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2-Amino-4-methylpyridinium trifluoroacetate: a monoclinic polymorph

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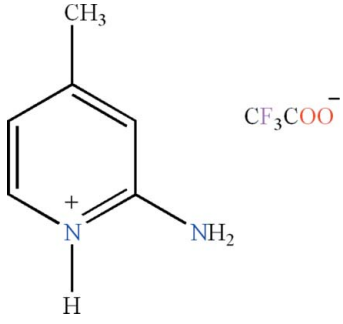
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.002 Å; R factor = 0.035; wR factor = 0.098; data-to-parameter ratio = 14.6.

The title salt, $C_6H_9N_2^+\cdot C_2F_3O_2^-$, is a monoclinic polymorph of a previously reported structure [Hemamalini & Fun (2010). *Acta Cryst.* E**66**, o781–o782]. In the crystal structure, the cations and anions are linked by two different types of N—H···O hydrogen bonds, forming cation–anion pairs. These pairs are hydrogen bonded to neighbouring pairs *via* another N—H···O hydrogen bonds involving an H atom of the NH_2 group and one of the O atoms of the COO^- group into a chain extended along the *b* axis.

Related literature

For a related structure and the triclinic polymorph of the title salt, see: Hemamalini & Fun (2010*a*,*b*).



Experimental

Crystal data

$C_6H_9N_2^+\cdot C_2F_3O_2^-$
M_r = 222.17
Monoclinic, $P2_1/c$
a = 8.5315 (7) Å
b = 11.4901 (9) Å
c = 9.7206 (8) Å
β = 90.820 (1)°
V = 952.79 (13) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.15 mm^{-1}
T = 100 K
0.30 × 0.20 × 0.10 mm

Data collection

Bruker SMART APEX diffractometer
10752 measured reflections
2197 independent reflections
1784 reflections with $I > 2\sigma(I)$
R_{int} = 0.036

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.098
S = 1.06
2197 reflections
150 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.29 e Å^{-3}
$\Delta\rho_{min}$ = −0.23 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1B···O2	0.952 (19)	1.82 (2)	2.7724 (14)	177.4 (18)
N2—H2C···O1	0.901 (18)	1.938 (19)	2.8376 (15)	176.3 (17)
N2—H2B···O2^{i}	0.923 (18)	2.055 (18)	2.8946 (15)	150.5 (15)

Symmetry code: (i) $-x+1, y-\frac{1}{2}, -z+\frac{3}{2}$.

Data collection: *SMART* (Bruker, 2005); cell refinement: *SAINT* (Bruker 2005); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

Support of this investigation by Ferdowsi University of Mashhad is gratefully acknowledged.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: NG2740).

References

Bruker (2005). *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Hemamalini, M. & Fun, H.-K. (2010*a*). *Acta Cryst.* E**66**, o691–o692.
Hemamalini, M. & Fun, H.-K. (2010*b*). *Acta Cryst.* E**66**, o781–o782.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

supporting information

Acta Cryst. (2010). E**66**, o844 [doi:10.1107/S1600536810008408]

2-Amino-4-methylpyridinium trifluoroacetate: a monoclinic polymorph

Mehrdad Pourayoubi, Maryam Toghraee, Arnold L. Rheingold and James A. Golen

S1. Comment

In the previous works, the structure determinations of 2-aminopyridinium trifluoroacetate and the triclinic polymorph of 2-amino-4-methylpyridinium trifluoroacetate (Hemamalini & Fun, 2010*a*,*b*) have been investigated; we report here on the crystal structure of title compound, 4-methyl-2-aminopyridinium trifluoroacetate (Fig. 1). The cation and anion are linked by two different types of N—H···O hydrogen bonds, forming the cation-anion pair. The pairs are hydrogen bonded to neighbouring pairs *via* another N—H···O hydrogen bonds between the hydrogen of NH_2 moiety and one of the oxygen atom of COO^- group into chain extended along the *b* axis (Fig. 2).

S2. Experimental

The title compound was obtained accidently from the reaction between 2,2,2-trifluoroacetamide, phosphorus pentachloride and formic acid and then the treatment of 2-amino-4-methylpyridine and triethylamine. The crystal was obtained from chloroform and n-heptane at room temperature.

S3. Refinement

The H atoms of the NH2 group were located from the difference Fourier synthesis and refined isotropically, no restraints were used. Finally, the geometrical and thermal parameters obtained for these H-atoms, as well as parameters of the hydrogen bonds for these H-atoms included, were rather realistic. The H(C) atom positions were calculated and refined in isotropic approximation in riding model with the Uiso(H) parameters equal to 1.2 Ueq(Ci) for the aromatic C atoms, for methyl groups equal to 1.5 Ueq(Cii), where U(Ci) and U(Cii) are respectively the equivalent thermal parameters of the carbon atoms to which corresponding H atoms are bonded.

