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Electronic structure of stable benzodiazasilylenes: photoelectron spectra and quantum-chemical investigations †

Philip Blakeman,[a] Barbara Gehrhus,[b] Jennifer C. Green,[a] Joachim Heinicke,[c] Michael F. Lappert,[b] Markus Kindermann[c] and Tamás Veszprémi *,[d]

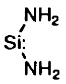
[a] *Inorganic Chemistry Laboratory, South Parks Road, Oxford OX1 3QR, UK*
[b] *School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ, UK*
[c] *Institut für Anorganische Chemie, EMA-Universität, D-17487 Greifswald, Germany*
[d] *Inorganic Chemistry Department, Technical University of Budapest, H-1521, Hungary*

Photoelectron spectra of 2,3-dihydro-1,3-di(neopentyl)-1*H*-1,3,2-benzodiazasilol-2-ylidene were investigated and compared to those of 2,3-dihydro-1,3-di(*tert*-butyl)-1*H*-1,3,2-diazasilol-2-ylidene and the related 2,3-dihydro-1,3-di(neopentyl)-1*H*-1,3,2-benzodiazasilole. The experimental spectra were assigned with the help of quantum-chemical calculations using the MP2/6-31G* level of theory. Trends in the orbital energies correspond well with the observed ionization energies. A 0.41 eV stabilization of the highest occupied molecular orbital level from the silane to the related silylene derivative indicates the incorporation of the silicon empty out-of-plane orbital into the π system. A good agreement was found between the calculated and experimental geometries. Delocalization stabilization of the investigated molecules is also supported by appropriate isodesmic reactions. The reaction energy indicates significant aromatic stabilization of the silylene derivatives. The stabilization is, however, reduced by a considerable ring strain.

Silylenes have long been known only as transient species, characterized by gas-phase or matrix spectroscopic investigations, as well as by trapping reactions.[1] The current interest in isolable low-co-ordinated compounds of main-group elements[2] stimulated efforts to synthesize persistent silylenes and to study their structural peculiarities and their reactivity.

The first isolated silicon(II) compounds, obtained in 1989–1990, were stabilized sterically by co-ordinating silicon to two pentamethylcyclopentadienyl ligands,[3] or by chelating with soft phosphine ligands,[4] resulting, however, in uncommon linear and tetrahedral structures. For normal 'bent' singlet silylenes considerable electronic stabilization is expected by interaction with one or two lone-pair donor substituents, especially amino groups.[5–8] Nevertheless, the diaminosilylene **1** is unknown (and probably would readily lose ammonia). Although no persistent acyclic representatives are known, four cyclic diazasilylenes have recently been prepared.[8–10] The most stable are the bulky substituted 2,3-dihydro-1,3-di(*tert*-butyl)-1*H*-1,3,2-diazasilol-2-ylidene **II**, described by Denk *et al.*,[9] and the two benzoannellated diaminosilylenes 2,3-dihydro-1,3-di(neopentyl)-1*H*-1,3,2-benzodiazasilol-2-ylidene **III** and its 5-methyl derivative.[10] They may be stored under nitrogen for more than a year under ambient conditions and distil or sublime without significant decomposition. A fourth representative, 1,3-di(*tert*-butyl)-1,3,2-diazasilolidine (the saturated analogue of **II**), was reported to dimerize reversibly at room temperature.[8] Since the steric shielding in the latter is comparable to that in **II** their different behaviour may be due to electronic factors as additional stabilizing contributions.

The nature of the electronic stabilization of the diazasilol-2-ylidene **II** has recently been the subject of photoelectron spectroscopic and quantum-chemical investigations.[8,11] According to this (*i*) the silicon $3p_\pi$ orbital is involved in the π system of the molecule and (*ii*) a delocalization energy of 13 kcal mol^{-1} was calculated by considering the hydrogenation at the C=C bond of **II** and of the analogous $Si^{IV}H_2$ compound.



