Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

5-*tert*-Butyl-4-bromo-1,2-dihydro-1*H*-pyrazol-3(2*H*)-one monohydrate

Daniel E. Lynch[a]* and Ian McClenaghan[b]

[a]School of Science and the Environment, Coventry University, Coventry CV1 5FB, England, and [b]Key Organics Ltd, Highfield Industrial Estate, Camelford, Cornwall PL32 9QZ, England

Correspondence e-mail: apx106@coventry.ac.uk

Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.004 Å
R factor = 0.030
wR factor = 0.069
Data-to-parameter ratio = 15.9

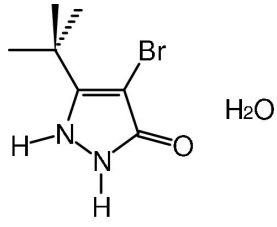
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 21 April 2005
Accepted 22 April 2005
Online 6 July 2005

The structure of the title compound, $C_7H_{11}BrN_2O\cdot H_2O$, exhibits an elaborate hydrogen-bonding network involving pyrazole N—H···O dimers and two other hydrogen-bonding motifs, both including water molecules. One motif is a distorted hexagonal $R_3^5(11)$ graph set, while the other is a distorted octagonal boat conformation $R_6^4(14)$ graph set.

Comment

In a series of studies on the preparation and hydrogen-bonding properties of 3,4,5-tri-substituted pyrazoles, we recently characterized the structure of 5-*tert*-butyl-4-nitro-1*H*-pyrazol-3-ol (Lynch & McClenaghan, 2005). We report here the structure of the title compound, (I). Similar to 5-*tert*-butyl-4-nitro-1*H*-pyrazol-3-ol, compound (I) originated from 3,5-di-*tert*-butylpyrazole. Compound (I) was prepared by reacting 3,5-di-*tert*-butylpyrazole with bromine in chloroform solution at room temperature. In these reactions, 3,5-di-*t*-butylpyrazole is attacked by either nitric acid (as in the case of 5-*tert*-butyl-4-nitro-1*H*-pyrazol-3-ol) or bromine to form the onium species, which then displaces one *tert*-butyl group. The subsequent vacant position is then filled by an OH group that, in the case of (I), tautomerizes to form the pyrazolone.



(I)

In the structure of (I) (Fig. 1), all strong hydrogen-bonding components are involved in the hydrogen-bonding network. The hydrogen-bonding geometry for this structure is listed in Table 1. The fourfold symmetry in (I) arises because of the unique hydrogen-bonded motif that is formed *via* contributions from eight pyrazole molecules and four water molecules. Each pyrazole molecule forms a centrosymmetric $R_2^2(8)$ graph set (Etter, 1990) dimer *via* N1—H···O5 interactions, at (x, y, z) and ($-x+\frac{3}{2}$, $-y+\frac{1}{2}$, $-z+\frac{1}{2}$), centred at ($\frac{3}{4}$, $\frac{1}{4}$, $\frac{1}{4}$). The N2/H group associates with O1*W*, at (x, y, z) and ($y+\frac{1}{4}$, $-x+\frac{5}{4}$, $z+\frac{1}{4}$). O1*W*, at (x, y, z), associates with two O5 atoms, one at (x, y, z) and the other at ($-y+\frac{5}{4}$, $x-\frac{3}{4}$, $-z+\frac{1}{4}$). Thus, each O5 atom is involved in a four-centre hydrogen-bonding association. For O5, at (x, y, z), the three non-H-atom contacts are O1*W* at (x, y, z), O1I at ($y+\frac{3}{4}$, $-x+\frac{5}{4}$, $-z+\frac{1}{4}$) and N1 at ($-x+\frac{3}{2}$, $-y+\frac{1}{2}$, $-z+\frac{1}{2}$) (Fig. 2). Three pyrazole molecules, at (x, y, z), ($-x+\frac{3}{2}$,

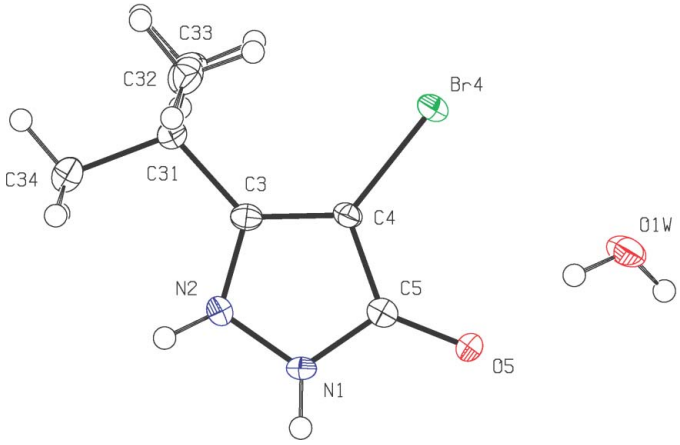


Figure 1
Molecular configuration and atom-numbering scheme for (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms are drawn as spheres of arbitrary radii.

