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Cholesteryl isobutylcarbonate

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Key indicators

Single-crystal X-ray study
T = 173 K
Mean σ(C–C) = 0.005 Å
Disorder in main residue
R factor = 0.058
wR factor = 0.169
Data-to-parameter ratio = 8.6

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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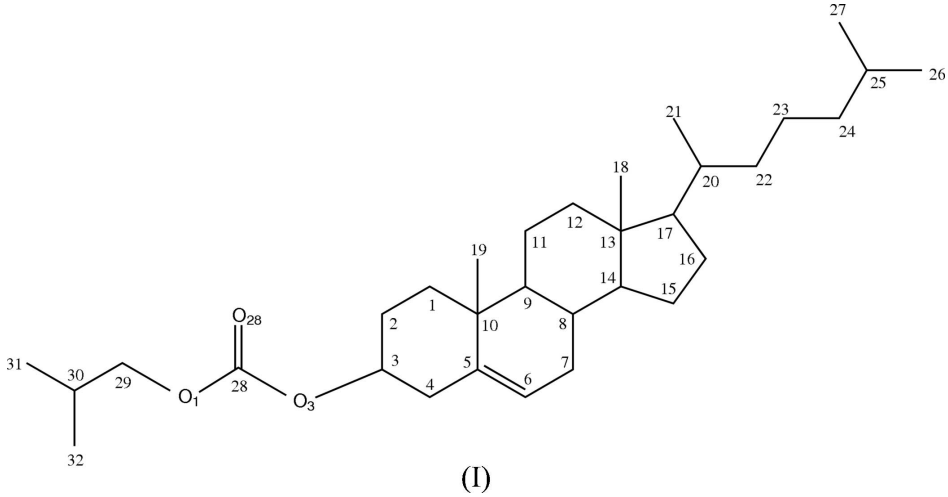
Cholesteryl isobutylcarbonate, $C_{32}H_{54}O_3$, contains two molecules (*A* and *B*) in the asymmetric unit. The isobutylcarbonate chain of molecule *A* and the isoprenoid tail of molecule *B* are each conformationally disordered over two positions. The two distinct molecules form separate stacks along the screw axes so that they are arranged in an antiparallel array, forming monolayers with a thickness of d_{001} = 19.412 Å. The central regions of the monolayers are characterized by efficient molecular packing and are separated by interface regions, which are more loosely packed.

Comment

A series of crystal structures of the esters and carbonates of cholesterol (Ahn & Park, 1990; Kang *et al.*, 1985; Yun *et al.*, 1989; Park & Shin, 2002; Park, 2004*a*,*b*) has been examined in order to obtain structural information relevant to the liquid crystalline phases and the possible modes of association of the cholesterol derivatives themselves, as well as of other substances in biological systems (Abrahamsson *et al.*, 1977). An examination of the unit-cell parameters of the cholesterol derivatives suggests that the majority of the derivatives might have one of three common crystal packing arrangements (Craven, 1986; Craven & DeTitta, 1976; Guerina & Craven, 1979; Suh *et al.*, 1988; Park & Craven, 1981). However, the crystal data of cholesteryl isobutylcarbonate, (I), obtained in this study indicate that this carbonate belongs to none of these three crystal structure types. Therefore, the primary aim of this study was to obtain structural information on the conformation and the type of molecular interactions.



(I)

Cholesteryl isobutylcarbonate contains two molecules (*A* and *B*) in the asymmetric unit. The bond lengths and angles agree well with those of other cholesterol derivatives. The conformations are quite similar for the tetracyclic ring systems in molecules *A* and *B*. The selected torsion angles in Table 1 are for the cholesteryl tails and carbonate chains, where the major differences in conformation occur. Because of the weak intermolecular forces in the non-polar cholesteryl isobutylcarbonate structure, there appears to be conformational and dynamic disorder. These effects are particularly severe in the tail at C17 and also in the carbonate chain. The isobutylcarbonate chain of molecule *A* (C28–C31/O1/O28) and the C17 isoprenoid tail of molecule *B* (C20–C27) are conformationally disordered over two positions. The C17–C26 tail of the two molecules is almost fully extended, as in most cholesterol derivatives. There are differences involving the last four atoms (C24–C27). The terminal isopropyl group of molecule (*A*) has a (−)-*gauche* conformation, but that of molecule (*B*) has a (+)-*gauche* conformation. The conformation at the carbonate chain in the two molecules is different; the carbonate chains of both molecules are fully extended.

