Synthesis, Structure and Photoluminescence of 1,2-Disila-acenaphthene $Si_2C_{10}H_{10}$ and 1,2-Diaryldisilane Reference Compounds

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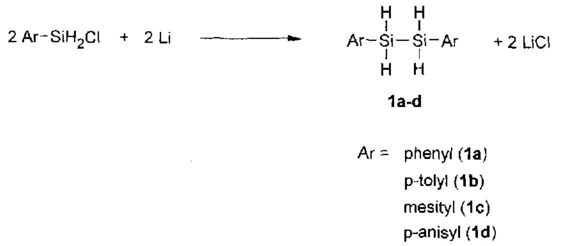
For the synthesis of the diaryldisilanes $Ar-SiH_2SiH_2-Ar$ (**1a**, Ar = phenyl; **1b**, Ar = *p*-tolyl; **1c**, Ar = mesityl; **1d**, Ar = *p*-anisyl) two convenient preparative routes are reported. The crystal structures of **1c** and **1d** have been determined in X-ray diffraction studies; the disilanes have a staggered trans-conformation with a crystallographically imposed center of inversion. For **1a–d** no photoluminescence phenomena can be observed. 1,2-Disila-acenaphthene (**2**) is synthesized in acceptable yield by treatment of 1,8-dilithionaphthalene with 1 equivalent of 1,2-bis[((trifluoromethyl)sulfonyl)oxy]disilane $Tf-SiH_2SiH_2-Tf$. The crystal structure of **2** has also been determined by X-ray diffraction. The molecule has no crystallographically imposed symmetry but closely follows the symmetry elements of point group C_{2v}. Solutions of **2** exhibit intense fluorescence in the near UV region at room temperature. The fluorescence spectra are discussed in comparison with data on acenaphthene and naphthalene.

Introduction

Groups with Si–Si bonds are strong UV chromophors[1]. As substituents to a π-system they have a marked effect on the optical properties of the substrate, and this is widely used in optical sensors, photolithographic and related devices[2][3]. The mutual influence of disilanyl units and arene π-systems on the photoluminescence has not been systematically investigated, however, and there are very few examples in the literature, where this question has been addressed[3]. As part of our ongoing studies of the intrinsic effect of silyl and disilanyl substituents on the optical properties of arenes[4][5][6] we have now investigated molecules where a disilanyl group is bridging two independent benzene rings or the two fused benzene rings of naphthalene. In order to minimize the influence of substituents at the disilane unit, the fully hydrogenated linkage $-SiH_2-SiH_2-$ was introduced.



$$2\,Ar-SiH_2Cl + 2\,Li \longrightarrow Ar-\overset{H}{\underset{H}{Si}}-\overset{H}{\underset{H}{Si}}-Ar + 2\,LiCl \qquad (1)$$

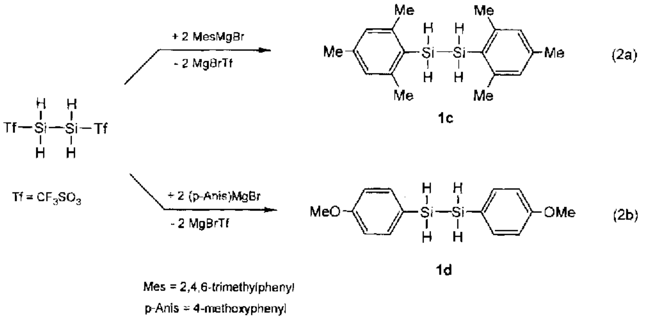
1,2-Diaryldisilanes $Ar-SiH_2-SiH_2-Ar$ (**1**) are accessible via several synthetic routes, but none of these is very satisfactory either regarding the yields of the products or the preparative effort[7][8]. We have now prepared the compounds with Ar = phenyl (Ph, **1a**), *p*-tolyl (*p*-Tol, **1b**)[9], mesityl (Mes, **1c**)[10], *p*-anisyl (*p*-Anis, **1d**) via convenient methods from simple starting materials in more acceptable yields and as single crystals. Only the crystal structure of **1b** was determined previously[9]. The structures of **1c,d** have been investigated in the present study in order to delineate any substituent effects on the configuration, which could be relevant for the discussion of the spectroscopic properties.

