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2,2′-Dimethyl-4,5′-dinitro-1*H*,3′*H*-1,4′-biimidazole monohydrate

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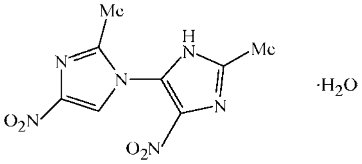
The two almost perfectly planar imidazole rings in the title compound, $C_8H_8N_6O_4 \cdot H_2O$, make a dihedral angle of 63.01 (10)°. The water molecule acts as a double donor and double acceptor of strong and linear hydrogen bonds, including an exceptionally short C—H···O bond. These bonds create a tight three-dimensional structure and are probably responsible for the relatively high melting point of the compound.

Comment

There are 28 organic and 62 organometallic crystal structures containing 2,2′-biimidazole in the Cambridge Structural Database (Version of November 2004, February 2005 updates; Allen, 2002). It therefore seems strange that for 1,5′-biimidazole there is only one known crystal structure (Kubicki *et al.*, 2001). What is more, examples of other biimidazoles are also scarce; there are only a few examples of 4,4′- (four structures) and 5,5′-biimidazoles (three examples).



(I)

Since the 4-nitroimidazole derivatives proved to be convenient subjects for studying weak intermolecular interactions in crystals (*e.g.* Kubicki, 2004, and references therein), it should be of interest to determine the crystal structures of their biimidazole analogues as well. Here, the crystal structure of one of the simplest members of this family, 2,2′-dimethyl-4,5′-dinitro-1*H*,3′*H*-1,4′-biimidazole, is reported. This compound crystallizes as a hydrate, (I).

Fig. 1 shows a perspective view of the molecule. Both imidazole rings are almost perfectly planar; the maximum deviations from the least-squares planes are 0.0032 (14) and 0.0008 (15) Å for rings *A* and *B* (hereinafter *A* will denote the non-primed and *B* the primed imidazole rings). The nitro groups are only slightly twisted with respect to the imidazole planes [the twist angles are 1.9 (3)° for *A* and 3.9 (4)° for *B*]. The dihedral angle between the imidazole rings is 63.01 (10)°; this value is large compared with the typical values for 2,2′-biimidazoles, for which angles significantly larger than a few degrees are observed only in the case of large substituents [for example, 60.5° in *cis*-1,1′-diacetyl-2,2′-biimidazole (Secondo *et al.*, 1996)] or for charged species, *i.e.* biimidazolium [for example, 89.0° in 2,2′-bi(1,3-diisopropyl-4,5-dimethylimidazolyl) bis(tetrafluoroborate) monohydrate (Kuhn *et al.*, 2001)]. The bond lengths and angles in (I) (Table 1) are typical.

The architecture of the crystal structure of (I) is determined mainly by hydrogen bonds involving the water molecule, which acts as a double donor and a double acceptor. It takes part in two O*W*—H···N hydrogen bonds, in which two different N atoms (*i.e.* N3 and N1′) from two different molecules are acceptors, and also accepts one N—H···O*W* and one exceptionally short C—H···O*W* hydrogen bond. The hydrogen-bonding geometry is given in Table 2. These four directional bonds (the *D*—H···*A* angles are larger than 156°) form a regular tetrahedral coordination of the water O atom (the H···O—H angles are in the range 98–125°). The three-dimensional hydrogen-bond network may be described using graph-set notation (Etter *et al.*, 1990; Bernstein *et al.*, 1995): $C_2^1(7)$ and $C_2^2(8)$ chains of biimidazole and water molecules are interwoven to produce some relatively large rings; two examples, $R_6^6(21)$ and $R_6^6(23)$, are shown in Fig. 2. This tight network of hydrogen bonds may be responsible for the relatively high melting point of the title compound (542–543 K). Such a correlation between the hydrogen-bond network and melting points was noticed, for example, in the case of two isomeric 2-hydroxybornane-3-carboxylic acids (Kubicki *et al.*, 2000).

