Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Redetermination of 6-amino-5-formyl-1,3-dimethyluracil monohydrate at 120 K: a polarized molecular structure and two interwoven hydrogen-bonded frameworks

José M. de la Torre,[a] Manuel Nogueras,[a] Justo Cobo,[a] John N. Low[b] and Christopher Glidewell[c]*

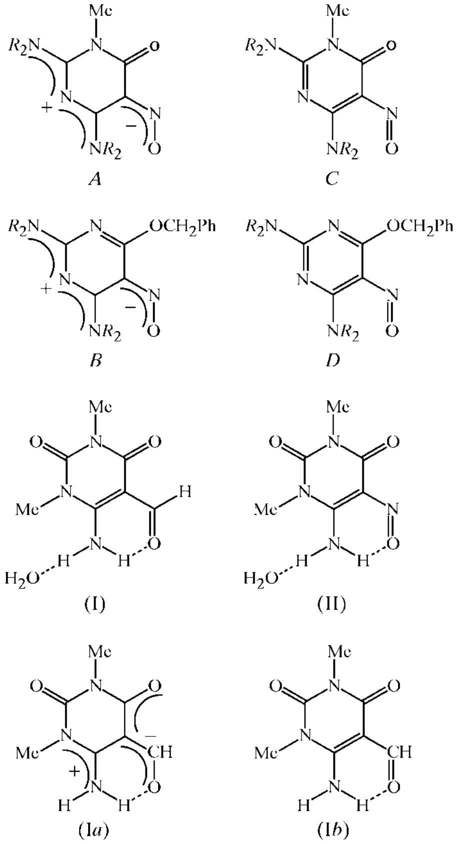
[a]Departamento de Química Inorgánica y Orgánica, Universidad de Jaén, 23071 Jaén, Spain, [b]Department of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen AB24 3UE, Scotland, and [c]School of Chemistry, University of St Andrews, Fife KY16 9ST, Scotland
Correspondence e-mail: cg@st-andrews.ac.uk

Received 11 September 2007
Accepted 12 September 2007
Online 13 October 2007

The title compound [systematic name: 6-amino-5-formyl-1,3-dimethylpyrimidine-2,4(1*H*,3*H*)-dione monohydrate], $C_7H_9N_3O_3\cdot H_2O$, has been reexamined at 120 K. The improved precision of the intramolecular dimensions provides evidence for a polarized molecular–electronic structure, and the molecular components are linked by one N—H···O and two O—H···O hydrogen bonds into two interwoven three-dimensional frameworks, which are weakly linked by the longer component of a three-centre N—H···(O)$_2$ hydrogen bond.

Comment

Recent studies (Low *et al.*, 2000; Quesada *et al.*, 2002; Melguizo *et al.*, 2003) of amino-substituted 5-nitrosopyrimidines have provided compelling evidence for the development of extensively polarized molecular–electronic structures, in which forms such as *A* (Low *et al.*, 2000) and *B* (Quesada *et al.*, 2002; Melguizo *et al.*, 2003) (see scheme) make important contributions to the overall molecular–electronic structures, normally represented by forms such as *C* and *D*. These polarized structures in turn lead to the formation of supramolecular networks built from charge-assisted (Gilli *et al.*, 1993) hydrogen bonds. With these recent findings in mind, we have now reinvestigated the structure of the title compound, (I) (Fig. 1). The structure of (I) was reported some years ago from diffraction data collected at ambient temperature (Low *et al.*, 1992), but the precision of that determination does not permit a detailed analysis of the intramolecular dimensions, nor did the earlier report contain any discussion of the supramolecular aggregation. We have now redetermined the structure of (I) using diffraction data collected at 120 K and we present here an analysis of the intramolecular geometry and a description of the supramolecular aggregation. The unit-cell dimensions, space group and atomic coordinates show that no phase transition occurs between ambient temperature and 120 K.



The organic component of compound (I) is effectively planar, apart from the H atoms of the methyl groups, and the coplanarity of the formyl unit with the ring may be associated with the intramolecular N—H···O hydrogen bond (Table 2). The intramolecular bond distances (Table 1) show a number of unusual features. The C6—N6 bond is short for its type (Allen *et al.*, 1987) and C51—O51 is long for its type, while C4—O4 is somewhat longer than C2—O2. At the same time, the lengths of the three bonds involving C5 span only a very small range, whereas in the classical representation the C5—C6 bond is a double bond, while the C5—C4 and C5—C51 bonds are single bonds. Finally, the C6—N1 bond is the shortest of the four independent C—N bonds within the ring. These observations, taken together, provide evidence for the importance of the polarized form (I*a*) of the organic component as a contributor to the overall molecular–electronic structure, in addition to the classical form (I*b*). It should perhaps be emphasized here that the similarity of the bond lengths involving C5, in particular, is not apparent from the results of the ambient-temperature study, nor is the lengthening of the C4—O4 bond. In form (I*a*), the anionic fragment resembles a 1,3-diketonate unit in the *syn–anti* conformation, while the cationic fragment most closely resembles an amidinium cation.

