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The chloride, bromide and iodide salts of 1-(diaminomethylene)thiouron-1-ium

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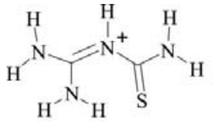
Crystals of 1-(diaminomethylene)thiouron-1-ium chloride, $C_2H_7N_4S^+\cdot Cl^-$, 1-(diaminomethylene)thiouron-1-ium bromide, $C_2H_7N_4S^+\cdot Br^-$, and 1-(diaminomethylene)thiouron-1-ium iodide, $C_2H_7N_4S^+\cdot I^-$, are built up from the nonplanar 1-(diaminomethylene)thiouron-1-ium cation and the respective halogenide anion. The conformation of the 1-(diaminomethylene)thiouron-1-ium cation in each case is twisted. Both arms of the cation are planar and rotated in opposite directions around the C—N bonds involving the central N atom. The dihedral angles describing the twisted conformation are 22.9 (1), 15.2 (1) and 4.2 (1)° in the chloride, bromide and iodide salts, respectively. Ionic and extensive hydrogen-bonding interactions join oppositely charged units into a supramolecular network. The aim of the investigation is to study the influence of the size of the ionic radii of the Cl^-, Br^- and I^- ions on the dimensionality of the hydrogen-bonding network of the 1-(diaminomethylene)thiouron-1-ium cation. The 1-(diaminomethylene)thiouron-1-ium system should be of use in crystal engineering to form multidimensional networks.

Comment

The present work continues our investigation of the characterization of compounds that in solids form multiple hydrogen-bonding systems (Janczak & Perpétuo, 2008*a*; Perpétuo & Janczak, 2007, 2008; Janczak & Kubiak, 2005*a*,*b*). Previously, we have investigated the crystal structure of commercially available 2-imino-4-thiobiuret (Aldrich, CAS No. 2114-02-05) and stated that it exists in the tautomeric form, *i.e.* 1-(diaminomethylene)thiourea (Janczak & Perpétuo, 2008*b*). 2-Imino-4-thiobiuret and its tautomer have several potential coordinating modes, since they can act as *N*,*N*′- or *N*,*S*-donor ligands and can form several different complexes with metal ions. The coordination of metals by this ligand is possible by either the neutral or a deprotonated (anionic) form. A search of the Cambridge Structural Database (Version 5.29 of November 2007; Allen, 2002) for structures containing this ligand yielded only three Pt complexes, in which the Pt atom is coordinated by 2-imino-4-thiobiuret or its deprotonated form (Doxiadi *et al.*, 2003). Besides these known Pt complexes with neutral and deprotonated negatively charged ligands, 2-imino-4-thiobiuret and 1-(diaminomethylene)thiourea can form salts, since both contain an N atom with a lone pair of electrons that can accept a H atom, forming positively charged 2-iminio-4-thiobiuret and 1-(diaminomethylene)thiouron-1-ium, respectively. In the present work, we investigate the crystal structures of three salts, namely 1-(diaminomethylene)thiouron-1-ium chloride, (I*a*), bromide, (I*b*), and iodide, (I*c*). In addition, the X-ray geometry and the conformation of the thiouronium cation is compared with that in the gas phase, as predicted for an isolated cation by density functional theory (Frisch *et al.*, 1998), as well as with the geometry of the neutral molecule reported previously (Janczak & Perpétuo, 2008*b*). *Ab initio* molecular orbital (MO) calculations were performed at the B3LYP/6–31+G* level and the results are illustrated in Fig. 1.



