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Impact of the anion and chalcogen on the crystal structure and properties of 4,6-dimethyl-2-pyrimido(thio)onium halides

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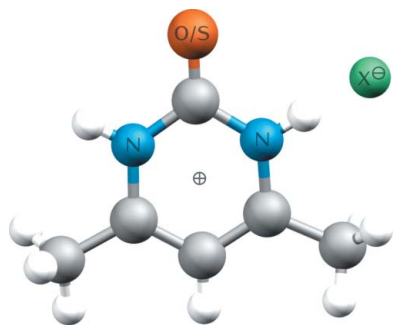
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By the reaction of urea or thiourea, acetylacetone and hydrogen halide (HF, HBr or HI), we have obtained seven new 4,6-dimethyl-2-pyrimido(thio)onium salts, which were characterized by single-crystal X-ray diffraction, namely, 4,6-dimethyl-2-oxo-2,3-dihydropyrimidin-1-ium bifluoride, $C_6H_9N_2O^+ \cdot HF_2^-$ or (dmpH) F_2H , 4,6-dimethyl-2-oxo-2,3-dihydropyrimidin-1-ium bromide, $C_6H_9N_2O^+ \cdot Br^-$ or (dmpH)Br, 4,6-dimethyl-2-oxo-2,3-dihydropyrimidin-1-ium iodide, $C_6H_9N_2O^+ \cdot I^-$ or (dmpH)I, 4,6-dimethyl-2-oxo-2,3-dihydropyrimidin-1-ium iodide–urea (1/1), $C_6H_9N_2O^+ \cdot I^- \cdot CH_4N_2O$ or (dmpH)I–ur, 4,6-dimethyl-2-sulfanylidene-2,3-dihydropyrimidin-1-ium bifluoride–thiourea (1/1), $C_6H_9N_2S^+ \cdot HF_2^- \cdot CH_4N_2S$ or (dmptH) $F_2H \cdot tu$, 4,6-dimethyl-2-sulfanylidene-2,3-dihydropyrimidin-1-ium bromide, $C_6H_9N_2S^+ \cdot Br^-$ or (dmptH)Br, and 4,6-dimethyl-2-sulfanylidene-2,3-dihydropyrimidin-1-ium iodide, $C_6H_9N_2S^+ \cdot I^-$ or (dmptH)I. Three HCl derivatives were described previously in the literature, namely, 4,6-dimethyl-2-oxo-2,3-dihydropyrimidin-1-ium chloride, (dmpH)Cl, 4,6-dimethyl-2-sulfanylidene-2,3-dihydropyrimidin-1-ium chloride monohydrate, (dmptH)–Cl·H₂O, and 4,6-dimethyl-2-sulfanylidene-2,3-dihydropyrimidin-1-ium chloride–thiourea (1/1), (dmptH)Cl·tu. Structural analysis shows that in 9 out of 10 of these compounds, the ions form one-dimensional chains or ribbons stabilized by hydrogen bonds. Only in one compound are parallel planes present. In all the structures, there are charge-assisted $N^+ \cdots H \cdots X^-$ hydrogen bonds, as well as weaker $C_{Ar}^+ \cdots H \cdots X^-$ and $\pi^+ \cdots X^-$ interactions. The structures can be divided into five types according to their hydrogen-bond patterns. All the compounds undergo thermal decomposition at relatively high temperatures (150–300 °C) without melting. Four oxopyrimidinium salts containing a $\pi^+ \cdots X^- \cdots \pi^+$ sandwich-like structural motif exhibit luminescent properties.

1. Introduction

It is well known that 1,3-dicarbonyl compounds condense with ureas and thioureas to give 2-pyrimidone and 2-pyrimidothione derivatives, respectively (Hale, 1914). Therefore 4,6-dimethyl-2-pyrimido(thio)onium salts can be easily prepared by condensation of acetylacetone with urea or thiourea in the presence of the appropriate acid. To our surprise, only the structures of chloride salts have been deposited to the Cambridge Structural Database (Groom *et al.*, 2016) so far (Lee *et al.*, 1984; Battaglia *et al.*, 1986; Seth *et al.*, 1996; Gaye *et al.*, 2009). When a cation is deprotonated to neutral 4,6-dimethyl-2-pyrimido(thio)ne, it can serve as an *S*- and *N*-donor ligand (Lang *et al.*, 2009).

The influence of anion type on crystal structure has been of increasing scientific interest for many years (*e.g.* Awaleh *et al.*, 2006; Altaf & Stoeckli-Evans, 2010). Recently, we have examined a series of mercury(II) complexes with different halides and thiourea ligands (Okuniewski *et al.*, 2015; Rosiak



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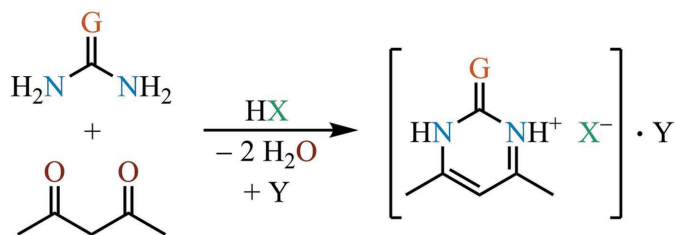


Figure 1

Synthetic procedure for the presented compounds. $G = \text{O}$ or S ; $X = \text{F}_2\text{H}$, Cl , Br or I ; $Y = \text{nil}$, H_2O , $\text{OC}(\text{NH}_2)_2$ or $\text{SC}(\text{NH}_2)_2$. The combinations of G , X and Y , and the corresponding compound numbers are summarized in Table 1.

et al., 2018). In our present studies, we were interested in finding out how the halide anion influences the crystal packing and properties of 4,6-dimethyl-2-pyrimido(thio)anium salts. The chosen compounds fulfill the basic requirements for industrial reagents – they are simple to synthesize, stable under ambient conditions and relatively cheap. Similar studies were performed by Owczarzak *et al.* (2013) on a simpler example, namely, commercially available 2-pyrimidothione was reacted with various acids to give the corresponding salts.

During our studies we synthesized 4,6-dimethyl-2-pyrimidonium salts, as well as their sulfur derivatives, so we can also obtain some information on the influence of a chalcogen atom on the crystal structure. The compounds are (dmpH) F_2H , (1), (dmpH)Br, (3), (dmpH)I, (4), (dmpH)I-ur, (5), (dmptH) F_2H -tu, (6), (dmptH)Br, (9), and (dmptH)I, (10), where dmpH is 4,6-dimethyl-2-oxo-2,3-dihydropyrimidin-1-ium or 4,6-dimethyl-2-pyrimidonium, dmptH is 4,6-dimethyl-2-sulfanylidene-2,3-dihydropyrimidin-1-ium or 4,6-dimethyl-2-pyrimidothionium, ur is urea and tu is thiourea. Most of the syntheses described in other articles were performed using water as solvent. Changing this to acetone in some cases allowed faster deposition of crystals and there was no need to heat the reaction mixture.

Besides basic research interest, similar compounds play an important pharmacological role. Thiopyrimidone derivatives (such as thiouracil derivatives) exhibit significant biological activity (Nagasaka & Hidaka, 1976). Propylthiouracil inhibits the thyroperoxidase enzyme and is one of the most frequently used thyrostatic drugs (Boron & Boulpaep, 2016).

2. Experimental

Melting points were measured on an SMP30 (Stuart, Stone, UK) and were uncorrected. The solid-state IR spectra were measured using a Nicolet iS50 FT-IR spectrometer equipped with a Specac Quest single-reflection diamond attenuated total reflectance (ATR) accessory controlled by Omnic computer software in the range 4000–400 cm^{-1} . The solid-state luminescence spectra were measured using an Opolette 355LD tunable laser as an excitation source ($\lambda_{\text{ex}} = 320 \text{ nm}$) and a Hamamatsu R928 photomultiplier as a detector.

2.1. Synthesis and crystallization

The described salts were synthesized by dissolving urea (1.00 mmol, 0.60 g) or thiourea (1.00 mmol, 0.76 g) and

Table 1

Compounds under consideration.

For an explanation of the symbols, see Fig. 1.

	G	X^-	Y	Reference
(1)	O	F_2H^-	–	This work
(2)	O	Cl^-	–	Lee <i>et al.</i> (1984)
(3)	O	Br^-	–	This work
(4)	O	I^-	–	This work
(5)	O	I^-	$\text{OC}(\text{NH}_2)_2$	This work
(6)	S	F_2H^-	$\text{SC}(\text{NH}_2)_2$	This work
(7)	S	Cl^-	H_2O	Battaglia <i>et al.</i> (1986) and Seth <i>et al.</i> (1996)
(8)	S	Cl^-	$\text{SC}(\text{NH}_2)_2$	Gaye <i>et al.</i> (2009)
(9)	S	Br^-	–	This work
(10)	S	I^-	–	This work

acetylacetone (9.68 mmol, 1.00 ml) in acetone (10 ml). Subsequently, 2.00 ml of the appropriate concentrated acid (HF, HCl, HBr or HI) were added to the mixture, which was stirred for several minutes. The solution was then left to evaporate slowly at room temperature. After a few hours, colourless crystals of (1)–(5) and pale-yellow crystals of (6), (7), (9) and (10) suitable for X-ray diffraction were isolated from the reaction mixture. We were unable to obtain crystals of (8) using this procedure. Crystals of (4) and (5) were separated manually from the single reaction mixture under a UV lamp. This was possible because (4) was luminescent, while (5) was not. The yields were calculated based on the masses of the isolated crystals.

For compound numbering and the synthetic scheme, see Fig. 1 and Table 1. Analytical data for the obtained products are presented in the following section.

