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High pressure optical studies of the chirality and phase behaviour of liquid crystalline blue phases

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The blue phase (BP) polymorphism of chiral *S*-(+)-4′-(2-methylbutyl)phenyl-4-decyloxy benzoate (CE6) and *S*-(+)-4′-(2-methylbutyl)phenyl-4-dodecyloxy benzoate (CE7) was studied at elevated transition pressures up to 280 MPa using optical activity measurements. The increased density causes an increase in phase chirality which in the case of CE6 manifests itself in the disappearance of BP II (BP I–BP II–BP III triple point) and in the case of CE7 in the appearance of BP II. At atmospheric pressure, CE6 exhibits BP I, BP II and BP III, while CE7 only possesses BP I. This pressure behaviour of CE6 and CE7 is contrary to that of cholesteryl nonanoate, which has been investigated previously. This result is particularly interesting when discussed in connection with the effect of elongation of the terminal *n*-alkylcarboxy chain of the cholesteryl *n*-alkanoates and of the terminal *n*-alkyloxy chain in the homologous series to which CE6 and CE7 belong. In the first case the phase chirality increases; in the second case it decreases. Since CE6 shows an obvious pretransitional optical activity in its isotropic liquid phase, pretransition and BP phase behaviour could be compared with each other at elevated transition pressures and temperatures. For those transition pressures or temperatures where anomalies in the BP phase behaviour occur, anomalies in the pretransition behaviour are also observed.

1. Introduction

Compounds of sufficiently high chirality can form liquid crystalline blue phases (BPs), which exist just below the clearing point. These fascinating phases have been the subject of much theoretical and experimental work. Apart from three publications by Pollmann and coworkers [1–3], however, nothing has been reported about the behaviour of BPs at elevated pressures. Chirality plays the decisive role in the polymorphism of BPs, and since one has good reason to assume that an increased transition pressure (which is equivalent to an increased density) would influence the chirality [1], it would be of great interest to study the polymorphism of BPs at elevated pressures. On the other hand, one has to take note of the previous results [1–3], which show no influence of pressure on the temperature range of BPs. The question arises as to whether or not this is generally characteristic for BPs or only for BPs of the few compounds investigated.

2. Experimental

The subjects of the present study were the chiral compounds *S*-(+)-4′-(2-methylbutyl)phenyl-4-decyloxy-benzoate (CE6), *S*-(+)-4′-(2-methylbutyl)phenyl-4-dodecyloxy benzoate (CE7), and cholesteryl nonanoate (CH9). Their molecular structures are given in figure 1. The materials were obtained from Merck Ltd. (Poole, England). Whereas CE6 and CE7 were used without

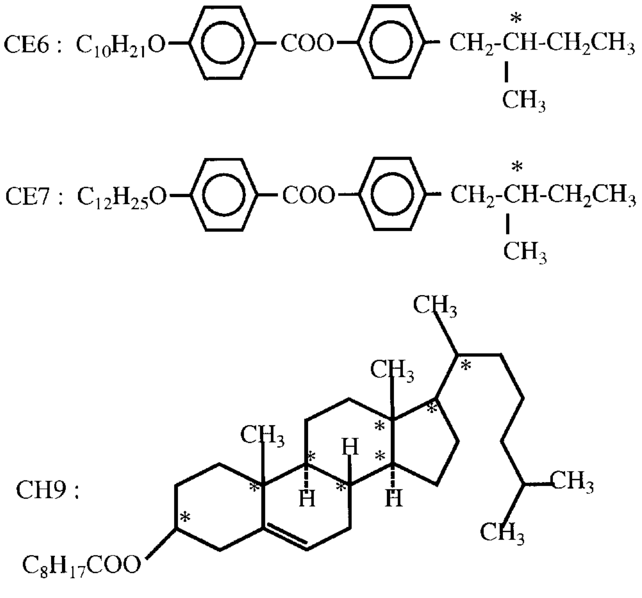

Figure 1. Molecular structures of the compounds studied.

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further purification, CH9 was purified by repeated recrystallization from a mixture of acetone/methanol.

A very precise and simple method for detecting phase transitions in the liquid crystalline range, even under high pressure, is the optical transmission technique. The transition is indicated by a discontinuity in the intensity of transmitted light or a change in its pressure dependence. Relevant measurements were carried out with a Cary 17 DH spectrophotometer. This method is not suitable for transitions where BPs are involved. In this case we chose as the quantity to be measured the angle of optical rotation. In addition the optical activity gives information within the blue phases and the pretransition region. The optical rotation was determined by a half-shade polarimeter (Schmidt and Haensch). The high pressure set-up is essentially the same as that previously described [3]. The accuracy in the determination of pressure was ±0·1% of the full scale reading of the gauge, of temperature ± 0·02 K, and of the angle of optical rotation ± 0·01 deg. For identifying the special liquid crystalline phases, particularly the different BPs and the detection of their transformations at atmospheric pressure, a polarizing microscope (Leitz, Ortholux II-Pol BK) was used.

3. Results and discussion

3.1. *General*

Chiral liquid crystals can exhibit up to three thermodynamically stable BPs occurring in a narrow temperature range between the cholesteric (N*) and the isotropic liquid (ISO) phase. Proceeding with increasing temperature the BPs are denoted as BP I, BP II, and BP III. Phase transitions involving BPs are first order. The BP III/ISO transition, however, seems to be an exception. There is evidence that the first order line of this transition can end at a critical point like that of the isotropic liquid/gas transition [4]. Responsible for this phenomenon is the chirality of the system. The chirality also determines the BP polymorphism: the number of BPs generally increases as the chirality increases, e.g. in a multicomponent system. However, this correlation is not universal, since experimental evidence has been obtained that in mixed systems of very high chirality the BP II can disappear [5].

