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(3*R*,4*S*)-3,4-Isopropylidenedioxy-5-phenylsulfonylmethyl-3,4-dihydro-2*H*-pyrrole 1-oxide

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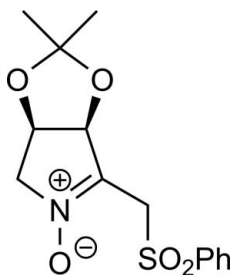
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Key indicators: single-crystal X-ray study; $T = 298$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; R factor = 0.034; wR factor = 0.084; data-to-parameter ratio = 13.0.

The title compound, $\text{C}_{14}\text{H}_{17}\text{NO}_5\text{S}$, was prepared by oxidation of (2*R*,3*S*,4*R*)-2-phenylsulfonylmethyl-1-hydroxy-3,4-isopropylidenedioxypyrrolidine. Its crystal structure confirms unequivocally its configuration. Two intermolecular C—H...O interactions help to establish the packing.

Related literature

For the preparation, see: Flores *et al.* (2010). For the standard oxidation of hydroxylamines to nitrones with manganese dioxide, see: Cicchi *et al.* (2001). For background to organocatalysts, see: Berkessel & Groger (2005); Macmillan (2008). For analogues of the organocatalyst L-proline, see: Andrey *et al.* (2004); Cobb *et al.* (2004); Tanaka *et al.* (2004); Wang *et al.* (2005).



Experimental

Crystal data

$\text{C}_{14}\text{H}_{17}\text{NO}_5\text{S}$
 $M_r = 311.35$
Orthorhombic, $P2_12_12_1$
 $a = 5.6424$ (2) Å

$b = 15.5592$ (7) Å
 $c = 16.9097$ (8) Å
 $V = 1484.52$ (11) Å³
 $Z = 4$

Cu $K\alpha$ radiation
 $\mu = 2.14$ mm⁻¹

$T = 298$ K
 $0.10 \times 0.08 \times 0.06$ mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (SADABS; Bruker, 2006)
 $T_{\min} = 0.815$, $T_{\max} = 0.880$

8018 measured reflections
2487 independent reflections
2159 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.030$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.034$
 $wR(F^2) = 0.084$
 $S = 1.06$
2487 reflections
192 parameters

H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.14$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.15$ e Å⁻³
Absolute structure: Flack (1983), Flack parameter: 0.06 (2)

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{C4}-\text{H4}\cdots\text{O4}^{\text{i}}$	0.98	2.50	3.389 (2)	151
$\text{C12}-\text{H12}\cdots\text{O3}^{\text{ii}}$	0.93	2.51	3.270 (4)	139

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

Data collection: APEX2 (Bruker 2006); cell refinement: SAINT (Bruker 2006); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: Mercury (Macrae *et al.*, 2008); software used to prepare material for publication: SHELXTL (Sheldrick, 2008).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT5495).

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(3*R*,4*S*)-3,4-Isopropylidenedioxy-5-phenylsulfonylmethyl-3,4-dihydro-2*H*-pyrrole 1-oxide

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S1. Comment

Recently there has been an enormous interest in organocatalysis (Berkessel & Groger *et al.* 2005 and Macmillan, 2008). Among the many known organocatalysts *L*-proline is perhaps the one which has been most studied. This fact has led to the appearance of many analogues (Andrey *et al.*, 2004; Wang *et al.*, 2005; Cobb *et al.*, 2004; Tanaka *et al.*, 2004). In our research group we have developed new organocatalyst using nitrones as starting material (Flores *et al.*, 2010). This catalyst was obtained from chiral hydroxylamine (I) (Fig. 1). Here we communicate the oxidation of this compound into nitron II and the crystal structure determination.

