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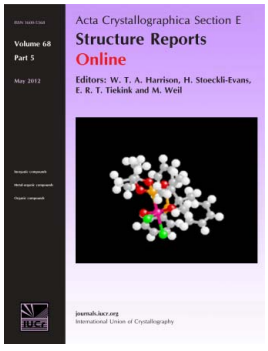

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1-Azaniumylcyclobutane-1-carboxylate monohydrate

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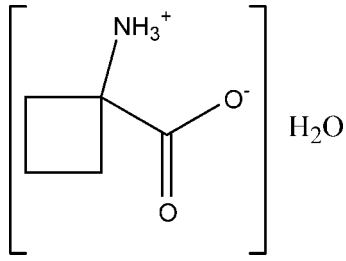
Key indicators: single-crystal X-ray study; T = 123 K; mean σ(C–C) = 0.002 Å; disorder in main residue; R factor = 0.038; wR factor = 0.103; data-to-parameter ratio = 11.8.

In the title compound, $C_5H_9NO_2\cdot H_2O$, the amino acid is in the usual zwitterionic form involving the α-carboxylate group. The cyclobutane backbone of the amino acid is disordered over two conformations, with occupancies of 0.882 (7) and 0.118 (7). In the crystal, N—H···O and O—H···O hydrogen bonds link the zwitterions [with the water molecule involved as both acceptor (with the NH_3^+) and donor (through a single carboxylate O from two different aminocyclobutane carboxylate moities)], resulting in a two-dimensional layered structure lying parallel to (100).

Related literature

For the eighty amino acids that have been detected in meteorites or comets, see: Burton *et al.* (2012); Pizzarello *et al.* (2004), (2006). For the role of the H atom on the α-C atom in enhancing the rate of racemization, see: Yamada *et al.* (1983). For the mechanism of racemization of amino acids lacking an α-H atom, see: Pizzarello & Groy (2011). For the role that crystallization can play in the enrichment of L-isovaline and its structure, see: Butcher *et al.* (2013). For normal bond lengths and angles, see: Orpen (1993). For the hydrochloride salt of the title compound and related non-proteinogenic amino acids, see: Chacko & Zand (1975); Butcher *et al.* (2013); Brewer *et al.* (2013). For conformational studies on model proteins with 1-aminocyclobutane-1-carboxylic acid residues, see: Balaji *et al.* (1995). For involvement of the title compound in ethylene production that leads to the ripening and spoilage of fruit, see: Nakatsuka *et al.* (1998); Bulantseva *et al.* (2003).



Experimental

Crystal data

$C_5H_9NO_2\cdot H_2O$
M_r = 133.15
Monoclinic, $P2_1/c$
a = 10.25082 (19) Å
b = 6.13117 (9) Å
c = 10.9209 (2) Å
β = 100.8735 (18)°
V = 674.05 (2) Å^3
Z = 4
Cu $K\alpha$ radiation
μ = 0.92 mm^{-1}
T = 123 K
0.41 × 0.34 × 0.16 mm

Data collection

Agilent Xcalibur (Ruby, Gemini) diffractometer
Absorption correction: multi-scan (*CrysAlis PRO*; Agilent, 2012)
T_{min} = 0.784, T_{max} = 1.000
4405 measured reflections
1400 independent reflections
1360 reflections with $I > 2\sigma(I)$
R_{int} = 0.022

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.103
S = 1.06
1400 reflections
119 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.36 e Å^{-3}
$\Delta\rho_{min}$ = −0.19 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O1W—H1W1···O1^{i}	0.87 (2)	1.92 (2)	2.7935 (12)	175.2 (18)
O1W—H1W2···O2^{ii}	0.82 (2)	2.01 (2)	2.8268 (12)	175.7 (19)
N1—H1N···O2^{iii}	0.922 (18)	1.923 (18)	2.8087 (12)	160.6 (15)
N1—H2N···O1^{iv}	0.930 (17)	1.913 (17)	2.8351 (12)	171.2 (14)
N1—H3N···O1W	0.902 (17)	1.895 (17)	2.7673 (13)	162.3 (15)

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

Data collection: *CrysAlis PRO* (Agilent, 2012); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

RJB wishes to acknowledge the NSF–MRI program (grant CHE-0619278) for funds to purchase the diffractometer. GB wishes to acknowledge support of this work from NASA (NNX10AK71A)

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: ZS2282).

