Products of the interaction of (1-diaminomethylene)thiourea with hydrofluoric acid

Małgorzata Hołyńska* and Maria Kubiak

Faculty of Chemistry, University of Wrocław, 14 Joliot-Curie Street, 50-383 Wrocław, Poland

Correspondence e-mail: holynska@wcheto.chem.uni.wroc.pl

The salts 1-(diaminomethylene)thiouron-1-ium hydrogen difluoride, $C_2H_7N_4S^+\cdot HF_2^-$, (I), and bis[1-(diaminomethylene)-thiouron-1-ium] hexafluoridosilicate, $2C_2H_7N_4S^+\cdot SiF_6^{2-}$, (II), have both been obtained from the reaction of (1-diaminomethylene)thiourea (HATU) with hydrofluoric acid. Both compounds contain extensive networks of $N-H\cdots F$ hydrogen bonds. The hydrogen difluoride salt contains four independent asymmetric $[HF_2]^-$ anions. In the hexafluoridosilicate salt, the centrosymmetric $[SiF_6]^{2-}$ anion is distorted, although this distortion is not clearly correlated with the $N-H\cdots F$ hydrogen-bonding network.

Comment

(1-Diaminomethylene)thiourea (HATU) is known to be capable of participating in an extensive network of interactions (Janczak & Perpétuo, 2008a). This capability has been utilized in cage-like complexes, such as $[Ni_6(ATU)_8Cl](ClO_4)_3$ (Vilar et al., 1998), which could serve as sensors for the identification of chloride anions in solution. HATU also forms complex hydrogen-bonded systems in its simple salts, such as the hydrogen sulfate and dihydrogen phosphate (Janczak & Perpétuo, 2008b). The crystal structures of several halide salts of HATU are also known, namely the chloride, bromide and iodide, all obtained from the reaction of HATU with the corresponding hydrogen halide in aqueous solution (Perpétuo & Janczak, 2008). The products of the reaction of HATU with hydrogen fluoride have not been hitherto reported. The present work is thus a continuation of our studies on the reactivity and complexing properties of (1-diaminomethylene)thiourea (Hołyńska & Kubiak, 2008), in which HATU halides can also be used as substrates.

Compound (I), obtained in the reaction of either concentrated or dilute hydrofluoric acid with HATU in a Teflon reaction vessel, comprises 1-(diaminomethylene)thiouron-1-ium cations and hydrogen difluoride anions (see scheme and Fig. 1). A similar reaction using very dilute hydrofluoric acid in a quartz vessel gave compound (II), while recrystallization of (I) from water in a quartz vessel gave a third product, possibly $[HATUH]_3[SiF_6]F\cdot H_2O$ (see Experimental). The hydrogen difluoride anion is an important model for strong hydrogen bonding (Williams & Schneemeyer, 1973). Such hydrogen bonding has been widely investigated, e.g. for arylammonium (Harmon et al., 1974) or alkylammonium (Gennick, Harmon & Potvin, 1977; Gennick, Harmon & Hartwig, 1977) fluorides.
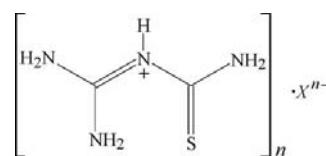
(I) $X = [HF_2]$, $n = 1$

