# Electronic Structure of a Stable Silylene: Photoelectron Spectra and Theoretical Calculations of Si(NRCHCHNR), $Si(NRCH_2CH_2NR)$ and $SiH_2(NRCHCHNR)$ *

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The He I and He II photoelectron spectra are reported and assigned for three closely related molecules, $Si(Bu^tNCHCHNBu^t)$, $Si(Bu^tNCH_2CH_2NBu^t)$ and $SiH_2(Bu^tNCHCHNBu^t)$, providing evidence for an energetically significant contribution from the silicon 3pπ orbital to the ring π system of $Si(Bu^tNCHCHNBu^t)$. Theoretical calculations on the model compounds Si(HNCHCHNH), $Si(HNCH_2CH_2NH)$ and $SiH_2(HNCHCHNH)$ have been carried out and there is good agreement between the calculated and experimental geometries. Trends in the orbital energies corresponded closely with the trends found for the ionization energies of the photoelectron bands. Calculated singlet–triplet splittings predict singlet ground states for the model silylenes. Calculated heats of hydrogenation at the ring carbons of Si(HNCHCHNH) and $SiH_2(HNCHCHNH)$ show the latter to be more exothermic by 13 kcal $mol^{-1}$ providing evidence for aromatic cyclic $(4n + 2)$-π delocalization in $Si(Bu^tNCHCHNBu^t)$. Estimates of Si–N double-bond character are obtained by *ab initio* calculations on rotamers of the model compound $Si(NH_2)_2$ and compared with analogous values for $C(NH_2)_2$.

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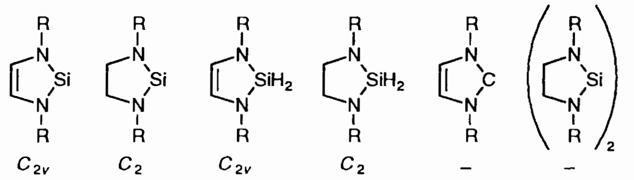
In 1994 the isolable silylene $Si(Bu^tNCHCHNBu^t)$ **I** was reported.[1] Its stability resembles that of the previously reported analogous carbenes, C(RNCHCHNR)[2–4] and germylene, $Ge(Bu^tNCHCHNBu^t)$.[5] The exceptional stability of **I** was attributed to cyclic $(4n + 2)$-π delocalization in this molecule. Experimental evidence to back this explanation stems from the chemical behaviour of **I**, its NMR data and electron diffraction structure.[1]

The electronic structure of the carbenes has been the subject of theoretical calculations[4,6,7] and an experimental diffraction determination of the electron density using X-ray and neutron diffraction.[8] The conclusion from this work is that the imidazole carbenes are carbenic rather than ylidic and that π donation from the nitrogen to the two-co-ordinate carbon atom plays only a minor role.

The question arises, therefore, as to whether the pπ orbital on the divalent centre is available for acceptance of π density from both the adjacent nitrogen atoms. It is normally accepted that such π bonding is less effective for silicon than carbon due to the larger covalent radius of the $Si^{II}$ centre. To gain experimental evidence for such π bonding in **I** we have investigated the photoelectron (PE) spectrum of **I** and those of the C–C-saturated derivative **II** and the $Si^{IV}$ compound **III**. In these last two compounds the π system is perturbed, by hydrogenation of the silicon in **III**, and by hydrogenation of the $(CH)_2$ unit in **II**. We have also undertaken an *ab initio* study of the model compounds **1**–**4**. This enables a theoretical comparison of the energy change of hydrogenation at the double bond of the unsaturated ring present in **I** and **1**, with that of the unsaturated ring found in the silicon(IV) compounds **III** and **3**.

To estimate the potential for N–Si double-bond character, we also carried out *ab initio* calculations of the model compounds $Si(NH_2)_2$ (**5**–**7**) and $C(NH_2)_2$ (**8**–**10**) in various conformations (Fig. 1).



| | $C_{2v}$ | $C_2$ | $C_{2v}$ | $C_2$ | – | – |
|---|---|---|---|---|---|---|
| | (Zero imaginary frequencies) | | | | | |
| R = H | | | | | | |
| | **1** | **2** | **3** | **4** | – | – |
| $R = Bu^t$ | | | | | | |
| | **I** | **II** | **III** | **IV** | **V** | **VI** |

Comparison of the PE spectra of **I** with those of **V** and $Ge(Bu^tNCHCHNBu^t)$, assigned with the help of density functional theory calculations, indicate a difference in ionization energy ordering between the carbene and the two heavier congeners and differences in the total electron-density distribution.[4] The PE spectrum of **I** is also presented and assigned here to facilitate its comparison with **II** and **III**.

## Experimental

The compound **I** was synthesized according to the literature method.[9] Compound **II** was prepared by the reaction of $SiF_2(Bu^tNCH_2CH_2NBu^t)$ (obtained from $Bu^tNHCH_2CH_2NHBu^t$[10] by lithiation with $LiBu^n$ followed by reaction with $SiF_4$) with Riecke magnesium in tetrahydrofuran. NMR: $^1H$, δ 1.28 [s, $C(CH_3)_3$] and 3.14 (s, $CH_2$); $^{13}C$, δ 52.5 [s, $C(CH_3)_3$], 46.5 (t, $CH_2$, $\pm {}^1J = 138.2$) and 31.7 [q, $C(CH_3)_3$, $^1J = 125.7$ Hz]. Though **II** dimerizes in the solid state, it has been shown to sublime as a monomer.[11] Compound **III** was prepared from $Bu^tNCHCHNBu^t$ and $SiH_2Cl_2$ in a manner analogous to that of tom Dieck and Zettlitzer[12] in synthesizing $SiCl_2(Bu^tNCHCHNBu^t)$ and $SiHCl(Bu^tNCHCHNBu^t)$. NMR: $^1H(C_6D_6)$, δ 1.18 [s, $C(CH_3)_3$], 5.65 (s, =CH) and 6.00 (d, $SiH_2$,

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* *Non-SI units employed:* cal = 4.184 J, eV ≈ $1.60 \times 10^{-19}$ J.

