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# Synthesis and structure of stable 1,2-diaryldisilyne*

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*Abstract*: A novel 1,2-diaryldisilyne, BbtSi≡SiBbt (Bbt = 2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl), was synthesized as a stable compound by reduction of the corresponding 1,2-dibromodisilene, Bbt(Br)Si=Si(Br)Bbt. The spectral and structural features of this first stable 1,2-diaryldisilyne are revealed, and the Si≡Si triple-bond character is evaluated with the aid of detailed theoretical calculations. The triple-bond characters of BbtSi≡SiBbt and BbtGe≡GeBbt are compared based on experimental and theoretical results.

*Keywords*: dibromodisilene; digermyne; disilyne; kinetic stabilization; triple bond.

## INTRODUCTION

Synthesis and isolation of stable multiple-bond compounds of heavier main group elements have long been acknowledged as difficult because of their extremely high reactivity. Nevertheless, many chemists have sought to discover the intrinsic nature of such unique multiple-bond compounds between heavier main group elements as objects of fundamental interest. Especially, heavier congeners of alkene and alkyne, i.e., multiple-bond compounds between heavier group 14 elements, have attracted much attention from the viewpoint of comparison with the corresponding organic compounds, most of which are known as stable multiple-bond compounds. The idea of kinetic stabilization using bulky substituents has been helpful, leading to the isolation of various stable double-bond compounds that can be formed with heavier group 14 elements [1], since the first isolation of a stable distannene, $Dis_2Sn{=}SnDis_2$ [Dis = $CH(SiMe_3)_2$], by M. F. Lappert et al. in 1973 [2] and a stable disilene, $Mes_2Si{=}SiMes_2$ (Mes = mesityl), by R. West et al. in 1981 [3]. With the stable double-bond compounds between heavier group 14 elements (dimetallenes) in hand, the bonding character of the dimetallenes has been revealed in detail based on experimental and theoretical results. Recently, the chemistry of multiply bonded systems of heavier group 14 elements has emphasized the heavier element analogs of alkyne (dimetallynes), i.e., disilynes, digermynes, distannynes, and diplumbynes [4]. Pioneering works on the synthesis and isolation of the stable 1,2-diaryldigermynes [5], distannynes [6], and diplumbynes [7] using bulky *m*-terphenyl type ligands such as 2,6-$Dip_2C_6H_3$ or 2,6-$Tip_2C_6H_3$ (Dip = 2,6-diisopropylphenyl, Tip = 2,4,6-triisopropylphenyl) have been reported by P. P. Power et al. and have contributed to our knowledge of the unique structures and properties of these dimetallynes. The bonding properties of the Ge–Ge and Sn–Sn bonds of 1,2-diaryldigermynes (ArGeGeAr) and 1,2-diaryldistannynes (ArSnSnAr)

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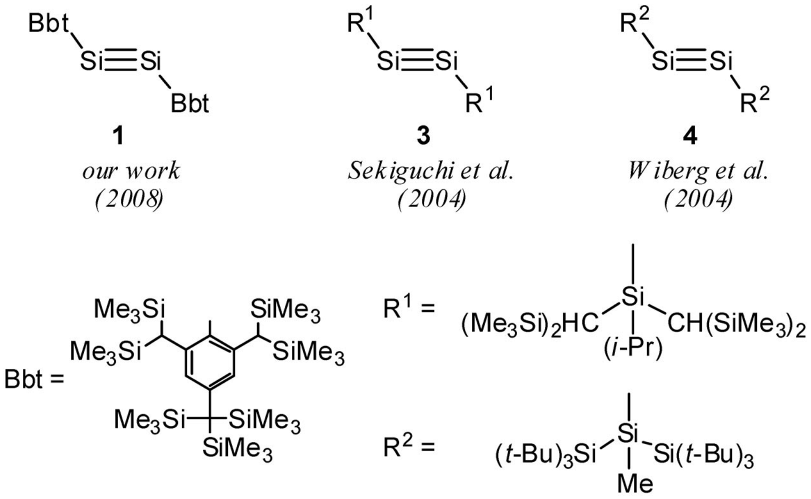
can be considered as multiple bonds, but their "bond order" has remained controversial. In fact, ArMMAr (M = Ge, Sn) are sometimes discussed as biradical species (·M=M·) or bis-metallylene species (:M–M:) with dependence on the electronic properties of the *m*-terphenyl ligands in their crystalline state [4,8]. A crystallographic analysis of the diplumbyne, ArPbPbAr (Ar = 2,6-$Tip_2C_6H_3$), suggested that the Pb–Pb bond of the diplumbyne displays single-bond character in the crystalline state, i.e., the structure of the diplumbyne should be described as the bis-plumbylene, Ar–Pb:–Pb:–Ar [7]. It is particularly interesting that these 1,2-diaryldimetallynes (ArMMAr, M = Ge, Sn, Pb) exhibit a pronounced multiple-bond character in solution based on their electronic spectra and theoretical calculations [9]. Attempted synthesis of 1,2-diaryldisilyne bearing *m*-terphenyl ligand was unsuccessful because of the intramolecular cyclization of the silicon moiety with the bulky *m*-terphenyl ligand [10]. Wiberg [11] and Sekiguchi [4c,12] independently designed the bulky silyl groups, $SiMe[Si(t\text{-}Bu)_3]_2$ and $Si(Dis)_2(i\text{-}Pr)$ [Dis = $CH(SiMe_3)_2$], respectively, for stabilization of a disilyne based on theoretical calculations showing that the electropositive ligand such as a silyl group should thermodynamically stabilize the Si–Si triple bond of disilynes [13] (Scheme 1). As a result, the Si–Si bonds of the silyl-substituted disilynes exhibit a considerable triple-bond character in the solid state and even in solution [4c,12].

