

Crystal structure and Hirshfeld surface analysis of 3-(3-hydroxyphenyl)-1-(1*H*-pyrrol-2-yl)prop-2-en-1-one hemihydrate

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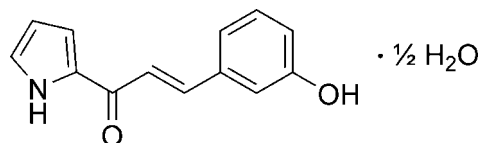
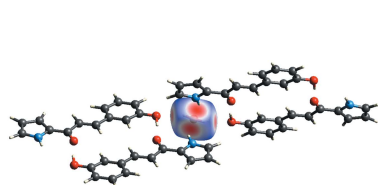
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High-quality single crystals of the title compound, $2C_{13}H_{11}NO_2 \cdot H_2O$, were grown and a structural analysis was performed. The asymmetric unit comprises one molecule of 3-(3-hydroxyphenyl)-1-(1*H*-pyrrol-2-yl)prop-2-en-1-one (**3HPPP**), which was recently discovered to be a promising anti-MRSA candidate, and a half-molecule of water. The compound crystallizes in the monoclinic space group *P2*/*c*. The crystal structure features intermolecular pyrrole-N—H···O (water), carbonyl/keto-C—O···H—O-phenol and phenol-C—O···H (water) hydrogen bonds, which help to consolidate the crystal packing. A Hirshfeld surface analysis for the components in the asymmetric unit showed that H···H (40.9%) and H···C/C···H (32.4%) contacts make the largest contributions to the intermolecular interactions of **3HPPP**. Considering the presence of water, in its vicinity H···O/O···H and H···C/C···H are the most significant contacts, contributing 48.7 and 29.8%, respectively.

1. Chemical context

Chalcones are 1,3-diphenyl-2-propen-1-ones with an α,β -unsaturated carbonyl system in between two aromatic rings (Zhuang *et al.*, 2017; Attarde *et al.*, 2010). Chalcones are widely used as precursors for the biosynthesis of compounds in the flavonoid class, and can be chemically synthesized by various reactions such as aldol condensation, and Suzuki and Wittig reactions (Zhuang *et al.*, 2017). To date, chalcones have continued to attract great interest from researchers because of their simple chemistry and diverse applications in medicinal and synthetic chemistry (Zhuang *et al.*, 2017), analytical chemistry (Sun *et al.*, 2012), materials chemistry and lighting technology (Anandkumar *et al.*, 2017; Danko *et al.*, 2012).



Chalcone analogues have been reported with a wide range of biological activities, including anti-inflammatory, anti-microbial, and anticancer properties (Kar Mahapatra *et al.*, 2019; Lin *et al.*, 2002; Nowakowska, 2007). Recently, we discovered a new promising anti-microbial candidate, 3-(3-hydroxyphenyl)-1-(1*H*-pyrrol-2-yl)prop-2-en-1-one (**3HPPP**), which showed remarkable inhibitory activity on methicillin-



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resistant *Staphylococcus aureus* (MRSA, ATCC 700699) with MIC and MBC values of 0.23 mg ml⁻¹ and 0.47 mg ml⁻¹, respectively (Gunasekharan *et al.*, 2021). However, as yet the crystal structure of this compound has remained elusive. The molecular structure of its hydrate is analysed and discussed herein.

2. Structural commentary

The molecular structure of the asymmetric unit of **3HPPP** plus the symmetry-completed water molecule are shown in Fig. 1. The asymmetric unit consists of a molecule of **3HPPP** in a neutral state plus half a water molecule of crystallization. The investigated bioactive compound crystallized in the monoclinic crystal system, space group *P2₁/c*, with the unit cell containing four molecules of **3HPPP** together with two molecules of water. Four water molecules reside on four of the cell edges on the crystallographic *c*-axis and are shared between the unit and adjacent cells. Further analysis of the metrical parameters of the molecule showed no anomalies compared to the available literature data for related compounds. The planarity of **3HPPP** is confirmed as both the aromatic pyrrole (N1/C1–C4) and phenyl (C8–C13) rings are aligned in the plane of the aliphatic α,β -unsaturated ketone linker, making dihedral angles of 0.91 (7) and 5.98 (7)°, respectively with the linker.

