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3,4,4a,5,6,7,8,8a-Octahydro-8a-hydroxy-2-quinolone and its 8a-Hydroperoxy Derivative

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Abstract

The crystal structures of the title compounds, 3,4,4a,5,6,-7,8,8a-octahydro-8a-hydroxy-2-quinolone [$C_9H_{15}NO_2$, (I)] and 3,4,4a,5,6,7,8,8a-octahydro-8a-hydroperoxy-2-quinolone [$C_9H_{15}NO_3$, (II)], show a *trans-* and a *cis*-fused-ring configuration, respectively, with the cyclohexane rings in a chair conformation in both compounds. In (I), the molecules are linked about 2_1

axes *via* intermolecular N—H···O hydrogen bonds, forming an infinite helix; further O—H···O interactions result in a two-dimensional hydrogen-bond network. In (II), the molecules form centrosymmetric dimers *via* pairwise N—H···O interactions, and these dimers are connected by O—H···O hydrogen bonds, giving infinite parallel chains.

Comment

Recently, we reported an efficient new procedure for the synthesis of 6-hydroxy-3,4,5,6-tetrahydro-2-pyridones and 6-hydroperoxy-3,4,5,6-tetrahydro-2-pyridones, by hydration–cyclization of δ-ketonitriles with basic hydrogen peroxide (Citterio *et al.*, 1997). The first class of compounds are useful intermediates in acyliminium chemistry (Murahashi *et al.*, 1993), whereas the latter are quite stable hydroperoxides. Applied to 2-(2-cyano-ethyl)cyclohexanone, this procedure affords compounds (I) and (II) as a mixture of the corresponding *cis* and *trans* isomers. The stereochemistry of (I) and (II) was

(I)   (II)
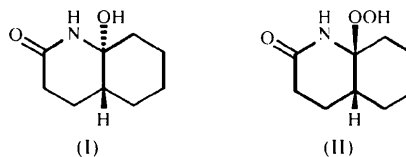
difficult to elucidate by NMR spectroscopy, and in order to confirm their identity and to determine the relative stereochemistry, an X-ray structural investigation was carried out on pure epimers obtained by selective crystallization. In both compounds, the cyclohexane ring adopts a chair conformation. The ring fusion in (I) is *trans*, with a torsion angle O2—C9—C10—H10 of 176.9 (10)° and with the hydroxy substituent in an axial position, which is the only conformation possible for this compound (Fig. 1). In (II), the two rings have a *cis*-fused stereochemistry, with a torsion angle O2—C9—C10—H10 of 54.9 (12)° and the hydroperoxy group in an equatorial position. Within the piperidone rings of both compounds, the carbonyl and the N_{sp^2} groups are nearly coplanar [r.m.s. deviations are 0.045 and 0.021 Å for (I) and (II), respectively], with the C4 and C10 atoms lying below and above the least-squares mean planes, respectively. Bond distances and angles in both compounds are in agreement with the expected values, with the exception of the bond angles around atoms C9 and C10, where significant deviation from C_{sp^3} geometry is observed (Tables 1 and 3), probably due to the different ring junctions. The conformation around the C9—O2 bond is approximately *gauche*. The value of the torsion angles N—C9—O2—H2O for (I) and N—C9—O2—O3 for (II) are, respectively, −46.0 (13) and −57.31 (16)°, slightly smaller than those reported for a similar structural motif (64–67°) in the

Cambridge Structural Database (Allen *et al.*, 1983). The antiperiplanar orientation of the C—N bond relative to the O-atom lone pair seems to be related to the anomeric effect associated with the N—C—O linkage and to the $n \rightarrow \sigma^*$ molecular-orbital interaction involving the heteroatom lone pair and the vacant C—N or C—O antibonding orbital (Deslongchamps, 1983; Salzner & Schleyer, 1994).
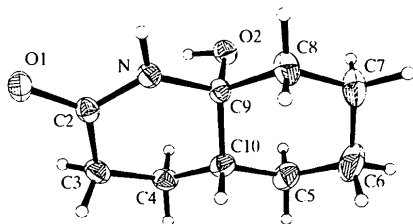

Fig. 1. View of molecule (I), showing the atom-labelling scheme. Displacement ellipsoids are plotted at the 20% probability level, while the H atoms are of an arbitrary size.
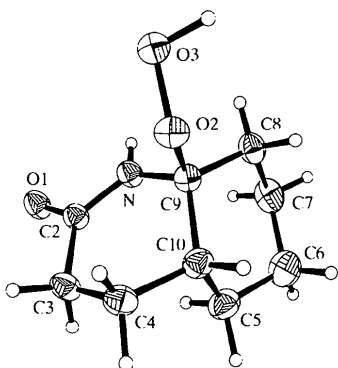

Fig. 2. View of molecule (II), showing the atom-labelling scheme. Displacement ellipsoids are plotted at the 20% probability level, while the H atoms are of an arbitrary size.

