Table 3. *Hydrogen-bonding geometry (Å, °)*

	D—H···*A*	H···*A*	*D*···*A*	*D*—H···*A*
(I)	N2—H2N···N1^{i}	2.11 (2)	3.007 (2)	166 (2)
(II)	N2—H2N···N1^{i}	2.09 (2)	2.956 (2)	177 (2)

Symmetry code: (i) $-x, 1-y, 1-z$.

For both structures, the positional parameters of the H atoms were refined: compound (I), C—H range 0.91 (2)–1.00 (2) and N—H distance 0.90 (2) Å; compound (II), C—H range 0.90 (2)–0.99 (2) and N—H distance 0.87 (2) Å.

For both compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1985); program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1985); program(s) used to refine structures: *TEXSAN*; software used to prepare material for publication: *TEXSAN*, *PLUTON*92 (Spek, 1992) and *ORTEP*II (Johnson, 1976).

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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: FR1017). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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1-Styrylsilatrane

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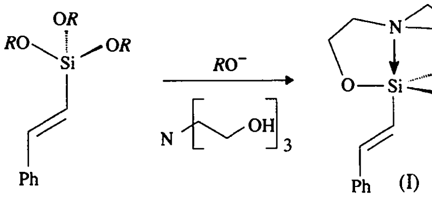
Abstract

The structure of (*E*)-1-(2-phenylethenyl)-2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecane, $C_{14}H_{19}NO_3Si$, has been determined by X-ray analysis. The N—Si dative bond length of 2.127 (4) Å is in agreement with structural trends found for such systems. The C atoms linked to the N atom are disordered, an effect which has been observed in other silatrane structures.

Comment

Over the past two decades, silicon atranes or 'silatranes' have attracted considerable attention. In addition to demonstrating unique patterns of chemical reactivity, silatranes also exhibit interesting biological activity, such as the stimulation of hair growth (Voronkov, 1979). However, possibly the most intriguing aspect of these compounds is their nominally pentacoordinate structure. The distorted trigonal bipyramid geometry and short transannular silicon–nitrogen 'bond' possessed by silatranes was first demonstrated by use of single-crystal X-ray diffraction in 1968 (Turley & Boer, 1968). Since then, crystallographic data compiled from numerous other silatrane structures have demonstrated that the length of this silicon–nitrogen transannular interaction in the solid state is dependent primarily upon the substituent bound to the silicon center (Schmidt, Windus & Gordon, 1995, and references therein). This transannular interaction has been extensively studied by a variety of techniques, including multinuclear magnetic resonance spectroscopy (Iwamiya & Maciel, 1993).

The stabilization of β-carbocations is a well documented facet of organosilicon chemistry. It has been demonstrated that the extent of this 'β-effect' can be correlated to the electron-withdrawing ability of the groups on silicon (Brook & Neuy, 1990). This was shown by using the degree of *syn* addition of bromine to (*E*)-β-silylstyrenes as a measure of the stabilizing ability of the silicon center. Recently, these studies have been expanded to include the title compound, (I), a styrene-substituted silatrane.



(I)

Most silatrane structures possess silicon–nitrogen distances in the range of 2.05–2.20 Å (Hencsei, 1991). While this distance is considerably shorter than the sum of the van der Waals radii, 3.5 Å, it is significantly longer than the typical silicon–nitrogen single-bond distance of 1.7–1.8 Å (Turley & Boer, 1968). As a result, this transannular interaction is often categorized as a 'dative' bond, the length of which, with some exceptions, is inversely proportional to the electronegativity of the substituent on silicon. Perhaps surprisingly, the shortest known bond occurs for the chloro-substituted silatrane (2.02 Å) rather than the fluoro-substituted analog (2.04 Å) (Schmidt, Windus & Gordon, 1995, and references therein). The silicon–nitrogen distance in the title compound [2.127 (4) Å] is equal within experimental error to the related distance of 2.132 Å measured for the γ-modification of phenylsilatrane (Párkányi, Nagy & Simon, 1975), but is considerably shorter than the distance of 2.193 (5) Å found for α-phenylsilatrane (Turley & Boer, 1968).

While the Si1—C12 length of 1.857 (5) Å found in the title compound is approximately 0.024 Å shorter than in the α-modification of phenylsilatrane (Turley & Boer, 1968), it is still considerably longer than an average silicon–carbon(sp^2) bond. It has also been found that as the length of the aforementioned dative bond decreases, the silicon–carbon(sp^2) bond lengthens (Párkányi, Nagy & Simon, 1975). These observations have previously been rationalized in terms of a decrease in $d\pi$–$p\pi$ interactions between the neighboring π-system and the silicon center, resulting from d-orbital participation in the formation of the silatrane structure. However, it is not possible from these structural data to conclusively distinguish between a π-contribution of this type, one using σ^* orbitals on silicon, or a simple inductive effect.

