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Substituent Effects on the Structure and Aromaticity of 4-Silatriafulvene

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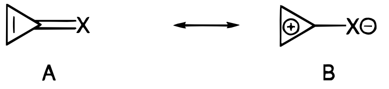
The structure and aromaticity of several 4-silatriafulvene derivatives are studied using correlated ab initio MO calculations. Electronegative substituents on silicon have been found to stabilize a nonplanar structure around the formal Si═C double bond, while π-electron acceptors planarize the molecule. To assess the aromaticity, the geometry index ΣCC, the nucleus-independent chemical shift (NICS), and the Bird indices are employed. Appropriate substituents on 4-silatriafulvene to enhance the aromatic character have been shown to cause the significant decrease of the Si═C π-bond strength. In cyclopropenylidene-1-silacyclopentadiene derivatives, both the three- and five-membered rings have low aromaticity, irrespective of the pyramidality of the molecular skeleton. Remarkably high aromaticity of the three-membered rings have been found in cyclopropenylidene-2-silaallene and 1-cyclopropenylidene-3-cyclopentadienylidene-2-silaallene.

Introduction

Triafulvene analogs (Chart 1, X = CH_2, O, S, PH, SiH_2, etc.) have been the subject of long-standing theoretical interest because of their unusual electronic structure and novel chemical reactions. The high strain of the three-membered ring of a triafulvene is, at least partly, compensated by the contribution of resonance structure **B** with a 2π aromatic ring.

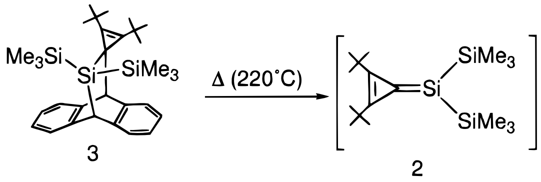
CHART 1



The aromaticity and geometrical structure of triafulvenes have been extensively studied in recent years;[1−10] some of these molecules are regarded as aromatic, while others are regarded as nonaromatic or even antiaromatic species, on the basis of different experimental and theoretical arguments. For example, cyclopropenone, the most extensively studied 4-heterosubstituted triafulvene, is usually considered to be an aromatic molecule,[3,5,7,8,11−13] although some earlier papers[14] question this finding based on the very small magnetic susceptibility anisotropy or the electron distribution of the molecule. In contrast, methylenecyclopropene was found by many researchers to be either an aromatic,[15] a nonaromatic,[1,7,10] or an antiaromatic molecule.[16] The experimental and theoretical considerations of the aromaticity of these molecules are well-summarized in the literature.[8]

Among the various 4-heterosubstituted triafulvenes, 4-silatriafulvene (**1**; Chart 1, X = SiH_2) is quite unique because it has an exo Si═C double bond that is intrinsically polarized as $Si^+−C^-$. We have recently reported the first generation of a 4-silatriafulvene derivative, 1,2-di-*tert*-butyl-4,4-bis(trimethylsilyl)-4-silamethylenecyclopropene (**2**),[17] via a sila-Peterson reaction[18] of di-*tert*-butylcyclopropenone with tris(trimethylsilyl)silyllithium or thermolysis of an anthracene adduct of **2** (**3**) at 220 °C (Scheme 1). The study has revealed unusually low reactivity of **2** toward alcohols and its facile isomerization to the corresponding silacyclobutadienes.

SCHEME 1



In our previous theoretical paper,[19] we have studied structures and reactions of 4-silatriafulvene (**1**) in details using ab initio molecular orbital calculations. At the equilibrium structure, **1** shows severe bending around the Si═C double bond. A planar structure with the cross-conjugated double bonds is the transition state for flopping between the two degenerate bent structures, while the energy barrier is within 1 kcal/mol at the MP2/6-311++G** + ZPE level (Figure 1). The competition between the Si−C π-bond formation and the ring aromatization diminishes the gross stabilization of the molecule. Unusually low reactivity of **1** toward water is ascribed to the less polar Si═C double-bond in **1** in comparison with the bond in simple silenes, due to the significant contribution of resonance structure **B** (X = SiH_2) in **1**.

In this paper, we have investigated extensively the substituent effects on the geometry, electronic structure, and stability of 4-silatriafulvene. Aromaticity of the three-membered ring in a 4-silatriafulvene is discussed in relation to the planarity around an exo silicon atom and the Si−C double bond character. The

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present results will be useful for design of novel cross-conjugated sila-π systems.

