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Diethyl 4-(3-ethoxy-4-hydroxyphenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate

N. L. Prasad and Noor Shahina Begum*

Department of Studies in Chemistry, Central College Campus, Bangalore University, Bangalore 560 001, Karnataka, India. *Correspondence e-mail: noorsb@rediffmail.com

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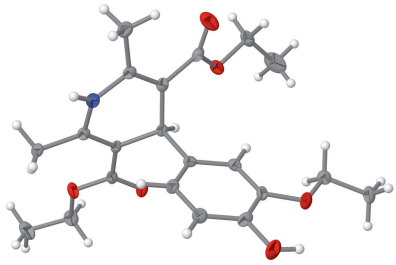
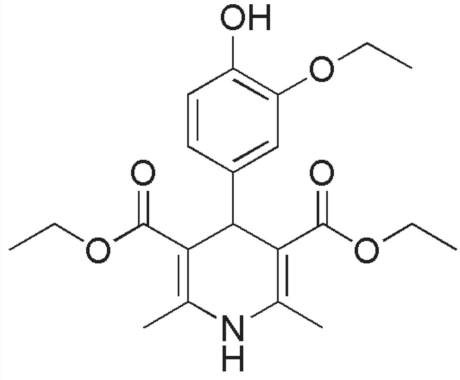
Structural data: full structural data are available from iucrdata.iucr.org

In the title compound, $C_{21}H_{27}NO_6$, the 1,4-dihydropyridine ring adopts a shallow boat conformation, with the 3-ethoxy-4-hydroxyphenyl substituent in an axial orientation [dihedral angle between ring planes = 85.49 (12)°]. In the crystal, N—H···O and O—H···O hydrogen bonds link the molecules into (001) sheets. The packing is consolidated by C—H···O and π–π stacking interactions, which leads to a three-dimensional network.

3D view



Chemical scheme



Structure description

Hantzsch 1,4-dihydropyridines (1,4-DHPs) display a number of biological activities (Reddy *et al.*, 2017). As part of our ongoing studies of 1,4-dihydropyridines (Prasad & Begum, 2016), we report herein the synthesis and crystal structure of the title compound (Fig. 1).

The dihedral angle between 3-ethoxy-4-hydroxyphenyl and dihydroxypyridine rings is 85.49 (12)°. The heterocyclic ring is significantly puckered and adopts a boat conformation, with atoms C2 and C5 displaced by −0.036 (2) and −0.229 (2) Å, respectively, from the mean plane of the other four atoms (C3/C4/C6/N1). The C═O group of the exocyclic ester at atom C5 adopts a *trans* orientation with respect to the C5═C6 double bond [C6═C5—C11═O4 = −173.5 (3)°], whereas the carbonyl group attached to atom C3 adopts a *cis* orientation [C2—C3—C8═O2 = 17.8 (4)°]. This may be due to the presence of the bulky 3-ethoxy-4-hydroxyphenyl substituent. Otherwise, the bond lengths and angles in the title compound are in good agreement with the corresponding data reported for related structures (Bai *et al.*, 2009).

In the crystal, molecules are linked by various types of hydrogen bonds (Table 1). The N1—H1···O4^{i} and O5—H5···O2^{ii} interactions generate (001) sheets incorporating $R_2^2(20)$ loops (Fig. 2). The weak C13—H13*C*···O5^{i} hydrogen bonds form infinite chains along the *c*-axis direction (Fig. 3). In addition, two weak C—H···π interactions involving both rings as acceptors are observed, which connect the layers into a three-dimensional network (Fig. 4).

