



## Crystal structure of 4,6-diamino-2-(methylsulfanyl)pyridine-3-carbonitrile

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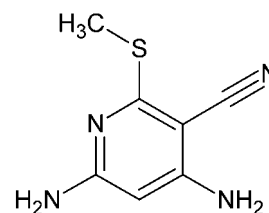
The title pyrimidine derivative, C<sub>7</sub>H<sub>8</sub>N<sub>4</sub>S, is essentially planar, with a maximum deviation of 0.029 (2) Å from the mean plane of the non-H atoms. In the crystal, molecules are linked by an intermolecular bifurcated N—H...N hydrogen bond between the cyano N atom and the two amino groups, an N—H...N hydrogen bond between the two amino groups and a weak C—H...π interaction, forming a three-dimensional network.

**Keywords:** crystal structure; 4,6-diamino-2-(methylsulfanyl)pyridine-3-carbonitrile; multifunctional pyridines.

**CCDC reference:** 1049335

### 1. Related literature

For the abundance of pyridines in pharmaceuticals and natural products, see: Zhang *et al.* (2010). For various applications of pyridine-containing compounds, see: Murata *et al.* (2003). For the use of polyfunctional pyridines in preparing a variety of heterocyclic compounds, see: Al-Haiza *et al.* (2003). For the synthesis of the title compound, see: Abu-Shanab (1999). For a similar structure, see: Mohamed *et al.* (2014).



### 2. Experimental

#### 2.1. Crystal data

C<sub>7</sub>H<sub>8</sub>N<sub>4</sub>S  
M<sub>r</sub> = 180.23  
Orthorhombic, P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>  
a = 5.0863 (7) Å  
b = 12.698 (2) Å  
c = 13.069 (2) Å

V = 844.1 (2) Å<sup>3</sup>  
Z = 4  
Mo Kα radiation  
μ = 0.33 mm<sup>-1</sup>  
T = 200 K  
0.40 × 0.09 × 0.05 mm

#### 2.2. Data collection

Bruker SMART X2S benchtop diffractometer  
Absorption correction: multi-scan (SADABS; Bruker, 2008)  
T<sub>min</sub> = 0.833, T<sub>max</sub> = 0.984

9083 measured reflections  
1487 independent reflections  
1353 reflections with I > 2σ(I)  
R<sub>int</sub> = 0.037

#### 2.3. Refinement

R[F<sup>2</sup> > 2σ(F<sup>2</sup>)] = 0.026  
wR(F<sup>2</sup>) = 0.062  
S = 1.06  
1487 reflections  
122 parameters  
6 restraints

H atoms treated by a mixture of independent and constrained refinement  
Δρ<sub>max</sub> = 0.20 e Å<sup>-3</sup>  
Δρ<sub>min</sub> = -0.13 e Å<sup>-3</sup>  
Absolute structure: Flack (1983)  
Absolute structure parameter: 0.01 (4)

**Table 1**

Hydrogen-bond geometry (Å, °).

D—H...A	D—H	H...A	D...A	D—H...A
N2—H2A...N3 <sup>i</sup>	0.86 (3)	2.43 (3)	3.225 (4)	155 (3)
N2—H2B...N4 <sup>ii</sup>	0.86 (2)	2.26 (3)	3.083 (4)	161 (3)
N3—H3B...N4 <sup>iii</sup>	0.85 (2)	2.31 (2)	3.128 (3)	161 (2)
C7—H7A...Cg1 <sup>iv</sup>	0.98	2.77	3.552 (4)	137

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

Data collection: APEX2 (Bruker, 2009); cell refinement: SAINT (Bruker, 2009); data reduction: SAINT; program(s) used to solve structure: SHELXS2014 (Sheldrick, 2008); program(s) used to refine structure: SHELXL2014 (Sheldrick, 2008); molecular graphics: ORTEP-3 for Windows (Farrugia, 2012); software used to prepare material for publication: PLATON (Spek, 2009).

### Acknowledgements

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Supporting information for this paper is available from the IUCr electronic archives (Reference: IS5390).

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## supporting information

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## Crystal structure of 4,6-diamino-2-(methylsulfanyl)pyridine-3-carbonitrile

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### S1. Comment

The pyridine ring is a core structure in a number of pharmaceuticals and natural products (Zhang *et al.*, 2010). 2-Amino-3-cyanopyridines have been identified as IKK- $\beta$  inhibitors (Murata *et al.*, 2003). Besides this, they are important and useful intermediates in preparing variety of heterocyclic compounds (Al-Haiza *et al.*, 2003). Such findings and following to our on-going study on synthesis of bio-active heterocyclic molecules we report in this study the synthesis and crystal structure determination of the title compound.

