Acta Cryst E CRYSTALLOGRAPHIC COMMUNICATIONS

OPEN ACCESS

ISSN 2056-9890

Crystal structure of 4-formylpyridine semicarbazone hemihydrate

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Received 24 March 2015; accepted 11 April 2015

Edited by M. Lopez-Rodriguez, Universidad de La Laguna, Tenerife

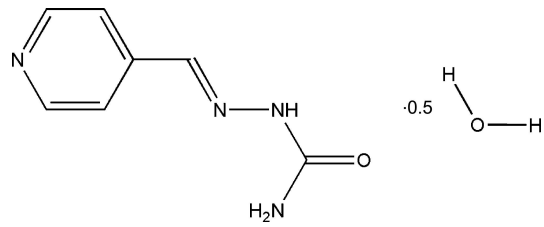
The molecule of the title compound $C_7H_8N_4O{\cdot}0.5H_2O$, alternatively called (*E*)-1-(pyridin-4-ylmethylene)semicarbazide hemihydrate, is in the *E* conformation and is almost planar; the r.m.s. deviation of the positions of the atoms of the pyridine ring from the best-fit plane is 0.0039 Å. The C, N and O atoms of the rest of the molecule sits close on this plane with a largest deviation of 0.115 (4) Å for the O atom of the semicarbazone moiety. There is an intramolecular N—H···N hydrogen bond. In the crystal, molecules are linked into an infinite three-dimensional network by classical N—H···O_s (s = semicarbazone) and O_w—H···N (w = water) hydrogen bonds.

Keywords: crystal structure; 4-formylpyridine semicarbazone hemihydrate; N—H···O hydrogen bonds.

CCDC reference: 1059160

1. Related literature

For the preparation of coordination compounds of 4-formylpyridine semicarbazone with cobalt and zinc, see: Zhou *et al.* (2006*a*,*b*). For the spectroscopic (FT–IR, NMR and UV–vis) properties of 4- and 3-formylpyridine semicarbazones, see: Beraldo *et al.* (2001). For the crystal structure of 4-formylpyridine thiosemicarbazone, see: Restivo & Palenik (1970). For the crystal structures of 2-formylpyridine semicarbazone and several coordination compounds published by our group, see: Garbelini *et al.* (2008, 2009, 2011, 2012). Geometrical analysis was performed with *Mogul* (Bruno *et al.*, 2004).



2. Experimental

2.1. Crystal data

$2C_7H_8N_4O{\cdot}H_2O$
M_r = 346.36
Monoclinic, *C*2/*c*
a = 25.0636 (13) Å
b = 5.3725 (3) Å
c = 13.0124 (7) Å
β = 111.717 (3)°
V = 1627.81 (16) Å^3
Z = 4
Mo *Kα* radiation
μ = 0.11 mm^{-1}
T = 296 K
0.82 × 0.27 × 0.20 mm

2.2. Data collection

Bruker X8 Kappa APEXII diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2014)
T_{min} = 0.860, T_{max} = 0.937
20739 measured reflections
1795 independent reflections
1502 reflections with $I > 2\sigma(I)$
R_{int} = 0.029

2.3. Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.094
S = 1.04
1795 reflections
127 parameters
1 restraint
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.23 e Å^{-3}
$\Delta\rho_{min}$ = −0.20 e Å^{-3}

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*NA*···N3	0.852 (18)	2.273 (18)	2.6541 (16)	107.3 (13)
N1—H1*NB*···O1^{i}	0.917 (19)	1.998 (18)	2.9046 (15)	169.3 (16)
N2—H2*N*···O1^{ii}	0.898 (17)	2.022 (17)	2.9141 (14)	171.9 (16)
O1*W*—H1*WA*···N4	0.87 (3)	2.08 (3)	2.9373 (16)	168 (3)

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

Data collection: *APEX2* (Bruker, 2014); cell refinement: *SAINT* (Bruker, 2014); data reduction: *SAINT*; program(s) used to solve structure: *SHELXT2014* (Sheldrick, 2015); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *DIAMOND* (Crystal Impact, 2014); software used to prepare material for publication: *SHELXL2014*.