(II) $X = [SiF_6]$, $n = 2$

The $[HF_2]^-$ anion can be either symmetric (Wilson et al., 1989; Rush et al., 1972) or asymmetric (Williams & Schneemeyer, 1973; Ramos Silva et al., 2000), depending on its local environment. Ramos Silva et al. (2000) reported the structure of L-argininium hydrogen difluoride, which has the shortest
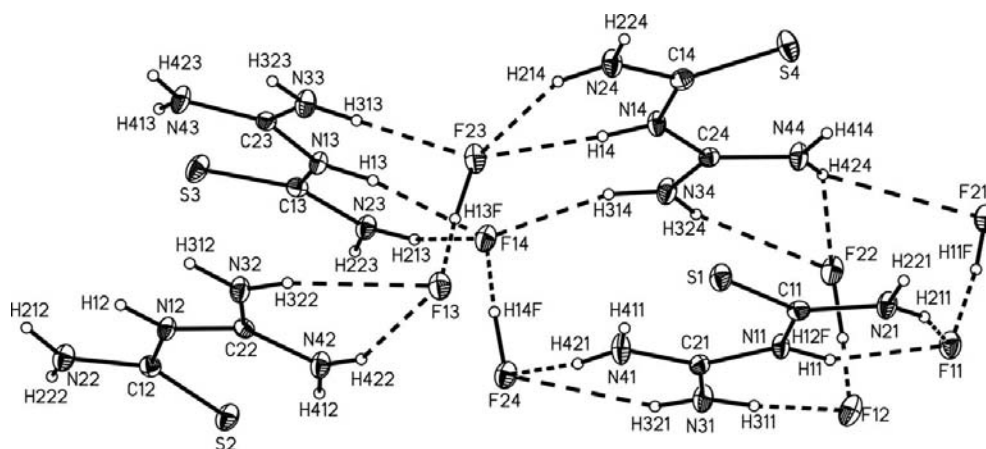

Figure 1
A view of the asymmetric unit of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. Hydrogen bonds are denoted by dashed lines.
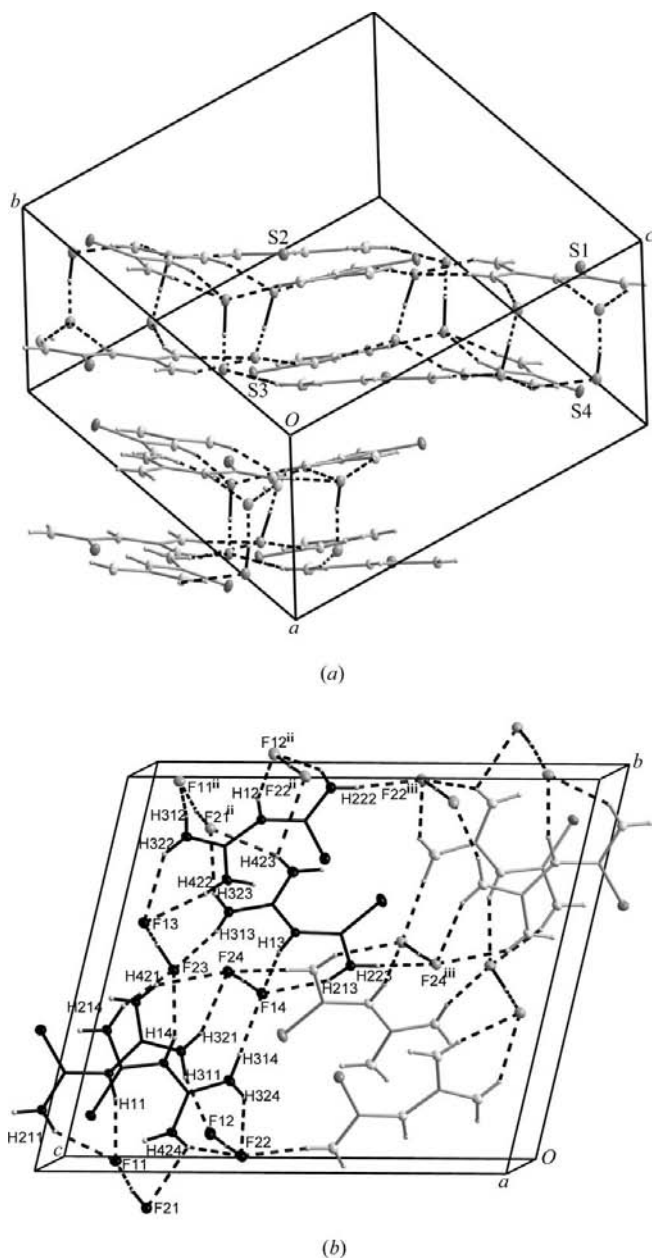
(a)

(b)

Figure 2
A view of (*a*) the hydrogen-bonded layers in (I) and (*b*) the structural motif of one of the hydrogen-bonded layers in (I). Symmetry-independent atoms are coloured black. Hydrogen bonds are shown as dashed lines. [Symmetry codes: (ii) $x + 1$, $y + 1$, z; (iii) $-x + 1$, $-y + 1$, $-z + 1$.]

