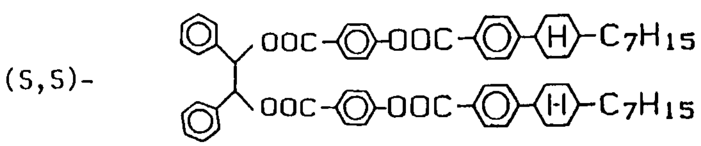
By means of optical polarizing microscopy, we have studied the occurrence of blue phases in induced-cholesteric mixtures using the chiral compounds described in [9]. For preliminary investigation, contact preparations between a nematogenic compound and each of these dopants were studied. More detailed investigations were performed using mixtures containing as the non-chiral component the wide temperature range nematic mixture RO–TN 404 (Hoffmann La Roche) which consists of cyano-substituted pyrimidine and biphenyl derivates. In particular, results are reported here for three mixtures containing RO–TN 404 and each of the following chiral additives:



(1)



(2)



(3)

In order to determine the helical twisting power the cholesteric pitch was measured using the Cano method [10] for solutions exhibiting concentrations of the chiral dopant between 0·1 per cent and 2·0 per cent (by weight). The HTP values for the compounds (1) and (2) were reported earlier [9], whereas HTP for compound (3) is presented here for the first time.

The occurrence of blue phases requires higher fractions of the chiral compound than those mixtures used in the Cano experiment. In order to investigate mixtures of high chirality, the Bragg peaks of the cholesteric phase and the blue phases were investigated in back reflection using a multielement spectoradiometer PR-702 A (Photo Research) [11]. The Bragg wavelengths observed spectroscopically are related to the pitch of a cholesteric phase by

$$\lambda_{\mathrm{Ch}} = n_{\mathrm{Ch}} p \cos \vartheta, \qquad (1)$$

or to the lattice constant a_{BP} of a cubic blue phase by

$$\lambda_{hkl} = \frac{2\bar{n}a\cos\vartheta}{\sqrt{(h^2 + k^2 + l^2)}}. \qquad (2)$$

Here n_{Ch} and $\bar{n}$ are mean refractive indices, (h, k, l) are the Miller indices of a family of planes in the cubic lattice and ϑ is the angle between the direction of light incidence and the respective reciprocal lattice vector. For these spectroscopic investigations, the sample was covered by two glass slides and contained in a copper block. The temperature of this block was controlled by a Haake F3/S thermostat and the temperature close to the cell was measured separately using chromel–alumel thermocouples allowing an accuracy of ± 0·03°C.

Phase diagrams were studied by microscopic observation of the textures occurring in transmission between crossed polarizers. In this experiment, a Mettler hot stage FP 2 with an accuracy of better than 0·1°C was used in order to determine the transition temperatures.

In order to determine the clearing temperature for mixtures of very high chirality, a new method was employed in which the effect of field-induced phase transitions from blue phases to the cholesteric phase was utilized. For mixtures in which the Bragg wavelength of the blue phase is expected to be in the UV region, optical observation allows us only to determine the temperature where the cholesteric phase vanishes if the sample is heated. A blue phase occurring in this mixture cannot be distinguished from the isotropic phase since both phases appear dark between crossed polarizers. It is well-known [12], however, that by applying a sufficiently high voltage, the cholesteric phase can be induced in the blue phase temperature range, but not for temperatures above the clearing point [13]. The induced cholesteric phase appears with a bright focal conic texture for mixtures with positive dielectric anisotropy. Thus, the clearing temperature can be determined either by optical observation or by recording the output of a photomultiplier connected to the microscope tube. This method allows us to distinguish between the temperature region of homogeneous blue phase and the temperature region of coexistence of two phases close to the clearing point. It does not allow us to determine whether the observed blue phases are BP I, BP II or BP III. When using this procedure, we applied an AC voltage of 60 V to a sample of 9 μm thickness. In order to avoid hysteresis, this voltage was modulated (on/off) with a frequency of 1 Hz while heating the sample very slowly (< 0·2°C/min).

