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The Structure of Mesophases of Cholesteryl Esters†

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Abstract—The mesophases and the isotropic melt phase of several cholesteryl esters of saturated aliphatic acids have been studied by X-ray diffraction. The data are presented and briefly analyzed in terms of the angular position of the diffraction lines, their intensity, their integral width, and their shape. Both the cholesteric and the smectic phases are characterized by layer-structures with the long molecular axes perpendicular to the layers. Within the layers of the mesophases, the molecules are arranged anti-parallel to each other; the lateral order is nearly random. The isotropic phase is also characterized by groups of parallel molecules. Just above the temperature of transition into this phase, the molecules are still in their extended form.

1. Introduction

X-ray diffraction studies of the cholesteric and smectic liquid crystalline structure are few in number. Most papers are mainly concerned with qualitative interpretation of the diffraction patterns which were obtained for these mesophases;[1–5] Chistyakov *et al.*,[6,7] characterized the mesophases in terms of radial distribution functions. Bernal and Crowfoot[8] studied the solid states of substances which are able to form a thermotropic cholesteric state. They did not succeed in deriving information about the mesophase. Recently, de Vries[9–12] has published several papers dealing with diffraction studies on the nematic and smectic mesophases. Very recently, an elegant piece of work on X-ray diffraction from smectic ethyl *p*-azoxybenzoate in the Grandjean terrace structure has been reported.[13] However this study was carried out at only one temperature, hence the effect of temperature upon the structure was

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not delineated. The work reported in the present paper is part of a program for the evaluation of the structure of various phases and of the transitions between these phases for several cholesteryl esters of saturated aliphatic acids. Previous work dealt with studies on the transitions of cholesteryl acetate,[14] nonanoate,[15] myristate,[16] and stearate.[17] This paper deals with the characterization at a series of temperatures by X-ray diffraction of the structure of the mesophases as well as of the isotropic melts of these substances. Subsequent papers will report our results on the structure of the solid states.

2. Experimental

Samples of cholesteryl acetate, nonanoate, myristate and stearate were obtained from Eastman Kodak Company, Rochester, New York. The samples were purified by recrystallizing three times from *n*-pentanol and washed and dried as described previously.[16]

The X-ray diffraction data were taken with a General Electric XRD5 diffraction unit. The diffracted intensity was measured using a Geiger counter and was recorded on a chart. Nickel filtered Cu Kα radiation was used. The collimation used was: beam slit, 0.4°; counter slit, 0.2°; Soller slit, medium resolution; the background due to the primary beam divergence, air scattering, window scattering, etc., was determined by running a diffractometer scan without the sample, and was subtracted from the total intensity observed with the sample in place.

Corrections for instrumental broadening were treated by conventional methods.[18] These corrections were small. The sample was contained in a cell consisting of a steel ring with an inner diameter of about 1 cm and a thickness of about 1 mm and two thin mylar windows. The cell was attached to a larger copper block which could be heated. A hole was drilled through the block in a way which made transmission experiments possible. The desired temperature of the sample was maintained within $\pm\frac{1}{4}$°C by pumping thermostatted oil through the copper block. The temperature of the sample was checked with a thermocouple and a digital thermocouple thermometer. In addition, two mylar windows at the surface of the copper block and asbestos insulation of the block improved the temperature control. Our studies covered a temperature range from

room temperature to 130 °C. X-ray photographic diffraction patterns showed the absence, within the sample, of orientation which might have interfered with our measurements. This observed lack of orientation is consistent with our optical observations of these samples which showed no single observable texture over areas comparable to that of the X-ray beam. The results were analyzed in terms of (a) the angular position of the diffraction lines, (b) the intensity of the lines, (c) the integral width and the half-width of the lines and (d) the shape of the lines. We now will discuss these points in more detail: (a) In general, it is possible to calculate a spacing, X, from the position of the diffraction maximum by a formula of the type:

