A Curtius-type Rearrangement in the Silicon Series; an *ab initio* Study of the Model Silylnitrene–Silanimine Isomerization†

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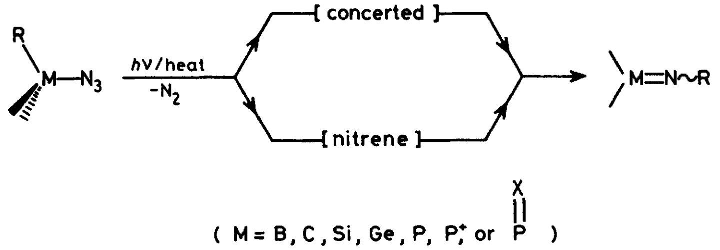
The model silylnitrene–silanimine rearrangement ($H_3SiN: \longrightarrow H_2Si{=}NH$) has been examined in four electronic states, namely the closed- and open-shell singlet, triplet, and cationic states. *Ab initio* calculations have demonstrated that the silylnitrene has a triplet ground state ($^3A_2$), while its closed-shell singlet ($^1A'$) and cationic ($^2A''$) states correspond to saddle points. The 1,2-hydrogen migration connecting ^3H_3SiN to $^3H_2SiNH$ has an energy barrier of 83 kcal mol^{-1}. Hence both species can exist in the lowest triplet state, where they are energetically equivalent. Silanimine (H_2SiNH) exhibits a triplet–singlet separation of 39 kcal mol^{-1} and a first adiabatic ionization energy of 8.8 eV. Calculations indicate that the Curtius-type rearrangement occurring during the thermolysis or direct photolysis of silyl azide does *not* involve silylnitrene as an intermediate. However, preliminary data suggest that the excited $^1(n \longrightarrow \pi^*)$ state of silylnitrene might play a role in a photochemically sensitized decomposition of silyl azide.

Along with other compounds containing second-row atoms in lower co-ordination states, the silicon analogues of imines (silanimines) are long-sought molecules. The transient existence of silanimines during the thermolysis of silyl azides was first postulated in 1964.[1] Conclusive evidence for their direct generation in both condensed and gas phases was provided a decade later by Sommer and his co-workers.[2] These authors identified unsaturated silicon–nitrogen reactive intermediates by use of various chemical trapping agents. The isolation of stable silanimines possessing bulky substituents has only very recently been reported, by several groups. Wiberg *et al.*[3] have been successful in preparing and structurally characterizing (*X*-ray) a solid silanimine which forms a stable complex with tetrahydrofuran at the silicon atom. Formation of silanimines in an inert matrix and in solution at low temperature has also been reported by Ando's and West's groups.[4,5] These compounds are yellow in colour and show typical $n \longrightarrow \pi^*$ and $\pi \longrightarrow \pi^*$ electronic absorption bands.

Thermolysis and photolysis of silyl azides have proved to be the methods of choice for silanimine generation.[6] Such reactions involve the more general Curtius-type rearrangement [equation (1)], the main features of which have recently been reviewed.[7]



(1)

$$(\ M = B, C, Si, Ge, P, P^{+}\ \text{or}\ \overset{\overset{\displaystyle X}{\|}}{P}\ )$$

From a mechanistic viewpoint, recent experimental studies[7,8] suggested that the transformation of azides into silanimines [equation (1), M = Si] involves, as in the carbon series, a concerted migration–nitrogen loss pathway. Reported data do not, however, preclude the formation of silylnitrenes as reactive intermediates. As part of our continuing theoretical study of the Curtius-type rearrangement,[9–11] we now describe *ab initio* calculations on the model interconversion of silylnitrene (H_3SiN) and silanimine ($H_2Si{=}NH$). The reaction was considered in the three lowest-lying singlet and triplet electronic states, and in the cationic state, in order to provide information on the possible role of silylnitrene as a discrete intermediate.

Calculations

In order to facilitate comparison, the computational procedures used were identical with those used previously.[9–11] In brief, they involved geometry optimization at the single determinant SCF level with the 3-21G* basis set (*d* functions on silicon only).[12] Energy differences between stationary points were computed with values obtained by Møller–Plesset perturbation theory at fourth order (MP4SDQ including only single, double, and quadruple electron excitations; triple substitutions have been neglected),[13] using SCF wavefunctions computed at 3-21G*-optimized geometries with the 6-31++G* basis set[14] for generating electronic configurations (the latter is of the 6-31G type expanded with a set of *d* polarizations and *sp* diffuse functions on silicon and nitrogen and a set of *s* diffuse functions on hydrogen). The unrestricted formalism (UHF, UMP) was employed for the doublet and triplet states and a restricted RHF–CI for the open-shell singlet states. Harmonic vibrational frequencies and some thermochemical parameters were determined with the 3-21G* basis set; some molecular properties were computed at the HF/6-31++G* model. All calculations were carried out with the MONSTERGAUSS[15] and GAUSSIAN 82[16] programs.

