Refinement

Refinement on F	$(\Delta/\sigma)_{max} = 0.168$
Final $R = 0.037$	$\Delta\rho_{max} = 0.3$ e Å^{-3}
$wR = 0.050$	$\Delta\rho_{min} = -0.7$ e Å^{-3}
$S = 0.55$	Atomic scattering factors
997 reflections	from *International Tables*
98 parameters	*for X-ray Crystallogra-*
Only H-atom U's refined	*phy* (1974, Vol. IV, Table
Calculated weights w =	2.2B)
$1/[\sigma^2(F)+0.0070F^2]$	

Data collection: Nicolet *R3m/V* software, release 4.11. Cell refinement: Nicolet *R3m/V* software. Data reduction: Nicolet *R3m/V* software. Program(s) used to solve structure: *SHELXTL-Plus* (Sheldrick, 1987). Program(s) used to refine structure: *SHELXTL-Plus*. Software used to prepare material for publication: *PARST* (Nardelli, 1983), *PLATON* (Spek, 1982), *MISSYM* (Le Page, 1987).

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}
Ge(1)	0.0	0.02457 (6)	0.25	0.0448
O(1)	−0.0965 (2)	−0.6461 (4)	0.3928 (3)	0.0768
O(2)	−0.2113 (2)	−0.7006 (3)	0.1983 (3)	0.0654
C(1)	0.0672 (3)	0.1507 (5)	0.4059 (4)	0.0686
C(2)	−0.0620 (2)	−0.1309 (4)	0.2672 (4)	0.0479
C(3)	−0.0457 (2)	−0.2816 (4)	0.2228 (3)	0.0378
C(4)	−0.0657 (2)	−0.4168 (4)	0.2729 (3)	0.0380
C(5)	−0.1316 (2)	−0.5059 (4)	0.2025 (3)	0.0359
C(6)	−0.1970 (3)	−0.4918 (4)	0.0571 (4)	0.0573
C(7)	−0.1412 (2)	−0.6234 (4)	0.2774 (3)	0.0416
C(8)	−0.2282 (4)	−0.8154 (6)	0.2618 (5)	0.0908

Table 2. *Geometric parameters* (Å, °)

Ge(1)—C(1)	1.929 (4)	C(3)—C(3^i)	1.550 (6)
Ge(1)—C(2)	1.950 (5)	C(3)—C(4)	1.504 (6)
O(1)—C(7)	1.184 (4)	C(4)—C(5)	1.327 (5)
O(2)—C(7)	1.332 (4)	C(5)—C(6)	1.492 (5)
O(2)—C(8)	1.447 (8)	C(5)—C(7)	1.483 (6)
C(2)—C(3)	1.539 (6)		
C(1)—Ge(1)—C(2)	113.1 (2)	C(2)—C(3)—C(4)	110.0 (3)
C(1)—Ge(1)—C(1^i)	110.6 (2)	C(3)—C(4)—C(5)	126.6 (3)
C(1)—Ge(1)—C(2^i)	113.5 (2)	C(4)—C(5)—C(7)	116.3 (3)
C(2)—Ge(1)—C(2^i)	92.1 (2)	C(4)—C(5)—C(6)	124.9 (3)
C(7)—O(2)—C(8)	115.9 (3)	C(6)—C(5)—C(7)	118.7 (3)
Ge(1)—C(2)—C(3)	104.8 (3)	O(2)—C(7)—C(5)	111.2 (3)
C(2)—C(3)—C(3^i)	107.6 (3)	O(1)—C(7)—C(5)	127.0 (4)
C(4)—C(3)—C(3^i)	111.7 (3)	O(1)—C(7)—O(2)	121.7 (4)

C(2)—Ge(1)—C(2^i)—C(3^i)	−14.1(3)
Ge(1)—C(2^i)—C(3^i)—C(3)	39.2(3)
C(2^i)—C(3^i)—C(3)—C(2)	−53.2(4)

Symmetry code: (i) $-x, y, \tfrac{1}{2} - z$.

The title compound was obtained from free singlet dimethylgermylene, which is generated by thermolysis of a 7-germanorbornadiene (Neumann, 1991), and methyl (E)-2-methyl-2,4-pentadienoate at 343 K in benzene (Wienken & Neumann, 1992) and is separated from the isomeric *cis*-3,4-dialkenyl-1-germacyclopentane by repeated crystallization. The crystals were obtained from methanol at room temperature, m.p. 384 K (yield 16%). The lattice parameters were determined from a symmetry-constrained least-squares fit. Refinement was based on full-matrix least-squares methods with H atoms in calculated positions (C—H 0.96 Å). One common isotropic temperature factor was refined for the H atoms of the methyl groups and another was refined for the remaining H atoms.

