

# Crystal structure and Hirshfeld surface analysis of 3,6-bis(pyrimidin-2-yl)-1,4-dihydro-1,2,4,5-tetrazine dihydrate

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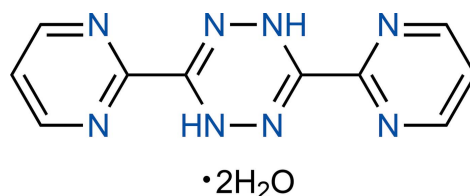
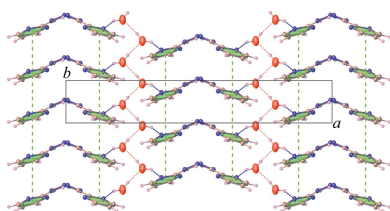
**Keywords:** crystal structure; hydrogen bonds; Hirshfeld surface; pyrimidine.**CCDC reference:** 1986751**Supporting information:** this article has supporting information at journals.iucr.org/e

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In the title compound, C<sub>10</sub>H<sub>8</sub>N<sub>8</sub>·2H<sub>2</sub>O or H<sub>2</sub>bmtz·2H<sub>2</sub>O [bmtz = 3,6-bis(2'-pyrimidyl)-1,2,4,5-tetrazine], the asymmetric unit consists of one-half molecule of H<sub>2</sub>bmtz and one water molecule, the whole H<sub>2</sub>bmtz molecule being generated by a crystallographic twofold rotation axis passing through the middle point of the 1,4-dihydro-1,2,4,5-tetrazine moiety. In the crystal, N—H···O, N—H···N, O—H···O hydrogen bonds and aromatic  $\pi$ – $\pi$  stacking interactions link the components into a three-dimensional supramolecular network. Hirshfeld surface analysis was used to further investigate the intermolecular interactions in the crystal structure.

## 1. Chemical context

The chemistry of nitrogen-containing heterocyclic compounds has attracted the attention of the scientific community for over a century. Many compounds of this class are bioactive (Jubeen *et al.*, 2018) and show promising pharmacological properties (Alcaide *et al.*, 2016; Varano *et al.*, 2016). Among these, numerous pyrimidine derivatives have been studied extensively in the context of synthetic organic chemistry and coordination chemistry (Kaim, 2002). For instance, the tetrazine-based ligand 3,6-bis(2'-pyrimidyl)-1,2,4,5-tetrazine (bmtz) has been used as a polydentate ligand for the formation of silver(I) coordination polymers (Chainok *et al.*, 2012) and for the self-assembly of the highly stable Fe<sup>II</sup> pentagonal metal-lacycles (Giles *et al.*, 2011). Herein, the crystal and molecular structures of the dihydrotetrazine-based compound 3,6-bis(pyrimidin-2-yl)-1,4-dihydro-1,2,4,5-tetrazine dihydrate, C<sub>10</sub>H<sub>8</sub>N<sub>8</sub>·2H<sub>2</sub>O or H<sub>2</sub>bmtz·2H<sub>2</sub>O (**I**), is described along with an analysis of its Hirshfeld surface.



## 2. Structural commentary

The molecular structure of (**I**) is shown in Fig. 1. The asymmetric unit consists of one-half molecule of H<sub>2</sub>bmtz and one water molecule, in which the whole molecule of the H<sub>2</sub>bmtz is