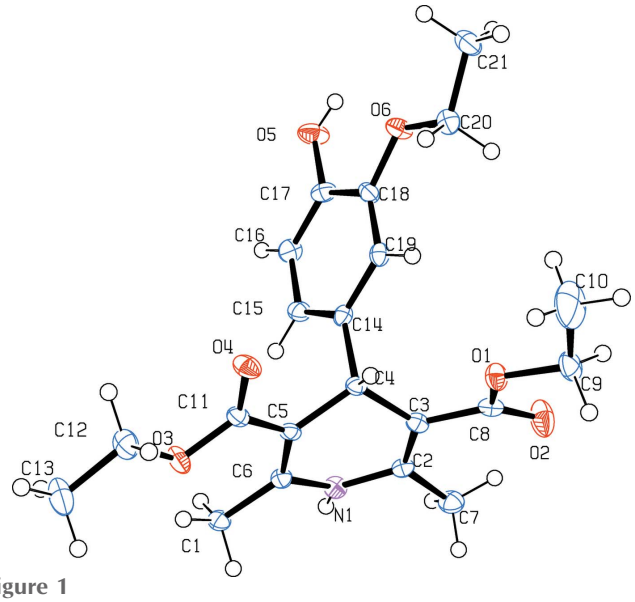


Figure 1
The molecular structure of the title compound, with displacement ellipsoids drawn at the 50% probability level.

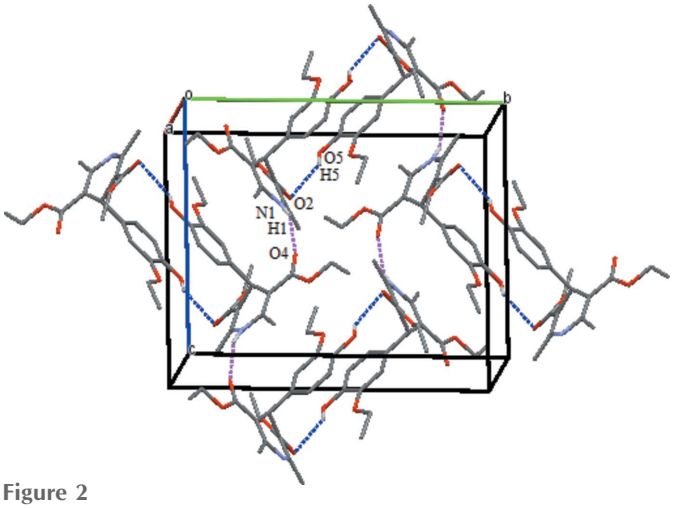


Figure 2
The unit-cell packing of the title compound, showing O—H···O and N—H···O hydrogen-bond interactions with dotted lines. H atoms not involved in hydrogen bonding have been omitted.

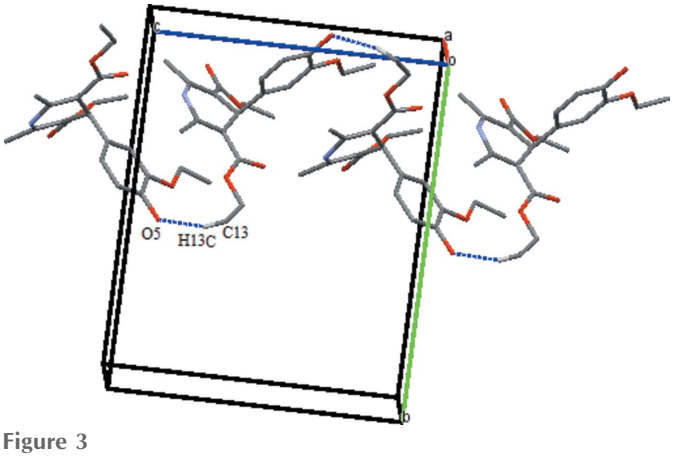


Figure 3
The partial unit-cell packing of the title compound, showing C—H···O hydrogen-bond interactions with dotted lines. H atoms not involved in hydrogen bonding have been omitted.

