Acta Cryst E STRUCTURE REPORTS

OPEN ACCESS

ISSN 1600-5368

Crystal structure of 3-methoxycarbonyl-2-(4-methoxyphenyl)-8-oxo-1-azaspiro-[4.5]deca-1,6,9-trien-1-ium-1-olate

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Received 14 October 2014; accepted 22 October 2014

Edited by W. T. A. Harrison, University of Aberdeen, Scotland

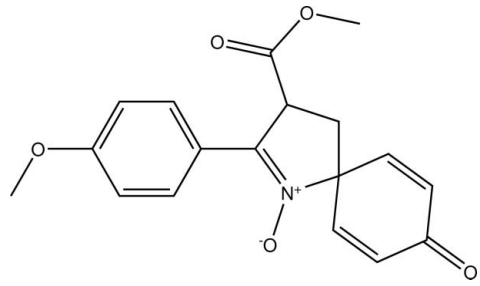
The title compound, $C_{18}H_{17}NO_5$, was prepared by a synthetic strategy based on the Heck reaction from Morita–Baylis–Hillman adducts. The five-membered ring adopts a slightly twisted conformation on the C_a—C_m (a = aromatic and m = methylene) bond. The dihedral angle between the five-membered ring and the spiro aromatic ring is 89.35 (7)°; that between the five-membered ring and the 4-methoxybenzene ring is 4.65 (7)°. Two short intramolecular C—H···O contacts occur. In the crystal, molecules are linked by C—H···O hydrogen bonds to generate a three-dimensional network.

Keywords: single-crystal X-ray study; spirohexadienone structure; Morita–Baylis–Hillman aducts.

CCDC reference: 1030399

1. Related literature

For compounds that contain a spirohexadienone moiety in their structures, see: Wright & König (1993); König *et al.* (1990); Beil *et al.* (1998) and for their biological activities, see: Glushkov *et al.* (2010); Pereira *et al.* (2007). For strategies for the synthesis of spiro-hexadienones from Morita–Baylis–Hillman adducts, see: Coelho *et al.* (2002); Ferreira *et al.* (2009); Pirovani *et al.* (2009); Martins *et al.* (2014). For the biological activity of compounds containing a nitrone group, see: Fangour *et al.* (2009); Floyd *et al.* (2008); Halliwell & Gutteridge (1999); Fevig *et al.* (1996). For a discussion about non-classical hydrogen bonds, see: Desiraju (2005).



2. Experimental

2.1. Crystal data

$C_{18}H_{17}NO_5$
M_r = 327.32
Triclinic, $P\overline{1}$
a = 6.0916 (11) Å
b = 8.7713 (16) Å
c = 15.167 (3) Å
α = 80.255 (6)°
β = 81.703 (6)°
γ = 80.122 (6)°
V = 781.3 (2) Å^3
Z = 2
Cu $K\alpha$ radiation
μ = 0.85 mm^{-1}
T = 100 K
0.47 × 0.20 × 0.17 mm

2.2. Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2010)
T_{min} = 0.813, T_{max} = 1.000
14656 measured reflections
2771 independent reflections
2727 reflections with $I > 2\sigma(I)$
R_{int} = 0.033

2.3. Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.105
S = 1.11
2771 reflections
220 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.28 e Å^{-3}
$\Delta\rho_{min}$ = −0.35 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
C8—H1*C*···O1^{i}	0.98	2.59	3.4941 (18)	153
C4—H3···O1^{i}	0.95	2.38	3.1345 (16)	136
C3—H4···O1	0.95	2.22	2.8725 (17)	125
C14—H8···O3	0.95	2.57	3.3431 (18)	138
C15—H9···O5^{ii}	0.95	2.56	3.3821 (17)	146
C18—H13···O2^{iii}	0.95	2.54	3.4309 (17)	155
C17—H14···O3^{iv}	0.95	2.38	3.2408 (18)	151
C12—H15*A*···O5^{v}	0.99	2.60	3.5402 (18)	159
C9—H16···O1^{vi}	1.00	2.31	3.2045 (16)	148

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

Data collection: *APEX2* (Bruker, 2010); cell refinement: *SAINT* (Bruker, 2010); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2008); molecular graphics: *WinGX* (Farrugia, 2012) and *PLATON* (Spek, 2009); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Acknowledgements

The authors acknowledge Dr Cristiane Storck Schwalm for the data collection and preliminary data processing and structure refinement and thank the Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP 2009/18390–4 and 2009/51602–5), the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES) and the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) for financial support. RA is the recipient of a research grant from CNPq.

