

Electronic Spectra of Ethynyl- and Vinylsilylenes: Experiment and Theory[§]

Yitzhak Apeloig,^{*,†} Miriam Karni,[†] Robert West,^{*,‡} and Kevin Welsh[‡]

Contribution from the Departments of Chemistry, Technion—Israel Institute of Technology, 32000 Haifa, Israel, and University of Wisconsin, Madison, Wisconsin 53706

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Abstract: Electronic absorption spectra are reported for four ethynylsilylenes (λ_{\max} , nm), $\text{MesSiC}\equiv\text{CH}$ (524), $\text{MesSiC}\equiv\text{CSiMe}_3$ (545), $\text{MesSiC}\equiv\text{CPh}$ (500), and $\text{CH}_3\text{SiC}\equiv\text{CSiMe}_3$ (473), generated in 3-methylpentane matrices by photolysis of the corresponding trisilanes, $\text{RR'Si}(\text{SiMe}_3)_2$. Calculations of the $^1\text{A}' \rightarrow ^1\text{A}''$ ($n \rightarrow 3p$) transition energies for these and for some vinyl- and phenylsilylenes, by *ab initio* methods including the use of spin-projection methods, provided results in good agreement with experiment. Vinyl, ethynyl, and aryl groups all decrease the transition energy of silylenes, compared with Me_2Si : (i.e., they cause a red shift). Also when H in HSiMe is replaced by vinyl or phenyl groups, a bathochromic (red) shift results, but ethynyl induces a small blue shift. The calculated stabilization energies of the two electronic states suggests that the bathochromic shift is due to an excited-state stabilization (resulting from interaction of the singly-occupied $3p(\text{Si})$ orbital with the π^* orbital on the substituent) which is larger than the stabilization of the corresponding ground state.

Introduction

Following the first direct observation of an organosilylene in 1979,¹ several silylenes have been studied in either argon or hydrocarbon matrices.² In 1986, a paper from one of our laboratories³ reported the electronic spectra of 22 different organosilylenes generated by photolysis of trisilanes⁴ in a 3-methylpentane (3-MP) glass (eq 1).



At about the same time, unrestricted Hartree–Fock (UHF) calculations on the $n\text{--}3p$ electronic transition energies for simple silylenes were published from the other of our laboratories.⁵ In general the calculated and observed electronic absorption energies agreed, qualitatively if not quantitatively. Notable disagreement was, however, found for mesitylethynylsilylene, $\text{MesSiC}\equiv\text{CH}$, which had a λ_{\max} of 524 nm, bathochromically shifted from the values for other mesitylsilylenes. In contrast, the UHF calculations predicted a “blue” shift rather than a “red” shift for ethynyl substitution.⁵ The UHF calculations also predicted a blue shift for vinyl substitution in silylenes, compared to either H or CH_3 ,⁵ but at that time experimental measurements for comparison were not available. While this work was in progress, the first spectra of two vinylsilylenes were reported by Kira et al.,⁶ and their absorption was red shifted compared to dimethylsilylene, in disagreement with the original calculations.⁵

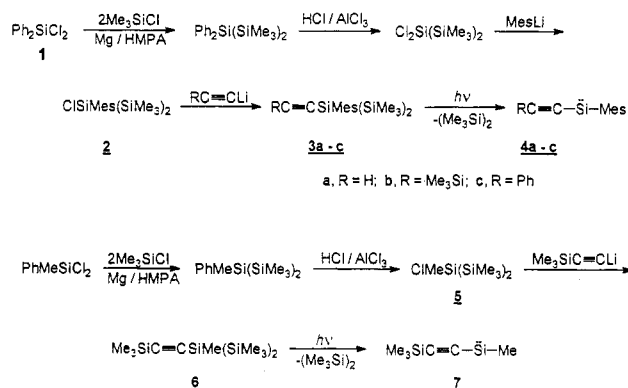
The discrepancy between our previous theoretical results⁵ and the experimental data concerning the excitation energies of vinylsilylenes and ethynylsilylenes has prompted us to restudy the problem theoretically, for these two silylene classes and also

for the related aryl-substituted silylenes. Concurrently, we have also prepared several additional ethynylsilylenes and studied experimentally their electronic spectrum. The new experimental and computational results, which are in excellent agreement, are reported in this paper.

Results

A. Experimental Results. The general procedure for the synthesis of the trisilanes used as precursors for the generation of silylenes is outlined in Scheme 1.

Scheme 1. Routes for Preparation of Trisilane Precursors and Ethynylsilylenes



The useful intermediate 2-chloro-2-mesitylhexamethyltrisilane (2) obtained from diphenyldichlorosilane (1) by standard coupling,⁷ dephenylation, and arylation reactions was treated with ethynyllithium compounds to give mesitylethynyltrisilanes 3a–c. A similar sequence starting from phenylmethyldichlorosilane led to the trisilane precursor 6.

To generate the silylenes, the trisilanes were photolyzed with 254 nm light in degassed 3-MP glasses at 77 K. The photolysis was monitored by electronic spectroscopy; the formation of silylenes was noted by the growth of new electronic absorption bands. A typical curve is shown in Figure 1. Two maxima were usually seen, a UV band at 313–350 nm and a visible absorption at 473–550 nm.

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[†] Technion—Israel Institute of Technology.

[‡] University of Wisconsin.

[§] Dedicated to Professor P. v. R. Schleyer on the occasion of his 65th birthday.

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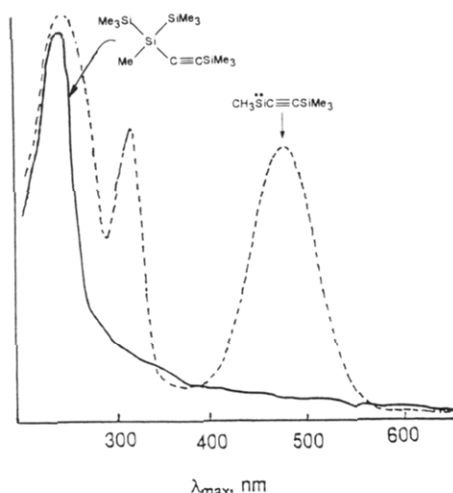


Figure 1. UV spectra of $\text{Me}_3\text{SiC}\equiv\text{CSiMe}$ obtained in the photolysis of $\text{Me}_3\text{SiC}\equiv\text{CSiMe}(\text{SiMe}_3)_2$ at 77 K in 3-methylpentane.

The silylenes **4a**, **4b**, and **7** were further identified by carrying out the photolysis in a 3-MP glass containing triethylsilane, in order to trap the silylene by Si–H insertion (eq 2). In each case GC of the solutions after warming showed that silylenes were transformed in more than 90% conversion to a single trapping product, **8a–c**.



The products were not fully characterized, but were simply identified by high-resolution mass spectrometry. For silylene **4c**, trapping with Et_3SiH was unsuccessful, and the more reactive trapping agent *tert*-butyl alcohol was therefore used, producing a product with a mass spectrum consistent with the expected silylene trapping product: *t*-BuO(H)MeSiC \equiv CPh.

The absorption maxima for the ethynylsilylenes are listed in Table 1, together with those of some previously known silylenes for comparison. It is apparent that the ethynyl groups lead to significant bathochromic shifts, compared with methyl substituents.

Table 1. Measured Absorption Maxima of Silylenes, RSiR' , in 3-Methylpentane at 77 K

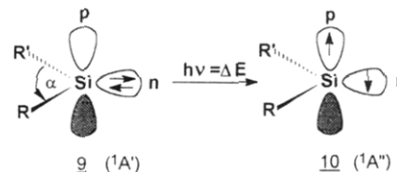
silylene	R	R'	λ_{max} , nm	annealed	ref
	mesityl	CH_3	495	397	3
	mesityl	H	497	412	3
	mesityl	Ph	530	455	3
4a	mesityl	$\text{C}\equiv\text{CH}$	524	430	<i>a</i>
4b	mesityl	$\text{C}\equiv\text{CSiMe}_3$	545, 350	440	<i>a</i>
4c	mesityl	$\text{C}\equiv\text{CPh}$	550, 330		<i>a</i>
	CH_3	CH_3	453	345	1, 3
	CH_3	H	480		1, 3
	CH_3	Ph	490	420	3
7	CH_3	$\text{C}\equiv\text{CSiMe}_3$	473, 313	410	<i>a</i>

^a This work.

Earlier experiments have shown that the careful annealing of a hydrocarbon glass containing a silylene results in silylene dimerization to give disilenes, which depending on the substituents may be transient or stable.³ When matrices containing silylenes **4a**, **4b**, and **7** were warmed slowly, the silylene absorption bands decreased and were replaced by absorptions near 400 nm. These maxima are similar to those observed for other conjugated disilenes

and are probably due to the disilenes formed by dimerization of **4a**, **4b**, and **7**.

B. Theoretical Results. 1. Method of Calculation. In the $^1\text{A}'$ ground state of simple silylenes two electrons occupy an orbital of σ symmetry [$n(\text{Si})$] while the 3p orbital on silicon of π -symmetry is vacant (see structure **9**). The lowest electronic transition involves the promotion of one of the $n(\text{Si})$ electrons to the empty 3p(Si) orbital (i.e., **9** \rightarrow **10**), forming the $^1\text{A}''$ excited state.⁵



Our calculations followed the strategy outlined in our previous communication,⁵ according to which the energy of the first transition in the UV–visible spectra of silylenes, ΔE , is calculated using UHF *ab initio* methods, from the energy difference between the total energies of the $^1\text{A}'$ ground-state singlet and the “vertical” (i.e., confined to have the geometry of the ground state) $^1\text{A}''$ excited-state singlet, i.e., $\Delta E = E(^1\text{A}'') - E(^1\text{A}')$.

