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Structures and Stabilities of Heteroatom-Substituted Disilenes and Related Compounds: Four-Center π Systems

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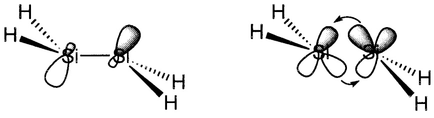
The geometries of $(H_2X)HE{=}EH(XH_2)$, $(H_2X)HE{=}EH(XH_2)^{2+}$, and $HX{=}EHHE{=}XH$ ($E =$ Si, C; $X =$ Al, B, P, N) have been studied using ab initio molecular orbital calculations. Relative stabilities of the stereoisomers of the four-center π systems were explained by the orbital-phase continuity of the terminal atoms. Isodesmic reaction energies show that π conjugation is effective for stabilization of compounds with AlH_2 and BH_2 substituents on the unsaturated silicon, and therefore, aluminum- and boron-substituted disilenes can be potential synthetic targets.

Introduction

Disilene, a silicon analogue of ethylene, exists as a trans-bent equilibrium structure,[1] which differs from the planar D_{2h} structure of ethylene. The trans-bent structure was described using the Carter, Goddard, Malrieu, and Trinquier (CGMT) model,[2] in which the Si−Si double bond is partly a π type and partly a charge-transfer type.



π type   charge-transfer type

We have recently reported on the dimeric structures of bis(diisopropylamino)silylene, $(i\text{-}Pr_2N)_2Si$:, and their spectroscopic characteristics using ab initio molecular orbital calculations.[3] In earlier theoretical predictions[4] and experimental studies,[5,6] a double-bonded dimer was not observed for silylenes that carry electronegative and π-donating substituents, such as NH_2, OH, and F. However, our calculations of amino-substituted silylenes have demonstrated that a Si−Si-bonded structure of $((i\text{-}Pr_2N)_2Si)_2$ exists as the most stable dimer. The calculated absorption maximum of the bonded dimer was in good agreement with recently reported UV absorption measurements of $((i\text{-}Pr_2N)_2Si)_2$.[7] The tuning of the singlet−triplet energy separation, ΔE_{ST}, of diaminosilylene fragments by the steric bulkiness of the substituents at nitrogen was the key in resolving the conflict between previous[4−6] and recent[3,7] studies of the dimeric structure. According to the CGMT model,[2] smaller values of ΔE_{ST} lead to a bonded dimer. Interaction between the vacant 3p orbital of the silicon and the lone-pair orbital of nitrogen plays a significant role in the tuning of ΔE_{ST}. The optimized structure of $((i\text{-}Pr_2N)_2Si)_2$ was markedly twisted and bent, and the Si−Si bond distance was relatively large (2.472 Å). Experimentally, several examples of strongly twisted and bent disilenes have been reported.[6,8] For the unusual structure of $((i\text{-}Pr_2N)_2Si)_2$, two of the nitrogen atoms, in a cis arrangement, were roughly coplanar ($\delta(NSiSiN) = 2°$), as shown in Chart 1.

Although substituent effects on the structures of double-bonded silicon compounds have been reported,[9,10] structural and energetic differences of the four-center π systems have yet to be studied. In this paper,

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Chart 1

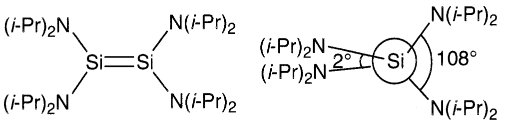
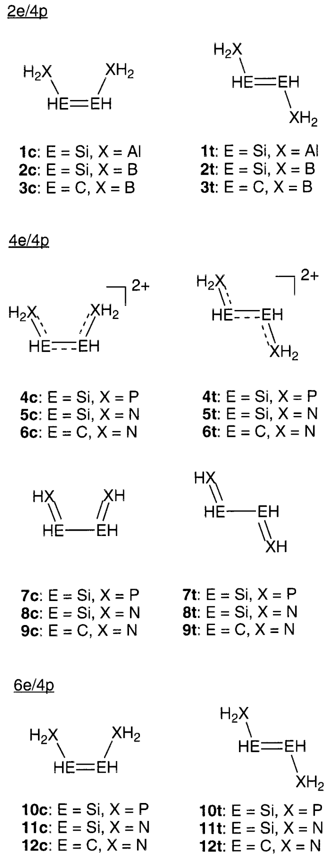


