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[(1*R**,3*S**,4*S**)-3-(2-Hydroxybenzoyl)-1,2,3,4-tetrahydro-1,4-epoxynaphthalen-1-yl]methyl 4-nitrobenzoate

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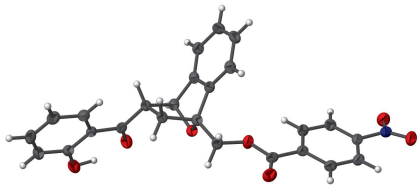
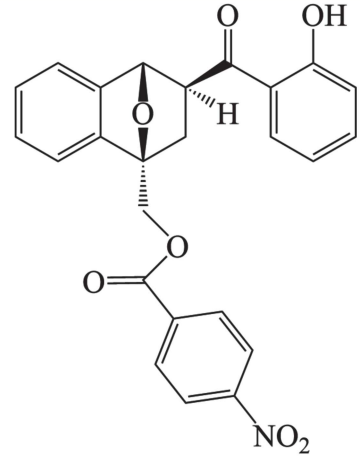
Structural data: full structural data are available from iucrdata.iucr.org

The relative stereo- and regiochemistry of the racemic title compound, $C_{25}H_{19}NO_7$, were established from the crystal structure. The fused benzene ring forms dihedral angles of 77.3 (1) and 60.3 (1)° with the hydroxy-substituted benzene ring and the nitro-substituted benzene ring, respectively. The dihedral angle between the hydroxy-substituted benzene ring and the nitro-substituted benzene ring is 76.4 (1)°. An intramolecular O—H···O hydrogen bond closes an *S*(6) ring. In the crystal, weak C—H···O hydrogen bonds connect the molecules, forming layers parallel to (100). Within these layers, there are weak π–π stacking interactions with a ring centroid–ring centroid distance of 3.555 (1) Å.

3D view



Chemical scheme



Structure description

In past years, our research group (Ballantine *et al.*, 2009; Edmunds *et al.*, 2015; Hill & Tam, 2019; Edmunds *et al.*, 2016; Raheem *et al.*, 2014) has investigated the effects of various C_1-substituted oxabenzonorbornadienes (OBD) on controlling the regioselectivity of ring-opening reactions. In 2015, Nagamoto and Nishimura reported the iridium-catalysed hydroacylation reaction of bicyclic alkenes with 2-hydroxybenzaldehyde and its derivatives. Based upon these findings, we set out to determine the effect of C_1 substitution on controlling the regioselectivity in the iridium-catalysed hydroacylation reaction with salicylaldehyde **II** (see Fig. 1) on unsymmetrical oxabenzonorbornadienes. Reaction of C_1-substituted OBD (**I**) with salicylaldehyde **II** in the presence of $[Ir(COD)Cl]_2$ (COD = 1,5-cyclooctaiene), and 5 *M* KOH afforded exclusively the title C_3 regioisomer (**III**) in a 82% yield. The relative stereo- and regiochemistry of the adduct system was determined by single-crystal X-ray analysis. There are two possible stereoisomers as the addition can occur on the *exo* or the *endo* face, and two possible regioisomers as the addition can occur

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

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3O···O2	0.94 (2)	1.67 (2)	2.5321 (15)	151.7 (19)
C3—H3A···O3^{i}	1.00	2.48	3.4510 (17)	163
C8—H8A···O1^{ii}	0.95	2.38	3.2782 (17)	157
C9—H9A···O7^{iii}	0.95	2.49	3.4057 (19)	161

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

at the C_2 or C_3 position. Of the four possible stereo- and regio-isomers, only the *exo*-C_3 isomer was obtained. The title compound is racemic: in the arbitrarily chosen asymmetric unit, the stereogenic centres are as follows: C1 *R*; C3 *S*; C4 *S*.