For representing the chirality of a system, a so-called chirality parameter is often used which is proportional to the reciprocal pitch of the cholesteric phase (pitch near the N*/BP I transition). The variation of the blue phase polymorphism of the cholesteryl *n*-alkanoates with this reciprocal pitch z^{-1} is demonstrated in figure 2 [6]. Whereas cholesteryl propionate only has BP I, the higher homologues are di- or tri-morphic. Obviously, the elongation of the terminal *n*-alkylcarboxy chain causes an increase of the reciprocal pitch. Elongation of this chain also means an increase in the flexibility of the molecules which perhaps is one reason for a stronger induction of phase chirality by the molecules in this case.

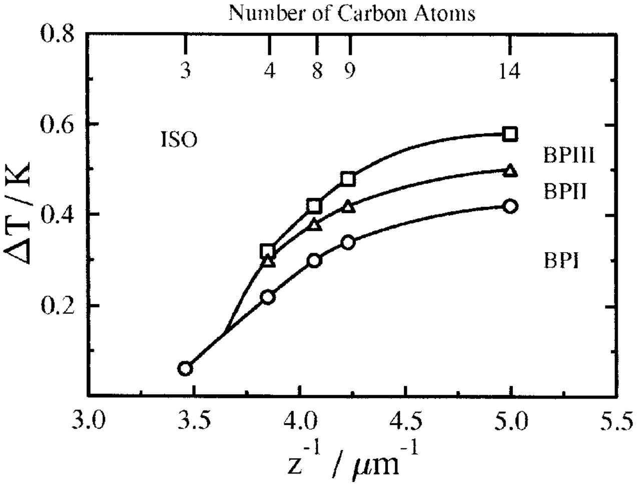

Figure 2. Blue phase temperature range ΔT vs. reciprocal pitch z^{-1} of the cholesteryl *n*-alkanoates.

The opposite is observed when the terminal *n*-alkyloxy chain (*R*) of the homologous series to which CE6 and CE7 belong is elongated. Unfortunately the cholesteric pitch of the known homologues CE4, CE5, CE6, and CE7 is so small that for all four compounds only an extrapolated value of about 160 nm is given [5]. This small value indicates a high chirality of the N* phase. The variation of the BP polymorphism with the length of the *n*-alkyloxy chain, however, clearly speaks for a decrease of chirality with elongation of the chain (see table 1). In CE7 the chirality is reduced to such an extent that only BP I remains.

By application of pressure, one has the chance to change the flexibility of a given molecule. Generally the density of a phase at a transition point, briefly called transition density, increases with increasing transition temperature caused by rising pressure [7]. Increasing density lowers molecular flexibility, particularly that of the end chain [7], so that one can examine whether this change in flexibility has a similar effect on chirality and BP polymorphism to that induced by elongation of the chain.

Table 1. Blue phase polymorphism of four CE*X* homologues.

CE*X*	*R*	Blue phases
CE4	$n\text{-}C_6H_{13}O$	BP I, BP III
CE5	$n\text{-}C_8H_{17}O$	BP I, BP III
CE6	$n\text{-}C_{10}H_{21}O$	BP I, BP II, BP III
CE7	$n\text{-}C_{12}H_{25}O$	BP I

3.2. *BP pressure behaviour of CH9*

In the case of cholesteryl nonanoate (CH9) with all three BPs, a rise from atmospheric pressure to 35 MPa increases the clearing temperature by 15 K and the transition density by 5% [7]; the latter value seems to be somewhat too high [8]. It is not clear to which phase the given transition density is related (BP III?). In [7] the authors only report that the measurements were performed in the vicinity of the clearing transition. Since they do not mention the existence of any BP, probably the narrow BP range escaped their notice. In any case, there is an increase in density on the BP side of the BP/ISO transition. What then is the effect of increasing density, meaning also decreasing molecular flexibility, on the chirality and BP polymorphism of CH9? To answer this question we can make use of previous light reflection measurements on CH9 up to 120 MPa [9]. Figure 3 displays all the measured wavelengths of maximum light reflection at the phase transition points to which N*, BP I and BP II refer. The impression created by figure 3 is somewhat confusing: BP I and BP II exhibit two different wavelengths. The explanation is the following: starting in the N* phase oriented in the Grandjean texture, with decreasing pressure (at constant temperature), a reflecting lattice plane of BP I and BP II is observed, different from that seen with increasing pressure when starting from the ISO phase [9].

All λ_t are linearly shifted to higher wavelengths with increasing transition pressure and temperature in the same way. Since

$$\lambda = \bar{n}\, z \qquad (1)$$

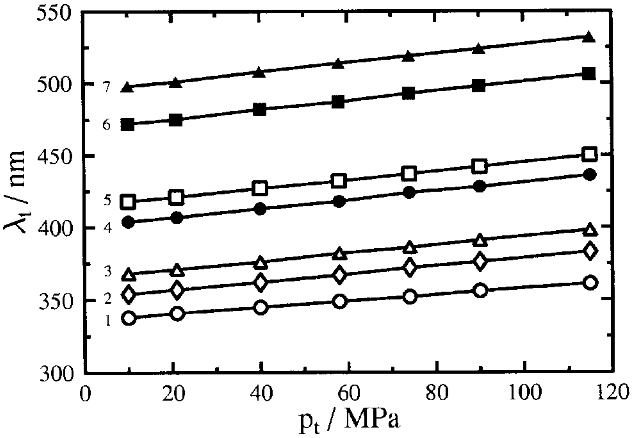

Figure 3. Wavelength of maximum light reflection of CH9 at the phase transition point, λ_t, vs. phase transition pressure, p_t. 1: λ_t'(BP II/BP III); 2: λ_t'(N*/BP I); 3: λ_t'(N*/BP I); 4: λ_t(BP III/BP II); 5: λ_t(BP II/BP I); 6: λ_t(BP II/BP I); 7: λ_t (BP I/N*). (λ_t' with decreasing pressure, λ_t with increasing pressure; the bar above a phase symbol denotes the phase in which λ_t has been measured.)

