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4-Cyanoanilinium perchlorate

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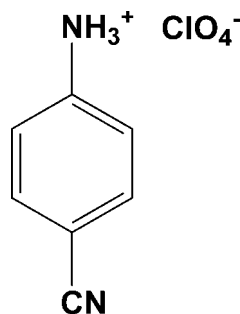
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 Key indicators: single-crystal X-ray study; $T = 298$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.036; wR factor = 0.097; data-to-parameter ratio = 16.6.

 The title compound, $\text{C}_7\text{H}_7\text{N}_2^+\cdot\text{ClO}_4^-$, comprises discrete ions which are interconnected by $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds, leading to a neutral one-dimensional network along the $[100]$ direction.

Related literature

 For the chemistry of nitrile derivatives, see: Xiong *et al.* (2002); Jin *et al.* (1994); Brewis *et al.* (2003); Fu *et al.* (2008); Duncia *et al.* (1991); Fu & Zhao (2007); Dai & Fu (2008); Smith *et al.* (2000).


Experimental

Crystal data

 $\text{C}_7\text{H}_7\text{N}_2^+\cdot\text{ClO}_4^-$
 $M_r = 218.60$
 Triclinic, $P\bar{1}$
 $a = 4.9905$ (10) Å
 $b = 6.9465$ (14) Å
 $c = 13.998$ (3) Å
 $\alpha = 94.87$ (3)°
 $\beta = 95.68$ (3)°

 $\gamma = 103.99$ (3)°
 $V = 465.57$ (17) Å³
 $Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 0.40$ mm⁻¹
 $T = 298$ (2) K
 $0.25 \times 0.15 \times 0.15$ mm

Data collection

 Rigaku Mercury2 diffractometer
 Absorption correction: multi-scan
 (*CrystalClear*; Rigaku, 2005)
 $T_{\min} = 0.941$, $T_{\max} = 1.000$
 (expected range = 0.886–0.942)

 4861 measured reflections
 2126 independent reflections
 1851 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.023$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.036$
 $wR(F^2) = 0.097$
 $S = 1.05$
 2126 reflections

 128 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.25$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.34$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

| $D-\text{H}\cdots A$ | $D-\text{H}$ | $\text{H}\cdots A$ | $D\cdots A$ | $D-\text{H}\cdots A$ |
|--|--------------|--------------------|-------------|----------------------|
| $\text{N1}-\text{H1A}\cdots\text{O2}^{\text{i}}$ | 0.89 | 2.04 | 2.881 (2) | 158 |
| $\text{N1}-\text{H1B}\cdots\text{O3}^{\text{ii}}$ | 0.89 | 1.98 | 2.855 (2) | 166 |
| $\text{N1}-\text{H1C}\cdots\text{O4}^{\text{iii}}$ | 0.89 | 2.04 | 2.871 (2) | 156 |

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

 Data collection: *CrystalClear* (Rigaku, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008) and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXTL*.

This work was supported by a Start-up Grant from Southeast University to Professor Ren-Gen Xiong.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BX2181).

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supporting information

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4-Cyanoanilinium perchlorate

Jing Dai

S1. Comment

Nitrile derivatives have found wide range of applications in industry and coordination chemistry as ligands. For example, phthalonitriles have been used as starting materials for phthalocyanines (Jin *et al.*, 1994), which are important components for dyes, pigments, gas sensors, optical limiters and liquid crystals, and which are also used in medicine, as singlet oxygen photosensitisers for photodynamic therapy (Brewis *et al.*, 2003). And nitrile compounds are the precursor of tetrazole complexes (Duncia *et al.*, 1991; Xiong *et al.*, 2002; Fu *et al.*, 2008). Recently, a series of benzonitrile compounds have been reported (Fu & Zhao, 2007; Dai & Fu, 2008; Smith *et al.*, 2000). As an extension of these work on the structural characterization, we report here the crystal structure of the title compound *p*-cyanoanilinium perchloride. The crystal data show that in the title compound, the N1 atom of the amine group is protonated. The nitrile group and the benzene ring are essentially coplanar. The C1≡N2 bond length of 1.135 (3) Å is within the normal range (Fig. 1). The crystal packing is stabilized by cation–anion N—H⋯O hydrogen bonds, building an infinite one-dimensional chain parallel to the *a* axis. (Table 1, Fig. 2).

