

Reversible Transformation between a Diaminosilylene and a Novel Disilene

Thomas A. Schmedake,[†] Michael Haaf,[†] Yitzhak Apeloig,^{*,‡}
Thomas Müller,[§] Sergey Bukalov,[#] and Robert West^{*,†}

Department of Chemistry, University of Wisconsin—Madison
Madison, Wisconsin 53706

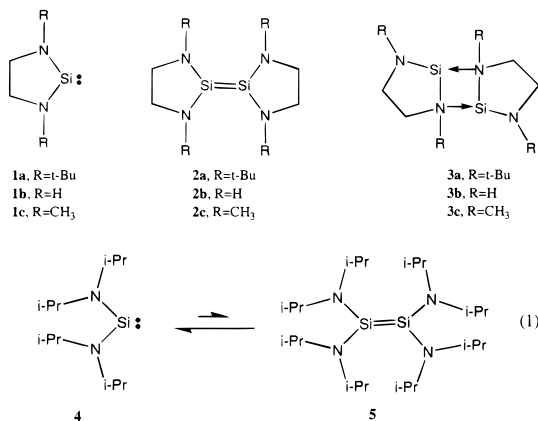
Department of Chemistry and Lise Meitner-Minerva
Center for Computational Quantum Chemistry
Technion, Haifa, Israel

Institut für Anorganische Chemie der Universität Frankfurt
Frankfurt, Germany

INEOS, Russian Academy of Sciences
Moscow, Russia

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Since the first report of the saturated silylene **1a** in 1996,¹ several papers have mentioned its inherent instability in the solid state.² Although colorless crystals of **1a** can be grown on a cold-finger, the crystals transform to a red powder within a few hours at 25 °C. Different structures have been considered for the red “decomposed” product. A tetraaminodisilene structure, **2a**, would be consistent with the red color, and recently Kira and co-workers proposed an equilibrium between an acyclic diaminosilylene **4** and the tetraaminodisilene **5** based on low-temperature UV studies (eq 1).³ Another possible dimeric structure, **3a**, was also considered,⁴ but it did not seem to account for the red color.



Recently, we were able to obtain a crystal structure of the red compound (Figure 1) and found that the actual solid-state structure is a Z-diaminodisilyldisilene (**7**)—a tetramer of silylene **1a**.⁵ **7** is similar to the diaminodisilyldigermenes synthesized recently by Weidenbruch and co-workers.⁶ The crystal structure of **7** is remarkable in several respects. The unit cell is unexpectedly long along one of the axes (18.22 Å × 91.44 Å × 12.54 Å), giving a

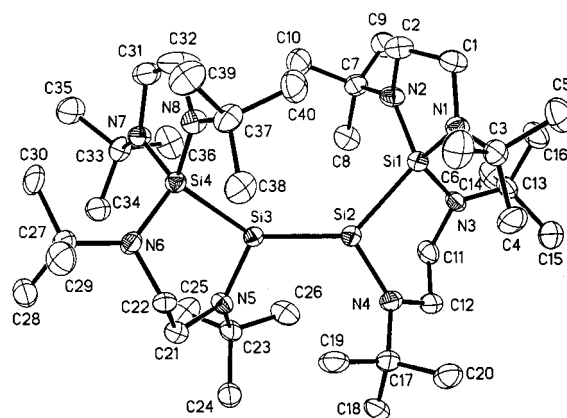


Figure 1. Structure of Z-diaminodisilyldisilene **7**.

Table 1. Selected Bond Lengths (Å), Angles (degree) and Torsion Angles (degree) for **7**

