

7-1-2015

# Crystal structure of *cis*-2-(2-carboxycyclopropyl)-glycine (CCG-III) monohydrate

Sergey V. Lindeman

Marquette University, [sergey.lindeman@marquette.edu](mailto:sergey.lindeman@marquette.edu)

Nathaniel J. Wallock

Marquette University

William A. Donaldson

Marquette University, [william.donaldson@marquette.edu](mailto:william.donaldson@marquette.edu)



Received 12 April 2015

Accepted 14 June 2015

Edited by W. T. A. Harrison, University of  
Aberdeen, Scotland**Keywords:** crystal structure; cyclopropane;  
conformationally restricted glutamate analog**CCDC reference:** 1406594**Supporting information:** this article has  
supporting information at journals.iucr.org/e

# Crystal structure of *cis*-2-(2-carboxycyclopropyl)-glycine (CCG-III) monohydrate

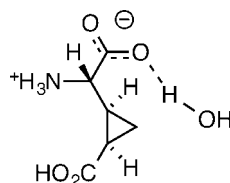
Sergey Lindeman, Nathaniel J. Wallock and William A. Donaldson\*

Department of Chemistry, Marquette University, PO Box 1881, Milwaukee, WI 53201-1881, USA. \*Correspondence  
e-mail: william.donaldson@marquette.edu

The title compound,  $C_6H_9NO_4 \cdot H_2O$  [systematic name: ( $\alpha R,1R,2S$ )-*rel*- $\alpha$ -amino-2-carboxycyclopropaneacetic acid monohydrate], crystallizes with two organic molecules and two water molecules in the asymmetric unit. The space group is  $P2_1$  and the organic molecules are enantiomers, thus this is an example of a 'false conglomerate' with two molecules of opposite handedness in the asymmetric unit (r.m.s. overlay fit = 0.056 Å for one molecule and its inverted partner). Each molecule exists as a zwitterion, with proton transfer from the amino acid carboxylic acid group to the amine group. In the crystal, the components are linked by  $N-H \cdots O$  and  $O-H \cdots O$  hydrogen bonds, generating (100) sheets. Conformationally restricted glutamate analogs are of interest due to their selective activation of different glutamate receptors, and the naturally occurring (+)-CCG-III is an inhibitor of glutamate uptake and the key geometrical parameters are discussed.

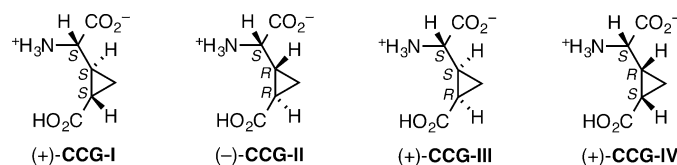
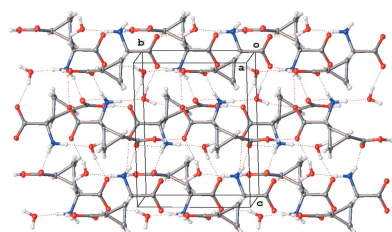
## 1. Chemical context

2-(2'-Carboxycyclopropyl)glycines **CCG-I**, **CCG-III** and **CCG-IV** (Fig. 1) are naturally occurring conformationally restricted analogs of glutamate isolated from *Aesculus parviflora*, *Blighia sapida* (Fowden, *et al.*, 1969), *Ephedra foeminea* (Caveney & Starratt, 1994), and *Ephedra altissima* (Starratt & Caveney, 1995). While not naturally occurring, both enantiomers of **CCG-II** (Fig. 1) have been prepared in the laboratory (Shimamoto, *et al.*, 1991) and all of the diastereomeric CCGs are useful tools for investigating the mechanism of glutamate function. The crystal structure of the title hydrate, ( $\pm$ )-**CCG-III**· $H_2O$ , is now reported.

