

2,4,6-Triamino-1,3,5-triazine-
1*H*-isoindole-1,3(2*H*)-dione (1/3)Genivaldo Júlio Perpétuo^a and Jan Janczak^{b*}

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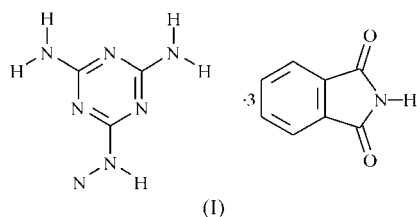
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The asymmetric unit of the title compound, $C_3H_6N_6 \cdot 3C_8H_5NO_2$, contains a melamine and a phthalimide [1*H*-isoindole-1,3(2*H*)-dione] molecule, both residing on a mirror plane, and a second phthalimide molecule residing on a general position. The two components are linked by almost linear $N-H \cdots O$ and $N-H \cdots N$ hydrogen bonds, forming an essentially planar superstructure. These aggregates, related by a twofold screw axis, interact through weak $C-H \cdots O$ contacts, forming chains parallel to the *b* axis, while those related by translation along the *c* axis interact *via* $\pi-\pi$ interactions between the π clouds of the aromatic triazine and phthalimide rings to form a stacked structure.

Comment

The present study is a continuation of our investigations into the characterization of hydrogen-bonding networks 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 because of their ability to form 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 materials arises from the possibility of their displaying nonlinear optical properties (Janczak & Perpétuo, 2002; Marchewka *et al.*, 2003; Perpétuo & Janczak, 2006). We present here the 2,4,6-triamino-1,3,5-tria-

zine-tris(phthalimide) cocrystal, (I), which contains multiple $N-H \cdots N$ and $N-H \cdots O$ hydrogen-bonding interactions.

The asymmetric unit of (I) comprises half a melamine and one and a half phthalimide molecules (Fig. 1). These units through a crystallographic mirror plane form an almost planar triazine-phthalimide (1/3) aggregate. The triazine ring in melamine is essentially planar [the deviation of the N and C atoms from the mean plane is less than 0.037 (2) Å], but exhibits significant distortion from the ideal hexagonal form (D_{3h} symmetry). The internal C–N–C angles are smaller than 120°, while the internal N–C–N angles are greater than 120°. This distortion results from the steric effect of the lone-pair electrons, predicted by the valence-shell electron-pair repulsion theory (Gillespie, 1963, 1992). The *ab initio* gas-phase geometry calculated for an isolated melamine molecule shows similar correlation between the internal C–N–C and N–C–N angles within the ring (Drozd & Marchewka, 2005). Thus, the ring distortions result mainly from the steric effect of the lone pairs of electrons on the ring N atoms and, to a lesser degree, from the hydrogen-bonding arrangement, which diminishes the steric effect of these electron lone pairs by about 2° compared with the *ab initio* results (Drozd & Marchewka, 2005). The phthalimide molecule has a similar geometry to that found in the pure phthalimide crystal (Matzat, 1972; Ng, 1992; Zakaria *et al.*, 2002).

An extensive set of almost linear hydrogen bonds (Table 1) link the components of (I) into essentially planar triazine-phthalimide (1/3) aggregates with pseudo-threefold symmetry. These aggregates, related by a twofold symmetry screw axis, interact *via* $C-H \cdots O$ contacts, forming chains parallel to the *b* axis (Fig. 2), while the plane defined by the atoms of the triazine-phthalimide (1/3) aggregates of the chain is inclined by 27.6° to the (001) plane. Each melamine molecule is involved in a maximum of nine hydrogen bonds; in six of these it acts as a donor and in the remaining three as an acceptor

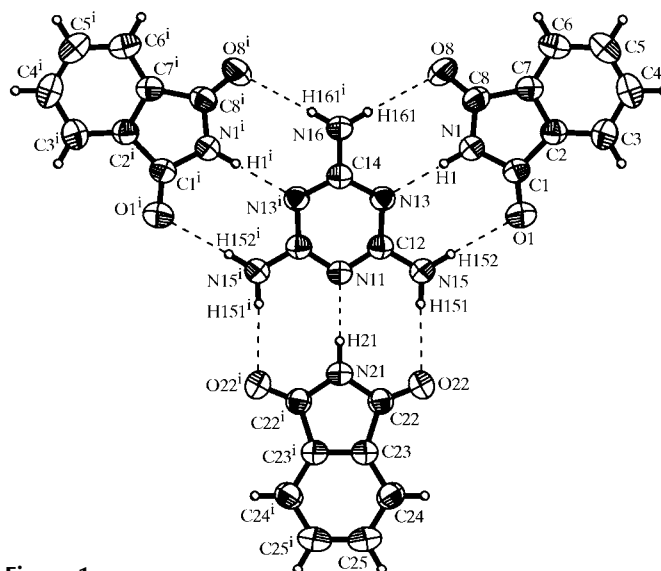


Figure 1

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. [Symmetry code: (i) $x, -y + \frac{1}{2}, z$.]