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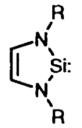
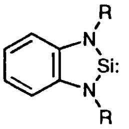
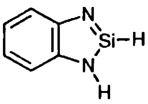


2 R = H
II R = Bu^t



3 R = H
III R = CH$_2$Bu^t



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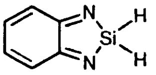

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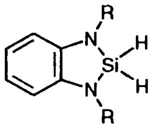

6 R = H
VI R = CH$_2$Bu^t

The aim of this work was to study the electronic structure of the benzo-bridged diaminosilylene (**3** and **III**) and to specify the type and magnitude of electronic stabilization by comparison with **2** as well as with isomeric benzodiazasiloles **4**,**5** and the related 2,3-dihydro-1,3-di(neopentyl)-1*H*-1,3,2-benzodiazasilole **6** (and **VI**).

Experimental

Compound **III** was synthesized by reductive dechlorination of 2,2-dichloro-2,3-dihydro-1,3-di(neopentyl)-1*H*-1,3,2-benzodiazasilole, and its crystal and molecular structure was determined by X-ray diffraction.[10] Compound **VI** was obtained by $LiAlH_4$ reduction of the dichloro derivative (yield 35%). B.p. 104 °C (0.05 Torr). NMR (C_6D_6): ^1H ($SiMe_4$), δ 0.88 (s, CCH_3), 2.90 (s, CH_2) 5.67 (s, SiH), 6.68–6.72 (m, $CH^{4,7}$) and 6.84-6.87 (m, $CH^{5,6}$); ^{13}C, δ 28.22 (CH_3), 34.16 (CMe_3), 56.61 (NCH_2), 141.89 (NC_{ar}), 109.21 ($C^{4,7}$) and 118.0 ($C^{5,6}$); ^{29}Si, δ −15.33 ($^1J_{HSi}$ 230 Hz).

Photoelectron spectra of compounds **III** and **VI** were recorded using a PES Laboratories 0078 photoelectron spectrometer equipped with a hollow-cathode helium-discharge

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† *Non-SI units employed:* cal = 4.184 J, Torr ≈ 133 Pa, eV ≈ 1.60×10^{-19} J, E_h (Hartree) ≈ 4.36×10^{-18} J.

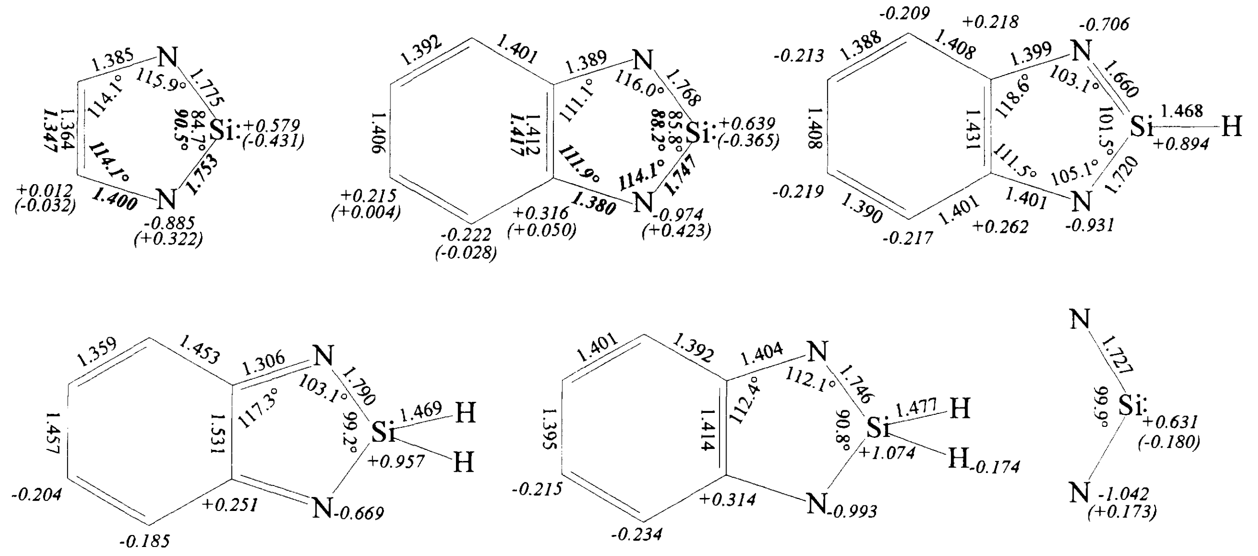

Fig. 1 Calculated and observed (bold) geometry (distances in Å), total charge density (in italics) and π-charge density (in italics and parentheses)

lamp able to provide both He (I) and He (II) radiation. The pale yellow, crystalline **III** and the pale viscous oil **VI** sublimed cleanly and rapidly at *ca.* 100 °C (10^{-5} Torr). Data were collected by repeated scans on an Atari microprocessor. Spectra were calibrated using N_2, Xe and He.

