Acta Cryst E CRYSTALLOGRAPHIC COMMUNICATIONS

ISSN 2056-9890

Crystal structure of 1-anilino-5-methyl-1*H*-1,2,3-triazole-4-carboxylic acid monohydrate

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Received 16 April 2019
Accepted 25 April 2019

Edited by J. Ellena, Universidade de São Paulo, Brazil

Keywords: crystal structure; triazole compounds; crystal packing; hydrogen bonding; Hirshfeld surface analysis..

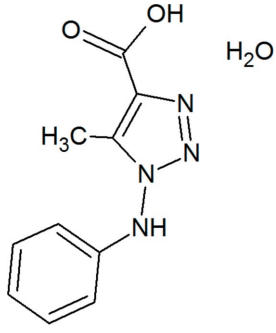
CCDC reference: 1912546

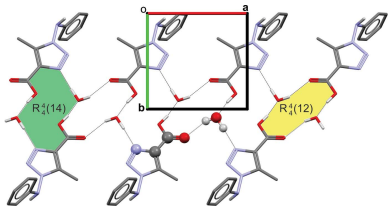
Supporting information: this article has supporting information at journals.iucr.org/e

In the molecular structure of the title compound, $C_{10}H_{10}N_4O_2\cdot H_2O$, the angle between the triazole and arene rings is 87.39 (5)°. The water of crystallization connects the molecules in the crystal packing. The crystal structure exhibits N—H···O, O—H···O and O—H···N interactions, resulting in the formation of a three-dimensional framework. The intermolecular interactions were identified and quantified using Hirshfeld surface analysis.

1. Chemical context

Triazoles are a class of compounds that have aroused chemical interest because of their wide range of applications, including their biological relevance and the development of new materials. Triazoles have potent antifungal activity, being an important class of drugs (Peyton *et al.*, 2015). Their antitubercular (Zhang *et al.*, 2017), anticancer (Teixeira *et al.*, 2019), antimicrobial (Yadav *et al.*, 2018) and antiviral (Jordão *et al.*, 2009) activities have also been evaluated. This class of compounds has also aroused interest in materials chemistry, mainly in the development of systems with uptake capacity for both CO_2 and H_2 (Mukherjee *et al.*, 2019).





2. Structural commentary

The title molecule (Fig. 1) is formed by planar aniline and triazolic rings, which subtend a dihedral angle of 87.41 (5)°. Atoms O1 and O2 are located 0.237 (2) and 0.208 (2) Å, respectively, outside the plane of the triazole ring. The methyl group exhibits occupational disorder of the hydrogen atoms.

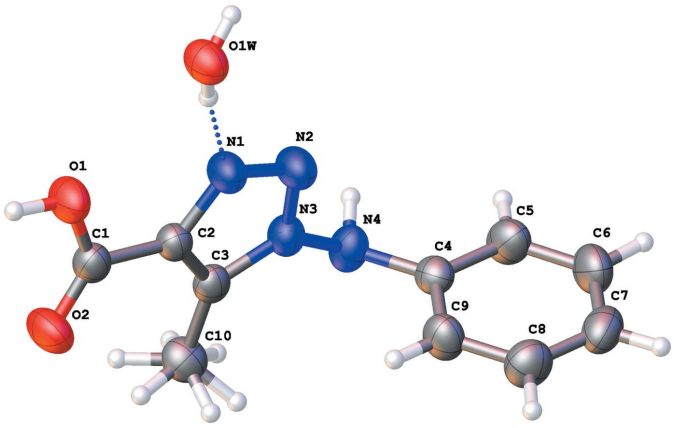


Figure 1
The molecular structure of the title compound with anisotropic atomic displacement ellipsoids shown at the 50% probability level.

