Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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Version of record first published: 21 Mar 2007.

To cite this article: Joachim H. Wendorff & Fraser P. Price (1974): X-Ray Diffraction Studies of the Solid Phases of Cholesteryl Acetate, Molecular Crystals and Liquid Crystals, 25:1-2, 71-82

To link to this article: http://dx.doi.org/10.1080/15421407408083406

Mol. Cryst. Liq. Cryst., 1974, Vol. 25, pp. 71-82
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Printed in Dordrecht, Holland

X-Ray Diffraction Studies of the Solid Phases of Cholesteryl Acetate[†]

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(Received January 16, 1973; in revised form September 16, 1973)

The solid phases of cholesteryl acetate were studied by x-ray diffraction techniques. The data were analyzed in terms of the angular position of the reflections, their intensity, and their integral width. The unit cell is monoclinic with the parameters a, b, c, and β respectively equal to 10.00 A, 7.36 A, 37.2 A and 95°. The space group is either c2 or cm. The dimensions of the unit cell are the same for all three solid phases. Temperature dependent measurements show that the broad melting range of the transition into the isotropic phase is not a true melting range. Increasing lack of short range order occurring along the direction of the long axis of the molecule causes an increase of the expansion coefficient in that range.

INTRODUCTION

The saturated aliphatic esters of cholesterol are a class of compounds which exhibit mesophase behavior. That is, they can exist in a number of stable states whose order is intermediate between that of a crystalline solid and that of the isotropic liquid[1]. Studies of mesophase structure by means of x-ray diffraction are few in number[2-11]. Further, with a few notable recent exceptions[13,16] they have been concerned with determination of position, rather than shape and intensity of the diffraction lines. The same situation prevails with respect to structure determination of the crystalline solids which form mesophases upon heat-

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[†] This work was supported by Grant No. 13188 from the National Institutes of Health.

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ing[17-19]. The present paper is concerned with x-ray diffraction studies on the solid cholesteryl acetate. This ester exhibits no detectable smectic mesophase and its cholesteric mesophase is monotropic with a transition temperature of 94°C. The solid-isotropic transition occurs at 112°C. It has been shown that the ester has several solid crystalline states[20,21] depending on the mode of crystallization, the temperature of crystallization, and the temperature of the sample.

We have designated these solids as SI, SII and SIII. The SI solid is the one which melts at 112°C. It is formed directly from the liquid in the range 94-107°C. The SII solid is formed from the cholesteric phase below 94°C, transforms reversibly to SIII at 41°C and irreversibly to SI above 94°C.

The purpose of this work is first to investigate the structures of the different solid phases and, if possible, the reasons for differences among them. Second, it is also intended to get information about the transition from the solid to the isotropic state. Dilatometric studies[20] have shown the occurrence of a broad melting range, inexplicable solely on the basis of impurities present. Imperfections were suggested as a reason for this behavior. This study will permit a check on this idea. Third, the studies were made to collect data which will permit characterization of mixtures of cholesteryl esters in their various crystalline phases.

EXPERIMENTAL

The cholesteryl acetate was obtained from Eastman Kodak Company, Rochester, New York. The samples were recrystallized three times from n-pentanol and washed and and dried as described previously[20]. The sample was then subjected to different treatments in order to get the different solid phases.

These treatments, the basis for which had been previously established[20], are stated in Table I. The designation, solution crystallized, implies that the solvent was removed below the melting point of the solid, 112°. The melt-crystallized

TABLE I

Conditions for preparation of the various solid states of cholesteryl acetate

State	Melt crystallization range (°C)	Comments
SI	94°–107°	Reversible behavior up to 114°
SII	40°– 94°	Transforms reversibly to SIII around 40° and irreversibly to SI above 94°
SIII	below 40°	Transforms reversibly to SII around 40°
Soln. Cryst.	No treatment	

specimens were obtained by melting the solution-crystallized samples to 120° and then treating as indicated in Table I.

