Synthesis, spectroscopic and structural studies of spirocyclic pseudosilatranes

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Abstract

Spirocyclic pseudosilatranes have been prepared from the condensation of $(HOCH_2CH_2)_2NMe$ with dihydrophenazasilines or by alcohol exchange with dialkoxyphenazasilines. The structures have been investigated in solution by ^1H, ^{13}C and ^{29}Si NMR spectroscopy and in the solid state by X-ray diffraction. The interatomic $Si \cdots N$ distance in the 1,3-dioxa-6-aza-2-silacyclooctane ring in two 5-methyl-2,8-dioxa-5-aza-1-silacyclooctane-1-*spiro*-(2,8-dibromo-5-alkyl-10-silaphenzasiline) derivatives is 2.968 and 2.986 Å which indicates a weak nitrogen–silicon interaction such as might occur in an intermediate stage of nucleophilic substitution at tetrahedral silicon. The solution data support an equilibrium between a boat–boat conformation (closed form with presumed pentacoordinate Si) and the chair–chair conformation (open form, tetrahedral Si). The spirocyclic pseudosilatranes and related acyclic pseudosilatranes are compared.

Introduction

Organosilicon compounds that contain pentacoordinate silicon have been the subject of several recent reviews [1–4]. One of the oldest recognized examples is the silatrane derived from the condensation of triethanolamine with $RSi(OMe)_3$ [5]. Pseudosilatranes, I, are organosilicon ethers derived from diethanolamine. In both sets of derivatives the degree of interaction of the nitrogen with silicon can vary from bonded to non-bonded. Several pseudosilatranes have been studied by spectroscopic methods [6,7] and a few solid state structures have been reported [6e,7,8]. The transannular coordinate bond distance reported in the solid state for the dioxaazasilacyclooctanes of type I vary from 2.30 to 3.19 Å for the five derivatives listed [7,8d] as compared to a proposed standard five-coordinate Si–N distance of 1.823 Å [9]. The series exhibits an interesting variation in conformation of the eight-membered dioxaazasilacyclo-octane ring from the boat–boat (BB) form shown for I, observed for Ia and Ib, to the chair–chair (CC) form adopted by Id and Ie. The transition between these two forms is exhibited by Ic. The bond distance between

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[†] Deceased.

silicon and nitrogen in I, appears to increase as the bulk of the acyclic substituent at nitrogen increases [6b,e]. In a solution of I, an equilibrium between the BB and CC forms has been reported [6].

A few examples of spirocyclic pseudosilatranes, II, III and IV that have 2, 3 and 4 bonds to oxygen, have been reported. Although the structure in III is disordered, the SiN distance in both II and III is approximately 2.30 Å, a distance achieved in Ia only where there is a hydrogen substituent on nitrogen. In Ia, II and III there is minimal steric hindrance to the approach of the N center in the axial position of the trigonal bipyramid. Derivatives of structural type IV with four bonds to oxygen should have the most acidic silicon center in addition to minimal steric hindrance to the approach of the N center and in these cases the Si–N distance is shorter and varies from 2.004 Å (IVa) to 2.247 Å (IVb).

In I–IV the nitrogen center of the dioxaazasilacyclooctane occupies an axial position in the trigonal bipyrqamid. We speculated that a more congested spirocycle might provide evidence for the attack of the nitrogen "nucleophile" in the equatorial position. In this report we describe the synthesis and spectroscopic studies of spirocyclic pseudosilatranes V based on a tricyclic silicon unit and the single crystal X-ray analysis of two derivatives, Va and Vb.
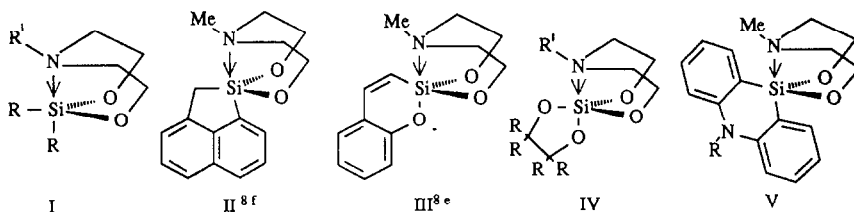
Structure I				Structure IV		
R	R′			R	R′	
Ph	H	Ia [7]		H	H	IVa [8b]
Ph	Me	Ib [8d]		Me	Me	IVb [8c]
Ph	'Bu	Ic [8d]		CF$_3$	Me	IVc [8a]
Ph	Ph	Id [8d]				
Ph	Ph	Id [8d]				
Me	Ph	Ie [8d]				

Experimental

All reactions were performed in flame dried glassware under an atmosphere of dry nitrogen or argon. Toluene was distilled over sodium benzophenone ketyl. The diethanolamine was dried over charged molecular sieves for several days. ^{1}H NMR spectra were recorded in CDCl$_3$ on a Varian T-60 or a Varian XL-300 MHz spectrometer. ^{13}C and ^{29}Si NMR data were recorded on the Varian XL-300 spectrometer operating in a Fourier Transform mode using proton decoupling. The concentrations of the samples for ^{29}Si spectra were 100 mg/0.5 ml CDCl$_3$. A small amount of Cr(acac)$_3$ (4 mg) was added to reduce the relaxation time for silicon nuclei. TMS was used as internal reference in all NMR experiments. Mass spectral data were recorded on an AEIMS 1201B mass spectrometer.