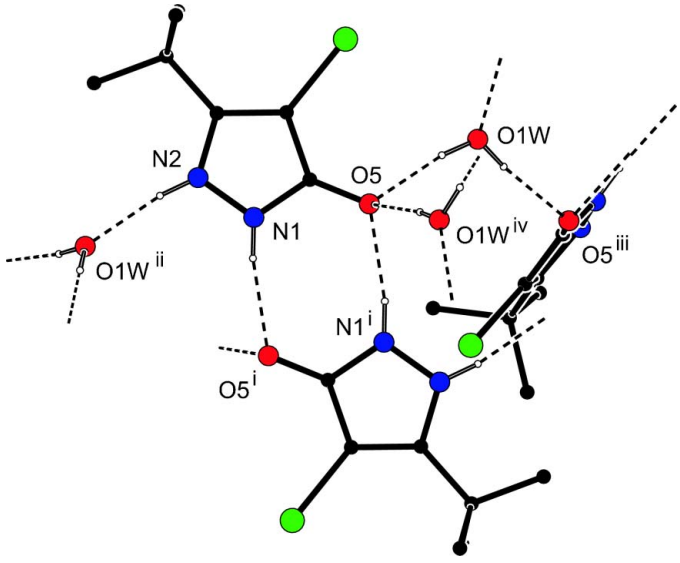


Figure 2
Hydrogen-bonding environment for (I), at (*x*, *y*, *z*), showing the centrosymmetric $R_2^2(8)$ N1—H···O5 dimer, the two hydrogen-bonding associations from O1*W*, and the four-centre hydrogen-bonding association involving O5. For clarity, H atoms not involved in the hydrogen-bonding interactions have been omitted. Hydrogen bonds are shown as dashed lines. [Symmetry codes: (i) $-x+\frac{3}{2}, -y+\frac{1}{2}, -z+\frac{1}{2}$; (ii) $y+\frac{1}{4}, -x+\frac{5}{4}, z+\frac{1}{4}$; (iii) $-y+\frac{5}{4}, x-\frac{3}{4}, -z+\frac{1}{4}$; (iv) $y+\frac{3}{4}, -x+\frac{5}{4}, -z+\frac{1}{4}$.]

$-y+\frac{1}{2}, -z+\frac{1}{2}$) and ($-y+\frac{5}{4}, x-\frac{3}{4}, -z+\frac{1}{4}$), and two water molecules, at (*x*, *y*, *z*) and ($-y+\frac{5}{4}, x-\frac{3}{4}, -z+\frac{1}{4}$), form a distorted hexagonal hydrogen-bonding motif [graph set $R_3^5(11)$], adjoining the N1—H···O5 dimer, fused *via* the same interaction (Fig. 3). The hexagonal motifs are also fused with each other *via* the O1*W*—H···O5 interaction at (*x*, *y*, *z*). The resulting arrangement also creates a distorted octagonal boat conformation hydrogen-bonding motif [graph set $R_6^4(14)$] involving four pyrazole groups, at (*x*, *y*, *z*), ($-x+\frac{3}{2}, -y+\frac{1}{2}, -z+\frac{1}{2}$), ($x-\frac{1}{2}, y, -z+\frac{1}{2}$) and ($1-x, -y+\frac{1}{2}, z$), and two water molecules, at ($y+\frac{1}{4}, -x+\frac{5}{4}, z+\frac{1}{4}$) and ($-y+\frac{3}{4}, x-\frac{3}{4}, z+\frac{1}{4}$)

