J. Am. Chem. Soc. **1984**, *106*, 603-609

Theoretical Study of the Relative Stabilities of C_2H_2 and Si_2H_2 Conformers[†]

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Received May 11, 1983

Abstract: The low-lying singlet and triplet conformations of C_2H_2 and Si_2H_2 have been studied theoretically by using ab initio electronic structure theory. The most stable conformation of Si_2H_2 is found to be a nonplanar bridged structure when polarization functions are included in the basis set. Electron-correlation effects, computed by using fourth-order Møller–Plesset perturbation theory, further stabilize this form relative to silasilene ($H_2Si{=}Si$) which is computed to be 11.3 kcal mol^{-1} less stable than bridged disilyne. There is an analogous nonplanar bridged conformation of C_2H_2 which was found to lie 72.1 kcal mol^{-1} above acetylene. No stable linear conformation of Si_2H_2 (analogous to acetylene) was found even when electron correlation was taken into account. For the Si_2H_2 compounds, inclusion of polarization functions in the basis set has a larger effect on stability ordering than does electron correlation.

I. Introduction

There is growing evidence from both theory and experiment that the unsaturated silicon hydrides, Si_2H_2 and Si_2H_4, exhibit chemical features that are quite dissimilar from the analogous carbon-containing compounds. This is not altogether surprising—rather simple qualitative arguments indicate that p-type atomic orbitals play a more important role than s orbitals in hybridization in silicon hydrides.[1] This is in contrast to carbon hydrides in which s and p functions are comparably balanced in the formation of sp-, sp^2, and sp^3-hybrid orbitals. As a result, certain chemical properties, particularly equlibrium geometries, can exhibit striking features in these compounds.

Unfortunately there are few experimental data for compounds that contain Si–Si multiple bonds. West et al.[2] and Boudjouk et al.[3] have reported the isolation and characterization of $(Mes)_2Si{=}Si(Mes)_2$ where Mes = mesitylene (2,4,6-trimethylphenyl). Masamune et al.[4] discovered a synthetic pathway to an analogous compound tetrakis(2,6-dimethylphenyl)disilene by first forming hexakis(2,6-dimethylphenyl)cyclotrisilane. These appear to be the only experimentally observed compounds that contain Si–Si double bonds. To date, there has been no direct experimental evidence concerning Si_2H_2. There is, however, considerable interest in these molecules; both Si_2H_4 and Si_2H_2 have been suggested as intermediates in the thermal decomposition of silane (SiH_4).[5-9]

Si_2H_4 has been the subject of several recent theoretical studies. Synder and Wasserman[10] used Hartree–Fock theory with a split-valence 4-31G basis set to determine equlibrium geometries and total energies of the most-stable singlet-state conformations of Si_2H_4. They found silylsilylene (H_3SiSiH) to be slightly more stable than disilene ($H_2Si{=}SiH_2$) and that disilene was nonplanar with a trans-bent conformation.

More recently, several theoretical studies of Si_2H_4 have appeared[11-14] that used more sophisticated methods than those employed by Synder and Wasserman. Poirier and Goddard[11] considered the low-lying electronic triplets in addition to singlets. They performed calculations at the Hartree–Fock level with split-valence basis sets which included polarization functions and determined electron-correlation corrections from configuration-interaction calculations carried out with smaller split-valence basis sets. Contrary to the findings of Synder and Wasserman, Poirier and Goddard concluded that planar disilene is the most stable form of Si_2H_4.

Lischka and Kohler[12,13] studied the singlets and triplets of Si_2H_4, C_2H_4, and $SiCH_4$ using split-valence plus polarization basis sets with electron-correlation effects determined with use of the coupled electron pair approximation (CEPA). This study also included harmonic frequency calculations at the Hartree–Fock level with a split-valence plus polarization basis set in order to properly characterize the stationary points on the Si_2H_4 potential energy surface. Their CEPA calculations with the largest basis set used indicate that disilene and silylsilylene are almost equally stable.

Krogh-Jespersen,[14] using third-order Møller-Plesset perturbation theory and split-valence plus polarization basis sets, systematically studied the relative stabilities of singlet Si_2H_4. He found that planar disilene is not a minimum on the potential surface and that trans-bent disilene is the most stable conformation of this compound when electron correlation is taken into account with a split-valence plus polarization basis set.

Disilyne, Si_2H_2, is the next smaller unsaturated silicon hydride that could exist as a singlet in its electronic ground state. Several possible conformations of this compound are shown in Figure 1. This molecule has been studied recently by Snyder et al.[15] and Ohno et al.[16] Synder et al. determined equilibrium geometries of five prototypical conformations using Hartree–Fock theory with a split-valence 4-31G basis set[17] which does not contain any polarization functions. The conformations they considered are a subset of those shown in Figure 1 and comprise bridged disilyne (**1**), silasilene (**2**), trans-bent disilyne (**4**), twisted disilyne (**5**), and linear disilyne (**6**). This level of theory predicts silasilene (**2**) to be the most stable species.

