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Crystal Structure of Cholesteryl Ethyl Carbonate

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Cholesteryl ethyl carbonate, $C_{30}O_3H_{50}$, $M_r = 458.7$, monoclinic, $P2_1$, $a = 18.681(2)$, $b = 11.7697(10)$, $c = 13.5656(10)$ Å, $\beta = 105.37(2)°$, $V = 2876.0(4)$ Å^3, $Z = 4$, $D_c = 1.059$ mgm^{-3}, $\mu = 0.506$ mm^{-1}, $F(000) = 1016$, λ (Cu K_α) = 1.5418 Å, final R and wR2 are 0.0727 and 0.2125 respectively.

Keywords: Crystal structure; cholesteryl ethyl carbonate

INTRODUCTION

Crystal structure determination of cholesteryl esters has been under taken by many workers, [1–9] as the structure prefigures the mesogenicity and the molecular arrangement in the mesomorphic state. A knowledge of the properties and structures of cholesterogens in crystalline solid phases and mesophases, particularly of those esters involved in unsaturated fatty carbon chains, may lead to a better understanding of molecular association in arterial fatty deposits [10–12] and further give insight into their involvement in biological functions. Cholesteric mesophases have unusual optical [13], and thermochromic properties which have led to wide technological applications [14]. A number of studies have been made on the structural relationships between crystals [15, 16] and mesophases [17, 18]. The crystal structure studies of a number of cholesteryl derivatives have been reported [19–21].

Presently we have under taken the crystal and molecular structure of cholesterogenic material cholesteryl ethyl carbonate.

EXPERIMENTAL

The colourless crystal obtained from a solution in acetone melts into a cholesteric phase at 83°C and turns into isotropic liquid at 105°C. The accurate cell dimensions and orientation matrix were obtained by a least-squares fit to the setting angles of 25 reflections on Enraf-Nonius computer controlled four circle diffractometer employing CuK_α radiation. Two reflections measured every one hour showed no deterioration of the crystal. Lorentz and polarization corrections were applied. The crystal structure was solved by SHELXS-86 [22] and was refined by full matrix least-squares using SHELXL-93 [23] [3853 unique reflections with $I > 2\sigma(I)$]. The atom C(1) of molecule 1 and C(51) of molecule 2 were refined isotropically and the remaining atoms by anisotropic refinement since we find disorder in the terminal group as is usually found in other cholesteric compounds. The difference Fourier maps were used to locate the positions of hydrogen atoms. However, the hydrogens [H(4A), H(54A)] were fixed in calculated positions (C—H 1.05).986 parameters have been refined using 3853 unique reflections with $R = 0.0727$, $wR2 = 0.2125$. In the final difference map $(\Delta\sigma)_{max} = 0.039$ and $(\Delta\sigma)_{min} = -0.244$, $(\Delta\sigma)_{max} = 0.626$ eÅ^{-3}. All calculations were performed on MicroVax 3100 computer.

RESULTS AND DISCUSSION

The positional parameters and equivalent temperature factors for non-hydrogen atoms are given in Table I. Anisotropic thermal parameters (U_{ij}) for the non-hydrogen atoms are listed in Table II. Table III gives the bond distances and angles of non-hydrogen atoms. Table IV shows selected torsion angles. Figure 1 represents the ORTEP [24] diagram of the molecule with thermal ellipsoid at 42% probability. Figure 2 shows the packing of molecules down b-axis. Figure 3 shows the packing of the molecules viewed down [021].

The dihedral angles between planes are given in Table V. The dihedral angles between the adjacent planes of the steroid molecules are consistent with those observed in steroid structures. The dihedral angle between the least-squares plane through the atoms of the cholestrol ring and that