The molecular structure of the title compound is shown in Fig. 2. The fused benzene ring (C5–C10) forms dihedral angles of 77.3 (1) and 60.3 (1)° with the hydroxy-substituted benzene ring (C12–C17) and the nitro-substituted benzene ring (C20–C25), respectively. The dihedral angle between the hydroxy-substituted benzene ring and the nitro-substituted benzene ring is 76.4 (1)°. An intramolecular O—H···O hydrogen bond is observed. In the crystal, weak C—H···O hydrogen bonds

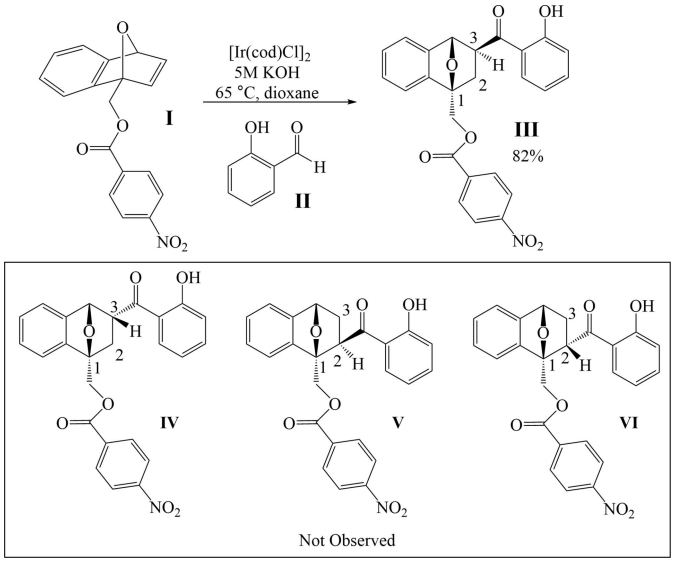


Figure 1
The reaction scheme.

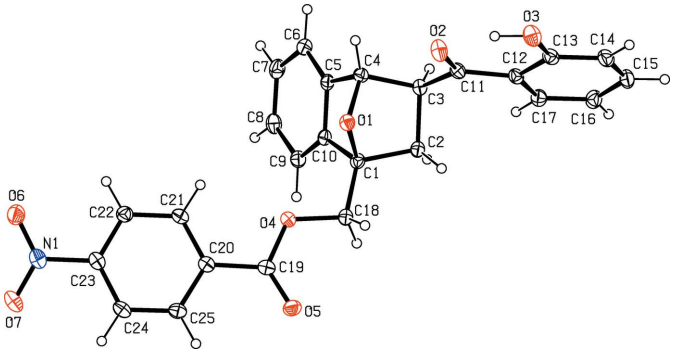


Figure 2
The molecular structure of the title compound with displacement ellipsoids drawn the 30% probability level.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{25}H_{19}NO_7$
M_r	445.41
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	150
a, b, c (Å)	14.7455 (10), 11.9504 (8), 11.9649 (8)
β (°)	101.898 (2)
V (Å^3)	2063.1 (2)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.11
Crystal size (mm)	0.32 × 0.30 × 0.16
Data collection	
Diffractometer	Bruker Kappa APEX DUO PHOTON II
Absorption correction	Multi-scan (Krause *et al.*, 2015)
T_{min}, T_{max}	0.623, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	40054, 4727, 3399
R_{int}	0.059
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.650
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.036, 0.093, 1.01
No. of reflections	4727
No. of parameters	302
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.25, −0.21

Computer programs: *APEX3* and *SAINT* (Bruker, 2019), *SHELXT2014* (Sheldrick, 2015*a*), *SHELXL2018* (Sheldrick, 2015*b*), *PLATON* (Spek, 2020) and *publCIF* (Westrip, 2010).

(Table 1) connect the molecules, forming layers lying parallel to (100) (Fig. 3). Within these layers, there are weak π–π stacking interactions with a ring centroid–ring centroid