F···F distances observed so far for an asymmetric $[HF_2]^-$ anion, at 2.233 (2) and 2.248 (3) Å in two independent anions [see also Ramos Silva *et al.* (2000) for a detailed discussion of F···F distances in other hydrogen-bonded compounds]. Recently, the hydrogen difluoride anion has been considered of importance in the description of the magnetism in a new antiferromagnet, *viz.* $[Cu(HF_2)(pyz)_2]BF_4$ (pyz is pyrazine; Manson *et al.*, 2006).

Compound (I) contains four independent $[HF_2]^-$ anions all lying in general positions, with F···F distances in the range 2.287 (2)–2.291 (2) Å, although the degree of asymmetry varies markedly between them (Table 1 and Fig. 1). The
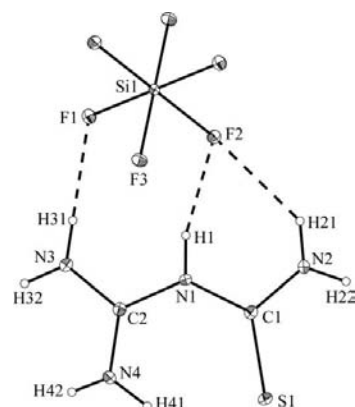

Figure 3
A view of the cation and anion in (II), showing the atom-labelling scheme. Unlabelled atoms are generated by the symmetry operation $(-x, -y + 2, -z)$. Displacement ellipsoids are drawn at the 30% probability level. Hydrogen bonds are denoted by dashed lines. $R_2^2(8)$ and $R_2^1(6)$ graph-set motifs are formed (Etter *et al.*, 1990).

compound adopts a layered arrangement (Fig. 2*a*) and each layer is stabilized by N—H···F hydrogen bonds (Fig. 2*b*). Within each layer, two cation layers can be distinguished, linked by the anions (Fig. 2*b*). Hydrogen-bonding motifs characteristic of 1-(diaminomethylene)thiouron-1-ium salts (Janczak & Perpétuo, 2008*b*) are present, such as $R_2^1(6)$ (Etter *et al.*, 1990), with two ammine groups acting as the donors and an F atom from an $[HF_2]^-$ anion acting as acceptor.

Compound (II) comprises 1-(diaminomethylene)thiouron-1-ium cations and hexafluoridosilicate anions which lie across inversion centres (Fig. 3). The anion is linked *via* N—H···F hydrogen bonds to six $[HATUH]^+$ cations; the symmetry-independent cation and five cations are related by the following symmetry operations: $(-x, 2 - y, -z)$, $(1 - x, 1 - y, -z)$, $(-x, 2 - y, 1 - z)$, $(1 - x, 1 + y, z)$ and $(x, y, z - 1)$. The distortion of the anion from ideal O_h symmetry was rationalized in terms of hydrogen bonding [*e.g.* in the case reported by Reiß (1998), the F atom bonded to the Si atom with the shortest Si—F bond does not participate in any hydrogen bond]. In the case of (II), the distortion of the anion is towards D_{2h} and its dependence on the hydrogen-bonding network (Table 3) is not as clear as in the case reported by Reiß (1998). The deformation in (II) affects the Si—F bond lengths, but not the F—Si—F angles. For comparison, in cubic $K_2[SiF_6]$ no such anion distortion is observed and the Si—F distance is 1.683 (2) Å (Loehlin, 1984). The geometric parameters of the 1-(diaminomethylene)thiouron-1-ium cation in both (I) and (II) are normal and comparable with those previously reported for other salts (Janczak & Perpétuo, 2008*b*; Perpétuo & Janczak, 2008).

In (II), the hydrogen-bonded layers lie perpendicular to [110] (Fig. 4*a*). Within each such layer, $[HATUH]^+$ cations interact with $[SiF_6]^{2-}$ anions through N—H···F hydrogen bonds (Fig. 4*b*) with the formation of many specific graph-set motifs (Etter *et al.*, 1990), such as $R_2^2(8)$, $R_2^1(6)$ [also present in (I)] and $R_1^2(4)$ [absent from (I)].

