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2-Amino-4,6-dimethoxy-5-nitrosopyrimidine–water (4/3): seven independent molecular components are linked into a three-dimensional framework by six three-centre and eight two-centre hydrogen bonds

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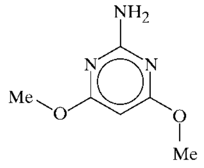
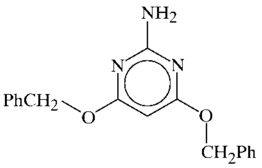
In the title compound, $4C_6H_8N_4O_3 \cdot 3H_2O$, the pyrimidine molecules all exhibit a polarized molecular electronic structure; the seven-component asymmetric unit can be selected as a closed cyclic aggregate and the linking of these aggregates can be analysed in terms of translational chain motifs running parallel to [110], [210] and [011], which combine to generate a single three-dimensional framework.

Comment

In 2-amino-4,6-dimethoxypyrimidine, (I), both N—H bonds are involved in the formation of N—H···N hydrogen bonds, so forming a chain of edge-fused rings containing two distinct $R_2^2(8)$ motifs (Low *et al.*, 2002). The benzyloxy analogue, 2-amino-4,6-bis(benzyloxy)pyrimidine, (II), on the other hand, utilizes only one of the N—H bonds in forming an N—H···N hydrogen bond, again forming an $R_2^2(8)$ motif, while the other N—H bond forms an N—H···O hydrogen bond which generates a simple *C*(6) chain motif; the combination of the ring and chain motifs generates a molecular ladder (Quesada, Marchal *et al.*, 2002). There are no $R_2^2(8)$ rings in 2-amino-4,6-bis(benzyloxy)-5-nitrosopyrimidine, (III), the nitrosated analogue of (II) (Quesada, Low *et al.*, 2002). Instead, one N—H bond participates in a three-centre N—H···(N,O) hydrogen bond, while the other forms an N—H···π(arene) hydrogen bond; the overall supramolecular structure is again one-dimensional. Thus, the supramolecular structures of (I)–(III) involve two, one or zero distinct $R_2^2(8)$ rings, respectively, containing paired N—H···N hydrogen bonds. Intrigued by the differences in structural behaviour, not only between (I) and (II), but also between (II) and (III), we have now investigated the nitrosated analogue of (I), namely 2-amino-4,6-dimethoxy-5-nitrosopyrimidine, which upon crystallization from acetone, as used for (I) and (III), yields the stoichiometric hydrate $4C_6H_8N_4O_3 \cdot 3H_2O$, (IV).


(I)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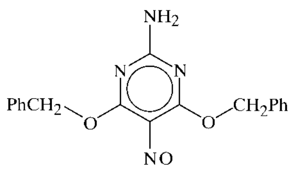
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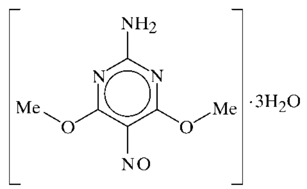
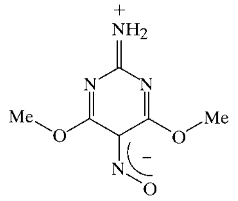

(IV)


(IV*a*)

Compound (IV) (Fig. 1) crystallizes in the non-centrosymmetric triclinic space group *P*1, with four pyrimidine molecules and three water molecules in the asymmetric unit. Each of the pyrimidine molecules adopts a conformation in which the two methyl C atoms are essentially in the plane of the ring, but directed away from the nitroso substituent, just as in (III) (Quesada, Low *et al.*, 2002). In each of the pyrimidine molecules in (IV), the N*n*1—C*n*6 and N*n*3—C*n*4 bonds (n = 1–4) are short for their type (Allen *et al.*, 1987) and the C*n*2—N*n*2 bonds are much shorter than both the N*n*1—C*n*2 and C*n*2—N*n*3 bonds (Table 1); in addition, the C*n*5—N*n*5 bonds are shorter and the N*n*5—O*n*5 bonds longer than the corresponding bonds in simple unpolarized aryl–nitroso compounds. All of these distances point to the charge-separated form (IV*a*) as an important contributor to the overall molecular–electronic structure.

