Dimers of Diaminosilylenes: Doubly Bonded or Bridged? The Dimers of (i-$Pr_2N)_2Si$:

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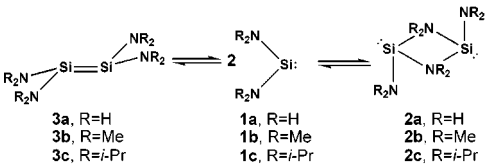
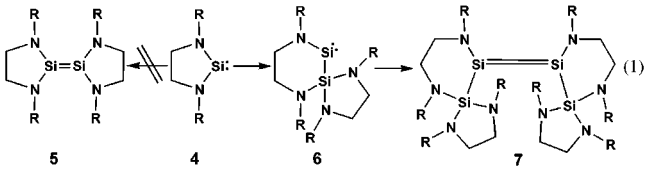
Disilenes, $R_2Si{=}SiR_2$, are generally synthesized by the dimerization of the corresponding silylenes, R_2Si:.[1] A significant number of disilenes were synthesized by this method, but only few disilenes which carry heteroatom substituents, i.e., one bis(trimethylsilylamino)-substituted disilene[2a] and one dialkoxydisilene,[2b] have so far been isolated.[3] Disilenes having **four** heteroatom substituents, i.e., $X_2Si{=}SiX_2$ (X = OR, NR_2, F, etc.), are not yet known. This raises the fundamental question if such disilenes, e.g., $(R_2N)_2Si{=}Si(NR_2)_2$ which formally result from the dimerization of diaminosilylenes, $(R_2N)_2Si$:, can exist? On the basis of ab initio calculations, two of us have predicted[4] that the parent $(H_2N)_2Si$:, **1a**, dimerizes to the novel (μ-NH_2)-bridged species, **2a**, and furthermore the disilene $(H_2N)_2Si{=}Si(NH_2)_2$ (**3a**) (Scheme 1) is not a minimum on the potential energy surface (PES) and therefore is not an existing molecule. This theoretical prediction was supported by scrambling experiments in the dimerization of (i-$Pr_2N)_2Si$: (**1c**), carried out in the Sendai laboratories, which were interpreted to be consistent with the intermediacy of bridged **2c**, although a more complex sequence of reactions, involving **3c**, could not be excluded.[5] Additional support for the theoretical

Scheme 1



prediction that tetraaminodisilenes do not exist is the recent finding by West et al.[6] that the stable cyclic diaminosilylene **4**, R = t-Bu, does not dimerize to the corresponding tetraaminodisilene, **5**, R = t-Bu, but instead undergoes an insertion reaction leading to silylene **6**, R = t-Bu, which dimerizes to a **diamino**disilyl disilene **7**, R = t-Bu (eq 1).[6] In full agreement with these findings, calculations predict that **7**, R = Me, is a minimum on the PES, while the **tetraamino**disilene, **5**, R = Me, which can be obtained from dimerization of **4**, R = Me, is not.[6]



However, recent experimental evidence, reported by the Sendai group, of a low-temperature equilibrium between **1c** and the tetraaminodisilene **3c**[7] stands in apparent conflict with the theoretical predictions[4,6] and the implications from previous experiments.[5,6]

In this paper we report results of detailed quantum mechanical calculations as well as new experiments, which illuminate the role of the conformation of the amino substituents in determining which type(s) of silylene dimers (N-bridged, Si=Si bonded, or weakly Si···Si bonded) exist and what are their relative energies and geometries.

Calculations were carried out at the correlated ab initio MP2/6-311G(d,p) and CCSD(T)/6-311G(d,p) levels[8] and at the hybrid-density functional B3LYP/6-311G(d,p) level.[9,10] The calculations show that the parent tetraaminodisilene (**3a**) is **not** a minimum on the PES (similarly to **5**[6]), in agreement with our previous lower level calculations.[4a] Thus, **1a** dimerizes without a barrier to give the bridged **2a** which is lower in energy than two molecules of **1a** by 16.3 and 17.9 kcal mol^{-1} (at CCSD(T)/6-311G(d,p) and MP2/6-311G(d,p), respectively).[11,12] In contrast to **3a**, the N-dimethyl- and N-di-i-Pr-substituted tetraaminodisilenes, **3b** and **3c**, are calculated to be bound species.