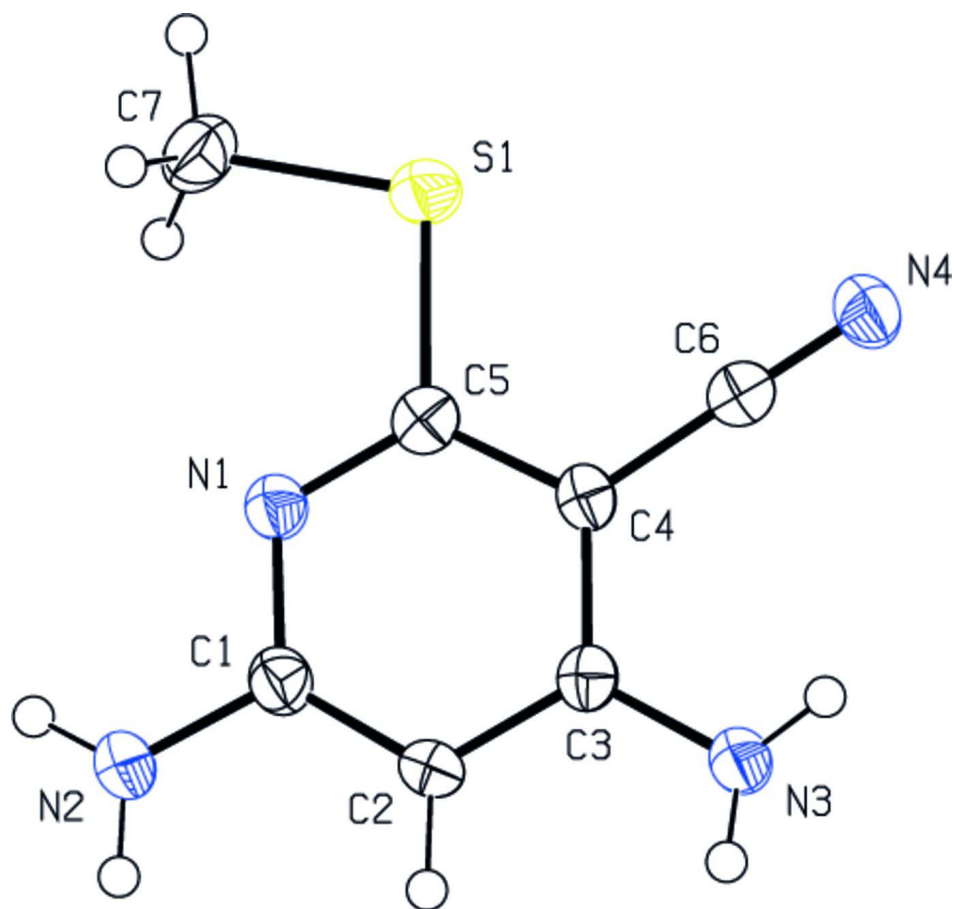
The molecule of the title compound, Fig. 1, is a tetra-substituted pyrimidine derivative, which is essentially planar with C7–S1–C5–C4, C3–C2–C1–N2, N3–C3–C4–C5 and C6–C4–C3–C2 torsion angles being 180.0 (2), 179.9 (2), 179.0 (2) and 179.7 (2)°, respectively. All bond lengths and bond angles are normal and comparable to those observed in a similar structure (Mohamed *et al.*, 2014). In the crystal structure, intermolecular N—H $\cdots$ N hydrogen bonds and a weak C—H $\cdots$  $\pi$  interaction feature in the crystal packing (Table 1, Fig. 2).

### S2. Experimental

The title compound was prepared according to the reported method (Abu-Shanab, 1999). Crystals of the product were obtained in a good yield (77%) and were suitable for X-ray diffraction (*M.p.* 426–428 K).

