

A Theoretical Investigation of Donor-Acceptor Bonding between Amines and Silylenes

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The dative Si-N bond dissociation enthalpy D_0 in $\text{SiH}_2\leftarrow\text{NH}_3$ has been estimated as 97 ± 10 kJ mol^{-1} at the G2 level of theory. D_0 values for substituted analogs and cyclic complexes closed by intramolecular Si-N bonds have been obtained by means of isodesmic reactions, and strains in four-, five-, and six-membered rings are shown to be small. D_0 in $\text{SiH}_2\leftarrow(\text{NH}_3)_2$ is estimated to be 7 ± 20 kJ mol^{-1} . Kinetic implications of D_0 are discussed. Vibrational frequencies and UV/visible spectra of various silylenes and silaylides are predicted, to obtain changes in the $S_0 \rightarrow S_1$ energy relative to SiH_2 . Ylide formation is seen to increase this gap, and CIS/6-31+G* results suggest that complexation of SiH_2 with NH_3 shifts the absorption from 485 to 301 nm.

1. Introduction

This work is an *ab initio* study of the thermochemistry and spectroscopy of dative bonds¹ between amines and silylenes (silanediyls). These bonds are formed through donation of the lone electron pair on the N atom into the empty p orbital on the Si atom. The existence of such bonds has recently been demonstrated in silylenes stabilized by coordination to Lewis bases, which contain intramolecular amine groups.^{2,3} X-ray structure determinations on these coordinate complexes containing the silaylide arrangement revealed a relatively large Si-N separation of about 2.05 Å.³ This may be compared to the normal Si-N distance of, e.g., about 1.72 Å calculated for silylamine.⁴ These complexes involve five-membered rings containing Si-N bonds, which are therefore a focus in this work. Similar donation of lone electron pairs on O atoms into silylenes has been investigated experimentally by several groups,⁵⁻¹² while Ando *et al.*¹³ and Gillette *et al.*¹⁴ have studied the changes in the electronic spectrum of silylenes caused by donor-acceptor adduct formation. There have also been recent studies of the isoelectronic donor-acceptor complexes formed between amines and alanes.^{1,15}

The UV-visible spectra of several silylenes have previously been analyzed in terms of the Hartree-Fock wave functions of the ground and first excited singlet states by Apeloig and Karni;¹⁶ here we assess the usefulness of the CIS method recently described by Pople and co-workers¹⁷ and compare results from both approaches with experimental data for free silylenes and silylenes complexed to amines.

Silylene-amine bonding is of potential practical significance in plasma-enhanced chemical vapor deposition of silicon nitride from ammonia/silane mixtures, where the gas-phase reaction of SiH_2 with NH_3 may be an important step.^{18,19} The theoretical work of Raghavachari *et al.* predicts that SiH_2 and NH_3 initially combine to form a silaylide adduct, which has a significant barrier to isomerization to the more stable SiH_3NH_2 .⁴ Part of the present work forecasts the vibrational and electronic properties to aid the design of experiments to study the $\text{SiH}_2 + \text{NH}_3$ reaction. The results obtained are also considered in the context of recent experiments on possible cyclic amine/silylene complexes.²⁰ Strain energies for four-, five-, and six-membered rings containing Si-N dative bonds are estimated, and kinetic implications of the thermochemistry are discussed.

2. Theoretical Method

Results were obtained by use of the GAUSSIAN90 program,²¹ implemented on a VAX 6310 and a Solbourne 5E/902 computer. Standard *ab initio* molecular orbital theory was employed to optimize the energy as a function of nuclear coordinates,²² and calculations were performed using the split-valence 3-21G(*),

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6-31G*, and 6-311G** atomic basis sets. The first basis set includes polarization functions on Si, and the second includes polarization functions on all but the H atoms, while the third basis set includes polarization functions on all atoms. A full geometry optimization was carried out for the ground state of each closed-shell (S_0) molecule using the spin-restricted Hartree-Fock (RHF) method. RHF harmonic vibrational frequencies were calculated to verify each equilibrium structure as a true minimum. HF frequencies are typically about 10% higher than experimental and, thus, were scaled by a standard factor of 0.922 before zero-point vibrational energies (ZPE) were computed.

