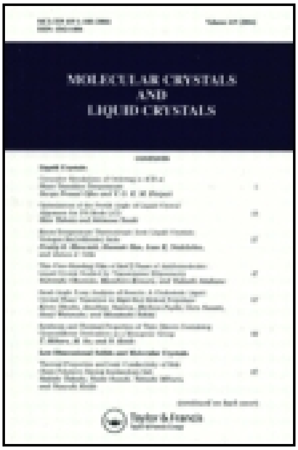

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High Pressure Investigations of the Phase Transitions in Cholesteryl Pentanoate and Cholesteryl Hexanoate

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HIGH PRESSURE INVESTIGATIONS OF THE PHASE TRANSITIONS IN CHOLESTERYL PENTANOATE AND CHOLESTERYL HEXANOATE

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Abstract: At high pressures too cholesteryl n-pentanoate (CH-5) and cholesteryl n-hexanoate (CH-6) exhibit only a cholesteric liquid crystalline phase. Our light reflection measurements up to 2600 bars yield no indication of a pressure induced smectic phase which was suggested by Tikhomirova and Ginzberg[1] for CH-5 at about 850 bars and 120°C. The obtained pressure(p_t)-temperature (T_t) phase diagrams show the expected widening of the cholesteric range with p_t and T_t. In the case of CH-5 the marked crystallization curve besides a melting curve could be explained by the transformation of the cholesteric into a metastable crystalline solid phase.

Introduction In the homologous series of the cholesteryl n-alkanoates the lower homologues exhibit only cholesteric mesophases at atmospheric pressure, but from the heptanoate both smectic A and cholesteric mesophases are observed. Therefore, we suppose, the pressure induced phase of cholesteryl pentanoate (CH-5) found by the Russian workers Tikhomirova and Ginzberg[1] is assumed by them to be a smectic. Because our laboratory is equipped with an optical high pressure apparatus for sensitive detection of smectic phases and the available pressure(p_t)-temperature(T_t*⁾)phase diagrams of CH-5[1,3,4] differ very much from one another, we have re-investigated the p_t-T_t phase behaviour of this alkanoate.

Compared with the CH-5 pressure induced smectic behaviour is rather to be expected for the hexanoate (CH-6) (see above). On that account the phase behaviour of this cholesteryl ester was studied too.

Results and discussion A smectic A phase (S_A) in addition to a cholesteric phase (CH) can be established by the divergence of the maximum wavelength of the selective light reflection λ_R of the latter phase near the phase transition CH/S_A. This effect is shown in figure 1 for cholesteryl nonanoate at atmospheric pressure. An analogous behaviour of λ_R occurs when the cholesteric compound is pressurized to the CH/S_A transition

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*⁾Index t means transition

at constant temperature.

The supposed induced smectic mesophase of CH-5 was obtained by Tikhomirova and Ginzberg[1] at about 850 bars and 120°C. No divergence of λ_R, however, was found by us in our experimental range up to 2600 bars and 169.4°C.

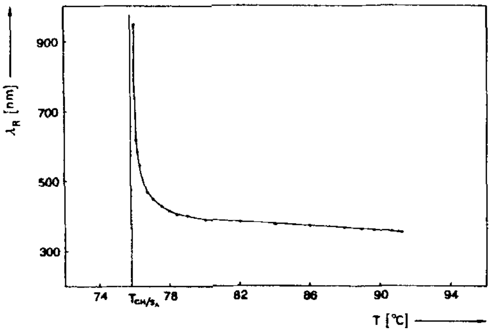

FIGURE 1 Temperature (T) dependence of the maximum wavelength of the selective light reflection λ_R for cholesteryl nonanoate at atmospheric pressure
T_{CH/S_A} = phase transition temperature cholesteric (CH)/ smectic A (S_A)

A slight red shift of λ_R with pressure was only observed at different constant temperatures as shown in figure 2 for 169.4°C.

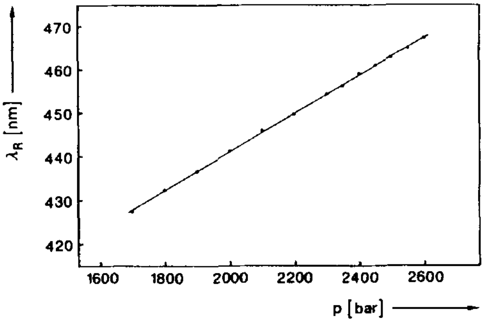

FIGURE 2 Pressure (p) dependence of the maximum wavelength of the selective light reflection λ_R for cholesteryl pentanoate at 169.4°C

The upper pressure limit of the isotherm is the phase transition pressure cholesteric (CH)/crystalline (C). For CH-6 too in the range 1-1225 bars and 93.62 - 136.02°C no divergence of λ_R was observed. The transition points CH/C as well as cholesteric (CH)/isotropic (I) which was also determined are indicated by the sudden disappearance of the light reflection of the cholesteric phase. Because CH-5 as well as CH-6 exhibit a blue phase (BP), upon closer consideration the transition CH/I must be replaced by CH/BP and BP/I respectively. The range of the BP, however, is only about 0.5 degrees, and therefore ignored here and in the following.*)

Not shown in this paper are the numerous isotherms of λ_R versus pressure necessary for the determination of the p_t-T_t phase diagrams of CH-5 and CH-6. For CH-5, however, the slopes of these isotherms $(\partial\lambda_R/\partial p)_T$ are given in figure 3 as functions of temperature.

