**Silicon Clusters**

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# A Stable Derivative of the Global Minimum on the $Si_6H_6$ Potential Energy Surface**

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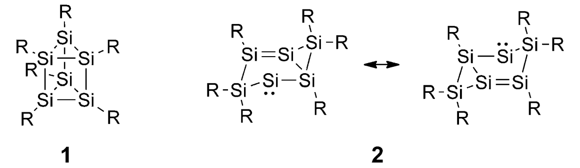
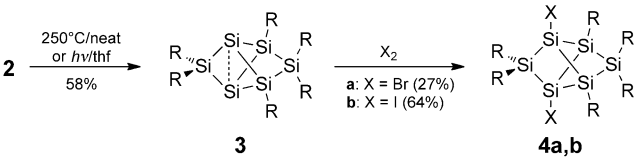
The aromatic benzene molecule is by far the lowest-energy structure with the empirical formula $C_6H_6$.[1] The high aromatic stabilization that is conferred by the cyclic delocalization of six $\pi$ electrons distinguishes benzene from its approximately 200 theoretically known isomers and accounts for the ubiquitous occurrence of the benzene motif in many areas of chemistry. Despite impressive progress regarding the synthesis of stable compounds with Si–Si $\pi$ bonds,[2] homonuclear aromatic entities based on silicon are still rare and restricted to systems with less than five ring atoms.[2a,3–6] While stable derivatives of monosilabenzene,[7] 1,2-,[8] and 1,4-disilabenzene[9] have been reported, knowledge on all-silicon aromatic six-membered rings stems exclusively from numerous computational studies.[10] In addition, the parent hexasilabenzene has been repeatedly used as a benchmark for computational methods designed to evaluate aromaticity.[11]

In marked contrast to the $C_6H_6$ potential energy surface, however, the lower thermodynamic stability of silicon $\pi$ bonding[2] accounts for an energetic preference for cluster-like structures in the case of the $Si_6H_6$ manifold.[12] As a consequence, the only known stable substituted derivative of an $Si_6H_6$ isomer was until recently the hexasilaprismane **1** (Scheme 1).[13] All silicon atoms of **1** are tetracoordinate and consequently it does not exhibit $\pi$ aromaticity in the classical sense.[14] Recently, we reported the tricyclic hexasilabenzene isomer **2** (Tip = 2,4,6-$i$Pr$_3$C$_6$H$_2$), which we identified as being aromatic on the basis of its unusually high thermal stability and various calculations on model compounds.[15] We suggested the term "dismutational aromaticity" for this new type of cyclic delocalization in isomers of Hückel aromatics that involve permutation of $\pi$-type, $\sigma$-type, and nonbonding electrons as shown in Scheme 1. Computational analysis of the magnetically induced ring current across the central $Si_4$ moiety of **2** revealed it to be strongly diamagnetic and akin in nature to the cluster current of three-dimensional aromatic structures.[16]



***Scheme 1.*** Stable $Si_6R_6$ isomers (**1**: R = Dip = 2,6-$i$Pr$_2$C$_6$H$_3$; **2**: R = Tip = 2,4,6-$i$Pr$_3$C$_6$H$_2$).

We now report the isolation and characterization of an aryl-substituted version of the likely global minimum on the $Si_6H_6$ potential energy surface.[12f] Thus, the thermal or photolytic rearrangement of the silicon scaffold of **2** affords the valence isomeric **3** as orange crystals in 58% yield after crystallization from hexane (Scheme 2).[17] The electron impact mass spectrum with the most intense peak corresponding to the molecular ion at $m/z$ 1388 is in agreement with the expected formula $Si_6C_{90}H_{138}$. Apparently, **3** is readily transferred into the gas phase despite its high molecular weight; indeed short-path distillation of the compound is possible at $10^{-2}$ mbar and approximately 350 °C with only slight decomposition. The kinetic stability of **3**, however, is significantly less pronounced than in the isomeric **2**, as **3** decomposes within minutes upon exposure to air in solution and the crystalline state.



***Scheme 2.*** Rearrangement of **2** to **3** and addition of halogens to **3** (R = Tip = 2,4,6-$i$Pr$_3$C$_6$H$_2$).

Single crystals of **3** suitable for X-ray diffraction analysis were obtained as the hexane solvate **3**·$(C_6H_{14})_{1.75}$, but disorder of some of the peripheral groups and the included solvent molecules required extensive modeling and reduced the quality of the resulting data (see the Supporting Information). A better data set was acquired by using crystals obtained from a thf solution of **3**. Both structural models unequivocally confirm the constitution of a persilapropellane in which two

