Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Nicotinium trifluoroacetate

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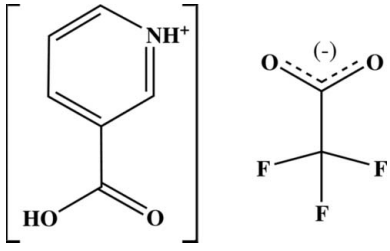
Received 13 April 2007; accepted 18 April 2007

Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.005 Å; disorder in main residue; R factor = 0.053; wR factor = 0.087; data-to-parameter ratio = 9.7.

In the title compound, $C_6H_6NO_2^+\cdot C_2O_2F_3^-$, the carboxyl group is twisted from the planar pyridine ring by an angle of 5.2 (6)°. The protonated cations and the anions are linked through N—H···O and O—H···O hydrogen bonds, forming a $C_2^1(8)$ chain motif with two-dimensional lamellar sheets parallel to (010). These sheets are separated by a distance of 3.092 (4) Å and there are no hydrogen bonds between them. The F atoms are each disordered unequally over two positions.

Related literature

For related literature on hydrogen-bond motifs, see: Etter *et al.* (1990). For values of bond lengths and angles, see: Allen (2002). For information on the pharmacological properties of nicotinic acid, see: Athimoolam & Rajaram (2005*a*,*b*). For a related structure, see: Athimoolam & Natarajan (2006).



Experimental

Crystal data

$C_6H_6NO_2^+\cdot C_2O_2F_3^-$
M_r = 237.14
Triclinic, $P\overline{1}$
a = 8.1981 (7) Å
b = 8.6292 (8) Å
c = 8.8580 (6) Å
α = 62.036 (11)°
β = 86.867 (14)°
γ = 61.818 (9)°
V = 476.53 (11) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.17 mm^{-1}
T = 293 (2) K
0.22 × 0.19 × 0.15 mm

Data collection

Nonius MACH3 diffractometer
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.963, T_{max} = 0.995
2060 measured reflections
1674 independent reflections
809 reflections with $I > 2\sigma(I)$
R_{int} = 0.016
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.053
$wR(F^2)$ = 0.088
S = 0.96
1674 reflections
173 parameters
9 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.14 e Å^{-3}
$\Delta\rho_{min}$ = −0.16 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O22^{i}	0.86	1.82	2.675 (3)	170
O1B—H1B···O22	0.82	1.82	2.639 (3)	177

Symmetry code: (i) $x-1, y, z$.

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: *SHELXTL/PC* (Bruker, 2000); program(s) used to refine structure: *SHELXTL/PC*; molecular graphics: *ORTEP-3* (Farrugia, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXTL/PC*.

The authors thank the Department of Science and Technology, Government of India for establishing the single-crystal diffractometer facility at the School of Physics, Madurai Kamaraj University, Madurai, through the FIST programme. The authors also thank the UGC for the SAP programme.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SJ2293).

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supplementary materials

Acta Cryst. (2007). E**63**, o2656 [**doi:10.1107/S1600536807019216**]

Nicotinium trifluoroacetate

S. Athimoolam and S. Natarajan

Comment

Nicotinic acid (pyridine-3-carboxylic acid) is a B vitamin known as niacin, and has a variety of pharmacological properties as detailed in our previous publications (Athimoolam & Rajaram, 2005a,b). As vitamin B is one of the important biological compounds in many fields such as the pharmaceutical industry, it is very useful to study ionic crystals of the vitamin in inorganic/organic acid environment. The planar nicotinic acid ligand has potential sites for hydrogen-bonding interactions, *viz*., the pyridine N atom, and the carboxylic O atoms. These effective hydrogen-bonding sites make this molecule to act as an important supramolecular organic synthon. The present work is part of our ongoing work on vitamin-inorganic/organic complexes to study the different hydrogen-bond motifs.