where $\bar{n}$ is the average refractive index and z the pitch of the cholesteric helix, it follows from straight line 2 in figure 3 that the pitch at the N*/BP I transition point is enlarged by increasing transition pressure. This result also holds if one takes into account the transition pressure dependence of $\bar{n}$ at the phase transition point (increase by approximately 2% [10]). The result is a small reduction in chirality at higher transition pressure and temperature. Does this reduction affect the polymorphism of CH9? Figure 4 gives the answer: neither the pressure range of BP I, nor that of BP II is changed with increasing transition temperature. The same should be valid for BP III.

In the following sections, the pressure behaviour of CE6 and CE7 is reported and compared with that of CH9. The pressure (p)-temperature(T) diagrams for both compounds are essentially similar. The diagram for CE6 is shown in figure 5. The pressure dependence of the

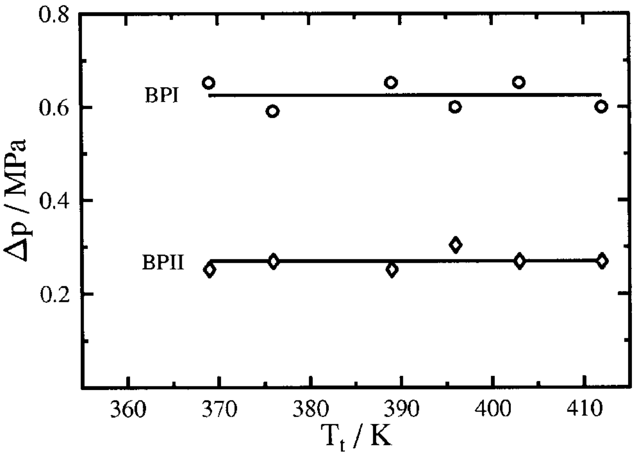

Figure 4. Pressure range Δp of BP I and BP II of CH9 vs. phase transition temperature T_t.

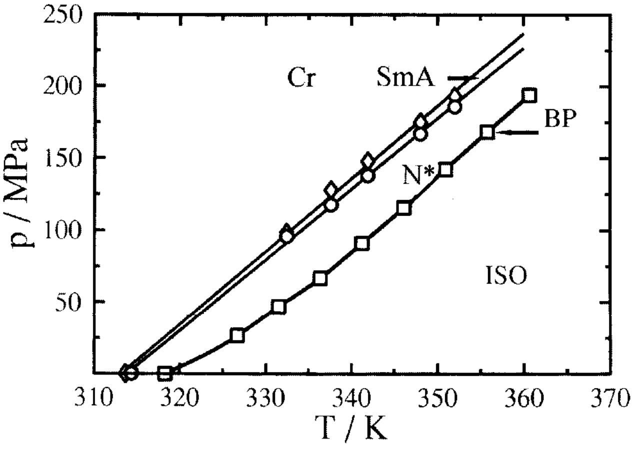

Figure 5. The pressure–temperature phase diagram of CE6. Cr, crystal; SmA, smectic A; N*, cholesteric; BP, blue phase; ISO, isotropic liquid phase.

phase transition temperatures, other than those concerning BPs, was studied by the optical transmission technique. The diagram exhibits no unusual features. On account of the very small temperature span of the BPs, the BP range appears only as a single line.

3.3. *BP pressure behaviour of CE6*

For indicating phase transitions involving BPs, use has been made of the high optical activity of these phases. This method has proved to be sufficiently sensitive and has the advantage of including BP III, which is not possible using the light reflection method.

Before presenting the *p–T* phase diagrams for the BPs of CE6 and CE7, the influence of elevated transition pressure on their chirality will be investigated. Unfortunately, all experiments failed to orient CE6 and CE7 in such a way that at high pressure the determination of the wavelength of maximum light reflection of the BPs (λ_R) was possible. In this case the recording of the optical rotatory dispersion (ORD) of the BPs of CE6 offered an opportunity of obtaining at least the pressure trend of λ_R. The results are given in figure 6. In figure 6 (*a*), the ORD of all three BPs in the visible wavelength region is shown. The pressure level to which the measurements are related is represented by a clearing pressure of 95·2 MPa at 341·4 K. Only BP I exhibits a tendency towards a divergence of the ORD. The value of the corresponding λ_R should be about 500 nm. On increasing the temperature to 356·1 K, the clearing pressure rises to 168·5 MPa; BP II has now disappeared and λ_R of BP I is lowered to about 475 nm (figure 6 (*b*)). This decrease of λ_R with pressure is consistent with the value of 600 nm given in [11] for atmospheric pressure. λ_R of the N* phase should behave in the same manner, so that one can tentatively conclude an increasing trend with pressure for the chirality.

