

1990); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1184). Services for accessing these data are described at the back of the journal.

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Structures of Chiral Hydroxylamines. VI. (3*R*,4*S*)-*N*-Benzyl-4,5-dihydroxy-3-(hydroxyamino)-4,5-*O*-isopropylidene-1-pentynyl†

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Abstract

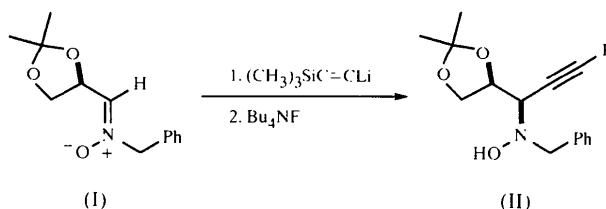
The structure of the title compound, C₁₅H₁₉NO₃, confirms the crystal structure previously assigned on the basis of chemical evidence. The packing in the crystal

† Alternative name: *N*-benzyl-*N*-[1-(2,2-dimethyl-1,3-dioxolan-4-yl)prop-2-ynyl]hydroxylamine.

is influenced by an intermolecular hydrogen-bond interaction [O—H...O 2.841 (2) Å].

Comment

In order to prepare new building blocks useful in developing a new method for the synthesis of optically pure allylamines, we described a procedure in which the chiral nitron, (I), was used (Merino, Anoro *et al.*, 1996). In two steps, compound (I) was transformed into propargyl hydroxylamine, (II), a key intermediate not only in the synthesis of allylamines, but also in the preparation of *N*-hydroxy α -amino acids (Merino *et al.*, 1997).



The stereochemistry of the title hydroxylamine, (II), was determined on the basis of chemical evidence, by transformation into the corresponding 1,3-oxazolidin-2-one. The present structural determination serves to confirm the previously assigned *syn* stereochemistry between the substituents attached to atoms C3 and C4.

The molecular geometry and numbering scheme are shown in Fig. 1. Bond distances and angles are in good agreement with the values reported for related chiral hydroxylamines (Merino *et al.*, 1995; Merino, Junquera *et al.*, 1996). The absolute configuration of (II) was not determined, since the configuration of the starting nitron, (I), was known to be *S* (Dondoni *et al.*, 1994). The torsion angles given in Table 1 show the configuration at the newly-formed C3 chiral center to be *R*.

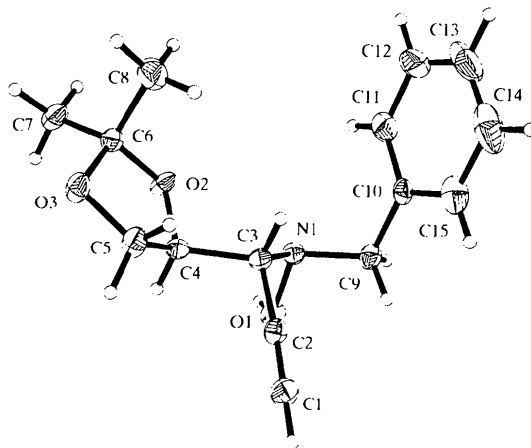


Fig. 1. The molecular structure of (II), showing the atom numbering. Displacement ellipsoids are shown at the 30% probability level.

The five-membered dioxolane ring has a total puckering amplitude (Cremer & Pople, 1975) of 0.299 (4) Å and a conformation intermediate between envelope and half-chair, with a local pseudo-mirror running along O3 and the midpoint of the O2—C4 bond, and a local pseudo-twofold axis running along O2 and the midpoint of O3—C5.

The phenyl plane and that through the dioxolane ring form a dihedral angle of 78.0 (1)°; the same planes form dihedral angles of 87.0 (2) and 52.8 (2)°, respectively, with the central, almost planar, C4—C3—N1—C9 system. Their orientation with respect to this plane is *syn*, and is defined by the torsion angles quoted in Table 1.

The packing is mainly governed by the O1—H···O1¹ hydrogen bond, whose geometry is defined by the following parameters: H···O1¹ 2.01, O1···O1¹ 2.841 (2) Å and O1—H···O1¹ 171° [symmetry code: (i) $-y, x-y, z-\frac{1}{3}$].