3. Supramolecular features

The crystal packing is stabilized by N—H···O, O—H···N and O—H···O hydrogen bonds between the water molecule and the organic molecule. The supramolecular arrangement is formed by four hydrogen bonds (Table 1): (*A*) N4—H4···O1*W*^{ii}, (*B*) O1—H1···O1*W*^{i}, (*C*) O1*W*—H1*WA*···O2^{iii} and (*D*) O1*W*—H1*WB*···N1. Separately, these hydrogen bonds do not form nets in the structure. However, when combined, they generate interesting supramolecular systems. The combination of the (*A*:*B*), (*B*:*C*) and (*B*:*D*) interactions result in intermolecular rings with $R_2^4(18)$, $R_4^4(12)$ and $R_4^4(14)$ motifs, respectively. Representations of the $R_4^4(12)$ and $R_4^4(14)$ motifs are illustrated in Fig. 2). A $C_2^2(9)$ motif is observed along [$\bar{1}$10] (*A*:*C* interactions) (Fig. 3*a*), a $C_2^2(7)$ motif along [010] (*A*:*D* interactions) (Fig. 3*b*) and a $C_2^2(7)$ motif along [100] (*C*:*D* interactions).

4. Hirshfeld surface analysis

For an unequivocal description of the supramolecular system, Hirshfeld Surface (HS) analysis was performed. The isosurface was plotted for the weight function equal to 0.5. The red areas in Fig. 4 correspond to short contacts between atoms inside and outside the surface atom, d_i and d_e. There are three spots on the surface, and in the corresponding fingerprint plot (FPP; Fig. 5), they are represented as sharp spikes. Chemically, they correspond to classical hydrogen bonds. Two of these involve interactions between the carboxyl group and the water molecule while the third is the interaction between *N*-triazole and the water molecule. These hydrogen bonds are the shortest contacts, assigned in the FPP as O···H and N···H. The N···H interaction contributes 15.8% to the HS, while the O···H interaction corresponds to 18.1%. The majority of the interactions are H···H, being equal to 36.0%.

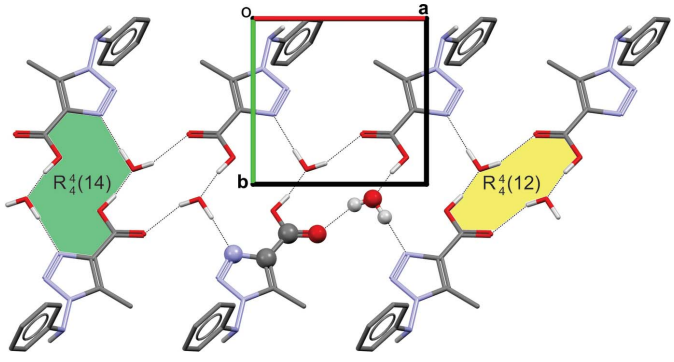


Figure 2
A partial packing diagram showing the hydrogen-bond network along the *a* axis and the $R_4^4(12)$ (green) and $R_4^4(14)$ (yellow) motifs. All hydrogen atoms bonded to carbon are omitted for clarity.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O1*W*^{i}	0.94 (2)	1.68 (3)	2.6030 (19)	167 (2)
N4—H4···O1*W*^{ii}	0.91 (2)	2.22 (2)	3.111 (2)	169.2 (19)
O1*W*—H1*WA*···O2^{iii}	0.82 (3)	1.99 (3)	2.773 (2)	159 (2)
O1*W*—H1*WB*···N1	0.92 (3)	1.88 (3)	2.800 (2)	172 (2)

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

5. Database survey

A research of the Cambridge Structural Database (CSD version 5.40, update of November 2018; Groom *et al.*, 2016) for *N*-phenyl-1*H*-1,2,3-triazol-1-amine derivatives gave 18 hits for structures that include atomic coordinates. These results include alcohols, esters and a carbohydrazide. The molecular structures of these compounds show dihedral angles between the triazole and aniline rings in the range 76 to 89°. These

