Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Nicotinohydrazide

Gustavo Portalone* and Marcello Colapietro

Chemistry Department, 'Sapienza' University of Rome, P. le A. Moro, 5, I-00185 Rome, Italy
Correspondence e-mail: g.portalone@caspur.it

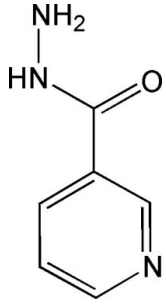
Received 30 October 2007; accepted 11 December 2007

Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.005 Å; R factor = 0.042; wR factor = 0.131; data-to-parameter ratio = 12.2.

In the title compound (alternative name: pyridine-3-carbohydrazide, $C_6H_7N_3O$), the asymmetric unit contains a single molecule. In contrast with nicotinic acid and nicotinamide, the C=O bond is found to be oriented *cis* with respect to the C_{ipso}···C···N fragment in the pyridine ring. The pyridine ring and the hydrazide group make a dihedral angle of 34.0 (2)°. In the crystal structure, molecules are associated into a three-dimensional framework by a combination of N—H···N and three-centre N—H···O hydrogen bonds.

Related literature

The structure of the same compound has been determined independently and is reported in the preceding paper (Priebe *et al.*, 2008). For related literature, see: Bhat *et al.* (1974); Kutoglu & Scheringer (1983); Miwa *et al.* (1999); Portalone (2007); Portalone & Colapietro (2007). For computation of ring patterns formed by hydrogen bonds in crystal structures, see: Etter *et al.* (1990); Bernstein *et al.* (1995); Motherwell *et al.* (1999).



Experimental

Crystal data

$C_6H_7N_3O$
M_r = 137.15
Orthorhombic, $P2_12_12_1$
a = 3.8727 (10) Å
b = 10.481 (2) Å
c = 15.855 (2) Å
V = 643.6 (2) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.10 mm^{-1}
T = 298 (2) K
0.15 × 0.05 × 0.05 mm

Data collection

Oxford Diffraction Xcalibur S CCD diffractometer
Absorption correction: none
3076 measured reflections
1139 independent reflections
695 reflections with $I > 2\sigma(I)$
R_{int} = 0.019

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.131
S = 1.19
1139 reflections
93 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.22 e Å^{-3}
$\Delta\rho_{min}$ = −0.22 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H21···N1^{i}	0.89 (4)	2.09 (4)	2.964 (4)	168 (4)
N3—H31···O1^{ii}	0.84 (5)	2.57 (5)	3.146 (4)	127 (4)
N3—H32···O1^{iii}	1.00 (5)	2.08 (5)	3.027 (4)	157 (4)

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

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2006); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

We thank MIUR (Rome) for 2006 financial support of the project 'X-ray diffractometry and spectrometry'.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BH2149).

References

Altomare, A., Burla, M. C., Camalli, M., Cascarano, G. L., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.
Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Bhat, T. N., Singh, T. P. & Vijayan, M. (1974). *Acta Cryst.* B**30**, 2921–2922.
Etter, M. C., MacDonald, J. C. & Bernstein, J. (1990). *Acta Cryst.* B**46**, 256–262.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Kutoglu, A. & Scheringer, C. (1983). *Acta Cryst.* C**39**, 232–234.
Miwa, Y., Mizuno, T., Tsuchida, K., Taga, T. & Iwata, Y. (1999). *Acta Cryst.* B**55**, 78–84.
Motherwell, W. D. S., Shields, G. P. & Allen, F. H. (1999). *Acta Cryst.* B**55**, 1044–1056.
Oxford Diffraction (2006). *CrysAlis CCD* and *CrysAlis RED*. Versions 1.171.32.3. Oxford Diffraction Ltd, Abingdon, Oxfordshire, England.
Portalone, G. (2007). *Acta Cryst.* E**63**, o3232.
Portalone, G. & Colapietro, M. (2007). *Acta Cryst.* C**63**, o655–o658.
Priebe, J. P., Mello, R. S., Nome, F. & Bortoluzzi, A. J. (2008). *Acta Cryst.* E**64**, o302–o303.
Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.

  doi:10.1107/S1600536807066561

supporting information

Acta Cryst. (2008). E**64**, o304 [https://doi.org/10.1107/S1600536807066561]

Nicotinohydrazide

Gustavo Portalone and Marcello Colapietro

S1. Comment

As a part of a more general study of multiple-hydrogen-bonding *N* -heterocyclic systems as potential supramolecular reagents (Portalone, 2007; Portalone & Colapietro, 2007), we report here the structure of the title compound (I, Fig. 1). The asymmetric unit of (I) comprises one independent molecule, and the angle between the mean planes of the acid hydrazine group and the pyridine ring is 34.0 (2)°. Noteworthy, in contrast to nicotinic acid (Kutoglu & Scheringer, 1983) and nicotinamide (Miwa *et al.*, 1999), the C?O bond is oriented *cis* with respect to the C2—C3 bond.