It is suspected that the reaction of HATU with hydrofluoric acid carried out at different concentrations of the reagents and
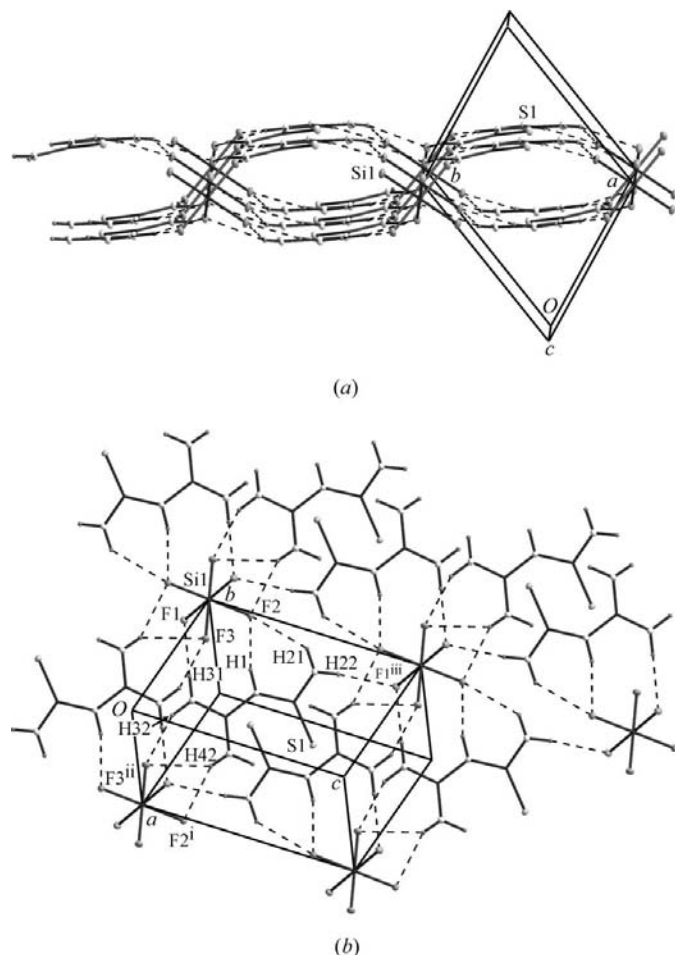
Figure 4
Two different views, (*a*) and (*b*), of one of the hydrogen-bonded layers present in (II). Hydrogen bonds are denoted by dashed lines. [Symmetry codes: (i) $x + 1$, $y - 1$, z; (ii) $-x + 1$, $-y + 1$, $-z$; (iii) x, y, $z + 1$.]

at different temperatures will yield further interesting hydrogen-bonded systems, although our preliminary investigations have so far invariably led to compound (I).

Experimental

Caution! Hydrogen fluoride is extremely corrosive and harmful to human tissue, causing painful burns which heal with difficulty. All handling should be conducted in an efficient fume hood and suitable body protection should be worn. Suitable palliative preparations, such as calcium gluconate gel, should be to hand before work with HF commences.

For the synthesis of (I), HATU (Aldrich) (0.05 g) was dissolved in concentrated (40%) hydrofluoric acid in a Teflon vessel. On slow evaporation of the solution, crystals of (I) in the form of colourless plates were obtained. Compound (I) reacts readily with glass and if stored in air it readily loses hydrogen fluoride gas. Compound (I) is also obtained when 5% hydrofluoric acid is used as the substrate.

The same reaction with an excess of 5% hydrofluoric acid carried out in a quartz glass vessel yields crystalline (II) (colourless blocks). On recrystallization of (I) from water, carried out in a quartz glass vessel, a third crystalline compound, (III), was obtained in the form of colourless blocks. Compound (III) seems to be [HATUH]$_3$[SiF$_6$]-

F·H$_2$O [$P2_1/n$, $a = 8.212$ (3) Å, $b = 22.234$ (5) Å, $c = 11.806$ (4) Å, $\beta = 100.81$ (3)°]. Compound (III) comprises three symmetry-independent [HATUH]$^+$ cations, one [SiF$_6$]$^{2-}$ anion lying in a general position and apparently one water molecule along with one fluoride anion disordered over two sites with half-occupancy factors. The assumed structure model is arbitrary and it is difficult to prove it unambiguously using standard analytical methods.

