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Structure and Bonding in Bissilylated Arenium Ions[†]

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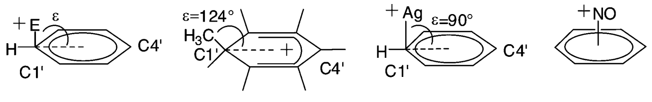
The aryl-bridged disilyl cations **8** with an 1,8-naphthalenediyl backbone were synthesized and were identified by NMR spectroscopy. In addition the $[B(C_6F_5)_4]^-$ salt of the tolyl-bridged cation **8b** was characterized by X-ray crystallography. The NMR spectroscopic and the structural data indicate the arenium ion nature of disilyl cations **8**. Results of quantum mechanical computations corroborate the experimental findings, and a Bader-type topological analysis of the electron density in model cation **6** gives a refined picture of the bonding in aryl-bridged disilyl cations **6** and **8**.

Introduction

The nature of the interaction of silylium ions with aryl groups has been a subject of extensive discussion since the work of Lambert et al., who proposed the formation of the free triethylsilylium ion Et_3Si^+ (**1**) in toluene as solvent.[1] Subsequent work indicated that the generated silyl cation is interacting with the solvent toluene.[2] The bonding situation of the cation $[Et_3Si{\cdot}toluene]^+$ (**2**) has been interpreted as a σ-bonded silylated arenium ion[2] or as a π-complex.[3a,b] Reed proposed this structure to be a point along a $\sigma-\pi$ continuum,[3c] on the basis of the discussion of structural features. Central to this discussion is the angle ϵ, which is defined by the vector between the electrophile E^+ and the *ipso* carbon atom C1′ and by the C1′−C4′ vector (Scheme 1). Typical arenium ions (σ-complexes) are characterized by wide angles ϵ; that is, for heptamethylbenzenium ion **3**[4,5] $\epsilon = 124°$ and for protonated arenium ions angles ϵ between 116° and 142° are reported.[5] In contrast, π-complexes have more acute angles. Thus, in the case of the Ag^+ complex **4** the angle ϵ is 90°.[6] Even more acute angles are found in π-complexes of NO^+ with arenes, such as **5**, investigated by Kochi and co-workers.[7] In these molecules the NO^+ cation is located above the centroid of the arene ring.

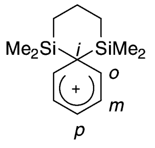
Scheme 1. Structural Diversity of Electrophile−Arene Complexes[a]



3 **4** **5**

[a] The bonding angle ϵ is defined as $\epsilon[deg] = E-C1'-C4'$.

The bissilylated benzenium ion **6** and a series of higher alkylated analogues were synthesized and characterized in our laboratories.[8] These cations, formed by the hydride transfer procedure,[9] have been identified as σ-complexes by multinuclear NMR spectroscopy supported by the results of quantum mechanical calculations. The experimental ^{13}C NMR spectra and the calculated structures exhibit characteristic features of arenium ions: (i) the typical ^{13}C NMR chemical shift pattern with strongly deshielded carbon atoms in the *ortho* and *para* positions, (ii) a shielded carbon atom C*ipso*, and (iii) a significant C−C bond length alternation in the aryl rings.[8]



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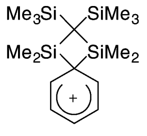

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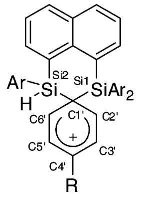
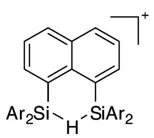


8a Ar=Ph, R=H
8b Ar=Tol, R=Me



11a Ar=Ph
11b Ar=Tol

Recently, Lickiss and co-workers[10] isolated the related cation **7** from a complex mixture of equilibrating species. On the basis of the results of quantum mechanical calculations of nucleus-independent chemical shifts[11] (NICS(1)) the authors assign to the π-system of the bridging phenyl group an almost unperturbed

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[†] This paper is dedicated in memory of Prof. Nils Wiberg in recognition of his ground breaking contributions to organosilicon chemistry.

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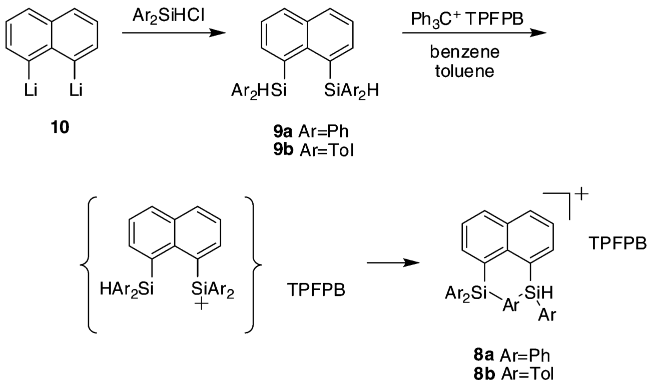
Scheme 2. Synthesis of the Precursor Compounds 9 and the Cations 8 (TPFPB, tetrakis(pentafluorophenyl) borate, $[B(C_6F_5)_4]^-$)



character comparable to the aromatic molecule benzene. They argued that the structure of disilyl cation **7** is "not fitting with the conventional view of benzenium ions but being closer to that for a neutral main group compound containing a bridging Ph group".[10,12] This report prompted us to communicate our own structural and spectroscopic results on disilyl cations **8**. In addition, we present a theoretical analysis of the bonding situation in the strongly related cations **6** and **8**. Both theoretical as well as experimental data indicate that in agreement with our previous work on cation **6** the disilyl cations **8** are best termed as arenium ions.

Results and Discussion

The precursor compounds **9** were obtained by reaction of 1,8-dilithionaphthalene[13] **10** with stoichiometric amounts of the corresponding diarylchlorosilane in low yields and were characterized by standard methods (see Scheme 2 and Experimental Section).