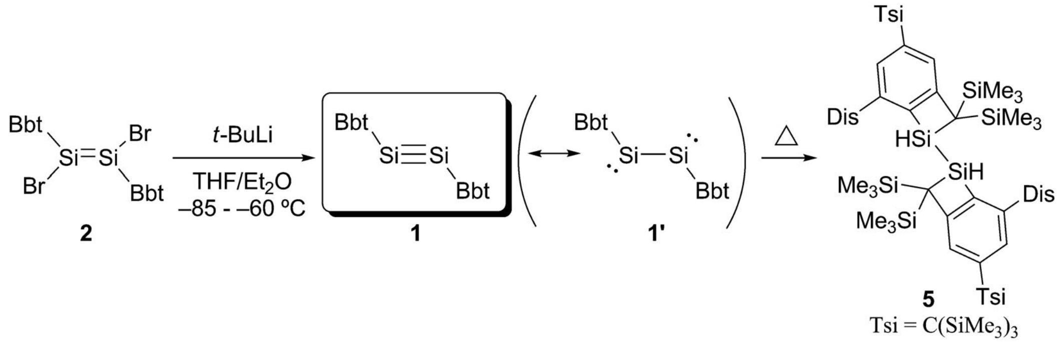


**Scheme 1** Stable disilynes.

We have published a preliminary report on the first stable 1,2-diaryldisilyne, BbtSi≡SiBbt (**1**), bearing 2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl (denoted as Bbt) groups by the reaction of the corresponding (*E*)-1,2-diaryl-1,2-dibromodisilene, Bbt(Br)Si=Si(Br)Bbt (**2**) with *t*-BuLi [14]. In this report, the synthesis and properties of 1,2-diaryldisilyne **1** are described from the viewpoint of the Si≡Si triple-bond character of **1**. With disilyne and digermyne bearing the same substituents, Bbt groups, in hand, the triple-bond character of **1** and BbtGe≡GeBbt [15] can be compared systematically.

## RESULTS AND DISCUSSION

In the preliminary report, results showed that dibromodisilene **2** was reduced with *t*-BuLi at –100 °C in tetrahydrofuran (THF) to afford 1,2-diaryldisilyne **1** as a mixture of **1** and **2** (**1**:**2** = 55:45 as judged by $^1H$ NMR spectrum) [14]. The synthetic method of **1** has been revised as follows (Scheme 2).



**Scheme 2** Synthesis of 1,2-diaryldisilyne.

Dibromodisilene **2** in THF/$Et_2O$ (1:9) was treated with *t*-BuLi at –85 °C. After stirring at –85 °C for 70 min, the temperature was increased to –60 °C. After stirring 30 min, volatile contents were removed under reduced pressure. Fractional crystallization of the crude product in a glove box filled with argon afforded dark yellow crystals of disilyne **1** in 61 % isolated yield [16]. In the $^1H$ NMR spectrum of **1** at ambient temperature, only one set of signals corresponding to the Bbt group was observed, suggesting the symmetric structure of **1** in solution. The $^{29}Si$ NMR spectrum of **1** showed a characteristic singlet signal at 18.7 ppm assignable to the central triply bonded silicon nuclei. The $^{29}Si$ chemical shift of 1,2-diaryldisilyne **1** is considerably more upfield-shifted than those of the previously reported bis-silyldisilynes [$\delta_{Si}$ = 89.9 for $(Dis)_2(i\text{-}Pr)Si–Si{\equiv}Si–Si(Dis)_2(i\text{-}Pr)$ (**3**) [12], $\delta_{Si}$ = 91.5 for $[(t\text{-}Bu)_3Si]_2MeSi–Si{\equiv}Si–SiMe[Si(t\text{-}Bu)_3]_2$ (**4**) [11]]. Because the previously reported $^{29}Si$ NMR chemical shifts for stable tetraaryldisilenes ($\delta_{Si}$ = ca. 53–66) are known to be higher than those for the stable tetrasilyldisilenes ($\delta_{Si}$ = ca. 142–154), the apparent difference of $^{29}Si$ NMR chemical shifts between **1** and bis-silyldisilynes **3** and **4** is probably attributable to the electronic effect of the substituents and the paramagnetic effect [17]. In addition, the higher chemical shift of **1** than those of tetraaryldisilenes is expected to be attributable to the isotropic effect of the two π-bonds of the Si–Si triple bond, as in the case of acetylene.