Supporting information for this paper is available from the IUCr electronic archives (Reference: HB7301).

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supporting information

Acta Cryst. (2014). E**70**, o1200–o1201 [doi:10.1107/S1600536814023277]

Crystal structure of 3-methoxycarbonyl-2-(4-methoxyphenyl)-8-oxo-1-azaspiro-[4.5]deca-1,6,9-trien-1-ium-1-olate

Lucimara Julio Martins, Deborah de Alencar Simoni, Ricardo Aparicio and Fernando Coelho

S1. Introduction

Natural products, isolated both from terrestrial or marine sources, display great structural diversity and exhibit remarkable biological activities, many of them bearing in their structures a spiro-hexadienone moiety (Wright & König (1993); Beil *et al.* (1998)). Owing to the high conjugation, provided by the presence of a carbonyl group and two double bonds, this structural moiety acts as an efficient Michael acceptor and this chemical property is routinely associated with some biological activities, such as cytotoxic (Pereira *et al.* (2007); Glushkov *et al.* (2010)).

Compounds presenting a nitrone group in their structures can present biological activity related to radical trapping in chemical systems (Fangour *et al.* (2009); Floyd *et al.* (2008); Halliwell *et al.* (1999)). The presence of radicals is normally associated to several type of pathologies. Our interest in preparing spiro-hexadienones with great structural diversity combinated with the biological effect that can be associated to nitrone groups stimulated us to synthesize new spiro compounds containing a nitrone group into their structures and evaluate the biological profiles of these new compounds.

A strategy for the synthesis of spiro-hexadienones from Morita-Baylis-Hillman aducts had been developed. This strategy is based on the Heck reaction, followed by phenolic oxidation of functionalized b-ketoester mediated by a hypervalent iodine reagent (Coelho *et al.* (2002); Ferreira *et al.* (2009); Floyd *et al.* (2008); Halliwell *et al.* (1999)). As far as we know, we synthesized for the first time new functionalized azaspiro compounds from Morita-Baylis-Hillman.

S2. Experimental

S2.1. Synthesis and crystallization

Some *β*-ketoesters, prepared from Morita-Baylis-Hillman adducts, were treated with hydroxylamine hydrochloride to furnish a diastereomeric mixture of oximes, in which the E isomer cyclizes spontaneously to the corresponding isoxazoles. The Z oxime was treated with PIFA [phenyliodine(III) bis(trifluoroacetate)] to furnish the new azaspiro compounds in moderate overall yield (3-17%). The obtained 3-(Methoxycarbonyl)-2-(4-methoxyphenyl)-8-oxo-1-aza-spiro[4.5]deca-1,6,9-trien-1-ium-1-olate (33 mg, 0.1 mmol) was dissolved in absolute chloroform-D1 (1 mL), followed by stirring until total dissolution was achieved. The solution was kept in the freezer. After two weeks, the resulting solution was filtered using a vacuum, washed with small portions of cold chloroform and dried in a desiccator to furnish colourless prisms.

S2.2. Refinement

A riding model was used to calculate the positions of included H atoms, with aromatic and methyl C—H bond lengths of 0.95 and 0.98 A °, respectively. The isotropic displacement parameters values (Uiso(H)) were fixed at 1.5Ueq(C) for

methyl H atoms and 1.2Ueq(C) for all other attached H atoms.

