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(*Z*)-*N*-[(2*R*,3*R*)-2-(*tert*-Butoxycarbonylamino)-3-(*tert*-butyldiphenylsiloxy)butylidene]benzylamine *N*-Oxide

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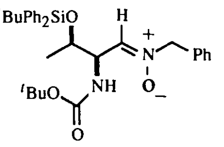
Abstract

The title compound, $C_{32}H_{42}N_2O_4Si$, is a key intermediate in the stereoselective synthesis of α,β-diaminoaldehydes, α,β-diaminoacids and chiral 1,2-diamines. The X-ray structure determination shows that the nitrone [C—CH=N$^+$(O$^-$)—C] system is planar with torsion angles of 175 (H1—C1—N1—O1) and 175.0° (C2—C1—N1—C5).

Comment

As part of a project directed toward the synthesis of chiral α,β-diaminoaldehydes, α,β-diaminoacids and 1,2-diamines, we described a stereodivergent procedure in which chiral nitrones derived from natural α-amino acids were used as suitable starting materials. The arrangement of the protecting groups in the nitrone is crucial for the selectivity of the process (Dondoni, Merchan, Merino, Tejero & Bertolasi, 1994).

Study the interaction of the nitrone functionality with its vicinal groups should aid the elucidation of the reactivity of the title nitrone, (I), derived from L-threonine. The present structure analysis shows that a plausible hydrogen bond O1···H(N2) is, in fact, impossible as a result of the bulkiness of the *tert*-butyldiphenylsilyl group. The molecular geometry and numbering scheme are shown in Fig. 1. The *Z* configuration of the nitrone is confirmed, as well as the planarity of the important nitrone atoms C1, H1, N1 and O1. Atoms C2 and C5 are also coplanar with the nitrone moiety.



(I)

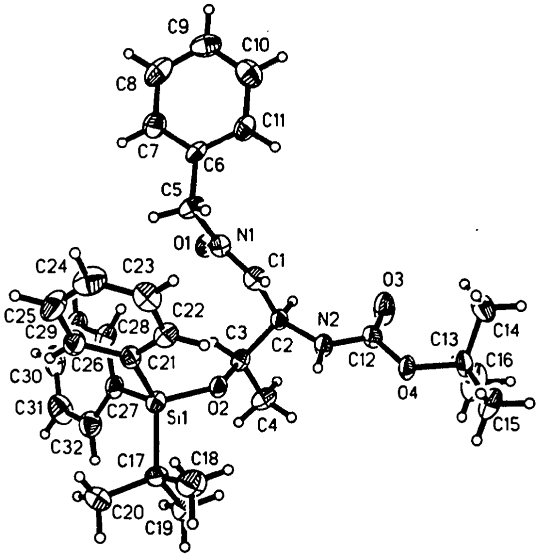


Fig. 1. Molecular configuration and atom-numbering scheme of the title compound. Displacement ellipsoids are plotted at the 30% probability level.

Experimental

The synthesis was carried out by reaction of the corresponding aldehyde with *N*-benzylhydroxylamine by the method described previously (Dondoni, Franco, Junquera, Merchan, Merino & Tejero, 1994). The compound was purified by column chromatography and crystals suitable for X-ray experiments were obtained by slow evaporation of the solvents [m.p. = 400 K; $[\alpha]_D = -24.3°$ (c 1.2 g 100 ml^{-1}, chloroform)].

Crystal data

$C_{32}H_{42}N_2O_4Si$
$M_r = 546.77$
Orthorhombic
$P2_12_12_1$
$a = 10.002\,(2)$ Å
$b = 14.274\,(3)$ Å
$c = 21.976\,(4)$ Å
$V = 3137.5\,(11)$ Å^3
$Z = 4$
$D_x = 1.158$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 39 reflections
$\theta = 9.45–21.85°$
$\mu = 0.111$ mm^{-1}
$T = 293\,(2)$ K
Transparent block
$0.5 \times 0.3 \times 0.2$ mm
Colourless

Data collection

Siemens *P*4 diffractometer
Profile data from $2\theta/\omega$ scans
Absorption correction: semi-empirical (ellipsoidal) refined from ψ scan (North, Phillips & Mathews, 1968)
$T_{\min} = 0.652$, $T_{\max} = 0.841$
3015 measured reflections
2827 independent reflections

1648 observed reflections [$I > 2\sigma(I)$]
$R_{\rm int} = 0.0633$
$\theta_{\max} = 22.50°$
$h = -1 \rightarrow 10$
$k = -1 \rightarrow 15$
$l = -1 \rightarrow 23$
3 standard reflections monitored every 97 reflections
intensity decay: 7.26%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0568$
$wR(F^2) = 0.1148$
$S = 1.132$
2824 reflections
398 parameters
H atoms refined as riding model (except for H1)
$w = 1/[\sigma^2(F_o^2) + (0.0580P)^2 + 0.7204P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.004$
$\Delta\rho_{\max} = 0.211$ e Å^{-3}
$\Delta\rho_{\min} = -0.176$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0047 (12)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

