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6-Chloro-4-(dimethylaminomethyleneamino)-2-(methylsulfanyl)pyrimidine

José M. de la Torre,[a] Justo Cobo,[a] Manuel Nogueras[a] and John Nicolson Low[b]*

[a]Departamento de Química Inorgánica y Orgánica, Universidad de Jaén, 23071 Jaén, Spain, and [b]Department of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen, AB24 3UE, Scotland.

Correspondence e-mail: che562@abdn.ac.uk

Key indicators

Single-crystal X-ray study
T = 120 K
Mean σ(C–C) = 0.003 Å
R factor = 0.040
wR factor = 0.106
Data-to-parameter ratio = 18.3

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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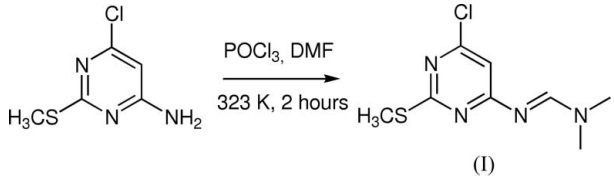
The molecules in the title compound, $C_8H_{11}ClN_4S$, are linked in pairs by a π–π stacking interaction. There are, however, no other direction-specific interactions.

Comment

In our search for good candidates for intermediates in the synthesis of new pyrimidine fused ring systems, we have prepared the title compound, (I), (Fig. 1), a formyl derivative of 4-amino-6-chloro-2-(methylsulfanyl)pyrimidine, using the Vilsmeier formylation reaction (Vilsmeier & Haack, 1927).



(I)

The bond lengths and angles show no unusual features. The essentially planar group consisting of atoms N4, C41, N42, C43 and C44 forms a dihedral angle of 31.49 (8)° with that of the planar pyrimidine ring. The leading torsion angles are given in Table 1. The molecules are linked into pairs by a π–π stacking

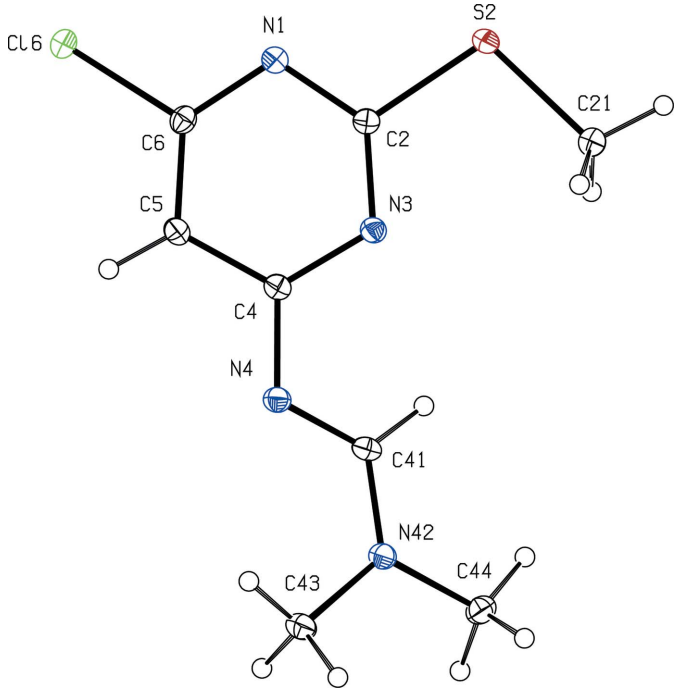


Figure 1
A view of (I) with our numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

interaction (Fig. 2). The molecules at (x, y, z) and $(1-x, 1-y, 1-z)$ are parallel, with an interplanar spacing of 3.4661 (2) Å. The ring-centroid separation is 3.359 (2) Å corresponding to a ring offset of 0.857 Å.

Experimental

The Vilsmeier reagent was prepared in an ice-bath by adding phosphorus oxychloride (1.8 mmol) to *N*,*N*-dimethylformamide (38 mmol) and stirring for 15 min. 4-Amino-6-chloro-2-(methylsulfanyl)pyrimidine (0.2 g, 1.14 mmol) was then added and the reaction temperature raised to 323–333 K, and the mixture stirred for 2 h. The reaction mixture was then poured on to crushed ice and neutralized with NaOH (10% in water) until the pH was raised to 8–9. The resulting white solid was filtered off and recrystallized from DMSO-d_6 producing white crystalline blocks suitable for single-crystal X-ray diffraction (yield 60%; m.p. 374–376 K). MS (70 eV): 232/230 (38:100, M+2/M^+), 217/215 (17/18, $[(M+2/M) - CH_3]^+$), 186/184 (17/18, $[(M+2/M) - SCH_2]^+$), 149 (31, $[M - SCH_3 - Cl]^+$), 71 (4, $[N{=}CH{-}N(CH_3)_2]^+$).

