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tert-Butyl 2-(dihydroxyboryl)pyrrole-1-carboxylate

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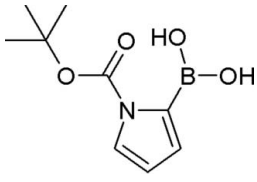
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.002 Å; R factor = 0.031; wR factor = 0.077; data-to-parameter ratio = 14.1.

In the title compound, $C_9H_{14}BNO_4$, the carbonyl and boronic acid groups are essentially coplanar with the pyrrole ring and the boronic acid group has an *exo-endo* conformation. The *exo*-oriented OH is engaged in an intramolecular O—H···O interaction, while the *endo*-oriented one is involved in intermolecular hydrogen bonding to form centrosymmetric dimers. A supramolecular assembly is achieved through interactions involving the *tert*-butyl groups, forming infinite chains along the crystallographic *b* axis. There are, in addition, face-to-face and center-to-edge stacking interactions [distance between the pyrrole ring centroid and an N atom from a neighbouring molecule = 3.369 (8) Å].

Related literature

For related literature, see: Dabrowski *et al.* (2006); Parry *et al.* (2002); Saygili *et al.* (2004); Seminario *et al.* (1998); Thompson *et al.* (2005); Wang *et al.* (2002).



Experimental

Crystal data

$C_9H_{14}BNO_4$
M_r = 211.02
Orthorhombic, *Pbca*
a = 12.9179 (12) Å
b = 9.5885 (7) Å
c = 17.5811 (15) Å
V = 2177.7 (3) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.10 mm^{-1}
T = 100 (2) K
0.71 × 0.34 × 0.22 mm

Data collection

Kuma KM4 CCD diffractometer
Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction 2005)
T_{min} = 0.95, T_{max} = 0.98
19290 measured reflections
2713 independent reflections
1911 reflections with $I > 2\sigma(I)$
R_{int} = 0.021

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.031
$wR(F^2)$ = 0.076
S = 0.96
2713 reflections
193 parameters
All H-atom parameters refined
$\Delta\rho_{max}$ = 0.26 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
O1—H1*O*···O3	0.917 (15)	1.704 (15)	2.5941 (10)	162.9 (13)
O2—H2*O*···O1^{i}	0.922 (16)	1.855 (17)	2.7728 (11)	173.7 (13)

Symmetry code: (i) $-x+1, -y+1, -z+1$.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2005); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2005); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *SHELXL97*.

This work was supported by the Aldrich Chemical Company through the donation of chemicals and equipment and by the Warsaw University of Technology. The X-ray measurements were undertaken in the Crystallographic Unit of the Physical Chemistry Laboratory at the Chemistry Department of the University of Warsaw.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BG2173).

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supporting information

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tert-Butyl 2-(dihydroxyboryl)pyrrole-1-carboxylate

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S1. Comment

Nitrogen-containing boronic acids are the object of interest to many chemists because of their application as potential saccharide sensors (Wang *et al.*, 2002). However, no crystal structure of any boronic acid containing a pyrrole ring has been elucidated to date. The only crystal data concerning nitrogen-containing heterocyclic boronic acids involve some pyrydine (Parry *et al.*, 2002), (Thompson *et al.*, 2005), (Dabrowski *et al.*, 2006) and pyrimidine (Saygili *et al.*, 2004) derivatives.

The molecular structure of the title compound $C_9H_{14}BO_4N$ (I) is shown in Fig. 1. The carbonyl and boronic acid groups are essentially coplanar with the pyrrole ring [torsion angles O3—C5—N1—C1 = -1.31 (1)° and N1—C1—B1—O1 = -2.8 (2)° respectively]. The conformation between C9 from the *tert*-butyl- and the carbonyl groups is antiperiplanar. The boronic acid group has an *exo*-*endo* conformation. The *exo*-oriented OH is engaged in an intramolecular O—H···O interaction with O3. The *endo*- oriented one, instead, is involved into intermolecular hydrogen bonding to form centrosymmetric dimers (Fig. 2). The supramolecular assembly is achieved through interactions involving *tert*-butyl groups, forming infinite chains along the crystallographic *b* axis. Examination of the crystal packing reveals the presence of face to face, center to edge stacking (FFCE) (Seminario *et al.*, 1998). These interactions are represented by a relatively short distance (3.369 (8) Å) between the pyrrole ring centroid and the nitrogen atom from neighbouring molecules (Fig. 3).