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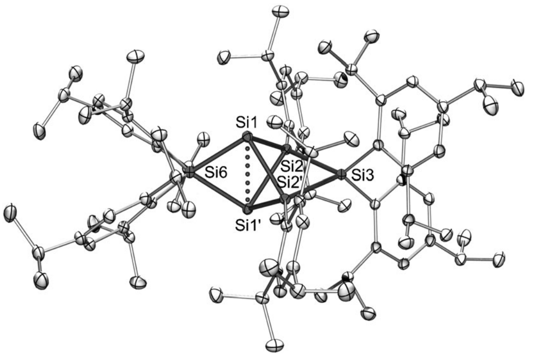

***Figure 1.*** Solid-state structure of **3**·thf$_3$ (thermal ellipsoids at 30%; hydrogen atoms and thf molecules are omitted for clarity). Selected bond lengths [Å] and angles [°]: Si1−Si1′ 2.7076(8), Si1−Si2 2.3536(6), Si1−Si2′ 2.3819(5), Si1−Si6 2.3806(6), Si2−Si3 2.3782(6); Si2-Si1-Si6 97.465(19), Si2-Si1-Si2′ 75.64(2), Si6-Si1-Si2′ 96.693(18), Si1-Si2-Si3 93.649(18), Si1-Si2-Si1′ 69.74(2), Si2′-Si3-Si2 75.25(2), Si1-Si6-Si1′ 69.32(2).

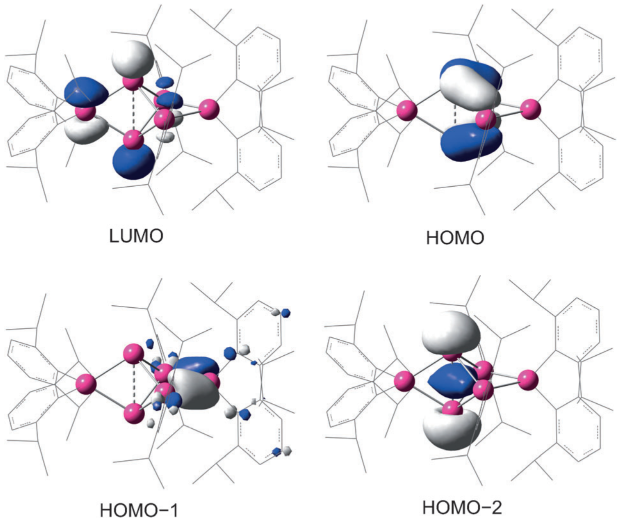

***Figure 2.*** Molecular orbitals at isovalue 0.05 calculated for **3 Dip** at the B3LYP/6-31G(d) level of theory.

of the "propeller blades" are connected by an additional SiTip$_2$ unit (Figure 1).[17]

The following discussion, however, is based on the thf solvate **3**·thf$_3$ exclusively (which has a crystallographic $C_2$ axis coincident with the Si6⋯Si3 vector). The distance between the unsubstituted bridgehead silicon atoms Si1−Si1′ (2.7076(8) Å) is significantly longer than the corresponding distance in the pentasilapropellane Si$_5$Mes$_6$ (2.636 Å, Mes = 2,4,6-Me$_3$C$_6$H$_2$), which was recently prepared by Breher et al.[18] All other Si−Si bond lengths are within the typical range for single bonds. The presence of the additional bridging silicon unit (Si3) between Si2 and Si2′ results in a smaller angle between these two "propeller blades" and a widened angle to the untethered "blade" (Si1-Si1′-Si2/Si1-Si1′-Si2′: 96.7°; Si1-Si1′-Si2/Si1-Si1′-Si6: 131.64°). The angles at the bridging silicon atoms are, as to be expected, approximately the same (Si1-Si2-Si1′: 69.74(2)°; Si1-Si6-Si1′: 69.32(2)°).

In light of the recent attention devoted to diradical(oid) main group compounds in general[19] and heavier Group 14 propellanes in particular,[20] the UV/Vis spectrum of **3** deserved special consideration as an approximate measure of the HOMO–LUMO gap. For their unbridged persilapropellane Breher et al. observed a very weak band at $\lambda_{\max} = 546$ nm that they assigned to the lowest energy singlet–triplet transition (S–T).[18] Conversely, the longest wavelength absorption of **3** at $\lambda_{\max} = 473$ nm is relatively intense ($\varepsilon = 700\,\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$) and therefore unlikely to be associated with a formally forbidden transition. Indeed, TD-DFT calculations on the slightly simplified model compound **3 Dip** (R = Dip = 2,6-*i*Pr$_2$C$_6$H$_3$) show that this absorption band is due to the HOMO–LUMO vertical singlet excitation ($\lambda_{\max,\mathrm{calc}} = 474.6$).[21] The corresponding band for Si$_5$Mes$_6$ was found at $\lambda_{\max} = 396$ nm by Breher and co-workers.[18] As in the case of Si$_5$Mes$_6$, the HOMO of **3 Dip** does not correspond to the predominantly nonbonding orbitals on the bridgehead atoms, but rather to cluster bonding electrons (Figure 2). The large redshift of this transition in **3** compared to that of Si$_5$Mes$_6$ is due to the lifted degeneracy of the HOMO on grounds of a reduction in idealized symmetry ($C_2$ for **3** vs. $D_{3h}$ for Si$_5$Mes$_6$). The value for the lowest-energy vertical triplet excitation of **3** is calculated as 50.5 kcal mol$^{-1}$, which corresponds to $\lambda_{\max} = 566.5$ nm. The fact that the corresponding absorption is not observed for **3** may be due to the more rigid structure and thus less vibronic coupling or possibly the tailing of the intense band at 473 nm.