The starting materials, 2,8-dibromo-5-alkyl-10,10-dihydrophenazasiline (VII) and 2,8-dibromo-5-alkyl-10,10-dialkoxyphenasiline (VI) were prepared by a previously reported method [10].

Analyses were performed by Galbraith Laboratories Inc., Knoxville, Tennessee.

Synthesis of 5-Alkyl-2,8-dioxa-5-aza-1-silacycloocta-1-spiro-(2,8-dibromo-5-alkyl-10-phenasiline), VIa and VIb

a. Alcohol exchange. A mixture of VIa (1.2 g, 2.8 mmol) and *N*-methyldiethanolamine (0.33 g, 2.8 mmol) in toluene (30 ml) was heated at reflux for 48 h under a nitrogen atmosphere. Removal of the solvent gave a solid. Recrystallization from hexanes/methylene, chloride, 30/70, provided Va, m.p. 241–243°C (0.87 g, 64%). ^{1}H NMR δ(ppm): 2.64 (s, 2.9H, N–Me), 2.76–2.79 (t, 4.0H, NCH$_2$), 3.53 (s, 3.0H, N–Me), 3.9–3.93 (t, 3.9H, O–CH$_2$), 7.0–7.8 (m, 6.2H, arom). ^{13}C δ(ppm): 38.35, 46.12, 57.32, 62.43, 113.35, 117.33, 123.90, 132.99, 136.09, 150.34. ^{29}Si NMR δ(ppm): −45.34. m/e = 482 (M^+ based on ^{79}Br). Anal. Found: C, 44.63; H, 4.16. C$_{18}$H$_{20}$Br$_2$O$_2$N$_2$Si calcd.: C, 44.63; H, 4.13%.

By a similar procedure, Vb was prepared from VIb (1.0 g, 2.3 mmol) and *N*-methyldiethanolamine (0.27 g, 2.3 mmol). Recrystallization from hexanes/methylene chloride, 50/50, gave a solid, m.p. 182–183°C (0.77 g, 67%). ^{1}H NMR δ(ppm): 1.36–1.41 (t, 3.0H, NCH$_2$CH$_3$), 2.60 (s, 2.9H, N–Me), 3.85–3.88 (t, 3.9H, OCH$_2$), 4.0–4.08 (q, 3.1H, NCH$_2$CH$_3$), 7.06–7.08 (m, 6.1H, arom). ^{13}C NMR δ(ppm): 13.69, 45.05, 46.32, 57.66, 62.63, 118.41, 124.64, 133.20, 136.36, 149.60. ^{29}Si NMR δ(ppm): −45.39. m/e = 494 (M^+ based on ^{79}Br).

b. Dehydrogenative condensation. To a round bottom flask was added VIIa (1.0 g, 2.7 mmol), *N*-methyldiethanolamine (0.31 g, 2.7 mmol) and toluene (20 ml). The evolution of hydrogen gas took place spontaneously. The solutions were stirred under nitrogen for 6 h. After this period the solvent was removed. A hexanes–methylene chloride mixture 40/60, was added to the residue and insoluble material removed by filtration. The product Va (0.33 g, 25%) crystallized from the filtrate.

c. Alcoholysis in the presence of ClRh(PPh$_3$)$_3$. To a round bottom flask with a side arm was added ClRh(PPh$_3$)$_3$ (10 mg), *N*-methyldiethanolamine (0.30 mg, 2.6 mmol), dissolved in toluene (15 ml). The dihydrophenazasiline, VIIb (1.0 g, 2.6 mmol). dissolved in toluene (15 ml) was injected into the flask through a septum. The mixture was refluxed overnight and the volatiles removed. The residue was recrystallized from hexanes/methylene chloride, 50/50, to give Vb (0.37 g, 29%).

Synthesis of 5-Hydro-2,8-dioxa-5-aza-1-silacyclooctane-1-spiro-(2,8-dibromo-5-methyl-10-phenazasiline

Similarly, Vc was prepared from VIa (1.0 g, 2.7 mmol) and diethanolamine (0.28 g, 2.7 mmol). Recrystallization from hexanes/methylene chloride, 30/70, gave a solid, m.p. 234–235°C (0.76 g, 60%). ^{1}H NMR δ(ppm): 2.1–2.2 (bs, 1H, NH), 3.0–3.03 (t, 4.0H, NCH$_2$), 3.48 (s, 2.8H NCH$_3$), 3.85–3.89 (t, 3.9H, NCH$_2$), 6.9–7.7 (m, 6.3H, arom). ^{13}C NMR δ(ppm): 37.90, 47.37, 61.12, 113.71, 117.12, 128.55, 132.05, 135.36, 150.78. Vc decomposes on standing.

