1084 J. Am. Chem. Soc. 1983, 105, 1084-1088

Vibrational Frequencies for Silaacetylene and Its Silylidene and Vinylidene Isomers

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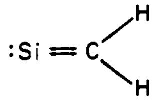
Abstract: The molecular structures, vibrational frequencies, and relative energies of silaacetylene and its vinylidene and silylidene isomers have been investigated via nonempirical molecular electronic theoretical methods. Basis sets of double ζ (DZ) and double-ζ plus d function quality have been used 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, $:Si{=}CH_2$, which lies ~50 kcal below the linear silaacetylene. The vinylidene isomer $H_2Si{=}C:$ 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 Å, about 0.08 Å shorter than a "standard" Si=C double-bond distance. The silicon–carbon stretching vibrational frequency is predicted to be ~1100 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

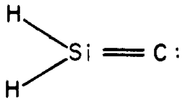
Now that a variety of synthetic techniques are available[1,2] for the laboratory preparation of molecules with carbon–silicon double bonds, it is inevitable that organic chemists will begin to devise schemes for the synthesis of carbon–silicon triple bonds. Theory should be able to provide guidance in this regard, and several studies[3-6] 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 (**1**) 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 Lien[4] were the first to appreciate that, within the self-consistent-field (SCF) approximation, **2** rearranges to the silylidene (**1**) without a barrier. However, the work of Gordon and Pople[5] at a higher level of theory suggests that electron correlation may bring into existence a small barrier for the rearrangement **2** → **1**.


1

$$H-Si\equiv C-H$$

2

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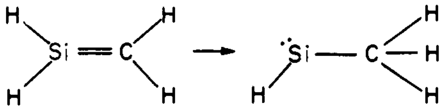
Theoretical Approach

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-ζ (DZ)[8] and double ζ plus d function (DZ+d) sets. In the latter DZ+d basis, sets of six d-like functions (x^2, y^2, x^2, xy, xz, xz 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(11s7p1d/6s4p1d), C(9s5p1d/4s2p1d), 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 at six 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 rearrangement[9] and for the simpler vinylidene[10] and formaldehyde[11] isomerizations,



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(1) L. E. Gusel'nikov and N. S. Nametkin, *Chem. Rev.*, **79**, 529 (1979); B. Coleman and M. Jones, *Rev. Chem. Intermed.*, **4**, 297 (1981).

(2) For a semipopular review, see *Chem. Eng. News*, 18 (March 30, 1981).

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(7) For early matrix infrared studies of the Si=C double bond, see O. L. Chapman, C. C. Chang, J. Kolc, M. E. Jung, J. A. Lowe, T. J. Barton, and M. L. Tumey, *J. Am. Chem. Soc.* **98**, 7844 (1976); M. R. Chedekel, M. Skogland, R. L. Kreeger, and H. Schechter, *ibid.*, **98**, 7846 (1976).

(8) T. H. Dunning and P. J. Hay, "Modern Theoretical Chemistry", Vol. 3, H. F. Schaefer, Ed., Plenum, New York, 1977, pp 1–27.

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(10) Y. Osamura, H. F. Schaefer, S. K. Gray, and W. H. Miller, *J. Am. Chem. Soc.*, **103**, 1900 (1981).

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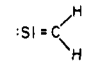
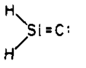
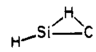
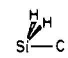
Table I. Total and Relative Energies for Stationary Points on the $SiCH_2$ Potential Energy Hypersurface[a]

		H–Si≡C–H			
		Total Energies			
DZ SCF	−327.835 67	−327.736 66	−327.680 64	−327.646 98	−327.646 19
DZ+d SCF	−327.864 48	−327.772 54	−327.727 61	−327.696 25	−327.694 75
DZ+d CI	−328.066 84	−327.985 66	−327.921 71	−327.910 19	−327.895 14
		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

[a] Total energies are in hartrees and relative energies in kcal.

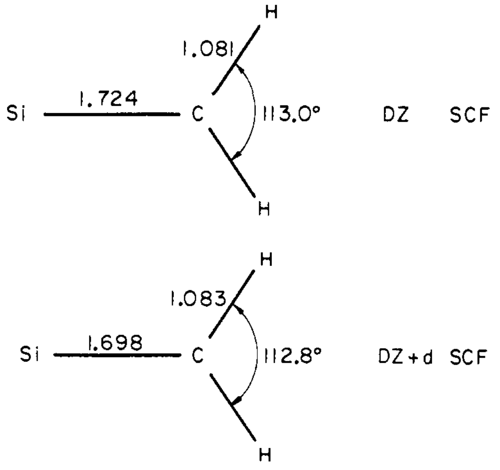


Figure 1. Theoretical structures predicted for the silylidene isomer of silaacetylene. Bond distances are in Å.

these approximations are relatively unimportant.