Crystal data

$C_8H_{11}ClN_4S$	V = 518.31 (15) Å^3
M_r = 230.72	Z = 2
Triclinic, $P\overline{1}$	D_x = 1.478 Mg m^{-3}
a = 7.4817 (2) Å	Mo $K\alpha$ radiation
b = 8.5739 (2) Å	μ = 0.54 mm^{-1}
c = 9.818 (3) Å	T = 120 (2) K
α = 111.973 (2)°	Block, colourless
β = 91.661 (2)°	0.30 × 0.30 × 0.20 mm
γ = 114.566 (2)°	

Data collection

Nonius KappaCCD diffractometer	12192 measured reflections
φ and ω scans	2378 independent reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)	2015 reflections with $I > 2\sigma(I)$
T_{min} = 0.856, T_{max} = 0.901	R_{int} = 0.032
	θ_{max} = 27.5°

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0456P)^2 + 0.5109P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)]$ = 0.040	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2)$ = 0.106	$\Delta\rho_{max}$ = 0.43 e Å^{-3}
S = 1.13	$\Delta\rho_{min}$ = −0.36 e Å^{-3}
2378 reflections	
130 parameters	
H-atom parameters constrained	

Table 1
Selected torsion angles (°).

N3—C2—S2—C21	0.17 (18)	N4—C41—N41—C43	−3.4 (3)
N1—C2—S2—C21	−179.75 (14)	N4—C41—N41—C44	175.22 (18)
N3—C4—N4—C41	−25.4 (3)	C2—N1—C6—Cl6	−177.26 (13)
C5—C4—N4—C41	156.38 (18)	C4—C5—C6—Cl6	175.75 (14)
C4—N4—C41—N41	174.23 (17)		

H atoms were treated as riding atoms, with aromatic C—H = 0.95 Å and U_{iso}(H) = 1.2U_{eq}(C), and C—H = 0.98 Å and U_{iso}(H) = 1.5U_{eq}(C). The positions of all methyl H atoms were checked in a difference map.

Data collection: *COLLECT* (Bruker–Nonius, 2004); cell refinement: *DIRAX/LSQ* (Duisenberg *et al.*, 2000); data reduction: *EVALCCD* (Duisenberg *et al.*, 2003); program(s) used to solve structure: *SIR2004* (Burla *et al.*, 2005); program(s) used to refine structure: *OSCAIL* (McArdle, 2003) and *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *WORDPERFECT* macro *PRPKAPPA* (Ferguson, 1999).

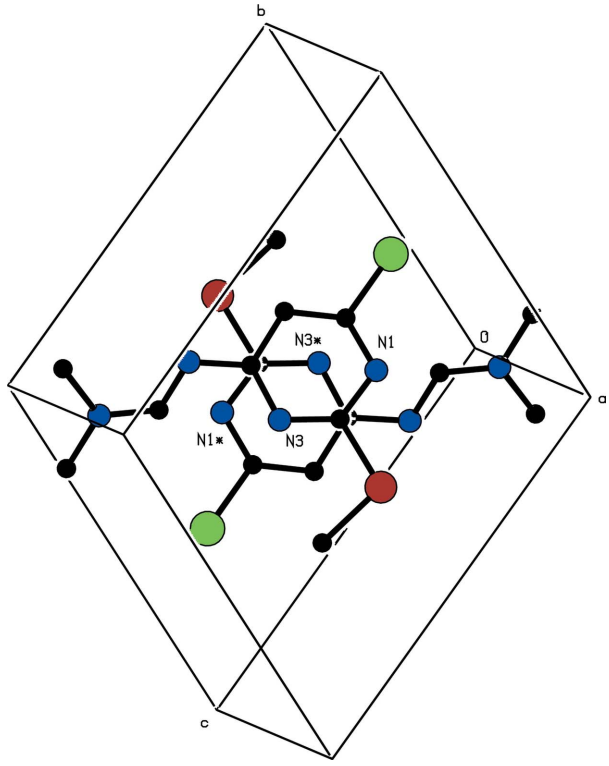


Figure 2
A view of the π–π stacking viewed perpendicular to the plane of the pyrimidine ring. Atoms labelled with an asterisk (*) are in the molecule at $(1-x, 1-y, 1-z)$. For the sake of clarity, all H atoms have been omitted.

