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N′-[(*E*)-4-Methylbenzylidene]pyridine-4-carbohydrazide monohydrate

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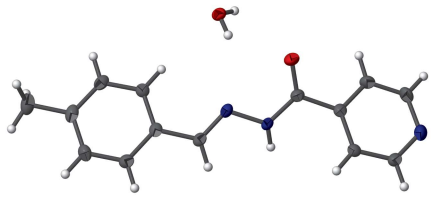
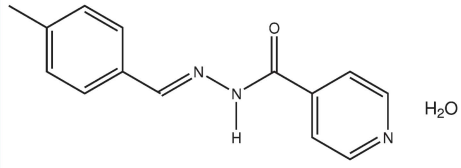
Structural data: full structural data are available from iucrdata.iucr.org

In the title hydrate, $C_{14}H_{13}N_3O\cdot H_2O$, the C=N double bond adopts an *E* conformation and the dihedral angle between the aromatic rings is 16.36 (10)°. In the crystal, N—H···O, O—H···O and O—H···N hydrogen bonds link the components into (001) sheets.

3D view



Chemical scheme



Structure description

N-Acylhydrazone (NAH) derivatives show various biological properties including anti-tumor (Maia *et al.*, 2014), antimalarial (Melnyk *et al.*, 2006) and anti-inflammatory (Moldovan *et al.*, 2011) activities and, therefore, are potential therapeutic agents.

The method of synthesis of the title compound was a condensation reaction between a hydrazide and an aldehyde, and the asymmetric unit of the crystal structure is made up of one molecule of *N*′-[(*E*)-(4-methylphenyl) methylidene] pyridine-4-carbohydrazide and one water molecule (Fig. 1).

The title compound presents an (*E*) conformation relative to the C8=N2 bond, with the pyridine ring and the central spacer unit (C4–C8–N2–N1–C9–C10) being essentially planar (r.m.s. deviations of 0.006 and 0.066 Å, respectively), as in other reported NAH derivatives (Bhat *et al.*, 2012; de Souza *et al.*, 2007; Shafiq *et al.*, 2009). The dihedral angle between the pyridine ring and the spacer unit is 16.36 (10)° and the structure shows the following torsion angles: C5—C4—C8—N2 = −169.34 (18)°, C4—C8—N2—N1 = −172.76 (15)°, C8—N2—N1—C9 = −173.08 (17)°, N2—N1—C9—C10 = −172.66 (16)° and N1—C9—C10—C11 = −33.6 (3)°.

In the crystal, hydrogen bonds occur between the NAH and water molecules (Table 1). The N1—H1···O2 bond is nearly linear (173°) as is observed in analogous monohydrated NAH structures bearing different phenyl substituents (Bhat *et al.*, 2012; de Souza *et al.*,

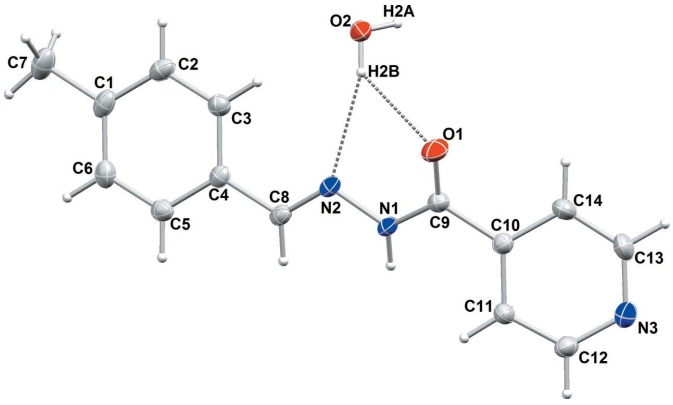


Figure 1
The molecular structure of the title compound with 50% probability displacement ellipsoids. Hydrogen bonds are shown as dashed lines

2007). The present compound has O2—H2*A*···N3 and N1—H1···O2 hydrogen bonds forming a chain in the [010] direction, while another chain is built along [100] from O2—H2*B*···N2, O2—H2*B*···O1 and N1—H1···O2 hydrogen bonds (Fig. 2). Taken together, (001) sheets arise.

