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Crystal Structure of Cholesteryl Perfluoropropionate at 173 K

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The molecular structure of cholesteryl perfluoropropionate(CPFP) was determined by X-ray analysis. The side chain at C(17) has an extended conformation, while the perfluoropropionate chain at C(3) is disordered in a bent conformation. The molecules, the best planes through the tetracyclic ring-system of which are nearly parallel to the ac plane, form a layered structure.

In the previous works[1,2] on phase transitions in a series of cholesteryl fluoroalkanoates([$C_{27}H_{45}OCO(CF_2)_mCF_3$] and [$C_{27}H_{45}OCO(CF_2)_nCF_2H$]), it was found that the number of mesophases of cholesteryl fluoroalkanoates is generally smaller than that of the corresponding cholesteryl n-alkanoates; the title compound has two transition points near 148 and 128 K without producing a mesophase, while cholesteryl n-propionate has a cholesteric phase. The crystal structure analysis of CPFP was undertaken to clarify the relationship between structural characteristics and phase transitions.

In the structure of CPFP at room temperature, the large thermal vibration and conformational disorder obscured the atomic details of perfluoropropionate chain.[3] The low-temperature study, therefore, was carried out to give more accurate atomic

parameters of the perfluoropropionate chain. The conformational structure of the chain was revealed to be disordered even at the low temperature.

Colorless crystals of CPFP were synthesized by the same procedure as described previously[2] and recrystallized by very slow evaporation from an acetone solution. The cell dimensions and diffraction intensities were measured at 173 K on a Rigaku four-circle diffractometer equipped with a Rigaku low temperature device(liquid nitrogen as the coolant) and Ni-filtered CuKα radiation. Among 2317 independent reflections with 2θ values up to 120°, 2053 with $|F_o|>2\sigma(F_o)$ were used in structure refinement.

Crystal data were as follows: $C_{30}H_{45}O_2F_5$, F.W.=532.7, monoclinic, space group $P2_1$, Z=2, a=13.294(2), b=9.158(1), c=12.362(1) Å, β=104.91(1)°, V=1454.3(3) Å^3, D_x=1.217 Mgm^{-3}(173 K), D_m=1.17 Mgm^{-3}(294 K).

An effort to determine the structure with the MULTAN 80[4] has come to nothing. A set of the cholesteryl coordinates of cholesteryl 2,2,3,3-tetrafluoropropionate[5] was adopted as the parameters of trial model of the isomorphous CPFP. In the difference electron density, some atoms of the perfluoropropionate chain were so highly disordered that the two chain conformations with the least R values were obtained by rotating the geometry about C(28)-C(29) bond. Keeping the positional parameters of the disordered chain obtained above to be fixed and occupancy factor to be 0.5, the structure parameters were refined by the block-diagonal least-squares method. The final R value was 0.12.

Molecular Structure. The perspective view of CPFP is depicted in Fig.1. Bond lengths and angles of non-hydrogen atoms are shown in Table 1. Those of cholesteryl moiety agree fairly well with those of other cholesteryl derivatives.[6] The bond lengths of the C(25)-C(26) single bond(1.46 Å) and C(5)-C(6) double bond(1.32 Å) are shorter than their respective normal bond lengths. The improper torsion angle C(19)-C(10)--C(13)-C(18) is -9°. It is a measure of the twist within the tetracyclic ring-system. In other related structures[7] the magnitude of this angle is found in the range of 5° to 18°. The chain at C(17) has an extended conformation as shown in Table 2, while the disordered perfluoropropionate chain takes a bent conformation as in the corresponding chain of cholesteryl δ-monohydrofluoropentanoate.[8] The torsion angle O(1)-C(28)-C(29)-C(30) is 2.5° in the model 1 and -35° in the model 2.

Crystal Structure. The crystal structure is shown in Fig.2. The molecules,

the best planes through the tetracyclic ring-system of which are nearly parallel to the ac plane, form a layered structure. Each layer is composed of rows of molecules packed head to tail within each row, and with molecular long axes parallel to the [2 0 1] direction. There are no intermolecular contacts shorter than the van der Waals distance except for the disordered perfluoropropionate chain.

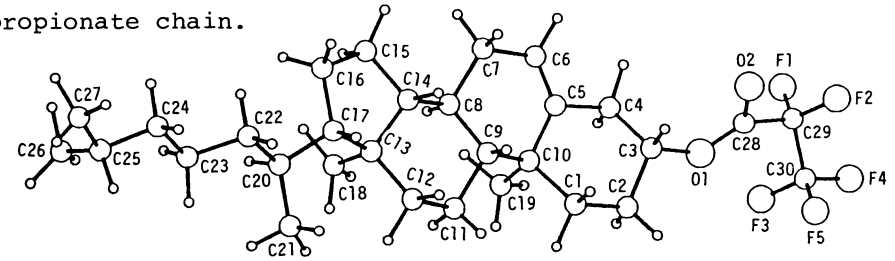

Fig.1. Perspective view of CPFP(model 2).

