organic compounds

2-Amino-1,3-thiazolium dihydrogen phosphate

Irena Matulková,[a,b]* Jaroslav Cihelka,[b] Ivan Němec,[a] Michaela Pojarová[b] and Michal Dušek[b]

[a]Department of Inorganic Chemistry, Faculty of Science, Charles University in Prague, Hlavova 2030, 128 40 Prague 2, Czech Republic, and [b]Institute of Physics of the ASCR, Na Slovance 2, 182 21 Prague 8, Czech Republic
Correspondence e-mail: irena.mat@atlas.cz

In the title compound, $C_3H_5N_2S^+\cdot H_2PO_4^-$, the dihydrogen phosphate anions form infinite chains along [001] via short O—H···O hydrogen bonds. The 2-aminothiazolium cations interconnect these chains into a three-dimensional network by short linear or bifurcated N—H···O and weak C—H···O hydrogen bonds.

Related literature

For metal complexes of 2-aminothiazole and its derivatives used in medicine, see: De *et al.* (2008); Aridoss *et al.* (2009); Cukurovali *et al.* (2006); Franklin *et al.* (2008); Li *et al.* (2009); Alexandru *et al.* (2010); Mura *et al.* (2005). For the use of 2-aminothiazole in the decontamination of aqueous media or ethanol fuel, see: Cristante *et al.* (2006, 2007); Takeuchi *et al.* (2007). For uses of 2-aminothiazole and its derivatives as anticorrosive films, see: Ciftci *et al.* (2011); Solmaz (2011). For non-linear optical properties and for structural properties of closely related compounds, see: Yesilel *et al.* (2008); Matulková *et al.* (2007, 2008, 2011a,b).
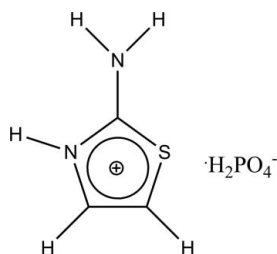
Experimental

Crystal data

$C_3H_5N_2S^+\cdot H_2PO_4^-$
M_r = 198.14
Monoclinic, $P2_1/c$
a = 9.7581 (2) Å
b = 9.8826 (2) Å
c = 8.2794 (1) Å
β = 90.680 (2)°
V = 798.37 (2) Å^3

Z = 4
Cu $K\alpha$ radiation
μ = 5.35 mm^{-1}
T = 120 K
0.47 × 0.17 × 0.13 mm

Data collection

Agilent Xcalibur Atlas Gemini ultra diffractometer
Absorption correction: multi-scan (*CrysAlis PRO*; Agilent, 2010)
  T_{min} = 0.453, T_{max} = 1.000

7670 measured reflections
1419 independent reflections
1389 reflections with $I > 2\sigma(I)$
R_{int} = 0.025

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.027
$wR(F^2)$ = 0.070
S = 1.07
1419 reflections

100 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.30 e Å^{-3}
$\Delta\rho_{min}$ = -0.37 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1N1···O2^i	0.87	1.96	2.815 (2)	167
N1—H2N1···O1^{ii}	0.80	2.31	3.076 (2)	162
N1—H2N1···O2^{ii}	0.80	2.56	3.194 (2)	137
N2—H1N2···O3^i	0.99	1.73	2.726 (2)	175
O1—H1O1···O2^{iii}	0.90	1.61	2.504 (2)	176
O4—H1O4···O3^{iv}	0.94	1.65	2.593 (2)	179
C2—H1C2···O4^v	0.93	2.40	3.268 (2)	155

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

Data collection: *CrysAlis PRO* (Agilent, 2010); 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: *PLATON* (Spek, 2003); software used to prepare material for publication: *publCIF* (Westrip, 2010).