(I*a*) *X* = Cl
(I*b*) *X* = Br
(I*c*) *X* = I

The asymmetric units of the title salts are illustrated in Fig. 2. The geometry of the 1-(diaminomethylene)thiouron-1-ium cation in these salts is not planar. However, both arms of the cation, containing atoms N1/C2/N3/N4 and N1/C1/N2/S1, are planar. The maximum deviations of the non-H atoms from these planes are 0.029 (2) and 0.014 (2) Å, respectively. The two arms of the cation are turned in opposite directions around the C—N bonds involving the central N1 atom. Thus, the conformation of the thiouronium cation is twisted. The dihedral angles between the planes are 22.9 (1), 15.2 (1) and 4.2 (1)° in the chloride, bromide and iodide salts, respectively. The rotation angles correlate with the electronegativity of the halogen: 3.16 for Cl, 2.96 for Br and 2.66 for I (Pauling, 1960). A similar twisted conformation is observed in the crystal

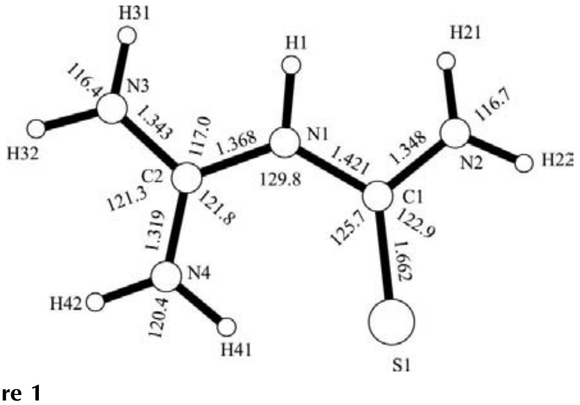


Figure 1
Results of the optimized molecular orbital calculations (B3LYP/6–31+G*) for the 1-(diaminomethylene)thiouronium cation (Å, °).

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structure of neutral 1-(diaminomethylene)thiourea [22.2 (1)°; Janczak & Perpétuo, 2008*b*]. The gas-phase conformation of the 1-(diaminomethylene)thiouron-1-ium cation as shown by *ab initio* MO calculations is also twisted, with a dihedral angle of 6.2°. The difference between the conformation of the cation in the crystal and in the gas phase results from the interionic and hydrogen-bonding interactions present in the crystal structures.

In the present salts, the corresponding C—N and C═S bond lengths are essentially the same. The C—N bond lengths involving the central N1 atom are significantly longer than the other C—N bond lengths linking the amine groups (Tables 1, 3 and 5). The C1═S1 bond lengths in these salts are comparable to those in thiourea derivatives (where the average C═S distance is 1.663 Å; Allen *et al.*, 1997). However the gas-phase data for thioformaldehyde, $H_2C{=}S$, give a value of 1.6109 (8) Å for the C═S bond distance, which represents 100% double-bond character (Johnson *et al.*, 1971), while C═S bond lengths of *ca* 1.74 Å are cited as representing 50% double-bond character, as observed in dithiolate anions (Abrahams, 1956; Allen *et al.*, 1987). The planarity of the amine groups indicates *sp*^{2}-hybridization of the orbitals on the amine N atoms, and the lone pair of electrons occupies the *p* orbital, which is perpendicular to the plane of the NH_2 groups. The *p* orbitals of the C and S atoms, forming the π bonds of the C2═N1 and C1═S1 double bonds, are also perpendicular to the plane; therefore, partial delocalization, due to the symmetry of the *p* orbitals, of the π electrons over the whole cation is possible, and leads to elongation of the C1═S1 and C2═N1 double bonds and to shortening of the other, single, C—N bonds (Tables 1, 3 and 5). Thus, the bond order of the C1═S1 and C2═N1 bonds is smaller than 2, and the bond order of the C—N bonds linking the amine groups is greater than 1. The bond order of the C—N bonds joining the amine groups is greater than the bond order of the C—N bonds involving the central N1 atom. The repulsion between the S atom and the amine group at N4 causes the rotation of both arms of the cation around the C—N1 bonds and is responsible for the twisted conformation of the cation. This interaction decreases the overlap of the *p* orbitals of atoms C2 and N1 and of atoms N1 and C1, and leads to elongation of the C2—N1 and N1—C1 bonds compared with the other $C—N_{amine}$ bonds, in which the overlap of the *p* orbitals is more effective. The steric interaction between atom S1 and amine atom N4 is also responsible for the distortion of the N—C—N, C—N1—C and N—C1—S1 angles, as expected for *sp*^{2}-hybridization. A similar correlation between the bond lengths and angles can be found in the gas-phase structure as obtained by *ab initio* MO calculations (Fig. 1). The protonation of the central N1 atom leads to a decrease of the steric effect of the lone pair of electrons on atom N1 and makes the C2—N1—C1 angle greater by ~6° than that in the neutral 1-(diaminomethylene)thiourea molecule (Janczak & Perpétuo, 2008*b*). This is consistent with the valence-shell electron-pair repulsion model (Gillespie, 1963, 1992), according to which the lone pair of electrons on the N atom occupies a wider region than the N—H bonding pair.