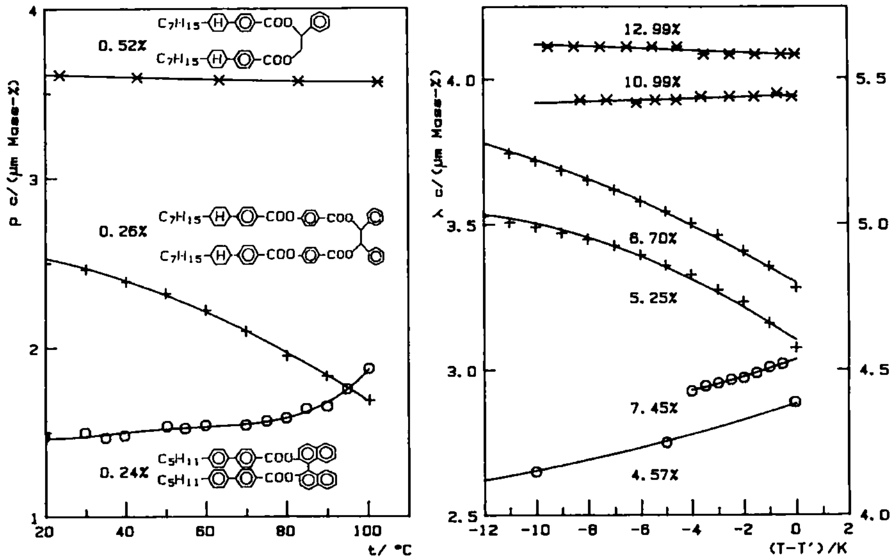
In order to investigate electrostrictive effects and phase diagrams in the electric field-temperature plane, AC voltages (f = 1 kHz) up to 60 V were applied to 9 μm cells with transparent electrodes and TN-type surface treatment. The selective reflection and the textures under the influence of the electric field were observed with a polarizing microscope as described previously. In addition, measurements of the dielectric permittivity as a function of applied field strength were performed. For this purpose, the variable 1 kHz voltage was modulated with a constant measuring voltage of 1·5 V at $f = 16\,\text{kHz}$. A signal proportional to the capacitance of the cell was obtained by measuring the voltage drop at a capacitor with $C = 1\,\mu\text{F}$ in series with the cell using a lock in amplifier, selectively for $f = 16\,\text{kHz}$ [14].

3. Results and discussion

3.1. *Occurrence of blue phases and temperature dependence of the lattice constants*

The investigation of contact preparations shows that blue phases occur in mixtures of nematic RO–TN 404 with one of the chiral dopants (1) (designated as compound '7' in [9]), (2) ('2' in [9]) or (3) as well as with compounds '6' and '14' in [9]. For compounds (1) to (3) which are investigated here more closely, we also checked whether blue phases occur in mixtures made with the nematic material EN 18 (Chisso), which exhibits a negative dielectric anisotropy. Blue phases were found for mixtures of EN 18 with either compound (2) or (3).

A comparison of the pitch values measured by the Cano method and by Bragg reflections in mixtures with higher chiral concentration shows (see figure 1) that the product of pitch and concentration is almost constant for the same reduced temperature. Furthermore the large temperature dependence of the twisting power observed



(*a*) (*b*)

Figure 1. Temperature dependence of the cholesteric pitch for mixtures of the chiral compounds with RO–TN 404. (*a*) Product of pitch, *P* (measured by the Cano method [10]) and concentration, *c*, versus temperature, *t*. (*b*) Product of the Bragg wavelength of the cholesteric phase and the concentration versus the shifted temperature (T' being the temperature for the phase transition from the cholesteric phase to either the blue phase or isotropic phase for the respective mixture). (o) compound (1), (∗) compound (2), (+) compound (3).

