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# Crystal structure, Hirshfeld surface analysis and geometry optimization of 2-hydroxyimino-*N*-[1-(pyrazin-2-yl)ethylidene]propanohydrazide

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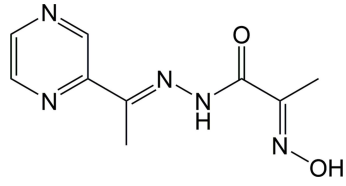
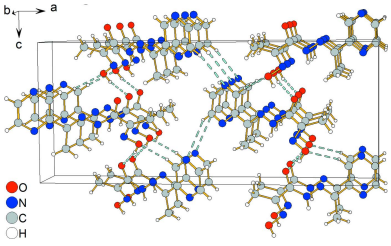
In the molecule of the title compound, $C_9H_{11}N_5O_2$, the oxime and hydrazide groups are situated in a *cis*-position in relation to the C—C bond linking the two functional groups. The $CH_3C(=NOH)C(O)NH$ fragment deviates from planarity because of a twist between the oxime and amide groups. In the crystal, molecules are linked by O—H···O hydrogen bonds, forming zigzag chains in the [013] and [0$\bar{1}$3] directions.

## 1. Chemical context

The combination in one molecule of two donor sets of a different nature, such as oxime and hydrazide, might be the key to creating new asymmetric polynucleative ligands suitable for the formation of polynuclear complexes. In recent decades, a number of ligands based on 2-hydroxyimino-propanehydrazide have been obtained. It was shown that such a type of ligand reveals a strong tendency for the formation of polynuclear complexes (Anwar *et al.*, 2011, 2012; Fritsky *et al.*, 2006; Jin *et al.*, 2022).






The title compound, 2-hydroxyimino-*N*-[1-(pyrazin-2-yl)ethylidene]propanohydrazide (**1**), was first described in the work of Feng and co-workers (Feng *et al.*, 2018). It acts as a ligand in three new polynuclear heterometal porous coordination polymers, which have displayed high $CO_2$ adsorption uptake and high adsorption selectivity of $CO_2$ over $N_2$ and $CH_4$. The present work is devoted to the synthesis, crystal structure, spectroscopic characterization, Hirshfeld surface analysis and quantum mechanical geometry optimization of **1**.

## 2. Structural commentary

The title compound, **1**, crystallizes in space group $Pca2_1$ (Fig. 1). The N—O and C—N bond lengths of the oxime group

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O2—H2···O1$^{i}$ | 0.82 | 1.94 | 2.741 (3) | 167 |
| C2—H2$A$···O2$^{ii}$ | 0.93 | 2.35 | 3.243 (5) | 161 |
| C4—H4$A$···N2$^{iii}$ | 0.93 | 2.67 | 3.451 (6) | 142 |

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

are 1.382 (3) and 1.278 (4) Å, respectively, which is typical for neutral moieties of this type (Fritsky *et al.*, 1998, 2004). The N—N, N—C and C—O bond lengths of the hydrazide group [1.370 (3), 1.332 (4) and 1.229 (4) Å, respectively] are typical for 2-(hydroxyimino)propanehydrazide derivatives (Hegde *et al.*, 2017; Malinkin *et al.*, 2012; Moroz *et al.*, 2009*a*,*b*; Plutenko *et al.*, 2011). The oxime and the hydrazide groups are situated in a *cis*-position about the C7—C8 bond, which is also typical for 2-(hydroxyimino)propanehydrazide derivatives. Such a conformation is stabilized additionally by an H4···N5 attractive interaction (2.33 Å). Despite the distance being shorter than the sum of the van der Waals radii (2.67 Å; Zefirov, 1997) the interaction cannot be classified as an intramolecular hydrogen bond because of the acute N4—H···N5 angle (101°).

The $CH_3C(=NOH)C(O)NH$ fragment deviates from planarity (r.m.s. deviation of 0.362 Å) because of a twist between the oxime and the amide groups about the C7—C8 bond. The maximum deviations are 0.8763 (9) and 0.3355 (18) Å, respectively, for hydrogen (H9*C*) and non-hydrogen (O1) atoms. The O1—C7—C8—N5 torsion angle is 165.1 (3)°, significantly less than the average value in 2-(hydroxyimino)propanehydrazide derivatives published previously [172.1 (4)°]. Thus, such a twist distortion of the molecule seems to be a result of the crystal packing.

