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ISSN 2414-3146

Pyrazine-2(1*H*)-thione

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Received 22 September 2021
Accepted 21 October 2021

Edited by G. Diaz de Delgado, Universidad de Los Andes, Venezuela

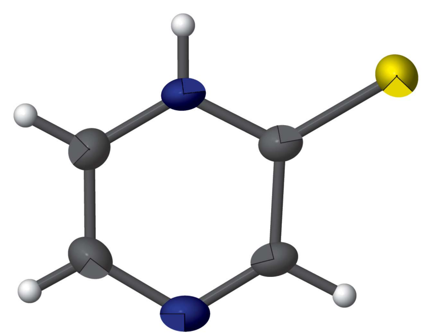
Keywords: crystal structure; 2-mercapto-pyrazine; hydrogen bonds; Hirshfeld surface analysis.

CCDC reference: 2117037

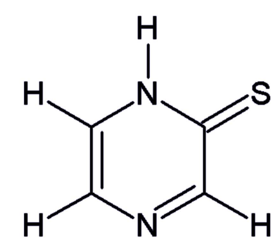
Structural data: full structural data are available from iucrdata.iucr.org

The title compound, $C_4H_4N_2S$, was obtained by the reduction of 2-mercapto-pyrazine (during its crystallization with 2-mercaptopyrazine and isonicotinic acid *N*-oxide in ethanol solution. It crystallizes in the monoclinic space group $P2_1/m$. In the crystal, the molecules are linked by N—H···N and C—H···S hydrogen bonds.

3D view



Chemical scheme



Structure description

Pyrazine is an aromatic six-membered hetrocyclic that contains two nitrogen atoms in positions 1 and 4. As a result, pyrazine has weaker basic properties than pyridine, pyridazine and pyrimidine. Pyrazine derivatives play an important role in chemotherapy (Wu *et al.*, 2012; Polshettiwar & Varma 2008; Goya *et al.*, 1997). Its derivatives possess diverse biological activities such as antidiabetic, diuretic (Pranab *et al.*, 2011), anti-inflammatory (Chandrakant & Naresh, 2004), antimicrobial (Mallesha & Mohana 2011), analgesic (Doležal *et al.*, 2007) and anticancer (Kayagil & Demirayak, 2011). In addition, 2-mercaptopyrinosine derivatives are known to be cancer inhibitors (Mallesha & Mohana, 2011; Bonde & Gaikwad, 2004).

The title compound pyrazine-2(1*H*)-thione (I) was obtained as a yellow solid by reduction of 2-mercaptopyrazine (II) during its crystallization with 2-mercaptopyrazine (II) and isonicotinic acid *N*-oxide (III) in ethanol solution (Fig. 1). Pyrazine-2(1*H*)-thione crystallizes in the monoclinic space group $P2_1$/m. The atomic labelling scheme is shown in Fig. 2. In pyrazine-2(1*H*)-thione, being a reduced form of (II), there is one hydrogen atom at atom N1.

The C—C bond lengths are within the expected values known for aromatic systems. The N1—C2 and N1—C6 bond lengths [1.354 (3) and 1.355 (3) Å, respectively] are longer than those for N4—C3 and N4—C5 [1.299 (3) Å and 1.366 (3) Å)], respectively. This is the result of the protonation of the N1 atom. The C2—S2 bond length [1.671 (2) Å] is comparable within the 3σ criterion. All of the angles have usual values.

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

D—H···A	D—H	H···A	D···A	D—H···A
C5—H5···S2^{i}	0.86 (3)	2.94 (3)	3.797 (3)	171 (3)
C6—H6···S2^{ii}	0.90 (3)	2.88 (3)	3.775 (2)	173 (2)
C3—H3···S2^{iii}	0.99 (3)	2.98 (3)	3.716 (2)	132 (2)
N1—H1···N4^{iv}	0.85 (4)	2.04 (4)	2.893 (3)	178 (3)
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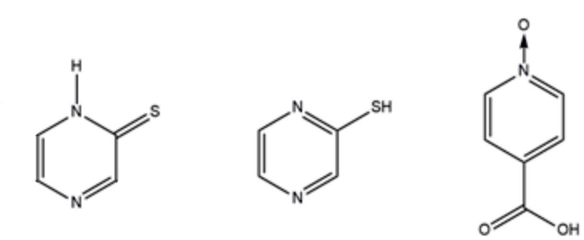
N1—H1···N4^{iv}	0.85 (4)	2.04 (4)	2.893 (3)	178 (3)

