Registry No. 1a, 58356-65-3; **1b**, 32195-55-4; LiOCl, 13840-33-0; styrene, 100-42-5; 4-cyanopyridine, 100-48-1; 4-methylpyridine, 108-89-4; 2,6-dimethylpyridine, 108-48-5; 2,6-di-*tert*-butylpyridine, 585-48-8; 3,5-dimethylpyridine, 591-22-0; *cis*-stilbene, 645-49-8; α-methylstyrene, 98-83-9; cyclohexene, 110-83-8; 1-methylcyclohexene, 591-49-1; cyclooctene, 931-88-4; 2-methyl-2-heptene, 627-97-4; 2-methyl-1-heptene, 15870-10-7; 1-octene, 111-66-0; pyridine, 110-86-1; benzyldimethyltetradecylammonium chloride, 139-08-2; *p*-methoxystyrene, 637-69-4; sodium hypochlorite, 7681-52-9; norbornene, 498-66-8; 3-carene, 13466-78-9.

Substituent Effects on the Carbon–Silicon Double Bond. Monosubstituted Silenes

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Abstract: A series of isomeric silenes $H_2C{=}SiHR$ (**1**) and $H_2Si{=}CHR$ (**2**) where R = CH_3, SiH_3, F, OH, $OSiH_3$, CN, and NO_2 were studied at the RHF/3-21G and 6-31G* levels. The two basis sets give in general similar results. The calculated r(C=Si) are (3-21G, values (in Å) for **1** followed by **2**) 1.717 (R = H), 1.716, 1.725 (CH_3), 1.724, 1.721 (SiH_3), 1.698, 1.730 (F), 1.705, 1.746 (OH), 1.705, 1.749 ($OSiH_3$), 1.711, 1.727 (CN), 1.707, and 1.726 (NO_2). The experimental r(C=Si) of 1.764 Å in $(Me_3Si)_2Si{=}C$(adamantyl)$(OSiMe_3)$ is electronically elongated and consistent with our calculations and with a r(C=Si) of 1.70 Å in unperturbed silenes but contrasts with the electron diffraction measurement of 1.83 Å. The **2** - **1** energy differences (ΔE) are determined by the bond energies of Si–R vs. C–R and of Si–H vs. C–H: ΔE (6-31G*, kcal mol^{-1}) 8.9 (R = CH_3), -3.6 (SiH_3), 53.9 (F), 41.2 (OH), 51.1 ($OSiH_3$), 3.0 (CN), 2.7 (NO_2). Substituent effects (SE) on the thermodynamic stability of the C=Si bond are generally small. The calculated energies of the equations **1** + SiH_4 → **1**, R = H and H_3SiR, **2** + CH_4 → **2**, R = H and H_3CR, that also model the SE on the dimerization energies of **1** and **2** are, respectively, (6-31G*, kcal mol^{-1}), R = CH_3, 0.1, 0.3, H_3Si, 2.9, 6.0, F, -2.0, -7.8, OH, 0.3, 0.4, $OSiH_3$, -0.2, -2.8, CN, -1.4, 3.8, and NO_2, -3.4, 2.4. SE on the charge distributions and on the energies and coefficients of the frontier orbitals of **1** and **2** are evaluated and used for analyzing the factors that control their kinetic stability. A "reversed polarity" of the π-bond, i.e., $C^{\delta+}{=}Si^{\delta-}$, is the most important single electronic factor that reduces the reactivity of silenes; the energies of the π- and π*-orbitals are less significant.

Silicon–carbon double bonds (silenes) have become recently the subject of considerable experimental and theoretical interest.[1] The theoretical as well as most of the experimental studies have centered on the parent $H_2C{=}SiH_2$[2] and on the methyl-substituted silenes.[1c,3] Recently Brook et al. have succeeded for the first time to isolate stable silenes of the general formula $(Me_3Si)_2Si{=}CR(OSiMe_3)$.[4] This important achievement focused attention to the possible role of the substituents in stabilizing the C=Si bond. While steric effect definetively play an important role in stabilizing these silenes[4] the contribution of electronic effects which may be even more significant is unknown. Knowledge of substituent effects is of great importance in selecting new silenes as possible candidates for synthesis or for understanding silene reactions. Disappointingly, very little is known in this respect either experimentally or theoretically. Experimentally, Brook reported that attempts to stabilize silenes with aryl or trifluoromethyl groups were unsuccessful.[4c] Theoretically only methyl[3] and fluorine[5a] substituions were studied. When this paper was being written, Gordon and George pulbished calculations on hydroxy substitution,[5b] but as the prime interest of these authors was entirely different from ours there is no overlap between the discussions of the two papers. In an attempt to supply this vital basic information we have undertaken an extensive theoretical study of a series of substituted silenes. Both mono- and disubstituted silenes were studied. The substituents that were chosen, i.e., OH, $OSiH_3$, SiH_3, CN, and NO_2, span wide range of electronic properties.[6] Hydroxy and silyloxy are strong π-donors, due to the presence of lone-pair electrons on the oxygen, but weak σ-acceptors. The nitro and the nitrile groups on the other hand are strong π-acceptors and also powerful σ-acceptors. Silyl exerts a much milder electronic effect, it is a weak π-acceptor and a weak σ-donor. For completion we have included methyl and fluorine which were studied previously.[3,5] Methyl is a weak π- and σ-donor, while fluorine is a strong σ-acceptor and a weak π-donor.[6]

In this paper we report the results of molecular orbital calculations at the ab initio level for the monosubstituted silenes. Substitution at both the silicon (**1**) and the carbon (**2**) ends of

$$\underset{\mathbf{1}}{H_2C{=}SiHR} \qquad \underset{\mathbf{2}}{RCH{=}SiH_2}$$

R = H, CH_3, SiH_3, OH, $OSiH_3$, F, CN, NO_2

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Table I. 3-21G Optimized Geometries of Silicon-Substituted Silenes $H_2C{=}SiHR$ (**1**)[a]

R	Si=C	Si—R	RSiC[b]	HSiC	HCSi[c]	HCSi[d]	additional parameters
H[e]	1.718	1.474	122.2	122.2	122.6	122.6	Si-H = 1.474, C-H = 1.074
CH_3[e]	1.716	1.907	124.7	120.1	121.9	122.7	Si-H = 1.482, C-H = 1.074
SiH_3[f,h]	1.725	2.359	122.2	119.5	122.3	122.3[n]	Si-H[i] = 1.482, C-H = 1.075
OH[g]	1.705	1.659	126.5	126.4	123.4	120.8	HOSiC = 180, HOSi = 128.7, O-H = 0.959, Si-H = 1.464, C-H = 1.074
$OSiH_3$[j]	1.705	1.633	125.5	123.9	123.2	120.6	SiOSiC = 180, SiOSi = 178.1, H_3Si-O = 1.654, Si-H[i] = 1.471, C-H = 1.074
F[e]	1.698	1.628	127.7	128.0	120.4	123.2	C-H = 1.074, Si-H = 1.466
CN	1.711	1.852	121.0	126.8	122.1	121.7	C-N = 1.143, Si-H = 1.466, C-H = 1.074
NO_2	1.702	1.863	115.6	134.8	120.2	122.8	planar, N-O[k] = 1.247, ONSi[l] = 118.0, ONSi[m] = 116.8, Si-H = 1.457, C-H = 1.074

[a] Bond lengths in Å, bond angles in deg. [b] The angle with the first atom in R bonded to silicon (e.g., N in NO_2). [c] Cis to R. [d] Trans to R. [e] See ref 5a for additional parameters. [f] C_s symmetry, HSiSi = 0. [g] Similar geometries were reported in ref 5b. [h] The SiH_3 parameters: H eclipsing C=Si, Si—H = 1.487, HSiSi = 108.6; hydrogens out of the C_s plane, Si—H = 1.492, HSiH = 108.4, SiSiX (X lies on the HSiH bisector) = 126.6. [i] H bonded to Si=C. [j] The SiH_3 group was taken to be tetrahedral with Si-H optimized at 1.484 Å. [k] The N-O bond lengths were assumed to be equal. [l] Cis to C=Si. [m] Trans to C=Si. [n] The two HCSi angles were optimized together.

