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Thermodynamic, structural and morphological studies on liquid-crystalline blue phases

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Invited Article

Thermodynamic, structural and morphological studies on liquid-crystalline blue phases

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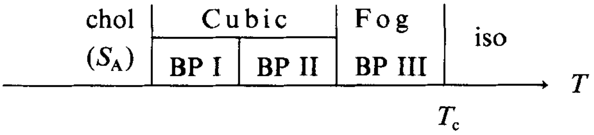
This article describes the progress in experimental studies of liquid-crystalline blue phases during the past 5 years. Additionally, these results are compared critically with the predictions of theories of the blue phases. Areas considered in this review include (i) the thermodynamic stability of the three polymorphic blue phases and the influence of the cholesteric pitch on this; (ii) the phase diagrams of blue phases; (iii) electric field effects on the blue phase structure and stability; (iv) the morphology and growth of liquid single crystals of blue phases; (v) the symmetry and structural properties of the blue phases.

1. Introduction

Blue phases (BPs) are liquid-crystalline phases which exist in a very small temperature span just below the clearing point usually between the isotropic liquid phase and cholesterics of sufficiently short pitches. In several systems up to *three* BPs are thermodynamically stable (cf. experimental results reported in §2).



During the past decade the blue phase has attracted the attention of a growing number of scientists and this has lead to numerous publications in this field. An earlier review has been made of the experimental results [1] and recently a progress report emphasizing the theoretical aspects [2] has been given. As long ago as 1906 Lehmann [3] detected the blue phase as a stable optically-isotropic modification not identical with the cholesteric phase. The very first observation of a blue phase, was however, described in 1888 by Reinitzer in his famous letter to Lehmann [4]. He reported a blue-violet light reflection just below the clearing point of cholesteryl benzoate which is actually caused by the BP I (for details cf. [1], p. 174).

The crucial point was to discover a BP structure which explains both the zero birefringence of bulk blue phases [5, 6] as well as their cholesteric-like optical properties [6, 7]. In 1969 Saupe [8] proposed a chiral *cubic* BP structure but without giving any proof. The first experimental evidence for a cubic structure was obtained by Meiboom and Sammon [9] from light scattering studies of the bulk BP. More striking evidence was derived by Johnson *et al.* [10] from Bragg reflection measurements for individual platelets of a polycrystalline BP texture which fulfils the Bragg equation for normal incidence

$$\lambda(hkl) = 2nd(h^2 + k^2 + l^2)^{-1/2}. \qquad (1)$$

Here λ is the reflection wavelength, h, k, l, are the Miller indices, n is the refractive index and the lattice parameter is d. From these results a face-centred cubic structure could be excluded but no decision was possible between a body-centred and a simple cubic structure, a question which has not been solved even to this day. Important evidence for a cubic BP structure is given by liquid single crystals of a cubic habit first grown in 1981 by Onusseit and Stegemeyer (cf. figure 14) [11]. The crystallographic aspects of three-dimensional blue phase single crystals leading to special space groups for BP I and II will be discussed in §4.

Extensive theoretical studies on blue phase problems have been made mainly by Hornreich and Shtrikman. They predicted stable body-centred cubic and simple cubic BP structures by means of an approach [12, 13] based on Landau theory. A complete solution of the BP structure problem demands the knowledge of the spatial molecular distribution function which of course cannot be derived unequivocally from the blue phase space group symmetry. In this respect the study of electric field effects on BPs may be helpful; these are discussed in §3.

2. Thermodynamics and blue phase stability

2.1. *Pitch effect on blue phase stability—critical pitches*

Blue phases only occur in cholesteric systems of sufficiently small pitches. If the cholesteric pitch, p, exceeds a critical value, p_c, then BP no longer exists. This is shown in figure 1 for a mixed system of cholesteryl nonanoate (CN) with the nematogen p-n-pentylphenyl-2-chloro-4-(p-n-pentylbenzoyloxy)-benzoate (PCPB) [14]; the total BP I/II range (ΔT) decreases with increasing cholesteric pitch p_u and becomes zero at p_c equal to 383 nm. For comparison of different systems p_u is measured at the cholesteric-blue phase transition temperature. In compensatable systems with cholesterogenic

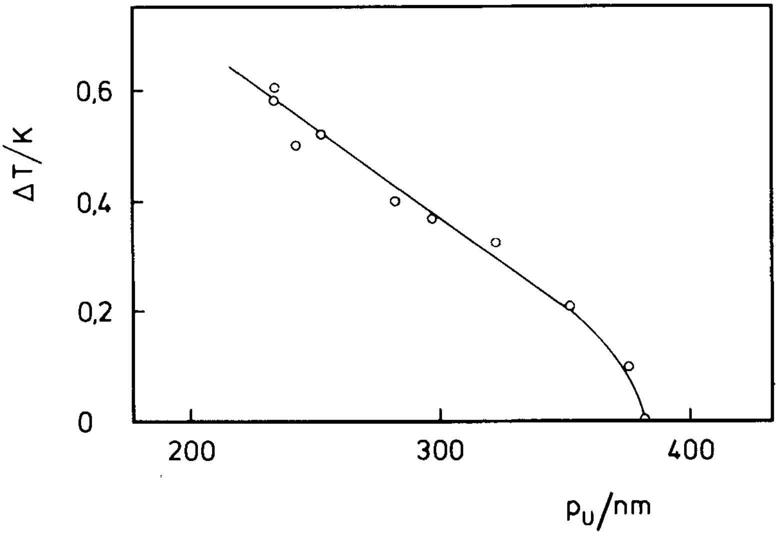


Figure 1. Total blue phase range ΔT versus cholesteric pitch p_u for CN/PCPB.

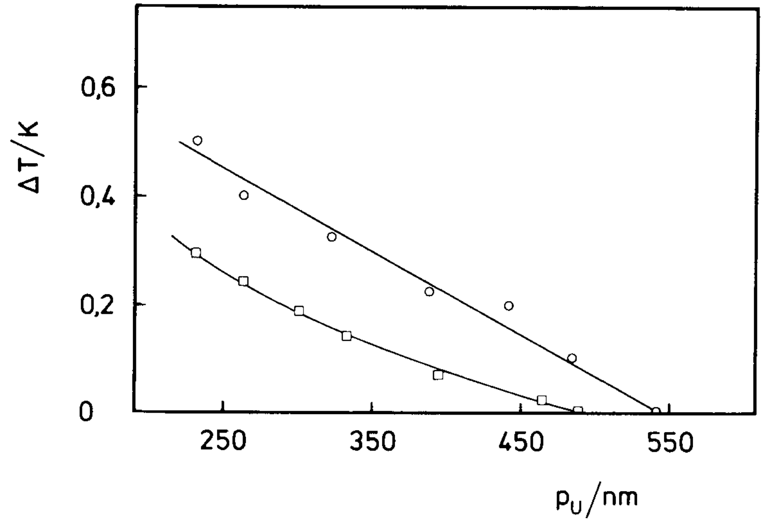


Figure 2. ΔT versus p_u for the compensatable system CN/CC.

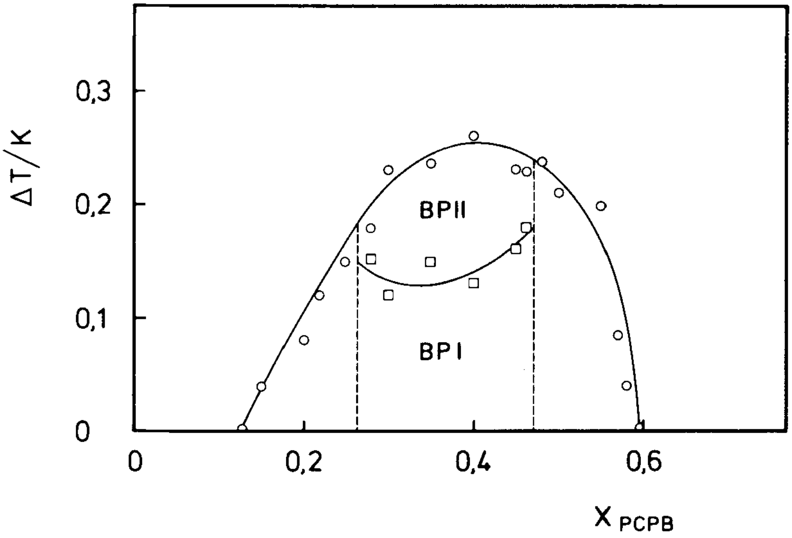


Figure 3. Phase diagram for the induced blue phases for CA/PCPB.

compounds of opposite helical sense, e.g. cholesteryl chloride/cholesteryl nonanoate, the BPs break down at medium mole fractions where the pitch begins to diverge [15, 16]. In such cases the plot of ΔT versus p_u splits into two branches (cf. figure 2) [14, 15]. These results demonstrate the important influence of p_u on the stability of blue phases.

Consequently, it is obvious that *induced BPs* can be found in binary mixed systems with compounds which do not exhibit blue phases by themselves because their pitches are too large. If p_u passes through a minimum as a function of composition then blue phases occur at medium mole fractions where $p_u < p_c$ [17]. As an example the phase diagram of the induced BPs for the system PCPB/cholesteryl acetate is shown in figure 3; the values of the critical pitches can be obtained from figure 4. The largest critical

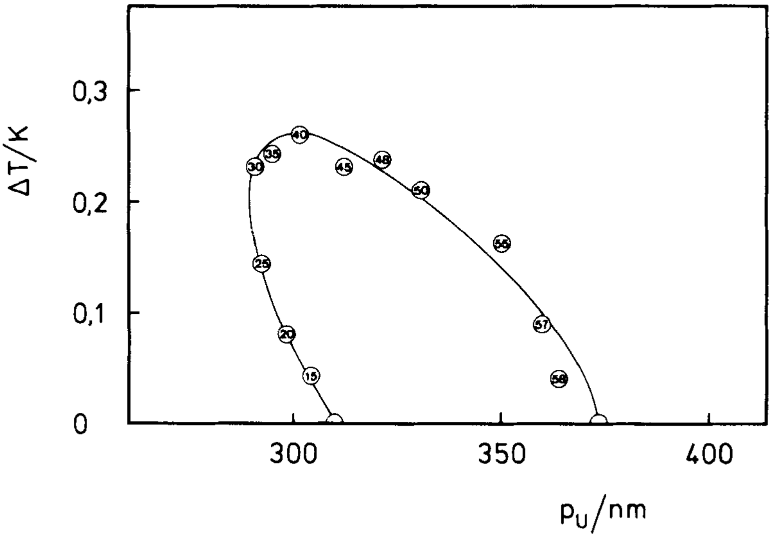


Figure 4. The dependence of ΔT on p_u for CA/PCPB. The numbers shown are the mol per cent of PCPB.

Table 1. Critical pitches for monomorphic (p_c) and dimorphic blue phases (p_m) in cholesteric mixed systems (at $T_{ch/BP}$).