Synthesis and crystallization

An equimolar mixture of isonicotinic acid hydrazide and 4-methylbenzaldehyde were refluxed in ethanol for 10 h, followed by solvent removal in a rotatory evaporator. The residue was washed three times with a hot 1:1 mixture of hexane–ethyl acetate and the residual solvent was removed by filtration. Light brown needles (m.p. 192–194°C) were obtained by recrystallization from reagent-grade ethanol (ethanol/water, 97:3 *v*/*v*) solution.

^{1}H NMR (d_6-DMSO, 500 MHz) *d* 12.04 (*s*, 1H, H1); 8.46 (*s*, 1H, H8); 8.79 (*dd*, *J* = 1.6 and 4.5 Hz, 2H, H12 and H13); 7.85 (*dd*, *J* = 1.6 and 4.5 Hz, 2H, H11 and H14); 7.66 (*d*, *J* = 8 Hz, 2H, H3 and H5); 7.30 (*d*, *J* = 8 Hz, 2H, H2 and H6); 2.37 (*s*, 3H, H7).

^{13}C NMR (d_6-DMSO, 125 MHz) *d* 161.9 (C9), 150.78 (C12, C13), 149.53 (C8), 141.02 (C10), 140.77 (C4), 131.84 (C1), 129.99 (C3, C5), 127.71 (C2, C6), 122.05 (C11, C14), 21.53 (C7).

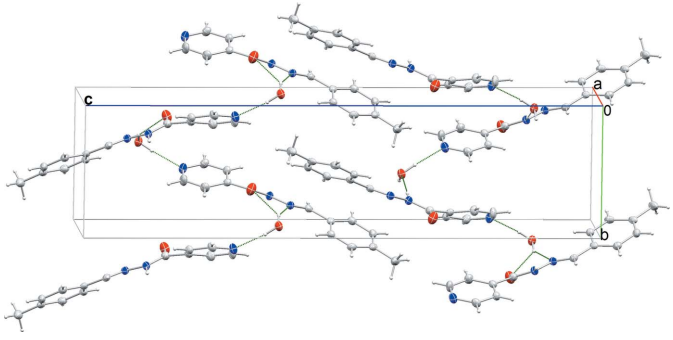


Figure 2
Crystal packing of the title compound, showing hydrogen-bonding interactions as dashed lines.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O2^{i}	0.85 (2)	1.93 (2)	2.775 (2)	173 (2)
O2—H2*A*···N3^{ii}	0.87 (3)	1.97 (3)	2.832 (2)	169 (2)
O2—H2*B*···O1	0.84 (3)	2.25 (3)	2.919 (2)	136 (2)
O2—H2*B*···N2	0.84 (3)	2.44 (3)	3.184 (2)	147 (2)

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{14}H_{13}N_3O\cdot H_2O$
M_r	257.29
Crystal system, space group	Orthorhombic, $P2_12_12_1$
Temperature (K)	150
a, *b*, *c* (Å)	6.3268 (8), 7.2868 (10), 28.272 (4)
V (Å^3)	1303.4 (3)
Z	4
Radiation type	Mo *Kα*
μ (mm^{-1})	0.09
Crystal size (mm)	0.30 × 0.23 × 0.11
Data collection	
Diffractometer	Bruker *APEX* CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2010)
T_{min}, T_{max}	0.701, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	13953, 2546, 2426
R_{int}	0.023
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.617
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.030, 0.079, 1.06
No. of reflections	2546
No. of parameters	182
H-atom treatment	H-atom parameters not refined
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.17, −0.15

Computer programs: *APEX2* and *SAINT* (Bruker, 2010), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *Mercury* (Macrae *et al.*, 2006), *OLEX2* (Dolomanov *et al.*, 2003) and *publCIF* (Westrip, 2010).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Acknowledgements

