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The Crystal and Molecular Structure of Cholesteryl Formate

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Cholesteryl formate ($HCOOC_{27}H_{45}$) is monoclinic, space group $P2_1$, with $a=15.757$ (1), $b=6.073$ (1), $c=13.592$ (2) Å, $\beta=94.1$ (1)°, $Z=2$. Intensities were measured, using an automatic diffractometer with graphite-monochromated Cu-Kα radiation. The structure was solved by a direct method and refined by least-squares method. The final R factor was 0.087 for 1640 observed reflections. There are no unusual bond distances and angles. The molecules are arranged in antiparallel array forming monolayers of thickness $d_{100}=15.757$ Å. Adjacent cholesteryl ring groups are related by the translation operation along the *b* axis.

Introduction

Cholesterol[1-3] is the most abundant steroid in the animal kingdom. In addition to being a primary metabolic precursor for many of the steroid hormones, it and some of its esters play an important role in the structural stabilization of membranes.[4] The phase interactions of the cholesterol-phospholipid systems that comprise many membranes tend to be very complicated, and thus an important first step towards deriving detailed structural membrane models is a study of the stereochemistry and packing of cholesterol and its derivatives.

Though the crystal structures of cholesteryl chloroformate[5] and many other cholesteryl esters[6-16] were solved, the structure of cholesteryl formate has not yet been reported. From consideration of the crystal data of the cholesteryl formate it seemes interesting to study its crystal structure, because the different modes of cholesteryl-cholesteryl packing tend to be present in this compound.

TABLE 1: Crystal Data

Cholesteryl formate	:	$HCOOC_{27}H_{45}$	
Mw	:	414.35	
m.p.	:	100.9°C	
Unit Cell Parameter	:	a =	15.757(1) Å
		b =	6.073 (1) Å
		c =	13.592 (2) Å
		β =	94.1 (1)°
		V =	1297.3 (2) Å^3
		Z =	2
μ(Cu-Kα)	:	4.22 cm^{-1}	
Crystal System	:	monoclinic	
Space Group	:	$P2_1$	
Density	:	Dc = 1.061 g/cm^3	
		Dm = 1.04 g/cm^3	
F(000)	:	460.00	

Experimental

Cholesteryl formate from Tokyo Kasei Kogyo Co., Ltd. was crystallized by slow evaporation of an acetone solution. The resulting monoclinic lath-shaped crystals melted at 100.9°.

Preliminary crystal data obtained from X-ray Weissenberg photographies were agreement with those of Barnard and Lydon.[17] Subsequent X-ray data collection was carried out at room temperature using a Rigaku AFC diffractometer with Cu-Kα graphite-monochromated radiation. The crystal lattice parameters (Table 1) were obtained by a least-squares fit of 13 reflections with $15°\leqslant\theta\leqslant26°$C. X-ray intensities with $2\theta\leqslant120°$ were collected by $\omega/2\theta$ scan, and 1640 reflections with $F_o>3\sigma(F_o)$ were used in structure determination. No absorption corrections were applied. The crystal density measured by the flotation method in a mixture of methanol and KI aqueous solution was 1.04g cm^{-3}.

Determination and Refinement of the Structure

The structure amplitudes were converted to normalized structure factors and the structure was solved using MULTAN[18] with 238 E values ($E\geqslant1.40$).

Initial attempts to determine the structure from the E map computed with the set of the best figure of merit failed. Although the seventeen peaks selected from the E map were consistent with a chemically reasonable cholesterol fragment and the successive routine structure analyses gave a plausible

stereochemistry and a packing mode of the molecules, the refinements were terminated at the step of R = 0.35.

But fortunately, we observed that the above E map revealed the another set of a tetracyclic cholesterol fragment among the highest sixty peaks. There were seven peaks, of which each peak

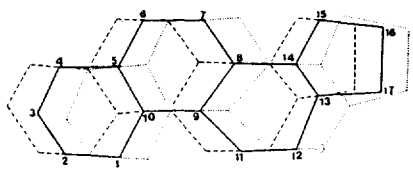

Figure 1. Average structure system for cholesteryl tetracyclic rings.