For silaacetylene only, a significantly more advanced theoretical prediction of the equlibrium 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 C_1 (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 studies[3-6] of these systems, there are not 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≡C triple bond. However, as noted in an earlier paper[14] 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.

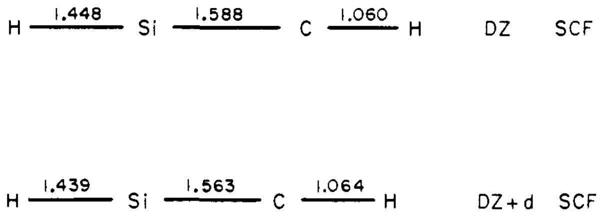


Figure 2. Self-consistent-field (SCF) structures for linear, closed-shell singlet silaacetylene. Bond distances are in Å.

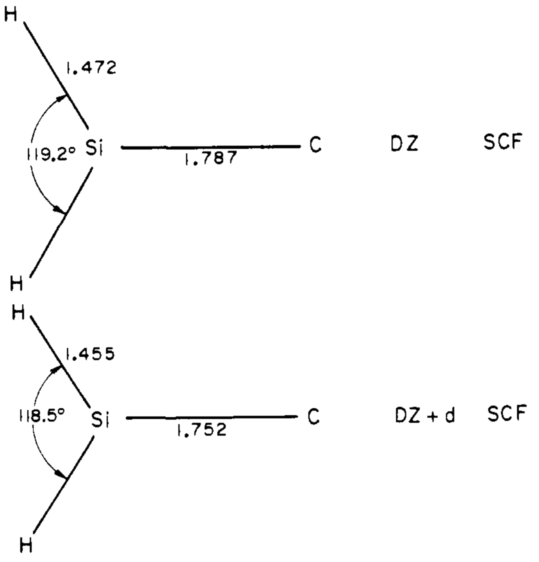


Figure 3. Predicted geometrical structure for the C_{2v} constrained vinylidene, a possible isomer of silaacetylene. Bond distances are in Å.

Theoretical studies of silaethylene and dimethylsilaethylene have now firmly established[15-17] 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 understood[19] as being

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(11) J. D. Goddard, Y. Yamaguchi, and H. F. Schaefer, *J. Chem. Phys.*, **75**, 3459 (1981).

(12) B. R. Brooks, W. D. Laidig. P. Saxe, and H. F. Schaefer, *J. Chem. Phys.*, **72**, 3837 (1980).

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(14) D. J. Fox, D. Ray, P. R. Rubesin, and H. F. Schaefer, *J. Chem. Phys.*, **73**, 3246 (1980).

(15) D. M. Hood and H. F. Schaefer, *J. Chem. Phys.*; **68**, 2985 (1978).

(16) Y. Yoshioka, J. D. Goddard, and H. F. Schaefer, *J. Am. Chem. Soc.*, **103**, 2452 (1981).

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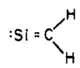
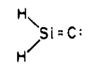
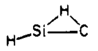
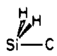
(18) A. Brook, S. C. Nyburg, F. Abdesaken, B. Gutekunst, G. Gutekunst, R. Krishna, M. R. Kallury, Y. C. Poon, Y.-M. Chang, and W. Wong-Ng, *J. Am. Chem. Soc.*, **104**, 5667 (1982).

Table II. Predicted Vibrational Frequencies (in cm^{-1}) for Stationary Points on the $SiCH_2$ Potential Energy Hypersurface

		$H-Si\equiv C-H$			
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)	313*i* (π)	426 (b_2)	340i (a″)	493*i* (a″)
	601 (b_2)		406 (b_1)	870i (a′)	691*i* (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)	340i (π)	464 (b_1)	342i (a″)	456i (a″)
	500 (b_2)		459 (b_2)	815i (a′)	732i (a′)

somewhat elongated because of its four bulky substituents (two trimethylsilyl groups, one adamantyl, and one $-OSi(CH_3)_3$ substituent). Given this background, inspection of Figures 1–3 shows immediately that the vinylidene structure (**3**) possesses a long silicon–carbon double bond, the silyidene (**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 studies[20] 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 Si═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'nikov[21] and Nefedov[22] have assigned the Si═C stretching frequency in dimethylsilaethylene as 1001 and 1003 cm^{-1}, respectively. Finally the 853- and 500-cm^{-1} fundamentals may be assigned in the harmonic approximation to the wag (out-of-plane) and rock frequencies, respectively.