1,2-Disila-acenaphtene (**2**) was first prepared by Chernyshev et al. in 1971, but the information on the compound is very limited[11]. The *Si,Si'*-tetrachloro precursor (**2a**) was obtained in small quantities by passing 1-trichlorosilylnaphthalene and $HSiCl_3$ through a hot tube (650°C). $LiAlH_4$ reduction of **2a** gave **2** in low yield. Methylation of **2a** (with MeMgI in diethyl ether) afforded the Si,Si'-tetramethyl homologue **2b**, the structure of which has been determined[12].

Preparation, Properties and Structures of 1,2-Diaryldisilanes 1a–d

Starting from chemicals readily available, two preparative routes, which were used successfully for other syntheses, have now also been employed for the present purposes[6a][13]. Treatment of chloro(phenyl)silane with lithium powder in a 2:1 mixture [v/v] of tetrahydrofuran and hexane gives a 30% yield of **1a** after a reaction time of 2 h at 20°C [Eq. (1)], and for **1c,d** the yields are similar. Since the precursors $Cl(Mes)SiH_2$ and $Cl(p\text{-}Anis)SiH_2$ are less readily accessible than $Cl(Ph)SiH_2$, compounds **1c,d** are better prepared by converting **1a**/**b** into 1,2-bis[((trifluoromethyl)sulfonyl)oxy]disilane[9][14], which is then treated with two equivalents of the corresponding Grignard reagent [Eq. (2a,b)]. The yields for this alternative synthesis are low

(10−20%), but the work-up is easier (Experimental Section).



Compound **1a** is a colorless liquid, while compounds **1b−d** are colorless crystalline solids, stable to air at ambient temperature (except for **1d**), and soluble in most aprotic organic solvents. Analytical and mass spectrometry data confirm their composition, and the NMR spectra are proof for the connectivities of the atoms (Experimental Section). The ^{29}Si NMR resonance of **1c** at −79.3 ppm shows that the silicon atoms of this compound are strongly shielded, possibly as a result of steric congestion. This was not confirmed, however, by the structure determination, which revealed a quite regular molecular geometry.

Crystals of **1c** (at −68°C) are triclinic, space group $P\bar{1}$ with one molecule in the unit cell, and compound **1d** crystallizes monoclinically in the space group $P2_1/c$ (at −80°C) with two molecules in the unit cell (Table 1). Both lattices contain isolated molecules with no sub-van-der-Waals contacts. The disilanes have the staggered trans conformation with a crystallographically imposed center of inversion in the middle of the Si−Si linkage (Figures 1, 2). The molecular dimensions are very similar, although it appears that the bulky mesityl groups are causing a slight lengthening of Si−C and even Si−Si bonds. These differences are also obvious in a comparison with the data for the related 1,2-di(*p*-tolyl)disilane **1b**, which has the same *s-trans* conformation[9]. The changes are hardly significant taking into account the standard deviations of the data, and a discussion in the light of electronic (**1a**, **1b**, **1d**) or steric effects (**1c**) is not meaningful. It is important to note that all three 1,2-diarylsilanes (**1b−d**) have the same conformation (*s-trans*) which suggests that it is justified to trace the optical spectra to a common molecular constitution. Interestingly enough the meso-isomer of the isoelectronic dimesityl*diphosphane* structurally investigated recently also shows the *trans* conformation with a crystallographically imposed center of inversion[15]. The bond length PH−PH (2.23 Å) is slightly shorter than the SiH_2-SiH_2 bond of the corresponding disila derivative **1c**.

In the UV/vis spectra of the 1,2-diaryldisilanes the dominant absorption bands appear in the region of

Table 1. Crystal data, data collection, and structure refinement for compounds **1c**, **1d** and **2**

	1c	**1d**	**2**
Crystal data			
Formula	$C_{18}H_{26}Si_2$	$C_{14}H_{18}O_2Si_2$	$C_{10}H_{10}Si_2$
M_r	298.58	274.46	186.36
Crystal system	triclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$I2/a$
a (Å)	7.6819(7)	7.215(1)	14.966(1)
b (Å)	8.1224(7)	7.589(1)	8.401(1)
c (Å)	8.1951(7)	14.172(2)	16.037(1)
α (°)	78.695(5)	90	90
β °)	69.532(6)	96.78(1)	109.14(1)
γ (°)	65.569(7)	90	90
V (Å^3)	435.38(7)	770.6(2)	1904.9(3)
ρ_{calc} (g cm^{-3})	1.139	1.183	1.300
Z	1	2	8
$F(000)$	162	292	784
μ(Mo-K_α) (cm^{-1})	1.94	2.22	3.11
Data collection			
T (°C)	−68	−80	−74
Scan mode	ω−θ	ω	ω
hkl range	0→9, −8→10, −9→10	−8→8, 0→9, 0→16	−18→18, −10→0, −20→0
sin(θ/λ)$_{max}$ (Å^{-1})	0.64	0.64	0.64
Measured reflections	1888	1464	2141
Refls. used for refinement	1884	1413	2068
Refinement			
Refined parameters	143	82	149
H atoms (found/calcd.)	13/0	9/0	10/0
Final R values [$I>2\sigma(I)$]			
$R1$[a]	0.0298	0.0680	0.0308
$wR2$[b]	0.0873	0.1919	0.0852
(shift/error)$_{max}$	<0.001	<0.001	<0.001
ρ_{fin}(max/min) (e Å^{-3})	0.250/−0.208	1.803/−0.258	0.216/−0.252

