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Anthryl-Substituted Trialkyldisilene Showing Distinct Intramolecular Charge-Transfer Transition

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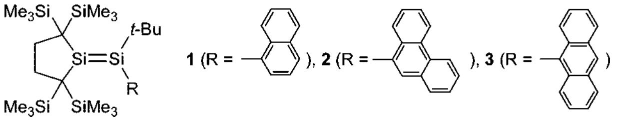
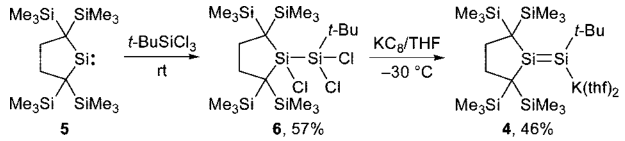
Although many stable disilenes hitherto reported[1] have organic π-electron systems as bulky sterically protecting substituents, very few studies have been directed toward understanding the characteristics of the electronic communication including conjugation and intramolecular charge transfer (ICT) interaction between a Si=Si double bond (πSi) and a carbon π-electron system (πC).[2] All known disilenes bound to πC systems have multiple πSi−πC interactions and, hence, are not suitable for defining the nature of a single πSi−πC interaction.[2] We would like to report the synthesis and properties of a series of trialkyldisilenes with single polycyclic aromatic substituents **1**−**3**.[3] These disilenes allowed elucidation of the unprecedented ICT interaction between πSi and πC systems, while no appreciable πSi−πC conjugation is expected because of their mutually perpendicular arrangement. Anthryl-substituted disilene **3** having a low-lying π*(aryl) LUMO showed a distinct ICT absorption band due to the charge transfer from a πSi donor to a πC acceptor.



To synthesize disilenes **1**−**3**, new disilenide **4** was prepared by reduction of trichlorodisilane **6**, which was obtained from isolable dialkylsilylene **5**[4] and t-BuSiCl$_3$,[5] with excess KC$_8$ in THF (Scheme 1).[6,7] While stable disilenides have been extensively investigated by Scheschkewitz[8] and Sekiguchi et al.,[9] **4** is unique in that it is a trialkyldisilenide without any π substituents.

Scheme 1



Disilenes **1**−**3** were synthesized by reactions of **4** with the corresponding aryl bromides.[6] Recrystallization from diethyl ether at −30 °C gave air-sensitive colored crystals of disilenes: 1-naphthyldisilene **1** (10%, yellow), 9-phenanthryldisilene **2** (20%, yellow), and 9-anthryldisilene **3** (41%, blue-purple).[10]

Molecular structures of disilenes **1**−**3** determined by X-ray analysis are shown in Figure 1.[6] All disilenes have a *trans*-bent geometry around the Si=Si double bond with bent angles[11] of 23.8° and 12.2°, 26.7° and 12.9°, and 11.4° and 6.9° around Si1 and Si2 atoms of **1**, **2**, and **3**, respectively. The Si=Si bond lengths [2.1943(14), 2.209(2), and 2.1754(12) Å for **1**−**3**] are in the region of those for typical acyclic disilenes.[1] It should be noted that disilene π (πSi) and aromatic π (πC) systems are almost perpendicular to each other with a dihedral angle δ[11] of 83°, 80°, and 88° for **1**, **2**, and **3**.

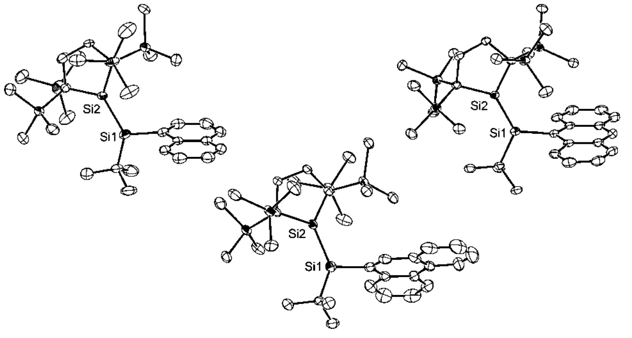


Figure 1. Molecular structures of **1** (left), **2** (middle), and **3** (right). Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity.