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

The crystal packing of pyrazine-2(1*H*)-thione is determined by hydrogen bonds of the N—H···N and C—H···S type (Table 1). Firstly, N1—H1···N4 hydrogen bonds [C···S = 2.893 (2) Å] between neighbouring molecules form a chain. As a result, the molecules are ordered along the [100] direction. This parallel arrangement is additionally stabilized by further interactions between adjacent molecules [C3—H3···S2 = 3.716 (2) Å, C5—H5···S2 = 3.797 (3) Å and C6—H6···S2 = 3.775 (3) Å], as shown in Fig. 3.

Molecular Hirshfeld surface (Spackman & Jayatilaka, 2009) and fingerprint plots (Spackman & McKinnon, 2002), were generated with *Crystal Explorer 3.1* (Wolff *et al.*, 2012) using the automatic procedures implemented in the program. The surfaces are mapped with a normalized contact distance (d_{norm}), with values ranging from −0.58 to 1.05 a.u. Graphical



(I) (II) (III)

Figure 1
. Molecular formulae of pyrazine-2(1*H*)-thione (I), 2-mercaptopyrazine (II) and isonicotinic acid *N*-oxide (III).

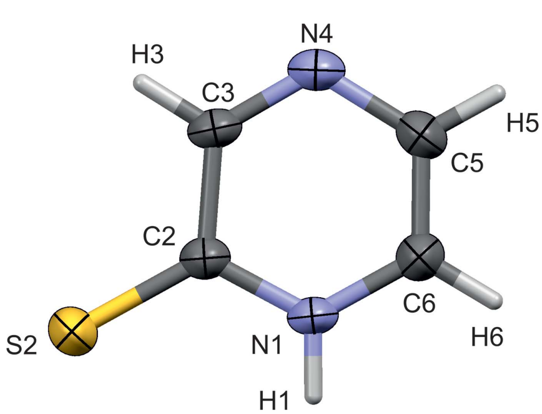


Figure 2
The molecular structure of pyrazine-2(1*H*)-thione, showing the atom-labelling scheme and displacement ellipsoids at the 50% probability level.

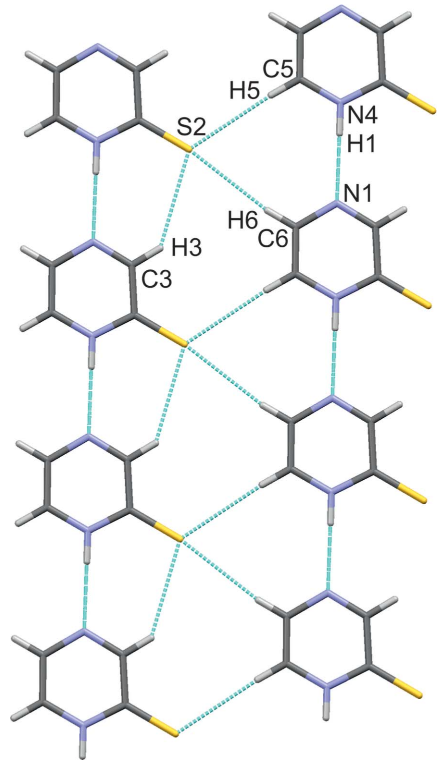


Figure 3
N–H···N and C—H···S hydrogen bonds between adjacent pyrazine-2(1*H*)-thione molecules.

representations of the Hirshfeld fingerprint plots for selected types of intermolecular interactions are presented in Fig. 4. The C—H···S and N—H···N hydrogen bonds make major contribution to the overall Hirshfeld surface with 36.8% and 13.8% contributions, respectively. In addition, H···H (24.8%) and H···C (11.7%) contacts make a significant contribution to the crystal packing.

