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3-Aminophenylboronic acid monohydrate

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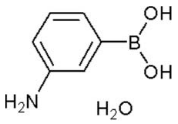
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.002 Å; R factor = 0.032; wR factor = 0.088; data-to-parameter ratio = 10.8.

In the title compound, $C_6H_8BNO_2\cdot H_2O$, the almost planar boronic acid molecules (r.m.s. deviation = 0.044 Å) form inversion dimers, linked by pairs of O—H⋯O hydrogen bonds. The water molecules link these dimers into [100] chains by way of O—H⋯O hydrogen bonds, and N—H⋯O links generate (100) sheets.

Related literature

For background to the synthesis, structures and applications of phenylboronic acid derivatives, see: Barba & Betanzos (2007); Barba *et al.* (2004, 2006); Bernstein *et al.* (1995); Christinat *et al.* (2008); Dreos *et al.* (2002); Fujita *et al.* (2008); Höpfl (2002); Hall (2005); Lulinski *et al.* (2007); Miyaura & Suzuki (1995); Severin (2009); Shinkai *et al.* (2001); Smith *et al.* (2008); Zhang *et al.* (2007).



Experimental

Crystal data

$C_6H_8BNO_2\cdot H_2O$
M_r = 154.96
Monoclinic, $P2_1/c$
a = 7.1211 (8) Å
b = 13.8548 (15) Å
c = 7.8475 (8) Å
β = 100.663 (2)°
V = 760.88 (14) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.11 mm^{-1}
T = 100 K
0.44 × 0.38 × 0.34 mm

Data collection

Bruker SMART APEX CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min}$ = 0.89, $T_{\max}$ = 1.00
7077 measured reflections
1341 independent reflections
1258 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.022

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.088
S = 1.03
1341 reflections
124 parameters
6 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}$ = 0.29 e Å^{-3}
$\Delta\rho_{\min}$ = −0.17 e Å^{-3}

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O1—H1′⋯O2$^{\rm i}$	0.84 (1)	1.92 (1)	2.7583 (13)	174 (2)
N1—H1A⋯O31$^{\rm ii}$	0.86 (1)	2.21 (1)	3.0661 (15)	177 (1)
N1—H1B⋯O1$^{\rm iii}$	0.86 (1)	2.43 (1)	3.1854 (15)	147 (1)
O2—H2′⋯O31	0.84 (1)	1.91 (1)	2.7159 (13)	161 (2)
O31—H31A⋯N1$^{\rm iv}$	0.84 (1)	2.07 (1)	2.9040 (15)	173 (2)
O31—H31B⋯O1$^{\rm v}$	0.84 (1)	2.05 (1)	2.8810 (13)	170 (2)

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

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT-Plus-NT* (Bruker, 2001); data reduction: *SAINT-Plus-NT*; program(s) used to solve structure: *SHELXTL-NT* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL-NT*; molecular graphics: *SHELXTL-NT*; software used to prepare material for publication: *PLATON* (Spek, 2009) and *publCIF* (Westrip, 2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5409).

References

Barba, V. & Betanzos, I. (2007). *J. Organomet. Chem.* **692**, 4903–4908.
Barba, V., Höpfl, H., Farfán, N., Santillan, R., Beltrán, H. I. & Zamudio-Rivera, L. S. (2004). *Chem. Commun.* pp. 2834–2835.
Barba, V., Villamil, R., Luna, R., Godoy-Alcantar, C., Höpfl, H., Beltrán, H. I., Zamudio-Rivera, L. S., Santillan, R. & Farfán, N. (2006). *Inorg. Chem.* **45**, 2553–2561.
Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed.* **34**, 1555–1573.
Bruker (2000). *SMART*. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2001). *SAINT-Plus-NT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Christinat, N., Scopelliti, R. & Severin, K. (2008). *Angew. Chem. Int. Ed.* **47**, 1848–1852.
Dreos, R., Nardin, G., Randaccio, L., Siega, P. & Tauzher, G. (2002). *Eur. J. Inorg. Chem.* pp. 2885–2890.
Fujita, N., Shinkai, S. & James, T. D. (2008). *Chem. Asian J.* **3**, 1076–1091.
Hall, D. G. (2005). *Boronic Acids: Preparation, Applications in Organic Synthesis and Medicine*. Weinheim: Wiley-VCH.
Höpfl, H. (2002). *Struct. Bond.* **103**, 1–56.
Lulinski, S., Madura, I., Serwatowski, J., Szatylowicz, H. & Zachara, J. (2007). *New J. Chem.* **31**, 144–154.
Miyaura, N. & Suzuki, A. (1995). *Chem. Rev.* **95**, 2457–2483.
Severin, K. (2009). *Dalton Trans.* pp. 5254–5264.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Shinkai, S., Ikeda, M., Sugasaki, A. & Takeuchi, M. (2001). *Acc. Chem. Res.* **34**, 494–503.
Smith, A. E., Clapham, K. M., Batsanov, A. S., Bryce, M. R. & Tarbit, B. (2008). *Eur. J. Org. Chem.* pp. 1458–1463.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**. Submitted.
Zhang, Y., Li, M., Chandrasekaran, S., Gao, X., Fang, X., Lee, H.-W., Hardcastle, K., Yang, J. & Wang, B. (2007). *Tetrahedron*, **63**, 3287–3292.