Within the selected asymmetric unit, the independent components of (I) are linked by an N—H···O hydrogen bond (Fig. 1 and Table 2). These bimolecular aggregates are then

DOI: 10.1107/S0108270107044563

linked by two independent O—H···O hydrogen bonds and an N—H···O hydrogen bond which is, in fact, the longer weaker component of a planar three-centre N—H···$(O)_2$ hydrogen bond, in which both acceptors are formyl O atoms (Table 2). It is convenient to consider the actions of the two independent O—H···O hydrogen bonds, firstly acting in isolation, and secondly acting together. Water atom O1 at (x, y, z) acts as a hydrogen-bond donor, *via* atom H1*A*, to amidic atom O4 at (x, $1 - y$, $\frac{1}{2} + z$), so completing a $C_2^2(8)$ (Bernstein *et al.*, 1995) chain running parallel to the [001] direction and generated by the *c*-glide plane at $y = \frac{1}{2}$. The same water atom also acts as a hydrogen-bond donor, this time *via* atom H1*B*, to atom O2 at ($\frac{1}{2} + x$, $\frac{1}{2} - y$, $\frac{1}{2} + z$), so completing a second $C_2^2(8)$ chain, now running parallel to the [101] direction and generated by the *n*-glide plane at $y = \frac{1}{4}$. These two chain motifs, generated by different glide planes, are sufficient to generate a three-dimensional framework, within which it is possible to identify a third simple chain motif, involving both O—H···O hydrogen bonds and this time running parallel to the [010] direction (Fig. 2). The combination of the hydrogen-bonded chains along [010], [001] and [101] necessarily generates a three-dimensional structure. The framework thus formed encompasses only half of the molecules within the unit cell, and this three-dimensional substructure conforms exactly to *Cc* symmetry. A second such substructure is related to the first by the twofold rotation axes, and the two substructural frameworks are continuously interwoven. They are linked by the inter-aggregate N—H···O hydrogen bond, which is the weaker component of the three-centre system in which the amino atom N6 at (x, y, z) acts as donor to the formyl atoms O51 at both (x, y, z) and ($2 - x$, y, $\frac{3}{2} - z$), so forming a cyclic motif generated by the twofold rotation axis along (1, y, $\frac{3}{4}$) in which an $R_2^2(4)$ motif comprising two double donors and two double acceptors is embedded within an outer $R_2^2(12)$ ring (Fig. 3).

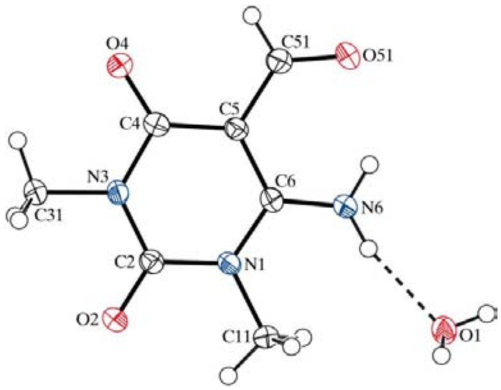


Figure 1
The independent molecular components of compound (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. The dashed line indicates the N—H···O hydrogen bond linking the components within the selected asymmetric unit.

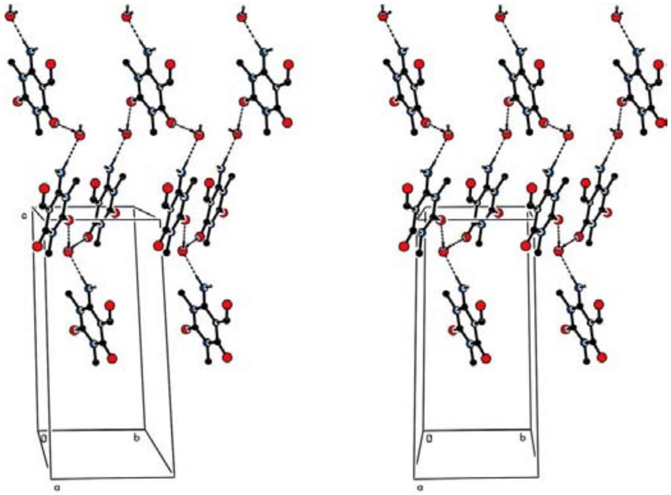


Figure 2
A stereoview of part of the crystal structure of compound (I), showing the formation of a hydrogen-bonded chain along the [010] direction containing three types of intermolecular hydrogen bond. For the sake of clarity, H atoms bonded to C atoms have been omitted

