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The Structure of Cholesteryl Laurate at 198 K

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Abstract

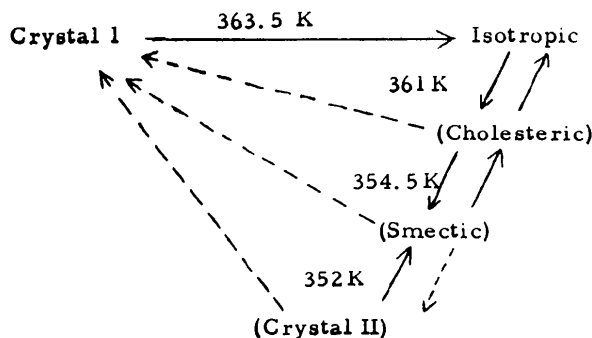
Cholesteryl laurate ($C_{39}H_{68}O_2$) at 198 K is monoclinic, space group $P2_1$ with $a = 12.983$ (3), $b = 8.838$ (1), $c = 31.803$ (4) Å, $\beta = 90.41$ (2)° and $Z = 4$. Integrated intensities for 3825 reflections with $I > 2\sigma(I)$ were measured at 198 K, using an automatic diffractometer and graphite-monochromated $Cu K\alpha$ radiation. Atomic coordinates for the 82 non-hydrogen atoms from the cholesteryl laurate room-temperature structure were used as a starting model. Refinement by block-diagonal least-squares methods gave a final R factor of 0.062. In contrast to the room-temperature structure, all atoms are clearly resolved and 127 of the 136 H atoms were experimentally located. The molecules are packed in an antiparallel array in the crystal structure forming monolayers of thickness $d_{(001)} = 31.8$ Å. The central regions of the monolayers are characterized by efficient molecular packing and are separated by interface regions which are more loosely packed. The major differences between the room-temperature and low-temperature structures occur in this interface region. At 298 K the laurate chain of molecule (B) has an almost extended conformation with possible disordering, but at 198 K the (B) chain is distally bent and is well ordered.

Introduction

A series of X-ray crystal structure determinations of cholesteryl esters has been undertaken. These structures are of interest as they may provide models for molecular associations in less ordered lipid systems. At room temperature, the crystal structures of cholesteryl nonanoate (Guerina & Craven, 1979), decanoate (Pattabhi & Craven, 1979), undecanoate (Sawzik & Craven, 1980), and laurate (Dahlén, 1979; Sawzik & Craven, 1979a) are isostructural and have been designated type I monolayers in order to distinguish them from other structure types in the cholesteryl ester series (Guerina & Craven, 1979). A notable feature of type I monolayer structures is the contrast between the molecular close packing within the layer, and the loose packing of the interface region between layers. In the cholesteryl laurate structure at 298 K, large apparent thermal vibrational averaging and possibly conformational disordering obscure atomic details in the interface region. The room-temperature study represents a desirable compromise in that the crystal structure is near a phase transition, yet the number of available X-ray intensity data is adequate for structure determination. We report here the low-temperature (198 K) crystal structure of cholesteryl laurate. This

provides more detail and accuracy for the structure prior to the onset of severe thermal averaging effects.

The crystalline and liquid-crystalline phases of cholesteryl laurate undergo phase transformations which have been summarized by Small (1970) as follows:



(---> indicates that transformation takes place on supercooling).

The cholesteric and smectic mesophases as well as a second crystalline form are monotropic with respect to the stable crystalline phase. That is, their transition temperatures are lower than the crystal melting point, but they do not appear when the crystal is heated to melting. Crystal form I is stable at room temperature and has the monolayer type I crystal structure reported in this paper. Form II crystallizes isothermally from the smectic phase (Sawzik & Craven, 1979*b*) as well as by supercooling. Powder patterns from form II indicate that it has a monolayer type II structure, similar to cholesteryl oleate (Craven & Guerina, 1979*a*) and cholesteryl octanoate (Craven & Guerina, 1979*b*) with $d_{(001)} = 16.5 \text{ \AA}$. Crystal polymorphism is common in the cholesteryl ester series. Thus, the phase diagrams for undecanoate and nonanoate esters are similar to that of the laurate.*

Experimental

Cholesteryl laurate obtained from Supelco Chemical Co., Bellefonte, PA, was crystallized by slow evaporation of an *n*-pentanol solution at room temperature. A plate-like crystal elongated along the crystal *b* axis melted at 363.2 K. X-ray data were collected at 198 K using a Nonius CAD-4 diffractometer equipped with an Enraf-Nonius Universal Low Temperature device

* Recently, we have grown crystals of the nonanoate from solution at room temperature which are different from those containing monolayers of type I (Guerina & Craven, 1979). This appears to be the crystal form reported by Barnard & Lydon (1974). The cell data are consistent with a structure containing monolayers of type II. The dimorphism of cholesteryl nonanoate appears to have escaped previous attention, although the phase equilibria for this ester have been extensively studied.

(liquid nitrogen as the coolant) and Cu $K\alpha$ graphite-monochromated radiation. A crystal with dimensions $0.5 \times 0.2 \times 0.4 \text{ mm}$ was mounted with the b^* axis 6° from the diffractometer φ axis and 1101 X-ray intensities were measured. During diffractometer maintenance, the crystal was lost and a second crystal with dimensions $0.6 \times 0.15 \times 0.3 \text{ mm}$ was mounted with the crystal b^* axis 10° from the diffractometer φ axis. X-ray intensities for 5475 reflections were measured for this crystal. A $\theta/2\theta$ scan was used in measuring intensity data for all reflections with $\sin \theta/\lambda < 0.56 \text{ \AA}^{-1}$. Unit-cell parameters were determined by a least-squares fit of $\sin^2 \theta$ values for 65 reflections with $19^\circ \leq \theta \leq 43^\circ$ that were measured at $\pm\theta$ (Table 1).

