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2-(8-Bromoimidazo[1,2-a]pyridin-2-yl)-N'-[(E)-4-diethylamino-2-hydroxybenzylidene]acetohydrazide dihydrate

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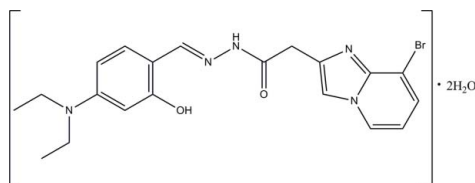
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Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.027; wR factor = 0.077; data-to-parameter ratio = 21.9.

In the title compound, $\text{C}_{20}\text{H}_{22}\text{BrN}_5\text{O}_2 \cdot 2\text{H}_2\text{O}$, the Schiff base molecule exists in an *E* conformation with respect to the acyclic $\text{C}=\text{N}$ bond. An $S(6)$ ring motif is formed *via* an intramolecular $\text{O}-\text{H} \cdots \text{N}$ hydrogen bond. The dihedral angle between the imidazo[1,2-*a*]pyridine system and the benzene ring is 84.62 (5)°. In the crystal, $\text{N}-\text{H} \cdots \text{O}$, $\text{O}-\text{H} \cdots \text{O}$, $\text{O}-\text{H} \cdots \text{N}$, $\text{C}-\text{H} \cdots \text{O}$ and $\text{C}-\text{H} \cdots \text{Br}$ hydrogen bonds link the molecules into a three-dimensional network. The crystal packing is further stabilized by $\text{C}-\text{H} \cdots \pi$ and $\pi-\pi$ interactions [centroid-centroid distance = 3.5365 (7) Å].

Related literature

For background to and applications of hydrazones, see: Seleem *et al.* (2011); Rollas & Küçüküzgel (2007). For background to and applications of imidazopyridine, see: Ertepinar *et al.* (1995); Liang *et al.* (2007); Hamdouchi *et al.* (1999); Gudmundsson & Johns (2007); Biftu *et al.* (2006); Fisher & Lusi (1972); Bochis *et al.* (1981). For hydrogen-bond motifs, see: Bernstein *et al.* (1995). For the stability of the temperature controller used for the data collection, see: Cosier & Glazer (1986).



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§ Thomson Reuters ResearcherID: C-7581-2009.

Experimental

Crystal data

$\text{C}_{20}\text{H}_{22}\text{BrN}_5\text{O}_2 \cdot 2\text{H}_2\text{O}$
 $M_r = 480.37$
Triclinic, $P\bar{1}$
 $a = 8.4370$ (4) Å
 $b = 10.6711$ (5) Å
 $c = 11.7559$ (5) Å
 $\alpha = 92.914$ (1)°
 $\beta = 96.949$ (1)°

$\gamma = 93.978$ (1)°
 $V = 1046.23$ (8) Å³
 $Z = 2$
Mo $K\alpha$ radiation
 $\mu = 2.00$ mm⁻¹
 $T = 100$ K
 $0.37 \times 0.20 \times 0.07$ mm

Data collection

Bruker SMART APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
 $T_{\min} = 0.529$, $T_{\max} = 0.869$

22937 measured reflections
6491 independent reflections
5841 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.023$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.027$
 $wR(F^2) = 0.077$
 $S = 1.05$
6491 reflections
297 parameters

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.63$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.24$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

Cg1 is the centroid of the N1/C1/N2/C6/C7 ring and Cg3 is the centroid of the $\text{C11}-\text{C16}$ ring.

$D-\text{H} \cdots A$	$D-\text{H}$	$\text{H} \cdots A$	$D \cdots A$	$D-\text{H} \cdots A$
$\text{N3}-\text{H1N3} \cdots \text{O2W}^{\text{i}}$	0.894 (17)	1.908 (17)	2.7956 (15)	171.7 (17)
$\text{O2}-\text{H1O2} \cdots \text{O1W}^{\text{ii}}$	0.87 (3)	2.42 (3)	2.9423 (15)	119 (2)
$\text{O2}-\text{H1O2} \cdots \text{N4}$	0.87 (3)	1.99 (3)	2.7181 (16)	142 (2)
$\text{O1W}-\text{H1W1} \cdots \text{N1}$	0.86 (2)	1.98 (2)	2.8315 (14)	176 (2)
$\text{O1W}-\text{H2W1} \cdots \text{O1}^{\text{iii}}$	0.85 (3)	1.92 (2)	2.7361 (14)	162 (2)
$\text{O2W}-\text{H1W2} \cdots \text{O1W}^{\text{i}}$	0.80 (2)	2.08 (2)	2.8311 (15)	157 (2)
$\text{O2W}-\text{H2W2} \cdots \text{O1W}$	0.86 (2)	1.87 (2)	2.7245 (15)	172.9 (17)
$\text{C5}-\text{H5A} \cdots \text{O1}^{\text{iv}}$	0.93	2.50	3.3121 (17)	146
$\text{C10}-\text{H10A} \cdots \text{O2W}^{\text{i}}$	0.93	2.54	3.3256 (17)	142
$\text{C17}-\text{H17B} \cdots \text{Br}^{\text{v}}$	0.97	2.85	3.6569 (15)	142
$\text{C3}-\text{H3A} \cdots \text{Cg3}^{\text{vi}}$	0.93	2.61	3.4734 (15)	154
$\text{C17}-\text{H17A} \cdots \text{Cg1}^{\text{vii}}$	0.97	2.70	3.5863 (15)	152

