organic compounds

2-Amino-3-nitropyridinium perchlorate

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The title compound, $C_5H_6N_3O_2^+ \cdot ClO_4^-$, is comprised of discrete perchlorate anions and 2-amino-3-nitropyridinium cations. The anion has a typical tetrahedral geometry while the cation presents a nearly planar [maximum deviation = 0.007 (8) Å] pyridinium ring. Undulating $[C_5H_6N_3O_2^+]_n$ chains extending along the *c*-axis direction are linked *via* N—H⋯O hydrogen bonds. The cations are further connected to the anions by N—H⋯O hydrogen bonds and weak C—H⋯O interactions, leading to the formation of a three-dimensional network.

Related literature

For related structures, see: Akriche & Rzaigui (2000, 2009*a*,*b*,*c*); Nicoud *et al.* (1997). For details of hydrogen bonding, see: Steiner & Saenger (1994). For bond lengths in related structures, see: Aakeröy *et al.* (1998); Messai *et al.* (2009).
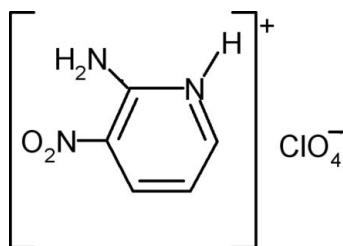
Experimental

Crystal data

$C_5H_6N_3O_2^+ \cdot ClO_4^-$
M_r = 239.58
Monoclinic, $P2_1/c$
a = 5.888 (2) Å
b = 18.342 (6) Å
c = 9.170 (4) Å
β = 116.61 (3)°

V = 885.3 (6) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.45 mm^{-1}
T = 293 K
0.29 × 0.25 × 0.21 mm

Data collection

Enraf–Nonius TurboCAD-4 diffractometer
Absorption correction: multi-scan (Blessing, 1995)
T_{min} = 0.725, T_{max} = 0.912
3574 measured reflections

2130 independent reflections
1109 reflections with $I > 2\sigma(I)$
R_{int} = 0.046
2 standard reflections every 120 min intensity decay: 1%

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.062
$wR(F^2)$ = 0.189
S = 1.00
2130 reflections
136 parameters

66 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.52 e Å^{-3}
$\Delta\rho_{min}$ = −0.30 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N1—H1⋯O1	0.86	2.28	2.927 (5)	133
N1—H1⋯O1^i	0.86	2.44	2.969 (5)	121
N2—H2A⋯O2^{ii}	0.86	2.03	2.886 (5)	173
N2—H2B⋯O5	0.86	2.04	2.633 (5)	126
N2—H2B⋯O6^{iii}	0.86	2.32	2.917 (5)	126
C5—H5⋯O3^{iv}	0.93	2.57	3.270 (5)	133

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

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS86* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *DIAMOND* (Brandenburg & Putz, 2005); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

References

Aakeröy, C. B., Beatty, A. M., Nieuwenhuyzen, M. & Zou, M. (1998). *J. Mater. Chem.* pp. 1385–1389.
Akriche, S. & Rzaigui, M. (2000). *Z. Kristallogr. New Cryst. Struct.* **215**, 617–618.
Akriche, S. & Rzaigui, M. (2009*a*). *Acta Cryst.* E**65**, m123.
Akriche, S. & Rzaigui, M. (2009*b*). *Acta Cryst.* E**65**, o1648.
Akriche, S. & Rzaigui, M. (2009*c*). *Acta Cryst.* E**65**, o793.
Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–38.
Brandenburg, K. & Putz, H. (2005). *DIAMOND*. Crystal impact GbR, Bonn, Germany.
Enraf–Nonius (1994). *CAD-4 EXPRESS*. Enraf–Nonius, Delft, The Netherlands.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Harms, K. & Wocadlo, S. (1995). *XCAD4*. University of Marburg, Germany.
Messai, A., Direm, A., Benali-Cherif, N., Luneau, D. & Jeanneau, E. (2009). *Acta Cryst.* E**65**, o460.
Nicoud, J. F., Masse, R., Bourgogne, C. & Evans, C. (1997). *J. Mater. Chem.* **7**, 35–39.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Steiner, T. & Saenger, W. (1994). *Acta Cryst.* B**50**, 348–357.

supporting information

2-Amino-3-nitropyridinium perchlorate

Samah Toumi Akriche, Mohamed Rzaigui, Noura Al-Hokbany and Refaat Mohamed Mahfouz

S1. Comment

Salts of 2-amino-3-nitropyridine attracted more attention as non linear optical (NLO) materials after discovering the promising properties of 2-amino-3-nitropyridinium chloride (Nicoud *et al.*,1997). With the purpose of obtaining non-centrosymmetric crystals of 2-amino-3-nitropyridine salts, its interaction with various acids has been studied and we have elaborated a serie of new materials with this organic molecule (Akriche & Rzaigui, 2000; Akriche & Rzaigui, 2009a; 2009b; 2009c). In this paper, we describe the crystal structure of the title compound (I).

