

Pentasila-1,4-diene: Homoconjugation between Si=Si Double Bonds via a SiMe₂ Unit

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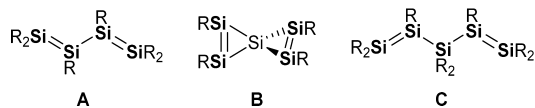
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S Supporting Information

ABSTRACT: Although the synthesis of several bis-(disilenes) has already been reported, the number of reported conjugation modes between the Si=Si double bonds remains limited. Herein, we report the properties of the stable pentasila-1,4-diene **1**, which was obtained from the reaction of two equivalents of disilenide **4** with dichlorodimethylsilane. The $\pi(\text{Si}=\text{Si}) \rightarrow \pi^*(\text{Si}=\text{Si})$ absorption band of **1** is considerably broadened and red-shifted compared to those of the corresponding monodisilene and hexasila-1,5-diene, but blue-shifted relative to those of typical tetrasila-1,3-dienes. The bathochromic shift and the broadening of the absorption band in **1** should be attributed to the homoconjugation between Si=Si double bonds through the SiMe₂ unit.

Conjugation is a key concept in the design of the molecular architecture of advanced functional materials. In addition to classic π -conjugation, various other modes of conjugation such as cross-,¹ homo-,² and spiroconjugation³ afford a rich diversity of molecular and electronic structures in π -electron systems. Recently, π -electron systems involving Si=Si double bonds (disilenes) have been considered as promising prospects for advanced functional π -electron systems, owing to the inherently narrow HOMO–LUMO gap in disilenes.⁴ Even though several stable compounds containing two or more Si=Si double bonds have been synthesized so far, modes of conjugation between the Si=Si double bonds have been restricted to π -conjugation between two directly connected Si=Si double bonds (A in Chart 1),^{5–8} or to spiro-conjugation

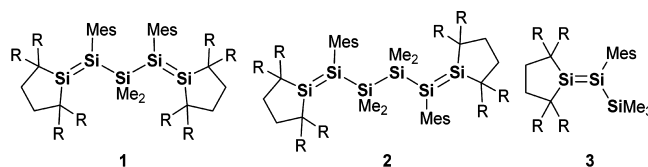
Chart 1. Conjugation Modes between Si=Si Double Bonds



(B), i.e., a through-space interaction between two perpendicularly arranged double bonds connected by a spiro center.⁹ Homoconjugation (C), i.e., the orbital overlap of two π -systems separated by a nonconjugating group such as CH₂² should also be possible for Si=Si double bonds, considering their similarity to π -electron systems based on elements of the second row. Nevertheless, compounds exhibiting such interactions still remain elusive,¹⁰ except for spiroconjugation (B), which constitutes a special case of homoconjugation within a spirocyclic structure.³ Significant homoconjugation between

Si=Si double bonds may thus represent another fundamental interaction in functional compounds based on Si=Si double bonds. Herein, we report the synthesis of stable pentasila-1,4-diene **1**, which bears two Si=Si double bonds separated by a SiMe₂ group (Chart 2). The red-shifted absorption band of **1**

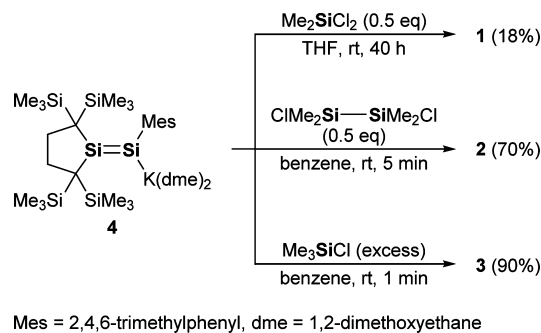
Chart 2. Pentasila-1,4-diene 1, Hexasila-1,5-diene 2, and Monodisilene 3 (R = SiMe₃, Mes = 2,4,6-trimethylphenyl)



relative to those of hexasila-1,5-diene **2** and monodisilene **3** indicates remarkable interactions between two Si=Si double bonds via the SiMe₂ unit, and thus constitutes the first example of homoconjugation between two Si=Si double bonds.

