organic compounds

N′-Hydroxypyridine-2-carboximidamide

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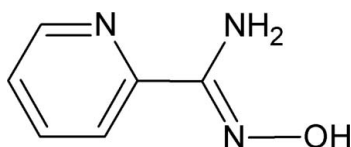Correspondence e-mail: drsreenivasa@yahoo.co.in

The title molecule, $C_6H_7N_3O$, is almost planar (r.m.s. deviation = 0.0068 Å) and adopts an E conformation about the C=N double bond. In the crystal, molecules are linked by pairs of strong N—H⋯N hydrogen bonds, forming inversion dimers with $R_2^2(10)$ motifs. The dimers are further linked into $C(3)$ chains through O—H⋯N hydrogen bonds.

Related literature

For the pharmaceutical and biological activity of substituted N′-hydroxybenzamidines and 1,2,4-oxadiazole derivatives, see: Kundu et al. (2012); Sakamoto et al. (2007); Tyrkov & Sukhenko (2004). For a related structure, see: Sreenivasa et al. (2012)

Experimental

Crystal data

$C_6H_7N_3O$	c = 13.003 (3) Å
M_r = 137.15	β = 105.468 (12)°
Monoclinic, $C2/c$	V = 1242.0 (5) Å^3
a = 21.367 (5) Å	Z = 8
b = 4.6382 (11) Å	Mo $K\alpha$ radiation

μ = 0.11 mm^{-1}	0.33 × 0.25 × 0.20 mm
T = 293 K	

Data collection

Bruker APEXII CCD area-detector diffractometer	8242 measured reflections
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)	1086 independent reflections
T_{min} = 0.966, T_{max} = 0.979	982 reflections with $I > 2\sigma(I)$
	R_{int} = 0.038

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.031	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2)$ = 0.081	
S = 1.08	$\Delta\rho_{max}$ = 0.19 e Å^{-3}
1086 reflections	$\Delta\rho_{min}$ = −0.18 e Å^{-3}
103 parameters	
2 restraints	

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O1—H1⋯N3[i]	0.903 (18)	1.859 (19)	2.7537 (14)	170.5 (17)
N2—H2N2⋯N1[ii]	0.86 (1)	2.44 (1)	3.1753 (16)	144 (1)

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

Data collection: *APEX2* (Bruker, 2009); cell refinement: *APEX2* and *SAINT-Plus* (Bruker, 2009); data reduction: *SAINT-Plus* and *XPREP* (Bruker, 2009); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *Mercury* (Macrae et al., 2008); software used to prepare material for publication: *SHELXL97*.

References

Bruker (2009). *APEX2, SADABS, SAINT-Plus* and *XPREP*. Bruker AXS Inc., Madison, Wisconsin, USA.

Kundu, M., Singh, J., Singh, B., Ghosh, T., Maiti, B. C. & Maity, T. K. (2012). *Indian J. Chem. Sect. B*, **51**, 493–497.

Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., van de Streek, J. & Wood, P. A. (2008). *J. Appl. Cryst.* **41**, 466–470.

Sakamoto, T., Cullen, M. D., Hartman, T. L., Watson, K. M., Buckheit, R. W., Pannecouque, C., DeClercq, E. & Cushman, M. (2007). *J. Med. Chem.* **50**, 3314–3319.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Sreenivasa, S., ManojKumar, K. E., Suchetan, P. A., Mohan, N. R. & Palakshamurthy, B. S. (2012). *Acta Cryst.* E**68**, o3402.

Tyrkov, A. G. & Sukhenko, L. T. (2004). *Pharm. Chem. J..* **38**(7), 30–38.

supporting information

N′-Hydroxypyridine-2-carboximidamide

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S1. Comment

Substituted *N*′-hydroxybenzamidines are important intermediates obtained during the synthesis of pharmaceutically important 1,2,4-oxadiazole derivatives (Kundu *et al.*, 2012). 1,2,4-Oxadiazole derivatives are well known for their biological activities such as anti-HIV (Sakamoto *et al.*, 2007) and anti-microbial (Tyrkov *et al.*, 2004). In this view, we synthesized the title compound to study its crystal structure.