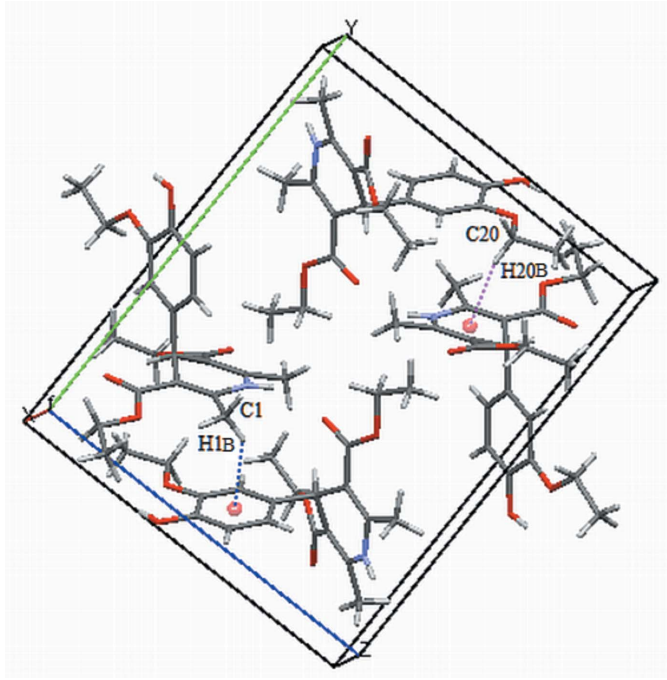


Figure 4
The unit-cell packing, depicting the C—H···π interactions with dotted lines.

Synthesis and crystallization

A mixture of 3-ethoxy-4-hydroxybenzaldehyde (1 mmol), ethyl acetoacetate (2 mmol) and aqueous ammonia (1.5 mmol) was refluxed in dry ethanol (20 mmol) for 12 h (Fig. 5). The progress of the reaction was monitored by thin-layer chromatoghraphy (TLC). Upon completion, the reaction mixture was cooled to room temperature and allowed to stand for 2 d to allow the formation of solid. The resulting solid product was washed with methanol and recrystallized from ethanol to yield colourless blocks (yield 87%; m.p. 423–425 K). TLC information: *n*-hexane–ethyl acetate (8:2), R_F = 0.25. Colourless solid; IR (KBr cm^{-1}): 3496, 3310, 3246, 1686, 1639, 1490, 1192, 1088, 1019, 758, 696; ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.81 (*d*, *J* = 2.5 Hz, 1H), 6.69–6.74 (*m*, 2H), 5.58 (*s*, 1H), 5.49 (*s*, 1H), 4.89 (*s*, 1H), 4.02–4.13 (*m*, 6H), 2.30 (*s*, 6H), 1.39 (*t*, *J* = 7.5 Hz, 3H), 1.21 (*t*, *J* = 7.5 Hz, 6H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 14.7, 15.3, 18.7, 38.6, 59.3, 64.2, 102.7, 113.7, 115.7, 120.1, 140.0, 145.3, 145.5, 146.2, 167.6; MS (*m*/*z*): 388 *M* − 1, 387 *M* − 2 (base peak), 359, 358, 330, 301, 252.

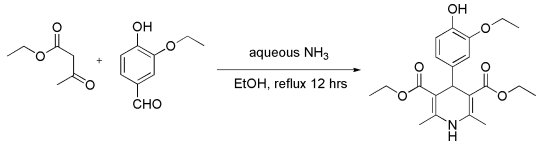


Figure 5
The reaction scheme for the preparation of the title compound.

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

*Cg*1 and *Cg*2 are the centroids of the C14–C19 and N1/C2–C6 rings, respectively.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O4^{i}	0.88	2.11	2.898 (4)	149
O5—H5···O2^{ii}	0.84	2.38	3.035 (5)	135
C13—H13*C*···O5^{i}	0.98	2.62	3.519 (3)	152
C1—H1*B*···*Cg*1^{iii}	0.98	2.69	3.370 (2)	136
C20—H20*B*···*Cg*2^{iii}	0.99	2.66	3.654 (2)	146

