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Crystal packing of two 5-substituted 2-methyl-4-nitro-1*H*-imidazoles

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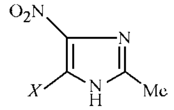
Infinite chains connected by N—H···N hydrogen bonding form the primary packing motif in two closely related 4-nitroimidazole derivatives, *viz.* 5-bromo-2-methyl-4-nitro-1*H*-imidazole, $C_4H_4BrN_3O_2$, (I), and 2-methyl-4-nitro-1*H*-imidazole-5-carbonitrile, $C_5H_4N_4O_2$, (II). These chains are almost identical, even though in (II) there are two symmetry-independent molecules in the asymmetric unit. The differences appear in the interactions between the chains; in (I), there are strong C—Br···O halogen bonds, which connect the chains into a two-dimensional grid, while in (II), the cyano group does not participate in specific interactions and the chains are only loosely connected into a three-dimensional structure.

Comment

Nitroimidazoles have been intensively investigated as radiosensitizers of hypoxic tumor cells and as veterinary drugs (Smithen & Hardy, 1982). Moreover, the 5(4)-bromo and 5(4)-cyano derivatives of nitroimidazoles have been proved to be excellent starting materials for purine derivative synthesis (*e.g.* Suwiński *et al.*, 1996, and references therein). For some time, we have studied weak intermolecular interactions in 4-nitroimidazole derivatives (*e.g.* Kubicki *et al.*, 2001, 2002). We describe here the intermolecular interactions in two closely related 4(5)-nitroimidazole derivatives, *viz.* 5(4)-bromo-2-methyl-4(5)-nitroimidazole, (I), and 2-methyl-4(5)-nitroimidazole-5(4)-carbonitrile, (II). In the previously reported pair of 5-cyanoimidazoles with blocked N1 atom (Kubicki, 2004*a*), which differed by the presence of a Cl atom, we observed chloro–cyano halogen bonds or cyano–cyano interactions.



(I) *X*=Br
(II) *X*=CN

The conformation of the molecules (Figs. 1 and 2) can be defined by the dihedral angle between the planar imidazole ring [the maximum deviation from the plane is 0.001 (3) Å in (I) and 0.002 (1) Å in (II)] and the nitro group. The values of these angles are small [2.3 (6)° in (I), and 5.2 (3) and 2.3 (2)° in the two independent molecules of (II)]; therefore, the whole molecules are approximately planar.

In both crystal structures, N—H···N hydrogen bonds form the primary motif of crystal packing (Table 1). Such chains are often observed in the crystal structures of N-unsubstituted nitroimidazole derivatives (*e.g.* De Bondt *et al.*, 1993). The chains created by these hydrogen bonds are almost identical in both cases (Figs. 3 and 4), even though in the asymmetric unit of (II) there are two symmetry-independent molecules. It has been shown (Kubicki, 2005) that the percentage of structures with $Z' > 1$ (*i.e.* more than one symmetry-independent molecule) for simple imidazole derivatives is above the average value for organic molecules. In the structure of (II), the symmetry-independent molecules are almost identical, and the intermolecular interactions in which they take part are also almost identical. The only difference is that one of these molecules is connected to its centrosymmetric partner by a

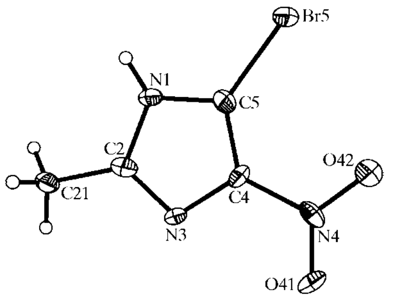


Figure 1
An anisotropic displacement ellipsoid representation (at the 50% probability level) of the molecule of (I), together with the atomic numbering scheme.

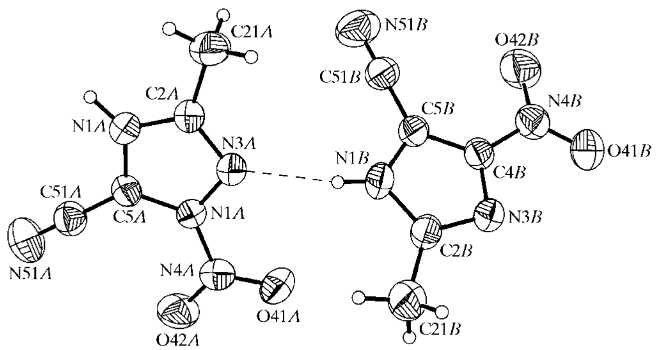


Figure 2
An anisotropic displacement ellipsoid representation (at the 50% probability level) of both symmetry-independent molecules of (II), together with the atomic numbering scheme. The intermolecular N—H···N hydrogen bond is shown as a dashed line.