The title compound, (I), crystalizes with a single molecule in the asymmetric unit. This is in contrast to (*E*)-3-chloro-*N*′-hydroxybenzene-1-carboximidamide, (II), (Sreenivasa *et al.*, 2012) which crystalizes with two molecules in its asymmetric unit. Compound (I) adopts an *E* configuration across the C=N double bond, as the OH group and the benzene ring are on opposite sides of the double bond, while the H atom of the hydroxy group is directed away from the NH$_2$ group. This is similar as observed in (II). In the packing, the molecules are linked to one another through strong intermolecular N—H···N hydrogen bonds into $R_2^2(10)$ motifs forming inversion dimers. The dimers are further linked into C(3) chains through O—H···N hydrogen bonds.

S2. Experimental

To a solution of 2-cyanopyridine (1 mmol) in ethanol was added triethyl amine (2.5 mmol) and hydroxyl amine hydro-chloride, NH$_2$OH.HCl (3.5 mmol). The reaction mixture was stirred at room temperature for 12hrs. (The reaction was monitored by TLC). The solvent was removed and the crude product was purified by column chromatography using hexane and ethyl acetate as the eluent.

Single crystals required for X-ray diffraction measurements were obtained from slow evaporation of the solution of the compound in a mixture of ethanol and dichloromethane (1:4).

S3. Refinement

The hydrogen atoms attached to N and O were located in difference maps and refined isotropically. The remaining H atoms were positioned geometrically and refined using a riding model, with C–H = 0.93 Å with isotropic displacement parameters set to 1.2 times of the U_{eq} of the parent atom.
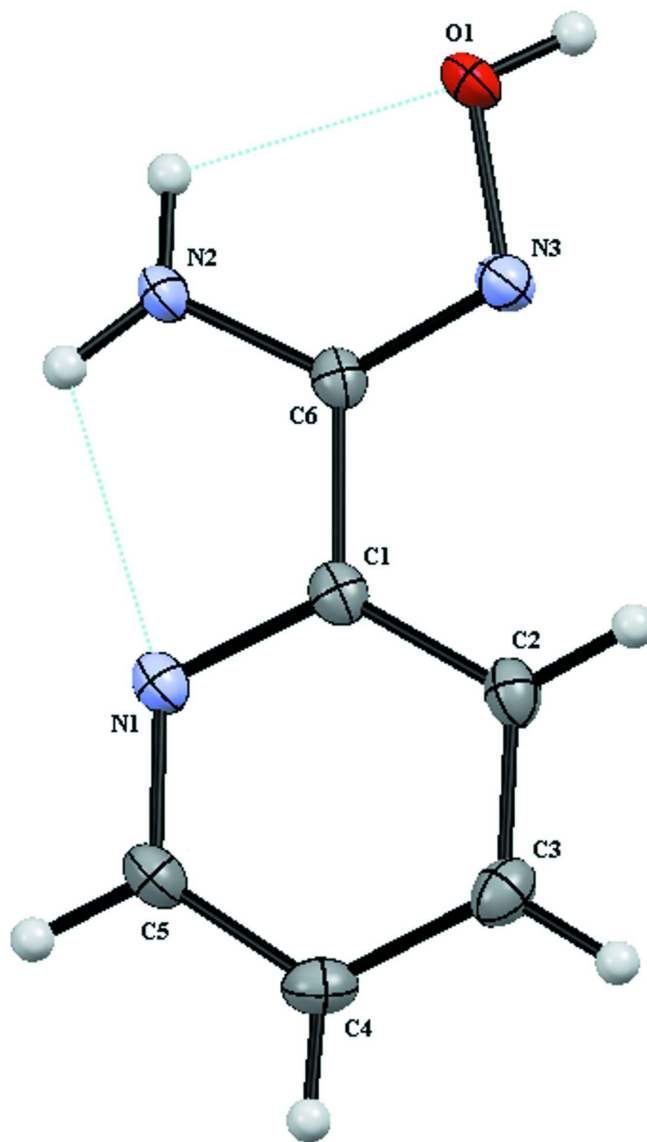
Figure 1