Disilenes **1** and **2** in 3-methylpentane show similar three absorption bands (bands I−III) in the UV−vis region as typically shown for **1** in Figure 2a.[12] Band I having fine structures is observed at 287 and 304 nm for **1** and **2**, respectively, and assignable to the ^1L_a band of the corresponding πC systems because the reported ^1L_a band maxima of 1-(pentamethyldisilanyl)naphthalene and 9-(pentamethyldisilanyl)phenanthrene are 287 and 302 nm.[13] The other two major bands of **1** and **2** (bands II and III) are very similar to each other, and hence, these bands are assigned to the transition originating from the common disilene moiety; λ_{max}/nm 342 and 376 for **1** and 343 and 378 for **2**.[14] An apparent spectral feature of anthryldisilene **3** is very different from those of **1** and **2** as shown in Figure 2b, but the intense structured band between 320 and 450 nm with an ε of 19.7 × 10^3 is regarded as band I overlapped with bands II and III, because the ^1L_a band of 9-(pentamethyldisilanyl)anthracene appears at 373 nm with an ε of 8.42 × 10^3.[13] All these spectral features are in good accord with the picture that the πSi and πC systems are independent of each other and there is no significant conjugation between the two π systems, as expected by the mutually perpendicular arrangement of the two π systems.

A noticeable spectral feature of **3** is the presence of a weak but distinct absorption band at 525 nm (ε 420) in 3-methylpentane (band IV), which red-shifts to 535 nm (ε 480) in more polar 1,2-dichlorobenzene,[15] suggesting the ICT nature of this band.

To elucidate the nature of the absorption bands of **1**−**3**, DFT calculations at the B3LYP/6−311G(d) level[16] are carried out for model compounds **1′**−**3′**, where SiMe$_3$ groups in **1**−**3** are replaced by SiH$_3$ groups. The molecular structures of disilenes **1**−**3**

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determined by X-ray crystallography are reproduced well in optimized structures of **1′**−**3′**. The almost perpendicular geometry between the Si=Si bond and aromatic π plane in **1′**−**3′** (δ 82°, 81°, and 83° for **1′**, **2′**, and **3′**) supports compounds **1**−**3** having similar perpendicular geometry even in solution. Frontier Kohn−Sham orbitals of **1′**−**3′** are almost pure π and π* orbitals of disilene and aryl moieties, and their energy levels are almost the same as those of the component πSi and πC systems,[16] indicating no significant conjugative interaction between the two π systems (Figure 3). The calculated absorption maxima and oscillator strengths of **1′**−**3′** using the TD-DFT method show good qualitative agreement with those of **1**−**3**: the band positions and relative intensities for **1′** and **3′** are shown using vertical bars in Figure 2.

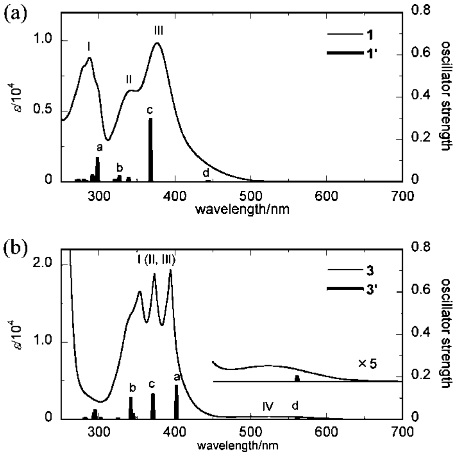

Figure 2. UV−vis spectra of (a) **1** and (b) **3** in 3-methylpentane at 298 K superimposed by the calculated band positions of **1′** and **3′**. Selected theoretical transitions: a: π(aryl)→π*(aryl), b: π(Si=Si)→σ*(ring Si−C), c: π(Si=Si)→π*(Si=Si), d: π(Si=Si)→π*(aryl).

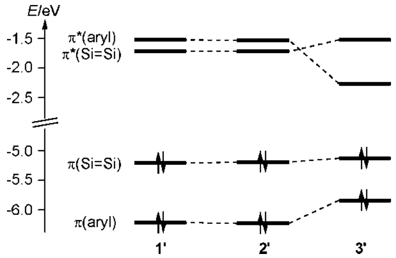

Figure 3. Orbital energy diagram of aryldisilenes **1′**−**3′** calculated at the B3LYP/6−311++G(d,p)//B3LYP/6−311G(d) level.

