1,2-Dialkynyldisilenes: silicon analogues of (E)-enediyne[†]

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Reductions of bulky alkynyl-substituted dihalosilanes, BbtSiX₂(C \equiv CR) (Bbt = 2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl, R = SiMe₃ or Ph groups, X = halogen), with 2.0 equiv. of lithium naphthalenide gave the first stable 1,2-dialkynyl-substituted disilenes, which constituted extended π -conjugated systems between Si \equiv Si bond and ethynylene units.

Since the isolation of the first molecular compound with a Si=Si bond (disilene) by West et al. in 1981,¹ numerous disilenes that are kinetically stabilized by bulky substituents have been reported.² Recently, several new disilene systems have been designed and investigated to evaluate the conjugation between the Si=Si unit and the connected aryl sp²-carbon conjugated systems.³ Although those disilenes exhibited optically and electrochemically unique properties, such π -conjugated systems are structurally limited; on the other hand, a diverse array of all-the-carbon conjugated systems has been reported: for example, conjugated 3-ene-1,5-diyne units are important building blocks in the area of synthetic polymers and nanostructures using the electronic structures of alkynyl groups. Therefore, the synthesis and isolation of the alkynylsubstituted disilenes-the silicon analogues of enedivnes-are attractive from the viewpoint of elucidation of the conjugation between the Si=Si and sp-carbon units. We present herein the syntheses, structures, and properties of novel π -conjugated 1,2-dialkynyldisilenes.



Only one example of the heavier group 14 element (Si, Ge, Sn, Pb) analogues of eneyne derivatives has been reported in the literature. Weidenbruch *et al.* reported the synthesis and isolation of ethynylene-bridged bis(germaethene)s [Ar₂Ge=C(R)C = CC(R)=GeAr₂; Ar = 4,5,6-trimethyl-2-*tert*-butylphenyl, R = *n*-Bu or Ph] and experimentally revealed the π -conjugation between the Ge=C and C = C units.⁴ However, no dimetallene systems bearing (an) alkynyl

substituent(s) has been reported to date.⁵ Most likely, the difficulty of the synthesis and isolation of such metallenes is due to the inherent high reactivity of the dimetallene moiety toward an alkynyl substituent⁶ and the sterically small size of an alkynyl group as a steric protection group. We have synthesized and isolated the stable 1,2-dibromodimetallenes $[Bbt(Br)M=M(Br)Bbt, M = Si^7 \text{ or } Ge^8]$ and 1,2-diarylsubstituted dimetallynes (BbtM \equiv MBbt, M = Si⁷ or Ge⁹) by taking advantage of the effective steric protection group, 2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl (Bbt). All of them are highly reactive low-coordinated heavier group 14 element compounds. These results strongly suggest that the Bbt group can stabilize disilenes bearing a rather small substituent such as an alkynyl group. Based on this observation, we have initiated the syntheses of stable 1,2-dialkynyldisilenes, 1a and 1b, bearing Bbt groups.

