

4-amino-2-chloro-5-nitro-6-(propylamino)pyrimidine

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Key indicators

Single-crystal X-ray study
 $T = 295\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.007\text{ \AA}$
 R factor = 0.050
 wR factor = 0.158
Data-to-parameter ratio = 13.1For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

4-Amino-2-chloro-5-nitro-6-(propylamino)pyrimidine

The title compound, $\text{C}_7\text{H}_{10}\text{ClN}_5\text{O}_2$, was synthesized as part of a study to demonstrate the reactivity of 4-amino-2,6-dichloro-5-nitropyrimidine with respect to various amine substitutions. The structure determination allowed unambiguous assignment of the regioselectivity of the substitution of the propylamine group at the 6-position. Intra- and intermolecular $\text{N}-\text{H}\cdots\text{O}$ and $\text{N}-\text{H}\cdots\text{N}$ hydrogen bonding yields polymeric chains of coplanar molecules. There are two independent molecules in the asymmetric unit.

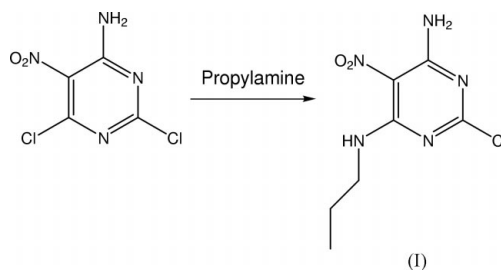
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Comment

The title compound, (I), was synthesized by substitution of one chloro substituent of 4-amino-2,6-dichloro-5-nitropyrimidine with propylamine. While it was clear from the spectroscopic data that monosubstitution had been achieved, the question remained as to whether the chloro group at the 2- or 6-position had been substituted. NMR experiments could not answer this question satisfactorily and so crystals of (I) were grown. The determination of the crystal structure has allowed the assignment of the regioselectivity of the substitution at the 6-position.



The crystal structure of (I) contains two independent molecules in the asymmetric unit disposed across a pseudo-centre of symmetry (Fig. 1). Relevant bond lengths and angles are listed in Table 1. With the exception of the peripheral propylamine substituents, both molecules are essentially coplanar.

Each molecule exhibits two intramolecular $S(6)$ (Bernstein *et al.*, 1995) $\text{N}-\text{H}\cdots\text{O}$ hydrogen-bonding interactions. The first of these is between the *ortho* amine and the nitro groups on C4 and C5 (*cf.* McKeveney *et al.*, 2004; Glidewell *et al.*, 2003), and the second is between the *ortho* propylamine and the nitro groups on C6 and C5 (Table 2 and Fig. 2).

Two intermolecular hydrogen-bonding interactions are also observed between the two independent molecules. The first is an $R_2^2(8)$ $\text{N}-\text{H}\cdots\text{N}$ interaction between the *ortho* amino group and the ring N3 atom (*cf.* Glidewell *et al.*, 2003; Lynch & McClenaghan, 2004). The second is an $R_2^2(12)$ $\text{N}-\text{H}\cdots\text{O}$

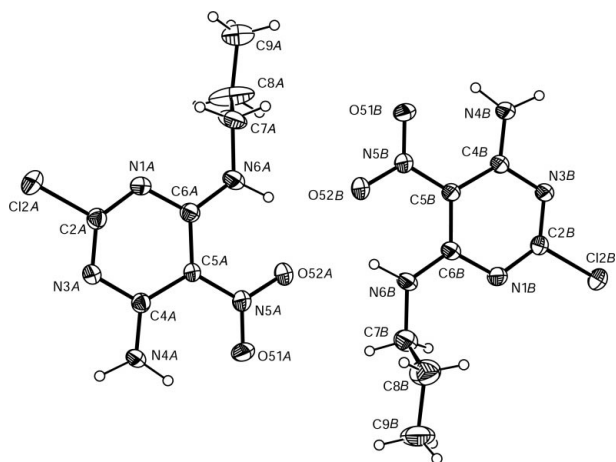


Figure 1

The two independent molecules of (I), showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

