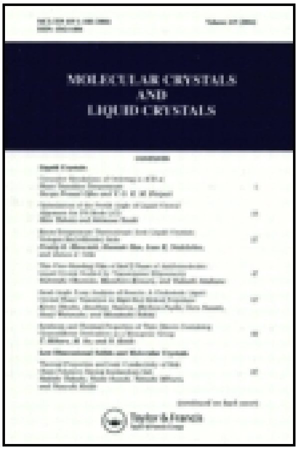

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Pitch Behavior of the Cholesteric Helix at the Phase Transition Point Cholesteric/Smectic A up to 2500 Bars. Study of Some Cholesteryl *n*-Alkanoates.

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Experimental evidence is given, for the first time, for a finite pitch of the cholesteric helix at the phase transition point cholesteric/smectic A (Ch/S_A). This finite pitch changes into an infinite one at a given point on the phase equilibrium line Ch/S_A. Therefore this point is called the pitch infinity point (PIP).

With increasing *n*-alkyl chain length of the investigated cholesteryl *n*-alkanoates the pressure coordinate of the PIP is shifted to higher values up to a chain length of 13 C atoms. For the alkanoates with 13, 15 and 17 C atoms the same PIP pressure of about 1000 bars was determined.

The Ch/S_A phase equilibrium line of the cholesteryl esters could at best be followed up to 2600 bars. The respective transition enthalpies were measured at normal pressure and the corresponding changes in volume calculated by means of the Clausius-Clapeyron equation.

INTRODUCTION

The pitch of a cholesteric helix increases very rapidly as a sample is cooled or pressurized to the cholesteric/smectic A (Ch/S_A) transition point. This is primarily due to the growth of smectic-like clusters[1,2] in the

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cholesteric phase. This phase transition can be of first or second order, that is, the enthalpy and volume may change discontinuously or continuously at the transition point. Until now the correlation between the change in enthalpy and volume on the one hand and the pitch behavior near the phase transition Ch/S_A on the other hand has not been demonstrated. Regardless of the transition order the pitch seems to approach infinity at the transition point. For the case of cholesteryl tetradecanoate with a relatively high transition enthalpy, a finite pitch at the phase transition point has been suggested by Müller for the first time,[3] but this has not been established conclusively by the experiments. In this paper, however, experimental evidence for a finite pitch at the transition has been given, from which very interesting conclusions can be drawn.

EXPERIMENTAL

The pitch behavior of the cholesteric helix was observed by determining the maximum wavelength of the selective light reflection which is characteristic of a cholesteric mesophase. This light reflection causes a quasi-absorption and therefore could be followed with a Cary 17 DH absorption spectrophotometer. The wavelength of maximum "absorption" corresponds to the wavelength of maximum reflection. The accuracy of the pressure gauges was 0.1% of full-scale reading, the temperature within the test cell was stabilized to better than 0.01 K. Details of the pressure equipment are described in a previous publication.[4] The following four cholesteryl *n*-alkanoates were investigated: cholesteryl decanoate (CD), cholesteryl tridecanoate (CT), cholesteryl pentadecanoate (CP) and cholesteryl heptadecanoate (CH). They were obtained from Merck (CD) and Sigma (CT, CP, CH). All compounds were recrystallized from a mixture of acetone/ethanol.

RESULTS AND DISCUSSION

According to

$$\lambda_R = \bar{n} \cdot z \tag{1}$$

the wavelength of maximum light reflection λ_R of a cholesteric mesophase is proportional to the pitch z of the cholesteric helix, where the average refractive index $\bar{n}$ of the phase is the proportionality coefficient.[5] Therefore the pitch behavior—in our case near and at the phase transition point cholesteric/smectic A (Ch/S_A)—could be observed via λ_R. If one works at normal pressure one can study for one compound only one phase transition point. Therefore a high pressure optical cell was developed[4] to study the behavior of λ_R along the phase transition line Ch/S_A. Moreover, λ_R can be influenced more sensitively by pressure variation at constant temperature than vice versa (as in the case of measurements at normal pressure).

The investigated 4 compounds (see above) all have a first order phase transition Ch/S_A at normal pressure. As a quantity for the strength of the first order transition we chose the transition enthalpy $\Delta_u H$. Although $\Delta_u H$ is already known in some cases,[6,7] it was measured for all of the four cholesteryl *n*-alkanoates for better comparison. The results are listed in Table I.[8]

TABLE I

Enthalpy changes $\Delta_u H$ of the phase transition cholesteric/smectic A at normal pressure for six cholesteryl *n*-alkanoates[a]

Cholesteryl *n*-alkanoate	$\Delta_u H$[Jmol^{-1}]
Nonanoate	444
Decanoate	695
Tridecanoate	1430
Tetradecanoate	1500
Pentadecanoate	1766
Heptadecanoate	1989

[a] For comparison $\Delta_u H$ of cholesteryl nonanoate and cholesteryl tetradecanoate are additionally listed.[8]