The use of UHF theory for calculating ΔE raises a special problem. The excited singlets which are calculated at UHF are nearly 1:1 mixtures of the wave functions of the “pure” excited singlet and of the corresponding “pure” triplet. In our previous study⁵ we estimated the energy of the “pure” excited singlet, $E(\text{S})$, which is the relevant energy for calculating ΔE , by “extracting” the triplet “contamination” out of the calculated E (“mixed state”), by way of eq 3. In eq 3, E (“mixed state”) is the total energy of the excited $^1\text{A}''$ singlet which is obtained by the UHF calculations, $E(\text{S})$ and $E(\text{T})$ denote the calculated energies of the “pure” excited singlet and triplet states, and $\langle S^2 \rangle$ is the calculated expectation value for the “mixed states”.

$$E(\text{“mixed state”}) = 0.5[\langle S^2 \rangle E(\text{T}) + (2 - \langle S^2 \rangle) E(\text{S})] \quad (3)$$

As will be discussed in detail below, we find that, for silylenes with calculated $\langle S^2 \rangle$ values close to 1.0, eq 3 gives reasonable agreement with the experimental spectra. Two examples are $(\text{CH}_3)_2\text{Si}$ and HSiOH , where $\langle S^2 \rangle$ is calculated to be 1.037 and 1.048, respectively.⁵ On the other hand, for ethynylsilylenes and vinylsilylenes where the theoretical–experimental agreement is poor, the calculated UHF $\langle S^2 \rangle$ values are significantly higher: 1.094 and 1.216, respectively, indicating significant contamination from spin states higher than the first triplet. The fact that it is in these cases that we find disagreement between the computational predictions and the experimental spectra (see below) suggested that in cases with $\langle S^2 \rangle$ values greater than ca. 1.05 the use of eq 3 for extracting the contaminations of high spin states from the wave function of the excited singlet is not sufficient. As a result the energies calculated for the $^1\text{A}''$ state *via* eq 3 are too high. Consequently, this procedure predicts blue shifts for these silylenes, in contrast to experiment.

In this paper we use a rigorous theoretical method (which was published after our previous study was completed), the spin-projection method,^{8a} for annihilating spin contaminations (resulting from higher spin states) from the first excited singlet.^{8b} This method has been shown to improve significantly the agreement

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Table 2. Calculated Total Energies of RSiR', Energy Differences between Their ¹A' and ¹A'' States (ΔE), the Corresponding Absorption Wavelengths (λ_{\max}), and the Substituent Effects on this Shift ($\Delta\lambda$)

R	R'	no.	total energies ^a		ΔE^d	$\Delta\Delta E^{d,e}$	λ_{\max}^f	$\Delta\lambda^g$	$\Delta\lambda^h$
			¹ A' ^b	¹ A'' ^c					
H	H		-290.090 00	-290.004 26	53.8	0.0	532	0	54
H	Me		-329.285 09	-329.195 13	56.5	2.7	507	-25	29
Me	Me		-368.481 16	-368.385 66	59.9	6.1	478	-54	0
H	OH		-365.200 07	-365.078 91	76.0	22.2	376	-156	-102
H	OH (per) ⁱ		-365.181 17	-365.082 35	62.0	8.2	462	-70	-16
H	C≡CH	11	-366.049 40	-365.361 79	55.0	1.2	520	-12	42
H	C≡CMe	13	-405.242 53	-405.155 30	54.7	0.9	523	-9	45
H	C≡CSiH ₃	14	-656.240 47	-656.154 08	54.2	0.4	528	-4	50
Me	C≡CH	12	-405.246 07	-405.152 89	58.5	4.7	489	-43	11
Me	C≡CSiH ₃	15	-695.437 16	-695.345 60	57.5	3.7	498	-34	20
H	CH=CH ₂	16	-367.261 77	-367.180 70	50.9	-2.9	563	31	85
H	CH=CH ₂ (per) ^j		-367.250 56	-367.170 53	50.2	-3.6	570	38	92
Me	CH=CH ₂	17	-406.457 76	-406.370 90	54.5	0.7	525	-7	47
CH=CH ₂	CH=CH ₂	19	-444.433 90	-444.352 72	50.9	-2.9	563	31	85
C≡CH	CH=CH ₂	18	-443.222 55	-443.135 72	54.5	0.7	525	-7	47
H	phenyl ^k	20	-520.473 70	-520.393 46	50.4	-3.4	568	36	90
H	phenyl ^k (per) ^l		-520.460 48	-520.378 90	51.2	-2.6	559	27	81
	(CH ₂ =C)(CH ₂) ₃	21	-483.640 41	-483.553 67	54.4	0.6	526	-6	48
	(H ₂ C=C)(CH ₂) ₂	22	-521.624 43	-521.542 99	51.1	-2.7	560	28	82
	(CH ₂) ₄	23	-445.656 00	-445.558 00	61.5	7.7	465	-67	-13

^a In hartrees. ^b At MP4SDTQ/6-31G*. ^c At UMP4SDTQ/6-31G* (after spin projection⁸), at the optimized geometry of the ¹A' state. ^d In kcal/mol. ^e Relative to H₂Si: ^f λ_{\max} (in nm) calculated from $2.8618 \times 10^4 / \Delta E$. ^g $\lambda_{\max}(\text{RR'Si}) - \lambda_{\max}(\text{H}_2\text{Si})$, in nm. ^h $\lambda_{\max}(\text{RR'Si}) - \lambda_{\max}(\text{Me}_2\text{Si})$, in nm. ⁱ $\angle\text{HSiOH} = 90^\circ$. ^j $\angle\text{C}=\text{CSiH} = 90^\circ$. ^k The geometry was optimized at the 3-21G level. ^l $\angle\text{CCSiH} = 90^\circ$.

between calculated and experimental transition energies, for example, for SiH₂.^{9,10}

For all calculations we have used the Gaussian 88^{11a} and Gaussian 92^{11b} series of programs. The geometries of the ground states of all silylenes were optimized at the RHF/6-31G* level of theory¹² using standard gradient techniques,¹¹ and these geometries were identified to be minima on the potential energy surface by characterizing the calculated Hessian matrix.¹¹ The effect of electron correlation was included by carrying out single-point energy calculations at the 6-31G*-optimized geometries, with the Moller-Plesset perturbation theory up to fourth order, including all single, double, triple, and quadrupole excitations (denoted as MP4SDTQ/6-31G**//6-31G*).¹³ The energy of the "vertical" first excited ¹A'' state was calculated at the geometry of the ground state using the unrestricted Hartree-Fock (UHF) method,¹⁴ i.e., at the UMP4SDTQ/6-31G**//6-31G* level. The level of theory used in the current study is significantly higher than used in our previous work (i.e., 6-31G**//3-21G).⁵

2. Computational Results. The "vertical" transition energies were calculated for a series of mono- and disubstituted vinyl- and ethynylsilylenes, 11–19, as well as for HSiC₆H₅ (20). Calculations were also carried out for the mono- and disubstituted vinylsilylenes 21 and 22, respectively, which were recently prepared by Kira *et al.*,⁶ and for cyclopentylsilylene 23. For comparison with our previous calculations Me₂Si and HSiOH were recalculated using the spin-projection method.

(9) Using a large basis set and a correlated level (i.e., MP4/6-31G++G-(3d,3p)//HF/6-31G*), Francisco and co-workers^{10a} calculated that the ¹A₁–¹B₁ excitation energy in SiH₂ is 31.6 kcal/mol. Inclusion of the spin-projection method increased the ¹A₁–¹B₁ excitation energy to 44.1 kcal/mol,^{10a} in excellent agreement with the measured value of 44.4 kcal/mol.^{10b}

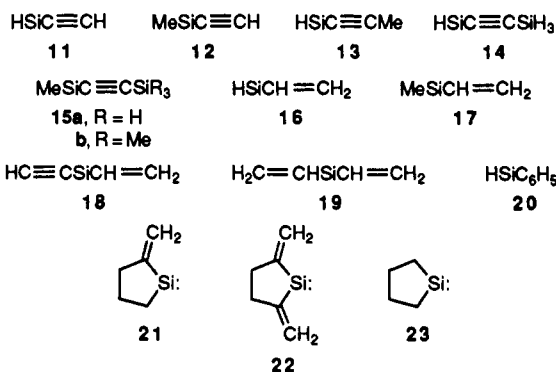
(10) (a) Francisco, J. S.; Barnes, R.; Thomas, J. W., Jr. *J. Chem. Phys.* **1988**, *88*, 2334. (b) Dubois, I.; Herzberg, G.; Verma, R. D. *J. Chem. Phys.* **1967**, *47*, 4262. Dubois, I. *Can. J. Phys.* **1968**, *46*, 2485.

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The calculated optimized geometries of the ¹A' state of 11–23 are given in Figure 2. The calculated total energies of the ¹A' and ¹A'' states of 11–23 and the calculated excitation energies are given in Table 2.

Discussion

Let us examine first the effect of the spin-projection method on the calculated transition of dimethylsilylene, a case where $\langle S^2 \rangle$ is only 1.037 at UHF/6-31G**//3-21G. Using eq 3 we have previously calculated that the excitation energy for the $n(\text{Si}) \rightarrow 3p(\text{Si})$ transition of Me₂Si is 57.9 kcal/mol at 6-31G**//3-21G,⁵ and 58.7 kcal/mol at MP4/6-31G**//6-31G*. Using the spin-projection method we calculate a ΔE of 59.9 kcal/mol. Thus, in this case the effect of spin contamination on ΔE is relatively small. Similar conclusions are reached for HSiOH, for which $\langle S^2 \rangle = 1.048$, and $\Delta E = 74.9, 75.6$, and 76.0 kcal/mol at 6-31G**//3-21G, at MP4/6-31G**//6-31G*, and at MP4/6-31G**//6-31G* + spin projection, respectively.