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

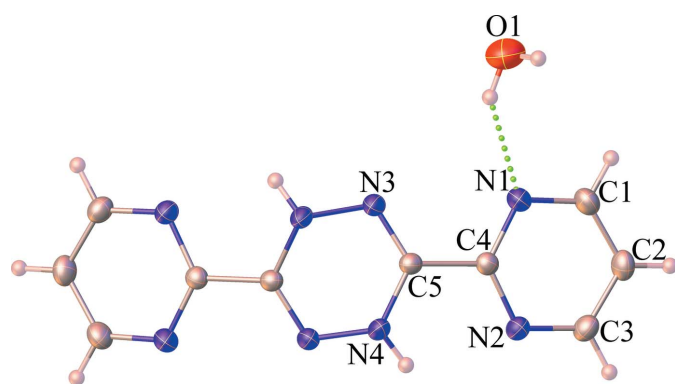
| $D-H\cdots A$          | $D-H$    | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|------------------------|----------|-------------|-------------|---------------|
| $O1-H1A\cdots O1^i$    | 0.88 (1) | 1.81 (1)    | 2.642 (4)   | 156 (2)       |
| $O1-H1B\cdots N1$      | 0.86 (1) | 2.15 (4)    | 2.863 (3)   | 140 (5)       |
| $N4-H4\cdots N2^{ii}$  | 0.85 (1) | 2.57 (1)    | 3.221 (1)   | 133 (2)       |
| $C2-H2\cdots O1^{iii}$ | 0.93     | 2.43        | 3.278 (3)   | 151           |

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

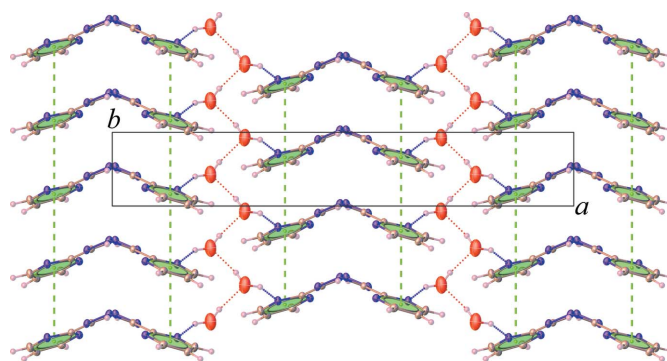
generated by a crystallographic twofold rotation axis passing through the middle point of the 1,4-dihydro-1,2,4,5-tetrazine moiety. The  $H_2bmtz$  molecule is therefore not planar (r.m.s. deviation from planarity = 0.598 Å) with a  $C4-C5-N3-N4^i$  torsion angle of 178.46 (14)° [symmetry code: (i)  $-x, y, \frac{3}{2} - z$ ]. The pyrimidine rings are twisted with respect to each other, making a dihedral angle of 43.67 (9)°. The 1,4-dihydro-1,2,4,5-tetrazine moiety adopts a twist-boat conformation with a  $C5-N3-N4^i-C5^i$  torsion angle of  $-41.17$  (17)°. The  $N3-N4^i$  and  $C5-N4$  bond lengths of 1.423 (2) and 1.395 (2) Å, confirm their single-bond character, while the  $C3-N5$  bond length of 1.278 (2) Å, is consistent with a double bond (compare QORNAM, Glöckle *et al.*, 2001; ZASTAQ, Chainok *et al.*, 2012). The C–C and C–N bond lengths in the pyrimidine ring are characteristic for a delocalized double bond and a typical single bond (QORNAM, Glöckle *et al.*, 2001).

### 3. Supramolecular features

In the crystal, the  $H_2bmtz$  molecules are stacked along [010] into columns through  $\pi$ – $\pi$  interactions between the pyrimidine rings [centroid-to-centroid distance = 3.726 (2) Å]. At the same time, the water molecules are connected by  $O-H\cdots O$  hydrogen bonds (Table 1), resulting in the formation of a zigzag chain. These motifs are then connected together through  $N-H\cdots O$  hydrogen bonds involving the tetrazine nitrogen atoms and the water molecules to form a sheet structure propagating in the  $ab$  plane, as shown in Fig. 2. The sheets are further linked into an overall three-dimensional



**Figure 1**  
 Molecular structure of (I) with displacement ellipsoids drawn at the 50% probability level. Unlabelled atoms are generated by the symmetry operation  $-x, y, 3/2 - z$ .