[a] $R = \Sigma(\|F_o| - |F_c\|)/\Sigma|F_o|$. − [b] $wR2 = \{[\Sigma w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$; $p = (F_o^2 + 2F_c^2)/3$; a = 0.0496 (**1c**), 0.1049 (**1d**), 0.0473 (**2**); b = 0.10 (**1c**), 154 (**1d**), 1.12 (**2**).

Figure 1. Molecular structure of compound **1c** (ORTEP drawing with 50% probability ellipsoids, C–*H* atoms omitted for clarity). Selected bond lengths [Å]: Si–Si′ 2.339(1), Si–C1 1.876(1)

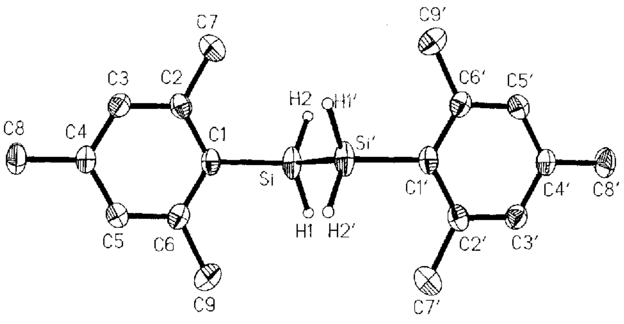
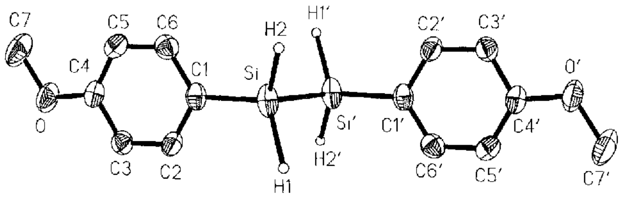


Figure 2. Molecular structure of compound **1d** (ORTEP drawing with 50% probability ellipsoids, C–*H* atoms omitted for clarity). Selected bond lengths [Å]: Si–Si′ 2.323(2), Si–C1 1.862(3)



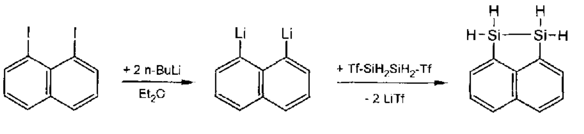
210–280 nm with a characteristic fine structure (selected data see Table 2). The absorption maxima are similar in their wave-lengths and intensities. The most intense absorptions occur in the region of 220–235 nm, followed by much weaker absorptions in the region of 250–280 nm. No photoluminescence phenomena were observed for all four compounds **1a–d**.

Table 2. UV spectra of disilanes **1a**, **1b** and **2** and reference compounds

Compound	λ_{max} [nm]	ε_{max} [$l \cdot mol^{-1} \cdot cm^{-1}$]	λ [nm]
1,2-Diphenyldisilane (**1a**)	224	$7.37 \cdot 10^{4}$	214; 265; 272
1,2-Di(*p*-tolyl)disilane (**1b**)	231	$7.78 \cdot 10^{4}$	213; 265; 271
Naphthalene	220	$1.34 \cdot 10^{5}$	265; 275; 283
Acenaphthene	227	$1.50 \cdot 10^{5}$	278; 288; 299
1,2-Disila-acenaphthene (**2**)	229	$9.02 \cdot 10^{4}$	280; 290; 301

Preparation, Properties and Structure of 1,2-Disila-acenaphthene 2

The title compound was first prepared by hydride-reduction of a minor component of the product mixture generated in the copyrolysis of trichlorosilylnaphthalene and silicochloroform in a hot tube at 650 °C[11]. In order to open up a more rational synthetic route we have now reacted 1,8-dilithio-naphthalene with 1,2-bis(triflato)disilane[10][14]. The dilithium naphthalide is readily available via literature methods[16], and each of the compounds **1a–d** can be used as the substrate for protodearylation with triflic acid to give Tf–SiH_2SiH_2–Tf. After purification by vacuum sublimation the product (**2**) is obtained in ca. 41% yield, m.p. 103–104 °C. Naphthalene is the major by-product of the reaction.