$^1J$ = 222.8): $^{13}$C, δ 113.4 (dd, =CH, $^1J$ = 179.5, $^2J$ = 9.0), 50.9 [s, $C(CH_3)_3$] and 30.2 [q, $C(CH_3)_3$, $^1J$ = 125.7 Hz].

The photoelectron spectra were measured using a PES Laboratories 0078 photoelectron spectrometer which has a hollow-cathode helium discharge lamp capable of providing both He I and He II radiation. Compounds **I** and **II** were held at temperatures between 40 and 46 °C, and **III** was held at room temperature external to the spectrometer. Data were collected by repeated scans on an Atari microprocessor. The spectra were calibrated with reference to $N_2$, Xe and He.

All equilibrium geometries were computed with the help of the GAUSSIAN 92 program.[13] The geometric parameters were optimized with maintenance of the $C_{2v}$ (**1**, **I**, **3**, **III**) and $C_2$ (**2**, **II**, **4**, **IV**) symmetry point groups. The theoretical levels HF/3-21G* and HF/6-31G* were employed for geometry optimization.[14] To reveal which structures represent minima on the potential-energy surface, analysis of their harmonic vibrational frequencies was carried out at the RHF/3-21G* level. As the number of imaginary force constants obtained depends only slightly on either the size of the basis set or on consideration of electron correlation,[14] we restricted calculations of vibrational frequencies to this theoretical level. Structures which possess no imaginary frequencies represent minima on the potential energy surface.

Final electronic energies were obtained by single point calculations at the MP4 level in the 6-31G* basis with the optimized HF/6-31G* geometries. Triplet structures were calculated as UHF (unrestricted Hartree–Fock) and singlet structures under the RHF (restricted Hartree–Fock) approximation. The energy difference between the triplet and singlet structures, $\Delta E_{ST}$, is defined as $E_T - E_S$, so that a positive value indicates a singlet ground state.

Zero-point energies were multiplied by 0.89 to correct for anharmonicity.[14] For evaluation of relative energies at 0 K (final estimations for the heats of hydrogenation given in the text) these zero-point vibrational contributions were added to the relative electronic energies (conversion factor, 1 Hartree = 627.5095 kcal mol$^{-1}$ = 27.087 eV ≈ 4.36 × $10^{-18}$ J).

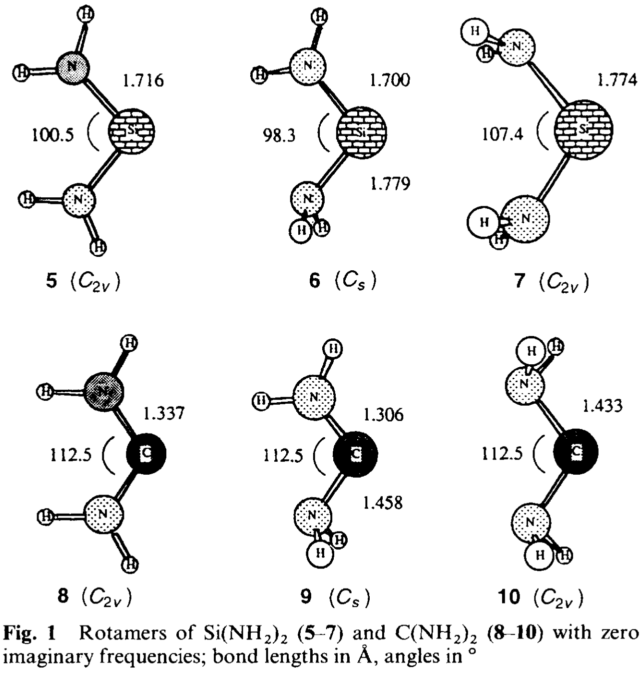
## Results and Discussion

The assignment and significance of the PE spectra are most readily appreciated in the context of a simple molecular orbital (MO) scheme for the unsaturated silylene, **1**. Such an orbital scheme is constructed for **1** by considering the interaction of *cis*-HNCHCHNH with a silicon atom. Diazabutadiene has four butadiene-like π orbitals, $\pi_1$–$\pi_4$, two of which, $\pi_1$ and $\pi_2$ are occupied. In the $C_{2v}$ symmetry of **1**, assuming the coordinate system shown in Fig. 2 with the molecule lying in the *xz* plane, $\pi_1$ and $\pi_3$ transform as $b_2$ and $\pi_2$ and $\pi_4$ as $a_2$. In addition two symmetry-adapted orbitals $n_+$ ($a_1$ symmetry) and $n_-$ ($b_1$ symmetry) represent the σ lone pairs on the nitrogens. The remaining valence electrons occupy orbitals which form the σ framework of the molecule. The ns and three np orbitals of Si transform as $a_1$ (3s), $b_1$ ($3p_x$), $b_2$ ($3p_y$) and $a_1$ ($3p_z$). The $n_+$ and $n_-$ lone-pair orbitals donate into $a_1$ and $b_1$ orbitals of Si, two of the Si electrons occupy another orbital of $a_1$ symmetry and two are transferred into a π orbital of $b_2$ symmetry built from $\pi_3$ and the Si $3p_y$ orbital. Fig. 2 gives a schematic MO scheme for **1** together with representations of the diazabutadiene MOs. Fig. 3 shows schematic representations of the MOs of **1**.

