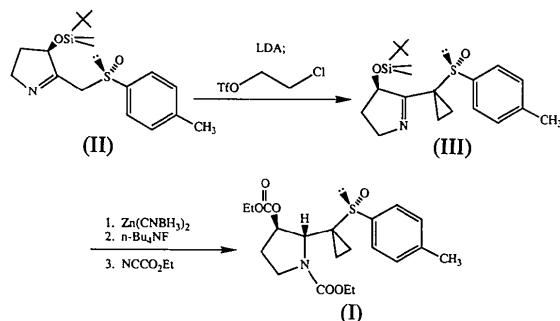


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was isolated unexpectedly [yield 55%, based on 26% recovery of (II)]. Subsequent stereoselective reduction of (III) with zinc cyanoborohydride followed by desilylation with tetra-*n*-butylammonium fluoride and then ethoxycarbonylation with 3 equivalents of LDA and 2.5 equivalents of ethyl cyanoformate gave the title compound (I);  $[\alpha]_D^{22} = +34.4^\circ$  (*c* 0.5,  $\text{CHCl}_3$ ), m.p. 369–374 K (recrystallized from  $\text{CH}_2\text{Cl}_2$ –hexane).



The C(7)—C(8) bond in the cyclopropyl ring of (I) is shorter [1.48(1) Å] than both the normal distance for cyclopropane (1.51 Å) (Vollhardt, 1987) and the C(6)—C(7) and C(6)—C(8) bonds. In addition, the bond angle S(1)—C(6)—C(2) [123.2(6)°] is substantially larger than the corresponding angle (115°) in cyclopropane.

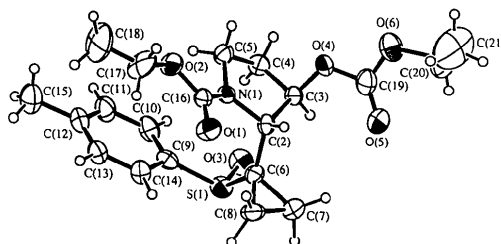


Fig. 1. Molecular configuration and atom-numbering scheme with thermal ellipsoids at the 30% probability level. H atoms are shown as unlabeled circles of arbitrary radius.

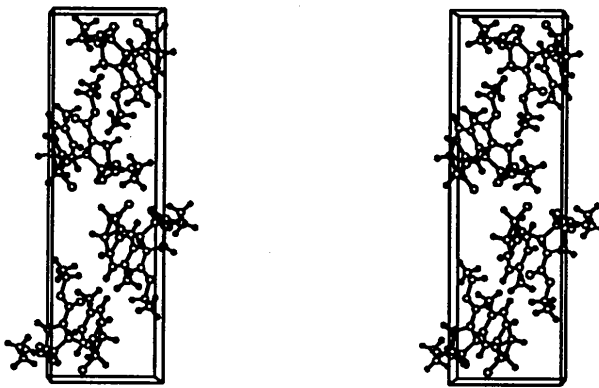


Fig. 2. Stereoscopic illustration of the molecular packing. The origin is at the lower-right-front, *a* is into the plane of the paper, *b* is vertical, and *c* is horizontal.

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### Ethyl (2*R*,3*R*,*S**R*)-3-(Ethoxycarbonyloxy)-2-[1-(*p*-tolylsulfinyl)cyclopropyl]-1-pyrrolidinecarboxylate

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#### Abstract

The title compound, derived in four steps beginning with the cyclopropanation reaction of the anion of the  $\alpha$ -sulfinyl ketimine (4*R*,*SS*)-4-(*tert*-butyldimethylsilyloxy)-3,4-dihydro-5-[(*p*-tolylsulfinyl)methyl]-2*H*-pyrrole with 2-chloroethyl trifluoromethanesulfonate, contains a shorter than expected bond [C(7)—C(8) 1.48 (1) Å] and a larger than expected angle [S(1)—C(6)—C(2) 123.2 (6)°] in the cyclopropane framework.

#### Comment

The title compound (I) was synthesized using  $\alpha$ -sulfinyl ketimine chemistry (Hua, Bharathi, Panagadan & Tsujimoto, 1991) as part of our investigations into the asymmetric total synthesis of the anti-tumor agent indicine *N*-oxide (Kovach, Ames, Powis, Moertel, Hahn & Cregan, 1979). When (4*R*,*SS*)-4-(*tert*-butyldimethylsilyloxy)-3,4-dihydro-5-[(*p*-tolylsulfinyl)methyl]-2*H*-pyrrole (II) was treated with 1.3 equivalents of lithium diisopropylamide (LDA) in THF at 195 K followed by 2-chloroethyl trifluoromethanesulfonate, 5-cyclopropyldihydropyrrole (III)

<sup>†</sup> Fellow of the Alfred P. Sloan Foundation, 1989–1993.