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supplementary materials

2-Amino-1,3-thiazolium dihydrogen phosphate

I. Matulková, J. Cihelka, I. Nemec, M. Pojarová and M. Dusek

Comment

2-Aminothiazole and its derivatives have been investigated as potential compounds for the modification of TiO_2 or SiO_2 particles used for the sorption and photocatalytic reduction of Hg(II) (Cristante *et al.*, 2006) or phenol (Cristante *et al.*, 2007) in aqueous solutions. 2-Aminothiazole can be also used for electrode modification (Ciftci *et al.*, 2011; Solmaz, 2011) or for the detection of metal impurities (Takeuchi *et al.*, 2007) in ethanol fuel.

Metal complexes of 2-aminothiazole and its derivatives have been studied for treatment of Alzheimers disease (Li *et al.*, 2009), antitumor activity (Alexandru *et al.*, 2010), and activity against leukemia (Mura *et al.*, 2005). Thiazole derivatives have been used as antioxidants (De *et al.*, 2008), antibacterial drugs (Aridoss *et al.*, 2009) and fungicides (Cukurovali *et al.*, 2006). Anti-inflammatory, analgesic and antipyretic activities were observed for thiazolyl and benzothiazolyl derivatives (Franklin *et al.*, 2008).

Only one salt, bis(2-aminothiazolium) squarate dihydrate (Yesilel *et al.*, 2008), was studied in detail for the extensive system of hydrogen bonds, which are very attractive not only in the biological and biochemical processes but also in the field of material and supramolecular chemistry.

The title salt was prepared during the research motivated by the study of salts or cocrystals of the highly related aminotriazoles (Matulková *et al.*, 2011*a*, 2008, 2007) and 2-aminothiazole (Matulková *et al.*, 2011*b*), while searching for materials with potential non-linear optical properties. Unfortunately, the title salt, 2-aminothiazolium dihydrogen phosphate (Fig. 1), crystallizes in the monoclinic system in the centrosymmetric space group $P2_1/c$, which excludes the existence of the second order non-linear optical properties. The crystal structure of the title compound is based on chains of anions interconnected *via* two O—H···O hydrogen bonds with donor-acceptor distances 2.504 (2) and 2.596 (2) Å. Chains are interconnected by 2-aminothiazolium(1+) cations *via* N—H···O (2.728 (2)–3.202 (3) Å) and weak C—H···O (3.271 (3) Å) hydrogen bond interactions into a three-dimensional network. Each cation interacts with three anionic chains by means of two linear hydrogen bonds towards one of the chains, one linear hydrogen bond to another chain and one bifurcated hydrogen bond to the third chain (Fig. 3). The anionic chains are oriented along the axis *c* (see Fig. 2).

Experimental

Crystals of the title compound were obtained from a solution of 1.0 g of 2-aminothiazole (97%, Aldrich) and 0.67 ml of phosphoric acid (85%, Lachema) in 200 ml of water. The solution was left to crystallize at room temperature for several weeks. The colourless crystals obtained were filtered off, washed with methanol and dried in vacuum desiccator over KOH.

supplementary materials

Refinement

H atoms attached to C atoms were calculated in geometrically idealized positions, Csp^2 - H = 0.93 Å. The positions of H atoms attached to O and N atoms were localized in difference Fourier maps. All hydrogen atoms were constrained to ride on their parent atoms during refinement, with $U_{iso}(H) = 1.2\ U_{eq}$(pivot atom).
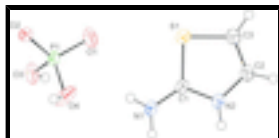
Figures

Fig. 1. The molecular structure of 2-aminothiazolium dihydrogen phosphate. Displacement ellipsoids are drawn at the 50% probability level.
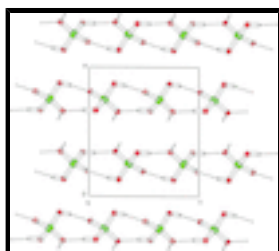

Fig. 2. Packing scheme of the anions in the crystals of 2-aminothiazolium dihydrogen phosphate (projection to *ac* plane). Dashed lines indicate the hydrogen bonds.
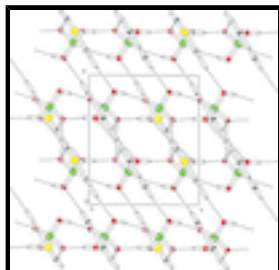

Fig. 3. Packing scheme of the structure of 2-aminothiazolium dihydrogen phosphate (projection to *ac* plane). Hydrogen bonds are indicated by dashed lines.

