leau 1, les distances et les angles dans le Tableau 2.* L'étude cristallographique a montré que ce composé existe préférentiellement dans la conformation (1*a*), la plus encombrée stériquement, confirmant les résultats inattendus obtenus par étude en RMN du proton.

Littérature associée. Libre rotation des hétérocycles autour de la liaison d'assemblage dans le (phényl-2)-1 pyrrole (Jones & Wright, 1968); couplage à longue distance observé dans les aldéhydes pyrroliques ayant une configuration bloquée (Roques & Combrisson, 1973); conformation S—O *cis* décrite dans le thénaldehyde-2 (Roques, Combrisson, Riche & Pascard-Billy, 1970).

Nous remercions les Professeurs S. Rault et M. Robba de nous avoir fourni ce composé.

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* Les listes des facteurs de structure, des facteurs d'agitation thermique anisotrope, des paramètres des atomes d'hydrogène, distances de van der Waals et calculs des plans moyens ont été déposées au dépôt d'archives de la British Library Document Supply Centre (Supplementary Publication No. SUP 54104: 10 pp.). On peut en obtenir des copies en s'adressant à: The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, Angleterre.

Acta Cryst. (1991). C**47**, 2224–2226

Chiral Organosilicon Compounds. 5.* Structure of (Cholest-5-en-3*β*-yloxy)(3,3-dimethylbuten-2-yloxy)dimethylsilane

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(*Received* 28 *December* 1990; *accepted* 4 *April* 1991)

Abstract. $C_{35}H_{63}O_2Si$, M_r = 544·07, monoclinic, *C*2, a = 23·648 (8), b = 8·998 (2), c = 17·118 (4) Å, β = 103·88 (2)°, V = 3536 (3) Å^3, Z = 4, D_x = 1·02 Mg m^{-3}, Mo $K\alpha$, λ = 0·7107 Å, μ = 0·062 mm^{-1}, $F(000)$ = 1212, R = 0·083 for 1765 independent reflections. In this pinacolone silyl enol ether, a cholesteryloxy moiety is bound to the Si atom, inducing asymmetry about the reactive silyl enol ether site.

Experimental. The title compound was prepared as part of an investigation into the use of chiral organosilicon compounds (Kaye & Learmonth, 1990) in asymmetric synthesis; the X-ray work was expected to provide a basis for exploring solution conformations and, more particularly, transition-state interactions crucial to effective stereocontrol. In an adaptation of a literature procedure (Walkup, 1987), pinacolone, dichlorodimethylsilane, triethylamine and cholesterol were added sequentially to a solution of lithium diisopropylamide in Et_2O. Work-up and flash chromatography on silica (elution with hexane) afforded the title compound (62%), m.p. 350–352 K; $[\alpha]_D^{25\,^\circ C}$ − 22·68° (c 1·1 in hexane) which gave satisfactory elemental (combustion) and spectroscopic (IR, MS, and ^{1}H and ^{13}C NMR) analyses. Crystal dimensions 0·45 × 0·3 × 0·2 mm, Enraf–Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$ radiation, ω–2θ scans, lattice parameters from 24 high-θ reflections, loss in intensity of 29 monitored reflexions < 3%, 3435 measured with $2 < 2\theta < 50°$; *hkl*: h −26–27, k 0–10, l 0–20, 1765 unique with $I > \sigma(I)$; structure solved by direct methods, refined using full-matrix least squares based on F_c with calculated H-atom positions; due to poor resolution at the extreme ends of the molecule, C—C bond lengths in the *tert*-butyl and isopropyl groups constituting those ends had to be constrained to 1·54 Å

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* Part 4: Kaye & Learmonth (1990).