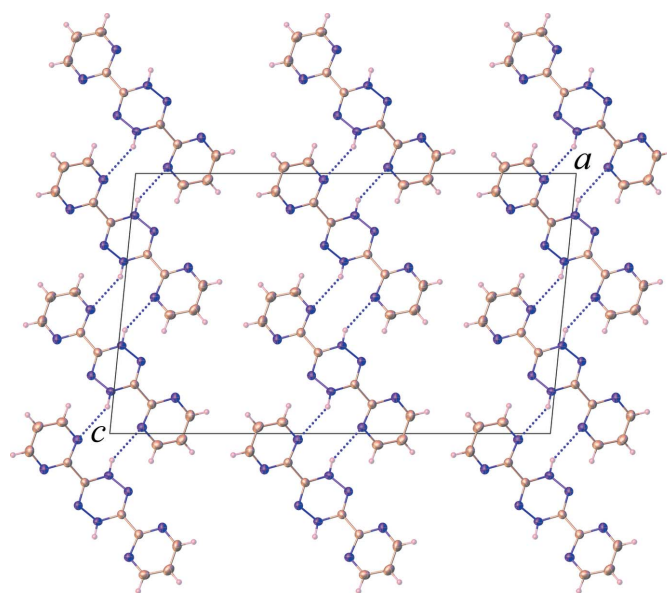


**Figure 2**  
 Partial packing diagram of (I), showing the  $O-H\cdots O$  and  $O-H\cdots N$  hydrogen bonds (dashed lines) and  $\pi$ – $\pi$  stacking interactions propagating in the  $ab$  plane.

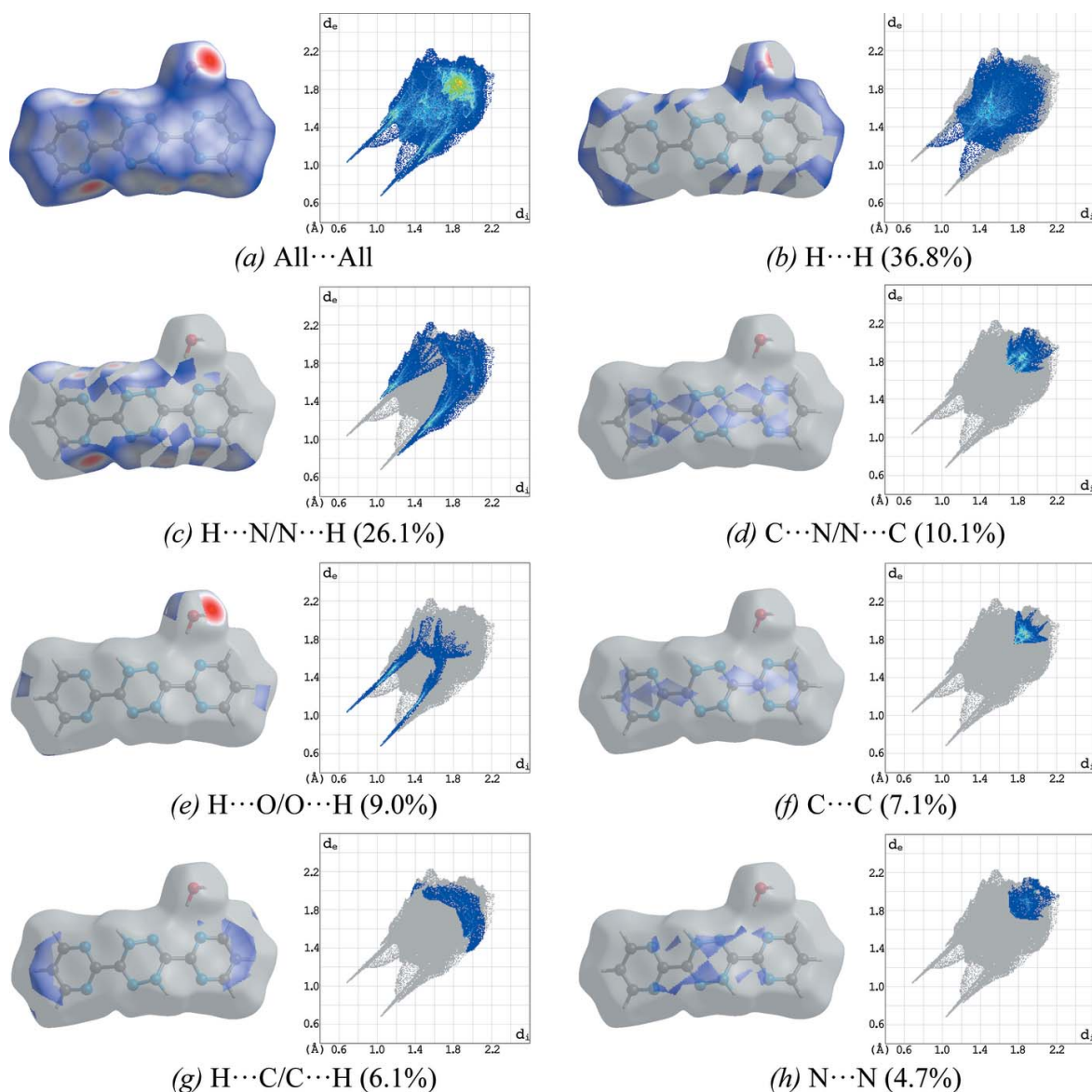
supramolecular network through  $N-H\cdots N$  hydrogen bonds with an  $R_2^2(10)$  ring motif, Fig. 3, which involve the dihydro nitrogen atoms and the pyrimidine nitrogen atoms. A weak  $C-H\cdots O$  interaction is also noted (Table 1).