Si(1)—Si(2)	2.3910(14)	N(4)—Si(2)—Si(3)	118.11(11)
Si(2)—Si(3)	2.2890(14)	Si(2)—Si(3)—Si(4)	123.17(5)
Si(3)—Si(4)	2.3835(14)	Si(2)—Si(3)—N(5)	117.73(11)
Si(2)—N(4)	1.746(3)	Si(4)—Si(3)—N(5)	104.72(11)
Si(1)—Si(2)—Si(3)	124.63(5)	Si(1)—Si(2)—Si(3)—Si(4)	−81.97(8)
Si(1)—Si(2)—N(4)	103.82(10)	N(4)—Si(2)—Si(3)—N(5)	10.39(16)

total cell volume of 20 888 Å³. The Si(2)—Si(3) bond length of 228.9 pm (Table 1) is the longest yet reported for a disilene bond.^{7a} The structure is strongly trans-bent, with pyramidalization angles at the two silicon atoms differing slightly (32.3° Si(2) and 33.8° Si(3)), far larger than for other known disilenes.^{7b} Moreover, the torsion angle between the two Si—Si—N planes is exceptionally large, 25.1°.^{7c} However, the Raman spectrum of solid **7** exhibits an intense line at 533 cm^{−1}, very close in frequency to that of *E*-tBuMesSi=SiMes(tBu) at 522 cm^{−1}, which has been shown to contain predominantly the Si=Si stretching vibration.⁸

Surprisingly, a dynamic equilibrium exists between the silylene **1a** and the disilene **7**. ²⁹Si NMR of freshly dissolved red crystals of **7** shows a gradual disappearance of resonances due to **7**, at 119.5 and −29.0 ppm, and formation of the saturated silylene peak (118.9 ppm). The reversibility of the above reaction can also be demonstrated by UV–vis spectroscopy (Figure 2). When crystals of disilene **7** are dissolved in hexane, peaks assigned to **7** ($\lambda_{\text{max}} = 476$ and 360 nm) disappear, with formation of new peaks belonging to the silylene **1a** ($\lambda_{\text{max}} = 292$ and 268 nm). Presumably, the formation of **7** proceeds (eq 2) by (a) formation of an aminosilylsilylene **6a** via Si—N insertion of one silylene into the Si—N bond of another,⁹ followed by (b) rapid dimerization to the disilene **7**. Evidence for the intermediacy of **6a** was obtained by reacting crystals of **7** with methanol. Instead of producing the

(6) (a) Schäfer, A.; Saak, W.; Weidenbruch, M. *Z. Anorg. Allg. Chem.* **1998**, 624, 1405. (b) Schäfer, A.; Saak, W.; Weidenbruch, M. *Chem. Ber./Recueil* **1997**, 130, 1733. (c) Weidenbruch, M. *Eur. J. Inorg. Chem.* **1999**, 373.

(7) (a) For a review of disilene structural parameters, see: Okazaki, R.; West, R. *Adv. Organomet. Chem.* **1996**, 39, 231. The average Si=Si distance for carbon-substituted disilenes is 216 pm, while silicon-substituted disilenes are typically 10 pm longer. (b) Previously reported trans-bent pyramidalization angles fall in the range of 0°–18°, where the pyramidalization angle is defined as the angle of intersection between the Si=Si vertex and the plane made up of the silicon atom and its two substituents. (c) By comparison, all of the other known disilenes have torsion angles between 0° and 14°.

(8) Leites, L. A.; Bukalov, S. S.; Garbuzova, I. A.; West, R.; Mangette, J.; Spitzner, H. *J. Organomet. Chem.* **1997**, 536–537, 425.

(9) Calculations performed at the B3LYP/6-311+G** level for a constrained (H₂N)₂Si=Si(NH₂)₂ show that an alternative mechanism for the formation of **7**, involving intermediate formation of **2a** followed by a 1,2 migration of an amino group, is energetically improbable.

[†] University of Wisconsin.

[‡] Technion.

[§] Universität Frankfurt.

[#] INEOS.

(1) West, R.; Denk, M. *Pure Appl. Chem.* **1996**, 68, 785.

(2) Denk, M.; Green, J. C.; Metzler, N.; Wagner, M. *J. Chem. Soc., Dalton Trans.* **1994**, 2405.

(3) Tsutsui, S.; Sakamoto, K.; Kira, M. *J. Am. Chem. Soc.* **1998**, 120, 9955.

(4) Apeloig, Y.; Müller, T. *J. Am. Chem. Soc.* **1995**, 117, 5363.