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Table 1. *Fractional coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors* ($Å^2 \times 10^3$)

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

	x	y	z	U/U_{eq}
Si	- 580 (2)	- 4168	- 8236 (2)	81 (1)
O(1)	- 751 (3)	- 2999 (10)	- 7625 (4)	71 (2)
C(3)	- 1016 (4)	- 3371 (14)	- 6970 (6)	64 (3)
C(2)	- 548 (5)	- 3363 (15)	- 6203 (6)	69 (3)
C(1)	- 819 (4)	- 3672 (14)	- 5490 (6)	60 (3)
C(4)	- 1487 (5)	- 2268 (14)	- 6948 (6)	64 (3)
C(5)	- 1747 (5)	- 2436 (12)	- 6221 (6)	54 (3)
C(6)	- 2303 (4)	- 2471 (12)	- 6281 (6)	50 (3)
C(7)	- 2596 (4)	- 2573 (14)	- 5609 (5)	60 (3)
C(8)	- 2182 (4)	- 2322 (13)	- 4794 (6)	48 (2)
C(9)	- 1600 (4)	- 3110 (13)	- 4746 (5)	52 (3)
C(10)	- 1298 (4)	- 2540 (13)	- 5412 (5)	54 (3)
C(19)	1029 (6)	- 981 (14)	- 5192 (7)	78 (4)
C(11)	- 1194 (4)	- 3130 (16)	- 3901 (6)	65 (3)
C(12)	- 1494 (4)	- 3683 (14)	- 3252 (5)	64 (3)
C(13)	- 2050 (4)	- 2771 (13)	- 3258 (6)	53 (3)
C(14)	- 2441 (4)	- 2893 (13)	- 4113 (5)	49 (2)
C(15)	- 3016 (4)	- 2224 (14)	- 4035 (6)	63 (3)
C(16)	- 3064 (4)	- 2802 (15)	- 3185 (6)	67 (3)
C(17)	- 2475 (4)	- 3481 (13)	- 2785 (5)	56 (3)
C(18)	- 1904 (5)	- 1160 (13)	- 3006 (7)	66 (3)
C(20)	- 2339 (4)	- 3320 (15)	- 1860 (5)	68 (3)
C(21)	- 1726 (5)	- 3929 (18)	- 1443 (7)	88 (4)
C(22)	- 2801 (5)	- 4076 (16)	- 1548 (5)	75 (3)
C(23)	- 2780 (5)	- 3788 (18)	- 668 (6)	92 (4)
C(24)	- 3330 (6)	- 4462 (17)	- 428 (7)	94 (4)
O(2)	- 188 (4)	- 5422 (12)	- 7677 (5)	109 (3)
C(30)	22 (8)	- 6734 (24)	- 7858 (11)	146 (7)
C(31)	69 (11)	- 7033 (34)	- 8629 (16)	225 (11)*
C(32)	133 (6)	- 7879 (17)	- 7190 (10)	112 (5)
C(25)	- 3346 (6)	- 4401 (25)	440 (8)	171 (8)
C(26)	- 3899 (6)	- 5149 (20)	582 (10)	136 (6)*
C(27)	- 2963 (9)	- 3256 (23)	995 (12)	190 (9)*
C(28)	- 124 (7)	- 3069 (21)	- 8802 (9)	126 (5)*
C(29)	- 1246 (7)	- 5021 (21)	- 8899 (10)	131 (6)*
C(33)	- 401 (7)	- 8010 (27)	- 6828 (10)	168 (7)*
C(34)	616 (8)	- 7177 (26)	- 6527 (11)	177 (8)*
C(35)	304 (10)	- 9448 (18)	- 7411 (13)	192 (9)*

* Isotropic temperature factor.

Table 2. *Selected bond lengths* (Å) *and angles* (°)

Si—O(1)	1·61 (1)	Si—O(2)	1·62 (1)
Si—C(28)	1·89 (2)	Si—C(29)	1·87 (2)
O(1)—C(3)	1·45 (1)	C(5)—C(6)	1·29 (2)
C(9)—C(10)	1·57 (2)	C(13)—C(17)	1·57 (2)
O(2)—C(30)	1·35 (2)	C(30)—C(31)	1·38 (4)
O(1)—Si—O(2)	105·7 (5)	O(1)—Si—C(28)	104·8 (6)
O(2)—Si—C(28)	110·7 (6)	O(1)—Si—C(29)	110·9 (7)
O(2)—Si—C(29)	110·6 (6)	C(28)—Si—C(29)	113·8 (7)
Si—O(1)—C(3)	125·3 (8)	C(4)—C(5)—C(6)	122·7 (9)
C(4)—C(5)—C(10)	114·5 (9)	C(6)—C(5)—C(10)	122·7 (10)
C(5)—C(6)—C(7)	126·6 (9)	O(2)—C(30)—C(31)	121 (2)
Si—O(2)—C(30)	131·7 (10)	C(31)—C(30)—C(32)	123 (2)
O(2)—C(30)—C(32)	116 (2)		