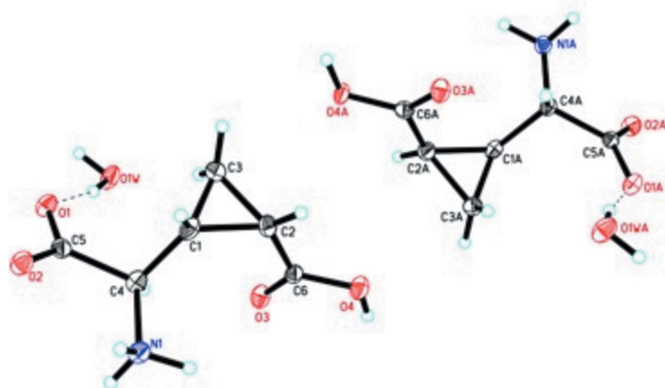


## 2. Structural commentary

The racemic title compound (Fig. 2) crystallizes as a 'false conglomerate' with two molecules of opposite handedness in



**Figure 1**  
Structures of the diastereomers of 2-(2'-carboxycyclopropyl)glycine.

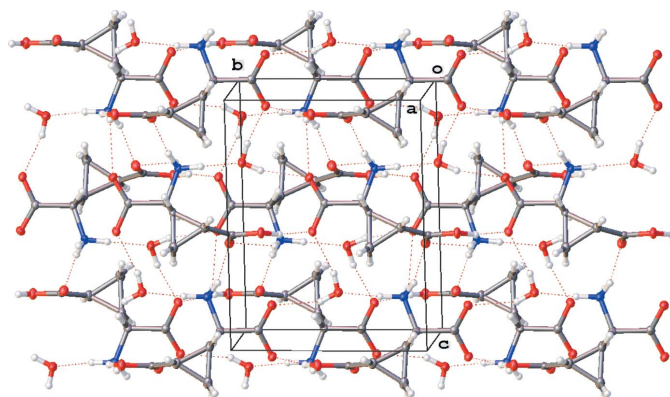


**Figure 2**  
The asymmetric unit of the title compound, showing 50% displacement ellipsoids.

the asymmetric unit. Each of molecules of 2-(2'-carboxycyclopropyl)glycine has a molecule of water hydrogen bonded to the glycine carboxylate group. It has been estimated that only 1% of organic compounds are false conglomerates (Bishop & Scudder, 2009).

The torsion angles  $O3-C6-C2-X = -4.3^\circ$  and  $O3A-C6A-C2A-X = -11.1^\circ$  (where  $X$  is the midpoint of the distal cyclopropane bond) indicate that the carboxylic acid attached to the cyclopropane ring adopts a bisected conformation (Allen, 1980). The cyclopropane C—C bonds proximal to the C2 carboxylic group are roughly equal [ $C1-C2 = 1.532$  (3);  $C2-C3 = 1.512$  (3);  $C1A-C2A = 1.520$  (3);  $C2A-C3A = 1.516$  (2) Å] and are longer than the cyclopropane bonds distal to the C2 carboxylic acid [ $C1-C3 = 1.489$  (2);  $C1A-C3A = 1.484$  (2) Å]. These distances and torsion angles are consistent with other cyclopropane carboxylic acids (Allen, 1980).

Conformationally restricted glutamic acid analogs can be classified into one of four categories, which are characterized by the distances between the nitrogen atom of the amino group and the  $\gamma$ -carboxylate carbon atom ( $d_1$ ), between the  $\alpha$ - and  $\gamma$ -carboxylate carbon atoms ( $d_2$ ), and their sum ( $d_1 + d_2$ ).



**Figure 3**  
The packing for the title compound viewed approximately down [100], with hydrogen bonds shown as dashed lines.

