

4-Amino-2,6-dimethoxypyrimidine: hydrogen-bonded sheets of $R_2^2(8)$ and $R_6^6(28)$ rings, reinforced by an aromatic π - π -stacking interaction

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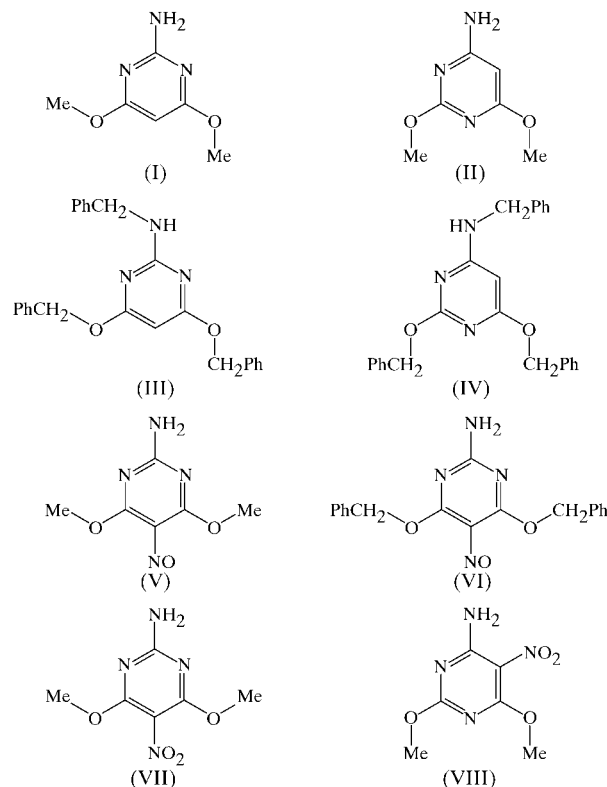
Molecules of the title compound, $C_6H_9N_3O_2$, are linked by an N—H \cdots O hydrogen bond [$H\cdots O = 2.29 \text{ \AA}$, $N\cdots O = 3.169(2) \text{ \AA}$ and $N-H\cdots O = 173^\circ$] and an N—H \cdots N hydrogen bond [$H\cdots N = 2.12 \text{ \AA}$, $N\cdots N = 2.999(2) \text{ \AA}$ and $N-H\cdots N = 175^\circ$] into sheets containing centrosymmetric $R_2^2(8)$ and $R_6^6(28)$ rings; the sheets are reinforced by a single aromatic π - π -stacking interaction.

Comment

The supramolecular structure of 2-amino-4,6-dimethoxy-pyrimidine, (I) (Low *et al.*, 2002), consists of chains of edge-fused $R_2^2(8)$ rings generated solely by N—H \cdots N hydrogen bonds, and these chains are linked into a three-dimensional framework by means of aromatic π - π -stacking interactions. We now report the molecular and supramolecular structure of the isomeric compound 4-amino-2,6-dimethoxypyrimidine, (II), which proves to adopt a conformation different from that of (I) and a two-dimensional supramolecular structure involving both N—H \cdots N and N—H \cdots O hydrogen bonds, and aromatic π - π -stacking interactions.

Whereas compound (I), which could in principle adopt a conformation having C_{2v} ($mm2$) molecular symmetry adopts a conformation with one methoxy group *anti* to the amino group and one methoxy group *syn*, in compound (II), by contrast, both methoxy groups are *anti* to the amino substituent (Fig. 1 and Table 1). A similar pattern of molecular conformation has been observed in the isomeric tribenzyl compounds (III) and (IV) (Glidewell *et al.*, 2003a); on the other hand, the 5-nitroso compounds (V) (Glidewell *et al.*, 2002) and (VI) (Quesada, Low *et al.*, 2002) both exhibit the third possible conformational

arrangement of the alkoxy substituents. Of the two isomeric nitropyrimidines (VII) and (VIII) (Glidewell *et al.*, 2003b), (VII) adopts an alkoxy conformation similar to those in (V) and (VI), while (VIII) adopts a conformation similar to those in (II) and (IV). The consistency of these conformational arrangements, independent of the nature, in particular the bulk, of the alkyl substituent, suggests that the underlying causes determining the selection of the conformations may be intramolecular rather than intermolecular in origin.