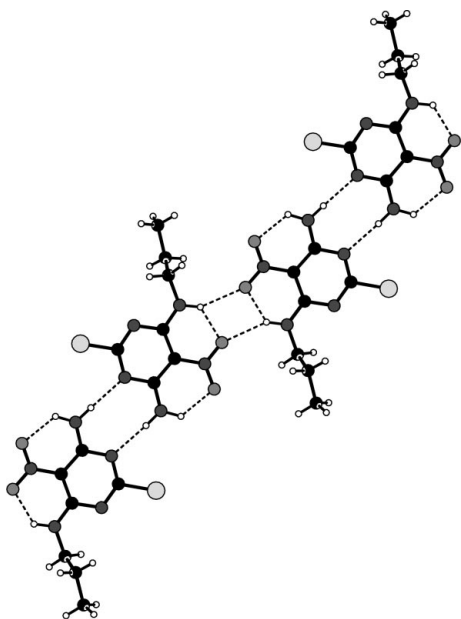


Figure 2

The hydrogen-bonding interactions in (I), shown as dashed lines.

interaction between the *ortho* propylamine and the nitro groups (Table 2, Fig. 2). This complex hydrogen-bonding pattern results in the formation of polymeric chains of coplanar molecules, which lie approximately parallel to the *bc* plane and along the direction of the crystallographic *c* axis.

Experimental

4-Amino-2,6-dichloro-5-nitropyrimidine (40 mg, 0.19 mmol) was taken up in CHCl_3 (4 ml) at 273 K. Propylamine (32 μl , 0.38 mmol), which had been distilled before use, was added and the reaction left to stir. After 4 h, thin-layer chromatography and gas chromatography–mass spectroscopy analysis indicated the reaction was complete. Purification on a column (silica gel, CHCl_3) followed by slow evaporation of the solvent gave a pale-yellow crystalline solid

suitable for X-ray diffraction studies (32 mg, 72.7% yield; m.p. 463–465 K). Spectroscopic analysis: ^1H NMR (d_6 -DMSO, δ , p.p.m.): 9.48 (*brs*, NH), 8.84 (*brs*, NH_2), 3.43 (CH_2), 1.58 (CH_2), 0.89 (*t*, CH_3); ^{13}C NMR (d_6 -DMSO, δ , p.p.m.): 160.76, 159.61, 157.32, 110.69, 42.82, 21.79, 11.11.

Crystal data

$\text{C}_7\text{H}_{10}\text{ClN}_5\text{O}_2$
 $M_r = 231.65$
 Triclinic, $P\bar{1}$
 $a = 7.406$ (3) \AA
 $b = 11.074$ (3) \AA
 $c = 13.886$ (5) \AA
 $\alpha = 112.54$ (2) $^\circ$
 $\beta = 94.82$ (3) $^\circ$
 $\gamma = 101.69$ (3) $^\circ$
 $V = 1013.4$ (7) \AA^3

$Z = 4$
 $D_x = 1.518$ Mg m^{-3}
 Mo $K\alpha$ radiation
 Cell parameters from 25 reflections
 $\theta = 12.7$ – 17.4 $^\circ$
 $\mu = 0.37$ mm^{-1}
 $T = 295$ K
 Prism, pale yellow
 $0.30 \times 0.15 \times 0.10$ mm

Data collection

Rigaku AFC-7R diffractometer
 $\omega/2\theta$ scans
 Absorption correction: none
 3994 measured reflections
 3565 independent reflections
 1948 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.025$

$\theta_{\text{max}} = 25.0$ $^\circ$
 $h = -8 \rightarrow 8$
 $k = -12 \rightarrow 13$
 $l = -16 \rightarrow 7$
 3 standard reflections
 every 150 reflections
 intensity decay: 2.9%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.050$
 $wR(F^2) = 0.158$
 $S = 1.02$
 3565 reflections
 272 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0687P)^2 + 0.5417P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.41$ e \AA^{-3}
 $\Delta\rho_{\text{min}} = -0.32$ e \AA^{-3}

Table 1

Selected geometric parameters (\AA , $^\circ$).