System	p_c/nm	p_m/nm	p_m/p_c
	Cholesteric/nematic mixtures		
CN/PCPB	383	333	0·87
CN/CCH 7	439	410	0·93
CN/PCH 7	410	356	0·87
CN/CB 7	398	336	0·84
CC/CCH 7	407	330	0·81
CC/PCH 7	395	345	0·87
CC/CB 7	350	271	0·77
CV/8OBE	415	340	0·82
CM/8OBE	390	265	0·68
CB/8OBE	355	270	0·76
	Compensated mixtures		
CN/CBAC	647	343	0·53
	573	556	0·97
CN/CC	540	472	0·87
	490	370	0·76
	Induced BPs		
CA/PCPB	310	305	0·98
	373	309	0·83
CEEC/EBBA	610	462	0·76
	490	413	0·84

Abbreviations: CA cholesteryl acetate; CV cholesteryl valerate; CC cholesteryl chloride; CN cholesteryl nonanoate; CM cholesteryl myristate; CB cholesteryl benzoate; CEEC cholesteryl ethoxyethoxyethylcarbonate; EBBA 4-ethoxybenzylidene-4′-n-butylaniline; CBAC 4-cyanobenzylidene-4′-aminocinnamic acid opt.act.amylester; PCPB p-pentylphenyl-2-chloro-4-(p-n-pentylbenzoyloxy)-benzoate; 8OBE 4-n-octyloxyphenyl-4′-n-octyloxybenzoate.

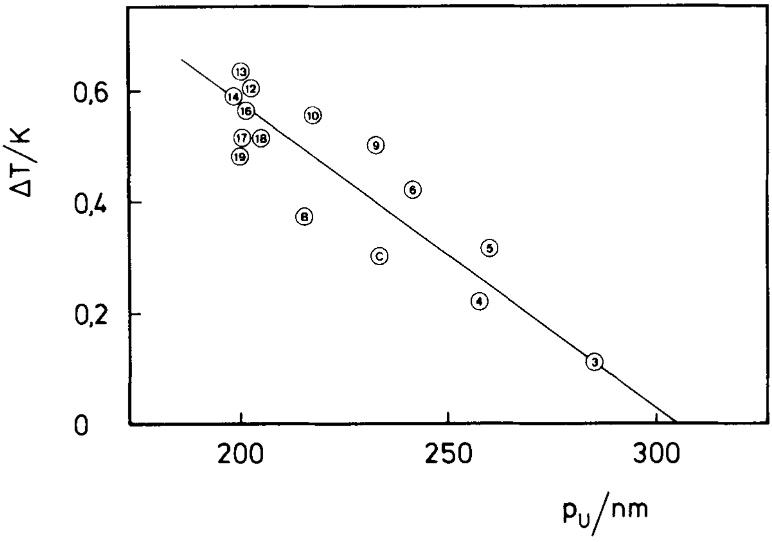


Figure 5. The variation of ΔT with p_u for cholesteryl alkanoates. The number of carbon atoms in the alkyl chain is given in the circles; B, cholesteryl benzoate; C, cholesteryl chloride.

pitch we observed was p_c equal to 647 nm in the compensatable system of cholesteryl nonanoate with the chiral nematic 4-cyanobenzylidene-4′-aminocinnamic acid amylester (opt. act.) (CBAC). Probably no blue phase will be stable in systems with cholesteric pitches larger than p_u of approximately 700 nm.

Comparison of figures 1, 2 and 4 together with the data listed in table 1 shows that the critical pitch, p_c, does *not adopt a universal value* but depends on both the molecular structure and the composition of the system. The influence of these parameters is also demonstrated by the plotted ΔT versus p_u of the induced BP system PCPB/cholesteryl acetate given in figure 4: the maximum BP temperature span does not occur in the mixture with the smallest pitch (30 mol per cent PCPB) but in the 40 per cent mixture with a somewhat large p_u value.

The non-universality of p_c can be understood in terms of the Hornreich–Shtrikman theory of blue phases [12, 13]. It has been predicted that a cubic BP structure is only stable if the coefficient of the cubic term in the Landau free energy expansion is smaller than the chiral one. As for the mixtures listed in table 1 the chirality has been varied by mixing compounds of different molecular structure, other Landau coefficients will also be changed resulting in different p_c values for different systems. To avoid a simultaneous change of chirality on the one hand and molecular structure on the other hand, mixtures of chiral and racemic forms of the same compound have been investigated [18, 19]. In such a mixture of 4-(2-methylbutyl)phenyl-4′-decyloxybenzoate (designated by BDH Chemicals as CE 6) Tanimoto *et al.* [20] observed a critical pitch, p_c, of 330 nm. As PCPB exhibits a rather similar molecular structure to CE 6 it is obvious that the p_c values of the PCPB/cholesteryl acetate system are of the same order of magnitude (cf. table 1).

Within the series of cholesteryl alkanoates the homologues with the smallest p_u exhibit the largest blue phase range. From a plot of ΔT versus p_u (cf. figure 5) a critical

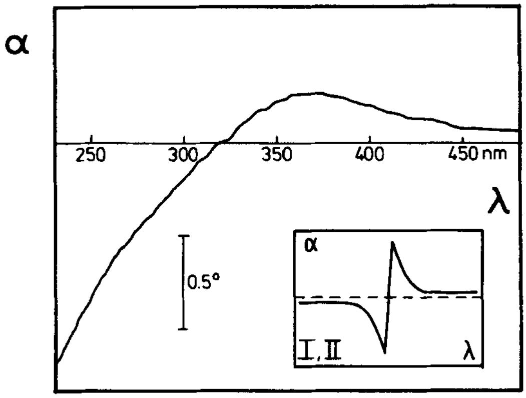


Figure 6. Optical rotatory dispersion spectrum of the BP III for cholesteryl nonanoate (from [30]). Right bottom: schematical optical rotatory dispersion spectrum of BP I and II.

pitch for this ester series can be found, by extrapolation of $\Delta T \to 0$, to be approximately 300 nm. It has been found [14, 21] that cholesteryl propionate is the shortest homologue which exhibits a BP. The helical pitches of cholesteryl acetate and formate are too large ($p_u > p_c$) to allow blue phases [14]. Addition of small amounts of nematogenic PCPB to cholesteryl acetate decreases the pitch until in a mixture with 87 mol per cent cholesteryl acetate a BP occurs at p_c equal to 310 nm (cf. table 1). This value agrees with the extrapolated p_c value for the cholesteryl ester series.

The maximum total BP temperature range which we observed in low pitch systems ($p_u \approx 200$ nm) was $\Delta T \approx 0{\cdot}6$ K. The cholesterogenic compound 4-(2-methylbutylphenyl)-4′-(2-methylbutyl)-4″-biphenylcarboxylate, (designated by BDH Chemicals as CE 2) exhibits an extremely low pitch of about 100 nm because of its two chiral centres [22]. Consequently, the largest total BP range known at present ($\Delta T \approx 2$ K) has been found for CE 2 [23]; although still larger values have sometimes been reported [24]. In mixed systems, however, two-phase regions involving the blue and isotropic phases must be taken into account; these are the broader the larger the differences between the clearing temperatures and/or the clearing enthalpies of both components are. Blümel [25] has calculated in some cases two-phase regions larger than 3 K. If the BP range is determined by polarizing microscopy it can often happen that a two-phase region will be identified erroneously as a blue phase which results in values of ΔT which are too large. It is doubtful also from a theoretical point of view [13] if systems can be found with a BP range considerably larger than several Kelvin.

2.2. *Blue phase polymorphism*

Evidence for *two* polymorphic forms BP I and BP II was obtained in 1979 by Bergmann and Stegemeyer [26] by DSC thermograms as well as by selective reflection and optical rotation measurements [7, 27].

2.2.1. *BP III—is the fog a stable phase?*

The possibility of a *third* BP was first mentioned in 1980 [1]: by polarizing microscopy we detected a 'grey texture' between the isotropic liquid and the BP II platelet texture (cf. figures 13 and 14 in [1]). Marcus [28] and Meiboom and Sammon [29] also observed such a texture and called it a 'blue fog' or a 'fog phase'. The

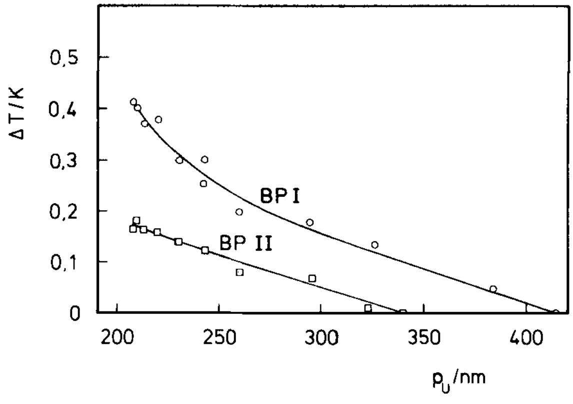


Figure 7. Temperature range, ΔT, of the BP I and II as a function of the cholesteric pitch, p_u, for the system CV/8OBE.

temperature range of this texture, however, was so small ($< 0{\cdot}1$ K) that a proof of its thermodynamic stability could not be obtained at that time.

Convincing evidence for the stability of a BP III has been found recently by Collings [30] from optical rotatory dispersion measurements. In a temperature range of a few hundredth Kelvin below the clearing point he observed optical rotatory dispersion spectra with a pattern (figure 6) quite different from the anomalous spectra of the BP I and II [1], indicating a different structured phase between the isotropic liquid and BP II. Kleiman *et al.* [31] resolved directly the BP II/BP III as well as the BP III/isotropic transition by high-precision specific heat measurements. From these results the thermodynamic stability of the fog phase is quite obvious and it has been named BP III. The clearing enthalpy in liquid-crystalline systems exhibiting the phase sequence cholesteric/BP I/BP II/BP III/isotropic is caused predominantly by the BP III/isotropic transition [30, 31].

2.2.2. *The monomorphic blue phase*

From the phase diagram of the induced BP system PCPB/cholesteryl acetate (cf. figure 3) it can be seen that two blue phases (BP I and BP II) exist in an intermediate concentration range with the lowest p_u values. At lower or higher PCPB concentrations where p_u increases up to values close below p_c only *one* BP has been found (cf. figure 3) [17]. The change of dimorphic to monomorphic blue phase behaviour is determined obviously by the helical pitch of the system. We define a *monomorphic pitch* p_m above which only *one* BP is stable; the range of the monomorphic BP is $p_m < p < p_c$ and values of p_m are given in table 1.

