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Synthesis, structures and Hirshfeld surface analyses of 2-hydroxy-*N*′-methylacetohydrazide and 2-hydroxy-*N*-methylacetohydrazide

Oleksandr V. Vashchenko,[a] Dmytro M. Khomenko,[a,b] Viktoriya V. Dyakonenko[c,d]* and Rostyslav D. Lampeka[a]

[a]Department of Chemistry, Taras Shevchenko National University of Kyiv, Volodymyrska str. 64/13, 01601 Kyiv, Ukraine, [b]Enamine Ltd. (www.enamine.net), Winston Churchill str. 78, 02094 Kyiv, Ukraine, [c]SSI "Institute for Single Crystals" of the National Academy of Sciences of Ukraine, Nauki Ave 60, Kharkiv 61001, Ukraine, and [d]V. I. Vernadskii Institute of General and Inorganic Chemistry of the National Academy of Sciences of Ukraine, Prospect Palladina 32/34, 03680 Kyiv, Ukraine. *Correspondence e-mail: dyakvik@gmail.com

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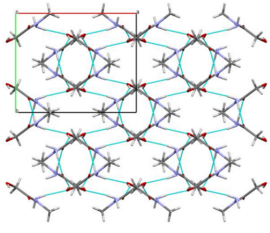
The structures of the title compounds 2-hydroxy-*N*′-methylacetohydrazide, **1**, and 2-hydroxy-*N*-methylacetohydrazide, **2**, both $C_3H_8N_2O_2$, as regioisomers differ in the position of the methyl group relative to the N atoms in 2-hydroxy-acetohydrazide. In the structure of **1**, the 2-hydroxy-acetohydrazide core [OH—C—C(=O)—NH—NH] is almost planar and the methyl group is rotated relative to this plane. As opposed to **1**, in the structure of **2** all non-hydrogen atoms lie in the same plane. The hydroxyl and carbonyl groups in structures **1** and **2** are in *trans* and *cis* positions, respectively. The methyl amino group and carbonyl group are in the *cis* position relative to the C—N bond in structure **1**, while the amino group and carbonyl group are in the *trans* position relative to the C—N bond in stucture **2.** In the crystal, molecules of **1** are linked by N—H···O and O—H···N intermolecular hydrogen bonds, forming layers parallel to the *ab* crystallographic plane. A Hirshfeld surface analysis showed that the H···H contacts dominate the crystal packing with a contribution of 55.3%. The contribution of the H···O/O···H interaction is somewhat smaller, amounting to 30.8%. In the crystal, as a result of the intermolecular O—H···O hydrogen bonds, molecules of **2** form dimers, which are linked by N—H···O hydrogen bonds and a three-dimensional supramolecular network The major contributors to the Hirshfeld surface are H···H (58.5%) and H···O/O···H contacts (31.7%).

1. Chemical context

N-substituted hydrazides are widely used compounds in organic synthesis. Aza-peptides containing the *N*-alkyl hydrazide fragment have been investigated as wide-spectrum antibiotics (Amabili *et al.*, 2020), drugs for inflammatory acne treatment (Fournier *et al.*, 2018), antiviral agents (Breidenbach *et al.*, 2021) and selective protease inhibitors (Corrigan *et al.*, 2020). Additionally, *N*-alkyl hydrazides are very important starting reagents for the synthesis of 1,2-substituted 1,2,4-triazoles (Nguyen & Hong, 2021; Peese *et al.*, 2020), 3-substituted 1,3,4-thiadiazol-2-ones and 1,3,4-oxodiazol-2-ones (Kuzmina *et al.*, 2019; Bi *et al.*, 2019), 2,3-dihydro-1H-pyrazoles (Shaker Ardakani *et al.*, 2021), and other heterocyclic or spyrocyclic compounds (Kobayashi & Ainai, 2018; Tian *et al.*, 2022).