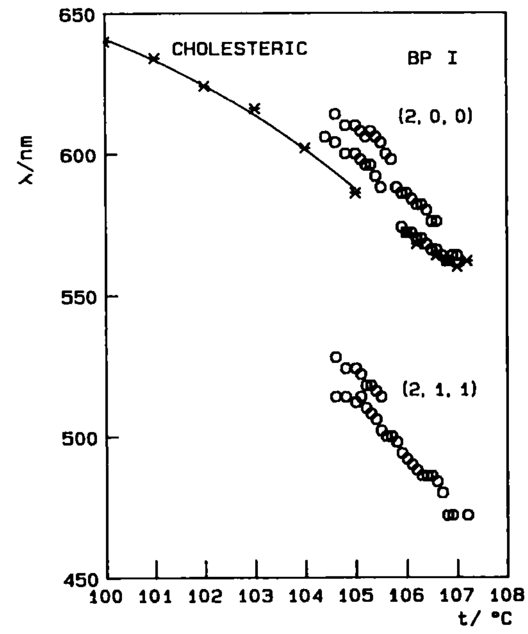


Figure 2. Temperature dependence of the Bragg wavelengths for the cholesteric phase and the BP I observed on heating (*) and cooling (O) for a mixture of 5·25 mass % of compound (3) with RO–TN 404.

for compounds (1) and (3) by the Cano method occurs also in mixtures with a high concentration of the chiral compound.

For the mixtures containing compound (2) or (3), BP I and BP II were observed. For the mixtures of compound 2 with RO–TN 404, which exhibit a cholesteric pitch independent of temperature, the temperature dependence of the lattice contants of BP I and BP II is in agreement with previous observations for other materials [1]. A decrease of the lattice constant with increasing temperature is observed in BP I, whereas BP II shows a lattice constant which is independent of temperature. The same behaviour was observed in mixtures of compound (3) with RO–TN 404, except that the decrease of the lattice constant of BP I with increasing temperature (see figure 2) is very large (about 4 per cent/°C).

However, a completely different behaviour compared to the systems studied so far is shown by a mixture of compond (1) with RO–TN 404. In this mixture, an increase of the lattice constant of BP I with increasing temperature was found (see figure 3 (*a*)). The solution of 8·55 per cent of compound (1) in RO–TN 404 shows only one blue phase. This phase was identified as BP I by studying the angular dependence of the selective reflection. As shown previously [11], a family of planes (*hkl*) which are not parallel to the sample surface can also be observed in our scattering experiment if the second interface of the sample is reflecting. The Bragg wavelength corresponding to these planes can increase with increasing angle, θ, of light incidence with respect to the surface normal, provided that the angle ϑ between the corresponding reciprocal lattice vector and the direction of light incidence decreases with increasing θ. For BP I, two peaks showing this unusual behaviour can be observed in the wavelength range between the first and the second Bragg peak whereas for BP II only one peak showing this behaviour is observed in the respective wavelength range [11]. Thus, the angular

