Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Hydrogen-bonded networks in crystals of 1-(diaminomethylene)thiouron-1-ium perchlorate, hydrogen sulfate, dihydrogen phosphate and dihydrogen arsenate

Jan Janczak[a]* and Genivaldo Julio Perpétuo[b]

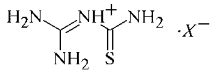
[a]Institute of Low Temperatures and Structures Research, Polish Academy of Sciences, PO Box 1410, 50-950 Wrocław, Poland, and [b]Departamento de Fisica, Instituto de Ciências Exatas e Biológicas, Universidade Federal de Ouro Preto, CEP 35.400-000 Ouro Preto, MG, Brazil
Correspondence e-mail: j.janczak@int.pan.wroc.pl

Received 10 April 2008
Accepted 7 May 2008
Online 21 May 2008

Crystals of the title compounds, namely 1-(diaminomethylene)-thiouron-1-ium perchlorate, $C_2H_7N_4S^+\cdot ClO_4^-$, 1-(diaminomethylene)thiouron-1-ium hydrogen sulfate, $C_2H_7N_4S^+\cdot HSO_4^-$, 1-(diaminomethylene)thiouron-1-ium dihydrogen phosphate, $C_2H_7N_4S^+\cdot H_2PO_4^-$, and its isomorphic relative 1-(diaminomethylene)thiouron-1-ium dihydrogen arsenate, $C_2H_7N_4S^+\cdot H_2AsO_4^-$, are built up from a nonplanar 1-(diaminomethylene)thiouron-1-ium cation and the respective anion linked together *via* N—H···O hydrogen bonds. Both arms of the cation are planar, but they are twisted with respect to one another around the central N atom. Ionic and extensive hydrogen-bonding interactions join oppositely charged units into layers in the perchlorate, double layers in the hydrogen sulfate, and a three-dimensional network in the dihydrogen phosphate and dihydrogen arsenate salts. This work demonstrates the usefulness of 1-(diaminomethylene)-thiourea in crystal engineering for the formation of supramolecular networks with acids.

Comment

1-(Diaminomethylene)thiourea and its imino tautomer, *i.e.* 2-imino-4-thiobiuret, are potentially interesting compounds that can be used in crystal engineering to build up extended frameworks, since they contain arrays of hydrogen-bonding sites (Janczak & Perpétuo, 2008). In addition, both tautomers have different potential coordination modes, since they can act as *N*,*N*′- or *N*,*S*-bidentate ligands and can form several different types of complexes with metal ions. The coordination of metal ions by these tautomers is possible by both the neutral and the deprotonated (anionic) forms (Doxiadi *et al.*, 2003). Beyond these known complexes, 2-imino-4-thiobiuret and 1-(diaminomethylene)thiourea can form salts with acids (Perpétuo & Janczak, 2008). We present here the crystal structures of 1-(diaminomethylene)thiouron-1-ium perchlorate, (I*a*), and hydrogen sulfate, (I*b*), as well as the isomorphic dihydrogen phosphate, (I*c*), and dihydrogen arsenate, (I*d*); the conformations of the cations are compared with that of the neutral molecule and with those in the chloride, bromide and iodide salts.


$$H_2N{-}C(NH_2){=}NH^+{-}C({=}S){-}NH_2\ \cdot X^-$$

(I*a*) $X = ClO_4^-$
(I*b*) $X = HSO_4^-$
(I*c*) $X = H_2PO_4^-$
(I*d*) $X = H_2AsO_4^-$

The asymmetric units of the title compounds are illustrated in Figs. 1(*a*)–1(*d*). The two arms of the 1-(diaminomethylene)thiouron-1-ium cation containing the N1/C2/N3/N4 and N1/C1/N2/S1 fragments are planar but twisted from coplanarity at the central N1 atom. The dihedral angle between the planes defined by the N1/C2/N3/N4 and N1/C1/N2/S1 arms is 1.4 (1)° in (I*a*), 9.8 (1)° in (I*b*), 4.4 (1)° in (I*c*) and 2.1 (1)° in (I*d*). Therefore, the 1-(diaminomethylene)thiouron-1-ium cations in the crystal structures of (I*a*) and (I*d*) are almost planar [the deviations of the non-H atoms from the mean planes are smaller than 0.021 (1) Å in (I*a*) and 0.058 (1) Å in (I*d*); see Table 5]. A similar nonplanar twisted conformation of the cation is observed in the crystal structures of other salts, as shown by their dihedral angles [22.9 (1)° for the chloride, 15.2 (1)° for the bromide and 4.2 (1)° for the iodide (Perpétuo & Janczak, 2008)]. *Ab initio* molecular orbital (MO) calculations indicate that the most stable conformation of the 1-(diaminomethylene)thiouron-1-ium cation is twisted with a dihedral angle of 6.2° (Perpétuo & Janczak, 2008). In single crystals, the neutral 1-(diaminomethylene)thiourea molecule also has a twisted conformation, with a dihedral angle of 22.2 (1)°, while the MO-calculated dihedral angle is 6.6° (Janczak & Perpétuo, 2008).