Using these geometries, Synder et al. included electron-correlation effects using perfect-pairing generalized valence-bond theory (PP-GVB)[18] with a smaller single-valence basis set in which the core electrons (1s to 2p of the silicon atoms) were replaced with the coreless Hartree-Fock (CHF) effective potential of Melius et al.[19,20] On the basis of these calculations, Snyder et

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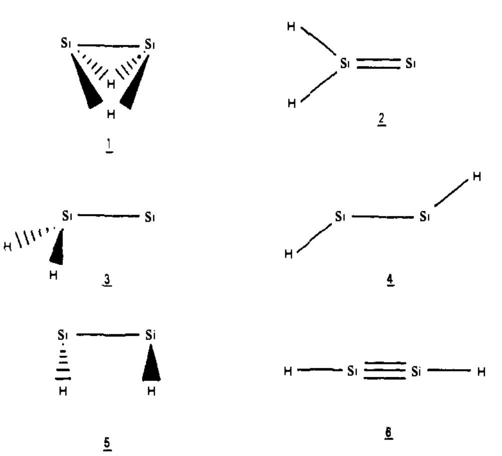

Figure 1. Si_2H_2 conformations: **1**, bridged disilyne (C_{2v}); **2**, silasilene (C_{2v}); **3**, bent silasilene (C_s); **4**, trans-bent disilyne (C_{2h}); **5**, twisted disilyne (C_2); and **6**, linear disilyne ($D_{\infty h}$).

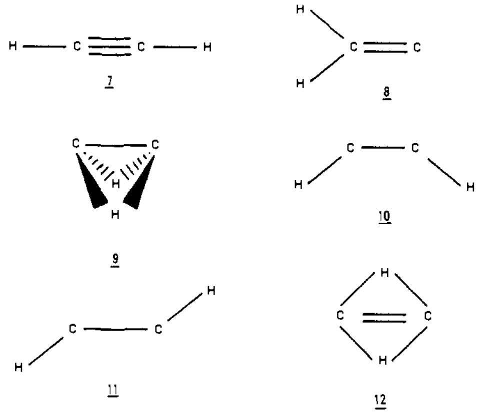

Figure 2. C_2H_2 conformations: **7**, acetylene ($D_{\infty h}$); **8**, vinylidene (C_{2v}); **9**, bridged acetylene (C_{2v}); **10**, cis-bent dimethyne (C_{2v}); **11**, trans-bent dimethyne (C_{2h}); and **12**, planar bridged acetylene (D_{2h}).

al. predicted that the most stable conformation of Si_2H_2 is silasilene; the least stable conformer was found to be linear Si_2H_2.

Following the work by Synder et al., Ohno et al.[16] compared linear and bent forms of Si_2H_2 with the corresponding C_2H_2 species using Hartree–Fock theory and the minimal STO-3G basis set. At this level of theory, they concluded that the equilibrium geometry of Si_2H_2 is twisted rather than linear.

These predictions are very different from the situation observed in first-row chemistry where acetylene, the analogue of linear disilyne, is clearly the most stable conformation of C_2H_2 and is thought to be ~42 kcal mol^{-1} more stable than vinylidene.[21] Earlier theoretical studies by Apeloig et al.[22], in search of dilithioacetylene, identified a planar bridged form of C_2H_2 similar to **1** (see structure **12** in Figure 2) that was considerably higher in energy relative to acetylene (~100 kcal mol^{-1}). In light of the possible technical importance of Si_2H_2 and its significant dissimilarities with respect to the analogous first-row compounds, it is of considerable interest to extend these calculations in an effort to further understand the chemistry of unsaturated silicon hydrides.

The aim of this paper is to study the singlet and triplet conformations of C_2H_2 and Si_2H_2 by using reliable ab initio methods. The only species in this set of molecules for which there are experimental data is acetylene. The previous studies of Si_2H_4 clearly indicate the importance of adequate basis sets and inclusion of electron-correlation effects. Therefore, the calculational approach in this study consists of using multiple-valence (double- and triple-ζ quality) basis sets that are augmented with polarization functions on both the heavy atoms (C and Si) and hydrogen along with treatment of electron-correlation effects by using Møller–Plesset perturbation theory carried out to fourth order.[23,24] This is in some respects preferable to the PP-GVB approach used by Snyder et al.[15] that involves rather arbitrary selection of pairs of orbitals that are correlated together. Furthremore, since the molecules involved are relatively small, the use of effective potentials is avoided.

The next section describes the computational methods employed. The third section presents the details of the equilibrium-geometry calculations along with a discussion of the relative energies of the various isomers of C_2H_2 and Si_2H_2. Finally, discussion is presented concerning the anomalous bonding observed in Si_2H_2.

II. Computational Methods

Equilibrium geometries at the Hartree–Fock level of theory were determined using a split-valence plus polarization basis set (6-31G**[25,26]). The restricted (RHF) formalism is Roothaan[27] was used for closed-shell species, and the unrestricted (UHF) method of Pople and Nesbet[28] was used for open-shell species. This level of theory is denoted HF/6-31G**. For each stoichiometry, optimizations were carried out with several assumed symmetry constraints. Upon completion of each geometry optimization, harmonic frequencies were calculated analytically.[29] These calculations determined the nature of a stationary point (minimum, saddle point) and produce zero-point-energy corrections for use in energetic comparisons.

