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## Structure Reports

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## 4,6-Dimethoxy-2-(methylsulfanyl)-pyrimidinium chloride

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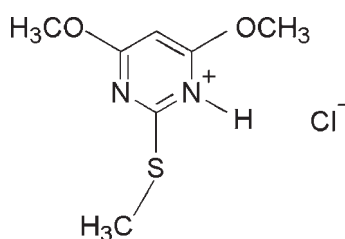
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Key indicators: single-crystal X-ray study;  $T = 100$  K; mean  $\sigma(\text{C}-\text{C}) = 0.002$  Å;  
R factor = 0.027; wR factor = 0.078; data-to-parameter ratio = 17.0.

In the title compound,  $\text{C}_7\text{H}_{11}\text{N}_2\text{O}_2\text{S}^+\cdot\text{Cl}^-$ , the 4,6-dimethoxy-2-(methylsulfanyl)pyrimidinium cation is essentially planar (r.m.s. deviation = 0.043 Å). In the crystal, the anions and cations are connected by intermolecular  $\text{N}-\text{H}\cdots\text{Cl}$  and  $\text{C}-\text{H}\cdots\text{Cl}$  hydrogen bonds, forming a two-dimensional network parallel to (011). Adjacent networks are cross-linked via  $\pi-\pi$  interactions involving the pyrimidinium ring [centroid-centroid distance = 3.5501 (8) Å].

## Related literature

For general background to substituted pyrimidines, see: Salas *et al.* (1995); Holy *et al.* (1974); Hunt *et al.* (1980); Baker & Santi (1965); Balasubramani & Fun (2009); For bond-length data, see: Allen *et al.* (1987). For the stability of the temperature controller used for the data collection, see: Cosier & Glazer (1986).



## Experimental

## Crystal data

$\text{C}_7\text{H}_{11}\text{N}_2\text{O}_2\text{S}^+\cdot\text{Cl}^-$   
 $M_r = 222.69$   
Triclinic,  $P\bar{1}$   
 $a = 6.6934$  (2) Å

$b = 8.4713$  (2) Å  
 $c = 8.8123$  (2) Å  
 $\alpha = 79.774$  (1)°  
 $\beta = 87.294$  (1)°

$\gamma = 84.494$  (1)°  
 $V = 489.24$  (2) Å<sup>3</sup>  
 $Z = 2$   
Mo  $K\alpha$  radiation

$\mu = 0.57$  mm<sup>-1</sup>  
 $T = 100$  K  
 $0.32 \times 0.22 \times 0.14$  mm

## Data collection

Bruker SMART APEXII CCD  
area-detector diffractometer  
Absorption correction: multi-scan  
(SADABS; Bruker, 2009)  
 $T_{\min} = 0.836$ ,  $T_{\max} = 0.922$

9438 measured reflections  
2126 independent reflections  
1889 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.022$

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.027$   
 $wR(F^2) = 0.078$   
 $S = 1.03$   
2126 reflections  
125 parameters

H atoms treated by a mixture of  
independent and constrained  
refinement  
 $\Delta\rho_{\text{max}} = 0.41$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.31$  e Å<sup>-3</sup>

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N2}-\text{H2}\cdots\text{Cl1}^{\text{i}}$	0.96 (3)	2.00 (3)	2.9606 (13)	172 (2)
$\text{C6}-\text{H6A}\cdots\text{Cl1}^{\text{ii}}$	0.96	2.77	3.4896 (16)	132
$\text{C6}-\text{H6B}\cdots\text{Cl1}$	0.96	2.80	3.7002 (15)	157
$\text{C7}-\text{H7A}\cdots\text{Cl1}^{\text{iii}}$	0.96	2.76	3.5524 (15)	141

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

Data collection: APEX2 (Bruker, 2009); cell refinement: SAINT (Bruker, 2009); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Sheldrick, 2008); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL and PLATON (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CI5011).

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## supporting information

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## 4,6-Dimethoxy-2-(methylsulfanyl)pyrimidinium chloride

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### S1. Comment

Pyrimidine and aminopyrimidine derivatives are biologically important compounds as they occur in nature as components of nucleic acids. Some aminopyrimidine derivatives are used as antifolate drugs (Hunt *et al.* 1980; Baker & Santi, 1965). We have recently reported the crystal structure of 4,6-dimethoxy-2-(methylsulfanyl)pyrimidine (Balasubramani & Fun, 2009). In continuation of our studies of pyrimidinium derivatives, the crystal structure determination of the title compound has been undertaken.