### 4. Hirshfeld surface analysis

To further quantify the nature of the intermolecular interactions present in the crystal structure, Hirshfeld surfaces (McKinnon *et al.*, 2007) and their associated two-dimensional fingerprint plots (Spackman & McKinnon, 2002) were generated using *CrystalExplorer17* (Turner *et al.*, 2017). The shorter and longer contacts are indicated as red and blue spots, respectively, on the Hirshfeld surfaces, and contacts with distances approximately equal to the sum of the van der Waals radii are represented as white spots. The contribution of interatomic contacts to the  $d_{norm}$  surface of the title compound



**Figure 3**  
 Partial packing diagram of (I) viewed along the  $b$  axis, showing the  $N-H\cdots N$  hydrogen bonds (dashed lines).


**Figure 4**

Two-dimensional fingerprint plots of the title compound (**I**), showing (a) all interactions, and those delineated into (b)  $\text{H}\cdots\text{H}$ , (c)  $\text{H}\cdots\text{N}/\text{N}\cdots\text{H}$ , (d)  $\text{C}\cdots\text{N}/\text{N}\cdots\text{C}$ , (e)  $\text{H}\cdots\text{O}/\text{O}\cdots\text{H}$ , (f)  $\text{C}\cdots\text{C}$ , (g)  $\text{H}\cdots\text{C}/\text{C}\cdots\text{H}$ , and (h)  $\text{N}\cdots\text{N}$  contacts [ $d_e$  and  $d_i$  represent the distances from a point on the Hirshfeld surface to the nearest atoms outside (external) and inside (internal) the surface, respectively].

is shown in Fig. 4. Analysis of the two-dimensional fingerprint plots, Fig. 4, reveals that  $\text{H}\cdots\text{H}$  (36.8%) contacts are the major contributors toward the Hirshfeld surface, whereas  $\text{H}\cdots\text{N}/\text{N}\cdots\text{H}$  (26.1%) contacts (*i.e.*  $\text{N}-\text{H}\cdots\text{N}$ ) make a less significant contribution. The contribution of the  $\text{H}\cdots\text{O}/\text{O}\cdots\text{H}$  (9.0%) contacts (*i.e.*  $\text{C}-\text{H}\cdots\text{O}$  and  $\text{O}-\text{H}\cdots\text{O}$ ) and other contacts such as  $\text{C}\cdots\text{C}$  (7.1%) (*i.e.*  $\pi-\pi$  stacking),  $\text{H}\cdots\text{C}/\text{C}\cdots\text{H}$  (6.1%) and  $\text{N}\cdots\text{N}$  (4.7%) make a small contribution to the entire Hirshfeld surface.