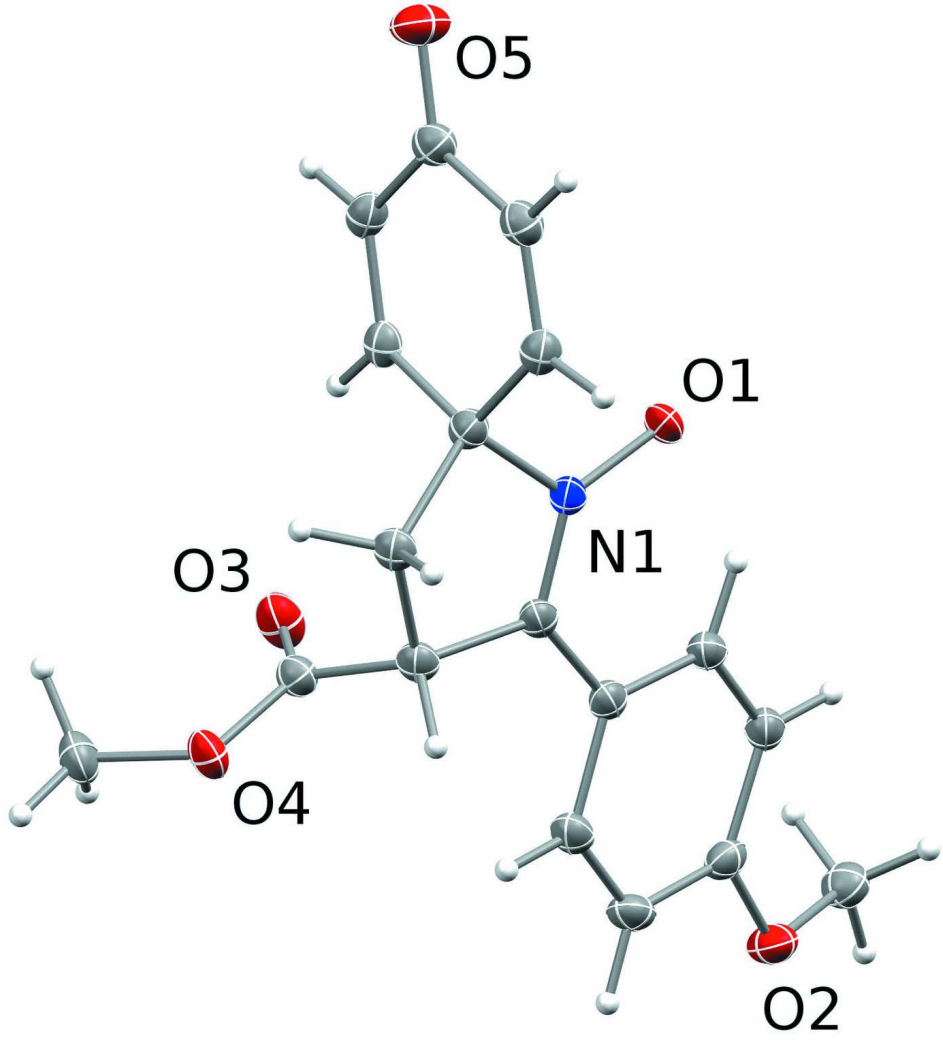

Figure 1

The molecular structure of the title compound with 50% probability displacement ellipsoids.

