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Theoretical Investigations on Some C_2SiH_4 Isomers

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Abstract: A part of the C_2SiH_4 potential energy surface has been explored using a nonempirical pseudopotential method. The computed relative stabilities of the five isomers, silylacetylene (0 kcal/mol) < silacyclopropene (**3**) and silacyclopropylidene (**2**) (both 17 kcal/mol) < 2-silaallene (46 kcal/mol) < 2-silapropyne (61 kcal/mol), differ significantly from those of the analogous carbon compounds: propyne < allene < cyclopropene ≪ cyclopropylidene. Silacyclopropylidene (**2**) has a singlet while the carbene analogue a triplet ground state. The relative stabilities of the two cyclic structures **2** and **3** have been analyzed further using extensive CI calculations. The results do not suggest an aromatic character for **3**.

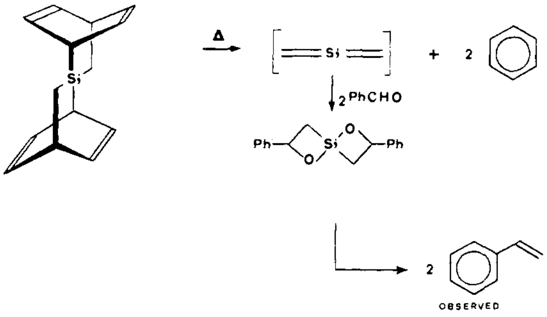
Introduction

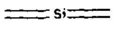
Silylacetylene (**5**) has been a well-known compound[2] for many years and its structure has been elucidated. More recently, derivatives of silacyclopropene (**3**) have been observed,[3] and in 1978 Bertrand, Manuel, and Mazerolles[4] suggested the existence of a digonal (i.e., sp-hybridized) silicon compound, 2-silaallene (**1**), as a possible intermediate in the copyrolysis of the adduct (2,8-dimethyl-3,9-dichloro-6-sila[5.5]spiroundecatetra-2,4,8,10-ene + methyl acetylenedicarboxylate) and benzaldehyde; see Scheme I.

In this context, we thought it might be of some interest to examine theoretically the existence and relative stability of such an intermediate in comparison with other possible isomers (especially those containing the C–Si–C linkage).

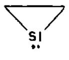
To this end, ab initio valence-only calculations have been carried out for the following C_2SiH_4 isomers: 2-silaallene (**1**), silacyclopropylidene (**2**), which is topologically very similar to the former, silacyclopropene (**3**), and 2-silapropyne (**4**), which also contain the C–Si–C linkage; as a test of reliability for the computational method used, silylacetylene (**5**), for which many experimental data are available, was also investigated.

Scheme I





1



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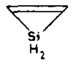

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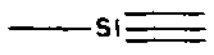

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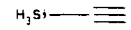

5

Method

All the SCF calculations were performed according to the PSIBMOL algorithm[5] using the pseudopotential method proposed by Durand and Barthelat.[6] This method is well adapted for calculations on molecules involving silicon atoms since it does not require more computing effort than for the analogous carbon compounds. Recent works[7] have shown that pseudopotential methods lead to results of the same quality as those obtained from an all-electron SCF method.

For each atom, the core electrons are taken into account through a nonempirical atomic pseudopotential determined from the double ζ atomic Hartree-Fock calculations of Clementi and Roetti.[8] The atomic pseudopotentials have the following analytical form:

$$W(r) = \sum_l W_l(r)P_l - z/r \qquad (1)$$

where z is the number of valence electrons for the neutral atom, P_l the projector on the lth subspace of the spherical harmonics, and

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Table I. Pseudopotential Parameters

atom	l	α_l	n_1	C_1	n_2	C_2
carbon	0	0.650 84	2	1.152 10	−2	−0.226 76
	1	7.222 29	0	−2.278 44		
silicon	0	0.484 28	2	2.697 96	−2	−0.161 49
	1	0.419 52	2	1.832 06	−2	−0.076 83
	2	1.554 08	0	−1.455 46		