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full crystallographic data

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Crystal data

$C_{14}H_{13}N_3O·H_2O$
M_r = 257.29
Orthorhombic, $P2_12_12_1$
a = 6.3268 (8) Å
b = 7.2868 (10) Å
c = 28.272 (4) Å
V = 1303.4 (3) Å^3
Z = 4
F(000) = 544
D_x = 1.311 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 6782 reflections
θ = 2.9–28.1°
μ = 0.09 mm^{-1}
T = 150 K
Block, light brown
0.30 × 0.23 × 0.11 mm

Data collection

Bruker APEX CCD diffractometer
Radiation source: fine-focus sealed tube
Detector resolution: 8.3333 pixels mm^{-1}
phi and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2010)
T_{min} = 0.701, T_{max} = 0.746
13953 measured reflections
2546 independent reflections
2426 reflections with $I > 2\sigma(I)$
R_{int} = 0.023
θ_{max} = 26.0°, θ_{min} = 1.4°
h = −7→5
k = −8→8
l = −34→34

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.030
$wR(F^2)$ = 0.079
S = 1.06
2546 reflections
182 parameters
0 restraints
Hydrogen site location: mixed
H-atom parameters not refined
$w = 1/[\sigma^2(F_o^2) + (0.0433P)^2 + 0.2529P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.17 e Å^{-3}
$\Delta\rho_{min}$ = −0.15 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	0.6820 (2)	0.1768 (2)	0.82914 (5)	0.0324 (4)
N1	0.3922 (3)	0.2683 (2)	0.87038 (5)	0.0191 (3)
H1	0.264 (4)	0.305 (3)	0.8707 (7)	0.023*
N2	0.5160 (2)	0.3223 (2)	0.90852 (5)	0.0198 (3)
N3	0.1151 (3)	0.0996 (3)	0.70795 (6)	0.0287 (4)
C1	0.7141 (3)	0.6081 (3)	1.06567 (7)	0.0243 (4)
C2	0.8199 (3)	0.5942 (3)	1.02236 (7)	0.0239 (4)
H2	0.9561	0.6410	1.0195	0.029*
C3	0.7252 (3)	0.5121 (3)	0.98366 (7)	0.0208 (4)
H3	0.7981	0.5045	0.9552	0.025*
C4	0.5213 (3)	0.4408 (2)	0.98708 (6)	0.0189 (4)
C5	0.4149 (3)	0.4541 (3)	1.03019 (6)	0.0221 (4)
H5	0.2787	0.4073	1.0331	0.027*
C6	0.5113 (3)	0.5370 (3)	1.06885 (7)	0.0248 (4)
H6	0.4385	0.5448	1.0974	0.030*
C7	0.8197 (4)	0.6995 (3)	1.10712 (7)	0.0340 (5)
H7A	0.9438	0.6316	1.1158	0.051*
H7B	0.7237	0.7029	1.1334	0.051*
H7C	0.8589	0.8225	1.0986	0.051*
C8	0.4135 (3)	0.3616 (2)	0.94615 (6)	0.0194 (4)
H8	0.2689	0.3396	0.9475	0.023*
C9	0.4911 (3)	0.2065 (3)	0.83144 (6)	0.0209 (4)
C10	0.3516 (3)	0.1727 (3)	0.78939 (7)	0.0198 (4)
C11	0.1448 (3)	0.1115 (3)	0.79248 (7)	0.0213 (4)
H11	0.0809	0.0950	0.8218	0.026*
C12	0.0350 (3)	0.0753 (3)	0.75110 (7)	0.0246 (4)
H12	−0.1027	0.0314	0.7536	0.030*
C13	0.3135 (3)	0.1616 (3)	0.70536 (7)	0.0308 (5)
H13	0.3714	0.1810	0.6755	0.037*
C14	0.4377 (3)	0.1987 (3)	0.74447 (7)	0.0265 (4)
H14	0.5758	0.2401	0.7409	0.032*
O2	0.9875 (2)	0.4131 (2)	0.87689 (5)	0.0234 (3)
H2A	0.972 (4)	0.478 (3)	0.8513 (9)	0.035*
H2B	0.878 (4)	0.348 (4)	0.8789 (8)	0.035*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0160 (7)	0.0502 (10)	0.0311 (7)	0.0006 (7)	−0.0008 (6)	−0.0098 (7)
N1	0.0147 (7)	0.0234 (9)	0.0190 (8)	0.0002 (6)	−0.0037 (6)	−0.0016 (6)
N2	0.0182 (7)	0.0210 (8)	0.0201 (8)	−0.0004 (6)	−0.0052 (6)	0.0000 (6)
N3	0.0286 (9)	0.0357 (10)	0.0218 (8)	−0.0023 (8)	−0.0022 (7)	−0.0051 (8)
C1	0.0321 (10)	0.0163 (9)	0.0244 (9)	0.0019 (8)	−0.0099 (8)	0.0015 (7)
C2	0.0220 (9)	0.0185 (10)	0.0312 (10)	−0.0016 (9)	−0.0060 (8)	0.0010 (8)
C3	0.0222 (9)	0.0188 (10)	0.0214 (9)	0.0003 (8)	0.0003 (7)	0.0012 (7)