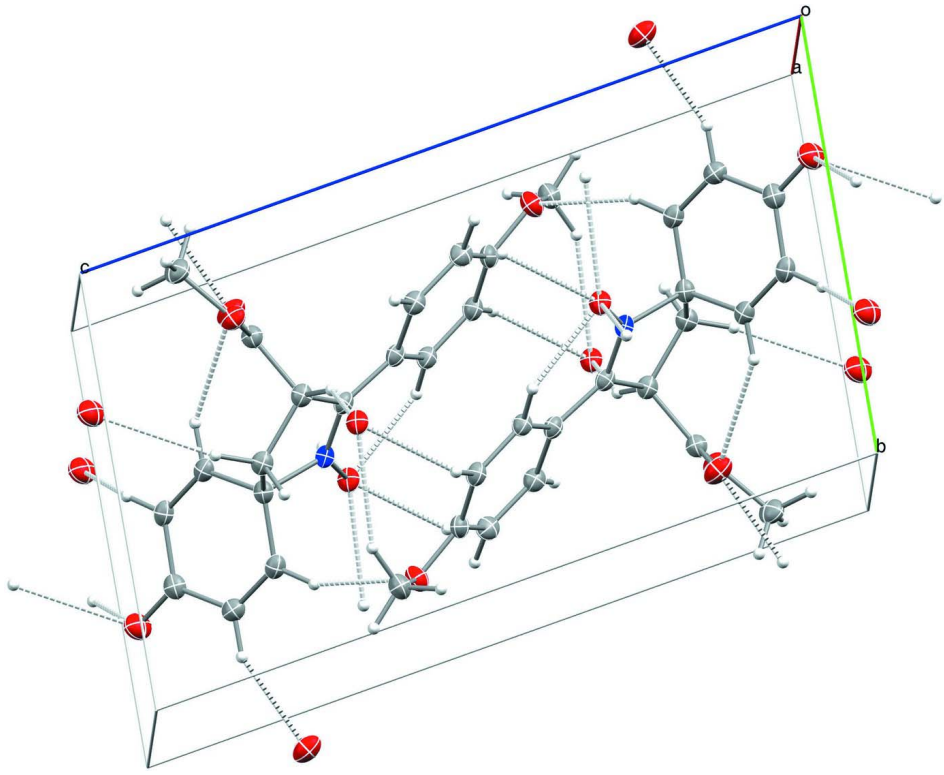

Figure 2

Crystal packing of the title compound, showing hydrogen bonding interactions.

3-Methoxycarbonyl-2-(4-methoxyphenyl)-8-oxo-1-azaspiro[4.5]deca-1,6,9-trien-1-ium-1-olate

Crystal data

$C_{18}H_{17}NO_5$
$M_r = 327.32$
Triclinic, $P\overline{1}$
Hall symbol: -P 1
$a = 6.0916\ (11)$ Å
$b = 8.7713\ (16)$ Å
$c = 15.167\ (3)$ Å
$\alpha = 80.255\ (6)°$
$\beta = 81.703\ (6)°$
$\gamma = 80.122\ (6)°$
$V = 781.3\ (2)$ Å^3
$Z = 2$
$F(000) = 344$
$D_x = 1.391$ Mg m^{-3}
Cu $K\alpha$ radiation, $\lambda = 1.54178$ Å
Cell parameters from 109 reflections
$\theta = 9.0–38.4°$
$\mu = 0.85$ mm^{-1}
$T = 100$ K
Prismatic, colourless
0.47 × 0.20 × 0.17 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Detector resolution: 8.3333 pixels mm^{-1}
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2010)
$T_{min} = 0.813$, $T_{max} = 1.000$
14656 measured reflections
2771 independent reflections
2727 reflections with $I > 2\sigma(I)$
$R_{int} = 0.033$
$\theta_{max} = 67.7°$, $\theta_{min} = 3.0°$
$h = -5\rightarrow7$
$k = -10\rightarrow10$
$l = -18\rightarrow17$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.105$
$S = 1.11$
2771 reflections
220 parameters
0 restraints
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0542P)^2 + 0.3281P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.28$ e Å^{-3}
$\Delta\rho_{min} = -0.35$ e Å^{-3}
Extinction correction: *SHELXL2014* (Sheldrick, 2014), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.043 (2)

