$-18 \leq l \leq 18$ were measured. The data were corrected for Lorentz–polarization but not for absorption effects because of the small absorption coefficient, and averaged ($R_{\rm int} = 0.105$) to 2090 unique reflections, 1567 of which had $F \geq 4.0\sigma(F)$. The systematic absences (hkl) $h + k = 2n + 1$ conform to the space groups $C2$, Cm and $C2/m$. The structure was solved *via* direct methods and $\Delta\rho$ maps in space group $C2$. It was refined (on F) using full-matrix least squares with anisotropic displacement parameters for all non-H atoms and a common isotropic displacement parameter for the H atoms, which were placed in geometrically calculated positions (C—H 0.96 Å). 200 parameters were refined. Weights $w = 1.0/[\sigma^2(F) + (0.0040F^2)]$ led to a featureless analysis of variance in terms of $\sin\theta$ and F_o. The refinement (damping factor damp = 1000 on the L.S. card of *SHELX76*; Sheldrick, 1976) converged to $S = 0.97$, $R = 0.054$, $wR = 0.073$, $(\Delta/\sigma)_{\rm max} = 0.23$ (no extinction correction). The largest peaks in the final $\Delta\rho$ map were $\pm 0.2\,(1)$ e Å^{-3}. The correctness of the space-group choice was checked by using *MISSYM* (Le Page, 1987) and the extra symmetries m (at $y = 0.097$) and $\bar{1}$ were indicated. A refinement in space group $C2/m$ led to unreasonable results ($R = 0.165$, $wR = 0.258$, $S = 3.1$, unreasonable atomic displacement parameters) and this space group was discarded. Atomic scattering factors for neutral atoms and real and imaginary dispersion terms were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). The programs used were *PARST* (Nardelli, 1983), *SHELX76* (Sheldrick, 1976), *SHELXTL-Plus* (Sheldrick, 1987), *PCK83* (Williams, 1984), *PLATON* (Spek, 1982). The molecule and the numbering scheme are shown in Fig. 1 and a stereoscopic view of the unit-cell contents is in Fig. 2. Positional parameters and the equivalent values of the anisotropic displacement parameters for the non-H atoms are given in Table 1.* Bond lengths, bond angles, least-squares planes and dihedral angles are given in Table 2.

Related literature. Appropriately substituted aniles of p-CN-benzophenone have potential use as complexation agents for the spectrophotometric determination of some metals. The general method for synthesis of aniles has been reported (Layer, 1963).

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* Lists of structure factors, anisotropic displacement parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54687 (16 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AL0501]

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Structure of a Novel Twist-Boat Spiroketal

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Abstract. 10-(*tert*-Butyldiphenylsilyloxy)-2-methoxy-2,3,8-trimethyl-1,7-dioxaspiro[5.5]undecan-5-one, $C_{29}H_{40}O_5Si$, $M_r = 496{\cdot}72$, monoclinic, $C2/c$, $a = 38{\cdot}29\,(5)$, $b = 7{\cdot}774\,(2)$, $c = 20{\cdot}65\,(2)$ Å, $\beta = 109{\cdot}05\,(8)°$, $V = 5810\,(8)$ Å^3, $Z = 8$, $D_x = 1{\cdot}136$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 1{\cdot}09$ cm^{-1}, $F(000) = 2144$, $T = 298$ K, $R = 0{\cdot}075$ for 1469 observed reflections. The structure consists of two substituted and spiro-fused tetrahydropyran rings. One tetrahydropyran ring is in a chair conformation with intra-ring torsion angles alternating ± in the range 55–58°; both its methyl and *tert*-

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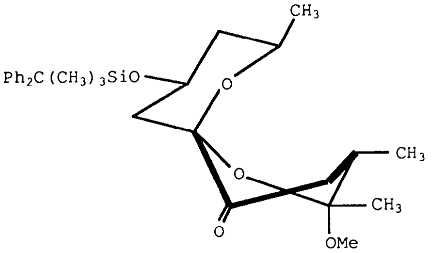
butyldiphenylsiloxane substituents are equatorial. The tetrahydropyran-3-one ring is in the more unusual twist-boat conformation with cyclic intraring torsion angles −23, −28, +60, −34, −16, +49 (± 1°); its two adjacent methyl substituents are equatorial while the methoxy is axial. Average ring distances are C—O = 1.44 (1), C—C (sp^3) = 1.53 (1) and C—C (sp^2) = 1.51 (1) Å.