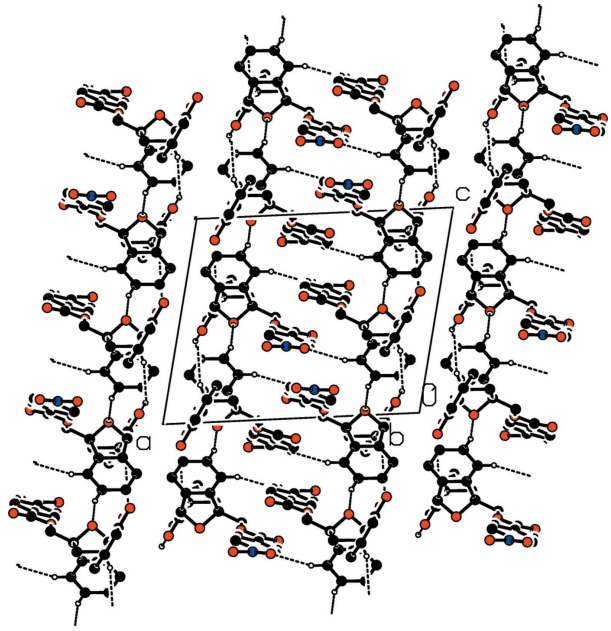


Figure 3
Part of the crystal structure with weak hydrogen bonds shown as dashed lines. Only H atoms involved in hydrogen bonds are shown.

distance of 3.555 (1) Å for $Cg\cdots Cg(1-x, -y, 1-z)$ where Cg is the centroid of the C20–C25 ring.

Synthesis and crystallization

To a dried screw-cap vial, was added $[Ir(COD)Cl]_2$ (10 mg, 5 mol%), C_1-substituted oxabenzonorbornadiene (**I**) (Fig. 1) (0.3 mmol, 1.2 equiv.), salicylaldehyde **II** (27 µl, 1 equiv.) and 5*M* KOH (0.03 mmol, 10 mol%) dissolved in 2 ml of 1,4-dioxane. The reaction was left to stir at 338 K for 20 h, the resultant mixture was loaded directly onto a column and the crude reaction mixture was purified by flash chromatography (EtOAc:hexanes 25:75) to obtain the adduct product **III** (101 mg, 0.23 mmol, 82%) as a yellow solid. The product was then subsequently recrystallized from solution in pure hexanes by slow evaporation of the solvent to give product **III** as colourless crystals.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Acknowledgements

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References

Ballantine, M., Menard, M. L. & Tam, W. (2009). *J. Org. Chem.* **74**, 7570–7573.
Bruker (2019). *APEX3* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Edmunds, M., Menard, M. L. & Tam, W. (2015). *Synth. Commun.* **45**, 458–466.
Edmunds, M., Raheem, M.-A., Boutin, R., Tait, K. & Tam, W. (2016). *Beilstein J. Org. Chem.* **12**, 239–244.
Hill, J. & Tam, W. (2019). *J. Org. Chem.* **84**, 8309–8314.
Krause, L., Herbst-Irmer, R., Sheldrick, G. M. & Stalke, D. (2015). *J. Appl. Cryst.* **48**, 3–10.
Nagamoto, M. & Nishimura, T. (2015). *Chem. Commun.* **51**, 13791–13794.
Raheem, M. A., Edmunds, M. & Tam, W. (2014). *Can. J. Chem.* **92**, 888–895.
Sheldrick, G. M. (2015*a*). *Acta Cryst.* A**71**, 3–8.
Sheldrick, G. M. (2015*b*). *Acta Cryst.* C**71**, 3–8.
Spek, A. L. (2020). *Acta Cryst.* E**76**, 1–11.
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

full crystallographic data

IUCrData (2020). **5**, x200265 [https://doi.org/10.1107/S2414314620002655]

[(1*R**,3*S**,4*S**)-3-(2-Hydroxybenzoyl)-1,2,3,4-tetrahydro-1,4-epoxynaphthalen-1-yl]methyl 4-nitrobenzoate

Alan J. Lough, Angel Ho and William Tam

[(1*R,3*S**,4*S**)-3-(2-Hydroxybenzoyl)-1,2,3,4-tetrahydro-1,4-epoxynaphthalen-1-yl]methyl 4-nitrobenzoate**

Crystal data

$C_{25}H_{19}NO_7$
M_r = 445.41
Monoclinic, $P2_1/c$
a = 14.7455 (10) Å
b = 11.9504 (8) Å
c = 11.9649 (8) Å
β = 101.898 (2)°
V = 2063.1 (2) Å^3
Z = 4
$F(000)$ = 928
D_x = 1.434 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 9213 reflections
θ = 2.4–27.2°
μ = 0.11 mm^{-1}
T = 150 K
Shard, colourless
0.32 × 0.30 × 0.16 mm

