Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Pyrazine-2-carbohydrazide: a three-dimensional hydrogen-bonded framework structure

Solange M. S. V. Wardell,[a] Marcus V. N. de Souza,[a] James L. Wardell,[b] John N. Low[c] and Christopher Glidewell[d]*

[a]Instituto de Tecnologia em Fármacos, Far-Manguinhos, FIOCRUZ, 21041-250, Rio de Janeiro, RJ, Brazil, [b]Instituto de Química, Departamento de Química Inorgânica, Universidade Federal do Rio de Janeiro, CP 68563, 21945-970 Rio de Janeiro, RJ, Brazil, [c]Department of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen AB24 3UE, Scotland, and [d]School of Chemistry, University of St Andrews, Fife KY16 9ST, Scotland

Correspondence e-mail: cg@st-andrews.ac.uk

Key indicators

Single-crystal X-ray study
T = 120 K
Mean σ(C–C) = 0.003 Å
R factor = 0.059
wR factor = 0.138
Data-to-parameter ratio = 15.3

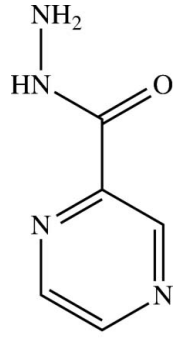
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 27 July 2006
Accepted 28 July 2006

Molecules of the title compound, $C_5H_6N_4O$, are linked into a three-dimensional framework structure by a combination of N—H···O, N—H···N and C—H···O hydrogen bonds.

Comment

As part of our general study of the supramolecular structures of amine and hydrazine derivatives, we report here the molecular and supramolecular structure of the title compound, (I). Within the hydrazino fragment, the coordination at C7 and N2 is planar within experimental uncertainty, while the coordination at N3 is markedly pyramidal (Fig. 1). Apart from the H atoms bonded to atom N3, the molecule is effectively planar, as shown by the key torsion angles (Table 1); the bond distances and angles show no unexpected features.



(I)

The molecules are linked by hydrogen bonds (Table 2) into a three-dimensional framework of some complexity, whose formation can, nonetheless, be readily analysed in terms of two simple substructures. In the first of these substructures, atom N3 in the molecule at (*x*, *y*, *z*) acts as hydrogen-bond donor, *via* H31 and H32, respectively, to atoms O1 in the molecules at $(1-x, 1-y, 1-z)$ and $(-x, 1-y, 1-z)$, so generating by inversion a chain of edge-fused $R_2^2(10)$ (Bernstein *et al.*, 1995) rings running along $(x, \frac{1}{2}, \frac{1}{2})$ (Fig. 2). The rings containing H31 are centred at $(n+\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, where *n* = zero or an integer) and those containing H32 are centred at $(n, \frac{1}{2}, \frac{1}{2})$ (*n* = zero or integer).

In the second substructure, atom N2 in the molecule at (*x*, *y*, *z*), which lies in the chain of rings along $(x, \frac{1}{2}, \frac{1}{2})$, acts as hydrogen-bond donor to atom N4 in the molecule at $(1-x, \frac{1}{2}-y, \frac{1}{2}+z)$, which lies in the chain along (*x*, 0, 1); at the same time, atom C3 at $(1-x, \frac{1}{2}-y, \frac{1}{2}+z)$ acts as donor to atom N1 in the molecule at (*x*, *y*, *z*), so forming an $R_2^2(8)$ motif (Fig. 3). Propagation of this motif by the symmetry operations of the space group then links the chain of rings along $(x, \frac{1}{2}, \frac{1}{2})$ directly

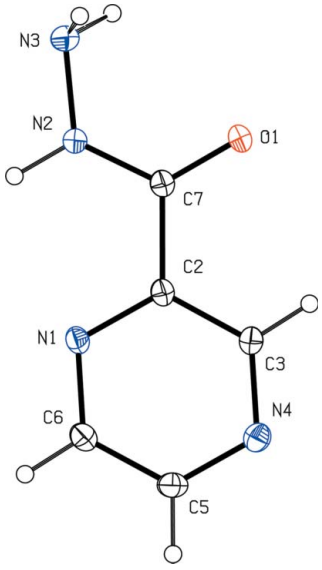


Figure 1
The molecular structure of compound (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

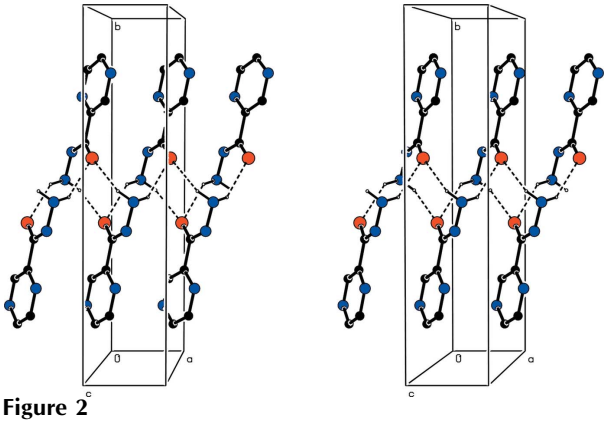


Figure 2
A stereoview of part of the crystal structure of compound (I), showing the formation of a chain of edge-fused rings along $(x, \frac{1}{2}, \frac{1}{2})$. For the sake of clarity, H atoms not involved in the motifs shown have been omitted.