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supporting information

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$\alpha = 111.973$ (2)°
$\beta = 91.661$ (2)°
$\gamma = 114.566$ (2)°
$V = 518.31$ (15) Å^3
$Z = 2$
$F(000) = 240$
$D_x = 1.478$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å
Cell parameters from 2378 reflections
$\theta = 4.2$–27.5°
$\mu = 0.54$ mm^{-1}
$T = 120$ K
Block, colourless
0.30 × 0.30 × 0.20 mm

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Nonius KappaCCD diffractometer
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Absorption correction: multi-scan (SADABS; Sheldrick, 2003)
$T_{min} = 0.856$, $T_{max} = 0.901$
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2378 independent reflections
2015 reflections with $I > 2\sigma(I)$
$R_{int} = 0.032$
$\theta_{max} = 27.5°$, $\theta_{min} = 4.2°$
$h = -9 \rightarrow 9$
$k = -11 \rightarrow 11$
$l = -12 \rightarrow 12$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.106$
$S = 1.13$
2378 reflections
130 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-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0456P)^2 + 0.5109P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.43$ e Å^{-3}
$\Delta\rho_{min} = -0.36$ e Å^{-3}

Special details

Experimental. The scale factors in the experimental table are calculated from the 'size′ command in the *SHELXL97* input file.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
N1	0.7202 (2)	0.4345 (2)	0.35311 (18)	0.0187 (3)
C2	0.7336 (3)	0.4427 (3)	0.4933 (2)	0.0171 (4)
S2	0.71334 (8)	0.23243 (7)	0.49580 (5)	0.02132 (15)
C21	0.7347 (3)	0.2824 (3)	0.6919 (2)	0.0255 (4)
N3	0.7589 (2)	0.5869 (2)	0.62132 (18)	0.0176 (3)
C4	0.7747 (3)	0.7458 (3)	0.6112 (2)	0.0172 (4)
N4	0.8032 (2)	0.9024 (2)	0.73831 (18)	0.0192 (3)
C41	0.7393 (3)	0.8703 (3)	0.8511 (2)	0.0183 (4)
N41	0.7704 (2)	1.0073 (2)	0.98542 (18)	0.0195 (3)
C43	0.8898 (3)	1.2062 (3)	1.0181 (2)	0.0241 (4)
C44	0.6831 (3)	0.9661 (3)	1.1064 (2)	0.0234 (4)
C5	0.7678 (3)	0.7549 (3)	0.4712 (2)	0.0191 (4)
C6	0.7360 (3)	0.5939 (3)	0.3494 (2)	0.0185 (4)
Cl6	0.70810 (8)	0.58526 (7)	0.16889 (5)	0.02420 (15)
H21A	0.7244	0.1718	0.7059	0.038*
H21B	0.6262	0.3111	0.7275	0.038*
H21C	0.8652	0.3914	0.7495	0.038*
H41	0.6665	0.7426	0.8370	0.022*
H43A	0.9684	1.2170	0.9409	0.036*
H43B	0.9814	1.2724	1.1170	0.036*
H43C	0.8002	1.2632	1.0183	0.036*
H44A	0.5920	0.8302	1.0680	0.035*
H44B	0.6078	1.0377	1.1441	0.035*
H44C	0.7910	1.0027	1.1885	0.035*
H5	0.7842	0.8662	0.4618	0.023*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0197 (8)	0.0177 (8)	0.0186 (8)	0.0086 (7)	0.0043 (6)	0.0077 (6)
C2	0.0159 (9)	0.0168 (9)	0.0173 (9)	0.0072 (7)	0.0030 (7)	0.0064 (7)
S2	0.0301 (3)	0.0171 (2)	0.0182 (3)	0.0133 (2)	0.00435 (19)	0.00624 (19)
C21	0.0362 (12)	0.0228 (10)	0.0195 (10)	0.0149 (9)	0.0050 (8)	0.0094 (8)
N3	0.0191 (8)	0.0167 (8)	0.0170 (8)	0.0088 (6)	0.0024 (6)	0.0065 (6)
C4	0.0153 (8)	0.0160 (9)	0.0185 (9)	0.0069 (7)	0.0023 (7)	0.0062 (7)
N4	0.0217 (8)	0.0176 (8)	0.0172 (8)	0.0098 (7)	0.0023 (6)	0.0055 (6)
C41	0.0179 (9)	0.0154 (9)	0.0188 (9)	0.0087 (7)	0.0017 (7)	0.0036 (7)
N41	0.0220 (8)	0.0178 (8)	0.0184 (8)	0.0100 (7)	0.0032 (6)	0.0064 (7)
C43	0.0299 (11)	0.0174 (9)	0.0222 (10)	0.0112 (8)	0.0031 (8)	0.0054 (8)
C44	0.0266 (10)	0.0270 (10)	0.0187 (9)	0.0146 (9)	0.0064 (8)	0.0091 (8)
C5	0.0203 (9)	0.0163 (9)	0.0210 (9)	0.0084 (8)	0.0040 (7)	0.0084 (8)
C6	0.0174 (9)	0.0222 (9)	0.0174 (9)	0.0097 (8)	0.0040 (7)	0.0093 (8)
Cl6	0.0333 (3)	0.0244 (3)	0.0183 (2)	0.0146 (2)	0.00694 (19)	0.0109 (2)