Previously, we have obtained a series of *N*1- and *N*2-alkylated 1,2,4-triazoles (Khomenko *et al.*, 2022; Ohorodnik *et al.*, 2023). The separation of the resulting regioisomers was achieved through flash column chromatography. The use of pure *N*-methyl regioisomers of hydrazides in the synthesis of



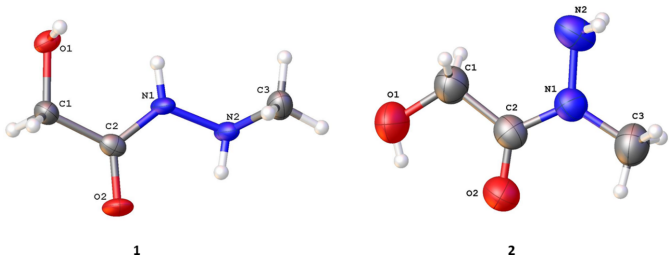
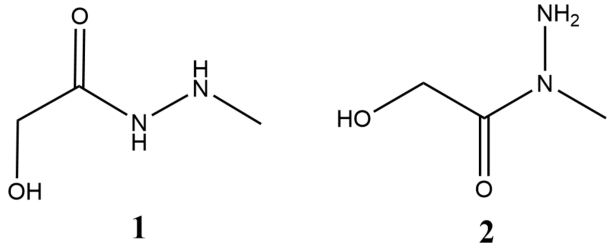


Figure 1
The molecular structures of **1** and **2** with atom labeling and displacement ellipsoids drawn at the 50% probability level.

1,2,4-triazoles allows for the direct formation of the desired *N*1- and *N*2-methylated compounds, thereby eliminating the need for an expensive flash chromatography step.

Usually, the interaction of carboxylic acid derivatives with *N*-alkyl hydrazines leads to a mixture of regioisomers (Condon, 1972), while the desired *N*- or *N*′- regioisomer can be obtained from BOC or CBZ-protected *N*-alkyl hydrazines (Amabili *et al.*, 2020; Peese *et al.*, 2020). This method, however, has several disadvantages: expensive reagents, more steps, and the need for protecting other functional groups.



In this work, we report the one-step synthesis and purification procedure of 2-hydroxy-*N*′-methylacetohydrazide (**1**) and 2-hydroxy-*N*-methylacetohydrazide (**2**) using inexpensive reagents, their crystal structures and Hirshfeld surface analyses.

2. Structural commentary

Structures **1** and **2** are regioisomers and differ in the position of the methyl group relative to the N atoms in 2-hydroxy-acetohydrazide (Fig. 1). Compound **1** crystallizes in the orthorhombic space group *Pbca*, while **2** crystallizes in the monoclinic space group *C*2/*c*.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···N2^{i}	0.87 (5)	1.90 (5)	2.767 (5)	172 (4)
N1—H1*A*···O2^{ii}	0.71 (4)	2.17 (4)	2.848 (5)	159 (4)

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

Table 2
Hydrogen-bond geometry (Å, °) for **2**.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O2^{i}	0.78 (4)	2.39 (4)	3.078 (4)	148 (3)
N2—H2*A*···O2^{ii}	1.00 (3)	2.08 (3)	3.062 (4)	169 (2)
N2—H2*B*···O1^{iii}	0.92 (3)	2.21 (3)	3.129 (4)	173 (2)

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

In the structure of **1**, the 2-hydroxy-acetohydrazide core [OH—C—C(=O)—NH—NH] is almost planar (r.m.s. deviation is 0.016 Å). The methyl group is rotated relative to this plane [the C2—N1—N2—C3 torsion angle is −124.1 (4)°]. The hydroxyl and carbonyl groups are in *trans* positions. The methyl amino group and carbonyl group are in the *cis* position relative to the C2—N1 bond. The O–C–N–N fragment shows features of conjugation, supported by the pronounced shortening of the C2—N1 [1.300 (6) Å] single bond compared to the average value of 1.355 Å (Orpen *et al.*, 1994). This may be enhanced by the formation of the N1—H1*A*···O2′ intermolecular hydrogen bond (Table 1).

As opposed to **1**, in the structure of **2** all non-hydrogen atoms lie in the same plane (r.m.s. deviation is 0.028 Å). The hydroxyl and carbonyl groups are in *cis* positions. The amino group and carbonyl group are in the *trans* position relative to the C2—N1 bond. Both the C2—O2 [1.251 (3) Å] and the N1—N2 [1.434 (3) Å] bonds are elongated compared to the average values of 1.234 and 1.420 Å, respectively (Orpen *et al.*, 1994). The elongation of the N1—N2 bond, together with the absence of a shortening of the C1—N2 bond, may indicate a slight disruption of the conjugation within the O–C–N–N core. That is consistent with amino group rotation: C2—N1—N2—H torsion angles are +12° and −116°, indi-

