1-(4-Chlorophenyl)-2-methyl-4-nitro-5-(1-piperidyl)-1H-imidazole

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Abstract
The only specific interactions that influence the crystal packing of the title compound, C15H17ClN4O2, are weak C-H...N and C-H...Cl hydrogen bonds, even though there is a possibility of, for example, pi-pi stacking or halogen bonding. The dihedral angle between the mean planes of the imidazole and benzene rings is 59.82 (5) degrees. The length of the C-N bond connecting the imidazole and piperidine fragments is correlated with the degree of pyramidalization of the piperidine N atom.

Keywords
methyl, 5, piperidyl, 1h, 2, 1, chlorophenyl, 4, nitro, imidazole

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The only specific interactions that influence the crystal packing of the title compound, C_{15}H_{17}ClN_{4}O_{2}, are weak C–H⋯N and C–H⋯Cl hydrogen bonds, even though there is a possibility of, for example, π–π stacking or halogen bonding. The dihedral angle between the mean planes of the imidazole and benzene rings is 59.82 (5)°. The length of the C–N bond connecting the imidazole and piperidine fragments is correlated with the degree of pyramidalization of the piperidine N atom.

Comment

Nitroimidazoles have been intensively investigated as radiosensitizers of hypoxic tumour cells and as veterinary drugs (Smithen & Hardy, 1982). In particular, 4-nitro-5-aminoimidazole derivatives have been relatively widely studied, due to their expected radiosensitizing activity combined with good water solubility (see, for example, Wolska et al., 1993, 1994). More recently, in the crystal structure of 1,2-dimethyl-5-morpholino-4-nitroimidazole hydrate, the interesting case of centrosymmetric–non-centrosymmetric ambiguity was found (Kubicki et al., 2003). Moreover, a number of simple 4-nitroimidazole derivatives have been used for studying different intermolecular interactions (see, for example, Kubicki, 2005, and references therein). The structure of another 5-amino-4-nitroimidazole, the title compound, (I), is reported here. The ability of 4-nitroimidazoles to undergo nucleophilic substitution has been widely investigated (see, for example, Mąkosza, 1992) and provides a convenient way of modifying azole derivatives. Some amino derivatives have also been synthesized in this way (Mąkosza & Bialecki, 1998; Suwiński & Świerczek, 1996).

Fig. 1 shows a displacement ellipsoid representation of (I). The benzene and imidazole rings are almost perfectly planar, and the dihedral angle between them is 59.82 (5)°. The sum of the valence angles around the amino N atom (Fig. 2) is correlated with the C–N bond length (see, for example, Kubicki, 2005, and references therein).

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**Figure 1**
A view of the molecule of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

**Figure 2**
The correlation between the C–N bond length and the sum of the valence angles around the amino N atom for 5-(cyclic)aminoimidazoles.
The molecular geometry of (I) is quite typical. In this type of compound, there is an interesting correlation between the C5—N51 bond length and the sum of the bond angles around N51: the longer the bond, the larger the pyramidalization of the N atom, i.e. the cis angle is larger than the trans one (Kubicki, 2004b).

The piperidine ring is in a chair conformation. The asymmetry parameters (Duax & Norton, 1975) show only minor distortions from ideal C3v symmetry (the maximum value of the ΔC2 parameter is 3.83°, and of ΔC3 is −3.15°).

In the crystal structure of (I), there are infinite chains of molecules extending along the [100] direction, created by C—N hydrogen bonds. Using graph-set notation (Etter et al., 1990; Bernstein et al., 1995), this motif can be described as a C(7) chain. Neighbouring chains are bound by weak three-centred C—H···Cl hydrogen bonds {C(12)[R2(5)]} chains along the [001] direction. These two kinds of weak interactions close larger rings of molecules of motif R2(30) (Fig. 3). The geometric details of these interactions are given in Table 2. Interestingly, in this case no other specific interatomic interactions (e.g. π···π stacking or halogen bonds) take part in the creation of the supramolecular structure, even though these interactions could compete successfully with weak hydrogen bonding.

