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ISSN 2414-3146

5-Methylpyrazine-2-carboxamide

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Received 13 July 2017
Accepted 24 July 2017

Edited by H. Stoeckli-Evans, University of Neuchâtel, Switzerland

Keywords: crystal structure; amide; pyrazine; hydrogen bonding.

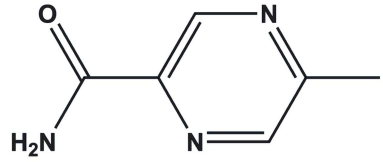
CCDC reference: 1564289

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

The title compound, $C_6H_7N_3O$, is nearly planar, with a dihedral angle of 2.14 (11)° between the pyrazine ring and the mean plane of the carboxamide group [C—C(═O)—N]. In the crystal, molecules are linked *via* pairs of N—H···O hydrogen bonds forming inversion dimers with an $R_2^2(8)$ ring motif. These dimers are further linked by a pair of N—H···N hydrogen bonds, enclosing an $R_2^2(10)$ ring motif, and C—H···O hydrogen bonds, forming ribbons lying parallel to the *ab* plane. The ribbons are linked by offset π–π interactions [intercentroid distance = 3.759 (1) Å], forming two sets of mutually perpendicular slabs parallel to planes (110) and (1$\bar{1}$0).

3D view

Chemical scheme



Structure description

The title compound, is an intermediate in the preparation of 2-bromo-5-methylpyrazine (Madhusudhan *et al.*, 2009). The latter compound has been used to synthesize 5,5′-dimethyl-2,2′-bipyrazine (Pefkianakis *et al.*, 2008) derivatives as bidentate ligands to coordinate to transition metals. The molecular structure of the title compound is illustrated in Fig. 1. The bond lengths of the methylpyrazine component are similar to those found in methyl 5-methyl-2-pyrazinecarboxylate (Rillema *et al.*, 2017). The molecule is planar with a dihedral angle of 2.14 (11)° between the pyrazine ring (N2/N3/C2–C5) and the mean plane of the carboxamide group [atoms C2—C1(═O1)—N1].

In the crystal, molecules are linked *via* pairs of N—H···O hydrogen bonds, forming classical amide–amide inversion dimers with an $R_2^2(8)$ ring motif (Table 1 and Fig. 2). These dimers are further linked by pairs of N—H···N hydrogen bonds, enclosing $R_2^2(10)$ ring motifs, and C—H···O hydrogen bonds, forming ribbons lying parallel to (001); see Table 1 and Fig. 2. The ribbons are linked in the *a*-axis direction by offset π–π interactions, forming two sets of mutually perpendicular slabs parallel to (110) and (1$\bar{1}$0), as shown in Fig. 3 [$Cg\cdots Cg^{i,ii}$ = 3.759 (1) Å, *Cg* is the centroid of the pyrazine ring, inter-

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1B···O1^{i}	0.94 (2)	1.96 (2)	2.905 (2)	178 (2)
N1—H1A···N2^{ii}	0.92 (2)	2.34 (2)	3.072 (2)	136 (2)
C4—H4···O1^{iii}	0.95	2.40	3.339 (3)	168

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

planar distance = 3.386 (1) Å, slippage = 1.63 Å, symmetry codes: (i) −1 + x, y, z; (ii) 1 + x, y, z].

Synthesis and crystallization

Methyl 5-methyl-2-pyrazinecarboxylate (80.0 g, 0.657 mole) (Rillema *et al.*, 2017) was added to 600 ml of methanol in a 1 litre round-bottomed flask. The flask was immersed in an ice bath, the contents were cooled to *ca* 273 K, stirred with a magnetic stirrer and then purged with ammonia gas for 4 h. The reaction progress was monitored by thin-layer chromatography (TLC). After completion of the reaction, the product was separated by filtration and washed with pre-cooled

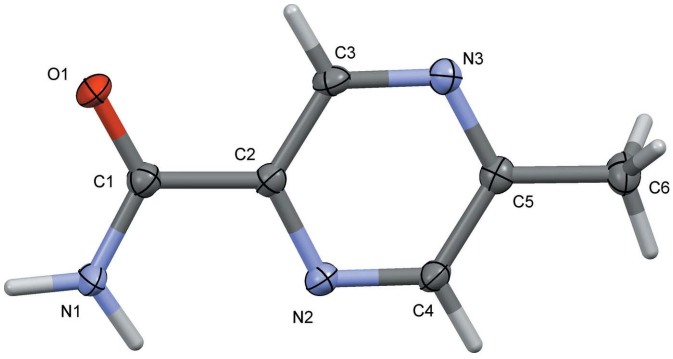


Figure 1
The molecular structure of the title compound, with the atom labelling and 50% probability displacement ellipsoids.