$Si{=}CH_2$ 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 $H_2C{=}C{:}$, the transition state would be expected[10] 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**).

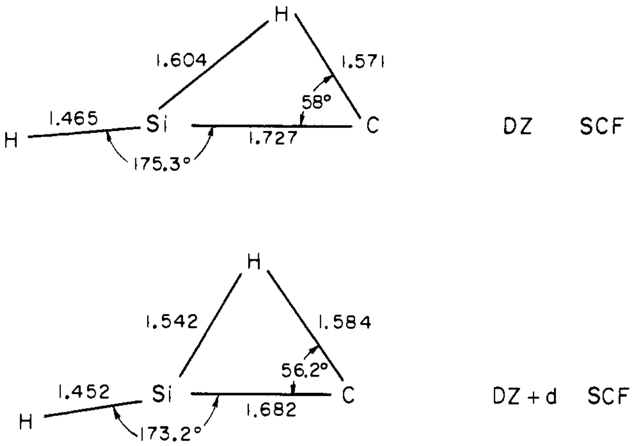


Figure 4. Expected transition state for the rearrangement of the vinylidene structure (see Figure 3) to silaacetylene. Bond distances are in Å. Note that there are two imaginary vibrational frequencies associated with this stationary point.

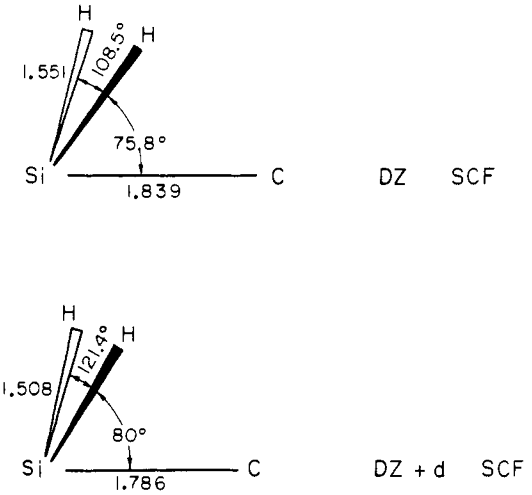


Figure 5. A $SiCH_2$ stationary point analogous to that found to be the absolute minimum on the Si_2H_2 potential surface. These $SiCH_2$ structures were determined to have two imaginary vibrational frequencies (see text).

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 (340*i*) 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 found[23] for the triplet vinylidene 1,2 hydrogen shift.

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[19] H. F. Schaefer, *Acc. Chem. Res.*, **15**, 283 (1982).

[20] Y. Yamaguchi and H. F. Schaefer, *J. Chem. Phys.*, **73**, 2310 (1980).

[21] L. E. Gusel'nikov, V. V. Volkova, V. G. Avakyan, and N. S. Nametkin, *J. Organomet. Chem.*, **201**, 123 (1980).

[22] O. M. Nefedov, A. K. Maltsev, V. N. Khabashesku, and V. A. Korolev, *J. Organomet. Chem.*, **201**, 123 (1980).

[23] M. P. Conrad and H. F. Schaefer, *J. Am. Chem. Soc.*, **100**, 7820 (1978).

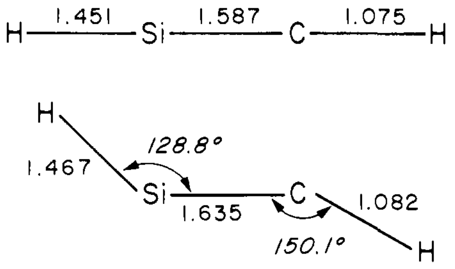
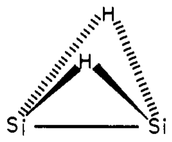


Figure 6. Predicted structure of trans-bent silaacetylene at a significantly higher level of theory than reported elsewhere. Bond distances are in Å. For comparison the analogous geometry of the constrained linear HSiCH is also presented.

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 Liu[26] 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 **4**. 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.



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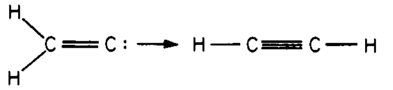
In conclusion, it must be admitted that we have not found a transition state leading from the vinylidene structure (**3**). However, such a transition state must lie less than 4.9 kcal above **3** at the DZ+d CI level of theory. Furthermore, two high-level studies[10,27] of the singlet parent vinylidene 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 reduce[28] (or entirely eliminate[27]) 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 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. It 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.