Table II. Atomic Gaussian Basis Sets

atom	orbital	exponent	contraction coefficients
hydrogen	1s	13.247 9	0.019 255
		2.003 13	0.134 420
		0.455 867	0.469 565
		0.124 695	1.0
carbon	2s	48.522 8	−0.008 584
		6.269 28	−0.056 339
		0.424 916	0.584 091
		0.142 208	1.0
	2p	8.630 74	0.037 893
		2.044 42	0.202 280
		0.561 436	0.501 596
		0.155 381	1.0
silicon	3s	6.914 84	−0.013 820
		1.388 19	−0.172 552
		0.215 849	0.673 119
		0.085 339	1.0
	3p	4.699 18	−0.010 118
		0.326 834	0.394 774
		0.114 730	0.566 626
		0.044 579	0.156 942
	3d	0.30	1.0

Table III. Pseudopotential SCF Relative Energies

C_2SiH_4 isomers		ΔE, kcal/mol
silylacetylene (**5**)		0
silacyclopropene (**3**)		16.63
silacyclopropylidene (**2**)	$^1A_1$ singlet	16.99
	$^3B_1$ triplet	51.59
2-silaallene (**1**)		45.73
2-silapropyne (**4**)		60.74

$$W_l(r) = \left[\sum_i C_i/r^{n_i}\right] \exp(-\alpha_l r^2) \qquad (2)$$

The values of the parameters are listed in Table I. The s and p components were obtained from the (ns^2np^2) ^3P ground state of the C and Si atoms, and the Si d component from the $(3s^2\ 3p\ 3d)$ ^3D state.

For each atom, a valence basis set was optimized in a pseudopotential SCF calculation of the ground state of the atom using a quadruple ζ Gaussian basis set. These four Gaussian functions were contracted to the double ζ level by means of a 3 + 1 procedure (except for the p basis set of Si, where a 2 + 2 procedure has been used). For silicon a 3d Gaussian function was added as a polarization function. The chosen orbital exponent has the value determined by Roos and Siegbahn.[9] The basis sets used here are given in Table II.

Some excited states of **1** and the triplet state of **2** were investigated using an open-shell Hartree–Fock–Roothaan procedure. Moreover, extended CI calculations were carried out with the CIPSI algorithm[10] for the two cyclic compounds **2** and **3**. It has been shown that the use of pseudopotential techniques coupled with large-scale CIs allows accurate calculations of valence electronic correlation energies.[11]

All the equilibrium geometries were determined by optimizing independently the geometrical parameters at the Hartree–Fock level.

Results and Discussion

Relative SCF energies are given in Table III and the corresponding geometries are reported in Figure 1.

First, the silylacetylene molecule was computed in order to compare our SCF pseudopotential results with the experimentally available microwave,[12] infrared,[13] and dipole moment[14] data (cf. Table IV). Although interatomic distances (especially the Si–C one) seem to be slightly overestimated, the calculated geometry agrees fairly well with experiment. With regard to force constants and dipole moment, it is known that better values can hardly be expected from an SCF level calculation.

The first main result is that, on the total potential energy surface, there is a minimum corresponding to the allenic structure. We have verified that all deviations from this D_{2d} optimized geometry lead to positive second derivatives of the total energy. Therefore this structure can exist, although it is not the most stable one.

A. Relative Stability. It should be pointed out that the order of calculated thermodynamic stabilities for these isomers is in line with their experimental observation. The new main result is that silacyclopropylidene (**2**) is predicted to be more stable than 2-silaallene (**1**). Since no proton migration is involved in the conversion of **1** to **2** only a small energy barrier may be expected, and, therefore, if **1** is formed as an intermediate in the above-mentioned reaction at 500 °C, it would probably rearrange to the more stable silylene form **2**.