In fact, **1** is stable in the solid state at room temperature and in heptane solution at –40 °C for more than 3 weeks, but it decomposes slowly in etheral or aromatic solution. The half-life of **1** in benzene is 40 h at 25 °C. The possible structure of the major thermal decomposition product is intramolecular cyclized compound **5** [18], which would be generated via the C–H insertion of the possible isomer of **1**, bis-silylene **1'**. The structure of 1,2-diaryldisilyne **1** was revealed by X-ray crystallographic analysis (Fig. 1) [19]. Disilyne **1** has a crystallographic $C_2$ axis through the central Si≡Si bond. It has *trans*-bent structure similar to the case of silyl-substituted disilyne **3**. The Si–Si–C bond angle and the C–Si–Si–C torsion angle of **1** are 133.0 (3)° and of 164.1 (8)°, respectively, whereas those of **3** are, respectively, 137.44 (4)° and 179.4° [12]. The smaller Si–Si–C bond angle and the C–Si–Si–C torsion angle of diaryldisilyne **1** suggest a weaker triple-bond character than that of silyl-substituted disilyne **3** based on the valence electron bonding model (Fig. 2). In addition, the Si≡Si bond length of **1** is 2.108(5) Å, which is considerably shorter than those of previously reported tetraaryldisilenes (ca. 2.14 Å) and slightly longer than that of **3** [2.0622(9) Å]. Consequently, 1,2-diaryldisilyne of **1** is expected to exhibit a strong Si≡Si triple-bond character; the Si≡Si triple bond of **1** is expected to be weaker than that of **3**.

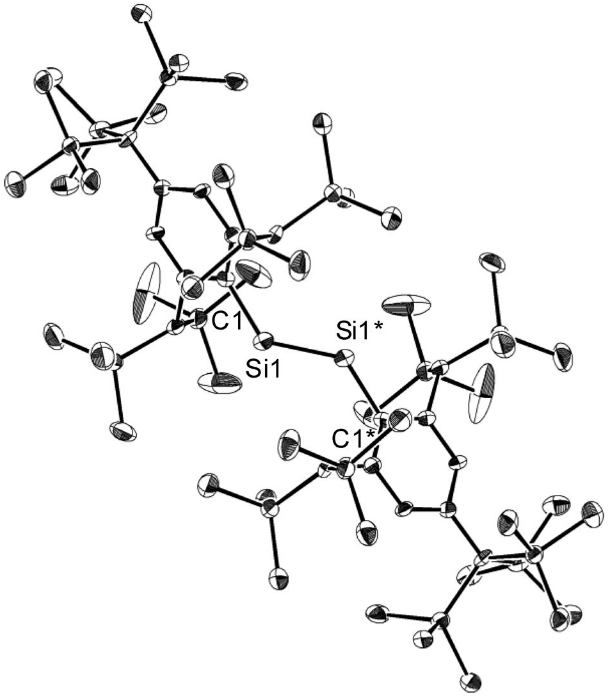


**Fig. 1** Molecular structure of 1,2-diaryldisilyne **1**. The toluene molecules were omitted for clarity. Displacement ellipsoids were drawn at the 30 % probability level. Selected structural parameters: Si1–Si1*, 2.108 (5) Å; C1–Si1–Si1*, 133.0 (3)°; C1–Si1–Si1*–C1*, 164.1 (8)°. *Symmetry transformations used to generate equivalent atoms: *y*, *x*, –*z* + 2.