ESI–MS spectra were collected on a micrOTOF-Q device for samples prepared as solutions in methanol. Positive ions were analysed. For (I) and (II) the most intensive peak was observed at m/Z 119.0 (ascribed to the [HATUH]$^+$ cation). For comparison purposes, spectra for HATU and other halides of HATU were also collected. Hydrogen chloride, hydrogen bromide and hydrogen iodide were prepared according to the literature procedures of Perpétuo & Janczak (2008). As shown below, their MS spectra lead to some observations worth noting. In the MS spectrum collected for HATU, a very weak peak [$M + 1$] at m/Z 119.0 is detected. The highest peak is observed at m/Z 304.3. A similar peak at m/Z 304.3 is observed for hydrogen chloride. In the MS spectrum collected for hydrogen bromide and hydrogen iodide, the peak at m/Z 119.0 is more visible than for HATU. For hydrogen iodide, the most intense peak in the MS spectrum is at m/Z 365.0 (with characteristic isotope distribution), which is the sum of double the mass of a HATU molecule, a single H$^+$ cation and a single I$^-$ anion. Similarly for hydrogen bromide, the highest peak in the MS spectrum (with characteristic isotope distribution) corresponds to double the sum of the mass of a HATU molecule, a single H$^+$ cation and a single Br$^-$ anion.

Compound (I)

Crystal data

C$_2$H$_7$N$_4$S$^+$·HF$_2^-$	$\gamma = 104.50$ (3)°
$M_r = 158.18$	$V = 1337.5$ (8) Å^3
Triclinic, $P\bar{1}$	$Z = 8$
$a = 8.199$ (3) Å	Mo $K\alpha$ radiation
$b = 12.203$ (4) Å	$\mu = 0.44$ mm^{-1}
$c = 14.158$ (4) Å	$T = 100$ K
$\alpha = 100.78$ (3)°	$0.19 \times 0.09 \times 0.07$ mm
$\beta = 93.87$ (3)°	

Data collection

Oxford Diffraction KM-4-CCD area-detector diffractometer	20685 measured reflections
	7461 independent reflections
Absorption correction: analytical (*CrysAlis RED*; Oxford Diffraction, 2006)	5387 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.051$
$T_{\min} = 0.897$, $T_{\max} = 0.979$	

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.056$	421 parameters
$wR(F^2) = 0.129$	Only H-atom coordinates refined
$S = 1.01$	$\Delta\rho_{\max} = 0.41$ e Å^{-3}
7461 reflections	$\Delta\rho_{\min} = -0.29$ e Å^{-3}

Compound (II)

Crystal data

2C$_2$H$_7$N$_4$S$^+$·SiF$_6^{2-}$	$\gamma = 66.15$ (3)°
$M_r = 380.44$	$V = 345.2$ (3) Å^3
Triclinic, $P\bar{1}$	$Z = 1$
$a = 6.537$ (3) Å	Mo $K\alpha$ radiation
$b = 7.390$ (3) Å	$\mu = 0.55$ mm^{-1}
$c = 7.884$ (4) Å	$T = 100$ K
$\alpha = 83.65$ (3)°	$0.25 \times 0.23 \times 0.09$ mm
$\beta = 83.44$ (3)°	