Calculations

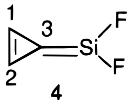
Quantum−chemical calculations were carried out with the GAUSSIAN 94[20] program package. In our previous paper,[19] we investigated the effects of basis sets and level of theory using the standard 6-31G* and 6-311++G** basis sets at the HF, MP2, MP3, MP4SDQ, CCSD, and QCISD levels of electron correlation. The results were not sensitive to the basis set, but were significantly modified by inclusion of the electron correlation. For **1**, the HF calculations gave a more bent structure with a longer Si−C bond by about 0.1 Å than the correlated methods; considerable differences were found in the C−C bond lengths and the C−C−C bond angles. Since the deviation among the results of the higher level calculations was small, we ignored the HF calculations and drew conclusions only from the MP2 results.

The geometries of all the investigated molecules were optimized at the MP2/6-31G* level and at the MP2/6-311++G** level for relatively small systems. Second derivatives and harmonic vibration frequencies were calculated for planar and nonplanar equilibrium structures. The number of imaginary frequencies was checked.

The aromaticity of the ring systems was estimated on the basis of geometry index ΣCC,[21] the nucleus-independent chemical shift (NICS) criteria, which are newly developed by Schleyer et al.,[22] and Bird's aromaticity index.[23] NICS(2.0)[22b] instead of the original NICS was used for three-membered ring compounds.

Results and Discussion

The structures and energies of various substituted 4-silatriafulvene derivatives (**4**−**10**) as well as some reference molecules (**11**−**25**) were investigated at the MP2/6-31 1++G** level.



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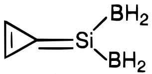

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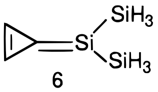

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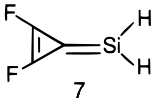

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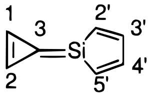

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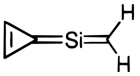

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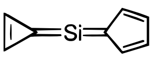

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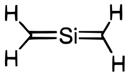


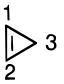
11

$H_2C{=}SiH_2$

12

$H_3C{-}SiH_3$

13



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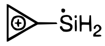

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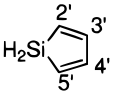

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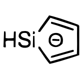

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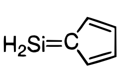

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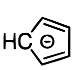

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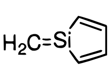

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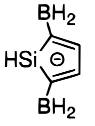

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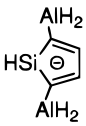

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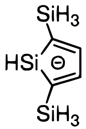

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The calculated geometrical data are shown in Table 1. The C−C bond lengths in the fully delocalized cyclopropenium cation (**16**) are 1.372 Å, while in the saturated cyclopropane (**15**) they are 1.511 Å. In cyclopropene (**14**), the bond lengths indicate the existence of fully localized single and double bonds. To elucidate the characteristics of the Si−C bond in a 4-silatriafulvene derivative, silaethene (**12**, Si−C: 1.712 Å) and methylsilane (**13**, Si−C: 1.877 Å) are the most appropriate model molecules.

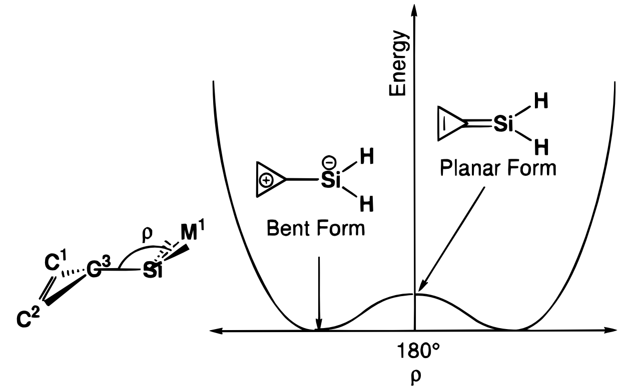


Figure 1. Schematic potential energy curve for bending motion of 4-silatriafulvene. ρ is the $M^1{-}Si{-}C^3$ angle and $M^1{-}Si$ is the line bisecting the H−Si−H angle.