Table II. 3-21G Optimized Geometries of Carbon-Substituted Silenes $H_2Si{=}CHR$ (**2**)[a]

R	Si=C	C—R	RCSi[b]	HCSi	HSiC[c]	HSiC[d]	additional parameters
H[e]	1.718	1.074	122.6	122.6	122.2	122.2	Si-H = 1.474, C-H = 1.074
CH_3[e]	1.725	1.514	124.6	120.1	123.8	120.1	Si-H = 1.479 (cis), 1.477 (trans)
SiH_3[f,h]	1.721	1.880	126.2	117.4	122.9	122.9	Si-H[i] = 1.477, C-H = 1.079
OH[g]	1.746	1.378	131.1	119.4	121.5	117.9	HOCSi = 180, HOC = 113.3, O-H = 0.960, Si-H[c] = 1.474, Si-H[d] = 1.469, C-H = 1.073
$OSiH_3$[j]	1.749	1.364	130.8	118.1	123.3	116.8	SiOCSi = 180, SiOC = 134.7, Si-O = 1.682, Si-H[c] = 1.474, Si-H[d] = 1.470, C-H = 1.075
F[e]	1.730	1.378	121.9	125.8	122.0	118.4	C-H = 1.072, Si-H[c] = 1.469, Si-H[d] = 1.471
CN	1.727	1.409	125.0	119.3	122.8	120.4	C-N = 1.44, Si-H = 1.471, C-H = 1.075
NO_2	1.731	1.419	121.4	125.8	127.2	116.6	planar, N-O[k] = 1.255, ONC[l] = 118.2, ONC[m] = 117.5, Si-H = 1.467, C-H = 1.067

[a] Bond lengths in Å, bond angles in deg. [b] The angle with the first atom in R bonded to silicon (e.g., N in NO_2). [c] Cis to R. [d] Trans to R. [e] See ref 5a for additional parameters. [f] C_s symmetry, HSiCSi = 0. [g] Similar geometries were reported in ref 5b. [h] The SiH_3 parameters: H eclipsing C=Si, Si—H = 1.487, HSiC = 109.8; hydrogens out of the C_s plane, Si-H = 1.492, HSiH = 107.0, SiSiX (X lies on the HSiH bisector) = 128.7. [i] H bonded to Si=C. [j] The SiH_3 was taken to be tetrahedral with Si-H optimized at 1.482 Å. [k] The N-O bond lengths were assumed to be equal. [l] Cis to C=Si. [m] Trans to C=Si. [n] The two HCSi angles were optimized together.

Table III. Total Energies (hartrees) and Relative Energies (kcal/mol^{-1}) of $H_2C{=}SiHR$ and of $H_2Si{=}CHR$ at 3-21G and at 6-31G*//3-21G[a]

	total energies, hartrees				relative energies,[b] kcal mol^{-1}	
	$H_2C{=}SiHR$ (**1**)		$H_2Si{=}CHR$ (**2**)			
R	3-21G	6-31G*	3-21G	6-31G*	3-21G	6-31G*
H[c]	-327.30167	-329.03598	-327.30167	-329.03598	0.0	0.0
CH_3[c]	-366.14165	-368.08348	-366.12028	-368.06987	13.4	8.5
SiH_3	-615.85903	-619.12057	-615.86308	-619.12631	-2.5	-3.6
OH[d]	-401.79663	-403.94036	-401.72494	-403.87471	45.0	41.2
$OSiH_3$	-690.40624	-694.06840	-690.31813	-693.99088	55.3	48.6
F[c]	-425.68656	-427.95200	-425.60051	-427.86611	54.0	53.9
CN	-418.53823	-420.78274	-418.52681	-420.77799	7.2	3.0
NO_2	-529.61353	-532.50585	-529.59194	-532.50155	13.5	2.7

[a] At the 3-21G optimized geometries (Tables I and II). [b] Between isomers, i.e., $E(H_2Si{=}CHR) - E(H_2C{=}SiHR)$. Positive values indicate that **1** is more stable than **2**. [c] From ref 5a. [d] Very similar energies were reported in ref 5b.

the double bonds are examined and the effect of substitutents on the thermodynamic and the kinetic stabilities of these silenes is discussed. The related study on disubstituted silenes will be published elsewhere.[7]

I. Results and Discussion

We have used standard RHF ab initio methods.[8] The geometries of **1** and **2** were fully optimized at the RHF/3-21G level[9a] by using gradient techniques,[9b] and the results are given in Tables I and II, respectively. Single-point 6-31G* calculations[9c] at the 3-21G optimized geometries (denoted as 6-31G*//3-21G) followed. The total energies of **1** and **2** at both levels are presented in Table III.

II. Geometries

The most interesting structural feature of the silenes is the C=Si bond length. Before proceeding with a detailed discussion it is important to note that a split-valence basis set such as 3-21G is believed to be sufficiently reliable for estimating C=Si bond lengths.[1c] In the parent $H_2C{=}SiH_2$, for example, the C=Si internuclear distance is 1.717 Å at 3-21G, only slightly longer than the best calculated value of 1.705 Å which was obtained by using a polarized basis set and including electron correlation effects.[1c]

The data in Tables I and II show that the C=Si bond lengths which fall in the range of 1.70–1.75 Å change quite substantially upon monosubstituted. C—Si single bonds are considerably longer, e.g., 1.93 Å in H_3CSiH_3 at 3-21G.[10] Substitution at silicon (i.e., **1**) shortens the C=Si bond relative to $H_2C{=}SiH_2$ (except for R = SiH_3) while substitution at carbon (i.e., **2**) causes elongation. An especially large elongation is observed in **2**, R = OH, $OSiH_3$. As a result of this opposite substituent effect the C=Si bonds are shorter (except for R = SiH_3) in $RHSi{=}CH_2$ than in the isomeric $RCH{=}SiH_2$. The bond-length differences between isomers may

(7) Apeloig, Y.; Karni, M., manuscript in preparation.

(8) A modified version of the GAUSSIAN80 series of programs was used: Binkley, J. S.; Whiteside, R. A.; Krishnan, R.; Seeger, R.; Defrees, D. J.; Schlegel, H. B.; Topiol, S.; Kahn, L. R.; Pople, J. A. Program No. 406 Quantum Chemistry Program Exchange, Indiana University, Bloomington, IN. We thank Dr. S. Topiol for a copy of the program.

