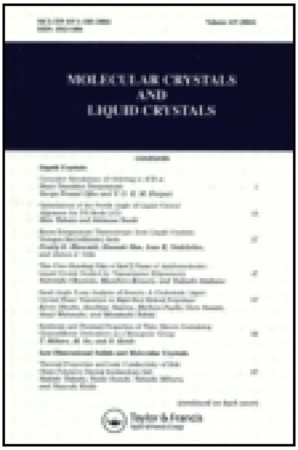

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Helix Inversion of Cholesteric Liquid Crystals at High Pressure. Selective Light Reflection Measurements on Binary Mixtures up to 3000 Bar and 130°C

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Helix Inversion of Cholesteric Liquid Crystals at High Pressure. Selective Light Reflection Measurements on Binary Mixtures up to 3000 Bar and 130°C

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The pitch-concentration relationship of Bak and Labes for binary cholesteric–cholesteric liquid crystal mixtures was used to determine the pressure dependence of the nematic temperature for the first time. The resulting helix inversion lines were obtained on the experimental basis of the temperature–pressure dependence of the peak light reflection wavelength. Measurements were performed on cholesteryl nonanoate/cholesteryl chloride mixtures.

INTRODUCTION

Whereas in a nematic liquid crystal the molecules with their long axes are on average only aligned parallel to each other, in the cholesteric phase this orientation is characterized by a helical arrangement. The cholesteric helix, which can be right- or left-handed, repeats itself over a distance called its pitch.

Mixtures of two cholesteric components of opposite chirality can compensate and form a nematic liquid crystal at a certain temperature T_n (nematic temperature). At $T < T_n$ they can form a left (right)-handed helix and a right (left)-handed one at $T > T_n$; in other words, at T_n an inversion of the helix occurs.

In 1982 we[1] studied such helix inversions for the first time at elevated pressures. For a given $T(= T_n)$ the corresponding nematic pressure p_n could be determined by observation of texture changes in the liquid crystal phase. The resulting function $T_n = f(p_n)$ can be called a helix inversion line. In this work we will show that such an inversion line can also be evaluated on the basis of the experimentally obtainable temperature and pressure dependence of the selective light reflection of the cholesteric liquid crystal phase.

THEORY

Basing their work on de Gennes[2] concept for induced cholesteric phases, Bak and Labes[3,4] derived a pitch-concentration relationship for the general case of cholesteric–cholesteric mixtures (in the following, a two-component mixture of A and B):

$$(2 \cdot z \cdot M)^{-1} = N \cdot [\beta_A \cdot x_A^2 + \beta_B \cdot (1 - x_A)^2 + 2 \cdot \beta_{A,B} \cdot x_A \cdot (1 - x_A)], \quad (1)$$

where

z is the pitch of the cholesteric helix in the mixture,
M the molar density of the mixture (reciprocal molar volume),
N Avogadro's number,
$\beta_{A(B)}$ the molecular "twisting power" between $A(B)$ molecules only [when $\beta_{A(B)}$ is positive (negative), the helical structure is right (left) handed],
x_A the mole fraction of the cholesteric component A, and
$\beta_{A,B}$ the molecular "twisting power" between A and B molecules (and vice versa, respectively).

When the special case

$$\beta_{A,B} = \frac{1}{2} \cdot (\beta_A + \beta_B) \quad (2)$$

cannot be applied, a new parameter

$$\delta\beta_{A,B} \equiv 2\beta_{A,B} - \beta_A - \beta_B \quad (3)$$

is introduced which is a measure of the deviation of $\beta_{A,B}$ from the mean value of β_A and β_B.