The question has to be answered if the BP I or the BP II vanishes first on increasing the pitch or if the monomorphic BP is of quite different structure. By means of polarizing microscopy using a contact preparation Blümel and Stegemeyer [32] found that the monomorphic blue phase is identical with the BP I. On increasing p_u the BP II vanishes first at p_m whereas the BP I survives until p_u is equal to p_c as shown in figure 7. From the critical pitches given in table 1 it follows that there is also no universal value for p_m and even the ratio p_m/p_c depends on the structure of the mixed systems. In mixed systems with a given cholesterogenic component (cholesteryl nonanoate or chloride) p_c and p_m increases in the order CB 7, PCH 7, CCH 7 of the nematogenic

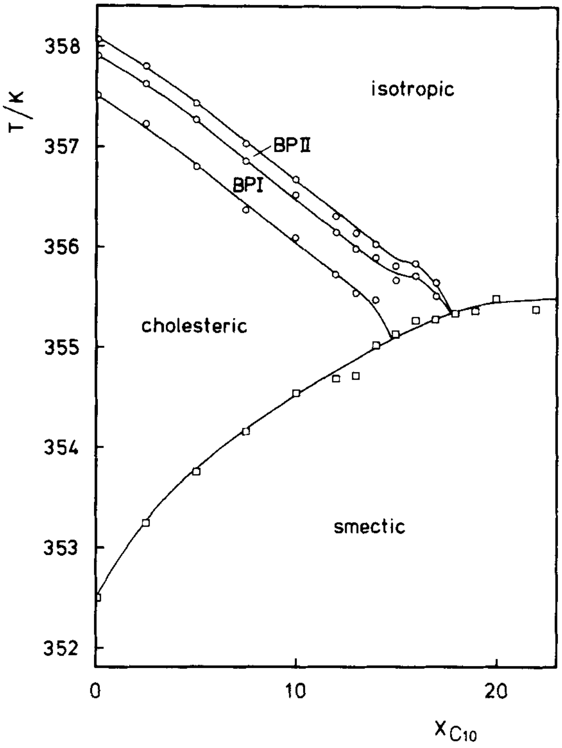


Figure 8. Partial phase diagram for CM/C_{10} showing a direct transition from the smectic A phase to BP I.

component. The anisotropy of the permittivity $\Delta\varepsilon$ decreases in the same order. Obviously, the BPs are still stable at large critical pitches (that means small chirality) if the dispersion interaction is small which is the case with small $\Delta\varepsilon$.

Within the homologous series of cholesteryl n-alkanoates we found that the propionate with a rather large pitch p_u of 284 nm only exhibits the BP I whereas the blue phase of the butyrate and the higher homologues are dimorphic [14].

2.2.3. *Direct smectic A–blue phase transition*

Generally, blue phases occur between the cholesteric and the isotropic liquid state. In polymorphic liquid-crystalline systems the phase sequence

$$S_A \rightarrow Ch \rightarrow BP \rightarrow I$$

has been found on increasing temperature whenever the cholesteric pitch is small enough. Recently, we investigated the blue phase stability of cholesteryl myristate (CM) on admixing 4,4′-di-n-decylazoxybenzene (C_{10}) which exhibits only a smectic A phase [33]. A partial phase diagram of the CM/C_{10} system is shown in figure 8. On increasing the C_{10} concentration the cholesteric range decreases finally to zero at 15 mol per cent whereas the BP ranges remain nearly constant. In mixtures of 15 to 18 mol per cent C_{10} a direct $S_A \rightarrow$ BP I transition occurs. This phase behaviour is quite exceptional and seems to be caused by an overcompensation of the helical twisting power by the smectic layer organization forces. The smectic A phase increases

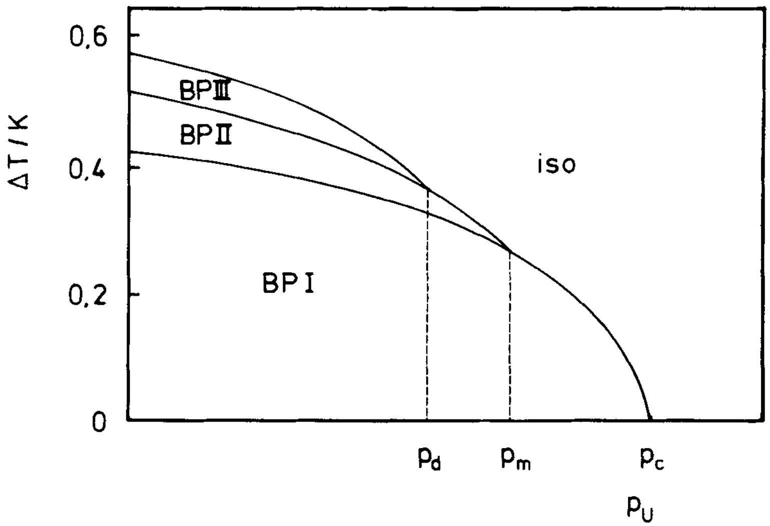


Figure 9. Schematic phase diagram showing ΔT as a function of p_u for all three blue phases.

at the expense of the cholesteric whereas the blue phase is the last portion of the chiral phase to become unstable relative to the smectic A phase. It is obvious from these results that the occurrence of a blue phase does not require the simultaneous existence of a cholesteric phase. Thus, the designation 'cholesteric' blue phase which is often used should be avoided.

2.3. *Phase diagrams of the blue phases*

We have observed a change of blue phase dimorphism to monomorphism on increasing the cholesteric pitch with the BP I surviving as mentioned in §2.2.2.

Collings [30] has found that the BP III exists only in systems with very short pitches. The BP III span is extremely small ($\lesssim 0{\cdot}05$ K), it decreases with increasing pitch and becomes zero at a so-called dimorphic pitch, p_d. The variation of blue phase polymorphism with p is demonstrated by the schematic phase diagram in figure 9. Experimental phase diagrams containing data of all three BPs have been obtained by Blümel *et al.* [34] using polarizing microscopy, optical rotatory dispersion and selective reflection measurements. In figure 10 a typical phase diagram for the pure cholesteryl alkanoates is shown. The BP span is given here as a function of p^{-1} since this is proportional to the chirality parameter κ used in the Hornreich–Shtrikman theory [12]. Recently, Collings [36] reported the phase diagram of the CE6 chiral/racemic mixture which exhibits BP I, II, and III. Values of p_d, p_m and p_c for some blue phase systems are listed in table 2.

Theoretical BP phase diagrams have been predicted using a Landau theory approach [12, 13] and two examples are shown in figure 11. The thermodynamic boundaries between the isotropic and cholesteric phases and the BPs are given as a function of a chirality parameter $\kappa = 2\pi\xi_R p^{-1}$ where ξ_R is the correlation length at the clearing point (a typical value of ξ_R is 25 nm [35]). The temperature scale is given in reduced units $t = (T - T^*)/(T_c - T^*)$ with the clearing temperature T_c and the Landau temperature T^* which occurs as $\xi_R \rightarrow \infty$. All boundaries correspond to first order phase transitions as found experimentally [26, 31]. The blue phase symmetry

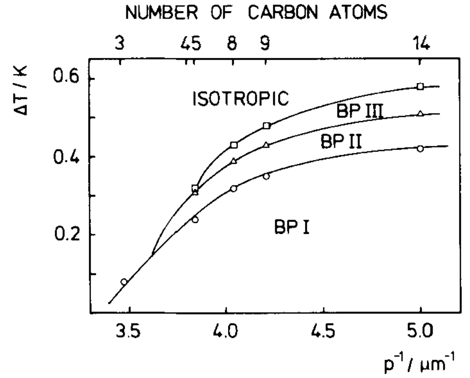


Figure 10. Blue phase diagram with ΔT versus p^{-1} for the pure cholesteryl alkanoates [34].

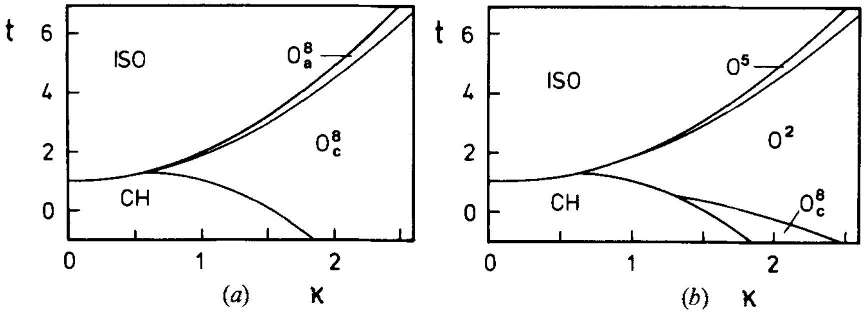


Figure 11. Theoretical phase diagrams with (*a*) two blue phases and (*b*) three blue phases (after Grebel *et al.* [13]).

Table 2. Characteristic pitches for some blue phase systems.

	8OBE/CV [25]	CN/CC	Cholesteryl alkanoates	CE 6 (chiral/racemic) [20, 36]
p_d/nm	270	329	261	193
p_m/nm	340	450	278	236
p_c/nm	415	560	300	330

Abbreviations: 8OBE: p-n-octyloxyphenyl-p′-octyloxy benzoate; CV: cholesteryl valerate.

given in figure 11 will be discussed in §4. None of the theoretical diagrams include a phase with BP III properties of lacking long-range periodic order. In principle, the theoretical phase diagrams resemble their experimental counterparts [34] which show a change of blue phase monomorphism to dimorphism and an increase of the BP temperature ranges on increasing the chirality. However, some of these diagrams (e.g. figure 11 (*b*)) predict the occurrence of a third blue phase at very high chirality $\kappa > 1{\cdot}3$ [13] which has not yet been found experimentally. The topology of the theoretical phase diagrams is very sensitive to parameter variation and depends on the number of higher harmonics taken into account in the theoretical treatment [13]. Because of the extremely small differences in free energy between the three blue phases [14, 26, 31] a universal phase diagram is not expected from a theoretical point of view. Further, the use of only two characteristic parameters ξ_R and T^* also does not seem to allow a universality of a temperature versus p^{-1} plot because the wide variety of systems

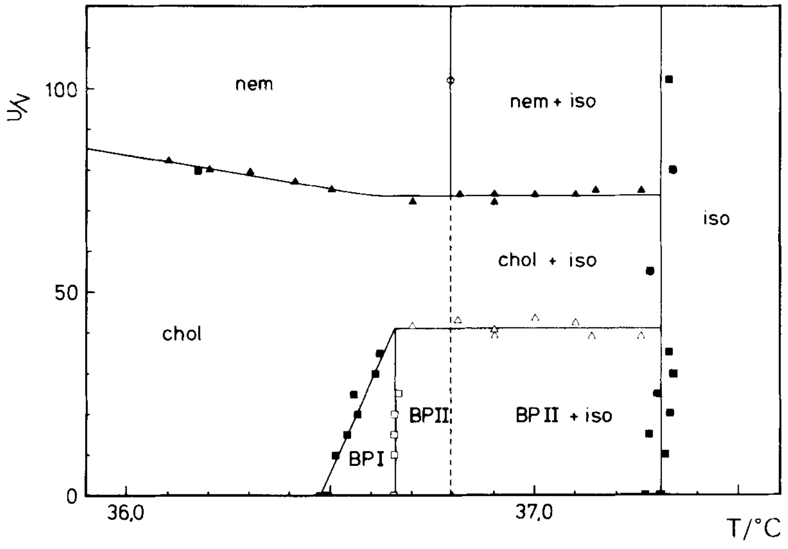


Figure 12. A phase diagram showing voltage against temperature for a M 18/CB 15 mixture (47 mol per cent CB 15).

with different molecular structures cannot be taken into account in this way. This also follows from the results given in the last column of table 1, which shows that the ratio p_m/p_c is not constant for different systems. The experimental results [20, 32, 34], however, point to one type of phase diagram with different values of the characteristic pitches p_d, p_m and p_c but universal only in topology. A direct $S_A \rightarrow$ BP transition as shown in figure 8 remains unexplained by the blue phase theories presently available [13].