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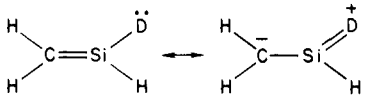
be substantial and large enough to be observed experimentally. For example, the C=Si bond length in H_2C=SiH(OH) is 1.705 Å compared to 1.746 Å in H_2Si=CH(OH). We note that calculations using the minimal STO-3G basis set give shorter C=Si bond lengths than 3-21G, i.e., in the range 1.64–1.67 Å. The trends regarding the substituent effects are, however, the same as at 3-21G.[12]

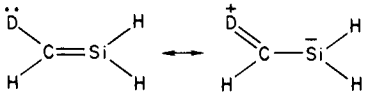
The effect of the substituents on the C=Si bond length is best understood in terms of the bond polarity. The C—Si bond in H_2C=SiH_2 is polarized so that the silicon atom is positively charged and the carbon is negatively charged (**3**). Substituents

$$H_2C^{\delta-}=^{\delta+}SiH_2$$
3

that increase this polarization and thus the degree of ionicity of the C=Si bond are expected to shorten this bond.[13] A detailed analysis of the effect of substituents on the charge distribution in silenes is presented below (section IVa). For the discussion of the C=Si bond lengths it is sufficient to realize that the *total* charges at silicon and carbon, that can serve as a measure of bond ionicity, are determined primarily by the substituent's electronegativity. Thus, in **1**, electron-withdrawing substituents (e.g., F, NO_2) increase the positive charge at silicon (Table V) and thus the degree of bond ionicity. As a result the C=Si bond shortens. The reverse is true for **2**. Electronegative substituents decrease the negative charge at carbon, the bond ionicity decreases, and the C=Si bond lengthens. π-Conjugation between the substituent and the double bond is apparently of little importance in determining the C=Si bond length. This is best exemplified by examining the isomeric **1** and **2**, where R is a good π-donor (D), e.g., OH. If π-conjugation effects contribute significantly then the C=Si bond in *both* **1** and **2**, R = OH, is expectd to be *longer* than in H_2C=SiH_2, due to contributions from resonance structures **4a** and **5a**, respectively. The calculations show however that although the C=Si bond in **2**, R = OH, is longer than that in H_2C=SiH_2, in **1**, R = OH, it is shorter than that in H_2C=SiH_2. The same analysis holds for π-acceptors such as CN.



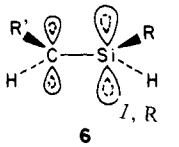
4 **4a**



5 **5a**

D = π-donor

An extensive study of the geometry of 200 substituted-benzene derivatives by Domenicano et al. leads to the same conclusions.[14] The major structural distortions are related to the σ-electronegativity of the substituent; its π-donor/acceptor properties are less important.[14] The exceptional effect of R = SiH_3, the only σ-donor that we have investigated, can be also understood. **1**, R = SiH_3, is the only silene substituted at silicon for which the positive charge at silicon is smaller than in H_2C=SiH_2 (Table V). The C=Si bond is consequently lengthened by ca. 0.01 Å in contrast to the other silenes of type **1** where it is shortened relative to H_2C=SiH_2 (Table I). In substituted ethylene substitution usually causes very small changes in the C=C bond length. For example, the bond length in H_2C=CHOH and in ethylene are essentially the same (1.315 Å at 4-31G)[15] while the C=Si distance in the analogous **2**, R = OH, is by 0.028 Å longer than in H_2C=SiH_2. This contrast in the behavior of the two isoelectronic double bonds supports our interpretation that changes in bond polarity play the major role in determining the substituent effects on the C=Si bond lengths. Bond polarities similar to that in H_2C=SiH_2 may be achieved only in heavily substituted "push-pull" type olefins.[16] Changes in the sizes of the valence orbitals of carbon and silicon as a result of substitution may also contribute to the changes in the C=Si internuclear distances. Silicon valence orbitals are more diffuse than those of carbon. Contraction of the silicon orbitals by the attachment of an electron-withdrawing substituent, as in **1**, is therefore expected to increase the C—Si overlap and thus to shorten the bond as observed. The opposite is true of **2** where an electron-withdrawing substituent contracts the already smaller carbon orbitals, thus reducing the C—Si overlap and lengthening the bond. These considerations are presented schematically for the π(C=Si) orbital in structure **6**. A similar rationalization relating the Mo—Mo bond distance in a series of Mo_2L_4 (L = ligand) complexes to a charged-induced contraction of the metal orbitals was suggested recently by Cotton et al.[17]



1, R

6

–, H_2C=SiH_2; ···, 1, R = electron withdrawing, R′ = H; - - -, 2, R′ = electron withdrawing, R = H.

Our calculations have an important bearing on the experimental–theoretical discrepancy regarding the carbon–silicon double bond length.[18] Schaefer pointed out in a stimulating review[1c] that calculations at fairly high levels of sophistication (polarized basis set + configuration interaction) predict that the C=Si bond length in H_2C=$Si(CH_3)_2$ is 1.705 Å, significantly shorter than the value of 1.83 Å determined by electron diffraction.[19] The experimental–theoretical difference of 0.12 Å appears to be too large to be attributed solely to inherent errors in the theoretical methods.[1c] Brook et al., who have succeeded recently to isolate the first solid silene, $(Me_3Si)_2Si$=C(OSiMe$_3$)(adamantyl), carried out its crystal structure analysis which gives a C=Si bond distance of 1.76 Å.[4b] This value is intermediate between the experimental and the theoretical bond distances in H_2C=$Si(CH_3)_2$.[1c] Due to the heavy substitution of the central bond and the absence of data on the effect of substituents on the C=Si bond length, Brook's data could not be compared directly with that for H_2C=$Si(CH_3)_2$ and could not be used to resolve the experimental–theoretical discrepancy. Such comparisons are, however, possible now with that aid of Tables I and II. Furthermore, additional calculations of a large number of silenes reveal that the effect of substituents on the C=Si bond length is approximately additive.[7] An example will clarify this point. According to Tables I and II an OH group attached to carbon elongates the C=Si bond length by 0.028 Å (i.e., 1.746–1.718 Å), and an H_3Si group attached to silicon lengthens the bond by 0.007 Å (i.e., 1.725–1.718 Å). Assuming additivity, r(C=Si) in H_3SiHSi=CH(OH) is predicited to be 1.718 + 0.007 + 0.028 = 1.753 Å, essentially identical with the actual value obtained by a 3-21G geometry optimization. A close electronic model for Brook's silene is $(H_3Si)_2Si$=CCH_3(OSiH_3), where H_3Si and CH_3 substitute the $SiMe_3$ and the adamantyl groups. Assuming additivity for the substituent effects the C=Si bond length in $(H_3Si)_2Si$=CCH_3(OSiH_3) is calculated to be 1.718 + 0.031 (for H_3SiO) + 2(0.007) (for SiH_3) + 0.007 (for CH_3) = 1.770 Å. This calculated distance is essentially the same as the experimentally measured bond length of 1.764 Å. Although this excellent agreement may be somewhat fortuitous the general trend in not! Note also the excellent agreement between the calculated Si–Si bond length in **1**, R = SiH_3, of 2.36 Å and Brook's

