

Theoretical Prediction of Vertical Transition Energies of Diaminosilylenes and Aminosubstituted Disilenes

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Dedicated to Professor Paul von R. Schleyer

ABSTRACT: Vertical electronic transition energies of diaminosilylenes and their dimers (disilenes and nitrogen-bridged) were investigated by *ab initio* and density functional calculations. A good linear correlation was found between the observed UV transition energies of various silylenes and disilenes and those of model compounds calculated using the CIS and TD-DFT methods. On the basis of these computations the experimental UV absorption maximum observed for the dimer of (*i*-Pr₂N)₂Si: (λ_{max} 439 nm at 77 K), could be assigned to an Si—Si bonded dimer with an unusually long Si—Si distance of 2.472 Å, and the isomeric amino-bridged cyclic dimer could be discarded. © 2001 John Wiley & Sons, Inc. J Comput Chem 22: 1536–1541, 2001

Keywords: silylenes; disilenes; UV spectra; TD-DFT; CIS; quantum mechanical calculations

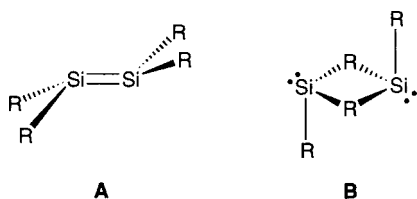
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Introduction

Silylenes $R_2Si:$ are known to dimerize to give disilenes $R_2Si=SiR_2$.¹ However, for silylenes carrying electronegative and π -donating substituents R such as NH_2 , OH , and F , it was predicted theoretically that the doubly bonded disilene, **A**, does not exist and bridged structures $RSi(\mu-R)_2SiR$, **B**, are favored.^{2,3} This surprising theoretical finding can be rationalized by a model suggested by Carter and Goddard,⁴ and Malrieu and Trinquier² (CGMT), which relates the structure of the dimer $(ER_2)_2$ to the singlet-triplet energy separation, ΔE_{ST} , of the $R_2E:$ fragments. According to this model silylenes that have a singlet ground state and a large ΔE_{ST} , such as diamino- and difluoro-silylenes, are predicted to give N- and F-bridged dimers, **B**, respectively, instead of the conventional disilene, **A**.^{2,3}

A nitrogen-bridged dimer of type **B** was suggested to be involved as an intermediate (or a transition state) in the scrambling observed in a reaction in which diaminosilylenes **1** and **2** are formed as intermediates.⁵ In addition, West et al. have found recently that the stable cyclic diaminosilylene **3** does not dimerize to the corresponding tetraaminodisilene, but instead, reacts with another molecule of **3** to yield a different silylene (with one amino and one silyl substituents), which then dimerizes to a diaminodisilyldisilene.⁶ These observations supported the previous theoretical predictions that simple tetraaminodisilenes are not minima on the potential energy surface.³ In apparent contrast to these predictions, it was recently proposed that at low temperature $(i\text{-}Pr_2N)_2Si:$ (**1**) does dimerize to the corresponding tetraaminodisilene $(i\text{-}Pr_2N)_2Si=Si(NPr\text{-}i_2)_2$, (**4**), and not to the bridged dimer $(i\text{-}Pr_2N)Si(\mu\text{-}(i\text{-}Pr_2N))_2Si(NPr\text{-}i_2)$ (**5**). The suggestion that the observed species is the disilene **4** was made on the basis of a long-wave absorption maximum at 439 nm in the UV spectra.⁷ This seems incompatible with the theoretical prediction, which indicated that diaminosilylene dimers should adopt a bridged structure.^{3c, 3d}



