

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/11884493>

# Dimers of diaminosilylenes: doubly bonded or bridged? The dimers of (i-Pr(2)N)(2)Si:.

ARTICLE in JOURNAL OF THE AMERICAN CHEMICAL SOCIETY · FEBRUARY 2001

Impact Factor: 12.11 · Source: PubMed

CITATIONS

6

READS

17

6 AUTHORS, INCLUDING:



Kenkichi Sakamoto

Shizuoka University

94 PUBLICATIONS 1,226 CITATIONS

SEE PROFILE



Mitsuo Kira

Tohoku University

314 PUBLICATIONS 5,739 CITATIONS

SEE PROFILE



Yitzhak Apeloig

Technion - Israel Institute of Technology

246 PUBLICATIONS 5,937 CITATIONS

SEE PROFILE

## Dimers of Diaminosilylenes: Doubly Bonded or Bridged? The Dimers of (*i*-Pr<sub>2</sub>N)<sub>2</sub>Si:

Masae Takahashi,<sup>†</sup> Shinobu Tsutsui,<sup>‡</sup> Kenkichi Sakamoto,<sup>‡</sup> Mitsuo Kira,<sup>\*,‡</sup> Thomas Müller,<sup>\*,‡</sup> and Yitzhak Apeloig<sup>§\*</sup>

Photodynamics Research Center

The Institute of Physical and Chemical Research (RIKEN)  
519-1399, Aoba, Aramaki, Aoba-ku, Sendai 980-0845, Japan

Department of Chemistry, Graduate School of Science  
Tohoku University, Aoba-ku, Sendai 980-8578, Japan

Institut für Anorganische Chemie der Goethe  
Universität Frankfurt, Marie Curie-Strasse 11

D-60439 Frankfurt/Main, Federal Republic of Germany

Department of Chemistry and the Lise Meitner-Minerva

Center for Computational Quantum Chemistry

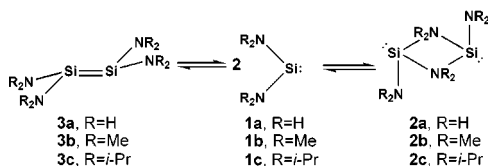
Technion-Israel Institute of Technology, 32000 Haifa, Israel

Received September 22, 2000

Revised Manuscript Received October 18, 2000

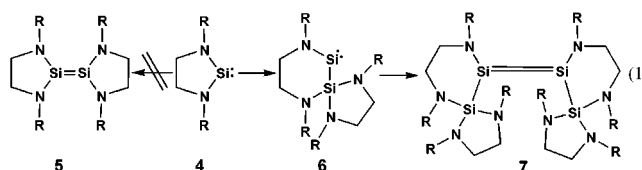
Disilenes, R<sub>2</sub>Si=SiR<sub>2</sub>, are generally synthesized by the dimerization of the corresponding silylenes, R<sub>2</sub>Si:.<sup>1</sup> A significant number of disilenes were synthesized by this method, but only few disilenes which carry heteroatom substituents, i.e., one bis(trimethylsilylamino)-substituted disilene<sup>2a</sup> and one dialkoxydisilene,<sup>2b</sup> have so far been isolated.<sup>3</sup> Disilenes having **four** heteroatom substituents, i.e., X<sub>2</sub>Si=SiX<sub>2</sub> (X = OR, NR<sub>2</sub>, F, etc.), are not yet known. This raises the fundamental question if such disilenes, e.g., (R<sub>2</sub>N)<sub>2</sub>Si=Si(NR<sub>2</sub>)<sub>2</sub> which formally result from the dimerization of diaminosilylenes, (R<sub>2</sub>N)<sub>2</sub>Si:, can exist? On the basis of ab initio calculations, two of us have predicted<sup>4</sup> that the parent (H<sub>2</sub>N)<sub>2</sub>Si:, **1a**, dimerizes to the novel (*μ*-NH<sub>2</sub>)-bridged species, **2a**, and furthermore the disilene (H<sub>2</sub>N)<sub>2</sub>Si=Si(NH<sub>2</sub>)<sub>2</sub> (**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<sub>2</sub>N)<sub>2</sub>Si: (**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.<sup>5</sup> Additional support for the theoretical

### Scheme 1



prediction that tetraaminodisilenes do not exist is the recent finding by West et al.<sup>6</sup> 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).<sup>6</sup> In full agreement with these findings, calculations predict that **7**, R = Me, is a minimum on the PES, while the **tetraaminodisilene**, **5**, R = Me, which can be obtained from dimerization of **4**, R = Me, is not.<sup>6</sup>