The experimentally determined λ_{\max} in Me₂Si is 453 nm, corresponding to a ΔE of 63.2 kcal/mol.^{1,3} Thus, at MP4SDTQ/6-31G**//6-31G*, even when spin projection is included, the calculations do not precisely duplicate the experimental excitation energies, the calculated ΔE being too small by 3.3 kcal/mol.^{15a} Assuming that this correction of 3.3 kcal/mol applies also to other silylenes,^{15b} it can be used to correct the calculated excitation energies of other silylenes. We will see below that this correction

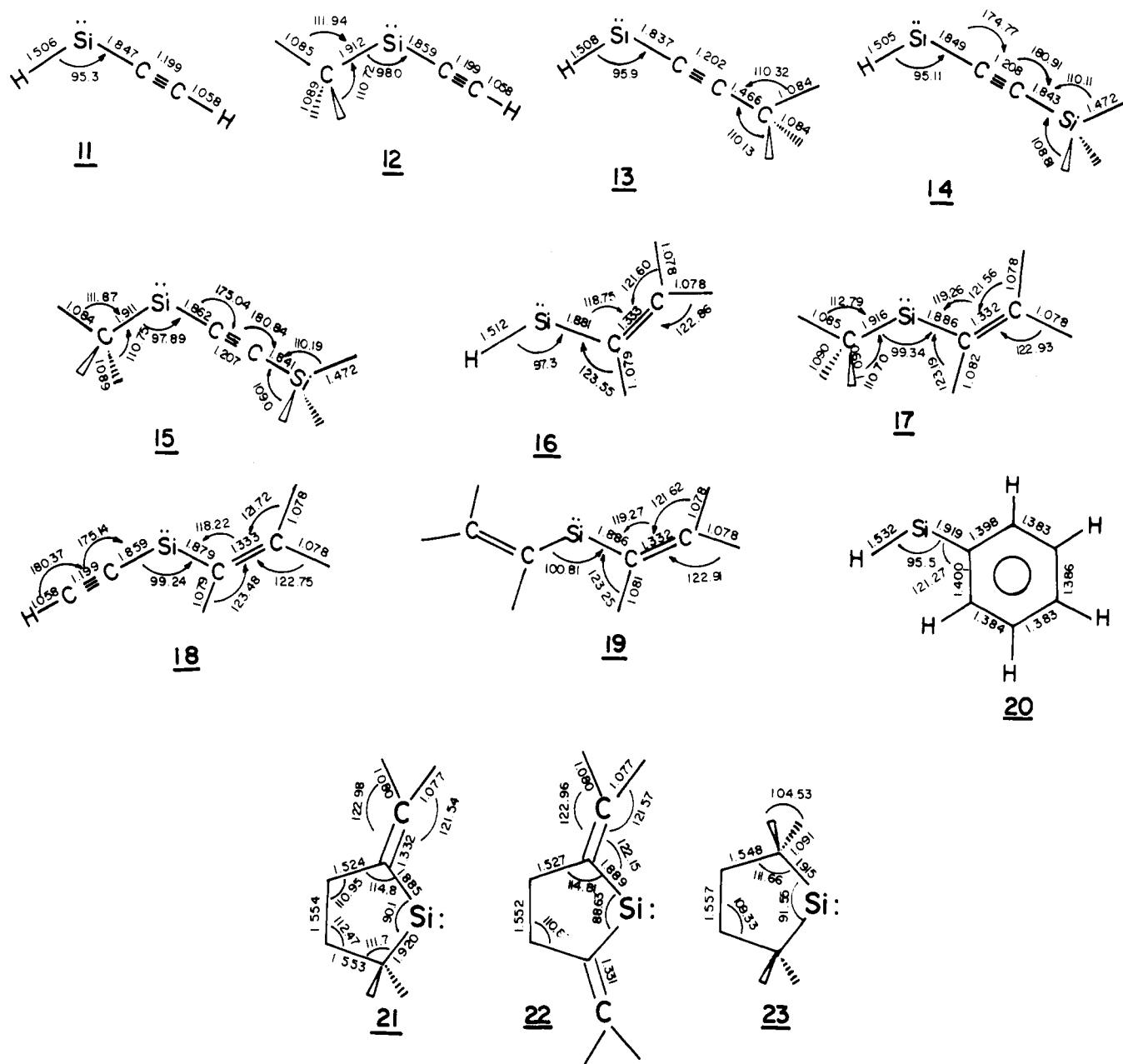


Figure 2. Optimized geometries (C_s symmetry) at 6-31G* of various silylenes.

indeed brings the calculations into a better quantitative agreement with experiment.

A. Ethynylsilylenes. The comparison of the measured λ_{\max} values for Me_2Si and $\text{MeSiC}\equiv\text{CSiMe}_3$ shows a red shift of 20 nm (Table 1). However, as our attempts to observe $\text{MeSiC}\equiv\text{CH}$ failed, it could not be established whether the observed red shift is due to the ethynyl group or to the Me_3Si substitution, which according to the calculations⁵ is indeed expected to induce a red shift. This analysis can be done using the computational results.

The calculated transition energies along the series $\text{H}_2\text{Si} \rightarrow \text{HSiC}\equiv\text{CH} \rightarrow \text{HSiC}\equiv\text{CSiH}_3$ and $\text{MeSiH} \rightarrow \text{MeSiC}\equiv\text{CH} \rightarrow \text{MeSiC}\equiv\text{CSiH}_3$ show that, in both series, substitution of hydrogen by ethynyl or by silylethynyl substituents induces a very small blue shift in the $n\text{--}3p$ transition (Scheme 2A). In the first series

we find that the $n\text{--}3p$ excitation energy is increased by 1.2 kcal/mol ($\Delta\lambda = -12$ nm) by ethynyl substitution. Similar results are obtained for the disubstituted silylene series: The ethynyl substituent increases ΔE by 2.0 kcal/mol, i.e., causing a blue shift of 18 nm. In our previous calculations using eq 3, the predicted blue shift due to ethynyl substitution in H_2Si was much larger (i.e., $\Delta\lambda = -71$ nm, $\Delta\Delta E = 8.2$ kcal/mol).⁵

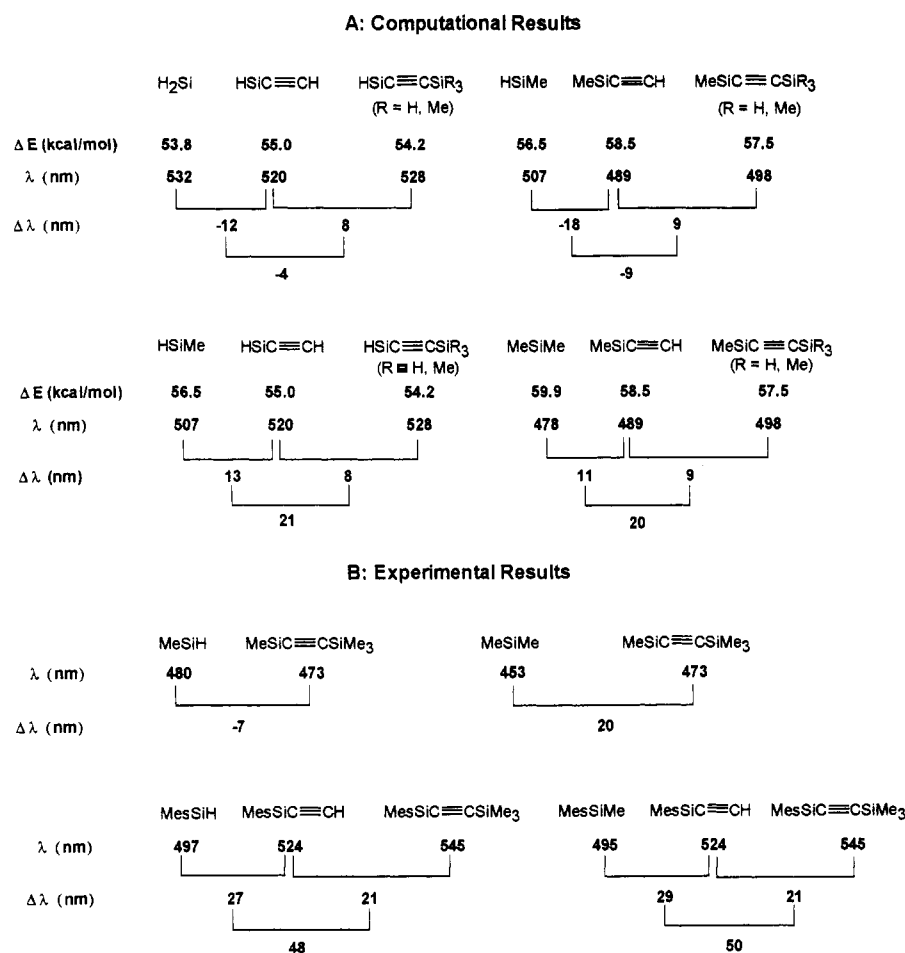
In both series, substitution of the hydrogen on the ethynyl group by a silyl group induces a small red shift, 8 and 9 nm for $\text{HSiC}\equiv\text{CSiH}_3$ and $\text{MeSiC}\equiv\text{CSiH}_3$, respectively (Scheme 2A). So overall, substitution of hydrogen by a $\text{C}\equiv\text{CSiH}_3$ group induces a small blue shift, of only 4 and 9 nm in the primary and secondary silylenes, respectively (Scheme 2A). Further, the calculations show that substitution of the SiH_3 group by a SiMe_3 group has no effect on λ_{\max} (Scheme 2A).

The computational conclusion is that, in both series, substitution of hydrogen by an ethynyl substituent introduces a small blue shift of ca. 12–18 nm, and further substitution of the ethynyl hydrogen by SiH_3 or SiMe_3 reduces the blue shift to only 4–9 nm.

