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Odd-even effect in the smectic A-cholesteric tricritical pressure of the cholesteryl n-alkanoates. High pressure studies on nine homologues

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Odd-even effect in the smectic A-cholesteric tricritical pressure of the cholesteryl *n*-alkanoates

High pressure studies on nine homologues

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The tricritical pressure, p_{TCP}, for the smectic A-cholesteric phase transition was determined by optical measurements for nine members of the homologous series of the cholesteryl *n*-alkanoates. p_{TCP} shows a clear odd-even effect with the length of the *n*-alkyl chain. The dependence of p_{TCP} on the length of the chain is not the same as that of the total smectic A-cholesteric transitional enthalpy, ΔH, at 1 bar. A comparison of both dependences gives hints to a different influence of the chain length on the pretransitional and discontinuous part of ΔH.

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1. Introduction

If the smectic A-cholesteric phase transition is second order (continuous), the enthalpy and volume undergo continuous changes at the transition, and a divergence of the cholesteric helical pitch to infinity is observed [1]. This behaviour of the pitch is expected theoretically; following de Gennes [2, 3] a divergence of the correlation length (the length over which smectic-like ordering occurs in the cholesteric phase), is present if the transition is second order. This divergence of the correlation length causes a divergence of the twist elastic constant, which in turn is correlated with a divergence of the pitch. The S_A-Ch transition can change from first order at atmospheric pressure to second order at elevated pressure. The crossover point on the S_A-Ch phase boundary line is called a tricritical point. As long as the transition is first order, the pitch of the cholesteric helix reaches only a finite value at the S_A-Ch transition. With increasing transition pressure, however, this value increases until finally the pitch diverges to infinity, indicating that the transition has become second order and a tricritical point exists. We have already verified this for cholesteryl tetradecanoate (Ch-14) [1]. Here we investigate the influence of the length of the *n*-alkyl chain on the tricritical behaviour for the homologous series of the cholesteryl *n*-alkanoates.

2. Experimental

The pressure-temperature dependence of the pitch, Z, of the cholesteric helix was determined from the wavelength of maximum light reflection, λ_R ($Z \sim \lambda_R$), with a Cary 17 DH photometer. The high pressure equipment has been described earlier [4]. A Perkin-Elmer DSC 2 was used for additional measurements of transitional enthalpies at atmospheric pressure.

All of the cholesteryl *n*-alkanoates, Ch-*n* ($n = 9$ to 17), were repeatedly recrystallized from mixtures of acetone/methanol and tested for purity by thin-layer

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chromatography. The S_A–Ch and Ch-I transition temperatures of the compounds at atmospheric pressure agreed with the corresponding data in [5] to within ±1·0°C.

3. Results and discussion

The position of the tricritical point can be fixed on the phase boundary line by its pressure coordinate, the tricritical pressure, p_{TCP}. We shall demonstrate the determination of p_{TCP} with the example of Ch-14. Since the pitch, Z, of the cholesteric helix is proportional to the wavelength of maximum light reflection, λ_R, the pressure-temperature behaviour of λ_R directly reflects that of Z. This selective light reflection causes a quasiabsorption, so that the reflection can be followed with an absorption spectrophotometer (see Experimental). The wavelength of maximum absorption in figure 1 corresponds to λ_R. The spectra were taken at constant temperature, $T = 82{\cdot}6$°C, near the S_A–Ch phase transition. In approaching the transition by increasing the pressure from $p = 164$ to 167 bar, λ_R is red shifted. Further increase of pressure to 169 bar, however, does not shift λ_R any more, indicating that the transition pressure has been reached and the band disappears. Just before the transition an unsettled increase of intensity takes place (see figure 1), which then is followed by a rapid decrease. At this point the cholesteric phase has transformed into the S_A phase with a finite value for λ_R of 393 nm corresponding to a finite pitch. This special λ_R at the transition point is denoted by λ_t in the following discussion. The break-off behaviour of λ_R indicates that the transition is still first order as has been found at atmospheric pressure by optical as well as by thermodynamic measurements. The latter show a discontinuous change in volume. Repeating this procedure at a higher temperature, we find that λ_t increases. As shown in figure 2, λ_t increases rapidly with transition pressure, p_t. This behaviour of λ_t encouraged us to determine the tricritical pressure, p_{TCP}, that is the lowest transition pressure, p_t, where $\lambda_t = \infty$. For that reason we used the function

