

Crystal structure of (4*R*,5*S*)-4-methyl-3-methylsulfinyl-5-phenyl-1,3-oxazolidin-2-one

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The absolute structure of the chiral asymmetric indole precursor title compound, C₁₁H₁₃NO₃S, was confirmed by refinement of the Flack and Hooft parameters and is that expected based on the starting materials for the synthesis. The phenyl group subtends a dihedral angle of 56.40 (5)° with the mean plane of the oxazolidinone ring, which adopts an envelope conformation, with the C atom bearing the methyl group as the flap. In the crystal, no significant directional interactions beyond van der Waals contacts are observed.

Keywords: crystal structure; oxazolidinone; asymmetric indole.

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1. Related literature

For general background to the preparation of naturally occurring alkaloids, see: Marino *et al.* (1992). For further synthetic details, see: Silveira & Marino, 2013. For related structures, see: Evans *et al.* (1992); Silveira *et al.* (2013); Silveira *et al.* (2012); Clara-Sosa *et al.* (2004); Romanenko *et al.* (2003). A statistical analysis (Hooft *et al.*, 2008) was used to corroborate that the correct enantiomorph of the space group and hence handedness of the molecule had been determined.

2. Experimental

2.1. Crystal data

C ₁₁ H ₁₃ NO ₃ S	<i>V</i> = 1123.12 (13) Å ³
<i>M_r</i> = 239.28	<i>Z</i> = 4
Orthorhombic, <i>P</i> 2 ₁ 2 ₁ 2 ₁	Mo <i>K</i> α radiation
<i>a</i> = 6.1605 (4) Å	<i>μ</i> = 0.28 mm ⁻¹
<i>b</i> = 11.8490 (8) Å	<i>T</i> = 100 K
<i>c</i> = 15.3861 (11) Å	0.22 × 0.09 × 0.06 mm

2.2. Data collection

Bruker X8 APEXII CCD diffractometer	30938 measured reflections
Absorption correction: multi-scan (<i>SADABS</i> ; Sheldrick, 2007)	3761 independent reflections
<i>T</i> _{min} = 0.707, <i>T</i> _{max} = 0.746	3507 reflections with <i>I</i> > 2σ(<i>I</i>)
	<i>R</i> _{int} = 0.032

2.3. Refinement

<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.027	Δρ _{min} = -0.18 e Å ⁻³
<i>wR</i> (<i>F</i> ²) = 0.070	Absolute structure: Flack <i>x</i>
<i>S</i> = 1.03	determined using 1431 quotients
3761 reflections	[(<i>I</i> ⁺) - (<i>I</i> ⁻)] / [(<i>I</i> ⁺) + (<i>I</i> ⁻)] (Parsons <i>et al.</i> , 2013)
147 parameters	Absolute structure parameter:
H-atom parameters constrained	-0.012 (16)
Δρ _{max} = 0.31 e Å ⁻³	

Data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINTE* (Bruker, 2008); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2008); molecular graphics: *XP in SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *XCIF* (Sheldrick, 2008), *enCIFer* (Allen *et al.*, 2004) and *pubCIF* (Westrip, 2010).

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Supporting information for this paper is available from the IUCr electronic archives (Reference: HB7309).

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Crystal structure of (4*R*,5*S*)-4-methyl-3-methylsulfinyl-5-phenyl-1,3-oxazolidin-2-one

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S1. Introduction

Our research group has interest in the development of new methodologies to the synthesis of chiral sulfur compounds (Silveira & Marino, 2013). Thus, we have been preparing chiral oxazolidinones (Silveira, Oliver & Noll, 2013) to the synthesis of asymmetric indole derivatives (Pozza Silveira *et al.*, 2012) as precursors to the preparation of naturally occurring alkaloids (Marino *et al.*, 1992).

S2. Experimental

Experimental discussion

S2.1. Synthesis and crystallization

411 mg of (4*R*,5*S*)-4-methyl-5-phenyloxazolidin-2-one (2.32 mmol) and 25 mL of dry THF were added to a 50 mL flame-dried round bottom flask charged with argon gas at 0 °C. To this 1.21 mL of *n*-butyl lithium (1.83 M, 2.21 mmol) was added dropwise into the solution during five minutes and the mixture obtained cooled to -78 °C. Subsequently, 320 mg of sulfinyl chloride was added. After 10 min. the reaction was quenched with 6.5 mL of saturated NH₄Cl solution. The aqueous layer was extracted with 25 mL of ethyl acetate and the organic phase washed with 8 mL of saturated NaHCO₃ solution and 10 mL of saturated NaCl solution, respectively. The organic phase was dried over Na₂SO₄ and the salt removed by filtration. The solvent was removed under reduced pressure to give a white solid. The crude solid was dissolved with ethyl acetate and hexanes were added dropwise to the solution until a cloudy suspension was observed. The ethyl acetate / hexanes solution was left overnight to evaporate yielding 238 mg of clear colorless rods (45%).