In view of the interesting three-dimensional supramolecular structure found for compound (I), we have also briefly analysed the supramolecular aggregation of the isoelectronic analogue (II), using the published atomic coordinates. This structure was reported (Low *et al.*, 1992) in space group *Pnam*, a nonstandard setting of *Pnma*, although the CIF retrieved (17 August 2007) from the IUCr archive records the structure as

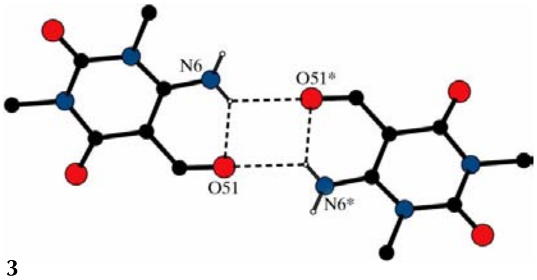


Figure 3
Part of the crystal structure of compound (I), showing the formation of the cyclic motif which links the two frameworks. For the sake of clarity, the unit-cell outline and H atoms bonded to C atoms have been omitted. Atoms marked with an asterisk (*) are at the symmetry position ($2 - x$, y, $\frac{3}{2} - z$).

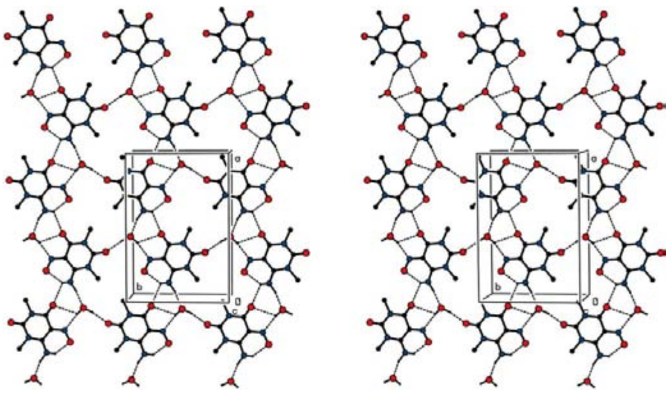


Figure 4
A stereoview of part of the crystal structure of compound (II), showing the formation of a hydrogen-bonded sheet parallel to (001). The published atomic coordinates (Low *et al.*, 1992) have been used. For the sake of clarity, H atoms bonded to C atoms have been omitted.

having space group $Pna2_1$, which had been considered by the authors and rejected by them. Scrutiny of the $Pna2_1$ structure using the ADDSYM option in *PLATON* (Spek, 2003) showed a 100% fit to space group *Pnam*, as deduced by the earlier authors. A combination of three hydrogen bonds, one each of the N—H···O, O—H···O and O—H···N types, links the molecular components of (II) into complex sheets parallel to (001) and containing four types of ring, with chains of edge-fused $R_5^6(19)$ rings along [100] alternating with strings of edge-fused $S(6)$, $R_1^2(5)$ and $R_3^2(6)$ rings (Fig. 4). Thus, a rather modest change in the constitution of the organic component between compounds (I) and (II) leads to a major change in the hydrogen-bonded supramolecular aggregation.

Experimental

A mixture of phosphoryl chloride (10.7 mmol) and dimethylformamide (2 ml) was stirred at 273 K for 15 min, and then a suspension of 6-amino-1,3-dimethyluracil (6.4 mmol) in dimethylformamide (8 ml) was added. The mixture was heated at 323–333 K in a water bath for another 15 min and then poured on to crushed ice. The resultant solution was heated to boiling and neutralized with solid sodium hydroxide. The mixture was allowed to cool to ambient temperature and the resulting solid product was collected by filtration, washed with a little ice-cold water and recrystallized from water (yield 98%, m.p. 465–467 K). Crystals of (I) suitable for single-crystal X-ray diffraction were obtained by slow evaporation of a solution in ethanol–water (97:3 *v*/*v*).

