

Andrei S. Batsanov

Department of Chemistry, University of
Durham, South Road, Durham DH1 3LE,
EnglandCorrespondence e-mail:
a.s.batsanov@durham.ac.uk

Key indicators

Single-crystal X-ray study
 $T = 120$ K
Mean $\sigma(\text{C}-\text{C}) = 0.003$ Å
 R factor = 0.049
 wR factor = 0.128
Data-to-parameter ratio = 12.2For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

Pyridinium nitrate at 120 K

The structural unit of pyridinium nitrate, $\text{C}_5\text{H}_6\text{N}^+\cdot\text{NO}_3^-$, is a pyridinium–nitrate ion pair, held together by a strong $\text{N}-\text{H}\cdots\text{O}$ hydrogen bond.Received 15 November 2004
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Comment

The present paper reports the low-temperature study of the title compound, (I). For the introduction and the room-temperature results, see the preceding paper (Batsanov, 2004).

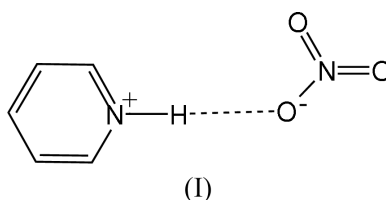
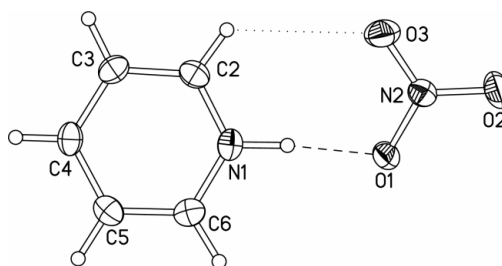
Cooling of (I) from 290 to 120 K resulted in an approximately 4% decrease of the unit-cell volume, which was shown (by fast determinations at 160, 200 and 250 K) to be practically linear in this range. It is noteworthy that, whilst at room temperature $\beta > 90^\circ$, on cooling it decreases, passing through 90° at 250 K. Therefore, in the present report, the non-standard cell setting with $\beta < 90^\circ$ is used, for compatibility with the room-temperature data (Serewicz *et al.*, 1965; Batsanov, 2004).The structure at 120 K (Fig. 1) is similar to that at room temperature (see Table 1), with the anisotropic displacement parameters approximately three times lower [U_{eq} of non-H atoms averaging 0.08 (1) Å² at 290 K *versus* 0.027 (5) Å² at 120 K]. The asymmetric unit comprises one pyridinium cation and one nitrate anion, the ionic nature of which is proven by the location of H atoms. Both ions are planar, and the dihedral angle between them increases from 13.7 (1)° at 290 K to 21.1 (1)° at 120 K. This change can be best approximated as a rotation of the anion around atom O1, which is hydrogen bonded to the cation (Table 2). The deviations of the nitrate

Figure 1

The molecular structure of (I) at 120 K. Displacement ellipsoids are drawn at the 50% probability level. The dashed and dotted lines indicate strong and weak hydrogen bonds, respectively.

anion atoms from the pyridine ring plane illustrate this point, *viz.* O1 $-0.302(4)$, O2 $0.081(6)$, O3 $0.174(5)$ and N2 $-0.006(5)$ Å at 290 K *versus* O1 $-0.265(4)$, O2 $0.274(5)$, O3 $0.496(4)$ and N2 $0.173(4)$ Å at 120 K.