## 3. Supramolecular features

In the crystal, molecules are linked by O2—H2···O1$^{i}$ and C2—H2$A$···O2$^{ii}$ intermolecular hydrogen bonds [symmetry codes: (i) $-x+\frac{3}{2}, y+1, z+\frac{1}{2}$; (ii) $-x+\frac{3}{2}, y-1, z-\frac{1}{2}$], forming zigzag chains in the [013] and [0$\bar{1}$3] crystallographic directions (Fig. 2). These chains alternate in the [100] direction and are linked by C4—H4$A$···N2$^{iii}$ intermolecular hydrogen bonds [symmetry code: (iii) $-x+1, -y-1, z+\frac{1}{2}$]. Details of the hydrogen-bond geometry are given in Table 1.

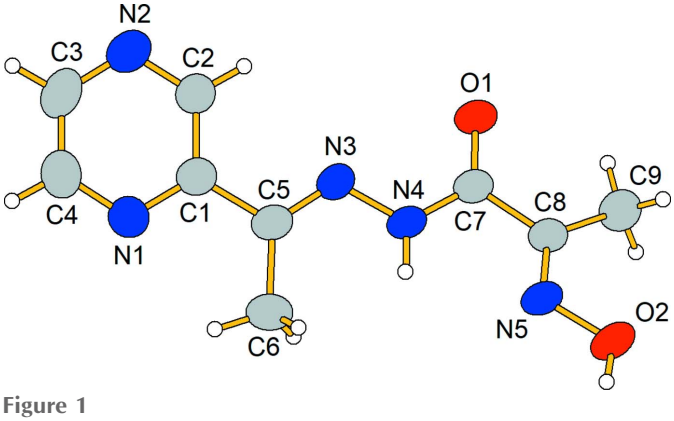



**Figure 1**
The molecular structure of the title compound **1** with displacement ellipsoids shown at the 50% probability level.

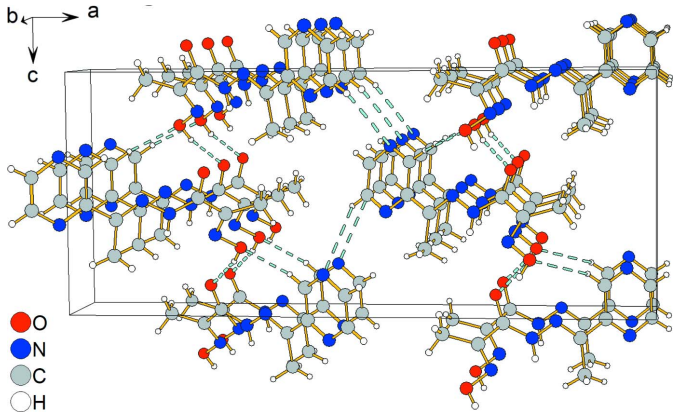



**Figure 2**
Crystal packing of the title compound **1**. Hydrogen bonds are indicated by dashed lines.

## 4. Hirshfeld surface analysis

The Hirshfeld surface analysis (Spackman & Jayatilaka, 2009) and the associated two-dimensional fingerprint plots (McKinnon *et al.*, 2007) were performed with *Crystal-*