The crystal contains an unique molecule in the asymmetric unit (Fig. 2). The title molecule consists of a pyrroline-N-oxide ring with a phenylsulfonylmethyl group and an isopropylidenedioxy group as substituents. All the bond lengths and angles are within the normal ranges. Statistically no difference is observed between the S1—O4 = 1.4310 (19) Å and S1—O5 = 1.4334 (18) Å distances suggesting that the two oxygen are very similar. The S1—C8 and S1—C9 bond lengths are 1.784 (2) Å and 1.755 (3) Å, respectively. The C—S—C and O—S—O angles are 104.02 (12)° and 119.46 (14)°, respectively. The large O—S—O angle and this deviation from the optimal 109.5° angle can be explained by the repulsion of the lone pairs of the oxygen placing the oxygen atoms as far away from each other as possible and thus minimizing the C—S—C angle. The molecule is twisted at the C—S bond being the C2—C8—S1—C9 torsion angle of -59.4 (7)°. The carbonyl group at atom N1 is desviated from the planar conformation with the pyrroline ring being the O3—N1—C3—C4 torsion angle of 165.9 (5)°.

Crystal packing (Fig. 3) is stabilized by two intermolecular C-H...O interactions. One occurs between the carbon atom (C4) of the isopropylidenedioxypyrroline group and the oxygen atom (O4) of the phenylsulfonylmethyl group of the neighboring molecule oriented in the opposite direction along *c* axis with $d(\text{C4-H4}\cdots\text{O4}) = 3.389$ (2) Å and $\langle \text{C4-H4}\cdots\text{O4} \rangle = 151^\circ$. This leads to infinite molecular chains running along the [001] direction, which are joined each other along the *b* axis by another intermolecular interaction between the oxygen atom (O3) of the pyrroline group and the carbon atom (C12) of the phenyl group of the next molecule with $d(\text{C12-H3}\cdots\text{O3}) = 3.270$ (1) Å and $\langle \text{C12-H3}\cdots\text{O3} \rangle = 139^\circ$.

S2. Experimental

The title N-oxide, (II), was obtained by spontaneous oxidation of (2*R*,3*S*,4*R*)-2-Phenylsulfonylmethyl-1-hydroxy-3,4-isopropylidenedioxypyrrolidine (I) (Flores *et al.* 2010) in a 30% of yield. Our attention was then turned to the synthesis of this nitron because of the important role nitrones play in organic syntheses, particularly in the field of alkaloids, nitrogen containing natural products or bioactive analogues. Taking this into account we tried the standard oxidation of hydroxylamines to nitrones with manganese dioxide according to the methodology described by Cicchi *et al.* (2001). MnO₂ (107.2 mg, 1.11 mmol) was added to a solution of hydroxylamine I (234 mg, 0.74 mmol) in DCM (1.5 ml) at 0° C. The resulting

mixture was stirred for 2 h, then it was filtered through celite; and concentrated. The resulting crude residue was purified by flash chromatography (silica gel, hexane/ EtAcO 1:1) to obtain the nitron II (229 mg, 98%) (Flores *et al.*, 2010). Well shaped colourless single crystals were obtained by crystallization from EtOAc/Et₂O. $[\alpha]_D^{20} = +110.7$ ($c = 1.17$, CHCl₃). IR (film): 3376 (broad), 3058, 2995, 2967, 1580 cm⁻¹. ¹H NMR (200 MHz, CDCl₃, δ p.p.m.): 7.94 (2H, m, H_{orto}), 7.69–7.58 (3H, m, H_{meta} H_{para}), 5.58 (1H, d, $J = 6.2$ Hz, H-4), 4.87 (1H, t, $J = 6.2$ and 12 Hz H-3), 4.04 (2H, d, $J = 4.4$ Hz, H-2), 3.96 (2H, s, 2H-1) 1.38 (3H, s, Me-acetonide), 1.37 (3H, s, Me-acetonide). ¹³C NMR (50 MHz, CDCl₃, δ p.p.m.): 139.7 (C—Ar), 134.62 (CH-*para*), 134.0 (C-5), 129.6 (2CH-*meta*), 128.1 (2CH-*orto*), 112.6 (C-acetonide), 80.8 (CH-4), 71.7 (CH-3), 68.1 (CH₂-2), 52.1 (CH₂-1), 27.2 (Me-acetonide), 25.8 (Me-acetonide). HRMS (EI): C₁₄H₁₇NO₅S requires ($M+Na$)⁺, 334.0725, found 334.0703.

S3. Refinement

The hydrogen atoms were positioned geometrically with C—H distances constrained to 0.93 Å (aromatic CH), 0.96 Å (methyl groups), 0.97 Å (methylene groups) and refined using a riding mode with $U_{iso}(H) = xU_{eq}(C)$, where $x = 1.5$ for methyl H atoms and $x = 1.2$ for all other atoms.

