

## 2,4-Diamino-6-methyl-1,3,5-triazin-1-ium trifluoroacetate

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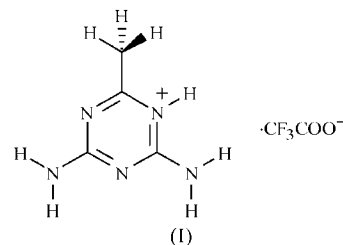
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Crystals of the title compound,  $C_4H_8N_5^+ \cdot C_2F_3O_2^-$ , are built up of singly protonated 2,4-diamino-6-methyl-1,3,5-triazin-1-ium cations and trifluoroacetate anions. The  $CF_3$  group of the anion is disordered. The oppositely charged ions interact *via* almost linear  $N-H \cdots O$  hydrogen bonds, forming a  $CF_3COO^- \cdots C_4H_8N_5^+$  unit. Two units related by an inversion centre interact through a pair of  $N-H \cdots N$  hydrogen bonds, forming planar  $(CF_3COO^- \cdots C_4H_8N_5^+ \cdots C_4H_8N_5^+ \cdots CF_3COO^-)$  aggregates that are linked by a pair of  $N-H \cdots O$  hydrogen bonds into chains running along the *c* axis.

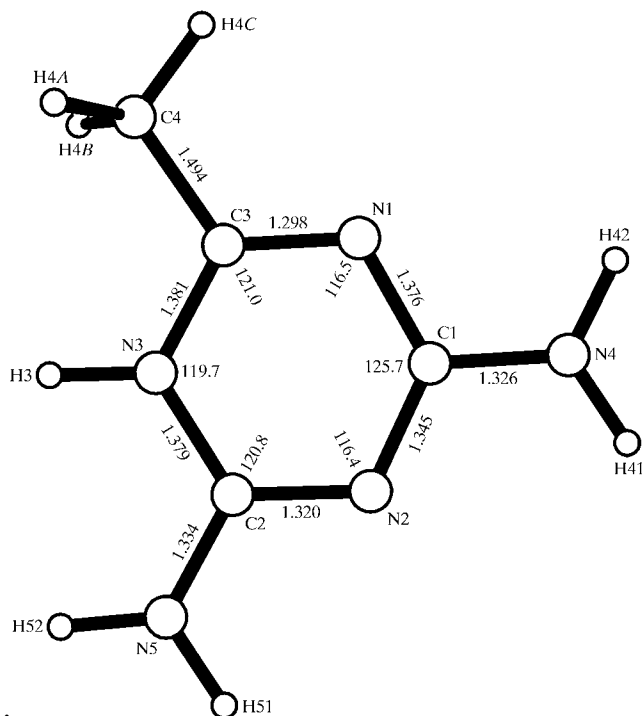
## Comment

The present study is a continuation of our investigations on the characterization of the hydrogen-bonding system formed by triazine derivatives in the solid state (Perpétuo & Janczak, 2005; Janczak & Kubiak, 2005). Triazine and its derivatives, especially 2,4,6-triamino-1,3,5-triazine, *i.e.* melamine and its organic and inorganic complexes or salts, can develop well defined noncovalent supramolecular architectures *via* multiple hydrogen bonds since they contain components of complementary arrays of hydrogen-bonding sites (Desiraju, 1990; MacDonald & Whitesides, 1994; Row, 1999; Krische & Lehn, 2000; Sherrington & Taskinen, 2001). Our interest in these types of compounds arises from the possibility of obtaining materials for nonlinear optics (Janczak & Perpétuo, 2002; Marchewka *et al.* 2003; Perpétuo & Janczak, 2006). In order to expand the understanding of the solid-state physical-organic chemistry of compounds that form multiple  $N-H \cdots N$  and  $N-H \cdots O$  hydrogen-bonding systems, we present here the solid-state structure of 2,4-diamino-6-methyl-1,3,5-triazin-1-ium trifluoroacetate, (I), and compare the results with the structure predicted for isolated oppositely charged units by *ab initio* fully optimized geometry calculations at the B3LYP/6-31G(*d*) level (Frisch *et al.*, 1998). The molecular orbital (MO) calculations were carried out on isolated ions corresponding to the gas phase, and results are shown in Fig. 1.

