$C_{31}H_{32}N_2O_{12}$

The structural information on the POD derivatives should prove useful in understanding the structure–activity relationships between this important group of drugs and how they interact with their cellular receptors.

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# Structure of a Lactone, (3α,4α,6α)-4-(*tert*-Butyldimethylsiloxy)-3,4,5,6-tetrahydro-6-methyl-3-(2-oxopropyl)-2*H*-pyran-2-one
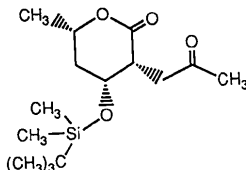
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**Abstract.** $C_{15}H_{28}O_4Si$, $M_r = 300.5$, monoclinic, $P2_1/a$, $a = 11.194$ (4), $b = 10.944$ (3), $c = 14.815$ (5) Å, $\beta = 95.01$ (3)°, $V = 1808$ (2) Å$^3$, $D_x = 1.104$ g cm$^{-3}$, $Z = 4$, $\lambda$(Mo $K\alpha$) = 0.71069 Å, $\mu = 1.43$ cm$^{-1}$, $F(000) = 656$, $T = 293$ K, final $R = 0.052$, $wR = 0.058$ for 1630 reflections with $I > 3\sigma(I)$. The valerolactone ring is in a boat conformation and the three ring substituents are *cis*.

**Experimental.** Colorless crystals from ethyl acetate/hexane, $0.06 \times 0.26 \times 0.33$ mm plate-like specimen; Enraf–Nonius CAD-4 diffractometer; cell parameters and crystal orientation from 25 automatically



centered reflections in the range $6.0 < \theta < 16.4$°; $2\theta$–$\theta$ scans over $\Delta\theta$ range of $1.5(1.0 + 0.14\tan\theta)$°; variable $\theta$ scan speed of $5.49$–$0.82$° min$^{-1}$; each scan recorded in 96 steps and post-processed with a reflection profile program (Lehmann & Larsen, 1974; Ammon, 1986); diffractometer controlled with

Digital Equipment Corp. MicroVAX II computer with version 5.0 of CAD-4 diffractometer control program; six standard reflections monitored at 1 h intervals of X-ray exposure, $-2.1$–$0.1\%$ intensity variation, $-0.5\%$ average, correction applied; $2 < \theta < 25$°, *hkl* range for data collection of $h = -13$–13, $k = 0$–13, $l = 0$–17; 3676 total data measured including standards and systematically absent data, 3367 unique data, 1630 data with $I > 3\sigma(I)$; $R_{int} = 0.01$ for 135 twice-measured data; absorption correction (*DIFABS*; Walker & Stuart, 1983) following a full isotropic structure refinement, transmission factor range of $0.670$–$1.220$, average of $0.974$. All crystallographic calculations performed with the *TEXSAN* (Molecular Structure Corporation, 1989) program system on DEC MicroVAX II or VAXStation II computers; structure solved with the *MITHRIL* (Gilmore, 1983) direct methods program incorporated in *TEXSAN*. Full-matrix least-squares refinement, $\sum[w(F_o - F_c)^2]$ minimized with $w = 1/\sigma^2(F_o)$, reflections with $I < 3\sigma(I)$ excluded from refinement; correction for secondary isotropic extinction (Zachariasen, 1968) applied, $g = 0.37$ (4) $\times 10^{-6}$; C, O and Si refined with anisotropic temperature factors; H atoms positioned from the C-atom framework, individual isotropic temperature factors refined; 209 total variables; atomic scattering factors

Table 1. *Fractional coordinates and equivalent isotropic temperature factors* ($\text{Å}^2$) *with e.s.d.'s in parentheses*

