

A simple compound with an unexpectedly complex structure: 4-pyridone 6/5-hydrate

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The crystal structure of the title compound, $C_5H_5NO \cdot \frac{6}{5}H_2O$, contains five independent molecules of pyridone and six independent water molecules. The space group is $P2_1$, but four of the pyridones and four waters correspond closely to $P2_1/n$. The packing involves two layers; one consists of head-to-tail chains of pyridone molecules 1–4 linked by $N-H \cdots O$ hydrogen bonds, and a second layer involves all the waters and the fifth pyridone. The layers are linked by hydrogen bonds from water to pyridone oxygen. The four water O atoms that accept only one classical hydrogen bond have their environment completed by $C-H \cdots O$ interactions.

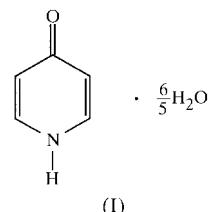
Comment

We are interested in the structures of pyridines substituted at the 4-position, and in particular in their secondary bonding interactions, which often lead to the formation of chains of molecules. We have recently published the structures of 4-iodopyridine (Ahrens & Jones, 1999), with $N \cdots I$ ‘halogen bonds’ (Corradi *et al.*, 2000), 4-halopyridinium halides (Jones *et al.*, 1999), with halogen–halogen contacts and $N-H \cdots$ halide hydrogen bonds, and ‘4-mercaptopypyridine’ (pyridine-4-thione; Flakus *et al.*, 2001), with $N-H \cdots S$ hydrogen bonds.

We have now turned our attention to ‘4-hydroxypyridine’, which is known from spectroscopic studies to exist in the keto form as 4-pyridone; standard texts such as Meisslich (1962) and Smith (1979) review the evidence. The structure of 2-pyridone has been determined several times, including low-temperature neutron diffraction and charge–density studies; see Yang & Craven (1998) and references therein. For a brief discussion of tautomerism in hydroxypyridines, the reader is referred to Freytag & Jones (1999) and Wijaya *et al.* (1999).

Various derivatives, adducts and complexes of 4-pyridone have been investigated by X-ray methods, *e.g.* 2-amino-4-pyridones, used in some early crystal engineering studies (Toledo *et al.*, 1994), the 1:1 adduct of 4-pyridone with 4-nitrophenol (Evans *et al.*, 1998), the 2:1 adduct with nitric acid (Goodgame *et al.*, 1993), and the complex

$ZnCl_2(C_5H_5NO)_2$ (Masse & Le Fur, 1998). However, perhaps surprisingly, there appears to be no report of the structure of the parent compound itself. Well formed colourless crystals were obtained by evaporation from supposedly anhydrous acetone but the structure determination, reported here, shows these to be the hydrate 4-pyridone-6/5 H_2O , (I), presumably formed by the influence of adventitious water.



The asymmetric unit contains five independent molecules of 4-pyridone (atoms are numbered with the first digit 1 for molecule 1, *etc.*, and the second digit corresponding to the standard ring numbering) and six independent water molecules. The five pyridone molecules are all closely similar. In particular, the bond lengths reflect the quinone-like distribution of single and double bonds, with $N-C$ 1.341 (3)–1.355 (3), average 1.346 Å, $C_{n2}-C_{n3}$ and $C_{n5}-C_{n6}$ 1.356 (3)–1.372 (3), average 1.362 Å, $C_{n3}-C_{n4}$ and $C_{n4}-C_{n5}$ 1.417 (3)–1.433 (3), average 1.426 Å, and $C_{n4}=O$ 1.258 (2)–1.278 (2), average 1.272 Å. The $C=O$ bond of the fifth molecule is significantly shorter than the others, which may be due to its different hydrogen-bonding environment (see below). The ring angles are all slightly greater than 120° except for the angle at C_{n4} , which is narrowed to an average of 115.40° . Closely similar dimensions, where applicable, are also observed in the analogous 4-thione (Flakus *et al.*, 2001) and the 4-nitrophenol adduct (Evans *et al.*, 1998). Individual values for each molecule are available in the deposited material.

