IUCrData

ISSN 2414-3146

(*R*,*R*/*S*,*S*)-9-Benzyl-3-methyl-7-phenyl-1,6-dioxa-3,9-diazaspiro[4.4]nonane-2,8-dione

Craig M. Forsyth[a]* and Zohreh Nazarian[b,a]

[a]School of Chemistry, Monash University, Clayton 3800, Australia, and [b]School of Chemistry, Shahid Beheshti University G. C., Evin, Tehran 1983963113, Iran. *Correspondence e-mail: craig.forsyth@monash.edu

Received 15 February 2019
Accepted 16 April 2019

Edited by G. S. Nichol, University of Edinburgh, Scotland

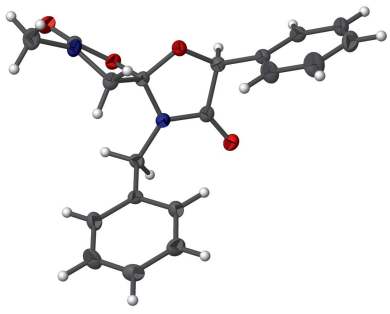
Keywords: crystal structure; spirocyclic compounds; cyclization reactions; oxazolidinone.

CCDC reference: 1486263

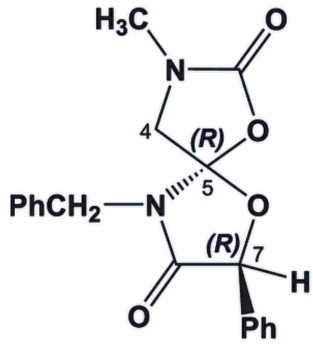
Structural data: full structural data are available from iucrdata.iucr.org

The title compound, $C_{19}H_{18}N_2O_4$, a rare example of a spirocyclic orthoamide, was synthesized by a double cyclization of a *N*-Boc protected sarcosine derivative. The crystal structure of the racemic (*R*,*R*/*S*,*S*) modification reveals two near-orthogonal five-membered heterocyclic ring systems, each in an envelope configuration.

3D view



Chemical scheme



Structure description

The biological significance of spirocyclic molecules has inspired considerable research towards the discovery of new synthetic routes to such compounds (Rios, 2012). We have recently reported (Nazarian & Forsyth, 2016) the preparation of 1,6-dioxa-3,9-diazaspiro[4,4]nonane-2,8-diones, a new class of spirocyclic othoamide. These were achieved by double cyclization of *O*-acylated hydroxamides utilizing a modification of an analogous procedure for 2-oxy-1,3-oxazolidin-4-ones (Kamimura *et al.*, 2002, 2003, 2006).

As part of this study, we prepared the title compound (**B**) from the *N*-Boc-protected sarcosine derivative (**A**). Two diastereomers, solid **B1** and liquid **B2** (Fig. 1) were formed with the solid diastereomer **B1** as the major product. However, attempted crystallization of **B1** in EtOH resulted instead in the formation of crystals of the racemic modification (*R*,*R*/*S*,*S*), presumably due to thermal instability of the spirocyclic nonane and subsequent change in the configuration profile during crystal growth.

The molecular structure and atom numbering scheme of the title compound are shown in Fig. 2. The structure comprises two approximately orthogonal five-membered heterocyclic ring systems [angle between least squares planes = 87.12 (5)°]. The geometry about the central C1 atom is slightly distorted, with a larger N2—C1—C2 angle of 117.4 (1)°, presumably due to the steric influence of the CH_2Ph substituent on N2. The individual heterocycles each have an envelope configuration, on C2 (ring I) and on O3

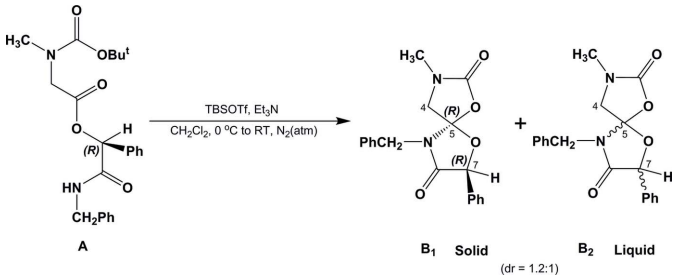


Figure 1
Reaction scheme for the synthesis of 9-benzyl-3-methyl-7-phenyl-1,6-dioxa-3,9-diazaspiro[4,4]nonane-2,8-dione from the sarcosine derivative **A**.