$\Delta_u H$ increases with the length of the *n*-alkyl chain. What is the λ_R ($\propto$ pitch z) behavior at the phase transition point and how does the λ_R behavior change with the chain length? Figure 1 shows for CD ($n - C_{10}$) a strong red shift of λ_R (maximum of A_{BR}) with increasing pressure at 85.40°C. The spectra show the expected broadening with λ. All measured λ_R values are plotted versus pressure in Figure 2. The highest value of λ_R which could be measured was about 1400 nm at 241 bars. A further increase of pressure shifted λ_R out of the photometer range before the phase transition pressure was reached. It follows that in the case of CD we observe a continuous shift of λ_R to the infrared without being able to decide whether λ_R has a finite or infinite value at the phase transition point Ch/S_A. Because of the proportionality between λ_R and z a value of infinity for λ_R means that the helical arrangement of the long molecular axes has turned into a parallel one. CT ($n - C_{13}$), CP ($n - C_{15}$) and CH

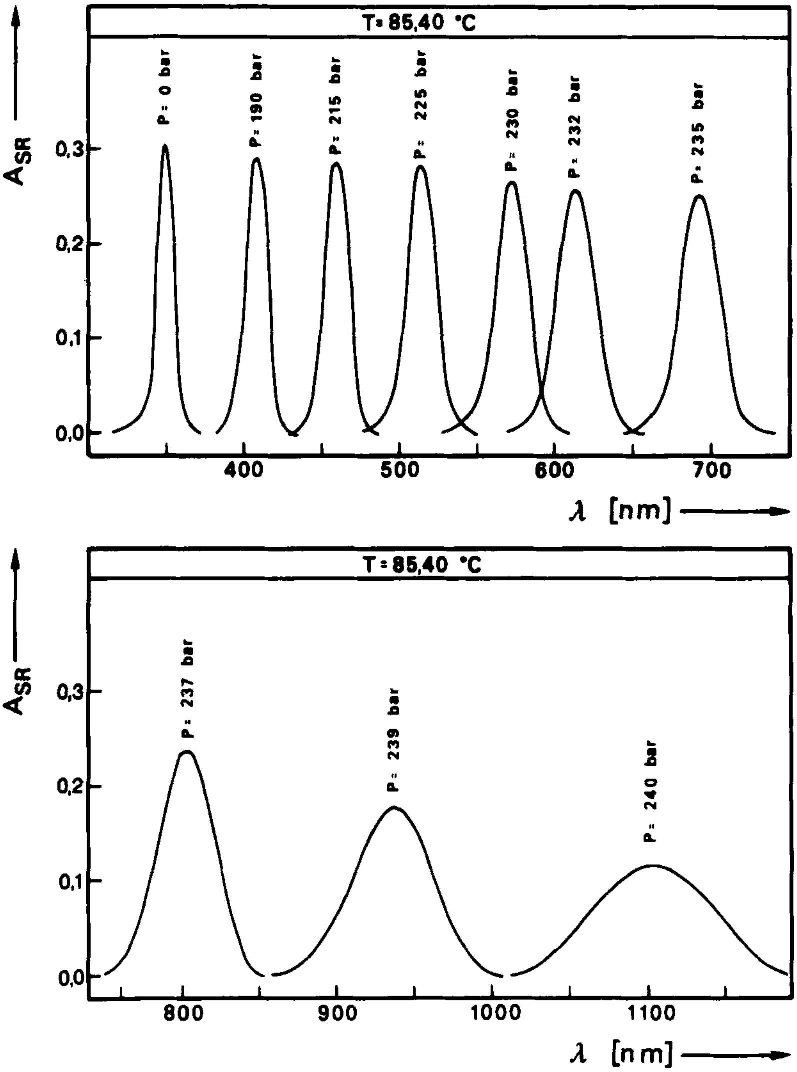

FIGURE 1 Quasi-absorption A_{SR} as a function of wavelength λ at various pressures and constant temperature $T = 85.40$°C. Compound: Cholesteryl decanoate. SR = Selective reflection.

($n - C_{17}$) show quite a different behavior of λ_R in the available experimental range. This is demonstrated by that of CP in Figure 3. As long as the phase transition pressure has not been reached, λ_R is shifted towards red (Figure 3a). Then between 292 and 295 bars a strong decrease of the reflected light intensity occurs with no shift of $\lambda_R = 396$ nm (Figure 3b).

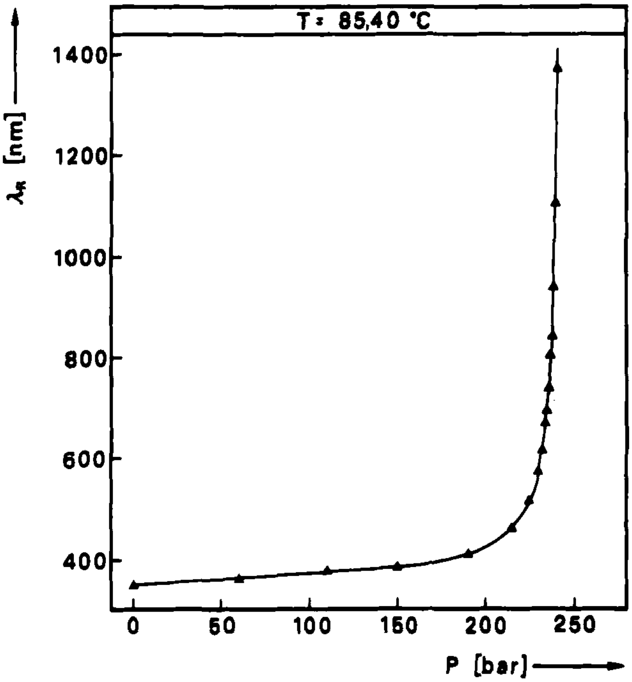

FIGURE 2 Wavelength of maximum light reflection λ_R as a function of pressure P at $T = 85.40$°C. Compound: Cholesteryl decanoate.

