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2-Amino-4-methoxy-6-methylpyrimidin-1-ium trifluoroacetate

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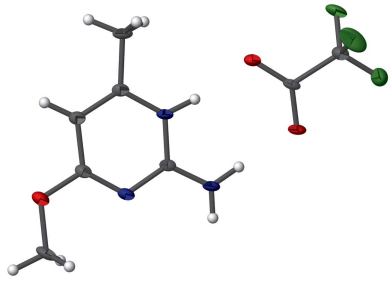
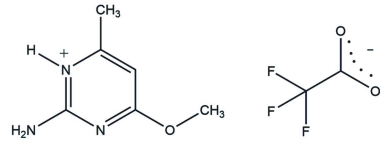
Structural data: full structural data are available from iucrdata.iucr.org

In the title molecular salt, $C_6H_{10}N_3O^+\cdot C_2F_3O_2^-$, the pyrimidinium cation is essentially planar, with a maximum deviation of 0.042 (3) Å for all non-H atoms. In the crystal, the cations and anions are linked *via* N—H···O hydrogen bonds, forming a centrosymmetric 2 + 2 aggregate with $R_2^2(8)$ and $R_4^2(8)$ ring motifs. These motifs are further linked through a pair of C—H···O hydrogen bonds into a supramolecular tape along the [101] direction.

3D view



Chemical scheme



Structure description

Pyrimidine and aminopyrimidine derivatives are biologically very important compounds and they occur in nature as components of nucleic acids such as cytosine, uracil and thymine. Pyrimidine derivatives are very important molecules in biology and have many applications in the areas of pesticide and pharmaceutical agents (Condon *et al.*, 1993). For example, imazosulfuron, ethirmol and mepanipyrim have been commercialized as agrochemicals (Maeno *et al.*, 1990). Pyrimidine derivatives have also been developed as antiviral agents, such as AZT, which is the most widely used anti-AIDS drug (Gilchrist, 1997). Trifluoroacetic acid is a very strong carboxylic acid, easily volatile and used for protein purification. An example of the crystal structure of a trifluoroacetate salt has been reported (Rodrigues *et al.*, 2001). In order to study potential hydrogen-bonding interactions, the crystal structure determination of the title compound was carried out.

The molecular structure of the title molecular salt is illustrated in Fig. 1. The proton transfers from the one of the carboxyl group oxygen atoms (O2) to atom N2 of the cation resulted in the widening of C3—N2—C4 angle of the pyrimidinium ring to 121.9 (2)°,

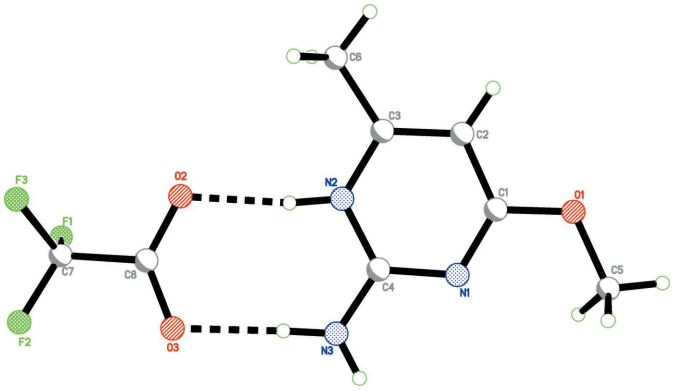


Figure 1
The molecular structure of the title compound, showing the atom labelling and 50% probability displacement ellipsoids. The N—H···O hydrogen bonds are shown as dashed lines (see Table 1).

compared to the corresponding angle of 116.01 (18)° in neutral 2-amino-4-methoxy-6-methylpyrimidine (Glidewell *et al.*, 2003). The cation is essentially planar, with a maximum deviation of 0.042 (3) Å for atom C5.

In the crystal, Fig. 2, the protonated N2 atom and the 2-amino group (N3) are hydrogen bonded to the carboxylate oxygen atoms (O2 and O3) *via* a pair of intermolecular N2—H1*N*2···O2 and N3—H2*N*3···O3 hydrogen bonds, forming an $R_2^2(8)$ ring motif. These motifs are linked by pairs of N3—H1*N*3···O3^{i} hydrogen bonds (Table 1), to produce a *DDAA* array (where *D* is a hydrogen-bond donor and *A* is a hydrogen-bond acceptor) of four hydrogen bonds. This set of fused rings can be represented by the graph-set notations $R_2^2(8)$, $R_4^2(8)$ and $R_2^2(8)$. This type of motif has been reported in the crystal structures of trimethoprim hydrogen glutarate (Robert *et al.*, 2001) and 2-amino-6-methylpyridinium 3-chlorobenzoate (Thanigaimani *et al.*, 2013). These arrays are further interlinked with a neighboring array through a pair of C2—H2*A*···O1^{ii} hydrogen bonds (Table 1 and Fig. 2), leading to the formation of hydrogen-bonded supramolecular tapes propagating along [101].