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

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINTE* (Bruker, 2009); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BQ2340).

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2-(8-Bromoimidazo[1,2-*a*]pyridin-2-yl)-*N'*-[(*E*)-4-diethylamino-2-hydroxy-benzylidene]acetohydrazide dihydrate

Hoong-Kun Fun, Wan-Sin Loh, Seema Shenvi, Arun M. Isloor and Gurumurthy Hegde

S1. Comment

Hydrazone constitute an important class of biologically active drug molecules (Seleem *et al.*, 2011) which has attracted attention of medicinal chemists due to their wide range of pharmacological properties. These compounds are being synthesized as drugs by many researchers in order to combat diseases with minimal toxicity and maximal effects. A number of hydrazone derivatives have been reported to exert notably antimicrobial, antihypertensive, anticonvulsant, analgesic, anti-inflammatory, antituberculosis, antitumoral, antiproliferative and antimalarial activities (Rollas & Küçükgüzel, 2007). Imidazopyridine is the fundamental heterocyclic component of principal anthelmintic drugs. In addition, the imidazopyridine ring possesses many anti-infective properties including antibacterial (Ertepinarl *et al.*, 1995; Liang *et al.*, 2007), antiviral (Hamdouchi *et al.*, 1999; Gudmundsson & Johns, 2007), antiprotozoal (Biftu *et al.*, 2006) and especially anthelmintic (Fisher & Lusi, 1972; Bochis *et al.*, 1981) activities. Therefore, the imidazopyridine ring could replace the benzimidazole ring in the design and the development of new anthelmintic agents. In view of its biological importance, we hereby report the crystal structure of (I).

The title compound (Fig. 1) consists of one 2-(8-bromoimidazo[1,2-*a*]pyridin-3-yl)-*N'*-{(*E*)-[4-(diethylamino)-2-hydroxyphenyl]methylidene}acetohydrazide molecule and two water molecules. The Schiff base molecule exists in an *E* configuration with respect to the acyclic C=N bond. An *S*(6) ring motif (Bernstein *et al.*, 1995) is formed *via* the intramolecular O2—H1O2···N4 hydrogen bond. The dihedral angle between the imidazo[1,2-*a*]pyridine (C1—C5/N2/C6/C7/N1) and the benzene (C11—C16) rings is 84.62 (5)°.

In the crystal packing (Fig. 2), intermolecular N3—H1N3···O2W, O2—H1O2···O1W, O2—H1O2···N4, O1W—H1W1···N1, O1W—H2W1···O1, O2W—H1W2···O1W, O2W—H2W2···O1W, C5—H5A···O1, C10—H10A···O2W and C17—H17B···Br1 hydrogen bonds link the molecules into a three-dimensional network. The crystal packing is further stabilized by C—H··· π interactions, involving the 1*H*-imidazole (N1/C1/N2/C6/C7; *Cg*1; Table 1) and benzene (*Cg*3; Table 1) rings. Weak π — π interactions were observed involving 1*H*-imidazole, pyridine (N2/C1—C5; *Cg*2) and benzene rings. [*Cg*1···*Cg*1 = 3.5365 (7) Å; symmetry code: 1 - *x*, 1 - *y*, 1 - *z*; *Cg*1···*Cg*2 = 3.6210 (7) Å; symmetry code: 1 - *x*, 1 - *y*, 1 - *z*; *Cg*3···*Cg*3 = 3.6253 (8) Å; symmetry code: -*x*, -*y*, 2 - *z*].

