organic compounds

Two 1-substituted 4-nitroimidazoles

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Crystalline 4-nitro-1-phenylimidazole, $C_9H_7N_3O_2$, (I), and 4′-nitro-1-phenyl-4,1′-biimidazole, $C_{12}H_9N_5O_2$, (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).

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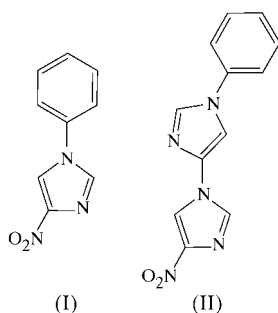
In (I), both the benzene and imidazole rings are almost perfectly planar [maximum deviations from the least-squares planes are 0.0070 (9) and 0.0048 (7) Å for the benzene and imidazole rings, respectively] and the dihedral angle between these planes is 26.78 (5)°. The nitro group is twisted slightly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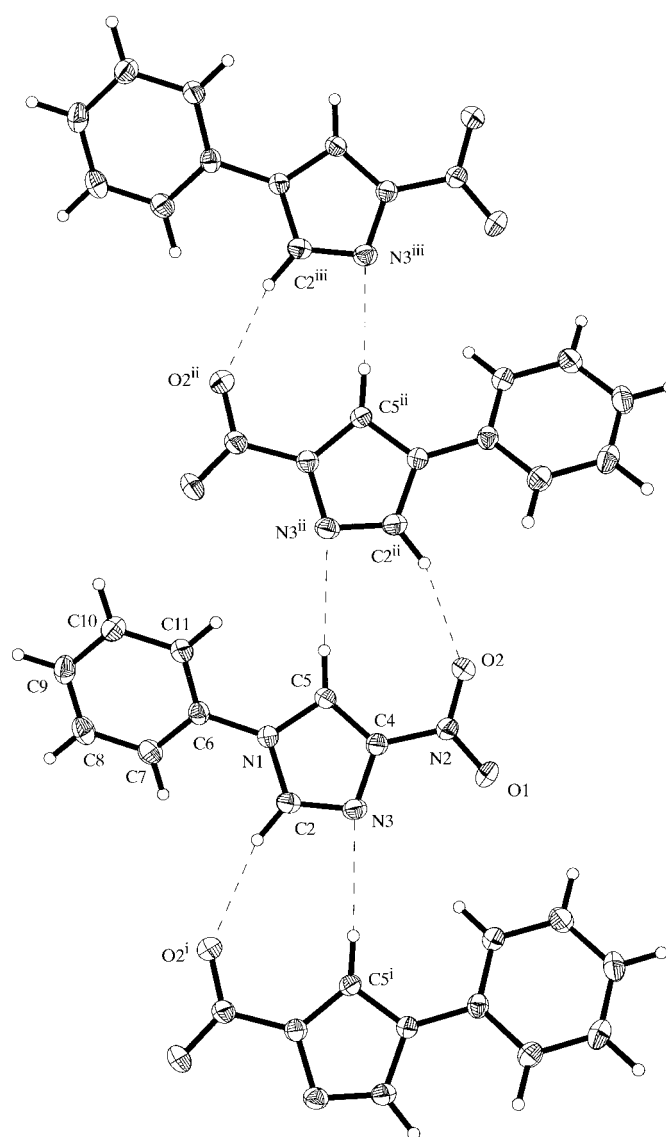

Figure 1
View of the hydrogen-bonded motif of compound (I) (Siemens, 1989) with the atomic labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and the H atoms are depicted as spheres of arbitrary radii. [Symmetry codes: (i) $x - \frac{1}{2}, \frac{1}{2} - y, 1 - z$; (ii) $\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$; (iii) $1 + x, y, z$.]