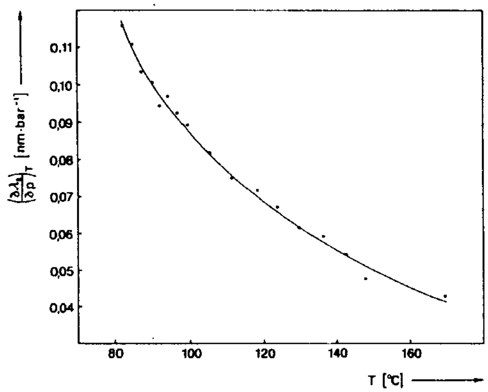

FIGURE 3 Temperature dependence of the first derivative of the λ_R (p) values $(\partial\lambda_R/\partial p)_T$ for cholesteryl pentanoate Meaning of letters as in figure 1 and 2

The observed decrease of $(\partial\lambda_R/\partial p)_T$ with temperature is an additional argument against a pressure induced smectic phase. $(\partial\lambda_R/\partial p)_T$ could be easily determined, because the isotherms are all linear in the respective upper pressure ranges. The decrease of $(\partial\lambda_R/\partial p)_T$ with increasing temperature cannot according to

$$\lambda_R = \bar{n} \cdot z \qquad (1)$$

$\bar{n}$ = average refractive index of the cholesteric phase
z = pitch of the cholesteric helix

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*) p_t-T_t phase behaviour of the BP see^5

be attributed to the pressure (p)-temperature(T) behaviour of $\bar{n}$ and the density, which has a direct influence on z. Both effects have been estimated. In the case of $\bar{n}$ we have made use of the measurements of Horn[6] who observed the p-T dependence of the two refractive indices of a nematic up to 2000 bars. For z we determined the direct dependence on the density from the p-V-T data of CH-5[4] assuming an isotropic compressibility. The influences of $\bar{n}$ as well as of z and of the density respectively on λ_R are of no importance and moreover cancel out. Hence there remains a significant decrease of the pressure dependence of z (according to eq. (1)) with increasing temperature which means a decrease of that of the twist angle ($\propto z^{-1}$).

In figure 4 and 5 the p_t-T_t phase diagrams of CH-5 and CH-6 based upon our light reflection measurements are presented. The diagrams show the cholesteric liquid crystal (CH) between the crystalline solid (C) and the isotropic liquid phase (I) (The very small blue phase region has been neglected). In both cases the cholesteric range is widened by pressure. Furthermore, a crystallization (a) and a melting curve (b) can be clearly distinguished with remarkable small deviations of the experimental points from CH-5 crystallization curve (see fig. 4, curve a).

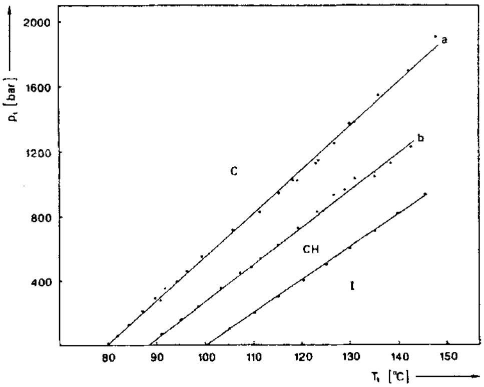

FIGURE 4 p_t-T_t phase diagram of cholesteryl pentanoate
(C = crystalline, CH = cholesteric, I = isotropic)
p_t, T_t = phase transition pressure and temperature respectively
a = crystallization curve, b = melting curve

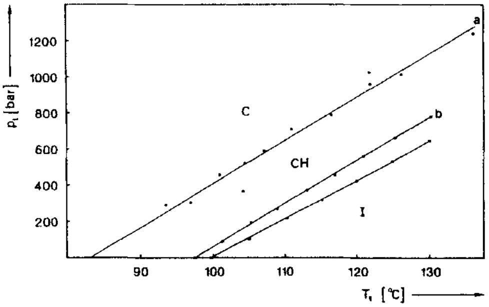

FIGURE 5 p_t-T_t phase diagram of cholesteryl hexanoate
(C = crystalline, CH = cholesteric, I = isotropic)
p_t, T_t = phase transition pressure and temperature respectively
a = crystallization curve, b = melting curve

For this curve a of CH-5, contrary to CH-6, a transformation of the cholesteric into a metastable crystalline phase could be established by X-ray measurements[7].

The accordance of our p_t-T_t phase diagrams with those of two Russian groups[1,4,8] is low. While our data of the phase transition temperatures at atmospheric pressure agree well with those given in the literature, those of[1,4,8] do not. According to[4,8] CH-5 and CH-6 should show smectic behaviour even at atmospheric pressure. However as outlined above, no smectic behaviour could be observed by us at higher pressures too. The slopes (dp_t/dT_t) for the melting and clearing curve of CH-5 and CH-6 in this work, however, differ very little from those obtained by Robberecht[3] who investigated these compounds already in 1938 up to 760 bars.

Acknowledgement

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