The crystal structure of cholesteryl isobutylcarbonate consists of antiparallel molecules arranged to form monolayers that are parallel to the crystal plane (001), with a thickness of d_{001} = 19.412 Å. Each layer comprises a row of twofold screw-related pairs of molecules *A* and molecules *B*, packed tail to tail. The monolayers are regions of closely packed molecules that are separated by interface regions where the atoms are more loosely packed. A significant level of cholesteryl–alkyl packing is present at the centre of the monolayers. These are between the *A*-cholesteryl and the first part of the *A*-isoprenoid tails (C20–C23), *B*-cholesteryl and *B*-isoprenoid tails, *B*-isoprenoid and a part of the *A*-cholesteryl, and *A*-isoprenoid and a part of the *B*-cholesteryl groups. The isobutylcarbonate chains of both molecules *A* and *B* as well as the second part of the isoprenoid tails (C24–C27) of molecules *A*, are loosely packed to form a monolayer interface region. In this crystal structure, the C17 isoprenoid tails do not pack with each other.

As expected, the crystals do not belong to any of the three main crystal structure types, but have a structure similar to that of cholesteryl isobutyrate (Kim *et al.*, 1989). Both crystal structures form monolayers. The main structural differences are the packing mode and the degree of overlap of the cholesteryl ring systems at the centre of the monolayers, with more efficient cholesteryl packing in the isobutyrate than in the isobutylcarbonate. Most of the layered structures show liquid crystalline states (Barrall, 1979), but these were not observed in the crystals of cholesteryl isobutylcarbonate and cholesteryl isobutyrate.

Experimental

The title compound was obtained from Tokyo Kasei Kogyo Co. Ltd. Crystals were obtained by recrystallization from an acetone solution.

Crystal data

$C_{32}H_{54}O_3$
M_r = 486.75
Monoclinic, $P2_1$
a = 15.005 (3) Å
b = 10.2992 (19) Å
c = 19.602 (4) Å
β = 97.984 (3)°
V = 3000.0 (10) Å^3
Z = 4
D_x = 1.078 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4364 reflections
θ = 2.4–28.1°
μ = 0.07 mm^{-1}
T = 173 (2) K
Block, colourless
0.75 × 0.65 × 0.43 mm

Data collection

Bruker SMART CCD area-detector diffractometer
ω scans
Absorption correction: none
16321 measured reflections
6790 independent reflections
5207 reflections with $I > 2\sigma(I)$
R_{int} = 0.036
θ_{max} = 27.0°
$h = -9 \rightarrow 19$
$k = -13 \rightarrow 13$
$l = -24 \rightarrow 25$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.058
$wR(F^2)$ = 0.169
S = 1.04
6790 reflections
788 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1004P)^2 + 0.2345P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.003
$\Delta\rho_{max}$ = 0.31 e Å^{-3}
$\Delta\rho_{min}$ = −0.22 e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.0021 (9)

Table 1
Comparison of selected torsion angles (°).

	Molecule *A*	Molecule *B*
C2—C3—O3—C28	72.4 (7)[a] 105.5 (12)[b]	137.3 (4)
C3—O3—C28—O1	−178.4 (6) −173.3 (13)	−171.9 (3)
C3—O3—C28—O28	2.5 (13) 2 (4)	4.6 (7)
O3—C28—O1—C29	−178.1 (8) 177.2 (16)	175.9 (4)
C28—O1—C29—C30	103.8 (11) 174.0 (17)	−158.8 (4)
O1—C29—C30—C31	176.9 (11) −177.4 (18)	178.9 (4)
O1—C29—C30—C32	−55.3 (14) 70.6 (19)	−56.1 (10)
C13—C17—C20—C21	−55.3 (4)	−77.8 (6)[c] −60.7 (9)[d]
C13—C17—C20—C22	−177.6 (3)	160.2 (7) −178.8 (9)
C17—C20—C22—C23	−165.9 (3)	179.5 (8) −173.8 (11)
C20—C22—C23—C24	179.2 (3)	168.9 (10) −173.3 (16)
C22—C23—C24—C25	176.3 (5)	−178.6 (10) 173.3 (18)
C23—C24—C25—C26	−173.0 (5)	170.1 (9) 167.1 (19)
C23—C24—C25—C27	69.8 (7)	−66.4 (12) −67 (2)

Occupancy factors: (*a*) 0.600 (8), (*b*) 0.400 (8), (*c*) 0.621 (8), (*d*) 0.379 (7).

