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4-Cyano-1-methylpyridinium iodide

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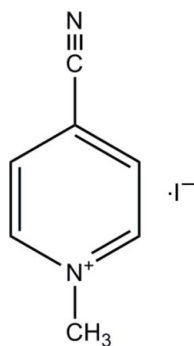
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Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; R factor = 0.020; wR factor = 0.048; data-to-parameter ratio = 19.5.

In the crystal structure of the title compound, $\text{C}_7\text{H}_7\text{N}_2^+\cdot\text{I}^-$, the cations form inversion-related dimers *via* weak pairwise $\text{C}-\text{H}\cdots\text{N}$ hydrogen bonds. In the dimers, the pyridinium rings are parallel to one another with their mean planes separated by a normal distance of *ca* 0.28 Å. Weak $\text{C}-\text{H}\cdots\text{N}$ interactions between adjacent dimers generate a layer lying parallel to (10 $\bar{1}$). The remaining H atoms form $\text{C}-\text{H}\cdots\text{I}$ interactions, which link the layers into a three-dimensional structure.

Related literature

For the structure of 3-cyano-1-methylpyridinium iodide, see: Koplitz *et al.* (2003). For the structure of 1-methylpyridinium iodide, see: Lalancette *et al.* (1978). For related structures see: Mague *et al.* (2005); Koplitz *et al.* (2012).



Experimental

Crystal data

$\text{C}_7\text{H}_7\text{N}_2^+\cdot\text{I}^-$
 $M_r = 246.05$
 Monoclinic, $P2_1/n$
 $a = 5.0734$ (3) Å
 $b = 11.4528$ (7) Å
 $c = 15.0751$ (9) Å
 $\beta = 99.679$ (1)°

$V = 863.46$ (9) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 3.64$ mm⁻¹
 $T = 100$ K
 $0.14 \times 0.07 \times 0.05$ mm

Data collection

Bruker SMART APEX CCD diffractometer
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.614$, $T_{\max} = 0.836$

12786 measured reflections
 1792 independent reflections
 1572 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.040$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.020$
 $wR(F^2) = 0.048$
 $S = 1.07$
 1792 reflections

92 parameters
 H-atom parameters constrained
 $\Delta\rho_{\max} = 0.88$ e Å⁻³
 $\Delta\rho_{\min} = -0.47$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{C3}-\text{H3}\cdots\text{N2}^{\text{i}}$	0.95	2.58	3.434 (4)	149
$\text{C1}-\text{H1B}\cdots\text{N2}^{\text{ii}}$	0.98	2.71	3.513 (4)	140
$\text{C1}-\text{H1A}\cdots\text{I1}^{\text{iii}}$	0.98	3.04	3.999 (3)	166
$\text{C1}-\text{H1C}\cdots\text{I1}^{\text{iv}}$	0.98	3.06	3.870 (3)	141
$\text{C2}-\text{H2}\cdots\text{I1}^{\text{v}}$	0.95	2.99	3.796 (3)	144
$\text{C5}-\text{H5}\cdots\text{I1}^{\text{vi}}$	0.95	2.94	3.839 (3)	158
$\text{C6}-\text{H6}\cdots\text{I1}^{\text{iii}}$	0.95	3.01	3.916 (3)	161

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

Data collection: APEX2 (Bruker, 2010); cell refinement: SAINT (Bruker, 2009); data reduction: 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]. MNK was supported by Louisiana Board of Regents grant LEQSF(2007–12)-ENH-PKSFI-PES-03 during the summer of 2011.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SU2473).

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supporting information

Acta Cryst. (2012). E68, o2514 [https://doi.org/10.1107/S1600536812032230]

4-Cyano-1-methylpyridinium iodide

Michael N. Kammer, Lynn V. Koplitz and Joel T. Mague

S1. Comment

Previously reported structures of four other cyano-1-methylpyridinium salts (Koplitz *et al.*, 2003; Mague *et al.*, 2005; Koplitz *et al.*, 2012) include three layered compounds with all atoms, except the methyl H atoms, lying on crystallographic mirror planes. Interestingly, none of the iodide salts of the 4-, 3- and 2-cyano-1-methylpyridinium cation adopt this layer structure, possibly because the larger size and weaker hydrogen-bonding ability of iodide as compared with the smaller chloride and bromide ions provides a less restrictive set of interionic interactions.

