

Fig. 2. Newman projections around C(5)–C(1) and C(6)–C(7).

Table 5. Ring conformations

	Ring A (cyclopentane)	Ring B (seven-membered)	Ring C (lactone)
Description	Deformed envelope	Deformed twist-chair	Half-chair
Approximate symmetry	C_s	C_2	C_2
Pseudo-symmetry element from atom to the midpoint of bond	m C(5) C(2)–C(3)	2 C(7) C(1)–C(10)	2 C(12) C(6)–C(7)
Average torsion angle (magnitude)	29.2°	61.0°	14.4°
Asymmetry parameter (Duax, Weeks & Rohrer, 1976)	7.8°	12.8°	0.7°

The conformations of the three fused rings given by the torsion angles in Table 4 are described in another way with some further comments in Table 5. The torsion angles of the cyclopentane ring indicate a somewhat deformed, highly puckered envelope conformation.

In the seven-membered ring the C_2 symmetrized values of the torsion angles, *i.e.* 58, -70 , 79, -36° , are quite similar to those (54, -72 , 88, -39) proposed by Hendrickson (1967) for a cycloheptane molecule with equal bond lengths and in a perfect twist-chair conformation.

The lactone ring shows a relatively flat half-chair conformation which induces only a small torsion angle [$C(5)–C(6)–C(7)–C(8) = -27^\circ$] in the seven-membered ring; as a consequence, perfect C_2 symmetry in that ring conformation in the four bonds between C(5) and C(9) is destroyed.

The hysterin molecules are linked together by hydrogen bonds between the O(15)–H hydroxyl group and O(12) of the lactone carbonyl group; O(15)···O(12) is 2.79 Å. These bonds form infinite chains parallel to [100].

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Structure of Cholesteryl Undecanoate

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Abstract. $C_{38}H_{66}O_2$, monoclinic, $P2_1$, $a = 13.008$ (6), $b = 9.006$ (7), $c = 31.063$ (9) Å, $\beta = 90.60$ (4)°, $Z = 4$ (2 molecules/asymmetric unit), $d_{meas} = 1.009$ (floatation in aqueous sucrose), $d_{calc} = 1.013$ Mg m $^{-3}$. The final R factor for 1888 observed reflections is 0.127. The molecular packing in the crystal structure of cholesteryl undecanoate is isostructural with the cholesteryl n -alkanoate series $C_9–C_{12}$.

Introduction. The structure of cholesteryl undecanoate is one of a series of cholesteryl ester structure determinations we have undertaken. These structures are of interest as they may provide models for molecular associations in less ordered lipid systems. The liquid-crystalline phases of cholesteryl undecanoate are monotropic. For samples recrystallized from n -pentanol, the solid–isotropic transition occurs at 364.5

Table 1. Atomic positional parameters ($\times 10^4$) in cholesteryl undecanoate

E.s.d.'s are in parentheses.

