

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

4-Cyano-1-methylpyridinium perchlorate

Vu D. Nguyen,^a Cameron A. McCormick,^b Lynn V. Koplitz^a and Joel T. Mague^{c*}^aDepartment of Chemistry, Loyola University, New Orleans, LA 70118, USA,^bDepartment of Physics, Loyola University, New Orleans, LA 70118, USA, and^cDepartment of Chemistry, Tulane University, New Orleans, LA 70118, USA

Correspondence e-mail: joelt@tulane.edu

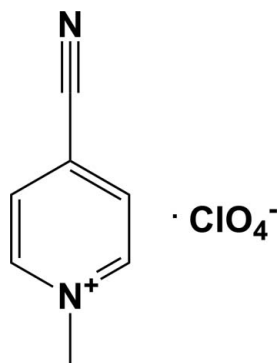
Received 30 May 2014; accepted 3 June 2014

Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.034; wR factor = 0.097; data-to-parameter ratio = 19.2.

The title salt, $\text{C}_7\text{H}_7\text{N}_2^+\cdot\text{ClO}_4^-$, crystallizes with alternating cations and anions in wavy sheets, which are formed by a number of $\text{C}-\text{H}\cdots\text{O}$ and $\text{C}-\text{H}\cdots\text{N}$ hydrogen bonds, lying approximately parallel to (001).

Related literature

For the crystal structures of other 4-cyano-1-methylpyridinium salts, see: McCormick *et al.* (2013); Kammer *et al.* (2012*a,b*); Hardacre *et al.* (2008, 2010); Glavcheva *et al.* (2004); Bockman & Kochi (1989, 1992). For the structure of 3-cyano-1-methylpyridinium perchlorate, see: McCormick *et al.* (2014) and for the structure of 4-cyanoanilinium perchlorate, see: Dai (2008). For a discussion of anion- π interactions, see: Frontera *et al.* (2011).



Experimental

Crystal data

 $\text{C}_7\text{H}_7\text{N}_2^+\cdot\text{ClO}_4^-$ $M_r = 218.60$ Orthorhombic, *Pbca* $a = 10.232$ (2) Å $b = 10.872$ (3) Å $c = 16.769$ (4) Å $V = 1865.3$ (7) Å³ $Z = 8$ Mo $K\alpha$ radiation $\mu = 0.40$ mm⁻¹ $T = 100$ K

0.23 × 0.16 × 0.12 mm

Data collection

Bruker SMART APEX CCD

diffractometer

Absorption correction: multi-scan

(SADABS; Bruker, 2010)

 $T_{\min} = 0.86$, $T_{\max} = 0.95$

30647 measured reflections

2475 independent reflections

2235 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.054$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.034$ $wR(F^2) = 0.097$ $S = 1.07$

2475 reflections

129 parameters

H-atom parameters constrained

 $\Delta\rho_{\text{max}} = 0.38$ e Å⁻³ $\Delta\rho_{\text{min}} = -0.39$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{C1}-\text{H1A}\cdots\text{O4}^{\text{i}}$	0.98	2.37	3.245 (2)	149
$\text{C1}-\text{H1C}\cdots\text{O2}^{\text{ii}}$	0.98	2.61	3.2540 (19)	123
$\text{C2}-\text{H2}\cdots\text{O1}^{\text{ii}}$	0.95	2.46	3.4001 (18)	173
$\text{C2}-\text{H2}\cdots\text{O2}^{\text{ii}}$	0.95	2.63	3.2549 (18)	123
$\text{C3}-\text{H3}\cdots\text{N2}^{\text{iii}}$	0.95	2.67	3.3098 (18)	125
$\text{C3}-\text{H3}\cdots\text{O3}^{\text{iv}}$	0.95	2.46	3.300 (2)	148
$\text{C6}-\text{H6}\cdots\text{O4}^{\text{i}}$	0.95	2.50	3.351 (2)	149

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

Data collection: *APEX2* (Bruker, 2010); cell refinement: *SAINT* (Bruker, 2010); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg & Putz, 2012); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008').

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.