Calculations were carried out on model compounds **1**–**6** with hydrogen in place of *tert*-butyl or neopentyl substituents using the GAUSSIAN 92[12] quantum-chemical package and the standard 6-31G* basis set at the Hartree-Fock (HF) level and second-order (frozen-core) Moeller-Plesset (MP2) perturbation theory. Geometry optimizations were performed using the gradient method. Harmonic vibrational frequencies were calculated at the equilibrium geometries of the HF level to ensure that these geometries were real minima of the potential surface. Since the structural differences between HF and MP2 levels are small, further frequency calculations on the MP2 level were not carried out for economic reasons. Nevertheless, in order to test the adequacy of the level of theory used, we performed a series of calculations on the five-membered silylene **2** using a larger basis set (6-311G*) and higher level of correlation [MP2(full), CCSD(T)] without finding any significant deviation in the results. Therefore, in this paper all of the results and conclusions drawn are based on MP2/6-31G*//MP2/6-31G* calculations.

Results and Discussion

(*a*) Geometry

The calculated geometries of the model compounds **1**–**6** are compiled in Fig. 1, which also shows the X-ray diffraction data for **III**[10] and electron diffraction (ED) data for **II**.[9] The calculated results are in good agreement with the observed values indicating that the level of theory used is appropriate for the structural investigation. The similarity of the solid state and the calculated (and ED investigated) gas-phase structure suggests that the molecule has a rigid skeleton. Indeed, the lowest calculated vibrational frequency of **3** is 181 cm^{-1} which belongs to the C–H out-of-plane bending and the lowest ring frequency is 509 cm^{-1} (at the HF/6-31G* level).

No significant differences can be seen between structure **2** and its benzo-condensed derivative **3** except that the C=C bond length in the five-membered rings differ due to the influence of annellation.

Systematic trends can be found when comparing **3** to its isomers **4** and **5** and to the dihydrogenated derivative **6**, in both the bond lengths and angles. The variation in the Si–N bond length may be a measure of the double-bond character and thus the possible aromaticity of the rings, and therefore requires further analysis. For comparison, we note that the Si–X bond lengths in silylenes (SiX_2) are longer than in silanes (SiX_2H_2) as a result of the larger p character of the bond.[5,13] Assuming that the difference in the bond lengths is a direct consequence of the larger covalent radii of Si^{II}, the difference in the calculated Si–H distances[14] in SiH_4 (1.4829 Å) and in SiH_2 (1.5185 Å) can be used as an additive constant for the Si^{II}–N distance in **3** compared with Si^{IV}–N distances. The corrected bond length obtained in this way for **3** (1.7324 Å) indicates a small but significant double-bond character as compared to the Si=N and Si–N distances of $H_2Si{=}NH$ (1.6170 Å) and that of **5** (1.790 Å). Such a comparison is not rigorous and hence does not lead to an unambiguous conclusion because of other possible effects (variation in the charge separation, the hyperconjugation of SiH_2 group, anomeric effect,[13] *etc.*).

(*b*) Photoelectron spectroscopy

The He (I) spectrum of compound **III** is shown in Fig. 2. A He (II) spectrum was also obtained, but no significant differences in the relative intensities of the bands were found. The vertical ionization energies (i.e.s) are shown in Table 1. Five distinct bands are expected to be attributable to ionization from π orbitals and the silicon lone pair. To help in their assignment, the He (I) spectrum of compound **VI** was also obtained (Fig. 2). Again, no significant differences in the relative intensities of the bands were apparent in the He (II) spectrum.