2.2. Analytical data

For (1), yield 83%; $T_{\text{dec}} = 150\text{--}170^\circ\text{C}$; IR (ATR, cm^{-1}): $\nu_{\text{C=O}}$ 1750; $\lambda_{\text{max,em}}$ (nm): 419, 504. For (2) (see Lee *et al.*, 1984), yield 91%; $T_{\text{dec}} = 240\text{--}280^\circ\text{C}$; IR (ATR, cm^{-1}): $\nu_{\text{C=O}}$ 1734; $\lambda_{\text{max,em}}$ (nm): 563. For (3), yield 85%; $T_{\text{dec}} = 250\text{--}290^\circ\text{C}$; IR (ATR, cm^{-1}): $\nu_{\text{C=O}}$ 1736; $\lambda_{\text{max,em}}$ (nm): 562. For (4), yield 91%; $T_{\text{dec}} = 270\text{--}290^\circ\text{C}$; IR (ATR, cm^{-1}): $\nu_{\text{C=O}}$ 1744; $\lambda_{\text{max,em}}$ (nm): 415, 683. For (5), yield 5%; $T_{\text{dec}} = 150\text{--}180^\circ\text{C}$; IR (ATR, cm^{-1}): $\nu_{\text{C=O(ur)}}$ 1677, $\nu_{\text{C=O(dmpH)}}$ 1745. For (6), yield 86%; $T_{\text{dec}} = 170\text{--}180^\circ\text{C}$; IR (ATR, cm^{-1}): $\nu_{\text{C=S(tur)}}$ 730, $\nu_{\text{C=S(dmptH)}}$ 844. For (7) [see Battaglia *et al.* (1986) and Seth *et al.* (1996)]: yield 94%; $T_{\text{dec}} = 200\text{--}235^\circ\text{C}$; IR (ATR, cm^{-1}): $\nu_{\text{C=S}}$ 861. For (8), see Gaye *et al.* (2009). For (9), yield 83%; $T_{\text{dec}} = 190\text{--}240^\circ\text{C}$; IR (ATR, cm^{-1}): $\nu_{\text{C=S}}$ 844. For (10), yield 91%; $T_{\text{dec}} = 200\text{--}210^\circ\text{C}$; IR (ATR, cm^{-1}): $\nu_{\text{C=S}}$ 831.

2.3. Refinement

Crystal data, data collection and structure refinement details for (1), (3)–(6), (9) and (10) are summarized in Table 2. Most H atoms were placed at calculated positions ($\text{C–H} = 0.95\text{--}0.98 \text{ \AA}$ and $\text{N–H} = 0.88 \text{ \AA}$) and treated as riding on their parent atoms, with $U_{\text{iso}}(\text{H})$ values set at $1.2\text{--}1.5U_{\text{eq}}(\text{C})$ or $1.2U_{\text{eq}}(\text{N})$. The H atoms of the methyl groups on mirror planes

Table 2
Experimental details.

Experiments were carried out at 120 K with Mo $K\alpha$ radiation using a Stoe IPDS 2T diffractometer. Absorption correction was by integration [*X-RED32* (Stoe & Cie, 2009), analogous to Coppens (1970)]. For (4), (5) and (9), H-atom parameters were constrained, and for (1), (3), (6) and (10), H atoms were treated by a mixture of independent and constrained refinement.

	(1)	(3)	(4)	(5)
Crystal data				
Chemical formula	$C_6H_9N_2O^+ \cdot HF_2^-$	$C_6H_9N_2O^+ \cdot Br^-$	$C_6H_9N_2O^+ \cdot I^-$	$C_6H_9N_2O^+ \cdot I^- \cdot CH_4N_2O$
M_r	164.16	205.06	252.05	312.11
Crystal system, space group	Monoclinic, $P2_1/m$	Orthorhombic, $Pnma$	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/c$
a, b, c (Å)	7.9253 (16), 5.9962 (14), 8.433 (2)	14.4984 (18), 6.722 (2), 8.113 (7)	7.1803 (10), 7.2139 (18), 8.6574 (12)	8.772 (1), 11.5579 (10), 14.0700 (16)
α, β, γ (°)	90, 113.551 (18), 90	90, 90, 90	90, 100.603 (11), 90	90, 127.378 (7), 90
V (Å ³)	367.39 (16)	790.6 (7)	440.78 (14)	1133.6 (2)
Z	2	4	2	4
μ (mm ⁻¹)	0.14	5.13	3.57	2.81
Crystal size (mm)	0.25 × 0.04 × 0.04	0.35 × 0.20 × 0.03	0.66 × 0.37 × 0.14	0.49 × 0.42 × 0.19
Data collection				
T_{min}, T_{max}	0.949, 0.983	0.639, 0.905	0.274, 0.624	0.258, 0.579
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	6035, 1075, 1009	10482, 1130, 971	5622, 1166, 1143	16324, 2995, 2800
R_{int}	0.028	0.050	0.066	0.050
($\sin \theta/\lambda$) _{max} (Å ⁻¹)	0.688	0.682	0.682	0.682
Refinement				
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.035, 0.096, 1.05	0.031, 0.096, 1.09	0.059, 0.165, 1.09	0.032, 0.093, 1.07
No. of reflections	1075	1130	1166	2995
No. of parameters	84	75	49	129
No. of restraints	1	12	0	0
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å ⁻³)	0.39, -0.32	0.74, -0.59	1.55, -1.29	0.84, -1.25
	(6)	(9)	(10)	
Crystal data				
Chemical formula	$C_6H_9N_2S^+ \cdot F_2H^- \cdot CH_4N_2S$	$C_6H_9N_2S^+ \cdot Br^-$	$C_6H_9N_2S^+ \cdot I^-$	
M_r	256.34	221.12	268.11	
Crystal system, space group	Monoclinic, $P2_1/m$	Monoclinic, $C2/c$	Orthorhombic, $Cmcm$	
a, b, c (Å)	6.3876 (11), 8.8268 (13), 10.500 (2)	8.4675 (11), 14.9142 (19), 6.8814 (9)	8.7198 (14), 15.095 (3), 7.0716 (11)	
α, β, γ (°)	90, 99.355 (15), 90	90, 101.575 (10), 90	90, 90, 90	
V (Å ³)	584.15 (17)	851.35 (19)	930.8 (3)	
Z	2	4	4	
μ (mm ⁻¹)	0.46	5.02	3.60	
Crystal size (mm)	0.32 × 0.2 × 0.07	0.21 × 0.14 × 0.04	0.17 × 0.12 × 0.05	
Data collection				
T_{min}, T_{max}	0.853, 0.967	0.262, 0.740	0.520, 0.837	
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	3316, 1532, 1375	5070, 933, 871	7434, 708, 661	
R_{int}	0.047	0.118	0.058	
($\sin \theta/\lambda$) _{max} (Å ⁻¹)	0.669	0.639	0.680	
Refinement				
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.071, 0.220, 1.18	0.064, 0.168, 1.05	0.025, 0.060, 1.07	
No. of reflections	1532	933	708	
No. of parameters	80	49	42	
No. of restraints	0	0	6	
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å ⁻³)	0.55, -0.49	2.21, -1.62	1.10, -0.88	

Computer programs: *X-AREA* (Stoe & Cie, 2009), *X-RED32* (Stoe & Cie, 2009), *SHELXT* (Sheldrick, 2015a), *SHELXL2018* (Sheldrick, 2015b) and *OLEX2* (Dolomanov *et al.*, 2009).

were found from difference maps and constrained with C—H = 0.980 (1) Å and H...H = 1.600 (1) Å.

3. Results and discussion

X-ray structural analysis revealed that all the compounds obtained consist of 4,6-dimethyl-2-pyrimidonium cations or

their sulfur analogs and the relevant halide anions. When HF was used in the synthesis, this ion is bifluoride, HF_2^- , and in other cases, it is a simple Cl^- , Br^- or I^- ion. Also, urea, thiourea or water molecules have been incorporated in some structures. For the numbering of the compounds, see Fig. 1 and Table 1. Besides the seven new compounds, *viz.* (1), (3)–(6), (9) and (10), we will also discuss the already known chloride

analogues (dmpH)Cl, (2), (dmptH)Cl·H₂O, (7), and (dmptH)Cl·tu, (8). Appropriate references are summarized in Table 1.

Despite the analogous molecular structures, the discussed compounds crystallize in as many as four different space groups of the monoclinic system [compounds (1), (4)–(6) and (9)] and three of the orthorhombic system [compounds (2), (3), (7), (8) and (10)]. Only compound (7) crystallizes in a noncentrosymmetric space group (*Pca2*₁).

Due to this variety of space groups, only one pair of isostructural compounds can be found, *i.e.* (2) and (3). The unit-cell identity parameter (Fábíán & Kálmán, 1999; for identical unit cells $\Pi = 0$) calculated with our algorithm (Okuniewski, 2018) is very small, *i.e.* $\Pi = 0.014$. We have also manually calculated the isostructurality index *I'* (taking into account only heavy atoms) according to the formula of Kubicki & Szafranski (1998) (for two identical structures, $I' = 1$). In this case, $I' = 0.981$ (for the space group *Pnma*, the parameter $q = {}^{64}I_7$).

Hydrogen-bonding patterns were analyzed with standard settings of *Mercury* (Version 4.3.0; Macrae *et al.*, 2020), but ‘Require hydrogen atom to be present’ was turned on and ‘unclassified F’ was checked as an acceptor. In all the structures presented here, there are strong charge-assisted N⁺–H···X[−] hydrogen bonds connecting heterocyclic cations and halide anions. We can distinguish five types of hydrogen-bond patterns (denoted **A–E**, see Fig. 2). In types **A** and **B**, the only hydrogen bonds present are those mentioned before. They allow the formation of straight (**A**) or zigzag (**B**) noncentrosymmetric chains (however, the overall structures are centrosymmetric). In types **C** and **D**, additional urea and

Table 3
Hydrogen-bond geometry (Å, °) for (1).

<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···F1	0.88	1.75	2.6240 (15)	175

Table 4
Hydrogen-bond geometry (Å, °) for (3).

<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···Br1	0.88	2.41	3.284 (2)	174
N6–H6···Br1 ¹	0.88	2.43	3.308 (3)	176

Symmetry code: (i) $x + \frac{1}{2}, y, -z + \frac{3}{2}$.

Table 5
Hydrogen-bond geometry (Å, °) for (4).