The $^{29}$Si NMR spectrum of **3** in [D$_6$]benzene showed four signals at $\delta = 174.6$, 14.8, 7.5, and $-274.2$ ppm in a 1:1:2:2 ratio in accordance with the change in symmetry of **3** ($C_2$ vs. $C_i$ for **2**). The dispersion of chemical shifts of **3** ($\Delta\delta = 448.8$ ppm) is even larger than in the case of the recently reported charge-separated tetrasilacyclobutadiene.[5a] The highest-field resonance at $\delta = -274.2$ ppm was assigned to the unsubstituted bridgehead silicon atoms on the basis of a 2D-$^{29}$Si/$^{1}$H correlation spectrum. Further corroboration for this assignment is provided by comparison with Breher's Si$_5$Mes$_6$, which shows an almost identical $^{29}$Si NMR shift for the bridgehead atoms at $\delta = -273.2$ ppm.[18] At first glance the low-field resonance of **3** at $\delta = 174.6$ ppm seemed to be at odds with the solid-state structure, suggesting a formally sp$^2$-hybridized silicon atom such as in tetrasilyl disilenes[2] or silylium cations (e.g. Mes$_3$Si$^+$B(C$_6$F$_5$)$_4^-$ in [D$_6$]benzene: $\delta = 225.5$ ppm).[22] On the basis of the 2D-$^{29}$Si/$^{1}$H correlation of **3**, however, this signal is assigned to one of the SiTip$_2$ units and hence to a tetracoordinate silicon atom. The $^{29}$Si NMR shifts computed for **3 Dip** ($\delta = 207.0$, 32.1, 20.4, and $-267.0$ ppm)[21] are very similar to the experimental NMR shifts of **3** and confirm that the most deshielded silicon atom is that of the untethered "propeller blade" (Si6). To the best of our knowledge, this represents the by far most deshielded $^{29}$Si NMR signal of a tetracoordinate silicon atom in a molecular environment void of transitions metals.[23] For comparison, even the silicon atoms of donor-stabilized silylium cations show resonances at far higher field (e.g. [Et$_3$Si(C$_6$H$_6$)]$^+$B(C$_6$F$_5$)$_4^-$ in [D$_6$]benzene: $\delta = 92.3$ ppm).[24]

The topology of the magnetically induced currents readily explained the $^{29}$Si NMR chemical shifts of the dismutational