$$2X \sin \theta = Kn\lambda. \tag{1}$$

Here 2θ is the diffraction angle measured between incident and diffracted beams, λ is the wavelength of the radiation, n is the order of the reflection (assumed to be unity) and K is a constant depending on the arrangement and shape of the molecules.[1-7] The choice of K value depends on the orientational order within a phase (i.e., upon the order and shape of the molecules) and on the particular spacing we are concerned with. De Vries[9-12] has discussed the equations, their application and their limits in detail. In all our measurements we were concerned with only two spacings, a long spacing, l, and a short spacing, d. The d values for all phases were calculated using $K = 1.117$. For the long spacing, l, in the isotropic phase we used $K = 1.229$. The l values of the smectic state were calculated using Bragg's law, $K = 1$, and the cholesteric state, because of its peculiar structure, was treated in the manner discussed below. (b) The corrected maximum height of the diffraction line, I_0, was chosen as a measure of relative intensity only when comparing lines having the same integral widths. (c) The integral width is defined as:

$$\delta\beta = \frac{\int I(\mathbf{b})\, \mathrm{d}b}{I_0} \tag{2}$$

where

$$\mathbf{b} = \frac{\mathbf{s} - \mathbf{s}_0}{\lambda}; \quad |b| = \frac{2 \sin \theta}{\lambda} \tag{3}$$

$I =$ intensity and $\mathbf{s}_0$ and $\mathbf{s}$ are unit vectors in the direction of the

primary and diffracted beam. The half width is defined as the width at half-maximum.

3. Results and Discussion

We shall discuss sequentially in separate sections the results on the smectic, cholesteric and isotropic phases.

The Smectic Phase

The smectic phases of cholesteryl nonanoate and myristate are characterized by a very sharp diffraction line of high intensity at small angles and a broad diffraction line of low intensity at an angle, 2θ, of about 17°. This behavior is shown in Figs. 1 and 2 for the myristate.

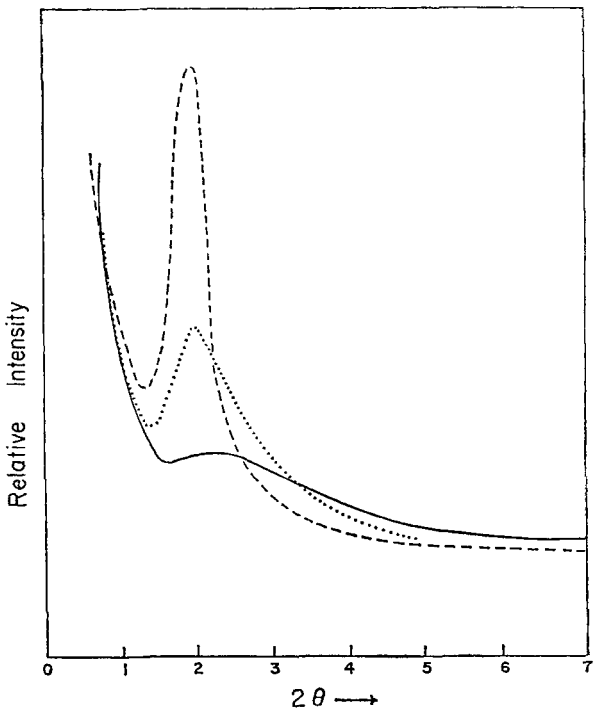

Figure 1. Plots of the relative Intensity versus the angular position 2θ for the small angle diffraction peaks of cholesteryl myristate. Smectic phase, – – –; cholesteric phase, . . .; isotropic phase, ——.