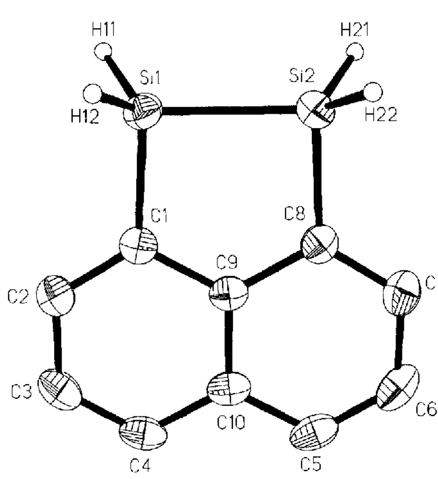


(3)

2

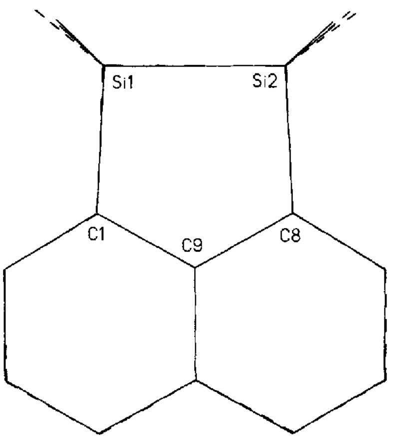
Compound **2** is a colorless, crystalline solid, soluble in most common organic solvents. Crystals (at −74 °C) are monoclinic, space group *I*2/a with 8 molecules in the unit cell (Table 1). The molecules have no crystallographically imposed symmetry, but the molecular geometry closely follows the symmetry elements of point group C_{2v} (Figure 3).

Figure 3. Molecular structure of compound **2** (ORTEP drawing with 50% probability ellipsoids, C–*H* atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Si1–Si2 2.309(1), Si–C1 1.884(2); C1–Si1–Si2 93.11(5), C8–Si2–Si1 92.89(5) Si1–C1–C9 116.02(10), Si2–C8–C9 116.31(10)



The molecular structure of the tetrahydride **2** is surprisingly similar to that of the tetramethyl homologue[12]. A superposition of the diagrams shows an almost perfect match of the planar $C_{10}H_6Si_2$ unit (Figure 4). The dimension of the naphthalene skeleton is also virtually unchanged relative to free naphthalene in the crystal[17].

Figure 4. Superposition of compound $C_{10}H_{10}Si_2$, **2**, and the tetra*methyl* homologue $C_{14}H_{18}Si_2$



The Si–Si and Si–C bond lengths are similar to those in the non-cyclic reference compounds (**1b–d**), which could mean that there is little strain in the five-membered ring. This is also suggested by the endocyclic angles Si1–C1–C9 and Si2–C8–C9, which differ only by ca. 3.5° from the ideal 120° angle. It is worth noting that 120° is not really "ideal" for free naphthalene, because the angles H1–C1–C9/H8–C8–C9 are actually 1.8° smaller than 120° in the unsubstituted hydrocarbon (H1 and H8 designating the hydrogen atoms at C1 and C8, respectively).

At any rate, however, the distortion of the angles in **2** is much less than for acenaphthene, where a bridging of the peri-positions of naphthalene by a shorter CH_2–CH_2 bridge leads to a narrowing of the corresponding C–C–C angles by more than 12°[18]. While this argument again suggests that disila-acenaphthene **2** suffers from less "mechanical strain" than acenaphthene itself, the angles at the CH_2 and SiH_2 units seem to indicate the opposite: Both Si2–Si1–C1 [93.11(5)°] and Si1–Si2–C8 [92.89(5)°] are far away from the ideal tetrahedral angle of 109.48°, while in acenaphthene the corresponding values are 105.3° (average), only 4° from the tetrahedral reference. The overall situation thus shows that compound **2** indeed has less severe strain than the parent acenaphthene, because all bond lengths and most bond angles can be kept normal, and only the "soft" angles at the heavier elements (Si) need to be readjusted, which is energetically least costly.

