Angewandte Chemie

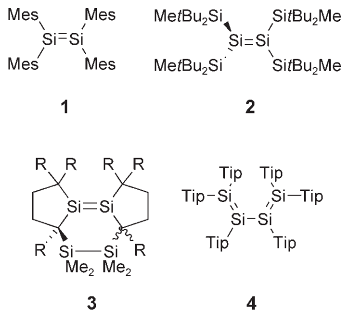
DOI: 10.1002/anie.200701744

VIP Silicon–Silicon Double Bonds

Two Si–Si Double Bonds Connected by a Phenylene Bridge**

*Iulia Bejan and David Scheschkewitz**

The chemistry of disilenes, that is, compounds with Si–Si double bonds,[1] has developed explosively since the discovery of the first stable derivative **1** by West, Michl, and Fink in 1981.[2] Compared to their carbon analogues, disilenes are characterized by a smaller gap between the highest occupied and lowest unoccupied molecular orbitals (HOMO–LUMO gap).[1a] The corresponding π–π* transition is responsible for the intense color of disilenes, which distinguishes them from the often colorless olefins. Moreover, disilenes exhibit considerable conformational flexibility.[1a] This flexibility can have enormous impact on the HOMO–LUMO gap, as demonstrated by the blue, twisted disilene **2**[3] and by the isomeric disilenes *cis*-**3** (yellow) and *trans*-**3** (red) with differing degrees of *trans* bending (Scheme 1).[4]

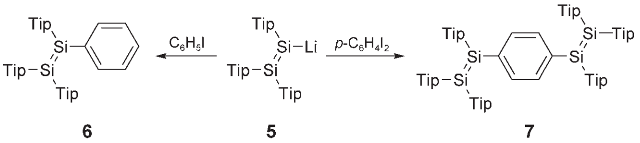


Scheme 1. Mes = 2,4,6-$Me_3C_6H_2$, R = $SiMe_3$, Tip = 2,4,6-$iPr_3C_6H_2$.

In the case of carbon compounds, it is textbook knowledge that the HOMO–LUMO gap is lowered by conjugation of double bonds; this principle underlies charge transport in conducting and semiconducting organic polymers.[5] In light of the peculiarities discussed above, interesting electronic and optical properties can be expected for conjugated systems containing Si–Si double bonds. The synthesis of the first tetrasilabutadiene **4** by Weidenbruch et al. was a breakthrough in this regard.[6a] Tetrasilabutadienes exhibit a considerable red shift of the π–π* transition by about 100 nm with respect to the corresponding disilenes.[6] Other noteworthy compounds with two Si–Si π bonds include a trisilaallene,[7] a spiro-conjugated pentasiladiene,[8] and a disilyne.[9]

Conversely, compounds with phenylene-bridged Si–Si double bonds have not been reported to date. In the case of carbon, poly(phenylenevinylene)s (PPVs) have attracted much interest owing to their electroluminescent properties and the resulting applications in organic light emitting devices.[10] Recently, in groundbreaking work by the groups of Protasiewicz and Gates, PPV analogues based on P=P and P=C fragments have been synthesized.[11] Herein, we report the remarkable, straightforward synthesis of a compound containing two Si–Si double bonds linked by a phenylene moiety, that is, a model system for hitherto unknown Si=Si-containing PPV analogues.[12]

Silyl anions have only occasionally been arylated by reaction with halogenated arenes.[13] Nonetheless, the successful application of disilenides, that is, disila analogues of vinyl anions, as transfer reagents for Si–Si double bonds,[14] encouraged us to investigate their behavior towards iodoarenes. To test the feasibility of our approach, we treated **5**[15] in benzene with one equivalent of iodobenzene at room temperature (Scheme 2). No color change of the orange reaction mixture was observed. However, ^{29}Si NMR signals at $\delta = 71.76$ and 55.23 ppm showed the quantitative formation of a new Si=Si-containing species, which was identified as the anticipated phenyl-substituted disilene **6** by NMR and UV/Vis spectroscopy and isolated as yellow crystals from hexane in 58 % yield (m.p. 156–157 °C, dec.).