2-Amino-1,3-thiazolium dihydrogen phosphate

Crystal data
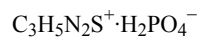
$C_3H_5N_2S^+ \cdot H_2PO_4^-$	$F(000) = 408$
$M_r = 198.14$	$D_x = 1.648$ Mg m^{-3}
Monoclinic, $P2_1/c$	Cu $K\alpha$ radiation, $\lambda = 1.5418$ Å
Hall symbol: -P 2ybc	Cell parameters from 6931 reflections
$a = 9.7581\ (2)$ Å	$\theta = 4.5–66.8°$
$b = 9.8826\ (2)$ Å	$\mu = 5.35$ mm^{-1}
$c = 8.2794\ (1)$ Å	$T = 120$ K
$\beta = 90.680\ (2)°$	Plate, colourless
$V = 798.37\ (2)$ Å^3	$0.47 \times 0.17 \times 0.13$ mm
$Z = 4$	

Data collection

Agilent Xcalibur Atlas Gemini ultra diffractometer	1419 independent reflections
Radiation source: Enhance Ultra (Cu) X-ray Source mirror	1389 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.025$
Detector resolution: 10.3874 pixels mm^{-1}	$\theta_{max} = 66.9°$, $\theta_{min} = 4.5°$
Rotation method data acquisition using ω scans	$h = -11 \rightarrow 11$
Absorption correction: multi-scan (*CrysAlis PRO*; Agilent, 2010)	$k = -11 \rightarrow 11$
$T_{min} = 0.453$, $T_{max} = 1.000$	$l = -9 \rightarrow 7$
7670 measured reflections	

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.027$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.070$	H-atom parameters constrained
$S = 1.07$	$w = 1/[\sigma^2(F_o^2) + (0.0339P)^2 + 0.5451P]$ where $P = (F_o^2 + 2F_c^2)/3$
1419 reflections	$(\Delta/\sigma)_{max} = 0.001$
100 parameters	$\Delta\rho_{max} = 0.30$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.37$ e Å^{-3}

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. The hydrogen atoms were be localized from the difference Fourier map. Despite of that,all hydrogen atoms connected to C were constrained to ideal positions. The distance in N—H and O—H groups were left unrestrained. The isotropic temperature parameters of hydrogen atoms were calculated as $1.2*U_{eq}$ of the parent atom.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($Å^2$)

	x	y	z	$U_{iso}*/U_{eq}$
C1	0.66442 (17)	0.80237 (17)	0.1326 (2)	0.0234 (4)
C2	0.85753 (17)	0.75229 (19)	−0.0086 (2)	0.0283 (4)
H1C2	0.9367	0.7716	−0.0657	0.034*

C3	0.81429 (18)	0.62710 (18)	0.0206 (2)	0.0301 (4)
H1C3	0.8591	0.5492	−0.0132	0.036*
N1	0.57066 (15)	0.87839 (15)	0.20091 (19)	0.0303 (4)
H1N1	0.5829	0.9648	0.2168	0.036*
H2N1	0.5099	0.8487	0.2540	0.036*
N2	0.77265 (14)	0.85134 (15)	0.05485 (17)	0.0237 (3)
H1N2	0.7837	0.9509	0.0454	0.028*
O1	0.66404 (15)	0.33219 (15)	0.06047 (15)	0.0400 (4)
H1O1	0.6636	0.3367	−0.0481	0.048*
O2	0.65458 (14)	0.14664 (14)	0.25914 (15)	0.0338 (3)
O3	0.80601 (12)	0.12283 (11)	0.01267 (14)	0.0243 (3)
O4	0.87030 (12)	0.28418 (13)	0.23071 (15)	0.0301 (3)
H1O4	0.8469	0.3189	0.3326	0.036*
P1	0.74805 (4)	0.21447 (4)	0.14002 (5)	0.02120 (14)
S1	0.66311 (4)	0.62775 (4)	0.13014 (5)	0.02763 (15)