Single-point calculations using these geometries were then carried out by using the larger 6-31++G** basis set[31] and fourth-order Møller–Plesset perturbation theory (MP4).[23,24] The 6-31++G** basis is comprised of the same basis functions as 6-31G** plus an additional set of valence functions on all atoms (i.e., s and p functions on carbon and silicon and an s function on hydrogen) and is therefore of triple-ζ plus polarization quality. This computational approach is referred to as MP4/6-31++G**//HF/6-31G** where the double slash separates the procedures used for final energy evaluation and geometry determination, respectively. Core electrons (carbon 1s; silicon 1s, 2s, and 2p) were "frozen" in the MP4 calculations. Fourth-order perturbation theory utilizes the second-order perturbed wave function[23,24] and therefore involves up to quadrupole substitutions out of the Hartree–Fock determinant.

Note that UHF wave functions are not necessarily eigenfunctions of the total spin operator S^2. In order to assess the degree of higher-multiplicity spin contamination, expectation values of this operator have been computed at the HF/6-31++G**//HF/6-31G** level for the open-shell molecules that were included in this study.

For several conformations of Si_2H_2 it was desirable to perform additional geometry optimizations in which different levels of theory were used. To facilitate comparisons with the work of Snyder et al.[15] several conformations of Si_2H_2 were optimized at the HF/6-31G level of theory. This level of theory is analogous to the HF/6-31G** method (defined above) except that all polarization functions have been omitted and is therefore close to the level of theory used by Snyder et al.[15] (When the notation defined in this paper is used, their method is referred to as HF/4-31G.)

Electron-correlation effects often have an important effect on equilibrium geometries. Therefore, further optimizations for selected conformations of Si_2H_2 were performed by using the MP2/6-31G* method. This consists of second-order Møller–Plesset perturbation theory[30] used with the 6-31G* basis set. This level of perturbation theory (MP2) is the lowest that incorporates electron-correlation effects. These calculations therefore serve to test the validity of geometries determined by using the HF/6-31G** method. The 6-31G* basis set is analogous to 6-31G** except that polarization functions have been omitted from the hydrogen atoms; polarization functions are retained on silicon. Geometry opti-

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Table I. HF/6-31G** Equilibrium Geometries, Total Energies, and Harmonic Frequencies for C_2H_2 Conformers

					harmonic frequencies	
conformer[a]	symmetry constraint	electronic state	geometrical parameter[b]	HF/6-31G** total energy[c]	symmetry of mode	value[d]
acetylene (7)	$D_{\infty h}$	$^1\Sigma_g^+$	r_{CC} 1.186[e]	−76.82184	Σ_g	2242
						3584
			r_{CH} 1.057[e]		Π_u	3696
						800
						878
vinylidene (**8**)	C_{2v}	$^1A_1$	r_{CC} 1.293	−76.76736	A_1	1369
						1849
			r_{CH} 1.078			3308
					B_1	924
			∠HCC 120.1		B_2	546
						3396
bridged acetylene (**9**)	C_{2v}	$^1A_1$	r_{CC} 1.285	−76.69658	A_1	1452
						1854
			r_{XH} 1.097			2451
					A_2	512
			∠HXH 99.8		B_1	2479
					B_2	330
cis-bent dimethyne (**10**)	C_{2v}	$^3B_2$	r_{CC} 1.316	−76.72416	A_1	913
						1785
			r_{CH} 1.080			3317
					A_2	946
			∠HCC 128.7		B_2	1179
						3278
triplet vinylidene (**8**)	C_{2v}	$^3B_2$	r_{CC} 1.342	−76.73811	A_1	1408
						1596
			r_{CH} 1.080			3242
					B_1	850
			∠HCC 121.3		B_2	1087
						3327
trans-bent dimethyne (**11**)	C_{2h}	^3B_u	r_{CC} 1.317	−76.71170	A_g	1211
						1772
			r_{CH} 1.075			3371
					A_u	1024
			∠HCC 130.8		B_u	842
						3351
trans-bent dimethyne (**11**)	C_{2h}	^3A_u	r_{CC} 1.359	−76.69306	A_g	1199
						1544
			r_{CH} 1.083			3285
					A_u	942
			∠HCC 123.0		B_u	1236 i
						3268
planar bridged acetylene (**12**)	D_{2h}	$^1A_{1g}$	r_{CC} 1.298	−76.62726	A_g	1548
						2642
			r_{XH} 1.004		B_{1u}	779 i
					B_{2u}	2882
					B_{3g}	2165
					B_{3u}	1741 i

[a] The name of each conformation is accompanied by the number of the corresponding structure in Figure 2. [b] Bond lengths in angstroms and bond angles in degrees. X denotes the midpoint of the C–C bond. [c] Total energies in hartree atomic units. [d] Harmonic frequencies in cm^{-1}. Imaginary frequencies denoted by i. Note that species with imaginary frequencies are not minima but rather are transition structures on the C_2H_2 energy hypersurface; see text. [e] Experimental values for acetylene (ref 32) are r_{CC} = 1.203 Å and r_{CH} = 1.061 Å.

mizations at the MP2/6-31G* level were performed by using analytical MP2 energy gradients computed by using the method of Pople et al.;[29] harmonic frequencies at this level of theory and determined by finite differencing of the analytically computed energy first derivatives. In these calculations no electrons were "frozen".