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3-Aminophenylboronic acid monohydrate

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S1. Comment

Substituted phenylboronic acid derivatives have been prepared mainly for applications in organic synthesis (Miyaura & Suzuki, 1995; Hall, 2005) and for molecular recognition of biochemically active molecules (Shinkai *et al.*, 2001). More recently, such boronic acid derivatives have attracted attention also as building blocks for the self-assembly of macrocyclic and polymeric assemblies. For this purpose, the boronic acid is generally converted to an ester (boronate) via condensation with an aliphatic or aromatic diol, which is then assembled to a macromolecular structure via reaction of the additional functional group attached to the *B*-phenyl ring (Höpfl, 2002; Fujita *et al.*, 2008; Severin, 2009). In this context, 3-aminophenylboronic acid has been employed for the generation of macrocycles and cages (Dreos *et al.*, 2002; Barba *et al.*, 2004 and 2006; Barba & Betanzos, 2007; Christinat *et al.*, 2008).

We report herein on the molecular and crystal structure of 3-aminophenylboronic acid monohydrate (**I**).

The asymmetric unit of **I** contains one 3-aminophenylboronic acid and one water molecule (Figure 1). The boronic acid molecules are associated through the well-known -$B(OH)_2\cdots(HO)_2B$-synthon (motif **A**) with the graph set $R_2^2(8)$ (Bernstein *et al.*, 1995), in which each $B(OH)_2$ group has *syn-anti* conformation (with respect to the H atoms), thus allowing for the formation of additional hydrogen bonds with the water molecules included in the crystal lattice. These (B)O—H···O_w hydrogen bonds give rise to a cyclic water-expanded motif **B** [graph set $R_6^6(12)$] of the boronic acid homodimer, thus generating a 1D chain along axis *a* (Figure 2). The $(OH)_6$ ring has chair-conformation and has been observed previously in the crystal structures of 3,5-dibromo-2-formylphenylboronic acid monohydrate (Lulinski *et al.*, 2007), 5-quinolineboronic acid monohydrate (Zhang *et al.*, 2007) and 2,6-dichloro-3-pyridylboronic acid hemihydrate (Smith *et al.*, 2008). The 1D chains are interconnected through O_w—H···N, N—H···O_w and N—H···O(B) hydrogen bonds to give an overall 3D hydrogen bonded network (Table 1).

S2. Experimental

3-Aminophenylboronic acid monohydrate is a commercially available product that has been crystallized from a solvent mixture of benzene, methanol and water to generate colourless blocks of (I); M.p. 368 K.

S3. Refinement

H atoms were positioned geometrically and constrained using the riding-model approximation [$C\text{-}H_{aryl} = 0.93$ Å, $U_{iso}(H_{aryl}) = 1.2\ U_{eq}(C)$]. Hydrogen atoms bonded to O (H1′, H2′, H31A and H31B) and N (H1A and H1B) were located in difference Fourier maps. The coordinates of the O—H and N—H hydrogen atoms were refined with distance restraints: O—H = 0.84±0.01 Å, N—H = 0.86 Å ±0.01 and [$U_{iso}(H) = 1.5\ U_{eq}(O,N)$].

