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6-Amino-5-hydroxyiminomethyl-1-methyluracil Hydrate

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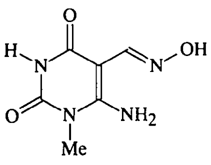
Abstract

In the title compound, 6-amino-5-hydroxyimino-1-methyl-2,4(1*H*,3*H*)-pyrimidinedione hydrate, $C_6H_8N_4O_3.H_2O$, the uracil moieties are linked by N—H···O hydrogen bonds [N···O 2.814 (3) Å] resulting in centrosymmetric base-paired dimers which are then linked in a three-dimensional network through hydrogen bonding with a water molecule of crystallization [N···O 3.105 (3), O···O 2.748 (3) and 2.817 (3), and 2.873 (3) Å]. There is also an intramolecular N—H···N hydrogen bond [N···N 2.680 (3) Å] between adjacent amino and hydroxyimino groups. All available hydrogen-bond donors are utilized.

Comment

The study of the title molecule, (I), is part of a series of analyses of various uracil and related derivatives in our laboratories aimed at determining the nature of their hydrogen bonding and molecular geometry (Low, Scrimgeour, Egglishaw, Howie, Moreno-Carretero & Hueso-Ureña, 1994; Low, Ferguson, Moreno-Carretero & Hueso-Ureña, 1994).



(I)

A view of the molecule of (I) is shown in Fig. 1 and Fig. 2 shows a view of both the molecular packing in the unit cell and the hydrogen bonding. The molecular geometry is very similar to that of 6-amino-1,3-dimethyl-5-hydroxyiminomethyluracil (II) (Low, Ferguson, Moreno-Carretero & Hueso-Ureña, 1994), with no bonds differing by more than 3σ except for C4═O4, which is 1.249 (3) Å in the present structure and 1.234 (3) Å in compound (II). Presumably this slight (0.015 Å) lengthening is associated with atom O4 being involved as an acceptor (see Fig. 2) for two hydrogen bonds in (I), compared with only one in (II). The availability of an additional N—H group, on atom N3, to participate in hydrogen bonding in (I) compared with (II) and the incorporation of a water molecule of

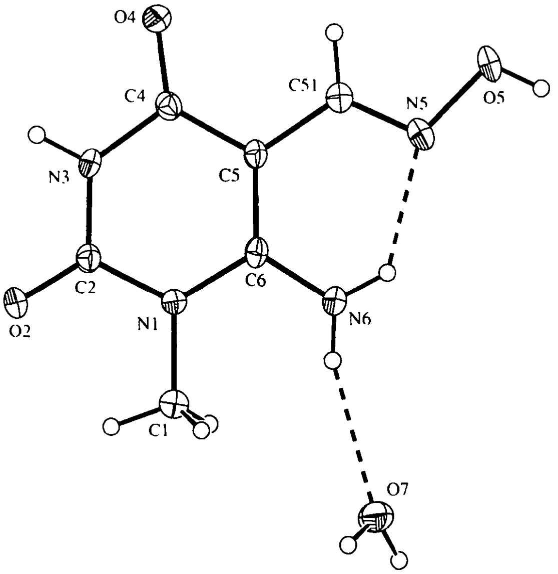


Fig. 1. The molecular structure of (I) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

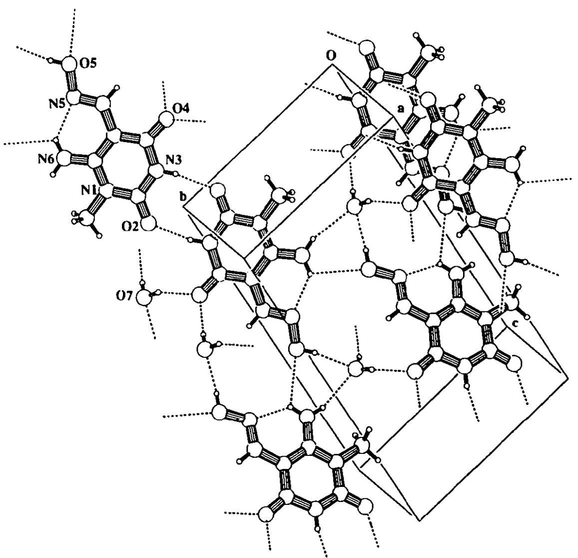


Fig. 2. A view of the molecular packing of (I) showing the hydrogen bonding.

