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Mark R. Hoffman, Yasunori Yoshioka,
and Henry F. Schaefer III

April 1982

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Vibrational Frequencies for Silaacetylene and
its Silylidene and Vinylidene Isomers

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Abstract

The molecular structures, vibrational frequencies, and relative energies of silaacetylene and its vinylidene and silylidene isomers have been investigated via nonempirical molecular electronic theoretical methods. Basis sets of double zeta (DZ) and double zeta (DZ) and double zeta plus d function quality have been used for this purpose in conjunction with self-consistent-field (SCF) and configuration interaction (CI) wave functions. The largest CI included in a completely variational manner 8,001 configurations, and analytic CI gradient methods were used to determine the structure and harmonic vibrational frequencies of silaacetylene itself. The absolute minimum on the potential energy hypersurface is the silylidene, $:\text{Si}=\text{CH}_2$, which lies ~ 50 kcal below the linear silaacetylene. The vinylidene isomer $\text{H}_2\text{Si}=\text{C}:$ is either an extremely shallow minimum or, more likely, not a genuine relative minimum at all. Silaacetylene is predicted to have a trans bent equilibrium geometry, with HSiC angle 128.8° , HCSi angle 150.1° , and a silicon-carbon bond distance of $1.635 \text{ \AA}$, about $0.08 \text{ \AA}$ shorter than a "standard" $\text{Si}=\text{C}$ double bond distance. The silicon-carbon stretching vibrational frequency is predicted to be $\sim 1100 \text{ cm}^{-1}$, or 10% higher than found experimentally for dimethylsilaethylene. It is concluded that the silicon-carbon linkage in trans bent silaacetylene is intermediate between a double and triple bond. There appears to be no cis isomer of silaacetylene.

Introduction

Now that a variety of synthetic techniques are available^{1,2} for the laboratory preparation of molecules with carbon-silicon double bonds, it is inevitable that organic chemists will begin to devise schemes for the synthesis of carbon-silicon triple bonds. Theory should be able to provide guidance in this regard and several studies³⁻⁶ of the unsubstituted silaacetylene have already appeared. All of these theoretical studies affirm the prediction, first made by Murrell, Kroto, and Guest,³ that the silylidene isomer

represents the absolute minimum on the SiCH_2 potential energy hypersurface. The issue of whether the silaacetylene isomer is a true minimum has not yet been given a completely definitive answer. Hopkinson and Lien⁴ were the first to appreciate that, within the self-consistent-field (SCF) approximation

rearranges to the silylidene (1) without a barrier. However, the work of Gordon and Pople⁵ at a higher level of theory suggests that electron correlation may bring into existence a small barrier for the rearrangement (2)→(1).

The experimental technique which seems at present most likely to provide the initial observation of silaacetylene or the silylidene

isomer (1) is matrix isolation infrared spectroscopy.⁷ For this reason, the present theoretical study is aimed primarily at the determination of the vibrational frequencies of (1), (2), and the vinylidene isomer

In addition an attempt has been made to locate and characterize stationary points connecting species (1), (2), and (3).

Theoretical Approach

In this work, stationary points have been for the most part located and characterized (in terms of their harmonic vibrational frequencies) at the self-consistent-field (SCF) level of theory. This has been accomplished using two basis sets, the relatively standard double zeta (DZ)⁸ and double zeta plus d function (DZ+d) sets. In the latter DZ+d basis, sets of six d-like functions ($x^2, y^2, z^2, xy, xz, yz$ times $e^{-\alpha r^2}$) were centered on silicon ($\alpha=0.6$) and carbon ($\alpha=0.75$). The technical specification of the larger basis set is thus Si(11s 7p 1d/6s 4p 1d), C(9s 5p 1d/4s 2p 1d), H(4s/2s). Following optimization of the DZ+d SCF stationary point geometries, single calculations were carried out at these geometries with extensively correlated wave functions. These configuration interaction (CI) wave functions included all singly- and doubly-

excited configurations relative to the respective SCF reference configuration, with the restriction that the core-like orbitals (six lowest occupied SCF orbitals and 6 highest virtual orbitals; Si 1s, 2s, 2p_x, 2p_y, 2p_z, and C 1s in character) were excluded. For the C_{2v} structures (1) and (3) this amounts to 2253 configurations, while for planar (point group C_s) stationary points there are 4321 configurations in the CISD wave functions.

