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

William P. Schaefer, Vijaya Subramanian and Andrew G. Myers

Division of Chemistry and Chemical Engineering† and The Beckman Institute, Mail Code 139-74, California Institute of Technology, Pasadena, California 91125, USA

Abstract

The title compound, $(4S,5S,8R,10Z)$-2,2,5,6,8,10-hexamethyl-4-phenyl-1,3-dioxa-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). α,β-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.
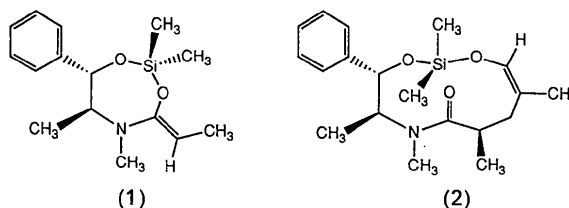

(1)   (2)

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.
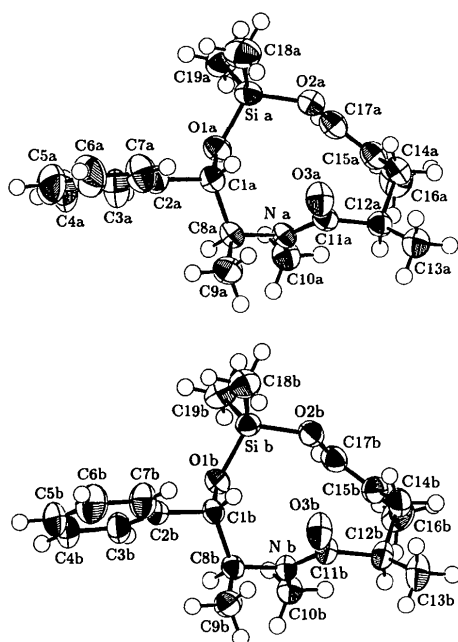
Fig. 1. An *ORTEP* drawing of molecules *A* (top) and *B* (bottom) with 50% probability ellipsoids showing the numbering system for the non-H atoms. H atoms are shown as spheres of arbitrary small diameter.
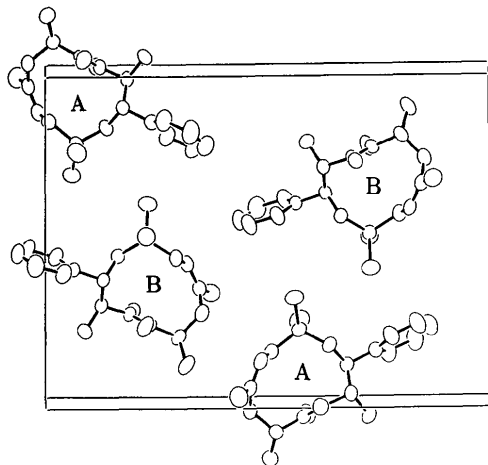

Fig. 2. An *ORTEP* projection of the contents of one unit cell onto the *bc* plane (one unit cell outlined). The molecules *A* and *B* are so indicated; H atoms are not shown. The *b* axis is horizontal.

Experimental

Crystal data

$C_{19}H_{29}NO_3Si$
$M_r = 347.53$
Monoclinic
$P2_1$
$a = 6.562\ (4)$ Å
$b = 20.473\ (11)$ Å
$c = 15.202\ (6)$ Å
$\beta = 94.73°$

$D_x = 1.13$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 14$–$16°$
$\mu = 0.125$ mm^{-1}
$T = 293$ K

$V = 2035.3\ (18)$ Å^3
$Z = 4$

$0.65 \times 0.35 \times 0.18$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer
ω scans
Absorption correction: none
7473 measured reflections
3685 independent reflections
3685 observed reflections
$R_{int} = 0.026$

$\theta_{max} = 25°$
$h = -7 \rightarrow 7$
$k = -24 \rightarrow 24$
$l = 0 \rightarrow 18$
3 standard reflections frequency: 150 min intensity variation: slight linear decay