To investigate the influence of the terminal groups, trimethylsilyl- and phenylethynylacetylene were used to synthesize the suitable precursors, dihalosilanes 7 and 8, the synthetic procedures of which are summarized in Scheme 1. In the reaction of **6a** with NBS in CCl_4 [conditions (f)], we expected the generation of dibromosilane 8a, but obtained only dichlorosilane 7a. In addition, the reaction of 6a with NCS in CCl₄ did not afford 7a.¹⁰ On the other hand, the reactions of 6a and 6b with NBS in benzene afforded the corresponding dibromosilanes 8a and 8b. As the final step, according to the well-established procedure for the syntheses of disilenes, dihalosilanes 7a, 8a, and 8b were reduced with 2.0 mol equiv. of lithium naphthalenide in THF at -78 °C to afford the title compounds, 1,2-diethynyldisilenes 1, as stable crystals (1a, yellow, 23% from 7a, 53% from 8a; 1b, orange, 41% from 8b) (Scheme 2).[‡] In their ¹³C NMR spectra, the signals assignable to the C \equiv C units of **1a** (112.2, 116.7 ppm) and 1b (95.0, 119.6 ppm) appeared in the lower field compared to the those of related enediyne frameworks $[e.g., (E)-R-C \equiv C-(H)C \equiv C(H)-C \equiv C-R: 102.9, 103.9 \text{ ppm}$ $(R = SiMe_3)$, 88.1, 94.9 ppm (R = Ph)].¹¹ In their ²⁹Si NMR spectra, the signals attributable to the sp^2 Si atoms of **1a** and 1b appeared at 44.6 and 42.6 ppm, respectively. To the best of our knowledge, these values are the most high-field shifted among those of the carbon-substituted and acyclic disilenes. For example, tetraaryl- and tetraalkyl-substituted, acyclic disilenes exhibited ²⁹Si NMR signals of their sp² Si atoms at 57-73 and 90-103 ppm,² respectively. Probably, the noticeable high-field shift of the central Si atoms in 1 results from the magnetic anisotropy effect of their $C \equiv C$ moieties. Actually, the high-field shift caused by the effect of an alkynyl group was observed for ²⁹Si NMR signals of sp³-silicon compounds [e.g., trimethylsilylacetylene $(-17.3 \text{ ppm in } C_6 D_6)$ compared with tetramethylsilane (0.0 ppm in C_6D_6)].

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Scheme 1 Preparation of alkynyl-substituted dihalosilanes 7 and 8. *Reagents and conditions: (a) tert*-BuLi (2.1 eq), THF, -78 °C. (*b*) HSi(OMe)₃, THF, -78 °C to r.t. (*c*) BBr₃ (1.0 eq), hexane, r.t. (*d*) RC \equiv CLi, THF, -50 °C. (*e*) LiAlH₄, Et₂O, 0 °C. (*f*) NBS, CCl₄, r.t. (*g*) NBS, benzene, 6 °C.

Crystals of 1a and 1b suitable for X-ray diffraction analysis were obtained by slow evaporation from benzene/THF and hexane solution, respectively. The molecular structures of 1a and 1b are presented in Fig. 1.§ Their structures have a centre and an axis of symmetry at the middle point of the Si1-Si1* bond. For 1b, the phenylethynyl groups were disordered with a 1:1 ratio (See Fig. S4, ESI⁺). The Si1-Si1^{*} bonds [1a: 2.202(2) Å, 1b: 2.1871(10) Å] are shorter than those reported for typical Si-Si single-bond compounds (2.33-2.37 Å)¹² and within the range reported for carbon-substituted disilenes.² The *trans*-bent angles, which are defined as angles between the respective axes of Si=Si bonds and the plane of $C(Ar_{inso})$ -Si(1)-C(1), were 8.9° (1a) and 11.3° (1b). The bond lengths of C(1)–C(2) [1a, 1.213(6) Å; 1b, 1.214(3) Å] are almost equal to that of the C(sp)-C(sp) bond in bis(trimethylsilyl)acetylene [1.208(3) Å].¹³ The structural parameters for the $C \equiv C - Si = Si - C \equiv C$ skeletons of **1a** and **1b** are almost identical and neither of them shows apparent elongation of their Si=Si and C \equiv C bonds. It is noteworthy that **1b** has sufficient planarity, giving rise to conjugation between the Si=Si bond and phenyl moieties.

In the UV-vis spectra of **1a** and **1b** in hexane, the longest absorption maxima (λ_{max}) of **1a** and **1b** appeared at 437 nm ($\varepsilon = 2.4 \times 10^4$) and 469 nm ($\varepsilon = 3.1 \times 10^4$), respectively (Fig. 2). Compared with λ_{max} of trimethylsilylethynylsubstituted disilene **1a**, that of the phenylethynyl-substituted disilene **1b** showed 32 nm of red-shift together with increased molar absorptivity. In addition, the λ_{max} of **1b** is longer than those of tetraaryl-substituted disilenes. For example, Mes₂Si=SiMes₂ and Tip₂Si=SiTip₂ exhibited their λ_{max} values at 420 and 432 nm, respectively.² These results strongly demonstrate the effective π -conjugation between the Si=Si unit and two phenyl groups of **1b** through the ethynylene moieties.