Because of the lack of significant anomalous scattering, Friedel pairs could not be used to determine the absolute configuration. Therefore, they were merged before the final refinement. The absolute configuration was assigned on the basis of the known configuration of the cholesteryl hexanoate molecule. All H atoms were placed in calculated positions in a riding model, with C—H distances

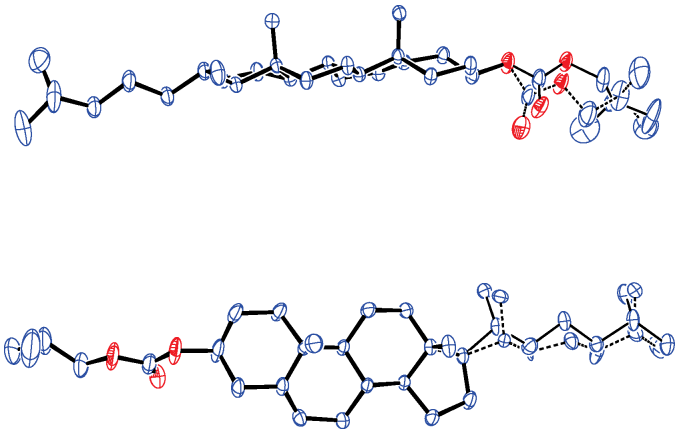


Figure 1
The molecular conformations of the two crystallographically independent molecules of cholesteryl isobutylcarbonate. The dashed lines indicate the bonds of the minor disorder components of the molecules. Displacement ellipsoids are drawn at the 30% probability level and H atoms have been omitted for clarity.

in the range 0.95–1.00 Å and with U_{iso}(H) = 1.2U_{eq}(C) or 1.5U_{eq}(C) for the methyl groups.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT-Plus* (Bruker, 1999); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996); software used to prepare material for publication: *SHELXL97*.

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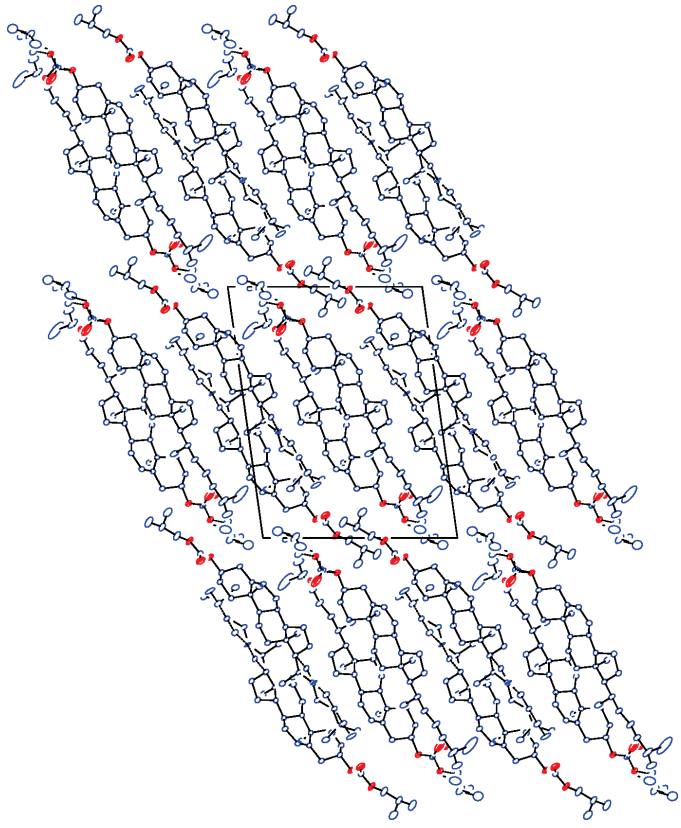

Figure 2
The crystal packing viewed down the *b* axis. The *c* axis is horizontal. H atoms have been omitted.

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