$$\lambda_t = A(1 - p_t/p_{TCP})^{-B}, \qquad (1)$$

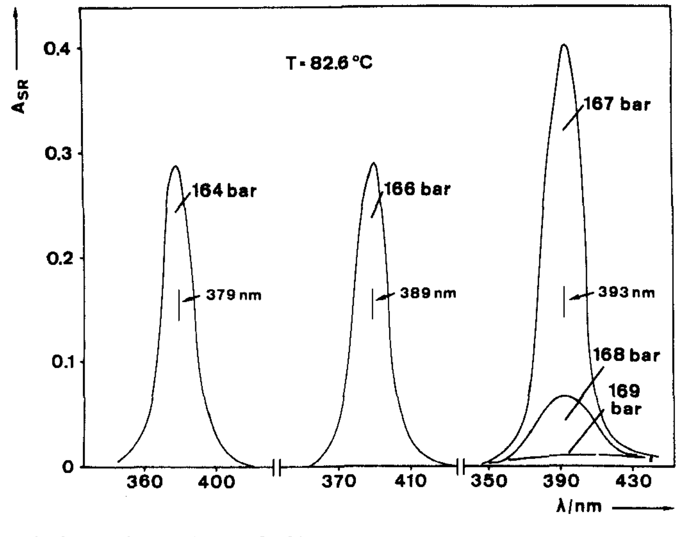

Figure 1. Quasi-absorption, A_{SR}, of Ch-14 versus wavelength λ at various pressures and constant temperature $T = 82{\cdot}6$°C near and at the S_A–Ch phase transition (SR = selective reflection).

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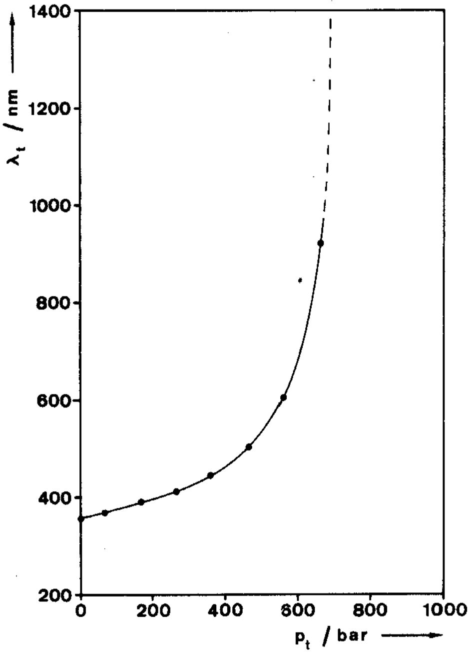

Figure 2. Wavelength of maximum light reflection at the S_A–Ch phase transition, λ_t, of Ch-14 versus the phase transition pressure, p_t.

where A, B and p_{TCP} are adjustable parameters. The curve in figure 2 gives λ_t as a function of p_t according to equation (1). The tendency of λ_t towards infinity with increasing p_t is more clearly demonstrated by plotting λ_t^{-1} versus p_t as shown in figure 3. For $\lambda_t = \infty$ and $\lambda_t^{-1} = 0$, $p_t = p_{TCP} = 701$ bar. That means that at this p_t the helix is totally unwound before the Ch phase is transformed into the S_A phase. The transition has changed from first to second order. p_{TCP} for the homologues Ch-13, Ch-15 and Ch-17 was determined in this same way, yielding the values listed in the table.

Despite the monotropic S_A–Ch transition of the homologues Ch-9 and Ch-10 at atmospheric pressure, p_t could be measured, but unfortunately not λ_t. For Ch-9 the required break-off behaviour of λ_R could not be observed, because the reflection wavelength was too high to be recorded in our photometer. For Ch-10 this behaviour

Tricritical pressure p_{TCP} of nine cholesteryl *n*-alkanoates (cholesteryl nonanoate (Ch-9) to cholesteryl heptadecanoate (Ch-17).