To obtain the *p–T* diagram for the BP transitions of CE6, the pressure dependence of the angle of optical rotation α was determined at various constant temperatures. Because of the large heat capacity of the high pressure optical cell, it was more practical to vary the pressure at constant temperature than *vice versa*. Figure 7 shows two representative isothermal pressure dependences of α at one temperature with all three BPs (*a*) and a different temperature with only BP I and BP III (*b*). At both temperatures, measurements were performed with increasing pressure starting in the ISO phase and with decreasing pressure in the N* phase. The vertical lines indicate the probable 'transition point', obtained by repeatedly passing through the transition. Generally the pressure was varied in equal steps in order to show a greater change in α near a transition.

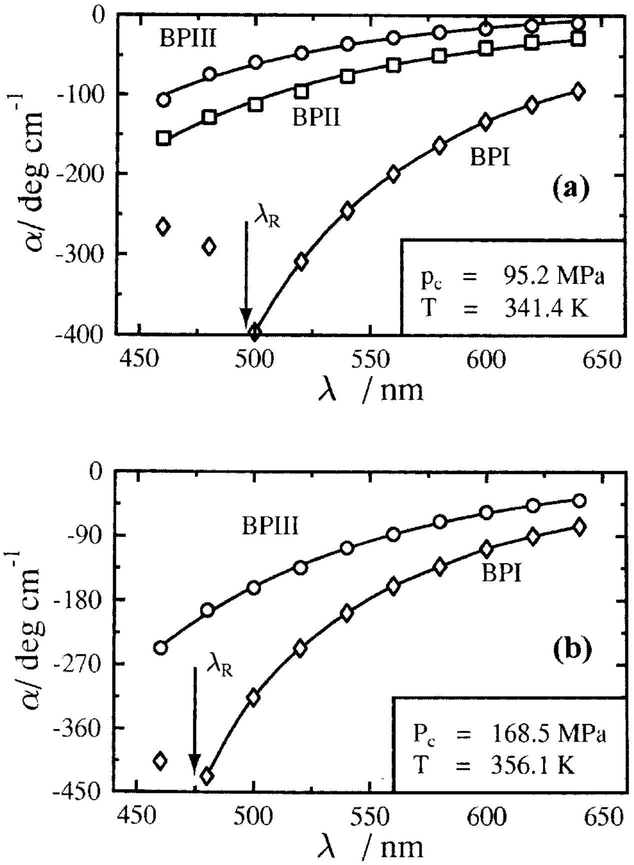

Figure 6. Optical rotatory dispersion of the BPs of CE6 at two different ((a) and (b)) clearing pressures (p_c) and temperatures (T). (The vertical arrow points to the approximate wavelength of maximum light reflection, λ_R, of BP I.)

(*a*) Starting in the ISO phase with increasing pressure, the transition to BP III can easily be observed by a jump in α associated with a change from a positive to a negative sign. The following BP III/BP II transition can just be seen by a bend in the α curve, whereas the BP II/BP I transition is indicated again by a jump in α, with increasing as well as with decreasing pressure. The BP I/N* transition, however, appears only with decreasing pressure when starting in the N* phase, because the BP I is superpressurized. The N* phase has a considerably higher optical activity (with a small light transmission) than BP I and cannot be measured by our polarimeter. When reaching BP I from the N* phase with decreasing pressure, the optical activity is measurable again which means that the N*/BP I transition has occurred. Obviously α now is higher than with increasing pressure. This effect will be discussed later. The pressure dependence of α is also stronger and thus both curves still intersect in the BP I range. Very low values of α follow in the BP II range so that one observes no BP II/BP III transition. There seems to be a direct transition to the ISO phase. This behaviour is thermodynamically incomprehensible. It is always observable when starting

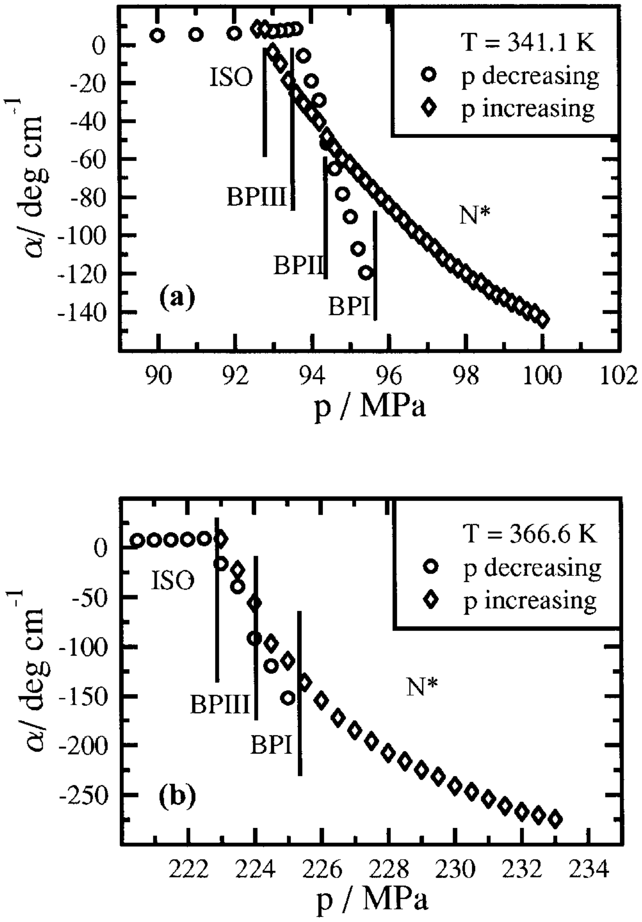

Figure 7. Variation of the angle of optical rotation α of CE6 with pressure at constant temperature in the p-T range where (*a*): all three BPs (*b*): only BP I and BP III exist. (Wavelength of the light: 675 nm, optical path length: 8 mm.)

in the N* phase and not observable when starting below the N*/BP I transition without any formation of the N* phase.