Chart 2



structures and stabilities are studied for several heteroatom-substituted disilene derivatives and related compounds (Chart 2): $(H_2X)HE{=}EH(XH_2)$ (**1**−**3**, **10**−**12**), $(H_2X)HE{=}EH(XH_2)^{2+}$ (**4**−**6**), and $HX{=}EHHE{=}XH$ (**7**−**9**) (E = Si, C; X = Al, B, P, N). In these compounds, the four p orbitals are involved in the π conjugation. Compounds **1**−**3**, **4**−**9**, and **10**−**12** have two (2e/4p system), four (4e/4p system), and six (6e/4p system) conjugative electrons, respectively. The basis of the relative stability of the stereoisomers of the four-center π systems is examined.

Calculations

Ab initio MO calculations[11a] were performed using the Gaussian 98 software package.[11b] In our preceding study on Si−Si double-bond systems,[12] excellent results were obtained by both MP2 and B3LYP methods using the 6-311++G(d,p) basis set for the molecular geometry. On the other hand, the 6-311+G(3df,2p) basis set was recommended for the calculations of second-row species to obtain a reliable geometry.[13] Thus, we carried out the calculations of compounds **1**−**12** at both the MP2/6-311++G(d,p) and MP2/6-311+G(3df,2p) levels. Optimized geometries at both levels are almost the same.[14] For some molecules, however, only the MP2/6-311++G(d,p) calculation gives reliable results, which shows that a diffuse function on hydrogen atoms is essential for them.[15] Consequently, the results at the MP2/6-311++G(d,p) level were used for subsequent discussions. Second derivatives and harmonic vibrational frequencies were calculated for all molecules, and all frequency modes were checked as positive. The $\pi-\sigma^*$ delocalization energy was obtained by deletion of selected antibonds using the NBO 4.0 module of the Gaussian 98 software package.[16]

Results and Discussion

Optimized Structures. The geometrical parameters of compounds **1**−**12** are listed in Table 1. For each compound, the isomer with a larger dihedral angle, δ(XEEX), is denoted as **t**, and its counterpart as **c**. Isomers **6c** and **8c** are not optimized as minimum stationary points. The E−E distances of **1**−**3** are elongated by 0.02−0.03 Å from those of their parent disilene (**13**) or ethylene (**14**). The trans isomers **2t** and **3t** have planar structures, but **1t** exists as a slightly trans-bent structure. Isomer **3c** has a planar $BHC{=}CHB$ skeleton with a twisted BH_2 group (Figure 1), whereas isomers

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(14) Maximum and average differences between the results of the MP2/6-311+G(3df,2p) and MP2/6-311++G(d,p) calculations for compounds **1**−**12** are 0.029 Å (for **11t**) and 0.007 Å in bond length, respectively; in pyramidality, the difference is 1° on average and 6° at most (for **10c**). Structural features such as planar, trans-bent, and twisted do not depend on the level of calculation, except for **1c** and **2c**. The optimized structures of **1c** and **2c** at the MP2/6-311+G(3df,2p) level are planar, while those at the MP2/6-311++G(d,p) level are slightly trans-bent.

(15) The average difference in relative stabilities between the results of both calculations for compounds **1**−**12** is 0.5 kcal/mol. The dominant isomer is the same, independent of the level of calculation, except for **3**. In the case of compound **3**, the cis isomer is more stable than the trans isomer by 0.6 kcal/mol at the MP2/6-311+G(3df,2p) level, while the trans isomer is more stable than the cis isomer by 2.2 kcal/mol at the MP2/6-311++G(d,p) level. The 6-311+G(3df,2p) basis contains high-exponent d and f functions, but it does not contain a diffuse function on hydrogen which is included in the 6-311++G(d,p) basis. To check the effects of the diffuse function, single-point calculations were performed using the basis sets with both high-exponent d and f functions and the diffuse function on hydrogen (MP2/6-311++G(3df,-2p)) at the MP2/6-311+G(3df,2p) geometry of **3**. The calculation shows that the trans isomer is more stable by 2.1 kcal/mol. The result demonstrates that the diffuse function on hydrogen atoms is important for the energetics of **3**.

