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S-Methyl 5-methylpyrazine-2-carbothioate

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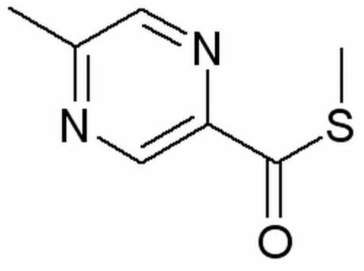
Key indicators: single-crystal X-ray study; T = 105 K; mean σ(C–C) = 0.001 Å; R factor = 0.040; wR factor = 0.109; data-to-parameter ratio = 33.0.

The title compound, $C_7H_8N_2OS$, can be a key synthetic intermediate for the preparation of various pyrazine compounds of biological interest. It was prepared by the hydrolysis of 2-tris(methylsulfanyl)methyl-5-methylpyrazine using the $HgCl_2/CaCO_3$ system. The molecule is quasi-planar; the H atoms of the methyl group linked to the pyrazine ring break the molecular mirror pseudosymmetry. One of these H atoms is involved in an intermolecular hydrogen bond with the carbonyl group of a neighbouring molecule. Two molecules related by an inversion centre interact through C—H···N hydrogen bonds, forming $R_2^2(6)$ dimers. Neighbouring dimers interact through longer C—H···N contacts and form infinite planes parallel to $(10\bar{3})$. These planes interact together through C—H···O hydrogen bonds and π–π interactions (pyrazine centroids are separated by 3.99 Å and the interplanar spacing is 3.38 Å).

Related literature

For the synthesis of the title compound, see: Mamane *et al.* (2007). For details of the pharmacological properties of pyrazine compounds, see: Sato (1995). For graph-set analysis, see: Bernstein *et al.* (1995).



Experimental

Crystal data

$C_7H_8N_2OS$
M_r = 168.21
Monoclinic, $P2_1/n$
a = 3.9934 (2) Å
b = 13.8082 (5) Å
c = 14.3502 (4) Å
β = 97.008 (4)°
V = 785.38 (5) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.35 mm^{-1}
T = 105 (2) K
0.51 × 0.26 × 0.26 mm

Data collection

Oxford Diffraction XCalibur diffractometer
Absorption correction: analytical [*CrysAlis RED* (Oxford Diffraction, 2007) using a multi-faceted crystal model (Clark & Reid, 1995)]
T_{min} = 0.900, T_{max} = 0.941
37490 measured reflections
3362 independent reflections
3009 reflections with $I > 2\sigma(I)$
R_{int} = 0.033

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.109
S = 1.14
3362 reflections
102 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.68 e Å^{-3}
$\Delta\rho_{min}$ = −0.25 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
C6—H6···N1^{i}	0.95	2.55	3.344 (1)	141 (1)
C9—H9B···N4^{ii}	0.98	2.65	3.626 (1)	173 (1)
C7—H7C···O1^{iii}	0.98	2.52	3.451 (1)	158 (1)

Symmetry codes: (i) $-x+1, -y, -z$; (ii) $x-\frac{3}{2}, -y+\frac{1}{2}, z-\frac{1}{2}$; (iii) $-x+\frac{3}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2007); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2007); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *POVRay* (Persistence of Vision Development Team, 2005); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BH2136).

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supplementary materials

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S-Methyl 5-methylpyrazine-2-carbothioate

E. Aubert, V. Mamane and Y. Fort

Comment

The title compound (I) (Fig. 1) is a pyrazine derivative (Sato, 1995), which has a quasi planar molecular structure with a r.m.s. deviation from planarity of 0.03 Å. Two molecules related by an inversion centre interact through C—H···N hydrogen bonds, forming $R_2^2(6)$ dimers (Bernstein *et al.*, 1995) (Table 2). Neighbouring dimers interact through longer C—H···N contacts (H9B···N4 = 2.65 Å) and form infinite planes parallel to (1 0 $\overline{3}$) (Fig. 2). The cohesion between these molecular planes is done through C—H···O hydrogen bonds (Table 2, Fig. 3), which induce a rotation of the methyl groups linked to the pyrazine rings (Fig. 1; the H7A—C7—C5—N4 torsion angle is −26.6°). π–π interactions are also present between these molecular planes (Figs. 3 and 4), the pyrazine centroids being separated by 3.99 Å (the interplane spacing is 3.38 Å).

