al., 1995) and the crystals (I*a*) with crystals (II). The structure of (I) was solved by taking the published coordinates of the non-H atoms (Mazurek *et al.*, 1995). The structure of (II) was solved by direct methods (*SHELXS*86; Sheldrick, 1990) and its refined coordinates were used as a starting model for (I*a*). In the structure of (II) we noted rather high values for the anisotropic displacement parameters of the atoms forming the tolyl groups, especially the value of 0.284 (10) for U_{11} of C69. We tried unsuccessfully to develop a satisfactory disorder model for this group.

Although compound (II) has a higher value of μ than compound (I), an absorption correction was applied to the latter only: this was because the much larger crystal results in a higher value of μR (where R is the mean crystal radius) for (I) (*ca* 0.8) compared with that for (II) (0.4).

For all compounds, data collection: *KM*4 (Kuma Diffraction, 1987); cell refinement: *KM*4; data reduction: *KM*4; program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *ORTEP*II (Johnson, 1976)

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry, together with a structural diagram of (I*a*), have been deposited with the IUCr (Reference: BM1069). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Redetermination of Cholesteryl *p*-Toluenesulfonate at 150 K

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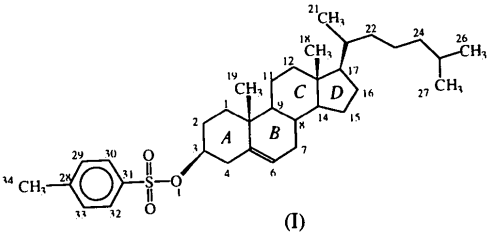
Abstract

Compared to a previous room-temperature study, the apparent shortening of the bond lengths in the C17 side chain of cholesteryl *p*-toluenesulfonate, $C_{34}H_{52}O_3S$, is much less pronounced at 150 K, and the uncertainties associated with the molecular geometry are much improved.

Comment

Room-temperature X-ray studies of cholesteryl derivatives may show bond-length anomalies or disorder in the C17 side chain (El-Shora, Palmer, Singh, Bhardwaj & Paul, 1984; Buchanan, Cox & Wardell, 1996*a*). We have recently used cholesteryl *p*-toluenesulfonate in the synthesis of metallated steroids (Buchanan, Cox & Wardell, 1996*b*) and have observed unusual geometries in this chain. The previously determined room-temperature crystal structure of the title compound (I) (Chandross & Bordner, 1977) exhibits such features but geometrical uncertainties are high. The current low-temperature study was performed to obtain a better molecular geometry of the steroid. The R value has improved from 0.092 to 0.049, the bond length uncertainties have decreased by a factor of about three and the apparent shortening of C—C bonds in the C17 side chain is less obvious at 150 K. For example, C24—C25 is 1.405 (26) Å at room temperature and 1.496 (7) Å at 150 K; the corresponding values for C25—C26 are 1.479 (32) and 1.505 (7) Å, respectively. It is probable that high anisotropic displacement parameters caused librational shortening of the C—C bond lengths in the room-temperature study.



(I)

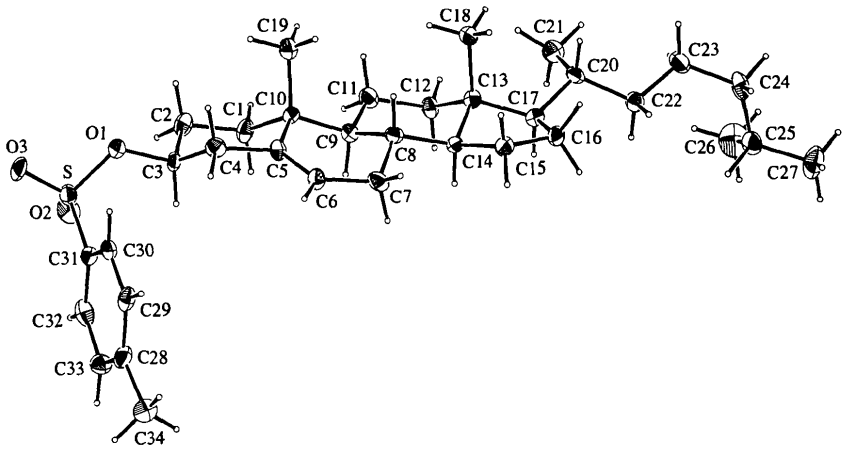


Fig. 1. The atomic arrangement in the molecule. Displacement ellipsoids are shown at the 50% probability level.