Air-sensitive red crystals of **1** were obtained in 18% yield from the reaction of two equivalents of disilenide **4**¹¹ with dichlorodimethylsilane in THF (Scheme 1). Scheschkewitz et

Scheme 1. Synthesis of Disilenes 1–3

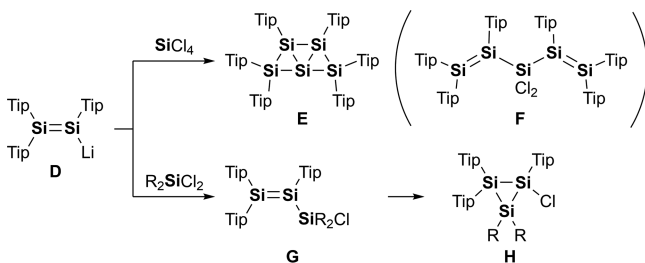


al. have reported that the reaction of triaryldisilenide **D** with silicon tetrachloride provided tricyclic siliconoid **E** instead of 3,3-dichloropentasila-1,4-diene **F**.^{12a} Conversely, the reaction with dichlorodimethylsilane affords chlorosilyldisilene **G**, which undergoes an isomerization in THF to furnish cyclotrisilane **H** (Scheme 2).^{12b} In our case, however, a similar isomerization to generate a cyclotrisilane was not observed, which is probably due to the steric bulk of the terminal R^H₂ groups (R^H₂ = 1,1,4,4-

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Scheme 2. Related Reactions of Triaryldisilenide D



Tip = 2,4,6-triisopropylphenyl, R = Me and Ph

tetrakis(trimethylsilyl)butane-1,4-diyl). Disilenide **4** can also be used to synthesize **2** (70%) and **3** (90%), which were obtained as orange and yellow crystals, respectively.¹³ The molecular structures of **1–3** were unequivocally determined by a combination of multinuclear NMR spectroscopy, mass spectrometry, and single-crystal X-ray diffraction (XRD) analysis.

The molecular structures of **1–3**, derived from XRD analyses, are shown in Figures 1 and S26. The five silicon

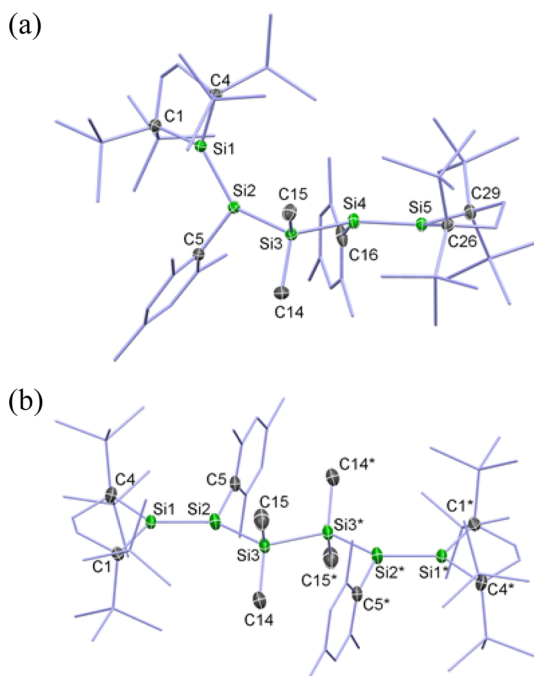


Figure 1. ORTEP representations of (a) **1** and (b) **2** (atomic displacement parameters set at 50% probability; hydrogen atoms omitted for clarity). Selected bond lengths (Å) and angles (deg) for **1**: Si1–Si2 2.2089(6), Si2–Si3 2.3710(6), Si3–Si4 2.3711(6), Si4–Si5 2.2032(6), Si1–Si2–Si3 128.42(2), Si2–Si3–Si4 106.57(2), Si3–Si4–Si5 132.07(2), Si1–Si2–Si3–Si4 –99.06(3), Si2–Si3–Si4–Si5 167.34(3). Selected bond lengths (Å) and angles (deg) for **2**: Si1–Si2 2.1918(12), Si2–Si3 2.3702(12), Si3–Si3* 2.3753(16), Si1–Si2–Si3 128.55(5), Si2–Si3–Si3* 108.80(6), Si1–Si2–Si3–Si3* 177.06(6), Si2–Si3–Si3*–Si2* 180.00.