3. Supramolecular features

Fig. 2 illustrates the unit cell of **3HPPP** viewed along the crystallographic *b*-axis and the supramolecular association within and around it. In the crystal, molecules are linked into dimers *via* multiple intermolecular hydrogen bonds (Table 1). The dimers are arranged in planes with two distinct orientations and at an angle of roughly 61° to each other, while the water molecules act as hinges. This represents a zigzag pattern when viewed along the the *ac* diagonal. Furthermore, the **3HPPP** dimers are arranged in a stair-like fashion, which

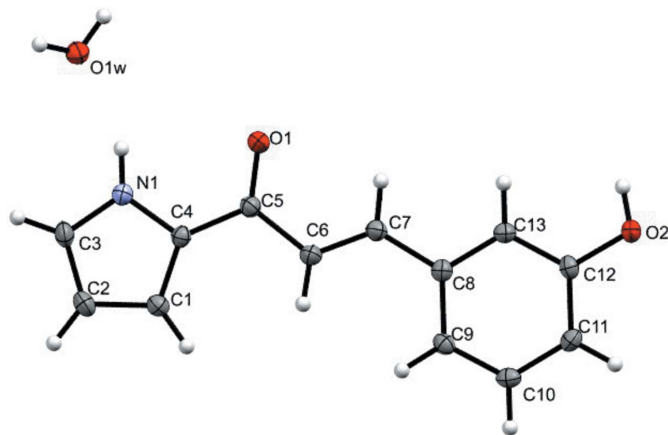


Figure 1
ORTEP (Burnett & Johnson, 1996) diagram of compound **3HPPP** plus the symmetry-completed water molecule with the atom-labelling scheme and 50% probability ellipsoids.

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>
O2–H2O···O1 ⁱ	0.901 (19)	1.828 (19)	2.7257 (11)	174.2 (16)
N1–H1N···O3	0.888 (17)	2.041 (17)	2.8722 (13)	155.4 (14)
C13–H13···O1 ⁱ	0.95	2.51	3.2050 (13)	130
O3–H3O···O2 ⁱⁱ	0.864 (18)	2.320 (18)	2.9430 (7)	129.2 (16)

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

Table 2
Percentage contribution of interatomic contacts to the calculated Hirshfeld surfaces for the individual constituents in the asymmetric unit of **3HPPP**.

Contact	Percentage contribution	
	3HPPP	Water
H···H	40.9	16.2
H···O/O···H	19.4	48.7
H···C/C···H	32.4	29.8
H···N/N···H	2.0	4.6

ascends/descends roughly in the *b*-axis direction. Intermolecular hydrogen bonds C13–H13···O1ⁱ [symmetry code: (i) $-x + 1, -y + 1, -z + 1$] between two molecules of **3HPPP** can be observed connecting these non-covalently. Molecules of **3HPPP** are linked into inversion dimer–dimer chains through these weak interactions. Moreover, the lattice water molecules act as donors and acceptors in hydrogen bonds with the phenol and pyrrole moieties of **3HPPP** [O3–H3O···O2ⁱⁱ and N1–H1N···O3; symmetry code: (ii) $x - 1, -y + 1, z - \frac{1}{2}$;

