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Chiral Hydroxylamines. I. 1-(*N*-Benzyl-*N*-hydroxyamino)-1-deoxy-2,3-*O*-isopropylidene-1-(1-methylimidazol-2-yl)-D-*threo*-triitol

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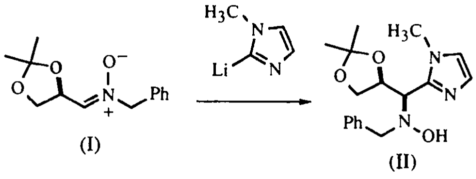
Abstract

The molecular structure of the title compound, *N*-benzyl-*N*-[(2,2-dimethyl-1,3-dioxolan-4-yl)(1-methylimidazol-2-yl)methyl]hydoxylamine, $C_{17}H_{23}N_3O_3$, determined from X-ray data, confirms the structure previously assigned on the basis of chemical evidence. One type of O—H···N hydrogen-bond interaction and van der Waals forces stabilize the crystal structure.

Comment

In the course of our studies aimed at the preparation of chiral hydroxyaminomethyl heterocycles with synthetic utility, we prepared the *N*-methylimidazole derivative (II) by the addition of the corresponding organometallic heterocyclic reagent to the nitrone (I). The experimental conditions concerning the synthesis of (II) have been reported previously (Dondoni, Franco, Merchan, Merino & Tejero, 1993*b*). Since the addition of other heterocyclic systems (*e.g.* thiazole and furan) afforded *syn* adducts when they were added to chiral nitrones (Dondoni, Franco, Merchan, Merino & Tejero, 1993*a*,*b*), we assumed *syn* stereochemistry for (II). The present structural determination of the title compound confirms our previous assignment and demonstrates that the attack of the organometallic reagent occurs at the less-hindered *Re* face, in a similar way to that proposed by us for the attack of 2-lithiofuran (Dondoni, Junquera, Merchan, Merino & Tejero, 1994). The determination of the absolute configuration was not undertaken since the starting nitrone (I) was enantiomerically pure, having an *S* configuration at the only asymmetric centre.



The molecular geometry and numbering scheme of the title compound are shown in Fig. 1. The dioxolane ring has an envelope conformation and the imidazole ring is planar. Both atoms C4 and C5, which are bonded to the azole ring, are coplanar with it. Since the absolute configuration at C6 is known to be *S*, the torsion angles given in Table 2 show the configuration at C5 to be *R*. The packing in the crystal is entirely due to hydrogen-bond interactions of 2.722 (5) Å between atoms O1 and N3, and van der Waals forces. A view of the crystal packing showing the intermolecular hydrogen-bond interactions is shown in Fig. 2.

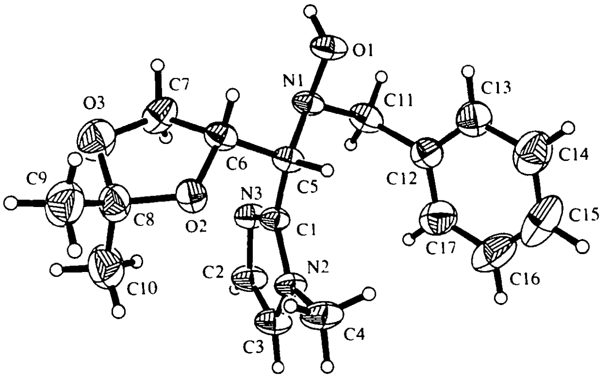


Fig. 1. The molecular geometry and numbering scheme for the title compound, (II). Displacement ellipsoids are plotted at the 30% probability level.

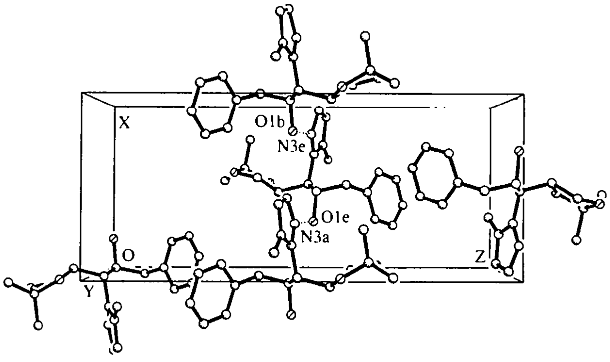


Fig. 2. Crystal packing of the hydroxylamine (II).

Experimental

Crystals suitable for X-ray analysis were obtained by slow evaporation of a solution of (II) in 1:4 hexane–diethyl ether solution. The melting point was found to be 376 K. $[\alpha]_D$ was found to be +17.2° (*c* 15.5 g l^{-1}, chloroform).