At 295 bars almost no reflection can be observed. Further pressurizing yields no reflection band, although the wavelength range of the photometer would have allowed a measurement in this case. Upon lowering the pressure to 293 bars the reflection at 396 nm returns (Figure 3c). This behavior can be explained by a finite limiting value $\lambda_u = 396$ nm of λ_R at the phase transition point Ch/S_A at 294 bars and 85.43°C. All measured λ_R values at 85.43°C are plotted versus pressure in Figure 4. The isotherm ends at 294 bars.

All obtained isotherms in the case of CP are presented in Figure 5. *Only for the isotherms 1–8 could experimental evidence of a finite* λ_u at the transition point be given. All isotherms, however, will be needed later for constructing a phase equilibrium line Ch/S_A. A very similar behavior of λ_R, as mentioned above, was found for CT and CH. For all these compounds λ_u shifts to higher values with increasing transition pressure (see e.g. Figure 5, 1–8).

In order to examine this effect more closely, the λ_u values for CT, CP and CH were plotted versus the phase transition pressure P_u (Figure 6).

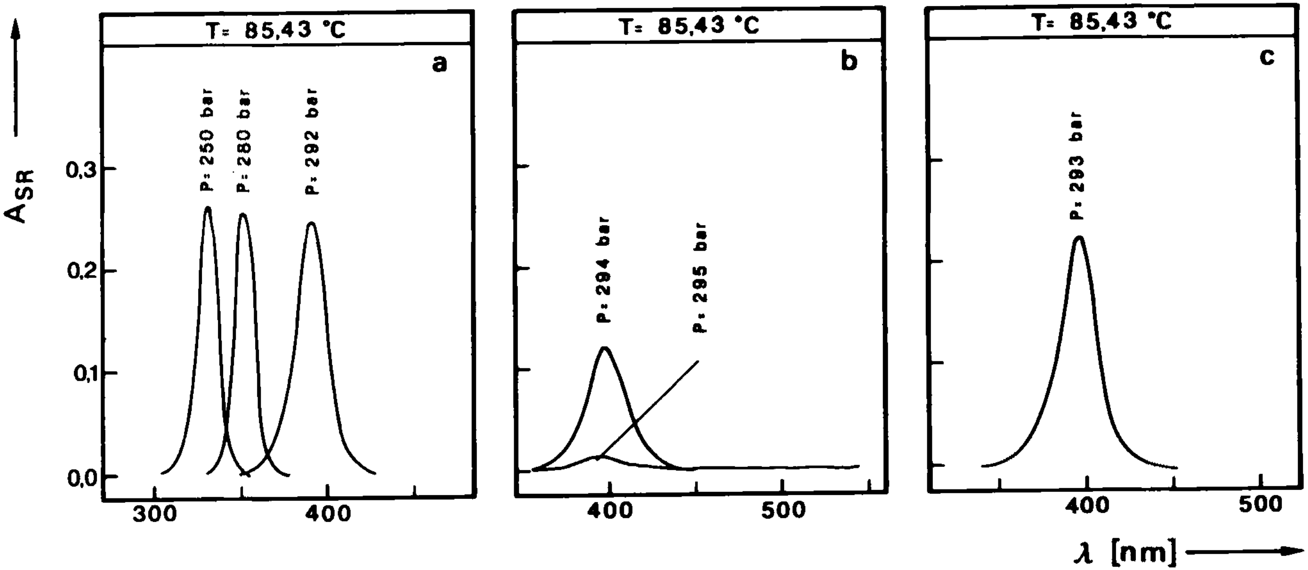

FIGURE 3 Quasi-absorption A_{SR} as a function of wavelength λ at various pressures and constant temperature $T = 85.43°C$. Compound: Cholesteryl pentadecanoate.

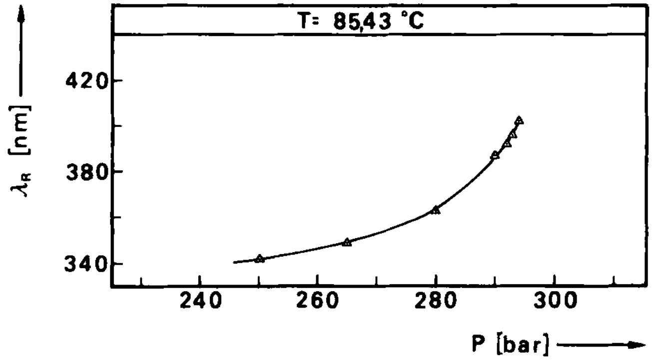

FIGURE 4 Wavelength of maximum light reflection λ_R as a function of pressure P at $T = 85.43$°C. Compound: Cholesteryl pentadecanoate.

One notices the following surprising result: In spite of the different compounds, on increase of P_u, λ_u approaches infinity with nearly the same function $f(P_u)$. A plot of the reciprocal of λ_u versus P_u makes this behavior still more obvious (Figure 7): a transition pressure P_t exists where λ_u^{-1} equals zero and λ_u infinity respectively. The dependence of λ_u^{-1} on P_u can be well described by a fourth order polynomial (see solid curve for CP in Figure 7). Then P_t can be determined fairly precisely by extrapolation of $\lambda_u^{-1} = f(P_u)$ to $\lambda_u^{-1} = 0$ (see broken curve in Figure 7): about 1000 bars. Nearly the same value for P_t results for CT and CH.

