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An X-ray Diffraction Study of Crystalline Cholesteryl Myristate and Cholesteryl Stearate†

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Abstract—Powdered samples of the solid crystalline phase of cholesteryl myristate and stearate, crystallized at various temperatures from the melt and from solution, were studied by X-ray diffraction. The type and parameters of the unit cell were determined. The myristate and the stearate have monoclinic unit cells that are nearly identical except that the stearate has a larger *c* parameter. The structure has essentially no similarity to the corresponding structure in the mesophase. Temperature dependent measurements show that in a temperature range below the melting point imperfections are introduced. These imperfections are concentrated in directions perpendicular to the long axis of the molecules. This result is discussed in terms of the structure of the mesophase.

1. Introduction

X-ray diffraction studies on the solid crystalline phase of compounds which are able to form mesophases are relatively few in number. Bernal and Crowfoot⁽¹⁾ derived the crystal structure at room temperature of several substances which give liquid crystals on heating. They observed imbricated molecular arrangements in the solid crystalline states of typical nematogenic compounds. The inference was strong that such a parallel arrangement of molecules in a less perfect way would occur in the nematic phase itself. Herrmann^(2,3) observed tilted layer structures in the solid crystalline phases of substances which form tilted layer structures in the smectic phase.

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Thus it was inferred that the crystal structure can often give information about the possible arrangement of the molecules in the mesophases. Further examples are given in review articles.^(4,5,6)

One purpose of the work reported here was to find out how close is the relation between the molecular arrangement in the mesophases and in the solid phase. If there is a close relation we might be able to get information about the forces that cause mesophases to form. In a future paper, we will report our results on the structures of the mesophases of those compounds, the solid states of which we study now.⁽⁷⁾ These substances are cholesteryl esters of saturated fatty acids of different chain lengths. This paper is concerned with cholesteryl myristate and stearate.

A second purpose of this paper is to check the idea that, possibly, the solid crystalline phase undergoes slight changes at elevated temperatures slightly below the melting point and that these changes occur in a direction towards the structure of the mesophases. We might expect these changes both near a transition to a mesophase, and near a transition to an isotropic state in cases where on cooling a monotropic mesophase is formed. This idea is based on two observations. Firstly, Bulkin *et al.*⁽⁸⁾ observed, that in the solid state of several compounds which form a nematic phase on heating, several IR bands disappear gradually as the transition to the mesophase is approached. These authors were led to the conclusion that this was due to the actual movement of molecules from lattice sites to interstitial sites (lattice defect model). The authors, however, could not detect these effects for solid-smectic transitions. Secondly, our studies involving dilatometric measurements of the solid-liquid transitions of cholesteryl esters^(9,10,11) showed melting ranges which could not be explained totally on the basis of impurity effects. We considered the influence of the lattice defects on the melting properties. The present study could yield more information about the intimate nature of these transitions.

Finally, the third purpose of this paper is the collection of X-ray diffraction data of both the reflections and their intensities of various crystalline cholesteryl esters. These data then will allow us to define the different phases which can be observed at different temperatures in mixtures of these esters. Often optical observations, viscometric studies and DSC measurements are not specific enough to identify

the nature of the phases. The X-ray diffraction technique is a very sensitive tool for this purpose.

2. Experimental

SAMPLE PREPARATION

The samples were obtained from Eastman Kodak Co., Rochester, N.Y. They were purified by recrystallizing three times from *n*-pentanol and washed and dried as described in a previous publication.⁽⁹⁾ Some samples were not molten during the drying process. We shall refer to these samples as "solution crystallized".

X-RAY DIFFRACTION STUDIES

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 K α 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 obtained using powdered quartz and were treated by conventional methods. 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 $\pm \frac{1}{4}^{\circ}\text{C}$ 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 photographs, obtained by the forward scattering pinhole

technique, were used to make sure that the orientation of the crystals in the sample was random and that the number of scattering crystals was large enough to give continuous scattering rings.

As in this technique all information is taken from the equatorial plane, limitations are imposed on the interpretation. This is due to the possibility of superposition of different reflections and a lack of resolution between other reflections. If one of the spacings is very much longer than the others as is the case in our experiments, many reflections may be superimposed. Furthermore, we study powder samples of organic materials. Thus, we encounter broad lines due to lattice defects and small crystal sizes as well as strongly decreasing intensities with increasing angle, 2θ . These effects reduce the accuracy of the data. We nevertheless used the powdered samples for our studies because these seemed to be the optimal compromise among the three different purposes of our work, cited in the introduction.