(ring II) and are similar to previous examples of isolated oxazolidin-2-one or oxazolidine-4-one ring systems (Obijalska *et al.*, 2010; El Bouakher *et al.*, 2016).

The crystal packing of molecules of **B1** reveals a weak intermolecular offset π–π ring interaction between parallel, inversion-related, phenyl rings [$Cg1\cdots Cg1^{i}$ 4.608 (1) Å, offset 3.196 Å, interplanar separation *ca* 3.32 Å, *Cg1* defined by atoms C7–C12; symmetry code: (i) $-x, -y, -z$]. In addition, there are minor C—H···O and C—H···π contacts that link molecules into a supramolecular network (Table 1).

A search of the Cambridge Structural Database (CSD Version 5.39, August 2018; Groom *et al.* 2016) for the 1,6-dioxa-3,9-diazaspiro[4,4]nonane-2,8-dione skeleton yielded hits for three substituted analogues from our previous study (CSD refcodes IAPDIO, IAPDOU, IAPDUA; Nazarian & Forsyth, 2016). Additionally, there was one example of an oxazolidine-4-one ring in a spirocyclic multi-ring natural product analogue (CSD refcode KEMXOR; Oguri *et al.*, 2012)

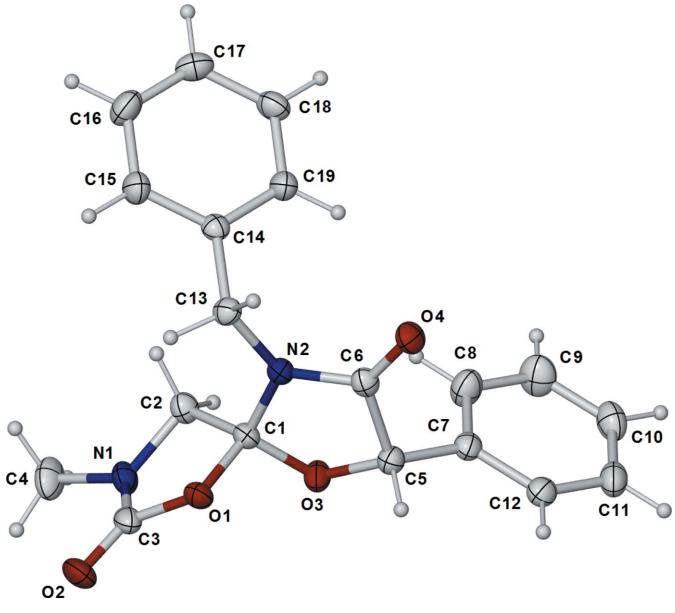


Figure 2
Molecular structure of (*R*,*R*/*S*,*S*)-9-benzyl-3-methyl-7-phenyl-1,6-dioxa-3,9- diazaspiro[4,4]nonane-2,8-dione with non-hydrogen atoms represented by 50% displacement ellipsoids and hydrogen atoms as spheres of arbitrary size. The 5-*S*,7-*S* diastereomer is shown.

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

*Cg*2 is the centroid of the C14–C19 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C18—H18···O2^{i}	0.95	2.34	3.1642 (19)	144
C10—H10···*Cg*2^{ii}	0.95	2.80	3.6106 (16)	144

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

in which the heterocyclic ring has an envelope configuration on the ether oxygen atom, similar to the current structure.

Synthesis and crystallization

(*R*)-2(Benzylamino)-2-oxo-1-phenylethyl-2-{(*t*-butoxycarbonyl)(methyl)amino}acetate (A).