Experimental

The synthesis follows a published procedure (Mamane *et al.*, 2007). $HgCl_2$ (3.3 mmol, 897 mg) and $CaCO_3$ (3.3 mmol, 330 mg) were added to a stirred solution of 2-tris(methylthio)methyl-5-methylpyrazine (1.5 mmol, 369 mg) in CH_3CN/H_2O (4/1, 15 ml) at 298 K. After stirring for 4 h., the mixture was filtered over celite and dichloromethane was added until no spot of product appeared on TLC. More water was added and the organic phase was separated and dried over $MgSO_4$. After solvent evaporation the residue was purified by chromatography on silica gel (hexanes/ethyl acetate, 4/1) to give 210 mg of a white powder (83%). *M*.p. 375 K. Single crystals were obtained by slow evaporation of a dilute solution of (I) in dichloromethane / hexane (1/1) at 298 K.

Refinement

All H atoms were located in difference Fourier maps. The final structure was constructed using riding models for C—H bonds with interatomic distances fixed at 0.95 (aromatic C) and 0.98 Å (methyl C), and U_{iso}(H) fixed at $1.2U_{eq}$(C) (aromatic C) and $1.5U_{eq}$(C) (methyl C). At the end of the refinement, residuals in a difference map revealed that the most important electron density residues are associated with valence density.

Figures

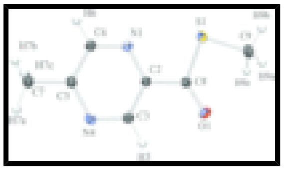

Fig. 1. Molecular structure of (I). Atomic displacement ellipsoids are plotted at the 50% probability level. Image rendered with *PovRay* (Persistence of Vision Development Team, 2005)

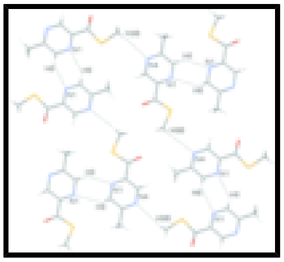

Fig. 2. Molecules of (I) aggregate has infinite planes parallel to $(1\ 0\ \bar{3})$, interacting through C—H···N hydrogen bonds (displayed as dashed lines).

Fig. 3. Crystal structure of (I) viewed along [0 1 0], displaying the C—H···O hydrogen bonds (dashed lines) linking the $(1\ 0\ \bar{3})$ planes.

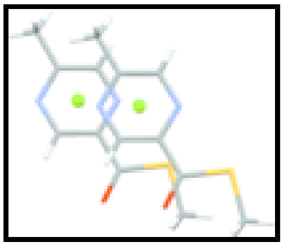

Fig. 4. View along $[1\ 0\ \bar{3}]^*$ showing two (I) molecules belonging to two adjacent (1 0 3) planes. The distance between the pyrazine ring centroids (displayed as green spheres) is 3.99 Å, whereas the distance from one pyrazine centroid to the mean plane of the second pyrazine ring is 3.38 Å.

S-Methyl 5-methylpyrazine-2-carbothioate

Crystal data

$C_7H_8N_2OS$

$M_r = 168.21$

Monoclinic, $P2_1/n$

Hall symbol: -P 2yn

$a = 3.9934\ (2)$ Å

$b = 13.8082\ (5)$ Å

$c = 14.3502\ (4)$ Å

$\beta = 97.008\ (4)$°

$V = 785.38\ (5)$ Å^3

$Z = 4$

$F_{000} = 352$

$D_x = 1.423$ Mg m^{-3}

Melting point: 375.15 K

Mo *K*α radiation
$\lambda = 0.71073$ Å

Cell parameters from 37490 reflections

$\theta = 3.3$–34.7°

$\mu = 0.35$ mm^{-1}

$T = 105\ (2)$ K

Block, pale brown

0.51 × 0.26 × 0.26 mm

Data collection

Oxford Diffraction XCalibur diffractometer

Radiation source: Enhance (Mo) X-ray Source

Monochromator: graphite

$T = 105(2)$ K

oscillation scans

Absorption correction: analytical [CrysAlis RED (Oxford Diffraction, 2007) using a multifaceted crystal (Clark & Reid, 1995)]