A CI calculation has been performed for the two cyclic compounds **2** and **3** in their optimized geometry since it is well-known that electronic correlation energy may be important in cyclic frameworks. The calculation of valence correlation energies, performed according to the CIPSI algorithm, first selected the doubly excited determinants which have a weight larger than 0.026 in the perturbed wave function. The resulting variational multiconfigurational zeroth-order wave functions have been perturbed to the second order in energy, involving up to 3.6×10^5 determinants and bringing about 200 kcal/mol valence correlation energies. Two definitions of the nonperturbed Hamiltonian have been used; the most popular Möller-Plesset[15] definition leads to a final 1.98 kcal/mol difference in favor of the sylilene molecule **2**, while the use of the energy-shifted denominators of the Epstein-Nesbet[16] definition of H_0 leads to a larger value (4.51 kcal/mol) in favor of the same. The estimation of accurate values for *differences* between correlation energies is difficult, but it would appear that the silylene molecule **2** is definitely more stable than its

Table IV. Calculated and Experimental Values of Geometrical Parameters, Force Constants, and Dipole Moments for Silylacetylene

	geometry, Å and deg					force constants, mdyn/Å					dipole moment, D
	Si—C	C≡C	C—H	Si—H	∠HSiH	k_{Si-C}	$k_{C\equiv C}$	k_{C-H}	k_{Si-H}	k_{HSiH}	
PSIBMOL theoretical values (this work)	1.86	1.21	1.07	1.49	109.7	3.67	18.58	7.19	3.31	0.67	0.47
exptl data	1.83	1.21	1.06	1.49	110.1	3.30	15.59	5.87	2.89	0.26	0.32
ref			12					13			14

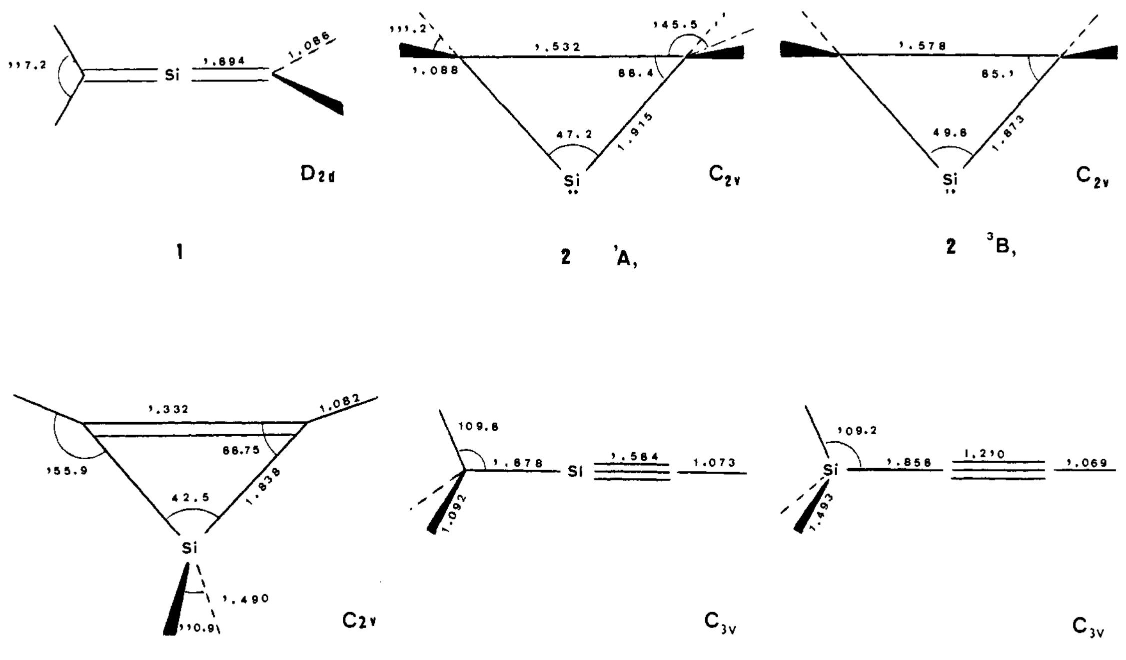


Figure 1. Optimized geometries of C_2SiH_4 isomers 1–5: interatomic distances in ångströms, bond angles in degrees.

