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Methyl 5-methylpyrazine-2-carboxylate

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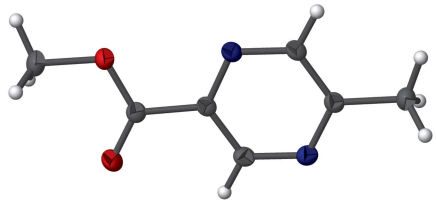
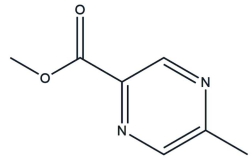
In the structure of methyl 5-methyl-2-pyrazinecarboxylate, $C_7H_8N_2O_2$, the non-H atoms of the molecule are nearly planar, with a dihedral angle of 5.4 (1)° between the plane of the pyrazine ring and the plane defined by C—C(O)—O. In the crystal, molecules are linked *via* C—H···N and C—H···O hydrogen bonds, forming layers parallel to (100).

3D view



Chemical scheme



Structure description

The title compound, Fig. 1, is an intermediate in the preparation of 5,5′-dimethyl-2,2′-bipyrazine derivatives used to coordinate to transition metals for use in solar energy conversion studies (Toma *et al.*, 2004; Rillema *et al.*, 2007; Kirgan *et al.*, 2007). The bond lengths of the methyl pyrazine component are similar to those found in 5,5-dimethyl-2,2′-bipyrazine (Eller *et al.*, 2004).

Two identical molecules are located in the unit cell related to each other by a twofold screw axis. In the crystal, molecules are linked by C—H···N and C—H···O hydrogen bonds (Table 1), forming sheets parallel to the (100) plane, Fig. 2. The sheets are further linked by C—H···N and C—H···O hydrogen bonds, forming a three-dimensional network, Fig. 3.

Synthesis and crystallization

The procedure followed one reported earlier (Madhusudhan *et al.* 2009) To a stirred solution of 5–methylpyrazine-2-carboxylic acid (50 g, 0.362 mol) in methanol (150 ml) at 0–5° C, concentrated sulfuric acid (4 ml) was added dropwise. After addition of sulfuric acid was complete, the reaction mixture was stirred at 65° C for 8 h. Then the solution was cooled to room temperature and excess methanol was removed from the solution by rotary evaporation at 30° C. The crude compound was partitioned between water

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

D—H···A	D—H	H···A	D···A	D—H···A
C1^{i}—H1A^{i}···N2^{i}	0.98	2.72	3.592	148
C1^{i}—H1B^{i}···O1^{i}	0.98	2.55	3.455	154
C3^{i}—H3^{i}···O1^{i}	0.95	2.41	3.299	155

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

(200 ml) and toluene (300 ml). The water layer was separated from the toluene layer and extracted with toluene (3 × 200 ml). The combined organic layers were washed with 2% aqueous sodium hydroxide solution (50 ml), dried over

