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2-Amino-3-nitropyridinium hydrogen oxalate

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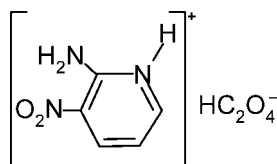
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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; R factor = 0.034; wR factor = 0.088; data-to-parameter ratio = 8.1.

In the non-centrosymmetric title compound, $\text{C}_5\text{H}_6\text{N}_3\text{O}_2^+\cdot\text{C}_2\text{HO}_4^-$, the hydrogen oxalate anions form corrugated chains parallel to the c axis, linked by $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds. The 2-amino-3-nitropyridinium cations are anchored between these chains by $\text{N}-\text{H}\cdots\text{O}$ and $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds and van der Waals and electrostatic interactions, creating a three-dimensional network.

Related literature

For related structures, see: Akriche & Rzaigui (2000, 2009); Le Fur *et al.* (1998); Nicoud *et al.* (1997); For a discussion of hydrogen bonding, see: Desiraju (1989, 1995).



Experimental

Crystal data

 $\text{C}_5\text{H}_6\text{N}_3\text{O}_2^+\cdot\text{C}_2\text{HO}_4^-$ $M_r = 229.16$ Orthorhombic, $Pna2_1$ $a = 15.268$ (4) Å $b = 6.921$ (3) Å $c = 8.807$ (2) Å $V = 930.6$ (5) Å³ $Z = 4$ Mo $K\alpha$ radiation $\mu = 0.15$ mm⁻¹ $T = 293$ K $0.33 \times 0.25 \times 0.21$ mm

Data collection

Enraf–Nonius Turbo CAD-4

diffractometer

Absorption correction: none

2228 measured reflections

1190 independent reflections

1003 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.020$

2 standard reflections

frequency: 120 min

intensity decay: 1%

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.034$ $wR(F^2) = 0.088$ $S = 1.06$

1190 reflections

147 parameters

1 restraint

H-atom parameters constrained

 $\Delta\rho_{\text{max}} = 0.33$ e Å⁻³ $\Delta\rho_{\text{min}} = -0.20$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{O3}-\text{H3}\cdots\text{O2}^{\text{i}}$	0.82	1.82	2.632 (2)	171
$\text{N1}-\text{H1}\cdots\text{O2}$	0.86	1.85	2.706 (3)	175
$\text{N2}-\text{H2A}\cdots\text{O1}$	0.86	1.99	2.837 (3)	170
$\text{N2}-\text{H2B}\cdots\text{O5}$	0.86	2.09	2.673 (3)	124
$\text{N2}-\text{H2B}\cdots\text{O4}^{\text{ii}}$	0.86	2.51	3.188 (3)	136
$\text{C3}-\text{H3A}\cdots\text{O5}^{\text{iii}}$	0.93	2.44	3.178 (3)	136
$\text{C4}-\text{H4}\cdots\text{O1}^{\text{iv}}$	0.93	2.33	3.258 (3)	174
$\text{C5}-\text{H5}\cdots\text{O6}^{\text{v}}$	0.93	2.57	3.262 (3)	132

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

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1996); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *DIAMOND* (Brandenburg & Putz, 2005); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: KJ2116).

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supplementary materials

Acta Cryst. (2009). E65, o793 [doi:10.1107/S1600536809008666]

2-Amino-3-nitropyridinium hydrogen oxalate

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Comment

The search for new molecular materials for the non-linear optics lies at the basis of our ongoing study of 2-amino-3-nitropyridinium salts. Our strategy is aimed at the production of very cohesive non-centrosymmetric packing of chromophores. We have previously reported two centrosymmetric structures of 2-amino-3-nitropyridinium (Akriche & Rzaigui, 2000; Akriche & Rzaigui, 2009). We report here a new non-centrosymmetric structure, 2-amino-3-nitropyridinium hydrogenoxalate.

The asymmetric unit of the title compound consists of one $(\text{HC}_2\text{O}_4)^-$ anion and one $(2\text{-NH}_2\text{-3-NO}_2\text{C}_5\text{H}_3\text{NH})^+$ cation (Fig. 1). In the hydrogenoxalate $(\text{HC}_2\text{O}_4)^-$, the H atom is located at O3 as is also indicated by elongation of the corresponding C—O distance [O3—C7 is 1.314 (3) Å]. The bond length of C6—C7 is relatively long [1.545 (3) Å] as expected for an oxalate anion. In the 2-amino-3-nitropyridinium cation, nitro and amino groups are *ortho* to one another, which explains the presence of the intra-cation contact N2—H2B···O5 (Le Fur *et al.*, 1998; Nicoud *et al.*, 1997).