Experimental. The synthesis and reaction rationale has been discussed (Stolze, Perron-Sierra, Heeg & Albizati, 1991). The structure (I) was undertaken specifically to confirm the twist-boat conformation of the tetrahydropyran-3-one ring.



(I)

Colorless flat rod-shaped crystals, 0.08 × 0.24 × 0.16 mm; Nicolet *R*3 diffractometer, monochromated Mo $K\alpha$; $\theta/2\theta$ scans; $6 \leq 2\theta \leq 45°$; lattice parameters from 25 reflections ($2\theta > 15°$) constrained monoclinic; $0 \leq h \leq 42$, $0 \leq k \leq 9$, $-23 \leq l \leq 23$; three standard reflections fluctuated < 2%; 4801 total reflections, 3829 unique, 1469 observed with $I_o \geq 2.5\sigma(I)$. Direct methods; full-matrix refinement *via SHELX76* (Sheldrick, 1976) on *F* values minimizing $\sum w(|F_o| - |F_c|)^2$; phenyl C atoms were refined in a rigid body and isotropically; all other non-hydrogen atoms were anisotropic; hydrogen atoms were placed in observed and calculated positions, assigned $U(\mathrm{H}) \sim 1.5U(\mathrm{C})$ and held invariant. Number of parameters varied was 232. For observed reflections $R = 0.075$, $wR = 0.067$, $S = 1.7$, $w = (\sigma_F^2 + 0.0003F^2)^{-1}$. In the final cycle $(\Delta/\sigma)_{\max} < 0.001$, $(\Delta\rho)_{\max} = 0.28$, $(\Delta\rho)_{\min} = -0.28$ e Å^{-3}. No correction for absorption or extinction was made. Neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV). Overall the crystal gave poor diffraction at high angles due to the small sample size. Weak data were collected at 3° min^{-1}. Table 1* gives the atomic coordinates and Table 2 lists torsion angles. Fig. 1 illustrates the geometry and labelling scheme.

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters*

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

	x	y	z	U_{eq}(Å^2)
O1	0.0982 (2)	1.2712 (9)	0.0214 (3)	0.051 (3)
C1	0.0703 (3)	1.375 (2)	−0.0266 (5)	0.061 (5)
C2	0.0726 (3)	1.546 (1)	0.0088 (6)	0.095 (7)
O2	0.0355 (2)	1.290 (1)	−0.0389 (4)	0.072 (4)
C3	0.0260 (3)	1.247 (2)	0.0213 (6)	0.111 (8)
C4	0.0751 (3)	1.381 (2)	−0.0974 (5)	0.061 (5)
C5	0.0470 (3)	1.498 (1)	−0.1485 (5)	0.090 (6)
C6	0.0724 (3)	1.198 (1)	−0.1263 (5)	0.060 (5)
C7	0.0884 (3)	1.066 (2)	−0.0720 (5)	0.056 (5)
O3	0.0811 (3)	0.917 (1)	−0.0816 (4)	0.108 (5)
C8	0.1138 (3)	1.131 (1)	−0.0037 (5)	0.040 (4)
O4	0.1455 (2)	1.1903 (8)	−0.0200 (3)	0.047 (3)
C9	0.1744 (2)	1.260 (1)	0.0379 (5)	0.047 (5)
C10	0.2052 (3)	1.318 (1)	0.0110 (5)	0.075 (5)
C11	0.1872 (2)	1.129 (1)	0.0951 (4)	0.051 (4)
C12	0.1545 (2)	1.065 (1)	0.1162 (4)	0.040 (4)
C13	0.1248 (3)	0.997 (1)	0.0519 (5)	0.049 (4)
O5	0.1672 (2)	0.9242 (8)	0.1639 (3)	0.048 (3)
Si1	0.15455 (7)	0.8957 (4)	0.2319 (1)	0.043 (1)
C14	0.1830 (2)	1.0412 (7)	0.3029 (3)	0.046 (3)
C15	0.1729 (2)	1.0776 (7)	0.3604 (3)	0.061 (3)
C16	0.1957 (2)	1.1792 (7)	0.4130 (3)	0.069 (3)
C17	0.2286 (2)	1.2444 (7)	0.4080 (3)	0.069 (3)
C18	0.2388 (2)	1.2080 (7)	0.3504 (3)	0.070 (3)
C19	0.2160 (2)	1.1064 (7)	0.2979 (3)	0.060 (3)
C20	0.1038 (1)	0.9499 (9)	0.2123 (3)	0.043 (3)
C21	0.0768 (1)	0.8306 (9)	0.1787 (3)	0.064 (3)
C22	0.0395 (1)	0.8724 (9)	0.1626 (3)	0.077 (4)
C23	0.0292 (1)	1.0336 (9)	0.1801 (3)	0.073 (4)
C24	0.0563 (1)	1.1529 (9)	0.2137 (3)	0.086 (4)
C25	0.0936 (1)	1.1111 (9)	0.2298 (3)	0.062 (3)
C26	0.1675 (3)	0.664 (1)	0.2575 (5)	0.054 (5)
C27	0.1485 (3)	0.600 (1)	0.3072 (5)	0.068 (5)
C28	0.1563 (3)	0.545 (1)	0.1944 (6)	0.080 (6)
C29	0.2094 (3)	0.654 (1)	0.2926 (5)	0.084 (6)