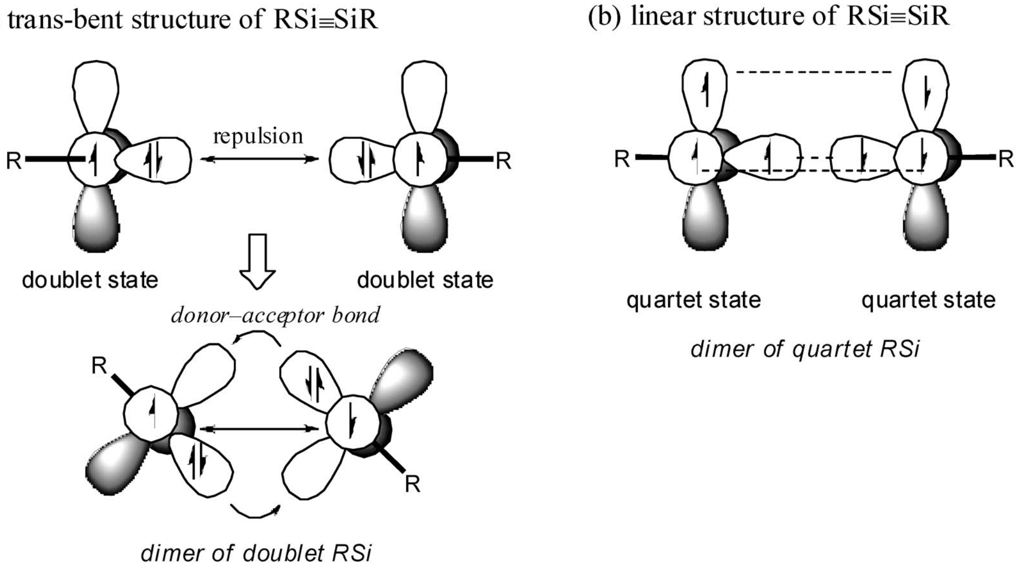


**Fig. 2** Interaction modes of two RSi units.

To understand the triple-bond characters of the Si≡Si bond of **1**, density functional theory (DFT) calculations were performed (Table 1). Based on the previous report on the structural optimization of **3** at various calculation levels [20], the better results were obtained at B3PW91/6-311+G(2df)[Si]: 6-31G(d)[C,H] level. Therefore, we decided to perform the calculations at the same level. At this stage, three structures of **1** were located [21]. One has $C_2$ symmetry (**1-C2**); the other two are asymmetric (**1-A**, **1-B**) (Fig. 3). Structural parameters of **1-C2** (e.g., Si≡Si: 2.119 Å, C–Si≡Si: 135.9°, C–Si≡Si–C: 171.2°) show the best agreement with those experimentally observed for **1** [Si≡Si: 2.108(5) Å, C–Si≡Si: 133.0 (3)°, C–Si≡Si–C: 164.1 (8)°] among those of the optimized structures, and the relative energies (kcal/mol) of **1-C2** (set as 0.0) are the lowest among those for the asymmetric structures (+0.9 for **1-A**, +0.3 for **1-B**). A contrast is the case of BbtGe≡GeBbt, the $C_2$-symmetric structure of which is less stable than the asymmetric structures (as described later) [15]. In addition, $\delta_{\mathrm{Si}}$ of the triply bonded silicon nuclei were calculated at the GIAO-B3PW91/6-311+G(2df)[Si]: 6-31G(d)[C,H] level. The $^{29}$Si NMR chemical shift for **1-C2** was computed as 16.7 ppm, which is expected to agree with the observed value for **1** (18.7 ppm), although the computed chemical shifts of $\delta_{\mathrm{Si}}$ of the other structures, **1-A** (47.6 and –14.5 ppm), and **1-B** (51.1 and –17.6 ppm) differ considerably from the observed value. Considering these results, it can be concluded that disilyne **1** exhibits a geometry resembling the optimized structure of **1-C2** in the solution as well as in the crystalline state.

**Table 1** Optimized and observed parameters for BbtSi≡SiBbt. Theoretical calculations were performed at B3PW91/6-311+G(2df)[Si]: 6-31G(d)[C,H] level.

| | **1**[a] | **1-C2**[b] | **1-A**[b] | **1-B**[b] |
|---|---|---|---|---|
| Si–Si (Å) | 2.108 (5) | 2.119 | 2.122 | 2.124 |
| C–Si–Si(deg) | 133.0 (3) | 135.9 | 132.9<br>139.0 | 132.4<br>139.2 |
| C–Si–Si–C (deg.) | 164.1 (8) | 171.2 | 173.6 | 174.9 |
| BE (kcal/mol) | – | 44.0 | – | – |
| $^{29}$Si NMR (ppm) | +18.7 | +16.7 | +47.6<br>–14.5 | +51.1<br>–17.6 |
| UV (nm) | 385 ($\varepsilon$ 43000)<br>480 ($\varepsilon$ 1500) | 394.5 ($f$ 0.840)<br>516.0 ($f$ 0.009) | – | – |
| Rel. energy (kcal/mol) | – | 0.0 | +0.9 | +0.3 |

[a] observed.
[b] calculated.