The calculated i.e.s are based on quantum-chemical methods using Koopmans' theorem.[15] The first eight molecular orbitals (MOs) of compound **3** relevant for the spectrum are illustrated in Fig. 3. As a comparison the MO contours of **2** are also included. To illustrate the assignment and to find the relationship of the spectral bands of **1**–**3** a MO scheme based on the calculated orbital energies is shown in Fig. 4, indicating the similarities and the development of the orbital structures of **2** and **3** from their parent molecules. Starting from the orbitals of **1** we observe a definite stabilization of both the silicon and nitrogen lone pairs as an effect of either ethylene or benzene substitution. This stabilization may be caused by either or both (*i*) the distortion of the N–Si–N angle in the ring or (*ii*) the electronic effect of the unsaturated moiety attached. The effect of distortion was estimated by calculating **1** in the ring geometry. It was found that while the first (a_1) level shifted from 8.73 (at the optimum, 99.9°) to 9.47 eV (at 84.7° which matches

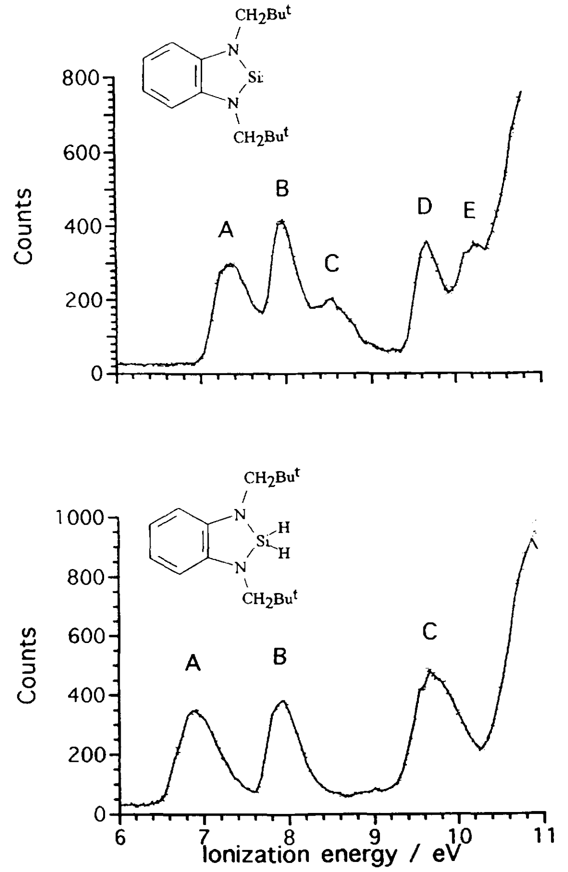

Fig. 2 Photoelectron spectra of compounds **III** and **VI**

Table 1 Calculated and observed ionization energies (eV) for compounds **II**, **III** and **VI**

III		VI		II		
obs.	calc.	obs.	calc.	obs.	calc.	Assignment
7.32	7.43	6.91	7.10	6.96	7.37	b_1 ring π
7.96	8.46	7.95	8.35	—	—	a_2 phenyl π
8.55	9.61	—	—	8.21	9.30	a_1 Si lone pair
9.67	12.08	9.70	12.22	8.92	11.32	a_2 N lone pair
10.22	12.11		11.37	—	—	b_1 phenyl π
—	—		13.17	—	—	b_1 SiH_2
	13.36		13.22	—	—	a_1 phenyl σ
	13.66		13.47	10.76	14.15	b_2 phenyl σ
			14.45			a_1 N–Si–N
	15.32		15.56		14.55	b_1 ring π

the geometry of **II**), the second (a_2) level shifted in the opposite direction, from 10.45 (99.9) to 9.89 eV (84.7°). The third level (b_1) is insensitive to the N–Si–N angle. The electronic effect of the unsaturated groups on the orbital structure of the N–Si–N moiety can be elucidated considering the variation of the charge distribution in the molecules (Fig. 1). Although the total charge at the silicon in **1**–**3** does not change considerably, the variation of the charge on the in-plane and out-of-plane orbitals (σ- and π-charge distribution) is quite large, and, as a consequence of the classical $+I$ and $-M$ effects, is in opposite directions. As the π charge on the silicon varies from -0.18 (in **1**) to -0.431 (**2**) and to -0.365 (**3**), the σ charge shifts from $+0.811$ (**1**) to $+1.010$ (**2**) and to $+1.004$ (**3**). Therefore a strong stabilization of the in-plane lone pair of silicon is expected. A similar (but opposite) effect stabilizes the out-of-plane lone pairs of nitrogen; in this case the electron density decreases in the out-of-plane orbitals (and increases in the in-plane orbital) during the substitution. A strong interaction found between the π orbital of ethylene (benzene) and that of **1** drastically splits the respective levels, and forms, eventually, the highest occupied molecular orbital (HOMO) of **2** and **3**. The reason why the first two MOs are in reverse order in the analogous carbene compound[11] is that in the carbene analogue of **1**, NH_2–C–NH_2, the respective π level is much 'deeper' in energy (according to our MP2/6-31G* calculation, 13.84 eV compared to 11.95 eV in **1**) and so the combination with the ethylene π level is not as effective as in the cyclic silylenes.