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supplementary materials

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1-Azaniumylcyclobutane-1-carboxylate monohydrate

Ray J. Butcher, Greg Brewer, Aaron S. Burton and Jason P. Dworkin

1. Comment

The alpha amino acids are essential for life as they are the building blocks of all proteins and enzymes. Nature uses almost exclusively the *L* form of the nineteen common chiral amino acids. The title compound is achiral due to the symmetry of the alpha carbon atom. It also lacks a hydrogen atom on the alpha carbon atom, which is critical in the racemization of the proteinogenic amino acids (Yamada *et al.*, 1983). Little is known about the mechanism of racemization of amino acids lacking an alpha hydrogen atom (Pizzarello & Groy, 2011). Mechanistic investigation of racemization pathways of appropriate derivatives of the title compound may shed light on the racemization of this class of amino acids. Over eighty amino acids that have been identified in meteorites (Burton *et al.*, 2012; Pizzarello *et al.*, 2006). The title compound has not been detected to date in extraterrestrial sources but a higher analog, cycloleucine, has been reported (Pizzarello *et al.*, 2004). The title compound has been incorporated into peptides for conformational studies on model proteins with 1-aminocyclobutane-1-carboxylic acid residues (Balaji *et al.*, 1995). In addition the title compound has been shown to inhibit the enzyme 1-aminocyclopropane-1-carboxylate synthase, part of the pathway for ethylene production that leads to the ripening and spoilage of fruit (Nakatsuka *et al.*, 1998; Bulantseva *et al.*, 2003). The structures of some related non-proteinogenic amino acids have recently been reported (Butcher *et al.*, 2013; Brewer, *et al.*, 2013).

The structure of the title compound has not been reported to the CCDC but there is a report of its hydrochloride salt as a monohydrate (Chacko & Zand, 1975). In the structure of the title compound the amino acid is in the usual zwitterionic form involving the *α* carboxylate group and all the the bond lengths and angles are in the normal range for such compounds (Orpen, 1993). The metrical parameters of the title compound and its hydrochloride salt do not differ significantly apart from the C—O bond lengths which are equivalent in the title compound but differ significantly in the hydrochloride salt. The cyclobutane backbone of the amino-acid is disordered over two conformations with occupancies of 0.882 (7) and 0.118 (7). There is extensive N—H···O and O—H···O hydrogen bonding (Table 1) linking the zwitterions into a two-dimensional layered structure lying parallel to (100) (Fig. 2).

2. Experimental

1-Aminocyclobutane carboxylic acid was purchased from Sigma Aldrich. Crystals of the title compound were grown by evaporation from an aqueous solution of the achiral amino acid.

3. Refinement

H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms with a C—H distances of 0.98 and 0.99 Å. The protons on the N and O were refined isotropically with the O—H distances for the water H's constrained to be 0.82 Å and the H—O—H angle close to 104.5°. The cyclobutane backbone of the amino-acid was disordered over two conformations with occupancies of 0.882 (7) and 0.118 (7).

Computing details

Data collection: *CrysAlis PRO* (Agilent, 2012); cell refinement: *CrysAlis PRO* (Agilent, 2012); data reduction: *CrysAlis PRO* (Agilent, 2012); program(s) used to solve structure: *SHELXS97* (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).