TABLE I Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) with e.s.d.'s in parentheses for the nonhydrogen atoms. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor

	x	*y*	*z*	*U(eq)*
C(1)	18562(10)	705(23)	4015(15)	244(7)
C(2)	17636(8)	1256(14)	2634(9)	181(4)
C(3)	17937(6)	850(15)	3620(6)	200(7)
C(4)	17362(5)	277(10)	4053(6)	142(3)
C(5)	16658(5)	936(8)	4009(5)	125(2)
C(6)	16108(4)	271(6)	4391(4)	99(2)
C(7)	15414(3)	896(5)	4446(3)	90(1)
C(8)	14988(4)	1282(6)	3380(4)	108(2)
C(9)	14941(3)	189(4)	4988(3)	82(1)
C(10)	15394(3)	−122(5)	6106(3)	90(1)
C(11)	14832(3)	−164(5)	6757(3)	87(1)
C(12)	14082(3)	−134(4)	5968(3)	78(1)
C(13)	14193(3)	655(4)	5123(3)	82(1)
C(14)	14284(4)	1899(4)	5472(4)	99(2)
C(15)	13507(4)	502(6)	4212(4)	104(2)
C(16)	12785(3)	749(7)	4511(4)	109(2)
C(17)	12694(3)	104(5)	5437(4)	90(1)
C(18)	13399(3)	141(4)	6336(3)	79(1)
C(19)	13323(3)	−690(5)	7200(4)	89(1)
C(20)	12586(4)	−618(5)	7374(5)	103(2)
C(21)	11986(4)	−111(5)	6767(5)	104(2)
C(22)	12005(4)	472(6)	5789(4)	100(2)
C(23)	11999(5)	1785(6)	5972(5)	112(2)
C(24)	11310(4)	120(10)	4938(6)	135(3)
C(25)	10571(5)	294(14)	5262(9)	164(5)
C(26)	10603(5)	−398(10)	6165(12)	169(5)
C(27)	11281(4)	−70(7)	7094(6)	119(2)
O(1)	9958(3)	−230(6)	6578(7)	175(3)
C(28)	9484(5)	−1061(9)	6521(6)	122(2)
O(2)	9557(5)	−1952(9)	6222(8)	201(4)
O(3)	8936(3)	−689(6)	6843(5)	137(2)
C(29)	8356(7)	−1457(11)	6870(10)	180(4)
C(30)	7765(6)	−974(12)	7158(9)	171(4)
C(51)	−975(16)	320(31)	10678(23)	311(13)
C(52)	−870(10)	2343(21)	10975(17)	240(8)
C(53)	−622(8)	1253(20)	10900(17)	221(7)
C(54)	−36(8)	1205(26)	10342(10)	274(14)
C(55)	617(5)	1078(16)	10597(9)	191(6)
C(56)	1167(5)	1095(11)	10012(8)	147(3)
C(57)	1973(4)	1247(6)	10515(5)	110(2)
C(58)	2284(4)	255(9)	11227(7)	134(3)
C(59)	2406(3)	1522(5)	9750(4)	91(1)
C(60)	2108(4)	2581(6)	9087(5)	107(2)
C(61)	2746(3)	3130(5)	8794(4)	90(1)
C(62)	3378(3)	2281(4)	9117(3)	76(1)
C(63)	3244(3)	1755(4)	10107(3)	80(1)
C(64)	3449(3)	2589(5)	11022(4)	90(1)
C(65)	3760(3)	711(4)	10353(4)	83(1)
C(66)	4560(3)	1020(4)	10441(4)	80(1)
C(67)	4688(3)	1630(3)	9506(3)	68(1)
C(68)	4156(3)	2639(4)	9196(3)	73(1)

TABLE I (*Contd.*)

	x	*y*	*z*	*U*(*eq*)
C(69)	4216(3)	3129(4)	8170(3)	82(1)
C(70)	4993(3)	3171(4)	8081(3)	79(1)
C(71)	5567(3)	2671(4)	8703(3)	72(1)
C(72)	5511(3)	1948(3)	9609(3)	70(1)
C(73)	5832(3)	2629(5)	10600(3)	87(1)
C(74)	5967(3)	847(4)	9621(3)	79(1)
C(75)	6742(3)	1042(4)	9521(4)	87(1)
C(76)	6719(3)	1689(4)	8552(3)	81(1)
C(77)	6331(3)	2816(4)	8551(3)	82(1)
O(4)	7496(2)	1885(4)	8548(3)	96(1)
C(78)	7627(4)	2117(7)	7642(5)	108(2)
O(5)	7162(3)	2159(8)	6841(3)	150(2)
O(6)	8338(3)	2279(5)	7808(4)	121(1)
C(79)	8590(6)	2506(13)	6924(7)	169(4)
C(80)	9357(7)	2616(13)	7158(9)	174(4)

