Reverse Si═C Bond Polarization as a Means for Stabilization of Silabenzenes: A Computational Investigation

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Quantum-chemical calculations at the B3LYP/6-31+G(d,p) hybrid density functional level reveal that reverse polarization, i.e., reduction of the partial positive charge at Si by π-electron donation from ortho and/or para substituents, is a viable tool to increase the thermodynamic stability of silabenzenes. With 2,4,6-triamino substitution the silabenzene is dominated by zwitterionic resonance structures that place negative charge on Si, and this silabenzene is nearly equally stable as a monomer as it is as a dimer. Ipso silyl substitution further increases the stability so that 1-silyl-2,4,6-triaminosilabenzene is more stable as a monomer than as a dimer. However, bond geometrical data and nucleus-independent chemical shifts indicate that aromaticity decreases with increasing importance of reverse polarization. To design novel silabenzenes that are stable at ambient temperatures, one can work with three parameters: the steric bulk of the substituents, the inductive stabilization obtained through ipso-silyl substitution, and the conjugative stabilization achieved through π-donor groups in ortho and/or para positions.

Introduction

Aromatic compounds play an important role in organic chemistry and are found in a wide range of applications.[1] It is thus natural that attention also has been given to the possible formation of heavier group 14 analogues of these compounds.[2] Until fairly recently, silaaromatic compounds had only been found as transient reaction intermediates,[3] and they had been observed spectroscopically when generated in low-temperature matrixes or formed pyrolytically in the gas phase.[4,5] Their structures and stabilities had also been investigated by quantum-chemical calculations.[2e,6] The synthesis and isolation of a silaaromatic compound that is stable at ambient temperature was hampered by the high reactivity of Si═C double bonds. However, in 1988 Märkl and Schlosser succeeded in forming a silabenzene that is stable in THF/Et_2O/petroleum ether (4/1/1) solutions at −100 °C,[7] and just a few years ago Tokitoh, Okazaki, and their co-workers managed to synthesize and characterize the first neutral silaaromatic species that is stable at ambient temperatures, a 2-silanaphthalene, by taking advantage of an efficient steric protection group, the 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt) group.[8]

Recently, the synthesis of a stable 1-Tbt-silabenzene was reported, and its structure was confirmed by X-ray crystallography, revealing a planar ring.[9] The lengths of the two Si−C bonds of the ring were found to be essentially equal (1.765 and 1.770 Å) and intermediate

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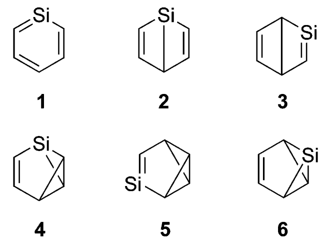
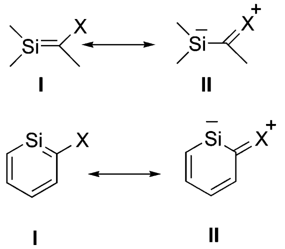
Chart 1



between Si═C double-bond and Si−C single-bond lengths (1.70 and 1.87 Å, respectively).[10,11] Furthermore, the C−C bond lengths in this silabenzene are almost equal to each other (1.381−1.399 Å), and they resemble those of benzene (1.39−1.40 Å).[1] The structural data thus indicated that 1-Tbt-silabenzene has a delocalized six-π-electron ring system similar to that of benzene. Quantum-chemical calculations on model compounds of 1-Tbt-silabenzene at the B3LYP/6-31G(d) level revealed that the bond lengths of the silabenzene ring are little affected by Si substituents,[9b] and calculations of nucleus-independent chemical shifts (NICS) further confirmed that the parent silabenzene (**1**; Chart 1) is nearly as aromatic as benzene.[8a] Subsequently, the syntheses and structural characterizations of 2-Tbt-germanaphthalene and 1-Tbt-germabenzene were reported, and quantum-chemical calculations of the parent germabenzene indicated that this compound is also aromatic.[12,13] Of late, Tilley and co-workers also successfully formed a Ru complex containing a much less sterically congested silabenzene, 1-*tert*-butylsilabenzene.[14]

Wakita et al. computed several silabenzene isomers **2**−**6** and concluded that the second and third most stable SiC_5H_6 isomers are the Dewar silabenzenes **2** and the silabenzvalene **4**.[9b] These species were found to be less stable than **1** by 43 and 48 kcal/mol, respectively. Priyakumar and Sastry later studied 15 different SiC_5H_6 isomers at the CCSD(T)/6-31G(d)//MP2/6-31G(d,p) level of theory and found that **1** is more stable than **2** by 37 kcal/mol.[15] However, they also revealed that lower energy isomers exist that are best described as distorted silabenzvalenes similar in structure to **6** and that are 21−25 kcal/mol above **1** in relative energy. Even though these isomers are not reached thermally, several studies have clarified that both Dewar silabenzenes and silabenzvalenes can be reached photochemically. Maier and co-workers showed that the Dewar silabenzene is formed from **1** upon irradiation,[4d] whereas the 1-Tbt-silabenzene of Tokitoh and Okazaki gave a silabenzvalene.[9b]

Scheme 1



Silabenzenes that are not sufficiently sterically protected often dimerize at low temperatures, and very bulky substituents must be used to slow or prevent this process. Silatoluene forms a [4 + 2] cycloadduct,[4a] whereas the bulkier 1,4-di-*tert*-butylsilabenzene forms [2 + 2] adducts.[3c] Stabilization of reactive species such as silenes and silabenzenes can be obtained through two methodologies: thermodynamic and kinetic stabilization. The former is achieved through stabilization of the ground state by mesomeric effects of neighboring heteroatoms, i.e., attachment of electron-donating or -withdrawing substituents, or complexation with transition metals. In the second methodology one takes advantage of sterically protective groups to raise the energies of the transition states for e.g. oligomerizations and additions of oxygen and water. Only kinetic stabilization was utilized in the Tbt-substituted silaaromatic compounds,[8,9,16] whereas coordination of 1-*tert*-butylsilabenzene to a Ru fragment thermodynamically stabilized this reactive species.[14]

Considering that silabenzene is highly reactive, in contrast to benzene, one may feel that it is not aromatic, but its reactivity can be ascribed to the fact that the Si═C bond is inherently more reactive than the C═C double bond. The Si═C bond in silenes is polar and electrophilic because of the electronegativity difference between C and Si; however, the polarity of this bond can be reduced by π-electron-donating groups at the C end of the silene (Scheme 1). Such substitution raises the barrier for water addition and lowers the dimerization energy.[17,18] Indeed, Apeloig and Karni concluded from their quantum-chemical calculations that "reversed polarity of the π-bond, i.e., $Si^{\delta-}=C^{\delta+}$, is the most important single electronic factor that reduces the reactivity of silenes".[19] The first solid silene that is stable at ambient temperature made by Brook and co-workers is an example where reversed Si═C polarization plays a role,[20] and several other silenes and 2-silenolates that take advantage of this effect have been reported.[21−26]

A reduction in the positive charge at Si of a silabenzene can be effected through the zwitterionic resonance structure **II** (cf. reverse polarization; Scheme 1), similar to that for silenes,[18] when π-electron-donating groups are placed in ortho and/or para positions. We now intend

