organic compounds

2-Ureido-1,3-thiazol-3-ium dihydrogen phosphate

Kateryna Gubina,* Iuliia Shatrava, Vladimir Ovchynnikov and Vladimir Amirkhanov

National Taras Shevchenko University, Department of Chemistry, Volodymyrska Street 64, 01033 Kyiv, Ukraine

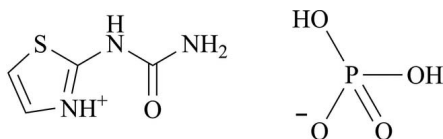Correspondence e-mail: katlig@univ.kiev.ua

The title compound, $C_4H_6N_3OS^+ \cdot H_2PO_4^-$, (I), was obtained as a result of hydrolysis of [(1,3-thiazol-2-ylamino)carbonyl]-phosphoramidic acid, (II), in water. X-ray analysis has shown that the N—P bond in (II) breaks, leading to the formation of the substituted carbamide (I). This compound exists as an internal salt. The unit cell consists of a urea cation and an anion of $H_2PO_4^-$. Protonation of the N atom of the heterocyclic ring was confirmed by the location of the H atom in a difference Fourier map. The molecules of substituted urea are connected by O⋯O hydrogen bonds into unlimited planes. In turn, those planes are connected to each other via N—H⋯O hydrogen bonds with molecules of phosphoric acid, forming a three-dimensional polymer.

Related literature

For background to the chemistry of phosphorus–organic compounds, see: Ly & Woollins (1998). For details of the synthesis and properties of the [(1,3-thiazol-2-ylamino)-carbonyl]phosphoramidic acid, see: Kirsanov & Levchenko (1957); Smaliy *et al.*(2003). For structural analogues of phosphorylated carbacylamides and their properties, see: Amirkhanov *et al.* (1997). For a structural investigation of phosphortriamidic compounds, see: Ovchynnikov *et al.* (1997). For the synthesis of the aminothiazol-containing phosphor-triamides, see: Shatrava *et al.* (2009). For a description of the attractive interaction in thiazole compounds, see: Burling & Goldstein (1992); Angyan *et al.* (1987).

Experimental

Crystal data

$C_4H_6N_3OS^+ \cdot H_2PO_4^-$	V = 947.37 (19) Å^3
M_r = 241.16	Z = 4
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
a = 11.9038 (11) Å	μ = 0.51 mm^{-1}
b = 9.7936 (10) Å	T = 293 K
c = 8.1914 (12) Å	$0.30 \times 0.20 \times 0.20$ mm
β = 97.231 (9)°	

Data collection

Siemens SMART CCD area-detector diffractometer	2644 measured reflections
	2239 independent reflections
Absorption correction: empirical (using intensity measurements) (*SADABS*; Bruker, 1999)	1893 reflections with $I > 2\sigma(I)$
	R_{int} = 0.014
T_{min} = 0.861, T_{max} = 0.904	

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.038	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2)$ = 0.109	
S = 1.05	
2239 reflections	$\Delta\rho_{max}$ = 0.58 e Å^{-3}
150 parameters	$\Delta\rho_{min}$ = −0.43 e Å^{-3}

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N2—H2⋯O2	0.86	1.93	2.697 (2)	148
N3—H3⋯O3	0.80 (3)	1.91 (3)	2.710 (2)	174 (3)
N1—H1A⋯O1^i	0.87 (3)	2.09 (3)	2.898 (2)	155 (2)
N1—H1B⋯O5^{ii}	0.82 (3)	2.20 (3)	3.007 (2)	170 (3)
O5—H5⋯O2^{iii}	0.81 (4)	1.77 (4)	2.546 (2)	162 (4)
O4—H4⋯O3^{iv}	0.80 (4)	1.82 (4)	2.613 (2)	170 (4)

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

Data collection: *SMART-NT* (Bruker, 1999); cell refinement: *SAINT-NT* (Bruker, 1999); data reduction: *SAINT-NT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *XP* within *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: DN2693).

References

Amirkhanov, V. M., Ovchynnikov, V. A., Glowiak, T. & Kozlowski, H. (1997). *Z. Naturforsch. Teil B*, **52**, 1331–1336.

Angyan, J. G., Poirier, R. A., Kucsman, A. & Csizmadia, I. G. (1987). *J. Am. Chem. Soc.* **109**, 2237–2245.

Bruker (1999). *SMART-NT, SAINT-Plus-NT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.

Burling, F. T. & Goldstein, B. M. (1992). *J. Am. Chem. Soc.* **114**, 2313–2320.

