

## 6-Methyl-2-pyridone pentahydrate

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## Key indicators

Single-crystal X-ray study  
 $T = 150$  K  
Mean  $\sigma(\text{C}-\text{C}) = 0.003$  Å  
 $R$  factor = 0.047  
 $wR$  factor = 0.133  
Data-to-parameter ratio = 12.8For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.

Crystals of the title compound,  $\text{C}_6\text{H}_7\text{NO}\cdot 5\text{H}_2\text{O}$ , were grown over a period of several weeks from an aqueous solution of the commercial compound. The molecule crystallizes in space group  $P\bar{1}$  and there are two independent 6-methyl-2-pyridone (Hmhp) molecules in the asymmetric unit, together with ten molecules of water. Packing diagrams reveal stacks of hydrogen-bonded Hmhp dimers surrounded by channels of water molecules. The Hmhp molecules pack with face-to-face  $\pi$ - $\pi$  stacking, a common feature of pyridone crystal structures. Each water molecule serves twice as hydrogen-bond donor and twice as acceptor, and is thus pseudo-tetrahedral. The water molecules are arranged in hydrogen-bonded five- and six-membered rings and the rings are fused together, with the five-membered rings adopting an envelope conformation and the six-membered rings adopting either a chair or boat conformation. This structure is further evidence that Hmhp exists in the solid state as the pyridone tautomer and not the pyridinol tautomer.

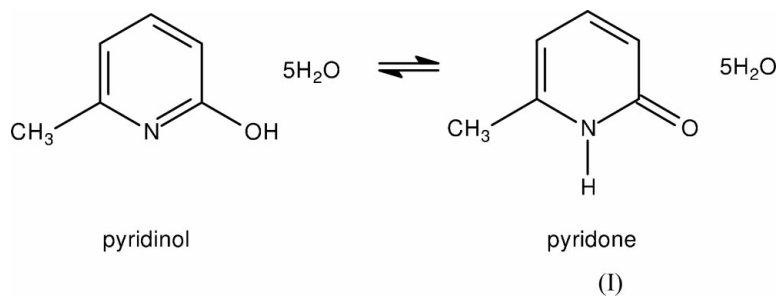
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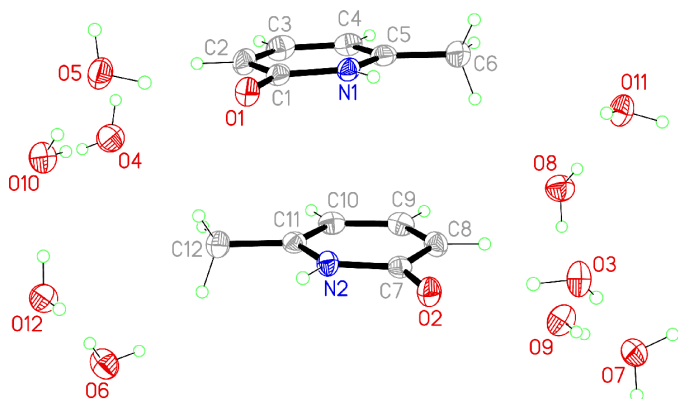
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## Comment

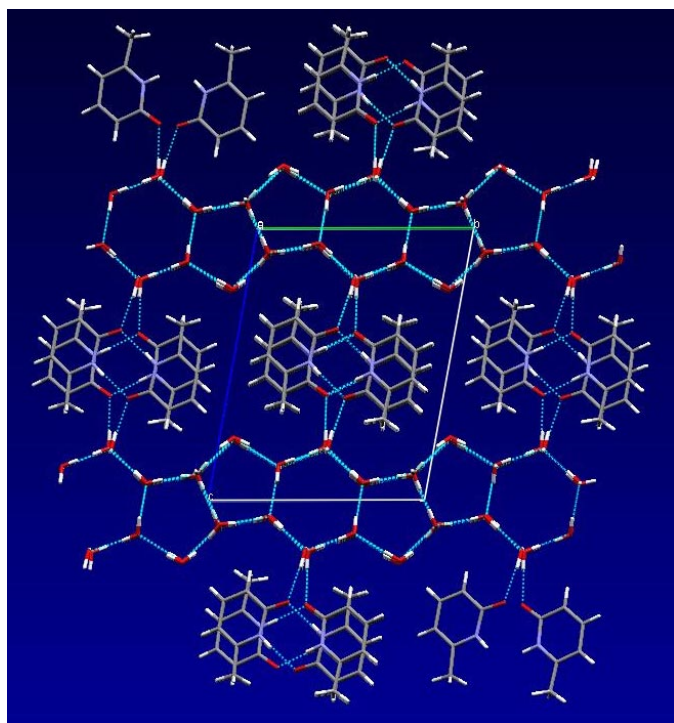
The molecule 2-hydroxypyridine and the family of 6-substituted derivatives have been extensively used as ligands in transition metal coordination chemistry, and a detailed review has been published (Rawson & Winpenny, 1995). There is also much interest in the chemistry of the ligands themselves, in particular, the keto-enol tautomerism which is observed in the gas phase and in solution.