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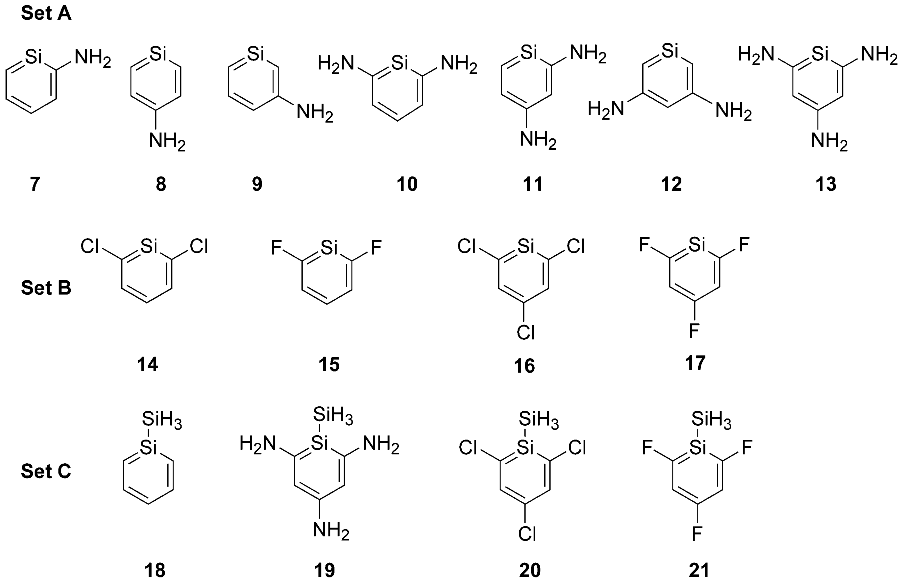
Chart 2



to probe if reverse polarization thermodynamically stabilizes silabenzenes toward dimerization in a manner similar to that for silenes. We considered amino and halo substituents at the different C atoms of the silabenzene (sets A and B, Chart 2) and silyl substitution at Si (set C). A few of these silabenzenes were previously considered by Baldridge and Gordon through HF/3-21G//HF/STO-2G calculations.[6b] They found that the ipso position is preferred by both halo and amino substituents by 30−45 kcal/mol and that the energy difference between ortho, meta, and para positions was less than 10 kcal/mol, favoring the meta position. For halo substituents, the meta position led to the most aromatic silabenzene, whereas for amino substituents it was the ipso position. However, what is the situation upon further substitution? In zwitterionic silenes, the Si atoms adopt pyramidal configurations that resemble those of silyl anions, and the Si═C double bond transforms into an Si−C single bond.[18] If such geometric distortions occur in the substituted silabenzenes, will they still be aromatic? Moreover, will such silabenzenes have a reduced tendency to dimerize? And will they be prone to rearrange? We hope to resolve these questions and hope that our study can guide synthetic efforts toward the preparation of further isolable silabenzenes that exist at ambient temperatures.

Computational Methods

Density functional theory (DFT) calculations were carried out with the Gaussian 98 program.[27] The geometries of benzene and silabenzenes were fully optimized using the three-parameter hybrid DFT of Becke (B3LYP)[28] together with the 6-31G(d,p) and 6-31+G(d,p) basis sets.[29] For dimers of silabenzenes, energy calculations were performed at the B3LYP/6-31+G(d,p)//B3LYP/6-31G(d,p) level. Atomic charges were calculated with the natural bond orbital (NBO) program[30] implemented in the G98 package, using B3LYP/6-31+G(d,p) densities. Nucleus-independent chemical shifts (NICS)[31] have been computed at the GIAO-B3LYP/6-311+G(d,p)//B3LYP/6-31+G(d,p) level. The NICS values were calculated at a distance 1.0 Å above the ring center (NICS(1)), since it has been found that the local effect of CH and CC σ-bonds thereby are diminished in comparison to ring current effects.[32] For silabenzenes with C_s or no symmetry there is an ambiguity on which side of the molecule the NICS value should be computed.

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Table 1. Collected Computed Data of Benzene and Silabenzenes 1 and 7−21 at the B3LYP/6-31+G(d,p) Level[a]

compd	sym	ΣSi	ΣN	NICS(1)[b]	q(Si)	Δq(Si)[c,d]	q(C2, C6)[c]
benzene	D_{6h}			−10.1			
1	C_{2v}	360.0		−9.2	1.212		−0.803
7	C_1	360.0	344.3	−9.0	1.116	−0.096	−0.316 (C2), −0.788 (C6)
8	C_s	359.9	341.2	−8.6	1.135	−0.077	−0.771
9	C_1	360.0	346.3	−7.6	1.244	0.032	−0.863 (C2), −0.847 (C6)
10	C_s	332.6	353.2	−6.0	0.808	−0.404	−0.212
11	C_1	342.2	350.3, 345.3	−6.9	0.924	−0.288	−0.231 (C2), −0.704 (C6)
12	C_s	359.9	345.3	−6.4	1.273	0.061	−0.899
13	C_s	306.1	357.2, 351.4	−3.3	0.611	−0.601	−0.131
14	C_{2v}	360.0		−9.1	1.258	0.046	−0.592
15	C_{2v}	360.0		−10.3	1.049	−0.163	−0.068
16	C_{2v}	360.0		−9.1	1.254	0.042	−0.579
17	C_{2v}	360.0		−10.4	1.026	−0.186	−0.051
18	C_s	360.0		−8.7	0.993	−0.219	−0.780
19	C_s	305.1		−3.0	0.476	−0.736	−0.136
20	C_s	360.0		−9.1	1.025	−0.187	−0.556
21	C_s	360.0		−10.4	0.790	−0.422	−0.036

[a] Angles are given in deg, NICS(1) values in ppm, and atomic charges in electrons. [b] NICS(1) values were calculated at the GIAO-B3LYP/6-311+G(d,p)//B3LYP/6-31+G(d,p) level. [c] Atomic charges were obtained from natural population analyses at the B3LYP/6-31+G(d,p) level. [d] Δq(Si) = q(Si,substituted silabenzene) − q(Si,**1**).

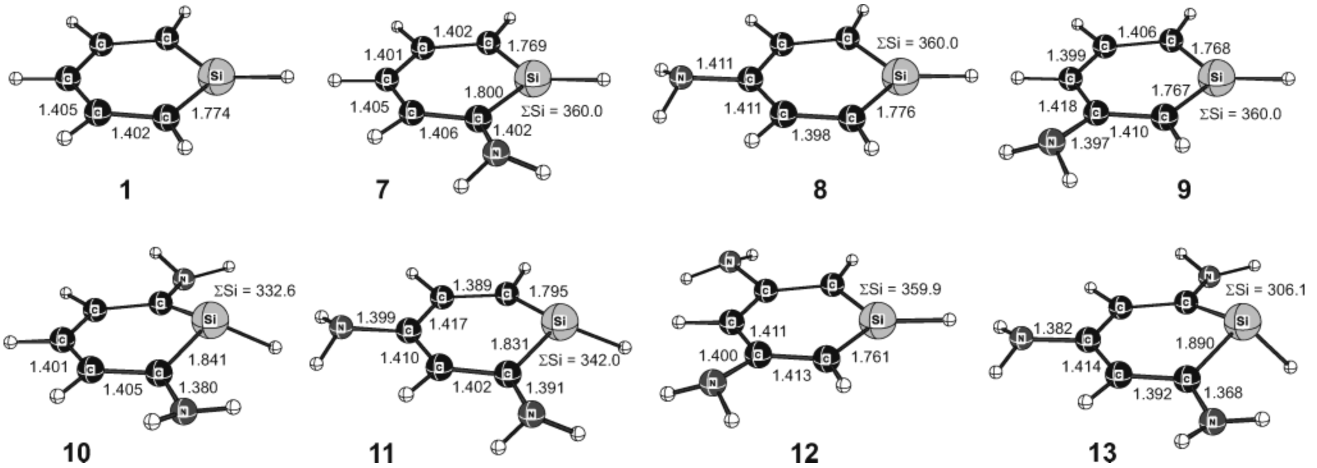

Figure 1. Optimized geometries of silabenzenes **1** and **7**−**13** calculated at the B3LYP/6-31+G(d,p) level. Distances are given in Å and angles in deg.

