Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

N′-[(*E*)-(3-Fluoropyridin-2-yl)methylidene]benzohydrazide monohydrate

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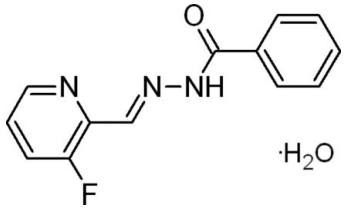
Received 10 July 2012; accepted 8 August 2012

Key indicators: single-crystal X-ray study; T = 296 K; mean σ(C–C) = 0.002 Å; R factor = 0.032; wR factor = 0.096; data-to-parameter ratio = 11.8.

The title compound, $C_{13}H_{10}FN_3O\cdot H_2O$, exists in the *E* conformation with respect to the azomethane C=N double bond. The molecule is close to planar with a maximum deviation of 0.286 (2) Å. The pyridine ring is essentially coplanar with the central C(=O)N_2C unit [dihedral angle = 2.02 (3)°] and the phenyl ring exhibits a dihedral angle of 14.41 (10)° with respect to the central unit. The crystal structure features O—H···N, N—H···O and O—H···O hydrogen-bond interactions between the solvent water and the benzohydrazide molecules, as well as C—H···O hydrogen bonds and C—F···π [3.0833 (18) Å] interactions.

Related literature

For background to the use of benzohydrazides as catalysts, see: Heravi *et al.* (2007); Hou *et al.* (2005) and for their biological activity, see: Sreeja *et al.* (2004). For the synthesis of related compounds, see: Fun *et al.* (2008). For related structures, see Mangalam *et al.* (2009).



Experimental

Crystal data

$C_{13}H_{10}FN_3O\cdot H_2O$
M_r = 261.26
Orthorhombic, *Pbca*
a = 8.2540 (4) Å
b = 11.5489 (4) Å
c = 26.1962 (11) Å
V = 2497.14 (18) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.11 mm^{-1}
T = 296 K
0.35 × 0.30 × 0.25 mm

Data collection

Bruker Kappa APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2004)
T_{min} = 0.964, T_{max} = 0.974
34264 measured reflections
2192 independent reflections
1817 reflections with $I > 2\sigma(I)$
R_{int} = 0.027

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.096
S = 1.07
2190 reflections
185 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.18 e Å^{-3}
$\Delta\rho_{min}$ = −0.13 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N3—H3′···O1W	0.901 (18)	1.914 (18)	2.7917 (17)	164.3 (16)
O1W—H1A···O1^{i}	0.84 (3)	2.08 (3)	2.9187 (19)	172 (2)
O1W—H1A···N2^{i}	0.84 (3)	2.48 (2)	2.9494 (17)	116.1 (19)
O1W—H1B···N1^{i}	0.89 (2)	1.95 (3)	2.8420 (18)	178 (2)
C9—H9···O1W	0.93	2.30	3.209 (2)	165

Symmetry code: (i) $-x+\frac{3}{2}, y-\frac{1}{2}, z$.

Data collection: *APEX2* (Bruker, 2004); cell refinement: *APEX2* and *SAINT* (Bruker, 2004); data reduction: *SAINT* and *XPREP* (Bruker, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *DIAMOND* (Brandenburg, 2010); software used to prepare material for publication: *SHELXL97* and *publCIF* (Westrip, 2010).

The authors are thankful to Dr Shibu M. Eapen, SAIF, Cochin University of Science and Technology, for the data collection.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: ZL2494).

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supplementary materials

Acta Cryst. (2012). E**68**, o2709 [doi:10.1107/S1600536812035179]

N′-[(*E*)-(3-Fluoropyridin-2-yl)methylidene]benzohydrazide monohydrate

Yamuna Nair, M. Sithambaresan and M. R. Prathapachandra Kurup

Comment

Interest in coordination chemistry of benzohydrazide has been a subject of enthusiastic research since their complexes show a wide range of catalytic properties (Heravi *et al.*, 2007; Hou *et al.*, 2005). Benzohydrazone derivatives are also important due to their wide spectrum of biological activities (Sreeja *et al.*, 2004).

