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6-Amino-3-methyl-5-nitrosopyrimidine-2,4(1*H*,3*H*)-dione forms a three-dimensional hydrogen-bonded framework structure

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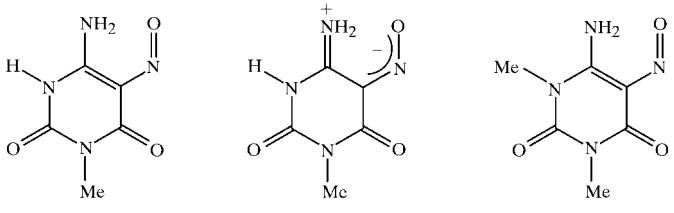
Molecules of the title compound, $C_5H_6N_4O_3$, are linked into a single three-dimensional framework by a two-centre N—H···O hydrogen bond [H···O = 1.92 Å, N···O = 2.785 (2) Å and N—H···O = 168°], a two-centre N—H···H hydrogen bond [H···N = 2.19 Å, N···N = 3.017 (2) Å and N—H···N = 157°] and the intermolecular component of an effectively planar three-centre N—H···$(O)_2$ hydrogen bond [H···O = 2.03 and 2.31 Å, N···O = 2.645 (2) and 2.957 (2) Å, N—H···O = 126 and 130°, and O···H···O = 101°].

Comment

We have recently reported (Cuesta *et al.*, 2001; Low *et al.*, 2003; López Garzón *et al.*, 2003) on the structures of the hydrated sodium, strontium and barium complexes of the 6-amino-3-methyl-5-nitrosopyrimidine-2,4(1*H*,3*H*)-dionate anion, which is derived from the title compound, the neutral pyrimidine (I), and we report here the molecular and supramolecular structures of (I) itself.



Within the molecule of (I) (Fig. 1), the C5—C6 bond distance (Table 1) is much longer than the mean value (1.330 Å; Allen *et al.*, 1987) for a double bond between two three-connected C atoms, whereas the C4—C5 distance does not differ significantly from the mean value (1.455 Å) for a single bond between a pair of three-connected C atoms in a conjugated system. At the same time, the C6—N6 distance is significantly shorter than the mean value (1.355 Å) for a C_{aryl}—NH_2 distance involving planar nitrogen, while the C5—N5 and N5—O5 distances differ by only *ca* 0.08 Å. The remaining distances show no unexpected values. Hence, it can be concluded that the polarized form, (I*a*), is a significant contributor to the overall molecular–electronic structure, alongside the classically localized form, (I).

The molecules exhibit the usual intramolecular N—H···O hydrogen bonding, with nitroso atom O5 as the acceptor (Table 2). In addition, there are three intermolecular N—H···O and N—H···N hydrogen bonds, which link the molecules into layers. Amino atom N6 in the molecule at (x, y, z) acts as a hydrogen-bond donor, *via* H6*A*, to nitroso atom N5 in the molecule at (x, $\frac{1}{2}-y$, $\frac{1}{2}+z$), while atom N6 at (x, $\frac{1}{2}-y$, $\frac{1}{2}+z$) in turn acts as a donor to atom N5 at (x, y, $1+z$), so forming a zigzag *C*(5) chain (Bernstein *et al.*, 1995) running parallel to the [001] direction and generated by the *c*-glide plane at $y=\frac{1}{4}$. Atom N6 also utilizes atom H6*B* to form an effectively planar three-centre N—H···$(O)_2$ hydrogen bond, in which the two acceptors are nitroso atom O5 at (x, y, z), so

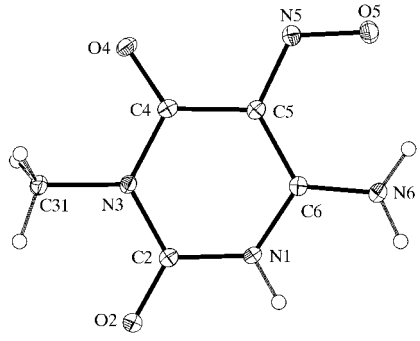


Figure 1
A view of the molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids have been drawn at the 30% probability level.