The asymmetric unit of (I) is composed of a perchlorate anion and a 2-amino-3-nitropyridinium (2 A3NP) cation (Fig. 1). The anions are surrounded by two cations *via* hydrogen bonds which play an important role in stabilizing the crystal structure (Fig. 2). In the crystal structure, one can distinguish the ondulated chains of the cations extending along the *c* axis. The adjacent cations are joined by the N2—H2B···O6 (Table 1) hydrogen bond with N···O distance of 2.917 (5) Å. The cations are also connected to the chlorate anions by hydrogen bonds, of the type N—H···O with N···O distances in the range 2.886 (5) - 2.969 (5) Å, and weak C5—H5···O3 interaction with C5···O3 separation 3.270 (5) Å (Fig. 2, Table 1). The C—H···O bonds have already been evidenced by several authors in molecular crystals (Steiner *et al.*, 1994).

The anion displays a typical tetrahedral geometry around Cl atom and the Cl···O distances compare well with previously reported values (Messai *et al.*, 2009). The Cl—O bond distances and O—Cl—O bond angles (Table: Geometric parameters) confirm a tetrahedral conformation, similar to other perchlorates quoted above.

The pyridinium ring of the cation is nearly planar, with maximum deviation from planarity being 0.007 (8) Å for C1 atom. The diedral angle between the planes of the NO_2 group and the pyridinium ring is 9.7 (2) ° indicating a deviation of the NO_2 group from being co-planar with the ring since its oxygen atoms are involved in various types of inter- and intramolecular hydrogen bonds. Moreover, the C—NH_2 (1.313 (5) Å) and C—NO_2 (1.448 (5) Å) distances in the 2 A3NP cation are respectively shortened and lengthened with respect to the C—NH_2 (1.337 (4) Å) and C—NO_2 (1.429 (4) Å) observed in the crystal structure of 2-amino-3-nitropyridine (Aakeröy *et al.*, 1998). All the 2-amino-3-nitropyridinium cations hosted in various organic or inorganic matrices show the same changes in C—NH_2 and C—NO_2 distances, revealing a weak increase of π bond character in C—NH_2 and a decrease in C—NO_2. The bond lengths of cation in (I) are normal and comparable with the corresponding values observed in the related structure (Akriche & Rzaigui, 2000; Akriche & Rzaigui, 2009a; 2009b, 2009c).

S2. Experimental

2-Amino-3-nitropyridine (4 mmol, 354 mg) was dissolved in a solution of perchloride acid (4 mmol in 20 ml water). The mixture was stirred for about 30 min at 333 K and evaporated in the air giving colorless block crystals of the title compound suitable for X-ray analysis.

S3. Refinement

H atoms were treated as riding, with C—H = 0.93 A ° and N—H = 0.86 A ° and with U_{iso}(H) = 1.2Ueq(C or N). The atoms of the chlorate ion were refined using isotropic U_{ij} restraints.
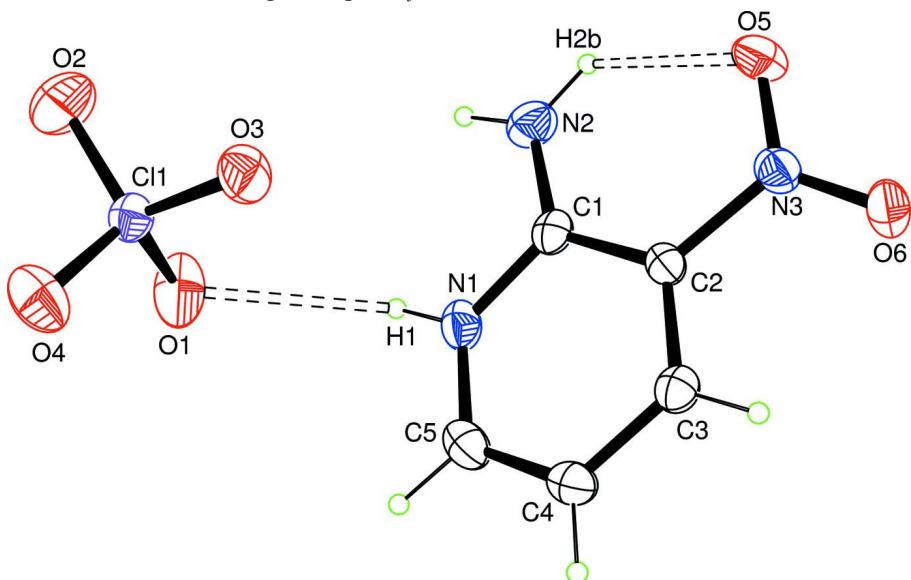
Figure 1

