

# Crystal structure of 3-carbamothioylpyridinium thiocyanate

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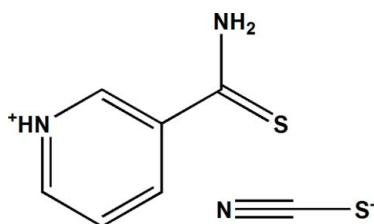
In the cation of the title salt, C<sub>6</sub>H<sub>7</sub>N<sub>2</sub>S<sup>+</sup>·SCN<sup>-</sup>, the C=S bond is oriented *trans* with respect to the C—C=N fragment in the pyridine ring. The planes of the aromatic ring and the thioamide fragment of the cation make a dihedral angle of 38.31 (4)°. In the crystal, the components are linked by N—H···S and N—H···N, hydrogen bonds, forming a two-dimensional network parallel to (10 $\bar{1}$ ).

**Keywords:** crystal structure; 3-carbamothioylpyridinium cation; thiocyanate anion; N—H···S hydrogen bonding.

**CCDC reference:** 1037011

## 1. Related literature

For isomeric thionicotinamide structures, see: Downie *et al.* (1972); Form *et al.* (1973); Colleter & Gadret (1967). For a related structure, see: Sharif *et al.* (2009). For the structural interest of thionicotinamides, see: Fonari *et al.* (2007).



## 2. Experimental

### 2.1. Crystal data

C<sub>6</sub>H<sub>7</sub>N<sub>2</sub>S<sup>+</sup>·CNS<sup>-</sup>

*M<sub>r</sub>* = 197.28

Monoclinic, *P*2<sub>1</sub>/*n*  
*a* = 7.2495 (2) Å  
*b* = 9.3759 (3) Å  
*c* = 13.5949 (3) Å  
 $\beta$  = 94.454 (1)°  
*V* = 921.26 (4) Å<sup>3</sup>

*Z* = 4  
Mo *K*α radiation  
 $\mu$  = 0.52 mm<sup>-1</sup>  
*T* = 295 K  
0.2 × 0.16 × 0.1 mm

### 2.2. Data collection

Bruker APEXII diffractometer  
Absorption correction: multi-scan  
(*SADABS*; Sheldrick, 2002)  
*T*<sub>min</sub> = 0.679, *T*<sub>max</sub> = 0.746

12686 measured reflections  
3313 independent reflections  
2563 reflections with *I* > 2σ(*I*)  
*R*<sub>int</sub> = 0.023

### 2.3. Refinement

*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.045  
*wR*(*F*<sup>2</sup>) = 0.140  
*S* = 1.04  
3313 reflections

109 parameters  
H-atom parameters constrained  
 $\Delta\rho_{\text{max}} = 0.58 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.26 \text{ e } \text{Å}^{-3}$

**Table 1**

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>
N1—H1A···S11 <sup>i</sup>	0.86	2.54	3.3450 (15)	156
N1—H1B···S11 <sup>ii</sup>	0.86	2.55	3.3975 (14)	171
N2—H2···N11 <sup>iii</sup>	0.86	1.88	2.709 (2)	162

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

Data collection: *APEX2* (Bruker, 2011); cell refinement: *SAINT* (Bruker, 2011); data reduction: *SAINT*; program(s) used to solve structure: *SIR2002* (Burla *et al.*, 2005); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and *DIAMOND* (Brandenburg & Berndt, 2001); software used to prepare material for publication: *WinGX* (Farrugia, 2012).

## Acknowledgements

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Supporting information for this paper is available from the IUCr electronic archives (Reference: BQ2397).

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## supporting information

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## Crystal structure of 3-carbamothioylpyridinium thiocyanate

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### S1. Comment

There are three isomeric thionicotinamides of general formula  $C_6H_6N_2S$ , 2-thioamidopyridine (Downie *et al.*, 1972), 3-thioamidopyridine (Form *et al.*, 1973) and 4-thioamidopyridine (Colleter & Gadret, 1967), then three possible coordination sites. The structural interest to these compounds has centered on the parameters of the thioamide group and the consequent electron arrangement within the group (Fonari *et al.*, 2007). The thioamide group and the pyridine ring are not coplanar.

