effects of allene strain, due to in-plane bending and diminished π-bonding, and strain in the $-(CH_2)_n-$ linkage.

For moderate to large ring sizes (>6 carbons), the C_2 chiral structures are global minima, with racemization occurring through a bent planar diradical. The allene triplet also should have a minimum at this geometry, with a small singlet–triplet gap[15,38] and a nearly identical geometry. However, as noted above, the singlet is predicted to lie below the triplet.

A second excited singlet minimum is predicted to occur for the lowest closed-shell state, which corresponds to a zwitterion.[9,15] This is of higher energy than the open-shell singlet because of one additional electron intrapair repulsion.

Our calculations permit a quantitative estimate of the strain inherent in allenes **5** and **6**. Previous calculations by Pople and co-workers show that allenes should racemize through a C_{2v} biradical species, with a bending angle of ca. 130°.[15] The in-plane bending potential is relatively soft.[16] Thus, for **5** and **6**, the racemization transition states **5**-¹D and **6**-¹D, with bending angles 123 and 127°, respectively, should be essentially unstrained. Roth has measured an experimental racemization barrier of 46.2 kcal/mol in 2,3-pentadiene, another disubstituted allene.[39] Combining this value with our predicted MCSCF inversion barriers (4.9 and 15.0 kcal/mol) yields strain estimates of 41.3 and 31.2 kcal/mol, respectively, for **5** and **6**. Dimerization or other reactions would be accompanied by substantial strain release.

Conclusions

One of the lessons which has been learned during the past several decades is the degree to which hydrocarbons may be structurally distorted and yet remain thermodynamically stable (if reactive) molecules.[2a] Cyclic allenes further demonstrate the remarkable tenacity of π-bonding. Thus, while a chiral allenic structure for 1,2-cyclohexadiene may have seemed only remotely possible, experiment and theory now have converged on this remarkable conclusion. For the smaller homologue, 1,2-cyclopentadiene, our calculations slightly favor a chiral structure, but the energy difference is within reasonable estimates for computational error bounds, and confirmation must await the results of careful experimentation.

We are continuing to explore other strained cyclic allene structures, as well as cyclic butatrienes, the next homologous cumulene. The smallest isolable cyclic butatriene probably is 1,2,3-cyclononatriene, which we have recently prepared for the first time.[40]

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Structural and Energetic Features of Fully Substituted Silylenes, Disilenes, and Silylsilylenes (SiX₂, X₂SiSiX₂, and XSiSiX₃; X = Li, CH₃, and F)

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Abstract: Ab initio molecular orbital calculations with basis sets of split valence plus polarization function quality (6-31G*) have been carried out on some fully substituted silylenes, disilenes, and silylsilylenes (SiX₂, X₂SiSiX₂, and XSiSiX₃; X = Li, CH₃, and F). The silylenes SiH_2, $Si(CH_3)_2$, and SiF_2 are all strongly bent in both their singlet ground and triplet excited states, but $SiLi_2$ has a triplet ground state with a linear geometry and a bent singlet excited state. Singlet–triplet separations are calculated (CISD/6-31G*//6-31G*) in SiH_2, $Si(CH_3)_2$, SiF_2, and $SiLi_2$ as 17.6, 22.9, 74.0, and −10.3 kcal/mol, respectively. The $Si_2(CH_3)_4$ isomers resemble the analogous Si_2H_4 species with respect to structural and energetic features. Thus, the singlet disilenes and silylsilylenes are almost isoenergetic, the disilene dissociation energies toward two simple silylenes are comparable, and both disilenes feature very flat potential energy surfaces for bending of the geminal groups in a mutual trans fashion or twisting around the SiSi bond. In contrast, no closed shell singlet minimum could be located for F_2SiSiF_2 corresponding to a disilene; a minimum for a diradical-like triplet ·F₂SiSiF₂· species was obtained, but this structure is considerably less stable ($\approx$25 kcal/mol; HF/6-31G*//6-31G⁺) than the singlet silylsilylene, :FSiSiF₃. For the model Si_2Li_4 species, there is no minimum corresponding to a conventional disilene or a silylsilylene. A distorted, planar structure with two bridging Li atoms (LiSiLi₂SiLi, C_{2h} symmetry) has been located as the global minimum for singlet Si_2Li_4.

I. Introduction

There is at present considerable interest in molecules featuring trivalent or divalent silicon.[1] Experimental determinations of physical parameters for these generally short-lived, reactive silicon species are difficult to obtain and hence largely nonexistent. Such systems are, however, amenable to accurate theoretical investigations, and it is desirable to explore the possibility and opportunity to obtain reliable information in this manner. This paper presents results from ab initio molecular orbital calculations on fully substituted silylenes, disilenes, and silylsilylenes (SiX₂, X₂SiSiX₂, and XSiSiX₃; X = Li, CH₃, and F) with the aim to assess structural and energetic substituent effects on the parent systems

(1) Review: Gusel'nikov, L. E.; Nametkin, N. S. *Chem. Rev.* **1979**, *79*, 529. Gaspar, P. P. "Reactive Intermediates"; Moss, R. A., Jones, M., Jr., Eds.; Wiley, New York, 1985; Vol. 3, Chapter 9.