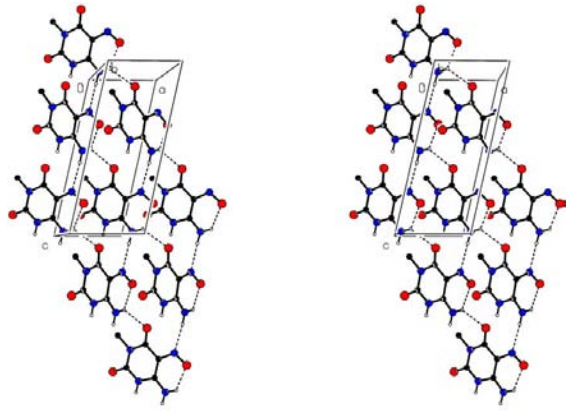


Figure 2
A stereoview of part of the crystal structure of (I), showing the combination of [001] and [201] chains to form a (010) sheet. For the sake of clarity, H atoms bonded to C atoms have been omitted.

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forming an $S(6)$ motif, and amide atom O4 in the molecule at $(1+x, \frac{1}{2}-y, \frac{1}{2}+z)$. This latter interaction gives rise to a zigzag $C(6)$ chain running parallel to the [201] direction and generated by the same c-glide plane at $y=\frac{1}{4}$. The combination of the [001] and [201] chains generates a sheet parallel to (010) in the form of a (4,4)-net (Batten & Robson, 1998) containing equal numbers of $S(6)$ and $R_4^5(16)$ rings (Fig. 2). Two sheets of this type pass through each unit cell, in the domains $-0.03 < y < 0.53$ and $0.47 < y < 1.03$, and one further hydrogen bond serves to link the (010) sheets.

Atom N1 in the molecule at (x, y, z) acts as hydrogen-bond donor to atom O4 in the molecule at $(1-x, 1-y, 1-z)$, so forming an $R_2^2(8)$ ring centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ (Fig. 3). The molecules at (x, y, z) and $(1-x, 1-y, 1-z)$ are components of sheets lying in the $-0.03 < y < 0.53$ and $0.47 < y < 1.03$ domains, respectively, and propagation of this $R_2^2(8)$ motif by the space group links all the (010) sheets into a single three-dimensional framework. In this manner, all potential donors and all potential acceptors of hard hydrogen bonds are involved in the overall molecular aggregation.

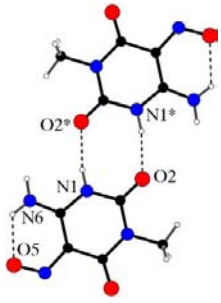

Figure 3
Part of the crystal structure of (I), showing the formation of the centrosymmetric $R_2^2(8)$ motif that links the (010) sheets. For the sake of clarity, the unit-cell box and H atoms bonded to C atoms have been omitted. Atoms marked with an asterisk (*) are at the symmetry position $(1-x, 1-y, 1-z)$.

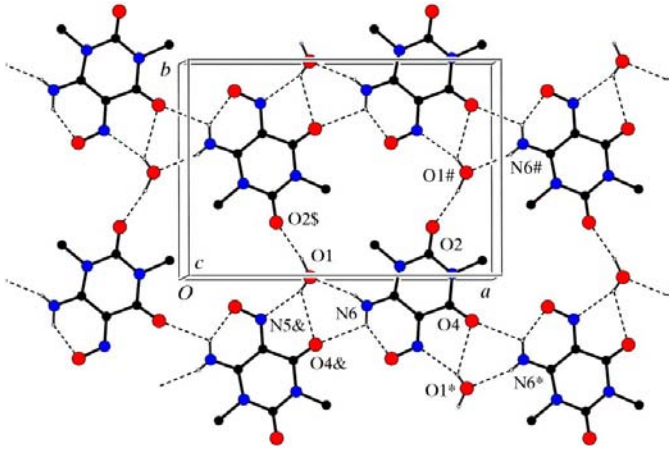

Figure 4
Part of the crystal structure of (II), showing the formation of a (001) sheet. The original cell setting and atoms labels (Low *et al.*, 1992) have been used. For the sake of clarity, H atoms bonded to C atoms have been omitted. Atoms marked with an asterisk (*), hash (#), dollar sign ($) or ampersand (&) are at the symmetry positions $(\frac{1}{2}+x, -\frac{1}{2}-y, \frac{1}{4})$, $(\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{4})$, $(-\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{4})$ and $(-\frac{1}{2}+x, -\frac{1}{2}-y, \frac{1}{4})$, respectively.

