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High pressure optical measurements on BP III and the isotropic phase of a highly chiral liquid crystal

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The optical activity and light transmission of the blue phases and isotropic phase of 4''-(2-methylbutylphenyl)-4'-(2-methylbutyl)-4-biphenylcarboxylate (CE2) are investigated under high pressure. The temperature ranges of the first (BP I) and third (BP III) blue phases show only the slightest change, if any, with increasing pressure. This is the first time BP III, a phase which is not understood at all, has been investigated under pressure. In addition, an alternative analysis to the one reported previously is reported which confirms that the pretransitional optical activity in the isotropic phase changes very slightly due to pressure, and even this small change seems to be due to small changes in pitch and index of refraction. Taken together, these observations indicate that high pressure has little effect on both the BP III phase and the transition to the isotropic phase in highly chiral systems, even though the BP III phase differs significantly from the other blue phases and strong short range fluctuations make the transition appear continuous optically.

1. Introduction

Highly chiral liquid crystals have received a great deal of theoretical and experimental attention due to the rich phenomena which occur near the transition to the isotropic phase. Unique phases called the blue phases only exist in highly chiral systems, and the transition to the isotropic phase itself becomes much more complex as the chirality is increased. Perhaps the most important effect is that short range fluctuations in the isotropic phase become more intense at high chirality, producing a significant amount of light scattering and optical activity. Consult [1] for a recent review of this work.

These intense fluctuations in the isotropic phase cause the transition to take with a much more continuous character at high chirality. This is best illustrated by the optical activity data of [2] and the light scattering data of [3]. While thermodynamic data clearly show that the transition is discontinuous in samples of low chirality [4, 5], there is new evidence that the discontinuity decreases as the chirality is increased toward an amount present in the most highly chiral liquid crystals [6]. These results are even more difficult to explain theoretically due to a lack of knowledge of the structure of BP III. In the past, high pressure experiments have been extremely useful in investigating phase transitions in liquid crystals, yet little high pressure work has been done with highly chiral samples. Just after the blue phases were discovered, Pollmann and Scherer [7]

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used high pressure to confirm that two blue phases actually exist. Later, the same workers measured the temperature range of these two blue phases under pressure, demonstrating that there was no change as the pressure was increased to above 1000 bars [8].

Although this past work shows that pressure has little effect on the first two blue phases and the isotropic transition in liquid crystals of moderate chirality, this may not be the case in highly chiral systems where both the structure of BP III and the nature of the isotropic transition are so different. In order to investigate this, methods to record the blue phase temperature ranges and measure the pretransitional fluctuations under pressure are necessary. As reported in this article, light transmission and optical activity measurements on a highly chiral sample under pressure are quite suitable for this. The pretransitional optical activity data were described in a brief report previously, with an analysis assuming a linear relationship between the effects of temperature changes versus the effects of pressure changes [9]. We present an alternative analysis in this report, concentrating on the effects of temperature changes at constant pressure. Our results show that despite the differences in the transition and phases which occur in highly chiral liquid crystals, the temperature range of BP III and the fluctuations which occur in the isotropic phase are not significantly affected by pressure changes up to 1000 bars.

2. Theory

There are a number of contributions to the optical activity in the isotropic phase of a chiral nematic liquid crystal [10–13]. The first contribution is due to the intrinsic molecular optical activity and is relatively temperature independent. The second contribution stems from the short range orientational order which fluctuates increasingly as the transition to the liquid crystal phase is approached. The orientational order in chiral nematic systems can be expressed as a linear combination of structural modes. Two of these modes, the conical spiral mode and the planar spiral mode, both contribute to the optical activity in the isotropic phase and are strongly temperature dependent. Each has its own correlation length and second order transition temperature at which the fluctuations of the mode tend to diverge. If the contributions from these two modes are calculated through a Landau–de Gennes continuum theory [14], then corrections are necessary since the theory is not appropriate over all length scales.