**Table 1**  
Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$N1-H1A \cdots O3A^i$	0.94 (2)	2.03 (2)	2.9444 (18)	162.1 (17)
$N1-H1B \cdots O2A^{ii}$	0.86 (2)	2.39 (2)	2.9454 (18)	123.1 (16)
$N1-H1C \cdots O1WA^i$	0.98 (3)	1.83 (3)	2.795 (2)	167 (2)
$O4-H4 \cdots O1^{iii}$	0.81 (3)	1.79 (3)	2.5851 (18)	166 (3)
$O1W-H1WA \cdots O2A^{iv}$	0.82 (3)	2.01 (3)	2.8072 (19)	166 (2)
$O1W-H1WB \cdots O1$	0.86 (2)	1.90 (2)	2.7449 (16)	169 (2)
$N1A-H1AA \cdots O3^v$	0.90 (2)	2.01 (2)	2.9087 (18)	173 (2)
$N1A-H1AB \cdots O3A^{vi}$	0.87 (2)	2.38 (2)	3.1151 (19)	141.7 (17)
$N1A-H1AC \cdots O1W^v$	0.93 (2)	1.87 (2)	2.785 (2)	165.6 (18)
$O4A-H4AA \cdots O1A^{vii}$	0.98 (3)	1.60 (3)	2.5672 (16)	168 (2)
$O1WA-H1WC \cdots O2^{viii}$	0.83 (3)	2.07 (3)	2.8628 (19)	158 (2)
$O1WA-H1WD \cdots O1A$	0.81 (2)	1.98 (3)	2.7717 (17)	166 (3)

Symmetry codes: (i)  $-x+1, y-\frac{1}{2}, -z$ ; (ii)  $x-1, y-1, z-1$ ; (iii)  $x, y+1, z$ ; (iv)  $-x+1, y-\frac{3}{2}, -z+1$ ; (v)  $-x+1, y+\frac{1}{2}, -z+1$ ; (vi)  $-x+2, y+\frac{3}{2}, -z+1$ ; (vii)  $x, y-1, z$ ; (viii)  $-x+1, y+\frac{3}{2}, -z$ .

The classifications 'folded', 'semi-folded', 'semi-extended', and 'extended' are defined by  $(d_1 + d_2) \leq 7.5$  Å,  $7.5$  Å  $\leq (d_1 + d_2) \leq 8.0$  Å,  $8.0$  Å  $\leq (d_1 + d_2) \leq 8.5$  Å, and  $(d_1 + d_2) \geq 8.5$  Å, respectively (Pellicciari, *et al.*, 2002). The two enantiomeric molecules in the crystal structure evidence the following distances/sums:  $d_1$ , 3.65 and 3.71 Å;  $d_2$ , 4.59 and 4.59 Å;  $(d_1 + d_2)$ , 8.24 and 8.30 Å, respectively. From these values, these conformers of CCG-III can be considered to be in the 'semi-extended' class.

**Table 2**  
Experimental details.

Crystal data	
Chemical formula	$C_6H_9NO_4 \cdot H_2O$
$M_r$	177.16
Crystal system, space group	Monoclinic, $P2_1$
Temperature (K)	100
$a, b, c$ (Å)	8.9688 (8), 8.0063 (8), 10.9628 (10)
$\beta$ (°)	106.015 (4)
$V$ (Å <sup>3</sup> )	756.65 (12)
$Z$	4
Radiation type	Cu $K\alpha$
$\mu$ (mm <sup>-1</sup> )	1.18
Crystal size (mm)	0.37 × 0.32 × 0.10
Data collection	
Diffractometer	Bruker APEXII CCD detector
Absorption correction	Multi-scan (SADABS; Bruker, 2005)
$T_{min}, T_{max}$	0.669, 0.891
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	6086, 2164, 2154
$R_{int}$	0.018
$\theta_{max}$ (°)	61.0
$(\sin \theta/\lambda)_{max}$ (Å <sup>-1</sup> )	0.567
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.021, 0.055, 1.06
No. of reflections	2164
No. of parameters	305
No. of restraints	1
H-atom treatment	All H-atom parameters refined
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å <sup>-3</sup> )	0.15, -0.16
Absolute structure	Flack (1983), 836 Friedel pairs
Absolute structure parameter	0.57 (15)

Computer programs: APEX2 and SAINT (Bruker, 2005), SHELXTL and SHELXL97 (Sheldrick, 2008).

### 3. Supramolecular features

In the crystal, the molecules are linked by N—H···O and O—H···O hydrogen bonds, forming sheets parallel to (100); Table 1 and Fig. 3.

### 4. Synthesis and crystallization

The racemic title compound was prepared according to the literature procedure (Wallock & Donaldson, 2004). A sample for X-ray diffraction analysis was recrystallized from water.