As regards crystal packing, amide groups are known to afford hydrogen-bonded dimers or chains (Berkovitch-Yellin & Leiserowitz, 1983). The structures of (I) and (II) show two different hydrogen-bonding topologies. In both structures, the carbonyl O atoms are bifurcated acceptors of hydrogen bonds, while the hydroxyl O atoms act only as hydrogen-bond donors. In (I), each molecule is linked *via* intermolecular N—H···O1 hydrogen bonds to two neighbours related to it by a 2_1 screw axis, forming an infinite helix along **b** (see Fig. 3). The chains are themselves cross-linked by O2—H···O1 interactions between the carbonyl and the hydroxyl O atoms, into an infinite two-dimensional network extending parallel to the *bc* plane. No hydrogen bonds are present between these layers. According to the Etter notation (Etter *et al.*, 1990), the chain hydrogen-bond motif may be designated as $C(4)$ and the interchain hydrogen-bond pattern (ring motif) as $R_2^2(12)$. In

the crystals of (II), each molecule is linked to a single neighbour, related to it by a centre of symmetry, *via* two mutual N—H···O1 hydrogen bonds, forming a planar eight-membered pseudo-cycle [graph set $R_2^2(8)$] (Fig. 4). Further O3—H···O1 interactions result in infinite parallel chains of dimers along the *a* axis [graph set $R_4^2(14)$]. The overall hydrogen-bonding network may account for the high stability of compound (II), which decomposes only at its melting point (413 K) and is stable for years at 298 K.
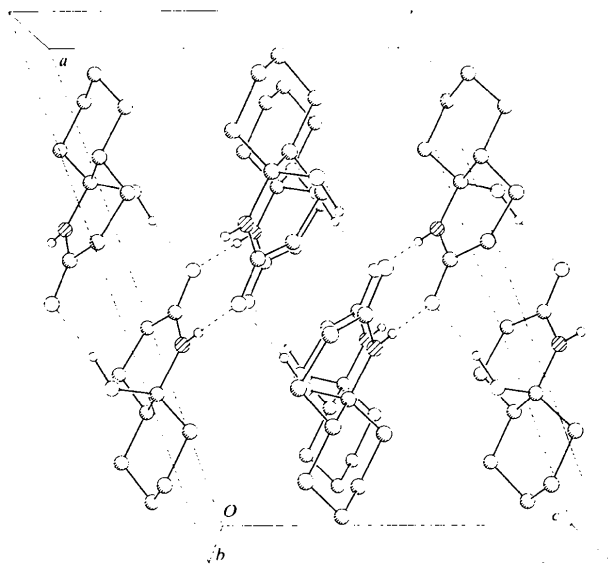

Fig. 3. Packing arrangement of (I) viewed along the *b* axis, showing the hydrogen-bond system (dashed lines).
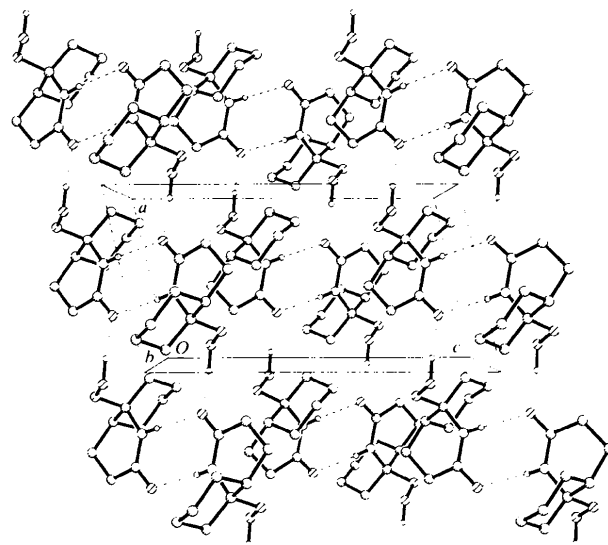

Fig. 4. Packing arrangement of (II) viewed along the *b* axis, showing the hydrogen-bond system (dashed lines).

