

In Search of Triplet Silylenes

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Abstract: Substituent effects on singlet-triplet splittings in silylenes SiR₂ are investigated by ab initio quantum mechanical techniques with the goal of providing keys to the formation of ground-state triplet silylenes. Bending potential energy curves for the singlet and triplet states of dimethylsilylene, (H₃C)₂Si, and disilylsilylene, (H₃Si)₂Si, are generated to determine the central silylene angle at which the electronic states cross. Triplet dimethylsilylene is found to be the ground state for angles greater than 140°, whereas triplet disilylsilylene is more stable for angles greater than 115°. These results suggest that it will be excruciatingly difficult to produce a ground-state triplet dialkylsilylene via introduction of sterically overloaded alkyl groups. Substituted disilylsilylenes, on the other hand, should require only moderately sized ligands to produce a triplet ground state. Model studies of three different β-substituents (R = F, CH₃, SiH₃) in disilylsilylenes, (R₃Si)₂Si, suggest that R = CH₃ is the best choice. Comparison of the current results with similar studies on SiH₂, for which accurate quantum mechanical and experimental results are in agreement, suggest that bis(trimethylsilyl)silylene has a singlet-triplet splitting of only about 3 or 4 kcal/mol. Thus, to produce a ground-state triplet silylene in the laboratory, we recommend that synthetic efforts be directed to the generation of bis(trialkylsilyl)silylenes with alkyl groups larger than methyl.

Introduction

Silylenes SiR₂ are ubiquitous reactive intermediates in silicon chemistry.¹ The parent silylene, SiH₂, is a ground-state singlet, 21 kcal/mol more stable than the lowest lying triplet state.²⁻⁴ This is in contrast with the parent carbene, methylene, which has a triplet ground state, 9 kcal/mol below the lowest lying singlet state.⁴⁻⁶ The existence of two low-lying spin states of methylene is no doubt responsible for much of the interest in this reactive intermediate, as their characteristic reactions differ. For example, triplet carbenes abstract hydrogens and add to double bonds in a nonstereospecific fashion, whereas insertion reactions and stereospecific addition are characteristic of singlet carbenes.⁷

The thrill of carbene chemistry is certainly enhanced by the ready availability of carbenes with either singlet or triplet ground states. For example, methylene and most aryl- and alkylcarbenes are ground-state triplets, whereas lone pair bearing substituents such as the halogens, OR, and NR₂ generally yield ground-state singlets.⁸⁻¹⁷ This is not the case for silylenes.^{15,18-22} To our knowledge, no evidence has yet been presented for an experimentally observed triplet silylene, and it is certainly not from a lack of interest or effort!

The stumbling block to the successful synthesis of a ground-state triplet silylene is the unavailability of suitable ligands for stabilizing the triplet state. While it is known from theoretical studies that electropositive ligands such as lithium are capable of producing ground-state triplet silylenes,¹⁹⁻²² these are not attractive candidates for laboratory study. More generally, it seems to be the π-acceptor or -donor capability of the substituents that determines the singlet-triplet splittings of carbenes,⁹⁻¹² with π-acceptors such as CN, CHO, Li, and BeH preferentially stabilizing the triplets and π-donors like NH₂, OH, and halogens stabilizing singlets. Similar correlations exist for silylenes as well. A potential disadvantage to using strong π-acceptors, like CHO, is the possibility of rearrangement during the crucial silylene-generating step to yield Si-O bonded products as in, for example, the observed photolytic rearrangement of acylsilanes to siloxycarbenes.²³ This problem might be circumvented by thermal generation of the silylene, as in Seyferth's silirane thermolysis.²⁴

A method for obtaining ground-state triplet silylenes that is likely to be eventually successful rests on the observation that, at linear geometries, the triplet state should be more stable than the singlet state by Hund's rules, as both the in-plane σ-orbital and the out-of-plane p-orbital are then degenerate components of a π-orbital. Thus, if sufficiently bulky groups can be attached to silicon, one can hope to eventually generate a ground-state triplet

silylene simply by opening up the angle at silicon toward linearity. This approach has been investigated theoretically by Gordon,²⁵ who found that the energies of the ground-state ¹A₁ surface and the excited-state ³B₁ surface cross at about 130° for SiH₂, similar to results of Rice and Handy.²⁶ Subsequent studies by Gordon

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and Schmidt²² on di-*tert*-butylsilylene found that the optimized singlet-state C–Si–C angle was 111.7°, still well short of 130°, and they predicted that the singlet state was at least 10 kcal/mol more stable than the triplet. Gaspar and co-workers²⁷ have investigated the chemistry of diadamantylsilylene, generated from 1,1-diadamantylsilirane, with the initial hope that it would be sufficiently bulky to yield a triplet silylene, but the reactions of this sterically loaded silylene are all indicative of singlets.²⁷

