Two 1-substituted 4-nitroimidazoles

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Abstract
Crystalline 4-nitro-1-phenylimidazole, C$_{9}$H$_{7}$N$_{3}$O$_{2}$, (I), and 4′-nitro-1-phenyl-4,1′-biimidazole, C$_{12}$H$_{9}$N$_{5}$O$_{2}$, (II), contain C—H⋯O and C—H⋯N hydrogen bonds, connecting the molecules into infinite chains. The aromatic fragments in both compounds are nearly planar. The dihedral angles between the benzene and imidazole rings are 26.78 (5)° in (I) and 29.36 (8)° in (II).

Keywords
1, substituted, 4, nitroimidazoles, two

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Two 1-substituted 4-nitroimidazoles

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Crystalline 4-nitro-1-phenylimidazole, C₇H₇N₂O₂, (I), and 4'-nitro-1-phenyl-4,1'-biimidazole, C₁₇H₁₄N₄O₂, (II), contain C—H···O and C—H···N hydrogen bonds, connecting the molecules into infinite chains. The aromatic fragments in both compounds are nearly planar. The dihedral angles between the benzene and imidazole rings are 26.78 (5)° in (I) and 29.36 (8)° in (II).

Comment

The imidazole ring is present in a number of biologically active compounds, as well as in many natural products (Josephy & Mason, 1985). 1-Substituted 4-nitroimidazoles are generated in excellent yields from the reaction of 1,4-dinitroimidazoles with primary amines (Suwiński & Salwińska, 1990; Suwiński & Wagner, 1997). We present here the crystal structures of two compounds of this kind, i.e. (I) and (II).

In (I), both the benzene and imidazole rings are almost perfectly planar [maximum deviations from the least-squares planes are 0.0070 (9) and 0.0048 (7) Å for the benzene and imidazole rings, respectively] and the dihedral angle between these planes is 26.78 (5)°. The nitro group is twisted slightly but significantly [by 6.91 (14)°] with respect to the plane of the five-membered ring. The C2—N3 bond length is shorter than C2—C4 [1.311 (2) and 1.363 (2) Å, respectively].

In (II), all rings are also planar, with maximum deviations from the least-squares planes of 0.0039 (13), 0.0046 (12) and 0.0049 (17) Å for the nitroimidazole, imidazole and benzene rings, respectively. The dihedral angle between the benzene and imidazole rings is 29.36 (8)° [a similar value was found for (I)], while the angle between the two imidazole rings is significantly smaller, 11.28 (13)°. The reason for this may be geometrical; the five-membered rings afford more space around the junction bond than the six-membered ring. The twist angle of the nitro group is smaller than in (I) [3.3 (3)°].

In compound (I), there is a statistically significant deformation of the endocyclic bond angles pattern in the benzene ring due to the influence of the electron-accepting nitroimidazole substituent. These deformations are generally consistent with those described by Domenicano (1988) and are comparable with those found for the cyano group. In (II), these effects are negligible because of the weaker electron-
accepting properties of imidazole compared with nitro-
imidazole.

In both compounds, there are weak though important C—
H· · · O and C—H· · · N hydrogen bonds (see Table 3). In (I),
two such bonds connect the molecules into infinite chains
(Fig. 1). Isolated chains have also been found in the crystal
structure of (II); in this case, however, chains are comprised of
hydrogen-bonded centrosymmetric dimers. The linearity of

![Figure 2](image)

View of the hydrogen-bonded motif of compound (II) (Siemens, 1989)
with the atomic labelling scheme. Displacement ellipsoids are drawn at
the 50% probability level and the H atoms are depicted as spheres of
arbitrary radii. [Symmetry codes: (i) x, y, z; (ii) x, y, z; (iii) x, y, z.]

these contacts, as well as their determinative role in the crystal
packing, justify the use of the term ‘hydrogen bonds’ in these
cases (Desiraju & Steiner, 1999). We have not detected any
interplanar interactions, the distances between chains being
close to the sums of van der Waals radii. In the nitro group of
(I), the N1—O2 bond is significantly shorter than N1—O1.
This could be related to the fact that the O2 atom acts as a
hydrogen-bond acceptor. However, no such shortening could
be found in (II) and therefore it probably should be labelled as
an artefact.

**Experimental**

The syntheses of compounds (I) and (II) have been described else-
where (Suwinski & Salwinski, 1990; Suwinski & Wagner, 1997).
Crystals appropriate for data collection were obtained by slow
evaporation from methanol solution.

