

- CREMER, D. & POPLE, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
- HALL, S. R. & STEWART, J. M. (1987). Editors. *XTAL2.2 User's Manual*. Univs. of Western Australia, Australia, and Maryland, USA.
- JEFFREY, G. A. (1979). *Am. Chem. Soc. Symp. Ser.* **87**, 50–62.
- JEFFREY, G. A. & YATES, J. H. (1979). *Carbohydr. Res.* **74**, 319–322.
- JOHNSON, C. K. (1971). *ORTEP*. Report ORNL-3794, revised. Oak Ridge National Laboratory, Tennessee, USA.
- LUGER, P. & BÜLOW, R. (1983). *J. Appl. Cryst.* **16**, 431–432.
- PÉREZ, S., ST-PIERRE, J. & MARCHESSAULT, R. H. (1978). *Can. J. Chem.* **56**, 2866–2871.
- SHELDRICK, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- SMIATACZ, Z., MYSZKA, H. & CIUNIK, Z. (1988). *Carbohydr. Res.* **172**, 171–182.
- WOLFROM, M. L. & THOMSON, A. (1963). *Methods Carbohydr. Chem.* **2**, 427.
- ZACHARIASEN, W. H. (1963). *Acta Cryst.* **16**, 1139–1144.
- ZACHARIASEN, W. H. (1967). *Acta Cryst.* **23**, 558–564.

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Structure of an *anti*-Aldol Addition Product of Benzaldehyde and a Pseudoephedrine-Derived *O*-Silyl Ketene *N,O*-Acetal

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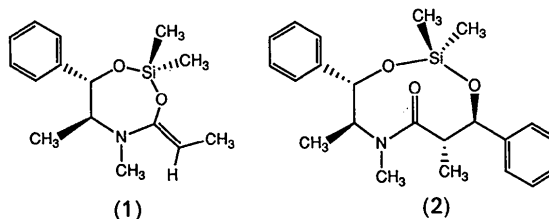
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Abstract. [4*S*-(4*R**,5*R**,8*R**,9*S**)]-2,2,5,6,8-Pentamethyl-4,9-diphenyl-1,3-dioxo-6-aza-2-silacyclononan-7-one, C₂₂H₂₉NO₃Si, *M_r* = 383.56, monoclinic, *P*2₁, *a* = 6.550 (3), *b* = 17.318 (6), *c* = 20.129 (6) Å, β = 98.83 (3)°, *V* = 2256.2 (14) Å³, *Z* = 4, *D_x* = 1.13 g cm⁻³, λ(Mo *K*α) = 0.71073 Å, μ = 1.18 cm⁻¹, *F*(000) = 824, room temperature, *R* on *F* = 0.039 for 4305 reflections with *F_o*² > 3σ(*F_o*²). The two independent molecules in this structure have nearly the same configuration and geometry. The Si atoms are tetrahedrally coordinated, with average Si—C bond distances of 1.842 (3) Å and average Si—O bond distances of 1.636 (7) Å; angles at Si differ from 109.5° by an average of 3.5°. The nine-membered rings are fully extended and the planes of the phenyl groups are approximately perpendicular to the nine-membered ring.

Introduction. Further studies of the reactions of *O*-silyl ketene *N,O*-acetals with aldehydes have revealed interesting aspects of the mechanism of the transformation (Myers, Widdowson & Kukkola, 1992). Crucial to these studies is the fact that (*S,S*)-pseudoephedrine-derived *O*-silyl ketene *N,O*-acetal (1) reacts readily with benzaldehyde to form product (2), whereas the corresponding ephedrine-derived acetal does not react. The structure of *anti*-aldol product (2), described herein, is similar to that derived from *S*-prolinol, previously reported (Schaefer, Widdowson & Myers, 1991; Myers &

Widdowson, 1990) and provides further support for the proposed mechanism involving hypervalent organosilicon intermediates (Myers, Widdowson & Kukkola, 1992; Myers & Widdowson, 1990).