An *ORTEP* view of (I) with the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms are represented by spheres of arbitrary radii. Hydrogen bonds are represented as dashed lines.
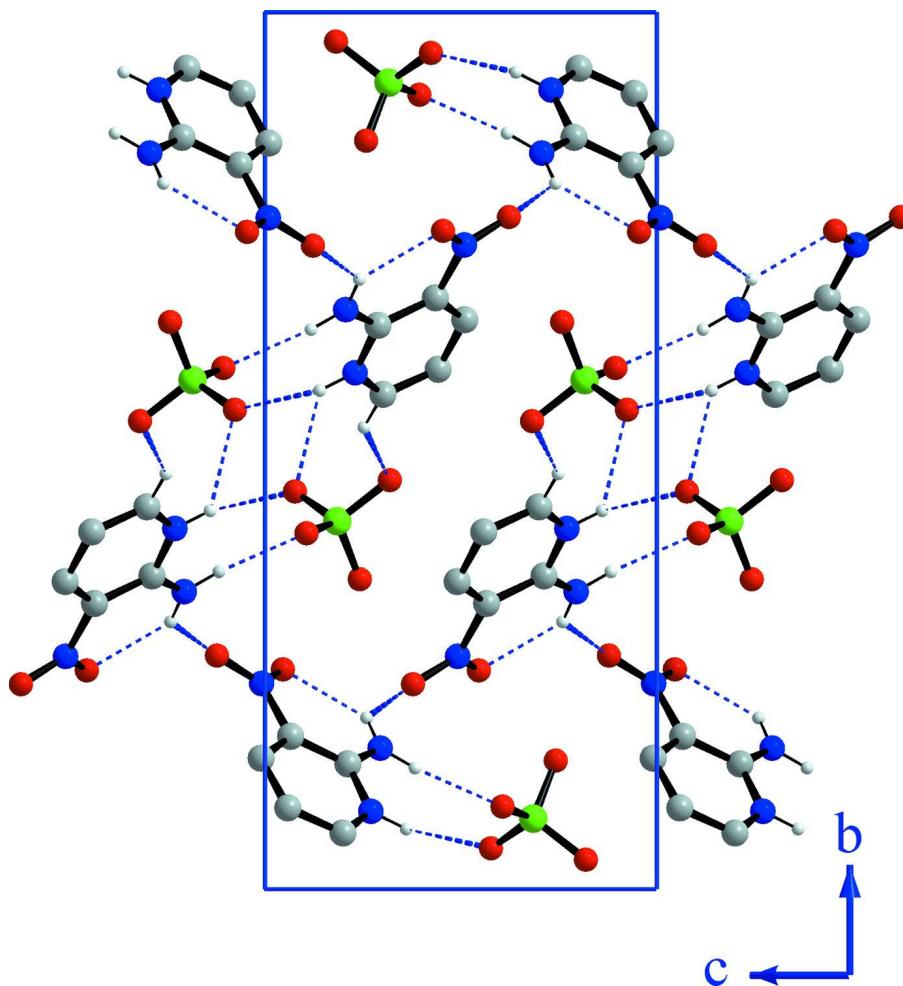
Figure 2
Projection of (I) down the *a* axis. The H-atoms not involved in H-bonding are omitted.