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

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. H atoms were placed at calculated positions in the riding-model approximation, with C—H = 0.95, 1.00 and 0.96 Å for aromatic, methyne and methyl H atoms, respectively, and with $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl H atoms and $1.2U_{eq}(C)$ for other H atoms.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{21}H_{27}NO_6$
M_r	389.44
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	100
a, b, c (Å)	9.6064 (16), 15.924 (2), 13.129 (2)
β (°)	96.013 (5)
V (Å^3)	1997.4 (5)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.10
Crystal size (mm)	0.16 × 0.15 × 0.15
Data collection	
Diffractometer	Bruker SMART APEX CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 1998)
T_{min}, T_{max}	0.985, 0.986
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	15758, 3520, 2204
R_{int}	0.087
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.595
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.056, 0.151, 1.02
No. of reflections	3520
No. of parameters	259
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.30, −0.32

Computer programs: *SMART* and *SAINT* (Bruker, 1998), *SHELXS97*, *SHELXL97* and *SHELXTL* (Sheldrick, 2008).

Acknowledgements

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full crystallographic data

IUCrData (2017). **2**, x171022 [https://doi.org/10.1107/S2414314617010227]

Diethyl 4-(3-ethoxy-4-hydroxyphenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate

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Diethyl 4-(3-ethoxy-4-hydroxyphenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate

Crystal data

$C_{21}H_{27}NO_6$
M_r = 389.44
Monoclinic, $P2_1/c$
a = 9.6064 (16) Å
b = 15.924 (2) Å
c = 13.129 (2) Å
β = 96.013 (5)°
V = 1997.4 (5) Å^3
Z = 4
$F(000)$ = 832
D_x = 1.295 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 3520 reflections
θ = 2.0–25.0°
μ = 0.10 mm^{-1}
T = 100 K
Block, colorless
0.16 × 0.15 × 0.15 mm

Data collection

Bruker SMART APEX CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω scans
Absorption correction: multi-scan (SADABS; Bruker, 1998)
T_{min} = 0.985, T_{max} = 0.986
15758 measured reflections
3520 independent reflections
2204 reflections with $I > 2\sigma(I)$
R_{int} = 0.087
θ_{max} = 25.0°, θ_{min} = 2.0°
h = −11→11
k = −17→18
l = −15→15

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.056
$wR(F^2)$ = 0.151
S = 1.02
3520 reflections
259 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0777P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.30 e Å^{-3}
$\Delta\rho_{min}$ = −0.32 e Å^{-3}

Special details

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

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.1199 (3)	0.27480 (17)	0.8627 (2)	0.0200 (7)
H1A	0.0768	0.3244	0.8282	0.030*
H1B	0.1505	0.2885	0.9343	0.030*
H1C	0.0515	0.2290	0.8600	0.030*
C2	0.4545 (3)	0.16274 (15)	0.8465 (2)	0.0174 (6)
C3	0.5028 (3)	0.18745 (15)	0.7580 (2)	0.0175 (6)
C4	0.4016 (3)	0.22685 (16)	0.67425 (19)	0.0157 (6)
H4	0.4548	0.2680	0.6358	0.019*
C5	0.2851 (3)	0.27365 (15)	0.71935 (19)	0.0152 (6)
C6	0.2435 (3)	0.24810 (16)	0.8102 (2)	0.0173 (6)
C7	0.5302 (3)	0.11523 (17)	0.9340 (2)	0.0245 (7)
H7A	0.6121	0.0872	0.9109	0.037*
H7B	0.4673	0.0731	0.9587	0.037*
H7C	0.5606	0.1543	0.9896	0.037*
C8	0.6507 (3)	0.17556 (16)	0.7410 (2)	0.0198 (7)
C9	0.8343 (3)	0.22798 (18)	0.6487 (2)	0.0263 (7)
H9A	0.8765	0.1717	0.6612	0.032*
H9B	0.8845	0.2681	0.6970	0.032*
C10	0.8471 (4)	0.2542 (3)	0.5425 (3)	0.0666 (13)
H10A	0.8004	0.2130	0.4951	0.100*
H10B	0.9463	0.2577	0.5316	0.100*
H10C	0.8032	0.3093	0.5301	0.100*
C11	0.2228 (3)	0.34133 (16)	0.6544 (2)	0.0173 (6)
C12	0.0678 (3)	0.45631 (16)	0.6272 (2)	0.0256 (7)
H12A	0.0267	0.4335	0.5606	0.031*
H12B	0.1427	0.4964	0.6144	0.031*
C13	−0.0426 (3)	0.49978 (18)	0.6804 (2)	0.0365 (9)
H13A	−0.1158	0.4595	0.6933	0.055*
H13B	−0.0836	0.5454	0.6371	0.055*
H13C	−0.0005	0.5229	0.7457	0.055*
C14	0.3440 (3)	0.15860 (16)	0.59973 (19)	0.0158 (6)
C15	0.2251 (3)	0.11367 (16)	0.6148 (2)	0.0192 (6)
H15	0.1758	0.1268	0.6718	0.023*
C16	0.1759 (3)	0.04974 (16)	0.5487 (2)	0.0211 (7)
H16	0.0943	0.0192	0.5607	0.025*

