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# Crystal structure of 2,6-bis(3-hydroxy-3-methylbut-1-yn-1-yl)pyridine monohydrate

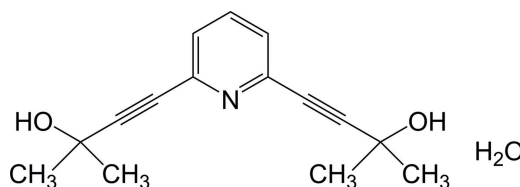
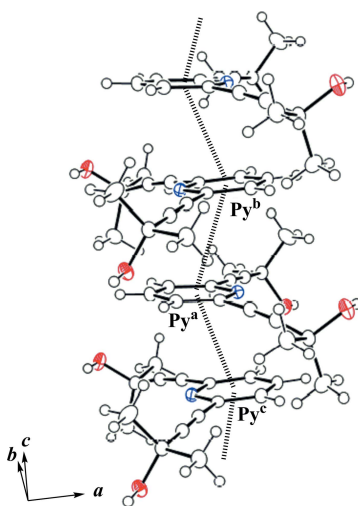
Take-aki Koizumi\* and Toshikazu Takata

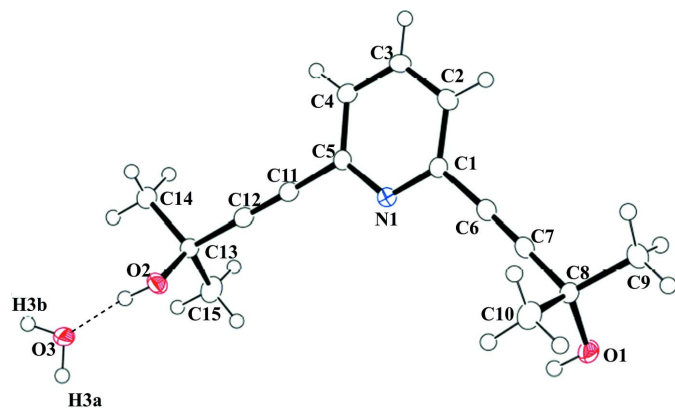
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In the title pyridine derivative,  $C_{15}H_{17}NO_2 \cdot H_2O$ , the two OH groups are oriented in directions opposite to each other with respect to the plane of the pyridine ring. In the crystal, hydrogen bonds between the pyridine molecule and the water molecule, *viz.*  $O_{\text{hydroxy}}-H \cdots O_{\text{water}}$ ,  $O_{\text{hydroxy}}-H \cdots O_{\text{hydroxy}}$ ,  $O_{\text{water}}-H \cdots O_{\text{hydroxy}}$  and  $O_{\text{water}}-H \cdots N_{\text{pyridine}}$ , result in the formation of a ribbon-like structure running along [011].

## 1. Chemical context

Pyridine derivatives with propargyl alcohol groups as substituents in the 2,6-positions are interesting compounds that have been used as synthons of many reactive compounds (Furusko *et al.*, 2004) and polymers (Miyagawa *et al.*, 2010, 2011), as starting materials of helical polymers (Inouye *et al.*, 2004; Waki *et al.*, 2006; Abe, Machiguchi *et al.*, 2008; Abe, Murayama *et al.*, 2008), and as ligands for transition-metal complexes (Hung *et al.*, 2009). Since such compounds have rigid structures containing one pyridine nitrogen and two alcoholic OH groups, they can be used to construct a higher order structure by coordination with metals and/or hydrogen-bond formation at multiple points. The crystal structures of 2,6-bis(3-methylbutyn-3-ol)pyridine, **1**, and its complex with triphenylphosphine oxide (**1**-OPPh<sub>3</sub>) were reported by Holmes *et al.* (2002). In the crystal of **1**, the molecules form intermolecular hydrogen bonds with the pyridine ring and the two OH groups; the O—H  $\cdots$  O hydrogen bonds from a 2<sub>1</sub> helical chain along the *b*-axis direction. The chains are linked by intermolecular N  $\cdots$  H—O hydrogen bonds, forming a layer structure, and then form a stacking structure *via* C—H  $\cdots$  O interactions between the layers. In contrast, in the case of **1**-OPPh<sub>3</sub>, each of the two OH groups forms a hydrogen bond with the O atom of OPPh<sub>3</sub> without forming a network structure. Hence, it is expected that the crystal packing of **1** strongly depends on the presence or absence of hydrogen bonding. However, to our knowledge, the present examples have only been structurally analysed with 2,6-bis(propargyl alcohol)-substituted pyridines. In this paper, we report the crystal structure of 2,6-bis(3-methylbutyn-3-ol)pyridine monohydrate, **1**·H<sub>2</sub>O.