It occurred to us that while the introduction of bulky substituents is a good idea, electronic effects may make the choice for carbon-based substituents less than optimal. The reason is that methyl groups alone are known to increase the singlet–triplet splitting²⁸ in silylene by about 6–7 kcal/mol, which could easily increase the singlet–triplet crossing angle by 10° or more. On the other hand, silyl- and disilylsilylene have been shown in theoretical studies^{19,29} to have much smaller singlet–triplet energy differences than SiH₂. Thus, one might wonder whether it would not be more efficacious to use a combination of electronic and steric effects, in the form of bulky silyl substituents, to produce ground-state triplet silylenes. An obvious potential drawback to this approach is that the longer Si–Si distance, compared to Si–C, may make it more difficult to force open the central angle past the singlet–triplet crossing angle.

Mueller et al.¹² have shown that singlet–triplet splittings in carbenes also correlate well with empirical resonance substituent constants, σ_r^0 , and independent studies, reviewed by Bassindale and Taylor,³⁰ find that SiF₃ is a strong resonance acceptor, although its field and inductive effects appear to be dominant. A related phenomena, summarized by Bock and Solouki,³¹ is that trifluorosilyl groups dramatically raise ionization potentials (IP's) of neighboring lone pairs such as those in amines or phosphines. There are two ways to view the importance of this observation as it relates to singlet–triplet splittings. One is that SiF₃ will stabilize the singlet state by lowering the energy of the, mainly s-type, lone pair in a singlet carbene or silylene, which would jibe with earlier speculations about the crucial role of electronegative substituents in stabilizing singlets.^{8,10} The other is that the SiF₃ group would stabilize the triplet state through Si(p) → SiF(σ*) negative hyperconjugation. A priori, it is not clear which effect would win out.

Theoretical studies by Dixon³² on (trifluoromethyl)carbenes found very little difference in singlet–triplet splittings upon substitution of hydrogen by CF₃. Bis(trifluoromethyl)carbene was found to have a slightly more stable triplet state, by 3.8 kcal/mol, than CH₂. Dixon noted, however, that this may be reduced if rotation of the CF₃ groups had been allowed, and he mainly ascribed the difference to the bulk of the CF₃ groups compared to hydrogens, as evidenced by the larger angle at carbon, 112.6° in (F₃C)₂C compared to 102.5° in CH₂. Coupling the observed correlations of carbene singlet–triplet splittings with empirical resonance substituent constants and large positive σ_R for SiF₃ with the already small energy difference^{19,25} in (H₃Si)₂Si, near 5 kcal/mol, it is certainly worth investigating the possibility that bis(trifluorosilyl)silylene may have a triplet ground state. In this case, however, the difference in bulk between SiH₃ and SiF₃ is not likely to provide a differential advantage to the triplet state. From a more general point of view, this relates to the general question of the effect of β substituents on singlet–triplet splittings, which has not been systematically investigated to date.

In this paper, we investigate many of the questions raised above using ab initio quantum mechanical methods. Specifically, we have determined the energies of both the singlet and triplet states

of (H₃C)₂Si and (H₃Si)₂Si as a function of the angle about the central silicon atom, optimizing all other degrees of freedom within the constraints of C_{2v} symmetry, to determine the angle at which the singlet and triplet states cross. The geometries and energies of the singlet and triplet states of bis(trifluorosilyl)silylene have also been determined. Finally, two model bulky silylenes, bis(trisilylsilyl)silylene, [(H₃Si)₃Si]₂Si, and bis(trimethylsilyl)silylene, [(H₃C)₃Si]₂Si, have been investigated to elucidate the β-silyl and β-methyl group effects. Our studies suggest that none of these are ground-state triplets, although bis(trimethylsilyl)silylene is quite close. Nonetheless, the idea of attaching sterically overloaded silyl substituents to a silylene center appears to be a promising strategy and, bulk-for-bulk, β-alkyl groups are preferable.

