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4,6-Dimethoxy-2-phthalimidopyrimidine: sheets built from π-stacked hydrogen-bonded chains

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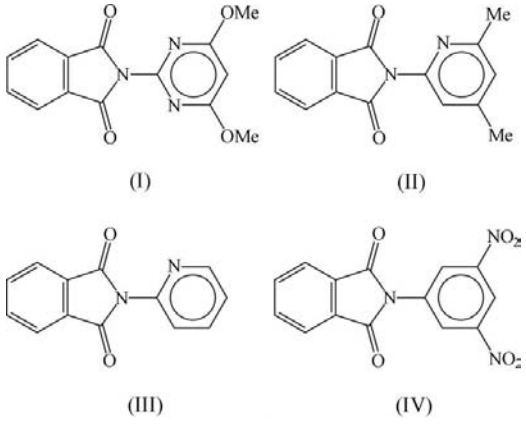
The molecules of the title compound, $C_{14}H_{11}N_3O_4$, have approximate but noncrystallographic twofold rotational symmetry. The molecules are linked into chains by a C—H···O hydrogen bond, and these chains are linked into sheets by a π–π stacking interaction. The significance of this study lies in its comparison of the modes of supramolecular aggregation in the title compound and those in some close analogues.

Comment

An attractive possibility as a protecting group for aminopyrimidines is the phthalimide unit, which can be readily introduced by reaction of the aminopyrimidine with phthalic anhydride using microwave irradiation under solvent-free conditions. We report the molecular and supramolecular structures of the title compound, (I) (Fig. 1), synthesized in this fashion from 2-amino-4,6-dimethoxypyrimidine, and we compare its mode of supramolecular aggregation with that observed in several closely analogous compounds.



The torsion angles defining the conformations of the two independent methoxy groups (Table 1) indicate that the molecule overall has approximate, although noncrystallographic, twofold rotational symmetry. The dihedral angle between the mean planes of the pyrimidine ring and the phthalimide fragment is 46.4 (2)°, while the two independent methoxy C atoms are displaced by only 0.186 (2) and 0.068 (2) Å from the plane of the pyrimidine ring. Despite this near coplanarity of the methoxy C atoms with the pyrimidine ring, the two exocyclic bond angles at each of C14 and C16 are fairly similar (Table 1), in contrast to the difference of *ca* 10° typically found in methoxyarene derivatives. The bond distances in (I) present no unusual values.

The molecules of (I) are linked by a single C—H···O hydrogen bond (Table 2) into *C*(10) (Bernstein *et al.*, 1995) chains running parallel to the [001] direction and consisting of molecules related by translation. Chains of this type are weakly linked into sheets by a single π–π stacking interaction. The pyrimidine and arene rings in the molecules at (*x*, *y*, *z*) and ($x+\frac{1}{2}$, $-y+\frac{3}{2}$, $z-\frac{1}{2}$), respectively, make a dihedral angle of 11.6 (2)°; the ring-centroid separation is 3.618 (2) Å and the interplanar spacing is *ca* 3.31°, corresponding to a ring-centroid offset of *ca* 1.46 Å. The effect of this interaction is to link the hydrogen-bonded [001] chains into a sheet parallel to (100) (Fig. 2). Two sheets of this type pass through each unit cell, containing molecules related by the *n*-glide planes at $y=\frac{1}{4}$ and $y=\frac{3}{4}$, but there are no direction-specific interactions between adjacent sheets.

There appear to be no analogues of (I) containing the same ring system, regardless of substituents, recorded in the Cambridge Structural Database (CSD; Allen, 2002). However, the structures of the disubstituted 2-pyridyl analogue (II) (CSD refcode JUBLOH; Rodier *et al.*, 1992) and the unsubstituted 2-pyridyl compound (III) (CSD refcode VEXNES; Liang & Li, 2007) have been reported, although in neither of