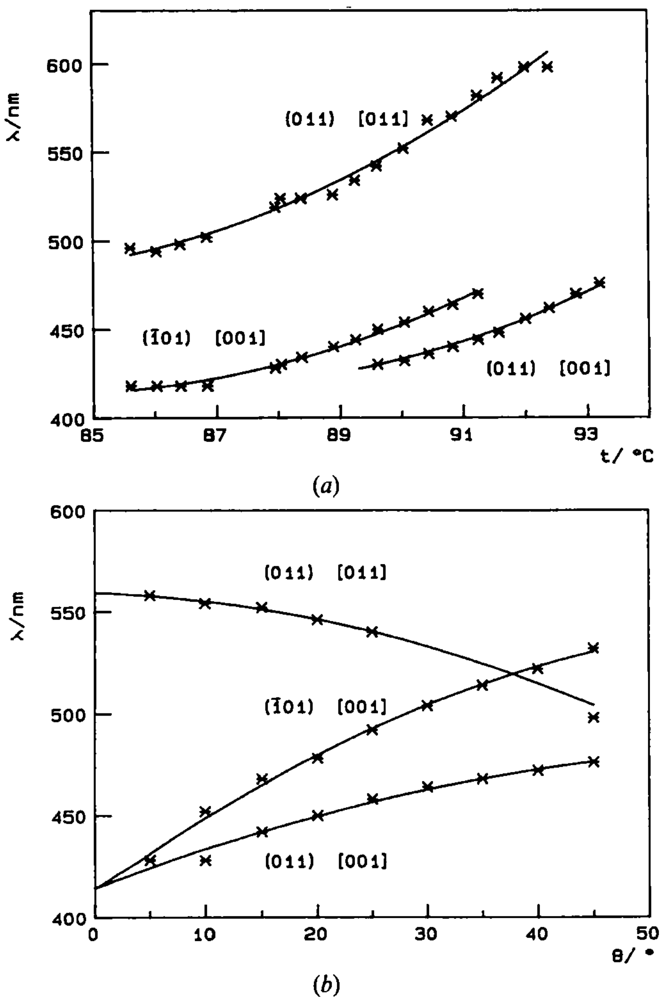


Figure 3. (*a*) Temperature dependence of the Bragg wavelength for the blue phase occurring in a mixture of 8·55 mass % of compound (1) in RO–TN 404 (angle of light incidence 10°, heating rate 0·1°C/min). (*b*) Angular dependence of the Bragg wavelengths at 90·5°C for the same sample.

dependence represented in figure 3 (*b*) is in agreement with the body centred cubic structure of BP I.

Another remarkable property of the mixtures of compound (1) with RO–TN 404 is the very wide blue phase temperature range (see figure 4). Note that the temperature range of the blue phase increases with increasing chirality up to 11°C. Since the investigated system is a multicomponent mixture, we observed BP–isotropic two phase regions close to the clearing temperature, as indicated in figure 4. But even compared to the two phase regions in other multicomponent systems the BP temperature range observed here is unusually large. So far, a larger temperature range has been reported only in the paper by Gerber [6]. However, in Gerber's work the transition temperatures were determined by cooling so that the temperature interval includes also the metastable range of the supercooled BP I which can be much larger than the thermodynamically stable interval corresponding to the transition temperatures determined, as in figure 4, by heating.

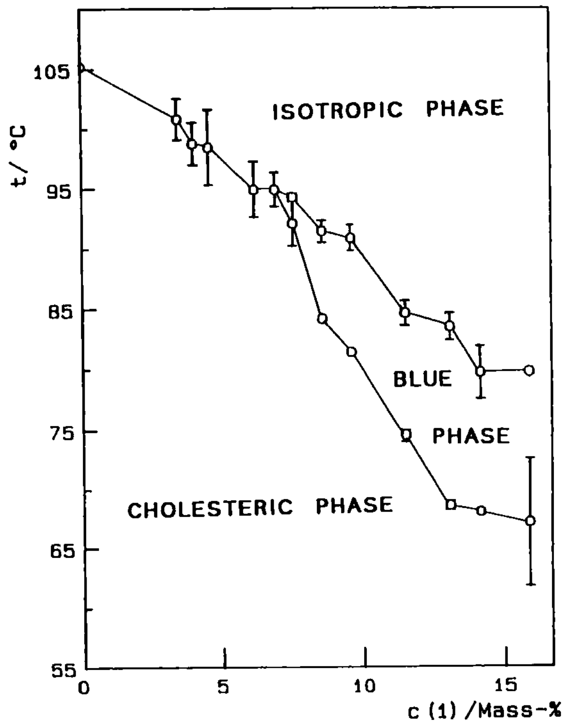


Figure 4. Phase diagram in the chirality-temperature plane for mixtures of compound (1) with RO–TN 404. The transition temperatures were determined on heating. Vertical bars indicate the temperature region of coexistence of two phases. For the mixtures exhibiting lattice constants in the UV region ($c > 9{\cdot}7$ mass %), the clearing temperatures are determined by switching from the non-visible BP to the field-induced cholesteric phase.