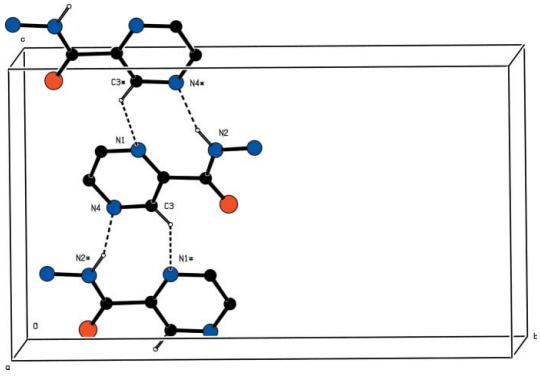


Figure 3
Part of the crystal structure of compound (I), showing the concerted action of the N—H···N and C—H···N hydrogen bonds. For the sake of clarity, H atoms not involved in the motif shown have been omitted. Atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions $(1 + x, \frac{1}{2} - y, \frac{1}{2} + z)$ and $(-1 + x, \frac{1}{2} - y, -\frac{1}{2} + z)$, respectively.

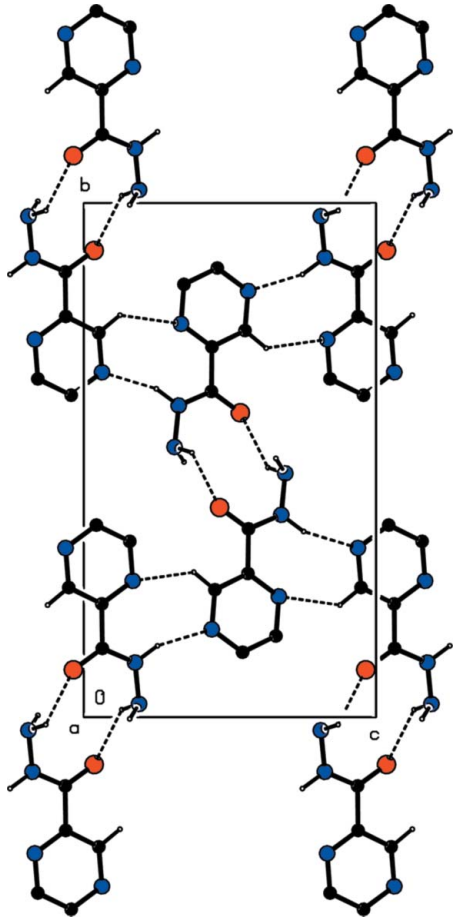


Figure 4
A projection down [100] of part of the crystal structure of compound (I), showing the linking of the chain of rings along $(x, \frac{1}{2}, \frac{1}{2})$ to four adjacent chains. For the sake of clarity, H atoms not involved in the motifs shown have been omitted.

to the four chains along $(x, 0, 0)$, $(x, 0, 1)$, $(x, 1, 0)$ and $(x, 1, 1)$, thence linking all of the [100] chains into a single three-dimensional framework structure (Fig. 4).

Experimental

A solution of methyl pyrazinecarboxylate and a fivefold molar excess of hydrazine hydrate was held at 353 K for 12 h. The solvent was removed under reduced pressure and the residue was purified by washing successively with cold ethanol and with diethyl ether to give crystalline (I) (yield 87%, m.p. 431–432 K). NMR (DMSO-d_6): δ(H) 10.14 (1H, *s*, NH), 9.13 (1H, *d*, J = 1.2 Hz, H3), 8.84 (1H, *d*, J = 2.8 Hz, H6), 8.70 (1H, *dd*, J = 1.2 and 2.8 Hz, H5), 4.70 (2H, *s*, NH_2); δ(C) 161.4, 147.2, 144.8, 143.4, 143.1. IR (KBr disk, cm^{-1}) 3306–3238 (NH), 1648 (CO).