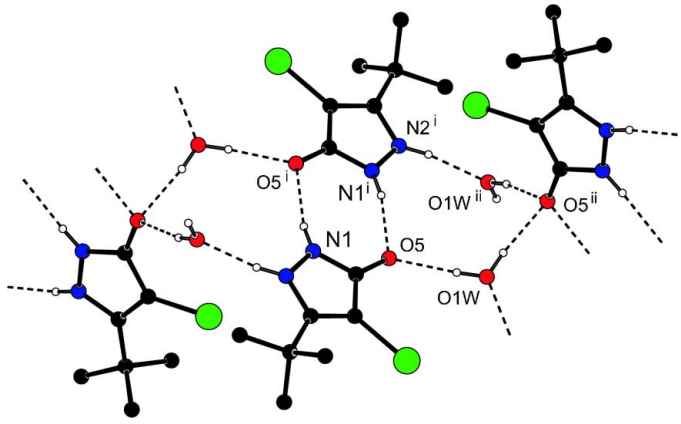


Figure 3
Part of the structure of (I), at (*x*, *y*, *z*), showing the distorted $R_3^5(11)$ hexagonal motif, and its position with respect to the N1—H···O5 dimer. For clarity, H atoms not involved in the hydrogen-bonding interactions have been omitted. Hydrogen bonds are shown as dashed lines. [Symmetry codes: (i) $-x+\frac{3}{2}, -y+\frac{1}{2}, -z+\frac{1}{2}$; (ii) $-y+\frac{5}{4}, x-\frac{3}{4}, z-\frac{1}{4}$.]

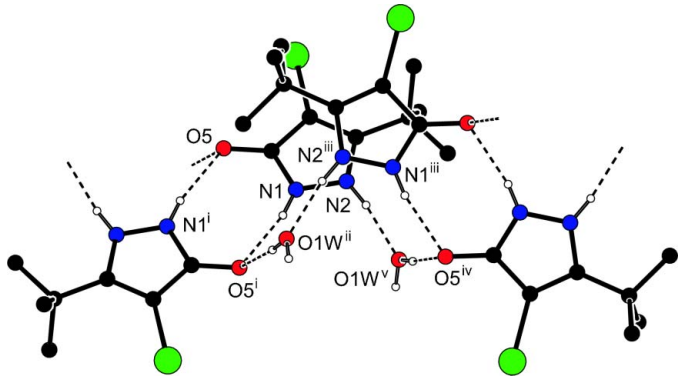


Figure 4
Part of the structure of (I), at (*x*, *y*, *z*), showing the distorted $R_6^4(14)$ octagonal boat motif and its position with respect to the N1—H···O5 dimer. For clarity, H atoms not involved in the hydrogen-bonding interactions have been omitted. Hydrogen bonds are shown as dashed lines. [Symmetry codes: (i) $-x+\frac{3}{2}, -y+\frac{1}{2}, -z+\frac{1}{2}$; (ii) $-y+\frac{3}{4}, x-\frac{3}{4}, z+\frac{1}{4}$; (iii) $1-x, -y+\frac{1}{2}, z$; (iv) $x-\frac{1}{2}, y, -z+\frac{1}{2}$; (v) $y+\frac{1}{4}, -x+\frac{5}{4}, z+\frac{1}{4}$.]

(Fig. 4). A stereoview of the unit cell contents of (I) is shown in Fig. 5. The Br atom does not contribute to the hydrogen-bonding network; atom Br4 is 3.469 (3) Å from O1*W*, and 3.412 (3) Å from N2($-y+\frac{5}{4}, x-\frac{1}{4}, z-\frac{1}{4}$).

Experimental

The title compound was obtained from Key Organics Ltd, and crystals were grown from an ethanol solution.

Crystal data

$C_7H_{11}BrN_2O\cdot H_2O$
$M_r = 237.10$
Tetragonal, $I4_1/a$
$a = 13.6840\ (4)$ Å
$c = 21.4734\ (8)$ Å
$V = 4020.9\ (2)$ Å^3
$Z = 16$
$D_x = 1.567$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2331 reflections
$\theta = 2.9$–$27.5°$
$\mu = 4.06$ mm^{-1}
$T = 150\ (2)$ K
Prism, colourless
0.36 × 0.27 × 0.20 mm

Data collection

Nonius KappaCCD diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.288, T_{max} = 0.444
12 489 measured reflections
1977 independent reflections