The tosylate group is β to the cholesteryl moiety with H3α and ring conformations are *A* chair, *B* half-chair (the best plane is through C10, C5, C6 and C7 with C8β and C9α), *C* chair, and *D* half-chair with C13β and C14α. The S atom is in a distorted tetradehral environment with bond lengths and valence angles as given in Table 2. The cell volume at 150 K is 4.1% smaller than that at room temperature.

Experimental

Cholesteryl *p*-toluenesulfonate, was produced by tosylation of cholesterol, as described by Wallis, 1937 and recrystallized from acetone.

Crystal data

$C_{34}H_{52}O_3S$
M_r = 540.82
Monoclinic
$P2_1$
a = 12.893 (4) Å
b = 6.215 (2) Å
c = 18.800 (8) Å
β = 95.06 (3)°
V = 1500.6 (9) Å^3
Z = 2
D_x = 1.197 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 250 reflections
θ = 1.84–25.09°
μ = 0.140 mm^{-1}
T = 150 K
Lozenge
0.32 × 0.26 × 0.24 mm
Colourless

Data collection

Delft Instruments FAST diffractometer with Oxford Cryosystems low temperature device (Cosier & Glazer, 1986)
Area detector scans
Absorption correction: none
6774 measured reflections

4411 independent reflections
2136 observed reflections [$I > 2\sigma(I)$]
R_{int} = 0.0755
θ_{max} = 25.09°
$h = -14 \rightarrow 12$
$k = -5 \rightarrow 7$
$l = -21 \rightarrow 21$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.0494
$wR(F^2)$ = 0.1066
S = 0.659
4411 reflections
345 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0235P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.042
$\Delta\rho_{max}$ = 0.26 e Å^{-3}
$\Delta\rho_{min}$ = −0.22 e Å^{-3}

Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Absolute configuration: Flack (1983)
Flack parameter = −0.08 (13)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
S	0.28067 (12)	−0.2479 (2)	0.48083 (7)	0.0320 (4)
O1	0.1787 (3)	−0.3303 (5)	0.5114 (2)	0.0326 (10)
O2	0.2836 (3)	−0.0205 (5)	0.4817 (2)	0.0404 (11)
O3	0.2826 (3)	−0.3578 (6)	0.4151 (2)	0.0407 (11)
C1	0.0260 (5)	0.0108 (8)	0.6307 (3)	0.034 (2)
C2	0.0670 (4)	−0.0727 (8)	0.5616 (3)	0.034 (2)
C3	0.1515 (4)	−0.2326 (8)	0.5784 (2)	0.0242 (13)
C4	0.1182 (4)	−0.4149 (8)	0.6241 (3)	0.034 (2)
C5	0.0712 (4)	−0.3338 (7)	0.6914 (3)	0.0257 (14)
C6	0.1009 (4)	−0.4182 (8)	0.7539 (3)	0.0293 (15)
C7	0.0569 (4)	−0.3606 (8)	0.8215 (3)	0.0327 (14)
C8	−0.0437 (4)	−0.2417 (9)	0.8083 (2)	0.0266 (12)
C9	−0.0344 (4)	−0.0680 (8)	0.7512 (3)	0.0274 (14)
C10	−0.0127 (4)	−0.1686 (7)	0.6799 (2)	0.0208 (13)
C11	−0.1226 (4)	0.0987 (8)	0.7459 (3)	0.0327 (15)
C12	−0.1568 (4)	0.1746 (8)	0.8166 (2)	0.0308 (15)
C13	−0.1807 (4)	−0.0124 (7)	0.8657 (3)	0.0244 (13)
C14	−0.0799 (4)	−0.1435 (8)	0.8770 (2)	0.0227 (13)
C15	−0.0960 (4)	−0.2908 (8)	0.9385 (2)	0.0304 (14)
C16	−0.1623 (4)	−0.1611 (8)	0.9850 (3)	0.0305 (14)
C17	−0.1991 (4)	0.0437 (8)	0.9428 (3)	0.0297 (15)
C18	−0.2706 (4)	−0.1460 (8)	0.8306 (2)	0.0315 (14)
C19	−0.1113 (4)	−0.2717 (8)	0.6424 (3)	0.0363 (14)
C20	−0.3055 (4)	0.1200 (8)	0.9608 (3)	0.0281 (14)
C21	−0.3493 (4)	0.3068 (8)	0.9155 (3)	0.042 (2)
C22	−0.3077 (4)	0.1727 (8)	1.0396 (2)	0.0314 (15)
C23	−0.4111 (4)	0.2366 (10)	1.0643 (3)	0.045 (2)
C24	−0.4148 (4)	0.2500 (10)	1.1439 (3)	0.043 (2)
C25	−0.3439 (4)	0.4101 (9)	1.1826 (3)	0.039 (2)