Data collection

Bruker Kappa APEX DUO PHOTON II diffractometer
Radiation source: sealed tube with Bruker Triumph monochromator
φ and ω scans
Absorption correction: multi-scan (Krause *et al.*, 2015)
T_{min} = 0.623, T_{max} = 0.746
40054 measured reflections
4727 independent reflections
3399 reflections with $I > 2\sigma(I)$
R_{int} = 0.059
θ_{max} = 27.5°, θ_{min} = 1.4°
h = −19→19
k = −15→15
l = −15→15

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.093
S = 1.01
4727 reflections
302 parameters
0 restraints
Primary atom site location: dual
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.039P)^2 + 0.5845P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.25 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.21520 (6)	0.45410 (8)	0.52221 (8)	0.0254 (2)
O2	0.09918 (8)	0.66077 (8)	0.55530 (9)	0.0357 (3)
O3	0.08195 (8)	0.86474 (10)	0.60434 (9)	0.0376 (3)
H3O	0.0802 (14)	0.7862 (18)	0.6067 (18)	0.069 (6)*
O4	0.37771 (6)	0.32000 (8)	0.53811 (9)	0.0295 (2)
O5	0.53204 (7)	0.32594 (9)	0.60060 (9)	0.0336 (2)
O6	0.35631 (8)	−0.23766 (9)	0.63820 (10)	0.0430 (3)
O7	0.50514 (8)	−0.25121 (9)	0.65612 (9)	0.0393 (3)
N1	0.43308 (9)	−0.19667 (10)	0.64302 (10)	0.0317 (3)
C1	0.27856 (9)	0.46052 (11)	0.44429 (11)	0.0239 (3)
C2	0.26049 (9)	0.58196 (11)	0.39894 (12)	0.0247 (3)
H2A	0.275088	0.590603	0.322264	0.030*
H2B	0.296733	0.637046	0.451839	0.030*
C3	0.15431 (9)	0.59376 (11)	0.39449 (11)	0.0238 (3)
H3A	0.120016	0.605331	0.314073	0.029*
C4	0.13143 (9)	0.47745 (11)	0.43864 (12)	0.0249 (3)
H4A	0.072919	0.474098	0.468439	0.030*
C5	0.13776 (9)	0.39344 (11)	0.34635 (12)	0.0249 (3)
C6	0.07283 (10)	0.33873 (12)	0.26533 (13)	0.0302 (3)
H6A	0.008319	0.348599	0.261361	0.036*
C7	0.10549 (11)	0.26840 (12)	0.18949 (13)	0.0332 (3)
H7A	0.062396	0.228731	0.133444	0.040*
C8	0.19923 (11)	0.25522 (12)	0.19418 (12)	0.0319 (3)
H8A	0.219548	0.206293	0.141757	0.038*
C9	0.26456 (10)	0.31274 (11)	0.27481 (12)	0.0283 (3)
H9A	0.329065	0.304773	0.277455	0.034*
C10	0.23228 (9)	0.38140 (11)	0.35039 (11)	0.0235 (3)
C11	0.13163 (9)	0.68588 (11)	0.47082 (11)	0.0254 (3)
C12	0.14368 (9)	0.80400 (11)	0.44234 (12)	0.0250 (3)
C13	0.11508 (10)	0.88844 (12)	0.50972 (12)	0.0283 (3)
C14	0.11990 (10)	1.00024 (12)	0.47954 (14)	0.0349 (4)
H14A	0.100414	1.056998	0.524970	0.042*
C15	0.15290 (11)	1.02872 (12)	0.38389 (14)	0.0369 (4)
H15A	0.155158	1.105273	0.363255	0.044*
C16	0.18300 (10)	0.94724 (12)	0.31691 (13)	0.0340 (3)
H16A	0.206590	0.967947	0.251714	0.041*
C17	0.17825 (10)	0.83600 (12)	0.34613 (12)	0.0287 (3)
H17A	0.198678	0.780174	0.300444	0.034*
C18	0.37610 (10)	0.43650 (11)	0.50427 (12)	0.0279 (3)
H18A	0.419456	0.449528	0.452497	0.034*
H18B	0.394223	0.485260	0.572100	0.034*
C19	0.46027 (9)	0.27418 (12)	0.57989 (11)	0.0253 (3)
C20	0.45169 (9)	0.15105 (11)	0.59774 (11)	0.0247 (3)
C21	0.36672 (9)	0.09770 (12)	0.56869 (12)	0.0274 (3)
H21A	0.312763	0.139404	0.536667	0.033*