The molecular structure of the title compound is illustrated in Fig. 1. In the crystal, the cations form inversion dimers *via* weak pairwise C2—H2···N2 hydrogen bonds (Table 1). In the dimers the pyridinium rings are parallel to one another with their mean planes separated by a normal distance of *ca* 0.28 Å. Weak C1—H1B···N2 interactions between adjacent dimers generate a layer lying parallel to (10 $\bar{1}$), with the remaining hydrogen atoms forming C—H···I interactions (Table 1). The latter reinforce the construction of the layers as well as tying them together into a three-dimensional structure (Fig. 2).

In contrast to 3-cyano-1-methylpyridinium iodide (Koplitz *et al.*, 2003) where each iodide ion interacts with three C—H groups, in the title compound each anion is linked by five C—H groups which may reflect the more linear shape of the cation in the present structure.

S2. Experimental

4-Cyanopyridine (10.55 g) was dissolved in benzene (40 ml). Iodomethane (9.5 ml) was added to this solution slowly with stirring and the solution was refluxed for 75 minutes. A yellow solid was collected by vacuum filtration (*M.p.* 462 - 466 K). Addition of ethanol to the supernatant (*ca* 2:1 benzene:ethanol) resulted in the the growth overnight of thin plate-like yellow crystals of the title compound, suitable for X-ray diffraction.

S3. Refinement

The C-bound H-atoms were included in calculated positions and treated as riding atoms: C—H = 0.95 and 0.98 Å for CH and CH₃ H-atoms, respectively, with $U_{\text{iso}}(\text{H}) = k \times U_{\text{eq}}(\text{C})$, where $k = 1.5$ for CH₃ H-atoms and 1.2 for other H-atoms.

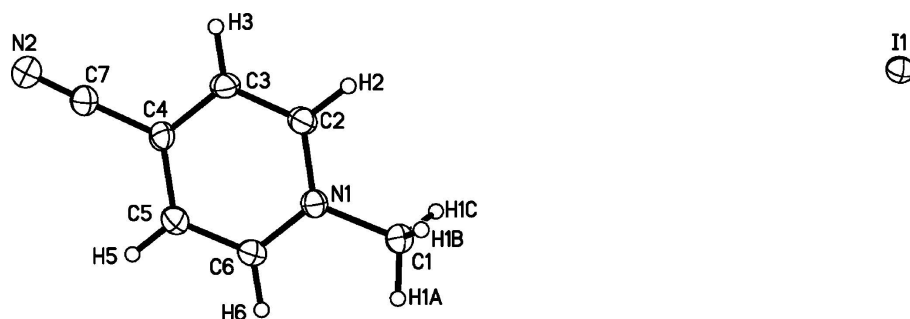


Figure 1

A perspective view of the asymmetric unit of the title compound with atom numbering. Displacement ellipsoids are drawn at the 50% probability level.

