# 2-Sulfanylidene-1,3-dithiolo[4,5-b]pyrazine-5,6-dicarbonitrile

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In the title compound, $C_7N_4S_3$, the molecular entity consisting of a 1,3-dithiole-2-thione with a fused pyrazine ring is planar, with an r.m.s. deviation of 0.042 (3) Å from the least-squares plane. In the crystal, molecules are linked via short intermolecular S···N contacts [3.251 (4) and 3.308 (3) Å] between the S atom of the thiocarbonyl group and N atoms of the cyano groups.

**3D view**
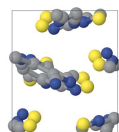


**Chemical scheme**
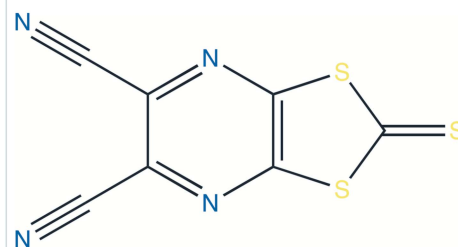


## Structure description

Molecules containing an 1,3-dithiolo[4,5-b]pyrazine-2-thione framework are important synthetic precursors of multi-dimensional organic superconductors and conductors. Intermolecular S···N and S···S contacts involving peripheral S and N atoms may increase the dimensionality in the solid state and suppress metal–insulator transitions (Williams et al., 1992; Ishiguro et al., 1998). In addition, such contacts may lead to the formation of unique molecular networks which have special functions, such as inclusion properties (Yamashita & Tomura, 1998). Fused pyrazine units are expected to extend the π-conjugated system, resulting in decreased Coulombic repulsion (Tomura & Yamashita, 1995; Belo et al., 2004; Nomura et al., 2009), and coordinate to transition metals (Imakubo et al., 2006; Rabaça & Almeida, 2010; Imakubo & Murayama, 2013), constructing organometallic coordination polymers. We report here the molecular and crystal structure of the title compound.

The title compound crystallizes in the space group $P2_12_12_1$ with one molecule in the asymmetric unit. The molecular structure is shown in Fig. 1. The molecular geometry is comparable to that found in the parent thione (2-thioxo-1,3-dithiolo[4,5-b]pyrazine; Rabaça et al., 2013), although the parent molecule lies on a mirror plane. The molecular entity of the title compound is planar, with an r.m.s. deviation of 0.042 (3) Å from the least-squares plane. In the crystal, a short intermolecular S···N contact [3.251 (4) Å for S1—N4($-x + \frac{1}{2}, -y + 1, z - \frac{1}{2}$)] is observed between the S atom of the thiocarbonyl group
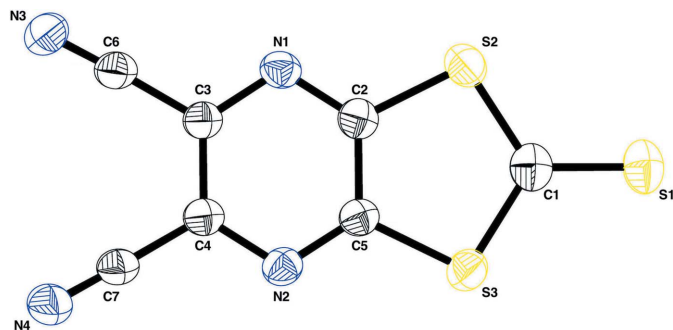
**Figure 1**
The molecular structure of the title compound, showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

and the N atom of the cyano group, constructing a zigzag molecular tape network extending along the $c$ axis (Fig. 2). The molecular tapes are linked *via* short intertape $S \cdots N$ interactions [3.308 (3) Å for $S1 \cdots N3(-x - \frac{1}{2}, -y + 1, z - \frac{1}{2})$].

## Synthesis and crystallization

According to the literature method of Tomura *et al.* (1994), the title compound was synthesized by the reaction of 2,3-dichloropyrazine-5,6-dicarbonitrile with sodium sulfide and thiophosgene. The details will be reported elsewhere. Decomposition point: 463 K, MS (EI): $m/z$ 236 ($M^+$). Orange crystals suitable for X-ray analysis were grown from an acetonitrile solution.

## Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. One reflection (205) was omitted due to bad agreement between the observed and calculated intensities.