The asymmetric unit of the title compound (I) contains a nicotinium cation and a trifluoroacetate anion (Fig 1). The fluorine atoms of the trifluoroacetate are observed to have 'rotational disorder' about the C—C bond. Deprotonation of the anion and protonation of the cation are confirmed by the C—N and C—O bond distances (Table 1). Characteristic features of the protonated nicotinium structure are the twisting of the carboxylic acid plane out of the pyridine ring plane and a significant widening of the C—N—C angle in the pyridine ring (>120°) (Cambridge Structural Database; Version 5.28 of 2008; Allen, 2002). Both these features are observed in (I) (Table 1), with the angle of twisting between the carboxylic acid and pyridine ring planes being 5.2 (6)°. The deviations of the atoms O1A and O1B from the plane of the pyridine ring are observed to be -0.112 (5) and 0.090 (5) Å, respectively.

Anions link cations through N—H···O and O—H···O hydrogen bonds forming a $C_2^1(8)$ chain motif (Etter *et al.*, 1990). Normally, nicotinium cations are linked together interactions leading to a sheet like structure (Athimoolam & Natarajan, 2006). But in (I), cations and anions are linked leading to a sheet like structure parallel to the ac plane of the crystal (Fig. 2; Table 2). These two-dimensional hydrogen-bonded sheets are separated by a distance of 3.092 (4) Å . There are no hydrogen bonding interactions between these sheets.

Experimental

The title compound (I) was crystallized from an aqueous mixture containing nicotinic acid and trifluoroacetic acid, in the stochiometric ratio of 1:1, by the technique of slow evaporation.

Refinement

All the H atoms were positioned geometrically and refined using a riding model, with C—H = 0.93 Å, N—H = 0.86 Å and O—H = 0.82 Å and U_{iso}(H) = 1.2 - 1.5 U_{eq} (parent atom). The F atoms of the trifluoroacetate are disordered over two positions with the site occupancies of 0.57 (1) and 0.43 (1). Despite attempts to model this disorder effectively, the displacement parameters for the F atoms remain very high.

Figures

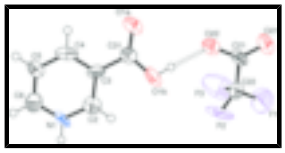

Fig. 1. The molecular structure of (I), shwoing the atom-numbering scheme and 50% probability displacement ellipsoids. Hydrogen bonds are shown as dashed lines. Only the major component of the disordered F atoms are shown.

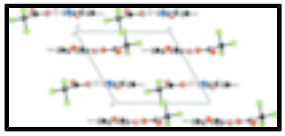

Fig. 2. Packing diagram of the molecules viewed down the *c*-axis. Minor components of the disordered F atoms are omitted for clarity. H-bonds are shown as dashed lines.

Nicotinium trifluoroacetate

Crystal data

$C_6H_6NO_2^+ \cdot C_2O_2F_3^-$	$Z = 2$
$M_r = 237.14$	$F_{000} = 240$
	$D_x = 1.653$ Mg m^{-3}
Triclinic, $P\overline{1}$	$D_m = 1.65$ (1) Mg m^{-3} D_m measured by flotation using a mixture of xylene and bromoform
Hall symbol: -P 1	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$a = 8.1981$ (7) Å	Cell parameters from 25 reflections
$b = 8.6292$ (8) Å	$\theta = 9.5$–15.1°
$c = 8.8580$ (6) Å	$\mu = 0.17$ mm^{-1}
$\alpha = 62.036$ (11)°	$T = 293$ (2) K
$\beta = 86.867$ (14)°	Block, colourless
$\gamma = 61.818$ (9)°	0.22 × 0.19 × 0.15 mm
$V = 476.53$ (11) Å^3	