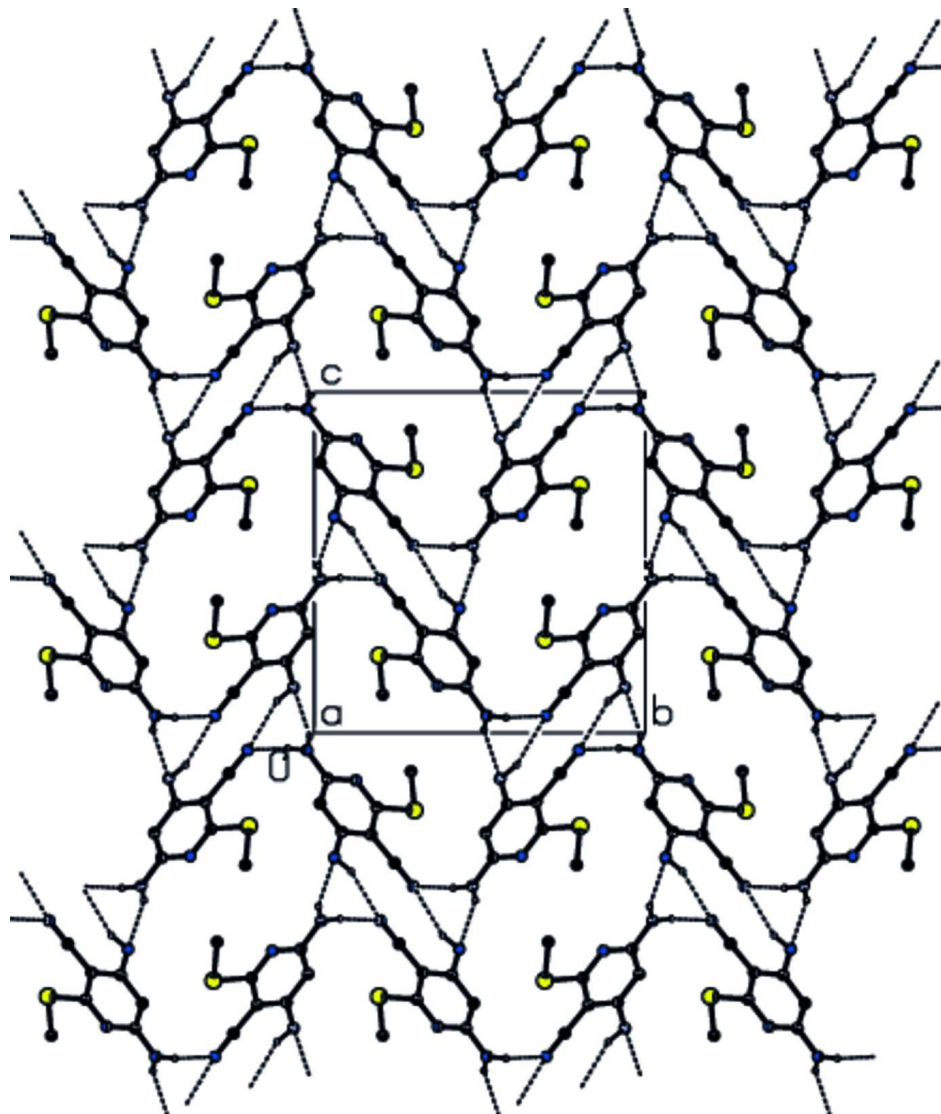
### S3. Refinement

H-atoms attached to carbon were placed in calculated positions (C—H = 0.95–0.98 Å) and refined as riding with  $U_{\text{iso}}(\text{H}) = 1.2$  or  $1.5U_{\text{eq}}(\text{C})$ . The H atoms attached to N2 and N3 were found in a difference Fourier map and their positions were refined with bond length and angle restraints of N—H = 0.86 (1) and H $\cdots$ H = 1.40 (3) Å, and with  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{N})$ .



**Figure 1**

The molecular structure of the title compound with the atom numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 50% probability level.

**Figure 2**

The hydrogen bonding (dashed lines) and packing of the title compound viewed down the *a* axis.

#### 4,6-Diamino-2-(methylsulfanyl)pyridine-3-carbonitrile

##### *Crystal data*

$C_7H_8N_4S$

$M_r = 180.23$

Orthorhombic,  $P2_12_12_1$

Hall symbol: P 2ac 2ab

$a = 5.0863$  (7) Å

$b = 12.698$  (2) Å

$c = 13.069$  (2) Å

$V = 844.1$  (2) Å<sup>3</sup>

$Z = 4$

$F(000) = 376$

$D_x = 1.418$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 3713 reflections

