

José M. de la Torre,^a Justo Cobo,^a
 Manuel Noguera^a and
 John Nicolson Low^{b*}

^aDepartamento de Química Inorgánica y
 Orgánica, Universidad de Jaén, 23071 Jaén,
 Spain, and ^bDepartment 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 $\sigma(\text{C}-\text{C}) = 0.003 \text{ \AA}$
 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>.

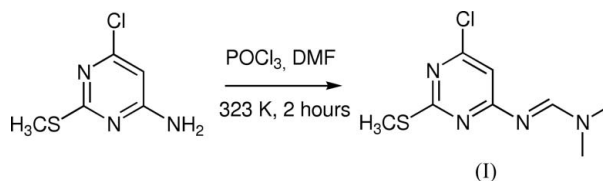
6-Chloro-4-(dimethylaminomethyleneamino)- 2-(methylsulfanyl)pyrimidine

The molecules in the title compound, $\text{C}_8\text{H}_{11}\text{ClN}_4\text{S}$, are linked in pairs by a $\pi-\pi$ stacking interaction. There are, however, no other direction-specific interactions.

Received 24 July 2006
 Accepted 14 August 2006

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).



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 $31.49(8)^\circ$ with that of the planar pyrimidine ring. The leading torsion angles are given in Table 1. The molecules are linked into pairs by a $\pi-\pi$ stacking

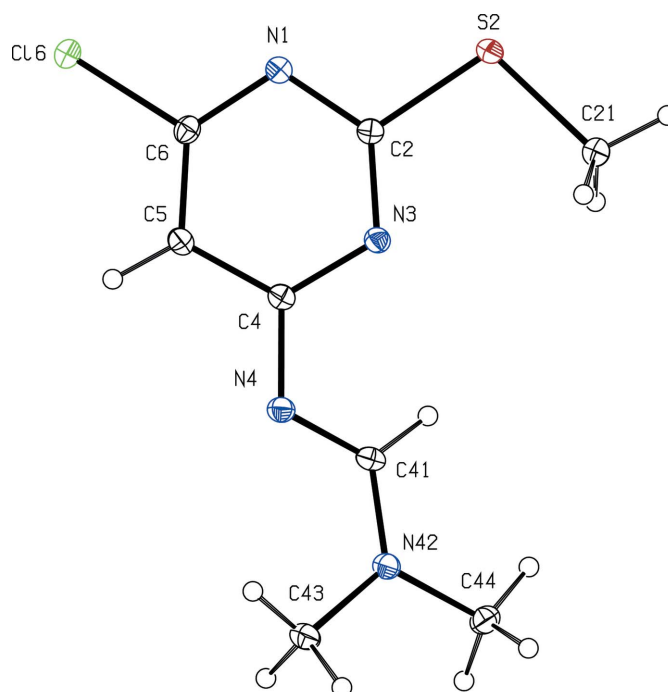


Figure 1
 A view of (I) with our numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

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, $[(M+2/M) - \text{CH}_3]^+$), 186/184 (17/18, $[(M+2/M) - \text{SCH}_2]^+$), 149 (31, $[M - \text{SCH}_3 - \text{Cl}]^+$), 71 (4, $[\text{N}=\text{CH}-\text{N}(\text{CH}_3)_2]^+$).

Crystal data

| | |
|---|---|
| $\text{C}_8\text{H}_{11}\text{ClN}_4\text{S}$ | $V = 518.31 (15) \text{ \AA}^3$ |
| $M_r = 230.72$ | $Z = 2$ |
| Triclinic, $P\bar{1}$ | $D_x = 1.478 \text{ Mg m}^{-3}$ |
| $a = 7.4817 (2) \text{ \AA}$ | Mo $K\alpha$ radiation |
| $b = 8.5739 (2) \text{ \AA}$ | $\mu = 0.54 \text{ mm}^{-1}$ |
| $c = 9.818 (3) \text{ \AA}$ | $T = 120 (2) \text{ K}$ |
| $\alpha = 111.973 (2)^\circ$ | Block, colourless |
| $\beta = 91.661 (2)^\circ$ | $0.30 \times 0.30 \times 0.20 \text{ mm}$ |
| $\gamma = 114.566 (2)^\circ$ | |

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 $I > 2\sigma(I)$ |
| $T_{\min} = 0.856$, $T_{\max} = 0.901$ | $R_{\text{int}} = 0.032$ |
| | $\theta_{\text{max}} = 27.5^\circ$ |

Refinement

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

Table 1

Selected torsion angles ($^\circ$).

| | | | |
|---------------|--------------|----------------|--------------|
| 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 $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$, and C–H = 0.98 Å and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$. 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:

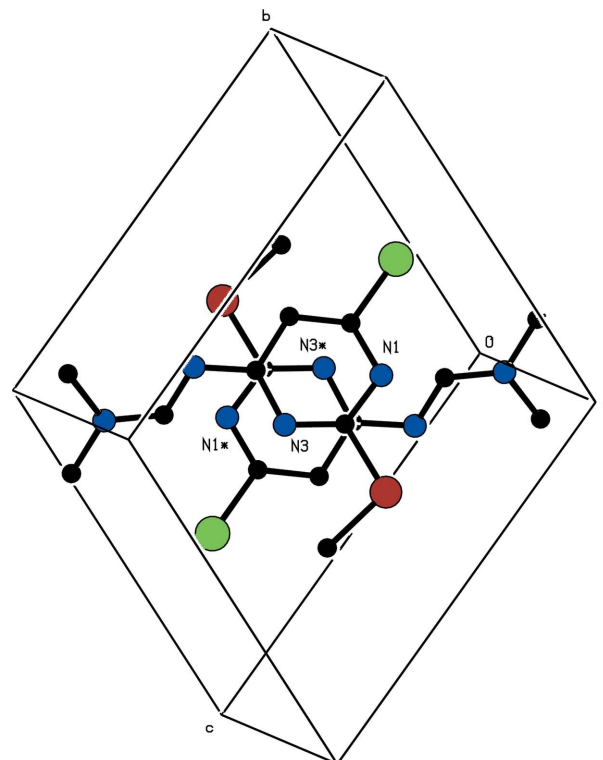


Figure 2

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.

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).

JT, MN and JC thank the Consejería de Innovación, Ciencia y Empresa (Junta de Andalucía, Spain) and the Universidad de Jaén, Spain, for financial support. JT thanks also the Universidad de Jaén for a research scholarship.

References

- Bruker–Nonius (2004). *COLLECT*. Bruker–Nonius BV, Delft, The Netherlands.
- Burla, M. C., Caliandro, R., Camalli, M., Carrozzini, B., Cascarano, G. L., De Caro, L., Giacovazzo, C., Polidori, G. & Spagna, R. (2005). *J. Appl. Cryst.* **38**, 381–388.
- Duisenberg, A. J. M., Hooft, R. W. W., Schreurs, A. M. M. & Kroon, J. (2000). *J. Appl. Cryst.* **33**, 893–898.
- Duisenberg, A. J. M., Kroon-Batenburg, L. M. J. & Schreurs, A. M. M. (2003). *J. Appl. Cryst.* **36**, 220–229.
- Ferguson, G. (1999). *PRPKAPPA*. University of Guelph, Canada.
- McArdle, P. (2003). *OSCAIL for Windows*. Version 10. Crystallography Centre, Chemistry Department, NUI Galway, Ireland.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Sheldrick, G. M. (2003). *SADABS*. Version 2.10. University of Göttingen, Germany.
- Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
- Vilsmeier, A. & Haack, A. (1927). *Chem. Ber.* **60**, 119–122.