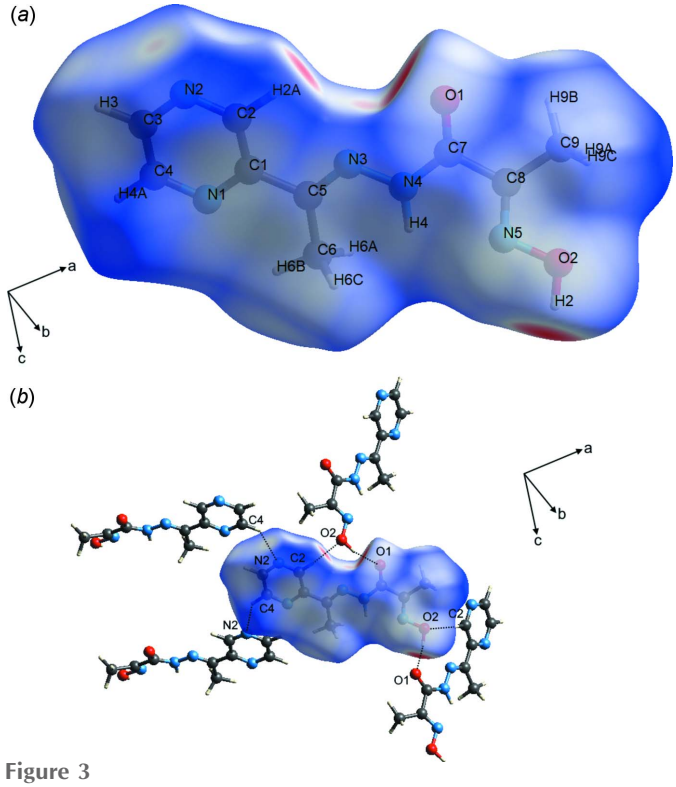



**Figure 3**
The Hirshfeld surface of the title molecule **1** mapped over $d_{norm}$, showing the close contacts.

*Explorer17* (Turner *et al.*, 2017). The Hirshfeld surfaces of the complex anions are colour-mapped with the normalized contact distance ($d_{norm}$) from red (distances shorter than the sum of the van der Waals radii) through white to blue (distances longer than the sum of the van der Waals radii). The Hirshfeld surface of the title compound mapped over $d_{norm}$, in the colour range −0.6441 to 1.3084 a.u. is shown in Fig. 3. According to the Hirshfeld surface, O2—H2···O1 and C4—H4*A*···N2 are the most noticeable intermolecular interactions. In addition, a C2—H2*A*···O2 weak intermolecular interaction is observed.

A fingerprint plot delineated into specific interatomic contacts contains information related to specific intermolecular interactions. The blue colour refers to the frequency of occurrence of the ($d_i$, $d_e$) pair with the full fingerprint plot outlined in grey. Fig. 4 shows the two-dimensional fingerprint plots of the sum of the contacts contributing to the Hirshfeld surface represented in normal mode. The most significant contribution to the Hirshfeld surface is from H···H (41.9%) contacts. In addition, N···H/H···N (20.5%) and O···H/H···O (15.4%) are highly significant contributions to the total Hirshfeld surface. The O···H/H···O fingerprint plot (Fig. 4*d*) reveals two sharp spikes along 1.9 Å < $d_i$ + $d_e$ < 2.4 Å, which are associated with the O2—H2···O1 hydrogen bond.

## 5. Geometry optimization

The DFT quantum-chemical calculations were performed at the B3LYP/6-311 G(d,p) level (Becke, 1993) as implemented in *PSI4* software package (Parrish *et al.*, 2017). The GFN2-xTB (Bannwarth *et al.*, 2019) calculations were applied with *xtb 6.4* package (Grimme, 2019). The structure optimization of the title compound was performed starting from the X-ray geometry and the resulting geometric values were compared with experimental values (Table 2, Fig. 5). The r.m.s. deviations are 0.380 and 0.362 Å for DFT and GFN2-xTB, respectively.

**Table 2**
Comparison of selected geometric data (A,°) from calculated and X-ray data.

| | X-ray | DFT | GFN2-xTB |
|---|---|---|---|
| Oxime moiety | | | |
| C8═N5 | 1.278 (4) | 1.285 | 1.273 |
| N5—O2 | 1.382 (3) | 1.394 | 1.389 |
| C8—N5—O2 | 111.4 (2) | 112.1 | 116.0 |
| Hydrazide moiety | | | |
| C7═O1 | 1.229 (4) | 1.218 | 1.208 |
| C7—N4 | 1.332 (4) | 1.382 | 1.368 |
| N3—N4 | 1.370 (3) | 1.351 | 1.336 |
| O1—C7—N4 | 124.1 (3) | 124.6 | 124.7 |
| Other | | | |
| C5═N3 | 1.278 (4) | 1.292 | 1.279 |
| O1—C7—C8—N5 | 165.1 (3) | 179.9 | 179.0 |

The calculated geometric parameters are in good agreement with experimental values. It is important to note that the accuracy of the semi-empirical GFN2-xTB method is close to that of the DFT calculations, even though GFN2-xTB calculations are significantly computationally 'cheaper' (∼$2{\cdot}10^3$ times faster for the calculations described here).