$T_{min} = 0.900$, $T_{max} = 0.941$

37490 measured reflections

3362 independent reflections

3009 reflections with $I > 2\sigma(I)$

$R_{int} = 0.033$

$\theta_{max} = 34.7$°

$\theta_{min} = 3.3$°

$h = -6 \rightarrow 6$

$k = -22 \rightarrow 21$

$l = -22 \rightarrow 22$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.040$

$wR(F^2) = 0.109$

$S = 1.14$

3362 reflections

102 parameters

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

$w = 1/[\sigma^2(F_o^2) + (0.0569P)^2 + 0.29P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.68$ e Å^{-3}

$\Delta\rho_{min} = -0.25$ e Å^{-3}

Extinction correction: none

Special details

Refinement. The high ratio of maximum / minimum residual density (2.70) is explained by the accumulation of valence electron density in covalent chemical bonds and in non-spherical electron density of the S atoms, as evidenced in a final difference map.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	0.39777 (6)	0.269288 (17)	−0.055470 (16)	0.01819 (8)
O1	0.7218 (2)	0.36238 (5)	0.08893 (6)	0.02209 (15)
N4	1.1412 (2)	0.11198 (6)	0.22049 (6)	0.01882 (16)
N1	0.6955 (2)	0.10828 (6)	0.05344 (6)	0.01678 (15)
C8	0.6575 (2)	0.28398 (7)	0.05203 (6)	0.01546 (15)
C2	0.7927 (2)	0.19143 (7)	0.09611 (6)	0.01430 (15)
C7	1.1770 (3)	−0.06478 (8)	0.22269 (8)	0.02189 (18)
H7A	1.3923	−0.0524	0.2614	0.033*
H7B	1.2114	−0.1116	0.1734	0.033*
H7C	1.0148	−0.0910	0.2621	0.033*
C3	1.0136 (2)	0.19323 (7)	0.17937 (6)	0.01804 (16)
H3	1.0752	0.2539	0.2077	0.022*
C6	0.8185 (2)	0.02717 (7)	0.09494 (7)	0.01737 (16)
H6	0.7522	−0.0334	0.0671	0.021*
C5	1.0433 (2)	0.02814 (7)	0.17854 (6)	0.01624 (16)
C9	0.2807 (3)	0.39414 (8)	−0.07722 (7)	0.02153 (18)
H9A	0.1853	0.4204	−0.0227	0.032*
H9B	0.1124	0.3982	−0.1328	0.032*
H9C	0.4808	0.4317	−0.0879	0.032*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.01976 (12)	0.01688 (12)	0.01668 (12)	0.00107 (7)	−0.00283 (8)	0.00022 (7)

O1	0.0296 (4)	0.0141 (3)	0.0211 (3)	0.0002 (3)	−0.0029 (3)	−0.0018 (2)
N4	0.0213 (3)	0.0177 (4)	0.0161 (3)	−0.0004 (3)	−0.0034 (3)	0.0011 (3)
N1	0.0196 (3)	0.0141 (3)	0.0157 (3)	−0.0009 (3)	−0.0016 (2)	−0.0009 (2)
C8	0.0158 (3)	0.0153 (4)	0.0149 (3)	0.0001 (3)	0.0003 (3)	0.0002 (3)
C2	0.0156 (3)	0.0133 (3)	0.0138 (3)	0.0000 (3)	0.0007 (2)	0.0004 (3)
C7	0.0230 (4)	0.0184 (4)	0.0232 (4)	0.0023 (3)	−0.0011 (3)	0.0053 (3)
C3	0.0218 (4)	0.0154 (4)	0.0157 (4)	−0.0015 (3)	−0.0028 (3)	−0.0007 (3)
C6	0.0206 (4)	0.0146 (4)	0.0162 (4)	−0.0012 (3)	−0.0008 (3)	−0.0005 (3)
C5	0.0172 (3)	0.0157 (4)	0.0156 (3)	0.0005 (3)	0.0011 (3)	0.0023 (3)
C9	0.0221 (4)	0.0198 (4)	0.0219 (4)	0.0039 (3)	−0.0004 (3)	0.0045 (3)

Geometric parameters (Å, °)