Electronic Absorption and Emission Spectra of 2

In Table 2, selected UV/vis data of **2**, acenaphthene and naphthalene are summarized. Absorption bands with a fine structure are located in the region of 210–320 nm. The most intense absorption appears between 220 and 230 nm, whereas the intensity of the absorptions between 240 and 320 nm is low. The absorption maxima of **2** and acenaphthene show a bathochromic shift compared with naphthalene. Similar extinction coefficients can be observed for acenaphthene and naphthalene, whereas **2** shows a significantly lower coefficient ε_{max}. For compound **2**, the bathochromic shift may be explained by the destabilization of the HOMO by silyl groups at the 1- and 8-position, analogous to the effects noticed for 1,4-bis(trimethylsilyl)naphthalene and silyl-substituted benzenes in general[19][20].

2 shows intense fluorescence in solution in the near UV region, as shown in Figure 5. A $2.5 \cdot 10^{-6}$ M solution of 1,2-disila-acenaphthene (**2**) in hexane has a maximum in the excitation spectrum at 293 nm. The emission spectrum has a maximum at 336 nm; at 348 nm a shoulder can be observed. In Table 3, the excitation and emission maxima of **2**, naphthalene and acenaphthene are listed; the latter are in accordance with literature data[21][22].

Substitution with the disilanyl unit causes a red shift of the emission maximum compared with naphthalene and acenaphthene, while the excitation maximum of both **2** and acenaphthene are shifted to longer wavelength compared with the parent naphthalene. Although **2** shows the least intense absorption in the UV/vis region, it exhibits the most intense emission in the fluorescence spectra. This result indicates that substitution of hydrogen atoms of naphthalene by silyl groups strongly increases the quantum yield φ of the fluorescence. The phenomenon appears to be a specific electronic effect of the disilanyl unit as part of a rigid, but strainfree arene skeleton[19].

Figure 5. Emission and excitation spectra of 1,2-disila-acenaphthene **2** compared with acenaphthene and naphthalene ($2.5 \cdot 10^{-6}$ M in chloroform; excitation slit and emission slit, 5 nm)

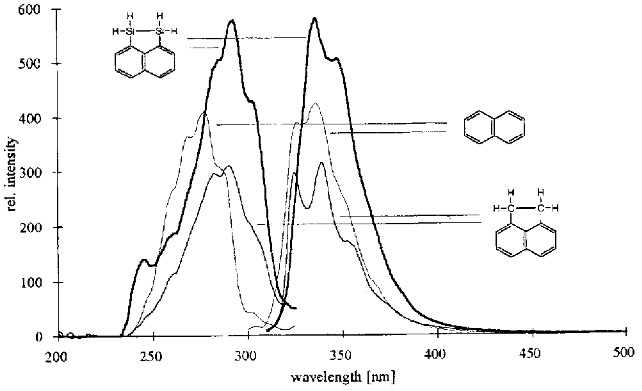


Table 3. Excitation and emission maxima of 1,2-disila-acenaphthene **2**, acenaphthene and naphthalene ($2.5 \cdot 10^{-6}$ M solutions in chloroform)

Compound	Excitation maximum [nm]	Emission maxima [nm]
1,2-Disila-acenaphthene (**2**)	293	336; 348 (shoulder)
Acenaphthene	290	325; 340; 353 (shoulder)
Naphthalene	278	327; 336; 353 (shoulder)

We thank *J. Riede* for establishing the X-ray data sets, Dr. *G. Raudaschl-Sieber* for the measurement of the UV spectra and Dr. *G. Rabe* for assistance.

Experimental Section

All experiments were routinely carried out under an atmosphere of dry, pure nitrogen. Solvents were appropriately dried, distilled and saturated with nitrogen prior to use, glassware was oven-dried and filled with nitrogen. NMR spectra were obtained on a Jeol JNM-GX 400 spectrometer using dry degassed C_6D_6 as the solvent. Infrared spectra were recorded on a Perkin-Elmer FT-IR 577 spectrometer. GLC-MS analyses were performed on a HP 5890/II gas liquid chromatography system with a mass-selective detector HP 5971 A (EI, 70 eV). UV Spectra were recorded on a Perkin-Elmer UV/vis Lambda 2 spectrometer. Luminescence measurements were performed on a Perkin-Elmer LS 50 B luminescence spectrometer. Elemental analyses were performed at the Microanalytical Laboratory of the Technische Universität München. Carbon contents were generally too low due to formation of silicon carbide. In case of 1,2-disila-acenaphthene only the classical analysis according to Pregl led to reasonable data for the carbon content. 1,8-Dilithionaphthalene[16], chloro(phenyl)silane[13], chloro(*p*-ansiyl)silane[6a] and 1,2-bis[(trifluoromethylsulfonyl)oxy]disilane[9][14] were prepared following literature procedures.