Crystal data

$C_5H_6N_4O$
M_r = 138.14
Monoclinic, $P2_1/c$
a = 3.7193 (5) Å
b = 16.978 (2) Å
c = 9.7858 (10) Å
β = 99.185 (8)°
V = 610.01 (13) Å^3
Z = 4
D_x = 1.504 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 0.11 mm^{-1}
T = 120 (2) K
Plate, colourless
0.50 × 0.18 × 0.01 mm

Data collection

Bruker–Nonius KappaCCD diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.965, T_{max} = 0.999
6568 measured reflections
1395 independent reflections
1080 reflections with $I > 2\sigma(I)$
R_{int} = 0.057
θ_{max} = 27.5°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.059
$wR(F^2)$ = 0.138
S = 1.08
1395 reflections
91 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0462P)^2 + 0.4947P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.20 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-3}

Table 1
Selected torsion angles (°).

N1—C2—C7—N2	−1.9 (3)	C2—C7—N2—N3	179.60 (18)

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2···N4^{i}	0.96	2.06	2.976 (3)	160
N3—H31···O1^{ii}	0.92	2.31	3.079 (3)	140
N3—H32···O1^{iii}	0.92	2.25	3.138 (2)	161
C3—H3···N1^{iv}	0.95	2.59	3.312 (3)	133

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

All H atoms were located in difference maps, and then treated as riding atoms, with C—H = 0.95 Å and N—H = 0.92 (NH_2) or 0.96 Å (NH), with $U_{iso}(H) = 1.2U_{eq}(C,N)$.

Data collection: *COLLECT* (Hooft, 1999); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *OSCAIL* (McArdle, 2003) and *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *OSCAIL* and *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

X-Ray data were collected at the EPSRC National X-ray Crystallography Service, University of Southampton, England; the authors thank the staff of the Service for all their help and advice. JLW thanks CNPq and FAPERJ for financial support.

References

Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Ferguson, G. (1999). *PRPKAPPA*. University of Guelph, Canada.
Hooft, R. W. W. (1999). *COLLECT*. Nonius BV, Delft, The Netherlands.
McArdle, P. (2003). *OSCAIL for Windows*. Version 10. Crystallography Centre, Chemistry Department, NUI Galway, Ireland.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Sheldrick, G. M. (2003). *SADABS*. Version 2.10. University of Göttingen, Germany.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.

supporting information

Acta Cryst. (2006). E**62**, o3765–o3767 [https://doi.org/10.1107/S1600536806029394]

Pyrazine-2-carbohydrazide: a three-dimensional hydrogen-bonded framework structure

Solange M. S. V. Wardell, Marcus V. N. de Souza, James L. Wardell, John N. Low and Christopher Glidewell

Pyrazine-2-carbohydrazide

Crystal data

$C_5H_6N_4O$
$M_r = 138.14$
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
$a = 3.7193\ (5)$ Å
$b = 16.978\ (2)$ Å
$c = 9.7858\ (10)$ Å
$\beta = 99.185\ (8)°$
$V = 610.01\ (13)$ Å^3
$Z = 4$
$F(000) = 288$
$D_x = 1.504$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 1395 reflections
$\theta = 4.2–27.5°$
$\mu = 0.11$ mm^{-1}
$T = 120$ K
Plate, colourless
0.50 × 0.18 × 0.01 mm

Data collection

Bruker–Nonius KappaCCD diffractometer
Radiation source: Bruker–Nonius FR591 rotating anode
Graphite monochromator
Detector resolution: 9.091 pixels mm^{-1}
φ and ω scans
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)
$T_{min} = 0.965$, $T_{max} = 0.999$
6568 measured reflections
1395 independent reflections
1080 reflections with $I > 2\sigma(I)$
$R_{int} = 0.057$
$\theta_{max} = 27.5°$, $\theta_{min} = 4.2°$
$h = -4\rightarrow4$
$k = -22\rightarrow19$
$l = -12\rightarrow12$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.059$
$wR(F^2) = 0.138$
$S = 1.08$
1395 reflections
91 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-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0462P)^2 + 0.4947P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.20$ e Å^{-3}
$\Delta\rho_{min} = -0.24$ e Å^{-3}