Obvious weaknesses of this theoretical procedure are the failure to include polarization functions (p functions) on hydrogen and the lack of complete geometrical optimizations at the highest level of theory. However for the more exhaustively studied silaethylene rearrangement⁹

and for the simpler vinylidene¹⁰ and formaldehyde¹¹ isomerizations, these approximations are relatively unimportant.

For silaacetylene only, a significantly more advanced theoretical prediction of the equilibrium geometry was carried out. Using the DZ + d basis, the molecular structure and vibrational frequencies were determined using explicitly correlated wave functions. To determine the vibrational frequencies, calculations in both C_s and C₁ (no elements of symmetry other than the identity) are required, and the CISD

wave functions included 4321 and 8001 configurations, respectively, for these two cases. Recently developed analytic configuration interaction gradient techniques^{12,13} were used to determine both the silaacetylene structure and vibrational frequencies.

Equilibrium Structures and Energetics

The predicted structures of (1), (2), and (3) are given in Figures 1, 2, and 3 and their total and relative energies in Table I. In light of previous theoretical studies³⁻⁶ of these systems, there are no striking surprises in either the geometries or energetics. At the SCF level, the addition of d functions to the basis set serves to decrease the predicted Si-C bond distances by only ~ 0.03 Å. Despite its high energy, the linear HSiCH structure is clearly seen to possess a very short bond distance, in this sense precisely what would be expected for a Si $\equiv$ C triple bond. However, as noted in an earlier paper¹⁴ on aluminum-carbon multiple bonds, the electronic and geometrical manifestations of multiple bonds need not necessarily be accompanied by the anticipated energetic stability. Nevertheless, for the formally double-bonded vinylidene (3) and silylidene (1) structures there is a correlation between bond energy and bond order. That is, the lower energy silylidene structure has a Si=C bond distance 0.054 Å less than the vinylidene Si=C distance. The most reliable level of theory given in Table I predicts linear silaacetylene and its vinylidene isomer to lie 49.1 and 90.0 kcal, respectively, above silylidene.

Theoretical studies of silaethylene and dimethylsilaethylene have now firmly established¹⁵⁻¹⁷ that a "normal" Si=C double bond length is of the order of 1.71 Å. The only reliably established experimental Si=C bond distance for a silaolefin is that of Brook,¹⁸ and his distance of 1.764 Å is readily understood¹⁹ as being somewhat elongated due to its four bulky substituents (two trimethylsilyl groups, one adamantyl, and one -OSi(CH₃)₃ substituent). Given this background, inspection of Figures 1-3 shows immediately that the vinylidene structure (3) possesses a long silicon-carbon double bond, the silylidene (2) Si=C bond distance is "normal" or very slightly short, while the linear silaacetylene bond distance at 1.563 Å is much too short to be classified as a double bond.

In light of Gordon and Pople's novel prediction that electron correlation introduces an energy barrier (apparently nonexistent at the SCF level) between (2) and (1), it was decided to further pursue this issue at the DZ+d CI level of theory. These results will be described in the final section of this report.

Silylidene Vibrational Frequencies

Table II summarizes the harmonic vibrational frequencies predicted for the different stationary points considered here. Since only the silylidene structure (1) is likely to be observed in the near future, our discussion focuses on this aspect of the present research. The reader should also be advised that systematic studies²⁰ of vibrational frequencies at the DZ and DZ+d SCF levels of theory typically show the predicted frequencies to be ~ 10%

larger than experiment. Thus the two predicted C-H stretching frequencies of silylidene (1) might be expected to be actually observed at 3012 and 2941 cm^{-1} . The frequency predicted at 1521 (DZ) or 1517 (DZ+d) cm^{-1} is a methylene bending frequency. The all-important $\text{Si}=\text{C}$ stretching mode occurs at 997 cm^{-1} (DZ) or 1026 cm^{-1} (DZ+d), both of which lie in the general vicinity expected^{21,22} for a silicon-carbon double bond. Specifically, the Russian workers Gusel'nikov²¹ and Nefedov²² have assigned the $\text{Si}=\text{C}$ stretching frequency in dimethylsilaethylene as 1001 and 1003 cm^{-1} , respectively. Finally the 853 cm^{-1} and 500 cm^{-1} fundamentals may be assigned in the harmonic approximation to the wag (out-of-plane) and rock frequencies, respectively.