TABLE 2: Fractional Atomic Coordinates of Average Molecular Fragment

Atom	Peak No.[a]	Molecular fragment A			Average			Peak No.	Molecular fragment B		
C(1)	12	0.718(x)	0.114(y)	0.189(z)	0.758	0.112	0.224	47	0.798	0.110	0.258
C(2)	27	0.638	0.150	0.129	0.678	0.132	0.159	12	0.718	0.114	0.189
C(3)	5	0.634	0.293	0.043	0.673	0.266	0.080	25	0.712	0.238	0.117
C(4)	11	0.710	0.196	−0.024	0.748	0.197	0.010	1	0.786	0.198	0.043
C(5)	1	0.786	0.198	0.043	0.830	0.205	0.071	13	0.873	0.211	0.099
C(6)	19	0.860	0.307	0.002	0.899	0.302	0.033	2	0.939	0.297	0.061
C(7)	2	0.939	0.297	0.061	0.980	0.315	0.091	10	1.021	0.333	0.120
C(8)	7	0.960	0.161	0.138	0.999	0.176	0.173	4	1.037	0.190	0.208
C(9)	3	0.879	0.112	0.193	0.917	0.120	0.226	14	0.954	0.128	0.259
C(10)	8	0.803	0.062	0.132	0.841	0.087	0.163	3	0.879	0.112	0.193
C(11)	18	0.899	−0.027	0.278	0.939	0.005	0.312	20	0.978	0.037	0.345
C(12)	20	0.978	0.037	0.345	[b]1.018	0.037	0.379	[c]			
C(13)	41	1.061	0.056	0.286	1.096	0.056	0.321	17	1.130	0.057	0.356
C(14)	4	1.037	0.190	0.208	1.073	0.196	0.237	9	1.109	0.202	0.266
C(15)	42	1.119	0.240	0.170	1.156	0.255	0.205	6	1.192	0.269	0.240
C(16)	6	1.192	0.269	0.240	1.229	0.275	0.275	21	1.266	0.281	0.310
C(17)	16	1.143	0.175	0.349	1.179	0.189	0.380	15	1.215	0.204	0.410

[a] The order of peak height in the E map. [b] Derived from the coordinate of C(12) of the molecular fragment A. [c] Missing peak.

TABLE 3: Fractional Atomic Coordinates ($\times 10^4$) and Anisotropic Temperature Factors ($\times 10^3$) for the non-hydrogen Atoms of Cholesteryl Formate