A search of the Cambridge Structural Database (CSD version 5.41, November 2019; Groom *et al.*, 2016) for 2-mercaptopyrazine with no disorder, no other errors and only organic compounds yielded 79 structures. However, the

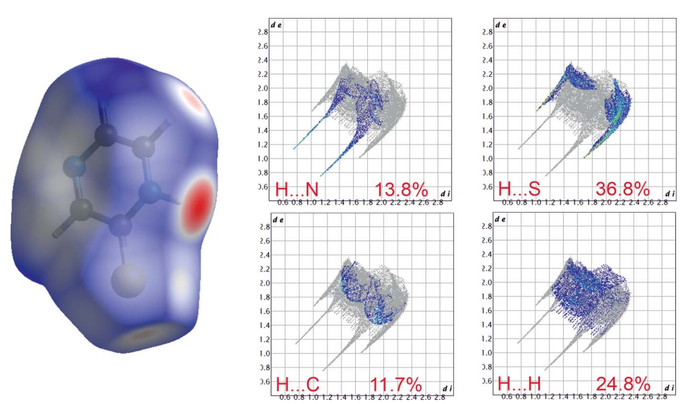


Figure 4
The molecular Hirshfeld surfaces of pyrazine-2(1*H*)-thione mapped with d_{norm}. Red areas represent intermolecular contacts of distances shorter than the van der Waals separation.

structure of this compound and its oxidised form were not found.

Synthesis and crystallization

Crystals suitable for *X*-ray measurements were obtained from commercially available reagents (Aldrich Chemical Co.) which were used without further purification. 0.5 mmol of 2-mercaptopyrazine (II) was mixed with 0.5 mmol of isonicotinic acid *N*-oxide (III) and dissolved in ethanol (4 ml). The obtained solution was kept at room temperature. Crystals (yellow plates) for *X*-ray diffraction were obtained after slow evaporation of the solvent within 2 weeks.

Refinement

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_4H_4N_2S$
M_r	112.15
Crystal system, space group	Monoclinic, $P2_1/m$
Temperature (K)	150
a, b, c (Å)	5.6113 (3), 6.4370 (6), 7.0923 (4)
β (°)	100.325 (6)
V (Å^3)	252.03 (3)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.49
Crystal size (mm)	0.18 × 0.06 × 0.04
Data collection	
Diffractometer	XtaLAB Synergy, Dualflex, HyPix
Absorption correction	Analytical (*CrysAlis PRO*; Rigaku OD, 2015)
T_{min}, T_{max}	0.991, 0.997
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	2812, 562, 496
R_{int}	0.035
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.627
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.031, 0.088, 1.13
No. of reflections	562
No. of parameters	55
H-atom treatment	All H-atom parameters refined
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.24, −0.19

Computer programs: *CrysAlis PRO* (Rigaku OD, 2015), *SHELXT2018*/2 (Sheldrick, 2015*a*), *SHELXL2018*/3 (Sheldrick, 2015*b*) and *SHELXTL* (Sheldrick, 2008).

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full crystallographic data

IUCrData (2021). **6**, x211102 [https://doi.org/10.1107/S2414314621011020]

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Pyrazine-2(1*H*)-thione

Crystal data

$C_4H_4N_2S$
M_r = 112.15
Monoclinic, $P2_1/m$
a = 5.6113 (3) Å
b = 6.4370 (6) Å
c = 7.0923 (4) Å
β = 100.325 (6)°
V = 252.03 (3) Å^3
Z = 2
F(000) = 116
D_x = 1.478 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 1374 reflections
θ = 3.2–29.1°
μ = 0.49 mm^{-1}
T = 150 K
Plate, yellow
0.18 × 0.06 × 0.04 mm

Data collection

XtaLAB Synergy, Dualflex, HyPix diffractometer
Detector resolution: 10.4052 pixels mm^{-1}
ω scans
Absorption correction: analytical (CrysAlisPro; Rigaku OD, 2015)
T_{min} = 0.991, T_{max} = 0.997
2812 measured reflections
562 independent reflections
496 reflections with $I > 2\sigma(I)$
R_{int} = 0.035
θ_{max} = 26.5°, θ_{min} = 2.9°
$h = -7 \rightarrow 6$
$k = -7 \rightarrow 8$
$l = -8 \rightarrow 8$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.031
$wR(F^2)$ = 0.088
S = 1.13
562 reflections
55 parameters
0 restraints
Primary atom site location: difference Fourier map
Hydrogen site location: difference Fourier map
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0411P)^2 + 0.0767P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.24 e Å^{-3}
$\Delta\rho_{min}$ = −0.19 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.

