

A 1:1 cocrystal of 4-(dimethylamino)-benzaldehyde and 6-phenyl-1,3,5-triazine-2,4-diamine

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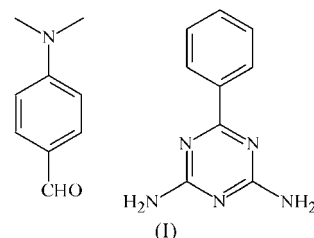
The crystal structure of the title compound, C₉H₁₁NO·C₉H₉N₅, contains one molecule of each component in the asymmetric unit. Approximately planar clusters of four molecules are formed by N—H···N and N—H···O hydrogen bonds, and further N—H···N hydrogen bonds link adjacent clusters to form pleated ribbons. π – π interactions are found between triazine and aldehyde benzene rings in different clusters, generating stacks along the monoclinic *b* axis. The intramolecular geometry of the two components is similar to that found in other crystal structures containing these molecules. Both molecules are approximately planar, except for methyl H atoms, with a small twist about the C—C bond linking the phenyl and triazine rings.

Comment

Hydrogen bonding plays a key role in chemical, catalytic and biochemical processes, as well as in supramolecular chemistry and crystal engineering (Epstein & Shubina, 2002). Heterocycles are very important in studies of new pharmaceuticals and agrochemicals. In recent years, many new chemicals have been synthesized that have structures containing heterocyclic rings, such as triazine (Chen *et al.*, 2001). Triazine derivatives have demonstrated a broad range of biological activities, including anti-angiogenesis, herbicidal effects, antimetastatic effects, Erm methyltransferase inhibition, antimicrobial effects (Bork *et al.*, 2003), the inhibition of the differentiation of endothelial progenitor cells (Park *et al.*, 2003) and the prevention of the early cell death of transplanted myogenic cells (El Fahime *et al.*, 2003). The crystal structure of the title compound, (I), consists of 4-dimethylaminobenzaldehyde and 6-phenyl-1,3,5-triazine-2,4-diamine molecules, with one of each in the asymmetric unit (Fig. 1).

Although the unit-cell parameters have been reported for 4-dimethylaminobenzaldehyde (Reffner & McCrone, 1959), there is no report of the crystal structure of this compound.

The structure of its hydrobromide is known (Dattagupta & Saha, 1973), as are those of a 1:1 complex in which it acts as a guest molecule in channels (Herbstein *et al.*, 1984), and of a tin complex in which it serves as a ligand coordinating through its O atom (Mahadevan *et al.*, 1982). In each case, the aldehyde group is essentially coplanar with the benzene ring, and the same is true of the dimethylamino group when it remains unprotonated. Relevant torsion angles for the title cocrystal are given in Table 1.



The crystal structure of 6-phenyl-1,3,5-triazine-2,4-diamine has been reported (Diaz-Ortiz *et al.*, 2004), as have a number of cocrystals (Deak, Radics *et al.*, 2001; Bertolasi *et al.*, 2001; Bishop *et al.*, 2002), salts (Wijaya *et al.*, 2004; Adachi *et al.*, 2005; Sheshmani *et al.*, 2006; Aghabozorg *et al.*, 2006) and a metal complex in which it serves as a ligand (Deák, Kálmán *et al.*, 2001). In most cases, the two rings are approximately coplanar, usually with a small twist around the bond linking them, as is found in the title cocrystal, but torsion angles range up to 33°.

Based on their work on *s*-triazine derivatives, Główka & Iwanicka (1989*a,b*) concluded that the endocyclic bond angles at all N atoms are less than 120°, while those at the C atoms are larger than 120°, irrespective of their hybridization. The 1,3,5-triazine ring in the title cocrystal has the same characteristics: the endocyclic bond angles at the N atoms lie in the range 124.7 (1)–126.6 (1)° and those at the C atoms lie in the range 113.9 (1)–114.9 (1)°. The values of the N—C bond lengths within the 1,3,5-triazine ring (Table 1) are comparable with those found in crystal structures of other N-heteroaro-