With Eq. (2) and the relationship of de Vries,[5]

$$z = \lambda_R \cdot \bar{n}^{-1}, \quad (4)$$

where λ_R denotes the wavelength of maximum reflection and $\bar{n}$ the average refractive index of a quasi nematic layer in a cholesteric phase, Eq. (1) can be rewritten as

$$(2 \cdot \lambda_R \cdot \bar{n}^{-1} \cdot M)^{-1} = N \cdot [(\beta_A - \beta_B) \cdot x_A + \beta_B + \delta\beta_{A,B} \cdot x_A \cdot (1 - x_A)] \quad (5)$$

Using the condition

$$N[(\beta_A - \beta_B) \cdot x_A + \beta_B + \delta\beta_{A,B} \cdot x_A \cdot (1 - x_A)] = 0 \quad (6)$$

at the nematic temperature T_n and pressure $p_n(z \sim \lambda_R = \infty)$, Eq. (5) can be employed to determine the pressure dependence of T_n.

EXPERIMENTAL

The binary mixtures studied in this work consist of the two cholesterics cholesteryl chloride and cholesteryl nonanoate. Both compounds were purified by repeated recrystallization from a mixture of acetone/methanol.

The pressure dependence of the nematic temperature T_n of the binary mixtures was obtained from measurements of the temperature and pressure dependence of their wavelength of maximum light reflection. The selective light reflection was measured by a Cary 17 DH spectrophotometer. The high pressure equipment was described earlier.[6]

The more direct determination of T_n by observation of texture changes in the cholesteric mixtures was performed by means of a Schmidt and Haensch spectropolarimeter. The high pressure equipment was similar to that used in the reflection measurements.

RESULTS

Eq. (5) can be converted into an equation of a straight line:

$$(2\lambda_R \cdot \bar{n}^{-1} \cdot M)^{-1} - N \cdot \delta\beta_{A,B} \cdot x_A \cdot (1 - x_A) = (N \cdot \beta_A - N \cdot \beta_B) \cdot x_A + N \cdot \beta_B \quad (7)$$

For a given temperature T and pressure p all parameters can be determined by means of the mole fraction dependence of λ_R, $\bar{n}$ and M. The future test of Eq. (7) by the experimental data will show that the parameter $N \cdot \delta\beta_{A,B}$ can be adjusted independently of the molar fraction x_A. The molar twisting powers $N \cdot \beta_A$ and $N \cdot \beta_B$ can be obtained by extrapolating the straight line according to Eq. (7) to $x_A = 1$ and 0.

First the temperature–pressure dependence of λ_R of five binary mixtures consisting of cholesteryl nonanoate (Ch-9, left handed helix) and cholesteryl chloride (CC, right handed helix) was measured. The results are shown in Figures 1–5, where λ_R is plotted vs. pressure p for different temperatures (in °C).

For simplicity we chose nearly the same temperatures for all five mixtures and tried to maintain the same pressure range for the corresponding temperatures as far as possible, considering the somewhat different clearing pressures. In some mole fraction ranges, no measurements could be performed for the following reasons:

a) $0 < x_{\text{Ch-9}} < 0.100$: The mixtures can partially crystallize, since the cholesteric phase is metastable with respect to the cholesteric/CC-crystalline two phase region.

b) $0.220 < x_{\text{Ch-9}} < 0.500$: The pitches of the mixtures are so high that λ_R cannot be measured.

c) $x_{\text{Ch-9}} > 0.740$: The mixtures were not studied since at lower temperatures the pretransitional effects of the cholesteric/smectic-A phase transition influence λ_R.