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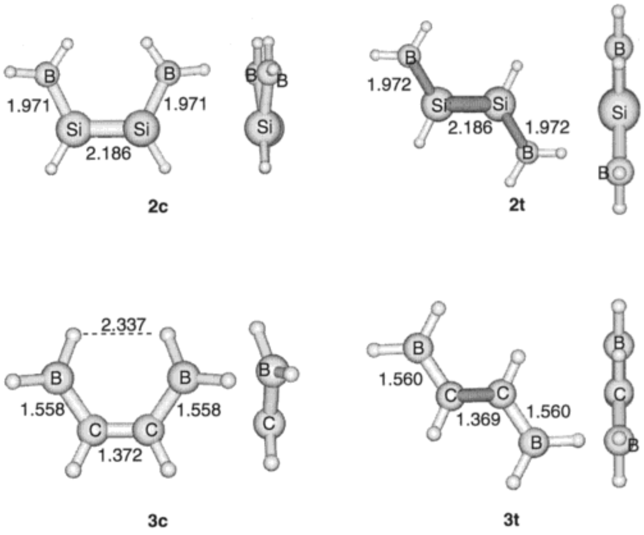
Table 1. Structural and Electronic Properties of 1−12[a]

	bond length		dihedral angle	pyramidality[b]			
compd	*r*(EE)	*r*(EX)	δ(XEEX)	E	X	δ[c]	hybridization[d]
1c	2.185	2.411	28.3	357	360	51.6	p_π
1t	2.180	2.408	180.0	358	360	±89.8	p_π
2c	2.186	1.971	−17.2	359	360	−80.0	p_π
2t	2.186	1.972	180.0	360	360	±90.0	p_π
3c	1.372	1.558	0.0	360	360	±63.7	p_π
3t	1.369	1.560	180.0	360	360	90.0	p_π
4c	2.381	2.131	−27.0	355	322	−104.6	p_π
4t	2.369	2.121	180.0	353	331	±105.9	p_π
5c	2.410	1.645	−55.9	360	360	−90.4	p_π
5t	2.403	1.644	180.0	360	360	−90.0	p_π
6t	1.493	1.285	180.0	360	360	±90.0	p_π
7c	2.301	2.088	−33.5				p_π
7t	2.295	2.089	180.0				p_π
8t	2.306	1.623	180.0				p_π
9c	1.490	1.283	−38.2				p_π
9t	1.477	1.286	180.0				p_π
10c	2.161	2.250	28.7	353	285	−9.1	$s^1p^{0.9}$
10t[e]	2.169	2.254	−173.7	349	285	−87.0	$s^1p^{0.9}$
		2.251		350	288	4.2	$s^1p^{0.9}$
11c	2.297	1.724	41.3	334	360	26.1	p_π
11t	2.298	1.724	180.0	335	359	±24.5	p_π
12c	1.346	1.415	−4.4	360	333	79.5	$s^1p^{5.1}$
12t	1.345	1.417	−165.0	360	333	−71.1	$s^1p^{4.8}$
$H_2Si{=}SiH_2$ (**13**)	2.163			350			
$H_2C{=}CH_2$ (**14**)	1.338			360			

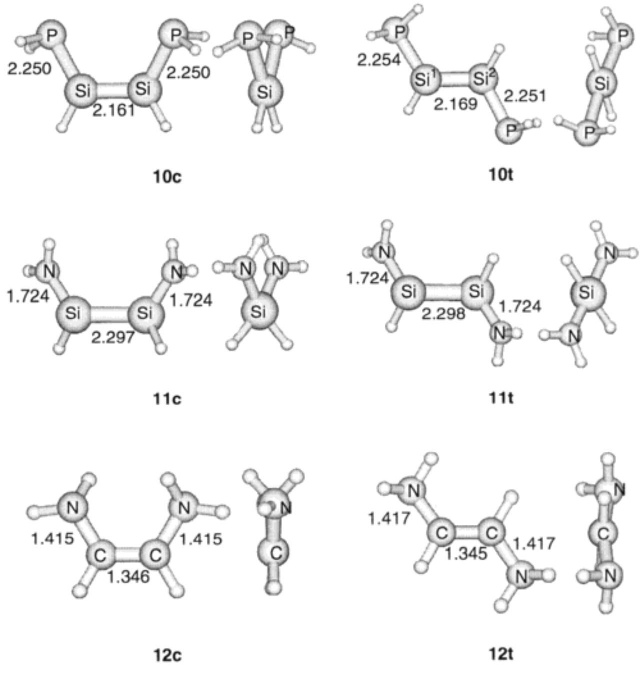
[a] Results at the MP2/6-311++G(d,p) geometry. Bond lengths and dihedral angles are given in Å and in deg, respectively. [b] Pyramidality at E and X. The sum of the three bond angles at E and X is given in deg. [c] Dihedral angle (δ), MXEE, in deg. MX is the bisector of HXH. δ = ½(δ(HXEE) + δ(H′XEE)). [d] Hybridization of lone pairs of X. [e] Unsymmetrical structure.