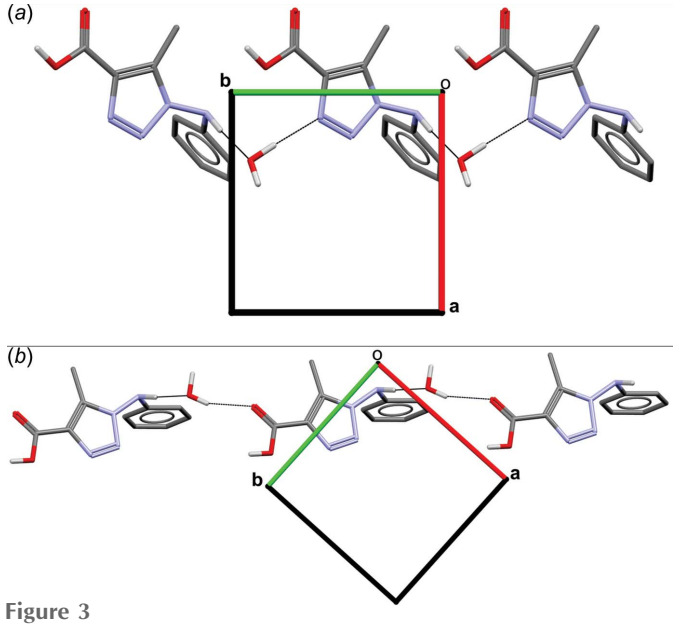


Figure 3
Views along the *c* axis showing the layers consolidated by the hydrogen-bond network: (*a*) a $C_2^2(7)$ chain along the *b*-axis direction and (*b*) a $C_2^2(9)$ chain along [$\bar{1}$10]. All hydrogen atoms bonded to carbon are omitted for clarity.

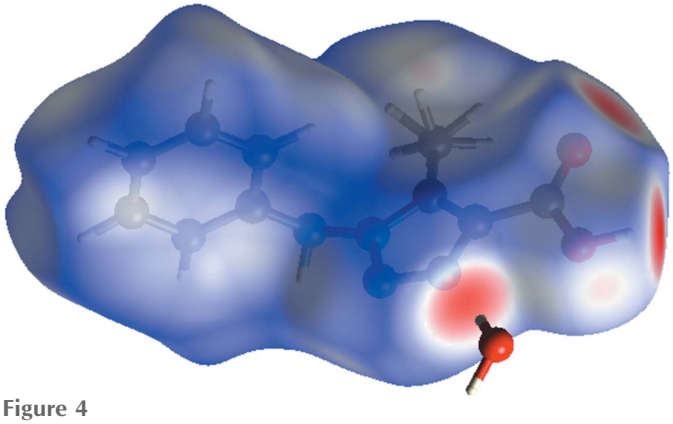


Figure 4
Hirshfeld surface mapped with d_{norm}.

values are affected by the hydrogen bonds in the crystal packing. In addition, in studies of halogenated phenyl derivatives, differences in C—H$\cdots\pi$ interactions were shown to result in changes in the crystal packing (Jordão *et al.*, 2012).

6. Vibrational spectrum

Fig. 6 shows the IR spectrum measured in ATR mode (ν_{max}, cm^{-1}) which exhibits the following characteristic bands: 3205 (N—H stretching); 2984 (methyl C—H stretching); 1725 (C═O stretching); 1600 (>C═N stretching); 1496 (aromatic C═C stretching); 1348 (C—N stretching of triazole); 1208 (C—O stretching) for the esther and 3431 (OH stretching); 3268 (N—H stretching); 1695 (C═O stretching); 1589 (>C═N stretching); 1496 (aromatic C═C stretching); 1381 (C—N stretching of triazole); 1259 (C—O stretching) for the acid.

7. Synthesis and crystallization

The title compound was synthesized by the alkaline hydrolysis of 5-methyl-1-(phenylamino)-1*H*-[1,2,3]-triazole-4-carboxylic acid ethyl ester (Jordão *et al.*, 2009), **1**. 3.6 mmol of **1** were dissolved in 30.0 ml of a sodium hydroxide solution (0.1 mol L^{-1}) (NaOH, VETEC). This mixture was refluxed at

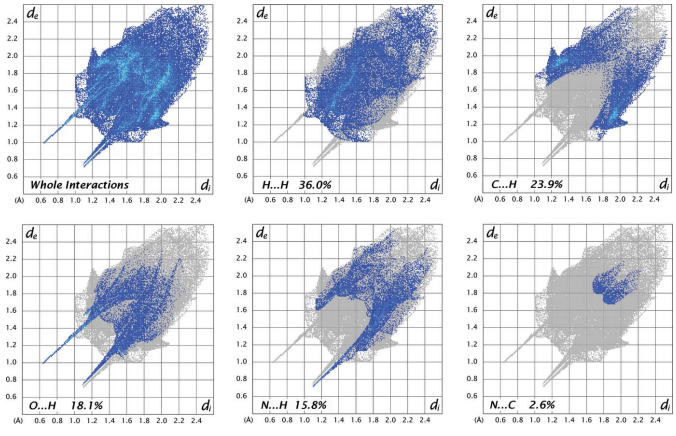


Figure 5
The fingerprint plots for the title compound.