The two data sets were scaled using intensities of 100 reflections which were measured for both crystals. The variance in an integrated intensity was assumed to be $\sigma^2(I) = \sigma^2 + (0.02I)^2$ where σ^2 is the variance due to counting statistics. The final data set consisted of 5690 symmetry-independent reflections of which 3825 had $I > 2\sigma(I)$ and were used in structure refinement.

Atomic positional and thermal parameters from the room-temperature laurate structure (Sawzik & Craven, 1979*a*) were used as an initial model. A structure factor calculation with all 82 non-hydrogen atoms gave an *R* factor of 0.26. The structure refinement was carried out by a block-diagonal least-squares procedure in which the function minimized was $\sum w\Delta^2$, where $\Delta = |F_{\text{obs}}| - |F_{\text{calc}}|$, and $w = 1/\sigma^2(F_{\text{obs}})$. The X-ray scattering factors used were those of Cromer & Waber (1965) for C and O and Stewart, Davidson & Simpson (1965) for H.

After three cycles of refinement the *R* factor dropped to 0.12. At this point the C atoms at the ends of the C(17) tails and ester chains were omitted and relocated in a Fourier map. Two additional cycles of refinement gave an *R* of 0.10. Of the 136 H atoms, 127 were located near their expected positions in a difference Fourier synthesis. The remaining nine H atoms, bonded to C(27) and C(39) of molecule (A) and C(39) of molecule (B), were fixed at their expected positions which were calculated by assuming C-H bond distances of 1.0 Å and standard bond angles. Isotropic thermal parameters were also fixed for the H atoms with values equivalent to those of the C atoms to which each is bonded.

Table 1. Crystal data for cholesteryl laurate at 198 K

$\text{C}_{39}\text{H}_{68}\text{O}_2$, $M_r = 569.0$, m.p. 363.2 K
Space group $P2_1$
$a = 12.983(3)$, $b = 8.838(1)$, $c = 31.803(4) \text{ \AA}$
$\beta = 90.41(2)^\circ$
$Z = 4$ (two molecules/asymmetric unit)
$V = 3649(2) \text{ \AA}^3$
$D_c = 1.036 \text{ Mg m}^{-3}$ (198 K); $D_m = 1.007 \text{ Mg m}^{-3}$ (298 K)
$\lambda(\text{Cu } K\alpha) = 1.5418 \text{ \AA}$

Table 2. Fractional atomic coordinates ($\times 10^4$, $\times 10^3$ for H) and isotropic thermal parameters (equivalent values for heavy atoms)

Estimated standard deviations are in parentheses. Fixed-parameter values are shown with 0 for the e.s.d. $B_{eq.} = \frac{1}{3} \sum_{i=1}^3 B_{i,r}$. The $B_{iso.}$ values for H atoms are given according to the expression $\exp(-T) = \exp(-B \sin^2 \theta / \lambda^2)$.