	Molecule A			Molecule B		
	x	y	z	x	y	z
C(1)	-4796 (24)	2160 (36)	1620 (9)	-2775 (19)	968 (36)	-469 (8)
C(2)	-5396 (21)	1745 (36)	1209 (8)	-3286 (22)	695 (35)	-923 (9)
C(3)	-5137 (27)	245 (36)	1084 (10)	-2334 (22)	783 (38)	-1242 (8)
C(4)	-5367 (23)	-814 (32)	1466 (9)	-1558 (23)	-432 (36)	-1157 (9)
C(5)	-4895 (20)	-423 (34)	1866 (8)	-1162 (20)	-223 (32)	-696 (9)
C(6)	-4404 (24)	-1455 (41)	2070 (9)	-153 (20)	-208 (34)	-619 (8)
C(7)	-3876 (33)	-1093 (43)	2501 (11)	355 (19)	-176 (35)	-204 (8)
C(8)	-4170 (21)	317 (34)	2727 (9)	-392 (17)	-460 (31)	156 (8)
C(9)	-4255 (20)	1553 (32)	2372 (9)	-1404 (19)	334 (31)	68 (8)
C(10)	-5000 (20)	1169 (39)	2002 (9)	-1952 (19)	-215 (37)	-357 (10)
C(11)	-4435 (19)	3139 (40)	2571 (9)	-2141 (19)	300 (35)	460 (8)
C(12)	-3656 (23)	3524 (36)	2920 (9)	-1636 (21)	794 (33)	877 (8)
C(13)	-3546 (17)	2250 (41)	3270 (8)	-664 (18)	33 (32)	948 (9)
C(14)	-3352 (21)	813 (36)	3046 (8)	37 (19)	146 (28)	570 (8)
C(15)	-3090 (23)	-285 (42)	3406 (10)	1110 (19)	-444 (35)	745 (8)
C(16)	-2547 (24)	635 (51)	3723 (11)	1176 (18)	28 (35)	1213 (9)
C(17)	-2660 (22)	2344 (43)	3598 (11)	104 (20)	703 (31)	1326 (7)
C(18)	-4591 (25)	2274 (47)	3527 (10)	-906 (20)	-1673 (36)	1047 (9)
C(19)	-6153 (19)	1419 (36)	2149 (9)	-2476 (21)	-1772 (35)	-311 (8)
C(20)	-2713 (25)	3615 (52)	3967 (10)	-161 (23)	483 (38)	1778 (9)
C(21)	-2859 (29)	5107 (47)	3825 (12)	-1256 (21)	747 (37)	1912 (8)
C(22)	-1670 (28)	3379 (57)	4229 (12)	653 (20)	1318 (36)	2085 (8)
C(23)	-1721 (37)	3781 (73)	4653 (17)	514 (22)	1001 (46)	2569 (10)
C(24)	-571 (46)	3569 (93)	4918 (20)	1313 (25)	1761 (52)	2834 (10)
C(25)	-693 (46)	3030 (92)	5404 (19)	1453 (33)	1350 (71)	3323 (14)
C(26)	-1526 (49)	4292 (87)	5476 (19)	2345 (35)	2101 (102)	3473 (13)
C(27)	283 (48)	4077 (87)	5463 (19)	313 (40)	1435 (95)	3495 (15)
C(28)	-5448 (20)	285 (34)	328 (8)	-2634 (25)	1325 (45)	-1993 (9)
C(29)	-6103 (20)	-331 (37)	-20 (9)	-3136 (23)	867 (42)	-2406 (10)
C(30)	-6019 (19)	364 (33)	-460 (8)	-3090 (30)	2010 (56)	-2774 (12)
C(31)	-6785 (20)	-223 (37)	-791 (8)	-3660 (24)	1466 (47)	-3145 (10)
C(32)	-6799 (23)	540 (36)	-1224 (9)	-3556 (34)	2556 (57)	-3486 (14)
C(33)	-7679 (20)	-30 (38)	-1521 (48)	-4237 (38)	2338 (56)	-3899 (14)
C(34)	-7746 (22)	782 (41)	-1943 (10)	-4118 (56)	3262 (81)	-4287 (22)
C(35)	-8666 (26)	506 (45)	-2175 (10)	-5113 (42)	2889 (70)	-4643 (14)
C(36)	-8745 (26)	1346 (48)	-2601 (12)	-5398 (68)	3816 (78)	-4917 (18)
C(37)	-9724 (36)	936 (65)	-2865 (13)	-5849 (46)	2875 (89)	-5269 (19)
C(38)	-9756 (42)	1659 (97)	-3223 (17)	-6163 (48)	3922 (87)	-5589 (19)
O(3)	-5818 (13)	-190 (23)	707 (6)	-2863 (15)	568 (25)	-1651 (6)
O(28)	-4752 (13)	1180 (25)	282 (5)	-1885 (19)	2135 (38)	-1994 (7)

K. Cholesteric and smectic phases appear on cooling at 360.9 and 251.9 K respectively (Davis & Porter, 1970).

Cholesteryl undecanoate (Supelco Chemical Co., Bellefonte, PA) was recrystallized from an *n*-pentanol solution as plates (001) elongated on **b**, m.p. 365 K. X-ray data were measured at room temperature using a Nonius CAD-4 diffractometer and Cu $K\alpha$ graphite-monochromated radiation ($\lambda = 1.5418 \text{ \AA}$). Unit-cell parameters were determined by a least-squares fit of $\sin^2 \theta$ values for 17 reflections with $18^\circ \leq \theta \leq 40^\circ$ which were measured at $\pm \theta$. X-ray intensities for 2417 symmetry-independent reflections with $\sin \theta / \lambda \leq 0.42 \text{ \AA}^{-1}$ were measured using ω scans. 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. Only 1888 reflections with $I > 2\sigma(I)$ were used in the structure determination.

Since the crystal data for cholesteryl undecanoate were similar to those of cholesteryl laurate (Sawzik & Craven, 1979; Dahlén, 1979), atomic positional parameters from the latter were used as a starting model for refinement. A structure factor calculation with 64 atoms from the model gave $R = 0.32$. The 16 C atoms which were excluded from this calculation were at the terminal regions of the hydrocarbon chains [C(24), C(25), C(26), C(27), C(35), C(36), C(37), C(38)] in each molecule (Fig. 1). All were located in three subsequent cycles of Fourier refinement. H atoms were included in the structure factor calculation with fixed parameters obtained by assuming bond lengths of 1.0 \AA and standard bond angles. Each H atom was assigned an isotropic thermal parameter equivalent to that of the C atom to which it is bonded. Block-diagonal least-squares refinement of positional and anisotropic thermal parameters for the 80 non-