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very weak, in fact disputable, C—N···C—N interaction [the N···C distances are 3.516 (3) Å].

The differences in crystal packing are clearly seen at the next level of analysis, in the interactions between the chains. In (I), relatively short C—Br···O(nitro) halogen bonds connect neighbouring chains. The Br···O contact of 2.986 (4) Å is one of the shortest contacts of this type. The contact to the other O atom of the nitro group is relatively long [3.363 (4) Å]. Such an unsymmetrical situation is typical; examples of (almost) symmetrical halogen bonds of this type are rare (*cf.* Kubicki, 2004*b*, and references therein). In (I), additional weak π–π interactions between molecules related by a *b*-glide plane perpendicular to *a* also contribute to the determination of the structure. The molecules are almost parallel; the dihedral angle between the mean planes is 1.3 (3)° and the distance between these planes is 3.487 Å (taking into account the offset, the distance between the mid-points is 3.730 Å).

On the other hand, in (II), it is hard to indicate any specific, directional interactions that could act between the chains (the cyano–cyano distances are far too long to play any role in the determination of crystal packing). Therefore, it is probable that just van der Waals forces are the driving factor for the packing of the hydrogen-bonded chains.

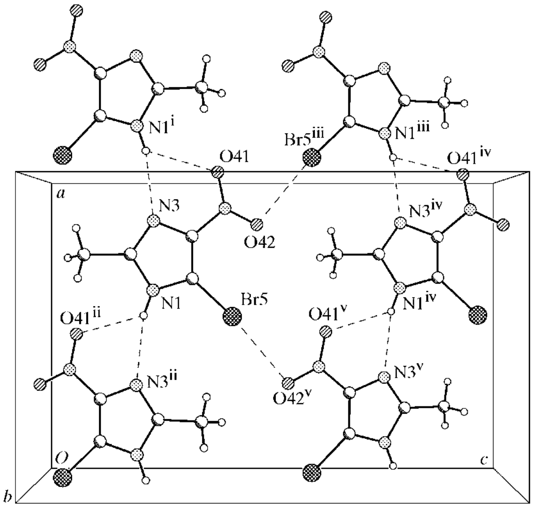

Figure 3

A fragment of the hydrogen- and halogen-bonded structure of (I). [Symmetry codes: (i) $x+\frac{1}{2}, y, -z+\frac{1}{2}$; (ii) $x-\frac{1}{2}, y, -z+\frac{1}{2}$; (iii) $x+\frac{1}{2}, -y+\frac{3}{2}, -z+1$; (iv) $x, -y+\frac{3}{2}, z+\frac{1}{2}$; (v) $x-\frac{1}{2}, -y+\frac{3}{2}, -z+1$.]

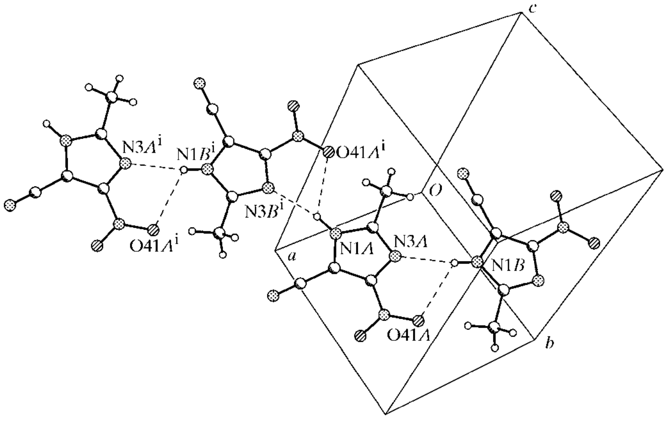

Figure 4

The hydrogen-bonded chain of molecules in (II). [Symmetry code: (vi) $x+1, y-1, z$.]

