

4-Cyanoanilinium iodide

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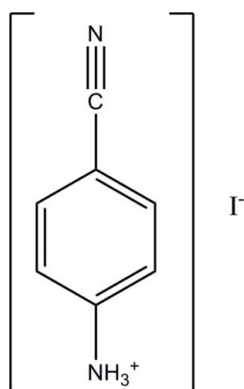
Received 12 July 2012; accepted 24 July 2012

Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; disorder in main residue; R factor = 0.012; wR factor = 0.029; data-to-parameter ratio = 12.3.

In the title compound, $\text{C}_7\text{H}_7\text{N}_2^+\cdot\text{I}^-$, the cation is located on a site of $4mm$ symmetry and is thus disordered about the fourfold axis so that there are two perpendicular orientations of the six-membered ring and four rotational orientations of the $\{-\text{NH}_3^+\}$ group. In the crystal, there are two layers perpendicular to the c axis, each containing iodide ions and the $\{-\text{NH}_3^+\}$ portions of the cations, with the remainder of the cations extending outwards from these layers.

Related literature

For the structure of 4-cyanoanilinium chloride, see: Colapietro *et al.* (1981). For the structure of 4-cyanoanilinium bromide, see: Vumbaco *et al.* (2012). For the structure of anilinium iodide, see: Fecher & Weiss (1986).



Experimental

Crystal data

| | |
|---|---|
| $\text{C}_7\text{H}_7\text{N}_2^+\cdot\text{I}^-$ | $Z = 2$ |
| $M_r = 246.05$ | Mo $K\alpha$ radiation |
| Tetragonal, $P4/nmm$ | $\mu = 3.83 \text{ mm}^{-1}$ |
| $a = 4.9930$ (4) Å | $T = 100$ K |
| $c = 16.445$ (2) Å | $0.26 \times 0.20 \times 0.05 \text{ mm}$ |
| $V = 409.98$ (8) Å ³ | |

Data collection

| | |
|--|---------------------------------------|
| Bruker SMART APEX CCD diffractometer | 7082 measured reflections |
| Absorption correction: multi-scan (<i>SADABS</i> ; Sheldrick, 2009) | 382 independent reflections |
| $T_{\min} = 0.362$, $T_{\max} = 0.844$ | 381 reflections with $I > 2\sigma(I)$ |
| | $R_{\text{int}} = 0.039$ |

Refinement

| | |
|---------------------------------|--|
| $R[F^2 > 2\sigma(F^2)] = 0.012$ | 31 parameters |
| $wR(F^2) = 0.029$ | H-atom parameters constrained |
| $S = 1.14$ | $\Delta\rho_{\text{max}} = 0.46 \text{ e \AA}^{-3}$ |
| 382 reflections | $\Delta\rho_{\text{min}} = -0.56 \text{ e \AA}^{-3}$ |

Table 1

Hydrogen-bond geometry (Å, °).

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|--|-------|-------------|-------------|---------------|
| $\text{N1}-\text{H1}\cdots\text{I1}$ | 0.88 | 2.72 | 3.5813 (5) | 165 |
| $\text{N1}-\text{H1A}\cdots\text{I1}^i$ | 0.88 | 2.87 | 3.5813 (5) | 139 |
| $\text{N1}-\text{H1B}\cdots\text{I1}^{ii}$ | 0.88 | 2.87 | 3.5813 (5) | 139 |

Symmetry codes: (i) $x - 1, y, z$; (ii) $x, y - 1, z$.

Data collection: *APEX2* (Bruker, 2010); cell refinement: *S SAINT* (Bruker, 2009); data reduction: *S SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

We thank the Chemistry Department of Tulane University for support of the X-ray laboratory and the Louisiana Board of Regents through the Louisiana Educational Quality Support Fund (grant LEQSF (2003–2003)–ENH–TR–67) for the purchase of the APEX diffractometer.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: RK2373).

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supporting information

Acta Cryst. (2012). E68, o2623 [doi:10.1107/S1600536812033466]