Experimental

The title compounds were prepared according to the procedure published by Citterio *et al.* (1997). Crystals of (I), suitable for X-ray diffraction analysis, were obtained by crystallization of a 97:3 epimer mixture from ethyl acetate, whereas crystals of (II) were obtained by double crystallization of a 45:55 epimer mixture from methanol.

Compound (I)

Crystal data

$C_9H_{15}NO_2$	Cu $K\alpha$ radiation
$M_r = 169.22$	$\lambda = 1.54178$ Å
Monoclinic	Cell parameters from 24
$P2_1/c$	reflections
$a = 14.574\,(8)$ Å	$\theta = 22–38°$
$b = 6.5096\,(16)$ Å	$\mu = 0.710$ mm^{-1}
$c = 10.103\,(5)$ Å	$T = 293\,(2)$ K
$\beta = 109.82\,(4)°$	Trigonal prism
$V = 901.7\,(7)$ Å^3	$0.60 \times 0.50 \times 0.40$ mm
$Z = 4$	Colourless
$D_x = 1.247$ Mg m^{-3}	
D_m not measured	

Data collection

Siemens *P4* diffractometer	$\theta_{max} = 68.85°$
$\theta/2\theta$ scans	$h = -17 \rightarrow 17$
Absorption correction: none	$k = -1 \rightarrow 7$
2231 measured reflections	$l = -1 \rightarrow 11$
1604 independent reflections	3 standard reflections
1497 reflections with	every 200 reflections
$I > 2\sigma(I)$	intensity decay: $<0.5\%$
$R_{int} = 0.027$	

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} = 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.037$	$\Delta\rho_{max} = 0.17$ e Å^{-3}
$wR(F^2) = 0.107$	$\Delta\rho_{min} = -0.16$ e Å^{-3}
$S = 1.070$	Extinction correction:
1604 reflections	SHELXL97
138 parameters	Extinction coefficient:
H atoms: see below	0.0147 (12)
$w = 1/[\sigma^2(F_o^2) + (0.0524P)^2$	Scattering factors from
$+ 0.2042P]$	International Tables for
where $P = (F_o^2 + 2F_c^2)/3$	Crystallography (Vol. C)

Table 1. *Selected geometric parameters (Å, °) for (I)*

O1—C2	1.2483 (16)	O2—C9	1.4175 (16)
N—C2	1.3341 (17)	C9—C10	1.5286 (18)
N—C9	1.4624 (17)		
C2—N—C9	125.64 (11)	O2—C9—C10	112.17 (11)
C2—C3—C4	115.75 (11)	C8—C9—C10	110.62 (12)
O2—C9—C8	105.55 (11)	C4—C10—C5	114.13 (13)
C9—N—C2—C3	11.37 (19)	C2—N—C9—C8	-153.35 (13)
N—C2—C3—C4	-13.97 (19)	C2—N—C9—O2	91.28 (15)
O2—C9—C10—H10	176.9 (10)	N—C9—O2—H2O	-46.0 (13)

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

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2O···O1^i	0.94 (2)	1.89 (2)	2.826 (2)	172 (2)
N—H1N···O1^{ii}	0.85 (2)	2.14 (2)	2.989 (2)	178 (2)

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

Compound (II)

Crystal data

$C_9H_{15}NO_3$	Cu $K\alpha$ radiation
$M_r = 185.22$	$\lambda = 1.54178$ Å
Monoclinic	Cell parameters from 36
$P2_1/c$	reflections
$a = 6.9120\,(10)$ Å	$\theta = 15–40°$
$b = 10.905\,(2)$ Å	$\mu = 0.806$ mm^{-1}
$c = 12.848\,(2)$ Å	$T = 293\,(2)$ K
$\beta = 102.620\,(10)°$	Block
$V = 945.0\,(3)$ Å^3	$0.60 \times 0.30 \times 0.20$ mm
$Z = 4$	Colourless
$D_x = 1.302$ Mg m^{-3}	
D_m not measured	