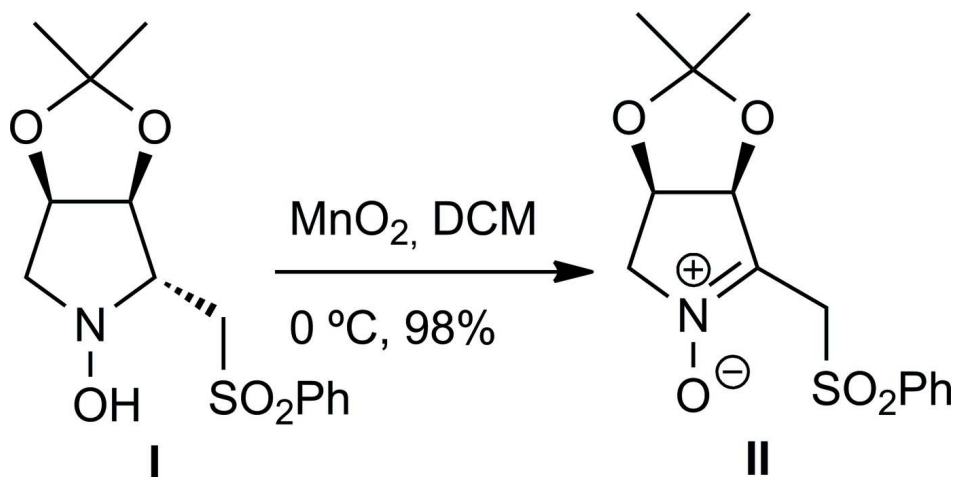


Figure 1

Reaction scheme.