We found that in two of the silabenzenes the difference between NICS(1) values at either sides was 0.7 ppm but in all others was much smaller, and we therefore list average values. Finally, electronic excitation energies were calculated with time-dependent (TD) B3LYP using the 6-31+G(d,p) basis set.

Results and Discussion

Amino substituents at the C end of a silene have been found to give the largest proportion of reverse Si═C bond polarization.[18] A variety of amino-substituted silabenzenes, and also the chloro and fluoro analogues, were therefore investigated. NPA charges at Si, the extent of pyramidalization at Si and N, and NICS(1) values of the silabenzenes are collected in Table 1. Optimized geometries are found in Figures 1, 3, and 4, and the corresponding absolute and relative energies are listed in Table 2. Not all possible amino-, halo-, and silyl-substituted silabenzenes were investigated but a limited number, from which an understanding of substituent effects is obtained.

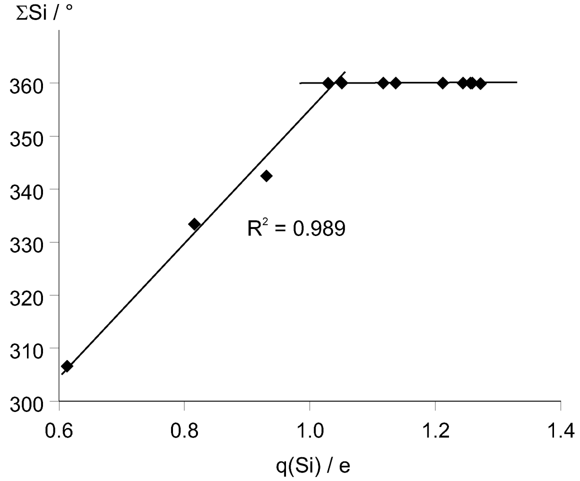

Figure 2. Dependence of the pyramidalization of Si (ΣSi) on the atomic charge of this atom (q(Si)). Charges were obtained from natural population analysis at the B3LYP/6-31+G(d,p) level.

Amino Substitution (Set A). Due to the electronegativity difference between silicon and carbon, the Si atoms in silenes bear large positive charges. For example, the q(Si) value in $H_2Si{=}CH_2$ is 0.936 e at the

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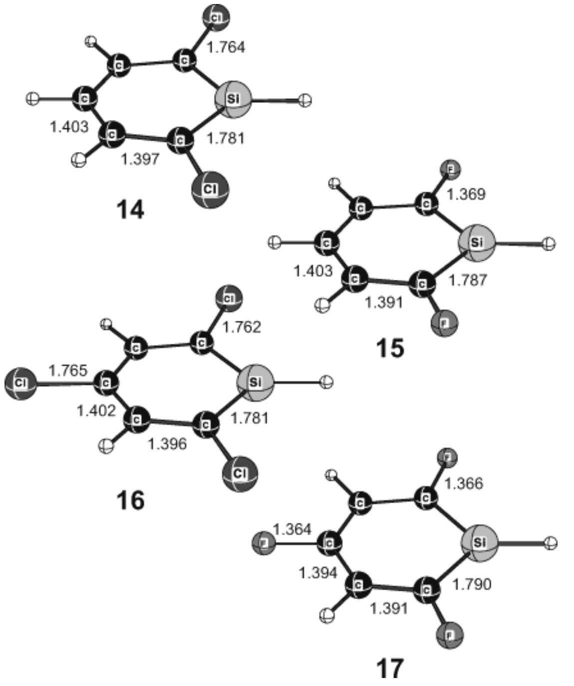


Figure 3. Optimized geometries of halo-substituted silabenzenes **14**−**17** at the B3LYP/6-31G+G(d,p) level. Distances are given in Å and angles in deg.

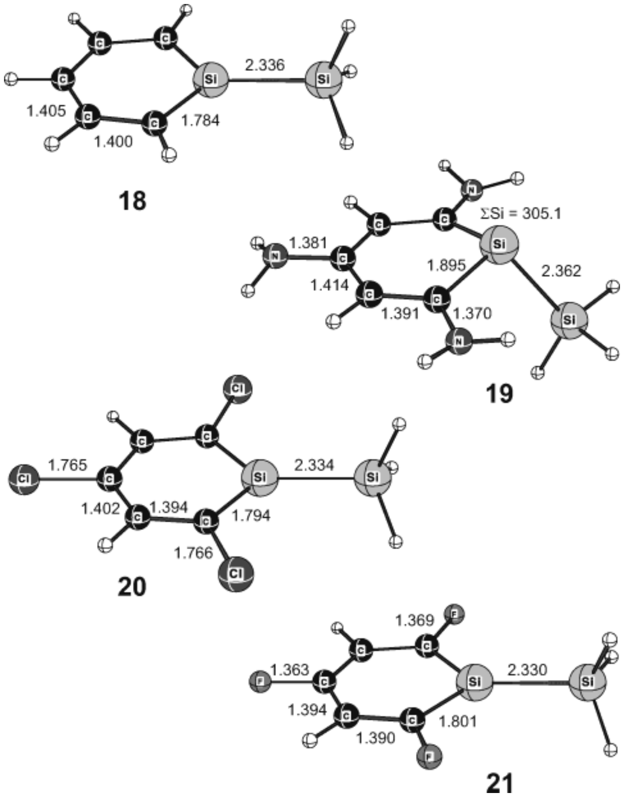


Figure 4. Optimized geometries of silyl-substituted silabenzenes **18**−**21** at the B3LYP/6-31+G(d,p) level. Distances are given in Å and angles in deg.