S2.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. All non-hydrogen atoms were refined with anisotropic thermal displacement parameters. Hydrogen atoms were included in geometrically calculated positions riding on the carbon to which they are bonded. C—H bond distances were restrained to 0.95 Å (aromatic), 0.98 Å (methyl) and 1.00 Å (methylene). Hydrogen thermal parameters were set as $U_{\text{iso}}(\text{H}) = 1.2 \times U_{\text{eq}}(\text{C})_{\text{aromatic/methylene}}$ and $1.5 \times U_{\text{eq}}(\text{C})_{\text{methyl}}$.

The absolute stereochemistry was determined both by the known chirality that was retained during synthesis and by comparison of intensities of Friedel pairs of reflections. Both a direct measurement in the differences in intensities (Flack *x* parameter = -0.012 (3), (Parsons *et al.*, 2013)) and a statistical analysis (Hooft *y* parameter = -0.015 (17), Hooft *et al.*, 2008) corroborate that the correct enantiomorph of the space group and hence handedness of the molecule were determined. All three techniques agree and the correct chirality is shown.

S3. Results and discussion

The structure of the oxazolidinone is as expected. The stereochemistry from the parent reactants was retained through the synthesis. Surprisingly, no significant intermolecular interactions are observed in the crystal. The phenyl group which could exhibit either $\pi\cdots\pi$ interactions or C—H $\cdots\pi$ interactions shows no sign or indication of such arrangements.

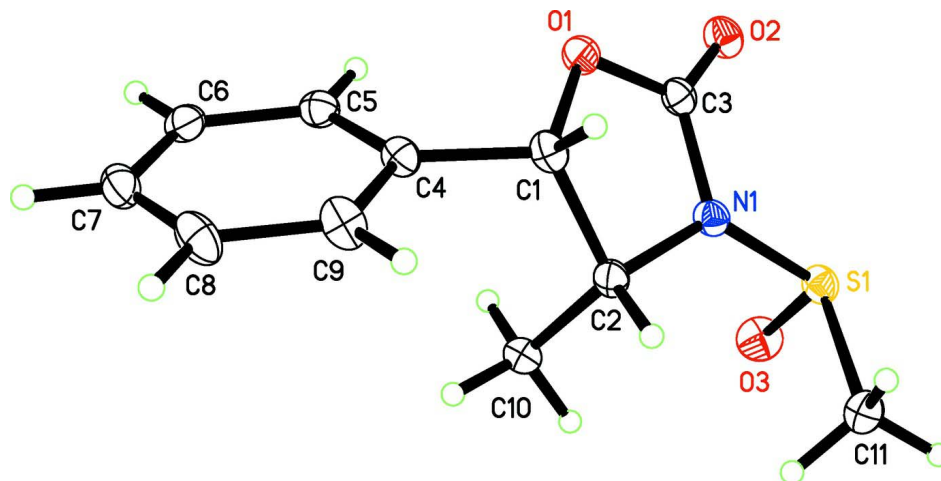


Figure 1

Labelling scheme for (4*R*,5*S*)-4-methyl-3-methylsulfinyl-5-phenyl-1,3-oxazolidin-2-one. Thermal displacement ellipsoids are depicted at the 50% probability level.

(4*R*,5*S*)-4-Methyl-3-methylsulfinyl-5-phenyl-1,3-oxazolidin-2-one

Crystal data

C₁₁H₁₃NO₃S

M_r = 239.28

Orthorhombic, *P*2₁2₁2₁

a = 6.1605 (4) Å

b = 11.8490 (8) Å

c = 15.3861 (11) Å

V = 1123.12 (13) Å³

Z = 4

F(000) = 504

D_x = 1.415 Mg m⁻³

Mo *K*α radiation, λ = 0.71073 Å

Cell parameters from 9865 reflections

θ = 3.2–31.4°

μ = 0.28 mm⁻¹

T = 100 K

Rod, colorless

0.22 × 0.09 × 0.06 mm

Data collection

Bruker X8 APEXII CCD
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: 8.33 pixels mm⁻¹

φ and ω scans

Absorption correction: multi-scan
(*SADABS*; Sheldrick, 2007)

T_{min} = 0.707, *T_{max}* = 0.746

30938 measured reflections

3761 independent reflections

3507 reflections with *I* > 2σ(*I*)

R_{int} = 0.032

θ_{max} = 31.6°, θ_{min} = 2.2°

h = -8→9

k = -17→17

l = -21→22

Refinement

Refinement on *F*²

Least-squares matrix: full

R[*F*² > 2σ(*F*²)] = 0.027

wR(*F*²) = 0.070

S = 1.03

3761 reflections

147 parameters

0 restraints

Hydrogen site location: inferred from neighbouring sites
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0431P)^2 + 0.127P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.31 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.18 \text{ e } \text{\AA}^{-3}$
 Absolute structure: Flack x determined using
 1431 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
 Absolute structure parameter: -0.012 (16)

