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Possible Strategies toward the Elusive Tetraaminodisilene

Thomas Müller*,† and Yitzhak Apeloig*,‡

Contribution from the Institut für Anorganische Chemie der Goethe Universität Frankfurt,
Marie Curie-Strasse 11, D-60439 Frankfurt/Main, Federal Republic of Germany, and
Department of Chemistry and the Lise Meitner-Minerva Center for Computational Quantum
Chemistry, Technion-Israel Institute of Technology, 32000 Haifa, Israel

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Abstract: In this paper we predict, using quantum mechanical calculations, which diaminosilylenes would dimerize to produce strongly bound tetraaminodisilenes, which so far have proven to be elusive. The central idea is that diaminosilylenes with a small singlet−triplet energy difference would dimerize to strongly bonded disilenes. Calculations at the B3LYP/6-311++G(3df,2p)//MP2/6-31G(d) level of theory showed that the energy difference between the singlet and the triplet states (ΔE_{ST}) of diaminosilylenes $(R_2N)_2Si{:}$ (**1**) strongly depends on (i) the twist angle φ between the SiN_2 and the R_2N planes and (ii) the NSiN bond angle α at the divalent silicon. ΔE_{ST} decreases with increased twisting (larger φ) and with widening of α. ΔE_{ST} is reduced from 70.7 kcal mol^{-1} for planar $(H_2N)_2Si{:}$ (**1a**) to $\Delta E_{ST} = 21.7$ kcal mol^{-1} when φ is held at 90°. Likewise, the bicyclic diaminosilylenes 1,4-diaza-7-silabicyclo[2.2.1]hepta-7-ylidene and 1,5-diaza-9-silabicyclo[3.3.1]nona-9-ylidene (**4a,b**), with the nitrogens in the bridgehead positions ($\varphi = 90°$), have ΔE_{ST} values of 45.1 and 38.3 kcal mol^{-1}, respectively. When dimerized, these silylenes form strongly bonded disilenes **5** ($E_{dim} = -32.2$ kcal mol^{-1} (**4a**) and -41.3 kcal mol^{-1} (**4b**)) with Si═Si bond lengths of 2.239 Å (**4a**) and 2.278 Å (**4b**) (MP2/6-31G(d)//MP2/6-31G(d)). These theoretical predictions pave the way for the synthesis of the first strongly bonded tetraaminodisilene. Due to the steric requirements, also silyl substitution at nitrogen has a significant effect on ΔE_{ST} and $[(H_3Si)_2N]_2Si{:}$ (**1d**) is predicted to form a stable Si═Si bonded dimer ($E_{dim} = -24.1$ kcal mol^{-1}). However, the larger size of the Me_3Si substituent prevents the formation of a Si═Si bonded dimer of $[(Me_3Si)_2N]_2Si{:}$ (**1e**).

Introduction

Dimerization of heavier group 14 carbene analogues, ER_2, usually leads to the formation of E═E double bonds.[1] However, the actual shape of the ER_2 dimer and even the existence of doubly bonded species depend strongly on E and R and more specifically on the energy difference between the singlet and triplet states (ΔE_{ST}) of the R_2E fragments forming the $R_2E{=}ER_2$ dimer.[1] According to a model suggested independently by Carter and Goddard[2] and by Trinquier and Malrieux[3] (the CGMT model), E═E′ bonds are expected to be formed only when the sum of the ΔE_{ST} values of the ER_2 and $E'R_2$ fragments ($\sum\Delta E_{ST}$) is smaller than the E═E′ bond energy ($E_{\sigma+\pi}$). When $\sum\Delta E_{ST} > E_{\sigma+\pi}$, the E═E′ bond does not exist and cyclic bridged dimers are favored.[3] Silylenes are ground-state singlets, and ΔE_{ST} depends strongly on the substituents at silicon.[3−5] Thus, while in dimethylsilylene $\Delta E_{ST} = 26.1$ kcal mol^{-1}, in $(H_2N)_2Si{:}$ (**1a**) $\Delta E_{ST} = 56.7$ kcal mol^{-1}, due to the presence of the strongly electron donating amino substituents.[6,7]