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
F21—H11F···F11	0.92 (3)	1.38 (3)	2.291 (2)	172 (3)
F22—H12F···F12	1.10 (3)	1.20 (3)	2.291 (2)	177 (3)
F23—H13F···F13	1.14 (3)	1.16 (3)	2.287 (2)	172 (3)
F24—H14F···F14	1.06 (3)	1.23 (3)	2.289 (2)	177 (3)
N11—H11···F11	0.87 (3)	1.89 (3)	2.711 (3)	157 (3)
N21—H211···F11	0.82 (3)	2.10 (3)	2.823 (3)	148 (3)
N21—H221···F21[i]	0.88 (3)	2.00 (3)	2.873 (3)	179 (3)
N31—H311···F12	0.86 (3)	1.90 (3)	2.732 (3)	166 (3)
N31—H321···F24	0.81 (3)	2.24 (3)	2.955 (3)	147 (3)
N41—H421···F24	0.79 (3)	2.14 (3)	2.867 (3)	152 (3)
N12—H12···F12[ii]	0.83 (3)	1.96 (3)	2.744 (3)	159 (3)
N22—H212···F12[ii]	0.86 (3)	1.99 (3)	2.768 (3)	151 (3)
N22—H222···F22[iii]	0.80 (3)	2.05 (3)	2.847 (3)	173 (3)
N32—H312···F11[ii]	0.87 (3)	1.89 (3)	2.734 (3)	165 (3)
N32—H322···F13	0.83 (3)	2.24 (3)	2.953 (3)	144 (3)
N42—H422···F13	0.76 (3)	2.16 (3)	2.862 (3)	153 (3)
N13—H13···F14	0.87 (3)	1.87 (3)	2.708 (3)	162 (3)
N23—H213···F14	0.86 (3)	2.01 (3)	2.796 (3)	151 (3)
N23—H223···F24[iii]	0.86 (3)	1.99 (3)	2.851 (3)	173 (3)
N33—H323···F21[ii]	0.84 (3)	2.18 (3)	2.940 (3)	150 (3)
N33—H313···F23	0.80 (3)	1.98 (3)	2.768 (3)	166 (3)
N43—H423···F21[ii]	0.82 (3)	2.20 (3)	2.928 (3)	149 (3)
N43—H423···F22[ii]	0.82 (3)	2.53 (3)	2.958 (3)	114 (3)
N14—H14···F23	0.82 (3)	2.02 (3)	2.789 (3)	156 (3)
N24—H214···F23	0.87 (3)	1.99 (3)	2.788 (3)	151 (3)
N24—H224···F13[iv]	0.86 (3)	1.96 (3)	2.821 (3)	174 (3)
N34—H324···F22	0.81 (3)	2.24 (3)	2.933 (3)	145 (3)
N34—H314···F14	0.86 (3)	1.92 (3)	2.750 (3)	163 (3)
N44—H424···F21	0.75 (3)	2.52 (3)	2.891 (3)	112 (3)
N44—H424···F22	0.75 (3)	2.19 (3)	2.865 (3)	151 (3)

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

Table 2
Selected geometric parameters (Å, °) for (II).

Si1—F1	1.6911 (11)	Si1—F3	1.6788 (11)
Si1—F2	1.7086 (10)		
F1—Si1—F2	90.02 (5)	F3—Si1—F2	90.12 (5)
F3—Si1—F1	89.77 (5)		

Table 3
Hydrogen-bond geometry (Å, °) for (II).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1···F2	0.85 (2)	2.01 (2)	2.823 (2)	162 (2)
N2—H22···F1[i]	0.85 (2)	2.10 (2)	2.938 (2)	173 (2)
N2—H21···F2	0.87 (2)	2.31 (2)	3.023 (2)	139 (2)
N3—H31···F1	0.86 (2)	2.00 (2)	2.864 (2)	179 (2)
N3—H32···F3[ii]	0.89 (2)	2.05 (2)	2.873 (2)	153 (2)
N4—H42···F2[iii]	0.76 (2)	2.32 (2)	2.978 (2)	146 (2)
N4—H42···F3[ii]	0.76 (2)	2.38 (2)	3.021 (2)	143 (2)

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

(Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

Data collection

Oxford Diffraction KM-4-CCD area-detector diffractometer	4487 measured reflections
	1837 independent reflections
Absorption correction: analytical (*CrysAlis RED*; Oxford Diffraction, 2006)	1582 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.021$
$T_{min} = 0.870$, $T_{max} = 0.953$	

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.026$	125 parameters
$wR(F^2) = 0.071$	All H-atom parameters refined
$S = 1.01$	$\Delta\rho_{max} = 0.38$ e Å^{-3}
1837 reflections	$\Delta\rho_{min} = -0.28$ e Å^{-3}

In (I), the H-atom coordinates were freely refined, with $U_{iso}(H) = 1.2U_{eq}$(nearest F atom) or $1.2U_{eq}(N)$. The range of N—H bond lengths is 0.75 (3)–0.88 (3) Å for (I) and the highest peak in the difference map (0.41 e Å^{-3}) is located 0.82 Å from atom S4. In (II), all H-atom parameters were freely refined. The range of N—H bond lengths is 0.76 (2)–0.89 (2) Å, and the highest peak in the difference map (0.38 e Å^{-3}) is located 0.59 Å from atom N1 and 0.82 Å from atom C1.

For both compounds, data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2006); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg & Putz, 2005) and *SHELXTL-NT*

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