Electronic energies were calculated for the first excited singlet (S_1) and triplet (T) states of each molecule at its S_0 RHF geometry, by means of unrestricted Hartree-Fock (UHF) theory. Spin contamination was monitored via the value of $\langle S^2 \rangle$. Energies of the pure first excited singlets ($E[S_{1,pure}]$) were derived from the triplet energies and the energies of the contaminated UHF singlets (which have $\langle S^2 \rangle \approx 1$ and are mixtures of the wave functions of the pure excited singlets and triplets) using the relation proposed by Apeloig and Karni:¹⁶

$$E[S_{1,pure}] = [2E[S_{1,contaminated}] - \langle S^2 \rangle E(T)] / (2 - \langle S^2 \rangle) \quad (1)$$

Their fix of spin contamination is not highly satisfactory because $E[S_{1,pure}]$ becomes indeterminate as $\langle S^2 \rangle$ approaches 2. Accordingly, an alternative method to derive the vertical energy separation between the S_0 and S_1 states is evaluated here. The S_0 geometry was optimized at the RHF/6-31G* level and the energy gap was derived using configuration interaction with single excitations,¹⁷ with the 6-31+G* basis set. The "+" indicates the inclusion of diffuse functions that aid the description of any Rydberg character in the excited-state wave function.

For the thermochemical analysis single-point energies for ground states were obtained at the RHF/6-31G* geometries by means of second-order and fourth-order Møller-Plesset perturbation theory (MP2 and MP4) using the frozen core approximation with the 6-31G* and 6-311G** basis sets. Finally, the ground-state energy of the $H_3N \rightarrow SiH_2$ complex was computed at the Gaussian-2 (G2) level of theory.²³⁻²⁵ Briefly, the G2 procedure is based on MP4 energies calculated with the 6-311G** basis set at the MP2/6-31G*-optimized geometry, modified by a series of additive corrections to approximate a full QCISD-(T)/6-311+G(3df,2p) calculation.

3. Results and Discussion

3.1. Geometry. Six molecules were examined for the purpose of studying the Si-N bond dissociation energy: H_3NSiH_2 (molecule A), $(H_3N)_2SiH_2$ (B), $CH_3(H_2)NSi(H)CH_3$ and linear and cyclic $HSi(CH_2)_xNH_2$ ($x = 2, 3, 4$; C-H) (see Figures 1 and 2). Selected results of the geometry optimizations of the first two species are shown in Figure 1. For A the calculated Si-N bond length increases from 2.043 to 2.089 Å upon increasing the flexibility of the atomic basis set from 3-21G(*) to 6-31G* and, unlike most bonds,²² decreases when electron correlation is included at the MP2=FULL/6-31G* level, back to 2.063 Å. Similar decreases have been noted for the calculated Al-N separation of about 2.08 Å in the isoelectronic $AlH_3 \leftarrow NH_3$ molecule,¹⁵ as well as other dative bonds.²² These distances compare well with the measured intramolecular Si-N separation of 2.046 Å in a more complicated base-stabilized silaylide.³ For $CH_3(H_2)NSi(H)CH_3$ the Si and N atoms are 2.027 Å apart at the RHF/

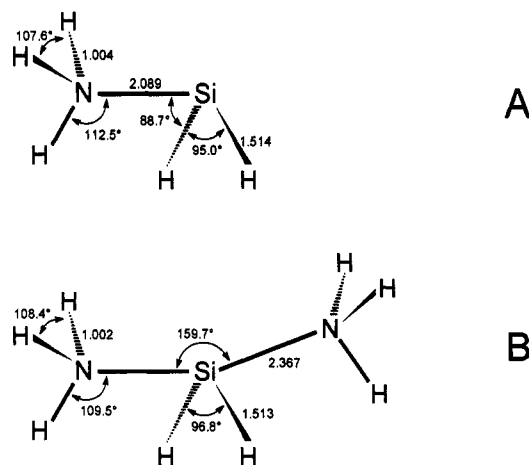


Figure 1. Structures of complexes of NH_3 with SiH_2 , showing selected bond lengths (Å) and angles (deg) calculated at the HF/6-31G* level of theory.

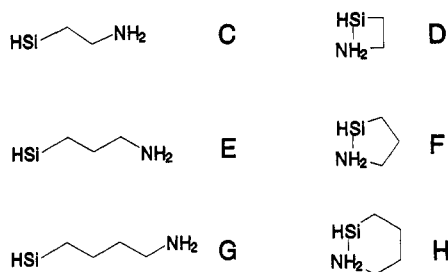


Figure 2. Structures of the linear and cyclic silylenes $HSi(CH_2)_xNH_2$ ($x = 2, 3, 4$).

