

Crystal structure and DFT study of 8-hydroxy-1,2,3,5,6,7-hexahydropyrido[3,2,1-*ij*]quinoline-9-carbaldehyde

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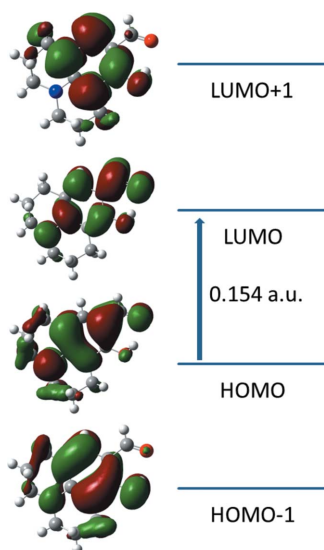
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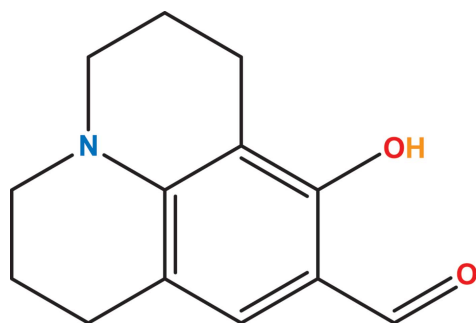
In the title compound, C₁₃H₁₅NO₂, the fused non-aromatic rings of the julolidine moiety adopt envelope conformations. The hydroxy group forms an intramolecular hydrogen bond to the aldehyde O atom, generating an *S*(6) ring motif. Weak intermolecular C—H...O hydrogen bonds help to stabilize the crystal structure. Density functional theory (DFT) optimized structures at the B3LYP/6–311 G(d,p) level are compared with the experimentally determined molecular structure in the solid state.

1. Chemical context

Julolidine is chemically an aniline derivative with two *N*-alkyl substituents forming rings back to the aromatic ring; the fused rings lock the nitrogen lone-pair of electrons into conjugation with the aromatic ring leading to unusual reactivity. The presence of the julolidine ring system in some molecules makes them useful for chromogenic naked-eye detection of copper, zinc, iron and aluminium ions as well as fluoride ions (Wang *et al.*, 2013; Choi *et al.*, 2015; Kim *et al.*, 2015; Jo *et al.*, 2015). Julolidine dyes exhibit excited-state intramolecular proton transfer (Nano *et al.*, 2015). Compounds containing julolidine rings are also used as fluorescent probes for the measurement of cell-membrane viscosity. Julolidine-based materials are also used as red emitters in OLEDs when linked to dicyanomethylpyran modules (Lee, *et al.*, 2012). The julolidine unit plays an important role as it has strong electronic-donating properties for chelating (Nano, *et al.*, 2013). Julolidine malononitrile acts as a ‘push–pull’ molecule with large hyperpolarizability and is used as a model system for understanding the non-linear optical properties of molecules (Mennucci *et al.*, 2009).

There are many reports in the literature on julolidine-based Schiff bases and their applications as sensors for metal ions (Park *et al.*, 2014; Lee *et al.*, 2014; Kim *et al.*, 2016). The present work is a part of an ongoing structural study of Schiff bases based on the julolidine ring system (Faizi *et al.*, 2016, 2017). We report here the crystal structure and DFT computational calculation of the title julolidine compound (I). The results of calculations by density functional theory (DFT) on (I) carried out at the B3LYP/6–311 G(d,p) level are compared with the experimentally determined molecular structure in the solid state.





2. Structural commentary

The molecular structure of the title compound (I) is shown in Fig. 1. The π -conjugated system is nearly planar, with a $2.5(1)^\circ$ twist between the aromatic and aldehyde groups. The julolidine ring system comprises three fused rings and one locked nitrogen atom. The C1—O1 and C3—O2 bond lengths are of 1.231(3) and 1.345(3) Å, respectively, indicate double- and single-bond character for these bonds. The two fused non-aromatic rings of the julolidine moiety adopt slightly distorted envelope conformations with atoms C9 and C12 displaced from the plane through the remaining ring atoms by 0.654(2) and 0.648(2) Å, respectively. The intramolecular O2—H2···O1 hydrogen bond forms an *S*(6) ring motif (Fig. 1 and Table 1) between the phenol and aldehyde groups. Such an intramolecular hydrogen bond is common in salicylaldehyde derivatives, and the metrical parameters are comparable to those for related structures such as hydroxybenzaldehyde (Kirchner *et al.*, 2011).