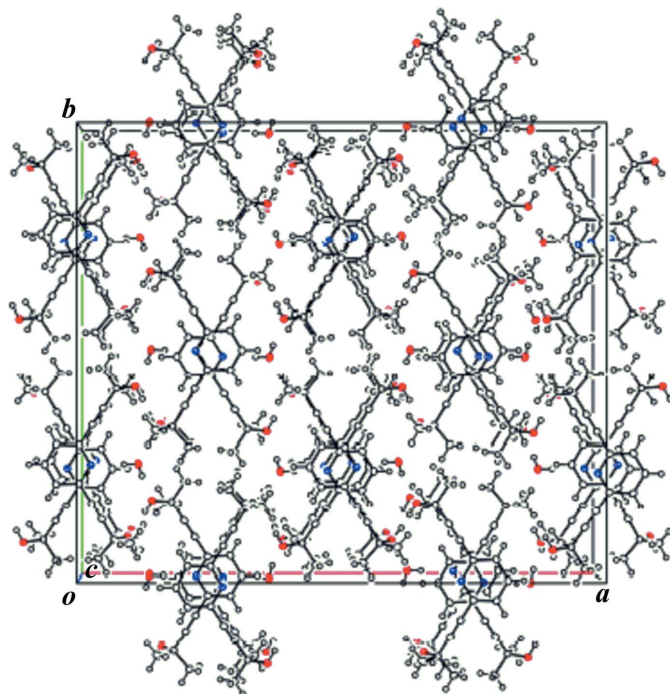




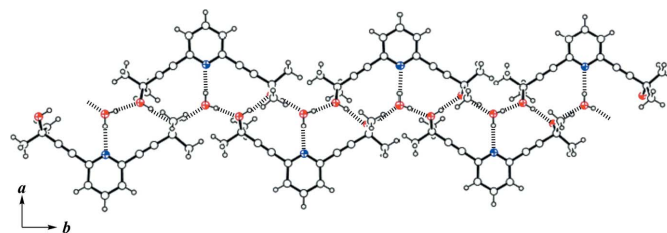
**Figure 1**  
The molecular structure of the title compound with the atom labelling. Displacement ellipsoids are drawn at the 50% probability level. A dashed line indicates the O—H...O hydrogen bond.

## 2. Structural commentary

The molecular structure of the title compound is depicted in Fig. 1. The bond lengths of two C≡C triple bonds (C6≡C7 and C11≡C12) are 1.199 (2) and 1.191 (2) Å, respectively, consistent with the triple-bond character. The  $C_{ipso}$ —C≡C (C1—C6≡C7 and C5—C11≡C12) and C≡C—C(OH) (C6≡C7—C8 and C11≡C12—C13) bond angles are 176.0 (2), 176.4 (2), 174.6 (2) and 178.5 (2)°, respectively. C6≡C7—C8 is slightly distorted from a linear structure compared to the other bonds. The two OH groups are oriented in directions opposite to each other with respect to the plane of the pyridine ring, and the pyridine ring makes dihedral