3-21G(*) level, which indicates that simple alkyl substitution has little influence on the Si-N distance. The RHF/3-21G(*) distances in the cyclic species D, F, and H are 2.045, 2.017, and 2.018 Å, respectively. In B the Si-N distance is predicted at the RHF/3-21G(*) and RHF/6-31G* levels to be 2.274 and 2.367 Å. As shown below, the longer Si-N bonds in this molecule are much weaker than in the other silaylides analyzed here.

The Mulliken charges on Si and N in free SiH_2 and NH_3 at the RHF/6-31G* level are +0.32 and -1.00, respectively, and change to +0.18 and -1.02 upon formation of A. Alternatively, if H atom charges are summed with heavy atoms, then the Mulliken charges on the SiH_2 and NH_3 groups within A are ± 0.20 . Thus there is no large charge separation in the donor-acceptor complex and any description of the complex as "zwitterionic" is best regarded as a formal representation.

3.2. Vibrational Frequencies. The results of normal mode analyses for A and B are listed in Table 1. For A the modes below 1000 cm^{-1} show strong coupling between SiH_2 and NH_3 motions and have mixed character. Si-N stretching is mainly in the mode predicted to lie at 833 cm^{-1} , where it is coupled to scissoring of the SiH_2 group and inversion, i.e., umbrella motion of the NH_3 group. In B, symmetric Si-N stretching is estimated to occur at 188 cm^{-1} while the IR-active asymmetric stretching is found at 125 cm^{-1} . Promising spectral regions for IR detection of A and B must contain reasonably intense absorption bands that are well-separated from the absorptions of SiH_2 and NH_3 that are likely to be present in an attempted synthesis of A. Such regions lie at approximately 352 and 1288 cm^{-1} for A, and for B at approximately 125 , 511 , and 865 cm^{-1} . The most intense features in their spectra will be the Si-H stretching bands at $\approx 1900\text{ cm}^{-1}$, and it might

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Table 1. Calculated Vibrational Frequencies of SiH₂/NH₃ Adducts^a

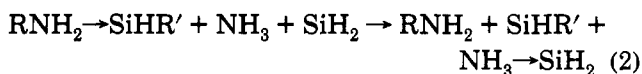
ν , cm ⁻¹	I , km ^b	SiH ₂ NH ₃ descrptn ^c	ν , cm ⁻¹	I , km ^b	SiH ₂ (NH ₃) ₂ descrptn ^c
149	0.6	SiH ₂ , NH ₃ rock	82	0.0	torsion
352	44	NH ₃ rock	95	18	torsion
525	0.4	SiH ₂ , NH ₃ def, torsion	125	130	asym SiN str
543	3.8	SiH ₂ scis, NH ₃ inv	131	36	NSiN bend
819	47	NH ₃ def, torsion	186	9.0	torsion
833	130	SiH ₂ scis, NH ₃ inv, SiN str	188	0.0	sym SiN str
984	140	HSiN bend	389	0.0	NH ₃ rock
1288	210	NH ₃ rock	401	0.0	NH ₃ rock
1646	32	NH ₃ def	509	41	NH ₃ rock
1648	42	NH ₃ def	513	58	NH ₃ rock
1929	540	SiH str	830	0.0	SiH ₂ twist
1946	379	SiH str	865	170	SiH ₂ rock
3321	29	NH str	959	140	SiH ₂ scis
3435	52	NH str	1166	440	NH ₃ inv
3440	59	NH str	1168	8.0	NH ₃ inv
			1650	61	NH ₃ def
			1650	0.0	NH ₃ def
			1651	2.4	NH ₃ def
			1652	50	NH ₃ def
			1918	590	SiH str
			1931	378	SiH str
			3331	22	NH str
			3332	0.6	NH str
			3455	1.6	NH str
			3455	39	NH str
			3457	2.4	NH str
			3458	41	NH str

^a HF/6-31G* frequencies scaled by a factor of 0.9. ^b IR absorption intensity. ^c Str, stretch; def, deformation; inv, inversion; scis, scissor.

be possible to detect ylide formation using high-resolution IR spectroscopy to monitor small shifts in these Si-H stretching frequencies.