The asymmetric unit of (I) consists of a 2,4-diamino-6-methyl-1,3,5-triazin-1-ium cation, singly protonated at one of the ring N atoms located between the methyl and amine

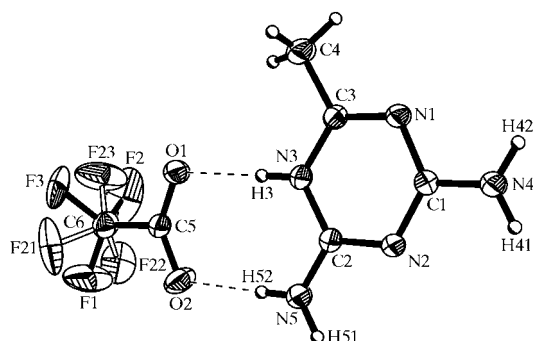


groups, and a trifluoroacetate anion, which shows disorder of the  $CF_3$  group (Fig. 2). The two oppositely charged units of (I) interact *via* a pair of almost linear  $N-H \cdots O$  hydrogen bonds with a graph-set motif of  $R_2^2(8)$ , which is one of the 24 most frequently observed bimolecular cyclic hydrogen-bonded units in organic crystal structures (Steiner, 2002; Stanley *et al.*, 2002; Raj *et al.*, 2003). The triazine ring is essentially planar [the deviation of the N and C atoms from the mean plane is smaller than 0.0256 (2) Å], but exhibits significant distortion from the ideal hexagonal form (Table 1). The internal C—N—C angle at the protonated N atom in the ring is greater than the other two C—N—C angles within the ring. This distortion results from the steric effect of the lone-pair electrons, predicted by the valence-shell electron-pair repulsion theory (Gillespie, 1963, 1992). According to the theory, the lone pair of electrons on the ring N atoms occupies a wider region than the bonding pair NH, causing the internal angle at the latter to be greater than that at the nonprotonated ring N atoms. As a result of the protonation, the internal N—C—N angle invol-



**Figure 1**  
Results of the optimized molecular-orbital calculations (Å, °) for the 2,4-diamino-6-methyl-1,3,5-triazin-1-ium cation.

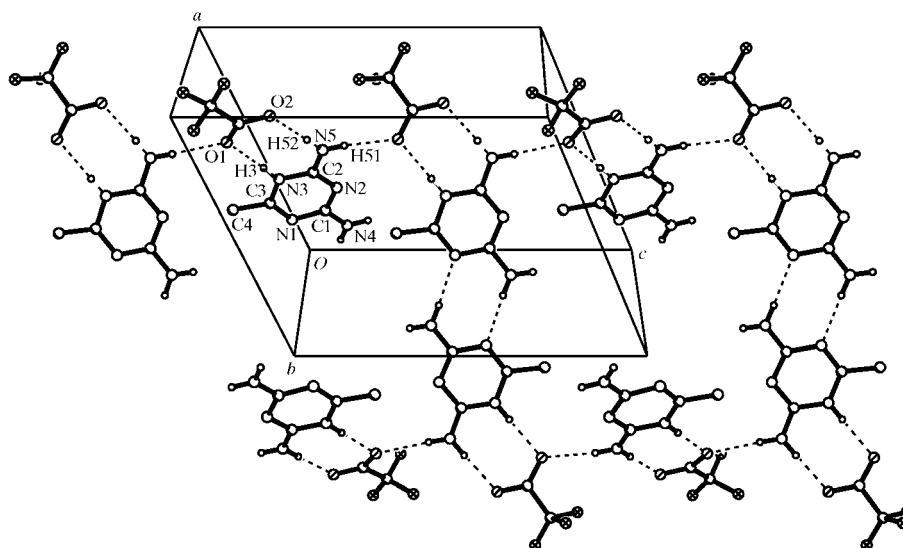
ving only nonprotonated N atoms is significantly greater than the remaining two N—C—N angles involving both protonated and nonprotonated N atoms (Table 1). The *ab initio* gas-phase geometry calculated for the isolated singly protonated 2,4-diamino-6-methyl-1,3,5-triazin-1-ium cation (Fig. 1) shows quite similar correlation between the internal C—N—C and N—C—N angles within the ring. Thus the ring distortions result mainly from the protonation and, to a lesser degree, from the hydrogen-bonding system, interionic interactions and the crystal-packing forces. Protonation of the triazine ring also disturbs the C—N bonds within the ring when compared with the neutral 2,4-diamino-6-methyl-1,3,5-triazine molecule (Aoki *et al.*, 1994). A search of Cambridge Structural Database (Version 5.27; Allen, 2002) for crystals containing the protonated 2,4-diamino-6-methyl-1,3,5-triazine residue yields only one structure (Wijaya *et al.*, 2004), which shows very similar ring distortions to those found in the present structure.



