electronic origin is the most intense band of the complete spectrum. The structural changes are therefore smaller than the elongation of the classical harmonic oscillator at the zero-point energy, otherwise the intensity would initially increase with increasing quantum number. The electronic ground state also has the same symmetry and almost the identical geometry as the electronic excited state. For the latter, only the delocalized structure is applicable, and hence this structure must also be assigned to the ground state.

Experimental Section

MA was synthesized following the method of Vogel and Roth[8] and purified by distillation. The ultracold supersonic jet was produced by the expansion of a mixture of MA (1.3 mbar) along with the helium carrier (2 bar) through a pulsed nozzle of 0.5 mm diameter. A dye laser pumped by an excimer laser was used for fluorescence excitation, and a second dye laser/excimer laser pair was used for the double-resonance measurements. The laser bandwidth (FWHM) limited resolution to 0.2 cm^{-1} in the survey spectra; for the measurement of the rotational structures a Fabry–Perot interferometer inside the laser cavity improved the resolution to 0.1 cm^{-1}.

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Silynes ($\mathrm{RC{\equiv}SiR'}$) and Disilynes ($\mathrm{RSi{\equiv}SiR'}$): Why Are Less Bonds Worth Energetically More?**

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*Dedicated to Professor Zvi Rappoport
on the occasion of his 65th birthday*

Since the first isolation in 1981 of stable silaethylene[1] and disilene[2] a variety of new compounds containing doubly bonded silicon have been synthesized and their chemistry explored.[3] The next challenge has become the syntheses of compounds in which silicon has a triple bond.[4] Until recently $\mathrm{HSi{\equiv}N}$ was the only known silicon species with a triple bond, and was prepared by matrix isolation and identified by UV and infrared (IR) spectroscopy.[5a] Other attempts to isolate $\mathrm{RSi{\equiv}N}$ resulted in the isomeric RNSi species.[5b–g] While the formation of transients of the form $\mathrm{RSi{\equiv}SiR}$ (R = Me[6a] and $\mathrm{Tip_2C_6H_3}$,[6b] (Tip = 2,4,6-triisopropyphenyl)) was suggested, no conclusive evidence has been presented to support these assignments. Only recently has the existence of stable $\mathrm{FSi{\equiv}CH}$ and $\mathrm{ClSi{\equiv}CH}$, under gas-phase conditions, been demonstrated.[7] This successful assignment followed previous theoretical predictions.[8] The computational studies[7–9] have shown, however, that $\mathrm{HSi{\equiv}CH}$ and $\mathrm{HSi{\equiv}SiH}$ possess a *trans*-bent geometry (Figure 1, **1B** and **2B**) in contrast to the linear geometry of acetylene (**3**). Moreover, the linear isomers **1L** and **2L** are not even minima on the potential-energy surface (substituted silynes and disilynes behave likewise[7, 8, 9d]). *Trans*-bending appears also in analogous $\mathrm{E{\equiv}E}$ species (E = Ga, Ge, Sn, Pb) which are formally triply bonded,[10] and it seems to be a characteristic feature of multiple bonding in higher-row compounds. The inherent preference for bending raises fundamental questions about the nature of CSi or SiSi bonding.[11] Is it truly a triple bond such as $\mathrm{C{\equiv}C}$? What is the

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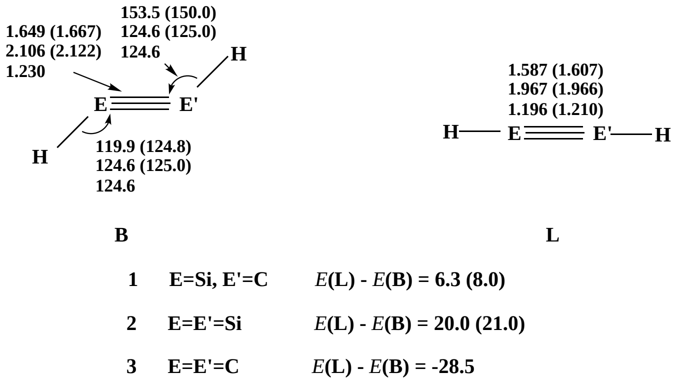

