

## References

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tetracoordinate allyl silanes (Cerveau, 1987), and this reactivity is believed to arise from particularly effective hyperconjugation between the Si—C  $\sigma$ -electrons and the C=C  $\pi$ -system (Fig. 1). Thus, we were interested in investigating whether the hyperconjugation in (I) would lead to any observable structural effects, such as lengthening of the Si—allyl bond, lengthening of the C=C double bond or a decrease in the intrabridgehead N $\cdots$ Si distance, as expected from contributions from the resonance form, (Ia), compared with similar saturated analogues in which hyperconjugation is absent.

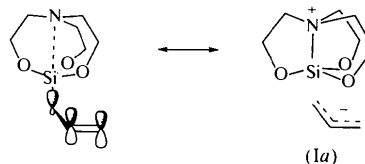


Fig. 1. Hyperconjugation in allylsilatrene.

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## Low-temperature structure of allyl silatrane

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### Abstract

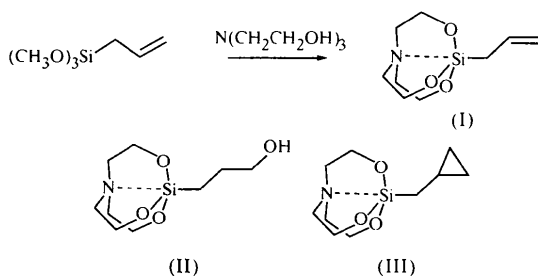
The structure of the title compound, 1-allyl-2,8,9-trioxo-5-aza-1-silabicyclo[3.3.3]undecane (C<sub>9</sub>H<sub>17</sub>NO<sub>3</sub>Si), was determined in order to study the structural effects which arise from hyperconjugation between the C—Si bond and the allyl double bond. The dative N $\cdots$ Si distance is 2.140 (1) Å.

### Comment

As part of our general interest in the structural consequences of hyperconjugation in silicon compounds (White, 1995), we chose to determine the structure of allyl silatrane, (I). Allyl silatrane has been shown to undergo reaction with electrophiles more readily than

The structure of (I) was determined at 130 K to eliminate the unwanted effects of thermal motion. Although the bicyclic moiety was well ordered, the allyl group was disordered over two positions, with occupancies of 52 (1) and 48 (1)%. This disorder arises from rotation about the C12—C13 bond. Intrabridgehead interaction between the amino group and the Si atom is evidenced by the N5 $\cdots$ Si distance of 2.140 (1) Å, which is considerably shorter than the sum of the van der Waals radii for Si and N (3.65 Å; Bondi, 1964). As a result of this interaction, the Si distorts from a regular tetrahedral geometry towards a trigonal bipyramid, with N5 and C12 at the apical positions and O2, O8 and O9 at the basal positions. This distortion is best exemplified by the bond angles about the Si: the mean O—Si—O angle is 118.7, the mean O—Si—C12 angle is 96.4 and the mean N $\cdots$ Si—O angle is 83.58°.

Owing to the disorder of C13 and C14, the bond distances involving these atoms must be treated as somewhat suspect. Therefore, we cannot make any conclusions regarding structural effects arising from hyperconjugation between the Si—C12 bond and the C13=C14 double bond. However, the Si—C12—C13—C14 torsion angle of 106.8 (3)° is close to the optimum conformation required for this interaction. Consideration of the interatomic distances in the ordered part of the structure of (I) does provide some tentative structural evidence for hyperconjugation between the Si—C12 bond and the allyl  $\pi$ -system. Thus, the N $\cdots$ Si bond of 2.140 (1) Å is slightly shorter than the corresponding distance observed in the analogous structures, (II) [2.173 (2) Å; Hencsei *et al.*, 1988] and (III) [2.177 (4) Å; Hencsei *et al.*, 1989]. Furthermore, the Si—C12 distance of 1.896 (1) Å is slightly longer than the corresponding distances in (II)



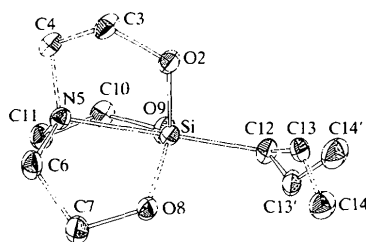


Fig. 2. ZORTEP (Zsolnai, 1994) diagram of (I). Displacement ellipsoids are at the 30% probability level and H atoms have been omitted for clarity.

and (III), which are 1.869 (2) and 1.872 (4) Å, respectively, and this is consistent with contributions from the resonance form, (Ia).

## Experimental

The title compound was prepared by reaction of allyltrimethoxysilane with triethanolamine (Cerveau, 1987). Crystals of (I) (m.p. 396–397 K) were grown from ether.