Data collection

Nonius MACH3 sealed tube diffractometer	$R_{int} = 0.016$
Radiation source: fine-focus sealed tube	$\theta_{max} = 25.0^\circ$
Monochromator: graphite	$\theta_{min} = 2.7^\circ$
$T = 293$(2) K	$h = -1 \rightarrow 9$
ω–2θ scans	$k = -9 \rightarrow 10$
Absorption correction: ψ scan (North *et al.*, 1968)	$l = -10 \rightarrow 10$
$T_{min} = 0.963$, $T_{max} = 0.995$	3 standard reflections
2060 measured reflections	every 60 min
1674 independent reflections	intensity decay: none
809 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.053$	$w = 1/[\sigma^2(F_o^2) + (0.0354P)^2 +]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.088$	$(\Delta/\sigma)_{max} < 0.001$
$S = 0.96$	$\Delta\rho_{max} = 0.15$ e Å^{-3}
1674 reflections	$\Delta\rho_{min} = -0.16$ e Å^{-3}
173 parameters	Extinction correction: none
9 restraints	
Primary atom site location: structure-invariant direct methods	
Secondary atom site location: difference Fourier map	

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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 $F^2 > 2$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}	Occ. (<1)
N1	−0.0844 (3)	0.2751 (3)	−0.0477 (3)	0.0451 (6)	
H1	−0.1676	0.2813	0.0163	0.054*	
C2	0.0696 (4)	0.2693 (3)	0.0028 (3)	0.0422 (8)	
H2	0.0836	0.2719	0.1050	0.051*	
C3	0.2086 (4)	0.2595 (4)	−0.0934 (4)	0.0460 (8)	
C31	0.3802 (5)	0.2516 (5)	−0.0425 (4)	0.0503 (8)	
O1A	0.5100 (3)	0.2306 (3)	−0.1179 (3)	0.0652 (7)	
O1B	0.3770 (3)	0.2727 (4)	0.0958 (3)	0.0719 (7)	
H1B	0.4762	0.2643	0.1226	0.108*	
C4	0.1767 (4)	0.2599 (4)	−0.2455 (4)	0.0582 (9)	
H4	0.2633	0.2589	−0.3179	0.070*	
C5	0.0163 (4)	0.2618 (4)	−0.2902 (4)	0.0531 (9)	
H5	−0.0009	0.2561	−0.3900	0.064*	
C6	−0.1164 (4)	0.2718 (4)	−0.1907 (4)	0.0587 (9)	
H6	−0.2256	0.2763	−0.2220	0.070*	
O21	0.8754 (3)	0.2793 (3)	0.3340 (3)	0.0650 (7)	

O22	0.6891 (3)	0.2585 (3)	0.1815 (3)	0.0633 (6)	
C21	0.7513 (4)	0.2472 (4)	0.3171 (4)	0.0477 (8)	
C22	0.6485 (6)	0.1903 (8)	0.4611 (6)	0.0757 (12)	
F1	0.7186 (18)	0.157 (2)	0.6044 (12)	0.172 (6)	0.57
F2	0.4680 (8)	0.2901 (13)	0.4224 (12)	0.094 (3)	0.57
F3	0.6864 (17)	−0.0022 (13)	0.5179 (17)	0.151 (6)	0.57
F1'	0.7359 (19)	0.1224 (14)	0.6155 (11)	0.085 (4)	0.43
F2'	0.4762 (15)	0.316 (2)	0.4358 (17)	0.231 (10)	0.43
F3'	0.665 (2)	0.012 (2)	0.499 (2)	0.134 (7)	0.43