Crystal data

$C_{17}H_{23}N_3O_3$
$M_r = 317.38$

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å

Orthorhombic
$P2_12_12_1$
$a = 8.388\,(2)$ Å
$b = 10.527\,(2)$ Å
$c = 19.730\,(4)$ Å
$V = 1742.2\,(6)$ Å^3
$Z = 4$
$D_x = 1.210$ Mg m^{-3}

Cell parameters from 62 reflections
$\theta = 6.62$–$24.66°$
$\mu = 0.084$ mm^{-1}
$T = 293\,(2)$ K
Transparent block
$0.6 \times 0.4 \times 0.2$ mm
Colourless

Data collection

Siemens *P*4 diffractometer
Profile data from $2\theta/\omega$ scans
Absorption correction: none
1822 measured reflections
1659 independent reflections
1120 observed reflections [$I > 2\sigma(I)$]
$R_{\rm int} = 0.0196$

$\theta_{\rm max} = 22.55°$
$h = -1 \rightarrow 9$
$k = -1 \rightarrow 11$
$l = -1 \rightarrow 21$
3 standard reflections monitored every 97 reflections intensity decay: 3.70%

Refinement

Refinement on F^2
$R(F) = 0.0467$
$wR(F^2) = 0.1251$
$S = 1.029$
1659 reflections
214 parameters
H atoms refined as riding model
$w = 1/[\sigma^2(F_o^2) + (0.0524P)^2 + 0.5028P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = -0.021$

$\Delta\rho_{\rm max} = 0.308$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.147$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0103 (17)
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)

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

	x	y	z	$U_{\rm eq}$
O2	0.0258 (4)	0.1100 (3)	0.5841 (2)	0.0582 (11)
N2	0.2508 (5)	0.1032 (4)	0.4522 (2)	0.0523 (12)
O1	−0.1923 (4)	−0.1630 (3)	0.4750 (2)	0.0596 (11)
N3	0.3036 (5)	−0.0913 (4)	0.4818 (2)	0.0547 (12)
N1	−0.0216 (5)	−0.1590 (4)	0.4683 (2)	0.0481 (12)
C5	0.0174 (6)	−0.0294 (4)	0.4876 (3)	0.0465 (14)
C1	0.1911 (6)	−0.0081 (5)	0.4748 (3)	0.0466 (13)
C3	0.4096 (7)	0.0876 (6)	0.4452 (3)	0.069 (2)
C7	0.0549 (9)	−0.1007 (5)	0.6110 (3)	0.072 (2)
C4	0.1661 (8)	0.2206 (5)	0.4378 (3)	0.074 (2)
C6	−0.0263 (7)	−0.0117 (5)	0.5619 (3)	0.0533 (14)
C8	0.1097 (9)	0.0992 (6)	0.6461 (3)	0.075 (2)
C12	−0.0270 (9)	−0.0932 (6)	0.3448 (3)	0.065 (2)
O3	0.0845 (6)	−0.0266 (4)	0.6684 (2)	0.096 (2)
C11	0.0142 (7)	−0.1909 (5)	0.3980 (3)	0.062 (2)
C2	0.4412 (7)	−0.0327 (6)	0.4638 (3)	0.068 (2)
C17	0.0879 (10)	−0.0207 (7)	0.3153 (3)	0.091 (2)
C9	0.0365 (10)	0.1823 (7)	0.6985 (3)	0.105 (3)
C13	−0.1809 (9)	−0.0752 (6)	0.3250 (3)	0.077 (2)
C16	0.0484 (16)	0.0694 (9)	0.2686 (4)	0.114 (3)
C10	0.2807 (8)	0.1264 (9)	0.6338 (4)	0.106 (3)
C15	−0.1046 (16)	0.0894 (9)	0.2509 (4)	0.122 (4)
C14	−0.2189 (11)	0.0158 (8)	0.2784 (4)	0.106 (3)

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

O2—C8	1.416 (6)	C7—O3	1.399 (7)
O2—C6	1.423 (6)	C7—C6	1.509 (7)
N2—C1	1.350 (6)	C8—O3	1.412 (7)
N2—C3	1.349 (7)	C8—C10	1.482 (9)
N2—C4	1.454 (6)	C8—C9	1.488 (9)
O1—N1	1.439 (5)	C12—C13	1.362 (9)
N3—C1	1.295 (6)	C12—C17	1.360 (8)
N3—C2	1.355 (6)	C12—C11	1.509 (8)
N1—C5	1.454 (6)	C17—C16	1.364 (11)
N1—C11	1.459 (6)	C13—C14	1.365 (10)
C5—C1	1.495 (7)	C16—C15	1.346 (11)
C5—C6	1.523 (7)	C15—C14	1.346 (12)
C3—C2	1.345 (8)		
C8—O2—C6	110.2 (4)	C2—C3—N2	106.3 (5)
C1—N2—C3	107.2 (5)	O3—C7—C6	104.7 (4)
C1—N2—C4	128.4 (4)	O2—C6—C7	102.9 (4)
C3—N2—C4	124.5 (5)	C7—C6—C5	115.7 (4)
C1—N3—C2	106.6 (4)	O3—C8—O2	105.7 (5)
O1—N1—C5	103.1 (4)	C7—O3—C8	107.2 (4)
N1—C5—C1	108.4 (4)	C3—C2—N3	109.4 (5)
N3—C1—N2	110.5 (4)		
C5—C1—N3—C2	178.9 (6)	C6—C7—O3—C8	−31.2 (7)
C1—N3—C2—C3	−0.5 (6)	C7—O3—C8—O2	26.3 (7)
N3—C2—C3—N2	0.3 (7)	N1—C5—C6—C7	58.4 (6)
C2—C3—N2—C4	179.6 (5)	N1—C5—C6—O2	174.1 (4)

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

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1141). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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