S2. Experimental

N-tert-butoxycarbonyl-pyrrole-2-boronic acid was obtained from Aldrich, crystallized from tetrahydrofurane and dried in air.

S3. Refinement

All of hydrogen atoms were located geometrically and their positions were refined while temperature factors were not. The maximum electron-density peak in the final difference map is 0.80 Å from atom C1.

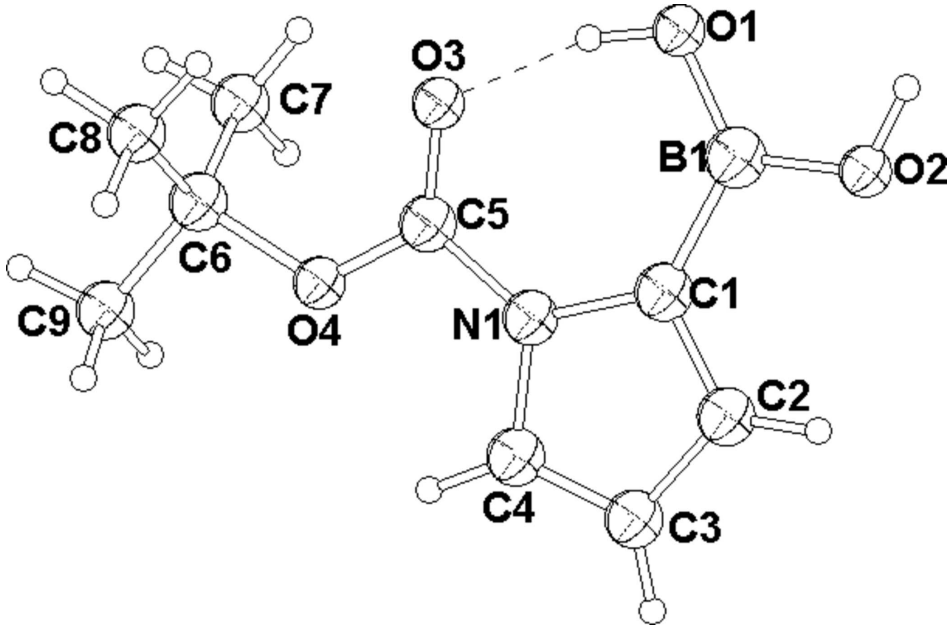

Figure 1

The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids for all non-H atoms are drawn at the 50% probability level.