ATOM	X	Y	Z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(1)	7585(3)	1298(12)	2201(4)	38(2)	81(4)	50(3)	3(3)	10(2)	−8(3)
C(2)	6727(3)	1287(13)	1581(4)	33(2)	81(4)	83(4)	−17(4)	5(3)	−6(3)
C(3)	6792(3)	2867(11)	739(5)	36(3)	53(3)	92(4)	−9(3)	−14(3)	1(2)
C(4)	7463(3)	2128(10)	80(4)	49(3)	49(3)	68(3)	−1(3)	−14(3)	−8(3)
C(5)	8323(3)	2013(8)	660(3)	37(2)	43(3)	38(2)	−3(2)	1(2)	0(2)
C(6)	8984(3)	3088(10)	356(4)	42(2)	61(3)	46(2)	16(3)	−3(2)	2(2)
C(7)	9854(3)	3227(9)	850(4)	41(2)	47(3)	59(3)	18(3)	−8(2)	−2(2)
C(8)	9978(3)	1533(8)	1703(3)	31(2)	40(2)	33(2)	0(2)	5(2)	2(2)
C(9)	9184(3)	1385(8)	2262(3)	36(2)	32(2)	50(3)	6(2)	5(2)	0(2)
C(10)	8363(3)	761(0)	1631(3)	40(2)	39(3)	43(3)	1(2)	0(2)	−2(2)
C(11)	9332(3)	−81(11)	3197(4)	51(3)	70(4)	46(3)	17(3)	−1(2)	−20(3)
C(12)	10113(3)	628(10)	3867(4)	47(3)	64(4)	54(3)	11(3)	−1(3)	2(3)
C(13)	10915(3)	681(8)	3292(4)	40(2)	32(2)	55(3)	6(2)	−2(2)	4(2)
C(14)	10723(3)	2230(8)	2415(3)	41(2)	31(2)	38(2)	0(2)	3(2)	−3(2)
C(15)	11607(3)	2684(10)	1981(4)	34(2)	67(4)	56(3)	12(3)	0(2)	−8(3)
C(16)	12215(3)	2702(10)	2937(4)	42(2)	58(3)	60(3)	5(3)	−4(3)	3(2)
C(17)	11706(3)	1914(8)	3797(3)	46(3)	38(3)	47(3)	−1(2)	−3(2)	4(2)
C(18)	11177(4)	−1615(10)	2977(4)	66(3)	36(3)	82(4)	0(3)	−11(3)	4(3)
C(19)	8357(4)	−1726(10)	1365(4)	59(4)	36(3)	79(4)	−2(3)	−4(3)	−9(2)
C(20)	12263(3)	691(11)	4621(4)	50(3)	62(3)	56(3)	9(3)	−13(3)	3(3)
C(21)	11763(4)	−179(17)	5430(5)	70(4)	122(6)	73(4)	36(4)	−10(3)	−22(4)
C(22)	12968(3)	2265(13)	5037(4)	56(3)	81(4)	68(3)	5(3)	−30(3)	−14(3)
C(23)	13625(3)	1156(17)	5782(4)	62(3)	124(6)	65(3)	12(4)	−24(3)	−4(4)
C(24)	14345(5)	2602(17)	6072(5)	87(4)	112(7)	83(4)	14(5)	−40(4)	−13(5)
C(25)	15038(7)	1729(29)	6830(10)	111(7)	184(13)	154(8)	62(10)	−86(7)	−55(8)
C(26)	15723(7)	3387(34)	7081(9)	117(7)	290(22)	169(9)	84(14)	−79(7)	−69(11)
C(27)	15094(9)	−257(45)	7145(16)	123(10)	274(24)	307(20)	112(21)	−130(12)	−28(13)
C(28)	5708(5)	4882(7)	−138(7)	64(4)	79(5)	139(7)	−19(5)	−37(4)	23(5)
O(3)	5972(3)	2956(8)	175(4)	42(2)	63(3)	119(4)	−5(3)	−31(2)	0(2)
O(28)	6107(4)	6497(2)	−118(8)	101(4)	63(4)	281(10)	15(5)	−80(6)	−1(3)

did doubly correspond to two different atoms of the cholesterol fragments, A and B, and only one peak corresponding to C(12) of fragment B missing as shown in Figure 1 and Table 2. The above trial cholesterol nucleus corresponded to the fragment A. These two steroid nucleus were found which proved to have the correct orientation but an incorrect position in the unit cell. The structure was shifted to bring its proper position and the coordinates of the seventeen atom steroid nucleus were averaged. It is not quite understandable why the averaged structure derived from the two distinct fragments gave the correct answer. A similar example of heptahelicene was investigated by P.T. Buerskens and Th.E.M.van den Hark.[19]

The first trial structure based on 17 atoms gave an R value of 0.46 for all reflections. The remaining non-hydrogen atoms were located by doing several cycles of Fourier syntheses. The refinement was carried out by the full-matrix least-squares method using the SHELX 76 Program.[20] Three cycles of refinement using isotropic temperature factors resulted in R value of 0.17. In two further cycles with all non-hydrogen atoms treated anisotropically R decreased to 0.12. Most of hydrogen atoms

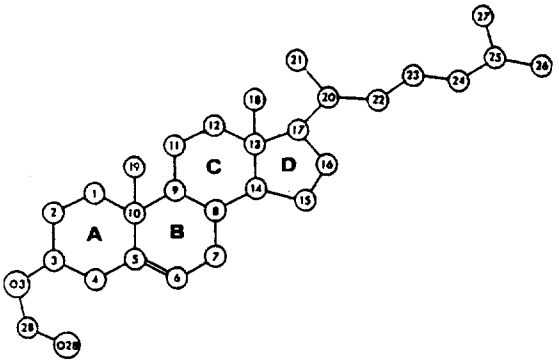

Figure 2. Atomic numbering of cholesteryl formate.