The apparatus employed and the experimental methods used have been described previously[19]. In the present case of the cholesteryl acetate, as in the cases of the myristate and the stearate, the absence of large crystals or of oriented crystals was checked by photographic techniques. In all the work reported here there was never any evidence of orientation.

RESULTS AND DISCUSSION

The diffraction patterns of all the samples are characterized by only a small number of detectable reflections that usually occur in groups and are relatively broad. This situation results in the overlapping of reflections, which in turn decreases the accuracy of the derived information. The intensity of the reflections decreases strongly with increasing angle 2Θ. Surprisingly, the **d** spacings were identical for all three solids (SI, SII, and SIII) and only somewhat different for the solution-crystallized sample. They are displayed in the last column in Tables II and III. The error of ± 0.05° in the line position introduces an error of ± 0.02 A in all the observed **d** spacings except the (001), (002) and (003) reflections for which the errors are 0.8, 0.3 and 0.1 A, respectively. From the calculated **d** spacings of all three solids (SI, SII, and SIII), the unit cells are monoclinic and identical. The parameters, measured at room temperature for the SI and SIII samples and between 40° and 50° for SII, are 10.00 ± 0.04 A, 7.36 ± 0.03 A, 37.2 ± 0.3 A and 95° ± 1° for a, b, c and β respectively. The errors in the unit cell parameters are sufficiently great so that the density change in the SIII–SII transition (0.8%) would not be detected[20] by the present x-ray diffraction method. For the solution crystallized matrial measured at room, temperature, the parameters are 10.15 ± 0.04 A, 7.48 ± 0.03 A, 38.0 ± 0.3 A and 95° ± 1°. The errors in all these figures are those derivable from an error in diffraction line position of 0.05°. These unit cell parameters, combined with the previously-determined density, indicate that there are four molecules per unit cell. The calculated and observed **d** spacings for the melt- and solution-crystallized samples are displayed in Tables II and III, respectively. The fit is satisfactory.

It should be noted that the values of a, b and β given above are close to those previously calculated for crystalline cholesteryl myristate and stearate. However, the c dimension is slightly less than twice the long dimension of the cholesteryl acetate molecule, as indicated in Figure 1, and not the significantly higher multiple of the molecular length as was found in the cases of cholesteryl myristate and stearate.

The unit cell for the solution-crystallized specimen is very similar to that of the melt-crystallized specimens. The observation that it is somewhat different is

TABLE II

Calculated and observed d spacings in solid I of cholesteryl acetate

Reflection	d calc(A)	d obs(A)
001	36.85	37.10
002	18.43	18.70
003	12.28	12.38
100	9.96	–
101	9.41	
102	8.46	
103	7.43	
010	7.34	–
011	7.20	
012	6.81	
013	6.31	
110	5.91	5.91
111	5.79	5.80
112	5.54	5.53
113	5.22	5.23
200	4.98	4.98
201	4.88	4.87
202	4.71	4.72
203	4.48	4.49
210	4.12	–
211	4.06	
212	3.96	
213	3.82	
020	3.67	3.67
021	3.65	3.64
022	3.60	3.59
023	3.52	–
120	3.44	–
121	3.42	
122	3.37	
123	3.29	
220	2.95	(2.95)
221	2.93	2.92
222	2.89	2.89
223	2.84	–
300	3.32	–
301	3.28	
302	3.21	
303	3.14	
310	3.02	3.02
311	2.99	2.98
312	2.95	(2.95)
313	2.88	