S2. Experimental

The mixture of 2-(8-bromoimidazo[1,2-*a*]pyridine-3-yl)acetohydrazide (200 mg, 0.00074 mol), 4-(diethylamino)-2-hydroxy benzaldehyde (143.6 mg, 0.00074 mol) and a catalytic quantity of acetic acid (0.1 ml) and ethanol (10 ml) was stirred overnight at 90°C. On cooling, orange plate-shaped crystals of the product begins to separate. It was collected by filtration and recrystallized from ethanol. Yield: 307.7 mg, 93.2%. m.p. 401–402 K.

S3. Refinement

O- and N-bound H atoms were located from the difference Fourier map and were refined freely [O—H = 0.80 (3) to 0.87 (3) Å; N—H = 0.896 (19) Å]. The remaining H atoms were positioned geometrically and refined with a riding model with $U_{\text{iso}}(\text{H}) = 1.2$ or $1.5U_{\text{eq}}(\text{C})$ [C—H = 0.93 to 0.97 Å]. A rotating group model was applied to the methyl groups. Three outliers were omitted in the final refinement, 230, $\bar{5}41$ and $3\bar{6}5$.

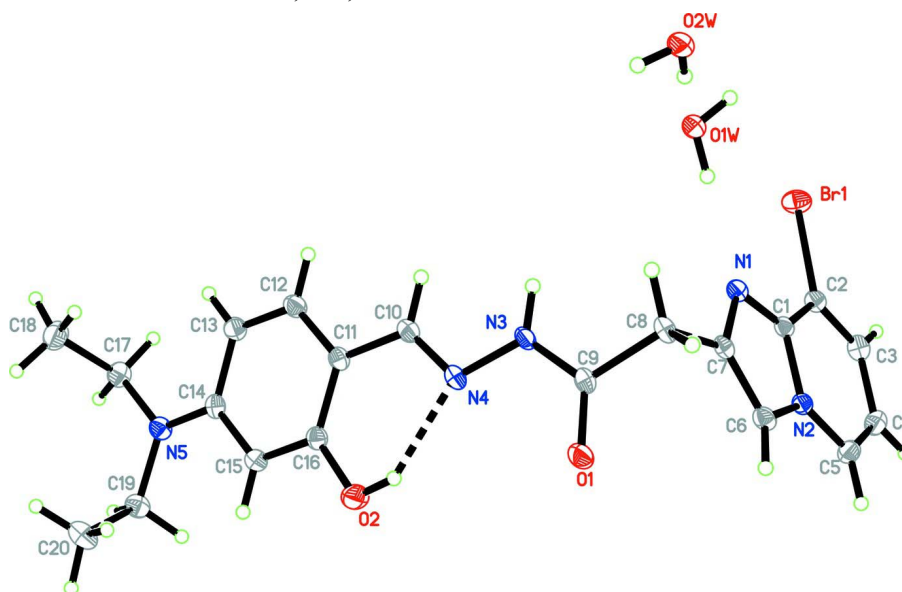
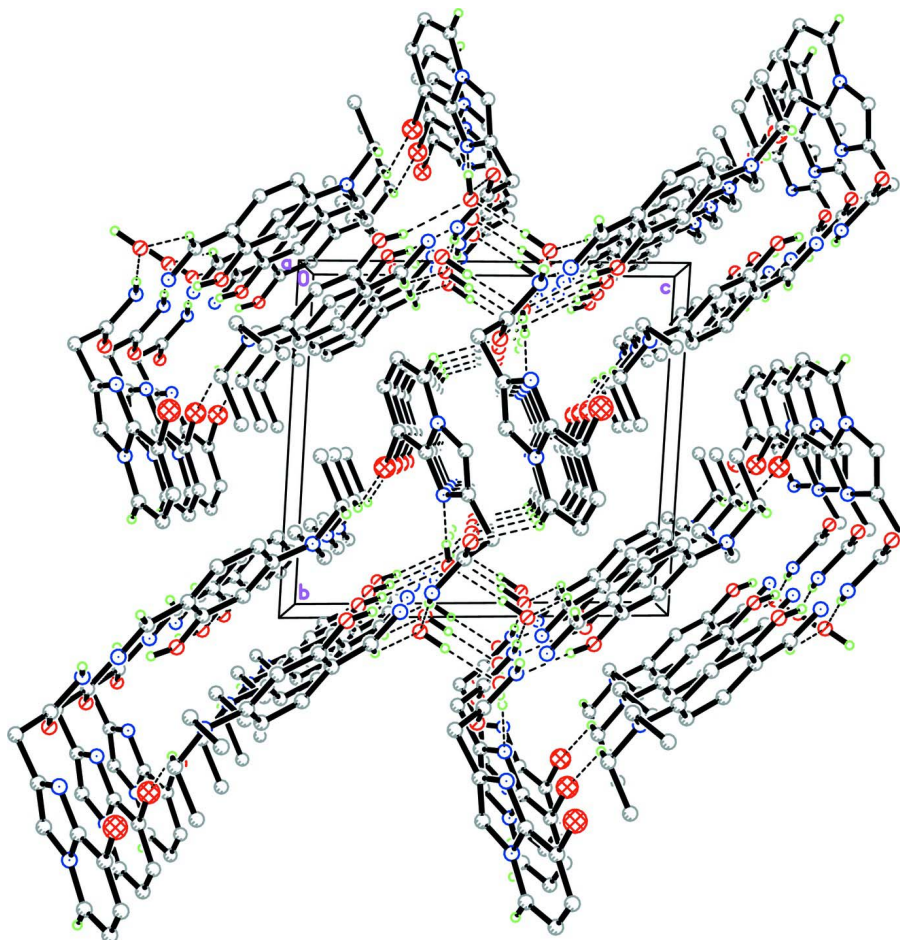