The influence of the planar spiral mode decreases rapidly above the isotropic transition and can be neglected when the temperature is more than 1 K above the transition temperature, T_c . In this region the optical activity can be written

$$\alpha = \alpha_0 + AT[(T - T_3^*)^{-1/2} - B], \quad (1)$$

where α_0 is the molecular optical activity, A and B are temperature-independent constants, T is the temperature, and T_3^* is the second order transition temperature for the conical spiral mode ($T_3^* < T_c$). The constants A and B are given by

$$A = k_0^2 q k_B / [48\pi n^2 (a_0 b)^{1/2} (1 + c/2b)^{3/2}] \quad (2a)$$

$$B = 4(a_0/b)^{1/2} l / [\pi(1 + c/2b)^{1/2}], \quad (2b)$$

where k_0 is the wavevector of the light, q is the chirality ($4\pi/P$, where P is the pitch), k_B is the Boltzmann constant, n is the index of refraction, a_0 , b , c are coefficients in the Landau–de Gennes theory, and l is the intermolecular distance [12]. In equation (1),

the first term in the brackets is the contribution from the conical spiral mode while the second term in the brackets is the correction to the continuum theory.

In the vicinity of the phase transition ($T - T_c < 1$ K), the contribution from the planar spiral mode increases more rapidly than the contribution from the conical spiral mode because its second order transition temperature, T_1^* , is higher than T_3^* ($T_3^* < T_1^* < T_c$). Since the two contributions are of opposite sign, this causes the optical activity to reach a maximum and start to decrease just before the transition to the liquid crystal phase. An expression for this contribution enters in the next highest power of k_0/q and involves a $(T - T_1^*)^{-3/2}$ factor. Unfortunately, it cannot simply be added to equation (1), because a similar contribution from the conical spiral mode also enters at this level in the expansion [12, 13]. Optical activity measurements have been performed for a number of highly chiral liquid crystals, and the results are in good agreement with the theory [12, 15–19]. As the chirality increases, the importance of the planar spiral contribution grows as $T_c - T_1^*$ decreases and $T_c - T_3^*$ increases. If the chirality is high enough, the short range fluctuations are large enough for the transition to appear continuous.

With this theoretical perspective, it is difficult to ascertain what effects high pressure might have on this transition. Pressure directly couples to the density, which is not an important parameter in the theory. One might expect little change. On the other hand, the structure of BP III is unknown and, unlike other liquid crystal to isotropic transitions, large fluctuations are present. It is therefore conceivable that the density plays a more important role in either the formation of the BP III phase or the fluctuations in the isotropic phase. Thus, an experiment to measure the pressure dependence of both the temperature range of BP III and the optical activity due to these fluctuations is important.

3. Experiment

The highly chiral nematic liquid crystal investigated was 4''-(2-methylbutylphenyl)-4'-(2-methylbutyl)-4-biphenylcarboxylate (CE2), which was obtained from Merck Ltd. (Poole, England) and used without further purification. The optical activity was measured by means of a half-shade polarimeter using light at 633 nm from a HeNe Laser. The angle of optical rotation could be determined with an accuracy of $\pm 0.04^\circ$.

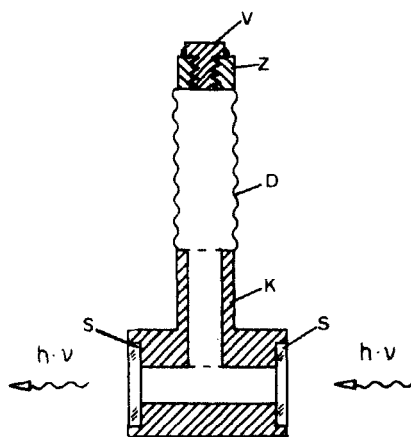


Figure 1. Schematic diagram of the high pressure cuvette. See text for description.

The high pressure apparatus was identical to that used earlier for light reflection measurements [20]. The windows of the optical high pressure cell were made of Schott SF 57 glass (Mainz, Germany), an optical glass with very small birefringence. A schematic diagram of the cuvette is shown in figure 1. The pressure was transmitted to the sample by a steel tube (D) made from steel foil 0.1 mm thick. The tube was welded to the steel cuvette body (K) and the upper plug (Z). The cuvette was sealed by two glass windows (S) made of SF 57 glass, and a screw (V) closed the tube at the top. The optical path length was 8 mm. In addition to measuring the optical rotation for the light which passed through the sample, a Cary 17 D spectrometer was used to measure the intensity of the transmitted light.