## 5. Database survey

A search of the Cambridge Crystallographic Database (CSD version 5.41, November 2019 update; Groom *et al.*, 2016) using *ConQuest* gave 4261 hits, reflecting the large number of pyrimidine-containing heterocyclic compounds that have been

characterized. However, searches for compounds related to  $\text{H}_2\text{bmtz}$  yielded just two hits for  $\mu_2$ -1,4-dihydro-3,6-bis[(2'-pyrimidyl)-1,2,4,5-tetrazine]bis[bis(triphenylphosphine)copper(I)] bis(tetrafluoroborate) dichloromethane solvate (QORNAM, Glöckle *et al.*, 2001) and *catena*-[[ $\mu_2$ -3,6-di(pyrimidin-2-yl)-1,4-dihydro-1,2,4,5-tetrazine][ $\mu_2$ -(dicyanoethenylidene)amido][[dicyanoethenylidene)amido]acetonitriledi-silver(I)] (ZASTAQ, Chainok *et al.*, 2012).

## 6. Synthesis and crystallization

All commercially available chemicals and solvents were of reagent grade and were used as received without further purification.  $\text{H}_2\text{bmtz}$  was synthesized according to a literature method (Kaim & Fees, 1995). Single crystals for X-ray struc-

ture analysis were obtained by recrystallization from mixed solvents of CH<sub>2</sub>Cl<sub>2</sub>/H<sub>2</sub>O (1:1, v/v).

### 7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All H atoms were located in difference-Fourier maps: the carbon-bound H atoms were relocated to idealized positions and refined as riding atoms with C–H = 0.93 Å and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ . The 1,4-dihydro-1,2,4,5-tetrazine and water H atoms were located in difference-Fourier maps and were constrained to N–H = 0.86 ± 0.01 Å with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$  and O–H = 0.84 ± 0.01 Å with  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$ , respectively.

### Acknowledgements

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**Table 2**  
Experimental details.

|  |  |
|--|--|
| Crystal data   |  |
| Chemical formula   | C <sub>10</sub> H <sub>8</sub> N <sub>8</sub> ·2H <sub>2</sub> O             |
| <i>M<sub>r</sub></i>   | 276.28   |
| Crystal system, space group  | Monoclinic, C2/c   |
| Temperature (K)  | 296  |
| <i>a</i> , <i>b</i> , <i>c</i> (Å)   | 23.4730 (12), 3.7262 (2),<br>13.9102 (7)                                     |
| β (°)  | 95.687 (2)   |
| <i>V</i> (Å <sup>3</sup> )   | 1210.67 (11)   |
| <i>Z</i>   | 4  |
| Radiation type   | Mo Kα  |
| μ (mm <sup>-1</sup> )  | 0.11   |
| Crystal size (mm)  | 0.32 × 0.2 × 0.2   |
| Data collection  |  |
| Diffractometer   | Bruker D8 QUEST CMOS<br>PHOTON II  |
| Absorption correction  | Multi-scan (SADABS; Bruker,<br>2016)   |
| <i>T<sub>min</sub></i> , <i>T<sub>max</sub></i>  | 0.714, 0.746   |
| No. of measured, independent and<br>observed [ <i>I</i> > 2σ( <i>I</i> )] reflections                          | 11339, 1487, 1145  |
| <i>R<sub>int</sub></i>   | 0.030  |
| (sin θ/λ) <sub>max</sub> (Å <sup>-1</sup> )  | 0.667  |
| Refinement   |  |
| <i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i> | 0.053, 0.174, 1.05   |
| No. of reflections   | 1487   |
| No. of parameters  | 103  |
| No. of restraints  | 4  |
| H-atom treatment   | H atoms treated by a mixture of<br>independent and constrained<br>refinement |
| Δρ <sub>max</sub> , Δρ <sub>min</sub> (e Å <sup>-3</sup> )   | 0.26, -0.39  |