**Experimental***Crystal data*C<sub>20</sub>H<sub>27</sub>NO<sub>6</sub>SM<sub>r</sub> = 409.50

Orthorhombic

P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>

a = 9.622 (2) Å

b = 27.282 (7) Å

c = 8.107 (2) Å

V = 2128.1 (8) Å<sup>3</sup>

Z = 4

D<sub>x</sub> = 1.278 Mg m<sup>-3</sup>

Mo Kα radiation

λ = 0.71069 Å

Cell parameters from 24 reflections

θ = 8.1–11.2°

μ = 1.77 cm<sup>-1</sup>

T = 296 K

Platy

0.51 × 0.28 × 0.06 mm

Colorless

*Data collection*

Rigaku AFC-5S diffractometer

ω scans

Absorption correction: none

2197 measured reflections

2172 independent reflections

1169 observed reflections

[I &gt; 2σ(I)]

No equivalent reflections measured

θ<sub>max</sub> = 25°

h = 0 → 11

k = 0 → 32

l = 0 → 9

3 standard reflections

monitored every 100 reflections

intensity variation: +1.1%

*Refinement*Refinement on F<sup>2</sup>

Final R = 0.056

wR = 0.053

S = 1.58

1169 reflections

253 parameters

H-atom parameters not refined

w = 4F<sub>o</sub><sup>2</sup>/σ<sup>2</sup>(F<sub>o</sub><sup>2</sup>)(Δ/σ)<sub>max</sub> = 0.0003Δρ<sub>max</sub> = 0.23 e Å<sup>-3</sup>Δρ<sub>min</sub> = -0.21 e Å<sup>-3</sup>

Extinction correction:

Zachariasen type 2 Gaussian isotropic

Extinction coefficient: none

Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.3.1)

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1985). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1988). Program(s) used to solve structure: *MITHRIL* (Gilmore, 1984) and *DIRDIF* (Beurskens, 1984). Program(s) used to refine structure: *TEXSAN LS*. Molecular graphics: *TEXSAN ORTEP* (Johnson, 1965). Software used to prepare material for publication: *TEXSAN FINISH*.

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (Å<sup>2</sup>)
$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U <sub>eq</sub>
S(1)	0.1489 (2)	0.93719 (8)	0.0718 (3)	0.067 (1)
O(1)	0.3395 (7)	0.7922 (2)	0.2042 (7)	0.075 (2)
O(2)	0.1728 (7)	0.7747 (2)	0.3920 (7)	0.079 (2)
O(3)	0.1107 (6)	0.9766 (2)	0.1903 (7)	0.083 (2)
O(4)	0.4211 (6)	0.9169 (2)	0.5737 (7)	0.060 (2)
O(5)	0.5869 (7)	0.9582 (3)	0.440 (1)	0.107 (3)
O(6)	0.6147 (7)	0.9275 (3)	0.696 (1)	0.112 (3)
N(1)	0.2417 (6)	0.8513 (2)	0.3627 (7)	0.045 (2)
C(2)	0.3354 (8)	0.8900 (2)	0.308 (1)	0.047 (2)
C(3)	0.3228 (9)	0.9285 (2)	0.445 (1)	0.052 (2)
C(4)	0.182 (1)	0.9200 (3)	0.521 (1)	0.059 (3)

