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Molecular structure of *N*-trimethylsilylaziridine in the gas phase

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N-Trimethylsilylaziridine, $Me_3SiNC_2H_4$ **1**, prepared by a literature procedure has been studied by gas-phase IR and NMR spectroscopy of the nuclei ^1H, ^{13}C, ^{15}N, ^{29}Si. The molecular structure of **1** has been determined in the gas phase by analysis of electron diffraction (GED) data augmented by geometric and vibrational amplitude restraints derived from *ab initio* calculations employing the second order Møller–Plesset (MP2) level of theory and the 6-311G(d,p) basis set. The molecule was found to adopt C_s symmetry and has a pyramidal arrangement around the nitrogen atom with a slightly elongated Si–N bond [1.770(4) Å], relative to those in other Si–N species having a planar nitrogen co-ordination. The results for the principal distances (r_a) and angles from the combined GED/*ab initio* study of $Me_3SiNC_2H_4$ are (uncertainties: one sigma): r(Si–N) = 1.770(4), $r(\text{Si–C}_{\text{in-plane}})$ = 1.868(4), $r(\text{Si–C}_{\text{out-of-plane}})$ = 1.881(2), r(C–N) = 1.459(3) Å, C–N–C 61.1(5), N–Si–$C_{\text{in-plane}}$ 109.7(7), N–Si–$C_{\text{out-of-plane}}$ 107.8(10), Si–N–C 121.9(4)°. The structure data are complemented by natural bond orbital analyses, and calculation of the barrier to inversion at the nitrogen centre, which is predicted to be 21.4 kJ mol^{-1}. Calculations on the simpler model compound $H_3SiNC_2H_4$ [up to QCISD/6-311G(d,p)] gave geometrical and energetic results similar to those of **1**. The steeply pyramidal nitrogen co-ordination is attributed to the strain of the aziridine ring, as was found by comparison with the results of other calculations on acyclic systems and those with larger rings.

Introduction

The structural chemistry of silicon–nitrogen compounds has been the focus of interest of many studies in the past as the Si–N bond was found to be unexpectedly strong and is distinct in its chemistry and structure from the related C–N bond. Nitrogen atoms in typical alkylamines form bonds in a pyramidal array and have considerable basicity. Exceptions do occur where there is massive steric overcrowding, an example being $(^i\text{Pr})_3N$ which was reported to have a planar nitrogen NC_3 core in the gas phase,[1] but is pyramidal in the crystal.[2] In contrast, silylamines generally possess planar nitrogen atoms and the compounds show very little basicity. In most cases just one silyl substituent bound to the nitrogen is sufficient to achieve a complete flattening of the nitrogen co-ordination sphere. The whole process of flattening of the nitrogen containing core is associated with a decrease in the height of the barrier to inversion in alkylamines caused by the presence of silicon substituents. While in most cases the barrier vanishes, in some cases there remains either a very shallow potential or a small barrier. Such small barriers probably exist in H_3SiNMe_2, which exhibits a slightly pyramidal $NSiC_2$ core,[3] and in compounds with very bulky silyl substituents carrying a NH_2 group.[4] Recently inherently pyramidal SiN containing molecules were found when the structures of *N*-silylhydroxylamines were investigated. The observation was ascribed to the influence of the high electronegativity of the alkoxy substituent bound to the nitrogen atom which causes a high barrier to inversion, thus overcoming the counter influence of the silicon substituent. Examples are provided by $(H_3Si)_2NOMe$[5] and $(H_3Si)MeNOMe$[6] which have slightly and steeply pyramidal cores respectively.

Electronic reasons for planar nitrogen containing cores in silylamines are the subject of many publications, the latest, in which $N(SiH_3)_3$ and H_2NSiH_3 are discussed, contains arguments in favour of a polar σ effect, which is said to give rise to electrostatic repulsion between the substituents at the nitrogen atom.[7] Only for compounds with very electronegative substituents as in $(H_3Si)MeNOMe$, a significant amount of electrostatic attraction occurs thus leading to steeply pyramidal silylamines.

The influence of ring strain on the geometry around the nitrogen atom in Si–N compounds is of current interest. Very recently a crystal structure of the silyl aziridine $Ph_3SiNC_2H_4$ was published, showing this compound to have a steeply pyramidal nitrogen atom in the crystal lattice.[8] This poses the question as to whether the observation of a pyramidal nitrogen core is a consequence of crystal packing as was seen in the case of $(^i\text{Pr})_3N$, see above. The molecule $Ph_3SiNC_2H_4$ is thought unlikely to exhibit sufficient stability in the gas phase to allow investigation of the influence of crystal packing. However, the trimethyl analogue, $Me_3SiNC_2H_4$ **1**, which was prepared by Scherer and Schmidt as early as 1965,[9] was thought likely to be suitable for a gas-phase investigation. Therefore in this paper are reported the results of *ab initio* calculations and gas-phase electron diffraction studies on **1**.