The high ΔE_{ST} of $(H_2N)_2Si{:}$ raises the fundamental question of whether disilenes, having *four amino substituents*, can exist, as $\sum\Delta E_{ST}$ in this case is expected to be larger than $E_{\sigma+\pi}$ of the disilene. On the basis of quantum mechanical calculations, we have previously predicted that diaminosilylene (**1a**) dimerizes to the bridged dimer **2a** (Scheme 1) and that the corresponding disilene $(H_2N)_2Si{=}Si(NH_2)_2$ (**3a**) is not a minimum on the potential energy surface (PES).[6] Subsequently, we showed that the conformation of the amino substituents strongly affects ΔE_{ST}, and that $(R_2N)_2Si{:}$ with bulky alkyl substituents R have strongly reduced ΔE_{ST} values (e.g., 44.4 kcal mol^{-1} for **1c** (R = *i*-Pr)),[7] and this enables (in agreement with the CGMT

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* To whom correspondence should be addressed. E-mail: (T.M.) Dr.Thomas.Mueller@chemie.uni-frankfurt.de; (Y.A.) chrapel@techunix.technion.ac.il. Fax: (T.M.) 6979829188; (Y.A.) 97248233735.

† Goethe Universität Frankfurt .

‡ Technion-Israel Institute of Technology.

(1) For recent reviews, see: (a) Driess, M.; Grützmacher, H. *Angew. Chem., Int. Ed. Engl*. **1996**, *35*, 828. (b) Power, P. P. *Chem. Rev.* **1999**, *99*, 3463. (c) Okazaki, R.; West, R. *Adv. Organomet. Chem.* **1996**, *39*, 231. (d) Weidenbruch, M. In *The chemistry of organic silicon compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley-Intersience: New York, 2001; Vol. 3, p 391.

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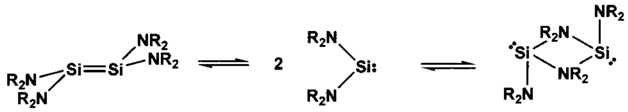
Scheme 1



3a, R=H	**1a**, R=H	**2a**, R=H
3b, R=Me	**1b**, R=Me	**2b**, R=Me
3c, R=*i*-Pr	**1c**, R=*i*-Pr	**2c**, R=*i*-Pr
3d, R=SiH_3	**1d**, R=SiH_3	**2d**, R=SiH_3
3e, R=$SiMe_3$	**1e**, R=$SiMe_3$	**2e**, R=$SiMe_3$

model) the formation of **3c** at low temperatures.[7,8] However, **3c** is very weakly bonded (i.e., by only 3.8 kcal mol^{-1} relative to **1c**);[9] it has a very long Si−Si bond of 2.472 Å and is strongly twisted and pyramidalized around the silicon atoms. These data clearly indicate that **3c** is *not* a disilene and is better described as a weak complex of two silylenes.[7] In this paper we will present results of quantum mechanical calculations (see Table 1) which point to new strategies for the synthesis of *stable disilenes having four nitrogen substituents, and still maintaining short and relatively strong Si═Si double bonds*.

Computational Details

Calculations[11] were carried out initially at the hybrid density functional B3LYP/6-31G(d) level.[12] Frequency analysis at this level has been performed to identify the optimized structures as minima. Refined structures have been obtained at the correlated ab initio MP2/6-31G(d) level.[13] All geometrical parameters cited in the text are optimized at the MP2/6-31G(d) level, and the values calculated at B3LYP/6-31G(d) are given in Table 1 and Figures 1 and 3 for comparison. ΔE_{ST} values have been calculated at B3LYP/6-311++G(3df,2p) for optimized geometries of the ^{1}A and the ^{3}B states of the silylenes at MP2/6-31G(d). Dimerization energies, E_{dim}, have been calculated at MP2/6-31G(d)//MP2/6-31G(d), if not stated otherwise, since it has been shown previously[7a] that in critical cases the B3LYP method severely underestimates the stability of the dimers relative to their silylene precursors.

