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

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Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.007 Å
R factor = 0.050
wR factor = 0.158
Data-to-parameter ratio = 13.1

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

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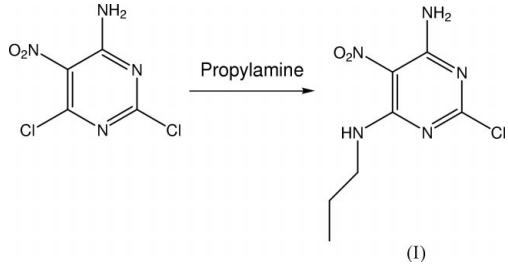
The title compound, $C_7H_{10}ClN_5O_2$, was synthesized as part of a study to demonstrate the reactivity of 4-amino-2,6-dichloro-5-nitropyrimidine with respect to various amine substitutions. The structure determination allowed unambiguous assignment of the regioselectivity of the substitution of the propylamine group at the 6-position. Intra- and intermolecular N—H···O and N—H···N hydrogen bonding yields polymeric chains of coplanar molecules. There are two independent molecules in the asymmetric unit.

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.



(I)

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) N—H···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 $R_2^2(8)$ N—H···N interaction between the *ortho* amino group and the ring N3 atom (*cf.* Glidewell *et al.*, 2003; Lynch & McClenaghan, 2004). The second is an $R_2^2(12)$ N—H···O

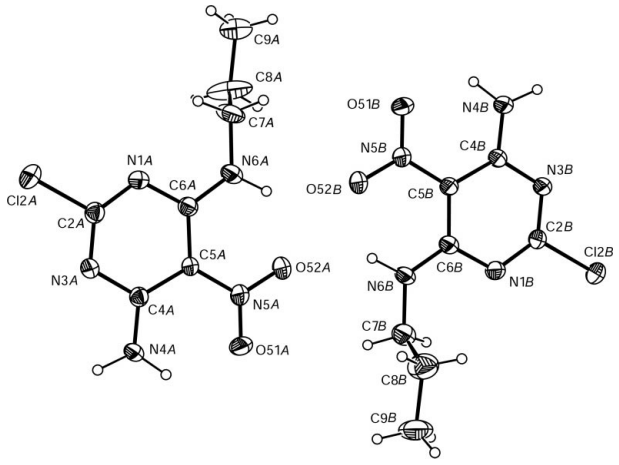


Figure 1
The two independent molecules of (I), showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

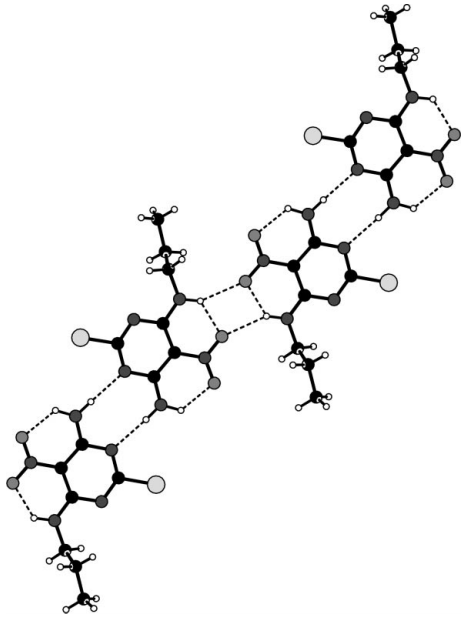


Figure 2
The hydrogen-bonding interactions in (I), shown as dashed lines.

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: ^{1}H 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

$C_7H_{10}ClN_5O_2$	$Z = 4$
$M_r = 231.65$	$D_x = 1.518$ Mg m^{-3}
Triclinic, $P\overline{1}$	Mo $K\alpha$ radiation
$a = 7.406$ (3) Å	Cell parameters from 25 reflections
$b = 11.074$ (3) Å	$\theta = 12.7$–$17.4°$
$c = 13.886$ (5) Å	$\mu = 0.37$ mm^{-1}
$\alpha = 112.54$ (2)°	$T = 295$ K
$\beta = 94.82$ (3)°	Prism, pale yello
$\gamma = 101.69$ (3)°	0.30 × 0.15 × 0.10 mm
$V = 1013.4$ (7) Å^3	