Supporting information for this paper is available from the IUCr electronic archives (Reference: SU2740).

References

- Bockman, T. M. & Kochi, J. K. (1989). *J. Am. Chem. Soc.* **111**, 4669–4683.
 Bockman, T. M. & Kochi, J. K. (1992). *New J. Chem.* **16**, 39–49.
 Brandenburg, K. & Putz, H. (2012). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
 Bruker (2010). *APEX2*, *SADABS* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
 Dai, J. (2008). *Acta Cryst.* **E64**, o2025.
 Frontera, A., Gamez, P., Mascari, M., Mooibroek, T. J. & Reedijk, J. (2011). *Angew. Chem. Int. Ed.* **50**, 9564–9583.
 Glavcheva, Z., Nakanishi, H., Okdad, S. & Umezawa, H. (2004). *Mater. Lett.* **58**, 2466–2471.
 Hardacre, C., Holbrey, J. D., Mullan, C. L., Nieuwenhuyzen, M., Reichert, W. M., Seddon, K. R. & Teat, S. J. (2008). *New J. Chem.* **32**, 1953–1967.
 Hardacre, C., Holbrey, J. D., Mullan, C. L., Nieuwenhuyzen, M., Youngs, T. G. A., Bowron, D. T., Teat, S. J. (2010). *Phys. Chem. Chem. Phys.* **12**, 1842–1853.
 Kammer, M. N., Koplitz, L. V. & Mague, J. T. (2012*a*). *Acta Cryst.* **E68**, o2514.

Kammer, M. N., Mague, J. T. & Koplitz, L. V. (2012*b*). *Acta Cryst.* **E68**, o2409.
McCormick, C. A., Nguyen, V. D., Koplitz, L. V. & Mague, J. T. (2014). *Acta Cryst.* **E70**, o811.

McCormick, C. A., Nguyen, V. D., Renfro, H. E., Koplitz, L. V. & Mague, J. T. (2013). *Acta Cryst.* **E69**, o981–o982.
Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.

supporting information

Acta Cryst. (2014). E70, o756–o757 [https://doi.org/10.1107/S1600536814012860]

4-Cyano-1-methylpyridinium perchlorate

Vu D. Nguyen, Cameron A. McCormick, Lynn V. Koplitz and Joel T. Mague

S1. Comment

The title compound, Fig. 1, crystallizes with alternating cations and anions in wavy sheets, which are formed by a number of C—H \cdots O and C—H \cdots N hydrogen bonds, which are approximately parallel to (001) [see Table 1 and Fig. 2].

As with 3-cyano-1-methylpyridinium perchlorate (McCormick *et al.*, 2014), the perchlorate ions are located near the pyridinium nitrogen atoms as the result of electrostatic attraction but the remainder of the two structures differ considerably due to the different position of the cyano group and the effect this has on the weak interionic interactions.

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. Yellow solid 4-cyano-1-methylpyridinium iodide (m.p. 189–193° C) was collected by vacuum filtration. This solid (0.98 g) was then dissolved in a solution of silver perchlorate previously prepared by reacting Ag₂O (0.47 g) with 0.5 M aqueous HClO₄ (8.0 ml). After stirring, precipitated AgI was removed by vacuum filtration and the filtrate containing 4-cyano-1-methylpyridinium perchlorate (m.p. 114–119° C) was slowly evaporated to dryness to form crystals of the title compound.

S3. Refinement

H-atoms were placed in calculated positions (C—H = 0.95 - 0.98 Å) and included as riding contributions with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C-methyl})$ and $= 1.2U_{\text{eq}}(\text{C})$ for other H atoms.