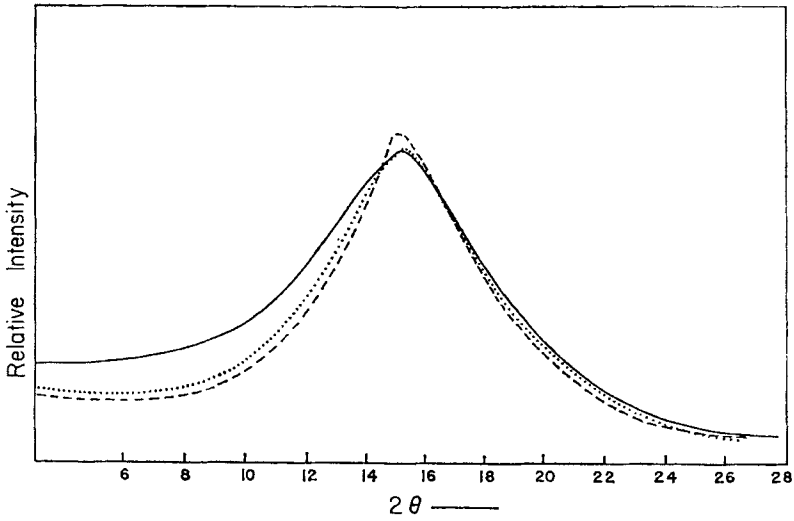

Figure 2. Plots of the relative intensity versus the angular position 2θ for the wide angle diffraction peaks of cholesteryl myristate. Smectic phase, – – –; cholesteric phase, . . .; isotropic phase, ——.

Diffraction lines of higher order could not be detected. With increasing temperature, the small angle line decreases in intensity, shifts slightly to larger angles and maintains a constant integral width. This behavior is shown in Table1 where in are displayed as a function of temperature, the long distances, l, and the relative intensities of the small angle lines for both the nonanoate and the myristate. For the smectic phases of both substances at all temperatures noted in the table, the integral width was $0.59 \pm 0.01°$. The uncertainties in l and the relative intensities are estimated at 0.05 and 0.02 A, respectively. The angular position, of course, also depends on the chain length of the ester, an increase of which results in a shift to smaller angles.

The broad high angle diffraction lines remain unchanged over the temperature range studied, and have the characteristics indicated by Table 2. The angular position of the line and its half width depend on the chain length of the ester and here an increase of the length causes a shift to larger angles (small distances d) and an increase of the half width.

TABLE 1 The influence of Temperature on the Small Angle Diffraction Lines of the Smectic Phase of Two Cholesteryl Esters

T(°C)	l-distance (A)	Relative intensity
	Nonanoate	
51.0	27.65	1.00
58.0	27.43	0.92
63.5	27.33	0.85
68.0	27.25	0.77
70.0	27.24	0.73
	Myristate	
63.5	33.95	1.00
64.2	33.85	1.00
68.0	33.55	0.89
68.5	33.40	0.89
71.8	33.40	0.77
73.4	33.35	0.73
74.0	33.35	0.68
75.0	33.40	0.67
76.0	33.30	0.65
77.0	33.25	0.63
77.6	33.20	0.57

TABLE 2 Position, d-Spacing and Half Width of the Wide Angle Diffraction Lines of Several Phases of Some Cholesteryl Esters

Ester	Phase	2θ (deg)	Distance d (A)	Half width (deg)
Acetate	Iso	15.30	6.48	5.5
Nonanoate	Smectic	16.70	5.95	4.90
	Chol	16.40	6.05	5.60
	Iso	15.90	6.23	6.15
Myristate	Smectic	17.40	5.69	5.00
	Chol	17.30	5.73	5.70
	Iso	17.15	5.81	6.3
Stearate	Iso	17.60	5.57	6.5

It seems not unreasonable to assume as others have[19–21] that the diffraction line at smaller angles is related to the length of the molecules and the broad line at larger angles to the perpendicular distances between molecules. If we take into account the results of optical studies on the smectic phase,[22] we have to conclude that the

line at smaller angles is caused by an assembly of smectic layers. The calculated value of l is related to the thickness of these layers. The broad line at larger angles is a consequence, of the specific arrangement of the molecules within the layers.