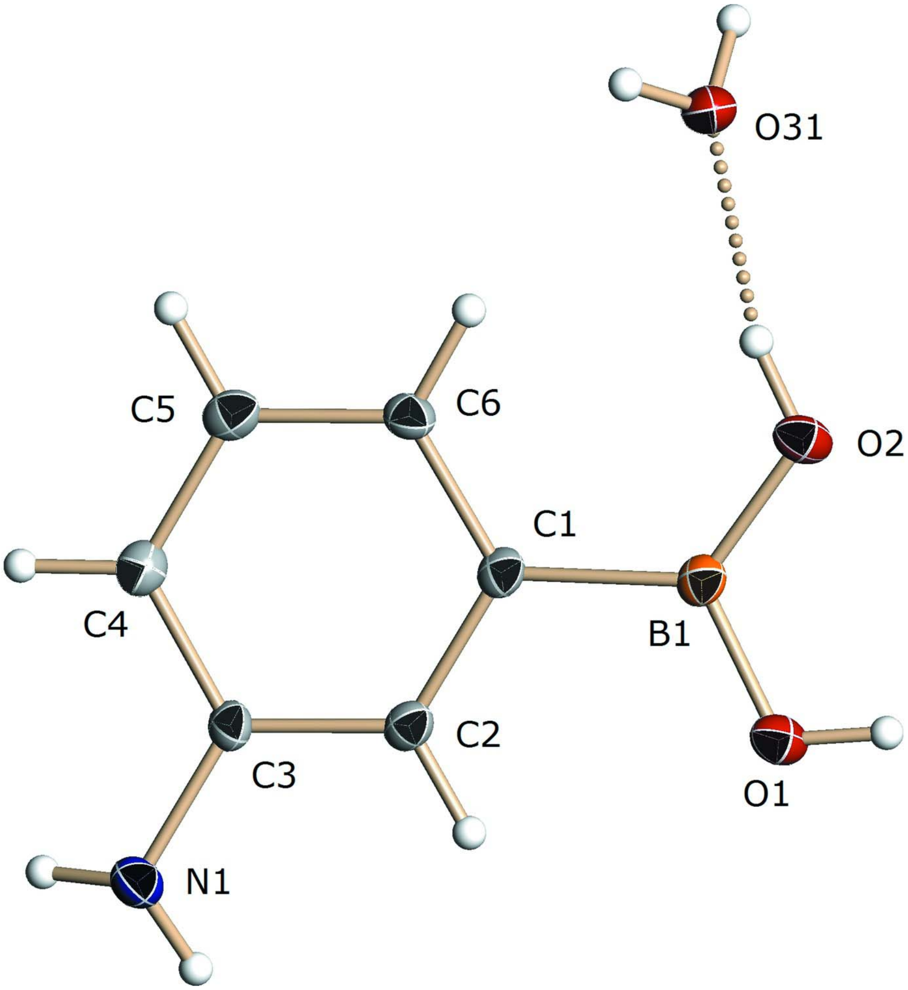

Figure 1

Perspective view of (I) with displacement ellipsoids drawn at the 50% probability level.