Refinement

Refinement on F^2
Final $R = 0.043$ for $F_o^2 > 0$
Final $R = 0.034$ for $F_o^2 > 3\sigma(F_o^2)$
$wR = 0.05$
$S = 1.72$
3685 reflections
432 parameters

H-atom parameters not refined
$w = 1/[\sigma^2(F_o^2)+(0.014I)^2]$
$(\Delta/\sigma)_{max} = 0.01$
$\Delta\rho_{max} = 0.19$ e Å^{-3}
$\Delta\rho_{min} = -0.19$ e Å^{-3}
Atomic scattering factors from Cromer & Waber (1974), Cromer (1974)

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$$U_{eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Sia	0.8192 (2)	0.5709	0.2286 (1)	0.0480 (2)
O1a	0.8906 (3)	0.6384 (1)	0.1832 (2)	0.0479 (6)
O2a	0.8445 (4)	0.5084 (1)	0.1626 (2)	0.0506 (6)
C1a	0.7693 (5)	0.6772 (2)	0.1200 (2)	0.0432 (8)
C2a	0.7234 (6)	0.7420 (2)	0.1616 (2)	0.0521 (9)
C3a	0.8751 (7)	0.7767 (2)	0.2091 (3)	0.0728 (12)
C4a	0.8357 (10)	0.8370 (3)	0.2444 (4)	0.0998 (17)
C5a	0.6416 (12)	0.8636 (3)	0.2314 (4)	0.1039 (19)
C6a	0.4920 (9)	0.8302 (3)	0.1847 (4)	0.1000 (17)
C7a	0.5299 (7)	0.7698 (2)	0.1495 (3)	0.0762 (13)
C8a	0.8889 (5)	0.6864 (2)	0.0381 (2)	0.0447 (8)
C9a	0.7724 (6)	0.7268 (2)	−0.0332 (2)	0.0622 (10)
Na	0.9627 (4)	0.6244 (1)	0.0035 (2)	0.0392 (6)
C10a	1.1854 (5)	0.6178 (2)	0.0095 (2)	0.0522 (9)
C11a	0.8283 (5)	0.5798 (2)	−0.0321 (2)	0.0414 (8)
O3a	0.6415 (3)	0.5879 (1)	−0.0300 (2)	0.0586 (7)
C12a	0.9030 (5)	0.5187 (2)	−0.0757 (2)	0.0434 (8)
C13a	0.7700 (6)	0.5051 (2)	−0.1603 (3)	0.0609 (10)
C14a	0.8975 (6)	0.4602 (2)	−0.0114 (3)	0.0546 (10)
C15a	1.0609 (6)	0.4611 (2)	0.0626 (3)	0.0523 (10)
C16a	1.2705 (7)	0.4359 (2)	0.0445 (3)	0.0811 (13)
C17a	1.0295 (6)	0.4844 (2)	0.1412 (3)	0.0533 (10)
C18a	0.5445 (6)	0.5720 (2)	0.2467 (3)	0.0799 (12)
C19a	0.9895 (7)	0.5606 (2)	0.3304 (3)	0.0705 (11)
Sib	0.1939 (1)	0.7299 (1)	0.4965 (1)	0.0421 (2)
O1b	0.2820 (3)	0.6653 (1)	0.5499 (1)	0.0423 (5)
O2b	0.2422 (3)	0.7965 (1)	0.5547 (2)	0.0492 (6)
C1b	0.1829 (4)	0.6315 (2)	0.6176 (2)	0.0371 (7)
C2b	0.1220 (5)	0.5642 (2)	0.5847 (2)	0.0417 (7)
C3b	0.2651 (6)	0.5238 (2)	0.5515 (3)	0.0611 (10)
C4b	0.2135 (8)	0.4604 (2)	0.5254 (3)	0.0773 (13)
C5b	0.0176 (9)	0.4381 (2)	0.5319 (3)	0.0833 (16)
C6b	−0.1246 (8)	0.4777 (2)	0.5634 (4)	0.0882 (15)
C7b	−0.0724 (6)	0.5405 (2)	0.5903 (3)	0.0675 (11)
C8b	0.3321 (4)	0.6274 (2)	0.7002 (2)	0.0387 (7)
C9b	0.2464 (6)	0.5896 (2)	0.7750 (2)	0.0546 (9)
Nb	0.4128 (3)	0.6916 (1)	0.7301 (2)	0.0358 (6)
C10b	0.6341 (5)	0.6988 (2)	0.7282 (2)	0.0451 (8)
C11b	0.2842 (5)	0.7366 (2)	0.7591 (2)	0.0406 (7)
O3b	0.0980 (3)	0.7267 (1)	0.7558 (2)	0.0591 (7)