Judging from the comparison between experimental and theoretical UV−vis spectra, bands I, II, and III of disilenes **1**−**3** are assignable to transitions a [π(aryl)→π*(aryl)], b [π(Si=Si)→σ*(ring Si−C)], and c [π(Si=Si)→π*(Si=Si)]. Theoretical calculations confirm that the broad 320−450 nm band of **3** is due to the overlap of bands a, b, and c. The weak absorption at 525 nm of **3** (band IV) is assigned as an ICT transition from π(Si=Si) to π*(aryl) orbitals (transition d). Because similar πSi→π*C ICT transition bands are predicted at 444 and 444 nm for **1′** and **2′**, the broad tails of band III of **1** and **2** may be assigned to the ICT absorption bands. The absorption spectra of **1**−**3** suggests that a πC system having a lower-lying π* LUMO such as anthracene and longer acenes is indispensable for a distinct longer-wavelength ICT band.[17]

The present study offers a guideline to designing unique materials showing effective ICT interaction between a πSi donor and a πC acceptor.[18]

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Supporting Information Available: Experimental details for **1**−**4**, details for the calculations of **1′**−**3′** and related compounds, and X-ray crystallographic data of **1**−**4** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(1) For recent comprehensive reviews of disilenes, see: (a) Okazaki, R.; West, R. *Adv. Organomet. Chem.* **1996**, *39*, 231. (b) Weidenbruch, M. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; John Wiley & Sons: Chichester, U.K., 2001; Vol. 3, p 391. (c) West, R. *Polyhedron* **2002**, *21*, 467. (d) Kira, M.; Iwamoto, T. *Adv. Organomet. Chem.* **2006**, *54*, 73.

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(5) Ishida, S.; Iwamoto, T.; Kabuto, C.; Kira, M. *Silicon Chem.* **2003**, *2*, 137.

(6) For details of synthesis and X-ray analysis of **1**−**4**, see Supporting Information.

(7) In the solid state, disilenide **4** adopts a dimeric structure with a four-membered ring made of Si(sp^2)−K−Si(sp^2)−K atoms, while disilenides reported by Scheschkewitz[8] and Sekiguchi et al.[9] are monomeric.

(8) Scheschkewitz, D. *Angew. Chem., Int. Ed.* **2004**, *43*, 2965.

(9) (a) Ichinohe, M.; Sanuki, K.; Inoue, S.; Sekiguchi, A. *Organometallics* **2004**, *23*, 3088. (b) Inoue, S.; Ichinohe, M.; Sekiguchi, A. *Chem. Lett.* **2005**, *34*, 1564. (c) Ichinohe, M.; Sanuki, K.; Inoue, S.; Sekiguchi, A. *Silicon Chem.* **2005**, *3*, 111.

(10) The reaction of **4** with bromobenzene gave a complex mixture.

(11) Bent angle is defined as the angle between the axis through the Si=Si bond and R−Si(sp^2)−R plane, and dihedral angle δ is defined as the angle between the two axes that bisect Si(sp^2)−Si(sp^2)−C(*t*-Bu) and C(sp^2)−C(ipso)−C(sp^2) angles as viewed along the Si(sp^2)−C(aryl) bond axis.

(12) See Supporting Information for details of UV−vis spectrum of **2**.

(13) The $\lambda_{\max}$ (ε) of the ^1L_a of 1-naphthyl-, 9-phenanthryl-, and 9-anthryl-substituted pentamethyldisilanes are reported to be 287 nm (9.94×10^3), 302 nm (1.62×10^4), and 373 nm (8.42×10^3), respectively. Shizuka, H.; Sato, Y.; Ueki, Y.; Ishikawa, M.; Kumada, M. *J. Chem. Soc., Faraday Trans. 1* **1984**, *80*, 341.

(14) Tetraalkyldisilene $[(Me_3Si)_2CH]_2Si{=}Si[CH(SiMe_3)_2]_2$ shows two absorption bands: $\lambda_{\max}$ (ε), 357 nm (8.6×10^3), 390 nm (12.6×10^3). Masamune, S.; Eriyama, Y.; Kawase, T. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 584.

(15) Dielectric constants are 1.84 for 3-methylpentane and 9.93 for 1,2-dichlorobenzene. Christian, R. In *Solvent and Solvent Effects in Organic Chemistry*; Wiley-VCH, New York, 2004; p 472. Disilene **3** decomposed in CH_3CN.

(16) See Supporting Information for details of calculations for **1′**−**3′** and related compounds.

(17) Dabestani, R.; Ivanov, I. N. *Photochem. Photobiol.* **1999**, *70*, 10.

(18) Preliminarily, when band I of **3** was excited in hexane, emission from anthryl ππ* state was observed at 415 nm with a lower quantum yield (0.14) than that for 9-anthrylpentamethyldisilane (0.73).[13] Excitation of the ICT band showed no emission.

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