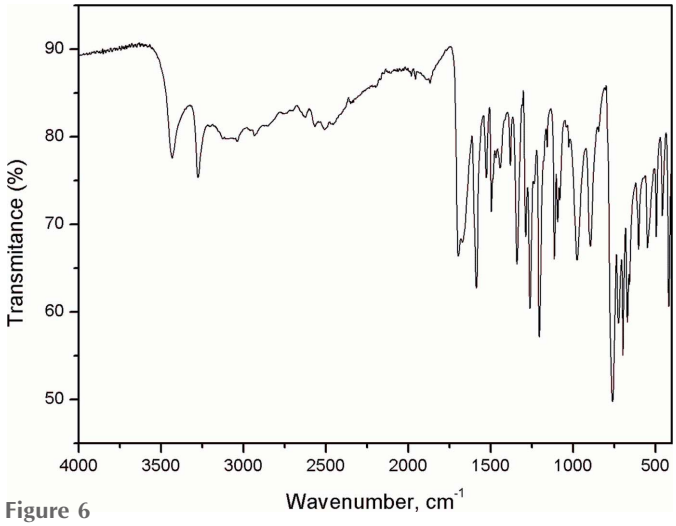


Figure 6
IR spectrum of the title compound.

373 K for about 48 h. The product was neutralized using dilute hydrochloric acid (HCl, VETEC), filtered and dried *in vacuo*. The title compound was dissolved in methanol and kept at room temperature. After a few days, colourless block-shaped crystals, suitable for X-ray analysis, were obtained by slow evaporation (yield 83%).

^{1}H NMR (500 MHz, C_2D_6OS): 10.218 (1H, *s*), 9.887 (1H, *s*), 7.215 (2H, *m*), 6.872 (1H, *m*), 6.390(2H, *d*, *J* = 3Hz), 3.295 (1H, *s*).

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{10}H_{10}N_4O_2{\cdot}H_2O$
M_r	236.24
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	298
a, *b*, *c* (Å)	7.2288 (14), 6.8265 (14), 23.922 (5)
β (°)	98.69 (3)
V (Å^3)	1167.0 (4)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.10
Crystal size (mm)	0.24 × 0.20 × 0.06
Data collection	
Diffractometer	Bruker KappaCCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2008)
T_{min}, T_{max}	0.701, 0.745
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	11378, 2207, 1559
R_{int}	0.042
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.609
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.041, 0.100, 1.04
No. of reflections	2207
No. of parameters	191
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.18, −0.15

Computer programs: *COLLECT* (Bruker, 2004), *DIRAX/LSQ* (Duisenberg, 1992), *EVALCCD* (Duisenberg *et al.*, 2003), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2016* (Sheldrick, 2015*b*), *OLEX2* (Dolomanov *et al.*, 2009) and *Mercury* (Macrae *et al.*, 2008).

8. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All H atoms were located in a difference-Fourier map and freely refined except for hydrogen atoms bound to C10 which are disordered (occupancy 0.5) and were refined using a riding model with C—H = 0.96 Å and $U_{iso}(H) = 1.5U_{eq}(C)$.

Acknowledgements

The authors would like to thank LAME–UFF and LDRX–UFF for analyses.

Funding information

Funding for this research was provided by: Fundação Carlos Chagas Filho de Amparo à Pesquisa do Estado do Rio de Janeiro; Conselho Nacional de Desenvolvimento Científico e Tecnológico (grant No. 311142/2017-6).

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supporting information

Acta Cryst. (2019). E**75**, 738-741 [https://doi.org/10.1107/S2056989019005711]

Crystal structure of 1-anilino-5-methyl-1*H*-1,2,3-triazole-4-carboxylic acid monohydrate

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Computing details

Data collection: *COLLECT* (Bruker, 2004); cell refinement: *DIRAX/LSQ* (Duisenberg, 1992); data reduction: *EVALCCD* (Duisenberg *et al.*, 2003); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2016* (Sheldrick, 2015b); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009) and *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009).