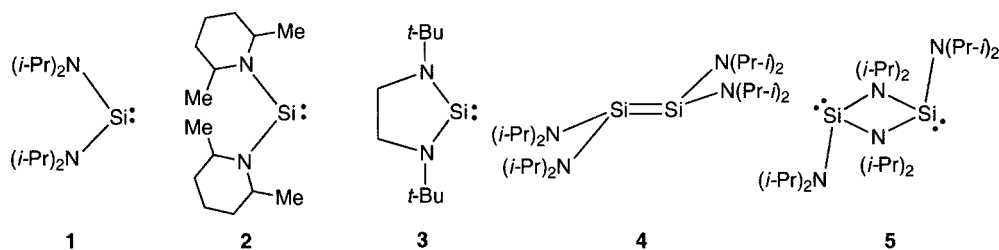
The first step to resolve this apparent theoretical/experimental contradiction was to unequivocally determine the structure of the experimentally detected species. As providing additional experimental evidence for the structure of the elusive **4** proved to be extremely difficult we turned to theory for support. As the assignment of the structure of **4** was based on UV-spectroscopy and as this method is one of the major tools for studying silylenes and their dimerization process, it is of major importance to evaluate the reliability of various theoretical methods for calculating the long wave UV absorption of disilenes and silylenes. Some previous calculations on the UV absorption of silylenes are available,^{3d, 8} but the methods used in 1985 are now outdated, and they do not allow the calculations of the large system which are of interest here.

In this article, we present results that show that *ab initio* molecular orbital calculations [at the CIS/6-311++G(3df,2p) level of theory] as well as density functional calculations [at the TD-B3LYP/6-311++G(d,p) level of theory] can be applied reliably to determine the long-wave UV transitions (i.e., the lowest energy transitions) of silylenes and their dimers, i.e., disilenes **A** and their cyclic isomers **B**.

Computational Details

Quantum mechanical calculations^{9a} were performed with the Gaussian 98 software package.^{9b} Geometries were fully optimized at the MP2/6-31G(d) level of theory. For geometry optimizations of dimers **4** and **5**, density functional methods^{10a, 10b} with the hybrid B3LYP functional^{10c, 10d} along with the 6-31G(d) basis set^{9a} were used. These levels of theory are suitable for these geometry optimizations because they reproduce well-known structures of disilenes including the weak bending modes of the Si=Si bond.^{6, 11}

UV absorption maxima and oscillator strengths were calculated using the configuration interaction-singles (CIS) method.¹² Previous studies have shown that in combination with the CIS method a judicious choice of basis set is essential,¹² and we found that the very large extended 6-311++G(3df,2p) basis set is required to give consistent results for the vertical transition energies of known silylenes and disilenes (see below). In general, the MP2/6-31G(d) optimized geometries were used for the UV calculations (except for **4** and **5**, for which B3LYP/6-31G(d) optimized geometries were used). For example, the basis-set dependency of CIS calculations for the tetramethyldisilene (**6**)



using the MP2/6-31G(d) geometry was as follows: 280 nm [6-31G(d)]; 303 nm [6-31+G(d)]; 302 nm [6-311+G(d)]; 324 nm [6-311++G(d,p)]; 327 nm [6-311++G(3df,2p)]. With the more recently developed time-dependent-B3LYP (TD-B3LYP) method¹³ the smaller 6-311++G(d,p) basis already gives converged results. The use of the TD-B3LYP method allows to calculate the vertical transition energies of larger molecules, which in size and complexity are closer to the experimentally studied species.

Results and Discussion

The calculated absorption wavelengths and the oscillator strengths for disilenes **6–12** and silylenes **13** and **14** at both the CIS and TD-B3LYP levels of theory are listed in Table I along with the corresponding experimental values for related compounds. In the calculated model compounds hydro-

gens generally replace the alkyl groups in the experimentally investigated disilenes and vinyl groups replace phenyl groups (see Table I). In **13**, the experimentally used *iso*-propyl groups are replaced in the calculations by methyl groups.

All optimized structures of disilenes **6–12** reveal the expected^{1–3} *trans*-bent structure around the Si=Si double bond. In addition, **9** and **10** are markedly twisted around the Si=Si bond. The dihedral angles $\Theta(\text{NSiSiN})$ and $\Theta(\text{CSiSiC})$ are -40.5° , 73.3° for **9**, R = H and 35.6° , -73.3° for **9**, R = Me. In **10**, the two NSiSiC dihedral angles are 65.3° , -39.8° for R = H and 67.3° , -34.7° for R = Me. The angle δ (Fig. 1) between the π -orbital of the Si=Si bond and the lone pair on nitrogen or oxygen (or the π -orbital in **11** R' = CH₂=CH) of the substituents in **7–12**, or between the vacant 3p orbital of the silylene and the lone pair of nitrogen in **13**, which indicates the degree of conjugation, is also included in Table I.

