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

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.002 Å
R factor = 0.043
wR factor = 0.127
Data-to-parameter ratio = 16.1

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

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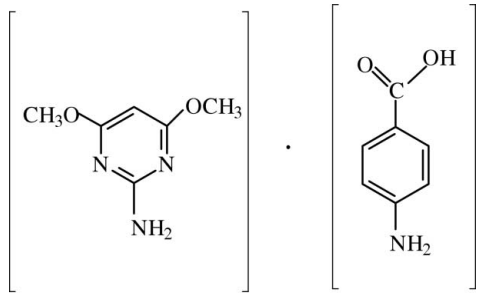
In the title cocrystal, $C_6H_9N_3O_2\cdot C_7H_7NO_2$, the 2-amino-4,6-dimethoxypyrimidine molecule interacts with the carboxyl group of the 4-aminobenzoic acid molecule through N—H···O and O—H···N hydrogen bonds, forming a cyclic hydrogen-bonded motif [$R_2^2(8)$]. This motif further self-organizes through N—H···O hydrogen bonds to generate an array of six hydrogen bonds with the rings having the graph-set notation $R_2^3(6)$, $R_2^2(8)$, $R_4^2(8)$, $R_2^2(8)$ and $R_2^3(6)$. The 4-aminobenzoic acid molecules self-assemble *via* N—H···O hydrogen bonds to form a supramolecular chain along the *c* axis.

Comment

Pyrimidine and aminopyrimidine derivatives are biologically important compounds as they occur in nature as components of nucleic acids. Some aminopyrimidine derivatives are used as antifolate drugs (Hunt *et al.*, 1980; Baker & Santi, 1965). The adducts of carboxylic acids with 2-aminoheterocylic ring systems form a graph-set motif of $R_2^2(8)$ (Lynch & Jones, 2004). The crystal structure of 2-amino-4,6-dimethoxy pyrimidine has also been reported (Low *et al.*, 2002). The crystal structure of 4-aminobenzoic acid (Lai & Marsh, 1967) is known. The interplay of strong N—H···O and O—H···N hydrogen bonds, and weak C—H···O interactions, forms supramolecular motifs, involved in the molecular packing of organic solids. (Taylor & Kennard, 1982). In the present study, the hydrogen-bonding patterns in the 2-amino-4,6-dimethoxypyrimidine–4-aminobenzoic acid (1/1) cocrystal, (I), are investigated.



(I)

The asymmetric unit (Fig. 1) contains one 2-amino-4,6-dimethoxypyrimidine molecule and one 4-aminobenzoic acid molecule, which are linked by N2—H2*B*···O3 and O4—H4···N1 hydrogen bonds (Table 1), forming an eight-membered ring of graph-set notation $R_2^2(8)$ (Etter, 1990; Bernstein *et al.*, 1995). This type of pairing has been observed in the crystal structure of 2-aminopyrimidine–fumaric acid (Goswami *et al.*, 1999) and 2-aminopyrimidine–(+)-camphoric

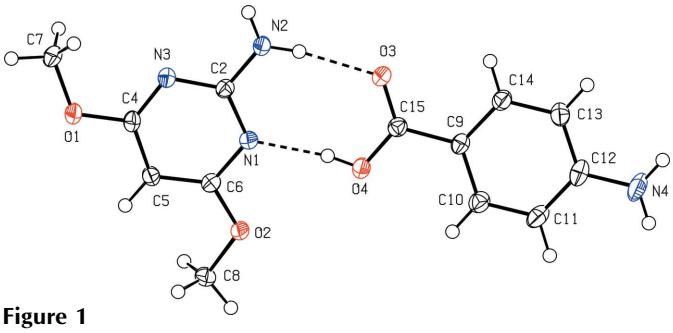


Figure 1
A view of the asymmetric unit of (I), showing 50% probability displacement ellipsoids. Dashed lines indicate hydrogen bonds.

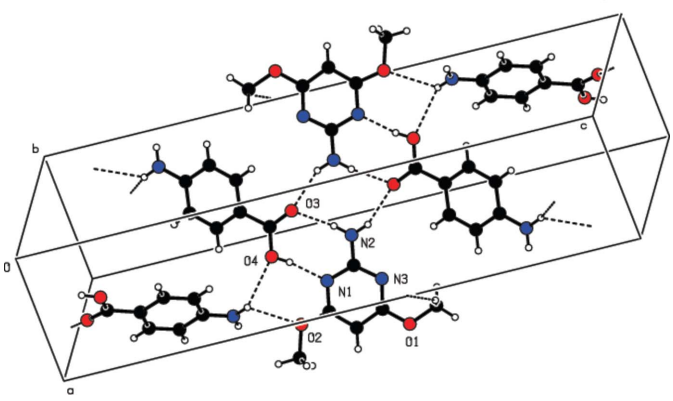


Figure 2
Hydrogen-bonding (dashed lines) patterns in compound (I).