Results and discussion

The background to our study is as follows. Initially attempts were made to synthesize $H_3SiNC_2H_4$. Two methods were used. The first required the condensation of bromosilane and aziridine in the presence of 2,6-dimethylpyridine as an auxiliary base, while in the second lithioaziridine, $LiNC_2H_4$, was allowed to react with bromosilane. The first method was completely unsuccessful, probably because of the sensitivity of aziridine towards ring opening by acids. The second method produced a volatile compound, which condensed onto the walls of a cold trap at −60 °C after the volatile constituents of the reaction mixture (when the mixture was warmed to maximum −78 °C) were pumped through to other cold traps. However, upon removing the coolant, the liquid condensate that had been

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trapped at $-60\,^{\circ}$C turned immediately and irreversibly to a solid as the temperature was raised slightly. The solid was not soluble in common aprotic organic solvents. If silylaziridine was formed by the second reaction, which could not be proved unequivocally, it probably decomposed by reaction of the Si–H functions with the aziridine ring, a reaction which has previously been described as alkali metal catalysed, *e.g.* see the reaction of Et_2SiH_2 and HNC_4H_4.[10] It should also be noted that this was not the first attempt to prepare this compound.[11]

Having failed to make the parent compound of the homologous series it was decided to study **1**, so eliminating the problem of the incompatibility of Si–H and aziridine functions. A new preparative method was adopted in which lithioaziridine was allowed to react with Me_3SiCl, eqn. (1). The desired

$$\mathrm{Me_3SiCl + LiNC_2H_4 \longrightarrow \underset{\mathbf{1}}{Me_3SiNC_2H_4} + LiCl} \quad (1)$$

material was easily purified by fractional condensation in a high vacuum system to give a sample suitable for structure determination by gas-phase electron diffraction. Characterisation of **1** in solution was undertaken by multi-nuclear NMR spectroscopy. The ^{1}H and ^{13}C NMR data deserve no comment and are listed in the Experimental section. In the ^{29}Si NMR spectrum a multiplet appears at δ −19.7, which is about 20 ppm to lower frequency than chemical shifts reported for other typical silylamines [$(Me_3Si)_2NH$ (δ 2.2), $(Me_3Si)_3N$ (2.4)[12] and Me_2NSiMe_3 (6.5)].[13] The unique value obtained here for a silylamine suggests the presence of a different bonding situation at silicon and a different type of Si–N bond in **1** to those observed in other silylamines. This interpretation is confirmed by data from ^{15}N NMR spectroscopy which gave a signal at δ −348.5, which bears two pairs of satellites identified by their relative intensities as coupling to the ring carbon atoms with $^{1}J_{NC} = 2.9$ Hz and a coupling to the silicon centre with $^{1}J_{SiN} = 4.8$ Hz. The latter value is exceptionally low for a monosilylamine (coupling constants of about 20 Hz are seen normally[14]) suggesting the presence of a weak and relatively long Si–N bond. Such small $^{1}J_{SiN}$ coupling constants have, however, been observed for *N*-silylhydroxylamines, which have been shown to have pyramidal nitrogen containing cores and weak Si–N bonds.[15]

Gas-phase electron diffraction data for compound **1** were obtained using the Reading apparatus and an all-glass nozzle as described below. The data were interpreted using the SARACEN method,[16] to overcome the difficulties often experienced in refining a complete molecular geometry from electron diffraction data alone. Geometry restraints derived from *ab initio* calculations using the second-order Møller–Plesset (MP2) level of theory up to the 6-311G(d,p) basis set [MP2/6-311G(d,p)] were used to augment the experimental data, and a force field calculated at MP2/6-31G(d) was employed to calculate the vibrational amplitudes, perpendicular amplitude corrections and centrifugal distortions by the normal co-ordinate analysis program ASYM40.[17]

A model with C_s symmetry was proposed for compound **1** with C3, Si1, N2 and the mid-point of the C6–C7 bond [see Fig. 3 for the atomic numbering scheme] defining the plane of symmetry. The model was defined by the seventeen parameters and restraints listed in Table 1. Shown in Fig. 1 are the molecular scattering intensity curves while in Fig. 2 is depicted the radial distribution curve obtained from Fourier transformation of the molecular intensity data. The small residuals exhibited in the difference curves [see Figs. 1 and 2] indicate that a good fit was achieved between the experimental and calculated curves, the latter being obtained using the proposed molecular model and the values for the parameters given in Table 1. The validity of the proposed model was also substantiated by the final R_G value of 0.0647.