3. Electric field effects on blue phases

3.1. *Voltage temperature phase diagram*

In §2 we have shown that the blue phases become unstable if the cholesteric pitch, p, exceeds a critical value, p_c. It is well known that p can be enhanced by an electric field up to infinity thus transforming the cholestric helical structure into a nematic. Our original idea was to increase the cholesteric pitch by an electric field up to values $p > p_c$ in order to obtain field-induced BP → Ch phase transitions. We investigated the voltage/temperature phase diagrams of mixtures of the polar compounds 4-n-hexyloxy-4′-cyanobiphenyl, M 18, and its chiral 2-methylbutyl derivative CB 15 (both of these are BDH Chemicals designations) in the range of 47 to 57 mol per cent CB 15. The applied field strengths were about 10 kV/cm with frequencies up to 400 Hz to avoid electrohydrodynamic effects. In consequence, the phase transition temperatures could be determined statically by polarizing microscopy. In figure 12 we present the U/T phase diagram of the mixture with 47 mol per cent CB 15. Besides the well-known cholesteric → nematic transition a BP I → Ch phase transition is indeed induced by the field as it has been described qualitatively by Armitage and Cox [23] and Finn and Cladis [37]. We also found a field-induced BP II → Ch transition in all CB 15/M 18 mixtures (cf. figure 12). A BP II → nematic transition as reported for this system [37] was not reproducible in our investigations. Actually, the observed BP I, II → Ch transitions take place at field strengths at which the cholesteric pitch is only increased by about 2 per cent with respect to the zero-field value and thus at pitches far below p_c. The magnitude of the cholesteric pitch does not therefore play an important role during the field-induced phase transitions. A BP I → BP II transition could not be induced by the field as we also found for less polar cholesteryl esters. This result is not in agreement with the conclusions drawn by Heppke *et al.* [38] from electro-optical effects in blue phases but will be demonstrated by the considerations given in §3.2. Recently, Pieranski *et al.* [39] have given some arguments for a field-induced hexagonal blue phase which has been predicted theoretically [40, 41].

3.2. *Field dependence of the BP I → Ch transition*

It is obvious from figure 12 that the coexistence line for the BP I → Ch transition is inclined towards the ordinate; this means that the transition temperature T_u is field-dependent. This is not the case for the BP I → BP II and the BP II → isotropic transition. The field shift ΔT of T_u can be understood in terms of a relation given by Kirkwood [42, 43],

$$\Delta T = \frac{T_u M}{2\varrho \Delta_u H}(\varepsilon_1 - \varepsilon_2)\varepsilon_0 E^2 \qquad (2)$$

because the transition enthalpy $\Delta_u H$ for BP I → Ch is extremely small (≈ 50 J/mole) [1] while the permittivity difference is non-zero ($\Delta\varepsilon \approx 2$) [44]. In equation (2) M is the molar mass, ϱ is the mean density, and ε_0 is the permittivity of free space. For the BP I → BP II and the BP II → isotropic transition, $\Delta\varepsilon$ is zero and/or $\Delta_u H$ too large and no field shift of T_u occurs at least according to equation (2). In the U/T diagram there is a triple point where BP I, BP II and the cholesteric phase coexist.

The coexistence line between BP II and the cholestric phase runs parallel to the abscissa, i.e. the critical field strength, E_{BC}, for BP II → Ch is independent of temperature. In terms of the Kirkwood equation (2) this can be achieved if $\Delta_u H = 0$ for this transition. However, because of Hess' law this cannot be true as the $\Delta_u H$ values for the transitions Ch → BP I and BP I → BP II are finite [26]. We are unable therefore to explain why E_{BC} is independent of temperature.

3.3. *Field induced optical biaxiality*

A detailed study of the BP I → Ch transition [44] has revealed a field dependence of T_u with a power less than 2, contrary to the quadratic prediction of Kirkwood's equation (2)

$$\Delta T = \text{const}.\, E^m, \quad \text{with } m < 2. \qquad (2a)$$

This result can be explained in terms of a non-linear dielectric effect which occurs in BP I. If we cool a mixture of CB 15/M 18 from the BP II into the BP I state in an external field of about 18 kV/cm a typical striated texture of the BP I develops as shown in figure 13. A sample with such parallel alternately light and dark striations could be brought four times into extinction positions by a rotation of 2π. This indicates a birefringence induced by the field. It must be emphasized that this birefringence was observed parallel to the field direction. A distortion of the cubic BP I structure into a tetragonal one with the long-axis parallel to the field direction would lead to pseudo-isotropy. The observed birefringence can only be understood

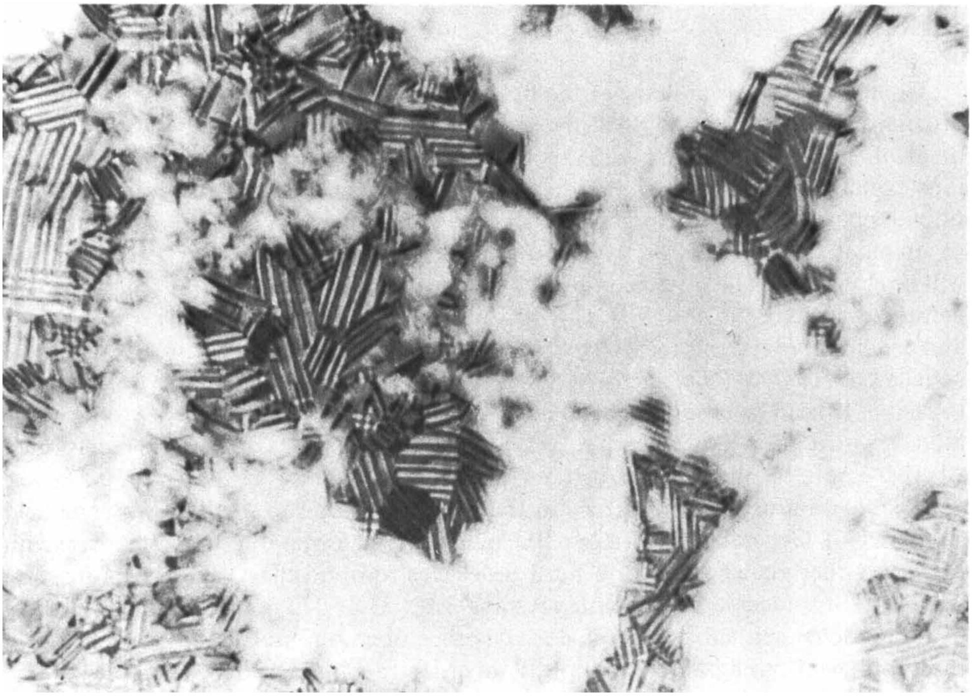


Figure 13. The phase transition BP II → BP I for a M 18/CB 15 mixture in an electric field of 18 kV/cm (49·6 mol per cent CB 15, 30·90°C).

if the optic axis is not parallel to the observation direction. A detailed investigation [45] led to the conclusion that the cubic structure must have been distorted by the field thus inducing an optical biaxiality. The observed birefringence increased with field strength up to a maximum value of about 0·02.

The biaxial BP I anisotropy obviously results from a non-linear dielectric behaviour,

$$\varepsilon_{\mathrm{BP}} = \varepsilon^0_{\mathrm{BP}} + \xi_1 E + \xi_2 E^2 + \cdots, \tag{3}$$

where ξ_1 and ξ_2 are tensors of third and fourth rank, respectively. ξ_1 exhibits the symmetry of the piezo-electric tensor and vanishes in crystals of the class 432. As there is some evidence that the BP I belongs just to this class (see §4) the linear term and all odd terms in equation (3) are to be cancelled and thus a quadratic field dependence of the electro-optic effect in BP I is expected. Inserting the modified equation (3) for $\varepsilon_{\mathrm{BP}}$ into the Kirkwood equation (2) it follows straightforwardly that the field dependence of the transition temperature T_u can be described formally by an exponent $m < 2$, as found experimentally.

From crystallographic considerations it can be shown that a biaxial crystal will be obtained only if the field direction is parallel to a rotation axis C_n of the cubic structure with $n \leqslant 2$ [46]. This situation can be realized in 432 crystals with the field normal to (110) lattice planes. From electric field effects on the Bragg scattering we obtained experimental evidence that this situation obtains for BP I [47].

In the BP II no optical biaxiality could be induced by an electric field [45]. This indicates that **E** must have been applied normal to a lattice plane with a C_n rotation axis of $n > 2$ [46]. For BP II crystals these planes can be (100) or (200) with $n = 4$.

Concluding, the symmetry of the field-deformed blue phase structures should be discussed. We have found that the cubic BP II crystals will be deformed into a uniaxial *tetragonal* structure with the longest crystal axis parallel to the field direction thus explaining the observed pseudo-isotropy [45]. As a result of the optical activity of blue phases only two tetragonal classes are possible: 4 (C_4) or 422 (D_4).

In cubic BP I crystals we have also found that the crystal axis parallel to the field will be elongated. The observed optical biaxiality requires that the axis relation of the deformed structure is $a \neq b \neq c \neq a$ which only occurs in the *triclinic*, *monoclinic* and *orthorombic* system, respectively. Only the following biaxial classes show optical activity: 1 (C_1), 2 (C_2) and 222 (D_2). The striated field-deformed BP I texture (cf. figure 13) can be brought into an identical position after rotation by 180° [45] which indicates a rotation axis C_n with $n \leqslant 2$ parallel to the field. Therefore, the deformed BP I structure belongs to one of these classes.

The field-induced birefringence in the BP I was found to increase with the field strength [45]. Generally, the extent of the blue phase deformation should increase with the field either via a second or a third order electro-optic effect. This open question is important to decide between the crystal classes 23 or 432 governing the symmetry of the undeformed cubic blue phases. Another open question is the existence of a threshold field strength to be applied in order to obtain a deformed blue phase structure.

4. Blue phase structures

The elucidation of the phase structure of blue phases requires the knowledge of the molecular distribution function. A helical molecular arrangement cannot be built in three dimensions without any frustration which lead necessarily to a disclination lattice of spatial regularity. By whatever type of disclinations this lattice may be built its symmetry must be cubic because of the absence of birefringence. The question to be answered first is the determination of the space group which describes the blue phase lattice symmetry. This can be achieved by Bragg scattering measurements as well as by morphological studies of blue phase liquid single crystals which are discussed in this section.

4.1. *Bragg scattering*

In 1978 Bergmann and Stegemeyer [6] observed that the blue light selectively reflected from the blue phases of cholesteryl esters is circularly polarized showing a Bragg-like angular dependence and a wavelength jump at the BP II–BP I transition [27]. Crooker's pioneering work on Bragg scattering from polycrystalline BP platelets [10] mentioned in §1 provided evidence for a cubic lattice built up from periodical disclinations with helically structured matter in between. In CB 15/E 9 mixtures Crooker *et al.* [10, 19] found four reflection peaks both for BP I and BP II which were assigned to the (110), (200), (211), and (220) planes of a body-centred cubic structure. To decide clearly between this and a simple cubic structure it is necessary to observe at least seven Bragg peaks because a reflection at (321) is the first one in a body centred cubic structure without a counterpart in a simple cubic. However, this observation is rather difficult because the spectral range to observe selectively reflected peaks is limited to short wavelengths by the self-absorption of the material ($\lesssim 300\,\mathrm{nm}$). At long wavelengths the critical pitch sets a limit at $\lambda_R = \bar{n}p_c$.