Geometric parameters (Å, º)

N1—C6	1.337 (2)	C41—H41	0.95
N1—C2	1.350 (2)	N41—C43	1.455 (3)
C2—N3	1.331 (2)	N41—C44	1.460 (3)
C2—S2	1.7553 (19)	C43—H43A	0.98
S2—C21	1.796 (2)	C43—H43B	0.98
C21—H21A	0.98	C43—H43C	0.98
C21—H21B	0.98	C44—H44A	0.98
C21—H21C	0.98	C44—H44B	0.98
N3—C4	1.360 (2)	C44—H44C	0.98
C4—N4	1.378 (2)	C5—C6	1.367 (3)
C4—C5	1.406 (3)	C5—H5	0.95
N4—C41	1.296 (3)	C6—Cl6	1.748 (2)
C41—N41	1.330 (2)		
C6—N1—C2	113.18 (16)	C41—N41—C44	121.80 (17)
N3—C2—N1	127.66 (17)	C43—N41—C44	116.60 (16)
N3—C2—S2	119.89 (14)	N41—C43—H43A	109.5
N1—C2—S2	112.44 (14)	N41—C43—H43B	109.5
C2—S2—C21	102.86 (9)	H43A—C43—H43B	109.5
S2—C21—H21A	109.5	N41—C43—H43C	109.5
S2—C21—H21B	109.5	H43A—C43—H43C	109.5
H21A—C21—H21B	109.5	H43B—C43—H43C	109.5
S2—C21—H21C	109.5	N41—C44—H44A	109.5
H21A—C21—H21C	109.5	N41—C44—H44B	109.5
H21B—C21—H21C	109.5	H44A—C44—H44B	109.5
C2—N3—C4	116.74 (16)	N41—C44—H44C	109.5
N3—C4—N4	120.58 (17)	H44A—C44—H44C	109.5
N3—C4—C5	120.53 (17)	H44B—C44—H44C	109.5
N4—C4—C5	118.87 (17)	C6—C5—C4	115.92 (17)
C41—N4—C4	116.07 (17)	C6—C5—H5	122.0
N4—C41—N41	123.31 (18)	C4—C5—H5	122.0
N4—C41—H41	118.3	N1—C6—C5	125.91 (18)
N41—C41—H41	118.3	N1—C6—Cl6	114.60 (14)
C41—N41—C43	121.59 (17)	C5—C6—Cl6	119.48 (15)
C6—N1—C2—N3	0.3 (3)	C4—N4—C41—N41	174.23 (17)
C6—N1—C2—S2	−179.79 (13)	N4—C41—N41—C43	−3.4 (3)
N3—C2—S2—C21	0.17 (18)	N4—C41—N41—C44	175.22 (18)
N1—C2—S2—C21	−179.75 (14)	N3—C4—C5—C6	2.7 (3)
N1—C2—N3—C4	−0.5 (3)	N4—C4—C5—C6	−179.04 (17)
S2—C2—N3—C4	179.60 (13)	C2—N1—C6—C5	1.6 (3)
C2—N3—C4—N4	−179.32 (17)	C2—N1—C6—Cl6	−177.26 (13)
C2—N3—C4—C5	−1.1 (3)	C4—C5—C6—N1	−3.1 (3)
N3—C4—N4—C41	−25.4 (3)	C4—C5—C6—Cl6	175.75 (14)
C5—C4—N4—C41	156.38 (18)		