To a solution of *R*-*N*-benzyl-2-hydroxy-2-phenylacetamide (0.30 g,1.24 mmol) in anhydrous CH_2Cl_2 at 0°C, were added *N*-Boc-sarcosine (0.234 g, 1.24 mmol), EDCl·HCl (0.378 g, 1.98 mmol) and DMAP (0.124 g, 0.015 mmol) under an atmosphere of N_2. To the resulting suspension, dried Et_3N (1.61 mmol) was added dropwise while stirring vigorously. The mixture was warmed to room temperature and stirred for 7–8 h. The resulting mixture was diluted with CH_2Cl_2, washed successively with 1*M* HCl(aq) and water, then dried over $MgSO_4$. Solvent removal *in vacuo* gave a yellow oil that was purified by flash chromatography (20% EtOAc/hexanes) to afford the title compound (0.449 g, 88%) as a white foam. (Mixture of two rotomers) **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47–7.20 (*m*, 10 H, Ar*H*), 6.15 (*s*, 1 H, *H*7), 4.54–4.32 (*m*, 2 H, PhCH_2NH), 4.15–3.82 (*m*, 2 H, *H*4), 2.91 and 2.89 (2 × *s*, 3 H, NCH_3), 1.37 and 1.30 (2 × *s*, 9 H, C(CH_3)$_3$). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.5 and 168.3 (O*C*=O), 168 (PhCH_2N(H)*C*=O), 156.8 (O*C*O-*t*-Bu), 138.0 (Ar*C* quaternary), 135.2 (Ar*C* quaternary), 129.2 (Ar*C*), 128.9 (Ar*C*), 128.8 (Ar*C*), 128.7 (Ar*C*), 128.5 (Ar*C*), 127.7 (Ar*C*), 127.6 (Ar*C*), 127.5 (Ar*C*), 127.3 (Ar*C*), 127.3 (Ar*C*), 80.7 and 80.4 (*C*(CH$_3$)$_3$), 76.0 (*C*7), 51.3 and 51.0 (*C*4), 43.2 (Ph*C*H$_2$NH), 36.3 and 35.5 (NCH$_3$), 28.2 and 28.1 (C(*C*H$_3$)$_3$). **IR** ν_{max} 3301 (*br*, *w*), 2975 (*w*), 2929 (*w*), 1754 (*m*), 1663 (*s*), 1536 (*w*), 1453 (*w*), 1389 (*m*), 1366 (*m*), 1239 (*w*), 1144 (*s*), 732 (*w*), 696 (*w*) cm^{-1}. **HRMS** calculated for $C_{23}H_{28}N_2O_5$ $[M+Na]^+$ *m*/*z* = 435.1890; found 435.1891. **Specific rotation** $[\alpha]_D$ −51.8 (*c* 1.0, CH_2Cl_2).

9-Benzyl-3-methyl-7-phenyl-1,6-dioxa-3,9-diazaspiro[4,4]-nonane-2,8-dione (B)

To a stirring solution of **A** (0.191 g, 0.463 mmol) in dry CH_2Cl_2 at 0°C under N_2, was added Et_3N (0.161 ml, 1.15 mmol), followed by TBSOTf (0.301 mL, 1.15 mmol). The reaction mixture was stirred at 0°C for 15–20 min, then warmed to room temperature and stirred for a further 13–14 h. The solvent was removed *in vacuo* and the crude product was purified by flash chromatography, eluting with a solvent gradient of 20–40% EtOAc/hexanes to yield the title compound as a mixture of diastereomers in a 1:1.2 dr ratio (87 mg, 56% combined yield). **Major diastereomer B1 (solid)**