In the present crystal structures, the respective C—N and C═S bond lengths are very similar (Table 6). The C—N bonds involving the central N1 atom are significantly longer than the C—N bonds linking the amine groups. The values of the C1═S1 bond lengths in these salts are shorter than that in the neutral molecule of 1-(diaminomethylene)thiourea [1.7364 (9) Å; Janczak & Perpétuo, 2008] and are comparable to those found in the crystals of 1-(diaminomethylene)thiouron-1-ium chloride, bromide and iodide (Perpétuo & Janczak, 2008), as well as in some thiourea derivatives (for which the average C—S distance is 1.663 Å; Allen *et al.*, 1997). The C1═S1 bond lengths in (I*a*)–(I*d*) are slightly longer than the pure double C═S bond as observed in thioformaldehyde, CH_2S [1.6109 (8) Å; Johnson *et al.*, 1971], but shorter than the distance of 1.74 Å which represents 50% double-bond character (Abrahams, 1956; Allen *et al.*, 1987). Thus, the bond order of C1═S1 in (I*a*)–(I*d*) is somewhat less than 2, because of the partial delocalization of the π electrons of the double C1═S1 and C2═N1 bonds over the single C—N bonds linking the NH_2 groups. This results in a shortening of the

DOI: 10.1107/S0108270108013504

single C—NH$_2$ bonds and an elongation of the double C1═S1 and C2═N1 bonds. Thus, the bond order of the C—N bonds linking the amine groups is greater than that of the C—N bonds involving the central N1 atom. *Ab initio* MO calculations show that interaction of atom S1 with the amine group (N4) leads to rotation of both arms of the 1-(diaminomethylene)thiouron-1-ium cation around the C—N1 bond by 6.2°, as well as distortion of the C—N═C, N—C—N and N—C═S angles from 120°, as expected for sp^2 hybridization. The protonation of the central N1 atom decreases the steric effect of the lone pair of electrons at atom N1 and makes the C1—N1═C2 angle greater by ~6° in comparison with that in the neutral molecule (Janczak & Perpétuo, 2008), which is consistent with the valence-shell electron-pair repulsion model (Gillespie, 1992). The anionic species of (I*a*)–(I*d*) each exhibit a slightly distorted tetrahedral geometry, with bond lengths and angles typical of those found in several crystals of this kind (Allen, 2002).

In all of the title crystal structures, besides the interionic interactions, the oppositely charged units interact through hydrogen-bonding systems. Atom S1 contains two lone-pair electrons and so acts as a hydrogen-bond acceptor. The non-bonded S···H contact requires that the distance between the S and H atoms is shorter than the sum of the van der Waals radii of these atoms [r_S = 1.80 Å (Bondi, 1964) and r_H = 1.10 Å (Rowland & Taylor, 1996)]. Besides S···H contacts, N—H···O contacts between the oppositely charged units with distances shorter than the sum of the van der Waals radii of O and H atoms are observed in these structures (r_O = 1.52 Å and r_H = 1.10 Å; Bondi, 1964; Pauling, 1960). In (I*a*) (Table 1), 1-(diaminomethylene)thiouron-1-ium cations related by inversion interact *via* a pair of N—H···S hydrogen bonds, forming a dimeric structure (Fig. 2*a*). These dimers are linked *via* N—H···O hydrogen bonds with ClO_4^- anions, forming layers that are arranged almost parallel to the (102) crystallographic plane and are separated by a distance of ~3.58 Å.

