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From Silaallene to Cyclotrisilanylidene

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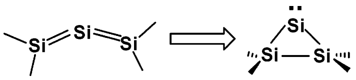
Four possible structural isomers at the Si_3H_4 potential surface, a trisilene, a trisilaallene, and two structurally different silylenes, have been studied by quantum chemical methods. With the investigation of the Si−Si−Si bond angle the different structures could be distinguished and characterized. $\alpha > 100°$ represents silaallenes with Si═Si double bonds and C_2 symmetry. In the $80° < \alpha < 100°$ region the Si═Si bond order is about 1.5 and the molecule is planar or almost planar and can be characterized with an in-plane lone electron pair and a delocalized π-system. A cyclic silylene with single Si−Si bonds and C_2 symmetry can be found in the $\alpha < 80°$ region. With systematic variation of the substituents using π-donor or -acceptor groups both silylenes can be stabilized. Some possible stabilized structures of each type are suggested.

Introduction

In 2003 Kira and co-workers synthesized the first stable trisilaallene.[1,2] In contrast to the carbon analogue allene (and similarly to the tin analogue[3]), this molecule is significantly bent: the Si═Si═Si bond angle is 136°, which indicates that the central silicon is between the sp and sp[2] hybridization. More recently trigermaallene and 1,3-digermasilaallene[4] and also some novel allenic anionic species consisting of two silicon atoms and a gallium or indium atom were prepared and isolated.[5] Since the surprising stability of these molecules is most likely caused by the steric hindrance of the huge groups at the terminal silicon (germanium) atoms, the synthesis of a more bent structure with appropriate substituents seems to be also possible. In this case, however, instead of sila- or germaallene, the existence of a new class of silylenes (germylenes) has to be considered:



The isolation and characterization of thermally stable silylenes in the 1990s brought the low-coordinated compounds of group 14 elements in the center of interest. Silylenes are frequent intermediates in thermal and photochemical reactions. Their existence was first proposed as transient molecules in organosilicon chemistry.[6] Then later they were isolated in matrix at low temperature[7] and still later as stable species.[8] For today the basic principles of the chemistry of divalent silicon species are well founded. Several tips and tricks are known for the synthesis and stabilization of elusive compounds, and their chemical and physical characteristics are well investigated. Review articles and book chapters[9] are available that summarize the latest progress of the field.

The stability of silylenes depends on several factors: the effect of substituents, the strain at the divalent silicon, the possible cyclic delocalization, and the shielding of bulky groups around the sensitive part of the molecule. A systematic study of these factors may help to design and synthesize novel compounds.

The aim of this work was to study the possible structural variation and stability of the new three-membered ring and related class of silylenes. We studied the potential surface of Si_3H_4 and its substituted derivatives using quantum chemical methods, seeking the stability criteria of allene and silylene structures.

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(1) Ishida, S.; Iwamoto, T.; Kabuto, C.; Kira, M. *Nature* **2003**, *421*, 725.

(2) "Allene" is a common name but allowed the usage instead of "propadiene" by the IUPAC rule. We have no proper bases to name one for a linear molecule but the other for a bent one. Both "trisilaallene" and "trisiladiene" can be used for a molecule having two cumulative Si═Si double bonds. If we allowed using the name "disilene" for a bent and/or twisted disilene, we should allow using the name trisilaallene for a bent trisilaallene.

(3) Wiberg, N.; Lerner, H. W.; Vasisht, S. K.; Wagner, S.; Karaghiosoff, K.; Nöth, H.; Ponikwar, W. *Eur. J. Inorg. Chem.* **1999**, 1211.

(4) Iwamoto, T.; Masuda, H.; Kabuto, C.; Kira, M. *Organometallics* **2005**, *24*, 197.

(5) Nakata, N.; Izumi, R.; Lee, V. Y.; Ichinohe, M.; Sekiguchi, A. *J. Am. Chem. Soc.* **2004**, *126*, 5058.