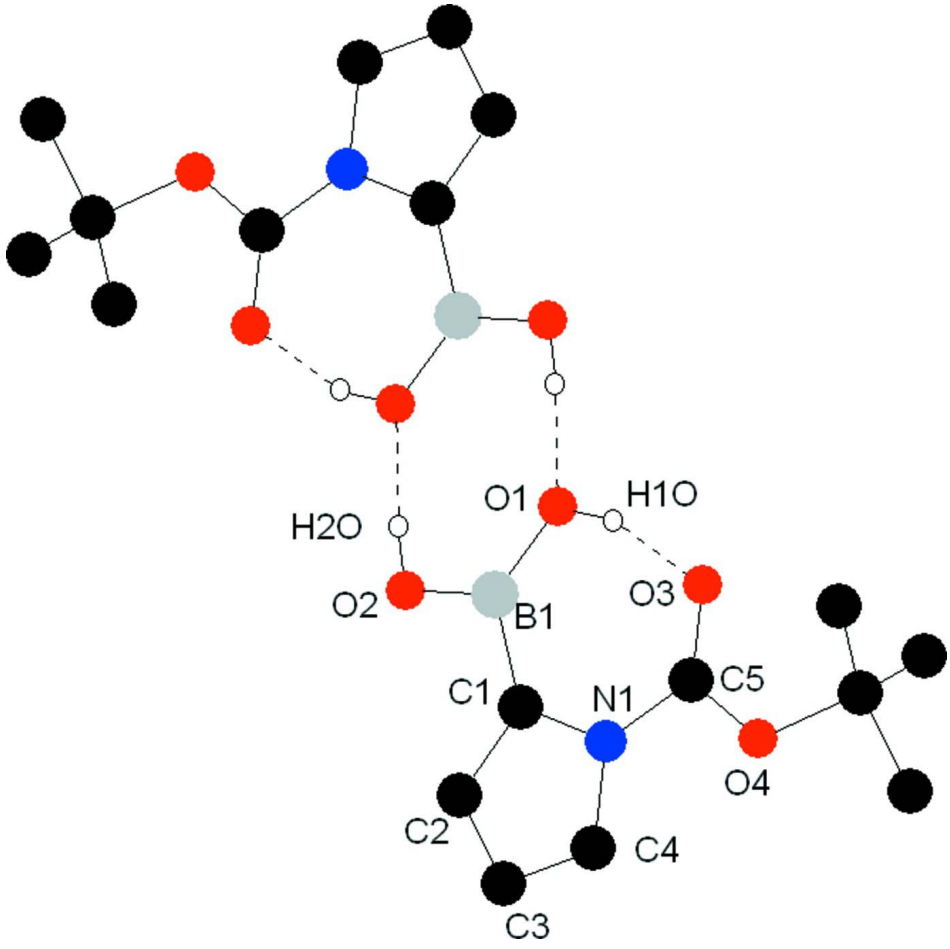

Figure 2

The hydrogen-bonding pattern for (I). Hydrogen bonds are shown as dashed lines.