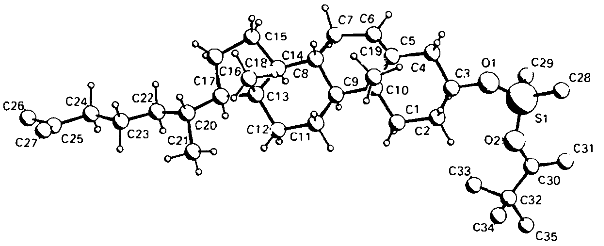

Fig. 1. Molecular structure of (cholest-5-en-3β-yloxy)(3,3-dimethylbuten-2-yloxy)dimethylsilane, viewed from the direction giving minimum overlap; poorly defined H atoms have been omitted.

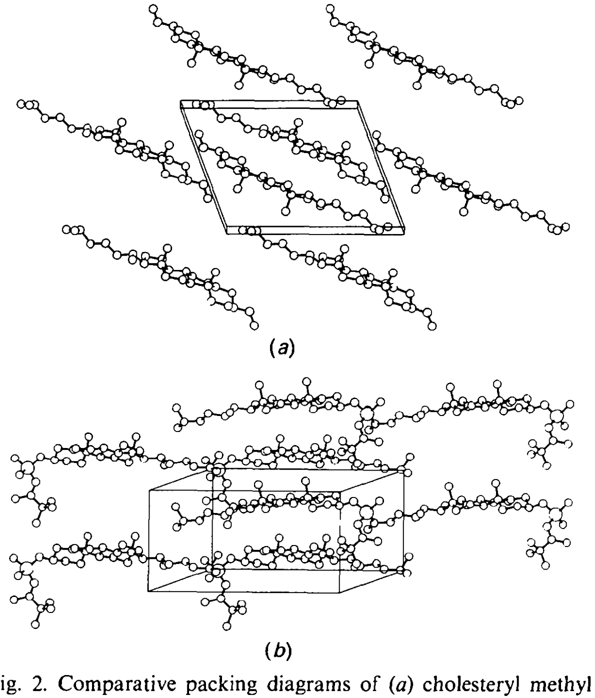

Fig. 2. Comparative packing diagrams of (*a*) cholesteryl methyl ether and (*b*) the title compound viewed approximately parallel to the mean plane of the cholesteryl group and perpendicular to the major axis of the molecules. Unit-cell outlines are shown.

and final temperature factors of the terminal C atoms were correspondingly high. $R = 0{\cdot}083$ (unit weights), $(\Delta/\sigma)_{max}$ in final cycle < 0·01, $\Delta\rho$ excursion in final difference map within ± 0·5 e Å^{-3}; f, f' and f'' from *International Tables for X-ray Crystallography* (1974, Vol. IV); the programs *SHELXS* (Sheldrick, 1984) and *SHELX*76 (Sheldrick, 1976) were used. Atomic coordinates and selected derived parameters are listed in Tables 1 and 2.* A minimum-overlap plot of the molecule is presented in Fig. 1. Bond lengths and angles lie within expected ranges.

Related literature. The poor definition of the electron density map at the ends of the molecule (one of which is the main point of interest) suggests that the compound packs rather uneasily in the crystal. Recently, the crystal and molecular structure of cholesteryl methyl ether has been described (Yun, Park, Shin & Craven, 1989): the same lack of definition was noted. Despite the obvious influence of the bulky cholesteryloxy group, substitution of the methyl group by the pinacolone silyl enol results in a completely different packing (Fig. 2). The *tert*-butyl group, comprising C32–C35, is in close proximity

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* Lists of structure factors, H-atom positions and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54137 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

with the *A* ring system (C1–C5 and C10) to the extent that the sphere of influence of the methyl group (radius 2·28 Å) is only 0·08 Å from the van der Waals sphere of all H atoms bound to C2. This may be due to packing forces.

We thank Rhodes University, the University of Cape Town and the Foundation for Research Development for financial and technical support.

