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1-Methyl-4-thiocarbamoylpyridin-1-ium iodide

Ibukun O. Shotonwa^{b,a} and René T. Boéré^{b*}

^aDepartment of Chemistry, Lagos State University, Ojo, Lagos, Nigeria, and ^bDepartment of Chemistry and Biochemistry, University of Lethbridge, 4401 University Drive West, Lethbridge, Alberta, T1K3M4, Canada. *Correspondence e-mail: boere@uleth.ca

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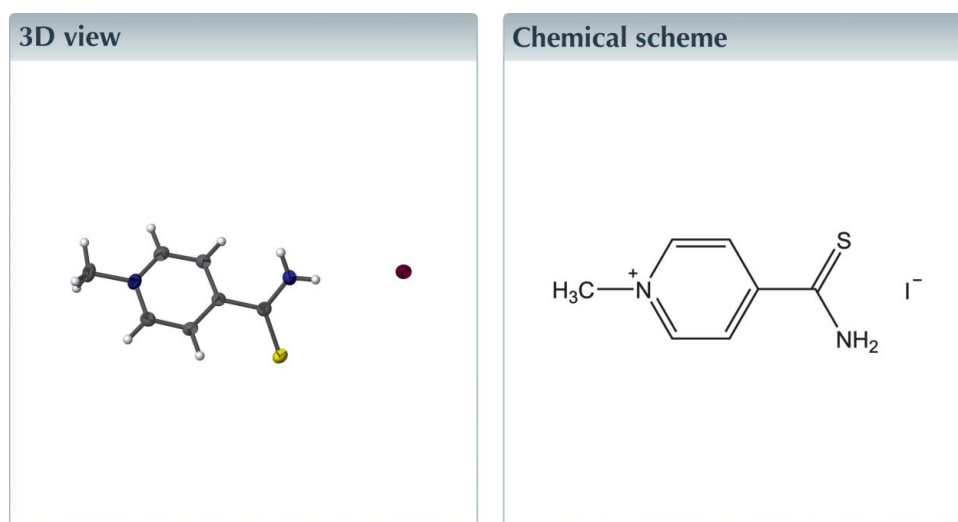
Edited by S. Bernès, Benemérita Universidad Autónoma de Puebla, México

Keywords: crystal structure; hydrogen bonds; heteroelements.

CCDC reference: 1874701

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

In the title compound, $C_7H_9N_2S^+I^-$, the thioamide moiety is twisted out of the aromatic plane by $38.98(4)^\circ$ and forms $N-H \cdots I$ hydrogen bonds. In the crystal, hydrogen-bonded centrosymmetric dimers $[C_7H_9N_2S^+I^-]_2$ are linked *via* additional short contacts from an aromatic CH group to the iodide anion into ribbons parallel to the (010) plane.



Structure description

Methylation at the pyridine nitrogen was used as a protecting group in synthetic attempts to prepare the corresponding 3,5-dipyridyl-1,2,4-dithiazolium salts. In the title compound (I), the cation and anion are linked pairwise in a centrosymmetric hydrogen-bonded dimer (N1, I1, N1ⁱ and I1ⁱ; see Table 1 for symmetry code, and Fig. 1). The pyridine ring is planar (r.m.s. deviation = 0.0054 Å), as is the thioamide functional group (r.m.s. deviation = 0.0020 Å), and the two planes make a dihedral angle of $38.98(4)^\circ$. The N1/I1/N1ⁱ/I1ⁱ plane makes a dihedral angle of $26.67(2)^\circ$ with the thioamide moiety, and the H1A and H1B hydrogen atoms deviate from this plane by $-0.39(2)$ and $0.12(2)$ Å, respectively. The cation structure is closely related to that of the protonated analogue, $C_6H_7N_2S^+I^-$ (Shotonwa & Boéré, 2014) and all comparable intramolecular distances are indistinguishable within standard uncertainties [Cambridge Structural Database (CSD) Version 5.39, with updates to November 2017 (Groom *et al.*, 2016), refcode: TODDAT].

In the crystal (Fig. 2), the only significant intermolecular contacts are non-classical hydrogen bonds between H5 and I1ⁱⁱ, with a separation 0.22 Å shorter than the sum of van der Waals radii (Table 1, entry 3). These link the dimers of ion pairs into ribbons parallel to the (010) plane.