The compounds **2** and **3** result from hydrogenation of **1** at two different sites. In the saturated silylene, **2**, the two C 2pπ orbitals have been removed from the π system, resulting in a major reorganization of the π levels. The lower-occupied π level of $b_2$ symmetry will consist of a bonding in-phase combination of the three pπ orbitals from Si and the two N atoms. The higher-occupied π level, of $a_2$ symmetry, is an out-of-phase non-bonding combination of the N pπ orbitals. The lone-pair orbital is relatively unaffected. Representations of the orbitals are given in Fig. 3. Hydrogenation at Si to form **3** results in removal of the $a_1$ Si lone-pair orbital, and removal of the Si pπ orbital from the ring system. The removal of the Si pπ orbital is expected to destabilize the occupied $b_2$ π levels if it does contribute significantly to them, but not to perturb the $a_2$ π level to which it does not contribute. The consequent MOs are shown in Fig. 3.

*PE Spectral Assignment*.—The PE spectra of the three compounds are given in Figs. 4–6; vertical ionization energies (IE) are listed in Table 1. They differ significantly in the low IE region (below 11 eV). The broad complex band centred around 12.5 eV contains ionizations characteristic of the tertiary butyl group.

The PE spectrum of **I** (Fig. 4) shows three separate bands, A–C, at low ionization energy. The second band B, at 8.21 eV, is less intense than either band A or band C which have comparable intensities in both the He I and He II spectra. The first band shows clear vibrational structure with three



**5** ($C_{2v}$) **6** ($C_s$) **7** ($C_{2v}$)

**8** ($C_{2v}$) **9** ($C_s$) **10** ($C_{2v}$)

**Fig. 1** Rotamers of $Si(NH_2)_2$ (**5**–**7**) and $C(NH_2)_2$ (**8**–**10**) with zero imaginary frequencies; bond lengths in Å, angles in °

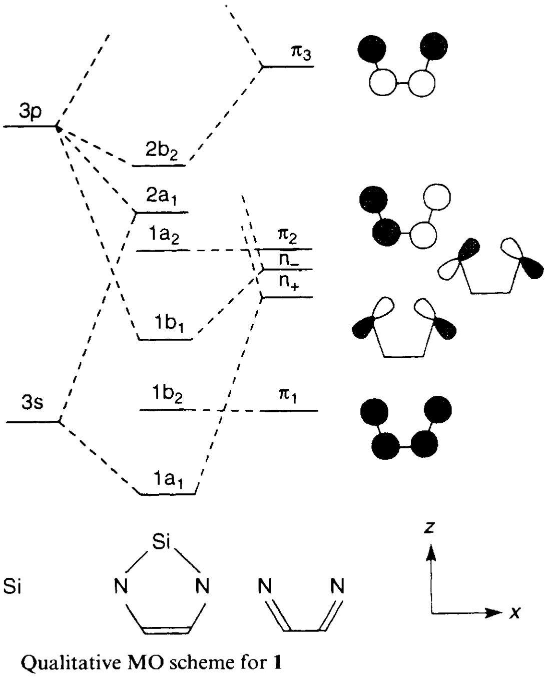
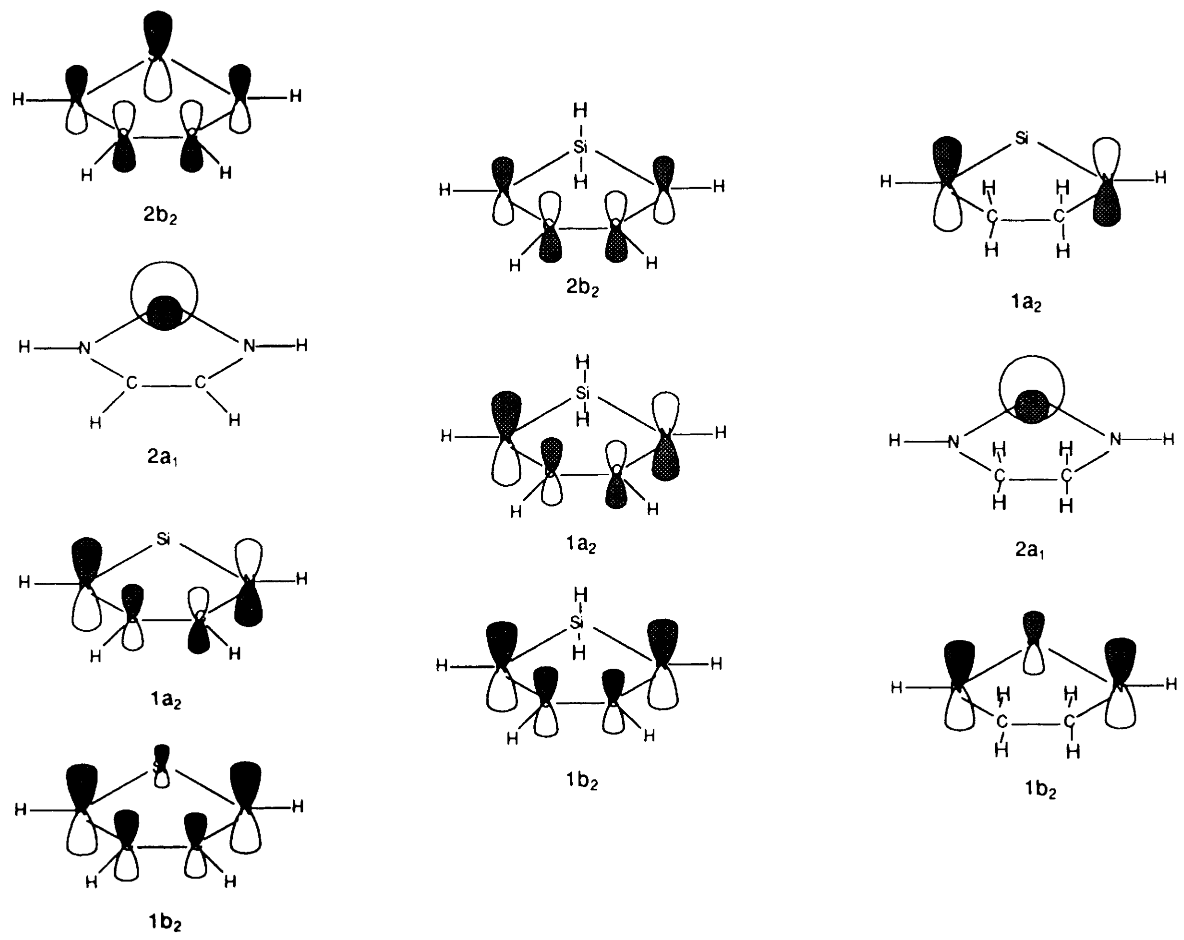