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0231 (14)	0.0605 (16)	0.0562 (16)	−0.0302 (13)	0.0134 (12)	−0.0239 (13)
C2	0.046 (2)	0.0277 (16)	0.0353 (16)	−0.0162 (16)	0.0041 (16)	−0.0059 (14)
C3	0.045 (2)	0.055 (2)	0.0469 (18)	−0.0248 (17)	0.0243 (16)	−0.0340 (16)
C31	0.048 (2)	0.067 (2)	0.054 (2)	−0.0385 (18)	0.0198 (18)	−0.0347 (18)
O1A	0.0443 (13)	0.0908 (16)	0.0751 (15)	−0.0427 (13)	0.0229 (12)	−0.0445 (13)
O1B	0.0434 (15)	0.1169 (19)	0.0796 (16)	−0.0543 (15)	0.0182 (13)	−0.0530 (15)
C4	0.050 (2)	0.065 (2)	0.063 (2)	−0.0296 (19)	0.0355 (18)	−0.0353 (19)
C5	0.0347 (19)	0.071 (2)	0.058 (2)	−0.0268 (18)	0.0097 (18)	−0.0348 (18)
C6	0.052 (2)	0.067 (2)	0.0424 (19)	−0.0227 (19)	0.0014 (18)	−0.0232 (18)
O21	0.0561 (15)	0.0838 (16)	0.0779 (16)	−0.0486 (13)	0.0148 (12)	−0.0434 (13)
O22	0.0612 (14)	0.0983 (16)	0.0577 (13)	−0.0576 (13)	0.0292 (12)	−0.0428 (13)
C21	0.040 (2)	0.069 (2)	0.0364 (19)	−0.0394 (19)	0.0130 (16)	−0.0166 (17)
C22	0.060 (3)	0.133 (4)	0.104 (3)	−0.060 (3)	0.037 (3)	−0.098 (3)
F1	0.185 (13)	0.368 (15)	0.103 (7)	−0.201 (12)	0.079 (7)	−0.159 (8)
F2	0.032 (4)	0.126 (6)	0.106 (6)	−0.031 (4)	0.043 (4)	−0.057 (5)
F3	0.098 (7)	0.103 (6)	0.168 (10)	−0.044 (6)	0.041 (6)	−0.017 (7)
F1'	0.089 (9)	0.087 (5)	0.042 (5)	−0.033 (5)	0.004 (5)	−0.018 (4)
F2'	0.092 (9)	0.191 (12)	0.073 (8)	0.069 (7)	0.038 (7)	0.026 (7)
F3'	0.188 (16)	0.188 (12)	0.128 (10)	−0.153 (14)	0.050 (9)	−0.094 (10)

Geometric parameters (Å, °)

N1—C6	1.324 (3)	C5—C6	1.359 (4)
N1—C2	1.334 (3)	C5—H5	0.9300
N1—H1	0.8600	C6—H6	0.9300
C2—C3	1.379 (3)	O21—C21	1.206 (3)
C2—H2	0.9300	O22—C21	1.273 (3)
C3—C4	1.385 (4)	C21—C22	1.505 (4)
C3—C31	1.462 (4)	C22—F2'	1.256 (10)
C31—O1A	1.211 (3)	C22—F1	1.266 (9)
C31—O1B	1.317 (3)	C22—F2	1.274 (7)
O1B—H1B	0.8200	C22—F1'	1.299 (10)
C4—C5	1.384 (4)	C22—F3'	1.352 (11)
C4—H4	0.9300	C22—F3	1.362 (9)
C6—N1—C2	123.6 (3)	O21—C21—O22	126.4 (3)