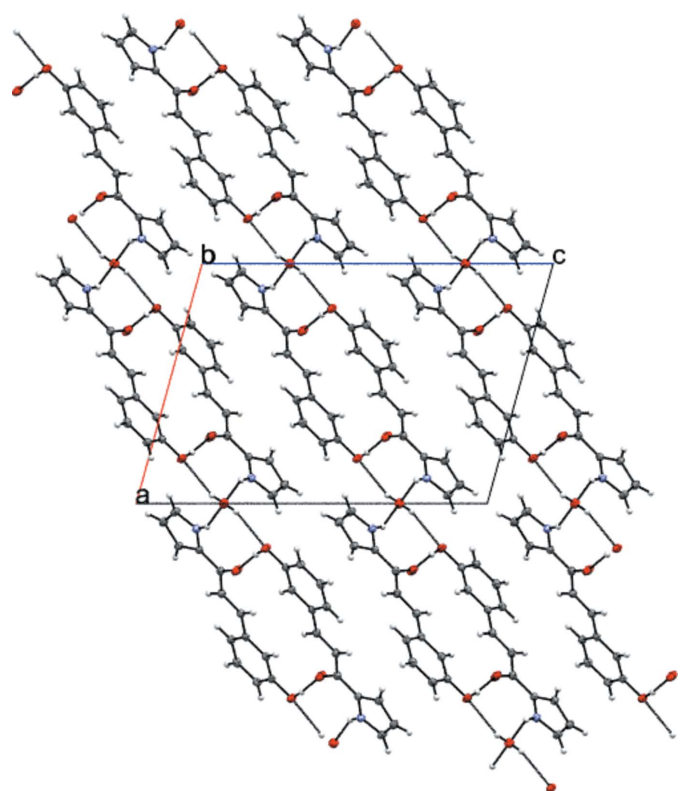


Figure 2
The crystal packing of compound **3HPPP** viewed along the *b* axis. The intermolecular interactions are indicated by dashed lines.

Table 2]. All hydrogen atoms and all lone pairs of the water molecule are engaged in hydrogen bonding (Fig. 2). These hydrogen bonds connect two of the **3HPPP** dimers in different planes comparably strongly and further consolidate the crystal packing.

4. Database survey

A database survey of the Cambridge Structural Database (WEBCSD version 1.9.32, updated September 2022; Groom *et al.*, 2016) revealed that no structure of a compound with a close similarity to the entire **3HPPP** molecule as been reported. However, focusing on the pyrrole ene-one side yielded three [refcodes HIXGAW (Norsten *et al.*, 1999); RICFEP (Camarillo *et al.*, 2007) and RICFEP01 (Jones, 2013)] similar compounds with a 77–88% similarity score relative to the title compound. The title compound differs from those at the substituted ethyl-phenol (C6–C13) side. The overall conformation of the title compound and HIXGAW are very nearly planar and the other two (RICFEP and RICFEP01) are planar. A notable difference relates to the substitution on the keto side. The respective dihedral angles in the studied compound and in HIXGAW are in the range of 5.49–24.65°.

5. Hirshfeld surface analysis

Crystal Explorer 21 (Spackman *et al.*, 2021) was used to calculate the Hirshfeld surfaces to obtain further insight into the intermolecular interactions in the crystal structure of the title compound. The three-dimensional Hirshfeld surfaces

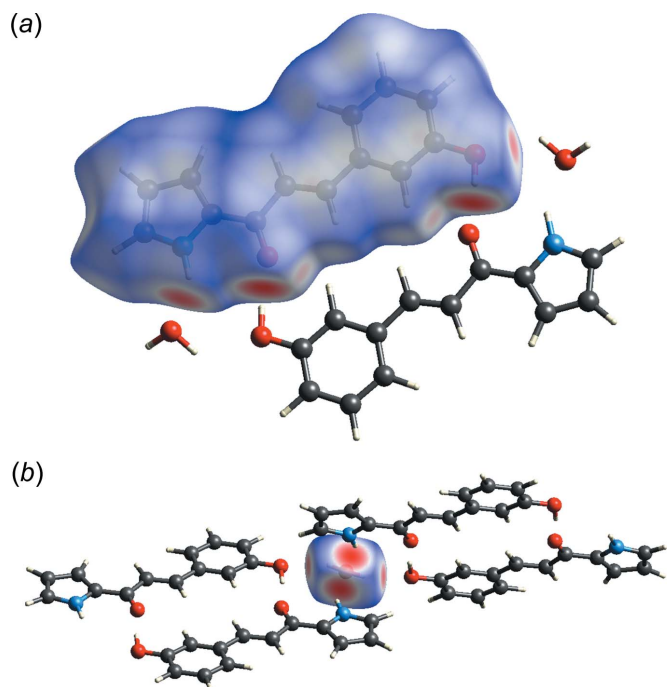


Figure 3
Three-dimensional Hirshfeld surfaces plotted over d_{norm} in the range -0.667 to 1.118 a.u. of (a) compound **3HPPP** and (b) the water molecule, generated with *Crystal Explorer* (Spackman *et al.*, 2021).