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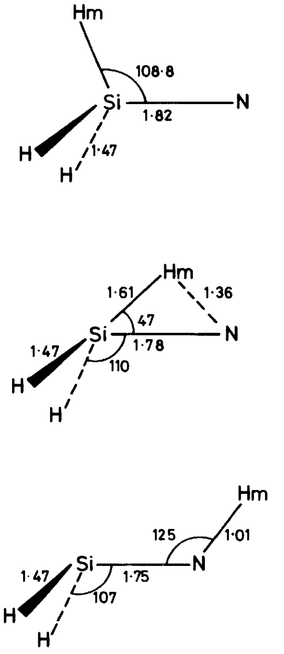
† *Non-S.I. units employed:* 1 cal = 4.184 J; 1 eV = 1.6 × 10^{-19}J.

Table 1. Total (a.u.) and relative (kcal mol^{-1}, in parentheses) energies^a and some thermochemical parameters of three stationary points on the triplet [$SiNH_3$] energy surface

	(1)	(2)	(3)
UHF/3-21G*	−343.319 96^f	−343.154 03^f	−343.296 68^f
	(0.0)	(104.1)	(14.6)
UHF/6-31++G*	−345.049 99^f	−344.886 97^f	−345.034 58^f
	(0.0)	(102.3)	(9.7)
MP2/6-31++G*	−345.226 91	−345.090 53	−345.234 16
	(0.0)	(85.6)	(−4.5)
MP3/6-31++G*	−345.255 66	−345.116 09	−345.258 09
	(0.0)	(87.6)	(−1.5)
MP4SDQ/6-31++G*	−345.261 71	−345.124 05	−345.263 93
	(0.0)	(86.4)	(−1.4)
ZPE^b	17.7	14.6	18.4
Estimated^c	0.0	83.3	−0.7
S^d	59.1	61.8	61.7
$C_p{}^e$	11.6	12.1	12.5

Reaction (1) ⟶ (3) ΔH (298 K) = −0.4 kcal mol^{-1}
$\Delta H^‡$ (298 K) = 83.5 kcal mol^{-1}
ΔG (298 K) = −1.2 kcal mol^{-1}
$\Delta G^‡$ (298 K) = 82.7 kcal mol^{-1}

^{a} Using UHF/3-21G* geometries given in Figure 1. ^{b} Zero-point vibrational energies at UHF/3-21G* (kcal mol^{-1}). ^{c} Using MP4SDQ/6-31G* and ZPE. ^{d} Entropy at 298 K (cal mol^{-1} K^{-1}). ^{e} Specific heat capacity at 298 K (cal mol^{-1} K^{-1}). ^{f} The $<S^2>$ values of UHF wavefunctions are: (1) 2.02, (2) 2.09, and (3) 2.02 in both basis sets. The values of (2) seem reasonable for a transition structure.



(1)($^3A_2$)

(2)($^3A''$)

(3)($^3A''$)

Figure 1. Optimized geometries (UHF/3-21G*) for three stationary points on the triplet [$SiNH_3$] energy surface; bond lengths in Å and bond angles in degrees

Results and Discussion

Triplet States.—Three stationary points of interest on the triplet [$SiNH_3$] energy surface are silylnitrene (**1**), the transition structure (**2**), and silanimine (**3**). Geometries and energies of both minimum-energy species (**1**) and (**3**) have been discussed in detail in previous papers.[17,18] The only new point is the transition structure (**2**). To emphasize the geometrical changes along the reaction pathway, the HF/3-21G*-optimized geometries of all three points are shown in Figure 1. Table 1 lists calculated total and relative energies considered at three levels of theory; some relevant thermodynamic properties [zero-point energies (ZPE), entropies (S), specific heat capacities (C_p), enthalpies (ΔH) and free energies (ΔG)] are also included.