$$B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

|     | $x$ | $y$ | $z$ | $B_{eq}$ |
|-----|-----|-----|-----|-----|
| Si  | 0.7541 (1) | 0.0294 (1) | 0.19004 (8) | 4.62 (5) |
| O1  | 0.7482 (3) | -0.2532 (3) | 0.4494 (2) | 6.1 (2) |
| O2  | 0.6063 (3) | -0.3391 (3) | 0.3600 (2) | 7.5 (2) |
| O3  | 0.4288 (3) | 0.0717 (3) | 0.3707 (2) | 6.7 (2) |
| O4  | 0.7200 (2) | -0.0667 (2) | 0.2689 (2) | 4.3 (1) |
| C2  | 0.6458 (4) | -0.2477 (4) | 0.3953 (3) | 5.2 (2) |
| C3  | 0.5920 (3) | -0.1223 (4) | 0.3829 (3) | 4.3 (2) |
| C4  | 0.6903 (3) | -0.0345 (3) | 0.3578 (2) | 4.0 (2) |
| C5  | 0.7995 (4) | -0.0428 (4) | 0.4259 (3) | 4.9 (2) |
| C6  | 0.7884 (4) | -0.1412 (4) | 0.4953 (3) | 5.2 (2) |
| C7  | 0.9037 (5) | -0.1691 (6) | 0.5505 (4) | 7.3 (3) |
| C8  | 0.4818 (4) | -0.1238 (4) | 0.3163 (3) | 5.0 (2) |
| C9  | 0.4068 (4) | -0.0091 (4) | 0.3165 (3) | 5.2 (2) |
| C10 | 0.3023 (5) | -0.0006 (7) | 0.2468 (4) | 7.8 (3) |
| C11 | 0.8921 (8) | 0.1137 (8) | 0.2265 (4) | 9.9 (4) |
| C12 | 0.6409 (7) | 0.1395 (6) | 0.1654 (5) | 8.8 (4) |
| C13 | 0.7764 (4) | -0.0694 (4) | 0.0902 (3) | 5.6 (2) |
| C14 | 0.811 (1) | 0.0092 (7) | 0.0115 (4) | 10.4 (4) |
| C15 | 0.6587 (7) | -0.139 (1) | 0.0631 (6) | 11.2 (5) |
| C16 | 0.875 (1) | -0.1607 (8) | 0.1129 (5) | 10.6 (5) |

Table 2. *Bond lengths* ($\text{Å}$), *bond angles* (°) *and torsional angles* (°) *with e.s.d.'s in parentheses*