plotted over d_{norm} ranging from -0.667 to 1.118 a.u. are shown in Fig. 3. For compound **3HPPP** (Fig. 3a), the most prominent interactions in the crystal packing are the hydrogen bonds, which are represented by four bright-red spots on the mapped d_{norm} surface. The bright-red spots around O1 and O2 correspond to the hydrogen bonding between hydroxyl and carbonyl/keto functional groups of two molecules of **3HPPP**. The other two bright-red spots are due to hydrogen bonding between the pyrrole-N–H functional group and the water molecule, and between the water molecule and the hydroxyl group of **3HPPP**. In addition to these four spots, two faint-red spots appear around O1 and H13, representing the non-classical hydrogen-bond interaction of an aromatic C–H and the carbonyl/keto functional group. The intensities of all these red spots indicate the relative strengths of the interactions, as well

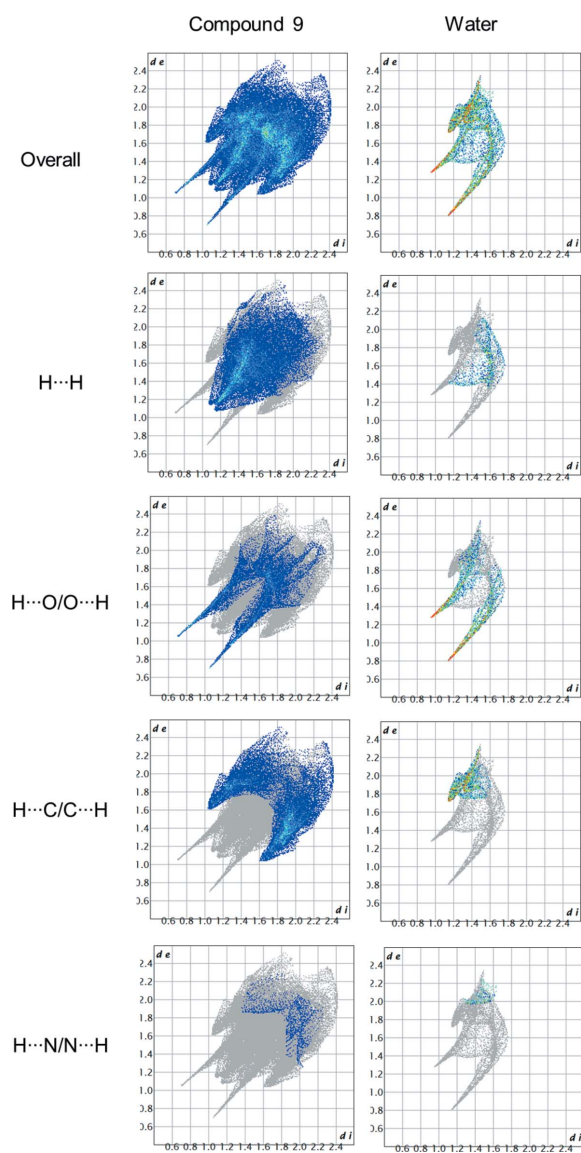


Figure 4
Overall two-dimensional fingerprint plots for compound **3HPPP** and the water molecule together with those delineated into H...H, H...O/O...H, H...C/C...H and H...N/N...H interactions, generated with *Crystal Explorer* (Spackman *et al.*, 2021).

as the distances of the contacts. The d_{norm} Hirshfeld surface for the water molecules present in the crystal lattice was also calculated and mapped (Fig. 3*b*). Four bright-red spots are observed, which are due to the pyrrole-to-water and water-to-hydroxyl hydrogen bonds and are thereby mirrors of the interactions involving water described above.