C22	0.36020 (10)	−0.01641 (12)	0.58624 (12)	0.0287 (3)
H22A	0.302095	−0.053641	0.568005	0.034*
C23	0.44020 (10)	−0.07438 (12)	0.63079 (11)	0.0273 (3)
C24	0.52603 (10)	−0.02386 (12)	0.65983 (12)	0.0293 (3)
H24A	0.579934	−0.066435	0.689955	0.035*
C25	0.53146 (10)	0.09052 (12)	0.64388 (12)	0.0284 (3)
H25A	0.589463	0.127695	0.664342	0.034*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0287 (5)	0.0252 (5)	0.0235 (5)	0.0008 (4)	0.0085 (4)	0.0022 (4)
O2	0.0536 (7)	0.0288 (5)	0.0292 (5)	0.0063 (5)	0.0189 (5)	0.0028 (4)
O3	0.0493 (7)	0.0330 (6)	0.0332 (6)	0.0069 (5)	0.0145 (5)	−0.0052 (5)
O4	0.0247 (5)	0.0248 (5)	0.0380 (6)	0.0019 (4)	0.0040 (4)	0.0041 (4)
O5	0.0259 (5)	0.0370 (6)	0.0358 (6)	−0.0032 (5)	0.0019 (4)	0.0034 (5)
O6	0.0423 (7)	0.0330 (6)	0.0484 (7)	−0.0031 (5)	−0.0029 (5)	0.0024 (5)
O7	0.0485 (7)	0.0354 (6)	0.0344 (6)	0.0168 (5)	0.0097 (5)	0.0035 (5)
N1	0.0408 (8)	0.0302 (7)	0.0224 (6)	0.0058 (6)	0.0027 (5)	−0.0004 (5)
C1	0.0258 (7)	0.0230 (7)	0.0245 (7)	−0.0012 (5)	0.0085 (6)	0.0011 (5)
C2	0.0277 (7)	0.0212 (6)	0.0260 (7)	−0.0009 (5)	0.0074 (6)	0.0007 (5)
C3	0.0272 (7)	0.0219 (7)	0.0228 (7)	0.0008 (5)	0.0059 (5)	0.0002 (5)
C4	0.0236 (7)	0.0241 (7)	0.0278 (7)	0.0015 (5)	0.0072 (6)	0.0017 (6)
C5	0.0278 (7)	0.0193 (6)	0.0280 (7)	−0.0008 (5)	0.0069 (6)	0.0025 (5)
C6	0.0279 (7)	0.0254 (7)	0.0360 (8)	−0.0022 (6)	0.0036 (6)	0.0018 (6)
C7	0.0402 (9)	0.0258 (7)	0.0307 (8)	−0.0053 (6)	0.0007 (7)	−0.0019 (6)
C8	0.0441 (9)	0.0242 (7)	0.0284 (7)	0.0012 (6)	0.0098 (7)	−0.0032 (6)
C9	0.0311 (8)	0.0251 (7)	0.0305 (8)	0.0010 (6)	0.0105 (6)	0.0011 (6)
C10	0.0265 (7)	0.0202 (6)	0.0242 (7)	−0.0012 (5)	0.0058 (5)	0.0031 (5)
C11	0.0273 (7)	0.0263 (7)	0.0220 (7)	0.0039 (6)	0.0036 (6)	0.0020 (6)
C12	0.0250 (7)	0.0240 (7)	0.0239 (7)	0.0026 (5)	0.0003 (5)	0.0000 (5)
C13	0.0268 (7)	0.0280 (7)	0.0279 (7)	0.0035 (6)	0.0010 (6)	−0.0021 (6)
C14	0.0317 (8)	0.0259 (7)	0.0440 (9)	0.0040 (6)	0.0005 (7)	−0.0062 (7)
C15	0.0372 (9)	0.0223 (7)	0.0460 (9)	0.0010 (6)	−0.0032 (7)	0.0046 (7)
C16	0.0354 (8)	0.0305 (8)	0.0338 (8)	−0.0035 (6)	0.0015 (7)	0.0066 (6)
C17	0.0307 (7)	0.0267 (7)	0.0269 (7)	−0.0006 (6)	0.0018 (6)	0.0006 (6)
C18	0.0282 (7)	0.0227 (7)	0.0322 (8)	−0.0011 (6)	0.0044 (6)	0.0022 (6)
C19	0.0237 (7)	0.0326 (8)	0.0197 (7)	0.0025 (6)	0.0049 (5)	−0.0008 (6)
C20	0.0265 (7)	0.0281 (7)	0.0200 (6)	0.0027 (6)	0.0060 (5)	−0.0010 (5)
C21	0.0244 (7)	0.0293 (7)	0.0286 (7)	0.0057 (6)	0.0053 (6)	−0.0008 (6)
C22	0.0269 (7)	0.0287 (7)	0.0305 (7)	0.0004 (6)	0.0058 (6)	−0.0025 (6)
C23	0.0336 (8)	0.0277 (7)	0.0208 (7)	0.0061 (6)	0.0062 (6)	−0.0002 (5)
C24	0.0289 (8)	0.0335 (8)	0.0243 (7)	0.0090 (6)	0.0030 (6)	0.0004 (6)
C25	0.0248 (7)	0.0344 (8)	0.0251 (7)	0.0023 (6)	0.0035 (6)	−0.0018 (6)