Crystal data

$C_7H_9N_3O_3 \cdot H_2O$
$M_r = 201.19$
Monoclinic, $C2/c$
$a = 15.5815\ (4)$ Å
$b = 7.4458\ (4)$ Å
$c = 16.8575\ (8)$ Å
$\beta = 116.408\ (4)^\circ$
$V = 1751.67\ (15)$ Å^3
$Z = 8$
Mo $K\alpha$ radiation
$\mu = 0.13$ mm^{-1}
$T = 120\ (2)$ K
0.60 × 0.50 × 0.10 mm

Data collection

Bruker Nonius KappaCCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{\min} = 0.946$, $T_{\max} = 0.988$
19726 measured reflections
2012 independent reflections
1418 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.042$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.142$
$S = 1.06$
2012 reflections
129 parameters
H-atom parameters constrained
$\Delta\rho_{\max} = 0.34$ e Å^{-3}
$\Delta\rho_{\min} = -0.33$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

N1—C2	1.387 (2)	C2—O2	1.223 (2)
C2—N3	1.375 (2)	C4—O4	1.237 (2)
N3—C4	1.405 (2)	C5—C51	1.432 (3)
C4—C5	1.425 (3)	C51—O51	1.228 (2)
C5—C6	1.417 (2)	C6—N6	1.317 (2)
C6—N1	1.368 (2)		
C4—C5—C51—O51	178.91 (19)		

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

D—H···A	D—H	H···A	D···A	D—H···A
N6—H6A···O1	0.86	1.99	2.831 (2)	166
N6—H6B···O51	0.86	1.98	2.686 (2)	138
N6—H6B···O51$^{\rm i}$	0.86	2.38	3.030 (2)	133
O1—H1A···O4$^{\rm ii}$	0.82	1.93	2.7465 (18)	174
O1—H1B···O2$^{\rm iii}$	0.82	2.00	2.8177 (18)	172

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

The systematic absences permitted *Cc* and *C*2/*c* as possible space groups. *C*2/*c* was selected and confirmed by the refinement. All H atoms were located in difference maps and then treated as riding atoms, with C—H = 0.95 (formyl) or 0.98 Å (methyl), N—H = 0.86 Å and O—H = 0.82 Å, and with $U_{\rm iso}({\rm H}) = kU_{\rm eq}$(carrier), with $k = 1.5$ for the methyl and water H atoms, and 1.2 for all other H atoms.

Data collection: *COLLECT* (Nonius, 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, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

The authors thank the Servicios Técnicos de Investigación of the Universidad de Jaén and the staff for data collection. JMT, MN and JC thank the Consejería de Innovación, Ciencia y Empresa (Junta de Andalucía, Spain) and the Universidad de Jaén for financial support. JMT also thanks the Universidad de Jaén for a scholarship grant.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN3062). Services for accessing these data are described at the back of the journal.

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.

Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.

Burla, M. C., Caliandro, R., Camalli, M., Carrozzini, B., Cascarano, G. L., De Caro, L., Giacovazzo, C., Polidori, G. & Spagna, R. (2005). *J. Appl. Cryst.* **38**, 381–388.

Duisenberg, A. J. M., Hooft, R. W. W., Schreurs, A. M. M. & Kroon, J. (2000). *J. Appl. Cryst.* **33**, 893–898.

Duisenberg, A. J. M., Kroon-Batenburg, L. M. J. & Schreurs, A. M. M. (2003). *J. Appl. Cryst.* **36**, 220–229.

Ferguson, G. (1999). *PRPKAPPA*. University of Guelph, Canada.

Gilli, P., Bertolasi, V., Ferretti, V. & Gilli, G. (1993). *J. Am. Chem. Soc.* **116**, 909–915.

Low, J. N., Howie, R. A., Hueso-Ureña, F. & Moreno-Carretero, M. N. (1992). *Acta Cryst.* C**48**, 145–147.

Low, J. N., López, M. D., Arranz Mascarós, P., Cobo Domingo, J., Godino, M. L., López Garzón, R., Gutiérrez, M. D., Melguizo, M., Ferguson, G. & Glidewell, C. (2000). *Acta Cryst.* B**56**, 882–892.

McArdle, P. (2003). *OSCAIL for Windows*. Version 10. Crystallography Centre, Chemistry Department, NUI Galway, Ireland.

Melguizo, M., Quesada, A., Low, J. N. & Glidewell, C. (2003). *Acta Cryst.* B**59**, 263–276.

Nonius (1999). *COLLECT*. Nonius BV, Delft, The Netherlands.

Quesada, A., Marchal, A., Melguizo, M., Nogueras, M., Sánchez, A., Low, J. N., Cannon, D., Farrell, D. M. M. & Glidewell, C. (2002). *Acta Cryst.* B**58**, 300–315.

Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.

Sheldrick, G. M. (2003). *SADABS*. Version 2.10. University of Göttingen, Germany.

Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.