The overall two-dimensional fingerprint plots of both molecules, water and **3HPPP**, and those delineated into H...H, H...O/O...H, H...C/C...H and H...N/N...H interactions are shown in Fig. 4, while the percentage contributions are listed in Table 2. The two-dimensional fingerprint plots for compound **3HPPP** show that H...H and H...C/C...H are the most significant interatomic interactions in the crystal packing, contributing 40.9 and 32.4%, respectively, to the Hirshfeld surface. The H...O/O...H (19.4%) and other minor contacts (H...N/N...H = 2.0%) further contribute to the Hirshfeld surfaces. On the other hand, the most prominent interatomic contacts for the water molecule are H...O/O...H, as expected, with a 48.7% contribution while H...H and H...C/C...H contacts contribute 16.2 and 29.8%, respectively.

6. Synthesis and crystallization

The 3-hydroxypyrrolylated chalcone **3HPPP** was synthesized by a Claisen–Schmidt condensation reaction between 2-acetylpyrrole (2 mmol) and 3-hydroxybenzaldehyde (2 mmol) under ethanolic (10 ml) conditions. The resulting mixture was stirred for 5 min followed by the dropwise addition of 3 ml of a 40% aqueous NaOH solution (Fig. 5). The mixture was stirred overnight at room temperature. After the reaction was essentially complete, it was quenched by pouring the resultant solution onto crushed ice and extraction with ethyl acetate (3 × 10 ml). The organic layer was washed with distilled water (3 × 10 ml), filtered, dried over anhydrous MgSO₄ and concentrated *in vacuo*. Finally, the collected crudes were purified by gravity column chromatography using hexane:ethyl acetate (ratio of 7:3) as solvent system. Multiple spectroscopic analyses confirmed the chemical structure (Mohd Faudzi *et al.*, 2020). The obtained pure **3HPPP** was then recrystallized by slow evaporation of an ethanol solution, giving crystals suitable for X-ray diffraction analysis.

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. The hydrogen atoms bound to oxygen or nitrogen were found in difference maps and refined freely. The carbon-bound hydrogen atoms, which are all

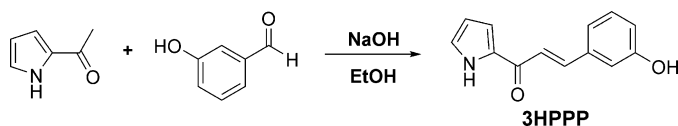


Figure 5
Synthetic route towards 3-(3-hydroxyphenyl)-1-(1*H*-pyrrol-2-yl)prop-2-en-1-one (**3HPPP**).

Table 3
Experimental details.

Crystal data	
Chemical formula	2C ₁₃ H ₁₁ NO ₂ ·H ₂ O
M_r	444.47
Crystal system, space group	Monoclinic, <i>P2/c</i>
Temperature (K)	100
a, b, c (Å)	11.9096 (1), 5.5836 (1), 16.8121 (2)
β (°)	105.356 (1)
V (Å ³)	1078.07 (3)
Z	2
Radiation type	Cu $K\alpha$
μ (mm ⁻¹)	0.78
Crystal size (mm)	0.18 × 0.17 × 0.13
Data collection	
Diffractometer	XtaLAB Synergy, Dualflex, AtlasS2
Absorption correction	Gaussian (<i>CrysAlis PRO</i> ; Rigaku OD, 2021)
$T_{\text{min}}, T_{\text{max}}$	0.676, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	13888, 2221, 2067
R_{int}	0.028
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.627
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.034, 0.095, 1.04
No. of reflections	2221
No. of parameters	163
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	0.30, -0.19

Computer programs: *CrysAlis PRO* (Rigaku OD, 2021), *SHELXT2018/2* (Sheldrick, 2015*a*), *SHELXL2018/3* (Sheldrick, 2015*b*), *OLEX2* 1.3 (Dolomanov *et al.*, 2009) and *publCIF* (Westrip, 2010).

aromatic, were geometrically placed and refined using a riding model with C—H = 0.95 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

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Computing details

Data collection: *CrysAlis PRO* 1.171.41.121a (Rigaku OD, 2021); cell refinement: *CrysAlis PRO* 1.171.41.121a (Rigaku OD, 2021); data reduction: *CrysAlis PRO* 1.171.41.121a (Rigaku OD, 2021); program(s) used to solve structure: *SHELXT2018/2* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2018/3* (Sheldrick, 2015b); molecular graphics: Olex2 1.3 (Dolomanov *et al.*, 2009); software used to prepare material for publication: *publCIF* (Westrip, 2010).