Experimental. A tablet-shaped crystal, 0.15 × 0.51 × 0.61 mm, was used for data collection on a CAD-4 diffractometer with ω scans. 25 reflections with 25 < 2θ < 32° were used for determination of the cell dimensions. No absorption correction was made. (sinθ/λ)_{max} = 0.54 Å⁻¹; *h* from -7 to 7, *k* from -18 to 18, *l* from -19 to 19. Three standard reflections (055, 114 and 018) showed no variations greater than those predicted by counting statistics. 6162 reflections were measured, of which 5887 were independent. Goodness of fit for merging was 0.87 (*R*_{merge} = 0.019 for 177 reflections with exactly two observations). All reflections were used in solution and refinement of the structure. The Si atoms were found from a Patterson map and the remaining atoms located by successive structure factor–Fourier calculation; the *y* coordinate of atom Si1 was fixed at 0.7 to define the origin. *F_o*² magnitudes were used in

† Contribution No. 8513.

Table 1. Final heavy-atom coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^4$)
$$U_{\text{eq}} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U_{eq}
Si1	1888 (2)	7000	499 (1)	466 (2)
O1	2660 (3)	6991 (1)	1315 (1)	490 (6)
O2	2264 (3)	6173 (1)	148 (1)	486 (6)
O3	6582 (4)	5651 (1)	1042 (1)	558 (7)
N1	3504 (4)	5263 (2)	1302 (1)	440 (8)
C1	4679 (5)	7070 (2)	1687 (2)	501 (9)
C2	4632 (7)	7648 (2)	2244 (2)	650 (13)
C3	6129 (9)	8189 (3)	2387 (2)	1050 (18)
C4	6066 (16)	8698 (4)	2915 (4)	1649 (34)
C5	4527 (19)	8653 (5)	3302 (4)	1624 (40)
C6	3041 (12)	8135 (4)	3160 (3)	1372 (27)
C7	3085 (8)	7612 (3)	2627 (2)	896 (15)
C8	5480 (5)	6280 (2)	1984 (2)	449 (9)
C9	7761 (5)	6350 (2)	2299 (2)	621 (11)
C10	5250 (6)	5698 (2)	1409 (2)	444 (9)
C11	1937 (5)	5268 (2)	1751 (2)	603 (11)
C12	2887 (5)	4916 (2)	646 (2)	490 (10)
C13	2100 (7)	4088 (2)	685 (2)	789 (14)
C14	1283 (5)	5446 (2)	223 (2)	474 (9)
C15	504 (6)	5115 (2)	-450 (2)	544 (11)
C16	-1448 (7)	4810 (3)	-594 (2)	775 (14)
C17	-2136 (10)	4484 (3)	-1203 (3)	1057 (19)
C18	-921 (13)	4470 (3)	-1694 (3)	1184 (23)
C19	1040 (10)	4785 (3)	-1561 (3)	1071 (19)
C20	1730 (7)	5102 (3)	-942 (2)	787 (14)
C21	-893 (6)	7219 (2)	407 (2)	642 (11)
C22	3345 (6)	7696 (2)	65 (2)	623 (11)
Si3	6077 (2)	3283 (1)	4411 (1)	616 (3)
O31	7371 (4)	4067 (2)	4666 (1)	612 (7)
O32	5214 (3)	3282 (1)	3608 (1)	555 (6)
O33	4557 (5)	5067 (2)	3296 (1)	748 (8)
N31	7576 (5)	4487 (2)	3193 (2)	576 (9)
C31	6626 (6)	4833 (2)	4717 (2)	621 (12)
C32	7378 (8)	5144 (2)	5411 (2)	683 (13)
C33	6072 (8)	5557 (3)	5755 (3)	917 (15)
C34	6787 (12)	5876 (3)	6380 (3)	1185 (22)
C35	8773 (13)	5773 (4)	6666 (3)	1214 (24)
C36	10066 (9)	5381 (4)	6336 (3)	1119 (20)
C37	9413 (8)	5060 (3)	5719 (2)	935 (16)
C38	7318 (7)	5339 (2)	4164 (2)	735 (13)
C39	6577 (10)	6179 (3)	4197 (2)	1271 (23)
C40	6386 (8)	4970 (2)	3507 (2)	597 (12)
C41	9786 (6)	4372 (3)	3405 (2)	820 (14)
C42	6496 (5)	3937 (2)	2700 (2)	520 (10)
C43	7508 (6)	3864 (2)	2066 (2)	649 (11)
C44	6264 (5)	3157 (2)	3046 (2)	570 (10)
C45	5060 (7)	2596 (2)	2569 (2)	558 (11)
C46	3014 (8)	2709 (2)	2347 (2)	745 (13)
C47	1904 (8)	2233 (3)	1876 (2)	915 (15)
C48	2850 (13)	1630 (4)	1632 (3)	1225 (24)
C49	4861 (13)	1483 (4)	1856 (4)	1320 (24)
C50	5987 (8)	1974 (3)	2323 (3)	997 (15)
C51	3732 (7)	3199 (3)	4806 (2)	900 (14)
C52	7933 (7)	2488 (3)	4635 (2)	961 (16)