In the title compound, (I), the asymmetric unit contains one 3-3-carbamothioylpyridinium and one thiocyanate ions. The molecular geometry and the atom-numbering scheme are shown in Fig 1. In the cation moiety, the C=S bond is oriented *trans* with respect to the C—C—N fragment in the pyridine ring. The aromatic ring and the thioamide fragment of the thionicotinamide molecule make a dihedral angle of  $38.31(4)^\circ$  similar to that found in 3-carbamothioylpyridinium iodide (*trans*) ( $30.02(3)^\circ$ ) (Sharif *et al.*, 2009) and 3-thioamido-pyridine (*cis*) ( $33.76(7)^\circ$ ) (Form *et al.* 1973). The crystal packing is stabilized by weak N—H $\cdots$ N and N—H $\cdots$ S hydrogen bonds forming a two-dimensional network (Fig. 2).

### S2. Experimental

3-Thionicotinamide (690 mg, 0.5 mmol) was added dropwise to a solution of KSCN (48.6 mg, 0.5 mmol) in water/ethanol (10 ml/10 ml). The mixture was then refluxed with stirring for 3 h and the resulting solution was left to stand at room temperature. After several days, single crystals suitable for X-ray diffraction were obtained.

### S3. Refinement

Approximate positions for all H atoms were first obtained from the difference electron density map. However, the H atoms were situated into idealized positions and the H-atoms have been refined within the riding atom approximation. The applied constraints were as follow: C—H = 0.93 Å and N—H = 0.86 Å with  $U_{iso} = 1.2U_{eq}(C \text{ or } N)$ .

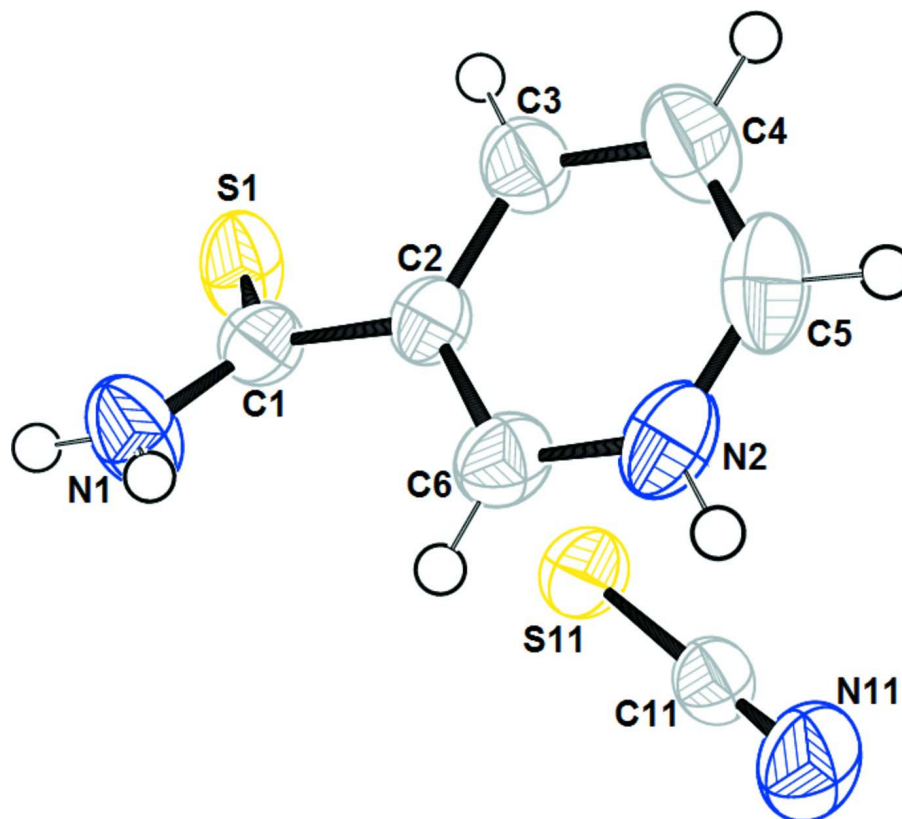


Figure 1

The molecular structure of, (I), with displacement ellipsoids drawn at the 50% probability level. H atoms are represented as small spheres of arbitrary radii.