(6) (a) Drahnak, T. J.; Michl, J.; West, R. J. *J. Am. Chem. Soc.* **1979**, *101*, 5427. (b) West, R. J.; Fink, M. J.; Michl, J. *Science* **1981**, *214*, 1343.

(7) (a) Michalczik, M. J.; Fink, M. J.; De Joung, D. J.; Carlson, C. W.; Welsh, K. M.; West, R.; Michl, J. *Silicon, Germanium, Tin, Lead Comput.* **1986**, *9*, 75. (b) Punanik, D. B.; Fink, M. J. *J. Am. Chem. Soc.* **1989**, *111*, 5951.

(8) (a) Jutzi, P.; Holtmann, U.; Kanne, D.; Krüger, C.; Blom, R.; Gleiter, R.; Hyla-Kryspin *Chem. Ber.* **1989**, *122*, 1629. (b) Karsch, H. H.; Keller, U.; Gamper, S.; Müller, G. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 195. (c) Denk, M.; Lennon, R.; Hayashi, R.; West, R.; Belyakov, A. V.; Verne, H. P.; Haaland, A.; Wagner, M.; Metzler, N. *J. Am. Chem. Soc.* **1994**, *116*, 2691. (d) Denk, M.; Green, J. C.; Metzler, N.; Wagner, M. J. *J. Chem. Soc., Dalton Trans.* **1994**, 2405. (e) West, R.; Denk, M. *Pure Appl. Chem.* **1996**, *68*, 785. (f) Kira, M.; Ishida, S.; Iwamoto, T.; Kabuto, C. *J. Am. Chem. Soc.* **1999**, *121*, 9722.

(9) Reviews for silylenes, see: (a) Apeloig, Y. Theoretical Aspects of Organosilicon Compounds. In *The Chemistry of Organic Silicon Compounds,* Patai, S. Rappaport, Z., Eds.; Wiley: New York, 1989; pp 167−184. (b) Almond, J. L. *Short-Lived Molecules*; Ellis Horwood: New York, 1990; pp 93−120. (c) Zybill, C. The Coordination Chemistry of Low Valent Silicon. In *Topics in Current Chemistry, Vol. 160*; 1991. (d) Weidenbruch, M. *Coord. Chem. Rev.* **1994**, *130*, 275. (e) Denk, M.; West, R.; Hayashi, R.; Apeloig, Y.; Pauncz, R.; Karni, M. Silylenes, Stable and Unstable. In *Organosilicon Chemistry II. From Molecules to Materials*; Auner, N., Weis, J., Eds.; VCH: Weinheim, 1996. (f) Nyulászi, L.; Veszprémi, T. *Silylenes.* In *Encyclopedia of Computational Chemistry*; Schleyer, P. v. R., Ed.; Wiley: Chichester, 1998. (g) Gaspar, P. P.; West, R. Silylenes. In *The Chemistry of Organic Silicon Compounds*, Vol. 2; Rappaport, Z., Apeloig, Y., Eds.; Wiley: New York, 1998. (h) Weidenbruch, M. *Eur. J. Inorg. Chem.* **1999**, 373. (i) Veszprémi, T. *Adv. Mol. Struct. Res.* **2000**, *6*, 267.