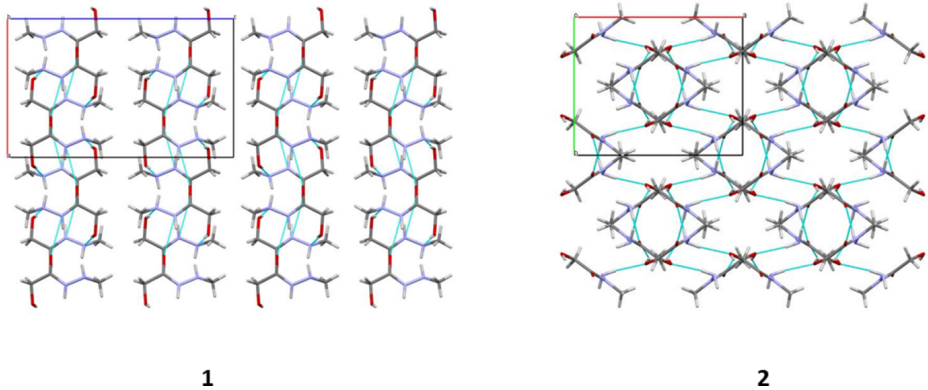


Figure 2
Crystal packing of **1** viewed along the *b* axis (left) and **2** viewed along *c* axis (right). The hydrogen bonds are shown as blue dotted lines.

cating an in-plane position of the lone pair of the N2 atom, stabilized by the N2—H2*A*···O2 and N2—H2*B*···O1 intermolecular hydrogen bonds (Table 2), so this lone pair cannot participate in the π-conjugation of the O–C–N–N fragment. The minor elongation of the C2═O2 double bond is probably caused by the presence of the intermolecular bi-directional hydrogen bond O1—H1···O2 with the O—H group of an adjacent molecule and the N2—H2*B*···O2″ hydrogen with another molecule (Table 2).

The N2 atom is pyramidal in both structures **1** and **2** (the sums of the valence angles is 225.93 and 317.93° in **1** and **2**, respectively). The pyramidal configuration of the N2 atom is stabilized by intermolecular hydrogen bonds O1—H1···N2 (in **1**, Table 1) and N2—H2*B*···O1, N2—H2*A*···O2 (in **2**, Table 2).

3. Supramolecular features and Hirshfeld surface analysis

In the crystal, molecules of **1** are linked by N—H···O and O—H···N hydrogen bonds (Table 1), forming layers parallel to the *ab* crystallographic plane (Fig. 2).

The intermolecular interactions in the crystal structure of **1** were further analyzed by means of the d_{norm} property (Fig. 3) mapped over the Hirshfeld surface (Spackman & Jayatilaka, 2009), which was calculated using the *CrystalExplorer21* program (Spackman *et al.*, 2021). The strongest contacts, which are visualized on the Hirshfeld surface as the dark-red spots, correspond to the N—H···O and O—H···N hydrogen bonds between molecules. The majority of the intermolecular interactions of **1** are weak, and are represented in blue on the Hirshfeld surface.

For further exploration of the intermolecular interactions, two-dimensional fingerprint plots (McKinnon *et al.*, 2007) were generated, as shown in Fig. 4. The major contributions to the crystal structure are from the H···H (55.3%) and H···O/O···H (30.8%) interactions. The N···H/H···N (9.2%) and

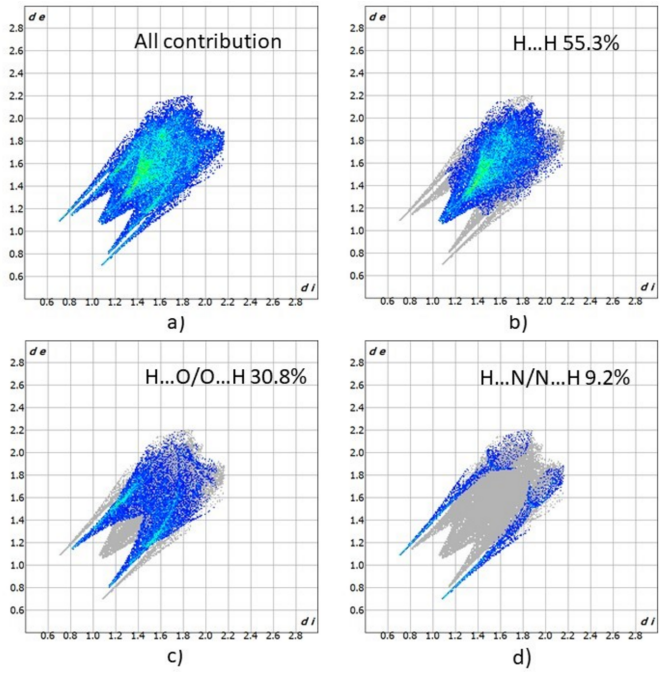


Figure 4
Two-dimensional fingerprint plots for **1** showing (*a*) all interactions, and (*b*)–(*d*) delineated into contributions from other contacts (blue areas) [d_e and d_i represent the distances from a point on the Hirshfeld surface to the nearest atoms outside (external) and inside (internal) the surface, respectively].