2c **2t**

3c **3t**

Figure 1. Structures of compounds **2** and **3** optimized at the MP2/6-311++G(d,p) level. The top and side views are shown on the left and right, respectively. The selected bond lengths are given in Å.



10c **10t**

11c **11t**

12c **12t**

Figure 2. Structures of compounds **10**−**12** optimized at the MP2/6-311++G(d,p) level. The top and side views of each structure are shown on the left and right, respectively. The selected bond lengths are given in Å.

1c and **2c** have slightly trans-bent structures. The structures of the dications **4**−**6** are similar to those of the deprotonated compounds, dienes **7**−**9**, but dissimilar from those of the corresponding neutral disilenes **10**−**12**. The E−E bonds of dications **4**−**6** are elongated from those of the corresponding neutral compounds **10**−**12**, and in contrast, the P−Si, N−Si, and N−C bond distances are shortened. The cis (or cisoid) isomers **4c**, **5c**, **7c**, and **9c** have twisted skeletons, and the trans (or transoid) isomers **5t**−**9t**, but not **4t**, have planar structures. The Si−Si bond lengths of diaminodisilenes **11c** and **11t** are markedly longer by 0.14 Å than that of parent **13**, whereas the bond lengths of **10c** and **10t** are comparable to that of **13**. As shown in Figure 2, disilene derivatives **10c**, **10t**, and **11t** exist as trans-bent structures around the Si═Si bond, but **11c** takes a trans-bent structure twisted around the Si═Si double bond. Diaminoethylenes **12c** and **12t** have trans-bent and twisted skeletons, respectively, although the skeletal deviation from planarity is small. Compounds **11c** and **11t** exhibit strong pyramidality at the silicon (the summations of three bond angles at silicon are 334 and 335°, respectively). The pyramidality of **10c** and **10t** is

Table 2. Delocalization Energy, E_d, between $\pi_{E=E}$ and σ^*_{E-E}

compd	E_d[a]	compd	E_d[a]
10c	7.6	**12c**	0.0
10t	11.2	**12t**	0.0
11c	39.9	**13**	11.0
11t	40.3		

[a] Energies in kcal/mol calculated at the B3LYP/6-311++G(d,p)//MP2/6-311++G(d,p) level.

similar to that of the parent disilene **13** (~350°). Pyramidality was not observed for the AlH_2 and BH_2 moieties of **1**−**3** (the summation of three bond angles at aluminum and boron is 360°), while the PH_2 group of **4** and **10** exhibits strong pyramidality (the summation of three bond angles at phosphorus is 285−331°). The amino group bonded to silicon (compounds **5** and **11)** does not show pyramidality,[17] whereas the amino group bonded to carbon (compound **12**) has a pyramidal structure.

Since geminal hyperconjugation between $\pi_{E=E}$ and σ^*_{E-E} (E = Si, C) was expected to play an important role in the bent structure,[2] geminal hyperconjugation energies of compounds **10**−**12** were calculated and are listed in Table 2. The delocalization energy for olefin **12** is negligible. The energy of diphosphinodisilene **10** is less than that of **11**, although similar to that of **13**. The largest stabilization energy was obtained for diaminodisilene **11**, which is attributable to its significantly bent structure.