Scheme 2. Syntheses of **6** and **7**. (Details are given in the Supporting Information.)

Encouraged by this result, we tried the reaction of two equivalents of **5** with *para*-diiodobenzene under identical conditions (Scheme 2). An immediate color change from orange to dark red occurred. The only detectable product exhibited ^{29}Si NMR resonances at $\delta = 70.73$ and 56.79 ppm, very similar to those of **6**. Phenylene-bridged tetrasiladiene **7** crystallized from pentane in 72 % yield (dec. 190 °C). Its constitution was deduced from the simple ^{1}H and ^{13}C NMR spectra indicating a *para*-disubstituted benzene moiety.

UV/Vis spectroscopy (Figure 1) revealed a large red shift of $\Delta\lambda = 69$ nm of the longest wavelength absorption of **7**

---

[*] Dipl.-Chem. I. Bejan, Dr. D. Scheschkewitz
Institut für Anorganische Chemie
Julius-Maximilians-Universität Würzburg
Am Hubland, 97074 Würzburg (Germany)
Fax: (+49) 931-888-4623
E-mail: scheschkewitz@mail.uni-wuerzburg.de
Homepage: http://www-anorganik.chemie.uni-wuerzburg.de/

[**] Funding by the DFG (Sche 906/3-1), the Fonds der Chemischen Industrie and the Dr. Otto-Röhm-Gedächtnis-Stiftung is gratefully acknowledged. We thank Prof. K. Klinkhammer for stimulating discussions, Prof. H. Braunschweig for generous support, and Dr. R. Bertermann for NMR spectroscopy.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

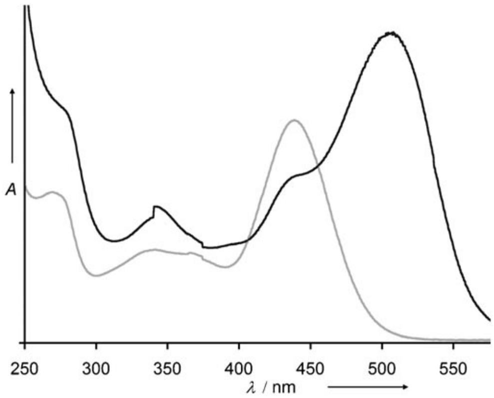


Figure 1. Normalized UV/Vis spectra of **6** (gray) and **7** (black) in hexane at 25 °C.

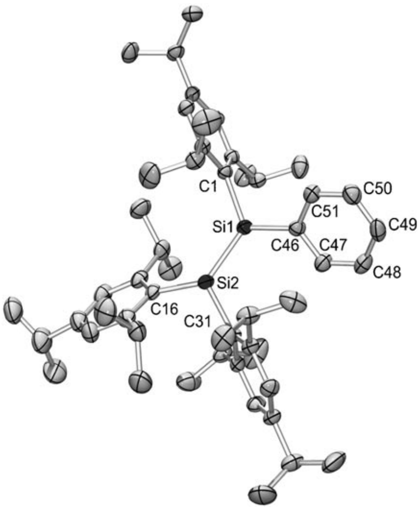


Figure 2. Crystal structure of **6**. Thermal ellipsoids are set at 50% probability. Hydrogen atoms and the second molecule in the asymmetric unit are omitted for clarity. Selected bond lengths [pm]: Si1–Si2 217.54(11), Si1–C46 187.3(3), Si1–C1 188.4(2), Si2–C16 189.5(3), Si2–C31 189.8(2).