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S1. Comment

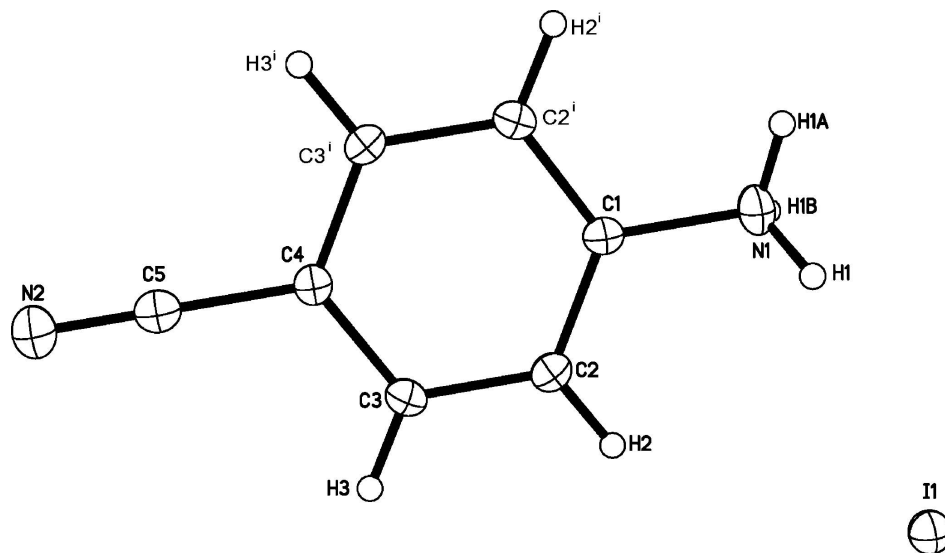
In the title compound, $(C_7H_7N_2)^+I^-$, the cation is located on a site of $4mm$ symmetry so is disordered over 2 sites rotated 90° from one another about the $N1-C1\cdots C4-C5\equiv N2$ axis. This leads to a more extensive disorder of the $(-NH_3^+)$ group so it is likely that there are a variety of $N-H\cdots I$ interactions of different geometries. To illustrate what one set of these could be, the best estimate of the rotational orientation of the $(-NH_3^+)$ group obtained from a difference map was used to generate the values given in Table 1. These interactions lead to a layer of anions with the $(-NH_3^+)$ groups largely in the layer and the remainder of the cations projecting perpendicular to the layer. Two of these layers are then associated in a head-to-head fashion *via* electrostatic $N1^+\cdots I1^-$ interactions of $3.513(1)\text{\AA}$ leading to a bilayer of iodide and $(-NH_3^+)$ groups with the remainders of the cations projecting out from both sides (Fig. 2). A similar layer structure is adopted by anilinium iodide (Fecher & Weiss, 1986) while the packings for 4-cyanoanilinium bromide (Vumbaco *et al.*, 2012) and the corresponding chloride salt (Colapietro *et al.*, 1981) are quite different.

S2. Experimental

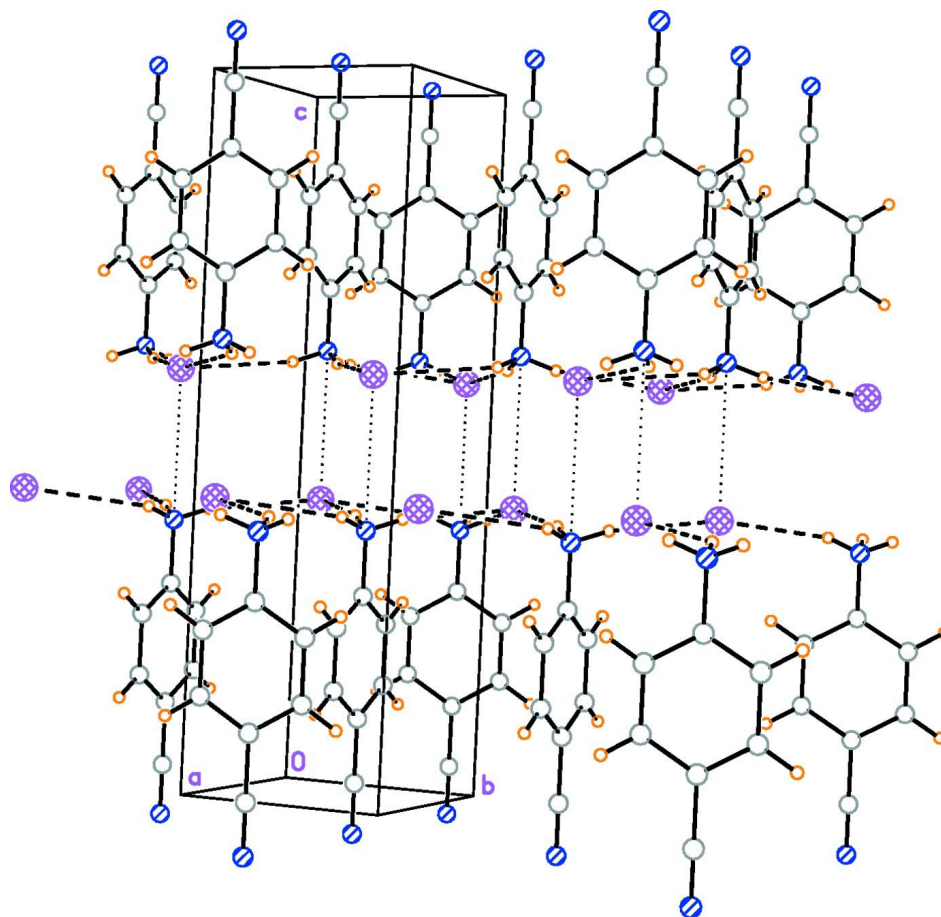
The 0.55 g of 4-cyanoaniline and 1.0 ml of aqueous hydroiodic acid (47% by mass) were combined in 10 ml of ethanol. This solution was slowly evaporated to dryness under ambient conditions to form crystals of the title compound.