Substitution of the silylene hydrogen in $\text{HSiC}\equiv\text{CH}$ or in $\text{HSiC}\equiv\text{CSiH}_3$ by a methyl group, to give $\text{MeSiC}\equiv\text{CH}$ and

(15) (a) In more elaborate calculations which were performed by Grev and Schaefer, a value of 456 nm ($\Delta E = 62.8$ kcal/mol) was calculated for the "vertical" transition in Me_2Si (these calculations, which achieved a much better agreement with experiment, used a triple- ζ quality basis set and a CI treatment which included all singly- and doubly-excited configurations (CISD) and the Davidson's correction for quadrupole excitation); see: Grev, R.; Schaefer, H. F., III. *J. Am. Chem. Soc.* 1986, 108, 5804. (b) The correction in λ_{\max} ($\Delta\lambda$) depends on the absorption maximum and is given by the equation: $\Delta\lambda(\text{nm}) = 2.8618 \times 10^4 \times 3.3 / [\Delta E_{\text{cal}}(\Delta E_{\text{cal}} + 3.3)]$.

Scheme 2. n-3p Electronic Transition Energies for Ethynylsilylenes



$\text{MeSiC}\equiv\text{CSiH}_3$, increases ΔE by 3.5 and 3.3 kcal/mol, respectively. A similar methyl effect is found along the series H_2Si : $\rightarrow \text{HMeSi}$: $\rightarrow \text{Me}_2\text{Si}$: ($\Delta E = 53.8, 56.5, 59.5$ kcal/mol, respectively). In the latter series the calculated effect of the methyl group is in excellent agreement with the experimental results (see Tables 1 and 2). Relative to Me_2Si , λ_{max} of $\text{MeSiC}\equiv\text{CH}$ is calculated to be *red shifted* by 11 nm (Scheme 2A). This *red shift* results from the fact that substitution of hydrogen in HSiMe by a methyl group causes a *larger blue shift* (i.e., 29 nm) than substitution of hydrogen by an ethynyl group (i.e., 18 nm). The red shift relative to methyl is increased to 20 nm by changing $\text{C}\equiv\text{CH}$ to $\text{C}\equiv\text{CSiH}_3$ or $\text{C}\equiv\text{CSiMe}_3$.

The agreement between the above theoretical results and our new experimental measurements is excellent, as seen by comparing Scheme 2A (calculated values) and Scheme 2B (experimental values). Thus, the calculated blue shift of 9 nm observed when comparing MeSiH with $\text{MeSiC}\equiv\text{CSiMe}_3$ is almost identical to the experimental value of 7 nm. Similarly, the calculated and experimental red shift of 20 nm when comparing MeSiMe with $\text{MeSiC}\equiv\text{CSiMe}_3$ is incidentally identical. Furthermore, inclusion of the above mentioned empirical correction of 3.3 kcal/mol brings the calculated and measured λ_{max} into excellent agreement (Scheme 2). For example, the "corrected" calculated λ_{max} for $\text{MeSiC}\equiv\text{CSiMe}_3$ is $498-27^{15b} = 471$ nm, incidentally identical to the value measured for $\text{MeSiC}\equiv\text{CSiMe}_3$ (Table 1). As explained above, the calculations allow us to conclude reliably that the red shift of 20 nm observed when comparing Me_2Si and $\text{MeSiC}\equiv\text{CSiMe}_3$ does not reflect the inherent tendency of the ethynyl group to decrease the $^1A' - ^1A''$ gap. On the contrary, an ethynyl group induces a blue shift compared to hydrogen, which, however, is smaller than the effect of a methyl group, causing, therefore, a red shift relative to methyl.

An interesting experimental observation is that, in mesitylsilylenes, substitution of hydrogen or methyl by $\text{C}\equiv\text{CH}$ or by $\text{C}\equiv\text{CSiMe}_3$ causes a much larger shift in λ_{max} than in the corresponding methylsilylenes (Scheme 2B). For example, in going from MesSiMe to $\text{MesSiC}\equiv\text{CSiMe}_3$, λ_{max} is red shifted by 50 nm compared to a shift of only 20 nm on going from Me_2Si to $\text{MeSiC}\equiv\text{CSiMe}_3$. The larger red shifts in the mesitylsilylenes may reflect specific geminal electronic interactions between the aromatic substituent and the ethynyl group, but they may also reflect problems in the assignment of the experimental absorptions. Unfortunately, for such large silylenes we are not yet able to carry out calculations which will allow detailed analysis of these interesting spectral shifts.




B. Vinyl and Phenyl Substitution. The most relevant calculated and experimental data regarding vinyl- and phenyl-substituted silylenes are presented in Scheme 3.

The calculations predict that substitution of the parent silylene with a vinyl substituent causes a significant red shift of 31 nm, in contrast to a similar substitution by an ethynyl group which induces a blue shift of 12 nm. In methylsilylene, substitution of H by a vinyl group causes a smaller red shift of 18 nm ($\text{MeSiH} \rightarrow \text{MeSiCH}=\text{CH}_2$, Scheme 3A). The smaller effect of a vinyl substituent when it is a second substituent is expected, as the electronic demand on the vinyl substituent is reduced compared to the case where it is a single substituent.¹⁶ Substitution of a methyl group by either a vinyl or an ethynyl substituent causes a red shift, but the shifts are significantly larger for vinyl substitution. Thus, red shifts of 56 and 47 nm are calculated for the comparisons: $\text{HSiMe} \rightarrow \text{HSiCH}=\text{CH}_2$ and $\text{MeSiMe} \rightarrow$

(16) (a) Troung, T.; Gordon, M. S.; Boudjouk, P. *Organometallics* **1984**, 3, 484. (b) See also: Apeloig, Y. In *Heteroatom Chemistry*; Block, E., Ed.; VCH: New York, 1990; p 27.

Scheme 3. *n*-3p Electronic Transition Energies for Vinyl- and Arylsilylenes**A: Computational Results****a) Vinyl Substitution**




	H ₂ Si	HSiCH=CH ₂	(H ₂ C=CH) ₂ Si:	MeSiH	MeSiMe	MeSiCH=CH ₂
ΔE (kcal/mol)	53.8	50.9	50.9	56.5	59.9	54.5
λ (nm)	532	563	563	507	478	525
Δλ (nm)		31	0		29	47

	MeSiMe	MeSiCH=CH ₂	(H ₂ C=CH) ₂ Si:	MeSiMe			
ΔE (kcal/mol)	59.9	54.5	50.9	59.9	61.5	54.4	51.1
λ (nm)	478	525	563	478	465	526	560
Δλ (nm)		47	38		-13	61	34
			85			48	

b) Phenyl Substitution

	H ₂ Si	HSiPhenyl	HSiMe	HSiPhenyl
ΔE (kcal/mol)	53.8	50.4	56.5	50.4
λ (nm)	532	568	507	568
Δλ (nm)		36		61

B: Experimental Results**a) Vinyl Substitution**

	MeSiMe				
λ (nm)		453	436	475	505
$\Delta\lambda$ (nm)			-17	39	30
				22	

b) Phenyl Substitution

	MeSiH	MeSiPhenyl	MeSiMe	MeSiPhenyl
λ (nm)	480	490	453	490
Δλ (nm)		10		37

	HSiMe	HSiMes	MeSiMe	MeSiMes
λ (nm)	480	497	453	495
Δλ (nm)		17		42

MeSiCH=CH₂, respectively (Scheme 3A), compared to only 13 and 11 nm for the corresponding ethynyl substitutions (Scheme 2A).

Unfortunately, the UV-visible spectra of simple vinyl-substituted silylenes such as HSiCH=CH₂ or MeSiCH=CH₂ which can be compared directly with the calculations have not yet been measured. However, Kira and Sakurai have recently reported the electronic spectra of the vinylsilylenes **21** and **22**.⁶ An appropriate reference molecule for elucidating the effect of the vinyl substituents in **21** and **22** is the cyclic silylene **23**.¹⁷ The measured λ_{max} for **21** is 475 nm, and it is therefore red shifted

by 39 nm relative to **23**. This shift is in reasonably good agreement with the predicted shift of 47 nm, which results from the comparison of the calculated λ_{max} for Me₂Si and MeSiCH=CH₂. The measured λ_{max} for the divinyl-substituted silylene **22**, at 505 nm, is red shifted by 30 nm relative to **21**. This result is in very good agreement with the theoretical model calculations; i.e.,

(17) λ_{max} of **23** is at 436 nm, blue shifted by 17 nm relative to Me₂Si³ (this is in good agreement with the calculated shift of 13 nm). We believe that this shift is due to the smaller angle around the silicon center in **23** (91.5°), relative to 98.0° in Me₂Si (both values at 6-31G*). As discussed previously,⁵ the more acute angle in **23** results in a higher excitation energy.

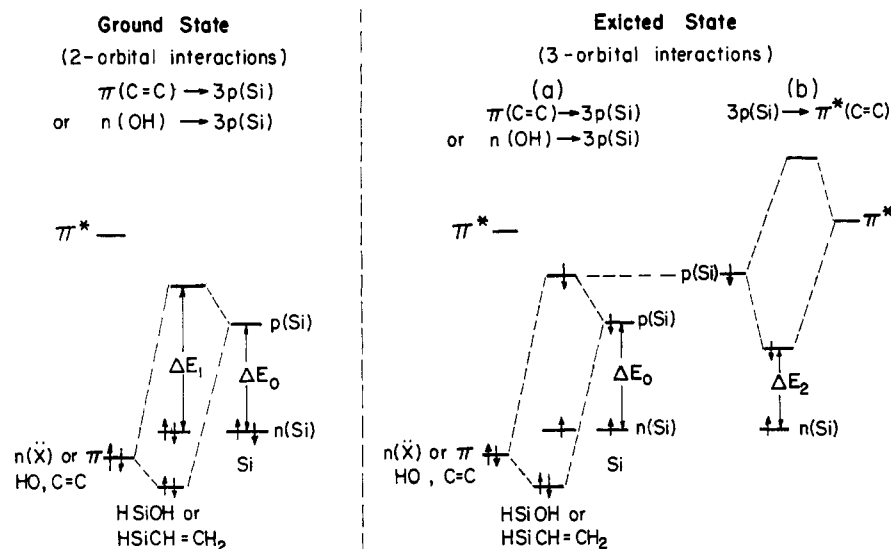


Figure 3. Schematic orbital interaction diagram for HSiCH=CH₂ and HSiOH in the ground state and in the excited state. ΔE_0 , ΔE_1 , and ΔE_2 denote the vertical excitation energies in H₂Si, HSiOH, and H₂C=CHSiH, respectively.

comparison of the calculated λ_{\max} in **17** and **19** predicts a red shift of 38 nm (Scheme 3A).

