organic papers

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Key indicators

Single-crystal X-ray study
T = 120 K
Mean σ(C–C) = 0.003 Å
R factor = 0.049
wR factor = 0.128
Data-to-parameter ratio = 12.2

For 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, $C_5H_6N^+\cdot NO_3^-$, is a pyridinium–nitrate ion pair, held together by a strong N—H$\cdots$O hydrogen bond.

Comment

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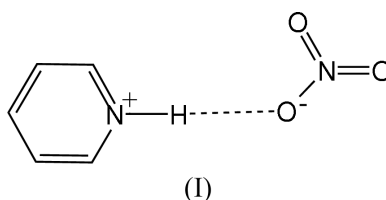

(I)

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 $\beta > 90°$, on cooling it decreases, passing through 90° at 250 K. Therefore, in the present report, the non-standard cell setting with $\beta < 90°$ 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) Å^2 at 290 K *versus* 0.027 (5) Å^2 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
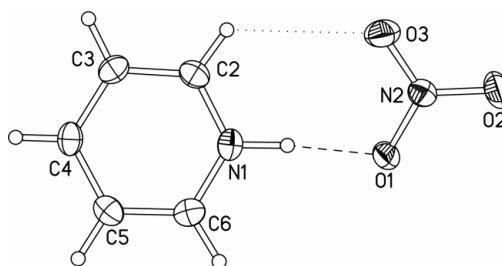
Figure 1
The molecular structure of (I) at 120 K. Displacement ellipsoids are drawn at the 50% probability level. The dashed and dotted lines indicate strong and weak hydrogen bonds, respectively.

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⋯O1 hydrogen bond (Table 2). The N1⋯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⋯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⋯O bonds are substantially stronger: the C⋯O distances range from 3.175 (4) to 3.214 (4) Å *versus* 3.229 (3) Å in (I), and the H⋯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⋯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⋯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$_3^-$	$D_x = 1.521$ Mg m^{-3}
$M_r = 142.12$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 851
$a = 3.7756$ (9) Å	reflections
$b = 12.336$ (3) Å	$\theta = 10.4–24.9°$
$c = 13.353$ (3) Å	$\mu = 0.13$ mm^{-1}
$\beta = 88.60$ (1)°	$T = 120$ (1) K
$V = 621.8$ (4) Å^3	Plate, colourless
$Z = 4$	$0.42 \times 0.37 \times 0.03$ mm

Data collection

Bruker SMART 1K CCD area-detector diffractometer	1006 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.065$
Absorption correction: none	$\theta_{max} = 27.5°$
3711 measured reflections	$h = -4 \rightarrow 4$
1408 independent reflections	$k = -10 \rightarrow 15$
	$l = -17 \rightarrow 17$

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