$\theta = 2.2$ – $25.0^\circ$

$\mu = 0.33$  mm<sup>-1</sup>

$T = 200$  K

Needle, yellow

$0.40 \times 0.09 \times 0.05$  mm

*Data collection*

Bruker SMART X2S benchtop diffractometer	9083 measured reflections
Radiation source: XOS X-beam microfocus source	1487 independent reflections
Doubly curved silicon crystal monochromator	1353 reflections with $I > 2\sigma(I)$
$\omega$ scans	$R_{\text{int}} = 0.037$
Absorption correction: multi-scan (SADABS; Bruker, 2008)	$\theta_{\text{max}} = 25.0^\circ$ , $\theta_{\text{min}} = 3.1^\circ$
$T_{\text{min}} = 0.833$ , $T_{\text{max}} = 0.984$	$h = -6 \rightarrow 6$
	$k = -15 \rightarrow 12$
	$l = -15 \rightarrow 15$

*Refinement*

Refinement on $F^2$	H atoms treated by a mixture of independent and constrained refinement
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.0294P)^2 + 0.1689P]$
$R[F^2 > 2\sigma(F^2)] = 0.026$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.062$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.06$	$\Delta\rho_{\text{max}} = 0.20 \text{ e } \text{\AA}^{-3}$
1487 reflections	$\Delta\rho_{\text{min}} = -0.13 \text{ e } \text{\AA}^{-3}$
122 parameters	Absolute structure: Flack (1983)
6 restraints	Absolute structure parameter: 0.01 (4)
Hydrogen site location: mixed	

*Special details*

**Geometry.** Bond distances, angles *etc.* have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell e.s.d.'s are taken into account in the estimation of distances, angles and torsion angles

**Refinement.** Refinement on  $F^2$  for ALL reflections except those flagged by the user for potential systematic errors. Weighted  $R$ -factors  $wR$  and all goodnesses 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 observed criterion of  $F^2 > \sigma(F^2)$  is used only for calculating  $-R$ -factor-obs *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 ( $\text{\AA}^2$ )*

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	1.05518 (13)	0.80355 (6)	0.72687 (5)	0.0304 (2)
N1	0.8883 (4)	0.62615 (18)	0.63890 (15)	0.0256 (7)
N2	0.7653 (6)	0.4785 (2)	0.55086 (19)	0.0410 (9)
N3	0.3276 (4)	0.5616 (2)	0.86570 (18)	0.0282 (7)
N4	0.6450 (4)	0.7998 (2)	0.94969 (16)	0.0322 (7)
C1	0.7297 (5)	0.5407 (2)	0.6340 (2)	0.0277 (8)
C2	0.5369 (5)	0.5181 (2)	0.70666 (18)	0.0268 (8)
C3	0.5066 (4)	0.5834 (2)	0.79017 (17)	0.0222 (8)
C4	0.6745 (5)	0.67178 (19)	0.79768 (17)	0.0217 (8)
C5	0.8576 (4)	0.6892 (2)	0.71847 (18)	0.0238 (7)
C6	0.6581 (5)	0.7431 (2)	0.88141 (19)	0.0242 (8)
C7	1.2520 (6)	0.7927 (3)	0.6128 (2)	0.0387 (10)
H2	0.42720	0.45820	0.69870	0.0320*
H2A	0.894 (5)	0.487 (3)	0.509 (2)	0.0620*
H2B	0.682 (6)	0.4202 (18)	0.545 (3)	0.0620*
H3A	0.210 (5)	0.5167 (19)	0.849 (2)	0.0420*

H3B	0.286 (6)	0.6117 (17)	0.9060 (19)	0.0420*
H7A	1.32830	0.72190	0.60900	0.0580*
H7B	1.39330	0.84510	0.61490	0.0580*
H7C	1.14140	0.80510	0.55260	0.0580*

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
S1	0.0274 (3)	0.0303 (4)	0.0334 (3)	-0.0054 (3)	0.0014 (3)	-0.0023 (3)
N1	0.0259 (13)	0.0261 (12)	0.0249 (11)	0.0002 (10)	0.0014 (9)	-0.0017 (10)
N2	0.0562 (18)	0.0331 (16)	0.0338 (14)	-0.0117 (13)	0.0185 (12)	-0.0121 (12)
N3	0.0290 (13)	0.0291 (13)	0.0266 (12)	-0.0026 (11)	0.0033 (10)	-0.0050 (10)
N4	0.0355 (12)	0.0340 (14)	0.0270 (11)	-0.0016 (12)	-0.0010 (10)	-0.0054 (12)
C1	0.0328 (15)	0.0254 (15)	0.0248 (13)	0.0026 (12)	0.0010 (11)	-0.0012 (12)
C2	0.0305 (14)	0.0224 (14)	0.0275 (13)	-0.0049 (12)	0.0014 (12)	-0.0042 (11)
C3	0.0222 (15)	0.0245 (14)	0.0200 (12)	0.0035 (10)	-0.0029 (10)	0.0026 (11)
C4	0.0213 (12)	0.0242 (15)	0.0195 (12)	0.0044 (10)	-0.0036 (9)	-0.0002 (10)
C5	0.0207 (12)	0.0268 (13)	0.0240 (11)	0.0031 (11)	-0.0051 (10)	0.0041 (13)
C6	0.0207 (12)	0.0261 (14)	0.0258 (14)	0.0003 (11)	-0.0032 (11)	0.0034 (12)
C7	0.0364 (15)	0.045 (2)	0.0347 (15)	-0.0091 (15)	0.0057 (12)	0.0038 (15)

