

Acta Crystallographica Section E

## Structure Reports

Online

ISSN 1600-5368

# tert-Butyl 1-hydroxypiperidine-2-carboxylate

 Oliver Brücher,<sup>a</sup> Uwe Bergsträsser,<sup>a</sup> Harald Kelm<sup>b</sup> and Jens Hartung<sup>a\*</sup>
<sup>a</sup>Fachbereich Chemie, Organische Chemie, Technische Universität Kaiserslautern, Erwin-Schrödinger-Strasse, D-67663 Kaiserslautern, Germany, and <sup>b</sup>Fachbereich Chemie, Anorganische Chemie, Technische Universität Kaiserslautern, Erwin-Schrödinger-Strasse, D-67663 Kaiserslautern, Germany

Correspondence e-mail: hartung@chemie.uni-kl.de

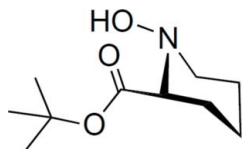
Received 17 June 2011; accepted 5 July 2011

 Key indicators: single-crystal X-ray study;  $T = 150$  K; mean  $\sigma(\text{C}-\text{C}) = 0.003$  Å;  $R$  factor = 0.049;  $wR$  factor = 0.146; data-to-parameter ratio = 14.1.

The title compound,  $\text{C}_{10}\text{H}_{19}\text{NO}_3$ , is a disubstituted piperidine bearing substituents in two equatorial positions. One of the substituents is a hydroxy group bound to nitrogen and the second a *tert*-butyl ester group bound to the carbon next to the endocyclic nitrogen. Enantiomers of the title compound form hydrogen-bridged dimers across a center of inversion.

## Related literature

For bond lengths, see: Allen *et al.* (1987). For structural features associated with hydroxylamine, see: Chung-Phillips & Jebber (1995). For details of vanadium(V)- and molybdenum(VI)-catalysed oxidations, see: Hartung & Greb (2002); Reinhardt (2006). For a related structure, see: Kliegel *et al.* (2002). For the synthesis of 1-hydroxy piperidine-2-carboxylic acid, see: Murahashi & Shiota (1987).



## Experimental

### Crystal data

 $\text{C}_{10}\text{H}_{19}\text{NO}_3$ 
 $M_r = 201.26$ 

 Monoclinic,  $P2_1/n$   
 $a = 10.1685$  (3) Å  
 $b = 12.1271$  (2) Å  
 $c = 10.2083$  (3) Å  
 $\beta = 110.377$  (3)°  
 $V = 1180.06$  (5) Å<sup>3</sup>
 $Z = 4$   
 Cu  $K\alpha$  radiation  
 $\mu = 0.68$  mm<sup>-1</sup>  
 $T = 150$  K  
 $0.24 \times 0.21 \times 0.19$  mm

### Data collection

 Oxford Diffraction Gemini S Ultra diffractometer  
 Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2008)  
 $T_{\min} = 0.854$ ,  $T_{\max} = 0.882$ 

 5815 measured reflections  
 1851 independent reflections  
 1440 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.026$ 

### Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.049$   
 $wR(F^2) = 0.146$   
 $S = 1.09$   
 1851 reflections

 131 parameters  
 H-atom parameters constrained  
 $\Delta\rho_{\max} = 0.39$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.23$  e Å<sup>-3</sup>

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{O3}-\text{H3}\cdots\text{N1}^i$	0.84	2.12	2.8136 (19)	139

 Symmetry code: (i)  $-x, -y + 2, -z$ .

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2008); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2008); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

This work was supported by the Deutsche Bundesstiftung Umwelt (grant No. 20007/885; scholarship for OB).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: NC2235).

## References

- Allen, F. H., Kennard, O. & Watson, D. G. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
- Chung-Phillips, A. & Jebber, K. A. (1995). *J. Chem. Phys.* **102**, 7080–7087.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Hartung, J. & Greb, M. (2002). *J. Organomet. Chem.* **661**, 67–84.
- Kliegel, W., Riebe, U., Patrick, B. O., Rettig, S. J. & Trotter, J. (2002). *Acta Cryst. E* **58**, o509–o510.
- Murahashi, S. & Shiota, T. (1987). *Tetrahedron Lett.* **28**, 6469–6472.
- Oxford Diffraction (2008). *CrysAlis RED* and *CrysAlis CCD*. Oxford Diffraction Ltd, Abingdon, England.
- Reinhardt, G. (2006). *J. Mol. Catal. A*, **251**, 177–184.
- Sheldrick, G. M. (2008). *Acta Cryst. A* **64**, 112–122.