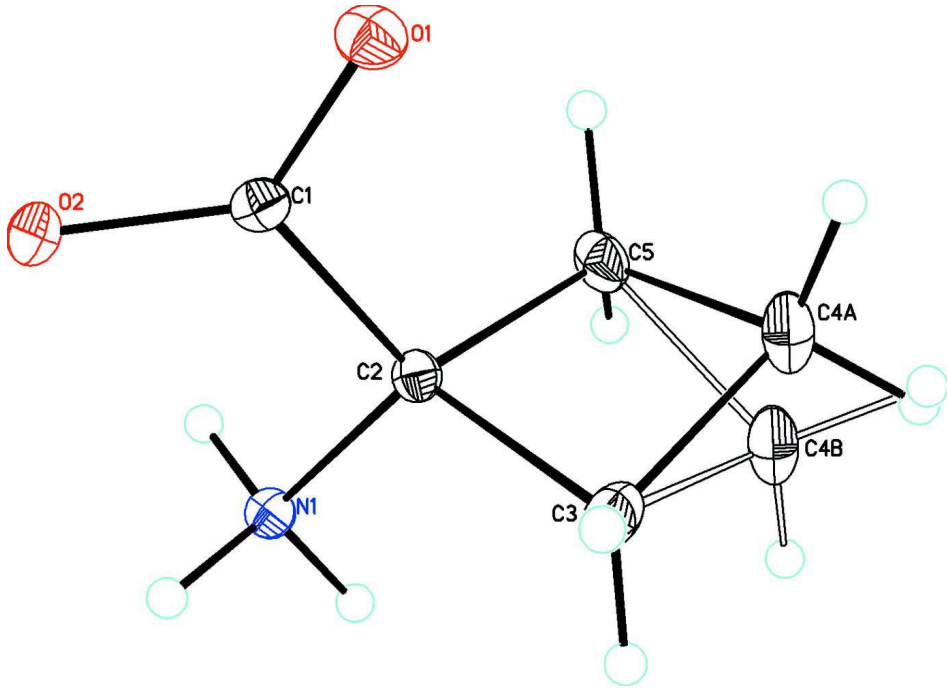

Figure 1

Fif. 1. Diagram of the title compound showing atom labeling. Atomic displacement parameters are at the 30% probability level. The disorder in the backbone is shown with atoms in the the minor component connected with unfilled bonds. Hydrogen bonds are shown as dashed lines.

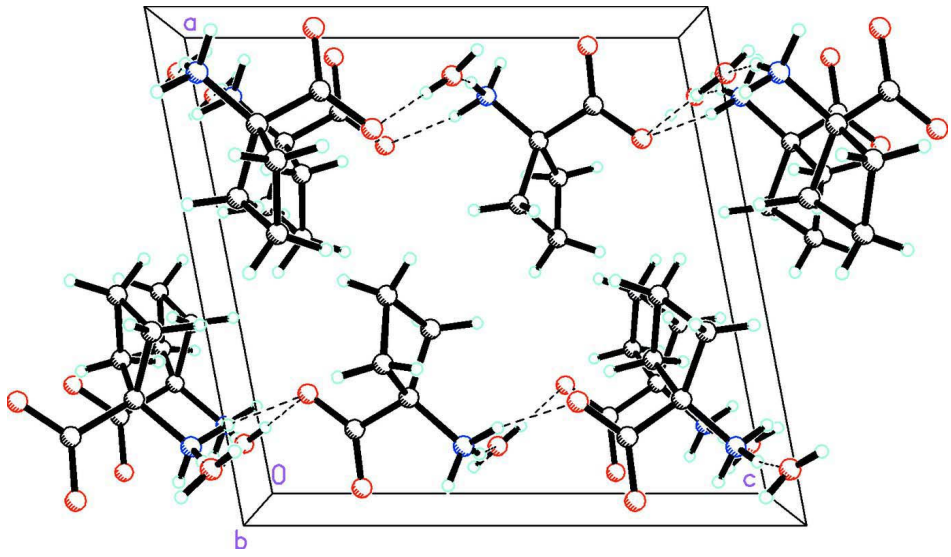

Figure 2

Packing diagram of the title compound (major component only) viewed along the *b* axis showing the N—H···O and O—H···O hydrogen bonds as dashed lines.

1-Azaniumylcyclobutane-1-carboxylate monohydrate

Crystal data

$C_5H_9NO_2·H_2O$
M_r = 133.15
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
a = 10.25082 (19) Å
b = 6.13117 (9) Å
c = 10.9209 (2) Å
β = 100.8735 (18)°
V = 674.05 (2) Å^3
Z = 4
$F(000)$ = 288
D_x = 1.312 Mg m^{-3}
Cu $K\alpha$ radiation, λ = 1.54184 Å
Cell parameters from 4146 reflections
θ = 4.1–77.2°
μ = 0.92 mm^{-1}
T = 123 K
Prism, colorless
0.41 × 0.34 × 0.16 mm

Data collection

Agilent Xcalibur (Ruby, Gemini) diffractometer
Radiation source: Enhance (Cu) X-ray source
Graphite monochromator
Detector resolution: 10.5081 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*CrysAlis PRO*; Agilent, 2012)
T_{min} = 0.784, T_{max} = 1.000
4405 measured reflections
1400 independent reflections
1360 reflections with $I > 2\sigma(I)$
R_{int} = 0.022
θ_{max} = 77.4°, θ_{min} = 8.3°
h = −12→12
k = −6→7
l = −13→13

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.103
S = 1.06
1400 reflections
119 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 atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0616P)^2 + 0.2169P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.36$ e Å^{-3}
$\Delta\rho_{min} = -0.19$ e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.016 (4)