The most significant difference between the calculated and X-ray geometries is the absence of a twist deformation between the oxime and the amide groups in the case of QM calculated geometries. This might be additional evidence that the twist distortion of the molecule is due to effects of the crystal packing. The largest differences between the X-ray and calculated bond lengths are observed for the hydrazide moiety: N3—N4 is slightly longer (0.019 and 0.034 Å for DFT and GFN2-xTB, respectively) and C7—N4 is shorter (0.050 and 0.036 Å for DFT and GFN2-xTB, respectively) than calculated. Such calculation errors are probably typical for

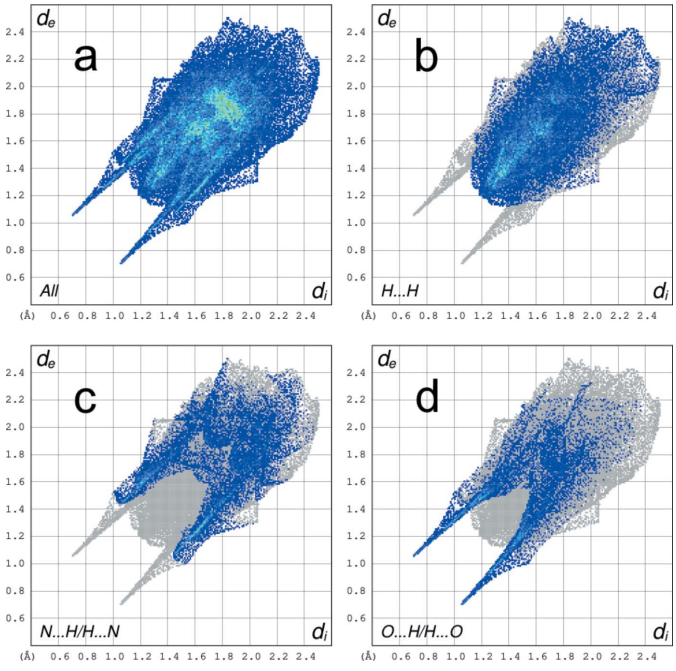



**Figure 4**
A view of the two-dimensional fingerprint plots for the title compound **1** showing (*a*) all interactions, and delineated into (*b*) H···H (41.9%), (*c*) N···H/H···N (20.5%) and (*d*) O···H/H···O (15.4%) contacts.

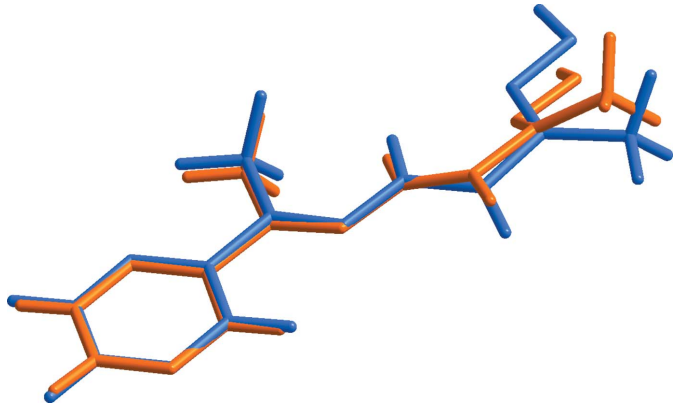


**Figure 5**
Overlay between the molecule obtained from experimental (orange) and DFT optimization (blue).

hydrazide derivatives at this level of theory (Anitha *et al.*, 2019; Malla *et al.*, 2022). The HOMO–LUMO gap calculated by DFT method is 0.159 a.u. and the frontier molecular orbital energies, $E_{HOMO}$ and $E_{LUMO}$ are −0.23063 and −0.07178 a.u., respectively.

