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$_9$H$_{11}$N$_5$O$_2$, 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$_3$C(═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 [0T3] 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 polynucleatic 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 Pca$_2_1$ (Fig. 1). The N—O and C—N bond lengths of the oxime group...
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., 2009a,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···C1/C1/C1/N5 angle (101°).

The CH3C(==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) 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···O1i and C2—H2A···O2ii intermolecular hydrogen bonds [symmetry codes: (i) −x + 1, y + 1, z − 1; (ii) −x + 1, y − 1, z + 1], forming zigzag chains in the [013] and [013] crystallographic directions (Fig. 2). These chains alternate in the [100] direction and are linked by C4—H4A···N2iii intermolecular hydrogen bonds [symmetry code: (iii) −x + 1, −y − 1, z + 1]. Details of the hydrogen-bond geometry are given in Table 1.

### 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-
Explorer17 (Turner et al., 2017). The Hirshfeld surfaces of the complex anions are colour-mapped with the normalized contact distance \((d_{\text{norm}})\) 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 \(d_{\text{norm}}\), in the colour range \(-0.6441\) to \(1.3084\) a.u. is shown in Fig. 3. According to the Hirshfeld surface, O2—H2
dC1/C1/C1O1 and C4—H4
A/C1/C1/C1N2 are the most noticeable intermolecular interactions. In addition, a C2—H2
A/C1/C1/C1O2 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. 4d) reveals two sharp spikes along \(1.9 \text{ Å} < d_i + d_e < 2.4 \text{ Å}\), which are associated with the O2—H2···O1 hydrogen bond.

5. Geometry optimization

The DFT quantum-chemical calculations were performed at the B3LYP/6-311G(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.

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’ (\(\sim 2\times 10^3\) 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

### Table 2

|                | 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    |

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, $E_{\text{HOMO}}$ and $E_{\text{LUMO}}$ 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., 2009a;b; Plutenko et al., 2011). Most of them deviate slightly from planarity: r.m.s. deviations are 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 3d and 4f 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$_9$H$_{11}$N$_5$O$_2$: C 48.49, H 5.22, N 31.42%; 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 $U_{iso} = n U_{eq}$ 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$_9$H$_{11}$N$_5$O$_2$ |
| $M_r$ | 221.23 |
| Crystal system, space group | Orthorhombic, Pca$_2_1$ |
| 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 Kα |
| $\mu$ (mm$^{-1}$) | 0.10 |
| Crystal size (mm) | 0.8 × 0.4 × 0.1 |

| Data collection | Diffractometer Xcalib3 |
|-----------------|------------------------|
| 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 |
| $R_{int}$ (sin $\theta$/λ)$_{max}$ (Å$^{-1}$) | 0.023 |
| Refinement | 0.595 |
| $R[F^2 > 2\sigma(F^2)]$, 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 |
| $\Delta$ρ$_{max}$, $\Delta$ρ$_{min}$ (e Å$^{-3}$) | 0.11, −0.13 |
| Absolute structure | Flack x determined using 351 |
| Absolute structure parameter | quotients [(I$^+$−(I$^-$))/(I$^+$)+(I$^-$)]] |
| (Parsons et al., 2013) | 1.7 (10) |

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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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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

C9H11N5O2
Mr = 221.23
Orthorhombic, Pca2₁
a = 24.367 (2) Å
b = 4.3979 (5) Å
c = 10.1424 (9) Å
V = 1086.89 (18) Å³
Z = 4
F(000) = 464

Data collection

Xcalibur3
diffractometer
area detector scans
Absorption correction: multi-scan
(CrysAlisPro; Rigaku OD, 2019)
Tmin = 0.646, Tmax = 1.000
2381 measured reflections

Refinement

Refinement on F²
Least-squares matrix: full
R[F² > 2σ(F²)] = 0.037
wR(F²) = 0.088
S = 1.01
1540 reflections
148 parameters
1 restraint
Hydrogen site location: mixed
H-atom parameters constrained

