Indole-3-thiouronium iodide

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Indole-3-thiouronium iodide

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In the title compound, C₉H₁₀N₃S⁺·I⁻, the indole ring system and the thiouronium group are essentially perpendicular, with a dihedral angle of 89.87 (8)°. By intermolecular hydrogen bonding, a three-dimensional network is formed, which is additionally supported by intermolecular C–H···π interactions.

Related literature

For the synthesis of the title compound, see: Harris (1969); van der Geer et al. (2007). For the crystal structures of similar compounds, see: Lutz et al. (2007); Ng (1995). For the characterization of C–H···π interactions, see: Malone et al. (1997). For thermal-motion analysis, see: Schomaker & Trueblood (1998). For the Cambridge Structural Database (update of August 2007), see: Allen (2002).

Table 1

Hydrogen-bond geometry (Å, °).

| D—H···A | D—H | H···A | D···A | D—H···A |
|---------|------|-------|-------|---------|
| N1—H1···I1 | 0.76 (2) | 2.91 (2) | 3.6295 (17) | 158 (2) |
| N2—H2···I1 | 0.86 (3) | 2.76 (3) | 3.5736 (18) | 158 (2) |
| N2—H3···I1ii | 0.80 (2) | 2.97 (2) | 3.6269 (17) | 141 (2) |
| N3—H4···I1iii | 0.75 (3) | 2.86 (3) | 3.5990 (19) | 165 (2) |
| N3—H5···I1 | 0.81 (2) | 2.95 (2) | 3.7258 (19) | 149 (2) |
| C1—H1···Cg1iv | 0.91 (2) | 2.91 (2) | 3.794 (2) | 161.2 (18) |

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

Data collection: COLLECT (Nonius, 1999); cell refinement: PEAKREF (Schreurs, 2005); data reduction: EVAL14 (Duisenberg et al., 2003) and SADABS (Sheldrick, 2002); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: PLATON (Spek, 2003); software used to prepare material for publication: SHELXL97.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT2659).

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Indole-3-thiouronium iodide

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Comment

Uronium and thiouronium ions are positively charged with the charge delocalized over the N—C—N group. In crystal engineering this group is therefore complementary to the negatively charged carboxylate group, not only in charge distribution but also in hydrogen-bonding ability.

The molecular geometry of the cation of title compound indole-3-thiouronium iodide (I) (Fig. 1) is very similar to the corresponding nitrate salt (Lutz et al., 2007). The C—N bond lengths of 1.306 (2) and 1.317 (2) Å show significant double bond character while the C—S bond of 1.7533 (19) Å is in the expected range for a single bond. Similar distances and angles have also been found in the benzylthiouronium cation (Ng, 1995).

As in the nitrate salt, the cation consists of two planar subunits, i.e. the indole and the thiouronium moieties, which are perpendicular to each other with an angle of 89.87 (8)° between the corresponding least squares planes. The weighted $R$ value of a thermal motion analysis using the program THMAl1 (Schomaker & Trueblood, 1998) results in a low weighted $R$ value of 0.106, which is slightly higher than in the nitrate salt (0.084).

The iodide anion is surrounded by five N—H groups which act as hydrogen bond donors (Fig. 2). This results in a three dimensional hydrogen bonded network. The H⋯I distances of 2.76 (3) to 2.97 (2) Å are in the same range as found for other N—H⋯I hydrogen bonds in the Cambridge Structural Database (update August 2007; Allen, 2002), where we calculate an average H⋯I distance of 2.80 Å. In general, N—H⋯I hydrogen bonds are relatively weak; the average hydrogen bonded intermolecular N⋯I distance is 3.65 Å in the Cambridge Structural Database, which is not shorter than the sum of van der Waals radii of 1.55 (nitrogen) plus 1.98 Å (iodine).

In addition to the N—H⋯I hydrogen bonds there are weak intermolecular C—H⋯π interactions between H1 and the six-membered ring of the indole moiety (Fig. 3). The distance of H1 to the least squares plane of the six-membered ring is 2.83 (2) Å and the distance to the center of gravity of this ring is 2.91 (2) Å (Table 2). According to the classification of Malone et al. (1997) this is a "Type I" C—H⋯π interaction.

Experimental

Indole-3-thiouronium iodide was prepared as described in literature (Harris, 1969; van der Geer et al., 2007) and crystallized by diethyl ether vapor diffusion into an acetone solution.

Refinement

All H atoms were freely refined.
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Figures

Fig. 1. The molecular structure of (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

Fig. 2. Hydrogen bonded environment of the iodide in (I). C—H hydrogen atoms are omitted for clarity. Symmetry operations i: 1 + x, y, z; ii: 1 - x, 1 - y, -z; iii: x, 0.5 - y, z - 1/2.