(*b*) With further increasing transition pressure and temperature, finally only two BPs remain. Which BP has disappeared? Since there was no possibility of observing the BPs microscopically, this question can only be answered indirectly (table 2). At a pressure where all three BPs still exist (110 MPa) the slopes of all transition lines involving BPs were determined. Whereas the slopes of three transition lines are nearly equal, the slope of the BP II/BP III transition line is clearly greater. Hence suppression of the BP II range can be concluded.

Table 2. Slopes of BP transition lines $(\mathrm{d}p/\mathrm{d}T)_t$ of CE6 at 110 MPa.

Phase transition line	$(\mathrm{d}p/\mathrm{d}T)_t$/MPa K^{-1}
N*/BP I	5·1
BP I/BP II	5·2
BP II/BP III	6·1
BP III/ISO	5·2

Another hint is the following: the light depolarization by the polycrystalline sample is different in the BPs and gives rise to a characteristic shading in the analyser of the polarimeter. The observed shading in BP II is particularly conspicuous compared with that in BP I or BP III, so that the absence of this peculiarity above 120 MPa also suggests the disappearance of BP II. The pressure behaviour of α in figure 7 (*b*) can briefly be described. The new BP I/BP III transition is indicated by a jump in α, with increasing as well as with decreasing pressure. The same now is true for the BP III/ISO transition, contrary to case (*a*). The behaviour of α at the N*/BP I transition corresponds to that in (*a*).

In figure 8 some additional experimental details are presented concerning the pressure behaviour of α. (*a*) The increase of pressure is stopped when the BP I range is reached. The isotherms obtained with increasing and decreasing pressure are identical within the margin of experimental error. The same is valid for the BP III/ISO transition. (*b*) The pressure is increased up to the metastable range of the BP I, but immediately lowered to that of the stable range. At first one distinguishes higher values of α with decreasing pressure, and then, on account of the stronger pressure dependence of α, lower values. (*c*) The experimental procedure is similar to that in (*b*); the pressure, however, is maintained in the metastable range of BP I and in the stable range of the N* phase for 12 h, so that one can be sure that with decreasing pressure BP I grows from the N* phase. At the N*/BP I transition, again α is higher than with increasing pressure, but the difference now is greater than in (*b*). The transition to the ISO phase occurs earlier than with increasing pressure without any detectable formation of BP III (figure 7 (*a*)). What is the reason for the difference in α at the N*/BP I transition?

A certain orienting influence of the N* phase on BP I is found for path lengths $<30\,\mu$m. Under these conditions BP I exhibits different reflection peaks according to the phase from which it develops, e.g. as in this case from BP II or the N* Grandjean texture [1]. The path length in this study, however, is 8 mm. Probably the most important reason is an increased magnitude of the BP I domains when the sample has passed through the N* phase. BP I single crystals of CH9 show an essentially greater optical activity than BP I polycrystals [12].

Since the regions of existence of the BPs are very small, the usual p–T phase diagram had to be varied. In figure 9 the pressure difference Δp of the BP transitions from the corresponding N*/BP I transition is plotted

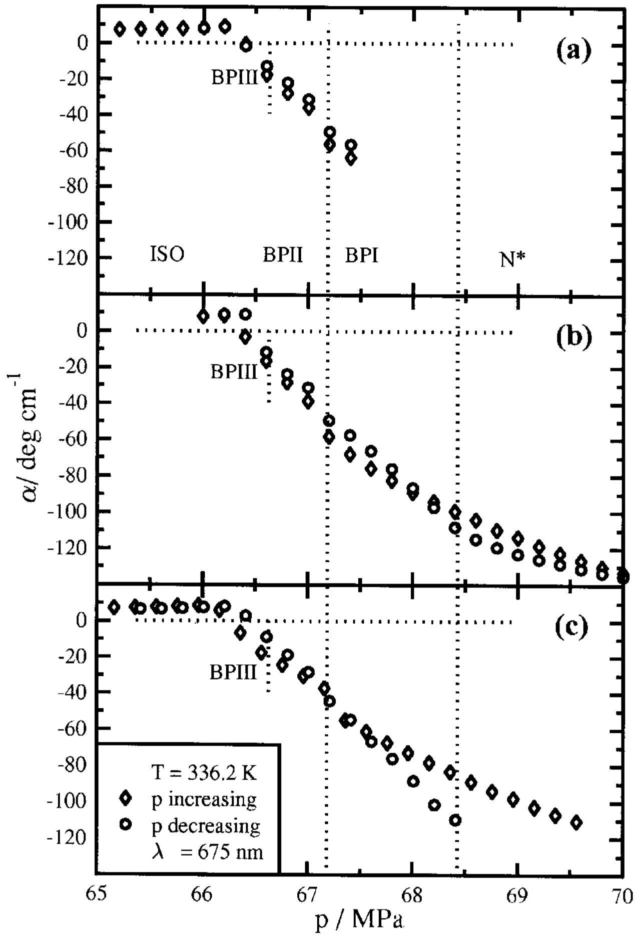

Figure 8. Variation of the angle of optical rotation α of CE6 with pressure under differing test conditions. Start in the ISO phase and stop pressurizing (a): in the stable range of BP I (b): in the metastable range of BP I (BP I/N* transition superpressurized) and immediately return to the stable range (c): in the metastable range of BP I (BP I/N* transition superpressurized) and return to the stable range, but not before 12 h. In all cases, the decrease in pressure is continued until the formation of the ISO phase. (Optical path length: 8 mm.)