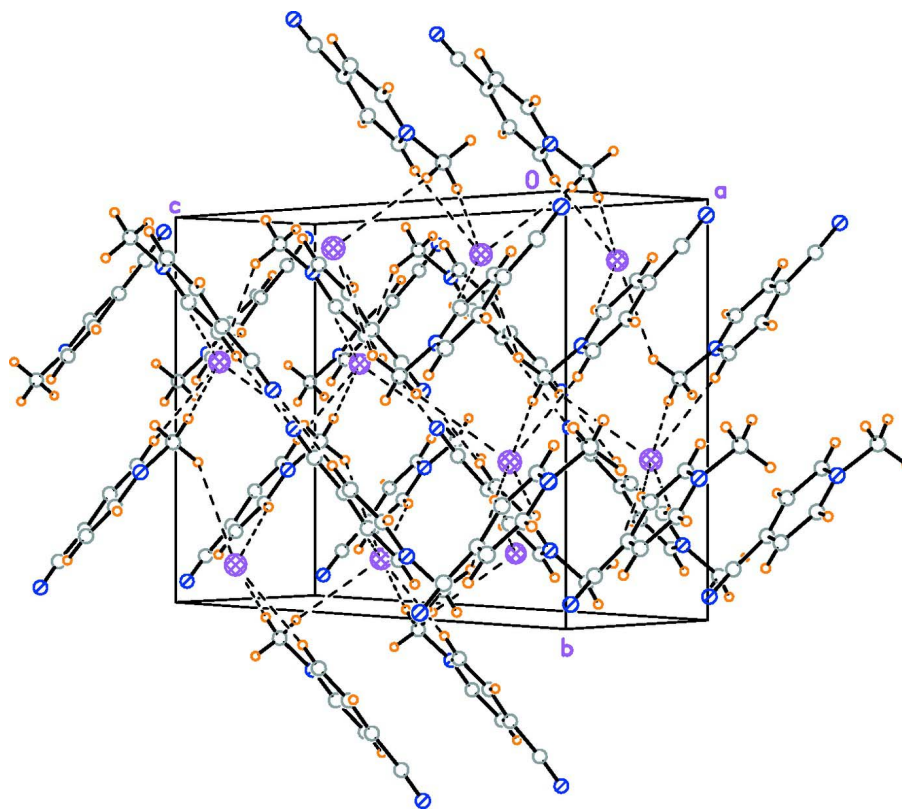


Figure 2

A view of the crystal packing of the title compound, showing the interpenetrating sheets of cations [colour key: C = gray, H = orange, N = blue, I = purple; C—H...I interactions are depicted as dashed lines].

4-Cyano-1-methylpyridinium iodide

Crystal data

$C_7H_7N_2^+I^-$

$M_r = 246.05$

Monoclinic, $P2_1/n$

Hall symbol: $-P 2_1n$

$a = 5.0734 (3) \text{ \AA}$

$b = 11.4528 (7) \text{ \AA}$

$c = 15.0751 (9) \text{ \AA}$

$\beta = 99.679 (1)^\circ$

$V = 863.46 (9) \text{ \AA}^3$

$Z = 4$

$F(000) = 464$

$D_x = 1.893 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
 Cell parameters from 8899 reflections
 $\theta = 2.3\text{--}28.6^\circ$
 $\mu = 3.64 \text{ mm}^{-1}$

$T = 100 \text{ K}$
 Plates, yellow
 $0.14 \times 0.07 \times 0.05 \text{ mm}$

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, 1996)
 $T_{\min} = 0.614$, $T_{\max} = 0.836$

12786 measured reflections
 1792 independent reflections
 1572 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.040$
 $\theta_{\max} = 26.5^\circ$, $\theta_{\min} = 2.3^\circ$
 $h = -6 \rightarrow 6$
 $k = -14 \rightarrow 14$
 $l = -18 \rightarrow 18$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.020$
 $wR(F^2) = 0.048$
 $S = 1.07$
 1792 reflections
 92 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
 $w = 1/[\sigma^2(F_o^2) + (0.0159P)^2 + 1.1195P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.002$
 $\Delta\rho_{\max} = 0.88 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.47 \text{ e \AA}^{-3}$

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. H-atoms were placed in calculated positions (C—H = 0.95 - 0.98 \AA) and included as riding contributions with isotropic displacement parameters 1.2 - 1.5 times those of the attached carbon atoms.

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	0.95185 (3)	0.378404 (15)	0.854589 (12)	0.02114 (7)
N1	0.6792 (5)	0.3458 (2)	0.18850 (15)	0.0201 (5)
N2	0.7382 (5)	0.0466 (2)	-0.07663 (17)	0.0307 (6)
C1	0.6477 (6)	0.4209 (3)	0.26587 (19)	0.0233 (6)
H1A	0.5052	0.4779	0.2472	0.035*
H1B	0.8159	0.4621	0.2871	0.035*
H1C	0.6013	0.3726	0.3146	0.035*
C2	0.8704 (6)	0.2626 (3)	0.19989 (19)	0.0218 (6)
H2	0.9858	0.2554	0.2562	0.026*
C3	0.8996 (6)	0.1883 (3)	0.13096 (19)	0.0219 (6)
H3	1.0361	0.1306	0.1387	0.026*
C4	0.7265 (6)	0.1986 (2)	0.04961 (18)	0.0207 (6)
C5	0.5356 (6)	0.2869 (3)	0.03797 (19)	0.0243 (6)
H5	0.4201	0.2965	-0.0181	0.029*