Analysis of the crystal packing of (I) shows that, at variance with isonicotinohydrazide (Bhat *et al.*, 1974), for which the crystal structure is stabilized by a network of N—H···N hydrogen bonds, in compound (I) two of the three independent N—H bonds act as donor in three-centre N—H···O systems (Table 1, entries 2 and 3), and the third is involved in a N—H···N interaction (Table 1, entry 1). These hydrogen bonds delineate patterns in which rings are the most prominent features (Fig. 2). Two small rings with descriptor $R_2^2(10)$ (Etter *et al.*, 1990; Bernstein *et al.*, 1995; Motherwell *et al.*, 1999) are then formed by NH_2 functionalities and two symmetry-related carbonyl O atoms [O1^{ii} and O1^{iii}, symmetry codes: (*ii*) *x* + 1/2, -*y* + 1/2, -*z*; (*iii*) *x* - 1/2, -*y* + 1/2, -*z*]. The formation of the N—H···N hydrogen bonds between the N—H groups and the pyridyl N atoms [N1^{i}, symmetry code: (*i*) -*x* + 1, *y* + 1/2, -*z* + 1/2] leads to the formation of larger $R_6^6(30)$ rings.

S2. Experimental

1 mmol of the title compound (purchased from Sigma-Aldrich at 97% purity) was dissolved in a mixture benzene/ethanol (8:1, 50 ml) and refluxed for 1 h. After cooling the solution to ambient temperature, a colorless precipitate was formed, which was collected by filtration and washed with benzene/ethanol (8:1). Crystals suitable for single-crystal X-ray diffraction were grown from a benzene solution, by slow evaporation of the solvent.

S3. Refinement

Diffraction from the very small crystals was weak; nevertheless, these data gave good structural results, albeit with a lower data/parameter ratio than usual. All H atoms were detected in a difference map, after the first cycles of the isotropic refinement. The final full-matrix least-squares refinement was carried out on F^2 with anisotropic non-H atoms and isotropic H atoms. C-bonded H atoms were positioned with idealized geometry and refined using a riding model, with C—H bond lengths fixed to 0.95 Å and U_{iso}(H) = 1.2U_{eq}(carrier C). H atoms bonded to N atoms were refined freely with U_{iso}(H) = 1.2U_{eq}(carrier N). In the absence of significant anomalous scattering in this light-atom study, measured Friedel pairs were merged.