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solvation leads, not unexpectedly, to a completely different crystal packing in (I) compared with (II) which crystallizes in space group $I4_1/a$. The present compound crystallizes in the lower symmetry space group $P2_1/n$, with the water molecule of crystallization playing an important role in the packing of the structure through its hydrogen-bonding interactions. Compound (I) forms base-paired centrosymmetric dimers through N3—H···O2^i [symmetry code: (i) $-x, 2-y, -z$] interactions [N···O 2.814 (3) Å] and these dimers are further linked to form a three-dimensional hydrogen-bonded network *via* O—H···O and N—H···O hydrogen bonds involving the water molecule (Table 3). In both compounds (I) and (II), there is an intramolecular N—H···N hydrogen bond (Table 3) which in each case causes the plane of the hydroxyiminomethyl group to be held close to the plane of the uracil moiety [the C6—C5—C51—N5 torsion angle is 3.7 (4)° in compound (I) and −4.6 (4)° in (II)].

Experimental

Compound (I) was prepared by formylation of 6-amino-1-methyluracil with acetic anhydride and formic acid, followed by condensation of the formyl derivative with hydroxylamine in a pyridine medium. Recrystallization from water afforded crystals suitable for the X-ray analysis.

Crystal data

$C_6H_8N_4O_3.H_2O$
$M_r = 202.18$
Monoclinic
$P2_1/n$
$a = 4.6528\,(6)$ Å
$b = 8.9800\,(9)$ Å
$c = 20.5944\,(14)$ Å
$\beta = 91.752\,(8)°$
$V = 860.1\,(2)$ Å^3
$Z = 4$
$D_x = 1.561$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 8–15.50°$
$\mu = 0.132$ mm^{-1}
$T = 294\,(1)$ K
Plate
0.39 × 0.22 × 0.07 mm
Yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
2083 measured reflections
1865 independent reflections
1079 observed reflections [$I > 2\sigma(I)$]

$R_{\rm int} = 0.015$
$\theta_{\rm max} = 26.91°$
$h = -5 \rightarrow 5$
$k = 0 \rightarrow 11$
$l = 0 \rightarrow 26$
3 standard reflections frequency: 120 min intensity decay: variation 1.3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0453$
$wR(F^2) = 0.1159$
$S = 0.968$
1861 reflections
129 parameters
H atoms riding [*SHELXL*93 (Sheldrick, 1993) defaults: C—H 0.93–0.96, N—H 0.86, O—H 0.82 Å]

$w = 1/[\sigma^2(F_o^2) + (0.0560P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.203$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.238$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
N1	0.5037 (4)	0.7869 (2)	0.07818 (9)	0.0275 (4)
C1	0.5242 (6)	0.6336 (3)	0.05459 (13)	0.0442 (7)
C2	0.2967 (5)	0.8765 (2)	0.04842 (10)	0.0261 (5)
O2	0.1293 (3)	0.8286 (2)	0.00657 (8)	0.0357 (4)
N3	0.2964 (4)	1.0207 (2)	0.06786 (9)	0.0274 (4)
C4	0.4756 (5)	1.0847 (2)	0.11535 (10)	0.0265 (5)
O4	0.4486 (4)	1.2207 (2)	0.12620 (8)	0.0365 (4)
C5	0.6728 (5)	0.9871 (2)	0.14712 (10)	0.0250 (5)
C51	0.8513 (5)	1.0455 (3)	0.20011 (11)	0.0317 (5)
N5	1.0421 (4)	0.9678 (2)	0.23036 (9)	0.0357 (5)
O5	1.1821 (4)	1.0518 (2)	0.27963 (9)	0.0492 (5)
C6	0.6842 (5)	0.8384 (2)	0.12733 (10)	0.0260 (5)
N6	0.8695 (4)	0.7419 (2)	0.15363 (10)	0.0345 (5)
O7	0.9572 (4)	0.4021 (2)	0.13473 (9)	0.0484 (5)

Table 2. *Selected geometric parameters (Å, °)*

N1—C1	1.464 (3)	C4—C5	1.414 (3)
N1—C2	1.383 (3)	C5—C6	1.397 (3)
N1—C6	1.375 (3)	C5—C51	1.449 (3)
C2—O2	1.222 (2)	C51—N5	1.276 (3)
C2—N3	1.356 (3)	N5—O5	1.408 (2)
N3—C4	1.390 (3)	C6—N6	1.327 (3)
C4—O4	1.249 (3)		
C2—N3—C4—C5	−1.5 (3)	C6—C5—C51—N5	3.7 (4)
O4—C4—C5—C51	3.9 (4)	C4—C5—C51—N5	−177.6 (2)
N3—C4—C5—C51	−175.9 (2)	C5—C51—N5—O5	−179.7 (2)

Table 3. *Hydrogen-bond parameters (Å, °)*

D—H···A	D—H	H···A	D···A	D—H···A
N3—H3···O2$^{\rm i}$	0.86	1.97	2.814 (3)	167.2
O5—H5···O7$^{\rm ii}$	0.82	1.95	2.748 (3)	163.3
N6—H6A···O7	0.86	2.28	3.105 (3)	161.5
N6—H6B···N5	0.86	2.03	2.680 (3)	131.9
O7—H71···O4$^{\rm iii}$	0.82	2.04	2.817 (3)	158.2
O7—H72···O4$^{\rm iv}$	0.82	2.06	2.873 (3)	172.6

Symmetry codes: (i) $-x, 2-y, -z$; (ii) $\frac{5}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; (iii) $1+x, y-1, z$; (iv) $x, y-1, z$.