Special details

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

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
O2	0.20642 (16)	0.89397 (12)	0.62486 (6)	0.0247 (3)
O5	0.19082 (18)	0.28804 (12)	0.01392 (7)	0.0309 (3)
O1	0.19910 (14)	0.44109 (11)	0.32280 (6)	0.0199 (2)
O4	0.91693 (15)	0.79511 (11)	0.19091 (7)	0.0228 (3)
O3	0.54105 (16)	0.85337 (11)	0.19863 (7)	0.0281 (3)
N1	0.38917 (17)	0.48769 (12)	0.29230 (7)	0.0166 (3)
C8	−0.0287 (2)	0.92550 (17)	0.65513 (10)	0.0252 (3)
H1A	−0.1106	0.9720	0.6036	0.038*
H1B	−0.0535	0.9985	0.6991	0.038*
H1C	−0.0827	0.8276	0.6833	0.038*
C5	0.2673 (2)	0.80731 (16)	0.55566 (9)	0.0202 (3)
C4	0.1260 (2)	0.72330 (16)	0.52570 (9)	0.0200 (3)
H3	−0.0222	0.7203	0.5551	0.024*
C3	0.2017 (2)	0.64391 (15)	0.45269 (9)	0.0189 (3)
H4	0.1048	0.5855	0.4333	0.023*
C2	0.4179 (2)	0.64816 (15)	0.40712 (9)	0.0177 (3)
C1	0.4981 (2)	0.57613 (15)	0.32644 (9)	0.0173 (3)
C13	0.4972 (2)	0.44582 (15)	0.20162 (9)	0.0180 (3)
C14	0.3688 (2)	0.55382 (15)	0.13203 (9)	0.0186 (3)
H8	0.3569	0.6635	0.1312	0.022*
C15	0.2712 (2)	0.50353 (16)	0.07177 (9)	0.0202 (3)
H9	0.1934	0.5777	0.0293	0.024*
C16	0.2811 (2)	0.33526 (16)	0.06944 (9)	0.0216 (3)
C7	0.5596 (2)	0.73034 (16)	0.44026 (9)	0.0207 (3)
H11	0.7083	0.7332	0.4114	0.025*
C6	0.4867 (2)	0.80683 (16)	0.51396 (9)	0.0223 (3)
H12	0.5863	0.8593	0.5363	0.027*
C18	0.4924 (2)	0.27616 (15)	0.20004 (9)	0.0197 (3)