Atomic displacement parameters ($Å^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0219 (8)	0.0251 (9)	0.0234 (9)	−0.0034 (6)	0.0016 (6)	−0.0005 (6)
C2	0.0210 (8)	0.0331 (9)	0.0310 (9)	0.0010 (7)	0.0049 (7)	−0.0035 (8)
C3	0.0220 (9)	0.0288 (10)	0.0398 (10)	0.0024 (7)	0.0051 (7)	−0.0049 (7)
N1	0.0277 (8)	0.0262 (8)	0.0373 (9)	−0.0053 (6)	0.0157 (7)	−0.0039 (6)
N2	0.0216 (7)	0.0245 (7)	0.0250 (7)	−0.0023 (5)	0.0050 (5)	−0.0015 (6)
O1	0.0515 (9)	0.0436 (8)	0.0247 (7)	0.0265 (7)	−0.0028 (6)	−0.0091 (6)
O2	0.0347 (7)	0.0371 (7)	0.0300 (7)	−0.0138 (6)	0.0155 (5)	−0.0113 (6)
O3	0.0287 (6)	0.0216 (6)	0.0227 (6)	0.0031 (5)	0.0089 (5)	0.0001 (4)
O4	0.0228 (6)	0.0444 (8)	0.0231 (6)	−0.0071 (5)	0.0070 (5)	−0.0071 (5)
P1	0.0201 (2)	0.0230 (2)	0.0207 (2)	0.00071 (15)	0.00549 (16)	−0.00254 (15)
S1	0.0252 (2)	0.0228 (2)	0.0351 (3)	−0.00293 (15)	0.00515 (18)	−0.00053 (16)

Geometric parameters (Å, °)

C1—N1	1.317 (2)	N1—H2N1	0.7980
C1—N2	1.334 (2)	N2—H1N2	0.9934
C1—S1	1.726 (2)	O1—P1	1.564 (1)
C2—C3	1.330 (3)	O1—H1O1	0.8996
C2—N2	1.389 (2)	O2—P1	1.508 (1)
C2—H1C2	0.9300	O3—P1	1.505 (1)
C3—S1	1.741 (2)	O4—P1	1.562 (1)
C3—H1C3	0.9300	O4—H1O4	0.9413
N1—H1N1	0.8718		
N1—C1—N2	123.9 (2)	C1—N2—C2	113.9 (2)
N1—C1—S1	124.79 (13)	C1—N2—H1N2	119.0
N2—C1—S1	111.3 (2)	C2—N2—H1N2	127.1
C3—C2—N2	113.3 (2)	P1—O1—H1O1	117.0
C3—C2—H1C2	123.4	P1—O4—H1O4	113.5
N2—C2—H1C2	123.4	O3—P1—O2	115.19 (7)

C2—C3—S1	111.3 (1)	O3—P1—O4	108.11 (7)
C2—C3—H1C3	124.3	O2—P1—O4	110.24 (7)
S1—C3—H1C3	124.3	O3—P1—O1	110.61 (7)
C1—N1—H1N1	121.9	O2—P1—O1	106.73 (8)
C1—N1—H2N1	123.4	O4—P1—O1	105.54 (8)
H1N1—N1—H2N1	112.3	C1—S1—C3	90.21 (8)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1N1···O2[i]	0.87	1.96	2.815 (2)	167
N1—H2N1···O1[ii]	0.80	2.31	3.076 (2)	162
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C2—H1C2···O4[v]	0.93	2.40	3.268 (2)	155