## 6. Database survey

A search in the Cambridge Structural Database (CSD version 5.43, update of March 2022; Groom *et al.*, 2016) resulted in seven hits for 2-(hydroxyimino)propanehydrazide derivatives: CUDBEJ, DUDHOA, OBUXIU, PUVPED, PUVPED01, WARCEZ and WARCID (Hegde *et al.*, 2017; Malinkin *et al.*, 2012; Moroz *et al.*, 2009*a*,*b*; Plutenko *et al.*, 2011). Most of them deviate slightly from planarity: r.m.s. deviations are in the range 0.247-0.390 Å with maximum deviations of non-hydrogen atoms from the best plane in the range 0.098–0.340 Å. At the same time PUVPED and PUVPED01 are not planar, mainly because of a twist of the dicarbonylhydrazine group [the C—N—N—C torsion angle is 96.54 (15)°].

157 hits relate to organometallic substances based on 2-(hydroxyimino)propanehydrazide derivatives. Most of them are polynuclear 3*d* and 4*f* metal complexes (discrete molecules and MOFs). The maximum number of metal centres per molecule for the discrete complexes of this type is 12 (Anwar *et al.*, 2011, 2012; Moroz *et al.*, 2012).

## 7. Synthesis and crystallization

The title compound was prepared according to a slightly modified procedure (Feng *et al.*, 2018). A solution of 2-(hydroxyimino)propanehydrazide (0.702 g, 5 mmol) in methanol (50 ml) was treated with 2-acetylpyrazine (0.732 g, 5 mmol) and the mixture was heated under reflux for 1.5 h. After that, the solvent was evaporated under vacuum and the product was recrystallized from methanol. Yield 1.141 g (86%). $^1$H NMR, 400.13 MHz, (DMSO-$d_6$): 11.97 (*s*, 1H, OH), 10.21 (*s*, 1H, NH), 9.31 (*s*, 1H, pyrazine-3), 8.56 (*s*, 1H, pyrazine-5), 8.55 (*s*, 1H, pyrazine-6), 2.37 (*s*, 3H, hydrazonic $CH_3$), 2.02 (*s*, 3H, $CH_3$). IR (KBr, cm$^{-1}$): 1658 (CO amid I), 1034 (NO oxime). Analysis calculated for $C_9H_{11}N_5O_2$: C 48.86, H 5.01, N 31.66%; found: C 48.49, H 5.22, N 31.42%.

## 8. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. All the hydrogen atoms were positioned geometrically (N—H = 0.85, C—H = 0.93–0.96 Å) and refined using a riding model with $U_{iso} = nU_{eq}$ of the carrier atom ($n$ = 1.5 for methyl groups and $n$ = 1.2 for other hydrogen atoms).

**Table 3**
Experimental details.

| | |
|---|---|
| Crystal data | |
| Chemical formula | $C_9H_{11}N_5O_2$ |
| $M_r$ | 221.23 |
| Crystal system, space group | Orthorhombic, $Pca2_1$ |
| Temperature (K) | 293 |
| $a$, $b$, $c$ (Å) | 24.367 (2), 4.3979 (5), 10.1424 (9) |
| $V$ (Å$^3$) | 1086.89 (18) |
| $Z$ | 4 |
| Radiation type | Mo $K\alpha$ |
| $\mu$ (mm$^{-1}$) | 0.10 |
| Crystal size (mm) | 0.8 × 0.4 × 0.1 |
| | |
| Data collection | |
| Diffractometer | Xcallibur3 |
| Absorption correction | Multi-scan (*CrysAlis PRO*; Rigaku OD, 2019) |
| $T_{min}$, $T_{max}$ | 0.646, 1.000 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 2381, 1540, 1254 |
| $R_{int}$ | 0.023 |
| (sin $\theta/\lambda)_{max}$ (Å$^{-1}$) | 0.595 |
| | |
| Refinement | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.037, 0.088, 1.01 |
| No. of reflections | 1540 |
| No. of parameters | 148 |
| No. of restraints | 1 |
| H-atom treatment | H-atom parameters constrained |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 0.11, −0.13 |
| Absolute structure | Flack $x$ determined using 351 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013) |
| Absolute structure parameter | −1.7 (10) |

Computer programs: *CrysAlis PRO* (Rigaku OD, 2019), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2016/6* (Sheldrick, 2015*b*), *DIAMOND* (Brandenburg, 2009) and *OLEX2* (Dolomanov *et al.*, 2009).