S3. Refinement

The cation sits on a special position requiring 4 mm symmetry with the 4-fold axis running through both N atoms and the attached carbons. Thus the carbon atoms at the 2- and 3-positions are effectively disordered over two sites and two orientations of each were used in the refinement. H atoms attached to these carbons were placed in calculated positions with $C-H = 0.95\text{\AA}$. A small peak in a position to be one location for a hydrogen bound to N1 could be seen in a difference map and its position was used to calculate positions for the remainder of one of the orientations of the $-NH_3^+$ unit in which the $N-H$ distance was adjusted to be 0.88\AA . All H atoms were included as riding contributions with $U_{iso}(H) = 1.2U_{eq}(C, N)$.

**Figure 1**

View of the cation–anion pair with with the atom numbering scheme. Displacement ellipsoids are drawn at 50% probability level. H atoms are presented as a small spheres of arbitrary radius. Symmetry code: (i) $-x+1/2, -y+1/2, z$.

**Figure 2**

Packing showing the cation–anion bilayer perpendicular to the c axis. N—H \cdots I interactions are shown as dashed lines and the electrostatic N $^+$ \cdots I interactions as dotted lines. Colour key: purple = I, blue = N, gray = C, orange = H.

4-Cyanoanilinium iodide

Crystal data

$C_7H_7N_2^+I^-$
 $M_r = 246.05$
 Tetragonal, $P4/nmm$
 Hall symbol: $-P\ 4a\ 2a$
 $a = 4.9930\ (4)\ \text{\AA}$
 $c = 16.445\ (2)\ \text{\AA}$
 $V = 409.98\ (8)\ \text{\AA}^3$
 $Z = 2$
 $F(000) = 232$

$D_x = 1.993\ \text{Mg m}^{-3}$
 Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$
 Cell parameters from 8495 reflections
 $\theta = 2.5\text{--}29.1^\circ$
 $\mu = 3.83\ \text{mm}^{-1}$
 $T = 100\ \text{K}$
 Plate, colourless
 $0.26 \times 0.20 \times 0.05\ \text{mm}$

Data collection

Bruker SMART APEX CCD
 diffractometer
 Radiation source: fine-focus sealed tube
 Graphite monochromator
 φ and ω scans

Absorption correction: multi-scan
 (*SADABS*; Sheldrick, 2009)
 $T_{\min} = 0.362$, $T_{\max} = 0.844$
 7082 measured reflections
 382 independent reflections
 381 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.039$
 $\theta_{\text{max}} = 29.1^\circ$, $\theta_{\text{min}} = 2.5^\circ$
 $h = -6 \rightarrow 6$

$k = -6 \rightarrow 6$
 $l = -22 \rightarrow 22$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.012$
 $wR(F^2) = 0.029$
 $S = 1.14$
 382 reflections
 31 parameters
 0 restraints
 Primary atom site location: heavy atom

Secondary atom site location: difference Fourier map
 Hydrogen site location: inferred from neighbouring sites
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0165P)^2 + 0.1447P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.002$
 $\Delta\rho_{\text{max}} = 0.46 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.56 \text{ e } \text{\AA}^{-3}$

Special details

Experimental. The diffraction data were obtained from 3 sets of 400 frames, each of width 0.5° in ω , collected at $\varphi = 0.00^\circ$, 90.00° and 180.00° and 2 sets of 800 frames, each of width 0.45° in φ , collected at $\omega = -30.00^\circ$ and 210.00° . The scan time was 10 sec/frame.