C12b	0.3670 (5)	0.8013 (2)	0.7979 (2)	0.0458 (8)
C13b	0.2527 (6)	0.8191 (2)	0.8777 (3)	0.0656 (11)
C14b	0.3402 (6)	0.8541 (2)	0.7260 (3)	0.0554 (10)
C15b	0.4870 (5)	0.8482 (2)	0.6558 (3)	0.0512 (9)
C16b	0.7008 (6)	0.8737 (2)	0.6771 (3)	0.0732 (12)
C17b	0.4357 (5)	0.8206 (2)	0.5791 (2)	0.0495 (9)
C18b	−0.0888 (5)	0.7296 (2)	0.4781 (3)	0.0633 (10)
C19b	0.3273 (6)	0.7321 (2)	0.3951 (2)	0.0647 (10)

Table 2. Selected bond lengths (Å) and angles (°)

Sia—O1a	1.630 (4)	Sib—O1b	1.633 (2)
Sia—O2a	1.644 (4)	Sib—O2b	1.641 (3)
Sia—C18a	1.846 (4)	Sib—C18b	1.853 (4)
Sia—C19a	1.845 (4)	Sib—C19b	1.835 (4)
O1a—C1a	1.435 (4)	O1b—C1b	1.439 (4)
O2a—C17a	1.372 (4)	O2b—C17b	1.384 (4)
C1a—C2a	1.512 (5)	C1b—C2b	1.508 (4)
C1a—C8a	1.536 (5)	C1b—C8b	1.531 (4)
C2a—C3a	1.378 (6)	C2b—C3b	1.378 (5)
C2a—C7a	1.390 (6)	C2b—C7b	1.374 (5)
C3a—C4a	1.379 (7)	C3b—C4b	1.391 (6)
C4a—C5a	1.383 (8)	C4b—C5b	1.375 (7)
C5a—C6a	1.350 (8)	C5b—C6b	1.352 (7)
C6a—C7a	1.378 (7)	C6b—C7b	1.384 (6)
C8a—C9a	1.518 (5)	C8b—C9b	1.520 (5)
C8a—Na	1.472 (4)	C8b—Nb	1.474 (4)
Na—C10a	1.463 (4)	Nb—C10b	1.462 (4)
Na—C11a	1.351 (4)	Nb—C11b	1.348 (4)
C11a—O3a	1.240 (4)	C11b—O3b	1.235 (4)
C11a—C12a	1.517 (5)	C11b—C12b	1.532 (5)
C12a—C13a	1.518 (5)	C12b—C13b	1.523 (5)
C12a—C14a	1.548 (5)	C12b—C14b	1.536 (5)
C14a—C15a	1.489 (5)	C14b—C15b	1.501 (5)
C15a—C16a	1.515 (6)	C15b—C16b	1.507 (6)
C15a—C17a	1.319 (5)	C15b—C17b	1.314 (5)
O2a—Sia—O1a	110.8 (2)	O2b—Sib—O1b	111.1 (1)
C18a—Sia—O1a	111.8 (2)	C18b—Sib—O1b	112.4 (1)
C19a—Sia—O1a	106.1 (2)	C19b—Sib—O1b	105.3 (2)
C18a—Sia—O2a	104.4 (2)	C18b—Sib—O2b	103.3 (2)
C19a—Sia—O2a	109.8 (2)	C19b—Sib—O2b	110.4 (2)
C19a—Sia—C18a	114.1 (2)	C19b—Sib—C18b	114.5 (2)
C1a—O1a—Sia	126.1 (2)	C1b—O1b—Sib	125.7 (2)
C17a—O2a—Sia	124.0 (2)	C17b—O2b—Sib	125.0 (2)
C2a—C1a—O1a	108.9 (3)	C2b—C1b—O1b	109.0 (2)
C8a—C1a—O1a	108.6 (2)	C8b—C1b—O1b	108.5 (2)
C8a—C1a—C2a	111.3 (3)	C8b—C1b—C2b	110.9 (2)
C9a—C8a—C1a	112.6 (3)	C9b—C8b—C1b	113.0 (3)
Na—C8a—C1a	112.8 (3)	Nb—C8b—C1b	113.2 (2)