H13	0.5580	0.2010	0.2454	0.024*
C17	0.4002 (2)	0.22581 (16)	0.13799 (9)	0.0213 (3)
H14	0.4117	0.1164	0.1379	0.026*
C12	0.7367 (2)	0.48121 (15)	0.20051 (9)	0.0196 (3)
H15A	0.7956	0.5274	0.1394	0.024*
H15B	0.8389	0.3846	0.2199	0.024*
C9	0.7139 (2)	0.59949 (15)	0.26787 (9)	0.0186 (3)
H16	0.8422	0.5732	0.3049	0.022*
C10	0.7081 (2)	0.76464 (16)	0.21684 (9)	0.0195 (3)
C11	0.9377 (3)	0.93704 (17)	0.12808 (10)	0.0270 (3)
H18A	0.8704	0.9329	0.0738	0.040*
H18B	1.0968	0.9470	0.1118	0.040*
H18C	0.8601	1.0274	0.1561	0.040*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O2	0.0232 (5)	0.0323 (6)	0.0211 (5)	−0.0051 (4)	−0.0046 (4)	−0.0084 (4)
O5	0.0324 (6)	0.0323 (6)	0.0319 (6)	−0.0051 (5)	−0.0150 (5)	−0.0066 (4)
O1	0.0130 (5)	0.0267 (5)	0.0208 (5)	−0.0079 (4)	−0.0007 (4)	−0.0017 (4)
O4	0.0166 (5)	0.0233 (5)	0.0272 (5)	−0.0063 (4)	0.0016 (4)	−0.0003 (4)
O3	0.0188 (5)	0.0246 (5)	0.0372 (6)	−0.0016 (4)	−0.0037 (4)	0.0044 (4)
N1	0.0128 (5)	0.0199 (5)	0.0161 (5)	−0.0027 (4)	−0.0024 (4)	0.0005 (4)
C8	0.0252 (7)	0.0298 (7)	0.0210 (7)	−0.0038 (6)	−0.0018 (6)	−0.0061 (6)
C5	0.0233 (7)	0.0216 (7)	0.0158 (6)	−0.0023 (5)	−0.0067 (5)	−0.0005 (5)
C4	0.0179 (6)	0.0231 (7)	0.0183 (6)	−0.0047 (5)	−0.0025 (5)	0.0008 (5)
C3	0.0180 (6)	0.0209 (6)	0.0184 (6)	−0.0057 (5)	−0.0048 (5)	0.0004 (5)
C2	0.0163 (6)	0.0187 (6)	0.0174 (6)	−0.0028 (5)	−0.0051 (5)	0.0022 (5)
C1	0.0143 (6)	0.0185 (6)	0.0182 (6)	−0.0023 (5)	−0.0051 (5)	0.0019 (5)
C13	0.0139 (6)	0.0229 (7)	0.0166 (6)	−0.0016 (5)	−0.0014 (5)	−0.0023 (5)
C14	0.0140 (6)	0.0202 (6)	0.0190 (6)	−0.0005 (5)	0.0006 (5)	−0.0004 (5)
C15	0.0148 (6)	0.0250 (7)	0.0184 (6)	−0.0002 (5)	−0.0023 (5)	0.0011 (5)
C16	0.0156 (6)	0.0280 (7)	0.0214 (7)	−0.0036 (5)	−0.0017 (5)	−0.0039 (6)
C7	0.0153 (6)	0.0238 (7)	0.0229 (7)	−0.0043 (5)	−0.0045 (5)	−0.0001 (5)
C6	0.0199 (7)	0.0245 (7)	0.0246 (7)	−0.0054 (5)	−0.0094 (5)	−0.0019 (5)
C18	0.0159 (6)	0.0216 (7)	0.0195 (6)	0.0000 (5)	−0.0017 (5)	0.0000 (5)
C17	0.0180 (7)	0.0208 (7)	0.0243 (7)	−0.0027 (5)	−0.0017 (5)	−0.0021 (5)
C12	0.0136 (6)	0.0226 (7)	0.0219 (7)	−0.0013 (5)	−0.0027 (5)	−0.0017 (5)
C9	0.0130 (6)	0.0218 (7)	0.0204 (6)	−0.0021 (5)	−0.0037 (5)	−0.0006 (5)
C10	0.0159 (6)	0.0231 (7)	0.0197 (7)	−0.0041 (5)	−0.0013 (5)	−0.0033 (5)
C11	0.0275 (8)	0.0252 (7)	0.0277 (7)	−0.0109 (6)	0.0023 (6)	0.0002 (6)

Geometric parameters (Å, º)

O2—C5	1.3705 (17)	C13—C14	1.5066 (18)
O2—C8	1.4339 (17)	C13—C12	1.5395 (17)
O5—C16	1.2301 (17)	C14—C15	1.3289 (19)
O1—N1	1.2905 (14)	C14—H8	0.9500

O4—C10	1.3345 (16)	C15—C16	1.473 (2)
O4—C11	1.4462 (17)	C15—H9	0.9500
O3—C10	1.2059 (17)	C16—C17	1.4732 (19)
N1—C1	1.3121 (17)	C7—C6	1.380 (2)
N1—C13	1.5121 (16)	C7—H11	0.9500
C8—H1A	0.9800	C6—H12	0.9500
C8—H1B	0.9800	C18—C17	1.332 (2)
C8—H1C	0.9800	C18—H13	0.9500
C5—C4	1.3908 (19)	C17—H14	0.9500
C5—C6	1.393 (2)	C12—C9	1.5519 (18)
C4—C3	1.3884 (19)	C12—H15A	0.9900
C4—H3	0.9500	C12—H15B	0.9900
C3—C2	1.3996 (19)	C9—C10	1.5197 (18)
C3—H4	0.9500	C9—H16	1.0000
C2—C7	1.4067 (18)	C11—H18A	0.9800
C2—C1	1.4554 (19)	C11—H18B	0.9800
C1—C9	1.5014 (18)	C11—H18C	0.9800
C13—C18	1.4977 (19)		