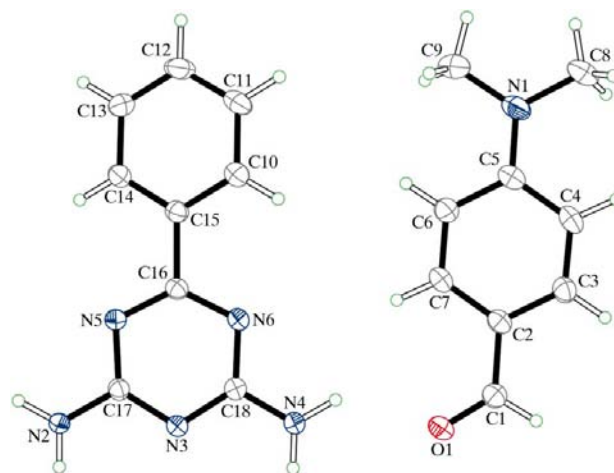


Figure 1
The asymmetric unit of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

matic derivatives (Allen *et al.*, 1987; Chen *et al.*, 2001). Triazine itself, (HCN)₃, has a C–N bond distance in the same range at low temperature [1.338 (4) Å; Smith & Rae, 1978], though it appears to be shorter at room temperature (Wheatley, 1955; Coppens, 1967), probably because of libration effects. The exocyclic C–N bond distances for the 1,3,5-triazine ring [1.3323 (17)–1.3598 (16) Å] are significantly larger than those in other similar triazine molecules (1.325–1.333 Å). The narrow CNC angles (*ca* 113°) and the wide NCN angles (*ca* 126°) in the present compound are very similar to the CNC [114.8 (10)°] and NCN [125.2 (10)°] angles of (HCN)₃. The two amine groups lie essentially in the triazine ring plane (Table 2). The dihedral angle between the connected phenyl and triazine rings is 13.8 (1)°.

The supramolecular structure of the title cocrystal involves hydrogen bonding (Table 2) and π – π stacking. The hydrogen-bond donors are the four N–H bonds of the two amino groups, while the acceptors are the aldehyde O atom and two of the three triazine ring N atoms; the third ring N atom and the dimethylamino N atom do not take part in hydrogen bonding. Pairs of triazine molecules form centrosymmetric dimers *via* N–H...N hydrogen bonds, and two aldehyde molecules are linked to this dimer by two N–H...O hydrogen bonds each, to give an approximately planar cluster of four molecules with six hydrogen bonds (Fig. 2). Each such cluster

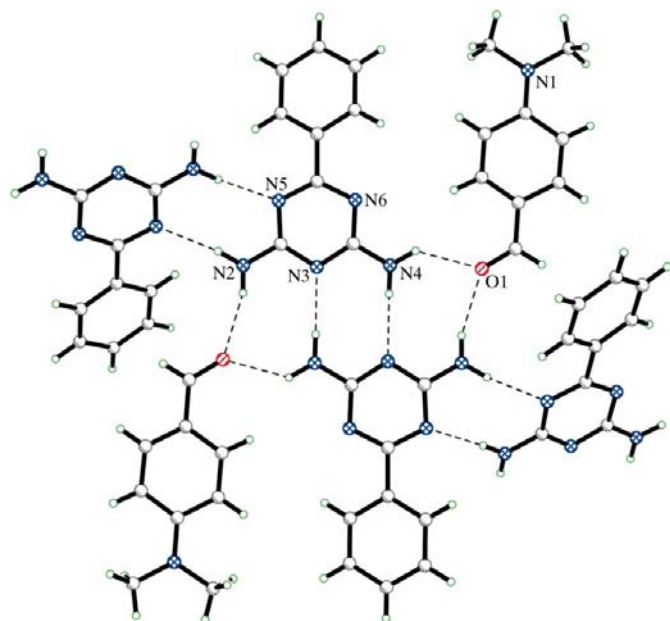


Figure 2
The hydrogen bonding (dashed lines) connecting two molecules of each component of (I) into an approximately planar centrosymmetric unit and linking each of these units to two adjacent units.

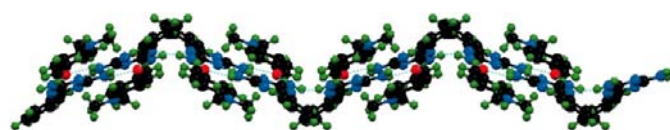


Figure 3
The formation of pleated sheets of molecules of (I) *via* hydrogen bonding.