<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···I1	0.88	2.70	3.571 (7)	170

thiourea molecules, respectively, are incorporated, allowing the formation of further strong hydrogen bonds (with cations, anions and each other). As a result, centrosymmetric ribbons are formed. The urea molecules in type **C** are arranged in such a way that weak bifurcated N–H···O interactions are preferred in contrast to thiourea in type **D**, where S···S contacts play a more important role. In the case of type **E**, containing additional water molecules, hydrogen-bonded planes are formed. These planes are noncentrosymmetric, as is the whole structure. Hydrogen-bond parameters are summarized in Tables 3–9. The atom-numbering schemes differ

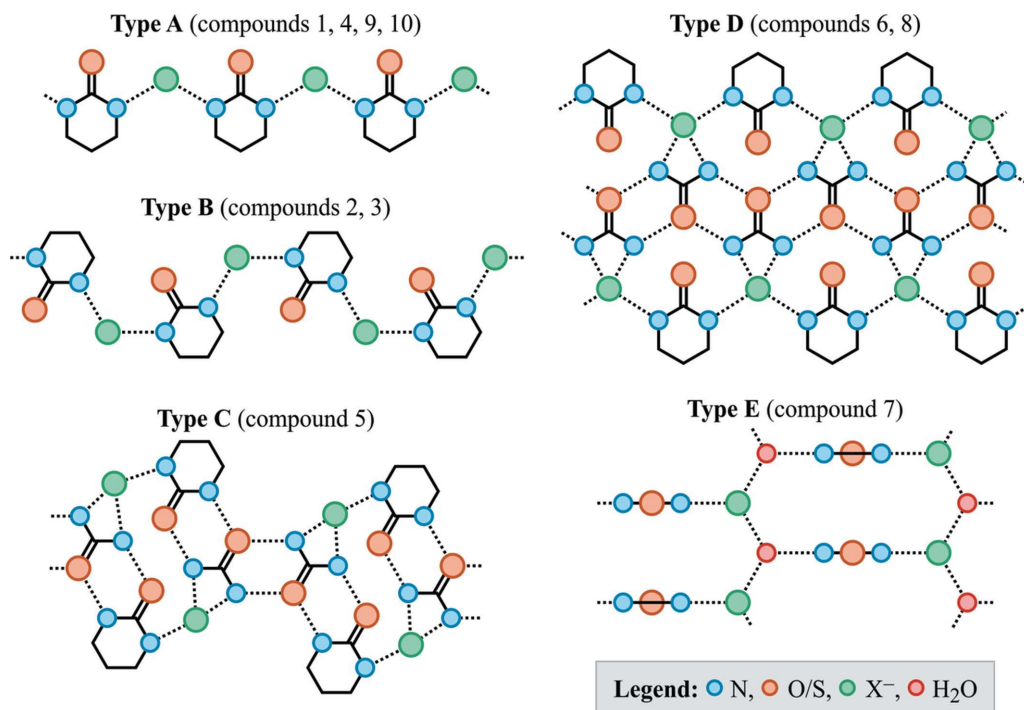


Figure 2

Schematic representation of the hydrogen-bond patterns present in the described compounds. Methyl groups and H atoms have been omitted for clarity. Type **A–D** structures are depicted perpendicular to the direction of chain/ribbon propagation, while the **E** structure is shown perpendicular to the hydrogen-bond plane, so that heterocyclic cations are seen from the ‘bottom’ (orange disc with stroke) or from ‘above’ (otherwise).

Table 6
Hydrogen-bond geometry (Å, °) for (5).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$N2-H2 \cdots I1$	0.88	2.59	3.4692 (19)	173
$N6-H6 \cdots O1U$	0.88	1.80	2.666 (3)	167
$N1U-H1UA \cdots O1$	0.88	2.21	3.070 (3)	167
$N1U-H1UB \cdots I1^i$	0.88	3.11	3.883 (2)	148
$N2U-H2UA \cdots O1U^{ii}$	0.88	2.06	2.940 (3)	179
$N2U-H2UB \cdots I1^i$	0.88	2.71	3.565 (2)	166

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

Table 7
Hydrogen-bond geometry (Å, °) for (6).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$N1T-H1TA \cdots F1$	0.88	1.99	2.874 (4)	179
$N1T-H1TB \cdots S1T^i$	0.88	2.66	3.528 (3)	170
$N2-H2 \cdots F1$	0.88	1.76	2.610 (4)	163

Symmetry code: (i) $-x + 1, -y + 1, -z + 2$.

between the structures due to the different symmetries and compositions, so the reader is referred to the CIF file available online. Rod group symmetry symbols (Kopský & Litvin, 2010) for describing chains and ribbons are as follows: (1) $\rho m11$, (2) and (3) $\rho mc2_1$, (4) and (9) $\rho 211$, (5) $\rho \bar{1}$, (6) $\rho 112_1/m$, (8) ρmcm and (10) $\rho m2m$. The layer group symbol (Kopský & Litvin, 2010) for the planes found in (7) is $p11b$.

Table 8
Hydrogen-bond geometry (Å, °) for (9).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$N2-H2 \cdots Br1$	0.88	2.52	3.399 (4)	174

Table 9
Hydrogen-bond geometry (Å, °) for (10).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$N2-H2 \cdots I1$	0.88	2.68	3.561 (3)	175

Taking a look at the coordination of the anions, we can again distinguish five types of structural motifs (denoted **a–e**, see Fig. 3). In type **a** (most common), the halide anion is sandwiched between two heterocyclic cations ($\pi^+ \cdots X^- \cdots \pi^+$ interaction). All parameters are typical for anion– π interactions (Mooibroek *et al.*, 2008). Additionally, two $N^+ - H \cdots X^-$ hydrogen bonds are present (part of the **A** and **B** type chains). Also, weaker $C_{Ar}^+ - H \cdots X^-$ interactions can be found. Type **b** is similar to **a**, but instead of a single $C_{Ar}^+ - H \cdots X^-$ interaction there are two very weak $C_{Me} - H \cdots X^-$ interactions stabilized by $C_{Ar}^+ - H \cdots O$ interactions. In type **c**, one of the $\pi^+ \cdots X^-$ interactions is substituted with pseudo-ring interactions and a bifurcated urea–iodide hydrogen bond is present. Type **d** is similar to **a**, but the $C_{Ar}^+ - H \cdots X^-$

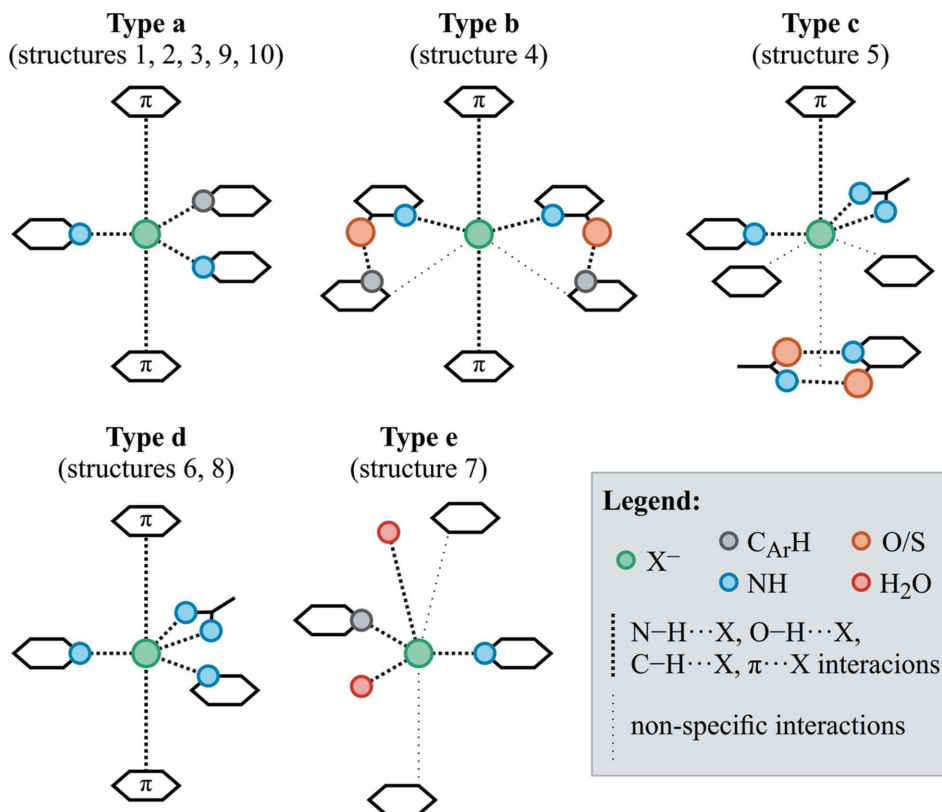


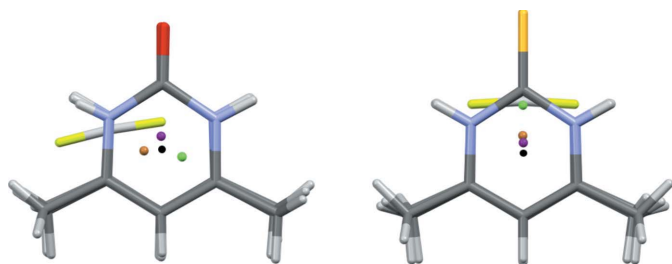
Figure 3
The anion coordination types found in the described structures. As the structures are quite complex, the heterocyclic cations have been simplified as flattened hexagons, urea/thiourea as a flattened trigonal shape and only donor/acceptor atoms/groups are visible. Types **c–e** are found in the cocrystals or the hydrate.

Table 10

 Distances (Å) between halogen and the mean ring planes (p) and centroids (d) of dmpH^+ (or dmptH^+).

 Structure (7) was excluded since it has no sandwich feature. When parameters for the upper and lower plane differ, two values are provided. Hydrogen-bonding motif $R_2^2(8)$ is regarded as the upper ring of the sandwich in structure (5). The shift was calculated using a Pythagorean equation based on the distance to the centroid, d , and the distance perpendicular to the mean plane, p ; $\text{shift} = \sqrt{d^2 - p^2}$. All values are in Å. vdW is van der Waals.