TABLE II Anisotropic displacement parameters ($Å^2 \times 10^3$) for nonhydrogen atoms with e.s.d's in parentheses. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + \cdots + 2hka^*b^*U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(2)	221(11)	175(10)	147(8)	−9(7)	50(8)	−18(9)
C(3)	147(7)	328(19)	103(5)	62(8)	−5(5)	−105(10)
C(4)	116(5)	181(8)	115(5)	40(5)	6(4)	−46(6)
C(5)	145(6)	120(5)	102(4)	18(4)	16(4)	−30(5)
C(6)	120(4)	100(4)	74(3)	2(3)	19(3)	−18(3)
C(7)	129(4)	76(3)	59(2)	−6(2)	13(2)	−5(3)
C(8)	152(5)	106(4)	69(3)	15(3)	33(3)	16(4)
C(9)	119(4)	69(2)	51(2)	−4(2)	9(2)	−5(2)
C(10)	108(3)	90(3)	60(2)	9(2)	−2(2)	−4(3)
C(11)	104(3)	92(3)	58(2)	8(2)	9(2)	1(3)
C(12)	102(3)	63(2)	59(2)	1(2)	5(2)	−5(2)
C(13)	115(4)	70(2)	51(2)	−3(2)	6(2)	12(2)
C(14)	154(5)	67(3)	80(3)	0(2)	41(3)	6(3)
C(15)	121(4)	120(4)	57(2)	2(3)	1(2)	16(4)
C(16)	112(4)	142(5)	61(2)	0(3)	1(2)	31(4)
C(17)	97(3)	86(3)	76(3)	−12(2)	5(2)	7(3)
C(18)	101(3)	67(2)	59(2)	−1(2)	3(2)	0(2)
C(19)	98(4)	80(3)	86(3)	8(2)	20(3)	−1(3)
C(20)	126(5)	82(3)	100(4)	7(3)	26(3)	−10(3)
C(21)	122(5)	81(3)	104(4)	−9(3)	21(3)	−8(3)
C(22)	108(4)	100(4)	83(3)	−8(3)	9(3)	16(3)
C(23)	137(5)	100(4)	97(4)	2(3)	27(3)	30(4)
C(24)	103(4)	176(8)	115(4)	−31(5)	7(4)	3(5)
C(25)	106(6)	220(13)	154(7)	−43(8)	10(5)	21(7)
C(26)	106(5)	136(7)	273(15)	−78(9)	62(8)	−12(5)
C(27)	100(4)	109(4)	148(6)	−11(4)	34(4)	−3(4)
O(1)	116(4)	135(4)	293(9)	−75(5)	85(5)	−22(4)
C(28)	116(5)	121(5)	119(5)	−24(4)	15(4)	2(5)