C17	0.2463 (3)	0.03096 (16)	0.4654 (2)	0.0204 (7)
C18	0.3672 (3)	0.07531 (16)	0.4488 (2)	0.0179 (6)
C19	0.4164 (3)	0.13826 (16)	0.5158 (2)	0.0169 (6)
H19	0.4995	0.1678	0.5049	0.020*
C20	0.5481 (3)	0.09391 (16)	0.3377 (2)	0.0208 (7)
H20A	0.6276	0.0823	0.3901	0.025*
H20B	0.5315	0.1553	0.3351	0.025*
C21	0.5797 (3)	0.06224 (17)	0.2347 (2)	0.0258 (7)
H21A	0.6027	0.0023	0.2396	0.039*
H21B	0.6594	0.0933	0.2127	0.039*
H21C	0.4977	0.0705	0.1847	0.039*
N1	0.3203 (2)	0.18583 (13)	0.86434 (16)	0.0177 (5)
H1	0.2813	0.1594	0.9130	0.021*
O1	0.68648 (18)	0.22551 (11)	0.66499 (14)	0.0221 (5)
O2	0.7345 (2)	0.12903 (13)	0.78730 (16)	0.0373 (6)
O3	0.12502 (18)	0.38864 (11)	0.69286 (14)	0.0231 (5)
O4	0.25831 (19)	0.35563 (11)	0.56969 (14)	0.0229 (5)
O5	0.1961 (2)	−0.03123 (12)	0.39926 (14)	0.0288 (5)
H5	0.2464	−0.0345	0.3508	0.043*
O6	0.42503 (19)	0.05071 (10)	0.36239 (13)	0.0223 (5)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0189 (16)	0.0278 (16)	0.0138 (14)	−0.0007 (13)	0.0048 (13)	−0.0006 (13)
C2	0.0195 (16)	0.0164 (15)	0.0159 (15)	−0.0018 (12)	0.0002 (13)	−0.0022 (12)
C3	0.0197 (15)	0.0157 (15)	0.0176 (15)	−0.0003 (12)	0.0036 (13)	−0.0021 (12)
C4	0.0161 (15)	0.0174 (15)	0.0140 (14)	−0.0021 (12)	0.0033 (12)	−0.0012 (12)
C5	0.0162 (15)	0.0140 (14)	0.0154 (14)	−0.0025 (12)	0.0026 (12)	−0.0050 (12)
C6	0.0175 (15)	0.0172 (15)	0.0172 (15)	−0.0009 (12)	0.0010 (13)	−0.0023 (12)
C7	0.0290 (18)	0.0265 (16)	0.0179 (16)	0.0017 (14)	0.0026 (14)	0.0017 (13)
C8	0.0256 (17)	0.0200 (16)	0.0140 (15)	−0.0010 (14)	0.0034 (14)	−0.0032 (13)
C9	0.0165 (16)	0.0268 (17)	0.0367 (18)	−0.0040 (13)	0.0087 (14)	−0.0052 (15)
C10	0.029 (2)	0.127 (4)	0.047 (2)	0.005 (2)	0.0204 (19)	0.028 (2)
C11	0.0154 (15)	0.0172 (15)	0.0201 (16)	−0.0046 (12)	0.0048 (13)	−0.0065 (13)
C12	0.0296 (18)	0.0226 (16)	0.0251 (17)	0.0089 (14)	0.0046 (14)	0.0081 (13)
C13	0.0288 (19)	0.038 (2)	0.044 (2)	0.0140 (15)	0.0100 (16)	0.0063 (16)
C14	0.0144 (15)	0.0177 (15)	0.0150 (15)	0.0005 (12)	−0.0005 (12)	0.0025 (12)
C15	0.0221 (16)	0.0207 (15)	0.0151 (14)	0.0006 (13)	0.0036 (13)	0.0007 (13)
C16	0.0189 (16)	0.0236 (16)	0.0211 (16)	−0.0055 (13)	0.0045 (13)	0.0013 (13)
C17	0.0268 (17)	0.0169 (15)	0.0168 (15)	−0.0020 (13)	−0.0008 (13)	−0.0021 (13)
C18	0.0196 (16)	0.0186 (15)	0.0159 (15)	0.0058 (13)	0.0044 (13)	0.0005 (13)
C19	0.0146 (14)	0.0171 (15)	0.0190 (15)	0.0013 (12)	0.0018 (12)	0.0039 (13)
C20	0.0201 (16)	0.0204 (16)	0.0221 (16)	0.0012 (13)	0.0032 (13)	0.0024 (13)
C21	0.0283 (17)	0.0270 (17)	0.0236 (16)	0.0067 (14)	0.0097 (14)	−0.0006 (14)
N1	0.0192 (13)	0.0205 (13)	0.0142 (12)	−0.0031 (10)	0.0060 (10)	0.0053 (10)
O1	0.0166 (11)	0.0250 (11)	0.0255 (11)	−0.0004 (9)	0.0055 (9)	0.0030 (9)
O2	0.0276 (13)	0.0487 (14)	0.0368 (13)	0.0149 (11)	0.0086 (11)	0.0188 (11)