C4	0.0209 (9)	0.0151 (9)	0.0206 (9)	0.0029 (8)	−0.0033 (7)	0.0018 (7)
C5	0.0202 (8)	0.0216 (10)	0.0246 (9)	−0.0001 (8)	−0.0011 (8)	0.0034 (8)
C6	0.0329 (10)	0.0230 (10)	0.0185 (8)	0.0023 (9)	−0.0006 (8)	0.0011 (7)
C7	0.0471 (13)	0.0257 (11)	0.0292 (11)	−0.0039 (10)	−0.0114 (10)	−0.0015 (9)
C8	0.0187 (8)	0.0182 (10)	0.0212 (9)	−0.0002 (7)	−0.0039 (7)	0.0036 (7)
C9	0.0178 (9)	0.0216 (9)	0.0232 (9)	−0.0013 (8)	0.0001 (7)	−0.0005 (7)
C10	0.0197 (9)	0.0181 (9)	0.0215 (9)	0.0016 (7)	0.0002 (7)	−0.0020 (8)
C11	0.0200 (9)	0.0240 (10)	0.0199 (9)	−0.0001 (7)	0.0020 (7)	−0.0009 (8)
C12	0.0198 (9)	0.0282 (10)	0.0259 (9)	−0.0023 (8)	−0.0001 (8)	−0.0048 (9)
C13	0.0333 (10)	0.0412 (13)	0.0179 (9)	−0.0055 (9)	0.0050 (9)	0.0001 (9)
C14	0.0216 (9)	0.0311 (11)	0.0268 (10)	−0.0054 (8)	0.0043 (8)	0.0000 (9)
O2	0.0171 (6)	0.0320 (8)	0.0211 (7)	−0.0004 (6)	−0.0024 (5)	0.0034 (6)

Geometric parameters (Å, º)

