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

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Key indicators

Single-crystal X-ray study

T = 295 K

Mean r(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.

The title compound, C7H10ClN5O2, 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.

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...
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 CHCl₃ (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, CHCl₃) 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 (δ, ppm): 9.48 (brs, NH), 8.84 (brs, NH₂), 3.43 (CH₃), 1.58 (CH₃), 0.89 (t, CH₃); ¹³C NMR (δ, ppm): 160.76, 159.61, 157.32, 110.69, 42.82, 21.79, 11.11.

**Crystal data**

C₁₂H₁₀Cl₂N₅O₂, Z = 4  
Mᵣ = 231.65  
Triclinic, P̅T  
Cell parameters from 25 reflections  
θ = 12.7–17.4°  
μ = 0.37 mm⁻¹  
T = 298 K  
Prism, pale yellow

**Data collection**

Rigaku AFC-7R diffractometer  
θ/2θ scans  
Absorption correction: none  
3994 measured reflections  
3565 independent reflections  
1948 reflections with I > 2σ(I)  
Rint = 0.025  
3 standard reflections  
every 150 reflections  
intensity decay: 2.9%

**Refinement**

Refinement on F²  
R[F² > 2σ(F²)] = 0.050  
wR(F²) = 0.158  
S = 1.02  
3565 reflections  
272 parameters  
H-atom parameters constrained

**Table 1**

<table>
<thead>
<tr>
<th>Bond</th>
<th>D/A (Å)</th>
<th>E/A (°)</th>
<th>E/B (°)</th>
<th>E/C (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl₁₀—Cl₂⁴</td>
<td>1.738 (4)</td>
<td>N₆₄—C₇⁴</td>
<td>1.453 (7)</td>
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<tr>
<td>Cl₂⁴—Cl₃⁸</td>
<td>1.732 (4)</td>
<td>N₁₈—C₂⁸</td>
<td>1.361 (5)</td>
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<tr>
<td>O₅₁—N₅₄</td>
<td>1.228 (5)</td>
<td>N₁⁵—C₂⁵</td>
<td>1.355 (5)</td>
<td></td>
</tr>
<tr>
<td>O₅₂—N₅₄</td>
<td>1.233 (4)</td>
<td>N₃⁵—C₂⁸</td>
<td>1.361 (6)</td>
<td></td>
</tr>
<tr>
<td>O₅₅—N₅₈</td>
<td>1.235 (5)</td>
<td>N₃⁸—C₄⁸</td>
<td>1.356 (5)</td>
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<td>O₅₂—N₅₈</td>
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<td>N₄⁸—C₄⁸</td>
<td>1.324 (5)</td>
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<td>N₁₄—C₂⁴</td>
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<td>N₅₈—C₅⁸</td>
<td>1.410 (5)</td>
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<td>N₁₄—C₆⁶</td>
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<td>N₆⁶—C₆⁶</td>
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<td>N₃₄—C₄⁴</td>
<td>1.360 (5)</td>
<td>N₆⁶—C₇⁴</td>
<td>1.469 (7)</td>
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<td>N₃₄—C₄⁴</td>
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<td>C₄⁴—C₅₄</td>
<td>1.430 (5)</td>
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<td>N₄₄—C₄⁴</td>
<td>1.319 (5)</td>
<td>C₅₄—C₆₄</td>
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<tr>
<td>N₅₄—C₅₄</td>
<td>1.406 (5)</td>
<td>C₄⁸—C₅⁸</td>
<td>1.422 (5)</td>
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<tr>
<td>N₆₆—C₆⁶</td>
<td>1.327 (6)</td>
<td>C₅⁸—C₆⁶</td>
<td>1.439 (6)</td>
<td></td>
</tr>
</tbody>
</table>


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

<table>
<thead>
<tr>
<th>N6A−H6A···O52A</th>
<th>D−H</th>
<th>H···A</th>
<th>D···A</th>
<th>D−H···A</th>
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</thead>
<tbody>
<tr>
<td>N6A−H6A···O52B</td>
<td>0.95</td>
<td>1.91</td>
<td>2.601 (5)</td>
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<td>N6B−H6B···O52A</td>
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<td>2.22</td>
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<td>N4A−H41A···O51A</td>
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<td>1.94</td>
<td>2.607 (4)</td>
<td>125</td>
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<tr>
<td>N4B−H41B···O51B</td>
<td>0.95</td>
<td>1.94</td>
<td>2.607 (4)</td>
<td>125</td>
</tr>
<tr>
<td>N4A−H42A···N3B</td>
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<td>2.07</td>
<td>3.024 (4)</td>
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</tr>
<tr>
<td>N4B−H42B···N3A</td>
<td>0.95</td>
<td>2.06</td>
<td>3.003 (4)</td>
<td>176</td>
</tr>
</tbody>
</table>

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 (Molecular Structure Corporation, 1997–2001); data reduction: TEXSAN for Windows; 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