C6	0.5167 (6)	0.3604 (3)	0.10929 (19)	0.0223 (6)
H6	0.3883	0.4215	0.1023	0.027*
C7	0.7369 (6)	0.1158 (3)	-0.0225 (2)	0.0244 (6)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
I1	0.01891 (11)	0.02214 (12)	0.02205 (11)	0.00126 (7)	0.00256 (7)	0.00040 (7)
N1	0.0211 (12)	0.0212 (12)	0.0191 (12)	0.0000 (9)	0.0065 (9)	0.0021 (9)
N2	0.0343 (15)	0.0328 (15)	0.0257 (14)	0.0058 (12)	0.0071 (11)	-0.0015 (12)
C1	0.0265 (15)	0.0239 (15)	0.0201 (14)	0.0037 (12)	0.0055 (12)	0.0008 (11)
C2	0.0190 (14)	0.0260 (15)	0.0204 (14)	0.0032 (11)	0.0035 (11)	0.0053 (11)
C3	0.0197 (14)	0.0238 (15)	0.0237 (15)	0.0060 (11)	0.0078 (11)	0.0048 (11)
C4	0.0250 (15)	0.0217 (14)	0.0171 (14)	0.0001 (11)	0.0082 (11)	0.0021 (11)
C5	0.0229 (15)	0.0301 (17)	0.0190 (14)	0.0041 (12)	0.0010 (11)	0.0021 (12)
C6	0.0219 (14)	0.0228 (15)	0.0219 (14)	0.0053 (11)	0.0029 (11)	0.0033 (11)
C7	0.0253 (15)	0.0256 (16)	0.0234 (15)	0.0017 (12)	0.0073 (12)	0.0027 (12)

Geometric parameters (Å, °)

N1—C6	1.343 (4)	C2—H2	0.9500
N1—C2	1.350 (4)	C3—C4	1.388 (4)
N1—C1	1.480 (4)	C3—H3	0.9500
N2—C7	1.139 (4)	C4—C5	1.390 (4)
C1—H1A	0.9800	C4—C7	1.451 (4)
C1—H1B	0.9800	C5—C6	1.381 (4)
C1—H1C	0.9800	C5—H5	0.9500
C2—C3	1.370 (4)	C6—H6	0.9500
C6—N1—C2	121.4 (2)	C2—C3—H3	120.5
C6—N1—C1	119.8 (2)	C4—C3—H3	120.5
C2—N1—C1	118.7 (2)	C3—C4—C5	119.8 (3)
N1—C1—H1A	109.5	C3—C4—C7	120.6 (3)
N1—C1—H1B	109.5	C5—C4—C7	119.5 (3)
H1A—C1—H1B	109.5	C6—C5—C4	118.8 (3)
N1—C1—H1C	109.5	C6—C5—H5	120.6
H1A—C1—H1C	109.5	C4—C5—H5	120.6
H1B—C1—H1C	109.5	N1—C6—C5	120.3 (3)
N1—C2—C3	120.6 (3)	N1—C6—H6	119.9
N1—C2—H2	119.7	C5—C6—H6	119.9
C3—C2—H2	119.7	N2—C7—C4	176.3 (3)
C2—C3—C4	119.0 (3)		
C6—N1—C2—C3	-1.6 (4)	C7—C4—C5—C6	175.8 (3)
C1—N1—C2—C3	177.5 (3)	C2—N1—C6—C5	2.4 (4)
N1—C2—C3—C4	-1.1 (4)	C1—N1—C6—C5	-176.7 (3)
C2—C3—C4—C5	2.9 (4)	C4—C5—C6—N1	-0.5 (4)
C2—C3—C4—C7	-175.0 (3)	C3—C4—C7—N2	76 (5)

C3—C4—C5—C6

−2.2 (4)

C5—C4—C7—N2

−102 (5)

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>
C3—H3 \cdots N2 ⁱ	0.95	2.58	3.434 (4)	149
C1—H1B \cdots N2 ⁱⁱ	0.98	2.71	3.513 (4)	140
C1—H1A \cdots I1 ⁱⁱⁱ	0.98	3.04	3.999 (3)	166
C1—H1C \cdots I1 ^{iv}	0.98	3.06	3.870 (3)	141
C2—H2 \cdots I1 ^v	0.95	2.99	3.796 (3)	144
C5—H5 \cdots I1 ^{vi}	0.95	2.94	3.839 (3)	158
C6—H6 \cdots I1 ⁱⁱⁱ	0.95	3.01	3.916 (3)	161

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