atoms of the silicon backbone in **1** adopt an anticlinal-antiperiplanar conformation with dihedral Si1–Si2–Si3–Si4 and Si2–Si3–Si4–Si5 angles of –99.06(3)° and 167.34(3)°,¹⁴ respectively. In contrast, the silicon backbone in **2** adopts an all-*anti*-conformation. The Si=Si double bond distances in **1** [Si1=Si2: 2.2089(6) Å; and Si4=Si5: 2.2032(6) Å] are

slightly longer than those in **2** [2.1918(12) Å] and **3** [2.1794(6) Å], and comparable to those of typical disilenes (2.16–2.25 Å).⁴ The two Si=Si double bonds in **1** are in close spatial proximity with respect to each other, which is evident from the distance between neighboring three-coordinate silicon atoms [Si2⋯Si4 = 3.8013(7) Å]. This distance is much shorter than those in spiropentasiladiene **B** [Chart 1, R = Si(*t*-BuMe₂Si)₃, 4.322(3) Å]⁶ and **2** [Si2⋯Si2' = 5.947(1) Å], as well as the sum of the van der Waals radii (4.2 Å).¹⁶ The two Si=Si double bonds in **1** are twisted relative to each other, i.e., an angle of 72° was observed between the π -orbital axis vectors (POAVs)¹⁷ on Si2 and Si4 (Figure S29). The mesityl rings in **1–3** are aligned almost perpendicularly with respect to the Si=Si double bonds (84–88°).¹⁸

The NMR spectra of **1** in C₆D₆ showed two equivalent spectra of **1** in C₆D₆ showed two equivalent disilene moieties (R^H₂Si=SiMes) on the NMR time scale, as evident from the relative intensities of the ¹H NMR signals. This result suggests facile rotation around the Si(Mes)–SiMe₂ bonds in **1** in solution. The silicon backbone in **1** afforded three ²⁹Si resonance signals at 166.1 (R^H₂Si=), 43.0 (=SiMes–), and –16.4 (SiMe₂) ppm.

The UV–vis absorption spectra of **1** in hexane revealed remarkable interactions between the two Si=Si double bonds. In the visible region, two absorption bands were observed at $\lambda_{\text{abs}} = 445$ nm and $\lambda_{\text{abs}} = 368$ nm (Figure 2). The longest-

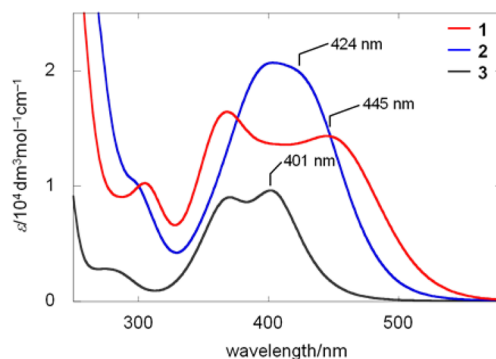


Figure 2. UV–vis absorption spectra of **1** (red), **2** (blue), and **3** (black) in hexane.

wavelength absorption band of **1** at $\lambda_{\text{max}} = 445$ nm is thereby considerably red-shifted relative to those of monodisilene **3** ($\lambda_{\text{max}} = 401$ nm) and bis(disilene) **2** ($\lambda_{\text{max}} = \sim 424$ nm), whereas it is blue-shifted with respect to those of typical tetrasil-1,3-dienes ($\lambda_{\text{max}} = 510$ –531 nm).⁵ The longest-wavelength absorption band of **1** is moreover broadened and tails up to 550 nm, suggesting the contribution of several transitions from the Si=Si double bonds. This spectral feature suggests homoconjugation between the two Si=Si double bonds in **1**. Replacement of the SiMe₂ unit in **1** with (SiMe₂)₂ in **2** induces a blue-shift of this absorption band, which is indicative of reduced interactions between the Si=Si double bonds in **2**.

The nature of the absorption bands of **1** was also examined by theoretical calculations on **1–3** (for details, see SI). Structures of **1–3** were optimized at the B3PW91-D3/6-31G(d) level of theory (**1**_{opt}–**3**_{opt}) and are in good agreement with those obtained from the XRD analysis (for details, see SI). The band positions and intensities determined by TD-DFT calculations on the optimized structures also fitted well with those obtained from the experimental spectra (Figure 3a and