III. Results and Discussion

This section discusses aspects of the equilibrium geometries and relative energies of the various conformations of C_2H_2 and Si_2H_2 along with a comparison of the previous calculations by Snyder et al.[15] Since the analysis by Ohno et al.[16] was carried out with small basis sets and omitted electron correlation, no significant comparisons can be made between their results and those presented here.

C_2H_2 Conformers. Equilibrium geometries for the conformations of C_2H_2 are listed in Table I; energetic information is given in Table II. In both tables, each conformation is accompanied by its point-group symmetry and electronic state. Refer to Figure 2 for diagrams of the different conformations. Acetylene was found to be the most stable C_2H_2 species; this is the only molecule in this study that has been studied experimentally. The computed geometrical parameters of acetylene are in good agreement with the experimentally observed[32] values of r_{CC} = 1.203 Å and r_{CH} = 1.061 Å. This molecule has been the object of numerous other theoretical studies.[33]

The second lowest energy conformation of C_2H_2 is singlet vinylidene (**8**) which is 39.6 kcal mol^{-1} less stable than acetylene at the MP4/6-31++G**//HF/6-31G** level of theory. This

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Table II. C_2H_2 Energetic Results

			energies[c]			
conformer[a]	symmetry constraint	electronic state	zero point[b]	HF/6-31++G**// HF/6-31G**[d]	MP4/6-31++G**// HF/6-31G**[d]	rel[d]
acetylene (**7**)	$D_{\infty h}$	$^1\Sigma_g^+$	0.02934	−76.82727	−77.11287	0
vinylidene (**8**)	C_{2v}	$^1A_1$	0.02595	−76.77371	−77.04630	39.6
bridged acetylene (**9**)	C_{2v}	$^1A_1$	0.02068	−76.70326	−76.98937	72.1
cis-bent dimethyne (**10**)	C_{2v}	$^3B_2$	0.02601	−76.72876	−76.97475	84.6
triplet vinylidene (**8**)	C_{2v}	$^3B_2$	0.02622	−76.74160	−76.96526	90.7
trans-bent dimethyne (**11**)	C_{2h}	^3B_u	0.02636	−76.71703	−76.96137	93.2
trans-bent dimethyne (**11**)	C_{2h}	^3A_u	0.02332	−76.69959	−76.95184	97.3
planar bridged acetylene (**12**)	D_{2h}	$^1A_{1g}$	0.02104	−76.63586	−76.93384	107.1

[a] The number accompanying each conformation refers to the structures shown in Figure 2. [b] Zero-point energies, in hartree atomic units, computed from harmonic frequencies listed in Table I. [c] Total energies in hartree atomic units. [d] Relative energies in kcal mol^{-1} relative to acetylene. On the basis of combined MP4/6-31++G**//HF/6-31G** total energies and HF/6-31G** zero-point corrections.

molecule has been the topic of several recent theoretical studies[21] that have attempted to describe the energetics of the 1,2-hydrogen-migration reaction with acetylene. The level of theory used in this study closely parallels that used by Pople et al.,[21] who found vinylidene to lie 41.4 kcal mol^{-1} above acetylene with use of a somewhat smaller basis set.

Bridged acetylene (**9**) was found to be the next most stable conformation in this study. On the basis of an early study by Apeloig et al.,[22] geometry searches were initially conducted for the planar D_{2h} conformation (**12**). The planar species was found to be 107.1 kcal mol^{-1} less stable than acetylene. However, the spectrum of harmonic frequencies calculated at the HF/6-31G** level of theory (Table I) contains two imaginary frequencies, indicating that this species does not correspond to a stable conformation on the C_2H_2 hypersurface. Relaxation of the symmetry from D_{2h} to C_{2v} resulted in the bridged form (**9**) which was found to lie 72.1 kcal mol^{-1} above acetylene at the MP4/6-31++G**//HF/6-31G** level of theory.

The remaining conformations of C_2H_2 were all found to have triplet electronic states and are less stable than the bridged form (**9**). In energy order they are cis-bent dimethyne ($^3B_2$, 84.6 kcal mol^{-1} above acetylene), triplet vinylidene ($^3B_2$, 90.7 kcal mol^{-1} above acetylene), and trans-bent dimethyne (^3B_u, 93.2 kcal mol^{-1} above acetylene). A trans-bent ^3A_u conformation of dimethyne was also investigated and was found to be 97.3 kcal mol^{-1} less stable than acetylene. This species has one imaginary frequency (Table I) and is therefore not a minimum on the C_2H_2 hypersurface at the HF/6-31G** level of theory. Expectation values of S^2 for the triplets at the HF/6-31++G** level are 2.0045 (C_{2v}, $^3B_2$), 2.3977 (C_{2v}, $^3B_2$), 2.0052 (C_{2h}, ^3B_u), and 2.0200 (C_{2h}, ^3A_u), respectively, indicating only slight to moderate contamination from states of higher multiplicity.