The molecular packing was expected to be straightforward, with chains of pyridone molecules linked by head-to-tail hydrogen bonds of the form $N-H \cdots O$; this structure type is

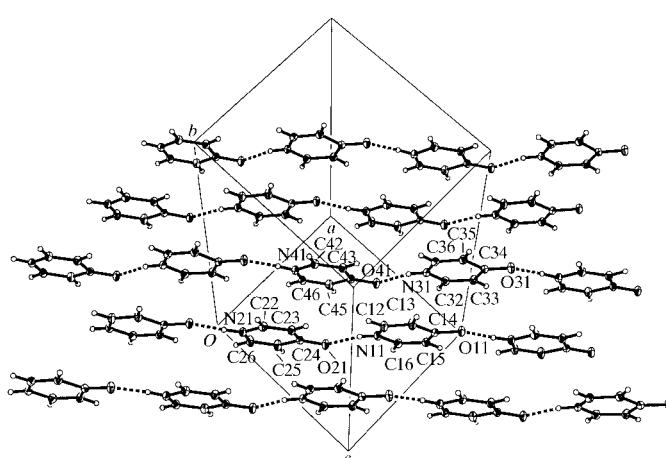


Figure 1

The layer of four independent 4-pyridone molecules at $y \approx 0.4$, showing the atom-numbering scheme. Ellipsoids correspond to 30% probability levels and H-atom radii are arbitrary. Hydrogen bonds are indicated by dashed lines.

observed for the sulfur analogue (Flakus *et al.*, 2001). In one region of the structure, at $y \approx 0.4$, such chains are indeed observed (Fig. 1) parallel to the diagonal [101]. One chain is composed of molecules 1 and 2, and another of molecules 3 and 4. The chains are slightly angled at the H atoms of the NH groups (Table 2) and rather more so at the O atoms [$H \cdots O=C$ 129.9 (8)–136.0 (8) $^\circ$]. There is no additional secondary bonding between the two chains. All four independent molecules are approximately coplanar [interplanar angles: molecule 1/molecule 2 1.39 (7), 3/4 2.03 (7), and 2/3 2.38 (7) $^\circ$].

The second region of the structure, at $y \approx 0.15$, consists of layers involving pyridone molecule 5 and all six water molecules (Fig. 2). There are two clearly defined chain substructures in the layer, both parallel to the x axis. One is composed solely of water molecules 1–4, connected by hydrogen bonds, the other is of the form $[\cdots \text{pyridone}-(\text{H}_2\text{O})_2 \cdots]_n$, whereby the two waters O5 and O6 are acceptors in a three-centre hydrogen bond from the NH group of one pyridone and donors to the O=C group of the next. It is this chain that is responsible for the overall lack of inversion symmetry. The two chains are linked by O5–H \cdots O1W and O6–H \cdots O4W hydrogen bonds, but also involve some non-classical hydrogen bonds (see below).

The two main components of the packing, the purely pyridone layer and the pyridone/water layer, are linked (Fig. 3) by four independent hydrogen bonds of the form water H \cdots pyridone O. Pyridone molecule 5 is approximately perpendicular to the pyridones of the first layer [e.g. 4/5, interplanar angle 85.85 (5) $^\circ$].

The hydrogen bonding described so far exhausts the set of classical hydrogen-bond donors, but the waters numbered 2, 3,

5 and 6 still have an acceptor site free. Accordingly, non-classical hydrogen bonds of the form C–H \cdots O are observed in the water/pyridone layer (Fig. 2; H53 \cdots O2W, H56 \cdots O3W and H52 \cdots O6W) and between layers (H22 \cdots O5W; this interaction is not shown in Fig. 3 because the C22–H22 bonds are eclipsed).

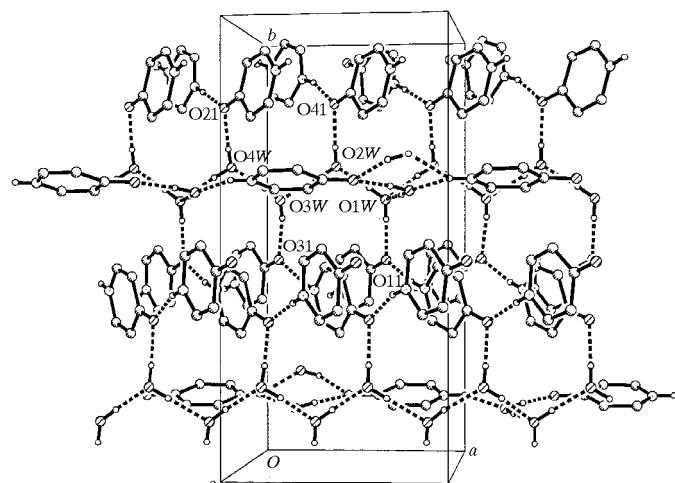


Figure 3

Side view of the layer structure of the title compound, showing the hydrogen bonds that connect the layers. All radii are arbitrary. H atoms not involved in hydrogen bonding have been omitted.