**Figure 2**  
Packing diagram of the title compound, viewed down the  $c$  axis.

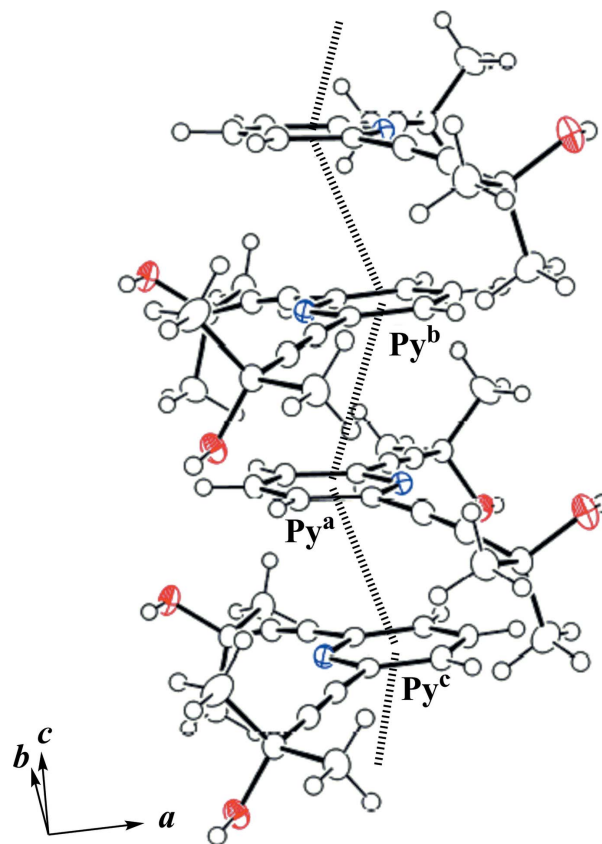


**Figure 3**  
Partial packing diagram of the title compound, showing the O—H...O and O—H...N hydrogen bonds (dashed lines) between **1** and water molecules.

angles of 50.50 (17) and 57.58 (15)°, respectively, with the C7/C8/O1 and C12/C13/O2 planes.

## 3. Supramolecular features

Fig. 2 depicts the packing of **1**·H<sub>2</sub>O along the  $c$  axis. The water molecules present as the crystallization solvent form intermolecular O—H...O and O—H...N interactions with the hydroxyl groups and the N atoms of the pyridine unit of molecule **1** (Table 1), resulting in a ribbon-like structure along [011] (Fig. 3). The pyridine ring forms  $\pi$ — $\pi$  stacking interactions with that in a neighboring ribbon in an *anti*-parallel



**Figure 4**  
Partial packing diagram of the title compound, showing the chain formation along the  $c$  axis by  $\pi$ — $\pi$  interactions (dashed lines). [Symmetry codes: (b)  $-x + \frac{1}{2}, -y + 1, z + \frac{1}{2}$ ; (c)  $-x + \frac{1}{2}, -y + 1, z - \frac{1}{2}$ .]

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

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
O1–H1...O2 <sup>i</sup>	0.86 (3)	1.90 (3)	2.7640 (15)	175 (3)
O2–H2...O3	0.89 (3)	1.82 (2)	2.7052 (17)	170 (3)
O3–H3A...N1 <sup>ii</sup>	0.86 (3)	2.02 (3)	2.8790 (18)	179 (3)
O3–H3B...O1 <sup>iii</sup>	0.83 (3)	2.01 (3)	2.8361 (19)	173 (3)

Symmetry codes: (i)  $-x + \frac{3}{4}, y - \frac{1}{4}, z + \frac{1}{4}$ ; (ii)  $-x + \frac{3}{4}, y + \frac{1}{4}, z - \frac{1}{4}$ ; (iii)  $x, y + \frac{1}{2}, z - \frac{1}{2}$ .

mode, resulting in a  $\pi$ – $\pi$  network along the *c* axis (Fig. 4). The centroid–centroid distance between the pyridine rings [*Cg*...*Cg*<sup>iv</sup>; symmetry code: (iv)  $-x + \frac{1}{2}, -y + 1, z + \frac{1}{2}$ ] is 3.5538 (11) Å. In the crystal of non-solvated **1** (space group *P*2<sub>1</sub>/*c*; Holmes *et al.*, 2002), such  $\pi$ – $\pi$  stacking interactions between the pyridine rings are not found.

#### 4. Database survey

The Cambridge Structural Database (CSD version 5.41, update of March 2020; Groom *et al.*, 2016) has 138 entries for structures containing 2,6-diethynylpyridine scaffolds, and for 2,6-bis(1-propyn-3-ol) derivatives gave two hits. The non-solvated compound 2,6-bis(3-methylbutyn-3-ol)pyridine (refcode LUMYEX) and its complex with O=PPh<sub>3</sub> (LUMYIB) have been reported (Holmes *et al.*, 2002). The benzene derivative containing two propargyl alcohol units at the 1,3-positions gives 34 hits; however, there is no report of a simple benzene derivative having a structure similar to that of **1**.