X-Ray diffraction study of Va and Vb

Colorless crystals of compound Va and Vb were grown by slow evaporation of a saturated solution of a methylene chloride–hexane mixture. The crystals were

Table 1

Crystallographic data collection and structure refinement parameters of Va and Vb [a]

	Va	Vb
Molecular formula	$C_{18}H_{20}N_2O_2SiBr_2$	$C_{19}H_{22}N_2O_2SiBr_2$
Formula weight g/mol	484.3	498.3
Radiation	Mo-K_α ($\lambda = 0.71069$ Å)	
Temperature (K)	298	298
Crystal size (mm)	$0.8 \times 0.8 \times 0.2$	$0.7 \times 0.5 \times 0.4$
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/n$	$P2_12_12_1$
Cell constants		
a, Å	12.772(3)	7.912(4)
b, Å	7.500(2)	13.360(6)
c, Å	20.962(4)	18.892(8)
β, degrees	106.19(2)	–
V, Å^3	1928.2(8)	1997.0(16)
Z	4	4
D_{calc} (Mg m^{-3})	1.668	1.657
μ (mm^{-1})	4.24	4.09
2θ Range	3.5 to 52.0°	4.0 to 45.0°
Reflections collected	4190	8839
Independent reflections	3710 ($R_{int} = 5.42\%$)	3269 ($R_{int} = 2.96\%$)
Observed reflections	709 ($F > 4.0\sigma(F)$)	1430 ($F > 6.0\sigma(F)$)
Ratio data/parameter	6.4:1	10.2:1
Absorption correction	N/A	Semi empirical
R	4.23%	2.87%
R_w	4.40%	3.83%

[a] Estimated standard deviation of least significant figure(s) are given in parentheses for this table and subsequent tables.

mounted on a glass fiber in random orientation. Preliminary examination and data collection were carried out with Mo-K_α radiation on a Siemens R3 diffractometer. Final cell constants were obtained by least squares analysis of 25 automatically centered reflections ($20 < 2\theta < 25°$). Data were collected by $\theta-2\theta$ scan technique, and the intensity of three reflections was monitored every 50 reflections. There was no significant change in intensities of the three standard reflections during data collection. Crystal data and intensity collection parameters are summarized in Table 1.

Data reduction, structure solution and refinement were carried out by SHELXTL-PLUS structure solution software package [11a]. The structures were solved by Patterson Methods for heavy atom positions and the rest of the atoms were located from difference Fourier maps. Full matrix least squares refinement was carried out by minimizing $\Sigma w(F_o - F_c)^2$. Final positional parameters are given in Tables 2 and 3. Hydrogen atoms were included at their calculated positions. The final difference Fourier maps had a maximum electron density of 0.37 and 0.64 e/Å^3 for Va and Vb, respectively. All calculations were performed on a VAX Station II GPX computer.

Lists of positional and isotropic temperature factors for H-atoms and calculated and observed structure factors are available from the authors.

Table 2

Atomic coordinates ($\times 10^4$) of non-hydrogen atoms for N–Me pseudosilatrane (Va)

	x	y	z	U_{eq} [a]
Br(1)	8951(2)	8906(3)	465(1)	85(1)
Br(2)	1488(2)	11477(3)	1748(1)	93(1)
Si	4961(4)	7827(6)	1101(2)	42(1)
O(1)	4429(7)	8228(12)	301(4)	49(3)
O(2)	5141(8)	5729(13)	1294(4)	47(3)
N(1)	6256(10)	9250(17)	2423(6)	53(4)
N(2)	2838(9)	5968(16)	601(6)	48(4)
C(1)	7023(11)	8686(19)	892(7)	46(5)
C(2)	8135(12)	9109(20)	1055(7)	46(5)
C(3)	8582(13)	9543(18)	1722(7)	49(5)
C(4)	7971(12)	9609(19)	2164(8)	52(5)
C(5)	4714(12)	10723(20)	2694(8)	54(5)
C(6)	3692(13)	11261(21)	2555(8)	62(5)
C(7)	2958(14)	10760(22)	1951(9)	65(6)
C(8)	3358(12)	9733(19)	1531(7)	47(5)
C(9)	6875(12)	9193(19)	1985(7)	42(5)
C(10)	6385(11)	8707(19)	1315(7)	36(4)
C(11)	5166(13)	9703(19)	2271(7)	46(5)
C(12)	4418(12)	9138(20)	1653(7)	45(5)
C(13)	3847(11)	6977(19)	−193(7)	51(5)
C(14)	2777(11)	6521(21)	−68(7)	58(5)
C(15)	4357(12)	4528(20)	1417(7)	65(6)
C(16)	3414(12)	4285(20)	786(7)	62(5)
C(17)	1828(13)	5983(25)	752(7)	96(7)
C(18)	6854(13)	9310(21)	3136(7)	81(6)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Results and discussion