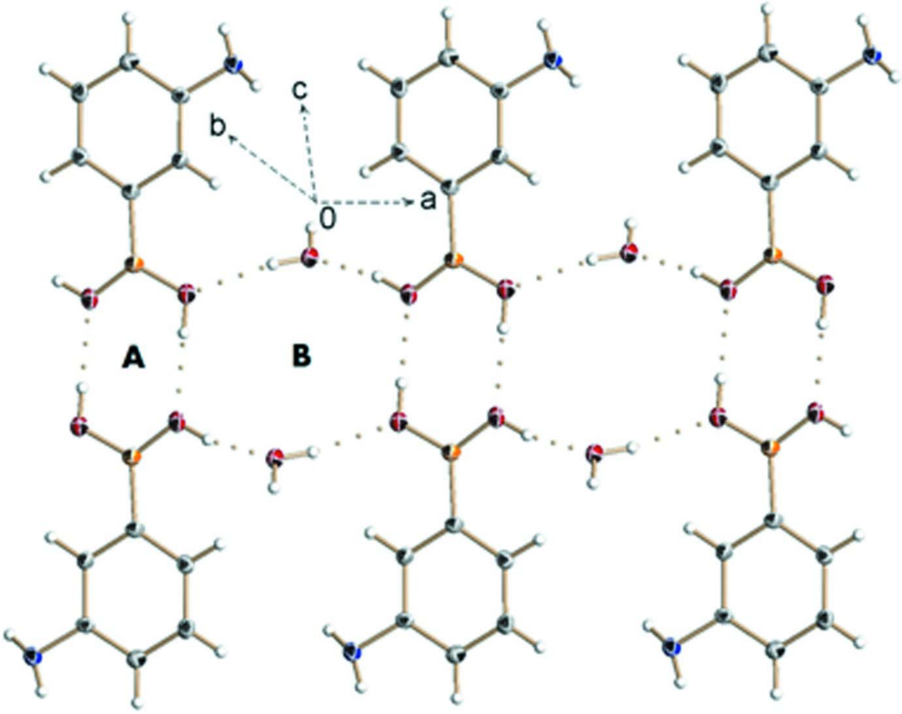

Figure 2

In the crystal structure of (I) homodimeric boronic acid motifs **A** and water-expanded motifs **B** are linked to 1D hydrogen-bonded chains.

3-Aminophenylboronic acid monohydrate

Crystal data

$C_6H_8BNO_2 \cdot H_2O$
M_r = 154.96
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
a = 7.1211 (8) Å
b = 13.8548 (15) Å
c = 7.8475 (8) Å
β = 100.663 (2)°
V = 760.88 (14) Å^3
Z = 4
$F(000)$ = 328
D_x = 1.353 Mg m^{-3}
Melting point: 368 K
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 4929 reflections
θ = 2.9–28.3°
μ = 0.11 mm^{-1}
T = 100 K
Block, colourless
0.44 × 0.38 × 0.34 mm

Data collection

Bruker SMART APEX CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 8.3 pixels mm^{-1}
phi and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.89, T_{max} = 1.00
7077 measured reflections
1341 independent reflections
1258 reflections with $I > 2\sigma(I)$
R_{int} = 0.022
θ_{max} = 25.0°, θ_{min} = 2.9°
$h = -8 \rightarrow 8$
$k = -16 \rightarrow 16$
$l = -9 \rightarrow 9$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.088$
$S = 1.03$
1341 reflections
124 parameters
6 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
$w = 1/[\sigma^2(F_o^2) + (0.0487P)^2 + 0.3165P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.29$ e Å^{-3}
$\Delta\rho_{min} = -0.17$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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}
B1	0.5617 (2)	0.06346 (10)	0.24383 (18)	0.0160 (3)
N1	1.02034 (15)	0.15487 (8)	0.78329 (14)	0.0186 (3)
H1A	1.030 (2)	0.1547 (11)	0.8942 (3)	0.022 (4)*
H1B	1.0986 (18)	0.1138 (9)	0.753 (2)	0.029 (4)*
O1	0.71516 (12)	0.03223 (7)	0.17614 (11)	0.0180 (2)
H1′	0.682 (3)	0.0084 (12)	0.0767 (10)	0.038 (5)*
O2	0.38624 (12)	0.05950 (6)	0.13944 (11)	0.0179 (2)
H2′	0.2917 (15)	0.0828 (12)	0.175 (2)	0.036 (5)*
C1	0.60035 (17)	0.10356 (8)	0.43486 (16)	0.0151 (3)
C2	0.78720 (17)	0.10598 (8)	0.52950 (16)	0.0158 (3)
H2	0.8881	0.0809	0.4786	0.019*
C3	0.82923 (17)	0.14429 (8)	0.69650 (16)	0.0151 (3)
C4	0.68011 (18)	0.17961 (9)	0.77225 (16)	0.0171 (3)
H4	0.7062	0.2051	0.8866	0.021*
C5	0.49436 (18)	0.17741 (9)	0.68042 (16)	0.0181 (3)
H5	0.3935	0.2018	0.7322	0.022*
C6	0.45380 (17)	0.13999 (9)	0.51337 (16)	0.0163 (3)
H6	0.3257	0.1391	0.4519	0.020*
O31	0.05437 (12)	0.14588 (7)	0.17821 (12)	0.0199 (2)
H31A	0.048 (3)	0.2022 (5)	0.217 (2)	0.041 (5)*
H31B	−0.0485 (14)	0.1179 (12)	0.186 (2)	0.040 (5)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
B1	0.0179 (7)	0.0120 (7)	0.0181 (7)	−0.0012 (5)	0.0037 (6)	0.0013 (5)
N1	0.0161 (6)	0.0235 (6)	0.0156 (6)	0.0018 (4)	0.0016 (4)	−0.0009 (4)
O1	0.0155 (5)	0.0228 (5)	0.0152 (5)	0.0002 (4)	0.0017 (3)	−0.0049 (4)
O2	0.0143 (5)	0.0221 (5)	0.0172 (5)	0.0019 (4)	0.0026 (4)	−0.0047 (4)
C1	0.0174 (6)	0.0110 (6)	0.0171 (6)	−0.0019 (5)	0.0034 (5)	0.0016 (5)
C2	0.0167 (6)	0.0137 (6)	0.0179 (6)	0.0010 (5)	0.0058 (5)	0.0014 (5)
C3	0.0164 (6)	0.0126 (6)	0.0158 (6)	−0.0008 (5)	0.0019 (5)	0.0030 (5)
C4	0.0206 (7)	0.0153 (6)	0.0156 (6)	−0.0012 (5)	0.0038 (5)	−0.0013 (5)
C5	0.0177 (6)	0.0159 (6)	0.0219 (7)	0.0011 (5)	0.0072 (5)	−0.0007 (5)
C6	0.0135 (6)	0.0157 (6)	0.0190 (6)	−0.0015 (5)	0.0013 (5)	0.0004 (5)
O31	0.0154 (5)	0.0228 (5)	0.0219 (5)	0.0007 (4)	0.0045 (4)	−0.0031 (4)