Compound X	(1) F_2H	(2) Cl	(3) Br	(4) I	(5) I	(6) F_2H	(8) Cl	(9) Br	(10) I
Distance $X \cdots p$	2.998	3.334	3.361	3.566	3.559, 3.632	3.188, 3.051	3.323	3.464	3.536
Distance $X \cdots d$	3.054	3.366	3.385	3.601	3.515, 3.530	3.828, 3.279	3.490	3.338	3.545
Type	a	a	a	b	c	d	d	a	a
Symmetry	m on ring	m on ring	m on ring	2 on I	1 (none)	vertical m on F_2H	m on ring and $mm2$ on Cl	2 on Br	m on ring and $mm2$ on I
$R_{\text{vdW}}(X)$ (Mantina <i>et al.</i> , 2009)	1.40	1.74	1.82	1.99	1.99	1.40	1.74	1.82	1.99
Plane proximity	1.598	1.594	1.541	1.576	1.569, 1.642	1.788, 1.651	1.583	1.644	1.546
Shift	0.582	0.463	0.402	0.501	0.558, 0.854	2.119, 1.201	1.067	0.926	0.252


Figure 4

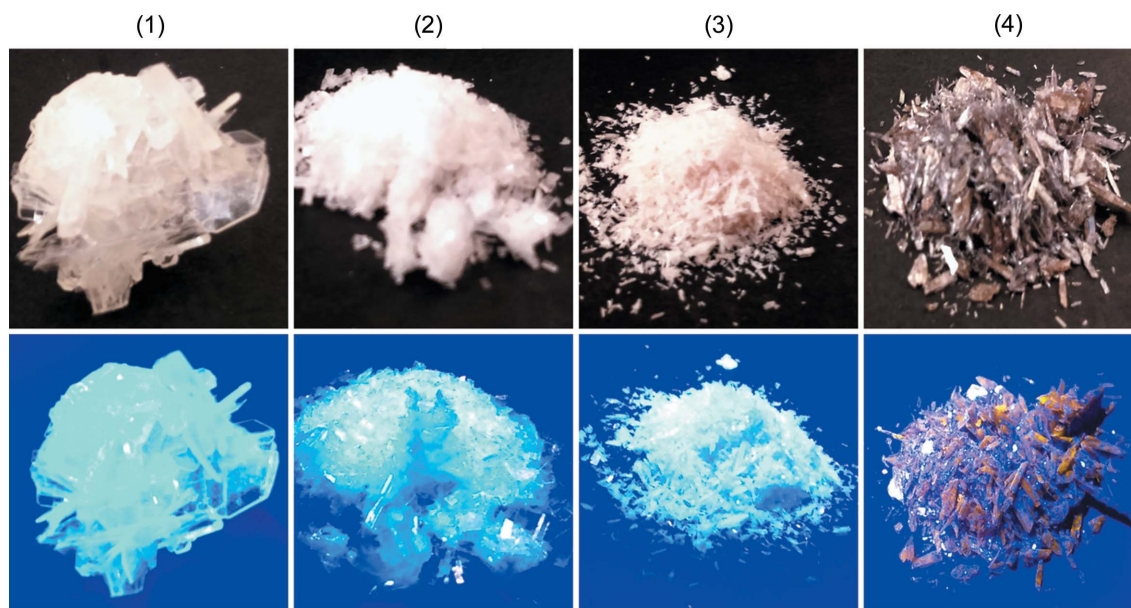
 The superposition of the dmpH^+ and dmptH^+ salts seen in the stack direction. Colour key for anions: pale-green F^- , green Cl^- , brown Br^- and purple I^- . The black dots indicate the geometric centres of the dmpH^+ and dmptH^+ rings.

 interaction is replaced by a bifurcated thiourea–halide hydrogen bond. Type **e** (likewise **E**) is represented by compound (7) and is different because water molecules are present in the structure. Two such molecules form hydrogen bonds to the chloride ion. Additionally, there is one N^+ –

 $\text{H} \cdots \text{Cl}^-$ and one $\text{C}_{\text{Ar}}^+ - \text{H} \cdots \text{Cl}^-$ interaction. Finally, some nonspecific interactions with heterocyclic cations can be found (no $\pi^+ \cdots \text{Cl}^-$ interactions).

 The heavier (bigger) halide anions tend to be located closer to the geometric centre of the cation ring in sandwiches (Fig. 4). This may indicate the diminishing role of electrostatic attractions for heavier halides and the shift of the electric charge centre about the centre of the cation ring towards the N atoms (for numerical values, see Table 10). Plane proximity given in Table 10 was calculated as the distance from the halide to the aromatic plane, corrected for van der Waals radii, so it shows the distance of the plane to ‘the edge’ of the X^- anion. This value is rather uniform and shows no clear tendencies, which indicates no extra interactions. The degree of delocalization of positive charge is likely to be different for oxo and thio derivatives.

We have observed that under UV light compounds (1)–(4) exhibit luminescent properties (Fig. 5). Spectrofluorimetric measurements showed that compounds (1)–(3) gave very


Figure 5

 Photographs of luminescent crystals (1)–(4) in daylight (top) and in *ca* 395 nm UV light (bottom).

broad peaks covering almost the whole visible region with maxima at the blue or green colours (see §2.2). For this reason, those compounds emit pale-blue–white light. The spectrum of compound (4) is more discrete. The largest maximum covers the UV–blue region, but a peak at the red region is also present, which is visible in Fig. 6. After turning off the excitation light, the compounds exhibit phosphorescence that lasts from several seconds for (1) but which disappears almost immediately for (4). Lowering the temperature with liquid nitrogen elongates the glowing time.

4. Conclusions

The reaction of urea (or thiourea) with a *ca* 10-fold molar excess of acetylacetonate in the presence of at least a 30-fold excess of hydrogen halide HX gives the relevant pyrimidonium salts or their cocrystals with still unreacted urea or thiourea. Using a simple one-step synthesis, we obtained seven new crystalline 4,6-dimethyl-2-pyrimido(thio)onium salts, namely, (dmpH)₂F₂H, (dmpH)Br, (dmpH)I, (dmpH)I·ur, (dmptH)₂F₂H·tu, (dmptH)Br and (dmptH)I. Three chloride derivatives were described previously in the literature.

The structure of the simple salts is dictated mainly by strong charge-assisted hydrogen bonds of the N⁺–H···X[−] type, which leads to the linear structures of type **A** (simple chain) and type **B** (zigzag chain). Simple chains exhibit more distant (8.5–9.0 Å) positively charged rings than zigzag chains (7.9–8.1 Å), but are probably destabilized by repulsive contacts of the closer methyl substituents. All simple salts exhibit sandwich-like coordination of the anions due to π⁺···X[−]···π⁺ interaction, between the chains. This is the second structure forming factor. In the case of (5), the sandwich is composed of dmpH⁺ cations, iodide anions and quasi-aromatic R₂²(8) hydrogen-bonded pseudo-rings.

Cocrystals with urea and thiourea cannot follow the same scheme and form structures of type **C** (with urea) and **D** (with thiourea), which are essentially ribbons including the neutral molecules inside charge-assisted hydrogen bonding located at the edges of the ribbon. Type **D** shows short S···S contacts [3.283 and 3.348 Å for (6) and (8), respectively]. The C–S···S

angles are in the range 170–180°. Since one molecule is a cation, one can think of charge-assisted S···S chalcogen bonding due to donor–acceptor interactions regardless of the lack of classical geometry for the electron-density hole and the asymmetry of the electron distribution at the S atoms.

Luminescent properties were observed within the structures where anions were sandwiched between 4,6-dimethyl-2-pyrimidonium cations (π⁺···X[−]···π⁺ interaction). The inclusion of the hydrogen-bond motif R₂²(8) instead of the aromatic ring in the sandwich of (5) caused a significant change in the structure and, for this reason, the compound is not luminescent. Due to quenching ability, all sulfur analogs were also not luminescent. The time of phosphorescence shortens with halide mass and can be extended by lowering the temperature with liquid nitrogen.

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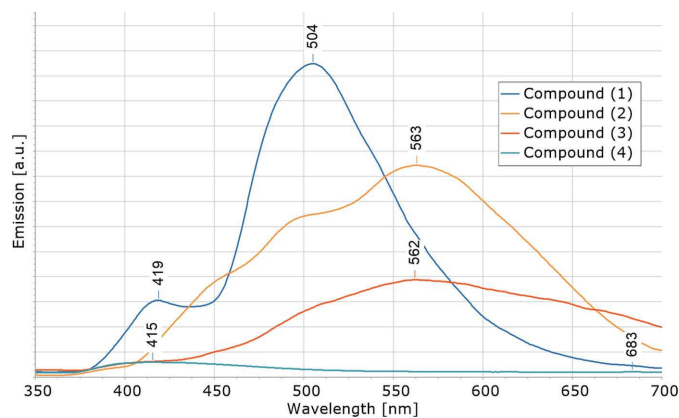


Figure 6

The luminescence spectra of compounds (1)–(4) recorded at 320 nm excitation. For experimental details, see §2.

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supporting information

Acta Cryst. (2020). C76, 468-475 [https://doi.org/10.1107/S2053229620005525]

Impact of the anion and chalcogen on the crystal structure and properties of 4,6-dimethyl-2-pyrimido(thio)onium halides

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Computing details

For all structures, data collection: *X-AREA* (Stoe & Cie, 2009); cell refinement: *X-AREA* (Stoe & Cie, 2009); data reduction: *X-RED32* (Stoe & Cie, 2009); program(s) used to solve structure: *SHELXT* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2018* (Sheldrick, 2015b); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009).

4,6-Dimethyl-2-oxo-2,3-dihydropyrimidin-1-ium bifluoride (1)

Crystal data

$C_6H_9N_2O^+ \cdot HF_2^-$
 $M_r = 164.16$
 Monoclinic, $P2_1/m$
 $a = 7.9253$ (16) Å
 $b = 5.9962$ (14) Å
 $c = 8.433$ (2) Å
 $\beta = 113.551$ (18)°
 $V = 367.39$ (16) Å³
 $Z = 2$

$F(000) = 172$
 $D_x = 1.484$ Mg m⁻³
 Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
 Cell parameters from 1096 reflections
 $\theta = 3.0$ – 29.4 °
 $\mu = 0.14$ mm⁻¹
 $T = 120$ K
 Block, colourless
 0.25 × 0.04 × 0.04 mm

Data collection

Stoe IPDS 2T
 diffractometer
 Radiation source: microfocus sealed X-ray tube,
 GeniX Mo, 0.05 × 0.05 mm²
 Parabolic x-ray mirror monochromator
 Detector resolution: 6.67 pixels mm⁻¹
 rotation method scans
 Absorption correction: integration
 [X-RED32 (Stoe & Cie, 2009), analogous to
 Coppens (1970)]

$T_{\min} = 0.949$, $T_{\max} = 0.983$
 6035 measured reflections
 1075 independent reflections
 1009 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.028$
 $\theta_{\max} = 29.3$ °, $\theta_{\min} = 4.3$ °
 $h = -10 \rightarrow 10$
 $k = -8 \rightarrow 8$
 $l = -11 \rightarrow 11$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.035$
 $wR(F^2) = 0.096$
 $S = 1.05$
 1075 reflections
 84 parameters

1 restraint
 Primary atom site location: dual
 Hydrogen site location: mixed
 H atoms treated by a mixture of independent
 and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0471P)^2 + 0.1674P]$
 where $P = (F_o^2 + 2F_c^2)/3$

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

$$\Delta\rho_{\max} = 0.39 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.32 \text{ e } \text{\AA}^{-3}$$