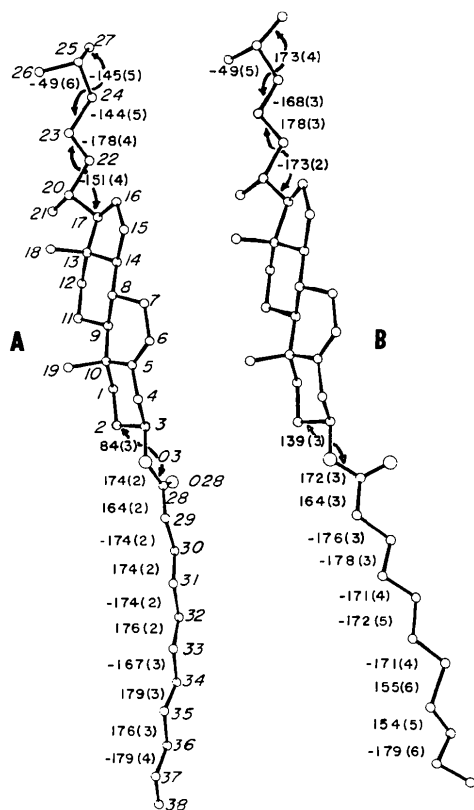


Fig. 1. Atomic numbering system and selected torsion angles ($^{\circ}$) for cholesteryl undecanoate, molecules *A* and *B*. Estimated standard deviations are in parentheses. The molecules are shown in their observed configurations with the tetracyclic ring systems in the same orientation.

hydrogen atoms followed. 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 were those of Cromer & Waber (1965) for C and O, and Stewart, Davidson & Simpson (1965) for H. The refinement converged with $R = \sum |\Delta| / \sum |F_{\text{obs}}| = 0.127$. Final atomic parameters are in Table 1.*

Discussion. The crystal structure of cholesteryl undecanoate is isostructural with the series of cholesteryl *n*-alkanoate esters C_9 – C_{12} (C_9 , Guerina & Craven, 1979; C_{10} , Pattabhi & Craven, 1979; C_{12} , Sawzik & Craven, 1979). The undecanoate molecules are arranged in layers which are parallel to the crystal (001) planes and have a thickness of $d_{001} = 31.06 \text{ \AA}$ (Fig. 2). Within these layers, hydrocarbon chains of *A* and *B* molecules have close-neighbor cholesteryl ring systems. There is

* Lists of structure factors, temperature factors, H atom positional parameters, and atomic bond distances and bond angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34795 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

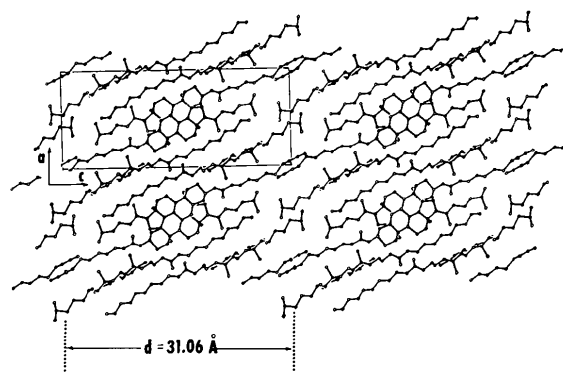


Fig. 2. The crystal structure of cholesteryl undecanoate in projection down the *b* axis. Undecanoate *A* molecules are those with the ring system viewed on edge. The monolayer repeat distance is shown, with the interface region indicated by dotted lines.

efficient cholesteryl packing of the *B* molecules with each other in stacks along the crystallographic *b* axis. In contrast, the interface region between layers is loosely packed. The major structural differences in the cholesteryl ester C_9 – C_{12} series occur in this region. The space available for the ester chains of *B* molecules seems to depend on the packing arrangement of the $C(17)$ tails of the *A* molecules. In the undecanoate structure, the slightly twisted *B* alkanate chains are required to overlap one another to a greater extent than the *B* chains of the other esters in this series. The $C(17)$ hydrocarbon tail of molecule *B* is almost fully extended but in the *A* molecule there is a moderate twisting of the tail to avoid contact with the tail of its symmetry-related neighbor in the interface region of the structure (Fig. 1). The most prominent difference in conformation of the undecanoate *A* and *B* molecules is a difference of 55° in the rotation of the ester bond. The ester chain of each molecule is in an extended conformation (Fig. 1).

The bond lengths and angles* in the cholesteryl undecanoate crystal structure are consistent with those observed in the related structures determined at room temperature (Guerina & Craven, 1979; Pattabhi & Craven, 1979; Sawzik & Craven, 1979).

The tetracyclic ring systems of molecules *A* and *B* in the undecanoate structure are quite similar. A best least-squares fit for superposability of the $C(1)$ – $C(19)$ fragments for the two molecules gave an r.m.s. displacement between corresponding atoms of 0.091 \AA . The atoms of the ethylenic groups [$C(4)$, $C(5)$, $C(6)$, $C(7)$, $C(10)$] and the ester group [$O(3)$, $C(28)$, $C(29)$, $O(28)$] are coplanar within experimental error for both molecules. The thermal motions of the atoms in the $C(17)$ hydrocarbon tails and ester chains show an effect observed in the other so-called type I monolayer

* See deposition footnote.

cholesteryl ester structures (Pattabhi & Craven, 1979). The ester chains of molecule *A* and C(17) tails of molecule *B* are surrounded by cholesteryl ring systems in the crystal structure and have a smaller average amplitude of vibration than the *B* chains and *A* tails which project into the layer interface. It has been suggested that this may be related to the stiffening effect of cholesterol on phospholipid membranes (Pattabhi & Craven, 1979).

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