full-matrix least-squares refinement, which minimized $\sum w(F_o^2 - F_c^2)^2$. H atoms were placed at calculated positions (C—H = 0.095 Å) with staggered geometry. Positional and anisotropic displacement parameters of all non-H atoms (y of Si1 fixed) were refined; H-atom parameters were not refined, but the atoms were repositioned once near the end of the refinement. For 5616 reflections with $F_o^2 > 0$ $R = 0.054$, for 4305 reflections with $F_o^2 > 3\sigma(F_o^2)$ $R = 0.039$, wR (on F^2) = 0.006; $S = 1.43$. Weights were taken as $1/\sigma^2(F_o^2)$; variances $[\sigma^2(F_o^2)]$ were derived from counting statistics plus an additional term, $(0.014I)^2$; variances of the merged data by propagation of e.s.d. plus another additional term, $(0.014I)^2$. In the final least-squares cycle the $(\Delta/\sigma)_{\text{max}}$

Table 2. Selected distances (Å) and angles ($^\circ$)

Si1—O1	1.643	Si3—O31	1.640 (3)
Si1—O2	1.632	Si3—O32	1.628 (2)
Si1—C21	1.842	Si3—C51	1.841 (4)
Si1—C22	1.839	Si3—C52	1.846 (5)
O1—C1	1.423 (4)	O31—C31	1.422 (5)
O2—C14	1.433 (4)	O32—C44	1.428 (4)
O3—C10	1.230 (4)	O33—C40	1.220 (5)
N1—C10	1.358 (4)	N31—C40	1.363 (5)
N1—C11	1.468 (4)	N31—C41	1.459 (5)
N1—C12	1.450 (4)	N31—C42	1.475 (5)
C1—C2	1.505 (4)	C31—C32	1.507 (6)
C1—C8	1.553 (5)	C31—C38	1.540 (6)
C8—C9	1.536 (5)	C38—C39	1.537 (6)
C8—C10	1.525 (5)	C38—C40	1.511 (6)
C12—C13	1.530 (5)	C42—C43	1.531 (5)
C12—C14	1.548 (5)	C42—C44	1.537 (5)
C14—C15	1.486 (5)	C44—C45	1.503 (5)
O2—Si1—O1	112.4	O32—Si3—O31	113.2 (1)
C21—Si1—O1	104.5	C51—Si3—O31	110.8 (2)
C22—Si1—O1	112.3	C52—Si3—O31	104.6 (2)
C21—Si1—O2	110.5	C51—Si3—O32	104.0 (2)
C22—Si1—O2	104.2	C52—Si3—O32	110.9 (2)
C22—Si1—C21	113.3	C52—Si3—C51	113.4 (2)
C1—O1—Si1	130.0	C31—O31—Si3	128.9 (2)
C14—O2—Si1	128.8	C44—O32—Si3	130.6 (2)
C11—N1—C10	123.4 (3)	C41—N31—C40	124.1 (3)
C12—N1—C10	118.9 (3)	C42—N31—C40	117.3 (3)
C12—N1—C11	116.1 (3)	C42—N31—C41	117.4 (3)
C2—C1—O1	109.4 (3)	C32—C31—O31	109.5 (3)
C8—C1—O1	110.4 (3)	C38—C31—O31	109.6 (3)
C8—C1—C2	110.1 (3)	C38—C31—C32	112.1 (3)
C9—C8—C1	109.8 (3)	C39—C38—C31	112.2 (3)
C10—C8—C1	107.6 (3)	C40—C38—C31	105.5 (3)
C10—C8—C9	110.0 (3)	C40—C38—C39	110.5 (4)
N1—C10—O3	121.8 (3)	N31—C40—O33	121.6 (4)
C8—C10—O3	120.2 (3)	C38—C40—O33	119.3 (4)
C8—C10—N1	118.0 (3)	C38—C40—N31	118.9 (4)
C13—C12—N1	113.0 (3)	C43—C42—N31	112.9 (3)
C14—C12—N1	109.1 (3)	C44—C42—N31	109.5 (3)
C14—C12—C13	112.2 (3)	C44—C42—C43	113.0 (3)
C12—C14—O2	107.6 (3)	C42—C44—O32	108.6 (3)
C15—C14—O2	109.9 (3)	C45—C44—O32	109.6 (3)
C15—C14—C12	112.5 (3)	C45—C44—C42	110.9 (3)