## supporting information

*Acta Cryst.* (2011). E67, o2061 [doi:10.1107/S1600536811026894]

***tert*-Butyl 1-hydroxypiperidine-2-carboxylate**

Oliver Brücher, Uwe Bergsträsser, Harald Kelm and Jens Hartung

**S1. Comment**

1-Hydroxypiperidine-2-carboxylate (Murahashi & Shiota, 1987) attracted our attention, because the compound was expected to bind as dianion to early transition metal ions, such as vanadium(V) or molybdenum(VI). Complexes formed from vanadium(V) or molybdenum(VI) ions are formally  $d^0$ -metal centers. Complexes having such an electron configuration are able to activate peroxides at low temperatures, which is of importance for modern sustainable oxidation catalysis, for example in natural product synthesis (Hartung & Greb, 2002) or bleaching (Reinhardt, 2006). Since impurities from the synthesis of 1-hydroxypiperidine-2-carboxylate were difficult to separate from standard liquid/liquid and liquid/solid partitioning processes, we chose to convert this acid into a derived *O-tert*-butyl ester for subsequent sublimation. Colorless crystals of the title compound that deposited from the sublimation process were investigated *via* X-ray diffraction, in order to obtain a deeper structural insight into the product class of *N*-hydroxy  $\alpha$ -aminocarboxylic acid esters.

The central structural element of the title compound, is a disubstituted piperidine ring. The N-heterocycle bears a hydroxy substituent at nitrogen and a *tert*-butyl O-ester substituent at the carbon next to the endocyclic nitrogen. Both substituents are bonded to equatorial sites in piperidine (Figure 1). A distorted *gauche* arrangement of subunits C6–N1–O3–H3 =  $-90.30^\circ$  and C2–N1–O3–H3  $151.18^\circ$ , in combination with a N1–O3 distance of 1.4477 (18) Å, reflect typical structural characteristics of compounds having a nitrogen oxygen single bond, such as hydroxylamine (Chung-Phillips & Jebber, 1995) or *N*-hydroxypiperidinium chloride (Kliegel *et al.*, 2002). The geometrical parameters for the *tert*-butyl O-ester group in terms of bond distances and angles agree with reference data reported previously (Allen *et al.*, 1987).

In the crystal, association of the title compound, occurs predominantly *via* H-bonding. Enantiomers of the title compound thus form H-bridged dimers (Figure 2 and Table 1) across a center of inversion [ $N1^i \cdots H3-O3 = 2.12$  Å,  $N1^i \cdots O3 = 2.8136$  (19)].