O···C/C···O (2.5%) interactions are less impactful in comparison.

In the crystal of **2**, as a result of the O—H···O intermolecular hydrogen bonds (Table 2) the molecules form dimers, which are linked by N—H···O intermolecular hydrogen bonds to form a 3D supramolecular network (Fig. 2).

Fig. 5 shows the Hirshfeld surface of **2** plotted over d_{norm} (normalized contact distance) and Fig. 6 the 2D fingerprint

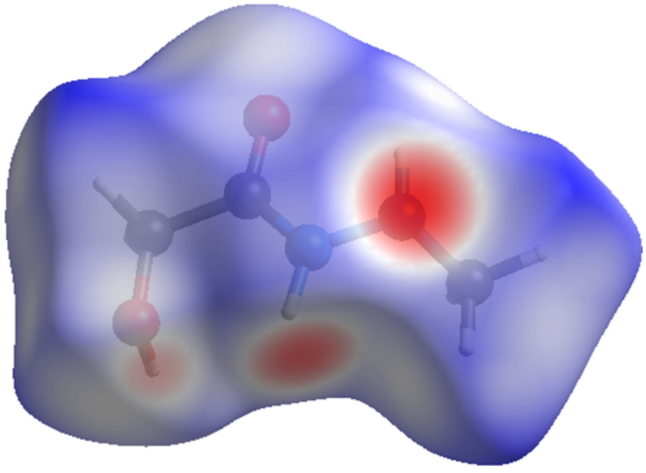


Figure 3
The Hirshfeld surface mapped over d_{norm} for visualizing the intermolecular contacts of compound **1**.

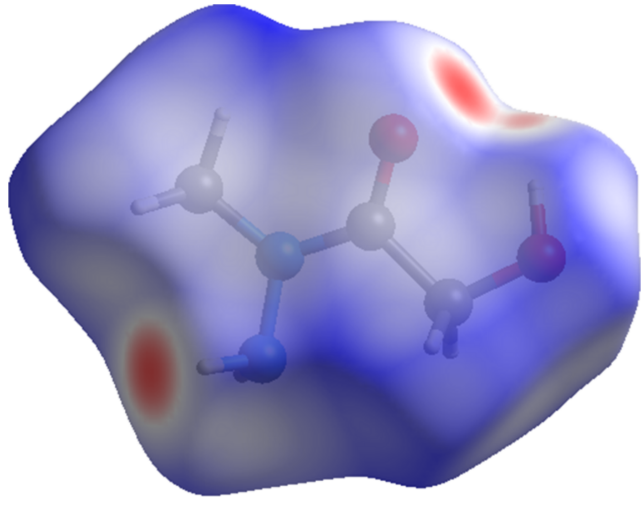


Figure 5
The Hirshfeld surface mapped over d_{norm} for visualizing the intermolecular contacts of compound **2**.

Table 3
Experimental details.

	1	2
Crystal data		
Chemical formula	$C_3H_8N_2O_2$	$C_3H_8N_2O_2$
M_r	104.11	104.11
Crystal system, space group	Orthorhombic, *Pbca*	Monoclinic, *C*2/*c*
Temperature (K)	296	296
a, *b*, *c* (Å)	9.4484 (8), 7.0977 (7), 15.3781 (14)	11.646 (10), 9.304 (10), 10.514 (10)
α, β, γ (°)	90, 90, 90	90, 105.65 (4), 90
V (Å^3)	1031.28 (16)	1097.0 (18)
Z	8	8
Radiation type	Mo *K*α	Mo *K*α
μ (mm^{-1})	0.11	0.11
Crystal size (mm)	0.3 × 0.2 × 0.1	0.2 × 0.15 × 0.09
Data collection		
Diffractometer	Bruker APEXII CCD	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Krause *et al.*, 2015)	Multi-scan (*SADABS*; Krause *et al.*, 2015)
T_{min}, T_{max}	0.602, 0.746	0.554, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	10003, 909, 841	5355, 1259, 503
R_{int}	0.072	0.099
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.595	0.650
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.103, 0.199, 1.34	0.050, 0.126, 0.81
No. of reflections	909	1259
No. of parameters	77	77
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.32, −0.35	0.14, −0.16