**Figure 2**  
A view of (I), showing displacement ellipsoids at the 50% probability level and H atoms as spheres of arbitrary radii. Hydrogen bonds are drawn as dashed lines. The two orientations of the CF<sub>3</sub> group (each 50% occupancy) are shown as solid and open bonds.

The trifluoroacetate anion exhibits disorder, caused by the rotation of the CF<sub>3</sub> group around the single C—C bond. The conformation of the trifluoroacetate ion in the crystal is described by the O1—C5—C6—F1 torsion angle of  $-174.1(1)^\circ$  (one rotational conformer) and by the O1—C5—C6—F21 torsion angle of  $-100.4(1)^\circ$  (the second rotational conformer). MO calculations performed for the isolated trifluoroacetate ion show a minimum on the potential energy surface (PES) for a conformation quite similar to the first rotational conformer in the crystal (the O1—C5—C6—F1 torsion angle is  $-175.2^\circ$ ). The other minima on the PES appear when the CF<sub>3</sub> group is rotated by about 60 or 120°; however, these conformations are different from the second rotational conformer present in the crystal. Undoubtedly, this results from the interaction with the neighbouring cations, the N—H···F hydrogen bond and the crystal-packing forces. The C—O bond lengths in the carboxylate group are intermediate between single  $Csp^2$ —O (1.308–1.320 Å) and double  $Csp^2=O$  bond values (1.214–1.224 Å; Allen *et al.* 1987), indicating delocalization of the charge onto both O atoms of the COO<sup>−</sup> group. The average C—F bond length in the crystal of 1.287 Å is slightly shorter than those for the gas phase obtained by MO calculations (1.334 Å; Frisch *et al.*, 1998). The X-ray O—C—O angle in the COO<sup>−</sup> group is smaller by about 3.5° than that in the *ab initio* MO calculations (132.88°). Thus, in the crystal, the repulsive interactions between the O atoms of COO<sup>−</sup> as well as the steric effects of the lone pair of electrons on both O atoms are decreased as a result of the formation of the N—H···O hydrogen bonds.

An extensive set of hydrogen bonds (Table 2) links the components of (I) into a continuous framework superstructure. Each 2,4-diamino-6-methyl-1,3,5-triazin-1-ium residue is involved in seven hydrogen bonds; in five of these it acts as a donor and in the remaining two as an acceptor. One



**Figure 3**  
A view of the crystal packing in (I), showing the hydrogen-bonded (CF<sub>3</sub>COO<sup>−</sup>···C<sub>4</sub>H<sub>8</sub>N<sub>5</sub><sup>+</sup>···C<sub>4</sub>H<sub>8</sub>N<sub>5</sub><sup>+</sup>···CF<sub>3</sub>COO<sup>−</sup>) aggregates that interact *via* N—H···O hydrogen bonds, forming chains parallel to the *c* axis. H atoms of methyl groups have been omitted for clarity.