1633 reflections with $I > 2\sigma(I)$
R_{int} = 0.069
θ_{max} = 26.0°
$h = -16 \rightarrow 16$
$k = -15 \rightarrow 14$
$l = -19 \rightarrow 26$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.030
$wR(F^2)$ = 0.069
S = 1.02
1977 reflections
124 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0247P)^2 + 7.0406P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.30 e Å^{-3}
$\Delta\rho_{min}$ = −0.64 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O5^{i}	0.82 (3)	1.97 (3)	2.773 (3)	168 (3)
N2—H2···O1W^{ii}	0.85 (3)	1.80 (3)	2.646 (3)	171 (3)
O1W—H1W···O5	0.83 (2)	1.91 (2)	2.733 (3)	169 (3)
O1W—H2W···O5^{iii}	0.83 (2)	1.91 (2)	2.739 (3)	173 (3)

Symmetry codes: (i) $-x+\frac{3}{2}, -y+\frac{1}{2}, -z+\frac{1}{2}$; (ii) $y+\frac{1}{4}, -x+\frac{5}{4}, z+\frac{1}{4}$; (iii) $-y+\frac{5}{4}, x-\frac{3}{4}, -z+\frac{1}{4}$.

All *tert*-butyl H atoms were included in the refinement at calculated positions, in the riding-model approximation, with C—H distances of 0.98 Å. All NH H atoms involved in the hydrogen-bonding associations (Table 1) were located in Fourier syntheses and positional parameters were refined. The water H atoms were located and were refined with O—H distance restraints of 0.83 (2) Å and H···H restraints of 1.40 (2) Å. The isotropic displacement parameters for all H atoms were set equal to $1.25U_{eq}$ of the carrier atom.

Data collection: *COLLECT* (Hooft, 1998); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON97* (Spek, 1997); software used to prepare material for publication: *SHELXL97*.

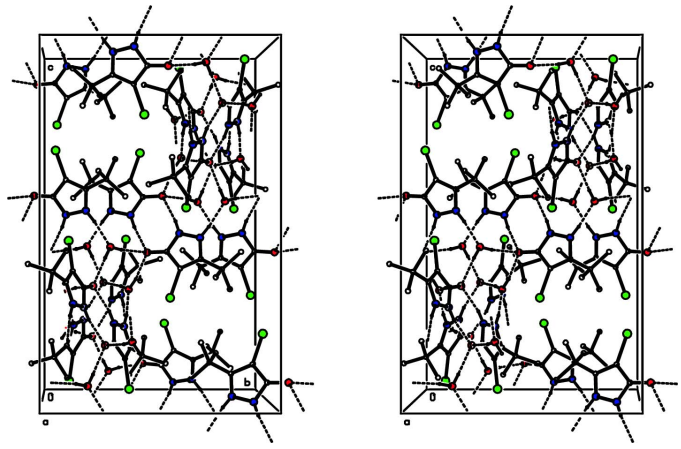


Figure 5
Stereoview of the unit cell contents of (I).

The authors thank the EPSRC National Crystallography Service (Southampton, England).

References

Etter, M. C. (1990). *Acc. Chem. Res.* **23**, 120–126.
Hooft, R. W. W. (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.
Lynch, D. E. & McClenaghan, I. (2005). *Acta Cryst.* E**61**, o2347–o2348.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Sheldrick, G. M. (2003). *SADABS*. Version 2.10. Bruker AXS Inc., Madison, Wisconsin, USA.
Spek, A. L. (1997). *PLATON9*. University of Utrecht, The Netherlands.

supporting information

Acta Cryst. (2005). E**61**, o2349–o2351 [https://doi.org/10.1107/S1600536805012791]

5-*tert*-Butyl-4-bromo-1,2-dihydro-1*H*-pyrazol-3(2*H*)-one monohydrate

Daniel E. Lynch and Ian McClenaghan

5-*tert*-Butyl-4-bromo-1,2-dihydro-1*H*-pyrazol-3(2*H*)-one monohydrate

Crystal data

$C_7H_{11}BrN_2O\cdot H_2O$
$M_r = 237.10$
Tetragonal, $I4_1/a$
Hall symbol: -I 4ad
$a = 13.6840\ (4)$ Å
$c = 21.4734\ (8)$ Å
$V = 4020.9\ (2)$ Å^3
$Z = 16$
$F(000) = 1920$
$D_x = 1.567$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 2331 reflections
$\theta = 2.9$–$27.5°$
$\mu = 4.06$ mm^{-1}
$T = 150$ K
Prism, colourless
0.36 × 0.27 × 0.20 mm