This molecule adopts an *E* conformation with respect to the C6=N2 bond and it exists in the amido form with a C7=O1 bond length of 1.2258 (17) Å which is very close to the reported C=O bond length of a similar structure (Mangalam *et al.*, 2009). The O1 and N2 atoms are in a *Z* conformation with respect to C7–N3 having a torsional angle of -0.4 (2)°. The molecule is almost planar with a maximum deviation of 0.286 (2) Å for the atom C12 from its least square plane. The pyridyl ring is essentially coplanar with the central C(=O)N_2C unit (dihedral angle 2.02 (3) °), the phenyl ring exhibits a dihedral angle of 14.41 (10)° with respect to the central unit.

The water molecule forms six H-bonds with two different benzohydrazone molecules. Hydrogen bond interactions such as O–H···N, O–H···O, N–H···O and C–H···O are present in the crystal system between the H atoms attached to the O1W atom and N1, N2, N3, C9 and O1 atoms of two adjacent molecules with D···A distances of 2.842 (2), 2.9495 (17), 2.7917 (17), 3.209 (2) and 2.9188 (18) Å respectively as shown in Table 1. Both H-atoms of the water molecule form bifurcated hydrogen bonds with the azomethine nitrogen, the pyridyl nitrogen and the carbonyl oxygen atoms of one neighboring molecule (Fig. 2). The water molecule acts as a hydrogen bond acceptor towards another benzohydrazone molecule through an N–H···O hydrogen bond. Through these interactions the molecules are interconnected through the water molecule to form infinite chains parallel to the *b* axis of the unit cell (Fig. 2). Benzohydrazone molecules within these chains also interact through weak C–F···π [3.0833 (18) Å] interactions (Fig. 2) that augment the stronger O–H···N, O–H···O, N–H···O hydrogen bonds.

Experimental

The title compound was prepared by adapting a reported procedure (Fun *et al.*, 2008). A solution of 3-fluoropyridine-2-carbaldehyde (1.25 g,1 mmol) in ethanol (10 ml) was mixed with an ethanolic solution (10 ml) of benzohydrazide (1.36 g,1 mmol). The mixture was boiled under reflux for 12 h after adding few drops of glacial acetic acid and then cooled to room temperature. Colorless block shaped crystals, suitable for single-crystal analysis, were obtained in 61.8% yield after slow evaporation of the solution in air for a few days. ^{1}H NMR spectrum, DMSO-d_6, δ, p.p.m.: 12.12 (s, 1H, NH), 8.66 (s, 1H, CH=N), 8.53 (d, 1H, py–H(C1)), 7.54–7.95 (m, 7H, Ar–H (C2, C3, C9, C10, C11, C12, C13)). IR spectrum, ν (cm^{-1}): 3421, 3059, 1683,1650, 1597, 1441, 1350, 1295, 1273, 1167, 1134, 1073, 922, 801, 706, 674.

Refinement

The atoms H3′, H1A and H1B were located from a difference Fourier map and refined isotropically. The remaining hydrogen atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C–H

distances of 0.93 Å, and with isotropic displacement parameters 1.2 times that of the parent carbon atoms. Omitted owing to bad disagreement were the reflections (0 0 2) and (1 0 2).

Computing details

Data collection: *APEX2* (Bruker, 2004); cell refinement: *APEX2* and *SAINT* (Bruker, 2004); data reduction: *SAINT* and *XPREP* (Bruker, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *DIAMOND* (Brandenburg, 2010); software used to prepare material for publication: *SHELXL97* (Sheldrick, 2008) and *publCIF* (Westrip, 2010).