In a mixture of cholesteryl nonanoate and chloride Kitzel and Prokhorov [48] detected five Bragg peaks in the BP I with the following assignment: (110), (200), (211), (310) and (321). However, the (220) reflection was not observed. In the BP II they found reflections at only (100) and (110). They derived the space group $I\,4_1 32 (O^8)$ for BP I and $P\,4_2 32 (O^2)$ for BP II but this latter conclusion is not convincing.

The determination of space groups from Bragg reflections is based on selection rules derived theoretically by Grebel *et al.* (tables III and IV in [12]). For example these rules forbid a reflection of circularly polarized light at (111) planes of all simple cubic space groups and at the (200) plane of the body-centred cubic space group $I\,432 (O^5)$. Taking into account these results a body-centred cubic structure clearly follows for the BP I most probably with the space group $I\,4_1 32 (O^8)$ [19, 48, 49]. The BP II structure remains controversial [19, 48, 49] and cannot be determined only from Bragg measurements. In the following section we shall give additional results derived from the morphology of blue phase liquid single crystals.

4.2. *Blue phase liquid single crystals*

4.2.1. *Habit and morphology*

In the polycrystalline blue phase platelet texture [50] obtained by rapid cooling from the isotropic state the different coloured platelets are separated by sharp grain boundaries which resemble the situation in the mosaic texture of positionally long-range ordered smectic phases (e.g. smectic B) and indicate an exceptional stiffness of the blue phase structure though it contains only long-range orientationally ordered molecules. Thus in retrospect it does not seem too surprising that blue phases can be obtained as liquid single crystals of well defined habit. Those single crystals were observed in 1981 by Onusseit and Stegemeyer [11, 14, 51]. Regarding the polymorphic phase behaviour (cf. figure 9) we are now able to differentiate between the growth conditions of differently shaped blue phase single crystals.

(i) $p < p_d$. In cholesterics of very short pitches we have the phase sequence isotropic → BP III (fog) → BP II → BP I on decreasing the temperature (cf. figure 9). If we cool those systems (e.g. pure cholesteryl esters) from the isotropic liquid state by an extremely slow rate, large BP II single crystals of quadratic habit grow very rapidly from the fog phase (BP III). A microphotograph is given in figure 14(*a*); the square crystal with blue selective reflections represents the crystallographic form {100} which has been observed in all cholesteryl esters and their short pitch mixtures. Figure 14 (*b*) shows the situation 10 s later; the BP II crystal has grown by 65 per cent demonstrating the high growth rate which is typical for all BP II crystals developing from the fog phase. A further typical feature of the cubic BP II crystals are the more or less rounded edges which indicate the fluid properties of the crystals. Cooling the BP II crystal the selective reflection colour changes from blue to green just at the phase transition BP II → BP I (figure 14(*c*)). Immediately, the growth stops and a crosshatching occurs which is well developed in a cholesteryl myristate crystal shown in figure 15. The striations run diagonally to the square sides in the ⟨110⟩ direction [11, 52] and broaden slowly with time on annealing the BP I crystal for several hours.

(ii) $p_m < p < p_c$. In monomorphic blue phase systems with rather long pitches BP I single crystals grow directly from the isotropic liquid phase (cf. figure 9).

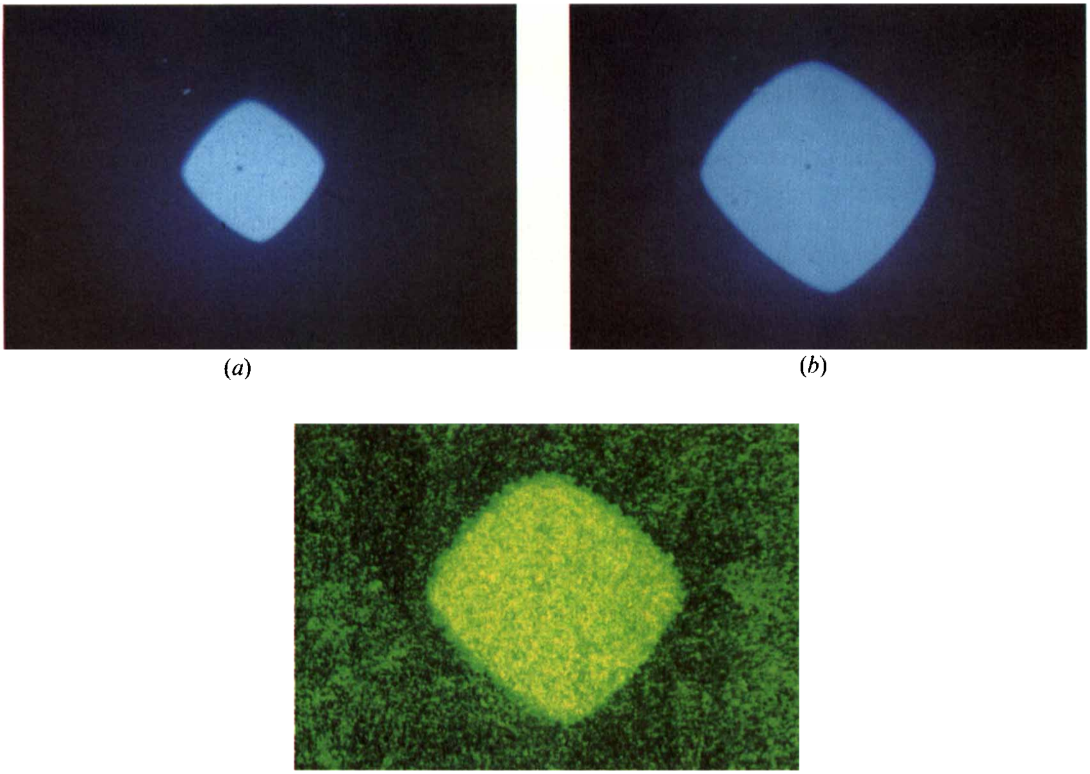

(a)
(b)
(c)

Figure 14. Microphotographs of blue phase single crystals of the system CN/CBAC (80 mol per cent CN, crossed polarizers, magnification 160 ×, in reflection). (a) BP II crystal, 92·90°C; (b) the same crystal after 10 s; (c) the same crystal after the transition to the BP I, 92·55°C.

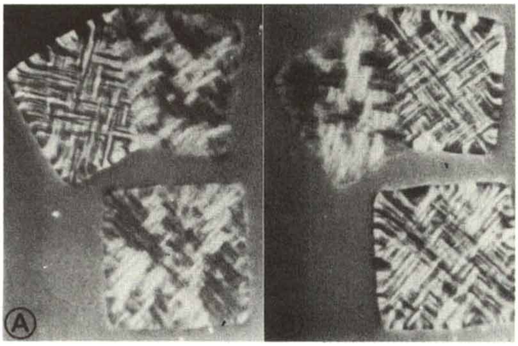


Figure 15. A, Liquid single crystals for the BP I of cholesteryl myristate; B, after sample rotation by 45° (magnification 230 ×).

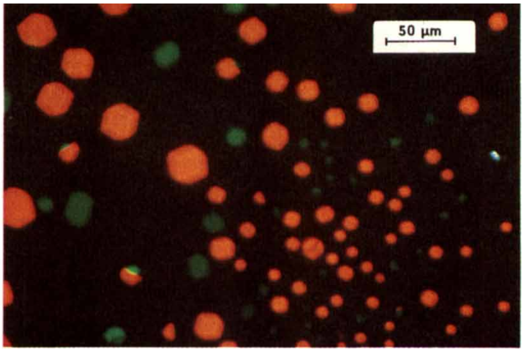


Figure 16. Orange three-dimensional crystals of BP I with {110} faces (8OBE/CB with 30 mol per cent CB; in reflection, sample thickness 30 μm, 100·9°C).

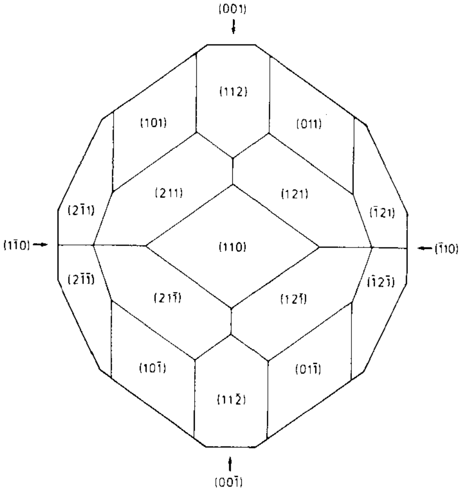


Figure 17. BP I crystal in final habit with $\{110\}$, $\{211\}$, and $\{100\}$ (8OBE/CB with 30 mol per cent CB; in reflection, sample thickness $30\,\mu$m, 100·2°C).

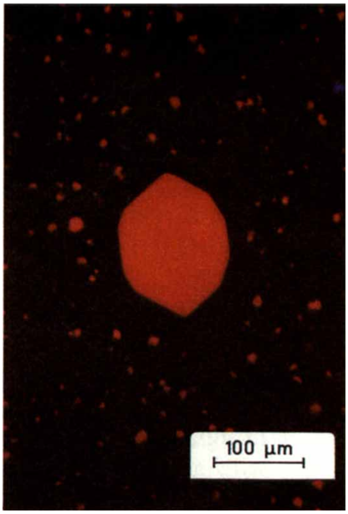


Figure 18. Construction of a crystal with $\{110\}$, $\{211\}$ and $\{100\}$.

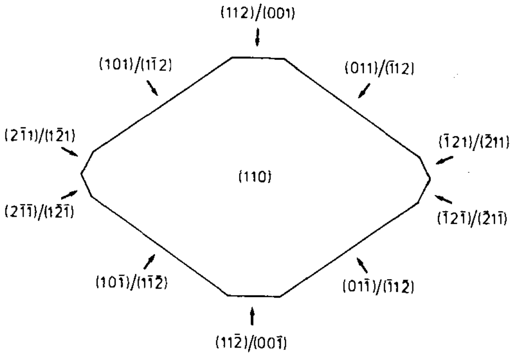


Figure 19. Microphotograph of a BP I single crystal with a rhomb-like shape (CB/8OBE with 32 mol per cent CB, 95·75°C, in reflection; sample preparation without spacer).