C12A—C2A	1.738 (4)	N6A—C7A	1.453 (7)
C12B—C2B	1.732 (4)	N1B—C2B	1.316 (5)
O51A—N5A	1.228 (5)	N1B—C6B	1.355 (5)
O52A—N5A	1.233 (4)	N3B—C2B	1.316 (6)
O51B—N5B	1.235 (5)	N3B—C4B	1.356 (5)
O52B—N5B	1.239 (4)	N4B—C4B	1.324 (5)
N1A—C2A	1.306 (5)	N5B—C5B	1.410 (5)
N1A—C6A	1.352 (5)	N6B—C6B	1.323 (6)
N3A—C4A	1.360 (5)	N6B—C7B	1.469 (7)
N3A—C2A	1.314 (6)	C4A—C5A	1.430 (5)
N4A—C4A	1.319 (5)	C5A—C6A	1.430 (6)
N5A—C5A	1.406 (5)	C4B—C5B	1.422 (5)
N6A—C6A	1.327 (6)	C5B—C6B	1.439 (6)
C2A—N1A—C6A	115.7 (4)	C4A—C5A—C6A	117.7 (3)
C2A—N3A—C4A	115.6 (3)	N5A—C5A—C6A	122.1 (3)
O51A—N5A—O52A	120.0 (3)	N6A—C6A—C5A	123.9 (4)
O51A—N5A—C5A	121.1 (3)	N1A—C6A—N6A	115.9 (4)
O52A—N5A—C5A	118.9 (3)	N1A—C6A—C5A	120.1 (4)
C6A—N6A—C7A	124.9 (4)	N6A—C7A—C8A	116.2 (5)
C2B—N1B—C6B	115.9 (4)	C12B—C2B—N1B	114.7 (3)
C2B—N3B—C4B	115.7 (3)	C12B—C2B—N3B	114.4 (3)
O51B—N5B—O52B	119.8 (3)	N1B—C2B—N3B	130.9 (4)
O52B—N5B—C5B	119.6 (3)	N4B—C4B—C5B	125.3 (3)
O51B—N5B—C5B	120.6 (3)	N3B—C4B—C5B	119.9 (3)
C6B—N6B—C7B	124.5 (4)	N3B—C4B—N4B	114.8 (3)
C12A—C2A—N1A	114.5 (3)	N5B—C5B—C4B	120.5 (3)
C12A—C2A—N3A	114.2 (3)	C4B—C5B—C6B	118.1 (3)
N1A—C2A—N3A	131.2 (4)	N5B—C5B—C6B	121.5 (3)
N3A—C4A—C5A	119.7 (3)	N1B—C6B—N6B	116.9 (4)
N3A—C4A—N4A	115.1 (3)	N6B—C6B—C5B	123.8 (4)
N4A—C4A—C5A	125.2 (3)	N1B—C6B—C5B	119.3 (4)
N5A—C5A—C4A	120.2 (3)	N6B—C7B—C8B	111.4 (5)

Table 2
Hydrogen-bonding 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>
N6A—H6A···O52A	0.95	1.91	2.601 (5)	128
N6A—H6A···O52B	0.95	2.24	3.076 (5)	147
N6B—H6B···O52A	0.95	2.22	3.052 (5)	146
N6B—H6B···O52B	0.95	1.89	2.599 (5)	129
N4A—H41A···O51A	0.95	1.94	2.607 (4)	125
N4B—H41B···O51B	0.95	1.94	2.607 (4)	125
N4A—H42A···N3B ⁱ	0.95	2.07	3.024 (4)	177
N4B—H42B···N3A ⁱⁱ	0.95	2.06	3.003 (4)	176

Symmetry codes: (i) *x*, *y*, *z* − 1; (ii) *x*, *y*, 1 + *z*.

H atoms were constrained in the riding-model approximation, fixed to their parent C or N atoms, with C—H and N—H distances of 0.95 Å and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C,N})$.

Data collection: *MSC/AFC-7 Diffractometer Control for Windows* (Molecular Structure Corporation, 1999); cell refinement: *MSC/AFC-7 Diffractometer Control for Windows*; data reduction: *TEXSAN for Windows* (Molecular Structure Corporation, 1997–2001); program(s) used to solve structure: *TEXSAN for Windows*; program(s) used to refine structure: *TEXSAN for Windows* and *SHELXL97* (Sheldrick,

1997); molecular graphics: *PLATON for Windows* (Spek, 2001) and *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *TEXSAN for Windows* and *PLATON for Windows*.

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References

- Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Glidewell, C., Low, J. N., Melguizo, M. & Quesada, A. (2003). *Acta Cryst.* **C59**, o14–o18.
- Lynch, D. E. & McClenaghan, I. (2004). *Cryst. Eng.* **6**, 1–14.
- McKeveney, D., Quinn, R. J., Janssen, C. O. & Healy, P. C. (2004). *Acta Cryst.* **E60**, o241–o243.
- Molecular Structure Corporation (1999). *MSC/AFC-7 Diffractometer Control for Windows*. Version 1.02. MSC, 9009 New Trails Drive, The Woodlands, TX 77381-5209, USA.
- Molecular Structure Corporation (1997–2001). *TEXSAN for Windows*. Version 1.06. MSC, 9009 New Trails Drive, The Woodlands, TX 77381-5209, USA.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Spek, A. L. (2001). *PLATON for Windows*. Version 121201. University of Utrecht, The Netherlands.