In (I*b*), the 1-(diaminomethylene)thiouron-1-ium cations are discrete and are surrounded by the HSO_4^- counter-ions (Fig. 2*b*). HSO_4^- anions related by inversion interact *via* a pair of O3—H3···O1^i hydrogen bond [symmetry code: (i) $-x + 1, -y, -z + 1$], forming centrosymmetric dimers. The discrete 1-(diaminomethylene)thiouron-1-ium cations interact *via* N—H···O hydrogen bonds with the $(HSO_4^-)_2$ dimers, forming double layers that are parallel to the (001) crystallographic plane (Table 2). The sheets in the double layers are interconnected by N—H···O hydrogen bonds, while no hydrogen bonds are observed between the double layers (Fig. 2*b*). The sheets in the double layer are separated by a distance of ~3.22 Å and the double layers are separated by ~2.92 Å.

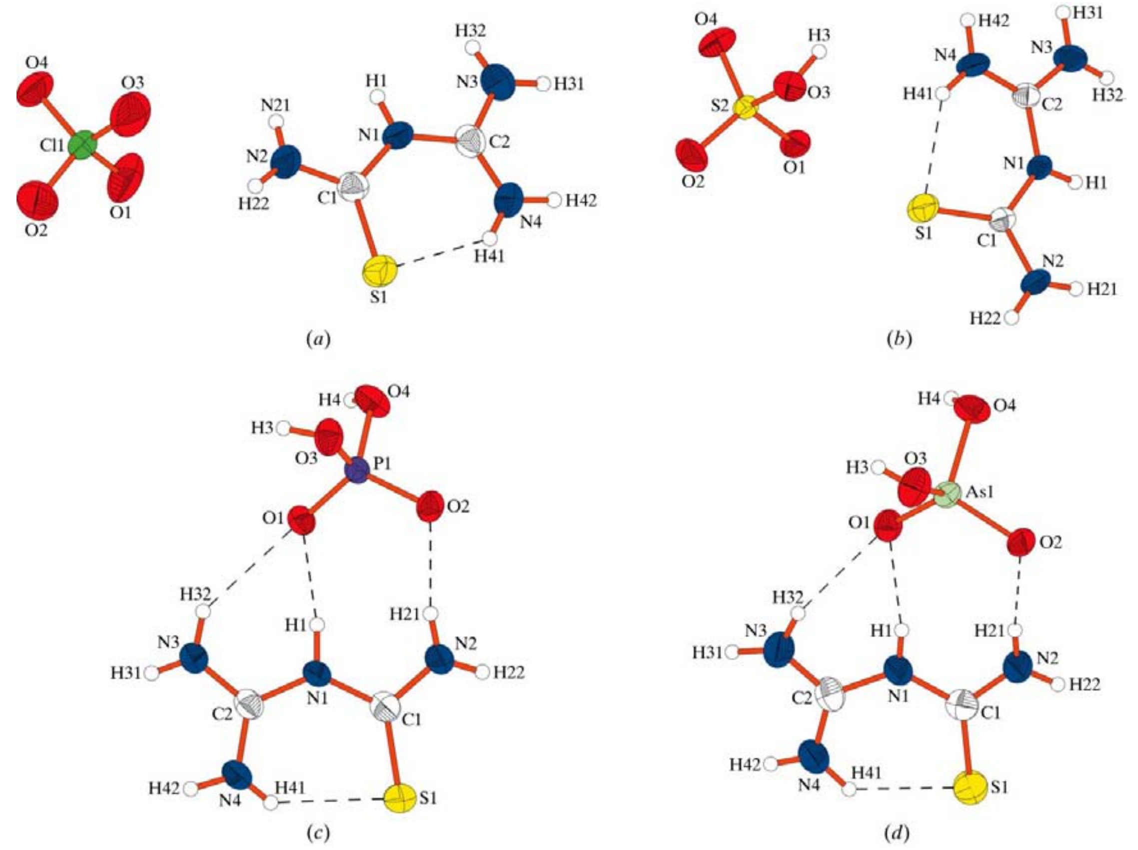


Figure 1
Views of (*a*) (I*a*), (*b*) (I*b*), (*c*) (I*c*) and (*d*) (I*d*), showing the atom-labelling schemes. Displacement ellipsoids are drawn at the 50% probability level and H atoms as spheres of arbitrary radii. Dashed lines indicate hydrogen-bond contacts.