Comparing the photoelectron band structures of compounds **II**[11] with **III** two important factors should be stressed. First, the number of bands in the low-ionization-energy region increases indicating the inclusion of ionizations from the phenylene unit. Secondly, the bands of **III** shift towards higher energy. Given the charge distribution of molecule **3** (Fig. 1), the latter fact is not surprising; it clearly indicates the electron-withdrawing effect of the phenylene ring. Although the nitrogen atoms are somewhat more negative in **3** than in **2** both the silicon and the two carbon atoms become more positive. Analysing again the σ- and π-charge distribution on nitrogen, it is found that the out-of-plane p orbital is more positive in **3** while the in-plane orbitals carry more negative charge. Therefore it is expected that bands originating from the five-membered ring in **3** are usually stabilized when compared to the corresponding bands of **2**. The only exception, as expected, is a band assigned to the N–C or N–Si σ bonds.

On this basis, it is a simple matter to assign the bands in Fig. 2. Ionization from band A is 0.41 eV lower in energy for compound **VI** than **III** and is assigned to the $2b_1$ HOMO. Ionization from band B is identical in both cases, and is assigned to the $2a_2$ orbital. Band C in the spectrum of **III** is absent altogether from that of **VI** and hence is assigned to the silicon lone pair ($1a_1$) orbital. Band C of **VI** has a much larger area under the peak than either band D or E of **III**, so it is likely that the $1a_2$ and $1b_1$ levels overlap. Band D of **III** and C of **VI** occur at the same energy, consequently D is assigned to the $1a_2$ level. Band E (of **III**) moves to lower i.e. by 0.54 eV to be part of C of **VI**. It is thus assigned to the $1b_1$ level. These results are summarized in Table 1.

It is interesting that the $1a_1$ orbital lies at a noticeably higher i.e. for compound **III** than for **II**. This implies that the silicon lone pair is less nucleophilic in **III** than in **II**.

The position of the asymmetric combination of the nitrogen lone-pair orbitals is almost the same in compounds **III** and **VI** at about 9.7 eV. This energy is about 0.8 eV higher than in **II** as indicated in Fig. 4 because of the interaction with the orbital of the phenyl ring of the same symmetry.

(*c*) Stability

Almost all the MOs are stabilized on going from compound **6** to **3** indicating that the reduction from Si^{IV} to Si^{II} results in a stabilization of the molecule. The stabilization of the HOMO by 0.41 eV (0.33 eV in the calculations) is of crucial importance, because it indicates that the silicon out-of-plane orbital is incorporated in the π system. Studying the orbital correlation, it seems that the stabilization is not restricted to the π system; a possible delocalization is only one of the factors which makes silylenes **2** and **3** particularly stable.

Comparing the energies of the isomeric molecules **3**–**5** (Table 2) it can be seen that the silylene derivative is the most stable, its relative energy being >30 kcal mol^{-1} lower than for the other isomers. The contribution of delocalization stabilization can be estimated from the energies of isodesmic bond separation reactions as follows in equations (1)–(4). All fragments and possible conformers of the fragments of the equations have been optimized at the HF/6-31G* and at the MP2(fc)/6-31G* level. Second derivatives have also been calculated at both levels