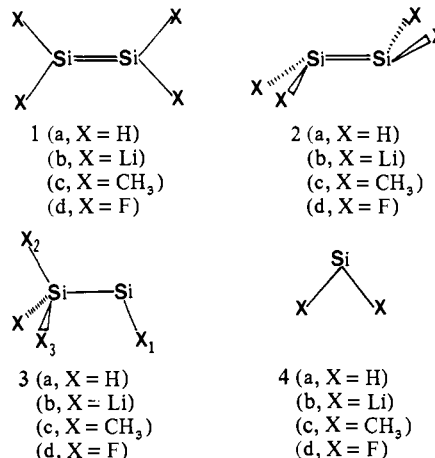**Table I.** Optimized Structures for the Two Lowest States of SiX$_2$ (X = H, Li, CH$_3$, and F)[a]

X	state[b]	parameter	HF/6-31G	HF/6-31G$^+$	HF/6-31G*
H	$^1A_1$	SiH	1.545	1.515	1.514
		HSiH	93.5	93.2	93.2
	$^3B_1$	SiH	1.492	1.477	1.477
		HSiH	118.6	117.9	117.9
Li	$^1A_1$	SiLi	2.588	2.538	2.533
		LiSiLi	93.4	91.8	92.0
	$^3\Sigma_g^-$	SiLi	2.442	2.428	2.429
CH$_3$[c]	$^1A_1$	SiC	1.962	1.921	1.926
		CSiC	98.1	99.2	98.8
	$^3B_1$	SiC	1.944	1.909	1.914
		CSiC	118.5	117.7	117.7
F	$^1A_1$	SiF	1.680	1.626	1.598
		FSiF	96.3	98.8	99.6
	$^3B_1$	SiF	1.683	1.626	1.598
		FSiF	115.0	112.8	113.6

[a] Bond lengths in angstrom, angles in degrees. [b] All term symbols refer to the C_{2v} point group with the exception of triplet SiLi$_2$ which has $D_{\infty h}$ symmetry. [c] CH$_3$ groups kept tetrahedral (CH = 1.085 Å) and "staggered" with respect to the unique Si 3p(π) orbital.

(SiH$_2$, H$_2$SiSiH$_2$, and HSiSiH$_3$).

The presence of reactive intermediates with a SiSi double bond had repeatedly been inferred from analysis of reaction products,[2-5] but with the more recent reports[6,7] on the successful isolation and characterization of heavily substituted disilenes (**1** or **2**; e.g., X = 2,4,6-trimethylphenyl[6a-c,7a] and 2,6-diethylphenyl[7b]), all further doubts regarding the existence of compounds possessing a true Si=Si double bond can be dismissed. Comparisons with ethylenes indicate several intriguing aspects associated with the structural and energetic properties of disilenes. For example, whereas simply substituted or unstrained ethylenes do not show tendencies toward adopting distinctly nonplanar geometries,[8] there are indications that disilenes may be very susceptible to distortions.[9] High level ab initio calculations on disilene, Si$_2$H$_4$, gave a nonplanar, trans-bent equilibrium geometry (**2a**),[9] and the recently published X-ray structures show nonplanar, slightly trans-bent and/or twisted Si$_2$C$_4$ skeletons.[7] There is considerable experimental and theoretical evidence that digermenes and distannenes possess strongly trans-bent equilibrium structures[10] and Si could hence be the pivotal group 14 element in this regard. In addition, disilenes may be almost isoenergetic with the isomeric silylsilylenes (**3**). Thus, the apparently similar thermodynamic stability of **1** and **3** (X = H or CH$_3$, respectively) as well as their possible interconversion in the gas phase at elevated temperatures[3,11] stand in marked contrast to the calculated energy difference of ca. 75 kcal/mol between singlet ethylene and methylmethylene (:HC–CH$_3$);[12] in fact, it is doubtful that the latter species even represents a minimum structure. Furthermore, evidence for the facile gas-phase dimerization of organosilylenes to produce disilenes has been presented;[3c,4] e.g., the dimerization of **4c** to **1c** occurs even in the presence of a tenfold excess of propyne. The possibility

1 (a, X = H)
(b, X = Li)
(c, X = CH$_3$)
(d, X = F)

2 (a, X = H)
(b, X = Li)
(c, X = CH$_3$)
(d, X = F)

3 (a, X = H)
(b, X = Li)
(c, X = CH$_3$)
(d, X = F)

4 (a, X = H)
(b, X = Li)
(c, X = CH$_3$)
(d, X = F)

of analogous SiF$_2$ (**4d**) dimerization[5] and its importance in mechanistic studies of SiF$_2$–alkene reactions is a subject of current debate.[13] Ethylene formation by dimerization of carbenes, although not unknown, is not likely to occur when alkenes or alkynes are present in the reaction mixture.

Olefinic compounds with Si doubly bonded to C and the isomeric carbenes and silylenes have received wide attention.[14] The detailed investigations of doubly bonded Ge and Sn species seem to be just getting under way.[10,15] Only the parent Si$_2$H$_4$ species have previously been investigated with reliable theoretical methods, and the structural and energetic effects of substituents on **1–3** are unknown. The simple silylenes, SiX$_2$ (**4**), have been included in this study of substituent effects partly for comparison purposes and partly because physical data are available on a few of these silylenes which may be used to judge the accuracy of the applied calculational methodology.

II. Computational Details

Ab initio molecular orbital calculations have been carried out with the GAUSSIAN 80[16a] and 82[16b] series of programs on a DEC

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Table II. Total and Relative Energies of SiX$_2$ (X = H, Li, CH$_3$, and F) at HF/6-31G* Optimized Geometries

X	state	HF/6-31G*[a]	MP2/6-31G*[a,b]	MP3/6-31G*[a,b]	CISD/6-31G*[a,c]	ΔE$_{ST}$[d]
H	$^1A_1$	-290.00014 (0.0)	-290.06936 (0.0)	-290.08696 (0.0)	-290.09580 (0.0)	0.0
	$^3B_1$	-289.99271 (4.7)	-290.04819 (13.3)	-290.06190 (15.7)	-290.06843 (17.2)	17.6
Li	$^3\Sigma_g^-$	-303.76269 (0.0)	-303.83938 (0.0)	-303.85463 (0.0)	-303.85980 (0.0)	0.0
	$^1A_1$	-303.65856 (24.8)	-303.75608 (14.3)	-303.77464 (12.4)	-303.80487 (10.5)	10.3
CH$_3$	$^1A_1$	-368.09144 (0.0)	-368.42709 (0.0)	-368.46375 (0.0)	-368.47494 (0.0)	0.0
	$^3B_1$	-368.07663 (9.3)	-368.39584 (19.6)	-368.42908 (21.8)	-368.43971 (22.1)	22.9
F	$^1A_1$	-487.88278 (0.0)	-488.30343 (0.0)	-488.30360 (0.0)	-488.31341 (0.0)	0.0
	$^3B_1$	-487.79401 (55.7)	-488.19013 (71.1)	-488.18649 (73.5)	-488.19574 (73.8)	74.0

[a] Total energies in hartrees, relative energies (in parentheses) in kilocalories/mole. [b] MP2 and MP3 denote correlation energy calculations based on Møller–Plesset perturbation theory to second and third order, ref 20b. [c] This includes the size-consistency correction, ref 20a. [d] Vibrational zero-point energies were calculated at the HF/3-21G level, ref 21. ΔE$_{ST}$ = ΔE$_{ST}$(CISD) + ΔE$_{ST}$(ZPE).