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

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

	x	y	z	$U_{\rm eq}$
Si1	0.1246 (2)	0.78695 (15)	0.20606 (11)	0.0546 (7)
O1	−0.0369 (6)	0.7720 (4)	0.0152 (2)	0.065 (2)
O2	0.1262 (5)	0.6910 (3)	0.1658 (2)	0.0525 (14)
O3	0.1054 (7)	0.4455 (4)	0.0132 (3)	0.100 (3)
O4	0.2803 (6)	0.4099 (3)	0.0725 (2)	0.063 (2)
N1	0.0914 (7)	0.7677 (5)	0.0154 (3)	0.055 (2)
N2	0.1858 (7)	0.5468 (4)	0.0802 (3)	0.059 (2)
C1	0.1579 (10)	0.6998 (7)	0.0374 (4)	0.057 (2)
C2	0.0907 (8)	0.6208 (5)	0.0685 (4)	0.049 (2)
C3	0.0258 (8)	0.6509 (5)	0.1274 (4)	0.052 (2)
C4	−0.0431 (11)	0.5714 (7)	0.1594 (5)	0.075 (3)
C5	0.1614 (9)	0.8486 (6)	−0.0107 (4)	0.067 (3)
C12	0.1836 (9)	0.4668 (6)	0.0505 (4)	0.059 (3)
C13	0.3025 (10)	0.3178 (6)	0.0456 (4)	0.065 (3)
C14	0.3316 (21)	0.3272 (12)	−0.0206 (5)	0.140 (6)
C15	0.4256 (9)	0.2841 (6)	0.0796 (5)	0.083 (3)
C16	0.1822 (12)	0.2566 (8)	0.0570 (9)	0.122 (5)
C17	0.1880 (9)	0.7518 (6)	0.2820 (4)	0.060 (2)
C18	0.3295 (10)	0.7140 (9)	0.2736 (5)	0.094 (3)
C19	0.1073 (14)	0.6734 (7)	0.3090 (5)	0.092 (3)
C20	0.1950 (13)	0.8346 (8)	0.3262 (4)	0.093 (3)
C6	0.1243 (8)	0.8702 (6)	−0.0730 (4)	0.052 (2)
C7	0.0612 (9)	0.9496 (7)	−0.0878 (6)	0.074 (3)
C8	0.0371 (11)	0.9726 (8)	−0.1475 (7)	0.090 (3)
C9	0.0711 (11)	0.9128 (10)	−0.1930 (6)	0.087 (3)
C10	0.1299 (11)	0.8309 (9)	−0.1781 (5)	0.086 (3)
C11	0.1576 (9)	0.8087 (6)	−0.1174 (5)	0.068 (3)
C21	0.2363 (9)	0.8712 (6)	0.1683 (4)	0.056 (2)
C22	0.3434 (9)	0.8423 (7)	0.1335 (4)	0.063 (2)
C23	0.4251 (10)	0.9048 (9)	0.1038 (5)	0.078 (3)
C24	0.4053 (12)	0.9988 (9)	0.1094 (5)	0.089 (3)
C25	0.3016 (13)	1.0286 (8)	0.1455 (5)	0.096 (4)
C26	0.2204 (11)	0.9667 (6)	0.1746 (4)	0.074 (3)
C27	−0.0437 (8)	0.8425 (6)	0.2073 (5)	0.058 (2)
C28	−0.0941 (9)	0.8828 (6)	0.1557 (5)	0.065 (3)
C29	−0.2168 (11)	0.9262 (6)	0.1530 (6)	0.079 (3)
C30	−0.2891 (11)	0.9334 (7)	0.2036 (7)	0.090 (3)
C31	−0.2455 (12)	0.8969 (8)	0.2558 (7)	0.100 (4)
C32	−0.1233 (11)	0.8504 (7)	0.2581 (5)	0.078 (3)

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

O1—N1	1.285 (8)	C1—C2	1.480 (11)
O2—C3	1.431 (8)	C1—H1	0.86 (6)
N1—C1	1.271 (10)	C2—C3	1.510 (10)
N1—C5	1.467 (9)	C3—C4	1.503 (10)
C1—N1—O1	124.1 (8)	N1—C1—H1	125 (4)
C1—N1—C5	120.0 (7)	C2—C1—H1	113 (4)
O1—N1—C5	115.9 (7)	N2—C2—C1	109.9 (7)
N1—C1—C2	121.3 (8)	C1—C2—C3	112.0 (7)
C2—C1—N1—C5	175.0 (7)	H1—C1—N1—O1	−175 (5)

Data collection: *XSCANS* (Siemens, 1992). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXL*93. Software used to prepare material for publication: *SHELXL*93.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1167). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Two Products of Ring Opening Reactions of an Arylthionitrooxirane

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Abstract

Crystal structure determination of the products, *S*-(4-methylphenyl) (αR,4*R*)-α-bromo-2,2-dimethyl-1,3-dioxolane-4-thioacetate, $C_{14}H_{17}BrO_3S$, (2), and *S*-(4-methylphenyl) (αR,4*R*)-α-(benzyloxycarbonylamino)-2,2-dimethyl-1,3-dioxolane-4-thioacetate, $C_{22}H_{25}NO_5S$, (3), of the two reactions, including absolute-structure assignment, shows that they proceed stereospecifically with inversion of configuration. Common groups of the two structures have essentially the same bond lengths and angles, but different conformations, arising from weak hydrogen bonding and van der Waals interactions.