Silicon−Silicon Triple Bonds: Do Substituents Make Disilynes Synthetically Accessible?

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Summary: Effects of substituents on silicon−silicon triple bonds are investigated using density functional theory. The electronic and steric effects of electropositive silyl groups play an important role in making disilynes ($RSi\equiv SiR$) an interesting synthetic target.

As represented by ethylene and acetylene, carbon−carbon double and triple bonds have played an important role in organic chemistry. For many years, the synthesis of the silicon analogues was a major challenge in silicon chemistry. Since the first isolation of a stable disilene ($R_2Si{=}SiR_2$) derivative in 1981,[1] a number of synthetic methods have been developed for silicon−silicon double bonds, as summarized in a recent review.[2] Despite several attempts, however, stable compounds containing a silicon−silicon triple bond, disilynes ($RSi\equiv SiR$), are still unknown, except for the proposal of transient existence of $MeSi\equiv SiMe$ as an intermediate.[3]

For the parent disilyne, it has been repeatedly calculated that its linear structure (**1**) does not correspond to a minimum on the potential energy surface of Si_2H_2; it has two imaginary frequencies and collapses to a trans-bent structure (**2**). In addition, **2** isomerizes to a more stable bridged or 1,2-H-shifted (**3**) isomer.[4] Accordingly, a bridged structure has been detected through the millimeter- and submillimeterwave spectra.[5] This contrasts with the well-known linear structure of $HC\equiv CH$; the bridged and 1,2-H-shifted isomers are very unstable or not minima.[6]

$H-Si\equiv Si-H$

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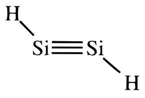

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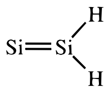

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It is an interesting question whether linear disilynes are synthetically accessible if they are properly substituted. However, little has been known about the substituent effects.[7] Thus, we have undertaken the theoretical calculations of $RSi\equiv SiR$ with R = H, Me, SiH_3, SiF_3, $Si(SiH_3)_3$, $SiMe_3$, $SiPh_3$, Si(t-Bu)$_3$, and $SiDep_3$ (Dep = 2,6-$Et_2C_6H_3$). Geometries were fully optimized with nonlocal hybrid density functional theory at the B3LYP level[8] using the GAUSSIAN 94 program.[9] The 3-21G* basis set[10a] was used throughout this work because of the size of substituents, while the 6-31G* basis set[10b] was also employed for the case of smaller substituents.

Table 1. Relative Energies (kcal/mol) of the Linear (1), Trans-Bent (2), and 1,2-R-Shifted (3) Structures of $RSi\equiv SiR$ at the B3LYP/3-21G* and B3LYP/6-31G* (in Parentheses) Levels

R	1	2	3
H	0.0	−20.3 (−22.1)	−28.2 (−30.7)
Me	0.0	−18.4 (−20.4)	−25.3 (−28.2)
SiH_3	0.0	−10.1 (−12.1)	−15.7 (−17.7)
SiF_3	0.0	−13.3 (−15.8)	−30.1 (−25.6)
$SiMe_3$	0.0	−7.0 (−8.5)	−10.5 (−11.4)
$SiPh_3$	0.0	−7.2	−17.3
$Si(SiH_3)_3$	0.0	−10.4	−16.6
Si(t-Bu)$_3$	0.0	−4.0	5.7
$SiDep_3$	0.0	−5.5	6.5

To calibrate the present calculations, we calculated the parent disilyne and made comparison with available high-level calculations. As Table 1 shows, the trans-bent structure (**2**) is 20.3 (3-21G*) and 22.1 (6-31G*) kcal/mol more stable than the linear structure (**1**). These data agree well with the value of 20.5 kcal/mol at the CISD/TZd level.[4b] The trans-bent H−Si−Si angle and Si−Si distance of 124.9° and 2.093 Å (3-21G*) and 124.4° and 2.111 Å (6-31G*) of **2** are in good agreement with those of 125.8° and 2.103 Å (CISD/TZd)[4b] and 124.2° and 2.121 Å (CCSD(T)/TZ2df).[4c] It was also calculated that the 1,2-H-shifted isomer (**3**) is 28.2 (3-21G*), 30.7 (6-31G*), and 32.1 (CISD/TZd)[4b] kcal/mol more stable than **1,** while the doubly-bridged isomer is 35.8 (3-21G*), 38.8 (6-31G*), and 43.1 (CISD/TZd)[4b] kcal/mol more stable than **1**.