#### 5. Synthesis and crystallization

2,6-Bis(3-methylbutyn-3-ol)pyridine was prepared by using a modified Potts method (Potts *et al.*, 1993). 2,6-Dibromopyridine (9.1 g, 38 mmol) was reacted with 2-methyl-3-butyn-2-ol (13 g, 151 mmol) using CuI (225 mg, 1.3 mmol)/PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (840 mg, 1.3 mmol) as a catalyst in a THF (50 mL)–NEt<sub>3</sub> (150 mL) solvent for 19 h at room temperature. The resulting dark-brown solution was quenched with an aqueous NH<sub>4</sub>Cl solution and the obtained solid was eliminated by celite filtration. The solution was extracted by AcOEt, and the organic phase was dried over MgSO<sub>4</sub>. After filtering off the desiccant, the filtrate was concentrated and subjected to silica-gel chromatography (eluent: AcOEt:hexane 3:2). Single crystals suitable for X-ray diffraction studies were obtained from an ethyl acetate solution *via* slow evaporation in air.

#### 6. Refinement

Crystal data, data collection and refinement details are summarized in Table 2. Water H atoms and alcohol H atoms were located in a difference-Fourier map, and were refined freely. All of the C-bound H atoms were positioned geometrically (C–H = 0.93 or 0.98 Å), and were refined using a

**Table 2**  
Experimental details.

Crystal data	
Chemical formula	C <sub>15</sub> H <sub>17</sub> NO <sub>2</sub> ·H <sub>2</sub> O
<i>M<sub>r</sub></i>	261.31
Crystal system, space group	Orthorhombic, <i>Fdd</i> 2
Temperature (K)	113
<i>a</i> , <i>b</i> , <i>c</i> (Å)	31.9834 (14), 27.7358 (13), 6.6610 (4)
<i>V</i> (Å <sup>3</sup> )	5908.9 (5)
<i>Z</i>	16
Radiation type	Cu <i>K</i> α
$\mu$ (mm <sup>−1</sup> )	0.66
Crystal size (mm)	0.34 × 0.1 × 0.1
Data collection	
Diffractometer	Rigaku XtaLAB Synergy R, DW system, HyPix
Absorption correction	Multi-scan ( <i>CrysAlis PRO</i> ; Rigaku OD, 2019)
<i>T</i> <sub>min</sub> , <i>T</i> <sub>max</sub>	0.817, 1.000
No. of measured, independent and observed [ <i>I</i> > 2σ( <i>I</i> )] reflections	4676, 2071, 2045
<i>R</i> <sub>int</sub>	0.015
(sin θ/λ) <sub>max</sub> (Å <sup>−1</sup> )	0.626
Refinement	
<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.029, 0.082, 1.04
No. of reflections	2071
No. of parameters	192
No. of restraints	1
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}$ , $\Delta\rho_{\min}$ (e Å <sup>−3</sup> )	0.18, −0.20
Absolute structure	Flack <i>x</i> determined using 495 quotients [( <i>I</i> <sup>+</sup> ) − ( <i>I</i> <sup>−</sup> )]/[( <i>I</i> <sup>+</sup> ) + ( <i>I</i> <sup>−</sup> )] (Parsons <i>et al.</i> , 2013)
Absolute structure parameter	0.02 (11)

Computer programs: *CrysAlis PRO* (Rigaku OD, 2019), *Olex2.solve* (Bourhis *et al.*, 2015), *Olex2.refine* (Bourhis *et al.*, 2015) and *OLEX2* (Dolomanov *et al.*, 2009).

riding model, with *U*<sub>iso</sub>(H) = 1.2*U*<sub>eq</sub> (aromatic-C) or 1.5*U*<sub>eq</sub> (methyl-C).

#### Acknowledgements

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## supporting information

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## Crystal structure of 2,6-bis(3-hydroxy-3-methylbut-1-yn-1-yl)pyridine monohydrate

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### Computing details

Data collection: *CrysAlis PRO* (Rigaku OD, 2019); cell refinement: *CrysAlis PRO* (Rigaku OD, 2019); data reduction: *CrysAlis PRO* (Rigaku OD, 2019); program(s) used to solve structure: *Olex2.solve* (Bourhis *et al.*, 2015); program(s) used to refine structure: *Olex2.refine* (Bourhis *et al.*, 2015); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009).