Theoretical Methods

All the structures considered here have been precisely optimized within the given symmetry constraints by employing restricted Hartree–Fock (RHF) self-consistent-field (SCF) analytic gradient techniques.³³ Residual Cartesian gradients are in all cases less than 10⁻⁵ au. Analytic second-derivative methods³⁴ were used to evaluate the quadratic force constants and resulting harmonic vibrational frequencies whenever possible. Many of the singlet states have also been optimized by two configuration SCF (TCSCF) methods, as this is known to be important for providing a simple balanced description of the singlet and triplet state energies,⁸ and TCSCF is absolutely essential at larger angles. These optimizations employed analytic TCSCF gradient methods,³⁵ and harmonic vibrational frequencies at the TCSCF geometries were obtained by analytic determination of the TCSCF second-derivative matrix.³⁶

The basis sets used are of double-ζ plus polarization quality (DZP) on the silylene center and all directly attached atoms. In many cases, those atoms not directly attached to the divalent silicon center are described with a more economical DZ basis set, i.e., without polarization functions. When employing basis sets of this mixed quality, we will designate the resulting basis set as DZ(d) and reserve the notation DZP for those results obtained with polarization functions attached to all atoms. For silicon and hydrogen, the standard Huzinaga–Dunning³⁷ DZ basis sets designated (11s7p/6s4p) and (4s/2s) are appended with Cartesian polarization functions with exponents $\alpha_d(\text{Si}) = 0.5$ and $\alpha_p(\text{H}) = 0.75$. For the first-row atoms carbon and fluorine,³⁷ the basis set is (9s5p/4s2p), with polarization functions $\alpha_d(\text{C}) = 0.75$ and $\alpha_d(\text{F}) = 1.0$. To reduce the number of contracted basis functions and thus make theoretical studies possible, for bis(trisilylsilyl)silylene, [(H₃Si)₃Si]₂Si, and bis(trimethylsilyl)silylene, [(H₃C)₃Si]₂Si, the basis set employed is of split-valence type from Pople and co-workers.³⁸ Specifically, this set consists of 6-31G* on the central and attached silicons, 6-31G on the pendant silicons or carbons, and 3-21G on the hydrogens, which we will designate as 6-31G(d) despite the convention that this usually designates a basis set in which all heavy atoms are given polarization functions. This results in a total of 171 contracted basis functions for [(H₃Si)₃Si]₂Si and 147 contracted functions for [(H₃C)₃Si]₂Si.

Electron correlation effects have been included by the method of configuration interaction (CI), with the frozen core approximation. Thus, all corelike (Si, 1s, 2s, 2p; C, F 1s) orbitals have been omitted from the CI procedure. Otherwise, all single and double excitations from the appropriate SCF or TCSCF reference configuration are included (CISD).³⁹ Improved estimates of the relative energies are obtained by adding the Davidson correction,⁴⁰ or its two-reference analogue, for un-

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Table I. Total Energies (hartrees) and Relative Energies (kcal/mol, Given in Parentheses) of the Substituted Silylenes Investigated in this Study^a

molecule	state	basis set	SCF/TCSCF	CISD	CISD+Q
(H ₃ Si) ₂ Si	¹ A ₁	DZ(d)	-870.176 23 (0.2)	-870.415 12 (0.4)	-870.443 80 (0.4)
	¹ A	DZ(d)	-870.176 48 (0.0)	-870.415 71 (0.0)	-870.444 47 (0.0)
	³ B ₁	DZ(d)	-870.171 89 (2.9)	-870.409 88 (3.7)	-870.438 07 (4.0)
	¹ A	DZP	-870.187 88 (0.0)	-870.473 81 (0.0)	-870.509 56 (0.0)
	³ B ₁	DZP	-870.183 33 (2.9)	-870.468 06 (3.6)	-870.503 24 (4.0)
	¹ A	6-31G(d)	-870.179 02 (0.0)	-870.416 95 (0.0)	-870.446 37 (0.0)
(F ₃ Si) ₂ Si	¹ A ₁	DZ(d)	-1463.849 00 (0.0)	-1464.572 00 (0.0)	-1464.684 73 (0.0)
	³ B ₁	DZ(d)	-1463.844 73 (2.7)	-1464.567 21 (3.0)	-1464.679 43 (3.3)
	¹ A ₁	DZP	-1463.933 27 (0.0) ^b		
	³ B ₁	DZP	-1463.929 71 (2.2) ^b		
[(SiH ₃) ₃ Si] ₂ Si	¹ A ₁	6-31G(d)	-2610.375 54 (0.0) ^c		
	³ B ₁	6-31G(d)	-2610.368 61 (4.3)		
[(CH ₃) ₃ Si] ₂ Si	¹ A ₁	6-31G(d)	-1104.344 05 (0.0) ^c		
	³ B ₁	6-31G(d)	-1104.345 99 (-1.2)		

^a Singlet-state energies are from two-configuration self-consistent-field (TCSCF) reference wave functions. ^b Determined at the DZ(d) basis set optimized geometry. ^c TCSCF energy at the SCF optimized geometry.

linked quadruple excitations (CISD+Q).