Figure 1. Optimized structures of bent (**B**) and linear (**L**) silyne (**1**), disilyne (**2**), and acetylene (**3**). Bond lengths [Å], angles [°] calculated at B3LYP/6-311G* are given in each case in the order **1**–**3** from top to bottom (CCSD(T)/cc-pVTZ values in parentheses) and the relative energies [kcal mol^{-1}] at the same computational levels.

effect of *trans*-bending on the bond energies? Why do these molecules prefer to be bent while acetylene remains linear?

Herein we address these questions by using valence bond (VB) computations. The VB analysis shows that approximately 2.5 bonds connect the heavy atoms in *trans*-bent HSiCH (**1B**) and HSiSiH (**2B**). But these 2.5 bonds are stronger than the triple bonds in linear HSi≡CH (**1L**) and HSi≡SiH (**2L**) as a result of a remarkable *strengthening* upon *bending* of the σ(C–Si) and σ(Si–Si) bonds, respectively.

Two complementary VB approaches[12] were used. The first is the spin coupled (SC) method,[12a, 13] which utilizes semi-localized atomic orbitals (AOs). As such, the ionic character of the electron-pair bond is embedded in a formally covalent SC wavefunction.[14, 15] This method provides the indices to quantify the number of bonds in the CSi and SiSi moieties.[13] The conclusions from the SC method can be compared with other bond indices.[16] For each of the target molecules, we treated as active the 10 valence electrons, with simultaneous relaxation of the inactive orbitals that accommodate the core electrons.

The second VB approach enables the determination of the in situ π-bond energies.[17] The essence of the method is illustrated in Figure 2. In the **II** state, called quasiclassical (QC), the two p_π electrons of the π bond are unpaired (and maintain opposite spins) so that their net interaction is zero.[17] The energy difference of state **II**, relative to the ground state **I** (determined by a normal VB calculation), gives the in situ π-bond energy (D_π) that does not involve geometric reorganization of the dissociated fragments. Similarly in a case of a triple bond, we can unpair two π bonds and obtain directly the total π-bond energy ($D_{2\pi}$ in Figure 2b). These calculations were carried out with the VB package TURTLE.[12b, 17, 18]

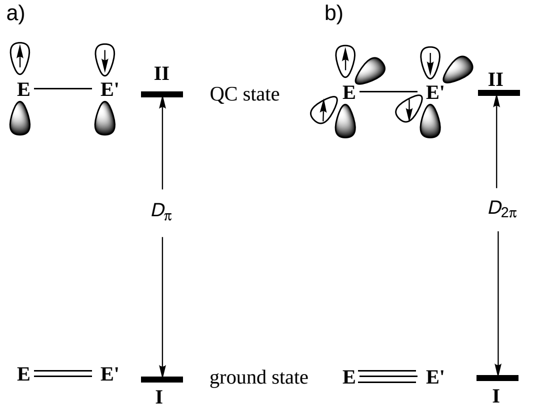

Figure 2. Definition of in situ π-bond energy based on the quasiclassical (QC) state reference a) for one π bond and b) for two π bonds.