The Si–N bond, at 1.770(4) Å, is comparatively long. Typical Si–N bonds for comparable gas-phase geometries cover the range of 1.710(5) Å in Me_3SiNMe_2[18] to 1.755(3) Å in $(Me_3Si)_3N$,[19] with the values for Me_3SiNCS [1.743(6) Å],[20] for Me_3SiNCO [1.740(4) Å],[20] for H_3SiNMe_2 [1.713(5) Å][3,22] and for $Me_3SiNHMe$ [1.738(5) Å][23] lying in between. The major reason for this lengthening can be attributed to the very different co-ordination geometry at nitrogen in compound **1**, where it is steeply pyramidal, as is indicated by the sum of angles formed at nitrogen by the three bonds [305.0(11)°] and the declination of the Si–N vector from the C_2N plane of the aziridine ring of 52.1(5)°. In two of the compounds mentioned above, Me_3SiNMe_2[18] and $(Me_3Si)_3N$,[19] the nitrogen atom and the three atoms bonded to it are coplanar. Only in H_3SiNMe_2 a slight deviation from planarity is observed as revealed by the sum of the angles subtended at the nitrogen atom [353.9(8)°].[3,22]

The geometry of the ring is similar to that of the parent aziridine[24] and deserves no further comment. The distortion of

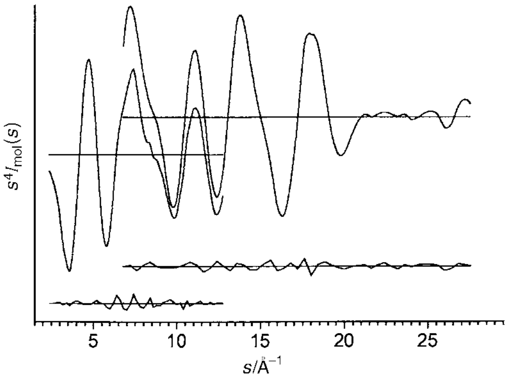

Fig. 1 Experimental scattering intensity (s^4I mol(s)) and final difference curves (*vs.* model) for gaseous $Me_3SiNC_2H_4$.

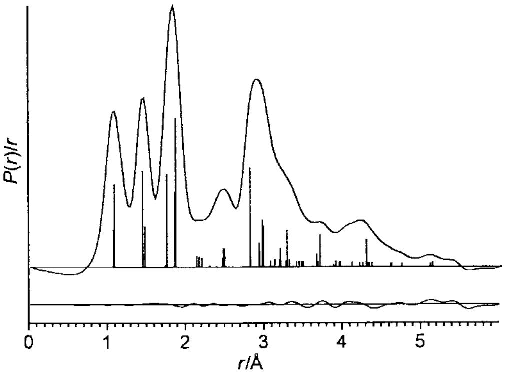

Fig. 2 Radial distribution and difference curves for the electron diffraction refinement of $Me_3SiNC_2H_4$. Before Fourier inversion the data were multiplied by $s\cdot\exp[(-0.002s^2)/(Z_{Si} - f_{Si})/(Z_N - f_N)]$. Vertical lines indicate atom pairs with their height being proportional to their scattering contribution.

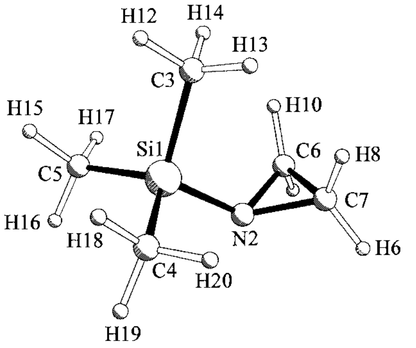

Fig. 3 Molecular structure of $Me_3SiNC_2H_4$ in the gas phase with atom numbering scheme.

Table 1 Parameter definition, parameter values and restraints for the gas-phase electron diffraction (GED) least squares refinement of the geometry of $Me_3SiNC_2H_4$. Results from the *ab initio* calculations are listed for comparison

Parameter[a]		Experimental result	Restraint[b]	Theoretical results MP2/6-311G(d,p)
Independent				
p^1	r(Si–N)	1.770(4)		1.753
p^2	r(Si–C(4))	1.881(2)	$p^2 - p^1 = 0.131(10)$	1.884
p^3	r(Si–C(3))	1.868(4)	$p^3 - p^2 = -0.012(5)$	1.872
p^4	r(N–C)	1.459(3)		1.462
p^5	$r(C\text{–}H_{ring})$	1.082(4)		1.086/1.090
p^6	$r(C\text{–}H_{methyl})$	1.091(2)	$p^6 - p^5 = 0.007(5)$	1.094–1.096
p^7	N–Si–C(4)	107.8(10)		106.8
p^8	N–Si–C(3)	109.7(7)		112.6
p^9	Si–N–C	121.9(4)		123.6
p^{10}	C–N–C	61.1(5)		61.3
p^{11}	C4–Si–C5	116.9(16)		111.4
p^{12}	Si–C(4)–H	111.4(6)		110.6
p^{13}	Si–C(3)–H	110.9(8)	$p^{13} - p^{12} = -0.7(10)$	109.9
p^{14}	N–C–H	117.5(11)	$p^8 = 118.8(15)$	118.8
p^{15}	τCSiCH	−66.4(75)		−57.6
p^{16}	τCNCH(8)	104.4(28)	$p^{16} = 106.3(30)$	106.3
p^{17}	τCNCH(9)	−109.7(27)	$p^{17} = -110.4(30)$	−109.7
Dependent				
p^{18}	r(C–C)	1.484(7)	$p^{18} - p^4 = -0.028(10)$	1.490
p^{19}	C–C–N	59.4(2)		59.4
p^{20}	Σ angles (at N)	305.0(11)		308.5