2-Amino-3-nitropyridinium perchlorate

Crystal data
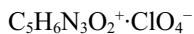
$C_5H_6N_3O_2^+ \cdot ClO_4^-$	$F(000) = 488$
$M_r = 239.58$	$D_x = 1.797$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 25 reflections
$a = 5.888$ (2) Å	$\theta = 9$–11°
$b = 18.342$ (6) Å	$\mu = 0.45$ mm^{-1}
$c = 9.170$ (4) Å	$T = 293$ K
$\beta = 116.61$ (3)°	Prism, colorless
$V = 885.3$ (6) Å^3	$0.29 \times 0.25 \times 0.21$ mm
$Z = 4$	

Data collection

Enraf–Nonius TurboCAD-4 diffractometer	Non–profiled ω scans
Radiation source: fine-focus sealed tube	Absorption correction: multi-scan (Blessing, 1995)
Graphite monochromator	$T_{min} = 0.725$, $T_{max} = 1.101$

3574 measured reflections	$h = -7 \rightarrow 7$	
2130 independent reflections	$k = -24 \rightarrow 0$	
1109 reflections with $I > 2\sigma(I)$	$l = -11 \rightarrow 12$	
$R_{\text{int}} = 0.046$	2 standard reflections every 120 min	
$\theta_{\text{max}} = 28.0°$, $\theta_{\text{min}} = 2.2°$	intensity decay: 1%	

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.062$

$wR(F^2) = 0.189$

$S = 1.00$

2130 reflections

136 parameters

66 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

$w = 1/[\sigma^2(F_o^2) + (0.096P)^2]$
  where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} < 0.001$

$\Delta\rho_{\text{max}} = 0.52$ e Å^{-3}

$\Delta\rho_{\text{min}} = -0.30$ e Å^{-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. 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 (Å^2)

	x	y	z	U_{iso}*/U_{eq}
O1	0.6409 (9)	0.45343 (19)	0.9234 (4)	0.0967 (12)
O2	0.9810 (6)	0.4058 (2)	0.8940 (5)	0.1130 (15)
O3	0.6657 (6)	0.46634 (17)	0.6814 (4)	0.0750 (9)
O4	0.5876 (7)	0.35339 (19)	0.7581 (5)	0.0970 (12)
N1	0.3798 (6)	0.58877 (17)	0.7702 (4)	0.0563 (8)
H1	0.4836	0.5686	0.8602	0.068*
N2	0.7098 (6)	0.6608 (2)	0.7939 (4)	0.0663 (10)
H2A	0.8051	0.6381	0.8826	0.080*
H2B	0.7720	0.6953	0.7592	0.080*
N3	0.3603 (7)	0.73452 (18)	0.4915 (4)	0.0562 (9)
C1	0.4694 (7)	0.6428 (2)	0.7117 (4)	0.0453 (9)
C2	0.2906 (7)	0.67427 (18)	0.5653 (4)	0.0419 (8)
C3	0.0457 (7)	0.6493 (2)	0.4903 (5)	0.0498 (9)
H3	−0.0702	0.6705	0.3932	0.060*
C4	−0.0302 (7)	0.5927 (2)	0.5582 (5)	0.0544 (10)
H4	−0.1957	0.5750	0.5077	0.065*
C5	0.1418 (9)	0.5641 (2)	0.6989 (5)	0.0591 (11)
H5	0.0944	0.5265	0.7475	0.071*
O5	0.5840 (6)	0.75060 (17)	0.5457 (4)	0.0767 (9)
O6	0.1928 (6)	0.76632 (17)	0.3776 (4)	0.0757 (9)

