

2,4,6-Triamino-1,3,5-triazin-1-ium 4-methylbenzenesulfonate monohydrate

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The asymmetric unit of the new title melaminium salt, $C_3H_7N_6^+ \cdot C_7H_7O_3S^- \cdot H_2O$, comprises a melaminium cation, a 4-methylbenzenesulfonate anion and a water molecule. Extensive intermolecular interactions, including hydrogen bonding, feature in the crystal structure.

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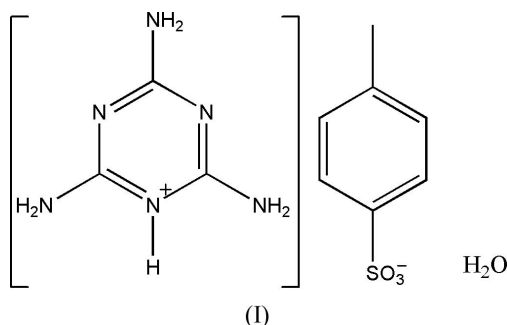
Comment

Recently, the solid-state physical–organic chemistry of melamine has attracted great interest. In their crystal structures, many hydrogen-bond interactions between melaminium cations and various anions have been established (Janczak & Perpétuo, 2001*a,b,c,d*, 2002*a,b*, 2003, 2004; Perpétuo & Janczak, 2002; Zhang *et al.*, 2004; Choi *et al.*, 2004). We present here the results of the crystal structure analysis of another ion-pair adduct having monoprotonated melaminium, 4-methylbenzenesulfonate and solvent water, (I) (Fig. 1 and Table 1).

Key indicators

Single-crystal X-ray study
 $T = 293$ K
 Mean $\sigma(C-C) = 0.004$ Å
 R factor = 0.046
 wR factor = 0.136
 Data-to-parameter ratio = 12.4

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.



The six-membered aromatic rings of monoprotonated melaminium exhibit significant distortions from the ideal hexagonal form. Thus, the internal C–N–C angle at the protonated N atom (C1–N1–C2) is significantly greater than the other two ring angles (*i.e.* C2–N2–C3 and C1–N3–C3), and the internal N2–C3–N3 angle, containing only non-protonated N atoms, is greater than either of the remaining N–C–N angles containing both protonated and non-protonated N atoms (Table 1). This feature of the structure is similar to the other reported monoprotonated melaminium cations (Janczak & Perpétuo, 2001*a,c,d*, 2002*b*, 2003, 2004; Perpétuo & Janczak, 2002; Zhang *et al.*, 2004; Choi *et al.*, 2004). In the 4-methylbenzenesulfonate anion, the O–S bond lengths are in the range 1.426 (2)–1.433 (2) Å and are slightly shorter than those [1.4439 (13)–1.4670 (12) Å] of the *p*-hydroxybenzenesulfonate anion in melaminium bis(4-hydroxybenzenesulfonate) dihydrate (Janczak & Perpétuo, 2001*b*).

Both charged residues and the water molecules interact extensively by a combination of ionic and hydrogen bonds (Table 2), as well as π – π interactions, as shown in Figs. 2 and 3. Neighboring melaminium residues are interconnected by

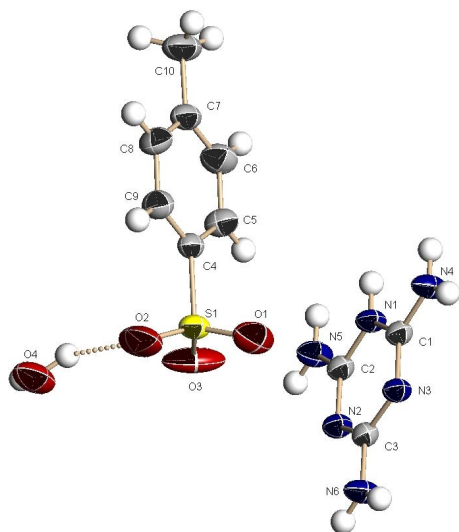


Figure 1
The structure of the title compound, with displacement ellipsoids drawn at the 50% probability level for non-H atoms. The dotted line represents a hydrogen bond.