Refinement. Hydrogen atoms of aromatic rings were introduced in calculated positions with idealized geometry and constrained using a rigid body model with isotropic displacement parameters equal to 1.2 the equivalent displacement parameters of the parent atoms. The H atom of the NH group was located in a difference Fourier map and freely refined.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
S2	0.96392 (11)	0.750000	0.80505 (9)	0.0517 (3)
N1	0.8466 (3)	0.750000	0.4242 (3)	0.0354 (5)
N4	0.3609 (3)	0.750000	0.4191 (3)	0.0371 (5)
C3	0.5132 (4)	0.750000	0.5802 (3)	0.0335 (5)
C2	0.7722 (4)	0.750000	0.5956 (3)	0.0321 (5)
C6	0.6909 (4)	0.750000	0.2544 (4)	0.0418 (6)
C5	0.4506 (4)	0.750000	0.2523 (4)	0.0436 (6)
H5	0.355 (5)	0.750000	0.143 (5)	0.051 (8)*
H6	0.743 (5)	0.750000	0.142 (4)	0.047 (8)*
H3	0.458 (5)	0.750000	0.704 (4)	0.037 (7)*
H1	0.999 (7)	0.750000	0.426 (5)	0.069 (10)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S2	0.0290 (4)	0.0950 (6)	0.0300 (4)	0.000	0.0026 (2)	0.000
N1	0.0185 (9)	0.0561 (13)	0.0327 (10)	0.000	0.0074 (8)	0.000
N4	0.0215 (9)	0.0495 (12)	0.0409 (11)	0.000	0.0069 (8)	0.000
C3	0.0217 (10)	0.0436 (13)	0.0371 (12)	0.000	0.0108 (9)	0.000
C2	0.0231 (10)	0.0414 (13)	0.0326 (11)	0.000	0.0076 (9)	0.000
C6	0.0301 (12)	0.0672 (18)	0.0292 (12)	0.000	0.0085 (10)	0.000
C5	0.0270 (12)	0.0693 (18)	0.0323 (13)	0.000	−0.0008 (10)	0.000

Geometric parameters (Å, º)

S2—C2	1.671 (2)	C3—C2	1.437 (3)
N1—C2	1.354 (3)	C3—H3	0.99 (3)
N1—C6	1.355 (3)	C6—C5	1.346 (3)
N1—H1	0.85 (4)	C6—H6	0.90 (3)
N4—C3	1.299 (3)	C5—H5	0.86 (3)
N4—C5	1.366 (3)		
C2—N1—C6	123.0 (2)	N1—C2—S2	123.03 (17)
C2—N1—H1	117 (2)	C3—C2—S2	123.25 (18)
C6—N1—H1	120 (2)	C5—C6—N1	119.6 (2)
C3—N4—C5	118.37 (19)	C5—C6—H6	118.2 (19)
N4—C3—C2	124.3 (2)	N1—C6—H6	122.2 (19)
N4—C3—H3	121.6 (15)	C6—C5—N4	121.0 (2)
C2—C3—H3	114.1 (15)	C6—C5—H5	118 (2)
N1—C2—C3	113.7 (2)	N4—C5—H5	121 (2)
C5—N4—C3—C2	0.000 (1)	N4—C3—C2—S2	180.000 (1)
C6—N1—C2—C3	0.000 (1)	C2—N1—C6—C5	0.000 (1)
C6—N1—C2—S2	180.000 (1)	N1—C6—C5—N4	0.000 (1)
N4—C3—C2—N1	0.000 (1)	C3—N4—C5—C6	0.000 (1)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C5—H5···S2^{i}	0.86 (3)	2.94 (3)	3.797 (3)	171 (3)
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Symmetry codes: (i) *x*−1, *y*, *z*−1; (ii) *x*, *y*, *z*−1; (iii) *x*−1, *y*, *z*; (iv) *x*+1, *y*, *z*.