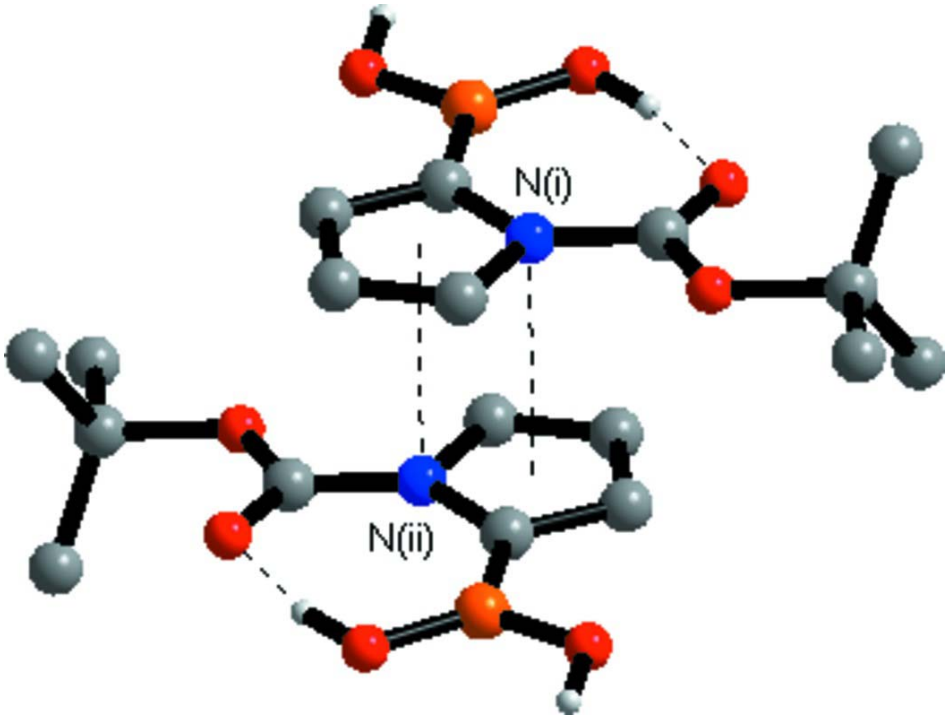

Figure 3

The crystal packing for (I), showing π-π interactions as dotted lines [Symmetry codes: (i) -1/2 + x, 1.5 - y, 1 - z; (ii) 0.5 - x, -1/2 + y, z].

tert-Butyl 2-(dihydroxyboryl)pyrrole-1-carboxylate

Crystal data

$C_9H_{14}BNO_4$
M_r = 211.02
Orthorhombic, *Pbca*
Hall symbol: -P 2ac 2ab
a = 12.9179 (12) Å
b = 9.5885 (7) Å
c = 17.5811 (15) Å
V = 2177.7 (3) Å^3
Z = 8
$F(000)$ = 896
D_x = 1.287 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 19290 reflections
θ = 2.8–28.7°
μ = 0.10 mm^{-1}
T = 100 K
Prismatic, colourless
0.71 × 0.34 × 0.22 mm

Data collection

Kuma KM4 CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 8.6479 pixels mm^{-1}
ω scan
Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction 2005)
T_{min} = 0.95, T_{max} = 0.98
19290 measured reflections
2713 independent reflections
1911 reflections with $I > 2\sigma(I)$
R_{int} = 0.021
θ_{max} = 28.7°, θ_{min} = 2.8°
h = −17→17
k = −12→12
l = −23→23

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.076$
$S = 0.97$
2713 reflections
193 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
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0461P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.26$ e Å^{-3}
$\Delta\rho_{min} = -0.19$ e Å^{-3}
Extinction correction: *SHELXL*, $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0033 (7)

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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.54350 (6)	0.63771 (7)	0.45212 (4)	0.02586 (19)
O2	0.40336 (6)	0.64180 (8)	0.53731 (4)	0.02619 (19)
O3	0.60617 (5)	0.83554 (7)	0.36263 (4)	0.02260 (18)
O4	0.56150 (5)	1.04637 (7)	0.31656 (4)	0.02186 (18)
N1	0.46192 (6)	0.95162 (8)	0.40642 (4)	0.01800 (19)
C1	0.42176 (8)	0.85423 (10)	0.45945 (5)	0.0187 (2)
C2	0.33504 (8)	0.91604 (11)	0.48868 (6)	0.0223 (2)
C3	0.32126 (8)	1.05007 (11)	0.45569 (6)	0.0242 (2)
C4	0.39900 (8)	1.06957 (10)	0.40571 (6)	0.0218 (2)
C5	0.54985 (8)	0.93691 (9)	0.36119 (5)	0.0186 (2)
C6	0.64575 (8)	1.04984 (10)	0.25803 (5)	0.0225 (2)
C7	0.63032 (10)	0.93008 (12)	0.20274 (6)	0.0285 (3)
C8	0.75028 (9)	1.04896 (12)	0.29709 (6)	0.0269 (2)
C9	0.62477 (10)	1.18889 (12)	0.22011 (7)	0.0304 (3)
B1	0.46066 (9)	0.70564 (12)	0.48297 (6)	0.0204 (2)
H1O	0.5763 (11)	0.6964 (15)	0.4187 (8)	0.056 (4)*
H2O	0.4234 (12)	0.5504 (17)	0.5442 (8)	0.060 (5)*
H2	0.2915 (8)	0.8741 (11)	0.5269 (5)	0.018 (2)*
H3	0.2680 (9)	1.1122 (12)	0.4668 (6)	0.028 (3)*
H4	0.4168 (8)	1.1463 (11)	0.3729 (6)	0.020 (3)*
H7A	0.5580 (11)	0.9321 (12)	0.1830 (7)	0.038 (3)*
H7B	0.6429 (9)	0.8387 (12)	0.2253 (6)	0.029 (3)*
H7C	0.6788 (9)	0.9424 (11)	0.1603 (6)	0.029 (3)*