Acknowledgements

MHI, RAB and FSN thank CNPq for research fellowships. The diffractometer was supported by the Financiadora de Estudos e Projetos (FINEP, CT Infra 03/2001).

Supporting information for this paper is available from the IUCr electronic archives (Reference: LR2134).

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supporting information

Acta Cryst. (2015). E**71**, o317–o318 [doi:10.1107/S2056989015007276]

Crystal structure of 4-formylpyridine semicarbazone hemihydrate

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S1. Structural commentary

The title molecule crystallizes in the E conformation and is almost ideally planar. The root mean square deviation of the postions of the atoms of the pyridine ring (C3/C4/C5/C6/C7/N4) from the best fit plane is 0.0039 Å. The C, N & O atoms of the rest of the molecule sits close on this plane with the largest deviation of 0.115 (4) Å for O1. The torsion angles of the side arm, C1—N2—N3—C2 (-174.35 (11)°, N2—N3—C2—C3 (-177.87 (10)° and N3—C2—C3—C6 (-1.76 (18)°) reflect this planarity. The shorter bond distance between C2 and N3 of 1.2752 (15) Å compared with 1.3366 (18) Å of N2—C1 along with the double bond character of C1=O1 at 1.2399 (14) Å is in accordance with the carbonyl tautomeric form. The longer than normal double bond length for N2—N3, 1.3706 (13) Å, and shorter than normal single bond length for C2—C3, 1.4616 (15) Å, indicates a resonance of the side chain with the pyridine ring.

There is an extensive three dimensional network of hydrogen bonding interactions formed between the 4-formylpyridine semicarbazone molecules, N2—H2N···O1 = 2.022 (18)Å and N1—H1NB···O1 = 1.998 (19)Å, and between the pyridine N4 atoms of the 4-formylpyridine semicarbazone molecules and the water molecules, O1W—H1WA···N4 = 2.077 (18)Å.

S2. Database survey

An analysis of the geometry of the 4-formylpyridine semicarbazone molecule with Mogul (Bruno *et al.*, 2004) showed all bond lengths, bond angles, dihedral angles and ring geometry as not unusual, with the largest |z-score| = 1.254 for the C6–C3–C2 angle.

S3. Synthesis and crystallization

Reagent grade chemicals were used in this work. The compound was prepared based on a similar reaction for the 2-formylpyridine semicarbazone (Garbelini *et al.* 2009).

In an round bottom flask 2.4 g (21 mmol) of semicarbazide hydrochloride were dissolved in 20 mL of ethanol and 5 mL of water and mixed with 1.7 g (21 mmol) of sodium acetate and 15 mL of water. The mixture was kept under stirring and heating at 70°C until the complete dissolution. Then, 2.0 mL (21 mmol) of 4-formylpyridine was added and the resulting solution was cooled at -15 °C overnight. Colourless crystals were collected by filtration, washed with water and cold ethanol and dried under vacuum. The yield was 2.3 g (67%).

S4. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. Crystal data, data collection and structure refinement details are summarized in Table 1. Crystal data, data collection and structure refinement details are summarized in Table 1. The final structure was refined with SHELXL2014 (Sheldrick, 2015) with anisotropic displacement parameters for all non-hydrogen atoms; hydrogen atoms were refined isotropically as riding atoms at their theoretical ideal positions. Drawings were made with Crystal Impact Diamond 3.