Homologue	p_{TCP}/bar
Ch-9	23
Ch-10	195
Ch-11	508
Ch-12	708
Ch-13	869
Ch-14	701
Ch-15	867
Ch-16	796
Ch-17	836

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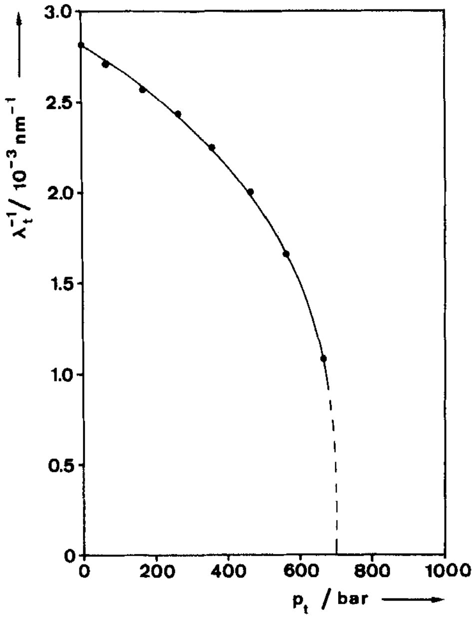

Figure 3. Reciprocal of the wavelength of maximum light reflection at the S_A-Ch phase transition, λ_t^{-1}, of Ch-14 versus the phase transition pressure, p_t.

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could not be identified with certainty. Thus the possibility exists that their S_A-Ch transition is second order at atmospheric pressure ($\lambda_t = \infty$). To answer this question we have mixed Ch-9 and Ch-10 with 4,4′-didecylazoxybenzene (C_{10}). With increasing mole fraction of C_{10} the reflection wavelength of the mixtures decreases so that a break-off behaviour of λ_R can be observed. p_{TCP} of three mixtures was determined, allowing p_{TCP} for the mole fraction $x_{C_{10}} = 0$ to be obtained by extrapolation (see figure 4). The value of 23 bar for p_{TCP} of Ch-9 reveals that the S_A-Ch transition of this

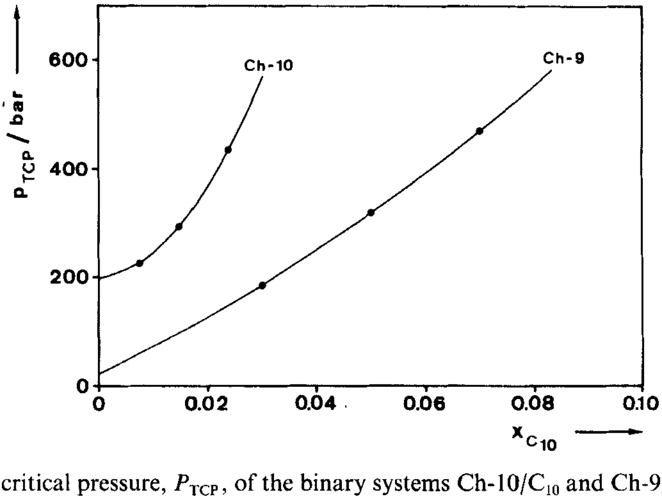

Figure 4. Tricritical pressure, P_{TCP}, of the binary systems Ch-10/C_{10} and Ch-9/C_{10} versus the mole fraction of C_{10}, $x_{C_{10}}$.

compound is almost second order at atmospheric pressure. For the Ch-11, Ch-12 and Ch-16 homologues, the wavelength range of the reflection is situated in the visible near the S_A-Ch transition, so that for this reason the break-off behaviour of λ_R should be observable. For fear of crystallization, there was nevertheless no chance to observe the S_A-Ch transition under elevated pressure, because at atmospheric pressure this transition occurs about 10°C below the melting point.