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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.71017 (14)	0.250000	0.91063 (13)	0.0205 (2)
N2	0.72246 (15)	0.250000	0.64423 (14)	0.0140 (2)
H2	0.601583	0.250000	0.592192	0.017*
N6	0.99054 (14)	0.250000	0.89619 (14)	0.0137 (2)
H6	1.046662	0.250000	1.009730	0.016*
C1	0.80061 (17)	0.250000	0.82331 (16)	0.0140 (3)
C3	0.81877 (18)	0.250000	0.54510 (16)	0.0142 (3)
C4	1.00892 (18)	0.250000	0.62426 (16)	0.0155 (3)
H4	1.080338	0.250000	0.556716	0.019*
C5	1.09434 (17)	0.250000	0.80387 (17)	0.0142 (3)
C7	0.7107 (2)	0.250000	0.35340 (17)	0.0196 (3)
C8	1.29731 (18)	0.250000	0.90421 (19)	0.0192 (3)
F1	0.36129 (11)	0.250000	0.50873 (11)	0.0214 (2)
H1	0.255 (2)	0.250000	0.3699 (12)	0.064 (9)*
F2	0.13833 (15)	0.250000	0.23660 (11)	0.0316 (3)
H7A	0.790 (3)	0.250000	0.294 (3)	0.030 (5)*
H8A	1.362 (3)	0.250000	0.827 (3)	0.032 (6)*
H8B	1.331 (2)	0.120 (3)	0.9768 (18)	0.031 (4)*
H7B	0.631 (2)	0.121 (3)	0.3222 (19)	0.033 (4)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0167 (5)	0.0302 (6)	0.0178 (5)	0.000	0.0102 (4)	0.000
N2	0.0121 (5)	0.0156 (5)	0.0135 (5)	0.000	0.0044 (4)	0.000
N6	0.0122 (5)	0.0164 (5)	0.0120 (4)	0.000	0.0041 (4)	0.000
C1	0.0134 (6)	0.0147 (6)	0.0144 (6)	0.000	0.0059 (4)	0.000
C3	0.0184 (6)	0.0111 (5)	0.0138 (5)	0.000	0.0071 (5)	0.000
C4	0.0172 (6)	0.0159 (6)	0.0164 (6)	0.000	0.0100 (5)	0.000
C5	0.0136 (5)	0.0122 (5)	0.0175 (6)	0.000	0.0071 (5)	0.000
C7	0.0244 (7)	0.0204 (6)	0.0122 (6)	0.000	0.0055 (5)	0.000
C8	0.0123 (6)	0.0229 (7)	0.0218 (6)	0.000	0.0062 (5)	0.000
F1	0.0143 (4)	0.0300 (5)	0.0168 (4)	0.000	0.0029 (3)	0.000
F2	0.0386 (6)	0.0322 (5)	0.0140 (4)	0.000	0.0001 (4)	0.000

Geometric parameters (\AA , $^\circ$)

O1—C1	1.2156 (16)	C4—C5	1.3904 (18)
N2—H2	0.8800	C5—C8	1.4886 (18)
N2—C1	1.3846 (16)	C7—H7A	0.95 (2)
N2—C3	1.3385 (16)	C7—H7B	0.967 (16)
N6—H6	0.8800	C7—H7B ⁱ	0.967 (16)
N6—C1	1.3800 (16)	C8—H8A	0.98 (2)
N6—C5	1.3396 (16)	C8—H8B	0.962 (16)
C3—C4	1.3831 (18)	C8—H8B ⁱ	0.962 (16)
C3—C7	1.4968 (18)	F1—H1	1.1360 (15)
C4—H4	0.9500	F2—H1	1.1360 (15)
C1—N2—H2	117.9	N6—C5—C4	119.24 (12)
C3—N2—H2	117.9	N6—C5—C8	116.40 (12)
C3—N2—C1	124.28 (11)	C4—C5—C8	124.36 (12)
C1—N6—H6	118.1	C3—C7—H7A	111.2 (13)
C5—N6—H6	118.1	C3—C7—H7B	108.9 (9)
C5—N6—C1	123.71 (11)	C3—C7—H7B ⁱ	108.9 (9)
O1—C1—N2	123.07 (12)	H7A—C7—H7B	110.5 (11)
O1—C1—N6	122.18 (12)	H7A—C7—H7B ⁱ	110.5 (11)
N6—C1—N2	114.75 (11)	H7B—C7—H7B ⁱ	106.7 (18)
N2—C3—C4	118.80 (12)	C5—C8—H8A	111.1 (13)
N2—C3—C7	116.86 (12)	C5—C8—H8B ⁱ	109.1 (9)
C4—C3—C7	124.34 (12)	C5—C8—H8B	109.1 (9)
C3—C4—H4	120.4	H8A—C8—H8B ⁱ	109.5 (11)
C3—C4—C5	119.22 (12)	H8A—C8—H8B	109.5 (11)
C5—C4—H4	120.4	H8B—C8—H8B ⁱ	108.5 (17)

Symmetry code: (i) $x, -y+1/2, z$.Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N2—H2 \cdots F1	0.88	1.75	2.6240 (15)	175

4,6-Dimethyl-2-oxo-2,3-dihydropyrimidin-1-ium bromide (3)

Crystal data

 $C_6H_9N_2O^+Br^-$ $M_r = 205.06$ Orthorhombic, $Pnma$ $a = 14.4984$ (18) \AA $b = 6.722$ (2) \AA $c = 8.113$ (7) \AA $V = 790.6$ (7) \AA^3 $Z = 4$ $F(000) = 408$ $D_x = 1.723$ Mg m^{-3} Mo $K\alpha$ radiation, $\lambda = 0.71073$ \AA

Cell parameters from 16240 reflections

 $\theta = 3.8\text{--}29.7^\circ$ $\mu = 5.13$ mm^{-1} $T = 120$ K

Plate, colourless

 $0.35 \times 0.20 \times 0.03$ mm

Data collection

Stoe IPDS 2T diffractometer	$T_{\min} = 0.639$, $T_{\max} = 0.905$ 10482 measured reflections
Radiation source: microfocus sealed X-ray tube, GeniX Mo, 0.05 x 0.05 mm ²	1130 independent reflections 971 reflections with $I > 2\sigma(I)$
Parabolic x-ray mirror monochromator	$R_{\text{int}} = 0.050$
Detector resolution: 6.67 pixels mm ⁻¹ rotation method scans	$\theta_{\max} = 29.0^\circ$, $\theta_{\min} = 3.8^\circ$ $h = -19 \rightarrow 19$
Absorption correction: integration [X-RED32 (Stoe & Cie, 2009), analogous to Coppens (1970)]	$k = -9 \rightarrow 8$ $l = -11 \rightarrow 11$

Refinement

Refinement on F^2	Hydrogen site location: mixed
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.031$	$w = 1/[\sigma^2(F_o^2) + (0.0666P)^2 + 0.2083P]$
$wR(F^2) = 0.096$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.09$	$(\Delta/\sigma)_{\max} = 0.001$
1130 reflections	$\Delta\rho_{\max} = 0.74 \text{ e } \text{\AA}^{-3}$
75 parameters	$\Delta\rho_{\min} = -0.59 \text{ e } \text{\AA}^{-3}$
12 restraints	
Primary atom site location: dual	

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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.35196 (2)	0.250000	0.50127 (2)	0.02388 (16)
O1	0.58317 (14)	0.250000	0.8135 (2)	0.0371 (5)
N2	0.57782 (16)	0.250000	0.5322 (3)	0.0226 (4)
H2	0.517129	0.250000	0.532890	0.027*
N6	0.71848 (15)	0.250000	0.6681 (3)	0.0248 (4)
H6	0.751254	0.250000	0.759377	0.030*
C3	0.6210 (2)	0.250000	0.3855 (3)	0.0245 (5)
C5	0.7641 (2)	0.250000	0.5243 (3)	0.0242 (5)
C4	0.71538 (19)	0.250000	0.3791 (3)	0.0254 (5)
H4	0.746603	0.250000	0.276126	0.031*
C1	0.62334 (19)	0.250000	0.6826 (3)	0.0266 (5)
C7	0.5611 (2)	0.250000	0.2362 (3)	0.0326 (6)
C8	0.8668 (2)	0.250000	0.5294 (4)	0.0360 (7)
H7A	0.5971 (13)	0.250000	0.1340 (16)	0.049 (12)*
H7B	0.5221 (2)	0.13098 (8)	0.2398 (17)	0.068 (8)*
H8A	0.8902 (18)	0.250000	0.6427 (11)	0.057 (11)*
H8B	0.8890 (9)	0.13099 (8)	0.4719 (10)	0.054 (9)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0223 (2)	0.0298 (2)	0.0195 (2)	0.000	-0.00044 (6)	0.000
O1	0.0251 (9)	0.0693 (15)	0.0169 (9)	0.000	0.0028 (7)	0.000
N2	0.0199 (10)	0.0304 (11)	0.0176 (7)	0.000	0.0006 (8)	0.000
N6	0.0217 (9)	0.0374 (12)	0.0151 (8)	0.000	-0.0005 (7)	0.000
C3	0.0306 (13)	0.0276 (12)	0.0152 (10)	0.000	0.0005 (10)	0.000
C5	0.0230 (13)	0.0293 (12)	0.0204 (9)	0.000	0.0048 (9)	0.000
C4	0.0272 (12)	0.0328 (13)	0.0163 (10)	0.000	0.0024 (9)	0.000
C1	0.0243 (11)	0.0367 (14)	0.0188 (11)	0.000	-0.0009 (10)	0.000
C7	0.0327 (14)	0.0472 (16)	0.0179 (11)	0.000	-0.0034 (10)	0.000
C8	0.0241 (12)	0.057 (2)	0.0273 (11)	0.000	0.0020 (12)	0.000

Geometric parameters (\AA , $^\circ$)

O1—C1	1.211 (3)	C5—C4	1.373 (4)
N2—H2	0.8800	C5—C8	1.490 (4)
N2—C3	1.345 (3)	C4—H4	0.9500
N2—C1	1.387 (3)	C7—H7A	0.9799 (12)
N6—H6	0.8800	C7—H7B ⁱ	0.9800 (8)
N6—C5	1.340 (3)	C7—H7B	0.9800 (8)
N6—C1	1.384 (3)	C8—H8A	0.9802 (12)
C3—C4	1.369 (3)	C8—H8B ⁱ	0.9802 (8)
C3—C7	1.490 (4)	C8—H8B	0.9802 (8)
C3—N2—H2	118.1	O1—C1—N2	122.8 (3)
C3—N2—C1	123.9 (2)	O1—C1—N6	123.6 (3)
C1—N2—H2	118.1	N6—C1—N2	113.5 (2)
C5—N6—H6	117.8	C3—C7—H7A	112.1 (14)
C5—N6—C1	124.4 (2)	C3—C7—H7B	108.2 (7)
C1—N6—H6	117.8	C3—C7—H7B ⁱ	108.2 (7)
N2—C3—C4	119.9 (2)	H7A—C7—H7B	109.44 (13)
N2—C3—C7	116.6 (3)	H7A—C7—H7B ⁱ	109.44 (13)
C4—C3—C7	123.5 (2)	H7B—C7—H7B ⁱ	109.43 (16)
N6—C5—C4	119.5 (3)	C5—C8—H8A	111.8 (16)
N6—C5—C8	118.0 (3)	C5—C8—H8B ⁱ	108.4 (8)
C4—C5—C8	122.5 (2)	C5—C8—H8B	108.4 (8)
C3—C4—C5	118.8 (2)	H8A—C8—H8B ⁱ	109.39 (13)
C3—C4—H4	120.6	H8A—C8—H8B	109.39 (13)
C5—C4—H4	120.6	H8B—C8—H8B ⁱ	109.40 (16)

Symmetry code: (i) $x, -y+1/2, z$.Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N2—H2 \cdots Br1	0.88	2.41	3.284 (2)	174



N6—H6...Br1ⁱⁱ 0.88 2.43 3.308 (3) 176

Symmetry code: (ii) $x+1/2, y, -z+3/2$.