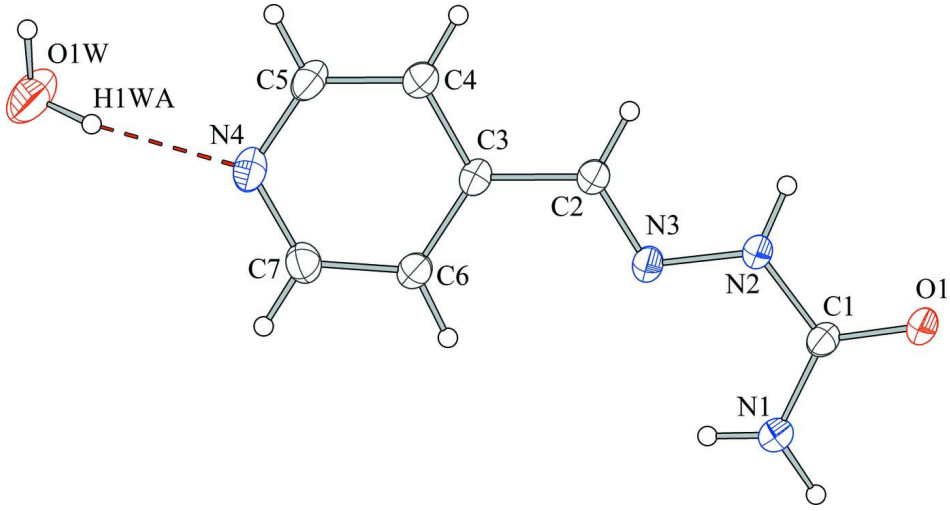

Figure 1

View of the title molecule.Displacement ellipsoids are drawn at the 50% probability level.

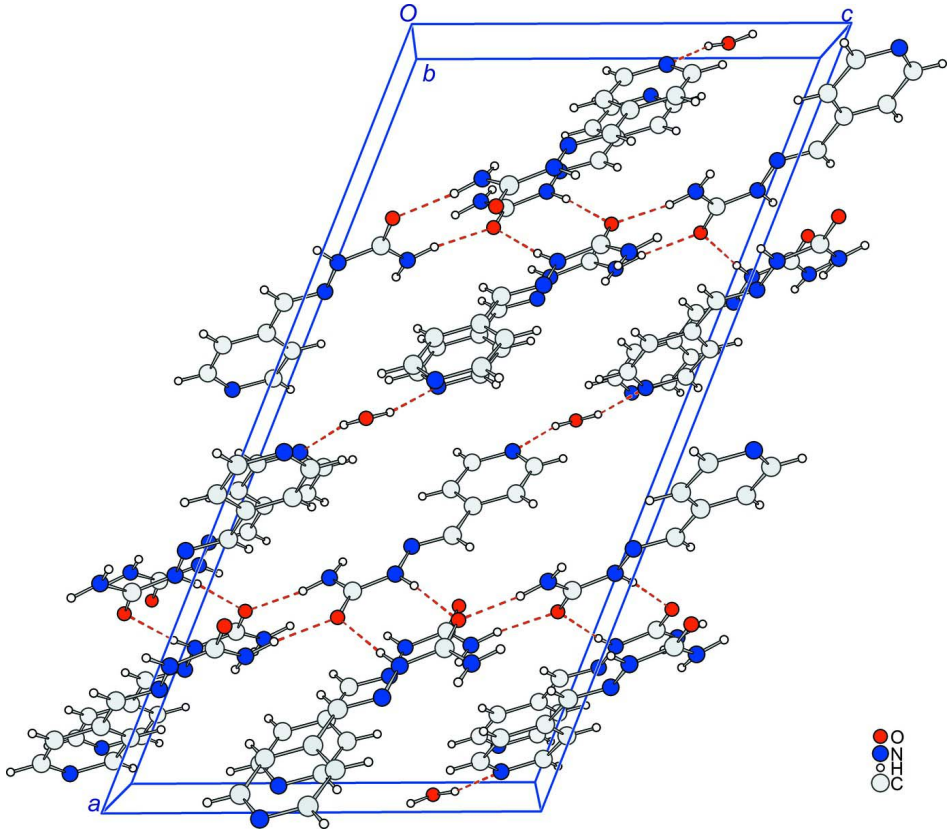

Figure 2

The molecular packing viewed down the crystallograpic *b* axis, with the *a* axis pointed down, showing the three dimensional hydrogen bonding network.