The phase transitions were identified by monitoring the transmitted light at 450 nm as the temperature was held constant and the pressure varied. Whereas the chiral nematic to BP I and BP I to BP III transitions exhibited clear discontinuities in the light transmission (BP I/BP III less pronounced), the BP III to isotropic transition revealed itself only as a change in the pressure dependence of the transmitted intensity. The data for these three transitions are shown in figure 2, and the slopes of the three transition lines are given in table 1. The BP I/BP III transition could also be detected by a discontinuity in the pressure dependence of the optical activity, and determinations using this method were fully consistent with the transmission results.

Because of the large heat capacity of the high pressure chamber, it was easier to measure the pressure dependence of the optical activity at constant temperature, than to measure the temperature dependence at constant pressure. For this reason, the pressure dependence of the optical activity was measured in very small temperature steps and the results were used to construct optical activity curves as a function of temperature at constant pressure for five different pressures (1, 150, 300, 500 and

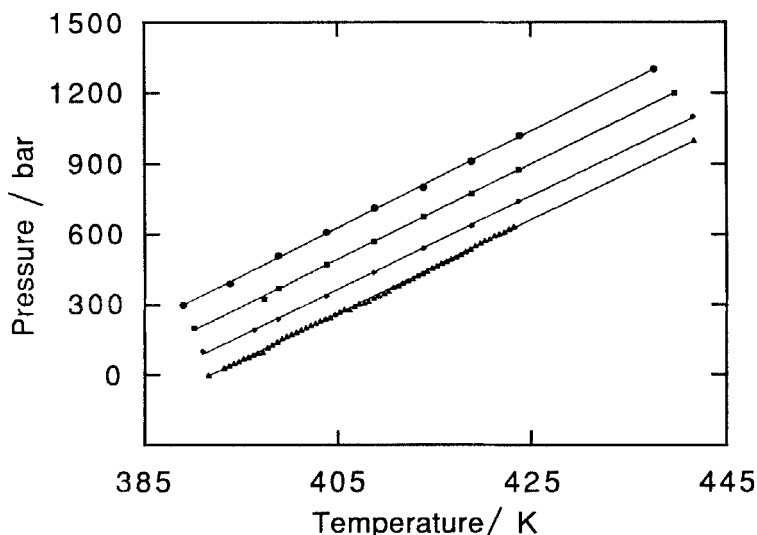


Figure 2. Three transition lines and the line of maximum optical activity in the isotropic phase of CE2. Values for the slopes are given in table 1. ●, N*–BP I; ■, BP I–BP III; ◆, BP III–BP I; ▲, OA_{\max} . The N*–BP I, BP I–BP III, and BP III–I transition lines have been displaced upward by 300, 200 and 100 bars, respectively, so that all the data can be seen clearly.

Table 1. Least-squares-fitted values for the slopes of the various transition lines and maximum optical activity line.

Line	Slope/bar K ⁻¹
N*–BP I	20.58 ± 0.15
BP I–BP III	20.29 ± 0.14
BP III–isotropic	19.90 ± 0.13
Optical activity maximum	19.98 ± 0.06

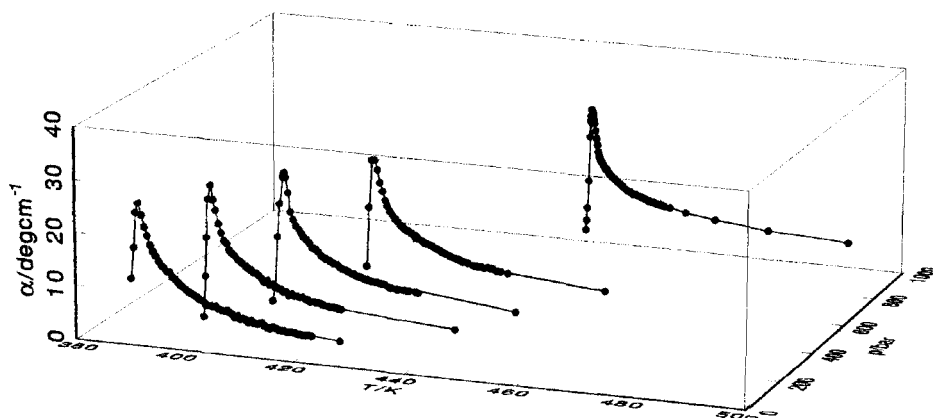


Figure 3. Temperature dependence of the optical activity at five different pressures. Some of the last data points for BP III and all of the data points for the isotropic phase are shown. The wavelength of the light is 633 nm.