The strengths of the interactions between the π orbital of disilene and p orbitals of the substituents were deduced from δ angles, which are listed in Table 1. Efficient interactions are expected for compounds with δ angles of approximately 90°, such as for compounds **1**−**6** and **12**. For compound **11**, the δ angle is less than 30°, and thus the interaction would be weak. The δ angle for **10c** is small (9°), and therefore interaction would not be expected. It is notable that **10t** has an unsymmetrical structure, with a large δ (87°) and a small δ (4°) angle, and therefore only one lone pair can interact with the disilene π orbitals, resulting in two distinct Si−P bond lengths ($r(Si^1P)$ = 2.254 Å, $r(Si^2P)$ = 2.251 Å). As mentioned previously, compounds **1**−**3**, **4**−**9**, and **10**−**12** were assigned to the 2e/4p, 4e/4p, and 6e/4p systems, respectively, and considering their δ values, compound **11** was judged to be a weakly conjugated 6e/4p system. However, **10** was not assigned to the 4p system: compounds **10c** and **10t** belong to the 2e/2p and 4e/3p systems, respectively.

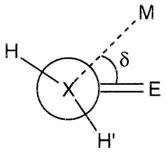
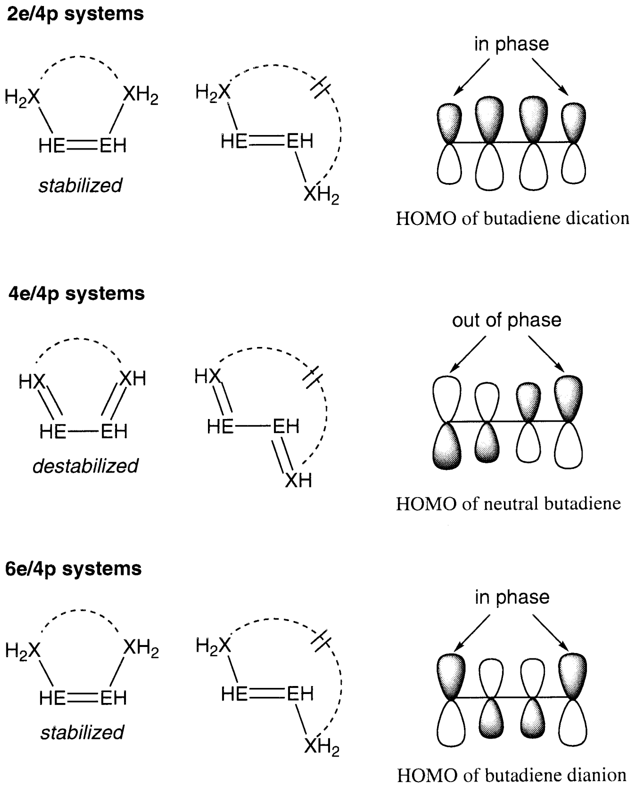


Table 3. Relative Energies, Δ*E*, of the Cis to Trans Isomers

compd	Δ*E*[a]	compd	Δ*E*[a]
1	0.1	**7**	0.4
2	−1.2	**8**	
3	2.2	**9**	6.8
4	1.3	**10**	0.1
5	0.8	**11**	−0.8
6		**12**	−3.6

[a] Energies in kcal/mol calculated at the MP2/6-311++G(d,p) level.

Chart 3



Differences between compounds **10** and **11** or **12** are attributable to the hybridization of the lone pairs. The lone pairs of the nitrogen in **11** and **12** exhibit p character (p_π for **11** and sp^5 for **12**), whereas those of the phosphorus in **10** show sp hybridization. The spherical shape of the sp-hybridized orbital allows the two lone pairs of **10c** to face each other in the nodal plane of the π orbital of disilene without significant repulsion.

Relative Energies. The total energies of the cis (or cisoid) isomers relative to those of the trans (or transoid) isomers are listed in Table 3. Generally, the orbital-phase continuity of terminal atoms in the highest occupied molecular orbital (HOMO) determines the relative stability of the isomers.[18] The orbitals in phase stabilize and those out of phase destabilize the cis isomers via through-space interaction. For the trans isomers, the interaction is negligible because of a longer distance between the terminal atoms. The prototypes of 2e/4p, 4e/4p, and 6e/4p systems are butadiene dication, neutral butadiene, and butadiene dianion, respectively. Judging from the orbital-phase continuity of HOMO shown in Chart 3, dominant isomers for 2e/4p, 4e/4p, and 6e/4p systems are cis, trans, and cis isomers,

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(17) The planarity of the tricoordinate nitrogen atom bonded to the silicon atom was an established phenomenon. See the review: Kaftory, M.; Kapon, M.; Botoshansky, M. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: New York, 1998; Vol. 2, Part 1, Chapter 5.