Spirocyclic pseudosilatranes, V, were generated by two methods as summarized in Scheme 1. The preferred route is through alcohol exchange of a 10,10-dialkoxyphenazasiline, VI, with diethanolamine. Dialkoxyphenazasilines are generated from VII and ROH in the presence of a Rh^I catalyst [10]. The exchange reaction with a diethanolamine requires refluxing the components in anhydrous toluene for 48 h. Removal of solvent gives about 60–67% yields of V after purification. Reaction of VII with diethanolamine gave spontaneous evolution of hydrogen gas when the two compounds were mixed in toluene. A low yield (25%) of spirocyclic pseudosilatrane was obtained along with insoluble oligomeric (or polymeric) material. The pseudosilatrane was soluble in CH_2Cl_2/hexanes and could be separated from the oligomers. Condensation of diethanolamine and VII in the presence of Rh^I which normally catalyzes alcoholysis reactions provided only a marginal improvement in the yields of pseudosilatranes. Although the sequence, VII–VI–V, requires two steps the overall yield is about 50%. Spectroscopic data (^{1}H and ^{13}C) are assigned in the Experimental section.
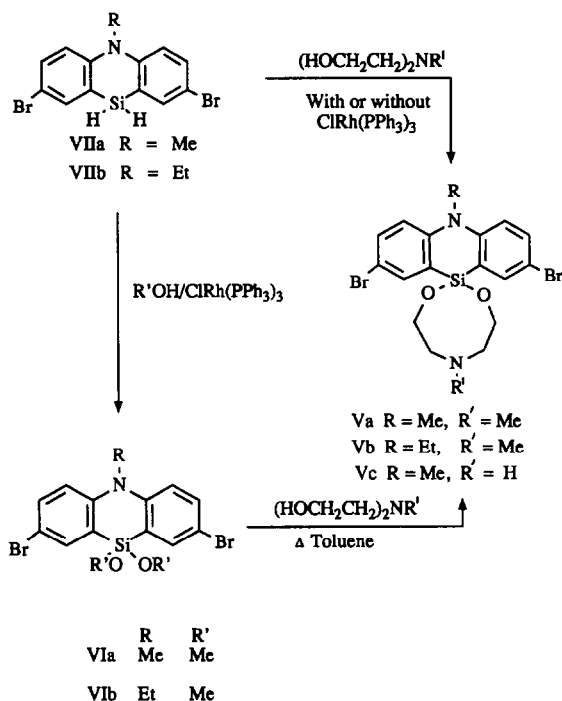
Table 3

Atomic coordinates ($\times 10^4$) of non-hydrogen atoms for N–Et pseudosilatrane (Vb)

	x	y	z	U_{eq} [a]
Br(1)	785(2)	2601(1)	5070(1)	58(1)
Br(2)	960(2)	4671(1)	−425(1)	45(1)
Si	3142(3)	3275(2)	2270(1)	24(1)
O(1)	3147(7)	4448(4)	2520(3)	30(2)
O(2)	4953(7)	2721(4)	2321(3)	30(2)
N(1)	749(11)	1537(5)	1920(3)	30(3)
N(2)	5739(10)	4458(5)	1492(3)	30(3)
C(1)	1755(11)	2842(6)	3620(5)	30(3)
C(2)	738(13)	2287(6)	4083(4)	33(2)
C(3)	−282(11)	1522(7)	3840(5)	35(3)
C(4)	−311(11)	1298(6)	3135(5)	31(3)
C(5)	−113(12)	2129(7)	751(5)	30(3)
C(6)	−78(11)	2839(6)	234(5)	31(3)
C(7)	951(13)	3674(6)	306(4)	27(2)
C(8)	1918(12)	3813(7)	905(5)	25(2)
C(9)	740(12)	1823(6)	2652(4)	24(2)
C(10)	1761(10)	2596(6)	2896(4)	22(2)
C(11)	875(12)	2265(6)	1377(4)	26(2)
C(12)	1925(11)	3103(6)	1439(4)	22(2)
C(13)	4545(12)	5085(7)	2606(5)	41(3)
C(14)	5368(12)	5350(8)	1908(5)	42(3)
C(15)	6395(11)	2771(7)	1862(5)	42(3)
C(16)	7054(12)	3827(7)	1801(5)	38(3)
C(17)	6177(14)	4700(9)	777(5)	61(3)
C(18)	177(12)	521(7)	1726(5)	41(3)
C(19)	1332(12)	36(7)	1186(5)	42(3)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