The pseudo-pentacoordinate distorted trigonal bipyramidal geometry common to silatranes is readily apparent in the title compound. The C12—Si1—N5 angle is almost linear at 178.8 (3)°, while the O2—Si1—O8, O2—Si1—O9 and O8—Si1—O9 angles are 119.4 (2), 117.7 (2) and 118.9 (2)°, respectively. Moreover, the C12—Si1—O angles are much closer to optimal trigonal bipyramidal geometry (90°) than tetrahedral geometry (109.5°).

From the molecular packing diagram (Fig. 2), it is observed that the styrylsilatrane units pack lengthwise in an orientation which is almost perpendicular to the long c axis. There are no unusually close intermolecular contacts.

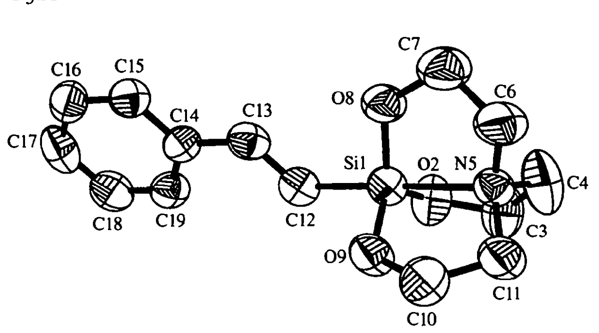


Fig. 1. The molecular structure of the title compound showing 50% probability displacement ellipsoids. For clarity, the H atoms have been omitted and only the more abundant conformation is presented.

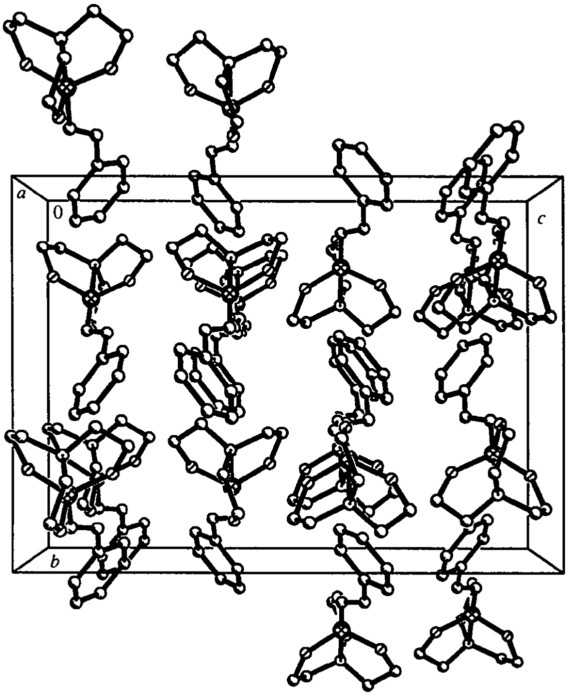


Fig. 2. A packing diagram of the title compound, viewed down the a axis. The Si atoms are displayed as dotted spheres.

Experimental

The title compound was prepared in good yield by the reaction of triethanolamine with styrylsilane. Single crystals were grown from dichloromethane at room temperature. A specimen of suitable dimensions for X-ray diffraction studies was obtained from a large single crystal cut under paraffin oil. The fragment was then mounted in a 0.2 mm diameter capillary tube.

Crystal data

$C_{14}H_{19}NO_3Si$	Ag $K\alpha$ radiation
$M_r = 277.39$	$\lambda = 0.56086$ Å

Orthorhombic
Pbca
$a = 10.839(2)$ Å
$b = 13.519(3)$ Å
$c = 18.939(4)$ Å
$V = 2775.2(10)$ Å^3
$Z = 8$
$D_x = 1.328$ Mg m^{-3}
$D_m = 1.337$ Mg m^{-3}
D_m measured by flotation in a CH_2Cl_2–$CHCl_3$ mixture

Cell parameters from 25 reflections
$\theta = 7.58$–$14.82°$
$\mu = 0.098$ mm^{-1}
$T = 293(2)$ K
Irregular fragment
0.2 × 0.2 × 0.2 mm
Colorless

Data collection

Siemens *P*3 diffractometer
ω scans
Absorption correction: none
3366 measured reflections
2636 independent reflections
725 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.0673$