C5—O2—C8	116.78 (10)	C16—C15—H9	119.3
C10—O4—C11	115.74 (11)	O5—C16—C15	121.67 (13)
O1—N1—C1	128.90 (11)	O5—C16—C17	121.42 (13)
O1—N1—C13	116.85 (10)	C15—C16—C17	116.89 (12)
C1—N1—C13	114.09 (10)	C6—C7—C2	121.25 (12)
O2—C8—H1A	109.5	C6—C7—H11	119.4
O2—C8—H1B	109.5	C2—C7—H11	119.4
H1A—C8—H1B	109.5	C7—C6—C5	120.13 (12)
O2—C8—H1C	109.5	C7—C6—H12	119.9
H1A—C8—H1C	109.5	C5—C6—H12	119.9
H1B—C8—H1C	109.5	C17—C18—C13	123.01 (12)
O2—C5—C4	124.47 (12)	C17—C18—H13	118.5
O2—C5—C6	115.89 (12)	C13—C18—H13	118.5
C4—C5—C6	119.64 (12)	C18—C17—C16	121.73 (13)
C3—C4—C5	119.90 (12)	C18—C17—H14	119.1
C3—C4—H3	120.1	C16—C17—H14	119.1
C5—C4—H3	120.1	C13—C12—C9	105.07 (10)
C4—C3—C2	121.34 (12)	C13—C12—H15A	110.7
C4—C3—H4	119.3	C9—C12—H15A	110.7
C2—C3—H4	119.3	C13—C12—H15B	110.7
C3—C2—C7	117.62 (12)	C9—C12—H15B	110.7
C3—C2—C1	123.04 (12)	H15A—C12—H15B	108.8
C7—C2—C1	119.31 (12)	C1—C9—C10	112.58 (11)
N1—C1—C2	125.30 (12)	C1—C9—C12	103.83 (10)
N1—C1—C9	110.32 (11)	C10—C9—C12	109.86 (11)
C2—C1—C9	124.32 (11)	C1—C9—H16	110.1
C18—C13—C14	113.42 (11)	C10—C9—H16	110.1
C18—C13—N1	109.22 (10)	C12—C9—H16	110.1
C14—C13—N1	106.44 (10)	O3—C10—O4	124.52 (12)

C18—C13—C12	112.45 (11)	O3—C10—C9	125.53 (12)
C14—C13—C12	113.17 (11)	O4—C10—C9	109.87 (11)
N1—C13—C12	101.15 (10)	O4—C11—H18A	109.5
C15—C14—C13	123.35 (12)	O4—C11—H18B	109.5
C15—C14—H8	118.3	H18A—C11—H18B	109.5
C13—C14—H8	118.3	O4—C11—H18C	109.5
C14—C15—C16	121.39 (12)	H18A—C11—H18C	109.5
C14—C15—H9	119.3	H18B—C11—H18C	109.5

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C8—H1*C*···O1^{i}	0.98	2.59	3.4941 (18)	153
C4—H3···O1^{i}	0.95	2.38	3.1345 (16)	136
C3—H4···O1	0.95	2.22	2.8725 (17)	125
C14—H8···O3	0.95	2.57	3.3431 (18)	138
C15—H9···O5^{ii}	0.95	2.56	3.3821 (17)	146
C18—H13···O2^{iii}	0.95	2.54	3.4309 (17)	155
C17—H14···O3^{iv}	0.95	2.38	3.2408 (18)	151
C12—H15*A*···O5^{v}	0.99	2.60	3.5402 (18)	159
C9—H16···O1^{vi}	1.00	2.31	3.2045 (16)	148

Symmetry codes: (i) −*x*, −*y*+1, −*z*+1; (ii) −*x*, −*y*+1, −*z*; (iii) −*x*+1, −*y*+1, −*z*+1; (iv) *x*, *y*−1, *z*; (v) −*x*+1, −*y*+1, −*z*; (vi) *x*+1, *y*, *z*.