Computer programs: *APEX3* and *SAINTE* (Bruker, 2016), *SHELXT* (Sheldrick, 2015a), *SHELXL2018* (Sheldrick, 2015b) and *OLEX2* (Dolomanov *et al.*, 2009).

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## supporting information

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## Crystal structure and Hirshfeld surface analysis of 3,6-bis(pyrimidin-2-yl)-1,4-dihydro-1,2,4,5-tetrazine dihydrate

**Kenika Khotchasanthong, Siripak Jittirattanakun and Kittipong Chainok**

### Computing details

Data collection: *APEX3* (Bruker, 2016); cell refinement: *SAINTE* (Bruker, 2016); data reduction: *SAINTE* (Bruker, 2016); program(s) used to solve structure: *SHELXT* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2018* (Sheldrick, 2015b); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009).

### 3,6-Bis(pyrimidin-2-yl)-1,4-dihydro-1,2,4,5-tetrazine dihydrate

#### Crystal data

$C_{10}H_8N_8 \cdot 2H_2O$

$M_r = 276.28$

Monoclinic, *C2/c*

$a = 23.4730$  (12) Å

$b = 3.7262$  (2) Å

$c = 13.9102$  (7) Å

$\beta = 95.687$  (2)°

$V = 1210.67$  (11) Å<sup>3</sup>

$Z = 4$

$F(000) = 576$

$D_x = 1.516$  Mg m<sup>-3</sup>

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

Cell parameters from 4681 reflections

$\theta = 3.3$ – $28.1$ °

$\mu = 0.11$  mm<sup>-1</sup>

$T = 296$  K

Block, orange

$0.32 \times 0.2 \times 0.2$  mm

#### Data collection

Bruker D8 QUEST CMOS PHOTON II diffractometer

Radiation source: sealed x-ray tube

Graphite monochromator

Detector resolution: 7.39 pixels mm<sup>-1</sup>

$\varphi$  and  $\omega$  scans

Absorption correction: multi-scan (SADABS; Bruker, 2016)

$T_{\min} = 0.714$ ,  $T_{\max} = 0.746$

11339 measured reflections

1487 independent reflections

1145 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.030$

$\theta_{\max} = 28.3$ °,  $\theta_{\min} = 2.9$ °

$h = -30 \rightarrow 29$

$k = -4 \rightarrow 4$

$l = -18 \rightarrow 18$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.053$

$wR(F^2) = 0.174$

$S = 1.05$

1487 reflections

103 parameters

4 restraints

Primary atom site location: dual

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.1061P)^2 + 0.7279P]$

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

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.26$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.39$  e Å<sup>-3</sup>