3. Results and Discussion

The cholesteryl myristate crystallized from the melt shows only a small number of resolvable reflections. These are relatively broad and most occur in groups. The intensities both within groups and the average group intensities from group to group decrease strongly with increasing diffraction angle. The diffraction patterns are independent of the temperature of crystallization. The half widths (0.4° – 0.5°) of resolvable reflection were independent of the order of the reflection.

The solution crystallized myristate compared to the melt crystallized substance shows much smaller intensity of the reflection at low angles but larger intensities at larger angles. Further the intensity within a group of reflections decreases more strongly with increasing angle than it does with the melt crystallized material.

The results of the diffraction studies at room temperature for the myristate are displayed in Table 1. Here are shown the " d " spacings calculated from Braggs Law and the indices for these spacings calculated for values, respectively, of a , b , c and β of the monoclinic unit cell of 10.26, 7.6, 101.4 Å and $94^\circ 23'$ for the solution grown crystals and 10.07, 7.48, 97.07 Å and $94^\circ 23'$ for the melt crystallized samples.

TABLE 1 Calculated and Observed Spacings (in Å) for Cholesteryl Myristate

Spacing	Melt Crystallized			Solution Crystallized		
	d_{calc}	d_{obs}	Error	d_{calc}	d_{obs}	Error
002	48.39	48.5	1.3	50.55	—	—
004	24.19	24.15	0.35	25.28	25.23	0.35
006	16.13	16.14	0.15	16.85	16.80	0.16
008	12.10	12.14	0.09	12.64	—	—
102	10.81	10.85	0.04	—	—	—
100	10.04	10.02	0.05	10.23	10.20	0.05
104	9.03	9.06	0.05	9.24	9.18	0.09
106	8.24	8.10	0.04	8.46	—	—
010	7.48	7.46	0.04	7.60	7.58	0.04
012	7.39	7.38	0.04	7.52	7.50	0.04
014	7.14	7.12	0.03	5.58	5.57	0.02
016	6.79	6.80	0.03	—	—	—
110	5.99	5.98	0.02	6.10	6.09	0.02
114	5.76	5.75	0.02	5.87	5.88	0.02
116	5.54	5.47	0.02	5.65	5.57	0.02
118	5.28	5.18	0.02	—	—	—
200	5.02	5.02	0.02	5.12	5.10	0.02
205	4.78	4.77	0.01	4.87	4.88	0.02
208	4.20	4.55	0.01	4.62	4.62	0.02
210	4.16	4.16	0.01	4.24	4.22	0.02
214	4.06	4.05	0.01	4.14	4.10	0.02
218	3.88	3.88	0.01	3.94	—	—
120	3.50	3.50	0.01	3.55	3.55	0.02
220	2.99	2.99	0.01	—	—	—
020	3.74	3.74	—	3.80	3.81	0.02
022	3.73	—	—	3.78	—	—
024	3.69	not	—	3.74	not	—
resolved				resolved		

The unit cell parameters for the solution grown crystals are those assigned by Professor B. M. Cravens and Mr. G. T. DeTitta of the University of Pittsburgh who currently are undertaking a structure determination of this substance using single crystal methods. They have found that there are eight molecules per unit cell (two in the asymmetric unit), that the space group is A2 and that the absent spectra (hkl) have $k+l$ odd. We wish to express our thanks to Professor Cravens and Mr. DeTitta for use of their results in this

premature manner.† The values of the unit cell parameters for the melt crystallized material were obtained by fixing b and β at 7.48 \AA and $94^\circ 23'$, respectively, and optimizing the fit of calculated to observed d values by varying a and c . The errors listed in Table 1 are those arising from a 0.05° uncertainty in the position of the line maximum.

The diffraction patterns of the melt crystallized cholesteryl stearate were very similar to those of the myristate. Samples of stearate which were crystallized from the melt below 25°C showed, when examined at room temperature, a slight increase in the c spacings and slightly smaller a and b spacings. Samples crystallized above 25°C and examined at room temperature showed slightly larger a and b spacings and smaller c spacings. The differences are all small and we confine ourselves to merely reporting the trend.

When crystallized from solution the cholesteryl stearate shows no 00 l reflections. There are, however, groups of reflections indicating, as in the myristate, a large c spacing. It seems probable that these absences represent merely an exaggeration of the effect found in going from melt to solution crystallized myristate. In the solution crystallized stearate the line width (0.5°) is independent of the order of the reflection.