Si_2H_2 Conformers. Equilibrium geometries at the HF/6-31G** level of theory and energetic results at the MP4/6-31++6**//HF/6-31G** level of theory for the Si_2H_2 species are given in Tables III and IV, respectively, along with symmetry constraints and electronic states (see also Figure 1). Theoretical geometries for selected conformations Si_2H_2 found by using the MP2/6-31G* and HF/6-31G methods are contained in Tables V and VI, respectively.

The most striking result is that at the MP4/6-31++G*//HF/6-31G** level of theory (Table IV) linear disilyne (the second-row analogue of acetylene) was found to be the *least* stable isomer of Si_2H_2. This result is consistent with the findings of Snyder et al.,[15] found with the use of the HF/4-31G theory. Furthermore, this species has an imaginary Π_u frequency at the HF/6-31G** level of theory indicating that it is not a minimum on Si_2H_2 hypersurface. These findings are essentially unmodified by geometry optimization at the MP2/6-31G* level of theory (Table V), where linear disilyne (**6**) still has an imaginary frequency and is therefore unstable with respect to relaxation of the $D_{\infty h}$ symmetry constraint.

At the MP4/6-31++G**//HF/6-31G** level of theory (Table IV), the most stable Si_2H_2 conformation was found to be the bridged form (**1**). This conformation is still found to be a minimum at the MP2/6-31G* level of theory (Table V). The stability ordering of bridged vs. the "vinylidene" form (**2**) obtained in the present study differs from the results of Snyder et al.,[15] who found the "vinylidene" form (**2**) to be 3.2 kcal mol^{-1} more stable at the HF/4-31G level of theory and 30.9 kcal mol^{-1} more stable at the PP-GVB level using a single-valence basis set with the core electrons replaced with an effective potential. At the HF/6-31G** level of theory, Table III, the bridged form is computed to be more stable than silasilene (**2**) by 3.9 kcal mol^{-1}. At the highest level considered here (i.e., extension of the basis set to the triple-ζ plus polarization level and inclusion of electron correlation at the MP4 level), bridged disilyne is found to be 11.3 kcal mol^{-1} more stable than silasilene.

The main improvements in the present calculations relative to those of snyder et al.[15] are the expansion of the basis set from single-ζ to triple-ζ, the inclusion of polarization functions on both the silicon and hydrogen atoms, and a significantly different treatment of electron correlation. Since the bridged form was already more stable than silasilene before expansion of the valence part of the basis set to triple-ζ (i.e., at the HF/6-31G** level, Table III), it was decided to see what effect the polarization functions had on the relative stabilities of these two conformations. Removal of the polarization functions (i.e., reduction of the basis set to 6-31G) and reoptimization of the geometries (Table VI) resulted in a reversal of the order of stability; at the HF/6-31G level of theory, silasilene is 9.2 kcal mol^{-1} more stable than bridged disilyne. Thus, inclusion of polarization functions (expansion from 6-31G to 6-31G**) stabilizes **1** relative to **2** by 13.1 kcal mol^{-1} at the Hartree–Fock level, and further expansion of the basis to 6-31++G** along with treatment of electron correlation at the MP4 level further stabilizes **1** relative to **2** by an additional 7.4 kcal mol^{-1}. Since basis set improvements and electron-correlation effects are both stabilizing structure **1** more than **2**, it is unlikely that further improvements in the calculations will reverse this feature.

The 6-31G basis set used here is very similar the 4-31G basis set used by Snyder et al.,[15] and the addition of polarization functions to their basis set should stabilize **1** relative to **2**. The large stabilization of the "vinylidene" form seen by Snyder et al. at the PP-GVB level probably results from the fact that the single-ζ basis set used in the PP-GVB calculations is so small that it can only include *left–right* correlations (which are clearly important in describing the mutiple bond in silasilene) while omitting radial (*in–out*) and angular correlations that are necessary for describing the bonding in bridged disilyne. These latter correlations require extension of the basis set to multiple ζ and inclusion of polarization functions, respectively.

A geometry search was carried out on the Si_2H_2 surface to locate the silicon analogue of structure **12** (i.e., planar bridged disilyne). This conformation was found to be 12.7 kcal mol^{-1} less stable then bridged disilyne (**1**) at the MP4/6-31++G**//HF/6-31G** level of theory. Furthermore, the B_{3u} vibrational frequency at the HF/6-31G** level of theory (Table III) is imaginary, indicating that this structure would collapse to structure **1** if the symmetry constraint was relaxed from D_{2h} to C_{2v}.