VAX 11/780. Geometries have been optimized[17] at the single determinant self-consistent-field (SCF) Hartree–Fock (HF) level[18a,b] with split-valence 6-31G basis sets[19a,b] (HF/6-31G//6-31G) and with the 6-31G basis sets augmented by a full set of d functions (6D) on Si,[19b] abbreviated 6-31G$^+$ (HF/6-31G$^+$//6-31G$^+$). In addition, geometries for the simple silylenes (**4**) were optimized with the 6-31G* basis set (HF/6-31G*//6-31G*),[19b,c] which includes full sets of d functions on all atoms except hydrogen; single point calculations on **1–3** were also carried out with this basis set (HF/6-31G*//6-31G$^+$). All methyl group geometries were kept fixed with CH = 1.085 Å and <HCH = 109.47°, and the local geometry also remained tetrahedral in the trimethylsilyl group of **3c**.

The electronic singlet–triplet energy differences in **4** were determined from configuration interaction calculations employing the 6-31G* basis set; all singly and doubly excited configurations not involving the core orbitals (Si(1s,2s,2p), Li(1s), C(1s), and F(1s)) were included (CISD/6-31G*//6-31G*).[20a] Finally, to evaluate the zero-point energy corrections to these electronic differences, the vibrational frequencies were calculated at the HF level[21] with the 3-21G basis set.[19d]

III. Results and Discussion

Electronic States of 4. SiH$_2$ and SiF$_2$. Some physical data are available for these two silylenes from experiment and theory. Dubois deduced a vibrationally averaged (r_0) structure for singlet SiH$_2$ from the UV spectrum (SiH = 1.516 (3) Å, <HSiH = 92.1°).[22] The calculated structure, Table I, shows a bond length (r_e) too long at the HF/6-31G//6-31G level (SiH = 1.545 Å, <HSiH = 93.5°), but it is in excellent agreement with the experimental data after reoptimization including the Si d functions (SiH = 1.515 Å, <HSiH = 93.2°; HF/6-31G*//6-31G*). Recent calculations by Colvin et al. (CGSB)[23a] with a basis set slightly larger than the 6-31G* basis set and two-configuration SCF (TCSCF) theory gave very similar structural parameters (1.505 Å, 93.9°) as did an earlier TCSCF calculation by Meadows and Schaefer with a near HF-limit basis set (1.508 Å, 94.3°).[23b] Promotion of an electron from the doubly occupied lone pair orbital (**5**), which is almost exclusively of Si 3s character in the singlet

ground state ($^1A_1$), into the out-of-plane Si 3p(π) orbital (**6**) leads for the triplet configuration ($^3B_1$) to an increase in bond angle to 117.9° and a decrease in SiH bond length to 1.477 Å (HF/6-31G*//6-31G*). Very similar structural data were previously

5   **6**
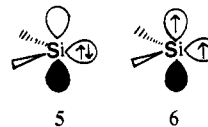
obtained by Schaefer and collaborators (e.g., 118.1° and 1.466Å, ref 23a). This favorable comparison between results obtained with the present methodology and the best available in the literature carries over to estimates for the singlet–triplet energy separation (Table II). CGSB obtain a ΔE$_{ST}$ of 16.8 kcal/mol at the CISD level, and the value calculated here is 17.2 kcal/mol (CISD/6-31G*//6-31G*); inclusion of zero-point corrections increases the difference to 17.6 kcal/mol. The only experimental value for ΔE$_{ST}$ in **4a** arises from the laser photodetachment study of SiH$_2^-$ by Lineberger et al.,[24] which produced an approximate upper bound of 0.6 eV ($\approx$14 kcal/mol). Expansions in the basis set or number of active orbitals used for the correlation energy calculations appears to only increase the calculated ΔE$_{ST}$ further.[25] An experimental reinvestigation of this fundamental silylene quantity is desirable.[23a]

Margrave et al. have obtained the following structure from the microwave spectrum of singlet SiF$_2$: SiF = 1.591 Å and <FSiF = 101.0°.[26] With the 6-31G basis set, the calculated SiF bond length is far too long (1.680 Å) and the bond angle too small (96.3°). The 6-31G$^+$ basis set gives a considerable improvement in the bond length to 1.626 Å and increases the bond angle to 98.8°. Finally, the addition of d-type functions on F (6-31G*) leads to excellent agreement with the experimental geometry since the calculated SiF bond length now is 1.598 Å and the FSiF angle 99.6°. The recent work of CGSB led to a shorter bond length (1.584 Å) but a similar angle (99.9°).[23a] The triplet state has no change in bond length but the usual opening of the bond angle (113.6°) relative to the singlet; comparable results were obtained by CGSB. ΔE$_{ST}$ is experimentally determined at 75.2 kcal/mol.[27] CGSB obtained a value of 73.5 kcal/mol, and our calculations give 73.8 kcal/mol (74.0 kcal/mol after zero-point energy corrections).

Si(CH$_3$)$_2$. Dimethylsilylene was first characterized by Drahnak, Michl, and West in 1979[28] although it had been implicated frequently as a reaction intermediate.[1] The singlet state of **4c** was considered by Gordon in his calculational study of SiC$_2$H$_6$ isomers,[29] but no calculations on the triplet have been reported. The

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(25) If all orbitals are included in the CI, the value for ΔE$_{ST}$ increases from 17.2 to 17.3 kcal/mol with the 6-31G* basis set. If p functions on H are added to the basis set (6-31G**), ΔE$_{ST}$ increases to 18.0 kcal/mol. The H p functions have negligible geometrical effects.