**Fig. 2** Qualitative MO scheme for **1**



1

3

2

**Fig. 3** Schematic representations of the upper-occupied MOs of **1**–**3**

**Table 1** Vertical ionisation energies (eV) for Si(Bu$^t$NCHCHNBu$^t$) **I**, Si(Bu$^t$NCH$_2$CH$_2$NBu$^t$) **II** and SiH$_2$(Bu$^t$NCHCHNBu$^t$) **III**

| I | II | III |
|---|---|---|
| 6.96, 7.13, 7.28 (A, 2b$_2$) | 7.54 (A, 1a$_2$) | 6.56 (A, 2b$_2$) |
| 8.21 (B, 2a$_1$) | 8.11 (B, 2a$_1$) | 8.92 (B, 1a$_2$) |
| 8.92 (C, 1a$_2$) | 9.08 (C, 1b$_2$) | 9.73 (X) |
| 10.76 | 10.66 | 10.52 |
| 11.27 | | |
| 12.48 | 12.57 | |
| 13.67 | 14.81 | |

identifiable components separated by 0.16 eV corresponding to a stretching frequency of the molecular ion in its ground state of 1291 (± 15) cm$^{-1}$.

The PE spectrum of **II** (Fig. 5) also shows three bands in this region, the second one, B, having an IE very similar to that of band B in the PE spectrum of **I**.

The PE spectrum of **III** (Fig. 6) shows two relatively intense bands, A and B, and a further weak band, X, in the low IE region. Band X is less apparent in the He II spectrum.

*Assignment of the PE spectrum of* Si(Bu$^t$NCHCHNBu$^t$) **I**. The PE spectrum of Si(Bu$^t$NCHCHNBu$^t$) is assigned in relation to this approximate MO scheme by comparison with previously reported PE spectra of Bu$^t$NCHCHNBu$^t$ [15] and its derivatives.[16] The first band is assigned to ionization from the 2b$_2$ π orbital. This is at a higher IE than found for $\pi_3$ ionizations in Al(Bu$^t$NCHCHNBt$^t$)$_2$ and Ga(Bu$^t$NCHCHNBu$^t$)$_2$.[16] The inferred corresponding stabilization of the orbital may well be due to the contribution of the Si p$_y$ orbital to the 2b$_2$ orbital.

The $\pi_2$ ionization band of Bu$^t$NCHCHNBu$^t$ has an IE of *ca.* 9.5 eV.[15] In the silicon derivative $\pi_2$ cannot interact on symmetry grounds with any silicon s or p orbital, but the IE can be affected by transfer of charge to the Bu$^t$NCHCHNBu$^t$ and increased electron–electron repulsion of the associated electrons. The third band, at 8.92 eV, is the most likely candidate for assignment to the 1a$_2$ π ionization.

This leaves the second band as the ionization of the 2a$_1$ silicon lone-pair orbital. Support for this assignment comes from the fact that bands A and C have similar intensities and are therefore likely both to arise from the two π orbitals.

The bands expected for ionization from the 1b$_1$ (n$_-$) and 2a$_1$ (n$_+$) orbitals must lie under the main band and may well give rise to part of the structure visible on the low IE edge. We assign the shoulder at 10.76 eV to the 1b$_1$ (n$_-$) orbital. They thus lie at higher IE than found in the aluminium and gallium compounds,[16] which is not unexpected as silicon has a higher nuclear charge than aluminium.

*Assignments of the PE spectrum of* SiH$_2$(Bu$^t$NCHCHNBu$^t$) **III**. Band A in the spectrum of **III** is assigned to the 2b$_2$ ionization. Its IE is 0.56 eV lower than the corresponding ionization in **I** consistent with the expectation that the silicon pπ orbital contributes to the stability of the 2b$_2$ electrons in **I** but not in **III**. There is no band between 7 and 8.7 eV where the silicon lone-pair ionization was found in **I** providing confirmation of the assignment given for the 2a$_1$ orbital. The second band B is assigned to the 1a$_2$ ionization and is unshifted from the position of the corresponding band in **I**. The shifts in the two π bands provide unambiguous evidence that the Si pπ orbital contributes to the 2b$_2$ MO.