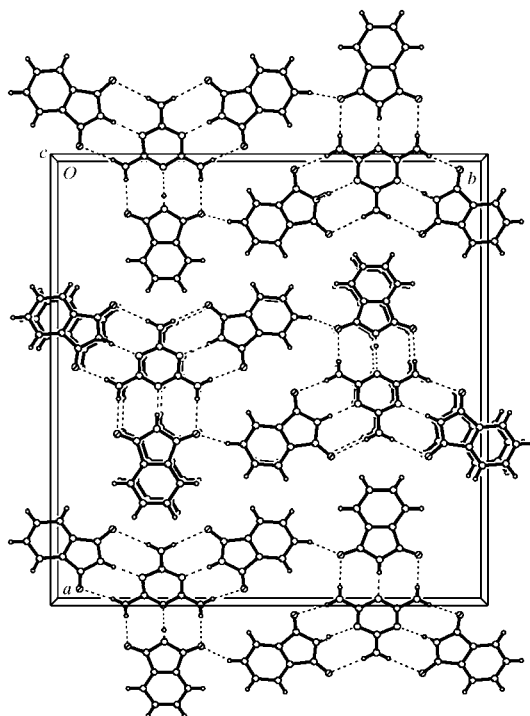


Figure 2
A view of the crystal packing in (I), showing the hydrogen-bonded triazine-phthalimide (1/3) aggregates interacting via C—H...O hydrogen bonds to form chains along the *b* axis.

(Table 1). Chains related by a translation along the *c* axis interact via π - π interactions between the π clouds of the aromatic triazine and phthalimide rings, forming a stacked structure. Within the stack, the triazine rings are separated by ~ 3.27 Å and the phthalimide molecules are separated by ~ 3.40 Å. These values indicate relatively strong π - π interactions within the stack, since they are comparable to the value of 3.4 Å for the interacting π aromatic ring system (Pauling, 1960).

Experimental

A mixture of 2,4,6-triamino-1,3,5-triazine (quality *ca* 98%) and phthalimide (quality > 99%) in a 1:3 molar ratio was heated under vacuum in a sealed glass ampoule in a temperature gradient (hot zone 473 K, cold zone 373 K). After several hours, colourless crystals formed in the cold zone, which proved to be suitable for single-crystal X-ray diffraction analysis.

Crystal data

$C_3H_6N_6 \cdot 3C_8H_5NO_2$	$V = 2612.6$ (10) Å ³
$M_r = 567.53$	$Z = 4$
Orthorhombic, <i>Pnma</i>	Mo $K\alpha$ radiation
$a = 26.709$ (5) Å	$\mu = 0.11$ mm ⁻¹
$b = 25.884$ (5) Å	$T = 295$ (2) K
$c = 3.779$ (1) Å	$0.30 \times 0.28 \times 0.22$ mm

Data collection

Kuma KM-4 CCD diffractometer	5001 measured reflections
Absorption correction: analytical, face-indexed (<i>SHELXTL</i> ; Sheldrick, 1990)	2555 independent reflections
$T_{\min} = 0.962$, $T_{\max} = 0.972$	1789 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.021$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.034$	211 parameters
$wR(F^2) = 0.092$	H-atom parameters constrained
$S = 1.00$	$\Delta\rho_{\text{max}} = 0.16$ e Å ⁻³
2555 reflections	$\Delta\rho_{\text{min}} = -0.13$ e Å ⁻³

Table 1

Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1...N13	0.86	1.96	2.818 (2)	174
N15—H151...O22	0.86	2.30	3.159 (2)	179
N15—H152...O1	0.86	2.27	3.124 (2)	169
N16—H161...O8	0.86	2.39	3.248 (2)	178
N21—H21...N11	0.86	1.95	2.803 (2)	173
C4—H4...O22 ⁱⁱ	0.93	2.51	3.278 (2)	139

Symmetry code: (ii) $-x + 1, -y + 1, -z$.

H atoms were placed in their geometrically defined positions, with $U_{\text{iso}}(\text{H})$ values of $1.2U_{\text{eq}}$ of the N or C atoms directly attached to the H atoms.

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: GG3088). Services for accessing these data are described at the back of the journal.

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