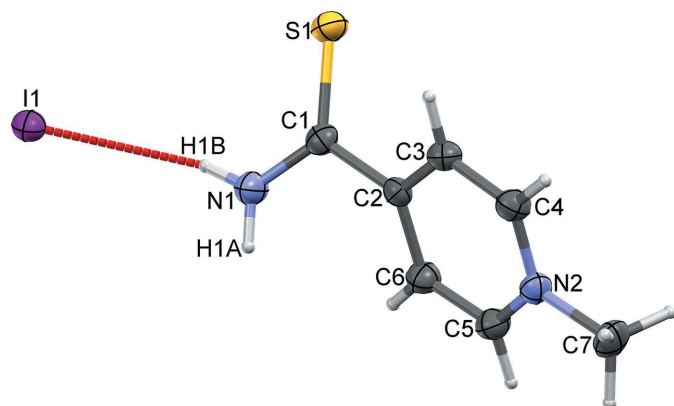


Figure 1
The molecular structure of the ion pair with the labelling scheme and 50% displacement ellipsoids.

Synthesis and crystallization

The title salt was prepared by a modification of a literature method for related compounds (Kosower, 1955): methyl iodide (0.57 g, 4 mmol) was added dropwise to 4-pyridine-thioamide (0.50 g, 4 mmol) in 5.00 ml of dry CH_3CN , with a colour change from yellow to deep orange. The mixture was stirred for 30 min. at room temperature, followed by reflux for 10 min., cooled, filtered and washed three times with cold CH_3CN . Recrystallization from boiling 99% ethanol afforded 0.21 g (35% yield) of (I) [CAS registry 749784–54-1]. The crystals are hygroscopic and were stored in a well sealed flask. ^1H NMR, (D_2O , $\delta/\text{p.p.m.}$): 8.84 (*d*, 2H Ar, $J = 6.9$ Hz), 8.23 (*d*, 2H Ar, $J = 6.9$ Hz), 4.38 (*s*, 3H, N– CH_3). mp = 219.3–220.9°C (lit. 220°C; Christ *et al.*, 1974).

Refinement

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

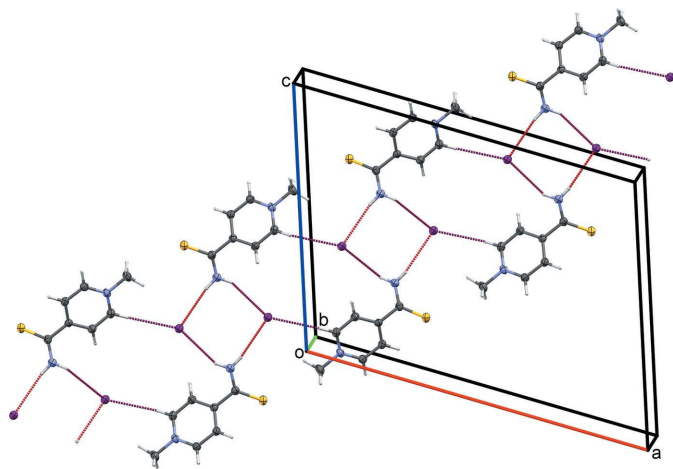


Figure 2
Packing viewed along the *b*-axis direction with classical and non-classical hydrogen bonds to the iodide anion shown as dashed lines.

Table 1
Hydrogen-bond geometry (\AA , $^\circ$).

<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–H1B···I1	0.83 (2)	2.79 (2)	3.6037 (16)	166 (2)
N1–H1A···I1 ⁱ	0.86 (2)	2.93 (2)	3.6367 (16)	141 (2)
C5–H5···I1 ⁱⁱ	0.95	2.96	3.8642 (17)	160