Determination of correlation energies beyond TCSCF for the largest silylenes reported in this work is not feasible, but the TCSCF(singlet)-SCF(triplet) method is already in very good agreement (usually within 1 or 2 kcal/mol) with more extensively correlated results. For example, the DZP TCSCF(singlet)-SCF(triplet) method gives $\Delta E = 16.4$ kcal/mol for SiH₂, and CISD+Q gives 18.1 kcal/mol, with 6-31G** results being almost identical with those of DZP. In fact, two-reference CISD+Q singlet-triplet splittings for CH₂ and SiH₂ with a DZP basis set are within 0.2 kcal/mol of FULL CI results.⁴ On the other hand, huge basis set multireference CI methods⁴ give $\Delta E = 20.4$ kcal/mol, which, after correcting for relativistic effects and zero-point vibrational energy differences, yield $T_0 = 20.9$ kcal/mol, in excellent agreement with the experimental value² of 21.0 kcal/mol. Thus, if the results for SiH₂ can be extrapolated to the molecules investigated in this study, we should expect that CISD+Q singlet-triplet splittings will be about 3 kcal/mol smaller, and TCSCF energy differences will be 4–5 kcal/mol smaller, than experimental values.

Dimethylsilylene and Disilylsilylene

The optimized geometries and relative energies of the singlet and triplet states of dimethylsilylene have been previously reported.²⁸ To summarize, the minimum on the ground-state singlet surface has C₂ symmetry, with an Si–C bond distance of 1.910 Å and a C–Si–C angle of 98.8° at the DZ(d) TCSCF level of theory. A C_{2v} symmetry transition-state structure with an identical Si–C bond distance and C–Si–C angle lies about 0.1 kcal/mol above the C₂ minimum. The minimum on the triplet surface has a bond distance of 1.897 Å, a C–Si–C angle of 117.9°, and C_{2v} symmetry. This ³B₁ state is 24.2 kcal/mol above the ¹A₁ ground state at the CISD+Q/DZ(d) level of theory. Single-point CISD+Q energy determinations with larger basis sets at the DZ(d) TCSCF(singlet) and SCF(triplet) C_{2v} optimized geometries increased the energy separation to 25.1 kcal/mol.

The TCSCF singlet and SCF triplet DZ(d) optimized geometries of disilylsilylene are shown in Figure 1. Disilylsilylene, (H₃Si)₂Si, is similar to dimethylsilylene in that the optimized geometry on the singlet surface has C₂ symmetry, with a C_{2v} symmetry transition state that differs only marginally in terms of structure and energy. There are only two significant structural differences between the C_{2v} transition state and the C₂ minimum; the silyl groups as a whole are rotated through a torsion angle of about 20°, and they are tilted (one up, one down) by a few degrees. Both of these geometrical distortions are approximately double the magnitude of those in dimethylsilylene. Thus, it is not surprising that the C₂ – C_{2v} energy difference is also larger for disilylsilylene than for dimethylsilylene, 0.4 kcal/mol instead of 0.1 kcal/mol. The Si–Si–Si bond angle is 95.8° for the C₂ symmetry minimum. The ³B₁ minimum has a bond angle of 124.8° and a significantly shorter Si–Si distance than the singlet, 2.335 Å compared to 2.399 Å. The trend of shorter distances in the triplet state of silylenes is a ubiquitous phenomenon and may be a minor hindrance in attempting to create a ground-state triplet by sterically induced opening of the central silicon bond angle, as the larger bond distances are characteristic of singlets.