We have gone one step further and have calculated directly the ΔE values in **21**, **22**, and **23**. The calculated λ_{\max} values of **23**, **21**, and **22** are 465, 526, and 560 nm, respectively. The absorption band for **22** is calculated to be red shifted relative to **21** by 34 nm, in very good agreement with the measured shift of 30 nm and with the calculated shift in the simpler model systems **19** → **17** (38 nm). The monovinyl cyclopentylsilylene **21** is calculated to be red shifted relative to **23** by 61 nm, 22 nm more than the value of 39 nm measured by Kira et al.⁶ Apparently, in this case, the calculations exaggerate the effect of the first vinyl substituent.

A second substitution usually has a smaller effect than the first, because the electronic demands on the substituent are smaller.¹⁶ This is revealed by both the experimental and the theoretical trends for the series **23** → **22** → **21** (Scheme 3). Interestingly, the calculations predict that substitution of hydrogen in HSiCH=CH₂ by a second vinyl group has no effect on λ_{\max} (Scheme 3A), so that λ_{\max} of (H₂C=CH)₂Si: and of H₂C=CHSiH are predicted to be identical, at 563 nm. Apparently, the expected small red shift which should result from the reduced resonance effect of the second vinyl group is precisely offset by the blue shift expected to result from the electron-withdrawing inductive effect of the vinyl group,⁵ which is more electronegative than hydrogen (the corresponding σ_1 values are 0.07 and 0.0, respectively¹⁸).

As the spectrum of many phenyl- or mesityl-substituted silylenes were measured experimentally, we have also calculated the ΔE gap in HSiPh. The calculations predict that phenyl and vinyl groups should have a similar effect on the absorption spectra of silylenes. Thus, substitution of H in H₂Si by a phenyl group induces a red shift of 36 nm, only 5 nm larger than the effect of a vinyl group. We therefore conclude that a vinyl group can serve as a good computational model for studying the effect of aryl substituents on the electronic spectra of silylenes. This conclusion is important because calculations for diarylsilylenes are not possible with our current computational resources.

The trends observed experimentally for aryl-substituted silylenes (Scheme 3B) are in qualitative agreement with the theoretical predictions, using the vinyl group as a model for phenyl, except that the calculated shifts are somewhat larger than the experimental values. The measured red shift in comparing MeSiH

and MeSiPh is 10 nm, compared to a calculated value of 18 nm (comparison of MeSiH and MeSiCH=CH₂). For the substitutions MeSiMe → MeSiPh and MeSiMe → MeSiMes, the experimentally measured red shifts are 37 and 42 nm, respectively. The calculated value for MeSiMe → MeSiCH=CH₂ of 47 nm (Scheme 3A) is in good qualitative agreement. The calculated prediction that a second vinyl group has no effect on λ_{\max} (Scheme 3A) combined with the similarity of the effects of vinyl and phenyl groups can explain why the λ_{\max} values for MeSiPh (490 nm) and PhSiPh (495 nm) are so similar, while in HSiMe substitution of Me by phenyl resulted in a red shift of ca. 61 nm (Scheme 3A).

On the basis of the excellent experimental-theoretical agreement demonstrated above, the calculations can be now used with confidence to analyze critically existing spectroscopic data and to predict the spectra of yet unknown silylenes. The two examples below illustrate this point: (1) the 17 nm red shift which was measured³ for the substitution HSiMe → HSiMes (Table 1 and Scheme 3B) is much smaller than the values of 56 and 61 nm calculated for the analogous vinyl substitution (i.e., HSiMe → HSiCH=CH₂) and phenyl substitution (i.e., HSiMe → HSiPh). Furthermore, the reported λ_{\max} values of HSiMes, MeSiMes, and MeSiPh are almost identical (i.e., 497, 495, and 490 nm, respectively). However, we found both theoretically and experimentally that substitution of a hydrogen by a methyl group, even when the silylene is already substituted by a second group, causes a blue shift of about 30–40 nm in λ_{\max} (see Tables 1 and 2). On the basis of the above considerations and the generally good agreement for similar systems between the calculations and experiment, we predict that HSiMes actually absorbs around 530 nm, and we therefore suggest that the absorption band at 497 nm originally attributed to HSiMes is actually due to a different species.^{19a} (2) Prediction of λ_{\max} for MeSiSiMe₃.^{19b} These two specific examples nicely demonstrate the importance of the experimental-theoretical collaboration in studying silylenes.

C. Analysis of the Effects of Ethynyl, Vinyl, and Phenyl Substituents on λ_{\max} . The discussion above shows that the calculations reproduce with good accuracy the measured substituent effects on the absorption maximum in the UV-visible spectra of substituted silylenes. In addition to this predictive power the calculations also provide an excellent tool for analyzing and understanding these substituent effects.

In general, substituents can affect λ_{\max} by both electronic and steric effects. Steric effects can affect the angle α at silicon and thus cause a red shift or a blue shift, depending on whether α increases or is reduced.^{5,17} Electronically, the substituent effects can be discussed in terms of their inductive and conjugative effects.

(18) Charton, M. *Prog. Phys. Org. Chem.* **1987**, *16*, 287. Exner, O. In *Correlation Analysis in Chemistry*; Chapman, N. B.; Shorter, J., Eds.; Plenum: London, 1978; Chapter 10.

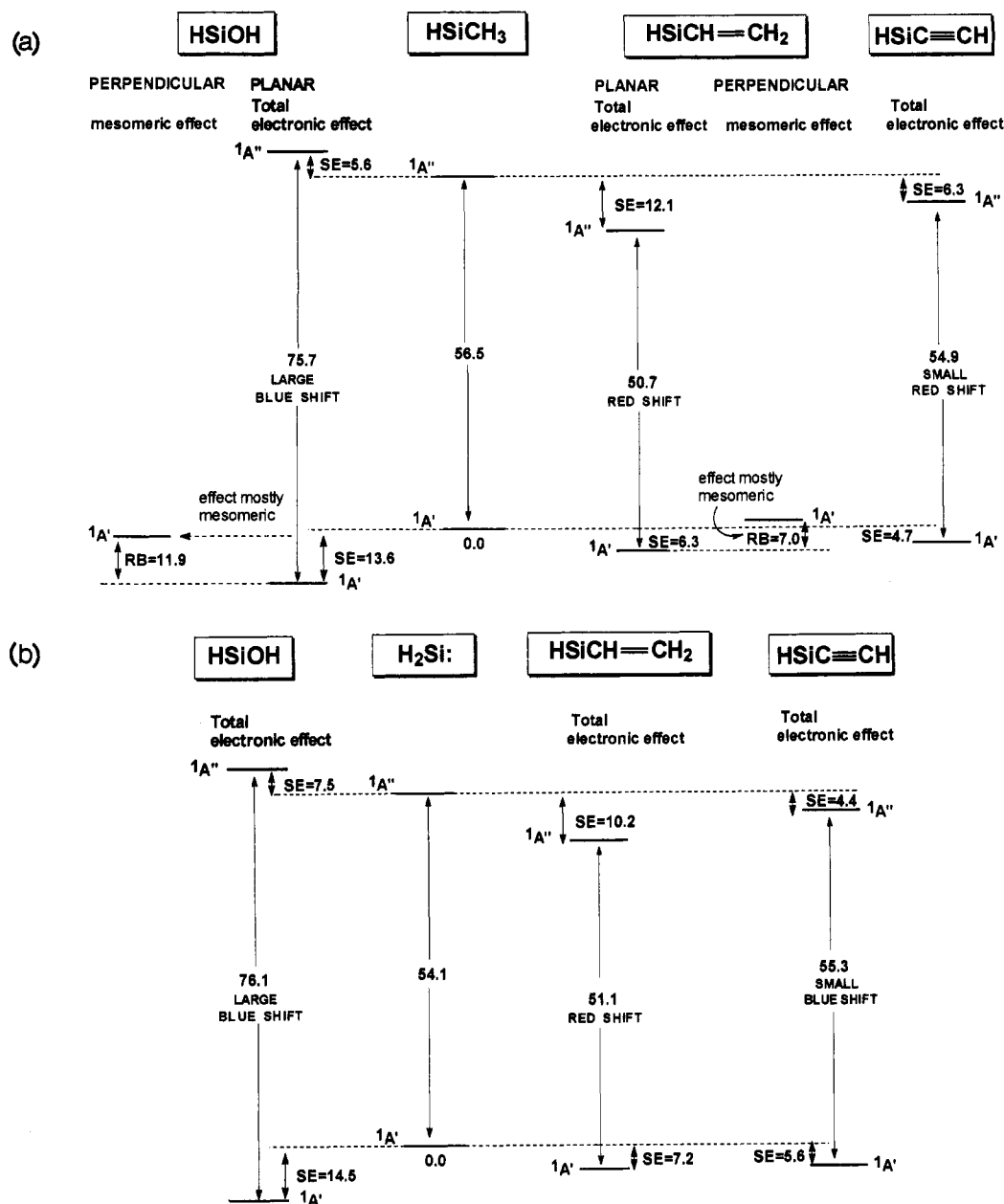


Figure 4. (a) Excitation and stabilization energies in the ground and first excited states relative to HSiCH_3 (eq 4) in RSiH , $\text{R} = \text{OH}$, $\text{H}_2\text{C}=\text{CH}$, and $\text{HC}\equiv\text{C}$, and rotation barriers in the ground states of HSiOH and $\text{HSiCH}=\text{CH}_2$ (all values in kcal/mol). (b) Excitation and stabilization energies (in kcal/mol) relative to H_2Si in the ground and first excited states (eq 5) of HSiOH , $\text{HSiC}\equiv\text{CH}$, and $\text{HSiCH}=\text{CH}_2$. The excitation energies in this figure are larger than in Figure 4a, resulting from the fact that they use eqs 4 and 5, respectively, the difference of which is 0.4 kcal/mol.