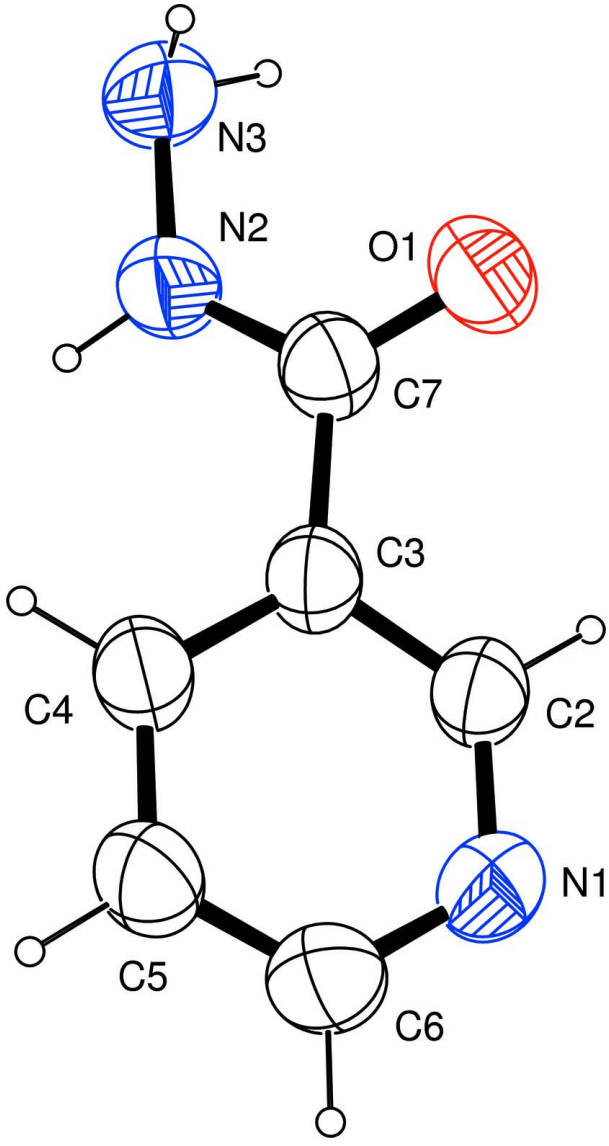


Figure 1

The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

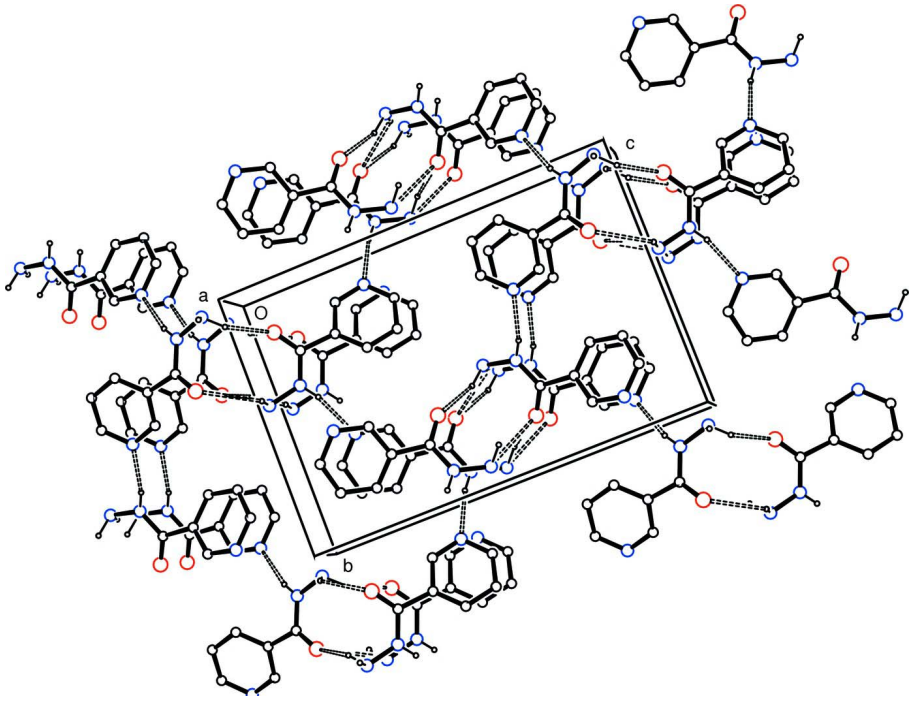


Figure 2

Crystal packing diagram for (I) viewed down [100]. All atoms are shown as small spheres of arbitrary radii. For the sake of clarity, H atoms not involved in hydrogen bonding have been omitted. Hydrogen bonding is indicated by dashed lines.

pyridine-3-carbohydrazide

Crystal data

$C_6H_7N_3O$
$M_r = 137.15$
Orthorhombic, $P2_12_12_1$
Hall symbol: P 2ac 2ab
$a = 3.8727$ (10) Å
$b = 10.481$ (2) Å
$c = 15.855$ (2) Å
$V = 643.6$ (2) Å^3
$Z = 4$

$F(000) = 288$
$D_x = 1.415$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å
Cell parameters from 6060 reflections
$\theta = 2.3$–$30.0°$
$\mu = 0.10$ mm^{-1}
$T = 298$ K
Plate, colourless
0.15 × 0.05 × 0.05 mm

Data collection

Oxford Diffraction Xcalibur S CCD diffractometer
Radiation source: Enhance (Mo) X-ray source
Graphite monochromator
Detector resolution: 16.0696 pixels mm^{-1}
ω and φ scans
3076 measured reflections

1139 independent reflections
695 reflections with $I > 2\sigma(I)$
$R_{int} = 0.019$
$\theta_{max} = 30.0°$, $\theta_{min} = 2.3°$
$h = -5 \rightarrow 5$
$k = -14 \rightarrow 14$
$l = -22 \rightarrow 22$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.131$
$S = 1.19$
1139 reflections
93 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
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
$w = 1/[\sigma^2(F_o^2) + (0.022P)^2 + 0.3733P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.22$ e Å^{-3}
$\Delta\rho_{min} = -0.22$ e Å^{-3}