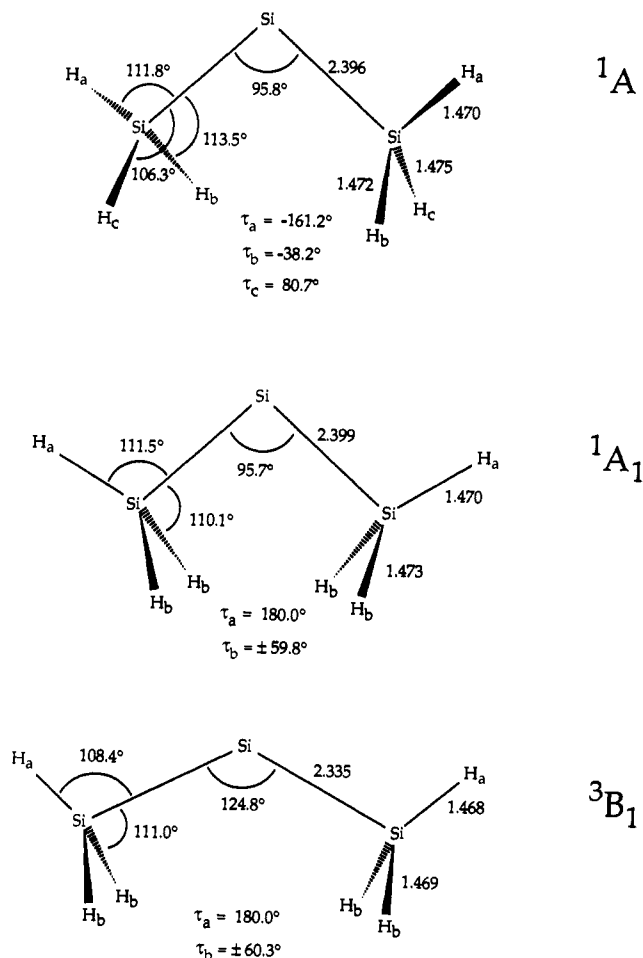


Figure 1. Optimized geometries of the ¹A₁ (C₂ symmetry) minimum, ¹A₁ (C_{2v} symmetry) transition state, and ³B₁ (C_{2v} symmetry) minimum electronic states of disilylsilylene using the DZ(d) basis set and TCSCF(singlet), SCF(triplet) methods. τ_i is the torsion angle of atom *i* relative to the Si₃ framework. Bond distances are in angstroms.

The singlet-triplet splitting of disilylsilylene at the CISD+Q/DZ(d) level of theory (Table I) is 4.0 kcal/mol. Gordon and Bartol²⁹ obtained a value of 5.8 kcal/mol by using 6-31G(d) basis sets and MP4 energies at 3-21G* SCF geometries. With the 6-31G(d) basis set used here (which differs from Gordon's in that we use the standard 6-31G* d-function exponent of 0.45, instead of the SiH₄ energy optimized value of 0.395 employed by Gordon), the CISD+Q energy difference is 5.0 kcal/mol. The difference in singlet-triplet splittings between the various basis sets may be at least partially related to the use of different d-function exponents, since in CH₂ the optimum d-function exponent for the

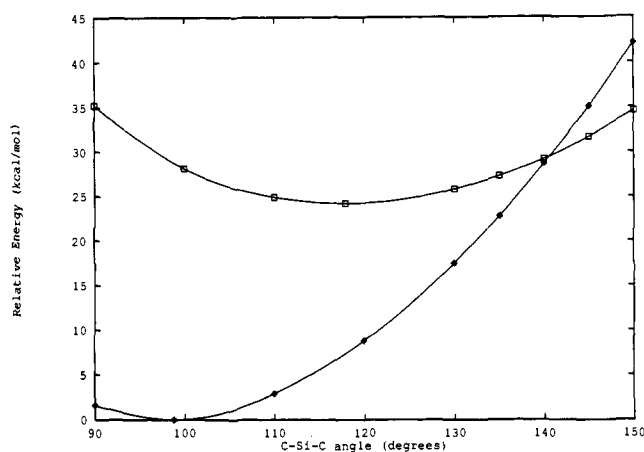


Figure 2. Bending potential energy curves for dimethylsilylene, $(\text{H}_3\text{C})_2\text{Si}$, determined from CISD+Q energies at C_{2v} symmetry constrained TCSCF(singlet), SCF(triplet) optimized geometries. The $^3\text{B}_1$ state is represented by the large squares and the $^1\text{A}_1$ state by the smaller diamonds. See text for details.

singlet state is more diffuse (has a smaller exponent) than that for the triplet state,^{8b} although this does not appear to be a universal trend.¹⁶ The strength of the TCSCF(singlet)–SCF(triplet) zeroth-order quantum mechanical description of silylenes is evident by the small change, from 2.9 to 4.0 kcal/mol, in the singlet–triplet splitting due to more extensive treatment of the effects of electron correlation via CISD. This is similar to results obtained in previous studies and will allow us to make accurate predictions of singlet–triplet splittings in cases where CISD or other correlation methods are not feasible, as in some of the large systems shown below.

We have also optimized the C_{2v} and C_2 symmetry singlet-state structures of disilylsilylene with single configuration SCF methods, but the geometries are not shown in Figure 1, as they differ almost imperceptibly from the TCSCF values. The torsion angles differ by about 3° , which has an inconsequential effect on the energy, and all other parameters differ by less than 1° for angles and 0.002 Å for bond distances. The addition of polarization functions to the hydrogens also has little effect on geometries or relative energies. Geometrically the only change is a constant 0.006-Å increase in Si–H distances, with no angle changing by more than 0.7° , and the DZP relative energies, given in Table I, are identical with those from the DZ(d) basis set to within 0.1 kcal/mol. Thus, for the large silylenes presented below, we will use SCF optimized geometries and determine single-point TCSCF energies for our final results.