S2. Experimental

p-cyanoaniline (3 mmol, 354 mg) was dissolved in the solution of distilled water (10 ml) and perchloric acid (0.5 ml), and evaporated in the air affording colorless block crystals of this compound suitable for X-ray analysis were obtained.

S3. Refinement

All H atoms attached to C and N atoms were fixed geometrically and treated as riding with C—H = 0.93 Å (aromatic) and N—H = 0.89 Å with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C or N})$.

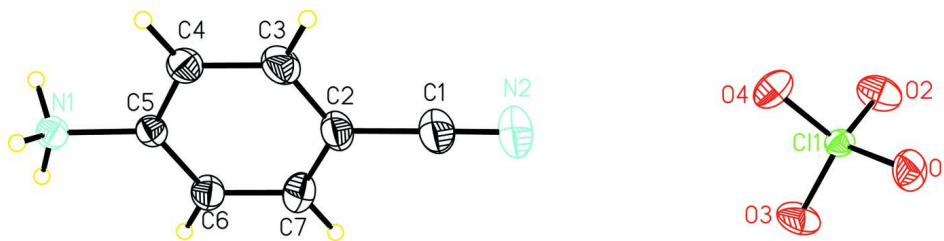
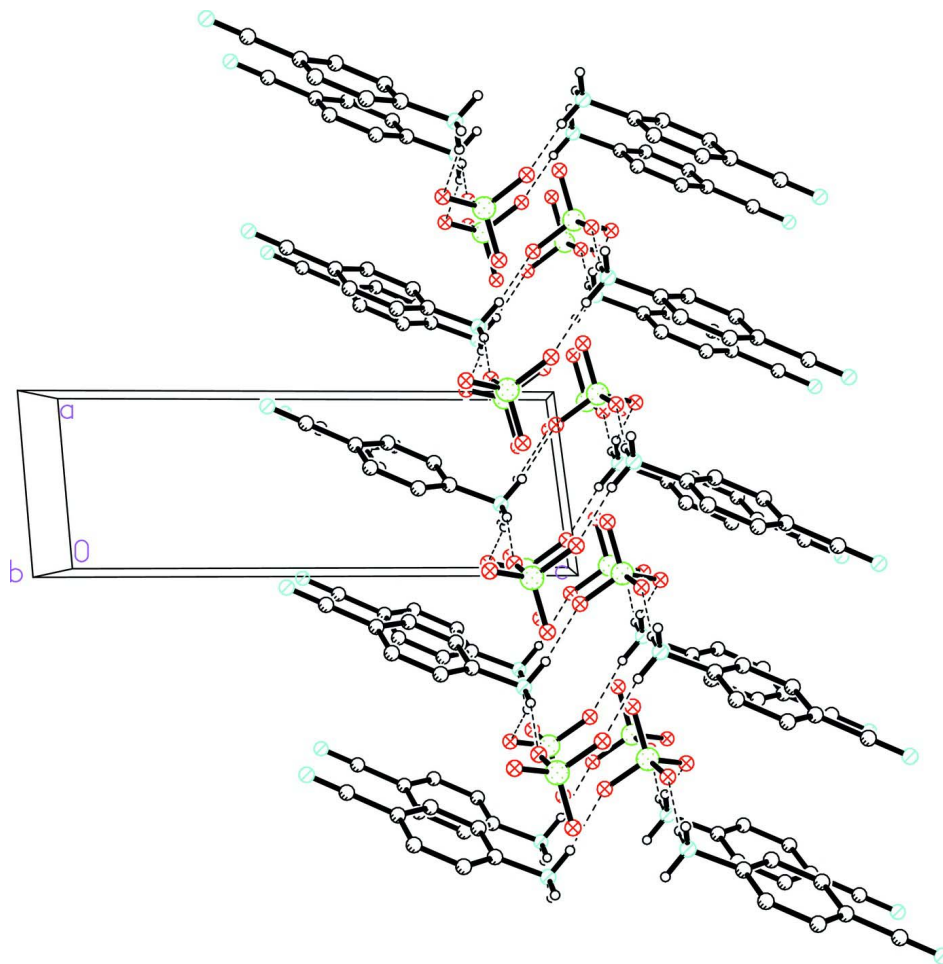


