organic compounds

A new polymorph of 5-nitrouracil monohydrate

P. S. Pereira Silva, S. R. Domingos, M. Ramos Silva, J. A. Paixão and A. Matos Beja*

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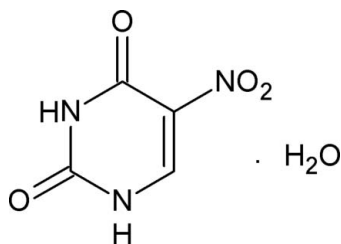Correspondence e-mail: psidonio@pollux.fis.uc.pt

In the title compound, $C_4H_3N_3O_4 \cdot H_2O$, molecules of 5-nitro-uracil are hydrogen bonded in pairs across crystallographic centers of symmetry. The resulting dimers are also hydrogen bonded to the water molecules, forming a three-dimensional network. The pyrimidine ring is almost planar (with a maximum deviation of 0.0156 (9) Å for the one of the N atoms) and the nitro group is rotated by 12.4 (1)° out of the uracil plane, while in the other polymorph the value for the same angle is 5°.

Related literature

For the non-linear optical properties of 5-nitrouracil, see: Bergman *et al.* (1972); Puccetti *et al.* (1993); Youping *et al.* (1992). For the crystal structure of another polymorph, see: Craven (1967). For related literature, see: Pettier & Byrn (1982); Rao *et al.* (1995).

Experimental

Crystal data

$C_4H_3N_3O_4 \cdot H_2O$	$a = 6.2799$ (1) Å
$M_r = 175.11$	$b = 7.8481$ (2) Å
Monoclinic, $P2_1/c$	$c = 13.8068$ (3) Å
$\beta = 93.842$ (1)°	$\mu = 0.16$ mm^{-1}
$V = 678.94$ (3) Å^3	$T = 293$ (2) K
$Z = 4$	$0.44 \times 0.22 \times 0.20$ mm
Mo $K\alpha$ radiation	

Data collection

Bruker APEXII CCD area-detector diffractometer	15135 measured reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)	2232 independent reflections
$T_{min} = 0.890$, $T_{max} = 0.969$	1918 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.018$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.042$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.131$	
$S = 1.00$	
2232 reflections	$\Delta\rho_{max} = 0.35$ e Å^{-3}
115 parameters	$\Delta\rho_{min} = -0.37$ e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N3—H3···O2^i	0.86	1.99	2.8503 (13)	173
N1—H1···O9^{ii}	0.86	1.88	2.6736 (12)	153
O9—H9A···O4^{iii}	0.87 (2)	1.92 (2)	2.7640 (13)	165 (2)
O9—H9A···O7^{iii}	0.87 (2)	2.41 (3)	2.9101 (13)	117 (2)
O9—H9B···O7^{iv}	0.84 (3)	2.29 (3)	3.0940 (15)	162 (2)

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

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT2713).

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supporting information

A new polymorph of 5-nitrouracil monohydrate

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S1. Comment

5-Nitrouracil (5NU) is an interesting molecule due to its nonlinear optical properties (Bergman *et al.*, 1972; Puccetti *et al.*, 1993; Youping *et al.*, 1992) and is also of relevance to biological and pharmaceutical sciences (Rao *et al.*, 1995; Pettier & Byrn, 1982).

In the framework of our study of new compounds with potential NLO properties, we have crystallized a new polymorph of 5-nitrouracil monohydrate (Fig.1). Molecules of 5NU are hydrogen bonded in pairs across crystallographic centers of symmetry. The resulting dimers are also hydrogen bonded by the water molecules forming a three dimensional network (Table 1; Fig. 2). The difference in intermolecular interactions between the two polymorphs seems to have a small effect on the molecular structure of the 5NU moiety, with all bond lengths and angles being in good agreement with the previously reported structure (Craven, 1967). The pyrimidine ring is almost planar and the main conformational difference is the large twist of the nitro group away from the plane of the ring [12.4 (1)°], whereas it approaches coplanarity in the other polymorph (5.0° for the same angle).

S2. Experimental

The title compound was prepared by adding 5-nitrouracil (Aldrich, 98%, 1 mmol) to *L*-serine (Aldrich 99%, 1 mmol) in a solution of water (10 ml) and piridine (Aldrich 99%, 30 ml). The solution was slowly warmed and then left to evaporate under ambient conditions. After a few days, small colourless single crystals were deposited.