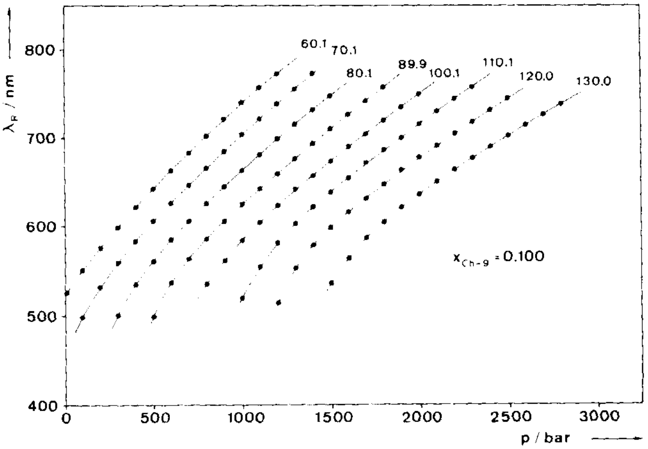

FIGURE 1 Wavelength of maximum light reflection λ_R vs. pressure p at various temperatures (numerical data in °C). Mixture Ch-9/CC with $x_{\text{Ch-9}} = 0{,}100$.

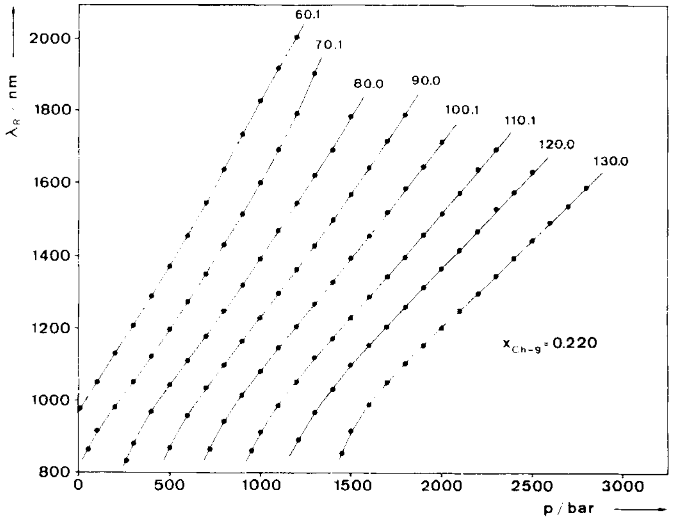

FIGURE 2 Wavelength of maximum light reflection λ_R vs. pressure p at various temperatures (numerical data in °C). Mixture Ch-9/CC with $x_{Ch\text{-}9}$ = 0,220.

After the x-T-p dependence of λ_R has been determined, the x-T-p dependence of $\bar{n}$ and M (or molar volume V) must be evaluated. Since $\bar{n}$ and V only depend weakly on temperature and pressure, an estimation of the functions $\bar{n} = f(p, T)$ and $V = f(p, T)$ for the five mixtures on the basis of data from a comparable pure compound

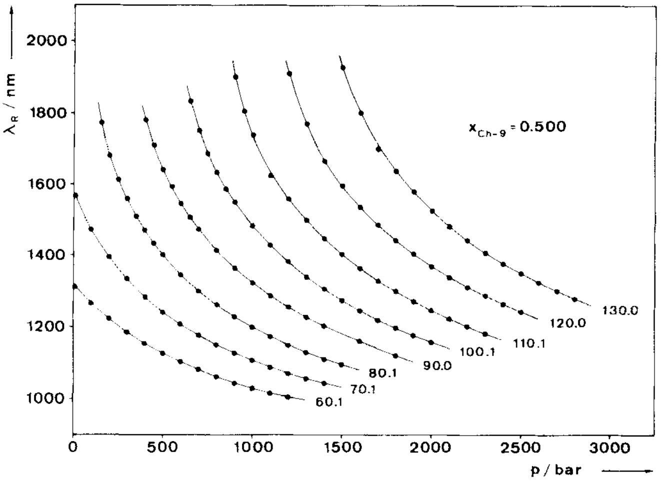

FIGURE 3 Wavelength of maximum light reflection λ_R vs. pressure p at various temperatures (numerical data in °C). Mixture Ch-9/CC with $x_{Ch\text{-}9}$ = 0,500.