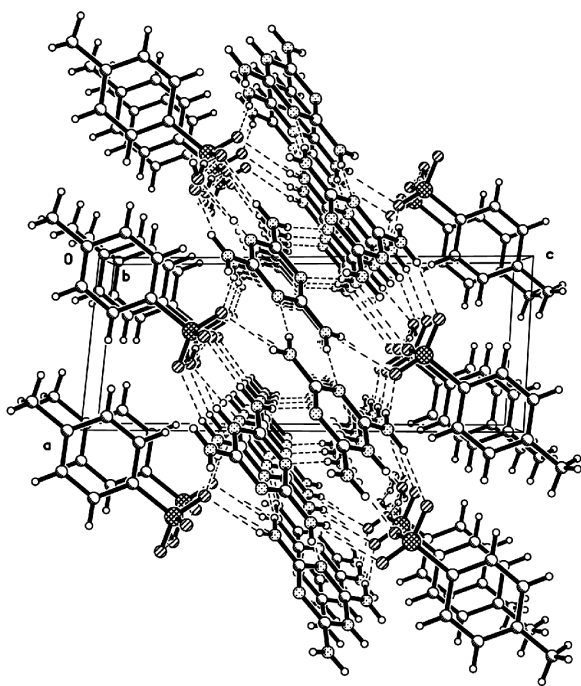


Figure 2
The packing of the title compound, viewed down the *b* axis, highlighting the stacking of the sheets along the *c* direction. Dashed lines indicate hydrogen bonds.

double N—H···N hydrogen bonds, forming a zigzag chain in the (114) plane extending in the **b** direction. The distance between successive zigzag chains is about 3.4 Å, affording π – π interactions and leading to the formation of layers. The zigzag layers are interspersed by layers comprising 4-methylbenzenesulfonate anions and water molecules so as to construct a sheet arrangement stacked along the *c* axis. Layers are held together by seven different hydrogen bonds, namely four N—H···O hydrogen bonds between four different SO₃ residues and four different melaminium amino groups, two

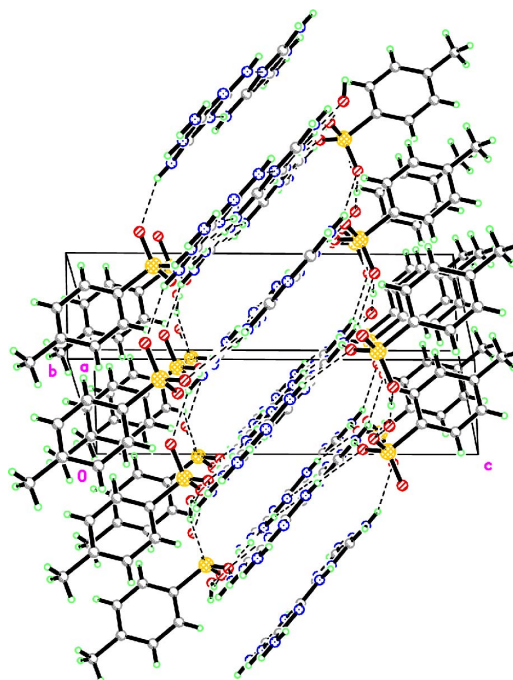


Figure 3
The packing of the title compound, highlighting the inclination between layers. Dashed lines indicate hydrogen bonds.

O—H···O hydrogen bonds between a water molecule and two different SO₃ residues, and finally another N—H···O hydrogen bond between the N_{ring}—H H atom and a water molecule (Table 2).

The plane of the melaminium residue is inclined at an angle of 65.9 (1)° to the plane of the 4-methylbenzenesulfonate ring, which is slightly smaller than that [72.2 (1)°] in melaminium bis(4-hydroxybenzenesulfonate) dihydrate (Janczak & Perpétuo, 2001*b*).

Experimental

Hot solutions of melamine and 4-methylbenzenesulfonic acid in a 1:1 molar ratio were mixed and, after allowing the mixture to stand at room temperature for a few days, suitable colorless crystals for the X-ray diffraction experiment were deposited.