H8A	0.7576 (9)	1.1342 (13)	0.3317 (7)	0.038 (3)*
H8B	0.7629 (9)	0.9613 (12)	0.3252 (6)	0.031 (3)*
H8C	0.8046 (10)	1.0547 (12)	0.2579 (7)	0.036 (3)*
H9A	0.6288 (8)	1.2649 (12)	0.2567 (7)	0.034 (3)*
H9B	0.5551 (10)	1.1878 (13)	0.1981 (6)	0.040 (3)*
H9C	0.6768 (9)	1.2037 (12)	0.1802 (7)	0.039 (3)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0238 (4)	0.0218 (4)	0.0320 (4)	0.0014 (3)	0.0056 (3)	0.0085 (3)
O2	0.0255 (4)	0.0253 (4)	0.0278 (4)	−0.0001 (3)	0.0051 (3)	0.0059 (3)
O3	0.0227 (4)	0.0186 (4)	0.0265 (4)	0.0021 (3)	0.0044 (3)	0.0032 (3)
O4	0.0240 (4)	0.0180 (4)	0.0235 (4)	0.0007 (3)	0.0031 (3)	0.0038 (3)
N1	0.0172 (4)	0.0178 (4)	0.0190 (4)	0.0001 (3)	−0.0011 (3)	−0.0005 (3)
C1	0.0181 (5)	0.0220 (5)	0.0159 (4)	−0.0040 (4)	−0.0023 (4)	−0.0013 (4)
C2	0.0188 (5)	0.0286 (6)	0.0194 (5)	−0.0018 (4)	−0.0009 (4)	−0.0039 (4)
C3	0.0195 (5)	0.0264 (6)	0.0267 (5)	0.0049 (5)	−0.0040 (4)	−0.0071 (4)
C4	0.0220 (5)	0.0194 (5)	0.0239 (5)	0.0029 (4)	−0.0061 (4)	−0.0022 (4)
C5	0.0203 (5)	0.0170 (5)	0.0186 (5)	−0.0027 (4)	−0.0026 (4)	−0.0011 (4)
C6	0.0245 (6)	0.0228 (5)	0.0203 (5)	−0.0023 (4)	0.0036 (4)	0.0031 (4)
C7	0.0341 (7)	0.0281 (6)	0.0233 (6)	−0.0037 (5)	0.0027 (5)	−0.0002 (4)
C8	0.0258 (6)	0.0270 (6)	0.0278 (6)	−0.0045 (5)	0.0011 (5)	0.0047 (5)
C9	0.0339 (7)	0.0270 (6)	0.0304 (6)	−0.0027 (5)	0.0012 (5)	0.0087 (5)
B1	0.0193 (6)	0.0230 (6)	0.0190 (5)	−0.0038 (5)	−0.0027 (5)	−0.0013 (5)

Geometric parameters (Å, º)

O1—B1	1.3652 (13)	C3—H3	0.931 (12)
O1—H1O	0.917 (15)	C4—H4	0.963 (10)
O2—B1	1.3547 (13)	C6—C8	1.5149 (15)
O2—H2O	0.922 (16)	C6—C9	1.5151 (14)
O3—C5	1.2143 (11)	C6—C7	1.5176 (14)
O4—C5	1.3191 (11)	C7—H7A	0.996 (13)
O4—C6	1.4981 (12)	C7—H7B	0.976 (11)
N1—C4	1.3928 (12)	C7—H7C	0.981 (12)
N1—C5	1.3937 (12)	C8—H8A	1.023 (13)
N1—C1	1.4178 (12)	C8—H8B	0.989 (12)
C1—C2	1.3676 (14)	C8—H8C	0.985 (13)
C1—B1	1.5665 (15)	C9—H9A	0.973 (12)
C2—C3	1.4211 (15)	C9—H9B	0.980 (13)
C2—H2	0.964 (10)	C9—H9C	0.983 (12)
C3—C4	1.3474 (15)		
B1—O1—H1O	108.9 (9)	O4—C6—C7	109.13 (8)
B1—O2—H2O	111.6 (9)	C8—C6—C7	113.78 (9)
C5—O4—C6	120.61 (7)	C9—C6—C7	111.13 (9)
C4—N1—C5	123.55 (8)	C6—C7—H7A	109.4 (7)