TABLE 4: Bond Lengths(Å) and Angles(°) for Cholesteryl Formate with e.s.d's in Parentheses

C(1) -C(2) 1.541(6)	C(1) -C(10) 1.531(6)	C(2) -C(3) 1.503(7)
C(3) -C(4) 1.502(6)	C(3) -O(3) 1.455(7)	C(4) -C(5) 1.520(6)
C(5) -C(6) 1.320(6)	C(5) -C(10) 1.521(6)	C(6) -C(7) 1.485(6)
C(7) -C(8) 1.552(7)	C(8) -C(9) 1.512(6)	C(8) -C(14) 1.527(6)
C(9) -C(10) 1.547(6)	C(9) -C(11) 1.556(6)	C(10)-C(19) 1.553(7)
C(11)-C(12) 1.539(7)	C(12)-C(13) 1.533(7)	C(13)-C(14) 1.532(7)
C(13)-C(17) 1.569(7)	C(13)-C(18) 1.524(8)	C(14)-C(15) 1.575(7)
C(15)-C(16) 1.558(8)	C(16)-C(17) 1.540(7)	C(17)-C(20) 1.561(7)
C(20)-C(21) 1.494(10)	C(20)-C(22) 1.542(8)	C(22)-C(23) 1.549(9)
C(23)-C(24) 1.466(11)	C(24)-C(25) 1.541(16)	C(25)-C(26) 1.498(21)
C(25)-C(27) 1.281(26)	C(28)-O(3) 1.303(9)	C(28)-O(28) 1.164(10)

C(1) -C(2) -C(3) 108.0(4)	C(1) -C(10)-C(5) 110.3(3)
C(1) -C(10)-C(9) 109.6(3)	C(1) -C(10)-C(19) 109.5(4)
C(2) -C(1) -C(10) 115.2(3)	C(2) -C(3) -C(4) 110.6(4)
C(2) -C(3) -O(3) 108.6(4)	C(3) -C(4) -C(5) 110.1(3)
C(3) -O(3) -C(28) 117.1(5)	C(4) -C(3) -O(3) 109.5(4)
C(4) -C(5) -C(6) 120.6(4)	C(4) -C(5) -C(10) 116.9(4)
C(5) -C(6) -C(7) 127.6(4)	C(5) -C(10)-C(9) 109.9(3)
C(5) -C(10)-C(19) 106.6(4)	C(6) -C(5) -C(10) 122.3(4)
C(6) -C(7) -C(8) 111.3(4)	C(7) -C(8) -C(9) 110.5(4)
C(7) -C(8) -C(14) 109.9(4)	C(8) -C(9) -C(10) 115.2(4)
C(8) -C(9) -C(11) 111.3(4)	C(8) -C(14)-C(15) 115.0(4)
C(8) -C(14)-C(15) 118.1(4)	C(9) -C(8) -C(14) 108.9(4)
C(9) -C(10)-C(19) 111.0(4)	C(9) -C(11)-C(12) 113.0(4)
C(10)-C(9) -C(11) 112.5(3)	C(11)-C(12)-C(13) 111.0(4)
C(12)-C(13)-C(14) 106.6(4)	C(12)-C(13)-C(17) 116.4(4)
C(12)-C(13)-C(18) 111.9(4)	C(13)-C(14)-C(15) 105.6(4)
C(13)-C(17)-C(16) 104.9(4)	C(13)-C(17)-C(20) 118.4(4)
C(14)-C(13)-C(17) 98.8(4)	C(14)-C(13)-C(18) 112.7(4)
C(14)-C(15)-C(16) 101.3(4)	C(15)-C(16)-C(17) 108.0(4)
C(16)-C(17)-C(20) 113.3(4)	C(17)-C(13)-C(18) 109.7(4)
C(17)-C(20)-C(21) 113.4(5)	C(17)-C(20)-C(22) 108.8(4)
C(20)-C(22)-C(23) 113.6(5)	C(21)-C(20)-C(22) 110.7(5)
C(22)-C(23)-C(24) 112.6(6)	C(23)-C(24)-C(25) 118.1(8)
C(24)-C(25)-C(26) 112.7(11)	C(24)-C(25)-C(27) 125.2(14)
C(26)-C(25)-C(27) 121.7(15)	O(3) -C(28)-O(28) 126.1(7)

