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Chiral Hydroxylamines. III. 1-(*N*-Benzyl-*N*-hydroxyamino)-1-deoxy-1-(2-furyl)-2,3:4,5-di-*O*-isopropylidene-L-*manno*-pentitol

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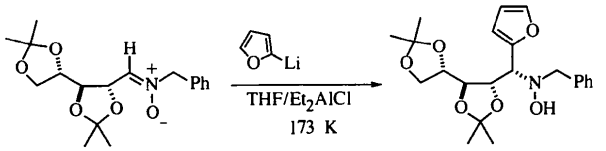
Abstract

The molecular structure of the title compound, $C_{22}H_{29}NO_6$, determined crystallographically, confirms the previous assignment on the basis of chemical and spectroscopic evidence. In addition, it supports the previously described furan sector rule for the determination of the absolute configuration of chiral 2-furylalkylhydroxylamines by the dichroic circular method. The crystal structure is stabilized entirely by van der Waals interactions.

Comment

We have recently described a stereodivergent methodology for the synthesis of 2-furylalkylhydroxylamines starting from chiral nitrones (Dondoni, Franco, Merchan, Merino & Tejero, 1993). The synthetic utility of this methodology was demonstrated by the further conversion of the prepared chiral hydroxylamines into optically active β-hydroxy-α-amino acids (Dondoni, Junquera, Merchan, Merino, & Tejero, 1994). Among the chiral hydroxylamines prepared was the arabinose-derived adduct (II), obtained from nitrone (I), whose stereochemistry was determined on the basis of chemical evidence. The present structural determination of the title compound, (II), confirms the previously assigned *anti* stereochemistry between the C5 and C6 atoms.



(I) (II)

The molecular geometry and atomic numbering scheme of the title compound are shown in Fig. 1. The furan and phenyl rings are coplanar with C5 and C10, respectively. Such planarity has already been observed in other 2-furylalkylbenzylhydroxylamines described previously by us (Merino, Merchan, Tejero & Lanaspa, 1996*a*,*b*). Compound (II) shows an alternate conformation between the furan ring and the C6 and N1 atoms, with torsion angles C6—C5—C4—C3 −55.9 (10) and N1—C5—C4—C3 70.4 (10)°, thus allowing the H5 atom to be eclipsed by the furan ring [O2—C4—C5—H5 7.6 (5)°].

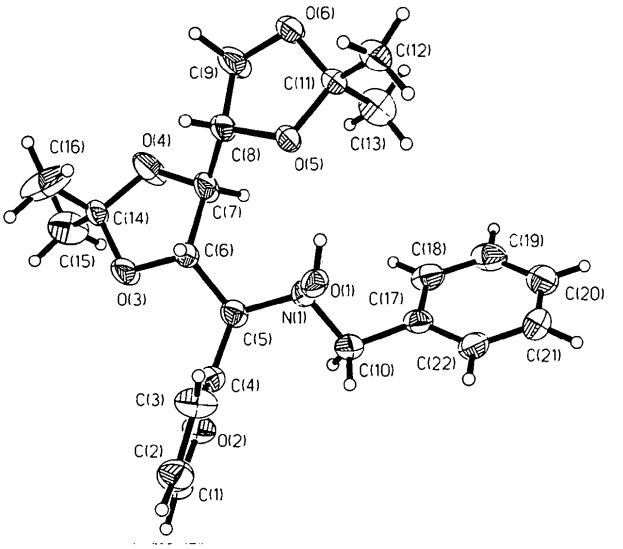


Fig. 1. The molecular geometry and numbering scheme for the title compound. Displacement ellipsoids are plotted at the 30% probability level.

The precision of the structure is relatively low, which may be due to unresolved disorder, as indicated by some high displacement parameters, but the results serve to confirm our previously proposed conformation based on molecular mechanics calculations and used to rationalize the observed Cotton effect in chiral 2-furylalkylhydroxylamines (Tejero, Franco, Junquera, Lanaspa, Merchan, Merino & Rojo, 1996).

The determination of the absolute configuration was not considered since the starting nitrone, (I), obtained from L-arabinose as described previously (Dondoni, Franco, Junquera, Merchan, Merino & Tejero, 1994), was known to be enantiomerically pure. The absolute configuration at C6 was known to be *S* and the torsion angles given in Table 2 show the configuration at the newly formed C5 chiral center to be *R*. There are no unusual intermolecular contacts, the crystal packing being entirely the result of van der Waals interactions.

Experimental

Full experimental and spectroscopic data concerning the synthesis of the title compound have been described previously (Dondoni, Junquera, Merchan, Merino & Tejero, 1994). The compound was purified by column chromatography and then crystallized from methanol. Crystals suitable for X-ray experiments were obtained by slow evaporation of the solvent. The melting point was found to be 353 K.