C6—N1—H1	118.2	O21—C21—C22	121.7 (3)
C2—N1—H1	118.2	O22—C21—C22	111.9 (3)
N1—C2—C3	121.3 (3)	F2'—C22—F1	102.8 (9)
N1—C2—H2	119.3	F1—C22—F2	113.9 (8)
C3—C2—H2	119.3	F2'—C22—F1'	109.9 (10)
C2—C3—C4	116.2 (3)	F2—C22—F1'	119.3 (8)
C2—C3—C31	123.2 (3)	F2'—C22—F3'	108.3 (11)
C4—C3—C31	120.6 (3)	F1—C22—F3'	104.7 (10)
O1A—C31—O1B	123.3 (3)	F2—C22—F3'	95.3 (8)
O1A—C31—C3	124.8 (3)	F1'—C22—F3'	95.3 (9)
O1B—C31—C3	111.9 (3)	F2'—C22—F3	113.9 (10)
C31—O1B—H1B	109.5	F1—C22—F3	97.2 (9)
C5—C4—C3	120.2 (3)	F2—C22—F3	101.7 (7)
C5—C4—H4	119.9	F1'—C22—F3	87.6 (8)
C3—C4—H4	119.9	F2'—C22—C21	117.8 (7)
C6—C5—C4	121.1 (3)	F1—C22—C21	114.0 (7)
C6—C5—H5	119.4	F2—C22—C21	117.8 (5)
C4—C5—H5	119.4	F1'—C22—C21	114.7 (7)
N1—C6—C5	117.5 (3)	F3'—C22—C21	108.4 (8)
N1—C6—H6	121.2	F3—C22—C21	109.2 (6)
C5—C6—H6	121.2		
C6—N1—C2—C3	0.1 (4)	O21—C21—C22—F2'	112.8 (11)
N1—C2—C3—C4	1.1 (4)	O22—C21—C22—F2'	−66.3 (11)
N1—C2—C3—C31	−179.6 (3)	O21—C21—C22—F1	−7.8 (9)
C2—C3—C31—O1A	175.3 (3)	O22—C21—C22—F1	173.1 (7)
C4—C3—C31—O1A	−5.5 (5)	O21—C21—C22—F2	129.5 (6)
C2—C3—C31—O1B	−5.5 (4)	O22—C21—C22—F2	−49.6 (7)
C4—C3—C31—O1B	173.8 (3)	O21—C21—C22—F1'	−18.9 (8)
C2—C3—C4—C5	−2.5 (4)	O22—C21—C22—F1'	162.0 (6)
C31—C3—C4—C5	178.2 (3)	O21—C21—C22—F3'	−123.9 (7)
C3—C4—C5—C6	2.8 (5)	O22—C21—C22—F3'	57.0 (8)
C2—N1—C6—C5	0.1 (4)	O21—C21—C22—F3	−115.2 (7)
C4—C5—C6—N1	−1.5 (4)	O22—C21—C22—F3	65.6 (7)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O22^{i}	0.86	1.82	2.675 (3)	170
O1B—H1B···O22	0.82	1.82	2.639 (3)	177

Symmetry codes: (i) *x*−1, *y*, *z*.

Fig. 1

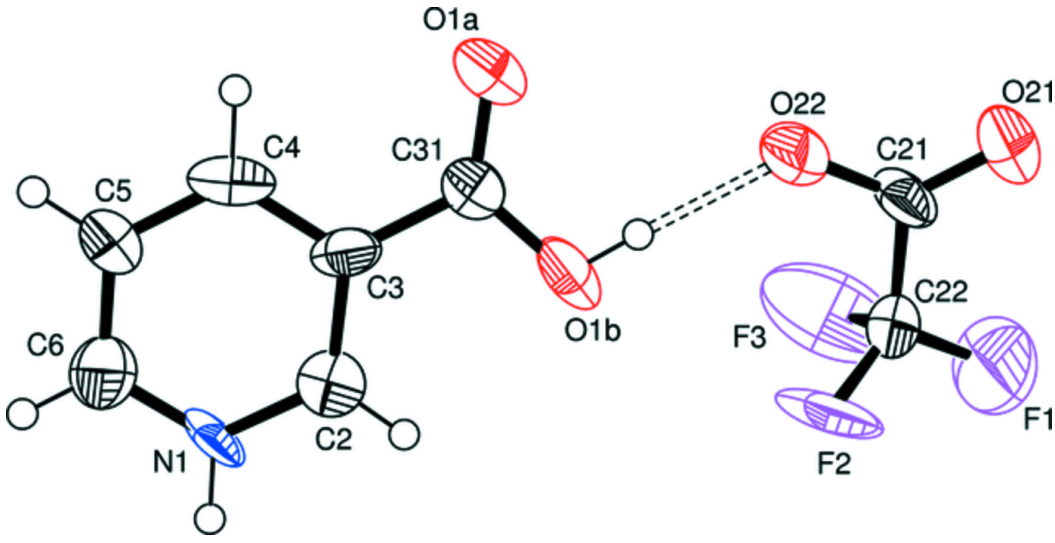

Fig. 2