(11) Our geometries, energies, and charge distributions are essentially identical to those reported recently by Gordon and George.[5b]
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(17) Cotton, F. A.; Dunbar, K. R.; Falvello, L. R.; Thomas, M.; Walton, R. A. *J. Am. Chem. Soc.* **1983**, *105*, 4950.
(18) For a preliminary communication, see: Apeloig, Y.; Karni, M. *J. Chem. Soc., Chem. Commun.* **1984**, 768.
(19) Mohaffy, P. G.; Gutowski, R.; Montgomery, L. K. *J. Am. Chem. Soc.* **1980**, *102*, 2854.

experimental values of 2.341 and 2.349 Å.[4b] We conclude, therefore, that the C=Si bond length in $(Me_3Si)_2Si$=C-$(OSiMe_3)$(adamantyl) is elongated relative to a "normal" silaethylene by the electronic effects of the substituents (mainly by $OSiMe_3$).[20] Elongation of the C=Si bond by steric repulsions between the bulky substituents or as a result of the 16° twisting about the C=Si bond[4b] are apparently of much smaller importance.[21,22] Most important, the agreement between the calculations and Brook's measurements strongly supports Schaefer's suggestion that the C-Si internuclear separation in simple silenes (e.g., H_2C=SiH_2, H_2C=$Si(CH_3)_2$) is ca. 1.70 Å.[1c] The much longer experimental value of 1.83 Å[19] is probably erronous. Measurements of the C=Si bond distance in additional silenes will hopefully clarify this important issue.

Several additional geometrical features of **1** and **2** warrant comment. In **1**, R = OH, F, SiH_3, the Si-R bond length are somewhat longer (by ca. 0.02 Å) than in the corresponding saturated silanes H_3SiR.[10] This contrasts with the general trend found for C-R bond distances, which are shorter for a sp^2 hybridized carbon than for a sp^3 carbon.[23] The longer Si-O bond in **1**, R = OH, relative to that in H_3SiOH (i.e., 1.633 Å)[10] is consistent with our conclusion that resonance contributions of type **4a** have little effect on the C=Si bond length (vide supra). The RSiC angles in **1** and the RCSi angles in **2** are larger than 120°. Remarkably, wide OCSi angles of ca. 131° are calculated for **2**, R = $OSiH_3$, OH. In $(Me_3Si)_2Si$=C$(OSiMe_3)$(adamantyl) this angle is much smaller—117.5°.[4b] We believe that this contracted angle is a result of steric repulsion between the $OSiMe_3$ and the adamantyl groups,[4b] and it remains to be seen if our prediction of wider OCSi angles will hold when the structures of less crowded silenes become available. Note, however, that the calculated COSi angle in **2**, R = $OSiH_3$, of 134.7° is in good agreement with the experimental value of 133.9° reported by Brook.[4b] This agreement lends some support to the computational prediction of an even larger bonding angle around oxygen in the isomeric H_2C=Si-$H(OSiH_3)$. Our experience shows that 3-21G tends to underestimate somewhat the bending forces for linerization at oxygen,[12] so that a realistic prediction is that the SiOSi bond angle in H_2C=$SiH(OSiH_3)$ is ca. 150–160°.[24] Similar wide bond angles were reported for disiloxane and related compounds.[25a,b] The fact that the 3-21G basis set does not include d functions argues against the view that the large SiOSi valence angle in **1**, R = $OSiH_3$, is due to p-d π-bonding between the oxygen and silicon atoms.[25c] The angles around the H_2Si unit in **2** are more distorted than those around the H_2C unit in **1**. In **1** the two HCSi angles are slightly larger than 120°. In **2**, the HSiC angles cis to R are larger than 120° while the HSiC angles trans to R are in most cases smaller than 120°.

III. Thermodynamic Stability

(a) Isomers. The silicon-substituted silenes **1** are generally more stable than the isomeric carbon substituted silenes **2**, except for R = SiH_3 (Table III). The following (**2** - **1**) energy differences are calculated at 6-31G* (in kcal mol^{-1}): R = H, 0.0, R = CH_3, 8.9; R = SiH_3, -3.6; R = OH, 41.2; R = $OSiH_3$, 48.6; R = F, 53.9; R = CN, 3.0; R = NO_2, 2.7.[26a] Note that the 3-21G and the 6-31G* eneregy differences are very similar[26b] (Table III) suggesting that the smaller 3-21G basis set can be used with some confidence for larger silene, where more elaborate calculations are not practical. The general higher stabilities of **1** compared with **2** reflect primarily the differences in the bond energies of Si-H vs. C-H and of Si-R vs. C-R. Si-H bonds are weaker than C-H bonds by ca. 16 kcal mol^{-1}.[27a] **1** is therefore expected to be more stable than **2**, unless the C-R bond is much stronger than the Si-R bond. For most of the substituents that we have studied the C-R bonds are weaker than the Si-R bonds,[27] and **1** is therefore more stable than **2**. Particularly large energy differences between the isomers are found for R = OH, $OSiH_3$, and F because the Si-O and the Si-F bonds are substantially stronger than the corresponding C-R bonds (i.e., by 48 and 54 kcal mol^{-1} in MH_3-R where M = C or Si and R = OH and F, respectively[27b]). The exceptional behavior of R = SiH_3, for which **2** is more stable than **1**, is also consistent with this interpretation. Thus, the bond dissociation energy of the C-Si bond (88 kcal mol^{-1} in H_3CSiH_3[27]) is significantly larger than that of the Si-Si bond (74 kcal mol^{-1} in H_3SiSiH_3[27]). In addition, **1**, R = SiH_3, is destabilized by electrostatic repulsion between the two positively charged silicon atoms, while the isomeric **2** is stabilized by the attraction between the positively charged H_3Si group and the negatively charged carbon (vide infra and Table V).

(b) Substituent Effects. The effect of substituents on the C=Si bond energy can be evaluated in several ways depending on the compounds that are chosen as reference. The most useful for our purpose are the isodesmic equations (1) and (2) in which the

$$\underset{\mathbf{1}}{H_2C{=}SiHR} + SiH_4 \rightarrow H_2C{=}SiH_2 + H_3SiR \qquad (1)$$

$$\underset{\mathbf{2}}{H_2Si{=}CHR} + CH_4 \rightarrow H_2C{=}SiH_2 + H_3CR \qquad (2)$$

substituent R is transferred from a C-Si double bond to a C-Si single bond. These equations measure only the additional interaction between the substituent and the C-Si double bond while effects that are related to the presence of a particular Si-R or a C-R bond approximately cancel out. In addition, such isodesmic equations are expected to be much less sensitive to electron correlation effects than the **1** - **2** energy difference where different types of bonds are compared. The calculated energies for eq 1 and 2 are given in Table IV. The discussion below is based on the more reliable 6-31G* values but the 3-21G values are similar (usually somewhat higher).