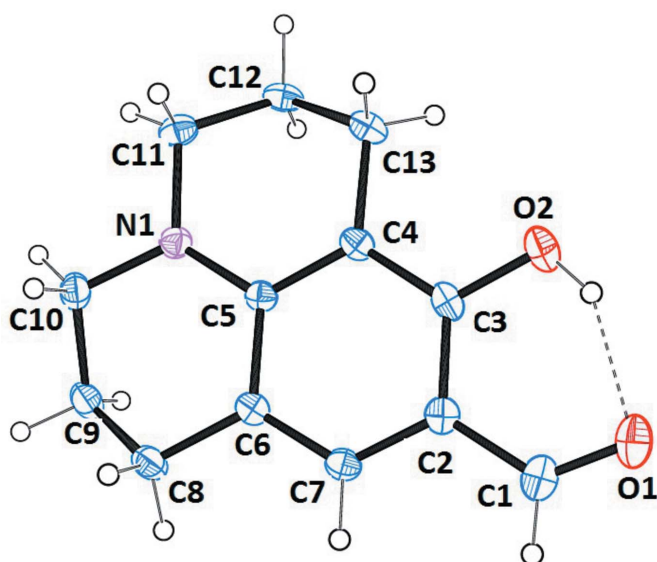


Figure 1
The molecular structure of the title compound, with the atom labelling. Displacement ellipsoids are drawn at the 30% probability level. The intramolecular O—H···O hydrogen bond is shown as a dashed line (see Table 1).

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—H2···O1	0.82	1.89	2.621(2)	148
C9—H9A···O2 ⁱ	0.97	2.50	3.324(3)	143
C9—H9B···O1 ⁱⁱ	0.97	2.55	3.438(3)	152
O2—H2···O1	0.82	1.89	2.621(2)	148
C9—H9A···O2 ⁱ	0.97	2.50	3.324(3)	143
C9—H9B···O1 ⁱⁱ	0.97	2.55	3.438(3)	152

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

3. Supramolecular features

In the crystal, molecules are linked by C—H···O hydrogen bonds, forming an *A*—*B*—*A*—*B*—*A*—*B* arrangement through the inversion centre and propagating along the *c*-axis direction (see Fig. 2 and Table 1). There are no other significant intermolecular contacts present in the molecule.

4. DFT study

The DFT quantum-chemical calculations were performed at the B3LYP/6–311 G(d,p) level (Becke, 1993; Lee *et al.*, 1988) as implemented in *GAUSSIAN09* (Frisch *et al.*, 2009). DFT structure optimization of (I) was performed starting from the X-ray geometry and the values compared with experimental values (see Table 2). From these results we can conclude that basis set 6–311 G(d,p) is well suited in its approach to the experimental data.

The DFT study of (I) shows that the HOMO and LUMO are localized in the plane extending from the whole julolidine ring to the salicylaldehyde ring. The electron distribution of the HOMO-1, HOMO, LUMO and the LUMO+1 energy levels are shown in Fig. 3. The molecular orbital of HOMO

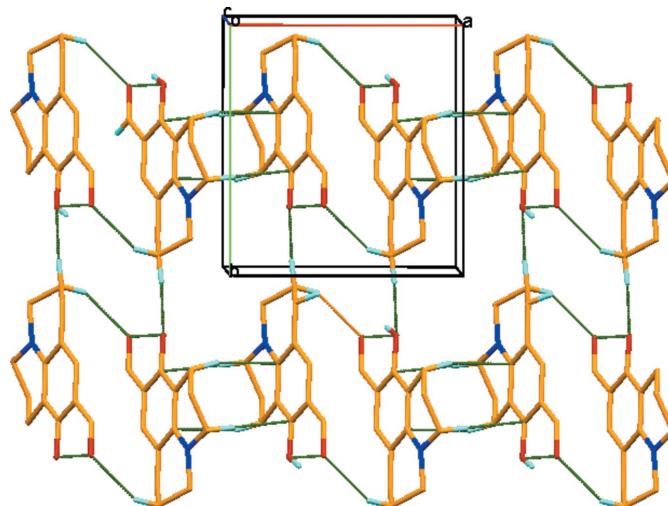


Figure 2
A view of the *A*—*B*—*A*—*B*—*A*—*B* arrangement in the crystal structure of the title compound. The hydrogen bonds are shown as dashed lines (see Table 1). For clarity, only the H atoms involved in hydrogen bonding have been included. The packing structure exhibits $R_2^2(16)$ and $R_4^4(10)$ graph-set motifs.