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We turn to substituted disilynes ($RSi\equiv SiR$). The linear structures were not minima, as in R = H, while the trans-bent structures were located as minima. As Table 1 shows, the energy difference between **1** and **2** decreases by ca. 2 kcal/mol when R = Me. Upon substitution by SiH_3 groups, this decrease is as large as ca. 10 kcal/mol. Consequently, **1** is only 10.1 (3-21G*) and 12.1 (6-31G*) kcal/mol less stable with R = SiH_3 than **2**. To confirm this large change, geometries and energies were recalculated with a larger 6-311G (2d) basis set.[10c] It was again found that **1** is 11.6 kcal/mol less stable than **2** for R = SiH_3. This suggests that the 3-21G* calculations are sufficiently reliable for the following discussion of larger systems.

The effect of SiH_3 groups is much more favorable than that of Me groups, as found for the strain energies of polyhedral silicon compounds.[11] This is interesting since alkyl groups are usually employed as a representative substituent. As is well-known, silicon has a low tendency to form hybrid orbitals with high p character because of the size difference between the valence s and p atomic orbitals.[11,12] Both Mulliken and natural[13] population analyses show that SiH_3 acts as an electropositive substituent while Me is electronegative. The advantage of electron-donating substituents over electron-accepting ones is ascribed to the fact that the increased negative charges on triply-bonded silicons decrease the size difference and make s–p hybridization favorable.[11,12] To make this clearer, substitution by different silyl groups, SiF_3, $SiMe_3$, $SiPh_3$, and $Si(SiH_3)_3$, was tested. The charge analyses show that the SiF_3, $SiMe_3$, and $SiPh_3$ groups are more electropositive than SiH_3, while $Si(SiH_3)_3$ is less electropositive. As Table 1 shows, the $Si(SiH_3)_3$ group slightly increases the energy difference between **1** and **2**, compared with the SiH_3 case. In contrast, more electropositive $SiPh_3$ and $SiMe_3$ groups make the energy difference as small as 7.2 and 7.0 kcal/mol, respectively. When R = SiF_3, however, **1** is 13–16 kcal/mol less stable than **2**; this is ascribed to the smaller electron donation onto the p orbitals of triply-bonded silicons.

It is instructive to view $HSi\equiv SiH$ as being composed of two SiH units. Two interaction modes (a and b) between SiH are shown in Figure 1. The SiH unit has a doublet ground state ($^2\Pi$) which is 42.6 (3-21G*) kcal/mol more stable than the quartet state ($^4\Sigma$). This contrasts with the CH case where the quartet state is only 17.9 (3-21G*) and 16.7 (spectroscopic data)[14] kcal/mol less stable than the doublet state. The more stable doublet state of SiH originates from the strong tendency of silicon to keep the $3s^23p^13p^1$ valence configuration without significant hybridization: two electrons remain to be singlet-paired in an orbital with high 3s atomic character (see Figure 1).

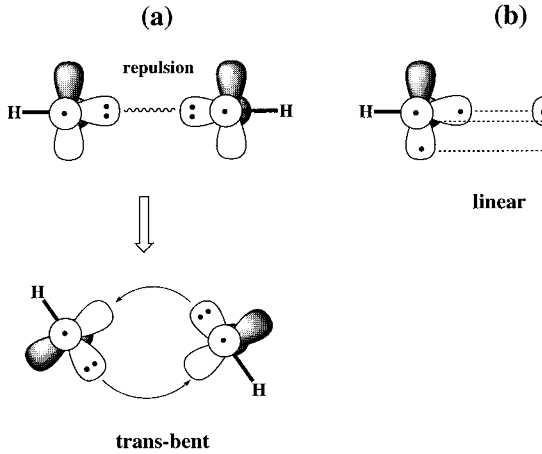

Figure 1. Two interaction modes (a and b) between SiH.

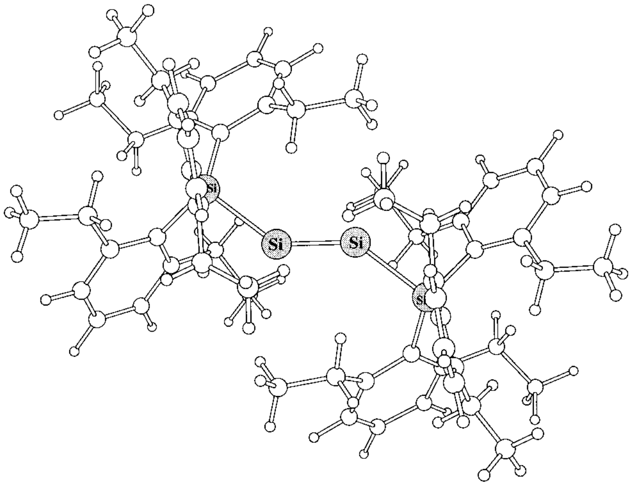

Figure 2. Optimized structures of $SiDep_3Si\equiv SiSiDep_3$ at the B3LYP/3-21G* level.

