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N′-Acetyl-5-amino-1-methyl-1*H*-pyrazole-4-carbohydrazonamide dihydrate

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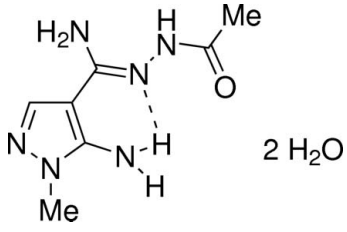
Key indicators: single-crystal X-ray study; T = 223 K; mean σ(C–C) = 0.003 Å; R factor = 0.052; wR factor = 0.141; data-to-parameter ratio = 13.9.

In the title compound, $C_7H_{12}N_6O\cdot 2H_2O$, the Z configuration of the hydrazone fragment is stabilized by an intramolecular N—H···N hydrogen bond involving one of the amino groups. In the crystal structure, the hydrazonamide molecules are connected *via* intermolecular N—H···O=C hydrogen bonds, forming $C(7)$ chains running along [010]. The chains form sheets parallel to the ($\bar{1}$01). The chains are cross-linked by water molecules to form a three-dimensional hydrogen-bonded network.

Related literature

For bioactive pyrazoles, see: Elguero *et al.* (2002); Lamberth (2007). For the use of pyrazoles as synthons in heterocyclic chemistry, see: Schenone *et al.* (2007); Dolzhenko *et al.* (2008). For the use of pyrazoles in metal-organic chemistry, see: Mukherjee (2000); Halcrow (2009). For the crystal structures of related 5-amino-1*H*-pyrazole-4-carboxylic acid derivatives, see: Zia-ur-Rehman *et al.* (2008, 2009); Caruso *et al.* (2009). For the crystal structure of *N*′-acetyl-2-phenylethanehydrazonamide, see: Ianelli *et al.* (2001). For the graph-set analysis of hydrogen bonding, see: Bernstein *et al.* (1995).



Experimental

Crystal data

$C_7H_{12}N_6O\cdot 2H_2O$
M_r = 232.26
Triclinic, $P\bar{1}$
a = 7.5496 (9) Å
b = 7.6208 (9) Å
c = 11.2518 (13) Å
α = 102.645 (2)°
β = 101.440 (2)°
γ = 110.810 (2)°
V = 562.75 (11) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.11 mm^{-1}
T = 223 K
0.45 × 0.12 × 0.10 mm

Data collection

Bruker SMART APEX CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2001)
T_{min} = 0.953, T_{max} = 0.989
3963 measured reflections
2548 independent reflections
2174 reflections with $I > 2\sigma(I)$
R_{int} = 0.021

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.052
$wR(F^2)$ = 0.141
S = 1.05
2548 reflections
183 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.31 e Å^{-3}
$\Delta\rho_{min}$ = −0.26 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O2W—H4W···N1^{i}	0.87 (3)	2.04 (3)	2.884 (2)	162 (3)
O2W—H3W···O1	0.86 (3)	2.11 (3)	2.885 (2)	150 (3)
O1W—H2W···O2W^{ii}	0.89 (3)	1.93 (3)	2.824 (2)	175 (3)
O1W—H1W···N5	0.81 (3)	2.24 (3)	2.982 (2)	153 (3)
N6—H6N···O1W^{iii}	0.84 (2)	2.07 (2)	2.905 (2)	177 (2)
N4—H42···O1W^{iii}	0.88 (2)	2.14 (3)	2.995 (2)	165 (2)
N4—H41···O1^{iv}	0.81 (2)	2.08 (2)	2.874 (2)	169 (2)
N3—H32···N5	0.86 (2)	2.18 (2)	2.791 (2)	128 (2)
N3—H31···O2W^{v}	0.83 (2)	2.27 (2)	3.082 (2)	163 (2)

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $x+1, y, z$; (iii) $-x+1, -y+1, -z$; (iv) $x, y-1, z$; (v) $-x+1, -y+2, -z+1$.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CI5086).