1,2-Diphenyldisilane (**1a**): A solution of chloro(phenyl)silane (10.0 g, 70 mmol) in a mixture of tetrahydrofuran (40 ml) and hexane (20 ml) is treated with lithium powder (0.7 g, 0.1 mol) for 2 h at 20°C with stirring. The mixture is filtered and the filtrate fractionally distilled in a vacuum. Phenylsilane and diphenylsilane can be separated as the major by-products. Colorless liquid (**1a**, yield 2.25 g, 30%), b.p. 98°C/0.05 Torr. – MS (EI, 70 eV): *m/z* = 214 (M^+). – IR (liquid, 25°C): 2128.9 cm^{-1} (vs, νSiH_2). – ^1H NMR (C_6D_6, 25°C): δ 4.50 (s, *J*(Si,H) = 193.2 Hz, 4 H, H_2Si), 7.05 (m, 6 H, $H^{3/4/5}$), 7.44 (m, 4 H, $H^{2/6}$). – $^{13}C\{^1H\}$ NMR (v.s.): δ 128.5 (s, $C^{3/5}$), 129.3 (s, C^1), 129.7 (s, C^4), 136.2 (s, $C^{2/6}$). – ^{29}Si NMR (DEPT, v.s.): δ –61.2 (ttt, *J*(Si,H) = 193.2, 6.5 and 6.5 Hz, respectively, SiH_2).

Mesitylsilane, MesSiH$_3$: A solution of mesityl(triethoxy)silane (7.5 g, 27 mmol; prepared by an in situ Grignard reaction) in 5 ml of diethyl ether is added dropwise to a suspension of lithiumaluminium hydride (0.8 g, 21mmol) in 40 ml of diethyl ether with stirring. After 1 h of continued agitation at 20°C the reaction mixture is poured onto crushed ice mixed with $NaHCO_3$ for neutralization. The organic layer is separated and washed three times with 50 ml of water, then dried with $MgSO_4$. The filtrate is fractionally distilled in a vacuum to give a colorless liquid ($MesSiH_3$, yield 2.70 g, 68%), b.p. 49–50°C/0.05 Torr, m.p. 12–13°C. – MS (EI, 70 eV): *m/z* = 150 (M^+). – ^1H NMR (C_6D_6, 25°C): δ 2.07 (s, 3 H, *p*-Me), 2.24 (s, 6 H, *o*-Me), 4.17 (s, *J*(Si,H) = 198.1 Hz, 3 H, H_3Si), 6.61 (s, 2 H, $H^{3/5}$). – $^{13}C\{^1H\}$ NMR (v.s.): δ 21.3 (s, *p*-Me), 23.7 (*o*-Me), 123.1 (s, C^1), 128.5 (s, $C^{3/5}$), 139.7 (s, C^4), 144.9 (s, $C^{2/6}$). – ^{29}Si NMR (DEPT, v.s.): δ –77.7 (q, *J*(Si,H) = 198.1 Hz, SiH_3).

Chloro(mesityl)silane, MesSiH$_2$Cl: Mesitylsilane (1.0 g, 6.7 mmol) is treated with a solution of BCl_3 (0.3 g, 2.6 mmol) in 10 ml of hexane for 14 h at 20°C. After removing the solvent, B_2H_6 and unreacted BCl_3, the product is obtained as a colorless liquid ($MesSiH_2Cl$, yield ca. 95%, derived from ^1H-NMR), which can be used without further purification. – MS (EI, 70 eV, GC-coupled): *m/z* = 184 (M^+). – ^1H NMR (C_6D_6, 25°C): δ 2.02(s, 3, *p*-Me), 2.28 (s, 6 H, *o*-Me), 5.21 (s, *J*(Si,H) = 234.4 Hz, 2 H, H_2Si), 6.56 (s, 2 H, $H^{3/5}$). – $^{13}C\{^1H\}$ NMR (v.s.): δ 21.3 (s, *p*-Me), 22.9 (*o*-Me), 125.6 (s, C^1), 129.0 (s, $C^{3/5}$), 141.8 (s, C^4), 144.8 (s, $C^{2/6}$). – ^{29}Si NMR (DEPT, v.s.): δ –29.5 (t, *J*(Si,H) = 234.4 Hz, SiH_2).