The corresponding temperature coordinates T_t taken from Figures 9, 10 and 11 (see below) are compiled in Table II.

TABLE II

Pressure (P_t)-temperature (T_t) coordinates of the cholesteric/smectic A phase transition point with the limiting wavelength of maximum reflection $\lambda_u = \infty$

Cholesteryl *n*-alkanoate	P_t [bar]	T_t [°C]
Tridecanoate	1000	105.01
Pentadecanoate	1000	102.36
Heptadecanoate	1000	101.15

The temperature coordinates are somewhat different because the phase equilibrium lines Ch/S_A of the three cholesteryl *n*-alkanoates do not coincide.

At $P_t \sim 1000$ bars the cholesteric phase with an infinite pitch coexists with the smectic A phase. We shall call this point on the phase equilibrium line Ch/S_A henceforth pitch infinity point (PIP).

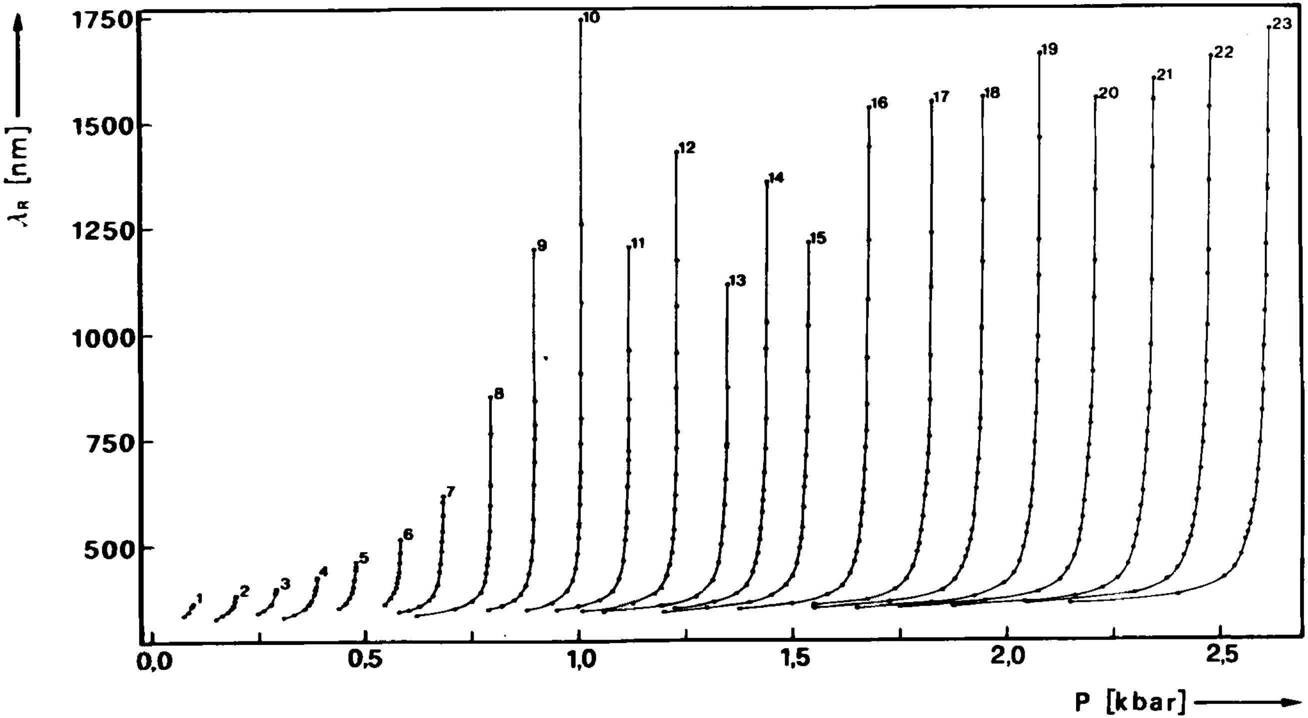

FIGURE 5 Wavelength of maximum light reflection λ_R as a function of pressure P at various temperatures. Compound: Cholesteryl pentadecanoate. 1—80.23°C; 2—82.82°C; 3—85.43°C; 4—87.81°C; 5—90.16°C; 6—92.65°C; 7—95.08°C; 8—97.61°C; 9—100.12°C; 10—102.61°C; 11—105.17°C; 12—107.61°C; 13—110.08°C; 14—112.04°C; 15—114.14°C; 16—116.99°C; 17—119.95°C; 18—122.45°C; 19—124.95°C; 20—127.55°C; 21—130.00°C; 22—132.47°C; 23—134.94°C