Table 1 shows the SC bond indices for the six target species alongside the NRT[16a–c] and Wiberg[16d] bond orders. The SC indices are itemized for the three bonds between the heavy atoms, that is, a σ bond (C–Si or Si–Si or C–C), a pseudo π bond in the molecular plane of the bent isomer (π_{in}) and a π bond which is perpendicular to the molecular plane (π_{out}). The first SC index $S_{i,j}$, gives the orbital overlap of the hybrids or AOs which constitute the respective bond. The second index P_s(i,j) is a measure of the extent of singlet coupling of the electrons in the bond.[13] The P_s(i,j) index is −0.75 for a pure singlet-coupled pair, +0.25 for a pure triplet, and zero for an uncoupled situation (deviations from −0.75 are a result of the involvement of spin coupling other than perfect pairing).[13] By comparison with the data for acetylene (**3L**), it is seen (Table 1) that the three E–E′ bonds are essentially singlet coupled, in both linear and *trans*-bent isomers. However, the orbital overlap index $S_{i,j}$ shows that the *trans*-bending weakens the overlap of the π_{in} bond significantly, which reduces it to ≤35–45% of its value in the linear isomer. Thus, the SC overlaps reveal that *trans*-bending reduces the C≡Si, Si≡Si, and C≡C multiple bonding from the formal three. According to calculated NRT and Wiberg bond orders, the bond order for the *trans*-bent isomers **1B**–**2B** is 2.5–2.6 (Table 1). Unlike the SC results, the NRT and Wiberg indices for **3L** and **3B** seem oddly equal. However, for **1** and **2**, all the bond-indices methods lead to the same conclusion of π-bond weakening because of bending.

Table 1. Bond-order indices for HCSiH (**1**), HSiSiH (**2**), and HCCH (**3**) in the linear (**L**) and *trans*-bent (**B**) isomers.

	SC calculations[a] $S_{i,j}$ [P_s(i,j)]			DFT calculations[b] bond orders	
	σ	π_{in}	π_{out}	NRT	Wiberg
1L	0.776 [−0.609]	0.607 [−0.599]	0.607 [−0.599]	2.9	2.8
1B	0.764 [−0.650]	0.207 [−0.635]	0.592 [−0.589]	2.6	2.5
2L	0.817 [−0.548]	0.620 [−0.572]	0.620 [−0.572]	2.9	3.0
2B	0.803 [−0.619]	0.277 [−0.577]	0.574 [−0.598]	2.6	2.6
3L	0.849 [−0.631]	0.688 [−0.617]	0.688 [−0.617]	2.9	3.0
3B	0.789 [−0.654]	0.264 [−0.641]	0.671 [−0.601]	2.9	3.0

[a] Using a cc-pVTZ basis set. [b] B3LYP/6-31G**.

Why should **1** and **2** undergo *trans*-bending if this causes reduction of the CSi and SiSi bonding? The density functional calculations (DFT) and CCSD(T)/cc-pVTZ,[19] as well as the SC calculations show that despite the reduction in π bonding, *trans*-bending results in a significant energy lowering, for example, 8.0 kcal mol^{-1} for **1B** and 21.0 kcal mol^{-1} for **2B** (Figure 1). The solution to this puzzle is revealed by the in situ bond energies[17] given in Table 2 as well as by the behavior of the QC state that represents the σ frame in Figure 3.

Table 2. In situ bond energies for the linear and *trans*-bent isomers of HCSiH (**1**), HSiSiH (**2**), and HCCH (**3**) in the linear (**L**) and *trans*-bent (**B**) isomers.[a]

		Bond energies [kcal mol^{-1}]					
		HCSiH		HSiSiH		HCCH	
Entry	Type	**1L**	**1B**	**2L**	**2B**	**3L**	**3B**[b]
1	$D(\pi_{out})$	57.7	556.5	545.5	534.0	88.2	574.1
2	$D(\pi_{in})$	557.7	~35[c]	545.5	~27[c]	88.2	~44[c]
3	$D_{2\pi}$	~105[c]	~71[c]	~80[c]	~56[c]	169.8	~110[c]
4	ΔE_σ[d]	−42.1		−53.0		−33.9	

[a] Calculated using the VB procedure described in ref. [17] with the 6-311G* basis set. The $D(\pi_{out})$ values are calculated with the BOVB method.[18] [b] The H-C-C angle was fixed at 124.6° (as in **2B**) and all other geometrical parameters were optimized. [c] These are estimated BOVB bond energies which were calculated by adding dynamic correlation increments obtained for the out-of-plane π bonds. For these cases BOVB calculations are too CPU-time demanding. [d] $\Delta E_\sigma = E_\sigma(\mathbf{B}) - E_\sigma(\mathbf{L})$. Obtained by comparing the total energy of the corresponding σ frames with all the π electrons uncoupled (Figure 3).