C(5)	0.1592 (8)	0.8649 (3)	0.507 (1)	0.060 (3)
C(6)	0.3089 (9)	0.9098 (3)	0.133 (1)	0.054 (2)
C(7)	0.430 (1)	0.9365 (3)	0.056 (1)	0.079 (3)
C(8)	0.390 (1)	0.8875 (3)	-0.007 (1)	0.070 (3)
C(9)	0.0288 (8)	0.8883 (3)	0.103 (1)	0.053 (3)
C(10)	-0.087 (1)	0.8968 (3)	0.198 (1)	0.069 (3)
C(11)	-0.189 (1)	0.8611 (4)	0.215 (1)	0.080 (4)
C(12)	-0.176 (1)	0.8164 (3)	0.137 (1)	0.069 (3)
C(13)	-0.062 (1)	0.8092 (3)	0.039 (1)	0.066 (3)
C(14)	0.0397 (9)	0.8441 (3)	0.020 (1)	0.063 (3)
C(15)	-0.288 (1)	0.7771 (4)	0.156 (1)	0.104 (2)
C(16)	0.259 (1)	0.8051 (3)	0.312 (1)	0.055 (3)
C(17)	0.175 (2)	0.7234 (3)	0.345 (1)	0.128 (4)
C(18)	0.042 (2)	0.7037 (4)	0.378 (2)	0.172 (8)
C(19)	0.546 (1)	0.9365 (4)	0.558 (2)	0.081 (4)
C(20)	0.753 (1)	0.9547 (5)	0.710 (2)	0.167 (7)
C(21)	0.841 (1)	0.9240 (8)	0.741 (3)	0.230 (8)

Table 2. Geometric parameters (Å, °)

S(1)—O(3)	1.487 (6)	C(2)—C(6)	1.53 (1)
S(1)—C(6)	1.783 (9)	C(3)—C(4)	1.51 (1)
S(1)—C(9)	1.783 (8)	C(4)—C(5)	1.52 (1)
O(1)—C(16)	1.220 (9)	C(6)—C(7)	1.51 (1)
O(2)—C(16)	1.342 (9)	C(6)—C(8)	1.51 (1)
O(2)—C(17)	1.45 (1)	C(7)—C(8)	1.48 (1)
O(4)—C(3)	1.441 (9)	C(9)—C(10)	1.38 (1)
O(4)—C(19)	1.32 (1)	C(9)—C(14)	1.38 (1)
O(5)—C(19)	1.20 (1)	C(10)—C(11)	1.38 (1)
O(6)—C(19)	1.32 (1)	C(11)—C(12)	1.38 (1)
O(6)—C(20)	1.53 (1)	C(12)—C(13)	1.37 (1)
N(1)—C(2)	1.459 (8)	C(12)—C(15)	1.53 (1)
N(1)—C(5)	1.463 (9)	C(13)—C(14)	1.37 (1)
N(1)—C(16)	1.335 (9)	C(17)—C(18)	1.42 (2)
C(2)—C(3)	1.536 (9)	C(20)—C(21)	1.22 (2)
O(3)—S(1)—C(6)	109.6 (4)	C(7)—C(6)—C(8)	58.8 (6)
O(3)—S(1)—C(9)	106.8 (4)	C(6)—C(7)—C(8)	60.5 (5)
C(6)—S(1)—C(9)	101.9 (3)	C(6)—C(8)—C(7)	60.6 (5)
C(16)—O(2)—C(17)	117.4 (7)	S(1)—C(9)—C(10)	118.6 (6)
C(3)—O(4)—C(19)	116.0 (8)	S(1)—C(9)—C(14)	122.2 (7)
C(19)—O(6)—C(20)	114 (1)	C(10)—C(9)—C(14)	118.7 (8)
C(2)—N(1)—C(5)	113.4 (6)	C(9)—C(10)—C(11)	120.8 (7)
C(2)—N(1)—C(16)	120.8 (7)	C(10)—C(11)—C(12)	120.6 (9)
C(5)—N(1)—C(16)	123.5 (7)	C(11)—C(12)—C(13)	117.8 (8)
N(1)—C(2)—C(3)	102.9 (6)	C(11)—C(12)—C(15)	121 (1)
N(1)—C(2)—C(6)	115.7 (6)	C(13)—C(12)—C(15)	121.6 (8)
C(3)—C(2)—C(6)	114.7 (6)	C(12)—C(13)—C(14)	122.4 (8)
O(4)—C(3)—C(2)	108.9 (6)	C(9)—C(14)—C(13)	119.6 (8)
O(4)—C(3)—C(4)	105.2 (6)	O(1)—C(16)—O(2)	124.0 (8)
C(2)—C(3)—C(4)	105.3 (6)	O(1)—C(16)—N(1)	125.0 (8)
C(3)—C(4)—C(5)	104.4 (6)	O(2)—C(16)—N(1)	111.0 (8)
N(1)—C(5)—C(4)	103.4 (6)	O(2)—C(17)—C(18)	107 (1)
S(1)—C(6)—C(2)	123.2 (6)	O(4)—C(19)—O(5)	125 (1)
S(1)—C(6)—C(7)	110.4 (5)	O(4)—C(19)—O(6)	107 (1)
S(1)—C(6)—C(8)	114.0 (6)	O(5)—C(19)—O(6)	127 (1)
C(2)—C(6)—C(7)	114.9 (7)	O(6)—C(20)—C(21)	107 (1)
C(2)—C(6)—C(8)	117.9 (7)		