Table 2. Dimerization Energies (E_{dimer}) of Benzene and Silabenzenes and Relative Energies (E_{rel}) of Isomeric Dimers[a]

dimer[b]	E_{dimer}	E_{rel}
DBenzene-42	57.6	0.0
DBenzene-22-exo	59.6	2.0
DBenzene-22-endo	63.2	5.6
D1-42-ht	−20.2	0.0
D1-42-hh	−6.4	13.8
D1-22-ht-exo	−18.4	1.8
D1-22-hh-exo	−1.1	19.1
D1-22-ht-endo	−17.3	2.9
D1-22-hh-endo	2.3	22.5
D1-42-ht(sp^2+sp^3)[b]	15.5	35.7
D10-42-ht	−17.3	0.0
D10-22-ht-exo	−6.7	10.6
D12-42-ht	−30.0	0.0
D12-22-ht-exo	−29.7	0.3
D13-42-ht	−5.8	0.0
D13-42-hh	4.1	9.9
D13-22-ht-exo	0.7	6.5
D13-22-hh-exo	5.8	11.6
D13-22-ht-endo	0.8	6.6
D13-22-hh-endo	11.7	17.5
D13-42-ht(sp^2+sp^3)[b]	19.4	25.2
D13A	5.4	11.2
D13B	−9.4	−3.6
D13C	−7.7	−1.9
D13D	−7.5	−1.7
D18-42-ht	−13.2	0.0
D18-22-ht-exo	−12.4	0.8
D19-42-ht	4.8	0.0
D19-22-ht-exo	8.8	4.0
D20-42-ht	−11.7	
D21-42-ht	−10.1	
D28-42-ht	−20.8	
D29-42-ht	*−10.2*[d]	
D30-42-ht	*−16.9*[d]	
D31-42-ht	*2.7*[d]	
D32-42-ht	*−10.1*[d]	

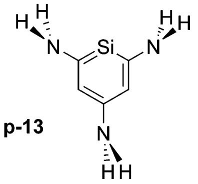
[a] Energies were obtained in kcal/mol from B3LYP/6-31G+G(d,p)//B3LYP/6-31G(d,p) calculations. [b] In the name of the dimers, **D** stands for dimer followed by the number of the corresponding monomer. The numbers **42** and **22** indicate whether it is a [4 + 2] or [2 + 2] adduct, **ht** and **hh** whether it is a head-to-tail or head-to-head adduct, and **exo** and **endo** whether it is an exo or endo adduct. [c] Silabenzene dimer in which one Si atom is sp^2 hybridized and the other is sp^3 hybridized. [d] Calculated at the B3LYP/6-31+G(d)//B3LYP/6-31G(d) level.

B3LYP/6-31+G(d,p) level, and q(Si) is even more positive in the parent silabenzene (Table 1). Attachment of one amino group in positions 2 and 4 of the silabenzene ring reduces the Si charge by ∼0.1 e (silabenzenes **7** and **8**), and attachment of two amino groups in positions 2 and 6 (silabenzene **10**) or positions 2 and 4 (silabenzene **11**) or of three amino groups in positions 2, 4, and 6 (silabenzene **13**) further lowers q(Si) by 0.3−0.6 e. Simultaneously, the charge at the C atoms bearing the amino substituent is lowered extensively. While the difference between q(Si) and q(C2) is 2.015 e in **1**, it is reduced to 0.742 e in **13** (Table 1). On the other hand, one amino group in position 3 (meta), as in **9**, or two in positions 3 and 5, as in **12**, raises q(Si) by respectively 0.03 and 0.06 e, because of the σ-electron-withdrawal effect of the NH_2 group. The charge at the ortho C atoms in these silabenzenes is also more positive than in **1**, thus increasing the Si−C bond polarity, and the charge difference becomes 2.172 e. The charge distribution thus suggests an increased contribution of a zwitterionic resonance structure such as **II** in **7**, **8**, **10**, **11**, and **13**. The difference in the effect of one amino group in an ortho or para position on q(Si) is small, within ∼0.02 e, with ortho substitution leading to the largest reduction of q(Si). However, when two amino groups are both placed in ortho positions (**10**), they cooperatively reduce q(Si) more than when one amino group is placed in a para and the other in an ortho position (**11**) (Table 1). Since π-electron-donating groups at meta positions do not lead to the desired change toward a zwitterionic silabenzene and because they lead to an increase of the q(Si) value, no meta-substituted silabenzenes other than **9** and **12** were studied.

As previously shown by Wakita et al.,[9b] the Si−C bond distance in **1** lies between double (1.70 Å) and single (1.89 Å) Si−C bond lengths, which implies that these bonds participate in the π-conjugation. The CC bonds in **1** are also similar in length to those in benzene (1.399 Å at B3LYP/6-31+G(d,p)). Upon amino substitution, the SiC bonds elongate when amino groups occupy ortho and/or para positions until reaching values typical for Si−C single bonds in **13**. The structure around Si further becomes gradually more pyramidal with increasing amino substitution at the ortho and para positions (Table 1), and for **13** the zwitterionic resonance structures should dominate the electronic structure. The ring also becomes slightly nonplanar upon ortho and para amino substitution, whereas amino substitution at meta positions does not distort the ring planarity. The degree of pyramidalization of Si in **13**, as determined by the sum of the valence angles ($\sum$Si), approaches that of the SiH_3^- and Me_2SiH^- anions at the B3LYP/6-31+G(d,p) level, ~285.6 and 291.4°, respectively, and it resembles that of the silolyl anion (c-C_4H_4-SiH^-; $\sum$Si is 306.4° at the B3LYP/6-31+G(d,p) level and 321.6° at the MP2/6-31+G(d,p) level[33]). The charge at Si in **13** is 0.611 e, compared to 0.330 e for Me_2SiH^-, and a plot of $\sum$Si against q(Si) reveals a connection between these properties similar to that for silenes[18] (Figure 2). Until q(Si) drops below a threshold, the structure around Si is planar. After this breakpoint the Si atom becomes gradually more pyramidal as q(Si) becomes less positive. Similar to the case for silenes,[18] there is a remarkable linear correlation between q(Si) and $\sum$Si for the pyramidalized silabenzenes ($R^2 = 0.981$). While the Si becomes more pyramidal, the opposite trend is seen for the amino groups as resonance structure **II** increases in importance (Table 1).

From the geometrical data one can infer that there is a loss of aromaticity as the reverse polarization effect becomes dominant. To quantify this loss of aromaticity, we calculated nucleus-independent chemical shifts (NICS). Our NICS calculations indicate aromaticity in **1**, as previously reported.[8] The *o*- and *p*-amino-substituted silabenzenes **7** and **8** have a slightly attenuated aromaticity. This attenuation is more pronounced in **10** and **11**, and **13** should presumably be regarded as nonaromatic. Clearly, negative charge localization at Si and the pyramidalization that follows lead to weakening of the overlap between the 2pπ(C) and 3pπ(Si) AOs and an eventual loss of conjugation in the ring. Similar conclusions have been made with regard to the silolyl anions.[2e,33] The lower degree of aromaticity of c-C_4H_4-SiH^- relative to c-$C_5H_5^-$ is mainly due to the pyramidal geometry around Si.[2e,33] For the very limited set composed of the pyramidal silabenzenes (**10**, **11**, and **13**) and the planar silabenzene which is closest to the breakpoint in Figure 2 (**17**), one obtains a good correlation between $\sum$Si and calculated NICS values ($R^2 = 0.962$). This supports the conclusion that the pyramidal geometry around Si causes the reduction in aromaticity. Finally, with regard to the *m*-amino-substituted silabenzenes **9** and **12**, it is interesting to note that the NICS calculations also suggest a weakening of the aromaticity in these compounds. Baldridge and Gordon arrived at the same conclusion for compound **9**.[6b]

Chart 3


p-13

The decrease in the SiC π-bond overlap as Si pyramidalizes is more than compensated by increased CN π-bonding. To measure the stabilization obtained by conjugation of the lp(N) orbitals with the π-system of the ring, we also calculated **p-13** (Chart 3), where the planes of the amino groups are oriented perpendicular to the ring plane. This structure, which is a third-order saddle point, is 19.5 kcal/mol above the optimal structure of **13** at the B3LYP/6-31+G(d,p) level, and its SiC bonds (1.782 and 1.792 Å), atomic charge at Si (1.178 e), and NICS(1) value (−9.3 ppm) are similar to those of **1**.