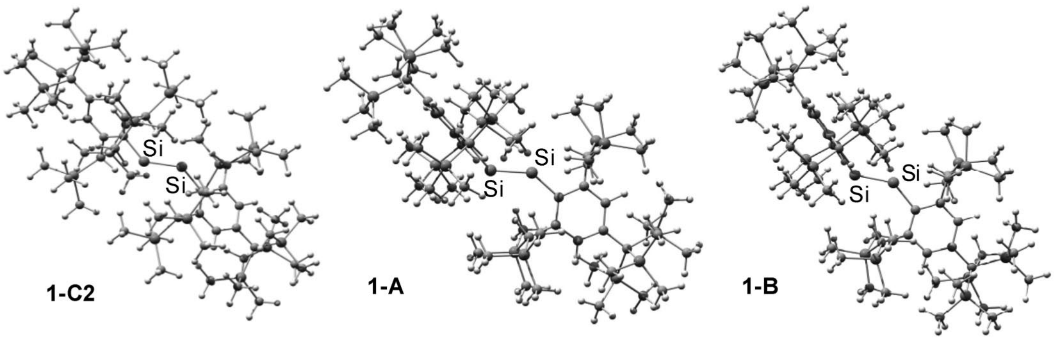


**Fig. 3** Optimized structures for BbtSi≡SiBbt.

It is important to consider the doublet–quartet energy differences of the RSi unit. It is instructive to view RSi≡SiR as a dimer of RSi, where the two interaction modes between RSi units (a) and (b) are conceivable as presented in Fig. 2. Generally, RSi has a larger energy difference between the doublet ground state ($^2\Pi$) and the quartet state ($^4\Sigma$) than that of the corresponding carbon system (RC unit). The larger doublet–quartet energy difference ($\Delta E_{D-Q}$) of RSi unit than that of carbon analog (RC unit) originates from the tendency of heavier main group elements to maintain the intrinsic valence electronic configuration such as $(ns)^2(np)^1(np)^1$ attributable to the size difference between ns and np orbitals ($n >$ 3). A stark contrast is the case of carbon, which can form hybridized orbitals easily. Therefore, RSi≡SiR is inferred to be formed from two RSi units with a *trans*-bent structure by the interaction mode (a) favorably rather than with a linear structure by the interaction mode (b) [1i,4].

Actually, $\Delta E_{D-Q}$ [= *E*(quartet RSi)–*E*(doublet RSi)] of BbtSi was computed as 44.8 kcal/mol, which is much larger than that of either $[(t\text{-Bu})_3\text{Si}]_2(\text{Me})\text{Si–Si}$ (25.6 kcal/mol) or $\text{Dis}_2(i\text{-Pr})\text{Si–Si}$ (18.9 kcal/mol) [19]. The small values of $\Delta E_{D-Q}$ of RSi (R = silyl group) are most likely interpreted in terms of the small size difference between 3*s* and 3*p* orbitals because of the electropositive silyl groups. The larger $\Delta E_{D-Q}$ of BbtSi than that of $\text{Dis}_2(i\text{-Pr})\text{Si–Si}$ is expected to make the Si≡Si triple bond of **1** weaker than that of **3**. Therefore, it engenders the longer Si≡Si bond length and smaller C–Si–Si bond angle of **1** than those of **3**. In addition, the calculated bonding energies (BEs) of the Si≡Si bonds suggest that the BE for the weaker Si≡Si bond of **1** (BE = 44.0 kcal/mol) is less than that of **3** (66.6 kcal/mol)

The multiple-bond compounds of heavier main group elements are generally colored because of the chromophore of the π-bonds. The electronic spectra are a good indicator of bonding character. In the UV–vis spectrum of hexane solution of **1** (Fig. 4), the characteristic two absorption maxima were observed at 385 nm ($\varepsilon$ 43 000) and 480 nm ($\varepsilon$ 1500), the former of which was a strong absorption, in contrast to the other weak one. These two absorptions are characteristic of dimetallynes with a *trans*-bent structure in solution [9]. As presented in Fig. 5, the DFT calculations show that the two π-orbitals of **1** are not equivalent because of the *trans*-bent structure, as in the case of bis-silyldisilyne **3** [4,22]. Consequently, the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO)+1 probably correspond to the out-of-plane π- and π*-orbitals with almost pure $p_x$-orbitals of the silicon atoms, respectively, whereas the HOMO-1 and LUMO, respectively, are expected to consist dominantly of in-plane slipped π- and π*-orbitals mixed with the σ*-orbital between the silicon atoms with *s*- and *p*-orbitals. The observed two absorption maxima of **1** should be assignable to the π–π* electron transitions as a mixed transition of "HOMO-1 to LUMO" and "HOMO to LUMO+1" based on results of time-dependent DFT (TDDFT) calculations (394.5 nm, $f = 0.840$; 516.0 nm, $f = 0.009$). Similarly, bis-silyldisilyne **3** reportedly shows two characteristic absorption maxima because of the π–π* electron transitions similarly to the case of **1** at 328 ($\varepsilon$ 5800) and 483 ($\varepsilon$ 120) nm. That is, the π–π* transitions of **1** were red-shifted compared to those of **3**, suggesting weaker π bonds of **1** than those of **3**. Although it was reported that **3** showed extremely weak absorption at the longer wavelength of 690 nm ($\varepsilon$ 14) assignable to the symmetry-forbidden HOMO–LUMO electron transition, such characteristic weak absorption was not observed for **1** even though the TDDFT calculations, suggesting the HOMO–LUMO transitions of **1** would be 942.0 nm ($f = 0.003$).