Results and Discussion

The calculated geometry of diaminosilylene (**1a**) in its ^{1}A state differs markedly from its structure in its ^{3}B state (Figure 1). While the favorable conjugation between the nitrogens' lone pairs and the empty 3p(Si) results in a perfectly planar structure for the singlet state, the triplet state adopts a perpendicular conformation, in which interaction between the singly occupied 3p(Si) and the nitrogens' lone pairs is avoided. The comparison of the calculated structures of **1a** in its ^{1}A and ^{3}B states suggest that two geometrical parameters determine ΔE_{ST} in **1a**: the twist angle between the planes spanned by the NH_2 and SiN_2 groups (φ) and the NSiN bond angle (α). The calculations show that the triplet state of **1a** is stabilized relative to the singlet ground state when φ and α increase[4a,14] (Figure 2): Twisting of the amino groups out of planarity reduces the conjugation between the nitrogens' lone pairs and the empty 3p(Si) orbital, destabilizing the singlet state and stabilizing the triplet state of **1a** and

Table 1. Important Geometrical Parameters of Silylenes in Their ^{1}A and ^{3}B States (Bond Lengths in angstroms, Bond and Dihedral Angles in degrees), Their ΔE_{ST} Values, and Their Dimerization Energies to Si═Si Bonded Dimers (E_{dim}(Si═Si)) and to Cyclic Dimers **2** (E_{dim}(cyclic)) (kcal mol^{-1})

compd	state	ΔE_{ST}[a]	r(SiN)[b]	bond angle α[b]	twist angle φ[b]	E_{dim}(Si═Si)[c]	E_{dim}(cyclic)[c]
1a	^{1}A	56.7	1.735	99.8	0.0	g	−19.7
			(1.729)	(100.1)	(0.0)		
	^{3}B		1.737	122.8	90.0		
			(1.758)	(119.3)	(90.0)		
anti-**1a**	^{1}A	21.7	1.776	103.6	−90.0	−55.0	
			(1.783)	(103.2)	(−90.0)		
	^{3}B		1.738	122.9	−90.0		
			(1.758)	(119.4)	(−90.0)		
syn-**1a**[d]	^{1}A	22.4	1.785	109.3	90.0		
			(1.789)	(109.5)	(90.0)		
1b	^{1}A	52.2	1.740	103.8	22.9	−6.7	−18.5
			(1.752)	(105.2)	(21.6)		
	^{3}B		1.739	126.1	90.0		
			(1.766)	(119.8)	(89.8)		
1c	^{1}A	44.4	1.757	105.3	26.4	−3.8[f]	12.2[f]
			(1.764)	(106.9)	(25.5)		
	^{3}B		1.750	125.3	86.8		
			(1.772)	(116.8)	(69.2)		
1d	^{1}A	46.6	1.767	104.7	30.2	−24.1	−8.1
			(1.773)	(105.8)	(30.0)		
	^{3}B		1.756	121.3	87.3		
			(1.766)	(121.4)	(83.5)		
1e	^{1}A	44.6[e]	(1.779)	(110.8)	(41.9)	g	h
	^{3}B		(1.779)	(123.3)	(51.0)		
4a	^{1}A	45.1	1.826	86.2	90.0	−32.2	h
			(1.831)	(86.0)	(90.0)		
	^{3}B		1.819	89.0	90.0		
			(2.018)	(75.8)	(90.0)		
4b	^{1}A	38.3	1.792	96.2	90.0	−41.3	h
			(1.797)	(96.1)	(90.0)		
	^{3}B		1.764	101.9	90.0		
			(1.773)	(99.9)	(90.0)		
Me_2Si:	^{1}A	26.1		97.3		−58.0	h
				(97.9)			
	^{3}B			118.1			
				(118.9)			

[a] At B3LYP/6-311++G(3df,2p)//MP2/6-31G(d). [b] At MP2/6-31G(d), in parentheses at B3LYP/6-31G(d). [c] At MP2/6-31G(d)//MP2/6-31G(d). [d] No triplet state in the *syn* conformation of **1a** could be located. [e] At B3LYP/6-311+G(d,p)//B3LYP/6-31G(d). [f] At MP2/6-31G(d)//B3LYP/6-31G(d), from ref 7a. [g] A Si═Si bonded dimer could not be located. [h] A cyclic dimer could not be located.

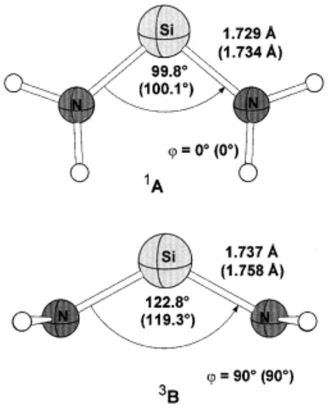


Figure 1. Calculated structures of silylene **1a** in its ^{1}A and ^{3}B states (at MP2/6-31G(d) and in parentheses at B3LYP/6-31G(d); φ is the angle between the NH_2 plane and the SiN_2 plane).