### 5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

### References

- Allen, F. H. (1980). *Acta Cryst.* **B36**, 81–96.  
Bishop, R. & Scudder, M. L. (2009). *Cryst. Growth Des.* **9**, 2890–2894.  
Bruker (2005). *APEX2*, *SAINTE* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.  
Caveney, S. & Starratt, A. (1994). *Nature*, **372**, 509.  
Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.  
Fowden, L., Smith, A., Millington, D. S. & Sheppard, R. C. (1969). *Phytochemistry*, **8**, 437–443.  
Pellicciari, R., Marinozzi, M., Camaioni, E., del Carmen Nùnez, M., Costantino, G., Gasparini, F., Giorgi, G., Macchiarulo, A. & Subramanian, N. (2002). *J. Org. Chem.* **67**, 5497–5507.  
Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.  
Shimamoto, K., Ishida, M., Shinozaki, H. & Ohfuné, Y. (1991). *J. Org. Chem.* **56**, 4167–4176.  
Starratt, A. N. & Caveney, S. (1995). *Phytochemistry*, **40**, 479–481.  
Wallock, N. J. & Donaldson, W. A. (2004). *J. Org. Chem.* **69**, 2997–3007.

## supporting information

*Acta Cryst.* (2015). E71, 844-846 [doi:10.1107/S2056989015011500]

## Crystal structure of *cis*-2-(2-carboxycyclopropyl)glycine (CCG-III) monohydrate

Sergey Lindeman, Nathaniel J. Wallock and William A. Donaldson

### Computing details

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT* (Bruker, 2005); program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

### (*αR,1R,2S*)-*rel-α*-Amino-2-carboxycyclopropaneacetic acid monohydrate

#### Crystal data

$C_6H_9NO_4 \cdot H_2O$

$M_r = 177.16$

Monoclinic,  $P2_1$

$a = 8.9688$  (8) Å

$b = 8.0063$  (8) Å

$c = 10.9628$  (10) Å

$\beta = 106.015$  (4)°

$V = 756.65$  (12) Å<sup>3</sup>

$Z = 4$

$F(000) = 376$

$D_x = 1.555$  Mg m<sup>-3</sup>

Cu  $K\alpha$  radiation,  $\lambda = 1.54178$  Å

Cell parameters from 5577 reflections

$\theta = 4-61^\circ$

$\mu = 1.18$  mm<sup>-1</sup>

$T = 100$  K

Plate, colorless

$0.37 \times 0.32 \times 0.10$  mm

#### Data collection

Bruker APEXII CCD detector  
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

$\omega$  scans

Absorption correction: multi-scan

(*SADABS*; Bruker, 2005)

$T_{\min} = 0.669$ ,  $T_{\max} = 0.891$

6086 measured reflections

2164 independent reflections

2154 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.018$

$\theta_{\max} = 61.0^\circ$ ,  $\theta_{\min} = 4.2^\circ$

$h = -10 \rightarrow 9$

$k = -8 \rightarrow 9$

$l = 0 \rightarrow 12$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.021$

$wR(F^2) = 0.055$

$S = 1.06$

2164 reflections

305 parameters

1 restraint

Primary atom site location: structure-invariant  
direct methods

Secondary atom site location: difference Fourier  
map

Hydrogen site location: difference Fourier map

All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0523P)^2 + 0.0652P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.15$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.16$  e Å<sup>-3</sup>

Absolute structure: Flack (1983), 836 Friedel  
pairs

Absolute structure parameter: 0.57 (15)

