

Melaminium phthalate

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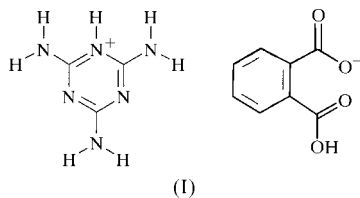
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The crystals of the new melaminium salt, 2,4,6-triamino-1,3,5-triazin-1-ium hydrogenphthalate, $C_3H_7N_6^+ \cdot C_8H_5O_4^-$, are built up from single protonated melaminium residues and single dissociated hydrogenphthalate(1⁻) anions. The protonated melaminium ring is almost planar. The best plane through the non-dissociated carboxyl group (COOH) of the hydrogenphthalate(1⁻) anion is inclined at an angle of 16.4 (2)° to the plane of the six-membered hydrogenphthalate ring, while the plane of the ionized COO⁻ group is roughly perpendicular [84.2 (2)°] to this plane. A combination of ionic and donor-acceptor hydrogen-bond interactions linking together the melaminium and hydrogenphthalate residues forms a three-dimensional network.

Comment

To extend the understanding of the physical organic chemistry of the solid state, we are studying the solid-state structure of the 1:1 cocrystal of melamine and phthalic acid. The asymmetric unit of the title compound, (I), consists of two well defined oppositely charged residues: a protonated moiety at one of the three N atoms of the melamine ring and a phthalate ion dissociated at one of the carboxyl groups (Fig. 1). To our knowledge, this is the second structurally characterized melaminium salt which is protonated at only one ring N atom; the first was a cocrystal of barbituric acid with melamine (Zerkowski *et al.*, 1994). In addition to these one-protonated melaminium salts, the diprotonated melaminium salt has also been structurally characterized (Martin & Pinkerton, 1995).



The almost planar six-membered aromatic ring of the melaminium residue $C_3H_7N_6^+$ shows a slight boat conformation character; the N2 and C11 atoms (the 1,4 positions in the

ring) deviate from the least-squares plane of the ring by up to 0.03 Å. Two of the three amine groups (N4 and N5) are approximately coplanar with the mean plane of the melamine ring, while the third amine group (N6) deviates slightly from the ring plane. The N6 atom of the amine group deviates by 0.146 (2) Å from the weighted least-squares plane through the ring. The first two amine groups (N4 and N5) are almost coplanar with the melaminium ring, but the third amine group at the N6 atom has a somewhat pyramidal character. This is likely a consequence of the intermolecular hydrogen-bonding interactions present in the crystal.

The ring of the melamine residue is significantly distorted from the ideal hexagonal form. The internal C9–N1–C11 and C10–N3–C11 angles of the melamine ring are smaller than the C10–N2–C9 angle protonated at the N atom. These differences between the C–N–C angles in the melaminium ring correlate with the steric effect of the lone-pair electrons and are fully consistent with the valence-shell electron-pair repulsion theory (VSEPR; Gillespie, 1972). A similar correlation between the angles within the ring are observed in the crystal of melamine in the X-ray as well as in the neutron structures (Hughes, 1941; Larson & Cromer, 1974; Varghese *et al.*, 1977) and several melamine derivatives (Mathias *et al.*, 1994; Zerkowski & Whitesides, 1994; Janczak & Kubiak, 1999). A greater difference between the corresponding angles (C–N–C 113° and N–C–N 127°) is observed in the X-ray and neutron structure of s-triazine (Coppens, 1967).

The hydrogenphthalate(1⁻) anion is almost planar except for the two carboxyl groups (dissociated and non-dissociated). Within the benzene ring, the greatest deviation from the weighted least-squares plane of the ring is observed for the C1 and C4 atoms. The plane defined by the atoms of the dissociated carboxyl group (COO⁻) is almost perpendicular [84.2 (2)°], while the plane defined as that of the non-dissociated carboxyl group (COOH) is inclined at an angle of 16.4 (2)° to the plane of the benzene ring. In the phthalic acid crystal, both carboxyl groups are oppositely inclined at angles of ±30° to the ring plane (Kuppers, 1981; Ermer, 1981). Within the ring, the endocyclic angles at the C1 and C2 atoms are slightly smaller than 120°, and correlate with the substitution effect of the COO⁻ and COOH groups. The interaction of the polar carboxyl (COO⁻ and COOH) groups results in a distortion of the C1–C2–C8 and C1–C7–O2 angles, which

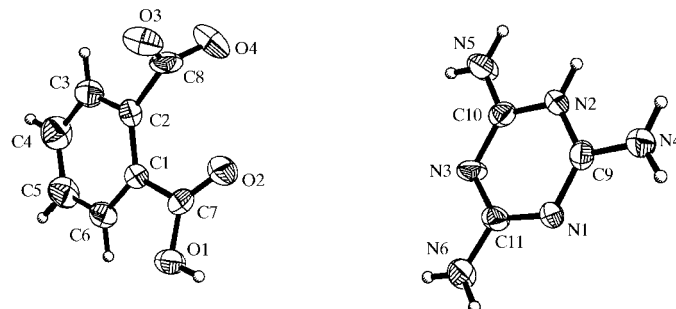


Figure 1

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

are substantially greater than 120°. The C—C bond length joining the ionized carboxyl group (C2—C8) is slightly longer than the C—C bond joining the non-dissociated carboxyl group (C1—C7), which is comparable with a distance of 1.491 (8) Å observed for the unconjugated $C_{\text{aromatic}}-Csp^2$ bond (Allen *et al.*, 1987).

