A Silicon–Silicon Triple Bond Surrounded by Bulky Terphenyl Groups

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In search of a stable disilyne, effects of bulky 2,6-bis(2,4,6-triisopropylphenyl)phenyl (Ar*) groups on silicon–silicon triple bonding are investigated using density functional theory. It is predicted that Ar*Si≡SiAr* is very stable to isomerization and dimerization.

Since the first synthesis in 1981,[1] a number of stable silicon–silicon doubly bonded compounds have been synthesized and isolated up to now.[2] However, stable silicon–silicon triply bonded compounds, disilynes (RSi≡SiR), are still unknown despite several attempts,[3] which are the focus of interest as an important target in silicon chemistry.[4] It has been calculated that the parent HSi≡SiH has a trans-bent structure and isomerizes readily to $\mathrm{SiSiH_2}$ or bridged structures.[5] As substituents become large, however, bridged structures are highly destabilized for steric reasons.[6] Therefore, it is important to prevent the 1,2-R shift in RSi≡SiR in order to realize a disilyne structure.

By providing theoretical insight into the nature of silicon–silicon triple bonding,[6] effects of bulky aryl groups such as Ar* = $\mathrm{C_6H_3}$-2,6-($\mathrm{C_6H_2}$-2,4,6-*i*-$\mathrm{Pr_3}$)$_2$ and Tbt = $\mathrm{C_6H_2}$-2,4,6-{$\mathrm{CH(SiMe_3)_2}$}$_3$ have recently been investigated[7] using density functional theory at the B3LYP/3-21G* level.[8] The Ar* and Tbt groups have served as representative bulky substituents, which are helpful for the synthesis and stabilization of doubly bonded species.[9] Despite the expected bulk of the Ar* group, it was calculated that Ar*Si≡SiAr* is 12.9 kcal mol^{-1} less stable than the 1,2-Ar* shifted isomer $\mathrm{SiSiAr^*_2}$ where the two bulky groups crowd more around one end of the Si–Si bond.[7] This has stimulated an elaborate search of the favorable conformation of Ar*Si≡SiAr*.

We now report that there is a more stable C_2 structure for Ar*Si≡SiAr*. The optimized structure is shown in Figure 1a.[10] It is noteworthy that the disilyne is 31.7 kcal mol^{-1} more stable at the B3LYP/3-21G* level than the 1,2-Ar* shifted isomer $\mathrm{SiSiAr^*_2}$ shown in Figure 1b. This energy difference is enough to prevent the 1,2-Ar* shift in Ar*Si≡SiAr*, which is larger than that of 18.5 kcal mol^{-1} for the TbtSi≡SiTbt case, reflecting the bulkier Ar* group. The Si–Si–Ar* bond angle (θ) is 130.5°. This trans-bending is almost the same as that in TbtSi≡SiTbt (θ = 130.9°). As the Ar*–Si–Si–Ar* dihedral angle (ω = 163.9°) shows, the skeleton of Ar*Si≡SiAr* is twisted 16.1° around the Si–Si bond, unlike the TbtSi≡SiTbt case (ω = 180.0°). In an attempt to reduce the crowding of substituents, the *i*-Pr groups on Ar* were replaced by H atoms. Upon this replacement, the trans-bending and twisting were highly enhanced (θ = 100.2° and ω = 97.9°) and the Si–Si bond was elongated by 0.258 Å. This result reveals that the *i*-Pr groups on Ar* are not decorative but indispensable to maintain a disilyne structure.[11] In addition, the *i*-Pr groups help to protect the central Si–Si bond from reactive reagents, as is apparent from Figure 1a.