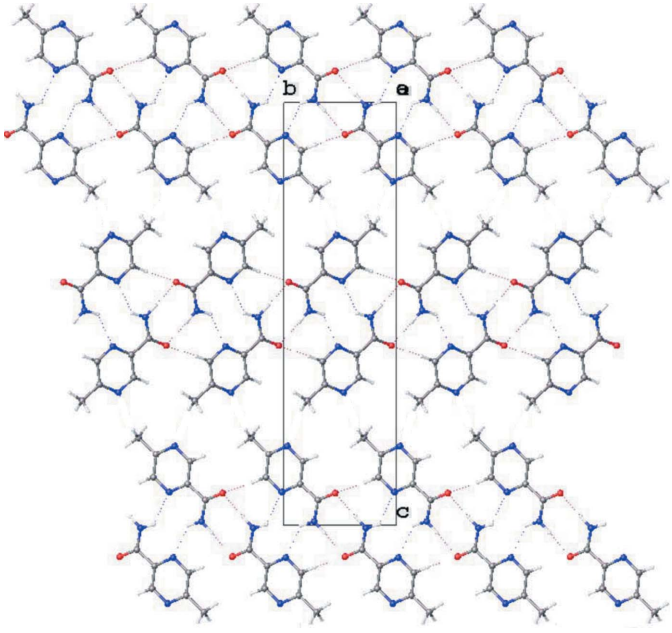


Figure 2
A view along the *a* axis of the crystal packing of the title compound. The hydrogen bonds are shown as dashed lines (see Table 1).

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_6H_7N_3O$
M_r	137.15
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	100
a, b, c (Å)	3.7592 (9), 6.7317 (13), 25.290 (5)
β (°)	93.106 (14)
V (Å^3)	639.0 (2)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.10
Crystal size (mm)	0.22 × 0.11 × 0.09
Data collection	
Diffractometer	Bruker X8 APEXII
Absorption correction	Multi-scan (*SADABS*; Bruker, 2013)
T_{min}, T_{max}	0.218, 0.259
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	7302, 1182, 849
R_{int}	0.046
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.604
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.043, 0.104, 1.03
No. of reflections	1182
No. of parameters	100
No. of restraints	2
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.20, −0.21

Computer programs: *APEX2* and *SAINT* (Bruker, 2013), *SAINT* (Bruker, 2013), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2014* (Sheldrick, 2015*b*), *OLEX2* (Dolomanov *et al.*, 2009), *Mercury* (Macrae *et al.*, 2008) and *PLATON* (Spek, 2009).

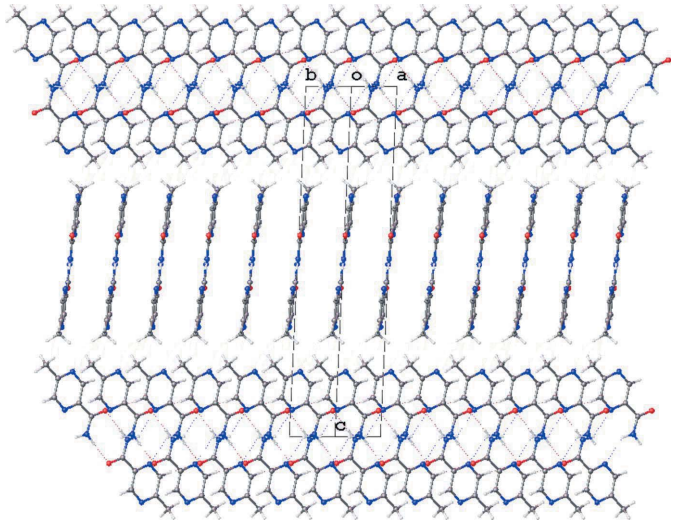


Figure 3
A view normal to the *ab* plane of the crystal packing of the title compound. Hydrogen bonds are shown as dashed lines (see Table 1).

methanol (2 × 30 ml) to give the title compound as a light-brown coloured solid. It was recrystallized by dissolving a small amount in methanol and then allowing the methanol to evaporate slowly, yielding colourless needles.

Refinement

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

Funding information

We are grateful for support from the National Science Foundation (EPSCoR), the Wichita State University Office of Research and the Department of Energy.

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full crystallographic data

IUCrData (2017). **2**, x171090 [https://doi.org/10.1107/S2414314617010902]

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Crystal data

$C_6H_7N_3O$
M_r = 137.15
Monoclinic, $P2_1/n$
a = 3.7592 (9) Å
b = 6.7317 (13) Å
c = 25.290 (5) Å
β = 93.106 (14)°
V = 639.0 (2) Å^3
Z = 4
$F(000)$ = 288
D_x = 1.425 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 1367 reflections
θ = 3.1–24.9°
μ = 0.10 mm^{-1}
T = 100 K
Needle, colourless
0.22 × 0.11 × 0.09 mm

Data collection

Bruker X8 APEXII diffractometer
Radiation source: sealed tube, fine-focus
Graphite monochromator
Detector resolution: 7.9 pixels mm^{-1}
ω and φ scans
Absorption correction: multi-scan (SADABS; Bruker, 2013)
T_{min} = 0.218, T_{max} = 0.259
7302 measured reflections
1182 independent reflections
849 reflections with $I > 2\sigma(I)$
R_{int} = 0.046
θ_{max} = 25.4°, θ_{min} = 3.1°
h = −4→4
k = −8→8
l = −30→30