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apex angle in singlet Si(CH$_3$)$_2$ (98.8°) is similar to that of SiF$_2$, but whereas the larger angle (relative to SiH$_2$) in SiF$_2$ most likely is a result of electrostatic repulsion between the negatively charged fluorines, the increased angle in Si(CH$_3$)$_2$ is the combined result of steric crowding and slight hyperconjugative donation into the formally empty Si 3p(π) orbital. The triplet structure has a shorter SiC (1.914 Å) bond length than the singlet (1.926 Å) and a widened angle (117.7°). This SiX bond length reduction is also apparent in SiH$_2$ (Table I) and is presumably due to the increased Si 3s character in the hybrids to C or H as the central angle opens. The large bond angle changes (15–25°) between the singlet and triplet state indirectly become reflected in large Stokes shifts between the maxima for the absorption and fluorescence bands of Si(CH$_3$)$_2$[28a] and known inorganic silylenes.[5a,24] The photoexcited singlet (^{1}B$_1$) differs in spin coupling but not in orbital occupancy from the triplet (^{3}B$_1$) considered here, and hence the equilibrium geometries of both excited silylene states should in general be very similar. This has indeed been verified by actual calculations on SiH$_2$ and SiF$_2$.[23]

The singlet–triplet energy separation in **4c** is calculated as 22.1 kcal/mol (ΔE_{ST} = 22.9 kcal/mol after vibrational corrections). At the same calculational level, ΔE_{ST} in HSiCH$_3$ is 19.2 kcal/mol so each methyl group stabilizes the silylene singlet state preferentially by 2–3 kcal/mol, certainly a much smaller effect than fluorine substitution. No direct measurement of ΔE_{ST} for **4c** is available, although it is certain that the ground state is the singlet.[28] The heat of formation for **4c** has been determined from decomposition studies of Si$_2$Me$_5$H and Me$_2$SiH$_2$ as ca. 16 kcal/mol[30a] and 42 kcal/mol,[30b] respectively. Bell et al.[31] have advanced the interesting suggestion that the difference between these two estimates (26 kcal/mol) arises from the formation of **4c** in different spin states in the two experiments. A recent ion cyclotron resonance spectroscopy experiment[30c] produced a value of 46 kcal/mol for the Si(CH$_3$)$_2$ heat of formation, whereas Walsh has derived a value of 26 kcal/mol on the basis of thermochemical arguments.[30d] The calculated value of ΔE_{ST} (22–23 kcal/mol) is compatible with the differences between the high and low heats of formation, but additional experimental and theoretical work is required to determine if the formation of triplet Si(CH$_3$)$_2$ is the actual source for the disagreement.

SiLi$_2$. This species is included in the study solely as a model representing the opposite extreme in electronegativity from SiF$_2$. A typically bent silylene structure (SiLi = 2.533 Å, <LiSiLi = 92.0°) can be located as a minimum for the closed shell singlet state (^{1}A$_1$), but there is no minimum with a bent geometry for the triplet. A linar structure with a shorter SiLi bond ($^3\Sigma_g^-$, 2.429 Å) is at the HF level about 25 kcal/mol more stable than the bent singlet. A singlet state with linear geometry ($^1\Delta_g$, SiLi = 2.426 Å) is 26.1 kcal/mol above the triplet.[32] Correlation energy corrections diminish the ^{1}A$_1$–$^3\Sigma_g^-$ energy gap considerably, and our final value for ΔE_{ST} in SiLi$_2$ is –10.3 kcal/mol.

Conclusions. Additional calculations show that HSiLi maintains a bent structure as a minimum for the triplet state (<HSiLi = 138.4°, SiH = 1.509 Å, SiLi = 2.394 Å) and that this state is just 4.0 kcal/mol (CISD/6-31G*//6-31G*) more stable than singlet, bent HSiLi (<HSiLi = 92.9°, SiH = 1.529 Å, SiLi = 2.612 Å). Highly electropositive substituents with empty, low-lying orbitals are hence required to establish the triplet state as the ground state in a silylene. Substituents more electronegative than Si preferentially stabilize the singlet silylene state, and so far all silylenes generated experimentally have had singlet ground states. These trends run parallel to those observed and calculated for carbenes[33] but triplet ground states are not uncommon among

carbenes. This may ultimately be related to the fact that in methylene (:CH$_2$) ΔE_{ST} is 8–10 kcal/mol in favor of the triplet; in silylene (:SiH$_2$), ΔE_{ST} is 15–20 kcal/mol in favor of the singlet. The substituent effects on ΔE_{ST} are not additive, however. The increase in ΔE_{ST} upon substitution of one H by CH$_3$ or F is 2.0 or 20.9[23a] kcal/mol, respectively; a second CH$_3$ or F produces an additional increase by 2.9 or 35.8[23a] kcal/mol. The first Li atom preferentially stabilizes the triplet by 21.2 kcal/mol whereas the second Li atom only gives an additional 6.5 kcal/mol decrease in ΔE_{ST}.

Where comparisons are possible, Table I and the experimental data given above in the text show that the sp 6-31G basis set produces too long bond lengths and that for accurate structure determinations of SiX$_2$ species (X = second row element or group), polarization functions at least on Si are necessary (6-31G$^+$ basis). The importance of additional d functions on X (6-31G*) is, as expected, largest for X = F but even then these functions provide largely a fine-tuning of the geometrical parameters. Two-configurational wave functions do not appear to be required for a good structural description of the silylene singlet ground states, however.[23] The energetic effects upon reoptimization are generally small, and quantitatively similar ΔE_{ST} values can be achieved by using the fully polarized basis sets at geometries optimized with either the 6-31G$^+$ or the 6-31G* basis set. Overall, the basis set containing d functions only on Si (6-31G$^+$) performs very well, which is important in studies of the larger molecules where, for example, geometry optimizations with 6-31G* basis sets are impossible to carry out.