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
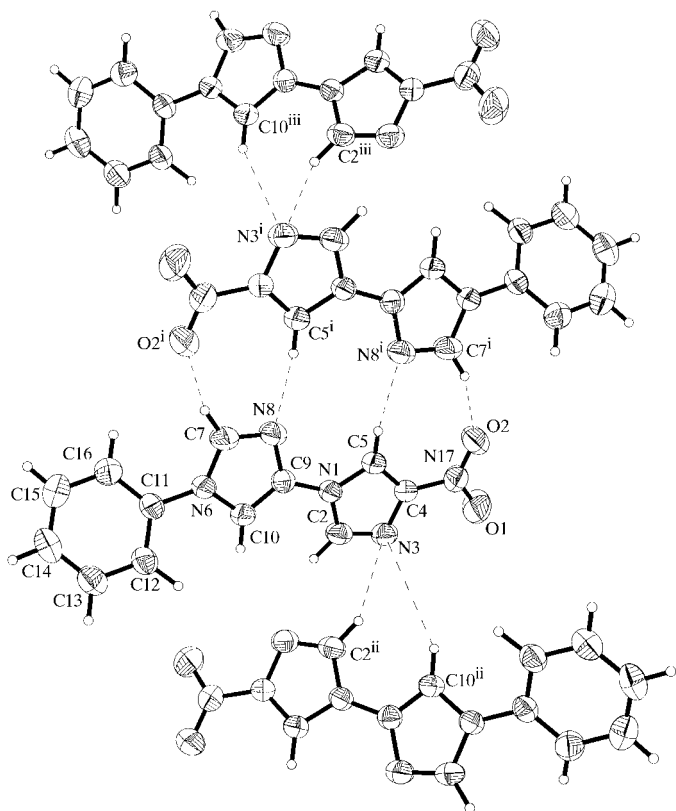

Figure 2
View of the hydrogen-bonded motif of compound (II) (Siemens, 1989) with the atomic labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and the H atoms are depicted as spheres of arbitrary radii. [Symmetry codes: (i) $-x, -y, 1 - z$; (ii) $-x, y - \frac{1}{2}, \frac{1}{2} - z$; (iii) $x, -\frac{1}{2} + y, \frac{1}{2} + z$.]

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 elsewhere (Suwiński & Salwińska, 1990; Suwiński & Wagner, 1997). Crystals appropriate for data collection were obtained by slow evaporation from methanol solution.

Compound (I)

Crystal data

$C_9H_7N_3O_2$	Mo $K\alpha$ radiation
$M_r = 189.18$	Cell parameters from 1027
Orthorhombic, $Pbca$	reflections
$a = 11.088\ (2)$ Å	$\theta = 1–50°$
$b = 6.8840\ (10)$ Å	$\mu = 0.110$ mm^{-1}
$c = 21.976\ (4)$ Å	$T = 293\ (2)$ K
$V = 1677.4\ (5)$ Å^3	Prismatic, colourless
$Z = 8$	$0.5 \times 0.2 \times 0.2$ mm
$D_x = 1.498$ Mg m^{-3}	

Data collection

Kuma KM4–CCD diffractometer	$R_{int} = 0.046$
$\omega/2\theta$ scans	$\theta_{max} = 27.10°$
8680 measured reflections	$h = -14 \rightarrow 14$
1846 independent reflections	$k = -5 \rightarrow 8$
1424 reflections with $I > 2\sigma(I)$	$l = -27 \rightarrow 28$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0573P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.035$	$+ 0.0033P]$
$wR(F^2) = 0.096$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.079$	$(\Delta/\sigma)_{max} = 0.001$
1846 reflections	$\Delta\rho_{max} = 0.22$ e Å^{-3}
156 parameters	$\Delta\rho_{min} = -0.23$ e Å^{-3}
H atoms treated by a mixture of	Extinction correction: $SHELXL$97
independent and constrained	(Sheldrick, 1997)
refinement	Extinction coefficient: 0.0045 (13)

Table 1
Selected geometric parameters (Å, °) for (I).