Table 2

Comparison of selected geometric data for (I) (Å, °) from calculated (DFT) and X-ray data.

Bonds	X-ray	B3LYP/6-311G(d,p)
C1–O1	1.231 (3)	1.231
C3–O2	1.345 (3)	1.345
C1–C2	1.431 (3)	1.431
N1–C5	1.381 (2)	1.381
O1–C1–C2	126.2 (2)	126.22
C1–C2–C3	121.34 (18)	120.25
C11–N1–C10	116.83 (15)	116.81

contain both σ and π character whereas HOMO-1 is dominated by π -orbital density. The LUMO is mainly composed of σ density while LUMO+1 has both σ and π electronic density. The HOMO–LUMO gap was found to be 0.154 a.u. and the frontier molecular orbital energies, E_{HOMO} and E_{LUMO} were -0.19624 and -0.04201 a.u., respectively.

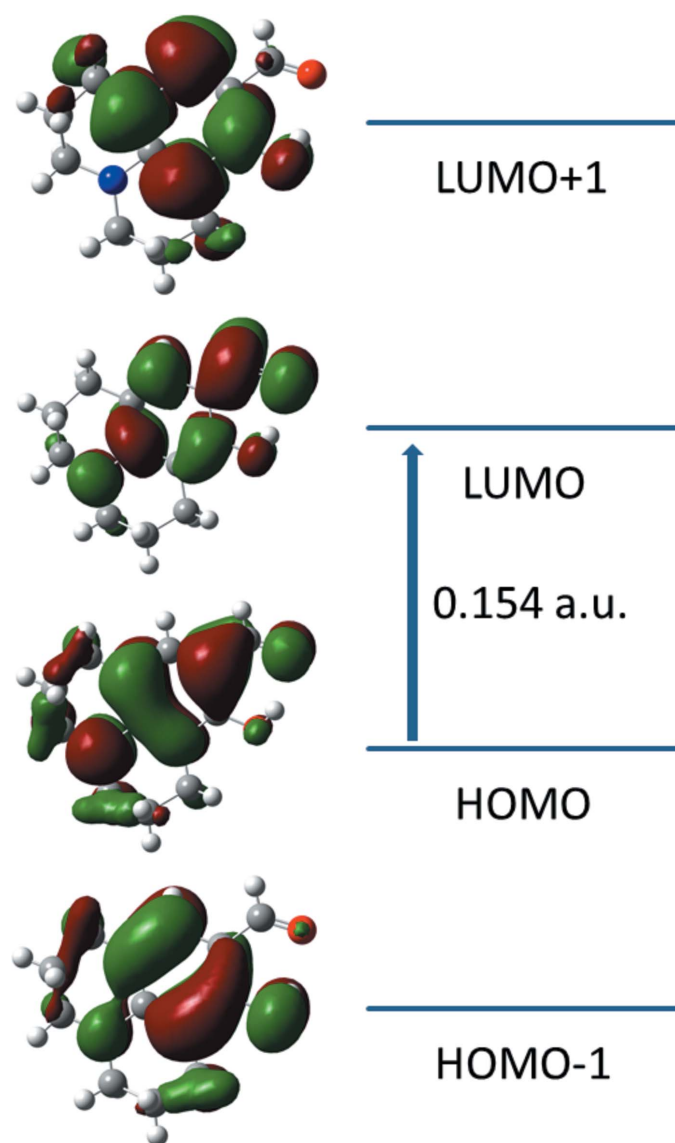


Figure 3
Electron distribution of the HOMO-1, HOMO, LUMO and the LUMO+1 energy levels for (I).

Table 3

Experimental details.

Crystal data	
Chemical formula	$\text{C}_{13}\text{H}_{15}\text{NO}_2$
M_r	217.26
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	100
a, b, c (Å)	8.546 (3), 9.137 (3), 13.662 (4)
β (°)	95.984 (6)
V (Å ³)	1061.0 (6)
Z	4
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	0.09
Crystal size (mm)	0.18 × 0.15 × 0.11
Data collection	
Diffractometer	Bruker SMART CCD area detector
Absorption correction	Multi-scan (<i>SADABS</i> ; Sheldrick, 2004)
$T_{\text{min}}, T_{\text{max}}$	0.985, 0.991
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	5787, 2083, 1530
R_{int}	0.026
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.617
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.066, 0.231, 1.11
No. of reflections	2083
No. of parameters	145
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	0.64, -0.27

Computer programs: *SMART* and *SAINT* (Bruker, 2003), *SHELXTL* and *SHELXL97* (Sheldrick, 2008).