Molecule (A)				$B_{eq.}/B_{iso.}$ (\AA^2)	Molecule (B)			$B_{eq.}/B_{iso.}$ (\AA^2)	
	x	y	z		x	y	z		
C(1)	-4844 (4)	2240 (8)	1569 (2)	3.7 (3)	C(1)	-2828 (4)	848 (7)	-485 (2)	3.0 (3)
C(2)	-5444 (5)	1773 (7)	1174 (2)	3.5 (3)	C(2)	-3274 (4)	620 (7)	-927 (2)	3.5 (3)
C(3)	-5161 (4)	165 (7)	1054 (2)	3.2 (3)	C(3)	-2410 (5)	738 (8)	-1242 (2)	3.7 (3)
C(4)	-5417 (5)	-912 (7)	1418 (2)	3.6 (3)	C(4)	-1616 (5)	-460 (7)	-1159 (2)	3.9 (4)
C(5)	-4895 (4)	-423 (7)	1819 (2)	3.2 (3)	C(5)	-1206 (4)	-359 (7)	-712 (2)	2.9 (3)
C(6)	-4389 (5)	-1446 (8)	2046 (2)	4.2 (4)	C(6)	-194 (4)	-367 (7)	-644 (2)	3.0 (3)
C(7)	-3841 (5)	-1105 (8)	2450 (2)	4.2 (4)	C(7)	321 (4)	-281 (7)	-221 (2)	3.0 (3)
C(8)	-4139 (4)	415 (7)	2647 (2)	3.4 (3)	C(8)	-436 (4)	-527 (7)	142 (2)	2.7 (3)
C(9)	-4238 (4)	1609 (7)	2302 (2)	3.1 (3)	C(9)	-1459 (4)	284 (6)	50 (2)	2.5 (3)
C(10)	-5037 (4)	1190 (7)	1958 (2)	3.3 (3)	C(10)	-1987 (4)	-284 (7)	-361 (2)	2.8 (3)
C(11)	-4408 (5)	3185 (8)	2491 (2)	4.2 (4)	C(11)	-2177 (4)	235 (7)	430 (2)	3.3 (3)
C(12)	-3632 (5)	3595 (8)	2837 (2)	4.6 (4)	C(12)	-1672 (4)	792 (7)	840 (2)	3.4 (3)
C(13)	-3620 (5)	2445 (8)	3189 (2)	4.0 (4)	C(13)	-678 (4)	-70 (7)	941 (2)	2.8 (3)
C(14)	-3365 (4)	922 (8)	2978 (2)	4.0 (3)	C(14)	17 (4)	80 (6)	549 (2)	2.5 (3)
C(15)	-3140 (5)	-149 (9)	3345 (2)	5.5 (4)	C(15)	1053 (4)	-538 (7)	709 (2)	3.2 (3)
C(16)	-2575 (5)	864 (10)	3664 (2)	6.2 (4)	C(16)	1122 (4)	-9 (7)	1167 (2)	3.3 (3)
C(17)	-2688 (5)	2524 (8)	3506 (2)	4.2 (4)	C(17)	31 (4)	607 (7)	1281 (2)	2.7 (3)
C(18)	-4634 (5)	2410 (10)	3430 (2)	6.0 (4)	C(18)	-924 (5)	-1750 (7)	1038 (2)	3.7 (3)
C(19)	-6154 (4)	1416 (7)	2110 (2)	3.9 (4)	C(19)	-2462 (4)	-1872 (7)	-305 (2)	3.3 (3)
C(20)	-2738 (5)	3670 (9)	3871 (2)	5.3 (4)	C(20)	-209 (3)	320 (7)	1752 (2)	3.5 (3)
C(21)	-2928 (7)	5296 (10)	3722 (2)	8.3 (6)	C(21)	-1311 (4)	735 (8)	1868 (2)	4.0 (3)
C(22)	-1723 (6)	3516 (10)	4137 (2)	6.7 (5)	C(22)	558 (4)	1178 (8)	2030 (2)	4.3 (4)
C(23)	-1776 (6)	4311 (11)	4558 (2)	8.3 (6)	C(23)	569 (5)	781 (10)	2491 (2)	5.9 (4)
C(24)	-784 (6)	4035 (12)	4820 (2)	8.2 (6)	C(24)	1341 (5)	1667 (10)	2744 (2)	6.8 (5)
C(25)	-771 (7)	4544 (16)	5256 (3)	13.6 (8)	C(25)	1419 (6)	1371 (10)	3194 (2)	7.3 (5)
C(26)	282 (7)	4306 (12)	5446 (3)	10.3 (7)	C(26)	428 (6)	1678 (11)	3423 (2)	7.7 (6)
C(27)	-1659 (8)	4646 (15)	5497 (3)	14.0 (8)	C(27)	2326 (6)	2191 (14)	3390 (3)	10.4 (7)
C(28)	-5505 (4)	180 (7)	312 (2)	3.2 (3)	C(28)	-2550 (5)	1304 (8)	-1982 (2)	4.9 (4)
C(29)	-6203 (4)	-440 (7)	-32 (2)	3.2 (3)	C(29)	-3143 (5)	912 (9)	-2382 (2)	5.3 (4)