[a] Distances (r_a) are in ångströms and angles are in degrees. Parenthesised values are σ. For atom numbering see Fig. 3. [b] Derived from *ab initio* calculations at MP2/6-311G(d,p), see next column. For derivation of uncertainties on restraints see text.

the SiC_3 moiety in compound **1** has been observed in a range of other compounds that contain the Me_3SiN fragment with one N–Si–C angle being different from the other two. The difference between the two angles is small in **1** [N–Si–C4 107.8(10), N–Si–C3 109.7(7)°], as in the case of $(Me_3Si)_2NH$ [109.5 and 111.9°],[25] while those in Me_3SiNSO[26] show a greater difference [101.5(18) and 107.9(13)°].

The gas-phase geometry around the nitrogen atom of $C_2SiNC_2H_4$ in compound **1** is similar to that found in the solid state for $Ph_3SiNC_2H_4$,[8] although the Si–N distances are different [1.731(1) Å in $Ph_3SiNC_2H_4$, 1.770(4) Å in **1**]. The sum of angles subtended at the nitrogen atom is 312.3° in $Ph_3SiNC_2H_4$ [305.0(11)° in **1**], and the declination of the Si–N vector from the C_2N plane is 47.2°(52.1° in **1**). The solid state structure of a related species having a four-membered NCCC ring, $Ph_3SiNC_3H_6$, was described as being much closer to the geometry of a planar nitrogen centre.[8]

Taking the typical deviations between r_a (electron diffraction) and r_e parameters (calculations) into account, the gas-phase geometry of $Me_3SiNC_2H_4$ is in reasonable agreement with the theoretical predictions obtained from Møller–Plesset calculations at the 6-311G(d,p) level of theory. The r_a/r_e differences are most pronounced in the Si–N distances [GED 1.770(4), MP2 1.753 Å]. There is also a substantial deviation between theory and experiment in the value of the C4–Si–C5 angle, which lies between the two symmetry-equivalent methyl groups. Refinement of experimental data gave 116.9(16)°, whereas a value of 111.4° was calculated *ab initio*. To investigate the discrepancy further refinements were executed. Initially the angle under consideration was set at the *ab initio* value, and secondly it was allowed to refine with a restraint of 1.0° in the uncertainty. In both cases a substantially poorer fit to the experimental scattering data was observed to that obtained previously when the angle was allowed to refine freely. The experimentally observed values for N–Si–C angles associated with the geometry of the trimethylsilyl group also differ somewhat from *ab initio* predictions. A value of 107.8(10)° was obtained for N–Si–C(4) and N–Si–C(5) whereas it is calculated at 106.8°. However, the in-plane angle N–Si–C(3) [109.7(7)°] is closer to the *ab initio* value of 112.6°.

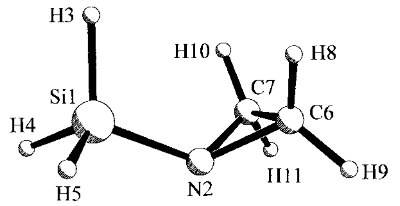

Fig. 4 Molecular structure of $H_3SiNC_2H_4$ as predicted by *ab initio* calculations at the QCISD/6-311G(d,p) level of theory.

Table 2 *Ab initio* molecular geometry of $H_3SiNC_2H_4$ as calculated at the MP2/6-311G(d,p) and the QCISD/6-311G(d,p) level of theory (core electrons not included in the correlation calculations)

Parameter[a]	MP2	QCISD
r(Si–N)	1.743	1.741
r(Si–H(3))	1.487	1.488
r(Si–H(4))	1.475	1.476
r(N–C)	1.465	1.464
r(C–C)	1.489	1.491
N–Si–H(4)	108.5	108.5
N–Si–H(3)	111.8	112.1
Si–N–C	121.2	122.2
C–N–C	61.1	61.2
Σ angles (at N)	303.5	305.6

[a] Distances (r_e) are in ångströms and angles are in degrees.

As attempts to prepare $H_3SiNC_2H_4$ were unsuccessful it was not possible to compare experimental data for this compound with those obtained for **1**. Theoretical calculations for $H_3SiNC_2H_4$ were carried out using the same basis set and level of theory as for **1** and, additionally, calculations with an improved treatment of electron correlation at the QCISD/6-311G(d,p) level. The results are shown in Table 2 and Fig. 4. A comparison of the theoretical structure of $H_3SiNC_2H_4$ with that of **1** (Table 1) shows the geometries of the Si–N–C_2 cores to be similar. An improvement of the theoretical level does not lead to significant changes in geometry. Thus the description of the structure and the suggested bonding model (see below) for **1** is transferable to $H_3SiNC_2H_4$.