TABLE 5: Selected Torsion Angles(°) in Cholesteryl Formate

Ring A		Ring B	
C(10)-C(1) -C(2) -C(3)	-56.0	C(10)-C(5) -C(6) -C(7)	2.1
C(1) -C(2) -C(3) -C(4)	62.7	C(5) -C(6) -C(7) -C(8)	11.8
C(2) -C(3) -C(4) -C(5)	-60.0	C(6) -C(7) -C(8) -C(9)	-39.5
C(3) -C(4) -C(5) -C(10)	50.1	C(7) -C(8) -C(9) -C(10)	57.4
C(4) -C(5) -C(10)-C(1)	-42.0	C(8)- C(9) -C(10)-C(5)	-42.7
C(5) -C(10)-C(1) -C(2)	45.0	C(9) -C(10)-C(5) -C(6)	12.5

$C_s^*(1)=14.69$	$C_2^*(1-2)=18.89$	$C_s(5)=22.27$	$C_2(5-6)=2.32$
$C_s(2)=10.58$	$C_2(2-3)=4.58$	$C_s(6)=19.48$	$C_2(6-7)=43.28$
$C_s(3)=4.13$	$C_2(3-4)=13.32$	$C_s(7)=41.71$	$C_2(7-8)=45.20$

$\langle C_s \rangle = 9.8 \pm 3.1$
$\langle C_2 \rangle = 12.3 \pm 4.2$

Ring C		Ring D	
C(11)-C(9) -C(8) -C(14)	-52.2	C(17)-C(13)-C(14)-C(15)	46.4
C(9) -C(8) -C(14)-C(13)	59.1	C(13)-C(14)-C(15)-C(16)	-35.1
C(8) -C(14)-C(13)-C(12)	-60.5	C(14)-C(15)-C(16)-C(17)	9.0
C(14)-C(13)-C(12)-C(11)	56.4	C(15)-C(16)-C(17)-C(13)	19.1
C(13)-C(12)-C(11)-C(9)	-55.5	C(16)-C(17)-C(13)-C(14)	-39.6
C(12)-C(11)-C(9) -C(2)	53.0		

$C_s(8)=5.91$	$C_2(8-9)=5.58$	$C_s(13)=12.29$	$C_2(13-14)=7.82$
$C_s(9)=3.18$	$C_2(9-11)=3.02$	$C_s(14)=23.07$	$C_2(14-15)=49.22$
$C_s(11)=2.94$	$C_2(11-12)=6.34$	$C_s(15)=49.86$	$C_2(15-16)=12.29$
		$C_s(16)=56.43$	$C_2(16-17)=23.07$
		$C_s(17)=41.77$	$C_2(17-13)=36.67$

$\langle C_s \rangle = 4.0 \pm 0.9$
$\langle C_2 \rangle = 5.0 \pm 1.0$

Tail		Chain	
C(13)-C(17)-C(20)-C(21)	-53.6	O(28)-C(28)-O(3) -C(3)	10.2
C(13)-C(17)-C(20)-C(22)	-177.2	C(2) -C(3) -O(3) -C(28)	139.3
C(16)-C(17)-C(20)-C(21)	-176.9	C(28)-O(3) -C(3) -C(4)	-99.8
C(16)-C(17)-C(20)-C(22)	59.4		
C(17)-C(20)-C(22)-C(23)	-173.6		
C(21)-C(20)-C(22)-C(23)	61.2		
C(20)-C(22)-C(23)-C(24)	172.8		
C(22)-C(23)-C(24)-C(25)	178.6		
C(23)-C(24)-C(25)-C(26)	-178.5		
C(23)-C(24)-C(25)-C(27)	8.8		

*$C_s(n)=[\Sigma_{i=1}^{m}(\Theta_i+\Theta_i')^2/m]^{1/2}$, and $C_2(n)=[\Sigma_{i=1}^{m}(\Theta_i-\Theta_i')^2/m]^{1/2}$; where $C_s(n)$ is a measure of the deviations from mirror symmetry about a plane passing through atom n and the diametrically opposed atom o, and $C_2(n-o)$ is a measure of the deviations from twofold symmetry about an axis bisecting bond $(n-o)$. The symmetry related torsion angles are Θ_i and Θ_i', and m is the number of such pairs.

could be located in a subsequent difference Fourier synthesis and the remaining hydrogen atoms were geometrically fixed on the assumption that C-H = 1.0Å and ∢ H-C-H = 109°. The final R value reduced to 0.087 for the 1640 observed reflections. The weighted $R_w = \left[\frac{\Sigma\omega\ (|F_o| - |F_c|)^2}{\Sigma\omega|F_o|^2}\right]^{1/2}$ was 0.098, where ω was $1.000/[\sigma^2(F_o) + 0.0453|F_o|^2]$. The final atomic coordinates and thermal parameters of the non-hydrogen atoms are given in Table 3.