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{19}H_{18}N_2O_4$
M_r	338.35
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	123
a, b, c (Å)	11.0914 (4), 13.6412 (4), 11.9739 (4)
β (°)	113.863 (4)
V (Å^3)	1656.78 (11)
Z	4
Radiation type	Cu $K\alpha$
μ (mm^{-1})	0.79
Crystal size (mm)	0.25 × 0.10 × 0.05
Data collection	
Diffractometer	Rigaku Xcalibur Ruby Gemini ultra
Absorption correction	Multi-scan (*CrysAlis PRO*; Rigaku OD, 2015)
T_{min}, T_{max}	0.927, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	17312, 2944, 2699
R_{int}	0.027
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.597
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.035, 0.088, 1.05
No. of reflections	2944
No. of parameters	227
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.20, −0.25

Computer programs: *CrysAlis PRO* (Rigaku OD, 2015), *SHELXS97* (Sheldrick, 2008), *SHELXL2018* (Sheldrick, 2015), *X-SEED* (Barbour, 2001), *PLATON* (Spek, 2009) and *publCIF* (Westrip, 2010).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44–7.25 (*m*, 10 H, Ar*H*), 5.52 (*s*, 1 H, *H*7), 5.10 (*d*, *J* = 15.6 Hz, 1 H, NCH_2Ph), 4.09 (*d*, *J* = 15.7 Hz, 1 H, NCH_2Ph), 3.58 (*d*, *J* = 11.1 Hz, 1 H, *H*4), 3.33 (*d*, *J* = 11.1 Hz, 1 H, *H*4), 2.80 (*s*, 3 H, NCH_3). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.4 (*C*8), 154.6 (*C*2), 135.4 (Ar*C* quaternary), 133.9 (Ar*C* quaternary), 129.3 (Ar*C*), 129.1 (Ar*C*), 129.0 (Ar*C*), 128.4 (Ar*C*), 127.9 (Ar*C*), 126.5 (Ar*C*), 111.8 (*C*5), 78.4 (*C*7), 54.2 (*C*4), 43.8 (N*C*H$_2$Ph), 30.2 (N*C*H$_3$). **IR** ν_{max} 3033 (*w*), 2928 (*w*), 1769 (*s*), 1731 (*s*), 1413 (*w*), 1396 (*m*), 1365 (*w*), 974 (*w*) cm^{-1}. **HRMS** calculated for $C_{19}H_{18}N_2O_4$ $[M+H]^+$ *m*/*z* = 339.1339; found 339.1345. **Specific rotation** $[\alpha]_D$ −86 (*c* 0.73, CH_3OH). **Minor diastereomer B2 (liquid) ^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55–7.26 (*m*, 10 H, Ar*H*), 5.48 (*s*, 1 H, *H*7), 5.04 (*d*, *J* = 15.5 Hz, 1 H, NCH_2Ph), 4.09 (*d*, *J* = 15.5 Hz, 1 H, NCH_2Ph), 3.56 (*d*, *J* = 11.0 Hz, 1 H, *H*4), 3.23 (*d*, *J* = 11.0 Hz, 1 H, *H*4), 2.78 (*s*, 3 H, NCH_3). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.9 (*C*8), 154.7 (*C*2), 135.4 (Ar*C* quaternary), 134.4 (Ar*C* quaternary), 129.2 (Ar*C*), 129.0 (Ar*C*), 128.7 (Ar*C*), 128.4 (Ar*C*), 126.6 (Ar*C*), 112.4 (*C*5), 79.7 (*C*7), 54.9 (*C*4), 43.9 (N*C*H$_2$Ph), 30.3 (N*C*H$_3$). **IR** ν_{max} 3032 (*w*), 2929 (*w*), 1768 (*s*), 1728 (*s*), 1413 (*w*), 1398 (*m*), 1364 (*w*), 976 (*w*) cm^{-1}. **HRMS** calculated for $C_{19}H_{18}N_2O_4$ $[M+H]^+$ 339.1339; found 339.1345. **Specific rotation** $[\alpha]_D$ +10.16 (*c* 0.41 CH_2Cl_2).

Attempted crystallization of the major diastereomer **B1** by dissolution of the solid compound in hot EtOH gave colourless prisms of the *R*,*R*/*S*,*S* racemate.

Refinement

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

Funding information

The authors are grateful for financial support from the Monash Institute of Graduate Research through the award of a PhD scholarship to ZN.