3.3. Thermochemistry. Total energies for the species considered here are listed in Table 2 and are employed together with the ZPE to calculate D_0 , the bond dissociation enthalpy at 0 K. The G2 calculation of D_0 for the SiH₂←NH₃ silaylide yields 97 kJ mol⁻¹ (Table 3). Because G2 theory has usually been found to agree well with experimental data, with a target accuracy of ±8 kJ mol⁻¹,²⁵ we assign an approximate uncertainty of ±10 kJ mol⁻¹ to this result. Our D_0 value is close to two previous calculations: an MP4/6-31G**//HF/6-31G* result of 105 kJ mol⁻¹ from Raghavachari *et al.*⁴ and a BAC-MP4 value of 109 ± 12 kJ mol⁻¹ by Melius.²⁶ These values are quite close to the D_0 calculated by Marsh *et al.* for AlH₃←NH₃ of 109 kJ mol⁻¹,¹⁵ while experiments by Haaland yielded a value for methyl-substituted alane of 130 kJ mol⁻¹.¹

D_0 for the other silaylides RNH₂→SiHR' are obtained by a two-step procedure. First, the bond dissociation enthalpy relative to that of NH₃→SiH₂, ΔD_0 , is derived as ΔH at 0 K for the isodesmic reaction



Then D_0 for the adduct RNH₂→SiHR' is obtained from

$$\Delta D_0 = D_0(\text{RNH}_2\text{-SiHR}') - D_0(\text{NH}_3\text{-SiH}_2) \quad (3)$$

where the G2 value of $D_0(\text{NH}_3\text{-SiH}_2)$ is employed. We expect D_0 derived in this way to be less sensitive to error than calculation of D_0 directly (also shown in Table 3) because errors in calculations below the G2 level arising

from inadequate basis set size and treatment of changes in correlation energy tend to cancel for reaction 2. Table 4 lists the mean D_0 values and their uncertainties, which represent an assessment of the scatter between D_0 values derived from different theoretical levels for a given molecule, combined with the initial uncertainty in the G2 bond strength for A.

As may be seen from Table 4, methyl substitution in A has a small effect on D_0 and apparently reduces the Si←N bond strength by only 4 kJ mol⁻¹. This might indicate a small degree of electron donation by the methyl group in the silylene into the Si p orbital, which would make donation of the lone pair on N into this orbital less favorable. Consistent with this idea, the electron-withdrawing SiH₃ group induces a slight increase in D_0 , of about 5 kJ mol⁻¹. It is reasonable to assume, on the grounds that the environments of the Si←N bonds are similar in both CH₃(H₂)NSi(H)CH₃ and the cyclic molecules D, F, and H, that the differences in D_0 may be attributed primarily to strain energy (i.e., strain enthalpy at 0 K) in the ring, E_S . Here we obtain E_S from

$$E_S \approx D_0(\text{H}_2(\text{CH}_3)\text{N-SiHCH}_3) - D_0(\text{HSi}(\text{CH}_2)_x\text{NH}_2) \quad (4)$$

As shown in Table 4, E_S is negligible for the five-membered cyclic silaylide (F), about 6 kJ mol⁻¹ for the six-membered ring (H), and 37 kJ mol⁻¹ for the four-membered ring (D). These modest values of E_S can be contrasted to the larger strain energies calculated by Boatz *et al.* for monosilacycloalkanes, of 103, 19, and 17 kJ mol⁻¹ for four-, five-, and six-membered rings, respectively.²⁷ The difference arises from the long Si←N bonds which accommodate larger angles in the carbon framework of the rest of the ring, while at the same time the dative bond into the p orbital on Si favors a 90° angle between the Si←N bond and other substituents at the Si atom (see Figure 1). Thus for cyclic HSi(CH₂)₃NH₂ (F) the NSiC angle is 86.8° at the RHF/3-21G(*)-optimized geometry, while the SiCC, CCC, CCN, and CNSi angles are close to tetrahedral, at 108.1°, 105.6°, 108.3°, and 108.8°, respectively. One consequence of the small strain energy is that formation of intramolecular Si←N bonds, as compared to intermolecular bonding, may be reasonably favorable on entropy grounds, *without* a large opposing enthalpy penalty.

