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(4S,5S)-(+)-4-Hydroxymethyl-2,5-diphenyloxazoline

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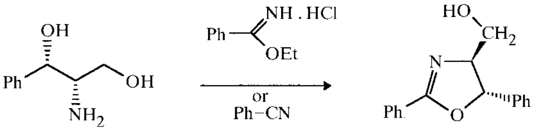
The absolute configuration of the title compound, alternatively called (+)-(4,5-dihydro-2,5-diphenyloxazol-4-yl)-methanol, $C_{16}H_{15}NO_2$, has been confirmed as 4S,5S. The hydroxymethyl group and phenyl ring at the asymmetric C atoms exhibit β and α orientations, respectively. The exocyclic C—C bonds at the asymmetric C atoms are mutually anticlinal (−*ac*). The hydroxyl group and the N atom of the oxazoline ring are involved in an intermolecular hydrogen bond leading to chains of molecules.

Comment

The synthesis of the title compound, (II), from (1S,2S)-(+)-2-amino-1-phenyl-1,3-propanediol, (I), and ethyl benzimidate hydrochloride or benzonitrile has recently been reported independently by three research groups (Allen & Williams, 1994; Hoarau *et al.*, 1997; Rozwadowska, 1998). Although the stereochemistry of (II) has been accepted as 4S,5S, the samples of oxazoline (II) prepared in these laboratories differed significantly in their physical data, *i.e.* in specific rotations, both in the sign and dimension, melting points and solubility, whereas the spectral data were much the same, within experimental error, for all the samples (see *Experimental*).



(I) (II)

Oxazoline (II), prepared in our laboratory from (I) and ethyl benzimidate hydrochloride or benzonitrile, showed positive rotation, as did the sample described by Hoarau *et al.* (1997), whereas Allen & Williams (1994) reported negative rotation. There were also differences in the melting points of all the samples: our sample melted at a much higher temperature (459–460 K) than the samples prepared by Allen & Williams (400–402 K) and Hoarau *et al.* (408 K). Moreover, we reported poor solubility of the compound in chloroform at room temperature. Since oxazolines are intermediates in the O → N acyl group migration in acylated 1,2-aminoalcohols, involving in some cases inversion of configuration, we decided to confirm unambiguously the structure of oxazoline (II) of m.p. 459–460 K and $[\alpha]_D^{20} = +51.0$ ($c = 0.54$, $CHCl_3$) by X-ray analysis.

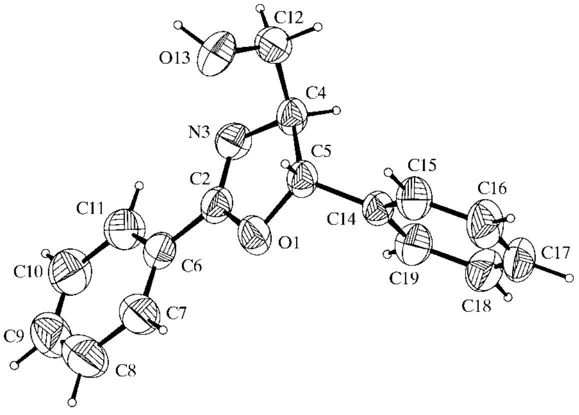


Figure 1
The molecular structure of (II) with displacement ellipsoids drawn at the 50% probability level. H atoms, treated as isotropic, are on an arbitrary scale.

For the (+)-enantiomer shown in Fig. 1, the tetrahedral C4 and C5 atoms are chiral centres. The absolute configuration of those atoms was established as 4S and 5S by the structure refinement using Bijvoet-pair reflections. The hydroxymethyl group at the asymmetric C4 atom exhibits a β-orientation, whereas the phenyl group at the asymmetric C5 atom is α-oriented. The torsion angle C12—C4—C5—C14 [−111.39 (13)°] indicates an anticlinal conformation of the C12 atom in the hydroxymethyl group with respect to the C14 atom of the phenyl group.

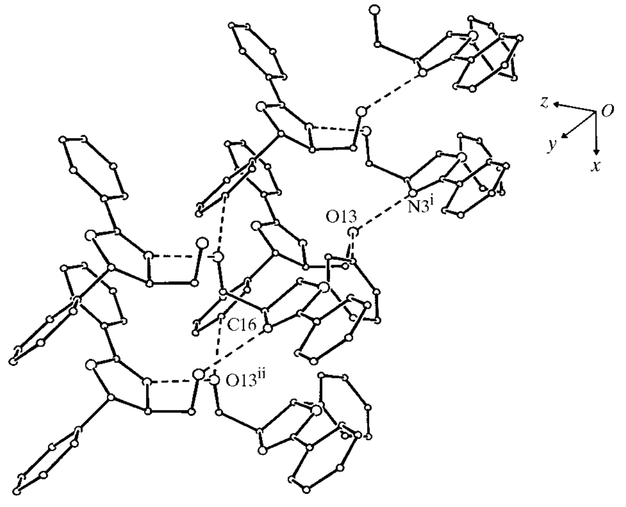


Figure 2
The hydrogen bonding in the crystal lattice of (II). The hydrogen bonds are indicated with dashed lines and the symmetry codes are explained in Table 2.