It is expected that the difference between the ring C−C bond lengths decreases and the $C^1{-}C^3{-}C^2$ angle approaches the ideal angle of 60°, as the extent of delocalization, i.e., the aromaticity of the ring, increases in a 4-silatriafulvene derivative. The sum of the double-bond characters of the ring C−C bonds (ΣCC) has been shown to be a good quantitative measure of the aromaticity of five-membered heterocycles.[21,24] For three-membered rings, the two limiting values of ΣCC are 100 and 205 for nonaromatic cyclopropene **14** and the aromatic cyclopropenium cation **16**, respectively. Magnetic shieldings computed at ring centers (NICS) have been shown to be a good criterion of aromaticity[22] for five- and six-membered rings. For the aromaticity of the three-membered rings, however, the nearby σ-bonds make the original NICS index unrealistic.[22b,c] We have applied the NICS(2.0) method for the three-membered rings,[22c] where the ghost atom 2.0 Å is placed above the ring center for all the three-membered rings. These values are shown in Table 2. These data indicate that the planar structures are less aromatic than the bent equilibrium structures. However, comparison of NICS(2.0) values between different molecules was not allowed; e.g., the same NICS(2.0) values were found for **5** and **15**.[25] Bird's aromaticity indices,[23] which are based upon statistical evaluation of the deviations of the bond orders in the rings, range between 13 for **14** and 100 for **16**. These three aromaticity indices of the investigated molecules are summarized in Table 2. The table also contains the number of total π-electrons of the rings calculated by the NBO analysis. Obviously, if the number approaches two and six for the three- and five-membered rings, respectively, they are supposed to be more aromatic.

The energy differences between the planar and nonplanar optimum geometric structures (ΔE_g) may also be related to the aromaticity of 4-silatriafulvene derivatives, because the contribution of the resonance structure **B** in Chart 1 is expected to be more important at the nonplanar geometry than at the planar geometry. The ΔE_g values are also shown in Table 2.

According to the Bird indices and the ΣCC values, both fluorine- (**4**) and boryl-substituted 4-silatriafulvenes (**5**) are somewhat more aromatic than unsubstituted 4-silatriafulvene **1**. These indices for silyl-substituted 4-silatriafulvene **6** show that silyl substituents on the unsaturated silicon of **1** are effective

TABLE 1: Selected Geometrical Data of Silatriafulvene Derivatives and Related Molecules[a]

	$r(\mathrm{Si-C^3})$/Å	$r(\mathrm{C^1-C^3})$/Å	$r(\mathrm{C^1-C^2})$/Å	$r(\mathrm{Si-C^{2'}})$/Å	$r(\mathrm{C^{2'}-C^{3'}})$/Å	$r(\mathrm{C^{3'}-C^{4'}})$/Å	$a(\mathrm{C^3-Si-M^1})$/deg
1	1.743(1.712)	1.460(1.468)	1.322(1.319)				138.7
4	1.917(1.660)	1.428(1.486)	1.336(1.309)				110.5
5	1.795	1.433	1.335				180.0
6[b]	1.764(1.740)	1.445(1.452)	1.323(1.320)				129.1
7	1.765(1.722)	1.460(1.470)	1.313(1.308)				130.6
8[b]	1.753(1.731)	1.449(1.453)	1.321(1.318)	1.838(1.823)	1.369(1.373)	1.464(1.460)	145.5
8a[b]	1.757(1.756)	1.437(1.437)	1.326(1.326)	1.811(1.810)	1.414(1.414)	1.426(1.422)	171.5
8b[b]	1.757(1.739)	1.444(1.448)	1.323(1.321)	1.838(1.820)	1.384(1.390)	1.454(1.448)	146.7
8c	1.888	1.397	1.358	1.771	1.420	1.414	180.0
9	1.912	1.419,1.417	1.344				
10[b]	1.921	1.407	1.341		1.372,1.370	1.451	
11	1.699						
12	1.712						
13	1.877						
14		1.515	1.306				
15		1.511	1.511				
16		1.372	1.372				
17	1.792	1.412	1.346				
18				1.873	1.359	1.486	
19				1.836(1.790)	1.406(1.425)	1.431(1.416)	
20	1.735				1.376	1.455	
21					1.420	1.420	
22	1.715			1.843	1.363	1.483	
23				1.793	1.460	1.386	
24				1.802(1.795)	1.445(1.449)	1.402(1.399)	
25				1.811(1.788)	1.426(1.437)	1.412(1.405)	

[a] Full optimized results at the MP2/6-311++G** level; the result for the planar molecule is in parenthesis. [b] Optimizations were performed at the MP2/6-31G* level.