We find that the effect of substituents on the C=Si bond strength is relatively small especially when R is bonded to silicon (i.e., in **1**). Hydroxy for exmaple, stabilizes either **1** or **2** by only 0.4 kcal mol^{-1}. The largest effects are exerted by R = F and SiH_3 when attached to carbon (i.e., **2**); silyl substitution is stabilizing

Table IV. Calculated Energies (kcal mol^{-1}) for Eq 1 and 2[a]

	eq 1[b]		eq 2[b]	
R	3-21G	6-31G*	3-21G	6-31G*
H	0.0	0.0	0.0	0.0
CH_3	0.5	0.1	3.7	0.3
SiH_3	2.0	2.9	7.6	6.0
OH	0.8	0.3	1.3	0.4
$OSiH_3$	0.3	-0.2	2.2	-2.8
F	-2.3	-2.0	-3.9	-7.8
CN	-0.8	-1.4	6.4	3.8
NO_2	-1.5	-3.4	7.5	2.4

[a] Using the energies in Table III and in ref 10. [b] Positive values indicate stabilization of the C=Si bond.

(20) Brook and his co-workers have concluded that "there is no reason to invoke significant stretching due to steric or other effects".[4b] However, due to the lack of appropriate structural data for comparison, their conclusion can be regarded as tentative. We strongly believe that in contrast to olefins, electronic effects cannot be ignored in the discussion of C=Si bond lengths.

(21) Also, in olefins, steric repulsions are relieved mainly by angle deformations and nonplanar double-bond distortions and not by elongation of the central bond. See: Ermer, O.; Lifson, S. *Tetrahedron* **1974**, *30*, 2425.

(22) A 16° twisting about the double bond in H_2C=SiH_2 results in a small lengthening of the C=Si bond (i.e., by 0.015 Å).[12]

(23) (a) Bent, H. A. *Chem. Rev.* **1961**, *61*, 275. (b) Pople, J. A.; Gordon, M. S. *J. Am. Chem. Soc.* **1967**, *89*, 4253.

(24) Similar problems were pointed out also with the polarized 3-21G* basis set. Even at MP2/6-31G* (i.e., including electron correlation) the bond angle in $H_3SiOSiH_3$ is 161°, still larger than the experimental value of 144°.[25a] See: Raghavachari, K.; Chandrasekhar, J.; Frisch, M. J. *J. Am. Chem. Soc.* **1982**, *104*, 3779.

(25) (a) Almenningen, A.; Bastiansen, O.; Ewing, V.; Hedberg, K.; Tratetteberg, M. *Acta Chem. Scand.* **1963**, *17*, 2455. (b) Shen, Q. *J. Mol. Struct.* **1983**, *102*, 325 and references therein. (c) Similar conclusions were reached by: Tossell, J. A.; Gibbs, G. V. *Acta Crystallogr., Sec. A* **1978**, *A34*, 463.

(26) (a) Electron correlation will probably reduce these energy differences by 10–20%. For R = OH, the **2** - **1** energy difference is 45.0 and 37.8 kcal/mol^{-1} at 3-21G and MP3/3-21G, respectively.[5b] (b) 3-21G usually overestimates the stability of **1** by a few kcal mol^{-1}.

(27) (a) Walsh, R. *Acc. Chem. Res.* **1981**, *14*, 246. (b) For a theoretical evaluation of C-R and Si-R bond-dissociation energies, see ref 10 and a subsequent paper in preparation.

by 6.0 kcal mol^{-1} while fluorine is destabilizing by 7.8 kcal mol^{-1} (Table IV). Similar conclusions are reached when different equations are used, e.g., $H_2C{=}SiHR + 2H_2 \rightarrow CH_4 + H_3SiR$.[12]

Many silenes undergo dimerization to give substituted disilacyclobutanes (e.g., eq 3 and 4) and the effect of substituents on

$$\underset{\mathbf{1}}{2H_2C{=}SiHR} \rightarrow RHSi\text{-}\overset{\lceil CH_2 \rceil}{CH_2}\text{-}SiHR \qquad (3)$$

$$\underset{\mathbf{2}}{2H_2Si{=}CHR} \rightarrow RHC\text{-}\overset{\lceil SiH_2 \rceil}{SiH_2}\text{-}CHR \qquad (4)$$

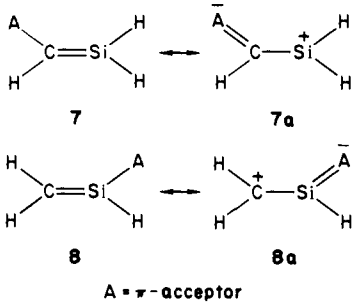
the energy of this reaction is thefore of interest. Ahlrichs and Heinzmann have calculated using a fairly large basis set that the head-to-tail dimerization of $H_2C{=}SiH_2$ (eq 3, R = H) is exothermic by ca. 76 kcal mol^{-1}.[2b] Explicit calculations of disubstituted disilacyclobutanes are prohibitive especially if geometry optimizations are attempted. Yet, eq 3 and 4 can be modeled quite accurately by eq 1 and 2, respectively. This comparison is justified because the major change in either eq 1 and 2 or eq 3 and 4 is the transfer of R from a doubly bonded to a singley bonded C–Si bond.

As the energies of eq 1 and 2 are relatively small (Table IV), we conclude that regardless of the substituent the head-to-tail dimerizations of substituted silenes are highly exothermic. The calculated dimerization energies for **1** and **2** range from 70 to 84 kcal mol^{-1}. Examination of the data in Tables 3 and 4 leads to a more important conclusion. Namely, that the *relative stability of two isomeric silenes* ***1*** *and* ***2*** *is of little importance in determining their thermodynamic stability toward dimerization.* The more stable isomer dimerizes to a more stable disilacyclobutane, so that its dimerization energy is approximately the same as for the less stable isomer.[28] An enlightening example is R = OH. $H_2C{=}SiH(OH)$ is more stable than $H_2Si{=}CH(OH)$ by 41.2 kcal mol^{-1}. However, the dimerization energies of the two isomers are essentially the same as indicated by the calculated energies of eq 1 and 2 for R = OH.

IV. Reactivity of Silenes

The major obstacle in isolating silenes is believed to be their high reactivity rather than their low thermodynamic stability.[1,4] The major processes that are believed to contribute to the fast destruction of the C–Si double bond are nucleophilic and electrophilic additions and dimerization to disilacyclbutanes. Another important reaction, the rearrangement of silenes that contain a =Si—H bond (e.g., **1** and **2**) to the isomeric silylenes (i.e., H_3CSiR and RCH_2SiH, respectively) will be discussed in a subsequent paper. A systematic study of the potential energy surfaces of the addition or the dimerization reactions is prohibitive. However, significant understanding of the reactivities of silenes may be gained by studying the effect of substituents on their ground-state properties. The energies and the coefficients of the silenes' frontier orbitals and the charge distribution within these molecules are the most relevant.[29] Similar analysis of a wide variety of organic molecules has proved to be highly successful and provided important insights into many reactivity problems.[29] Application of FMO theory to silenes is particularly attractive because their reactions are in general highly exothermic (e.g., dimerization, see above) and are therefore expected to proceed via relatively "early-reactant-like" transition states.[30] It is in these cases that FMO theory is most useful and highly reliable.[29]