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

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	1.0228 (9)	0.1920 (2)	0.10123 (15)	0.0690 (8)
N1	0.4952 (10)	0.1249 (3)	0.32513 (17)	0.0622 (8)
N2	0.8838 (10)	0.4009 (3)	0.10818 (16)	0.0613 (9)
H21	0.777 (5)	0.464 (3)	0.1359 (12)	0.074*
N3	0.9984 (11)	0.4321 (3)	0.02617 (17)	0.0670 (9)
H31	1.210 (6)	0.4151 (6)	0.0228 (2)	0.080*
H32	0.889 (3)	0.3722 (18)	−0.0149 (13)	0.080*
C2	0.6160 (10)	0.1529 (3)	0.2485 (2)	0.0565 (9)
H2	0.5944	0.0902	0.2056	0.068*
C3	0.7709 (10)	0.2678 (3)	0.22785 (19)	0.0517 (8)
C4	0.7961 (10)	0.3597 (3)	0.2905 (2)	0.0574 (9)
H4	0.8954	0.4406	0.2786	0.069*
C5	0.6755 (12)	0.3321 (3)	0.3700 (2)	0.0648 (11)
H5	0.6931	0.3932	0.4140	0.078*
C6	0.5291 (13)	0.2149 (4)	0.3845 (2)	0.0673 (10)
H6	0.4474	0.1966	0.4397	0.081*
C7	0.9030 (11)	0.2833 (3)	0.14019 (19)	0.0545 (8)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.089 (2)	0.0590 (14)	0.0593 (13)	0.0139 (16)	0.0077 (16)	−0.0061 (11)
N1	0.075 (2)	0.0528 (15)	0.0586 (15)	−0.0012 (19)	0.0015 (17)	0.0083 (13)
N2	0.083 (2)	0.0536 (15)	0.0468 (13)	0.0037 (17)	0.0062 (16)	0.0023 (12)
N3	0.083 (2)	0.0649 (17)	0.0526 (14)	−0.004 (2)	0.0038 (18)	0.0066 (13)
C2	0.071 (2)	0.0457 (15)	0.0528 (16)	0.0009 (18)	−0.0027 (18)	0.0009 (13)
C3	0.062 (2)	0.0440 (14)	0.0496 (15)	0.0019 (17)	−0.0038 (16)	−0.0007 (13)
C4	0.071 (2)	0.0475 (16)	0.0535 (16)	0.0034 (19)	−0.0040 (18)	−0.0040 (14)
C5	0.089 (3)	0.0574 (18)	0.0480 (16)	0.004 (2)	−0.004 (2)	−0.0041 (14)
C6	0.083 (3)	0.066 (2)	0.0526 (17)	0.005 (2)	0.002 (2)	0.0060 (16)
C7	0.063 (2)	0.0497 (15)	0.0505 (15)	0.0023 (18)	−0.0032 (17)	−0.0014 (14)

Geometric parameters (Å, º)

O1—C7	1.230 (4)	C2—H2	0.9500
N1—C2	1.334 (4)	C3—C4	1.387 (4)
N1—C6	1.340 (4)	C3—C7	1.490 (4)
N2—C7	1.335 (4)	C4—C5	1.375 (4)
N2—N3	1.412 (4)	C4—H4	0.9500
N2—H21	0.89 (4)	C5—C6	1.373 (5)
N3—H31	0.84 (5)	C5—H5	0.9500
N3—H32	1.00 (5)	C6—H6	0.9500
C2—C3	1.385 (4)		
C2—N1—C6	116.8 (3)	C5—C4—C3	119.1 (3)
C7—N2—N3	123.1 (3)	C5—C4—H4	120.5
C7—N2—H21	121.2	C3—C4—H4	120.5
N3—N2—H21	115.4	C6—C5—C4	118.9 (3)
N2—N3—H31	108.4	C6—C5—H5	120.6
N2—N3—H32	108.7	C4—C5—H5	120.6
H31—N3—H32	103.9	N1—C6—C5	123.5 (3)
N1—C2—C3	124.0 (3)	N1—C6—H6	118.2
N1—C2—H2	118.0	C5—C6—H6	118.2
C3—C2—H2	118.0	O1—C7—N2	123.2 (3)
C2—C3—C4	117.7 (3)	O1—C7—C3	120.9 (3)
C2—C3—C7	117.6 (3)	N2—C7—C3	115.8 (3)
C4—C3—C7	124.6 (3)		
C6—N1—C2—C3	0.0 (6)	C4—C5—C6—N1	−0.3 (7)
N1—C2—C3—C4	−1.1 (6)	N3—N2—C7—O1	0.2 (7)
N1—C2—C3—C7	178.1 (4)	N3—N2—C7—C3	179.8 (4)
C2—C3—C4—C5	1.5 (6)	C2—C3—C7—O1	−33.7 (6)
C7—C3—C4—C5	−177.6 (4)	C4—C3—C7—O1	145.5 (4)
C3—C4—C5—C6	−0.9 (6)	C2—C3—C7—N2	146.7 (4)
C2—N1—C6—C5	0.7 (7)	C4—C3—C7—N2	−34.2 (6)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H21···N1^{i}	0.89 (4)	2.09 (4)	2.964 (4)	168 (4)
N3—H31···O1^{ii}	0.84 (5)	2.57 (5)	3.146 (4)	127 (4)
N3—H32···O1^{iii}	1.00 (5)	2.08 (5)	3.027 (4)	157 (4)

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