### 4-[6-(3-Hydroxy-3-methylbut-1-yn-1-yl)pyridin-2-yl]-2-methylbut-3-yn-2-ol monohydrate

#### Crystal data

$C_{15}H_{17}NO_2 \cdot H_2O$

$M_r = 261.31$

Orthorhombic, *Fdd2*

$a = 31.9834$  (14) Å

$b = 27.7358$  (13) Å

$c = 6.6610$  (4) Å

$V = 5908.9$  (5) Å<sup>3</sup>

$Z = 16$

$F(000) = 2240$

$D_x = 1.175$  Mg m<sup>-3</sup>

Cu *Kα* radiation,  $\lambda = 1.54184$  Å

Cell parameters from 4276 reflections

$\theta = 4.2$ – $74.9^\circ$

$\mu = 0.66$  mm<sup>-1</sup>

$T = 113$  K

Plate, white

$0.34 \times 0.1 \times 0.1$  mm

#### Data collection

Rigaku XtaLAB Synergy R, DW system, HyPix diffractometer

Radiation source: Rotating-anode X-ray tube, Rigaku (Cu) X-ray Source

Mirror monochromator

Detector resolution: 10.0000 pixels mm<sup>-1</sup>

$\omega$  scans

Absorption correction: multi-scan (CrysAlisPro; Rigaku OD, 2019)

$T_{\min} = 0.817$ ,  $T_{\max} = 1.000$

4676 measured reflections

2071 independent reflections

2045 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.015$

$\theta_{\max} = 75.0^\circ$ ,  $\theta_{\min} = 4.2^\circ$

$h = -40 \rightarrow 25$

$k = -22 \rightarrow 34$

$l = -8 \rightarrow 5$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.029$

$wR(F^2) = 0.082$

$S = 1.04$

2071 reflections

192 parameters

1 restraint

Primary atom site location: iterative

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0555P)^2 + 3.7832P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.18$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.19$  e Å<sup>-3</sup>

Absolute structure: Flack  $x$  determined using  
 495 quotients  $[(F^-)-(F)]/[(F^+)+(F)]$  (Parsons *et al.*,  
 2013)  
 Absolute structure parameter: 0.02 (11)

### Special details

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

### Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.35948 (3)	0.32551 (4)	0.6275 (2)	0.0246 (3)
O2	0.34219 (3)	0.65799 (4)	0.3581 (2)	0.0216 (3)
O3	0.38487 (4)	0.74210 (5)	0.3415 (3)	0.0329 (4)
N1	0.27513 (4)	0.49371 (5)	0.5965 (3)	0.0166 (3)
H1	0.3733 (8)	0.3523 (9)	0.623 (5)	0.041 (7)*
H2	0.3550 (7)	0.6863 (9)	0.339 (5)	0.037 (6)*
H2A	0.195964	0.419764	0.615414	0.022*
H3	0.158347	0.492523	0.628127	0.023*
H3A	0.4117 (8)	0.7423 (8)	0.345 (5)	0.033 (6)*
H3B	0.3782 (8)	0.7679 (10)	0.288 (5)	0.042 (7)*
H4	0.194772	0.565882	0.611513	0.022*
H9A	0.313194	0.255773	0.504956	0.037*
H9B	0.271146	0.285849	0.469227	0.037*
H9C	0.290932	0.282373	0.689425	0.037*
H10A	0.353762	0.360767	0.264577	0.041*
H10B	0.310243	0.336577	0.202018	0.041*
H10C	0.350205	0.303410	0.244822	0.041*
H14A	0.303649	0.733924	0.513951	0.036*
H14B	0.271251	0.704803	0.651137	0.036*
H14C	0.269906	0.699027	0.412177	0.036*
H15A	0.369017	0.641198	0.719381	0.043*
H15B	0.333112	0.668096	0.843702	0.043*
H15C	0.364036	0.698483	0.703467	0.043*
C1	0.25351 (4)	0.45203 (5)	0.6000 (3)	0.0160 (3)
C2	0.21008 (5)	0.44989 (5)	0.6118 (3)	0.0182 (3)
C3	0.18798 (5)	0.49280 (6)	0.6182 (3)	0.0193 (4)
C4	0.20942 (4)	0.53608 (5)	0.6100 (3)	0.0183 (3)
C5	0.25298 (4)	0.53508 (5)	0.5995 (3)	0.0159 (3)
C6	0.27810 (5)	0.40863 (6)	0.5837 (3)	0.0186 (4)
C7	0.29850 (5)	0.37292 (5)	0.5576 (3)	0.0190 (4)
C8	0.32310 (5)	0.32951 (6)	0.5046 (3)	0.0179 (4)
C9	0.29729 (5)	0.28434 (6)	0.5457 (3)	0.0244 (4)
C10	0.33542 (6)	0.33286 (6)	0.2844 (3)	0.0275 (4)
C11	0.27666 (4)	0.57928 (5)	0.5862 (3)	0.0170 (3)
C12	0.29570 (4)	0.61579 (6)	0.5643 (3)	0.0178 (3)