Kirsanov, A. & Levchenko, V. (1957). *Zh. Obshch. Khim.* **27**, 2313–2320.

Ly, T. Q. & Woollins, J. D. (1998). *Coord. Chem. Rev.* **176**, 451–481.

Ovchynnikov, V. A., Amirkhanov, V. M., Timoshenko, T. P., Glowiak, T. & Kozlowski, H. (1997). *Z. Naturforsch. Teil B*, **53**, 481–484.

Shatrava, I., Ovchynnikov, O., Sliva, T., Amirkhanov, V. & Skopenko, V. (2009). *Zh. Dopov. Nac. Akad. Nauk*, **5**, 179–185.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Smaliy, R. V., Chaikovskay, A. A., Pinchyk, A. M. & Tolmachev, A. A. (2003). *Synthesis*, **16**, 2525–2529.

supporting information

2-Ureido-1,3-thiazol-3-ium dihydrogen phosphate

Kateryna Gubina, Iuliia Shatrava, Vladimir Ovchynnikov and Vladimir Amirkhanov

S1. Comment

The compound *N*-1,3-thiazol-2-yl-urea phosphate (I) can be synthesized by hydrolyzation of the [(1,3-thiazol-2-ylamino)-carbonyl]phosphoramidic acid (II) in the water solution by heating (Scheme 1). The crystal structure investigation shows that the break up of N—P bond in [(1,3-thiazol-2-ylamino)carbonyl]phosphoramidic leads to the forming of substituted carbamide (Fig.1).

The proton of the phosphoric acid locates at the nitrogen atom of the heterocyclic ring from difference-Fourier map. The molecules of substituted urea connected by hydrogen bonds O(4)H(4)O(3) and O(5)H(5)O(2) into unlimited planes (Table 1). In turn those planes are connected to each other forming three-dimensional polymer *via* hydrogen bonds with molecules of phosphoric acid: N(3)H(3)O(3), N(2)H(2)O(2) and N(1)H(1 A)O(1), N(1)H(1B)O(5) (Table 1, Fig.2). The interaction of nonbonded S and O atoms can be described as attractive (Angyan, *et al.*, 1987). In the molecule the S O nonbonded distances are significantly shorter (2.653 Å) than the sum of the corresponding van der Waals radii (3.25 Å).

S2. Experimental

The synthesis of [(1,3-thiazol-2-ylamino)carbonyl]phosphoramidic acid (II) was carried out according to the method described by Kirsanov (Kirsanov & Levchenko, 1957). The compound *N*-1,3-thiazol-2-yl-urea phosphate (I) was obtained due to hydrolyzation of (II) in the water solution (Smaliy *et al.*, 2003). The crystals (I) suitable for X-ray analysis were obtained by heating of [(1,3-thiazol-2-ylamino)carbonyl]phosphoramidic acid in water and evaporating the solvent at room temperature for about 2 days.

S3. Refinement

H2,H3A and H4A atoms were included in the refinement in the riding motion approximation but with refined isotropic thermal parameter. Other hydrogen atoms were refine isotropically.
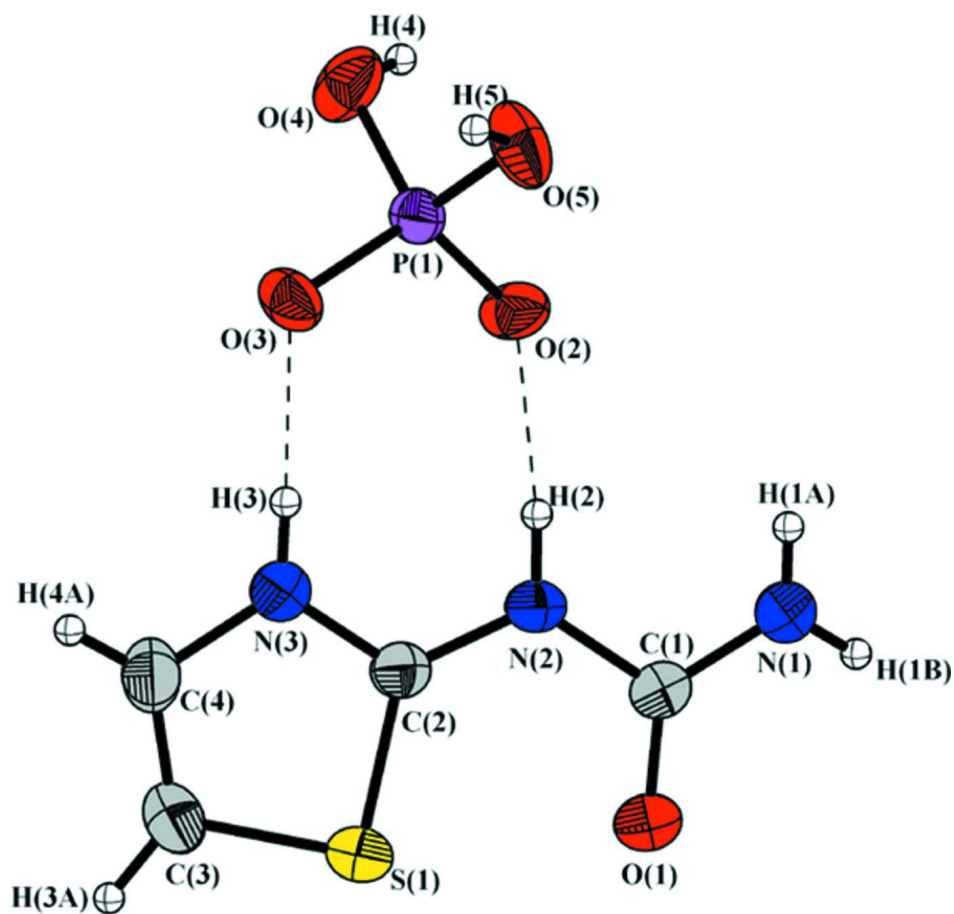
Figure 1