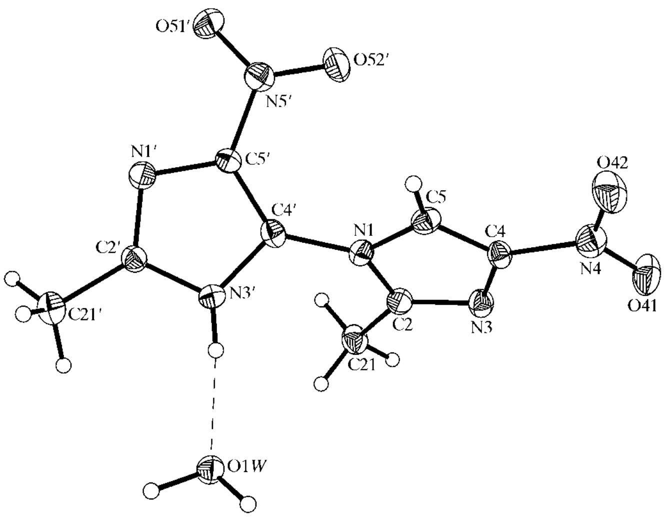


Figure 1
A view of (I) (Siemens, 1989). Displacement ellipsoids are drawn at the 50% probability level and H atoms are depicted as spheres of arbitrary radii. The intramolecular hydrogen bond is drawn as a dashed line.

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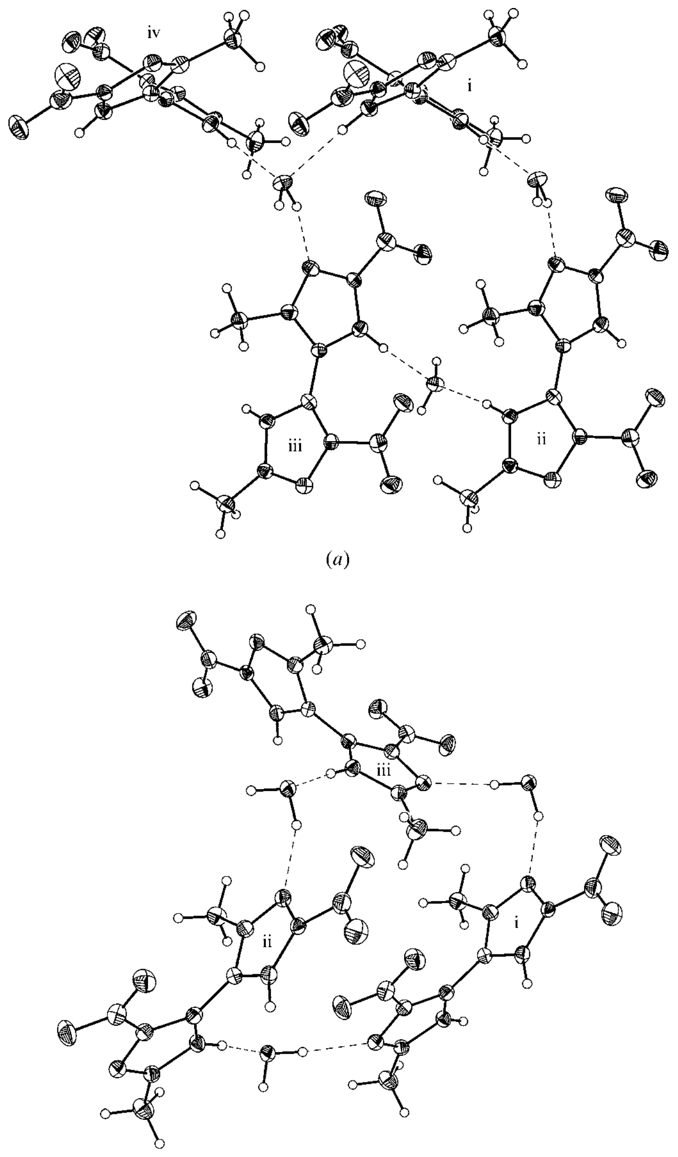

Figure 2
The elements of the three-dimensional network of hydrogen bonds. Displacement ellipsoids are drawn at the 50% probability level and H atoms are depicted as spheres of arbitrary radii. Hydrogen bonds are drawn as dashed lines. (*a*) The $R_6^6(21)$ ring and fragments of $C_1^2(7)$ and $C_2^2(8)$ chains. [Symmetry codes: (i) x, y, z; (ii) $-x + 1, y + \frac{1}{2}, -z + 1$; (iii) $-x + 2, y + \frac{1}{2}, -z + 1$; (iv) $x + 1, y, z$.] (*b*) The $R_6^6(23)$ ring. [Symmetry codes: (i) x, y, z; (v) $x, y, z - 1$; (vi) $-x + 1, z - \frac{1}{2}, -z$.]