TABLE 2: Various Aromaticity Indices, Energy Differences (ΔE_g), and π-Charges of Silatriafulvene Derivatives and Related Molecules[a]

	ΣCC		NICS[b]		Bird Index		ΔE_g[c]	π-charge[d]	
compd	3-ring	5-ring	3-ring	5-ring	3-ring	5-ring	(kcal/mol)	3-ring	5-ring
1b	145(139)		−1.7(−0.8)		45(40)		1.4	2.831(2.905)	
4	169(126)		−3.0(−0.6)		64(28)		10.4	2.234(3.235)[e]	
5	165		−1.9		62		0.0	2.505	
6[f]	159(154)		−2.0(−1.3)		52(48)		1.2	2.736(2.814)	
7	149(142)		−0.8(−0.1)		41(35)		2.1	2.987(3.035)[e]	
8[f]	156(154)	201(198)	−1.7(−0.8)	−4.5(−5.2)	49(46)	43(53)	0.9	2.758(2.819)	5.123(5.083)
8a[f]	165(165)	173(175)	−1.3(−1.1)	−6.5(−6.6)	56(56)	75(76)	0.3	2.644(2.651)	4.938(4.941)
8b[f]	160(157)	190(187)	−1.8(−0.9)	−4.1(−5.0)	52(50)	50(62)	0.9	2.709(2.763)[g]	5.143(5.115)[g]
8c	188	173	−3.2	−16.8	85	97		2.032	5.840
9	175		−3.0		71			2.254	
10[f]	187	205	−2.9	−6.2	75	65		2.177	5.333
14	100		−1.5		13				
15			−1.9						
16	205		−19.2		100			1.994	
17	179				75				
18		199		1.1		17			
19		179(167)		−9.1(−14.3)		58(89)	3.8		5.756(5.947)
20		198		−5.3		66	0.0		5.323
21		170		−14.0		100	0.0		5.954
22		197		1.1		37	0.0		4.733
23		146		−7.2		75	0.0		5.321
24		153(150)		−10.2(−10.1)		80(81)	0.6		5.533(5.611)
25		168(160)		−10.9(−12.0)		77(87)	1.5		5.688(5.820)

[a] Unless otherwise noted, fully optimized results at the MP2/6-311++G** level. The result for the planar molecule is in parenthesis. [b] The NICS of D_{6h} benzene is −9.6 ppm at the MP2/6-311++G** level. The NICS(2.0) value[22c] was calculated for a three-membered ring. [c] Without ZPE correction. ΔE_g = total energy (planar structure) − total energy (optimum structure). [d] Unless otherwise noted, NBO analysis was carried out at the MP2/6-311++G** level. [e] The charge at the HF/6-311++G** level. [f] The MP2/6-31G* geometry is used. [g] The charge at the MP2/6-3I+G** level.

in increasindg the aromaticity but to a smaller extent than fluorine and boryl substituents. On the other hand, comparison of the ΔE_g values among **1**, **4**−**7** indicates that the geometry around the Si=C double bond in **1** is very dependent on the substituents; the electronegative fluorine substituent in **4** stabilizes the nonplanar geometry, while the electropositive but π-accepting substituents like boryl and silyl groups favor the planar geometry. It may be concluded that whereas no direct correlation exists between the ring aromaticity and the nonplanarity around the exo silicon atom, the aromaticity correlates with the Si−C^3 bond length; the longer the bond length is, the more aromatic the three-membered ring is.[26] If we compare the planar and nonplanar forms in a molecule, the nonplanar form is more aromatic than the planar form, because planarization causes shortening of the Si−C^3 bond. Comparison of the aromaticity indices between **1** and **7** indicates no significant