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

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<sup>8</sup> and at the hybrid-density functional B3LYP/6-311G(d,p) level.<sup>9,10</sup> The calculations show that the parent tetraaminodisilene (**3a**) is **not** a minimum on the PES (similarly to **5**<sup>6</sup>), in agreement with our previous lower level calculations.<sup>4a</sup> 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<sup>-1</sup> (at CCSD(T)/6-311G(d,p) and MP2/6-311G(d,p), respectively).<sup>11,12</sup> 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 ( $\Delta E_{ST}$ ) of the corresponding silylenes, (R<sub>2</sub>N)<sub>2</sub>Si:. Carter and Goddard,<sup>13a</sup> as well as Malrieu and Trinquier<sup>13b,c</sup> (CGMT), pointed out that E = E' bonds (E, E' = C→Pb) are expected to be formed only when  $\Sigma \Delta E_{ST}$  of the ER<sub>2</sub>

(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**, in which **1a** inserts into a Si-N bond of a second **1a** molecule giving (H<sub>2</sub>N)<sub>3</sub>Si(H<sub>2</sub>N)Si: is also exothermic (by 9.4 kcal mol<sup>-1</sup>), but it involves a barrier of 7.3 kcal mol<sup>-1</sup> (at B3LYP/6-311+G(d,p)/B3LYP/6-311+G(d,p)). Dimerization of [(H<sub>2</sub>N)<sub>3</sub>Si](H<sub>2</sub>N)Si: can lead either to (H<sub>2</sub>N)<sub>3</sub>Si(H<sub>2</sub>N)Si=Si(NH<sub>2</sub>)<sub>3</sub> (exothermic by 24.6 kcal mol<sup>-1</sup>) and/or to the corresponding bridged dimer (H<sub>2</sub>N)<sub>3</sub>SiSi[μ(NH<sub>2</sub>)<sub>2</sub>SiSi(NH<sub>2</sub>)<sub>3</sub>] (the latter being by 2.2 kcal mol<sup>-1</sup> more stable). The fact that (H<sub>2</sub>N)<sub>3</sub>Si(H<sub>2</sub>N)Si=Si(NH<sub>2</sub>)Si(NH<sub>2</sub>)<sub>3</sub> is a minima on the PES is consistent (see below) with the much smaller singlet-triplet gap of [(H<sub>2</sub>N)<sub>3</sub>Si](H<sub>2</sub>N)Si: ( $\Delta E_{ST}$  = 41.6 kcal mol<sup>-1</sup> 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.

<sup>†</sup> The Institute of Physical and Chemical Research.

<sup>‡</sup> Tohoku University.

<sup>§</sup> Institut für Anorganische Chemie der Goethe Universität Frankfurt.

<sup>\*</sup> Technion-Israel Institute of Technology.

(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.; Millevalte, 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.

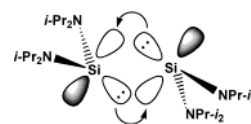
and  $ER'_2$  fragments is smaller than the  $E = E'$  bond energy ( $E_{\sigma+\pi}$ ). When  $\sum \Delta E_{ST} > E_{\sigma+\pi}$ , the  $E = E'$  isomer does not exist and bridged dimers of type **2** are favored.<sup>13</sup> Our previous studies<sup>4,14</sup> supported quantitatively the CGMT 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  $3p(\text{Si})$  orbital. Consequently  $\Delta E_{ST}$  of **1a** is large (79.3 kcal mol<sup>-1</sup>),<sup>15</sup> which explains<sup>13,14</sup> why **3a** does not exist. However, when the amino groups are twisted out of planarity  $\Delta E_{ST}$  is reduced considerably. Thus, **1a**,  $\theta = 90^\circ$  ( $\theta$  is the dihedral angle between the NSiN and the HNH planes), where the  $2p(\text{N})$  lone pairs are perpendicular to the empty  $3p(\text{Si})$  orbital, has a  $\Delta E_{ST}$  of only 26.4 kcal mol<sup>-1</sup>.<sup>15,16</sup> This large change in  $\Delta E_{ST}$  of  $(\text{H}_2\text{N})_2\text{Si}$ : should strongly influence the structure of its dimers.<sup>4,13,14</sup> Thus, a constrained  $(\text{H}_2\text{N})_2\text{Si}=\text{Si}(\text{NH}_2)_2$ , **3a'**, in which all amino groups are kept perpendicular (all HNSiSi dihedral angles are  $\pm 90^\circ$ ), has a planar doubly bonded structure with a short  $r(\text{Si}=\text{Si})$  of 2.129 Å (MP2/6-311G(d,p)), even shorter than in  $\text{H}_2\text{Si}=\text{SiH}_2$  (2.162 Å). **3a'** is by 58.9 kcal mol<sup>-1</sup> more stable than two **1a**,  $\theta = 90^\circ$ ; however, **3a'** is by 18.9 kcal mol<sup>-1</sup> 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  $\Delta E_{ST}$  is reduced<sup>17</sup> to 66.9 and 54.3 kcal mol<sup>-1</sup> for **1b** and **1c**, respectively.<sup>15</sup> The dimerizations of **1b,c** to **3b,c** are exothermic but only by 7.9 kcal mol<sup>-1</sup> and by 3.8 kcal mol<sup>-1</sup>, respectively.<sup>18</sup> The corresponding N-bridged dimers **2b,c** are also minima on the PES, **2b** being more stable than **3b** by 12.5 kcal mol<sup>-1</sup>.<sup>18</sup> In contrast, the *i*-Pr-substituted bridged dimer **2c** is by 16.0 kcal mol<sup>-1</sup> higher in energy than the SiSi bonded dimer **3c**.<sup>18</sup> 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  $\Delta E_{ST}$  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<sup>19</sup> is dramatically longer than regular Si=Si bonds (2.142 Å in  $\text{Me}_2\text{Si}=\text{SiMe}_2$ ) or than in the unusual **7** (2.289 Å<sup>6</sup>) and it even exceeds that of Si-Si single bonds (e.g., 2.368 Å in  $(\text{Me}_2\text{N})_3\text{Si}-\text{Si}(\text{NMe}_2)_3$ <sup>20a</sup> and 2.340 Å in  $\text{Me}_3\text{SiSiMe}_3$ <sup>20b</sup>). **3c** is strongly pyramidalized around the silicon atoms ( $\theta = 42.6^\circ$ , Figure S1), the torsion angle between the two NSiN planes is  $55.5^\circ$ , two of the vicinal *i*-Pr<sub>2</sub>N groups form a NSiSiN dihedral angle of  $108.4^\circ$ , while the other two are nearly eclipsed ( $\angle \text{NSiSiN} = 2.1^\circ$ ). **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  $3p(\text{Si})$  orbitals and formation of a  $\pi$ -bond. A significant singlet-biradical character of **3c** is implied.<sup>21</sup> The bonding between the silicon atoms in **3c** is best described by two **very weak** (3–8 kcal mol<sup>-1</sup>) **double donor–acceptor bonds** (Scheme 2).<sup>13c</sup>