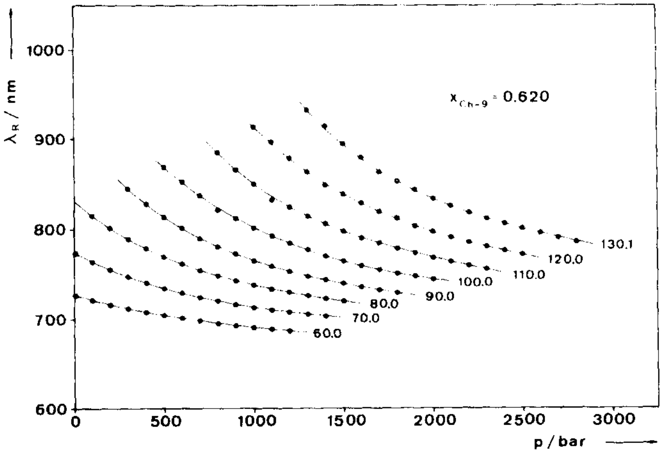

FIGURE 4 Wavelength of maximum light reflection λ_R vs. pressure p at various temperatures (numerical data in °C). Mixture Ch-9/CC with $x_{\text{Ch-9}} = 0{,}620$.

should be sufficient. V and $\bar{n}$ were determined in the cholesteric phase at the clearing point at atmospheric pressure $T_{c,o}$ (see Table 1).

The p,T-dependence of the Ch-9 molar volume V[7] was used for the 5 mixtures at $T_{c,o}$. For $\bar{n}$ the p,T data of the nematic compound 5 CB† [8] were used.

Using these results all three parameters ($N \cdot \beta_{\text{Ch-9}}$, $N \cdot \beta_{\text{CC}}$ and $N \cdot \delta\beta_{\text{Ch-9,CC}}$) could be determined for a given p, T-pair.

The comparison of Figures 6 and 7 reveals the influence of the parameter $N \cdot \delta\beta_{\text{Ch-9,CC}}$. On the assumption that Eq. (2) is valid (meaning $N \cdot \delta\beta_{\text{Ch-9,CC}} = 0$), the plot of $(2\lambda_R \cdot \bar{n}^{-1} \cdot M)^{-1}$ vs. $x_{\text{Ch-9}}$ (in Figure 6) for three constant pressures (1000, 1500, 2000 bar) at, for example, 100.1°C should yield straight lines. From Figure 6 it is seen that the data do not fall on a straight line. The plot of $(2\lambda_R\bar{n}^{-1} \cdot M)^{-1} - N \cdot \delta\beta_{\text{Ch-9,CC}} \cdot x_{\text{Ch-9}} \cdot (1 - x_{\text{Ch-9}})$ vs. $x_{\text{Ch-9}}$ in Figure 7 (according to Eq. (7) with $N \cdot \delta\beta_{\text{Ch-9,CC}} \neq 0$) yields straight lines. By extrapolating them to $x_{\text{Ch-9}} = 0$ and 1, the molar twisting powers $N \cdot \beta_{\text{CC}}$ and $N \cdot \beta_{\text{Ch-9}}$ of the pure compounds were obtained.‡

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†5 CB = 4-Cyano-4′-pentylbiphenyl.

‡The direct determination of the twisting power of CC from λ_R measurements is not possible due to the metastable cholesteric phase of this compound. For Ch-9 it is possible only in a very small region.

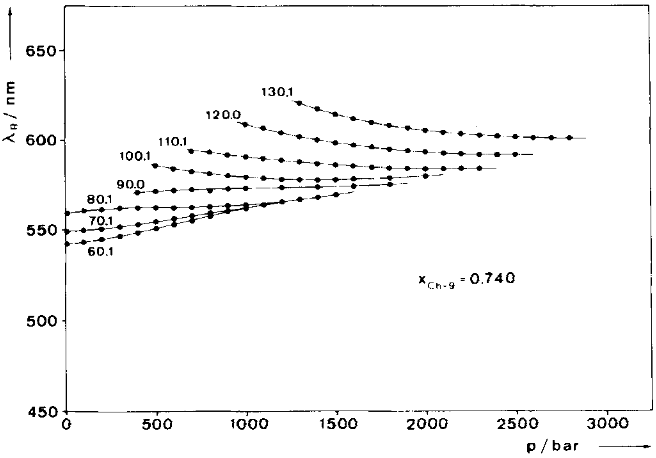

FIGURE 5 Wavelength of maximum light reflection λ_R vs. pressure p at various temperatures (numerical data in °C). Mixture Ch-9/CC with $x_{\text{Ch-9}}$ = 0,740.