S1—C8	1.7624 (9)	C7—H7A	0.9800
S1—C9	1.8035 (11)	C7—H7B	0.9800
O1—C8	1.2186 (12)	C7—H7C	0.9800
N4—C3	1.3390 (13)	C3—H3	0.9500
N4—C5	1.3409 (13)	C6—C5	1.4079 (13)
N1—C6	1.3338 (12)	C6—H6	0.9500
N1—C2	1.3363 (12)	C9—H9A	0.9800
C8—C2	1.4971 (13)	C9—H9B	0.9800
C2—C3	1.3963 (13)	C9—H9C	0.9800
C7—C5	1.5002 (14)		
C8—S1—C9	98.85 (5)	N4—C3—C2	121.93 (9)
C3—N4—C5	116.81 (8)	N4—C3—H3	119.0
C6—N1—C2	116.51 (8)	C2—C3—H3	119.0
O1—C8—C2	121.92 (8)	N1—C6—C5	122.29 (9)
O1—C8—S1	123.57 (8)	N1—C6—H6	118.9
C2—C8—S1	114.51 (7)	C5—C6—H6	118.9
N1—C2—C3	121.68 (8)	N4—C5—C6	120.76 (9)
N1—C2—C8	118.05 (8)	N4—C5—C7	118.65 (8)
C3—C2—C8	120.26 (8)	C6—C5—C7	120.59 (9)
C5—C7—H7A	109.5	S1—C9—H9A	109.5
C5—C7—H7B	109.5	S1—C9—H9B	109.5
H7A—C7—H7B	109.5	H9A—C9—H9B	109.5
C5—C7—H7C	109.5	S1—C9—H9C	109.5
H7A—C7—H7C	109.5	H9A—C9—H9C	109.5
H7B—C7—H7C	109.5	H9B—C9—H9C	109.5
C9—S1—C8—O1	−2.37 (10)	C5—N4—C3—C2	−0.85 (14)
C9—S1—C8—C2	176.96 (7)	N1—C2—C3—N4	0.41 (15)
C6—N1—C2—C3	0.51 (14)	C8—C2—C3—N4	−179.58 (9)
C6—N1—C2—C8	−179.50 (8)	C2—N1—C6—C5	−0.95 (14)
O1—C8—C2—N1	176.54 (9)	C3—N4—C5—C6	0.41 (14)
S1—C8—C2—N1	−2.80 (11)	C3—N4—C5—C7	−179.37 (9)
O1—C8—C2—C3	−3.47 (14)	N1—C6—C5—N4	0.52 (15)
S1—C8—C2—C3	177.19 (7)	N1—C6—C5—C7	−179.71 (9)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C6—H6···N1[i]	0.95	2.55	3.344 (1)	141 (1)
C9—H9B···N4[ii]	0.98	2.65	3.626 (1)	173 (1)
C7—H7C···O1[iii]	0.98	2.52	3.451 (1)	158 (1)

Symmetry codes: (i) −*x*+1, −*y*, −*z*; (ii) *x*−3/2, −*y*+1/2, *z*−1/2; (iii) −*x*+3/2, *y*−1/2, −*z*+1/2.