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N′-Acetyl-5-amino-1-methyl-1*H*-pyrazole-4-carbohydrazonamide dihydrate

Anna V. Dolzhenko, Anton V. Dolzhenko, Geok Kheng Tan, Lip Lin Koh and Giorgia Pastorin

S1. Comment

Pyrazoles have been well recognized as valuable ligands in metal-organic chemistry (Mukherjee, 2000; Halcrow, 2009). Pyrazoles also possess useful agricultural (Lamberth, 2007) and pharmacological (Elguero *et al.*, 2002) properties and serve as synthons for other pyrazolo fused bioactive heterocycles (Schenone *et al.*, 2007; Dolzhenko *et al.*, 2008).

Herein, we report molecular and crystal structure of *N*′-acetyl-5-amino-1-methyl-1*H*-pyrazole-4-carbohydrazonamide (Figs. 1 and 2). The compound can exist in two tautomeric forms, namely hydrazonamide and imidohydrazide (Fig. 3). The hydrazonamide tautomer can also exhibit (*E*-*Z*) isomerism by inversion of configuration of the hydrazono C═N linkage. We found that the compound crystallizes as a *N*′-acetyl-5-amino-1-methyl-1*H*-pyrazole-4-carbohydrazonamide tautomer. Similarly to previously reported *N*′-acetyl-2-phenylethanehydrazonamide (Ianelli *et al.*, 2001), the hydrazonamide group of *N*′-acetyl-5-amino-1-methyl-1*H*-pyrazole-4-carbohydrazonamide adopts (*Z*)-configuration. This configuration is stabilized by the intramolecular N(3)H···N5═C5 hydrogen bonding between the amino group and the hydrazone N5 atom, generating an *S*(6) graph-set motif (Bernstein *et al.*, 1995). Similar NH···O═C interactions were reported for the structurally related derivatives of 5-amino-1*H*-pyrazole-4-carboxylic acid (Zia-ur-Rehman *et al.*, 2008; Zia-ur-Rehman *et al.*, 2009; Caruso *et al.*, 2009). Planarity of the molecule is affected by slight twisting of the acetyl group [C5—N5—N6—C6 torsion angle is 170.14 (16)°].

In the crystal, the hydrazonamide molecules are arranged to form sheets parallel to the $(\bar{1}01)$ (Fig. 2). In the sheets, atom N4 of one molecule is involved in a intermolecular N—H···O═C interaction with the carbonyl atom O1 of adjacent molecule making *C*(7) chains along the [010] direction. The water molecules further stabilize packing by formation of the intermolecular hydrogen bond network (Fig. 2 and Table 1).

S2. Experimental

N′-Acetyl-5-amino-1-methyl-1*H*-pyrazole-4-carbohydrazonamide was prepared by treatment of ethyl *N*-(4-cyano-1-methyl-1*H*-pyrazol-5-yl)acetimidate with 3 eq. of hydrazine hydrate (40%) in ethanol. Detail procedure with proposed mechanism will be reported elsewhere. Single crystals suitable for the crystallographic analysis were grown by recrystallization from ethanol, m.p. 513 K.

S3. Refinement

All C-bound H atoms were positioned geometrically and included in the refinement in riding-motion approximation [0.95 Å for $C_{pyrazole}$–H, and 0.98 Å for methyl groups; $U_{iso}(H) = 1.2U_{eq}(C_{pyrazole})$ and $U_{iso}(H) = 1.5U_{eq}(C_{methyl})$] while the N- and O-bound H atoms were located in a difference map and refined freely.