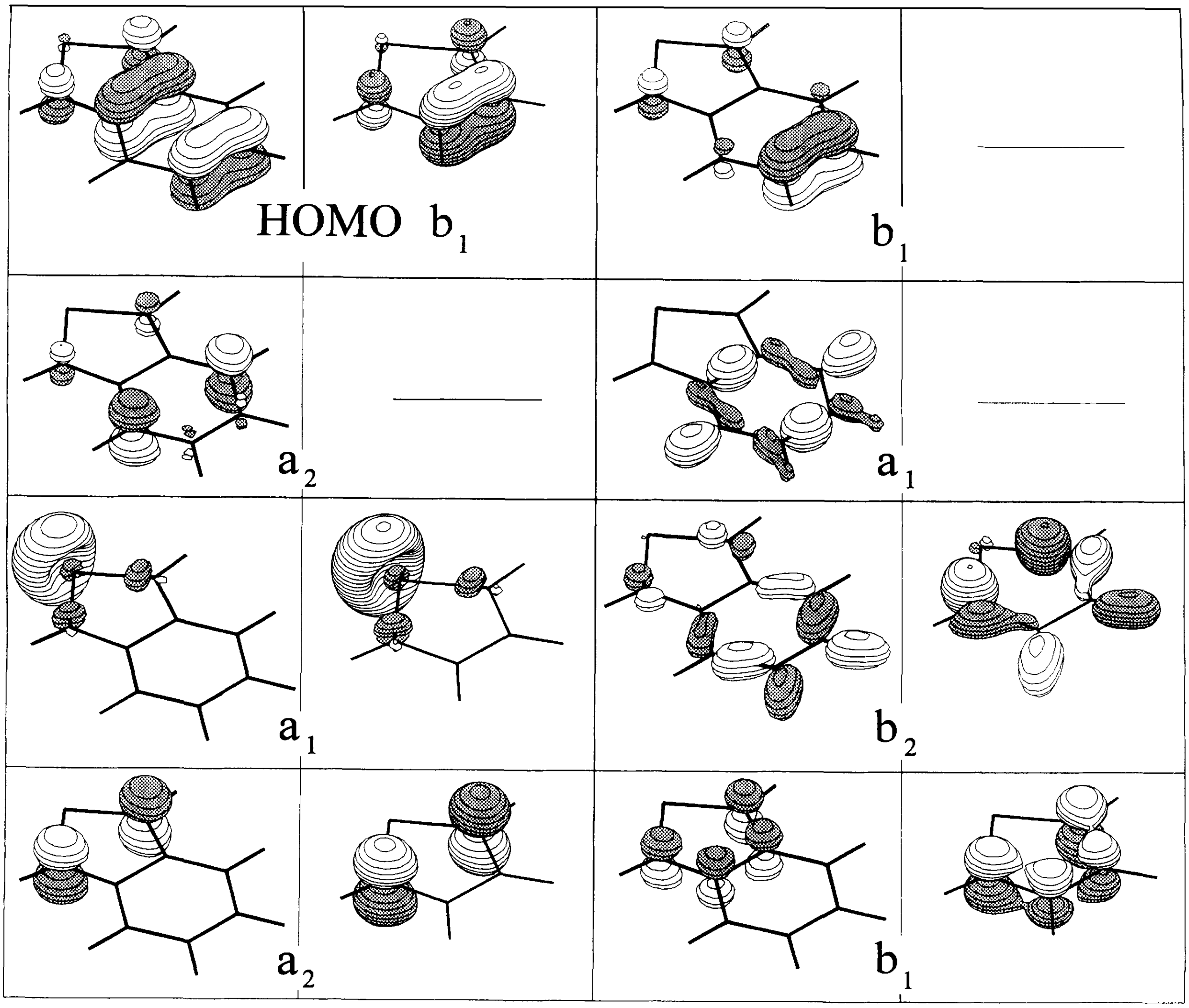

Fig. 3 Molecular orbitals of compounds **2** and **3** as shown by the MOLDEN program[16]

$$\mathbf{2} + 2NH_3 + 2CH_4 + SiH_2 \longrightarrow 2SiH{-}NH_2 + 2NH_2{-}CH_3 + CH_2{=}CH_2 \quad (1)$$

$$\mathbf{3} + 2NH_3 + 2CH_4 + SiH_2 \longrightarrow 2SiH{-}NH_2 + 2NH_2{-}CH_3 + C_6H_6 \quad (2)$$

$$\mathbf{4} + 2NH_3 + 2CH_4 + SiH_4 \longrightarrow SiH_3{-}NH_2 + SiH_2{=}NH + 2NH_2{-}CH_3 + C_6H_6 \quad (3)$$