The chirality in mixtures of compound (1) and RO–TN404 is limited by the solubility of the chiral dopant. Homogeneous mixtures were obtained only for solutions containing less than 16 per cent of compound (1). For a mixture of this maximum concentration the cholesteric pitch is as small as 130 nm. The longest pitch, p_{cr}, for which a blue phase is allowed is $p_{cr} \approx 325$ nm. For concentrations less than 10 per cent of the chiral component, the Bragg wavelengths are in the visible range. For these concentrations only one blue phase was observed, as for the 8·55 per cent mixture described previously. Not only the angular dependence of the selective reflection but also contact preparations with a well-known mixture of CB 15 and RO–TN404 [2] show that this modification is BP I.

For concentrations larger than 10 per cent of chiral compound (1), it cannot be excluded that the modifications BP II or BP III also occur in the blue phase temperature range. For these high concentrations, the Bragg wavelengths of the blue phases are in the ultraviolet region and the blue phases cannot be distinguished from the isotropic phase by optical observation between crossed polarizers. Thus, for these mixtures the electrooptic effect of the field-induced phase transition BP I/Ch has been used to determine the transition temperatures (as described previously). This method does not allow us to distinguish between the different blue phase modifications.

3.2. *Observation of reentrant behaviour in an electric field*

For a solution of 8·55 per cent of compound (1) in RO–TN404, which exhibits a large BP I temperature range and a BP I selective reflection in the visible spectral range, the behaviour under the influence of an electric field was investigated with respect to electrostrictive effects and with respect to field-induced phase transitions. With respect to electrostriction, a shift of the (110) peak to larger wavelength with increasing field strength was observed for the orientation [110] || **E**. This behaviour is in agreement with observations for other mixtures with positive dielectric anisotropy [2,4]. For the orientation [100] || **E**, which was obtained by heating the sample from the planar texture of the cholesteric phase (Grandjean texture), a peak corresponding to the (200) planes can be observed. For this orientation, no influence of the electric field on the (200) interplanar spacing could be detected within our experimental accuracy of ± 2 nm. This behaviour is also similar to other materials with positive dielectric anisotropy, in which a very small decrease of the lattice constant in the field direction with increasing field strength was found [4].

A very interesting phenomenon, however, was observed concerning the field-induced phase transition from BP I to the cholesteric phase. The field strength $E_{\mathrm{BP-Ch}}$ for this transition decreases with increasing temperature, as can be seen by optical observation of the sample (figure 5). This behaviour was established also by dielectric measurements (see figure 6). As a consequence of this behaviour, a reentrancy can be observed. If a constant voltage was applied to the sample and if the sample was heated with a very small heating rate ($< 0{\cdot}05$°C/min), the reentrant phase sequence Ch–BP I–Ch–I could be observed under the polarizing microscope. The corresponding phase diagram in the electric field-temperature plane is shown schematically in figure 7.

The unusual temperature dependence of the field strength $E_{\mathrm{BP-Ch}}$ which was observed here for the first time, can be explained by the large temperature dependence of the chirality in mixtures of compound (1). Previously, the influence of the concentration in other chiral nematic mixtures on the transition field strength $E_{\mathrm{BP-Ch}}$ close to the clearing temperature caused the value of $E_{\mathrm{BP-Ch}}$ to *increase* with increasing chirality [5]. The system investigated here exhibits, for constant composition, a *decreasing* chirality with increasing temperature. This chirality decrease is due to the temperature dependence of the twisting power of the chiral dopant (see figure 1). In the two phase region an additional decrease of chirality may occur due to a decrease of the concentration of the chiral component in the BP droplets. Thus, our observation that the transition field strength $E_{\mathrm{BP-Ch}}$ decreases with increasing temperature is in qualitative agreement with the previous results mentioned here [5].