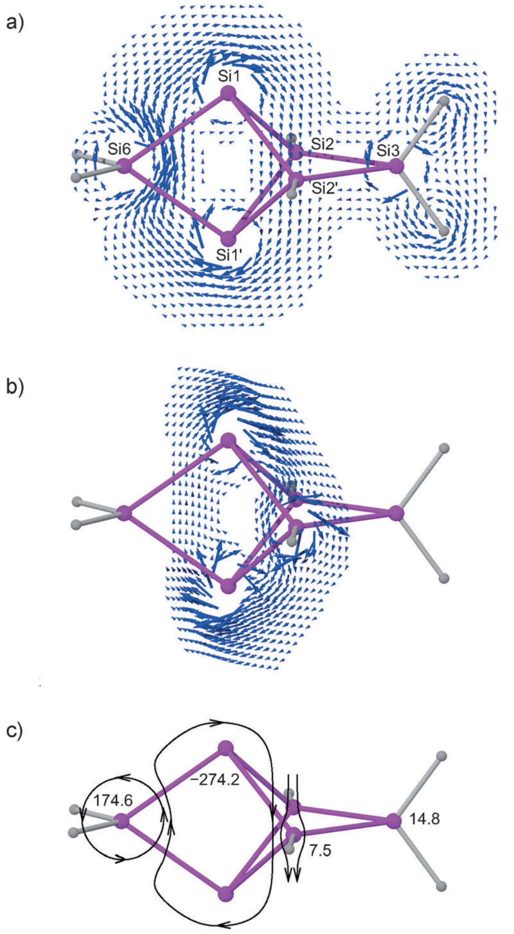

***Figure 3.*** Magnetically induced current density field vectors in **3 H**, calculated with the GIMIC[25] (gauge-including magnetically induced currents) method. The magnetic field (**B** vector) is parallel to Si2–Si2′, hence diatropic vortices are clockwise, paratropic vortices are counter-clockwise. Very small currents and very intense currents are omitted. The largest arrows displayed arise from the diatropic atomic Larmor currents of closed atomic subshells: a) Vectors in the Si6-Si1-Si1′-Si3 plane. b) Vectors in the Si1-Si1′-Si2′ plane. c) Dominating (non-Larmor) current vortices; experimental $^{29}$Si NMR chemical shifts of **3** in [D$_6$]benzene [ppm].

hexasilabenzene isomer **2**.[16] Similarly, the cluster current present in the bridged propellane derivative **3H** (R = H, Figure 3 a, see the Supporting Information) includes Si1 and Si1′ into a diatropic current loop, which thus exerts a magnetic shielding effect by back-induction. This strong current vortex excludes the close-by lying Si6 atom, which is in turn surrounded by a distinct paratropic current vortex, leading to the observed unusual $^{29}$Si NMR low-field resonance of $\delta = 174.6$ ppm for **3**. The main current vortex, interestingly, branches around Si2 and Si2′ (Figure 3 b). As a consequence shielding effects are approximately canceled out, yielding the comparably small chemical shifts of $\delta = 7.5$ ppm. Like in the case of **2**,[16] the innermost current vortex in **3H** is also diatropic, a typical feature of cluster currents as opposed to ring currents in 2D aromatic systems. The total induced molecular current (integrated through a half-plane parallel to the B-field and passing through the central vortex located between Si1 and Si1′) in **3H** amounts to a purely diamagnetic contribution of 10.0 nA$T^{-1}$ (0.0 nA$T^{-1}$ paramagnetic). Almost identical values were found for **2H**.[15]

First investigations with regards to further functionalization confirmed the high reactivity of the bridgehead silicon atoms of **3**. Treatment of **3** with elemental bromine or iodine affords the 1,5-dihalogenated derivatives **4 a,b** in moderate to good isolated yields as orange crystals (Scheme 2).[17] It is noteworthy that the color of the halogenated **4 a,b** is not as strongly affected by halogenation as commonly observed upon saturation of free valences in silicon compounds. The blue shift of longest wavelength absorptions in the UV/Vis compared to that of **3** (**3**: $\lambda_{max} = 473$; **4 a**: $\lambda_{max} = 436$; **4 b**: $\lambda_{max} = 463$ nm) is small to negligible. Conversely, the $^{29}$Si NMR shifts of both compounds are observed between $\delta = 21.2$ and $-77.4$ ppm and hence within the common range for small silicon rings, which provided further corroboration that the unusual shifts of **3** are indeed due to its nonbonding electron density being engaged in the cluster current.

The solid-state structures of **4 a,b** were determined by X-ray crystallography on single crystals (Figure S8 and S13 in the Supporting Information).[17] Remarkably, the molecular structures of **4 a,b** reveal a small but significant shortening of the distance between the bridgehead silicon atoms compared to the unsubstituted propellane-type structure **3** (**3**·thf$_3$: 2.7076(8); **4 a**: 2.6547(7); **4 b**: 2.6810(17) Å). This is in sharp contrast to the substantial elongation of the interbridgehead distance in the case of carbon-based propellanes upon substitution ([1.1.1]propellanes: 1.577 to 1.605 Å; bicyclo-[1.1.1]pentanes: 1.80 to 1.891 Å),[26] but qualitatively similar to previous observations for the addition of more electropositive reagents to heavier propellanes whereupon only slight elongations were found.[27] It is conceivable that the decrease in the distance between the bridgehead silicon atoms is associated with an increased s character of the cluster bonds—and thus an overall contraction of the silicon framework. Such an increased s character should be expected for electronegative substituents on the basis of Bent's rule.[28] We recently observed a related substituent effect in cyclotrisilanes.[29]

In summary, with the bridged propellane **3** we have reported a stable derivative of the assumed global minimum of the $Si_6H_6$ potential energy surface and thus the thermodynamic counterpart of benzene in the case of silicon. The magnetically induced cluster current in **3** is responsible for an unprecedented dispersion of $^{29}$Si NMR shifts and the most deshielded tetracoordinate silicon atom to date. The remarkable thermal stability of **3** allows its ready transfer into the gas phase suggesting its suitability for gas phase deposition techniques. Conversely, the halogenation of the bridgehead positions confirms the high reactivity, offering the possibility of further functionalization of the tricyclic silicon scaffold.

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