C(30)	-6073 (4)	315 (7)	-451 (2)	3.4 (3)	C(30)	-3088 (5)	2116 (9)	-2715 (2)	5.3 (4)
C(31)	-6857 (4)	-232 (7)	-773 (2)	3.5 (3)	C(31)	-3727 (5)	1725 (8)	-3093 (2)	5.2 (4)
C(32)	-6826 (4)	550 (7)	-1192 (2)	3.3 (3)	C(32)	-3682 (6)	2876 (9)	-3442 (2)	6.0 (5)
C(33)	-7673 (4)	41 (7)	-1497 (2)	3.8 (3)	C(33)	-4394 (6)	2507 (11)	-3813 (2)	7.8 (5)
C(34)	-7732 (4)	885 (8)	-1905 (2)	3.6 (3)	C(34)	-4342 (8)	3579 (12)	-4178 (3)	10.3 (7)
C(35)	-8674 (5)	525 (8)	-2173 (2)	4.3 (4)	C(35)	-5229 (9)	3319 (13)	-4505 (3)	12.6 (9)
C(36)	-8778 (5)	1484 (8)	-2564 (2)	5.1 (4)	C(36)	-5154 (8)	4183 (12)	-4906 (3)	11.5 (7)
C(37)	-9670 (5)	1049 (9)	-2854 (2)	5.7 (4)	C(37)	-5908 (7)	3915 (12)	-5263 (3)	10.7 (7)
C(38)	-9804 (6)	2048 (10)	-3229 (2)	6.8 (5)	C(38)	-6866 (7)	4664 (13)	-5133 (3)	11.6 (7)
C(39)	-10649 (7)	1530 (11)	-3546 (2)	9.0 (6)	C(39)	-7649 (8)	4534 (14)	-5509 (3)	12.9 (8)
O(3)	-5787 (3)	-342 (5)	695 (1)	3.5 (2)	O(3)	-2887 (3)	486 (5)	-1664 (1)	4.1 (2)
O(28)	-4804 (3)	1045 (5)	261 (1)	4.2 (3)	O(28)	-1847 (5)	2150 (8)	-1956 (1)	6.8 (4)
H1(1)	-421 (4)	223 (7)	149 (2)	3 (1)	H1(1)	-253 (3)	182 (6)	-47 (1)	2 (1)
H1(2)	-502 (4)	316 (6)	165 (1)	3 (1)	H1(2)	-339 (4)	80 (6)	-31 (1)	3 (1)
H2(1)	-612 (4)	176 (6)	120 (1)	2 (1)	H2(1)	-359 (4)	-21 (7)	-95 (2)	5 (2)
H2(2)	-534 (3)	245 (6)	93 (1)	2 (1)	H2(2)	-380 (4)	135 (6)	-99 (1)	3 (1)
H3(1)	-455 (4)	1 (7)	98 (2)	4 (2)	H3(1)	-223 (4)	157 (7)	-127 (2)	6 (2)
H4(1)	-523 (3)	-189 (6)	134 (1)	2 (1)	H4(1)	-110 (4)	-50 (6)	-133 (2)	5 (2)
H4(2)	-613 (4)	-95 (6)	145 (2)	3 (1)	H4(2)	-183 (4)	-159 (7)	-120 (2)	4 (1)
H6(1)	-426 (4)	-231 (7)	194 (2)	6 (2)	H6(1)	32 (4)	-41 (6)	-87 (1)	3 (1)
H7(1)	-307 (4)	-134 (7)	238 (2)	5 (2)	H7(1)	74 (3)	73 (6)	-17 (1)	2 (1)
H7(2)	-405 (4)	-199 (6)	264 (2)	3 (1)	H7(2)	95 (4)	-109 (7)	-21 (2)	4 (2)
H8(1)	-478 (4)	18 (7)	279 (2)	4 (2)	H8(1)	-59 (3)	-153 (5)	18 (1)	1 (1)
H9(1)	-365 (4)	162 (6)	217 (2)	4 (1)	H9(1)	-129 (4)	128 (6)	-1 (1)	2 (1)
H11(1)	-506 (4)	319 (6)	261 (2)	4 (1)	H11(1)	-244 (4)	-80 (6)	49 (2)	4 (1)
H11(2)	-440 (4)	401 (7)	229 (2)	6 (2)	H11(2)	-283 (4)	79 (6)	41 (1)	3 (1)
H12(1)	-377 (3)	445 (6)	295 (1)	2 (1)	H12(1)	-209 (4)	64 (6)	105 (1)	3 (1)
H12(2)	-297 (4)	364 (7)	271 (2)	5 (2)	H12(2)	-150 (4)	161 (6)	81 (2)	3 (1)
H14(1)	-279 (4)	101 (6)	284 (2)	3 (1)	H14(1)	16 (4)	116 (6)	54 (1)	3 (1)
H15(1)	-271 (4)	-91 (7)	326 (2)	6 (2)	H15(1)	164 (3)	-24 (6)	54 (1)	2 (1)
H15(2)	-385 (4)	-60 (7)	343 (2)	6 (2)	H15(2)	108 (4)	-156 (6)	70 (2)	3 (1)