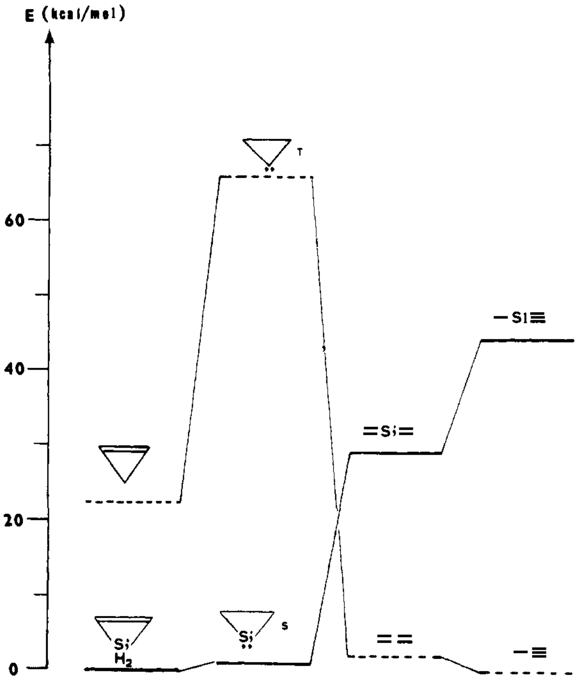


Figure 2. Comparison of the relative stabilities of C_2SiH_4 isomers containing the C–Si–C linkage (this work) and the corresponding C_3H_4 isomers (ref 17 except for cyclopropylidene (ref 20)).

more classical isomer silacyclopropene (3) by a few kilocalories per mole. It can be mentioned also that their interconversion will require considerable energy since it involves two proton migrations.

B. Comparison with the Carbon Series. With reference to the most refined ab initio calculations of Hariharan and Pople,[17] which agree with experimental data in the carbon series, one can see that the order of stability is quite different when a carbon atom is substituted by a silicon atom, especially when silicon is multiple bonded (see Figure 2). The reluctance of silicon for multiple-bond formation is well recognized and in the present instance it prefers to shift the unsaturation by forming either a ring or a silicon carbene.

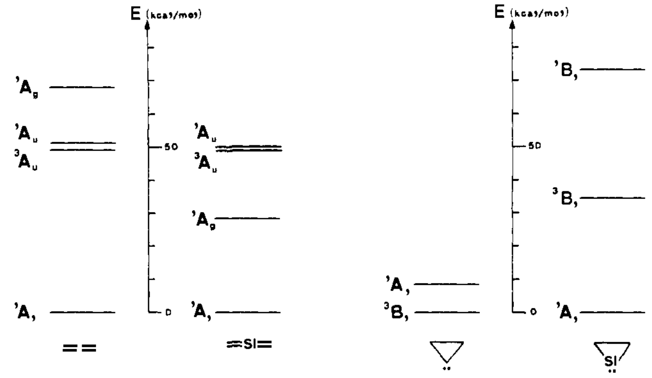


Figure 3. Electronically excited states of 2-silaallene, silacyclopropylidene, allene,[21] and cyclopropylidene.[20]

In Figure 3, the lower lying electronic states of 2-silaallene and silacyclopropylidene are compared with those of the corresponding carbon series.

For the silylene form 2, the computed ground state is a singlet, in good agreement with other calculations on silylenes.[18,19] The first $^3B_1$ triplet state lies 34.6 kcal/mol while the first excited $^1B_1$ singlet lies about 73.5 kcal/mol above the ground state. It is interesting to point out that the S–T energy gap for 2 is much higher than that of cyclopropylidene; like most carbenes, the latter has a triplet ground state and the T–S gap is 8.4 kcal/mol, according to the latest 4-31G calculations of Pasto et al.[20]

The first planar D_{2h} excited states of 2-silaallene (1) have been also investigated by Hartree–Fock–Roothaan open-shell calculations using a geometry estimated from the geometrical