4,6-Dimethyl-2-oxo-2,3-dihydropyrimidin-1-ium iodide (4)

Crystal data

$C_6H_9N_2O^+I^-$

$M_r = 252.05$

Monoclinic, $P2_1/n$

$a = 7.1803$ (10) Å

$b = 7.2139$ (18) Å

$c = 8.6574$ (12) Å

$\beta = 100.603$ (11)°

$V = 440.78$ (14) Å³

$Z = 2$

$F(000) = 240$

$D_x = 1.899$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 1779 reflections

$\theta = 3.4$ – 27.7°

$\mu = 3.57$ mm⁻¹

$T = 120$ K

Needles, colourless

$0.66 \times 0.37 \times 0.14$ mm

Data collection

Stoe IPDS 2T

diffractometer

Radiation source: microfocus sealed X-ray tube,

GeniX Mo, 0.05 x 0.05 mm²

Parabolic x-ray mirror monochromator

Detector resolution: 6.67 pixels mm⁻¹

rotation method scans

Absorption correction: integration

[X-RED32 (Stoe & Cie, 2009), analogous to

Coppens (1970)]

$T_{\min} = 0.274, T_{\max} = 0.624$

5622 measured reflections

1166 independent reflections

1143 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.066$

$\theta_{\max} = 29.0^\circ, \theta_{\min} = 3.4^\circ$

$h = -9 \rightarrow 9$

$k = -9 \rightarrow 9$

$l = -10 \rightarrow 11$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.059$

$wR(F^2) = 0.165$

$S = 1.09$

1166 reflections

49 parameters

0 restraints

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0966P)^2 + 2.7212P]$

where $P = (F_o^2 + 2F_c^2)/3$

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

$\Delta\rho_{\max} = 1.55$ e Å⁻³

$\Delta\rho_{\min} = -1.29$ e Å⁻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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
I1	0.250000	0.36113 (8)	0.750000	0.0398 (3)
C1	0.250000	0.4775 (14)	0.250000	0.0394 (19)
C3	0.2593 (9)	0.7723 (10)	0.3881 (9)	0.0394 (13)
N2	0.2632 (9)	0.5837 (9)	0.3837 (7)	0.0411 (12)
H2	0.275074	0.524688	0.473976	0.049*
C7	0.2664 (18)	0.8639 (11)	0.5416 (12)	0.056 (2)

H7A	0.143381	0.851002	0.574207	0.085*
H7B	0.295644	0.995667	0.532394	0.085*
H7C	0.364872	0.805749	0.620039	0.085*
O1	0.250000	0.3089 (13)	0.250000	0.058 (2)
C4	0.250000	0.8710 (12)	0.250000	0.041 (2)
H4	0.249999	1.002703	0.250000	0.049*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
I1	0.0384 (4)	0.0395 (4)	0.0419 (4)	0.000	0.0083 (2)	0.000
C1	0.038 (4)	0.031 (4)	0.048 (5)	0.000	0.006 (4)	0.000
C3	0.034 (3)	0.033 (3)	0.049 (3)	-0.003 (2)	0.003 (2)	0.003 (3)
N2	0.042 (3)	0.042 (3)	0.039 (3)	0.006 (2)	0.005 (2)	0.001 (2)
C7	0.074 (6)	0.045 (5)	0.050 (5)	-0.006 (3)	0.008 (4)	-0.003 (3)
O1	0.089 (7)	0.033 (4)	0.056 (5)	0.000	0.021 (4)	0.000
C4	0.042 (5)	0.025 (4)	0.053 (6)	0.000	0.004 (4)	0.000

Geometric parameters (\AA , $^\circ$)

C1—N2	1.377 (8)	N2—H2	0.8800
C1—N2 ⁱ	1.377 (8)	C7—H7A	0.9800
C1—O1	1.216 (14)	C7—H7B	0.9800
C3—N2	1.362 (9)	C7—H7C	0.9800
C3—C7	1.477 (12)	C4—H4	0.9500
C3—C4	1.382 (8)		
N2 ⁱ —C1—N2	112.4 (9)	C3—C7—H7A	109.5
O1—C1—N2 ⁱ	123.8 (4)	C3—C7—H7B	109.5
O1—C1—N2	123.8 (4)	C3—C7—H7C	109.5
N2—C3—C7	118.3 (7)	H7A—C7—H7B	109.5
N2—C3—C4	119.3 (7)	H7A—C7—H7C	109.5
C4—C3—C7	122.4 (7)	H7B—C7—H7C	109.5
C1—N2—H2	117.3	C3 ⁱ —C4—C3	118.0 (9)
C3—N2—C1	125.5 (7)	C3—C4—H4	121.0
C3—N2—H2	117.3	C3 ⁱ —C4—H4	121.0

Symmetry code: (i) $-x+1/2, y, -z+1/2$.

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N2—H2 \cdots I1	0.88	2.70	3.571 (7)	170

4,6-Dimethyl-2-oxo-2,3-dihydropyrimidin-1-ium iodide-urea (1/1) (5)

Crystal data

$C_6H_9N_2O^+ \cdot I^- \cdot CH_4N_2O$
 $M_r = 312.11$

Monoclinic, $P2_1/c$
 $a = 8.772 (1) \text{\AA}$

$b = 11.5579 (10) \text{ \AA}$
 $c = 14.0700 (16) \text{ \AA}$
 $\beta = 127.378 (7)^\circ$
 $V = 1133.6 (2) \text{ \AA}^3$
 $Z = 4$
 $F(000) = 608$
 $D_x = 1.829 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
 Cell parameters from 3188 reflections
 $\theta = 3.0\text{--}29.4^\circ$
 $\mu = 2.81 \text{ mm}^{-1}$
 $T = 120 \text{ K}$
 Prism, colourless
 $0.49 \times 0.42 \times 0.19 \text{ mm}$

Data collection

Stoe IPDS 2T
 diffractometer
 Radiation source: microfocus sealed X-ray tube,
 GeniX Mo, $0.05 \times 0.05 \text{ mm}^2$
 Parabolic x-ray mirror monochromator
 Detector resolution: $6.67 \text{ pixels mm}^{-1}$
 rotation method scans
 Absorption correction: integration
 [X-RED32 (Stoe & Cie, 2009), analogous to
 Coppens (1970)]

$T_{\min} = 0.258, T_{\max} = 0.579$
 16324 measured reflections
 2995 independent reflections
 2800 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.050$
 $\theta_{\max} = 29.0^\circ, \theta_{\min} = 3.4^\circ$
 $h = -11 \rightarrow 11$
 $k = -15 \rightarrow 15$
 $l = -19 \rightarrow 19$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.032$
 $wR(F^2) = 0.093$
 $S = 1.07$
 2995 reflections
 129 parameters
 0 restraints
 Primary atom site location: dual

Hydrogen site location: inferred from
 neighbouring sites
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.061P)^2 + 0.6546P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.84 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -1.25 \text{ e \AA}^{-3}$

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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
II	0.83377 (2)	0.74469 (2)	0.35562 (2)	0.02789 (9)
O1U	0.5613 (2)	0.14468 (14)	0.46992 (15)	0.0333 (3)
O1	0.6489 (3)	0.44215 (14)	0.44055 (16)	0.0342 (4)
N2	0.7967 (3)	0.44561 (16)	0.35149 (17)	0.0288 (4)
H2	0.809381	0.521263	0.359539	0.035*
N6	0.6879 (3)	0.27280 (16)	0.37324 (18)	0.0269 (4)
H6	0.627973	0.233371	0.395104	0.032*
N1U	0.4346 (3)	0.29408 (18)	0.5062 (2)	0.0337 (4)
H1UA	0.485102	0.345600	0.486678	0.040*
H1UB	0.365183	0.316836	0.528741	0.040*
C1	0.7072 (3)	0.39069 (18)	0.39252 (19)	0.0274 (4)
C5	0.7551 (3)	0.21480 (19)	0.32306 (19)	0.0279 (4)
C3	0.8663 (3)	0.39169 (18)	0.29974 (19)	0.0281 (4)