Fig. 3. C—H···π interaction in (I). View along the crystallographic b axis. Symmetry operation i: x, 0.5 - y, z - 1/2.

Indole-3-thiouromium iodide

Crystal data

C9H10N2S+I-

$F_{000} = 616$

$M_r = 319.16$

$L_x = 1.819 \text{ Mg m}^{-3}$

Monoclinic, $P2_1/c$

Hall symbol: -P 2yc

$a = 10.5098$ (2) Å

$b = 10.6264$ (3) Å

$c = 10.6951$ (4) Å

$\beta = 102.648$ (2)°

$V = 1165.46$ (6) Å³

$Z = 4$

$\lambda = 0.71073$ Å

Cell parameters from 11915 reflections

$\theta = 2.0{}^\circ - 27.5{}^\circ$

$\mu = 2.89$ mm$^{-1}$

$T = 150$ (2) K

Block, colourless

$0.30 \times 0.30 \times 0.30$ mm

Data collection

Nonius KappaCCD
differential

Radiation source: rotating anode

Mo Kα radiation

$R_{int} = 0.033$

$\theta_{max} = 27.5{}^\circ$

$\theta_{min} = 2.0{}^\circ$

$T_{min} = 0.24$, $T_{max} = 0.42$

SADABS; Sheldrick, 2002

15531 measured reflections

2668 independent reflections

$R_{int} = 0.033$

$R_{int} = 0.033$

$\theta_{max} = 27.5{}^\circ$

$\theta_{min} = 2.0{}^\circ$

$T_{min} = 0.24$, $T_{max} = 0.42$

SADABS; Sheldrick, 2002

15531 measured reflections

$\theta_{max} = 27.5{}^\circ$

$\theta_{min} = 2.0{}^\circ$

$T_{min} = 0.24$, $T_{max} = 0.42$

15531 measured reflections

$2470$ reflections with $I > 2\sigma(I)$

$2470$ reflections with $I > 2\sigma(I)$

$2470$ reflections with $I > 2\sigma(I)$

$2470$ reflections with $I > 2\sigma(I)$

Re�inement

Refinement on $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.018$

$wR(F^2) = 0.045$

$S = 1.09$

2668 reflections

Secondary atom site location: difference Fourier map

Hydrogen site location: difference Fourier map

All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0216P)^2 + 0.5241P]$ where $P = (F_o^2 + 2F_c^2)/3$

$\langle \Delta \rho \rangle_{\text{max}} = 0.003$

$\Delta \rho_{\text{max}} = 0.50$ e Å$^{-3}$
supplementary materials

167 parameters

Primary atom site location: structure-invariant direct methods

\[ \Delta \rho_{\text{min}} = -0.53 \text{ e/Å}^3 \]

Extinction correction: none

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 \( F^2 > 2 \sigma(F^2) \) 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 (Å²)

| Atom | \( x \)  | \( y \)  | \( z \)  | \( U_{eq} \) |
|------|---------|---------|---------|-----------|
| S1   | 0.43028 (5) | 0.17217 (4) | 0.29661 (4) | 0.02089 (10) |
| N1   | 0.08974 (16) | 0.33441 (15) | 0.18625 (17) | 0.0243 (3) |
| H1N  | 0.024 (2) | 0.343 (2) | 0.140 (2) | 0.017 (5)* |
| N2   | 0.49115 (18) | 0.34694 (16) | 0.13906 (16) | 0.0237 (3) |
| H2N  | 0.541 (3) | 0.384 (3) | 0.097 (2) | 0.039 (7)* |
| H3N  | 0.415 (2) | 0.365 (2) | 0.123 (2) | 0.025 (6)* |
| N3   | 0.65635 (17) | 0.21727 (17) | 0.23827 (18) | 0.0247 (3) |
| H4N  | 0.680 (2) | 0.170 (2) | 0.291 (2) | 0.025 (6)* |
| H5N  | 0.711 (2) | 0.251 (2) | 0.196 (3) | 0.040 (7)* |
| C1   | 0.18173 (18) | 0.24948 (18) | 0.17078 (18) | 0.0220 (4) |
| H1   | 0.168 (2) | 0.198 (2) | 0.101 (2) | 0.032 (6)* |
| C2   | 0.29152 (17) | 0.26651 (17) | 0.26602 (17) | 0.0193 (3) |
| C3   | 0.3378 (2) | 0.42952 (18) | 0.45307 (19) | 0.0238 (4) |
| H3   | 0.422 (2) | 0.402 (2) | 0.491 (2) | 0.022 (5)* |
| C4   | 0.2801 (2) | 0.52789 (19) | 0.5048 (2) | 0.0287 (4) |
| H4   | 0.325 (3) | 0.574 (3) | 0.577 (3) | 0.047 (8)* |
| C5   | 0.1524 (2) | 0.5675 (2) | 0.4494 (2) | 0.0312 (5) |
| H5   | 0.117 (2) | 0.635 (2) | 0.487 (2) | 0.027 (6)* |
| C6   | 0.0801 (2) | 0.5097 (2) | 0.3418 (2) | 0.0277 (4) |
| H6   | −0.004 (3) | 0.536 (2) | 0.304 (3) | 0.034 (7)* |
| C7   | 0.13841 (18) | 0.40987 (18) | 0.29061 (18) | 0.0218 (4) |
| C8   | 0.26581 (17) | 0.36941 (16) | 0.34426 (17) | 0.0189 (3) |
| C9   | 0.53403 (17) | 0.25457 (16) | 0.21755 (16) | 0.0183 (3) |
| I1   | 0.770943 (11) | 0.454617 (11) | 0.031246 (11) | 0.02163 (5) |