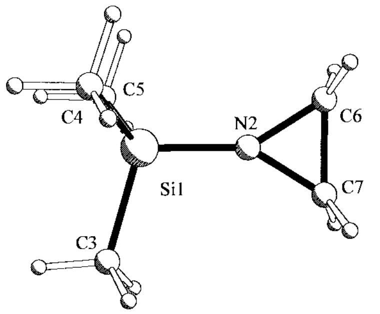

Fig. 5 Molecular structure of the transition state to inversion/rotation of $Me_3SiNC_2H_4$ as predicted by *ab initio* calculations at the MP2/6-311G(d,p) level of theory.

Table 3 *Ab initio* geometry of the transition state of $Me_3SiNC_2H_4$ as calculated at the MP2/6-311G(d,p) level of theory (core electrons not included in the correlation calculations)

Parameter[a]	Value
r(Si–N)	1.718
r(Si–C(3))	1.873
r(Si–C(4))	1.878
r(N–C(7))	1.431
r(N–C(4))	1.433
r(C(3)–C(4))	1.505
N–Si–C(5)	106.0
N–Si–C(3)	110.9
Si–N–C(7)	148.4
Si–N–C(6)	148.3
C(6)–N–C(7)	63.4

[a] Distances (r_e) are in ångströms and angles are in degrees.

Calculations of the transition state to nitrogen inversion

The main question that remains to be addressed is the reason for the non-planar co-ordination geometry of the nitrogen atom. A transition state having a planar C_2NSi skeleton was located by *ab initio* calculations. Such a geometry becomes a transition state to nitrogen inversion only if the Me_3Si group is concurrently rotated such that one of the methyl carbon atoms becomes coplanar with the C_2NSi core. The transition state is characterised by the occurrence of one imaginary frequency in the calculations such that it is a combined rotation/inversion process, *i.e.* rotation about the Si–N bond and inversion of the nitrogen centre. This transition state is predicted to be 21.4 kJ mol^{-1} higher in energy than the ground state [MP2/6-311G(d,p)], which is a substantial amount relative to the very low or even non-existent barriers in non-cyclic silylamines.

The geometry of the transition state is shown in Fig. 5 and the important geometric parameters are listed in Table 3. On adopting planarity the angles of the C_2NSi core open (Si–N–C(6) 148.3, *cf.* 121.9(4)° in ground-state experimental structure; C(6)–N–C(7) 63.4, *cf.* 61.1(5)° in ground-state experimental structure). This places the NC(6)C(7) ring under some strain compared to that in the parent 1-methylaziridine structure.[24] The biggest difference to the ground-state geometry is in the Si–N bond length, which is much shorter in the planar transition state (1.718 Å) than that calculated in the ground state (1.753 Å). The natural bond orbital (NBO) analysis of the Si–N bond in the transition state geometry indicates it consists of Si $sp^{2.25}d^{0.05}$ and N $sp^{1.76}$ hybrid orbitals, which represents a much smaller p contribution than in the pyramidal ground state, where the Si–N bond is described to be formed by Si $sp^{3.35}d^{0.08}$ and N $sp^{1.78}$ hybrid orbitals. It is worthy of note that it is the hybridisation of the silicon atom which changes between the transition state and ground state. In contrast the nitrogen atom, around which the co-ordination geometry undergoes a major change, retains the same hybridisation. This is not consistent with the simplistic expectation that a sp^2 hybridised nitrogen atom makes stronger bonds to its neighbours than one which is sp^3 hybridised. There is also a larger Si/N charge separation in the transition state (the atomic charges are 1.378 e for Si and −0.730 e for N, the "natural charges" being 1.92 and −1.00 e) than the ground state (Si atom bears +1.343 e and the N atom −0.668 e, the "natural charges" being 1.90 and −0.95 e) according to Mulliken population analyses.

We have performed further calculations for energy calibration purposes and to provide information suitable to rationalise further the steeply pyramidal co-ordination geometry at nitrogen in compound **1**. These results are compiled in Fig. 6. The barrier to nitrogen inversion of $H_3SiNC_2H_4$ was calculated at the MP2/6-311G(d,p) to be 21.9 kJ mol^{-1} and to be 22.4 kJ mol^{-1} at the more sophisticated QCISD(T)/6-311G(d,p) level of theory [based on a QCISD/6-311G(d,p) geometry]. This shows that the MP2/6-311G(d,p) level is suitable to provide a realistic estimate of the height of this barrier. The barrier for $H_3SiNC_2H_4$ is close to that in **1**, which leads to the conclusion that the substituents (Me and H) at the silicon atom do not change this barrier significantly.