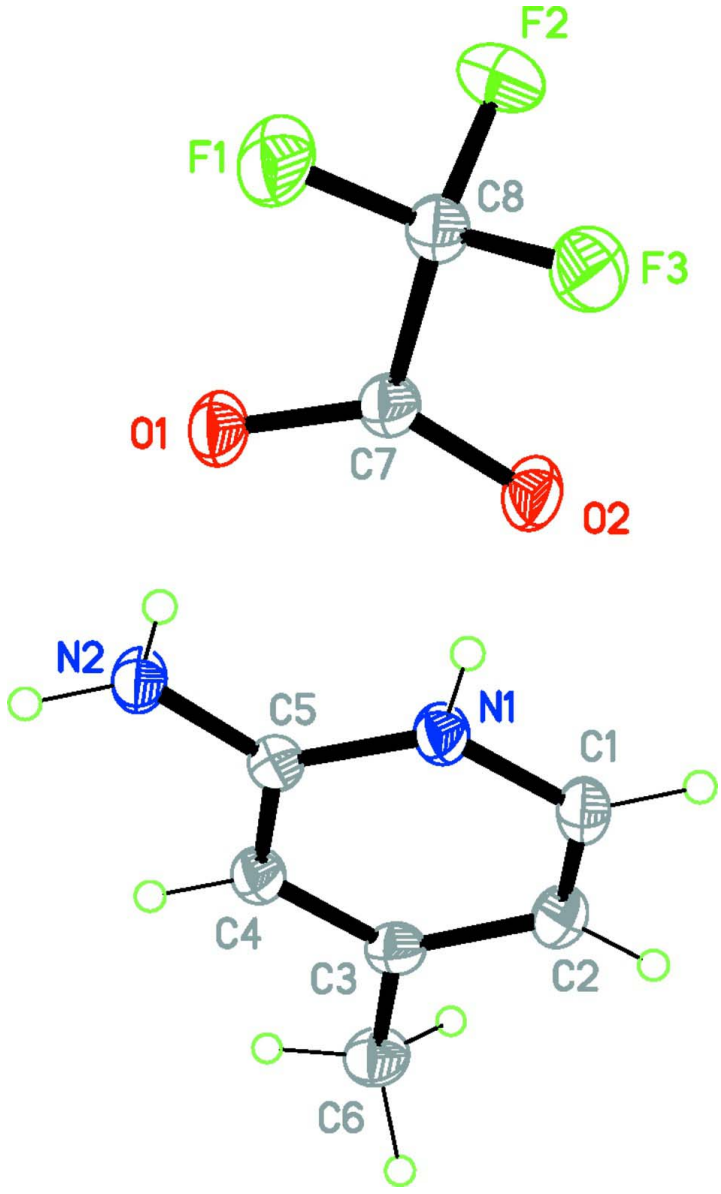


Figure 1

The molecular structure of the title salt, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50 % probability level.

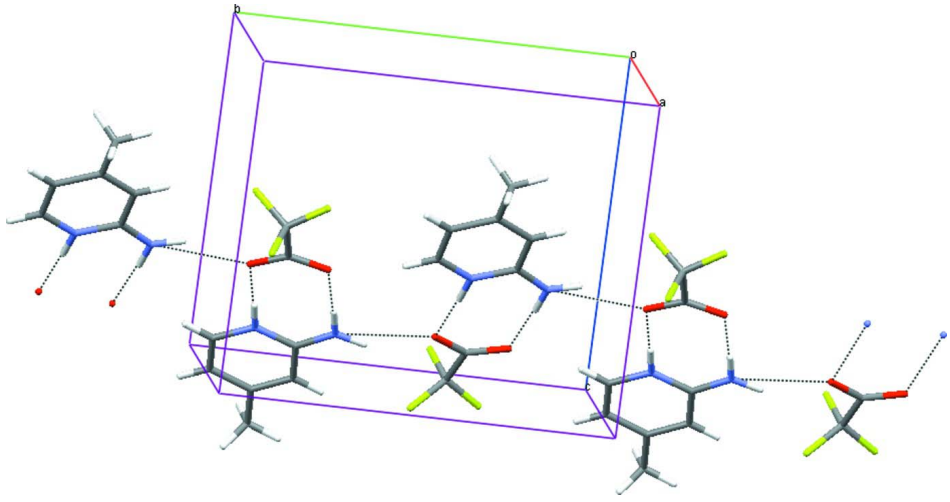


Figure 2

A view of crystal packing along the *b* axis, hydrogen bonds are shown by dashed lines.

