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5-Bromo-6-chloro-N^4-methylpyrimidine-2,4-diamine

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Key indicators

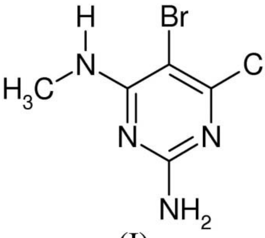
Single-crystal X-ray study
T = 120 K
Mean σ(C–C) = 0.002 Å
R factor = 0.018
wR factor = 0.043
Data-to-parameter ratio = 15.9

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

In the title compound, $C_5H_6BrClN_4$, intermolecular N—H···N hydrogen bonds link the molecules into tapes containing $R_2^2(8)$ loops.

Comment

The substituted pyrimidine title compound, $C_5H_6BrClN_4$, (I) (Fig. 1), is a precursor in the synthesis of a derivative of the natural product heteromine H.



(I)

In (I), the pyrimidine ring (C1–C4/N1/N2; centroid denoted Cg) is almost planar (r.m.s. deviation from mean plane = 0.018 Å) and atom C5 is the only non-H atom to be displaced significantly from the mean plane [deviation = 0.349 (3) Å]. The bond angle sum of 358° at N4 implies sp^2-hybridization for this atom, and the short C3—N4 bond length of 1.341 (2) Å indicates substantial double-bond character. The situation at N3 is ambiguous; the short C4—N3 bond of 1.358 (2) Å implies double-bond character, but the bond-angle sum of 346° and the mean bond angle of 115° are intermediate between typical sp^2 and sp^3 values. Otherwise, the geometrical parameters for (I) fall within expected ranges (Allen *et al.*, 1995).

The crystal packing of (I) is influenced by intermolecular N—H···N hydrogen bonds (Table 1). The two hydrogen bonds involving the NH_2 group assemble the molecules into tapes propagating along [001], with adjacent molecules linked by $R_2^2(8)$ loops (Bernstein *et al.*, 1995). There are two crystallographically distinct $R_2^2(8)$ loops, one generated by a centre of inversion and one generated by twofold rotation symmetry. The hydrogen-bonding situation for N4 is less clear cut. The N4/H3 group is involved in an intramolecular N—H···Br1 link, and also an intermolecular N—H···N interaction (Table 1). The pyrimidine rings form π–π stacking interactions across centres of inversion [$Cg\cdots Cg^{vi}$ = 3.9189 (9) Å; symmetry code: (vi) $\frac{1}{2}-x, \frac{1}{2}-y, -z$], and a relatively short $Br1\cdots C5^{vii}$ contact of 3.3434 (18) Å is also present [symmetry code (vii): $x-\frac{1}{2}, \frac{1}{2}-y, z-\frac{1}{2}$], compared with 3.55 Å for the sum of the van der Waals radii of Br and C (Bondi, 1964).

Experimental

4,6-Dichloro-5-bromopyrimidine (0.500 g, 2.06 mmol) was added to a flask under argon. This was followed by slow addition of methylamine in 33% ethanol/water (10 ml) and the solution was left to stir overnight for 12 h. The excess methylamine was removed *in vacuo* and flash column chromatography (hexane/ethyl acetate/triethylamine *v*/*v*/*v* 10:5:1) yielded crude (I) as a yellow solid with R_f = 0.39. Recrystallization from ethanol/acetone (*v*/*v* 1:1) with a few drops of water afforded 0.363 g (72% yield) of colourless blocks of (I), m.p. 447–449 K; ν_{max} (KBr) 3455, 3299 (NH_2), 1631 (NH_2), 1549 (C=N, conjugated, cyclic), 1449 (CH_3), 1059 (pyrimidyl Br).