1-Anilino-5-methyl-1*H*-1,2,3-triazole-4-carboxylic acid monohydrate

Crystal data

$C_{10}H_{10}N_4O_2·H_2O$
M_r = 236.24
Monoclinic, $P2_1/c$
a = 7.2288 (14) Å
b = 6.8265 (14) Å
c = 23.922 (5) Å
β = 98.69 (3)°
V = 1167.0 (4) Å^3
Z = 4
$F(000)$ = 496
D_x = 1.345 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 11378 reflections
θ = 3.1–25.2°
μ = 0.10 mm^{-1}
T = 298 K
Block, colourless
0.24 × 0.20 × 0.06 mm

Data collection

Bruker KappaCCD diffractometer
Horizonally mounted graphite crystal monochromator
Detector resolution: 9 pixels mm^{-1}
CCD scans
Absorption correction: multi-scan (SADABS; Bruker, 2008)
T_{min} = 0.701, T_{max} = 0.745
11378 measured reflections
2207 independent reflections
1559 reflections with $I > 2\sigma(I)$
R_{int} = 0.042
θ_{max} = 25.7°, θ_{min} = 3.1°
h = −8→8
k = −8→7
l = −28→29

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.100
S = 1.04
2207 reflections
191 parameters
0 restraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0451P)^2 + 0.2317P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max}$ = 0.18 e Å^{-3}
$\Delta\rho_{min}$ = −0.15 e Å^{-3}

Extinction correction: SHELXL2016 (Sheldrick, 2015b), $Fc^{*}=kFc[1+0.001xFc^{2}\lambda^{3}/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.016 (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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^{2})