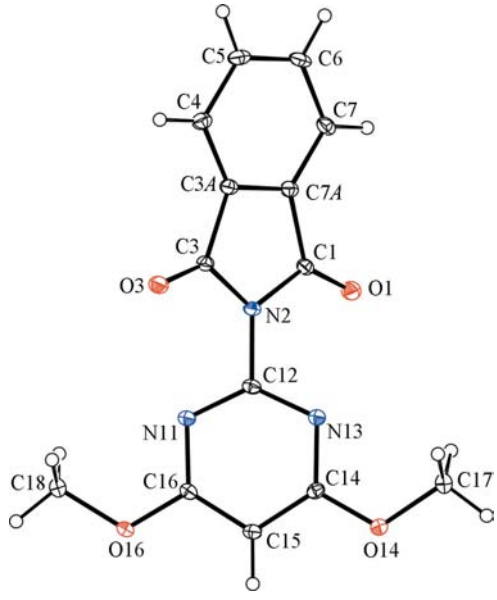


Figure 1
The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

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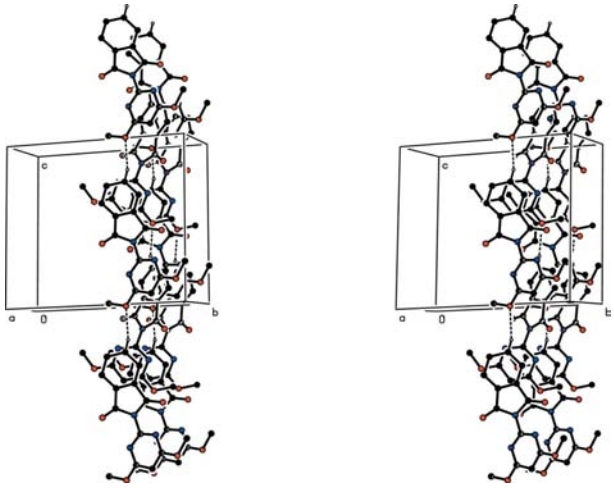

Figure 2
A stereoview of part of the crystal structure of (I), showing the formation of a sheet parallel to (100) built by the π stacking of the hydrogen-bonded chains running parallel to [001]. For the sake of clarity, H atoms not involved in the motif shown have been omitted.

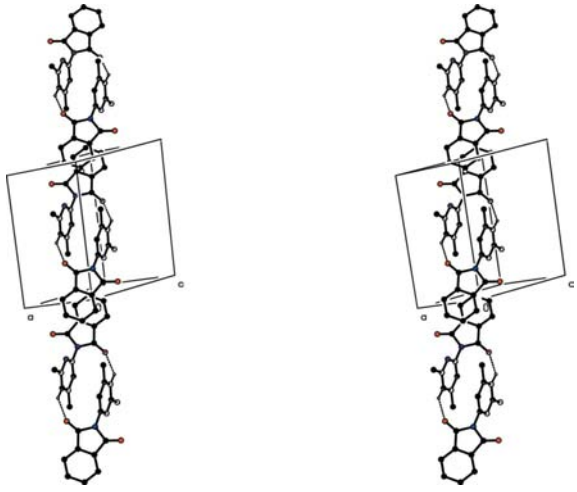

Figure 3
A stereoview of part of the crystal structure of (II), showing the formation of a chain of π-stacked hydrogen-bonded dimers. The original atom coordinates (Rodier *et al.*, 1992) have been used. For the sake of clarity, H atoms not involved in the motif shown have been omitted.

these reports is there any consideration of the intermolecular interactions and aggregation. It is thus of interest to analyse these two structures briefly here in order to compare them with the structure of (I).

In (II), the pattern of substitution matches that in (I), but on a pyridine ring rather than a pyrimidine ring. A combination of a C—H$\cdots$O hydrogen bond and a π–π stacking interaction between strictly parallel arene rings generates a chain of π-stacked hydrogen-bonded dimers running parallel to the [111] direction of the triclinic cell. Hydrogen-bonded $R_2^2(16)$ rings centred at $(n, n+\frac{1}{2}, n)$ (where n represents zero or an integer) alternate with π–π stacking interactions across $(n-\frac{1}{2}, n, n-\frac{1}{2})$ (where n represents zero or an integer) (Fig. 3). By

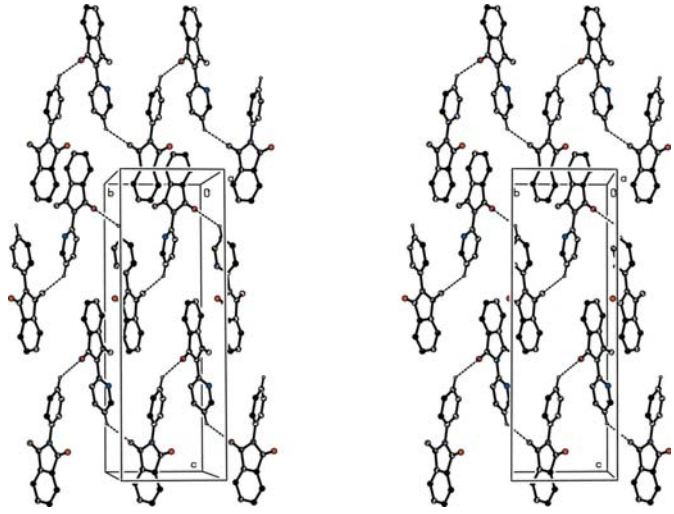

Figure 4
A stereoview of part of the crystal structure of (III), showing the formation of a sheet of π-stacked hydrogen-bonded chains. The original atom coordinates (Liang & Li, 2007) have been used. For the sake of clarity, H atoms not involved in the motif shown have been omitted.