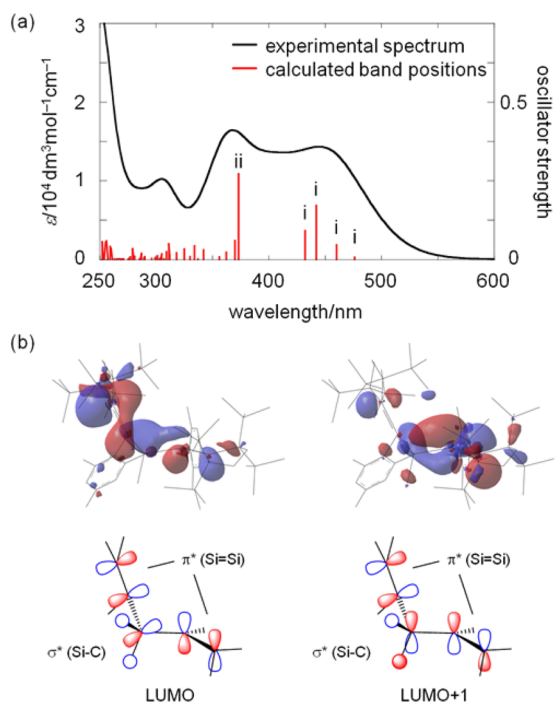


Figure 3. (a) Experimental UV–vis absorption spectrum (black) and calculated band positions (red) of **1**. i, $\pi(\text{Si}=\text{Si})\rightarrow\pi^*(\text{Si}=\text{Si})$ transition; ii, $\pi(\text{Si}=\text{Si})\rightarrow\pi^*(\text{Mes})$ transition. (b) LUMO and LUMO+1 of **1**_{opt} (isosurface value = 0.03). Hydrogen atoms are omitted for clarity.

Figure S32), suggesting that the structures of **1–3** in the crystalline state are also the predominant ones in solution. The frontier orbitals of **1**_{opt} are two split $\pi^*(\text{Si}=\text{Si})$ orbitals (LUMO and LUMO+1; Figure 3b) and two virtually degenerate $\pi(\text{Si}=\text{Si})$ orbitals (HOMO and HOMO–1; Figure S33). The splitting of the $\pi^*(\text{Si}=\text{Si})$ orbitals should result from the effective interactions between the two $\pi^*(\text{Si}=\text{Si})$ orbitals via the $\sigma^*(\text{Si}-\text{C})$ orbitals (Figure 3b). The degeneration of the $\pi(\text{Si}=\text{Si})$ orbitals is probably due to the large energy difference between the $\pi(\text{Si}=\text{Si})$ and the $\sigma^*(\text{Si}-\text{C})$ orbitals relative to that between the $\pi^*(\text{Si}=\text{Si})$ and the $\sigma^*(\text{Si}-\text{C})$ orbitals. Judging from the comparison between the experimentally observed and theoretically calculated UV–vis spectra, the broad absorption band at $\lambda_{\text{abs}} = 445 \text{ nm}$ (**1**) was assigned to the overlap of four $\pi\rightarrow\pi^*$ transitions of the $\text{Si}=\text{Si}$ double bonds (assignment i in Figure 3a), whereas the band at $\lambda_{\text{abs}} = 368 \text{ nm}$ was assigned to an intramolecular charge-transfer (ICT) transition from the $\pi(\text{Si}=\text{Si})$ to the $\pi^*(\text{mesityl})$ orbital (assignment ii).¹⁹ These features contrast sharply to those of **2**_{opt}. The frontier orbitals of **2**_{opt} are degenerated $\pi(\text{Si}=\text{Si})$ and $\pi^*(\text{Si}=\text{Si})$ orbitals, which indicates the absence of significant interactions between the two remote $\text{Si}=\text{Si}$ double bonds (Figure S33).²¹ The absorption band of **2** was assigned to a mixture of the $\pi\rightarrow\pi^*$ transition of the $\text{Si}=\text{Si}$ double bonds, the ICT transition from the disilene to the mesityl group, and the $\pi(\text{Si}=\text{Si})\rightarrow\sigma^*(\text{Si}-\text{C})$ transition.¹⁹ Based on these results, the remarkably broadened and red-shifted absorption band observed for **1** should be attributed to effective interactions between the two $\pi^*(\text{Si}=\text{Si})$ orbitals via the $\sigma^*(\text{Si}-\text{C})$ orbitals, i.e., a homoconjugation between the two $\text{Si}=\text{Si}$ double bonds (Figure 3b).²⁴

In conclusion, we synthesized pentasila-1,4-diene **1**, which represents the first example for homoconjugation between $\text{Si}=\text{Si}$

Si double bonds via a SiMe_2 group. The longest-wavelength absorption band of **1** is broadened and red-shifted relative to those of monodisilene **3** and hexasila-1,5-diene **2**, which is due to the homoconjugation between the two $\text{Si}=\text{Si}$ double bonds. However, this absorption band of **1** is also blue-shifted relative to those of typical tetrasila-1,3-dienes, indicating that although homoconjugation between the two $\text{Si}=\text{Si}$ double bonds via the SiMe_2 moiety is weaker than direct π -conjugation, it is still significant. Thus, homoconjugation should henceforth be considered a key interaction in functional compounds based on $\text{Si}=\text{Si}$ double bonds.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b11912.