Table 1. Bond lengths(Å) and angles(°) of non-hydrogen atoms

C(1) -C(2)	1.55(2)	C(8) -C(9)	1.52(2)	C(15)-C(16)	1.56(2)	C(24)-C(25)	1.54(3)
C(2) -C(3)	1.51(2)	C(9) -C(10)	1.55(2)	C(16)-C(17)	1.56(2)	C(25)-C(26)	1.46(3)
C(3) -C(4)	1.53(2)	C(10)-C(19)	1.54(2)	C(17)-C(13)	1.56(2)	C(25)-C(27)	1.52(3)
C(4) -C(5)	1.56(2)	C(9) -C(11)	1.55(2)	C(13)-C(18)	1.55(2)	C(3) -O(1)	1.50(2)
C(5) -C(10)	1.53(2)	C(11)-C(12)	1.55(2)	C(17)-C(20)	1.54(2)	O(1) -C(28)	1.30(2)
C(10)-C(11)	1.58(2)	C(12)-C(13)	1.53(2)	C(20)-C(21)	1.49(2)	C(28)-O(2)	1.19(3)
C(5) -C(6)	1.32(2)	C(13)-C(14)	1.54(2)	C(20)-C(22)	1.55(2)	C(28)-C(29)	1.52(2)
C(6) -C(7)	1.51(2)	C(14)-C(8)	1.51(2)	C(22)-C(23)	1.54(2)	C(29)-C(30)	1.54
C(7) -C(8)	1.55(2)	C(14)-C(15)	1.54(2)	C(23)-C(24)	1.53(2)	C -F	1.32

C(10)-C(1) -C(2)	114(1)	C(10)-C(9) -C(11)	113(1)	C(17)-C(20)-C(21)	114(1)
C(1) -C(2) -C(3)	108(1)	C(9) -C(11)-C(12)	112(1)	C(17)-C(20)-C(22)	109(1)
C(2) -C(3) -C(4)	113(1)	C(11)-C(12)-C(13)	111(1)	C(21)-C(20)-C(22)	112(1)
C(3) -C(4) -C(5)	109(1)	C(12)-C(13)-C(14)	105(1)	C(20)-C(22)-C(23)	114(1)
C(4) -C(5) -C(10)	117(1)	C(13)-C(14)-C(8)	115(1)	C(22)-C(23)-C(24)	113(1)
C(5) -C(10)-C(1)	110(1)	C(14)-C(8) -C(9)	111(1)	C(23)-C(24)-C(25)	117(1)
C(10)-C(5) -C(6)	124(1)	C(13)-C(14)-C(15)	104(1)	C(24)-C(25)-C(26)	111(2)
C(5) -C(6) -C(7)	125(1)	C(14)-C(15)-C(16)	104(1)	C(24)-C(25)-C(27)	109(2)
C(6) -C(7) -C(8)	112(1)	C(15)-C(16)-C(17)	106(1)	C(26)-C(25)-C(27)	113(2)
C(7) -C(8) -C(9)	111(1)	C(16)-C(17)-C(13)	105(1)	C(2) -C(3) -O(1)	106(1)
C(8) -C(9) -C(10)	112(1)	C(17)-C(13)-C(14)	101(1)	C(4) -C(3) -O(1)	107(1)
C(9) -C(10)-C(5)	110(1)	C(12)-C(13)-C(18)	112(1)	C(3) -O(1) -C(28)	116(1)
C(1) -C(10)-C(19)	108(1)	C(17)-C(13)-C(18)	109(1)	O(1) -C(28)-C(29)	121(1)
C(5) -C(10)-C(19)	108(1)	C(14)-C(13)-C(18)	112(1)	O(1) -C(28)-O(2)	130(1)
C(9) -C(10)-C(19)	113(1)	C(12)-C(13)-C(17)	117(1)	C(29)-C(28)-O(2)	108(1)
C(1) -C(10)-C(9)	107(1)	C(13)-C(17)-C(20)	118(1)	C(28)-C(29)-C(30)	109.5
C(8) -C(9) -C(11)	112(1)	C(16)-C(17)-C(20)	114(1)	F -C -F	109.5
				F -C -C	109.5

Table 2. Torsion angles(°)

C(13)-C(17)-C(20)-C(22)	-179	C(17)-C(20)-C(22)-C(23)	167
C(20)-C(22)-C(23)-C(24)	-178	C(22)-C(23)-C(24)-C(25)	-171
C(23)-C(24)-C(25)-C(26)	-59	C(23)-C(24)-C(25)-C(27)	177

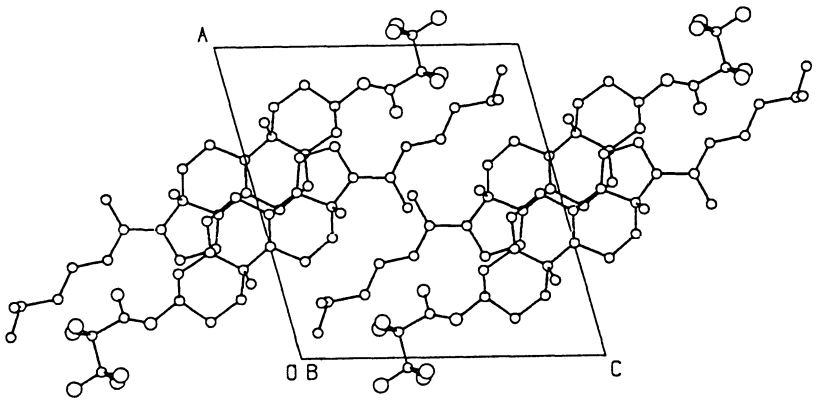

Fig.2. Crystal structure of CPFP(model 2) along the b axis.

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