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Table 4. Isodesmic Reaction Energies, E_{iso} (Eq 1)

compd	E_{iso}[a]	compd	E_{iso}[a]
1c	25.8	**10c**	7.1
1t	25.8	**10t**	7.3
2c	24.2	**11c**	1.9
2t	23.1	**11t**	1.1
3c	9.1	**12c**	20.2
3t	11.3	**12t**	16.6

[a] Energies in kcal/mol calculated at the MP2/6-311++G(d,p) level.

respectively. Experimentally, the more stable conformation of butadiene, a typical example of 4e/4p systems, was reported to be transoid.[19] The conformational preference of butadiene can be explained by the orbital-phase continuity.

For the 4e/4p systems (compounds **4**−**9**), we have observed that the trans isomers are more stable than the cis isomers, which is similar to the case for the butadiene isomers. In the cases of **6** and **8**, only the trans isomer exhibits a minimum on the potential energy surface. However, for the 2e/4p and 6e/4p systems (compounds **1**−**3**, **11,** and **12**), the relative stabilities are rather complicated. As expected from the orbital phase, the cis isomers are stable for **2**, **11**, and **12**. The difference of the stability between the isomers of **1** is small, since the interaction of the p orbitals of aluminum is negligible. However, the cis isomer of **3** is less stable as compared with the trans isomer, since the distance between the two hydrogens on the boron substituent of **3c** is less than the sum of their van der Waals radii (2.4 Å), thus resulting in a steric repulsion and destabilization of the cis isomer (Figure 1).

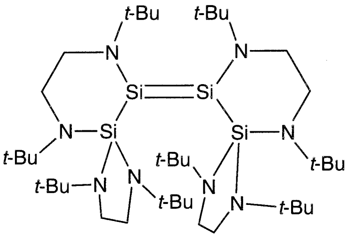
Isodesmic Reaction Energies. To determine the substituent effects of XH_2 on disilene and ethylene, isodesmic reactions (eq 1) are examined, and the results

$$H(H_2X)E{=}E(XH_2)H + 2EH_4 \rightarrow 2E(XH_2)H_3 + H_2E{=}EH_2 \quad (1)$$

are listed in Table 4. The reactions provide stabilization energies by the elongation of the π conjugation and by the increase of the π bond strength. For the 2e/4p system, the stabilization energies of **1** and **2** are about 25 kcal/mol, which are more than twice the energies of ethylene derivative **3** (ca. 10 kcal/mol). The planarity at the silicon in compounds **1** and **2** (the summation of three bond angles at silicon is 357−360°) results in the stabilization of the π bond, as compared to the bond of trans-bent disilene **13**. Consequently, the isodesmic reaction energies of compounds **1** and **2** contain both the elongation of the π conjugation and the increase of the π bond strength, but only the energy gain by the elongation of the π conjugation was obtained for compound **3** due to its originally planar structure of ethylene (**14**). For the 6e/4p system, stabilization energies of compounds **10** (7 kcal/mol) and **11** (1−2 kcal/mol) are relatively small as compared to those of the ethylene analogue **12**. It can thus be concluded from these isodesmic reactions that the conjugation of AlH_2 and BH_2 with silicon is effective but that of PH_2 and NH_2 is not effective.

Conclusion

The relative stabilities of the stereoisomers of heteroatom-substituted disilenes were explained by the orbital-phase continuity of the terminal atoms. The recently reported X-ray crystal structure of diaminodisilene **15** shows a cis configuration,[6] which is in accord with our results based on the orbital-phase continuity. Isodesmic reaction energies have demonstrated that π conjugation is effective for stabilization of compounds with AlH_2 and BH_2 substituents on the unsaturated silicon, and therefore, aluminum- and boron-substituted disilenes can be potential synthetic targets.



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Supporting Information Available: Figures showing the optimized structures of compounds **1**−**9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[19] (a) Almenningen, A.; Bastiansen, O.; Trættenberg, M. *Acta Chem. Scand.* **1958**, *12*, 1221. (b) Aten, C. F.; Hedberg, L.; Hedberg, K. *J. Am. Chem. Soc.* **1968**, *90*, 2463. (c) Kuchitsu, K.; Fukuyama, T.; Morino, Y. *J. Mol. Struct.* **1968**, *1*, 463.