1000 bars). These are shown in figure 3. Notice that the optical activity reaches a maximum and decreases sharply near the transition. This is in full accord with prior measurements at atmospheric pressure on CE2 [16]. This procedure also permitted measurement of the pressure at which the optical activity reached a maximum at each temperature, and these data are also graphed in figure 2 and the corresponding slope given in table 1.

In order to analyse the data in figure 3, the correction term in equation (1) was evaluated. Using values for a_0 ($0.92 \times 10^6 \text{ erg cm}^{-3} \text{ K}^{-1}$), and b ($6.2 \times 10^{-7} \text{ erg cm}^{-1}$) determined from prior measurements on CE2 [16], assuming that $b = c$ (for which there is good evidence [21, 22]), and letting $l = 5 \times 10^{-8} \text{ cm}$, B is equal to $0.063 \text{ K}^{-1/2}$. The data at each pressure were fitted to equation (1) using this value for B and letting α_0 , A and T_3^* be fitting parameters. Obviously, the fit was not very good in the vicinity of the phase transition, but improved as the lowest temperature points were dropped one at a time. The values for the fitting parameters shown in table 2 are for the fits which gave low χ^2 values with the fewest points dropped. These fits typically excluded data within about 1 K of the transition. Such a fit is shown for the 1000 bar data in figure 4.

One interesting feature of these fits is illustrated in figure 5. Note that both $T_c - T_3^*$ and A both decrease as the pressure is increased, with similar relative changes from data point to data point. It is very unlikely that this is an experimental artefact, since these two quantities are determined from very different aspects of the data. One of the quantities, $T_c - T_3^*$, even includes data which were not fits (T_c) and which are less certain.

Table 2. Least-square-fitted values for the optical activity using equation (1) for five different pressures along with the BP III–isotropic transition temperatures.

Pressure/bar	$\alpha_0/\text{deg cm}^{-1}$	$A/\text{deg cm}^{-1} \text{K}^{-1/2}$	T_3^*/K	T_c/K
1	-0.90 ± 0.11	0.129 ± 0.002	389.01 ± 0.07	391.10 ± 0.25
150	0.36 ± 0.16	0.106 ± 0.002	397.20 ± 0.07	398.93 ± 0.25
300	1.42 ± 0.15	0.088 ± 0.002	405.83 ± 0.05	407.29 ± 0.25
500	0.36 ± 0.15	0.103 ± 0.002	414.87 ± 0.07	416.76 ± 0.25
1000	3.23 ± 0.22	0.059 ± 0.001	440.71 ± 0.04	441.60 ± 0.25

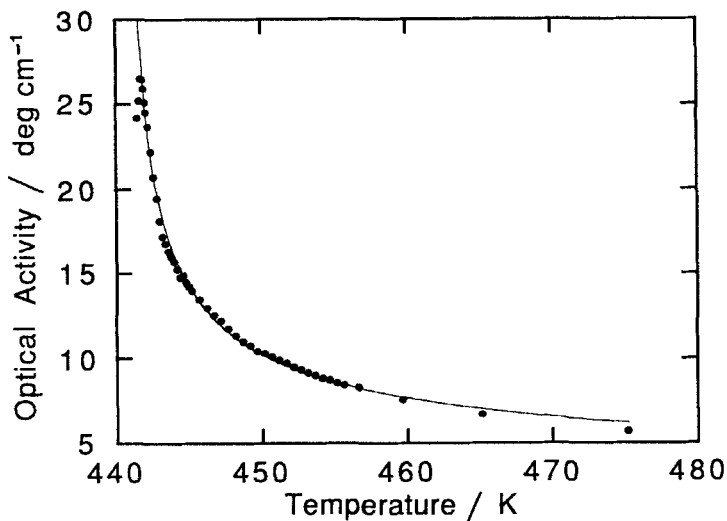


Figure 4. Least-squares-fit to the optical activity of CE2 at 1000 bars using equation (1). Only data points for the isotropic phase are shown. The least-squares-fitted parameters for the five pressures are given in table 2.