The ion pair is held together by a strong (Steiner, 2002) and nearly linear N1–H1 \cdots O1 hydrogen bond (Table 2). The N1 \cdots O1 distance decreases from 2.787(3) Å at 290 K to 2.699(2) Å at 120 K; *cf.* 2.730(3) Å in the structure of PyH $^+$ ·MeSO $_3^-$ at 173 K (Bolte *et al.*, 2001) and 2.664(4)–2.698(4) Å in PyH $^+$ ·F $_3$ CCO $_2^-$, (II), at 183 K (Palmore & McBride-Wieser, 1997). In (I), the ion pair is further stabilized by a weak (Desiraju & Steiner, 1999) hydrogen bond (C2–H2 \cdots O3) involving the *ortho* H atom, thus producing a seven-membered ring. This motif can be described by the graph set $R_2^2(7)$, according to Etter *et al.* (1990) and Bernstein *et al.* (1995). The same motif is realised in the structure of (II), where the C(*ortho*)–H \cdots O bonds are substantially stronger: the C \cdots O distances range from 3.175(4) to 3.214(4) Å *versus* 3.229(3) Å in (I), and the H \cdots O distances (for the C–H bond lengths corrected to 1.08 Å) from 2.28(3) to 2.42(4) Å *versus* 2.55(3) Å in (I). The weaker bonding in (I) can be easily explained, as atom H2 participates in a bifurcated hydrogen bond, with O3 of the same ion pair and with O2 of an adjacent ion pair. The latter bond is evidently the stronger, with the C \cdots O distance shorter by 0.15 Å. No such competition is possible in (II), which contains no O atoms not involved in intra-pair hydrogen bonds.

In fact, all H atoms in (I) participate in inter-pair C–H \cdots O contacts which are shorter than the sum of van der Waals radii (Rowland & Taylor, 1996), correspond to the stabilizing part of the potential curve (Desiraju & Steiner, 1999) and can be interpreted as weak hydrogen bonds (Table 2).

Due to protonation of N1, the C2–N1–C6 angle in (I) is widened in comparison with the neutral pyridine molecule [116.6(2)°; Mootz & Wusson, 1981] and coincides with those in PyH $^+$ ·MeSO $_3^-$ and (II).

Experimental

The crystals of (I) were grown by slow evaporation, at room temperature, of an aqueous solution of equimolar amounts of pyridine and nitric acid.

Crystal data

C $_5$ H $_6$ N $^+$ ·NO $_3^-$
 $M_r = 142.12$
 Monoclinic, $P2_1/c$
 $a = 3.7756(9)$ Å
 $b = 12.336(3)$ Å
 $c = 13.353(3)$ Å
 $\beta = 88.60(1)^\circ$
 $V = 621.8(4)$ Å 3
 $Z = 4$

$D_x = 1.521$ Mg m $^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 851 reflections
 $\theta = 10.4\text{--}24.9^\circ$
 $\mu = 0.13$ mm $^{-1}$
 $T = 120(1)$ K
 Plate, colourless
 $0.42 \times 0.37 \times 0.03$ mm

Data collection

Bruker SMART 1K CCD area-detector diffractometer
 ω scans
 Absorption correction: none
 3711 measured reflections
 1408 independent reflections

1006 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.065$
 $\theta_{\text{max}} = 27.5^\circ$
 $h = -4 \rightarrow 4$
 $k = -10 \rightarrow 15$
 $l = -17 \rightarrow 17$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.049$
 $wR(F^2) = 0.128$
 $S = 1.04$
 1408 reflections
 115 parameters
 All H-atom parameters refined

$$w = 1/[\sigma^2(F_o^2) + (0.045P)^2 + 0.4158P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.24 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.32 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

N1–C2	1.339(3)	C5–C6	1.370(3)
N1–C6	1.343(3)	O1–N2	1.272(2)
C2–C3	1.373(3)	O2–N2	1.237(2)
C3–C4	1.389(3)	O3–N2	1.245(2)
C4–C5	1.383(3)		
C2–N1–C6	122.2(2)	N1–C6–C5	119.6(2)
N1–C2–C3	120.3(2)	O2–N2–O3	121.32(18)
C2–C3–C4	118.7(2)	O2–N2–O1	119.44(18)
C5–C4–C3	119.8(2)	O3–N2–O1	119.24(17)
C6–C5–C4	119.5(2)		

Table 2

Hydrogen-bonding geometry (Å, °).