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

	x	*y*	*z*	U_{iso}*/U_{eq}
N1	0.2754 (5)	0.23490 (10)	0.66747 (17)	0.0223 (4)
C2	0.1216 (6)	0.27960 (12)	0.5616 (2)	0.0199 (5)
C3	−0.1032 (6)	0.24786 (13)	0.4486 (2)	0.0218 (5)
N4	−0.1773 (5)	0.17092 (11)	0.43778 (19)	0.0255 (4)
C5	−0.0225 (6)	0.12634 (13)	0.5431 (2)	0.0269 (5)
C6	0.1998 (6)	0.15799 (13)	0.6573 (2)	0.0255 (5)
C7	0.1993 (6)	0.36628 (12)	0.5634 (2)	0.0214 (5)
O1	0.0679 (4)	0.40779 (9)	0.46448 (15)	0.0273 (4)
N2	0.4142 (5)	0.39368 (10)	0.67541 (18)	0.0237 (4)
N3	0.5100 (6)	0.47441 (11)	0.6892 (2)	0.0305 (5)
H2	0.5180	0.3612	0.7520	0.028*
H3	−0.2086	0.2820	0.3763	0.026*
H5	−0.0659	0.0712	0.5400	0.032*
H6	0.3014	0.1239	0.7304	0.031*
H31	0.6722	0.4855	0.6300	0.037*
H32	0.3048	0.5034	0.6571	0.037*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0249 (10)	0.0235 (10)	0.0180 (8)	0.0030 (7)	0.0020 (7)	0.0022 (7)
C2	0.0195 (10)	0.0232 (11)	0.0173 (10)	0.0034 (8)	0.0036 (8)	0.0002 (8)
C3	0.0207 (10)	0.0253 (11)	0.0189 (10)	0.0014 (9)	0.0018 (8)	−0.0008 (8)
N4	0.0252 (10)	0.0275 (11)	0.0238 (9)	−0.0001 (8)	0.0038 (8)	−0.0027 (7)
C5	0.0317 (13)	0.0203 (11)	0.0291 (12)	−0.0021 (9)	0.0067 (10)	−0.0001 (9)
C6	0.0284 (12)	0.0242 (11)	0.0239 (11)	0.0042 (9)	0.0046 (9)	0.0031 (9)
C7	0.0211 (11)	0.0231 (11)	0.0200 (10)	0.0020 (9)	0.0028 (8)	0.0008 (8)
O1	0.0316 (9)	0.0237 (8)	0.0236 (8)	0.0014 (7)	−0.0048 (6)	0.0042 (6)
N2	0.0279 (10)	0.0201 (10)	0.0213 (9)	−0.0011 (7)	−0.0017 (7)	0.0006 (7)
N3	0.0340 (11)	0.0210 (10)	0.0333 (11)	−0.0015 (8)	−0.0039 (8)	0.0001 (8)

Geometric parameters (Å, º)

N1—C6	1.336 (3)	N3—H31	0.92
N1—C2	1.337 (3)	N3—H32	0.92
C2—C3	1.385 (3)	C3—N4	1.336 (3)
C2—C7	1.499 (3)	C3—H3	0.95
C7—O1	1.234 (2)	N4—C5	1.333 (3)
C7—N2	1.333 (3)	C5—C6	1.388 (3)
N2—N3	1.417 (3)	C5—H5	0.95
N2—H2	0.96	C6—H6	0.95
C6—N1—C2	115.99 (18)	H31—N3—H32	105.5
N1—C2—C3	121.8 (2)	N4—C3—C2	122.32 (19)
N1—C2—C7	119.37 (18)	N4—C3—H3	118.8

C3—C2—C7	118.81 (18)	C2—C3—H3	118.8
O1—C7—N2	123.8 (2)	C5—N4—C3	115.82 (19)
O1—C7—C2	120.01 (18)	N4—C5—C6	122.1 (2)
N2—C7—C2	116.19 (17)	N4—C5—H5	119.0
C7—N2—N3	121.63 (18)	C6—C5—H5	119.0
C7—N2—H2	123.7	N1—C6—C5	122.0 (2)
N3—N2—H2	114.6	N1—C6—H6	119.0
N2—N3—H31	108.5	C5—C6—H6	119.0
N2—N3—H32	107.6		

C6—N1—C2—C3	0.2 (3)	C2—C7—N2—N3	179.60 (18)
C6—N1—C2—C7	−178.60 (18)	N1—C2—C3—N4	−0.7 (3)
N1—C2—C7—O1	177.82 (19)	C7—C2—C3—N4	178.14 (19)
C3—C2—C7—O1	−1.0 (3)	C2—C3—N4—C5	0.4 (3)
N1—C2—C7—N2	−1.9 (3)	C3—N4—C5—C6	0.4 (3)
C3—C2—C7—N2	179.31 (18)	C2—N1—C6—C5	0.5 (3)
O1—C7—N2—N3	−0.1 (3)	N4—C5—C6—N1	−0.8 (3)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2···N4^{i}	0.96	2.06	2.976 (3)	160
N3—H31···O1^{ii}	0.92	2.31	3.079 (3)	140
N3—H32···O1^{iii}	0.92	2.25	3.138 (2)	161
C3—H3···N1^{iv}	0.95	2.59	3.312 (3)	133

Symmetry codes: (i) $x+1, -y+1/2, z+1/2$; (ii) $-x+1, -y+1, -z+1$; (iii) $-x, -y+1, -z+1$; (iv) $x-1, -y+1/2, z-1/2$.