In the isomorphic structures of (I*c*) and (I*d*) (Tables 3 and 4), and as found in (I*a*), the 1-(diaminomethylene)thiouron-1-ium cations interact *via* N—H···S hydrogen bonds, forming centrosymmetric dimers. The anions, *i.e.* $H_2PO_4^-$ and $H_2AsO_4^-$, are involved in two pairs of almost linear O—H···O hydrogen bonds to form pseudo-one-dimensional chains that run almost parallel to the [100] direction (Fig. 3*a*). The anionic chains interconnect the cationic dimers *via* N—H···O hydrogen bonds, forming a three-dimensional hydrogen-bonded network (Fig. 3*b*). In the crystal structures of (I*c*) and (I*d*), the dimeric cations form a stacking structure with distances between the mean planes of the dimers of 3.71 (1) and 3.42 (1) Å, respectively.

This study illustrates the utility of 1-(diaminomethylene)thiourea in crystal engineering for developing a variety of supramolecular structures, namely layers, double layers and three-dimensional networks.

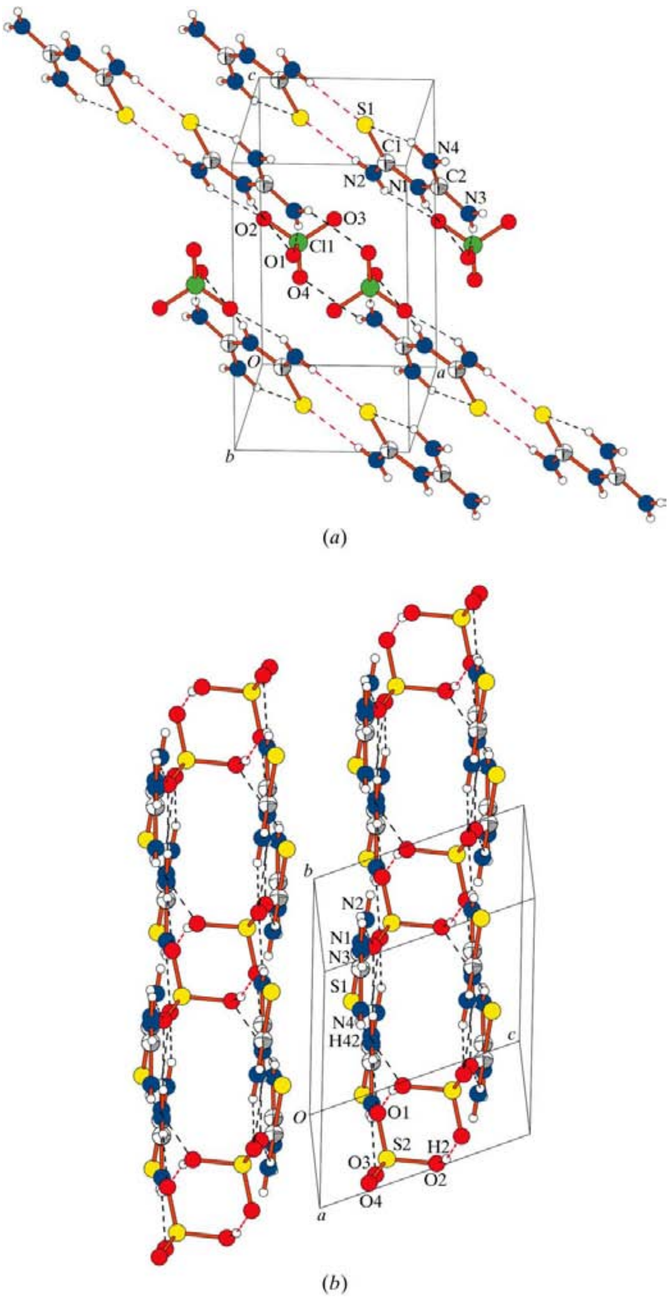


Figure 2
Views of the crystal packing of (I*a*) and (I*b*), showing (*a*) hydrogen-bonded layers in (I*a*) and (*b*) double layers in (I*b*). Dashed lines represent N—H···S hydrogen bonds in dimers of 1-(diaminomethylene)thiouron-1-ium and O—H···O bonds in dimers involving HSO_4^-.