The absolute values of the latter parameters decrease with increasing pressure at constant temperature (see Figures 8 and 9, respectively), whereas the parameter $|N \cdot \delta\beta_{\text{Ch-9}}|$ increases with increasing pressure (see Figure 10). The pressure dependence in Figure 10 seems to be nearly linear and independent of temperature.

Values of $N \cdot \beta_{\text{Ch-9}}$ and $N \cdot \beta_{\text{CC}}$ for atmospheric pressure can be compared with those from the literature.

From Figure 8, $N \cdot \beta_{\text{Ch-9}} = -11.7 \cdot 10^6\ \text{cm}^2 \cdot \text{mol}^{-1}$ at atmospheric pressure and 60.1°C, Chen and Wu found $-10.2 \cdot 10^6\ \text{cm}^2 \cdot \text{mol}^{-1}$ and $-9.8 \cdot 10^6\ \text{cm}^2 \cdot \text{mol}^{-1}$ from Ch-9/Ch-3† and Ch-9/Ch-4† mix-

TABLE I

Molar volume V and refractive index $\bar{n}$ of 5 mixtures Ch-9/CC at the clearing point at atmospheric pressure $T_{c,o}$ ($x_{\text{Ch-9}}$ = mole fraction of Ch-9)

$x_{\text{Ch-9}}$	$T_{c,o}$/°C	$\bar{n}$	V/cm^3 · mol^{-1}
0,100	67,7	1,511	426
0,220	69,0	1,507	445
0,500	75,3	1,499	489
0,620	78,2	1,496	508
0,740	82,2	1,492	527

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†Ch-3 = cholesteryl propionate; Ch-4 = cholesteryl butyrate

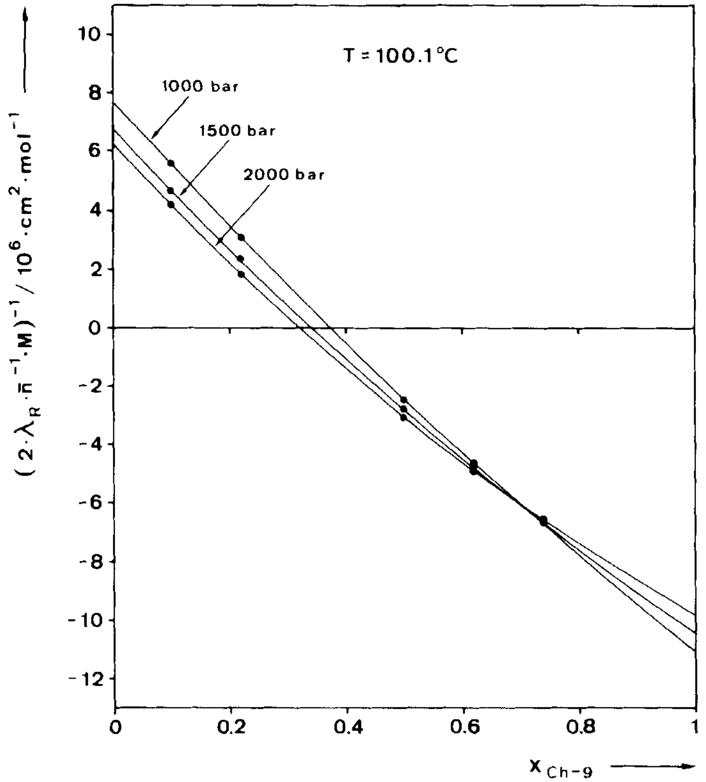

FIGURE 6 Plot of $(2\lambda_R \cdot \bar{n}^{-1} \cdot M)^{-1}$ vs. mole fraction $x_{\text{Ch-9}}$ for various pressures at $T = 100.1°C$. λ_R = wavelength of maximum light reflection. $\bar{n}$ = average refractive index; M = reciprocal molar volume.