TABLE II (*Contd.*)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O(2)	196(7)	143(5)	290(11)	−44(7)	113(8)	−14(5)
O(3)	116(3)	143(4)	153(4)	−12(4)	35(3)	−3(4)
C(29)	205(11)	145(8)	216(12)	−5(9)	98(10)	−34(9)
C(30)	174(8)	186(11)	179(8)	22(8)	95(7)	−13(8)
C(52)	219(15)	237(18)	305(21)	34(18)	139(15)	38(14)
C(53)	154(9)	223(16)	304(20)	−24(16)	95(11)	19(11)
C(54)	149(8)	514(40)	182(11)	140(18)	82(8)	87(16)
C(55)	121(6)	286(17)	190(9)	64(11)	86(7)	21(9)
C(56)	131(6)	172(9)	153(7)	27(6)	62(5)	27(6)
C(57)	120(5)	110(4)	115(4)	5(4)	58(4)	24(4)
C(58)	125(5)	152(7)	150(6)	48(5)	77(5)	20(5)
C(59)	106(4)	85(3)	86(3)	−1(2)	34(3)	10(3)
C(60)	107(4)	112(4)	102(4)	19(3)	28(3)	29(4)
C(61)	108(4)	82(3)	79(3)	8(2)	21(3)	7(3)
C(62)	111(4)	60(2)	56(2)	−6(2)	18(2)	2(2)
C(63)	106(3)	67(2)	70(2)	2(2)	31(2)	8(2)
C(64)	121(4)	81(3)	72(2)	−3(2)	35(3)	15(3)
C(65)	110(4)	63(2)	78(2)	10(2)	31(2)	7(2)
C(66)	98(3)	69(2)	75(2)	21(2)	25(2)	6(2)
C(67)	100(3)	50(2)	51(2)	−3(1)	15(2)	−6(2)
C(68)	106(3)	55(2)	53(2)	−3(2)	15(2)	2(2)
C(69)	115(4)	68(2)	56(2)	11(2)	11(2)	2(2)
C(70)	107(4)	65(2)	64(2)	8(2)	22(2)	−2(2)
C(71)	104(3)	51(2)	57(2)	−4(2)	17(2)	−6(2)
C(72)	93(3)	58(2)	52(2)	0(2)	9(2)	−6(2)
C(73)	111(4)	83(3)	60(2)	−10(2)	9(2)	−13(3)
C(74)	98(3)	64(2)	74(2)	14(2)	19(2)	−2(2)
C(75)	99(3)	71(3)	84(3)	10(2)	17(2)	−3(2)
C(76)	101(4)	72(2)	68(2)	−1(2)	20(2)	−4(2)
C(77)	106(4)	72(3)	68(2)	3(2)	23(2)	−17(2)
O(4)	104(3)	106(3)	80(2)	7(2)	29(2)	−7(2)
C(78)	128(5)	111(4)	92(4)	13(3)	43(4)	2(4)
O(5)	150(4)	225(7)	81(2)	21(3)	40(3)	8(5)
O(6)	122(3)	137(4)	119(3)	18(3)	58(3)	0(3)
C(79)	165(8)	225(13)	140(6)	43(8)	79(6)	−10(8)
C(80)	184(9)	183(10)	184(9)	35(9)	98(8)	11(8)

through the ethyl carbonate chain atoms in molecule 1 is 87.48(0.38)°, while that in molecule 2 of the asymmetric unit is 42.41(0.27)°. The dihedral angles of the tetracyclic ring plane with side chain group plane for molecules 1 and 2 are 12.54° and 16.80° respectively. The two molecules in the unit cell are related by a two fold rotation axis. The A and C rings are in the chair conformation, the ring B is in distortd chair conformation and the ring D has twisted envelope conformation for both molecules. This conformation can be understood by the torsional angles of the atoms of the rings A, B, C and D (Tab. IV). The side chain in both molecules is almost fully extended, as is the case in most of the cholesteryl ester structures. The torsion angles

TABLE III Bond lengths [Å] and angles [deg.] involving nonhydrogen atoms with e.s.d's in parentheses

C(1)–C(3)	1.16(2)
C(2)–C(3)	1.39(2)
C(3)–C(4)	1.513(12)
C(4)–C(5)	1.513(13)
C(5)–C(6)	1.491(10)
C(6)–C(7)	1.510(9)
C(7)–C(8)	1.524(8)
C(7)–C(9)	1.535(8)
C(9)–C(13)	1.556(9)
C(9)–C(10)	1.571(6)
C(10)–C(11)	1.541(8)
C(11)–C(12)	1.520(7)
C(12)–C(18)	1.524(8)
C(12)–C(13)	1.533(7)
C(13)–C(14)	1.534(7)
C(13) – C(15)	1.537(7)
C(15)–C(16)	1.536(9)
C(16)–C(17)	1.515(9)
C(17)–C(18)	1.541(7)
C(17)–C(22)	1.549(9)
C(18)–C(19)	1.561(7)
C(19) – C(20)	1.460(9)
C(20)–C(21)	1.343(9)
C(21)–C(27)	1.496(10)
C(21)–C(22)	1.502(9)
C(22)–C(24)	1.548(9)
C(22)–C(23)	1.565(10)
C(24)–C(25)	1.569(13)
C(25)–C(26)	1.46(2)
C(26)–O(1)	1.470(11)
C(26)–C(27)	1.580(14)
O(1)–C(28)	1.307(11)
C(28)–O(2)	1.145(12)
C(28)–O(3)	1.292(10)
O(3)–C(29)	1.419(12)
C(29)–C(30)	1.39(2)
C(51)–C(53)	1.28(4)
C(52)–C(53)	1.38(3)
C(53)–C(54)	1.49(2)
C(54)–C(55)	1.19(2)
C(55)–C(56)	1.455(12)
C(56)–C(57)	1.490(13)
C(57)–C(59)	1.510(8)
C(57)–C(58)	1.528(11)
C(59)–C(63)	1.536(8)
C(59)–C(60)	1.552(9)
C(60)–C(61)	1.498(9)
C(61)–C(62)	1.520(8)
C(62)–C(68)	1.490(7)
C(62)–C(63)	1.557(6)
C(63)–C(65)	1.542(7)
C(63)–C(64)	1.548(7)
C(65)–C(66)	1.512(8)