References

Barbour, L. J. (2001). *J. Supramol. Chem.* **1**, 189–191.
El Bouakher, A., Le Goff, R., Tasserie, J., Lhoste, J., Martel, A. & Comesse, S. (2016). *Org. Lett.* **18**, 2382–2386.
Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* B**72**, 171–179.
Kamimura, A., Omata, Y., Kakehi, A. & Shirai, M. (2002). *Tetrahedron*, **58**, 8763–8770.
Kamimura, A., Omata, Y., Tanaka, K. & Shirai, M. (2003). *Tetrahedron*, **59**, 6291–6299.
Kamimura, A., Tanaka, K., Hayashi, T. & Omata, Y. (2006). *Tetrahedron Lett.* **47**, 3625–3627.
Nazarian, Z. & Forsyth, C. M. (2016). *RSC Adv.* **6**, 55534–55538.
Obijalska, E., Mlostoń, G., Linden, A. & Heimgartner, H. (2010). *Helv. Chim. Acta*, **93**, 1725–1736.
Oguri, H., Mizoguchi, H., Oikawa, H., Ishiyama, A., Iwatsuki, M., Otoguro, K. & Ōmura, S. (2012). *Beilstein J. Org. Chem.* **8**, 930–940.
Rigaku OD (2015). *CrysAlis PRO*. Rigaku Oxford Diffraction, Yarnton, England.
Rios, R. (2012). *Chem. Soc. Rev.* **41**, 1060–1074.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Sheldrick, G. M. (2015). *Acta Cryst.* C**71**, 3–8.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

full crystallographic data

IUCrData (2019). **4**, x190520 [https://doi.org/10.1107/S2414314619005200]

(*R*,*R*/*S*,*S*)-9-Benzyl-3-methyl-7-phenyl-1,6-dioxa-3,9-diazaspiro[4.4]nonane-2,8-dione

Craig M. Forsyth and Zohreh Nazarian

(*R*,*R*/*S*,*S*)-9-Benzyl-3-methyl-7-phenyl-1,6-dioxa-3,9-diazaspiro[4.4]nonane-2,8-dione

Crystal data

$C_{19}H_{18}N_2O_4$
M_r = 338.35
Monoclinic, $P2_1/n$
a = 11.0914 (4) Å
b = 13.6412 (4) Å
c = 11.9739 (4) Å
β = 113.863 (4)°
V = 1656.78 (11) Å^3
Z = 4
$F(000)$ = 712
D_x = 1.356 Mg m^{-3}
Cu $K\alpha$ radiation, λ = 1.54184 Å
Cell parameters from 7087 reflections
θ = 3.2–66.9°
μ = 0.79 mm^{-1}
T = 123 K
Prism, colourless
0.25 × 0.10 × 0.05 mm

Data collection

Rigaku Xcalibur Ruby Gemini ultra diffractometer
Radiation source: fine focus sealed tube
Mirror monochromator
Detector resolution: 10.3389 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (CrysAlis PRO; Rigaku OD, 2015)
T_{min} = 0.927, T_{max} = 1.000
17312 measured reflections
2944 independent reflections
2699 reflections with $I > 2\sigma(I)$
R_{int} = 0.027
θ_{max} = 67.0°, θ_{min} = 4.6°
h = −13→13
k = −16→16
l = −13→14

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.088
S = 1.05
2944 reflections
227 parameters
0 restraints
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0431P)^2 + 0.5909P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.20 e Å^{-3}
$\Delta\rho_{min}$ = −0.25 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.

Refinement. Hydrogen atoms were included in the refinement at calculated positions with C—H = 0.95–0.98 Å and treated as riding with U_{iso}(H) = 1.2U_{eq}(C) or 1.5U_{eq}(methyl C). Geometrical calculations were performed using *PLATON* (Spek, 2009).