### Compound (I)

**Crystal data**

- C₆H₈N₂O₂
- Mₛ = 189.18
- Orthorhombic, Pnca
- a = 11.088 (2) Å
- b = 6.8840 (10) Å
- c = 21.976 (4) Å
- V = 1677.4 (5) Å³
- Z = 8
- Dᵣ = 1.498 Mg m⁻³

**Data collection**

- Kuma KM4—CCD diffractometer
- 8980 measured reflections
- 1846 independent reflections
- 1424 reflections with I > 2σ(I)

**Refinement**

- R[F²] = 0.035
- wR[F²] = 0.096
- S = 1.079
- 1846 reflections
- 156 parameters
- H atoms treated by a mixture of
- independent and constrained refinement

**Table 1**

<table>
<thead>
<tr>
<th></th>
<th>N1—O1</th>
<th>N1—C2</th>
<th>N2—O2</th>
<th>N1—C5</th>
<th>N3—C2</th>
<th>N3—C4</th>
<th>N2—O1</th>
<th>C7—C6—C11</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>1.3703 (15)</td>
<td>1.3677 (15)</td>
<td>1.3464 (15)</td>
<td>1.2216 (13)</td>
<td>1.2355 (13)</td>
<td>1.2396 (17)</td>
<td>1.3461 (17)</td>
<td>1.3641 (17)</td>
</tr>
</tbody>
</table>

**Table 2**

<table>
<thead>
<tr>
<th></th>
<th>C—H—A</th>
<th>D—H—A</th>
<th>H—A</th>
<th>D—A</th>
<th>D—H—A</th>
</tr>
</thead>
<tbody>
<tr>
<td>C2—H21—O2</td>
<td>0.953 (14)</td>
<td>2.353 (14)</td>
<td>3.2436 (16)</td>
<td>156.4 (11)</td>
<td>162.5 (12)</td>
</tr>
<tr>
<td>C5—H51—N3</td>
<td>0.952 (15)</td>
<td>2.514 (15)</td>
<td>3.4338 (18)</td>
<td>156.4 (11)</td>
<td>162.5 (12)</td>
</tr>
</tbody>
</table>

**Compound (II)**

**Crystal data**

- C₆H₈N₂O₂
- Mₛ = 255.24
- Monoclinic, P₂₁/c
- a = 14.143 (3) Å
- b = 3.8880 (10) Å
- c = 20.600 (4) Å
- β = 94.92 (3)°
- V = 1131.9 (4) Å³
- Z = 4

**Data collection**

- Mo Kα radiation
- Cell parameters from 531 reflections
- θ = 1.50°
- μ = 0.110 mm⁻¹
- T = 293 (2) K
- Plate, colourless
- 0.4 × 0.2 × 0.2 mm

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organic compounds

Data collection
Kuma KM4-CCD diffractometer
w20 scans
6713 measured reflections
2882 independent reflections
1046 reflections with I > 2σ(I)

Refinement
Refinement on F²
R[F²] = 2σ(F²) = 0.046
wR(F²) = 0.105
S = 0.781
2882 reflections
209 parameters
All H-atom parameters refined

w = 1/[σ²(Fo²) + (0.0453P)²]
where P = (Fo² + 2Fe²)/3
(Δρ)max = 0.16 e Å⁻³
Δρmin = -0.17 e Å⁻³
Extinction correction: SHELXL97
(Sheldrick, 1997)
Extinction coefficient: 0.0034 (10)

Table 4
Hydrogen-bonding geometry (Å, °) for (II).

<table>
<thead>
<tr>
<th>D—H···A</th>
<th>D—H</th>
<th>H···A</th>
<th>D···A</th>
<th>D···A</th>
</tr>
</thead>
<tbody>
<tr>
<td>C7—H71···O2</td>
<td>0.959 (19)</td>
<td>2.24 (2)</td>
<td>3.249 (3)</td>
<td>185.9 (15)</td>
</tr>
<tr>
<td>C5—H51···O6</td>
<td>0.955 (19)</td>
<td>2.56 (2)</td>
<td>3.505 (3)</td>
<td>168.7 (15)</td>
</tr>
<tr>
<td>C2—H21···N3</td>
<td>0.959 (19)</td>
<td>2.56 (2)</td>
<td>3.399 (3)</td>
<td>135.2 (16)</td>
</tr>
<tr>
<td>C10—H101···N3</td>
<td>0.919 (19)</td>
<td>2.65 (2)</td>
<td>3.460 (3)</td>
<td>148.0 (16)</td>
</tr>
</tbody>
</table>

Symmetry codes: (i) -x, -y, -z; (ii) -x, -y, z;

(Sheldrick, 1990); program(s) used to refine structure: SHELXL97
(Sheldrick, 1997); molecular graphics: Stereochemical Workstation
(Siemens, 1989); software used to prepare material for publication:
Stereochemical Workstation.

Supplementary data for this paper are available from the IUCr electronic
archives (Reference: DE1151). Services for accessing these data are
described at the back of the journal.

References
Chemistry and Biology. Oxford University Press.
Wrocław, Poland.
Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.