The reaction of the *peri*-substituted naphthyl disilanes **9** with 1 equiv of trityl tetrakis(pentafluorophenyl)borate (TPFPB) in aromatic solvents like benzene or toluene yields exclusively and quantitatively the arenium ions **8**, as indicated by NMR spectroscopy. The cation salts are obtained as light brown, glassy, amorphous solids. Interestingly, no NMR spectroscopic indications for the formation of the hydrogen-bridged disilyl cations **11**[14] were found. In the reaction of related peralkyl-substituted disilyl naphthalenes with trityl cations these hydrogen-bridged disilyl cations are the only product.[14b]

The ^{13}C NMR spectra of *benzene*-d_6 solutions of the salts of **8**·TPFPB show a characteristic chemical shift pattern (Table 1), which is typical for arenium ions.[8,15] That is, in cation **8a** the carbon atoms C2′/C6′ and C4′ of the bridging aryl ring are significantly deshielded compared to the starting compounds (C2′: $\delta^{13}C = 164.7$, $\Delta\delta^{13}C = +28.7$;[16] C6′: $\delta^{13}C = 165.8$, $\Delta\delta^{13}C = +29.8$;[16] C4′: $\delta^{13}C = 153.1$, $\Delta\delta^{13}C = +23.8$[16]). The signal of the *ipso* carbon C1′ appears with $\delta^{13}C = 95.1$ at higher field ($\Delta\delta^{13}C = -40.4$[16]) compared to the resonance of the corresponding carbon atom of the arylsilane **9a**. This indicates a change in its hybridization state from sp^2 in **9a** to sp^3 in **8a**. In addition, the ^{13}C NMR chemical shifts detected for the bridging aryl group in cations **8** are very near to those found for arenium ion **6**.[8] In agreement with the asymmetric structure of the cations **8** the $^{29}Si\{^1H\}$ NMR spectra show two distinct signals, which are deshielded upon cation formation (**8a**: $\delta^{29}Si(1) = -2.2$, $\Delta\delta^{29}Si(1) = +18.3$[16] and $\delta^{29}Si(2) = -9.7$, $\Delta\delta^{29}Si(2) = +10.8$;[16] **8b**: $\delta^{29}Si(1) = -3.3$, $\Delta\delta^{29}Si(1) = +17.6$[16] and $\delta^{29}Si(2) = -11.4$, $\Delta\delta^{29}Si(2) = +9.5$[16]). In the proton-coupled ^{29}Si NMR spectrum, the resonance at higher field splits up into a doublet with a relatively large coupling constant $^1J_{SiH}$ of 248 Hz.

The NMR parameters determined for **8a** in benzene-d_6 and toluene-d_8 are nearly identical, which indicates that no substantial interaction between the cation and the arene solvent is present.

Colorless crystals suitable for X-ray analysis were obtained from the salt **8b**·TPFPB by crystallization from hexafluorobenzene at 280 K. The asymmetric unit contains the cation **8b**, the TPFPB anion, and three and a half molecules of the solvent C_6F_6. The closest contact between cation and anion is 3.210(8) Å (C2−F83), which is beyond the sum of the van der Waals radii of 3.20 Å[17] (see Figure 1a). This indicates that no covalent interactions between anion and cation are present in the crystal. Interestingly, one relatively close contact between one molecule of hexafluorobenzene and the bridging ring is present (see Figure 1b). The closest distance between C*ortho* and F304 is 2.949(6) Å (C26−F304), which is significantly below the sum of the van der Waals radii. Additionally, this C_6F_6 molecule is oriented parallel to one of the rings of the tolyl substituents at Si2. The distance of the two ring planes of $d \approx 3.45$ Å suggests the presence of π-interactions between the two aryl rings,[18] which most likely are responsible for this particular spatial arrangement in the crystal.

The molecular structure of cation **8b** clearly reveals long−short−intermediate bond length variations in the bridging tolyl group (see Figure 2): That is, the C1′−C2′/C1′−C6′ bonds are rather long (1.443(9) Å/1.439(9) Å), the distances between the carbon atoms C2′−C3′/C6′−C5′ are relatively short (1.375(9) Å/1.363(9) Å), and the bonds between carbon atoms C3′−C4′/C5′−C4′ are of intermediate length (1.392(10) Å/1.421(10) Å). The values closely resemble those determined previously for the *para* toluenium ion $C_7H_9^+$ (C1′−C2′/C1′−C6′ = 1.448(8) Å/1.451(8) Å, C2′−C3′/C6′−C5′ = 1.336(8) Å/1.334(8) Å, C3′−C4′/C5′−C4′ = 1.409(7) Å/1.394(7) Å),[5] although the bond length variations in *para* $C_7H_9^+$ are more pronounced. Finally, the small C6′−C1′−C2′ bond angle $\alpha = 115.9(4)°$ indicates a change in the hybridization state of C1′ from sp^2 in **9b** to sp^3 in **8b**, a finding that is in agreement with the conclusions drawn from the analysis of the ^{13}C NMR data.

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[12] These diverging interpretations of the nature of the bridging phenyl groups in cations **6** and **7** are redolent of the debate on the nature of Cram's phenonium ion; see for example: (a) Sieber, S.; Schleyer, P. v. R.; Gauss, J. *J. Am. Chem. Soc.* **1993**, *116*, 6987. (b) Olah, G. A.; Head, N. J.; Rasul, G.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1995**, *117*, 875. We are grateful to one of the referees who brought this point into our attention.

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[16] The NMR chemical shift difference $\Delta\delta$ between cation and precursor compound is calculated according: $\Delta\delta^{13}C = \delta^{13}C(\text{cation}) - \delta^{13}C(\text{precursor})$ and $\Delta\delta^{29}Si = \delta^{29}Si(\text{cation}) - \delta^{29}Si(\text{precursor})$.