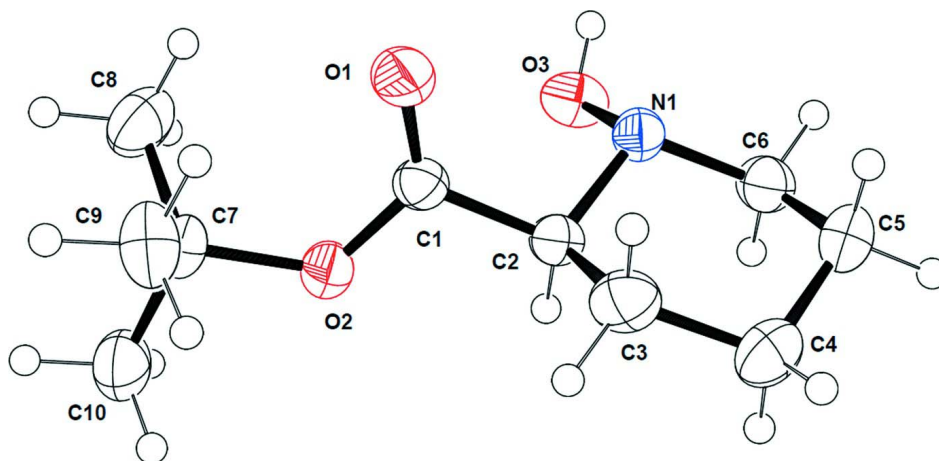
**S2. Experimental**

To a suspension of crude *N*-hydroxypiperidine-2-carboxylic acid (1.15 g, 8 mmol) (Murahashi & Shiota, 1987) in *tert*-butyl acetate (20 ml) was added at 298 K HClO<sub>4</sub> [0.2 ml, 70% (w/w)]. The mixture was stirred for 10 min at 298 K and treated with a second batch of HClO<sub>4</sub> [2 ml, 70% (w/w)]. Stirring was continued for 20 h at 298 K. pH of the reaction mixture was adjusted to 8–9 by addition of satd. aq. NaHCO<sub>3</sub> [150 ml, 10% (w/w)] and NaOH pellets (0.8 g, 20 mmol). The resulting mixture was extracted with EtOAc (4 x 40 ml). Combined organic washings were dried (MgSO<sub>4</sub>) and concentrated under reduced pressure to furnish a brown oily residue that was purified by chromatography [SiO<sub>2</sub>, pentane/EtOAc = 2:1 (v/v)]. Yield: 412 mg (25%); mp 356 K; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>,  $\delta_H$  p.p.m.): 1.20–1.30 (m, 1H), 1.47 (s, 9H), 1.52–1.78 (m, 4H), 1.97 (d,  $J = 11.1$  Hz, 1H), 2.52 (t,  $J = 9.1$  Hz, 1H), 3.02 (d,  $J = 10.6$  Hz, 1H), 3.37 (d,  $J = 10.2$  Hz, 1H), 6.56 (br s, 1H, OH). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>,  $\delta_C$  p.p.m.): 23.1, 25.1, 28.0, 29.3, 57.4, 71.2, 81.2, 171.9.

Anal. calcd. for  $C_{15}H_{23}NO_2$ : C, 59.68; H, 9.52; N, 6.96%; Found C, 59.96; H, 9.49; N 6.94%. Crystals suitable for X-ray diffraction were obtained by slow sublimation of (I) at 340 K and 0.1 mbar.

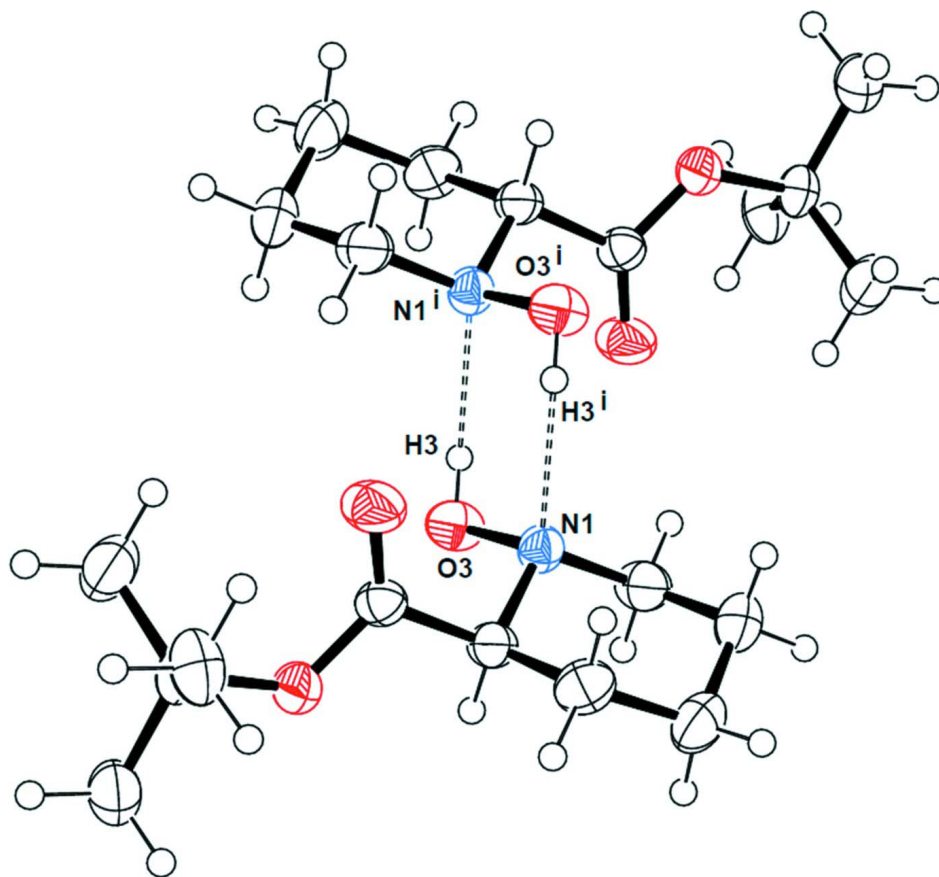
### S3. Refinement

All H atoms were positioned geometrically and treated as riding atoms, with C—H distances in the range 0.98–1.00 Å and with  $U_{\text{iso}}(\text{H})$  set at  $1.2U_{\text{eq}}(\text{CH}_2, \text{CH})$  or  $1.5U_{\text{eq}}(\text{CH}_3 \text{ and OH})$  of the parent atom. A free rotating group refinement was used for  $\text{CH}_3$  and OH H atoms.