Data collection

Siemens *P4* diffractometer	$\theta_{max} = 68.97°$
$\theta/2\theta$ scans	$h = -1 \rightarrow 7$
Absorption correction: none	$k = -13 \rightarrow 1$
2366 measured reflections	$l = -15 \rightarrow 15$
1685 independent reflections	3 standard reflections
1370 reflections with	every 200 reflections
$I > 2\sigma(I)$	intensity variation: $<0.3\%$
$R_{int} = 0.035$	

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} <0.001$
$R[F^2 > 2\sigma(F^2)] = 0.044$	$\Delta\rho_{max} = 0.19$ e Å^{-3}
$wR(F^2) = 0.127$	$\Delta\rho_{min} = -0.21$ e Å^{-3}
$S = 1.021$	Extinction correction:
1685 reflections	SHELXL97
143 parameters	Extinction coefficient:
H atoms: see below	0.0096 (14)
$w = 1/[\sigma^2(F_o^2) + (0.0665P)^2$	Scattering factors from
$+ 0.2071P]$	International Tables for
where $P = (F_o^2 + 2F_c^2)/3$	Crystallography (Vol. C)

Table 3. *Selected geometric parameters (Å, °) for (II)*

O1—C2	1.247 (2)	N—C2	1.333 (2)
O2—C9	1.441 (2)	N—C9	1.451 (2)
O2—O3	1.4599 (17)	C9—C10	1.531 (2)
C9—O2—O3	109.16 (12)	O2—C9—C10	103.27 (12)
C2—N—C9	126.27 (14)	C8—C9—C10	112.79 (14)
C2—C3—C4	115.91 (15)	C4—C10—C5	112.16 (16)
O2—C9—C8	110.62 (14)		
C2—N—C9—O2	-86.8 (2)	C2—N—C9—C8	151.30 (17)
C9—N—C2—C3	-3.8 (3)	O2—C9—C10—H10	-54.9 (12)
N—C2—C3—C4	8.2 (3)	N—C9—O2—O3	-57.31 (16)

Table 4. *Hydrogen-bonding geometry (Å, °) for (II)*

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3O···O1^i	1.02 (3)	1.71 (3)	2.718 (2)	171 (2)
N—H1N···O1^{ii}	0.84 (2)	2.13 (2)	2.953 (2)	169 (2)

Symmetry codes: (i) $1 + x, y, z$; (ii) $1 - x, -y, 1 - z$.

H atoms were located from difference Fourier maps and refined using a riding model; the positions of the N—H, O—H and C10—H H atoms were refined freely.

For both compounds, data collection: *XSCANS* (Siemens, 1994); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structures: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structures: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL/PC* (Sheldrick,

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

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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-pentyne†

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(*Received 7 October 1997; accepted 23 January 1998*)

Abstract

The structure of the title compound, $C_{15}H_{19}NO_3$, confirms the crystal structure previously assigned on the basis of chemical evidence. The packing in the crystal

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 nitrone, (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).
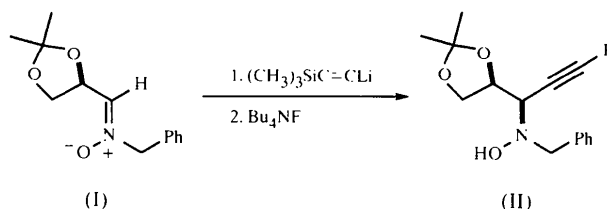
The stereochemistry of the title hydroxylamine, (II), was determined on the basis of chemical evidence, by transformation into the corresponding 1,3-oxazolidin-2-one. The present structural determination serves to confirm the previously assigned *syn* stereochemistry between the substituents attached 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 nitrone, (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*.
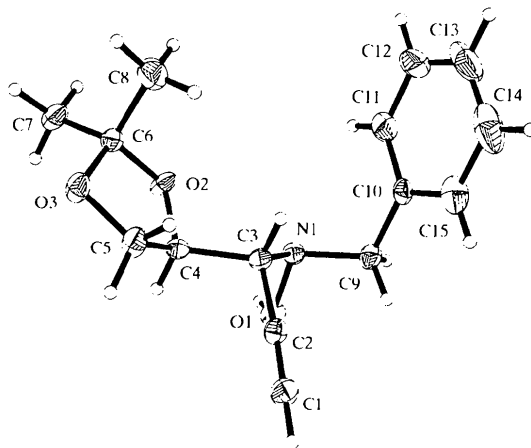
Fig. 1. The molecular structure of (II), showing the atom numbering. Displacement ellipsoids are shown at the 30% probability level.

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