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Table 1. Experimental and Calculated NMR Parameter of Cations 8

	$\delta(^{13}C)$, C1′	$\delta(^{13}C)$, C2′	$\delta(^{13}C)$, C3′	$\delta(^{13}C)$, C4′	$\delta(^{13}C)$, C5′	$\delta(^{13}C)$, C6′	$\delta(^{29}Si)$, Si1	$\delta(^{29}Si)$, Si2 ($^{1}J_{SiH}$ Hz)
8a^{a}	95.1	164.7	*d*	153.1	*d*	165.8	−2.2	−9.7 (248)
8a^{b}	95.4	164.9	*d*	153.3	*d*	166.1	−2.1	−9.8
8a^{c}	107.2	173.7	140.0	158.1	138.9	175.4	10.4	−3.5
8b^{a}	89.9	163.5	*d*	170.7	*d*	164.5	−3.3	−11.4 (249)
8b^{c}	102.1	172.7	141.0	177.1	139.7	173.6	8.0	−7.3

^{a} In benzene-d_6 at 303 K. ^{b}In toluene-d_8 at 303 K. ^{c} Calculated at GIAO/B3LYP/6-311G(2d,p)//B3LYP/6-31G(d,p). Chemical shifts δ reported relative to computed $\sigma(^{29}Si, TMS) = 328.3$ and $\sigma(^{13}C, TMS) = 183.3$. ^{d}No clear assignment of the *meta* carbon atoms could be done due to overlapping signals with the naphthyl backbone; see Experimental Section and Supporting Information.

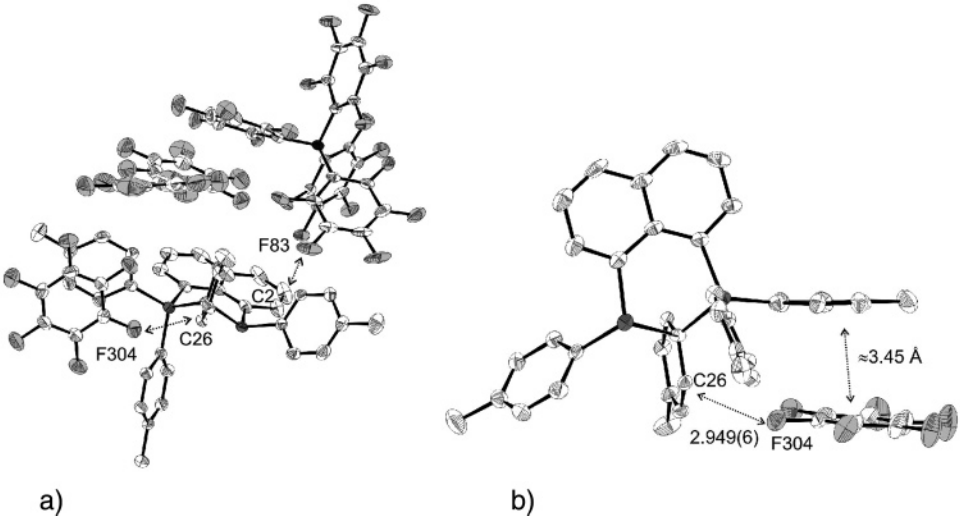

Figure 1. (a) Cation **8b** with the TPFPB anion and three molecules of C_6F_6. Hydrogen atoms are omitted for clarity. Important distances: F304−C26: 2.949(6) Å, C2−F83: 3.210(8) Å. (b) Cation **8b** along with one molecule of C_6F_6. Shown are the closest contacts between the cation and C_6F_6 (color code: B black, C white, Si dark gray, F light gray; distances in Å; thermal ellipsoids at the 30% probability level).

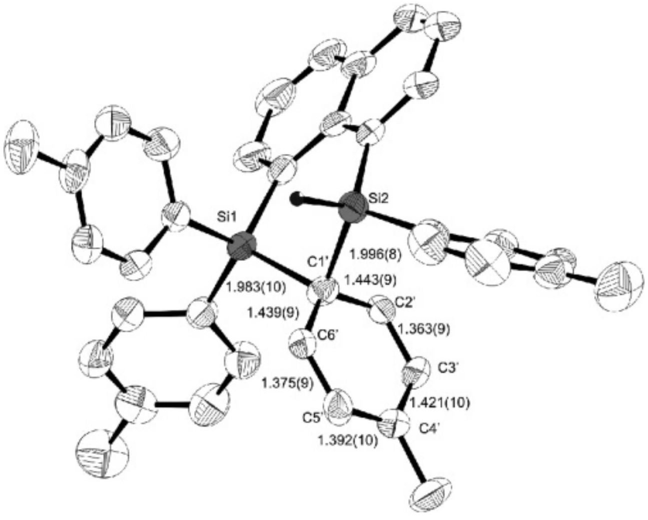

Figure 2. Molecular structure of cation **8b** in the crystal. Hydrogen atoms except for Si−H are omitted for clarity (color code: C white, Si dark gray, H black; bond lengths in Å; thermal ellipsoids at the 50% probability level).

Within the experimental error margins the Si1−C1′−Si2 linkage is almost symmetric, with Si1−C1′ = 1.983(10) Å and Si2−C1′ = 1.996(8) Å. The Si−C atom separations are significantly shorter than the Si−C bond lengths in the monosilylated compound **2** (2.195(11) Å) and the bissilylated cation **7** (2.104(8) Å/2.021(7) Å), but clearly longer than a regular Si−C(sp^3) bond (1.860 Å[19]). As the angle ϵ has been widely used as a structural criterion to distinguish between σ- and π-complexes,[3,5] a comparison of the structural data obtained for the cations **8b**, **7**, and **2** is appropriate: For **8b**, the angles ϵ(Si−C1′−C4′) are 140.5(3)° and 121.6(2)°, which is smaller than observed in the case of **7** (131.0(3)°/150.4(3)°), but wider than found for **2** (103.6(5)°). The bond angles α(C6′−C1′−*C*2′) around the *ipso* carbon atom C1′ are very similar for the cations **7**, **2**, and **8b** (**7**: $\alpha = 116.4(6)°$, **2**: $\alpha = 117.4(1.0)°$, **8b**: $\alpha = 115.9(4)°$). Since in cation **8b** the bridging ring is part of a six-membered ring, the angle β spanned by Si1−C1′−Si2 ($\beta = 98.08(2)°$) is larger than observed for **7** ($\beta = 78.5(2)°$), where C1′ is part of a more strained four-membered ring.