View of *N*-1,3-thiazol-2-yl-urea phosphate with the atom labeling scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms are represented as small spheres of arbitrary radii. Hydrogen bonds are shown as dashed lines.
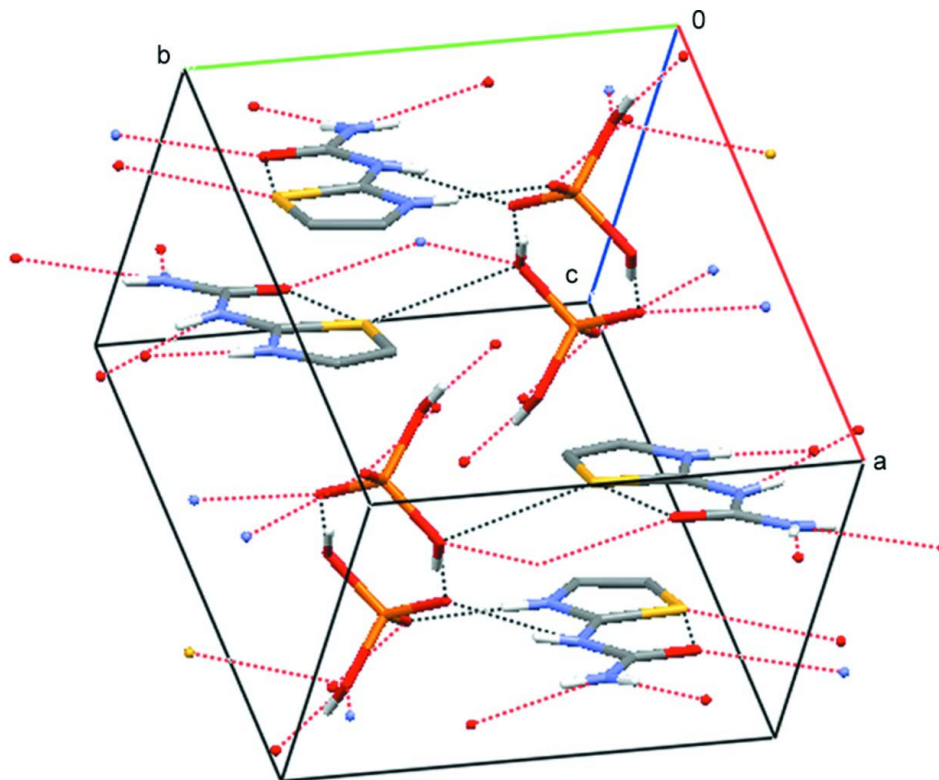
Figure 2

three-dimensional-view of the *N*-1,3-thiazol-2-yl-urea phosphate.
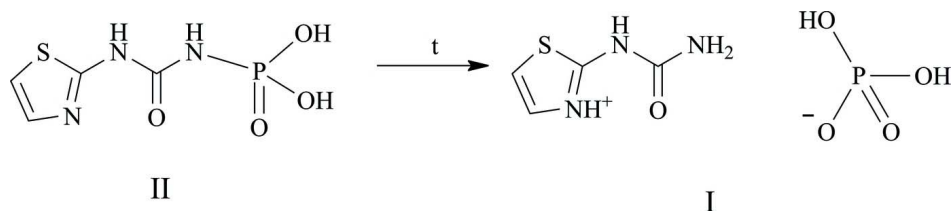
Figure 3

The formation of the title compound.