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

(9) This bond energy refers to the energy of two isolated silylenes as the reference state and does not therefore include the preparation energy term,[10] i.e., the energy required to deform the silylene geometry to the arrangement in the disilene, which is 10.4 kcal mol^{-1} in the case of the dimerization of **1c** (at MP2/6-31G(d)).

(10) For a definition of the preparation energy term, see: Jacobsen, H.; Ziegler, T. *J. Am. Chem. Soc.* **1994**, *116*, 3667.

(11) All calculations were performed with Gaussian 98 Revisions A3−A9, Gaussian, Inc., Pittsburgh, PA, 1999.

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(13) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.

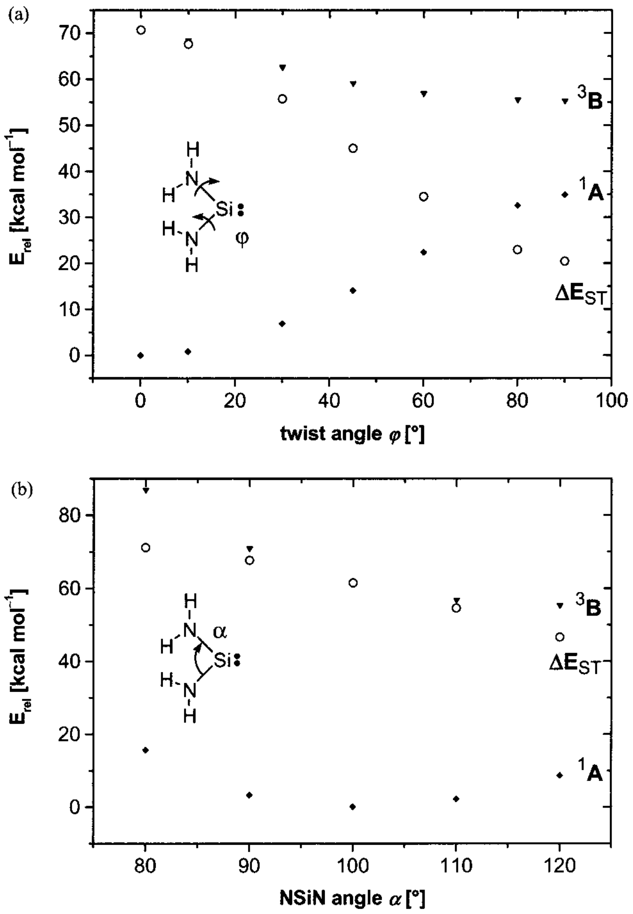
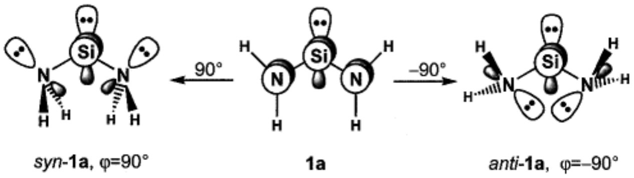


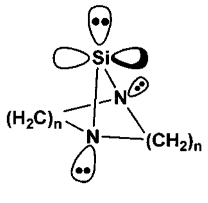
Figure 2. Relative energies of the ^{1}A (tilted squares) and the ^{3}B (triangles) states of **1a** and the resulting ΔE_{ST} (circles) (at B3LYP/6-311++G(3df,2p)//MP2/6-31G(d)) as a function of (a, top) the twist angle φ (the dihedral angle between the H_2N and N_2Si planes) and (b, bottom) the NSiN bond angle α.