Use of the isodesmic reaction 2 may be inappropriate for B because it is a more loosely bound complex, and direct *ab initio* D_0 values for the second Si←N bond are qualitatively different from the D_0 values for the other silaylides (see Table 3). This is reflected in the large scatter and uncertainty of the D_0 values. Nevertheless, the mean D_0 of 7 ± 20 kJ mol⁻¹ is clearly much smaller than the other values given in Table 4. The loose Si←N bonding in this diamine adduct may not compensate for the entropy loss required for formation of B. Consistent with this possibility, Probst *et al.* prepared a base-stabilized silylene where two equivalent intramolecular amine groups could bond to Si, but NMR spectroscopy revealed that only one amine was attached at a time.³

3.4. UV-Visible Spectroscopy. S₀ → S₁ transitions in the UV-visible spectrum of silylenes RSiH arise from n → p transitions in the Si atom, and the energy of this transition ΔE is raised if R is a π-donor, causing a blue

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Table 2. *Ab Initio* Energies

species	energy, au ^a					
	HF/3-21G(*)	HF/6-31G*	MP2/6-31G*// HF/6-31G*	MP4/6-31G*// HF/6-31G*	MP4/6-311G**// MP2=FULL/6-31G*	Gaussian-2
NH ₃	-55.872 20	-56.184 36	-56.353 71	-56.370 50	-56.428 04	-56.458 65 ^b
SiH ₂	-288.560 27	-289.999 78	-290.067 06	-290.090 03	-290.134 05	-290.167 71 ^b
H ₃ NSiH ₂	-344.494 45	-346.226 03	-346.473 26	-346.510 59	-346.612 48	-346.663 35
(H ₃ N) ₂ SiH ₂	-400.382 36	-402.416 86	-402.838 56	-402.891 98		
CH ₃ SiH	-327.398 61	-329.046 52 ^c	-329.246 83 ^c			
CH ₃ NH ₂	-94.681 66	-95.208 41 ^c	-95.504 56 ^c			
CH ₃ (H ₂)NSi(H)CH ₃	-422.137 39	-424.293 53 ^c	-424.804 14 ^c			
HSiSiH ₃	-577.203 78	-580.080 09 ^c	-580.225 82 ^c			
H ₃ NSi(H)SiH ₃	-633.139 82	-636.306 27 ^c	-636.634 51 ^c			
linear HSi(CH ₂) ₂ NH ₂	-420.924 71					
cyclic HSi(CH ₂) ₂ NH ₂	-420.966 89					
linear HSi(CH ₂) ₃ NH ₂	-459.744 48	-462.130 25 ^c	-462.754 35 ^c			
cyclic HSi(CH ₂) ₃ NH ₂	-459.801 51	-462.168 31 ^c	-462.804 68 ^c			
linear HSi(CH ₂) ₄ NH ₂	-498.618 99					
cyclic HSi(CH ₂) ₄ NH ₂	-498.563 19					

^a 1 au ≈ 2625 kJ mol⁻¹. MP2 and MP4 calculations were made with the frozen core approximation unless otherwise noted. ^b Data from ref 25. ^c Calculated at the HF/3-21G(*) geometry.

Table 3. *Ab Initio* Si-N Bond Dissociation Energies

level of calculation	D ₀ , kJ mol ⁻¹ ^a	isodesmic D ₀ , kJ mol ⁻¹ ^b
NH ₃ SiH ₂ → NH ₃ + SiH ₂		
HF/3-21G(*)	141	
HF/6-31G*	91	
MP2/6-31G*//HF/6-31G*	119	
MP4/6-31G*//HF/6-31G*	112	
MP4/6-311G**//MP2=FULL/ 6-31G*	113	
Gaussian 2	97	
(NH ₃) ₂ SiH ₂ → NH ₃ + NH ₃ SiH ₂		
HF/3-21G(*)	32	-12
HF/6-31G*	16	22
MP2/6-31G*//HF/6-31G*	29	7
MP4/6-31G*//HF/6-31G*	27	12
CH ₃ (H ₂)NSi(H)CH ₃ → CH ₃ NH ₂ + HSiCH ₃		
HF/3-21G(*)	133	89
HF/6-31G*//HF/3-21G(*)	84	90
MP2/6-31G*//HF/3-21G(*)	121	99
H ₃ NSi(H)SiH ₃ → NH ₃ + HSiSiH ₃		
HF/3-21G(*)	149	105
HF/6-31G*//HF/3-21G(*)	91	97
MP2/6-31G*//HF/3-21G(*)	126	104
Ring Opening in HSi(CH ₂) ₂ NH ₂		
HF/3-21G(*)	101	57
Ring Opening in HSi(CH ₂) ₃ NH ₂		
HF/3-21G(*)	136	92
HF/6-31G*//HF/3-21G(*)	87	93
MP2/6-31G*//HF/3-21G(*)	119	97
Ring Opening in HSi(CH ₂) ₄ NH ₂		
HF/3-21G(*)	132	88