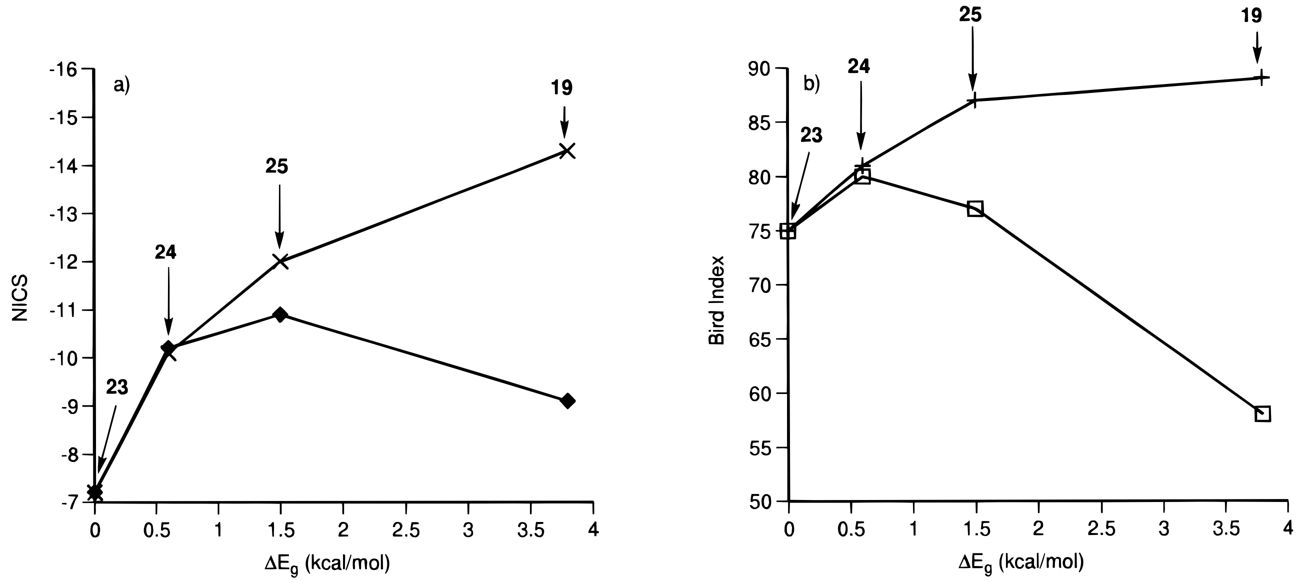
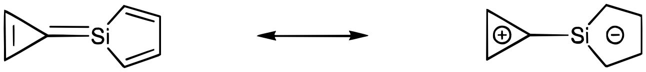


Figure 2. Plots of aromaticity indices vs energy difference between planar and nonplanar geometry (ΔE_g) of compounds **19**, **23**−**25**; (a) NICS for planar (×) and optimum geometry (◆), and (b) Bird Index for planar (+) and optimum geometry (□).

effect of fluorine substitution at the ring carbons on the aromaticity of three-membered ring.

The basic idea behind the investigation of **8**−**10** is that the enhanced intramolecular charge transfer from the three-membered ring to the five-membered ring via silicon may modify the ring aromaticity and also the geometry significantly (Chart 2).[27] In this relation, recent theoretical calculations have revealed considerable aromaticity of cyclopropenylidenecyclopentadiene[10] and cyclopropenylidenecyclononatetraene.[28]

CHART 2

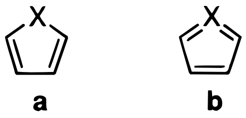


As shown in Table 1, however, the distance between the silicon atom and the three-membered ring carbon of **8** is shorter than the Si−C bond in the silole moiety. Bond-length equalization in **8** is observed neither in the cyclopropene nor the silole ring. The pyramidal geometry of silicon in the five-membered ring also indicates the lack of aromaticity in this half of the molecule. It seems that the silole ring is unable to accept the negative charge surplus of the lone electron pair on silicon. This finding is in accordance with recent experimental[29] and theoretical[30] results that silole and germole anions are nonaromatic or moderately aromatic, while the dianions are aromatic.[29c,31] A generally accepted explanation for this phenomenon is that the barrier to planarization about silicon is higher than the energy gain by aromatic stabilization.[32]

The ΔE_gvalue for **8** is somewhat smaller than that for **1**. This is because at the planar geometry in **8**, the three-membered ring is destabilized by losing the aromatic character but the energy loss is compensated in part by aromatic stabilization of the five-membered ring.