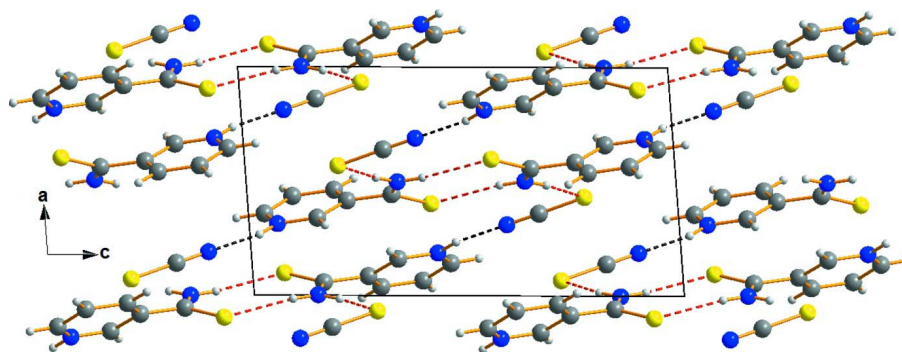


Figure 2

Packing diagram of (I) viewed along the *b* axis showing hydrogen bond as dashed lines [N—H...S in red and N—H...N in black]

### 3-Carbamothioylpyridinium thiocyanate

#### Crystal data

$C_6H_7N_2S^+ \cdot CNS^-$

$M_r = 197.28$

Monoclinic,  $P2_1/n$

$a = 7.2495 (2) \text{ \AA}$

$b = 9.3759 (3) \text{ \AA}$

$c = 13.5949 (3) \text{ \AA}$

$\beta = 94.454 (1)^\circ$

$V = 921.26 (4) \text{ \AA}^3$

$Z = 4$   
 $F(000) = 408$   
 $D_x = 1.422 \text{ Mg m}^{-3}$   
 Mo  $K\alpha$  radiation,  $\lambda = 0.71073 \text{ \AA}$   
 Cell parameters from 5267 reflections

$\theta = 2.6\text{--}32.1^\circ$   
 $\mu = 0.52 \text{ mm}^{-1}$   
 $T = 295 \text{ K}$   
 Prism, colorless  
 $0.2 \times 0.16 \times 0.1 \text{ mm}$

*Data collection*

Bruker APEXII diffractometer  
 Radiation source: sealed tube  
 Graphite monochromator  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: multi-scan (SADABS; Sheldrick, 2002)  
 $T_{\min} = 0.679$ ,  $T_{\max} = 0.746$

12686 measured reflections  
 3313 independent reflections  
 2563 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.023$   
 $\theta_{\max} = 32.5^\circ$ ,  $\theta_{\min} = 2.6^\circ$   
 $h = -10 \rightarrow 10$   
 $k = -14 \rightarrow 14$   
 $l = -20 \rightarrow 20$

*Refinement*

Refinement on  $F^2$   
 Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.045$   
 $wR(F^2) = 0.140$   
 $S = 1.04$   
 3313 reflections  
 109 parameters  
 0 restraints  
 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  
 $w = 1/[\sigma^2(F_o^2) + (0.0808P)^2 + 0.1946P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.58 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\min} = -0.26 \text{ e \AA}^{-3}$

*Special details*

**Geometry.** All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s 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  $F^2 > \sigma(F^2)$  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 ( $\text{\AA}^2$ )*

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.9430 (2)	0.08889 (15)	0.83615 (10)	0.0351 (3)
C2	0.91545 (18)	0.13467 (15)	0.73124 (9)	0.0322 (3)
C3	0.9619 (2)	0.27153 (17)	0.70337 (11)	0.0401 (3)
H3	1.0114	0.336	0.7503	0.048*
C4	0.9342 (3)	0.3117 (2)	0.60509 (13)	0.0536 (4)
H4	0.9675	0.4025	0.5854	0.064*
C5	0.8576 (3)	0.2168 (2)	0.53738 (12)	0.0552 (5)
H5	0.8365	0.2434	0.4716	0.066*
C6	0.8395 (2)	0.04215 (18)	0.65938 (10)	0.0392 (3)
H6	0.8072	-0.0501	0.6764	0.047*
C11	0.3607 (2)	0.10281 (16)	0.67580 (11)	0.0383 (3)

N1	0.9976 (2)	-0.04356 (15)	0.85163 (10)	0.0492 (3)
H1A	1.0153	-0.0983	0.8025	0.059*
H1B	1.0156	-0.0754	0.9109	0.059*
N2	0.81305 (19)	0.08559 (17)	0.56595 (9)	0.0464 (3)
H2	0.7655	0.027	0.5224	0.056*
N11	0.3114 (3)	0.0569 (2)	0.59942 (12)	0.0642 (5)
S1	0.90233 (7)	0.20284 (5)	0.92615 (3)	0.04789 (14)
S11	0.43232 (7)	0.16631 (5)	0.78372 (3)	0.04908 (14)