^a Bond dissociation enthalpy at 0 K, which includes changes in zero-point energies. ^b D₀ obtained via consideration of the isodesmic reaction 2 (see text).

shift in the electronic spectrum.¹⁶ Among the substituents considered by Apeloig and Karni, R = NH₂ caused the greatest increase in ΔE, 147 kJ mol⁻¹.¹⁶ We have employed their HF approach and also the CIS method, outlined in section 2, to derive the S₀ → S₁ transition energies listed in Table 5, together with the blue shifts relative to the SiH₂ absorption. It may be seen that the derived ΔE values are not strongly basis-set dependent. An approximate indication of the likely uncertainty in calculated wavelengths may be obtained via consideration of the HSiCH₃ and Si(CH₃)₂ molecules. λ ≈ 480 nm has been measured for HSiCH₃,²⁸ while the HF result of Apeloig and Karni¹⁶ is 509 nm and our CIS results is 463 nm. For Si(CH₃)₂ the

Table 4. Estimated Bond Energies and Strain Energies^a

molecule	estimated D ₀ , kJ mol ⁻¹	strain energy, kJ mol ⁻¹
H ₃ NSiH ₂	97 ± 10	
(H ₃ N) ₂ SiH ₂	7 ● 20	
(CH ₃) ₂ HSiN(CH ₃)H ₂	93 ± 15	
H ₃ NSi(H)SiH ₃	102 ● 15	
cyclic HSi(CH ₂) ₂ NH ₂	57 ± 15	37
cyclic HSi(CH ₂) ₃ NH ₂	94 ± 15	-1
cyclic HSi(CH ₂) ₄ NH ₂	88 ± 15	6

^a See text for discussion of estimation methods.

Table 5. Calculated Energy Difference between S₀ and S₁ States, ΔE, and Wavelength Shift Relative to Silylene from HF and CIS Theory

species	⟨S ² ⟩ ^b	Hartree-Fock results		configuration interaction results ^a	
		ΔE, kJ mol ⁻¹	blue shift, nm ^c	ΔE, kJ mol ⁻¹	blue shift, nm ^d
SiH ₂	1.034	225, ^e 225, ^f 224 ^g	0	247	0
HSiCH ₃		235 ^g	24	259	22
Si(CH ₃) ₂		242 ^g	40	278	54
HSiSiH ₃	1.044	157, ^e 153 ^g	-230, -250	187	-156
Si(SiH ₃) ₂	1.034	126 ^e	-417		
HSiNH ₂		367 ^g	206		
H ₃ NSiH ₂	1.012	474, ^e 441 ^f	279, 261	398	184
(H ₃ N) ₂ SiH ₂	1.015	496 ^f	291		
H ₃ NSi(H)SiH ₃				370	160
linear HSi(CH ₂) ₃ NH ₂	1.036	241 ^e	35	257	19
cyclic HSi(CH ₂) ₃ NH ₂	1.012	485 ^e	285	407	191

^a CIS/6-31+G* data. ^b For the UHF wave function of the S₁ state.

^c Relative to a theoretical λ = 532 nm for the S₀ → S₁ transition of SiH₂.

^d Relative to a theoretical λ = 485 nm for the S₀ → S₁ transition of SiH₂.

^e At the HF/3-21G(*) level. ^f At the HF/6-31G* level. ^g From ref 16, at the HF/6-31G* level.

S₀ → S₁ absorption maximum of λ ≈ 494 nm calculated by Apeloig and Karni¹⁶ at the HF level can be compared with our CIS result of λ ≈ 431 nm and the result of Grev and Schaefer²⁹ of λ ≈ 450 nm obtained through more extensive calculations, which is in accord with experimental values of 450–460 nm.^{28,30–32} A small blue shift of 35 nm

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(29) Grev, R. S.; Schaefer, H. F., III. *J. Am. Chem. Soc.* 1986, 108, 5804.