The asymmetric unit of the title compound (Fig. 1) consists of a chloride anion and a 4,6-dimethoxy-2-(methylsulfanyl)pyrimidinium cation. Protonation of the pyrimidine base on the N2 site is reflected in a change in the bond angle. The C4—N1—C1 angle at unprotonated atom N1 is 116.84(13) Å, whereas for protonated atom N2 the C4—N2—C3 angle is 120.03 (13) Å. The bond lengths and angles are normal (Allen *et al.* 1987).

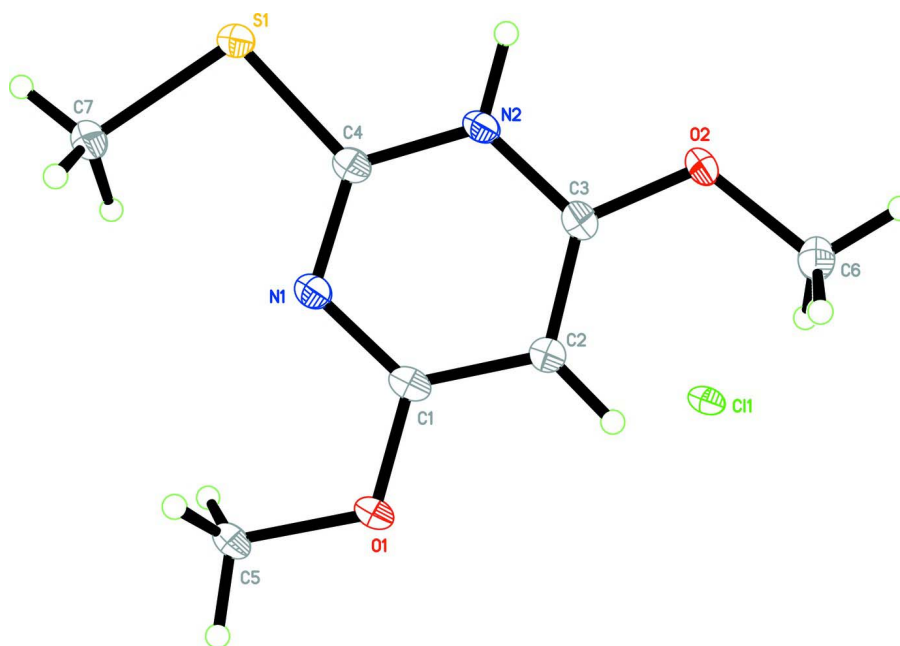
In the crystal packing (Fig. 2), atoms N2, C7 and C6 act as donors for intermolecular N—H...Cl and C—H...Cl hydrogen bonds with symmetry related chloride anions (Table 1), forming a two-dimensional network parallel to the (011). Adjacent networks are cross-linked *via*  $\pi$ - $\pi$  interactions involving the pyrimidinium ring with centroid...centroid distance = 3.5501 (8) Å (symmetry code -x, 1-y, 1-z).

### S2. Experimental

To a hot methanol solution (20 ml) of 4,6-dimethoxy-2-(methylsulfanyl)pyrimidine (46 mg, Aldrich) was added a few drops of hydrochloric acid. The solution was warmed over a water bath for a few minutes. The resulting solution was allowed to cool slowly to room temperature. Crystals of the title compound appeared from the mother liquor after a few days.

### S3. Refinement

Atom H2 was located in a difference Fourier map and refined freely. The remaining H atoms were positioned geometrically [C—H = 0.93 or 0.96 Å] and were refined using a riding model, with  $U_{\text{iso}}(\text{H}) = 1.2$  or  $1.5 U_{\text{eq}}(\text{C})$ . A rotating group model was applied to the methyl groups.



**Figure 1**

The molecular structure of the title compound, showing 50% probability displacement ellipsoids and the atom-numbering scheme.