2-ureido-1,3-thiazol-3-ium dihydrogen phosphate

Crystal data

$C_4H_6N_3OS^+ \cdot H_2PO_4^-$	$F(000) = 496$
$M_r = 241.16$	$D_x = 1.691$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 2646 reflections
$a = 11.9038$ (11) Å	$\theta = 1.7–28.0°$
$b = 9.7936$ (10) Å	$\mu = 0.51$ mm^{-1}
$c = 8.1914$ (12) Å	$T = 293$ K
$\beta = 97.231$ (9)°	Block, colourless
$V = 947.37$ (19) Å^3	$0.30 \times 0.20 \times 0.20$ mm
$Z = 4$	

Data collection

Siemens SMART CCD area-detector diffractometer	2644 measured reflections
Radiation source: fine-focus sealed tube	2239 independent reflections
Graphite monochromator	1893 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.014$
Absorption correction: empirical (using intensity measurements) (*SADABS*; Bruker, 1999)	$\theta_{max} = 28.0°$, $\theta_{min} = 1.7°$
	$h = -14 \rightarrow 15$
	$k = -12 \rightarrow 10$
	$l = -10 \rightarrow 10$
$T_{min} = 0.861$, $T_{max} = 0.904$	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.038$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.109$	
$S = 1.05$	H atoms treated by a mixture of independent and constrained refinement
2239 reflections	
150 parameters	$w = 1/[\sigma^2(F_o^2) + (0.0666P)^2 + 0.4134P]$ where $P = (F_o^2 + 2F_c^2)/3$
0 restraints	
Primary atom site location: structure-invariant direct methods	$(\Delta/\sigma)_{max} = 0.001$
	$\Delta\rho_{max} = 0.58$ e Å^{-3}
	$\Delta\rho_{min} = -0.43$ 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}
S1	0.76064 (4)	0.11536 (5)	0.89426 (7)	0.03929 (16)
O1	0.93971 (13)	0.18350 (15)	0.7497 (2)	0.0487 (4)
N1	1.00646 (16)	0.3959 (2)	0.7104 (3)	0.0450 (4)
C1	0.93508 (16)	0.30721 (18)	0.7630 (2)	0.0343 (4)
P1	0.71692 (4)	0.70375 (4)	0.89068 (5)	0.02801 (15)
N2	0.84692 (14)	0.36706 (16)	0.8367 (2)	0.0341 (3)
H2	0.8438	0.4545	0.8448	0.061 (8)*
C2	0.76722 (15)	0.29001 (18)	0.8948 (2)	0.0302 (4)
O2	0.77229 (12)	0.62295 (13)	0.76649 (16)	0.0368 (3)
N3	0.68142 (13)	0.34568 (18)	0.9603 (2)	0.0341 (3)
C3	0.63845 (18)	0.1230 (2)	0.9884 (3)	0.0456 (5)
H3A	0.5988	0.0467	1.0173	0.076 (9)*
O3	0.66290 (12)	0.61762 (13)	1.01208 (16)	0.0357 (3)
C4	0.60814 (17)	0.2511 (2)	1.0144 (3)	0.0414 (4)
H4A	0.5446	0.2745	1.0636	0.062 (8)*