5. Database survey

A search of the Cambridge Structural Database (CSD, Version 5.37, update May 2016; Groom *et al.*, 2016) gave 121 hits for the julolidine moiety. Of these, six have an OH group in position 8, and four also have a C=N group in position 1. The very similar compound 2-[(2,3,6,7-tetrahydro-1*H*,5*H*-benzo[*ij*]-quinolizin-9-yl)methylene]propanedinitrile (II) reported by Liang *et al.* (2009) has the aldehyde group in (I) replaced by dicyanovinyl groups and the hydroxy group replaced by hydrogen. The N1–C5 bond length [1.381 (2) Å] in the title compound is longer than in (II) [1.365 (3) Å] due to conjugation with dicyanovinyl group. In the julolidine-1,6-dione compound reported by Wu *et al.* (2007), the N atom of the julolidine moiety lies approximately in the plane of the benzene ring with a deviation of 0.023 (2) Å, similar to that in title compound [0.043 (2) Å], as might be expected for the maximum conjugation normally found for N-atom substituents on benzene rings.

6. Crystallization

2,3,6,7-Tetrahydro-8-hydroxy-1*H*,5*H*-benzo[*ij*]quinolizine-9-carboxaldehyde was purchased from Sigma Aldrich and crystallized by slow evaporation of methanol solution over a period of 2-3 days to yield quality crystal suitable for X-ray data collection.

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. All H atoms were located from difference-Fourier maps but in the final cycles of refinement they were included in calculated positions and treated as riding atoms: O–H = 0.84 Å, C–H = 0.93–0.98 Å with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$ and $1.2U_{\text{eq}}(\text{C})$ for other H atoms.

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Crystal structure and DFT study of 8-hydroxy-1,2,3,5,6,7-hexahydro-pyrido[3,2,1-*ij*]quinoline-9-carbaldehyde

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Computing details

Data collection: *SMART* (Bruker, 2003); cell refinement: *SMART* (Bruker, 2003); data reduction: *SAINTE* (Bruker, 2003); program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

8-Hydroxy-1,2,3,5,6,7-hexahydropyrido[3,2,1-*ij*]quinoline-9-carbaldehyde

Crystal data

C₁₃H₁₅NO₂

M_r = 217.26

Monoclinic, *P2₁/c*

a = 8.546 (3) Å

b = 9.137 (3) Å

c = 13.662 (4) Å

β = 95.984 (6)°

V = 1061.0 (6) Å³

Z = 4

F(000) = 464

D_x = 1.360 Mg m⁻³

Mo *K*α radiation, λ = 0.71073 Å

Cell parameters from 1494 reflections

θ = 2.4–28.1°

μ = 0.09 mm⁻¹

T = 100 K

Needle, colorless

0.18 × 0.15 × 0.11 mm

Data collection

Bruker SMART CCD area detector
diffractometer

Radiation source: sealed tube

Graphite monochromator

phi and ω scans

Absorption correction: multi-scan
(SADABS; Sheldrick, 2004)

T_{min} = 0.985, *T_{max}* = 0.991

5787 measured reflections

2083 independent reflections

1530 reflections with *I* > 2σ(*I*)

R_{int} = 0.026

θ_{\max} = 26.0°, θ_{\min} = 2.4°

h = -10→10

k = -8→11

l = -16→16

Refinement

Refinement on *F*²

Least-squares matrix: full

R[*F*² > 2σ(*F*²)] = 0.066

wR(*F*²) = 0.231

S = 1.11

2083 reflections

145 parameters

0 restraints

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

w = 1/[σ²(*F_o*²) + (0.1465*P*)² + 0.0857*P*]