C26	−0.3592 (6)	0.6339 (9)	1.1530 (3)	0.072 (2)
C27	−0.3542 (5)	0.4039 (11)	1.2611 (3)	0.070 (2)
C28	0.5318 (5)	−0.4887 (9)	0.6425 (3)	0.035 (2)
C29	0.4497 (4)	−0.6243 (9)	0.6192 (3)	0.0342 (14)
C30	0.3739 (4)	−0.5494 (8)	0.5685 (3)	0.033 (2)
C31	0.3763 (4)	−0.3442 (8)	0.5423 (2)	0.0231 (13)
C32	0.4588 (4)	−0.2158 (8)	0.5648 (3)	0.039 (2)
C33	0.5377 (5)	−0.2873 (9)	0.6142 (3)	0.037 (2)
C34	0.6107 (5)	−0.5653 (9)	0.7001 (3)	0.052 (2)

Table 2. *Selected geometric parameters (Å, °)*

S—O1	1.415 (3)	C20—C21	1.519 (6)
S—O2	1.414 (3)	C20—C22	1.519 (6)
S—O3	1.567 (4)	C22—C23	1.504 (7)
S—C31	1.722 (5)	C23—C24	1.504 (6)
O1—C3	1.469 (5)	C24—C25	1.496 (7)
C5—C6	1.312 (6)	C25—C27	1.494 (6)
C17—C20	1.518 (7)	C25—C26	1.505 (7)
O3—S—O2	119.4 (2)	C21—C20—C22	110.1 (4)
O3—S—O1	104.1 (2)	C23—C22—C20	116.8 (5)
O2—S—O1	110.2 (2)	C22—C23—C24	115.4 (5)
O3—S—C31	110.6 (2)	C25—C24—C23	116.6 (5)
O2—S—C31	108.8 (3)	C27—C25—C24	111.0 (5)
O1—S—C31	102.4 (2)	C27—C25—C26	111.6 (5)
C17—C20—C21	114.4 (4)	C24—C25—C26	112.4 (5)
C17—C20—C22	112.2 (4)		
C31—S—O1—C3	68.6 (4)		

The unit-cell and intensity data were collected on a Delft Instruments FAST diffractometer using the routines *ENDEX*, *REFINE* and *MADONL* in the *MADNES* software (Pflugrath & Messerschmidt, 1989) and processed using *ABSMAD* (Karaulov, 1992); detailed procedures are described by Darr, Drake, Hursthouse & Malik (1993). The non-H atoms were refined with anisotropic displacement parameters and H atoms were allowed to ride on their attached C atoms with a common isotropic displacement parameter.

Data collection: *MADNES* (Pflugrath & Messerschmidt, 1989). Cell refinement: *ABSMAD* (Karaulov, 1992). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ZORTEP* (Zsolnai, 1995).

The use of the EPSRC X-ray Crystallographic Service at The University of Wales, Cardiff, is gratefully acknowledged.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BM1066). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Naphtho[2,3-*b*]cholestane

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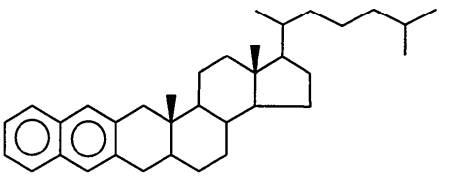
Abstract

The crystal structure of the title compound, naphtho-[2,3-*b*]cholestane, $C_{35}H_{50}$, is composed of independent molecules with normal molecular dimensions and no unusual contacts shorter than van der Waals distances.

Comment

In the course of our studies on the direct asymmetric introduction of a tricarbonylchromium moiety on prochiral arenes, we required pure optically active naphthalene ligands. The title compound, (1), has eight asymmetric centres and fulfills some of the requirements for a good chiral auxiliary: (i) good leaving-group ability, (ii) stable chiral information and (iii) easy recovery. In this paper, we report the crystal structure of the title compound. We did not determine the absolute configuration by X-ray methods, but the absolute configuration of the dibromocholestane has been established (Geise & Romers, 1966) and the structure and coordinates reported here refer to the same absolute configuration.



(1)