Following the lead established for the myristate by utilizing Cravens' results, we find unit cell parameters for the solution grown cholesteryl stearate of 10.23 , 7.6 , 110.0 \AA and $94^\circ 23'$ for a , b , c and β , respectively. There are eight molecules per unit cell. The fit of observed and calculated d values is shown in Table 2.‡

† In powder X-ray diffraction studies such as ours the number of data points are few (25 for the melt crystallized and 17 for the solution crystallized sample). Prior to becoming aware of the University of Pittsburgh work which produced some 5200 reflections, we had assigned unit cell parameters of a , b , c and β of 11.30 , 7.60 , 55.5 \AA , 116° , respectively, for the solution grown crystals and 11.11 , 7.48 , 54.0 \AA and 116° for the melt crystallized cholesteryl myristate. We determined four molecules per unit cell (half that of Cravens and DeTitta) and a space group of P2. In view of the overwhelming amount of their data, we do not feel justified in advocating too strongly these unit cell parameters.

‡ Here again before we became aware of the work of Cravens and DeTitta, we had calculated unit cell parameters for both the melt and solution grown cholesteryl stearate. They were 11.20 , 7.48 , 64.3 \AA , 116° and 11.35 , 7.6 , 62.8 \AA , 116° for a , b , c and β for the melt and solution grown crystals, respectively. We calculated four molecules per unit cell.

TABLE 2 Calculated and Observed Spacings (in Å) for Solution Crystallized Cholesteryl Stearate

Spacing	d_{calc}	d_{obs}	Error
002	54.84	—	—
004	27.42	—	—
006	18.28	—	—
100	10.20	10.20	0.05
104	9.33	9.36	0.05
106	8.63	—	—
108	7.67	—	—
200	5.10	5.10	0.02
204	4.95	4.88	0.02
208	4.67	4.68	0.02
010	7.60	7.60	0.04
012	7.53	7.53	0.04
014	7.32	7.34	0.04
020	3.80	3.80	0.02
022	3.79	unresolved	—
024	3.79		—
110	6.09	6.09	0.03
114	5.89	5.88	0.03
117	5.66	5.63	0.03
118	5.40	5.40	0.02
210	4.23	4.22	0.02
215	4.11	4.12	0.02
120	3.56	3.55	0.02

We have thus far been concerned with the unit cell dimensions and the number of molecules per unit cell and not with the specific arrangement of the molecules within the unit cell. Were our data sufficiently precise and numerous, it would be possible to calculate from it, corrected intensities or ideally the square of the scattering factors for the various reflections. Such calculations corrected for (a) incident intensity, (b) polarization of reflection, (c) Lorentz factor, (d) multiplicity of the reflection, (e) adsorption of scattered radiation by sample and (f) effect of temperature (Debye-Waller factor) allow inferences to be drawn about the distribution of matter within the unit cell. However, in our case the accuracy of the data is not very good and the data is sparse. Further, the presence of disorder of various kinds, local and long range, as well as crystal size complicates the picture. Thus while we measured the integrated intensities of the reflections of the melt and solution crystallized myristate and

stearate, and corrected these for everything except a , d , and f of the preceding expression, in view of the impending disclosure by Professor Cravens of much more numerous and precise results on the myristate, we do not deem it worthwhile to present our intensity calculation here. However, in the interest of recording X-ray powder data for possible identification studies, we present in Table 3 the observed

TABLE 3 Observed Intensities of Reflections from
Cholesteryl Myristate

Reflections	Melt Crystallized I_{obs}	Solution Crystallized I_{obs}
002	74	—
004	1000	250
006	238	45
102	15	—
100	74	135
104	82	103
010	126	330
012	93	227
014	37	—
016	22	—
110	520	1000
114	445	885
116	250	140
118	80	—
200	185	284
205	178	340
208	245	193
210	304	660
214	325	730
218	111	158
020	185	523
021	140	386
120	30	68

integrated intensities (maximum assumed to be 1000) for the melt and solution crystallized myristate. About all that can be said is that, most probably, the long axes of the cholesteryl ester molecules are parallel to the c axis of the unit cell. Further, as is shown by Fig. 1, the shape of these molecules when the ester part is extended is more like a war club than the frying pan usually depicted in structural formulae. The cholesterol part is the thick part and the ester moiety