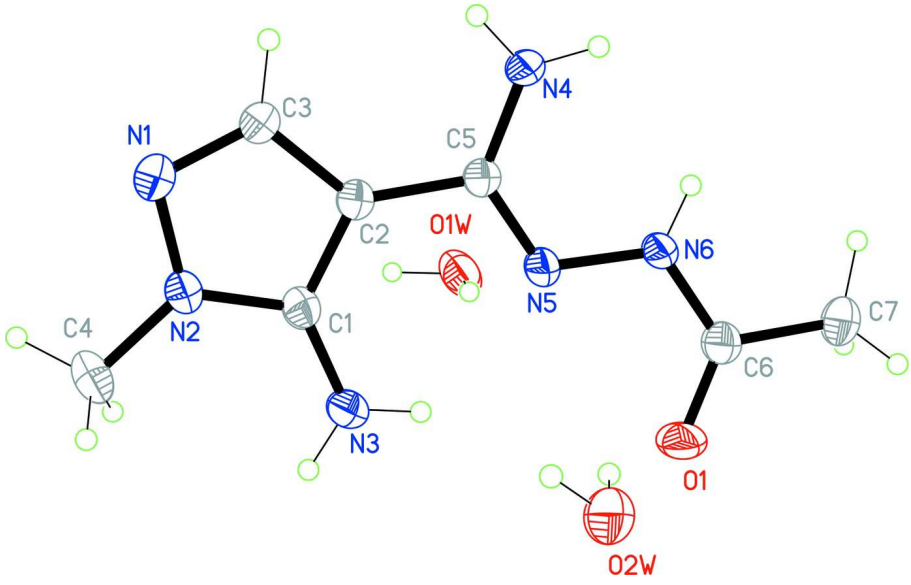

Figure 1

The molecular structure of *N*′-acetyl-5-amino-1-methyl-1*H*-pyrazole-4-carbohydrazonamide dihydrate showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

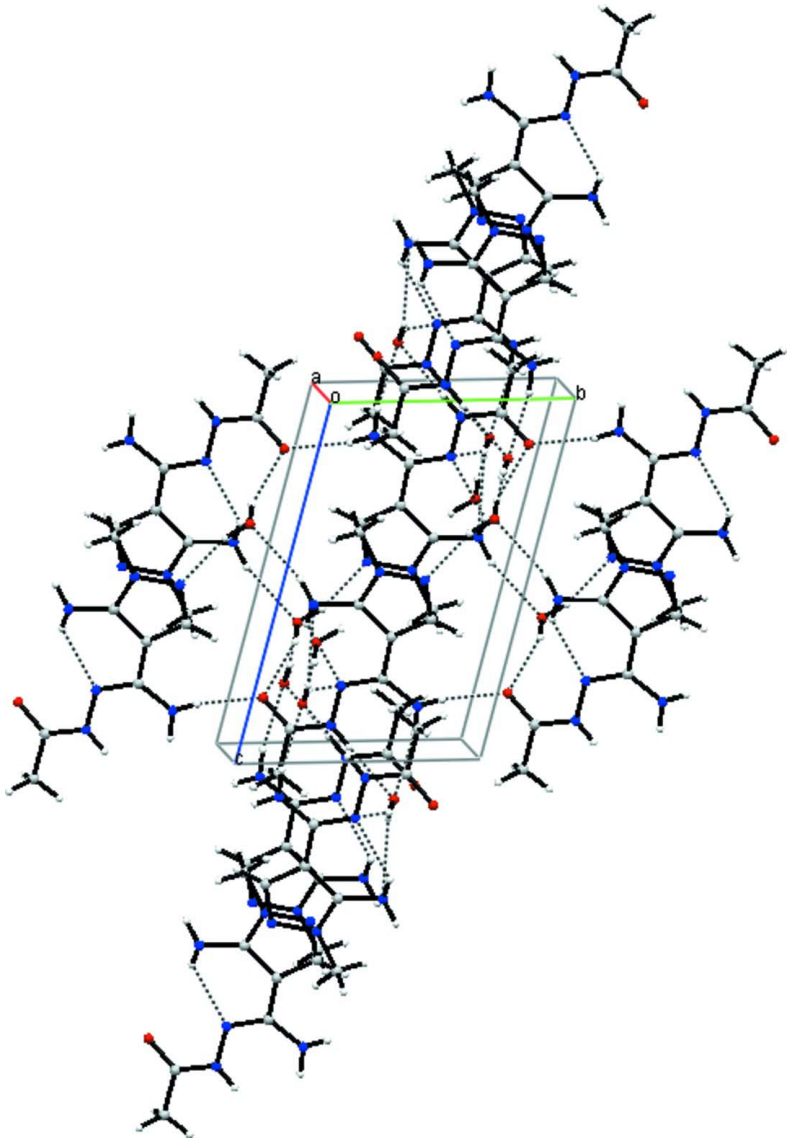

Figure 2

Crystal packing of the title compound, viewed along the *a* axis.

