

2-Cyano-1-methylpyridinium iodide

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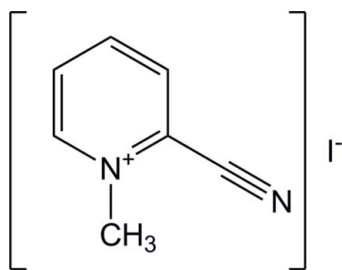
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Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.008$ Å; R factor = 0.036; wR factor = 0.091; data-to-parameter ratio = 574.1.

The cation in the title compound, $\text{C}_7\text{H}_7\text{N}_2^+\text{I}^-$, is planar (r.m.s. deviation for the nine fitted non-H atoms = 0.040 Å). The crystal packing is best described as undulating layers of cations and anions associated *via* $\text{C}-\text{H}\cdots\text{I}$ interactions.

Related literature

For the structure of 2-cyano-*N*-methylpyridinium nitrate, see: Koplitz *et al.* (2012). For structures of 3-cyano-*N*-methylpyridinium salts, see: Koplitz *et al.* (2003); Mague *et al.* (2005). For structures of 4-cyano-*N*-methylpyridinium salts, see: Kammer, Koplitz & Mague (2012); Kammer, Mague & Koplitz (2012).



Experimental

Crystal data

$\text{C}_7\text{H}_7\text{N}_2^+\text{I}^-$

$M_r = 246.05$

Orthorhombic, *Pbca*

$a = 9.5785$ (6) Å

$b = 8.5687$ (5) Å

$c = 20.2229$ (13) Å

$V = 1659.80$ (18) Å³

$Z = 8$

Mo $K\alpha$ radiation

$\mu = 3.79$ mm⁻¹

$T = 100$ K

$0.16 \times 0.14 \times 0.07$ mm

Data collection

Bruker SMART APEX CCD diffractometer

Absorption correction: multi-scan (*TWINABS*; Sheldrick, 2009)

$T_{\min} = 0.58$, $T_{\max} = 0.77$

58292 measured reflections

53390 independent reflections

40858 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.047$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.036$

$wR(F^2) = 0.091$

$S = 1.03$

53390 reflections

93 parameters

H-atom parameters constrained

$\Delta\rho_{\text{max}} = 1.14$ e Å⁻³

$\Delta\rho_{\text{min}} = -0.43$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{C1}-\text{H1B}\cdots\text{I1}^{\text{i}}$	0.98	3.20	4.014 (5)	141
$\text{C1}-\text{H1C}\cdots\text{I1}^{\text{ii}}$	0.98	3.11	4.021 (5)	156
$\text{C5}-\text{H5}\cdots\text{I1}^{\text{iii}}$	0.95	3.12	3.810 (5)	131
$\text{C6}-\text{H6}\cdots\text{I1}^{\text{iv}}$	0.95	3.03	3.677 (5)	126

Symmetry codes: (i) $-x + \frac{3}{2}, y + \frac{1}{2}, z$; (ii) $x + \frac{1}{2}, y + 1, -z + \frac{1}{2}$; (iii) $x + \frac{1}{2}, -y + \frac{3}{2}, -z$; (iv) $x + 1, y + 1, z$.

Data collection: *APEX2* (Bruker, 2013); cell refinement: *SAINT* (Bruker, 2013); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008b); program(s) used to refine structure: *SHELXL2013* (Sheldrick, 2013); molecular graphics: *DIAMOND* (Brandenburg & Putz, 2012); software used to prepare material for publication: *SHELXTL* and *CELL_NOW* (Sheldrick, 2008b).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: TK5240).

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supporting information

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S1. Comment

The three-dimensional, solid state structures of the salts of the three isomeric cyano-*N*-methylpyridinium cations are quite varied. These range from layered structures as seen in the chloride and bromide salts of the 3-cyano-*N*-methyl pyridinium cation (Koplitz, *et al.*, 2003; Mague, *et al.*, 2005) and in 2-cyano-*N*-methylpyridinium nitrate (Koplitz, *et al.*, 2012) through an open channel structure for 3-cyano-*N*-methyl pyridinium iodide (Koplitz, *et al.*, 2003) to complex networks as found for 4-cyano-*N*-methylpyridinium bromide and iodide (Kammer, Mague & Koplitz, 2012; Kammer, Koplitz & Mague, 2012). In all instances, the packing appears to be organized by weak C—H to anion hydrogen bonding and, in the case of 2-cyano-*N*-methylpyridinium nitrate, an anion- π interaction although we have yet to discern a pattern based on either the position of the cyano group on the ring or the size or shape of the anion. In the title compound, the packing of the cations and anions is organized by weak C—H \cdots I hydrogen bonding (Table 1). It can be described as "wavy" layers extending parallel to *c*. Fig. 2 presents a side view of the layers while Fig. 3 is a top view. From both of these, it is evident that the weak interionic interactions organize a three-dimensional network which is intermediate in complexity between those seen for 3-cyano-*N*-methylpyridinium iodide and 4-cyano-*N*-methylpyridinium bromide.