Figure 2 presents potential energy curves for singlet and triplet dimethylsilylene as a function of the C–Si–C angle. The curves are generated from CISD+Q energies determined at C_{2v} symmetry constrained TCSCF(singlet), SCF(triplet) optimized geometries for the $^1\text{A}_1$ and $^3\text{B}_1$ states in conjunction with the DZ(d) basis set. Thus, for a given C–Si–C angle, all of the six remaining totally symmetric internal coordinates in C_{2v} symmetry are optimized to yield the lowest energy. This curve is therefore the dimethyl analogue of those presented by Gordon²⁵ and Rice and Handy²⁶ for SiH_2 . In this case, the singlet and triplet states do not cross until the central angle is greater than 140° , compared to 130° for SiH_2 . If we assume that an increase of ~ 3 kcal/mol in the adiabatic singlet–triplet splitting for dimethylsilylene (see above) upon improving the silicon basis set will manifest itself as a constant lowering of the singlet surface at all angles, the actual crossing will occur at slightly larger angles. The exact angle at which the two states cross is not important, as other factors will make each case slightly different, but the fact that the crossing angle for dimethylsilylene is 10° or so larger than the crossing point for SiH_2 suggests that generating a ground-state triplet silylene by bulky carbon based ligands may be very difficult, indeed.

Curves for disilylsilylene analogous to those in Figure 2 for dimethylsilylene are shown in Figure 3. As in Figure 2, Figure

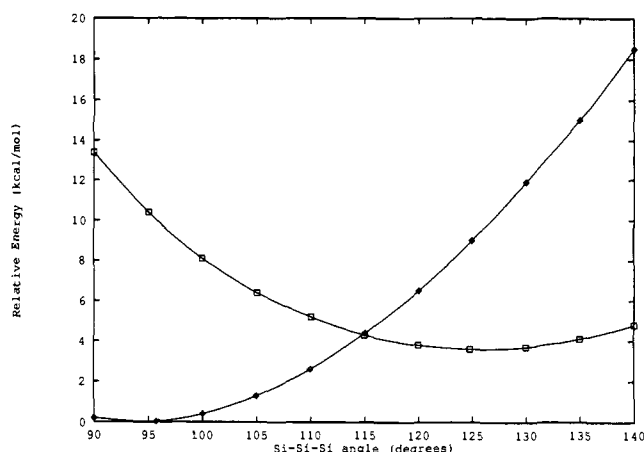


Figure 3. Bending potential energy curves for disilylsilylene, $(\text{H}_3\text{Si})_2\text{Si}$, determined from CISD+Q energies at C_{2v} symmetry constrained TCSCF(singlet), SCF(triplet) optimized geometries. The $^3\text{B}_1$ state is represented by the large squares and the $^1\text{A}_1$ state by the smaller diamonds. See text for details.

3 is obtained from CISD+Q energies at C_{2v} symmetry constrained optimized geometries by using the TCSCF(singlet)–SCF(triplet) prescription for a given angle about the central silicon atom. The smaller adiabatic singlet–triplet splitting of $(\text{H}_3\text{Si})_2\text{Si}$ compared to $(\text{H}_3\text{C})_2\text{Si}$, 4.0 and 24.2 kcal/mol, respectively, leads to a dramatically reduced curve-crossing angle of $\sim 115^\circ$. Even if our methodology underestimates the singlet–triplet splitting by 3 kcal/mol, and thus the actual crossing angle is nearer 120° , this appears to be a more reasonable and attainable goal.

Substituted Disilylsilylenes ($\text{R}_3\text{Si})_2\text{Si}$ ($\text{R} = \text{F}, \text{CH}_3, \text{SiH}_3$)

In this section, we investigate three separate per-substituted disilylsilylenes to determine the effects of β substituents on the geometries and singlet–triplet splittings of disilylsilylenes. The 4.0 kcal/mol splitting in the parent compound, $(\text{H}_3\text{Si})_2\text{Si}$, and the relatively small angle, 115° , at which the singlet- and triplet-state energies cross suggest that the choice of a proper silyl group, SiR_3 , in a molecule of $(\text{R}_3\text{Si})_2\text{Si}$ type should lead us to the ultimate goal of a ground-state triplet silylene. The question remains, however, as to what R is the optimal choice. One might simply employ the bulkiest R group available, but the possibility remains that the choice of β substituents can effect the outcome.