Figure 1

A view of the title compound with the atomic numbering scheme. Displacement ellipsoids were drawn at the 30% probability level.

**Figure 2**

The crystal packing of the title compound viewed along the *b* axis and all hydrogen atoms not involved in hydrogen bonding (dashed lines) were omitted for clarity.

4-Cyanoanilinium perchlorate

Crystal data

$C_7H_7N_2^+ \cdot ClO_4^-$

$M_r = 218.60$

Triclinic, $P\bar{1}$

Hall symbol: -P 1

$a = 4.9905 (10) \text{ \AA}$

$b = 6.9465 (14) \text{ \AA}$

$c = 13.998 (3) \text{ \AA}$

$\alpha = 94.87 (3)^\circ$

$\beta = 95.68 (3)^\circ$

$\gamma = 103.99 (3)^\circ$

$V = 465.57 (17) \text{ \AA}^3$

$Z = 2$

$F(000) = 224$

$D_x = 1.559 \text{ Mg m}^{-3}$

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

Cell parameters from 1806 reflections

$\theta = 3.0\text{--}27.5^\circ$

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

$T = 298 \text{ K}$

Block, colourless

$0.25 \times 0.15 \times 0.15 \text{ mm}$

Data collection

| | |
|--|--|
| Rigaku Mercury2 diffractometer | 4861 measured reflections 2126 independent reflections |
| Radiation source: fine-focus sealed tube | 1851 reflections with $I > 2\sigma(I)$ |
| Graphite monochromator | $R_{\text{int}} = 0.023$ |
| Detector resolution: 13.6612 pixels mm^{-1} | $\theta_{\text{max}} = 27.5^\circ$, $\theta_{\text{min}} = 3.0^\circ$ |
| ω scans | $h = -6 \rightarrow 6$ |
| Absorption correction: multi-scan (<i>CrystalClear</i> ; Rigaku, 2005) | $k = -8 \rightarrow 8$ |
| $T_{\text{min}} = 0.941$, $T_{\text{max}} = 1.000$ | $l = -18 \rightarrow 18$ |

Refinement

| | |
|---|--|
| Refinement on F^2 | Secondary atom site location: difference Fourier map |
| Least-squares matrix: full | Hydrogen site location: inferred from neighbouring sites |
| $R[F^2 > 2\sigma(F^2)] = 0.036$ | H-atom parameters constrained |
| $wR(F^2) = 0.097$ | $w = 1/[\sigma^2(F_o^2) + (0.0483P)^2 + 0.1253P]$ |
| $S = 1.05$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| 2126 reflections | $(\Delta/\sigma)_{\text{max}} < 0.001$ |
| 128 parameters | $\Delta\rho_{\text{max}} = 0.25 \text{ e } \text{\AA}^{-3}$ |
| 0 restraints | $\Delta\rho_{\text{min}} = -0.34 \text{ e } \text{\AA}^{-3}$ |
| Primary atom site location: structure-invariant direct methods | |

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.