(5) Crystal data for **7**: yellow crystals grown from THF at −20 °C, C₄₀H₈₈N₈Si₄, orthorhombic, group *Fdd2*, *a* = 18.22 Å, *b* = 91.44 Å, *c* = 12.54 Å, *V* = 20, 888 Å³, *Z* = 22, *T* = 293 K, *D*_{calcd} = 1.087 Mg/m³, *R*(*F*) = 0.0406 for 4896 observed reflections. All non-hydrogen atoms were refined with anisotropic displacement parameters. Full crystallographic information is given in the Supporting Information.

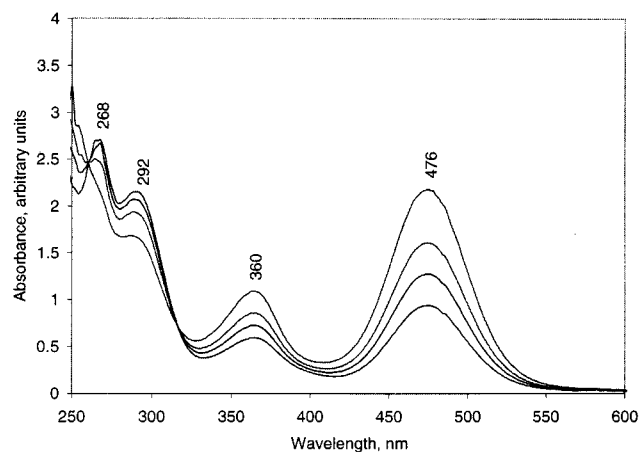
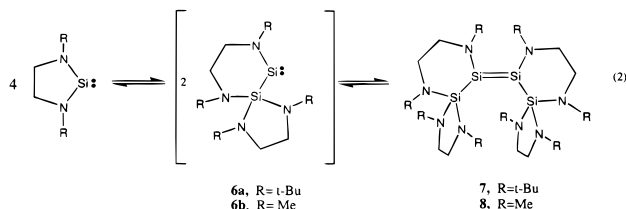


Figure 2. UV spectra of ca. 3×10^{-3} M solution of disilene **7** at 6 min intervals in hexane at 25 °C ($\lambda = 360$ and 476 nm), showing gradual transformation to silylene **1a** ($\lambda = 268$ and 292 nm). Eventually the peaks due to **7** disappear completely at this concentration.

disilene–methanol addition product, the major product was the methanol adduct of **6a**.¹⁰



Why does **1a** react in such an unusual way? Why does **1a** not simply dimerize to the corresponding disilene, **2a**? Previous ab initio calculations⁴ for the corresponding hydrogen-substituted derivatives showed that **1b** cannot dimerize to tetraaminodisilene **2b**, because the latter is not a viable molecule; i.e., **2b** does not correspond to a minimum on the potential energy surface (PES). **1a** was expected to behave similarly.⁴ However, these calculations also predicted that **1b** should dimerize to the bridged compound **3b**, which is 7.8 kcal/mol more stable than two separate **1b** silylenes.⁴ So why does **1a** not dimerize to the analogous bridged compound **3a**? Additional calculations,^{11a} using density functional theory (DFT)^{11b} at the hybrid B3LYP/6-31G* level,^{11c,d} for the methyl- (**1c–3c**) and the *tert*-butyl-substituted (**1a–3a**) systems show that, due to the large size of the *tert*-butyl substituents, two molecules of **1a** cannot approach each other to a reasonable Si–N bonding distance without encountering severe steric repulsions,¹² so that **3a**, in contrast to **3b** or **3c**, is *not a minimum* on the PES.

(10) Methanol adduct of **6a**: a colorless liquid; ¹H NMR (C₆D₆, δ) 1.231, 1.262, 1.344, 1.376 (36 H, singlet, C(CH₃)₃), 2.87–2.94 (8H, multiplet, CH₂–CH₂), 3.450 (3H, s, OCH₃); ²⁹Si (C₆D₆, δ) –24.77, –34.41.