In order to investigate the relation more quantitatively, we calculated from our pitch measurements extrapolated values for the cholesteric pitch in the temperature region close to the clearing point and plotted the field strength $E_{\mathrm{BP-Ch}}$ versus different powers of the pitch for the respective temperature. A good linear fit was obtained for a plot of $E_{\mathrm{BP-Ch}}$ versus p^{-2}. Of course, this relation describes only the behaviour of the particular mixture presented here. It is reasonable that a general law describing the relation between the chirality and the threshold field strength would have to take into account other quantities, such as the elastic coefficients for example, which are also dependent on the temperature and on the composition of the system, or the strain of the chirality [15].

4. Conclusions

It has been shown that mesogenic chiral compounds with very high helical twisting power can be used in order to obtain induced-cholesteric blue phase mixtures containing an unusually small amount (less than 10 per cent) of a chiral substance in a

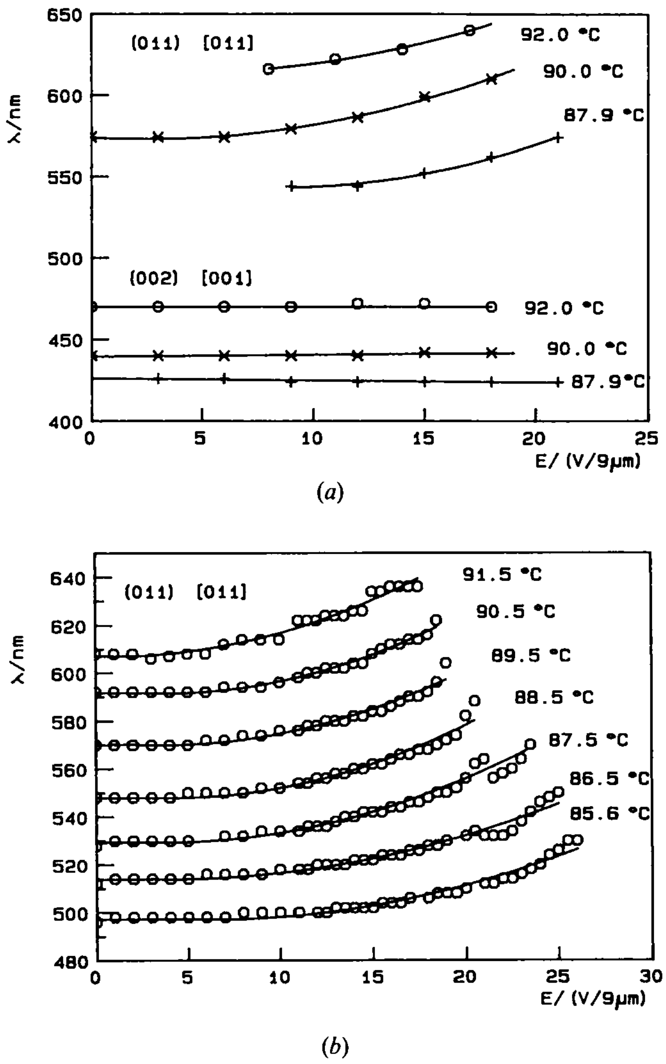


Figure 5. Bragg wavelengths as a function of electric field strength, measured in BP I for the mixture of 8·55 mass % of compound (1) in RO-TN 404. (*a*) BP I texture obtained on heating: Platelets with orientations [001] ∥ E and [011] ∥ E. (*b*) Uniform [011] orientation obtained on cooling. The lines are guides to the eye; the end of each line corresponds to the field strength where the field-induced transition BP I-Ch is observed for the respective temperature.

non-chiral nematogenic solvent. Since the chiral molecules presented here possess a very small permanent electric dipole moment, mixtures with either sign of the dielectric anisotropy can be produced depending on the dielectric anisotropy of the nematic component.