2-Amino-4-methylpyridinium trifluoroacetate

Crystal data

$C_6H_9N_2^+·C_2F_3O_2^-$
M_r = 222.17
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
a = 8.5315 (7) Å
b = 11.4901 (9) Å
c = 9.7206 (8) Å
β = 90.820 (1)°
V = 952.79 (13) Å^3
Z = 4
$F(000)$ = 456
D_x = 1.549 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 5265 reflections
θ = 2.7–28.0°
μ = 0.15 mm^{-1}
T = 100 K
Block, colorless
0.30 × 0.20 × 0.10 mm

Data collection

Bruker SMART APEX diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
10752 measured reflections
2197 independent reflections
1784 reflections with $I > 2\sigma(I)$
R_{int} = 0.036
θ_{max} = 28.2°, θ_{min} = 2.4°
h = −5→11
k = −14→14
l = −12→12

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.098
S = 1.06
2197 reflections
150 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0474P)^2 + 0.2454P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.29 e Å^{-3}
$\Delta\rho_{min}$ = −0.23 e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0084 (16)

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 $F^2 > \sigma(F^2)$ 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)

	x	*y*	*z*	U_{iso}*/U_{eq}
F1	0.16929 (11)	0.27679 (7)	1.06142 (10)	0.0350 (2)
F2	0.08357 (10)	0.40806 (8)	0.92121 (10)	0.0358 (2)
F3	0.25375 (10)	0.45302 (7)	1.07851 (9)	0.0316 (2)
O1	0.36035 (11)	0.23798 (8)	0.85540 (11)	0.0259 (2)
O2	0.41240 (11)	0.42938 (8)	0.83832 (10)	0.0257 (2)
N1	0.61429 (13)	0.37742 (9)	0.62595 (12)	0.0212 (2)
H1B	0.544 (2)	0.3930 (17)	0.699 (2)	0.048 (5)*
N2	0.56684 (13)	0.18015 (10)	0.63958 (12)	0.0223 (3)
H2C	0.504 (2)	0.1964 (16)	0.711 (2)	0.040 (5)*
H2B	0.588 (2)	0.1040 (16)	0.6158 (18)	0.034 (5)*
C1	0.68436 (16)	0.47274 (12)	0.56989 (15)	0.0251 (3)
H1A	0.6618	0.5480	0.6049	0.030*
C2	0.78596 (16)	0.46100 (12)	0.46475 (15)	0.0250 (3)
H2A	0.8341	0.5277	0.4261	0.030*
C3	0.81986 (15)	0.34848 (12)	0.41287 (14)	0.0214 (3)
C4	0.74763 (14)	0.25417 (11)	0.47012 (13)	0.0206 (3)
H4A	0.7689	0.1784	0.4359	0.025*
C5	0.64122 (14)	0.26797 (11)	0.58005 (14)	0.0196 (3)
C6	0.93335 (16)	0.33574 (13)	0.29694 (15)	0.0260 (3)
H6A	0.9287	0.2560	0.2612	0.039*
H6B	1.0398	0.3523	0.3307	0.039*
H6C	0.9055	0.3905	0.2233	0.039*
C7	0.34308 (14)	0.34184 (11)	0.88424 (14)	0.0200 (3)
C8	0.21258 (15)	0.36940 (11)	0.98849 (15)	0.0236 (3)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
F1	0.0412 (5)	0.0257 (5)	0.0385 (5)	−0.0036 (4)	0.0209 (4)	0.0027 (4)
F2	0.0220 (4)	0.0367 (5)	0.0488 (6)	0.0070 (3)	0.0017 (4)	−0.0026 (4)
F3	0.0328 (5)	0.0271 (5)	0.0350 (5)	−0.0012 (3)	0.0096 (4)	−0.0114 (4)
O1	0.0294 (5)	0.0168 (5)	0.0319 (6)	−0.0008 (4)	0.0099 (4)	−0.0027 (4)
O2	0.0292 (5)	0.0179 (5)	0.0303 (6)	−0.0033 (4)	0.0105 (4)	0.0005 (4)
N1	0.0223 (5)	0.0177 (5)	0.0237 (6)	0.0006 (4)	0.0044 (4)	−0.0015 (5)
N2	0.0250 (6)	0.0168 (6)	0.0253 (6)	−0.0007 (4)	0.0073 (5)	−0.0007 (5)
C1	0.0272 (7)	0.0168 (6)	0.0314 (8)	−0.0007 (5)	0.0026 (6)	−0.0014 (5)