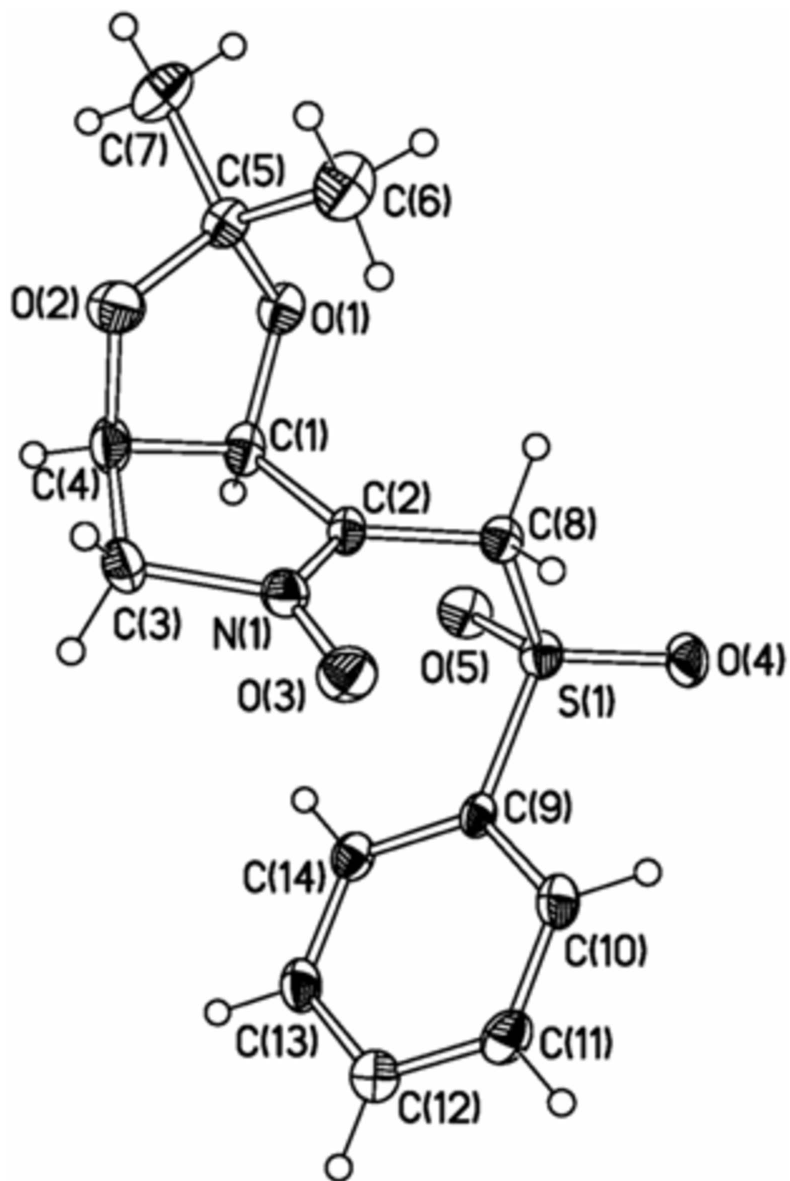


Figure 2

Molecular structure of $C_{14}H_{17}NO_5S$. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms are shown as spheres of arbitrary radius.

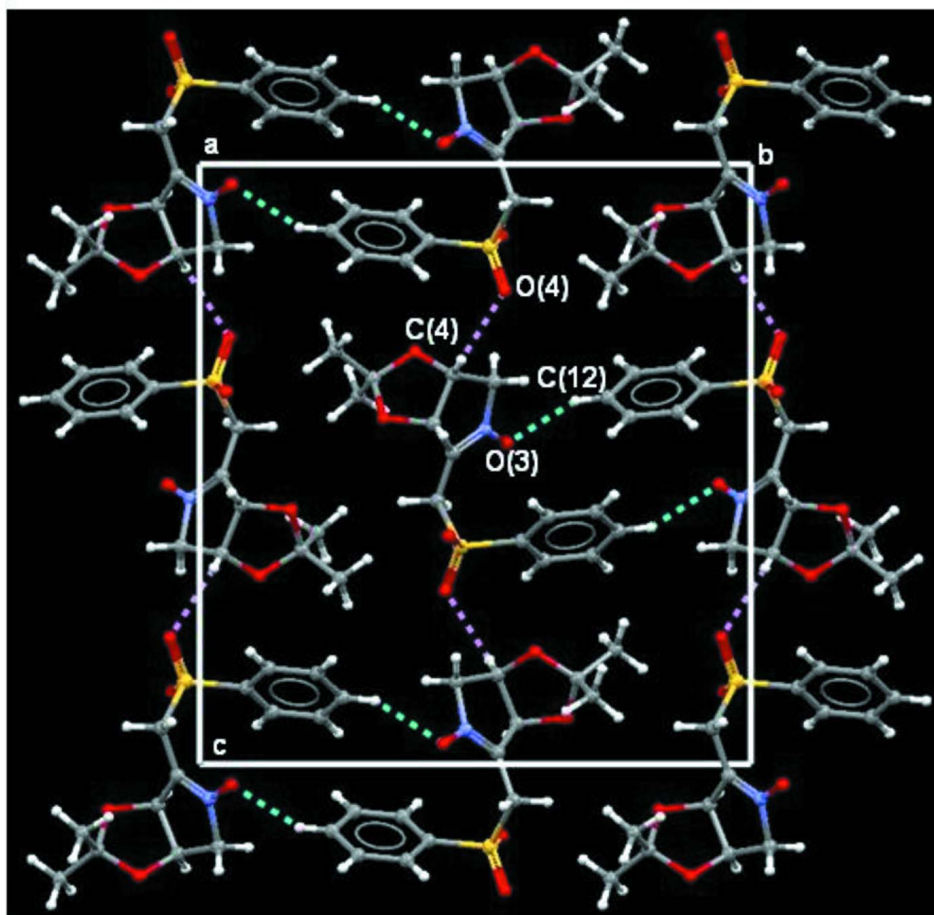


Figure 3

Crystal packing of $C_{14}H_{17}NO_5S$ view along a axis, showing intermolecular hydrogen bonding.