We shall now consider the low angle diffraction line in detail. As noted above if the temperature is increased, one observes a considerable decrease of the intensity of these lines for both substances studied while the widths of the lines remain constant. We observed a slight increase of the diffuse scattering around the lines with increasing temperature. A comparison of the diffraction patterns shows that the decrease of the intensity cannot be due to a partial melting of the smectic phase. Such melting would be accompanied by the appearance of peaks characteristic of the higher temperature cholesteric phase and no such peaks were formed. The marked decrease in intensity with increasing temperature is not unlike that which is to be expected from the effect of thermal vibrations. If these vibrations were only along the long axes of the molecules, it is possible to calculate minimum amplitudes of vibration of several angstroms.

The extended molecular lengths, L, as determined from space filling models are 22.7, 31.6, 37.4 and 41.9 A for the acetate, the nonanoate, the myristate and stearate, respectively. Table I shows that the calculated l values are less than L values, and that the l values decrease with increasing temperature. We can think of three possible explanations for this: (a) the molecules are tilted within the smectic layer; (b) the ester tail is not fully extended; and (c) the molecules in adjacent layers interpenetrate each other. We will now discuss these points in detail. (a) Optical studies indicate that in the cholesteryl esters the molecules are oriented perpendicular to the smectic layers. Thus, we reject the possibility. (b) This possibility we also are inclined to reject, but not so strongly. The decrease in spacing with increasing temperature is consistent with this concept but we have evidence, discussed below, that even in the isotropic state slightly above the transition temperature the ester tails are essentially fully extended. If this be true, it seems unreasonable that at lower temperatures they would be less extended. Thus, explanation (c) is favored by us because it is consistent with all observations. It can also account for the reasonably close lateral packing discussed below. The interpenetrating arrangement could result from trans-

lational motions of the molecules along their long axes and an increase of temperature resulting in a slightly stronger interpenetration of the molecules of adjacent layers would decrease the long spacing in the manner shown by Table 1. This interpenetration would be favored by an increase with temperature in the lateral spacing, d. We could not measure such an increase because the large width of the wide angle line precludes measurements of the necessary precision. However, for substances other than ours, de Vries observed, with increasing temperature, an extraordinary increase of the distance, d, in the nematic and smectic phase which was much larger than in the isotropic phase. de Vries did not report the dependence of the long spacing, l, on the temperature. If our model is correct, the depth $(L-l)$ of the penetration increases with increasing temperature from 4.0 to 4.4 A for the cholesteryl nonanoate and from 3.4 to 4.2 A for the cholesteryl myristate.

We assume that the breadth of the diffraction line at larger angles is due to the fact that the distribution of the molecules within the layers is nearly random (but not completely random as we shall see later). Laterally there is only a short range order as in normal liquids. The arrangement of the molecules within the layers will be discussed later.

The monotropic smectic phase of cholesteryl stearate was not studied because its transformation rate to the crystalline solid was too rapid.

The Cholesteric Phase

We studied the cholesteric phase of cholesteryl nonanoate, myristate and stearate. Crystallization interfered with our measurements in the case of cholesteryl acetate. For all substances studied, the cholesteric phase, like the smectic phase, is characterized by a narrow diffraction line at small angles and a broad line at larger angles. These phenomena are shown in Figs. 1 and 2 for the myristate and in Table 3 for all three esters. For the numbers in this table we estimate errors of 0.1 and 0.05 in the values of l^* and $\Delta\beta$, respectively. The line at small angles is broader than the corresponding line in the smectic phase; it has a lower intensity and lies at slightly higher angles. Within the cholesteric phase, as the temperature is increased,

TABLE 3 The Influence of Temperature on the Small Angle Diffraction Lines of the Cholesteric Phases of Cholesteryl Esters