ratio was 0.14. In the final difference Fourier map $0.45 \geq \Delta\rho \geq -0.34 \text{ e \AA}^{-3}$. Atomic scattering factors and values for f' and f'' were taken from Cromer & Waber (1974) and Cromer (1974). Programs used were those of the *CRYM* crystallographic computing system (Duchamp, 1964) and *ORTEP* (Johnson, 1976). Final refined parameters of the atoms are listed in Table 1 with selected distances and angles in Table 2.* The structure solution and preliminary refinement were with the data averaged in point group $2/m$ ($R_{\text{int}} = 0.028$ for 2530 duplicates, goodness of fit = 0.94 for 2826 multiples). The data were re-averaged in point group 2 for the final refinement. Structure factors with $f'' = 0.071$ for Si were better by about 2% for both R and goodness of fit, than for -0.071 , so final refinements were based on the positive value.

* Lists of assigned H-atom parameters, anisotropic displacement parameters, complete distances and angles, and observed and calculated structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55198 (32 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HH0589]

Discussion. There are two nearly identical molecules in the asymmetric unit of this compound (Fig. 1); this discussion will use average values of bond distances and angles for the two, indicated by sample e.s.d.'s within square brackets. Moreover, the molecules have a partial (non-crystallographic) symmetry to them, extending from the Si atom in both directions around the ring to the methyl C atoms, so that many bond distances quoted are averages of

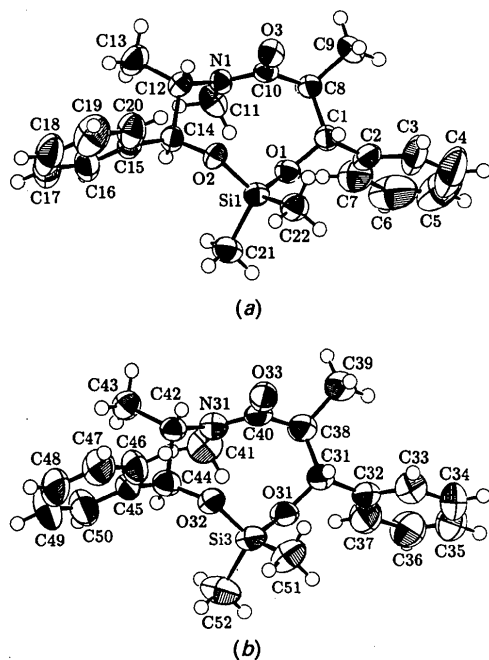


Fig. 1. ORTEPII (Johnson, 1976) drawings of (a) molecule 1 and (b) molecule 2, with 50% probability ellipsoids showing the numbering system. H atoms are shown as arbitrary small circles.