Why are **3b** and **3c** minima on the PES while the less congested **3a** is not? The answer lies in the conformation adapted by the amino substituents and its effect on the energy difference between the singlet and triplet states (ΔE_{ST}) of the corresponding silylenes, $(R_2N)_2Si$:. Carter and Goddard,[13a] as well as Malrieu and Trinquier[13b,c] (CGMT), pointed out that E = E′ bonds (E, E′ = C→Pb) are expected to be formed only when $\sum\Delta E_{ST}$ of the ER_2

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(1) For a recent review see: Okazaki, R.; West, R. *Adv. Organomet. Chem.* **1996**, *39*, 231.
(2) (a) Michalczyk, M. J.; West, R.; Michl, J. *Organometallics* **1985**, *4*, 826. (b) Gillette, G. R.; Noren, G.; West, R. *Organometallics* **1990**, *9*, 2925.
(3) However, similar attempts to synthesize amino- or fluoro-substituted disilenes were unsuccessful: Archibald, R. S.; Winkel, Y. v. d.; Millevolte, A. J.; Desper, J. M.; West, R. *Organometallics* **1992**, *11*, 3276.
(4) (a) Apeloig, Y.; Müller, T. *J. Am. Chem. Soc.* **1995**, *117*, 5363. (b) Apeloig, Y.; Karni, M.; Müller, T. In *Organosilicon Chemistry II*; Auner, N., Weis, J., Eds.; VCH: Weinheim, 1996; p 263.
(5) Sakamoto, K.; Tsutsui, S.; Sakurai, H.; Kira, M. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 253.
(6) Schmedake, T. A.; Haaf, M.; Apeloig, Y.; Müller, T.; Bukalov, S.; West, R. *J. Am. Chem. Soc.* **1999**, *121*, 9479.
(7) Tsutsui, S.; Sakamoto, K.; Kira, M. *J. Am. Chem. Soc.* **1998**, *120*, 9955.
(8) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.
(9) Koch, W.; Holthausen, M. C. *A Chemist's Guide to Density Functional Theory*; Wiley-VCH: Weinheim, 2000.
(10) (a) All calculations were performed with Gaussian 94, Revisions C2-E2, and Gaussian 98, Revisions A3-A7; Gaussian, Inc.: Pittsburgh, PA, 1995 and 1998. (b) Unless stated otherwise the following abbreviations are used: MP2/6-311G(d,p) denotes MP2/6-311G(d,p)//MP2/6-311G(d,p), B3LYP/6-311G(d,p) denotes B3LYP/6-311G(d,p)//B3LYP/6-311G(d,p), while CCSD(T)/6-311G(d,p) denotes CCSD(T)/6-311G(d,p)//MP2/6-311G(d,p).
(11) The relative energies of dimers **2a** and **3a′** (see text) relative to two molecules of **1a** are as follows: −10.5, 24.7 (B3LYP/6-311G(d,p)); −17.9, 18.9 (MP2/6-311G(d,p)); −16.3, 21.6 (CCSD(T)/6-311G(d,p)). These results demonstrate that the B3LYP method underestimates the stability (relative to the silylene monomers) of both types of dimers.
(12) The alternative reaction channel, similar to that observed for **4** → **6**,[6] in which **1a** inserts into a Si−N bond of a second **1a** molecule giving $(H_2N)_3Si(H_2N)Si$: is also exothermic (by 9.4 kcal mol^{-1}), but it involves a barrier of 7.3 kcal mol^{-1} (at B3LYP/6-311+G(d,p)//B3LYP/6-311+G(d,p)). Dimerization of $[(H_2N)_3Si](H_2N)Si$: can lead either to $(H_2N)_3Si(H_2N)Si{=}Si(NH_2)Si(NH_2)_3$ (exothermic by 24.6 kcal mol^{-1}) and/or to the corresponding bridged dimer $(H_2N)_3SiSi[\mu(NH_2)]_2SiSi(NH_2)_3$ (the latter being by 2.2 kcal mol^{-1} more stable). The fact that $(H_2N)_3Si(H_2N)Si{=}Si(NH_2)Si(NH_2)_3$ is a minima on the PES is consistent (see below) with the much smaller singlet−triplet gap of $[(H_2N)_3Si](H_2N)Si$: (ΔE_{ST} = 41.6 kcal mol^{-1} at B3LYP/6-311+G(d,p)) relative to that of **3a**.
(13) (a) Carter, E. A.; Goddard, W. A., III *J. Phys. Chem.* **1986**, *90*, 998. (b) Trinquier, G.; Malrieu, J.-P. *J. Am. Chem. Soc.* **1987**, *109*, 5303. (c) Malrieu, J.-P.; Trinquier, G. *J. Am. Chem. Soc.* **1989**, *111*, 5916.