The supramolecular aggregation of (I) can be contrasted with that of the dimethyl analogue, (II), which crystallizes as a monohydrate (Low *et al.*, 1992). In this hydrate, all the atoms lie on mirror planes in space group *Pnam* (*Pnma*; No. 62), and the molecules are linked into sheets by a combination of O—H···O, O—H···N and N—H···O hydrogen bonds (Fig. 4).

Experimental

An aqueous solution of potassium 6-amino-3-methyl-5-nitroso-pyrimidine-2,4(1*H*,3*H*)-dionate was neutralized with excess potassium aluminium sulfate dodecahydrate. The gelatinous precipitate that formed initially was filtered off and the resulting solution was set aside to crystallize, providing analytically pure crystals of (I), which were washed with cold water and then with ethanol. Analysis found: C 34.9, H 3.6, N 32.4%; $C_5H_6N_4O_3$ requires: C 35.2, H 3.5, N 32.9%.

Crystal data

$C_5H_6N_4O_3$	$D_x = 1.769$ Mg m^{-3}
$M_r = 170.14$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 1399 reflections
$a = 4.9634$ (3) Å	$\theta = 3.5$–$27.4°$
$b = 11.1829$ (9) Å	$\mu = 0.15$ mm^{-1}
$c = 11.7960$ (8) Å	$T = 120$ (2) K
$\beta = 102.665$ (4)°	Prism, pink
$V = 638.81$ (8) Å^3	0.15 × 0.10 × 0.06 mm
$Z = 4$	

Data collection

Nonius KappaCCD diffractometer	1399 independent reflections
φ scans, and ω scans with κ offsets	1106 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*DENZO–SMN*; Otwinowski & Minor, 1997)	$R_{int} = 0.040$
	$\theta_{max} = 27.4°$
$T_{min} = 0.972$, $T_{max} = 0.991$	$h = -5 \rightarrow 6$
4417 measured reflections	$k = -14 \rightarrow 13$
	$l = -15 \rightarrow 13$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0702P)^2 + 0.0762P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.045$	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2) = 0.118$	$\Delta\rho_{max} = 0.27$ e Å^{-3}
$S = 1.03$	$\Delta\rho_{min} = -0.37$ e Å^{-3}
1399 reflections	
110 parameters	
H-atom parameters constrained	

Crystals of (I) are monoclinic and the space group $P2_1/c$ was assigned uniquely from the systematic absences. All H atoms were

Table 1
Selected intramolecular distances (Å).

N1—C2	1.375 (2)	C2—O2	1.224 (2)
C2—N3	1.375 (2)	N3—C31	1.466 (2)
N3—C4	1.403 (2)	C4—O4	1.222 (2)
C4—C5	1.452 (2)	C5—N5	1.352 (2)
C5—C6	1.429 (2)	N5—O5	1.271 (2)
C6—N1	1.363 (2)	C6—N6	1.308 (2)

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O2^{i}	0.88	1.92	2.785 (2)	168
N6—H6A···N5^{ii}	0.88	2.19	3.017 (2)	157
N6—H6B···O5	0.88	2.03	2.645 (2)	126
N6—H6B···O4^{iii}	0.88	2.31	2.957 (2)	130

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

treated as riding atoms, with C—H distances of 0.98 Å and N—H distances of 0.88 Å.

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement and data reduction: *DENZO–SMN* (Otwinowski & Minor, 1997); structure solution: *SHELXS*97 (Sheldrick, 1997); structure refinement: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); 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: SK1637). Services for accessing these data are described at the back of the journal.

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