Both oppositely charged residues [$C_3H_7N_6^+$ and $C_6H_4(COOH)(COO)^-$] interact extensively by a combination of ionic and donor-acceptor hydrogen-bond interactions throughout the lattice to form a three-dimensional network (Fig. 2). For the purpose of this discussion, a hydrogen-bonding system has been defined as having $O\cdots H$ and $N\cdots H$ contacts shorter than 2.5 Å. All H atoms of the melaminium residue $C_3H_7N_6^+$ are involved in hydrogen bonds. The most noticeable feature is that the H21 atom (at the protonated N ring) forms a bifurcated hydrogen bond involving the O2 and O3 atoms. Additionally, both non-protonated N atoms of the melaminium residue act in the hydrogen bonds as acceptor. Thus, the melaminium moiety is involved in ten hydrogen bonds, of which four $N-H\cdots N$ bonds are almost linear with the neighbouring melamine residues, while five of the six $N-H\cdots O$ bonds are much more bent with respect to the neighbouring hydrogenphthalate(1-) residues. The H atom of the COOH group of the hydrogenphthalate(1-) anion is involved in the strongest $O1-H\cdots O3^{iv}$ hydrogen bond. Each of the O2, O3 and O4 atoms of the hydrogenphthalate(1-) residue are acceptors in two hydrogen bonds ($N-H\cdots O$) from neighbouring melamine residues.

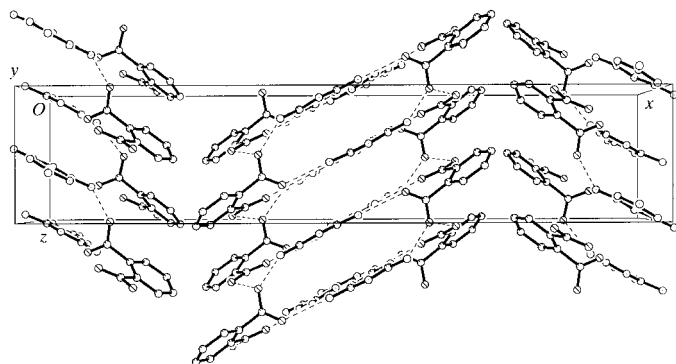


Figure 2
The molecular packing in the unit cell showing the hydrogen-bonding interactions (dashed lines). H atoms have been omitted for clarity.

In the crystal, the melaminium residues interconnected by four $N-H\cdots N$ hydrogen bonds form layers which are about $c/2$ apart (Fig. 2). These layers are almost parallel to the b axis and form angles of $\approx 30^\circ$ and $\approx 60^\circ$ with the a and c axes, respectively. The plane of the ring of the hydrogenphthalate(1-) residues is inclined at an angle of $7.6(1)^\circ$ to the plane of the melaminium ring, but the plane of the ionized carboxyl group is inclined at an angle of $68.6(1)^\circ$ to the melaminium ring, since both O atoms of the COO^- group (O3 and O4) act as acceptors of hydrogen bonds joining two neighbouring layers of melamine residues (Fig. 2). All H-atom geometric parameter details are given in Table 2.

Experimental

Melanine and phthalic acid in a 1:1 molar ratio were dissolved in hot water and the resulting solution was evaporated slowly. After several days, colourless crystals of the title salt appeared.

Crystal data

$C_3H_7N_6^+ \cdot C_8H_5O_4^-$
 $M_r = 292.27$
Orthorhombic, $Pbcn$
 $a = 33.622(7)$ Å
 $b = 10.562(2)$ Å
 $c = 7.0670(10)$ Å
 $V = 2509.6(8)$ Å³
 $Z = 8$
 $D_x = 1.547$ Mg m⁻³
 $D_m = 1.54$ Mg m⁻³

D_m measured by flotation in $CHCl_3/C_2Cl_4$
Mo $K\alpha$ radiation
Cell parameters from 2558 reflections
 $\theta = 5-25^\circ$
 $\mu = 0.122$ mm⁻¹
 $T = 293(2)$ K
Parallelepiped, colourless
 $0.35 \times 0.22 \times 0.20$ mm