Calculations on *N*-silylazetidine $H_3SiN(CH_2)_3$, which contains a larger ring system than compound **1**, and the open chain systems H_3SiNMe_2 and H_3SiNH_2 have been performed to demonstrate the effect of the R–N–R angle on the co-ordination geometry at nitrogen in R_2NSi systems. The compound $H_3SiN(CH_2)_3$ has a less steeply pyramidal nitrogen co-ordination, *i.e.* the declination of the Si–N vector from the C_2N plane is 33.8° [52.1(5)° in **1**]. However the ring strain exerted by the four- and three-membered rings in $H_3SiN(CH_2)_3$ and $H_3SiN(CH_2)_2$ (and **1**) leads to Si–N–C angles in these compounds [125.9 and 121.2°, compare that in $Ph_3SiN(CH_2)_3$[8] 127.6(1)°], which are slightly larger than those in the open-chain compounds H_3SiNMe_2 and H_3SiNH_2, the latter adopting Si–N–H angles of 119.4 and 119.6° and almost flat nitrogen co-ordination spheres. The barrier to nitrogen inversion of these open-chain systems is consequently much lower: 4.9 kJ mol^{-1} for H_3SiNMe_2 and 1.9 kJ mol^{-1} H_3SiNH_2 at MP2/6-311G(d,p). Improvement of the treatment of electron correlation in the calculations for H_3SiNH_2 does not change the height of this barrier substantially, as it is predicted to be 2.3 kJ mol^{-1} at QCISD(T)/6-311G(d,p) on the basis of a QCISD/6-311G(d,p) geometry (compare 2.1 kJ mol^{-1} in an earlier calculation by Gordon[27]).

Conclusion

The determination of the gas-phase structure of $Me_3SiNC_2H_4$ shows the steeply pyramidal nitrogen co-ordination to be an inherent phenomenon of the class of *N*-silylaziridines. This geometry is not imposed on the molecules by packing or dipole forces when studied in their crystalline forms. The pyramidal nitrogen co-ordination restricts the Si–N–C angles to 121.9(4)° (*cf.* 148.4° calculated for the planar transition state) and thus circumvents angle strain in addition to the ring strain of the aziridine ring.

Experimental

N-Trimethylsilylaziridine was prepared from aziridine (2.4 cm^3, 46 mmol), which was deprotonated in diethyl ether (20 cm^3) by 46 mmol of *n*-butyllithium (1.6 M in hexane) at −78 °C. Chlorotrimethylsilane (50 mmol) was added, the resulting suspension stirred for 1 h, and warmed to ambient temperature. The volatile products were distilled off *in vacuo* and separated by a trap to trap condensation, with the product being held in a −45 °C trap and obtained in 84% yield. *N*-Trimethylsilylazirine has been prepared before by another procedure[9] and our sample has the same properties as described therein. The following list contains new spectroscopic data. The NMR