C13	0.31907 (5)	0.66164 (5)	0.5422 (3)	0.0181 (4)
C14	0.28820 (5)	0.70362 (6)	0.5287 (3)	0.0238 (4)
C15	0.34897 (6)	0.66791 (7)	0.7178 (4)	0.0290 (4)

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
O1	0.0193 (5)	0.0161 (5)	0.0383 (9)	-0.0015 (4)	-0.0082 (6)	0.0042 (6)
O2	0.0195 (5)	0.0166 (5)	0.0287 (7)	-0.0014 (4)	0.0053 (6)	0.0013 (6)
O3	0.0154 (5)	0.0246 (6)	0.0586 (11)	-0.0014 (4)	0.0000 (7)	0.0166 (7)
N1	0.0161 (5)	0.0165 (6)	0.0173 (8)	0.0000 (4)	-0.0002 (6)	0.0005 (6)
C1	0.0187 (7)	0.0157 (7)	0.0138 (8)	0.0000 (5)	-0.0010 (7)	0.0008 (7)
C2	0.0186 (6)	0.0176 (7)	0.0182 (9)	-0.0035 (5)	-0.0006 (7)	0.0009 (7)
C3	0.0144 (6)	0.0230 (8)	0.0205 (9)	-0.0004 (6)	-0.0009 (7)	0.0010 (8)
C4	0.0175 (7)	0.0180 (7)	0.0195 (9)	0.0022 (5)	0.0000 (7)	0.0000 (7)
C5	0.0183 (7)	0.0157 (7)	0.0136 (9)	-0.0003 (5)	0.0001 (7)	0.0007 (7)
C6	0.0185 (7)	0.0174 (7)	0.0200 (9)	-0.0027 (5)	-0.0010 (7)	0.0019 (7)
C7	0.0178 (6)	0.0168 (7)	0.0225 (9)	-0.0029 (5)	0.0009 (7)	0.0029 (8)
C8	0.0163 (6)	0.0143 (7)	0.0232 (10)	0.0003 (5)	-0.0017 (7)	0.0024 (7)
C9	0.0228 (7)	0.0164 (7)	0.0339 (11)	-0.0046 (6)	-0.0014 (8)	0.0015 (8)
C10	0.0299 (8)	0.0245 (8)	0.0280 (11)	0.0067 (7)	0.0065 (8)	0.0042 (8)
C11	0.0174 (7)	0.0175 (7)	0.0161 (8)	0.0017 (5)	-0.0005 (7)	-0.0004 (7)
C12	0.0173 (6)	0.0172 (7)	0.0190 (9)	0.0025 (6)	-0.0001 (6)	-0.0009 (7)
C13	0.0179 (7)	0.0135 (7)	0.0229 (10)	0.0004 (5)	0.0002 (7)	0.0001 (7)
C14	0.0230 (7)	0.0161 (7)	0.0322 (11)	0.0031 (6)	0.0025 (8)	0.0023 (8)
C15	0.0340 (9)	0.0203 (8)	0.0327 (11)	-0.0043 (7)	-0.0129 (8)	0.0014 (8)