*Special details*

**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 ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.16905 (12)	-0.14281 (15)	0.09397 (9)	0.0171 (3)
O2	0.16680 (12)	-0.14746 (15)	-0.11118 (10)	0.0182 (3)
O3	0.17732 (12)	0.43933 (15)	0.13921 (10)	0.0179 (3)
O4	0.36153 (14)	0.61213 (15)	0.11160 (11)	0.0187 (3)
N1	0.10810 (17)	0.18398 (19)	-0.14010 (12)	0.0163 (3)
C1	0.34487 (17)	0.1610 (2)	0.03879 (15)	0.0167 (3)
C2	0.40767 (18)	0.3278 (2)	0.10039 (15)	0.0169 (3)
C3	0.42184 (19)	0.1692 (3)	0.17765 (16)	0.0203 (4)
C4	0.17508 (18)	0.1174 (2)	-0.00932 (14)	0.0147 (4)
C5	0.16579 (16)	-0.0746 (2)	-0.01143 (14)	0.0143 (4)
C6	0.30359 (18)	0.4620 (2)	0.11880 (14)	0.0139 (4)
H1A	0.150 (2)	0.128 (3)	-0.1987 (17)	0.020 (5)*
H1B	0.010 (3)	0.166 (3)	-0.1641 (18)	0.029 (5)*
H1C	0.131 (3)	0.303 (4)	-0.143 (2)	0.050 (7)*
H4	0.297 (3)	0.681 (4)	0.115 (2)	0.044 (7)*
H1	0.407 (2)	0.114 (2)	-0.0118 (16)	0.020 (5)*
H2	0.499 (2)	0.364 (2)	0.0793 (15)	0.017 (4)*
H3A	0.522 (2)	0.127 (3)	0.2107 (17)	0.020 (4)*
H3B	0.354 (2)	0.154 (3)	0.2312 (15)	0.017 (4)*
H4A	0.1176 (17)	0.159 (3)	0.0430 (14)	0.006 (4)*
O1W	0.15198 (15)	-0.01307 (17)	0.32148 (12)	0.0218 (3)
H1WA	0.152 (3)	-0.106 (3)	0.352 (2)	0.038 (7)*
H1WB	0.149 (2)	-0.042 (3)	0.246 (2)	0.034 (6)*
O1A	0.81679 (12)	1.13479 (15)	0.40666 (10)	0.0161 (3)
O2A	0.86473 (13)	1.14792 (16)	0.61824 (10)	0.0175 (3)
O3A	0.80378 (12)	0.55765 (16)	0.36274 (10)	0.0177 (3)
O4A	0.63822 (12)	0.38208 (15)	0.41642 (10)	0.0162 (3)
N1A	0.92671 (16)	0.8177 (2)	0.64801 (12)	0.0142 (3)
C1A	0.66918 (17)	0.8314 (2)	0.49476 (14)	0.0144 (4)
C2A	0.59847 (17)	0.6653 (2)	0.44103 (14)	0.0156 (3)
C3A	0.56440 (18)	0.8249 (2)	0.36381 (16)	0.0173 (4)
C4A	0.83802 (17)	0.8786 (2)	0.51986 (14)	0.0133 (4)
C5A	0.84454 (16)	1.0708 (2)	0.51702 (14)	0.0129 (4)
C6A	0.69085 (18)	0.5329 (2)	0.40323 (13)	0.0149 (4)
H1AA	0.892 (2)	0.864 (3)	0.710 (2)	0.028 (5)*

H1AB	1.025 (2)	0.842 (3)	0.6644 (16)	0.018 (4)*
H1AC	0.917 (2)	0.703 (3)	0.6570 (18)	0.024 (5)*
H4AA	0.709 (3)	0.295 (3)	0.404 (2)	0.044 (6)*
H1AD	0.6284 (17)	0.868 (2)	0.5597 (16)	0.008 (4)*
H2A	0.522 (2)	0.630 (2)	0.4774 (15)	0.013 (4)*
H3AA	0.6122 (17)	0.830 (3)	0.2982 (15)	0.006 (4)*
H3AB	0.465 (2)	0.868 (2)	0.3501 (14)	0.011 (4)*
H4AB	0.8848 (19)	0.827 (3)	0.4588 (16)	0.016 (4)*
O1WA	0.79114 (15)	1.00902 (16)	0.16619 (12)	0.0216 (3)
H1WC	0.796 (3)	1.099 (3)	0.130 (2)	0.041 (7)*
H1WD	0.804 (3)	1.030 (3)	0.241 (2)	0.041 (7)*