1,2-Di(mesityl)disilane (**1c**): A solution of chloro(mesityl)silane [from mesitylsilane (2.7 g, 18 mmol)] in 15 ml of diethyl ether is treated with lithium powder (0.2 g, 29 mmol) for 48 h at 20°C with stirring. The mixture is filtered, the solvent evaporated and the residue fractionally distilled in a vacuum. Mesitylsilane and di(mesityl)silane can be detected as the major volatile by-products. The separation of di(mesityl)silane from **1c** requires precise fractional distillation. The colorless liquid product (**1c**, yield 0.80 g, 30%) is collected at b.p. 147–150°C/0.05 Torr. It solidifies in the receiver, m.p. 100°C. – MS (EI, 70 eV): *m/z* = 298 (M^+). – ^1H NMR (C_6D_6, 25°C): δ 2.05 (s, 6 H, *p*-Me), 2.24 (s, 12 H, *o*-Me), 4.55 (s, *J*(Si,H) = 191.7 Hz, 4 H, H_2Si), 6.66 (s, 4 H, $H^{3/5}$). – $^{13}C\{^1H\}$ NMR (v.s.): δ 21.1 (s, *p*-Me), 23.9 (*o*-Me), 125.0 (s, C^1), 128.6 (s, $C^{3/5}$), 139.2 (s, C^4), 144.7 (s, $C^{2/6}$). – ^{29}Si NMR (DEPT, v.s.): δ –79.3 (tt, *J*(Si,H) = 191.7 and 6.4 Hz, respectively, SiH_2). – $C_{18}H_{26}Si_2$ (298.58): Found C 70.47, H 8.92; calcd. C 72.41, H 8.78.

1,2-Di(p-anisyl)disilane (**1d**): A solution of chloro(*p*-anisyl)silane [from *p*-anisylsilane (2.5 g, 18 mmol)] in 100 ml of diethyl ether is treated with lithium powder (0.2 g, 29 mmol) for 48 h at 20°C with stirring. The mixture is filtered, the solvent evaporated, and the residue distilled rapidly in a vacuum. *p*-Anisylsilane and di(*p*-anisyl)silane can be detected as the major volatile by-products. The separation of di(*p*-anisyl)silane from **1d** is difficult due to thermally induced decomposition reactions of **1d** and requires rapid fractionation. The colorless liquid product (**1d**, yield 0.50 g, 20%) is collected at b.p. 127–130°C/0.05 Torr. It solidifies in the receiver, m.p. 58–60°C. – MS (EI, 70 eV): *m/z* = 274 (M^+). – ^1H NMR (C_6D_6, 25°C): δ 3.21 (s, 6 H, Me), 4.60 (s, 4 H, H_2Si), 6.71 (d, *J*(H,H) = 8.5 Hz, 4 H, $H^{3/5}$), 7.43 (d, *J*(H,H) = 8.5 Hz, 4 H, $H^{2/6}$). – $^{13}C\{^1H\}$ NMR (v.s.): δ 54.5 (s, Me), 114.6 (s, $C^{3/5}$), 119.4 (s, C^1), 137.8 (s, $C^{2/6}$), 161.5 (s, C^4). – ^{29}Si NMR (DEPT, v.s.): δ –62.1 (ttt, *J*(Si,H) = 191.0, 6.4 and 6.4 Hz, respectively, SiH_2). – $C_{14}H_{18}O_2Si_2$: Found C 60.67, H 6.88; calcd. C 61.27, H 6.61.

1,2-Di(mesityl)disilane (**1c**). – *Alternative Synthesis:* A solution of mesitylmagnesium bromide [from mesityl bromide (5.0 g, 25 mmol)] in 25 ml of tetrahydrofuran is slowly added with stirring to a solution of $Tf-SiH_2SiH_2-Tf$ [from 1,2-di(*p*-tolyl)disilane (2.4 g, 10 mmol)] in 50 ml of toluene at –50°C. The reaction mixture is allowed to warm to 20°C, the magnesium salt is separated and the solvent evaporated. Hexane is added to precipitate all remaining salts, which are filtered off. After removing the hexane the major by-product, mesitylene, can readily be separated by fractional distillation in a vacuum. The colorless liquid product (**1c**, yield 0.42 g, 15%) is collected at b.p. 147–150°C/0.05 Torr. It solidifies in the receiver and is crystallized from hexane, m.p. 100–101°C.