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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.97856 (6)	0.27012 (3)	0.33636 (2)	0.01721 (9)
N1	0.8121 (2)	0.16070 (11)	0.31202 (8)	0.0153 (2)
O1	0.74140 (17)	0.00157 (9)	0.24121 (6)	0.0175 (2)
O2	1.04668 (18)	0.09415 (9)	0.20595 (7)	0.0194 (2)
O3	1.13406 (18)	0.23613 (11)	0.40470 (7)	0.0241 (2)
C1	0.5547 (2)	0.02282 (12)	0.29661 (9)	0.0156 (3)
H1	0.4376	0.0589	0.2612	0.019*
C2	0.6387 (2)	0.10893 (12)	0.36433 (9)	0.0152 (3)
H2	0.5236	0.1659	0.3775	0.018*
C3	0.8831 (2)	0.08716 (12)	0.24861 (9)	0.0154 (3)
C4	0.4715 (2)	-0.08568 (12)	0.33334 (9)	0.0155 (2)
C5	0.5964 (2)	-0.18255 (12)	0.33741 (10)	0.0169 (2)
H5	0.7380	-0.1831	0.3130	0.020*
C6	0.5153 (3)	-0.27897 (12)	0.37712 (9)	0.0190 (3)
H6	0.6021	-0.3451	0.3803	0.023*
C7	0.3081 (3)	-0.27882 (14)	0.41209 (9)	0.0208 (3)
H7	0.2528	-0.3447	0.4394	0.025*
C8	0.1815 (3)	-0.18222 (14)	0.40706 (10)	0.0221 (3)
H8	0.0387	-0.1823	0.4304	0.026*
C9	0.2623 (2)	-0.08596 (14)	0.36827 (10)	0.0204 (3)
H9	0.1755	-0.0198	0.3653	0.025*
C10	0.7241 (3)	0.05758 (13)	0.44793 (10)	0.0189 (3)
H10A	0.8343	0.0006	0.4342	0.028*
H10B	0.6043	0.0221	0.4796	0.028*
H10C	0.7889	0.1169	0.4840	0.028*
C11	0.7753 (3)	0.35377 (13)	0.38865 (10)	0.0211 (3)
H11A	0.7344	0.3184	0.4439	0.032*
H11B	0.6474	0.3592	0.3510	0.032*
H11C	0.8327	0.4295	0.3997	0.032*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.01616 (15)	0.01850 (15)	0.01696 (15)	−0.00282 (12)	−0.00025 (12)	0.00138 (12)
N1	0.0135 (5)	0.0171 (5)	0.0154 (5)	−0.0015 (4)	0.0024 (4)	0.0005 (4)
O1	0.0169 (5)	0.0178 (5)	0.0179 (5)	−0.0019 (4)	0.0058 (4)	−0.0002 (4)
O2	0.0158 (5)	0.0222 (5)	0.0202 (5)	0.0013 (4)	0.0045 (4)	0.0026 (4)
O3	0.0191 (5)	0.0288 (6)	0.0245 (5)	0.0005 (5)	−0.0068 (4)	−0.0011 (5)
C1	0.0114 (6)	0.0180 (6)	0.0174 (6)	0.0006 (5)	0.0021 (5)	0.0025 (5)
C2	0.0136 (6)	0.0147 (6)	0.0172 (6)	0.0011 (5)	0.0045 (5)	0.0010 (5)
C3	0.0147 (6)	0.0162 (6)	0.0152 (6)	0.0017 (5)	−0.0004 (5)	0.0027 (5)
C4	0.0133 (5)	0.0183 (6)	0.0149 (5)	−0.0014 (5)	−0.0004 (5)	0.0014 (5)
C5	0.0160 (6)	0.0185 (6)	0.0160 (6)	−0.0004 (5)	0.0011 (5)	−0.0016 (5)
C6	0.0243 (7)	0.0161 (6)	0.0166 (6)	−0.0003 (6)	−0.0016 (5)	−0.0021 (5)
C7	0.0245 (7)	0.0225 (7)	0.0155 (6)	−0.0078 (6)	−0.0025 (5)	0.0029 (6)
C8	0.0148 (6)	0.0311 (8)	0.0203 (7)	−0.0040 (6)	0.0007 (5)	0.0065 (6)
C9	0.0140 (6)	0.0252 (7)	0.0221 (7)	0.0015 (6)	−0.0004 (5)	0.0060 (6)
C10	0.0229 (7)	0.0185 (7)	0.0153 (6)	−0.0003 (6)	0.0031 (6)	0.0003 (5)
C11	0.0240 (7)	0.0173 (6)	0.0220 (7)	0.0020 (6)	0.0001 (6)	0.0004 (6)