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# supporting information

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## Crystal structure, Hirshfeld surface analysis and geometry optimization of 2-hydroxyimino-*N*-[1-(pyrazin-2-yl)ethylidene]propanohydrazide

**Maksym O. Plutenko, Svitlana V. Shishkina, Oleg V. Shishkin, Vadim A. Potaskalov and Valentina A. Kalibabchuk**

### Computing details

Data collection: *CrysAlis PRO* (Rigaku OD, 2019); cell refinement: *CrysAlis PRO* (Rigaku OD, 2019); data reduction: *CrysAlis PRO* (Rigaku OD, 2019); program(s) used to solve structure: *SHELXT* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2016/6* (Sheldrick, 2015b); molecular graphics: *DIAMOND* (Brandenburg, 2009); software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009).

### 2-hydroxyimino-*N*-[1-(pyrazin-2-yl)ethylidene]propanohydrazide

*Crystal data*

$C_9H_{11}N_5O_2$
$M_r = 221.23$
Orthorhombic, $Pca2_1$
$a = 24.367$ (2) Å
$b = 4.3979$ (5) Å
$c = 10.1424$ (9) Å
$V = 1086.89$ (18) Å$^3$
$Z = 4$
$F(000) = 464$
$D_x = 1.352$ Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 1825 reflections
$\theta = 2.4$–$25.3°$
$\mu = 0.10$ mm$^{-1}$
$T = 293$ K
Plate, colourless
0.8 × 0.4 × 0.1 mm

*Data collection*

Xcallibur3 diffractometer
area detector scans
Absorption correction: multi-scan (CrysAlisPro; Rigaku OD, 2019)
$T_{min} = 0.646$, $T_{max} = 1.000$
2381 measured reflections
1540 independent reflections
1254 reflections with $I > 2\sigma(I)$
$R_{int} = 0.023$
$\theta_{max} = 25.0°$, $\theta_{min} = 3.3°$
$h = -13 \rightarrow 28$
$k = -5 \rightarrow 4$
$l = -12 \rightarrow 10$

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.088$
$S = 1.01$
1540 reflections
148 parameters
1 restraint
Hydrogen site location: mixed
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0439P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.11$ e Å$^{-3}$
$\Delta\rho_{min} = -0.13$ e Å$^{-3}$
Absolute structure: Flack *x* determined using 351 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter: −1.7 (10)