C1U	0.4631 (4)	0.1814 (2)	0.5016 (2)	0.0303 (5)
N2U	0.3831 (3)	0.10581 (18)	0.5326 (2)	0.0411 (5)
H2UA	0.399411	0.030962	0.530629	0.049*
H2UB	0.314446	0.131331	0.554735	0.049*
C4	0.8454 (4)	0.2744 (2)	0.2849 (2)	0.0297 (4)
H4	0.892487	0.234216	0.248637	0.036*
C8	0.7286 (4)	0.08672 (19)	0.3136 (2)	0.0347 (5)
H8A	0.844970	0.049635	0.382072	0.052*
H8B	0.703908	0.059710	0.239327	0.052*
H8C	0.619515	0.066691	0.313008	0.052*
C7	0.9637 (4)	0.4651 (2)	0.2641 (2)	0.0354 (5)
H7A	0.877315	0.527494	0.211581	0.053*
H7B	0.997284	0.417626	0.221505	0.053*
H7C	1.080603	0.498420	0.335673	0.053*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
I1	0.03397 (14)	0.01755 (12)	0.03683 (14)	0.00064 (4)	0.02392 (11)	0.00024 (4)
O1U	0.0442 (9)	0.0230 (8)	0.0462 (9)	0.0034 (6)	0.0344 (8)	0.0025 (6)
O1	0.0461 (9)	0.0230 (8)	0.0480 (9)	0.0021 (6)	0.0360 (8)	-0.0009 (6)
N2	0.0394 (9)	0.0168 (8)	0.0387 (10)	0.0001 (7)	0.0282 (8)	-0.0003 (6)
N6	0.0320 (9)	0.0184 (7)	0.0359 (9)	-0.0007 (7)	0.0235 (8)	0.0006 (7)
N1U	0.0496 (12)	0.0185 (9)	0.0459 (11)	0.0028 (8)	0.0358 (10)	0.0011 (8)
C1	0.0304 (9)	0.0197 (9)	0.0350 (10)	0.0006 (7)	0.0215 (8)	0.0004 (7)
C5	0.0337 (10)	0.0193 (9)	0.0329 (10)	0.0011 (8)	0.0214 (9)	-0.0012 (8)
C3	0.0335 (10)	0.0221 (10)	0.0328 (10)	0.0011 (7)	0.0223 (8)	-0.0001 (7)
C1U	0.0362 (11)	0.0247 (11)	0.0363 (11)	0.0012 (8)	0.0253 (9)	0.0013 (8)
N2U	0.0621 (14)	0.0225 (9)	0.0674 (14)	-0.0010 (9)	0.0542 (12)	-0.0022 (9)
C4	0.0385 (12)	0.0209 (9)	0.0370 (11)	0.0014 (9)	0.0267 (10)	-0.0025 (9)
C8	0.0476 (13)	0.0187 (10)	0.0486 (13)	-0.0008 (9)	0.0348 (11)	-0.0020 (8)
C7	0.0512 (13)	0.0225 (10)	0.0482 (12)	-0.0027 (9)	0.0382 (11)	-0.0019 (9)

Geometric parameters (\AA , $^\circ$)

O1U—C1U	1.260 (3)	C3—C4	1.367 (3)
O1—C1	1.221 (3)	C3—C7	1.491 (3)
N2—H2	0.8800	C1U—N2U	1.348 (3)
N2—C1	1.379 (3)	N2U—H2UA	0.8800
N2—C3	1.353 (3)	N2U—H2UB	0.8800
N6—H6	0.8800	C4—H4	0.9500
N6—C1	1.379 (3)	C8—H8A	0.9800
N6—C5	1.342 (3)	C8—H8B	0.9800
N1U—H1UA	0.8800	C8—H8C	0.9800
N1U—H1UB	0.8800	C7—H7A	0.9800
N1U—C1U	1.336 (3)	C7—H7B	0.9800
C5—C4	1.381 (3)	C7—H7C	0.9800
C5—C8	1.492 (3)		

C1—N2—H2	117.6	N1U—C1U—N2U	117.8 (2)
C3—N2—H2	117.6	C1U—N2U—H2UA	120.0
C3—N2—C1	124.78 (19)	C1U—N2U—H2UB	120.0
C1—N6—H6	118.1	H2UA—N2U—H2UB	120.0
C5—N6—H6	118.1	C5—C4—H4	120.3
C5—N6—C1	123.8 (2)	C3—C4—C5	119.4 (2)
H1UA—N1U—H1UB	120.0	C3—C4—H4	120.3
C1U—N1U—H1UA	120.0	C5—C8—H8A	109.5
C1U—N1U—H1UB	120.0	C5—C8—H8B	109.5
O1—C1—N2	122.90 (19)	C5—C8—H8C	109.5
O1—C1—N6	123.1 (2)	H8A—C8—H8B	109.5
N2—C1—N6	113.95 (18)	H8A—C8—H8C	109.5
N6—C5—C4	119.6 (2)	H8B—C8—H8C	109.5
N6—C5—C8	116.7 (2)	C3—C7—H7A	109.5
C4—C5—C8	123.7 (2)	C3—C7—H7B	109.5
N2—C3—C4	118.4 (2)	C3—C7—H7C	109.5
N2—C3—C7	117.21 (19)	H7A—C7—H7B	109.5
C4—C3—C7	124.4 (2)	H7A—C7—H7C	109.5
O1U—C1U—N1U	122.3 (2)	H7B—C7—H7C	109.5
O1U—C1U—N2U	119.9 (2)		

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...I1	0.88	2.59	3.4692 (19)	173
N6—H6...O1U	0.88	1.80	2.666 (3)	167
N1U—H1UA...O1	0.88	2.21	3.070 (3)	167
N1U—H1UB...I1 ⁱ	0.88	3.11	3.883 (2)	148
N2U—H2UA...O1U ⁱⁱ	0.88	2.06	2.940 (3)	179
N2U—H2UB...I1 ⁱ	0.88	2.71	3.565 (2)	166

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

4,6-Dimethyl-2-sulfanylidene-2,3-dihydropyrimidin-1-ium bifluoride-thiourea (1/1) (6)

Crystal data

$C_6H_9N_2S^+ \cdot F_2H^- \cdot CH_4N_2S$

$M_r = 256.34$

Monoclinic, $P2_1/m$

$a = 6.3876$ (11) Å

$b = 8.8268$ (13) Å

$c = 10.500$ (2) Å

$\beta = 99.355$ (15)°

$V = 584.15$ (17) Å³

$Z = 2$

$F(000) = 268$

$D_x = 1.457$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 1229 reflections

$\theta = 3.1$ – 28.7°

$\mu = 0.46$ mm⁻¹

$T = 120$ K

Plate, yellow

$0.32 \times 0.2 \times 0.07$ mm

Data collection

Stoe IPDS 2T
diffractometer
Radiation source: microfocus sealed X-ray tube,
GeniX Mo, 0.05 x 0.05 mm²
Parabolic x-ray mirror monochromator
Detector resolution: 6.67 pixels mm⁻¹
rotation method scans
Absorption correction: integration
[X-RED32 (Stoe & Cie, 2009), analogous to
Coppens (1970)]

$T_{\min} = 0.853$, $T_{\max} = 0.967$
3316 measured reflections
1532 independent reflections
1375 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.047$
 $\theta_{\max} = 28.4^\circ$, $\theta_{\min} = 3.9^\circ$
 $h = -7 \rightarrow 8$
 $k = -10 \rightarrow 11$
 $l = -13 \rightarrow 13$

Refinement

Refinement on F^2
Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.071$
 $wR(F^2) = 0.220$
 $S = 1.18$
1532 reflections
80 parameters
0 restraints
Primary atom site location: dual

Hydrogen site location: mixed
H atoms treated by a mixture of independent
and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0998P)^2 + 1.0253P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.55 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.49 \text{ e } \text{\AA}^{-3}$

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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
S1T	0.5456 (2)	0.750000	1.04796 (11)	0.0367 (4)
S1	0.3578 (2)	0.250000	0.63525 (12)	0.0424 (4)
F1	0.2389 (4)	0.6231 (2)	0.5513 (2)	0.0494 (6)
N1T	0.4051 (4)	0.6196 (3)	0.8226 (3)	0.0321 (6)
H1TA	0.355387	0.620829	0.739409	0.038*
H1TB	0.429412	0.532580	0.863319	0.038*
N2	0.2256 (4)	0.3803 (3)	0.4084 (3)	0.0343 (6)
H2	0.252236	0.466934	0.449253	0.041*
C1T	0.4438 (6)	0.750000	0.8874 (4)	0.0281 (8)
C4	0.1035 (6)	0.250000	0.2147 (4)	0.0299 (9)
H4	0.046347	0.250000	0.125352	0.036*
C3	0.1457 (5)	0.3849 (4)	0.2805 (3)	0.0312 (7)
C7	0.1049 (5)	0.5375 (4)	0.2222 (4)	0.0377 (7)
H7A	-0.001766	0.589839	0.263414	0.056*
H7B	0.052706	0.527184	0.129569	0.056*
H7C	0.236850	0.596255	0.235186	0.056*
C1	0.2672 (7)	0.250000	0.4777 (5)	0.0357 (10)
H1	0.261 (15)	0.750000	0.545 (8)	0.08 (3)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1T	0.0486 (7)	0.0226 (6)	0.0379 (6)	0.000	0.0044 (5)	0.000
S1	0.0433 (7)	0.0448 (8)	0.0376 (6)	0.000	0.0023 (5)	0.000
F1	0.0736 (16)	0.0302 (11)	0.0444 (12)	-0.0082 (11)	0.0092 (10)	-0.0031 (9)
N1T	0.0333 (13)	0.0207 (12)	0.0411 (14)	-0.0006 (10)	0.0031 (10)	-0.0007 (10)
N2	0.0333 (13)	0.0276 (14)	0.0421 (14)	-0.0011 (10)	0.0066 (11)	-0.0023 (10)
C1T	0.0260 (18)	0.0223 (19)	0.035 (2)	0.000	0.0037 (15)	0.000
C4	0.0264 (18)	0.024 (2)	0.039 (2)	0.000	0.0062 (16)	0.000
C3	0.0273 (13)	0.0259 (15)	0.0414 (16)	-0.0020 (11)	0.0083 (11)	0.0001 (11)
C7	0.0381 (16)	0.0232 (15)	0.0515 (19)	-0.0008 (12)	0.0068 (13)	0.0017 (13)
C1	0.033 (2)	0.036 (2)	0.038 (2)	0.000	0.0056 (17)	0.000

Geometric parameters (\AA , $^\circ$)

S1T—C1T	1.706 (4)	N2—C1	1.363 (4)
S1—C1	1.662 (5)	C4—H4	0.9500
F1—H1	1.132 (14)	C4—C3 ⁱ	1.381 (4)
N1T—H1TA	0.8800	C4—C3	1.381 (4)
N1T—H1TB	0.8800	C3—C7	1.485 (4)
N1T—C1T	1.340 (3)	C7—H7A	0.9800
N2—H2	0.8800	C7—H7B	0.9800
N2—C3	1.357 (4)	C7—H7C	0.9800
H1TA—N1T—H1TB	120.0	N2—C3—C4	118.7 (3)
C1T—N1T—H1TA	120.0	N2—C3—C7	116.6 (3)
C1T—N1T—H1TB	120.0	C4—C3—C7	124.7 (3)
C3—N2—H2	117.9	C3—C7—H7A	109.5
C3—N2—C1	124.2 (3)	C3—C7—H7B	109.5
C1—N2—H2	117.9	C3—C7—H7C	109.5
N1T—C1T—S1T	120.7 (2)	H7A—C7—H7B	109.5
N1T ⁱⁱ —C1T—S1T	120.7 (2)	H7A—C7—H7C	109.5
N1T ⁱⁱ —C1T—N1T	118.5 (4)	H7B—C7—H7C	109.5
C3 ⁱ —C4—H4	120.4	N2 ⁱ —C1—S1	122.5 (2)
C3—C4—H4	120.4	N2—C1—S1	122.5 (2)
C3 ⁱ —C4—C3	119.1 (4)	N2—C1—N2 ⁱ	115.0 (4)

Symmetry codes: (i) $x, -y+1/2, z$; (ii) $x, -y+3/2, z$.Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1T—H1TA \cdots F1	0.88	1.99	2.874 (4)	179
N1T—H1TB \cdots S1T ⁱⁱⁱ	0.88	2.66	3.528 (3)	170
N2—H2 \cdots F1	0.88	1.76	2.610 (4)	163

Symmetry code: (iii) $-x+1, -y+1, -z+2$.