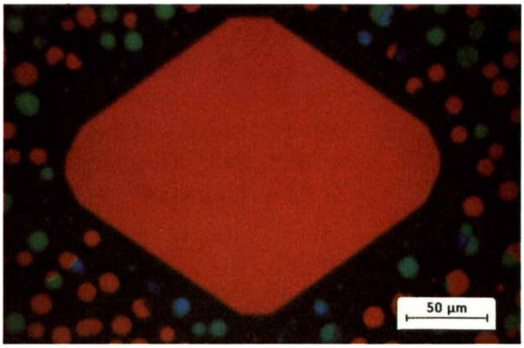


Figure 20. Construction of the crystal habit of the BP I single crystal shown in figure 19.

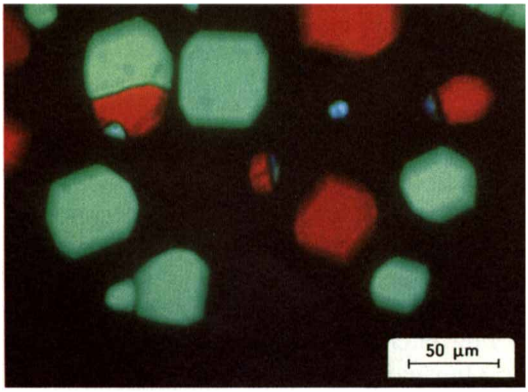


Figure 21. Microphotograph of BP I single crystals similar to those in figure 16 in addition showing *green* three dimensional crystals in (211) orientation (in transmission).

In such a system (cholesteryl benzoate/8OBE) Blümel *et al.* in 1983 obtained well developed *three-dimensional* BP I single crystals [53, 54] of a rhombic dodecahedral habit with well-developed (110) faces (figure 16). These BP I crystals grow rather slowly. In the initial stage of growth the habit of the three-dimensional crystals is only determined by the form $\{110\}$. Later on, additional sides develop and the number of edges increases. The final habit is shown in figure 17; this results from $\{211\}$ faces and from planes of $\{100\}$. A construction of the expected final habit involving the morphologically important forms $\{110\}$, $\{211\}$ and $\{100\}$ shown in figure 18 is in good agreement with the observed habit of the crystal in figure 17.

In thin samples without spacers the BP I crystal faces touch the surfaces of the glass cell and growth takes place only in two dimensions. In this way large rhomb-like BP I single crystals up to 0·3 mm in size could be obtained, an example of which is shown in figure 19 together with its constructed habit in figure 20. Besides these orange rhombic crystals of the CB/8OBE system with a Bragg reflection of 610 nm at (110) we found violet crystals of a quadratic habit with (h00) faces. Their reflection at 435 nm is obviously caused by Bragg scattering at (200) lattice planes because of the $\sqrt{2}$ relation to the 610 nm peak. Additionally, BP I crystals with a green selective reflection develop which can be seen in figure 16. They could be obtained as three-dimensional crystals with a habit which is determined mainly by the form $\{211\}$ (figure 21). Their selective reflection occurs at λ_R of 524 nm which cannot be understood by means of the Bragg equation (1) with the Miller indices 2, 1, 1. Blümel [25] has explained this discrepancy by an internal oblique reflection at (110) lattice planes with a light incidence to the (211) face. Recently, Cladis *et al.* [24, 55] have also observed well-faceted BP I single crystals of a quite similar habit with $\{110\}$ and $\{211\}$ in monomorphic CB 15 mixtures.

(iii) $p_d < p < p_m$. In this very small medium pitch range where the BP II develops directly from the isotropic liquid (cf. figure 9) the crystal growth situation is still unexplored. We have found that cubic BP II single crystals of 8OBE/CV grow much slower than those formed from the fog phase [56]. Additionally, we have observed single crystals of a diffuse triangular habit which are difficult to detect because either they reflect in the U.V. or the observation direction is normal to (111) lattice planes at which scattering of circularly polarized light is forbidden [12]. Cooling the sample to the BP I the squares as well as the triangles change their colours and the typical cross-hatching occurs in both of them. However, the triangles deserve further experimental attention.

4.2.2. *Blue phase crystal growth*

The growth rate, v, of cubic BP II single crystals developing from the fog phase BP III (cf. case (i) of §4.2.1) has been measured by Blümel [25]. The observed linear dependence of v on the pitch p_u (figure 22) explains why we found the largest and best developed cubic single crystals in the cholesteryl alkanoates with the longest alkyl chains since these exhibit pitches p_u of about 200 nm (cf. figure 5). For example, in cholesteryl myristate Onusseit grew cubic single crystals up to 2 mm in size. In

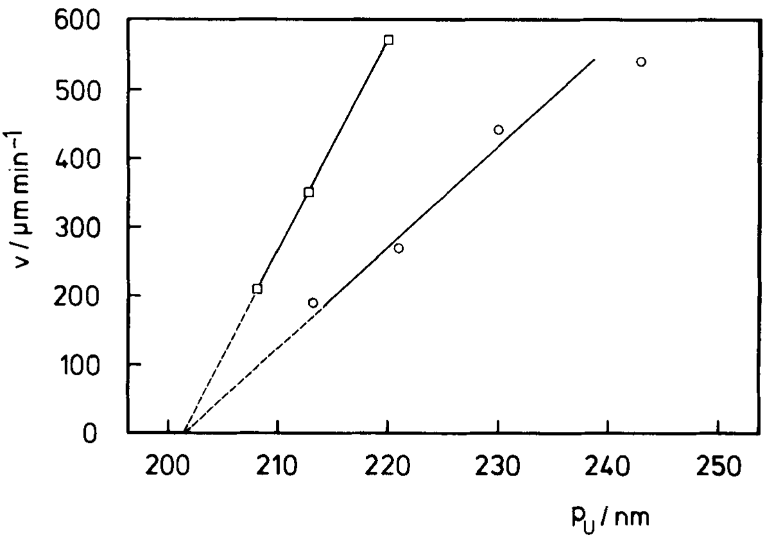


Figure 22. Growth rate, v, in the ⟨100⟩ direction of BP II crystals as a function of cholesteric pitch, p_u, in the system 8OBE/CV (○, $x_{CV} > 0{\cdot}7$; □, $x_{CV} < 0{\cdot}7$).

long-pitch cholesterics, however, a large number of crystallites nucleate and spread with a large growth rate which does not allow single crystal formation; this has been reported [11].

These results can be discussed in terms of the BP III model derived by Collings [30] from his optical rotatory dispersion results: the short-range ordered BP III is built from small BP II domains with randomly oriented crystallographic axes. Taking into account this model the BP III → BP II transition implies a rearrangement of small helically structured domains to a long-range periodic lattice of defects or disclinations. It is plausible that this process takes longer in short-pitch systems because more singularities must be created per unit volume according to the small lattice constants associated with those blue phase systems.

A quite different situation occurs for BP I crystals growing directly from the isotropic liquid (case (ii) in §4.2.1). For all faces involved in the growth of the BP I crystals given in figures 16, 17 and 19 Blümel [25] measured initial growth rates of about 2 µm min^{-1} which is smaller by a factor of 100 than that observed for the BP III → BP II transition (cf. figure 22). This large difference in growth rates is obviously due to the different growth mechanisms: if a BP I crystal develops directly from the isotropic liquid a helical molecular arrangement must be formed in addition to the defect lattice formation. In consequence the growth proceeds more slowly than from the fog phase.

In the mixed system 8OBE/CV with $x_{CV} < 0{\cdot}35$ the growth rate of BP II crystals has been found to be much smaller than in mixtures with $x_{CV} > 0{\cdot}35$ [25]. In a mixture with p_u equal to 296 nm a rate of 5 µm min^{-1} was measured [56] which is much smaller than expected from the plot of v versus p_u shown in figure 22. This behaviour seems to result from a BP II crystal growth from the isotropic liquid (case (iii) in §4.2.1, cf. figure 9). The reason for the slow growth is then the same as we have discussed for the isotropic → BP I transition.

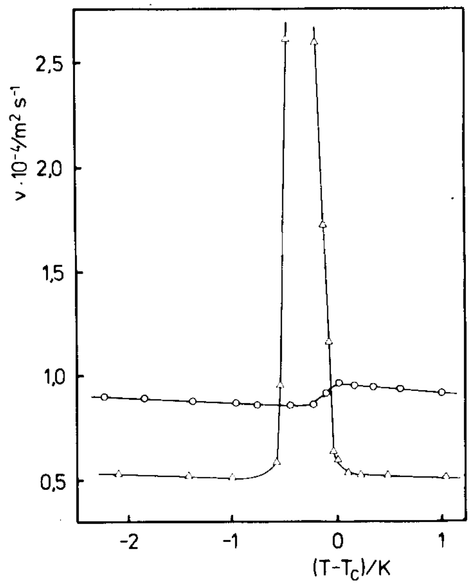


Figure 23. The temperature dependence of the kinematic viscosity for cholesteryl nonanoate/cholesteryl chloride mixtures (○, $x_{CC} = 0{\cdot}15$; △, $x_{CC} = 0{\cdot}50$).

4.2.3. *Paramorphism in blue phases*

From the experimental results reported in §§ 4.2.1 and 4.2.2 we have seen that the dominating growth determining form for BP II is $\{h00\}$ (h = 1 or 2) and $\{110\}$ for the BP I. Nevertheless, the BP I single crystals obtained by cooling the sample from the BP II state are quadratically shaped as shown in figure 14(*c*). The rapid growth of the BP II crystals stops immediately on arriving at the BP I state, the boundaries of the BP I squares become stable, and a crosshatching with striations along $\langle 110 \rangle$ occurs (cf. figure 15). It should be emphasized that analogous striations have never been observed in BP I crystals grown directly from the isotropic state (see, for example, figure 19).

We discuss those effects observed in the squares at the BP II → BP I transition in terms of a paramorphosis. From the change of the reflection colour shown in figures 14 (*b*) and (*c*) we can deduce that, according to the Bragg equation (1) either the blue phase space group (cf. §4.2.4) or the lattice parameter or both quantities change during this transition, whereas the crystal habit of the BP II squares is preserved. The much enhanced bulk viscosity of the blue phases with respect to the isotropic as well to the cholesteric state supports this suggestion. In a dimorphic blue phase system (cholesteryl nonanoate/cholesteryl chloride with 20 mol per cent cholesteryl chloride) we found an extremely high peak in the viscosity just below the clearing point (figure 23) [57]. However, the temperature measurement in the capillary viscosimeter was not precise enough to allow a clear decision if this extremely large bulk viscosity is due only to the BP I or to both blue phases. Visco-elasticity has also been observed for blue phases [24, 58]. The well-known ability of the BP I to be supercooled may be a result of these viscous properties. Consequently, it seems plausible that mechanical forces within a BP I structure of high stiffness result in the preservation of the BP II habit by paramorphosis.