tures, respectively, for these p,T conditions. From pitch measurements of Stegemeyer and Finkelmann[10] in CC/CEEC† and CC/CBAC† mixtures at 57°C, $N \cdot \beta_{CC} = 8.4 \cdot 10^6\ cm^2 \cdot mol^{-1}$ in good agreement with our extrapolated value of $8{,}5 \cdot 10^6\ cm^2 \cdot mol^{-1}$ for this temperature (Figure 9).

By means of the relationships in Figures 8–10, we are now able to determine the pressure dependence of the nematic temperature T_n. For a stated temperature $(= T_n)$ and mole fraction $x_{\text{Ch-9}}$ we are looking for that pressure $(= p_n)$ where $N \cdot \beta_{\text{Ch-9}}$, $N \cdot \beta_{CC}$ and $N \cdot$

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†CEEC = cholesteryl-2-(2-ethoxyethoxy)ethyl carbonate
CBAC = p-(4-cyanobenzalamino)-cinnamic acid active amyl ester

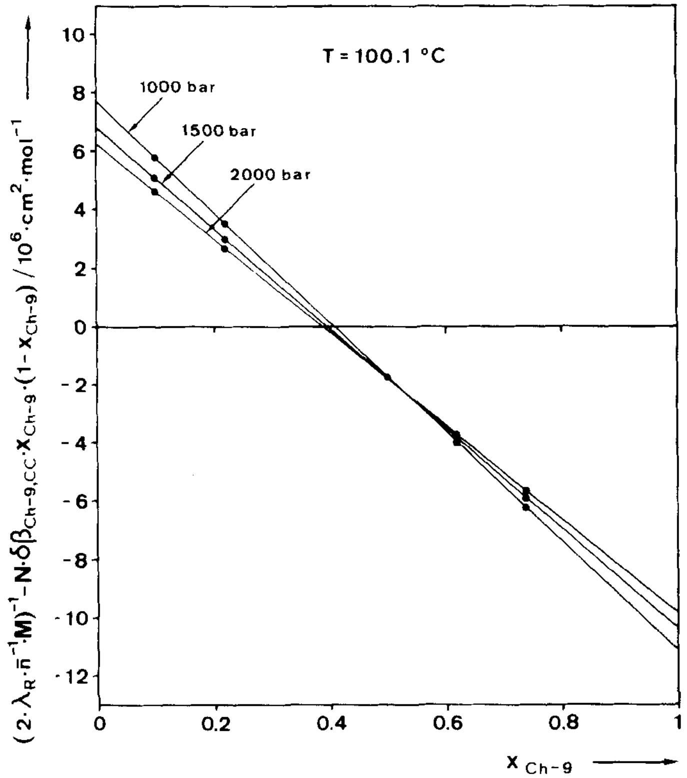

FIGURE 7 Plot of $(2\lambda_R \cdot \bar{n}^{-1} \cdot M)^{-1} - N \cdot \delta\beta_{\mathrm{Ch\text{-}9,CC}} \cdot x_{\mathrm{Ch\text{-}9}}\,(1 - x_{\mathrm{Ch\text{-}9}})$ vs. mole fraction $x_{\mathrm{Ch\text{-}9}}$ for various pressures at $T = 100.1$°C. λ_R = wavelength of maximum light reflection. $\bar{n}$ = average refractive index; M = reciprocal molar volume. The notation of $N \cdot \delta\beta_{\mathrm{Ch\text{-}9,CC}}$ is given in Eq. (3).