Table 2 (*cont.*)

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{\text{eq.}}/B_{\text{Iso.}}$ (\AA^2)		<i>x</i>	<i>y</i>	<i>z</i>	$B_{\text{eq.}}/B_{\text{Iso.}}$ (\AA^2)
H16(1)	-188 (5)	55 (8)	370 (2)	7 (2)	H16(1)	160 (4)	72 (7)	119 (2)	4 (2)
H16(2)	-293 (4)	70 (8)	395 (2)	6 (2)	H16(2)	130 (3)	-86 (5)	138 (1)	2 (1)
H17(1)	-207 (4)	291 (7)	334 (2)	5 (2)	H17(1)	2 (3)	151 (5)	125 (1)	2 (1)
H18(1)	-479 (4)	335 (7)	355 (2)	6 (2)	H18(1)	-141 (3)	-175 (6)	126 (1)	2 (1)
H18(2)	-516 (4)	220 (7)	326 (2)	4 (2)	H18(2)	-117 (4)	-227 (6)	80 (1)	3 (1)
H18(3)	-459 (4)	180 (7)	365 (2)	7 (2)	H18(3)	-34 (4)	-228 (6)	112 (2)	4 (1)
H19(1)	-634 (4)	239 (7)	215 (2)	5 (2)	H19(1)	-311 (4)	-184 (6)	-13 (2)	4 (1)
H19(2)	-662 (4)	101 (6)	189 (2)	4 (1)	H19(2)	-272 (4)	-239 (7)	-58 (2)	5 (2)
H19(3)	-626 (4)	85 (7)	234 (2)	4 (1)	H19(3)	-200 (4)	-263 (7)	-18 (2)	3 (1)
H20(1)	-338 (4)	346 (7)	404 (2)	5 (2)	H20(1)	-12 (4)	-63 (6)	183 (1)	3 (1)
H21(1)	-239 (5)	546 (8)	355 (2)	7 (2)	H21(1)	-138 (4)	180 (6)	180 (2)	4 (1)
H21(2)	-370 (7)	533 (13)	363 (3)	8 (4)	H21(2)	-177 (5)	21 (9)	176 (2)	10 (2)
H21(3)	-274 (5)	578 (8)	397 (2)	8 (2)	H21(3)	-137 (3)	65 (6)	215 (1)	3 (1)
H22(1)	-119 (5)	417 (8)	400 (2)	8 (2)	H22(1)	47 (4)	212 (8)	202 (2)	6 (2)
H22(2)	-153 (4)	267 (7)	416 (2)	6 (2)	H22(2)	116 (4)	119 (7)	193 (2)	6 (2)
H23(1)	-230 (4)	408 (7)	475 (2)	5 (2)	H23(1)	73 (4)	-51 (7)	254 (2)	6 (2)
H23(2)	-187 (4)	539 (8)	453 (2)	7 (2)	H23(2)	-3 (5)	82 (8)	260 (2)	6 (2)
H24(1)	-25 (5)	450 (8)	470 (2)	7 (2)	H24(1)	128 (5)	261 (8)	269 (2)	8 (2)
H24(2)	-71 (6)	289 (10)	487 (2)	13 (3)	H24(2)	202 (5)	186 (8)	261 (2)	7 (2)
H25(1)	-93 (5)	571 (10)	521 (2)	10 (2)	H25(1)	153 (4)	38 (8)	321 (2)	6 (2)
H26(1)	44 (5)	334 (8)	545 (2)	7 (2)	H26(1)	21 (5)	261 (8)	337 (2)	8 (2)
H26(2)	79 (6)	481 (10)	526 (2)	12 (3)	H26(2)	-23 (6)	90 (11)	334 (2)	15 (3)
H26(3)	40 (5)	486 (9)	567 (2)	10 (2)	H26(3)	59 (5)	161 (8)	375 (2)	9 (2)
H27(1)	-219 (0)	528 (0)	535 (0)	14 (0)	H27(1)	295 (5)	211 (8)	323 (2)	7 (2)
H27(2)	-155 (0)	538 (0)	573 (0)	14 (0)	H27(2)	255 (5)	176 (10)	366 (2)	12 (2)
H27(3)	-172 (0)	374 (0)	569 (0)	14 (0)	H27(3)	223 (5)	316 (9)	336 (2)	10 (2)
H29(1)	-689 (4)	-34 (7)	6 (2)	4 (2)	H29(1)	-376 (4)	96 (7)	-234 (2)	6 (2)
H29(2)	-598 (4)	-163 (7)	-5 (2)	6 (2)	H29(2)	-288 (4)	3 (7)	-248 (2)	4 (2)
H30(1)	-539 (4)	16 (6)	-55 (1)	3 (1)	H30(1)	-241 (4)	227 (7)	-277 (2)	4 (1)
H30(2)	-612 (3)	127 (6)	-41 (1)	2 (1)	H30(2)	-336 (4)	285 (6)	-263 (2)	4 (2)
H31(1)	-759 (4)	-15 (6)	-65 (2)	4 (1)	H31(1)	-442 (4)	145 (7)	-305 (2)	6 (2)
H31(2)	-675 (4)	-151 (7)	-84 (2)	5 (2)	H31(2)	-346 (4)	79 (7)	-319 (2)	4 (1)
H32(1)	-621 (3)	37 (6)	-134 (1)	2 (1)	H32(1)	-298 (5)	289 (8)	-356 (2)	9 (2)
H32(2)	-687 (4)	161 (6)	-116 (1)	3 (1)	H32(2)	-387 (4)	376 (8)	-335 (2)	6 (2)
H33(1)	-832 (4)	19 (7)	-135 (2)	5 (2)	H33(1)	-506 (5)	255 (8)	-375 (2)	8 (2)
H33(2)	-764 (4)	-106 (7)	-155 (2)	5 (2)	H33(2)	-427 (5)	138 (8)	-392 (2)	9 (2)
H34(1)	-708 (4)	70 (6)	-206 (1)	3 (1)	H34(1)	-362 (5)	349 (9)	-430 (2)	9 (2)
H34(2)	-775 (3)	190 (6)	-184 (1)	2 (1)	H34(2)	-430 (5)	464 (8)	-407 (2)	8 (2)
H35(1)	-934 (4)	52 (7)	-200 (2)	5 (2)	H35(1)	-582 (5)	373 (9)	-444 (2)	10 (2)
H35(2)	-858 (5)	-49 (7)	-230 (2)	7 (2)	H35(2)	-530 (5)	232 (9)	-457 (2)	9 (2)
H36(1)	-816 (4)	149 (7)	-271 (2)	5 (2)	H36(1)	-415 (6)	420 (9)	-500 (2)	11 (3)
H36(2)	-885 (4)	239 (7)	-250 (2)	5 (2)	H36(2)	-526 (5)	544 (9)	-470 (2)	9 (2)
H37(1)	-1023 (5)	98 (9)	-272 (2)	9 (2)	H37(1)	-625 (6)	261 (10)	-532 (2)	11 (3)
H37(2)	-965 (5)	-5 (8)	-296 (2)	8 (2)	H37(2)	-555 (8)	459 (13)	-559 (3)	10 (4)
H38(1)	-909 (5)	198 (10)	-339 (2)	10 (2)	H38(1)	-670 (8)	611 (15)	-501 (3)	16 (5)
H38(2)	-985 (5)	293 (9)	-315 (2)	9 (2)	H38(2)	-708 (5)	399 (8)	-485 (2)	8 (2)
H39(1)	-1052 (0)	46 (0)	-363 (0)	9 (0)	H39(1)	-733 (0)	494 (0)	-577 (0)	13 (0)
H39(2)	-1068 (0)	224 (0)	-379 (0)	9 (0)	H39(2)	-828 (0)	513 (0)	-545 (0)	13 (0)
H39(3)	-1135 (0)	168 (0)	-342 (0)	9 (0)	H39(3)	-784 (0)	345 (0)	-556 (0)	13 (0)