The seven independent molecular components in (IV) are linked into a three-dimensional framework by a combination of six three-centre hydrogen bonds, of which four are of the O—H···$(O)_2$ type and one each are of the O—H···(N,O) and N—H···$(O)_2$ types, and eight two-centre hydrogen bonds, one each of the O—H···O and N—H···N types and six of the N—H···O type (Table 2). The three-centre systems are, in general, distinctly asymmetric, but most are nearly planar;

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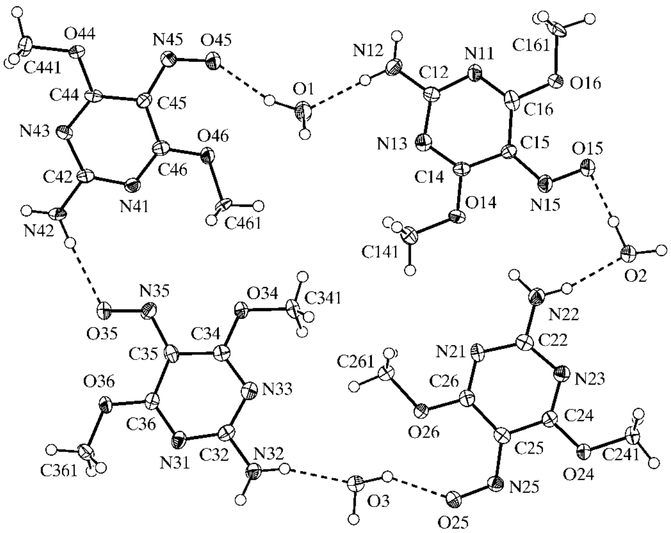

Figure 1
The independent molecular components of (IV), showing the atom-labelling scheme and the linking of the independent components into the cyclic asymmetric unit. Displacement ellipsoids are drawn at the 30% probability level. For the sake of clarity, only those hydrogen bonds which generate the outer $R^7_7(38)$ ring are shown.

their angle sums at the H atoms range from 340 to 359°, with a mean value of 351°. The $D-H\cdots A$ angles in the two-centre hydrogen bonds range from 149 to 177°, with a mean of 168°, and all are reasonably short, and thus reasonably strong, for their types.

In supramolecular systems such as this, the selection of the asymmetric unit is, to a large extent, arbitrary; however, in (IV), it is possible to select a compact cyclic asymmetric unit bounded by an $R^7_7(38)$ motif (Fig. 1) which incorporates three of the three-centre hydrogen bonds and five of the two-centre hydrogen bonds, leaving just six hydrogen bonds to link these cyclic aggregates into the continuous framework. The interior of this cyclic unit is occupied by four methoxy groups, one from each of the pyrimidine molecules. Because translation is the only symmetry operation available in $P1$, the formation of the framework itself can be readily analysed in terms of just three chain motifs linking the cyclic aggregates.

In the simplest of these chain motifs, the O1 water molecule in the aggregate at (x, y, z) acts as hydrogen-bond donor, *via* H11, to water atom O3 at $(1 + x, 1 + y, z)$, so generating a chain parallel to the [110] direction (Fig. 2). The second chain motif utilizes two different three-centre hydrogen bonds with which to link the cyclic aggregates; the O2 water molecule acts as hydrogen-bond donor, *via* H21, to both methoxy atom O36 and nitroso atom O35 in the pyrimidine molecule at $(x, 1 + y, 1 + z)$, while the N42 amino group acts as donor, *via* H42*B*, to methoxy atom O16 and nitroso atom O15 at $(x, -1 + y, -1 + z)$, and these three-centre interactions combine to generate a chain running parallel to [011] (Fig. 3). Finally, in the most complex of the chains, the N12 amino group acts as donor, *via* H12*A*, to nitroso atom N25 at $(2 + x, 1 + y, z)$, while the N32 amino group acts as donor, *via* H32*A*, to methoxy atom O44 at $(-2 + x, -1 + y, z)$, each hydrogen bond thus forming a chain along [210]; additionally, the O3 water molecule acts as donor, *via* H32, to both N45 and O45 at $(-2 + x, -1 + y, z)$, providing the final component of the [210] chain (Fig. 3). The combination of the [011] and [210] ladders generates a very elegant $(12\overline{2})$ sheet (Fig. 3), while the com-