Experimental

Compound (I) was synthesized by *N*-bromosuccinimide bromination of 4(5)-nitro-2-methylimidazole according to a previously described procedure (Salgado-Zamora *et al.*, 1999). Compound (II) was obtained by *cine* nucleophilic substitution of a nitro group from 1,4-dinitro-2-methylimidazole (Suwiński & Świerczek, 1998).

Compound (I)

Crystal data

$C_4H_4BrN_3O_2$
$M_r = 206.01$
Orthorhombic, *Pbca*
$a = 10.5281$ (10) Å
$b = 7.4585$ (11) Å
$c = 16.341$ (2) Å
$V = 1283.2$ (3) Å^3
$Z = 8$
Mo $K\alpha$ radiation
$\mu = 6.34$ mm^{-1}
$T = 100$ (1) K
0.2 × 0.15 × 0.15 mm

Data collection

Kuma KM-4 CCD four-circle diffractometer
Absorption correction: multi-scan (*CrysAlis RED*; Version 1.171.31.5; Oxford Diffraction, 2006)
$T_{\min} = 0.281$, $T_{\max} = 0.386$
9177 measured reflections
1187 independent reflections
965 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.073$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.050$
$wR(F^2) = 0.139$
$S = 1.08$
1187 reflections
92 parameters
H-atom parameters constrained
$\Delta\rho_{\max} = 1.47$ e Å^{-3}
$\Delta\rho_{\min} = -0.89$ e Å^{-3}

Compound (II)

Crystal data

$C_5H_4N_4O_2$
$M_r = 152.12$
Triclinic, $P\overline{1}$
$a = 7.7166$ (15) Å
$b = 8.1716$ (11) Å
$c = 11.715$ (2) Å
$\alpha = 74.278$ (14)°
$\beta = 77.630$ (17)°
$\gamma = 77.150$ (14)°
$V = 683.9$ (2) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.12$ mm^{-1}
$T = 295$ (1) K
0.3 × 0.2 × 0.15 mm

Data collection

Kuma KM-4 CCD four-circle diffractometer
4954 measured reflections
2360 independent reflections
1325 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.025$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.105$
$S = 0.97$
2360 reflections
209 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max} = 0.23$ e Å^{-3}
$\Delta\rho_{\min} = -0.22$ e Å^{-3}

In (I), H atoms were placed in ideal positions and refined as riding, with $U_{\rm iso}$(H) values set at 1.2 (NH) and 1.3 (CH) times $U_{\rm eq}$ of the carrier atoms. In (II), methyl H atoms were again treated as riding with $U_{\rm iso}$(H) values equal to $1.3U_{\rm eq}$(C). The remaining H atoms were refined freely.

Table 1
Hydrogen- and halogen-bond data (Å, °).

D—H···A or C—X···Y	D—H or C—X	H···A or X···Y	D···A	D—H···A or C—X···Y
Compound 1				
N1—H1···N3$^{\mathrm{ii}}$	0.86	2.25	3.085 (6)	164
N1—H1···O41$^{\mathrm{ii}}$	0.86	2.52	3.038 (6)	120
C21—H21A···O41$^{\mathrm{vii}}$	0.96	2.45	3.381 (6)	164
C5—Br5···O42$^{\mathrm{v}}$	1.855 (5)	2.986 (4)	–	173.2 (2)
C5—Br5···O41$^{\mathrm{v}}$	1.855 (5)	3.363 (4)	–	147.3 (2)
Compound 2				
N1B—H1B···N3A	0.82 (3)	2.07 (3)	2.864 (3)	163 (3)
N1B—H1B···O41A	0.82 (3)	2.72 (3)	3.119 (3)	111 (2)
N1A—H1A···N3B^{viii}	0.90 (3)	1.96 (3)	2.832 (3)	165 (2)
N1A—H1A···O41B^{viii}	0.90 (3)	2.58 (3)	3.057 (3)	114 (2)

Symmetry codes: (ii) $x - \frac{1}{2}, y, -z + \frac{1}{2}$; (v) $x - \frac{1}{2}, -y + \frac{3}{2}, -z + 1$; (vii) $-x + 2, y + \frac{1}{2}, -z + \frac{1}{2}$; (viii) $x + 1, y, z$.

For both compounds, data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2006); 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*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV3095). Services for accessing these data are described at the back of the journal.

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