The presence of a transannular Si $\cdots$ N interaction (N from the diethanolamine unit) is usually inferred from an upfield shift in the ^{29}Si NMR spectrum [3]. Solutions of Va or VB showed a single ^{29}Si resonance at −45 ppm compared to a value of −41 ppm in the model compiunds, 2,8-dibromo-5-alkyl-10,10-diethoxyphenazasiline. In related studies such upfield chemical shifts have been attributed to the presence of an equilibrium between the boat–boat conformer (pentacoordinate silicon as observed in the solid for Ia [7] and Ib [8d]) and the chair–chair form (tetracoordinate silicon, observed in the solid for Id [8a] and Ie [8d]) [6d,e]. Data available for acyclic systems with two phenyl groups bonded to silicon are summarized in Table 4. The Si $\cdots$ N transannular bond distance ranges from 2.30 Å (coordinated) to 3.16 Å (noncoordinated but less than the van der Waals distance). The differences in ^{29}Si chemical shifts in the acyclic systems relative to the model vary from 1 to 11 ppm and the equilibrium constants for the CC to BB equilibrium based on these values range from 0.36 to 0.96 [6e]. These data support an equilibrium between penta- and tetracoordinate silicon in solution starting from either coordination in the solid state. The difference of 4 ppm in the ^{29}Si resonance for V relative to the model diethoxy derivatives VId (R = Me, R′ = Et) and VIe (R = R′ = OEt) suggests the presence of conformational equilibria in solution. The crystal structure study of both Va and Vb was performed to

VIIa R = Me
VIIb R = Et

$(HOCH_2CH_2)_2NR'$

With or without
$ClRh(PPh_3)_3$

$R'OH/ClRh(PPh_3)_3$

Va R = Me, R' = Me
Vb R = Et,   R' = Me
Vc R = Me, R' = H

$(HOCH_2CH_2)_2NR'$
Δ Toluene

	R	R'
VIa	Me	Me
VIb	Et	Me

Scheme 1

determine the conformation adopted in the solid. Bond lengths and angles for the two compounds are provided in Table 5 using the numbering schemes shown in Figs. 1 and 2. The tricyclic skeleton exhibits a bend or butterfly angle of 147° (Va) and 145° (Vb) which is in the range observed for other phenazasilines [12]. The eight-membered dioxaazasilacyclooctane ring exists in a boat-chair conformation for both compounds. The transannular Si · · · N bonds in the eight-membered ring are 2.968 and 2.986 Å in Va and Vb, respectively. The suggested standard Si–N bond length in pentacoordinate silicon is 1.823 Å [9]. An upper limit of 2.72 Å has been proposed as a "minimal non-bonded approach" between Si and N and 2.69 Å as the "minimal non-bonded distance" [13]. The values obtained in this study are

Table 4

Solid and solution data for $Ph_2Si(OCH_2CH_2)_2NR$

R	Si · · · N (Å)	^{29}Si (δ obs.)	$\Delta^{29}Si$ [a]	K CC = BB	^{29}Si calc. ΔBB − CC	Ref.
H	2.30	− 44.7	12	0.36	46	7, 6e
CH$_3$	2.68	− 43.7	11	0.96	24	8d, 6f
Ph	3.08	− 33.4	1	[b]	[b]	8d, 6e
^{t}Bu	3.16	− 35.2	3	0.54	8	8d, 6f

[a] Difference between the pseudosilatrane and the model compound, $Ph_2Si(OEt)_2$ which exhibits a ^{29}Si resonance at − 32.4 ppm [6f]. [b] Crown form (CC) maintained in solution [8d].