S3. Refinement

All hydrogen atoms were located in a difference Fourier synthesis at an intermediate stage of the refinement. Hydrogen atoms bonded to N and C were placed at calculated positions and refined as riding on their parent atoms, using *SHELXL97* (Sheldrick, 2008) defaults [C—H = 0.93 Å, N—H = 0.86 Å and $U_{iso}(H) = 1.2U_{eq}(C,N)$]. The coordinates of the hydrogen atoms of the water molecule were refined with $U_{iso} = 1.5U_{eq}(O)$.
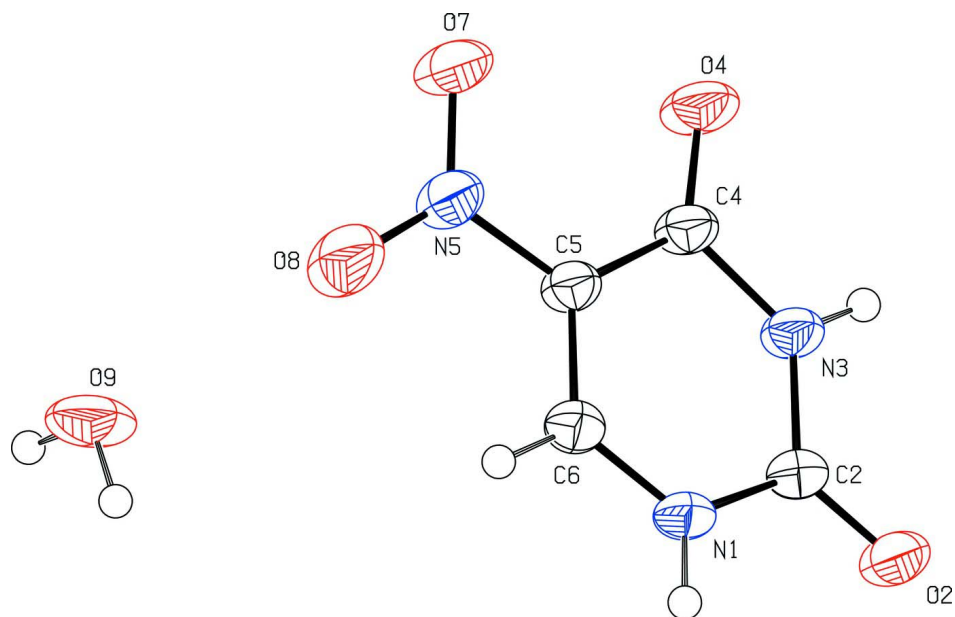
Figure 1

ORTEPII (Spek,2003) plot of the title compound. Displacement ellipsoids are drawn at the 50% probability level.
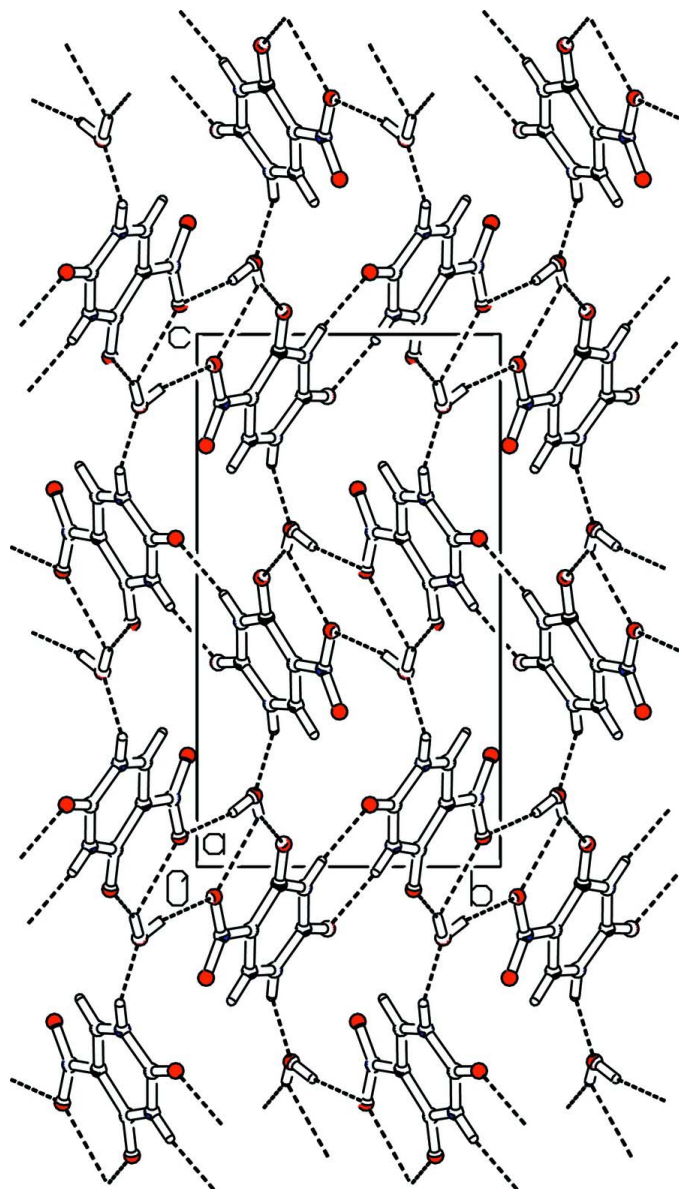
Figure 2