In monoamino-substituted silabenzenes the amino group is pyramidal; thus, conjugation between lp(N) and the π-system of the ring is not optimal. A property of amino groups is therefore that they can “switch off” reverse polarization. Halo substituents do not have this property, and even though they are weaker π-electron donors, they may have the same effect as amino substituents.

Halo Substitution (Set B). Chloro and fluoro substitutions in ortho and/or para positions have interesting effects on the charge distribution, since they act in opposite manners. Whereas F in **15** and **17** adds charge to the Si atom, Cl in **14** and **16** withdraws it. However, the influence of a fluorine is small when compared to that of an amino group in invoking reverse polarization, even though the lp(N) of the amino group could pyramidalize and thus weaken the conjugation with the pπ orbitals of the ring. Three fluoro substituents can only reduce q(Si) by a third of the amount of three NH_2 groups. Since fluorine was inferior to amino groups, we did not make an extensive exploration of fluoro-substituted silabenzenes.

When comparing the SiC and CC bond distances in **14**−**17** with the corresponding distances in **1** (Figures 1 and 3), one can note only small elongations of the SiC bonds by ~0.015 Å in the two F-substituted silabenzenes. With regard to the Cl-substituted silabenzene the changes in bond lengths are negligible when compared to **1**. Furthermore, the four halo-substituted silabenzenes are planar and aromatic on the basis of the NICS values (Table 1). Interestingly, the NICS values are similar or even more negative than for **1**, and we conclude that halosilabenzenes should display reactivities similar to that of **1**.

Silyl Substitution (Set C). Substitution of H1 in **1**, **13**, **16**, and **17** by a SiH_3 group leads to **18**−**21**, and it further reduces q(Si) by 0.1−0.2 e (Table 1). However, it does not significantly affect the geometries of the rings when compared to the corresponding silabenzenes that lack 1-silyl substituents. This agrees with the previous

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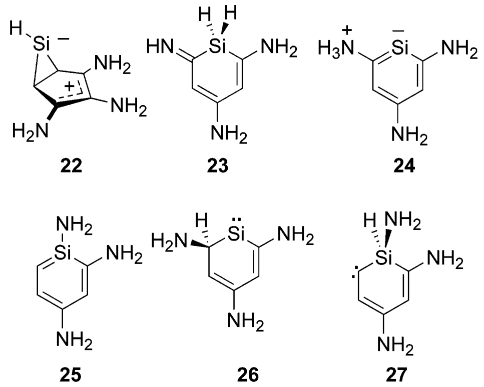
(33) Goldfuss, B.; Schleyer, P. v. R. *Organometallics* **1995**, *14*, 1553.

Chart 4



finding of Wakita et al., since neither a phenyl nor a Tbt group altered the bond lengths when compared to the parent silabenzene.[9b] One can also note that a silyl substituent at Si has no dramatic effect on the NICS value and, thus, does not affect the aromaticity of the ring.

To conclude, amino substitution at ortho and/or para positions, combined with a silyl substituent at Si, effectively reduces the positive charge at Si. Such silabenzenes should not be as prone to add water or other nucleophiles to Si, in a way similar to that found by Apeloig and co-workers for silenes that are influenced by reverse polarization.[17] For silenes it was also found that the increased importance of reverse polarization makes them less prone to dimerize, particularly if they are substituted by two strong π-donor groups at the C end.[18] Thus, will amino substituents in ortho and/or para positions make silabenzenes also less prone to dimerize? Moreover, can they undergo rearrangements not previously considered?

Rearrangement and Dimerization Processes. Previous calculations revealed that the silabenzene **1** is the most stable among the SiC_5H_6 isomers in Chart 1.[9,15] The difference in stability between **1** and the second most stable isomer, being a distorted form of silabenzvalene **6**, is 24.6 kcal/mol at the B3LYP/6-31+G(d,p) level: i.e., in accordance with the previous CCSD(T) result.[15] The lowest of the amino-substituted analogues of this isomer (**22**), which can be described as a zwitterion, is 12.4 kcal/mol higher in energy than **13**, but no facile pathway to this species could be found. A rearrangement from **13** to **22** thus seems unlikely. Moreover, triamino-substituted analogues of isomers **2**−**5** were disregarded because the energy differences between **1** and **2**−**5** are so large that we consider it unlikely that amino substituents will make any of them of lower energy relative to **13**.

Rearrangements other than those leading to the corresponding **2**−**6** could occur for amino-substituted silabenzenes. Our B3LYP/6-31+G(d,p) calculations established that **13** is 0.4 kcal/mol less stable than its imino isomer **23** (Chart 4), but the barrier for the unimolecular hydrogen shift is 47.0 kcal/mol, and this rearrangement pathway is therefore not plausible at ambient temperatures. Four additional isomers **24**−**27** were also investigated. The zwitterionic isomer **24**, in which a proton moves from Si to the NH_2 group, is 34.6 kcal/mol less stable than **13**. The isomeric silabenzene **25** is lower in energy than **13** by 14.6 kcal/mol. Silabenzene **25** is also considerably more aromatic than **13**, as its NICS(1) value is −7.2 ppm and the SiC bonds are 1.818 and 1.788 Å, similar to those of **1**. It also has a much less pyramidal Si atom ($\sum$Si = 348.8°) with a corresponding charge of 1.398 e, i.e., more positive than in **1**, a result of the inductive electron withdrawal caused by the ipso amino group.

However, formation of **25** following a unimolecular pathway is presumably stepwise, involving the silylene **26** as an intermediate, an isomer which is 15.7 kcal/mol less stable than **13**. It is interesting that the lp(N) of the amino group in **26** interacts with the empty 3pπ(Si) AO, reflected by the small N−C−Si angle of 70°. Formation of **25** from **13** should follow the route **13** → **26** → **25**; the energy barrier for the first rearrangement is 21.8 kcal/mol, and that of the second is 32.8 kcal/mol. The second barrier is sufficiently high so that formation of **25** from **13** should not occur at ambient temperatures. Finally, carbene **27** is 22.1 kcal/mol less stable than **13**, and its formation passes over a prohibitively high barrier of 66.9 kcal/mol.

The UV/vis absorption characteristics of **13** as compared to those of **1** could also be of interest for later experimental realizations of 2,4,6-triamino-substituted silabenzenes. TD-B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p) calculations reveal that the two lowest absorptions of **13** are found at longer wavelengths (λ 383.2 and 357.6 nm) than for **1** (λ 277.4 and 267.8 nm). The extinction coefficients for these transitions are of similar magnitudes in the two compounds. Since the first absorption of **1** is found experimentally at 320 nm,[4b] the TD-B3LYP calculation slightly exaggerates the energy needed for the first transition. If this is also the case for the first transition of **13**, this compound will likely absorb in the blue wavelength region. As other silabenzenes rearrange to either silabenzvalenes or Dewar silabenzenes upon irradiation, one could speculate that **13** has a likelihood of rearranging when exposed to ambient light. In this context, it is noteworthy that 1,4-disilabenzene was found to rapidly rearrange to Dewar 1,4-disilabenzene when irradiated at λ 405 nm.[34]

The substituted silabenzenes may also dimerize, as found for some of the previously generated silabenzenes,[3c,4a] or they may rearrange via bimolecular pathways. With regard to the cycloadduct dimers, we focused on dimers in which both of the Si atoms become sp^3 hybridized, and six isomeric dimers of this type can be formed for **1** and symmetrically substituted silabenzenes. We also calculated the [4 + 2] head-to-tail dimer of **1**, where one Si remains sp^2 hybridized. Exo and endo isomers could be formed for the [2 + 2] cycloadducts, but for the [4 + 2] adducts there is no such possibility. The dimerization energies discussed are from B3LYP/6-31+G(d,p)//B3LYP/6-31G(d,p) calculations, unless otherwise noted. In our nomenclature of the dimers, **D** stands for dimer followed by the number of the particular silabenzene. The numbers **42** and **22** indicate whether it is a [4 + 2] or [2 + 2] adduct, **ht** and **hh** whether it is a head-to-tail or head-to-head adduct, and **exo** and **endo** whether it is an exo or endo adduct.