$D\text{--}H\cdots A$	$D\text{--}H$	$H\cdots A$	$D\cdots A$	$D\text{--}H\cdots A$
N1–H1 \cdots O1	0.97(3)	1.74(3)	2.699(2)	171(3)
N1–H1 \cdots O3	0.97(3)	2.47(3)	3.160(3)	128(2)
C2–H2 \cdots O3	0.93(2)	2.63(2)	3.229(3)	122.4(18)
C2–H2 \cdots O2 $^{\text{ii}}$	0.93(2)	2.50(2)	3.076(3)	119.9(18)
C3–H3 \cdots O2 $^{\text{ii}}$	0.96(2)	2.62(2)	3.272(3)	125.3(17)
C4–H4 \cdots O3 $^{\text{iii}}$	0.94(2)	2.65(2)	3.244(3)	121.5(16)
C5–H5 \cdots O3 $^{\text{iii}}$	0.97(2)	2.61(2)	3.240(3)	122.8(18)
C6–H6 \cdots O1 $^{\text{iv}}$	0.97(2)	2.38(2)	3.215(3)	143.1(19)
C6–H6 \cdots O2 $^{\text{iv}}$	0.97(2)	2.60(2)	3.384(3)	137.8(18)

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

All H atoms were refined in an isotropic approximation without constraints.

Data collection: SMART (Bruker, 1997); cell refinement: SAINT (Bruker, 2001); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Bruker, 2001); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

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supporting information

Acta Cryst. (2004). E60, o2426–o2428 [https://doi.org/10.1107/S160053680403017X]

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pyridinium nitrate

Crystal data

$C_5H_6N^+ \cdot NO_3^-$

$M_r = 142.12$

Monoclinic, $P2_1/c$

Hall symbol: $-P\ 2_1/c$

$a = 3.7756$ (9) Å

$b = 12.336$ (3) Å

$c = 13.353$ (3) Å

$\beta = 88.60$ (1)°

$V = 621.8$ (4) Å³

$Z = 4$

$F(000) = 296$

$D_x = 1.521$ Mg m⁻³

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

Cell parameters from 851 reflections

$\theta = 10.4$ – 24.9 °

$\mu = 0.13$ mm⁻¹

$T = 120$ K

Plate, colourless

$0.42 \times 0.37 \times 0.03$ mm

Data collection

Bruker SMART 1K CCD area-detector
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: 8 pixels mm⁻¹

ω scans

3711 measured reflections

1408 independent reflections

1006 reflections with $I > 2\sigma(I)$

$R_{int} = 0.065$

$\theta_{max} = 27.5$ °, $\theta_{min} = 2.3$ °

$h = -4 \rightarrow 4$

$k = -10 \rightarrow 15$

$l = -17 \rightarrow 17$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.049$

$wR(F^2) = 0.128$

$S = 1.04$

1408 reflections

115 parameters

0 restraints

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map

Hydrogen site location: difference Fourier map

All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.045P)^2 + 0.4158P]$

where $P = (F_o^2 + 2F_c^2)/3$

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

$\Delta\rho_{max} = 0.24$ e Å⁻³

$\Delta\rho_{min} = -0.32$ e Å⁻³

Special details

Experimental. The data collection nominally covered over a hemisphere of reciprocal space, by a combination of 3 sets of ω scans; each set at different φ and/or 2θ angles and each scan (5 sec/frame exposure) covering 0.3° in ω . Crystal to detector distance 4.42 cm. Crystals are stable in dry air but deteriorate in atmospheric air.

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.