Since mixtures show a smaller tendency to crystallize, we tried to determine p_{TCP} for binary mixtures of cholesteryl n-alkanoates and to obtain p_{TCP} of the pure compounds by an extrapolation procedure. The investigations have proved, surprisingly, that if the difference of the n-alkyl chain length of both compounds is too great, a phase separation takes place at an elevated pressure shortly before the S_A-Ch transition. The latter effect is indicated by the appearance of two new reflection bands instead of one. Two mixed systems, Ch-11/Ch-14 and Ch-12/Ch-16, turned out to be usable (see figure 5 and 6). The tricritical pressures of the pure compounds were obtained by a three parameter fit according to

$$p_{TCP} = p_{TCP,1}x_1 + p_{TCP,2}(1 - x_1) - ax_1(1 - x_1). \qquad (2)$$

Here x_1 and $p_{TCP,1}$ are the mole fraction and the tricritical pressure, respectively, of compound 1, $p_{TCP,2}$, that of 2. The values of p_{TCP} obtained for the three compounds are also contained in the table.

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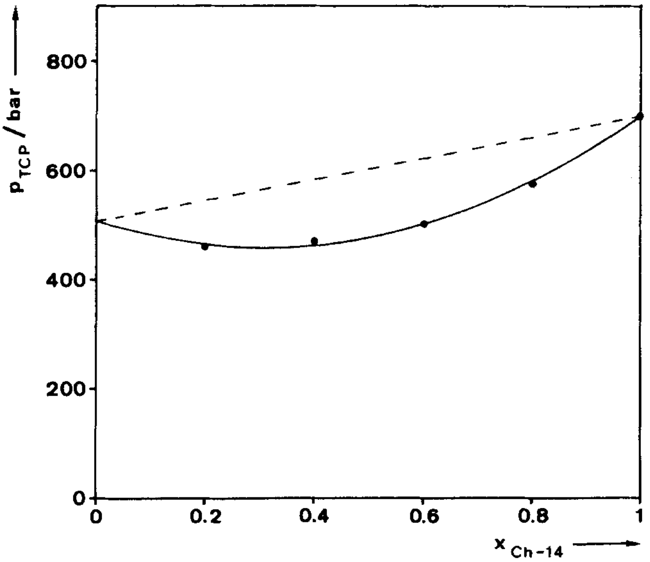

Figure 5. Tricritical pressure, p_{TCP}, of the binary system Ch-11/Ch-14 versus the mole fraction of Ch-14, x_{Ch-14}.

The dependence of p_{TCP} on the mole fraction in figure 5 and 6 exhibits for both systems a marked minimum. Since the effect of pressure on the S_A-Ch phase transitional enthalpy of all investigated cholesteryl n-alkanoates should be similar, this minimum should exist as well if we look at the dependence of this enthalpy on the mole fraction at atmospheric pressure. As our experimental results for the Ch-12/Ch-16 system in figure 7 show, this is indeed the case. When comparing figure 6 with 7 it should be borne in mind that our D.S.C. measurements of ΔH do not allow us to

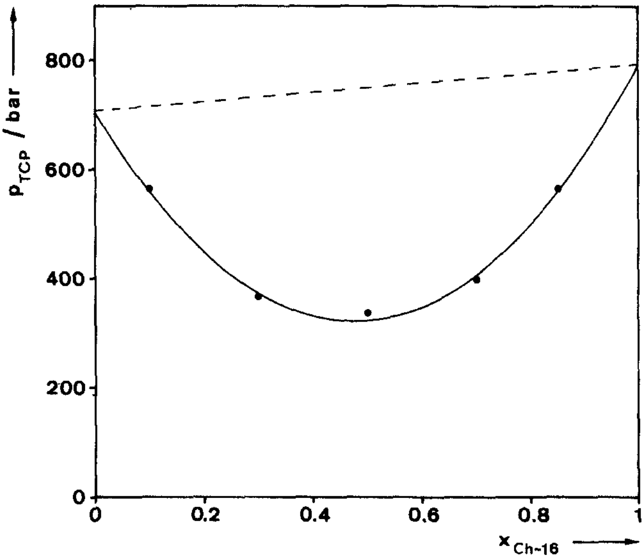

Figure 6. Tricritical pressure, P_{TCP}, of the binary system Ch-12/Ch-16 versus the mole fraction of Ch-16, $x_{Ch\text{-}16}$.