*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 (Å²)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| O1 | 0.76287 (9) | 0.3026 (5) | 0.3893 (2) | 0.0552 (6) |
| N1 | 0.54406 (13) | −0.2364 (8) | 0.5790 (3) | 0.0652 (9) |
| C1 | 0.58360 (13) | −0.1186 (7) | 0.5054 (3) | 0.0481 (9) |
| O2 | 0.80114 (8) | 0.9769 (6) | 0.7178 (3) | 0.0571 (6) |
| H2 | 0.785835 | 1.067394 | 0.778171 | 0.086* |
| C2 | 0.58576 (16) | −0.1796 (10) | 0.3721 (4) | 0.0696 (12) |
| H2A | 0.613875 | −0.093141 | 0.322655 | 0.084* |
| N2 | 0.54979 (15) | −0.3547 (9) | 0.3114 (3) | 0.0802 (11) |
| N3 | 0.66429 (11) | 0.1682 (6) | 0.4996 (3) | 0.0446 (6) |
| C3 | 0.51042 (17) | −0.4693 (10) | 0.3865 (5) | 0.0718 (13) |
| H3 | 0.483903 | −0.592846 | 0.348009 | 0.086* |
| N4 | 0.70225 (10) | 0.3562 (6) | 0.5568 (3) | 0.0457 (7) |
| H4 | 0.696761 | 0.411873 | 0.635489 | 0.055* |
| C4 | 0.50756 (17) | −0.4124 (11) | 0.5171 (4) | 0.0766 (13) |
| H4A | 0.479179 | −0.498671 | 0.565696 | 0.092* |
| N5 | 0.76423 (10) | 0.7824 (5) | 0.6578 (3) | 0.0447 (7) |
| C5 | 0.62427 (13) | 0.0788 (7) | 0.5713 (3) | 0.0467 (8) |
| C6 | 0.61725 (16) | 0.1548 (10) | 0.7154 (4) | 0.0674 (10) |
| H6A | 0.648915 | 0.087367 | 0.763582 | 0.101* |
| H6B | 0.585142 | 0.054609 | 0.748914 | 0.101* |
| H6C | 0.613240 | 0.370690 | 0.725479 | 0.101* |
| C7 | 0.74946 (14) | 0.4146 (6) | 0.4956 (3) | 0.0406 (7) |
| C8 | 0.78699 (12) | 0.6303 (7) | 0.5654 (3) | 0.0421 (7) |
| C9 | 0.84549 (13) | 0.6475 (9) | 0.5264 (4) | 0.0657 (11) |
| H9A | 0.853496 | 0.847820 | 0.494094 | 0.099* |
| H9B | 0.852677 | 0.501055 | 0.458348 | 0.099* |
| H9C | 0.868223 | 0.604687 | 0.601444 | 0.099* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| O1 | 0.0616 (13) | 0.0633 (14) | 0.0408 (14) | −0.0086 (12) | 0.0065 (12) | −0.0188 (13) |
| N1 | 0.0593 (18) | 0.086 (2) | 0.0508 (18) | −0.0195 (17) | −0.0002 (17) | 0.0000 (18) |
| C1 | 0.0450 (18) | 0.0568 (19) | 0.043 (2) | −0.0026 (16) | −0.0017 (17) | −0.0026 (18) |
| O2 | 0.0580 (13) | 0.0618 (14) | 0.0516 (14) | −0.0040 (12) | −0.0033 (13) | −0.0277 (12) |
| C2 | 0.065 (2) | 0.094 (3) | 0.050 (3) | −0.031 (2) | 0.004 (2) | −0.011 (2) |
| N2 | 0.077 (2) | 0.107 (3) | 0.056 (2) | −0.033 (2) | −0.003 (2) | −0.016 (2) |
| N3 | 0.0455 (14) | 0.0463 (14) | 0.0422 (14) | −0.0036 (13) | −0.0015 (14) | −0.0097 (13) |
| C3 | 0.061 (2) | 0.084 (3) | 0.071 (3) | −0.022 (2) | −0.017 (2) | −0.002 (3) |