As we noted in the Introduction, a general correlation between π -accepting ability and singlet–triplet splittings in carbenes has been observed, and SiF_3 has been independently studied and found to be a strong π -acceptor. Thus, $(\text{F}_3\text{Si})_2\text{Si}$ has been chosen as one compound to investigate, although it is unlikely that fluorine substituents would have a significant effect on the central silicon angle. Two other substituents, $\text{R} = \text{CH}_3$ and SiH_3 , with presumably more benign electronic effects, but that may serve to increase the angle about the silylene center, have also been chosen. The choice of $\text{R} = \text{SiH}_3$, however, is not taken without reservation. In organic chemistry, β -silyl groups are known to produce dramatic stabilizing effects on electron-deficient centers,^{30,41} just as we have here in the singlet silylenes with their formally empty π -type orbital. For example, Bassindale and Taylor³⁰ note that “in organic synthesis using silicon compounds, one of the most profound activating and directing effects is found in the stabilization of β -silylcarbonium ions, $\text{R}_3\text{SiCH}_2\text{CH}_2^+$ ”. While we are not aware of similar effects having been noted in compounds analogous to those we are interested in here, i.e., $\text{R}_3\text{SiSiR}_2\text{SiR}_2^+$, this may just be a reflection of the paucity of good thermochemical data in silicon chemistry as a whole.

The optimized geometries of the C_{2v} symmetry constrained $^1\text{A}_1$ (TCSCF) and $^3\text{B}_1$ (SCF) states of bis(trifluorosilyl)silylene are shown in Figure 4. The $^1\text{A}_1$ state has also been optimized by using the single configuration SCF method, and, as in di-

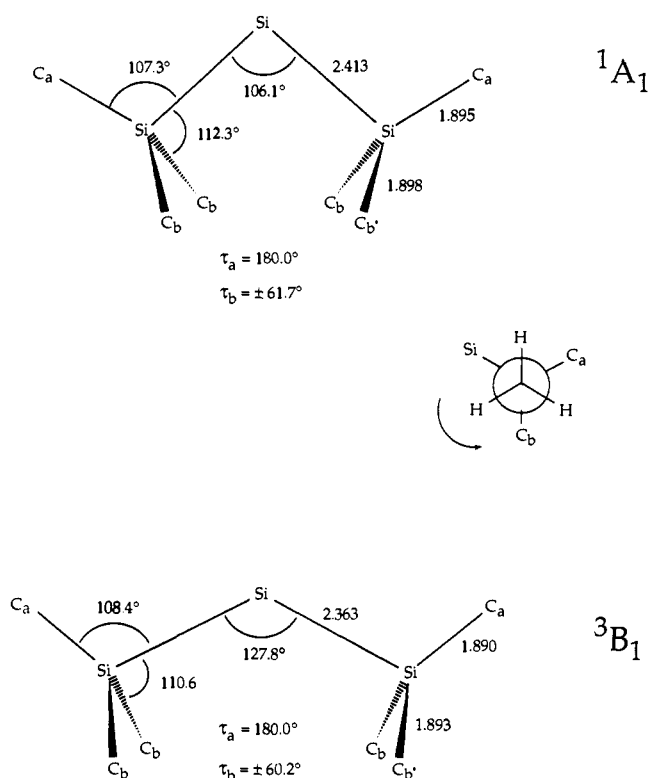


Figure 6. C_{2v} symmetry optimized geometries of the 1A_1 and 3B_1 electronic states of bis(trimethylsilyl)silylene using the 6-31G(d) basis set and SCF methods. The hydrogen atoms attached to the terminal carbons have been removed for clarity, but their internal rotation relative to an ideal staggered geometry is schematically shown in the center of the figure, relative to the atom labeled C_b in the figure. For the 1A_1 state, this rotation is $\sim 10^\circ$, and for the 3B_1 state it is $\sim 7^\circ$. τ_i is the torsion angle of atom i relative to the Si_3 framework. Bond distances are in angstroms.

methylsilyl)silylene is predicted to have a triplet ground state! To be sure, the triplet is lower by only 1.2 kcal/mol at this level of theory, and thus the singlet is most likely the actual ground state. If we assume the error at this level of theory is similar to that in SiH_2 , then we would predict the triplet to be about 3–4 kcal/mol above the singlet, and this ignores possible differential energy lowerings due to further geometry optimization in lower symmetry. Nonetheless, these results strongly suggest that a winning strategy for the experimental design of a triplet ground-state silylene is to produce, by whatever means, a bis-(trialkylsilyl)silylene, with alkyl being something larger than methyl. Given the apparent generality and ease of *singlet* silylene formation from siliranes,^{24,27} these seem to be obvious target precursors. On the other hand, the mode of decomposition of siliranes might change if ground-state *triplet* silylenes result!