### Crystal data

$C_9H_{17}NO_3Si$   
 $M_r = 215.33$   
 Monoclinic  
 $P2_1/n$   
 $a = 6.8422(8) \text{ \AA}$   
 $b = 12.400(1) \text{ \AA}$   
 $c = 12.609(1) \text{ \AA}$   
 $\beta = 94.825(8)^\circ$   
 $V = 1066.0(2) \text{ \AA}^3$   
 $Z = 4$   
 $D_x = 1.342 \text{ Mg m}^{-3}$   
 $D_m$  not measured

Mo  $K\alpha$  radiation  
 $\lambda = 0.71069 \text{ \AA}$   
 Cell parameters from 25 reflections  
 $\theta = 14\text{--}16^\circ$   
 $\mu = 0.203 \text{ mm}^{-1}$   
 $T = 130.0(1) \text{ K}$   
 Block  
 $0.4 \times 0.4 \times 0.3 \text{ mm}$   
 Colourless

### Data collection

Enraf–Nonius CAD-4S diffractometer  
 $\theta/2\theta$  scans  
 Absorption correction: none  
 2025 measured reflections  
 1861 independent reflections  
 1733 reflections with  $I > 2\sigma(I)$   
 $R_{int} = 0.015$

$\theta_{max} = 24.97^\circ$   
 $h = 0 \rightarrow 8$   
 $k = 0 \rightarrow 14$   
 $l = -14 \rightarrow 14$   
 3 standard reflections  
 frequency: 160 min  
 intensity decay: not significant

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.028$   
 $wR(F^2) = 0.074$   
 $S = 1.059$   
 1861 reflections  
 223 parameters  
 H atoms: see below  
 $w = 1/[\sigma^2(F_o^2) + (0.0406P)^2 + 0.4642P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{max} = 0.016$

$\Delta\rho_{max} = 0.359 \text{ e \AA}^{-3}$   
 $\Delta\rho_{min} = -0.236 \text{ e \AA}^{-3}$   
 Extinction correction: SHELXL97 (Sheldrick, 1997)  
 Extinction coefficient: 0.014 (2)  
 Scattering factors from International Tables for Crystallography (Vol. C)

Table 1. Selected geometric parameters (Å, °)

Si—O2	1.668 (1)	N5—C6	1.476 (2)
Si—O9	1.668 (1)	C6—C7	1.518 (2)
Si—O8	1.669 (1)	C7—O8	1.422 (2)
Si—C12	1.896 (1)	O9—C10	1.421 (2)
Si—N5	2.140 (1)	C10—C11	1.520 (2)
O2—C3	1.427 (2)	C12—C13'	1.472 (4)
C3—C4	1.517 (2)	C12—C13	1.538 (4)
C4—N5	1.475 (2)	C14—C13	1.314 (8)
N5—C11	1.476 (2)	C14'—C13'	1.312 (9)
O2—Si—O9	118.23 (5)	O9—Si—N5	83.60 (5)
O2—Si—O8	118.93 (5)	O8—Si—N5	83.62 (5)
O9—Si—O8	119.14 (5)	C12—Si—N5	178.97 (6)
O2—Si—C12	97.41 (6)	C4—N5—Si	105.00 (8)
O9—Si—C12	95.57 (6)	C11—N5—Si	104.50 (8)
O8—Si—C12	96.29 (6)	C6—N5—Si	104.45 (8)
O2—Si—N5	83.52 (5)		
Si—C12—C13'—C14'	-116.3 (4)	Si—C12—C13—C14	106.8 (3)

Data were collected at 130 K. The structure was solved by direct methods and refinement was performed using anisotropic displacement parameters for all non-H atoms, and isotropic displacement parameters for the H atoms. Despite the disorder on C13 and C14, the atoms in the region of the disorder refined well, including the H-atom positions, which were refined with restraint. The H atoms attached to C13 and C13' were assigned the same occupancies as their parent atoms. However, one of the H atoms attached to C14 is superimposed with one attached to C14' and this was therefore refined with an occupancy fixed at 1.

Data collection: CAD-4 Software (Enraf–Nonius, 1989). Cell refinement: CAD-4 Software. Data reduction: Process\_data (Gable *et al.*, 1994). Program(s) used to solve structure: SHELXS97 (Sheldrick, 1990). Program(s) used to refine structure: SHELXL97 (Sheldrick, 1997). Molecular graphics: ZORTEP (Zsolnai, 1994). Software used to prepare material for publication: SHELXL97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OA1074). Services for accessing these data are described at the back of the journal.

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