A comparison of the geometry and the aromaticity indices of the test molecules **18**−**22** may give an idea of the degree of aromaticity of the five-membered ring. The situation is somewhat more complicated when the geometry index, ΣCC, is applied to the five-membered heterocycles than in the case of the three-membered rings because two limiting nonaromatic mesomeric structures can be imagined (Chart 3). For pure structures **a** and **b**, ΣCC equals 200 and 100, respectively. Obviously, for an aromatic structure, the value of ΣCC should be expected to be between these two limits. The cyclopentadienyl anion **21**, which has the highest aromaticity of the five-membered rings, shows ΣCC = 170 with a large negative NICS value (−14) and a high Bird Index (100). For the nonaromatic silole **18** with a pure **a** structure, ΣCC = 199, the NICS value is almost zero, and the Bird index is low. The planar silacyclopentadienyl anion **19** shows high aromaticity (ΣCC = 167, NICS = −14.3, Bird index = 89), while the nonplanar equilibrium geometry of **19** is moderately aromatic (ΣCC = 179, NICS = −9.1, Bird index = 58).

CHART 3



Whereas the original idea to enhance the aromaticity of the three-membered ring through the charge transfer as shown in Chart 2 failed, the electronic structure of **8** may be modified by introducing appropriate substituents in the five-membered ring. First, the effects of BH_2, AlH_2, and SiH_3 substituents on the aromaticity of silacyclopentadienyl anion were investigated. It has been shown that the 17.2 kcal/mol barrier to planarity of phosphole is effectively reduced by appropriate π-electron accepting substituents.[33] Similarly, the effects of $SiMe_3$ groups have been shown to be important to planarize the tricoordinate phosphorus in the 1,2,4- triphosphole rings.[34] While the planarization barrier of **19** is much smaller (3.8 kcal/mol) than that of phosphole, parallel substituted effects are found; the silacyclopentadienyl anion with BH_2 substituents at the ring α-carbons (**23**) is planar in its equilibrium conformation and the AlH_2 (**24**) and SiH3 (**25**) substituents reduce the barrier to 1.5 and 0.6 kcal/mol, respectively. As shown in Figure 2, the aromaticity of the planar form increases with increasing barrier height; the planar transition state of **19** has the highest aromaticity and the planar ground state of **23** has the lowest aromaticity. Among the nonplanar equilibrium structures, the maximum aromaticity is observed at $\Delta E_g = 0.5-1.5$ kcal/mol.

The aromaticity indices in **8** indicate very low aromaticity of the silole ring, which is close to the planar nonaromatic

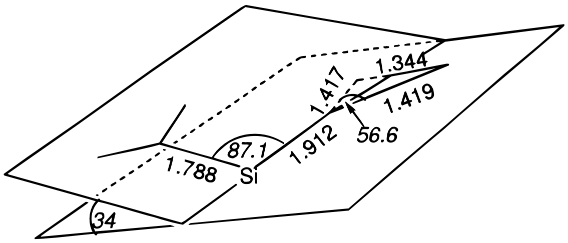
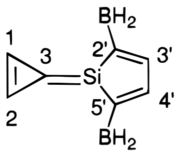
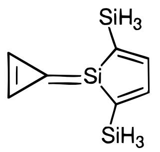


Figure 3. The optimized geometry of **9** at the MP2/6-311++G** level. Bond lengths are in Å, and bond and dihedral angles are in degrees.

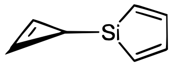
molecule **22**. In contrast to silol anion **19**, the aromaticity of the silol ring in **8** does not increase significantly in the planar geometry. The barrier to planarity for BH_2- and SiH_3-substituted cyclopropenylidene-1-silacyclopentadienes **8a** and **8b** is somewhat smaller than that for **8**, while the aromaticity of **8a** and **8b** is slightly higher both in the three- and five-membered rings. Relatively large bond equalization is found in **8a**; the ΣCC value of the five-membered ring in **8a** is 173, the value of which is close to that in a fully delocalized system **21**, being suggestive of high aromaticity in **8a**. However, the conclusion is not compatible with the long ring $Si-C^{2'}$ distance (1.811 Å). In this case, the ΣCC value is not a good measure of aromaticity but only indicative of high delocalization in cis-butadiene moiety of the ring as only the C−C bond distances are taken into account for the ΣCC index.[21]