## Acknowledgements

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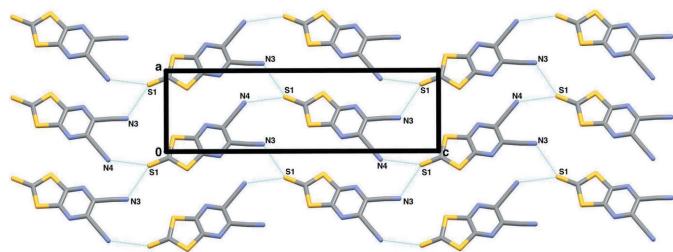
**Table 1**
Experimental details.

| | |
|---|---|
| **Crystal data** | |
| Chemical formula | $C_7N_4S_3$ |
| $M_r$ | 236.29 |
| Crystal system, space group | Orthorhombic, $P2_12_12_1$ |
| Temperature (K) | 173 |
| $a, b, c$ (Å) | 6.1657 (15), 7.0875 (19), 20.883 (6) |
| $V$ (Å$^3$) | 912.6 (4) |
| $Z$ | 4 |
| Radiation type | Mo $K\alpha$ |
| $\mu$ (mm$^{-1}$) | 0.77 |
| Crystal size (mm) | $0.30 \times 0.30 \times 0.05$ |
| | |
| **Data collection** | |
| Diffractometer | Rigaku/MSC Mercury CCD |
| Absorption correction | Multi-scan (*ABSCOR*; Higashi, 1995) |
| $T_{min}, T_{max}$ | 0.825, 1.000 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 8289, 2561, 2314 |
| $R_{int}$ | 0.031 |
| $(\sin \theta/\lambda)_{max}$ (Å$^{-1}$) | 0.721 |
| | |
| **Refinement** | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.041, 0.103, 1.11 |
| No. of reflections | 2561 |
| No. of parameters | 127 |
| $\Delta\rho_{max}, \Delta\rho_{min}$ (e Å$^{-3}$) | 0.29, −0.35 |
| Absolute structure | Flack $x$ determined using 803 quotients $[(I^+) - (I^-)]/[(I^+) + (I^-)]$ (Parsons *et al.*, 2013) |
| Absolute structure parameter | 0.07 (4) |

Computer programs: *CrystalClear* (Rigaku/MSC, 2006), *SIR2014* (Burla *et al.*, 2015), *SHELXL2016* (Sheldrick, 2015), *PLATON* (Spek, 2009) and *Mercury* (Macrae *et al.*, 2008).

**Figure 2**
A partial view along the $b$ axis of the crystal packing of the title compound. Dashed lines show the intermolecular $S \cdots N$ contacts.

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# full crystallographic data

## 2-Sulfanylidene-1,3-dithiolo[4,5-*b*]pyrazine-5,6-dicarbonitrile

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**2-Sulfanylidene-1,3-dithiolo[4,5-*b*]pyrazine-5,6-dicarbonitrile**

*Crystal data*

| | |
|---|---|
| $C_7N_4S_3$ | $D_x = 1.720$ Mg m$^{-3}$ |
| $M_r = 236.29$ | Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å |
| Orthorhombic, $P2_12_12_1$ | Cell parameters from 3015 reflections |
| $a = 6.1657$ (15) Å | $\theta = 2.0–30.7°$ |
| $b = 7.0875$ (19) Å | $\mu = 0.77$ mm$^{-1}$ |
| $c = 20.883$ (6) Å | $T = 173$ K |
| $V = 912.6$ (4) Å$^3$ | Prism, orange |
| $Z = 4$ | $0.30 \times 0.30 \times 0.05$ mm |
| $F(000) = 472$ | |