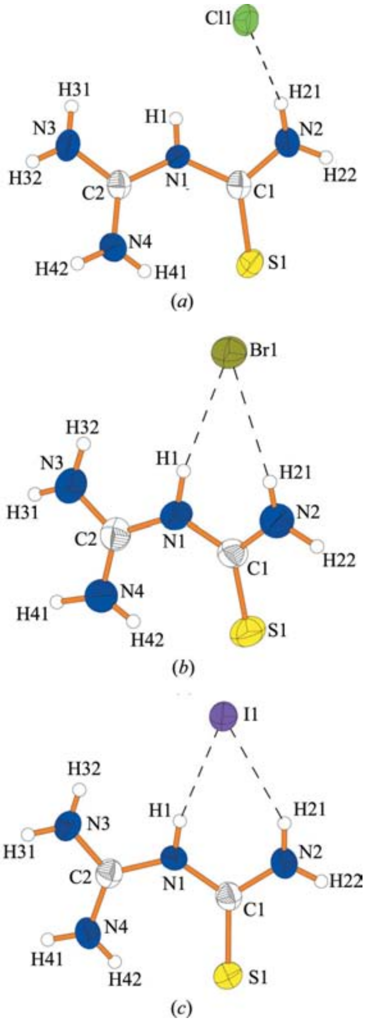

Figure 2
Views of (*a*) (I*a*), (*b*) (I*b*) and (*c*) (I*c*), showing the atom-labelling schemes. Displacement ellipsoids are shown at the 50% probability level and H atoms as spheres of arbitrary radii.

In the crystal structures, besides the interionic interactions, the oppositely charged units are linked by hydrogen bonds. In the crystal structure of (I*a*), the thiouronium cations are arranged almost parallel to the (100) crystallographic plane, forming layers separated by a distance of *a*/2 (~3.26 Å) (Fig. 3*a*). Within the layers, as well as between the layers, the cations are interconnected by N—H···Cl hydrogen bonds (Table 2). In the crystal structures of both (I*b*) and (I*c*), thiouronium cations related by an inversion centre interact *via* N—H···S hydrogen bonds, forming a dimeric structure (Figs. 3*b* and 3*c*). The S atom contains two lone pairs of electrons that can be involved in hydrogen bonds as acceptors. The nonbonded S···H contact requires that the distance between the S and H atoms should be less than the sum of the van der Waals radii of S and H atoms [r_S = 1.80 Å (Bondi, 1964) and r_H = 1.10 Å (Rowland & Taylor, 1996)]. S···H contacts shorter than 2.90 Å are observed in both (I*b*) and (I*c*) (Tables 4 and 6). The dimers of thiouronium cations in (I*b*) are interconnected by N—H···Br hydrogen bonds, forming layers that lie almost parallel to the (102) plane and are separated by a distance of ~3.16 Å. No hydrogen bonds of the Br···H type