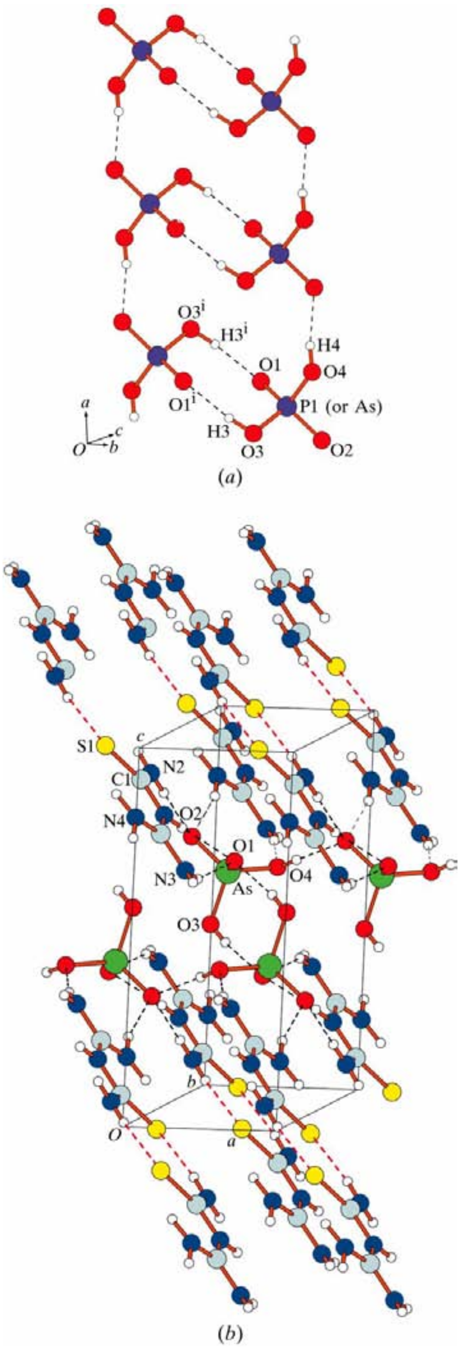


Figure 3
(*a*) A view of the anionic chains in the isomorphic structures of (I*c*) and (I*d*) [symmetry code: (i) $-x+1, -y+1, -z+1$], and (*b*) the crystal packing of (I*d*), showing the three-dimensional hydrogen-bonded network. Dashed lines represent N—H···S hydrogen bonds in dimers of 1-(diaminomethylene)thiouron-1-ium.

Experimental

Crystals of (I*a*), (I*b*), (I*c*) and (I*d*) were obtained from 2-imino-4-thiobiuret (purchased from Aldrich, 99% purity) dissolved in 5% aqueous solutions (100 ml) of $HClO_4$, H_2SO_4, H_3PO_4 and H_3AsO_4 acids, respectively. After several days at room temperature, suitable crystals were formed.

Compound (I*a*)

Crystal data

$C_2H_7N_4S^+\cdot ClO_4^-$
$M_r = 218.63$
Triclinic, $P\bar{1}$
$a = 5.8011\ (9)$ Å
$b = 8.4511\ (14)$ Å
$c = 9.430\ (2)$ Å
$\alpha = 109.15\ (2)^\circ$
$\beta = 91.441\ (10)^\circ$
$\gamma = 104.639\ (11)^\circ$
$V = 419.59\ (15)$ Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 0.69$ mm^{-1}
$T = 295\ (2)$ K
$0.37 \times 0.22 \times 0.14$ mm

Data collection

Kuma KM-4 diffractometer with a CCD area detector
Absorption correction: analytical (face-indexed; *SHELXTL*; Sheldrick, 2008)
$T_{\min} = 0.785$, $T_{\max} = 0.910$
5108 measured reflections
2110 independent reflections
1516 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.016$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.097$
$S = 1.00$
2110 reflections
137 parameters
All H-atom parameters refined
$\Delta\rho_{\max} = 0.29$ e Å^{-3}
$\Delta\rho_{\min} = -0.35$ e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °) for (I*a*).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O1$^{\rm i}$	0.81 (2)	2.40 (2)	3.159 (3)	156.5 (19)
N2—H21···O2$^{\rm i}$	0.78 (2)	2.32 (3)	3.050 (3)	156 (2)
N2—H22···S1$^{\rm ii}$	0.80 (3)	2.63 (3)	3.434 (2)	177 (2)
N3—H31···O4$^{\rm iii}$	0.85 (2)	2.44 (3)	3.245 (3)	158 (2)
N3—H31···O4$^{\rm iv}$	0.85 (2)	2.50 (2)	3.104 (2)	129 (2)
N3—H32···O1$^{\rm i}$	0.78 (3)	2.35 (3)	3.082 (3)	159 (3)
N4—H42···O2$^{\rm iii}$	0.86 (3)	2.22 (3)	3.014 (3)	153 (2)
N4—H41···S1	0.90 (3)	2.25 (3)	2.981 (2)	138 (3)