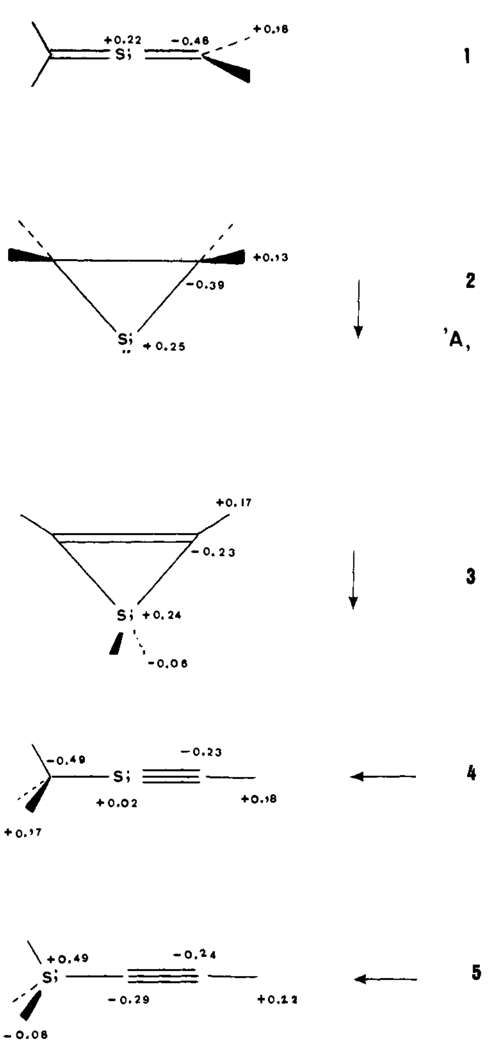


Figure 4. Net atomic charges for the C_2SiH_4 isomers **1–5**. The arrows indicate the direction of the dipole moments given in Table V.

changes known in the allene states. It is worthwhile to note that a ^3Au-^1Ag inversion appears, in contrast with the order obtained for the excited states of planar allene.[21]

C. Geometries, Force Constants, and Charges. The optimized geometries are not far from the expected ones (Figure 1). The ring angle on the silicon atom in **3** is 16% smaller than in cyclopropene (50.8°).[22] It increases to 47.2° in the singlet silylene form **2** and to 49.8° in the corresponding triplet state. The Si=C distance is shorter in **1** (1.69 Å) than in silaethylene (1.71 Å), that we have also computed for comparison; the same phenomenon occurs in going from ethylene (1.34 Å) to allene (1.31 Å). The trend in the Si-C bond distances is not surprising either, 1.91 > 1.87 Å for **2** singlet and **2** triplet, respectively, and 1.88 > 1.86 > 1.84 > 1.58 Å for **4** (Si—C), **5**, **3**, and **4** (Si≡C), respectively. The position of **3** in this sequence is due to a possible p_π-d_π overlap (vide infra). It is also worthwhile to point out that the Si≡C distance in the parent HSi≡CH calculated with the FSGO model[23] was found to be much shorter (1.50 Å).

Si-C and Si-H force constants have been calculated by parabolic fit and are reported in Table V. The variation of k_{Si-C} as a function of bond multiplicity (3.5, 6.6, 9.5 mdyn/Å) shows the same trend as in the carbon series. A weaker value can be noticed in the silylene form **2**.

Net atomic charges are given in Figure 4. The positive charge on the silicon atom has not drastically changed on going from silaethylene (+0.25) to 2-silaallene (+0.22). On the other hand, the digonal silicon in **4** would have an abnormally small charge but the corresponding calculated overall molecular moment (Table V) is very large and comparable with the FSGO value of 2.8 D for the parent HSi≡CH.[23] A rather weak value for the dipole moment (0.18 D) is predicted for **3**.