Cl1	0.71827 (18)	0.41956 (5)	0.81544 (11)	0.0530 (3)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.161 (4)	0.083 (2)	0.076 (2)	0.040 (2)	0.079 (2)	0.0169 (19)
O2	0.057 (2)	0.133 (4)	0.119 (3)	0.022 (2)	0.013 (2)	0.029 (3)
O3	0.090 (2)	0.078 (2)	0.0663 (19)	0.0100 (17)	0.0439 (17)	0.0197 (16)
O4	0.116 (3)	0.066 (2)	0.111 (3)	−0.024 (2)	0.052 (2)	−0.009 (2)
N1	0.068 (2)	0.0509 (19)	0.0523 (19)	0.0097 (18)	0.0286 (17)	0.0124 (16)
N2	0.048 (2)	0.077 (3)	0.065 (2)	0.0020 (18)	0.0174 (17)	0.003 (2)
N3	0.064 (2)	0.0459 (19)	0.070 (2)	0.0006 (18)	0.040 (2)	0.0018 (17)
C1	0.052 (2)	0.044 (2)	0.044 (2)	0.0093 (17)	0.0256 (18)	−0.0033 (16)
C2	0.054 (2)	0.0345 (17)	0.048 (2)	0.0019 (16)	0.0320 (18)	−0.0017 (15)
C3	0.051 (2)	0.052 (2)	0.046 (2)	0.0064 (18)	0.0219 (18)	0.0028 (18)
C4	0.053 (2)	0.055 (2)	0.062 (3)	−0.0066 (19)	0.032 (2)	−0.004 (2)
C5	0.078 (3)	0.049 (2)	0.065 (3)	−0.006 (2)	0.045 (2)	0.000 (2)
O5	0.073 (2)	0.067 (2)	0.103 (2)	−0.0138 (18)	0.0520 (19)	0.0072 (18)
O6	0.085 (2)	0.064 (2)	0.086 (2)	0.0191 (18)	0.0458 (19)	0.0309 (18)
Cl1	0.0554 (6)	0.0519 (6)	0.0498 (6)	0.0047 (5)	0.0219 (4)	0.0041 (5)

Geometric parameters (Å, º)

O1—Cl1	1.406 (3)	N3—O6	1.216 (4)
O2—Cl1	1.406 (3)	N3—O5	1.218 (4)
O3—Cl1	1.415 (3)	N3—C2	1.448 (5)
O4—Cl1	1.407 (3)	C1—C2	1.406 (5)
N1—C5	1.332 (5)	C2—C3	1.369 (5)
N1—C1	1.343 (5)	C3—C4	1.384 (5)
N1—H1	0.8600	C3—H3	0.9300
N2—C1	1.313 (5)	C4—C5	1.339 (6)
N2—H2A	0.8600	C4—H4	0.9300
N2—H2B	0.8600	C5—H5	0.9300
C5—N1—C1	124.8 (3)	C2—C3—C4	120.3 (4)
C5—N1—H1	117.6	C2—C3—H3	119.8
C1—N1—H1	117.6	C4—C3—H3	119.8
C1—N2—H2A	120.0	C5—C4—C3	118.0 (4)
C1—N2—H2B	120.0	C5—C4—H4	121.0
H2A—N2—H2B	120.0	C3—C4—H4	121.0
O6—N3—O5	123.1 (3)	N1—C5—C4	121.0 (4)
O6—N3—C2	118.5 (3)	N1—C5—H5	119.5
O5—N3—C2	118.4 (3)	C4—C5—H5	119.5
N2—C1—N1	118.1 (4)	O2—Cl1—O1	110.3 (3)
N2—C1—C2	126.8 (4)	O2—Cl1—O4	109.2 (3)
N1—C1—C2	115.1 (3)	O1—Cl1—O4	110.4 (2)
C3—C2—C1	120.8 (3)	O2—Cl1—O3	108.4 (2)
C3—C2—N3	118.4 (3)	O1—Cl1—O3	109.26 (19)

C1—C2—N3	120.8 (4)	O4—Cl1—O3	109.2 (2)
C5—N1—C1—N2	−179.1 (4)	O6—N3—C2—C1	−170.3 (3)
C5—N1—C1—C2	0.9 (5)	O5—N3—C2—C1	10.0 (5)
N2—C1—C2—C3	178.9 (3)	C1—C2—C3—C4	0.3 (5)
N1—C1—C2—C3	−1.1 (5)	N3—C2—C3—C4	−179.0 (3)
N2—C1—C2—N3	−1.8 (6)	C2—C3—C4—C5	0.7 (6)
N1—C1—C2—N3	178.3 (3)	C1—N1—C5—C4	0.1 (6)
O6—N3—C2—C3	9.0 (5)	C3—C4—C5—N1	−0.9 (6)
O5—N3—C2—C3	−170.7 (3)		

Hydrogen-bond geometry (Å, °)

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
N1—H1⋯O1	0.86	2.28	2.927 (5)	133
N1—H1⋯O1[i]	0.86	2.44	2.969 (5)	121
N2—H2*A*⋯O2[ii]	0.86	2.03	2.886 (5)	173
N2—H2*B*⋯O5	0.86	2.04	2.633 (5)	126
N2—H2*B*⋯O6[iii]	0.86	2.32	2.917 (5)	126
C5—H5⋯O3[iv]	0.93	2.57	3.270 (5)	133

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