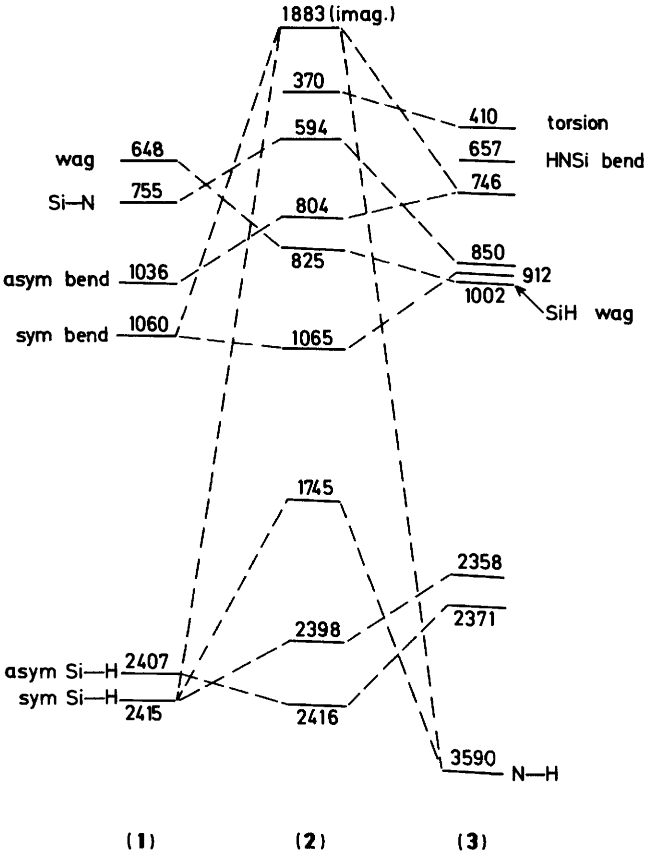


Figure 2. Vibrational frequency correlation diagram for three triplet species calculated at UHF/3-21G*; values in cm^{-1} (scale is arbitrary)

The transition state (**2**) has C_s symmetry, involving planar migration for the hydrogen atom. A similar situation has been observed for H_3CN[18–20] and H_3PN^+.[11] The angle of migration H_mSiN was calculated to be 47°, analogous to that in H_3PN^+ (50.3°).[11] It is the absence of the lone pair on triplet nitrene relative to singlet nitrene which reduces the electronic repulsion inherent to the hydrogen migration and consequently favours a symmetric transition structure (**2**).

At the UHF/6-31++G* level, the silylnitrene (**1**) ($^3A_2$) is lower in energy than the silanimine (**3**) ($^3A''$) by 9.7 kcal mol^{-1}, but the ordering reverses on inclusion of correlation energy. At the MP4SDQ/6-31++G* model with ZPE corrections, (**3**) becomes more stable than (**1**) by 0.7 kcal mol^{-1}. This is in line with previous results, showing the two structures to be energetically equivalent (at MP4SDTQ/6-31G** with 3-21G*-geometries).[17] As usual, incorporation of the polarization functions and correlation energies reduced the energy barrier for the unimolecular rearrangement (**1**) ⟶ (**3**) from 104.1 to 86.4 kcal mol^{-1}. With ZPE corrections, a barrier of 83.3 kcal mol^{-1} can be predicted. This is substantially higher than those obtained for triplet H_3CN (59 kcal mol^{-1}) and H_3PN^+ (45.2 kcal mol^{-1})[11] at similar levels of theory. Because the entropy variation is quite small (Table 1), the free energy values are dominated by the enthalpic terms. Our best estimate predicts values of 82.7 and −1.2 kcal mol^{-1} for the free energies of activation $\Delta G^‡$ (298 K) and reaction ΔG (298 K), respectively, for the transformation (**1**) ⟶ (**3**). It can thus be concluded

Table 2. Optimized geometries for $H_2Si{=}NH$ (**4**) at the HF level with different basis sets

Parameter[a]	3-21G	3-21G*	6-31G*	6-31G**[b]	DZP[c]
Si-N	1.611	1.547	1.573	1.576	1.586
N-H	1.002	0.987	0.997	0.997	1.006
Si-H(1)	1.483	1.475	1.476	1.479	1.481
Si-H(2)	1.469	1.463	1.463	1.478	1.471
H(1)SiN	132.8	180.0	126.7	125.2	122.4
H(2)SiN	127.9	128.7	128.7	128.6	128.6
NHSi	118.3	120.2	119.6	119.7	119.5

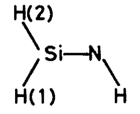
[a] See structure (**4**) for atom numbering. Bond lengths in Å; bond angles in degrees. [b] Ref. 21. [c] Ref. 18.

that the silylnitrene (**1**) and silanimine (**3**) will both exist in the lowest triplet state.

The harmonic vibrational frequencies of the points on the triplet pathway are represented as a correlation diagram in Figure 2. An imaginary frequency of 1 882 cm^{-1} is associated with hydrogen migration. The Si-N stretching frequency in (**1**) is 755 cm^{-1}; *cf.* 850 cm^{-1} in (**3**). Note that these calculated values are about 10—15% larger than the true ones. There tends to be a shift to lower frequencies in the transition structure (**2**) with respect to (**1**).