Data collection

Rigaku AFC-7*R* diffractometer	$\theta_{max} = 25.0°$
$\omega/2\theta$ scans	$h = -8 \rightarrow 8$
Absorption correction: none	$k = -12 \rightarrow 13$
3994 measured reflections	$l = -16 \rightarrow 7$
3565 independent reflections	3 standard reflections every 150 reflections
1948 reflections with $I > 2\sigma(I)$	intensity decay: 2.9%
$R_{int} = 0.025$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0687P)^2 + 0.5417P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.050$	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2) = 0.158$	$\Delta\rho_{max} = 0.41$ e Å^{-3}
$S = 1.02$	$\Delta\rho_{min} = -0.32$ e Å^{-3}
3565 reflections	
272 parameters	
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

Cl2*A*—C2*A*	1.738 (4)	N6*A*—C7*A*	1.453 (7)
Cl2*B*—C2*B*	1.732 (4)	N1*B*—C2*B*	1.316 (5)
O51*A*—N5*A*	1.228 (5)	N1*B*—C6*B*	1.355 (5)
O52*A*—N5*A*	1.233 (4)	N3*B*—C2*B*	1.316 (6)
O51*B*—N5*B*	1.235 (5)	N3*B*—C4*B*	1.356 (5)
O52*B*—N5*B*	1.239 (4)	N4*B*—C4*B*	1.324 (5)
N1*A*—C2*A*	1.306 (5)	N5*B*—C5*B*	1.410 (5)
N1*A*—C6*A*	1.352 (5)	N6*B*—C6*B*	1.323 (6)
N3*A*—C4*A*	1.360 (5)	N6*B*—C7*B*	1.469 (7)
N3*A*—C2*A*	1.314 (6)	C4*A*—C5*A*	1.430 (5)
N4*A*—C4*A*	1.319 (5)	C5*A*—C6*A*	1.430 (6)
N5*A*—C5*A*	1.406 (5)	C4*B*—C5*B*	1.422 (5)
N6*A*—C6*A*	1.327 (6)	C5*B*—C6*B*	1.439 (6)
C2*A*—N1*A*—C6*A*	115.7 (4)	C4*A*—C5*A*—C6*A*	117.7 (3)
C2*A*—N3*A*—C4*A*	115.6 (3)	N5*A*—C5*A*—C6*A*	122.1 (3)
O51*A*—N5*A*—O52*A*	120.0 (3)	N6*A*—C6*A*—C5*A*	123.9 (4)
O51*A*—N5*A*—C5*A*	121.1 (3)	N1*A*—C6*A*—N6*A*	115.9 (4)
O52*A*—N5*A*—C5*A*	118.9 (3)	N1*A*—C6*A*—C5*A*	120.1 (4)
C6*A*—N6*A*—C7*A*	124.9 (4)	N6*A*—C7*A*—C8*A*	116.2 (5)
C2*B*—N1*B*—C6*B*	115.9 (4)	Cl2*B*—C2*B*—N1*B*	114.7 (3)
C2*B*—N3*B*—C4*B*	115.7 (3)	Cl2*B*—C2*B*—N3*B*	114.4 (3)
O51*B*—N5*B*—O52*B*	119.8 (3)	N1*B*—C2*B*—N3*B*	130.9 (4)
O52*B*—N5*B*—C5*B*	119.6 (3)	N4*B*—C4*B*—C5*B*	125.3 (3)
O51*B*—N5*B*—C5*B*	120.6 (3)	N3*B*—C4*B*—C5*B*	119.9 (3)
C6*B*—N6*B*—C7*B*	124.5 (4)	N3*B*—C4*B*—N4*B*	114.8 (3)
Cl2*A*—C2*A*—N1*A*	114.5 (3)	N5*B*—C5*B*—C4*B*	120.5 (3)
Cl2*A*—C2*A*—N3*A*	114.2 (3)	C4*B*—C5*B*—C6*B*	118.1 (3)
N1*A*—C2*A*—N3*A*	131.2 (4)	N5*B*—C5*B*—C6*B*	121.5 (3)
N3*A*—C4*A*—C5*A*	119.7 (3)	N1*B*—C6*B*—N6*B*	116.9 (4)
N3*A*—C4*A*—N4*A*	115.1 (3)	N6*B*—C6*B*—C5*B*	123.8 (4)
N4*A*—C4*A*—C5*A*	125.2 (3)	N1*B*—C6*B*—C5*B*	119.3 (4)
N5*A*—C5*A*—C4*A*	120.2 (3)	N6*B*—C7*B*—C8*B*	111.4 (5)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
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 $U_{iso}(H) = 1.2U_{eq}(C,N)$.

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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