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
O1	0.0227 (6)	0.0139 (7)	0.0160 (6)	0.0011 (5)	0.0077 (4)	0.0020 (5)
O2	0.0242 (6)	0.0144 (7)	0.0163 (6)	0.0019 (5)	0.0061 (4)	-0.0010 (5)
O3	0.0197 (6)	0.0162 (7)	0.0203 (6)	-0.0010 (5)	0.0093 (5)	-0.0007 (5)
O4	0.0202 (6)	0.0130 (7)	0.0240 (6)	-0.0006 (5)	0.0082 (5)	-0.0009 (5)
N1	0.0187 (8)	0.0155 (9)	0.0154 (7)	0.0016 (7)	0.0057 (6)	0.0006 (6)
C1	0.0181 (8)	0.0125 (9)	0.0217 (8)	0.0024 (7)	0.0090 (6)	0.0006 (8)
C2	0.0145 (7)	0.0144 (9)	0.0217 (8)	-0.0031 (7)	0.0051 (6)	0.0013 (7)
C3	0.0160 (8)	0.0160 (9)	0.0258 (9)	-0.0004 (8)	0.0006 (7)	0.0015 (8)
C4	0.0188 (8)	0.0143 (10)	0.0129 (8)	0.0016 (7)	0.0075 (7)	0.0003 (6)
C5	0.0116 (7)	0.0148 (10)	0.0164 (9)	0.0006 (7)	0.0036 (6)	-0.0009 (7)
C6	0.0180 (9)	0.0130 (9)	0.0098 (7)	-0.0023 (7)	0.0022 (6)	0.0011 (6)
O1W	0.0361 (7)	0.0127 (7)	0.0171 (6)	0.0008 (6)	0.0081 (5)	-0.0008 (5)
O1A	0.0212 (6)	0.0127 (7)	0.0160 (5)	0.0013 (5)	0.0080 (4)	0.0014 (5)
O2A	0.0230 (6)	0.0144 (6)	0.0145 (5)	0.0006 (5)	0.0039 (4)	-0.0032 (5)
O3A	0.0196 (6)	0.0160 (7)	0.0203 (6)	-0.0017 (5)	0.0099 (5)	-0.0011 (5)
O4A	0.0178 (5)	0.0092 (7)	0.0228 (6)	-0.0013 (5)	0.0074 (5)	0.0003 (5)
N1A	0.0147 (7)	0.0116 (9)	0.0170 (7)	0.0001 (6)	0.0057 (6)	-0.0005 (6)
C1A	0.0184 (8)	0.0107 (9)	0.0159 (8)	0.0015 (7)	0.0076 (6)	0.0018 (7)
C2A	0.0143 (8)	0.0151 (9)	0.0177 (7)	-0.0001 (7)	0.0050 (6)	0.0011 (7)
C3A	0.0144 (8)	0.0155 (10)	0.0215 (8)	0.0015 (7)	0.0044 (7)	0.0006 (7)
C4A	0.0154 (8)	0.0112 (10)	0.0140 (8)	0.0005 (7)	0.0052 (6)	-0.0006 (6)
C5A	0.0101 (7)	0.0131 (10)	0.0166 (9)	0.0004 (7)	0.0056 (6)	0.0011 (7)
C6A	0.0155 (8)	0.0163 (10)	0.0108 (7)	-0.0012 (7)	0.0000 (6)	0.0015 (7)
O1WA	0.0342 (7)	0.0147 (7)	0.0160 (6)	0.0014 (6)	0.0068 (5)	-0.0003 (6)

*Geometric parameters (Å, °)*

O1—C5	1.271 (2)	O1A—C5A	1.273 (2)
O2—C5	1.2417 (19)	O2A—C5A	1.239 (2)
O3—C6	1.2270 (19)	O3A—C6A	1.2289 (19)
O4—C6	1.320 (2)	O4A—C6A	1.319 (2)
O4—H4	0.81 (3)	O4A—H4AA	0.98 (3)
N1—C4	1.492 (2)	N1A—C4A	1.492 (2)