TABLE I. Calculated and Experimental Absorption Wavelength, λ_{max} (nm), and Oscillator Strength, f , of the First UV Transition of Disilenes and Silylenes.^a

CIS Method (calc.) ^b				TD-B3LYP(calc.) ^c				Experiment		
Compounds	δ^d	λ_{max}	f	Compounds	δ^d	λ_{max}	f	Compounds	λ_{max}	Reference
6	—	327	0.397	6	—	341	0.330	6	344	18a
7 , R = Me	48	346	0.435	7 , R = Me	48	365	0.338	7 , R = Et	395	20
8 , R = H	67	355	0.438	8 , R = Me	65	373	0.355	8 , R = Et	408	20
9 , R = H	66	354	0.422	9 , R = Me	65	378	0.352	9 , R = Et	408	20
10 , R = H	12, 55 ^e	357	0.358	10 , R = Me	0, 65 ^e	382	0.314	10 , R = Et	417	7
11 , R = H, R' = CH=CH ₂	26	336	0.485	11 , R = Me, R' = Ph	52	358	0.369	11 , R = Me, R' = Ph	386	18b
12 , R = H, R' = H	35 ^f	307	0.284	12 , R = Me, R' = <i>t</i> -Bu	13 ^f	355	0.329	12 , R = Me, R' = <i>t</i> -Bu	373	20
13 , R = Me	23	254	0.141	13 , R = <i>i</i> -Pr	29	306	0.052	13 , R = <i>i</i> -Pr	335	19
14	—	422	0.055	14	—	450	0.039	14	453	20

^a The calculated transitions are $\pi \rightarrow \pi^*$ for the disilenes and $n \rightarrow 3p$ for the silylenes (Fig. 3).

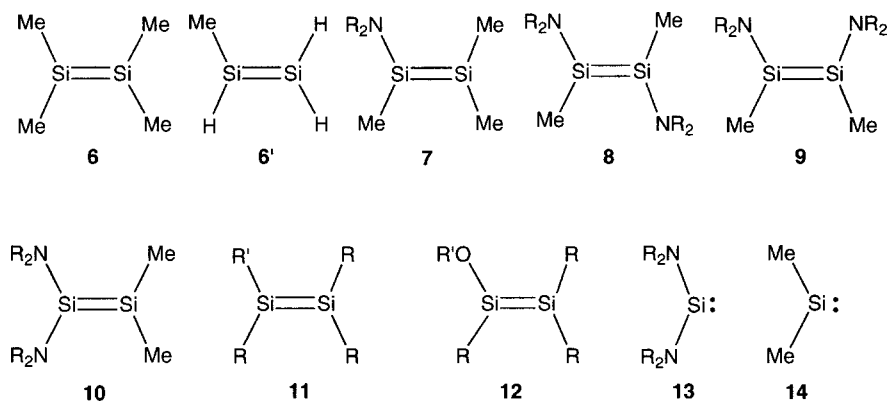
^b At the CIS/6-311++G(3df,2p) level.

^c At the TD-B3LYP/6-311++G(d,p) level.

^d See Figure 1 for definition of δ . $\delta(\text{deg}) = 90 - 0.5|d_{\text{RHSiSi}} + d_{\text{RHSiSi}'}|$, where d denotes dihedral angle (R = H, C; X = N, C).

^e The two nitrogen lone pairs gave two different δ values.

^f The ROSiSi (R = H, C) dihedral angle.