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Structure of a *syn*-Aldol Addition Product of Benzaldehyde and a Prolinol-Derived *O*-Silacyclopentyl Ketene *N,O*-Acetal

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Abstract

The compound (5*S*,6*S*,11a*S*)-hexahydro-6-methyl-5-phenylspiro[1*H*,7*H*-pyrrolo[2,1-*e*][1,3,6,2]dioxazasilonine-3,1′-silacyclopentan]-7-one (1) results from the silicon-directed condensation of the prolinol-derived

† Contribution No. 8633

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O-silacyclopentyl ketene *N,O*-acetal (2) with benzaldehyde. The five-membered pyrrolidine ring has an envelope conformation and the silacyclopentyl ring has an *en*-type conformation with C17 and C18 on opposite sides of the C16—Si—C19 plane. Both of these rings appear to be disordered.

Comment

The non-catalyzed condensation of *O*-silyl ketene *N,O*-acetals with aldehydes has been proposed to proceed *via* a pentavalent organosilicon intermediate (Myers & Widdowson, 1990; Myers, Widdowson & Kukkola, 1992). In further mechanistic studies of this reaction, the effect of constraining the alkyl groups bound to silicon in a ring was investigated. The reaction of the *O*-silyl ketene *N,O*-acetal (2) with benzaldehyde at 296 K forms both *syn* and *anti* aldol addition products; *syn* product (1) forms X-ray quality crystals (m.p. 430–434 K) upon slow evaporation of a benzene solution. The structural analysis of (1) is described herein.

This compound closely resembles the aldol condensation product (3) (Schaefer, Widdowson & Myers, 1991); the only difference is in the substituents of the Si atoms: a cyclic tetramethylene chain in (1) and two methyl groups in (3). The unit-cell dimensions are comparable, and the space group, packing and conformation of the nine-membered ring are the same.

(2) + (3) → (1)
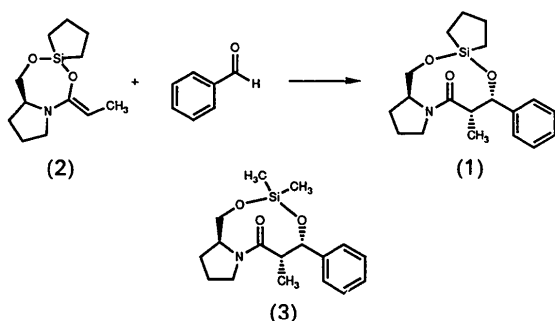
The molecule is shown in Fig. 1. The pyrrolidine ring has the common envelope conformation (Marsh & Donohue, 1967, and references therein) with 'flap' atom C12 lying 0.52 Å out of the (nearly exact) plane of C11, N, C13 and C14. We note that the large U_{ij}'s of C11, C12 and C13 suggest possible disorder involving inversion of the ring, as first found in crystals of L-leucyl-L-prolylglycine (Leung & Marsh, 1958; Marsh, 1980). Similar disorder in the five-membered ring containing Si may explain the surprisingly short C17–C18 distance [1.442 (9) Å]. The large anisotropic displacement parameters of these two atoms show that their apparent motion is primarily perpendicular to the bond between them. Correcting the observed distance for this apparent motion

gives a value of 1.50 or 1.51 Å, as expected for a —CH₂—CH₂— single bond. We have not attempted to model these possible disorders.
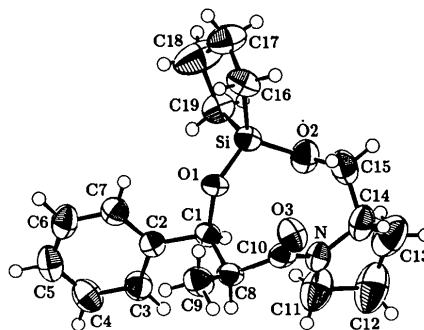

Fig. 1. An *ORTEP* drawing of the molecule with 50% probability ellipsoids showing the numbering system. H atoms are shown as circles of arbitrary small diameter.