The C_{2h} (^1A_g) conformation listed in Table IV that lies 14.2 kcal mol^{-1} above bridged disilyne has an imaginary frequency at

Table III. HF/6-31G** Equilibrium Geometries, Total Energies, and Harmonic Frequencies for Si_2H_2 Conformers

					harmonic frequencies	
conformer[a]	symmetry constraint	electronic state	geometrical parameter[b]	HF/6-31g** total energy[c]	symmetry of mode	value[d]
bridged disilyne (**1**)	C_{2v}	$^1A_1$	r_{SiSi} 2.181	−578.89134	A_1	600
						1069
			r_{XH} 1.276			1716
					A_2	972
			$\angle$HXH 102.2		B_1	1631
					B_2	1168
planar bridged disilyne	D_{2h}	$^1A_{1g}$	r_{SiSi} 2.346	−578.85866	A_g	504
						1917
			r_{SiX} 1.067		B_{1u}	1713
					B_{2u}	1632
					B_{3g}	1823
					B_{3u}	924 i
silasilene (**2**)	C_{2v}	$^1A_1$	r_{SiSi} 2.187	−578.88519	A_1	579
						986
			r_{SiH} 1.475			2356
					B_1	428
			$\angle$HSiSi 123.4		B_2	357
						2374
trans-bent disilyne (4)	C_{2h}	^1A_g	r_{SiSi} 2.083	−578.85288	A_g	550
						665
			r_{SiH} 1.478			2350
					A_u	360 i
			$\angle$HSiSi 127.5		B_u	42
						2351
bent silasilene (3)	C_s	$^3A''$	r_{SiSi} 2.300	−578.89795	A'	261
						479
			r_{SiH} 1.479			1032
						2337
			$\angle$YSiSi 159.8		A''	488
			$\angle$HSiH 108.2			2345
twisted disilyne (5)	C_2	^3B	r_{SiSi} 2.281	−578.86738	A	363
						444
			r_{SiH} 1.499			606
						2236
			$\angle$HSiSi 106.8		B	572
			γHSiSiH 44.3			2227
linear disilyne (6)	$D_{\infty h}$	$^1\Sigma_g^+$	r_{SiSi} 1.942	−578.82677	Σ_g	833
						2489
			r_{SiH} 1.451			2494
					Π_u	550 i
						522

[a] The name of each conformation is accompanied by the number of the corresponding structure in Figure 1. [b] Bond lengths in angstroms and bond angles in degrees. X denotes the midpoint of the Si–Si bond; Y is the common point on the bisector of the HSiH angle and the line connecting the two hydrogen atoms; γ denotes dihedral angle. [c] Total energies in hartree atomic units. [d] Harmonic frequencies in cm^{-1}. Imaginary frequencies denoted by i. Note that species with imaginary frequencies are not minima but rather are transition structures on the Si_2H_2 energy hypersurface; see text.

Table IV. Si_2H_2 Energetic Results

			energies			
conformer[a]	symmetry constraint	electronic state	zero point[b]	HF/6-31++G**// HF/6-31G**[c]	MP4/6-31++G**// HF/6-31G**[c]	rel[d]
bridged disilyne (1)	C_{2v}	$^1A_1$	0.01630	−578.89336	−579.10795	0
silasilene (2)	C_{2v}	$^1A_1$	0.01613	−578.88656	−579.08972	11.3
planar bridged disilyne	D_{2h}	$^1A_{1g}$	0.01729	−578.85995	−579.08864	12.7
trans-bent disilyne (4)	C_{2h}	^1A_g	0.01357	−578.85401	−579.08256	14.2
bent silasilene (3)	C_s	$^3A''$	0.01582	−578.89940	−579.07241	22.0
twisted disilyne (5)	C_2	^3B	0.01469	−578.86879	−579.05522	32.1
linear disilyne (6)	$D_{\infty h}$	$^1\Sigma_g^+$	0.01563	−578.82774	−579.04349	40.0

[a] The number accompanying each conformation refers to the structures shown in Figure 1. [b] Zero-point energies, in hartree atomic units, computed from harmonic frequencies listed in Table II. [c] Total energies in hartree atomic units. [d] Relative energies in kcal mol^{-1} relative to bridged disilyne. On the basis of combined MP4/6-31++G**//HF/6-31G** total energies and HF/6-31G** zero-point corrections.

the HF/6-31G** level, indicating that it is not a minimum on the Si_2H_2 hypersurface. Relaxation of the C_{2h} symmetry constraint results in collapse of this structure to the bridged form (**1**).

A geometry search was also carried out for singlet twisted Si_2H_2 (**5**) since Snyder et al.[15] reported such a structure. At the HF/6-31G** level of theory no such conformation appears to exist; every trial geometry collapsed to the bridged form (**1**). To further understand this, a geometry search was carried out by using the 6-31G basis set (Table VI). At this lower level of theory a stable minimum was found which is interpreted to be an artifact of the limited basis set (i.e., omission of polarization functions).