The structure projection in Fig. 2 shows that the oxalate ions are organized in corrugated chains extending along the *c* axis. The cations are located between these chains and manifest multiple H-bonds. In fact, in this structure there are three categories of H-bond (Table 1), O—H···O, N—H···O and C—H···O. Within each oxalate chain, the $(\text{HC}_2\text{O}_4)^-$ groups are interconnected by strong O—H···O hydrogen bonds. These chains are themselves interconnected by N—H···O interactions originating from the NH^+ and NH_2 groups of the cations. It is worth noticing the presence of long C—H···O contacts (Desiraju, 1989; Desiraju, 1995) occurring between cations and between cations and anions. The density of this H-bond scheme constitutes probably the main factor responsible for the formation of a non-centrosymmetric material.

Experimental

An aqueous solution containing 0.004 mol of $\text{H}_2\text{C}_2\text{O}_4$ in 10 ml of water, was added to 0.004 mol of 2-amino-3-nitropyridine in 20 ml of pure acetic acid. The obtained yellow solution was stirred at 333 K for 10 min and then left to stand at room temperature. Yellow single crystals of the title compound were obtained after some days.

Figures

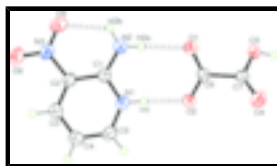


Fig. 1. View of the title compound with the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen bonds are represented as dashed lines.

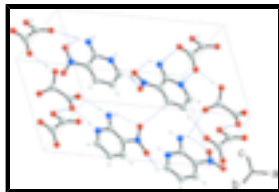
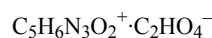


Fig. 2. A perspective view of the packing of the title compound. Hydrogen bonds are represented as dashed lines.

2-Amino-3-nitropyridinium hydrogen oxalate

Crystal data



$$M_r = 229.16$$

Orthorhombic, $Pna2_1$

$$a = 15.268 (4) \text{ \AA}$$

$$b = 6.921 (3) \text{ \AA}$$

$$c = 8.807 (2) \text{ \AA}$$

$$V = 930.6 (5) \text{ \AA}^3$$

$$Z = 4$$

$$F_{000} = 472$$

$$D_x = 1.636 \text{ Mg m}^{-3}$$

Mo $K\alpha$ radiation

$$\lambda = 0.71073 \text{ \AA}$$

Cell parameters from 25 reflections

$$\theta = 9\text{--}11^\circ$$

$$\mu = 0.15 \text{ mm}^{-1}$$

$$T = 293 \text{ K}$$

Rectangular prism, yellow

$$0.33 \times 0.25 \times 0.21 \text{ mm}$$

Data collection

Enraf–Nonius Turbo CAD-4 diffractometer

Monochromator: graphite

$$T = 293 \text{ K}$$

Nonprofiled ω scans

Absorption correction: none

2228 measured reflections

1190 independent reflections

1003 reflections with $I > 2\sigma(I)$

$$R_{\text{int}} = 0.020$$

$$\theta_{\text{max}} = 28.0^\circ$$

$$\theta_{\text{min}} = 2.7^\circ$$

$$h = -20 \rightarrow 0$$

$$k = -7 \rightarrow 9$$

$$l = -11 \rightarrow 0$$

2 standard reflections

every 120 min

intensity decay: 1%

Refinement

Refinement on F^2

Least-squares matrix: full

$$R[F^2 > 2\sigma(F^2)] = 0.034$$

$$wR(F^2) = 0.088$$

$$S = 1.06$$

1190 reflections

147 parameters

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0559P)^2 + 0.0295P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

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

$$\Delta\rho_{\text{max}} = 0.33 \text{ e \AA}^{-3}$$

$$\Delta\rho_{\text{min}} = -0.20 \text{ e \AA}^{-3}$$

1 restraint
 Extinction correction: SHELXL97 (Sheldrick, 2008),
 $F_c^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
 Primary atom site location: structure-invariant direct methods
 Extinction coefficient: 0.053 (6)

Special details

Geometry. H atoms were treated as riding, with C—H = 0.93 Å, N—H = 0.86 Å and O—H = 0.82 Å, and with $U_{iso}(H) = 1.2U_{eq}(C,N)$ and $1.5U_{eq}(O)$. 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 (Å²)