Computer programs: *APEX2* and *SAINT* (Bruker, 2008), *SHELXT2018/2* (Sheldrick, 2015*a*), *SHELXL2019/3* (Sheldrick, 2015*b*) and *OLEX2* (Dolomanov *et al.*, 2009).

plots. The strongest contacts, which are visualized on the Hirshfeld surface as the dark-red spots, correspond to the O–H···O and N—H···O hydrogen bonds between molecules. The major contributions to the crystal structure are from the H···H(58.5%) and H···O/O···H (31.7%) interaction. The N···H/H···N (4.0%) and H···C/C···H (3.2%), O···N/N···O interactions are of lower relevance.

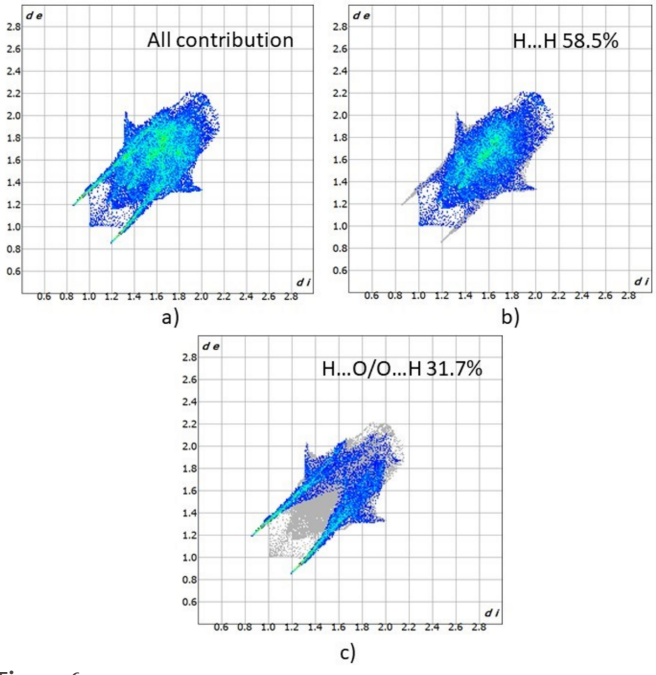


Figure 6
Two-dimensional fingerprint plots for **1** showing (*a*) all interactions, and (*b*)–(*c*) delineated into contributions from other contacts (blue areas) [d_e and d_i represent the distances from a point on the Hirshfeld surface to the nearest atoms outside (external) and inside (internal) the surface, respectively].

4. Database survey

A search of the Cambridge Structural Database (CSD, version 2024.2.0; Groom *et al.*, 2016) confirmed that the title compounds have not been previously published. Since hydrazides are very popular compounds and there are numerous entries in the database, the search was carried out for the specific fragment [OH—C—C(═O)—N—N—H], which represents the title structures albeit without the methyl substituent and excludes structures in which the terminal nitrogen atom is engaged in a double bond. As a result of the search, six structures were found in which the defined fragment bears different substituents: JESVIN (Beckmann & Brooker, 2006); LACBOG (Andre *et al.*, 1993); RAVZIX and RAVZOD (Andre *et al.*, 1997); UVUTIQ (Noshiranzadeh *et al.*, 2017); VOJBUS (Abu-Safieh *et al.*, 2008); WETGEL (Chen *et al.*, 2021). Four of these structures (LACBOG, RAVZIK, RAVZOD, WETGEL) have a pyramidal nitrogen, which is involved in the formation of intermolecular hydrogen bonds similar to what is observed in the crystals of the title compounds.

5. Synthesis and crystallization

To a solution of 12.14 ml (0.3 mol) of methylhydrazine in 50 ml of 2-propanole were added dropwise 9.5 ml (0.1 mol) of ethyl glycolate at room temperature and the obtained solution was heated under reflux for 6 h. After completion of the reaction, the reaction mixture was evaporated under reduced pressure to remove excess of methyl hydrazine and the residual oil was dissolved in 25 ml of 2-propanole for crystallization to obtain (**1**) as white crystals. The filtrate was evaporated under reduced pressure and compound (**2**) was extracted using boiling benzene (5 × 30 ml). The precipitated solid from the combined benzene fractions was filtered off and recrystallized from 25 ml of ethyl acetate to obtain hydrazide (**2**) as white crystals.