*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 ( $\text{\AA}^2$ )*

|     | <i>x</i>     | <i>y</i>    | <i>z</i>     | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|--------------|-------------|--------------|----------------------------------|
| O1  | 0.21290 (11) | 0.4286 (11) | 0.71824 (16) | 0.1166 (10)                      |
| H1A | 0.2318 (9)   | 0.594 (5)   | 0.7537 (16)  | 0.060 (8)*                       |
| H1B | 0.1796 (10)  | 0.400 (13)  | 0.738 (3)    | 0.19 (2)*                        |
| N1  | 0.14093 (6)  | 0.2128 (5)  | 0.86243 (11) | 0.0426 (4)                       |
| N2  | 0.07173 (6)  | 0.2495 (4)  | 0.97609 (10) | 0.0386 (4)                       |
| N3  | 0.05508 (6)  | 0.4046 (4)  | 0.72282 (9)  | 0.0372 (4)                       |
| N4  | −0.00726 (6) | 0.5326 (4)  | 0.83844 (9)  | 0.0381 (4)                       |
| H4  | −0.0111 (9)  | 0.481 (6)   | 0.8970 (8)   | 0.052 (6)*                       |
| C1  | 0.17826 (8)  | 0.0798 (6)  | 0.93187 (14) | 0.0488 (5)                       |
| H1  | 0.215005     | 0.024291    | 0.916985     | 0.059*                           |
| C2  | 0.16473 (8)  | 0.0213 (5)  | 1.02458 (14) | 0.0468 (5)                       |
| H2  | 0.190969     | −0.077223   | 1.071768     | 0.056*                           |
| C3  | 0.11048 (8)  | 0.1160 (5)  | 1.04382 (13) | 0.0441 (5)                       |
| H3  | 0.100261     | 0.086189    | 1.106236     | 0.053*                           |
| C4  | 0.08877 (6)  | 0.2840 (4)  | 0.88786 (11) | 0.0327 (4)                       |
| C5  | 0.04524 (7)  | 0.4139 (4)  | 0.81150 (11) | 0.0323 (4)                       |

*Atomic displacement parameters ( $\text{\AA}^2$ )*

|    | $U^{11}$    | $U^{22}$    | $U^{33}$    | $U^{12}$     | $U^{13}$    | $U^{23}$     |
|----|-------------|-------------|-------------|--------------|-------------|--------------|
| O1 | 0.0846 (16) | 0.196 (3)   | 0.0734 (14) | −0.0089 (18) | 0.0266 (13) | −0.0020 (18) |
| N1 | 0.0327 (8)  | 0.0553 (9)  | 0.0399 (8)  | 0.0017 (6)   | 0.0047 (6)  | −0.0006 (7)  |
| N2 | 0.0387 (8)  | 0.0453 (8)  | 0.0319 (7)  | 0.0027 (6)   | 0.0038 (6)  | 0.0021 (6)   |
| N3 | 0.0305 (7)  | 0.0496 (9)  | 0.0316 (7)  | −0.0050 (6)  | 0.0040 (5)  | −0.0019 (6)  |
| N4 | 0.0353 (7)  | 0.0527 (9)  | 0.0263 (7)  | 0.0066 (6)   | 0.0039 (5)  | −0.0024 (6)  |
| C1 | 0.0348 (9)  | 0.0596 (12) | 0.0516 (11) | 0.0081 (8)   | 0.0020 (8)  | −0.0018 (9)  |
| C2 | 0.0453 (10) | 0.0468 (10) | 0.0460 (10) | 0.0080 (8)   | −0.0072 (8) | 0.0021 (8)   |
| C3 | 0.0503 (11) | 0.0476 (10) | 0.0342 (8)  | 0.0041 (8)   | 0.0034 (7)  | 0.0033 (7)   |
| C4 | 0.0316 (8)  | 0.0331 (8)  | 0.0334 (8)  | −0.0012 (6)  | 0.0029 (6)  | −0.0029 (6)  |
| C5 | 0.0313 (8)  | 0.0347 (8)  | 0.0312 (8)  | −0.0022 (6)  | 0.0054 (6)  | −0.0014 (6)  |

*Geometric parameters ( $\text{\AA}$ ,  $^\circ$ )*

|        |            |       |           |
|--------|------------|-------|-----------|
| O1—H1A | 0.882 (10) | N4—H4 | 0.851 (9) |
| O1—H1B | 0.860 (10) | N4—C5 | 1.395 (2) |
| N1—C1  | 1.334 (2)  | C1—H1 | 0.9300    |
| N1—C4  | 1.334 (2)  | C1—C2 | 1.376 (3) |
| N2—C3  | 1.339 (2)  | C2—H2 | 0.9300    |
| N2—C4  | 1.334 (2)  | C2—C3 | 1.373 (3) |