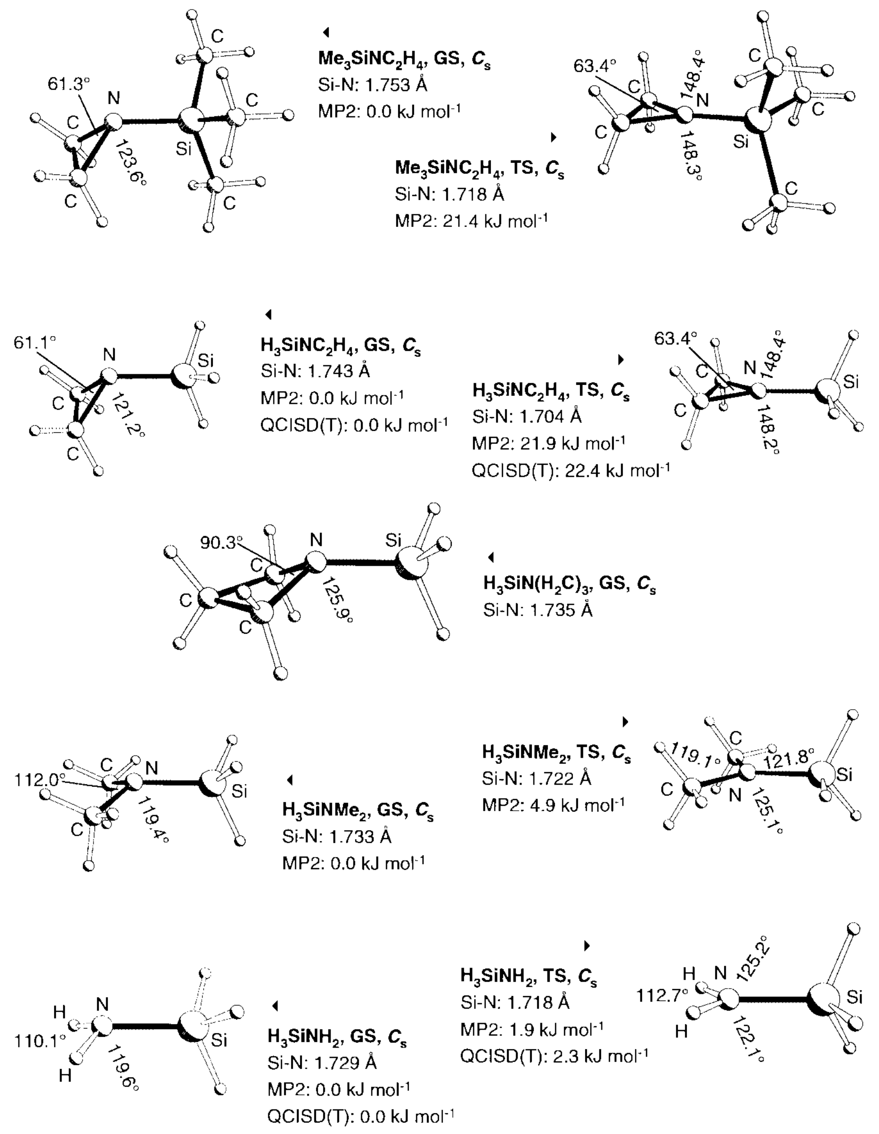

Fig. 6 Calculated molecular structures and selected geometrical parameters of the ground states (GS) of Me$_3$SiNC$_2$H$_4$ **1**, H$_3$SiNC$_2$H$_4$, H$_3$SiN(CH$_2$)$_3$, H$_3$SiNMe$_2$ and H$_3$SiNH$_2$ at the MP2/6-311G(d,p) level of theory. The geometries and relative energies for the transition states (TS) of nitrogen inversion are given for **1**, H$_3$SiNC$_2$H$_4$, H$_3$SiNMe$_2$ and H$_3$SiNH$_2$. For the model systems H$_3$SiNC$_2$H$_4$ and H$_3$SiNH$_2$ energy differences are also provided at the QCISD(T)/6-311G(d,p) level of theory, which are based on geometries optimised at QCISD/6-311G(d,p).

Table 4 Camera distances, data ranges, trapezoidal weighting function points, correlation parameters, scale factors, wavelengths and R values for the GED structure determination of Me$_3$SiNC$_2$H$_4$

Data set	Camera distance/mm	Sample T/°C	Nozzle T/°C	Δs/ Å^{-1}	s_{min}/ Å^{-1}	s_{max}/ Å^{-1}	s_1/ Å^{-1}	s_2/ Å^{-1}	Correlation parameter	Scale factor	Wavelength/ Å	R_g
1	496.12	33–36	42–47	0.2	2.4	12.8	4.4	11.8	0.1524	0.454(4)	0.058561	0.0686
2	245.54	38–40	48–50	0.4	6.8	27.6	8.8	23.6	−0.2077	0.413(10)	0.058561	0.0581

spectra were recorded at 21 °C on a JEOL JNM-LA400 spectrometer from a sample in a sealed tube with C$_6$D$_6$ as a solvent directly condensed onto the sample from K/Na alloy: ^{1}H NMR δ 0.0 (s, 9 H, H$_3$C) and 1.52 (s, 4 H, H$_2$C); ^{13}C NMR δ −2.87 (qp, $^1J_{CH}$ = 118.3, $^4J_{CH}$ = 1.8, (CH$_3$)$_3$Si) and 20.07 (qt, $^1J_{CH}$ = 168.8, $^3J_{CNCH}$ = 2.7 Hz, (CH$_3$)$_2$N); ^{15}N-{^{1}H} NMR δ −348.5 (s, $^1J_{NC}$ = 2.9, $^1J_{SiN}$ = 4.8 Hz); ^{29}Si NMR δ −19.7 (m). A vibrational spectrum was recorded in a gas cell in an FTIR spectrometer (Midac Prospect FTIR): 3042m, 2965s, 2913m, 2880w, 1288s, 1276s, 1258s, 1143m, 1073w, 955s, 949vs, 943s, 845vs, 744m, 682w, 649w, 556w cm^{-1}.

Electron diffraction experiments

GED data. Electron scattering intensity data for Me$_3$SiNC$_2$H$_4$ were recorded on Kodak Electron Image film using the University of Reading diffraction apparatus operating at 42 kV accelerating voltage.[28] Two sets of data were recorded at each of the two camera distances using nozzle temperatures between 42 and 50 °C. The wavelength (0.058561 Å) was calibrated against diffraction patterns of benzene. Optical densities were measured using a commercial AGFA II scanner.[29,30] Further experimental conditions and general parameters concerning the refinements are listed in Table 4. The least squares refinements were carried out using the program ED96[31] and applying the scattering factors established by Fink and co-workers.[32] The refined molecular parameters, their definition and the applied restraints, with selected interatomic distances including vibrational amplitudes and applied restraints, are given in Table 5; elements of the correlation matrix are given in Table 6.