Figure 1

The molecular structure of the title compound, showing 50% probability displacement ellipsoids. Dashed line indicates the intramolecular hydrogen bond.

**Figure 2**

The crystal packing of the title compound, viewed along the *a* axis, showing the three-dimensional network. H atoms not involved in the intermolecular interactions (dashed lines) have been omitted for clarity.

2-(8-Bromoimidazo[1,2-a]pyridin-2-yl)-*N'*-[(*E*)-4-diethylamino-2-hydroxybenzylidene]acetohydrazide dihydrate

Crystal data

$C_{20}H_{22}BrN_5O_2 \cdot 2H_2O$

$M_r = 480.37$

Triclinic, $P\bar{1}$

Hall symbol: $-P\ 1$

$a = 8.4370$ (4) Å

$b = 10.6711$ (5) Å

$c = 11.7559$ (5) Å

$\alpha = 92.914$ (1)°

$\beta = 96.949$ (1)°

$\gamma = 93.978$ (1)°

$V = 1046.23$ (8) Å³

$Z = 2$

$F(000) = 496$

$D_x = 1.525$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 9983 reflections

$\theta = 2.4$ – 30.9 °

$\mu = 2.00$ mm⁻¹

$T = 100$ K

Plate, orange

$0.37 \times 0.20 \times 0.07$ mm

Data collection

Bruker SMART APEXII CCD

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

φ and ω scans

Absorption correction: multi-scan

(SADABS; Bruker, 2009)

$T_{\min} = 0.529$, $T_{\max} = 0.869$

22937 measured reflections

6491 independent reflections

5841 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.023$

$\theta_{\max} = 30.9^\circ$, $\theta_{\min} = 1.8^\circ$

$h = -12 \rightarrow 12$

$k = -15 \rightarrow 15$

$l = -16 \rightarrow 16$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.027$

$wR(F^2) = 0.077$

$S = 1.05$

6491 reflections

297 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

$w = 1/[\sigma^2(F_o^2) + (0.0455P)^2 + 0.2952P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.002$

$\Delta\rho_{\max} = 0.63 \text{ e } \text{Å}^{-3}$

$\Delta\rho_{\min} = -0.24 \text{ e } \text{Å}^{-3}$

Special details

Experimental. The crystal was placed in the cold stream of an Oxford Cryosystems Cobra open-flow nitrogen cryostat (Cosier & Glazer, 1986) operating at 100.0 (1) K.

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	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.789019 (15)	0.424051 (13)	0.748329 (12)	0.02141 (5)
O1	-0.05933 (11)	0.23815 (10)	0.52050 (9)	0.02047 (19)
O2	-0.26058 (13)	0.04472 (10)	0.79255 (9)	0.0227 (2)
N1	0.44340 (12)	0.35221 (10)	0.59413 (9)	0.01348 (19)
N2	0.35279 (12)	0.54369 (10)	0.61740 (9)	0.01344 (19)
N3	0.10753 (13)	0.09994 (10)	0.60467 (9)	0.01444 (19)
N4	-0.00110 (13)	0.05569 (10)	0.67606 (9)	0.0150 (2)
N5	-0.25929 (13)	-0.22618 (11)	1.10154 (9)	0.0164 (2)
C1	0.47756 (14)	0.46769 (11)	0.64404 (10)	0.0127 (2)
C2	0.61422 (15)	0.52232 (12)	0.71616 (11)	0.0147 (2)
C3	0.62011 (16)	0.64472 (13)	0.75761 (11)	0.0174 (2)
H3A	0.7093	0.6799	0.8059	0.021*
C4	0.48898 (17)	0.71799 (12)	0.72639 (11)	0.0182 (2)
H4A	0.4935	0.8015	0.7542	0.022*
C5	0.35760 (16)	0.66812 (12)	0.65681 (11)	0.0175 (2)
H5A	0.2725	0.7167	0.6361	0.021*

