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Nonmerohedrally twinned 6-amino-3-methyluracil-5-carbaldehyde: a hydrogen-bonded ribbon containing four types of ring

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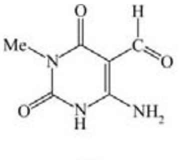
In the title compound [systematic name: 6-amino-5-formyl-3-methylpyrimidine-2,4(1*H*,3*H*)-dione], $C_6H_7N_3O_3$, the intramolecular dimensions provide evidence for some polarization of the electronic structure. There is an intramolecular N—H···O hydrogen bond; this and a combination of three intermolecular N—H···O hydrogen bonds generate an almost planar ribbon containing $S(6)$, $R_2^2(4)$, $R_2^1(6)$ and $R_4^4(16)$ rings. These ribbons are linked into sheets by a dipolar carbonyl–carbonyl interaction. The structure was refined as a nonmerohedral twin, with twin fractions 0.7924 (1) and 0.2076 (10).

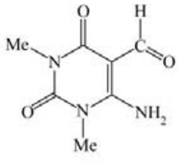
Comment

The title compound, (I), has been prepared as an intermediate for the preparation of fused pyrimidine derivatives. Its synthesis utilized the Vilsmeier–Haack formylation procedure applied to 6-amino-3-methyl-2-(methylsulfanyl)pyrimidin-4(3*H*)-one, in which the work-up using aqueous sodium hydroxide effected the hydrolysis of the methylsulfanyl group at C2, so providing the title compound in a single process. Compound (I) is closely related to the 1,3-dimethyl analogue (II), which, unlike (I), crystallizes as a monohydrate. The structure of (II) was first determined some years ago using diffraction data collected at ambient temperature (Low *et al.*, 1992); more recently, the structure of (II) was re-examined using data collected at 120 K (de la Torre *et al.*, 2007), and the improved precision afforded by the low-temperature data enabled a detailed examination of the intramolecular dimensions, which were interpreted in terms of a polarized electronic structure. A combination of three N—H···O hydrogen bonds and two O—H···O hydrogen bonds links the molecular components of the monohydrate of (II) into two linked and interwoven three-dimensional frameworks.

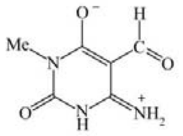
Prompted by the interesting molecular and supramolecular structures found in (II), we have now taken the opportunity to make a detailed comparison with the monomethyl analogue (I) (Fig. 1). Compound (I) crystallizes in solvent-free form in a unit cell whose dimensions bear no resemblance to those of the unit cell of (II). However, a similar pattern of bond distances is found (Table 1). In particular, the C5—C51 and C6—N6 bonds are both short for their types (Allen *et al.*, 1987), while C51—O5 is long for its type; in addition, the C4—O4 bond is significantly longer than C2—O2. These dimensions (Table 1) provide evidence for the importance of polarized forms (I*a*) and (I*b*) as contributors to the overall electronic structure. Despite the high degree of substitution of the rings in both (I) and (II), these rings are planar, although puckered pyrimidine rings are quite frequently observed in the presence of contiguous substituents (Melguizo *et al.*, 2003; Quesada *et al.*, 2003, 2004; Low *et al.*, 2007; Trilleras *et al.*, 2007; Cobo *et al.*, 2008). In (I), the maximum deviation of any ring atom from the mean plane is seen for atom N3 [0.013 (2) Å]. In these respects, therefore, (I) and (II) show considerable similarity. They differ, however, in their patterns of hydrogen bonding, dominated firstly by the presence of a water molecule in (II), which acts as a single acceptor and as a double donor of hydrogen bonds, and secondly by the presence in (I) of an additional N—H bond at N1.