Molecular structure of the title compound, showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level.
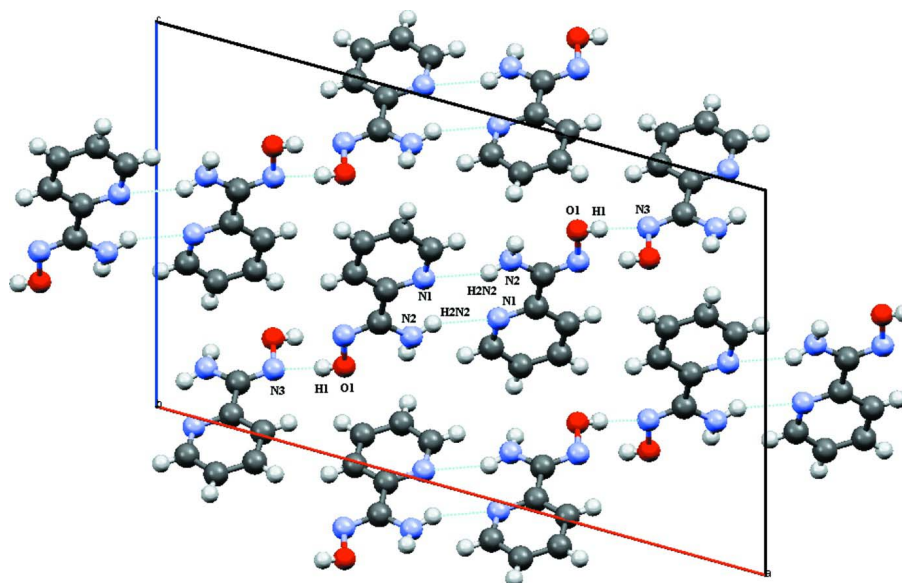
Figure 2

Packing of molecules displaying $R_2^2(10)$ loops and C(3) chains.

N′-**Hydroxypyridine-2-carboximidamide**

Crystal data

$C_6H_7N_3O$	$F(000) = 576$
$M_r = 137.15$	prism
Monoclinic, $C2/c$	$D_x = 1.467$ Mg m^{-3}
Hall symbol: -C 2yc	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 21.367$ (5) Å	Cell parameters from 1088 reflections
$b = 4.6382$ (11) Å	$\theta = 2.0$–$25.0°$
$c = 13.003$ (3) Å	$\mu = 0.11$ mm^{-1}
$\beta = 105.468$ (12)°	$T = 293$ K
$V = 1242.0$ (5) Å^3	Prism, colourless
$Z = 8$	$0.33 \times 0.25 \times 0.20$ mm

Data collection

Bruker APEXII CCD area-detector diffractometer	8242 measured reflections
Radiation source: fine-focus sealed tube	1086 independent reflections
Graphite monochromator	982 reflections with $I > 2\sigma(I)$
Detector resolution: 1.03 pixels mm^{-1}	$R_{int} = 0.038$
phi and ω scans	$\theta_{max} = 25.0°$, $\theta_{min} = 2.0°$
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)	$h = -24 \rightarrow 24$
	$k = -5 \rightarrow 5$
$T_{min} = 0.966$, $T_{max} = 0.979$	$l = -15 \rightarrow 15$

Refinement

Refinement on F^2	103 parameters
Least-squares matrix: full	2 restraints
$R[F^2 > 2\sigma(F^2)] = 0.031$	0 constraints
$wR(F^2) = 0.081$	Primary atom site location: structure-invariant direct methods
$S = 1.08$	
1086 reflections	

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0379P)^2 + 0.8786P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.011$
$\Delta\rho_{max} = 0.19$ e Å^{-3}
$\Delta\rho_{min} = -0.18$ e Å^{-3}