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

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|------------|------------|--------------|----------------------------------|
| N1 | 0.6157 (3) | 0.2508 (2) | 0.12597 (11) | 0.0399 (4) |
| H1A | 0.4771 | 0.2405 | 0.0791 | 0.048* |
| H1B | 0.6876 | 0.1460 | 0.1180 | 0.048* |
| H1C | 0.7468 | 0.3623 | 0.1238 | 0.048* |
| N2 | 0.0727 (7) | 0.2647 (4) | 0.5503 (2) | 0.1058 (10) |
| C1 | 0.1672 (6) | 0.2642 (4) | 0.47983 (19) | 0.0743 (8) |
| C2 | 0.2877 (5) | 0.2620 (3) | 0.38998 (16) | 0.0549 (5) |
| C3 | 0.2722 (5) | 0.4100 (3) | 0.33016 (17) | 0.0557 (5) |
| H3 | 0.1860 | 0.5101 | 0.3478 | 0.067* |
| C4 | 0.3859 (4) | 0.4064 (3) | 0.24466 (15) | 0.0458 (4) |
| H4 | 0.3789 | 0.5049 | 0.2041 | 0.055* |
| C5 | 0.5097 (3) | 0.2566 (3) | 0.21961 (13) | 0.0362 (4) |
| C6 | 0.5293 (4) | 0.1094 (3) | 0.27829 (14) | 0.0464 (5) |
| H6 | 0.6169 | 0.0104 | 0.2604 | 0.056* |
| C7 | 0.4158 (5) | 0.1127 (4) | 0.36408 (16) | 0.0574 (6) |
| H7 | 0.4252 | 0.0145 | 0.4046 | 0.069* |

| | | | | |
|-----|--------------|-------------|--------------|--------------|
| Cl1 | -0.00044 (8) | 0.22266 (6) | 0.91125 (3) | 0.03315 (14) |
| O1 | -0.2849 (3) | 0.1812 (2) | 0.92711 (11) | 0.0552 (4) |
| O2 | 0.1712 (3) | 0.3237 (2) | 0.99794 (12) | 0.0598 (4) |
| O3 | 0.0665 (3) | 0.0398 (2) | 0.88369 (13) | 0.0593 (4) |
| O4 | 0.0420 (4) | 0.3478 (2) | 0.83610 (12) | 0.0668 (5) |

Atomic displacement parameters (Å²)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|-------------|-------------|-------------|--------------|--------------|--------------|
| N1 | 0.0442 (8) | 0.0392 (8) | 0.0403 (9) | 0.0162 (7) | 0.0100 (6) | 0.0048 (6) |
| N2 | 0.141 (3) | 0.0996 (19) | 0.0746 (17) | 0.0122 (17) | 0.0625 (17) | -0.0038 (14) |
| C1 | 0.0839 (18) | 0.0741 (17) | 0.0597 (16) | 0.0059 (14) | 0.0296 (13) | -0.0047 (13) |
| C2 | 0.0545 (12) | 0.0599 (13) | 0.0450 (12) | 0.0039 (10) | 0.0167 (9) | -0.0053 (10) |
| C3 | 0.0560 (13) | 0.0514 (12) | 0.0617 (14) | 0.0159 (10) | 0.0210 (10) | -0.0056 (10) |
| C4 | 0.0485 (11) | 0.0424 (10) | 0.0506 (12) | 0.0168 (8) | 0.0126 (9) | 0.0046 (8) |
| C5 | 0.0328 (8) | 0.0375 (9) | 0.0366 (9) | 0.0068 (7) | 0.0046 (7) | 0.0004 (7) |
| C6 | 0.0547 (11) | 0.0455 (10) | 0.0441 (11) | 0.0205 (9) | 0.0097 (9) | 0.0072 (8) |
| C7 | 0.0714 (15) | 0.0609 (13) | 0.0425 (12) | 0.0163 (11) | 0.0126 (10) | 0.0140 (10) |
| Cl1 | 0.0306 (2) | 0.0284 (2) | 0.0426 (3) | 0.00948 (15) | 0.00733 (15) | 0.00697 (15) |
| O1 | 0.0333 (7) | 0.0667 (9) | 0.0627 (10) | 0.0079 (6) | 0.0146 (6) | -0.0046 (7) |
| O2 | 0.0531 (9) | 0.0534 (9) | 0.0661 (10) | 0.0147 (7) | -0.0150 (7) | -0.0090 (7) |
| O3 | 0.0595 (9) | 0.0396 (7) | 0.0839 (12) | 0.0271 (7) | 0.0058 (8) | -0.0036 (7) |
| O4 | 0.0880 (12) | 0.0539 (9) | 0.0623 (11) | 0.0127 (8) | 0.0217 (9) | 0.0293 (8) |