Crystal data

$C_5H_6BrClN_4$
M_r = 237.50
Monoclinic, $C2/c$
a = 9.6480 (2) Å
b = 10.8032 (3) Å
c = 15.1157 (3) Å
β = 105.2600 (14)°
V = 1519.95 (6) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 5.69 mm^{-1}
T = 120 (2) K
0.40 × 0.18 × 0.14 mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2003)
T_{min} = 0.209, T_{max} = 0.503 (expected range = 0.187–0.451)
15792 measured reflections
1761 independent reflections
1645 reflections with $I > 2\sigma(I)$
R_{int} = 0.034

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.018
$wR(F^2)$ = 0.043
S = 1.08
1761 reflections
111 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.49 e Å^{-3}
$\Delta\rho_{min}$ = −0.35 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N3—H1···N1^{i}	0.81 (2)	2.43 (2)	3.232 (2)	173.4 (19)
N3—H2···N2^{ii}	0.87 (2)	2.21 (2)	3.084 (2)	178.5 (19)
N4—H3···N3^{iii}	0.78 (2)	2.65 (2)	3.252 (2)	135 (2)
N4—H3···Br1	0.78 (2)	2.66 (2)	3.0851 (15)	115.8 (19)

Symmetry codes: (i) $-x+1, y, -z+\frac{1}{2}$; (ii) $-x+1, -y+1, -z$; (iii) $x-\frac{1}{2}, y-\frac{1}{2}, z$.

The N-bound H atoms were located in a difference Fourier map and their positions were refined freely with $U_{iso}(H) = 1.2U_{eq}(N)$. The methyl H atoms were placed in calculated positions (C—H = 0.98 Å) and refined as riding with the methyl group allowed to rotate about its local threefold axis, with $U_{iso}(H) = 1.5U_{eq}(C)$.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO*/*SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO*/*SCALEPACK*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

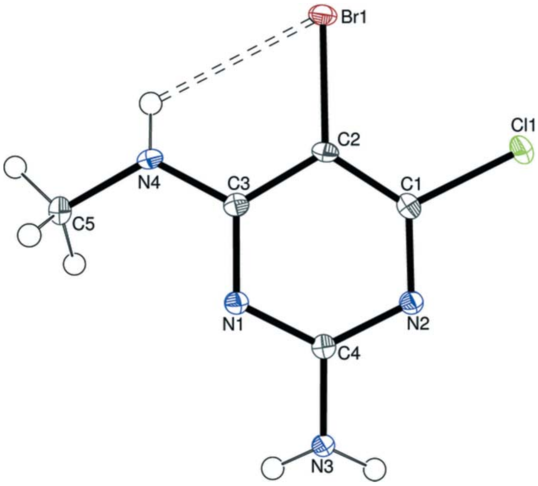


Figure 1
The molecular structure of (I) showing 50% displacement ellipsoids (arbitrary spheres for the H atoms). The N—H···Br interaction is shown with double-dashed lines.

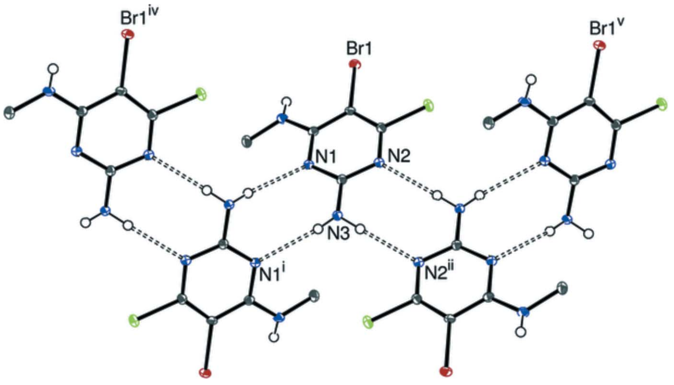


Figure 2
Fragment of a [001] tape in (I). Hydrogen bonds are indicated as double-dashed lines and methyl H atoms have been omitted. [Symmetry codes: (i) and (ii) as in Table 1; (iv) $x, 1-y, z+\frac{1}{2}$; (v) $x, 1-y, z-\frac{1}{2}$.]

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