Packing diagram, viewed down the *a* axis, with the hydrogen bonds depicted as dashed lines.

5-nitrouracil monohydrate

Crystal data

$C_4H_3N_3O_4 \cdot H_2O$

$M_r = 175.11$

Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

$a = 6.2799$ (1) Å

$b = 7.8481$ (2) Å

$c = 13.8068$ (3) Å

$\beta = 93.842$ (1)°

$V = 678.94$ (3) Å^3

$Z = 4$

$F(000) = 360$

$D_x = 1.713$ Mg m^{-3}

Mo *K*α radiation, $\lambda = 0.71073$ Å

Cell parameters from 8093 reflections

$\theta = 3.0–33.5°$

$\mu = 0.16$ mm^{-1}

$T = 293$ K

Block, colourless

$0.44 \times 0.22 \times 0.20$ mm

Data collection

Bruker APEXII CCD area-detector diffractometer	15135 measured reflections
Radiation source: fine-focus sealed tube	2232 independent reflections
Graphite monochromator	1918 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.018$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)	$\theta_{max} = 33.6°$, $\theta_{min} = 3.0°$
$T_{min} = 0.890$, $T_{max} = 0.969$	$h = -9 \rightarrow 9$
	$k = -10 \rightarrow 11$
	$l = -20 \rightarrow 20$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.042$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.131$	
$S = 1.00$	H atoms treated by a mixture of independent and constrained refinement
2232 reflections	
115 parameters	$w = 1/[\sigma^2(F_o^2) + (0.0782P)^2 + 0.1592P]$
0 restraints	where $P = (F_o^2 + 2F_c^2)/3$
Primary atom site location: structure-invariant direct methods	$(\Delta/\sigma)_{max} = 0.002$
	$\Delta\rho_{max} = 0.35$ e Å^{-3}
	$\Delta\rho_{min} = -0.37$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
O2	−0.10857 (13)	0.07025 (12)	0.38353 (6)	0.0403 (2)
O4	0.51917 (15)	0.21379 (14)	0.54232 (6)	0.0478 (3)
O7	0.75926 (14)	0.44337 (13)	0.44352 (7)	0.0459 (2)
O8	0.67663 (18)	0.46987 (19)	0.29111 (8)	0.0674 (4)
N1	0.11205 (14)	0.24517 (12)	0.30605 (6)	0.0306 (2)
H1	0.0210	0.2540	0.2569	0.037*
N3	0.20903 (15)	0.14746 (12)	0.46071 (6)	0.0330 (2)
H3	0.1773	0.0894	0.5106	0.040*
N5	0.63828 (16)	0.41810 (13)	0.37147 (7)	0.0371 (2)
C2	0.06017 (16)	0.14825 (13)	0.38398 (7)	0.0290 (2)
C4	0.40561 (16)	0.22918 (14)	0.46790 (7)	0.0309 (2)
C5	0.44553 (16)	0.32373 (13)	0.38070 (7)	0.0292 (2)
C6	0.29851 (16)	0.32614 (14)	0.30377 (7)	0.0307 (2)
H6	0.3287	0.3858	0.2481	0.037*
O9	0.90537 (17)	0.18878 (17)	0.13340 (7)	0.0555 (3)