Experimental

Anhydrous 4-pyridone (Sigma–Aldrich) was dissolved in acetone and the solvent was allowed to evaporate slowly. Much microcrystalline material was formed, but also some well formed tablets and prisms.

Crystal data

$C_5H_5NO \cdot \frac{6}{5}H_2O$	$D_x = 1.321 \text{ Mg m}^{-3}$
$M_r = 116.72$	Mo $K\alpha$ radiation
Monoclinic, $P2_1$	Cell parameters from 5938
$a = 8.6689 (8) \text{ \AA}$	reflections
$b = 17.6441 (16) \text{ \AA}$	$\theta = 2.3\text{--}30.2^\circ$
$c = 9.6101 (8) \text{ \AA}$	$\mu = 0.10 \text{ mm}^{-1}$
$\beta = 93.283 (3)^\circ$	$T = 133 (2) \text{ K}$
$V = 1467.5 (2) \text{ \AA}^3$	Rectangular tablet, colourless
$Z = 10$	$0.24 \times 0.18 \times 0.12 \text{ mm}$

Data collection

Bruker SMART1000 CCD diffractometer	$R_{\text{int}} = 0.035$
ω and φ scans	$\theta_{\text{max}} = 30.0^\circ$
18 869 measured reflections	$h = -12 \rightarrow 12$
4431 independent reflections	$k = -24 \rightarrow 24$
3403 reflections with $I > 2\sigma(I)$	$l = -13 \rightarrow 13$

Table 1
Selected geometric parameters (\AA , $^\circ$).

C14–O11	1.275 (2)	C44–O41	1.276 (2)
C24–O21	1.278 (2)	C54–O51	1.258 (2)
C34–O31	1.272 (2)		
C13–C14–C15	115.31 (16)	C43–C44–C45	115.49 (17)
C23–C24–C25	115.78 (16)	C53–C54–C55	114.95 (17)
C33–C34–C35	115.47 (17)		

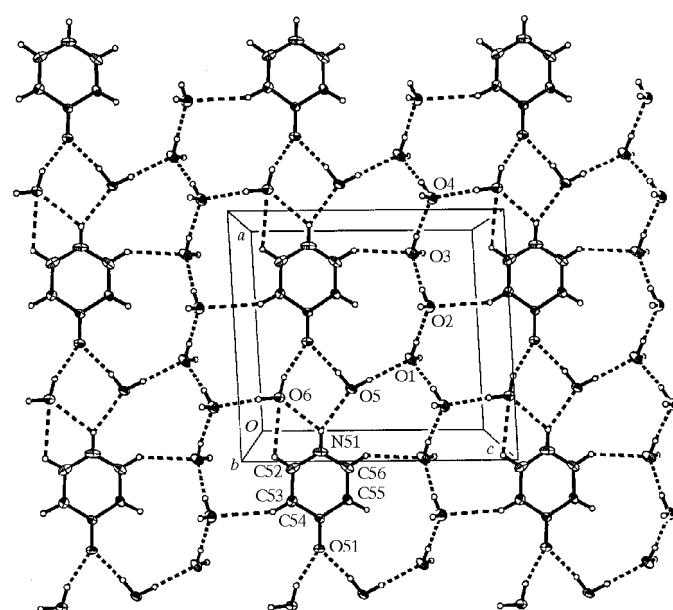


Figure 2

The layer of six independent waters and the fifth independent 4-pyridone molecule at $y \approx 0.15$, showing the atom-numbering scheme. Ellipsoids correspond to 30% probability levels and H-atom radii are arbitrary. Hydrogen bonds are indicated by dashed lines.

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.034$
 $wR(F^2) = 0.090$
 $S = 0.96$
4431 reflections
438 parameters

H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0548P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.32 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.18 \text{ e \AA}^{-3}$

Table 2
Hydrogen-bonding geometry (\AA , $^\circ$).