	<i>x</i>	<i>y</i>	<i>z</i>	U_{iso}^*/U_{eq}
O1	0.18864 (12)	0.6389 (3)	0.4311 (2)	0.0512 (5)
O2	0.10055 (11)	0.5552 (3)	0.2423 (2)	0.0408 (4)
O3	0.05130 (11)	0.5172 (3)	0.6129 (2)	0.0391 (4)
H3	0.0051	0.5043	0.6593	0.059*
O4	-0.03139 (11)	0.6833 (3)	0.4481 (2)	0.0494 (5)
O5	0.49613 (12)	0.5813 (3)	0.1226 (3)	0.0532 (5)
O6	0.52023 (11)	0.6750 (3)	-0.1071 (3)	0.0545 (5)
N1	0.23161 (12)	0.5903 (3)	0.0374 (3)	0.0375 (5)
H1	0.1920	0.5818	0.1065	0.045*
N2	0.33259 (15)	0.6060 (3)	0.2291 (3)	0.0462 (6)
H2A	0.2900	0.6012	0.2930	0.055*
H2B	0.3857	0.6133	0.2612	0.055*
N3	0.47122 (12)	0.6244 (3)	-0.0050 (3)	0.0367 (5)
C1	0.31649 (14)	0.6020 (3)	0.0827 (3)	0.0321 (5)
C2	0.37793 (14)	0.6148 (3)	-0.0380 (3)	0.0318 (5)
C3	0.35201 (16)	0.6188 (4)	-0.1871 (3)	0.0363 (5)
H3A	0.3936	0.6300	-0.2638	0.044*
C4	0.26384 (17)	0.6061 (4)	-0.2236 (3)	0.0437 (6)
H4	0.2452	0.6078	-0.3241	0.052*
C5	0.20572 (16)	0.5911 (4)	-0.1078 (3)	0.0421 (6)
H5	0.1463	0.5811	-0.1298	0.050*
C6	0.11677 (14)	0.5994 (3)	0.3773 (3)	0.0303 (5)
C7	0.03636 (14)	0.6065 (3)	0.4838 (3)	0.0302 (5)

Atomic displacement parameters (Å²)

U^{11} U^{22} U^{33} U^{12} U^{13} U^{23}

supplementary materials

O1	0.0315 (8)	0.0930 (14)	0.0292 (9)	-0.0146 (10)	-0.0004 (7)	-0.0040 (10)
O2	0.0286 (7)	0.0684 (11)	0.0254 (8)	-0.0040 (8)	0.0007 (7)	-0.0037 (9)
O3	0.0300 (8)	0.0618 (12)	0.0256 (7)	0.0005 (8)	0.0063 (7)	0.0065 (8)
O4	0.0346 (9)	0.0660 (12)	0.0475 (11)	0.0110 (8)	0.0040 (8)	0.0115 (10)
O5	0.0342 (9)	0.0727 (13)	0.0528 (12)	0.0094 (9)	-0.0082 (9)	0.0076 (11)
O6	0.0330 (9)	0.0779 (13)	0.0526 (12)	-0.0118 (9)	0.0125 (8)	-0.0050 (11)
N1	0.0243 (9)	0.0522 (14)	0.0361 (12)	-0.0015 (8)	0.0039 (8)	-0.0004 (9)
N2	0.0317 (10)	0.0773 (18)	0.0296 (11)	-0.0022 (10)	0.0002 (8)	0.0046 (11)
N3	0.0259 (9)	0.0401 (10)	0.0440 (12)	0.0007 (8)	0.0035 (9)	-0.0039 (9)
C1	0.0271 (10)	0.0372 (12)	0.0319 (12)	-0.0008 (9)	0.0024 (9)	0.0020 (9)
C2	0.0252 (10)	0.0356 (11)	0.0347 (12)	0.0013 (8)	0.0024 (9)	-0.0014 (10)
C3	0.0352 (12)	0.0427 (14)	0.0311 (12)	0.0002 (10)	0.0057 (10)	-0.0004 (10)
C4	0.0407 (13)	0.0592 (17)	0.0311 (13)	0.0026 (11)	-0.0038 (10)	-0.0018 (11)
C5	0.0271 (10)	0.0585 (16)	0.0406 (15)	0.0020 (10)	-0.0049 (10)	-0.0044 (12)
C6	0.0279 (10)	0.0391 (11)	0.0240 (10)	-0.0029 (9)	0.0015 (9)	0.0033 (9)
C7	0.0263 (10)	0.0382 (11)	0.0261 (11)	-0.0040 (8)	-0.0003 (8)	-0.0026 (9)

Geometric parameters (\AA , $^\circ$)