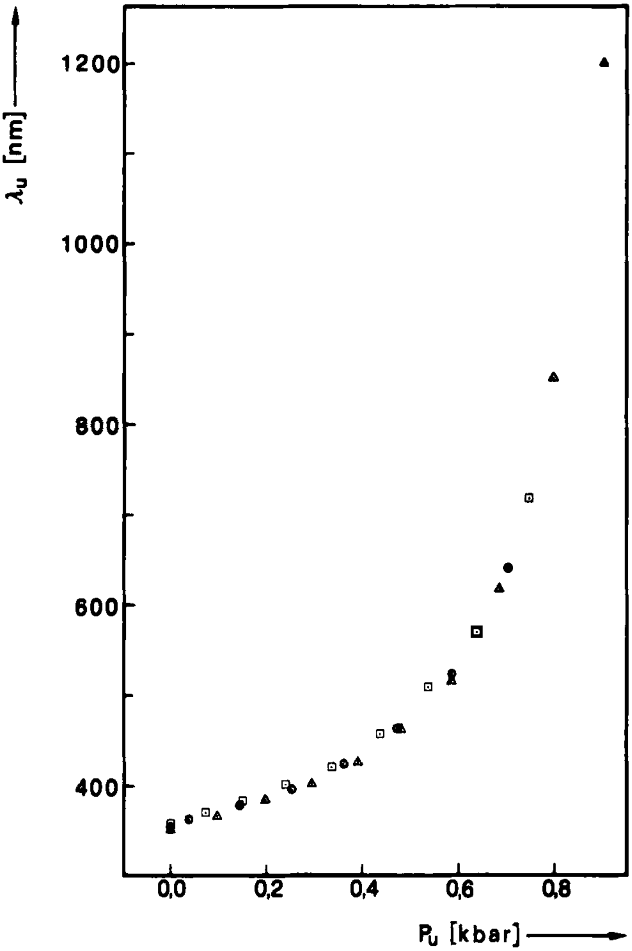

FIGURE 6 Limiting value of wavelength of maximum light reflection λ_u at the phase transition point cholesteric/smectic A as a function of the phase transition pressure P_u. Compounds: Cholesteryl tridecanoate (◘), cholesteryl pentadecanoate (▲), and cholesteryl heptadecanoate (◉). For comparison the highest measurable λ_R value of the lowest isotherm is plotted, where no "breakoff effect" could be observed (▲).

In a previous paper[9] we interpreted the intersection point of two straight lines representing the phase equilibrium behavior Ch/S_A of cholesteryl tetradecanoate [=cholesteryl myristate (CM)] as a tricritical point (TCP). The pressure coordinate of this point is 1050 bars! Because CM is positioned between CT and CP for which we found 1000 bars as pressure coordinate P_I of the PIP, we can suppose to a certain degree that this intersection point is a PIP. The same should be accepted for

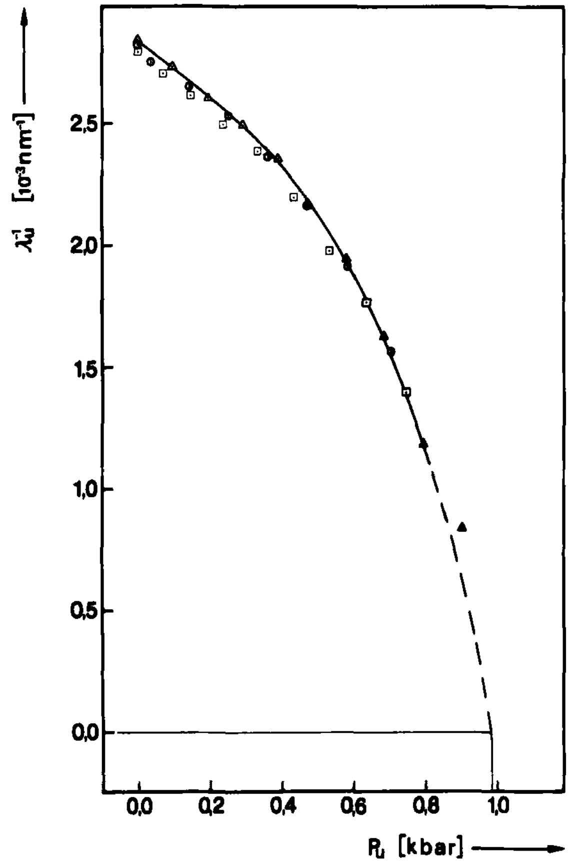

FIGURE 7 Reciprocal of λ_u as a function of P_u. Meaning of letters and symbols as in Figure 6

cholesteryl nonanoate (CN)[10] and CD (this work, see phase equilibrium line in Figure 8), although we obtained only 650 and 560 bars respectively, for the pressure coordinate of the intersection point. Probably an influence of the chain length on P_l exists in the case of cholesteryl *n*-alkanoates with shorter *n*-alkyl chains.

Hence the discrepancy between our interpretation of the intersection point as a TCP in the case of CN and CM and the results of Shashidhar[11] and Schneider *et al.*[12] is explained. Shashidhar (CN) and Schneider (CM) had found a finite value of $\Delta_u H$ at the coordinates of the particular intersection point. Moreover, according to Schneider, $\Delta_u H$ of CM does not approach zero before 3000 bars.

PHASE EQUILIBRIUM LINES CHOLESTERIC/SMECTIC A

As mentioned above λ_R is followed as a function of pressure at constant temperature. If a finite limiting value λ_u can be observed (see above), the corresponding pressure is the phase transition pressure P_u. If λ_R is shifted towards red out of the experimental range of the photometer, one cannot decide whether λ_u is finite or infinite at the transition point, because in general the pressure (P_I)-temperature (T_I) coordinates of the pitch infinity point (PIP) are not known. In the case $\lambda_u = \infty$ the relation

$$\lambda_R = \mathrm{A} \cdot (1 - P/P_u)^{-\mathrm{B}} \tag{2}$$

describes the behavior of λ_R as a function of P at constant T very well up to the phase transition point. Parameters A, B and also P_u can be determined on the basis of the measured quantities $\lambda_{R,i} | P_i$ near the transition point by minimization of the function

$$F = \sum [\lambda_{R,i} - \mathrm{A}(1 - P_i/P_u)^{\mathrm{B}}]^2 \tag{3}$$

using a nonlinear optimization method.[13]

If one measures above the PIP the optimized value for P_u should be the exact one. However, applying relation (2) below the PIP, the obtained value for P_u is always too big for systematic reasons. Nevertheless, the optimized value can be taken, because the difference between this value and that at the maximum pressure where λ_R still could be determined is only about 1 bar. The reason for this is the steep increase of λ_R with pressure near the transition point.