(3*R*,4*S*)-3,4-Isopropylidenedioxy-5-phenylsulfonylmethyl- 3,4-dihydro-2*H*-pyrrole 1-oxide

Crystal data

$C_{14}H_{17}NO_5S$

$M_r = 311.35$

Orthorhombic, $P2_12_12_1$

Hall symbol: $P\ 2ac\ 2ab$

$a = 5.6424\ (2)\ \text{\AA}$

$b = 15.5592\ (7)\ \text{\AA}$

$c = 16.9097\ (8)\ \text{\AA}$

$V = 1484.52\ (11)\ \text{\AA}^3$

$Z = 4$

$F(000) = 656$

$D_x = 1.393\ \text{Mg m}^{-3}$

$\text{Cu } K\alpha$ radiation, $\lambda = 1.54178\ \text{\AA}$

Cell parameters from 1922 reflections

$\theta = 3.9\text{--}55.3^\circ$

$\mu = 2.14\ \text{mm}^{-1}$

$T = 298\ \text{K}$

Prismatic, colourless

$0.10 \times 0.08 \times 0.06\ \text{mm}$

Data collection

Bruker APEXII CCD area-detector
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

phi and ω scans

Absorption correction: multi-scan
(*SADABS*; Bruker, 2006)

$T_{\min} = 0.815$, $T_{\max} = 0.880$

8018 measured reflections

2487 independent reflections

2159 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.030$
 $\theta_{\text{max}} = 67.5^\circ$, $\theta_{\text{min}} = 3.9^\circ$
 $h = -6 \rightarrow 5$

$k = -18 \rightarrow 15$
 $l = -18 \rightarrow 19$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.034$
 $wR(F^2) = 0.084$
 $S = 1.06$
 2487 reflections
 192 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-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0335P)^2 + 0.1514P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.14 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.15 \text{ e } \text{\AA}^{-3}$
 Absolute structure: Flack (1983), 907 Friedel
 pairs
 Absolute structure parameter: 0.06 (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.

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 $F^2 > \sigma(F^2)$ 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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.89076 (11)	0.02630 (4)	0.36234 (4)	0.05643 (18)
O1	0.8060 (3)	0.16596 (13)	0.57625 (11)	0.0614 (5)
O2	0.9722 (5)	0.10911 (14)	0.68680 (13)	0.0894 (7)
O3	1.3072 (4)	-0.05736 (13)	0.53437 (13)	0.0813 (6)
O4	0.9927 (4)	0.05353 (13)	0.28901 (11)	0.0739 (6)
O5	0.6496 (3)	0.04808 (13)	0.37996 (14)	0.0738 (6)
N1	1.1197 (4)	-0.01709 (14)	0.55737 (13)	0.0619 (6)
C1	0.8010 (4)	0.07555 (18)	0.56728 (16)	0.0587 (7)
H1	0.6470	0.0557	0.5477	0.070*
C2	0.9998 (4)	0.04067 (16)	0.51895 (15)	0.0521 (6)
C3	1.0217 (6)	-0.03387 (19)	0.63738 (19)	0.0805 (8)
H3A	1.1460	-0.0341	0.6770	0.097*
H3B	0.9384	-0.0884	0.6390	0.097*
C4	0.8538 (5)	0.0402 (2)	0.64986 (17)	0.0729 (8)
H4	0.7099	0.0231	0.6782	0.088*
C5	0.9533 (4)	0.18574 (16)	0.64286 (17)	0.0549 (6)
C6	1.1963 (5)	0.2119 (3)	0.6143 (2)	0.0922 (11)
H6A	1.2918	0.2289	0.6586	0.138*
H6B	1.1819	0.2592	0.5782	0.138*
H6C	1.2698	0.1642	0.5878	0.138*