2-Hydroxy-*N*'-methylacetohydrazide (1). Yield 3.9 g (37.5%), m.p. 350–3551 K (2-propanole). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.16 (1H, *br.s*, NHNCO), 5.34 (1H, *br.s*, OH), 4.81 [1H, *br.s*, NH(CH_3)], 3.82 (2H, *s*, CH_2), 2.42 (3H, *s*, CH_3). ^{13}C NMR (101 MHz, DMSO-d_6) δ 170.2, 61.0, 38.6. IR data (in KBr, cm^{-1}): 3410, 3296, 2924, 1664, 1444, 1348, 1076, 880, 656, 572. MS (*m*/*z*, CI) 87.0 $[M - OH]^+$,105.0 $[M + H]^+$. Analysis calculated for $C_3H_8N_2O_2$: C, 34.61; H, 7.75; N, 26.91. Found: C, 34.67; H, 7.88; N, 26.90.

2-Hydroxy-*N*-methylacetohydrazide (2). Yield 0.43 g (4.1%), m.p. 352–353 K (EtOAc). ^{1}H NMR (400 MHz, DMSO-d_6) δ 4.62 (2H, *s*, NH_2), 4.17 (2H, *s*, CH_2), 3.00 (3H, *s*, CH_3). ^{13}C NMR (101 MHz, DMSO-d_6) δ 173.3, 59.8, 37.6. IR data (in KBr, cm^{-1}): 3424, 3330, 2930, 1670, 1438, 1398, 1250, 1074, 1074, 808, 620, 572. MS (*m*/*z*, CI) 87.0 $[M - OH]^+$, 105.0 $[M + H]^+$. Analysis calculated for $C_3H_8N_2O_2$: C, 34.61; H, 7.75; N, 26.91. Found: C, 34.66; H, 7.80; N, 26.87.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. The low quality of the data is due to the fact that the quality of the crystals is not very good and we could not obtain bright distant reflections, which somewhat affects the final quantitative parameters·The O- and N-bound hydrogen atoms were identified in difference-Fourier maps and refined isotropically. The other H atoms were placed in calculated positions and refined using a riding model with Uiso(H) = nU_{eq} of the parent atom (n = 1.5 for methyl groups and n = 1.2 for other hydrogen atoms).

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supporting information

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Synthesis, structures and Hirshfeld surface analyses of 2-hydroxy-*N*′-methylacetohydrazide and 2-hydroxy-*N*-methylacetohydrazide

Oleksandr V. Vashchenko, Dmytro M. Khomenko, Viktoriya V. Dyakonenko and Rostyslav D. Lampeka

Computing details

2-Hydroxy-*N*′-methylacetohydrazide (1)

Crystal data

$C_3H_8N_2O_2$
M_r = 104.11
Orthorhombic, *Pbca*
a = 9.4484 (8) Å
b = 7.0977 (7) Å
c = 15.3781 (14) Å
V = 1031.28 (16) Å^3
Z = 8
F(000) = 448
D_x = 1.341 Mg m^{-3}
Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 3322 reflections
θ = 2.7–29.8°
μ = 0.11 mm^{-1}
T = 296 K
Block, colourless
0.3 × 0.2 × 0.1 mm

Data collection

Bruker APEXII CCD diffractometer
Graphite monochromator
φ and *ω* scans
Absorption correction: multi-scan (SADABS; Krause *et al.*, 2015)
T_{min} = 0.602, T_{max} = 0.746
10003 measured reflections
909 independent reflections
841 reflections with $I > 2\sigma(I)$
R_{int} = 0.072
θ_{max} = 25.0°, θ_{min} = 2.7°
h = −11→11
k = −8→8
l = −17→18

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.103
$wR(F^2)$ = 0.199
S = 1.34
909 reflections
77 parameters
0 restraints
Primary atom site location: iterative
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0435P)^2 + 3.1357P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.32 e Å^{-3}
$\Delta\rho_{min}$ = −0.35 e Å^{-3}