Equilibrium line of cholesteryl decanoate (CD)

All values of P_u for the different temperatures were determined by optimization, because no λ_u could be observed. The phase equilibrium line Ch/S$_A$ could be followed only up to 99.5°C (see Figure 8, upper part). At this temperature at a certain pressure crystallization occurs. Probably at this temperature a smectic A phase no longer exists. This effect results in a breakoff of the isotherms, which, however, can be distinguished from the effect leading to the breakoff at the phase transition point Ch/S$_A$ (see above). In the latter case the intensity of the reflection band disappears in a more or less small observable pressure interval and returns at the same pressure value when the pressure is lowered again. In the former case, however, the reflection band suddenly vanishes without a measurable interval and does not return until the pressure is lowered far below the crystallization point. These findings point to a supercooling effect,

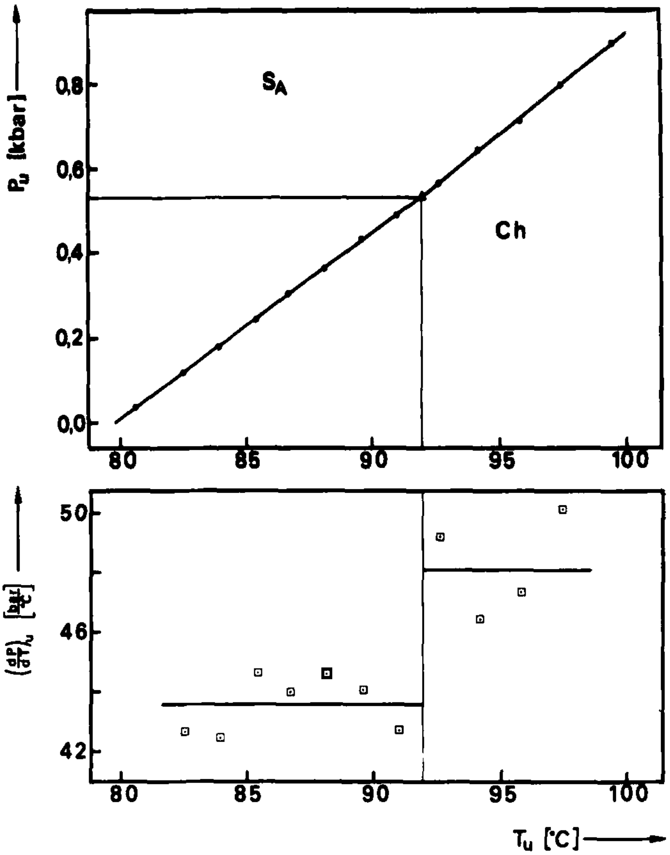

FIGURE 8 Upper part: Phase equilibrium line cholesteric/smectic A (Ch/S_A). Phase transition pressure P_u versus phase transition temperature T_u (Intersection point: ▲). Lower part: First derivative of the P_u (T_u) values versus T_u. Compound: Cholesteryl decanoate.

which is not observable for the Ch/S_A transition. Furthermore the highest wavelength λ_R attainable in the case of crystallization is considerably smaller than that obtained already for the Ch/S_A transition at lower pressures and temperatures. The data can be represented by two straight lines, which intersect at $P_u = 530$ bars and 91.95°C (see Figure 8, upper part). Here a PIP is to be assumed. Its coordinates are within an order of magnitude of those of cholesteryl nonanoate (CN) $^{10}P_u = 651$ bars and $T_u = 90.2$°C. The accuracy of the PIP coordinates of CD is not very high, because the equilibrium line could be measured only up to 895 bars and 99.5°C and the slopes of the straight lines above and below the PIP—contrary to CN—do not differ very much from each other (see Table III).

TABLE III

Slope $(dP/dT)_{u,a,b}$ of the phase equilibrium line cholesteric/smectic A of cholesteryl nonanoate and cholesteryl decanoate above (a) and below (b) the pitch infinity point

Compound	$\left(\frac{dP}{dT}\right)_{u,a}\left[\frac{\text{bar}}{^\circ\text{C}}\right]$	$\left(\frac{dP}{dT}\right)_{u,b}\left[\frac{\text{bar}}{^\circ\text{C}}\right]$
Cholesteryl nonanoate	53.8	44.6
Cholesteryl decanoate	48.1	43.6

Equilibrium line of cholesteryl pentadecanoate (CP)

The representation of the phase equilibrium line by two straight lines as in the case of CN and CD is not possible. The slope $(dP/dT)_u$ increases continuously with T_u beyond $P_l = 1000$ bars too (see Figure 9, lower part). The data, however, can very well be represented by the quadratic equation

$$P_u = a + b \cdot T_u + c \cdot T_u^2 \tag{4}$$

with $a = -1.7636 \cdot 10^3$ bar, $b = 9.4882$ bar/°C and $c = 1.7107 \cdot 10^{-1}$ bar/°C^2 (see solid curve Figure 9, upper part). The equilibrium line was followed up to 2632 bars and 134.94°C with no crystallization.