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distinguish between a discontinuous and a pretransitional part of ΔH, which is possible by the method of Thoen *et al.* [6]. At the tricritical point only the discontinuous part disappears, whereas the pretransitional contribution remains [1]; this will be discussed in more detail later. The minimum in figure 7 is nevertheless beyond doubt. What is the reason for its occurrence? In a recent paper we reported pressure-induced reentrant cholesteric phases of ternary Ch-3/Ch-9/Ch-14 mixtures [7]. As an explanation for this phase behaviour, we found an excess volume, which is formed when Ch-3 is added to a binary Ch-9/Ch-14 mixture. In the S_A phase, holes are

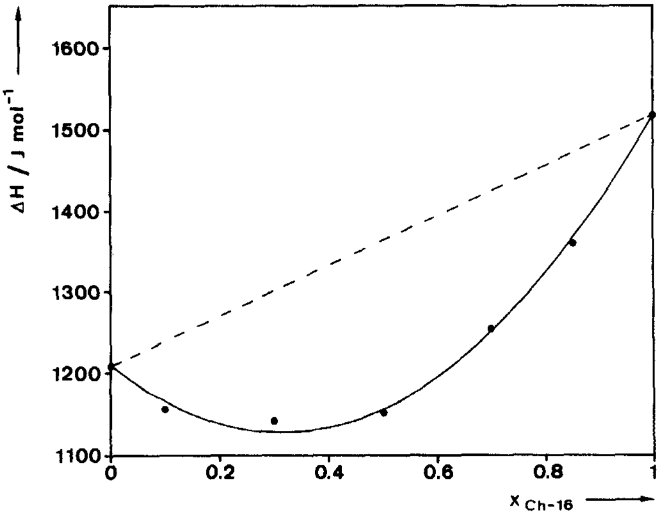

Figure 7. S_A–Ch transitional enthalpy, ΔH, of the binary system Ch-12/Ch-16 at atmospheric pressure versus the mole fraction of Ch-16, $x_{Ch\text{-}16}$.

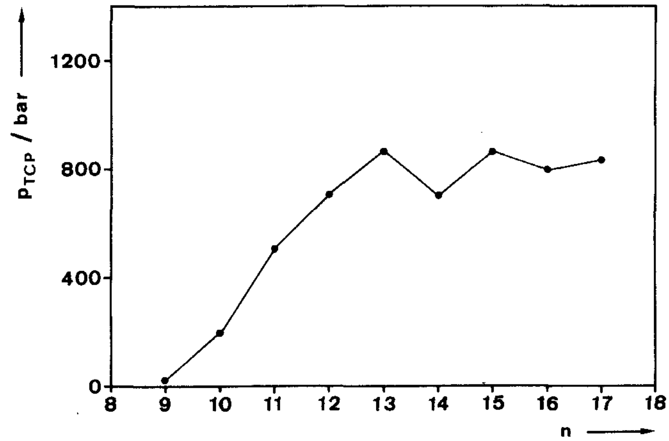

Figure 8. Tricritical pressure, p_{TCP}, of the cholesteryl n-alkanoates versus the number of carbon atoms in the acyl group, n.

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probably generated by the incorporation of the Ch-3 molecules, which have, compared with the other components, a very short n-alkyl chain. This effect destabilizes the S_A phase; the S_A-Ch transitional enthalpy, volume, and temperature decrease with increasing mole fraction of Ch-3. For the same reason the S_A phase of the respective pure component of the binary mixtures in figures 5 and 6 is destabilized by the incorporation of a partner with a different chain length.