IV. Disilenes

H$_2$SiSiH$_2$ and (CH$_3$)$_2$SiSi(CH$_3$)$_2$. Snyder and Wasserman were the first to calculate a trans-bent (**2a**, C$_{2h}$) rather than planar (**1a**, D$_{2h}$) equilibrium structure for the parent disilene. Basis sets containing only s and p functions on Si make singlet H$_2$SiSiH$_2$ distinctly nonplanar, e.g., α = 22.5° (Table III) with the 6-31G basis set (α = rocking angle = angle between the HSiH plane and the SiSi axis), and the planar conformation serves as a transition state for synchronous inversion of the geminal SiH$_2$ groups. Polarization functions decrease the equilibrium rocking angle and make the total potential energy surface extremely flat with respect to various angular deformations as shown by the following calculations. At the HF/6-31G*//6-31G* level, the energy difference between **1a** (α = 0) and **2a** (α = 11.2°) is ca. 0.01 kcal/mol; additional increases in α by 10°, 20°, and 30° above the equilibrium value lead to energy increases of only 0.1, 0.6, and 2.1 kcal/mol, respectively. Twisting each of the SiH$_2$ groups in **2a** by 5°, 10°, or 20° around the SiSi axis (C$_{2h}$ → C$_2$) gives energy increases of 0.2, 0.6, or 2.7 kcal/mol, respectively. The possibility of a cis-bent minimum can be safely dismissed since bending in a cis manner by 10°, 20°, or 30° raises the energy by 1.2, 4.6, or 10.2 kcal/mol, respectively. Correlation energy corrections preferentially favor the trans-bent form **2a**. Thus, geometry optimization including correlation via Møller–Plesset second-order perturbation theory and the 6-31G* basis set increases the rocking angle to 25.7° and the barrier toward planarity approaches 1.0 kcal/mol.[9a]

The equilibrium conformation for the fully methylated disilene is **2c** (α = 27.6°) at the HF/6-31G//6-31G level and **1c** is a transition state located 1.0 kcal/mol above **2c** (Table IV). The effect of Si d functions is, however, even more pronounced on the **2c** structure than on **2a** since this minimum (**2c**) actually disappears upon reoptimization with the 6-31G$^+$ basis set, and planar **1c** with SiSi = 2.133 Å, SiC = 1.898 Å, and <CSiC = 113.3° emerges as the potential energy minimum. As expected, the surface is still very soft for the trans-bending mode as evidenced by the modest energy increase of 1.5 kcal/mol (HF/6-31G$^+$// 6-31G$^+$) calculated for α = 30° (SiSi = 2.184 Å, SiC = 1.904 Å, <CSiC = 110.3°); cis-bending is again far less preferable with just a 10° distortion amounting to an energy increase of 3.1

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Table III. Optimized Structures for **1, 2, 7,** and **9**[a]

molecule (state)	parameter	HF/6-31G//6-31G				HF/6-31G+//6-31G+			
		X = H	X = Li	X = CH₃	X = F	X = H	X = Li	X = CH₃	X = F
1 (^1A_g)	SiSi	2.156	2.285	2.166	2.106	2.129	2.234	2.133	2.054
	SiX	1.484	2.492	1.927	1.660	1.470	2.498	1.898	1.606
	XSiX	116.2	124.8	114.1	111.8	115.3	126.8	113.3	109.3
2 (^1A_g)	SiSi	2.176		2.209		2.134			
	SiX	1.488		1.933		1.473			
	XSiX	113.7		110.4		114.7			
	α^b	22.5		27.6		11.2			
7 (^3B)	SiSi	2.368			2.377	2.349			2.348
	SiX₁	1.500			1.672	1.485			1.618
	SiX₂	1.498			1.675	1.484			1.621
	X₁SiX₂	109.4			106.5	108.9			106.6
	X₁SiSi	115.2			114.9	115.0			114.0
	X₂SiSi	112.8			105.5	112.1			107.9
	X₁SiSiX₃	68.8			59.7	65.0			45.7
9 (^1A_g)	SiSi		2.302				2.235		
	SiLi₁		2.461				2.442		
	SiLi₂		2.392				2.420		
	Li₁SiSi		65.3				65.9		
	Li₂SiSi		148.2				144.7		

[a] Bond lengths in angstrom, angles in degrees. [b] The rocking angle, α, is defined as the angle between the SiSi axis and the XSiX plane. [c] X₁ and X₃ are symmetry equivalent.

Table IV. Total and Relative Energies of Si₂X₄ Species (**1–3, 7,** and **9**)[a]

molecule point group	X	HF/6-31G//6-31G		HF/6-31G+//6-31G+		HF/6-31G*//6-31G+	
		E(tot)	E(rel)	E(tot)	E(rel)	E(tot)	E(rel)
1a (D_{2h})	H	−580.007 45	2.0	−580.076 67	2.8	−580.076 67	2.8
2a (C_{2h})	H	−580.007 82	1.7	−580.076 69	2.8	−580.076 69	2.8
3a (C_s)	H	−580.010 56	0.0	−580.081 13	0.0	−580.081 13	0.0
7a (C_2)	H	−580.007 71	1.8	−580.077 50	2.3	−580.077 50	2.3
1b (D_{2h})	Li	−607.529 81	13.3	−607.529 81	27.6	−607.533 44	29.0
9 (C_{2h})	Li	−607.550 93	0.0	−607.573 86	0.0	−607.579 64	0.0
1c (D_{2h})	CH₃	−736.134 87	2.7	−736.204 22	0.0	−736.252 13	
2c (C_{2h})	CH₃	−736.136 54	1.6	b		b	
3c (C_s)	CH₃	−736.139 14	0.0	−736.203 92	0.2	c	
1d (D_{2h})	F	−975.461 68	74.1	−975.628 69	60.0	−975.699 62	56.9
3d (C_s)	F	−975.579 80	0.0	−975.724 38	0.0	−975.790 33	0.0
7d (C_2)	F	−975.533 91	28.8	−975.684 81	24.8	−975.750 52	25.0

[a] Total energies in hartrees, relative energies in kilocalories/mole. [b] No longer a minimum structure; see text. [c] The low molecular symmetry and insufficient disk space made this calculation impossible to carry out.

kcal/mol. Twisting around the SiSi bond by 5° or 10° gives small energy increases of 0.2 and 0.7 kcal/mol, respectively. Since correlation energy corrections consistently favored **2a** preferentially over **1a** regardless of the basis set employed,[9a] the possibility of a nonplanar (trans-bent) equilibrium geometry of (CH₃)₂SiSi-(CH₃)₂ with a very small energy separation from planarity cannot be entirely excluded.