TABLE III

Calculated and observed d spacings of solution-crystallized cholesteryl acetate

Reflections	d calc(A)	d obs(A)
001	37.85	38.2
002	18.92	19.0
003	12.62	12.62
10ℓ	10.10 9.56	–
01ℓ	7.48 7.34	–
110	6.01	6.00
111	5.89	5.86
112	5.65	5.62
113	5.32	5.33
200	5.05	5.05
201	4.95	4.93
202	4.78	4.78
203	4.55	4.55
21ℓ	4.18 4.13	–
020	3.74	3.74
021	3.72	3.70
022	3.67	3.66
12ℓ	3.50 3.48	–
220	3.00	(3.00)
221	2.98	2.91
222	2.95	2.95
30ℓ	3.37 3.33	–
310	3.07	3.07
311	3.04	3.05
312	2.99	(3.00)
03ℓ	2.49 2.48	–

not without precedent. Different unit cells have been reported[22] for cholesteryl acetate crystallized from alcohol, from acetone below 58° or from petroleum ether above 58°. Values of a, b, c and β respectively have been reported of 17.65 A, 9.53 A, 16.54 A and 106.4° for the alcohol- or acetone-crystallized samples and 17.68 A, 9.23 A, 16.48 A and 91.74° for crystallization from petroleum ether. It is clear that the conditions under which the crystals were formed play an important role. In our case the solution- and melt-crystallized samples have nearly identical unit cells. This may result from the fact that in our case the designa-

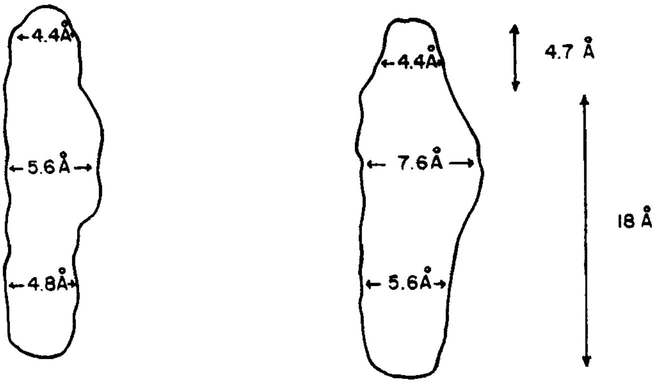

FIGURE 1 Axes and approximate shape and dimensions of the cholesteryl acetate molecule.

tion, solution crystallized, merely denotes that the sample was below its melting point (112°) during removal of solvent. Thus, the solution must have been quite concentrated during the drying and the crystallization conditions here must be very similar to those prevailing during crystallization from the pure melt. Although the unit cells of all the specimens are essentially identical, there are very marked variations in the intensity distributions and in the integral widths of the diffraction patterns of the various samples. These variations are probably the result of various kinds of order. This will be discussed below.

The data produced by the technique employed here are sufficient to determine unit cell dimensions and the number of molecules per unit cell and are useful for identification purposes. However, they are not sufficiently accurate or numerous to allow precise inferences to be drawn about the distribution of matter within the unit cell. Also, the situation is further complicated by diminished local and long-range order and by possible small crystallite size. Because of these qualifications, we can only draw qualitative conclusions concerning the structure of the solid state. We are mainly interested in the orientation of the molecules with respect to the axes of the unit cell and not in the accurate location of the molecules. This is so because we need only this information for the discussion of the melting behavior of the cholesteryl acetate.

Displayed in Table IV are the corrected integrated intensities for the various diffraction lines. These intensities are corrected for (a) polarization of reflection, (b) the Lorentz factor, and (c) absorption of scattered radiation and not for (i) effect of temperature (Debye-Waller factor), (ii) multiplicity of reflection, and (iii) incident intensity. These intensities are presented primarily for identification purposes and secondarily to allow us to draw some semiquantitative conclusions about the distribution of matter within the unit cell.

