

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

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## Key indicators

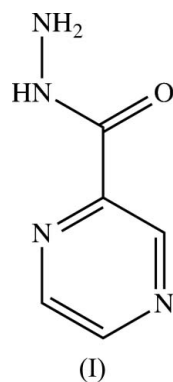
Single-crystal X-ray study  
 $T = 120$  K  
Mean  $\sigma(\text{C}-\text{C}) = 0.003$  Å  
 $R$  factor = 0.059  
 $wR$  factor = 0.138  
Data-to-parameter ratio = 15.3For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.Molecules of the title compound,  $\text{C}_5\text{H}_6\text{N}_4\text{O}$ , are linked into a three-dimensional framework structure by a combination of  $\text{N}-\text{H}\cdots\text{O}$ ,  $\text{N}-\text{H}\cdots\text{N}$  and  $\text{C}-\text{H}\cdots\text{O}$  hydrogen bonds.

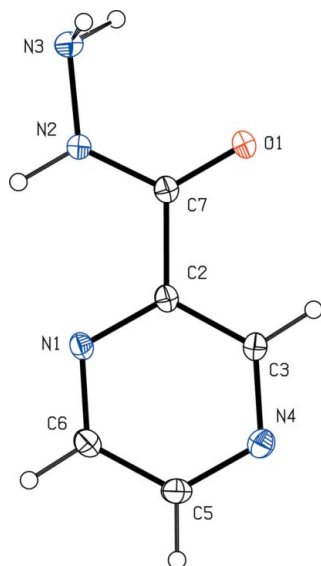
Received 27 July 2006

Accepted 28 July 2006

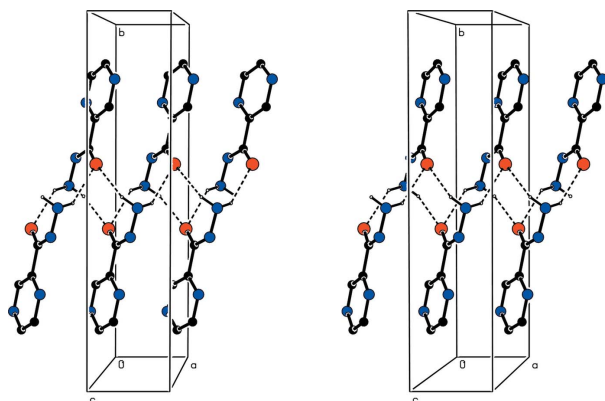
## Comment

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.

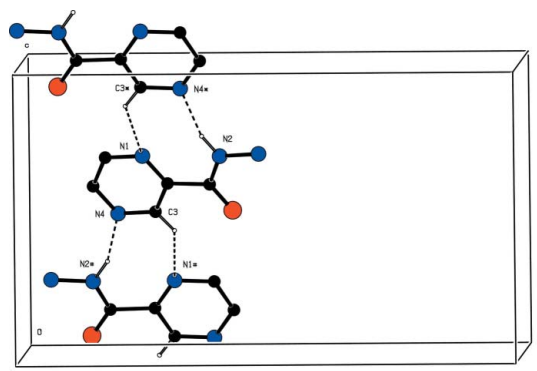
The molecules are linked by hydrogen bonds (Table 2) into a three-dimensional framework of some complexity, whose formation can, nonetheless, be readily analysed in terms of two simple substructures. In the first of these substructures, atom N3 in the molecule at  $(x, y, z)$  acts as hydrogen-bond donor, 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



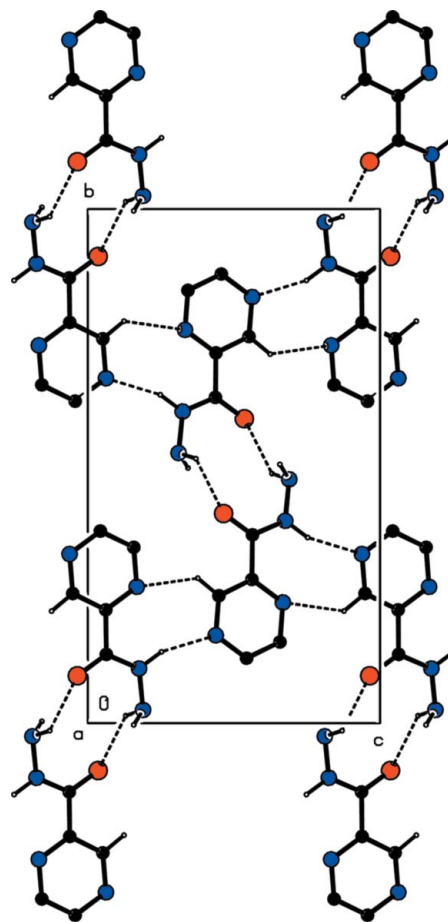
**Figure 1**  
The molecular structure of compound (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.



**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- $d_6$ ):  $\delta$ (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<sub>2</sub>);  $\delta$ (C) 161.4, 147.2, 144.8, 143.4, 143.1. IR (KBr disk,  $\text{cm}^{-1}$ ) 3306–3238 (NH), 1648 (CO).

## Crystal data

$\text{C}_5\text{H}_6\text{N}_4\text{O}$   
 $M_r = 138.14$   
Monoclinic,  $P2_1/c$   
 $a = 3.7193$  (5) Å  
 $b = 16.978$  (2) Å  
 $c = 9.7858$  (10) Å  
 $\beta = 99.185$  (8)°  
 $V = 610.01$  (13) Å<sup>3</sup>

$Z = 4$   
 $D_x = 1.504$  Mg m<sup>-3</sup>  
Mo  $K\alpha$  radiation  
 $\mu = 0.11$  mm<sup>-1</sup>  
 $T = 120$  (2) K  
Plate, colourless  
 $0.50 \times 0.18 \times 0.01$  mm

*Data collection*

Bruker–Nonius KappaCCD  
diffractometer  
 $\varphi$  and  $\omega$  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  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.057$   
 $\theta_{\text{max}} = 27.5^\circ$

*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  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.20 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.24 \text{ e } \text{\AA}^{-3}$

**Table 1**Selected torsion angles ( $^\circ$ ).

N1–C2–C7–N2	–1.9 (3)	C2–C7–N2–N3	179.60 (18)
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**Table 2**Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N2–H2 $\cdots$ N4 <sup>i</sup>	0.96	2.06	2.976 (3)	160
N3–H31 $\cdots$ O1 <sup>ii</sup>	0.92	2.31	3.079 (3)	140
N3–H32 $\cdots$ O1 <sup>iii</sup>	0.92	2.25	3.138 (2)	161
C3–H3 $\cdots$ N1 <sup>iv</sup>	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  $\text{\AA}$  and N–H = 0.92 (NH<sub>2</sub>) or 0.96  $\text{\AA}$  (NH), with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$ .

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.

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