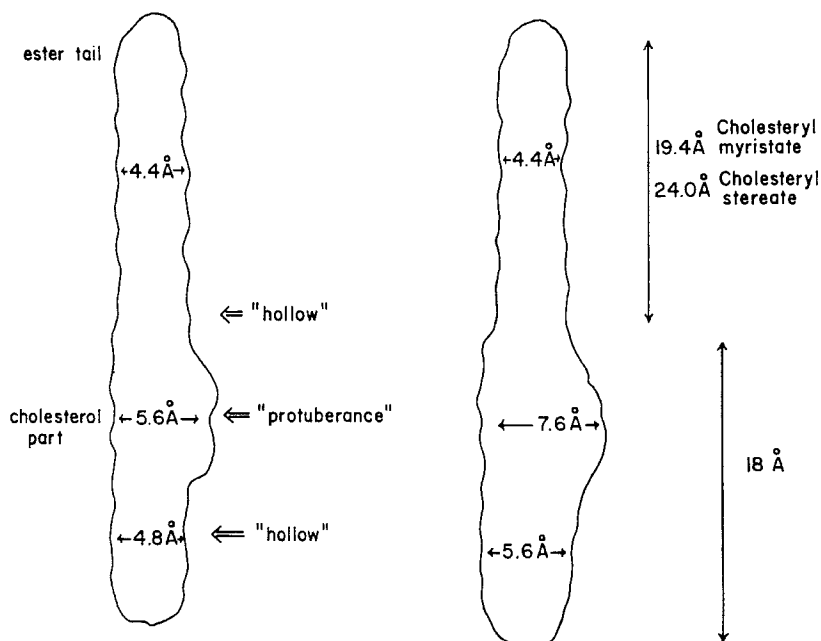


Figure 1. Approximate shapes and dimensions of cholesteryl myristate and cholesteryl stearate based on examination of space filling models.

the thin. We have evidence that the ester part is fully extended in both the mesophases and in the isotropic phase slightly above the transition temperature into that phase. It thus seems not improbable that the ester tail is fully extended in the crystal also. If these considerations are valid, it seems most probable that half the cholesteryl ester molecules are arranged in the unit cell with their ester tails pointing up and half with their tails pointing down. The arrangement is thus an interdigitated antiparallel array.

Diffraction patterns were obtained on all specimens between room temperature and 70° for the myristate and room temperature and 80° for the stearate. An increase of the observation temperature results in an increase of the lattice parameters. For instance, in the case of cholesteryl myristate, crystallized from the melt, between 25° and 65° the c parameter increases by about 1%. However, the inaccuracy of our data precludes calculation of sufficiently accurate expansion coefficients for the three directions to determine whether these values increase strongly near the melting point.

A more noticeable effect of the temperature occurs in a region below the melting point where the intensities of the reflections change strongly. The intensities of some reflections increase with increasing temperature, others decrease and some are not changed at all. Just below the melting point the intensity of all reflections drops. This behavior is shown in Fig. 2 for the 004, 114 and 220 reflections