Equilibrium line of cholesteryl heptadecanoate (CH)

CH has, as does CD, a monotropic phase transition Ch/S_A at normal pressure. As does CD at higher pressures and temperatures respectively, CH shows crystallization instead of the transition Ch/S_A. Therefore the equilibrium line ends at 1658 bars and 114.98°C (see Figure 10, upper part).

The increase of the slope $(dP/dT)_u$, however, is continuous (see Figure 10, lower part) and the data are well described as in the case of CP by a corresponding quadratic Eq. (4) with $a = -1.6851 \cdot 10^3$ bar, $b = 8.2279$ bar/°C and $c = 1.8108 \cdot 10^{-1}$ bar/°C^2 (see solid curve Figure 10, upper part).

Equilibrium line of cholesteryl tridecanoate (CT)

Since so far only the cholesteryl *n*-alkanoates with a monotropic Ch/S_A transition at normal pressure had shown crystallization of the cholesteric phase under pressure (CD, CH), crystallization of CT having as CP an enantiotropic Ch/S_A transition took place unexpectedly. The highest Ch/S_A transition was observed at 1065 bars and 106.49°C (see Figure 11,

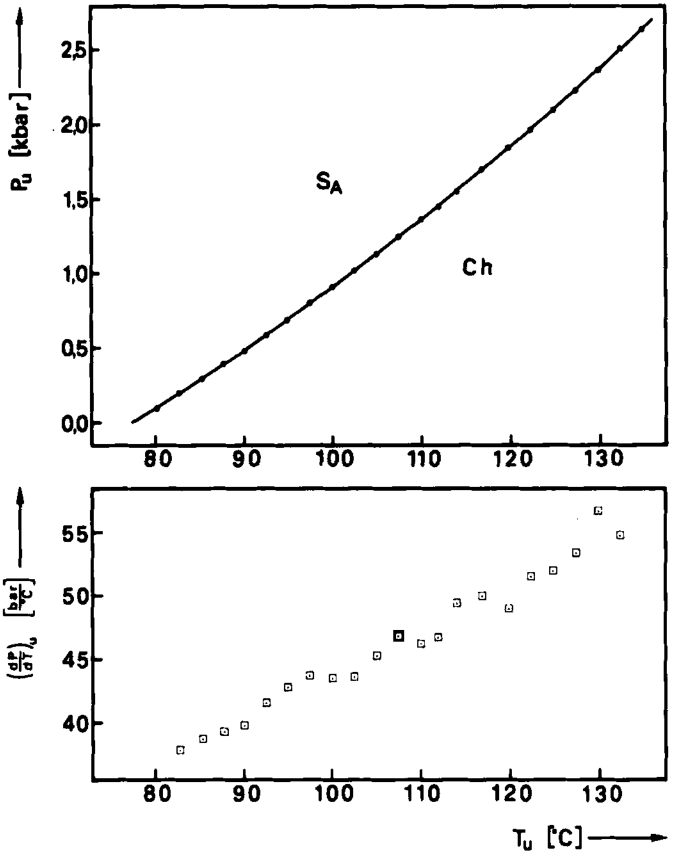

FIGURE 9 Upper part: Phase equilibrium line cholesteric/smectic A (Ch/S$_A$). Phase transition pressure P_u versus phase transition temperature T_u. Lower part: First derivative of the P_u (T_u) values versus T_u. Compound: Cholesteryl pentadecanoate.

TABLE IV

Slope $(dP/dT)_{u,o}$ of the phase equilibrium line cholesteric/smectic A of four cholesteryl *n*-alkanoates at normal pressure

Cholesteryl *n*-alkanoate	$\left(\frac{dP}{dT}\right)_{u,o}\left[\frac{\text{bar}}{°\text{C}}\right]$
Decanoate	43.6
Tridecanoate	36.1
Pentadecanoate	36.0
Heptadecanoate	35.9

upper part). In the observable P_u (T_u) range again the increase of the slope $(dP/dT)_u$ is continuous (see Figure 11, lower part) and the sequence of the $P_u | T_u$ values are very well represented by the relation (4) with $a = -1.8996 \cdot 10^3$ bar, $b = 1.1419 \cdot 10^1$ bar/°C and $c = 1.5423 \cdot 10^{-1}$ bar/°C^2 (see solid curve Figure 11, upper part).

Comparing the slopes of the phase equilibrium lines Ch/SA of the investigated cholesteryl *n*-alkanoates at normal pressure, one finds—similarly as in the case of the PIP coordinates—no influence of the *n*-alkyl chain length on the slope already from the CT on (see Table IV).