There is no significant bond fixation within the pyrimidine ring of (II) (Table 1) and the exocyclic bond lengths are also normal for their types (Allen *et al.*, 1987). In this respect, the molecular–electronic structure of (II) is markedly different from those in a large number of analogous pyrimidines carrying a 5-nitroso substituent, where highly polarized structures are the norm (Low *et al.*, 2000; Low, Cannon *et al.*, 2001; Low, Moreno *et al.* 2001; Quesada, Marchal *et al.*, 2002).

The two-dimensional supramolecular structure of (II) is most readily analysed using the substructure approach (Gregson *et al.*, 2000), which considers the effect of each of the intermolecular interactions in turn (Table 2). Amino atom N4 in the molecule at (x, y, z) acts as hydrogen-bond donor, *via* H4B, to O6 in the molecule at $(1 - x, \frac{1}{2} + y, \frac{3}{2} - z)$, while N4 at $(1 - x, \frac{1}{2} + y, \frac{3}{2} - z)$, in turn, acts as donor to O6 at $(x, 1 + y, z)$. In this manner, a $C(6)$ chain is formed, running parallel to the [010] direction and generated by the 2_1 screw axis along $(\frac{1}{2}, y, \frac{3}{2})$. Four such chains run through each unit cell. The same amino atom N4 also acts, this time *via* H4A, as hydrogen-bond donor to ring atom N3 in the molecule at $(1 - x, 1 - y, 1 - z)$, so generating a centrosymmetric $R_2^2(8)$ ring. The molecule at $(1 - x, 1 - y, 1 - z)$ forms part of the $C(6)$ chain generated by

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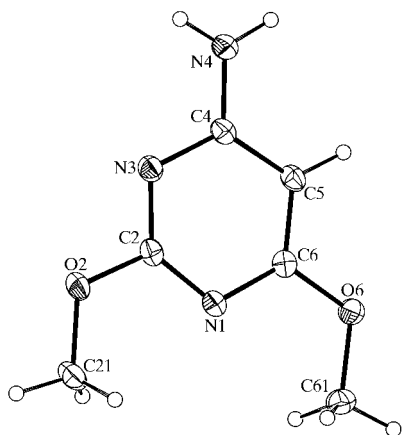


Figure 1

The molecule of (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

the 2_1 screw axis along $(\frac{1}{2}, -y, \frac{1}{4})$, and the effect of the N—H...N hydrogen bond is thus to link the C(6) chains into a sheet parallel to (100). This sheet contains $R_2^2(8)$ and $R_6^6(28)$ rings, both types centrosymmetric, arranged in a checkerboard fashion (Fig. 2). If the individual molecules are regarded as the nodes of the resulting net, then this is of the (6,3)-type, while if the $R_2^2(8)$ dimers are taken as the nodes, then the net is of the (4,4)-type (Batten & Robson, 1998).

The formation of the (100) sheet is reinforced by a single aromatic π – π -stacking interaction. The molecules at (x, y, z) and $(1 - y, -y, 1 - z)$ are components of the same $R_6^6(28)$ ring, and the pyrimidine rings in these molecules are strictly parallel, with an interplanar spacing of 3.371 (2) Å; the centroid–centroid separation is 3.624 (2) Å, corresponding to a centroid offset of 1.330 (2) Å.

There are two (100) sheets passing through each unit cell, in the domains $0.24 < x < 0.76$ and $0.75 < x < 1.26$, respectively; there are no direction-specific interactions between adjacent sheets nor is there any interweaving of the sheets.

Finally, we note briefly here some common features in the supramolecular aggregation of compounds (I)–(VIII), *i.e.* paired N—H...N hydrogen bonds occur in each of (I), (III), (IV) and (VIII), giving chains in (I) and dimers in the remainder, while a combination of N—H...O and N—H...N hydrogen bonds occurs in both (II) and (VII), giving sheets in each case.