$$\mathbf{6} + 2NH_3 + 2CH_4 + SiH_4 \longrightarrow 2SiH_3{-}NH_2 + 2NH_2{-}CH_3 + C_6H_6 \quad (4)$$

and only the real minima were accepted. Since no second derivatives have been calculated at the MP2 level for the benzo-condensed molecules **3**–**6**, zero-point energies (z.p.e.s) were calculated and used only at the HF level. These reactions make it possible to separate the conjugation of the five-membered ring from the benzene fragment of the molecules, therefore the calculated energies of **2** and **3** are comparable. Additionally, the delocalization stabilizations of the non-isomer molecules **3** and **6** are also comparable. No delocalization stabilization data for molecule **5** are included in Table 2 as a benzene unit cannot be separated from this molecule without drastic structural changes. To study the effects of the larger basis set and the higher correlated level some further calculations for molecule **2** were carried out at the MP2(full)/6-31G* and MP2(full)/6-311G* levels. From these data it could be concluded that the higher levels of sophistication reduce the bond-separation energy by about 3–6 kcal mol^{-1}, while the inclusion of z.p.e. increases it by about 6 kcal mol^{-1}.

As it can be seen from Table 2 the largest delocalization stabilization is found in compound **4**. The stabilization of **2** and **3** is about the same. This may indicate that the effect of the phenyl ring and the C=C double bond unit on the delocalization is similar. Since the stability of the obviously non-aromatic **6** is also quite close to that of **3** we may conclude that the silicon empty out-of-plane orbital in silylenes is not incorporated in the delocalized system. This proposal appears to contradict the previous conclusions, and therefore it is worthwhile to study the stabilization in detail by reference to equations (5)–(9).

$$\mathbf{2} + 2NH_3 + 2CH_4 \longrightarrow NH_2{-}Si{-}NH_2 + 2NH_2{-}CH_3 + CH_2{=}CH_2 \quad (5)$$

$$\mathbf{3} + 2NH_3 + 2CH_4 \longrightarrow NH_2{-}Si{-}NH_2 + 2NH_2{-}CH_3 + C_6H_6 \quad (6)$$

$$\mathbf{4} + 2NH_3 + 2CH_4 \longrightarrow NH_2{-}SiH{=}NH + 2NH_2{-}CH_3 + C_6H_6 \quad (7)$$

$$\mathbf{6} + 2NH_3 + 2\,CH_4 \longrightarrow NH_2{-}SiH_2{-}NH_2 + 2NH_2{-}CH_3 + C_6H_6 \quad (8)$$

$$NH_2{-}Si{-}NH_2 + SiH_2 \longrightarrow 2SiH{-}NH_2 \quad (9)$$

Table 2 Total energies (E_h), relative energies (kcal mol^{-1}), bond separations (b.s.) and ring-fragmentation (r.f.) energies (kcal mol^{-1})

			b.s.			r.f.	r.f. + strain[b]
Molecule	E_t[a]	E_{rel}[a]	HF	HF + z.p.e.	MP2	MP2	MP2
2	−476.551 77				26.41	35.31	43.40
	(−475.891 49)	—	14.79	21.18			
	−476.581 12[c]				21.16[c]	27.91[c]	36.33[c]
					27.21[d]		
	−476.843 45[e]				24.19[e]		
3	−629.722 81	0.0			25.00	33.90	40.90
	(−628.562 49)	(0.0)	14.59	22.54			
4	−629.669 77	33.26			30.07	19.86	31.57
	(−628.499 80)	(39.31)	16.35	22.72			
5	−629.652 39	44.16					
	(−628.508 17)	(34.06)	—	—	—	—	—
6	−630.885 35				23.82	17.80	22.86
	(−629.727 60)	—					

[a] Hartree-Fock energies in parentheses. [b] Energy of ring-fragmentation reaction and considering the ring strain. [c] Using the MP2(full)/6-31G* level. [d] Using the MP2(full)/6-31G* + z.p.e. level. [e] Using the MP2(full)/6-311G* level.