(*E*)-1-(Pyridin-4-ylmethylene)semicarbazide hemihydrate

Crystal data

$2C_7H_8N_4O·H_2O$
M_r = 346.36
Monoclinic, *C*2/*c*
a = 25.0636 (13) Å
b = 5.3725 (3) Å
c = 13.0124 (7) Å
β = 111.717 (3)°
V = 1627.81 (16) Å^3
Z = 4
F(000) = 728
D_x = 1.413 Mg m^{-3}
Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 5941 reflections
θ = 2.8–26.2°
μ = 0.11 mm^{-1}
T = 296 K
Block, clear light colourless
0.82 × 0.27 × 0.20 mm

Data collection

Bruker X8 Kappa APEXII diffractometer
Radiation source: sealed ceramic X ray tube, Siemens KFF
Graphite crystal monochromator
Detector resolution: 8.3333 pixels mm^{-1}
0.5 ° *ω* & *φ* scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2014)
T_{min} = 0.860, T_{max} = 0.937
20739 measured reflections
1795 independent reflections
1502 reflections with $I > 2\sigma(I)$
R_{int} = 0.029
θ_{max} = 27.1°, θ_{min} = 1.8°
h = −32→32
k = −6→6
l = −16→16

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.094
S = 1.04
1795 reflections
127 parameters
1 restraint
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0436P)^2 + 0.8364P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.23 e Å^{-3}
$\Delta\rho_{min}$ = −0.20 e Å^{-3}
Extinction correction: *SHELXL*
Extinction coefficient: 0.0067 (8)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.74966 (4)	−0.16017 (16)	0.36432 (7)	0.0411 (2)
N1	0.70517 (5)	0.2096 (2)	0.30449 (9)	0.0410 (3)
H1NA	0.6859 (8)	0.326 (3)	0.3188 (14)	0.061*
H1NB	0.7226 (7)	0.234 (3)	0.2545 (15)	0.061*
N2	0.69806 (5)	0.00971 (19)	0.45499 (9)	0.0373 (3)
H2N	0.7110 (7)	−0.107 (3)	0.5079 (14)	0.056*

N3	0.66491 (4)	0.20246 (18)	0.46659 (8)	0.0336 (3)
N4	0.54246 (5)	0.7238 (2)	0.61921 (10)	0.0430 (3)
C1	0.71939 (5)	0.0154 (2)	0.37260 (9)	0.0315 (3)
C2	0.65096 (5)	0.1908 (2)	0.55129 (10)	0.0329 (3)
H2	0.6646	0.0596	0.6007	0.039*
C3	0.61410 (5)	0.3783 (2)	0.57272 (9)	0.0309 (3)
C4	0.59797 (5)	0.3495 (2)	0.66315 (10)	0.0374 (3)
H4	0.6108	0.2134	0.71	0.045*
C5	0.56274 (6)	0.5251 (3)	0.68271 (11)	0.0431 (3)
H5	0.5526	0.5034	0.744	0.052*
C6	0.59294 (5)	0.5840 (2)	0.50545 (10)	0.0369 (3)
H6	0.6025	0.6106	0.4437	0.044*
C7	0.55757 (6)	0.7483 (2)	0.53140 (11)	0.0411 (3)
H7	0.5434	0.8843	0.4851	0.049*
O1W	0.5	1.0598 (3)	0.75	0.1046 (9)
H1WA	0.5078 (14)	0.965 (5)	0.703 (2)	0.157*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0538 (6)	0.0380 (5)	0.0420 (5)	0.0108 (4)	0.0303 (4)	0.0010 (4)
N1	0.0519 (7)	0.0410 (6)	0.0391 (6)	0.0099 (5)	0.0274 (5)	0.0071 (5)
N2	0.0484 (6)	0.0338 (5)	0.0396 (6)	0.0118 (5)	0.0278 (5)	0.0057 (4)
N3	0.0372 (5)	0.0318 (5)	0.0370 (5)	0.0045 (4)	0.0198 (4)	−0.0008 (4)
N4	0.0427 (6)	0.0411 (6)	0.0521 (7)	0.0027 (5)	0.0257 (5)	−0.0070 (5)
C1	0.0351 (6)	0.0328 (6)	0.0304 (6)	−0.0009 (5)	0.0164 (5)	−0.0032 (4)
C2	0.0353 (6)	0.0327 (6)	0.0349 (6)	0.0026 (5)	0.0178 (5)	0.0007 (4)
C3	0.0304 (6)	0.0318 (6)	0.0334 (6)	−0.0030 (4)	0.0150 (5)	−0.0058 (4)
C4	0.0397 (7)	0.0393 (6)	0.0385 (6)	0.0015 (5)	0.0208 (5)	0.0015 (5)
C5	0.0462 (7)	0.0492 (7)	0.0443 (7)	−0.0004 (6)	0.0289 (6)	−0.0046 (6)
C6	0.0427 (7)	0.0369 (6)	0.0363 (6)	0.0018 (5)	0.0206 (5)	−0.0003 (5)
C7	0.0435 (7)	0.0339 (6)	0.0472 (7)	0.0041 (5)	0.0185 (6)	0.0000 (5)
O1W	0.200 (3)	0.0427 (9)	0.1390 (19)	0	0.142 (2)	0