C6	0.23518 (14)	0.47094 (12)	0.54616 (11)	0.0153 (2)
H6A	0.1371	0.4957	0.5135	0.018*
C7	0.29303 (14)	0.35486 (12)	0.53359 (10)	0.0134 (2)
C8	0.20850 (15)	0.23836 (12)	0.46996 (11)	0.0155 (2)
H8A	0.2831	0.1737	0.4649	0.019*
H8B	0.1674	0.2574	0.3926	0.019*
C9	0.07088 (14)	0.19108 (12)	0.53330 (11)	0.0143 (2)
C10	0.05212 (15)	-0.02976 (12)	0.74143 (11)	0.0158 (2)
H10A	0.1519	-0.0582	0.7326	0.019*
C11	-0.03602 (15)	-0.08324 (12)	0.82756 (11)	0.0146 (2)
C12	0.03051 (15)	-0.17581 (13)	0.89465 (12)	0.0175 (2)
H12A	0.1274	-0.2048	0.8788	0.021*
C13	-0.04169 (15)	-0.22574 (12)	0.98328 (11)	0.0173 (2)
H13A	0.0055	-0.2883	1.0247	0.021*
C14	-0.18834 (15)	-0.18158 (12)	1.01136 (10)	0.0144 (2)
C15	-0.25764 (15)	-0.08989 (12)	0.94303 (11)	0.0156 (2)
H15A	-0.3549	-0.0610	0.9582	0.019*
C16	-0.18382 (15)	-0.04205 (12)	0.85370 (11)	0.0147 (2)
C17	-0.19118 (17)	-0.32564 (13)	1.16815 (12)	0.0196 (2)
H17A	-0.2326	-0.3243	1.2416	0.024*
H17B	-0.0760	-0.3076	1.1831	0.024*
C18	-0.2262 (2)	-0.45760 (14)	1.11027 (14)	0.0265 (3)
H18A	-0.1691	-0.5164	1.1555	0.040*
H18B	-0.1926	-0.4586	1.0351	0.040*
H18C	-0.3391	-0.4808	1.1038	0.040*
C19	-0.41481 (16)	-0.18615 (13)	1.12605 (11)	0.0186 (2)
H19A	-0.4149	-0.0958	1.1202	0.022*
H19B	-0.4286	-0.2039	1.2045	0.022*
C20	-0.55683 (17)	-0.25000 (16)	1.04598 (13)	0.0252 (3)
H20A	-0.6542	-0.2176	1.0652	0.038*
H20B	-0.5615	-0.3391	1.0544	0.038*
H20C	-0.5440	-0.2334	0.9680	0.038*
O1W	0.64543 (12)	0.15365 (9)	0.57170 (9)	0.01893 (19)
O2W	0.60246 (12)	0.01353 (10)	0.36855 (10)	0.01989 (19)
H1N3	0.205 (2)	0.0710 (17)	0.6120 (15)	0.018 (4)*
H1O2	-0.209 (3)	0.069 (3)	0.737 (2)	0.058 (8)*
H1W1	0.587 (3)	0.215 (2)	0.582 (2)	0.041 (6)*
H2W1	0.742 (3)	0.181 (2)	0.5720 (18)	0.031 (5)*
H1W2	0.518 (3)	-0.026 (2)	0.369 (2)	0.041 (6)*
H2W2	0.608 (2)	0.060 (2)	0.4315 (18)	0.026 (5)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.01455 (7)	0.02522 (8)	0.02311 (8)	0.00475 (5)	-0.00432 (5)	-0.00016 (5)
O1	0.0123 (4)	0.0243 (5)	0.0255 (5)	0.0016 (3)	0.0027 (4)	0.0083 (4)
O2	0.0220 (5)	0.0254 (5)	0.0236 (5)	0.0075 (4)	0.0069 (4)	0.0106 (4)
N1	0.0117 (4)	0.0156 (5)	0.0132 (5)	0.0004 (4)	0.0019 (4)	0.0016 (4)

