

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

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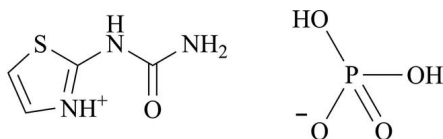
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Key indicators: single-crystal X-ray study;  $T = 293$  K; mean  $\sigma(\text{C}-\text{C}) = 0.003$  Å;  $R$  factor = 0.038;  $wR$  factor = 0.109; data-to-parameter ratio = 14.9.

The title compound,  $\text{C}_4\text{H}_6\text{N}_3\text{OS}^+\cdot\text{H}_2\text{PO}_4^-$ , (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  $\text{H}_2\text{PO}_4^-$ . 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  $\text{O}\cdots\text{O}$  hydrogen bonds into unlimited planes. In turn, those planes are connected to each other *via* N–H $\cdots\text{O}$  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 phosphortriamides, 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

$\text{C}_4\text{H}_6\text{N}_3\text{OS}^+\cdot\text{H}_2\text{PO}_4^-$   
 $M_r = 241.16$   
 Monoclinic,  $P2_1/c$   
 $a = 11.9038$  (11) Å  
 $b = 9.7936$  (10) Å  
 $c = 8.1914$  (12) Å  
 $\beta = 97.231$  (9)°

$V = 947.37$  (19) Å<sup>3</sup>  
 $Z = 4$   
 Mo  $K\alpha$  radiation  
 $\mu = 0.51$  mm<sup>-1</sup>  
 $T = 293$  K  
 $0.30 \times 0.20 \times 0.20$  mm

#### Data collection

Siemens SMART CCD area-detector diffractometer  
 Absorption correction: empirical (using intensity measurements) (SADABS; Bruker, 1999)  
 $T_{\min} = 0.861$ ,  $T_{\max} = 0.904$

2644 measured reflections  
 2239 independent reflections  
 1893 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.014$

#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.038$   
 $wR(F^2) = 0.109$   
 $S = 1.05$   
 2239 reflections  
 150 parameters

H atoms treated by a mixture of independent and constrained refinement  
 $\Delta\rho_{\text{max}} = 0.58$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.43$  e Å<sup>-3</sup>

**Table 1**

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N2–H2 $\cdots$ O2	0.86	1.93	2.697 (2)	148
N3–H3 $\cdots$ O3	0.80 (3)	1.91 (3)	2.710 (2)	174 (3)
N1–H1A $\cdots$ O1 <sup>i</sup>	0.87 (3)	2.09 (3)	2.898 (2)	155 (2)
N1–H1B $\cdots$ O5 <sup>ii</sup>	0.82 (3)	2.20 (3)	3.007 (2)	170 (3)
O5–H5 $\cdots$ O2 <sup>iii</sup>	0.81 (4)	1.77 (4)	2.546 (2)	162 (4)
O4–H4 $\cdots$ O3 <sup>iv</sup>	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

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**supplementary materials**

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

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### 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(1A)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).

### 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.

### 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.

### Figures

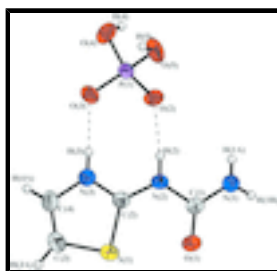


Fig. 1. View of *N*-1,3-thiazol-2-yl-urea phosphate with the atom labeling scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms are represented as small spheres of arbitrary radii. Hydrogen bonds are shown as dashed lines.

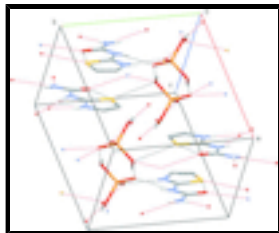


Fig. 2. three-dimensional-view of the *N*-1,3-thiazol-2-yl-urea phosphate.



Fig. 3. The formation of the title compound.