(a) Charge Distribution. The total charges and the π-charges at the two termini of the C=Si bond in both **1** and **2** are given in Table V (from the 6-31G* basis set). The silicon bond in $H_2C{=}SiH_2$ as well as in the substituted silenes is positively charged while the carbon is negative (Table V). Similarly, the hydrogens are negatively charged when attached to silicon but positively charged when bonded to carbon. Comparison of the total and the π-charges shows that charge polarization occurs mainly in the σ-framework. For example, in $CH_2{=}SiH_2$ the total charge at silicon is 0.46, of which 0.29 electron is associated with the σ-framework and only 0.17 electron results from polarization of the π-bond electrons away from the silicon atom. Although smaller than the σ-polarization, the π-polarization is probably more relevant to the discussion of the reactivity of the C–Si double bond. In general it is expected that the reactivity of a particular silene should increase as the the polarization of the C–Si π-bond (i.e., of the HOMO) increases. Inspection of the π-charges in Table V reveals that polarization of the C=Si bond by substituents is qualitatively similar to that of C=C π-bonds[6] and in agreement with arguments based on simple resonance theory. Thus, π-acceptors (e.g., CN, NO_2) bonded to carbon (or silicon) increase (or decrease) significantly the positive π-charge at silicon *relative* to that in the parent $H_2C{=}SiH_2$; see structures **7** ↔ **7a** and **8** ↔ **8a**. π-Donors (e.g., OH, $OSiH_3$) exert the opposite effect;



see structures **4** ↔ **4a** and **5** ↔ **5a**. The effect of CH_3 and SiH_3 is much milder and in the direction expected for weak π-donation or π-acceptance, respectively, by hyperconjugation.[6] Of special interest (vide infra) is the strong π-donation by $OSiH_3$ and OH that reverses the "natural" π-polarity of the C=Si bond, so that in $H_2Si{=}CH(OSiH_3)$ the π-charge at silicon is actually slightly negative. This result is consistent with the NMR spectrum of $Me_3SiOCR{=}Si(SiMe_3)_2$.[4d] Finally note that in cases where the σ- and π-effects of a particular substituent are reinforcing, the total charges may deviate significantly from those in $H_2C{=}SiH_2$ (i.e., Si +0.46; C −0.66). For example in $H_2C{=}SiH(OH)$ the total charges at silicon and carbon are +0.84 and −0.73, respectively, while in the isomeric $HOCH{=}SiH_2$ the charges are +0.26 and −0.06, respectively. Such large charge variations are expected to affect strongly the ^{29}Si NMR chemical shifts in substituted silenes and are therefore amenable to experimental probing.

(b) The Frontier Orbitals. According to FMO theory reactivity is dictated by the shapes and the energies of the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO, respectively). In silenes as in olefins these are naturally the π (HOMO) and the π^* (LUMO) orbitals of the double bond. In general, the interaction, ΔE, between two molecules (see eq 5)

$$\Delta E = \frac{C_1^2 C_2^2}{E(\text{HOMO} - \text{LUMO})} \qquad (5)$$

is stronger (and the reaction is faster) the higher the overlap and thus the orbital coefficients, C_1 and C_2, at the reacting sites and the smaller the energy gap between the HOMO of one molecule and the LUMO of the other, E(HOMO − LUMO).[29] According to eq 5 the nucleophilic reactivity of silenes is expected to increase the higher the energy of the C=Si π-bond and the orbital coefficient at the nucleophilic site. Similarly, the electrophic reactivity should increase the lower the energy of the π^*-orbital. Reactivity toward dimerization, where the silene acts as both the nucleophile and the electrophile, is therefore expected to diminish as the HOMO–LUMO energy gap increases. Furthermore, it is a general belief on the basis of eq 5 and on numerous empirical observations that only molecules with sizeable HOMO–LUMO gaps exhibit considerable kinetic stability (unless large steric effects

(28) Preliminary 3-21G calculations and average C–C, C–Si, and Si–Si bond energies[27] indicate that the head-to-head dimer is only a few kcal·mol^{-1} less stable than the head-to-tail dimer. The above conclusion is therefore probably valid also if isomeric **1** and **2** yield different types of dimers.

(29) Fleming, I. "Frontier Orbitals and Organic Chemical Reactions"; Wiley: London, 1976.

(30) Hammond, G. S. *J. Am. Chem. Soc.* **1955**, *77*, 334.

Table V. Calculated Charge Densities and the Coefficients and Energies of the Frontier Orbitals of **1** and **2**[a]

		charge at C		charge at Si		HOMO coefficients			LUMO coefficients			orbital energies, eV		
1, R =	**2**, R =	π^b	total	π^b	total	$C_C{}^c$	$C_{Si}{}^d$	C_C/C_{Si}	$C_C{}^c$	$C_{Si}{}^d$	C_C/C_{Si}	π	π^*	$(\pi - \pi^*)$
H	H	−0.15	−0.67	0.17	0.46	0.76	0.61	1.25	0.90	1.04	0.87	−8.4	2.5	10.9
CH_3	H	−0.18	−0.67	0.19	0.59	0.77	0.60	1.29	1.10	0.90	1.22	−8.1	3.0	11.1
H	CH_3	−0.08	−0.42	0.10	0.40	0.73	0.64	1.13	0.93	1.01	0.92	−7.9	2.6	10.5
SiH_3	H	−0.10	−0.62	0.12	0.28	0.73	0.63	1.17	0.85	0.83	1.02	−8.3	2.1	10.4
H	SiH_3	−0.16	−0.75	0.24	0.51	0.74	0.57	1.31	0.77	1.06	0.73	−8.6	1.9	10.5
OH	H	−0.30	−0.73	0.26	0.84	0.82	0.52	1.58	0.86	1.14	0.76	−8.2	3.4	11.6
H	OH	−0.01	−0.06	−0.07	0.26	0.63	0.72	0.87	1.02	0.96	1.06	−7.6	2.7	10.3
$OSiH_3$	H	−0.27	−0.71	0.24	0.83	0.81	0.54	1.50	0.87	1.14	0.76	−8.1	3.3	11.4
H	$OSiH_3$	−0.03	−0.05	−0.04	0.28	0.64	0.71	0.91	0.99	0.96	1.04	−7.6	2.7	10.3
F	H	−0.26	−0.72	0.25	0.91	0.80	0.54	1.48	0.87	1.11	0.78	−8.7	2.9	11.6
H	F	−0.03	0.10	0.08	0.37	0.71	0.66	1.08	0.95	1.01	0.94	−8.4	2.2	10.6
CN	H	−0.12	−0.63	0.13	0.56	0.76	0.62	1.21	0.85	0.90	0.94	−9.1	1.4	10.5
H	CN	−0.24	−0.53	0.32	0.59	0.72	0.52	1.38	0.73	1.05	0.70	−9.1	0.9	10.0
NO_2	H	−0.10	−0.63	0.13	0.67	0.73	0.63	1.17	0.73	0.72	1.02	−9.5	0.9	10.4
H	NO_2	−0.28	−0.32	0.43	0.64	0.81	0.48	1.68	0.54	1.01	0.54	−9.9	0.1	10.0

[a] At 6-31G*//3-21G. [b] In the C=Si π-orbital. [c] The orbital coefficient at carbon. [d] The orbital coefficient at silicon.

intervene). The energies and the coefficients of the π- and π^*-orbitals of **1** and **2** at the 6-31G* level are given in Table V. The coefficients of the π-orbital are of course related to the π-charge densities discussed above. It is worthwhile noting that the energies of the π- and π^*-orbitals as well as their energy differences are practically the same according to 6-31G* and to 3-21G,[12] suggesting that the smaller and more efficient basis set can be used reliably for larger silenes.