S2. Experimental

2-Cyanopyridine (10.5 g) was first melted in a warm water bath and then dissolved in benzene (40 ml). Iodomethane (9.5 ml) was added to this solution slowly with stirring and the solution was refluxed for 2 h. Yellow solid 2-cyano-*N*-methyl pyridinium iodide (m.p. 419–423 K) was collected by vacuum filtration.

S3. Refinement

The diffraction data were obtained from 3 sets of 400 frames, each of width 0.5° in ω , collected at $\varphi = 0.00, 90.00$ and 180.00° and 2 sets of 800 frames, each of width 0.45° in φ , collected at $\omega = -30.00$ and 210.00° . The scan time was 15 sec/frame. Analysis of 1649 reflections having $I/\sigma(I) > 15$ and chosen from the full data set with *CELL_NOW* (Sheldrick, 2008a) showed the crystal to belong to the orthorhombic system and to be twinned by a 180° rotation about *c*. The raw data were processed using the multi-component version of *SAINTE* under control of the two-component orientation file generated by *CELL_NOW*. The model was refined as a two-component twin which, although giving somewhat higher values for R_1 and wR_2 and the residual peaks in the final difference map than refinement as 1-component using the single component reflection file extracted from the full data set with *TWINABS*, provided a more reasonable suggested weighting scheme. H-atoms attached to carbon were placed in calculated positions (C—H = 0.95 - 0.98 Å). All were included as riding contributions with isotropic displacement parameters 1.2 - 1.5 times those of the attached atoms. The maximum and minimum residual electron density peaks of 1.14 and 0.43 eÅ⁻³, respectively, were located 0.02 Å and 1.86 Å from the I1 and N1 atoms, respectively.

I1

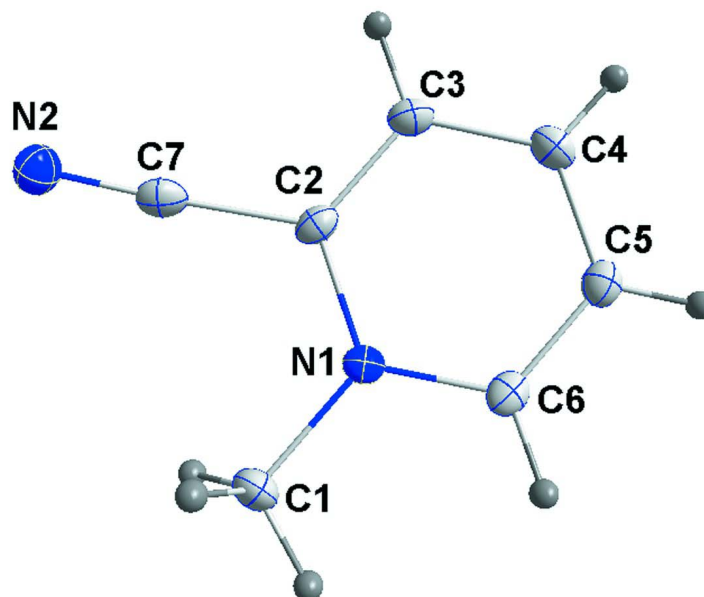


Figure 1
Perspective view of the title compound with 50% probability ellipsoids.