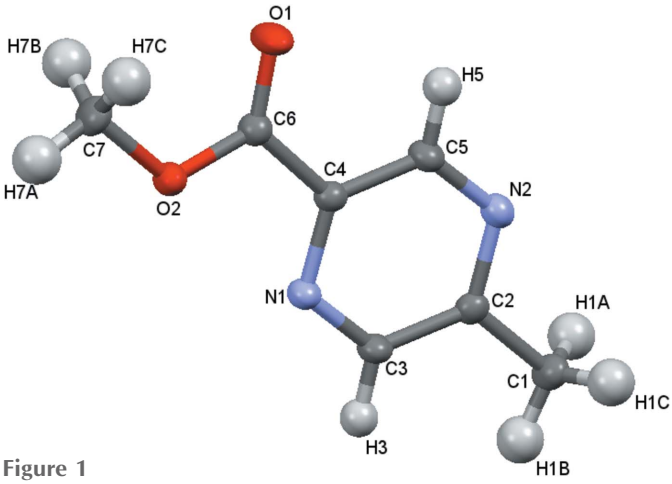


Figure 1
The molecular structure of the title compound with atom labels and 50% probability displacement ellipsoids.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_7H_8N_2O_2$
M_r	152.15
Crystal system, space group	Monoclinic, $P2_1$
Temperature (K)	150
a, b, c (Å)	3.8872 (1), 6.8386 (3), 13.6279 (5)
β (°)	93.303 (2)
V (Å^3)	361.67 (2)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.11
Crystal size (mm)	0.66 × 0.65 × 0.56
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Numerical (*SADABS*; Bruker, 2012)
T_{min}, T_{max}	0.925, 0.976
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	9931, 1556, 1495
R_{int}	0.015
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.641
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.029, 0.083, 1.14
No. of reflections	1556
No. of parameters	102
No. of restraints	1
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.20, −0.17
Absolute structure	Flack x determined using 659 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al*, 2013)
Absolute structure parameter	0.0 (2)

Computer programs: *SMART* and *SAINT* (Bruker, 2012), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2014* (Sheldrick, 2015*b*) and *OLEX2* (Dolomanov *et al.*, 2009).

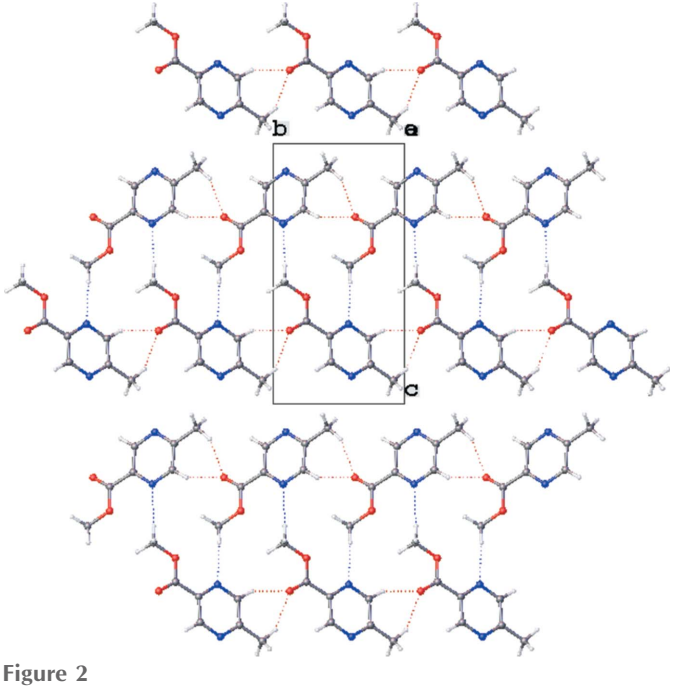


Figure 2
A view normal to the (100) plane of the crystal packing of the title compound. C—H···N (blue) and C—H···O (red) hydrogen bonds are shown as dashed lines.

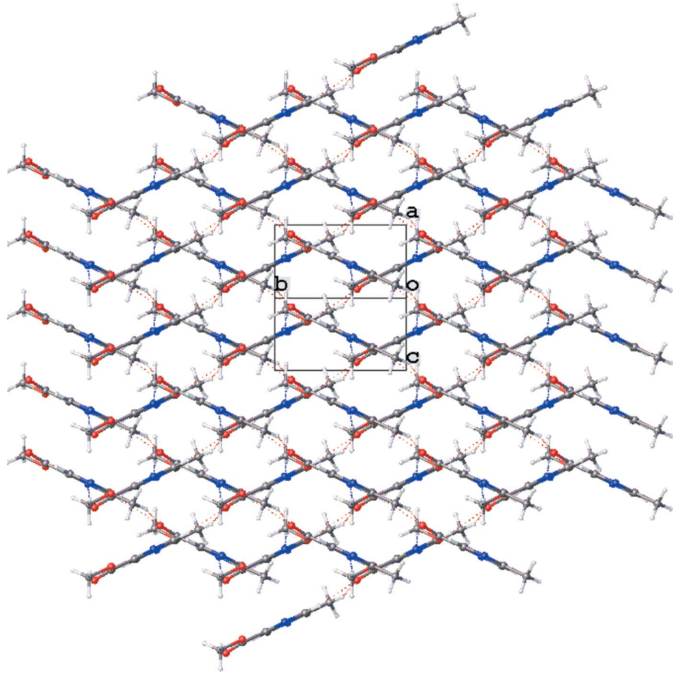


Figure 3
A view of the plane (101) of the crystal packing of the title compound. Hydrogen bonds are shown as dashed lines.