A linear correlation, shown in Figure 2(a), is found between the transition energies observed experimentally for disilenes and silylenes and the $\pi-\pi^*$ ¹⁴ or $n-3p$ ¹⁵ (Fig. 3) transition energies calculated for the corresponding model compounds at the CIS/6-311++G(3df,2p)//MP2/6-31G(d) level of theory. Linear regression of the data points gives eq. (1) (correlation coefficient: 0.99), which relates the experimental transition energies, Y , derived from the observed λ_{\max} , with the calculated vertical transition energies, X , for the model compounds.¹⁶

$$Y(\text{eV}) = 0.49X(\text{eV}) + 1.32 \quad (1)$$

where $X(\text{eV})$ is the calculated transition energies, and $Y(\text{eV})$ is the experimental transition energies.

For the same set of experimentally investigated compounds 6–14 TD-B3LYP/6-311++G(d,p) calculations were also performed but the TD-B3LYP method allowed to use more realistic substituents than with the CIS method. For example, in 8–10, the ethyl groups present in the experimentally investigated disilenes are replaced in the TD-B3LYP calcu-

lations by methyl groups instead of $R = \text{H}$ used in the CIS calculations (see Table I). The replacement of hydrogens by the more realistic methyl groups moved the calculated absorptions to a longer wavelength by ca. 20 nm than predicted by the CIS method, bringing the calculated results closer to the observed absorption maxima. A linear relationship (correlation coefficient = 0.98) shown in Figure 2b is found also between the experimental transition energies and the TD-DFT calculated values [eq. (2)].¹⁷ Thus, both the CIS and the TD-B3LYP methods give good linear correlation lines between the experimental and the theoretical results, but the TD-B3LYP values are generally closer (in their absolute values) to the experimental values. Considering this and the fact that the TD-B3LYP calculations are significantly faster than the CIS calculations and the ability to calculate more realistic models, we recommend the TD-B3LYP method for future applications.

$$Y(\text{eV}) = 0.78X(\text{eV}) + 0.52 \quad (2)$$

Substitution of one methyl group in disilene 6 by a phenyl group (11), by an alkoxy group (12) or by a dialkylamino group (7) results in an experimentally observed bathochromic (red) shift of the $\pi \rightarrow \pi^*$ transition by 42 nm (6/11), 29 nm (6/12) or 51 nm (6/7). This trend is well reproduced by the calculations, although the calculated changes are smaller than the observed ones; i.e., for the model pairs 6/11 (by 17 nm), 6/12 (by 14 nm), and 6/7 (by 24 nm) (at TD-B3LYP/6-311++G(d,p)), and 6'/11 (by 35 nm), 6'/12 (by 6 nm), and 6/7 (by 19 nm) (at CIS/6-311++G(3df,2p); calculated λ_{\max} for 6' = 301 nm). These red-shifts indicate conjugation between the substituent and the $\text{Si}=\text{Si}$ bond, which raises the HOMO-energy and thus reduces the π/π^* energy difference. Multiple substitution by electron donating substituents leads to additional bathochromic shifts, as shown, for example,

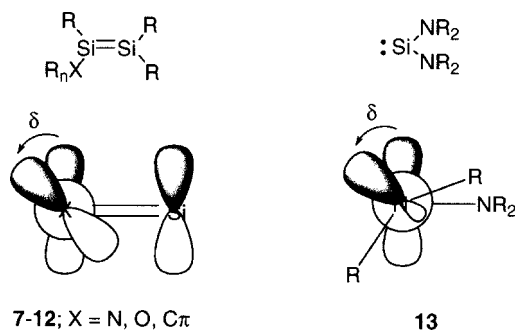


FIGURE 1. Definition of the angle δ between the axis of the π -orbital of the $\text{Si}=\text{Si}$ bond and that of the lone pair (or π -orbital) of the substituents in 7–12 (left), and between the axis of the vacant 3p orbital of the silylene and that of the lone pair of nitrogen in 13 (right).