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Crystal data

$C_{22}H_{29}NO_6$
M_r = 403.46
Monoclinic
$P2_1$
a = 9.747 (2) Å
b = 5.7470 (10) Å
c = 18.971 (4) Å
β = 91.08 (3)°
V = 1062.5 (4) Å^3
Z = 2
D_x = 1.261 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 40 reflections
θ = 10.51–24.75°
μ = 0.091 mm^{-1}
T = 205 (2) K
Block
0.40 × 0.35 × 0.28 mm
Colourless

Data collection

Siemens $P4$ diffractometer
$2\theta/\omega$ scans
Absorption correction: none
2922 measured reflections
2471 independent reflections
2043 observed reflections [$I > 2\sigma(I)$]
R_{int} = 0.0368

θ_{max} = 25.02°
$h = -1 \rightarrow 11$
$k = -1 \rightarrow 6$
$l = -22 \rightarrow 22$
3 standard reflections monitored every 97 reflections
intensity decay: 14.8%

Refinement

Refinement on F^2
$R(F)$ = 0.0732
$wR(F^2)$ = 0.1824
S = 1.038
2469 reflections
268 parameters
H atoms riding with group U_{iso}
$w = 1/[\sigma^2(F_o^2) + (0.0617P)^2 + 1.666P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = −0.005

$\Delta\rho_{max}$ = 0.594 e Å^{-3}
$\Delta\rho_{min}$ = −0.483 e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.022 (4)
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)*

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

	x	y	z	U_{eq}
N1	0.4376 (4)	−0.0164 (10)	0.8034 (2)	0.0498 (12)
O1	0.4865 (4)	0.2142 (8)	0.7889 (2)	0.0518 (10)
O2	0.0904 (4)	0.0167 (9)	0.8340 (2)	0.0642 (13)
O3	0.1852 (3)	−0.1113 (12)	0.6636 (2)	0.089 (2)
O4	0.3448 (4)	−0.3199 (15)	0.6076 (3)	0.128 (3)
O5	0.6247 (3)	0.0538 (10)	0.6714 (2)	0.068 (2)
O6	0.7628 (4)	−0.1386 (13)	0.5973 (2)	0.096 (2)
C1	0.0046 (6)	0.1950 (17)	0.8521 (3)	0.067 (2)
C2	0.0497 (8)	0.3912 (16)	0.8278 (4)	0.076 (2)
C3	0.1697 (7)	0.3374 (13)	0.7907 (4)	0.071 (2)
C4	0.1928 (6)	0.1146 (12)	0.7966 (3)	0.0496 (15)
C5	0.3012 (5)	−0.0411 (12)	0.7708 (3)	0.0527 (15)
C6	0.3125 (5)	−0.0239 (15)	0.6907 (3)	0.062 (2)
C7	0.4196 (5)	−0.1896 (16)	0.6590 (3)	0.077 (3)
C8	0.5349 (5)	−0.063 (2)	0.6221 (3)	0.098 (4)
C9	0.6304 (6)	−0.227 (3)	0.5851 (5)	0.134 (5)
C10	0.4304 (6)	−0.0371 (16)	0.8801 (3)	0.066 (2)
C11	0.7622 (5)	−0.0371 (15)	0.6643 (3)	0.055 (2)
C12	0.8603 (6)	0.1614 (14)	0.6659 (3)	0.063 (2)
C13	0.7900 (7)	−0.2062 (16)	0.7214 (4)	0.086 (2)
C14	0.2096 (5)	−0.2341 (12)	0.6016 (3)	0.052 (2)
C15	0.1157 (8)	−0.4349 (16)	0.5967 (5)	0.095 (3)
C16	0.1926 (12)	−0.0820 (19)	0.5401 (4)	0.125 (4)
C17	0.5691 (6)	−0.0835 (13)	0.9133 (3)	0.054 (2)
C18	0.6348 (7)	−0.2910 (16)	0.9001 (3)	0.071 (2)
C19	0.7588 (7)	−0.3425 (16)	0.9330 (4)	0.078 (2)
C20	0.8161 (7)	−0.1857 (18)	0.9792 (4)	0.079 (2)
C21	0.7523 (7)	0.0156 (17)	0.9931 (3)	0.075 (2)
C22	0.6291 (6)	0.0699 (14)	0.9603 (3)	0.062 (2)

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

O1—N1	1.437 (7)	N1—C5	1.463 (6)
N1—C10	1.462 (7)		
O1—N1—C10	106.8 (5)	N1—C5—C4	116.8 (5)
O1—N1—C5	108.1 (5)	N1—C5—C6	109.5 (4)
C10—N1—C5	110.7 (4)	C4—C5—C6	110.9 (5)
O3—C6—C5—N1	164.7 (6)	O5—C8—C7—C6	70.8 (8)
O3—C6—C5—C4	−64.9 (7)	O5—C8—C7—O4	−173.9 (7)

Refinement of the absolute structure Flack (1983) parameter [χ = −1 (3)] was inconclusive; the correct absolute configuration was deduced from the synthesis.

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: *SHELXTL-Plus* (Sheldrick, 1991). Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CF1124). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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