TABLE III (*contd.*)

C(66)–C(67)	1.532(6)
C(67)–C(68)	1.533(6)
C(67)–C(72)	1.551(7)
C(68)–C(69)	1.539(6)
C(69)–C(70)	1.489(8)
C(70)–C(71)	1.315(7)
C(71)–C(77)	1.504(7)
C(71)–C(72)	1.522(5)
C(72)–C(73)	1.543(6)
C(72)–C(74)	1.549(7)
C(74)–C(75)	1.507(8)
C(75)–C(76)	1.509(7)
C(76)–O(4)	1.471(7)
C(76)–C(77)	1.511(8)
O(4)–C(78)	1.343(7)
C(78)–O(5)	1.199(8)
C(78)–O(6)	1.301(9)
O(6)–C(79)	1.425(9)
C(79)–C(80)	1.39(2)
C(1)–C(3)–C(2)	127(2)
C(1)–C(3)–C(4)	119.0(14)
C(2)–C(3)–C(4)	112.2(9)
C(3)–C(4)–C(5)	117.1(10)
C(6)–C(5)–C(4)	112.9(7)
C(5)–C(6)–C(7)	116.2(6)
C(6)–C(7)–C(8)	109.7(4)
C(6)–C(7)–C(9)	111.7(4)
C(8)–C(7)–C(9)	113.2(5)
C(7)–C(9)–C(13)	120.8(4)
C(7)–C(9)–C(10)	111.0(5)
C(13)–C(9)–C(10)	103.8(4)
C(11)–C(10)–C(9)	106.6(4)
C(12)–C(11)–C(10)	103.7(4)
C(11)–C(12)–C(18)	118.0(4)
C(11)–C(12)–C(13)	105.0(4)
C(18)–C(12)–C(13)	114.1(4)
C(12)–C(13)–C(14)	111.9(4)
C(12)–C(13)–C(15)	106.3(5)
C(14)–C(13)–C(15)	111.1(5)
C(12)–C(13)–C(9)	100.2(4)
C(14)–C(13)–C(9)	110.2(5)
C(15)–C(13)–C(9)	116.6(4)
C(16)–C(15)–C(13)	111.7(4)
C(17)–C(16)–C(15)	115.0(5)
C(16)–C(17)–C(18)	112.5(5)
C(16)–C(17)–C(22)	113.6(5)
C(18)–C(17)–C(22)	110.7(4)
C(12)–C(18)–C(17)	110.4(4)
C(12)–C(18)–C(19)	111.3(4)
C(17)-C(18)-C(19)	110.4(4)
C(20)-C(19)-C(18)	111.2(5)
C(21)-C(20)-C(19)	126.6(6)
C(20)-C(21)-C(27)	119.3(6)
C(20)-C(21)-C(22)	122.2(6)

TABLE III (*contd.*)