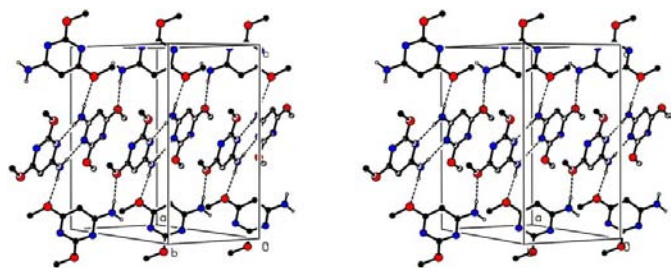


Figure 2

Stereoview of part of the crystal structure of (II), showing the formation of a (100) sheet of $R_2^2(8)$ and $R_6^6(28)$ rings, reinforced by a π – π -stacking interaction.

Experimental

A sample of (II) was purchased from Aldrich. Crystals suitable for single-crystal X-ray diffraction were grown by slow evaporation of a solution in *n*-butanol.

Crystal data

$C_6H_9N_3O_2$
 $M_r = 155.16$
 Orthorhombic, *Pbca*
 $a = 13.5867$ (6) Å
 $b = 7.8621$ (2) Å
 $c = 13.9932$ (6) Å
 $V = 1494.75$ (10) Å³
 $Z = 8$
 $D_x = 1.379$ Mg m⁻³

Mo K α radiation
 Cell parameters from 1703 reflections
 $\theta = 2.9$ – 27.4°
 $\mu = 0.11$ mm⁻¹
 $T = 120$ (2) K
 Needle, colourless
 $0.35 \times 0.08 \times 0.04$ mm

Data collection

Nonius KappaCCD diffractometer
 φ scans, and ω scans with κ offsets
 Absorption correction: multi-scan
 (DENZO-SMN; Otwinowski & Minor, 1997)
 $T_{\min} = 0.968$, $T_{\max} = 0.995$
 13 259 measured reflections

1703 independent reflections
 1056 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.081$
 $\theta_{\max} = 27.4^\circ$
 $h = -17 \rightarrow 17$
 $k = -8 \rightarrow 10$
 $l = -18 \rightarrow 14$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.047$
 $wR(F^2) = 0.125$
 $S = 1.05$
 1703 reflections
 103 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0626P)^2 + 0.1218P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.22$ e Å⁻³
 $\Delta\rho_{\min} = -0.22$ e Å⁻³
 Extinction correction: SHELXL97
 Extinction coefficient: 0.010 (2)

Table 1

Selected geometric parameters (Å, °).

| | | | |
|--------------|-----------|--------------|-----------|
| N1—C2 | 1.327 (2) | C2—O2 | 1.346 (2) |
| C2—N3 | 1.329 (2) | O2—C21 | 1.431 (2) |
| N3—C4 | 1.356 (2) | C4—N4 | 1.344 (2) |
| C4—C5 | 1.396 (2) | C6—O6 | 1.355 (2) |
| C5—C6 | 1.371 (2) | O6—C61 | 1.443 (2) |
| C6—N1 | 1.338 (2) | | |
| N1—C2—O2—C21 | −1.9 (2) | N1—C6—O6—C61 | −0.4 (2) |

Table 2

Hydrogen-bonding 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> |
|---------------------------|-------------|---------------|-----------------------|-------------------------|
| N4—H4A...N3 ⁱ | 0.88 | 2.12 | 2.999 (2) | 175 |
| N4—H4B...O6 ⁱⁱ | 0.88 | 2.29 | 3.169 (2) | 173 |

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

Crystals of (II) are orthorhombic and the space group *Pbca* was uniquely assigned from the systematic absences. H atoms were treated as riding, with C—H distances of 0.95 (aromatic) and 0.98 Å (CH₃), and N—H distances of 0.88 Å.

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; 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: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

X-ray data were collected at the EPSRC X-ray Crystallographic Service, University of Southampton, England; the authors thank the staff for all their help and advice. JNL thanks NCR Self-Service, Dundee, for grants which have provided computing facilities for this work.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1625). Services for accessing these data are described at the back of the journal.

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