Geometric parameters (Å, º)

O1—C1	1.2399 (14)	C2—H2	0.93
N1—C1	1.3294 (16)	C3—C4	1.3870 (16)
N1—H1NA	0.854 (18)	C3—C6	1.3875 (17)
N1—H1NB	0.917 (19)	C4—C5	1.3789 (17)
N2—C1	1.3639 (15)	C4—H4	0.93
N2—N3	1.3706 (13)	C5—H5	0.93
N2—H2N	0.899 (17)	C6—C7	1.3789 (17)
N3—C2	1.2752 (15)	C6—H6	0.93
N4—C5	1.3301 (18)	C7—H7	0.93
N4—C7	1.3366 (18)	O1W—H1WA	0.874 (17)
C2—C3	1.4616 (15)		

C1—N1—H1NA	117.8 (12)	C4—C3—C2	119.22 (11)
C1—N1—H1NB	120.2 (10)	C6—C3—C2	123.34 (10)
H1NA—N1—H1NB	120.5 (16)	C5—C4—C3	119.20 (12)
C1—N2—N3	119.97 (10)	C5—C4—H4	120.4
C1—N2—H2N	118.8 (11)	C3—C4—H4	120.4
N3—N2—H2N	120.3 (11)	N4—C5—C4	123.92 (12)
C2—N3—N2	115.43 (10)	N4—C5—H5	118.0
C5—N4—C7	116.50 (11)	C4—C5—H5	118.0
O1—C1—N1	124.12 (11)	C7—C6—C3	119.07 (11)
O1—C1—N2	118.79 (10)	C7—C6—H6	120.5
N1—C1—N2	117.08 (10)	C3—C6—H6	120.5
N3—C2—C3	121.72 (11)	N4—C7—C6	123.87 (12)
N3—C2—H2	119.1	N4—C7—H7	118.1
C3—C2—H2	119.1	C6—C7—H7	118.1
C4—C3—C6	117.43 (11)		

C1—N2—N3—C2	−174.35 (11)	C2—C3—C4—C5	−179.38 (11)
N3—N2—C1—O1	179.42 (10)	C7—N4—C5—C4	0.5 (2)
N3—N2—C1—N1	−1.82 (17)	C3—C4—C5—N4	0.4 (2)
N2—N3—C2—C3	−177.87 (10)	C4—C3—C6—C7	0.24 (17)
N3—C2—C3—C4	176.79 (11)	C2—C3—C6—C7	178.81 (11)
N3—C2—C3—C6	−1.76 (18)	C5—N4—C7—C6	−1.1 (2)
C6—C3—C4—C5	−0.74 (18)	C3—C6—C7—N4	0.7 (2)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
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N2—H2*N*···O1^{ii}	0.898 (17)	2.022 (17)	2.9141 (14)	171.9 (16)
O1*W*—H1*WA*···N4	0.87 (3)	2.08 (3)	2.9373 (16)	168 (3)

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