The next most stable conformation of Si_2H_2 is the C_s (^3A) species (**3**) which was found to be 22.0 kcal mol^{-1} less stable than bridged disilyne at the MP4/6-31++G**//HF/6-31G** level

Table V. MP2/6-31G* Equilibrium Geometries, Total Energies, and Harmonic Frequencies for Si_2H_2 Conformers

					harmonic frequencies	
conformer[a]	symmetry constraint	electronic state	geometrical parameter[b]	MP2/6-31g* total energy[c]	symmetry of mode	value[d]
bridged disilyne (**1**)	C_{2v}	$^1A_1$	r_{SiSi} 2.202	−579.06549	A_1	547
						1216
			r_{XH} 1.253			1721
					A_2	999
			∠HXH 104.5		B_1	1628
					B_2	1277
linear disilyne (**6**)	$D_{\infty h}$	$^1\Sigma_g^+$	r_{SiSi} 1.987	−579.01301	Σ_g	735
						2405
			r_{SiH} 1.464			2409
					Π_u	590 i
						410

[a] The name of each conformation is accompanied by the number of the corresponding structure in Figure 1. [b] Bond lengths in angstroms and bond angles in degrees. X denotes the midpoint of the Si-Si bond. [c] Total energies in hartree atomic units. [d] Harmonic frequencies in cm^{-1}. Imaginary frequencies denoted by i. Note that species with imaginary frequencies are not minima but rather are transition structures on the Si_2H_2 energy hypersurface; see text.

Table VI. HF/6-31G Equilibrium Geometries, Total Energies, and Harmonic Frequencies for Si_2H_2 Conformers

					harmonic frequencies	
conformer[a]	symmetry constraint	electronic state	geometrical parameter[b]	HF/6-31g total energy[c]	symmetry of mode	value[d]
bridged disilyne (**1**)	C_{2v}	$^1A_1$	r_{SiSi} 2.299	−578.81984	A_1	506
						1033
			r_{XH} 1.319			1549
					A_2	581
			∠HXH 101.1		B_1	1424
					B_2	875
silasilene (**2**)	C_{2v}	$^1A_1$	r_{SiSi} 2.314	−578.83447	A_1	542
						921
			r_{SiH} 1.490			2270
					B_1	377
			∠HSiSi 123.4		B_2	333
						2298
twisted disilyne (**5**)	C_2	^1A	r_{SiSi} 2.426	−578.82011	A	319
						361
			r_{SiH} 1.542			543
						2046
			∠HSiSi 93.9		B	364
			γHSiSiH 91.6			2041

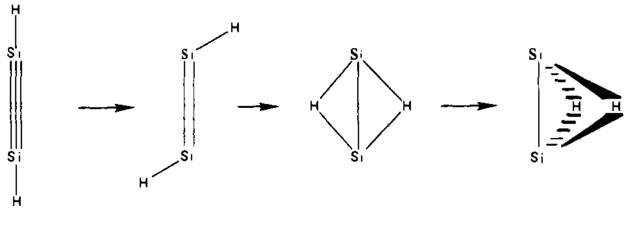
[a] The name of each conformation is accompanied by the number of the corresponding structure in Figure 1. [b] Bond lengths in angstroms and bond angles in degrees. X denotes the midpoint of the Si-Si bond. γ denotes dihedral angle. [c] Total energies in hartree atomic units.

of theory. The expectation value of S^2 for this molecule is 2.1114 at the HF/6-31++G**//HF/6-31G** level, indicating only slight contamination of the UHF wave function. This species is acutally 4 kcal mol^{-1} *more* stable than bridged disilyne at the Hartree–Fock level. This incorrect energy ordering, prior to inclusion of electron correlation, is not surprising and results from the fact that relative to closed-shell systems unrestricted Hartree–Fock wave functions for molecules involving open shells allow partial correlation of the motions of electrons of opposite spin.

The least-stable conformation found that corresponds to a minimum on the Si_2H_2 hypersurface was the C_2 (^3B) form (**5**). This species is 32.1 kcal mol^{-1} less stable than bridged disilyne (**1**) and its UHF wave function contains negligible higher-multiplicity contamination ($\langle S^2 \rangle = 2.0493$).

Si_2H_2 Bonding. In order to understand the anomalous bonding in Si_2H_2 it is useful to consider the sequence shown in Figure 3 in which the unstable linear conformer (**6**) is first distorted into trans-bent disilyne (**4**) followed by reduction in the HSiSi bond angles leading to the planar bridged species (**1a**) which is then folded along the Si–Si bond resulting in the minimum energy conformation **1**.

In the linear form **6**, the bonding formally involves sp hybridization between the silicon 3s and $3p_z$ orbitals. However, unlike carbon, the silicon valence s and p orbitals have disimilar orbital energies and spatial distributions. The resulting triple bond in **6** has strong overlap between the silicon valence s functions leading to a relatively short Si–Si bond in which the π orbitals are spatially crowded. Consequently, sp hybridization in this molecule is not energetically favorable.



6 4 1a 1

Figure 3. Stepwise distortion of linear disilyne (**6**) into the nonplanar bridged species (**1**).

Reduction of the symmetry from $D_{\infty h}$ to C_{2h} effectively redirects the s-orbital contribution into the Si–H bonds, resulting in less overlap betwen the silicon valence s orbitals. This permits a lengthening of the Si–Si bond from 1.942 to 2.083 Å, resulting in less repulsion in the remaining π orbital. This is accompanied by a significant increase in stabilization of 25.8 kcal mol^{-1} at the MP4/6-31++G**//HF/6-31G** level of theory.