Taken together the structural data of the cation **8b** are consistent with the formulation as a bissilylated arenium ion, that is, (i) a characteristic bond length alternation in the bridging ring, (ii) a significantly reduced C6′−C1′−C2′ bond angle α close to tetrahedral environment, and (iii) angles ϵ(Si(1/2)−C1′−C4′) that are significantly larger than 90°.

Quantum mechanical computations (for details see Supporting Information) at the hybrid density functional level B3LYP[20] and the correlated *ab initio* MP2 level of theory were performed (i) in order to find a rationalization for the exclusive formation of arenium ions **8** and (ii) to gain insight in the bonding situation of cations **6** and **8** (for technical details, see Supporting Information).

The energy differences between the isomeric arenium and hydrogen-bridged disilyl cations were computed for phenyl-substituted cations **8a** and **11a**. At the B3LYP level of theory,[20]

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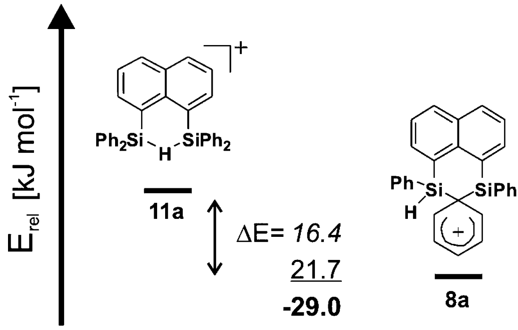


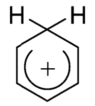
Figure 3. Plot of the relative energy of **8a** vs **11a**. $\Delta E = E^{\text{absolute}}(\mathbf{8a}) - E^{\text{absolute}}(\mathbf{11})$. B3LYP/6-31G(d,p) (*italic*), B3LYP/6-311G(d,p)//B3LYP/6-31G(d,p) (underlined), MP2/6-31G(d,p)//B3LYP/6-31G(d,p) (**bold**). Negative values correspond to an energetic preference of the arenium ion **8a**.

the formation of disilyl cation **11a** with a SiHSi 3c2e bond[14] is energetically preferred (Figure 3). This obviously contradicts the experimental finding that exclusively the arenium ion **8a** is formed. When the applied basis set is increased from double-ζ (6-31G(d,p)) to triple-ζ (6-311G(d,p)) quality, the energy difference between **8a** and **11a** increases from $\Delta E = 16.4$ kJ mol^{-1} to $\Delta E = 21.7$ kJ mol^{-1} in favor of the isomer **11a**. Only when a correlated *ab initio* method (Møller−Plesset second-order perturbation theory, MP2) is used, this energetic order is reversed. At the MP2/6-31G(d,p)//B3LYP/6-31G(d,p) level of theory, the arenium ion **8a** is 29.0 kJ mol^{-1} lower in energy than the hydrogen-bridged cation **11a**. It is notable that the results of computations with the widely used B3LYP hybrid density functional predict the wrong isomer to be the most stable one. Single-point calculations at the MP2 level of theory are necessary to correct this failure.[21]

The molecular structures of cations **8a**,**b**, which are obtained at the B3LYP/6-31G(d,p) level of theory, are very close to each other, and despite the deficiencies noted above for the energetic relation between cations **8**/**11**, the computed structure for cation **8b** agrees well with the experimental one; in particular the calculated C−C bond distances of the bridging ring are within the experimental error margins of the structure determined by X-ray diffraction. The calculated bond lengths show a long−short−intermediate bond length variation similar to that found experimentally (calculated: C1′−C2′/C1′−C6′ 1.438/1.438 Å; C2′−C3′/C6′−C5′ 1.381/1.382 Å; C3′−C4′/C5′−C4′ 1.410/1.409 Å; experimental: C1′−C2′/C1′−C6 1.443(9)/1.439(9) Å; C2′−C3′/C6′−C5′ 1.375(9)/1.363(9) Å; C3′−C4′/C5′−C4′ 1.392(10)/1.421(10) Å). The Si−C1′ atom distances are predicted to be slightly too long (Si1−C1′/Si2−C1′ 2.044/2.009 Å) compared to the experimental values (Si1−C1′ = 1.983(10) Å and Si2−C1′ = 1.996(8) Å).

In order to gain further insight into the bonding situation of cations **8**, the structural features and the topological properties of the electron density of disilyl cation **6**,[22] which serves as a close model for cations **8**, were analyzed and compared with cations **12** and **13** on the basis of quantum mechanical calculations.

Calculations of NMR chemical shifts at the B3LYP level of theory using the GIAO method[23] reveal for the bridging phenyl groups in both cations **6** and **13** very similar chemical shift



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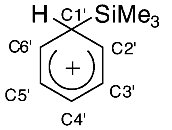

13

patterns that are typical for arenium ions (Table 2). For the benzenium ion **12** this pattern is reinforced; that is, the signal of the *ipso* carbon atom is calculated to appear at significantly higher field and the resonances of the *ortho* and *para* carbon atoms at much lower field than in **6** and **13**. The NICS(1)$_{zz}$[24] value of **6** is −26.0 different from those calculated for benzene (NICS(1)$_{zz}$ = −29.6), but also from that for benzenium ion **12** (NICS(1)$_{zz}$ = −14.6, see Table 2). That is, the NICS(1)$_{zz}$ computation suggests an intermediate nature of the disilyl cation **6** compared to aromatic benzene on one hand side and classical arenium ions like **12** on the other side.

