J. Am. Chem. Soc. **1981**, *103*, 2945–2947

Structure and Stability of a Silicon–Carbon Triple Bond

Mark S. Gordon* and John A. Pople†

Contribution from the Department of Chemistry, North Dakota State University, Fargo, North Dakota 58105, and Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213. *Received June 16, 1980*

Abstract: The stability of the carbon–silicon triple bond in silaethyne is investigated via an analysis of its isomerization to silylidene and through a study of its hydrogenation energy relative to acetylene and silaethylene. It is found that silaethyne is rather unstable in a thermodynamic sense. However, while SCF calculations predict this species to rearrange to its more stable isomer with no barrier, the introduction of perturbation corrections suggests the existence of a small barrier separating the two isomers.

I. Introduction

As part of a series of investigations of strained and unsaturated compounds containing silicon,[1–3] the present work focuses on a study of the stability of the carbon–silicon triple bond in its simplest prototype molecule, silaethyne. Three previous ab initio studies of a carbon–silicon triple bond have been carried out. Using a pseudopotential method with a better than double-ζ quality basis set, Barthelat and co-workers found 2-silapropyne to be the highest energy isomer of silaallene;[4] however, the corresponding silylidene was not considered. Hopkinson and Lien[5] find silylidene to be about 60 kcal/mol lower in energy than silaethyne, using a double-ζ basis set. Moreover, these authors suggest that silaethyne rearranges to its more stable isomer with no barrier, although no potential energy surface was presented. The preference of H_2CSi for the silylidene form has also been noted by Murrell, Kroto, and Guest.[6] In related calculations, Snyder has found three minima for Si_2H_2.[7] These occur at the silylidene, a bridged cyclobutane-like structure, and an open nonlinear structure.

In the present work the potential energy surface connecting silaethyne and silylidene is analyzed at two levels of approximation: SCF and SCF augmented by perturbation corrections. With the use of perturbation corrections, the hydrogenation energies of the silicon-containing species, including silaethylene, are compared with those of the corresponding hydrocarbons.

II. Methodology

Following the approach used in previous papers,[1,2] geometry optimizations have been carried out by using the split valence 3-21G basis set.[9] Single-point calculations were then performed by using the extended 6-31G* basis set[1,10] which includes d functions on the heavy atoms. With the use of the notation introduced by Pople and co-workers,[9] such a single-point calculation is denoted 6-31G*//3-21G. Second- and third-order Moller Plesset (MP2 and MP3)[8] perturbation corrections were added to the 6-31G* SCF results in order to account for the effect of correlation corrections on the calculated surface.

Full geometry optimizations within a specified point group were performed by using the analytical gradient scheme employed by the HONDO system of programs.[11a] MP3 calculations were carried out with the GAUSSIAN 80 program.[11b] The potential-energy surface connecting silaethyne with silyidene was followed by choosing the C–Si–H angle (α) as "reaction coordinate". Except for the obvious symmetry constraints of $C_{\infty v}$ for linear silaethyne and C_{2v} for silylidene, the geometry was fully optimized in C_1 symmetry for each value of α. These constrained variations were carried out in internal coordinates, using a numerical gradient technique.[12]

III. Results and Discussion

The 3-21G geometries for ethane, ethylene, acetylene, and methylsilane have been reported in previous papers.[9] For silaethylene the C=Si, CH, and SiH bond lengths are 1.717, 1.074, and 1.474 Å, respectively, while the HCH (HSiH) angle is 115.77° (114.90°). The structures of silaethyne and silylidene will be discussed below in connection with the surface which joins these two species.

Table I. Hydrogenation Energies (kcal/mol)[a]

molecule	3-21G// 3-21G	6-31G*// 3-21G	6-31G* + MP2//3-21G	exptl[b]
ethylene	−43.9	−44.0	−41.5	−31.0
acetylene	−51.5	−54.7	−47.2	−39.8
silaethylene	−63.7	−67.8	−56.9	
silaethyne	−82.7	−90.7	−71.7	
silylidene[c]	−22.3	−34.4	−31.0	

[a] The energy released upon the addition of 1 mol of H_2. [b] "Selected Values of Chemical Thermodynamic Properties", NBS Technical Note 270-3, National Bureau of Standards, Washington, D.C. [c] For this molecule the reaction is $H_2C{=}Si + H_2 \rightarrow H_2C{=}SiH_2$.