The intermolecular heavy-atom distances are all greater than 3.7 Å except for C6···C14 [3.673 (7) Å] which is still only a van der Waals contact and O3···C11 [3.363 (7) Å]. This latter value is short enough to suggest a weak hydrogen bond from C11 to the carbonyl O atom O3 but H11b···O3 (2.89 Å) is unremarkable and O3···H11b—C11 (113°) is severely bent. A packing drawing is shown in Fig. 2.
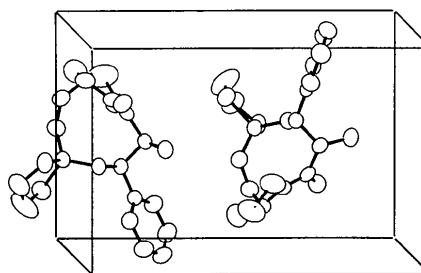

Fig. 2. An *ORTEP* drawing of the unit-cell contents (one unit cell outlined). The projection is roughly perpendicular to the *bc* plane, with the *b* axis horizontal; H atoms are not shown.

Experimental

Crystal data

C₁₉H₂₇NO₃Si	Mo *Kα* radiation
$M_r = 345.50$	$\lambda = 0.71073$ Å
Monoclinic	Cell parameters from 25
*P*2₁	reflections
$a = 6.410 (2)$ Å	$\theta = 6–16°$
$b = 15.438 (2)$ Å	$\mu = 0.14$ mm⁻¹
$c = 9.808 (2)$ Å	$T = 295$ K
$\beta = 104.06 (2)°$	Triangular prism
$V = 941.5 (3)$ Å³	0.44 × 0.24 × 0.24 mm
$Z = 2$	Colorless
$D_x = 1.22$ Mg m⁻³	

Data collection

Enraf-Nonius CAD-4 diffractometer

θ-2θ scans

Absorption correction: none

3582 measured reflections

1728 independent reflections

1728 observed reflections

R_{int} = 0.033 for 1384 reflections with 2 observations

θ_{max} = 25°

$h = -7 \to 7$

$k = -18 \to 18$

$l = 0 \to 11$

3 standard reflections frequency: 150 min intensity variation: within counting statistics

Refinement

Refinement on F^2

Final R = 0.055 for reflections with $F_o^2 > 0$, 0.043 for reflections with $F_o^2 > 3\sigma(F_o^2)$

wR = 0.007, 0.006

S = 1.75

1728 reflections

217 parameters

H-atom parameters not refined

$w = 1/[\sigma^2(F_o^2)]$

$(\Delta/\sigma)_{max}$ = 0.14

$\Delta\rho_{max}$ = 0.35 e Å^{-3}

$\Delta\rho_{min}$ = -0.28 e Å^{-3}

Extinction correction: Larson (1967)

Extinction coefficient: 1.2 (4)×10^{-6} (secondary)

Atomic scattering factors from Cromer & Waber (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}
Si	0.1889 (2)	0.5000	0.3812 (1)	0.0492 (3)
O1	0.2255 (4)	0.3970 (2)	0.3560 (3)	0.0498 (7)
O2	0.3040 (5)	0.5318 (2)	0.5408 (3)	0.0670 (9)
C1	0.4262 (6)	0.3527 (3)	0.3867 (4)	0.0448 (10)
C2	0.4719 (6)	0.3160 (3)	0.2539 (4)	0.0445 (9)
C3	0.6718 (7)	0.2829 (3)	0.2572 (5)	0.0579 (12)
C4	0.7147 (8)	0.2472 (3)	0.1375 (6)	0.0705 (14)
C5	0.5594 (9)	0.2442 (3)	0.0139 (6)	0.0713 (15)
C6	0.3614 (8)	0.2778 (3)	0.0098 (5)	0.0677 (14)
C7	0.3153 (7)	0.3140 (5)	0.1277 (5)	0.0554 (11)
C8	0.4202 (6)	0.2816 (3)	0.4978 (4)	0.0491 (10)
C9	0.2794 (8)	0.2057 (3)	0.4391 (5)	0.0645 (13)
C10	0.3390 (7)	0.3267 (3)	0.6131 (5)	0.0517 (11)
O3	0.1569 (5)	0.3181 (2)	0.6260 (3)	0.0652 (8)
N	0.4759 (6)	0.3849 (3)	0.6939 (4)	0.0541 (9)
C11	0.7113 (8)	0.3890 (5)	0.7140 (6)	0.0957 (19)
C12	0.7756 (10)	0.4441 (6)	0.8460 (7)	0.1245 (25)
C13	0.5964 (11)	0.5061 (5)	0.8377 (6)	0.1109 (21)
C14	0.3945 (8)	0.4551 (4)	0.7663 (5)	0.0709 (14)
C15	0.2293 (8)	0.5092 (4)	0.6619 (5)	0.0724 (14)
C16	−0.1024 (7)	0.5212 (3)	0.3208 (5)	0.0625 (13)
C17	−0.1143 (8)	0.5963 (4)	0.2206 (6)	0.0838 (16)
C18	0.0665 (11)	0.5995 (5)	0.1573 (8)	0.1213 (23)
C19	0.2796 (7)	0.5729 (3)	0.2575 (5)	0.0623 (13)