DFT/6-31G(d) and MP2/6-31G(d) model chemistries both predict very similar structures for the cations **6** and **12** (see Supporting Information for details). The structures differ slightly in the bond length alternation in the bridging aryl ring, which can be quantified using Julg's parameter A,[25] where n is the number of bonds in the ring, r_i is the individual C−C bond length, and r is the average C−C bond length.

$$A = 1 - (225/n)\sum(1 - r_i/r)^2$$

For cation **6** the A values ($A = 0.97$, 0.94[8] with MP2, B3LYP) are very close to that of benzene ($A = 1$) and the monosilylated cation **13** ($A = 0.98$, 0.97 with MP2, B3LYP), but show significant deviations from that of nonsilylated benzenium ions such as **12** ($A = 0.82$, 0.78 with MP2, B3LYP). For the calculated geometry of the toluenium ion **8b** an only marginally smaller A value was determined ($A = 0.93$, B3LYP), which should be compared to an experimental value of $A = 0.88$. These structural data indicate that silylated arenium ions like **6** or **8b** take an intermediate position compared to the cation **12** with a localized structure and the more delocalized cation **13**. Additionally, a topological analysis on the basis of the "atoms in molecules" approach[26,27] (AIM) gives valuable information about the bonding in arenium cations. In Figure 4 contour plots of the electron density ρ of the cations **6** and **13** are shown. For the arenium ion **6** bond paths and the corresponding bond critical points (bcp's) between the silicon atoms and the carbon atom C1′ have been found, with electron densities at the bcp's of 0.080 e bohr^{-3}. This is significantly lower than predicted for

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(21) Test calculations at higher levels for a smaller model system reveal a similar behavior (for details see Supporting Information).

(22) A C_1 symmetric structure of cation **6** exists, which is at MP2/6-31G(d) 0.12 kJ mol^{-1} lower in energy than the structure of C_s symmetry. Since NMR spectroscopic results[8] suggest the presence of a symmetric molecule, only the molecule with the symmetric structure is used for the analysis of bonding.

(23) For a monograph on the methodology, see*: Calculation of NMR and EPR Parameter;* Kaupp, M., Malkin, V. G., Bühl, M., Eds; Wiley-VCH: Weinheim, 2004.

(24) The NICS(1)$_{zz}$ value is defined as the negative out-of-plane eigenvalue of the shielding tensor of a ghost atom 1 Å above the plane of the ring at the average position of the six ring carbon atoms; see (a) Steiner, E.; Fowler, P.; Jennesskens, L. W. *Angew. Chem., Int. Ed.* **2001**, *40*, 362. (b) Fallah-Bagher-Shaidaei, H.; Wannere, C. S.; Corminboeuf, C.; Puchta, R.; Schleyer, P. v. R. *Org. Lett.* **2006**, 863. (c) Chen. Z.; Wannere, C. S.; Corminboeuf, C.; Puchta, R.; Schleyer, P. v. R. *Chem. Rev.* **2005**, *105*, 3842.

(25) The Julg parameter A is widely used as a structural criteria for aromaticity in cyclic conjugated compounds. In the present work it is solely used for a convenient description of bond length alternation. Julg, P. F. *Theor. Chim. Acta* **1967**, *7*, 249.

(26) For a monograph see: Bader, R. F. W. *Atoms in Molecules: A Quantum Theory*; Clarendon Press: Oxford, 1990.

(27) The AIM analysis was done using the AIM2000 program: (a) Biegler-König, F; Schönbohm, J.; Bayles, D. AIM2000−A Program to Analyze and Visualize Atoms in Molecules. *J. Comput. Chem.* **2001**, *22*, 545. (b) Biegler-König, F.; Schönbohm, J. An Update to the AIM2000−Program for Atoms in Molecules. *J. Comput. Chem.* **2002**, *23*, 1489.

Table 2. Calculated NMR Parameter and NICS Values for Benzenium Ions 6, 12, and 13 and Benzene[a]

	6	13	12	C_6H_6
δ Si	33.2	95.2		
δ C1′	105.9	102.1	52.5	134.3
δ C2′/6′	177.6/177.0	162.9	194.8	134.3
δ C3′/5′	140.1/141.4	141.7	142.6	134.3
δ C4′	159.5	156.6	182.7	134.3
NICS(1)$_{zz}$	−26.0		−14.6	−29.6

[a] Calculated at GIAO/B3LYP/6-311G(2d,p)//MP2/6-31G(d). Chemical shifts δ reported relative to computed $\sigma(^{29}Si) = 329.0$ and $\sigma(^{13}C) = 183.6$.

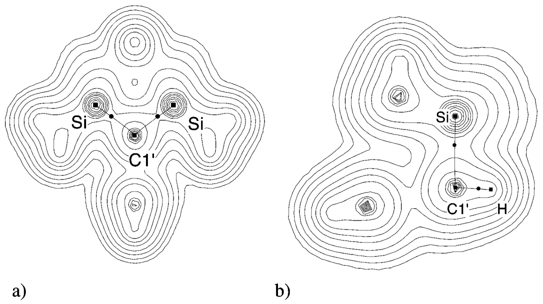


Figure 4. Plots of the electron densities in the plane containing the exocyclic substituent atoms at the C1′ atom, the C1′ atom (squares), and the corresponding bcp's (circles): (a) bissilylated benzenium ion **6**; (b) monosilylated benzenium ion **13**.