vs. the N*/BP I transition pressure. This modification shows clearly the individual BP ranges and also gives the pressure level for which the various isotherms $\alpha = f(p)$ have been measured. The striking feature of figure 9 is the triple point at about 120 MPa, where all three BPs are present; this is the first time that such a triple point of BPs has been found in a single component under pressure. At low pressures, the ranges of BP I and BP III enlarge with increasing pressure, while the range of BP II diminishes; finally BP II is suppressed. Above the triple point, the range of BP III remains constant whereas that of BP I passes through a maximum. At about 220 MPa the range of BP I also becomes constant.

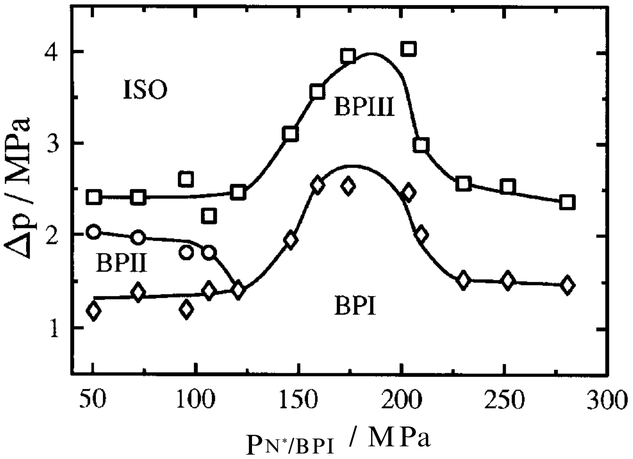

Figure 9. Pressure difference Δp between the BP transitions and the N*/BP I transition of CE6 vs. N*/BP I transition pressure.

3.4. *BP pressure behaviour of CE7*

In CE7, two homologues higher than CE6, the chirality is lowered so much that at atmospheric pressure only BP I is formed. Since increasing the transition pressure should increase the chirality of CE7 (as is the case for CE6), there is a chance of inducing a second BP by application of pressure. Indeed, even at about 40 MPa two BPs are observed. The pressure induced BP is probably BP II.

In figure 10 a representative isothermal pressure dependence of α is displayed in a p–T region with two BPs. The BP I/BP II and BP II/ISO transitions are indicated by jumps in α with both increasing and decreasing pressure. The variation of α at the N*/BP I transition is analogous to that of CE6. The p–T behaviour of the BPs of CE7 is presented in figure 11 in the same way as

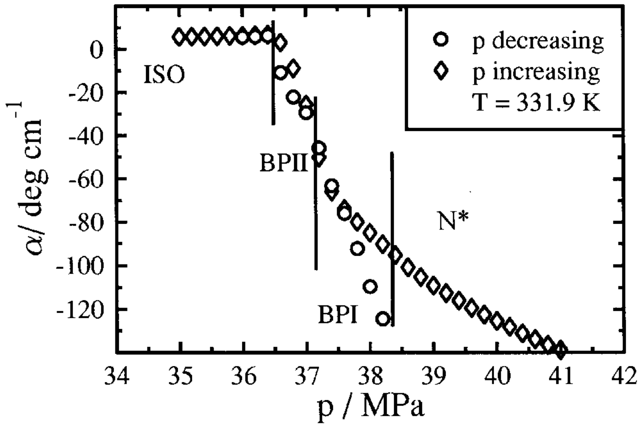

Figure 10. Variation of the angle of optical rotation α of CE7 with pressure at constant temperature. (wavelength of the light: 675 nm, optical path length: 8 mm).

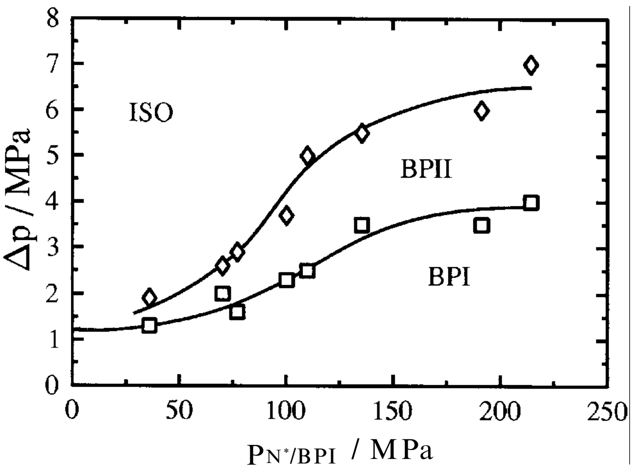

Figure 11. Pressure difference Δp between the BP transitions and the N*/BP I transition of CE7 vs. N*/BP I transition pressure.

for CE6. The range of BP I and BP II seems to become constant at higher pressures.

3.5. *Comparison of pretransitional and BP phase behaviour of CE6*

In [13] a correlation is described between the slope of the nematic/isotropic coexistence curve $\mathrm{d}T/\mathrm{d}p$ and the re-entrant behaviour of the nematic phase of a binary system with respect to its composition. Anomalies in $\mathrm{d}T/\mathrm{d}p$ as a function of mole fraction occur at those concentrations at which the re-entrant nematic phase makes its appearance and disappearance.