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Acta Cryst. (1991). C**47**, 2226–2227

Methyl 7-Methoxy-2-naphthoate

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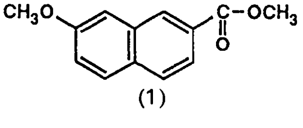
(*Received* 14 *November* 1990; *accepted* 20 *March* 1991)

Abstract. $C_{13}H_{12}O_3$, $M_r = 216{\cdot}2$, monoclinic, $P2_1/c$, $a = 3{\cdot}9886\,(2)$, $b = 11{\cdot}7995\,(9)$, $c = 22{\cdot}789\,(3)$ Å, $\beta = 92{\cdot}748\,(6)°$, $V = 1071{\cdot}3\,(3)$ Å^3, $Z = 4$, $D_x = 1{\cdot}341$ g cm^{-3}, $\lambda(\mathrm{Cu}\,K\alpha) = 1{\cdot}54184$ Å, $\mu = 7{\cdot}40$ cm^{-1}, $F(000) = 456$, $T = 295$ K, $R = 0{\cdot}034$ for 1835 observations (of 2177 unique data). The average deviation from planarity is 0·007 Å with a maximum of 0·014 (1) Å for the fused rings. Both the methoxy and the carboxy groups are nearly coplanar with the naphthalene system. The CH_3O—C—C torsion angle is $-1{\cdot}5\,(2)°$ with the methyl group *syn* to the neighboring α-carbon of the ring. In the ester the C—C—C—O torsion angles are $-0{\cdot}5\,(2)$ with the methoxy O atom and $178{\cdot}6\,(1)°$ with the carbonyl O atom.

Experimental. The title compound (1), was prepared by the palladium-catalyzed reaction of carbon monoxide and methanol on the corresponding triflate (Dolle, Schmidt & Kruse, 1987). Colorless laths of (1), m.p. 364·5–365·5 K, were isolated by recrystallization from ether. A fragment of size 0·15 × 0·35 × 0·38 mm, mounted on a glass fiber in random orientation, was used for data collection on an Enraf–Nonius CAD-4 diffractometer equipped with Cu $K\alpha$ radiation and a graphite monochromator. Cell dimensions from setting angles of 25 reflections having $25 < \theta < 30°$. Space group determined to be $P2_1/c$ from systematic absences $h0l$ with l odd, $0k0$ with k odd.



(1)

A hemisphere of data having $4 < 2\theta < 150°$, $0 \leq h \leq 4$, $-14 \leq k \leq 14$, $-28 \leq l \leq 28$ was collected using ω–2θ scans designed for $I = 25\sigma(I)$, subject to max. scan time = 60 s, scan rates varied 0·92–3·30° min^{-1}. Three reflections (100, 060, 008) were measured every 166 min, and their intensities exhibited only random fluctuations during data collection. A total of 4423 measurements was made. Lorentz and polarization corrections were applied. An empirical absorption correction based on a series of ψ scans was applied to the data. Relative transmission coefficients ranged from 0·8417 to 0·9962 with an average value of 0·9465. $R_{\rm int} = 0{\cdot}010$ for averaging the two equivalent quadrants. Structure solved by direct methods, using *MULTAN* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982), and refined by weighted full-matrix least squares; non-H atoms refined anisotropically; H atoms were located from difference maps and refined isotropically.

The function minimized was $\sum w(|F_o| - |F_c|)^2$ and weights were assigned as $w = 4\mathrm{F}_o{}^2\mathrm{Lp}[S^2(C + R^2B) + (0{\cdot}02F_o^2)^2]^{-1}$, where S = scan rate, C = total integrated peak count, R = scan time/background counting time, B = total background count, Lp = Lorentz–polarization factor, using Enraf–Nonius *SDP* (Frenz & Okaya, 1980), scattering factors of Cromer & Waber (1974), anomalous coefficients of Cromer (1974). Of 2177 unique data, 1835 reflections having $I > 3\sigma(I)$ were used in the refinement. The extinction coefficient (Larson, 1969) was refined in the least squares to $g = 1{\cdot}54\,(8) \times 10^{-5}$, where the correction factor $(1 + gI_c)^{-1}$ was applied to F_c; maximum correction 53·1% for the $12\bar{2}$ reflection. The

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0108-2701/91/102226-02$03.00