3-(3-Hydroxyphenyl)-1-(1H-pyrrol-2-yl)prop-2-en-1-one hemihydrate

Crystal data

2C₁₃H₁₁NO₂·H₂O
M_r = 444.47
 Monoclinic, *P2/c*
a = 11.9096 (1) Å
b = 5.5836 (1) Å
c = 16.8121 (2) Å
 β = 105.356 (1)°
V = 1078.07 (3) Å³
Z = 2

F(000) = 468
D_x = 1.369 Mg m⁻³
 Cu *K*α radiation, λ = 1.54184 Å
 Cell parameters from 9119 reflections
 θ = 3.8–76.1°
 μ = 0.78 mm⁻¹
T = 100 K
 Prism, colourless
 0.18 × 0.17 × 0.13 mm

Data collection

XtaLAB Synergy, Dualflex, AtlasS2
 diffractometer
 Radiation source: micro-focus sealed X-ray tube
 ω scans
 Absorption correction: gaussian
 (CrysAlisPro; Rigaku OD, 2021)
T_{min} = 0.676, *T_{max}* = 1.000
 13888 measured reflections

2221 independent reflections
 2067 reflections with *I* > 2σ(*I*)
R_{int} = 0.028
 θ_{\max} = 75.2°, θ_{\min} = 3.9°
h = -14→14
k = -6→7
l = -18→21

Refinement

Refinement on *F*²
 Least-squares matrix: full
R[*F*² > 2σ(*F*²)] = 0.034
wR(*F*²) = 0.095
S = 1.04
 2221 reflections
 163 parameters

0 restraints
 Primary atom site location: dual
 Secondary atom site location: difference Fourier
 map
 Hydrogen site location: mixed
 H atoms treated by a mixture of independent
 and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0512P)^2 + 0.3933P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

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

$$\Delta\rho_{\max} = 0.30 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.19 \text{ e } \text{\AA}^{-3}$$

Extinction correction: *SHELXL2018/3*

(Sheldrick, 2015b),

$$F_c^* = kFc[1 + 0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$$

Extinction coefficient: 0.0039 (5)

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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.27900 (7)	0.42189 (15)	0.33951 (5)	0.0268 (2)
O2	0.81284 (7)	0.95369 (15)	0.59533 (5)	0.0215 (2)
O3	0.000000	0.0526 (2)	0.250000	0.0208 (3)
N1	0.10566 (8)	0.45548 (17)	0.19188 (5)	0.0186 (2)
C1	0.17738 (9)	0.7925 (2)	0.15408 (6)	0.0178 (2)
H1A	0.225141	0.928386	0.153517	0.021*
C2	0.07695 (9)	0.7278 (2)	0.09255 (6)	0.0222 (3)
H2A	0.044033	0.812012	0.042726	0.027*
C3	0.03512 (9)	0.5190 (2)	0.11809 (6)	0.0222 (3)
H3	-0.032172	0.434067	0.088590	0.027*
C4	0.19382 (9)	0.62052 (19)	0.21594 (6)	0.0159 (2)
C5	0.28203 (9)	0.59293 (19)	0.29291 (6)	0.0177 (2)
C6	0.37555 (9)	0.7736 (2)	0.31381 (6)	0.0179 (2)
H6	0.376212	0.901776	0.276763	0.021*
C7	0.45937 (9)	0.75864 (19)	0.38443 (6)	0.0173 (2)
H7	0.455306	0.624717	0.418413	0.021*
C8	0.55672 (9)	0.92326 (19)	0.41588 (6)	0.0155 (2)
C9	0.56928 (9)	1.14020 (19)	0.37719 (6)	0.0174 (2)
H9	0.513693	1.186081	0.327786	0.021*
C10	0.66350 (9)	1.28752 (19)	0.41156 (6)	0.0184 (2)
H10	0.672229	1.433834	0.384975	0.022*
C11	0.74552 (9)	1.22472 (19)	0.48433 (6)	0.0181 (2)
H11	0.809769	1.326921	0.507080	0.022*
C12	0.73238 (9)	1.0110 (2)	0.52331 (6)	0.0166 (2)
C13	0.63891 (9)	0.86102 (19)	0.48899 (6)	0.0161 (2)
H13	0.630823	0.714363	0.515581	0.019*
H2O	0.7856 (15)	0.832 (3)	0.6202 (11)	0.050 (5)*
H1N	0.0948 (13)	0.324 (3)	0.2186 (9)	0.034 (4)*
H3O	-0.0335 (16)	-0.039 (4)	0.2091 (11)	0.062 (6)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0251 (4)	0.0272 (5)	0.0228 (4)	-0.0081 (3)	-0.0032 (3)	0.0089 (3)