Since CE6 exhibits a pretransitional optical activity in the ISO phase which is much higher than its molecular optical activity, the pressure dependence of α has been investigated at those elevated transition pressures and temperatures, where the disappearance of BP II and the maximum range of BP I have been observed.

A representative example of the isothermal pressure dependence of α in the ISO phase near the BP III/ISO transition is given in figure 12. Just before the transition, α seems to diverge, but then reaches a maximum and steeply decreases. This variation of α with pressure can theoretically be understood as a superposition of fluctuations in two structural modes, the conical spiral and the planar spiral mode. Both modes cause optical rotation in the opposite sense and thus a peak in the optical activity just before the transition to BP III (figure 12).

Even at a small distance from the BP III/ISO transition, the contribution of the planar spiral mode can be neglected and the data for $\alpha=f(p)$ in the ISO phase of CE6 described with a reduced form of a relation derived

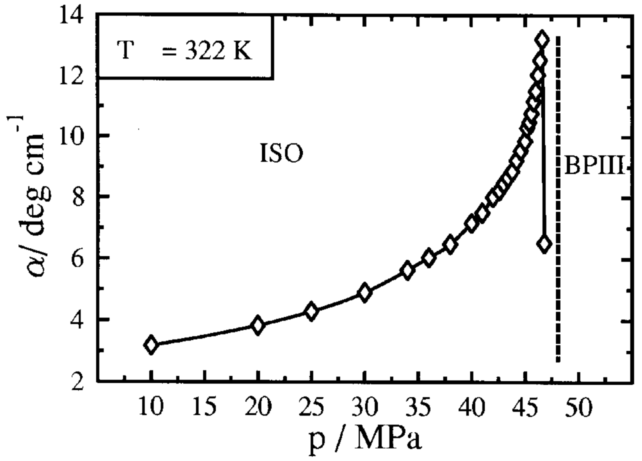

Figure 12. Variation of the angle of optical rotation α with pressure in the ISO phase of CE6 at constant temperature (wavelength of the light: 550 nm, optical path length: 8 mm).

by Demikhov [14]:

$$\alpha(p)=\alpha_0+\frac{k_0^2\,q\,k_B\,T}{48\,\Pi\,\varepsilon^2(1+c/2b)^{3/2}\,(a_0 b)^{1/2}\,\beta^{1/2}\,(p_1^*-p)^{1/2}} \qquad (2)$$

Due to equation (2), α consists of two terms: the angle of molecular optical rotation α_0 and the contribution of the conical spiral mode. The meaning of the other quantities in (2) is the following: p_1^* = pressure at which fluctuations in the conical spiral mode diverge ($p_1^*>p_c$ (clearing pressure)); $k_0=2\pi\cdot n/\lambda$ (wave vector of the light with wavelength λ; n, refractive index of the ISO phase); $q=4\pi/z$ (z, pitch of the N* phase near the N*/BP transition); k_B = Boltzmann's constant; ε = average dielectric constant; a_0, b, c are coefficients in the Landau-deGennes free energy expansion (pressure and temperature independent); β = slope of $T_1^*=f(p)$ (T_1^*, temperature at which fluctuations in the conical spiral mode diverge).

For determining p_1^*, the following fitting function was used:

$$(\alpha-\alpha_0)^{-2}=(AT^{-2})(p_1^*-p) \qquad (3)$$

A and p_1^* are the fitting parameters (α_0(550 nm) = 1·57 deg cm^{-1}). In a pressure range of 15 MPa in the vicinity of the clearing pressure, the resulting line is fairly straight. This fitting procedure was repeated with experimental data from ten additional isothermal pressure runs of α. Since the difference between the divergence pressure of the conical spiral mode and the clearing pressure $p_1^*-p_c=\Delta p^*$ is correlated with the chirality of the liquid crystal phase [15], Δp^* and not p_1^* is plotted vs. T_t (T_t = BP III/ISO transition temperature) in figure 13 (a). The remarkable result will be compared

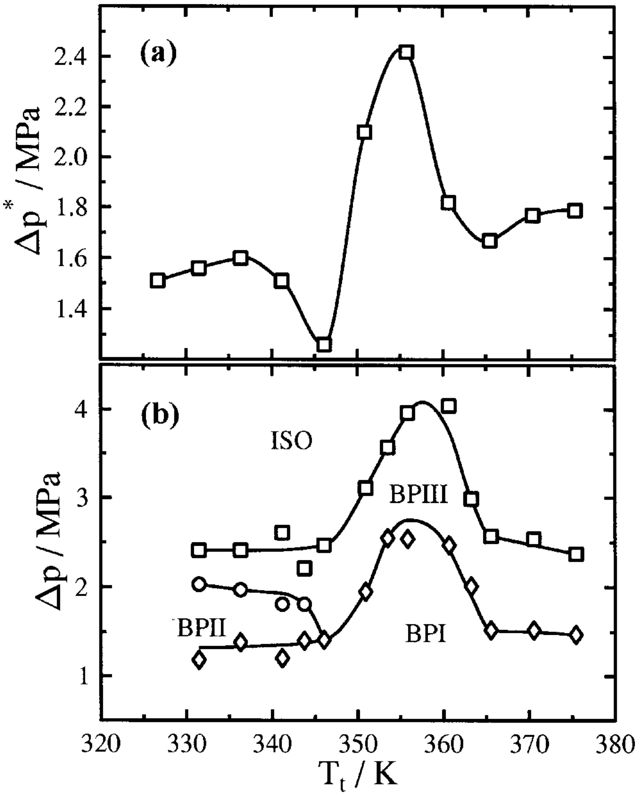

Figure 13. Difference between the divergence pressure and clearing pressure $p_1^* - p_c = \Delta p^*$ (p_c = BP III/ISO transition pressure) (*a*) and difference between the BP transition pressures and N*/BP I transition pressure Δp (*b*) vs. phase transition temperature T_t.

with that in figure 9. Before doing this the N*/BP I transition pressure abscissa in figure 9 is replaced by the corresponding transition temperature abscissa (see figure 13 (*b*)). This can be done easily, since the measuring temperatures are also the transition temperatures T_t of all transitions.