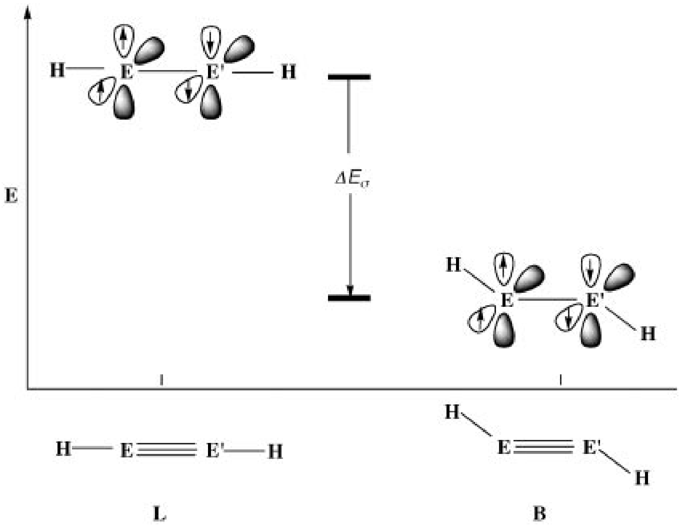

Figure 3. Representation of the stabilization of the σ frame of HE≡E′H upon *trans* distortion. The σ frame is represented by the QC state (see Figure 2).

Entries 1 and 2 in Table 2 show the individual π-bond energies determined by unpairing one bond at a time. It is seen that the in-plane pseudo π bond in the *trans*-bent isomer (**1B** and **2B**) is considerably weaker than the out-of-plane π bond. The $D_{2\pi}$ values (entry 3) obtained by unpairing simultaneously the two π bonds, also show that the total π bonding is weakened by 24–34 kcal mol^{-1} by *trans*-bending for both **1** and **2**. The same conclusion applies also to acetylene (**3**) the total π-bonding, $D_{2\pi}$, of which is weakened by 60 kcal mol^{-1} upon bending.

The behavior of the σ frame upon bending can be appreciated by inspection of Figure 3 and entry 4 in Table 2. Thus, as seen in Figure 3, the σ frame obtained by unpairing the two π bonds (the QC state of Figure 2b) is stabilized by the distortion of the linear frame. Entry 4 in Table 2 shows that these stabilization energies; the ΔE_σ values for **1**–**3**, are significant, 33.9–53.0 kcal mol^{-1}.[20] All the σ frames, including that of acetylene (**3**), prefer the bent structure, which strengthens σ bonding. This σ-bond strengthening[20] overrides the π-bond weakening in **1** and **2** and, therefore, the two molecules undergo *trans*-bending. In contrast, for acetylene (**3**) the π-bond weakening exceeds the σ-bond strengthening by a significant amount and the molecule remains linear.

What are the roots of the σ-bond strengthening? These appear to be a mix of a few effects:

a) The SC calculations show that in addition to the classical bond-pairing interactions, there are a variety of other spin-coupling modes[21] which involve interactions between the hybrids of π_{in} and those of all other σ bonds in the molecule. The net effect of these hyperconjugative interactions is some backbonding from E (E = Si, C) into the Si–H (or C–H) bond. To estimate this "backbonding" effect ($\Delta E_{backbond}$), the SC wavefunction was restricted to the perfectly paired (PP) structure. The SC energy of the PP structure was 7.4 and 7.0 kcal mol^{-1} higher than the full SC energy for HCSiH and HSiSiH, respectively. These increments account for only part of the full σ-bond strengthening effect in entry 4 of Table 2.
b) The second factor is caused by bond-length relaxation. Thus, the bond distance between the heavy atoms is too short in the linear structures for an optimal σ bond. The *trans*-bending lengthens the distance between the heavy atoms (Figure 1) and consequently the σ bond is strengthened. In **3** the bond lengthening confers 10.3 kcal mol^{-1} of σ-bond strengthening,[22] which is about one third of the entire effect (in entry 4 of Table 2). For **1** and **2**, the effects of bond-length relaxation are 8.2 and 9.3 kcal mol^{-1}. Clearly, the bond-length relaxation does not account for the entire effect. What remains from the total ΔE_σ in Table 2, appears to be associated with the increase of s-orbital participation in bonding through rehybridization caused by the *trans*-bending distortion.[23]