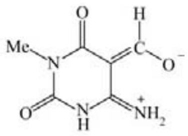
(I)



(II)



(I*a*)



(I*b*)

Within the molecule of (I), the N6—H62···O5 hydrogen bond (Table 2) generates an $S(6)$ (Bernstein *et al.*, 1995) motif; such an intramolecular motif is highly characteristic of both 6-amino-5-formylpyrimidines and 6-amino-5-nitrosopyrimi-

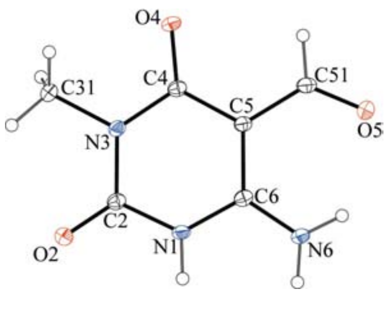


Figure 1
The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

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dines (Low *et al.*, 1997, 1999, 2000; Quesada *et al.*, 2002, 2004; Melguizo *et al.*, 2003; Cobo *et al.*, 2008), and it may well be a controlling factor in determining in (I) the near coplanarity of the formyl group with the uracil ring (Table 1); formyl atom O5 deviates from the mean plane of the ring by only 0.008 (2) Å. This intramolecular interaction is, in fact, the shorter component of the three-centre $\mathrm{N{-}H\cdots(O)_2}$ system, the longer component of which links pairs of molecules into a centrosymmetric dimer, characterized by an $R^{2}_{2}(12)$ motif; this motif is itself partitioned into a central $R^{2}_{2}(4)$ ring flanked by two symmetry-related $S(6)$ rings. Between the dimers related by translation along [100], atoms N1 and N6 both act as hydrogen-bond donors to amidic carbonyl atom O4 in the adjacent dimer, so forming an $R^{1}_{2}(6)$ ring. These interactions thus serve to link the centrosymmetric dimers into a ribbon along [100], in which $R^{2}_{2}(4)$ rings centred at $(n+\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, where n represents an integer, alternate with $R^{4}_{4}(16)$ rings centred at $(n, \frac{1}{2}, \frac{1}{2})$ (Fig. 2). Although the centrosymmetric dimer motif containing an $R^{2}_{2}(4)$ ring flanked by two $S(6)$ rings can also be identified within the three-dimensional structure of (II), the subsequent linking of these dimers is entirely different in (I) and (II), leading to hydrogen-bonded structures which are, respectively, one- and three-dimensional. It is of interest to note that, in (I), the hydrogen-bond formation involves the acceptor atoms O4 and O5, which carry enhanced negative charges owing to the charge polarization, but it does not involve atom O2, which is not involved in the polarization. The hydrogen bonds may thus all be regarded as charge-assisted hydrogen bonds (Gilli *et al.*, 1993).

With the exception of the H atoms in the methyl group, the ribbon is almost completely planar, providing a very compact structure. There are two hydrogen-bonded ribbons running through each unit cell in (I); although there are no hydrogen bonds between adjacent chains, the chains are weakly linked into sheets by a dipolar carbonyl–carbonyl interaction. Carbonyl atom O2 in the molecule at (x, y, z) makes a short contact with carbonyl atom C2 in the molecule at $(-x+1, y+\frac{1}{2}, -z+\frac{3}{2})$, with geometry $\mathrm{O2\cdots C2^{iii}}$ = 2.8978 (17) Å, $\mathrm{C2\cdots C2^{iii}}$ = 3.1791 (13) Å and $\mathrm{C2{-}O2\cdots C2^{iii}}$ = 142.14 (9)° [symmetry code: (iii) $-x+1, y+\frac{1}{2}, -z+\frac{3}{2}$], so conforming rather closely to the perpendicular type I carbonyl–carbonyl interaction (Allen *et al.*, 1998). The two molecules concerned are components of the hydrogen-bonded chains along $(x, \frac{1}{2}, \frac{1}{2})$ and $(x, 1, 1)$, respectively; hence propagation by the space-group symmetry of the carbonyl–carbonyl interaction links hydrogen-bonded ribbons into a sheet parallel to $(01\overline{1})$.