A total of ten cycles of block-diagonal least-squares refinement followed. Positional and anisotropic thermal parameters for C and O atoms were refined in the first four and last three cycles with damping factors of 0.50 for all parameters. For 127 of the H atoms (excluding the nine atoms with fixed parameters) positional and isotropic thermal parameters were refined in the other three cycles (damping factors 0.5 and 0.2 respectively). Refinement converged with $R = \sum | \Delta | /$

$\sum | F_{\text{obs}} | = 0.062$. Final atomic parameters are given in Table 2.*

* Tables of atomic temperature factors, interatomic bond distances and angles, observed and calculated structure factors, and intermolecular C...C contacts $< 4.5 \text{ \AA}$ have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35508 (55 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Intramolecular geometry

Within experimental error, bond distances and angles* for the independent molecules (*A*) and (*B*) are consistent with those found in the cholesteryl acetate crystal structure determination at 123 K (Sawzik & Craven, 1979c) and with those of the laurate room-temperature structure (Dahlén, 1979; Sawzik & Craven, 1979a). At low temperature, the average least-squares estimated standard deviation for bond distances is 0.009 Å and 0.5° for bond angles, while these values are 0.04 Å and 3° for the room-temperature structure. Those H atoms with refined parameters have a mean C–H bond distance of 0.96 Å and C–C–H, H–C–H angles have mean values of 109 and 107°, respectively.

The tetracyclic ring systems of molecules (*A*) and (*B*) have similar conformations. A best least-squares fit for superposition (Nyburg, 1974) of the C(1)–C(19) fragment from the two molecules results in an r.m.s. displacement of 0.03 Å. The effective steroid length, taken as the C(3)–C(16) distance, is 8.952 (9) Å for molecule (*A*) and 8.928 (8) Å for (*B*). A measure of the twist within the ring system is given by the C(19)–C(10)–C(13)–C(18) torsion angle, which has a value of 11.3 (5)° for molecule (*A*) and 9.5 (5)° for (*B*). In related structures, this torsion angle ranges from 7.9–15.0° (Pattabhi & Craven, 1979). The atoms within the ester and ethylenic groups of each cholesteryl laurate molecule are nearly coplanar (Table 3). The C(17) tails in both (*A*) and (*B*) molecules have extended conformations, with a difference of 88° rotation about the C(24)–C(25) bond (Fig. 1). One of the major conformational differences between the two independent molecules is the rotation about the ester linkage. The torsion angle C(2)–C(3)–O(3)–C(28) is 77.6 (6) and 141.7 (5)° in (*A*) and (*B*) respectively.

* See deposition footnote.

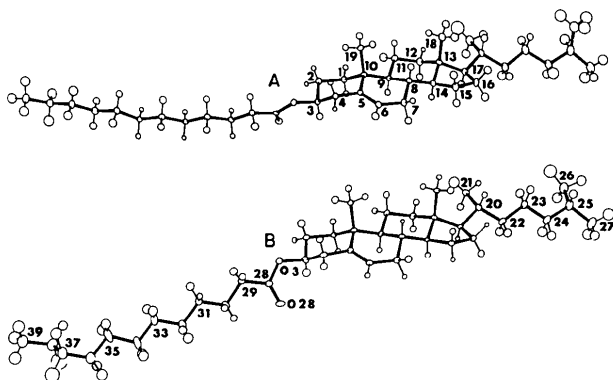


Fig. 1. Molecules (*A*) and (*B*) shown in their observed configuration with their tetracyclic ring systems in the same orientation. Atoms, including hydrogens, are represented as 25% probability thermal envelopes.

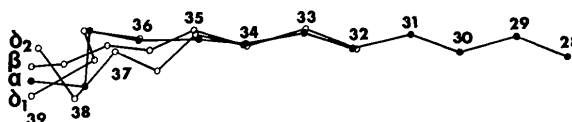


Fig. 2. The ester chain of molecule (*B*) as observed in the following structure determinations: α 198 K; β 298 K (Sawzik & Craven, 1979a); δ_1 , δ_2 disordered conformers at room temperature (Dahlén, 1979). A best least-squares fit for superposition of atoms C(28)–C(34) for the room-temperature chains with the low-temperature chains gave r.m.s. displacements <0.05 Å. Shown is the superposition of the first seven atoms of the chain and the conformational differences observed for the last five atoms.

The ester chain of (*A*) is in a nearly extended conformation for its full length, whereas in molecule (*B*) the first part of the chain is well extended and a twist occurs at the C(36)–C(37) bond (Fig. 2). Torsion angles about the sequence of bonds C(29)–C(30) through C(37)–C(38) are -174.3 (5), 175.8 (5), -176.1 (5), 174.8 (5), -171.0 (5), 174.6 (5), 175.2 (5), 177.0 (6), 174.8 (6)° for molecule (*A*) and -176.8 (6), -178.6 (6), -176.2 (6), -177.3 (7), 169.0 (7), -171.6 (8), 174.1 (9), 75.6 (10), 175.5 (9)° for molecule (*B*).

Conformations of the molecules in the two independent cholesteryl laurate crystal structure determinations at room temperature and low-temperature are not significantly different, except in the (*B*) ester chain from C(35)–C(39) (Fig. 2). In our room-temperature structure the (*B*) chain is slightly bowed at C(35), but otherwise in an extended conformation. Dahlén (1979) reports two disordered conformers as an interpretation of the electron density in this region of the structure. One of these conformers is extended and

Table 3. Best least-squares planes calculated for selected groups of atoms

The planes are: (1) tetracyclic ring system, C(1)–C(17); (2) ethylenic group, C(5), C(6), C(10), C(4), C(7); (3) ester group, O(3), C(28), C(29), O(28). Equations are in the form $ax + by + cz = d$, referred to crystallographic axes. The plane constants are in Å. Values for molecule (*A*) are above those for (*B*).