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.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.19134 (4)	0.1826 (2)	0.26040 (7)	0.0207 (3)
H1N2	0.0896 (7)	0.225 (3)	0.1797 (12)	0.027 (4)*
H2N2	0.0456 (6)	0.081 (3)	0.0861 (11)	0.027 (4)*
H1	0.2316 (9)	0.260 (4)	0.2779 (14)	0.043 (5)*
C1	0.12315 (6)	−0.2716 (3)	0.03188 (9)	0.0154 (3)
C2	0.17439 (6)	−0.4236 (3)	0.01036 (10)	0.0189 (3)
H2	0.2167	−0.3964	0.0520	0.023*
C3	0.16144 (6)	−0.6149 (3)	−0.07361 (10)	0.0208 (3)
H3	0.1949	−0.7164	−0.0904	0.025*
C4	0.09770 (6)	−0.6536 (3)	−0.13259 (10)	0.0211 (3)
H4	0.0874	−0.7834	−0.1891	0.025*
C5	0.05004 (6)	−0.4948 (3)	−0.10538 (10)	0.0203 (3)
H5	0.0073	−0.5229	−0.1449	0.024*
C6	0.13390 (5)	−0.0595 (3)	0.12070 (9)	0.0147 (3)
N1	0.06133 (5)	−0.3023 (2)	−0.02561 (8)	0.0176 (3)
N2	0.08163 (5)	0.0824 (2)	0.13540 (9)	0.0179 (3)
N3	0.19228 (5)	−0.0259 (2)	0.18081 (8)	0.0175 (3)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0156 (5)	0.0240 (5)	0.0199 (5)	−0.0027 (4)	0.0004 (4)	−0.0070 (4)
C1	0.0157 (6)	0.0151 (6)	0.0149 (6)	−0.0009 (5)	0.0032 (5)	0.0048 (5)
C2	0.0152 (6)	0.0215 (7)	0.0186 (6)	0.0008 (5)	0.0022 (5)	0.0038 (5)
C3	0.0225 (7)	0.0210 (7)	0.0205 (7)	0.0050 (5)	0.0087 (5)	0.0035 (5)
C4	0.0276 (7)	0.0199 (7)	0.0157 (6)	0.0005 (5)	0.0055 (5)	−0.0008 (5)
C5	0.0175 (6)	0.0231 (7)	0.0173 (6)	−0.0017 (5)	−0.0006 (5)	−0.0008 (5)
C6	0.0142 (6)	0.0154 (6)	0.0141 (6)	0.0000 (5)	0.0029 (5)	0.0046 (5)
N1	0.0155 (5)	0.0193 (6)	0.0162 (5)	−0.0008 (4)	0.0012 (4)	0.0004 (4)
N2	0.0130 (6)	0.0216 (6)	0.0162 (6)	0.0013 (5)	−0.0009 (5)	−0.0031 (5)

N3	0.0163 (5)	0.0177 (6)	0.0169 (5)	−0.0009 (4)	0.0018 (4)	−0.0017 (4)

Geometric parameters (Å, º)

O1—N3	1.4201 (13)	C4—C5	1.3773 (18)
O1—H1	0.903 (18)	C4—H4	0.9300
C1—N1	1.3407 (16)	C5—N1	1.3408 (16)
C1—C2	1.3918 (17)	C5—H5	0.9300
C1—C6	1.4878 (17)	C6—N3	1.2928 (16)
C2—C3	1.3765 (18)	C6—N2	1.3532 (16)
C2—H2	0.9300	N2—H1N2	0.862 (13)
C3—C4	1.3849 (19)	N2—H2N2	0.859 (13)
C3—H3	0.9300		
N3—O1—H1	104.9 (11)	C3—C4—H4	120.9
N1—C1—C2	123.03 (11)	N1—C5—C4	124.19 (12)
N1—C1—C6	115.35 (10)	N1—C5—H5	117.9
C2—C1—C6	121.61 (11)	C4—C5—H5	117.9
C3—C2—C1	118.91 (12)	N3—C6—N2	123.75 (11)
C3—C2—H2	120.5	N3—C6—C1	118.26 (10)
C1—C2—H2	120.5	N2—C6—C1	117.97 (10)
C2—C3—C4	118.86 (12)	C1—N1—C5	116.69 (10)
C2—C3—H3	120.6	C6—N2—H1N2	116.3 (10)
C4—C3—H3	120.6	C6—N2—H2N2	119.9 (10)
C5—C4—C3	118.28 (12)	H1N2—N2—H2N2	118.9 (14)
C5—C4—H4	120.9	C6—N3—O1	108.89 (9)
N1—C1—C2—C3	−0.07 (18)	N1—C1—C6—N2	−0.29 (16)
C6—C1—C2—C3	−179.35 (11)	C2—C1—C6—N2	179.05 (11)
C1—C2—C3—C4	−1.19 (18)	C2—C1—N1—C5	1.51 (17)
C2—C3—C4—C5	0.96 (18)	C6—C1—N1—C5	−179.17 (10)
C3—C4—C5—N1	0.6 (2)	C4—C5—N1—C1	−1.77 (18)
N1—C1—C6—N3	178.22 (10)	N2—C6—N3—O1	−0.96 (16)
C2—C1—C6—N3	−2.45 (17)	C1—C6—N3—O1	−179.38 (9)

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···N3[i]	0.903 (18)	1.859 (19)	2.7537 (14)	170.5 (17)
N2—H2*N*2···N1[ii]	0.86 (1)	2.44 (1)	3.1753 (16)	144 (1)

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