*Data collection*

| | |
|---|---|
| Rigaku/MSC Mercury CCD diffractometer | 8289 measured reflections |
| Radiation source: Rotating Anode | 2561 independent reflections |
| Graphite Monochromator monochromator | 2314 reflections with $I > 2\sigma(I)$ |
| Detector resolution: 14.7059 pixels mm$^{-1}$ | $R_{int} = 0.031$ |
| $\varphi$ & $\omega$ scans | $\theta_{max} = 30.8°$, $\theta_{min} = 2.0°$ |
| Absorption correction: multi-scan (ABSCOR; Higashi, 1995) | $h = -8 \rightarrow 6$ |
| | $k = -9 \rightarrow 8$ |
| $T_{min} = 0.825$, $T_{max} = 1.000$ | $l = -23 \rightarrow 28$ |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Secondary atom site location: difference Fourier map |
| Least-squares matrix: full | |
| $R[F^2 > 2\sigma(F^2)] = 0.041$ | $w = 1/[\sigma^2(F_o^2) + (0.0486P)^2 + 0.1364P]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| $wR(F^2) = 0.103$ | |
| $S = 1.11$ | $(\Delta/\sigma)_{max} < 0.001$ |
| 2561 reflections | $\Delta\rho_{max} = 0.29$ e Å$^{-3}$ |
| 127 parameters | $\Delta\rho_{min} = -0.35$ e Å$^{-3}$ |
| 0 restraints | Absolute structure: Flack $x$ determined using 803 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons *et al.*, 2013) |
| Primary atom site location: structure-invariant direct methods | |
| | Absolute structure parameter: 0.07 (4) |

*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**. Refinement of $F^2$ against ALL reflections. The weighted R-factor wR and goodness of fit S are based on $F^2$, conventional R-factors R are based on F, with F set to zero for negative $F^2$. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on $F^2$ are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

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

|  | $x$ | $y$ | $z$ | $U_{iso}*/U_{eq}$ |
|---|---|---|---|---|
| S1 | −0.17153 (16) | 0.55587 (14) | −0.06252 (4) | 0.0479 (3) |
| S2 | −0.21351 (14) | 0.62442 (14) | 0.07652 (4) | 0.0434 (2) |
| S3 | 0.17499 (14) | 0.43326 (12) | 0.02606 (4) | 0.0410 (2) |
| N1 | −0.0522 (4) | 0.5875 (4) | 0.19453 (13) | 0.0339 (6) |
| N2 | 0.3228 (4) | 0.4055 (4) | 0.14587 (13) | 0.0334 (6) |
| N3 | 0.0894 (5) | 0.6018 (5) | 0.35380 (15) | 0.0451 (7) |
| N4 | 0.6025 (5) | 0.3496 (4) | 0.28648 (16) | 0.0445 (7) |
| C1 | −0.0756 (6) | 0.5386 (5) | 0.00956 (17) | 0.0394 (7) |
| C2 | −0.0230 (5) | 0.5554 (5) | 0.13276 (16) | 0.0338 (6) |
| C3 | 0.1080 (5) | 0.5255 (4) | 0.23255 (15) | 0.0309 (6) |
| C4 | 0.2925 (5) | 0.4362 (4) | 0.20854 (15) | 0.0318 (6) |
| C5 | 0.1642 (5) | 0.4634 (4) | 0.10837 (15) | 0.0314 (6) |
| C6 | 0.0915 (5) | 0.5664 (5) | 0.30048 (17) | 0.0359 (7) |
| C7 | 0.4656 (5) | 0.3844 (5) | 0.25174 (16) | 0.0344 (7) |