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
N1	0.1134 (2)	0.5773 (2)	0.07579 (6)	0.0470 (4)	
N2	0.1952 (2)	0.4253 (2)	0.10201 (7)	0.0490 (4)	
N3	0.0553 (2)	0.3016 (2)	0.11042 (6)	0.0408 (4)	
N4	0.0956 (2)	0.1211 (2)	0.13675 (6)	0.0456 (4)	
O1	−0.11452 (18)	0.8386 (2)	0.01606 (6)	0.0548 (4)	
O2	−0.37050 (18)	0.6983 (2)	0.03987 (6)	0.0626 (4)	
C1	−0.2030 (3)	0.7017 (3)	0.04017 (7)	0.0416 (4)	
C2	−0.0763 (2)	0.5512 (3)	0.06831 (7)	0.0379 (4)	
C3	−0.1165 (2)	0.3727 (2)	0.09034 (7)	0.0375 (4)	
C4	0.1777 (2)	0.1351 (2)	0.19481 (7)	0.0387 (4)	
C5	0.3163 (3)	0.0044 (3)	0.21538 (9)	0.0536 (5)	
C6	0.3937 (3)	0.0088 (3)	0.27196 (9)	0.0608 (6)	
C7	0.3320 (3)	0.1427 (3)	0.30781 (9)	0.0552 (6)	
C8	0.1928 (3)	0.2721 (3)	0.28731 (9)	0.0575 (5)	
C9	0.1139 (3)	0.2681 (3)	0.23076 (8)	0.0502 (5)	
C10	−0.2922 (3)	0.2638 (3)	0.09330 (8)	0.0507 (5)	
H10A	−0.397146	0.341238	0.076648	0.076*	0.5
H10B	−0.290788	0.142584	0.073046	0.076*	0.5
H10C	−0.302575	0.237247	0.132110	0.076*	0.5
H10D	−0.263193	0.139474	0.111221	0.076*	0.5
H10E	−0.369552	0.338129	0.114823	0.076*	0.5
H10F	−0.357764	0.243466	0.055760	0.076*	0.5
O1W	0.3100 (2)	0.9111 (2)	0.05054 (6)	0.0509 (4)	
H1	−0.199 (3)	0.926 (4)	−0.0049 (10)	0.081 (7)*	
H9	0.022 (3)	0.353 (3)	0.2172 (8)	0.058 (6)*	
H5	0.359 (3)	−0.091 (3)	0.1907 (9)	0.067 (6)*	
H6	0.495 (3)	−0.078 (3)	0.2851 (9)	0.076 (7)*	
H7	0.388 (3)	0.149 (3)	0.3456 (10)	0.067 (6)*	
H8	0.139 (3)	0.367 (4)	0.3125 (10)	0.083 (7)*	
H4	0.170 (3)	0.056 (3)	0.1157 (9)	0.063 (6)*	
H1WA	0.415 (4)	0.876 (4)	0.0455 (10)	0.074 (8)*	
H1WB	0.241 (4)	0.800 (4)	0.0552 (10)	0.089 (8)*	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0395 (9)	0.0483 (9)	0.0530 (9)	0.0066 (7)	0.0060 (7)	0.0148 (8)
N2	0.0410 (9)	0.0486 (9)	0.0570 (10)	0.0059 (8)	0.0067 (7)	0.0150 (8)
N3	0.0423 (9)	0.0390 (8)	0.0404 (8)	0.0054 (7)	0.0043 (6)	0.0064 (7)
N4	0.0573 (10)	0.0355 (9)	0.0431 (9)	0.0114 (7)	0.0046 (7)	0.0046 (7)
O1	0.0467 (8)	0.0527 (8)	0.0641 (9)	0.0101 (7)	0.0057 (7)	0.0233 (7)
O2	0.0394 (8)	0.0704 (10)	0.0785 (10)	0.0141 (7)	0.0102 (7)	0.0187 (8)
C1	0.0426 (11)	0.0450 (11)	0.0374 (9)	0.0082 (9)	0.0068 (8)	0.0011 (8)
C2	0.0361 (10)	0.0419 (10)	0.0355 (9)	0.0054 (8)	0.0051 (7)	0.0020 (8)
C3	0.0407 (10)	0.0403 (10)	0.0313 (9)	0.0053 (8)	0.0053 (7)	−0.0019 (8)
C4	0.0390 (10)	0.0348 (9)	0.0428 (10)	0.0029 (8)	0.0080 (8)	0.0070 (8)
C5	0.0580 (13)	0.0519 (12)	0.0522 (12)	0.0201 (10)	0.0129 (10)	0.0078 (10)
C6	0.0533 (13)	0.0678 (15)	0.0594 (14)	0.0172 (11)	0.0027 (10)	0.0192 (12)
C7	0.0569 (13)	0.0638 (14)	0.0433 (11)	−0.0076 (11)	0.0022 (10)	0.0109 (11)
C8	0.0658 (14)	0.0566 (13)	0.0506 (12)	0.0041 (11)	0.0107 (10)	−0.0039 (11)
C9	0.0498 (12)	0.0487 (12)	0.0512 (12)	0.0146 (10)	0.0045 (9)	0.0020 (10)
C10	0.0478 (11)	0.0478 (11)	0.0557 (12)	−0.0048 (9)	0.0053 (9)	−0.0045 (9)
O1W	0.0430 (9)	0.0445 (8)	0.0649 (9)	0.0073 (7)	0.0074 (7)	0.0108 (7)

Geometric parameters (Å, º)

N1—N2	1.307 (2)	C5—H5	0.96 (2)
N1—C2	1.367 (2)	C6—C7	1.373 (3)
N2—N3	1.356 (2)	C6—H6	0.96 (2)
N3—C3	1.352 (2)	C7—C8	1.372 (3)
N3—N4	1.394 (2)	C7—H7	0.93 (2)
N4—C4	1.429 (2)	C8—C9	1.387 (3)
N4—H4	0.91 (2)	C8—H8	1.00 (2)
O1—C1	1.314 (2)	C9—H9	0.90 (2)
O1—H1	0.94 (2)	C10—H10A	0.9600
O2—C1	1.210 (2)	C10—H10B	0.9600
C1—C2	1.470 (2)	C10—H10C	0.9600
C2—C3	1.376 (2)	C10—H10D	0.9600
C3—C10	1.482 (2)	C10—H10E	0.9600
C4—C5	1.376 (3)	C10—H10F	0.9600
C4—C9	1.377 (3)	O1W—H1WA	0.82 (3)
C5—C6	1.385 (3)	O1W—H1WB	0.92 (3)
N2—N1—C2	109.36 (14)	C6—C7—H7	120.2 (13)
N1—N2—N3	105.80 (14)	C7—C8—C9	120.5 (2)
C3—N3—N2	112.91 (14)	C7—C8—H8	122.1 (13)
C3—N3—N4	126.55 (15)	C9—C8—H8	117.3 (14)
N2—N3—N4	120.53 (14)	C4—C9—C8	119.66 (19)
N3—N4—C4	114.07 (14)	C4—C9—H9	119.7 (13)
N3—N4—H4	106.5 (13)	C8—C9—H9	120.6 (13)
C4—N4—H4	112.3 (14)	C3—C10—H10A	109.5