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

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.30052 (8)	0.18504 (7)	0.42698 (8)	0.0240 (2)
O2	0.51661 (9)	0.15756 (9)	0.53756 (10)	0.0370 (3)
O3	0.13155 (9)	0.08339 (7)	0.30163 (8)	0.0262 (2)
O4	−0.09916 (9)	0.27442 (7)	0.23543 (8)	0.0265 (2)
N1	0.35613 (11)	0.05967 (8)	0.55571 (10)	0.0257 (3)
N2	0.07999 (10)	0.20997 (8)	0.39423 (9)	0.0212 (2)
C1	0.17850 (12)	0.13722 (9)	0.41040 (11)	0.0212 (3)
C2	0.21542 (12)	0.06973 (10)	0.52047 (12)	0.0245 (3)
H2A	0.195578	0.100051	0.586248	0.029*
H2B	0.169756	0.005773	0.497868	0.029*
C3	0.40365 (12)	0.13439 (10)	0.51217 (12)	0.0256 (3)
C4	0.43909 (16)	0.00450 (12)	0.66301 (14)	0.0382 (4)
H4A	0.531105	0.008769	0.673022	0.057*
H4B	0.411239	−0.064295	0.653082	0.057*
H4C	0.430920	0.031765	0.735349	0.057*
C5	0.03485 (12)	0.14058 (9)	0.20589 (11)	0.0229 (3)
H5	0.077093	0.173387	0.156165	0.028*
C6	−0.00674 (12)	0.21743 (9)	0.27596 (11)	0.0221 (3)
C7	−0.07615 (12)	0.07618 (9)	0.12528 (12)	0.0230 (3)
C8	−0.14058 (15)	0.01396 (11)	0.17482 (13)	0.0341 (3)
H8	−0.114380	0.011638	0.260766	0.041*
C9	−0.24301 (16)	−0.04480 (12)	0.09927 (15)	0.0389 (4)
H9	−0.286665	−0.087432	0.133586	0.047*
C10	−0.28201 (14)	−0.04155 (11)	−0.02631 (14)	0.0332 (3)
H10	−0.352334	−0.081813	−0.077997	0.040*
C11	−0.21818 (14)	0.02050 (11)	−0.07603 (13)	0.0309 (3)
H11	−0.244734	0.022950	−0.162014	0.037*
C12	−0.11513 (13)	0.07931 (10)	−0.00018 (12)	0.0259 (3)
H12	−0.071317	0.121773	−0.034527	0.031*
C13	0.08804 (12)	0.27981 (9)	0.48963 (11)	0.0224 (3)
H13A	0.053659	0.343955	0.451291	0.027*
H13B	0.181783	0.288903	0.545309	0.027*
C14	0.01220 (12)	0.24816 (9)	0.56362 (11)	0.0206 (3)
C15	0.06565 (13)	0.26214 (11)	0.68900 (12)	0.0288 (3)
H15	0.152564	0.287306	0.728776	0.035*
C16	−0.00679 (15)	0.23967 (11)	0.75711 (13)	0.0340 (3)
H16	0.030622	0.249980	0.842907	0.041*
C17	−0.13275 (14)	0.20246 (10)	0.70050 (13)	0.0305 (3)
H17	−0.182498	0.187761	0.746961	0.037*
C18	−0.18620 (13)	0.18667 (11)	0.57578 (13)	0.0294 (3)
H18	−0.272484	0.160259	0.536577	0.035*