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.104
S = 1.03
1182 reflections
100 parameters
2 restraints
Primary atom site location: dual
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0525P)^2 + 0.1949P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.20 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 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	0.9776 (4)	0.95545 (19)	0.42480 (5)	0.0240 (4)
N1	0.7790 (5)	0.7706 (3)	0.49219 (7)	0.0237 (5)
H1A	0.668 (5)	0.654 (3)	0.5011 (9)	0.034 (6)*
H1B	0.853 (6)	0.861 (3)	0.5190 (8)	0.039 (7)*
N2	0.5554 (4)	0.4823 (2)	0.42240 (6)	0.0179 (4)
N3	0.6419 (4)	0.5310 (2)	0.31371 (6)	0.0183 (4)
C1	0.8296 (5)	0.8043 (3)	0.44120 (7)	0.0181 (5)
C2	0.7022 (5)	0.6467 (3)	0.40302 (7)	0.0155 (5)
C3	0.7440 (5)	0.6691 (3)	0.34927 (7)	0.0176 (5)
H3	0.8497	0.7877	0.3372	0.021*
C4	0.4559 (5)	0.3434 (3)	0.38712 (7)	0.0177 (5)
H4	0.3536	0.2241	0.3994	0.021*
C5	0.4955 (5)	0.3657 (3)	0.33261 (7)	0.0164 (5)
C6	0.3727 (5)	0.2094 (3)	0.29402 (8)	0.0229 (5)
H6A	0.1921	0.2653	0.2689	0.034*
H6B	0.2696	0.0984	0.3131	0.034*
H6C	0.5755	0.1619	0.2748	0.034*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0332 (9)	0.0174 (7)	0.0215 (8)	−0.0117 (6)	0.0037 (6)	0.0002 (6)
N1	0.0357 (11)	0.0195 (9)	0.0161 (9)	−0.0138 (8)	0.0031 (8)	−0.0022 (8)
N2	0.0205 (10)	0.0153 (8)	0.0179 (9)	−0.0030 (7)	0.0007 (7)	0.0014 (7)
N3	0.0186 (9)	0.0183 (8)	0.0179 (9)	−0.0014 (7)	0.0001 (7)	0.0000 (7)
C1	0.0180 (11)	0.0173 (10)	0.0190 (11)	−0.0019 (9)	0.0005 (9)	0.0005 (8)
C2	0.0141 (11)	0.0146 (10)	0.0176 (10)	−0.0003 (8)	−0.0014 (8)	0.0008 (8)
C3	0.0166 (11)	0.0167 (9)	0.0194 (11)	−0.0029 (8)	0.0017 (9)	0.0038 (8)
C4	0.0199 (11)	0.0127 (9)	0.0206 (11)	−0.0029 (8)	0.0026 (9)	0.0005 (8)
C5	0.0123 (10)	0.0168 (10)	0.0200 (11)	0.0004 (8)	0.0009 (8)	−0.0009 (8)
C6	0.0225 (12)	0.0243 (11)	0.0223 (11)	−0.0050 (9)	0.0035 (9)	−0.0059 (9)

Geometric parameters (Å, º)

O1—C1	1.241 (2)	C2—C3	1.385 (3)
N1—H1A	0.923 (16)	C3—H3	0.9500
N1—H1B	0.941 (16)	C4—H4	0.9500
N1—C1	1.333 (2)	C4—C5	1.403 (3)
N2—C2	1.341 (2)	C5—C6	1.491 (3)
N2—C4	1.332 (2)	C6—H6A	0.9800
N3—C3	1.335 (2)	C6—H6B	0.9800
N3—C5	1.341 (2)	C6—H6C	0.9800
C1—C2	1.496 (3)		
H1A—N1—H1B	120 (2)	C2—C3—H3	118.6

C1—N1—H1A	118.2 (14)	N2—C4—H4	118.6
C1—N1—H1B	122.3 (14)	N2—C4—C5	122.85 (17)
C4—N2—C2	116.15 (16)	C5—C4—H4	118.6
C3—N3—C5	116.50 (16)	N3—C5—C4	120.43 (17)
O1—C1—N1	123.55 (18)	N3—C5—C6	118.08 (17)
O1—C1—C2	119.96 (16)	C4—C5—C6	121.48 (17)
N1—C1—C2	116.48 (16)	C5—C6—H6A	109.5
N2—C2—C1	118.25 (16)	C5—C6—H6B	109.5
N2—C2—C3	121.26 (17)	C5—C6—H6C	109.5
C3—C2—C1	120.47 (16)	H6A—C6—H6B	109.5
N3—C3—C2	122.80 (17)	H6A—C6—H6C	109.5
N3—C3—H3	118.6	H6B—C6—H6C	109.5

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*B*···O1^{i}	0.94 (2)	1.96 (2)	2.905 (2)	178 (2)
N1—H1*A*···N2^{ii}	0.92 (2)	2.34 (2)	3.072 (2)	136 (2)
C4—H4···O1^{iii}	0.95	2.40	3.339 (3)	168

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