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$\text{C}_7\text{H}_9\text{N}_2\text{S}^+\text{I}^-$
M_r	280.12
Crystal system, space group	Monoclinic, <i>C2/c</i>
Temperature (K)	173
<i>a</i> , <i>b</i> , <i>c</i> (\AA)	19.6249 (16), 7.2198 (6), 14.9117 (12)
β ($^\circ$)	108.592 (1)
<i>V</i> (\AA^3)	2002.5 (3)
<i>Z</i>	8
Radiation type	Mo $K\alpha$
μ (mm^{-1})	3.35
Crystal size (mm)	0.27 × 0.15 × 0.08
Data collection	
Diffractometer	Bruker APEXII CCD area-detector diffractometer
Absorption correction	Multi-scan (<i>SADABS</i> ; Bruker, 2008)
T_{min} , T_{max}	0.610, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	13927, 2294, 2121
R_{int}	0.018
($\sin \theta/\lambda$) _{max} (\AA^{-1})	0.650
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, <i>S</i>	0.014, 0.032, 1.07
No. of reflections	2294
No. of parameters	107
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e \AA^{-3})	0.35, –0.27

Computer programs: *APEX2* and *SAINT-Plus* (Bruker, 2008), *SHELXT* (Sheldrick, 2015a), *SHELXL* (Sheldrick, 2015b), *Mercury* (Macrae *et al.*, 2008) and *OLEX2* (Dolomanov *et al.*, 2009).

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full crystallographic data

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Crystal data

$C_7H_9N_2S^+I^-$

$M_r = 280.12$

Monoclinic, $C2/c$

$a = 19.6249$ (16) Å

$b = 7.2198$ (6) Å

$c = 14.9117$ (12) Å

$\beta = 108.592$ (1)°

$V = 2002.5$ (3) Å³

$Z = 8$

$F(000) = 1072$

$D_x = 1.858$ Mg m⁻³

Melting point: 493 K

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

Cell parameters from 13927 reflections

$\theta = 2.2$ – 27.5 °

$\mu = 3.35$ mm⁻¹

$T = 173$ K

Prism, clear orange

$0.27 \times 0.15 \times 0.08$ mm

Data collection

Bruker APEXII CCD area-detector
diffractometer

Radiation source: sealed tube

Graphite monochromator

Detector resolution: 8 pixels mm⁻¹

ω and φ scans

Absorption correction: multi-scan
(SADABS; Bruker, 2008)

$T_{\min} = 0.610$, $T_{\max} = 0.746$

13927 measured reflections

2294 independent reflections

2121 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.018$

$\theta_{\max} = 27.5$ °, $\theta_{\min} = 2.2$ °

$h = -25 \rightarrow 25$

$k = -9 \rightarrow 9$

$l = -19 \rightarrow 19$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.014$

$wR(F^2) = 0.032$

$S = 1.07$

2294 reflections

107 parameters

0 restraints

Primary atom site location: dual

Secondary atom site location: difference Fourier
map

Hydrogen site location: mixed

H atoms treated by a mixture of independent
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0118P)^2 + 2.1492P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.35$ e Å⁻³

$\Delta\rho_{\min} = -0.27$ e Å⁻³

Special details

Refinement. 1. Fixed Uiso At 1.2 times of: All C(H) groups, All N(H,H) groups At 1.5 times of: All C(H,H,H) groups 2.a Aromatic/amide H refined with riding coordinates: C5(H5), C3(H3), C4(H4), C6(H6) 2.b Idealised Me refined as rotating group: C7(H7A,H7B,H7C)