As seen in figure 13, Δp^* reaches a minimum just at that transition temperature where BP II disappears. At higher temperatures, Δp^* then passes a maximum where the BP I range (Δp) also exhibits a maximum. Finally Δp^* and Δp of BP I decrease to a level which is only a little higher than at atmospheric pressure.

According to [15], where optical activity measurements at atmospheric pressure were performed with CE2 (not a homologue of CE6!), the separation between T_c (clearing temperature) and T_1^* increases as the chirality is increased. On the other hand the liquid crystal/isotropic liquid transition is then expected to grow weaker.

Following these ideas and replacing $T_c - T_1^*$ by $p_1^* - p_1$ ($= \Delta p^*$) the BP III/ISO transition reveals its most discontinuous character where BP II disappears and the most continuous character where the BP I range is maximal. One has to be careful, however, with this interpretation of the T_t behaviour of Δp^* for as long as the influence of chirality on the character of a liquid crystal phase transition is not absolutely understood. Therefore it would be desirable to complete the above results by calorimetric measurements in this temperature region of the BP III/ISO transition.

4. Final remarks

Elongation of the terminal *n*-alkylcarboxy chain of the cholesteryl *n*-alkanoates causes, if the chain is not too long, an increase in phase chirality and BP polymorphism. Thus CH3 exhibits only BP I and CH9 exhibits BP I, BP II and BP III. Elongation of the terminal *n*-alkyloxy chain in the homologous series to which CE6 and CE7 belong shows a contrary effect. The decreasing chirality manifests itself in elimination of BP II in the case of CE5, which possesses only BP I and BP III, followed by CE6 with all three BPs and CE7 with only BP I. The investigations at higher transition pressures and temperatures carried out in this study were made at a higher density. The result for the above two homologous series is contrary again. The chirality of CH9 weakly decreases, and its polymorphism and its BP ranges remain unchanged. The chirality of CE6 and CE7, however, increases. CE6 loses its BP II and CE7 gains BP II.

In the beginning of the § 3, the elongation of the chain has been correlated with an increase in the flexibility of the molecules, and a higher density on the other hand with a decrease in flexibility. In this respect all results in this study are self-consistent. Using the variation of molecular flexibility as an explanation for the observed BP phase behaviour, however, remains superficial as long as one cannot answer the question of how the flexibility of the molecule, particularly that of the terminal *n*-alkylcarboxy and *n*-alkyloxy chains, affects the phase chirality.

In attempting to explain the contrary behaviour of the two homologous series, one has to take into account the fact that seven of the eight asymmetric carbon atoms of CH9 are incorporated in the rigid steroid skeleton and the eighth attached to the skeleton in the 20-position, whereas the single asymmetric carbon of CE6 and CE7 is in the 2-position of the terminal methylbutyl chain.

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References

[1] Pollmann, P., and Scherer, G., 1979, *Z. Naturforsch.*, **34a,** 255.

[2] Pollmann, P., and Scherer, G., 1980, *High Temperatures-High Pressures*, **12,** 103.
[3] Hollmann, J., Pollmann, P., and Collings, P. J., 1993, *Liq. Cryst.*, **15,** 651.
[4] Kutnjak, Z., Garland, C. W., Schatz, C. G., Collings, P. J., Booth, C. H., and Goodby, J. W., 1996, *Phys. Rev. E*, **53,** 4955.
[5] Yang, D. Y., and Crooker, P., 1987, *Phys. Rev. A*, **35,** 4419.
[6] Onusseit, H., 1983, PhD thesis, University of Paderborn.
[7] Keyes, P. H., and Daniels, W. B., 1979, *J. de Physique, C 3*, **40,** 380.
[8] Kuss, E., 1978, *Mol. Cryst. liq. Cryst.*, **47,** 71.
[9] Pollmann, P., and Scherer, G., 1980, *High Temperatures-High Pressures*, **12,** 103.
[10] Horn, R. G., 1978, *J. Physique*, **39,** 167.
[11] Vanweert, F., and Van Deel, W., 1993, *Liq. Cryst.*, **14,** 611.
[12] Belyakov, V. A., Demikhov, E. I., Dimitrienko, V. E., and Dolganov, V. K., 1985, *Zh. Eksp. Teor. Fiz.*, **89,** 2035 (1985, *Sov. Phys. JETP*, **62,** 1173).
[13] Shashidhar, R., 1983, *Mol. Cryst. liq. Cryst.*, **98,** 13.
[14] Demikhov, E., Hollmann, J., and Pollmann, P., 1993, *Europhys. Lett.*, **21,** 581.
[15] Battle, P. R., Miller, J. D., and Collings, P. J., 1987, *Phys. Rev. A*, **36,** 369.