Results and Discussion

The Molecular Structure. The bond distances and angles are in agreement, within experimental error, with those found in other cholesterol esters.[5-16] The bond distances in the tail and the formate group show the apparent shortening which is characteristic of cholesterol esters, and is caused by the high thermal vibrations in these regions. In this case, it is especially pronounced in the C(25)-C(27) bond (1.28 Å) and C(28) = O(28) bond (1.16 Å).

The ring torsion angles, along with the torsion angles within the tail are given in Table 5. Also given are the appropriate mirror plane and the two-fold asymmetry parameters of the ring as defined by Duax and Norton.[21] Rings A and C assume chair conformation, with ring A somewhat distorted. Ring B is a half chair, and ring D is the expected 13β, 14α half chair. The torsion angle C(2)-C(3)-O(3)-C(28) is 139°, so that the carbonyl bond is parallel to the C(3)-H bond. The C(17) side chain is almost fully extended.

The least-squares planes are listed in Table 6. The atoms within ethylenic group are nearly coplanar. The atoms of C(17), C(20), C(22)-C(26) are in a zigzag planar chain and C(21) and C(27) are out of the plane. Steroid nucleus best-plane makes an angle of 55.2° with the formate group and of 45.9° with the plane of C(17) side zigzag chain atoms.

The Molecular Packing. The packing diagram is shown in

TABLE 6: Least-squares Planes in Cholesteryl Formate. The Equation of Plane is Expressed in the form AX + BY + CZ = D where X,Y,Z are in Å and with Respect to Orthogonal Axes

Atoms included in plane	Atoms not included in plane	Distance in Å from the best plane	Given constant
(1) tetracyclic ring system, C(1) through C(17)			
			A = 0.157
			B = −0.922
			C = −0.354
			D = 0.352
(2) ethylenic group, C(4) through C(7) and C(10)			
C(5)		−0.028	A = 0.289
C(6)		−0.006	B = −0.820
C(10)		0.006	C = −0.493
C(4)		0.017	D = 2.300
C(7)		0.011	
(3) C(17) side chain, C(17), C(20), C(22) through C(26)			
C(17)		−0.081	A = 0.581
C(20)		−0.022	B = −0.380
C(22)		0.125	C = −0.720
C(23)		0.037	D = 6.275
C(24)		0.011	
C(25)		−0.043	
C(26)		−0.028	
	C(21)	1.070	
	C(27)	−0.227	

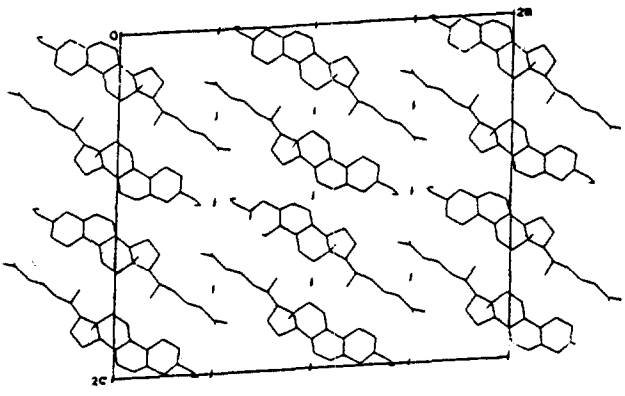

Figure 3a. The crystal structure of cholesteryl formate viewed down the *b*-axis.

