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

The Harvard community has made this article openly available. Please share how this access benefits you. Your story matters

Citation

Published Version
http://dx.doi.org/10.1107/S0108270192006851

Citable link
http://nrs.harvard.edu/urn-3:HUL.InstRepos:3198690

Terms of Use
This article was downloaded from Harvard University’s DASH repository, and is made available under the terms and conditions applicable to Other Posted Material, as set forth at http://nrs.harvard.edu/urn-3:HUL.InstRepos:dash.current.terms-of-use#LAA
Lists of structure factors, anisotropic thermal parameters, H-atom co-
ordinates and complete geometry have been deposited with the British Li-
brary 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

References
1984/1. Univ. of Nijmegen, The Netherlands.
Hua, D. H., Bharathi, S. N., Panagandan, J. A. K. & Tsujimoto, A.
tional Laboratory, Tennessee, USA.
Analysis Package. MSC, 3200 Research Forest Drive, The Wood-
lands, TX 77381, USA.
Molecular Structure Corporation (1988). MSC/AFC Diffra-
ctometer Control Software. MSC, 3200 Research Forest Drive, The Wood-
lands, TX 77381, USA.
Freeman.


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. SCHAFFER, 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

(Received 20 February 1992; accepted 25 June 1992)

Abstract
The title compound, (4S,5S,8R,10Z)-2,2,5,6,8,10-
hexamethyl-4-phenyl-1,3-dioxo-6-aza-2-silacyclo-
dec-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.

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 dis-
tances and angles in the two independent molecules
agree well; average values are quoted here, together
with the higher or higher 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 dis-
tances: 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
(O2b···H4b) 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.

0108-2701/92/112090-03$06.00 © 1992 International Union of Crystallography
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

\[ V = 2035.3 \, (18) \, \text{Å}^3 \]

\[ Z = 4 \]

Data collection

Enraf-Nonius CAD-4 diffractometer

\[ \theta_{\text{max}} = 25^\circ \]

\[ h = -7 \rightarrow 7 \]

\[ k = -24 \rightarrow 24 \]

\[ l = 0 \rightarrow 18 \]

Absorption correction: none

4743 measured reflections

3685 independent reflections

3685 observed reflections

\[ R_{e} = 0.026 \]

Refinement

Refinement on \( F^2 \)

Final \( R \) = 0.043 for \( F^2 > 0 \)

Final \( R = 0.034 \) for \( F^2 > 3 \sigma (F^2) \)

\[ wR = 0.05 \]

\[ S = 1.72 \]

3685 reflections

432 parameters

H-atom parameters not refined

\[ \Delta \sigma_{\text{max}} = 0.19 \, \text{e} \, \text{Å}^{-3} \]

\[ \Delta \sigma_{\text{min}} = -0.19 \, \text{e} \, \text{Å}^{-3} \]


**Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (Å²)**

<table>
<thead>
<tr>
<th>( x )</th>
<th>( y )</th>
<th>( z )</th>
<th>( U_{eq} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.8192 (2)</td>
<td>0.5709</td>
<td>0.2286 (1)</td>
<td>0.0480 (2)</td>
</tr>
<tr>
<td>0.8905 (3)</td>
<td>0.6898 (1)</td>
<td>0.1832 (2)</td>
<td>0.0479 (6)</td>
</tr>
<tr>
<td>0.9065 (4)</td>
<td>0.5084 (1)</td>
<td>0.1626 (2)</td>
<td>0.0506 (6)</td>
</tr>
<tr>
<td>0.7693 (5)</td>
<td>0.6772 (2)</td>
<td>0.1200 (2)</td>
<td>0.0432 (8)</td>
</tr>
<tr>
<td>0.7234 (6)</td>
<td>0.7420 (2)</td>
<td>0.1616 (2)</td>
<td>0.0521 (9)</td>
</tr>
<tr>
<td>0.8751 (7)</td>
<td>0.7767 (2)</td>
<td>0.2091 (3)</td>
<td>0.0728 (12)</td>
</tr>
<tr>
<td>0.8357 (10)</td>
<td>0.8370 (3)</td>
<td>0.2444 (4)</td>
<td>0.0998 (17)</td>
</tr>
<tr>
<td>0.6416 (12)</td>
<td>0.8636 (3)</td>
<td>0.2314 (4)</td>
<td>0.1039 (19)</td>
</tr>
<tr>
<td>0.4920 (9)</td>
<td>0.8302 (3)</td>
<td>0.1847 (4)</td>
<td>0.1000 (17)</td>
</tr>
<tr>
<td>0.7698 (2)</td>
<td>0.1495 (3)</td>
<td>0.0762 (13)</td>
<td></td>
</tr>
<tr>
<td>0.8889 (5)</td>
<td>0.6864 (2)</td>
<td>0.0381 (2)</td>
<td>0.0447 (8)</td>
</tr>
<tr>
<td>0.7724 (6)</td>
<td>0.7268 (2)</td>
<td>-0.0332 (2)</td>
<td>0.0622 (10)</td>
</tr>
<tr>
<td>0.9627 (4)</td>
<td>0.6244 (2)</td>
<td>0.0035 (2)</td>
<td>0.0392 (6)</td>
</tr>
<tr>
<td>1.1854 (5)</td>
<td>0.6178 (2)</td>
<td>0.0065 (2)</td>
<td>0.0522 (9)</td>
</tr>
<tr>
<td>0.8283 (5)</td>
<td>0.5798 (2)</td>
<td>-0.0321 (2)</td>
<td>0.0414 (8)</td>
</tr>
<tr>
<td>0.6415 (3)</td>
<td>0.5879 (1)</td>
<td>-0.0300 (2)</td>
<td>0.0586 (7)</td>
</tr>
<tr>
<td>0.9030 (5)</td>
<td>0.5187 (2)</td>
<td>-0.0757 (2)</td>
<td>0.0434 (8)</td>
</tr>
<tr>
<td>0.7700 (6)</td>
<td>0.5051 (2)</td>
<td>-0.1603 (3)</td>
<td>0.0609 (10)</td>
</tr>
<tr>
<td>0.8975 (6)</td>
<td>0.4602 (2)</td>
<td>-0.1114 (3)</td>
<td>0.0546 (10)</td>
</tr>
<tr>
<td>1.0690 (6)</td>
<td>0.4611 (2)</td>
<td>0.0626 (3)</td>
<td>0.0523 (10)</td>
</tr>
<tr>
<td>1.2705 (7)</td>
<td>0.4359 (2)</td>
<td>0.0445 (3)</td>
<td>0.0811 (13)</td>
</tr>
<tr>
<td>1.0295 (6)</td>
<td>0.4844 (2)</td>
<td>0.1412 (3)</td>
<td>0.0533 (10)</td>
</tr>
<tr>
<td>0.5445 (6)</td>
<td>0.5720 (2)</td>
<td>0.2467 (3)</td>
<td>0.0799 (12)</td>
</tr>
<tr>
<td>0.9895 (7)</td>
<td>0.5096 (2)</td>
<td>0.3094 (3)</td>
<td>0.0705 (11)</td>
</tr>
<tr>
<td>0.1939 (1)</td>
<td>0.7299 (1)</td>
<td>0.4965 (1)</td>
<td>0.0421 (2)</td>
</tr>
<tr>
<td>0.2820 (3)</td>
<td>0.6653 (1)</td>
<td>0.5499 (1)</td>
<td>0.0423 (5)</td>
</tr>
<tr>
<td>0.2422 (3)</td>
<td>0.7961 (1)</td>
<td>0.5547 (2)</td>
<td>0.0492 (6)</td>
</tr>
<tr>
<td>0.1829 (4)</td>
<td>0.6315 (2)</td>
<td>0.6176 (2)</td>
<td>0.0371 (7)</td>
</tr>
<tr>
<td>0.1220 (3)</td>
<td>0.5642 (2)</td>
<td>0.5847 (2)</td>
<td>0.0417 (7)</td>
</tr>
<tr>
<td>0.2651 (6)</td>
<td>0.5238 (2)</td>
<td>0.5515 (3)</td>
<td>0.0611 (10)</td>
</tr>
<tr>
<td>0.2125 (8)</td>
<td>0.4604 (2)</td>
<td>0.5254 (3)</td>
<td>0.0773 (13)</td>
</tr>
<tr>
<td>0.0176 (9)</td>
<td>0.4381 (2)</td>
<td>0.5319 (3)</td>
<td>0.0833 (10)</td>
</tr>
<tr>
<td>-0.1246 (8)</td>
<td>0.4777 (2)</td>
<td>0.5634 (3)</td>
<td>0.0882 (12)</td>
</tr>
<tr>
<td>0.2082 (6)</td>
<td>0.5405 (2)</td>
<td>0.5903 (3)</td>
<td>0.0867 (12)</td>
</tr>
<tr>
<td>0.3321 (4)</td>
<td>0.6274 (2)</td>
<td>0.7002 (2)</td>
<td>0.0387 (7)</td>
</tr>
<tr>
<td>0.2464 (6)</td>
<td>0.5896 (2)</td>
<td>0.7750 (2)</td>
<td>0.0546 (9)</td>
</tr>
<tr>
<td>0.4128 (3)</td>
<td>0.6916 (1)</td>
<td>0.7301 (2)</td>
<td>0.0358 (6)</td>
</tr>
<tr>
<td>0.6341 (5)</td>
<td>0.6988 (2)</td>
<td>0.7282 (2)</td>
<td>0.0451 (8)</td>
</tr>
<tr>
<td>0.2842 (5)</td>
<td>0.7366 (2)</td>
<td>0.7591 (2)</td>
<td>0.0406 (7)</td>
</tr>
<tr>
<td>0.0980 (3)</td>
<td>0.7267 (1)</td>
<td>0.7585 (2)</td>
<td>0.0591 (7)</td>
</tr>
</tbody>
</table>