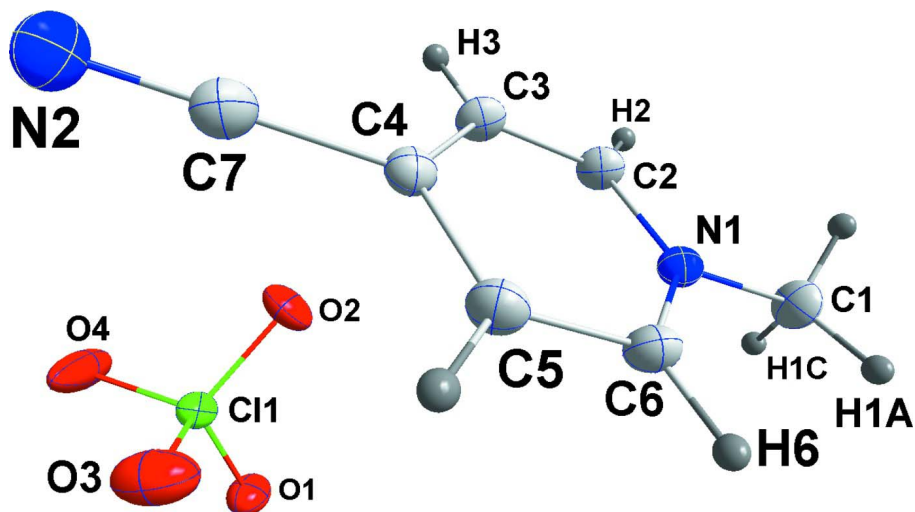


Figure 1

A view of the molecular structure of the title compound, with atom labelling. Displacement ellipsoids are drawn at the 50% probability level.

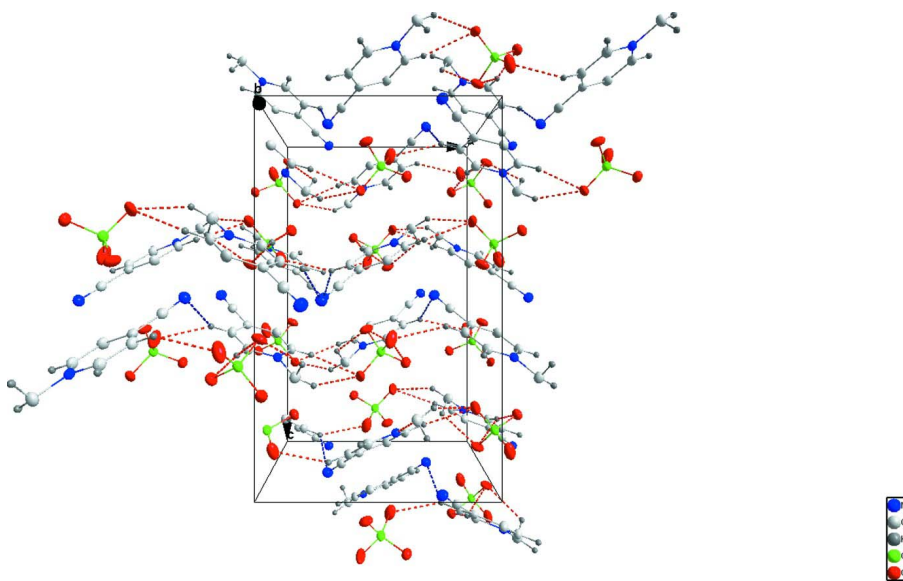


Figure 2

A view of the crystal packing along the *b* axis, with the C—H...O and C—H...N hydrogen bonds as red and blue dashed lines, respectively (see Table 1 for details).

4-Cyano-1-methylpyridinium perchlorate

Crystal data

$C_7H_7N_2^+ \cdot ClO_4^-$

$M_r = 218.60$

Orthorhombic, *Pbca*

Hall symbol: -P 2ac 2ab

$a = 10.232(2) \text{ \AA}$

$b = 10.872(3) \text{ \AA}$

$c = 16.769(4) \text{ \AA}$

$V = 1865.3(7) \text{ \AA}^3$

$Z = 8$

$F(000) = 896$

$D_x = 1.557 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 9543 reflections

$\theta = 3.0\text{--}29.1^\circ$

$\mu = 0.40 \text{ mm}^{-1}$
 $T = 100 \text{ K}$

Block, colourless
 $0.23 \times 0.16 \times 0.12 \text{ mm}$

Data collection

Bruker SMART APEX CCD
 diffractometer
 Radiation source: fine-focus sealed tube
 Graphite monochromator
 φ and ω scans
 Absorption correction: multi-scan
 (SADABS; Bruker, 2010)
 $T_{\min} = 0.86, T_{\max} = 0.95$