Electronegative substituents increase ΔE , as well as the singlet-triplet gap,^{20–22} and thus induce blue shifts in the UV–visible

(19) (a) This point is under further investigation in our laboratories. (b) The photolysis of $\text{MesSi}(\text{SiMe}_3)_3$ in 3-MP produced a species with a λ_{max} of 368 nm, assigned at the time to MesSiSiMe_3 .³ On the basis of the current calculations we conclude that this absorption is probably also due to a different molecule. Thus, on going from Me_2Si to MeSiSiH_3 a very large red shift of 17.7 kcal/mol (200 nm) is calculated, and MeSiSiH_3 is calculated to have a λ_{max} of 678 nm. As substitution of Me in Me_2Si by Mes causes a red shift of 42 nm (Scheme 3B), MesSiSiMe_3 is predicted by our calculations to absorb at ca. $678 + 42 = 720$ nm. Recently Kira, Sakurai, *et al.* (*Chem. Lett.* 1993, 1345) reported that MesSiSiMe_3 absorbs at 760 nm, in reasonable agreement with our prediction. Similar results were independently reported by Conlin *et al.* (XXV Silicon Symposium, Los Angeles, April 1992, Paper No. 7). A second substitution of Me by H_2Si also produces a large red shift (although smaller than the shift due to the first substitution) of $\Delta\lambda_{\text{max}} = 132$ nm ($\Delta\Delta E = 6.9$ kcal/mol). The yet noncharacterized $(\text{H}_2\text{Si})_2\text{Si}$ ($\alpha = 95.4^\circ$) is predicted to absorb at 810 nm. The absorption of the experimentally more accessible $(\text{Me}_3\text{Si})_2\text{Si}$ is predicted to be at a longer wavelength of 987 nm due to the larger angle at silicon ($\alpha = 106^\circ$).

(20) (a) Luke, B. T.; Pople, J. A.; Krogh-Jespersen, M.-B.; Apeloig, Y.; Karni, M.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* 1986, 108, 270. (b) Shin, S. K.; Goddard, W. A., III; Beauchamp, J. L. *J. Phys. Chem.* 1990, 94, 6963.

spectrum of silylenes. This can be understood in terms of Bent's rule²³ by the effect that such substituents have on the hybridization and energy of the $n(\text{Si})$ orbital.^{20–22}

Conjugation between the substituent and the empty $3p(\text{Si})$ orbital in the ground-state singlet and/or with the half-filled orbitals in the first excited state can have a strong effect on the electronic spectrum of silylenes.²² n donors such as OH and NH_2 significantly stabilize the singlet ground state by conjugation with the empty $3p(\text{Si})$ orbital, while the excited state is actually destabilized by these substituents (Figure 3, see also below). As

(21) For a similar consideration regarding carbenes, see: (a) Harrison, J. F.; Liedtke, R. C.; Liebman, J. F. *J. Am. Chem. Soc.* 1979, 101, 7162. (b) Liebman, J. F.; Simons, J. In *Molecular Structure and Energetics*; Liebman, J. F., Greenberg, A., Eds.; VCH Publishers: New York, 1986; Vol. 1, p 51. (c) Jones, M., Jr.; Moss, R. A. *Reactive Intermediates*; John Wiley & Sons, Inc.: New York, 1985; Vol. 3, p 45.

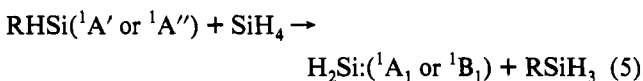
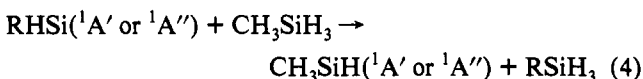
(22) For the effect of π donation on the singlet–triplet splitting in carbenes, see: Feller, D.; Borden, W. T.; Davidson, E. R. *Chem. Phys. Lett.* 1980, 71, 22.

(23) Bent, H. A. *J. Chem. Educ.* 1960, 37, 616; *J. Chem. Phys.* 1960, 33, 1258, 1259, 1260; *Chem. Rev.* 1961, 61, 275.

a result, n donors cause large blue shifts; e.g., ΔE in HSiOH is 75.7 kcal/mol compared to only 56.5 kcal/mol in HSiMe.²⁴

The ethynyl, vinyl, and phenyl substituents are all much weaker π donors than OH or NH₂, so the stabilization and thus the blue shift resulting from π conjugation are expected to be smaller. However, as discussed above, these unsaturated substituents actually produce red shifts relative to HSiMe. The different behavior of n donors such as OH and π donors such as vinyl is best understood qualitatively as resulting from the presence of a π^* orbital in the unsaturated ligands. According to simple frontier molecular orbital (FMO) theory,²⁵ the low-lying empty π^* orbital stabilizes the excited singlet by interacting with the half-filled 3p(Si) orbital (in contrast to the case with n -donor substituents where only the ground state is stabilized), reducing the $^1A' - ^1A''$ energy gap.²⁶ These FMO interactions are schematically displayed in Figure 3. In the ground state the $\pi(C\equiv C) \rightarrow 3p(Si)$ two-electron interaction results in a lowering of the π -electron energy (i.e., stabilization of the silylene). At the same time the empty 3p(Si) orbital is "pushed up" in energy, broadening the gap between the n orbital of Si (which to a first approximation remains unchanged²⁷) and the 3p(Si) orbital (i.e., $\Delta E_1 > \Delta E_0$). The situation in the excited state is more conveniently analysed in two steps: First, the same $\pi(C\equiv C) - 3p(Si)$ interactions occur, but now the 3p(Si) orbital is singly occupied. Second, the singly occupied 3p(Si) orbital interacts with the available low-lying empty π^* orbital, resulting in a significant lowering of the half-filled 3p(Si) orbital and therefore in an overall stabilization of the excited state and in a smaller excitation energy (i.e., $\Delta E_2 < \Delta E_0$, Figure 3).

Further insight and a more quantitative analysis of the effects of the vinyl, phenyl, and ethynyl substituents can be gained by calculating the stabilization energies (SEs) for the two states, relative to HMeSi (via the isodesmic equation 4) and relative to H₂Si (via isodesmic equation 5). The results are summarized in Table 3 and for HSiOH, HSiCH=CH₂, and HSiC≡CH also presented graphically in Figure 4.



Let us consider first a typical n donor, the hydroxyl group. The calculated SEs of eq 4 (Table 3) show that a hydroxyl substituent stabilizes strongly the $^1A'$ ground state (by 13.6 kcal/mol relative to a methyl group), but it destabilizes the excited state by 5.6 kcal/mol. As a result the $^1A' - ^1A''$ gap increases substantially, by 19.2 kcal/mol (Figure 4). As suggested qualitatively by Figure 3, the situation is entirely different for vinyl substitution. Both states are stabilized by a vinyl group, but the excited state is stabilized more strongly, i.e., by 6.3 and 12.1 kcal/mol for the $^1A'$ and $^1A''$ states, respectively (Figure 4a). As a result, the $^1A' - ^1A''$ energy gap is decreased by 5.8 kcal/mol relative to HSiMe (Figure 4a). In terms of the qualitative analysis in Figure 3, this indicates that the $\pi(C\equiv C) - 3p(Si)$ two-electron interaction present in the ground state is less stabilizing than the sum of the interactions: (a) the interaction

(24) Part of the 19.2 kcal/mol difference in ΔE can be attributed to the fact that the $n(Si)$ orbital in HSiOH is by 7.2 kcal/mol lower in energy than in HSiMe (at 6-31G*).

(25) Fleming, I. *Frontier orbitals and organic chemical reactions*; Wiley: London, 1976.

(26) This qualitative explanation was proposed also by Kira et al.,⁶ to explain the observed red shift in the spectra of 21 and 22, and previously also by West et al., to account for the bathochromic shift observed for arylsilylenes.^{1,3}

(27) The calculated energy of the $n(Si)$ orbital (at 6-31G*) is indeed only 0.3 kcal/mol lower in HSiCH=CH₂ than in HSiCH₃, while the calculated red shift for this substitution is 5.6 kcal/mol (56 nm).

between the single electron in the 3p(Si) orbital and the π^* ($C\equiv C$) orbital and (b) the $\pi(C\equiv C) - 3p(Si)$ three-electron interaction, present in the excited state.

Further understanding is gained by examining the barriers to rotation around the bond connecting the substituent to silicon in the ground state of the silylenes (Table 3 and Figure 4). To a first approximation these rotation barriers (RBs) measure the degree of conjugation between the silylene center and the substituent. As expected, the rotation barrier is the largest in HSiOH (11.9 kcal/mol) because the strongly stabilizing 2p(O) - 3p(Si) two-electron interaction in the planar form is "switched off" in the perpendicular conformation and is replaced by a four-electron destabilizing interaction between 2p(O) and $n(Si)$.²⁸ In H₂C=CHSiH and HSiPh the RBs are smaller, 7.0 and 7.3 kcal/mol, respectively, reflecting their weaker conjugation ability. The fact that in all these cases the SEs and the RBs are quite similar shows that π conjugation between the 3p(Si) orbital and the substituent indeed plays the major role in stabilizing the ground state of the silylenes.²⁹

A comparison of the rotation barriers in H₂C=CHSiH with those in H₂C=CHSiH₂⁺ and H₂C=CHSiH₂^{*} is of some interest. The calculated rotation barrier in H₂C=CHSiH₂⁺ is significantly higher (i.e., by 11.5 kcal/mol at MP4SDTQ/6-31G**//6-31G*)³⁰ than in H₂C=CHSiH. This is expected as in the cation the demand for resonance stabilization is larger than in the neutral silylene. A similar trend is observed when one compares the rotation barriers around the C-C bond in the allyl cation and in the corresponding vinyl carbene.³¹ The rotation barrier in the radical H₂C=CHSiH₂^{*}, 5.3 kcal/mol (MP4SDTQ/6-31G**//6-31G*), is significantly smaller than in H₂C=CHSiH and may serve as a model for the rotation barrier in the excited $^1A''$ state of H₂C=CHSiH²⁹ since in both cases the interaction that stabilizes the planar conformer involves a three-electron $\pi - 3p - (Si)$ interaction.