N1—H1A	0.94 (2)	N1A—H1AA	0.90 (2)
N1—H1B	0.86 (2)	N1A—H1AB	0.87 (2)
N1—H1C	0.98 (3)	N1A—H1AC	0.93 (2)
C1—C2	1.532 (3)	C1A—C2A	1.520 (3)
C1—C3	1.489 (2)	C1A—C3A	1.484 (2)
C1—C4	1.509 (2)	C1A—C4A	1.510 (2)
C1—H1	0.963 (19)	C1A—H1AD	0.933 (17)
C2—C3	1.512 (3)	C2A—C3A	1.516 (2)
C2—C6	1.473 (2)	C2A—C6A	1.474 (3)
C2—H2	0.953 (18)	C2A—H2A	0.925 (17)
C3—H3A	0.93 (2)	C3A—H3AA	0.934 (16)
C3—H3B	0.965 (18)	C3A—H3AB	0.929 (18)
C4—C5	1.539 (2)	C4A—C5A	1.541 (2)
C4—H4A	0.932 (17)	C4A—H4AB	0.976 (19)
O1W—H1WA	0.82 (3)	O1WA—H1WC	0.83 (3)
O1W—H1WB	0.86 (2)	O1WA—H1WD	0.81 (2)
C6—O4—H4	108.5 (19)	C6A—O4A—H4AA	111.5 (14)
C4—N1—H1A	110.8 (12)	C4A—N1A—H1AA	111.9 (13)
C4—N1—H1B	110.0 (14)	C4A—N1A—H1AB	111.6 (12)
C4—N1—H1C	110.3 (14)	C4A—N1A—H1AC	112.4 (11)
H1A—N1—H1B	106.2 (19)	H1AA—N1A—H1AB	107.1 (18)
H1A—N1—H1C	108.4 (19)	H1AA—N1A—H1AC	105 (2)
H1B—N1—H1C	111 (2)	H1AB—N1A—H1AC	108.5 (19)
C2—C1—H1	113.3 (11)	C2A—C1A—H1AD	111.2 (10)
C3—C1—C2	60.03 (12)	C3A—C1A—C2A	60.61 (11)
C3—C1—C4	120.41 (14)	C3A—C1A—C4A	121.37 (13)
C3—C1—H1	115.3 (10)	C3A—C1A—H1AD	118.2 (9)
C4—C1—C2	124.66 (14)	C4A—C1A—C2A	125.40 (14)
C4—C1—H1	113.3 (10)	C4A—C1A—H1AD	111.5 (9)
C1—C2—H2	113.0 (11)	C1A—C2A—H2A	112.3 (11)
C3—C2—C1	58.57 (11)	C3A—C2A—C1A	58.51 (11)
C3—C2—H2	116.3 (11)	C3A—C2A—H2A	116.0 (11)
C6—C2—C1	121.77 (14)	C6A—C2A—C1A	122.11 (13)
C6—C2—C3	119.62 (14)	C6A—C2A—C3A	119.45 (14)
C6—C2—H2	115.7 (11)	C6A—C2A—H2A	116.1 (11)
C1—C3—C2	61.40 (11)	C1A—C3A—C2A	60.89 (12)
C1—C3—H3A	120.3 (11)	C1A—C3A—H3AA	116.1 (9)
C1—C3—H3B	115.1 (10)	C1A—C3A—H3AB	117.8 (10)
C2—C3—H3A	116.6 (12)	C2A—C3A—H3AA	113.7 (12)
C2—C3—H3B	118.6 (12)	C2A—C3A—H3AB	115.9 (11)
H3A—C3—H3B	114.6 (15)	H3AA—C3A—H3AB	119.0 (14)
N1—C4—C1	110.69 (13)	N1A—C4A—C1A	109.69 (13)
N1—C4—C5	109.68 (13)	N1A—C4A—C5A	109.39 (13)
N1—C4—H4A	108.6 (10)	N1A—C4A—H4AB	106.7 (11)
C1—C4—C5	106.36 (14)	C1A—C4A—C5A	106.73 (14)
C1—C4—H4A	112.3 (10)	C1A—C4A—H4AB	111.6 (11)
C5—C4—H4A	109.2 (12)	C5A—C4A—H4AB	112.7 (13)