Geometric parameters (Å, º)

O1—C4	1.4471 (16)	C8—C9	1.396 (2)
O1—C1	1.4515 (15)	C8—H8A	0.9500
O2—C11	1.2410 (16)	C9—C10	1.3766 (19)
O3—C13	1.3523 (18)	C9—H9A	0.9500
O3—H3O	0.94 (2)	C11—C12	1.4715 (19)
O4—C19	1.3345 (16)	C12—C17	1.405 (2)
O4—C18	1.4487 (16)	C12—C13	1.4093 (19)
O5—C19	1.2066 (16)	C13—C14	1.390 (2)
O6—N1	1.2238 (16)	C14—C15	1.375 (2)
O7—N1	1.2287 (15)	C14—H14A	0.9500
N1—C23	1.4746 (19)	C15—C16	1.391 (2)
C1—C18	1.4968 (19)	C15—H15A	0.9500
C1—C10	1.5185 (18)	C16—C17	1.380 (2)
C1—C2	1.5531 (18)	C16—H16A	0.9500
C2—C3	1.5620 (19)	C17—H17A	0.9500
C2—H2A	0.9900	C18—H18A	0.9900
C2—H2B	0.9900	C18—H18B	0.9900
C3—C11	1.5112 (18)	C19—C20	1.4959 (19)
C3—C4	1.5486 (18)	C20—C21	1.3848 (19)
C3—H3A	1.0000	C20—C25	1.3942 (19)
C4—C5	1.5095 (19)	C21—C22	1.386 (2)
C4—H4A	1.0000	C21—H21A	0.9500
C5—C6	1.3788 (19)	C22—C23	1.3770 (19)
C5—C10	1.3920 (19)	C22—H22A	0.9500
C6—C7	1.393 (2)	C23—C24	1.380 (2)
C6—H6A	0.9500	C24—C25	1.385 (2)
C7—C8	1.381 (2)	C24—H24A	0.9500
C7—H7A	0.9500	C25—H25A	0.9500
C4—O1—C1	96.71 (9)	O2—C11—C12	120.38 (12)
C13—O3—H3O	104.6 (13)	O2—C11—C3	119.12 (12)
C19—O4—C18	117.40 (11)	C12—C11—C3	120.43 (12)
O6—N1—O7	124.11 (13)	C17—C12—C13	118.41 (13)
O6—N1—C23	118.42 (12)	C17—C12—C11	122.17 (12)
O7—N1—C23	117.46 (13)	C13—C12—C11	119.33 (13)
O1—C1—C18	111.35 (11)	O3—C13—C14	117.75 (13)
O1—C1—C10	101.05 (10)	O3—C13—C12	122.09 (13)
C18—C1—C10	118.44 (11)	C14—C13—C12	120.16 (14)
O1—C1—C2	100.78 (10)	C15—C14—C13	119.99 (14)
C18—C1—C2	115.17 (11)	C15—C14—H14A	120.0
C10—C1—C2	107.74 (11)	C13—C14—H14A	120.0
C1—C2—C3	101.24 (10)	C14—C15—C16	121.06 (14)
C1—C2—H2A	111.5	C14—C15—H15A	119.5
C3—C2—H2A	111.5	C16—C15—H15A	119.5
C1—C2—H2B	111.5	C17—C16—C15	119.31 (15)
C3—C2—H2B	111.5	C17—C16—H16A	120.3