C4—N1—C1	109.10 (8)	C6—C7—H7B	113.4 (6)
C5—N1—C1	127.35 (8)	H7A—C7—H7B	108.4 (10)
C2—C1—N1	105.15 (8)	C6—C7—H7C	108.2 (6)
C2—C1—B1	123.90 (9)	H7A—C7—H7C	109.3 (9)
N1—C1—B1	130.94 (9)	H7B—C7—H7C	108.1 (9)
C1—C2—C3	109.95 (9)	C6—C8—H8A	110.3 (7)
C1—C2—H2	124.0 (6)	C6—C8—H8B	112.2 (7)
C3—C2—H2	126.0 (6)	H8A—C8—H8B	111.5 (9)
C4—C3—C2	107.35 (9)	C6—C8—H8C	108.5 (7)
C4—C3—H3	126.8 (7)	H8A—C8—H8C	107.8 (9)
C2—C3—H3	125.9 (7)	H8B—C8—H8C	106.2 (9)
C3—C4—N1	108.44 (9)	C6—C9—H9A	111.0 (7)
C3—C4—H4	132.4 (6)	C6—C9—H9B	109.2 (7)
N1—C4—H4	119.1 (6)	H9A—C9—H9B	108.6 (10)
O3—C5—O4	125.51 (9)	C6—C9—H9C	108.6 (7)
O3—C5—N1	123.88 (8)	H9A—C9—H9C	109.1 (10)
O4—C5—N1	110.60 (8)	H9B—C9—H9C	110.4 (9)
O4—C6—C8	109.64 (8)	O2—B1—O1	119.54 (10)
O4—C6—C9	101.06 (8)	O2—B1—C1	114.96 (9)
C8—C6—C9	111.34 (9)	O1—B1—C1	125.49 (9)

C4—N1—C1—C2	0.54 (10)	C4—N1—C5—O3	178.49 (9)
C5—N1—C1—C2	−179.63 (8)	C1—N1—C5—O3	−1.32 (14)
C4—N1—C1—B1	179.79 (9)	C4—N1—C5—O4	−2.55 (12)
C5—N1—C1—B1	−0.38 (15)	C1—N1—C5—O4	177.64 (8)
N1—C1—C2—C3	−0.70 (10)	C5—O4—C6—C8	−64.93 (11)
B1—C1—C2—C3	179.99 (9)	C5—O4—C6—C9	177.47 (8)
C1—C2—C3—C4	0.62 (11)	C5—O4—C6—C7	60.31 (11)
C2—C3—C4—N1	−0.26 (11)	C2—C1—B1—O2	−1.97 (14)
C5—N1—C4—C3	179.99 (8)	N1—C1—B1—O2	178.91 (9)
C1—N1—C4—C3	−0.17 (10)	C2—C1—B1—O1	176.28 (10)
C6—O4—C5—O3	3.95 (14)	N1—C1—B1—O1	−2.85 (16)
C6—O4—C5—N1	−174.99 (7)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*O*···O3	0.917 (15)	1.704 (15)	2.5941 (10)	162.9 (13)
O2—H2*O*···O1^{i}	0.922 (16)	1.855 (17)	2.7728 (11)	173.7 (13)

Symmetry code: (i) −*x*+1, −*y*+1, −*z*+1.