Atomic displacement parameters (Å²)

|  | \( U^{11} \)  | \( U^{22} \)  | \( U^{33} \)  | \( U^{12} \)  | \( U^{13} \)  | \( U^{23} \)  |
|---|---------|---------|---------|---------|---------|---------|
| S1 | 0.0194 (2) | 0.0196 (2) | 0.0242 (2) | 0.00360 (16) | 0.00591 (17) | 0.00584 (17) |
### supplementary materials

|     |     |     |     |     |     |     |
|-----|-----|-----|-----|-----|-----|-----|
| N1  | 0.0146 (8) | 0.0273 (8) | 0.0288 (9) | 0.0010 (6) | −0.0001 (7) | −0.0015 (7) |
| N2  | 0.0188 (8) | 0.0262 (8) | 0.0259 (8) | 0.0001 (7) | 0.0045 (7) | 0.0077 (6) |
| N3  | 0.0202 (8) | 0.0272 (9) | 0.0278 (9) | 0.0059 (7) | 0.0076 (7) | 0.0069 (7) |
| C1  | 0.0210 (9) | 0.0227 (9) | 0.0222 (9) | −0.0008 (7) | 0.0047 (7) | −0.0001 (7) |
| C2  | 0.0160 (8) | 0.0200 (8) | 0.0227 (9) | 0.0001 (7) | 0.0058 (7) | 0.0032 (7) |
| C3  | 0.0238 (10) | 0.0234 (9) | 0.0232 (9) | −0.0020 (7) | 0.0032 (8) | 0.0034 (7) |
| C4  | 0.0367 (13) | 0.0238 (10) | 0.0251 (10) | −0.0043 (8) | 0.0059 (9) | −0.0023 (8) |
| C5  | 0.0365 (13) | 0.0231 (10) | 0.0378 (12) | 0.0020 (8) | 0.0165 (10) | −0.0032 (8) |
| C6  | 0.0219 (10) | 0.0273 (10) | 0.0354 (11) | 0.0049 (8) | 0.0094 (9) | 0.0003 (8) |
| C7  | 0.0180 (9) | 0.0211 (8) | 0.0266 (9) | 0.0004 (7) | 0.0058 (7) | 0.0023 (7) |
| C8  | 0.0185 (9) | 0.0184 (8) | 0.0210 (8) | −0.0006 (7) | 0.0067 (7) | 0.0042 (7) |
| C9  | 0.0198 (9) | 0.0175 (8) | 0.0173 (8) | −0.0007 (7) | 0.0031 (6) | −0.0014 (6) |
| I1  | 0.01614 (8) | 0.02314 (8) | 0.02444 (8) | 0.00029 (4) | 0.00192 (5) | 0.00236 (4) |