Ester	T (°C)	l^* (Bragg) (A)	K	Integral width (deg)	Relative intensity
Nonanoate	74.5	27.1	1.16	1.16	1.00
	76.5	27.0	1.17	1.12	0.91
	80.0	26.9	1.18	1.18	0.75
	85.0	26.8	1.18	1.19	0.57
	88.0	26.5	1.19	1.22	0.47
	89.5	26.0	1.21	1.34	0.45
	91.4	25.0	1.26	1.53	0.37
Myristate	78.8	32.3	1.16	1.10	1.00
	80.0	31.9	1.17	1.10	0.75
	80.4	33.9	1.17	1.07	0.73
	81.0	31.6	1.19	1.10	0.70
	81.4	31.6	1.19	1.07	0.66
	82.0	31.5	1.19	1.13	0.58
	82.5	31.4	1.19	1.11	0.57
	82.7	31.3	1.20	1.13	0.50
	83.4	31.1	1.21	1.32	0.43
Stearate	76.5	36.8	1.14	1.20	—

the line shifts to slightly higher angles, the intensity strongly decreases, the half width remains constant and the integral width remains nearly constant. There is an increase of the integral width in a small temperature range immediately below the transition into the isotropic melt. Density measurements showed premelting effects in this range.[14,16]

The broad diffraction line is similar to that of the smectic phase but its angular position is shifted to larger values and the half width is increased over that of the smectic phase. With increasing ester chain length, the average lateral distance, d, decreases and the half width of the wide angle line decreases.

For the same reasons as in the case of the smectic phase, we conclude that the diffraction line at small angles is due to a specific order in the direction of the long axes of the molecules, whereas the broad diffraction line is due to the lateral arrangements of the molecules perpendicular to this direction.

The greater width of the diffract on line at small angles of the

cholesteric phase compared with the smectic phase indicates that, whatever is the lack of order producing this width, it is greater in the cholesteric than in the smectic phase.

In the cholesteric phase as in the corresponding smectic phase, with increasing temperature, the integral width remains constant except in the pretransition region, but the intensity drops. In the cholesteric state, however, both the integral widths and the temperature sensitivity of the intensity are much greater. The effect is again reminiscent of the effects of thermal oscillation about fixed lattice points. This entire temperature behavior suggests a higher mobility and a stronger temperature dependence of mobility for molecules in the cholesteric phase compared to the same molecules in the smectic phase.

We reject partial melting as the basis of the decrease in intensity with temperature for the same reasons mentioned in the smectic case. Also as in the smectic case we observed an increase in diffuse scattering as the temperature is increased.

The angular position of the low angle line depends significantly on

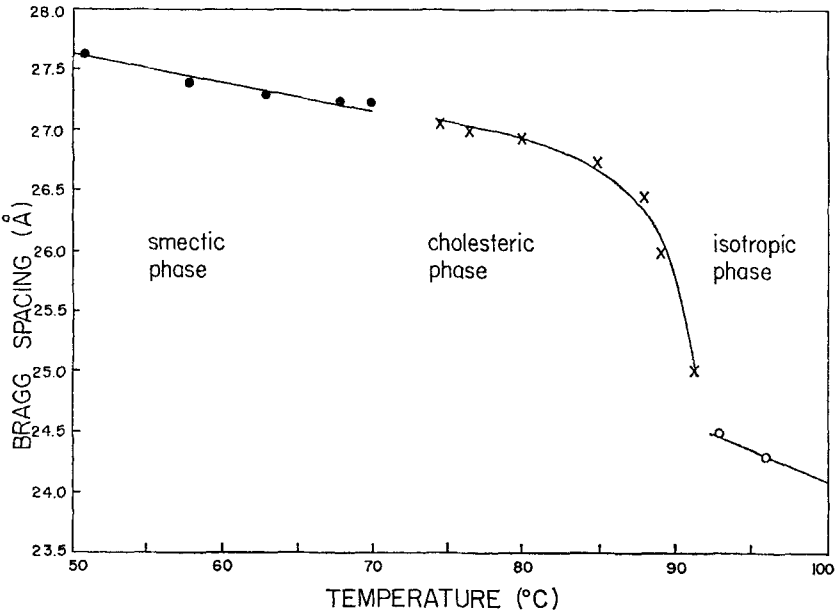

Figure 3. Plot of the Bragg spacing versus the temperature for cholesteryl nonanoate. Smectic phase, ●; cholesteric phase, × ; isotopic phase, ○.