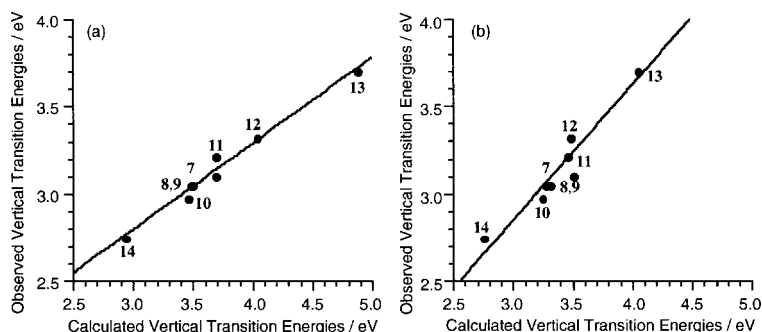


FIGURE 2. Correlation between observed and calculated (a) at CIS/6-311++G(3df,2p)//MP2/6-31G(d) and (b) at TD-B3LYP/6-311++G(d,p)//MP2/6-31G(d), transition energies (eV) of several silylenes and disilenes: **7**, (Me₂N)MeSi=SiMe₂ (CIS, TD-DFT)/(Et₂N)MeSi=SiMe₂ (obs.); **8**, (*E*)-(H₂N)MeSi=SiMe(NH₂) (CIS)/(*E*)-(Me₂N)MeSi=SiMe(NMe₂) (TD-DFT)/(Et₂N)MeSi=SiMe(NEt₂) (obs., stereochemistry not known); **9**, (*Z*)-(H₂N)MeSi=SiMe(NH₂) (CIS)/(*Z*)-(Me₂N)MeSi=SiMe(NMe₂) (TD-DFT)/(Et₂N)MeSi=SiMe(NEt₂) (obs., stereochemistry not known); **10**, (H₂N)₂Si=SiMe₂ (CIS)/(Me₂N)₂Si=SiMe₂ (TD-DFT)/(Et₂N)₂Si=SiMe₂ (obs.); **11**, H₂C=CHHSi=SiH₂ (CIS)/PhMeSi=SiMe₂ (TD-DFT, obs.); **12**, (HO)HSi=SiH₂ (CIS)/(*t*-BuO)MeSi=SiMe₂ (TD-DFT, obs.); **13**, (Me₂N)₂Si: (CIS)/(*i*-Pr₂N)₂Si: (TD-DFT, obs.); **14**, Me₂Si:

by the 13 nm red-shift observed for (*E*)- and (*Z*)-1,2-diamino-1,2-dimethyldisilenes **8** and **9**, relative to **7**. As the $n \rightarrow 3p$ transition in silylenes (Fig. 3) is forbidden the calculated oscillator strengths of this transition in silylenes **13**, R = Me or R = *i*-Pr and **14** are markedly smaller than those calculated for the $\pi \rightarrow \pi^*$ transition in disilenes **6–12** (Table I).

Photochemically generated (*i*-Pr₂N)₂Si: **1**, shows in 3-methylpentane at room temperature an ab-

sorption maximum at 335 nm (calculated 306 nm at TD-DFT, Table I). At 77 K, **1** dimerizes to a product of unknown structure with an absorption maximum at 439 nm.⁷ Calculations at the MP2/6-31G(d)//B3LYP/6-31G(d) level of theory reveal that both, the classical Si—Si bonded dimer **4** and the nitrogen bridged dimer **5**, are stable molecules, with **5** being less stable by 16.0 kcal mol⁻¹.²¹ However, the calculated structure of (*i*-Pr₂N)₂Si=Si(NPr-*i*)₂ (**4**) is rather unusual (Fig. 4). The Si—Si bond is extremely long (2.472 Å), the molecule is twisted around the Si—Si bond by 55.5° and both silicon atoms are strongly pyramidalized, the angle between the Si—Si vector and the SiN₂ plane being