To evaluate the conjugation between the Si \equiv Si and C \equiv C (and Ph in 1b) moieties, DFT calculations were conducted

7a	Li ⁺ [C ₁₀ H ₈] ⁻	1a	9h	Li ⁺ [C ₁₀ H ₈] ⁻	1b
8a	THF	53% from 8a	on -	THF	41%

Scheme 2 Syntheses of 1,2-diethynyldisilenes 1.



Fig. 1 Thermal ellipsoid plots of **1a** (left) and **1b** (right) are shown at the 50% probability level. The hydrogen atoms and one part of disorders on the phenylethynyl groups in **1b** were omitted for clarity. Selected bond lengths (Å) and bond angles (°) for **1a**: Si1–Si1* 2.202(2), Si1–C1 1.811(4), Si1–C(Ar) 1.881(4), C1–C2 1.213(6), C2–Si2 1.842(5), Si1*–Si1–C1 116.04(15), Si1*–Si1–C(Ar) 131.80(14), C(Ar)–Si1–C1 111.18(17), Si1–C1–C2 176.4(4), C1–C2–Si2 176.2(4). For **1b**: Si1–Si1* 2.1871(10), Si1–C1 1.8029(19), Si1–C(Ar) 1.8899(17), C1–C2 1.214(3), Si1*–Si1–C1 115.98(7), Si1*–Si1–C(Ar) 131.53(6), C(Ar)–Si1–C1 110.94(8), Si1–C1–C2 175.65(17).



Fig. 2 UV-vis spectra of 1a (grey) and 1b (black) in hexane at room temperature.

using simplified models 1' bearing 2,6-dimethylphenyl groups instead of Bbt groups. The HOMO and LUMO of 1' are shown in Fig. 3. The HOMOs of 1a' and 1b' were found to localize not only on their π orbitals of Si=Si bonds, but also on the two ethynylene units. The HOMO and LUMO of 1b' spread to the phenyl rings through the ethynylene units. The TD-DFT calculations¹⁴ for 1a' and 1b' [TD-B3LYP/6-311+G(2df,2p)//B3LYP/6-31G(d)] indicated values of 449 nm (f = 0.4042; 1a') and 511 nm (f = 0.7021; 1b') for their HOMO-LUMO transitions, respectively, supporting the experimental results of UV/vis spectroscopy for 1a and 1b.¹⁵

In conclusion, we synthesized and isolated the first stable 1,2-dialkynyldisilenes 1 and elucidated their structures using X-ray crystallography. In the UV/vis spectrum of 1, the absorption maximum of 1b was remarkably more red-shifted than that of 1a, indicating the π -conjugation between the Si \equiv Si bond and phenyl groups through the C \equiv C bonds. This result was supported by the results of MO calculations of 1b. Notwithstanding the different energy levels of π -orbitals between Si \equiv Si and C \equiv C bonds, these showed that conjugation was possible between Si \equiv Si and C \equiv C units. With a view to developing the chemistry of novel π -conjugated systems containing (a) disilene unit(s), substitution reactions of the



Fig. 3 Plots of HOMOs (a, 1a'; c, 1b') and LUMOs (b, 1a'; d, 1b') at the B3LYP/6-31G(d) (isosurface at ± 0.02 a.u).

trimethylsilyl groups on the sp carbons of **1a** are currently being studied.

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Notes and references

[‡] Synthesis of diethynyldisilene 1a. To a solution of 8a (1.24 g, 1.36 mmol) in THF (15 ml) was added a THF solution of lithium naphthalenide (0.50 M, 5.5 mL, 2.7 mmol) dropwise at -78 °C. After stirring at -40 °C for 2 h, the reaction mixture was allowed to warm to room temperature and concentrated *in vacuo*. Hexane was added to the residue and filtered through a plug of Celite⁴⁸. The filtrate was dried under reduced pressure and recrystallized from hexane several times to afford 1a (536 mg, 0.358 mmol, 53%) as yellow crystals. Similarly, using 7a and 8b as starting materials, 1a and 1b were isolated, respectively, in 23% and 41% yields.