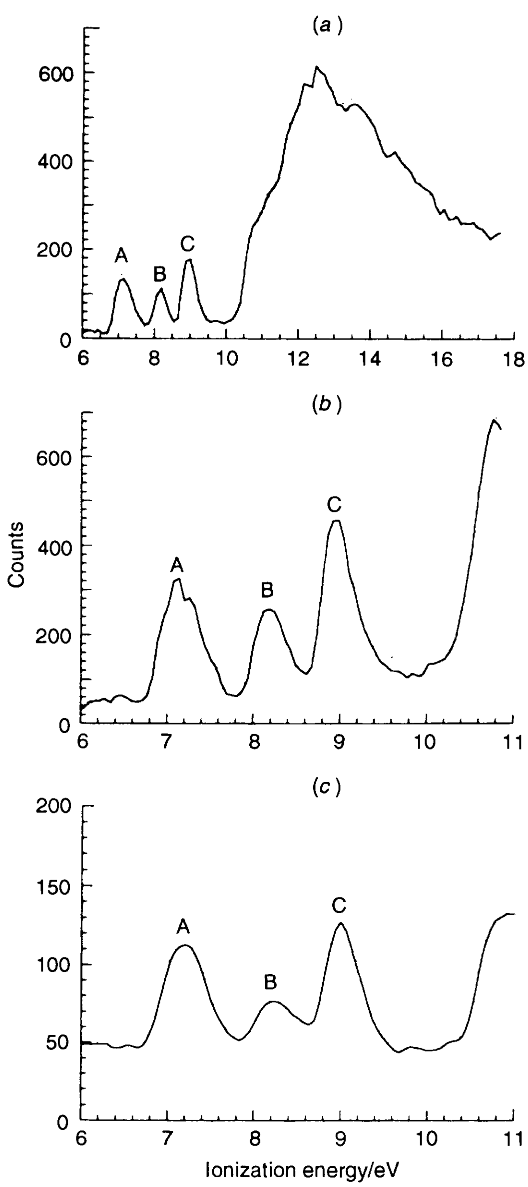


**Fig. 4** He I [(*a*) and (*b*)] and He II (*c*) photoelectron spectra of Si(Bu$^t$NCHCHNBu$^t$) **I**

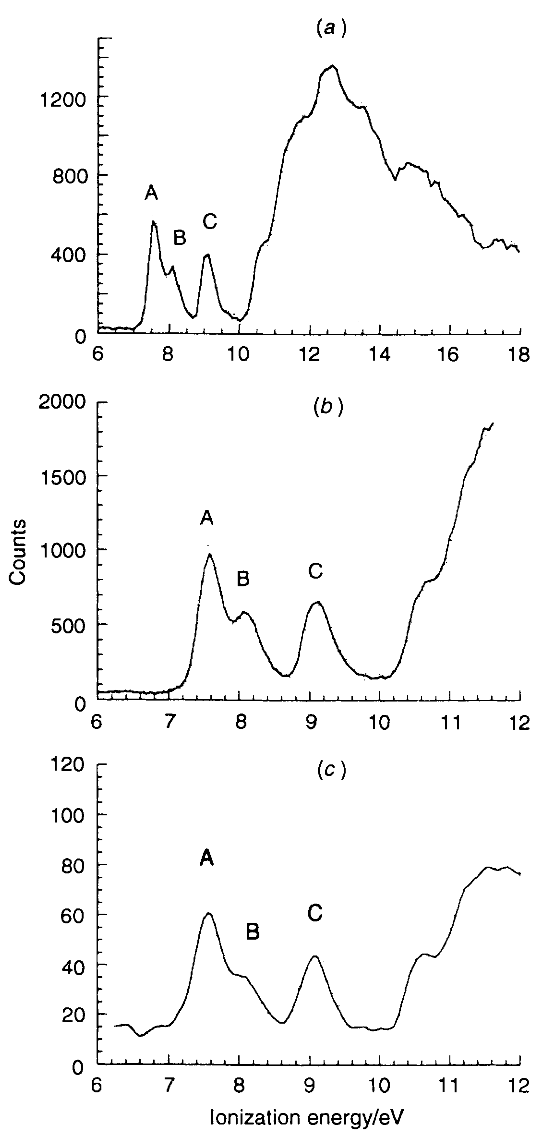


**Fig. 5** He I [(*a*) and (*b*)] and He II (*c*) photoelectron spectra of Si(Bu$^t$NCH$_2$CH$_2$NBu$^t$) **II**

**Table 2** Atomic charges for ring atoms in **1–4** and orbital energies (eV) for selected MOs of **1–3**

| | Atomic charge | | | Orbital energy | | | |
|---|---|---|---|---|---|---|---|
| | C | N | Si | b$_2$ | a$_1$ | a$_2$ | b$_2$ |
| **1** | 0.013 | −0.877 | 0.560 | −7.62 | −9.07 | −11.32 | −14.65 |
| **2** | 0.244 | −0.530 | 0.611 | | −9.40 | −8.78 | −11.24 |
| **3** | 0.011 | −0.926 | 1.058 | −7.10 | | −11.32 | −12.13 |
| **4** | −0.104 | −0.907 | 1.040 | | | | |

*Assignment of the PE spectrum of* Si(Bu$^t$NCH$_2$CH$_2$NBu$^t$) **II**. Band B, in the PE spectrum of **II**, lies at a similar IE to the lone-pair ionization band of **I**, and is similarly assigned to the 2a$_1$ orbital. Band A is assigned to the 1a$_2$ ionization undergoing a substantial lowering of IE from the corresponding band in **I** and **III** as the carbon 2pπ orbitals are no longer available for bonding. Band C arises from ionization of the 1b$_2$ electrons.

*Trends in Ionization and Orbital Energies*.—In Fig. 7 we juxtapose the trends found in the ionization energies of **I–III** with the trends calculated for the orbital energies of **1–3**. Given that the model compounds lack the *tert*-butyl groups present in the compounds studied experimentally, and that Koopmans' theorem is not strictly valid, it is still reasonable to expect that the *variations* in ionization energy in such a closely related series of molecules will be primarily controlled by the *variations* in the orbital energy. In fact the parallel between the two sets of data is good, giving us confidence both in the PE assignment and in the efficacy of the calculation.