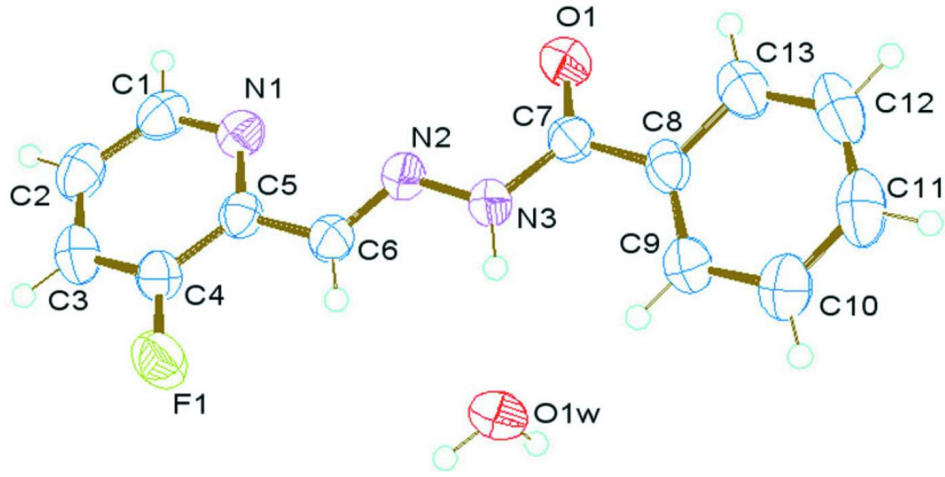

Figure 1

ORTEP diagram of *N*′-[(*E*)-(3-fluoropyridin-2-yl)methylidene]benzohydrazide monohydrate with 50% probability ellipsoids.