Crystal data

C₃H₇N₆⁺·C₇H₇O₃S[−]·H₂O
M_r = 316.35
 Triclinic, *P* $\bar{1}$
a = 6.413 (2) Å
b = 7.285 (3) Å
c = 15.654 (6) Å
 α = 97.229 (4)°
 β = 92.625 (4)°
 γ = 105.200 (5)°
V = 697.7 (4) Å³

Z = 2
D_x = 1.506 Mg m^{−3}
 Mo *K* α radiation
 Cell parameters from 1979 reflections
 θ = 2.6–26.9°
 μ = 0.26 mm^{−1}
T = 293 (2) K
 Block, colorless
 0.40 × 0.40 × 0.40 mm

Data collection

Bruker SMART 1K CCD area-detector diffractometer
 ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 2000)
T_{min} = 0.903, *T_{max}* = 0.903
 3382 measured reflections

2390 independent reflections
 2072 reflections with *I* > 2 σ (*I*)
R_{int} = 0.016
 θ_{max} = 25.0°
h = −7 → 6
k = −8 → 7
l = −18 → 18

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0813P)^2 + 0.2249P]$
$R[F^2 > 2\sigma(F^2)] = 0.046$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.136$	$(\Delta/\sigma)_{\max} = 0.004$
$S = 1.06$	$\Delta\rho_{\max} = 0.38 \text{ e } \text{\AA}^{-3}$
2390 reflections	$\Delta\rho_{\min} = -0.31 \text{ e } \text{\AA}^{-3}$
192 parameters	Extinction correction: <i>SHELXL97</i>
H-atom parameters constrained	Extinction coefficient: 0.061 (8)

Table 1

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

C1–N4	1.318 (3)	C2–N1	1.361 (3)
C1–N3	1.324 (3)	C3–N6	1.320 (3)
C1–N1	1.358 (3)	C3–N2	1.350 (3)
C2–N5	1.315 (3)	C3–N3	1.355 (3)
C2–N2	1.324 (3)		
N4–C1–N3	120.7 (2)	N2–C2–N1	121.0 (2)
N4–C1–N1	117.8 (2)	N6–C3–N2	117.7 (2)
N3–C1–N1	121.5 (2)	N6–C3–N3	116.0 (2)
N5–C2–N2	121.2 (2)	N2–C3–N3	126.3 (2)
N5–C2–N1	117.8 (2)	C1–N1–C2	120.03 (19)

Table 2

Hydrogen-bonding geometry (\AA , $^\circ$).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1–H1 \cdots O4 ⁱ	0.86	1.83	2.692 (3)	179
O4–H42 \cdots O1 ⁱⁱ	0.85	1.94	2.732 (3)	154
O4–H41 \cdots O2	0.85	2.26	2.906 (4)	133
N6–H6B \cdots N3 ⁱⁱⁱ	0.86	2.20	3.058 (3)	172
N6–H6A \cdots O3 ^{iv}	0.86	2.24	2.885 (3)	132
N5–H5B \cdots O1 ^v	0.86	2.12	2.957 (3)	165
N5–H5A \cdots N2 ^{vi}	0.86	2.19	3.049 (3)	172
N4–H4B \cdots O2 ^{vii}	0.86	2.20	2.989 (3)	153
N4–H4A \cdots O3 ^{viii}	0.86	2.06	2.906 (3)	167

Symmetry codes: (i) $x-1, y-1, z$; (ii) $x, 1+y, z$; (iii) $1-x, -y, 1-z$; (iv) $1-x, 1-y, 1-z$; (v) $x-1, y, z$; (vi) $-x, 1-y, 1-z$; (vii) $x, y-1, z$.

H atoms were placed in calculated positions and allowed to ride on their parent atoms, with $U_{\text{iso}}(\text{H})$ values set at $1.2U_{\text{eq}}(\text{parent atom})$ for aromatic, N- and O-bound H atoms, and $1.5U_{\text{eq}}(\text{parent atom})$ for methyl H atoms. The distances were fixed at $\text{Csp}^2\text{--H} = 0.93 \text{ \AA}$, $\text{Csp}^3\text{--H} = 0.96 \text{ \AA}$, $\text{O--H} = 0.85 \text{ \AA}$ and $\text{N--H} = 0.86 \text{ \AA}$.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL/PC* (Sheldrick, 1999); software used to prepare material for publication: *SHELXTL/PC*.

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