This tautomerism has been known since 1907 (Baker & Baly, 1907) and has been comprehensively investigated in solution by IR spectroscopy (Gibson *et al.*, 1955; Katritzky *et al.*, 1967; Mason, 1957) and nuclear magnetic resonance spectroscopy (Coburn & Dudek, 1968), and in the gas phase by IR spectroscopy (King *et al.*, 1972; Beak & Fry, 1973) and UV-vis spectroscopy (Beak *et al.*, 1976). Various theoretical studies have also been reported (Beak & Covington, 1978; Beak *et al.*, 1980; Parchment *et al.*, 1991; Wong *et al.*, 1992).



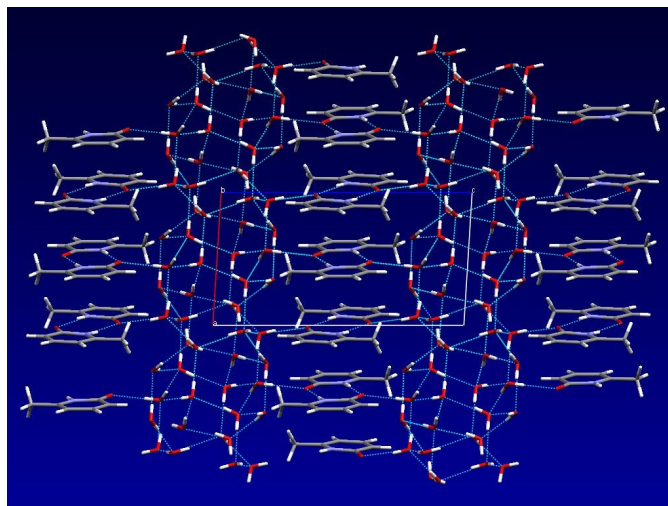
**Figure 1**  
The asymmetric unit of (I), with displacement ellipsoids drawn at the 50% probability level. H atoms are represented as small spheres of arbitrary size.



**Figure 2**  
Projection along the *a* axis, with hydrogen bonds in light blue, showing also the  $\pi$ - $\pi$  stacking.

Principal factors influencing the position of this equilibrium include solvent effects (polarity and pH) and substituent effects (position on the ring and electron-donating/withdrawing influence). Substituents at position 6 have the greatest effect; electron-withdrawing substituents are seen to drive the equilibrium towards the pyridinol tautomer, whereas electron-donating substituents favour the pyridone tautomer. The rationale behind this has already been explained in terms of resonance stabilization and destabilization by the substituent (King *et al.*, 1972).

Naturally, X-ray crystallography has played a key role in determining the preferred tautomers in the solid state. The structures of 6-chloro-2-hydroxypyridine (Kvick & Olovsson, 1969) and 6-bromo-2-hydroxypyridine (Kvick, 1976) are



**Figure 3**  
Projection along the *b* axis, showing the hydrogen-bonding network involving the water molecules and the 6-methyl-2-pyridone dimer.

already known. Both have electron-withdrawing substituents and both crystallize as the pyridinol form, confirming the conclusions derived from spectroscopic evidence which predicted that they would be observed as the pyridinol tautomer. If there is no substituent, the molecule crystallizes as the pyridone form (Penfold, 1953).