The flatness of the potential energy surfaces calculated for both the parent and alkylated disilene imply that crystal packing forces and temperature may affect the solid-state structures of isolated disilenes. Hence, experimentally determined conformations deviating from the predicted idealized gas-phase structures are likely. Two X-ray structures of heavily substituted disilenes have been published since the major part of these calculations were carried to completion.[7] The structure of tetramesityldisilene (**2**, X = 2,4,6-trimethylphenyl)[7a] shows a SiSi bond length of 2.16 Å, α = 18°, and an additional twist of 5° around the SiSi axis. The structure of tetrakis(2,6-diethylphenyl)disilene is planar around each Si atom (<CSiC = 117.6°) with a SiSi bond length of 2.140 Å and a twist angle of 10° around the SiSi bond. Given the additional bulkiness of the aryl groups and the possibility of direct conjugation with the SiSi double bond, the calculated results and the experimental structures are fully consistent with each other.

The preference for the nonplanar structure increases with the elements Ge and Sn. Ab initio HF calculations on digermene, H₂GeGeH₂, predict a strongly trans-bent structure ($\alpha \approx 35-40°$) and barriers to planarity of 2–3 kcal/mol.[10a,b] The IR and Raman spectra of tetramethyldigermene have recently been presented and were best interpreted according to a trans-bent geometry (C_{2h}).[10c] Preliminary ab initio results on distannene, H₂SnSnH₂, have

indicated a trans-bent equilibrium geometry with a barrier through planarity near 4 kcal/mol.[10b] A divalent tin species, Sn[CH-(SiMe₃)₂]₂, is a monomer in the gas phase but crystallizes as a singlet dimer with considerably pyramidalization around the Sn atoms (α = 41°, <CSnC = 112°); the Sn–Sn bond length (2.76 Å) is, however, indicative of a single bond without appreciable double bond character.[10d,e]

F₂SiSiF₂. There is no structural minimum corresponding to a closed shell singlet tetrafluorodisilene. Calculations with enforced D_{2h} symmetry (**1c**) leads to a geometry with a very short SiSi bond length (2.054 Å at HF/6-31G⁺) and a narrow FSiF angle (109.3°), but this species falls rapidly apart to two SiF₂ units without any activation energy barrier if the symmetry is decreased to C_{2h} by trans bending of the geminal SiF₂ groups.

Two adjacent SiF₂ units are often found in the reaction products of SiF₂ with alkene and alkyne derivatives, which suggests the possibly intermediacy of a dimeric species. This species could be diradical-like since a paramagnetic free radical species like [·(-SiF₂-)·]ₙ is present in concentrated condensed matrix solutions of SiF₂; in dilute systems only the monomer or dimer is present.[5b] There is no sign of diradical-like species in gas-phase SiF₂, but dimer intermediates might be formed upon condensation.

A search for the structure of triplet tetrafluorodisilene was initiated as a simple way of exploring the diradical possibility further. The triplet minimum has C_2 symmetry (**7**) and thus resembles triplet H₂SiSiH₂.[9b,c] Each Si atom is strongly pyramidalized (α = 55.2°, <FSiF = 106.5° in **7d**; α = 47.5°, <HSiH = 108.9° in **7a**), the terminal units are rotated to a gauche conformation (β = angle between the two SiF₂ bisectors = 80.5° in **7d**, 99.2° in **7a**), and the SiSi bond lengths (2.348 Å in **7d**, 2.349

7 (a, X = H)
(d, X = F)
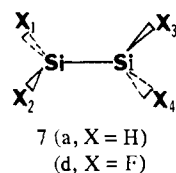
Å in **7a**) are indicative of single bonds. The triplet state **7d** is 31.9 kcal/mol below the hypothetical singlet structure **1d** at the HF/6-31G*//6-31G+ level. For comparison, the **2a–7a** separation is 0.5 kcal/mol at the same level, also with the triplet lowest in energy. These triplet states are obtained by unrestricted HF (UHF) calculations[18b] but show negligible spin contamination ($S^2 \approx 2.005$) from higher spin states. The corresponding open shell singlet diradical-like states, which differ formally from the triplets by just a spin flip, could hence be lying within a few kilocalories per mole of the triplets, but their positions are unknown at present.

Li₂SiSiLi₂. There is no stationary point with trans-bent geometry for tetralithiodisilene (**2b**) but a stationary point may be located under D_{2h} symmetry, resembling a classic olefin (**1b**) with a long SiSi bond (2.282 Å) and large LiSiLi angle (124.8°). The structure is not a minimum, however, since direct calculation of the force constant matrix shows two negative eigenvalues. Bridged structures are much lower in energy. The symmetrically bridged D_{2h} structure **8** (SiSi = 2.210 Å, SiLi₁ = 2.492 Å, and SiLi₂ = 2.334 Å; HF/6-31G//6-31G) is about 25 kcal/mol below **1b**, but it also has two negative eigenvalues of the force constant matrix.