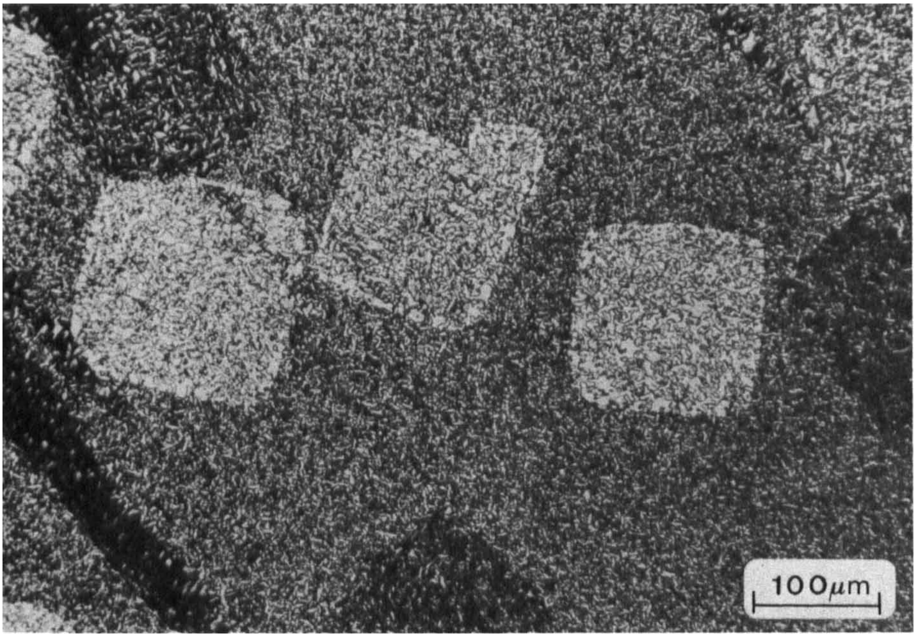


Figure 24. Paramorphic quadratic cholesteric structure of cholesteryl myristate obtained from supercooled BP I single crystals.

In a crosshatched quadratic BP I crystal the boundaries between the alternately light and dark ⟨110⟩ striations are seen to be sharp in the polarizing microscope if they are parallel to the axes of the polarizer and analyser, respectively. After rotation of the sample by 45° the crosshatching becomes diffuse as demonstrated in figure 15. This indicates that the crosshatching originates from birefringent areas within the squares. This birefringence can be induced by a mechanical stress resulting from a lattice change within the crystal whose (*h*00) faces are not in agreement with the new structure because of the paramorphosis. The crosshatching is then comparable with the striations resulting from the stress which is induced by an electric field applied to the ⟨110⟩ direction of the BP I (cf. §3.3).

Another type of paramorphosis has been observed in cholesterics developing from supercooled BP I single crystals (figure 24). Within the boundaries of (h00) faced BP I crystals a quadratic cholesteric texture grows, in which a perpendicular cholesteric helix orientation parallel to the square sides was detected [59]. This behaviour also indicates a high stiffness of the BP I structure.

4.2.4. *Blue phase space groups*

In solid crystals there is a close relation between habit and structure. The morphological aspects of the Donnay–Harker rule [60, 61] allow conclusions concerning the space group to be drawn from the morphologically important forms of a crystal. In contrast to solid crystals there is no positional long-range order in the blue phase liquid single crystals and the lattice planes are built from periodic defects. However, as the Donnay–Harker rule is based on the interfacial energies of the crystal faces concerned it is expected that there also exists an analogous relation between forms

Table 3. Space groups of cubic blue phase structures from the Donnay–Harker rule [60, 61].

Forms of growth	Space groups
	BP I
{110} {100} {211}	$I\,23\ (T^3)$; $I\,2_13\,(T^5)$; $I\,432\,(O^5)$; $\underline{I\,4_132\,(O^8)}$
	BP II
{100}	$P\,23\,(T^1)$; $\underline{P\,4_232\,(O^2)}$

and structure in blue phase crystals. In table 3 the morphologically important forms of BP I and II are given together with the possible space groups according to the Donnay–Harker rule. Because of the optical activity of blue phases only space groups of the enantiomorphic classes 23 and 432 are to be considered.

The situation for the BP I is quite clear: the two-fold rotation axis of the form {211} perpendicular to (110) (cf. figures 16–20) indicates that the crystal symmetry is higher than 23. Further, the field-induced optical biaxiality leads to the conclusion that the field direction is parallel to ⟨110⟩ with a C_2 symmetry (cf. §3.3). Additionally the symmetry of the violet, quadratic BP I crystals (§4.2.1, case (ii)) due to the 432 class. As the observed Bragg scattering with λ_R equal to 435 nm at (200) is forbidden for $I\,432$ because of the selection rules [12] the space group $I\,4_132\,(O^8)$ describes the BP I crystal symmetry, in agreement with the conclusion derived from Bragg scattering (cf. §4.1).

The situation for BP II crystals is less clear. Because only the form $\{h00\}$ with h equal to 1 occurs free of doubt the Donnay–Harker rule allows several space groups of which $P\,23$ and $P\,4_232$ are preferred [61]. Experimentally, four-fold rotation axes have been found in BP II crystals (cf. figure 14 (*a*) and (*b*)) providing that there is no hypermorphological effect. As we did not find a field-induced optical biaxiality in the BP II at a field direction parallel to [100] a C_4 axis characterizes the symmetry of the (100) planes. These results indicate the symmetry class 432. A serious problem is the question as to whether the BP II has a simple cubic or a body-centred cubic structure. We have found that the longest wavelength Bragg peak in the BP II is only compatible with a $(h00)$ reflection. Because of the selection rules [12] this is allowed for the simple cubic space groups $P\,23$ and $P\,4_232$ with h equal to 1 which most probably describe the BP II symmetry.

We obtained a further indication for the BP structures by the interpretation of Cano-lines observed in wedge-shaped blue phase samples [62] which are quite similar to that of cholesterics. The lines are edge dislocations in the defect lattice. For the BP I we found a body-centred cubic lattice with (110) parallel to the wedge planes, for the BP II, however, a simple cubic lattice with (100) planes parallel to the substrates is observed [25, 63].

4.3. *Blue phase models*

The first blue phase model was proposed by Saupe [8] with a body-centred cubic lattice of singular points and a twisted molecular arrangement in the intermediate space. This structure closely resembles the model subsequently derived from Landau theory [64]. To explain the zero birefringence as well as the cholesteric-like optical properties a uniaxial tilted helical blue phase structure has been proposed [65]. A spherical indicatrix results from a magic tilt angle of 54·7° between the local director and the helix axes. This model, given in our first review [1], is not tenable and should not be considered further.

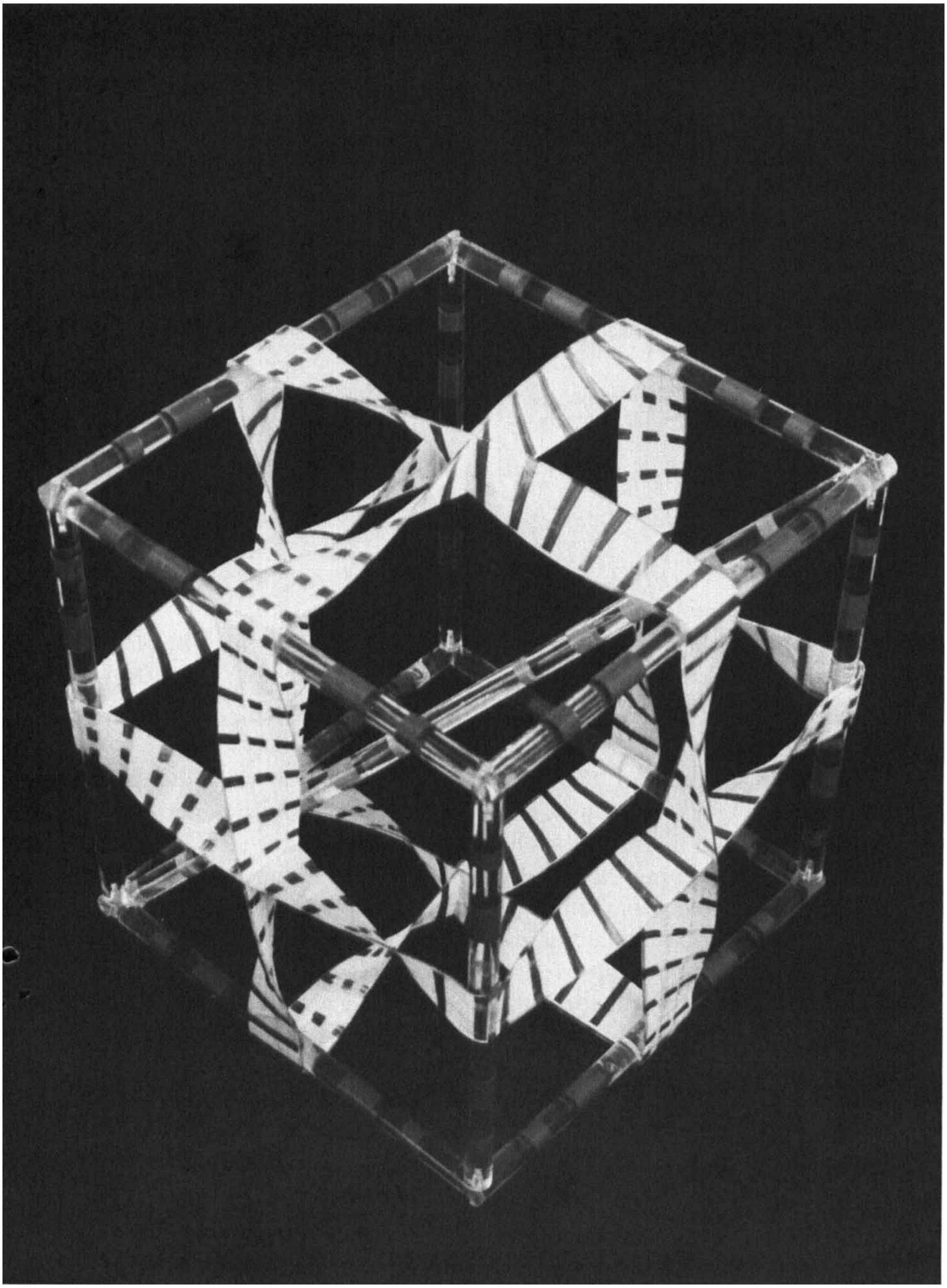


Figure 25. Molecular order in a blue phase structure with $I432$ symmetry (model from Hornreich and Shtrikman [64]).

The problem of setting up a molecular distribution function for the blue phases is to construct a continuous arrangement of form-anisotropic molecules both with cubic and chiral symmetry. This does not seem possible without creating singularities. Two different theories have been applied to develop blue phase structures: (i) the

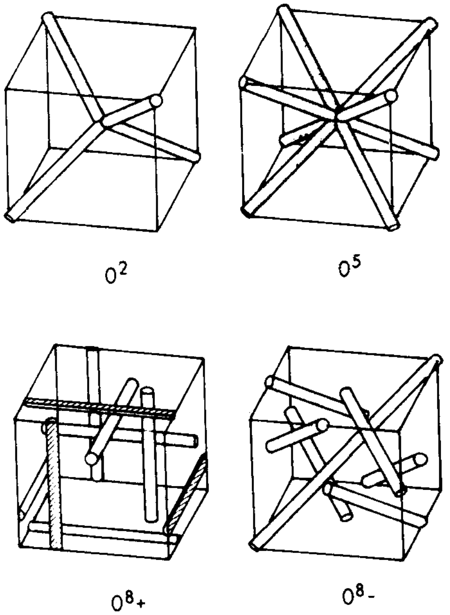


Figure 26. Configurations of blue phase disclinations lattices (after Berreman [67]).