In comparison to benzene, for which the lowest [2 + 2] and [4 + 2] dimers are 59.6 and 57.6 kcal/mol above

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(34) Maier, G.; Schöttler; Reisenauer, H. P. *Tetrahedron Lett.* **1985**, *26*, 4079.

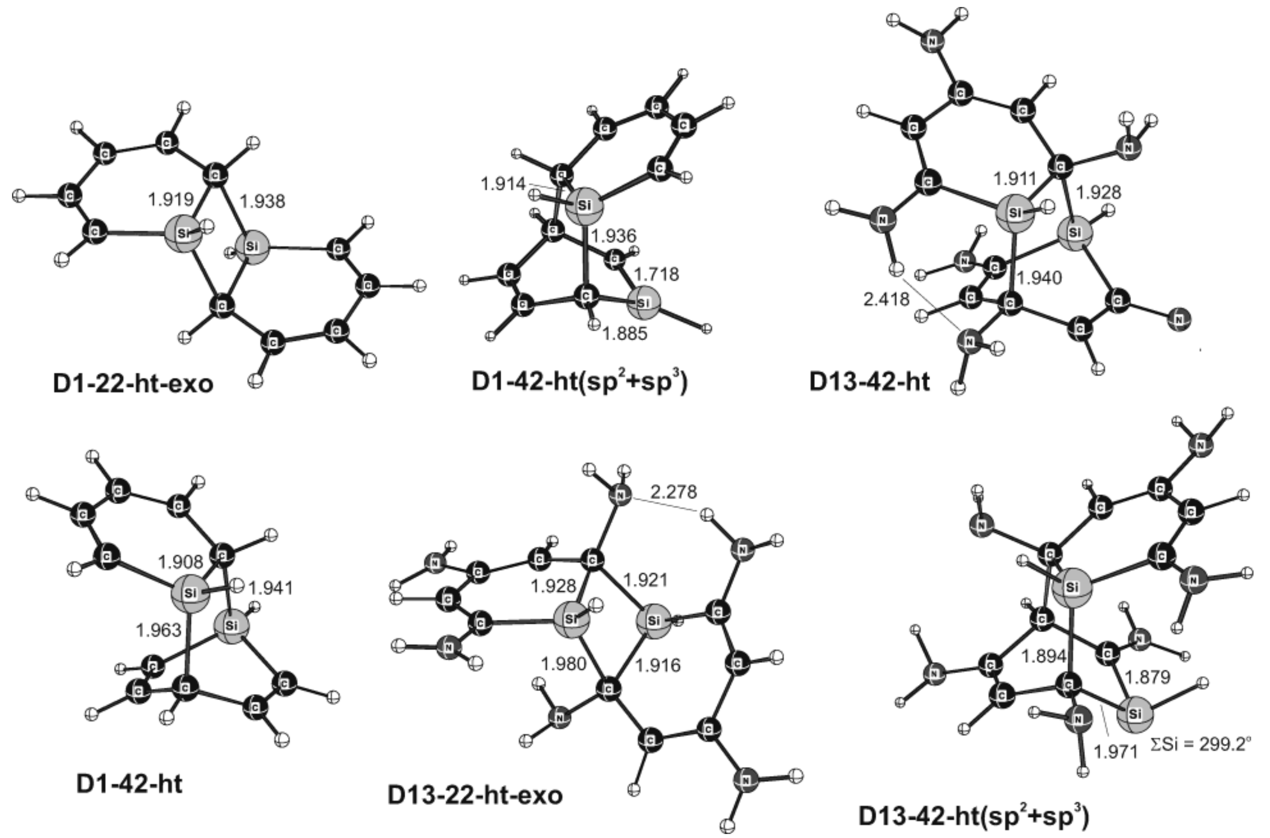

Figure 5. Optimized geometries of **D1-42-ht**, **D1-22-ht-exo**, **D1-42-ht(sp^2+sp^3)**, **D13-42-ht, D13-22-ht-exo**, and **D13-42-ht(sp^2+sp^3)** at the B3LYP/6-31G(d,p) level. Distances are given in Å and angles in deg.

two separated benzene molecules, dimerization of **1** is a highly exothermic process. The most stable [2 + 2] and [4 + 2] adducts of **1**, which are the [2 + 2] head-to-tail exo (**D1-22-ht-exo**) and [4 + 2] head-to-tail (**D1-42-ht**) cycloadducts (Figure 5), are 18.4 and 20.2 kcal/mol more stable than two separated molecules (Table 2). Our calculations further revealed that the head-to-tail dimerization products are clearly preferred over the head-to-head adducts. In this regard it is interesting to note that calculations by Brown and Borden on silabenzene and phosphabenzene,[6d] a compound that is stable at ambient temperatures,[35] showed that although the Si═C π bond energy is smaller than the P═C π bond energy, the major reason for the instability of silabenzene is the strength of the σ bonds formed to Si upon dimerization. As a result, the dimer in which one Si remains sp^2 hybridized (**D1-42-ht(sp^2+sp^3)**, Figure 5) has an energy considerably higher than for those in which both Si atoms are sp^3 hybridized (Table 2).

Since we want to know how reversed polarization influences the dimerization aptitude, we first examined the symmetric **13**: i.e., the silabenzene which is most affected by the zwitterionic resonance structure **II** (Scheme 2). We probed the relative stabilities of the six different dimer types where both Si atoms become sp^3 hybridized but also calculated the [4 + 2] head-to-tail dimer where one Si remains sp^2 hybridized (**D13-42-ht(sp^2+sp^3)**). For the substituted silabenzenes each dimer isomer can also adopt a vast number of different conformers varying with substituent orientation. Instead of computing the stability of each of the dimer conformers, we calculated those conformers that appear least congested, which admittedly introduces some ambiguity. Dimerization to the most stable [4 + 2] dimer of **13** (**D13-42-ht**) is exothermic by 5.8 kcal/mol, whereas dimerization to the most stable [2 + 2] adduct (**D13-22-ht-endo**) is endothermic by 0.7 kcal/mol. The energy gained upon dimerization of **13** is therefore much smaller than for **1**. Again, head-to-tail dimerization is more favorable than head-to-head dimerization, and the dimer that has one sp^2 hybridized Si is of highest energy, even though its relative energy is reduced when compared to the energy of the corresponding dimer of **1**.