It appears that mode a is dominant in disilyne, unlike the case of acetylene. Therefore, disilyne undergoes severe exchange repulsion between lone pairs in the linear form, as shown in Figure 1. The central Si–Si bond is not only elongated to avoid the repulsion[15] but its structure is trans-bent to gain stabilization due to electron transfer (denoted by arrows in Figure 1).[16] The doublet-quartet energy difference is somewhat increased to 46.2 kcal/mol for SiMe. However, the energy difference of silyl-substituted SiR becomes as small as 26.7 (R = $Si(SiH_3)_3$), 26.0 (R = SiH_3), 23.5 (R = $SiPh_3$), and 18.4 (R = $SiMe_3$) kcal/mol as the electropositivity of R increases; it is smallest for the most electropositive $SiMe_3$. Obviously, the doublet–quartet energy closeness makes interaction mode b favorable, leading to an energy decrease between **1** and **2** (and the linearity of disilynes).

However, it was found that silyl groups tend to raise the HOMO level of disilynes, leading to a higher reactivity. To suppress this reactivity, bulky silyl groups, $Si(t\text{-}Bu)_3$ and $SiDep_3$, were considered for

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(15) The elongation is 0.13–0.14 Å for R = H and Me while it is 0.06–0.09 Å for all silyl groups. As a result, the Si–Si distances in the trans-bent $RSi\equiv SiR$ are 2.093 (H), 2.104 (Me), 2.082 (SiH_3), 2.069 (SiF_3), 2.092 ($Si(SiH_3)_3$), 2.075 ($SiMe_3$), 2.078 ($SiPh_3$), 2.068 ($Si(t\text{-}Bu)_3$), and 2.072 ($SiDep_3$) Å at the 3-21G* level and 2.111 (H), 2.123 (Me), 2.100 (SiH_3), 2.094 (SiF_3), and 2.095 ($SiMe_3$) Å at the 6-31G* level.

(16) The trans-bent R–Si–Si angles are 124.9 (H), 129.2 (Me), 130.0 (SiH_3), 128.8 (SiF_3), 128.4 ($Si(SiH_3)_3$), 135.6 ($SiMe_3$), 133.5 ($SiPh_3$), 138.2 ($Si(t\text{-}Bu)_3$), and 141.0° ($SiDep_3$) at the 3-21G* level and 124.4 (H), 128.9 (Me), 130.0 (SiH_3), 126.6 (SiF_3), and 131.3° ($SiMe_3$) at the 6-31G* level. When R is bulky, the trans-bent disilyne structures are slightly further twisted around the Si–Si triple bond for steric reasons; the R–Si–Si–R dihedral angles are 179,7, 179.2, 170.5, 178.5, and 175.6° at the 3-21G* level for R = $SiMe_3$, $Si(SiH_3)_3$, $SiPh_3$, $Si(t\text{-}Bu)_3$, and $SiDep_3$, respectively.

RSi≡SiR. The doublet−quartet energy differences of the SiR part (18.6 kcal/mol for R = Si(t-Bu)$_3$ and 29.2 kcal/mol for R = SiDep$_3$ at the 3-21G* level) are comparable to and larger than that of 18.4 kcal/mol for R = SiMe$_3$, respectively. Owing to the bulk, however, **1** is now only 4.0 (R = Si(t-Bu)$_3$) and 5.5 (R = SiDep$_3$) kcal/mol less stable than **2**. As Figure 2 shows, these bulky groups protect the silicon−silicon triple bond from the attack of reactive species as well as its dimerization; they make also the trans-bending smallest.[16] The central Si−Si bond distances of 2.068 Å in Si(t-Bu)$_3$-Si≡SiSi(t-Bu)$_3$ and 2.072 Å in SiDep$_3$Si≡SiSiDep$_3$[15] are 0.13−0.18Å shorter than the Si-Si double bond distances of 2.202−2.251 Å observed for silyl-substituted disilenes,[17] confirming that two silicons are triply bonded.

Another major difficulty in preparing disilynes (**2**) is ascribed to the facile isomerization to more stable :Si═SiR$_2$ structures (**3**). As Table 1 shows, however, bulky silyl groups can reverse the order of stability. It is remarkable that the Si(t-Bu)$_3$ and SiDep$_3$ groups make **2** 9.7 and 12.0 kcal/mol more stable than **3**, preventing the isomerization.

In conclusion, both electronic and steric effects of substituents are very important in making disilynes synthetically accessible. Electropositive silyl groups have a remarkable effect on the stability of linear disilynes, in contrast to a recent theoretical study of substituent effects on silynes (RSi≡CR).[18] Disilynes bearing bulky silyl groups, such as Si(t-Bu)$_3$ and SiDep$_3$, are attractive as viable synthetic targets. Almost-linear disilynes are expected to be synthesized with bulkier silyl groups, such as SiTbt$_3$ (Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl). It is hoped that the theoretical interpretations of substituent effects will be of help in preparing the fruitful precursors of disilynes.

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