contrast, in the analogous compound (III), which differs from (II) only in its lack of the two methyl groups, a combination of a C—H$\cdots$O hydrogen bond and a π–π stacking interaction gives rise to a sheet parallel to (100) (Fig. 4). This sheet is formed by the π stacking of hydrogen-bonded $C(8)$ chains running parallel to the [010] direction; this type of aggregation is thus somewhat similar to that found in (I). The molecules of the dinitrophenyl analogue (IV), where the substituted ring now contains no N atoms, lie across twofold rotation axes in the space group $P2/n$ (Glidewell *et al.*, 2004), and the supramolecular aggregation consists of hydrogen-bonded chains of rings linked into sheets by dipolar O$\cdots$N and O$\cdots$C interactions.

Hence, (I), (II) and (IV), which have similar constitutions and very similar molecular shapes, all exhibit distinctly different patterns of supramolecular aggregation, namely π-stacked hydrogen-bonded chains in (I), π-stacked hydrogen-bonded dimers in (II) and hydrogen-bonded chains linked by dipolar interactions in (IV). The most similar structure types are those in (I) and (III), where the molecules concerned are, in fact, the least similar within this series.

Experimental

Finely ground 2-amino-4,6-dimethoxypyrimidine (1.29 mmol) and phthalic anhydride (1.29 mmol) were mixed thoroughly and the mixture was then subjected to microwave irradiation (8 min, maximum temperature 423 K and maximum power 150 W) in a monomode microwave CEM reactor. The resulting solid was shaken with sodium hydrogen carbonate (5 ml of a saturated aqueous solution), and the crude product, (I), was collected by filtration and washed with diethyl ether. Crystals suitable for single-crystal X-ray diffraction were obtained by slow evaporation of a solution in dimethyl sulfoxide (yield 65%, m.p. 465–466 K). HRMS found 285.0741; $C_{14}H_{11}N_3O_4$ requires 285.0750.

Crystal data

$C_{14}H_{11}N_3O_4$
$M_r = 285.26$
Monoclinic, $P2_1/n$
$a = 7.2904$ (8) Å
$b = 13.896$ (2) Å
$c = 12.5021$ (11) Å
$\beta = 96.476$ (7)°
$V = 1258.5$ (3) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.11$ mm^{-1}
$T = 120$ (2) K
0.37 × 0.24 × 0.22 mm

Data collection

Bruker–Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{min} = 0.953$, $T_{max} = 0.975$
29699 measured reflections
2893 independent reflections
2250 reflections with $I > 2\sigma(I)$
$R_{int} = 0.042$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.101$
$S = 1.12$
2893 reflections
192 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.27$ e Å^{-3}
$\Delta\rho_{min} = -0.30$ e Å^{-3}

Table 1
Selected bond and torsion angles (°).

N13—C14—O14	118.71 (14)	N11—C16—O16	119.05 (14)
C15—C14—O14	117.79 (14)	C15—C16—O16	117.28 (13)
C1—N2—C12—N11	−136.10 (15)	C17—O14—C14—N13	1.3 (2)
C1—N2—C12—N13	44.7 (2)	C18—O16—C16—N11	−6.6 (2)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C6—H6···O16^{i}	0.95	2.47	3.3920 (19)	163

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

The space group $P2_1/n$ was uniquely assigned from the systematic absences. All H atoms were located in difference maps and subsequently treated as riding atoms, with C—H distances of 0.95 (arene and pyrimidine) or 0.98 Å (methyl), and with $U_{iso}(H) = kU_{eq}(C)$, where $k = 1.5$ for the methyl groups and $k = 1.2$ for the ring H atoms.

Data collection: *COLLECT* (Hooft, 1999); cell refinement: *DIRAX/LSQ* (Duisenberg *et al.*, 2000); data reduction: *EVALCCD* (Duisenberg *et al.*, 2003); program(s) used to solve structure: *SIR2004* (Burla *et al.*, 2005); program(s) used to refine structure: *OSCAIL* (McArdle, 2003) and *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: HJ3078). Services for accessing these data are described at the back of the journal.

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