| | | | | | | |
|---|---|---|---|---|---|---|
| N4 | 0.0499 (15) | 0.0495 (15) | 0.0377 (14) | −0.0044 (13) | 0.0022 (15) | −0.0159 (13) |
| C4 | 0.063 (2) | 0.103 (3) | 0.064 (3) | −0.032 (2) | −0.006 (2) | 0.011 (3) |
| N5 | 0.0538 (17) | 0.0427 (13) | 0.0375 (16) | 0.0001 (13) | −0.0038 (14) | −0.0112 (13) |
| C5 | 0.0482 (18) | 0.0527 (18) | 0.0392 (18) | 0.0012 (16) | −0.0016 (18) | −0.0059 (16) |
| C6 | 0.069 (2) | 0.091 (3) | 0.042 (2) | −0.012 (2) | 0.005 (2) | −0.011 (2) |
| C7 | 0.0492 (17) | 0.0382 (15) | 0.0342 (19) | 0.0017 (14) | 0.0011 (16) | −0.0074 (16) |
| C8 | 0.0481 (16) | 0.0432 (15) | 0.0350 (17) | −0.0003 (14) | 0.0021 (16) | −0.0053 (16) |
| C9 | 0.0555 (19) | 0.080 (2) | 0.062 (3) | −0.0123 (19) | 0.014 (2) | −0.030 (2) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| O1—C7 | 1.229 (4) | N4—H4 | 0.8452 |
| N1—C1 | 1.325 (4) | N4—C7 | 1.332 (4) |
| N1—C4 | 1.336 (5) | C4—H4A | 0.9300 |
| C1—C2 | 1.379 (5) | N5—C8 | 1.278 (4) |
| C1—C5 | 1.477 (4) | C5—C6 | 1.509 (5) |
| O2—H2 | 0.8200 | C6—H6A | 0.9600 |
| O2—N5 | 1.382 (3) | C6—H6B | 0.9600 |
| C2—H2A | 0.9300 | C6—H6C | 0.9600 |
| C2—N2 | 1.319 (5) | C7—C8 | 1.496 (4) |
| N2—C3 | 1.325 (5) | C8—C9 | 1.482 (5) |
| N3—N4 | 1.370 (3) | C9—H9A | 0.9600 |
| N3—C5 | 1.279 (4) | C9—H9B | 0.9600 |
| C3—H3 | 0.9300 | C9—H9C | 0.9600 |
| C3—C4 | 1.350 (6) | | |
| | | | |
| C1—N1—C4 | 116.5 (3) | N3—C5—C1 | 115.8 (3) |
| N1—C1—C2 | 120.3 (3) | N3—C5—C6 | 124.7 (3) |
| N1—C1—C5 | 117.6 (3) | C5—C6—H6A | 109.5 |
| C2—C1—C5 | 122.2 (3) | C5—C6—H6B | 109.5 |
| N5—O2—H2 | 109.5 | C5—C6—H6C | 109.5 |
| C1—C2—H2A | 118.5 | H6A—C6—H6B | 109.5 |
| N2—C2—C1 | 123.1 (4) | H6A—C6—H6C | 109.5 |
| N2—C2—H2A | 118.5 | H6B—C6—H6C | 109.5 |
| C2—N2—C3 | 115.8 (4) | O1—C7—N4 | 124.1 (3) |
| C5—N3—N4 | 117.4 (3) | O1—C7—C8 | 120.5 (3) |
| N2—C3—H3 | 119.0 | N4—C7—C8 | 115.4 (3) |
| N2—C3—C4 | 122.1 (4) | N5—C8—C7 | 114.4 (3) |
| C4—C3—H3 | 119.0 | N5—C8—C9 | 125.9 (3) |
| N3—N4—H4 | 117.9 | C9—C8—C7 | 119.6 (3) |
| C7—N4—N3 | 120.1 (3) | C8—C9—H9A | 109.5 |
| C7—N4—H4 | 121.4 | C8—C9—H9B | 109.5 |
| N1—C4—C3 | 122.3 (4) | C8—C9—H9C | 109.5 |
| N1—C4—H4A | 118.9 | H9A—C9—H9B | 109.5 |
| C3—C4—H4A | 118.9 | H9A—C9—H9C | 109.5 |
| C8—N5—O2 | 111.4 (2) | H9B—C9—H9C | 109.5 |
| C1—C5—C6 | 119.5 (3) | | |

| | | | |
|---|---|---|---|
| O1—C7—C8—N5 | 165.1 (3) | N2—C3—C4—N1 | 0.2 (8) |
| O1—C7—C8—C9 | −16.1 (5) | N3—N4—C7—O1 | −2.1 (5) |
| N1—C1—C2—N2 | −0.3 (7) | N3—N4—C7—C8 | 178.2 (2) |
| N1—C1—C5—N3 | 174.5 (3) | N4—N3—C5—C1 | 178.8 (2) |
| N1—C1—C5—C6 | −4.0 (5) | N4—N3—C5—C6 | −2.7 (5) |
| C1—N1—C4—C3 | 0.1 (6) | N4—C7—C8—N5 | −15.2 (4) |
| C1—C2—N2—C3 | 0.6 (6) | N4—C7—C8—C9 | 163.6 (3) |
| O2—N5—C8—C7 | −179.9 (3) | C4—N1—C1—C2 | −0.1 (6) |
| O2—N5—C8—C9 | 1.4 (5) | C4—N1—C1—C5 | 179.5 (3) |
| C2—C1—C5—N3 | −5.8 (5) | C5—C1—C2—N2 | −179.9 (3) |
| C2—C1—C5—C6 | 175.6 (4) | C5—N3—N4—C7 | 168.4 (3) |
| C2—N2—C3—C4 | −0.5 (7) | | |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O2—H2···O1$^{i}$ | 0.82 | 1.94 | 2.741 (3) | 167 |
| C2—H2*A*···O2$^{ii}$ | 0.93 | 2.35 | 3.243 (5) | 161 |
| C4—H4*A*···N2$^{iii}$ | 0.93 | 2.67 | 3.451 (6) | 142 |

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