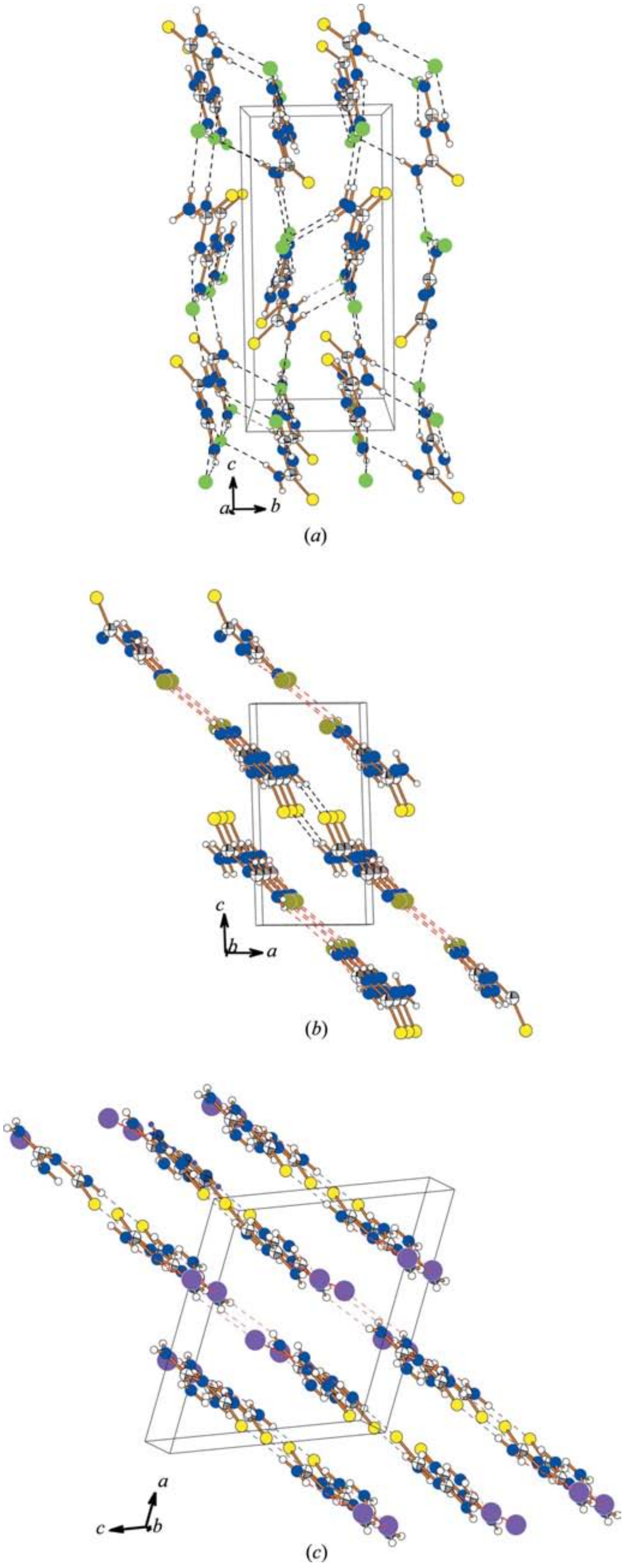

Figure 3
Views of the crystal packing in (I*a*), (I*b*) and (I*c*), showing (*a*) the hydrogen-bonded three-dimensional network in (I*a*), and the hydrogen-bonded layers in (*b*) (I*b*) and (*c*) (I*c*). Dashed lines represent hydrogen bonds.

with a distance shorter than the sum of the van der Waals radii of Br and H ($r_{\rm Br}$ = 1.81 Å and $r_{\rm H}$ = 1.10 Å; Rowland & Taylor, 1996; Pauling, 1960) were found between the layers; therefore, they interact only *via* van der Waals forces. In the crystal structure of (I*c*), the dimers interact *via* N—H···I hydrogen bonds, forming layers almost parallel to $(30\overline{2})$. Similar to the crystal structure of (I*b*), there are no I···H contacts with a distance shorter than the sum of the van der Waals radii of I and H ($r_{\rm I}$ = 2.20 Å; Pauling, 1960).

This study underscores the utility of 1-(diaminomethylene)thiourea for developing supramolecular structures with acids. Larger anions, such as Br^- and I^-, interconnect the 1-(diaminomethylene)thiouron-1-ium dimers into layers. The large anionic radii cause the layers to be separated by a distance greater than the sum of the van der Waals radii of I or Br and H atoms, and therefore there are no hydrogen-bonding interactions between the layers in (I*b*) and (I*c*). However, in the chloride salt, the smaller chloride anions link the thiouronium cations into layers that are interconnected *via* Cl···H interactions into a three-dimensional network.