#### Geometric parameters (Å, °)

|     |     |     |     |     |     |     |
|-----|-----|-----|-----|-----|-----|-----|
| S1—C2 | 1.7406 (18) | C1—H1 | 0.91 (2) |
| S1—C9 | 1.7533 (19) | C2—C8 | 1.438 (2) |
| N1—C1 | 1.359 (2) | C3—C4 | 1.383 (3) |
| N1—C7 | 1.379 (3) | C3—C8 | 1.396 (3) |
| N1—H1N | 0.76 (2) | C3—H3 | 0.94 (2) |
| N2—C9 | 1.306 (2) | C4—C5 | 1.407 (4) |
| N2—H2N | 0.86 (3) | C4—H4 | 0.95 (3) |
| N2—H3N | 0.80 (2) | C5—C6 | 1.377 (3) |
| N3—C9 | 1.317 (2) | C5—H5 | 0.94 (2) |
| N3—H4N | 0.75 (3) | C6—C7 | 1.396 (3) |
| N3—H5N | 0.88 (3) | C6—H6 | 0.93 (3) |
| C1—C2 | 1.374 (3) | C7—C8 | 1.404 (3) |
| C2—S1—C9 | 101.87 (9) | C3—C4—C5 | 121.3 (2) |
| C1—N1—C7 | 109.70 (16) | C3—C4—H4 | 122.2 (18) |
| C1—N1—H1N | 124.2 (16) | C5—C4—H4 | 116.5 (18) |
| C7—N1—H1N | 125.7 (16) | C6—C5—C4 | 121.3 (2) |
| C9—N2—H2N | 121.1 (18) | C6—C5—H5 | 119.9 (14) |
| C9—N2—H3N | 120.1 (17) | C4—C5—H5 | 118.8 (14) |
| H2N—N2—H3N | 118 (2) | C5—C6—C7 | 117.18 (19) |
| C9—N3—H4N | 118.3 (18) | C5—C6—H6 | 121.6 (15) |
| C9—N3—H5N | 120.9 (17) | C7—C6—H6 | 121.2 (15) |
| H4N—N3—H5N | 121 (2) | N1—C7—C6 | 129.98 (18) |
| N1—C1—C2 | 109.07 (17) | N1—C7—C8 | 107.73 (16) |
| N1—C1—H1 | 120.7 (15) | C6—C7—C8 | 122.29 (18) |
| C2—C1—H1 | 130.0 (15) | C3—C8—C7 | 119.67 (17) |
| C1—C2—C8 | 107.29 (17) | C3—C8—C2 | 134.13 (18) |
| C1—C2—S1 | 126.63 (15) | C7—C8—C2 | 106.20 (16) |
| C8—C2—S1 | 125.81 (14) | N2—C9—N3 | 121.41 (18) |
| C4—C3—C8 | 118.29 (19) | N2—C9—S1 | 121.45 (15) |
| C4—C3—H3 | 121.6 (14) | N3—C9—S1 | 117.12 (14) |
| C8—C3—H3 | 120.1 (14) | C4—C3—C8 | 129.98 (18) |
| C7—N1—C1—C2 | 1.0 (2) | C4—C3—C8—C7 | 0.1 (3) |
| N1—C1—C2—C8 | −0.6 (2) | C4—C3—C8—C2 | −179.7 (2) |
supplementary materials

N1—C1—C2—S1 173.64 (14) N1—C7—C8—C3 -179.32 (17)
C9—S1—C2—C1 96.99 (19) C6—C7—C8—C3 0.4 (3)
C9—S1—C2—C8 -89.75 (17) N1—C7—C8—C2 0.5 (2)
C8—C3—C4—C5 -0.3 (3) C6—C7—C8—C2 -179.74 (18)
C3—C4—C5—C6 0.1 (3) C1—C2—C8—C3 179.9 (2)
C4—C5—C6—C7 0.4 (3) S1—C2—C8—C3 5.5 (3)
C1—N1—C7—C6 179.4 (2) C1—C2—C8—C7 0.1 (2)
C1—N1—C7—C8 -0.9 (2) S1—C2—C8—C7 -174.27 (14)
C5—C6—C7—N1 179.0 (2) C2—S1—C9—N2 -11.53 (17)
C5—C6—C7—C8 -0.7 (3) C2—S1—C9—N3 170.10 (14)

Hydrogen-bond geometry (Å, °)

| D—H—A | D—H | H···A | D···A | D—H···A |
|--------|------|-------|-------|--------|
| N1—H1N···N1i | 0.76 (2) | 2.91 (2) | 3.6295 (17) | 158 (2) |
| N2—H2N···N1 | 0.86 (3) | 2.76 (3) | 3.5736 (18) | 158 (2) |
| N2—H3N···N1ii | 0.80 (2) | 2.97 (2) | 3.6269 (17) | 141 (2) |
| N3—H4N···N1iii | 0.75 (3) | 2.86 (3) | 3.5990 (19) | 165 (2) |
| N3—H5N···N1 | 0.88 (3) | 2.95 (3) | 3.7258 (19) | 149 (2) |
| C1—H1···Cg1iv | 0.91 (2) | 2.91 (2) | 3.794 (2) | 162.8 (18) |

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

Fig. 3