8   9
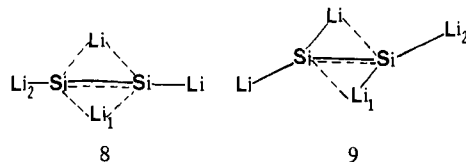
A distorted version of **8** with C_{2h} symmetry (**9**) is a minimum, about 2.0 kcal/mol below **8**. Based on its structural parameters (SiSi = 2.235 Å, SiLi₁ = 2.442 Å, SiLi₂ = 2.420 Å, <Li₁SiSi = 65.9°, and <Li₂SiSi = 144.7°) **9** may perhaps be viewed as a singlet coupled complex between two ground state triplet SiLi₂ species (<Li₁SiLi₂ = 149.4 in **9**, 180° in **4b**). The bridging Li atoms are bonded to both Si atoms, whereas the SiSi bonding is weak and mostly of π character. This structure appears to be the lowest energy singlet Si₂Li₄ isomer. A comprehensive search for nonplanar isomers,[34] including structures analogous to those suggested for C₂Li₄ by Epiotis,[35] failed to produce a singlet isomer with lower energy than **9**.

Disilene Structure and Stability Toward Dissociation. Both qualitative (e.g., atomic orbital size)[36] and semiquantitative (e.g., Mulliken overlap population analyses)[37] arguments indicate that Si utilizes considerable 3p-orbital character in its bonding. Thus, the SiSi σ bonding is mostly of the 3pσ type, and the π bonding is relatively weak. Most of the common substituents (including H) are more electronegative than Si; for example, on the Allred scale the respective electronegativities are Si = 1.90, H = 2.20, C = 2.55, F = 3.98, but Li = 0.98.[38] Consequently, it is to a large extent the substituent which controls the orbital composition of the SiX bond, and the SiSi bonding will adjust according to the demands exerted by X. Electronegative substituents will increase the preference for Si to adopt a tetrahedral environment through the enhanced degree of p character in the Si–X bonds, necessitating Si hybridization more like sp³ than sp². This is clearly reflected in the optimized (6-31G+ basis set) structures for **1** (Table III). The XSiX angle is already less than 120° for X = H (115.3°) and decreases to 113.3° upon replacement of H with

CH₃. X = F leads to a sp³-type angle (<FSiF = 109.3°), whereas the effective Si hybridization toward electropositive Li has more 3s and less 3p character, and a large LiSiLi angle of 126.8° results. The σ donation to C in **1c** leads to a SiSi bond length only slightly longer than that of **1a**, but F leaves Si with a highly positive charge in **1c** (+0.90; 6-31G* basis set). This increases the effective Si electronegativity considerably, the Si orbitals contract,[39] and for optimal SiSi bonding a short bond length (2.054 Å) is required. Naturally, Li has the opposite effect, and in **1b** Si has acquired an unfavorable negative charge (−0.20; 6-31G* basis set); the Si orbitals become diffuse due to the decreased effective electronegativity, and the SiSi bond length is long (2.234 Å).

Out-of-plane bending of the geminal groups initiates mixing of occupied and unoccupied orbitals, and as rationalized elsewhere for ethylene,[8b] this interaction is expected to favor trans (anti) over cis (syn) pyramidalization. Pyramidalization facilitates the withdrawal of σ-electron density toward X, lengthens the SiSi bond, and narrows the XSiX angle (Table III), but the anticipated immediate destabilization of the SiSi π orbital does not occur. The π bond mixes in Si 3s character and actually becomes slightly stabilized in energy for small values of α. This effect contributes to the softness of the bending mode. With sp basis sets, the orbital mixing in X₂SiSiX₂ leads to a preference for the nonplanar structures for X = H and CH₃. The d functions on Si present in the polarized basis set mix very strongly into the SiSi π orbital and decrease the tendency for nonplanarity in all the disilenes, resulting in planarity (X = CH₃) or near planarity (X = H) with low distortion energies toward trans bending. Pyramidalization further facilitates electron withdrawal from the SiSi bonding region in F₂SiSiF₂, and the molecule falls apart. The dissociation of **1d** to two ground-state SiF₂ species on a singlet surface maintaining D_{2h} symmetry is symmetry forbidden, but the process is allowed under C_{2h} symmetry. SiF₂ is, of course, an unusually stable silylene ($t_{1/2} \sim 100$ s),[5a] and the SiF bond in SiF₂ is exceptionally strong.[30d]

The substantial differences in disilene stabilities may be further illustrated by examination of the calculated energy changes for the dissociation reaction

$$X_2Si = SiX_2 \rightarrow 2\;:SiX_2 \qquad (1)$$

Although extensive recovery of electronic correlation energy clearly is essential for accurate determinations of the SiSi double bond strength from eq 1, our best HF values (HF/6-31G*//6-31G+) nevertheless are quite illustrative by themselves. For the parent disilene (X = H), reaction 1 is endothermic by 47.9 kcal/mol; with X = CH₃, the endothermicity is slightly diminished to 43.9 kcal/mol. These values are in accordance with reports that spontaneous dimerization of **4b** to **1b** indeed has been observed;[4b] also, the dimerization of **4a** to activated **2a** followed by rearrangement to **3a** has been proposed.[40] X = F leads to an exothermicity of 40.1 kcal/mol for reaction 1 using the planar singlet structure **1d** and 8.2 kcal/mol if the triplet diradical structure is used. For X = Li, eq 1, modified as **8** → 2 **4b**, is endothermic by 34.1 kcal/mol when the triplet ground state is used for **4b**. Thus, the prediction made by Blustin[41] that it would be difficult to find substituents, which can thermodynamically stabilize the SiSi double bond, has clearly been verified.

The effect of correlation energy corrections on the estimate for the energy of reaction 1 may be investigated for X = H. Inclusion of configuration interaction increases the calculated endothermicity of (1) to 57.7 kcal/mol (CISD/6-31G*//6-31G*).[42] The SiSi single bond energy in crystalline silicon is experimentally determined near 54 kcal/mol,[43] leading to an estimate for the π-bond strength of only ca. 4 kcal/mol. Walsh proposes considerably larger SiSi bond strengths (e.g., 74 kcal/mol in H₃SiSiH₃) which

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(42) E(CISD/6-31G*//6-31G*) = −580.283 54 au for **2a**.; E(CISD/6-31G*//6-31G*) = −580.252 90 au for **5a**.