pair of almost linear N—H···N hydrogen bonds links inversion-related 2,4-diamino-6-methyl-1,3,5-triazin-1-ium cations into a planar dimer. These dimers interact with two CF<sub>3</sub>COO<sup>−</sup> anions *via* N—H···O hydrogen bonds, forming almost planar (CF<sub>3</sub>COO<sup>−</sup>···C<sub>4</sub>H<sub>8</sub>N<sub>5</sub><sup>+</sup>···C<sub>4</sub>H<sub>8</sub>N<sub>5</sub><sup>+</sup>···CF<sub>3</sub>COO<sup>−</sup>) aggregates (Fig. 3). These aggregates are alternately located in the crystal almost parallel to the (120) and (1 $\bar{2}$ 0) planes. Additionally, the aggregates interact *via* N—H···O hydrogen bonds between the amine (N5) group and atom O2 of the COO<sup>−</sup> group (Fig. 3). Both O atoms of the COO<sup>−</sup> group act as acceptors in two hydrogen bonds. The ring N atom in the position *para* to the methyl group is not involved in any hydrogen bonds.

## Experimental

2,4-Diamino-6-methyl-1,3,5-triazine (98%) was resolved in 10% CF<sub>3</sub>COOH. After several days, colourless crystals had formed, which proved to be suitable for single-crystal X-ray diffraction analysis.

### Crystal data

C <sub>4</sub> H <sub>8</sub> N <sub>5</sub> <sup>+</sup> ·C <sub>2</sub> F <sub>3</sub> O <sub>2</sub> <sup>−</sup>	$V = 1027.5 (4) \text{ \AA}^3$
$M_r = 239.17$	$Z = 4$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 10.384 (2) \text{ \AA}$	$\mu = 0.15 \text{ mm}^{-1}$
$b = 8.187 (1) \text{ \AA}$	$T = 295 (2) \text{ K}$
$c = 13.013 (3) \text{ \AA}$	$0.32 \times 0.26 \times 0.22 \text{ mm}$
$\beta = 111.75 (2)^\circ$	

### Data collection

Kuma KM-4 CCD area-detector diffractometer	12223 measured reflections
Absorption correction: analytical, face-indexed (SHELXTL; Sheldrick, 1990)	2563 independent reflections
$T_{\min} = 0.953$ , $T_{\max} = 0.964$	1548 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.026$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.053$	177 parameters
$wR(F^2) = 0.165$	H-atom parameters constrained
$S = 1.11$	$\Delta\rho_{\text{max}} = 0.28 \text{ e \AA}^{-3}$
2563 reflections	$\Delta\rho_{\text{min}} = -0.25 \text{ e \AA}^{-3}$

**Table 1**

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

N1—C3	1.299 (2)	C2—N3	1.359 (2)
N1—C1	1.372 (2)	N3—C3	1.356 (2)
C1—N4	1.316 (2)	C3—C4	1.485 (2)
C1—N2	1.330 (2)	O1—C5	1.239 (2)
N2—C2	1.332 (2)	O2—C5	1.222 (2)
C2—N5	1.312 (2)	C5—C6	1.542 (3)
C3—N1—C1	115.75 (14)	C3—N3—C2	119.59 (16)
N2—C1—N1	125.66 (15)	N1—C3—N3	121.78 (15)
C1—N2—C2	116.02 (14)	O2—C5—O1	129.17 (18)
N2—C2—N5	120.76 (15)		

H atoms were positioned geometrically and treated as riding, with  $U_{\text{iso}}(\text{H})$  values of  $1.2U_{\text{eq}}(\text{N})$  or  $1.5U_{\text{eq}}(\text{C})$ .

**Table 2**

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N3—H3···O1	0.86	1.98	2.836 (2)	179
N5—H52···O2	0.86	1.94	2.799 (2)	178
N4—H41···O2 <sup>i</sup>	0.86	2.24	2.935 (2)	138
N4—H42···N1 <sup>ii</sup>	0.86	2.17	3.024 (2)	173
N5—H51···O1 <sup>iii</sup>	0.86	2.12	2.974 (2)	172
N5—H51···F23 <sup>iii</sup>	0.86	2.55	3.027 (7)	116

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

Data collection: *KM-4 CCD Software* (Kuma, 2004); cell refinement: *KM-4 CCD Software*; data reduction: *KM-4 CCD Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1990); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA3075). Services for accessing these data are described at the back of the journal.

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