$\delta\beta_{\mathrm{Ch\text{-}9,CC}}$ fulfill Eq. (6). In the case of the Ch-9/CC mixtures, Eq. (6) becomes

$$(N \cdot \beta_{\mathrm{Ch\text{-}9}} - N \cdot \beta_{\mathrm{CC}}) \cdot x_{\mathrm{Ch\text{-}9}} + N \cdot \beta_{\mathrm{CC}} + N \cdot \delta\beta_{\mathrm{Ch\text{-}9,CC}} \cdot x_{\mathrm{Ch\text{-}9}} \cdot (1 - x_{\mathrm{Ch\text{-}9}}) = 0 \quad \text{(6a)}$$

The helix inversion lines, $p_n = f(T_n)$, obtained in this manner for three mole fractions $x_{\mathrm{Ch\text{-}9}}$ are shown in Figure 11. It is seen that the slope of the inversion lines decreases slightly with increasing $x_{\mathrm{Ch\text{-}9}}$.

The clearing lines of all three mixtures nearly coincide. In Figure 11 the line for $x_{\mathrm{Ch\text{-}9}} = 0{,}354$ is plotted as an example. One can note

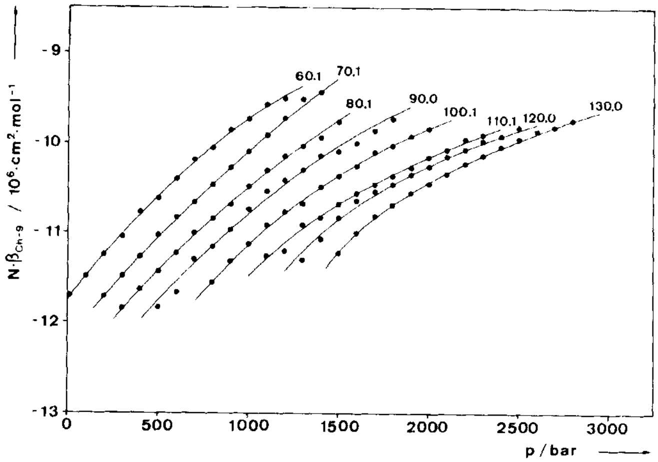

FIGURE 8 Molar twisting power $N \cdot \beta_{\mathrm{Ch\text{-}9}}$ vs. pressure p at various temperatures (numerical data in °C).

that the region of existence of the right-handed cholesteric helix, which is situated on the high temperature side of the inversion line, grows with increasing pressure for all three mixtures.

As already mentioned at the beginning, T_n and p_n can be determined directly by texture observations in the cholesteric phase.† We

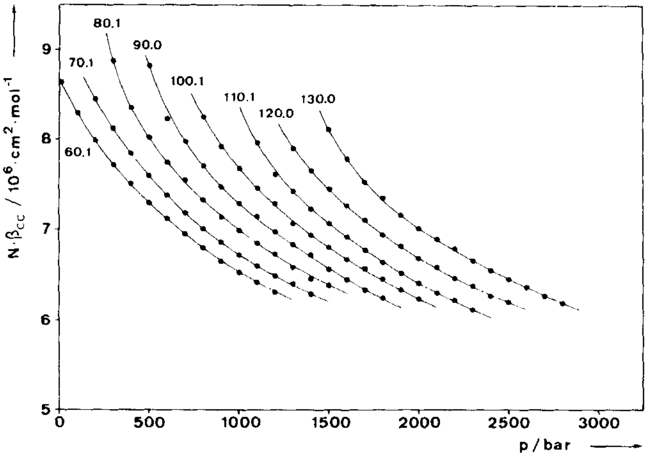

FIGURE 9 Molar twisting power $N \cdot \beta_{\mathrm{CC}}$ vs. pressure p at various temperatures (numerical data in °C).