C1—O1—H1	111.4 (14)	C3—C10—H10B	109.5
O2—C1—O1	124.32 (17)	H10A—C10—H10B	109.5
O2—C1—C2	122.91 (17)	C3—C10—H10C	109.5
O1—C1—C2	112.77 (15)	H10A—C10—H10C	109.5
N1—C2—C3	109.33 (15)	H10B—C10—H10C	109.5
N1—C2—C1	120.80 (15)	C3—C10—H10D	109.5
C3—C2—C1	129.87 (16)	H10A—C10—H10D	141.1
N3—C3—C2	102.58 (14)	H10B—C10—H10D	56.3
N3—C3—C10	123.43 (16)	H10C—C10—H10D	56.3
C2—C3—C10	133.97 (16)	C3—C10—H10E	109.5
C5—C4—C9	119.92 (18)	H10A—C10—H10E	56.3
C5—C4—N4	118.51 (16)	H10B—C10—H10E	141.1
C9—C4—N4	121.46 (16)	H10C—C10—H10E	56.3
C4—C5—C6	120.0 (2)	H10D—C10—H10E	109.5
C4—C5—H5	120.3 (13)	C3—C10—H10F	109.5
C6—C5—H5	119.7 (13)	H10A—C10—H10F	56.3
C7—C6—C5	120.3 (2)	H10B—C10—H10F	56.3
C7—C6—H6	120.8 (13)	H10C—C10—H10F	141.1
C5—C6—H6	118.8 (13)	H10D—C10—H10F	109.5
C8—C7—C6	119.7 (2)	H10E—C10—H10F	109.5
C8—C7—H7	120.1 (13)	H1WA—O1W—H1WB	108 (2)

C2—N1—N2—N3	0.73 (19)	N1—C2—C3—N3	0.32 (18)
N1—N2—N3—C3	−0.55 (19)	C1—C2—C3—N3	−179.89 (16)
N1—N2—N3—N4	178.75 (14)	N1—C2—C3—C10	−178.06 (18)
C3—N3—N4—C4	−114.38 (18)	C1—C2—C3—C10	1.7 (3)
N2—N3—N4—C4	66.4 (2)	N3—N4—C4—C5	−141.88 (17)
N2—N1—C2—C3	−0.69 (19)	N3—N4—C4—C9	41.9 (2)
N2—N1—C2—C1	179.51 (15)	C9—C4—C5—C6	−1.1 (3)
O2—C1—C2—N1	−168.96 (17)	N4—C4—C5—C6	−177.43 (18)
O1—C1—C2—N1	10.7 (2)	C4—C5—C6—C7	0.3 (3)
O2—C1—C2—C3	11.3 (3)	C5—C6—C7—C8	0.1 (3)
O1—C1—C2—C3	−169.10 (17)	C6—C7—C8—C9	0.2 (3)
N2—N3—C3—C2	0.13 (18)	C5—C4—C9—C8	1.4 (3)
N4—N3—C3—C2	−179.11 (15)	N4—C4—C9—C8	177.62 (18)
N2—N3—C3—C10	178.74 (15)	C7—C8—C9—C4	−1.0 (3)
N4—N3—C3—C10	−0.5 (3)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O1*W*^{i}	0.94 (2)	1.68 (3)	2.6030 (19)	167 (2)
N4—H4···O1*W*^{ii}	0.91 (2)	2.22 (2)	3.111 (2)	169.2 (19)
O1*W*—H1*WA*···O2^{iii}	0.82 (3)	1.99 (3)	2.773 (2)	159 (2)
O1*W*—H1*WB*···N1	0.92 (3)	1.88 (3)	2.800 (2)	172 (2)

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