Geometric parameters (Å, °)

S1—O3	1.4783 (12)	C5—C6	1.389 (2)
S1—N1	1.6948 (13)	C5—H5	0.9500
S1—C11	1.7882 (16)	C6—C7	1.385 (2)
N1—C3	1.3791 (18)	C6—H6	0.9500
N1—C2	1.4716 (18)	C7—C8	1.387 (2)
O1—C3	1.3428 (17)	C7—H7	0.9500
O1—C1	1.4534 (16)	C8—C9	1.380 (2)
O2—C3	1.2056 (17)	C8—H8	0.9500
C1—C4	1.4952 (19)	C9—H9	0.9500
C1—C2	1.547 (2)	C10—H10A	0.9800
C1—H1	1.0000	C10—H10B	0.9800
C2—C10	1.517 (2)	C10—H10C	0.9800
C2—H2	1.0000	C11—H11A	0.9800
C4—C5	1.3832 (19)	C11—H11B	0.9800
C4—C9	1.396 (2)	C11—H11C	0.9800
O3—S1—N1	109.93 (7)	C4—C5—H5	119.9
O3—S1—C11	106.55 (7)	C6—C5—H5	119.9
N1—S1—C11	95.73 (7)	C7—C6—C5	120.08 (14)
C3—N1—C2	110.71 (12)	C7—C6—H6	120.0
C3—N1—S1	116.62 (10)	C5—C6—H6	120.0
C2—N1—S1	129.58 (10)	C6—C7—C8	119.83 (14)
C3—O1—C1	109.49 (11)	C6—C7—H7	120.1
O1—C1—C4	110.13 (11)	C8—C7—H7	120.1
O1—C1—C2	104.16 (11)	C9—C8—C7	120.21 (14)
C4—C1—C2	115.28 (11)	C9—C8—H8	119.9

O1—C1—H1	109.0	C7—C8—H8	119.9
C4—C1—H1	109.0	C8—C9—C4	120.09 (14)
C2—C1—H1	109.0	C8—C9—H9	120.0
N1—C2—C10	112.29 (12)	C4—C9—H9	120.0
N1—C2—C1	98.58 (11)	C2—C10—H10A	109.5
C10—C2—C1	114.99 (12)	C2—C10—H10B	109.5
N1—C2—H2	110.2	H10A—C10—H10B	109.5
C10—C2—H2	110.2	C2—C10—H10C	109.5
C1—C2—H2	110.2	H10A—C10—H10C	109.5
O2—C3—O1	123.30 (13)	H10B—C10—H10C	109.5
O2—C3—N1	127.34 (14)	S1—C11—H11A	109.5
O1—C3—N1	109.34 (11)	S1—C11—H11B	109.5
C5—C4—C9	119.60 (13)	H11A—C11—H11B	109.5
C5—C4—C1	122.67 (12)	S1—C11—H11C	109.5
C9—C4—C1	117.65 (13)	H11A—C11—H11C	109.5
C4—C5—C6	120.18 (13)	H11B—C11—H11C	109.5
O3—S1—N1—C3	-88.16 (11)	C2—N1—C3—O2	-165.15 (14)
C11—S1—N1—C3	161.92 (11)	S1—N1—C3—O2	-3.1 (2)
O3—S1—N1—C2	69.87 (14)	C2—N1—C3—O1	13.73 (15)
C11—S1—N1—C2	-40.05 (14)	S1—N1—C3—O1	175.77 (9)
C3—O1—C1—C4	-145.05 (12)	O1—C1—C4—C5	19.91 (18)
C3—O1—C1—C2	-20.89 (14)	C2—C1—C4—C5	-97.55 (16)
C3—N1—C2—C10	96.80 (14)	O1—C1—C4—C9	-163.13 (12)
S1—N1—C2—C10	-62.25 (16)	C2—C1—C4—C9	79.41 (16)
C3—N1—C2—C1	-24.78 (14)	C9—C4—C5—C6	-0.9 (2)
S1—N1—C2—C1	176.17 (11)	C1—C4—C5—C6	175.97 (13)
O1—C1—C2—N1	26.31 (13)	C4—C5—C6—C7	0.6 (2)
C4—C1—C2—N1	147.08 (12)	C5—C6—C7—C8	0.2 (2)
O1—C1—C2—C10	-93.27 (14)	C6—C7—C8—C9	-0.8 (2)
C4—C1—C2—C10	27.50 (17)	C7—C8—C9—C4	0.5 (2)
C1—O1—C3—O2	-175.68 (13)	C5—C4—C9—C8	0.4 (2)
C1—O1—C3—N1	5.38 (15)	C1—C4—C9—C8	-176.66 (14)