Special details

Experimental. Absorption correction: CrysAlisPro (Agilent, 2012) 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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
O1W	0.11907 (10)	0.30045 (14)	0.47599 (9)	0.0268 (3)	
H1W1	0.1576 (18)	0.203 (3)	0.5293 (18)	0.037 (4)*	
H1W2	0.0713 (19)	0.231 (3)	0.4210 (19)	0.039 (5)*	
O2	0.04488 (8)	0.54177 (13)	0.20493 (7)	0.0218 (3)	
O1	0.23745 (8)	0.52875 (13)	0.13611 (7)	0.0213 (3)	
N1	0.13993 (9)	0.73526 (15)	0.41449 (8)	0.0159 (3)	
H1N	0.0661 (18)	0.809 (3)	0.3735 (16)	0.032 (4)*	
H2N	0.1799 (15)	0.815 (3)	0.4840 (15)	0.023 (4)*	
H3N	0.1179 (16)	0.603 (3)	0.4404 (15)	0.026 (4)*	
C1	0.16664 (10)	0.57917 (16)	0.21410 (9)	0.0155 (3)	
C2	0.23577 (10)	0.70405 (17)	0.32992 (9)	0.0151 (3)	
C3	0.30893 (12)	0.9136 (2)	0.30010 (12)	0.0247 (3)	
H3A	0.2845 (16)	0.967 (3)	0.2165 (16)	0.030*	
H3B	0.3019 (16)	1.021 (3)	0.3606 (16)	0.030*	
C4A	0.44072 (14)	0.7839 (3)	0.32757 (17)	0.0353 (6)	0.882 (7)
H4AA	0.4706	0.7309	0.2518	0.042*	0.882 (7)
H4AB	0.5134	0.8607	0.3837	0.042*	0.882 (7)
C4B	0.4308 (11)	0.845 (2)	0.3984 (14)	0.0353 (6)	0.118
H4BA	0.4366	0.9176	0.4802	0.042*	0.118 (7)
H4BB	0.5162	0.8543	0.3689	0.042*	0.118 (7)
C5	0.37127 (10)	0.6082 (2)	0.39333 (11)	0.0228 (3)	
H5A	0.3873 (16)	0.464 (3)	0.3693 (15)	0.027*	
H5B	0.3840 (16)	0.615 (3)	0.4822 (16)	0.027*	

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1W	0.0356 (5)	0.0181 (4)	0.0236 (5)	−0.0006 (3)	−0.0028 (4)	0.0030 (3)
O2	0.0172 (4)	0.0236 (5)	0.0229 (4)	−0.0017 (3)	−0.0010 (3)	−0.0053 (3)

O1	0.0237 (4)	0.0252 (5)	0.0150 (4)	0.0027 (3)	0.0035 (3)	−0.0017 (3)
N1	0.0166 (5)	0.0170 (5)	0.0139 (5)	0.0002 (3)	0.0023 (3)	−0.0002 (3)
C1	0.0186 (5)	0.0131 (5)	0.0134 (5)	0.0021 (4)	−0.0006 (4)	0.0021 (4)
C2	0.0143 (5)	0.0163 (5)	0.0141 (5)	0.0002 (4)	0.0017 (4)	0.0004 (4)
C3	0.0271 (6)	0.0214 (6)	0.0273 (6)	−0.0085 (4)	0.0098 (5)	−0.0027 (5)
C4A	0.0195 (8)	0.0404 (10)	0.0476 (11)	−0.0086 (6)	0.0105 (7)	−0.0069 (7)
C4B	0.0195 (8)	0.0404 (10)	0.0476 (11)	−0.0086 (6)	0.0105 (7)	−0.0069 (7)
C5	0.0148 (5)	0.0313 (7)	0.0204 (6)	0.0039 (4)	−0.0018 (4)	−0.0033 (4)

Geometric parameters (Å, º)