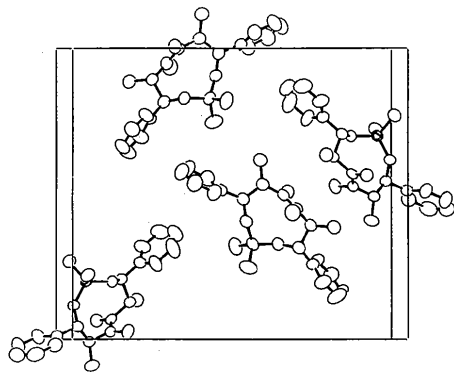


Fig. 2. An ORTEPII (Johnson, 1976) packing drawing projected down a showing the contents of a unit cell, with the unit cell outlined. The c axis is horizontal. Atoms are shown as 50% probability ellipsoids, with Si atoms in molecule 1 shaded. H atoms are not shown.

four values, not just two. Where comparisons are made to expected distances, the expected values are taken from the compilation of Allen, Kennard, Watson, Brammer, Orpen & Taylor (1987).

The bond distances and angles in the molecule are all within normal ranges. At the Si atom, Si—C averages 1.845 [5] vs 1.857 [18] Å expected; Si—O is 1.636 [7] vs 1.631 [22] Å expected. Similar comparisons hold for other bond lengths: O1—C1, O2—C14, O31—C31 and O32—C44, 1.427 [5] observed, 1.426 [19] Å expected; C—C (phenyl), 1.496 [19] observed, 1.506 [11] Å expected; C—C in phenyl rings, 1.368 [19] observed, 1.380 [13] Å expected; C1—C8, C12—C14, C31—C38 and C42—C44, 1.545 [7] observed, 1.542 [11] Å expected; and C—CH₃, 1.534 [4] observed, 1.524 [15] Å expected. For the remainder of the molecule we find: C8—C10, C38—C40 1.518 [10] observed, 1.511 [15] Å expected; C=O, 1.225 [7] observed, 1.231 [12] Å expected; C(=O)—N, 1.361 [4] observed, 1.352 [10] Å expected; N—CH₃, 1.464 [6] observed, 1.468 [9] Å expected and for C(CH₃)—N, 1.463 [18] observed, 1.469 [12] Å expected. The angles show a similar agreement, with the average value of the difference between corresponding angles in the two molecules being 1.2° in the central ring system. There are no close intramolecular contacts across the ring, but all atoms are at approximately van der Waals distances from each other.

Intermolecular contacts are also all at van der Waals or greater distances (Fig. 2). There are two H···H interactions less than 2.4 Å, one 2.34 and one 2.39 Å, the shorter being between an H atom of molecule 1 and a different H atom in the same molecule, one unit cell away along a. There are four H···O interactions at van der Waals distances (2.6 Å) or closer, suggestive of C—H···O hydrogen bonding. All of these contacts are to the carbonyl O atoms, clearly the best receptor in the molecule, with the shortest being from H11B to O33, at 2.49 Å.

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References

- ALLEN, F. H., KENNARD, O., WATSON, D. G., BRAMMER, L., ORPEN, A. G. & TAYLOR, R. (1987). *J. Chem. Soc. Perkin Trans.* pp. S1–S19.
- CROMER, D. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, pp. 149–151. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
- CROMER, D. T. & WABER, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, pp. 99–101. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
- DUCHAMP, D. J. (1964). CRYM crystallographic computing system. Am. Crystallogr. Assoc. Meet., Bozeman, Montana. Paper B14, p. 29.

JOHNSON, C. K. (1976). *ORTEPII*. Report ORNL-3794, third revision. Oak Ridge National Laboratory, Tennessee, USA.
 MYERS, A. G. & WIDDOWSON, K. L. (1990). *J. Am. Chem. Soc.* **112**, 9672–9674.