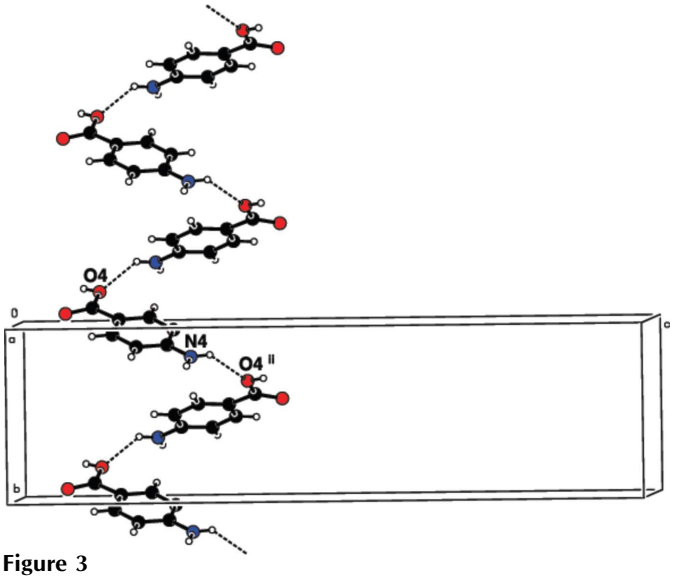


Figure 3
Hydrogen-bonding (dashed lines) patterns in the supramolecular chain in compound (I) [symmetry code: (ii) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$].

acid (Goswami *et al.*, 2000). This motif further self organizes through N—H···O hydrogen bonds (Fig. 2) to generate an array of six hydrogen bonds with the rings having the graph-set notations $R_2^3(6)$, $R_2^2(8)$, $R_4^2(8)$, $R_2^2(8)$ and $R_2^3(6)$. The 4-aminobenzoic acid molecules self-assemble *via* N—H···O hydrogen bonds to form a supramolecular chain along the *c* axis, with the graph-set notation $C(9)$; this is shown in Fig. 3. The pyrimidine ring is centrosymmetrically linked through a pair of C—H···O hydrogen bonds involving a methyl group (C7) and methoxy atom O2. A π–π stacking interaction between two aminopyrimidine groups (at x, y, z and $-x, 1-y, -z$), with a perpendicular separation of 3.306 Å, a centroid–centroid distance of 3.4129 (8) Å and a slip angle (the angle between the centroid vector and the normal to the plane) of 14.39° has also been observed. These are typical aromatic stacking values (Hunter, 1994).

Experimental

A hot methanol solution (20 ml) of 2-amino-4,6-dimethoxy pyrimidine (38 mg, Aldrich) and 4-aminobenzoic acid (34 mg, Loba Chemie) was warmed for half an hour over a water bath. The mixture was cooled slowly and kept at room temperature; after a few days, colourless plate-like crystals were obtained.

Crystal data

$C_6H_9N_3O_2\cdot C_7H_7NO_2$
$M_r = 292.30$
Monoclinic, $P2_1/c$
$a = 6.6358$ (4) Å
$b = 7.5560$ (5) Å
$c = 27.4226$ (16) Å
$\beta = 94.418$ (2)°
$V = 1370.89$ (15) Å^3
$Z = 4$
$D_x = 1.416$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.11$ mm^{-1}
$T = 293$ K
Plate, colourless
0.44 × 0.32 × 0.08 mm

Data collection

Bruker–Nonius KappaCCD area-detector diffractometer
φ and ω scans
Absorption correction: none
14577 measured reflections
3130 independent reflections
2469 reflections with $I > 2\sigma(I)$
$R_{int} = 0.032$
$\theta_{max} = 27.5°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.127$
$S = 1.03$
3130 reflections
194 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0746P)^2 + 0.4081P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.45$ e Å^{-3}
$\Delta\rho_{min} = -0.30$ e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.016 (4)

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2A···O3^{i}	0.86	2.07	2.8546 (17)	152
N2—H2B···O3	0.86	1.96	2.8180 (17)	172
O4—H4···N1	0.82	1.83	2.6426 (16)	171
N4—H4A···O2^{ii}	0.86	2.47	3.0621 (18)	127
N4—H4A···O4^{ii}	0.86	2.45	3.1566 (18)	140
C7—H7C···O2^{iii}	0.96	2.60	3.4578 (18)	150

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

All H atoms were positioned geometrically and were refined using a riding model. The C—H, O—H and N—H bond lengths are 0.93–0.96, 0.82 and 0.86 Å, respectively [U_{iso}(H) = 1.2U_{eq}(parent atom)].

Data collection: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT* (Hooft, 1998); cell refinement: *DENZO* and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics:

ORTEPII (Johnson, 1976); software used to prepare material for publication: *PLATON* (Spek, 2003).

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