Table 5

Bond distances (Å) and bond angles for pseudosilatranes Va and Vb

Distances	Va	Vb	Angles	Va	Vb
Br1–C2	1.83(2)	1.911(9)	O1–Si–O2	114.7(5)	114.8(3)
Si–O1	1.65(1)	1.637(6)	O2–Si–C10	102.8(6)	105.2(4)
Si–C10	1.87(1)	1.848(8)	O2–Si–C12	115.1(7)	117.0(4)
O1–C13	1.44(2)	1.40(1)	O1–Si–C10	106.1(6)	106.6(4)
N1–C9	1.37(2)	1.44(1)	O1–Si–C12	115.4(6)	111.4(3)
N1–C18	1.48(2)	1.48(1)	C10–Si–C12	100.2(7)	100.0(4)
N2–C16	1.46(2)	1.46(1)	Si–O1–C13	126.5(8)	128.0(5)
C1–C2	1.40(2)	1.40(1)	Si–O2–C15	126.9(9)	130.4(6)
C2–C3	1.40(2)	1.38(1)	C9–N1–C11	125.9(12)	121.0(6)
C4–C9	1.38(2)	1.42(1)	C9–N1–C18	116.6(12)	118.8(7)
C5–C11	1.41(2)	1.43(1)	C11–N1–C18	115.4(14)	118.2(7)
C7–C8	1.37(2)	1.38(1)	C14–N2–C16	113.2(12)	113.6(7)
C9–C10	1.42(2)	1.39(1)	C14–N2–C17	114.2(11)	111.9(7)
C13–C14	1.50(2)	1.51(1)	C16–N2–C17	111.9(13)	109.6(8)
Br2–C7	1.88(2)	1.919(8)	C2–C1–C10	126.1(13)	119.1(8)
Si–O2	1.62(1)	1.616(6)	Br1–C2–C1	123.1(11)	118.9(7)
Si–C12	1.80(2)	1.856(9)	Br1–C2–C3	123.1(12)	119.9(7)
O2–C15	1.42(2)	1.43(1)	C1–C2–C3	113.6(15)	121.3(8)
N1–C11	1.38(2)	1.42(2)	C2–C3–C4	122.5(14)	119.7(8)
N2–C14	1.44(2)	1.46(1)	C3–C4–C9	122.2(14)	120.6(8)
N2–C17	1.41(2)	1.43(1)	C6–C5–C11	125.5(14)	119.6(8)
C1–C10	1.36(2)	1.40(1)	C5–C6–C7	119.3(16)	120.1(8)
C3–C4	1.37(2)	1.37(1)	Br2–C7–C6	120.0(14)	119.3(6)
C5–C6	1.32(2)	1.36(1)	Br2–C7–C8	122.8(11)	119.7(6)
C6–C7	1.40(2)	1.39(1)	C6–C7–C8	117.2(15)	121.0(8)
C8–C12	1.38(2)	1.38(1)	C7–C8–C12	125.8(13)	120.5(8)
C11–C12	1.44(2)	1.40(1)	N1–C9–C4	122.7(13)	119.4(7)
C15–C16	1.53(2)	1.51(1)	N1–C9–C10	119.7(13)	121.0(7)
C18–C19	–	1.52(1)	C4–C9–C10	117.6(15)	119.6(7)
			Si–C10–C1	124.0(10)	120.7(6)
			Si–C10–C9	117.4(12)	119.7(6)
			C1–C10–C9	118.0(13)	119.6(8)
			N1–C11–C5	123.5(13)	118.2(7)
			N1–C11–C12	120.5(14)	122.1(7)
			C5–C11–C12	116.0(14)	119.7(7)
			Si–C12–C8	126.3(10)	122.3(6)
			Si–C12–C11	117.4(12)	118.5(6)
			C8–C12–C11	116.2(14)	119.0(8)
			O1–C13–C14	109.5(12)	112.4(7)
			N2–C14–C13	110.2(12)	111.4(8)
			O2–C15–C16	110.0(12)	111.4(7)
			N2–C16–C15	110.2(12)	108.9(7)
			N1–C18–C19	–	112.1(7)

outside the range suggested for the minimal non-bonded approach but are shorter than the Van der Waals distance of 3.65 Å proposed by Bondi [13c] by about 20%.

The bond angles about the silicon center which are summarized in Table 6 exhibit a distortion towards trigonal–bipyramidal geometry as revealed in the $N \cdots Si-C_{10}$ angles of 170°. The data in Table 6 and in Figs. 1 and 2 suggest an incipient nucleophilic attack of N at the axial position of the developing five-coordi-
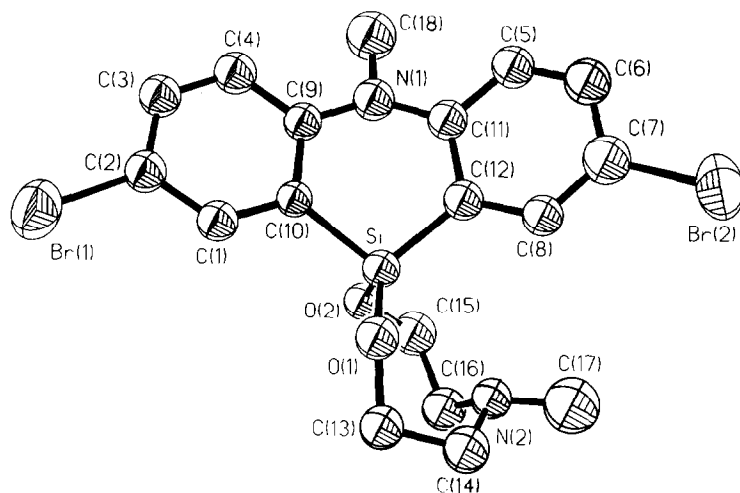
Fig. 1. Projection view of Va with atom labels.

nate silicon center. The related diphenylpseudosilatrane Ib exhibits a similar conformation but the transannular interaction gives a Si–N distance of 2.68 [8d].