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	0.5603 (3)	0.3926 (5)	0.8883 (2)	0.0278 (8)
H1	0.575 (4)	0.275 (7)	0.875 (3)	0.022 (12)*
O2	0.2107 (3)	0.4802 (6)	0.8076 (2)	0.0415 (10)
N1	0.4200 (4)	0.4761 (5)	0.7415 (2)	0.0251 (9)
N2	0.3656 (4)	0.5300 (5)	0.6594 (2)	0.0258 (9)
H2	0.283 (5)	0.534 (7)	0.670 (3)	0.024 (13)*
H1A	0.495 (5)	0.467 (5)	0.741 (3)	0.000 (10)*
C1	0.4115 (4)	0.4115 (7)	0.8943 (3)	0.0317 (12)
H1B	0.389895	0.509200	0.936369	0.038*
H1C	0.372361	0.294298	0.916087	0.038*
C2	0.3402 (4)	0.4592 (6)	0.8099 (3)	0.0251 (10)
C3	0.3999 (5)	0.3911 (7)	0.5928 (3)	0.0371 (13)
H3A	0.352088	0.422889	0.539704	0.056*
H3B	0.370059	0.268531	0.611778	0.056*
H3C	0.500296	0.390350	0.583003	0.056*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0221 (16)	0.0291 (18)	0.0321 (19)	0.0036 (13)	−0.0061 (13)	−0.0040 (14)
O2	0.0129 (16)	0.070 (3)	0.042 (2)	0.0013 (16)	0.0002 (13)	0.0016 (19)
N1	0.0095 (19)	0.038 (2)	0.028 (2)	0.0033 (17)	0.0011 (17)	0.0077 (18)
N2	0.0155 (18)	0.035 (2)	0.027 (2)	0.0017 (17)	0.0006 (16)	0.0096 (17)
C1	0.024 (2)	0.046 (3)	0.025 (3)	0.000 (2)	0.0034 (19)	0.000 (2)
C2	0.022 (2)	0.022 (2)	0.031 (3)	−0.0022 (18)	0.0041 (19)	−0.0043 (19)
C3	0.035 (3)	0.048 (3)	0.028 (3)	−0.007 (2)	0.000 (2)	0.001 (2)

Geometric parameters (Å, º)

O1—H1	0.87 (5)	N2—C3	1.458 (6)
O1—C1	1.415 (5)	C1—H1B	0.9700
O2—C2	1.233 (5)	C1—H1C	0.9700
N1—N2	1.416 (5)	C1—C2	1.502 (6)
N1—H1A	0.71 (4)	C3—H3A	0.9600
N1—C2	1.300 (6)	C3—H3B	0.9600
N2—H2	0.80 (5)	C3—H3C	0.9600
C1—O1—H1	106 (3)	C2—C1—H1B	108.7
N2—N1—H1A	112 (3)	C2—C1—H1C	108.7

C2—N1—N2	122.4 (4)	O2—C2—N1	122.8 (4)
C2—N1—H1A	126 (3)	O2—C2—C1	119.8 (4)
N1—N2—H2	101 (3)	N1—C2—C1	117.4 (4)
N1—N2—C3	111.3 (4)	N2—C3—H3A	109.5
C3—N2—H2	112 (3)	N2—C3—H3B	109.5
O1—C1—H1B	108.7	N2—C3—H3C	109.5
O1—C1—H1C	108.7	H3A—C3—H3B	109.5
O1—C1—C2	114.3 (4)	H3A—C3—H3C	109.5
H1B—C1—H1C	107.6	H3B—C3—H3C	109.5
O1—C1—C2—O2	−179.6 (4)	N2—N1—C2—C1	−176.7 (4)
O1—C1—C2—N1	0.7 (6)	C2—N1—N2—C3	−124.1 (4)
N2—N1—C2—O2	3.5 (7)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···N2^{i}	0.87 (5)	1.90 (5)	2.767 (5)	172 (4)
N1—H1*A*···O2^{ii}	0.71 (4)	2.17 (4)	2.848 (5)	159 (4)

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

2-Hydroxy-*N*-methylacetohydrazide (2)

Crystal data

$C_3H_8N_2O_2$
M_r = 104.11
Monoclinic, *C*2/*c*
a = 11.646 (10) Å
b = 9.304 (10) Å
c = 10.514 (10) Å
β = 105.65 (4)°
V = 1097.0 (18) Å^3
Z = 8

F(000) = 448
D_x = 1.261 Mg m^{-3}
Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 1019 reflections
θ = 2.8–30.1°
μ = 0.11 mm^{-1}
T = 296 K
Block, colourless
0.2 × 0.15 × 0.09 mm

Data collection

Bruker APEXII CCD diffractometer
Graphite monochromator
φ and *ω* scans
Absorption correction: multi-scan (SADABS; Krause *et al.*, 2015)
T_{min} = 0.554, T_{max} = 0.746
5355 measured reflections

1259 independent reflections
503 reflections with $I > 2\sigma(I)$
R_{int} = 0.099
θ_{max} = 27.5°, θ_{min} = 2.9°
h = −14→15
k = −12→12
l = −13→13