Experimental

The method of synthesis of compound (I) has been described elsewhere (Salwińska *et al.*, 1991; Walczak *et al.*, 2001). Crystals for data collection were grown from an aqueous solution by slow evaporation.

Crystal data

$C_8H_8N_6O_4 \cdot H_2O$
$M_r = 270.22$
Monoclinic, $P2_1$
$a = 6.5951$ (8) Å
$b = 13.4920$ (13) Å
$c = 7.2032$ (9) Å
$\beta = 113.084$ (12)°
$V = 589.63$ (13) Å^3
$Z = 2$
$D_x = 1.522$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2200 reflections
$\theta = 3$–20°
$\mu = 0.13$ mm^{-1}
$T = 100$ (1) K
Prism, colourless
$0.15 \times 0.1 \times 0.1$ mm

Data collection

Kuma KM-4 CCD four-circle diffractometer
ω scans
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995, 1997)
$T_{\min} = 0.989$, $T_{\max} = 0.989$
5482 measured reflections
1595 independent reflections
1060 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.039$
$\theta_{\max} = 29.8°$
$h = -9 \rightarrow 8$
$k = -18 \rightarrow 18$
$l = -8 \rightarrow 9$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.049$
$S = 0.84$
1598 reflections
192 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.01P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 0.21$ e Å^{-3}
$\Delta\rho_{\min} = -0.22$ e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.026 (2)

Table 1
Selected geometric parameters (Å, °).

N1—C5	1.376 (3)	N1′—C2′	1.325 (3)
N1—C2	1.391 (3)	N1′—C5′	1.367 (3)
N1—C4′	1.402 (3)	C2′—N3′	1.359 (3)
C2—N3	1.315 (3)	N3′—C4′	1.368 (3)
N3—C4	1.375 (3)		
C5—N1—C2	107.9 (2)	C2′—N1′—C5′	104.1 (2)
C5—N1—C4′	126.5 (2)	C2′—N3′—C4′	107.7 (2)
C2—N1—C4′	125.5 (2)	N3′—C4′—N1	121.5 (2)
N3—C2—N1	110.4 (2)	O51′—N5′—O52′	124.5 (2)
O41—N4—O42	124.7 (2)	O51′—N5′—C5′	118.0 (2)
O41—N4—C4	117.9 (2)	O52′—N5′—C5′	117.5 (2)
O42—N4—C4	117.4 (2)		

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C21—H21$B\cdots$O41$^{\rm vii}$	0.98	2.62	3.499 (3)	149
C5—H5$\cdots$O1$W^{\rm viii}$	0.96 (2)	2.20 (3)	3.155 (3)	175 (2)
N3′—H3′$\cdots$O1W	0.84 (2)	1.83 (2)	2.665 (3)	173 (2)
C21′—H21$F\cdots$O52$'^{\rm ix}$	0.98	2.64	3.381 (3)	133
O1W—H1$W\cdots$N3$^{\rm ii}$	0.99 (4)	1.86 (3)	2.799 (3)	157 (3)
O1W—H2$W\cdots$N1$'^{\rm x}$	0.91 (4)	1.94 (4)	2.840 (3)	170 (3)

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

The H atoms of CH groups were refined freely. Those of methyl groups were allowed to ride on the parent C atom and rotate as a rigid group around the C—C bond (C—H = 0.98 Å); one $U_{\rm iso}$ value was refined for each methyl group. The positions of the water H atoms were freely refined; a common $U_{\rm iso}$ value was also refined for these atoms.

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*.

The author thanks Dr P. Wagner for preparing the compound and for fruitful discussions.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: HJ1060). Services for accessing these data are described at the back of the journal.

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