N1—C2	1.3703 (15)	N2—O2	1.2355 (13)
N1—C5	1.3677 (15)	N3—C2	1.3106 (17)
N1—C6	1.4346 (15)	N3—C4	1.3631 (16)
N2—O1	1.2216 (13)	C4—C5	1.3641 (17)
C7—C6—C11	121.18 (11)		

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

D—H···A	D—H	H···A	D···A	D—H···A
C2—H21···O2^i	0.953 (14)	2.353 (14)	3.2466 (16)	156.0 (11)
C5—H51···N3^{ii}	0.952 (15)	2.514 (15)	3.4338 (18)	162.5 (12)

Symmetry codes: (i) $x - \frac{1}{2}, \frac{1}{2} - y, 1 - z$; (ii) $\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$.

Compound (II)

Crystal data

$C_{12}H_9N_5O_2$	$D_x = 1.498$ Mg m^{-3}
$M_r = 255.24$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 531
$a = 14.143\ (3)$ Å	reflections
$b = 3.8880\ (10)$ Å	$\theta = 1–50°$
$c = 20.660\ (4)$ Å	$\mu = 0.108$ mm^{-1}
$\beta = 94.92\ (3)°$	$T = 293\ (2)$ K
$V = 1131.9\ (4)$ Å^3	Plate, colourless
$Z = 4$	$0.4 \times 0.2 \times 0.02$ mm

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Data collection

Kuma KM4–CCD diffractometer	$R_{int} = 0.056$
$\omega/2\theta$ scans	$\theta_{max} = 29.35°$
6713 measured reflections	$h = -19 \rightarrow 15$
2882 independent reflections	$k = -5 \rightarrow 5$
1046 reflections with $I > 2\sigma(I)$	$l = -27 \rightarrow 28$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o{}^2) + (0.0453P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.046$	where $P = (F_o{}^2 + 2F_c{}^2)/3$
$wR(F^2) = 0.105$	$(\Delta/\sigma)_{max} < 0.001$
$S = 0.781$	$\Delta\rho_{max} = 0.16$ e Å^{-3}
2882 reflections	$\Delta\rho_{min} = -0.17$ e Å^{-3}
209 parameters	Extinction correction: *SHELXL*97
All H-atom parameters refined	(Sheldrick, 1997)
	Extinction coefficient: 0.0034 (10)

Table 3
Selected geometric parameters (Å, °) for (II).

N1—C2	1.357 (2)	N6—C11	1.423 (2)
N1—C5	1.360 (2)	N8—C7	1.317 (3)
N1—C9	1.415 (2)	C4—N3	1.362 (2)
N3—C2	1.308 (3)	C4—C5	1.353 (3)
N6—C7	1.353 (2)	C9—N8	1.354 (2)
N6—C10	1.374 (2)	C9—C10	1.345 (3)
C16—C11—C12	120.4 (2)		

For both compounds, data collection: *CrysAlis CCD* (Kuma Diffraction, 1999); cell refinement: *CrysAlis Red* (Kuma Diffraction, 1999) for compound (I), *CrysAlis CCD* for compound (II); data reduction: *CrysAlis Red* for compound (I), *CrysAlis CCD* for compound (II); program(s) used to solve structure: *SHELXS*97

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C7—H71$\cdots$O2^i	0.959 (19)	2.34 (2)	3.249 (3)	158.9 (15)
C5—H51$\cdots$N8^i	0.955 (19)	2.56 (2)	3.505 (3)	168.7 (15)
C2—H21$\cdots$N3^{ii}	0.959 (19)	2.56 (2)	3.309 (3)	135.2 (16)
C10—H101$\cdots$N3^{ii}	0.919 (19)	2.65 (2)	3.460 (3)	148.0 (16)

Symmetry codes: (i) $-x, -y, 1 - z$; (ii) $-x, \frac{1}{2} + y, \frac{1}{2} - z$.

(Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (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.

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