O3	0.0231 (11)	0.0248 (10)	0.0230 (11)	0.0096 (9)	0.0094 (9)	0.0038 (9)
O4	0.0301 (12)	0.0226 (11)	0.0173 (11)	0.0037 (9)	0.0088 (9)	0.0020 (9)
O5	0.0351 (13)	0.0277 (11)	0.0249 (12)	−0.0104 (10)	0.0086 (10)	−0.0106 (10)
O6	0.0259 (12)	0.0230 (11)	0.0192 (11)	−0.0019 (9)	0.0087 (9)	−0.0043 (9)

Geometric parameters (Å, º)

C1—C6	1.497 (3)	C11—O3	1.343 (3)
C1—H1A	0.9800	C12—O3	1.451 (3)
C1—H1B	0.9800	C12—C13	1.499 (4)
C1—H1C	0.9800	C12—H12A	0.9900
C2—C3	1.354 (3)	C12—H12B	0.9900
C2—N1	1.384 (3)	C13—H13A	0.9800
C2—C7	1.498 (4)	C13—H13B	0.9800
C3—C8	1.473 (4)	C13—H13C	0.9800
C3—C4	1.525 (4)	C14—C15	1.379 (3)
C4—C5	1.516 (3)	C14—C19	1.401 (3)
C4—C14	1.527 (3)	C15—C16	1.389 (3)
C4—H4	1.0000	C15—H15	0.9500
C5—C6	1.359 (3)	C16—C17	1.377 (4)
C5—C11	1.463 (4)	C16—H16	0.9500
C6—N1	1.387 (3)	C17—O5	1.371 (3)
C7—H7A	0.9800	C17—C18	1.396 (4)
C7—H7B	0.9800	C18—O6	1.372 (3)
C7—H7C	0.9800	C18—C19	1.384 (4)
C8—O2	1.210 (3)	C19—H19	0.9500
C8—O1	1.349 (3)	C20—O6	1.434 (3)
C9—O1	1.458 (3)	C20—C21	1.504 (3)
C9—C10	1.473 (4)	C20—H20A	0.9900
C9—H9A	0.9900	C20—H20B	0.9900
C9—H9B	0.9900	C21—H21A	0.9800
C10—H10A	0.9800	C21—H21B	0.9800
C10—H10B	0.9800	C21—H21C	0.9800
C10—H10C	0.9800	N1—H1	0.8800
C11—O4	1.218 (3)	O5—H5	0.8400
C6—C1—H1A	109.5	O3—C12—H12A	110.1
C6—C1—H1B	109.5	C13—C12—H12A	110.1
H1A—C1—H1B	109.5	O3—C12—H12B	110.1
C6—C1—H1C	109.5	C13—C12—H12B	110.1
H1A—C1—H1C	109.5	H12A—C12—H12B	108.4
H1B—C1—H1C	109.5	C12—C13—H13A	109.5
C3—C2—N1	118.5 (2)	C12—C13—H13B	109.5
C3—C2—C7	128.5 (2)	H13A—C13—H13B	109.5