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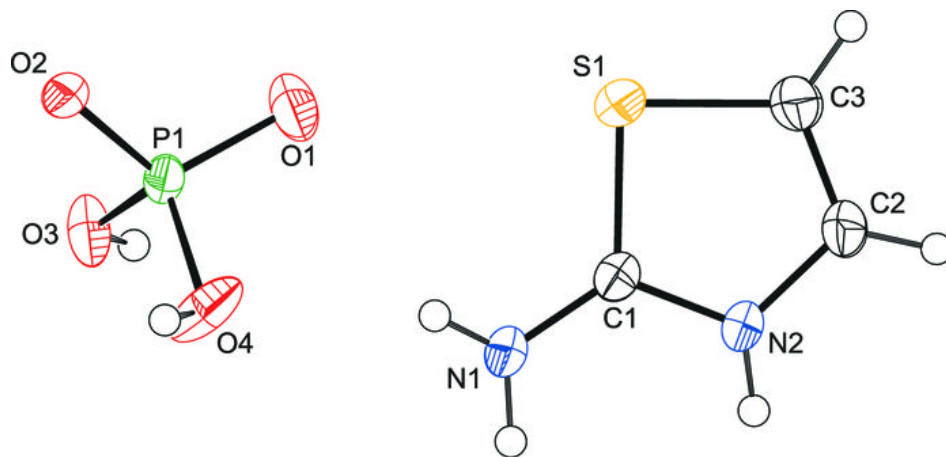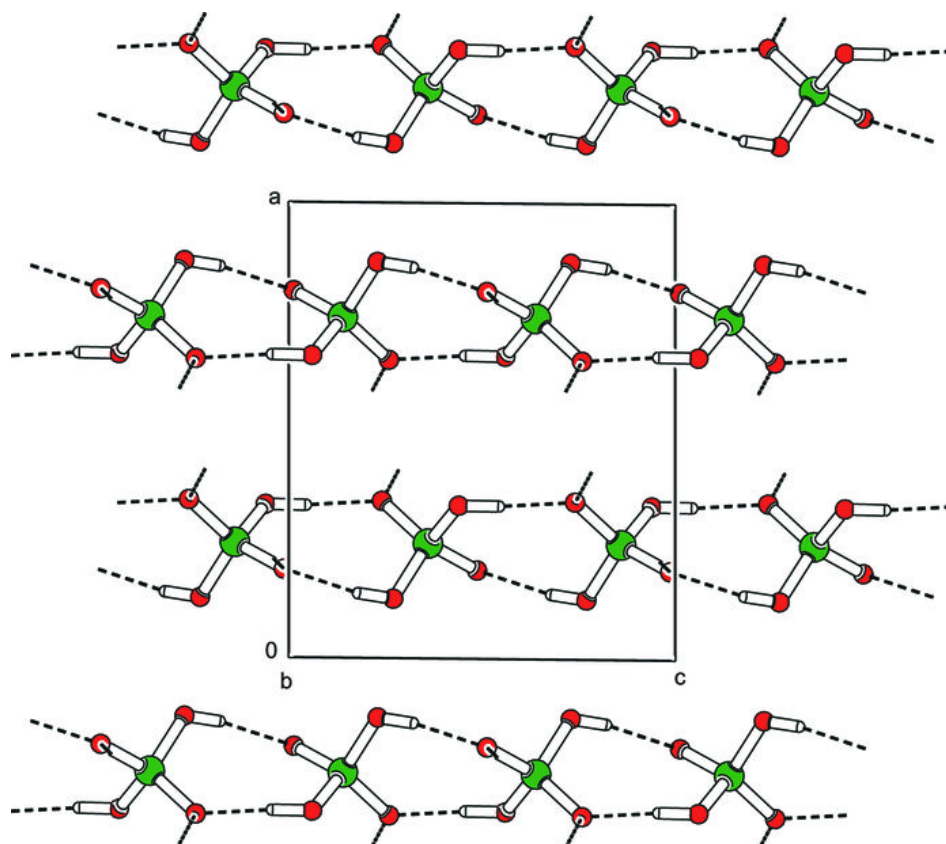
Fig. 1

Fig. 2

Fig. 3