$D\text{--H}\cdots A$	$D\text{--H}$	$H\cdots A$	$D\cdots A$	$D\text{--H}\cdots A$
N11-H11 \cdots O21	0.893 (16)	1.789 (17)	2.674 (2)	171 (2)
N31-H31 \cdots O41	0.885 (16)	1.816 (18)	2.667 (2)	161 (3)
N51-H51 \cdots O5W	0.868 (17)	2.18 (2)	2.925 (2)	143 (2)
N51-H51 \cdots O6W	0.868 (17)	2.41 (2)	3.011 (2)	127 (2)
O1W-H02 \cdots O2W	0.889 (15)	1.835 (16)	2.723 (2)	177 (3)
O2W-H03 \cdots O41	0.888 (15)	1.859 (16)	2.743 (2)	174 (2)
O2W-H04 \cdots O3W	0.879 (15)	1.884 (16)	2.762 (2)	176 (3)
O3W-H06 \cdots O4W	0.883 (15)	1.909 (16)	2.785 (2)	171 (3)
O5W-H09 \cdots O1W	0.875 (15)	1.972 (15)	2.845 (2)	176 (3)
N21-H21 \cdots O11 ⁱ	0.909 (16)	1.775 (17)	2.668 (2)	167 (2)
N41-H41 \cdots O31 ⁱ	0.870 (16)	1.841 (18)	2.686 (2)	163 (3)
O6W-H012 \cdots O4W ⁱ	0.876 (14)	1.922 (15)	2.796 (2)	175 (2)
O4W-H07 \cdots O21 ⁱⁱ	0.887 (15)	1.795 (16)	2.676 (2)	172 (2)
O4W-H08 \cdots O1W ⁱⁱ	0.895 (15)	1.852 (16)	2.744 (2)	174 (3)
O5W-H010 \cdots O51 ⁱⁱ	0.907 (15)	1.848 (16)	2.748 (2)	171 (3)
O6W-H011 \cdots O51 ⁱⁱ	0.870 (15)	1.887 (17)	2.715 (2)	158 (3)
O1W-H01 \cdots O11 ⁱⁱⁱ	0.895 (15)	1.818 (15)	2.704 (2)	170 (2)
O3W-H05 \cdots O31 ^{iv}	0.879 (15)	1.872 (18)	2.719 (2)	161 (3)
C53-H53 \cdots O2W ⁱⁱ	0.95	2.59	3.463 (3)	153
C56-H56 \cdots O3W ⁱⁱ	0.95	2.48	3.298 (3)	145
C22-H22 \cdots O5W ⁱⁱ	0.95	2.57	3.406 (2)	147
C52-H52 \cdots O6W	0.95	2.51	3.084 (2)	119

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

Despite centrosymmetric E -statistics, the structure could not be solved in space group $P2_1/m$, which was assigned by the crystallographic software. The space group was therefore changed to $P2_1$, whereupon direct methods yielded a solution with four recognisable pyridone molecules (numbers 1–4, see *Comment*) and four single peaks tentatively assigned as water O atoms (also numbers 1–4). The remaining residues (one pyridone and two waters) were identified, after appropriate refinement, in difference syntheses, but only as double images, from which the correct positions were obtained by trial and error. Inspection of the coordinates shows that the four pyridones and four waters originally located correspond closely to space group $P2_1/n$, with a pseudo-inversion centre at *ca* 0.25, 0.15, 0.25. The lack of systematic absences corresponding to $P2_1/n$ shows that the additional symmetry cannot be global.

H atoms bonded to N or O atoms were refined freely but with chemically equivalent $X\text{--H}$ bond lengths restrained equal. Other H

atoms were included using a riding model starting from calculated positions. Displacement parameter components along common bonds were restrained equal using the *DELU* instruction in *SHELXL97* (Sheldrick, 1997).

The anomalous scattering is not sufficient to determine the absolute structure, and Friedel pairs were therefore merged. A rigid-body libration correction (Schomaker & Trueblood, 1968) was successfully applied to all five 4-pyridone molecules; corrected bond lengths may be found in the deposited material. In the discussion, uncorrected values are quoted for consistency with other related structures.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1994); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1453). Services for accessing these data are described at the back of the journal.

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