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H1*N*3···O3^{i}	0.86 (4)	2.05 (4)	2.822 (3)	148 (3)
N3—H2*N*3···O3	0.90 (4)	1.88 (5)	2.782 (4)	178 (5)
N2—H1*N*2···O2	0.90 (4)	1.86 (4)	2.758 (3)	170 (4)
C2—H2*A*···O1^{ii}	0.95	2.58	3.514 (4)	168

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_6H_{10}N_3O^+\cdot C_2F_3O_2^-$
M_r	253.19
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	100
a, *b*, *c* (Å)	4.8087 (2), 11.0283 (5), 11.1135 (5)
α, β, γ (°)	108.704 (3), 96.174 (3), 100.533 (3)
V (Å^3)	540.03 (4)
Z	2
Radiation type	Mo *K*α
μ (mm^{-1})	0.15
Crystal size (mm)	0.37 × 0.21 × 0.07
Data collection	
Diffractometer	Bruker SMART APEXII CCD area-detector
Absorption correction	Multi-scan (*SADABS*; Bruker, 2009)
T_{min}, T_{max}	0.946, 0.989
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	8256, 2467, 1674
R_{int}	0.060
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.649
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.065, 0.245, 1.08
No. of reflections	2467
No. of parameters	168
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.40, −0.43

Computer programs: *APEX2* and *SAINT* (Bruker, 2009), *SHELXS97*, *SHELXL97* and *SHELXTL* (Sheldrick, 2008) and *PLATON* (Spek, 2009).

Synthesis and crystallization

To a hot methanol solution (20 ml) of 2-amino-4-methoxy-6-methylpyrimidine (69 mg, Aldrich) a few drops of trifluoroacetic acid were added. The solution was warmed over a heating magnetic-stirrer hotplate for a few minutes. The resulting solution was allowed to cool slowly at room temperature and crystals of the title compound appeared after a few days.

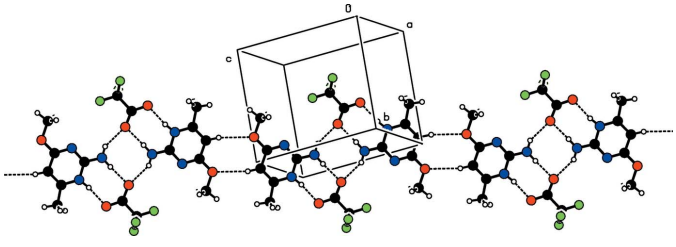


Figure 2
The crystal packing of the title compound, viewed along the *a* axis. H atoms not involved in the hydrogen bonds (dashed lines; see Table 1) have been omitted for clarity.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The N-bound H atoms were located in a difference Fourier map and freely refined.

Acknowledgements

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full crystallographic data

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Crystal data

$C_6H_{10}N_3O^+·C_2F_3O_2^-$
M_r = 253.19
Triclinic, $P\overline{1}$
Hall symbol: -P 1
a = 4.8087 (2) Å
b = 11.0283 (5) Å
c = 11.1135 (5) Å
α = 108.704 (3)°
β = 96.174 (3)°
γ = 100.533 (3)°
V = 540.03 (4) Å^3
Z = 2
$F(000)$ = 260
D_x = 1.557 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 2385 reflections
θ = 2.3–28.6°
μ = 0.15 mm^{-1}
T = 100 K
Plate, colourless
0.37 × 0.21 × 0.07 mm

Data collection

Bruker SMART APEXII CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
T_{min} = 0.946, T_{max} = 0.989
8256 measured reflections
2467 independent reflections
1674 reflections with $I > 2\sigma(I)$
R_{int} = 0.060
θ_{max} = 27.5°, θ_{min} = 2.0°
h = −6→6
k = −14→14
l = −14→14

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.065
$wR(F^2)$ = 0.245
S = 1.08
2467 reflections
168 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
$w = 1/[\sigma^2(F_o^2) + (0.1439P)^2 + 0.1968P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.40 e Å^{-3}
$\Delta\rho_{min}$ = −0.43 e Å^{-3}

Special details

Experimental. The crystal was placed in the cold stream of an Oxford Cryosystems Cobra open-flow nitrogen cryostat operating at 100.0 (1) K.