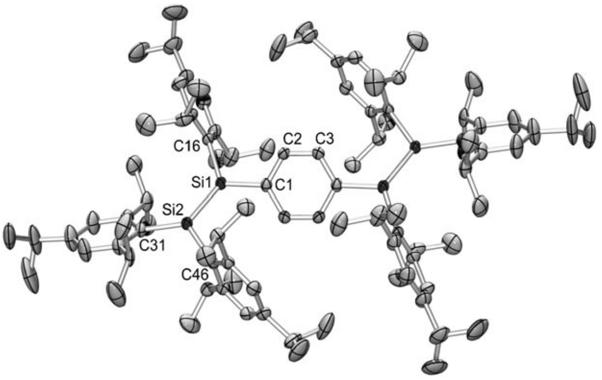


Figure 3. Crystal structure of **7** in the solid state. Thermal ellipsoids are set at 50% probability. Disordered *i*Pr groups, cocrystallized C_6H_6, and hydrogen atoms are omitted for clarity. Selected bond lengths [pm]: Si1–Si2 216.74(8), Si1–C1 187.00(19), Si1–C16 188.36(19), Si2–C46 188.73(19), Si2–C31 189.1(2), C1–C2 139.7(3), C2–C3 138.6(3), C1–C3′ 140.0(3).

($\lambda_{max} = 508$ nm, $\log\varepsilon = 4.45$) compared to that of **6** ($\lambda_{max} = 439$ nm, $\log\varepsilon = 4.28$). The value is similar to that of tetrasilabutadiene **4** ($\lambda_{max} = 518$ nm) without a phenylene linker between the Si=Si double bonds.[6a] As mentioned above, the narrowing of the HOMO–LUMO gap associated with such a red shift is widely accepted as evidence for conjugation.[1a,10,11] Moreover, the significantly higher extinction coefficient of the longest wavelength absorption of **7** replicates observations for phenylene-bridged P=P systems as well as those for corresponding carbon-based derivatives of 1,4-divinylbenzene.[11c] As is common for disilenes, both **6** and **7** exhibit thermochromic behavior. Especially the reversible color change of solid **7** from red at room temperature to almost black at 160 °C is noteworthy. The reversibility of this process was confirmed by NMR spectra of the heated sample and by differential scanning calorimetry, which shows exothermic decomposition of **7** only above 190 °C.

The structures of **6** and **7** in the solid state were determined by X-ray diffraction on single crystals[16] (Figures 2 and 3). Their comparison with regard to possible conjugation should be carried out with caution because of the aforementioned conformational flexibility of Si=Si double bonds. The Si=Si bond of disilene **6** (217.54(11) pm) is actually slightly longer than that of the phenylene-bridged tetrasiladiene **7** (216.74(8) pm). This somewhat counterintuitive observation can be rationalized by taking into account the more pronounced *trans* bending of **6** as indicated by the β values, defined by the angle between the Si=Si bond vector and the planes spanned by a Si atom and the pendant *ipso* C atoms (**6**: Si1 23.6(3)°, Si2 22.3(3)°; **7**: Si1 16.5(2)°, Si2 19.3(2)°). In fact, to our knowledge **6** and **7** represent the most *trans*-bent stable disilenes without strongly electron-donating substituents reported to date.[1a,17]

The disilenyl groups in **7** are severely rotated out of the plane of the bridging phenylene group (Si2-Si1-C1-C2 38.9(1)°), thereby avoiding unfavorable close contacts to the *ortho* H atoms. Nonetheless, the C−C bond lengths within the phenylene moiety of **7** point towards a small degree of quinoid character, as would be expected for a conjugated system (C1−C2 139.7(3), C2−C3 138.6(3), C1−C3′ 140.0(3) pm). These observations compare well with results obtained for the carbon-based system p-[Ph(C=CH$_2$)]$_2$C$_6$H$_4$ with a torsion angle of the double bond to the phenylene bridge of 39.5°.[18]

Having experimentally established the presence of a conjugated system in **7**, we carried out DFT calculations (B3LYP/6-31G(d,p))[19a] on the simplified model system **7Ph** (Ph instead of Tip) to shed light on the nature of the interaction. In general, the structure of **7** in the solid state is reproduced well (Table 1). Only the Si=Si bond lengths are slightly overestimated, which, however, is a known tendency for DFT calculations on compounds containing heavier main-group elements. TD-DFT calculations on **7Ph** yield a value of 564 nm as the longest wavelength absorption (assigned to the HOMO–LUMO transition), which is reasonably close to the experimental value of 508 nm for **7**.