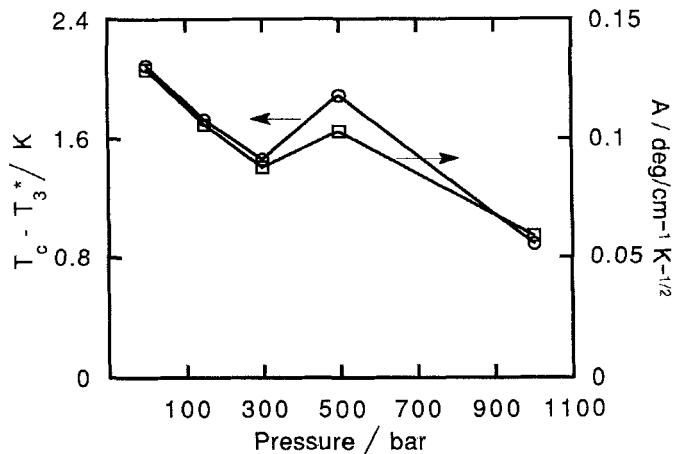


Figure 5. Pressure dependence of T_3^* (relative to T_c) and A , two of the parameters in equation (1).

4. Discussion

The most striking findings are (1) the constancy of the BP III temperature range as the pressure is increased, and (2) the qualitative similarity of the optical activity versus the temperature data of the isotropic phase at various pressures. The BP III temperature range might increase very slightly with increasing pressure (BP I may also), but the change is of the same order as the experimental error. These are the first pressure data for BP III, and the obvious conclusion is that, although the structure of BP III is quite different from the other two blue phases, pressure affects all of them similarly.

As clearly shown by figure 5, there are quantitative changes in the temperature dependence of the pretransitional optical activity as the pressure is increased. An increase in both $T_c - T_3^*$ and A was observed in mixtures of CE2 and a nematogen as the chiral fraction was increased [16], so the decrease in these two quantities as the pressure increases could point to a decrease in the chirality. This is in agreement with prior experiments on other systems, where an increase in the pitch was observed with increasing pressure [23]. It should also be pointed out that the index of refraction has also been observed to increase with pressure [24]. In fact, A is proportional to q/n^2 , while differences between the second order transition temperatures scale with q^2 . If the pitch ($q = 4\pi/P$) and index of refraction both increase with pressure, then one would expect both A and $T_c - T_3^*$ to decrease with pressure. This is fully consistent with the data, in that the second order transition temperatures for both the conical and planar spiral modes would be affected by the increase in pressure in the same way, leaving the temperature dependence of the optical activity qualitatively similar. One aspect of this explanation is troublesome, however. The decreases in A and $T_c - T_3^*$ amount to roughly 50 per cent over this pressure range, which is larger by about a factor of two than one might expect from observations of the pitch and dielectric constant for other liquid crystals under pressure.

5. Conclusions

These results provide strong evidence that the interactions which give rise to both the blue phases and the strong fluctuations which take place in highly chiral liquid crystals are entirely orientational in character, with a density dependence similar to other liquid crystalline systems with only orientational order. The important question to ask, therefore, is if this is also true for highly chiral smectic liquid crystals? Pressure does have a significant effect on some smectic phases, because the smectic order parameter is a density wave. Since the chiral smectic A* phase possesses such a density wave [25] and since it is known that strong fluctuations take place in the isotropic phase just above this phase [26], pressure measurements on the smectic A*-isotropic transition may be extremely revealing. Likewise, pressure may have a significant effect on the BP III-isotropic transition in systems which possess a smectic phase below a narrow chiral nematic phase, if smectic-like fluctuations are present in the isotropic phase.

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