Si CH₂ Rearrangement Pathways

An issue not addressed in prior theoretical studies of the silaacetylene potential energy hypersurface is the existence or nonexistence of a barrier between the vinylidene isomer (3) and silaacetylene. By comparison with the prototype vinylidene $\begin{array}{c} \text{H} \\ \diagdown \\ \text{C}=\text{C}: \\ \diagup \\ \text{H} \end{array}$ the transition state would be expected¹⁰ to be of the planar type exhibited in Figure 4. However Table II shows that this stationary point has associated with it (at both the DZ and DZ+d SCF levels of theory) two imaginary vibrational frequencies. Moreover, at the highest level of theory (unlinked cluster corrected DZ+d CI), this stationary point (Figure 4) lies only 4.9 kcal above the vinylidene isomer (3).

Beginning at the structure with two imaginary vibrational frequencies (Figure 4), an attempt was made (with the DZ SCF method) to locate a genuine transition state in adjacent regions of the

potential energy hypersurface. Noting that the lower (340i) of the two imaginary vibrational frequencies carries the migrating H atom out of the four atom plane, a search was begun for a nonplanar stationary point. Such a nonplanar transition state was previously found²³ for the triplet vinylidene 1,2 hydrogen shift. However, for the SiCH_2 system this portion of the DZ SCF energy surface is so flat that precision problems with our minicomputer (Harris Series 800; 11 significant figures) made this search unprofitable.

A final stationary point was suggested to us by the independent studies of Morokuma,²⁴ Binkley,²⁵ and Liu²⁶ on the related Si_2H_2 system. They predict the absolute minimum on the Si_2H_2 hypersurface to be a structure of the form

An analogous stationary point for SiCH_2 was found and is illustrated in Figure 5. However, Tables I and II show this structure to be quite high-lying energetically (104 kcal above silylidene) and furthermore to have two imaginary vibrational frequencies associated with it. Thus it may be reasonably concluded that the SiCH_2 system is quite different from Si_2H_2 in this regard.

In conclusion, it must be admitted that we have not found a transition state leading from the vinylidene structure (3). However, such a transition state must lie less than 4.9 kcal above (3) at the DZ+c CI level of theory. Furthermore, two high-level studies^{10,27}

of the singlet parent vinylidene rearrangement

indicate that a significant lowering of its barrier occurs beyond the DZ+d CISD level of theory. This line of reasoning suggests (but obviously does not prove) that the silicon-substituted vinylidene structure (3) is not a minimum on the SiCH_2 potential energy hypersurface.

Trans Bent Silaacetylene at a Higher Level of Theory

As mentioned earlier, the structure of trans bent HSiCH has also been determined at the DZ+d CI level of theory. This was done to further investigate Gordon and Pople's remarkable prediction that electron correlation actually introduces a barrier between silaacetylene and the lower energy silylidene form. More typically, of course, the effect of correlation is to reduce²⁸ (or entirely eliminate²⁷) barriers predicted at the SCF level of theory.

The predicted structure of trans bent silaacetylene at the DZ+d CI level of theory is reported in Figure 6. For completeness, the constrained linear structure was also determined at the same advanced level of theory and is likewise seen in Figure 6. Comparison of the two structures shows first of all that trans bending significantly lengthens the silicon-carbon bond distance from 1.587 Å

to 1.635 Å, an increase of 0.048 Å. Whereas the linear structure represents a true triple bond, the trans bent equilibrium geometry may alternately be considered a long triple bond or a very short double bond. If we again take 1.71 Å as the standard Si=C double bond distance,¹⁶ then the 1.635 Å predicted here for silaacetylene is 0.075 Å short of this standard measure.