The knowledge of p_{TCP} for all homologues from Ch-9 to Ch-17 now enables us to study the influence of the length of their n-alkyl chain (see figure 8, where n represents the number of carbon atoms of the acyl group). Beginning with $n = 9$, p_{TCP} increases with the chain length and approaches a limit of about 850 bar for the odd and about 800 bar for the even members of the homologous series. An odd-even effect is obvious, particularly from $n = 12$ on. This dependence of p_{TCP} on n should be reflected by the corresponding dependence of the S_A-Ch transitional enthalpies at atmospheric pressure. Since the enthalpy values have been reported by different authors, for better comparison all transitional enthalpies from Ch-9 to Ch-18 were once again measured in our laboratory. It must be pointed out again that DSC measurements do not allow a separation of ΔH into a pretransitional part ΔH_p and a discontinuous part ΔH_D. We see from figure 9 (●) that ΔH increases with the chain length as p_{TCP} does. This is in agreement with other investigations of homologous series. ΔH, however, does not exhibit a limit of transition pressure and we ask is ΔH_D or ΔH_p responsible for this behaviour? From our optical measurements we have learnt that the S_A-Ch transition of Ch-9 is almost second order at atmospheric pressure. The measured ΔH of 495 kJ/mol is therefore a pure ΔH_p. From volume-temperature measurements at atmospheric pressure on Ch-14 [1], we know that ΔH_p in this case is not larger than 35 per cent of ΔH, (= 1411 J/mole, see figure 9), or 494 J/mole, more likely smaller. Consequently ΔH_p does not change with the chain length from $n = 9$ to $n = 14$, but probably decreases. ΔH_D, however, must increase. Further, figure 8 reveals that Ch-13, Ch-15 and Ch-17 have nearly the same p_{TCP} of about 850 bar. This means that ΔH_D for all three homologues become zero at nearly the same transition pressure. Since the pressure coefficients of ΔH_D of these compounds will be very similar, ΔH_D at atmospheric pressure should also be nearly the same for these members. Beginning with $n = 9$, ΔH_D thus increases with the chain length and

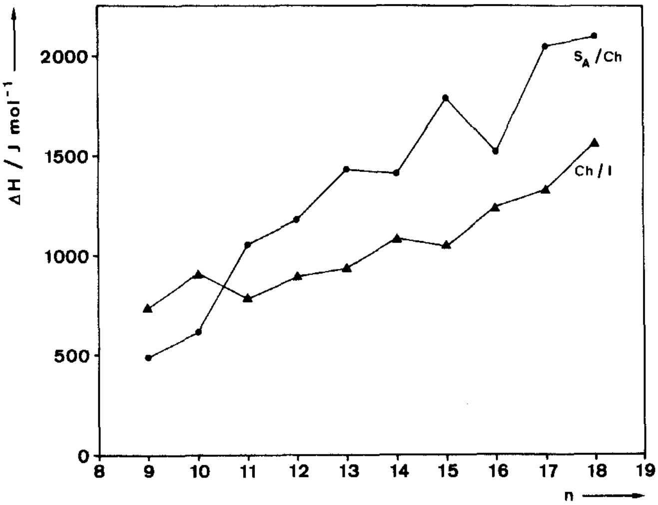

Figure 9. S_A–Ch and Ch–I transitional enthalpy, ΔH, of the cholesteryl *n*-alkanoates versus the number of carbon atoms in the acyl group, *n*.

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approaches a limit at $n = 13$. For the even members the same is valid: the limit ΔH_D should be somewhat lower and begin at $n > 14$.

It is, however, obvious from figure 9 that the total enthalpy effect ΔH alternatingly increases strongly for $n > 13$ ($n = 13$ to $n = 17$: by 625 J/mole). Only an increase of ΔH_p can be responsible for this, which means the gain in enthalpy of the Ch phase relative to the S_A phase by the prolongation of the *n*-alkyl chain is now diminished continuously at the transition to the S_A phase. The odd–even effect of p_{TCP} is, in principle, reflected by ΔH at atmospheric pressure. The S_A–Ch transitional entropies behave analogously to the transitional enthalpies (see figure 10), and since for the odd–even effect of the former a satisfactory explanation has already been given (see e.g. [8]), this explanation can also be accepted for the odd–even effect of p_{TCP}.