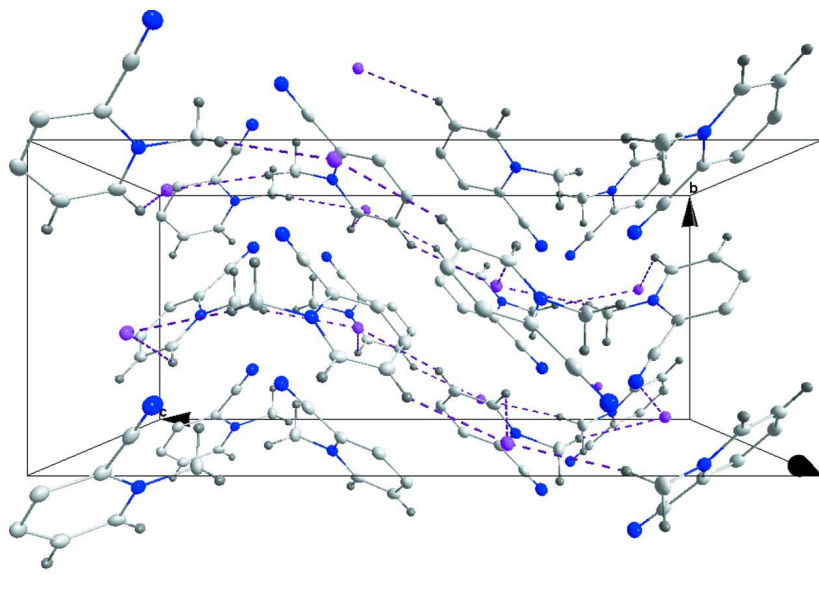
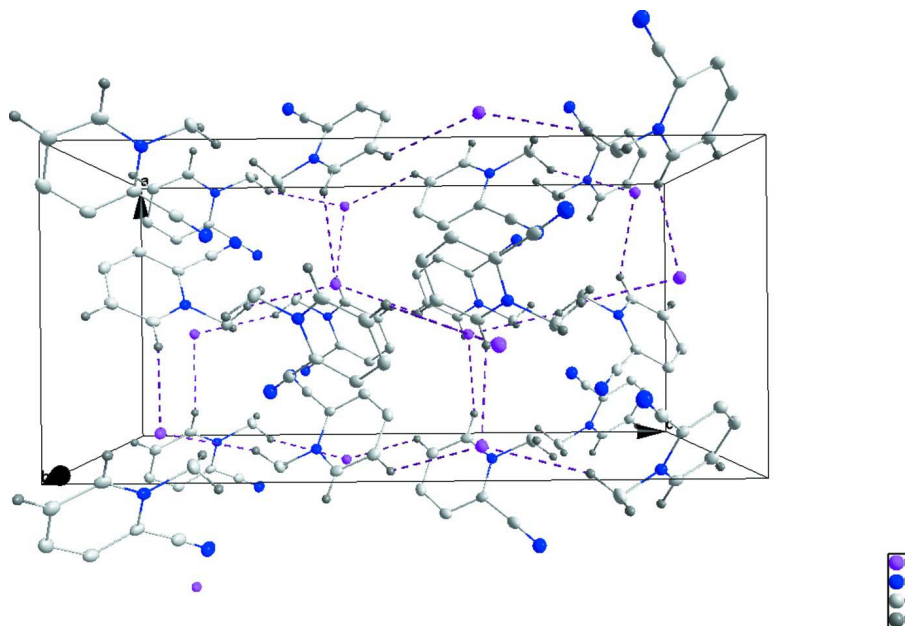


Figure 2
Packing projected down *a* showing the side view of the layers.

**Figure 3**

Packing projected down b showing the top view of the layers.

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Crystal data

$C_7H_7N_2^+I^-$

$M_r = 246.05$

Orthorhombic, $Pbca$

$a = 9.5785$ (6) Å

$b = 8.5687$ (5) Å

$c = 20.2229$ (13) Å

$V = 1659.80$ (18) Å³

$Z = 8$

$F(000) = 928$

$D_x = 1.969$ Mg m⁻³

Melting point: 146 K

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

Cell parameters from 4287 reflections

$\theta = 2.9$ – 28.7°

$\mu = 3.79$ mm⁻¹

$T = 100$ K

Slab, yellow

$0.16 \times 0.14 \times 0.07$ mm

Data collection

Bruker SMART APEX CCD

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: 8.3660 pixels mm⁻¹

φ and ω scans

Absorption correction: multi-scan

(*TWINABS*; Sheldrick, 2009)

$T_{\min} = 0.58$, $T_{\max} = 0.77$

58292 measured reflections

53390 independent reflections

40858 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.047$

$\theta_{\max} = 28.7^\circ$, $\theta_{\min} = 2.0^\circ$

$h = -12 \rightarrow 12$

$k = -11 \rightarrow 11$

$l = -26 \rightarrow 27$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.036$

$wR(F^2) = 0.091$

$S = 1.03$

53390 reflections

93 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

$$w = 1/[\sigma^2(F_o^2) + (0.0143P)^2 + 0.7747P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 1.14 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.43 \text{ e } \text{\AA}^{-3}$

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.