In their study Gordon and Pople⁵ did not explicitly optimize the geometrical structure of silaacetylene, but rather used an assumed reaction coordinate to examine the pathway from linear silaacetylene to the silylidene :Si=CH₂. For this purpose they defined the angle α to be the C-Si-H angle, where the hydrogen atom is migrating to form the silylidene, the absolute minimum on the SiCH₂ potential energy hypersurface. For a range of values of α between 180° (linear silaacetylene) and 21° (silylidene), the energy was minimized with respect to all other geometrical parameters. At the split valence (nearly DZ) and split valence plus d (essentially DZ+d) SCF levels of theory, the linear silaacetylene passes to the lower energy silylidene without a perceptible energy barrier. However when second- or third-order perturbation theory is applied, barriers of 16 kcal and 9 kcal, respectively, appear and evidence for a trans bent equilibrium geometry is indisputable. The barrier occurs near $\alpha=90^\circ$ and the trans minima near 140°. The latter value is seen to be in qualitative agreement with the prediction in Figure 6 of 128.8° for the equilibrium C-Si-H angle. For $\alpha=140^\circ$, Gordon and Pople⁵ find the optimum value of the SiC bond distance and HCSi angle to be 1.632 Å and 157.5°, in reasonable agreement with our

equilibrium geometry predictions of 1.635 Å and 150.1°, respectively.

The DZ+d CI total energies of linear and trans bent silaacetylene are -327.98642 and -327.99607 hartrees, respectively. The resulting energy difference of 6.1 kcal may be compared with Pople and Gordon's and is an obvious measure of the energy stabilization due to trans bending of the constrained linear structure shown in Table II to have two imaginary vibrational frequencies. A somewhat more reliable estimate of the linear-trans energy difference for silaacetylene is provided by adding the Davidson correction for quadruple excitations (unlinked clusters) to the CI energies. These corrections are 0.02414 hartrees for linear silaacetylene and 0.02874 hartrees for the trans bent structure, leading to final ΔE (linear-trans) of 8.9 kcal. This barrier to linearity was not directly predicted by Gordon and Pople, but graphical interpolation of their split valence plus d basis set, third-order perturbation results suggests a barrier of ~ 5 kcal.

Given the trans bent stationary point geometry, cartesian force constants were next determined at the DZ+d CI level of theory using recently developed analytic gradient techniques for explicitly correlated variational wave functions.^{12,13} Subsequently these force constants were subjected to a harmonic vibrational analysis, the results of which are seen in Table III. Note first that these silaacetylene frequencies should be significantly more reliable than the SCF results reported in Table II. For example, in a survey of four stable closed-shell molecules (H_2O , H_2CO , HCN , CH_4) for which experimentally determined harmonic vibrational frequencies are

available, Yamaguchi²⁰ found the DZ+P CI predictions to be 3.5% greater than experiment. The results in Table III of course do not include the effects of anharmonicity, which typically lowers the harmonic frequencies by the order of perhaps 4%.

If the above reduction of 7.5% is applied to our DZ+P CI prediction of the silicon-carbon stretching frequency, an empirical result of 1092 cm^{-1} is obtained. By comparison with the experimental values of 1001 and 1003 cm^{-1} for the Si=C double bond stretching frequency in dimethylsilaethylene^{21,22}, it is seen that the silaacetylene frequency is somewhat higher. This is consistent with the characterization of the silicon-carbon linkage in trans bent silaacetylene as an exceptionally strong double bond. Should a silaacetylene be prepared in the laboratory (perhaps with two very bulky substituents such as adamantyl replacing the hydrogen atoms in Figure 6), one would thus expect to observe a notably higher Si-C stretching frequency than for the analogous silaolefin.

Since the geometry optimization for trans bent silaacetylene was carried out in point group C_s , it was not obvious that a non-planar C_1 geometry might not be preferred. However, Table III shows that the planar structure is a genuine relative minimum of the DZ+P CI energy surface, i.e., all harmonic vibrational frequencies are real.³⁰ Moreover, the out-of-plane a'' frequency is 665 cm^{-1} , which is actually higher than the in-plane C-Si-H bend at 420 cm^{-1} . The magnitude of this torsional frequency at 665 cm^{-1} is not surprising when one appreciates that this corresponds to internal rotation about a silicon-carbon bond of order approximately $2\frac{1}{2}$.

Finally, an attempt was made to locate a cis bent equilibrium geometry for silaacetylene. Given the HSiC and HCSi trans bond angles of 128.8° and 150.1° , this is not an implausible possibility. However, the search proved fruitless. Starting from a cis structure obtained essentially via rotation of the trans geometry by 180° about the Si=C axis, no adjacent stationary point could be located. Gradient values in this region of the energy hypersurface were substantial and the total energy above that of the constrained linear structure. Thus it appears that there is no cis bent isomer of silaacetylene.