Table 5 Selected interatomic distances (r_a/Å), amplitudes of vibration (u/Å) and amplitude restraints as obtained in the least squares refinement of $Me_3SiNC_2H_4$

	Atom pair[a]	Distance	Amplitude	Restraint[b]
d^1	Si(1)–N(2)	1.770(4)	0.051(3)	$u^1 = 0.049(5)$
d^2	Si(1)–C(3)	1.868(4)	0.058(3)	$u^2/u^1 = 1.096(55)$
d^3	Si(1)–C(4)	1.881(2)	0.058(3)	$u^3/u^2 = 0.983(49)$
d^4	N(2)–C(6)	1.459(3)	0.046(3)	
d^5	C(6)–C(7)	1.484(7)	0.044(3)	$u^5/u^4 = 0.961(48)$
d^6	C(6)–H(8)	1.082(4)	0.064(2)	
d^7	C(3)–H(12)	1.091(2)	0.064(2)	Tied to u^6
d^8	Si(1)···C(6)	2.827(4)	0.044(10)	
d^9	N(2)···C(3)	2.939(18)	0.041(14)	
d^{10}	N(2)···C(4)	2.985(13)	0.045(15)	$u^{10}/u^9 = 1.094(55)$
d^{11}	C(3)···C(4)	2.999(27)	0.096(11)	$u^{11} = 0.106(11)$
d^{12}	C(4)···C(5)	3.206(28)	0.113(11)	$u^{12} = 0.108(11)$
d^{13}	C(3)···C(6)	3.295(25)	0.184(16)	$u^{13} = 0.186(19)$
d^{14}	C(4)···C(6)	4.316(9)	0.121(9)	$u^{14} = 0.115(12)$
d^{15}	C(4)···C(7)	3.724(11)	0.266(22)	$u^{15} = 0.257(26)$
d^{16}	N(2)···H(8)	2.182(13)	0.106(10)	
d^{17}	N(2)···H(9)	2.145(13)	0.106	Tied to u^{16}
d^{18}	C(6)···H(10)	2.177(26)	0.106	Tied to u^{16}
d^{19}	C(6)···H(11)	2.213(86)	0.106	Tied to u^{16}
d^{20}	Si(1)···H(12)	2.478(11)	0.099(5)	
d^{21}	Si(1)···H(13)	2.507(11)	0.097	Tied to u^{20}
d^{22}	Si(1)···H(15)	2.495(7)	0.097	Tied to u^{20}
d^{23}	Si(1)···H(16)	2.503(7)	0.097	Tied to u^{20}
d^{24}	Si(1)···H(17)	2.502(7)	0.097	Tied to u^{20}

[a] Uncertainties represent σ. For atom numbering see Fig. 3. [b] Restraints derived from *ab initio* at MP2/6-31G(d).

Table 6 Correlation matrix elements (×100) for $Me_3SiNC_2H_4$ with absolute values >50%

	p^1	p^4	p^8	p^{11}	p^{12}	u^1	u^2	u^4	u^5	u^6	u^7	u^9	u^{10}	u^{16}
p^9	−61		55											
p^{10}		−90												
p^{11}			51	100										
p^{15}				59										
u^2	59					76	100							
u^3	64					55	62							
u^5								55	100					
u^7										100				
u^8				70	−51							79	80	
u^{10}				65								98		
u^{20}														55
k^2								61	55	65	65			

GED model. The geometrical model for $Me_3SiNC_2H_4$ was defined in C_s symmetry. The atom numbering scheme is provided in Fig. 3. While fixing the differences between the parameters defining hydrogen atom positions (C–H distances, angles and torsion angles) to calculated values, a total of 17 parameters was used to refine the structures. The parameter definitions are listed in Table 1. Eight geometrical restraints based on the *ab initio* calculated values (MP2/6-311G(d,p)) were used to reduce correlation between parameters of similar nature (differences) or those describing hydrogen positions (absolute restraints). Their definition and values with assigned uncertainties based on an educated guess (experience with related structures) are also given in Table 1.

All vibrational amplitudes belonging to a pair of scatterers contributing more than 5% of the most important pair (Si–N) were refined. Restraints for these amplitudes were calculated from harmonic force fields obtained at the MP2/6-31G(d) level of theory, which were transformed into amplitudes by means of the program ASYM40.[17] Ratios between amplitudes were assigned an uncertainty of 10%, absolute restraints 20% of the calculated value. These amplitudes and restraints are given in Table 5.

Ab initio calculations. *Ab initio* molecular orbital calculations were carried out using the Gaussian 94 program.[33] Geometry optimisations and vibrational frequency calculations were performed from analytic first and second derivatives at the SCF and MP2 levels of theory. Calculations were undertaken at the SCF level using the standard 3-21G(d)[34–36] and 6-31G(d)[37–39] and 6-311G(d,p) basis sets, while the larger basis set was used for calculations at the MP2 level. For two model compounds higher level geometry optimisations were also undertaken with quadratic configuration interaction calculations including single and double substitutions (QCISD) and the energies were calculated single point further including the triple contribution substitutions [QCISD(T)].[40]

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