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.050
$wR(F^2)$ = 0.126
S = 0.81
1259 reflections
77 parameters

0 restraints
Primary atom site location: dual
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.060P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.14$ e Å^{-3}
$\Delta\rho_{min} = -0.16$ e Å^{-3}

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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.42646 (16)	0.2135 (2)	0.3887 (2)	0.0810 (7)
H1	0.446 (3)	0.251 (4)	0.331 (3)	0.106 (14)*
O2	0.61250 (14)	0.37066 (17)	0.37712 (16)	0.0690 (6)
N1	0.68310 (16)	0.40430 (19)	0.59936 (19)	0.0505 (6)
N2	0.6679 (2)	0.3683 (3)	0.7264 (2)	0.0644 (7)
H2A	0.650 (2)	0.461 (4)	0.765 (3)	0.112 (11)*
H2B	0.742 (2)	0.336 (3)	0.773 (3)	0.082 (9)*
C1	0.50426 (19)	0.2560 (3)	0.5132 (2)	0.0603 (7)
H1A	0.536650	0.171285	0.564015	0.072*
H1B	0.459633	0.310151	0.562713	0.072*
C2	0.60573 (19)	0.3481 (2)	0.4921 (2)	0.0480 (6)
C3	0.7826 (2)	0.4983 (3)	0.5913 (2)	0.0684 (8)
H3A	0.768514	0.593786	0.618254	0.103*
H3B	0.788558	0.500277	0.502060	0.103*
H3C	0.855570	0.462034	0.648489	0.103*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0648 (12)	0.1060 (18)	0.0656 (14)	−0.0291 (11)	0.0064 (11)	−0.0035 (12)
O2	0.0773 (13)	0.0799 (13)	0.0469 (11)	−0.0170 (9)	0.0118 (9)	0.0008 (9)
N1	0.0476 (11)	0.0557 (12)	0.0463 (12)	−0.0016 (10)	0.0095 (9)	0.0005 (10)
N2	0.0650 (16)	0.0812 (18)	0.0458 (14)	0.0090 (12)	0.0128 (12)	−0.0020 (12)
C1	0.0533 (14)	0.0660 (17)	0.0611 (17)	−0.0067 (13)	0.0146 (12)	−0.0046 (14)
C2	0.0486 (14)	0.0461 (15)	0.0464 (15)	0.0058 (11)	0.0079 (12)	0.0002 (12)
C3	0.0605 (16)	0.0652 (18)	0.0749 (19)	−0.0095 (13)	0.0102 (13)	−0.0013 (14)

Geometric parameters (Å, º)

O1—H1	0.78 (4)	N2—H2B	0.92 (3)
O1—C1	1.432 (3)	C1—H1A	0.9700
O2—C2	1.251 (3)	C1—H1B	0.9700
N1—N2	1.434 (3)	C1—C2	1.523 (3)
N1—C2	1.345 (3)	C3—H3A	0.9600
N1—C3	1.472 (3)	C3—H3B	0.9600
N2—H2A	1.00 (3)	C3—H3C	0.9600

C1—O1—H1	110 (2)	C2—C1—H1A	109.6
N2—N1—C3	119.29 (19)	C2—C1—H1B	109.6
C2—N1—N2	117.8 (2)	O2—C2—N1	122.8 (2)
C2—N1—C3	122.9 (2)	O2—C2—C1	119.3 (2)
N1—N2—H2A	105.6 (16)	N1—C2—C1	117.9 (2)
N1—N2—H2B	104.1 (16)	N1—C3—H3A	109.5
H2A—N2—H2B	109 (2)	N1—C3—H3B	109.5
O1—C1—H1A	109.6	N1—C3—H3C	109.5
O1—C1—H1B	109.6	H3A—C3—H3B	109.5
O1—C1—C2	110.3 (2)	H3A—C3—H3C	109.5
H1A—C1—H1B	108.1	H3B—C3—H3C	109.5
O1—C1—C2—O2	−2.5 (3)	N2—N1—C2—C1	2.8 (3)
O1—C1—C2—N1	176.05 (19)	C3—N1—C2—O2	0.3 (3)
N2—N1—C2—O2	−178.7 (2)	C3—N1—C2—C1	−178.2 (2)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O2^{i}	0.78 (4)	2.39 (4)	3.078 (4)	148 (3)
N2—H2*A*···O2^{ii}	1.00 (3)	2.08 (3)	3.062 (4)	169 (2)
N2—H2*B*···O1^{iii}	0.92 (3)	2.21 (3)	3.129 (4)	173 (2)

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