the temperature. Table 3 and Fig. 3 show the l^* spacings as calculated from Bragg's law. The quantity l^* is, of course, not the actual long spacing l; it is used here merely as a convenient way of expressing the data obtained, for as noted above, the equation for the calculation of the spacing depends on the order and on the shape of the molecules. As our knowledge of these properties is limited, we do not know the appropriate value or values of K to use in Eq. 1. However, we do know that K must lie between 1 (perfectly parallel molecules over a " long range ") and 1.229 (completely random orientation of molecules). Thus, we took another approach. We assumed that the molecules were in their completely extended form then having both X and θ used Eq. 1 to calculate K. Table 3, column 4, gives the results. It is seen that as might have been predicted, an " intermediate " degree of parallelism is indicated.

In a " normal " nematic phase where the axes of molecules are aligned in one direction,[22] there is a random displacement of centers along this direction. This random displacement has an average value reflected by a low angle X-ray scattering peak.[4] Such peaks are quite diffuse having integral widths of several degrees. In the cholesteric states of the substances here studied, the integral widths are much smaller (ca 1°, see Table 1). Further a " normal " nematic shows a small angle reflection very similar in intensity and shape to that of the isotropic liquid of the same substance.[25] In the case of the cholesteryl esters, the differences between the low angle lines of the cholesteric and the isotropic phases are much more marked. It is thus clear that these cholesteric states, whatever their structure, are not " normal " nematic structures with a superimposed twist. Rather, the relative sharpness of the low angle peak suggests the presence of a layered structure similar to the smectic but somewhat more disordered. It should be noted that our experiments are not concerned with structures on a larger scale, viz. on the scale of " long range order " and the twist as determined by optical measurements. The increase of the integral width in the " premelting range " gives us a hint about the nature of the premelting. Premelting is clearly not a partial melting caused by impurities but is probably due to increasing lateral distortions.

The breadth of the diffraction line at higher angles shows that a nearly random arrangement exists perpendicular to the long axis of

the molecules. We will discuss this order later. The temperature dependence of the d spacings were not measured for the same reasons as in the smectic case.

Isotropic Phase

The results of the diffraction studies on this phase are summarized in Figs. 1, 2, and 3 and in Table 4. The error in the position of the maximum in 2θ is estimated to be $\pm 0.08°$. The isotropic phase of all the substances studied is characterized by a broad, very weak diffraction peak at small angles and a broader peak at larger angles. This latter peak is similar to the corresponding peaks in the smectic and cholesteric phases. The peak at smaller angles becomes broader and weaker with increasing temperature while its position is shifted to larger angles. Figure 2 shows that the large angle diffuse line lies at slightly smaller angles and is somewhat broader than the corresponding line in the cholesteric state. Table 2 shows that increasing the

Table 4 The Influence of Temperature on the Small Angle Diffraction Lines of the Isotropic Phases of Several Cholesteryl Esters