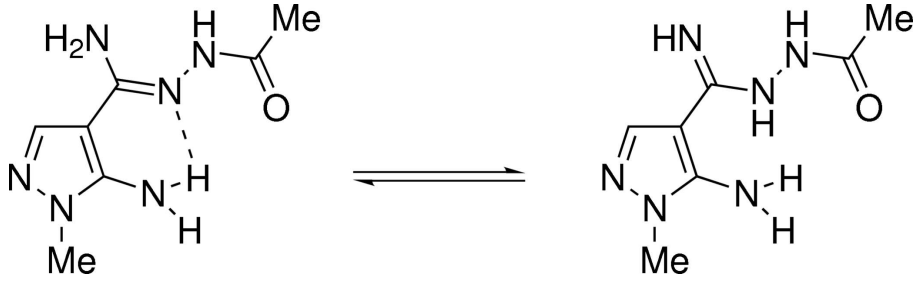

Figure 3

Hydrazonamide-imidohydrazide tautomerism in *N*′-acetyl-5-amino-1-methyl-1*H*-pyrazole-4-carbohydrazonamide

N′-Acetyl-5-amino-1-methyl-1*H*-pyrazole-4-carbohydrazonamide dihydrate

Crystal data

$C_7H_{12}N_6O·2H_2O$
$M_r = 232.26$
Triclinic, $P\overline{1}$
Hall symbol: -P 1
$a = 7.5496$ (9) Å
$b = 7.6208$ (9) Å
$c = 11.2518$ (13) Å
$\alpha = 102.645$ (2)°
$\beta = 101.440$ (2)°
$\gamma = 110.810$ (2)°
$V = 562.75$ (11) Å^3
$Z = 2$
$F(000) = 248$
$D_x = 1.371$ Mg m^{-3}
Melting point: 513 K
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 1515 reflections
$\theta = 3.0$–$27.5°$
$\mu = 0.11$ mm^{-1}
$T = 223$ K
Rod, colourless
0.45 × 0.12 × 0.10 mm

Data collection

Bruker SMART APEX CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2001)
$T_{min} = 0.953$, $T_{max} = 0.989$
3963 measured reflections
2548 independent reflections
2174 reflections with $I > 2\sigma(I)$
$R_{int} = 0.021$
$\theta_{max} = 27.5°$, $\theta_{min} = 3.0°$
$h = -9 \rightarrow 9$
$k = -9 \rightarrow 9$
$l = -14 \rightarrow 13$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.052$
$wR(F^2) = 0.141$
$S = 1.05$
2548 reflections
183 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0711P)^2 + 0.1961P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.31$ e Å^{-3}
$\Delta\rho_{min} = -0.26$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.3615 (2)	0.89463 (19)	0.14623 (12)	0.0421 (4)
N1	0.7337 (2)	0.3950 (2)	0.48625 (14)	0.0306 (4)