O1—C9	1.228 (2)	C5—H5	0.9300
N1—C9	1.344 (2)	C6—H6	0.9300
N1—N2	1.390 (2)	C7—H7A	0.9600
N1—H1	0.85 (2)	C7—H7B	0.9600
N2—C8	1.278 (2)	C7—H7C	0.9600
N3—C12	1.333 (3)	C8—H8	0.9300
N3—C13	1.337 (3)	C9—C10	1.501 (3)
C1—C6	1.387 (3)	C10—C11	1.385 (3)
C1—C2	1.399 (3)	C10—C14	1.395 (3)
C1—C7	1.504 (3)	C11—C12	1.386 (3)
C2—C3	1.383 (3)	C11—H11	0.9300
C2—H2	0.9300	C12—H12	0.9300
C3—C4	1.394 (3)	C13—C14	1.383 (3)
C3—H3	0.9300	C13—H13	0.9300
C4—C5	1.396 (3)	C14—H14	0.9300
C4—C8	1.462 (2)	O2—H2A	0.87 (3)
C5—C6	1.390 (3)	O2—H2B	0.84 (3)
C9—N1—N2	117.89 (15)	C1—C7—H7C	109.5
C9—N1—H1	123.9 (14)	H7A—C7—H7C	109.5
N2—N1—H1	115.9 (14)	H7B—C7—H7C	109.5
C8—N2—N1	115.04 (15)	N2—C8—C4	120.71 (17)
C12—N3—C13	116.90 (17)	N2—C8—H8	119.6
C6—C1—C2	118.19 (18)	C4—C8—H8	119.6
C6—C1—C7	121.7 (2)	O1—C9—N1	124.07 (18)
C2—C1—C7	120.07 (19)	O1—C9—C10	120.47 (17)
C3—C2—C1	121.08 (18)	N1—C9—C10	115.46 (16)
C3—C2—H2	119.5	C11—C10—C14	118.06 (17)
C1—C2—H2	119.5	C11—C10—C9	123.94 (17)
C2—C3—C4	120.45 (18)	C14—C10—C9	117.97 (16)
C2—C3—H3	119.8	C10—C11—C12	118.80 (18)
C4—C3—H3	119.8	C10—C11—H11	120.6
C3—C4—C5	118.76 (17)	C12—C11—H11	120.6

C3—C4—C8	121.58 (17)	N3—C12—C11	123.81 (17)
C5—C4—C8	119.58 (16)	N3—C12—H12	118.1
C6—C5—C4	120.34 (18)	C11—C12—H12	118.1
C6—C5—H5	119.8	N3—C13—C14	123.77 (19)
C4—C5—H5	119.8	N3—C13—H13	118.1
C1—C6—C5	121.17 (19)	C14—C13—H13	118.1
C1—C6—H6	119.4	C13—C14—C10	118.65 (17)
C5—C6—H6	119.4	C13—C14—H14	120.7
C1—C7—H7A	109.5	C10—C14—H14	120.7
C1—C7—H7B	109.5	H2A—O2—H2B	106 (2)
H7A—C7—H7B	109.5		

C9—N1—N2—C8	−173.08 (17)	N2—N1—C9—O1	7.9 (3)
C6—C1—C2—C3	0.1 (3)	N2—N1—C9—C10	−172.66 (16)
C7—C1—C2—C3	−179.5 (2)	O1—C9—C10—C11	145.9 (2)
C1—C2—C3—C4	−0.1 (3)	N1—C9—C10—C11	−33.6 (3)
C2—C3—C4—C5	0.1 (3)	O1—C9—C10—C14	−32.0 (3)
C2—C3—C4—C8	176.90 (18)	N1—C9—C10—C14	148.60 (19)
C3—C4—C5—C6	0.0 (3)	C14—C10—C11—C12	1.4 (3)
C8—C4—C5—C6	−176.91 (17)	C9—C10—C11—C12	−176.45 (18)
C2—C1—C6—C5	−0.1 (3)	C13—N3—C12—C11	0.4 (3)
C7—C1—C6—C5	179.5 (2)	C10—C11—C12—N3	−1.5 (3)
C4—C5—C6—C1	0.0 (3)	C12—N3—C13—C14	0.8 (3)
N1—N2—C8—C4	−172.76 (15)	N3—C13—C14—C10	−0.9 (3)
C3—C4—C8—N2	13.9 (3)	C11—C10—C14—C13	−0.2 (3)
C5—C4—C8—N2	−169.34 (18)	C9—C10—C14—C13	177.69 (19)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O2^{i}	0.85 (2)	1.93 (2)	2.775 (2)	173 (2)
O2—H2*A*···N3^{ii}	0.87 (3)	1.97 (3)	2.832 (2)	169 (2)
O2—H2*B*···O1	0.84 (3)	2.25 (3)	2.919 (2)	136 (2)
O2—H2*B*···N2	0.84 (3)	2.44 (3)	3.184 (2)	147 (2)

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