N2	0.0121 (4)	0.0152 (5)	0.0133 (5)	0.0009 (3)	0.0018 (4)	0.0027 (4)
N3	0.0107 (4)	0.0166 (5)	0.0165 (5)	-0.0009 (4)	0.0041 (4)	0.0021 (4)
N4	0.0126 (4)	0.0178 (5)	0.0147 (5)	-0.0017 (4)	0.0037 (4)	0.0009 (4)
N5	0.0165 (5)	0.0194 (5)	0.0136 (5)	0.0012 (4)	0.0030 (4)	0.0031 (4)
C1	0.0115 (5)	0.0154 (5)	0.0115 (5)	0.0013 (4)	0.0022 (4)	0.0031 (4)
C2	0.0130 (5)	0.0177 (6)	0.0131 (5)	0.0007 (4)	0.0007 (4)	0.0020 (4)
C3	0.0179 (6)	0.0194 (6)	0.0138 (5)	-0.0021 (4)	0.0005 (4)	0.0001 (4)
C4	0.0229 (6)	0.0151 (5)	0.0167 (6)	0.0017 (4)	0.0036 (5)	0.0013 (4)
C5	0.0199 (6)	0.0156 (6)	0.0178 (6)	0.0040 (4)	0.0036 (5)	0.0036 (4)
C6	0.0109 (5)	0.0197 (6)	0.0148 (5)	0.0000 (4)	-0.0001 (4)	0.0026 (4)
C7	0.0118 (5)	0.0171 (5)	0.0115 (5)	-0.0009 (4)	0.0030 (4)	0.0024 (4)
C8	0.0136 (5)	0.0188 (6)	0.0140 (5)	-0.0030 (4)	0.0039 (4)	0.0004 (4)
C9	0.0122 (5)	0.0160 (5)	0.0141 (5)	-0.0030 (4)	0.0017 (4)	0.0001 (4)
C10	0.0129 (5)	0.0173 (6)	0.0169 (6)	-0.0007 (4)	0.0024 (4)	0.0003 (4)
C11	0.0131 (5)	0.0164 (5)	0.0139 (5)	-0.0013 (4)	0.0010 (4)	0.0009 (4)
C12	0.0132 (5)	0.0200 (6)	0.0193 (6)	0.0014 (4)	0.0017 (4)	0.0029 (5)
C13	0.0154 (5)	0.0187 (6)	0.0176 (6)	0.0012 (4)	0.0004 (4)	0.0041 (4)
C14	0.0155 (5)	0.0152 (5)	0.0113 (5)	-0.0022 (4)	-0.0003 (4)	-0.0002 (4)
C15	0.0145 (5)	0.0173 (6)	0.0152 (6)	0.0010 (4)	0.0023 (4)	0.0007 (4)
C16	0.0144 (5)	0.0150 (5)	0.0144 (5)	-0.0004 (4)	0.0008 (4)	0.0007 (4)
C17	0.0227 (6)	0.0207 (6)	0.0158 (6)	0.0017 (5)	0.0024 (5)	0.0040 (5)
C18	0.0312 (8)	0.0201 (7)	0.0288 (8)	0.0007 (5)	0.0058 (6)	0.0029 (5)
C19	0.0193 (6)	0.0230 (6)	0.0145 (6)	0.0023 (5)	0.0055 (5)	0.0016 (5)
C20	0.0177 (6)	0.0342 (8)	0.0235 (7)	-0.0006 (5)	0.0040 (5)	-0.0005 (6)
O1W	0.0137 (4)	0.0173 (4)	0.0263 (5)	0.0007 (3)	0.0043 (4)	0.0026 (4)
O2W	0.0150 (4)	0.0182 (4)	0.0270 (5)	0.0005 (3)	0.0057 (4)	0.0000 (4)

Geometric parameters (Å, °)

Br1—C2	1.8809 (13)	C8—H8B	0.9700
O1—C9	1.2354 (16)	C10—C11	1.4444 (17)
O2—C16	1.3534 (16)	C10—H10A	0.9300
O2—H1O2	0.87 (3)	C11—C12	1.4007 (18)
N1—C1	1.3350 (16)	C11—C16	1.4134 (17)
N1—C7	1.3804 (16)	C12—C13	1.3804 (18)
N2—C5	1.3802 (16)	C12—H12A	0.9300
N2—C6	1.3837 (16)	C13—C14	1.4232 (18)
N2—C1	1.3887 (15)	C13—H13A	0.9300
N3—C9	1.3443 (17)	C14—C15	1.4108 (17)
N3—N4	1.3906 (14)	C15—C16	1.3856 (18)
N3—H1N3	0.896 (19)	C15—H15A	0.9300
N4—C10	1.2915 (17)	C17—C18	1.526 (2)
N5—C14	1.3690 (16)	C17—H17A	0.9700
N5—C17	1.4594 (17)	C17—H17B	0.9700
N5—C19	1.4642 (17)	C18—H18A	0.9600
C1—C2	1.4170 (17)	C18—H18B	0.9600
C2—C3	1.3662 (18)	C18—H18C	0.9600
C3—C4	1.4216 (19)	C19—C20	1.528 (2)