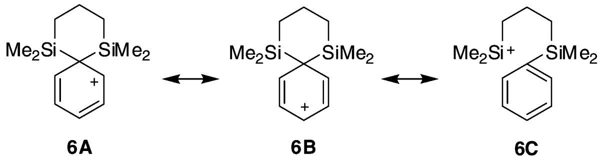
Table 3. Calculated Bond Ellipticities ϵ and Electron Densities ρ at the bcp's in the Aryl Rings of the Cations 6, 12, and 13

	12	6	13
ϵ (C1′−C2′/C1′−C6′)	0.044	0.109/0.108	0.145
ρ (C1′−C2′/C1′−C6′)	0.247	0.290/0.291	0.296
ϵ (C2′−C3′/C6′−C5′)	0.184	0.173/0.175	0.174
ρ (C2′−C3′/C6′−C5′)	0.325	0.314/0.315	0.314
ϵ (C3′−C4′/C5′−C4′)	0.113	0.142/0.143	0.148
ρ (C3′−C4′/C5′−C4′)	0.306	0.310	0.310

the Si−C bond in H_3Si-CH_3 ($\rho = 0.120$ e bohr^{-3}) but notably higher than the electron density found for the bcp (SiC1′) in cation **13** ($\rho = 0.057$ e bohr^{-3}).

The evaluation of the electron densities and bond ellipticities (ϵ) at the bcp's of the bridging aryl rings gives a refined picture of the bonding situation. The pronounced bond length alternation in benzenium ion $C_6H_7^+$ (**12**) is also reflected by the ellipticities at the bcp's. Ellipticities ϵ at the bcp's can, in general, be correlated with the degree of double-bond character of a given bond.[26,28] In **12**, the C1′−C2′/C1′−C6′ bonds show a small ellipticity ($\epsilon = 0.044$), while the bonds between C2′−C3′/C6′−C5′ and C3′−C4′/C5′−C4′ are characterized by high ($\epsilon = 0.184$) and intermediate ($\epsilon = 0.113$) ellipticities, respectively, consistent with the formulation of cyclohexadienyl resonance structures.[29] As summarized in Table 3, for **6** the ellipticities are calculated to be more uniform than in $C_6H_7^+$, **12**, and closer to that of benzene.[28] Comparatively high ϵ values are found between C1′−C2′/C1′−C6′ in benzenium ion **6** (**6**: $\epsilon = 0.109$ vs **12**: $\epsilon = 0.044$), a result of the hyperconjugative stabilizing effect of the two silyl groups, as detailed in Scheme 3. The C1′−Si hyperconjugation increases the double-bond character of the C1′−C2′ and the C1′−C6′ bonds by contributions of resonance structure **6C**. In general, the cation **6** possesses a significantly more delocalized structure than benzenium ion **12**, suggested by lower ϵ value between C2′−C3′/C6′−C5′ (mean value $\epsilon = 0.174$ (**6**) vs $\epsilon = 0.184$ (**12**)), but higher ellipticities between C3′−C4′/C5′−C4′ (mean value $\epsilon = 0.143$ (**6**) vs $\epsilon = 0.113$ (**12**)). For the ring in the silylated benzenium ion **13** calculations indicate an even more delocalized electronic structure, which is also reflected by a comparison of the electron densities at the bcp's, which are for cation **12** less uniform than for **6** and **13** (see Table 3). In summary, also the AIM model suggests an intermediate position of **6** between the benzenium ion **12** with a localized structure and the delocalized cation **13**.

Scheme 3. Resonance Structures of Cation 6



Conclusions

The synthesis and complete characterization of bissilylated arenium ions salts **8a**,**b**·TPFPB is reported. The cations **8a**,**b** are formed selectively by the hydride transfer reaction between the *peri*-substituted naphthylsilanes **9a**,**b** and the trityl cation. Isomeric hydrogen-bridged disilyl cations[14] are not formed. This suggests that the aryl groups in **8a**,**b** are stronger electron donors toward a silylium ion than the Si−H bond in **11a**,**b**. The molecular structure of disilyl cation **8b** clearly indicates its arenium ion nature, that is, a clear long−short−intermediate bond length alternation in the bridging tolyl substituent, and the SiC1′C4′ angles ϵ are larger than 120°. Further support comes from the strongly deshielded ^{13}C NMR chemical shifts found for *ortho* and *para* carbon atoms of the bridging arene ring in disilyl cations **8a**,**b**, which are reminiscent of its dienyl cation nature. The experimental work is supplemented by results of quantum mechanical computations at the hybrid density functional B3LYP and at the correlated ab initio MP2 level of theory, which uniformly favor the arenium ion nature of disilyl cations **8** and the closely related cation **6**. A comparison of the results of a topological analysis of the electron density for cation **6** and related arenium ions **12** and **13** supplies a refined picture of the bonding in **6** (and likewise for disilyl cations **8**). The results indicate the intermediate nature of disilyl cation **6**, framed by the highly localized benzenium ion **12** and the more delocalized silylated arenium ion **13**. The Si−C*ipso* hyperconjugation, operative in cation **6**, confers to the C*ipso*−C*ortho* bonds some double-bond character, which is pictorially shown by the no-bond resonance description **6C**. This leads to a somewhat attenuated but clearly detectable bond length variation in the arene ring compared to that found for the classical benzenium ion **12**. Therefore our combined experimental and theoretical results point to a distinct arenium ion character of disilyl cations **8**, and thereby they contrast the finding of Lickiss and colleagues[10] for the closely related cation **7**.

Experimental Section

General Procedures. Diethyl ether and hexane were distilled from sodium/benzophenone. Benzene, benzene-d_6, toluene, toluene-d_8, and pentane were distilled from sodium. Hexafluorobenzene was dried over P_4O_{10}. TMEDA was distilled freshly from calcium hydride. All reactions were carried out under inert conditions. IR spectra were recorded on a Shimadzu FTIR-8300 spectrometer.