C19	−0.11400 (13)	0.20934 (10)	0.50763 (12)	0.0263 (3)
H19	−0.151291	0.198200	0.421991	0.032*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0182 (4)	0.0298 (5)	0.0253 (5)	−0.0012 (4)	0.0101 (4)	0.0011 (4)
O2	0.0182 (5)	0.0530 (7)	0.0397 (6)	−0.0017 (4)	0.0116 (4)	−0.0089 (5)
O3	0.0244 (5)	0.0284 (5)	0.0216 (5)	0.0056 (4)	0.0049 (4)	−0.0035 (4)
O4	0.0241 (5)	0.0270 (5)	0.0255 (5)	0.0058 (4)	0.0071 (4)	0.0037 (4)
N1	0.0203 (5)	0.0271 (6)	0.0236 (6)	0.0049 (4)	0.0026 (4)	0.0001 (4)
N2	0.0189 (5)	0.0240 (5)	0.0202 (5)	0.0016 (4)	0.0076 (4)	−0.0005 (4)
C1	0.0167 (6)	0.0253 (6)	0.0215 (6)	0.0001 (5)	0.0077 (5)	−0.0005 (5)
C2	0.0222 (6)	0.0250 (6)	0.0244 (7)	0.0002 (5)	0.0074 (5)	0.0024 (5)
C3	0.0197 (6)	0.0321 (7)	0.0240 (6)	0.0027 (5)	0.0078 (5)	−0.0066 (5)
C4	0.0376 (8)	0.0362 (8)	0.0287 (7)	0.0121 (7)	0.0010 (6)	0.0022 (6)
C5	0.0227 (6)	0.0259 (7)	0.0199 (6)	0.0016 (5)	0.0082 (5)	0.0009 (5)
C6	0.0206 (6)	0.0227 (6)	0.0226 (6)	−0.0013 (5)	0.0083 (5)	0.0026 (5)
C7	0.0219 (6)	0.0240 (6)	0.0221 (6)	0.0038 (5)	0.0076 (5)	−0.0011 (5)
C8	0.0369 (8)	0.0383 (8)	0.0252 (7)	−0.0067 (6)	0.0108 (6)	0.0012 (6)
C9	0.0392 (8)	0.0355 (8)	0.0395 (9)	−0.0112 (7)	0.0134 (7)	0.0010 (7)
C10	0.0275 (7)	0.0293 (7)	0.0340 (8)	−0.0018 (6)	0.0034 (6)	−0.0050 (6)
C11	0.0272 (7)	0.0352 (7)	0.0240 (7)	0.0037 (6)	0.0038 (5)	−0.0035 (6)
C12	0.0248 (6)	0.0283 (7)	0.0246 (7)	0.0036 (5)	0.0098 (5)	0.0008 (5)
C13	0.0226 (6)	0.0226 (6)	0.0228 (6)	−0.0026 (5)	0.0098 (5)	−0.0046 (5)
C14	0.0202 (6)	0.0189 (6)	0.0230 (6)	0.0019 (5)	0.0090 (5)	−0.0017 (5)
C15	0.0246 (6)	0.0354 (7)	0.0237 (7)	−0.0044 (6)	0.0070 (5)	−0.0045 (6)
C16	0.0404 (8)	0.0407 (8)	0.0214 (7)	−0.0044 (7)	0.0131 (6)	−0.0027 (6)
C17	0.0362 (8)	0.0302 (7)	0.0331 (7)	−0.0002 (6)	0.0224 (6)	0.0009 (6)
C18	0.0218 (6)	0.0335 (7)	0.0347 (7)	−0.0031 (5)	0.0134 (6)	−0.0030 (6)
C19	0.0226 (6)	0.0334 (7)	0.0223 (6)	−0.0011 (5)	0.0083 (5)	−0.0031 (5)

Geometric parameters (Å, º)

O1—C3	1.3719 (16)	C8—C9	1.386 (2)
O1—C1	1.4418 (15)	C8—H8	0.9500
O2—C3	1.2058 (17)	C9—C10	1.387 (2)
O3—C1	1.3992 (15)	C9—H9	0.9500
O3—C5	1.4417 (15)	C10—C11	1.383 (2)
O4—C6	1.2199 (16)	C10—H10	0.9500
N1—C3	1.3457 (19)	C11—C12	1.391 (2)
N1—C2	1.4490 (17)	C11—H11	0.9500
N1—C4	1.4516 (18)	C12—H12	0.9500
N2—C6	1.3560 (16)	C13—C14	1.5105 (17)
N2—C1	1.4300 (16)	C13—H13A	0.9900
N2—C13	1.4622 (16)	C13—H13B	0.9900
C1—C2	1.5218 (18)	C14—C15	1.3862 (18)
C2—H2A	0.9900	C14—C19	1.3892 (18)