Table 2. *Torsion angles* (°)

O1—C1—O2—C3	53 (1)	O3—C7—C8—O4	113 (1)
O1—C1—C4—C5	−176.9 (9)	O3—C7—C8—C13	−6 (1)
O1—C1—C4—C6	60 (1)	C8—O4—C9—C10	−179.3 (8)
O1—C8—C7—C6	49 (1)	C8—O4—C9—C11	57.4 (9)
O1—C8—C7—O3	−129 (1)	C8—C13—C12—C11	−55.3 (9)
O1—C8—O4—C9	60.7 (8)	C8—C13—C12—O5	−172.6 (6)
O1—C8—C13—C12	−62.7 (9)	O4—C8—C13—C12	56.5 (9)
C1—O1—C8—C7	−23 (1)	O4—C9—C11—C12	−55.8 (9)
C1—O1—C8—O4	89.6 (9)	C9—O4—C8—C13	−57.5 (9)
C1—O1—C8—C13	−150.2 (8)	C9—C11—C12—C13	54.8 (9)
C1—C4—C6—C7	−34 (1)	C9—C11—C12—O5	172.3 (6)
C2—C1—O1—C8	−155.4 (8)	C10—C9—C11—C12	−175.4 (7)
C2—C1—O2—C3	−61 (1)	C11—C12—O5—Si1	140.2 (5)
C2—C1—C4—C5	−56 (1)	C12—O5—Si1—C14	−80.9 (6)
C2—C1—C4—C6	179.6 (9)	C12—O5—Si1—C20	38.9 (7)
O2—C1—O1—C8	84.1 (8)	C12—O5—Si1—C26	163.3 (6)
O2—C1—C4—C5	67 (1)	C13—C12—O5—Si1	−102.6 (6)
O2—C1—C4—C6	−55 (1)	O5—Si1—C26—C27	−164.5 (6)
C3—O2—C1—C4	172.3 (9)	O5—Si1—C26—C28	−44.1 (8)
C4—C1—O1—C8	−28 (1)	O5—Si1—C26—C29	76.0 (5)
C4—C6—C7—O3	161.5 (9)	C14—Si1—C26—C27	79.6 (7)
C4—C6—C7—C8	−16 (1)	C14—Si1—C26—C28	−160.0 (6)
C5—C4—C6—C7	−159.9 (8)	C14—Si1—C26—C29	−39.9 (5)
C6—C7—C8—O4	−67 (1)	C20—Si1—C26—C27	−43.0 (7)
C6—C7—C8—C13	171.8 (8)	C20—Si1—C26—C28	77.4 (7)
C7—C8—O4—C9	−179 (2)	C20—Si1—C26—C29	−162.5 (4)
C7—C8—C13—C12	172.0 (7)		

Related literature. Spiroketals are widely present as natural products and biological metabolites. The synthesis and reactions of spiroketals are important due to their role as pharmacological agents. A recent review of spiroketals has been published (Perron & Albizati, 1989). Another example of the twist-boat conformation in a related spiroketal is known in a trioxadispiroketal compound (Grenier-Loustalot,

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* Lists of anisotropic thermal parameters, H-atom parameters, bond lengths and angles and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54606 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