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[28] The ellipticities ϵ and electron densities ρ, calculated at the B3LYP/6-11G(2d,p)//MP2/6-31G(d) level of theory, at the bcp's of the C−C bonds for benzene $\epsilon = 0.200$, $\rho = 0.311$; C_2H_4 $\epsilon = 0.300$, $\rho = 0.349$; C_2H_6 $\epsilon = 0$, $\rho = 0.238$.

[29] Bader, R. F. W.; Slee, T. S.; Cremer, D.; Kraka, E. *J. Am. Chem. Soc.* **1983**, *105,* 5061.

Elemental analyses were carried out on a Foss-Heraeus CHN-O-RAPID. NMR spectra were recorded on a Bruker DPX-250 spectrometer at $T = 303$ K. ^{1}H and ^{13}C NMR spectra were calibrated using residual solvent signals δ^{1}H(CHCl$_3$) = 7.24, δ^{13}C(CDCl$_3$) = 77.0, δ^{1}H(C$_6$D$_5$H) = 7.20, δ^{13}C(C$_6$D$_6$) = 128.0, δ^{1}H(C$_6$D$_5$CD$_2$H) = 2.03, δ^{13}C(C$_6$D$_5$CD$_3$) = 20.4. ^{29}Si NMR spectra were calibrated using external Me$_2$SiHCl (δ^{29}Si = 11.1 vs TMS). ^{29}Si NMR spectra were recorded using the INEPT pulse sequence.

General Procedure for the Synthesis of the Precursor Silanes 9. A 12.5 mmol (2.5 M, 5 mL) sample of *n*-butyllithium was added slowly to a stirred solution of 10 mmol (2.07 g) of 1-bromonaphthalene in 30 mL of dry diethyl ether at −40 °C and stirred for a further 30 min. Stirring was stopped, and the supernatant clear solution was decanted off via a flexible Teflon tube. Then 50 mL dry hexane was added and the reaction mixture was stirred for a few minutes. Without stirring the clear supernatant was decanted off. This procedure was repeated three times. A 14 mmol amount of *n*-butyllithium (2.5 M, 5.2 mL) and 14 mmol (1.6 g) TMEDA were added to the resulting white precipitate. After heating the brown suspension to reflux for 3 h, it was cooled to −30 °C. Diethyl ether (30 mL) was added and the obtained 1,8-dilithionaphthalene was reacted with 20 mmol of diarylchlorosilane (**9a** 4.38 g of diphenylchlorosilane, **9b** 4.94 g of ditolylchorosilane). The dark brown suspension was allowed to warm to room temperature and heated to reflux for 1 h. **9a**: During the usual aqueous workup the product precipitated as a white solid, which was used without further purification. Yield: 1.35 g (2.7 mmol) as a pale yellow solid, 27% yield. ^{1}H NMR (250.131 MHz, CDCl$_3$): δ 6.06 (s, 2H, Si−H, $^{1}J_{\mathrm{Si-H}}$ = 205 Hz), 7.15−7.35 (m, 22H, Ar−H), 7.68−7.13 (m, 2H, H2/7), 7.83−7.87 (m, 2H, H4/5). ^{13}C{^{1}H} NMR (62.902 MHz, CDCl$_3$): δ 124.5 (C3/6), 127.8 (C3′), 129.3 (C4′), 132.1 (C4/5), 133.2 (C1/8), 134.2 (C10), 135.5 (C1′), 136.0 (C2′), 139.8 (C2/7), 142.8 (C9). ^{29}Si NMR (49.696 MHz, CDCl$_3$): δ −20.5 (d, $^{1}J_{\mathrm{Si-H}}$ = 208 Hz). Anal. Calc/Found for C$_{34}$H$_{28}$Si$_2$: C 82.87, H 5.73/C 82.77, H 5.86. IR: $\nu_{\mathrm{Si-H}}$ = 2154 cm^{-1} (KBr pellet). **9b**: After the usual aqueous workup the crude product was purified by column chromatography on silica using hexane−dichloromethane, 95:5 (R_f = 0.3). Yield: 1.35 g (2.5 mmol) as a pale yellow solid, 25% yield. ^{1}H NMR (250.131 MHz, CDCl$_3$): δ 2.32 (s, 12H, CH$_3$), 6.10 (s, 2H, Si−H, $^{1}J_{\mathrm{Si-H}}$ = 205 Hz), 7.08 (d, $^{3}J_{\mathrm{HH}}$ = 7.7 Hz, Ph−H), 7.27 (d, $^{3}J_{\mathrm{HH}}$ = 7.7 Hz, Ph−H), 7.38 (m, 2H, H3/6), 7.76 (m, 2H, H2/7), 7.88−7.92 (m, 2H, H4/5). ^{13}C{^{1}H} NMR (62.902 MHz, CDCl$_3$): δ 21.5 (CH$_3$), 124.5 (C3/6), 128.6 (C2′), 131.9 (C4/5), 132.2 (C1′), 133.9 (C1/8), 134.1 (C10), 136.0 (C3′), 139.1 (C4′), 139.6 (C2/7), 142.8 (C9). ^{29}Si NMR (49.696 MHz, CDCl$_3$): δ −20.9 (d, $^{1}J_{\mathrm{Si-H}}$ = 205 Hz). Anal. Calc/Found for C$_{38}$H$_{36}$Si$_2$: C 83.15, H 5.61/C 82.87, H 5.83.

General Procedure for the Generation of the Cations 8. A solution of 0.3 mmol (277 mg) of trityl TPFPB in benzene was added to a stirred solution of 0.3 mmol of 1,8-bis(diarylsilyl)-naphthalene in 2 mL of benzene at room temperature. The reaction was monitored by the disappearance of the orange color of the trityl cation. Stirring was stopped and the two phases were allowed to separate. The lower phase was transferred into an NMR tube and investigated by NMR spectroscopy. After evaporation of the NMR solvent, the brown cation salt was purified by washing with pentane to obtain a glassy solid.