**Figure 1**

Molecular structure of title compound in the solid state. Displacement ellipsoids are drawn at the 50% probability level.

**Figure 2**

H-bridged dimers of title compound in the solid state [hydrogen bonds shown as dashed lines symmetry code: (i)  $-x, -y + 2, -z$ ].

### ***tert*-Butyl 1-hydroxypiperidine-2-carboxylate**

#### *Crystal data*

$C_{10}H_{19}NO_3$

$M_r = 201.26$

Monoclinic,  $P2_1/n$

Hall symbol:  $-P\ 2_1n$

$a = 10.1685\ (3)\ \text{\AA}$

$b = 12.1271\ (2)\ \text{\AA}$

$c = 10.2083\ (3)\ \text{\AA}$

$\beta = 110.377\ (3)^\circ$

$V = 1180.06\ (5)\ \text{\AA}^3$

$Z = 4$

$F(000) = 440$

$D_x = 1.133\ \text{Mg m}^{-3}$

Melting point: 356 K

Cu  $K\alpha$  radiation,  $\lambda = 1.54184\ \text{\AA}$

Cell parameters from 2751 reflections

$\theta = 3.6\text{--}62.6^\circ$

$\mu = 0.68\ \text{mm}^{-1}$

$T = 150\ \text{K}$

Indifferent fragment, colourless

$0.24 \times 0.21 \times 0.19\ \text{mm}$

#### *Data collection*

Oxford Diffraction Gemini S Ultra diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution:  $16.1399\ \text{pixels mm}^{-1}$

$\omega$ -scans

Absorption correction: multi-scan

(*CrysAlis RED*; Oxford Diffraction, 2008)

$T_{\min} = 0.854, T_{\max} = 0.882$

5815 measured reflections

1851 independent reflections

1440 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.026$   
 $\theta_{\text{max}} = 62.7^\circ$ ,  $\theta_{\text{min}} = 6.4^\circ$   
 $h = -11 \rightarrow 11$

$k = -13 \rightarrow 12$   
 $l = -11 \rightarrow 11$

### Refinement

Refinement on  $F^2$   
 Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.049$   
 $wR(F^2) = 0.146$   
 $S = 1.09$   
 1851 reflections  
 131 parameters  
 0 restraints  
 Primary atom site location: structure-invariant  
 direct methods

Secondary atom site location: difference Fourier  
 map  
 Hydrogen site location: inferred from  
 neighbouring sites  
 H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.1003P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.001$   
 $\Delta\rho_{\text{max}} = 0.39 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.23 \text{ e } \text{\AA}^{-3}$

### Special details

**Experimental.** CrysAlis RED, Oxford Diffraction Ltd., (Version 1.171.31.8) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.

**Geometry.** All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

**Refinement.** Refinement of  $F^2$  against ALL reflections. The weighted  $R$ -factor  $wR$  and goodness of fit  $S$  are based on  $F^2$ , conventional  $R$ -factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > \sigma(F^2)$  is used only for calculating  $R$ -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement.  $R$ -factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and  $R$ -factors based on ALL data will be even larger.

### Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.22238 (18)	0.85238 (14)	-0.04530 (19)	0.0323 (4)
O1	0.11112 (15)	0.80571 (12)	-0.08516 (16)	0.0512 (5)
O2	0.32151 (13)	0.84628 (10)	-0.10296 (13)	0.0368 (4)
C2	0.27379 (18)	0.92188 (14)	0.08639 (18)	0.0330 (4)
H2	0.3532	0.9699	0.0850	0.040*
N1	0.15807 (15)	0.98997 (12)	0.09477 (14)	0.0313 (4)
O3	0.12723 (13)	1.06522 (10)	-0.02218 (14)	0.0401 (4)
H3	0.0425	1.0839	-0.0481	0.060*
C3	0.3223 (2)	0.84527 (16)	0.2126 (2)	0.0439 (5)
H3A	0.2449	0.7946	0.2093	0.053*
H3B	0.4019	0.8002	0.2085	0.053*
C4	0.3675 (2)	0.9091 (2)	0.3492 (2)	0.0541 (6)
H4A	0.4526	0.9528	0.3590	0.065*
H4B	0.3901	0.8572	0.4289	0.065*
C5	0.2493 (2)	0.9855 (2)	0.3503 (2)	0.0529 (6)
H5A	0.1686	0.9411	0.3532	0.063*
H5B	0.2814	1.0323	0.4351	0.063*
C6	0.2036 (2)	1.05791 (16)	0.2217 (2)	0.0427 (5)
H6A	0.1254	1.1060	0.2230	0.051*
H6B	0.2826	1.1056	0.2217	0.051*

C7	0.3043 (2)	0.77301 (16)	-0.22421 (19)	0.0386 (5)
C8	0.1799 (2)	0.8114 (2)	-0.3490 (2)	0.0554 (6)
H8A	0.1910	0.8897	-0.3664	0.083*
H8B	0.0931	0.8008	-0.3292	0.083*
H8C	0.1755	0.7683	-0.4317	0.083*
C9	0.2929 (3)	0.65452 (17)	-0.1852 (2)	0.0519 (6)
H9A	0.2054	0.6440	-0.1668	0.078*
H9B	0.3728	0.6360	-0.1012	0.078*
H9C	0.2932	0.6065	-0.2623	0.078*
C10	0.4397 (2)	0.79292 (19)	-0.2509 (2)	0.0509 (6)
H10A	0.5193	0.7704	-0.1688	0.076*
H10B	0.4481	0.8715	-0.2691	0.076*
H10C	0.4395	0.7498	-0.3322	0.076*

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C1	0.0292 (9)	0.0312 (9)	0.0348 (10)	0.0023 (7)	0.0091 (8)	-0.0018 (8)
O1	0.0362 (8)	0.0574 (9)	0.0610 (10)	-0.0095 (7)	0.0185 (7)	-0.0249 (7)
O2	0.0354 (7)	0.0415 (7)	0.0341 (7)	-0.0039 (5)	0.0131 (6)	-0.0072 (5)
C2	0.0282 (9)	0.0354 (9)	0.0346 (10)	0.0003 (7)	0.0099 (7)	-0.0031 (8)
N1	0.0323 (8)	0.0312 (8)	0.0297 (8)	0.0030 (6)	0.0100 (6)	0.0012 (6)
O3	0.0359 (7)	0.0372 (7)	0.0476 (8)	0.0030 (5)	0.0151 (6)	0.0163 (6)
C3	0.0411 (11)	0.0414 (10)	0.0452 (12)	0.0090 (8)	0.0097 (9)	0.0070 (9)
C4	0.0517 (12)	0.0692 (13)	0.0336 (11)	0.0100 (11)	0.0052 (9)	0.0044 (10)
C5	0.0500 (12)	0.0755 (14)	0.0312 (11)	0.0035 (11)	0.0117 (9)	-0.0094 (10)
C6	0.0361 (10)	0.0424 (11)	0.0490 (12)	-0.0018 (8)	0.0144 (9)	-0.0150 (9)
C7	0.0433 (11)	0.0444 (10)	0.0280 (9)	-0.0017 (8)	0.0120 (8)	-0.0086 (8)
C8	0.0564 (14)	0.0666 (14)	0.0355 (11)	-0.0055 (11)	0.0063 (10)	-0.0027 (10)
C9	0.0704 (15)	0.0476 (12)	0.0461 (12)	-0.0023 (10)	0.0307 (11)	-0.0073 (10)
C10	0.0546 (13)	0.0609 (13)	0.0411 (11)	-0.0055 (10)	0.0217 (10)	-0.0095 (10)