Landau theory, and (ii) the defect theory. A useful comparison of both theories has been given by Crooker [2].

In 1980 Hornreich and Shtrikman [64] reported a very instructive three-dimensional model for a blue phase structure with $I\,432\,(O^5)$ symmetry derived from the Landau theory. In figure 25 the direction and the highest eigenvalue of the order parameter is given showing the three-dimensional chirality across the unit cell faces as well as body centred cubic lattice points of disordered (isotropic) nature.

Attempts to determine blue phase structure by means of the defect theory have been made by Meiboom et al. [66] and Berreman [67]. They calculated the Oseen–Frank free energy for a disclination lattice for models with O^2, O^5, and O^8 symmetry. Four instructive models have been reported by Berreman [67]. In figure 26 the configuration of tubes surrounding disclinations is given; it is remarkable that two different configurations both with O^8 symmetry have been obtained (O^8+ and O^8-).

Grebel *et al.* [13] have recently obtained three different blue phase structures by means of the Landau theory, each with O^8 symmetry characterized by different assemblies of cylinders which describe the curling mode director configuration (O_a^8, O_b^8 and O_c^8). These results indicate the possibility of different molecular distribution functions of the same space group. Consequently, space group determination by means of Bragg scattering or morphological studies is only the first step to obtain the molecular arrangement in blue phases. Electric field effects on blue phases may provide additional information.

Finally, we discuss which of the calculated structures is valid for the BP I and II. In the phase diagrams predicted by Grebel *et al.* [13] the symmetry of the blue phases is included. In figure 11 we refer to two examples [13] with either two blue phases of O_a^8 and O_c^8 symmetry (figure 11 (*a*)) or three blue phases of O^2, O^5 and O_c^8 symmetry (figure 11 (*b*)). As a result none of the phase diagrams in [13] fits the experimentally observed symmetry of BP I and II except the situation in figure 11 (*b*) at higher

T	T	T
BP II O_a^8	BP II O^5	BP II O^2
BP I O_c^8	BP I O^2	BP I O_c^8
figure 11 (*a*))	(figure 11 (*b*))	(figure 11 (*b*), $\kappa > 1\cdot 3$)

chirality. Ignoring the high temperature blue phase with O^5 symmetry we can assign the O_c^8 phase to the BP I and O^2 to the BP II. However, in this case the BP II should survive on decreasing chirality in contradiction to our experimental results [32]. The question generally arises if the space group symmetry is universal for both blue phases in different systems. All these problems deserve further theoretical as well as experimental attention.

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References

[1] Stegemeyer, H., and Bergmann, K., 1980, *Springer Ser. Phys. Chem.* **11**, 161.

[2] Crooker, P. P, 1983, *Molec. Crystals liq. Crystals*, **98** 31.

[3] Lehmann, O., 1906, *Z. phys. Chem.*, **56**, 750.

[4] Reinitzer, F., 1888, *Monatsh. Chem.*, **9**, 421.

[5] Pelzl, G., and Sackmann, H., 1973, *Z. phys. Chem.*, **254**, 354.

[6] Bergmann, K., and Stegemeyer, H., 1978, *Ber. Bunsenges. phys. Chem.*, **82**, 1309.

[7] Bergmann, K., Pollmann, P., Scherer, G., and Stegemeyer, H., 1979, *Z. Naturf.* (*a*), **34**, 253.

[8] Saupe, A., 1969, *Molec. Crystals liq. Crystals*, **7**, 59.

[9] Meiboom, S., and Sammon, M., 1980, *Phys. Rev. Lett.*, **44**, 882.

[10] Johnson, D. L., Flack, J. H., and Crooker, P. P., 1980, *Phys. Rev. Lett.*, **45**, 641; 1981, *Physics Lett.* A, **82** 247.

[11] Onusseit, H., and Stegemeyer, H., 1981, *Z. Naturf.* (*a*), **36**, 1083.

[12] Grebel, H., Hornreich, R. M., and Shtrikman, S., 1983, *Phys. Rev.* A, **28**, 1114.

[13] Grebel, H., Hornreich, R. M., and Shtrikman, S., 1984, *Phys. Rev.* A, **30**, 3264.

[14] Onusseit, H., 1983, Thesis, University of Paderborn.

[15] Onusseit, H., and Stegemeyer, H., 1982, *Chem. Phys. Lett.*, **89**, 95.

[16] Keyes, P. H., and Nicastro, A. J., 1981, *Molec. Crystals liq. Crystals*, **67**, 59.

[17] Onusseit, H., and Stegemeyer, H., 1983, *Chem. Phys. Lett.*, **94**, 417.

[18] Marcus, M. A., and Goodby, J. W., 1982, *Molec. Crystals liq. Crystals*, **72**, 297.

[19] Flack, J. H., Crooker, P. P., Johnson, D. L., and Long, S., 1984, *Liquid Crystals Ordered Fluids*, **4**, 901.

[20] Tanimoto, K., Crooker, P. P., and Koch, G. C., 1985, *Phys. Rev.* A, **32**, 1983.

[21] Nicastro, A. J. and Keyes, P. H., 1983, *Phys. Rev.* A, **27**, 431.

[22] Gray, G. W., and McDonnell, D. G., 1978, *Molec. Crystals liq. Crystals*, **48**, 37.

[23] Armitage, D., and Cox, R. J., 1980, *Molec. Crystal liq. Crystals*, **64**, 41.

[24] Cladis, P. E., Pieranski, P., and Joanicot, M., 1984, *Phys. Rev. Lett.*, **52**, 542.

[25] Blümel, Th., 1984, Thesis, University of Paderborn.

[26] Bergmann, K., and Stegemeyer, H., 1979, *Z. Naturf.* (*a*), **34**, 251.

[27] Bergmann, K., and Stegemeyer, H., 1979, *Z. Naturf.* (*a*), **34**, 1031.

[28] Marcus, M., 1981, *J. Phys., Paris*, **42**, 61.

[29] Meiboom, S., and Sammon, M., 1981, *Phys. Rev.* A, **24**, 468.

[30] Collings, P. J., 1984, *Phys. Rev.* A, **30**, 1990; 1984, *Molec. Crystals liq. Crystals*, **113**, 277.

[31] Kleiman, R. N., Bischop, D. J., Pindak, R., and Taborek, P., 1984, *Phys. Rev. Lett.*, **53**, 2137.

[32] Blümel, Th., and Stegemeyer, H., 1984, *Physics Lett.* A, **104**, 277.
[33] Onusseit, H., and Stegemeyer, H., 1984, *Z. Naturf.* (*a*), **39**, 658.
[34] Blümel, Th., Collings, P. J., Onusseit, H., and Stegemeyer, 1985, *Chem. Phys. Lett.*, **116**, 529.
[35] Yang, C. C., 1972, *Phys. Rev. Lett.*, **28**, 955.
[36] Collings, P. J., *Phys. Rev.* A (in the press).
[37] Finn, P. L., and Cladis, P. E., 1982, *Molec. Crystals liq. Crystals*, **84**, 159.
[38] Heppke, G., Krumrey, M., and Oestreicher, F., 1983, *Molec. Crystals liq. Crystals*, **99**, 99.
[39] Pieranski, P., Cladis, P. E., and Barbet-Massin, R., 1985, *J. Phys. Lett.*, **46**, L-973.
[40] Brazowski, S. A., and Dimitriev, S. G., 1976, *Soviet. Phys. JETP*, **42**, 497.
[41] Hornreich, R. M., Kugler, M., and Shtrikman, S., 1985, *Phys. Rev. Lett.*, **54**, 2099.
[42] Kirkwood, J. G., and Oppenheim, I., 1961, *Chemical Thermodynamics* (McGraw-Hill Book Company, Inc.), p. 231.
[43] Helfrich, W., 1970, *Phys. Rev. Lett.*, **24**, 201.
[44] Stegemeyer, H., and Porsch, F., 1984, *Phys. Rev.* A, **30**, 3369.
[45] Porsch, .F., Stegemeyer, H., and Hiltrop, K., 1984, *Z. Naturf.* (*a*), **39**, 475.
[46] Nye, J. F., 1985, *Physical Properties of Crystals* (Clarendon Press), p. 245.
[47] Porsch, F., and Stegemeyer, H., *Chem. Phys. Lett.* (submitted). Porsch, F., 1983, Diplomarbeit, University of Paderborn.
[48] Kitzel, V. A., and Prokhorov, V. V., 1983, *J. exp. theor. Phys., Lett.*, **38**, 337; 1984, *J. exp. theor. Phys.*, **60**, 257.
[49] Meiboom, S., Sammon, M., and Berreman, D. W., 1983, *Phys. Rev.* A, **28**, 3553.
[50] Demus, D., and Richter, L., 1978, *Textures of Liquid Crystals* (Verlag Chemie, Weinheim), p. 184.
[51] Onusseit, H., and Stegemeyer, H., 1983, *J. Crystal Growth*, **61**, 409.
[52] Marcus, M., 1982, *Phys. Rev.* A, **25**, 2272.
[53] Blümel, Th., Onusseit, H., and Stegemeyer, H., 1983, *Proceedings of the 13th Freiburger Arbeitstagung Flüssigkristalle*, 23–25 March.
[54] Blümel, Th., and Stegemeyer, H., 1984, *J. Crystal Growth*, **66**, 163.
[55] Barbet-Massin, R., Cladis, P. E., and Pieranski, P., 1984, *Phys. Rev.* A, **30**, 1161.
[56] Blümel, Th., and Stegemeyer, H., 1985, *Z. Naturf.* (*a*), **40**, 260.
[57] Stegemeyer, H., and Pollmann, P., 1982, *Molec. Crystals liq. Crystals*, **82**, 123.
[58] Clark, N. A., Vohra, S. T., and Handschy, M. A., 1984, *Phys. Rev. Lett.*, **52**, 57.
[59] Onusseit, H., and Stegemeyer, H., 1983, *Z. Naturf.* (*a*), **38**, 1114.
[60] Donnay, J. D. H., and Harker, D., 1937, *J. Min. Soc. Am.*, **22**, 446.
[61] Kleber, W., 1983, *Einführung in die Kristallographie*, 15th edition (VEB Verlag Technik), p. 91.
[62] Kuczynski, W., and Stegemeyer, H., 1980, *Naturwissenschaften*, **67**, 310.
[63] Blümel, Th., and Stegemeyer, H., 1985, *Proceedings of the 15th Freiburger Arbeitstagung Flüssigkristalle*, 27–29 March.
[64] Hornreich, R. M., and Shtrikman, S., 1980, *Springer Ser. Chem. Phys.*, **11**, 185.
[65] Kuczynski, W., Bergmann, K., and Stegemeyer, H., 1980, *Molec. Crystals liq. Crystals*, **56**, 283.
[66] Meiboom, S., Sammon, M., and Brinkman, W. F., 1983, *Phys. Rev.* A, **27**, 438.
[67] Berreman, D. W., 1984, *Liq. Crystals Ordered Fluids*, **4**, 925.