C7	0.8367 (6)	0.2541 (2)	0.6910 (2)	0.0864 (10)
H7A	0.6857	0.2338	0.7094	0.130*
H7B	0.8143	0.3045	0.6591	0.130*
H7C	0.9351	0.2680	0.7355	0.130*
C8	1.0714 (4)	0.06909 (17)	0.43949 (14)	0.0520 (6)
H8A	1.2345	0.0520	0.4304	0.062*
H8B	1.0648	0.1313	0.4374	0.062*
C9	0.9226 (4)	-0.08537 (16)	0.37208 (15)	0.0523 (6)
C10	1.1198 (5)	-0.12509 (19)	0.33956 (16)	0.0653 (7)
H10	1.2338	-0.0933	0.3127	0.078*
C11	1.1429 (5)	-0.2125 (2)	0.3480 (2)	0.0754 (9)
H11	1.2732	-0.2400	0.3257	0.090*
C12	0.9786 (6)	-0.26022 (19)	0.38851 (18)	0.0705 (8)
H12	0.9981	-0.3193	0.3941	0.085*
C13	0.7836 (5)	-0.21963 (19)	0.42093 (19)	0.0703 (8)
H13	0.6707	-0.2516	0.4481	0.084*
C14	0.7551 (4)	-0.13237 (18)	0.41327 (17)	0.0609 (7)
H14	0.6245	-0.1051	0.4356	0.073*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0530 (3)	0.0692 (4)	0.0471 (3)	-0.0058 (3)	-0.0062 (3)	0.0034 (3)
O1	0.0476 (9)	0.0863 (13)	0.0503 (11)	0.0057 (8)	-0.0094 (9)	0.0002 (9)
O2	0.1365 (19)	0.0753 (12)	0.0565 (12)	-0.0047 (13)	-0.0356 (13)	0.0064 (10)
O3	0.0906 (14)	0.0759 (13)	0.0774 (15)	0.0194 (11)	0.0000 (12)	0.0008 (11)
O4	0.0948 (13)	0.0849 (13)	0.0421 (11)	-0.0213 (11)	-0.0065 (11)	0.0110 (9)
O5	0.0455 (9)	0.0819 (13)	0.0939 (16)	0.0066 (8)	-0.0109 (10)	-0.0017 (11)
N1	0.0731 (13)	0.0599 (12)	0.0528 (13)	-0.0067 (12)	0.0011 (13)	0.0040 (11)
C1	0.0440 (13)	0.0819 (18)	0.0503 (16)	-0.0131 (12)	0.0022 (12)	-0.0013 (14)
C2	0.0494 (12)	0.0638 (15)	0.0431 (13)	-0.0127 (12)	-0.0020 (12)	0.0028 (12)
C3	0.116 (2)	0.0678 (17)	0.0573 (17)	-0.0182 (17)	0.0092 (19)	0.0161 (16)
C4	0.0835 (18)	0.087 (2)	0.0485 (15)	-0.0228 (16)	0.0111 (16)	0.0062 (15)
C5	0.0470 (12)	0.0704 (15)	0.0471 (14)	0.0057 (11)	-0.0093 (13)	0.0006 (13)
C6	0.0543 (16)	0.135 (3)	0.087 (3)	-0.0178 (17)	-0.0027 (17)	-0.017 (2)
C7	0.077 (2)	0.117 (3)	0.065 (2)	0.0361 (18)	-0.0159 (17)	-0.0214 (19)
C8	0.0454 (13)	0.0655 (14)	0.0451 (14)	-0.0080 (11)	0.0019 (12)	0.0038 (11)
C9	0.0469 (13)	0.0682 (14)	0.0418 (14)	-0.0061 (11)	0.0018 (12)	-0.0013 (11)
C10	0.0524 (14)	0.0823 (18)	0.0612 (17)	-0.0056 (14)	0.0119 (15)	0.0050 (14)
C11	0.0662 (17)	0.0833 (19)	0.077 (2)	0.0129 (15)	0.0121 (18)	-0.0042 (16)
C12	0.0748 (18)	0.0687 (16)	0.068 (2)	-0.0018 (14)	-0.0025 (17)	0.0036 (15)
C13	0.0686 (17)	0.080 (2)	0.062 (2)	-0.0203 (15)	0.0052 (17)	0.0047 (15)
C14	0.0471 (13)	0.0774 (18)	0.0581 (18)	-0.0093 (13)	0.0092 (14)	-0.0027 (14)

Geometric parameters (Å, °)