Geometric parameters (Å, °)

B1—O2	1.3623 (17)	C2—C3	1.3941 (18)
B1—O1	1.3707 (17)	C2—H2	0.9500
B1—C1	1.5745 (18)	C3—C4	1.3980 (18)
N1—C3	1.4122 (16)	C4—C5	1.3846 (18)
N1—H1A	0.860 (3)	C4—H4	0.9500
N1—H1B	0.860 (13)	C5—C6	1.3894 (18)
O1—H1′	0.840 (10)	C5—H5	0.9500
O2—H2′	0.840 (13)	C6—H6	0.9500
C1—C2	1.3991 (17)	O31—H31A	0.842 (9)
C1—C6	1.4005 (18)	O31—H31B	0.841 (12)
O2—B1—O1	117.55 (11)	C2—C3—C4	119.02 (11)
O2—B1—C1	124.48 (11)	C2—C3—N1	120.86 (11)
O1—B1—C1	117.95 (11)	C4—C3—N1	119.91 (11)
C3—N1—H1A	112.3 (11)	C5—C4—C3	119.91 (11)
C3—N1—H1B	114.4 (11)	C5—C4—H4	120.0
H1A—N1—H1B	109.9 (15)	C3—C4—H4	120.0
B1—O1—H1′	112.2 (13)	C4—C5—C6	120.73 (11)
B1—O2—H2′	119.1 (12)	C4—C5—H5	119.6
C2—C1—C6	118.08 (11)	C6—C5—H5	119.6
C2—C1—B1	119.71 (11)	C5—C6—C1	120.52 (11)
C6—C1—B1	122.19 (11)	C5—C6—H6	119.7
C3—C2—C1	121.72 (11)	C1—C6—H6	119.7
C3—C2—H2	119.1	H31A—O31—H31B	107.4 (18)
C1—C2—H2	119.1		
O2—B1—C1—C2	−178.77 (11)	C1—C2—C3—N1	−173.67 (11)
O1—B1—C1—C2	−0.23 (17)	C2—C3—C4—C5	−0.90 (18)
O2—B1—C1—C6	−0.64 (19)	N1—C3—C4—C5	173.96 (11)
O1—B1—C1—C6	177.90 (11)	C3—C4—C5—C6	0.28 (18)
C6—C1—C2—C3	−0.73 (18)	C4—C5—C6—C1	0.13 (18)

B1—C1—C2—C3	177.47 (11)	C2—C1—C6—C5	0.08 (18)
C1—C2—C3—C4	1.14 (18)	B1—C1—C6—C5	−178.07 (11)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1′···O2^{i}	0.84 (1)	1.92 (1)	2.7583 (13)	174 (2)
N1—H1*A*···O31^{ii}	0.86 (1)	2.21 (1)	3.0661 (15)	177 (1)
N1—H1*B*···O1^{iii}	0.86 (1)	2.43 (1)	3.1854 (15)	147 (1)
O2—H2′···O31	0.84 (1)	1.91 (1)	2.7159 (13)	161 (2)
O31—H31*A*···N1^{iv}	0.84 (1)	2.07 (1)	2.9040 (15)	173 (2)
O31—H31*B*···O1^{v}	0.84 (1)	2.05 (1)	2.8810 (13)	170 (2)

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