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Melaminium maleate monohydrate

Jan Janczak[a]* and Genivaldo Julio Perpétuo[b]

[a]Institute of Low Temperature and Structure Research, Polish Academy of Sciences, PO Box 1410, 50-950 Wrocław, Poland, and [b]Departamento de Fisica, Instituto de Ciências Exatas e Biológicas, Universidade Federal de Ouro Preto, CEP 35.400-000, Ouro Preto, MG, Brazil
Correspondence e-mail: janczak@int.pan.wroc.pl

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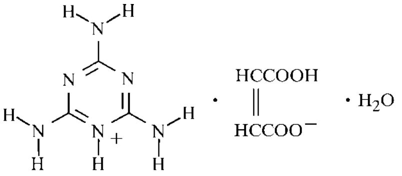
In the title compound, 2,4,6-triamino-1,3,5-triazin-1-ium maleate monohydrate, $C_3H_7N_6^+\cdot C_4H_3O_4^-\cdot H_2O$, containing singly protonated melaminium residues, maleate(1−) anions and water molecules, the components are linked by hydrogen bonds into a three-dimensional framework structure. The melaminium residues are connected by two pairs of N—H···N hydrogen bonds into chains in the form of stacks, with a distance of 3.26 (1) Å between the triazine rings, clearly indicating π–π interactions. The maleate anion contains an intramolecular O—H···O hydrogen bond and the anions interact with the water molecules *via* O—H···O hydrogen bonds, forming zigzag chains, also in the form of stacks, in which the almost-planar maleate anions are separated by 3.26 (1) Å. The experimental geometries of the ions are compared with molecular-orbital calculations of their gas-phase geometries.

Comment

The present study is a continuation of our investigations characterizing the hydrogen-bonding system formed by triazine derivatives in the solid state (Janczak & Perpétuo, 2003). Melamine and its organic and inorganic complexes or salts can develop well defined supramolecular structures *via* multiple hydrogen bonds by self-assembly of components containing complementary arrays of hydrogen-bonding sites (Desiraju, 1990; MacDonald & Whitesides, 1994; Guru Row, 1999; Krische & Lehn, 2000; Sherrington & Taskinen, 2001). In order to expand the understanding of the solid-state physical–organic chemistry of compounds containing multiple N—H···N, N—H···O and O—H···O hydrogen-bonding systems, we present here the solid-state structure of melaminium maleate monohydrate, (I). Additionally, the geometries of both ions are compared with the *ab initio* fully optimized parameters calculated at the HF/6-31G(*d*,*p*) level (*GAUSS*-94; Frisch *et al.*, 1995). The molecular-orbital calculations were carried out on the isolated ions, corresponding to the gas phase, and the results are illustrated in Fig. 1.

The asymmetric unit of (I) consists of a melaminium cation, singly protonated at a ring N atom, a maleate anion and a water molecule (Fig. 2). The six-membered aromatic triazine ring of the singly protonated melaminium residue is almost planar [the deviation of the N and C atoms from the mean plane is less than 0.08 (2) Å], but it exhibits significant distortions from the ideal hexagonal form (Table 1). The internal C—N—C angle at the protonated N atom in the melaminium cation is greater than the other two C—N—C angles within the ring. This is a result of the steric effect of a lone-pair electron, predicted by the valence-shell electron-pair repulsion theory (VSEPR; Gillespie, 1963, 1992). As a result of the protonation of the melamine ring at the one of the three ring N atoms, the internal N—C—N angle involving only non-protonated N atoms is significantly smaller than the N—C—N angles involving both protonated and non-protonated N atoms.



(I)

The *ab initio* optimized geometry calculated for the singly protonated melaminium residue corresponding to the gas phase shows a similar correlation between the C—N—C and N—C—N angles within the ring as that seen in the crystal of (I). Thus, the ring distortion of the singly protonated melaminium residue results mainly from the protonation and, to a lesser degree, from the hydrogen-bonding system and the crystal packing. The C—N bond lengths in the optimized melaminium residue are slightly shorter than those in the crystal. The lengthening of the C—N bonds of the melaminium rings in the crystal is likely to be due to interaction of the π–π clouds of the rings in the stacks, which are separated by 3.26 (1) Å, as well as to the hydrogen-bonding system. A similar correlation between the internal C—N—C and N—C—N angles within the melaminium ring has been reported for the crystals of barbituric acid with melamine (Zerkowski *et al.*, 1994), melaminium phthalate (Janczak & Perpétuo, 2001*a*), melaminium chloride hemihydrate (Janczak & Perpétuo, 2001*b*), bis(melaminium) sulfate dihydrate (Janczak & Perpétuo, 2001*c*), melaminium acetate (Perpétuo & Janczak, 2002), melaminium glutarate monohydrate (Janczak