Further reduction in the HSiSi bond angles, leading to the planar bridged conformation, does not produce significant additional stabilization relative to **4**. In fact, constraining the hydrogens to lie perpendicular to the Si-Si bond causes the Si-Si bond distance to increase to 2.346 Å, presumably due to repulsion between the hydrogen and silicon valence s orbitals.

Folding along the Si-Si bond, which results in structure **1**, reduces this repulsion, leading to a Si-Si bond distance of 2.181 Å. In this conformation the π-like orbitals (π_x and π_y if the Si-Si bond is oriented along the *z* axis) simultaneously serve in Si-Si and Si-H bonding.

The stepwise distortion from structure **6** to **1** is accompanied by an interesting change in the energies of the π orbitals. In structure **6** the highest occupied orbitals are π_x and π_y. This ordering is preserved in structure **4** although there is some participation of one of the π orbitals in bonding with the hydrogens. Further distortion to the planar bridged conformation results in significant stabilization of the π orbital that is in the plane of molecule (i.e., involved in bonding with the hydrogens). Distortion from D_{2h} to C_{2v} is accompanied by further stabilization of the remaining π orbital. When viewed in this manner, the anomalous bonding is bridged Si_2H_2 results from a drive toward better participation of the silicon valence p orbitals in π-like bonding.

IV. Conclusions

Clearly the Si_2H_2 hypersurface exhibits unusual characteristics. The absence of a stable linear form of disylyne is a striking feature and indicates that silicon is unwilling to participate in triple bonds. The span of relative energies for the stable Si_2H_2 conformations is much smaller than that of the C_2H_2 species (32.1 kcal mol^{-1} vs. 97.3 kcal mol^{-1}).

These calculations at the MP4/6-31++G**//HF/6-31G** level of theory suggest that the ground state of Si_2H_2 is the bridged form (**1**). Both the C_2H_2 and Si_2H_2 molecular systems were found to possess stable "vinylidene" (**2**, **8**) and bridged (**1**, **9**) conformations. With respect to the Si_2H_2 species, determination of the geometry using the electron correlated MP2/6-31G** approach does not modify these conclusions; linear $D_{\infty h}$ disilyne corresponds to a transition structure while bridged disilyne was found to be a minimum on the Si_2H_2 potential surface. The bridged form of C_2H_2 was found to exist although it is significantly less stable relative to acetylene than is vinylidene.

Several stable conformations with triplet electronic states exist on both the C_2H_2 and Si_2H_2 hypersurfaces. In the case of the C_2H_2 species there is a clear preference for planar structures while all the Si_2H_2 triplets were found to be nonplanar.

On the basis of comparisons with the calculations performed by Snyder et al.[15] it is clear that polarization functions are required in describing compounds such as these. The energy orderings predicted for the Si_2H_2 singlets are unaltered by inclusion of electron-correlation effects provided that the bais set contains polarization functions. This indicates that an adquate basis set is essential in obtaining reliable relative energies.

Registry No. **2**, 87970-40-9; **6**, 36835-58-2; **7**, 74-86-2; **8**, 2143-69-3.

Theoretical Study of Methylsilanone and Five of Its Isomers

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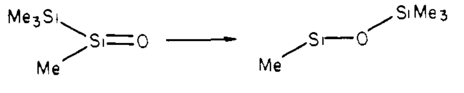
Abstract: By use of 3-21G SCF geometries and relative energies from MP3/6-31G* wave functions, methylsilanone has been found to be the most stable of the six isomers investigated. The relative stabilities of methylsilanone and silylformaldehyde are rationalized by the metathesis reaction $H_2SiO + C_2H_4 \rightarrow H_2CO + H_2CSiH_4$. This reaction is used to suggest that the C=O bond is about 10 kcal/mol stronger than Si=O.

Introduction

There has recently been considerable experimental[1-7] and theoretical[8] interest in silene to silylene rearrangements. Recently, Barton and co-workers[9] investigated the analogous silanone rearrangement



(1)

in which a Si=O double bond rearranges to the corresponding silylene. Based on their experimental evidence, the authors concluded that reaction 1 does not readily occur. In addition, it has been postulated[1] that a silene and a ketone may undergo a metathesis reaction

$$R_2Si{=}CR_2 + R_2C{=}O \rightarrow R_2Si{=}O + R_2C{=}CR_2 \quad (2)$$

to form a silanone and the corresponding alkene.

Reactions 1 and 2 suggest that it would be interesting to investigate the relative energies of the two isomers in (1) as well as the isomeric substituted formaldehyde and hydroxy-substituted silenes. Moreover, a reliable calculation of the energy difference in (2) will provide an estimate of the energy difference beteen the Si=O and Si=C bonds. To minimize the computational effort, the present work presents calculations on $CH_3SiH{=}O$ and five of its isomers.

Computational Methodology

Except for tests with larger basis sets for H_2SiO, all geometries were calculated by use of the 3-21G basis set[10] and the Schlegel

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