Na—C8a—C9a	112.1 (3)	Nb—C8b—C9b	111.7 (3)
C10a—Na—C8a	114.5 (2)	C10b—Nb—C8b	114.6 (2)
C11a—Na—C8a	120.2 (3)	C11b—Nb—C8b	119.4 (2)
C11a—Na—C10a	125.3 (3)	C11b—Nb—C10b	125.9 (3)
O3a—C11a—Na	120.9 (3)	O3b—C11b—Nb	121.3 (3)
C12a—C11a—Na	120.6 (3)	C12b—C11b—Nb	120.4 (3)
C12a—C11a—O3a	118.5 (3)	C12b—C11b—O3b	118.4 (3)
C13a—C12a—C11a	109.7 (3)	C13b—C12b—C11b	109.3 (3)
C14a—C12a—C11a	109.7 (3)	C14b—C12b—C11b	108.6 (3)
C14a—C12a—C13a	110.6 (3)	C14b—C12b—C13b	111.4 (3)
C15a—C14a—C12a	114.5 (3)	C16b—C15b—C14b	117.4 (3)
C16a—C15a—C14a	117.8 (3)	C17b—C15b—C14b	122.2 (3)
C17a—C15a—C14a	122.2 (3)	C17b—C15b—C16b	120.4 (3)
C17a—C15a—C16a	120.0 (4)	C15b—C17b—O2b	123.6 (3)
C15a—C17a—O2a	123.4 (3)		

The *y* coordinate of Sia was fixed to define the origin. The absolute configuration of the molecule about the C1—C2 bond was known so only the relative configurations at other chiral sites had to be determined. *f″* was ignored for all atoms, but *f′* was used for Si.

Computer programs of the *CRYM* Crystallographic Computing System (Duchamp, 1964) were used, together with *MULTAN* (Main *et al.*, 1980) and *ORTEP* (Johnson, 1976).

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endo-2-Phenyl-*exo*-3,4,5-trithiatricyclo-[5.2.1.0²,⁶]decane *exo*-4-Oxide

William H. Watson, Mariusz Krawiec, Tirthankar Ghosh and Paul D. Bartlett

Department of Chemistry, Texas Christian University, Fort Worth, Texas 76129, USA

Abstract

The three S atoms add to the *exo* face of norbornene forming a slightly distorted envelope conformation for the trithiolane ring. The sulfoxide is *exo* with respect to the ring, and the O atom is 2.41(2) Å from an H on the bridging C atom. The two C—S bonds differ by 0.047(2) Å while *AM1* calculations predict a difference of 0.029 Å.

Comment

Sulfur reacts with norbornene in *N,N*-dimethylformamide at 373 K to produce the *exo*-trithianorbornane and the *exo*-pentathiene (Ghosh, 1986). Oxidation of the trithiane