C2—H2B	0.9900	C15—C16	1.391 (2)
C4—H4A	0.9800	C15—H15	0.9500
C4—H4B	0.9800	C16—C17	1.379 (2)
C4—H4C	0.9800	C16—H16	0.9500
C5—C7	1.5025 (18)	C17—C18	1.383 (2)
C5—C6	1.5260 (18)	C17—H17	0.9500
C5—H5	1.0000	C18—C19	1.3898 (19)
C7—C12	1.3857 (18)	C18—H18	0.9500
C7—C8	1.388 (2)	C19—H19	0.9500

C3—O1—C1	109.17 (10)	C8—C7—C5	120.85 (12)
C1—O3—C5	109.46 (9)	C9—C8—C7	120.18 (14)
C3—N1—C2	111.10 (10)	C9—C8—H8	119.9
C3—N1—C4	121.89 (12)	C7—C8—H8	119.9
C2—N1—C4	121.95 (12)	C8—C9—C10	120.20 (14)
C6—N2—C1	111.95 (10)	C8—C9—H9	119.9
C6—N2—C13	124.08 (11)	C10—C9—H9	119.9
C1—N2—C13	123.00 (10)	C11—C10—C9	119.79 (13)
O3—C1—N2	105.19 (9)	C11—C10—H10	120.1
O3—C1—O1	109.93 (10)	C9—C10—H10	120.1
N2—C1—O1	109.14 (10)	C10—C11—C12	120.02 (13)
O3—C1—C2	110.92 (10)	C10—C11—H11	120.0
N2—C1—C2	117.40 (10)	C12—C11—H11	120.0
O1—C1—C2	104.22 (9)	C7—C12—C11	120.24 (13)
N1—C2—C1	100.97 (10)	C7—C12—H12	119.9
N1—C2—H2A	111.6	C11—C12—H12	119.9
C1—C2—H2A	111.6	N2—C13—C14	113.54 (10)
N1—C2—H2B	111.6	N2—C13—H13A	108.9
C1—C2—H2B	111.6	C14—C13—H13A	108.9
H2A—C2—H2B	109.4	N2—C13—H13B	108.9
O2—C3—N1	129.11 (13)	C14—C13—H13B	108.9
O2—C3—O1	121.61 (13)	H13A—C13—H13B	107.7
N1—C3—O1	109.27 (10)	C15—C14—C19	118.75 (12)
N1—C4—H4A	109.5	C15—C14—C13	120.01 (11)
N1—C4—H4B	109.5	C19—C14—C13	121.16 (11)
H4A—C4—H4B	109.5	C14—C15—C16	120.62 (13)
N1—C4—H4C	109.5	C14—C15—H15	119.7
H4A—C4—H4C	109.5	C16—C15—H15	119.7
H4B—C4—H4C	109.5	C17—C16—C15	120.23 (13)
O3—C5—C7	110.31 (10)	C17—C16—H16	119.9
O3—C5—C6	103.16 (9)	C15—C16—H16	119.9
C7—C5—C6	113.79 (10)	C16—C17—C18	119.64 (13)
O3—C5—H5	109.8	C16—C17—H17	120.2
C7—C5—H5	109.8	C18—C17—H17	120.2
C6—C5—H5	109.8	C17—C18—C19	120.16 (13)
O4—C6—N2	126.17 (12)	C17—C18—H18	119.9
O4—C6—C5	127.68 (11)	C19—C18—H18	119.9
N2—C6—C5	106.15 (10)	C14—C19—C18	120.59 (12)

C12—C7—C8	119.57 (13)	C14—C19—H19	119.7
C12—C7—C5	119.58 (12)	C18—C19—H19	119.7

Hydrogen-bond geometry (Å, º)

*Cg*2 is the centroid of the C14–C19 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C18—H18···O2^{i}	0.95	2.34	3.1642 (19)	144
C10—H10···*Cg*2^{ii}	0.95	2.80	3.6106 (16)	144

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