The following conclusions emerge from the data in Table V: (a) The strong π-electron-withdrawing substituents, CN and NO_2, lower considerably the energy of the π-orbital, while π-donors ($OSiH_3$, OH, SiH_3, and CH_3) push the HOMO to higher energies than in $H_2C{=}SiH_2$. The range of the π-orbital energies is quite large, i.e., 2.3 eV. The lowest HOMOs are calculated for O_2N-$CH{=}SiH_2$ (−9.9 eV) and for **1** and **2**, R = CN (−9.1 eV), while the highest HOMOs are found in **2**, R = OH, $OSiH_3$ (−7.6 eV). In most cases (i.e., except for R = NO_2 and SiH_3) the HOMO is lower in **1** than in the isomeric **2**. The rather limited experimental data are in good agreement with our calculations. The ionization potentials of $H_2C{=}SiH_2$ and of $(CH_3)_2Si{=}CH_2$ are 8.8[31] and 8.3 eV,[32] respectively; the calculations predict (using Koopmans' theorem[33]) 8.4 and 7.8 eV, respectively. Thus, although the calculated values are by 0.4 eV too low the substituent effect of methyl is reproduced. (b) The energy of the π^*-orbital is lowered by σ- and π-acceptors and pushed to higher energies by π-donors. The energy range is 3.3 eV somewhat larger than for the π-orbitals; extreme values are 0.1 eV in **2**, R = NO_2, and 3.4 eV in **1**, R = OH. (c) All of the substituents reduce the π–π^* energy difference (by 0.3–0.9 eV relative to that in $H_2C{=}SiH_2$) when attached to carbon (i.e., in **2**). In **1** the effect is more complex; the π–π^* gap is widened by π-donor by as much as 0.7 eV but reduced by up to 0.5 eV by π-acceptors and σ-donors (i.e., SiH_3). In all cases except for R = SiH_3, the π–π^* gap in **2** is considerably smaller than in the isomeric **1**. (d) The π-coefficients reflect the polarization of the C=Si π-bond and the trends induced by the substituents were discussed in section IVa. The degree of polarization is expressed conveniently by C (Table V), the ratio of the orbital coefficients at carbon (C_C) and at silicon (C_{Si}). Polarization increases as C moves further away from unity. In most cases the HOMO coefficients at carbon are higher than at silicon ($C > 1$) so that carbon is the nucleophilic site of the C=Si bond. The LUMO is generally concentrated at the silicon ($C < 1$) which is therefore the electrophilic site. The notable exceptions are **2**, R = OH, $OSiH_3$, where this trend is reversed (i.e., $C < 1$) and the silicon atom is calculated to be the nucleophilic site of the double bond. Comparison of the HOMO coefficients for a pair of isomers **1** and **2** follows the expected polarization patterns discussed in section IVa. (e) The effect of R on the orbital energies and on the orbital coefficients is often reversed. Substituents that raise the energy of the HOMO, thus increasing the nucleophilicity of the silene, usually reduce the π-coefficient at C, thus decreasing its nucleophilicity, e.g., $H_2Si{=}CHOH$. Similarly, reactivity differences between isomers **1** and **2** are expected to be smaller than those deduced by considering separately either the orbital coefficients or the orbital energies. (f) Substituent effects on the energies of the π- and π^*-orbitals of silenes are qualitatively similar to those in olefins.[29,34] The π-orbitals of silenes are, however, 1.0–2.5 eV higher in energy than those in the analogous olefins suggesting that silenes are much more potent nucleophiles than olefins. The orbital coefficients also follow similar trends to those found in olefins,[29,34] but in silenes the situation is more complex because polarization of the frontier orbitals by the substituent is acting on top of the "natural" polarity of the C=Si bond arising from electronegativity differences. For example, the polarization of the π-oribtal in $H_2C{=}CH(OH)$ is much larger than in H_2-$Si{=}CH(OH)$ because in the latter the contribution from resonance structure **5a** is partially counterbalanced by the reversed "natural" polarity in $H_2C{=}SiH_2$. This realization leads to an important distinction between olefins and silenes. *In olefins, substitutent effects on the energies and the coefficients of the frontier orbitals are generally reinforcing,[29,34] while in silenes they operate in opposite directions (vide supra point e).* Thus, the effect of an OH substituent, on both the orbital energies and the orbital coefficients, boosts the nucleophilic reactivity of $H_2C{=}CH(OH)$. In $H_2Si{=}CH(OH)$, on the other hand, the increased reactivity which is expected on the basis of the higher HOMO is counteracted by the π-polarization which is smaller and in the opposite direction than in $H_2C{=}SiH_2$ (C = 0.87 and 1.25, respectively), thus reducing its nucleophilicity.

In principle, the reactivity of silenes can be estimated, at least qualitatively, on the basis of the data in Table V by the application of simple FMO arguments.[29] For example, $H_2C{=}Si(CH_3)_2$ is expected to be more nucleophilic than $H_2C{=}SiH_2$, while H_2-$Si{=}CHCN$ is expected to be more electrophilic than both. However, the fact that most substituents have an opposite effect on the energies and the coefficients of the frontier orbitals complicates the FMO analysis rendering predictions for many silenes difficult and unreliable. Only extensive comparison between calcultions and experiment can lead to an understanding of the delicate balance between these factors and thus provide a working hypothesis, such as exists for olefins, for determining which of these factors is more important in dictating silene reactivity. Unfortunately the experimental data is scarce, and it is hoped that this paper will prompt further studies.

Of particular interest is the theoretical analysis of Brook's stable silenes, $(Me_3Si)_2Si{=}CR(OSiMe_3)$[4] (**9**), in an attempt to establish if electronic effects contribute to their remarkable stabilities. The shapes and the energies of the frontier orbitals in **9** can be ap-

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proximated from the data in Table V assuming that substituent effects are additive. The validity of this assumption is supported by calculations of disubstituted silenes, e.g., $H_3SiSiH{=}CH(OSiCH_3)$.[7] Using $(H_3Si)_2Si{=}CCH_3(OSiH_3)$ (**10**) as an electronic model for **9**, we calculate that this silene possesses a high-lying HOMO at ca. −7.5 eV[35] and a very small $\pi-\pi^*$ energy gap of ca. 9.0 eV. It is most satisfying that these values are consistent with the experimental data. The ionization potential of **9**, R = adamantyl, is 7.7 eV, and it absorbs at a much longer wavelength (340 mm)[4b] than either $H_2C{=}SiH_2$ or $H_2C{=}Si(CH_3)_2$ (258 and 244 mm, respectively)[36] for which we indeed calculate larger $\pi-\pi^*$ splitting of 10.9 and 11.3 eV, respectively. Both the high HOMO and the low $\pi-\pi^*$ splitting argue that **9** should be highly reactive. However, the polarization of the C=Si bond in **9** is small relative to that of other silenes. More important, the larger coefficient of the HOMO is located at the silicon end of the double bond, opposite to the situation in other silenes. Note that the gem-Me_3Si groups, modeled by H_3Si in **10**, reinforce the effect of the $OSiMe_3$ substituent and enhance the "reversed polarity" of the frontier orbitals. The remarkable stabilities of **9**, R = CMe_3, CEt_3, adamantyl, are certainly due largely to the bulkiness of R which reduce significantly the rate of dimerization. However, the observation that silenes of type **9**, even where R is less bulky, e.g., phenyl, are more stable than simple alkyl silenes[4c] argues strongly that electronic effects also contribute to this kinetic stability. At this point we are unable, neither are Brook et al.,[4] to quantify more accurately the relative importance of the steric and the electronic effects. However, calculations, which are in progress,[12] of the effect of substituents on the activation barriers for dimerization of various silenes will hopefully shed further light on this important question. With this reservation in mind, we conclude that the *"reversed polarity" of the C=Si bond plays a more important role than the energies of their frontier orbitals in controlling the reactivity of silenes (in particular* ***9****).*[37] The fact that **9** are the only known silenes that undergo head-to-head dimerization[4] supports this conclusion and it is consistent with the calculations which place the highest coefficients of both the HOMO and the LUMO at the silicon end of the double bond.