sodium sulfate, filtered and concentrated under vacuum at below 50° C to give the desired compound as a light-brown colored solid; 82% yield: The crystals were grown using the vapor diffusion technique. The inner vial contained methyl 5-methyl-2-pyrazinecarboxylate in dichloromethane (DCM) and the outer vial contained methanol. The crystals were harvested from the inner vial after 36 h.

Refinement

Crystal data, data collection and refinement details are summarized in Table 2. One low angle reflection with F_o <<< Fc may have been affected by the beamstop and was omitted from the final cycles of refinement.

Acknowledgements

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full crystallographic data

IUCrData (2017). **2**, x170997 [https://doi.org/10.1107/S241431461700997X]

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Crystal data

$C_7H_8N_2O_2$
M_r = 152.15
Monoclinic, $P2_1$
a = 3.8872 (1) Å
b = 6.8386 (3) Å
c = 13.6279 (5) Å
β = 93.303 (2)°
V = 361.67 (2) Å^3
Z = 2
$F(000)$ = 160
D_x = 1.397 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 7189 reflections
θ = 3.0–27.0°
μ = 0.11 mm^{-1}
T = 150 K
Block, clear colourless
0.66 × 0.65 × 0.56 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: sealed X-ray tube
Graphite monochromator
Detector resolution: 5.6 pixels mm^{-1}
φ and ω scans
Absorption correction: numerical (SADABS; Bruker, 2012)
T_{min} = 0.925, T_{max} = 0.976
9931 measured reflections
1556 independent reflections
1495 reflections with $I > 2\sigma(I)$
R_{int} = 0.015
θ_{max} = 27.1°, θ_{min} = 3.3°
h = −4→4
k = −8→8
l = −17→17

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.029
$wR(F^2)$ = 0.083
S = 1.14
1556 reflections
102 parameters
1 restraint
Primary atom site location: structure-invariant direct methods
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0504P)^2 + 0.0328P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.20 e Å^{-3}
$\Delta\rho_{min}$ = −0.17 e Å^{-3}
Absolute structure: Flack x determined using 659 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al*, 2013)
Absolute structure parameter: 0.0 (2)