relative to SiH_2 for linear $\text{HSi}(\text{CH}_2)_3\text{NH}_2$ (**E**) is estimated at the HF level, comparable to those predicted earlier for methyl and dimethylsilylene,¹⁶ and may be attributed to small electron donation from the alkyl group. At the CIS level we find a blue shift of 19 nm. For HSiSiH_3 the HF calculations predict $\lambda \approx 770$ nm, whereas the CIS result is 641 nm. The latter is much closer to the recently observed λ in several trimethylsilyl silylenes.²⁰

At the HF level, dative bonding in **A** is predicted to increase ΔE by about 249 kJ mol^{-1} (3-21G*) or 216 kJ mol^{-1} (6-31G*), which implies a large blue shift in absorption wavelength of around 270 nm. These changes in ΔE are seen to be overestimates by comparison with the observations of Ando *et al.*¹³ and Gillette *et al.*,¹⁴ which correspond to increases in ΔE of approximately 150 kJ mol^{-1} upon complexation of silylenes with amines. The CIS change in ΔE , 151 kJ mol^{-1} , corresponds to a decrease of λ from 485 to 301 nm and is in excellent agreement with experiment. Thus overall the CIS method appears to be more accurate than the HF approach and gives good accord with the observed spectra. The CIS method predicts a similar increase in ΔE for formation of the cyclic silaylide **F**.

Conlin and co-workers have prepared phenyl trimethylsilyl silylenes photolytically in a frozen 3-methylpentane matrix.²⁰ That work indicates that if an amine group is available for intramolecular coordination to Si in a five-membered ring, then the absorption band is shifted from 660 to 480 nm, i.e., ΔE is increased by about 68 kJ mol^{-1} . This is smaller than but in qualitative accord with the predicted shift in ΔE at the HF and CIS levels in the five-membered ring (**F**); the discrepancy with the larger change in ΔE predicted here may reflect the influence of the phenyl and trimethylsilyl groups. Consistent with this interpretation, the CIS result for HSiSiH_3 complexed with NH_3 demonstrates that a silyl group somewhat reduces the blue shift in λ (relative to SiH_2) caused by complexation: quantitative analysis of the combined influence of phenyl and trimethylsilyl groups remains a topic for future investigation.

3.5. Kinetic Implications. Initial experimental evidence²⁰ is that the reactions of the possible cyclic silaylide with known trapping agents for silylenes yield the same

products as would be expected from the silylene. There are alternative modes for trapping reactions with a silaylide, either that the silaylide first dissociates to the free silylene, or that Si–N bond fission is concerted with attack on the trap. A crude upper bound to the dissociation rate constant of the five-membered cyclic silaylide (**F**) is obtained by assuming that the activation energy is equal to D_0 and that the preexponential factor might be as large as 10^{17} s^{-1} . This implies a room temperature rate constant of at most about 10 s^{-1} , which is too small to account for the observations.²⁰ A similar result is derived from the D_0 value of Raghavachari *et al.*,⁴ and an even smaller upper bound to the dissociation rate constant would be obtained if the slight bond-strengthening effect (Table 4) of SiH_3 substitution (in the experimental silaylide²⁰) were taken into account. This lends support to the idea of a concerted reaction and suggests that the silaylides may react as hypercoordinated silylenes. In the absence of a trapping agent, the theoretical work of Raghavachari *et al.*⁴ suggests that a possible fate of silylene complexes with primary or secondary amines is isomerization to a more stable silylamine. Gillette *et al.*¹⁴ found, in the case of adducts to tertiary amines, that disilenes were ultimately formed, probably either by dimerization of two complexes or by reaction of a complex with a free silylene.

4. Conclusions

The geometries and vibrational and electronic properties of dative Si–N bonds formed between silylenes and amines have been estimated. The thermochemistry has been investigated, and the best estimate of the $\text{H}_3\text{N} \rightarrow \text{SiH}_2$ bond strength is $D_0 \approx 97 \pm 10 \text{ kJ mol}^{-1}$ from G2 theory. This value is used to derive D_0 for other silaylides via isodesmic reactions. The strain energies in cyclic silaylides were shown to be small. Two NH_3 molecules may be coordinated to SiH_2 , and the resulting second Si–N bonds are predicted to be weak, with $D_0 \approx 7 \pm 20 \text{ kJ mol}^{-1}$. $S_0 \rightarrow S_1$ energies have been calculated for several silylenes, including ones complexed to amine groups, and good agreement between CIS/6-31+G* results and experimental UV–visible spectra is found.

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