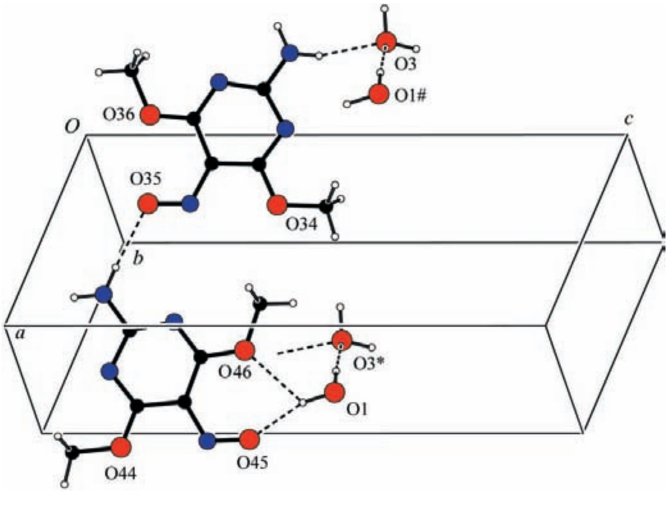

Figure 2
Part of the crystal structure of (IV), showing the formation of a chain along [110]. For the sake of clarity, H atoms bonded to C atoms have been omitted. Atoms marked with an asterisk (*) or hash (#) are at the symmetry positions $(1 + x, 1 + y, z)$ and $(-1 + x, -1 + y, z)$, respectively.

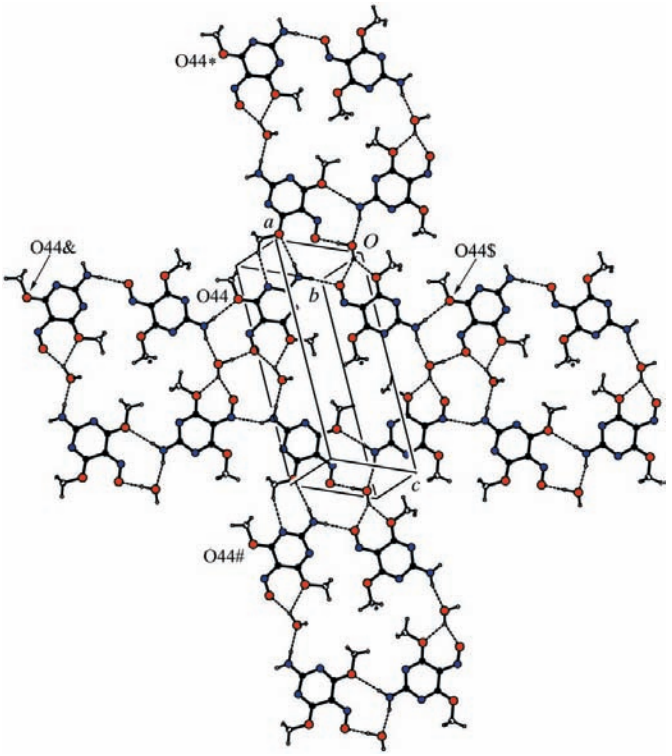

Figure 3
Part of the crystal structure of (IV), showing the formation of ladders along [011] and [210] and their combination to form a $(12\overline{2})$ sheet. Atoms marked with an asterisk (*), hash (#), dollar sign ($) or ampersand (&) are at the symmetry positions $(x, -1 + y, -1 + z)$, $(x, 1 + y, 1 + z)$, $(-2 + x, -1 + y, z)$ and $(2 + x, 1 + y, z)$, respectively.

bination of [110], [011] and [210] chains suffices to generate a single three-dimensional framework.

Experimental

A sample of (I) was purchased from Aldrich and converted to 2-amino-4,6-dimethoxy-5-nitrosopyrimidine according to the method of Marchal *et al.* (2002). Crystals suitable for single-crystal X-ray diffraction were grown by slow evaporation of a solution in acetone.

Crystal data

$4C_6H_8N_4O_3 \cdot 3H_2O$
$M_r = 790.70$
Triclinic, $P1$
$a = 6.9588 (4)$ Å
$b = 7.1984 (4)$ Å
$c = 17.4239 (11)$ Å
$\alpha = 101.181 (2)^\circ$
$\beta = 98.559 (2)^\circ$
$\gamma = 95.360 (4)^\circ$
$V = 839.95 (9)$ Å^3

$Z = 1$
$D_x = 1.563$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 6738 reflections
$\theta = 2.9$–27.4°
$\mu = 0.13$ mm^{-1}
$T = 120 (1)$ K
Plate, blue
$0.20 \times 0.20 \times 0.04$ mm

Data collection

Nonius KappaCCD diffractometer
φ scans, and ω scans with κ offsets
Absorption correction: multi-scan (*DENZO–SMN*; Otwinowski & Minor, 1997)
$T_{\min} = 0.964$, $T_{\max} = 0.992$
10 707 measured reflections