The hydrogenation energies for the molecules of interest are listed in Table I. The MP2 perturbation correction consistently reduces the calculated values and brings them into closer agreement with experiment. Not surprisingly, the correlation effect is greater for the triply bonded species. A greater percentage, as well as absolute, reduction is found for the silicon-containing molecules relative to the corresponding hydrocarbons. At all levels of calculation, the silylidene structure is found to be substantially lower in energy than the classical triple bond. This is in agreement with previous calculations.

Even though the calculated hydrogenation energies are somewhat overestimated, it is reasonable to conclude from the values listed in Table I that the silicon-containing multiple bonds are thermodynamically less stable than their hydrocarbon analogues.

---

* North Dakota State University.

† Carnegie-Mellon University.

(1) M. S. Gordon, *Chem. Phys. Lett.*, **76**, 163 (1980).

(2) M. S. Gordon, *J. Am. Chem. Soc.*, **102**, 7419 (1980).

(3) M. S. Gordon, *Chem. Phys. Lett.*, **54**, 9 (1978).

(4) J.-C. Barthelat, G. Trinquier, and G. Bertrand, *J. Am. Chem. Soc.*, **101**, 3785 (1979).

(5) A. C. Hopkinson and M. H. Lien, *J. Chem. Soc., Chem. Commun.*, 107, (1980).

(6) J. N. Murrell, H. W. Kroto, and M. F. Guest, *Chem. Commun.*, 619 (1977).

(7) L. C. Snyder, 14th Organosilicon Symposium, March, 1980, Fort Worth, TX.

(8) J. A. Pople, J. S. Binkley, and R. Seeger, *Int. J. Quantum Chem., Symp.*, **10**, 1 (1976).

(9) J. S. Binkley, J. A. Pople, and W. J. Hehre, *J. Am. Chem. Soc.*, **102**, 939 (1980); M. S. Gordon, J. S. Binkley, J. A. Pople, W. J. Pietro, and W. J. Hehre, *ibid.*, submitted.

(10) P. C. Hariharan and J. A. Pople, Chem. *Phys. Lett.*, **16**, 217 (1972).

(11) (a) H. F. King and M. Dupuis, *J. Comput. Phys.*, **21**, 144 (1976). M. Dupuis and H. F. King, *Int. J. Quantum Chem.*, *II*, 613 (1977); *J. Chem. Phys.*, **68**, 3998 (1978). (b) J. S. Binkley, R. A. Whiteside, R. Krishnan, and R. Seeger, D. J. DeFrees, and H. B. Schlegel, S. Topiol, L. R. Kahn, and J. A. Pople, Quantum Chemistry Program Exchange, Indiana University, 1980.

(12) J. B. Collins, P. v. R. Schleyer, J. S. Binkley, and J. A. Pople, *J. Chem. Phys.*, **64**, 5142 (1976).

0002-7863/81/1503-2945\$01.25/0

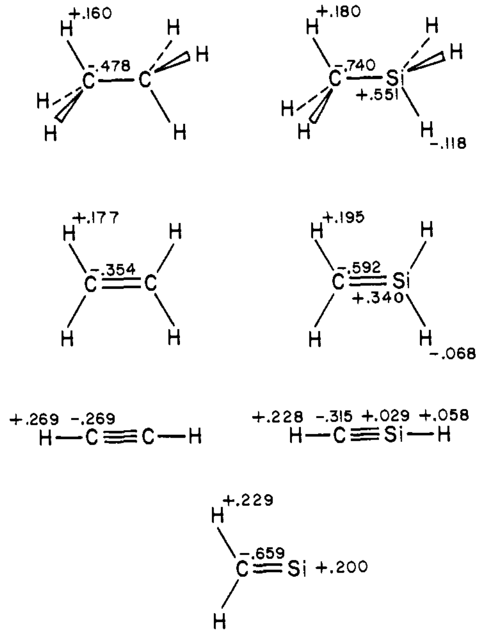

Figure 1. Net atomic charges (6-31G*//3-21G).