(a) Plane constants

Plane	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>
(1)	–11.86 –3.05	–0.41 –8.54	13.09 3.24	8.01 0.25
(2)	–10.81 –0.11	–2.15 –8.82	16.02 1.89	8.31 0.20
(3)	–8.05 –8.43	6.86 6.45	3.69 6.82	4.67 1.62

(b) Distances (Å) of atoms from the planes, e.s.d.'s are in parentheses.

Plane	C(5)	C(6)	C(10)	C(4)	C(7)
(2)	–0.022 (9) –0.007 (9)	0.013 (8) 0.002 (8)	0.008 (8) 0.002 (9)	0.004 (9) 0.002 (9)	–0.004 (9) 0.000 (8)
(3)	0.002 (8) –0.006 (8)	–0.007 (6) 0.021 (8)	0.002 (8) –0.006 (7)	0.003 (7) –0.009 (8)	

similar to the (*B*) chain of our room-temperature structure, and the second has a twist about the C(36)–C(37) bond, similar to that observed in the laurate structure at 198 K. Although we found no convincing evidence of disorder for the terminal portion of the (*B*) ester chain in our room-temperature structure, this possibility is not ruled out. The electron density in this region is quite diffuse at 298 K and it is difficult to distinguish the effect of high-amplitude thermal motion from disorder. There is no evidence of disorder in the low-temperature structure.

Molecular packing and thermal motion

In the crystal structure of cholesteryl laurate (Fig. 3) molecules are arranged to form monolayers that are parallel to the crystal planes (001). The two molecules (*A*, *B*) which are not related by crystal symmetry have their tetracyclic ring systems almost perpendicular to one another and all molecular long axes are nearly parallel to the [101] direction.

The monolayers are regions of closely packed molecules which are separated by interface regions where atoms are more loosely packed (Figs. 3, 4). There are 28 distinct intermolecular C...C distances less than 4.5 Å between atoms of (*B*)-molecule cholesteryl groups [C(1)–C(19)] which stack along twofold screw axes at the center of the monolayers (Figs. 3, 4). A significant amount of cholesteryl–alkyl

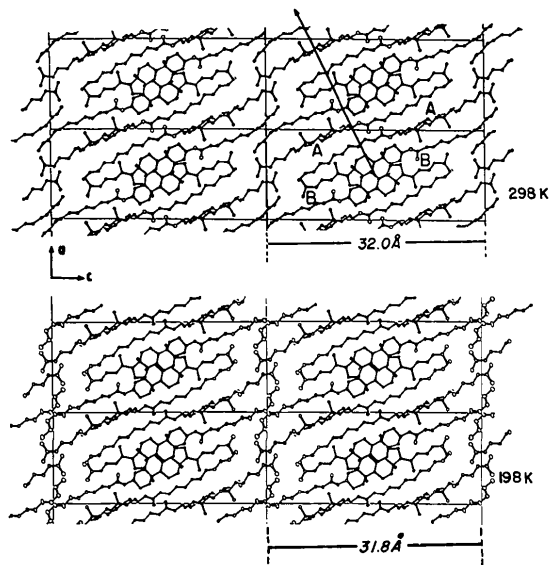


Fig. 3. Crystal structure of cholesteryl laurate in projection down the *b* axis. (a) At 298 K (Sawzik & Craven, 1979a), (b) at 198 K. The two molecules not related by symmetry are (*A*) (ring system viewed on edge) and (*B*). Adjacent monolayers extend vertically with the interface region occurring in vertical strips at the center and edges of the figure. The bold line through the 298 K structure indicates the [501] direction (see Fig. 4).

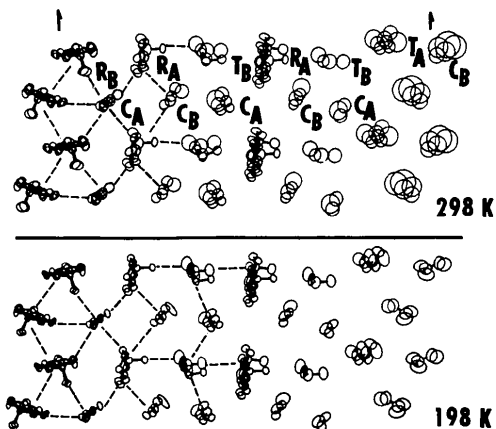


Fig. 4. A view of the crystal structure at 298 and 198 K as projected down the crystal [101] direction. The crystal *b* axis is vertical and the crystal [501] (see Fig. 3) direction is horizontal. For the purpose of clarity, only atoms within a slice of thickness 4.5 Å are included in the figure. The section begins at the center of a monolayer where cholesteryl groups of *B* atoms stack along twofold screw axes (far left) and ends at the center of an interface region (far right). Sections of each molecule are labeled: *R* for tetracyclic ring system, *T* for cholesteryl C(17) tail, and *C* for ester chain. Atoms are represented as 50% probability ellipsoids. Dashed lines indicate multiple intermolecular C...C distances less than 4.5 Å.

packing is also present. For nearest-neighbor molecules, C...C distances less than 4.5 Å between (*A*)-cholesteryl groups and each of the following groups: (*A*)-laurate chains [C(28)–C(39)], the first part of (*B*)-laurate chains [C(28)–C(34)] and (*B*)-cholesteryl tails [C(20)–C(27)], number 17, 21 and 11 respectively. There are 20 intermolecular C...C distances between (*B*)-cholesteryl groups and (*A*)-laurate chains that are less than 4.5 Å. The cholesteryl–alkyl packing in this crystal structure is important as it may be similar to the arrangements that occur when cholesterol is incorporated into phospholipid bilayers.

