

Hydrogen-bonding patterns in 2-amino-4,6-dimethylpyrimidine–cinnamic acid (1/2)

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Key indicators

Single-crystal X-ray study

T = 293 K

Mean $\sigma(\text{C}-\text{C}) = 0.004 \text{ \AA}$

R factor = 0.048

wR factor = 0.158

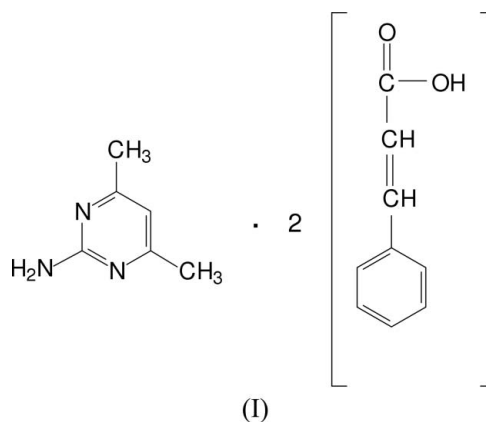
Data-to-parameter ratio = 13.0

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

In the title compound, $\text{C}_6\text{H}_9\text{N}_3 \cdot 2\text{C}_9\text{H}_8\text{O}_2$, an aminopyrimidine–cinnamic acid 1:2 cocrystal, the 2-amino-4,6-dimethylpyrimidine molecule forms two eight-membered hydrogen-bonded rings [$R_2^2(8)$ motif] with the carboxylic acid groups from two independent cinnamic acid molecules *via* $\text{N}-\text{H} \cdots \text{O}$ and $\text{O}-\text{H} \cdots \text{N}$ hydrogen bonds. The cinnamic acid molecules are linked by $\text{C}-\text{H} \cdots \text{O}$ hydrogen bonds to form chains along two axes.

Comment

Cinnamic acid derivatives are important building blocks in crystal engineering (Desiraju, 1989). Hydrogen bonding plays a key role in molecular recognition (Goswami & Ghosh, 1997) and crystal engineering research (Goswami *et al.*, 1998). The design of a highly specific solid-state structure is of considerable significance in organic chemistry due to important applications in the development of new optical, magnetic and electronic systems (Lehn, 1990). 2-Aminopyrimidine forms 1:1 adducts with different mono- and dicarboxylic acids (Etter & Adsmund, 1990) rather than individual self-assembly (Scheinbeim & Schempp, 1976). The adducts of carboxylic acids with 2-aminoheterocyclic ring systems form a graph-set motif of $R_2^2(8)$ (Lynch & Jones, 2004). Pyrimidine and aminopyrimidine derivatives are biologically important compounds as they occur in nature as components of nucleic acids. Some aminopyrimidine derivatives are used as anti-folate drugs (Hunt *et al.*, 1980; Baker & Santi, 1965).

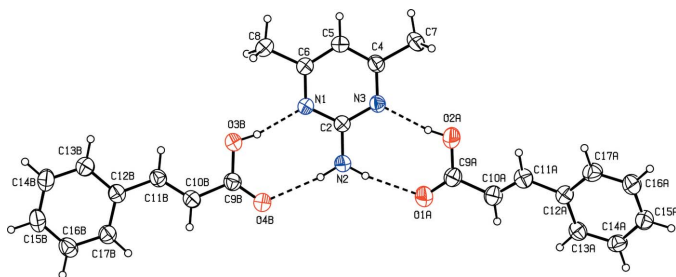


The crystal structures of aminopyrimidine derivatives (Schwalbe & Williams, 1982), aminopyrimidine carboxylates (Hu *et al.*, 2002) and co-crystal structures (Chinnakali *et al.*, 1999) have been reported. The crystal structures of 2-amino-4,6-dimethylpyrimidinium bromide 2-amino-4,6-dimethyl-

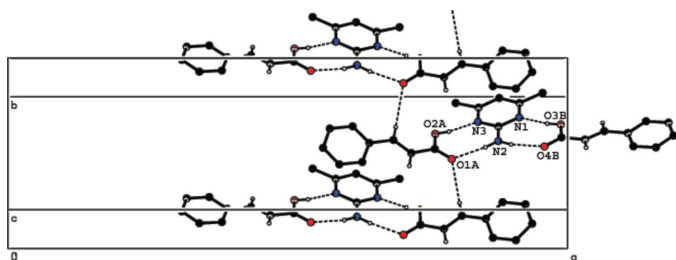
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**Figure 1**