However, crystallographic proof that electron-donating substituents generate a preference for the pyridone form has so far only been obtained *via* crystal structures of coordination compounds (Rawson & Winpenny, 1995, and references therein) or co-crystallized with (*S*)-malic acid (Aakeröy *et al.*, 2000). Unfortunately this is far from conclusive; a search of the Cambridge Structural Database (Version 5.25 plus two updates; Allen, 2002) for 6-methyl-2-pyridone, allowing all bonds to be of any type, returned 105 hits. Of these no fewer than 80 reported the ligand as the pyridinol form, rather than the pyridone form, and a handful of hits even contained mixtures of the two. In most cases, this is probably because the C—O bond was too long to be considered as a genuine double bond. In addition, the ligand has been deprotonated in its complexes; there is no longer the possibility of determining the presence of an O—H or N—H bond and hence decide upon pyridone or pyridinol structure; these are now resonance forms rather than discrete tautomers.

We have determined the crystal structure of 6-methyl-2-pyridone (Hmhp) as its pentahydrate, (I), crystallized from water (Fig. 1). There are two independent Hmhp molecules in the asymmetric unit and also ten molecules of water. Face-to-face  $\pi$ - $\pi$  stacking, a common feature of pyridone crystal structures, is observed here. One Hmhp molecule lies above the other, with the methyl groups oriented in opposite directions, as shown in Fig. 2. Both molecules are essentially planar, except for the methyl H atoms. Their mean planes are approximately parallel and 3.30 Å apart, just less than the sum of the van der Waals radii for two C atoms, which is 3.4 Å.

Packing diagrams of the structure show that Hmhp packs as hydrogen-bonded dimers; these then form stacks, separated by

channels of hydrogen-bonded water molecules (Fig. 2). Each water molecule serves twice as hydrogen-bond donor and twice as acceptor, making four hydrogen bonds in total. This pseudo-tetrahedral arrangement means that the O atoms form five- and six-membered rings. These rings are fused together; the five-membered rings adopt an envelope conformation and the six-membered rings adopt either a chair or boat conformation. The hydrogen-bonding network involving the water molecules, and also the hydrogen bonding between the Hmhp molecules, is shown in Fig. 3.

The C—O bond lengths are 1.272 (3) and 1.268 (3) Å for the two molecules and are in good agreement with those reported by Aakeröy *et al.* (2000) of 1.275 and 1.284 Å. These are a little on the long side for a C=O double bond. However, the data clearly show the presence of an H atom bonded to each N atom, and these have been refined freely. From this result, together with the lack of significant residual electron density next to the O atoms, the molecule is unambiguously in the pyridone form.

## Experimental

Commercially available 2-hydroxy-6-methylpyridine was obtained as a white powder. A sample was dissolved in distilled water with gentle heating and the sample vial stoppered. Storage in a cool cupboard resulted in large plate crystals growing over a period of several weeks.

### Crystal data

$C_6H_7NO \cdot 5H_2O$	$Z = 4$
$M_r = 199.21$	$D_x = 1.191 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 7.5134 (19) \text{ \AA}$	Cell parameters from 2910 reflections
$b = 11.261 (3) \text{ \AA}$	$\theta = 2.2\text{--}25.0^\circ$
$c = 13.859 (4) \text{ \AA}$	$\mu = 0.11 \text{ mm}^{-1}$
$\alpha = 99.674 (4)^\circ$	$T = 150 (2) \text{ K}$
$\beta = 90.793 (5)^\circ$	Plate, colourless
$\gamma = 105.622 (4)^\circ$	$0.20 \times 0.10 \times 0.01 \text{ mm}$
$V = 1111.0 (5) \text{ \AA}^3$	

### Data collection

Bruker SMART 1K CCD diffractometer	2768 reflections with $I > 2\sigma(I)$
Thin-slice $\omega$ scans	$R_{\text{int}} = 0.030$
Absorption correction: none	$\theta_{\text{max}} = 25.0^\circ$
8151 measured reflections	$h = -8 \rightarrow 8$
3872 independent reflections	$k = -13 \rightarrow 13$
	$l = -16 \rightarrow 16$

### Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0577P)^2 + 0.6174P]$
$R[F^2 > 2\sigma(F^2)] = 0.048$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.133$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.04$	$\Delta\rho_{\text{max}} = 0.32 \text{ e \AA}^{-3}$
3872 reflections	$\Delta\rho_{\text{min}} = -0.30 \text{ e \AA}^{-3}$
303 parameters	
H atoms treated by a mixture of independent and constrained refinement	

**Table 1**

Selected bond distances (Å).