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}
O2	0.2766 (3)	0.74768 (19)	0.59049 (8)	0.0235 (3)
O1	0.5934 (4)	0.8742 (2)	0.71764 (10)	0.0338 (4)
N2	0.3528 (4)	0.4025 (2)	0.89293 (10)	0.0223 (3)
N1	0.1414 (4)	0.4246 (2)	0.69310 (10)	0.0211 (3)
C6	0.4125 (4)	0.7469 (3)	0.68198 (12)	0.0204 (4)
C4	0.3192 (4)	0.5692 (2)	0.73882 (12)	0.0182 (4)
C3	0.0722 (4)	0.2702 (3)	0.74819 (12)	0.0216 (4)
H3	−0.0525	0.1642	0.7184	0.026*
C2	0.1754 (4)	0.2572 (2)	0.84819 (12)	0.0194 (4)
C1	0.0880 (5)	0.0836 (3)	0.90848 (13)	0.0267 (4)
H1A	0.2996	0.0283	0.9397	0.040*
H1B	−0.0271	−0.0151	0.8660	0.040*
H1C	−0.0660	0.1238	0.9593	0.040*
C5	0.4222 (5)	0.5576 (3)	0.83769 (12)	0.0222 (4)
H5	0.5466	0.6639	0.8673	0.027*
C7	0.3671 (5)	0.9159 (3)	0.53238 (13)	0.0288 (4)
H7A	0.2383	0.9115	0.4685	0.043*
H7B	0.6148	0.9136	0.5225	0.043*
H7C	0.3093	1.0361	0.5669	0.043*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O2	0.0286 (6)	0.0210 (6)	0.0206 (6)	−0.0053 (5)	−0.0005 (5)	0.0025 (5)
O1	0.0461 (9)	0.0243 (7)	0.0299 (7)	−0.0160 (7)	−0.0087 (6)	0.0030 (6)
N2	0.0241 (7)	0.0227 (7)	0.0197 (6)	−0.0011 (7)	−0.0008 (5)	−0.0011 (6)
N1	0.0240 (7)	0.0191 (7)	0.0200 (7)	−0.0038 (6)	−0.0006 (6)	−0.0012 (6)
C6	0.0219 (8)	0.0176 (8)	0.0215 (8)	0.0000 (7)	0.0004 (6)	0.0005 (7)
C4	0.0178 (8)	0.0162 (8)	0.0207 (8)	−0.0001 (6)	0.0012 (6)	−0.0011 (6)
C3	0.0242 (9)	0.0184 (8)	0.0220 (8)	−0.0050 (7)	−0.0003 (6)	−0.0018 (7)
C2	0.0165 (8)	0.0194 (8)	0.0225 (8)	0.0002 (7)	0.0018 (6)	0.0009 (7)
C1	0.0286 (10)	0.0258 (10)	0.0253 (9)	−0.0047 (8)	−0.0017 (7)	0.0079 (7)
C5	0.0249 (9)	0.0187 (8)	0.0225 (8)	−0.0023 (7)	−0.0018 (7)	−0.0029 (7)
C7	0.0343 (10)	0.0257 (9)	0.0264 (9)	−0.0040 (9)	0.0016 (7)	0.0085 (8)

Geometric parameters (Å, º)

O2—C6	1.3259 (19)	C3—C2	1.401 (2)
O2—C7	1.451 (2)	C2—C1	1.494 (2)
O1—C6	1.203 (2)	C1—H1A	0.9800
N2—C2	1.337 (2)	C1—H1B	0.9800
N2—C5	1.337 (2)	C1—H1C	0.9800
N1—C4	1.339 (2)	C5—H5	0.9500
N1—C3	1.332 (2)	C7—H7A	0.9800
C6—C4	1.497 (2)	C7—H7B	0.9800

C4—C5	1.386 (2)	C7—H7C	0.9800
C3—H3	0.9500		
C6—O2—C7	114.85 (14)	C2—C1—H1A	109.5
C2—N2—C5	116.65 (14)	C2—C1—H1B	109.5
C3—N1—C4	116.01 (13)	C2—C1—H1C	109.5
O2—C6—C4	113.23 (14)	H1A—C1—H1B	109.5
O1—C6—O2	124.67 (16)	H1A—C1—H1C	109.5
O1—C6—C4	122.10 (15)	H1B—C1—H1C	109.5
N1—C4—C6	119.51 (14)	N2—C5—C4	122.43 (16)
N1—C4—C5	121.52 (15)	N2—C5—H5	118.8
C5—C4—C6	118.97 (14)	C4—C5—H5	118.8
N1—C3—H3	118.6	O2—C7—H7A	109.5
N1—C3—C2	122.86 (15)	O2—C7—H7B	109.5
C2—C3—H3	118.6	O2—C7—H7C	109.5
N2—C2—C3	120.52 (15)	H7A—C7—H7B	109.5
N2—C2—C1	117.89 (14)	H7A—C7—H7C	109.5
C3—C2—C1	121.59 (15)	H7B—C7—H7C	109.5

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C1^{i}—H1*A*^{i}···N2^{i}	0.98	2.72	3.592	148
C1^{i}—H1*B*^{i}···O1^{i}	0.98	2.55	3.455	154
C3^{i}—H3^{i}···O1^{i}	0.95	2.41	3.299	155

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