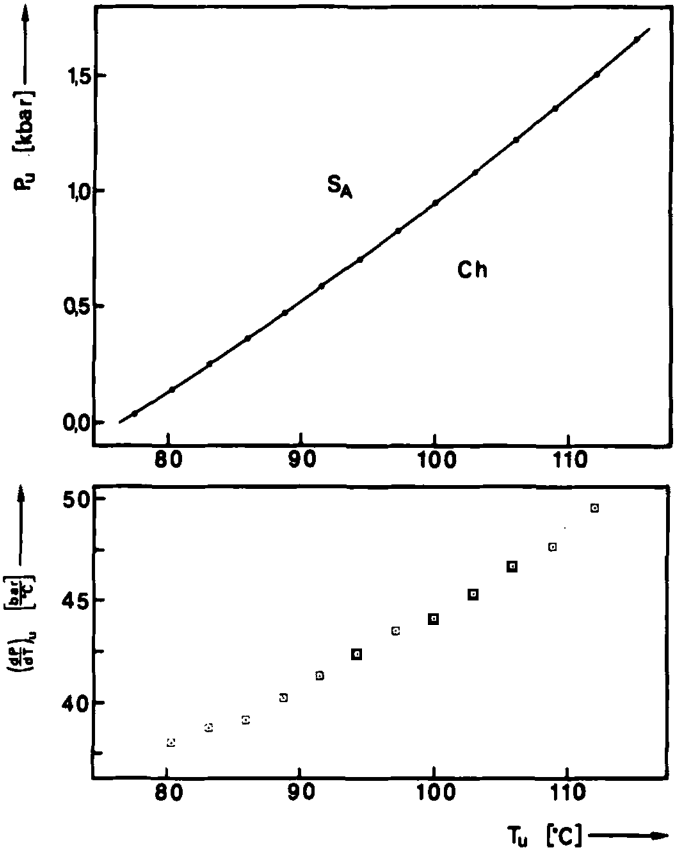

FIGURE 10 Upper part: Phase equilibrium line cholesteric/smectic A (Ch/S_A). Phase transition pressure P_u versus transition temperature T_u. Lower part: First derivative of the P_u (T_u) values versus T_u. Compound: Cholesteryl heptadecanoate.

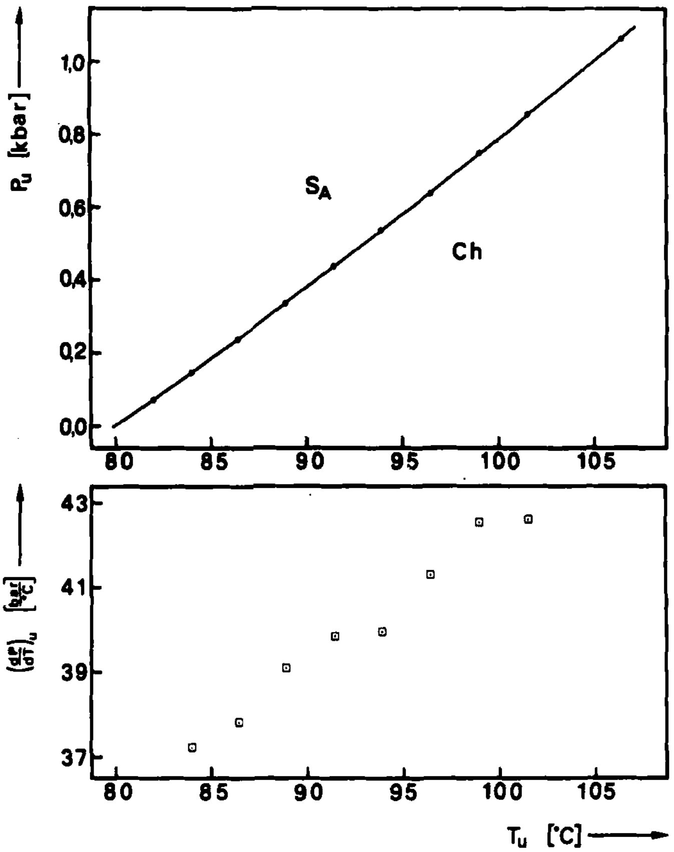

FIGURE 11 Upper part: Phase equilibrium line cholesteric/smectic A (Ch/S_A). Phase transition pressure P_u versus phase transition temperature T_u. Lower part: First derivative of the P_u (T_u) values versus T_u. Compound: Cholesteryl tridecanoate.

VOLUME DISCONTINUITIES AT THE PHASE TRANSITION CHOLESTERIC/SMECTIC A

Because the volume discontinuities ($\Delta_u V$) at the phase transition point Ch/S_A for the four investigated cholesteryl *n*-alkanoates are still not known and the slope of the phase equilibrium line at normal pressure could be determined with great accuracy, the four values of $\Delta_u V$ for normal pressure were calculated by means of the Clausius Clapeyron equation. The $\Delta_u H$ values were taken from Ref. 8. $\Delta_u V$ reveals a similar trend with respect to the *n*-alkyl chain length as $\Delta_u H$ (compare Tables I and V).

TABLE V

Calculated volume changes $\Delta_u V$ of the phase transition cholesteric/smectic A at normal pressure for six cholesteryl *n*-alkanoates.[a]

Cholesteryl *n*-alkanoate	$\Delta_u V$[cm^3 mol^{-1}]
Nonanoate	0.285
Decanoate	0.452
Tridecanoate	1.122
Tetradecanoate	1.028
Pentadecanoate	1.398
Heptadecanoate	1.586

[a] For comparison $\Delta_u V$ of cholesteryl nonanoate (CN) and cholesteryl tetradecanoate (CM) are also listed. Values for the slope of the phase equilibrium line are taken from previous work.[10] $\Delta_u H$ values see Table I.—Experimental values for CM: 1.015 cm^3 mol^{-1},[14] 1.333 cm^3 mol^{-1}.[15]

The influence of the chain length on $\Delta_u H$ has already been found by Barrall and Johnson[16] and is related to the stabilization of the smectic phase with increasing chain length.

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