Data collection

Nonius KappaCCD? diffractometer
Radiation source: Bruker-Nonius FR591 rotating anode
10 cm confocal mirrors monochromator
Detector resolution: 9.091 pixels mm^{-1}
φ and ω scans
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)
$T_{min} = 0.288$, $T_{max} = 0.444$
12489 measured reflections
1977 independent reflections
1633 reflections with $I > 2\sigma(I)$
$R_{int} = 0.069$
$\theta_{max} = 26.0°$, $\theta_{min} = 3.5°$
$h = -16\rightarrow16$
$k = -15\rightarrow14$
$l = -19\rightarrow26$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.069$
$S = 1.02$
1977 reflections
124 parameters
3 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
$w = 1/[\sigma^2(F_o^2) + (0.0247P)^2 + 7.0406P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.30$ e Å^{-3}
$\Delta\rho_{min} = -0.64$ e Å^{-3}

Special details

Experimental. The minimum and maximum absorption values stated above are those calculated in *SHELXL97* from the given crystal dimensions. The ratio of minimum to maximum apparent transmission was determined experimentally as 0.630689.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Br4	0.688965 (19)	0.380502 (19)	0.044971 (12)	0.02124 (11)
O5	0.78480 (12)	0.27537 (13)	0.16996 (8)	0.0182 (4)
N1	0.64408 (16)	0.31605 (16)	0.22405 (10)	0.0166 (5)
H1	0.660 (2)	0.295 (2)	0.2582 (14)	0.021*
N2	0.55701 (16)	0.36121 (16)	0.21224 (10)	0.0170 (5)
H2	0.520 (2)	0.374 (2)	0.2427 (14)	0.021*
C3	0.55559 (18)	0.39126 (18)	0.15299 (12)	0.0157 (5)
C31	0.46896 (19)	0.44595 (19)	0.12557 (12)	0.0181 (6)
C32	0.5036 (2)	0.5478 (2)	0.10536 (15)	0.0265 (7)
H31	0.5258	0.5844	0.1419	0.033*
H32	0.4495	0.5829	0.0855	0.033*
H33	0.5577	0.5413	0.0757	0.033*
C33	0.4290 (2)	0.3888 (2)	0.06939 (13)	0.0262 (6)
H34	0.4803	0.3823	0.0378	0.033*
H35	0.3732	0.4239	0.0516	0.033*
H36	0.4080	0.3237	0.0829	0.033*
C34	0.3868 (2)	0.4572 (2)	0.17367 (14)	0.0267 (7)
H37	0.3655	0.3925	0.1877	0.033*
H38	0.3316	0.4917	0.1547	0.033*
H39	0.4109	0.4947	0.2094	0.033*
C4	0.64375 (18)	0.36354 (18)	0.12658 (11)	0.0151 (5)
C5	0.70015 (19)	0.31513 (18)	0.17256 (12)	0.0153 (5)
O1W	0.86437 (18)	0.19982 (16)	0.06359 (9)	0.0364 (6)
H1W	0.833 (2)	0.223 (2)	0.0934 (9)	0.045*
H2W	0.898 (2)	0.1507 (16)	0.0717 (13)	0.045*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br4	0.02379 (17)	0.02565 (17)	0.01427 (16)	0.00435 (11)	0.00409 (11)	0.00462 (11)
O5	0.0139 (9)	0.0236 (10)	0.0169 (10)	0.0034 (7)	−0.0003 (7)	0.0021 (8)
N1	0.0178 (12)	0.0201 (12)	0.0120 (11)	0.0017 (9)	−0.0013 (9)	0.0039 (9)
N2	0.0168 (12)	0.0194 (12)	0.0146 (12)	0.0018 (9)	0.0028 (9)	−0.0005 (9)
C3	0.0191 (14)	0.0131 (13)	0.0150 (13)	−0.0019 (10)	−0.0010 (10)	0.0017 (10)
C31	0.0180 (14)	0.0184 (13)	0.0180 (14)	0.0025 (10)	0.0006 (11)	0.0024 (11)
C32	0.0234 (15)	0.0232 (15)	0.0330 (17)	0.0022 (12)	0.0005 (13)	0.0043 (13)
C33	0.0251 (15)	0.0294 (16)	0.0241 (16)	0.0032 (13)	−0.0074 (13)	−0.0003 (13)
C34	0.0207 (15)	0.0312 (16)	0.0283 (17)	0.0069 (12)	0.0014 (13)	0.0048 (13)
C4	0.0181 (13)	0.0153 (13)	0.0117 (13)	0.0000 (10)	0.0013 (10)	0.0019 (10)
C5	0.0185 (14)	0.0120 (13)	0.0154 (14)	−0.0031 (10)	0.0000 (11)	−0.0012 (10)
O1W	0.0584 (16)	0.0321 (13)	0.0186 (11)	0.0256 (11)	0.0121 (10)	0.0073 (9)