*Geometric parameters (Å, °)*

S1—C5	1.769 (3)	N2—H2B	0.86 (2)
S1—C7	1.801 (3)	N3—H3A	0.86 (2)
N1—C1	1.354 (3)	C3—C4	1.414 (3)
N1—C5	1.322 (3)	N3—H3B	0.85 (2)
N2—C1	1.355 (4)	C4—C5	1.410 (3)
N3—C3	1.371 (3)	C4—C6	1.423 (3)
N4—C6	1.149 (3)	C2—H2	0.9500
C1—C2	1.395 (4)	C7—H7A	0.9800
C2—C3	1.379 (3)	C7—H7B	0.9800
N2—H2A	0.86 (3)	C7—H7C	0.9800
C5—S1—C7	101.63 (14)	C5—C4—C6	120.2 (2)
C1—N1—C5	116.9 (2)	C3—C4—C5	118.2 (2)
N1—C1—N2	115.2 (2)	C3—C4—C6	121.6 (2)
N1—C1—C2	123.5 (2)	N1—C5—C4	124.1 (2)
N2—C1—C2	121.3 (2)	S1—C5—N1	118.61 (17)
C1—C2—C3	119.6 (2)	S1—C5—C4	117.28 (18)
C1—N2—H2A	123 (2)	N4—C6—C4	179.3 (3)
C1—N2—H2B	121 (3)	C1—C2—H2	120.00
H2A—N2—H2B	115 (3)	C3—C2—H2	120.00
N3—C3—C2	121.5 (2)	S1—C7—H7A	109.00
N3—C3—C4	120.8 (2)	S1—C7—H7B	109.00
C2—C3—C4	117.7 (2)	S1—C7—H7C	109.00
C3—N3—H3A	114.6 (18)	H7A—C7—H7B	109.00
C3—N3—H3B	117.3 (18)	H7A—C7—H7C	110.00

H3A—N3—H3B	119 (3)	H7B—C7—H7C	110.00
C7—S1—C5—C4	180.0 (2)	C1—C2—C3—N3	-177.1 (2)
C7—S1—C5—N1	-0.5 (2)	N3—C3—C4—C5	179.0 (2)
C1—N1—C5—C4	0.9 (4)	N3—C3—C4—C6	-2.3 (4)
C1—N1—C5—S1	-178.60 (18)	C2—C3—C4—C5	1.5 (3)
C5—N1—C1—C2	1.2 (4)	C2—C3—C4—C6	-179.7 (2)
C5—N1—C1—N2	179.4 (2)	C3—C4—C5—N1	-2.3 (4)
N2—C1—C2—C3	-179.9 (2)	C6—C4—C5—S1	-1.6 (3)
N1—C1—C2—C3	-1.8 (4)	C6—C4—C5—N1	179.0 (2)
C1—C2—C3—C4	0.4 (3)	C3—C4—C5—S1	177.24 (18)

*Hydrogen-bond geometry (Å, °)*

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N2—H2 <i>A</i> ...N3 <sup>i</sup>	0.86 (3)	2.43 (3)	3.225 (4)	155 (3)
N2—H2 <i>B</i> ...N4 <sup>ii</sup>	0.86 (2)	2.26 (3)	3.083 (4)	161 (3)
N3—H3 <i>B</i> ...N4 <sup>iii</sup>	0.85 (2)	2.31 (2)	3.128 (3)	161 (2)
C7—H7 <i>A</i> ...Cg1 <sup>iv</sup>	0.98	2.77	3.552 (4)	137

Symmetry codes: (i)  $-x+3/2, -y+1, z-1/2$ ; (ii)  $-x+1, y-1/2, -z+3/2$ ; (iii)  $x-1/2, -y+3/2, -z+2$ ; (iv)  $x+1, y, z$ .