C3—H3A	0.9300	C19—H19A	0.9700
C4—C5	1.3548 (19)	C19—H19B	0.9700
C4—H4A	0.9300	C20—H20A	0.9600
C5—H5A	0.9300	C20—H20B	0.9600
C6—C7	1.3701 (17)	C20—H20C	0.9600
C6—H6A	0.9300	O1W—H1W1	0.86 (3)
C7—C8	1.5057 (17)	O1W—H2W1	0.84 (2)
C8—C9	1.5242 (17)	O2W—H1W2	0.80 (3)
C8—H8A	0.9700	O2W—H2W2	0.86 (2)
C16—O2—H1O2	111.7 (18)	C12—C11—C16	116.99 (11)
C1—N1—C7	105.16 (10)	C12—C11—C10	119.37 (11)
C5—N2—C6	130.13 (11)	C16—C11—C10	123.53 (12)
C5—N2—C1	123.09 (11)	C13—C12—C11	122.76 (12)
C6—N2—C1	106.77 (10)	C13—C12—H12A	118.6
C9—N3—N4	120.60 (10)	C11—C12—H12A	118.6
C9—N3—H1N3	121.0 (12)	C12—C13—C14	120.09 (12)
N4—N3—H1N3	118.2 (12)	C12—C13—H13A	120.0
C10—N4—N3	113.55 (10)	C14—C13—H13A	120.0
C14—N5—C17	120.87 (11)	N5—C14—C15	121.23 (11)
C14—N5—C19	121.09 (11)	N5—C14—C13	121.24 (12)
C17—N5—C19	117.68 (11)	C15—C14—C13	117.54 (11)
N1—C1—N2	111.09 (10)	C16—C15—C14	121.34 (12)
N1—C1—C2	131.60 (11)	C16—C15—H15A	119.3
N2—C1—C2	117.31 (11)	C14—C15—H15A	119.3
C3—C2—C1	120.47 (12)	O2—C16—C15	116.85 (11)
C3—C2—Br1	121.18 (10)	O2—C16—C11	121.89 (12)
C1—C2—Br1	118.31 (9)	C15—C16—C11	121.25 (12)
C2—C3—C4	119.53 (12)	N5—C17—C18	114.42 (12)
C2—C3—H3A	120.2	N5—C17—H17A	108.7
C4—C3—H3A	120.2	C18—C17—H17A	108.7
C5—C4—C3	121.06 (12)	N5—C17—H17B	108.7
C5—C4—H4A	119.5	C18—C17—H17B	108.7
C3—C4—H4A	119.5	H17A—C17—H17B	107.6
C4—C5—N2	118.52 (12)	C17—C18—H18A	109.5
C4—C5—H5A	120.7	C17—C18—H18B	109.5
N2—C5—H5A	120.7	H18A—C18—H18B	109.5
C7—C6—N2	105.77 (11)	C17—C18—H18C	109.5
C7—C6—H6A	127.1	H18A—C18—H18C	109.5
N2—C6—H6A	127.1	H18B—C18—H18C	109.5
C6—C7—N1	111.22 (11)	N5—C19—C20	113.89 (11)
C6—C7—C8	127.58 (11)	N5—C19—H19A	108.8
N1—C7—C8	121.11 (11)	C20—C19—H19A	108.8
C7—C8—C9	109.35 (10)	N5—C19—H19B	108.8
C7—C8—H8A	109.8	C20—C19—H19B	108.8
C9—C8—H8A	109.8	H19A—C19—H19B	107.7
C7—C8—H8B	109.8	C19—C20—H20A	109.5
C9—C8—H8B	109.8	C19—C20—H20B	109.5