The water H atoms were initially located on a difference map, then allowed for as riding atoms with an O—H distance of 0.82 Å. Fig. 1 was prepared using *ORTEP*II (Johnson, 1976) as implemented in *PLATON* (Spek, 1995). The packing diagram (Fig. 2) was prepared using *PLUTON*92 (Spek, 1992). Examination of the structure with *PLATON* showed that there were no solvent-accessible voids in the crystal lattice.

Data collection: *CAD-4/PC Software* (Enraf–Nonius, 1992). Cell refinement: Enraf–Nonius *SET*4 (de Boer & Duisenberg, 1984) and *CELDIM*. Data reduction: *DATRD*2 in *NRCVAX*94 (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: *SOLVER* in *NRCVAX*94. Program(s) used to refine structure: *NRCVAX*94 and *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *NRCVAX*94, *PLATON* (Spek 1995) and *PLUTON* (Spek 1992). Software used to prepare material for publication: *NRCVAX*94, *SHELXL*93 and *WordPerfect*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1318). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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trans-1,2-Bis(8-hydroxy-2-quinolinyl)-ethene: Comparison with *trans*-Stilbene

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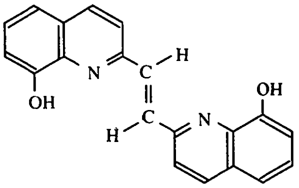
Abstract

The title compound, (*E*)-1,2-ethylenediylbis(2-quinolin-8-ol), $C_{20}H_{14}N_2O_2$, was isolated chromatographically from the Wittig reaction of 8-hydroxy-2-quinolinecarbaldehyde, triphenyl(2-methylene-8-hydroxyquinolinyl)-phosphonium chloride and *n*-butyllithium. The structure is almost planar with C_2 symmetry in the crystal. The olefinic C═C distance is 1.319 (3) Å and the structure consists of crystallographically equivalent molecules stacked along the **b** direction. These molecules are linked *via* zigzag hydrogen bonding between the quinolinol O atom of one molecule and the hydroxy H atom of another molecule. Such systematic hydrogen bonding on both sites of the molecule characterizes a novel backbone network.

Comment

Recently, *trans*-stilbene derivatives have attracted considerable interest because of their unusually short C═C bond distance (Ogawa, 1993). X-ray crystal structure reports of *trans*-1,2-disubstituted ethenes incorporating heteroaromatic compounds are known but limited in number. We describe herein a facile synthesis of *trans*-1,2-bis(8-hydroxy-2-quinolinyl)ethene, (I), *via* the Wittig reaction, and its structural characterization.



(I)

As shown in Fig. 1, the molecular structure of the title compound possesses an almost planar geometry, with torsion angles C9—C10—C10′—C9′ of 180° and N1—C9—C10—C10′ of 2.9 (3)°, the latter of which is small compared to the corresponding value found in *trans*-stilbene (Tirado-Rives, Fronczek & Gandour, 1985). The C10═C10′ double-bond distance of 1.319 (3) Å is in the range typical of ethylene C═C bond lengths [1.318 (5)–1.326 (3) Å] reported for *trans*-stilbene (Finder, Newton & Allinger, 1974; Bernstein, 1975; Boustra, Schouten & Kroon, 1984) and slightly shorter than the value of 1.332 (4) Å reported for *trans*-1,2-bis(2-methyl-4-quinazolinyl)ethylene (Wolfgang & Mehmet, 1990). The C9···C9′ distance is 3.821 Å in this compound and 3.873 Å in *trans*-stilbene, and the respective C9—C10—C10′ angles have comparable values of 124.4 (2) and 126.7 (2)°. These results can be explained by the steric effect of the intermolecular hydrogen bond [O1—H1···O 3.043 (4) Å] of the title compound. Fig. 2 shows the packing diagram viewed down the **a** direction of the molecule. Hydrogen bonds on both hydroxy groups of one molecule cause alignment of the zigzag molecules [O1—H1···O = 132 (2)°]. Thus, the structure exhibits a specific crystalline network in which the crystallographically equivalent molecules stack in a unique way, with molecules superimposed as shown in Fig. 2, similar to the situation seen in coronene (Robertson & White, 1944). The uniform stacking of planar π-donor molecules is ideal for both the design of molecular metals and the study of charge-transfer complexes.

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