The diffraction patterns of the different samples have some similar features, as

TABLE IV

Corrected intensities for diffraction patterns of various states of cholesteryl acetate

Reflections	Solid I	Solid II	Solid III	Solution crystallized
001	159	190	183	74
002	120	140	133	64
003	25	21	29	12
10ℓ	0	0	0	0
01ℓ	0	0	0	0
110	870	700	630	1070
111	90	190	80	109
112	390	286	244	422
113	56	146	68	56
200	1100	915	780	1690
201	350	480	322	320
202	1260	1000	910	1660
203	160	318	190	159
21ℓ	0	0	0	0
020	490	443	990	835
021	25	53	25	75
022	53	69	53	132
12ℓ	0	0	0	0
220	85	86	85	87
221	53	58	53	158
222	58	61	58	60
30ℓ	0	0	0	0
310	764	218	216	538
311	78	79	125	230
312	159	122	160	280

can be seen from Table IV. The (h,k,ℓ) reflections are absent if $h + k = 2n + 1$. This means that the unit cell is not primitive but is *c*-centered. Thus, the space group is either C_2, C_m, C_{2m}, C_c or C_{2c}. As there are no systematic absences which are indicative of glide planes or screw axes, the space group is either C_2, C_m or C_{2m}. The space group C_{2m} can be eliminated because it requires at least 8 molecules per unit cell while C_2 or C_m only require four molecules per unit cell for molecules possessing no symmetry element[23]. We have no further evidence to discriminate between the space groups C_2 and C_m. Another feature of the diffraction pattern is the systematic weakness of several reflections. Here generally the condition for systematic weakness is that $h + \ell = 2n + 1$ and $k + \ell = 2n + 1$. Together with the missing reflections for which $h + k = 2n + 1$, this is indicative of the near summetry situation of a face-centered structure. A monoclinic unit cell can not be face centered. Possibly the near symmetry situation is based on the small difference between the present monoclinic unit cell with an angle β of 95° and the corresponding orthorhombic unit cell with an angle β of 90°, which can be face centered.

As noted above, the sparseness and imprecision of the data make it unprofitable to speculate in depth about the arrangement of the molecules within the unit cell. However, the fact that there are four molecules per unit cell and that the *c* dimension corresponds to nearly twice the long molecular axis makes it seem very probable that here, as in the cases of cholosteryl myristate and stearate, the long molecular axis is nearly parallel to the *c* axis. Also, since interactions between the carbonyl of esters on neighboring molecules would be expected to be strong ones, and since the *c* dimension is slightly less than twice the long molecular axis, it seems most probable that in the unit cell half the molecules have their ester moieties pointing up and half pointing down. Thus, here, as in the case of crystalline cholesteryl myristate and stearate, there probably exists an antiparallel interdigitated array. It is noteworthy that antiparallel arrays of molecules in thermotropic mesophases have been postulated from a number of different studies.

With all phases, an increase of the temperature results in a small increase of

TABLE V

Effect of tenperature on intensity of selected diffraction lines in solid cholesteryl acetate (Intensity scales arbitrary)

Temp (°C)	Phase	I_{110}(s)	I_{112}(s)	I_{220}(s)	I_{202}(s)	I_{001}(w)	I_{002}(w)
24.0	III	79	33	41	40	54	74
32.0		79	33	42	40	54	74
40.0	II/III	80	33	43	40	56	80
48.0		80	33	44	40	57	81
50.5	II	82	33	44	40	58	82
60.8		83	33	44	41	61	83
71.6		83	34	44	42	65	85
80.0		84	36	44	44	68	92
86.5		85	37	44	45	67	92
88.0	II/I	89	39	45	46	67	88
92.0		95	44	46	48	58	80
94.0		101	50	51	52	51	70
24.0		95	42	48	49	49	64
55.0		96	42	48	51	49	65
70.0		98	43	48	51	50	66
80.0		100	45	48	51	50	69
87.0	I	102	46	48	51	50	71
93.0		104	49	50	51	51	73
96.0		109	50	52	53	50	69
100.0		111	54	53	54	41	61
103.0		111	53	54	54	44	58
107.5		111	53	54	53	41	56
110.0		103	50	51	49	38	54