Table 1: Experimental and calculated (B3LYP/6-31G(d,p)) distances [pm] and angles [°] of **7** and **7 Ph**.

	7	**7 Ph**
Si1=Si2	216.74(8)	219.3
Si1–C1	187.00(19)	187.5
C1–C2	139.7(3)	141.0
C2–C3	138.6(3)	139.2
β (Si1)	16.5(2)	22.1
β (Si2)	19.3(2)	22.5
Si2-Si1-C1-C2	38.9(1)	48.9

The almost degenerate HOMO and HOMO-1 of **7 Ph** are, as expected, of π symmetry (Figure 4). They are predominantly located on the silicon atoms with relatively minor participation from the p_z atomic orbitals (AOs) of the phenylene bridge. The LUMO exhibits much more significant contributions from the phenylene moiety with a pronounced quinoid appearance. HOMO-35 is the lowest lying mainly π-symmetric orbital. In addition to participation of the terminal phenyl groups, it is delocalized over all six phenylene carbon atoms in an all-bonding fashion and exhibits only very little admixture of silicon-centered AOs. The different energies of the 2p orbitals of carbon and the 3p orbitals of silicon obviously influence their respective contributions. It is well-established that secondary interactions between π and σ* MOs on the one hand and σ and π* MOs on the other hand are responsible for the *trans* bending of Si–Si double bonds.[1a] With that in mind, it is not surprising that second-order perturbation theory analysis reveals a similar situation for **7 Ph** (stabilization energies $\pi_{Si=Si}\rightarrow\sigma^*_{Si-Si}$ 2.72, $\sigma_{Si-Si}\rightarrow\pi^*_{Si=Si}$ 3.47 kcal mol^{-1}).[19b] However, even more favorable interactions are found between C=C π bonds of the phenylene bridge and Si=Si π* orbitals ($\pi_{C=C}\rightarrow\pi^*_{Si=Si}$ 4.91 kcal mol^{-1}), which strongly supports the presence of a conjugated system in **7 Ph**.

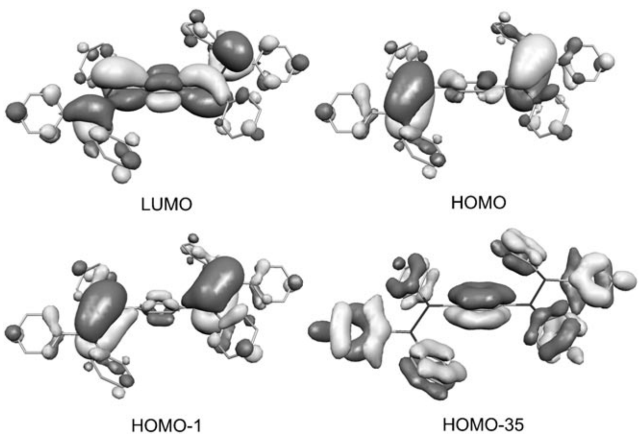


Figure 4. Plots of selected MOs of **7 Ph** (isosurface at ±0.02 a.u.).

To conclude, with **7** we have reported the first compound with phenylene-conjugated Si–Si double bonds. Experimental and computational evidence clearly indicates significant conjugation of the π-system. The remarkable thermal stability of **7** raises the hope of preparing more extended phenylene-conjugated systems containing Si–Si double bonds, the possibilities of which are currently under investigation.