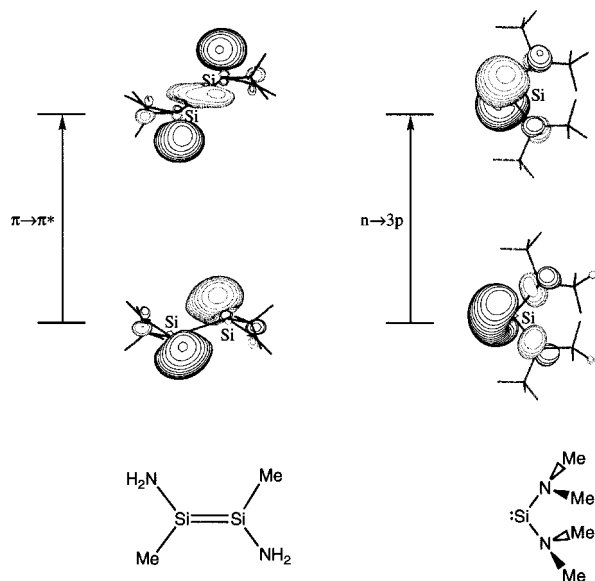


FIGURE 3. Shapes of the π and π^* orbitals of diaminodimethyldisilene and of the n and $3p$ orbitals of bis(dimethylamino)silylene. The threshold level of the orbitals is 0.060.

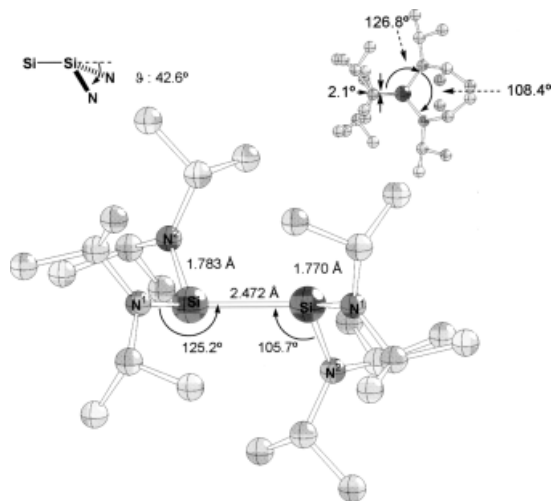


FIGURE 4. Calculated geometry of **4**, R = *i*-Pr, (C₂-symmetry) at the B3LYP/6-31G(d) level.

42.6°. ²¹ Calculations of the vertical transition energy for the model compound (H₂N)₂Si=Si(NH₂)₂, in which all the geometrical parameters are kept at the values calculated for **4** (only the NH bond lengths are optimized), using the CIS and the TD-B3LYP methods, and eqs. (1) and (2), respectively, predict absorption maxima for **4** at 434 and 452 nm, respectively. These calculated values are very close to the measured value of 439 nm of the species observed in the low-temperature dimerization of **1**.⁷ Similar calculations predict for the isomeric nitrogen-bridged dimer **5**, λ_{max} at 374 (CIS) and 354 nm (TD-B3LYP). Thus, the calculations of the vertical transition energies clearly favor the Si=Si bonded species **4** as the compound observed experimentally,⁷ and they definitely rule out the possibility that the experimentally observed species is the nitrogen-bridged dimer **5**.²¹

Acknowledgments

This article is dedicated to Professor Paul von Ragué Schleyer, one of the great pioneers of computational chemistry and of physical organic chemistry, on the occasion of his 70th birthday. Y.A. thanks the JSPS for a visiting Professor Scholarship during which this research was carried out.

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- The pyramidalization of aminosubstituted disilenes results in significant mixing of spⁿ type orbitals into the π orbital, and of σ^* -type orbitals into the π^* orbital. This is shown clearly in the final shape of the orbitals shown in Figure 3. For clarity we will, however, use the π - π^* notation for the long-wave absorption in these strongly distorted disilenes, although strictly this notation is not correct.
- In aminosilylenes the nitrogens lone pairs contribute significantly to 3p(Si) (see Fig. 3); however, the UV transitions is best described as an n(Si)-3p(Si) transition.
- With the smaller 6-31+G(d) basis set very similar calculated λ_{max} values were obtained: i.e., [340 nm (7), 349 (8), 348 (9), 353 (10), 330 (11), 296 (12), 253 (13), 425 (14)], giving the empirical correlation: $Y = 0.48X + 1.33$ with a correlation coefficient of 0.99.
- Similar λ_{max} values were obtained with the smaller 6-31+G(d) basis set: 363 (7), 371 (8), 376 (9), 380 (10), 356 (11), 353 (12), 306 (13), 452 (14), giving the empirical correlation: $Y = 0.76X + 0.56$, with a correlation coefficient of 0.97.
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