H2A—C2—H2B	109.3	C15—C16—H16A	120.3
C11—C3—C4	110.90 (11)	C16—C17—C12	121.05 (14)
C11—C3—C2	112.98 (11)	C16—C17—H17A	119.5
C4—C3—C2	101.22 (10)	C12—C17—H17A	119.5
C11—C3—H3A	110.5	O4—C18—C1	106.08 (11)
C4—C3—H3A	110.5	O4—C18—H18A	110.5
C2—C3—H3A	110.5	C1—C18—H18A	110.5
O1—C4—C5	101.80 (10)	O4—C18—H18B	110.5
O1—C4—C3	101.18 (10)	C1—C18—H18B	110.5
C5—C4—C3	107.26 (11)	H18A—C18—H18B	108.7
O1—C4—H4A	115.0	O5—C19—O4	124.08 (13)
C5—C4—H4A	115.0	O5—C19—C20	124.85 (12)
C3—C4—H4A	115.0	O4—C19—C20	111.08 (11)
C6—C5—C10	121.37 (13)	C21—C20—C25	120.42 (13)
C6—C5—C4	133.71 (13)	C21—C20—C19	121.05 (12)
C10—C5—C4	104.82 (11)	C25—C20—C19	118.53 (12)
C5—C6—C7	117.43 (13)	C20—C21—C22	120.16 (13)
C5—C6—H6A	121.3	C20—C21—H21A	119.9
C7—C6—H6A	121.3	C22—C21—H21A	119.9
C8—C7—C6	121.32 (14)	C23—C22—C21	118.22 (13)
C8—C7—H7A	119.3	C23—C22—H22A	120.9
C6—C7—H7A	119.3	C21—C22—H22A	120.9
C7—C8—C9	120.95 (13)	C22—C23—C24	123.04 (14)
C7—C8—H8A	119.5	C22—C23—N1	117.66 (13)
C9—C8—H8A	119.5	C24—C23—N1	119.26 (12)
C10—C9—C8	117.70 (13)	C23—C24—C25	118.24 (13)
C10—C9—H9A	121.2	C23—C24—H24A	120.9
C8—C9—H9A	121.2	C25—C24—H24A	120.9
C9—C10—C5	121.20 (13)	C24—C25—C20	119.91 (13)
C9—C10—C1	133.92 (12)	C24—C25—H25A	120.0
C5—C10—C1	104.80 (11)	C20—C25—H25A	120.0