(11) (a) All calculations were performed with Gaussian 94, Revision C.2-E2, Gaussian, Inc., Pittsburgh, PA, 1995. (b) Parr, R. G.; Yang, W. *Density-Functional Theory of Atoms and Molecules*; Oxford University Press: New York, 1989. (c) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785. (d) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(12) For example, a partial geometry optimization of **3a** at a Si–N distance of 203.3 pm (calculated to be the equilibrium distance for **3c**) results in a structure which is 50 kcal mol^{–1} higher in energy than two separated silylenes **1a**.

As the two dimerization routes of **1a**, either to **2a** or **3a**, are both blocked, a new reaction—the insertion of one silylene into the Si–N bond of a second silylene—takes place, leading to silylene **6a**. Calculations for the methyl-substituted systems (at the B3LYP/6-311+G**/B3LYP/6-31G* + ZPVE level) show that the silylene **6b** is 0.5 kcal/mol less stable than two separate **1c** silylenes and that the barrier for insertion is 10.9 kcal/mol. The new silylene **6b** then dimerizes to **8**, which is 27.3 kcal/mol lower in energy (at B3LYP/6-31G*). The reverse reaction, in which the disilene **7** dissociates into four molecules of **1a**, is entropically favored, accounting for the observed equilibrium.¹³

7, in contrast to **2a**, is a stable molecule because it has only two amino substituents connected to the Si=Si bond, while **2a** has four. This interpretation is fully consistent with previous calculations, which have shown that (H₂N)HSi=SiH(NH₂) is a minimum on the PES, having a bond dissociation energy of 17.6 kcal/mol.⁴ In **7** and **8**, the Si=Si bond is further strengthened by 8 kcal/mol by the two silyl substituents.¹⁴ The existence of **7**, but not of **2a**, is also consistent with the much larger energy difference between the singlet and triplet states^{14,15} of (Me₂N)₂Si (68.7 kcal/mol) than of (H₃Si)(Me₂N)Si (45.2 kcal/mol, both values at B3LYP/6-311G**). We note that the experimental structure of **7** (R = *t*Bu) is reproduced very well by the B3LYP/6-311G*-calculated structure of **8** (R = CH₃), including the unusual geometrical features such as the long Si=Si bond (calcd 228.5 pm) and the large twisting and bending angles (see Supporting Information). The long Si=Si bond and the strong bending and torsional angles at silicon are already apparent in simple model systems, e.g. (H₂N)HSi=SiH(NH₂),^{14,16} indicating that also in **7** and **8** their origin is mainly electronic in nature.

In conclusion, the diaminosilylene **1a**, which cannot dimerize to the disilene **2a** (prohibited electronically) or to the cyclic dimer **3a** (sterically blocked), circumvents these difficulties by dimerizing to silylaminosilylene **6a**, which can further dimerize to the corresponding disilyldiaminodisilene, **7**. This combined experimental–theoretical study demonstrates the crucial role that the substituents on the nitrogens play in the chemistry of diaminosilylenes. The theoretical prediction that, in contrast to the *tert*-butyl-substituted silylene **1a**, the methyl-substituted silylene **1c** should dimerize to the bridged dimer **3c** and not to the tetrameric disilene **8** will be tested experimentally.

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Supporting Information Available: ¹H and ²⁹Si NMR data for **1a**, **7**, and the methanol adduct of **6a**; structure data for **7**; and tables of the calculated energies of silylenes and their dimers, and of the calculated geometrical parameters of *E,Z*-**8** compared with the experimental structure of **7** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(13) The calculated contribution of the entropy, $T\Delta S$, to the free energy at 298 K for the dissociation of the disilene *Z*-(H₃Si)(H₂N)Si=Si(NH₂)(SiH₃) into (H₃Si)(H₂N)Si is 11.3 kcal/mol (B3LYP/6-31G*). Thus, we estimate the entropy contribution for the dissociation **7** → **1a** to be ca. 23 kcal/mol, in qualitative agreement with the observation that, in solution, **7** is in equilibrium with **1a**.

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(15) Trinquier, G.; Malrieu, J.-P. *J. Am. Chem. Soc.* **1991**, *113*, 8634.

(16) *Z*-(H₂N)HSi=SiH(NH₂): Si=Si, 233.4 pm; pyramidal angles at silicon, 47.4°; angle between the SiHN planes, 26.2° (B3LYP/6-311G**).