More often than for the S_A–Ch transition, the odd–even effect is discussed for the Ch–I, and N–I transitions. Comparing the effect of both transitions in figure 10, we

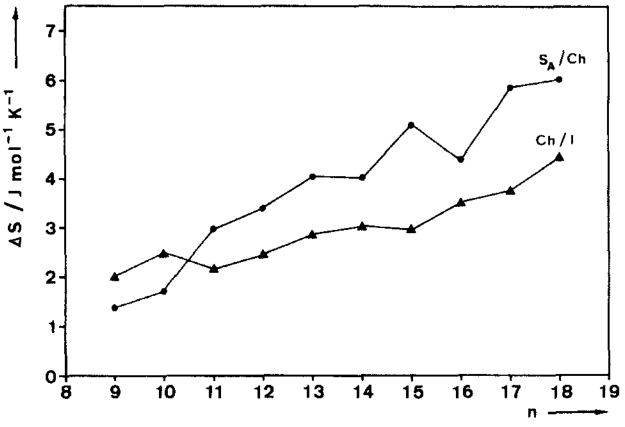

Figure 10. S_A–Ch and CH–I transitional entropy, ΔS, of the cholesteryl *n*-alkanoates versus the number of carbon atoms in the acyl group, *n*.

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see that the minima of ΔS for S_A-Ch are situated at even n, and for Ch-I at odd numbers of carbon atoms of the acyl group. Ennulat and Brown found the reverse behaviour for the cholesteryl ω-phenylalkanoates [9]. A rough attempt is made to explain the reverse alternation of ΔS for both transitions. The orientational order parameter, $\bar{P}_2$, of the molecules changes from a finite value to zero when the Ch phase transforms into the isotropic phase. $\bar{P}_2$(Ch) and the transitional entropy ΔS (Ch-I) therefore exhibit an analogous odd-even effect (see e.g. [8] and [10]). If the S_A-Ch transition is first order, $\bar{P}_2$(Ch) discontinuously increases to $\bar{P}_2(S_A)$, which alternates analogously with the chain length as $\bar{P}_2$(Ch) [11]. Since the alternation of $\bar{P}_2(S_A)$ is less pronounced than $\bar{P}_2$(Ch) [11], the difference $\bar{P}_2(S_A)$-$\bar{P}_2$(Ch) at the S_A-Ch phase transition, which is proportional to the related partial transitional entropy $\Delta S_{\bar{P}_2}(S_A\text{-Ch})$ of the total $\Delta S(S_A\text{-Ch})$, is smaller at the maxima than at the minima of $\bar{P}_2$(Ch)

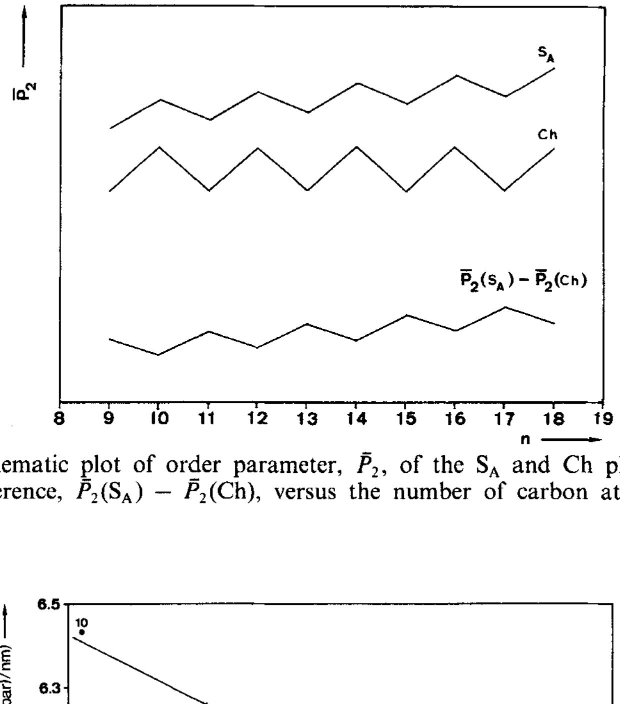

Figure 11. Schematic plot of order parameter, $\bar{P}_2$, of the S_A and Ch phases as well as their difference, $\bar{P}_2(S_A) - \bar{P}_2(Ch)$, versus the number of carbon atoms in the acyl group, n.