4,6-Dimethyl-2-sulfanylidene-2,3-dihydropyrimidin-1-ium bromide (9)

Crystal data

$C_6H_9N_2S^+Br^-$

$M_r = 221.12$

Monoclinic, $C2/c$

$a = 8.4675$ (11) Å

$b = 14.9142$ (19) Å

$c = 6.8814$ (9) Å

$\beta = 101.575$ (10)°

$V = 851.35$ (19) Å³

$Z = 4$

$F(000) = 440$

$D_x = 1.725$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 2102 reflections

$\theta = 3.8$ – 28.8 °

$\mu = 5.02$ mm⁻¹

$T = 120$ K

Prism, yellow

$0.21 \times 0.14 \times 0.04$ mm

Data collection

Stoe IPDS 2T
diffractometer

Radiation source: microfocus sealed X-ray tube,
GeniX Mo, 0.05 x 0.05 mm²

Parabolic x-ray mirror monochromator

Detector resolution: 6.67 pixels mm⁻¹

rotation method scans

Absorption correction: integration

[X-RED32 (Stoe & Cie, 2009), analogous to
Coppens (1970)]

$T_{\min} = 0.262$, $T_{\max} = 0.740$

5070 measured reflections

933 independent reflections

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

$R_{\text{int}} = 0.118$

$\theta_{\max} = 27.0$ °, $\theta_{\min} = 3.8$ °

$h = -10 \rightarrow 10$

$k = -18 \rightarrow 18$

$l = -8 \rightarrow 8$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.064$

$wR(F^2) = 0.168$

$S = 1.05$

933 reflections

49 parameters

0 restraints

Primary atom site location: dual

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.1393P)^2]$

where $P = (F_o^2 + 2F_c^2)/3$

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

$\Delta\rho_{\max} = 2.21$ e Å⁻³

$\Delta\rho_{\min} = -1.62$ e Å⁻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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.000000	0.19294 (3)	0.250000	0.0325 (3)
S1	0.500000	0.12830 (11)	0.250000	0.0368 (5)
N2	0.3645 (5)	0.2889 (2)	0.2528 (6)	0.0310 (8)
H2	0.273349	0.259950	0.248504	0.037*
C1	0.500000	0.2400 (4)	0.250000	0.0296 (12)
C3	0.3622 (5)	0.3795 (3)	0.2619 (5)	0.0307 (8)
C4	0.500000	0.4264 (4)	0.250000	0.0327 (12)
H4	0.500001	0.490054	0.249997	0.039*

C7	0.2091 (6)	0.4223 (3)	0.2835 (7)	0.0381 (9)
H7A	0.126072	0.410019	0.165295	0.057*
H7B	0.224963	0.487166	0.298873	0.057*
H7C	0.174921	0.397957	0.400812	0.057*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0298 (5)	0.0429 (5)	0.0265 (5)	0.000	0.0095 (3)	0.000
S1	0.0363 (8)	0.0359 (9)	0.0419 (9)	0.000	0.0168 (7)	0.000
N2	0.0274 (17)	0.0390 (16)	0.0292 (19)	0.0001 (15)	0.0117 (15)	0.0000 (14)
C1	0.026 (2)	0.033 (3)	0.032 (3)	0.000	0.011 (2)	0.000
C3	0.0262 (17)	0.041 (2)	0.0255 (18)	0.0037 (16)	0.0081 (14)	-0.0010 (15)
C4	0.035 (3)	0.039 (3)	0.025 (3)	0.000	0.008 (2)	0.000
C7	0.031 (2)	0.046 (2)	0.039 (2)	0.0046 (17)	0.0114 (19)	-0.0009 (17)

Geometric parameters (Å, °)

S1—C1	1.665 (6)	C3—C7	1.479 (6)
N2—H2	0.8800	C4—H4	0.9500
N2—C1	1.363 (5)	C7—H7A	0.9800
N2—C3	1.352 (5)	C7—H7B	0.9800
C3—C4	1.377 (5)	C7—H7C	0.9800
C1—N2—H2	118.1	C3 ⁱ —C4—C3	119.0 (6)
C3—N2—H2	118.1	C3—C4—H4	120.5
C3—N2—C1	123.8 (4)	C3 ⁱ —C4—H4	120.5
N2—C1—S1	122.4 (3)	C3—C7—H7A	109.5
N2 ⁱ —C1—S1	122.4 (3)	C3—C7—H7B	109.5
N2—C1—N2 ⁱ	115.2 (5)	C3—C7—H7C	109.5
N2—C3—C4	118.9 (4)	H7A—C7—H7B	109.5
N2—C3—C7	117.2 (4)	H7A—C7—H7C	109.5
C4—C3—C7	123.9 (4)	H7B—C7—H7C	109.5

Symmetry code: (i) $-x+1, y, -z+1/2$.*Hydrogen-bond geometry (Å, °)*

$D—H\cdots A$	$D—H$	$H\cdots A$	$D\cdots A$	$D—H\cdots A$
N2—H2 \cdots Br1	0.88	2.52	3.399 (4)	174

4,6-Dimethyl-2-sulfanylidene-2,3-dihydropyrimidin-1-ium iodide (10)*Crystal data* $C_6H_9N_2S^+I^-$ $M_r = 268.11$ Orthorhombic, $Cmcm$ $a = 8.7198$ (14) Å $b = 15.095$ (3) Å $c = 7.0716$ (11) Å $V = 930.8$ (3) Å³ $Z = 4$ $F(000) = 512$ $D_x = 1.913$ Mg m⁻³Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 1294 reflections



$\theta = 3.9\text{--}26.7^\circ$
 $\mu = 3.60\text{ mm}^{-1}$
 $T = 120\text{ K}$

Plate, yellow
 $0.17 \times 0.12 \times 0.05\text{ mm}$

Data collection

Stoe IPDS 2T
 diffractometer
 Radiation source: microfocus sealed X-ray tube,
 GeniX Mo, 0.05 x 0.05 mm²
 Parabolic x-ray mirror monochromator
 Detector resolution: 6.67 pixels mm⁻¹
 rotation method scans
 Absorption correction: integration
 [X-RED32 (Stoe & Cie, 2009), analogous to
 Coppens (1970)]

$T_{\min} = 0.520$, $T_{\max} = 0.837$
 7434 measured reflections
 708 independent reflections
 661 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.058$
 $\theta_{\max} = 28.9^\circ$, $\theta_{\min} = 4.0^\circ$
 $h = -11 \rightarrow 11$
 $k = -20 \rightarrow 20$
 $l = -9 \rightarrow 9$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.025$
 $wR(F^2) = 0.060$
 $S = 1.07$
 708 reflections
 42 parameters
 6 restraints
 Primary atom site location: dual

Hydrogen site location: mixed
 H atoms treated by a mixture of independent
 and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0431P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 1.10\text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.88\text{ e \AA}^{-3}$

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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
I1	0.000000	0.18528 (2)	0.750000	0.02004 (12)
S1	0.500000	0.12787 (8)	0.750000	0.0258 (3)
N2	0.3682 (3)	0.28725 (19)	0.750000	0.0195 (6)
H2	0.280127	0.258795	0.750000	0.023*
C1	0.500000	0.2378 (3)	0.750000	0.0198 (9)
C4	0.500000	0.4226 (3)	0.750000	0.0201 (9)
H4	0.499999	0.485535	0.750000	0.024*
C3	0.3643 (4)	0.3766 (2)	0.750000	0.0201 (6)
C7	0.2109 (5)	0.4189 (2)	0.750000	0.0298 (8)
H7A	0.220 (4)	0.4836 (3)	0.750000	0.062 (18)*
H7B	0.1549 (12)	0.3999 (11)	0.63687 (7)	0.049 (11)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
I1	0.01939 (17)	0.01578 (17)	0.02494 (19)	0.000	0.000	0.000
S1	0.0231 (6)	0.0113 (5)	0.0429 (8)	0.000	0.000	0.000

N2	0.0177 (12)	0.0140 (12)	0.0267 (15)	-0.0014 (10)	0.000	0.000
C1	0.021 (2)	0.015 (2)	0.024 (2)	0.000	0.000	0.000
C4	0.020 (2)	0.014 (2)	0.026 (3)	0.000	0.000	0.000
C3	0.0229 (15)	0.0128 (14)	0.0246 (17)	0.0039 (12)	0.000	0.000
C7	0.0262 (17)	0.0175 (15)	0.046 (3)	0.0071 (13)	0.000	0.000

Geometric parameters (Å, °)

S1—C1	1.659 (5)	C4—C3 ⁱ	1.372 (4)
N2—H2	0.8800	C3—C7	1.482 (5)
N2—C1	1.371 (4)	C7—H7A	0.9800 (11)
N2—C3	1.350 (4)	C7—H7B	0.9800 (7)
C4—H4	0.9500	C7—H7B ⁱⁱ	0.9800 (7)
C4—C3	1.372 (4)		
C1—N2—H2	117.8	N2—C3—C4	118.9 (3)
C3—N2—H2	117.8	N2—C3—C7	117.0 (3)
C3—N2—C1	124.5 (3)	C4—C3—C7	124.1 (3)
N2 ⁱ —C1—S1	123.0 (2)	C3—C7—H7A	111 (2)
N2—C1—S1	123.0 (2)	C3—C7—H7B	108.9 (10)
N2 ⁱ —C1—N2	113.9 (4)	C3—C7—H7B ⁱⁱ	108.9 (10)
C3—C4—H4	120.4	H7A—C7—H7B	109.43 (13)
C3 ⁱ —C4—H4	120.4	H7A—C7—H7B ⁱⁱ	109.43 (13)
C3—C4—C3 ⁱ	119.2 (4)	H7B—C7—H7B ⁱⁱ	109.43 (16)

Symmetry codes: (i) $-x+1, y, -z+3/2$; (ii) $x, y, -z+3/2$.

Hydrogen-bond geometry (Å, °)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N2—H2 \cdots I1	0.88	2.68	3.561 (3)	175