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

| | <i>x</i> | <i>y</i> | <i>z</i> | $U_{\text{iso}}^*/U_{\text{eq}}$ | Occ. (<1) |
|-----|------------|----------|---------------|----------------------------------|-----------|
| I1 | 0.7500 | 0.7500 | 0.588552 (10) | 0.01472 (8) | |
| N1 | 0.2500 | 0.2500 | 0.62508 (16) | 0.0199 (5) | |
| H1 | 0.3662 | 0.3662 | 0.6057 | 0.024* | 0.25 |
| H1A | 0.0887 | 0.2904 | 0.6073 | 0.024* | 0.125 |
| H1B | 0.2904 | 0.0887 | 0.6073 | 0.024* | 0.125 |
| N2 | 0.2500 | 0.2500 | 1.03941 (17) | 0.0226 (6) | |
| C1 | 0.2500 | 0.2500 | 0.71467 (18) | 0.0139 (5) | |
| C2 | 0.4934 (6) | 0.2500 | 0.75539 (17) | 0.0174 (5) | 0.50 |
| H2 | 0.6576 | 0.2500 | 0.7262 | 0.021* | 0.50 |
| C3 | 0.4936 (6) | 0.2500 | 0.84022 (16) | 0.0171 (5) | 0.50 |
| H3 | 0.6583 | 0.2500 | 0.8692 | 0.020* | 0.50 |
| C4 | 0.2500 | 0.2500 | 0.88189 (18) | 0.0143 (5) | |
| C5 | 0.2500 | 0.2500 | 0.97006 (19) | 0.0174 (6) | |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|----|-------------|-------------|--------------|----------|----------|----------|
| I1 | 0.01513 (9) | 0.01513 (9) | 0.01392 (11) | 0.000 | 0.000 | 0.000 |
| N1 | 0.0236 (8) | 0.0236 (8) | 0.0126 (11) | 0.000 | 0.000 | 0.000 |

| | | | | | | |
|----|-------------|-------------|-------------|-------|--------------|-------|
| N2 | 0.0252 (9) | 0.0252 (9) | 0.0174 (12) | 0.000 | 0.000 | 0.000 |
| C1 | 0.0129 (8) | 0.0129 (8) | 0.0158 (12) | 0.000 | 0.000 | 0.000 |
| C2 | 0.0132 (12) | 0.0225 (14) | 0.0163 (11) | 0.000 | 0.0020 (10) | 0.000 |
| C3 | 0.0129 (12) | 0.0226 (13) | 0.0157 (11) | 0.000 | -0.0022 (11) | 0.000 |
| C4 | 0.0146 (8) | 0.0146 (8) | 0.0136 (13) | 0.000 | 0.000 | 0.000 |
| C5 | 0.0161 (9) | 0.0161 (9) | 0.0200 (14) | 0.000 | 0.000 | 0.000 |

Geometric parameters (Å, °)

| | | | |
|---------------------------|-------------|------------------------|-------------|
| N1—C1 | 1.473 (4) | C2—C3 | 1.395 (4) |
| N1—H1 | 0.8800 | C2—H2 | 0.9500 |
| N1—H1A | 0.8800 | C3—C4 | 1.396 (3) |
| N1—H1B | 0.8800 | C3—H3 | 0.9500 |
| N2—C5 | 1.141 (4) | C4—C3 ⁱ | 1.396 (3) |
| C1—C2 ⁱ | 1.388 (3) | C4—C5 | 1.450 (4) |
| C1—C2 | 1.388 (3) | | |
| C1—N1—H1 | 111.2 | C1—C2—H2 | 120.8 |
| C1—N1—H1A | 109.4 | C3—C2—H2 | 120.3 |
| H1—N1—H1A | 109.4 | C2—C3—C4 | 119.3 (3) |
| C1—N1—H1B | 109.4 | C2—C3—H3 | 120.1 |
| H1—N1—H1B | 109.4 | C4—C3—H3 | 120.5 |
| H1A—N1—H1B | 108.0 | C3 ⁱ —C4—C3 | 121.2 (3) |
| C2 ⁱ —C1—C2 | 122.3 (3) | C3 ⁱ —C4—C5 | 119.39 (15) |
| C2 ⁱ —C1—N1 | 118.85 (16) | C3—C4—C5 | 119.39 (15) |
| C2—C1—N1 | 118.85 (16) | N2—C5—C4 | 180.000 (1) |
| C1—C2—C3 | 118.9 (3) | | |
| C2 ⁱ —C1—C2—C3 | 0.000 (2) | C1—C2—C3—C4 | 0.000 (2) |
| N1—C1—C2—C3 | 180.000 (1) | C2—C3—C4—C5 | 180.000 (1) |

Symmetry code: (i) $-x+1/2, -y+1/2, z$.*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—H1...I1 | 0.88 | 2.72 | 3.5813 (5) | 165 |
| N1—H1A...I1 ⁱⁱ | 0.88 | 2.87 | 3.5813 (5) | 139 |
| N1—H1B...I1 ⁱⁱⁱ | 0.88 | 2.87 | 3.5813 (5) | 139 |

Symmetry codes: (ii) $x-1, y, z$; (iii) $x, y-1, z$.