C(27)–C(21)–C(22)	118.4(6)
C(21)–C(22)–C(24)	108.9(6)
C(21)–C(22)–C(17)	111.2(5)
C(24)–C(22)–C(17)	107.3(5)
C(21)–C(22)–C(23)	108.0(5)
C(24)–C(22)–C(23)	110.1(6)
C(17)–C(22)–C(23)	111.5(6)
C(22)–C(24)–C(25)	112.5(6)
C(26)–C(25)–C(24)	108.7(9)
C(25)–C(26)–O(1)	113.0(10)
C(25)–C(26)–C(27)	112.2(9)
O(1)–C(26)–C(27)	103.3(9)
C(21)–C(27)–C(26)	109.8(7)
C(28)–O(1)–C(26)	119.2(7)
O(2)–C(28)–O(3)	127.6(10)
O(2)–C(28)–O(1)	124.2(10)
O(3)–C(28)–O(1)	108.2(8)
C(28)–O(3)–C(29)	118.2(8)
C(30)–C(29)–O(3)	114.6(11)
C(51)–C(53)–C(52)	131(2)
C(51)–C(53)–C(54)	105(2)
C(52)–C(53)–C(54)	112(2)
C(55)–C(54)–C(53)	134.0(14)
C(54)–C(55)–C(56)	131.2(12)
C(55)–C(56)–C(57)	121.7(9)
C(56)–C(57)–C(59)	111.8(6)
C(56)–C(57)–C(58)	111.5(7)
C(59)–C(57)–C(58)	114.5(5)
C(57)–C(59)–C(63)	120.6(5)
C(57)–C(59)–C(60)	113.3(5)
C(63)–C(59)–C(60)	102.6(5)
C(61)–C(60)–C(59)	108.2(5)
C(60)–C(61)–C(62)	104.6(5)
C(68)–C(62)–C(61)	120.3(4)
C(68)–C(62)–C(63)	115.2(4)
C(61)–C(62)–C(63)	102.7(4)
C(59)–C(63)–C(65)	116.8(4)
C(59)–C(63)–C(64)	112.3(4)
C(65)–C(63)–C(64)	108.9(4)
C(59)–C(63)–C(62)	100.5(4)
C(65)–C(63)–C(62)	105.7(4)
C(64)–C(63)–C(62)	112.2(4)
C(66)–C(65)–C(63)	111.9(4)
C(65)–C(66)–C(67)	114.6(4)
C(66)–C(67)–C(68)	111.0(4)
C(66)–C(67)–C(72)	114.0(3)
C(68)–C(67)–C(72)	113.1(3)
C(62)–C(68)–C(67)	110.5(4)
C(62)–C(68)–C(69)	110.2(4)
C(67)–C(68)–C(69)	109.9(4)
C(70)–C(69)–C(68)	113.1(4)
C(71)–C(70)–C(69)	125.5(4)
C(70)–C(71)–C(77)	120.2(4)
C(70)–C(71)–C(72)	123.3(4)
C(77)–C(71)–C(72)	116.5(4)

TABLE III (*contd.*)

C(71)–C(72)–C(73)	108.6(3)
C(71)–C(72)–C(74)	108.6(4)
C(73)–C(72)–C(74)	109.8(4)
C(71)–C(72)–C(67)	109.9(3)
C(73)–C(72)–C(67)	110.6(4)
C(74)–C(72)–C(67)	109.2(3)
C(75)–C(74)–C(72)	114.3(4)
C(74)–C(75)–C(76)	110.4(4)
O(4)–C(76)–C(75)	106.4(4)
O(4)–C(76)–C(77)	109.6(4)
C(75)–C(76)–C(77)	110.3(4)
C(71)–C(77)–C(76)	111.9(4)
C(78)–O(4)–C(76)	117.0(5)
O(5)–C(78)–O(6)	127.7(6)
O(5)–C(78)–O(4)	125.0(7)
O(6)–C(78)–O(4)	107.2(6)
C(78)–O(6)–C(79)	115.6(7)
C(80)–C(79)–O(6)	112.1(9)

TABLE IV Selected torsion angles [deg.]

Molecule 1		
143.94	(1.96)	C1–C3–C4–C5
−51.59	(1.63)	C2–C3–C4–C5
−179.22	(0.39)	C6–C7–C9–C13
−54.77	(0.58)	C8–C7–C9–C13
58.98	(0.53)	C6–C7–C9–C10
−176.57	(0.48)	C8–C7–C9–C10
Ring D		
16.23	(0.53)	C13–C9–C10–C11
11.68	(0.55)	C9–C10–C11–C12
−36.22	(0.51)	C10–C11–C12–C13
46.07	(0.44)	C11–C12–C13–C9
−37.19	(0.44)	C10–C9–C13–C12
Ring C		
−61.43	(0.49)	C18–C12–C13–C15
56.73	(0.64)	C12–C13–C15–C16
−52.65	(0.78)	C13–C15–C16–C17
46.76	(0.72)	C15–C16–C17–C18
57.40	(0.51)	C13–C12–C18–C17
−47.41	(0.58)	C16–C17–C18–C12
Ring B		
60.81	(0.59)	C22–C17–C18–C19
−42.79	(0.59)	C17–C18–C19–C20
13.33	(0.87)	C18–C19–C20–C21
−0.11	(1.00)	C19–C20–C21–C22
16.92	(0.80)	C20–C21–C22–C17
−46.67	(0.66)	C18–C17–C22–C21