With stable digermyne and disilyne bearing the same substituents (Bbt groups) in hand, we can compare the respective bonding characters Si≡Si and Ge≡Ge triple bonds. Results show that BbtGe≡GeBbt (**6**) exhibits a considerable Ge≡Ge triple-bond character based on its spectroscopic and structural features [15], chemical reactivities, and theoretical calculations, in contrast to the characters of the previously reported ArGe≡GeAr (Ar = $2,6\text{-Dip}_2\text{-C}_6\text{H}_3$ or $2,6\text{-Tip}_2\text{-C}_6\text{H}_3$) [4,6]. Three geometries of BbtGe≡GeBbt (**6**) were located as **6-C2**, **6-A**, and **6-B** [15,23]. In fact, **6-C2** has $C_2$ symmetry; the others are not symmetrical. While the experimentally observed structures of **6**, which has two independent molecules in the unit cell, are similar to those of **6-A** and **6-B**, the relative energies of **6-A** (–0.50 kcal/mol) and **6-B** (–1.07 kcal/mol) are slightly lower than that of **6-C2** (0.00 kcal/mol), in contrast to the cases of **1-C2**, **1-A**, and **1-B** (as described herein). The UV–vis spectrum of digermyne **5**

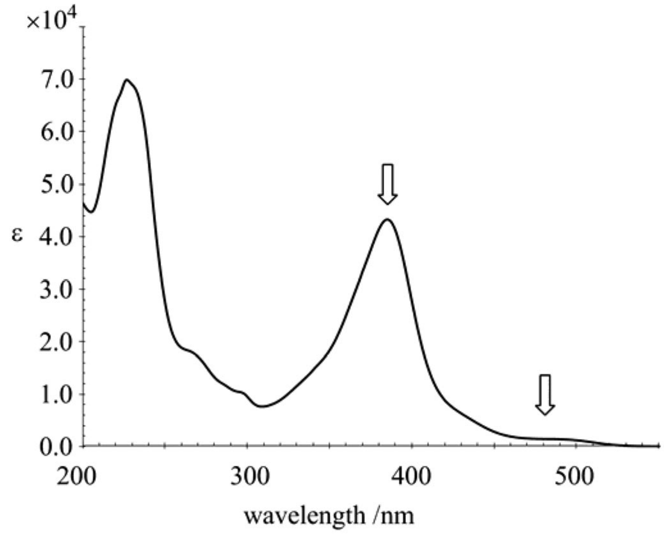


**Fig. 4** UV–vis spectrum of BbtSi≡SiBbt (**1**) (0.22 mM in hexane).

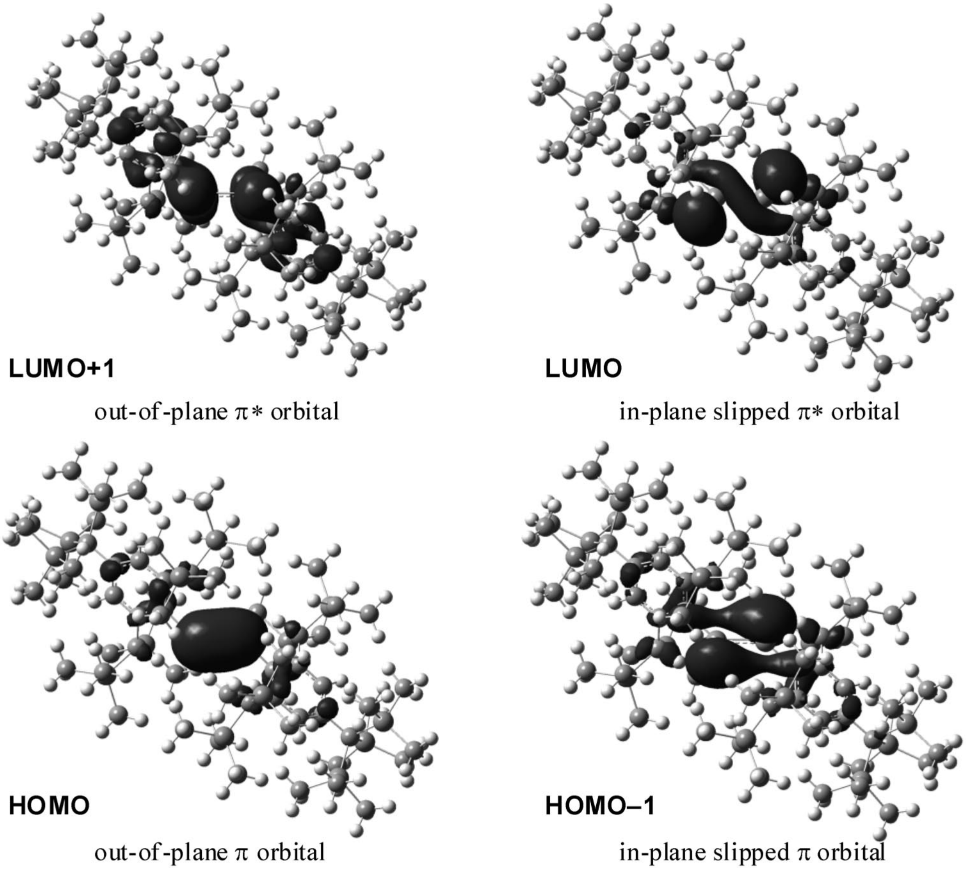


**Fig. 5** Calculated orbitals of BbtSi≡SiBbt (**1-C2**).

showed the characteristic two absorption maxima at 373 ($\varepsilon$ 32 000) and 495 ($\varepsilon$ 1500) nm, assignable to the π–π* electron transitions because of the mixed transition of "HOMO-1 to LUMO" and "HOMO to LUMO+1," as in the case of disilyne **1**. The observed absorptions were supported by TDDFT calculations for the optimized structures **6-C2** (405.2 nm, $f = 0.425$; 513.0 nm, $f = 0.013$), **6-A** (406.0 nm, $f = 0.490$; 513.4 nm, $f = 0.007$), and **6-B** (399.6 nm, $f = 0.582$; 502.5 nm, $f = 0.003$). Thus, the two characteristic absorptions observed for disilyne **1** and digermyne **6** are mutually similar, suggesting similar electronic properties of their Si≡Si and Ge≡Ge triple bonds. On the other hand, the calculated value of $\Delta E_{\mathrm{D-Q}}$ of BbtGe (47.1 kcal/mol) is equivalent to or slightly larger than that of BbtSi (44.8 kcal/mol), suggesting that the intrinsic nature of heavier elements to maintain intrinsic valence electronic configuration such as $(\mathrm{n}s)^2(\mathrm{n}p)^1(\mathrm{n}p)^1$ should be slightly enhanced in the case of germanium as compared to the case of silicon. Furthermore, the BEs of Ge≡Ge triple bonds in **6-C2**, **6-A**, and **6-B** were computed, respectively, as 36.6, 37.1, and 37.7 kcal/mol. Those values are somewhat smaller than that of the Si≡Si triple bond in **1-C2** (44.0 kcal/mol). Consequently, results showed that the electronic properties of the Ge≡Ge triple bond are expected to be similar to those of the Si≡Si triple bond, although the former is expected to be merely a slightly weaker bond than the Si≡Si bond because of the different intrinsic natures of germanium and silicon.

## CONCLUSION

A novel 1,2-diaryldisilyne with a Si≡Si triple bond was synthesized as a stable crystalline compound. The BbtSi≡SiBbt (**1**) structure was revealed by X-ray crystallographic analysis. Although **1** was expected to have a weaker triple bond than the previously reported silyl-substituted disilyne **3** based on spectral and structural features and theoretical studies, the aryl-substituted disilyne (**1**) was found to exhibit a strong triple-bond character between the silicon atoms in spite of its highly *trans*-bent structure. The silyl substituent is expected to make the doublet–quartet energy-difference ($\Delta E_{\mathrm{D-Q}}$) of the RSi unit smaller than in the case of carbon-substituted system; the small $\Delta E_{\mathrm{D-Q}}$ is expected to enhance BE of the Si≡Si triple bond. In addition, a comparison of the properties between Bbt-substituted disilyne **1** and digermyne **6** indicated that the bonding properties of Si≡Si and Ge≡Ge bonds should be mutually similar, but the Si≡Si triple bond is expected to be slightly stronger than the Ge≡Ge triple bond.

It is of great importance that the electronic effect of the silyl groups toward the Si≡Si triple bond can be clarified based on the comparison of silicon-substituted disilynes with the carbon-substituted disilyne. Moreover, matching of theoretical calculations with experimental results was shown to be extremely important and useful to elucidate the intrinsic nature of new chemical bindings of heavier main group elements. We hope that application of the kinetic stabilization to the chemistry of heavier π-electron systems will engender further progress in materials science.