**Experimental**

The title compound was synthesized by nucleophilic replacement of bromine at the 5-position of the imidazole ring by piperidine (see scheme). The reaction was carried out in boiling methanol with an excess of piperidine over 24 h with a high yield. In contrast with the reactivity of the 1-alkyl derivative, in which double substitution of the imidazole moiety. Crystals of (I) suitable for X-ray data collection were grown from a methanol solution.

**Crystal data**

C15H17ClN4O2

Mo Kα radiation

Cell parameters from 2320 reflections

θ = 3.39(1)°

μ = 0.28 mm−1

T = 90 (1) K

Needle, colourless

0.4 × 0.15 × 0.1 mm

**Data collection**

Kuma KM-4 CCD four-circle diffractometer

ω scans

Absorption correction: multi-scan

(SORTAV; Blessing, 1989)

Tmin = 0.958, Tmax = 0.972

15516 measured reflections

Refinement

Reﬁnement on F2

ℜ(F2) = 2σ(F2) = 0.031

wR(F2) = 0.054

S = 0.93

4069 reflections

257 parameters

All H-atom parameters refined

**Table 1**

Selected geometric parameters (Å, °).

<table>
<thead>
<tr>
<th></th>
<th>N1—C2</th>
<th>N3—C4</th>
<th>N1—C5</th>
<th>N4—O42</th>
<th>C2—N3</th>
<th>C5—N51</th>
<th>O42—N4—O41</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.383 (2)</td>
<td>1.376 (2)</td>
<td>1.391 (2)</td>
<td>1.234 (2)</td>
<td>1.302 (2)</td>
<td>1.361 (2)</td>
<td>1.232 (2)</td>
</tr>
<tr>
<td>C2—N1—C5</td>
<td>108.1 (1)</td>
<td>118.9 (1)</td>
<td>124.7 (1)</td>
<td>117.8 (1)</td>
<td>127.1 (1)</td>
<td>120.7 (1)</td>
<td>121.2 (1)</td>
</tr>
<tr>
<td>C2—N1—C11</td>
<td>127.1 (1)</td>
<td>127.1 (1)</td>
<td>117.8 (1)</td>
<td>120.7 (1)</td>
<td>121.2 (1)</td>
<td>114.9 (1)</td>
<td>114.9 (1)</td>
</tr>
</tbody>
</table>

**Acknowledgements**

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The positions of the H atoms were freely refined [C—H = 0.93 (2)—1.02 (2) Å. For each group of these atoms, i.e. for the methyl group, for each CH₂ group and for ring H atoms, one common U_iso(H) parameter was refined.

Data collection: CrysAlis CCD (Oxford Diffraction, 2002); cell refinement: CrysAlis CCD; data reduction: CrysAlis RED (Oxford Diffraction, 2002); program(s) used to solve structure: SHELXS97 (Sheldrick, 1990); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: Stereochemical Workstation Operation Manual (Siemens, 1989); software used to prepare material for publication: SHELXL97.

Symmetry codes: (i) x+1, y, z; (ii) −x+3/2, −y, z−1/2.

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### Table 2
Hydrogen-bond geometry (Å, °).

<table>
<thead>
<tr>
<th>D—H · · · A</th>
<th>D—H</th>
<th>H · · · A</th>
<th>D—A</th>
<th>D—H · · · A</th>
</tr>
</thead>
<tbody>
<tr>
<td>C13—H13 · · · N3i</td>
<td>0.97 (2)</td>
<td>2.45 (2)</td>
<td>3.424 (2)</td>
<td>180 (1)</td>
</tr>
<tr>
<td>C54—H54 · · · Cl14ii</td>
<td>0.98 (2)</td>
<td>3.06 (2)</td>
<td>3.705 (2)</td>
<td>125 (1)</td>
</tr>
<tr>
<td>C55—H55 · · · Cl14ii</td>
<td>0.97 (2)</td>
<td>2.95 (1)</td>
<td>3.564 (2)</td>
<td>122 (1)</td>
</tr>
</tbody>
</table>

Symmetry codes: (i) x+1, y, z; (ii) −x+3/2, −y, z−1/2.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TAI498). Services for accessing these data are described at the back of the journal.

### References

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**organic compounds**