N2	0.7791 (2)	0.5933 (2)	0.51428 (13)	0.0264 (3)
N3	0.7066 (3)	0.8221 (2)	0.42298 (16)	0.0302 (4)
H31	0.748 (3)	0.907 (3)	0.495 (2)	0.036 (6)*
H32	0.613 (3)	0.821 (3)	0.365 (2)	0.039 (6)*
N4	0.3308 (2)	0.2471 (2)	0.11287 (15)	0.0297 (4)
H41	0.350 (3)	0.158 (3)	0.132 (2)	0.032 (5)*
H42	0.260 (3)	0.223 (3)	0.034 (2)	0.040 (6)*
N5	0.4378 (2)	0.5945 (2)	0.18078 (13)	0.0294 (4)
N6	0.3198 (2)	0.5816 (2)	0.06398 (13)	0.0267 (3)
H6N	0.269 (3)	0.479 (3)	0.000 (2)	0.037 (6)*
C1	0.6808 (2)	0.6344 (2)	0.41838 (15)	0.0239 (4)
C2	0.5664 (2)	0.4541 (2)	0.32050 (15)	0.0236 (4)
C3	0.6068 (3)	0.3143 (3)	0.37018 (16)	0.0272 (4)
H3	0.5496	0.1780	0.3256	0.033*
C4	0.9204 (3)	0.7328 (3)	0.63443 (17)	0.0359 (4)
H4A	1.0140	0.8443	0.6188	0.054*
H4C	0.9916	0.6687	0.6766	0.054*
H4D	0.8504	0.7791	0.6886	0.054*
C5	0.4374 (2)	0.4304 (2)	0.19753 (15)	0.0225 (3)
C6	0.2965 (3)	0.7431 (3)	0.05365 (16)	0.0278 (4)
C7	0.1873 (3)	0.7318 (3)	−0.07661 (17)	0.0354 (4)
H7A	0.0729	0.7603	−0.0721	0.053*
H7B	0.1431	0.6000	−0.1353	0.053*
H7C	0.2751	0.8278	−0.1066	0.053*
O1W	0.8443 (2)	0.7733 (2)	0.15574 (13)	0.0380 (4)
H1W	0.752 (5)	0.757 (4)	0.186 (3)	0.069 (9)*
H2W	0.949 (5)	0.780 (4)	0.213 (3)	0.065 (8)*
O2W	0.1806 (2)	0.8169 (2)	0.34309 (14)	0.0393 (4)
H3W	0.253 (4)	0.812 (4)	0.294 (3)	0.064 (9)*
H4W	0.189 (4)	0.731 (4)	0.381 (3)	0.060 (8)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0739 (10)	0.0235 (7)	0.0262 (7)	0.0259 (7)	0.0028 (7)	0.0046 (5)
N1	0.0382 (8)	0.0292 (8)	0.0260 (8)	0.0170 (7)	0.0052 (6)	0.0107 (6)
N2	0.0311 (7)	0.0255 (7)	0.0195 (7)	0.0118 (6)	0.0023 (6)	0.0060 (6)
N3	0.0413 (9)	0.0219 (7)	0.0218 (8)	0.0130 (7)	0.0021 (7)	0.0032 (6)
N4	0.0436 (9)	0.0173 (7)	0.0228 (8)	0.0136 (6)	−0.0018 (6)	0.0053 (6)
N5	0.0403 (8)	0.0219 (7)	0.0197 (7)	0.0141 (6)	−0.0034 (6)	0.0043 (6)
N6	0.0375 (8)	0.0195 (7)	0.0174 (7)	0.0128 (6)	−0.0022 (6)	0.0029 (6)
C1	0.0268 (8)	0.0265 (8)	0.0186 (7)	0.0119 (7)	0.0058 (6)	0.0071 (6)
C2	0.0286 (8)	0.0225 (8)	0.0199 (8)	0.0119 (6)	0.0046 (6)	0.0072 (6)
C3	0.0342 (9)	0.0228 (8)	0.0241 (8)	0.0138 (7)	0.0037 (7)	0.0076 (6)
C4	0.0374 (10)	0.0406 (11)	0.0206 (8)	0.0142 (8)	−0.0003 (7)	0.0043 (8)
C5	0.0274 (8)	0.0211 (8)	0.0188 (7)	0.0114 (6)	0.0045 (6)	0.0061 (6)
C6	0.0353 (9)	0.0264 (8)	0.0217 (8)	0.0143 (7)	0.0048 (7)	0.0085 (7)
C7	0.0447 (11)	0.0370 (10)	0.0273 (9)	0.0227 (9)	0.0026 (8)	0.0136 (8)

O1W	0.0406 (8)	0.0395 (8)	0.0236 (7)	0.0125 (6)	0.0021 (6)	0.0044 (6)
O2W	0.0518 (9)	0.0414 (8)	0.0299 (7)	0.0253 (7)	0.0082 (7)	0.0145 (6)

Geometric parameters (Å, º)