The Si · · · N bond distance may not provide the best view of the position of a structure in the transition from tetrahedral to trigonal bipyramidal forms. An alternative approach has been developed based on the difference between the sums of equatorial and apical angles [14]. The differences in these angle sums would be 0° for the ideal tetrahedron and 90° for the trigonal bipyramid. This correlation was first demonstrated for pseudostannatranes [14]. Table 7 summarizes these
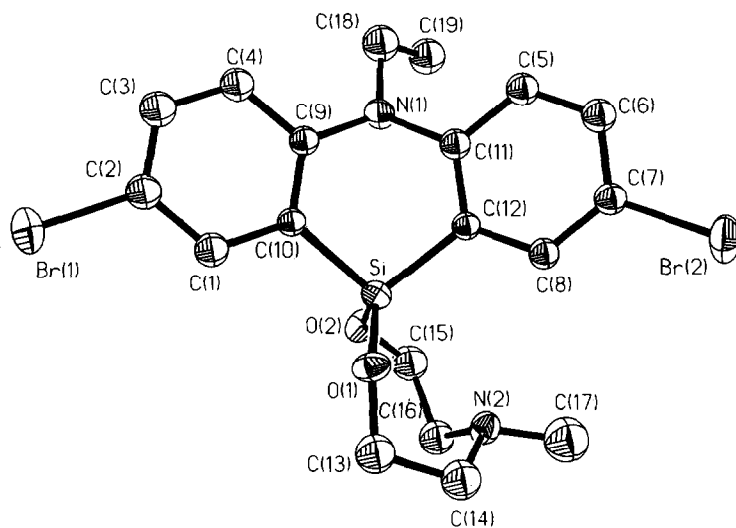
Fig. 2. Projection view of Vb with atom labels.

Table 6

Angles about silicon for Va and Vb

	Va	Vb
C10–Si–O1	106	107
C10–Si–O2	103	105
C10–Si–C12	100	100
C10–Si···N2	170	170
O1–Si–O2	115	115
O1–Si–C12	115	112
O2–Si–C12	115	117
O1–Si···N2	70	68
O2–Si···N2	72	70
C12–Si···N2	90	91

values for pseudosilatranes as well as a related dibenzosilazocine. Overall, as the Si···N distance decreases the differences between the sum of the equatorial angles and axial angles increases towards that of the trigonal bipyramid although the relationship is by no means linear. Another view of this transition is provided by the displacement of the silicon center from the plane defined by the three atoms that eventually form the trigonal plane of the trigonal bipyramid. These data are also

Table 7

Comparison of distortion towards trigonal bipyramidal geometry in pseudosilatranes and related derivatives

Subst. [a]	NR' [b]	Δ [c] (Å)	$\Sigma eq - \Sigma ax$ [d] (°)	Si atom displacement [e] (Å)	Ref.
Tetrahedral			0		
Ie	Ph	1.37	12		8d
Ic	^tBu	1.34	17	0.49	8d
Id	Ph	1.26	19		8d
[f]	^tBu	1.13	25	0.49	15
Vb	Et	1.16	31	0.40	this work
Va	Me	1.14	36	0.38	this work
Ib	Me	0.86	37	0.38	8d
Ia	H	0.49	59	0.25	7
III	Me	0.47	[g]	[g]	8e
II	Me	0.44	75 [h]	0.16	8f
IVc	Me	0.21	80	0.088	8a
IVa	H	0.18	78	0.101	8b
Trigonal bipyramidal			90	0	

[a] Substituents on I, II, III, IV and V. [b] Substituent on N in 8-membered ring. [c] (Si···N)$_{obs}$ = 1.823 Å (Si–N single bond in pentacoordinate derivative[9]). [d] Sum of equatorial angles around silicon – sum of axial angles. [e] Distance of silicon atom above the plane defined by the equatorial atoms. [f] 6-(1,1-dimethylethyl)-12,12-dimethyl-5,6-dihydro-7H,12H-dibenzo[c,f][1,5]silazocine. [g] Insufficient data provided in Ref. 8e to determine the value. [h] Calculated from the bond distance and angle data provided in Ref. 8f.

provided in Table 7 and exhibit a trend similar to that exhibited by the angle differences. The series of eight N-(halogeno-dimethylsilylmethyl)lactams have provided models for the intermediate stages of an S_N2 substitution at tetrahedral silicon. In this related series of compounds the displacement of the Si center ranged from 0.348 to −0.286 [16]. The tricyclic pseudosilatranes that are the subject of the current study are close to the upper range of this lactam series and correspond to the [4 + 1] case of a distorted tetrahedral silicon center with a secondary Si ··· Nuc bond. Only the pseudosilatranes IVa and IVc come close to the case where the Si center becomes coplanar with the three equatorial substituents [3 + 2] or trigonal bipyramid). The displacement of silicon from the equatorial plane of the three oxygens in silatranes correlates well with the length of the Si ··· N bond [17].