the dimensions of the unit cell. However, due to the imprecision of these data resulting from the experimental technique, we can not calculate expansion coefficients with satisfactory precision. A more noticeable effect of the increase of the temperature and of the change of the phase is a change of the relative intensities of the different reflections. This dependence is shown in Table V and in Figure 2. Here the intensities noted are the heights of the diffraction peaks on a relative scale. The validity of this procedure rests on the observation that the shapes of the peaks were essentially independent of temperature as exemplified by the constant integral widths of 0.51 ± 0.01 and 0.46 ± 0.01 of the 110 and the 002 peaks, respectively. The intensity of the peaks is designated by (s) or (w), respectively, for strong or weak inserted alongside the $I_{hk\ell}$. In Table V intensities of different reflections for different lines are not comparable, only the effect of temperature on intensity of the lines should be noted. In going from SIII to SII, the strong reflections increase slightly in intensity and remain constant in integral width, while the

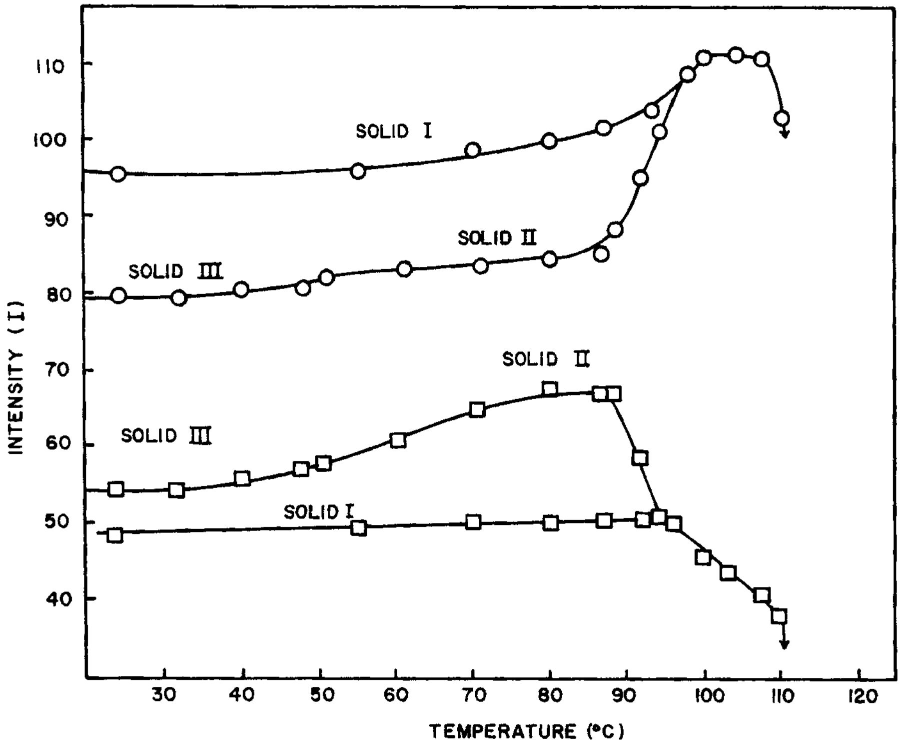

FIGURE 2 Plot of intensity versus temperature for selected diffraction lines of crystalline cholesteryl acetate. O = I_{110}; □ = I_{001}.