$\theta_{\rm max} = 20°$
$h = -1 \rightarrow 13$
$k = -1 \rightarrow 16$
$l = -1 \rightarrow 23$
3 standard reflections every 97 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0554$
$wR(F^2) = 0.1305$
$S = 0.761$
2628 reflections
182 parameters
H atoms not refined
$w = 1/\{\sigma^2(F_o^2) + [0.0346(F_o^2 + 2F_c^2)/3]^2\}$

$(\Delta/\sigma)_{\rm max} = -0.019$
$\Delta\rho_{\rm max} = 0.241$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.184$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U^{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Si1	0.15713 (14)	0.79420 (10)	0.10774 (8)	0.0548 (4)
O2	0.2678 (3)	0.8772 (2)	0.1012 (2)	0.0705 (12)
C3	0.3925 (5)	0.8529 (4)	0.0924 (3)	0.089 (2)
C4†	0.4190 (8)	0.7526 (6)	0.1200 (6)	0.097 (4)
C4*A*‡	0.395 (5)	0.745 (4)	0.073 (4)	0.097 (4)
N5	0.3072 (4)	0.6928 (3)	0.1076 (2)	0.0548 (11)
C6†	0.2845 (9)	0.6228 (7)	0.1636 (4)	0.087 (3)
C6*A*‡	0.331 (6)	0.685 (4)	0.187 (2)	0.087 (3)
C7	0.2036 (6)	0.6727 (4)	0.2166 (3)	0.088 (2)
O8	0.1272 (3)	0.7439 (2)	0.1854 (2)	0.0674 (12)
O9	0.1167 (3)	0.7338 (2)	0.0352 (2)	0.0658 (11)
C10	0.1785 (5)	0.6491 (4)	0.0110 (3)	0.080 (2)
C11†	0.3069 (9)	0.6461 (7)	0.0373 (4)	0.081 (3)
C11*A*‡	0.266 (5)	0.611 (4)	0.066 (3)	0.081 (3)
C12	0.0262 (4)	0.8828 (3)	0.1058 (3)	0.0554 (14)
C13	−0.0674 (5)	0.8907 (3)	0.1494 (3)	0.059 (2)
C14	−0.1725 (5)	0.9584 (4)	0.1461 (3)	0.0525 (14)
C15	−0.2744 (5)	0.9416 (4)	0.1884 (3)	0.061 (2)
C16	−0.3758 (5)	1.0027 (4)	0.1847 (3)	0.070 (2)
C17	−0.3789 (6)	1.0817 (5)	0.1391 (3)	0.079 (2)
C18	−0.2761 (6)	1.0990 (4)	0.0986 (3)	0.076 (2)
C19	−0.1758 (5)	1.0387 (4)	0.1011 (3)	0.0612 (15)

† Site occupancy = 0.851 (12). ‡ Site occupancy = 0.149 (12).

Table 2. *Selected geometric parameters (Å, °)*

Si1—O2	1.647 (3)	Si1—C12	1.857 (5)
Si1—O8	1.652 (3)	Si1—N5	2.127 (4)
Si1—O9	1.657 (3)	C12—C13	1.312 (6)
O2—Si1—O8	119.4 (2)	O9—Si1—C12	95.7 (2)
O2—Si1—O9	117.7 (2)	O2—Si1—N5	83.2 (2)
O8—Si1—O9	118.9 (2)	O8—Si1—N5	83.4 (2)
O2—Si1—C12	96.6 (2)	O9—Si1—N5	83.3 (2)
O8—Si1—C12	97.6 (2)	C12—Si1—N5	178.8 (3)

The final refined structure was based on a disordered model in which the five-membered rings of the silatrane unit could exist in one of two non-planar conformations. Based on the observed thermal displacement ellipsoids, it was assumed that only the positions of the three C atoms bound to the N atom were significantly affected by this disorder. The occupancy of the two conformations was allowed to refine as a free variable (final ratio of approximately 85:15) and then H atoms for each unique component of the disorder were added at calculated positions with occupancy factors equal to the occupancy factor of the associated C atom. All H atoms were refined using a riding model with isotropic displacement parameters equal to 1.2 times the equivalent isotropic displacement parameter of their attached C atom. The distances between the partially populated atom sites are 0.925, 1.073 and 0.842 Å for C4—C4*A*, C6—C6*A* and C11—C11*A*, respectively. This conformational disorder has been observed in a variety of other silatrane crystal structures, including the α-1-phenyl- (Turley & Boer, 1968), *para*-tolyl-, 1-(*meta*-chlorophenoxy)- and 1-fluoro- (Párkányi, Hencsei, Bihátsi & Müller, 1984) derivatives.

Data collection: *P*3 (Siemens, 1990). Cell refinement: *P*3. Data reduction: *XDISK* (Siemens, 1989). Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1994). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*.

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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: FR1023). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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