The question of the nature of the equilibrium that occurs in solution for pseudosilatranes appears to be quite complicated and has not yet been resolved [18]. In all cases where pentacoordinate silicon species have been observed in solution the ^{29}Si NMR resonance shifts upfield relative to a tetracoordinate model [3]. Anionic pentacoordinate derivatives exhibit ^{29}Si resonances furthest upfield but tetracoordinate models are often not available for comparison [3]. In silatranes (derivatives of triethanolamine) the chemical shift differences range from about 12 to 27 ppm^3 whereas for the pseudosilatranes, for which measurements have been reported, range from 3 to 11 ppm (see Table 4). The values for Va and Vb fall at the low end of this range. The effect of weak interactions between tetrahedral silicon and a fifth ligand are difficult to predict but the upfield shift is consistent with the trends observed in penta- and hexacoordinate systems. A 1,5-interaction has been observed in other 8- and 9-membered ring silicon heterocycles, such as VIII. The relationship between VIII (X = N^{t}Bu) and V is given in Table 7. The solid-state structures of VIII [X = SS (two derivatives, R = Me, Ph) and X = SeSe] have been reported as well as the spectroscopic data for the series X = SO$_2$, S, Se, S$_2$, Se$_2$ [18]. In VIII (X = SS, SeSe) the Si ··· S(Se) distances are 25–30% shorter than the Van der Waals distance and in the R = Ph series the ^{29}Si chemical shift differences relative to the tetrahedral model range from 3.5 to 4.7 ppm, similar to that observed by Va and Vb.


(VIII)
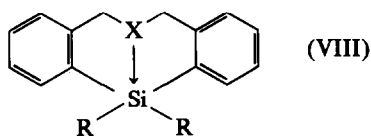
In the solid structure for diphenylpseudosilatrane, Ib, the equatorial phenyl substituent is oriented approximately in the equatorial plane (the plane defined by CSiO$_2$). In the corresponding heterocyclic pseudosilatrane this aryl group is forced out of the plane in the direction of the incoming nitrogen. The resulting orientation of the aryl group in V prevents a close approach of the nitrogen to the silicon center and accounts for the long Si ··· N distance observed in V compared to Ib, II and III. The structure which involves equatorial entry of the nitrogen center, thus avoiding the aryl group of the tricycle, is apparently not formed. If the solid state structure reflects the lowest energy conformation then axial entry is preferred to equatorial entry as suggested by calculations [19].

The interpretation or implications of the weak interactions observed in the eight-membered rings of the pseudosilatranes, I–V, or the eight- and nine-membered rings in VIII are not straightforward but these compounds are by no means

the only systems where such weak interactions have been reported. The structure of H_3SiCN has been determined in the gas phase, in solution and in the solid state (100 K). The solid state is characterized by near-linear chains of $\cdots Si-CN \cdots Si-CN$ with a nonbonded $N \cdots Si$ distance of 2.789 Å. The solution data appeared to support an interaction between cyanide groups and silyl groups that was intermediate between those in the gas and solution phases [20]. Two additional examples are exhibited by IX and X. A series of azasilatranes has been reported by Verkade and coworkers where hydrogen substituents at nitrogen (IX, R = H) are successively replaced by trimethylsilyl groups. The ^{29}Si resonance changes gradually from -68 ppm for IX (R = H) to -26 for IX (R = Me$_3$Si). The structure of the latter azasilatrane was determined and the $N_{ax}-Si$ bond distance was found to be 2.775 Å (24% shorter than the Van der Waals distance), the longest recorded for an azasilatrane. Consistent with the weak interaction is an upfield shift of the ^{29}Si resonance of 15 ppm relative to the tetrahedral model [21]. In X the dative bond between N and Si changes from 1.96 to 2.69 Å when the substituents at Si are changed from R = F to R = Me [9,22]. Haaland relates this considerable change to the sensitivity of the $N \rightarrow Si$ interaction to inductive effects [23]. Changes in inductive effects will be only one of the factors that contribute to the range of $N \cdots Si$ interactions observed in the pseudosilatranes.

In cases where Si $\cdots$ N "nonbonded" distances in the solid state are less than the Van der Waals distance there appear to be additional distortions in angles about the silicon center that are consistent with a weak dative bond interaction. In solution, spectroscopic data can be interpreted in terms of possible changes from a tetrahedral to pentacoordinate environment at silicon but these conclusions are more tenuous and in the case of pseudosilatranes are probably complicated by other conformational changes that can occur in solution.

IX

X
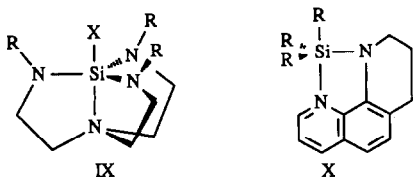
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