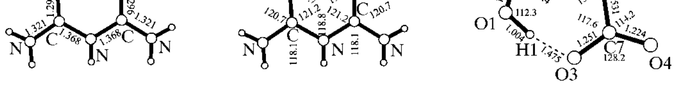


Figure 1
The results of the optimized molecular orbital calculations for (*a*) the melaminium cation and (*b*) the maleate(1−) ion. Bond lengths are given in angstroms (Å) and angles in degrees (°).

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& Perpétuo, 2002*a*), melaminium phosphate (Janczak & Perpétuo, 2002*b*), melaminium citrate (Perpétuo & Janczak, 2003) and melaminium selenate (Marchewka *et al.*, 2003), *i.e.* those singly protonated melaminium salts that have been previously structurally characterized.

An extensive series of hydrogen bonds (Table 2) links the independent components of (I) into a continuous framework structure. Each melaminium residue is involved in nine hydrogen bonds. In seven of these it acts as a donor and in the remaining two it acts as an acceptor. Two pairs of almost-linear N—H···N hydrogen bonds link pairs of melaminium cations, related to one another by inversion centres, to form chains in the form of stacks parallel to [100] (Fig. 3). This chain formation is different from that found in melaminium citrate, where the cations form centrosymmetric hydrogen-bonded dimers (Perpétuo & Janczak, 2003). Within one such stack, the melaminium residues are separated by 3.26 (1) Å. This distance is shorter than that between π-aromatic ring systems (3.4 Å; Pauling, 1960) and indicates strong π–π interactions between the triazine rings of the melaminium moieties within the stack. Five more N—H···O hydrogen bonds (Table 2) link each cation to two maleate anions and two water molecules.

The maleate anion of (I) deviates slightly from the planar conformation predicted by gas-phase molecular-orbital calculations, due to the intermolecular hydrogen-bonding system, which makes the C4—C5—C6—C7 torsion angle 1.7 (1)° and which leads to rotations of the COO$^-$ and COOH groups along the C6—C7 [1.0 (1)°] and C4—C5 [1.1 (1)°] bonds, respectively. This almost-planar conformation of the maleate ion is stabilized by an intramolecular hydrogen bond between atoms O1 and O3, which is confirmed as asymmetric, in agreement with the results of alkene-*cis*-dicarboxylic acids (Hechtfischer *et al.*, 1970), maleic acid (James & Williams, 1974) and several singly dissociated maleate salts (Allen, 2002). The O···O distance of 2.470 (2) Å is shorter than that found in maleic acid (2.502 Å; James & Williams, 1974) and compares well with other singly dissociated maleate salts (Allen, 2002). The intramolecular O1—H···O3 angle is almost linear in the gas phase, while in the crystal it is more bent, possibly due to the intermolecular hydrogen bond.

As revealed by the structure analysis, the ethylenic C5—C6 bond distance in (I) is normal for a simple Csp^2=Csp^2 double bond (Allen *et al.*, 1987), in agreement with the results of our molecular-orbital (MO) calculations. Comparison of the two Csp^2—Csp^2 single bonds of the non-dissociated (C4—C5) and dissociated (C6—C7) carboxyl groups shows that these two bonds are not identical. It is of interest to note that the shorter C4—C5 bond links the non-dissociated carboxyl group, while a longer bond (C6—C7) links the dissociated carboxyl group. 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 on both O atoms of the COO$^-$ group. The longer C—O bond of the carboxylate group is involved in the intramolecular hydrogen bond and this is entirely consistent with the MO calculations.

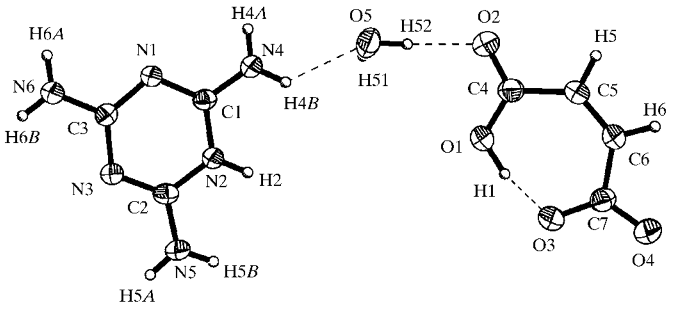

Figure 2
The molecular structure of (I), shown with 50% probability displacement ellipsoids. H atoms are shown as spheres of arbitrary radii.