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†For details see Reference 1.

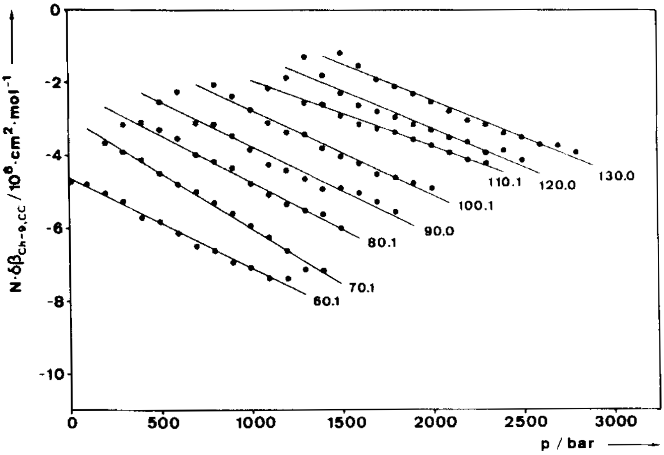

FIGURE 10 $N \cdot \delta\beta_{\text{Ch-9,CC}}$ vs. pressure p at various temperatures (numerical data in °C). The notation of $N \cdot \delta\beta_{\text{Ch-9,CC}}$ is given in Eq. (3).

have performed such observations with mixtures of the three mole fractions in Figure 11. The obtained data points (·) are also plotted in Figure 11. The agreement with the results from λ_R-p-T measurements is satisfactory. The latter are a little more extensive than the texture observations but yield results with greater accuracy.

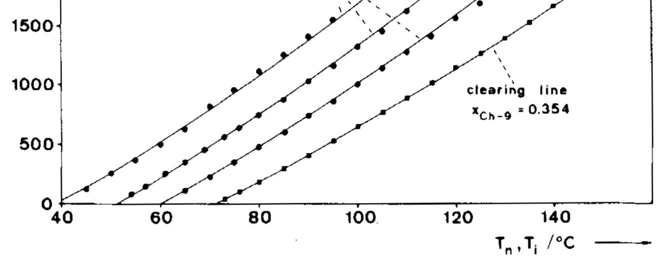

FIGURE 11 Helix inversion lines of three mixtures Ch-9/CC ($x_{\text{Ch-9}}$: 0,334; 0,354; 0,374) and clearing line of one mixture Ch-9/CC ($x_{\text{Ch-9}}$: 0,354). p_n,T_n: nematic pressure and temperature, respectively. p_i,T_i: clearing pressure and temperature, respectively.

As long as a calculation of helix inversion lines based on molecular interactions is not possible, the use of the empirical temperature-pressure dependence of λ_R in the pitch-concentration relationship of Bak and Labes[3,4] should be an acceptable method.

Acknowledgment

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References

1. P. Pollmann and B. Wiege, *Z. Naturforsch.*, **37a**, 1099 (1982).
2. P. G. de Gennes, *The Physics of Liquid Crystals* (Clarendon, Oxford, Chaps. 3 and 6 (1974)).
3. C. S. Bak and M. M. Labes, *J. Chem. Phys.*, **62**, 3066 (1975).
4. C. S. Bak and M. M. Labes, *J. Chem. Phys.*, **63**, 805 (1975).
5. H. de Vries, *Acta Crystallogr.* **4**, 219 (1951).
6. P. Pollmann, *J. Phys.* E **7**, 490 (1974).
7. V. K. Semenchenko, V. M. Byankin and V. Ya. Baskakov, *Kristallografiya* **20**, 187 (1975).
8. R. G. Horn, *J. Physique* **39**, 167 (1978).
9. S.-H. Chen and J. J. Wu, Mol. Cryst. Liq. Cryst. 87, 197 (1982).
10. H. Stegemeyer and H. Finkelmann, *Ber. Bunsenges. Phys. Chem.* **78**, 869 (1974).