Benzenium ion 8a: 0.3 mmol (277 mg) of trityl TPFPB, 0.3 mmol (148 mg) of **9a**. Yield: 0.334 g (0.285 mmol) as a brown glassy solid, 95% yield. ^{1}H NMR (250.131 MHz, C$_6$D$_6$): δ 5.21 (s, 1H, Si−H, $^{1}J_{\mathrm{Si-H}}$ = 247 Hz), 6.60−6.63 (m, 2H), 6.80−7.53 (m), 7.96−8.00 (m), 8.20−8.24 (m, 1H, μ-Ph, H6′), 8.67−8.70 (m, 1H, μ-Ph, H2′). ^{13}C NMR (62.902 MHz, C$_6$D$_6$):[30] δ 95.1 (μ-Ph, C1′), 121.7 (C$_q$), 122.6 (C$_q$), 124.3 (C$_q$), 125.1 (C$_q$), 126.1, 126.1, 126.7, 127.4 (C$_q$), 128.8, 129.4, 129.6, 132.6, 133.0, 133.8 (C$_q$), 134.7, 134.9, 135.0, 135.1, 135.6, 136.6, 137.1, 138.7, 139.4, 140.9 (C$_q$), 153.1 (μ-Ph, C4′), 164.7 (μ-Ph, C2′), 165.8 (μ-Ph, C6′), 138.1 ($^{1}J_{\mathrm{C-F}}$ = 232.6 Hz, CF, [B(C$_6$F$_5$)$_4$]), 149.1 ($^{1}J_{\mathrm{C-F}}$ = 240.1 Hz, CF, [B(C$_6$F$_5$)$_4$]). ^{13}C NMR (62.902 MHz, C$_6$D$_5$CD$_3$):[31] 95.4 (C1′), 153.3 (C4′), 164.9 (C2′), 166.1 (C6′). ^{29}Si NMR (49.696 MHz, C$_6$D$_6$): δ −2.2, −9.7 (d, $^{1}J_{\mathrm{Si-H}}$ = 248 Hz). ^{29}Si NMR (49.696 MHz, C$_6$D$_5$-CD$_3$): δ −2.1, −9.8.

Toluenium ion 8b: 0.3 mmol (277 mg) of trityl TPFPB, 0.3 mmol (165 mg) of **9b**. Yield. 0.361 g (0.294 mmol) as a brown glassy solid, 98% yield. ^{1}H NMR (250.131 MHz, C$_6$D$_6$): δ 1.66 (s, 3H, CH$_3$), 2.17 (s, 3H, CH$_3$), 2.21 (s, 3H, CH$_3$), 2.30 (s, 3H, CH$_3$), 5.34 (s, 1H, Si−H, $^{1}J_{\mathrm{Si-H}}$ = 243 Hz), 6.70−8.00 (m), 8.21−8.25 (m, 1H, μ-Ph, H2′), 8.69−8.72 (m, 1H, μ-Ph, H-6′). ^{13}C NMR (62.902 MHz, C$_6$D$_6$):[30] δ 21.1 (CH$_3$), 21.2 (CH$_3$), 21.4 (CH$_3$), 23.3 (CH$_3$), 89.9 (μ-Ph, C1′, C$_q$), 121.3 123.5 (C$_q$), 124.3 (C$_q$), 124.9 (C$_q$), 126.1, 126.3 (C$_q$), 126.6, 128.9, 129.5, 130.2, 133.8 (C$_q$), 134.4, 134.9, 135.3, 135.6, 136.4, 137.0, 137.3, 138.6, 139.3, 141.2 (C$_q$), 143.2 (C$_q$), 143.7 (C$_q$), 143.8 (C$_q$), 163.5 (μ-Ph, C2′), 164.5 (μ-Ph, C6′), 170.7 (μ-Ph, C4′), 149.2 ($^{1}J_{\mathrm{C-F}}$ = 242.0 Hz, CF, [B(C$_6$F$_5$)$_4$]$^-$). ^{29}Si NMR (49.696 MHz, C$_6$D$_6$): δ −3.3, −11.4 (d, $^{1}J_{\mathrm{Si-H}}$ = 249 Hz).

X-ray Crystallographic Analysis for 8b·TPFPB·3.5C$_6$F$_6$. Colorless crystals of **8b**·TPFPB·3.5C$_6$F$_6$ were obtained by crystallization from hexafluorobenzene at 7 °C. X-ray crystal structure analyses were performed on a STOE IPDS: Mo Kα radiation, λ = 0.71073 Å, graphite monochromator at 173(2) K. C$_{83}$H$_{35}$BF$_{41}$-Si$_2$, MW = 1878.10, crystal size 0.47 × 0.26 × 0.13 mm^3, triclinic, space group $P\bar{1}$, a = 13.1319(15) Å, b = 13.4079(15) Å, c = 22.577(3) Å, α = 91.468(10)°, β = 98.749(10)°, γ = 90.850(9)°; V = 3926.9(8) Å^3, Z = 2, D_{calc} = 1.588 Mg m^{-3}; F(000) = 1870; 50 932 reflections collected, of which 14 806 [R(int) = 0.0834] were independent; final R indices [$I > 2\sigma(I)$]: R1 = 0.0801, wR2 = 0.1602; GOF = 0.965. Cambridge data base file CCDC 637148.

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Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

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[30] No clear assignment of the missing C−F resonances of the anion could be done due to overlapping signals; see Supporting Information.

[31] Only the ^{13}C NMR chemical shifts of the bridging aryl group are mentioned. No clear assignment of the *meta* carbon atoms could be done due to overlapping signals with the naphthyl backbone; see Supporting Information.