Table II. Geometries along the HC≡SiH → H_2C=Si Reaction Path[a]

α	R(CH)	R(CSi)	R(SiH)	β(HCSi)
180	1.055	1.590	1.448	180.00
160	1.058	1.602	1.453	167.03
140	1.062	1.632	1.466	157.49
120	1.065	1.677	1.486	159.33
100	1.067	1.723	1.512	167.93
88.6	1.067	1.732	1.528	173.70
80	1.068	1.730	1.550	180.10
60	1.065	1.689	1.643	185.50
40	1.062	1.676	1.922	163.13
21.27	1.080	1.730	2.491	123.19

[a] Bond lengths in Å, angles in deg. The molecule remains nearly planar throughout the reaction path. α = 21.27 corresponds to silylidene.

Table III. Effect of Geometry on Calculated Energy Differences[a]

	6-31G*//3-21G			6-31G*//6-31G*		
α	SCF	MP2	MP3	SCF	MP2	MP3
180	6.2	−5.2	1.0	6.1	−2.6	2.6
120	0.0	0.0	0.0	0.0	0.0	0.0
90	−2.7	9.7	5.5	−2.9	9.4	5.2

[a] See ref 14; energy differences in kcal/mol.

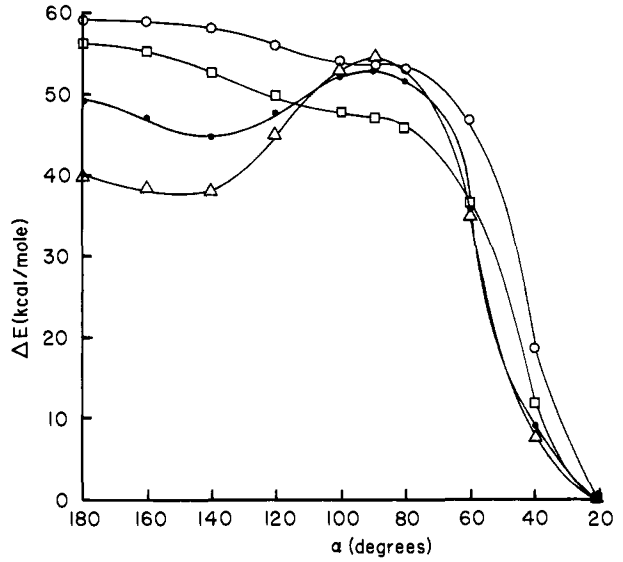

Figure 2. Energy (relative to silylidene) as a function of α. Note that α = 21° corresponds to silylidene and α = 180° corresponds to silaethyne. Key: ○, 3-21G//3-21G; □, 6-31G*//3-21G; △, 6-31G*//3-21G + MP2; ●, 6-31G*//3-21G + MP3.

An exception to this conclusion appears to occur for silylidene. The 6-31G* + MP2 energy for vinylidene published by Pople and co-workers[13] yields a hydrogenation energy of −97.2 kcal/mol for this molecule, about three times that of its silicon-containing counterpart.

The electron-density distributions (calculated at the 6-31G*//3-21G level) for the molecules of interest are displayed in Figure 1. As expected, in the hydrocarbons the electron density shifts from hydrogen to carbon as the amount of s character in the carbon hybrids increases. For the silicon-containing species, this is more difficult to follow since it is not immediately clear if the electron-density shifts are occurring between a heavy atom and its attached hydrogens or between the two heavy atoms themselves. A qualitative way of separating these possibilities is as follows. On going from methylsilane to silaethylene, assume that the +0.18 charge on the removed methyl hydrogen is added to the carbon and that the carbon gains 0.03 electron due to the greater positive charge on hydrogen in silaethylene. If this were the case, the net charge on carbon would be −0.590. The fact that this value is virtually identical with the actual calculated charge is evidence that the electron-density shift on carbon is essentially a C–H phenomenon similar to that in the hydrocarbons. A similar consideration predicts the charge on the silicon in silaethylene to be +0.333.

One can proceed in the same manner to estimate what the charges on carbon and silicon should be if no carbon–silicon density shift occurs on going from silaethylene to silaethyne. The result in this case is rather different. Here, the carbon in silaethyne should have a charge of −0.430 if the shifts are contained within the CH bonds, whereas the calculated charge on carbon is −0.315. A similar pair of numbers is found for silicon. This implies that removal of two hydrogens from silaethylene to form silaethyne results in a net shift of about 0.1 electron from carbon to silicon. Since, as has been noted previously,[1] silicon seems to prefer being a positive center, it is likely that this unusually small positive charge on Si in silaethyne contributes to its instability. Indeed, silaethyne is unusually unstable, even accounting for the lower stability of carbon–silicon multiple bonds, as may be verified by calculating the ratio of triple to double bond hydrogenation energies in Table I. Finally, note that the positive charge on silicon in silylidene is much larger than that in silaethyne. This is consistent with the greater stability of the former isomer.