(28) At the same time a destabilizing four-electron $sp^2(O) - n(Si)$ interaction in the planar form is replaced by a stabilizing two-electron $sp^2(O) - 3p(Si)$ interaction in the perpendicular conformer, but this change is apparently less important.

(29) The RBs in the excited states cannot be calculated rigorously using single-determinant theory because in the perpendicular conformation the ground state and the first excited state have both C₁ symmetry. Interestingly, we found that, by using the ALTER procedure, the Gaussian program allows one to calculate the perpendicular conformation of the first excited state exhibiting the *desired* electronic configuration. Using this procedure we calculate the following RBs for the $^1A''$ excited states (MP4/6-31G**//6-31G*, the planar and the perpendicular conformers having both the optimized geometries of the ground states): HSiOH (-2.2 kcal/mol, the perpendicular form is the more stable); H₂C=CHSiH (7.0 kcal/mol); C₆H₅SiH (8.3 kcal/mol). Using this data and keeping in mind the above-mentioned caution, the following interesting conclusion can be reached: The similar rotation barriers in the ground state (Table 3) and in the excited singlet states of vinyl- and phenylsilylenes indicate that rotation of these groups should not affect significantly the first excitation energy of these silylenes. We therefore attribute the red shift observed on going from PhSiPh (495 nm) to MesSiPh (530 nm) and the MesSiMes (577 nm) mainly to a widening of the RSiR' angle (α) as a result of steric congestion, rather than to rotations of the aryl groups. Relatively small changes in α are required to produce the observed shifts. For example, in HSiPh, widening of α from 95.5° (fully optimized geometry) to 100°, 105°, and 110° produces red shifts of 37, 85, and 144 nm, respectively (at MP4SDTQ/6-31G**//6-31G* and including spin projection). Thus, according to these calculations α is predicted to be around 100° and 105° in MesSiPh and MesSiMes, respectively. In contrast to vinyl and phenyl, rotation of a hydroxy (or amino) substituent away from a planar conformation is predicted to cause a relatively large change in the absorption wavelength. These findings support our previous interpretation that the blue shift observed upon annealing of matrices containing (aryloxy)silylenes, e.g., ArOSiMes, is due to relaxation of the geometry of the silylene from a trapped rotated conformation with λ_{max} 425-430 nm to a more stable planar conformer absorbing at 400 nm. (Gillett, G. R.; Noren, G.; West, R. *Organometallics* 1990, 9, 2925. Ar = mesityl and 2,6-diisopropylphenyl.) A similar relaxation phenomenon might be responsible for the inner inconsistency between the reported λ_{max} values for HSiOMe and MeSiOMe of 340 and 355 nm, respectively (Maier, G.; Reisenauer, H. P.; Schottler, K.; Wessolek-Kraus, U. *J. Organomet. Chem.* 1989, 366, 25), indicating a "red" shift due to methyl substitution. In all other known cases (see Tables 1 and 2) a methyl group induces blue shifts of ca. 25-40 nm. The theoretically predicted λ_{max} for HSiOH is 376 - 15^{15b} = 361 nm.

(30) Apeloig, Y. Unpublished results.

(31) Dorigo, A. E.; Li, Y.; Houk, K. N. *J. Am. Chem. Soc.* 1989, 111, 6942.

Table 3. Stabilization Energies (SEs) Relative to HMeSi (Eq 4) and H₂Si (Eq 5) of RSiH, R = OH, H₂C=CH, C₆H₅, and HC≡C, and Rotation Barriers (RBs) around the Si-Substituent Bond in the Ground State of HSiOH, H₂C=CHSiH, and HSiC₆H₅^a

silylene	state	SE (eq 4) ^b	SE (eq 5) ^c	RB ^d
HSiOH	¹ A'	13.6	14.5	11.9
	¹ A'' ^e	-5.6	-7.5	
H ₂ C=CHSiH	¹ A'	6.3	7.2	7.0
	¹ A'' ^e	12.1	10.2	
HSiC ₆ H ₅	¹ A'/ ^f	5.8		8.3 ^g
	¹ A'' ^e	12.9		
HC≡CSiH	¹ A'	4.7	5.6	
	¹ A'' ^e	6.3	4.4	

^a In kcal/mol. ^b Calculated at MP3/6-31G**//6-31G* according to eq 4. A positive value indicates that RSiH is more stable than MeSiH. ^c Calculated at MP3/6-31G**//6-31G* according to eq 5. ^d At MP4SDTQ/6-31G**//6-31G*. The geometries of the perpendicular conformers were fully optimized except for the HSiCC (or HSiOH) dihedral angle, which was kept at 90°. ^e At the geometry of the ¹A' state. ^f Geometry optimized at 3-21G. ^g At MP4SDTQ/6-31G**//3-21G.

The calculated stabilization energies (SEs) for the ethynyl group relative to a methyl group (eq 4) are quite modest: 4.7 kcal/mol for the ground state and 6.3 kcal/mol for the excited state. This difference between the stabilization of the two states of 1.5 kcal/mol is reflected in the small red shift of 13 nm in λ_{\max} of HSiC≡CH relative to HSiMe. For H₂C=CH the difference in the SEs (relative to HSiMe) between the two states is significantly larger (5.8 kcal/mol), and so is the resulting red shift. The calculations for eq 5 show that relative to H₂Si the shift is in the opposite direction for the ethynyl substituent which induces a blue shift of 12 nm (1.2 kcal/mol). This is due to the fact that the ground state is now stabilized more strongly (by 5.6 kcal/mol) than the excited state (4.4 kcal/mol, Table 3). In contrast, relative to H₂Si the vinyl group stabilizes the excited state more strongly than the ground state (eq 5) and a red shift of 3.0 kcal/mol results. As can be seen from Table 3, the major difference between the vinyl and ethynyl groups is in the better ability of the vinyl group to stabilize the excited ¹A'' state.

Conclusions. The MP4SDTQ/6-31G**//6-31G* + spin-projection calculations nicely reproduce the experimental electronic spectra of ethynyl-, vinyl-, and arylsilylenes.³² We find both experimentally and computationally that when H in HSiMe is replaced by vinyl or phenyl, a bathochromic (red) shift results, while ethynyl induces a comparable blue shift. On the other hand, ethynyl, vinyl, and aryl groups all decrease the transition energy in the substituted silylene compared with Me₂Si, but the induced red shift is much larger for vinyl and phenyl. The *ab initio* calculations allow one to analyze in detail the effect of these substituents on the energies of the ground (¹A') and excited (¹A'') states of these silylenes, and thus on the n(Si) → 3p(Si) transition energy. For example, the calculations show that the significant red shift induced by the substitution of a methyl by vinyl or aryl results mainly from a large stabilization of the excited state, due to efficient 3p(Si)- $\pi^*(C=C)$ interaction.

(32) For HSiR, R = H, CH₂C≡CH, and CH=CH₂, and Me₂Si we have also examined the ability of the CIS/6-31G* method (CIS = configuration interaction with single excitations³³) to reproduce the vertical excitation energies. For MeSiH and Me₂Si we find that the agreement between the spin-projection calculations (method a) and the CIS/6-31G* calculations (method b) is very good (i.e., the calculated $\Delta\lambda$ values (relative to H₂Si) are -25 nm (method a) and -23 nm (method b) for MeSiH and -54 nm (method a) and -51 nm (method b) for Me₂Si). However, large differences between the two methods are found for HSiC≡CH and HSiCH=CH₂. At CIS/6-31G*, λ_{\max} of HSiC≡CH is calculated to be blue shifted relative to H₂Si by 33 nm, significantly larger than the 12 nm calculated with the spin-projection method or the experimentally deduced shift (see text). For HSiCH=CH₂, the CIS/6-31G* calculations predict a blue shift of 41 nm relative to H₂Si, while the spin-projection method predicts a red shift (of 31 nm) in agreement with the experimental data. We conclude that the CIS method is not generally suitable for predicting the excitation energies of silylenes, and the spin-projection method should therefore be preferred.

(33) Foresman, J. B.; Head-Gordon, M.; Pople, J. A.; Frisch, M. J. *J. Phys. Chem.* 1992, 96, 135.

The good agreement between the calculations and the experiment for the systems studied here points to the calculations as a reliable tool for predicting the electronic spectra of yet unknown silylenes. The presence of substantial discrepancies between the calculated and the measured transitions probably points to a wrong assignment of certain absorptions to the presence of a silylene, and such cases should be restudied experimentally; two such cases have been point out in the paper.

Experimental Section

General Data. All reactions were carried out under an atmosphere of dry nitrogen or argon. Solvents were dried using standard techniques. 3-Methylpentane was washed repeatedly with sulfuric acid, dried over sodium sulfate, and distilled from fresh lithium aluminum hydride. All glassware was thoroughly dried in an oven at 110–120 °C prior to use. ¹H-NMR spectra were recorded on a Bruker WP-270 (270 MHz) spectrometer.

High-resolution mass spectrometry and exact mass determinations were performed on a Kratos MS-80 mass spectrometer operating at an ionizing voltage of 30 eV. A Kratos MS25 equipped with a Carlo Erba gas chromatograph fitted with a 30 m × 0.36 mm i.d. fused silica capillary column coated with 5% phenylmethylsilicone was used for GC-MS measurements.