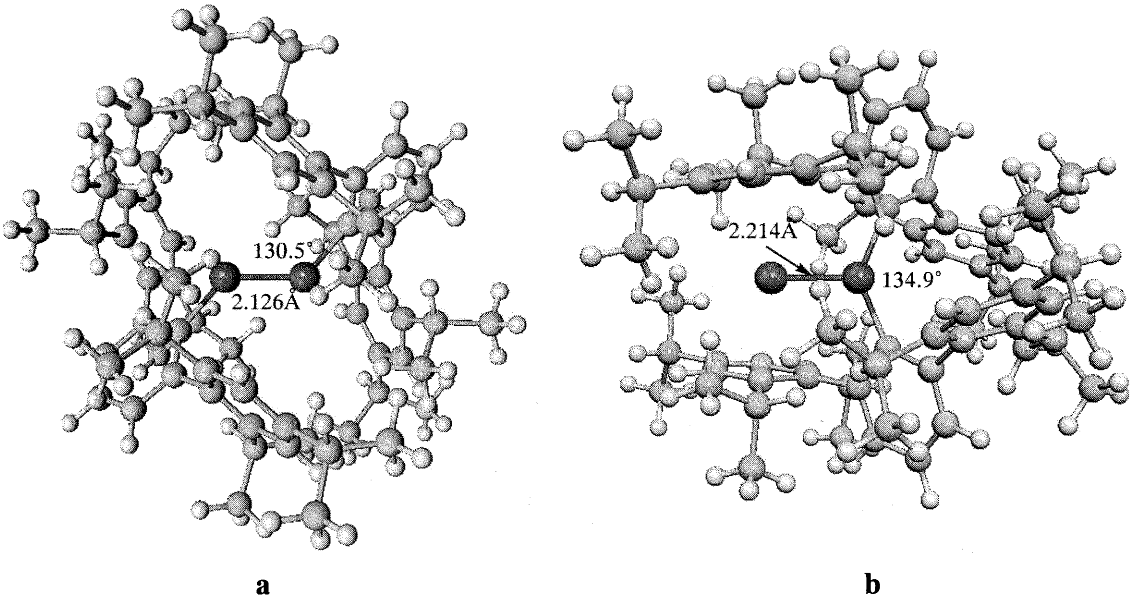

Figure 1. Optimized structures of (**a**) Ar*Si≡SiAr* and (**b**) $\mathrm{SiSiAr^*_2}$ at the B3LYP/3-21G* level.

Another important obstacle to the synthesis and isolation of RSi≡SiR is the facile dimerization that leads to tetrahedrane or more stable cyclobutadiene structures (Si_4R_4). When R is as bulky as $Si(t\text{-}Bu)_3$, the dimerization to tetrasilatetrahedrane is 80 kcal mol^{-1} exothermic.[7] In this context, it is interesting that the first synthesis and isolation of a stable tetrasilatetrahedrane was performed with the $Si(t\text{-}Bu)_3$ groups.[12]

To test if Ar*Si≡SiAr* is stable to dimerization, calculations were carried out using the two-layered ONIOM (B3LYP/3-21G*:AM1) method developed recently,[13] because of the size of molecules. This method can well reproduce the full B3LYP/3-21G* calculations. For example, the Si–Si distance, θ, and ω of 2.127 Å, 130.6°, and 168.4° calculated with the ONIOM method for Ar*Si≡SiAr* agree well with the values of 2.126 Å, 130.5°, and 163.9° at the full B3LYP level, respectively. The energy difference of 25.3 kcal mol^{-1} favoring Ar*Si≡SiAr* over $SiSiAr*_2$ calculated with the ONIOM method does not differ much from the full B3LYP value of 31.7 kcal mol^{-1}, for the present purpose.

The ONIOM calculations predict that the dimerization of Ar*Si≡SiAr* to tetrasilacyclobutadiene (Figure 2)[14] is 81 kcal mol^{-1} endothermic. This endothermicity, much larger than that of 42 kcal mol^{-1} for the TbtSi≡SiTbt case,[7] suggests that Ar*Si≡SiAr* is very stable to dimerization. It is interesting that the dimerization becomes 25 kcal mol^{-1} exothermic, only when the *i*-Pr groups on Ar* is replaced by Me groups; upon this replacement, the Si–Si distance increases by 0.04 Å, while the trans-bending and twisting are enhanced by 7 and 26°, respectively. These indicate again that the suitable crowding of substituents is very important.

In conclusion, Ar*Si≡SiAr* is very stable to isomerization and dimerization, which is worthy of experimental testing as an interesting synthetic target. Despite the bulk of the Ar* group, the energy required to cleave the Si–Si bond is as large as 31.7 kcal mol^{-1} at the B3LYP/3-21G* level. This suggests that Ar*Si≡SiAr* does not dissociate into two SiAr* fragments in solution. A drawback of the Ar* group is the somewhat long Si–Si distance of 2.126 Å, compared with those of 2.121 Å for TbtSi≡SiTbt[7] and 2.072 Å for $Dep_3SiSi{\equiv}SiSiDep_3$ (Dep = 2,6-diethylphenyl).[15] This trend is further enhanced for the still heavier germanium–germanium and tin–tin triple bonds.[16]

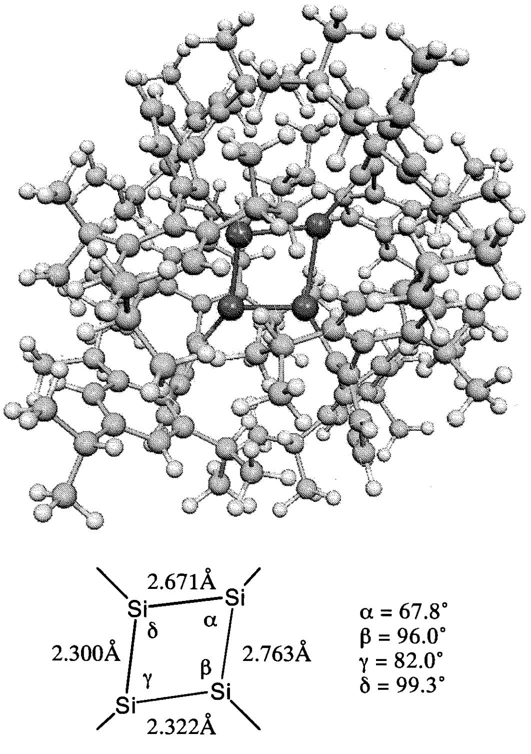

Figure 2. Optimized structure of Ar*-substituted tetrasilacyclobutadiene by the ONIOM method.

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Dedicated to Prof. Hideki Sakurai on the occasion of his 70th birthday.

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