The structures along the silaethyne–silylidene reaction path are presented in Table II, and the corresponding potential energy curves are displayed in Figure 2. It is clear from the table that the structural changes which occur do not correspond to a least motion pathway. In agreement with Hopkinson and Lien,[5] both basis sets at the SCF level predict silaethyne to rearrange to silylidene with no barrier, although the surface becomes rather flat at about α = 90°. The introduction of the second-order perturbation correction, however, introduces a barrier of more than 16 kcal/mol. The analogous hydrocarbon isomerization, acetylene → vinylidene, has been considered by Pople and co-workers[13] at the same levels of approximation. These authors find that the acetylene → vinylidene barrier increases by 2 kcal/mol when MP2 is added, whereas the vinylidene → acetylene barrier decreases by 16 kcal/mol. For the silicon system, the corresponding changes are +16 kcal/mol and −2 kcal/mol, so the effect of MP2 is rather different.

The calculations[13] on the acetylene–vinylidene surface revealed a substantial change in going from second-order (MP2) to third-order (MP3) perturbation corrections, so the surface rep-

---

(13) J. A. Pople, R. Krishnan, H. B. Schlegel, and J. S. Binkley, *Int. J. Quantum Chem.*, *14*, 545 (1978).

(14) For technical reasons a more recent version of the 6-31G* basis set (W. J. Hehre and J. A. Pople, to be published) has been used here. The SCF and MP2 curves in Figure 2 are virtually identical for the two basis sets.

resented in Table II was also followed with MP3.[14] As seen in Figure 2, this additional correction lowers the barrier to 8.5 kcal/mol. To investigate the effect of using 3-21G geometries, the structures at $\alpha = 180°$, 120°, and 90° were recalculated with the use of the 6-31G* basis set. As expected,[13] the main effect is to shorten the C–Si bond at all angles. The energy results are summarized in Table III. As before the SCF curve finds no barrier, while a barrier does appear at both MP2 and MP3 levels. The energy difference between $\alpha = 120°$ and $\alpha = 90°$ is only slightly reduced at both MP2 and MP3 (relative to Figure 2). Further, the addition of p functions on the hydrogens (6-31G**//6-31G*) has a very small effect at both the SCF and MP2 levels. Thus, it appears that there may be a significant barrier separating silaethyne and silylidene.

Since the perturbation correction corresponds to the addition of a large number of doubly excited configurations to the SCF wave function,[8] it is difficult to find a straightforward interpretation of the effect. A *qualitative* understanding may be obtained by simply carrying out a 2 × 2 CI, including the SCF configuration and the double excitation which removes a pair of electrons from the highest occupied orbital (HOMO) and places them in the lowest unoccupied orbital (LUMO). The latter orbital is one of two degenerate π^* MO's at $\alpha = 180$ and becomes a p_x antibonding orbital with a small mixing of s character as α decreases (the HOMO is the bonding counterpart). The effect of adding the second configuration at $\alpha = 140°$ and $\alpha = 88.6°$ is to change the energy difference ($E(\alpha = 88.6°) - E(\alpha = 140°)$) from −5.9 kcal/mol at the SCF(6-31G*) level to +6.1 kcal/mol. A further analysis reveals that the orbital energy of the LUMO is rather small (<0.1) throughout the surface and that the HOMO–LUMO splitting increases from $\alpha = 140°$ to $\alpha = 60°$. The small HOMO–LUMO splitting at all angles (about half that of acetylene) will give rise to unusually large interaction between the two configurations. Since the SCF surface is rather flat in the region from $\alpha = 140°$ to $\alpha = 80°$, this region may well be dominated by variations in the HOMO–LUMO interaction. A more quantitative analysis would require a study of all contributing configurations.