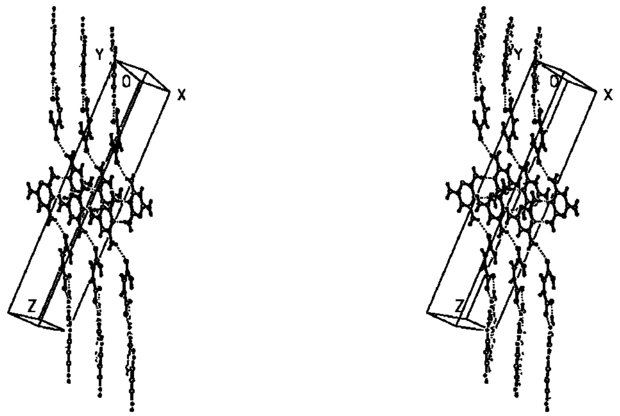

Figure 3
A stereoview of the crystal packing in (I), showing the stacking structure of the hydrogen-bonded melaminium and maleate residues, which stabilizes the N—H···O and O—H···O hydrogen bonds (dashed lines).

The COOH group in (I) shows the typical pattern of double and single C—O bonds. The two Csp^2—Csp^2—Csp^2 angles of the anion (C4—C5—C6 and C5—C6—C7) are almost equal but they are considerably larger than 120°, indicating in part the high degree of strain in the maleate anion. The O—C—O angle in the COO$^-$ group is only slightly larger than that in the non-dissociated COOH group. This relationship is quite different from that observed in the gas phase, as revealed by the MO calculations (Fig. 1), in which the O—C—O angle in the COO$^-$ group is significantly larger than that in the COOH group. The differences in the O—C—O angles between the crystal and gas-phase geometries of the maleate ion may be due to the hydrogen bonding present in the crystal, which leads to a decrease in the steric effect of lone pairs of electrons on both O atoms of the COO$^-$ and COOH groups in relation to the isolated anion in the gas phase, as shown by the MO calculations.

The maleate(1−) ions in (I), related by a 2_1 screw axis, are interconnected by water molecules *via* O—H···O hydrogen bonds in a head-to-tail fashion to form zigzag chains. These chains form stacks, with a distance of 3.36 (1) Å between the almost-planar maleate anions. Although the maleate anion is not aromatic, it does contain π electrons and polarized multiple bonds, and so the interchain separation can be compared with the stacking system in aromatic molecules (3.4 Å; Pauling, 1960). The interchain forces are relatively strong due to the close overlap of the π orbitals of the maleate ions in the stacks (Fig. 3). Both O atoms of the COO^- group are involved in two hydrogen bonds. Atom O4 is involved in hydrogen bonds with the water molecule and with the H atom of the protonated ring N atom of the melamine residue, while atom O3 acts as an acceptor for the NH_2 group of the same melamine residue and is involved in an intramolecular O1—H···O3 hydrogen bond. Atom O2 of the non-dissociated COOH group is also involved in two hydrogen bonds, with the water molecule and with the NH_2 group of the melamine residue, while the other O atom, O1, of the COOH group is involved only in the intramolecular O1—H···O3 hydrogen bond, if the relatively weak C6—H6···O1^{v} hydrogen bond is neglected [H6···O1^{v} = 2.57 Å, C6···O1^{v} = 3.218 (2) Å and C6—H6···O1^{v} = 127°; symmetry code: (v) $\frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$].

The water molecule is involved in four hydrogen bonds. In two it acts as a donor to two maleate ions and in the other two it acts as an acceptor for the NH_2 groups of two melamine moieties. The geometry of the hydrogen-bonding system in (I) is summarized in Table 2.

Experimental

Melamine and maleic acid, in a 1:1 molar ratio, were dissolved in boiling water and the resulting solution cooled to room temperature. After several days, colourless single crystals of (I) had formed.