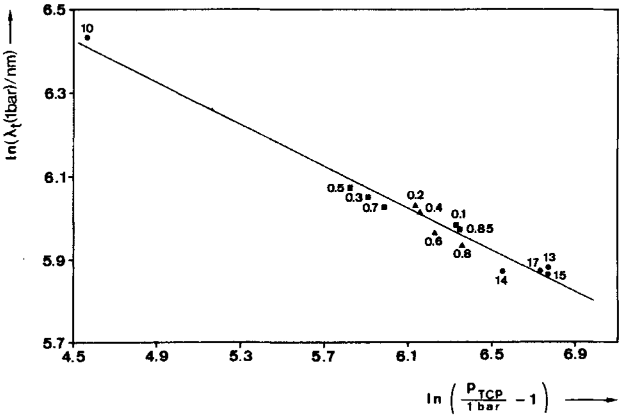

Figure 12. Ln-ln plot of the wavelength of maximum light reflection at the S_A-Ch phase transition, λ_t, of some cholesteryl n-alkanoates and binary systems versus $(p_{TCP}/1\text{ bar})$-$1(p_{TCP}$ = tricritical pressure). ●, pure compounds (n = 10; 13; 14; 15; 17); ▲, binary system Ch-11/Ch-14 ($x_{Ch\text{-}14}$ = 0·2; 0·4; 0·6; 0·8); ■, binary system Ch-12/Ch-16 ($x_{Ch\text{-}16}$ = 0·1; 0·3; 0·5; 0·7; 0·85).

(see figure 11). Hence $\Delta S_{\bar{P}_2}(S_A\text{–Ch})$ alternates in the reserve manner to $\Delta S(\text{Ch–I})$. $\Delta S_{\bar{P}_2}(S_A\text{–Ch})$ represents the main part of $\Delta S(S_A\text{–Ch})$ [12], so both behave in the same way.

Earlier it was shown that λ_t is enhanced when a S_A–Ch transition tends to second order ($\lambda_t = \infty$) with increasing transition pressure. This means that the Ch phase which coexists with the S_A phase exhibits an increased pitch. Consequently, there must be a correlation between λ_t at atmospheric pressure and p_{TCP}. In figure 12 all of the $\lambda_t - p_{TCP}$ pairs determined for pure compounds and for mixtures are used to test the plot ln λ_t as a function of ln $((p_{TCP}/1\,\text{bar}) - 1)$. The result is a linear relationship which can be used to predict approximate values of p_{TCP} from λ_t at atmospheric pressure.

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References

[1] Pollmann, P., and Schulte, K., 1985, *Ber. Bunsenges. phys. Chem.*, **89**, 780.
[2] De Gennes, P., 1972, *Solid St. Commun.*, **10**, 753.
[3] De Gennes, P., 1974, *The Physics of Liquid Crystals*, (Oxford).
[4] Pollmann, P., 1974, *J. Phys.* E, **7**, 490.
[5] Demus, D., 1974, *Flüssige Kristalle in Tabellen, VEB Deutscher Verlag für Grundstoffindustrie* (Leipzig).
[6] Thoen, J., Marynissen, H., and Van Dael, W., 1982, *Phys. Rev.* A, **26**, 2886.
[7] Pollmann, P., and Wiege, B., 1988, *Liq. Crystals*, **3**, 1203.
[8] Marcelja, S., 1974, *J. chem. Phys.*, **60**, 3599.
[9] Ennulat, R. D., and Brown, A. J., 1971, *Molec. Crystals liq. Crystals*, **12**, 367.
[10] Emsley, J. W., Luckhurst, G. R., and Shilstone, G. N., 1984, *Molec. Phys.*, **53**, 1023.
[11] Mukherjee, C. D., Bose, T. R., Ghosh, D., Roy, M. K., and Saha, M., 1985, *Molec. Crystals liq. Crystals*, **124**, 139.
[12] Bergmann, K., 1980, Dissertation, University of Paderborn.

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