The dipole moment is found to be larger in (**1**) (1.94 D) than in (**3**) (1.73 D); the transition structure (**2**) is the most polar (1.99 D). The spin populations indicate that the two unpaired electrons in the triplet H_3SiN are localized around the nitrogen atom. This situation changes regularly along the reaction pathway so that in the triplet H_2SiNH each of the two heavy atoms bears one α-electron.

Singlet States.—There have been some *ab initio* studies of the structures and stabilities of singlet $[SiNH_3]$ species.[17,18,21] Of particular interest is the geometry of the silanimine (**4**). Table 2 summarizes data determined using different basis sets. The 3-21G* set predicts a linear Si-N-H frame (C_{2v}) whereas the split-valence set and the sets including *d* functions on both Si and N atoms give a bent structure (C_s). The energy difference between the bent and linear conformations of (**4**) was, however, calculated to be much smaller (5—6 kcal mol^{-1})[21] than that in the carbon analogue (25 kcal mol^{-1}).[19] The stabilization of the linear silanimine arises from delocalization of the nitrogen lone pair into the 3*p* orbital of silicon. The presence of *d* functions only on silicon in the 3-21G* basis set thus artificially enhances this stabilization. This artefact can be overcome by employing a multiconfigurational SCF procedure.[21] Nevertheless, such a shallow potential energy curve should be quite sensitive to electronic and steric effects. Indeed, a recent *X*-ray study[3] revealed that the Si-N-Si bond angle in $Bu^t_2Si{=}N{-}SiBu^t_3$ is 177.8°. The corresponding Si-N bond length is 1.568 Å. The Si-N stretching frequency in (**4**) is calculated to be much larger (1 200—1 250 cm^{-1}) than that in the triplet (**3**).



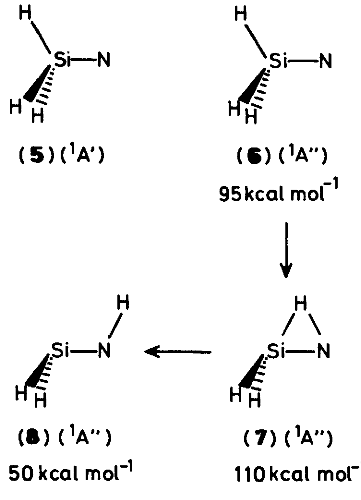
(**4**)

The triplet-singlet separation in silanimine (**4**) amounts to 39.7 kcal mol^{-1} and is thus similar to those of the isovalent species, namely $H_2C{=}NH$ (30), $H_2C{=}PH$ (39), and $H_2Si{=}PH$ (28 kcal mol^{-1}) (*cf.* ref. 11).

At the HF level, the singlet $H_3Si{-}N$ (**5**) ($^1A'$) is a local minimum. However, as in similar cases (CH_3N, H_3PN^+),[11,20,22] this nitrene collapses without energy barrier to the stable structure (**4**) when correlation energy is taken into account.

In a previous paper[19] the possibility that the excited singlet state $^1A''$ is involved in the photochemical decomposition of methyl azide has been suggested. We have considered the open-shell singlet states $^1A''$ of $[SiNH_3]$ species having the reference configuration ... $(3a'')^1(10a')^1$ and $a^1(n \longrightarrow \pi^*)$ character. On the basis of geometrical parameters partially optimized using a restricted Hartree–Fock (RHF) method and the 3-21G* basis set, and corresponding energies obtained by configuration interaction (CI) calculations employing the RHF/6-31++G* determinant as reference, the values shown in the Scheme have been estimated [with respect to the singlet silanimine (**4**)]. A small but real energy barrier (*ca.* 15 kcal mol^{-1}) separates the excited-singlet silylnitrene (**6**) from its more stable isomer (**8**). Hence, silylnitrene could exist as a local minimum on the open-shell singlet energy surface $^1A''$.

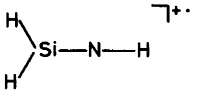
The $^1(n \longrightarrow \pi^*)$ state of silanimine (**8**) possesses a pyramidal C_s structure [as in the triplet (**3**)] and lies about 50 kcal mol^{-1} (2.2 eV) above the ground state $^1A'$ (**4**). Recently, electronic absorption bands located at 444—474 nm (2.8—2.6 eV) have been assigned to the $^1(n \longrightarrow \pi^*)$ transitions of substituted silanimines.[4,5] Surprisingly, the latter appear to be much smaller than the vertical transition energy of 3.8—3.9 eV obtained from recent MRD-CI calculations for the parent silanimine (**4**).[18]



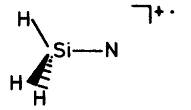
Scheme.