## EXPERIMENTAL SECTION

*General procedures*: All experiments were performed under an argon atmosphere unless otherwise noted. All solvents were purified using standard methods and/or The Ultimate Solvent System (Glass Contour Systems, Laguna, CA) prior to use [24]. $^1$H NMR (300 MHz), $^{13}$C NMR (75 MHz), and $^{29}$Si NMR (59 MHz) spectra were measured in $C_6D_6$ using a spectrometer (JNM AL-300; JEOL). A signal attributed to $C_6D_5H$ (7.15 ppm) was used as an internal standard in $^1$H NMR spectra, and that attributed to $C_6D_6$ (128 ppm) was used in $^{13}$C NMR spectra. A signal attributed to $Si(CH_3)_4$ (0.0 ppm) was used as an external standard in $^{29}$Si NMR spectra. Multiplicity of signals in $^{13}$C NMR spectra was determined using DEPT technique. The UV–vis spectra were measured (Ubest V-570; Jasco Inc.). All melting points were determined on a micro melting point apparatus (Yanaco Group); they were uncorrected. Elemental analyses were conducted at the Microanalytical Laboratory of the Institute for Chemical Research, Kyoto University. Then Bbt(Br)Si=Si(Br)Bbt (**2**) was prepared according to the reported procedure [14].

*Synthesis of 1,2-bis(2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl)-disilyne (***1***)*: To a stirred suspension of **2** (118 mg, 0.0802 mmol) in 9 ml of THF/$Et_2O$ (1:9 mixture) was added 239 µl of *t*-BuLi (0.705 M in *n*-heptane, 0.168 mmol) at –85 °C. After stirring for 70 min, the suspension changed to a clear deep green solution. The temperature was increased to –60 °C, and the additional stirring for 30 min stirring gave an orange–red solution. Volatile contents were removed under vacuum at low temperature. The residue was dissolved in hexane and filtered over a pad of Celite®. Removal of the solvent gave a yellow solid in which **1** (85 %) and **2** (15 %) were observed with no side products. Dark yellow crystals of **1** (63.8 mg, 61 %) were obtained by fractional crystallization from *n*-heptane. Mp slowly decolorized over 120 °C; $^1$H NMR (300 MHz, $C_6D_6$) $\delta$ 0.35 [s, 54H, $C(Si\mathit{Me}_3)_3$], 0.38 [s, 72H, $CH(Si\mathit{Me}_3)_2$], 3.43 (s, 4H, C*H*Si), 6.99 (s, 4H, Ar*H*); $^{13}$C NMR (75 MHz, $C_6D_6$) $\delta$ 1.7 [$CH(Si\mathit{Me}_3)_2$], 5.5 [$C(Si\mathit{Me}_3)_3$], 23.0 [$\mathit{C}(SiMe_3)_3$], 40.9 ($\mathit{C}HSiMe_3$), 125.8 [Ar*C*(3,5)], 139.0 [Ar*C*(1)], 146.1 [Ar*C*(4)], 150.5 [Ar*C*(2,6))]; $^{29}$Si NMR (60 MHz, $C_6D_6$) $\delta$ 0.9 [$C(\mathit{Si}Me_3)_3$], 2.3 [$CH(\mathit{Si}Me_3)_2$], 18.8 (*Si Si*).

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16. When THF was used as a solvent, disilyne **1** was obtained with an unidentified side product that was difficult to separate. No such side product was observed with the THF/$Et_2O$ mixed solvent system.
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18. NMR spectral data of **5**: $^1$H NMR (300 MHz, $C_6D_6$): $\delta$ 0.23 (s, 18H), 0.32 (s, 18H), 0.36 (s, 18H), 0.36 (s, 54H), 0.43 (s, 18H), 1.97 (s, 2H), 5.93 (s, 2H), 6.95 (d, $^4J_{HH}$ = 1.8 Hz, 2H), 7.00 (d, $^4J_{HH}$ = 1.8 Hz, 2H); $^{13}$C NMR (75 MHz, $C_6D_6$): $\delta$ 1.05 (q), 1.52 (q), 1.60 (q), 2.28 (q), 5.13 (q), 22.73 (s), 24.39 (d), 29.63 (d), 124.57 (d), 128.01 (d), 133.62 (s), 148.12 (s), 148.38 (s), 157.26 (s); $^{29}$Si NMR (59 MHz, $C_6D_6$): $\delta$ –25.1, 0.76, 0.99, 1.05, 1.59, 3.59.
19. Crystal data for [**1**·$2C_7H_8$]: $C_{74}H_{150}Si_{16}$, M = 1489.38, $T$ = 103 (2) K, tetragonal, $P4_22_12$ (no. 94), 0.10 × 0.05 × 0.02 mm$^3$, $a = b$ = 16.6701(4) Å, $c$ = 33.7498(11) Å, $V$ = 9378.8(4) Å$^3$, $Z$ = 4, $D_{calc}$ = 1.055 g·cm$^{-3}$, $\mu$ = 0.252 mm$^{-1}$, $2\theta_{max}$ = 50.0, 70378 measured reflections, 8253 independent reflections ($R_{int}$ = 0.1966), 446 refined parameters, GOF = 1.026, $R_1$ = 0.0723 and w$R_2$ = 0.1497 [$I > 2\sigma(I)$], $R_1$ = 0. 1762 and w$R_2$ = 0.2028 (for all data), largest diff. peak and hole 0.401 and –0.574 e.Å$^{-3}$.
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