O4	0.62286 (13)	0.79913 (17)	0.80225 (19)	0.0460 (4)
O5	0.80967 (14)	0.79873 (16)	0.98184 (19)	0.0457 (4)
H1A	1.001 (2)	0.483 (3)	0.731 (3)	0.042 (6)*
H1B	1.054 (3)	0.359 (3)	0.660 (3)	0.053 (8)*
H3	0.676 (2)	0.427 (3)	0.969 (3)	0.041 (6)*
H4	0.633 (3)	0.815 (4)	0.710 (5)	0.080 (11)*
H5	0.800 (3)	0.806 (4)	1.077 (4)	0.077 (11)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0400 (3)	0.0256 (2)	0.0531 (3)	0.00031 (17)	0.0089 (2)	0.00314 (18)
O1	0.0451 (8)	0.0277 (7)	0.0769 (11)	0.0041 (6)	0.0221 (8)	−0.0017 (7)
N1	0.0420 (9)	0.0316 (9)	0.0659 (12)	0.0008 (7)	0.0243 (9)	−0.0012 (8)
C1	0.0320 (9)	0.0295 (9)	0.0424 (10)	0.0045 (7)	0.0085 (7)	0.0015 (7)
P1	0.0337 (3)	0.0256 (3)	0.0268 (2)	0.00013 (16)	0.01202 (17)	0.00036 (15)
N2	0.0372 (8)	0.0241 (7)	0.0433 (8)	0.0027 (6)	0.0138 (7)	0.0017 (6)
C2	0.0316 (8)	0.0272 (9)	0.0320 (8)	0.0023 (6)	0.0052 (7)	0.0016 (6)
O2	0.0511 (8)	0.0299 (7)	0.0328 (7)	0.0094 (5)	0.0179 (6)	0.0025 (5)
N3	0.0340 (8)	0.0306 (8)	0.0390 (8)	0.0012 (6)	0.0099 (6)	0.0002 (6)
C3	0.0366 (10)	0.0407 (11)	0.0605 (13)	−0.0074 (8)	0.0107 (9)	0.0076 (9)
O3	0.0473 (8)	0.0300 (7)	0.0328 (6)	−0.0065 (5)	0.0171 (6)	−0.0001 (5)
C4	0.0321 (9)	0.0472 (12)	0.0461 (11)	−0.0024 (8)	0.0102 (8)	0.0043 (9)
O4	0.0461 (8)	0.0575 (10)	0.0377 (8)	0.0196 (7)	0.0185 (6)	0.0120 (6)
O5	0.0513 (9)	0.0550 (10)	0.0337 (7)	−0.0228 (7)	0.0174 (6)	−0.0071 (6)

Geometric parameters (Å, º)

S1—C2	1.7122 (18)	N2—C2	1.345 (2)
S1—C3	1.732 (2)	N2—H2	0.8600
O1—C1	1.218 (2)	C2—N3	1.329 (2)
N1—C1	1.324 (3)	N3—C4	1.383 (3)
N1—H1A	0.87 (3)	N3—H3	0.80 (3)
N1—H1B	0.82 (3)	C3—C4	1.330 (3)
C1—N2	1.403 (2)	C3—H3A	0.9300
P1—O2	1.5048 (12)	C4—H4A	0.9300
P1—O3	1.5083 (13)	O4—H4	0.80 (4)
P1—O5	1.5602 (16)	O5—H5	0.81 (4)
P1—O4	1.5642 (15)		
C2—S1—C3	89.80 (10)	C1—N2—H2	119.4
C1—N1—H1A	121.0 (16)	N3—C2—N2	121.65 (17)
C1—N1—H1B	113 (2)	N3—C2—S1	111.93 (14)
H1A—N1—H1B	126 (3)	N2—C2—S1	126.41 (14)
O1—C1—N1	125.79 (19)	C2—N3—C4	113.74 (18)
O1—C1—N2	119.90 (17)	C2—N3—H3	120.7 (19)
N1—C1—N2	114.29 (17)	C4—N3—H3	125.5 (18)
O2—P1—O3	114.27 (8)	C4—C3—S1	111.84 (15)

O2—P1—O5	107.05 (9)	C4—C3—H3A	124.1
O3—P1—O5	110.65 (8)	S1—C3—H3A	124.1
O2—P1—O4	110.48 (8)	C3—C4—N3	112.69 (18)
O3—P1—O4	107.43 (8)	C3—C4—H4A	123.7
O5—P1—O4	106.73 (10)	N3—C4—H4A	123.7
C2—N2—C1	121.12 (16)	P1—O4—H4	112 (3)
C2—N2—H2	119.4	P1—O5—H5	110 (3)
O1—C1—N2—C2	0.6 (3)	N2—C2—N3—C4	−179.63 (17)
N1—C1—N2—C2	179.39 (19)	S1—C2—N3—C4	0.8 (2)
C1—N2—C2—N3	−177.96 (17)	C2—S1—C3—C4	0.44 (19)
C1—N2—C2—S1	1.6 (3)	S1—C3—C4—N3	−0.1 (3)
C3—S1—C2—N3	−0.69 (15)	C2—N3—C4—C3	−0.4 (3)
C3—S1—C2—N2	179.74 (18)		

Hydrogen-bond geometry (Å, º)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N2—H2⋯O2	0.86	1.93	2.697 (2)	148
N3—H3⋯O3	0.80 (3)	1.91 (3)	2.710 (2)	174 (3)
N1—H1A⋯O1[i]	0.87 (3)	2.09 (3)	2.898 (2)	155 (2)
N1—H1B⋯O5[ii]	0.82 (3)	2.20 (3)	3.007 (2)	170 (3)
O5—H5⋯O2[iii]	0.81 (4)	1.77 (4)	2.546 (2)	162 (4)
O4—H4⋯O3[iv]	0.80 (4)	1.82 (4)	2.613 (2)	170 (4)

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