The title compound, C₄H₄N₂S, 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 
P2₁/m. In the crystal, the molecules are linked by N—H···N and C—H···S 
hydrogen bonds.

Structure description

Pyrazine is an aromatic six-membered heterocyclic 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(1H)-thione (I) was obtained as a yellow solid by 
reduction of 2-mercapto-
pyrazine (II) during its crystallization with 2-mercaptopyrazine and isonicotinic 
acid N-oxide (III) in ethanol solution (Fig. 1). Pyrazine-2(1H)-thione 
crystallizes in the monoclinic space group P2₁/m. The atomic labelling scheme is shown in 
Fig. 2. In pyrazine-2(1H)-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.
The crystal packing of pyrazine-2(1H)-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 ($d_{\text{norm}}$), with values ranging from ~0.58 to 1.05 a.u. Graphical 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

### Table 1

Hydrogen-bond geometry (Å, °).

| D—H···A   | D—H  | H···A | D···A  | D—H···A |
|-----------|-------|-------|--------|---------|
| C5—H5···S2i | 0.86 (3) | 2.94 (3) | 3.797 (3) | 171 (3) |
| C6—H6···S2ii | 0.90 (3) | 2.88 (3) | 3.775 (2) | 173 (2) |
| C3—H3···S2iii | 0.99 (3) | 2.98 (3) | 3.716 (2) | 132 (2) |
| N1—H1···N4iv | 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.

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![Figure 1](image1.jpg)

**Figure 1**

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

![Figure 2](image2.jpg)

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

![Figure 3](image3.jpg)

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

![Figure 4](image4.jpg)

**Figure 4**
The molecular Hirshfeld surfaces of pyrazine-2(1H)-thione mapped with $d_{\text{norm}}$. 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.

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Table 2
Experimental details.

| Crystal data                          | C8H8N2S |
|---------------------------------------|---------|
| Chemical formula                      |         |
| M_r                                   | 152.15  |
| 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 (Å³)                                | 252.03 (3) |
| Z                                      | 2       |
| Radiation type                        | Mo Kα   |
| μ (mm⁻¹)                              | 0.49    |
| Crystal size (mm)                     | 0.18 × 0.06 × 0.04 |

| Data collection                       | XtaLAB Synergy, Dualflex, HyPix Analytical (CrysAlis PRO; Rigaku OD, 2015) |
|---------------------------------------|---------------------------------------------------------------------------|
| Absorption correction                |                                                                            |
| T_min, T_max                          | 0.991, 0.997                                                               |
| No. of measured, independent and observed I > 2σ(I) reflections | 2812, 562, 496                                                             |
| Rint                                  | 0.035                                                                      |
| (sin θ/λ)max (Å⁻¹)                    | 0.267                                                                      |

Refinement
R[F² > 2σ(F²)], wR(F²), S               0.031, 0.088, 1.13
No. of reflections                     562
No. of parameters                      55
H-atom treatment                      All H-atom parameters refined
Δρ_max, Δρ_min (e Å⁻³)                 0.24, −0.19

Computer programs: CrysAlis PRO (Rigaku OD, 2015), SHELXTL2018/2 (Sheldrick, 2015a), SHELXL2018/3 (Sheldrick, 2015b) and SHELXTL (Sheldrick, 2008).

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Pyrazine-2(1H)-thione

Adrian Olszewski and Kinga Wzgarda-Raj

Pyrazine-2(1H)-thione

Crystal data

\[ \text{C}_4\text{H}_4\text{N}_2\text{S} \]

\[ M_r = 112.15 \]

Monoclinic, \( P2_1/m \)

\[ a = 5.6113 \ (3) \ \text{Å} \]

\[ b = 6.4370 \ (6) \ \text{Å} \]

\[ c = 7.0923 \ (4) \ \text{Å} \]

\[ \beta = 100.325 \ (6) ^\circ \]

\[ V = 252.03 \ (3) \ \text{Å}^3 \]

\[ Z = 2 \]

\[ \text{F}(000) = 116 \]

\[ D_\lambda = 1.478 \ \text{Mg m}^{-3} \]

Mo \( K\alpha \) radiation, \( \lambda = 0.71073 \ \text{Å} \)

Cell parameters from 1374 reflections

\[ \theta = 3.2-29.1^\circ \]

\[ \mu = 0.49 \ \text{mm}^{-1} \]

\[ T = 150 \ \text{K} \]

Plate, yellow

\[ 0.18 \times 0.06 \times 0.04 \ \text{mm} \]

Data collection

XtaLAB Synergy, Dualflex, HyPix

diffractometer

Detector resolution: 10.4052 pixels mm\(^{-1}\)

\( \omega \) scans

Absorption correction: analytical

\[ R_{\text{int}} = 0.035 \]

\[ \theta_{\text{max}} = 26.5^\circ, \theta_{\text{min}} = 2.9^\circ \]

\[ T_{\text{min}} = 0.991, T_{\text{max}} = 0.997 \]

562 independent reflections

496 reflections with \( I > 2\sigma(I) \)

\[ h = -7 \rightarrow 6 \]

\[ k = -7 \rightarrow 8 \]

\[ l = -8 \rightarrow 8 \]

2812 measured reflections

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

\[ w = 1/[(\sigma(F^2)^2 + (0.0411P)^2 + 0.0767P)] \]

where \( P = (F^2 + 2F_c^2)/3 \)

\[ (\Delta/\sigma)_{\text{max}} < 0.001 \]

\[ \Delta \rho_{\text{max}} = 0.24 \ \text{e Å}^{-3} \]

\[ \Delta \rho_{\text{min}} = -0.19 \ \text{e Å}^{-3} \]

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          | Uiso* / Ueq |
|-----|------------|-----------|------------|-------------|
| 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)

|     | U¹¹ | U¹² | U¹³ | U¹² | U¹³ | U¹³ |
|-----|-----|-----|-----|-----|-----|-----|
| 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, °)

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, °)

| 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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| 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) |

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