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

Compound (I*b*)

Crystal data

$C_2H_7N_4S^+\cdot HO_4S^-$
$M_r = 216.24$
Triclinic, $P\bar{1}$
$a = 7.8371\ (11)$ Å
$b = 8.103\ (2)$ Å
$c = 8.104\ (2)$ Å
$\alpha = 60.88\ (1)^\circ$
$\beta = 65.99\ (1)^\circ$
$\gamma = 87.54\ (2)^\circ$
$V = 402.85\ (17)$ Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 0.65$ mm^{-1}
$T = 295\ (2)$ K
$0.37 \times 0.27 \times 0.22$ mm

Data collection

Kuma KM-4 diffractometer with a CCD area detector
Absorption correction: analytical (face-indexed; *SHELXTL*; Sheldrick, 2008)
$T_{\min} = 0.796$, $T_{\max} = 0.871$
4199 measured reflections
1917 independent reflections
1731 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.005$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.070$
$S = 1.00$
1917 reflections
134 parameters
All H-atom parameters refined
$\Delta\rho_{\max} = 0.52$ e Å^{-3}
$\Delta\rho_{\min} = -0.49$ e Å^{-3}

Table 2
Hydrogen-bond geometry (Å, °) for (I*b*).

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3···O1$^{\rm i}$	0.86 (3)	1.83 (3)	2.6714 (19)	166 (2)
N1—H1···O2$^{\rm ii}$	0.84 (2)	2.29 (2)	3.073 (2)	155.2 (17)
N2—H21···O2$^{\rm ii}$	0.83 (2)	2.19 (2)	2.963 (2)	154.0 (19)
N2—H22···O4$^{\rm iii}$	0.89 (2)	2.30 (2)	3.164 (2)	166 (2)
N3—H31···O1$^{\rm iv}$	0.87 (2)	2.23 (2)	3.080 (2)	168 (2)
N3—H32···O4$^{\rm ii}$	0.85 (2)	2.19 (2)	3.031 (2)	168 (2)
N4—H41···S1	0.92 (2)	2.22 (2)	2.9798 (18)	140.4 (19)
N4—H41···O3$^{\rm i}$	0.92 (2)	2.47 (2)	3.029 (2)	119.6 (17)
N4—H42···O2$^{\rm iv}$	0.85 (3)	2.22 (3)	3.021 (2)	159 (2)

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

Compound (I*c*)

Crystal data

$C_2H_7N_4S^+\cdot H_2O_4P^-$
$M_r = 216.16$
Triclinic, $P\bar{1}$
$a = 4.5229\ (8)$ Å
$b = 8.3241\ (11)$ Å
$c = 11.574\ (2)$ Å
$\alpha = 88.160\ (12)^\circ$
$\beta = 86.191\ (11)^\circ$
$\gamma = 87.359\ (10)^\circ$
$V = 434.15\ (13)$ Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 0.54$ mm^{-1}
$T = 295\ (2)$ K
$0.38 \times 0.18 \times 0.17$ mm

Data collection

Kuma KM-4 diffractometer with a CDD area detector
Absorption correction: analytical (face-indexed; *SHELXTL*; Sheldrick, 2008)
$T_{\min} = 0.812$, $T_{\max} = 0.909$
4924 measured reflections
2067 independent reflections
1757 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.012$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.027$
$wR(F^2) = 0.071$
$S = 1.00$
2067 reflections
145 parameters
All H-atom parameters refined
$\Delta\rho_{\max} = 0.27$ e Å^{-3}
$\Delta\rho_{\min} = -0.26$ e Å^{-3}

Table 3
Hydrogen-bond geometry (Å, °) for (I*c*).