Experimental

Suitable crystals of (I*a*), (I*b*) and (I*c*) were obtained from 2-imino-4-thiobiuret (purchased from Aldrich, 99% purity) dissolved in 5% aqueous solutions of HCl, HBr and HI. Suitable crystals formed after several days at room temperature.

Compound (I*a*)

Crystal data

$C_2H_7N_4S^+\cdot Cl^-$
M_r = 154.63
Monoclinic, $P2_1/c$
a = 6.517 (1) Å
b = 6.807 (1) Å
c = 14.777 (3) Å
β = 90.36 (2)°
V = 655.51 (19) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.80 mm^{-1}
T = 295 (2) K
0.37 × 0.22 × 0.17 mm

Data collection

Kuma KM-4 diffractometer with a CCD area detector
Absorption correction: analytical, face-indexed (*SHELXTL*; Sheldrick, 2008)
$T_{\rm min}$ = 0.760, $T_{\rm max}$ = 0.878
6665 measured reflections
1635 independent reflections
1164 reflections with $\sigma > 2\sigma(I)$
$R_{\rm int}$ = 0.031

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.030
$wR(F^2)$ = 0.062
S = 0.99
1635 reflections
95 parameters
Only H-atom coordinates refined
$\Delta\rho_{\rm max}$ = 0.21 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.20 e Å^{-3}

Compound (I*b*)

Crystal data

$C_2H_7N_4S^+\cdot Br^-$
M_r = 199.09
Triclinic, $P\overline{1}$
a = 4.9661 (9) Å
b = 7.4841 (17) Å
c = 9.5739 (19) Å
α = 94.220 (14)°
β = 90.091 (11)°
γ = 104.012 (15)°
V = 344.23 (12) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 6.18 mm^{-1}
T = 295 (2) K
0.32 × 0.22 × 0.16 mm

Table 1
Selected geometric parameters (Å, °) for (I*a*).

S1—C1	1.6636 (17)	N1—C2	1.3565 (19)
C1—N2	1.319 (2)	C2—N4	1.300 (2)
C1—N1	1.3866 (19)	C2—N3	1.314 (2)
N2—C1—N1	112.45 (15)	N4—C2—N3	121.03 (15)
N2—C1—S1	123.43 (12)	N4—C2—N1	122.20 (15)
N1—C1—S1	124.07 (12)	N3—C2—N1	116.73 (15)
C2—N1—C1	130.32 (14)		

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$\cdots$Cl1^{i}	0.773 (17)	2.539 (18)	3.2305 (16)	149.9 (18)
N2—H21$\cdots$Cl1	0.86 (2)	2.54 (2)	3.3458 (18)	156.0 (16)
N2—H22$\cdots$Cl1^{ii}	0.85 (2)	2.48 (2)	3.3225 (18)	174.2 (18)
N3—H31$\cdots$Cl1^{i}	0.84 (2)	2.51 (2)	3.2804 (18)	152.9 (17)
N3—H32$\cdots$Cl1^{iii}	0.79 (2)	2.62 (2)	3.3084 (18)	146.9 (18)
N4—H41$\cdots$S1	0.806 (19)	2.390 (19)	3.0339 (17)	137.5 (18)
N4—H42$\cdots$Cl1^{iii}	0.844 (19)	2.46 (2)	3.2268 (17)	152.2 (17)

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

Table 3
Selected geometric parameters (Å, °) for (I*b*).