sup-1
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)**

| Atom | x     | y     | z     | Uiso* | Ueq  |
|------|-------|-------|-------|-------|------|
| 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) |
| C3   | 0.55042 (11) | 0.1682 (6) | 0.4996 (3) | 0.0446 (6) |
| C4   | 0.50756 (17) | 0.411873 | 0.635489 | 0.055* |
| H4A  | 0.479179 | −0.498671 | 0.565696 | 0.092* |
| N5   | 0.76423 (10) | 0.7824 (5) | 0.6578 (3) | 0.0447 (7) |
| C7   | 0.62427 (13) | 0.0788 (7) | 0.5713 (3) | 0.0467 (8) |
| C8   | 0.61725 (16) | 0.1548 (10) | 0.7154 (4) | 0.0674 (10) |
| H9A  | 0.48915 | 0.087367 | 0.763582 | 0.101* |
| H9B  | 0.585142 | 0.054609 | 0.748914 | 0.101* |
| H9C  | 0.613240 | 0.370690 | 0.725479 | 0.101* |
| H10  | 0.74946 (14) | 0.4146 (6) | 0.4956 (3) | 0.0406 (7) |
| C8   | 0.78699 (12) | 0.6303 (7) | 0.5653 (3) | 0.0421 (7) |
| C9   | 0.84549 (13) | 0.6475 (9) | 0.5264 (4) | 0.0657 (11) |
| H10A | 0.853496 | 0.847820 | 0.494094 | 0.099* |
| H10B | 0.852677 | 0.501055 | 0.458348 | 0.099* |
| H10C | 0.868223 | 0.604687 | 0.601444 | 0.099* |

**Atomic displacement parameters (Å²)**

|   | U11  | U22  | U33  | U12  | U13  | U23  |
|---|------|------|------|------|------|------|
| 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) |
### Geometric parameters (Å, °)

| Bond/Angle | Value (Å) | Value (°) |
|------------|-----------|-----------|
| O1—C7      | 1.229 (4) | 84.52     |
| N1—C1      | 1.325 (4) | 83.32     |
| N1—C4      | 1.336 (5) | 93.00     |
| C1—C2      | 1.379 (5) | 123.1 (4) |
| C1—C5      | 1.477 (4) | 124.7 (3) |
| O2—H2      | 0.8200    | 96.00     |
| O2—N5      | 1.382 (3) | 96.00     |
| C2—H2A     | 0.9300    | 109.5     |
| C2—N2      | 1.319 (5) | 149.6 (4) |
| N2—C3      | 1.325 (5) | 148.2 (5) |
| N3—N4      | 1.370 (3) | 96.00     |
| N3—C5      | 1.279 (4) | 96.00     |
| C3—H3      | 0.9300    | 96.00     |
| C3—C4      | 1.350 (6) |           |

| Bond/Angle | Value (Å) | Value (°) |
|------------|-----------|-----------|
| C1—C1—C4  | 116.5 (3) | 115.8 (3) |
| N1—C1—C2  | 120.3 (3) | 124.7 (3) |
| N1—C1—C5  | 117.6 (3) | 109.5     |
| C2—C1—C5  | 122.2 (3) | 109.5     |
| N5—O2—H2  | 109.5     |           |
| C1—C2—H2A | 118.5     | 109.5     |
| N2—C2—C1  | 123.1 (4) | 109.5     |
| N2—C2—H2A | 118.5     | 109.5     |
| C2—N2—C3  | 115.8 (4) | 124.1 (3) |
| C5—N3—N4  | 117.4 (3) | 120.5 (3) |
| N2—C3—H3  | 119.0     | 115.4 (3) |
| N2—C3—C4  | 122.1 (4) | 114.4 (3) |
| C4—C3—H3  | 119.0     | 125.9 (3) |
| N3—N4—H4  | 117.9     | 119.6 (3) |
| C7—N4—N3  | 120.1 (3) | 109.5     |
| C7—N4—H4  | 121.4     | 109.5     |
| N1—C4—C3  | 122.3 (4) | 109.5     |
| N1—C4—H4A | 118.9     | 109.5     |
| C3—C4—H4A | 118.9     | 109.5     |
| C8—N5—O2  | 111.4 (2) |           |
| 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—C2—N2—C3  0.6 (6)  N4—N3—C5—C6  178.2 (2)
N1—C1—C5—C6  174.5 (3)  N4—N3—C5—C6  −4.0 (5)
C1—N1—C4—C3  0.1 (6)  N4—N3—C5—C6  178.2 (2)
N1—C1—C5—C6  174.5 (3)  N4—N3—C5—C6  −4.0 (5)
C1—N1—C4—C3  0.1 (6)  N4—N3—C5—C6  178.2 (2)
C1—N1—C4—C3  0.1 (6)  N4—N3—C5—C6  −4.0 (5)
O2—N5—C8—C7  −179.9 (3)  C4—N1—C1—C2  −0.1 (6)
O2—N5—C8—C9  1.4 (5)  C4—N1—C1—C2  −0.1 (6)
C2—C1—C5—N3  −5.8 (5)  C5—C1—C2—N2  −179.9 (3)
C2—C1—C5—C6  175.6 (4)  C5—C1—C2—N2  −179.9 (3)
C2—N2—C3—C4  −0.5 (7)  C5—N3—N4—C7  168.4 (3)

Hydrogen-bond geometry (Å, °)

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

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