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3···O1$^{\rm i}$	0.84 (2)	1.76 (2)	2.5994 (17)	171.0 (19)
O4—H4···O2$^{\rm ii}$	0.79 (2)	1.73 (3)	2.5123 (15)	171 (3)
N1—H1···O1	0.890 (19)	1.948 (19)	2.8273 (18)	169.3 (16)
N2—H21···O2	0.855 (19)	2.035 (19)	2.874 (2)	166.4 (16)
N2—H21···O2	0.855 (19)	2.035 (19)	2.874 (2)	166.4 (16)
N2—H22···S1$^{\rm iii}$	0.81 (2)	2.68 (2)	3.4677 (19)	163.3 (18)
N4—H42···O2$^{\rm iv}$	0.893 (19)	2.00 (2)	2.8682 (19)	162.9 (16)
N4—H41···S1	0.790 (19)	2.36 (2)	3.0028 (19)	138.9 (17)
N3—H31···O4$^{\rm iv}$	0.81 (2)	2.16 (2)	2.964 (2)	171.0 (17)
N3—H32···O1	0.88 (2)	2.55 (2)	3.234 (2)	136.2 (17)
N3—H32···O4$^{\rm i}$	0.88 (2)	2.57 (2)	3.182 (2)	127.8 (17)

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

Compound (I*d*)

Crystal data

$C_2H_7N_4S^+ \cdot H_2AsO_4^-$
M_r = 260.11
Triclinic, $P\overline{1}$
a = 4.7250 (8) Å
b = 8.4071 (10) Å
c = 11.3841 (19) Å
α = 89.402 (11)°
β = 86.840 (12)°
γ = 88.871 (14)°
V = 451.41 (12) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 3.98 mm^{-1}
T = 295 (2) K
0.38 × 0.14 × 0.12 mm

Data collection

Kuma KM-4 diffractometer with a CCD area detector
Absorption correction: analytical (face-indexed; *SHELXTL*; Sheldrick, 2008)
$T_{\min}$ = 0.513, $T_{\max}$ = 0.641
4770 measured reflections
2149 independent reflections
1927 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.013

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.109
S = 1.01
2149 reflections
136 parameters
All H-atom parameters refined
$\Delta\rho_{\max}$ = 1.02 e Å^{-3}
$\Delta\rho_{\min}$ = −0.93 e Å^{-3}

Table 4
Hydrogen-bond geometry (Å, °) for (I*d*).

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3···O1$^{\rm i}$	0.78 (5)	1.83 (5)	2.599 (3)	169 (5)
O4—H4···O2$^{\rm ii}$	0.81 (5)	1.76 (5)	2.555 (3)	166 (6)
N1—H1···O1	0.80 (5)	2.03 (5)	2.806 (4)	166 (4)
N2—H21···O2	0.84 (4)	2.06 (4)	2.897 (4)	173 (5)
N2—H22···S1$^{\rm iii}$	0.83 (5)	2.66 (5)	3.449 (3)	160 (4)
N3—H31···O4$^{\rm iv}$	0.91 (6)	2.08 (6)	2.974 (4)	168 (5)
N3—H32···O1	0.86 (6)	2.35 (6)	3.133 (4)	150 (5)
N4—H41···S1	0.91 (5)	2.28 (5)	3.007 (4)	136 (4)
N4—H42···O2$^{\rm iv}$	0.84 (5)	2.05 (6)	2.867 (4)	164 (5)

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

Table 5
Deviations of the atoms from the mean least-squares plane defined by the non-H atoms of 1-(diaminomethylene)thiouron-1-ium in (I*a*), (I*b*), (I*c*) and (I*d*) and in the gas phase as obtained by MO calculations.

Atom	(I*a*)	(I*b*)	(I*c*)	(I*d*)	MO^a
N2	−0.0151 (13)	0.0939 (10)	−0.0030 (9)	−0.0297 (23)	−0.0551
C1	0.0051 (16)	−0.0080 (12)	−0.0018 (12)	−0.0066 (29)	0.0015
S1	0.0148 (10)	−0.1058 (8)	−0.0120 (8)	0.0090 (20)	0.0290
N1	0.0046 (15)	−0.0484 (12)	0.0257 (12)	0.0575 (28)	0.0757
C2	0.0007 (16)	0.0008 (16)	−0.0033 (13)	0.0067 (32)	0.0006
N3	0.0106 (12)	−0.0673 (10)	−0.0186 (10)	−0.0186 (25)	−0.0057
N4	−0.0207 (13)	0.1347 (10)	−0.0129 (10)	−0.0183 (25)	−0.0453

Note: (*a*) data from Perpétuo & Janczak (2008).