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C1	0.0405 (7)	0.0356 (6)	0.0286 (5)	-0.0036 (5)	-0.0012 (5)	-0.0032 (5)
C2	0.0340 (6)	0.0364 (6)	0.0257 (5)	0.0005 (5)	0.0004 (4)	-0.0029 (4)
C3	0.0481 (8)	0.0358 (7)	0.0358 (6)	0.0008 (6)	-0.0001 (6)	-0.0007 (5)
C4	0.0724 (12)	0.0460 (9)	0.0427 (8)	0.0019 (8)	0.0056 (8)	0.0102 (7)
C5	0.0638 (11)	0.0713 (12)	0.0299 (7)	0.0139 (9)	0.0000 (7)	0.0074 (7)
C6	0.0421 (7)	0.0435 (7)	0.0316 (6)	-0.0039 (6)	0.0007 (5)	-0.0066 (5)
C11	0.0440 (7)	0.0352 (7)	0.0356 (6)	0.0024 (6)	0.0029 (5)	0.0006 (5)
N1	0.0781 (10)	0.0370 (7)	0.0323 (6)	0.0049 (7)	0.0022 (6)	0.0002 (5)
N2	0.0484 (7)	0.0609 (9)	0.0286 (5)	0.0024 (6)	-0.0043 (5)	-0.0102 (5)
N11	0.0865 (12)	0.0625 (10)	0.0419 (7)	0.0034 (9)	-0.0070 (7)	-0.0116 (7)
S1	0.0704 (3)	0.0440 (2)	0.02793 (18)	0.01027 (18)	-0.00476 (16)	-0.00570 (13)
S11	0.0598 (3)	0.0521 (3)	0.0344 (2)	-0.00810 (19)	-0.00268 (16)	-0.00319 (15)

*Geometric parameters (Å, °)*

C1—N1	1.3154 (19)	C5—N2	1.337 (3)
C1—C2	1.4879 (18)	C5—H5	0.93
C1—S1	1.6677 (14)	C6—N2	1.3334 (19)
C2—C3	1.387 (2)	C6—H6	0.93
C2—C6	1.3879 (19)	C11—N11	1.155 (2)
C3—C4	1.388 (2)	C11—S11	1.6303 (16)
C3—H3	0.93	N1—H1A	0.86
C4—C5	1.367 (3)	N1—H1B	0.86
C4—H4	0.93	N2—H2	0.86
N1—C1—C2	116.23 (12)	N2—C5—H5	120.1
N1—C1—S1	123.75 (11)	C4—C5—H5	120.1
C2—C1—S1	120.02 (11)	N2—C6—C2	119.97 (15)
C3—C2—C6	118.52 (13)	N2—C6—H6	120
C3—C2—C1	120.76 (12)	C2—C6—H6	120
C6—C2—C1	120.71 (13)	N11—C11—S11	179.35 (17)
C2—C3—C4	119.60 (15)	C1—N1—H1A	120
C2—C3—H3	120.2	C1—N1—H1B	120
C4—C3—H3	120.2	H1A—N1—H1B	120
C5—C4—C3	119.51 (17)	C6—N2—C5	122.51 (14)
C5—C4—H4	120.2	C6—N2—H2	118.7

C3—C4—H4	120.2	C5—N2—H2	118.7
N2—C5—C4	119.88 (15)		
N1—C1—C2—C3	-142.88 (16)	C2—C3—C4—C5	1.4 (3)
S1—C1—C2—C3	37.84 (19)	C3—C4—C5—N2	-1.1 (3)
N1—C1—C2—C6	38.3 (2)	C3—C2—C6—N2	0.1 (2)
S1—C1—C2—C6	-140.98 (13)	C1—C2—C6—N2	178.93 (13)
C6—C2—C3—C4	-0.9 (2)	C2—C6—N2—C5	0.2 (2)
C1—C2—C3—C4	-179.75 (15)	C4—C5—N2—C6	0.3 (3)

*Hydrogen-bond geometry (Å, °)*

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
N1—H1A $\cdots$ S11 <sup>i</sup>	0.86	2.54	3.3450 (15)	156
N1—H1B $\cdots$ S1 <sup>ii</sup>	0.86	2.55	3.3975 (14)	171
N2—H2 $\cdots$ N11 <sup>iii</sup>	0.86	1.88	2.709 (2)	162

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