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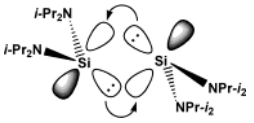
and ER'_2 fragments is smaller than the E = E′ bond energy ($E_{\sigma+\pi}$). When $\sum\Delta E_{ST} > E_{\sigma+\pi}$, the E = E′ isomer does not exist and bridged dimers of type **2** are favored.[13] Our previous studies[4,14] supported quantitatively the CGMT model for disilenes.

Diaminosilylene **1a** has a planar (C_{2v}-symmetry) equilibrium structure, reflecting the strong conjugation between the nitrogens' lone pairs and the empty 3p(Si) orbital. Consequently ΔE_{ST} of **1a** is large (79.3 kcal mol^{-1}),[15] which explains[13,14] why **3a** does not exist. However, when the amino groups are twisted out of planarity ΔE_{ST} is reduced considerably. Thus, **1a**, $\theta = 90^o$ (θ is the dihedral angle between the NSiN and the HNH planes), where the 2p(N) lone pairs are perpendicular to the empty 3p(Si) orbital, has a ΔE_{ST} of only 26.4 kcal mol^{-1}.[15,16] This large change in ΔE_{ST} of $(H_2N)_2Si$: should strongly influence the structure of its dimers.[4,13,14] Thus, a constrained $(H_2N)_2Si{=}Si(NH_2)_2$, **3a′**, in which all amino groups are kept perpendicular (all HNSiSi dihedral angles are ±90°), has a planar doubly bonded structure with a short r(Si=Si) of 2.129 Å (MP2/6-311G(d,p)), even shorter than in $H_2Si{=}SiH_2$ (2.162 Å). **3a′** is by 58.9 kcal mol^{-1} more stable than two **1a**, $\theta = 90°$; however, **3a′** is by 18.9 kcal mol^{-1} less stable than two planar **1a**, and full geometry optimization results in its spontaneous dissociation.

In contrast to **1a**, a SiSi bonded dimer of type **3** exists for both **1b** and **1c**. This can be understood by the fact that as the steric bulk of the R substituents at the nitrogens increases the amino groups are twisted out of planarity and ΔE_{ST} is reduced[17] to 66.9 and 54.3 kcal mol^{-1} for **1b** and **1c**, respectively.[15] The dimerizations of **1b**,**c** to **3b**,**c** are exothermic but only by 7.9 kcal mol^{-1} and by 3.8 kcal mol^{-1}, respectively.[18] The corresponding N-bridged dimers **2b**,**c** are also minima on the PES, **2b** being more stable than **3b** by 12.5 kcal mol^{-1}.[18] In contrast, the *i*-Pr-substituted bridged dimer **2c** is by 16.0 kcal mol^{-1} higher in energy than the SiSi bonded dimer **3c**.[18] The very large change in the relative stabilities of the N-bridged (**2**) and the disilene-type (**3**) isomers between R = Me and *i*-Pr results, in addition to the change in ΔE_{ST} of the corresponding silylenes, also from the severe steric interactions between the bulky *i*-Pr groups in **2c**, interactions which are smaller in **3c**.

3c (as well as **3b**) has a very unusual geometry (see Figure S1, Supporting Information). The calculated SiSi distance of 2.472 Å[19] is dramatically longer than regular Si=Si bonds (2.142 Å in $Me_2Si{=}SiMe_2$) or than in the unusual **7** (2.289 Å[6]) and it even exceeds that of Si−Si single bonds (e.g., 2.368 Å in $(Me_2N)_3$-$Si{-}Si(NMe_2)_3$[20a] and 2.340 Å in $Me_3SiSiMe_3$[20b]). **3c** is strongly pyramidalized around the silicon atoms ($\vartheta = 42.6°$, Figure S1), the torsion angle between the two NSiN planes is 55.5°, two of the vicinal *i*-Pr_2N groups form a NSiSiN dihedral angle of 108.4°, while the other two are nearly eclipsed (∠NSiSiN = 2.1°). **The unusual structure of 3c (or 3b) is not consistent with the presence of a Si=Si double bond**. The large twisting around the SiSi axis prevents effective interactions between the 3p(Si) orbitals and formation of a π-bond. A significant singlet-biradical character of **3c** is implied.[21] The bonding between the silicon atoms in **3c** is best described by two **very weak** (3-8 kcal mol^{-1}) **double donor−acceptor bonds** (Scheme 2).[13c]