H9A	0.790 (4)	0.206 (3)	0.0966 (18)	0.083*
H9B	0.975 (4)	0.119 (3)	0.1021 (18)	0.083*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O2	0.0332 (4)	0.0481 (5)	0.0381 (4)	−0.0115 (3)	−0.0090 (3)	0.0058 (3)
O4	0.0397 (5)	0.0639 (6)	0.0370 (4)	−0.0138 (4)	−0.0176 (3)	0.0143 (4)
O7	0.0378 (5)	0.0521 (5)	0.0457 (5)	−0.0136 (4)	−0.0137 (4)	0.0035 (4)
O8	0.0525 (6)	0.1010 (10)	0.0474 (6)	−0.0336 (6)	−0.0066 (4)	0.0276 (6)
N1	0.0274 (4)	0.0381 (4)	0.0251 (4)	−0.0006 (3)	−0.0067 (3)	0.0008 (3)
N3	0.0301 (4)	0.0406 (5)	0.0271 (4)	−0.0066 (3)	−0.0066 (3)	0.0064 (3)
N5	0.0308 (4)	0.0408 (5)	0.0387 (5)	−0.0065 (4)	−0.0055 (3)	0.0064 (4)
C2	0.0272 (4)	0.0313 (4)	0.0278 (4)	−0.0005 (3)	−0.0046 (3)	−0.0010 (3)
C4	0.0278 (5)	0.0353 (5)	0.0286 (4)	−0.0025 (4)	−0.0067 (3)	0.0020 (3)
C5	0.0259 (4)	0.0324 (5)	0.0285 (4)	−0.0023 (3)	−0.0040 (3)	0.0017 (3)
C6	0.0292 (5)	0.0358 (5)	0.0264 (4)	0.0003 (4)	−0.0030 (3)	0.0022 (3)
O9	0.0458 (5)	0.0762 (7)	0.0413 (5)	0.0151 (5)	−0.0218 (4)	−0.0152 (5)

Geometric parameters (Å, º)

O2—C2	1.2234 (12)	N3—C4	1.3888 (13)
O4—C4	1.2169 (11)	N3—H3	0.8600
O7—N5	1.2268 (13)	N5—C5	1.4320 (13)
O8—N5	1.2206 (14)	C4—C5	1.4502 (14)
N1—C6	1.3345 (13)	C5—C6	1.3601 (13)
N1—C2	1.3745 (13)	C6—H6	0.9300
N1—H1	0.8600	O9—H9A	0.87 (2)
N3—C2	1.3651 (12)	O9—H9B	0.84 (3)
C6—N1—C2	122.44 (8)	N3—C2—N1	115.09 (9)
C6—N1—H1	118.8	O4—C4—N3	118.84 (9)
C2—N1—H1	118.8	O4—C4—C5	128.88 (10)
C2—N3—C4	127.78 (9)	N3—C4—C5	112.29 (8)
C2—N3—H3	116.1	C6—C5—N5	117.19 (9)
C4—N3—H3	116.1	C6—C5—C4	120.62 (9)
O8—N5—O7	122.28 (10)	N5—C5—C4	122.19 (9)
O8—N5—C5	118.20 (10)	N1—C6—C5	121.72 (9)
O7—N5—C5	119.52 (9)	N1—C6—H6	119.1
O2—C2—N3	123.33 (9)	C5—C6—H6	119.1
O2—C2—N1	121.57 (9)	H9A—O9—H9B	104 (2)
C4—N3—C2—O2	179.00 (11)	O7—N5—C5—C4	−11.85 (17)
C4—N3—C2—N1	−1.51 (16)	O4—C4—C5—C6	179.88 (12)
C6—N1—C2—O2	−177.51 (10)	N3—C4—C5—C6	0.19 (15)
C6—N1—C2—N3	2.99 (15)	O4—C4—C5—N5	−0.29 (19)
C2—N3—C4—O4	−179.72 (11)	N3—C4—C5—N5	−179.97 (10)
C2—N3—C4—C5	0.00 (16)	C2—N1—C6—C5	−2.99 (16)

O8—N5—C5—C6	−12.45 (17)	N5—C5—C6—N1	−178.58 (10)
O7—N5—C5—C6	168.00 (11)	C4—C5—C6—N1	1.27 (17)
O8—N5—C5—C4	167.71 (13)		

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
N3—H3···O2[i]	0.86	1.99	2.8503 (13)	173
N1—H1···O9[ii]	0.86	1.88	2.6736 (12)	153
O9—H9A···O4[iii]	0.87 (2)	1.92 (2)	2.7640 (13)	165 (2)
O9—H9A···O7[iii]	0.87 (2)	2.41 (3)	2.9101 (13)	117 (2)
O9—H9B···O7[iv]	0.84 (3)	2.29 (3)	3.0940 (15)	162 (2)

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