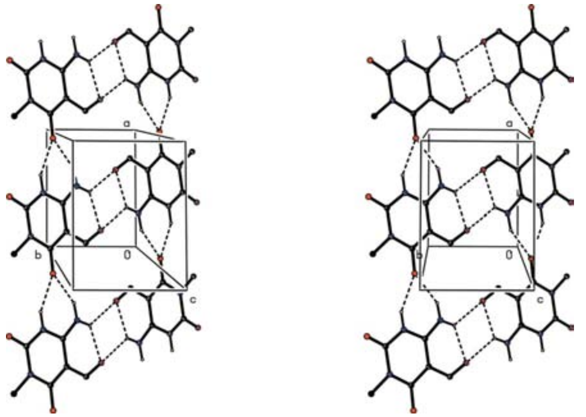

Figure 2
A stereoview of part of the crystal structure of (I), showing the formation of a hydrogen-bonded ribbon containing four types of ring and running parallel to [100].

Experimental

Phosphoryl chloride (12 mmol) was added dropwise to a suspension of 6-amino-3-methyl-2-(methylsulfanyl)pyrimidin-4(3*H*)-one (10 mmol) in dimethylformamide (30 ml) cooled in an ice–water bath. The mixture was stirred at room temperature for 1 h and then poured on to crushed ice (400 ml). The mixture was permitted to warm to ambient temperature and was then heated to boiling whereupon sodium hydroxide pellets were added until the solution was basic. The resulting mixture was allowed to cool to ambient temperature and the white solid which formed was collected by filtration, washed with ethanol, dried and recrystallized from ethanol [yield 50%; decomposition without melting at 573 K; literature m.p. > 573 K (Cherdantseva *et al.*, 1983)]. Crystals suitable for single-crystal X-ray diffraction analysis were grown by slow evaporation of a solution in dimethyl sulfoxide.

Crystal data

$C_6H_7N_3O_3$
M_r = 169.14
Monoclinic, $P2_1/c$
a = 6.6749 (4) Å
b = 5.0712 (5) Å
c = 19.7422 (4) Å
β = 99.996 (2)°
V = 658.12 (8) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.14 mm^{-1}
T = 120 K
0.29 × 0.23 × 0.12 mm

Data collection

Bruker–Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{\min}$ = 0.972, $T_{\max}$ = 0.983
9103 measured reflections
9103 independent reflections
7474 reflections with $I > 2\sigma(I)$

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.058
$wR(F^2)$ = 0.152
S = 1.08
9103 reflections
111 parameters
H-atom parameters constrained
$\Delta\rho_{\max}$ = 0.30 e Å^{-3}
$\Delta\rho_{\min}$ = −0.32 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

N1—C2	1.3650 (16)	C2—O2	1.2006 (15)
C2—N3	1.3753 (16)	N3—C31	1.4619 (16)
N3—C4	1.3733 (17)	C4—O4	1.2360 (15)
C4—C5	1.4215 (18)	C5—C51	1.4163 (18)
C5—C6	1.3966 (18)	C51—O5	1.2229 (15)
C6—N1	1.3522 (16)	C6—N6	1.3037 (16)
C4—C5—C51—O5	−177.67 (13)	C6—C5—C51—O5	1.6 (2)

All H atoms were located from difference maps and then treated as riding atoms, with C—H distances of 0.95 or 0.98 Å and N—H distances of 0.88 Å, and with $U_{\rm iso}({\rm H}) = kU_{\rm eq}$(carrier) ($k$ = 1.2 or 1.5). Conventional refinement then converged to R = 0.165 for 1513 reflections (1284 labelled observed), with $R_{\rm int}$ = 0.057, but analysis

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O4^{i}	0.88	2.02	2.8172 (14)	150
N6—H61···O4^{i}	0.88	2.00	2.7910 (14)	149
N6—H62···O5	0.88	2.05	2.6880 (14)	129
N6—H62···O5^{ii}	0.88	2.19	2.8314 (14)	130

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

with *PLATON*/*TwinRotMat* (Spek, 2009) of this solution indicated nonmerohedral twinning about a twofold rotation axis $(20\overline{1})$ (which makes an angle of 0.26° with [100]). The *TwinRotMat* routine was used to prepare a modified .hkl file for use with the HKLF5 option in *SHELXL97* (Sheldrick, 2008). The resulting twin fractions were 0.2076 (10) and 0.7924 (10).

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: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL97* and *PLATON*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3315). Services for accessing these data are described at the back of the journal.

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