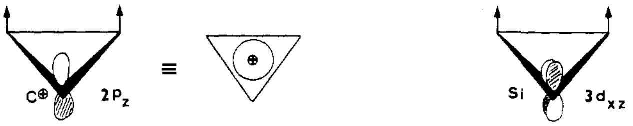
Table V. Si-C and Si-H Calculated Force Constants and Dipole Moments in C_2SiH_4 Isomers **1–5** and Silaethylene

compd	k, mdyn/Å Si-C	Si-H	μ, D
silaethylene	6.70		
2-silaallene (**1**)	6.56		0
silacyclopropylidene (**2**) (singlet)	2.50		0.44
silacyclopropene (**3**)	3.15	3.63	0.18
2-silapropyne (**4**)	9.48 (Si≡C) 3.35 (Si—C)		3.97
silylacetylene (**5**)	3.67	3.31	0.47

Table VI. Comparison between CNDO/2[24] and SCF Results (This Work) on Silacyclopropene

	CNDO/2	pseudopotential SCF results
C=C distance, Å	1.37	1.33
C—Si overlap population	0.99	0.80
C—C overlap population	0.98	1.22
net atomic charge on silicon	+0.06	+0.24

D. The Problem of Aromaticity in Silacyclopropene. Simple chemical intuition suggests that the $3d_{xz}$ orbital of silicon could play the same role as the vacant positive $2p_z$ carbon atomic orbital in the cyclopropenyl cation which, with its two π electrons, is aromatic.



This is indeed supported by the recent CNDO/2 calculation of Jones and White.[24] This method gives the following results: (1) the C=C bond length in various derivatives of silacyclopropene ranges from 1.37 to 1.39 Å, which is slightly shorter than a C=C aromatic bond. (2) Mulliken overlap populations are nearly the same in the Si-C (0.99) and the C-C (0.98) bonds. (3) The net atomic charge on the silicon atom in silacyclopropene (+0.06) is reduced with respect to that in silacyclopropane (+0.11) calculated with the same method.

However, our results are in complete disagreement with those obtained by CNDO/2 calculations (see Table VI). According to our SCF results, the aromatic character of **3** would be very small, although a certain p_π-d_π overlap exists between carbon and silicon atoms, and **3** would be more compatible with the model acetylene + silylene if indeed **3** could be visualized as being formed in the interaction between these two entities.[20] The discrepancy again shows[25] how much a CNDO/2 Hamiltonian can overestimate the d AO's participation and underlines the need for restraint in the interpretation of CNDO results.

E. Allene-Cyclopropylidene Conversion. A recent STO-3G study of Pasto et al.[20] demonstrated the complexity of the reaction path in the ring opening of cyclopropylidene to allene both for singlet and triplet states; this conversion involves three distinct processes in the singlet pathway, namely, disrotatory opening and monorotatory and conrotatory conversions. It was not our aim to compute such a complete pathway for intermediates the existence of which is not ascertained. In our case, where the silylenic ring is predicted to be much more stable than the allenic form, it is not even certain that an energy barrier for the conversion of **1** to **2** actually exists.

Conclusion

Our theoretical investigation, at an ab initio double ζ quality level of reliability, (1) shows the known thermodynamic stability of silylacetylene, (2) confirms the reluctance of silicon to engage in double-bond or in triple-bond formation, supporting the conclusion of previous FSGO calculations,[23] (3) suggests that the stability of silacyclopropene cannot be attributed to a high degree of aromatic character, and (4) predicts an unusual stability for singlet ground state silacyclopropylidene as a result of (2).

The silacyclopropylidene ring has not yet been observed and attempts to synthesize and characterize this species would be worthwhile. Detection of this intermediate may not depend solely on its intrinsic thermodynamic stability, however, since other reactions such as dimerizations could rapidly destroy the basic skeleton, as shown by Ahlrichs and Heinzmann for the case of silaethylene.[26] The same remarks must especially be kept in mind concerning the recently proposed intermediacy of 2-silaallene; although there is a minimum in the potential surface, the lifetime of this isomer might be very short, especially with regard to possible cyclization to the much more stable silacyclopropylidene structure.

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