Received: April 19, 2007

Keywords: conjugation · disilene · double bonds · Group 14 elements · silicon

---

[1] Recent reviews: a) M. Kira, T. Iwamoto, *Adv. Organomet. Chem.* **2006**, *54*, 73; b) V. Y. Lee, A. Sekiguchi, *Organometallics* **2004**, *23*, 2822; c) M. Weidenbruch, *Angew. Chem.* **2003**, *115*, 2322; *Angew. Chem. Int. Ed.* **2003**, *42*, 2222; d) A. Sekiguchi, V. Y. Lee, *Chem. Rev.* **2003**, *103*, 1429; e) M. Weidenbruch, *Organometallics* **2003**, *22*, 4348; f) R. West, *Polyhedron* **2002**, *21*, 467; g) M. Weidenbruch, *J. Organomet. Chem.* **2002**, *646*, 39; h) M. Kira, *Pure Appl. Chem.* **2000**, *72*, 2333.

[2] R. West, M. J. Fink, J. Michl, *Science* **1981**, *214*, 1343.

[3] A. Sekiguchi, S. Inoue, M. Ichinohe, Y. Arai, *J. Am. Chem. Soc.* **2004**, *126*, 9626.

[4] R. Tanaka, T. Iwamoto, M. Kira, *Angew. Chem.* **2006**, *118*, 6519; *Angew. Chem. Int. Ed.* **2006**, *45*, 6371.

[5] Review: V. Coropceanu, J. Cornil, D. A. da Silva Filho, Y. Olivier, R. Silbey, J.-L. Brédas, *Chem. Rev.* **2007**, *107*, 926.

[6] a) M. Weidenbruch, S. Willms, W. Saak, G. Henkel, *Angew. Chem.* **1997**, *109*, 2612; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2503; b) M. Ichinohe, K. Sanuki, S. Inoue, A. Sekiguchi, *Organometallics* **2004**, *23*, 3088.

[7] S. Ishida, T. Iwamoto, C. Kabuto, M. Kira, *Nature* **2003**, *421*, 725.

[8] T. Iwamoto, M. Tamura, C. Kabuto, M. Kira, *Science* **2000**, *290*, 504.

[9] A. Sekiguchi, R. Kinjo, M. Ichinohe, *Science* **2004**, *305*, 1755.

[10] Review: A. Kraft, A. C. Grimsdale, A. B. Holmes, *Angew. Chem.* **1998**, *110*, 416; *Angew. Chem. Int. Ed.* **1998**, *37*, 402.

[11] a) V. A. Wright, D. P. Gates, *Angew. Chem.* **2002**, *114*, 2495; *Angew. Chem. Int. Ed.* **2002**, *41*, 2389; b) R. C. Smith, J. D. Protasiewicz, *J. Am. Chem. Soc.* **2004**, *126*, 2268; c) R. C. Smith, J. D. Protasiewicz, *Eur. J. Inorg. Chem.* **2004**, 998; d) V. A. Wright, B. O. Patrick, C. Schneider, D. P. Gates, *J. Am. Chem. Soc.* **2006**, *128*, 8836.

[12] DFT calculations on disila- and digerma-PPVs: Y. Wang, J. Ma, Y. Jiang, *J. Phys. Chem. A* **2005**, *109*, 7197.

[13] a) R. A. Benkeser, R. G. Severson, *J. Am. Chem. Soc.* **1951**, *73*, 1424; b) A. G. Brook, S. Wolfe, *J. Am. Chem. Soc.* **1957**, *79*, 1431; c) M. A. Shippey, P. B. Dervan, *J. Org. Chem.* **1977**, *42*, 2654; d) A. Postigo, R. A. Rossi, *Org. Lett.* **2001**, *3*, 1197.

[14] a) T. Nguyen, D. Scheschkewitz, *J. Am. Chem. Soc.* **2005**, *127*, 10174; b) D. Scheschkewitz, *Angew. Chem.* **2005**, *117*, 3014; *Angew. Chem. Int. Ed.* **2005**, *44*, 2954; c) K. Abersfelder, D. Güclü, D. Scheschkewitz, *Angew. Chem.* **2006**, *118*, 1673; *Angew. Chem. Int. Ed.* **2006**, *45*, 1643; d) S. Inoue, M. Ichinohe, A. Sekiguchi, *Angew. Chem.* **2007**, *119*, 3410; *Angew. Chem. Int. Ed.* **2007**, *46*, 3346; e) I. Bejan, D. Güclü, S. Inoue, M. Ichinohe, A. Sekiguchi, D. Scheschkewitz, *Angew. Chem.* **2007**, *119*, 3413; *Angew. Chem. Int. Ed.* **2007**, *46*, 3349.