MYERS, A. G., WIDDOWSON, K. L. & KUKKOLA, P. J. (1992). *J. Am. Chem. Soc.* **114**, 2765–2767.
 SCHAEFER, W. P., WIDDOWSON, K. L. & MYERS, A. G. (1991). *Acta Cryst. C* **47**, 2575–2578.

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Structure of Thiamine Bromide Sesquihydrate

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Abstract. 3-[(4-Amino-2-methyl-5-pyrimidinyl)-methyl]-5-hydroxyethyl-4-methylthiazolium bromide sesquihydrate, $C_{12}H_{17}N_4OS^+ \cdot Br^- \cdot 1.5H_2O$, $M_r = 372.28$, monoclinic, $P2_1/a$, $a = 11.676$ (2), $b = 24.819$ (7), $c = 12.344$ (3) Å, $\beta = 113.74$ (2)°, $V = 3274$ (1) Å³, $Z = 8$, $D_x = 1.51$ g cm⁻³, $\rho(Mo K\alpha) = 0.71069$ Å, $\mu = 26.2$ cm⁻¹, $F(000) = 1528$, $T = 293$ K, $R = 0.062$ for 2720 observed reflections. Both the independent thiamine molecules *A* and *B* in the asymmetric unit adopt the common *F* conformation. A bromide anion is held by four neighbouring thiamine molecules through C(2)—H \cdots Br hydrogen bonds and Br \cdots thiazolium-ring electrostatic interactions. Another bromide anion (or a water molecule) bridges the pyrimidine and thiazolium moieties of molecule *A* (or *B*) through a hydrogen bond with the amino group and an electrostatic interaction with the thiazolium ring.

Introduction. The pyrophosphate of thiamine is a coenzyme in a number of important enzymes which include the α -keto acid decarboxylases and the transketolases. Thiamine C(2) adducts are intermediates in a proposed mechanism for thiamine action (Breslow, 1958). X-ray studies on the thiamine–anion compounds show that a thiamine molecule captures an anion in the vicinity of the C(2) catalytic site *via* both hydrogen-bond and electrostatic interactions, serving as a model of coenzyme–substrate interactions in the enzyme systems (Aoki & Yamazaki, 1985; Aoki, Yamazaki, Waragai & Itokawa, 1988). The crystal structure of thiamine bromide sesquihy-

drate reported here is an additional example of such a thiamine–anion complexation.

Experimental. Thiamine.Br.1.5H₂O was prepared by mixing aqueous solutions of thiamine.Cl.HCl and NaBr in a 1:2 molar ratio and adjusting the pH to 7 with dilute NaOH solution. Colourless tabular crystals formed after a few weeks. A crystal of dimensions 0.15 × 0.51 × 0.52 mm was used for data collection on a Nicolet R3m diffractometer, with graphite-monochromated Mo *K* α radiation. Cell parameters were determined from a least-squares fitting of diffractometer setting angles for 21 centred reflections ($10 < 2\theta < 28^\circ$). Data were collected using ω scans, scan speed 5.88° min⁻¹, scan width 1.25°, 2θ range 3–42°, and $h - 11 \rightarrow 10$, $k 0 \rightarrow 29$, $l 0 \rightarrow 14$. A total of 3811 unique reflections were measured, of which 2720 with $I > 2\sigma(I)$ were used in the refinement. One standard reflection showed no significant intensity variation. *Lp* and empirical absorption corrections (maximum and minimum transmission coefficients 0.99 and 0.47) were applied. The structure was solved by the heavy-atom method and refined by block-diagonal least squares on *F*. The hydroxyethyl side chain of a thiamine molecule and a water molecule were disordered, with each atom in two positions. The occupancy factors were estimated on the basis of their electron densities. The non-H atoms were refined anisotropically, except the minor disordered ones which refined isotropically. The positions of 29 of the 40 H atoms were determined from a difference map and their stereochemistry, and fixed in the final cycles of the refinement ($U = 0.06$ Å²). $R = 0.062$, $wR = 0.080$, S

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