1a: yellow crystals; m.p. 251 °C (dec.); ¹H NMR (300 MHz, C₆D₆, 298 K): δ 0.14 (s, 18H), 0.40 (s, 90H), 0.48 (s, 36H), 3.28 (s, 4H), 7.04 (s, 4H); ¹³C NMR (75 MHz, C₆D₆, 298 K): δ –0.15 (q), 1.59 (q), 5.70 (q) 22.56 (d), 28.95 (d), 112.16 (s), 116.73 (s), 126.25 (s), 127.68 (d), 150.31 (s), 153.16 (s); ²⁹Si NMR (60 MHz, C₆D₆, 298 K): δ –19.0 (C=C-SiMe₃), 0.9 [C(SiMe₃)₃], 1.2 [CH(SiMe₃)₂], 2.7 [CH(SiMe₃)₂], 44.6 (Si=Si); HRMS (FAB) m/z calcd for C₇₀H₁₅₂Si₁₈ 1496.7741 ([M⁺]), found: 1496.7736 ([M⁺]); Anal. Calcd for C₇₀H₁₅₂Si₁₈: C, 56.07; H, 10.22. Found: C, 55.86; H, 10.05. UV/vis (hexane, r.t.): λ_{max} = 437 nm (ε = 2.4 × 10⁴).

b orange crystals; m.p. 280–282 °C; ¹H NMR (300 MHz, C₆D₆, 323 K): δ 0.40 (s, 72H), 0.43 (s, 54H), 3.39 (s, 4H), 6.86–6.96 (m, 6H), 7.08 (s, 4H), 7.41–7.47 (m, 4H); ¹³C NMR (100 MHz, C₆D₆, 323 K): δ 2.41 (q), 6.06 (q), 31.87 (d), 37.46 (d), 94.97 (s), 119.57 (s), 124.35 (s), 127.21 (d), 128.50 (d), 128.62 (d), 130.83 (s), 132.26 (d), 148.13 (s), 152.63(s); ²⁹Si NMR (60 MHz, C₆D₆, 343 K): δ 1.0 [C(*Si*Me₃)₃], 2.1 ([CH(*Si*Me₃)₂]), 42.6 (*Si*=*Si*); HRMS *m*/*z* calcd for C₇₆H₁₄₄Si₁₆: 1504.7576 ([M⁺]), Found: 1504.7594 ([M⁺]). UV/vis (hexane, r.t.): $\lambda_{max} = 469$ nm ($\epsilon = 3.1 \times 10^4$).

§ *Crystal data* for **1a**: $C_{70}H_{152}Si_{18}$, M = 1499.54; triclinic; space group P-1 (no. 2); a = 13.4469(16), b = 13.4846(13), c = 15.106(2) Å; $\alpha = 69.666(5)$, $\beta = 68.255(8)$, $\gamma = 72.742(8)^{\circ}$; V = 2340.9(5) Å³; Z = 1; $D_{calcd.} = 1.064$ g cm⁻³; $\mu = 0.277$ mm⁻¹; $2\theta_{max} = 50^{\circ}$; T = 103 K; $R_1 [I > 2\sigma(I)] = 0.0706$; wR_2 (all data) = 0.2022; GOF = 1.128 for 17115 reflections and 421 parameters.

Crystal data for **1b**: $C_{76}H_{144}S_{16}$, M = 1507.35; monoclinic; space group C2/c (no. 15); a = 32.0708(5), b = 13.4092(2), c = 23.4405(9) Å; $\beta = 114.0243(16)^{\circ}$; V = 9207.2(3) Å³; Z = 4; $D_{calcd.} = 1.087$ g cm⁻³; $\mu = 0.257$ mm⁻¹; $2\theta_{max} = 50^{\circ}$; T = 103 K; $R_1 [I > 2\sigma(I)] = 0.0322$; wR_2 (all data) = 0.0843; GOF = 1.019 for 38386 reflections and 477 parameters. CCDC 770194 and 770195.†

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