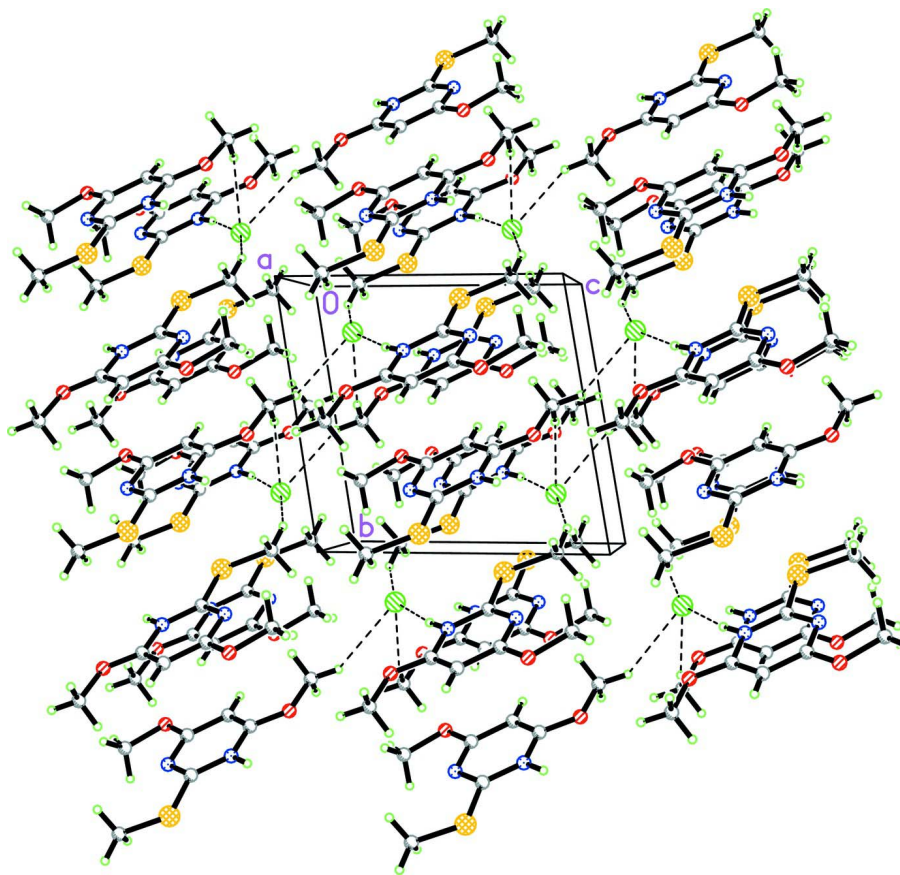


Figure 2

The crystal packing of the title compound, viewed along the  $a$  axis.

#### 4,6-Dimethoxy-2-(methylsulfanyl)pyrimidinium chloride

##### Crystal data

$C_7H_{11}N_2O_2S^+Cl^-$   
 $M_r = 222.69$   
 Triclinic,  $P\bar{1}$   
 Hall symbol: -P 1  
 $a = 6.6934$  (2) Å  
 $b = 8.4713$  (2) Å  
 $c = 8.8123$  (2) Å  
 $\alpha = 79.774$  (1)°  
 $\beta = 87.294$  (1)°  
 $\gamma = 84.494$  (1)°  
 $V = 489.24$  (2) Å<sup>3</sup>

$Z = 2$   
 $F(000) = 232$   
 $D_x = 1.512$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å  
 Cell parameters from 6382 reflections  
 $\theta = 2.4\text{--}30.1^\circ$   
 $\mu = 0.57$  mm<sup>-1</sup>  
 $T = 100$  K  
 Block, colourless  
 $0.32 \times 0.22 \times 0.14$  mm

##### Data collection

Bruker SMART APEXII CCD area-detector  
 diffractometer  
 Radiation source: fine-focus sealed tube  
 Graphite monochromator  
 $\varphi$  and  $\omega$  scans

Absorption correction: multi-scan  
 (SADABS; Bruker, 2009)  
 $T_{\min} = 0.836$ ,  $T_{\max} = 0.922$   
 9438 measured reflections  
 2126 independent reflections  
 1889 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.022$   
 $\theta_{\text{max}} = 27.0^\circ$ ,  $\theta_{\text{min}} = 2.4^\circ$   
 $h = -7 \rightarrow 8$