Scheme 2

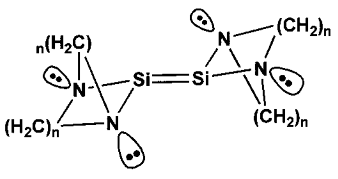


thereby decreasing ΔE_{ST} (see Figure 2a and Scheme 2). Thus, the perpendicular *anti*-**1a**, $\varphi = -90°$, where the 2p(N) lone pairs are perpendicular to the empty 3p(Si) orbital (Scheme 2), has a ΔE_{ST} of 21.7 kcal mol^{-1} (ΔE_{ST}(*syn*-**1a**, $\varphi = 90°$) = 22.4 kcal mol^{-1}), 35.0 kcal mol^{-1} smaller than that calculated from the energies of the planar ^{1}A and the perpendicular ^{3}B equilibrium structures ($\Delta E_{ST} = 56.7$ kcal mol^{-1}; see Table 1). The maximum ΔE_{ST} of 70.7 kcal mol^{-1} is predicted for **1a** when also the ^{3}B state is forced to be planar (see Figure 2a), a situation which is met in cyclic diaminosilylenes. Widening of α in **1a** from 80° to 120° has a smaller effect, resulting in a decrease in ΔE_{ST} by ca. 24.6 kcal mol^{-1} (Figure 2b).[4,14]

An intriguing prediction which emerges from these considerations is that if a diaminosilylene can be constrained to be in a conformation in which the nitrogens' lone pairs are forced to be in a nearly perpendicular plane to the empty 3p(Si) orbital (as in **1a**, $\varphi = 90°$), it will have a small ΔE_{ST} and according to the CGTM model[2,3] it should dimerize to *a strongly bonded disilene*. Indeed, the bicyclic silylene **4a** for which $\Delta E_{ST} = 45.1$ kcal mol^{-1} dimerizes to a strongly bonded disilene, **5a**, which is 32.2 kcal mol^{-1} lower in energy than two **4a** silylenes.[15] Although the twist angle φ of 90° in **4a** is optimal for a small ΔE_{ST}, the bond angle α of 86.2° is not; it is 23.1° smaller than that for *syn*-**1a**, $\varphi = 90°$, thus increasing ΔE_{ST}. This undesirable effect can be reduced by increasing the ring size of the bicyclic silylene. Thus, for **4b** where the NSiN angle is wider, α = 96.2°, ΔE_{ST} is reduced to 38.3 kcal mol^{-1}.[16] Consequently, the dimerization energy (E_{dim})[17] of **4b** to form **5b** is −41.3 kcal mol^{-1}, 9.1 kcal mol^{-1} more exothermic than E_{dim} of **4a**. The Si═Si bond energy in **5b** is only 16.7 kcal mol^{-1} weaker than that in $Me_2Si{=}SiMe_2$ ($E_{dim} = -58.0$ kcal mol^{-1}). Not only is the much stronger Si═Si bond of tetraaminodisilenes of type **5** over simple alkyl-substituted tetraaminodisilenes (e.g., **3c**, for which $E_{dim} = -3.8$ kcal mol^{-1}) due to the reduced ΔE_{ST} of the silylene fragments (ΔE_{ST}(**1c**) = 44.4 kcal mol^{-1}), but the higher steric crowding around the Si═Si bond in **3c**[7a] also contributes.

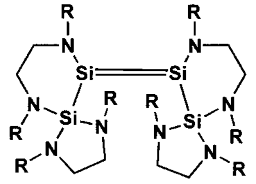


4a, n = 2
4b, n = 3



5a, n = 2
5b, n = 3

The relatively high Si═Si bond energies of disilenes **5a,b** are remarkable in light of the fact that the parent **3a** is not a bound molecule. Furthermore, the Si═Si bond energy in the tetraaminodisilenes **5a** and **5b** is larger than that of the *diamino*disilene **6**, R = Me ($E_{dim} = -27.3$ kcal mol^{-1}),[18] whose



6

t-Bu-substituted analogue **6**, R = *t*-Bu, exists at room temperature in equilibrium with its precursor silylene. *On the basis of these considerations, we predict that both* **5a** *and* **5b** *should exist at room temperature.*[19]

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[14] (a) Gordon, M. S. *Chem. Phys. Lett.* **1985**, *114*, 348. (b) Grev, R. S.; Schafer, H. F., III; Gaspar, P. P. *J. Am. Chem. Soc.* **1991**, *113*, 5638.

[15] Steric reasons preventing proper alignment of the lp(N) and 3p(Si) orbitals precludes the formation of cyclic bridged species of type **2**. However, the formation of dimers of **4** with only one dative lp(N) → 3pSi bond is possible. In the case of **4a** this dimer is bonded by 33.3 kcal mol^{-1}. Additional alkyl substitution at the α-carbon atoms will severely hamper the formation of such singly bonded dimers, without significant influence on the reactivity of the silicon center.