Fig. 1

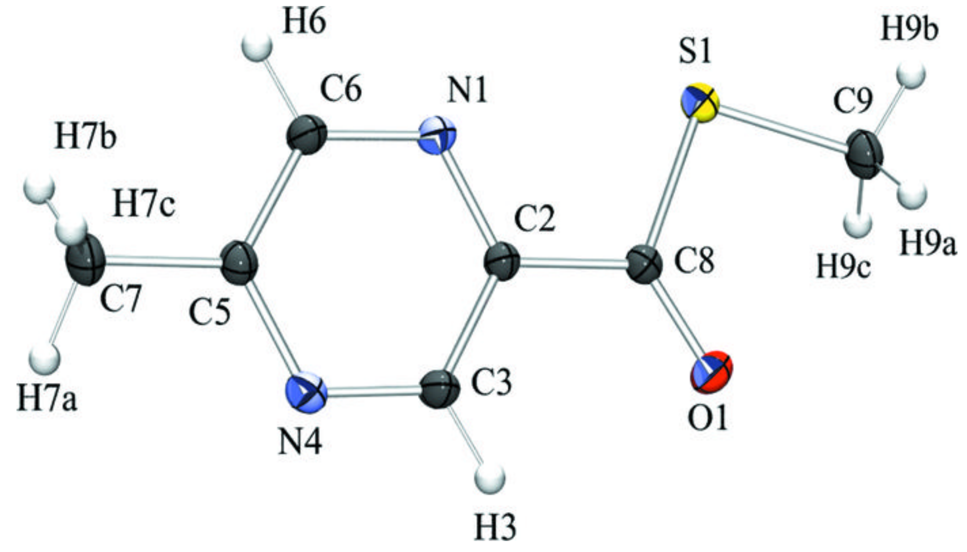

Fig. 2

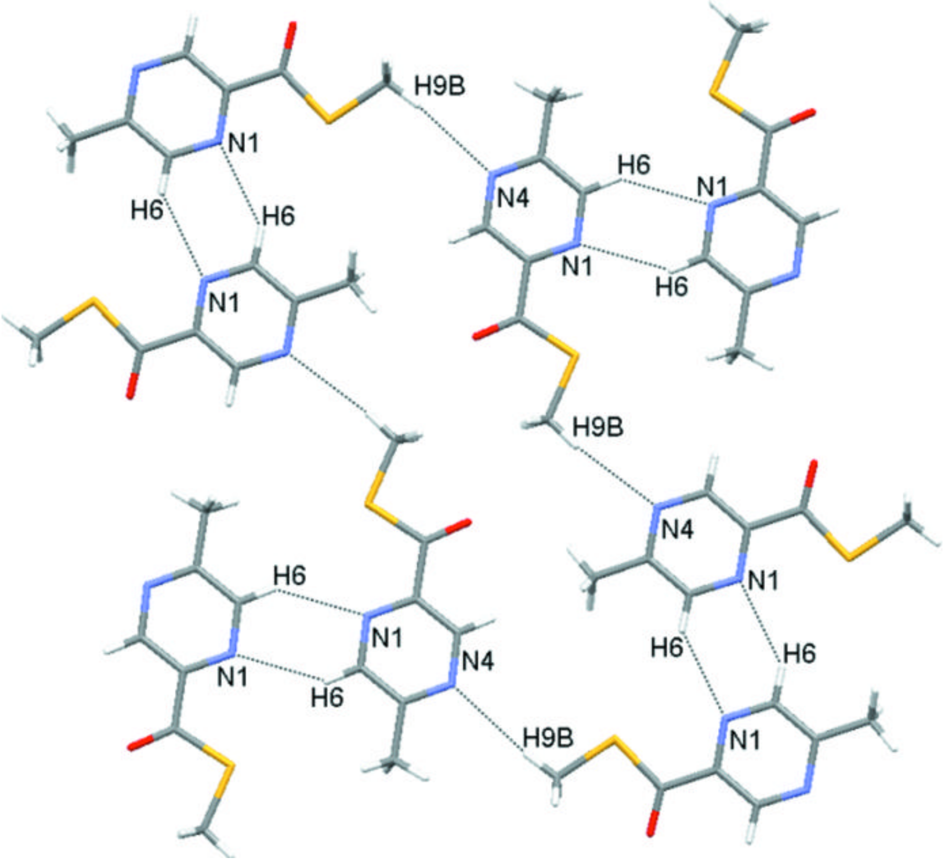
H9B
N1
H6
H6
N4
H6
N1
N1
N1
H6
H9B
H9B
N4
N1
H6
H6
H6
N1
N1
N4
H6
H9B
N1

Fig. 3

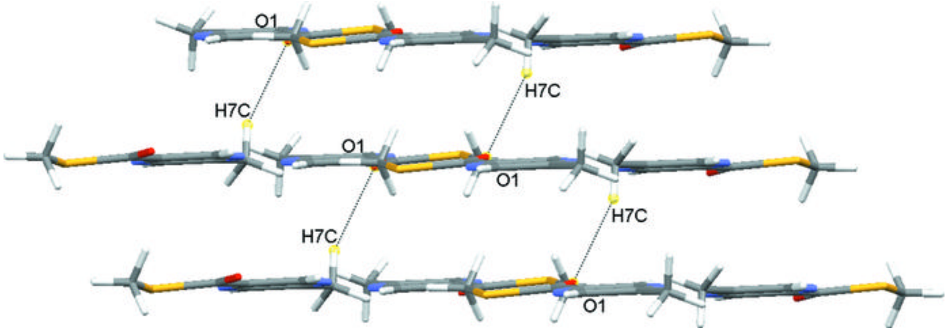

Fig. 4