Alkyl–alkyl group interactions occur in the monolayer region between atoms of (*B*)-cholesteryl tails and (*A*)-laurate chains giving 14 intermolecular C–C distances less than 4.5 Å and (*B*)-laurate chains from opposing monolayers overlap in the interface region with eight such distances.

In the crystal structure of cholesteryl laurate at 198 K and at 298 K, the thermal motion of the atoms in the tetracyclic ring systems, C(1)–C(19) of both (*A*) and (*B*) molecules, is nearly consistent with that of a rigid body (Schomaker & Trueblood, 1968) (Fig. 5, Table 4). Librational motion for molecule (*B*) and translational motion for both molecules is significantly reduced at low temperature. For molecule (*B*) (198 K) the r.m.s. principal values for *T* and ω are similar to those of cholesteryl acetate molecule (*A*) (123 K) which stacks in a similar manner along a twofold screw

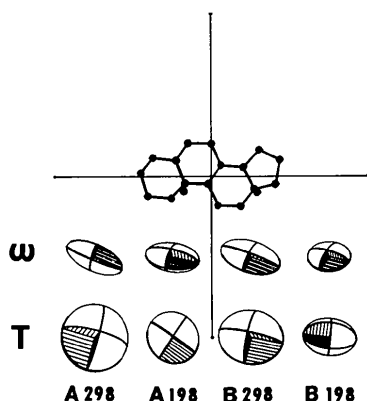


Fig. 5. Rigid-body parameters for the C(1)–C(19) fragment of molecules (A) and (B) for cholesteryl laurate at 198 and 298 K. The ω tensors are drawn at the same level of probability, and likewise the T tensors. These and the atoms of the C(1)–C(19) fragment are all shown with respect to the principal inertial axes of the fragment. The r.m.s. principal values for ω and T are given in Table 4.

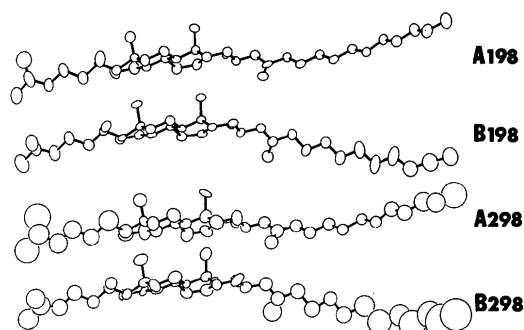


Fig. 6. Thermal ellipsoids for (A) and (B) molecules as seen in cholesteryl laurate structures at 198 and 298 K. Atoms are represented as 25% probability ellipsoids.

axis (Sawzik & Craven, 1979c). Librational corrections to bond distances and angles for the laurate low-temperature structure (ranging from 0.0014–0.0069 Å and 0.001–0.170° respectively) were within the calculated standard deviations for these parameters and were not applied.

Thermal motion for the atoms of the cholesteryl laurate molecules (Fig. 6) is consistent with their crystal-packing arrangements. In the 198 K and 298 K structures, the ester chains of (A) molecules and the C(17) tails of (B) molecules are surrounded by cholesteryl ring systems (Fig. 4) and have a smaller average amplitude of vibration than the (B) chains and (A) tails which project into the layer interface (Fig. 6). This difference has been observed for other type I monolayer cholesteryl ester structures and may be related to the stiffening effect that cholesterol has on phospholipid membranes (Pattabhi & Craven, 1979).

The most significant difference in thermal motion between the 198 K and 298 K structures is seen in the laurate chains and C(17) cholesteryl tails for both (A) and (B) molecules. For these alkyl groups the ratio of

Table 4. *R.m.s. magnitudes of principal values for rigid-body tensors T and ω for the molecular fragment C(1)–C(19)*

	T (Å)			ω (°)		
A(198 K)	0.17	0.20	0.22	2.12	1.45	5.05
A(298 K)	0.26	0.27	0.28	1.95	0.99	5.59
B(198 K)	0.15	0.15	0.22	2.02	1.32	3.30
B(298 K)	0.22	0.17	0.27	2.20	1.37	6.16

equivalent isotropic temperature factors* for corresponding atoms in the low- and room-temperature structures ranges from 0.2 to 0.7, whereas for atoms of the cholesteryl ring systems this range is 0.5 to 0.9. When the crystal is heated, it is probable that this trend will continue with increased thermal and conformational disordering of the laurate chains and cholesteryl tails. However, because of the efficient packing of the nearly rigid ring systems, the crystal melts at a temperature (363.5 K) beyond the range of stability for the smectic and cholesteric mesophases which form only on cooling at 354.5 K and 361 K respectively.

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$$* B_{eq} = \frac{1}{3} \sum_{i=1}^3 B_{ii} \text{ (units } \text{Å}^2\text{)}.$$

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