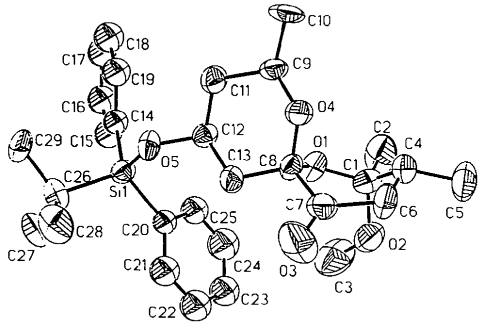

Fig. 1. A perspective view of the spiroketal with ellipsoids at 50% probability.

Metras, Cottier & Descotes, 1982). A discussion of the stereochemistry of five-, six- and seven-membered rings using torsion-angle analysis has been given by Toromanoff (1980).

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(*R*)-(1-Methyloxiranyl)methyl 4-Nitrobenzenesulfonate

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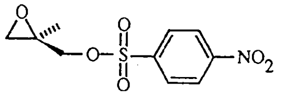
Abstract. $C_{10}H_{11}NO_6S$, $M_r = 273.3$, monoclinic, $P2_1$, $a = 10.2612\ (8)$, $b = 8.1670\ (8)$, $c = 15.2974\ (12)$ Å, $\beta = 108.885\ (6)°$, $V = 1213.0\ (2)$ Å^3, $Z = 4$, $D_x = 1.496$ g cm^{-3}, $\lambda(\text{Cu}\ K\alpha) = 1.54184$ Å, $\mu = 25.39$ cm^{-1}, $F(000) = 568$, $T = 297$ K, $R = 0.046$ for 4453 observations having $I > 3\sigma(I)$ (of 4798 unique data). The two independent molecules in the asymmetric unit differ conformationally, principally in torsion angle differences about the two bonds to the CH_2 group that link the oxirane three-membered ring to the 4-nitrobenzenesulfonate group. In molecule (*A*), the C(ring)—C—C—O torsion angle is −23.0 (4)°, while in molecule (*B*) that torsion angle is −146.8 (3)°. The S—O—C—C torsion angle in molecule (*A*) is 133.2 (2)°, while in molecule (*B*), it is −143.9 (2)°. The C—S—O—C torsion angles are −80.9 (2)° in molecule (*A*) and 76.5 (2)° in molecule (*B*). The molecules pack with a pseudocenter near $\frac{1}{2}, \frac{1}{2}, \frac{3}{4}$ as a pseudoracemate. Only the position of the epoxy O atom greatly deviates from a centrosymmetric motif.

Experimental. Pale yellow prisms of (1), m.p. 313.5–314.5 K, were isolated by two successive recrystallizations from ethanol of the crude product prepared by the reaction of (*S*)-(−)-2-methylglycidol with 4-nitrobenzenesulfonyl chloride in dichloromethane at 273 K. Crystal size 0.28 × 0.35 × 0.45 mm, mounted in capillary in random orientation on an Enraf–Nonius CAD-4 diffractometer equipped with a graphite monochromator, Cu *Kα* radiation. Cell dimensions from setting angles of 25 reflections having $12 < \theta < 30°$. The space group was determined from systematic absences $0k0$ with k odd and the known chirality of the compound.



(1)

A hemisphere of data having $4 < 2\theta < 150°$, $0 \leq h \leq 12$, $-10 \leq k \leq 10$, $-19 \leq l \leq 19$ was measured using ω–2θ scans designed for $I = 25\sigma(I)$, subject to maximum scan time of 90 s, scan rates varied 0.66–3.30° min^{-1}. Data corrected for background, Lorentz and polarization effects. Intensities of standard reflections 300, 020, 004 varied only randomly, and no decay correction was applied. Absorption corrections were based on ψ scans, and relative transmission coefficients ranged from 0.8982 to 0.9975 with an average value of 0.9593. The extinction coefficient was refined in the least squares to $g = 2.9\ (2) \times 10^{-6}$ where the correction factor $(1 + gI_c)^{-1}$ was applied to F_c. A total of 5090 data was measured. $R_{\text{int}} = 0.020$ for averaging redundant data. The structure was solved by direct methods, using *RANTAN* (Yao, 1981), and was refined by weighted full-matrix least squares; non-H atoms refined aniso-

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