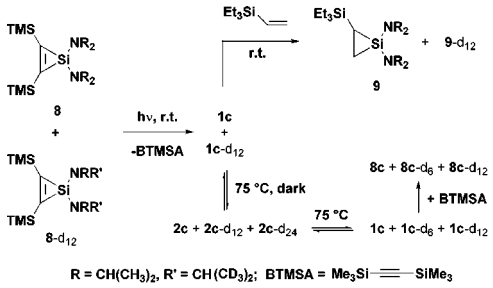
Scheme 2



Is the calculated structure of **3c** consistent with the observation that the product formed in the photochemical dimerization of **1c** has a λ_{max} of 439 nm?[7] Calculations at the TD-DFT level[22] of the electronic transitions of 8 experimentally observed (or of closely related models) amino- and alkyl-substituted silylenes and disilenes show a good linear correlation: Y(eV) = 0.58X(eV) + 1.16 ($r = 0.94$; see Figure S2, Supporting Information) between the calculated (X) and the experimental (Y) UV transition energies. These calculations rule out the possibility that the observed species[7] is the N-bridged **2c**, since calculations predict for **2c** a λ_{max} at 368 nm.[23] On the other hand, a λ_{max} of 441 nm is predicted for **3c**,[23] very close to that observed experimentally (439 nm).[7]

One important point remains to be explained: Why does dimerization of $(i\text{-}Pr_2N)_2Si$: (**1c**) when formed via reduction of the corresponding dichlorosilanes in boiling benzene lead to the bridged **2c**[5] while when **1c** is generated photolytically it dimerizes to the Si···Si bonded isomer **3c**?[7] New experiments (Scheme 3) suggest that **the bridged 2c is formed only above room temperature**, **while the Si···Si bonded isomer 3c is formed at lower temperatures.** Thus, cophotolysis at room temperature of a 1:1 mixture of **8** and **8**-d_{12} in C_6D_6 followed by thermal trapping of the generated diaminosilylenes **1c** and **1c**-d_{12} by bis(trimethylsilyl)acetylene **at 75 °C** (in the dark) produced the corresponding silacyclopropenes [**8**]:[**8**-d_{12}]:[**8**-d_6] in a ratio of 3:3:2 in 10% conversion. These results, showing scrambling, point clearly to the intermediacy of bridged dimer **2c**. On the other hand, co-photolysis of a 1:1 mixture of **8** and **8**-d_{12} in the presence of triethylvinylsilane in hexane **at room temperature** gave **9** and **9**-d_{12}; **no** scrambled product, e.g., **9**-d_6, was obtained (Scheme 3).[24]

Scheme 3



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Supporting Information Available: Tables with absolute energies, ΔE_{ST} values, and Cartesian coordinates for compounds **1**−**3**, Figure S1 showing the calculated geometry of **3c** and Figure S2 showing the correlation between experimental and calculated UV λ_{max} absorptions of silylenes and disilenes (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA003463D

(14) (a) Karni M.; Apeloig, Y. *J. Am. Chem. Soc*. **1990,** *112*, 8599. (b) Maxka, J.; Apeloig, Y. *J. Chem. Soc., Chem. Commun*. **1990**, 737.

(15) At B3LYP/6-311++G(3df,2p)//MP2/6-31G(d).

(16) **1a**, $\theta = 90°$ is 33 kcal mol^{-1} higher in energy than **1a**, $\theta = 0°$.

(17) The widening of the NSiN bond angle also contributes but the effect is relatively small.

(18) **2b** and **3b** at MP2/6-311G(d,p)//MP2/6-311G(d,p) and **2c** and **3c** at MP2/6-31G(d)//B3LYP/6-31G(d).[11]

(19) In **3b**, the SiSi distance is even longer: 2.595 Å at B3LYP/6-31G(d), 2.655 Å at B3LYP/6-311G(2d,p), and 2.537 Å at MP2/6-311G(d)).

(20) (a) Wan, J.; Verkade, J. G. *Inorg. Chem.* **1993**, *32*, 341. (b) Beagley, B.; Monaghan, J. J.; Hewitt, T. G. *J. Mol. Struct*. **1971**, *8*, 401.

(21) The calculated spin density at the silicon atoms in **3c** is ±0.69 (at UB3LYP/6-31G(d)); however, the first triplet state is 24.8 kcal mol^{-1} (at UB3LYP/6-31G(d)) higher in energy.

(22) Review: Burke, K.; Gross, E. K. U. In *Lecture Notes in Physics*; Joubert, D., Ed.; Springer: Heidelberg, 1998; Vol. 500.

(23) Modeled computationally by **2a** and **3a** in which all geometrical parameters are kept at the values calculated for **2c** and **3c**, respectively.

(24) Products which may result from an insertion reaction of one silylene into the other, similar to **6** or **7**,[6] were not observed in agreement with the calculations.[12]