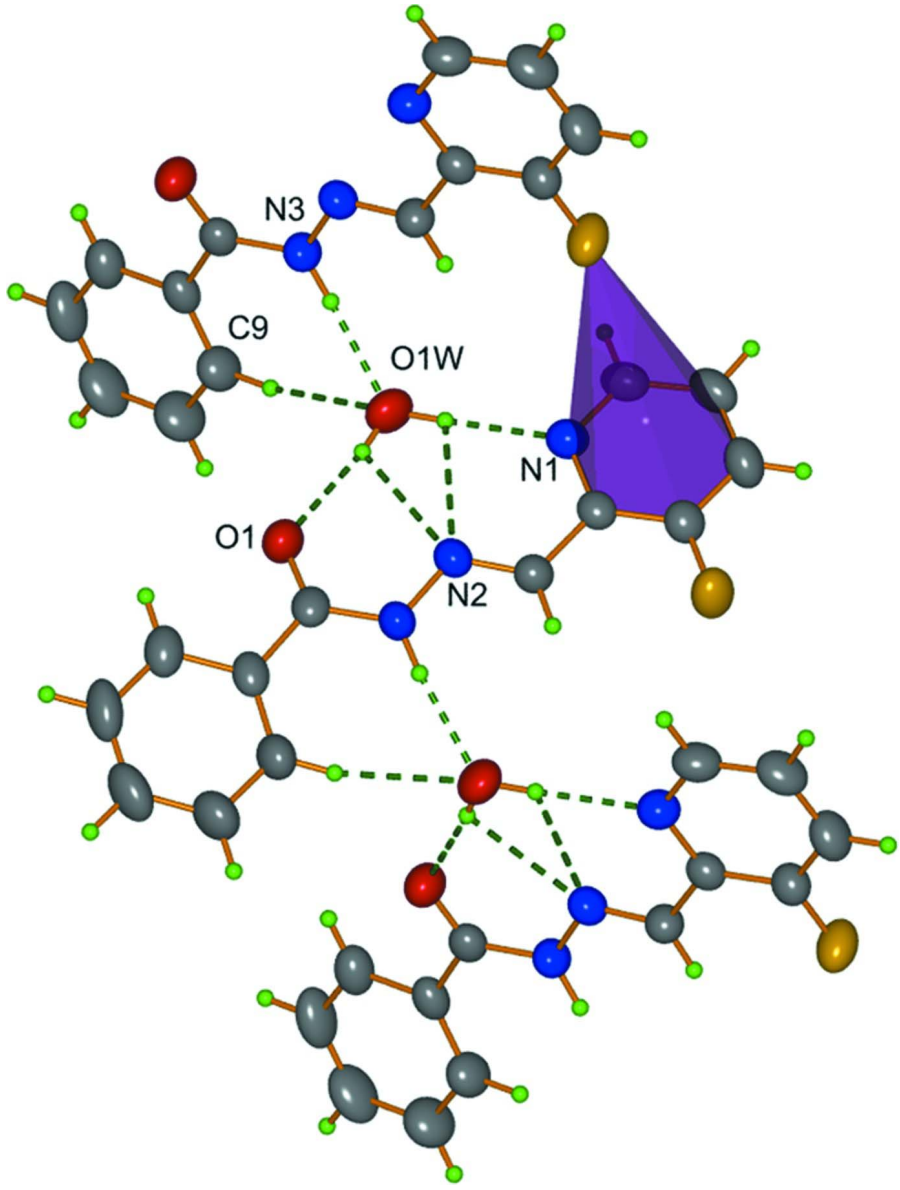

Figure 2

Hydrogen-bonding interactions showing an infinite chain in the crystal structure of *N*′-[(*E*)-(3-fluoropyridin-2-yl)methylidene]benzohydrazide hydrate and the interconnection of the chains *via* weak C–F···π interactions.

N′-[(*E*)-(3-Fluoropyridin-2-yl)methylidene]benzohydrazide monohydrate

Crystal data

$C_{13}H_{10}FN_3O\cdot H_2O$
$M_r = 261.26$
Orthorhombic, *Pbca*
Hall symbol: -P 2ac 2ab
$a = 8.2540\ (4)$ Å
$b = 11.5489\ (4)$ Å
$c = 26.1962\ (11)$ Å
$V = 2497.14\ (18)$ Å^3
$Z = 8$
$F(000) = 1088$
$D_x = 1.390$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 9884 reflections
$\theta = 5.8$–$54.5°$
$\mu = 0.11$ mm^{-1}
$T = 296$ K
Block, colorless
0.35 × 0.30 × 0.25 mm

Data collection

Bruker Kappa APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω and φ scan
Absorption correction: multi-scan (*SADABS*; Bruker, 2004)
T_{min} = 0.964, T_{max} = 0.974

34264 measured reflections
2192 independent reflections
1817 reflections with $I > 2\sigma(I)$
R_{int} = 0.027
θ_{max} = 25.0°, θ_{min} = 3.1°
h = −9→9
k = −13→13
l = −31→31

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.096
S = 1.07
2190 reflections
185 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
$w = 1/[\sigma^2(F_o^2) + (0.0425P)^2 + 0.6736P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.18 e Å^{-3}
$\Delta\rho_{min}$ = −0.13 e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0073 (8)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s 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 $F^2 > \sigma(F^2)$ 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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
F1	0.75071 (13)	0.87133 (8)	1.09485 (3)	0.0629 (3)
O1	0.82638 (15)	1.12491 (9)	0.86590 (4)	0.0561 (3)
O1W	0.90084 (17)	0.73757 (10)	0.93534 (6)	0.0600 (3)
N1	0.60294 (15)	1.12483 (10)	1.03176 (5)	0.0462 (3)
N2	0.79363 (14)	1.02906 (10)	0.95707 (4)	0.0413 (3)
N3	0.88214 (15)	0.97616 (11)	0.91928 (4)	0.0418 (3)
C1	0.51707 (19)	1.17020 (13)	1.06961 (6)	0.0514 (4)
H1	0.4633	1.2397	1.0637	0.062*
C2	0.5032 (2)	1.12006 (14)	1.11710 (6)	0.0562 (4)
H2	0.4420	1.1552	1.1425	0.067*
C3	0.5812 (2)	1.01773 (15)	1.12616 (6)	0.0557 (4)
H3	0.5742	0.9811	1.1577	0.067*
C4	0.66988 (18)	0.97122 (13)	1.08709 (5)	0.0444 (4)
C5	0.68155 (16)	1.02434 (11)	1.04024 (5)	0.0392 (3)
C6	0.77636 (17)	0.97353 (12)	0.99866 (5)	0.0416 (3)