Table 2. *Bond lengths (Å) and angles (°)*

Si—O1	1.636 (3)	C8—C9	1.505 (6)
Si—O2	1.635 (3)	C8—C10	1.523 (6)
Si—C16	1.846 (5)	C10—O3	1.211 (5)
Si—C19	1.849 (5)	C10—N	1.366 (6)
O1—C1	1.423 (5)	N—C11	1.475 (7)
O2—C15	1.427 (6)	N—C14	1.460 (6)
C1—C2	1.513 (6)	C11—C12	1.520 (10)
C1—C8	1.555 (6)	C12—C13	1.482 (10)
C2—C3	1.373 (6)	C13—C14	1.531 (9)
C2—C7	1.392 (6)	C14—C15	1.530 (7)
C3—C4	1.383 (7)	C16—C17	1.510 (7)
C4—C5	1.370 (8)	C17—C18	1.442 (9)
C5—C6	1.363 (7)	C18—C19	1.533 (9)
C6—C7	1.378 (7)		

O2—Si—O1	112.9 (2)	C10—C8—C1	105.5 (3)
C16—Si—O1	107.1 (2)	C10—C8—C9	111.0 (4)
C19—Si—O1	114.4 (2)	O3—C10—C8	122.6 (4)
C16—Si—O2	116.1 (2)	N—C10—C8	116.3 (4)
C19—Si—O2	107.8 (2)	N—C10—O3	120.8 (4)
C19—Si—C16	97.8 (2)	C11—N—C10	126.8 (4)
C1—O1—Si	126.2 (2)	C14—N—C10	121.0 (4)
C15—O2—Si	123.9 (3)	C14—N—C11	112.2 (4)
C2—C1—O1	110.6 (3)	C12—C11—N	101.3 (5)
C8—C1—O1	108.2 (3)	C13—C12—C11	105.5 (6)
C8—C1—C2	112.4 (3)	C14—C13—C12	104.5 (5)
C3—C2—C1	119.6 (4)	C13—C14—N	104.0 (4)
C7—C2—C1	121.7 (4)	C15—C14—N	110.5 (4)
C7—C2—C3	118.7 (4)	C15—C14—C13	113.3 (5)
C4—C3—C2	120.3 (4)	C14—C15—O2	111.9 (4)
C5—C4—C3	120.9 (5)	C17—C16—Si	103.4 (3)
C6—C5—C4	118.9 (5)	C18—C17—C16	112.8 (5)
C7—C6—C5	121.2 (5)	C19—C18—C17	113.5 (6)
C6—C7—C2	120.0 (4)	C18—C19—Si	102.2 (4)
C9—C8—C1	113.3 (3)		

The goodness-of-fit for merging (point group $2/m$) 1599 reflections with multiple observations was 1.01. The coordinates of the Si atom were found from a Patterson map and those of the C, N and O atoms from subsequent structure factor-Fourier cycles. All reflections, F_o^2 positive and negative, were used in the refinement. H atoms were placed at calculated postions (C— H 0.95 Å) and re-positioned once near the end of the refinement. The variances ($\sigma^2 I$) were derived from counting statistics plus an additional term $(0.014I)^2$; variances of the merged data were obtained by propagation of error plus another additional term $(0.014\bar{I})^2$. Atomic scattering factors and values for $\Delta f'$ were taken from Cromer & Waber (1974) and Cromer (1974). The programs used were *CRYM* (Duchamp, 1964) and *ORTEP* (Johnson, 1976). The chirality of the molecule was known from its synthesis. Near the conclusion of the refinement, the intensities were re-averaged in point group 2 and refinements carried out for both chiralities; the correct one gave slightly smaller residuals (0.0642 *versus* 0.0645 for R, 1.52 *versus* 1.53 for S). There were no significant differences between the three sets of coordinates ($\Delta f'_{Si}$ = 0.071 e$^-$).