To summarize, the major findings of this work are as follows: (a) the carbon–silicon triple bond is particularly unstable in a thermodynamic sense, as is evidenced by the calculated hydrogenation energies and by the isomerization energy relative to silylidene. (b) At the highest level of computation, a slightly bent form of silaethyne is found to be separated from its more stable isomer by a small barrier. It should be recognized, however, that the height of the barrier might be altered by higher order effects or by a modification of the reaction path due to correlation effects.

Acknowledgment. This work was supported by National Science Foundation Grants No. CHE78-18070 and CHE77-09293 and by a generous allotment of computer time from the North Dakota State University Computer Center. One of us (M.S.G.) has benefitted from interactions with Professors R. D. Koob and P. Boudjouk during the course of this work.

Sensitivity of Polypeptide Conformation to Geometry. Theoretical Conformational Analysis of Oligomers of α-Aminoisobutyric Acid

Yvonne Paterson,[1a] Shirley M. Rumsey,[1a] Ettore Benedetti,[1b] George Némethy,[1a] and Harold A. Scheraga*[1a]

Contribution from the Baker Laboratory of Chemistry, Cornell University, Ithaca, New York 14853, and Istituto Chimico, Universitá di Napoli, 80134 Napoli, Italy.
Received October 10, 1980

Abstract: Empirical observations by other workers have suggested that peptides containing α-aminoisobutyric acid obligatorily adopt 3_{10}-helical forms in the crystal state. The reasons for this conformational preference have not been understood heretofore, and this question is addressed in the present study. The preferred conformations of *N*-acetyl-*N'*-methyl(α-aminoisobutyryl)$_n$amide (with $n = 1, 2, 3$) have been determined by empirical conformational energy calculations; minimum energy conformations were located by minimizing the energy with respect to all the dihedral angles of the molecule. The conformational space of the α-aminoisobutyric acid residue is sterically severely restricted and therefore sensitive to the covalent geometry assigned to this residue, in particular to the bond angles between the substituents on the C^α atom. Tetrahedral symmetrical geometry for these substituents favors the α-helical conformation for the α-aminoisobutyric acid residue (and di- and tripeptides thereof) whereas asymmetric geometry, derived from well-refined X-ray structures, gives the 3_{10} conformation as the preferred structure. Analysis of pairwise atomic interactions indicates that favorable backbone–backbone interactions lower the overall energy of the molecule in the 3_{10} conformation when the substitution on the C^α atom is asymmetric.

The wide occurrence of α-aminoisobutyric acid (abbreviated Aib) in microbial peptides, particularly in the peptaibophols,[2,3] has long been attributed to its role in constraining the peptide backbone, because of the two methyl substituents on the C^α atom. Recent experimental work has demonstrated unequivocally that the Aib residue in peptide crystals always occurs in the right- or left-handed 3_{10}-helical conformation;[4-12] this is in conflict with early theoretical studies[13-15] of the Aib residue, using confor-

---

[1] (a) Baker Laboratory of Chemistry, Cornell University. (b) Istituto Chimico, Università di Napoli.

[2] Pandey, R. C.; Meng, H.; Cook, J. C.; Rinehart, K. L. *J. Am. Chem. Soc.* **1977**, *99*, 5203–5205.

[3] Pandey, R. C.; Cook, J. C.; Rinehart, K. L. *J. Am. Chem. Soc.* **1977**, *99*, 5205–5206.

[4] Flippen, J. L.; Karle, I. L. *Biopolymers* **1976**, *15*, 1081–1092.

[5] Shamala, N.; Nagaraj, R.; Balaram, P. *Biochem. Biophys. Res. Comm.* **1977**, *79*, 292–298.

[6] Shamala, N.; Nagaraj, R.; Balaram, P. *J. Chem. Soc., Chem. Commun.* **1978**, 996–997.

[7] Aubry, A.; Protas, J.; Boussard, G.; Marraud, M.; Néel, J. *Biopolymers* **1978**, *17*, 1693–1711.

[8] Prasad, B. V. V.; Shamala, N.; Nagaraj, R.; Chandrasekaran, R.; Balaram, P. *Biopolymers* **1979**, *18*, 1635–1646.

[9] Nagaraj, R.; Shamala, N.; Balaram, P. *J. Am. Chem. Soc.* **1979**, *101*, 16–20.

0002-7863/81/1503-2947$01.25/0 © 1981 American Chemical Society