However, the effect of reverse polarization in reducing the dimerization energy becomes less convincing if one considers **10**. Its geometry suggests that it is considerably influenced by the zwitterionic resonance structure **II**, but it releases 17.3 kcal/mol upon dimerization into **D10-42-ht** (Table 2): i.e., 11.5 kcal/mol more than dimerization of **13** into **D13-42-ht**. It seems that an extensive influence of reverse polarization is needed before a significant lowering in the dimerization energy of the silabenzene is found. A similar onset in the reduction of the dimerization energies was also first observed for reverse-polarized silenes when they had sufficiently strong π-donor groups at the C end.[18] On the other hand, with the two amino groups in meta positions (**12**) the energy released upon formation of **D12-42-ht** is instead larger by 9.8 kcal/mol when compared to the corresponding energy of **1**.

When possible hydrogen bonds in the dimeric cycloadducts of **13** are considered, the closest NH- - -H

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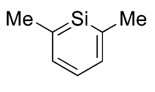
(35) (a) Ashe, A. J., III. *J. Am. Chem. Soc.* **1971**, *93*, 3293. (b) Ashe, A. J., III. *Acc. Chem. Res.* **1978**, *11*, 153. (c) Märkl, G.; Lieb, F. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 733.

Chart 5



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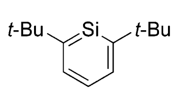

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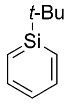

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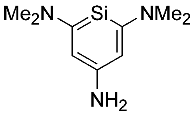
Chart 6



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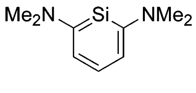

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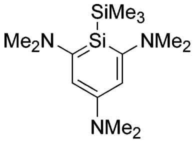

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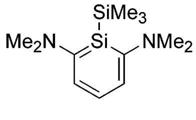

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distance is found in **D13-22-ht-exo**, where it is 2.278 Å (Figure 5). No other close NH---H contacts were found in this or any of the other dimers. This implies that hydrogen bonding is not important for the stabilization of the dimers of **13**. The steric bulk imposed by the amino groups is also very modest. 2,6-Dimethyl substitution as in **28** (Chart 5) should cause approximately the same steric congestion in the dimer as do the amino groups in **13**. However, the 2,6-dimethyl substitution in **28** even increases the energy released for dimerization into the [4 + 2] head-to-tail adduct by 0.6 kcal/mol when compared to **1** (Table 2). The stabilization toward dimerization observed in **13** is therefore not an effect of either H-bonding or steric bulk but instead a result of the reverse polarization in amino-substituted silabenzenes. Even 2,6-di-*tert*-butyl substitution as in **29** does not reduce the dimerization energy to the same extent as the amino substitution in **13**, since **29** releases 10.2 kcal/mol upon dimerization into the [4 + 2] head-to-tail adduct at the B3LYP/6-31+G(d)//B3LYP/6-31G(d) level. Also, when the H1 atom in **1** is replaced by a bulky *t*-Bu group (**30**), the dimerization energy is reduced by merely 3.3 kcal/mol at this level. This shows that very bulky groups, such as Tbt, are required to kinetically prevent dimerization of silabenzenes that are not affected by reversed polarization. Only through coordination to a transition metal can **30** be protected from further reactions.[14]

Replacement of the NH_2 groups at the ortho positions of **13** by NMe_2 groups leads to the silabenzene **31** (Chart 6), which is more stable in its monomeric than in its dimeric form by 2.7 kcal/mol. In this calculation we assumed that the [4 + 2] head-to-tail dimer is the most stable, as for **13**. This assumption could be oversimplified, but the difference from our calculated dimerization energy and the dimerization energy of an even more stable isomeric dimer of **31** should at most be a few kcal/mol. Interestingly, when the amino group in a para position is removed, yielding silabenzene **32**, the energy released upon formation of **D32-42-ht** is 10.1 kcal/mol, not much different from that of **29**.

Further reductions in the dimerization energies by 7−11 kcal/mol are achieved when a silyl group is added to the 1-positions of **1** and **13**, leading to **18** and **19**. Two separate monomers of **19** are more stable than the [4 + 2] head-to-tail dimer by 4.8 kcal/mol. In reality, one would use a Me_3Si group instead of an H_3Si group, which also adds some steric bulk and further increases the relative stability of the monomers when compared to the dimer.

When the [4 + 2] head-to-tail dimers of **18**, **20**, and **21** are compared, it becomes clear that trihalo substitution also makes the dimerization slightly less exothermic. Furthermore, as concluded above, **20** and **21** are as aromatic as **1** and benzene according to our NICS calculations. To achieve a stable silabenzene, one can thus work with three parameters: the steric bulk of the substituents, the inductive stabilization obtained through ipso silyl substitution, and the π-conjugative stabilization achieved through ortho and/or para substituents. Making use of these findings, we conclude that two silabenzenes that most likely prefer to exist as monomers rather than as dimers are 1-(trimethylsilyl)-2,4,6-tris(dimethylamino)silabenzene (**33**) and 1-(trimethylsilyl)-2,6-bis(dimethylamino)silabenzene (**34**) (Chart 6). Silabenzenes that are slightly less influenced by the zwitterionic resonance structure **II**, and thus more aromatic, will exist as monomers in cases where their substituents have some more steric bulk.

However, dimers of the zwitterionic silabenzenes other than [2 + 2] and [4 + 2] cycloadducts may form. For **13**, we also considered the dimers **D13A**−**D13E** (Figure 6). The first of these is a donor−acceptor complex in which the Si of one molecule of **13** coordinates to the C2 atom of the other, the latter atom resembling a C atom of an iminium cation. This complex is at a relative energy of 5.4 kcal/mol; thus, it is slightly less stable than two separate molecules of **13**. This complex is also separated from two monomeric **13** molecules by a transition state of 14.1 kcal/mol. However, this complex is set up for a proton transfer from N to Si, as indicated by the short Si---H distance of 2.457 Å. This process is also facile, as it proceeds over a transition state of 12.5 kcal/mol relative to two monomeric **13** molecules, and the compound formed, **D13B**, is at a lower relative energy (−9.4 kcal/mol). It is therefore crucial to prevent formation of **D13A**, as it functions as a trap for further rearrangement to **D13B**. Formation of **D13A** can presumably be hindered by NMe_2 instead of NH_2 substitution. Support for this conclusion comes from the corresponding complex of **31**, which is 28.9 kcal/mol above two molecules of **31** at the B3LYP/6-31+G(d)//B3LYP/6-31G(d) level. The steric bulk of a $SiMe_3$ ipso substituent will also destabilize dimers of the type **D13A**.

A hydrogen can also be transferred from one Si to the other in **D13A**, so that **D13C** is formed (Figure 6). This process leads to a return of aromaticity for one of the rings, whereas the other ring loses its aromaticity as its Si becomes sp^3 hybridized. The dimer **D13C** is 7.7 kcal/mol lower in energy than two separate **13** molecules, but the transition state that leads from **D13A** to **D13C** is at a relative energy of 23.1 kcal/mol. This should slow formation of **D13C**.

In the dimer **D13D** there are two hydrogen bonds between two of the amino groups in ortho positions and the partially negatively charged Si atoms (Figure 6).