H6	0.8237	0.9010	1.0026	0.050*
C7	0.89290 (17)	1.03168 (12)	0.87370 (5)	0.0416 (3)
C8	0.99453 (17)	0.97527 (13)	0.83362 (5)	0.0427 (3)
C9	1.0457 (2)	0.86099 (14)	0.83555 (6)	0.0543 (4)
H9	1.0176	0.8148	0.8633	0.065*
C10	1.1385 (2)	0.81533 (17)	0.79643 (6)	0.0664 (5)
H10	1.1715	0.7384	0.7978	0.080*
C11	1.1819 (2)	0.88324 (18)	0.75569 (7)	0.0692 (5)
H11	1.2441	0.8522	0.7294	0.083*
C12	1.1337 (2)	0.99666 (18)	0.75360 (6)	0.0650 (5)
H12	1.1645	1.0427	0.7261	0.078*
C13	1.03959 (19)	1.04278 (15)	0.79213 (6)	0.0529 (4)
H13	1.0062	1.1196	0.7903	0.064*
H3′	0.908 (2)	0.9010 (16)	0.9235 (6)	0.057 (5)*
H1A	0.838 (3)	0.699 (2)	0.9166 (9)	0.102 (9)*
H1B	0.902 (3)	0.701 (2)	0.9653 (9)	0.100 (8)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
F1	0.0738 (6)	0.0639 (6)	0.0511 (5)	0.0185 (5)	0.0040 (5)	0.0128 (4)
O1	0.0757 (8)	0.0461 (6)	0.0467 (6)	0.0037 (5)	0.0021 (5)	0.0061 (5)
O1W	0.0761 (8)	0.0452 (6)	0.0589 (8)	−0.0080 (6)	0.0070 (7)	0.0081 (6)
N1	0.0496 (7)	0.0422 (7)	0.0468 (7)	0.0015 (5)	0.0020 (6)	−0.0028 (5)
N2	0.0454 (7)	0.0418 (6)	0.0366 (6)	−0.0004 (5)	0.0024 (5)	−0.0031 (5)
N3	0.0500 (7)	0.0406 (7)	0.0348 (6)	0.0017 (5)	0.0046 (5)	−0.0004 (5)
C1	0.0508 (9)	0.0451 (8)	0.0583 (10)	0.0016 (7)	0.0051 (7)	−0.0096 (7)
C2	0.0529 (9)	0.0628 (10)	0.0528 (10)	−0.0014 (8)	0.0107 (7)	−0.0155 (8)
C3	0.0571 (9)	0.0704 (11)	0.0395 (8)	−0.0017 (8)	0.0053 (7)	−0.0008 (7)
C4	0.0447 (8)	0.0492 (8)	0.0395 (8)	0.0006 (7)	−0.0027 (6)	−0.0008 (6)
C5	0.0381 (7)	0.0417 (7)	0.0377 (7)	−0.0032 (6)	−0.0013 (6)	−0.0039 (6)
C6	0.0459 (8)	0.0401 (8)	0.0388 (7)	0.0034 (6)	−0.0001 (6)	−0.0008 (6)
C7	0.0458 (8)	0.0415 (8)	0.0375 (8)	−0.0089 (6)	−0.0036 (6)	−0.0003 (6)
C8	0.0421 (8)	0.0527 (8)	0.0333 (7)	−0.0109 (6)	−0.0020 (6)	−0.0007 (6)
C9	0.0643 (10)	0.0551 (9)	0.0433 (8)	−0.0037 (8)	0.0112 (8)	−0.0003 (7)
C10	0.0736 (12)	0.0708 (11)	0.0550 (10)	0.0039 (9)	0.0161 (9)	−0.0077 (9)
C11	0.0611 (11)	0.1001 (15)	0.0463 (10)	−0.0034 (10)	0.0143 (8)	−0.0098 (10)
C12	0.0576 (10)	0.0987 (14)	0.0386 (9)	−0.0147 (10)	0.0058 (7)	0.0105 (9)
C13	0.0519 (9)	0.0651 (10)	0.0418 (8)	−0.0110 (8)	−0.0024 (7)	0.0068 (7)

Geometric parameters (Å, º)

F1—C4	1.3481 (17)	C4—C5	1.376 (2)
O1—C7	1.2258 (17)	C5—C6	1.4639 (19)
O1W—H1A	0.84 (3)	C6—H6	0.9300
O1W—H1B	0.89 (2)	C7—C8	1.494 (2)
N1—C1	1.3266 (19)	C8—C9	1.387 (2)
N1—C5	1.3480 (18)	C8—C13	1.388 (2)
N2—C6	1.2721 (18)	C9—C10	1.384 (2)
N2—N3	1.3736 (16)	C9—H9	0.9300