A Hewlett-Packard 5890 gas chromatograph with a flame ionization detector and a 10 m × 0.56 mm i.d. megabor column coated with 5% phenylmethylsilicone was used for analytical gas chromatography. Preparative gas chromatography was performed on a Gow Mac Model 550P gas chromatograph using a thermal conductivity detector and helium as the carrier gas. Normally, a 6 ft × 0.25 in. column packed with 5% SE-30 absorbed on Chromosorb-W was used.

2,2-Dichlorohexamethyltrisilane. To a solution of 2,2-diphenylhexamethyltrisilane⁷ (25.0 g, 76 mmol) in 100 mL of benzene was added 2.0 g of aluminum trichloride. Anhydrous HCl was bubbled through the solution, and the reaction was monitored by gas chromatography. Shortly after the introduction of the HCl, the mixture became bright yellow and then orange, and the solvent began to reflux. After 20 min the mixture returned to room temperature as the reaction reached completion. The AlCl₃ was precipitated with 2 mL of dry acetone, the solvent was removed, and the residue was distilled at 41–60 °C/0.04 Torr to afford 16.3 g (87%) of 2,2-dichlorohexamethyltrisilane as a clear, colorless oil, easily hydrolyzed: ¹H-NMR (CDCl₃) δ 0.12 (s).

2-Chloro-2-mesitylhexamethyltrisilane, 2. Mesityllithium was prepared by the treatment of 2-bromomesitylene (22.0 g, 11.1 mmol) in 125 mL of diethyl ether with 1.6 M *n*-butyllithium (*n*-Buli) in hexane 70.0 mL, 11.2 mmol). Once the addition of the BuLi was complete the reaction mixture was warmed to a gentle reflux and was stirred for 4 h. The precipitated mesityllithium was removed by filtration under an inert atmosphere and washed several times with hexane.

2,2-Dichlorohexamethyltrisilane (26.6 g, 11.0 mmol) was dissolved in 100 mL of benzene and brought to reflux. To the solution was added a slurry of the mesityllithium, prepared as above, in 200 mL of benzene. The mixture was stirred at reflux for 24 h, the salts were removed by filtration, the benzene was stripped, and 18.8 g (52%) of **2** was obtained by distillation at 95 °C/0.1 Torr: ¹H-NMR (CDCl₃) δ 6.68 (s, 2H), 2.50 (s, 6H), 2.36 (s, 3H), 0.26 (s, 18H); mass spectrum *m/e* 328 (1), 313 (5), 220 (62), 205 (94), 73 (100); HRMS calcd for C₁₅H₂₉ClSi₃ 328.1258, obsd 328.1265.

2-Ethynyl-2-mesitylhexamethyltrisilane, 3a. Ethynyllithium was prepared *in situ* by the dropwise addition of 1.6 M *n*-BuLi in hexane (17.4 mL, 30 mmol) to a saturated solution of acetylene in THF (100 mL), cooled to -78 °C. Vigorous mechanical stirring was maintained for 15 min while the reaction mixture was kept at -78 °C. During the addition and subsequent stirring, lithium acetylide precipitated from the solution. A solution of **2** (9.2 g,

28 mmol) in 50 mL of THF was slowly added to the lithium acetylide; care was taken to maintain the temperature at -78°C . After 6 h of stirring, the mixture was allowed to warm to room temperature, and following an aqueous workup, the residue was distilled under reduced pressure to give 0.28 g (9%) of ethynyl-trisilane **3a** as a colorless oil, bp $73\text{--}75^{\circ}\text{C}/0.01\text{ Torr}$: $^1\text{H-NMR}$ (CDCl_3) 6.72 (s, 2H), 2.68 (s, 6H), 2.23 (s, 3H), 0.24 (s, 18H); mass spectrum m/e 318 (27), 303 (42), 259 (45), 245 (86), 229 (24), 205 (100); HRMS calcd for $\text{C}_{17}\text{H}_{30}\text{Si}_3$ 318.1647, obsd 318.1654. Anal. Calcd: C, 64.08; H, 9.49. Found: C, 63.67; H, 9.58.

2-((Trimethylsilyl)ethynyl)-2-mesitylhexamethyltrisilane, 3b. Ethynyltrimethylsilane (0.44 g, 4.7 mmol) in 20 mL of hexane was added in a dropwise manner to a solution of 4.7 mmol of lithium diisopropylamide in 20 mL of hexane. After 20 min a solution of **2** (1.54 g, 4.7 mmol) in hexane was introduced. Aqueous workup followed by stripping of the solvent gave **3b** as a colorless oil (1.47 g, 80%): $^1\text{H-NMR}$ (CDCl_3) 6.78 (s, 2H), 2.25 (s, 9H), 0.22 (s, 9H), 0.18 (s, 18H); mass spectrum m/e 390 (65), 375 (15), 317 (12), 220 (25), 205 (100); HRMS calcd for $\text{C}_{20}\text{H}_{34}\text{Si}_4$ 390.2040, obsd 390.2031.

2-(Phenylethynyl)-2-mesitylhexamethyltrisilane, 3c. To a solution of 0.43 g (4.2 mmol) of phenylacetylene in 10 mL of pentane, cooled to -78°C , was added 1.6 M *n*-BuLi in hexane (2.6 mL, 4.2 mmol). After being stirred for 10 min, the solution was warmed to room temperature and 1.38 g (4.2 mmol) of **2** in 10 mL of pentane was added. The reaction mixture was refluxed for 48 h and given an aqueous workup. Stripping of the solvent afforded a yellow oil, which was passed through a silica gel column, yielding 1.24 g (75%) of **3c** as a clear colorless oil: $^1\text{H-NMR}$ (C_6D_6) 7.5–7.4 (m, 2H), 6.95 (m, 3H), 6.78 (s, 2H), 2.68 (s, 6H), 2.11 (s, 3H), 0.35 (s, 18H); mass spectrum m/e 394 (9), 379 (5), 321 (15), 205 (22); HRMS calcd for $\text{C}_{23}\text{H}_{34}\text{Si}_3$ 394.1959, obsd 394.1955. Anal. Calcd: C, 69.97; H, 8.61. Found: C, 69.36; H, 8.59.

2-((Trimethylsilyl)ethynyl)heptamethyltrisilane, 6. The preparation of **6** was similar to that employed for **3c**. (Trimethylsilyl)acetylene (0.44 g, 4.7 mmol), *n*-butyllithium, and **5** (1.06 g, 4.7 mmol) afforded **6** as a colorless oil (1.08 g, 80%): $^1\text{H-NMR}$ (CDCl_3) 0.18 (s, 3H), 0.14 (s, 27H); mass spectrum m/e 286 (2), 221 (5), 213 (4), 207 (60), 73 (100); HRMS calcd for $\text{C}_{12}\text{H}_{30}\text{Si}_4$ 286.1416, obsd 286.1430. For all of the silylene precursors, **3a–c** and **6**, proton NMR spectra indicated that impurities were less than 4%.

Hydrocarbon Glass Experiments. All spectroscopic and chemical trapping experiments performed in 3-methylpentane glass at 77 K employed a specially modified cuvette constructed from Suprasil glass measuring $3 \times 1 \times 1\text{ cm}$. Attached to the cuvette was a stem with a high-vacuum stopcock and an O-ring joint. The cuvette was suspended in a liquid nitrogen filled quartz Dewar

equipped with Suprasil windows for spectroscopic measurements. UV–visible spectra were obtained on a Perkin-Elmer Model 3840 lambda array spectrophotometer connected to a PE Series 7000 computer.

In a typical experiment 1–3 mg of the appropriate trisilane was dissolved in 5 mL of 3-methylpentane. The cuvette was charged with 4 mL of the solution, and the remainder was reserved for comparison following the photolysis. The sample was thoroughly degassed at $5 \times 10^{-6}\text{ Torr}$ prior to irradiation. A Rayonet Model RPR-100 photoreactor equipped with low-pressure mercury lamps was employed for the photolyses.

Chemical Trapping Experiments. The trapping reactions from the glass were performed in a manner similar to that described for the spectroscopic experiments. Approximately 5 mg of the trisilane was dissolved in 5 mL of 3-methylpentane, and 50 mg of triethylsilane or *tert*-butyl alcohol was added. After being degassed under high vacuum, the sample was immersed in liquid nitrogen and irradiated at 254 nm for approximately 30 min. The sample was then warmed to room temperature, recooled, and irradiated for another 30 min period. This cycle was repeated until the characteristic color of the silylene failed to appear upon exposure to ultraviolet light. The sample was then removed from the photolysis vessel, concentrated *in vacuo*, and analyzed by gas chromatography and high-resolution mass spectrometry.

8a: mass spectrum m/e 288 (17), 259 (68), 245 (6), 231 (10); HRMS calcd for $\text{C}_{17}\text{H}_{28}\text{Si}_2$ 288.1722, obsd 288.1718.

8b: mass spectrum m/e 360 (22), 345 (5), 331 (15), 287 (15), 273 (15), 257 (20), 147 (100); HRMS calcd for $\text{C}_{20}\text{H}_{36}\text{Si}_3$ 360.2115, obsd 360.2125.

8c: mass spectrum m/e 256 (8), 227 (10), 199 (14), 171 (22); HRMS calcd for $\text{C}_{12}\text{H}_{28}\text{Si}_3$ 256.2491, obsd 256.1499. **Trapping product from 3c and tert-butyl alcohol:** mass spectrum m/e 322 (15), 307 (10), 266 (50), 251 (45), 220 (45).

Note Added in Proof. After submission of our paper, Maier *et al.* reported the matrix isolation of $\text{HSiC}\equiv\text{CH}$. (See: Maier, G.; Reisenauer, H. P.; Pack, H. *Angew. Chem.* **1994**, *106*, 1347; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1248.). The reported λ_{max} of 500 nm (a broad peak) is red shifted relative to HSiMe by 20 nm, in good agreement with the calculated red shift of 13 nm (Scheme 2A), supporting our theoretical conclusion that substitution of *hydrogen* by an ethynyl substituent introduces a small blue shift.

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