C2	0.0250 (7)	0.0200 (7)	0.0302 (8)	−0.0033 (5)	0.0032 (5)	0.0040 (5)
C3	0.0181 (6)	0.0239 (7)	0.0223 (7)	−0.0005 (5)	0.0013 (5)	0.0008 (5)
C4	0.0206 (6)	0.0187 (6)	0.0224 (7)	0.0006 (5)	0.0019 (5)	−0.0010 (5)
C5	0.0185 (6)	0.0181 (6)	0.0221 (6)	0.0003 (4)	−0.0005 (5)	−0.0005 (5)
C6	0.0236 (7)	0.0298 (7)	0.0247 (7)	−0.0021 (5)	0.0052 (5)	0.0023 (6)
C7	0.0200 (6)	0.0185 (6)	0.0217 (7)	−0.0005 (5)	0.0022 (5)	−0.0010 (5)
C8	0.0227 (6)	0.0182 (6)	0.0299 (7)	−0.0008 (5)	0.0060 (5)	−0.0015 (5)

Geometric parameters (Å, º)

F1—C8	1.3337 (15)	C1—H1A	0.9500
F2—C8	1.3475 (16)	C2—C3	1.4190 (19)
F3—C8	1.3429 (16)	C2—H2A	0.9500
O1—C7	1.2352 (15)	C3—C4	1.3688 (18)
O2—C7	1.2523 (15)	C3—C6	1.5033 (18)
N1—C5	1.3552 (16)	C4—C5	1.4209 (17)
N1—C1	1.3650 (17)	C4—H4A	0.9500
N1—H1B	0.952 (19)	C6—H6A	0.9800
N2—C5	1.3290 (16)	C6—H6B	0.9800
N2—H2C	0.901 (18)	C6—H6C	0.9800
N2—H2B	0.923 (18)	C7—C8	1.5490 (18)
C1—C2	1.356 (2)		
C5—N1—C1	122.40 (12)	N2—C5—N1	118.49 (12)
C5—N1—H1B	122.1 (12)	N2—C5—C4	123.85 (12)
C1—N1—H1B	115.5 (12)	N1—C5—C4	117.67 (12)
C5—N2—H2C	118.0 (12)	C3—C6—H6A	109.5
C5—N2—H2B	121.1 (11)	C3—C6—H6B	109.5
H2C—N2—H2B	120.5 (16)	H6A—C6—H6B	109.5
C2—C1—N1	120.62 (12)	C3—C6—H6C	109.5
C2—C1—H1A	119.7	H6A—C6—H6C	109.5
N1—C1—H1A	119.7	H6B—C6—H6C	109.5
C1—C2—C3	119.61 (12)	O1—C7—O2	129.54 (12)
C1—C2—H2A	120.2	O1—C7—C8	115.80 (11)
C3—C2—H2A	120.2	O2—C7—C8	114.62 (11)
C4—C3—C2	118.79 (12)	F1—C8—F3	107.24 (12)
C4—C3—C6	121.75 (12)	F1—C8—F2	106.89 (11)
C2—C3—C6	119.46 (12)	F3—C8—F2	106.54 (10)
C3—C4—C5	120.90 (12)	F1—C8—C7	113.06 (11)
C3—C4—H4A	119.5	F3—C8—C7	112.88 (11)
C5—C4—H4A	119.5	F2—C8—C7	109.85 (11)
C5—N1—C1—C2	−0.3 (2)	C3—C4—C5—N2	179.68 (13)
N1—C1—C2—C3	−0.1 (2)	C3—C4—C5—N1	−0.10 (19)
C1—C2—C3—C4	0.5 (2)	O1—C7—C8—F1	18.42 (18)
C1—C2—C3—C6	−179.60 (13)	O2—C7—C8—F1	−163.72 (12)
C2—C3—C4—C5	−0.37 (19)	O1—C7—C8—F3	140.38 (12)
C6—C3—C4—C5	179.73 (12)	O2—C7—C8—F3	−41.76 (17)

C1—N1—C5—N2	−179.33 (12)	O1—C7—C8—F2	−100.87 (14)
C1—N1—C5—C4	0.46 (19)	O2—C7—C8—F2	76.99 (14)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*B*···O2	0.952 (19)	1.82 (2)	2.7724 (14)	177.4 (18)
N2—H2*C*···O1	0.901 (18)	1.938 (19)	2.8376 (15)	176.3 (17)
N2—H2*B*···O2^{i}	0.923 (18)	2.055 (18)	2.8946 (15)	150.5 (15)

Symmetry code: (i) −*x*+1, *y*−1/2, −*z*+3/2.