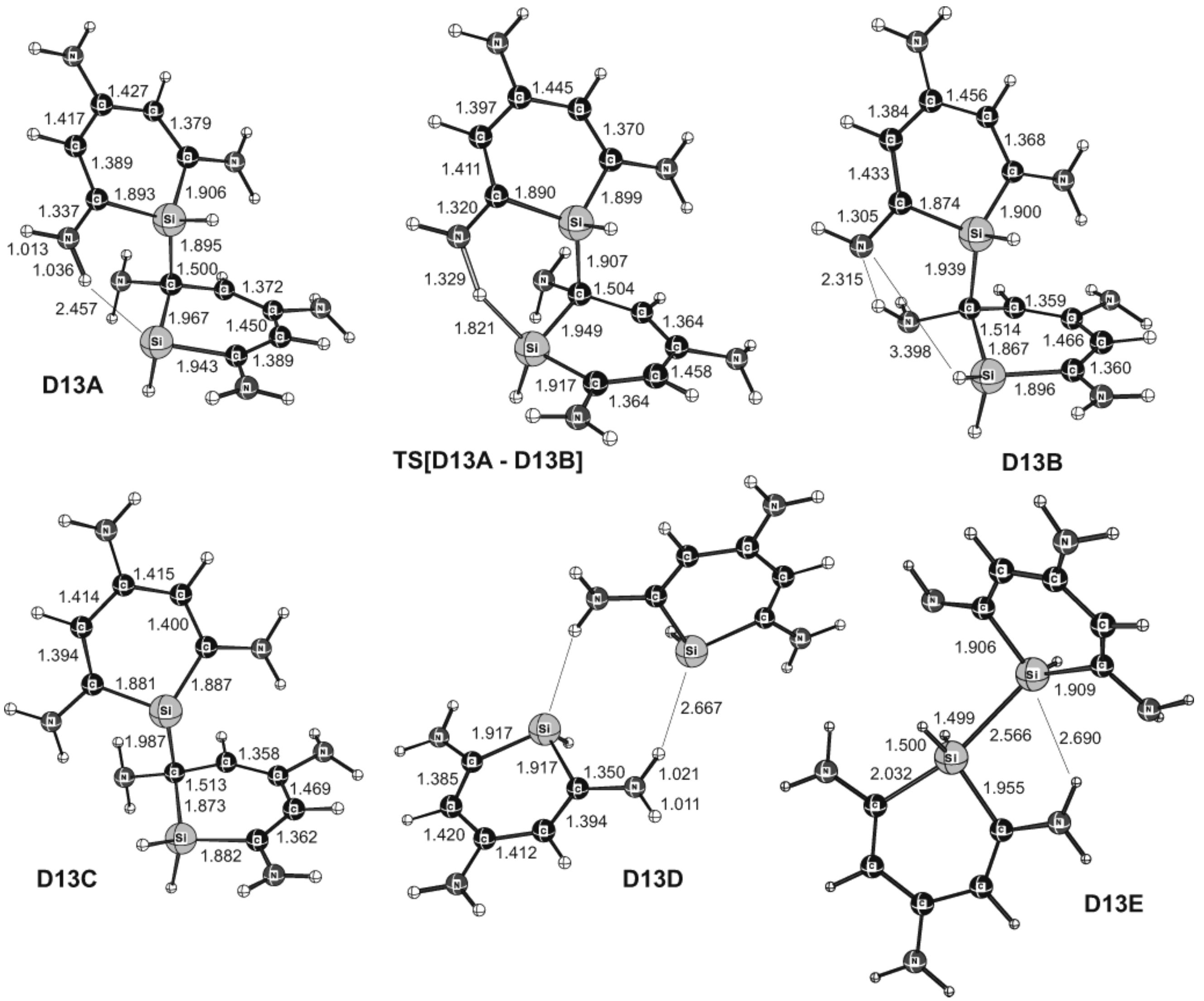

Figure 6. Optimized geometries at the B3LYP/6-31G(d,p) level of **D13A**−**D13E** and the transition states leading from **D13A** to **D13B**. Distances are given in Å.

This complex has C_2 symmetry, and it is 7.5 kcal/mol below two monomeric **13** molecules. The two silabenzene molecules in this dimer are also not distorted. However, one could argue that this dimer is set up for further rearrangement into two imines **23** through H atom transfer between the two silabenzenes. We found that this process is stepwise, involving the dimer **D13E**, where one Si is pentacoordinated and the other adopts an apical position of the trigonal bipyramid. This species is at a relative energy of 9.8 kcal/mol, and the transition states that lead to and from **D13E** are at 18.0 and 21.8 kcal/mol, respectively. However, as NMe_2 substitution prevents formation of hydrogen-bonded dimers such as **D13D**, such substitution should effectively eliminate the possibility for formation of **D13E** and imines via a bimolecular pathway. The calculations further indicate that the silabenzene is stabilized thermodynamically by ipso-silyl substitution and steric bulk. Thus, through variation of the three stabilizing effects discussed, it should be possible to prevent formation of complexes of the types **D13A**, **D13C**, and **D13D** so as to achieve new silabenzenes that are monomeric at ambient temperatures.

Conclusions

Density functional computations at the B3LYP level have been undertaken to study stabilization of silabenzenes through reverse Si═C bond polarization using amino and halo substituents as π-electron-donating groups. The results, which also should be applicable to germa- and stannabenzenes, can be summarized as follows.

(i) The partial positive charge at Si in silabenzene is reduced by ortho and/or para amino substitution. This is particularly the case in 2,4,6-triaminosilabenzene, a compound that should be dominated by zwitterionic resonance structures in which negative charge is placed on Si. The pyramidalization at Si correlates linearly with q(Si). Halo substitution has only modest effects on the charge distributions and structures of silabenzenes, and alkoxy substituents should take intermediate positions between halo and amino substituents in the ability to donate charge to Si. Silyl substituents at Si do not change the geometries of silabenzenes but have considerable impact on the reduction of q(Si).

(ii) The parent silabenzene is as aromatic as benzene on the basis of NICS calculations, but reverse polarization reduces aromaticity, since it decreases ring planarity and disrupts π-conjugation.

(iii) Six isomers of 2,4,6-triaminosilabenzene were investigated, and two of these are of lower relative energy. However, the pathways that lead to these isomers are blocked by barriers that cannot be overcome at ambient temperatures.

(iv) Dimerization into [2 + 2] and [4 + 2] cycloadducts was considered. It was found that [4 + 2] adducts are preferred for both the parent silabenzene and 2,4,6-triaminosilabenzene. In contrast to benzene, dimerization of the parent silabenzene is highly exothermic. However, triamino substitution at the ortho and para positions dramatically decreases dimerization energies and this effect increases even further with the attachment of a silyl group to Si. By combining the three ways to achieve stabilization of silabenzenes, i.e., ipso-silyl substitution, π-donor substituents in ortho and para positions, and steric bulk, it should be possible to design a series of silabenzenes that are more stable as monomers than as [4 + 2] and [2 +2] cycloadducts. More steric bulk is required for monomeric silabenzenes that are less affected by the zwitterionic resonance structures such as **II**, whereas only moderate steric bulk should be needed for those that can be stabilized extensively by such resonance structures and ipso-silyl substitution.

(v) A few other dimers in addition to [2 + 2] and [4 + 2] cycloadducts were found to be thermodynamically more stable than two separated 2,4,6-triaminosilabenzene monomers. However, their formations can be hindered by some moderate steric bulk of the substituents.

The study has clarified how reverse Si═C bond polarization functions in silaaromatic compounds, which should have significance for the general understanding of the properties of unsaturated heavy group 14 compounds. Furthermore, we hope that these computations can trigger and guide the synthesis of further stable and isolable silabenzenes that exist as monomers at ambient temperatures.

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Supporting Information Available: Listings of Cartesian coordinates of **1**−**32** and dimers together with their absolute energies. This material is available free of charge via the Internet at http://pubs.acs.org.

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