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

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	0.3911 (5)	0.31297 (14)	0.54178 (14)	0.0221 (4)
H1	0.269 (8)	0.374 (2)	0.573 (2)	0.055 (9)*
C2	0.4522 (5)	0.22606 (18)	0.59896 (16)	0.0235 (5)
H2	0.371 (6)	0.2287 (19)	0.6656 (18)	0.024 (6)*
C3	0.6197 (6)	0.13673 (18)	0.55879 (16)	0.0245 (5)
H3	0.659 (6)	0.074 (2)	0.6001 (18)	0.028 (6)*
C4	0.7247 (5)	0.13889 (18)	0.45835 (17)	0.0239 (5)
H4	0.827 (6)	0.0772 (18)	0.4280 (16)	0.018 (5)*
C5	0.6606 (6)	0.23012 (18)	0.40145 (17)	0.0248 (5)
H5	0.733 (6)	0.2309 (19)	0.3315 (19)	0.030 (6)*
C6	0.4892 (5)	0.31687 (19)	0.44450 (16)	0.0247 (5)
H6	0.437 (6)	0.3826 (19)	0.4075 (18)	0.028 (6)*
O1	0.0001 (4)	0.48032 (13)	0.61332 (11)	0.0286 (4)
O2	-0.1078 (5)	0.56343 (14)	0.75376 (12)	0.0361 (4)
O3	0.1735 (4)	0.41066 (14)	0.75319 (12)	0.0346 (4)
N2	0.0216 (5)	0.48502 (14)	0.70817 (13)	0.0232 (4)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0182 (8)	0.0201 (9)	0.0281 (10)	-0.0005 (7)	-0.0019 (7)	-0.0046 (8)
C2	0.0223 (10)	0.0284 (11)	0.0198 (10)	-0.0039 (9)	-0.0014 (8)	-0.0014 (9)
C3	0.0223 (11)	0.0233 (11)	0.0281 (11)	-0.0006 (9)	-0.0050 (8)	0.0032 (9)
C4	0.0174 (10)	0.0228 (11)	0.0314 (12)	0.0005 (8)	-0.0009 (8)	-0.0057 (9)
C5	0.0194 (10)	0.0333 (12)	0.0219 (10)	-0.0020 (9)	-0.0006 (8)	-0.0020 (9)
C6	0.0216 (10)	0.0262 (12)	0.0264 (11)	-0.0020 (9)	-0.0032 (9)	0.0038 (9)
O1	0.0367 (9)	0.0300 (9)	0.0193 (7)	0.0086 (7)	-0.0016 (6)	-0.0021 (7)
O2	0.0441 (10)	0.0357 (9)	0.0285 (9)	0.0109 (8)	0.0002 (7)	-0.0114 (7)
O3	0.0380 (9)	0.0379 (10)	0.0279 (9)	0.0104 (8)	0.0005 (7)	0.0102 (7)
N2	0.0231 (9)	0.0254 (10)	0.0212 (9)	-0.0017 (8)	0.0007 (7)	0.0001 (8)

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

N1—C2	1.339 (3)	C4—H4	0.94 (2)
N1—C6	1.343 (3)	C5—C6	1.370 (3)
N1—H1	0.97 (3)	C5—H5	0.97 (2)
C2—C3	1.373 (3)	C6—H6	0.97 (2)
C2—H2	0.93 (2)	O1—N2	1.272 (2)
C3—C4	1.389 (3)	O2—N2	1.237 (2)
C3—H3	0.96 (2)	O3—N2	1.245 (2)
C4—C5	1.383 (3)		

C2—N1—C6	122.2 (2)	C3—C4—H4	120.3 (13)
C2—N1—H1	117.5 (17)	C6—C5—C4	119.5 (2)
C6—N1—H1	120.3 (17)	C6—C5—H5	121.1 (15)
N1—C2—C3	120.3 (2)	C4—C5—H5	119.4 (15)
N1—C2—H2	117.2 (14)	N1—C6—C5	119.6 (2)
C3—C2—H2	122.5 (14)	N1—C6—H6	117.8 (14)
C2—C3—C4	118.7 (2)	C5—C6—H6	122.5 (14)
C2—C3—H3	119.8 (14)	O2—N2—O3	121.32 (18)
C4—C3—H3	121.6 (14)	O2—N2—O1	119.44 (18)
C5—C4—C3	119.8 (2)	O3—N2—O1	119.24 (17)
C5—C4—H4	119.8 (13)		

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—H1 \cdots O1	0.97 (3)	1.74 (3)	2.699 (2)	171 (3)
N1—H1 \cdots O3	0.97 (3)	2.47 (3)	3.160 (3)	128 (2)
C2—H2 \cdots O3	0.93 (2)	2.63 (2)	3.229 (3)	122.4 (18)
C2—H2 \cdots O2 ⁱ	0.93 (2)	2.50 (2)	3.076 (3)	119.9 (18)
C3—H3 \cdots O2 ⁱⁱ	0.96 (2)	2.62 (2)	3.272 (3)	125.3 (17)
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C6—H6 \cdots O1 ^{iv}	0.97 (2)	2.38 (2)	3.215 (3)	143.1 (19)
C6—H6 \cdots O2 ^{iv}	0.97 (2)	2.60 (2)	3.384 (3)	137.8 (18)

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