O1—C1	1.272 (3)	N1—H1N	0.81 (3)
O2—C7	1.268 (3)	N2—H2N	0.87 (3)

**Table 2**

Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O3—H1O $\cdots$ O2	0.816 (9)	1.876 (10)	2.690 (2)	175 (3)
O3—H2O $\cdots$ O7	0.813 (10)	1.944 (11)	2.750 (3)	171 (3)
O4—H4O $\cdots$ O6 <sup>i</sup>	0.816 (10)	1.967 (12)	2.766 (3)	166 (3)
O4—H3O $\cdots$ O6 <sup>ii</sup>	0.815 (10)	1.985 (12)	2.789 (3)	169 (2)
O5—H5O $\cdots$ O1	0.824 (9)	1.887 (11)	2.701 (2)	170 (3)
O5—H6O $\cdots$ O3 <sup>iii</sup>	0.822 (10)	1.939 (11)	2.751 (3)	169 (2)
O6—H7O $\cdots$ O12	0.813 (10)	1.935 (10)	2.744 (3)	173 (3)
O6—H8O $\cdots$ O8 <sup>iv</sup>	0.813 (10)	1.953 (10)	2.760 (3)	172 (3)
O7—H10O $\cdots$ O12 <sup>v</sup>	0.814 (10)	1.943 (11)	2.754 (2)	174 (3)
O7—H9O $\cdots$ O11 <sup>vi</sup>	0.810 (10)	1.965 (10)	2.774 (3)	176 (3)
O8—H11O $\cdots$ O11	0.820 (10)	2.006 (10)	2.823 (3)	175 (3)
O8—H12O $\cdots$ O9	0.818 (10)	1.963 (10)	2.780 (3)	177 (3)
O9—H13O $\cdots$ O7	0.824 (10)	1.990 (12)	2.801 (3)	168 (3)
O9—H14O $\cdots$ O4 <sup>iv</sup>	0.814 (10)	2.019 (12)	2.816 (3)	166 (3)
O10—H16O $\cdots$ O4	0.821 (9)	1.919 (10)	2.739 (3)	176 (3)
O10—H15O $\cdots$ O5	0.822 (10)	1.917 (11)	2.736 (3)	174 (2)
O11—H17O $\cdots$ O10 <sup>v</sup>	0.817 (10)	1.940 (10)	2.752 (2)	173 (3)
O11—H18O $\cdots$ O5 <sup>iii</sup>	0.818 (10)	1.927 (10)	2.743 (2)	175 (3)
O12—H19O $\cdots$ O3 <sup>vii</sup>	0.820 (10)	1.907 (10)	2.726 (2)	177 (3)
O12—H20O $\cdots$ O10	0.818 (9)	1.926 (10)	2.743 (3)	177 (3)
N1—H1N $\cdots$ O1 <sup>iii</sup>	0.81 (3)	2.00 (3)	2.798 (3)	171 (3)
N2—H2N $\cdots$ O2 <sup>iii</sup>	0.87 (3)	1.92 (3)	2.783 (3)	175 (2)

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

Methyl H atoms were positioned geometrically (C—H = 0.98 Å) and refined as riding, with free rotation about the C—C bond, and with  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ . Aromatic H atoms were also positioned geometrically (C—H = 0.95 Å) and refined as riding, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ . H atoms bonded to N and O atoms were found in a difference map and their positions were refined, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N}, \text{O})$ . Water O—H distances were restrained to 0.82 (1) Å and H $\cdots$ H distances restrained to 1.35 (2) Å, but N—H distances were not restrained.

Data collection: SMART (Bruker, 2001); cell refinement: SAINT (Bruker, 2001); data reduction: SAINT; program(s) used to solve structure: SIR92 (Altomare *et al.*, 1993); program(s) used to refine structure: SHELXTL (Sheldrick, 2001); molecular graphics: SHELXTL and MERCURY (Version 1.2; Bruno *et al.*, 2002); software used to prepare material for publication: SHELXTL and local programs.

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