The considerations developed above demonstrate that Brook has indeed found a very effective combination of substituents for stabilizing silenes kinetically via *electronic* effects. Other stable silenes may be constructed by using, in addition to $OSiMe_3$ or other OR groups that ensure the desired "reversed polarity" of the C=Si bond, substituents that do not change the polarity significantly but which lower the energy of the HOMO or increase the $\pi-\pi^*$ gap and thus reduce the reactivity. Examples are $R'_2Si{=}C(OSiMe_3)R$ and $R'_2Si{=}C(OBu\text{-}t)R$ where R′ = CN, $SiMe_3$, or alkyl and R = F, $SiMe_3$, or alkyl. Bulky alkyl groups will, of course, stabilize the silene also sterically. Note that alkyl substitution at silicon (i.e., R′ = alkyl) increases considerably the $\pi-\pi^*$ gap but induces a relatively small change in the silene's polarity, while silyl substitution at carbon lowers the energy of π and stabilizes the silene thermodynamically relative to R = alkyl (Table IV). We therefore believe that compounds of the general type $(alkyl)_2Si{=}C(OSiMe_3)(SiMe_3)$ should be relatively stable toward dimerization and are particularly attractive candidates for synthesis. Finally, Wiberg has reported recently the isolation of a moderately stable silene, $Me_2Si{=}CSiMe_3(SiMe(Bu\text{-}t)_2)$.[38] Our calculations show that this silene is polarized "naturally" (i.e., $C^{\delta-} = Si^{\delta+}$), and that its π- and π^*-energies are not very different from that of other known "short-lived" silenes. The stability of this silene was indeed attributed primerally to the bulky *tert*-butyl groups and not to electronic factors; the less crowded $Me_2Si{=}C(SiMe_3)_2$ dimerizes very rapidly.[38] Note, that the *gem*-disilyl substitution at carbon stabilizes this silene thermodynamically toward dimerization.

V. Conclusions

The following major conclusions can be drawn from this study: (1) Substituents can have a substantial effect on the C=Si bond length. Variations in r(C=Si) parallel the changes in the total ($\sigma + \pi$) bond polarity. An $OSiH_3$ substituent attached to carbon has an especially large effect, increasing r(C=Si) by 0.028 Å. The calculations suggest that the experimental C—Si bond length of 1.764 Å in $(Me_3Si)_2Si{=}C(adamantyl)(OSiMe_3)$[4b] is electronically elongated and that the unperturbed r(C=Si) is ca. 1.70 Å. This contrasts with the much longer r(C=Si) of 1.832 Å measured by electron diffraction of $H_2C{=}Si(CH_3)_2$.[19] (2) The energy difference between isomeric silenes, $RSiH{=}CH_2$ and $RCH{=}SiH_2$, can be very large, e.g., 48.6 kcal mol^{-1} for R = $OSiH_3$ (6-31G*). Substitution at silicon is more stabilizing than substitution at carbon, except for R = SiH_3. The relative thermodynamic stabilities of isomeric silenes are determined primarily by the bond energies of Si–R vs. C–R and of Si–H vs. C–H. (3) Substituent effects (SE) on the thermodynamic stability (or strength) of the C=Si bond are relatively small (generally up to 4 kcal mol^{-1}). The same applies to the dimerization reactions of silenes to disilacyclobutanes. Consequently, the relative stability of two isomeric silenes is of little importance in determining their thermodynamic stability toward dimerization. (4) Substituents have a strong effect on the charge distribution within the C=Si bond. Polarization of the σ-electrons is generally larger than of the π-electrons. In silenes with strong π-donors (e.g., OH) attached to carbon the "natural" $C^{\delta-}{=}Si^{\delta+}$ π-polarity is reversed to $C^{\delta+}{=}Si^{\delta-}$. (5) Substituent effects on the energies and the coefficients of the frontier molecular orbitals (FMO) of silenes are analyzed and then used to discuss the factors that determine their kinetic stabilities. SE on the energies of the π- and π^*-orbitals of silenes and olefins are qualitatively similar. The $\pi-\pi^*$ energy difference is however much smaller in silenes, in agreement with their extreme reactivity. An important difference between olefins and silenes is pointed out. In olefins, SE on the energies and the coefficients of the FMOs are generally reinforcing, while in silenes they operate in opposite directions. Comparison of the FMO analysis and the available experimental data suggests that the "reversed polarity" of the C=Si bond plays a more important role than the energies of their frontier orbitals in controlling the reactivity of silenes (in particular **9**). Consequently, $(NC)_2Si{=}CR(OSiMe_3)$, $(Me_3Si)_2Si{=}C(OSiMe_3)F$, $(Me_3Si)_2Si{=}C(OBu\text{-}t)R$, and $(Me_3Si)_2Si{=}C(OSiMe_3)SiMe_3$ are predicted to be electronically stabilized and probably also kinetically stable at room temperature. (6) The 3-21G and the 6-31G* results are in general very similar, suggesting that the smaller and more efficient basis set can be used with some confidence for calculating larger silenes (e.g., multisubstituted silenes). Furthermore, this agreement argues against a significant contribution from the d-orbitals of silicon to the properties of the silenes discussed in this paper.[39]

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Registry No. **1**, **2** (R = H), 51067-84-6; **1** (R = CH_3), 38063-40-0; **1** (R = SiH_3), 92126-76-6; **1** (R = OH), 88157-94-2; **1** (R = $OSiH_3$), 92126-77-7; **1** (R = F), 81875-06-1; **1** (R = CN), 92143-41-4; **1** (R = NO_2), 92126-78-8; **2** (R = CH_3), 38063-40-0; **2** (R = SiH_3), 92126-79-9; **2** (R = OH), 88157-97-5; **2** (R = $OSiH_3$), 92126-80-2; **2** (R = F), 81897-63-4; **2** (R = CN), 92126-81-3; **2** (R = NO_2), 92126-82-4.

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(37) Other theoretical studies have pointed out the important role of polarization.[2a,b] Ahlrichs and Heinzman have argued, however that an attempt to change this polarity by appropriate substituents would invariably weaken the π-bond and enhance reactivity.[2b] Our calculation and Brook's experiments suggest that this is not the case. The possible role of triplet states in determining the reactivity of silenes,[2a,b] in particular **9**, remains an open question.

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