Thus, by itself, the σ frame is *more* stable in the *trans*-bent geometry, but this comes at the expense of π-bond weakening. The final geometry of HE≡E′H is then a result of delicate interplay between the opposing effects of σ and π bonding. When the π bonding becomes very strong as in acetylene **3**, it overrides the σ frame and leads to a linear molecule. When π bonding gets weaker as in **1** or **2**, the σ frame overrides and the molecule adopts a *trans*-bent geometry with an extra strength in the σ frame. This σ–π interplay is reminiscent of the benzene story.[24]

In summary, the CSi and SiSi bonding in the bent structures is formally approximately 2.5 bonds. The propensity for *trans* bending arises from the remarkable *strengthening* upon *bending* of the σ(C–Si) and σ(Si–Si) bonds. Thus, HCSiH and HSiSiH demonstrate that "less bonds pay more" when the smaller number of bonds undergo significant strengthening. The generality of these findings will be explored in the future.

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[20] The same conclusion is reached by using an entirely different method. Thus, the total bond energy can be defined as (for a similar discussion, see: E. A. Carter, W. A. Goddard III, *J. Phys. Chem.* **1986**, *90*, 998): $D_{\mathrm{total}} = D_{\mathrm{diss}} + \Sigma\Delta E_{\mathrm{promotion}}$ where D_{diss} is obtained from the calculation of the dissociation energy (B3LYP/6-311G*) of $\mathrm{HE{\equiv}E'H}$ to the $\mathrm{HE}(^2\Pi)$ and $\mathrm{HE'}(^2\Pi)$ fragments in their ground state. $\Sigma\Delta E_{\mathrm{promotion}}$ is the sum of the promotion energy (B3LYP/6-311G*) of the fragments to the quartet states (i.e., $\Delta E(^2\Pi \rightarrow {}^4\Sigma^-)$, which are suitable for bonding. D_σ becomes then, $D_\sigma = D_{\mathrm{total}} - D_{2\pi}$. The values of D_σ [kcal mol^{-1}] for **1**–**3** are as follows: **1L**: $D_\sigma = 64.8$, **1B**: $D_\sigma = 105.6$, **2L**: $D_\sigma = 42.0$, **2B**: $D_\sigma = 87.4$, **3L**: $D_\sigma = 102.8$, **3B**: $D_\sigma = 134.2$.

[21] For 10 electrons there are 42 SC structures.

[22] Calculating **3L** at $r_{\mathrm{C-C}} = 1.196$ Å (equilibrium structure) and 1.23 Å (see Figure 1) with all the π electrons unpaired leads to a 10.3 kcal mol^{-1} σ-bond strengthening for the longer bond.

[23] The increase in s-orbital population is 0.044 e^- for **3**, 0.262 e^- for **1**, and 0.604 e^- for **2**. The same conclusion is obtained from a natural population analysis. The computed σ preference for *trans*-bending, **2** > **1** > **3**, follows the rehybridization effect. The increase of s-orbital participation is associated with partial reduction of the promotion energy ($\Delta E(^2\Pi \rightarrow {}^4\Sigma^-)$) of the EH (E = C, Si) fragments within the molecule. In the promoted $^4\Sigma^-$ state, the fragments are able to make a triple bond at the expense of raising their self-energies, because of the high population of their p-orbitals. *Trans*-bending triggers more s-orbital participation, which partially demotes the fragments back to their ground state situations. This demotion lowers the energy of the fragments and thereby stabilizes the σ frame.

[24] For similar notions on the σ–π interplay (as well as on the σ bond length relaxation effect), see, P. C. Hiberty, D. Danovich, A. Shurki, S. Shaik, *J. Am. Chem. Soc.* **1995**, *117*, 7760.