where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} < 0.001

Δρ_{max} = 0.64 e Å⁻³

Δρ_{min} = -0.27 e Å⁻³

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)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
O2	0.73084 (18)	0.25645 (16)	0.53899 (11)	0.0398 (5)
H2	0.691533	0.226583	0.587471	0.060*
O1	0.58740 (18)	0.27075 (18)	0.69921 (11)	0.0460 (5)
N1	0.83012 (18)	0.7058 (2)	0.37861 (11)	0.0288 (5)
C5	0.7743 (2)	0.6300 (2)	0.45521 (12)	0.0242 (5)
C4	0.7801 (2)	0.4768 (2)	0.45803 (13)	0.0269 (5)
C6	0.7080 (2)	0.7115 (2)	0.53120 (14)	0.0277 (5)
C2	0.6517 (2)	0.4816 (2)	0.60979 (14)	0.0282 (5)
C7	0.6468 (2)	0.6333 (2)	0.60434 (14)	0.0282 (5)
H7	0.599815	0.684412	0.652391	0.034*
C3	0.7204 (2)	0.4032 (2)	0.53505 (14)	0.0282 (5)
C10	0.8409 (2)	0.8646 (2)	0.37928 (14)	0.0333 (6)
H10A	0.840281	0.899757	0.312243	0.040*
H10B	0.939673	0.893952	0.415420	0.040*
C11	0.9103 (2)	0.6288 (2)	0.30450 (15)	0.0330 (6)
H11A	1.020944	0.618318	0.327631	0.040*
H11B	0.902214	0.685601	0.244223	0.040*
C13	0.8464 (2)	0.3888 (2)	0.37783 (14)	0.0336 (6)
H13A	0.786287	0.299427	0.365792	0.040*
H13B	0.954748	0.362366	0.398627	0.040*
C8	0.7061 (3)	0.8758 (2)	0.52940 (15)	0.0359 (6)
H8A	0.797720	0.912690	0.569753	0.043*
H8B	0.613101	0.910814	0.557226	0.043*
C1	0.5867 (2)	0.4043 (3)	0.68718 (15)	0.0358 (6)
H1	0.539410	0.460267	0.732734	0.043*
C12	0.8388 (2)	0.4791 (2)	0.28373 (14)	0.0330 (6)
H12A	0.895351	0.428934	0.235680	0.040*
H12B	0.730055	0.489689	0.256334	0.040*
C9	0.7061 (3)	0.9339 (2)	0.42599 (15)	0.0389 (6)
H9A	0.718103	1.039438	0.427433	0.047*
H9B	0.607130	0.910495	0.387813	0.047*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O2	0.0514 (11)	0.0255 (10)	0.0406 (9)	−0.0001 (6)	−0.0050 (7)	0.0021 (6)
O1	0.0469 (11)	0.0421 (11)	0.0470 (10)	−0.0075 (7)	−0.0054 (7)	0.0141 (7)
N1	0.0304 (9)	0.0301 (11)	0.0264 (9)	−0.0015 (7)	0.0044 (7)	−0.0016 (6)
C5	0.0233 (10)	0.0269 (13)	0.0217 (10)	−0.0009 (7)	−0.0011 (8)	−0.0033 (7)

C4	0.0289 (12)	0.0273 (12)	0.0233 (11)	0.0013 (7)	-0.0034 (8)	-0.0030 (7)
C6	0.0278 (11)	0.0275 (12)	0.0270 (10)	0.0021 (8)	-0.0007 (8)	-0.0016 (8)
C2	0.0263 (11)	0.0314 (13)	0.0256 (11)	-0.0007 (8)	-0.0041 (8)	0.0020 (8)
C7	0.0289 (11)	0.0307 (13)	0.0244 (10)	0.0010 (8)	-0.0005 (8)	-0.0043 (8)
C3	0.0286 (12)	0.0220 (11)	0.0319 (12)	0.0005 (7)	-0.0069 (9)	-0.0005 (8)
C10	0.0408 (13)	0.0294 (13)	0.0298 (11)	-0.0084 (8)	0.0032 (9)	0.0002 (8)
C11	0.0290 (11)	0.0437 (14)	0.0264 (11)	0.0013 (9)	0.0036 (8)	-0.0040 (9)
C13	0.0372 (13)	0.0295 (13)	0.0332 (12)	0.0069 (8)	-0.0002 (9)	-0.0071 (8)
C8	0.0484 (14)	0.0272 (13)	0.0323 (12)	0.0008 (9)	0.0050 (9)	-0.0049 (8)
C1	0.0291 (12)	0.0411 (14)	0.0353 (12)	-0.0037 (9)	-0.0051 (9)	0.0087 (9)
C12	0.0329 (12)	0.0389 (13)	0.0265 (11)	0.0085 (9)	0.0001 (8)	-0.0099 (8)
C9	0.0543 (14)	0.0252 (12)	0.0368 (12)	-0.0019 (9)	0.0028 (10)	-0.0026 (9)