3638 independent reflections
2498 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.076$
$\theta_{\max} = 27.4^\circ$
$h = -8 \rightarrow 8$
$k = -9 \rightarrow 9$
$l = -22 \rightarrow 22$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.053$
$wR(F^2) = 0.140$
$S = 1.00$
3638 reflections
504 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0793P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.32$ e Å^{-3}
$\Delta\rho_{\min} = -0.38$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

N11—C12	1.354 (7)	N31—C32	1.353 (7)
C12—N13	1.370 (7)	C32—N33	1.355 (7)
N13—C14	1.308 (7)	N33—C34	1.317 (7)
C14—C15	1.411 (7)	C34—C35	1.424 (7)
C15—C16	1.437 (8)	C35—C36	1.443 (7)
C16—N11	1.296 (7)	C36—N31	1.328 (7)
C12—N12	1.306 (7)	C32—N32	1.325 (7)
C15—N15	1.360 (7)	C35—N35	1.360 (7)
N15—O15	1.275 (6)	N35—O35	1.259 (6)
N21—C22	1.354 (7)	N41—C42	1.353 (7)
C22—N23	1.359 (7)	C42—N43	1.359 (7)
N23—C24	1.315 (7)	N43—C44	1.323 (6)
C24—C25	1.411 (7)	C44—C45	1.427 (7)
C25—C26	1.439 (7)	C45—C46	1.420 (7)
C26—N21	1.314 (7)	C46—N41	1.316 (7)
C22—N22	1.328 (7)	C42—N42	1.328 (7)
C25—N25	1.369 (7)	C45—N45	1.361 (7)
N25—O25	1.255 (6)	N45—O45	1.263 (6)
N13—C14—O14—C141	−5.4 (7)	N33—C34—O34—C341	0.1 (7)
N11—C16—O16—C161	−0.3 (7)	N31—C36—O36—C361	0.8 (7)
N23—C24—O24—C241	−1.6 (7)	N43—C44—O44—C441	−3.0 (7)
N21—C26—O26—C261	1.9 (6)	N41—C46—O46—C461	−1.3 (6)

Compound (IV) is triclinic and space group $P1$ was assumed and confirmed by the analysis. H atoms were treated as riding atoms, with distances C— H = 0.98 Å, N—H = 0.88 Å and O—H = 1.00 Å. In the absence of any significant anomalous scatterers, the Friedel equivalents were merged; the absolute structure could not be established.

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H12···O45	1.00	2.00	2.957 (5)	159
O1—H12···O46	1.00	2.35	2.977 (5)	120
N42—H42A···O35	0.88	2.13	3.011 (6)	177
N32—H32B···O3	0.88	2.12	2.962 (6)	161
O3—H31···O25	1.00	2.04	2.941 (5)	149
O3—H31···O26	1.00	2.12	2.882 (5)	132
N22—H22A···O14	0.88	2.31	3.183 (6)	172
N22—H22B···O2	0.88	2.00	2.855 (6)	165
O2—H22···O15	1.00	1.73	2.719 (6)	171
O2—H22···N15	1.00	2.23	3.090 (6)	143
N12—H12B···O1	0.88	1.95	2.825 (6)	177
O1—H11···O3$^{\rm i}$	1.00	1.82	2.817 (5)	170
O2—H21···O36$^{\rm ii}$	1.00	2.08	2.834 (5)	131
O2—H21···O35$^{\rm ii}$	1.00	2.16	2.951 (5)	135
N42—H42B···O15$^{\rm iii}$	0.88	2.43	2.991 (6)	122
N42—H42B···O16$^{\rm iii}$	0.88	2.46	3.337 (6)	173
N12—H12A···N25$^{\rm iv}$	0.88	2.24	3.027 (6)	149
O3—H32···O45$^{\rm v}$	1.00	1.78	2.767 (5)	168
O3—H32···N45$^{\rm v}$	1.00	2.32	3.145 (6)	139
N32—H32A···O44$^{\rm v}$	0.88	2.23	3.108 (6)	175

Symmetry codes: (i) $1+x, 1+y, z$; (ii) $x, 1+y, 1+z$; (iii) $x, y-1, z-1$; (iv) $2+x, 1+y, z$; (v) $x-2, y-1, z$.

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2002); software used to prepare material for publication: *SHELXL*97 and *PRPKAPPA* (Ferguson, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1591). Services for accessing these data are described at the back of the journal.

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