O1—C5—C4	115.33 (14)	O1A—C5A—C4A	114.98 (14)
O2—C5—O1	126.49 (17)	O2A—C5A—O1A	126.36 (17)
O2—C5—C4	117.97 (14)	O2A—C5A—C4A	118.46 (14)
O3—C6—O4	122.97 (16)	O3A—C6A—O4A	122.89 (16)
O3—C6—C2	124.64 (16)	O3A—C6A—C2A	124.66 (17)
O4—C6—C2	112.39 (14)	O4A—C6A—C2A	112.45 (14)
H1WA—O1W—H1WB	99 (2)	H1WC—O1WA—H1WD	107 (3)
N1—C4—C5—O1	-157.34 (12)	N1A—C4A—C5A—O1A	159.17 (12)
N1—C4—C5—O2	27.53 (18)	N1A—C4A—C5A—O2A	-25.74 (18)
C1—C2—C6—O3	31.9 (2)	C1A—C2A—C6A—O3A	-30.4 (2)
C1—C2—C6—O4	-148.40 (15)	C1A—C2A—C6A—O4A	150.15 (14)
C1—C4—C5—O1	82.93 (15)	C1A—C4A—C5A—O1A	-82.23 (15)
C1—C4—C5—O2	-92.20 (16)	C1A—C4A—C5A—O2A	92.87 (16)
C2—C1—C4—N1	83.47 (18)	C2A—C1A—C4A—N1A	-85.57 (18)
C2—C1—C4—C5	-157.45 (15)	C2A—C1A—C4A—C5A	156.02 (14)
C3—C1—C2—C6	-107.63 (17)	C3A—C1A—C2A—C6A	107.23 (16)
C3—C1—C4—N1	156.11 (16)	C3A—C1A—C4A—N1A	-159.79 (16)
C3—C1—C4—C5	-84.81 (19)	C3A—C1A—C4A—C5A	81.8 (2)
C3—C2—C6—O3	-37.4 (2)	C3A—C2A—C6A—O3A	38.8 (2)
C3—C2—C6—O4	142.30 (14)	C3A—C2A—C6A—O4A	-140.58 (14)
C4—C1—C2—C3	108.16 (17)	C4A—C1A—C2A—C3A	-109.43 (17)
C4—C1—C2—C6	0.5 (2)	C4A—C1A—C2A—C6A	-2.2 (2)
C4—C1—C3—C2	-115.01 (18)	C4A—C1A—C3A—C2A	115.80 (19)
C6—C2—C3—C1	111.25 (16)	C6A—C2A—C3A—C1A	-111.72 (16)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1A...O3A <sup>i</sup>	0.94 (2)	2.03 (2)	2.9444 (18)	162.1 (17)
N1—H1B...O2A <sup>ii</sup>	0.86 (2)	2.39 (2)	2.9454 (18)	123.1 (16)
N1—H1C...O1WA <sup>i</sup>	0.98 (3)	1.83 (3)	2.795 (2)	167 (2)
O4—H4...O1 <sup>iii</sup>	0.81 (3)	1.79 (3)	2.5851 (18)	166 (3)
O1W—H1WA...O2A <sup>iv</sup>	0.82 (3)	2.01 (3)	2.8072 (19)	166 (2)
O1W—H1WB...O1	0.86 (2)	1.90 (2)	2.7449 (16)	169 (2)
N1A—H1AA...O3 <sup>v</sup>	0.90 (2)	2.01 (2)	2.9087 (18)	173 (2)
N1A—H1AB...O3A <sup>vi</sup>	0.87 (2)	2.38 (2)	3.1151 (19)	141.7 (17)
N1A—H1AC...O1W <sup>v</sup>	0.93 (2)	1.87 (2)	2.785 (2)	165.6 (18)
O4A—H4AA...O1A <sup>vii</sup>	0.98 (3)	1.60 (3)	2.5672 (16)	168 (2)
O1WA—H1WC...O2 <sup>viii</sup>	0.83 (3)	2.07 (3)	2.8628 (19)	158 (2)
O1WA—H1WD...O1A	0.81 (2)	1.98 (3)	2.7717 (17)	166 (3)

Symmetry codes: (i)  $-x+1, y-1/2, -z$ ; (ii)  $x-1, y-1, z-1$ ; (iii)  $x, y+1, z$ ; (iv)  $-x+1, y-3/2, -z+1$ ; (v)  $-x+1, y+1/2, -z+1$ ; (vi)  $-x+2, y+1/2, -z+1$ ; (vii)  $x, y-1, z$ ; (viii)  $-x+1, y+3/2, -z$ .