O1W—H1W1	0.87 (2)	C3—C4A	1.547 (2)
O1W—H1W2	0.82 (2)	C3—H3A	0.958 (17)
O2—C1	1.2543 (13)	C3—H3B	0.943 (18)
O1—C1	1.2574 (13)	C4A—C5	1.542 (2)
N1—C2	1.4823 (13)	C4A—H4AA	0.9900
N1—H1N	0.922 (18)	C4A—H4AB	0.9900
N1—H2N	0.930 (17)	C4B—C5	1.570 (12)
N1—H3N	0.902 (17)	C4B—H4BA	0.9900
C1—C2	1.5330 (14)	C4B—H4BB	0.9900
C2—C5	1.5465 (14)	C5—H5A	0.942 (17)
C2—C3	1.5527 (15)	C5—H5B	0.956 (17)
C3—C4B	1.545 (13)		
H1W1—O1W—H1W2	105.5 (18)	C2—C3—H3B	108.9 (10)
C2—N1—H1N	109.9 (11)	H3A—C3—H3B	112.9 (14)
C2—N1—H2N	109.5 (9)	C5—C4A—C3	89.22 (9)
H1N—N1—H2N	109.6 (14)	C5—C4A—H4AA	113.8
C2—N1—H3N	108.3 (10)	C3—C4A—H4AA	113.8
H1N—N1—H3N	111.2 (15)	C5—C4A—H4AB	113.8
H2N—N1—H3N	108.2 (14)	C3—C4A—H4AB	113.8
O2—C1—O1	126.43 (10)	H4AA—C4A—H4AB	111.0
O2—C1—C2	117.09 (9)	C3—C4B—C5	88.3 (6)
O1—C1—C2	116.46 (9)	C3—C4B—H4BA	113.9
N1—C2—C1	108.72 (8)	C5—C4B—H4BA	113.9
N1—C2—C5	114.52 (8)	C3—C4B—H4BB	113.9
C1—C2—C5	114.58 (9)	C5—C4B—H4BB	113.9
N1—C2—C3	115.28 (9)	H4BA—C4B—H4BB	111.1
C1—C2—C3	113.99 (9)	C4A—C5—C2	88.88 (9)
C5—C2—C3	88.84 (8)	C2—C5—C4B	88.6 (4)
C4B—C3—C2	89.3 (4)	C4A—C5—H5A	113.8 (10)
C4A—C3—C2	88.44 (9)	C2—C5—H5A	114.8 (10)
C4B—C3—H3A	142.0 (11)	C4B—C5—H5A	141.8 (11)
C4A—C3—H3A	115.0 (10)	C4A—C5—H5B	117.2 (9)
C2—C3—H3A	115.6 (10)	C2—C5—H5B	112.2 (10)
C4B—C3—H3B	82.1 (12)	C4B—C5—H5B	86.9 (11)
C4A—C3—H3B	113.6 (10)	H5A—C5—H5B	109.0 (14)
O2—C1—C2—N1	5.49 (13)	C2—C3—C4A—C5	−16.15 (9)
O1—C1—C2—N1	−176.10 (9)	C4A—C3—C4B—C5	−71.5 (8)

O2—C1—C2—C5	135.05 (10)	C2—C3—C4B—C5	16.8 (5)
O1—C1—C2—C5	−46.54 (13)	C3—C4A—C5—C2	16.21 (10)
O2—C1—C2—C3	−124.62 (10)	C3—C4A—C5—C4B	−72.9 (8)
O1—C1—C2—C3	53.79 (13)	N1—C2—C5—C4A	−133.55 (10)
N1—C2—C3—C4B	99.7 (6)	C1—C2—C5—C4A	99.82 (11)
C1—C2—C3—C4B	−133.6 (6)	C3—C2—C5—C4A	−16.16 (10)
C5—C2—C3—C4B	−17.0 (6)	N1—C2—C5—C4B	−100.6 (6)
N1—C2—C3—C4A	132.80 (10)	C1—C2—C5—C4B	132.7 (6)
C1—C2—C3—C4A	−100.42 (11)	C3—C2—C5—C4B	16.8 (6)
C5—C2—C3—C4A	16.10 (10)	C3—C4B—C5—C4A	73.3 (8)
C4B—C3—C4A—C5	74.9 (8)	C3—C4B—C5—C2	−16.9 (5)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H1*W*1···O1^{i}	0.87 (2)	1.92 (2)	2.7935 (12)	175.2 (18)
O1*W*—H1*W*2···O2^{ii}	0.82 (2)	2.01 (2)	2.8268 (12)	175.7 (19)
N1—H1*N*···O2^{iii}	0.922 (18)	1.923 (18)	2.8087 (12)	160.6 (15)
N1—H2*N*···O1^{iv}	0.930 (17)	1.913 (17)	2.8351 (12)	171.2 (14)
N1—H3*N*···O1*W*	0.902 (17)	1.895 (17)	2.7673 (13)	162.3 (15)

Symmetry codes: (i) *x*, −*y*+1/2, *z*+1/2; (ii) −*x*, *y*−1/2, −*z*+1/2; (iii) −*x*, *y*+1/2, −*z*+1/2; (iv) *x*, −*y*+3/2, *z*+1/2.