(43) Sanderson, R. T. "Chemical Bonds and Bond Energy"; Academic Press: New York, 1976.

Table V. Optimized Geometries for Singlet Silylsilylenes, $XSiSiX_3$ (3c,d)[a,b]

parameter	HF/6-31G//6-31G		HF/6-31G+//6-31G+	
	X = CH$_3$	X = F	X = CH$_3$	X = F
SiSi	2.500	2.491	2.426	2.416
SiX$_1$	1.984	1.689	1.943	1.637
SiX$_2$	1.939	1.665	1.911	1.615
SiX$_3$	1.939	1.662	1.911	1.608
SiSiX$_1$	98.1	92.9	99.5	93.8
SiSiX$_2$	109.5[d]	108.7	109.5[d]	110.2
SiSiY[c]	120.0[d]	116.0	120.0[d]	114.1
X$_3$SiY[c]	54.8[d]	52.9	54.8[d]	52.8

[a] Bond lengths in angstrom, angles in degrees. [b] Geometries for **3a** with the present basis sets may be found in ref 9a. [c] Y is a point on the line of intersection formed by the planes X$_3$SiX$_3$ and SiSiX$_1$, so that <YSiSiX$_1$ = 0. [d] Parameter kept fixed.

may indicate that not even this extent of correlation energy recovery is sufficient for determination of the π-bond strength. A separate measure for this quantity is provided by the singlet–triplet (**2a–5a**) energy difference, since the π bond is broken in the triplet (**5a**). A value of 19.3 kcal/mol is obtained at the CISD/6-31G*//6-31G* level,[42] in excellent agreement with the value calculated by Lischka and Köhler (19.7 kcal/mol).[9b] This π-bond strength is still significantly lower than the corresponding π-bond energies in ethylene (≈60 kcal/mol) or silaethylene (≈39 ± 5 kcal/mol).[14]

V. Silylsilylenes

Only the closed shell singlet states of the silylsilylenes with the two electrons in the in-plane lone pair orbital have been considered since **3a**, **3c**, and **3d** undoubtedly possess singlet ground states. Lischka and Köhler have calculated a singlet–triplet separation of 16.5 kcal/mol in **3a**.[9b] Substitution of H with the more electronegative CH$_3$ or F will increase this separation. It was not possible to locate a minimum for **3b**; the Li atoms immediately move toward bridging positions when permitted to do so. The optimized silylsilylene structures (Table V) resemble simple silylene structures closely; i.e., the angle at the divalent Si atom lies between 90–100°, and the bond lengths between the divalent Si atom and Si or X are long due to extensive p-orbital character.

Although a species of composition Si$_2$H$_4$ has not been experimentally isolated, intermediates with this stoichiometry have been suggested in, e.g., the pyrolysis of silanes. In particular, the formation of silylsilylene (**3a**) rather than disilene (**2a**) has been postulated in the pyrolysis of trisilane.[3a] With the 6-31G* basis set, **3a** is calculated to be more stable than **2a** by ca. 2.5 kcal/mol at the HF level. However, correlation energy corrections reverse the energetic order, and the current best estimate for the **2a–3a** energy difference is ca. 5.0 kcal/mol in favor of **2a**.[9a]

The fully methylated species **1c** and **3c** are also essentially isoenergetic at the HF level. **3c** is 1.6 kcal/mol more stable than **2c** with the 6-31G basis set, but calculations with the larger basis

set (6-31G+) changes the difference to 0.2 kcal/mol in favor of the disilene **1c**. As just mentioned, electron correlation stabilizes **2a** (and **1a**) preferentially by ca. 7 kcal/mol over **3a**. Presumably, **1c** could be preferentially stabilized by a similar amount over **3c** since the correlation energy associated with the (π, π*) orbitals in olefins or sila olefins consistently exceeds that of the (n$_\sigma$, p$_\pi$) pair in carbenes or silylenes. The total differential correlation energy is dominated by this difference[44] and the conclusion is that **3c** is less stable than **1c**, probably by 5–10 kcal/mol. Evidence has been presented for the interconversion of **1c** and **3c** in the gas phase at elevated temperatures.[3b]

Interestingly, the fluorinated singlet silylene **3d** is 55–60 kcal/mol more stable than singlet **1d** (D_{2h} symmetry enforced) but, most importantly, it is also 25.0 kcal/mol more stable than the triplet diradical **5d**. Correlation energy corrections should preferentially favor closed shell singlet **3d** further over open shell **5d**, and it is very likely that **3d** is the most stable Si$_2$F$_4$ isomer. These calculational results, combined with the exothermicity of reaction 1 for X = F, suggest that in mechanistic analyses of SiF$_2$ reactions, the possible intervention of **3d** should be considered, since two adjacent SiF$_2$ units could be introduced via this silylene as well.

VI. Concluding Remarks

As anticipated, electronegativity differences between Si and the substituents play a dominant role for the stabilities and structures of SiX$_2$ and Si$_2$X$_4$ species. The small differences in electronegativity between H and C do lead to analogous features and properties between Si$_2$H$_4$ and Si$_2$(CH$_3$)$_4$ isomers or the silylenes SiH$_2$ and Si(CH$_3$)$_2$. Methyl does not stabilize the SiSi double bond in a thermodynamic sense, and the main function of the bulky aryl or alkyl groups commonly on disilenes clearly is to exert a steric influence and protect the double bond. Extremes in electronegativities have dramatic effects on stabilities and structures as calculated for the lithio- or fluoro-substituted species. The considerable relative stability of silylenes with electronegative substituents is underscored by the emergence of the silylsilylene **3d** as the most stable Si$_2$F$_4$ isomer. The exotic nature of Li as a substituent is apparent in the triplet ground state of SiLi$_2$ and the distorted structure for the most stable Si$_2$Li$_4$ isomer, **9**.

(44) Trinquier, G.; Malrieu, J.-P. *J. Am. Chem. Soc.* **1981**, *103*, 6313.