Geometric parameters (Å, °)

O2—C3	1.345 (3)	C10—H10A	0.9700
O2—H2	0.8200	C10—H10B	0.9700
O1—C1	1.231 (3)	C11—C12	1.512 (3)
N1—C5	1.381 (2)	C11—H11A	0.9700
N1—C10	1.454 (3)	C11—H11B	0.9700
N1—C11	1.461 (2)	C13—C12	1.523 (3)
C5—C4	1.401 (3)	C13—H13A	0.9700
C5—C6	1.441 (3)	C13—H13B	0.9700
C4—C3	1.390 (3)	C8—C9	1.509 (3)
C4—C13	1.516 (3)	C8—H8A	0.9700
C6—C7	1.376 (3)	C8—H8B	0.9700
C6—C8	1.502 (3)	C1—H1	0.9300
C2—C7	1.389 (3)	C12—H12A	0.9700
C2—C3	1.423 (3)	C12—H12B	0.9700
C2—C1	1.431 (3)	C9—H9A	0.9700
C7—H7	0.9300	C9—H9B	0.9700
C10—C9	1.513 (3)		
C3—O2—H2	109.5	N1—C11—H11B	109.5
C5—N1—C10	121.51 (16)	C12—C11—H11B	109.5
C5—N1—C11	120.49 (19)	H11A—C11—H11B	108.1
C10—N1—C11	116.83 (15)	C4—C13—C12	109.65 (17)
N1—C5—C4	120.54 (16)	C4—C13—H13A	109.7
N1—C5—C6	118.7 (2)	C12—C13—H13A	109.7
C4—C5—C6	120.79 (17)	C4—C13—H13B	109.7
C3—C4—C5	119.32 (17)	C12—C13—H13B	109.7
C3—C4—C13	119.00 (19)	H13A—C13—H13B	108.2
C5—C4—C13	121.66 (17)	C6—C8—C9	111.45 (16)
C7—C6—C5	117.6 (2)	C6—C8—H8A	109.3
C7—C6—C8	121.81 (17)	C9—C8—H8A	109.3
C5—C6—C8	120.62 (17)	C6—C8—H8B	109.3
C7—C2—C3	118.46 (18)	C9—C8—H8B	109.3
C7—C2—C1	121.34 (18)	H8A—C8—H8B	108.0

C3—C2—C1	120.2 (2)	O1—C1—C2	126.2 (2)
C6—C7—C2	123.07 (18)	O1—C1—H1	116.9
C6—C7—H7	118.5	C2—C1—H1	116.9
C2—C7—H7	118.5	C11—C12—C13	110.52 (16)
O2—C3—C4	119.02 (17)	C11—C12—H12A	109.5
O2—C3—C2	120.24 (18)	C13—C12—H12A	109.5
C4—C3—C2	120.7 (2)	C11—C12—H12B	109.5
N1—C10—C9	111.68 (16)	C13—C12—H12B	109.5
N1—C10—H10A	109.3	H12A—C12—H12B	108.1
C9—C10—H10A	109.3	C8—C9—C10	108.80 (19)
N1—C10—H10B	109.3	C8—C9—H9A	109.9
C9—C10—H10B	109.3	C10—C9—H9A	109.9
H10A—C10—H10B	107.9	C8—C9—H9B	109.9
N1—C11—C12	110.87 (16)	C10—C9—H9B	109.9
N1—C11—H11A	109.5	H9A—C9—H9B	108.3
C12—C11—H11A	109.5		

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—H2...O1	0.82	1.89	2.621 (2)	148
C9—H9A...O2 ⁱ	0.97	2.50	3.324 (3)	143
C9—H9B...O1 ⁱⁱ	0.97	2.55	3.438 (3)	152
O2—H2...O1	0.82	1.89	2.621 (2)	148
C9—H9A...O2 ⁱ	0.97	2.50	3.324 (3)	143
C9—H9B...O1 ⁱⁱ	0.97	2.55	3.438 (3)	152

Symmetry codes: (i) *x*, *y*+1, *z*; (ii) $-x+1$, $-y+1$, $-z+1$.