N1—C2—C7	113.0 (2)	C12—C13—H13C	109.5
C2—C3—C8	121.0 (3)	H13A—C13—H13C	109.5
C2—C3—C4	119.2 (2)	H13B—C13—H13C	109.5
C8—C3—C4	119.7 (2)	C15—C14—C19	118.7 (2)

C5—C4—C3	111.2 (2)	C15—C14—C4	121.8 (2)
C5—C4—C14	111.5 (2)	C19—C14—C4	119.4 (2)
C3—C4—C14	109.3 (2)	C14—C15—C16	121.5 (2)
C5—C4—H4	108.2	C14—C15—H15	119.2
C3—C4—H4	108.2	C16—C15—H15	119.2
C14—C4—H4	108.2	C17—C16—C15	119.5 (3)
C6—C5—C11	126.3 (2)	C17—C16—H16	120.2
C6—C5—C4	119.5 (2)	C15—C16—H16	120.2
C11—C5—C4	114.1 (2)	O5—C17—C16	119.4 (2)
C5—C6—N1	118.4 (2)	O5—C17—C18	120.6 (2)
C5—C6—C1	129.8 (2)	C16—C17—C18	120.0 (2)
N1—C6—C1	111.8 (2)	O6—C18—C19	126.3 (2)
C2—C7—H7A	109.5	O6—C18—C17	113.6 (2)
C2—C7—H7B	109.5	C19—C18—C17	120.1 (2)
H7A—C7—H7B	109.5	C18—C19—C14	120.2 (2)
C2—C7—H7C	109.5	C18—C19—H19	119.9
H7A—C7—H7C	109.5	C14—C19—H19	119.9
H7B—C7—H7C	109.5	O6—C20—C21	106.9 (2)
O2—C8—O1	121.7 (2)	O6—C20—H20A	110.3
O2—C8—C3	127.1 (3)	C21—C20—H20A	110.3
O1—C8—C3	111.2 (2)	O6—C20—H20B	110.3
O1—C9—C10	109.0 (3)	C21—C20—H20B	110.3
O1—C9—H9A	109.9	H20A—C20—H20B	108.6
C10—C9—H9A	109.9	C20—C21—H21A	109.5
O1—C9—H9B	109.9	C20—C21—H21B	109.5
C10—C9—H9B	109.9	H21A—C21—H21B	109.5
H9A—C9—H9B	108.3	C20—C21—H21C	109.5
C9—C10—H10A	109.5	H21A—C21—H21C	109.5
C9—C10—H10B	109.5	H21B—C21—H21C	109.5
H10A—C10—H10B	109.5	C2—N1—C6	123.9 (2)
C9—C10—H10C	109.5	C2—N1—H1	118.0
H10A—C10—H10C	109.5	C6—N1—H1	118.0
H10B—C10—H10C	109.5	C8—O1—C9	116.9 (2)
O4—C11—O3	120.8 (2)	C11—O3—C12	115.4 (2)
O4—C11—C5	122.2 (2)	C17—O5—H5	109.5
O3—C11—C5	117.0 (2)	C18—O6—C20	117.7 (2)
O3—C12—C13	108.0 (2)		