Geometric parameters (Å, °)

| | | | |
|------------|-------------|-----------|-------------|
| N1—C5 | 1.462 (2) | C4—C5 | 1.371 (3) |
| N1—H1A | 0.8900 | C4—H4 | 0.9300 |
| N1—H1B | 0.8900 | C5—C6 | 1.380 (3) |
| N1—H1C | 0.8900 | C6—C7 | 1.378 (3) |
| N2—C1 | 1.135 (3) | C6—H6 | 0.9300 |
| C1—C2 | 1.447 (3) | C7—H7 | 0.9300 |
| C2—C7 | 1.385 (3) | Cl1—O4 | 1.4202 (15) |
| C2—C3 | 1.392 (3) | Cl1—O3 | 1.4215 (14) |
| C3—C4 | 1.375 (3) | Cl1—O1 | 1.4222 (14) |
| C3—H3 | 0.9300 | Cl1—O2 | 1.4346 (16) |
| C5—N1—H1A | 109.5 | C4—C5—C6 | 122.22 (18) |
| C5—N1—H1B | 109.5 | C4—C5—N1 | 118.25 (16) |
| H1A—N1—H1B | 109.5 | C6—C5—N1 | 119.50 (16) |
| C5—N1—H1C | 109.5 | C7—C6—C5 | 118.39 (19) |
| H1A—N1—H1C | 109.5 | C7—C6—H6 | 120.8 |
| H1B—N1—H1C | 109.5 | C5—C6—H6 | 120.8 |
| N2—C1—C2 | 179.6 (3) | C6—C7—C2 | 120.1 (2) |
| C7—C2—C3 | 120.66 (19) | C6—C7—H7 | 120.0 |
| C7—C2—C1 | 119.9 (2) | C2—C7—H7 | 120.0 |
| C3—C2—C1 | 119.4 (2) | O4—Cl1—O3 | 109.51 (11) |
| C4—C3—C2 | 119.1 (2) | O4—Cl1—O1 | 109.25 (11) |

| | | | |
|-------------|-------------|-------------|--------------|
| C4—C3—H3 | 120.4 | O3—C11—O1 | 108.89 (10) |
| C2—C3—H3 | 120.4 | O4—C11—O2 | 109.01 (11) |
| C5—C4—C3 | 119.54 (19) | O3—C11—O2 | 110.69 (10) |
| C5—C4—H4 | 120.2 | O1—C11—O2 | 109.47 (10) |
| C3—C4—H4 | 120.2 | | |
| C7—C2—C3—C4 | 0.0 (3) | C4—C5—C6—C7 | 1.1 (3) |
| C1—C2—C3—C4 | -179.7 (2) | N1—C5—C6—C7 | -176.89 (19) |
| C2—C3—C4—C5 | 0.6 (3) | C5—C6—C7—C2 | -0.4 (3) |
| C3—C4—C5—C6 | -1.2 (3) | C3—C2—C7—C6 | -0.1 (4) |
| C3—C4—C5—N1 | 176.83 (18) | C1—C2—C7—C6 | 179.6 (2) |

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> |
|-----------------------------------|-------------|---------------------|----------------------------|-------------------------------|
| N1—H1A \cdots O2 ⁱ | 0.89 | 2.04 | 2.881 (2) | 158 |
| N1—H1B \cdots O3 ⁱⁱ | 0.89 | 1.98 | 2.855 (2) | 166 |
| N1—H1C \cdots O4 ⁱⁱⁱ | 0.89 | 2.04 | 2.871 (2) | 156 |

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