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
I1	0.11514 (2)	0.17323 (2)	0.42525 (2)	0.02707 (4)
S1	0.14565 (2)	0.31395 (7)	0.75400 (3)	0.03144 (10)
N1	0.23622 (9)	0.2254 (2)	0.66302 (11)	0.0301 (3)
H1A	0.2776 (12)	0.196 (3)	0.6589 (15)	0.036*
H1B	0.2037 (12)	0.228 (3)	0.6114 (16)	0.036*
N2	0.40862 (7)	0.20871 (19)	0.98789 (10)	0.0241 (3)
C5	0.41537 (9)	0.2872 (2)	0.90990 (12)	0.0269 (4)
H5	0.461071	0.330808	0.910006	0.032*
C3	0.28424 (9)	0.1655 (2)	0.91256 (12)	0.0235 (3)
H3	0.238945	0.124022	0.915043	0.028*
C4	0.34445 (9)	0.1489 (2)	0.99079 (12)	0.0256 (3)
H4	0.340682	0.095014	1.047130	0.031*
C7	0.47204 (10)	0.1918 (3)	1.07418 (13)	0.0333 (4)
H7A	0.516062	0.208892	1.057507	0.050*
H7B	0.472432	0.068642	1.102007	0.050*
H7C	0.469549	0.286572	1.120068	0.050*
C6	0.35692 (9)	0.3056 (2)	0.82953 (12)	0.0263 (4)
H6	0.362264	0.360346	0.774227	0.032*
C2	0.28980 (8)	0.2431 (2)	0.82991 (11)	0.0207 (3)
C1	0.22502 (8)	0.2579 (2)	0.74402 (12)	0.0227 (3)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
I1	0.02370 (6)	0.03292 (7)	0.02592 (6)	−0.00189 (5)	0.00981 (4)	−0.00090 (5)
S1	0.01959 (19)	0.0456 (3)	0.0283 (2)	0.00281 (19)	0.00643 (16)	−0.0004 (2)
N1	0.0238 (7)	0.0447 (10)	0.0210 (7)	0.0019 (7)	0.0058 (6)	0.0001 (7)
N2	0.0204 (7)	0.0245 (8)	0.0247 (7)	0.0037 (6)	0.0032 (5)	−0.0017 (6)
C5	0.0213 (8)	0.0293 (9)	0.0301 (9)	−0.0016 (7)	0.0081 (7)	−0.0004 (7)
C3	0.0202 (7)	0.0248 (9)	0.0267 (8)	0.0003 (7)	0.0090 (6)	0.0009 (7)
C4	0.0254 (8)	0.0273 (9)	0.0250 (8)	0.0028 (7)	0.0094 (7)	0.0025 (7)
C7	0.0250 (9)	0.0398 (11)	0.0279 (9)	0.0039 (8)	−0.0018 (7)	−0.0002 (8)
C6	0.0243 (8)	0.0307 (10)	0.0249 (8)	−0.0020 (7)	0.0093 (7)	0.0014 (7)
C2	0.0207 (8)	0.0197 (8)	0.0221 (8)	0.0013 (6)	0.0074 (6)	−0.0028 (6)
C1	0.0219 (8)	0.0205 (8)	0.0251 (8)	−0.0021 (6)	0.0068 (6)	0.0012 (6)

Geometric parameters (\AA , $^\circ$)

S1—C1	1.6615 (17)	C3—C2	1.389 (2)
N1—C1	1.316 (2)	C3—H3	0.9500
N1—H1A	0.86 (2)	C4—H4	0.9500
N1—H1B	0.83 (2)	C7—H7A	0.9800
N2—C5	1.338 (2)	C7—H7B	0.9800
N2—C4	1.345 (2)	C7—H7C	0.9800
N2—C7	1.483 (2)	C6—C2	1.394 (2)

C5—C6	1.376 (2)	C6—H6	0.9500
C5—H5	0.9500	C2—C1	1.493 (2)
C3—C4	1.376 (2)		
C1—N1—H1A	123.2 (14)	N2—C7—H7A	109.5
C1—N1—H1B	123.0 (15)	N2—C7—H7B	109.5
H1A—N1—H1B	114 (2)	H7A—C7—H7B	109.5
C5—N2—C4	121.14 (14)	N2—C7—H7C	109.5
C5—N2—C7	120.07 (15)	H7A—C7—H7C	109.5
C4—N2—C7	118.76 (15)	H7B—C7—H7C	109.5
N2—C5—C6	120.80 (16)	C5—C6—C2	119.45 (16)
N2—C5—H5	119.6	C5—C6—H6	120.3
C6—C5—H5	119.6	C2—C6—H6	120.3
C4—C3—C2	119.89 (15)	C3—C2—C6	118.39 (15)
C4—C3—H3	120.1	C3—C2—C1	120.23 (14)
C2—C3—H3	120.1	C6—C2—C1	121.37 (15)
N2—C4—C3	120.31 (15)	N1—C1—C2	115.41 (14)
N2—C4—H4	119.8	N1—C1—S1	124.14 (13)
C3—C4—H4	119.8	C2—C1—S1	120.44 (12)

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—H1B \cdots I1	0.83 (2)	2.79 (2)	3.6037 (16)	166 (2)
N1—H1A \cdots I1 ⁱ	0.86 (2)	2.93 (2)	3.6367 (16)	141 (2)
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Symmetry codes: (i) $-x+1/2, -y+1/2, -z+1$; (ii) $x+1/2, -y+1/2, z+1/2$.