Experimental and theoretical details (PDF)

Crystallographic data for **1–4** and a starting material (CIF)

NMR data (ZIP)

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Notes

The authors declare no competing financial interest.

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(11) Initially, we investigated reactions between potassium trialkyldisilene $K^+[R^H_2Si=Si(t-Bu)]^-$ ($R^H_2 = 1,1,4,4$ -tetrakis(trimethylsilyl)butane-1,4-diyl); for details, see: Iwamoto, T.; Kobayashi, M.; Uchiyama, K.; Sasaki, S.; Nagendran, S.; Isobe, H.; Kira, M. *J. Am. Chem. Soc.* **2009**, *131*, 3156.) and dichlorodimethylsilane, as alkyl-substituted pentasila-1,4-dienes should allow an investigation into the intrinsic electronic effects of homoconjugation. However, these reactions afforded only complex mixtures, probably due to steric and electronic reasons. Subsequently, we developed dialkyldisilene **4**, which contains an aryl group on the anionic silicon atom (for synthetic details on **4**, see: [Supporting Information](#)).

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(13) Even though tetrasilabutadienes of the type $R^H_2Si=Si(Mes)-Si(Mes)=SiR^H_2$ ($R^H_2 = 1,1,4,4$ -tetrakis(trimethylsilyl)butane-1,4-diyl) should be useful for a comparison of the electronic structure, their attempted synthesis was unsuccessful so far.

(14) The corresponding carbon-based parent compound 1,4-pentadiene has three conformational isomers (C_2 , C_1 , and C_s).¹⁵ We confirmed that the parent pentasila-1,4-diene also adopts these C_2 , C_1 , and C_s isomers (dihedral angles of the silicon backbone: $-94^\circ/-94^\circ$ (C_2), $-97^\circ/97^\circ$ (C_1), and $-90^\circ/-2^\circ$ (C_s); for details, see: [SI](#)). The large deviation of **1** from the ideal conformations should be due to the severe steric repulsion between the two bulky mesityl and the eight trimethylsilyl groups.

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(18) The dihedral angle is defined as the angle between the two axes that bisect the $Si(sp^2)-Si(sp^2)-Si(sp^3)$ and $C(sp^2)-C(ipso)-C(sp^2)$ angles viewed along the $Si(sp^2)-C(ipso)$ bond axis.

(19) The absorption band of **1** observed at 368 nm in hexane (dielectric constant: 1.88)²⁰ was red-shifted to 371 nm in *o*-dichlorobenzene (*o*DCB, dielectric constant: 9.93),²⁰ which is indicative of an ICT character of this band, whereas the band position at 445 nm remained unchanged in *o*DCB ([Figure S31a](#)). For **2**, the shape of the broadened absorption band changed slightly in *o*DCB ([Figure S31b](#)), which also suggests a at least partial ICT character for this band. The observed solvatochromism of **1** and **2** is consistent with the results of the theoretical study, which also suggested ICT character.

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(21) In the all-*anti* conformation of the silicon backbone in **2**, which is suitable for conjugation between the $\sigma(Si-Si)$ orbitals,^{22,23} two $\pi(Si=Si)$ orbitals are arranged almost perpendicular to the $\sigma(Si-Si)$ orbital of the central disilanyl moiety, which is not a suitable geometry for effective conjugation between two $\pi(Si=Si)$ orbitals through the $\sigma(Si-Si)$ orbital ([Figure S34](#)). The UV-vis absorption spectrum of **2** also shows an intense shoulder at ~ 260 nm ([Figure S32a](#)), which is

close to that of a conformationally controlled peralkylhexasilanes bearing an all *anti/transoid*-conformation (267 nm).²³

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(24) Redox potentials should be another good indicator for homoconjugation. However, all attempts to measure the redox potentials of **1**–**3** by cyclic voltammetry were unfortunately unsuccessful.