C4—O1—C1—C18	−178.46 (11)	O2—C11—C12—C17	−178.58 (13)
C4—O1—C1—C10	−51.79 (11)	C3—C11—C12—C17	−1.5 (2)
C4—O1—C1—C2	58.90 (11)	O2—C11—C12—C13	−2.1 (2)
O1—C1—C2—C3	−35.63 (12)	C3—C11—C12—C13	174.94 (12)
C18—C1—C2—C3	−155.56 (11)	C17—C12—C13—O3	−179.28 (12)
C10—C1—C2—C3	69.79 (12)	C11—C12—C13—O3	4.1 (2)
C1—C2—C3—C11	118.93 (12)	C17—C12—C13—C14	1.1 (2)
C1—C2—C3—C4	0.30 (12)	C11—C12—C13—C14	−175.51 (13)
C1—O1—C4—C5	51.61 (11)	O3—C13—C14—C15	−179.85 (13)
C1—O1—C4—C3	−58.89 (11)	C12—C13—C14—C15	−0.2 (2)
C11—C3—C4—O1	−84.83 (12)	C13—C14—C15—C16	−0.9 (2)
C2—C3—C4—O1	35.28 (12)	C14—C15—C16—C17	1.0 (2)
C11—C3—C4—C5	168.93 (11)	C15—C16—C17—C12	−0.1 (2)
C2—C3—C4—C5	−70.96 (12)	C13—C12—C17—C16	−0.9 (2)
O1—C4—C5—C6	151.71 (15)	C11—C12—C17—C16	175.55 (13)
C3—C4—C5—C6	−102.49 (17)	C19—O4—C18—C1	171.18 (11)

O1—C4—C5—C10	−32.04 (13)	O1—C1—C18—O4	66.60 (13)
C3—C4—C5—C10	73.76 (13)	C10—C1—C18—O4	−49.87 (15)
C10—C5—C6—C7	1.7 (2)	C2—C1—C18—O4	−179.47 (11)
C4—C5—C6—C7	177.47 (14)	C18—O4—C19—O5	6.95 (19)
C5—C6—C7—C8	−0.9 (2)	C18—O4—C19—C20	−173.23 (11)
C6—C7—C8—C9	−0.5 (2)	O5—C19—C20—C21	−178.22 (13)
C7—C8—C9—C10	1.0 (2)	O4—C19—C20—C21	1.96 (18)
C8—C9—C10—C5	−0.2 (2)	O5—C19—C20—C25	1.4 (2)
C8—C9—C10—C1	−176.44 (14)	O4—C19—C20—C25	−178.39 (11)
C6—C5—C10—C9	−1.2 (2)	C25—C20—C21—C22	0.6 (2)
C4—C5—C10—C9	−178.00 (12)	C19—C20—C21—C22	−179.80 (13)
C6—C5—C10—C1	176.00 (12)	C20—C21—C22—C23	−1.2 (2)
C4—C5—C10—C1	−0.82 (13)	C21—C22—C23—C24	0.8 (2)
O1—C1—C10—C9	−150.10 (15)	C21—C22—C23—N1	−176.67 (12)
C18—C1—C10—C9	−28.3 (2)	O6—N1—C23—C22	−16.19 (19)
C2—C1—C10—C9	104.67 (17)	O7—N1—C23—C22	162.95 (12)
O1—C1—C10—C5	33.25 (12)	O6—N1—C23—C24	166.29 (13)
C18—C1—C10—C5	155.09 (12)	O7—N1—C23—C24	−14.57 (18)
C2—C1—C10—C5	−71.98 (13)	C22—C23—C24—C25	0.4 (2)
C4—C3—C11—O2	−0.02 (17)	N1—C23—C24—C25	177.78 (12)
C2—C3—C11—O2	−112.86 (14)	C23—C24—C25—C20	−1.1 (2)
C4—C3—C11—C12	−177.14 (12)	C21—C20—C25—C24	0.6 (2)
C2—C3—C11—C12	70.02 (15)	C19—C20—C25—C24	−179.03 (12)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3*O*···O2	0.94 (2)	1.67 (2)	2.5321 (15)	151.7 (19)
C3—H3*A*···O3^{i}	1.00	2.48	3.4510 (17)	163
C8—H8*A*···O1^{ii}	0.95	2.38	3.2782 (17)	157
C9—H9*A*···O7^{iii}	0.95	2.49	3.4057 (19)	161

Symmetry codes: (i) *x*, −*y*+3/2, *z*−1/2; (ii) *x*, −*y*+1/2, *z*−1/2; (iii) −*x*+1, −*y*, −*z*+1.