Ester	T (°C)	$2\theta^*_{max}$ (deg)	l (A)
Acetate	101.0	5.06	21.5 ± 0.2
	112.0	5.04	
	120.0	5.03	
	128.0	5.07	
Nonanoate	93.0	3.61	30.2
	96.0	3.65	29.8
	103.0	3.70	29.4 ± 0.5
	111.0	3.73	29.1
Myristate	84.8	3.04	35.6
	87.0	3.07	35.4
	90.0	3.07	35.4 ± 0.08
	93.0	3.15	34.4
Stearate	78.0	2.65	41.0
	81.0	2.70	40.2
	85.0	2.75	39.6 ± 0.9
	88.5	2.83	38.0

chain length of the ester shifts the line to larger angles and increases its half width. The values of l^* for the nonanoate calculate from Bragg's law are displayed in Fig. 3. This value is significantly smaller than those calculated for l using Eq. (1) with $K = 1.229$, as shown in Table 4. The values of l are quite close to the extended molecular lengths noted above, particularly at temperatures just above the cholesteric-isotropic transition temperature. The most reasonable explanation for the diffraction pattern is that just above the transition temperature the molecules are arranged with their axes more or less parallel and cluster into small groups. These small groups represent arrangements of minimum potential energy but the specific molecular population of these groups changes with time as the groups dissociate and are reconstituted. The molecules in these groups stiffen each other through mutual interaction and assume essentially the same extended form as in the solid state. The existence of groups of oriented molecules is a consequence of space-filling requirements and is further promoted by forces between the molecules. Rehage and Stuart [26] demonstrated the occurrence of groups in a two-dimensional model comprised of rod-shaped particles without interactions. Clusters always appear when the packing is sufficiently tight that anisotropic space filling becomes necessary.

Similar results were obtained experimentally for liquid paraffins from C_5 to C_{15},[27] alcohols from C_1 to C_{11},[19,20] normal fatty acids[20,21] and several mesophase-forming substances.[9-12] Increasing the temperature probably decreases the size of the groups as well as the order within the groups. The ester chain becomes more and more mobile as the temperature is increased. This results in the observed decrease of the l spacing. Gravatt and Brady[28] observed that in the isotropic state as the isotropic–nematic transition was approached for *p*-azoxyanisole, the correlation length for molecular ordering increased.

Let us now briefly discuss the arrangement of the molecules perpendicular to the direction of the long axis of the molecules. As is shown by Table 2, for all phases the d spacings decrease considerably with increasing chain length of the ester tail. If one compares these values with the dimensions of the molecules and if one builds models of the phases, one is forced to the conclusion that in all phases studied the molecules (with the probable exception of cholesteryl acetate) cannot be arranged side by side with their ester

tails pointing in the same direction. The arrangement of adjacent molecules must be antiparallel so that a cholesterol part is surrounded by ester tails, and an ester tail is surrounded by cholesterol parts. This conclusion is forced by the fact that the transverse dimensions of the cholesteryl moiety are 7.4 and 6.0 A. Only this alternating arrangement can account for the observed values of d and their dependence on the length of the ester tail. The packing gets less and less tight, going from the smectic to the cholesteric to the isotropic phase; the short-range order decreases. The order gets more distorted as the length of the ester tail increases. This shows the importance of the cholesterol part in preserving sufficient order.

It is worth noting that antiparallel molecular arrangements have been proposed for liquid crystal phases of other mesophase forming substances.[6] Also, some of our preliminary X-ray structure studies on solid cholesteryl myristate indicate a similar arrangement.

4. Summary

The essential features of the structure of the smectic, cholesteric and the isotropic phases do not depend on the specific length of the ester moiety. The smectic phase is characterized by an assembly of layers. Within the layers there is a lateral short range order similar to that of a normal liquid. The molecules are essentially in their extended form and are arranged within the layers in an antiparallel configuration. The degree of order is highest in the direction perpendicular to the smectic layers. The molecules interpenetrate adjacent layers. An increase of temperature results in an increase of thermal vibrations of the molecules and possibly in a significantly stronger interpenetration of the molecules of adjacent layers.

The cholesteric phase does not differ much from the smectic phase; the layered structure is still maintained. The order both within and perpendicular to the layers has merely decreased somewhat. The average distance, d, between the molecules has increased while the order perpendicular to the layers has decreased. Increasing the temperature results in stronger longitudinal vibrations of the molecules and possibly in a decrease of the orientational order.