Conclusions

With the goal of providing a realizable synthetic target for a ground-state triplet silylene, we have studied the bending potential curves of dimethylsilylene and disilylsilylene via ab initio quantum mechanical methods. These results suggest that a dialkylsilylene may be *very* difficult to convert to a ground-state triplet by sterically induced bond opening of the central silylene angle. Disilylsilylenes provide a much more realistic basis from which to start, since only moderately bulky β -substituents will be required to open the angle past the 115° crossing point. Still, it appears that the choice of β -substituent has some effect and, bulk-for-bulk, β -alkyl is to be preferred to β -silyl.

With TCSCF(singlet)–SCF(triplet) methods, we find triplet bis(trimethylsilyl)silylene to be 1.2 kcal/mol more stable than the singlet state. However, comparison of the methods used here with both highly accurate quantum mechanical studies and experimental results for SiH_2 suggests that the actual ground state is most likely the singlet, with the triplet state 3–4 kcal/mol higher.

Table II. Absolute Energy Differences (kcal/mol) between SCF- and TCSCF-Based Methods for Various Small-Angle Singlet Carbenes and Silylenes^a

molecule	ref	SCF/TCSCF	CISD	CISD+Q
CH_2	4a	13.4	2.4	0.3
HCF	16	13.7	4.1	1.7
HCCl	16	13.2	3.7	1.5
HCB	16	13.3	4.2	1.8
SiH_2	4b	12.4	1.8	-0.1
$Si(CH_3)_2$	28	11.7	4.3	1.8
$Si(SiH_3)_2$		10.5	3.4	1.3
$HSi(SiH_3)$		10.7	3.0	0.9
$HSi(SiH_2F)$		10.8	4.0	1.7
$Si(SiF_3)_2$		11.2	6.1	3.8

^a A positive energy implies that the TCSCF reference result is lower. These data provide the basis for the 5-2-0 rule (see text).

The related molecules bis(trisilylsilyl)silylene and bis(trifluorosilyl)silylene are predicted to be ground-state singlets, approximately 9 and 6 kcal/mol lower in energy than their corresponding triplets, respectively.

Finally, before leaving the subject of silylenes, we would like to document an observation that we refer to within this research group as the 5-2-0 rule. The 5-2-0 rule refers to expected differences in total energies of small-angle singlet carbenes and silylenes obtained by single-reference- and two-reference-based CISD and CISD+Q methods. As we have noted many times in this work, the TCSCF(singlet)–SCF(triplet) methodology provides a very well balanced approach for determining singlet–triplet splittings of carbenes and silylenes. If electron correlation effects cannot be determined by more rigorous methods, then the TCSCF–SCF method can be used to provide semiquantitative singlet–triplet splittings; if the central carbene or silylene angle becomes large (greater than 130° or so²⁵), then TCSCF methods for the singlet state are truly essential. However, for small-angle singlet states where CISD methods are feasible, single-reference wave functions for the singlet state are adequate. Furthermore, comparison of single-reference-based CISD and CISD+Q energies with TCSCF reference CISD and CISD+Q energies shows that they exhibit a very regular pattern. At the CISD level of theory, the absolute energy difference (for the singlet state) between single-reference- and two-reference-based methods is almost invariably less than 5 kcal/mol, and after appending the Davidson correction, the energy difference is almost invariably less than 2 kcal/mol. The results for bis(trifluorosilyl)silylene in this study are the first we have encountered that did not obey this rule and are also, we should note, the largest (in terms of numbers of correlated electrons) that we have ever studied. The zero in the 5-2-0 rule refers to the observation that there will be *no* important difference between the structures obtained at the TCSCF and SCF level of theory for small-angle singlet carbenes and silylenes. Table II shows the data on which we base this rule. Thus, provided electron correlation is included, the use of a TCSCF reference wave function for the singlet state is not necessary to produce accurate singlet–triplet splittings, and the errors relative to the more rigorous TCSCF-based methods are easily estimated with a high degree of accuracy.

Some researchers have taken the “TCSCF requirement” for singlet carbenes to extremes that seem unjustified, arguing, for example, that Woodward–Hoffman rules are not applicable in the system methylene plus ethylene yields cyclopropane because methylene requires a TCSCF description.⁴³ If we are required to judge the “one referenceness” of a particular molecule on the ability of single-reference SCF methods to accurately reproduce singlet–triplet splittings, then it strains the imagination to produce *even one* molecule that can truly be called a “single-reference problem”.

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