[16] For **4b**, the ^{3}A state (r(SiN) = 1.903 Å, α = 75.3°, $\varphi = 90°$) with considerable spin density at the nitrogen atoms is lower in energy than the ^{3}B state (by 11.5 kcal mol^{-1}). From a conceptual point of view, however, only the ^{3}B state, resulting from the configuration lp(Si)^1, 3p(Si)^1, is of interest here.

[17] E_{dim} stands for the Si═Si bond energy.

[18] Schmedake, T. A.; Haaf, M.; Apeloig, Y.; Müller, T.; Bukalov, S.; West, R. *J. Am. Chem. Soc.* **1999**, *121*, 9479.

[19] At 298.15 K, the reaction 2(**4b**) → **5b** is exergonic, $\Delta G = -16.6$ kcal mol^{-1} (at B3LYP/6-31G(d)//B3LYP/6-31G(d)).

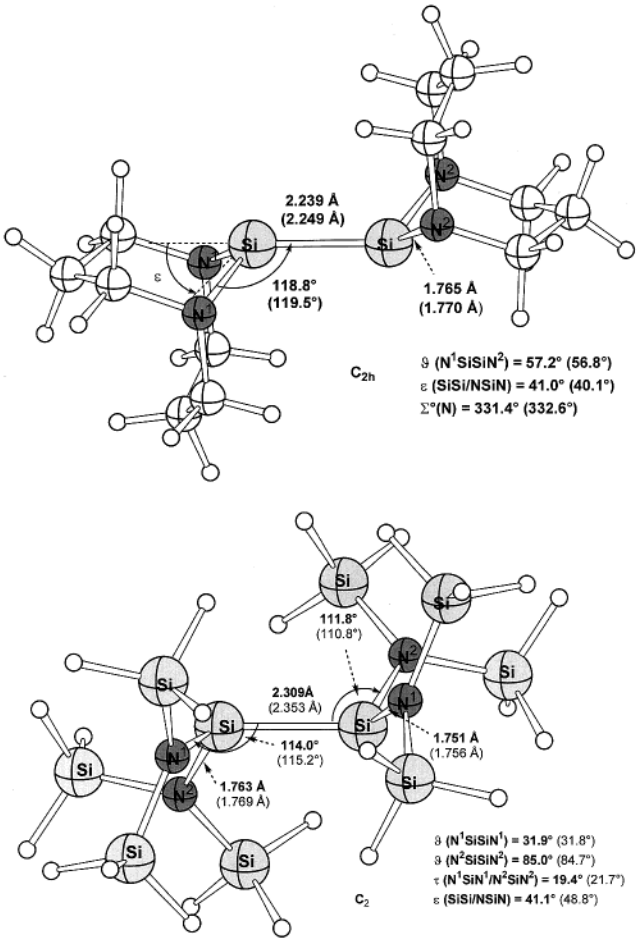

Figure 3. Calculated structure of disilenes (a, top) **5b** and (b, bottom) **3d** (at MP2/6-31G(d) and in parentheses at B3LYP/6-31G(d); ϵ is the pyramidalization angle; $\sum°$(N) is sum of bond angles around nitrogen; τ is the twist angle between the two $\mathrm{SiN_2}$ planes).

Disilenes **5a,b** have relatively long Si═Si double bonds (2.278 Å in **5a**, 2.239 Å in **5b)** compared to 2.180 Å for $\mathrm{Me_2Si{=}SiMe_2}$ or 2.143 Å for $\mathrm{Mes_2Si{=}SiMes_2}$,[20] and the silicon atoms are strongly *trans*-pyramidalized ($\epsilon = 47.3°$ (**5a**), $\epsilon = 41.0°$ (**5b**); see Figure 3a). However, the Si═Si bond in **5b** is shorter than that in **6**, R = *t*-Bu (2.289 Å),[18] consistent with its higher Si═Si bond energy.