[15] D. Scheschkewitz, *Angew. Chem.* **2004**, *116*, 3025; *Angew. Chem. Int. Ed.* **2004**, *43*, 2965.

[16] Crystal structure determinations. **6**: yellows blocks; $C_{51}H_{74}Si_2$, monoclinic, space group $P2_1$; $a = 1114.5(1)$, $b = 3006.4(3)$, $c = 1472.7(2)$ pm, $\beta = 106.094(2)°$, $V = 4741.4(9)\times10^{-30}$ m^3; $Z = 4$, $\rho_{calcd} = 1.041$ g cm^{-3}; crystal dimensions: $0.65\times0.60\times0.18$ mm^3; diffractometer: Bruker Smart Apex with CCD detector; $Mo_{K\alpha}$ radiation, 173 K; $2\theta_{max} = 51.36$; 73394 reflections, 18022 inde-

pendent ($R_{\text{int}} = 0.0298$), direct methods; absorption correction semiempirical ($\mu = 1.06\ \text{cm}^{-1}$); refinement (against F_o^2) with SHELXTL (version 5.1) and SHELXL-97,[20] 956 parameters, 1 restraint, $R_1 = 0.0503$ ($I > 2\sigma$) and wR_2(all data) $= 0.1296$, GOF $= 1.049$, max./min. residual electron density: 0.461/$-0.176 \times 10^{30}\ \text{e m}^{-3}$. **7**·$C_6H_6$: red blocks; $C_{102}H_{148}Si_4$, monoclinic, space group $C2/c$; $a = 3386.2(7)$, $b = 1478.0(3)$, $c = 1976.1(4)$ pm, $\beta = 104.065(4)°$, $V = 9593(3) \times 10^{-30}\ \text{m}^3$; $Z = 4$, $\rho_{\text{calcd}} = 1.029\ \text{g cm}^{-3}$; crystal dimensions: $0.40 \times 0.40 \times 0.10$ mm; diffractometer: Bruker Smart Apex with CCD detector; $\text{Mo}_{K\alpha}$ radiation, 173 K; $2\theta_{\max} = 50.70$; 35217 reflections, 8777 independent ($R_{\text{int}} = 0.0461$), direct methods; absorption correction semiempirical ($\mu = 1.04\ \text{cm}^{-1}$); refinement (against F_o^2) with SHELXTL (version 5.1) and SHELXL-97,[20] 586 parameters, 78 restraints, $R_1 = 0.0574$ ($I > 2\sigma$) and wR_2(all data) $= 0.1418$, GOF $= 1.062$, max./min. residual electron density: 0.355/$-0.187 \times 10^{30}\ \text{e m}^{-3}$. CCDC-643816 (**6**) and CCDC-643817 (**7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[17] Disilenes with amino groups on silicon exhibit considerably stronger *trans* bending: T. A. Schmedake, M. Haaf, Y. Apeloig, T. Müller, S. Bukalov, R. West, *J. Am. Chem. Soc.* **1999**, *121*, 9479.

[18] M. Klokkenburg, M. Lutz, A. L. Spek, J. H. van der Maas, C. A. van Walree, *Chem. Eur. J.* **2003**, *9*, 3544.

[19] a) Gaussian 98, g03 Revision B.04, M. J. Frisch et al., Gaussian, Inc., Pittsburgh PA, **2003**; b) NBO 5.0, E. D. Glendening et al., Theoretical Chemistry Institute, University of Wisconsin, Madison, WI, **2001**. See the Supporting Information.

[20] G. Sheldrick, SHELXL-97, Universität Göttingen, **1997**.