TABLE IV (*contd.*)

Ring A		
−48.23	(0.78)	C27–C21–C22–C24
51.82	(1.11)	C21–C22–C24–C25
−59.98	(1.30)	C22–C24–C25–C26
59.46	(1.10)	C24–C25–C26–C27
48.21	(0.94)	C22–C21–C27–C26
−53.62	(0.98)	C25–C26–C27–C21
Molecule 2		
−107.87	(4.20)	C51–C53–C54–C55
104.96	(4.03)	C52–C53–C54–C55
177.83	(0.68)	C56–C57–C59–C63
−54.11	(0.86)	C58–C57–C59–C63
55.78	(0.86)	C56–C57–C59–C60
−176.15	(0.67)	C58–C57–C59–C60
Ring D		
18.89	(0.59)	C63–C59–C60–C61
9.98	(0.59)	C59–C60–C61–C62
−34.73	(0.50)	C60–C61–C62–C63
−39.13	(0.47)	C60–C59–C63–C62
46.26	(0.45)	C61–C62–C63–C59
Ring C		
−59.11	(0.48)	C68–C62–C63–C65
55.26	(0.50)	C62–C63–C65–C66
−55.14	(0.55)	C63–C65–C66–C67
50.60	(0.50)	C65–C66–C67–C68
57.68	(0.44)	C63–C62–C68–C67
−50.04	(0.42)	C66–C67–C68–C62
Ring B		
58.64	(0.41)	C72–C67–C68–C69
−40.17	(0.50)	C67–C68–C69–C70
11.70	(0.66)	C68–C69–C70–C71
1.23	(0.69)	C69–C70–C71–C72
15.31	(0.53)	C70–C71–C72–C67
−45.20	(0.41)	C68–C67–C72–C71
Ring A		
−46.23	(0.45)	C77–C71–C72–C74
49.25	(0.45)	C71–C72–C74–C75
−57.20	(0.52)	C72–C74–C75–C76
58.47	(0.53)	C74–C75–C76–C77
51.02	(0.47)	C72–C71–C77–C76
−55.16	(0.51)	C75–C76–C77–C71

for the bonds along the chains C(7)–C(9) through C(4)–C(3) and C(57)–C(59) through C(54)–C(53) are as given in Table IV. The pseudo-torsion angles of C(22)–C(13) and C(72)–C(63) are 4.49° and 4.63°.

The conformation at the ester linkage is slightly different in the two molecules. The C(28)–O(1)–C(26)–C(27) torsion angle has a value of

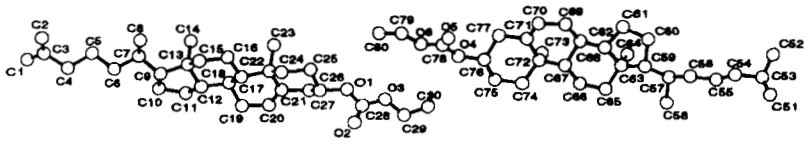

FIGURE 1 Projection of the molecules on the best plane.

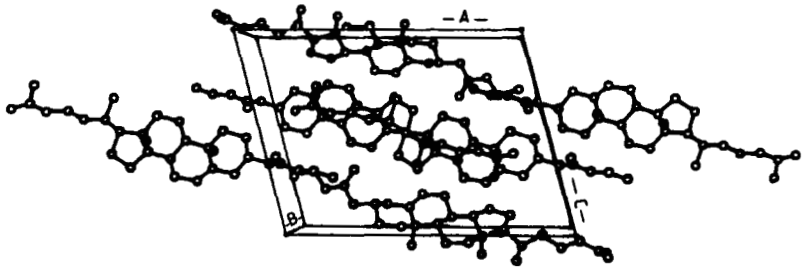

FIGURE 2 Packing of the molecules down b axis.