N3—C7	1.3582 (18)	C10—C11	1.372 (3)
N3—H3′	0.901 (18)	C10—H10	0.9300
C1—C2	1.377 (2)	C11—C12	1.370 (3)
C1—H1	0.9300	C11—H11	0.9300
C2—C3	1.366 (2)	C12—C13	1.381 (2)
C2—H2	0.9300	C12—H12	0.9300
C3—C4	1.368 (2)	C13—H13	0.9300
C3—H3	0.9300		

H1A—O1W—H1B	105 (2)	C5—C6—H6	120.2
C1—N1—C5	118.31 (13)	O1—C7—N3	122.14 (13)
C6—N2—N3	116.90 (12)	O1—C7—C8	121.16 (13)
C7—N3—N2	117.28 (12)	N3—C7—C8	116.67 (13)
C7—N3—H3′	123.2 (11)	C9—C8—C13	118.79 (14)
N2—N3—H3′	117.8 (11)	C9—C8—C7	124.09 (13)
N1—C1—C2	123.60 (15)	C13—C8—C7	117.12 (14)
N1—C1—H1	118.2	C10—C9—C8	120.27 (15)
C2—C1—H1	118.2	C10—C9—H9	119.9
C3—C2—C1	118.79 (14)	C8—C9—H9	119.9
C3—C2—H2	120.6	C11—C10—C9	120.18 (18)
C1—C2—H2	120.6	C11—C10—H10	119.9
C2—C3—C4	117.49 (15)	C9—C10—H10	119.9
C2—C3—H3	121.3	C12—C11—C10	120.13 (17)
C4—C3—H3	121.3	C12—C11—H11	119.9
F1—C4—C3	119.21 (13)	C10—C11—H11	119.9
F1—C4—C5	118.78 (13)	C11—C12—C13	120.19 (16)
C3—C4—C5	122.00 (14)	C11—C12—H12	119.9
N1—C5—C4	119.81 (13)	C13—C12—H12	119.9
N1—C5—C6	118.68 (12)	C12—C13—C8	120.43 (16)
C4—C5—C6	121.51 (13)	C12—C13—H13	119.8
N2—C6—C5	119.67 (12)	C8—C13—H13	119.8
N2—C6—H6	120.2		

C6—N2—N3—C7	176.10 (12)	N2—N3—C7—O1	−0.4 (2)
C5—N1—C1—C2	−0.2 (2)	N2—N3—C7—C8	177.81 (11)
N1—C1—C2—C3	−0.2 (2)	O1—C7—C8—C9	−166.31 (14)
C1—C2—C3—C4	0.3 (2)	N3—C7—C8—C9	15.5 (2)
C2—C3—C4—F1	178.90 (14)	O1—C7—C8—C13	13.8 (2)
C2—C3—C4—C5	0.1 (2)	N3—C7—C8—C13	−164.45 (13)
C1—N1—C5—C4	0.6 (2)	C13—C8—C9—C10	−0.7 (2)
C1—N1—C5—C6	179.89 (13)	C7—C8—C9—C10	179.37 (15)
F1—C4—C5—N1	−179.40 (12)	C8—C9—C10—C11	0.7 (3)
C3—C4—C5—N1	−0.5 (2)	C9—C10—C11—C12	0.1 (3)
F1—C4—C5—C6	1.4 (2)	C10—C11—C12—C13	−0.8 (3)
C3—C4—C5—C6	−179.78 (14)	C11—C12—C13—C8	0.8 (3)
N3—N2—C6—C5	−179.18 (11)	C9—C8—C13—C12	0.0 (2)
N1—C5—C6—N2	5.7 (2)	C7—C8—C13—C12	179.90 (14)
C4—C5—C6—N2	−175.10 (14)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3′···O1*W*	0.901 (18)	1.914 (18)	2.7917 (17)	164.3 (16)
O1*W*—H1*A*···O1^{i}	0.84 (3)	2.08 (3)	2.9187 (19)	172 (2)
O1*W*—H1*A*···N2^{i}	0.84 (3)	2.48 (2)	2.9494 (17)	116.1 (19)
O1*W*—H1*B*···N1^{i}	0.89 (2)	1.95 (3)	2.8420 (18)	178 (2)
C9—H9···O1*W*	0.93	2.30	3.209 (2)	165

Symmetry code: (i) −*x*+3/2, *y*−1/2, *z*.