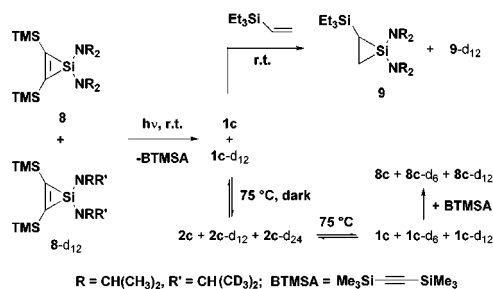
## Scheme 2



Is the calculated structure of **3c** consistent with the observation that the product formed in the photochemical dimerization of **1c** has a  $\lambda_{\text{max}}$  of 439 nm?<sup>7</sup> Calculations at the TD-DFT level<sup>22</sup> 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:  $Y(\text{eV}) = 0.58X(\text{eV}) + 1.16$  ( $r = 0.94$ ; 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<sup>7</sup> is the N-bridged **2c**, since calculations predict for **2c** a  $\lambda_{\text{max}}$  at 368 nm.<sup>23</sup> On the other hand, a  $\lambda_{\text{max}}$  of 441 nm is predicted for **3c**,<sup>23</sup> very close to that observed experimentally (439 nm).<sup>7</sup>

One important point remains to be explained: Why does dimerization of  $(i\text{-Pr}_2\text{N})_2\text{Si}$ : (**1c**) when formed via reduction of the corresponding dichlorosilanes in boiling benzene lead to the bridged **2c**<sup>5</sup> while when **1c** is generated photolytically it dimerizes to the Si···Si bonded isomer **3c**?<sup>7</sup> 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<sub>12</sub>** in  $\text{C}_6\text{D}_6$  followed by thermal trapping of the generated diaminosilylenes **1c** and **1c-d<sub>12</sub>** by bis(trimethylsilyl)acetylene at 75 °C (in the dark) produced the corresponding silacyclopropenes [**8**]:[**8-d<sub>12</sub>**]:[**8-d<sub>6</sub>**] 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, cophotolysis of a 1:1 mixture of **8** and **8-d<sub>12</sub>** in the presence of triethylvinylsilane in hexane at room temperature gave **9** and **9-d<sub>12</sub>**; no scrambled product, e.g., **9-d<sub>6</sub>**, was obtained (Scheme 3).<sup>24</sup>

## Scheme 3



**Acknowledgment.** This paper is dedicated to Prof. J. A. Pople on the occasion of his 75th birthday. This work was supported by the DFG (Scholarship to T.M.), by the German-Israeli Foundation for Scientific Research and Development (GIF), and the Minerva Foundation (Munich). Y.A. thanks the JSPS for a Visiting Professor scholarship.

**Supporting Information Available:** Tables with absolute energies,  $\Delta E_{ST}$  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  $\lambda_{\text{max}}$  absorptions of silylenes and disilenes (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA003463D

(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**,<sup>6</sup> were not observed in agreement with the calculations.<sup>12</sup>

(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**,  $\theta = 90^\circ$  is 33 kcal mol<sup>-1</sup> higher in energy than **1a**,  $\theta = 0^\circ$ .

(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).<sup>11</sup>

(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  $\pm 0.69$  (at UB3LYP/6-31G(d)); however, the first triplet state is 24.8 kcal mol<sup>-1</sup> (at UB3LYP/6-31G(d)) higher in energy.