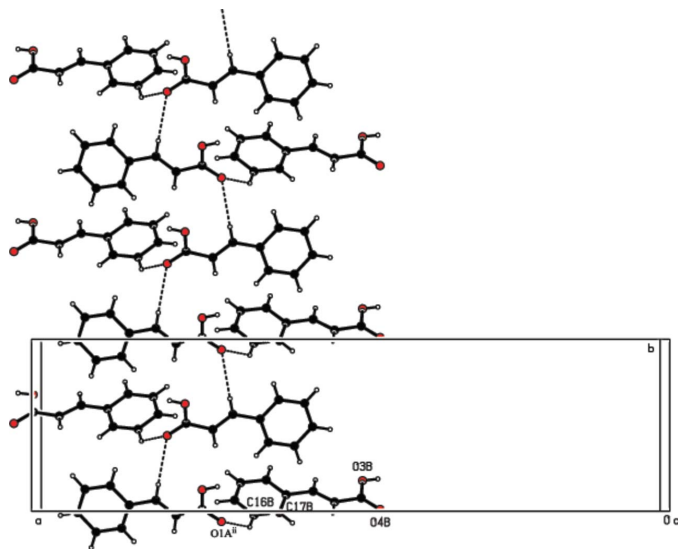
An ORTEP (Johnson, 1976) diagram of the asymmetric unit of (I), showing 50% probability displacement ellipsoids. The hydrogen bonds are shown as dashed lines.

**Figure 2**

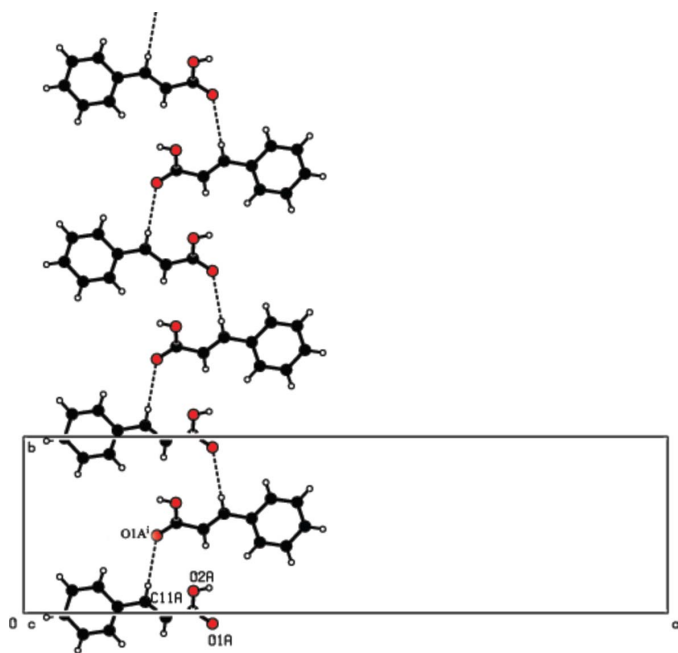
A view of the hydrogen bonding patterns in (I). H atoms not involved in hydrogen bonding have been omitted for clarity.

pyrimidine monohydrate (Panneerselvam *et al.*, 2004), 2-amino-4,6-dimethylpyrimidinium hydrogen sulfate (Hemamalini *et al.*, 2005) and bis(2,4-diamino-6-oxypyrimidinium) sulfate monohydrate (Muthiah *et al.*, 2004) have been recently reported from our laboratory. Most of the supramolecular crystals originate from strong N—H···O and O—H···N hydrogen bonds, and weak C—H···O bonds are known to play a significant role in determining the molecular packing of organic solids (Taylor & Kennard, 1982). In this paper, the hydrogen-bonding patterns in the 2-amino-4,6-dimethylpyrimidine–cinnamic acid (1/2) cocrystal, (I), are discussed.

An ORTEP (Johnson, 1976) view of (I) is shown in Fig. 1, and selected bond distances and angles are given in Table 1. The asymmetric unit contains one 2-amino-4,6-dimethylpyrimidine (AMPY) molecule and two cinnamic acid molecules (*A* and *B*). The acid molecules *A* and *B* make dihedral angles with the planar pyrimidine ring of 2.23 (10) and 26.75 (10)°, respectively. Within the asymmetric unit, atoms O3B, O2A and the 2-amino group (NH₂) act as hydrogen-bond donors to atoms N1, N3, O1A and O4B. The AMPY molecule is linked to the pair of cinnamic acid molecules by N—H···O and O—H···N intermolecular hydrogen bonds, to form two symmetry-independent eight-membered rings, each of which has the graph-set motif of R₂²(8) (Etter, 1990; Bernstein *et al.*, 1995). These units are further connected *via* a C—H···O hydrogen bond involving the acid molecule *A* as shown in Fig. 2 and Table 2. This type of pairing has been observed in the crystal structures of 2-aminopyrimidine–fumaric acid (Goswami, Mahapatra, Ghosh *et al.*, 1999 or Goswami, Mahapatra, Nigam *et al.*, 1999), 2-aminopyrimidine-(+)-camphoric acid (Goswami *et al.*, 2000), 2-aminopyrimidine–

**Figure 3**

C—H···O interactions observed in cinnamic acid molecules *A* and *B* [symmetry code: (ii) 1 - *x*, *y*, $\frac{3}{2}$ - *z*].