\[ D_T = 1.13 \, \text{Mg m}^{-3} \]

Mo Kα radiation

\[ \lambda = 0.71073 \, \text{Å} \]

Cell parameters from 25 reflections

\[ \theta = 14 - 16^\circ \]

\[ \mu = 0.125 \, \text{mm}^{-1} \]

\[ T = 293 \, \text{K} \]

\[ 0.65 \times 0.35 \times 0.18 \, \text{mm} \]
### Table 2. Selected bond lengths (Å) and angles (°)

<table>
<thead>
<tr>
<th>Bond Lengths</th>
<th>Angle Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Siₐ—Oₐ</td>
<td>1.630 (4)</td>
</tr>
<tr>
<td>Siₐ—Siₐ</td>
<td>2.379 (2)</td>
</tr>
<tr>
<td>Siₐ—C₇ₔ</td>
<td>1.924 (4)</td>
</tr>
<tr>
<td>C₇ₔ—Nₐ</td>
<td>1.472 (4)</td>
</tr>
<tr>
<td>Nₐ—Siₐ</td>
<td>1.354 (4)</td>
</tr>
<tr>
<td>C₁₄—O₃₃</td>
<td>1.240 (4)</td>
</tr>
<tr>
<td>C₁₂—C₂₂</td>
<td>1.489 (5)</td>
</tr>
<tr>
<td>C₁₅—C₁₆</td>
<td>1.515 (6)</td>
</tr>
<tr>
<td>C₁₅—C₁₆</td>
<td>1.519 (5)</td>
</tr>
<tr>
<td>O₂—Siₐ</td>
<td>1.108 (2)</td>
</tr>
<tr>
<td>C₈—Siₐ</td>
<td>1.118 (2)</td>
</tr>
<tr>
<td>C₉—Siₐ</td>
<td>1.106 (2)</td>
</tr>
<tr>
<td>O₂—Siₙ</td>
<td>1.106 (2)</td>
</tr>
<tr>
<td>Siₙ—O₂ₙ</td>
<td>1.924 (4)</td>
</tr>
<tr>
<td>Nₙ—Siₙ</td>
<td>1.472 (4)</td>
</tr>
<tr>
<td>C₇ₔ—Nₙ</td>
<td>1.354 (4)</td>
</tr>
<tr>
<td>O₃₃—C₁₄</td>
<td>1.240 (4)</td>
</tr>
<tr>
<td>C₂₂—C₁₂</td>
<td>1.489 (5)</td>
</tr>
<tr>
<td>C₁₆—C₁₅</td>
<td>1.515 (6)</td>
</tr>
<tr>
<td>C₁₆—C₁₅</td>
<td>1.519 (5)</td>
</tr>
<tr>
<td>O₃₃—C₁₄</td>
<td>1.240 (4)</td>
</tr>
<tr>
<td>C₁₄—C₁₃</td>
<td>1.489 (5)</td>
</tr>
<tr>
<td>C₁₃—C₁₂</td>
<td>1.515 (6)</td>
</tr>
<tr>
<td>C₁₃—C₁₂</td>
<td>1.519 (5)</td>
</tr>
</tbody>
</table>

**References**


---


**endo-2-Phenyl-exo-3,4,5-trithiatriacyclo-[5.2.1.0^2,6]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

(Received 13 March 1992; accepted 29 June 1992)

**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*-trithianonorbornene and the *exo*-pentathiene (Ghosh, 1986). Oxidation of the trithiane

© 1992 International Union of Crystallography