*Geometric parameters (Å, °)*

C1—O1	1.202 (2)	C5—H5A	0.9900
C1—O2	1.335 (2)	C5—H5B	0.9900
C1—C2	1.517 (2)	C6—H6A	0.9900
O2—C7	1.484 (2)	C6—H6B	0.9900
C2—N1	1.464 (2)	C7—C9	1.506 (3)
C2—C3	1.524 (3)	C7—C10	1.514 (3)
C2—H2	1.0000	C7—C8	1.522 (3)
N1—O3	1.4477 (18)	C8—H8A	0.9800
N1—C6	1.468 (2)	C8—H8B	0.9800
O3—H3	0.8400	C8—H8C	0.9800
C3—C4	1.520 (3)	C9—H9A	0.9800
C3—H3A	0.9900	C9—H9B	0.9800
C3—H3B	0.9900	C9—H9C	0.9800
C4—C5	1.521 (3)	C10—H10A	0.9800

C4—H4A	0.9900	C10—H10B	0.9800
C4—H4B	0.9900	C10—H10C	0.9800
C5—C6	1.512 (3)		
O1—C1—O2	126.22 (16)	H5A—C5—H5B	108.1
O1—C1—C2	123.69 (16)	N1—C6—C5	110.36 (16)
O2—C1—C2	109.97 (14)	N1—C6—H6A	109.6
C1—O2—C7	120.89 (13)	C5—C6—H6A	109.6
N1—C2—C1	109.21 (13)	N1—C6—H6B	109.6
N1—C2—C3	108.94 (15)	C5—C6—H6B	109.6
C1—C2—C3	108.69 (15)	H6A—C6—H6B	108.1
N1—C2—H2	110.0	O2—C7—C9	110.40 (15)
C1—C2—H2	110.0	O2—C7—C10	101.79 (14)
C3—C2—H2	110.0	C9—C7—C10	110.98 (17)
O3—N1—C2	104.77 (12)	O2—C7—C8	109.72 (16)
O3—N1—C6	106.58 (13)	C9—C7—C8	113.25 (18)
C2—N1—C6	110.82 (13)	C10—C7—C8	110.10 (17)
N1—O3—H3	109.5	C7—C8—H8A	109.5
C4—C3—C2	111.74 (16)	C7—C8—H8B	109.5
C4—C3—H3A	109.3	H8A—C8—H8B	109.5
C2—C3—H3A	109.3	C7—C8—H8C	109.5
C4—C3—H3B	109.3	H8A—C8—H8C	109.5
C2—C3—H3B	109.3	H8B—C8—H8C	109.5
H3A—C3—H3B	107.9	C7—C9—H9A	109.5
C3—C4—C5	109.27 (17)	C7—C9—H9B	109.5
C3—C4—H4A	109.8	H9A—C9—H9B	109.5
C5—C4—H4A	109.8	C7—C9—H9C	109.5
C3—C4—H4B	109.8	H9A—C9—H9C	109.5
C5—C4—H4B	109.8	H9B—C9—H9C	109.5
H4A—C4—H4B	108.3	C7—C10—H10A	109.5
C6—C5—C4	110.60 (17)	C7—C10—H10B	109.5
C6—C5—H5A	109.5	H10A—C10—H10B	109.5
C4—C5—H5A	109.5	C7—C10—H10C	109.5
C6—C5—H5B	109.5	H10A—C10—H10C	109.5
C4—C5—H5B	109.5	H10B—C10—H10C	109.5
O1—C1—O2—C7	-3.0 (3)	C1—C2—C3—C4	-176.65 (16)
C2—C1—O2—C7	173.14 (14)	C2—C3—C4—C5	54.3 (2)
O1—C1—C2—N1	-42.6 (2)	C3—C4—C5—C6	-53.9 (3)
O2—C1—C2—N1	141.07 (14)	O3—N1—C6—C5	-175.52 (14)
O1—C1—C2—C3	76.1 (2)	C2—N1—C6—C5	-62.1 (2)
O2—C1—C2—C3	-100.19 (17)	C4—C5—C6—N1	58.1 (2)
C1—C2—N1—O3	-65.86 (16)	C1—O2—C7—C9	-61.7 (2)
C3—C2—N1—O3	175.55 (13)	C1—O2—C7—C10	-179.57 (16)
C1—C2—N1—C6	179.56 (14)	C1—O2—C7—C8	63.8 (2)
C3—C2—N1—C6	60.98 (19)	C2—N1—O3—H3	152.19
N1—C2—C3—C4	-57.7 (2)	C6—N1—O3—H3	-90.30

*Hydrogen-bond geometry (Å, °)*

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
O3—H3 $\cdots$ N1 <sup>i</sup>	0.84	2.12	2.8136 (19)	139

Symmetry code: (i)  $-x, -y+2, -z$ .