Several points in the trends are particularly noteworthy. (*i*) The constancy of the 2a$_1$ IE between **I** and **II**, (*ii*) the constancy of the 1a$_2$ IE between **I** and **III** and (*iii*) the lowering of the 2b$_2$ IE between **I** and **III**. We attribute (*i*) to the fact that the lone pair is little affected by hydrogenation of the ring carbon atoms and (*ii*) is consistent with the lack of silicon 3pπ contribution to the 1a$_2$ MO. Most crucially (*iii*) is a strong indication that the silicon 3pπ orbital does contribute to the stabilization of the 2b$_2$ π orbital in **I**, as its removal by hydrogenation on the silicon significantly destabilizes the corresponding orbital in **III**.

A similar approach comparing the IE of the π bands of Δ$^4$-1,3,2-diazaborolines with 1,3,2-diazaborolidines established considerable delocalisation of the 6π electrons within the unsaturated five-membered heterocycle.[17]

The atomic charges found for C, N and Si for **1–4** and the

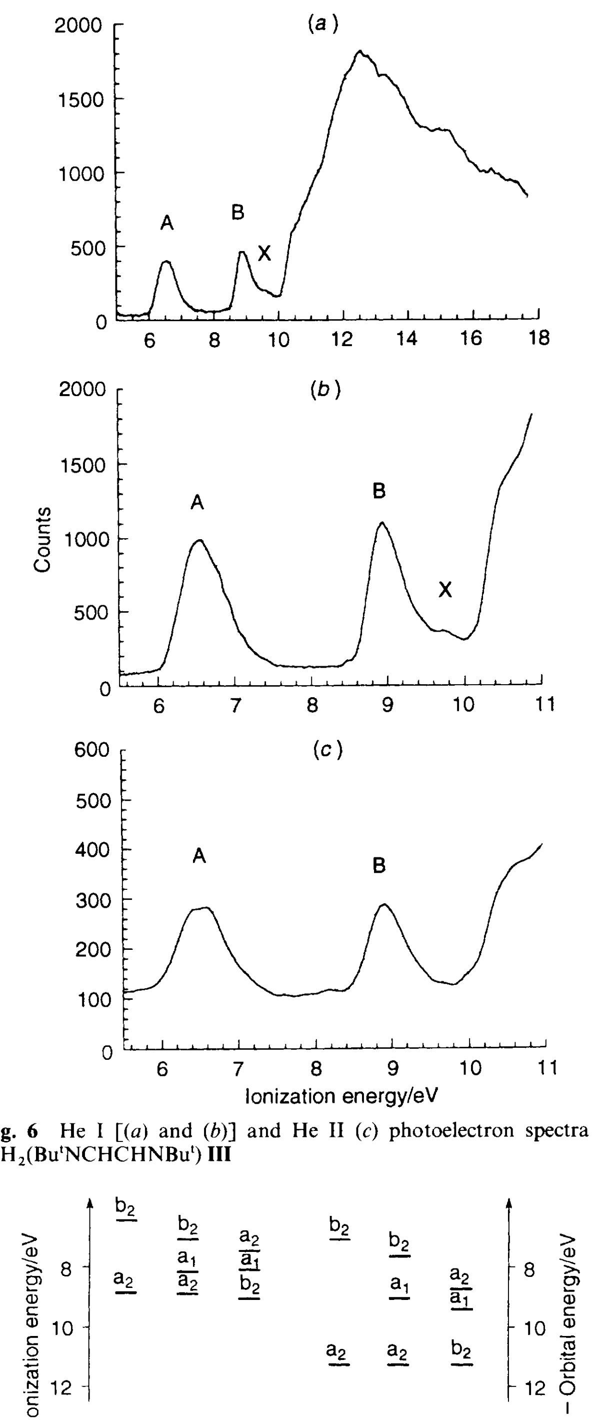


Fig. 6 He I [(*a*) and (*b*)] and He II (*c*) photoelectron spectra of $SiH_2(Bu^tNCHCHNBu^t)$ **III**

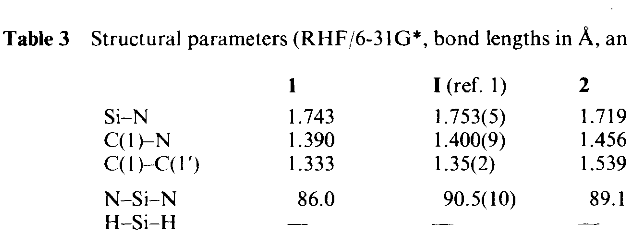


Fig. 7 Plot of the ionization energies of **I**–**III** and orbital energies of **1**–**3**

orbital energies for selected MOs of **1**–**3** are given in Table 2.

*Calculated and Experimental Geometries*.—A careful comparison of the geometries of **1** and C–C saturated **2** (Table 3) reveals an elongation of the Si–N bond by 0.024 Å in **1**. In the experimentally accessible **I** and **II**, this difference is even more pronounced [**I**, Si–N = 1.753(5);[1] **II**, Si–N = 1.719(3);[11] Δ(Si–N) = 0.034 Å]. In **2** the N pπ orbitals can only donate to the Si pπ orbital, whereas in **1** the hypothesis is that the N pπ electrons are cyclically delocalized, the Si–N bond order is thus reduced in **1** compared with **2**. This assumption is backed up by the fact that the C=C double bond in the silylene **1** is about 0.01 Å longer than in the silane **3**. A similar effect is not found in the C–C saturated **2** and **4** which rules out arguments based on mere σ skeleton or steric influences. The constancy of the Si–N bond length between **2** and **4** is attributed to a cancellation of the increase due to the absence of Si–N π bonding in **4** by the decrease in covalent radius between $Si^{II}$ and $Si^{IV}$. It is a striking observation, that the Si–N bond lengths in the bis(amino)silylenes **2** (cyclic), **5** and **II** (X-ray[11]) are virtually equal, the only exception being **1**. As mentioned earlier, the fact that the Si–N bonds in the bis(amino)silylenes and bis(amino)silanes are of equal length itself is a strong indication of Si–N π bonding.[1] In general, there is an excellent agreement between observed and calculated structural parameters.

