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

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In the title compound, C₇H₉N₂S⁺·I⁻, the thioamide moiety is twisted out of the aromatic plane by 38.98 (4)° and forms N—H···I hydrogen bonds. In the crystal, hydrogen-bonded centrosymmetric dimers [C₇H₉N₂S⁺·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, N1' and I1'; 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)°. The N1/I1/N1'/I1' plane makes a dihedral angle of 26.67 (2)° 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, C₆H₇N₂S⁺·I⁻ (Shotonwa & Boeré, 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 I1, 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.

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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 CH₃CN, 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 CH₃CN. 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.

Figure 1

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

1H NMR, (D₂O, δ/p.p.m.): 8.84 (d, 2 HA r, J = 6.9 Hz), 8.23 (d, 2H Ar, J = 6.9 Hz), 4.38 (s, 3H, N—CH₃). 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.

Table 1
Hydrogen-bond geometry (Å, °).

| D—H···A | D—H | H···A | D···A | D—H···A |
|----------|------|-------|-------|---------|
| N1—H1B···I1 | 0.83 (2) | 2.79 (2) | 3.6037 (16) | 166 (2) |
| N1—H1A···I1i | 0.86 (2) | 2.93 (2) | 3.6367 (16) | 141 (2) |
| C5—H5···I1ii | 0.95 | 2.96 | 3.8642 (17) | 160 |

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

Table 2
Experimental details.

| Crystal data | C₇H₉N₂S⁺I⁻ |
|--------------|-------------|
| M₀ | 280.12 |
| Crystal system, space group | Monoclinic, C2/c |
| Temperature (K) | 173 |
| a, b, c (Å) | 19.6249 (16), 7.2198 (6), 14.9117 (12) |
| V (Å³) | 2002.5 (3) |
| Z | 8 |
| Radiation type | Mo Kα |
| μ (mm⁻¹) | 3.35 |
| Crystal size (mm) | 0.27 × 0.15 × 0.08 |

| Data collection | Bruker APEXII CCD area-detector diffractometer |
|----------------|-----------------------------------------------|
| Absorption correction | Multi-scan (SADABS; Bruker, 2008) |
| Tmin, Tmax | 0.610, 0.746 |
| No. of measured, independent and observed [I > 2σ(I)] reflections | 13927, 2294, 2121 |
| Rint | 0.018 |
| Refinement | wR[F²]<2σ(F²), S |
| No. of reflections | 2294 |
| No. of parameters | 107 |
| H-atom treatment | H atoms treated by a mixture of independent and constrained refinement |
| Δρmax, Δρmin (e Å⁻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

\[ \text{C}_7\text{H}_9\text{N}_2\text{S}^+\cdot\text{I}^- \]

- Mr = 280.12
- Monoclinic, C2/c
- \( a = 19.6249 \) \( (16) \) Å
- \( b = 7.2198 \) \( (6) \) Å
- \( c = 14.9117 \) \( (12) \) Å
- \( \beta = 108.592 \) \( (1) \)°
- \( V = 2002.5 \) \( (3) \) Å\(^3\)
- \( Z = 8 \)
- \( F(000) = 1072 \)

- \( D_r = 1.858 \) Mg m\(^{-3}\)
- Melting point: 493 K

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)

- \( R_{	ext{int}} = 0.018 \)
- \( \theta_{\text{max}} = 27.5^\circ, \theta_{\text{min}} = 2.2^\circ \)
- \( h = -25 \rightarrow 25 \)
- \( k = -9 \rightarrow 9 \)
- \( l = -19 \rightarrow 19 \)

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
- \( w = 1/[\sigma(F_o^2) + (0.0118P)^2 + 2.1492P] \)
- \( P = (F_o^2 + 2F_C^2)/3 \)
- \( \Delta/\sigma_{\text{max}} = 0.001 \)
- \( \Delta \rho_{\text{max}} = 0.35 \) e Å\(^{-3}\)
- \( \Delta \rho_{\text{min}} = -0.27 \) 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)

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

|    | x         | y         | z         | U_{eq} / U_{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 | 0.362624     | 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 (Å²)

|    | U¹¹  | U¹²  | U¹³  | U²²  | U²³  | U³³  |
|----|------|------|------|------|------|------|
| 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 (Å, °)

|    | C1—C1 | C3—C2 | C3—H3 | C4—H4 | C7—H7A | C7—H7B | C7—H7C | C6—C2 |
|----|-------|-------|-------|-------|--------|--------|--------|-------|
| S1—C1| 1.6615 (17)| C3—C2| 1.389 (2)| 1.389 (2) | 1.389 (2) | 0.9500 | 0.9800 | 0.9800 |
| N1—C1| 1.316 (2)| C3—H3 | 0.9500 | 0.9500 | 0.9500 | 0.9800 | 0.9800 | 0.9800 |
| N1—H1A| 0.86 (2)| C4—H4 | 0.9500 | 0.9500 | 0.9500 | 0.9800 | 0.9800 | 0.9800 |
| N1—H1B| 0.83 (2)| C7—H7A | 0.9800 | 0.9800 | 0.9800 | 0.9800 | 0.9800 | 0.9800 |
| N2—C5| 1.338 (2)| C7—H7B | 0.9800 | 0.9800 | 0.9800 | 0.9800 | 0.9800 | 0.9800 |
| N2—C4| 1.345 (2)| C7—H7C | 0.9800 | 0.9800 | 0.9800 | 0.9800 | 0.9800 | 0.9800 |
| N2—C7| 1.483 (2)| C6—C2 | 1.394 (2)| 1.394 (2) | 1.394 (2) | 1.394 (2) | 1.394 (2) | 1.394 (2) |
| Bond       | Length (Å) | Bond          | Length (Å) |
|------------|------------|---------------|------------|
| C5—C6      | 1.376 (2)  | C6—H6         | 0.9500     |
| C5—H5      | 0.9500     | C2—C1         | 1.493 (2)  |
| C3—C4      | 1.376 (2)  |               |            |

| Bond                  | Angle (°) |
|-----------------------|-----------|
| C1—N1—H1A            | 123.2 (14) |
| C1—N1—H1B            | 123.0 (15) |
| H1A—N1—H1B           | 114 (2)    |
| C5—N2—C4             | 121.14 (14)|
| C5—N2—C7             | 120.07 (15)|
| C4—N2—C7             | 118.76 (15)|
| N2—C5—C6             | 120.80 (16)|
| N2—C5—H5             | 119.6      |
| C6—C5—H5             | 119.6      |
| C4—C3—C2             | 119.89 (15)|
| C4—C3—H3             | 120.1      |
| C2—C3—H3             | 120.1      |
| N2—C4—C3             | 120.31 (15)|
| N2—C4—H4             | 119.8      |
| C3—C4—H4             | 119.8      |

**Hydrogen-bond geometry (Å, °)**

| Bond                  | Length (Å) | Angle (°) |
|-----------------------|------------|-----------|
| N1—H1B···I1          | 0.83 (2)   | 2.79 (2)  | 3.6037 (16) | 166 (2) |
| N1—H1A···I1i         | 0.86 (2)   | 2.93 (2)  | 3.6367 (16) | 141 (2) |
| C5—H5···II           | 0.95       | 2.96      | 3.8642 (17) | 160     |

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