N1—C2—C3—C8	171.1 (2)	C3—C4—C14—C19	−88.5 (3)
C7—C2—C3—C8	−5.8 (4)	C19—C14—C15—C16	−0.5 (4)
N1—C2—C3—C4	−9.9 (4)	C4—C14—C15—C16	−177.8 (2)
C7—C2—C3—C4	173.2 (2)	C14—C15—C16—C17	−0.6 (4)
C2—C3—C4—C5	30.2 (3)	C15—C16—C17—O5	−178.9 (2)
C8—C3—C4—C5	−150.7 (2)	C15—C16—C17—C18	0.9 (4)
C2—C3—C4—C14	−93.3 (3)	O5—C17—C18—O6	0.6 (4)
C8—C3—C4—C14	85.7 (3)	C16—C17—C18—O6	−179.1 (2)
C3—C4—C5—C6	−28.9 (3)	O5—C17—C18—C19	179.6 (2)
C14—C4—C5—C6	93.4 (3)	C16—C17—C18—C19	−0.1 (4)

C3—C4—C5—C11	154.3 (2)	O6—C18—C19—C14	177.9 (2)
C14—C4—C5—C11	−83.4 (3)	C17—C18—C19—C14	−1.0 (4)
C11—C5—C6—N1	−176.3 (2)	C15—C14—C19—C18	1.2 (4)
C4—C5—C6—N1	7.3 (4)	C4—C14—C19—C18	178.6 (2)
C11—C5—C6—C1	6.3 (5)	C3—C2—N1—C6	−15.6 (4)
C4—C5—C6—C1	−170.1 (2)	C7—C2—N1—C6	161.8 (2)
C2—C3—C8—O2	17.7 (4)	C5—C6—N1—C2	17.0 (4)
C4—C3—C8—O2	−161.2 (3)	C1—C6—N1—C2	−165.1 (2)
C2—C3—C8—O1	−161.4 (2)	O2—C8—O1—C9	−6.7 (4)
C4—C3—C8—O1	19.6 (3)	C3—C8—O1—C9	172.5 (2)
C6—C5—C11—O4	−173.5 (3)	C10—C9—O1—C8	156.5 (3)
C4—C5—C11—O4	3.1 (4)	O4—C11—O3—C12	−0.3 (3)
C6—C5—C11—O3	7.5 (4)	C5—C11—O3—C12	178.7 (2)
C4—C5—C11—O3	−175.9 (2)	C13—C12—O3—C11	177.8 (2)
C5—C4—C14—C15	−34.5 (3)	C19—C18—O6—C20	−0.2 (4)
C3—C4—C14—C15	88.8 (3)	C17—C18—O6—C20	178.7 (2)
C5—C4—C14—C19	148.2 (2)	C21—C20—O6—C18	−173.6 (2)

Hydrogen-bond geometry (Å, º)

Cg1 and Cg2 are the centroids of the C14–C19 and N1/C2–C6 rings, respectively.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O4^{i}	0.88	2.11	2.898 (4)	149
O5—H5···O2^{ii}	0.84	2.38	3.035 (5)	135
C13—H13*C*···O5^{i}	0.98	2.62	3.519 (3)	152
C1—H1*B*···*Cg*1^{iii}	0.98	2.69	3.370 (2)	136
C20—H20*B*···*Cg*2^{iii}	0.99	2.66	3.654 (2)	146

Symmetry codes: (i) *x*, −*y*+1/2, *z*+1/2; (ii) −*x*+1, −*y*, −*z*+1; (iii) −*x*, *y*+1/2, −*z*+1/2.