A large temperature dependence of the helical twisting power of the chiral dopant can affect the temperature dependence of the lattice constant of the blue phases. Thus, a large increase of the lattice constant in BP I was observed for the first time in one of the mixtures investigated. Obviously, the strong decrease of the lattice constant of BP I with increasing temperature which has been observed previously [1] and which

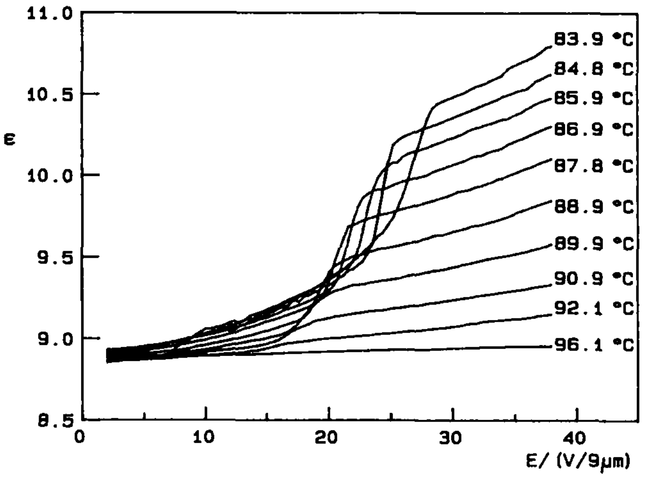


Figure 6. Dielectric permittivity as a function of field strength for different temperatures (cell thickness 9 μm, same composition as in figure 5). For weak electric field strength, a continuous change of ε is observed corresponding to the deformation of the blue phase structure. The phase transition BP I–Ch is indicated by a distinct step in ε.

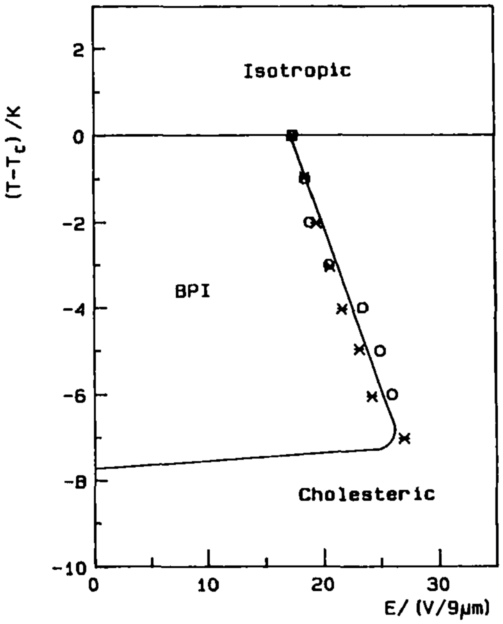


Figure 7. Schematic phase diagram in the electric field–temperature plane. The values for the transition field strength $E_{BP\text{-}Ch}$ are obtained by optical observation (O, compare figure 5) and by dielectric measurements ((∗), figure 6), respectively. Close to the clearing temperature the mixture exhibits a BP I-isotropic two-phase region as indicated in figure 4. Above T_c the sample is completely isotropic.

has been explained theoretically [16] occurs only for mixtures in which the temperature coefficient of the cholesteric pitch is zero or less than zero.

In one of the systems under investigation, an unusually large temperature range of the blue phase has been found on heating. To some extent this can be explained by the occurrence of two-phase regions close to the clearing temperature. In order to explain the large temperature interval of a homogeneous BP we might also consider a relation of the size of the BP temperature range to the temperature dependence of the chirality induced by the chiral dopant. It is well known that the occurrence of the blue phases requires high chirality (with the critical value depending on the material) and that the BP temperature range increases with increasing chirality. In the system studied here, an increase of the chirality can occur not only due to an increase of the concentration of the chiral compound, but also due to a decrease of the temperature. The latter effect may stabilize the blue phase additionally with respect to the cholesteric phase, thus providing a large blue phase temperature range. To study this relation more quantitatively, further investigations are necessary.