O2	0.0178 (4)	0.0239 (4)	0.0194 (4)	-0.0044 (3)	-0.0012 (3)	0.0032 (3)
O3	0.0218 (5)	0.0193 (6)	0.0208 (5)	0.000	0.0046 (4)	0.000
N1	0.0170 (4)	0.0199 (5)	0.0176 (4)	-0.0025 (4)	0.0025 (3)	0.0010 (4)
C1	0.0176 (5)	0.0187 (5)	0.0171 (5)	0.0015 (4)	0.0044 (4)	0.0011 (4)
C2	0.0214 (5)	0.0256 (6)	0.0167 (5)	0.0024 (4)	0.0000 (4)	0.0025 (4)
C3	0.0172 (5)	0.0277 (6)	0.0182 (5)	-0.0011 (4)	-0.0015 (4)	-0.0008 (4)
C4	0.0145 (5)	0.0173 (5)	0.0163 (5)	-0.0006 (4)	0.0045 (4)	-0.0010 (4)
C5	0.0173 (5)	0.0189 (5)	0.0167 (5)	0.0002 (4)	0.0043 (4)	0.0013 (4)
C6	0.0183 (5)	0.0185 (5)	0.0166 (5)	-0.0009 (4)	0.0040 (4)	0.0019 (4)
C7	0.0176 (5)	0.0170 (5)	0.0176 (5)	0.0003 (4)	0.0051 (4)	0.0014 (4)
C8	0.0153 (5)	0.0165 (5)	0.0156 (5)	0.0011 (4)	0.0056 (4)	-0.0016 (4)
C9	0.0190 (5)	0.0180 (5)	0.0150 (5)	0.0017 (4)	0.0043 (4)	0.0002 (4)
C10	0.0232 (5)	0.0144 (5)	0.0191 (5)	-0.0002 (4)	0.0083 (4)	0.0007 (4)
C11	0.0176 (5)	0.0176 (5)	0.0195 (5)	-0.0038 (4)	0.0055 (4)	-0.0030 (4)
C12	0.0150 (5)	0.0196 (5)	0.0147 (5)	0.0017 (4)	0.0034 (4)	-0.0014 (4)
C13	0.0172 (5)	0.0147 (5)	0.0170 (5)	0.0005 (4)	0.0059 (4)	0.0008 (4)

Geometric parameters (Å, °)