Geometric parameters (Å, º)

Br4—C4	1.873 (2)	C32—H31	0.98
O5—C5	1.281 (3)	C32—H32	0.98
N1—C5	1.346 (3)	C32—H33	0.98
N1—N2	1.366 (3)	C33—H34	0.98
N1—H1	0.82 (3)	C33—H35	0.98
N2—C3	1.337 (3)	C33—H36	0.98
N2—H2	0.85 (3)	C34—H37	0.98
C3—C4	1.386 (4)	C34—H38	0.98
C3—C31	1.521 (4)	C34—H39	0.98
C31—C34	1.534 (4)	C4—C5	1.417 (4)
C31—C32	1.535 (4)	O1W—H1W	0.83 (2)
C31—C33	1.538 (4)	O1W—H2W	0.83 (2)
C5—N1—N2	110.4 (2)	H32—C32—H33	109.5
C5—N1—H1	125 (2)	C31—C33—H34	109.5
N2—N1—H1	124 (2)	C31—C33—H35	109.5
C3—N2—N1	109.2 (2)	H34—C33—H35	109.5
C3—N2—H2	131 (2)	C31—C33—H36	109.5
N1—N2—H2	119 (2)	H34—C33—H36	109.5
N2—C3—C4	107.0 (2)	H35—C33—H36	109.5
N2—C3—C31	122.1 (2)	C31—C34—H37	109.5
C4—C3—C31	130.9 (2)	C31—C34—H38	109.5
C3—C31—C34	111.1 (2)	H37—C34—H38	109.5
C3—C31—C32	108.4 (2)	C31—C34—H39	109.5
C34—C31—C32	109.0 (2)	H37—C34—H39	109.5
C3—C31—C33	109.3 (2)	H38—C34—H39	109.5
C34—C31—C33	108.6 (2)	C3—C4—C5	108.5 (2)
C32—C31—C33	110.5 (2)	C3—C4—Br4	129.53 (19)
C31—C32—H31	109.5	C5—C4—Br4	121.99 (19)
C31—C32—H32	109.5	O5—C5—N1	123.7 (2)
H31—C32—H32	109.5	O5—C5—C4	131.3 (2)
C31—C32—H33	109.5	N1—C5—C4	104.9 (2)
H31—C32—H33	109.5	H1W—O1W—H2W	116 (3)
C5—N1—N2—C3	−0.6 (3)	C31—C3—C4—C5	179.2 (3)
N1—N2—C3—C4	0.5 (3)	N2—C3—C4—Br4	178.78 (19)
N1—N2—C3—C31	−178.9 (2)	C31—C3—C4—Br4	−1.8 (4)
N2—C3—C31—C34	−1.8 (4)	N2—N1—C5—O5	−178.3 (2)
C4—C3—C31—C34	178.8 (3)	N2—N1—C5—C4	0.4 (3)
N2—C3—C31—C32	117.9 (3)	C3—C4—C5—O5	178.5 (3)
C4—C3—C31—C32	−61.5 (4)	Br4—C4—C5—O5	−0.6 (4)
N2—C3—C31—C33	−121.6 (3)	C3—C4—C5—N1	−0.1 (3)
C4—C3—C31—C33	59.0 (4)	Br4—C4—C5—N1	−179.23 (17)
N2—C3—C4—C5	−0.3 (3)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O5^{i}	0.82 (3)	1.97 (3)	2.773 (3)	168 (3)
N2—H2···O1*W*^{ii}	0.85 (3)	1.80 (3)	2.646 (3)	171 (3)
O1*W*—H1*W*···O5	0.83 (2)	1.91 (2)	2.733 (3)	169 (3)
O1*W*—H2*W*···O5^{iii}	0.83 (2)	1.91 (2)	2.739 (3)	173 (3)

Symmetry codes: (i) −*x*+3/2, −*y*+1/2, −*z*+1/2; (ii) *y*+1/4, −*x*+5/4, *z*+1/4; (iii) −*y*+5/4, *x*−3/4, −*z*+1/4.