*Si–N π Bonding in Model Compounds* **5**–**10**.—In order to get an estimate of the possible energetic contribution of Si–N π bonding we studied the theoretical rotational barriers in $Si(NH_2)_2$ and the bond length in various rotamers (Fig. 1) and compared them with those of $C(NH_2)_2$.

On the MP2/6-31G* level the barrier of rotation about the first Si–N bond with pyramidalization of $NH_2$ was *E*(**6**) − *E*(**5**) = 13 kcal $mol^{-1}$, about the second bond *E*(**7**) − *E*(**6**) = 23 kcal $mol^{-1}$. Substitution of silicon for germanium gives essentially the same data, *i.e.* 13 and 22 kcal $mol^{-1}$ respectively (though the germanium results were calculated using the less sophisticated LANL 1DZ basis set[5]). In the case of the homologous carbene **8**, the rotational barriers were 19 and 48 kcal $mol^{-1}$. The high rotation barriers as well as the difference in energy for rotation about the first and second Si–N bond clearly shows the presence of significant $N–Si^{II}$ π interaction.

In the planar ground state **5**, both the nitrogen lone pairs are competing for the empty orbital on silicon. This causes 'resonance saturation' of this orbital and as a result none of the $NH_2$ groups exploits its full donor capacity. Therefore, in **6** the *in-plane* $NH_2$ group compensates for some of the charge density previously provided by the other $NH_2$ group. This effect also becomes evident by comparising the Si–N bond lengths in **5**–**7**. Upon orthogonalization, the N–Si bond length is elongated, whereas the N–Si bond of the still *in-plane* $NH_2$ group is shortened compared to the bond lengths in **5**.

*Singlet–Triplet Splittings and Dimerization*.—Both silylenes **1** and **2** are calculated as possessing a singlet ground state (**1**,

**Table 3** Structural parameters (RHF/6-31G*, bond lengths in Å, angles in °) of the cyclic silylenes **1** and **2** and the cyclic silanes **3** and **4**

| | **1** | **I** (ref. 1) | **2** | **II** (ref. 11) | **3** | **4** |
|---|---|---|---|---|---|---|
| Si–N | 1.743 | 1.753(5) | 1.719 | 1.719(3) | 1.730 | 1.718 |
| C(1)–N | 1.390 | 1.400(9) | 1.456 | 1.489(6) | 1.412 | 1.456 |
| C(1)–C(1′) | 1.333 | 1.35(2) | 1.539 | 1.52(1) | 1.322 | 1.538 |
| N–Si–N | 86.0 | 90.5(10) | 89.1 | 92.0(2) | 91.0 | 92.3 |
| H–Si–H | — | — | — | — | 104.9 | 105.1 |
| Si–N–C(1) | 114.6 | — | 116.8 | 113.2(3) | 110.6 | 112.70 |
| C(1)–N–C(2) | — | 120.4(22) | — | 116.4(3) | — | — |
| C(1)–N–H | 118.6 | — | 116.9 | — | 119.9 | 117.6 |
| N–C(1)–C(1′) | 112.2 | 114.1(5) | 106.1 | 106.2(7) | 113.9 | 106.3 |

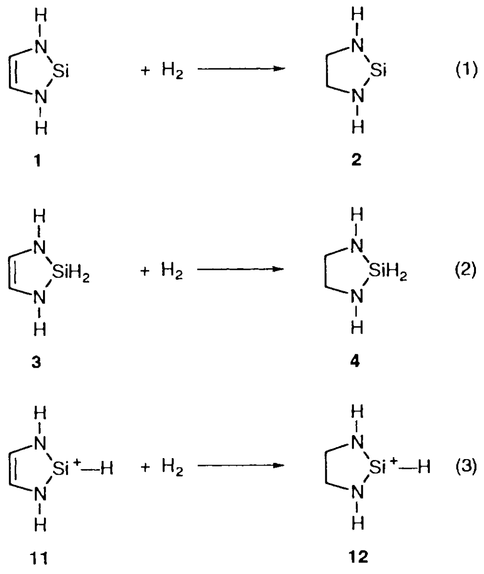
**Table 4** Heats of hydrogenation ($\Delta E$/kcal mol$^{-1}$) for reactions (1)–(3) and resonance energies of **1** ($\Delta E_{2-1}$/kcal mol$^{-1}$) and **11** ($\Delta E_{2-3}$/kcal mol$^{-1}$)

| | $\Delta E_1$ | $\Delta E_2$ | $\Delta E_3$ | $\Delta E_{2-1}$ | $\Delta E_{2-3}$ |
|---|---|---|---|---|---|
| LAN1DZ//LANL1DZ | −15.99 | −24.79 | — | −8.79 | — |
| 3-21G*//3-21G* | −16.64 | −25.05 | −26.26 | −8.41 | 1.21 |
| 6-31G*//6-31G* | −17.64 | −27.11 | −25.48 | −9.47 | −1.63 |
| MP2/6-31G*//6-31G* | −6.74 | −20.65 | −15.09 | −13.92 | −5.56 |
| MP4/6-31G*//6-31G* | −6.68 | −19.73 | — | −13.05 | — |