| | | | | | | |
|---|---|---|---|---|---|---|
| Si | O4 | 1.642 (3) | | C3 | C4 | 1.531 (5) |
| Si | C11 | 1.840 (6) | | C3 | C8 | 1.511 (5) |
| Si | C12 | 1.843 (5) | | C4 | C5 | 1.517 (5) |
| Si | C13 | 1.867 (5) | | C5 | C6 | 1.501 (5) |
| O1 | C2 | 1.342 (5) | | C6 | C7 | 1.499 (6) |
| O1 | C6 | 1.454 (5) | | C8 | C9 | 1.511 (6) |
| O2 | C2 | 1.196 (5) | | C9 | C10 | 1.494 (6) |
| O3 | C9 | 1.206 (5) | | C13 | C14 | 1.526 (7) |
| O4 | C4 | 1.431 (4) | | C13 | C15 | 1.544 (7) |
| C2 | C3 | 1.504 (5) | | | | |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| O4 | Si | C11 | 110.7 (2) | C3 | C4 | C5 | 110.8 (3) |
| O4 | Si | C12 | 110.1 (2) | C4 | C5 | C6 | 112.8 (3) |
| O4 | Si | C13 | 104.4 (2) | O1 | C6 | C5 | 109.0 (3) |
| C11 | Si | C12 | 109.0 (4) | O1 | C6 | C7 | 107.4 (4) |
| C11 | Si | C13 | 110.9 (3) | C5 | C6 | C7 | 113.7 (4) |
| C12 | Si | C13 | 111.8 (3) | C3 | C8 | C9 | 114.3 (4) |
| C2 | O1 | C6 | 117.0 (3) | O3 | C9 | C8 | 121.9 (4) |
| Si | O4 | C4 | 125.8 (2) | O3 | C9 | C10 | 121.2 (5) |
| O1 | C2 | O2 | 119.2 (4) | C8 | C9 | C10 | 116.9 (5) |
| O1 | C2 | C3 | 115.2 (4) | Si | C13 | C14 | 109.8 (4) |
| O2 | C2 | C3 | 125.5 (5) | Si | C13 | C15 | 108.7 (4) |
| C2 | C3 | C4 | 108.3 (5) | Si | C13 | C16 | 110.8 (4) |
| C2 | C3 | C8 | 111.4 (4) | C14 | C13 | C15 | 110.3 (7) |
| C4 | C3 | C8 | 114.3 (3) | C14 | C13 | C16 | 108.5 (5) |
| O4 | C4 | C3 | 107.4 (3) | C15 | C13 | C16 | 108.8 (7) |
| O4 | C4 | C5 | 111.0 (3) | | | | |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Si | O4 | C4 | C3 | 142.8 (3) | C2 | C3 | C4 | C5 | -52.7 (4) |
| Si | O4 | C4 | C5 | -95.9 (3) | C2 | C3 | C8 | C9 | 166.5 (3) |
| O1 | C2 | C3 | C4 | 49.7 (4) | C3 | C2 | O1 | C6 | 5.3 (5) |
| O1 | C2 | C3 | C8 | 176.2 (3) | C3 | C4 | C5 | C6 | 4.9 (5) |
| O1 | C6 | C5 | C4 | 47.9 (5) | C3 | C8 | C9 | C10 | 175.0 (4) |
| O2 | C2 | O1 | C6 | -176.2 (4) | C4 | O4 | Si | C11 | 63.0 (4) |
| O2 | C2 | C3 | C4 | -128.7 (4) | C4 | O4 | Si | C12 | -57.5 (4) |
| O2 | C2 | C3 | C8 | -2.2 (6) | C4 | O4 | Si | C13 | -177.6 (3) |
| O3 | C9 | C8 | C3 | -5.7 (6) | C4 | C3 | C8 | C9 | -70.4 (4) |
| O4 | Si | C13 | C14 | -179.1 (5) | C4 | C5 | C6 | C7 | 167.7 (4) |
| O4 | Si | C13 | C15 | 60.2 (6) | C5 | C4 | C3 | C8 | -177.5 (3) |
| O4 | Si | C13 | C16 | -59.3 (5) | C11 | Si | C13 | C14 | -59.9 (6) |
| O4 | C4 | C3 | C2 | 68.7 (4) | C11 | Si | C13 | C15 | 179.4 (6) |
| O4 | C4 | C3 | C8 | -56.1 (4) | C11 | Si | C13 | C16 | 59.9 (6) |
| O4 | C4 | C5 | C6 | -114.3 (4) | C12 | Si | C13 | C14 | 61.9 (6) |
| C2 | O1 | C6 | C5 | -55.9 (5) | C12 | Si | C13 | C15 | -58.8 (6) |
| C2 | O1 | C6 | C7 | -179.5 (4) | C12 | Si | C13 | C16 | -178.3 (6) |

from *International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 155–175); min. and max. $\Delta\rho$ of $-0.14$ and $0.23 \text{ e Å}^{-3}$; max. $\Delta/\sigma$ in final least-squares cycle of 0.15; $R$, $wR$ and $S$ of 0.052, 0.058 and 1.89. Atomic coordinates are listed in Table 1;* bond lengths, angles and torsion angles are given in Table 2. The *PLOTMD* (Luo, Ammon & Gilliland, 1989) program was used to display the *ORTEP* (Johnson, 1965) drawing on a VAXStation II monitor, label the drawing, and prepare a print file for a Hewlett-Packard Laser-Jet II printer (Fig. 1).

**Related literature.** An acid-catalyzed rearrangement of a pyranone derivative gave the title compound with three new stereogenic centers. This determination was performed to confirm the stereochemistry of the rearrangement product. A search of the January 1991 Cambridge Structural Database (Allen, Kennard & Taylor, 1983) revealed only one X-ray structure [5-(4-chlorophenyl)tetrahydro-3-phenyl-6-methyl($3\alpha,4\beta,6\alpha$)-$2H$-pyran-2-one; Axiotis, Dreux, Perrin & Royer (1982)] of a valerolactone with the same 3,4,6-substitution pattern as the title compound.