A scan rate of 3° min<sup>-1</sup> in ω was used. Weak reflections [I < 10σ(I)] were rescanned (maximum of two rescans) and the counts accumulated to improve accuracy. During the final stages of refinement, the methylene H atoms bound to C(7) and C(8) were included in difference map positions while the remaining H atoms were placed at assumed positions (C—H = 0.95 Å, U = 1.2 × U<sub>eq</sub> of the associated C atom) and fixed. The rotational orientation of the methyl groups was determined from a difference Fourier synthesis. The proper enantiomer was chosen on the basis of the known configuration of the substrate and was confirmed by a slightly superior refinement when compared to the antipode.

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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55376 (22 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CR1017]

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## Structure of an 11-Membered Cyclic Silyl Enol Ether from Condensation of Methacrolein and a Pseudoephedrine-Derived *O*-Silyl Ketene *N,O*-Acetal

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### Abstract

The title compound, (4*S*,5*S*,8*R*,10*Z*)-2,2,5,6,8,10-hexamethyl-4-phenyl-1,3-dioxo-6-aza-2-silacycloundec-10-en-7-one, crystallizes with two virtually identical molecules in the asymmetric unit, each with the same absolute configuration. Bond distances and angles are normal; the closest approaches across the ring between non-bonded atoms are all greater than

3.35 Å. The amide and enol ether groups are planar to within ±0.06 Å.

### Comment

The pseudoephedrine-derived *O*-silyl ketene *N,O*-acetal (1) undergoes facile aldol addition reactions with aldehydes to form 9-membered cyclic siloxane condensation products (Myers, Widdowson & Kukkola, 1992).  $\alpha,\beta$ -Unsaturated aldehydes react differently, forming, in the case of methacrolein, the 11-membered cyclic silyl enol ether (2) (Myers & Subramanian, 1992). The structure of this crystalline material has been established unambiguously by X-ray crystallography.

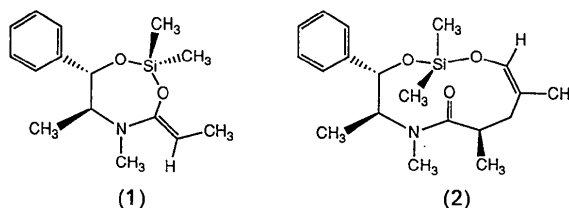


Fig. 1 shows the two independent molecules; both drawings have the same orientation relative to the least-squares plane of all their atoms, emphasizing their great similarity. Fig. 2 is a packing drawing showing the molecules in the unit cell. Bond distances and angles in the two independent molecules agree well; average values are quoted here, together with the higher or highest e.s.d.'s of the individual bonds. The Si—C and Si—O lengths average 1.842 (6) and 1.636 (3) Å. The angles at silicon differ from 109.5° by an average of 3.1°. There is some evidence of opening of the ring at the internal O atoms, where angles average 125.2 (9)°; the C—O distances, however, are normal [1.443 (5) Å to C1, 1.376 (6) Å to C17]. Other internal angles in the 11-membered ring are close to expected values. The grouping C8—N(C10)—C11(O3)—C12 is nearly planar in both molecules, with similar deviations from the least-squares plane. In molecule *A*, the two 'end' atoms, C8 and C12, are 0.057 Å out of the plane and the inner atoms (N, C10, C11 and O3) are −0.011, −0.045, −0.006 and −0.052 Å out of the plane respectively. In molecule *B*, the comparable distances are +0.047, and −0.017, −0.030, −0.009 and −0.037 Å. The non-bonded distances across the ring are all at or greater than van der Waals distances: O1...C10 3.42 and 3.48 Å, O2...C11 3.30 and 3.33 Å, O1...O3 3.66 and 3.67 Å, O2...O3 3.51 and 3.56 Å. Intermolecular contacts are also all at van der Waals distances or greater, the shortest (O2*b*...H4*b*) being 2.65 Å. The shortest H...H contact is 2.38 Å compared with an expected value of 2.4 Å.

† Contribution No. 8557.