The isotropic phase is characterized by small groups of parallel molecules. Compared with the cholesteric state, the distance, d,

between the molecules has decreased and the distribution of d has broadened. The molecules are still in their extended form just above the transition temperature; the ester chains probably lose their stiffness at higher temperatures.

An increase of the chain length of the ester results in an increase of the thickness of the smectic and cholesteric layers and in all phases in a decrease of the average distance, d, and in a decrease of the short-range order. The decrease of the average distance, d, is due to the antiparallel arrangement of the molecules in all phases. The decrease of the short-range order shows the importance of the cholesterol part for maintenance of this order.

Note Added in Proof

After this manuscript was finished, the authors became aware of the similar but more elegant and sophisticated work on cholesteryl nonanoate and myristate done by Prof. W. L. McMillan, *Phys. Rev.*, *A.* **6,** 936 (1972).

REFERENCES

1. Friedel, E. and de Broglie, M., *Compt. Rend.* **176,** 475, 738 (1923).
2. Friedel, E., *Compt. Rend.* **180,** 269 (1925).
3. Herrmann, K., *Trans. Faraday Soc.* **29,** 972 (1923).
4. Herrmann, K., *Krist. Z.*, **92,** 49 (1935).
5. Mabis, A. J., *Acta. Cryst.* **15,** 1152 (1962).
6. Chistyakov, I. G., *Soviet Phys.-Crystallography* **8,** 691, 1044 (1964).
7. Chistyakov, I. G., Schabischev, R. I., Jarenov, R. I. and Gusakova, L. A., *Mol. Cryst. and Liq. Cryst.* **7,** 279 (1969).
8. Bernal, J. D. and Crowfoot, D., *Trans. Faraday Soc.* **29,** 1032 (1933).
9. de Vries, A., *Mol. Cryst. and Liq. Cryst.* **10,** 31 (1970).
10. de Vries, A., *Mol. Cryst. and Liq. Cryst.* **10,** 219 (1970).
11. de Vries, A., *Mol. Cryst. and Liq. Cryst.* **11,** 361 (1970).
12. de Vries, A., to be published.
13. Krigbaum, W. E., Poirier, J. C. and Costello, M. J., to be published.
14. Price, F. P. and Wendorff, J. H., *J. Phys. Chem.* **75,** 2849 (1971).
15. Price, F. P. and Wendorff, J. H., *J. Phys. Chem.* **76,** 276 (1972).
16. Price, F. P. and Wendorff, J. H., *J. Phys. Chem.* **75,** 2839 (1971).
17. Price, F. P. and Wendorff, J. H., unpublished work.
18. Klug, H. P. and Alexander, L. E., *X-Ray Diffraction Procedures for Crystalline and Amorphous Materials*, John Wiley and Sons, New York, 1954.
19. Stewart, G. W., *Phys. Rev.* **30** 232 (1927).
20. Morrow, R. M., *Phys. Rev.* **31,** 10 (1928).

21. Katz, J. R., *Z. Physik* **45**, 97 (1927); **46**, 392 (1928).
22. Gray, G. W., *Molecular Structure and the Properties of Liquid Crystals*, Academic Press, London, 1962.
23. Guinier, A., *X-Ray Diffraction*, W. H. Freeman, San Francisco, 1963.
24. Hosemann, R., Lemm, K. and Wilke, W., *Mol. Cryst.* **1**, 333 (1967).
25. Stewart, G. W., *J. Chem. Phys.* **4**, 231 (1933).
26. Rehage, H. and Stuart, H. A., *Physik. Z.* **38**, 1027 (1937).
27. Stewart, G. W., *Phys. Rev.* **31**, 174; **32**, 153 (1928).
28. Gravatt, C. C. and Brady, G. W., *Mol. Cryst. and Liq. Cryst.* **7**, 355 (1969).