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 $F^2 > 2\text{sigma}(F^2)$ 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}
O1	1.4551 (4)	1.1091 (2)	0.17382 (19)	0.0228 (5)
N1	1.1022 (5)	1.0528 (2)	0.2807 (2)	0.0167 (5)
N2	0.7855 (5)	0.8428 (2)	0.1855 (2)	0.0163 (5)
N3	0.7455 (6)	0.9851 (3)	0.3832 (2)	0.0195 (6)
C1	1.2280 (6)	1.0222 (3)	0.1804 (3)	0.0158 (6)
C2	1.1430 (6)	0.9018 (3)	0.0739 (3)	0.0179 (6)
H2A	1.2385	0.8853	0.0017	0.021*
C3	0.9158 (6)	0.8112 (3)	0.0812 (3)	0.0171 (6)
C4	0.8787 (6)	0.9604 (3)	0.2842 (2)	0.0147 (6)
C5	1.5516 (7)	1.2318 (3)	0.2847 (3)	0.0251 (7)
H5A	1.7297	1.2834	0.2738	0.038*
H5B	1.5865	1.2115	0.3639	0.038*
H5C	1.4031	1.2825	0.2907	0.038*
C6	0.7968 (7)	0.6779 (3)	−0.0186 (3)	0.0230 (7)
H6A	0.5868	0.6619	−0.0380	0.035*
H6B	0.8501	0.6110	0.0140	0.035*
H6C	0.8753	0.6731	−0.0974	0.035*
F1	0.1552 (5)	0.49986 (19)	0.3587 (2)	0.0416 (6)
F2	−0.1411 (5)	0.6237 (2)	0.4158 (2)	0.0436 (6)
F3	−0.1740 (4)	0.50887 (18)	0.21656 (18)	0.0311 (5)
O2	0.3283 (4)	0.66321 (19)	0.20575 (18)	0.0214 (5)
O3	0.2727 (5)	0.8038 (2)	0.39445 (19)	0.0243 (5)
C7	0.0153 (7)	0.5820 (3)	0.3252 (3)	0.0223 (7)
C8	0.2262 (6)	0.6949 (3)	0.3065 (3)	0.0159 (6)
H1N3	0.807 (7)	1.059 (4)	0.446 (4)	0.022 (8)*
H2N3	0.592 (9)	0.925 (4)	0.385 (4)	0.035 (10)*
H1N2	0.628 (8)	0.792 (4)	0.197 (3)	0.023 (9)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0223 (11)	0.0158 (11)	0.0236 (11)	−0.0036 (8)	0.0021 (9)	0.0031 (9)
N1	0.0157 (12)	0.0118 (11)	0.0180 (11)	0.0001 (9)	−0.0016 (9)	0.0020 (9)
N2	0.0177 (13)	0.0098 (11)	0.0156 (11)	0.0005 (9)	−0.0003 (9)	−0.0010 (9)

N3	0.0196 (13)	0.0110 (12)	0.0194 (12)	−0.0012 (10)	0.0021 (10)	−0.0034 (10)
C1	0.0147 (14)	0.0122 (13)	0.0190 (13)	0.0029 (11)	−0.0009 (10)	0.0049 (11)
C2	0.0174 (14)	0.0161 (14)	0.0161 (13)	0.0017 (11)	−0.0003 (11)	0.0024 (11)
C3	0.0159 (14)	0.0160 (14)	0.0150 (12)	0.0021 (11)	−0.0024 (10)	0.0020 (11)
C4	0.0154 (13)	0.0111 (13)	0.0155 (12)	0.0035 (10)	−0.0015 (10)	0.0027 (10)
C5	0.0221 (16)	0.0120 (14)	0.0332 (16)	−0.0043 (11)	−0.0017 (13)	0.0039 (12)
C6	0.0294 (17)	0.0128 (14)	0.0177 (13)	0.0001 (12)	−0.0007 (12)	−0.0027 (11)
F1	0.0434 (13)	0.0260 (11)	0.0592 (14)	0.0030 (9)	−0.0028 (10)	0.0266 (10)
F2	0.0482 (14)	0.0313 (11)	0.0390 (12)	−0.0079 (10)	0.0241 (10)	0.0000 (9)
F3	0.0276 (11)	0.0195 (9)	0.0308 (10)	−0.0099 (8)	−0.0033 (8)	−0.0007 (8)
O2	0.0251 (12)	0.0133 (10)	0.0187 (10)	−0.0016 (8)	0.0035 (8)	−0.0006 (8)
O3	0.0291 (12)	0.0107 (10)	0.0226 (11)	−0.0026 (8)	0.0057 (9)	−0.0045 (8)
C7	0.0225 (15)	0.0172 (15)	0.0206 (14)	−0.0018 (12)	0.0019 (12)	0.0022 (12)
C8	0.0158 (14)	0.0085 (12)	0.0186 (13)	−0.0004 (10)	−0.0033 (10)	0.0019 (10)