Experimental

Full experimental data concerning the synthesis of the title compound have been described previously (Merino, Anoro *et al.*, 1996). Crystals of (II) were obtained by slow evaporation from a 4:1 hexane–diethyl ether solution. The melting point was found to be 388 K and $[\alpha]_D -24.4$ (*c* 7.2 g dm⁻³, chloroform).

Crystal data

C ₁₅ H ₁₉ NO ₃	Mo <i>K</i> α radiation
<i>M_r</i> = 261.31	$\lambda = 0.71069$ Å
Trigonal	Cell parameters from 39 reflections
<i>P</i> 3 ₂	$\theta = 9.19$ – 24.92°
<i>a</i> = 13.240 (5) Å	$\mu = 0.083$ mm ⁻¹
<i>c</i> = 7.157 (5) Å	<i>T</i> = 173 (2) K
<i>V</i> = 1086.5 (10) Å ³	Block
<i>Z</i> = 3	0.60 × 0.42 × 0.26 mm
<i>D_x</i> = 1.198 Mg m ⁻³	Yellow
<i>D_m</i> not measured	

Data collection

Siemens <i>P4</i> diffractometer	$\theta_{\max} = 25.49^\circ$
2 θ/ω scans	<i>h</i> = $-1 \rightarrow 15$
Absorption correction: none	<i>k</i> = $-15 \rightarrow 1$
1948 measured reflections	<i>l</i> = $-1 \rightarrow 8$
1604 independent reflections	3 standard reflections
1402 reflections with $I > 2\sigma(I)$	every 97 reflections
<i>R</i> _{int} = 0.049	intensity decay: 6.64%

Refinement

Refinement on <i>F</i> ²	$(\Delta/\sigma)_{\max} = 0.002$
$R[F^2 > 2\sigma(F^2)] = 0.041$	$\Delta\rho_{\max} = 0.154$ e Å ⁻³
$wR(F^2) = 0.102$	$\Delta\rho_{\min} = -0.145$ e Å ⁻³
<i>S</i> = 1.093	Extinction correction: none

1553 reflections

178 parameters

H atoms calculated

$$w = 1/[\sigma^2(F_o^2) + (0.0643P)^2 + 0.0988P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

Scattering factors from
*International Tables for
Crystallography* (Vol. C)

Table 1. Selected geometric parameters (Å, °)

O1—N1	1.455 (3)	N1—C9	1.474 (4)
O2—C4	1.421 (4)	C2—C1	1.170 (5)
O2—C6	1.437 (4)	C2—C3	1.484 (4)
O3—C6	1.415 (4)	C3—C4	1.530 (4)
O3—C5	1.418 (4)	C4—C5	1.526 (4)
N1—C3	1.471 (4)		
O1—N1—C3	106.0 (2)	C1—C2—C3	176.7 (3)
O1—N1—C9	105.2 (2)	N1—C3—C2	114.6 (2)
C3—N1—C9	111.9 (2)	N1—C3—C4	111.5 (2)
C2—C3—C4—O2	177.4 (2)	C3—N1—C9—C10	-68.9 (4)
O2—C4—C3—N1	-55.3 (3)	N1—C9—C10—C11	126.2 (4)

Refinement was on *F*² for all reflections except for 51 with very negative *F*² or flagged by the user for potential systematic errors. The low ratio of reflections to parameters is mainly due to the fact that Friedel pairs were not measured. In fact, although θ_{\max} was 25.49°, only a ratio of 8.72 was obtained. Friedel pairs were not measured because refinement of the absolute structure [Flack (1983) parameter] is inconclusive for molecules having N as the heaviest atom; see, for instance, previous crystallographic analyses of chiral hydroxylamines (Merino, Junquera *et al.*, 1996).

Data collection: XSCANS (Siemens, 1992). Cell refinement: XSCANS. Data reduction: XSCANS. Program(s) used to solve structure: SHELXS86 (Sheldrick, 1990). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: SHELXTL-Plus (Sheldrick, 1991). Software used to prepare material for publication: SHELXTL-Plus.

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