*Geometric parameters (Å, °)*

O2—C13	1.436 (2)	C4—C3	1.384 (2)
O2—H2	0.89 (3)	C13—C14	1.529 (2)
O1—C8	1.427 (2)	C13—C15	1.521 (3)
O1—H1	0.86 (3)	C2—H2A	0.9500
O3—H3A	0.86 (3)	C2—C3	1.385 (2)
O3—H3B	0.83 (3)	C3—H3	0.9500
N1—C1	1.3473 (19)	C9—H9A	0.9800
N1—C5	1.3488 (19)	C9—H9B	0.9800
C1—C6	1.442 (2)	C9—H9C	0.9800
C1—C2	1.393 (2)	C10—H10A	0.9800
C8—C7	1.481 (2)	C10—H10B	0.9800
C8—C9	1.525 (2)	C10—H10C	0.9800
C8—C10	1.522 (3)	C14—H14A	0.9800
C5—C4	1.3952 (19)	C14—H14B	0.9800
C5—C11	1.444 (2)	C14—H14C	0.9800
C12—C11	1.191 (2)	C15—H15A	0.9800
C12—C13	1.482 (2)	C15—H15B	0.9800
C7—C6	1.199 (2)	C15—H15C	0.9800
C4—H4	0.9500		

C13—O2—H2	107 (2)	C3—C2—C1	118.31 (13)
C8—O1—H1	109.4 (19)	C3—C2—H2A	120.8
H3A—O3—H3B	105 (2)	C4—C3—C2	119.44 (13)
C1—N1—C5	117.40 (12)	C4—C3—H3	120.3
N1—C1—C6	115.80 (12)	C2—C3—H3	120.3
N1—C1—C2	123.32 (13)	C8—C9—H9A	109.5
C2—C1—C6	120.85 (13)	C8—C9—H9B	109.5
O1—C8—C7	111.09 (14)	C8—C9—H9C	109.5
O1—C8—C9	105.94 (14)	H9A—C9—H9B	109.5
O1—C8—C10	110.27 (13)	H9A—C9—H9C	109.5
C7—C8—C9	109.73 (13)	H9B—C9—H9C	109.5
C7—C8—C10	108.51 (15)	C8—C10—H10A	109.5
C10—C8—C9	111.32 (16)	C8—C10—H10B	109.5
N1—C5—C4	122.83 (14)	C8—C10—H10C	109.5
N1—C5—C11	116.47 (12)	H10A—C10—H10B	109.5
C4—C5—C11	120.68 (14)	H10A—C10—H10C	109.5
C11—C12—C13	178.5 (2)	H10B—C10—H10C	109.5
C6—C7—C8	174.6 (2)	C13—C14—H14A	109.5
C5—C4—H4	120.7	C13—C14—H14B	109.5
C3—C4—C5	118.66 (14)	C13—C14—H14C	109.5
C3—C4—H4	120.7	H14A—C14—H14B	109.5
C12—C11—C5	176.4 (2)	H14A—C14—H14C	109.5
C7—C6—C1	176.0 (2)	H14B—C14—H14C	109.5
O2—C13—C12	106.48 (13)	C13—C15—H15A	109.5
O2—C13—C14	109.61 (14)	C13—C15—H15B	109.5
O2—C13—C15	109.95 (14)	C13—C15—H15C	109.5
C12—C13—C14	109.48 (12)	H15A—C15—H15B	109.5
C12—C13—C15	109.82 (15)	H15A—C15—H15C	109.5
C15—C13—C14	111.38 (14)	H15B—C15—H15C	109.5
C1—C2—H2A	120.8		
N1—C1—C2—C3	0.7 (3)	C5—N1—C1—C6	176.16 (16)
N1—C5—C4—C3	0.1 (3)	C5—N1—C1—C2	-1.8 (3)
C1—N1—C5—C4	1.3 (3)	C5—C4—C3—C2	-1.3 (3)
C1—N1—C5—C11	-177.20 (15)	C11—C5—C4—C3	178.62 (17)
C1—C2—C3—C4	0.9 (3)	C6—C1—C2—C3	-177.14 (17)

## Hydrogen-bond geometry (Å, °)

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
O1—H1 $\cdots$ O2 <sup>i</sup>	0.86 (3)	1.90 (3)	2.7640 (15)	175 (3)
O2—H2 $\cdots$ O3	0.89 (3)	1.82 (2)	2.7052 (17)	170 (3)
O3—H3A $\cdots$ N1 <sup>ii</sup>	0.86 (3)	2.02 (3)	2.8790 (18)	179 (3)
O3—H3B $\cdots$ O1 <sup>iii</sup>	0.83 (3)	2.01 (3)	2.8361 (19)	173 (3)

Symmetry codes: (i)  $-x+3/4, y-1/4, z+1/4$ ; (ii)  $-x+3/4, y+1/4, z-1/4$ ; (iii)  $x, y+1/2, z-1/2$ .