|                           |              |                           |              |
|---------------------------|--------------|---------------------------|--------------|
| N3—N4 <sup>i</sup>        | 1.423 (2)    | C3—H3                     | 0.9300       |
| N3—C5                     | 1.278 (2)    | C4—C5                     | 1.480 (2)    |
| H1A—O1—H1B                | 109 (2)      | C3—C2—C1                  | 116.54 (16)  |
| C1—N1—C4                  | 115.86 (15)  | C3—C2—H2                  | 121.7        |
| C4—N2—C3                  | 116.00 (15)  | N2—C3—C2                  | 122.46 (16)  |
| C5—N3—N4 <sup>i</sup>     | 111.21 (13)  | N2—C3—H3                  | 118.8        |
| N3 <sup>i</sup> —N4—H4    | 110.2 (15)   | C2—C3—H3                  | 118.8        |
| C5—N4—N3 <sup>i</sup>     | 113.47 (13)  | N1—C4—C5                  | 117.46 (14)  |
| C5—N4—H4                  | 111.5 (15)   | N2—C4—N1                  | 126.25 (15)  |
| N1—C1—H1                  | 118.6        | N2—C4—C5                  | 116.30 (14)  |
| N1—C1—C2                  | 122.79 (17)  | N3—C5—N4                  | 121.13 (14)  |
| C2—C1—H1                  | 118.6        | N3—C5—C4                  | 120.39 (14)  |
| C1—C2—H2                  | 121.7        | N4—C5—C4                  | 118.44 (13)  |
| N1—C1—C2—C3               | -1.6 (3)     | N4 <sup>i</sup> —N3—C5—C4 | 178.46 (14)  |
| N1—C4—C5—N3               | 10.4 (3)     | C1—N1—C4—N2               | 3.1 (3)      |
| N1—C4—C5—N4               | -172.09 (16) | C1—N1—C4—C5               | -176.87 (15) |
| N2—C4—C5—N3               | -169.62 (15) | C1—C2—C3—N2               | 1.8 (3)      |
| N2—C4—C5—N4               | 7.9 (2)      | C3—N2—C4—N1               | -3.0 (3)     |
| N3 <sup>i</sup> —N4—C5—N3 | 41.7 (2)     | C3—N2—C4—C5               | 176.97 (15)  |
| N3 <sup>i</sup> —N4—C5—C4 | -135.76 (15) | C4—N1—C1—C2               | -0.6 (3)     |
| N4 <sup>i</sup> —N3—C5—N4 | 1.0 (2)      | C4—N2—C3—C2               | 0.4 (3)      |

Symmetry code: (i)  $-x, y, -z+3/2$ .

*Hydrogen-bond geometry (Å, °)*

| <i>D</i> —H $\cdots$ <i>A</i>    | <i>D</i> —H | H $\cdots$ <i>A</i> | <i>D</i> $\cdots$ <i>A</i> | <i>D</i> —H $\cdots$ <i>A</i> |
|----------------------------------|-------------|---------------------|----------------------------|-------------------------------|
| O1—H1A $\cdots$ O1 <sup>ii</sup> | 0.88 (1)    | 1.81 (1)            | 2.642 (4)                  | 156 (2)                       |
| O1—H1B $\cdots$ N1               | 0.86 (1)    | 2.15 (4)            | 2.863 (3)                  | 140 (5)                       |
| N4—H4 $\cdots$ N2 <sup>iii</sup> | 0.85 (1)    | 2.57 (1)            | 3.221 (1)                  | 133 (2)                       |
| C2—H2 $\cdots$ O1 <sup>iv</sup>  | 0.93        | 2.43                | 3.278 (3)                  | 151                           |

Symmetry codes: (ii)  $-x+1/2, y+1/2, -z+3/2$ ; (iii)  $-x, -y+1, -z+2$ ; (iv)  $x, -y, z+1/2$ .