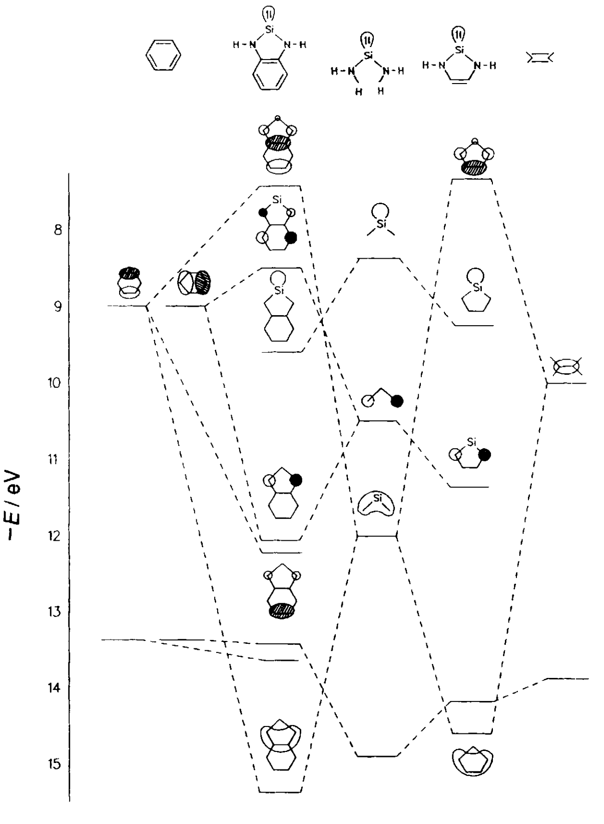

Fig. 4 A MO-correlation diagram for compounds **1**–**3**

An obvious limitation of reactions (1)–(4) is that the calculated delocalization energy is not clearly an aromatic stabilization by including the residual non-aromatic delocalization energy of the molecule and the ring strains. A better approximation of aromatic stabilization can be obtained using reactions (5)–(8). In these 'ring fragmentation' (r.f.) reactions the delocalization stabilization of the five-membered ring is compared to that of a N–Si–N unit. Since the stabilization exerted by a second amino group on a silylene is smaller than that caused by the first amino group [reaction (9) is exothermic[7]] the heat of reaction (5) is larger than that of (1) [reaction (5) represents the difference between (1) and (9)]. The delocalization stabilizations in NH_2–SiH=NH and in NH_2–SiH_2–NH_2 in reactions analogous to (9) are, however, endothermic (positive values). Therefore they diminish the original stabilization energy of equations (3) and (4) in reactions (7) and (8) indicating a large difference between the cyclic delocalization of rings containing Si^{II} or Si^{IV} (Table 2). The effect of (a part of) the ring strain on the delocalization can also be estimated considering the ring-fragmentation reactions with the energy of the corresponding N–Si–N units in the same geometry as that present in the ring. The results of these calculations are shown in the last column of Table 2. It is clear that the cyclic delocalization in the electronic structure and hence the stability of compounds **2** and **3** plays an important role. Although, in **4** the aromatic stabilization is also remarkably large, the ring strain in this molecule is the largest of all, and a considerable part of the aromatic stabilization compensates for the strain of the ring. As expected, the stabilization of **6** is the smallest and includes only the delocalization within the N–C=C–N moiety.

Conclusion

The molecular electronic structure of 2,3-dihydro-1,3-di(neopentyl)-1*H*-1,3,2-benzimidazol-2-ylidene and related compounds has been studied using UV-photoelectron spectroscopy and correlated *ab initio* quantum-chemical calculations. The photoelectron bands have easily been assigned using Koopmans' theory and the orbital correlations with the respective 2,3-dihydro-1,3,2-diazosilol-2-ylidene. The 0.41 eV stabilization of the HOMO level from the silane to the related silylene derivative indicates incorporation of the silicon empty out-of-plane orbital in the π system. Bond-separation reaction energies indicate, however, that the largest delocalization stabilization can be expected in compound **4** and the stability of the non-delocalized molecule **6** is close to that of the silylene **3**. This fact is in contradiction with the previous finding. Considering, however, the stability of the N–Si–N fragment of the molecules studied in proper ring-fragmentation reactions, it is clear that the cyclic delocalization in the stability of molecules **2**–**4** plays an important role. The largest ring strain can be estimated in **4** which compensates for a considerable part of the stabilization of the ring. Therefore the high stability of **2** and **3** is understandable.

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