$k = -9 \rightarrow 10$   
 $l = -11 \rightarrow 11$

### Refinement

Refinement on  $F^2$   
 Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.027$   
 $wR(F^2) = 0.078$   
 $S = 1.03$   
 2126 reflections  
 125 parameters  
 0 restraints  
 Primary atom site location: structure-invariant  
 direct methods

Secondary atom site location: difference Fourier  
 map  
 Hydrogen site location: inferred from  
 neighbouring sites  
 H atoms treated by a mixture of independent  
 and constrained refinement  
 $w = 1/[\sigma^2(F_o^2) + (0.0453P)^2 + 0.2271P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.001$   
 $\Delta\rho_{\text{max}} = 0.41 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.31 \text{ e } \text{\AA}^{-3}$

### Special details

**Experimental.** The crystal was placed in the cold stream of an Oxford Cyrosystems Cobra open-flow nitrogen cryostat (Cosier & Glazer, 1986) operating at 100.0 (1) K.

**Geometry.** All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

**Refinement.** Refinement of  $F^2$  against ALL reflections. The weighted  $R$ -factor  $wR$  and goodness of fit  $S$  are based on  $F^2$ , conventional  $R$ -factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > \sigma(F^2)$  is used only for calculating  $R$ -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement.  $R$ -factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and  $R$ -factors based on ALL data will be even larger.

### Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	-0.25972 (5)	0.07775 (4)	0.60806 (4)	0.01603 (11)
O1	0.34406 (15)	0.34047 (13)	0.69667 (11)	0.0171 (2)
O2	0.07854 (16)	0.42350 (13)	0.19722 (11)	0.0174 (2)
N1	0.06343 (18)	0.22322 (15)	0.65196 (14)	0.0143 (3)
N2	-0.05961 (19)	0.27213 (15)	0.40095 (14)	0.0145 (3)
C1	0.2115 (2)	0.31501 (18)	0.59794 (17)	0.0146 (3)
C2	0.2360 (2)	0.38881 (18)	0.44398 (17)	0.0154 (3)
H2A	0.3426	0.4501	0.4099	0.018*
C3	0.0918 (2)	0.36459 (17)	0.34645 (16)	0.0144 (3)
C4	-0.0672 (2)	0.20134 (17)	0.55095 (16)	0.0140 (3)
C5	0.3256 (2)	0.2515 (2)	0.85378 (17)	0.0187 (3)
H5A	0.4342	0.2717	0.9131	0.028*
H5B	0.3305	0.1384	0.8513	0.028*
H5C	0.2001	0.2860	0.9002	0.028*
C6	0.2314 (2)	0.52752 (19)	0.12795 (18)	0.0192 (3)
H6A	0.2041	0.5656	0.0211	0.029*
H6B	0.3610	0.4679	0.1365	0.029*
H6C	0.2299	0.6176	0.1806	0.029*
C7	-0.1949 (2)	0.0026 (2)	0.80670 (17)	0.0189 (3)

H7A	-0.2778	-0.0817	0.8498	0.028*
H7B	-0.2161	0.0886	0.8650	0.028*
H7C	-0.0563	-0.0391	0.8106	0.028*
C11	0.63752 (5)	0.19691 (4)	0.19642 (4)	0.01942 (12)
H2	-0.160 (4)	0.258 (3)	0.331 (3)	0.047 (6)*

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
S1	0.0151 (2)	0.0185 (2)	0.01466 (19)	-0.00449 (14)	-0.00315 (13)	-0.00105 (14)
O1	0.0169 (5)	0.0222 (6)	0.0127 (5)	-0.0044 (4)	-0.0054 (4)	-0.0020 (4)
O2	0.0207 (6)	0.0205 (6)	0.0106 (5)	-0.0057 (4)	-0.0044 (4)	0.0016 (4)
N1	0.0147 (6)	0.0160 (6)	0.0125 (6)	-0.0012 (5)	-0.0023 (5)	-0.0030 (5)
N2	0.0153 (6)	0.0164 (6)	0.0123 (6)	-0.0027 (5)	-0.0045 (5)	-0.0018 (5)
C1	0.0148 (7)	0.0156 (7)	0.0141 (7)	0.0013 (6)	-0.0044 (5)	-0.0048 (5)
C2	0.0155 (7)	0.0171 (7)	0.0136 (7)	-0.0037 (6)	-0.0020 (5)	-0.0016 (6)
C3	0.0166 (7)	0.0140 (7)	0.0123 (7)	0.0000 (6)	-0.0018 (5)	-0.0019 (5)
C4	0.0139 (7)	0.0144 (7)	0.0136 (7)	0.0007 (5)	-0.0026 (5)	-0.0029 (5)
C5	0.0201 (8)	0.0244 (8)	0.0115 (7)	-0.0044 (6)	-0.0058 (6)	-0.0001 (6)
C6	0.0225 (8)	0.0189 (8)	0.0157 (7)	-0.0048 (6)	-0.0003 (6)	0.0002 (6)
C7	0.0208 (8)	0.0216 (8)	0.0137 (7)	-0.0049 (6)	-0.0026 (6)	0.0007 (6)
C11	0.0191 (2)	0.0229 (2)	0.01680 (19)	-0.00531 (15)	-0.00808 (14)	-0.00133 (14)