Crystal data

$C_3H_7N_6^+ \cdot C_4H_3O_4^- \cdot H_2O$
$M_r = 260.23$
Monoclinic, $P2_1/n$
$a = 3.6720$ (7) Å
$b = 10.417$ (2) Å
$c = 28.749$ (6) Å
$\beta = 90.89$ (3)°
$V = 1099.6$ (4) Å^3
$Z = 4$
$D_x = 1.572$ Mg m^{-3}
$D_m = 1.57$ Mg m^{-3}
D_m measured by flotation in $CHCl_3/CHBr_3$
Mo $K\alpha$ radiation
Cell parameters from 1288 reflections
$\theta = 2.8$–27.0°
$\mu = 0.13$ mm^{-1}
$T = 293$ (2) K
Needle, colourless
0.46 × 0.12 × 0.10 mm

Data collection

Kuma KM-4 diffractometer with a CCD area-detector
ω scans
Absorption correction: analytical face-indexed (*SHELXTL/PC*; Sheldrick, 1990*b*)
$T_{min} = 0.938$, $T_{max} = 0.988$
11 241 measured reflections
2394 independent reflections
1788 reflections with $I > 2\sigma(I)$
$R_{int} = 0.036$
$\theta_{max} = 27.0°$
$h = -4 \rightarrow 4$
$k = -13 \rightarrow 13$
$l = -36 \rightarrow 36$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.050$
$S = 1.00$
2386 reflections
172 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0133P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.14$ e Å^{-3}
$\Delta\rho_{min} = -0.16$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—C4	1.2999 (17)	C6—C7	1.4899 (18)
O2—C4	1.2126 (15)	C7—O4	1.2422 (15)
C4—C5	1.4860 (19)	C7—O3	1.2648 (17)
C5—C6	1.3209 (16)		
C1—N1—C3	115.69 (12)	N6—C3—N3	117.36 (13)
N4—C1—N1	120.83 (13)	N1—C3—N3	125.61 (13)
N4—C1—N2	117.56 (13)	O2—C4—O1	121.18 (15)
N1—C1—N2	121.60 (13)	O2—C4—C5	119.82 (14)
C1—N2—C2	119.30 (12)	O1—C4—C5	118.98 (12)
N3—C2—N5	122.17 (14)	C6—C5—C4	131.15 (15)
N3—C2—N2	122.54 (13)	C5—C6—C7	131.67 (15)
N5—C2—N2	115.29 (13)	O4—C7—O3	122.91 (14)
C2—N3—C3	115.13 (12)	O4—C7—C6	116.23 (14)
N6—C3—N1	117.03 (13)	O3—C7—C6	120.85 (13)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2···O4^{i}	0.86	1.82	2.6570 (15)	165
N4—H4*B*···O5	0.86	2.26	2.8614 (17)	127
N4—H4*A*···N1^{ii}	0.86	2.17	3.0266 (16)	174
N5—H5*A*···O2^{iii}	0.86	2.30	3.0014 (16)	139
N5—H5*B*···O3^{i}	0.86	2.13	2.9912 (15)	174
N6—H6*A*···O5^{ii}	0.86	2.08	2.9234 (15)	168
N6—H6*B*···N3^{iv}	0.86	2.30	3.1585 (17)	173
O1—H1···O3	0.974 (9)	1.517 (9)	2.4704 (14)	165.1 (15)
O5—H1O5···O4^{v}	0.807 (18)	2.209 (18)	2.9315 (16)	149.3 (18)
O5—H2O5···O2	0.936 (17)	1.837 (17)	2.7697 (15)	174.5 (16)

Symmetry codes: (i) $\frac{5}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (ii) $1 - x, 1 - y, -z$; (iii) $1 + x, 1 + y, z$; (iv) $2 - x, 2 - y, -z$; (v) $\frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$.

H atoms bonded to C atoms were treated as riding, with C—H distances of 0.93 Å and with $U_{iso}(H) = 1.2U_{eq}(C)$. H atoms bonded to N atoms were also treated as riding, with N—H distances of 0.86 Å and with $U_{iso}(H) = 1.2U_{eq}(N)$. The coordinates of H atoms bonded to O atoms were refined, giving O—H distances in the range 0.807 (18)–0.974 (9) Å (Table 2).

Data collection: *KM*-4 *CCD Software* (Kuma, 2001); cell refinement: *KM*-4 *CCD Software*; data reduction: *KM*-4 *CCD Software*; program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990*a*); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL/PC* (Sheldrick, 1990*b*); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1299). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (2004). C**60**, o211–o214 Jan Janczak *et al.* • $C_3H_7N_6^+ \cdot C_4H_3O_4^- \cdot H_2O$ **o213**

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