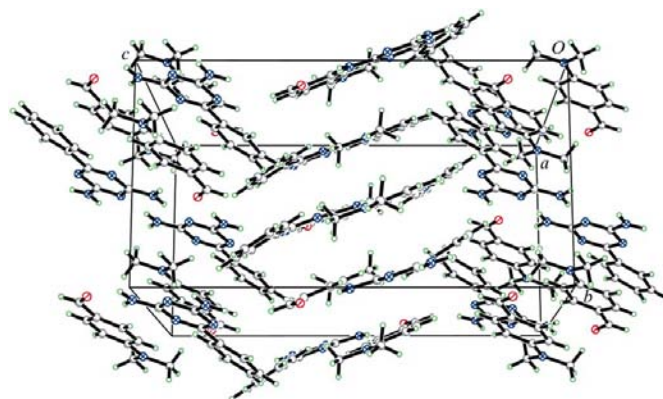


Figure 4
The stacking of molecules of (I) *via* π – π interactions.

is linked to two other clusters, one on each side, by pairs of N–H...N hydrogen bonds arranged around twofold rotation axes, with adjacent clusters inclined to each other by approximately 40°; these links are also shown in Fig. 2. The complete hydrogen bonding thus forms pleated ribbons along the *c* axis (Fig. 3).

The benzene rings of the aldehyde and triazine rings of (I) are stacked *via* π – π interactions along the *b* axis, having a centroid-to-centroid distance of 3.432 Å and a perpendicular interplanar distance of 3.341 Å, as shown in Fig. 4.

Experimental

The title compound, (I), was prepared by dissolving 4-(dimethylamino)benzaldehyde (1 mmol, 149 mg) and 6-phenyl-1,3,5-triazine-2,4-diamine (1 mmol, 187 mg) in chloroform (10 ml). The mixture was stirred at room temperature for 4 h. The solid product was filtered off and recrystallized from ethanol and dichloromethane (1:1 *v/v*), affording small colourless crystals.

Crystal data

C₉H₁₁NO·C₉H₉N₅
M_r = 336.40
 Monoclinic, *C2/c*
a = 15.848 (3) Å
b = 10.689 (2) Å
c = 20.078 (5) Å
 β = 91.380 (11)°

V = 3400.3 (13) Å³
Z = 8
 Mo *K* α radiation
 μ = 0.09 mm^{−1}
T = 150 (2) K
 0.30 × 0.20 × 0.20 mm

Data collection

Bruker SMART 1K CCD area-detector diffractometer
 14907 measured reflections

4131 independent reflections
 3134 reflections with *I* > 2 σ (*I*)
*R*_{int} = 0.027

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.045$
 $wR(F^2) = 0.129$
S = 1.05
 4131 reflections
 244 parameters

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\max} = 0.35 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.23 \text{ e \AA}^{-3}$

The amino H atoms were found in a difference map and refined freely. Other H atoms were placed in idealized positions and constrained to ride on their parent atoms, with C–H distances in the range 0.95–0.98 Å, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{Csp}^2)$ or $1.5U_{\text{eq}}(\text{Csp}^3)$.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINTE* (Bruker, 2001); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXTL* (Bruker, 2005); program(s) used to refine

Table 1

Selected geometric parameters (Å, °).

N2—C17	1.3355 (17)	N5—C16	1.3363 (16)
N3—C17	1.3392 (17)	N5—C17	1.3598 (16)
N3—C18	1.3469 (17)	N6—C16	1.3323 (17)
N4—C18	1.3292 (18)	N6—C18	1.3575 (17)
C17—N3—C18	114.98 (11)	N5—C16—N6	126.59 (12)
C16—N5—C17	114.48 (11)	N3—C17—N5	124.69 (12)
C16—N6—C18	113.87 (11)	N3—C18—N6	125.29 (12)
O1—C1—C2—C3	175.17 (14)	C9—N1—C5—C6	3.3 (2)
O1—C1—C2—C7	−3.6 (2)	C10—C15—C16—N5	169.71 (13)
C8—N1—C5—C4	−1.3 (2)	C10—C15—C16—N6	−11.58 (19)
C8—N1—C5—C6	179.27 (15)	C14—C15—C16—N5	−12.76 (19)
C9—N1—C5—C4	−177.29 (14)	C14—C15—C16—N6	165.95 (12)

Table 2

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>
N2—H2 <i>A</i> ...N5 ⁱ	0.902 (17)	2.066 (18)	2.9585 (18)	169.8 (15)
N2—H2 <i>B</i> ...O1 ⁱⁱ	0.855 (19)	2.173 (19)	2.9990 (16)	162.4 (16)
N4—H4 <i>A</i> ...O1	0.917 (19)	2.132 (19)	2.8575 (17)	135.2 (15)
N4—H4 <i>B</i> ...N3 ⁱⁱ	0.89 (2)	2.10 (2)	2.9895 (18)	177.9 (17)

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

structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and local programs.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SF3045). Services for accessing these data are described at the back of the journal.

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