O1—C6	1.236 (2)	C1—C2	1.401 (2)
N1—C3	1.317 (2)	C2—C3	1.402 (2)
N1—N2	1.372 (2)	C2—C5	1.459 (2)
N2—C1	1.344 (2)	C3—H3	0.94
N2—C4	1.445 (2)	C4—H4A	0.97
N3—C1	1.362 (2)	C4—H4C	0.97
N3—H31	0.83 (2)	C4—H4D	0.97
N3—H32	0.86 (2)	C6—C7	1.500 (2)
N4—C5	1.350 (2)	C7—H7A	0.97
N4—H41	0.81 (2)	C7—H7B	0.97
N4—H42	0.88 (2)	C7—H7C	0.97
N5—C5	1.303 (2)	O1W—H1W	0.81 (3)
N5—N6	1.3953 (19)	O1W—H2W	0.89 (3)
N6—C6	1.330 (2)	O2W—H3W	0.86 (3)
N6—H6N	0.84 (2)	O2W—H4W	0.87 (3)
C3—N1—N2	104.63 (14)	C2—C3—H3	123.7
C1—N2—N1	112.10 (14)	N2—C4—H4A	109.5
C1—N2—C4	127.04 (15)	N2—C4—H4C	109.5
N1—N2—C4	120.85 (14)	H4A—C4—H4C	109.5
C1—N3—H31	117.5 (15)	N2—C4—H4D	109.5
C1—N3—H32	110.8 (16)	H4A—C4—H4D	109.5
H31—N3—H32	119 (2)	H4C—C4—H4D	109.5
C5—N4—H41	116.7 (15)	N5—C5—N4	126.14 (15)
C5—N4—H42	123.9 (15)	N5—C5—C2	114.92 (14)
H41—N4—H42	118 (2)	N4—C5—C2	118.95 (15)
C5—N5—N6	117.52 (14)	O1—C6—N6	121.90 (15)
C6—N6—N5	117.50 (14)	O1—C6—C7	121.68 (16)
C6—N6—H6N	119.6 (15)	N6—C6—C7	116.42 (15)
N5—N6—H6N	122.8 (15)	C6—C7—H7A	109.5
N2—C1—N3	122.61 (15)	C6—C7—H7B	109.5
N2—C1—C2	106.59 (14)	H7A—C7—H7B	109.5
N3—C1—C2	130.72 (15)	C6—C7—H7C	109.5
C1—C2—C3	104.15 (14)	H7A—C7—H7C	109.5
C1—C2—C5	125.02 (15)	H7B—C7—H7C	109.5
C3—C2—C5	130.83 (15)	H1W—O1W—H2W	110 (3)
N1—C3—C2	112.53 (15)	H3W—O2W—H4W	103 (3)
N1—C3—H3	123.7		
C3—N1—N2—C1	0.66 (19)	N2—N1—C3—C2	−0.1 (2)
C3—N1—N2—C4	−178.36 (16)	C1—C2—C3—N1	−0.5 (2)
C5—N5—N6—C6	170.14 (16)	C5—C2—C3—N1	179.83 (17)
N1—N2—C1—N3	−177.99 (15)	N6—N5—C5—N4	−1.0 (3)

C4—N2—C1—N3	1.0 (3)	N6—N5—C5—C2	178.89 (14)
N1—N2—C1—C2	−0.95 (19)	C1—C2—C5—N5	1.9 (2)
C4—N2—C1—C2	178.00 (16)	C3—C2—C5—N5	−178.43 (17)
N2—C1—C2—C3	0.82 (18)	C1—C2—C5—N4	−178.18 (16)
N3—C1—C2—C3	177.53 (18)	C3—C2—C5—N4	1.5 (3)
N2—C1—C2—C5	−179.44 (15)	N5—N6—C6—O1	−6.2 (3)
N3—C1—C2—C5	−2.7 (3)	N5—N6—C6—C7	173.75 (16)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2*W*—H4*W*···N1^{i}	0.87 (3)	2.04 (3)	2.884 (2)	162 (3)
O2*W*—H3*W*···O1	0.86 (3)	2.11 (3)	2.885 (2)	150 (3)
O1*W*—H2*W*···O2*W*^{ii}	0.89 (3)	1.93 (3)	2.824 (2)	175 (3)
O1*W*—H1*W*···N5	0.81 (3)	2.24 (3)	2.982 (2)	153 (3)
N6—H6*N*···O1*W*^{iii}	0.84 (2)	2.07 (2)	2.905 (2)	177 (2)
N4—H42···O1*W*^{iii}	0.88 (2)	2.14 (3)	2.995 (2)	165 (2)
N4—H41···O1^{iv}	0.81 (2)	2.08 (2)	2.874 (2)	169 (2)
N3—H32···N5	0.86 (2)	2.18 (2)	2.791 (2)	128 (2)
N3—H31···O2*W*^{v}	0.83 (2)	2.27 (2)	3.082 (2)	163 (2)

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*+1; (ii) *x*+1, *y*, *z*; (iii) −*x*+1, −*y*+1, −*z*; (iv) *x*, *y*−1, *z*; (v) −*x*+1, −*y*+2, −*z*+1.