Geometric parameters (Å, º)

O1—C1	1.340 (3)	C3—C6	1.493 (4)
O1—C5	1.464 (4)	C5—H5A	0.9800
N1—C1	1.305 (3)	C5—H5B	0.9800
N1—C4	1.353 (3)	C5—H5C	0.9800
N2—C3	1.354 (3)	C6—H6A	0.9800
N2—C4	1.362 (3)	C6—H6B	0.9800
N2—H1N2	0.90 (4)	C6—H6C	0.9800
N3—C4	1.311 (3)	F1—C7	1.341 (4)
N3—H1N3	0.86 (4)	F2—C7	1.335 (3)
N3—H2N3	0.90 (4)	F3—C7	1.344 (3)
C1—C2	1.422 (4)	O2—C8	1.244 (3)
C2—C3	1.368 (4)	O3—C8	1.244 (3)
C2—H2A	0.9500	C7—C8	1.540 (4)
C1—O1—C5	116.5 (2)	O1—C5—H5B	109.5
C1—N1—C4	116.7 (2)	H5A—C5—H5B	109.5
C3—N2—C4	121.9 (2)	O1—C5—H5C	109.5
C3—N2—H1N2	125 (2)	H5A—C5—H5C	109.5
C4—N2—H1N2	113 (2)	H5B—C5—H5C	109.5
C4—N3—H1N3	119 (2)	C3—C6—H6A	109.5
C4—N3—H2N3	120 (2)	C3—C6—H6B	109.5
H1N3—N3—H2N3	121 (3)	H6A—C6—H6B	109.5
N1—C1—O1	119.1 (2)	C3—C6—H6C	109.5
N1—C1—C2	125.2 (3)	H6A—C6—H6C	109.5
O1—C1—C2	115.7 (2)	H6B—C6—H6C	109.5
C3—C2—C1	116.1 (2)	F2—C7—F1	107.4 (2)
C3—C2—H2A	121.9	F2—C7—F3	106.1 (2)
C1—C2—H2A	121.9	F1—C7—F3	106.5 (2)
N2—C3—C2	118.7 (2)	F2—C7—C8	113.2 (2)
N2—C3—C6	116.6 (2)	F1—C7—C8	111.1 (2)
C2—C3—C6	124.7 (2)	F3—C7—C8	112.1 (2)

N3—C4—N1	119.5 (2)	O2—C8—O3	129.4 (2)
N3—C4—N2	119.2 (3)	O2—C8—C7	114.8 (2)
N1—C4—N2	121.3 (2)	O3—C8—C7	115.8 (2)
O1—C5—H5A	109.5		
C4—N1—C1—O1	−178.3 (2)	C1—N1—C4—N3	179.4 (3)
C4—N1—C1—C2	2.0 (4)	C1—N1—C4—N2	−1.9 (4)
C5—O1—C1—N1	2.3 (4)	C3—N2—C4—N3	−179.4 (3)
C5—O1—C1—C2	−178.0 (2)	C3—N2—C4—N1	1.8 (4)
N1—C1—C2—C3	−1.9 (4)	F2—C7—C8—O2	−164.9 (3)
O1—C1—C2—C3	178.4 (2)	F1—C7—C8—O2	74.2 (3)
C4—N2—C3—C2	−1.7 (4)	F3—C7—C8—O2	−44.9 (4)
C4—N2—C3—C6	178.6 (2)	F2—C7—C8—O3	16.0 (4)
C1—C2—C3—N2	1.6 (4)	F1—C7—C8—O3	−105.0 (3)
C1—C2—C3—C6	−178.7 (3)	F3—C7—C8—O3	135.9 (3)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H1*N*3···O3^{i}	0.86 (4)	2.05 (4)	2.822 (3)	148 (3)
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