Data collection

Kuma KM-4 diffractometer with two-dimensional area CCD detector
 ω scans
Absorption correction: analytical face-indexed (SHELXTL; Sheldrick, 1990)
 $T_{\min} = 0.959$, $T_{\max} = 0.976$

22665 measured reflections
3384 independent reflections
1527 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.046$
 $\theta_{\max} = 29.56^\circ$
 $h = -45 \rightarrow 45$
 $k = -14 \rightarrow 14$
 $l = -8 \rightarrow 9$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.046$
 $wR(F^2) = 0.126$
 $S = 1.005$
3384 reflections
214 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.060P)^2 + 0.066P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.20$ e Å⁻³
 $\Delta\rho_{\min} = -0.24$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

O1—C7	1.307 (2)	C9—N4	1.319 (2)
O2—C7	1.226 (2)	C9—N2	1.367 (2)
O3—C8	1.272 (2)	N2—C10	1.366 (2)
O4—C8	1.236 (2)	C10—N5	1.315 (2)
C1—C7	1.484 (3)	C10—N3	1.334 (2)
C2—C8	1.500 (2)	N3—C11	1.348 (2)
N1—C9	1.321 (2)	C11—N6	1.323 (2)
N1—C11	1.351 (2)		
O2—C7—O1	122.9 (2)	C9—N1—C11	116.4 (2)
O2—C7—C1	123.3 (2)	N1—C9—N2	121.1 (2)
O1—C7—C1	113.8 (2)	C10—N2—C9	119.6 (2)
O4—C8—O3	124.5 (2)	N3—C10—N2	121.1 (2)
O4—C8—C2	117.7 (2)	C10—N3—C11	115.8 (2)
O3—C8—C2	117.5 (2)	N3—C11—N1	125.9 (2)

Table 2

Hydrogen-bonding geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1 \cdots O3 ⁱ	1.00 (2)	1.54 (2)	2.533 (3)	170 (2)
N2—H21 \cdots O3 ⁱⁱ	0.90 (2)	2.27 (2)	3.014 (3)	140 (2)
N2—H21 \cdots O2 ⁱⁱⁱ	0.90 (2)	2.46 (2)	3.185 (3)	138 (2)
N4—H41 \cdots O4 ^{iv}	0.93 (2)	2.10 (2)	3.010 (3)	169 (2)
N4—H42 \cdots O3 ^v	0.91 (2)	2.02 (2)	2.866 (3)	155 (2)
N5—H51 \cdots N3 ^v	0.93 (2)	2.08 (2)	3.004 (3)	172 (2)
N5—H52 \cdots O2 ⁱⁱⁱ	0.88 (2)	2.04 (2)	2.887 (3)	161 (2)
N6—H61 \cdots N1 ^{vi}	0.96 (2)	2.03 (2)	2.977 (3)	169 (2)
N6—H62 \cdots O4 ⁱ	0.96 (2)	1.99 (2)	2.796 (3)	140 (2)

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

The positions of H atoms of the melamine residue and the H atom of the COOH group of the hydrogenphthalate(1-) ion, *i.e.* all H atoms which are involved in hydrogen bonds, were refined.

Data collection: *KM-4 CCD Software* (Kuma, 1998); cell refinement: *KM-4 CCD Software*; data reduction: *KM-4 CCD Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1990); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1491). Services for accessing these data are described at the back of the journal.

References

- Allen, F. M., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
- Coppens, P. (1967). *Science*, **158**, 1577–1579.
- Ermer, O. (1981). *Helv. Chim. Acta*, **64**, 1902–1908.
- Gillespie, R. J. (1972). In *Molecular Geometry*. London: Van Nostrand Reinholds.
- Hughes, E. W. (1941). *J. Am. Chem. Soc.* **63**, 1731–1752.
- Janczak, J. & Kubiak, R. (1999). *Acta Chem. Scand.* **53**, 602–610.
- Kuma (1998). *KM-4 CCD Software*. Kuma Diffraction, Wroclaw, Poland.
- Kuppers, H. (1981). *Cryst. Struct. Commun.* **10**, 989–992.
- Larson, A. C. & Cromer, D. T. (1974). *J. Chem. Phys.* **60**, 185–192.
- Martin, A. & Pinkerton, A. A. (1995). *Acta Cryst.* **C51**, 2174–2177.
- Mathias, J. P., Simanek, E. E., Zerkowski, J. A., Seto, Ch. T. & Whitesides, G. M. (1994). *J. Am. Chem. Soc.* **116**, 4316–4325.
- Sheldrick, G. M. (1990). *SHELXTL*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Varghese, J. N., O'Connell, A. M. & Malsen, E. N. (1977). *Acta Cryst.* **B33**, 2102–2108.
- Zerkowski, J. A., McDonald, J. C. & Whitesides, G. M. (1994). *Chem. Mater.* **6**, 1250–1256.
- Zerkowski, J. A. & Whitesides, G. M. (1994). *J. Am. Chem. Soc.* **116**, 4298–4304.