* Lists of structure factors, anisotropic temperature factors and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54276 (25 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
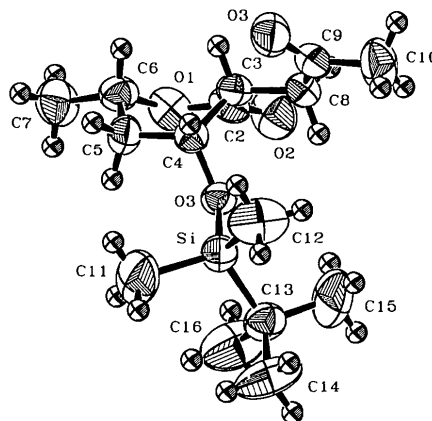


Fig. 1. *ORTEP* (Johnson, 1965). The C, O and Si atoms are shown as 50% ellipsoids and the H atoms are depicted as spheres with $B = 1.5 \text{ Å}^2$.

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# Structure of *N*-Methyl Benzaldehyde Nitrone

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**Abstract.** *N*-(Benzylidene)methylamine *N*-oxide, $C_8H_9NO$, $M_r = 135.2$, orthorhombic, *Pbca*, $a = 9.665$ (2), $b = 7.981$ (1), $c = 19.071$ (2) Å, $U = 1471.0$ Å$^3$, $Z = 8$, $D_x = 1.22$ g cm$^{-3}$, $\lambda(Mo\ K\alpha) = 0.71069$ Å, $\mu = 0.8$ cm$^{-1}$, $F(000) = 576$, $T = 298$ K, $R = 0.043$ and $wR = 0.050$ for 661 observed reflections with $|F^2| > 3\sigma(F^2)$. The geometry about the carbon–nitrogen double bond is $Z$, and there is little deviation from planarity.

**Experimental.** The compound was prepared by reaction of *N*-methylhydroxylamine with benzaldehyde, and crystals were obtained by recrystallization from benzene/light petroleum. A crystal of dimensions $0.35 \times 0.35 \times 0.08$ mm, cut from a larger plate crystal, was used for data collection. Unit-cell parameters by least squares fit of 25 reflections in the range $15 < 2\theta < 22°$, space group *Pbca* from systematic absences of $0kl$, $k$ odd; $h0l$, $l$ odd; $hk0$, $h$ odd; Enraf–Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$ radiation, $\theta$–$2\theta$ scan, $\Delta\theta = (0.8 + 0.35\tan\theta)°$, max. scan time 1 min, 1538 measured unique reflections for $2 < \theta < 25°$ and $h\ 0 \to 9$, $k\ 0 \to 11$, $l\ 0 \to 22$, 661 reflections for $|F^2| > 3\sigma(F^2)$, $\sigma(F^2) = [\sigma^2(I) + (0.04I)^2]^{1/2}/Lp$. Two standard reflections measured every hour showed 11.3% decay and a correction was applied to the data, Lorentz and polarization corrections, no absorption or extinction corrections. The structure was solved by direct methods using *SHELXS*86 (Sheldrick, 1985), refinement by full-matrix least squares with anisotropic thermal parameters. H atoms were located

from the difference map and refined with isotropic thermal parameters. With a weighting scheme of $w = 1/\sigma^2(F)$, $\sum w(|F_o| - |F_c|)^2$ minimized, the final residuals were $R = 0.043$, $wR = 0.050$ for 661 observed reflections, 127 variables, $S = 1.5$, $(\Delta/\sigma)_{max} = 0.01$, $(\Delta\rho)_{max,min} = +0.16$, $-0.18$ e Å$^{-3}$ on a final difference map. Programs from *SDP-Plus Structure Determination Package* (B. A. Frenz & Associates, Inc., 1984) were run on a MicroVAX II computer. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV). Atomic parameters are given in Table 1† and selected bond distances and angles are presented in Table 2. Fig. 1 shows the molecular structure and the numbering scheme.

**Related literature.** *Z*-Nitrones are generally the major products from this preparative route (Breuer, Aurich & Nielsen, 1988). The structure of the 4-chlorobenzaldehyde derivative has been determined (Folting, Lipscomb & Jerslev, 1964). The N—O bond is shorter and the C═N bond longer than in our case. In the derivative of 4-chloro-2,6-dimethylbenzaldehyde there is considerable deviation from planarity due to steric crowding (Jensen & Jerslev, 1969). Deviations from planarity are also noted in other highly substituted nitrones (Falshaw, Hashi &

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