Again, note that our values are only rough estimates of the energy ordering of the open-shell singlet states $^1A''$.

Cationic States.—As in the closed-shell singlet, the silylnitrene radical cation (**10**) is converted with zero barrier into the silanimine cation (**9**). This observation probably arises from the large difference between the first vertical ionization potentials of (**1**) (11.5 eV at MP4SDQ) and (**4**) (9.3 eV). In the

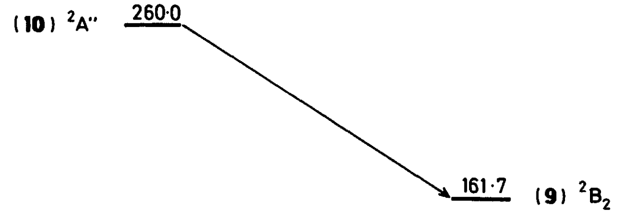


(**9**) ($^2B_2$)



(**10**) ($^2A''$)

neutral silanimine (**4**), the bonding π-(2a″) and non-bonding (10a′) orbitals are quite close in energy. Their relative ordering changes with the atomic basis employed.[17,18] A recent MRD-CI study[18] placed the vertical $^2A'(n)$ state 0.21 eV below the



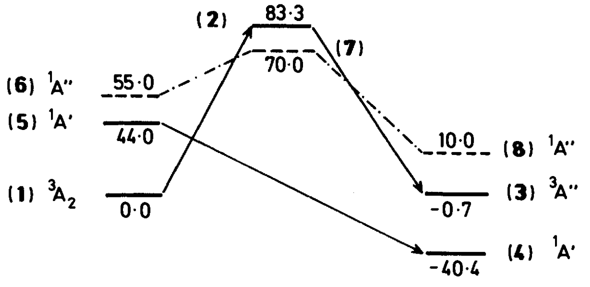


Figure 3. Schematic relative energies [ΔH(0 K) in kcal mol^{-1}] of the pathway for isomerization of H_3SiN to H_2SiNH in various electronic states

vertical $^2A''(\pi)$. However, as expected by these authors, extra stabilization due to elongation of the Si–N distance could lead to an $^2A''(\pi)$ ground state. Our geometry optimization confirms this view. The cation (**10**) has a planar structure with a linear Si–N–H frame (C_{2v}) and a $^2B_2(\pi)$ electronic ground state. The linearity of Si–N–H in (**9**) arises no doubt from strong delocalization and back-donation between Si and N atoms. The Si–N distance in (**10**) (1.622 Å) is larger than that in the neutral (**4**) but the corresponding calculated stretching frequency of 1 140 cm^{-1} (UHF/3-21G*) suggests a move towards double-bond character for this bond. Our best estimate predicts a first adiabatic ionization energy of 8.8 ± 0.3 eV for silanimine (**4**).

The Curtius-type Rearrangement.—The energy profile for the silylnitrene–silanimine rearrangement (Figure 3) is similar to those previously reported for the isovalent CH_3N [19,20,22] and isolectronic H_3PN^+ [11] species. Similar chemical behaviour can therefore be expected in the direct decomposition of the corresponding azides. There are three possibilities.

(*a*) If the decomposition occurs in the singlet ground state of the azide, the silanimine appears to be generated through another process such as that wherein nitrogen loss and migration of a substituent from silicon to nitrogen occur in a concerted manner rather than *via* the intermediacy of a singlet nitrene which does *not exist* as a discrete species.

(*b*) If the azide decomposes photochemically in its excited triplet state, a stable triplet silylnitrene should be formed and subsequently undergo typical reactions (with trapping agents, for example). In this case, silanimine was not observed as product.

(*c*) If the azide could be photochemically sensitized to rearrange in an electronic state higher lying than the closed-shell singlet and triplet states, then, the $^1(n \longrightarrow \pi^*)$ state of silylnitrene might play a role in that process.

Among these processes, case (*a*) appears the most likely since it best corroborates experimental findings.[2–8] This is in line with previous conclusions based on a stereochemical argument.[8] However, our preliminary results also suggest that the possibility (*c*) deserves further study. Finally, it should be pointed out that the fragmentation of unsubstituted silyl azide (H_3SiN_3) leads to the formation of H–N–Si;[21,23,24] the mechanistic aspects of this process are not the aim of the present paper (see ref. 21 for relevant calculations).

Acknowledgements

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