H atoms were located in difference Fourier maps and refined with isotropic displacement parameters in all structures.

For all compounds, data collection: *CrysAlis CCD* (Oxford Diffraction, 2005); cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2005); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg & Putz, 2006); software used to prepare material for publication: *SHELXL97*.

Table 6
A comparison of selected geometrical parameters for 1-(diaminomethylene)thiouron-1-ium in (I*a*), (I*b*), (I*c*) and (I*d*), and the *ab initio* MO-calculated values.

	(I*a*)	(I*b*)	(I*c*)	(I*d*)	MO^a
C1—S1	1.6656 (19)	1.6615 (16)	1.6800 (16)	1.686 (4)	1.662
C1—N1	1.396 (2)	1.3902 (18)	1.3827 (19)	1.378 (4)	1.421
C1—N2	1.308 (2)	1.3212 (19)	1.3130 (19)	1.305 (5)	1.348
N1—C2	1.364 (2)	1.3685 (19)	1.3639 (18)	1.364 (4)	1.368
C2—N3	1.322 (3)	1.313 (2)	1.309 (2)	1.322 (5)	1.343
C2—N4	1.283 (3)	1.303 (2)	1.303 (2)	1.292 (5)	1.319
N2—C1—N1	112.58 (18)	112.97 (14)	112.91 (14)	113.5 (3)	111.4
N2—C1—S1	122.50 (16)	121.75 (12)	122.04 (12)	122.0 (3)	122.9
N1—C1—S1	124.92 (14)	125.27 (11)	125.04 (11)	124.5 (3)	125.7
C2—N1—C1	130.08 (17)	129.74 (13)	130.34 (13)	130.4 (3)	129.9
N4—C2—N3	121.6 (2)	121.22 (15)	120.67 (15)	120.0 (3)	121.3
N4—C2—N1	122.37 (18)	121.83 (14)	123.09 (14)	123.8 (3)	121.8
N3—C2—N1	116.0 (2)	116.94 (14)	116.22 (14)	116.2 (3)	117.0
C2—N1—C1—N2	−178.84 (20)	−171.84 (15)	−177.85 (15)	−174.98 (35)	172.0
N3—C2—N1—C1	−179.55 (19)	−179.50 (15)	177.32 (15)	174.51 (37)	−174.8

Note: (*a*) data from Perpétuo & Janczak (2008).

This research was supported by a grant (No. 3 T09A 121 28) from the Polish State Committee for Scientific Research.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GA3088). Services for accessing these data are described at the back of the journal.

References

Abrahams, S. C. (1956). *Q. Rev. Chem. Soc.* **10**, 407–436.
Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Allen, F. H., Bird, C. M., Rowland, R. S. & Raithby, P. R. (1997). *Acta Cryst.* B**53**, 680–695.
Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.
Brandenburg, K. & Putz, H. (2006). *DIAMOND*. Version 3.0. University of Bonn, Germany.
Doxiadi, E., Vilar, R., White, A. J. P. & Williams, D. J. (2003). *Polyhedron*, **22**, 2991–2998.
Gillespie, R. J. (1992). *Chem. Soc. Rev.* **21**, 59–69.
Janczak, J. & Perpétuo, G. J. (2008). *Acta Cryst.* C**64**, o114–o116.
Johnson, D. R., Powell, F. X. & Kirchoff, W. H. (1971). *J. Mol. Spectrosc.* **39**, 136–143.
Oxford Diffraction (2005). *CrysAlis CCD* and *CrysAlis RED*. Versions 171.31.8. Oxford Diffraction Poland, Wrocław, Poland.
Pauling, L. (1960). *The Nature of the Chemical Bond*, 3rd ed., p. 260. Ithaca: Cornell University Press.
Perpétuo, G. J. & Janczak, J. (2008). *Acta Cryst.* C**64**, o264–o268.
Rowland, R. S. & Taylor, R. (1996). *J. Phys. Chem.* **100**, 7384–7391.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.