*Geometric parameters (Å, °)*

S1—C4	1.7380 (16)	C2—C3	1.375 (2)
S1—C7	1.8113 (15)	C2—H2A	0.93
O1—C1	1.3292 (17)	C5—H5A	0.96
O1—C5	1.4598 (18)	C5—H5B	0.96
O2—C3	1.3251 (17)	C5—H5C	0.96
O2—C6	1.4556 (19)	C6—H6A	0.96
N1—C4	1.3244 (18)	C6—H6B	0.96
N1—C1	1.336 (2)	C6—H6C	0.96
N2—C4	1.3519 (19)	C7—H7A	0.96
N2—C3	1.358 (2)	C7—H7B	0.96
N2—H2	0.97 (3)	C7—H7C	0.96
C1—C2	1.399 (2)		
C4—S1—C7	99.97 (7)	O1—C5—H5A	109.5
C1—O1—C5	116.16 (12)	O1—C5—H5B	109.5
C3—O2—C6	116.90 (12)	H5A—C5—H5B	109.5
C4—N1—C1	116.84 (13)	O1—C5—H5C	109.5
C4—N2—C3	120.03 (13)	H5A—C5—H5C	109.5
C4—N2—H2	121.1 (14)	H5B—C5—H5C	109.5
C3—N2—H2	118.8 (14)	O2—C6—H6A	109.5
O1—C1—N1	118.30 (13)	O2—C6—H6B	109.5
O1—C1—C2	117.18 (13)	H6A—C6—H6B	109.5
N1—C1—C2	124.51 (13)	O2—C6—H6C	109.5

C3—C2—C1	115.49 (14)	H6A—C6—H6C	109.5
C3—C2—H2A	122.3	H6B—C6—H6C	109.5
C1—C2—H2A	122.3	S1—C7—H7A	109.5
O2—C3—N2	112.49 (12)	S1—C7—H7B	109.5
O2—C3—C2	127.29 (14)	H7A—C7—H7B	109.5
N2—C3—C2	120.22 (13)	S1—C7—H7C	109.5
N1—C4—N2	122.85 (14)	H7A—C7—H7C	109.5
N1—C4—S1	120.43 (11)	H7B—C7—H7C	109.5
N2—C4—S1	116.73 (11)		
C5—O1—C1—N1	5.85 (19)	C4—N2—C3—C2	-1.1 (2)
C5—O1—C1—C2	-175.01 (13)	C1—C2—C3—O2	178.56 (14)
C4—N1—C1—O1	179.41 (12)	C1—C2—C3—N2	-1.0 (2)
C4—N1—C1—C2	0.3 (2)	C1—N1—C4—N2	-2.6 (2)
O1—C1—C2—C3	-177.67 (13)	C1—N1—C4—S1	177.53 (10)
N1—C1—C2—C3	1.4 (2)	C3—N2—C4—N1	3.0 (2)
C6—O2—C3—N2	178.64 (12)	C3—N2—C4—S1	-177.09 (10)
C6—O2—C3—C2	-0.9 (2)	C7—S1—C4—N1	-4.31 (13)
C4—N2—C3—O2	179.30 (12)	C7—S1—C4—N2	175.82 (11)

*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...Cl1 <sup>i</sup>	0.96 (3)	2.00 (3)	2.9606 (13)	172 (2)
C6—H6A...Cl1 <sup>ii</sup>	0.96	2.77	3.4896 (16)	132
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