$\Delta E_{ST}$ = 69; **2**, $\Delta E_{ST}$ = 74 kcal mol$^{-1}$).This is understandable not only in terms of maximising the N–S$^{II}$ π interaction, but also by the high electronegativity of the nitrogen atoms bonded to Si$^{II}$. A theoretical study of the substituted silylenes SiHF and $SiF_2$[18] and of methylated, silylated and lithiated silylenes[19] suggests that electronegative substituents stabilise the singlet state with respect to the triplet state. The singlet–triplet splitting calculated for **1** and **2** is indeed the highest yet found. For both the sum $\Sigma\Delta E_{ST}$ is well over the value of about 120 kcal mol$^{-1}$, above which disilylenes are predicted spontaneously to dissociate into the corresponding silylenes.[20]

The resonance of the N–Si–N moiety is likely to play an important role in stabilising the silicon(II) centre of **1**. However, comparison of the chemical behaviour of **I** and **II** clearly shows that there must be an additional stabilising effect in **I** which is absent in **II**. While **I** remains a monomeric white solid at room temperature, white crystals of monomeric **II** dimerize slowly under the same conditions ($t_{\frac{1}{2}}$ = 5 d) to yield orange **VI**. This dimerization is reversible; upon sublimation **VI** is cleaved again to give the monomer **II**.[11]

*Heats of Hydrogenation.*—A comparison of the calculated heats of hydrogenation at the ring carbons of **1** and the silicon(IV) compound **3** (Table 4) shows the latter to be more exothermic by 13 kcal mol$^{-1}$ [equations (1) and (2)]. We believe that this is due to the fact that in **1** hydrogenation of the C–C double bond is accompanied by the loss of cyclic (4*n* + 2)-π delocalization, which makes reaction (1) thermodynamically less favourable than reaction (2). Significant differences in the heats of hydrogenation of the unsaturated silylene and its protonated derivative, **11**, are also found upon comparison of reaction (1) and (3). Both structures **1** and **11** allow for cyclic (4*n* + 2)-π delocalization and thus in both molecules the inclusion of electron correlation results in a drastic increase of the resonance energy as would be expected for a highly delocalized structure.



## Conclusion

The experimental and theoretical evidence confirms the presence of significant Si–N pπ bonding in the cyclic silylenes and (4*n* + 2)-π delocalisation in **I**.

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## References

1 M. Denk, R. Lennon, R. Hayashi, R. West, A. Haaland, H. Belyakov, P. Verne, M. Wagner and N. Metzler, *J. Am. Chem. Soc.*, 1994, **116**, 2691.
2 A. J. Arduengo III, R. L. Harlow and M. Kline, *J. Am. Chem. Soc.*, 1991, **113**, 362.
3 A. J. Arduengo III, H. V. Rasika Dias, R. L. Harlow and M. Kline, *J. Am. Chem. Soc.*, 1992, **114**, 5530.
4 A. J. Arduengo III, H. Bock, H. Chen, M. Denk, D. A. Dixon, J. C. Green, W. A. Herrmann, N. Jones, M. Wagner and R. West, *J. Am. Chem. Soc.*, in the press.
5 W. A. Herrmann, M. Denk, J. Behm, W. Scherer, F. R. Klingan, H. Bock, B. Solouki and M. Wagner, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 1485.
6 D. A. Dixon and A. J. Arduengo III, *J. Phys. Chem.*, 1991, **95**, 4180.
7 J. Cioslowski, *J. Int. Quantum. Chem.: Quantum Chem. Symp.*, 1993, **27**, 309.
8 A. J. Arduengo III, H. V. Rasika Dias, D. A. Dixon, R. L. Harlow, W. T. Klooster and T. F. Koetzle, *J. Am. Chem. Soc.*, 1994, **116**, in the press.
9 M. Denk, R. K. Hayashi and R. West, *J. Chem. Soc., Chem. Commun.*, 1994, 33.
10 M. Denk, Ph.D. Thesis, Technische Universität München, 1992.
11 M. Denk, unpublished work.
12 H. tom Dieck and M. Zettlitzer, *Chem. Ber.*, 1987, **120**, 795.
13 M. J. Frisch, G. W. Trucks, M. Head-Gordon, P. M. W. Gill, M. W. Wong, J. B. Foresman, B. G. Johnson, H. B. Schlegel, M. A. Robb, E. S. Replogle, R. Gomperts, J. L. Anres, K. Raghavachari, J. S. Binkley, C. Gonzales, R. T. Martin, D. J. Fox, D. J. DeFrees, J. Baker, J. J. P. Steward and J. A. Pople, GAUSSIAN 92, Gaussian Inc., Pittsburgh PA, 1992.
14 W. J. Hehre, C. Radom, P. v. R. Schleyer and J. A. Pople, *Ab Initio Molecular Orbital Theory*, Wiley, New York, 1986.
15 J. N. Louwen, D. J. Stufkens and A. Oskam, *J. Chem. Soc., Dalton Trans.*, 1984, 2683.
16 F. G. N. Cloke, C. I. Dalby, P. J. Daff and J. C. Green, *J. Chem. Soc., Dalton Trans.*, 1991, 181.
17 J. Kroner, H. Nöth and K. Niedenzu, *J. Organomet. Chem.*, 1974, **71**, 165.
18 M. E. Colvin, J. Breulet and H. F. Schaefer III, *Tetrahedron*, 1985, **41**, 1429.
19 J. Kalcher and A. F. Sax, *J. Mol. Struct. THEOCHEM.*, 1992, **253**, 287.
20 M. Karni and Y. Apeloig, *J. Am. Chem. Soc.*, 1990, **112**, 8589.

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