*Atomic displacement parameters (Å²)*

|  | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| S1 | 0.0596 (6) | 0.0427 (5) | 0.0414 (5) | −0.0048 (5) | −0.0122 (4) | 0.0016 (4) |
| S2 | 0.0366 (4) | 0.0517 (5) | 0.0420 (5) | 0.0053 (4) | −0.0011 (3) | 0.0079 (4) |
| S3 | 0.0506 (5) | 0.0391 (4) | 0.0334 (4) | 0.0080 (4) | 0.0024 (3) | −0.0008 (4) |
| N1 | 0.0301 (12) | 0.0343 (14) | 0.0373 (15) | 0.0020 (11) | 0.0040 (10) | 0.0041 (12) |
| N2 | 0.0384 (12) | 0.0283 (13) | 0.0336 (14) | 0.0020 (11) | 0.0032 (11) | −0.0004 (11) |
| N3 | 0.0508 (15) | 0.0473 (18) | 0.0374 (17) | 0.0067 (14) | 0.0070 (13) | −0.0006 (14) |
| N4 | 0.0460 (15) | 0.0421 (18) | 0.0456 (18) | 0.0097 (13) | −0.0026 (13) | −0.0061 (14) |
| C1 | 0.0476 (17) | 0.0293 (17) | 0.0413 (19) | −0.0061 (14) | −0.0025 (14) | 0.0033 (14) |
| C2 | 0.0352 (14) | 0.0302 (15) | 0.0361 (17) | −0.0020 (12) | 0.0029 (12) | 0.0062 (13) |
| C3 | 0.0323 (13) | 0.0273 (16) | 0.0330 (16) | 0.0001 (11) | 0.0046 (11) | 0.0042 (12) |
| C4 | 0.0334 (13) | 0.0263 (14) | 0.0356 (16) | 0.0004 (12) | 0.0052 (12) | 0.0039 (12) |
| C5 | 0.0341 (14) | 0.0263 (14) | 0.0337 (16) | 0.0005 (12) | 0.0037 (12) | 0.0017 (12) |
| C6 | 0.0349 (14) | 0.0333 (16) | 0.0395 (19) | 0.0041 (13) | 0.0061 (12) | 0.0042 (14) |
| C7 | 0.0345 (15) | 0.0311 (16) | 0.0376 (17) | 0.0036 (13) | 0.0041 (13) | −0.0022 (14) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| S1—C1 | 1.622 (4) | N2—C4 | 1.340 (4) |
| S2—C2 | 1.732 (3) | N3—C6 | 1.141 (4) |
| S2—C1 | 1.746 (4) | N4—C7 | 1.140 (4) |
| S3—C5 | 1.733 (3) | C2—C5 | 1.420 (4) |
| S3—C1 | 1.750 (4) | C3—C4 | 1.395 (4) |

| | | | |
|---|---|---|---|
| N1—C2 | 1.322 (4) | C3—C6 | 1.452 (5) |
| N1—C3 | 1.341 (4) | C4—C7 | 1.445 (4) |
| N2—C5 | 1.319 (4) | | |
| | | | |
| S1···N4ⁱ | 3.251 (4) | S1···N3ⁱⁱ | 3.308 (3) |
| | | | |
| C2—S2—C1 | 96.57 (17) | N1—C3—C6 | 117.5 (3) |
| C5—S3—C1 | 96.24 (16) | C4—C3—C6 | 120.0 (3) |
| C2—N1—C3 | 114.9 (3) | N2—C4—C3 | 122.6 (3) |
| C5—N2—C4 | 115.2 (3) | N2—C4—C7 | 117.7 (3) |
| S1—C1—S2 | 122.6 (2) | C3—C4—C7 | 119.6 (3) |
| S1—C1—S3 | 122.5 (2) | N2—C5—C2 | 122.2 (3) |
| S2—C1—S3 | 114.9 (2) | N2—C5—S3 | 121.5 (2) |
| N1—C2—C5 | 122.6 (3) | C2—C5—S3 | 116.3 (2) |
| N1—C2—S2 | 121.4 (2) | N3—C6—C3 | 176.4 (4) |
| C5—C2—S2 | 116.0 (2) | N4—C7—C4 | 177.7 (4) |
| N1—C3—C4 | 122.4 (3) | | |
| | | | |
| C2—S2—C1—S1 | 179.2 (2) | N1—C3—C4—N2 | −0.2 (5) |
| C2—S2—C1—S3 | −1.0 (2) | C6—C3—C4—N2 | −175.7 (3) |
| C5—S3—C1—S1 | −179.3 (2) | N1—C3—C4—C7 | 175.8 (3) |
| C5—S3—C1—S2 | 1.0 (2) | C6—C3—C4—C7 | 0.3 (4) |
| C3—N1—C2—C5 | −0.4 (5) | C4—N2—C5—C2 | 1.3 (4) |
| C3—N1—C2—S2 | 179.7 (2) | C4—N2—C5—S3 | −179.4 (2) |
| C1—S2—C2—N1 | −179.4 (3) | N1—C2—C5—N2 | −0.7 (5) |
| C1—S2—C2—C5 | 0.7 (3) | S2—C2—C5—N2 | 179.2 (2) |
| C2—N1—C3—C4 | 0.8 (4) | N1—C2—C5—S3 | −180.0 (3) |
| C2—N1—C3—C6 | 176.4 (3) | S2—C2—C5—S3 | −0.1 (3) |
| C5—N2—C4—C3 | −0.9 (4) | C1—S3—C5—N2 | −179.8 (3) |
| C5—N2—C4—C7 | −177.0 (3) | C1—S3—C5—C2 | −0.6 (3) |

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