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

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
I1	0.41161 (3)	0.07802 (3)	0.10870 (2)	0.01550 (12)
N1	0.9765 (4)	1.0275 (5)	0.1442 (2)	0.0135 (9)
N2	0.7422 (4)	0.7530 (5)	0.2022 (2)	0.0205 (10)
C1	1.0446 (5)	0.9818 (6)	0.2072 (3)	0.0187 (11)
H1A	1.1337	1.0371	0.2116	0.028*
H1B	1.0615	0.8690	0.2072	0.028*
H1C	0.9837	1.0092	0.2443	0.028*
C2	0.8562 (5)	0.9559 (6)	0.1244 (3)	0.0142 (10)
C3	0.7917 (5)	0.9967 (6)	0.0661 (3)	0.0158 (11)
H3	0.7074	0.9471	0.0530	0.019*
C4	0.8517 (5)	1.1118 (6)	0.0268 (3)	0.0168 (11)
H4	0.8105	1.1395	-0.0143	0.020*
C5	0.9713 (5)	1.1848 (6)	0.0481 (3)	0.0166 (11)
H5	1.0122	1.2648	0.0220	0.020*
C6	1.0321 (5)	1.1424 (5)	0.1070 (3)	0.0149 (10)
H6	1.1140	1.1945	0.1216	0.018*
C7	0.7957 (5)	0.8415 (6)	0.1685 (3)	0.0165 (11)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
I1	0.01513 (19)	0.01697 (18)	0.01439 (19)	0.00131 (12)	-0.00021 (13)	-0.00058 (13)
N1	0.013 (2)	0.014 (2)	0.014 (2)	0.0017 (16)	0.0001 (18)	-0.0019 (17)
N2	0.022 (2)	0.020 (2)	0.019 (2)	-0.0019 (19)	0.001 (2)	-0.0010 (19)
C1	0.020 (3)	0.022 (3)	0.014 (3)	-0.001 (2)	-0.004 (2)	0.001 (2)
C2	0.012 (2)	0.014 (2)	0.016 (3)	-0.0010 (19)	0.003 (2)	-0.003 (2)
C3	0.013 (3)	0.016 (2)	0.018 (3)	0.0006 (19)	0.000 (2)	-0.003 (2)
C4	0.019 (3)	0.017 (2)	0.014 (3)	0.004 (2)	-0.001 (2)	-0.002 (2)
C5	0.017 (3)	0.014 (2)	0.020 (3)	0.0014 (19)	0.003 (2)	0.000 (2)
C6	0.012 (2)	0.011 (2)	0.021 (3)	0.0023 (18)	0.003 (2)	-0.002 (2)
C7	0.015 (2)	0.019 (3)	0.016 (3)	0.001 (2)	-0.001 (2)	-0.006 (2)

Geometric parameters (Å, °)

N1—C6	1.348 (6)	C2—C7	1.446 (7)
N1—C2	1.366 (6)	C3—C4	1.391 (7)
N1—C1	1.484 (6)	C3—H3	0.9500
N2—C7	1.141 (6)	C4—C5	1.375 (7)
C1—H1A	0.9800	C4—H4	0.9500
C1—H1B	0.9800	C5—C6	1.375 (7)
C1—H1C	0.9800	C5—H5	0.9500
C2—C3	1.375 (7)	C6—H6	0.9500
C6—N1—C2	119.8 (4)	C2—C3—H3	120.5
C6—N1—C1	119.9 (4)	C4—C3—H3	120.5
C2—N1—C1	120.3 (4)	C5—C4—C3	119.1 (5)
N1—C1—H1A	109.5	C5—C4—H4	120.4
N1—C1—H1B	109.5	C3—C4—H4	120.4
H1A—C1—H1B	109.5	C6—C5—C4	120.3 (5)
N1—C1—H1C	109.5	C6—C5—H5	119.8
H1A—C1—H1C	109.5	C4—C5—H5	119.8
H1B—C1—H1C	109.5	N1—C6—C5	120.6 (5)
N1—C2—C3	121.1 (4)	N1—C6—H6	119.7
N1—C2—C7	117.5 (4)	C5—C6—H6	119.7
C3—C2—C7	121.4 (5)	N2—C7—C2	176.9 (6)
C2—C3—C4	119.0 (5)		
C6—N1—C2—C3	1.3 (7)	C2—C3—C4—C5	-2.0 (7)
C1—N1—C2—C3	-180.0 (5)	C3—C4—C5—C6	1.2 (7)
C6—N1—C2—C7	-175.6 (4)	C2—N1—C6—C5	-2.2 (7)
C1—N1—C2—C7	3.1 (7)	C1—N1—C6—C5	179.1 (4)
N1—C2—C3—C4	0.7 (7)	C4—C5—C6—N1	0.9 (7)
C7—C2—C3—C4	177.5 (5)		

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>
C1—H1B...I1 ⁱ	0.98	3.20	4.014 (5)	141
C1—H1C...I1 ⁱⁱⁱ	0.98	3.11	4.021 (5)	156
C5—H5...I1 ⁱⁱⁱ	0.95	3.12	3.810 (5)	131
C6—H6...I1 ^{iv}	0.95	3.03	3.677 (5)	126

Symmetry codes: (i) $-x+3/2, y+1/2, z$; (ii) $x+1/2, y+1, -z+1/2$; (iii) $x+1/2, -y+3/2, -z$; (iv) $x+1, y+1, z$.