O1—C5	1.2417 (13)	C5—C6	1.4748 (14)
O2—C12	1.3683 (12)	C6—C7	1.3362 (14)
O2—H2O	0.901 (19)	C6—H6	0.9500
O3—H3O	0.864 (18)	C7—C8	1.4642 (14)
O3—H3O ⁱ	0.864 (18)	C7—H7	0.9500
N1—C3	1.3484 (13)	C8—C13	1.3973 (14)
N1—C4	1.3749 (13)	C8—C9	1.4015 (15)
N1—H1N	0.888 (17)	C9—C10	1.3879 (15)
C1—C4	1.3906 (14)	C9—H9	0.9500
C1—C2	1.4056 (14)	C10—C11	1.3932 (14)
C1—H1A	0.9500	C10—H10	0.9500
C2—C3	1.3804 (17)	C11—C12	1.3902 (15)
C2—H2A	0.9500	C11—H11	0.9500
C3—H3	0.9500	C12—C13	1.3903 (15)
C4—C5	1.4429 (14)	C13—H13	0.9500
C12—O2—H2O	109.4 (11)	C5—C6—H6	119.7
H3O—O3—H3O ⁱ	108 (3)	C6—C7—C8	127.97 (10)
C3—N1—C4	109.61 (9)	C6—C7—H7	116.0
C3—N1—H1N	122.9 (10)	C8—C7—H7	116.0
C4—N1—H1N	127.4 (10)	C13—C8—C9	119.15 (9)
C4—C1—C2	107.27 (10)	C13—C8—C7	117.69 (9)
C4—C1—H1A	126.4	C9—C8—C7	123.14 (9)
C2—C1—H1A	126.4	C10—C9—C8	119.53 (9)
C3—C2—C1	107.15 (9)	C10—C9—H9	120.2
C3—C2—H2A	126.4	C8—C9—H9	120.2
C1—C2—H2A	126.4	C9—C10—C11	121.19 (10)
N1—C3—C2	108.67 (10)	C9—C10—H10	119.4
N1—C3—H3	125.7	C11—C10—H10	119.4

C2—C3—H3	125.7	C12—C11—C10	119.33 (10)
N1—C4—C1	107.30 (9)	C12—C11—H11	120.3
N1—C4—C5	120.68 (9)	C10—C11—H11	120.3
C1—C4—C5	132.01 (10)	O2—C12—C11	118.55 (9)
O1—C5—C4	120.80 (10)	O2—C12—C13	121.51 (10)
O1—C5—C6	121.48 (9)	C11—C12—C13	119.94 (9)
C4—C5—C6	117.73 (9)	C12—C13—C8	120.84 (10)
C7—C6—C5	120.54 (10)	C12—C13—H13	119.6
C7—C6—H6	119.7	C8—C13—H13	119.6
C4—C1—C2—C3	-0.20 (12)	C5—C6—C7—C8	-178.53 (9)
C4—N1—C3—C2	0.25 (13)	C6—C7—C8—C13	-175.38 (10)
C1—C2—C3—N1	-0.03 (13)	C6—C7—C8—C9	6.06 (17)
C3—N1—C4—C1	-0.38 (12)	C13—C8—C9—C10	0.72 (14)
C3—N1—C4—C5	-179.58 (9)	C7—C8—C9—C10	179.26 (9)
C2—C1—C4—N1	0.35 (12)	C8—C9—C10—C11	-0.54 (15)
C2—C1—C4—C5	179.42 (11)	C9—C10—C11—C12	-0.24 (16)
N1—C4—C5—O1	-1.17 (16)	C10—C11—C12—O2	-179.10 (9)
C1—C4—C5—O1	179.86 (11)	C10—C11—C12—C13	0.84 (15)
N1—C4—C5—C6	178.55 (9)	O2—C12—C13—C8	179.27 (9)
C1—C4—C5—C6	-0.42 (17)	C11—C12—C13—C8	-0.67 (15)
O1—C5—C6—C7	-0.66 (16)	C9—C8—C13—C12	-0.12 (15)
C4—C5—C6—C7	179.62 (10)	C7—C8—C13—C12	-178.74 (9)

Symmetry code: (i) $-x, y, -z+1/2$.

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

<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>
O2—H2O \cdots O1 ⁱⁱ	0.901 (19)	1.828 (19)	2.7257 (11)	174.2 (16)
N1—H1N \cdots O3	0.888 (17)	2.041 (17)	2.8722 (13)	155.4 (14)
C13—H13 \cdots O1 ⁱⁱ	0.95	2.51	3.2050 (13)	130
O3—H3O \cdots O2 ⁱⁱⁱ	0.864 (18)	2.320 (18)	2.9430 (7)	129.2 (16)

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