Table III. Harmonic Vibrational Frequencies (in cm^{-1}) for the Trans-Bent Equilibrium Geometry of Silaacetylene[a]

	frequency	description
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

[a] These results were obtained via configuration interaction including all valence single and double excitations, in conjunction with a double-ζ plus d function basis set.

In their study Gordon and Pople[5] 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=CH_2. 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 $SiCH_2$ 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 and 9 kcal, respectively, appear, and evidence for a trans-bent equilibrium geometry is indisputable. The barrier occurs near $\alpha = 90°$ 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 equlibrium C–Si–H angle. For $\alpha = 140°$, Gordon and Pople[5] 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 equilbrium 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 to 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 hartree for linear silaacetylene and 0.02874 hartree for the trans-bend 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 the 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, Yamaguchi[20] found the DZ+d CI predictions to be 3.5% greater than experiment. The results in Table III, of course, do note include the effects of anharmonicity, which

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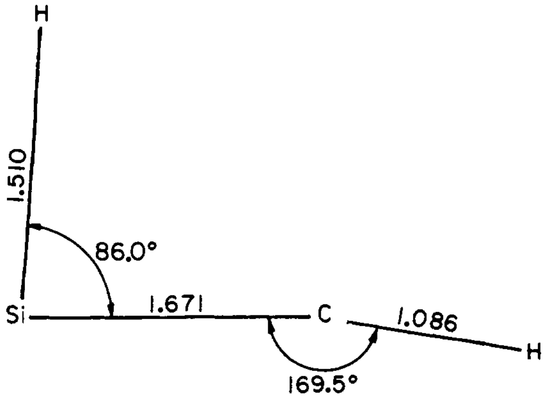

Figure 7. Transition state for the rearrangement of trans-bent silaacetylene to its silylidene isomer. The level of theory used was double-ζ plus d function (DZ+d) configuration interaction (CI), as in Figure 6.

typically lowers the harmonic frequencies by the order of perhaps 4%.

If the above reduction of 7.5% is applied to our DZ+d 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 is not obvious that a nonplanar C_1 geometry might not be preferred. However, Table III shows that the planar structure is a genuine relative minimum of the DZ+d CI energy surface; i.e., all harmonic vibrational frequences 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 $2^1/_2$.

Next, 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°, 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 was above that of the constrained linear structure. Thus it appears that there is no cis-bent isomer of silaacetylene.

Finally, the transition state from trans-bent silacetylene to the silylidene isomer was located at the DZ+d CI level of theory. This is shown in Figure 7 and corresponds to an energy of −327.98936 hartrees, or 4.2 kcal above the DZ+d CI energy of silaacetylene. When the Davidson correction is appended, the classical barrier increases somewhat, to 5.7 kcal. The latter result, of course, is consistent with the finding that correlation effects provide the origin of the barrier; i.e., the barrier vanishes within the Hartree–Fock approximation.

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 **1** 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 $2^1/_2$.

Acknowledgment. This research was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098. The Berkeley theoretical chemistry minicomputer is supported by the U.S. National Science Foundation, Grant CHE80-09320. We thank Professor Mark Gordon for helpful discussions and a copy of his paper (ref 5) with Professor John Pople prior to publication.

Note Added in Proof. The DZ SCF transition state for the unimolecular reaction of **3** was eventually found by using analytic *second* derivative methods. It is a nonplanar C_1 symmetry structure lying 17.8 kcal above **3**.

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Coordination in Benzene Dimer Cation Radical

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Abstract: Ab initio MO calculations are used to characterize coordinations in benzene dimer cation. Binding occurs for all arrangements which allow π overlap between parallel rings. Parity (orbital symmetry) is approximately conserved, and two manifolds which correspond to opposite parities are predicted. Stable species in either manifold exhibit slippery, spongy bonds. In the odd (even) manifold, these are 1-coordinate-like (6-coordinate-like) dimers which are bound by $\sim$12 (11) kcal/mol at inter-ring distances of $\sim$0.26 (0.32) nm. Analysis of the results suggests that such parity manifolds are generally expected of alternant aromatic dimer cations, and also to some extent of their oxidomer analogues. Application to the mechanism of benzene polymerization by aluminum chloride–cupric chloride is discussed.

Aromatic cation radicals have been suggested as intermediates for the oligomerization of polynuclear aromatic hydrocarbons[1,2] and the synthesis of poly(*p*-phenylene) from benzene–aluminum chloride–cupric chloride.[3-5] They may also be involved in the

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