8a



8b



8c

If the two ring planes are forced to be perpendicular to each other as in **8c**, no interaction can be assumed between the ring π-systems. Interestingly, the charge shift from the three- to the five-membered ring is the greatest at the perpendicular geometry during twisting around the exo Si−C bond of **8**, and therefore, high aromaticity of both the three- and five-membered rings of **8c** is given by all three aromaticity indices as well as the π-charge of both rings. As molecules having complete charge transfer from the three-membered ring to the five-membered ring as in **8c**, we have designed 2-silaallene derivatives **9** and **10**. Parent 2-silaallene **11** is a D_{2d} symmetry molecule with short Si═C bonds at both the HF and MP2 levels. Unexpectedly, the C−Si−C moiety in **9** and **10** is not linear but significantly bent with the bond angle of about 90°. The planes of the $Si{=}CH_2$ moiety in **9** (and $Si{=}CC_2$ moiety in **10**) are not perpendicular to the three-membered ring; at the MP2 level, the angle between the two planes is about 34°, while the angle is about 90° at the HF level (Figure 3). Nevertheless, aromaticity of the three-membered ring in **9** and **10** is estimated to be high and even comparable with that of silatriafulvene cation **17**, on the basis of the ΣCC values and Bird indices of these molecules. On the other hand, the five-membered ring of **10** is only moderately aromatic; the aromaticity is similar to that of parent 6-silapentafulvene **20**.

The small C−Si−C angles in **9** and **10** suggest strong s-character of the silicon lone-pair orbital and almost pure p character of the orbitals on the silicon making the Si−C σ-orbitals, which are characteristic of the bonding of second and higher row elements. This is why the $Si-C^3$ bond in **9** or **10** is longer than a usual single bond (Table 1) and the Si═C bond [1.790 Å for $Si{=}CH_2$ in **9** and 1.798 Å for Si═C (cyclopentadienylidene) in **10**] is longer than that in silaethene **12** or 6-silapentafulvene **20**. Molecules **9** and **10** can be described as systems with a $\sigma^2\lambda^3$-silicon.

Conclusions

We have investigated the structure of several 4-silatriafulvene derivatives using ab initio MO calculations at the MP2/6-311++G** level of theory. The aromaticity of these and related cyclic compounds has been estimated using three aromaticity criteria; ΣCC, the NICS, and the Bird indices. As the effective number of π-electrons in a ring is also characteristic for the aromaticity, we carried out NBO analysis for all the rings. The aromaticity indices of fluorine-(**4**) and boryl-substituted silatriafulvenes (**5**) are comparable, but the geometry around the silicon atom is quite different in each; electronegative fluorine stabilizes the bent structure around the silicon atom, while π-electron acceptors (BH_2) planarize the molecule. No direct correlation exists between the ring aromaticity and the nonplanarity around the exo silicon atom, while the aromaticity correlates with the $Si-C^3$ bond length; the longer the bond is, the more aromatic the three-membered ring is. In the cyclopropenylidenesilacyclopentadiene derivatives **8**, **8a**, and **8b**, the aromaticity of the three-membered ring does not change substantially with the substitution of the five-membered ring and is not sensitive to the barrier to planarity. However, highly aromatic species (**8c**, **9**, and **10**) can be derived by preventing conjugation between the two ring π-systems.

Considering the aromaticity indices used, the sequence of aromaticity of the investigated three-membered rings is **16** > **8c** > **10** > **17** > **9** > **4** > **5** > **8a** > **8b** > **6** > **8** > **1**, **7** > **14**. For the investigated five-membered rings, the order of aromaticity is **8c**, **21** > **25**, **24** > **19**, **23**, **8a** > **10**, **20** > **8**, **8b** > **22** > **18**.

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(25) As the distance between a three-membered ring and a measuring point becomes longer, the NICS values become smaller. The NICS values for **15** are −1.0, −0.6, −0.3, −0.2 and those for **5** are −1.1, −0.8, −0.6, −0.5 for the distances of 2.5, 3.0, 3.5, and 4.0 Å, respectively. The NICS value for **15** decreases more rapidly with increasing the distance, compared with that for **5**. The origin of the abnormally large NICS(2.0) value for nonaromatic compound **15** would be ascribed to the effects of the nearby C−H σ-bonds. Three-membered aromatic compounds have larger NICS values even at the longer distances; the NICS(3.5) values for **14** and **16** are −0.4 and −0.7, respectively. Nevertheless, we can conclude from the calculations that NICS values do not always give unambiguous order of the aromaticity for three-membered ring structures at any distances.

(26) For example, the Si−C^3 bond lengths of **4**, **5**, and **6**, which are 1.917, 1.795, 1.764 Å, respectively, are 0.222, 0.018, and 0.010 Å longer than the correspondiong Si−C bond distances of $Me_2C{=}SiF_2$, $Me_2C{=}Si(BH_2)_2$, and $Me_2C{=}Si(SiH_3)_2$, respectively.

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