Finally, we would like to consider the reentrant phase sequence Ch–BP I–Ch which was observed with increasing temperature for a mixture of compound (1) with RO–TN 404 under the influence of an electric field. This phenomenon can be explained by the large absolute value of the temperature coefficient of chirality in this system. Phase separation of the system very close to the clearing temperature can also affect the threshold voltage. The behaviour is in qualitative agreement with previous observations [5] showing that the threshold field strength for the field-induced phase transition BP–Ch increases with increasing chirality. Note that the effect observed here is a new example of a reentrant phase sequence. Reentrancy is of common interest; it occurs especially in liquid crystals [17] due to the very small latent heat connected with the transitions between different liquid-crystalline phases. Recently it was shown [15] that reentrancy in BP systems can also be caused by the uniaxial strain occurring in a Cano wedge. Since the latent heat for the phase transitions Ch–BP I, BP I–BP II and BP II–BP III have been found to be extremely small (between 1 J/mol and 20 J/mol [18]), blue phase systems may be especially suited to look for further reentrant phenomena.

We would like to thank Professor P. P. Crooker for critical revision of the manuscript. This work has been supported by the Deutsche Forschungsgemeinschaft (Sonderforschungsbereich 335, 'Anisotrope Fluide').

References

[1] Crooker, P. P., 1989, *Liq. Crystals*, **5**, 751.
[2] Heppke, G., Krumrey, M., and Oestreicher, F., 1983, *Molec. Crystals liq. Crystals*, **99**, 99.
[3] Porsch, F., and Stegemeyer, H., 1989, *Chem. Phys. Lett.*, **155**, 620.
[4] Heppke, G., Jérôme, B., Kitzerow, H.-S., and Pieranski, P., 1989, *J. Phys., Paris*, **50**, 2991.
[5] Jérôme, B., and Pieranski, P., 1989, *Liq. Crystals*, **5**, 799.
[6] Gerber, P. R., 1985, *Molec. Crystals liq. Crystals*, **116**, 197.
[7] Chanishvili, A. G., Chilaya, G. S., Elashvili, Z. M., Ivchenko, S. P., Khoshtaria, D. G., and Vinokur, K. D., 1986, *Molec. Crystals liq. Crystals Lett.*, **3**, 91.
[8] Coates, D., and Gray, G. W., 1975, *Physics Lett.* A, **51**, 335.
[9] Heppke, G., Lötzsch, D., and Oestreicher, F., 1986, *Z. Naturf.* (*a*), **41**, 1214.
[10] Cano, R., 1968, *Bull. Soc. Fr. Min. Crist.*, **91**, 20.
[11] Heppke, G., Kitzerow, H.-S., and Krumrey, M., 1987, *Molec. Crystals liq. Crystals* B, **150**, 265.
[12] Finn, P. L., and Cladis, P. E., 1982, *Molec. Crystals liq. Crystals*, **84**, 159.
[13] Stegemeyer, H., and Porsch, F., 1984, *Phys. Rev.* A, **30**, 3369.

[14] Heppke, G., Heyn, S., Kitzerow, H.-S., Krumrey, M., and Oestreicher, F., 1984, Experimental studies on the field induced deformation of blue phases, Poster presented at the 10th International Liquid Crystal Conference, York.

[15] Feldman, A. I., Crooker, P. P., and Goh, L. M., 1987, *Phys. Rev.* A, **35**, 842.

[16] Meiboom, S., Sammon, M., and Brinkman, W. F., 1983, *Phys. Rev.* A, **27**, 438.

[17] Cladis, P. E., 1988, *Molec. Crystals liq. Crystals*, **165**, 85.

[18] Thoen, J., 1989, *Phys. Rev.* A, **37**, 1754.