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

### Crystal data



$$M_r = 241.16$$

Monoclinic,  $P2_1/c$

Hall symbol: -P 2ybc

$$a = 11.9038 (11) \text{ \AA}$$

$$b = 9.7936 (10) \text{ \AA}$$

$$c = 8.1914 (12) \text{ \AA}$$

$$\beta = 97.231 (9)^\circ$$

$$V = 947.37 (19) \text{ \AA}^3$$

$$Z = 4$$

$$F(000) = 496$$

$$D_x = 1.691 \text{ Mg m}^{-3}$$

Mo  $K\alpha$  radiation,  $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 2646 reflections

$$\theta = 1.7\text{--}28.0^\circ$$

$$\mu = 0.51 \text{ mm}^{-1}$$

$$T = 293 \text{ K}$$

Block, colourless

$$0.30 \times 0.20 \times 0.20 \text{ mm}$$

### Data collection

Siemens SMART CCD area-detector diffractometer

Radiation source: fine-focus sealed tube graphite

$\omega$  scans

Absorption correction: empirical (using intensity measurements)

(*SADABS*; Bruker, 1999)

$$T_{\min} = 0.861, T_{\max} = 0.904$$

2644 measured reflections

2239 independent reflections

1893 reflections with  $I > 2\sigma(I)$

$$R_{\text{int}} = 0.014$$

$$\theta_{\max} = 28.0^\circ, \theta_{\min} = 1.7^\circ$$

$$h = -14 \rightarrow 15$$

$$k = -12 \rightarrow 10$$

$$l = -10 \rightarrow 10$$

### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$$R[F^2 > 2\sigma(F^2)] = 0.038$$

$$wR(F^2) = 0.109$$

$$S = 1.05$$

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

$$w = 1/[\sigma^2(F_o^2) + (0.0666P)^2 + 0.4134P]$$

2239 reflections  
150 parameters  
0 restraints

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

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

$$\Delta\rho_{\max} = 0.58 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.43 \text{ e } \text{\AA}^{-3}$$

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
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 ( $\text{\AA}^2$ )*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
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)

## supplementary materials

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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, °)*

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, °)

<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>
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 <sup>i</sup>	0.87 (3)	2.09 (3)	2.898 (2)	155 (2)
N1—H1B···O5 <sup>ii</sup>	0.82 (3)	2.20 (3)	3.007 (2)	170 (3)
O5—H5···O2 <sup>iii</sup>	0.81 (4)	1.77 (4)	2.546 (2)	162 (4)
O4—H4···O3 <sup>iv</sup>	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)  $x, -y+3/2, z-1/2$ .