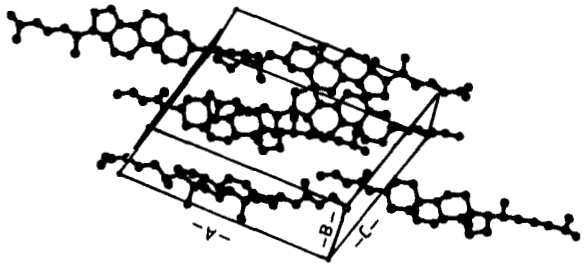

FIGURE 3 Packing of the molecules viewed down [021].

$-126.46(0.92)^\circ$ in molecule 1, where as it is $-81.22(0.59)^\circ$ for C(78)–O(4)–C(76)–C(77) in molecule 2. The effective steroid lengths taken from C(26) to C(10) and C(76) to C(60) are respectively 8.978Å and 8.896Å for the two molecules and are well within the expected range (8.86–9.01Å). The ethylenic linkages viz. C(21) and C(20) and C(71) and C(70) in the two molecules are within the standard deviations of the accepted value of 1.34Å. Some of the bond lengths, in particular, C(3)–C(1) and C(3)–C(2) for molecule 1 and C(55)–C(54), C(53)–C(51) and C(53)–C(52) for molecule 2 appear to be significantly different from the expected values. This effect could arise from large thermal disorder of the two side chains. The ring junctions B–C and C–D are trans where as the junction A–B is quasitrans. The main

TABLE V The dihedral angles between planes

	Plane 1	*Plane 2*	*Dihedral angles [deg.]*
Molecule 1	A1	A2	129.46(0.74)
	B3C1	B2	45.76(0.37)
	B3C1	C2	48.64(0.36)
	C3D1	C2	47.19(0.35)
	C3D1	D2	47.00(0.34)
	C3D1	D3	31.65(0.33)
	A	B	19.87(0.26)
	B	C	9.15(0.18)
	C	D	7.49(0.22)
Molecule 2	A1	A2	128.96(0.37)
	B3C1	B2	42.49(0.29)
	B3C1	C2	48.72(0.28)
	C3D1	C2	45.40(0.32)
	C3D1	D2	47.17(0.35)
	C3D1	D3	30.75(0.31)
	A	B	22.45(0.13)
	B	C	8.90(0.10)
	C	D	6.99(0.17)

where

Molecule 1

A1:C(25), C(26), C(27)
A2:C(24), C(25), C(27), C(21)
B2: C(20),C(19), C(17), C(22)
B3C1: C(19), C(18), C(17) C(16)
C2:C(18), C(16), C(15), C(12)
C3D1: C(15),C(13), C(12),C(11)
D2:C(13), C(11), C(10), C(9)
D3:C(12), C(11), C(10), C(9)
A:C(24), C(25),C(26),C(27), C(21), C(22)
B:C(21),C(20),C(19), C(18), C(17), C(22)
C:C(18), C(17), C(16), C(15), C(13), C(12)
D:C(13), C(12), C(11), C(10), C(9)

Molecule 2

A1: C(75), C(76), C(77)
A2: C(74), C(75), C(77), C(71)
B2: C(70), C(69), C(67), C(72)
B3C1:C(69), C(68), C(67), C(66)
C2: C(68), C(66), C(65), C(62)
C3D1:C(65), C(63), C(62), C(61)
D2: C(63), C(61), C(60), C(59)
D3: C(62), C(61), C(60), C(59)
A:C(74), C(75), C(76),C(77), C(71) ,C(72)
B:C(71), C(70), C(69), C(68), C(67), C(72)
C:C(68), C(67), C(66), C(65), C(63), C(62)
D:C(63), C(62), C(61), C(60), C(59)

conformational difference in the steriod rings A and B is in the twist at the ester linkages.

The crystal structure of cholesteryl ethyl carbonate consists of molecules stacked around 2_1 axes so that they are antiparallel. The space group $P2_1$ satisfies the requirement for a cholesterogen. The structure contains two distinct molecules in the asymmetric unit that form separate stacks with similar orientations and differing degrees of steriod overlap, as in the case of cholestryl acetate [1]. The molecules form stacks with steriod overlapping when viewed along [021]. In addition to this, layering of molecules is also seen with molecules packed head to head within each layer and tail to tail between alternate layers.

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