**Figure 4**

A view of the supramolecular chain observed for molecule *A* [symmetry code: (i) $\frac{1}{2}$ - *x*, $\frac{1}{2}$ + *y*, *z*].

succinic acid (Etter *et al.*, 1990) and 2-aminopyrimidine–terephthalic acid (Goswami, Mahapatra, Ghosh *et al.*, 1999 or Goswami, Mahapatra, Nigam *et al.*, 1999). The two crystallographically independent cinnamic acid molecules are connected *via* C—H···O hydrogen bonds, leading to the formation of a hydrogen-bonded supramolecular chain parallel to the *b* axis (Fig. 3). Symmetry-related cinnamic acid *A* molecules are linked to one another through a C—H···O interaction to form a chain extending in the *c* direction (Fig. 4). π – π interactions between the aromatic rings are also

observed. The N1/N3/C2/C4–C6 pyrimidine ring of AMPY has stacking interactions with the benzene rings (C12A–C17A and C12B–C17B) of both cinnamic acid molecules. The perpendicular separations are 3.402 and 3.648 Å, respectively, and the centroid-to-centroid distances are 3.7908 (16) and 3.9211 (15) Å, respectively. The slip angles (the angle between the centroid vector and the normal to the plane) are 26.3 and 22.2°, respectively. These values are typical for aromatic π – π stacking interactions (Hunter, 1994).

Experimental

A hot methanol solution of 2-amino-4,6-dimethylpyrimidine (31 mg, from Aldrich) and cinnamic acid (37 mg, from LOBA Chemie, India) were mixed in a 1:1 molar ratio and warmed for half an hour over a water bath. On slow evaporation, plate-like crystals of (I) were obtained.

Crystal data

$C_6H_9N_3 \cdot 2C_9H_8O_2$	Mo $K\alpha$ radiation
$M_r = 419.47$	Cell parameters from 25 reflections
Orthorhombic, <i>Pbcn</i>	$\theta = 10.3$ – 13.1°
$a = 32.045$ (2) Å	$\mu = 0.09$ mm $^{-1}$
$b = 8.7676$ (7) Å	$T = 293$ (2) K
$c = 15.9796$ (10) Å	Block, colourless
$V = 4489.6$ (5) Å 3	$0.3 \times 0.2 \times 0.15$ mm
$Z = 8$	
$D_x = 1.241$ Mg m $^{-3}$	

Data collection

Enraf–Nonius MACH3 single-crystal diffractometer	$R_{int} = 0.071$
$\omega/2\theta$ scans	$\theta_{max} = 25.0^\circ$
Absorption correction: ψ scan (North <i>et al.</i> , 1968)	$h = -38 \rightarrow 1$
$T_{min} = 0.970$, $T_{max} = 0.982$	$k = -1 \rightarrow 10$
5035 measured reflections	$l = -18 \rightarrow 1$
3956 independent reflections	1 standard reflection
2330 reflections with $I > 2\sigma(I)$	every 100 reflections
	intensity decay: none

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0666P)^2 + 1.8369P]$
$R[F^2 > 2\sigma(F^2)] = 0.048$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.158$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.03$	$\Delta\rho_{max} = 0.21$ e Å $^{-3}$
3956 reflections	$\Delta\rho_{min} = -0.18$ e Å $^{-3}$
305 parameters	
Only H-atom displacement parameters refined	

Table 1

Selected geometric parameters (Å, °).

O1A–C9A	1.201 (4)	N1–C2	1.349 (3)
O2A–C9A	1.326 (3)	N2–C2	1.333 (3)
O3B–C9B	1.316 (3)	N3–C2	1.346 (3)
O4B–C9B	1.209 (4)	N3–C4	1.338 (3)
N1–C6	1.338 (3)		
C2–N1–C6	117.5 (2)	N1–C2–N2	117.3 (2)
C2–N3–C4	117.2 (2)	N1–C2–N3	124.7 (2)
O1A–C9A–C10A	122.1 (3)	N2–C2–N3	118.0 (2)
O2A–C9A–C10A	114.7 (2)	N3–C4–C5	121.0 (2)
O1A–C9A–O2A	123.2 (3)	N3–C4–C7	116.6 (2)
O3B–C9B–O4B	123.5 (3)	N1–C6–C5	120.4 (2)
O3B–C9B–C10B	114.0 (2)	N1–C6–C8	116.8 (2)
O4B–C9B–C10B	122.5 (3)		

Table 2

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N2–H1 \cdots O1A	0.86	2.08	2.928 (3)	171
N2–H2 \cdots O4B	0.86	2.11	2.966 (3)	170
O2A–H2A \cdots N3	0.82	1.88	2.694 (3)	170
O3B–H3B \cdots N1	0.82	1.86	2.670 (3)	168
C11A–H11A \cdots O1A ⁱ	0.93	2.56	3.349 (4)	143
C16B–H16B \cdots O1A ⁱⁱ	0.93	2.55	3.230 (4)	130

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

The H atoms were included in calculated positions and refined using a riding model, with C–H, O–H and N–H distances of 0.93–0.96, 0.82 and 0.86 Å, respectively, and freely refined $U_{iso}(H)$.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *PLATON*.

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