S1—C1	1.676 (3)	N1—C2	1.362 (4)
C1—N2	1.322 (4)	C2—N4	1.286 (4)
C1—N1	1.372 (4)	C2—N3	1.308 (4)
N2—C1—N1	113.0 (3)	N4—C2—N3	121.2 (3)
N2—C1—S1	121.6 (2)	N4—C2—N1	123.0 (3)
N1—C1—S1	125.4 (2)	N3—C2—N1	115.9 (3)
C2—N1—C1	130.2 (3)		

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$\cdots$Br1	0.89 (4)	2.51 (4)	3.387 (3)	167 (3)
N2—H21$\cdots$Br1	0.83 (4)	2.95 (4)	3.580 (4)	134 (3)
N2—H22$\cdots$S1^{i}	0.96 (4)	2.50 (4)	3.426 (3)	161 (3)
N3—H31$\cdots$Br1^{ii}	0.79 (4)	2.61 (4)	3.361 (3)	159 (4)
N3—H32$\cdots$Br1^{iii}	0.90 (4)	2.76 (4)	3.372 (4)	126 (3)
N4—H41$\cdots$Br1^{ii}	0.97 (4)	2.73 (4)	3.601 (3)	149 (3)
N4—H42$\cdots$S1	0.82 (4)	2.32 (4)	3.031 (3)	147 (4)

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

Table 5
Selected geometric parameters (Å, °) for (I*c*).

S1—C1	1.674 (2)	N1—C2	1.355 (3)
C1—N2	1.326 (3)	C2—N3	1.309 (3)
C1—N1	1.377 (3)	C2—N4	1.312 (3)
N2—C1—N1	112.3 (2)	N3—C2—N4	120.6 (2)
N2—C1—S1	122.29 (19)	N3—C2—N1	116.9 (2)
N1—C1—S1	125.36 (16)	N4—C2—N1	122.5 (2)
C2—N1—C1	130.9 (2)		

Table 6
Hydrogen-bond geometry (Å, °) for (I*c*).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$\cdots$I1	0.84 (3)	2.75 (3)	3.571 (2)	165 (3)
N2—H21$\cdots$I1	0.86 (4)	2.98 (4)	3.741 (3)	149 (3)
N2—H22$\cdots$S1^{i}	0.85 (4)	2.59 (4)	3.434 (2)	171 (3)
N3—H31$\cdots$I1^{ii}	0.83 (4)	2.99 (5)	3.741 (3)	151 (3)
N4—H41$\cdots$I1^{ii}	0.82 (4)	2.88 (4)	3.667 (2)	160 (3)
N4—H42$\cdots$S1	0.82 (3)	2.33 (3)	3.007 (2)	140 (3)

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

Data collection

Kuma KM-4 diffractometer with a CCD area detector
Absorption correction: analytical, face-indexed (*SHELXTL*; Sheldrick, 2008) $T_{\min} = 0.244$, $T_{\max} = 0.441$
4034 measured reflections
1737 independent reflections
1295 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.017$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.085$
$S = 0.99$
1737 reflections
95 parameters
Only H-atom coordinates refined
$\Delta\rho_{\max} = 0.76$ e Å^{-3}
$\Delta\rho_{\min} = -0.51$ e Å^{-3}

Compound (Ic)

Crystal data

$C_2H_7N_4S^+\cdot I^-$
$M_r = 246.08$
Monoclinic, $P2_1/c$
$a = 10.929$ (3) Å
$b = 7.875$ (1) Å
$c = 9.456$ (2) Å
$\beta = 111.10$ (1)°
$V = 759.3$ (3) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 4.41$ mm^{-1}
$T = 295$ (2) K
0.38 × 0.24 × 0.22 mm

Data collection

Kuma KM-4 diffractometer with a CCD area detector
Absorption correction: analytical, face-indexed (*SHELXTL*; Sheldrick, 2008) $T_{\min} = 0.286$, $T_{\max} = 0.445$
10077 measured reflections
2001 independent reflections
1785 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.013$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.021$
$wR(F^2) = 0.055$
$S = 1.00$
2001 reflections
95 parameters
Only H-atom coordinates refined
$\Delta\rho_{\max} = 0.81$ e Å^{-3}
$\Delta\rho_{\min} = -0.68$ e Å^{-3}

H atoms were located in difference Fourier maps and their positions refined.

For all compounds, data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2006); 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*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3208). Services for accessing these data are described at the back of the journal.

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