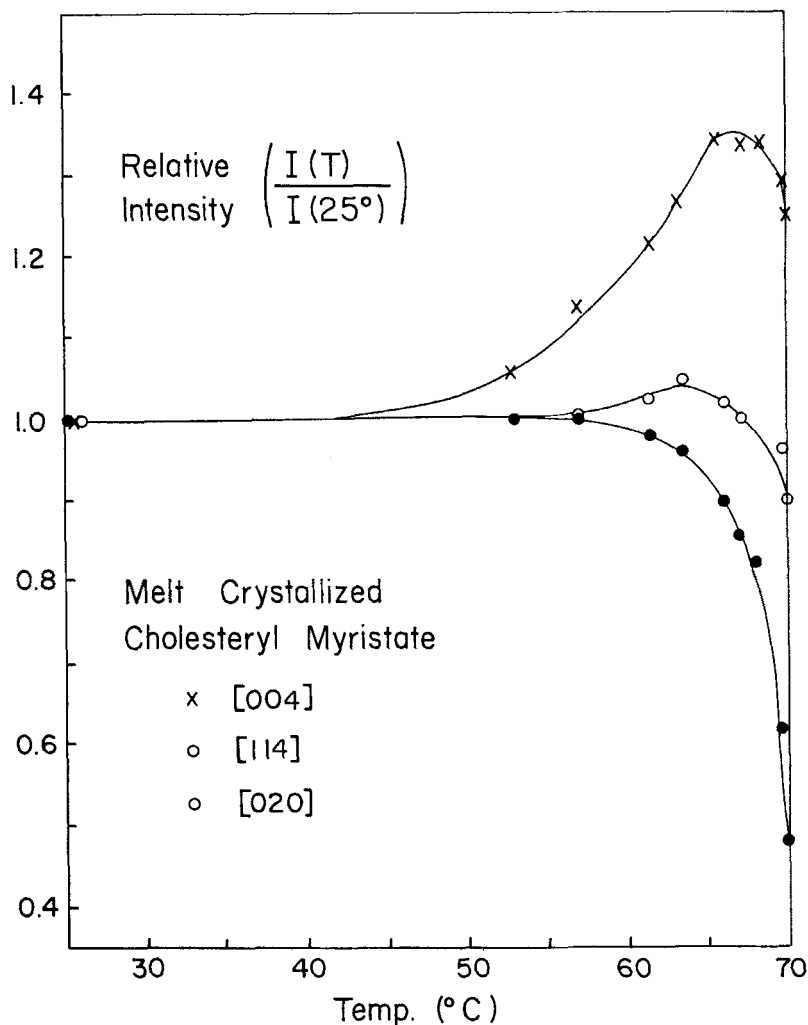


Figure 2. Plots of the temperature dependence of normalized intensities of three diffraction lines in cholesteryl myristate.

of the melt crystallized myristate. This behavior is typical and is shown by all the other myristate samples and to a lesser degree by the stearate samples. Over the temperature range studied the half width does not depend on the temperature within the sensitivity of our measurements. This is true for all samples and for all reflections. Just below the melting point we observed a strong increase of the intensity for the 002 reflections of melt crystallized cholesteryl myristate, and a smaller increase for the same reflections for cholesteryl stearate crystallized from the melt at room temperature. In this temperature range in all samples the intensities of the 00 l reflections go through a maximum while intensities of the 0 k 0 and h 00 reflections decrease. The latter effect is most noticeable for the 0 k 0 reflections. The intensities of reflections with mixed indices behave in a way which lies between the extremes. The temperature ranges over which this occurs are 10 °C for cholesteryl myristate, 10 °C for cholesteryl stearate if crystallized at room temperature and 5 °C if crystallized at 60 °C.

We now consider the basis for the changes of intensities in the premelting temperature range. In this range the reflections maintain a constant half width. This could mean that the samples are partially melting. If this is so, then we should observe diffraction patterns characteristic of smectic cholesteryl myristate or isotropic cholesteryl stearate being superimposed upon the solid crystalline patterns and becoming increasingly prominent as the transition point is approached. We have measured the diffraction patterns of the smectic myristate and the isotropic stearate. These patterns were not observed in the premelting regions until temperatures within 0.8 °C of the melting point were attained. We therefore conclude that partial melting is not the cause of the phenomenon.

Another possibility is that the changing intensities are due to increasing amplitudes of thermal vibrations. However, such an effect can explain only the monotonically decreasing intensities of the 0 k 0 and h 00 reflections and not the maxima in the 00 l reflection. Assuming the decrease in intensity is describable by an anisotropic Debye-Waller factor and that it is due only to rigid body translational vibrations, we calculate for cholesteryl myristate just below the melting minimum amplitudes of 0.13 Å and 1.8 Å for vibrations along the a and b axes, respectively. This calculation is made

assuming zero amplitudes of vibration at room temperature, so the actual amplitudes just below the melting point could be considerably greater.

As noted above, the maxima in the $00l$ reflections cannot be explained on this basis. It might be due to an increasing multiplicity of the d spacings which have been incorrectly assigned due to imprecise data. In the interests of presenting a consistent explanation, we are inclined to reject this and to ascribe the rising part of the maxima to increased magnitudes of periodic density variations along the c direction. That is, the order along the c direction tends to increase. This increase in order is coupled with the decreasing order perpendicular to this direction. As the temperature continues to rise the intensity weakening Debye-Waller effect discussed above eventually dominates and the intensity of the $00l$ reflections drops.

The intensity temperature dependence of reflections with mixed indices hkl is caused by superposition of both the above effects. The result is more or less temperature insensitive intensities.

5. Conclusions

For both substances studied the unit cell contains eight molecules and is almost orthogonal ($\beta = 94^\circ 23'$). Probably the molecules are arranged in the unit cell in some sort of antiparallel fashion of as yet undetermined kind and type. From these results it seems not possible to infer the structure of the mesophase from knowledge of the structure of its parent crystalline solid.

In a temperature range, whose size depends on the particular ester, slightly below the melting point the order in directions normal to the long axes of the molecules (the c axes) decreases markedly. The smectic and cholesteric states of these esters show long range order in directions of the c axes but essentially complete disorder normal to the c axes. Thus the pretransition disordering in the directions normal to the c axes is an anticipation of the transition to the mesomorphic state and as such is a second order process. On the other hand, the order in the direction of the c axis seems to be preserved and the rearrangement that takes place at the transition temperature is a first order process. The pretransition melting range is a superposition of first and second order processes. Very probably this is

the basis for the failure of the pretransition observed in our dilatometric work^(9,10,11) to conform to van't Hoff's Law.

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