systematic weak reflections increase moderately in intensity and integral width. Possibly this behavior is due to a small decrease of the order in the *c* axis direction. Further increase of the temperature results in a further intensity increase of the 001 reflections until their intensity sharply drops at the transition to Solid I. The transition to Solid I also results in a strong decrease of the intensity of the systematic weak reflections and an intensity increase of other reflections. This trend could already be observed within Solid II as the temperature increased. Apparently while the order along the *c* axis direction decreased, order perpendicular to this direction increased and the distribution of the molecules within the samples has become more "symmetrical". The constant integral width of the reflections, regardless of state, shows that the order is long range with the widths being attributable to local perturbations of this order. These could be thermal motions or frozen-in displacements. We believe that both of these perturbations of order are present. The peculiar shape of the molecules favors frozen-in translational shifts. The increased temperature favors thermal vibrations. In a temperature range of about 20°C just below the melting point, the intensity of the 00ℓ reflections decreases very strongly with increasing temperature, whereas the other reflections increased their intensity with increasing temperature up to about 108°C (4°C below the melting point). This 20° range is the range over which we observed a 'melting' in dilatometric studies[20]. From the X-ray results we now conclude that this range is not a true melting range. Melting should be accompanied by a decrease of the intensity of all reflections and by the appearance of a diffraction pattern of increasing intensity, characteristic of the isotropic state. We have examined the diffraction of the isotropic state and find no traces of it in the 20°C range below the melting-point. Thus, the change of the expansion coefficient in a broad temperature range below the melting point is due to decreasing order within the solid and not to a partial melting. Our studies on the solid state of cholesteryl myristate[19] led us to the same conclusion. There is, however, an important difference. In cholesteryl myristate imperfections introduced somewhat below the solid-smectic transition decreased the order in all directions perpendicular to the long axis of the molecule. The forces between molecules in these directions decreased, while the forces which restricted the ends of the molecules to be sensibly coplanar did not decrease or at least did not decrease at the same rate with increasing temperature. Consequently, the approximate coplanarity of the molecular ends characteristic of both the smectic and cholesteric states[2] is achieved and the transition resulted in a mesophase. In cholesteryl acetate, however, the situation is reversed; the order first breaks down in directions parallel to the long axes of the molecules. Thus, we might expect that the transition leads to either a nematic or, as is the case, to the isotropic state. Apparently the hydrocarbon ester chain has a significant influence in fixing the ends of the molecules at a certain position. This may explain why the smectic phase is observed only if the hydrocarbon ester chain has a minimum length. Only the less-ordered cholesteric phase is possible with smaller ester chain lengths.

It seems not improbable to ascribe the diminution of the 00ℓ reflection as the melting temperature is approched to thermal vibrations. If these vibrations are rigid body translational ones and the intensity decrease is described by an anisotropic Debye-Waller factor, a minimum amplitude of vibration of 3A is calculated at 107° (5° supercooling). This implies that the cholesteryl acetate molecules undergo vibrations of this magnitude along their long axes.

It is tempting to speculate further why the different solid phases occur and why they transform at the observed temperatures. Solids III and II must be formed by crystallization from the cholerestic phase because below 94°C, the cholesteric-solid transition is very fast. The crystals form and grow increasingly rapidly from the cholesteric state as the temperature is lowered below 94°. Solid I is formed by crystallizing from the isotropic melt. In this temperature range the crystals grow slowly. Solid II transforms into Solid I in the same temperature range in which the cholesteric state transforms into the isotropic state. In this range the solid state loses order in a direction parallel to the long axis while transforming from Solid II to Solid I in the same way as does the liquid crystal by going from the cholesteric state to the isotropic state. This suggests that similar forces are present in the solid and liquid crystal states and that some features of the structure of the liquid crystal state are incorporated into the solid state which originates from this liquid crystal state. It is conceivable that especially at fast transformation rates and with a high viscosity of the mother phase, specific imperfections of that phase are introduced into the solid state. We have no similar explanation for the transition SIII to SII. One speculation is that an as yet undetected monotropic smectic phase exists below 40°C.

CONCLUSIONS

The unit cells of the various solid phases of cholesteryl acetate do not differ much. The main differences among the various solid phases are the ocurrence of different degrees of order. Solid I has more imperfections in the c axis direction and less perpendicular to this direction than do the solid phases II and III. Within its unit cell the solid phase I has a near symmetry distribution of molecules. The symmetry decreases in the order: SI, SIII, SII. The melting range of about 20°C which was observed by dilatometric measurements is mainly caused by the decrease with temperature of the order along the *c* axis. Only within about 4°C of the melting point does actual melting occur.

The lack of order along the *c* axis is probably due to thermal vibrations of the molecules along this direction.

Acknowledgements

The authors wish to express their gratitude to Professor R. S. Stein and Professor R. S. Porter for much helpful discussion during the course of this study.

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