Fig. 1

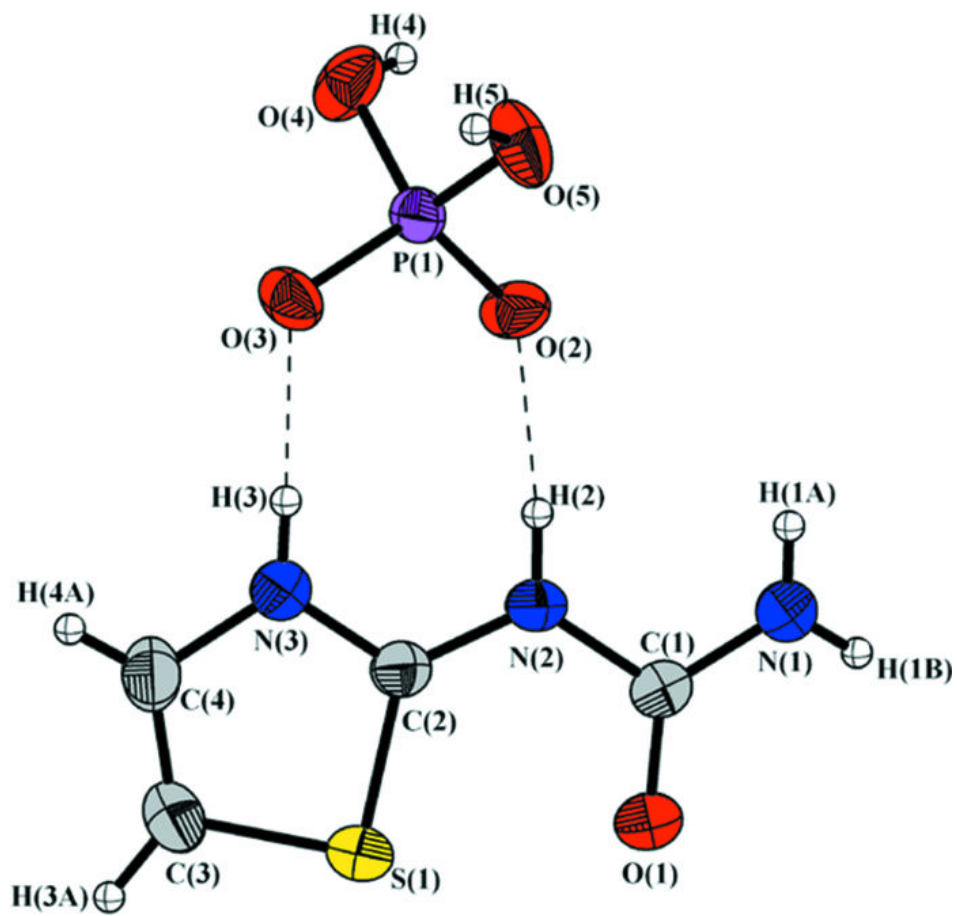




Fig. 2

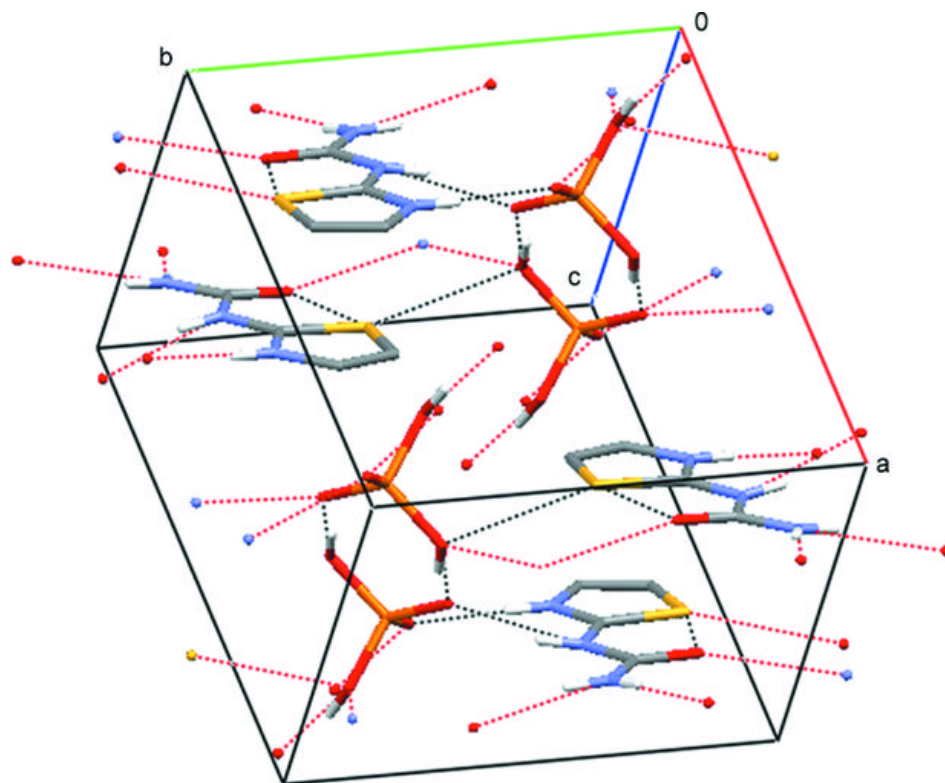


Fig. 3