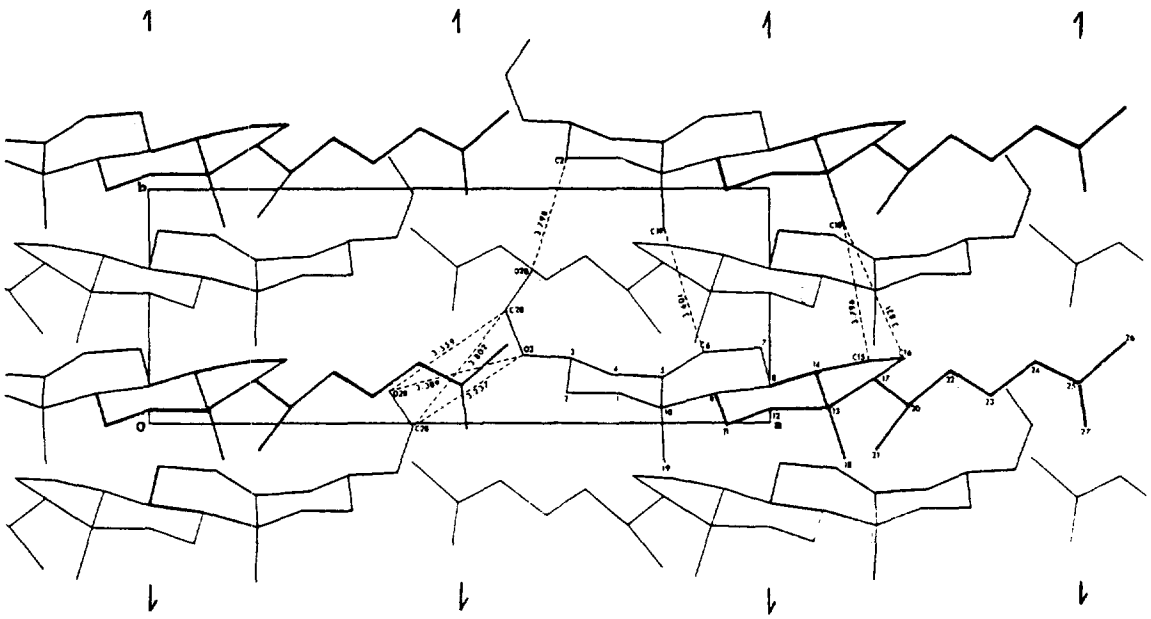

Figure 3b. The crystal structure of cholesteryl formate viewed down the *c*-axis.

Figure 3a and 3b. The plane of the cholesteryl group is parallel to the *ac* plane with the entire molecule orientated parallel to the [$\bar{1}02$] direction.

The most interesting feature is the close proximity of the cholesteryl ring group of one molecule to its translation-related neighbor along the *b* axis. The shortest distance (3.601 Å) is C(6)---C(19). As a result of this packing mode, d_{010} is only 6.073 Å, shortest of all cholesterol esters.

The crystal structure of cholesteryl formate contains antiparallel molecules packed to form monolayers which are parallel to the crystal (100) planes with a thickness $d_{100} = 15.757$ Å. Such monolayers are similar to those of cholesteryl hexanoate,[6] octanoate,[7] oleate[8] and chloroformate.[5] They are called monolayers of type II,[9] so as to distinguish them from the monolayers of type I which occur in cholesteryl nonanoate,[9] laurate[10] and decanoate.[11] At the center of the monolayers of type II there is an efficient packing of antiparallel cholesteryl groups which are related by 2_1 screw axis.

In the cholesteryl formate, the molecules are centered between four screw axes and there is no overlap of the cholesteryl rings within one unit cell as shown in Figure 3a. The cholesteryl tails are loosely packed to form the layer interface region. The formate atoms are closely packed along the 2_1 screw axis and there are four intermolecular contacts less than 3.9 Å, of which shortest (3.237 Å) is C(28)---O(3).

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Thermodynamic Properties of the Polymer Solutions

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A statistical mechanical approach to elucidate the solvent effects on the high polymer solutions has been carried out on the basis of the simple model of liquids improved by Pak. In our works, the partition function of the polymer solutions is formulated by the lattice model and our simple treatment of liquid structures. For the ideal polymer solutions proposed by Flory, thermodynamic functions of the polymer solutions are obtained and equations of mixing properties and partial molar quantities are derived from the presented partition function of the polymer solutions. Partial molar quantities are calculated for the rubber solutions in carbon disulfide, benzene and carbon tetrachloride. Comparisons have been made between our equations and those of Flory's original paper for partial molar properties of the rubber-benzene system. Comparing the experimental data of the osmotic pressure of polystyrene-cyclohexane system with our calculated values and those of Flory's, our values fit to the agreeable degrees better than those of Flory's.