The oxazoline ring is nearly planar with an r.m.s. deviation of 0.0306 Å. The C2 and C5 phenyl groups subtend very different interplanar angles of 8.82 (10) and 82.47 (4)°, respectively, to the oxazoline ring. The C2—C6 distance of 1.4723 (17) Å is shorter than the C5—C14 single bond of 1.4999 (16) Å by about 12σ. This indicates a weak conjugation effect between the C2 phenyl group and the oxazoline ring.

The bond distances and angles in the title molecule are consistent with those found in (4*S*,5*S*,*S*$_S$)-4-hydroxymethyl-2-[2-(4-methylphenylsulfinyl)phenyl]-4,5-dihydro-5-phenyl-1,3-oxazole (Bower *et al.*, 1996). Other hydroxymethyl-phenyl-oxazoline derivatives are not described in the Cambridge Structural Database (Version 5.18; Allen & Kennard, 1993).

The O13 atom of the hydroxyl group is synclinal with respect to the N3—C4 bond of the oxazoline ring [torsion angle O13—C12—C4—N3 of 68.15 (14)°]. We assume that this arrangement of the O13 atom is stabilized by the intermolecular O13—H13*A*···N3^{i} hydrogen bond (Table 2), which leads to chains of molecules parallel to the *x* axis. An intermolecular C16—H16*A*···O13^{ii} contact (Table 2) links neighbouring chains into a two-dimensional hydrogen-bond network parallel to the *xy* plane (Fig. 2).

Experimental

The title compound, (II), was prepared according to the literature procedure of Rozwadowska (1998). The crystals were grown from ethanol by slow evaporation of the solvent at room temperature. Some of physical and spectral characteristics of our sample and of the others are given below:

(II): m.p. 459–460 K; $[\alpha]_D^{20}$ = +51.0 (*c* = 0.54, CHCl$_3$), $[\alpha]_D^{20}$ = +70.0 (*c* = 0.5, CH$_3$OH), $[\alpha]_D^{20}$ = +88.5 (*c* = 1.0, DMSO); IR (KBr) cm^{-1}: 1648 (C=N); ^{1}H NMR (CDCl$_3$), p.p.m.: δ = 4.24 (*d*, *J* = 8.0 Hz, H4), 5.58 (*d*, *J* = 8.2 Hz, H5).

Allen & Williams (1994): m.p. 400–402 K; $[\alpha]_D^{25}$ = −44.6 (*c* = 5.4, CHCl$_3$); IR (KBr) cm^{-1}: 1670 (C=N); ^{1}H NMR (CDCl$_3$), p.p.m.: δ = 4.22 (H4), 5.56 (*d*, *J* = 8.0 Hz, H5).

Hoarau *et al.* (1997): m.p. 408 K; $[\alpha]_D^{20}$ = +74.2 (*c* = 1,0, DMSO); ^{1}H NMR (CDCl$_3$), p.p.m.: δ = 4.23 (*d*, *J* = 8.1 Hz, H4), 5.57 (*d*, *J* = 8.1 Hz, H5).

Crystal data

$C_{16}H_{15}NO_2$
M_r = 253.29
Orthorhombic, $P2_12_12_1$
a = 4.8995 (10) Å
b = 11.3300 (13) Å
c = 23.820 (3) Å
V = 1322.3 (4) Å^3
Z = 4
D_x = 1.272 Mg m^{-3}

Cu *Kα* radiation
Cell parameters from 48 reflections
θ = 15.4–30.3°
μ = 0.674 mm^{-1}
T = 293 (2) K
Needle, colourless
0.50 × 0.25 × 0.11 mm

Data collection

Kuma Diffraction KM-4 diffractometer
ω–2θ scans
2557 measured reflections
2406 independent reflections
2273 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.037

$\theta_{\max}$ = 70.04°
$h = -5 \rightarrow 5$
$k = 0 \rightarrow 13$
$l = 0 \rightarrow 29$
2 standard reflections every 100 reflections
intensity decay: 0.7%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.029
$wR(F^2)$ = 0.082
S = 1.076
2406 reflections
233 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0536P)^2 + 0.0663P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max}$ = 0.13 e Å^{-3}
$\Delta\rho_{\min}$ = −0.13 e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0047 (7)
Absolute structure: Flack (1983)
Flack parameter = −0.09 (19)

Table 1
Selected geometric parameters (Å, °).

O1—C2	1.3563 (14)	N3—C4	1.4660 (15)
O1—C5	1.4568 (16)	C4—C5	1.5479 (16)
C2—N3	1.2677 (16)	C5—C14	1.4999 (16)
C2—C6	1.4723 (17)		
C2—O1—C5	106.52 (9)	N3—C4—C5	104.34 (10)
N3—C2—O1	117.81 (10)	O1—C5—C4	103.13 (9)
C2—N3—C4	107.69 (9)		

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O13—H13*A*···N3^{i}	0.92 (2)	1.89 (2)	2.7948 (14)	169 (2)
C16—H16*A*···O13^{ii}	0.99 (2)	2.49 (2)	3.3314 (18)	142.3 (16)

Symmetry codes: (i) $x - \frac{1}{2}, \frac{3}{2} - y, -z$; (ii) $\frac{1}{2} + x, \frac{5}{2} - y, -z$.

The positions of the H atoms were obtained from difference Fourier maps and refined freely. The absolute configuration of (II) was established on the basis of 930 Friedel opposite reflections using the Flack parameter (Flack, 1983).

Data collection, cell refinement and data reduction: *Kuma KM*-4 *Software* (Kuma Diffraction, 1991); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976) and *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1397). Services for accessing these data are described at the back of the journal.

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