30647 measured reflections
 2475 independent reflections
 2235 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.054$
 $\theta_{\max} = 29.1^\circ, \theta_{\min} = 2.4^\circ$
 $h = -13 \rightarrow 14$
 $k = -14 \rightarrow 14$
 $l = -22 \rightarrow 22$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.034$
 $wR(F^2) = 0.097$
 $S = 1.07$
 2475 reflections
 129 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
 $w = 1/[\sigma^2(F_o^2) + (0.0474P)^2 + 1.204P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.38 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.39 \text{ e } \text{\AA}^{-3}$
 Extinction correction: SHELXL97 (Sheldrick,
 2008), $F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$
 Extinction coefficient: 0.0061 (7)

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 $F^2 > \sigma(F^2)$ 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. H-atoms were placed in calculated positions ($C-H = 0.95 - 0.98 \text{ \AA}$) 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>	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	0.07438 (11)	0.87020 (10)	0.65230 (6)	0.0173 (2)
N2	-0.23590 (12)	0.56153 (11)	0.49548 (7)	0.0259 (3)
C1	0.15878 (14)	0.95747 (13)	0.69622 (9)	0.0238 (3)
H1A	0.2307	0.9125	0.7215	0.036*
H1B	0.1071	0.9994	0.7372	0.036*
H1C	0.1944	1.0183	0.6590	0.036*
C2	-0.04511 (13)	0.90672 (12)	0.62884 (8)	0.0201 (3)
H2	-0.0730	0.9884	0.6394	0.024*
C3	-0.12714 (13)	0.82710 (12)	0.58970 (8)	0.0198 (3)
H3	-0.2115	0.8530	0.5731	0.024*

C4	−0.08458 (13)	0.70782 (12)	0.57475 (7)	0.0175 (3)
C5	0.03964 (13)	0.67124 (12)	0.59898 (8)	0.0204 (3)
H5	0.0700	0.5902	0.5887	0.024*
C6	0.11766 (14)	0.75535 (13)	0.63820 (8)	0.0200 (3)
H6	0.2026	0.7320	0.6554	0.024*
C7	−0.16859 (13)	0.62451 (12)	0.53131 (8)	0.0201 (3)
C11	0.01260 (3)	0.73669 (3)	0.35515 (2)	0.01939 (12)
O1	0.12396 (10)	0.79937 (10)	0.32127 (6)	0.0253 (2)
O2	−0.05193 (12)	0.81513 (10)	0.41181 (6)	0.0285 (3)
O3	0.05528 (12)	0.62622 (10)	0.39448 (9)	0.0386 (3)
O4	−0.07787 (11)	0.70787 (15)	0.29216 (7)	0.0432 (4)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0169 (5)	0.0170 (5)	0.0180 (5)	−0.0015 (4)	0.0016 (4)	0.0016 (4)
N2	0.0280 (6)	0.0231 (6)	0.0265 (6)	−0.0034 (5)	−0.0028 (5)	0.0021 (5)
C1	0.0233 (6)	0.0201 (6)	0.0278 (7)	−0.0042 (5)	−0.0028 (5)	−0.0017 (5)
C2	0.0206 (6)	0.0157 (6)	0.0241 (6)	0.0022 (5)	0.0010 (5)	0.0026 (5)
C3	0.0177 (6)	0.0184 (6)	0.0232 (6)	0.0023 (5)	−0.0001 (5)	0.0039 (5)
C4	0.0187 (6)	0.0182 (6)	0.0155 (5)	−0.0011 (5)	0.0017 (4)	0.0020 (4)
C5	0.0200 (6)	0.0183 (6)	0.0229 (6)	0.0040 (5)	0.0013 (5)	−0.0013 (5)
C6	0.0160 (6)	0.0210 (6)	0.0229 (6)	0.0030 (5)	0.0007 (5)	0.0007 (5)
C7	0.0208 (6)	0.0184 (6)	0.0211 (6)	0.0010 (5)	0.0005 (5)	0.0041 (5)
C11	0.01679 (17)	0.01989 (18)	0.02150 (19)	0.00045 (11)	0.00104 (11)	−0.00297 (11)
O1	0.0221 (5)	0.0261 (5)	0.0277 (5)	−0.0036 (4)	0.0033 (4)	0.0018 (4)
O2	0.0401 (6)	0.0236 (5)	0.0217 (5)	0.0050 (4)	0.0099 (4)	−0.0012 (4)
O3	0.0292 (6)	0.0213 (5)	0.0654 (9)	0.0055 (4)	0.0110 (6)	0.0133 (5)
O4	0.0193 (5)	0.0806 (10)	0.0297 (6)	−0.0081 (6)	−0.0003 (5)	−0.0213 (6)