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Comment

Synthesis of 2-[4-(dimethylamino)phenylimino]-3-oxo-N-phenylbutanamide (DPA) (Fig. 1) from acetanilide and N,N-dimethyl-4-nitroso-benzenamine (NDA) was undertaken as part of studies on charge-transfer complexes formed by 1-oxa-4-azabutadienes. The reaction mixture yielded the desired product but dark-green crystals, which had semiconductive properties, were also precipitated. On the basis of spectroscopic investigations, the structure of a polymeric quinhydrone-type charge-transfer complex of DPA and NDA was proposed (Moskal, Moskal & Milart, 1984). To verify this model we determined the crystal structure using X-ray diffraction methods.

Molecular Complex of 2-[4-(Dimethylamino)phenylimino]-3-oxo-N-phenylbutanamide and N,N-Dimethyl-4-nitrosoaniline

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Abstract

2-[4-(Dimethylamino)phenylimino]-3-oxo-N-phenylbutanamide and N,N-dimethyl-4-nitrosoaniline form a molecular complex in which they are linked by a hydrogen bond and π-π^* interactions. Intermolecular contacts shorter than 3.2 Å are also observed between adjacent complexes arranged in double layers. The geometry of the dimethylaminophenyl moiety in both molecules indicates a contribution from the *para*-quinonoid structure.
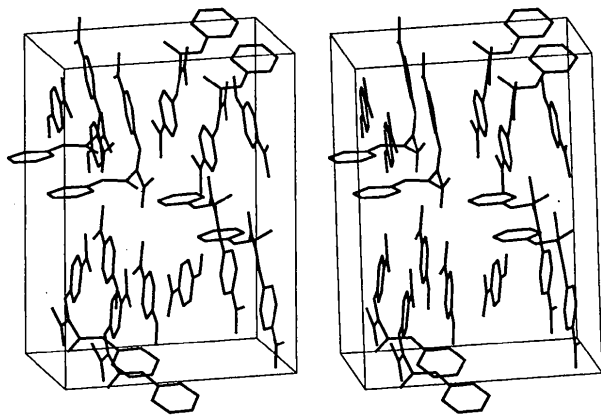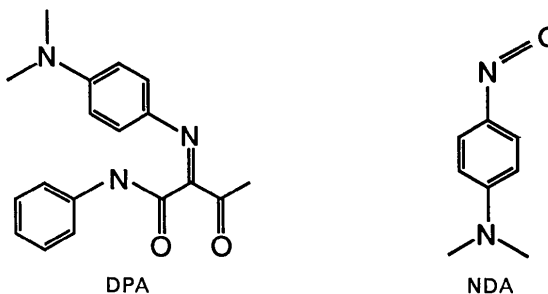
Fig. 1. Stereodrawing of the molecular packing. The origin is at the back lower right corner.

DPA　　　　　　　　　　　NDA

DPA (Fig. 2a) and NDA (Fig. 2b) molecules form double layers perpendicular to the [010] direction and related by a 2_1 axis. The mean separation between layers is about 3.5 Å. The DPA and NDA molecules are linked in pairs by a hydrogen bond between the anilide N atom of DPA and the nitroso O atom of NDA: N115···O209 = 2.813(2), H114···O209 = 1.98(2) Å and N115—H114···O209 = 162(2)°. As judged by the closest intermolecular contacts, which are 3.147(2) Å for O209—C102 and 3.339(2) Å for O209—C103, the nitroso group atoms are involved in π-π^* interactions with the same DPA molecule. Other short intermolecular contacts observed between molecules in the same layer are C210—N207 = 3.193(2) and C211—O122 = 3.101(2) Å. Although the structure contains potential charge-transfer donors and acceptors stacked along [010], all other intermolecular contacts are longer than 3.4 Å, thus the interactions between layers should be classified as van der Waals contacts.

The distances in the NDA molecule show some distortion from the values expected in an aromatic ring and indicate a large contribution of the *para*-quinonoid structure. The observed pattern of bond lengths and angles in NDA is analogous to that observed in the structures of NDA.HCl.H$_2$O (Drangfelt & Rømming, 1974) and the complexes CoCl(NDA)$_2$ (Sams & Doedens, 1979) and Cl$_2$Me$_2$(NDA)$_2$Sn (Matsubayashi & Nakatsu, 1982). Similar deformation is also observed in N,N-dimethylphenyl moiety of the DPA molecule, although to a lesser extent, presumably due to the formation of a double bond between N105 and C102 conjugated with