Silyl substituents are known to lower significantly the basicity of amines,[21,22] and we therefore hypothesized that this effect may also lower ΔE_{ST} of silylaminosilylenes and thus lead to strongly bonded tetraaminodisilenes. The bis(disilylamino)-silylenes **1d** and **1e** indeed deviate strongly from planarity, and the bond angle α is widened (**1d**, $\varphi = 30.2°$, $\alpha = 104.7°$; **1e**, $\varphi = 41.9°$, $\alpha = 110.8°$),[23a] resulting in greatly reduced ΔE_{ST} values of 46.6 and 44.6 kcal $\mathrm{mol^{-1}}$ for **1d** and **1e**, respectively.[23b] In line with its reduced ΔE_{ST}, **1d** dimerizes preferentially to a relatively strongly bonded disilene, **3d** ($E_{\mathrm{dim}} = -24.1$ kcal $\mathrm{mol^{-1}}$), while dimerization to the bridged dimer **2d** is less favorable ($E_{\mathrm{dim}} = -8.1$ kcal $\mathrm{mol^{-1}}$). Silyl substitution at N favors the formation of Si═Si bonded dimers more than alkyl substitution, as evident from E_{dim}(**1d**) = −24.1 kcal $\mathrm{mol^{-1}}$ vs E_{dim}(**1b**) = −6.7 kcal $\mathrm{mol^{-1}}$. This is due to the fact that the silyl groups in **1d** induce a larger twist around the Si−N bonds in the silylene than the methyl groups in **1b** ($\varphi = 22.9°$ (**1b**), $\varphi = 30.2°$ (**1d**)), which is reflected in the 5.6 kcal $\mathrm{mol^{-1}}$ smaller ΔE_{ST}(**1d**) vs ΔE_{ST}(**1b**). In addition, the computations reveal that the electronic effect of the silyl group[21,22] also contributes to the reduced ΔE_{ST} values of **1d** and **1e**. Thus, for singlet and triplet **1a,** fixed at the geometries of **1d** in its ^{1}A and ^{3}B states, respectively, ΔE_{ST} is calculated to be 53.2 kcal $\mathrm{mol^{-1}}$, 6.6 kcal $\mathrm{mol^{-1}}$ larger than that calculated for **1d** (46.6 kcal $\mathrm{mol^{-1}}$; see Table 1).

The structure of disilene **3d** is strongly distorted and resembles closely that of the diaminodisilene **6**, R = *t*-Bu.[18] Just like **6**, R = *t*-Bu, **3d** has a very long SiSi bond of 2.309 Å, approaching that of a single bond (e.g., 2.368 Å in $\mathrm{(Me_2N)_3Si{-}Si(NMe_2)_3}$)[24] with strongly pyramidalized silicon centers ($\epsilon = 41.1°$), and both $\mathrm{SiN_2}$ planes are twisted around the SiSi axis by $\tau = 19.4°$; thus, two of the vicinal $\mathrm{(H_3Si)_2N}$ groups form a NSiSiN dihedral of 84.7°, while the other two have a much smaller angle ($\angle$(NSiSiN) = 31.9°; see Figure 3b).

On the basis of the results for **1d** and the smaller ΔE_{ST} value of **1e**, **1e** appeared to be a promising candidate to dimerize to a strongly bonded tetraaminodisilene, **3e**. However, our calculations predict that **3e** and also the corresponding amino-bridged isomer **2e** are not bound compounds, due to steric overcrowding between the bulky $\mathrm{Me_3Si}$ groups in both **2e** and **3e**. This is in agreement with the recent observation that **1e** is monomeric in solution.[25]

In conclusion, the tetraaminodisilenes **5** are predicted to be more strongly bonded than several well-characterized disilenes,[18,26] and therefore, the prospect of the synthesis of this yet unknown group of disilenes by dimerization of the bicyclic diaminosilylenes **4a** and **4b** is very good. Experiments to test this prediction, as well as theoretical studies on the dimerization of other hetero-substituted silylenes to disilenes, are in progress.

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Supporting Information Available: Tables with calculated absolute energies and Cartesian coordinates for compounds **1**−**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(23) (a) Values for **1d** at MP2/6-31G(d) and for **1e** at B3LYP/6-31G(d); see Table 1 for data of **1d** at B3LYP/6-31G(d). (b) The relative small additional decrease of ΔE_{ST} for **1e** compared to **1d**, despite the considerable geometrical changes in the ^{1}A ground state, results from the fact that due to steric overcrowding **1e** in its ^{3}B state cannot take up the optimal perpendicular conformation ($\varphi = 90°$), but adopts in its equilibrium structure a significantly less twisted arrangement ($\varphi = 51.0°$, $\alpha = 123.3°$).

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