Geometric parameters (Å, °)

N1—C2	1.3443 (18)	C3—H3	0.9500
N1—C6	1.3458 (17)	C4—C5	1.3924 (19)
N1—C1	1.4793 (17)	C4—C7	1.4456 (18)
N2—C7	1.1420 (18)	C5—C6	1.3806 (19)
C1—H1A	0.9800	C5—H5	0.9500
C1—H1B	0.9800	C6—H6	0.9500
C1—H1C	0.9800	C11—O2	1.4373 (10)
C2—C3	1.3728 (19)	C11—O3	1.4382 (12)
C2—H2	0.9500	C11—O4	1.4389 (12)
C3—C4	1.3907 (18)	C11—O1	1.4441 (10)
C2—N1—C6	121.46 (12)	C3—C4—C7	119.27 (12)
C2—N1—C1	119.16 (11)	C5—C4—C7	120.72 (12)
C6—N1—C1	119.36 (11)	C6—C5—C4	118.54 (12)
N1—C1—H1A	109.5	C6—C5—H5	120.7
N1—C1—H1B	109.5	C4—C5—H5	120.7

H1A—C1—H1B	109.5	N1—C6—C5	120.52 (12)
N1—C1—H1C	109.5	N1—C6—H6	119.7
H1A—C1—H1C	109.5	C5—C6—H6	119.7
H1B—C1—H1C	109.5	N2—C7—C4	177.94 (14)
N1—C2—C3	120.65 (12)	O2—C11—O3	109.38 (7)
N1—C2—H2	119.7	O2—C11—O4	108.60 (7)
C3—C2—H2	119.7	O3—C11—O4	110.50 (9)
C2—C3—C4	118.86 (12)	O2—C11—O1	110.03 (7)
C2—C3—H3	120.6	O3—C11—O1	109.56 (7)
C4—C3—H3	120.6	O4—C11—O1	108.76 (7)
C3—C4—C5	119.97 (12)		
C6—N1—C2—C3	0.2 (2)	C3—C4—C5—C6	0.48 (19)
C1—N1—C2—C3	-178.38 (12)	C7—C4—C5—C6	178.09 (12)
N1—C2—C3—C4	0.0 (2)	C2—N1—C6—C5	-0.1 (2)
C2—C3—C4—C5	-0.4 (2)	C1—N1—C6—C5	178.49 (12)
C2—C3—C4—C7	-178.02 (12)	C4—C5—C6—N1	-0.3 (2)

Hydrogen-bond geometry (Å, °)

<i>D—H...A</i>	<i>D—H</i>	<i>H...A</i>	<i>D...A</i>	<i>D—H...A</i>
C1—H1A...O4 ⁱ	0.98	2.37	3.245 (2)	149
C1—H1C...O2 ⁱⁱ	0.98	2.61	3.2540 (19)	123
C2—H2...O1 ⁱⁱ	0.95	2.46	3.4001 (18)	173
C2—H2...O2 ⁱⁱ	0.95	2.63	3.2549 (18)	123
C3—H3...N2 ⁱⁱⁱ	0.95	2.67	3.3098 (18)	125
C3—H3...O3 ^{iv}	0.95	2.46	3.300 (2)	148
C6—H6...O4 ⁱ	0.95	2.50	3.351 (2)	149

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