S1—O4	1.4310 (19)	C5—C6	1.510 (4)
S1—O5	1.4334 (18)	C6—H6A	0.9600

S1—C9	1.755 (3)	C6—H6B	0.9600
S1—C8	1.784 (2)	C6—H6C	0.9600
O1—C1	1.415 (3)	C7—H7A	0.9600
O1—C5	1.433 (3)	C7—H7B	0.9600
O2—C5	1.409 (3)	C7—H7C	0.9600
O2—C4	1.409 (4)	C8—H8A	0.9700
O3—N1	1.290 (3)	C8—H8B	0.9700
N1—C2	1.299 (3)	C9—C14	1.383 (3)
N1—C3	1.485 (4)	C9—C10	1.387 (3)
C1—C2	1.490 (4)	C10—C11	1.374 (4)
C1—C4	1.530 (4)	C10—H10	0.9300
C1—H1	0.9800	C11—C12	1.371 (4)
C2—C8	1.471 (3)	C11—H11	0.9300
C3—C4	1.506 (5)	C12—C13	1.382 (4)
C3—H3A	0.9700	C12—H12	0.9300
C3—H3B	0.9700	C13—C14	1.373 (4)
C4—H4	0.9800	C13—H13	0.9300
C5—C7	1.492 (4)	C14—H14	0.9300
O4—S1—O5	119.46 (14)	C7—C5—C6	112.5 (3)
O4—S1—C9	109.47 (13)	C5—C6—H6A	109.5
O5—S1—C9	108.16 (12)	C5—C6—H6B	109.5
O4—S1—C8	107.06 (11)	H6A—C6—H6B	109.5
O5—S1—C8	107.58 (13)	C5—C6—H6C	109.5
C9—S1—C8	104.02 (12)	H6A—C6—H6C	109.5
C1—O1—C5	108.01 (19)	H6B—C6—H6C	109.5
C5—O2—C4	112.0 (2)	C5—C7—H7A	109.5
O3—N1—C2	127.8 (2)	C5—C7—H7B	109.5
O3—N1—C3	119.7 (2)	H7A—C7—H7B	109.5
C2—N1—C3	112.5 (2)	C5—C7—H7C	109.5
O1—C1—C2	113.9 (2)	H7A—C7—H7C	109.5
O1—C1—C4	104.8 (2)	H7B—C7—H7C	109.5
C2—C1—C4	102.9 (2)	C2—C8—S1	113.50 (17)
O1—C1—H1	111.6	C2—C8—H8A	108.9
C2—C1—H1	111.6	S1—C8—H8A	108.9
C4—C1—H1	111.6	C2—C8—H8B	108.9
N1—C2—C8	121.4 (2)	S1—C8—H8B	108.9
N1—C2—C1	111.7 (2)	H8A—C8—H8B	107.7
C8—C2—C1	126.8 (2)	C14—C9—C10	120.8 (3)
N1—C3—C4	103.1 (2)	C14—C9—S1	120.1 (2)
N1—C3—H3A	111.1	C10—C9—S1	119.10 (19)
C4—C3—H3A	111.1	C11—C10—C9	118.4 (3)
N1—C3—H3B	111.1	C11—C10—H10	120.8
C4—C3—H3B	111.1	C9—C10—H10	120.8
H3A—C3—H3B	109.1	C12—C11—C10	121.6 (3)
O2—C4—C3	110.3 (3)	C12—C11—H11	119.2
O2—C4—C1	102.9 (2)	C10—C11—H11	119.2
C3—C4—C1	105.6 (2)	C11—C12—C13	119.3 (3)

O2—C4—H4	112.5	C11—C12—H12	120.4
C3—C4—H4	112.5	C13—C12—H12	120.4
C1—C4—H4	112.5	C14—C13—C12	120.5 (3)
O2—C5—O1	106.07 (19)	C14—C13—H13	119.8
O2—C5—C7	110.4 (3)	C12—C13—H13	119.8
O1—C5—C7	109.1 (2)	C13—C14—C9	119.4 (3)
O2—C5—C6	109.1 (2)	C13—C14—H14	120.3
O1—C5—C6	109.4 (2)	C9—C14—H14	120.3

Hydrogen-bond geometry (Å, °)

<i>D—H...A</i>	<i>D—H</i>	<i>H...A</i>	<i>D...A</i>	<i>D—H...A</i>
C4—H4...O4 ⁱ	0.98	2.50	3.389 (2)	151
C12—H12...O3 ⁱⁱ	0.93	2.51	3.270 (4)	139

Symmetry codes: (i) $-x+3/2, -y, z+1/2$; (ii) $x-1/2, -y-1/2, -z+1$.