H8A—C8—H8B	108.3	H20A—C20—H20B	109.5
O1—C9—N3	124.94 (11)	C19—C20—H20C	109.5
O1—C9—C8	120.90 (12)	H20A—C20—H20C	109.5
N3—C9—C8	114.12 (11)	H20B—C20—H20C	109.5
N4—C10—C11	123.10 (12)	H1W1—O1W—H2W1	110 (2)
N4—C10—H10A	118.5	H1W2—O2W—H2W2	101 (2)
C11—C10—H10A	118.5		
C9—N3—N4—C10	-178.57 (11)	C7—C8—C9—O1	81.70 (15)
C7—N1—C1—N2	0.28 (13)	C7—C8—C9—N3	-95.99 (13)
C7—N1—C1—C2	-179.63 (13)	N3—N4—C10—C11	175.89 (11)
C5—N2—C1—N1	-179.26 (11)	N4—C10—C11—C12	179.87 (12)
C6—N2—C1—N1	-0.44 (13)	N4—C10—C11—C16	-4.1 (2)
C5—N2—C1—C2	0.66 (17)	C16—C11—C12—C13	-0.39 (19)
C6—N2—C1—C2	179.48 (11)	C10—C11—C12—C13	175.88 (12)
N1—C1—C2—C3	-179.62 (13)	C11—C12—C13—C14	-1.3 (2)
N2—C1—C2—C3	0.47 (18)	C17—N5—C14—C15	176.84 (12)
N1—C1—C2—Br1	2.65 (19)	C19—N5—C14—C15	3.84 (18)
N2—C1—C2—Br1	-177.26 (8)	C17—N5—C14—C13	-3.34 (18)
C1—C2—C3—C4	-1.02 (19)	C19—N5—C14—C13	-176.34 (12)
Br1—C2—C3—C4	176.64 (10)	C12—C13—C14—N5	-177.55 (12)
C2—C3—C4—C5	0.5 (2)	C12—C13—C14—C15	2.28 (19)
C3—C4—C5—N2	0.6 (2)	N5—C14—C15—C16	178.18 (12)
C6—N2—C5—C4	-179.72 (12)	C13—C14—C15—C16	-1.64 (18)
C1—N2—C5—C4	-1.20 (19)	C14—C15—C16—O2	179.42 (11)
C5—N2—C6—C7	179.12 (12)	C14—C15—C16—C11	-0.03 (19)
C1—N2—C6—C7	0.41 (13)	C12—C11—C16—O2	-178.35 (12)
N2—C6—C7—N1	-0.25 (14)	C10—C11—C16—O2	5.54 (19)
N2—C6—C7—C8	176.21 (11)	C12—C11—C16—C15	1.06 (18)
C1—N1—C7—C6	-0.01 (14)	C10—C11—C16—C15	-175.04 (12)
C1—N1—C7—C8	-176.73 (11)	C14—N5—C17—C18	-78.07 (16)
C6—C7—C8—C9	-68.28 (16)	C19—N5—C17—C18	95.16 (14)
N1—C7—C8—C9	107.87 (13)	C14—N5—C19—C20	77.22 (16)
N4—N3—C9—O1	-3.51 (19)	C17—N5—C19—C20	-96.00 (14)
N4—N3—C9—C8	174.06 (10)		

Hydrogen-bond geometry (\AA , $^\circ$)

Cg1 is the centroid of the N1/C1/N2/C6/C7 ring and Cg3 is the centroid of the C11—C16 ring.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N3—H1N3 \cdots O2W ⁱ	0.894 (17)	1.908 (17)	2.7956 (15)	171.7 (17)
O2—H1O2 \cdots O1W ⁱⁱ	0.87 (3)	2.42 (3)	2.9423 (15)	119 (2)
O2—H1O2 \cdots N4	0.87 (3)	1.99 (3)	2.7181 (16)	142 (2)
O1W—H1W1 \cdots N1	0.86 (2)	1.98 (2)	2.8315 (14)	176 (2)
O1W—H2W1 \cdots O1 ⁱⁱⁱ	0.85 (3)	1.92 (2)	2.7361 (14)	162 (2)
O2W—H1W2 \cdots O1W ⁱ	0.80 (2)	2.08 (2)	2.8311 (15)	157 (2)
O2W—H2W2 \cdots O1W	0.86 (2)	1.87 (2)	2.7245 (15)	172.9 (17)
C5—H5A \cdots O1 ^{iv}	0.93	2.50	3.3121 (17)	146

C10—H10A···O2 ^{iv}	0.93	2.54	3.3256 (17)	142
C17—H17B···Br1 ^v	0.97	2.85	3.6569 (15)	142
C3—H3A···Cg3 ^{vi}	0.93	2.61	3.4734 (15)	154
C17—H17A···Cg1 ^{vii}	0.97	2.70	3.5863 (15)	152

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