Concluding Remarks

Vibrational frequencies have been predicted for five different nondissociative stationary points on the SiCH_2 potential energy hypersurface. Among these the silylidene isomer $:\text{Si}=\text{C} \begin{smallmatrix} \text{H} \\ \diagup \\ \text{H} \end{smallmatrix}$ is the lowest lying energetically and therefore the most likely to be observed experimentally. Silaacetylene itself has a trans bent equilibrium geometry, corresponding to a silicon-carbon bond order of approximately $2 \frac{1}{2}$.

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Table I. Total and relative energies for stationary points on the SiCH₂ potential energy hypersurface. Total energies are in hartrees and relative energies in kcal.

Total Energies					
DZ SCF	-327.83567	-327.73666	-327.68064	-327.64698	-327.64619
DZ+d SCF	-327.86448	-327.77254	-327.72761	-327.69625	-327.69475
DZ+d CI	-328.06684	-327.98566	-327.92171	-327.91019	-327.89514
Relative Energies					
DZ SCF	0.0	62.1	97.3	118.4	118.9
DZ+d SCF	0.0	57.7	85.9	105.6	106.5
DZ+d CI	0.0	50.9	91.1	98.3	107.7
Davidson Corrected	0.0	49.1	90.0	94.9	104.2

Table II. Predicted vibrational frequencies (in cm^{-1}) for stationary points on the SiCH_2 potential energy hypersurface.

	$\text{H-Si}\equiv\text{C-H}$
DZ SCF	3366(b_2)	3604(σ)	2369(b_2)	2378(a')	1973(a')
	3273(a_1)	2485(σ)	2339(a_1)	1853(a')	1967(a'')
	1521(a_1)	1343(σ)	1013(a_1)	1069(a')	990(a')
	997(a_1)	738(π)	864(a_1)	621(a')	793(a')
	909(b_1)	3131(π)	426(b_2)	3401(a'')	4931(a'')
	601(b_2)		406(b_1)	8701(a')	6911(a')
DZ+d SCF	3347(b_2)	3574(σ)	2467(b_2)	2465(a')	2153(a'')
	3268(a_1)	2553(σ)	2443(a_1)	2078(a')	2152(a')
	1517(a_1)	1387(σ)	1069(a_1)	1154(a')	1010(a')
	1026(a_1)	743(π)	919(a_1)	685(a')	888(a')
	853(b_1)	3401(π)	464(b_1)	3421(a'')	4561(a'')
	500(b_2)		459(b_2)	8151(a')	7321(a')

Table III. Harmonic vibrational frequencies (in cm^{-1}) for the trans bent equilibrium geometry of silaacetylene. These results were obtained via configuration interaction including all valence single and double excitations, in conjunction with a double zeta plus d function basis set.

	<u>Frequency</u>	<u>Description</u>
a'	3362	C-H stretch
a'	2349	Si-H stretch
a'	1174	Silicon-Carbon stretch
a'	755	Si-C-H bend
a'	420	C-Si-H bend
a''	665	torsion

Figure Captions

1. Theoretical structures predicted for the silylidene isomer of silaacetylene. Bond distances are in Å.
2. Self-consistent-field (SCF) structures for linear, closed-shell singlet silaacetylene. Bond distances are in Å.
3. Predicted geometrical structure for the C_{2v} constrained vinylidene, a possible isomer of silaacetylene. Bond distances are in Å.
4. Expected transition state for the rearrangement of the vinylidene structure (see Figure 2) to silaacetylene. Bond distances are in Å. Note that there are two imaginary vibrational frequencies associated with this stationary point.
5. A $SiCH_2$ stationary point analogous to that found to be the absolute minimum on the Si_2H_2 potential surface. These $SiCH_2$ structures were determined to have two imaginary vibrational frequencies (see text).
6. Predicted structure of trans bent silaacetylene at a significantly higher level of theory than reported elsewhere. Bond distances are in Å. For comparison the analogous geometry of the constrained linear $HSiCH$ is also presented.

Figure 1

Figure 2

XBL 817 - 4062

Figure 3

XBL 817 - 4061

DZ SCF

DZ + d SCF

Figure 4

XBL817-4060

Figure 5

XBL817 - 4059

Figure 6

XBL8110 - 4317

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