O1—C6	1.226 (3)	N2—H2A	0.8600
O2—C6	1.252 (3)	N2—H2B	0.8600
O3—C7	1.314 (3)	N3—C2	1.455 (3)
O3—H3	0.8200	C1—C2	1.420 (3)
O4—C7	1.205 (3)	C2—C3	1.372 (3)
O5—N3	1.223 (3)	C3—C4	1.387 (3)
O6—N3	1.221 (3)	C3—H3A	0.9300
N1—C5	1.338 (4)	C4—C5	1.356 (4)
N1—C1	1.358 (3)	C4—H4	0.9300
N1—H1	0.8600	C5—H5	0.9300
N2—C1	1.313 (3)	C6—C7	1.545 (3)
C7—O3—H3	109.5	C2—C3—C4	120.0 (2)
C5—N1—C1	124.2 (2)	C2—C3—H3A	120.0
C5—N1—H1	117.9	C4—C3—H3A	120.0
C1—N1—H1	117.9	C5—C4—C3	117.8 (2)
C1—N2—H2A	120.0	C5—C4—H4	121.1
C1—N2—H2B	120.0	C3—C4—H4	121.1
H2A—N2—H2B	120.0	N1—C5—C4	121.7 (2)
O6—N3—O5	123.8 (2)	N1—C5—H5	119.1
O6—N3—C2	117.8 (2)	C4—C5—H5	119.1
O5—N3—C2	118.5 (2)	O1—C6—O2	126.8 (2)
N2—C1—N1	117.9 (2)	O1—C6—C7	118.0 (2)
N2—C1—C2	127.6 (2)	O2—C6—C7	115.25 (19)
N1—C1—C2	114.5 (2)	O4—C7—O3	125.6 (2)
C3—C2—C1	121.8 (2)	O4—C7—C6	122.5 (2)
C3—C2—N3	118.2 (2)	O3—C7—C6	111.85 (19)
C1—C2—N3	120.0 (2)		
C5—N1—C1—N2	177.8 (3)	C1—C2—C3—C4	-1.3 (4)
C5—N1—C1—C2	-0.2 (4)	N3—C2—C3—C4	178.7 (2)
N2—C1—C2—C3	-176.6 (3)	C2—C3—C4—C5	0.4 (4)

N1—C1—C2—C3	1.2 (3)	C1—N1—C5—C4	-0.7 (5)
N2—C1—C2—N3	3.3 (4)	C3—C4—C5—N1	0.6 (4)
N1—C1—C2—N3	-178.8 (2)	O1—C6—C7—O4	134.2 (3)
O6—N3—C2—C3	14.8 (3)	O2—C6—C7—O4	-45.0 (3)
O5—N3—C2—C3	-165.1 (2)	O1—C6—C7—O3	-46.9 (3)
O6—N3—C2—C1	-165.2 (2)	O2—C6—C7—O3	133.9 (2)
O5—N3—C2—C1	15.0 (3)		

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>
O3—H3...O2 ⁱ	0.82	1.82	2.632 (2)	171
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Fig. 1

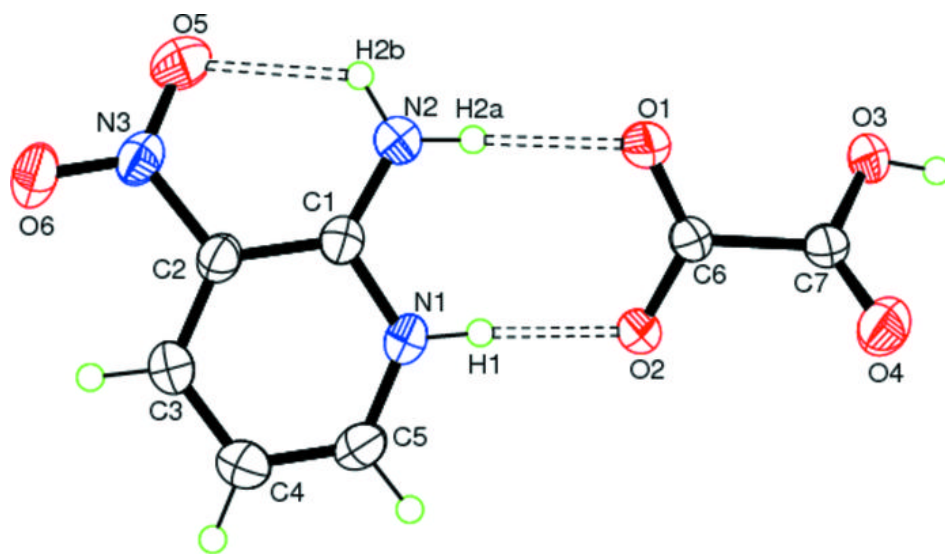


Fig. 2