1,2-Di(p-anisyl)disilane (1d). – *Alternative Synthesis:* A solution of *p*-anisylmagnesium bromide [from *p*-anisyl bromide (4.7 g, 25 mmol)] in 25 ml of tetrahydrofuran is slowly added with stirring to a solution of $Tf-SiH_2SiH_2-Tf$ [from 1,2-di(*p*-tolyl)disilane (2.4 g, 10 mmol)] in 50 ml of toluene at –50°C. The reaction mixture is allowed to warm to 20°C, the magnesium salt is separated, and the solvent evaporated. Hexane is added to precipitate all remaining salts, which are filtered off. After removing the hexane the volatile by-product (anisole) can readily be separated by distillation in a vacuum. The colorless liquid product (**1d**, yield 0.30 g, 11%) is collected by rapid fractionation at b.p. 127–130°C/0.05 Torr. It solidifies in the receiver and is crystallized from hexane, m.p. 60–61°C.

1,2-Disilaacenaphthene (**2**): A solution of 1,8-dilithionaphthalene [from 1,8-diiodonaphthalene (1.1 g, 2.9 mmol)] in 15 ml of diethyl ether is slowly added with stirring to a solution of $Tf-SiH_2-SiH_2-Tf$ [from 1,2-di(*p*-tolyl)disilane (0.7 g, 2.9 mmol)] in 25 ml of toluene at –50°C. The reaction mixture is allowed to warm to 20°C, the lithium triflate is separated, and the solvent removed in a vacuum. Hexane is added to precipitate all remaining salts. After removing the solvent all volatile by-products (mainly naphthalene) are separated by sublimation at 50°C/0.05 Torr. The colorless solid product (**2a**, yield 0.22 g, 41%) is purified by sublimation at 80°C/0.05 Torr and crystallized from hexane, m.p. 103–104°C. – MS (EI, 70 eV): *m/z* = 186 (M^+). – IR (CCl_4, 25°C): 2143.3 cm^{-1} (vs, νSiH_2). – ^1H NMR (C_6D_6, 25°C): δ 4.34 (s, *J*(Si,H) = 206.2 Hz, 4 H, H_2Si), 7.18 (dd, *J*(H,H) = 8.1 and 6.6 Hz, respectively, 2 H, $H^{3/6}$), 7.57 (d, *J*(H,H) = 8.1 Hz, 2 H, $H^{2/7}$), 7.66 (d, *J*(H,H) = 6.6 Hz, 2 H, $H^{4/5}$). – $^{13}C\{^1H\}$ NMR (v.s.): δ 125.7 (s, $C^{3/6}$), 130.1 (s, $C^{4/5}$), 133.9 (s, C^{10}), 134.0 (s, $C^{1/8}$), 135.6 (s, $C^{2/7}$), 147.9 (s, C^9). – ^{29}Si NMR (DEPT, v.s.): δ –69.6 (ttd, *J*(Si,H) = 206.2, 6.5 and 6.5 Hz, respectively, SiH_2). – $C_{10}H_{10}Si_2$ (186.36): Found C 64.18, H 5.68; calcd. C 64.45, H 5.41.

Crystal Structure Determinations: Specimens of suitable quality and size of compounds **1c**, **1d**, and **2** were mounted in glass capillaries and used for measurements of precise cell constants and intensity data collection on an Enraf Nonius CAD4 diffractometer [Mo-K_α radiation, λ(Mo-K_α) = 0.71073 Å] . During data collection, three standard reflections were measured periodically as a general check of crystal and instrument stability. No significant changes were observed for all three compounds. Lp correction was applied, but intensity data were not corrected for absorption effects.

The structures were solved by direct methods (SHELXS-86) and completed by full matrix least squares techniques against F^2 (SHELXL-93). The thermal motion of all non-hydrogen atoms was treated anisotropically. All hydrogen atoms were located and refined with isotropic contributions (compounds **1c** and **2**), whereas the Si$-H$ atoms of compound **1d** were allowed to ride on their corresponding silicon atoms with fixed isotropic contributions ($U_{iso(fix)} = 1.5 \times U_{eq}$ of the attached Si atom). Further information on crystal data, data collection and structure refinement are summarized in Table 1. Important interatomic distances and angles are shown in the corresponding Figure Captions. Anisotropic thermal parameters, tables of distances and angles, and atomic coordinates have been deposited with Fachinformationszentrum Karlruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen. The data are available on request on quoting CSD 407121 (**1c**), 407119 (**1d**), and 407120 (**2**).

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