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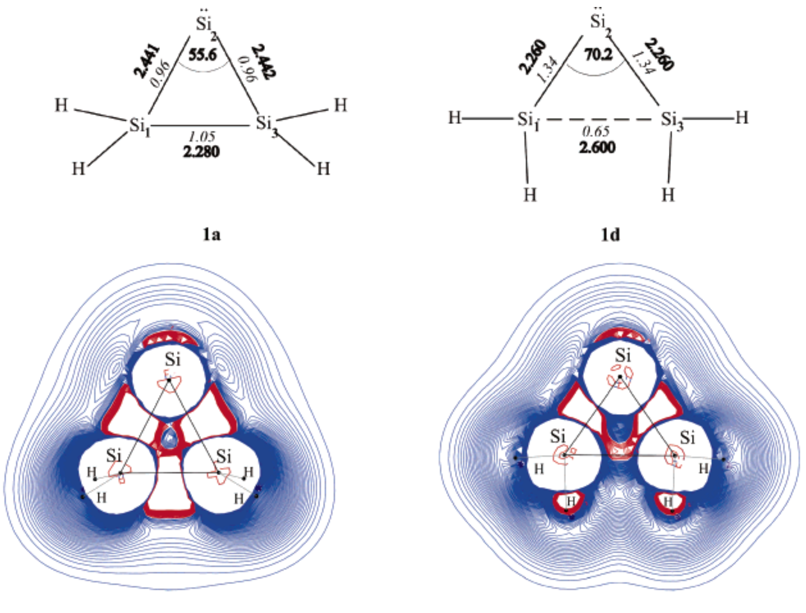
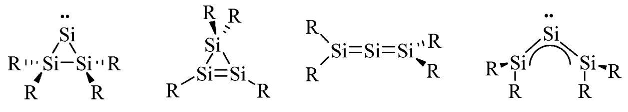


1a **1d**

1a **1d**

Figure 1. Geometry, Wiberg indices (italics), and Laplacian distributions of **1a** and **1d.** Bond lengths in Å and bond angles in deg (bold).

Chart 1



a **b** **c** **d**

Results and Discussion

Simple chemical wisdom suggests the possible Si_3H_4 (**1**) isomers (**a**−**d**[10]) shown in Chart 1 (−R = −H). Studying, however, the potential energy surface it can be found that while **1a**, **1b**, and **1d** are true minima, the linear **1c** is a second-order saddle point.[11] Although, at first glance **1d** is close in structure to **1a**, a deeper comparison indicates a large difference between the two structures (Figure 1, Table 1.). **1d** is more stable than **1a** by 5.42 kcal/mol at the DFT level (2.73 kcal/mol at the CCSD level). While **1a** has C_2 symmetry (CCSD/6-311++g** calculations predict almost C_{2v}), **1d** has C_s symmetry. **1a** is a cyclic silylene, with a bond angle of 55.6°, and **1d** is a strongly bent ($\alpha(Si_1{-}Si_2{-}Si_3) = 70.2°$) but open chain molecule with a delocalized π-system over the three silicon atoms. The investigation of the critical points obtained from the topological analysis of the electron density shows a ring critical point in **1a**, which is missing in **1d**. The Wiberg bond indices of the molecules indicate three single bonds between the ring atoms in **1a**, but a weak interaction between Si_1 and Si_3 and strong interaction (bond order is 1.34) between Si_1, Si_2 and Si_2, Si_3 in **1d** (Figure 1). The latter molecule is, however, essentially different also from silaallene. The Laplacian distributions of electron densities demonstrate the appearance of an in-plane electron pair on Si_2 in both **1a** and **1d**, proving that they are silylenes (Figure 1). In **1d** there is a delocalized π-system perpendicular to the plane containing the three silicon atoms, while in the allenic structures two perpendicular π-bonds are expected. (The symmetry of the pure allene is D_{2d}.)

The transition from **1a** to **1d** can be seen studying the energy change as the function of Si−Si−Si bond angle, α (Figure 2, continuous line). Since we optimized all the other parameters, the diagram includes **1a**, **1c**, and **1d** structures. It can also be seen that **1c** changes to **1d** without any energy barrier, but a small energy transition state exists between **1a** and **1d**. It is very close to **1a** in both energy and geometry.[12] Although **1b** is a different structural isomer, we also displayed its position in the figure. Comparing the optimized and the fully planar C_{2v} structures (Figure 2, dotted line) it can be seen that at $\alpha = 90°$ the two curves meet. This point indicates the clearest **d**-structure. Between $\alpha = 80°$ and $100°$ the curves run close and almost parallel. Below 80° the steric hindrance of the approaching hydrogen atoms increases the energy of the planar structure. At about $\alpha = 100°$ a breaking point on the optimum curve separates the two curves, suggesting some increasing stabilization effect of the allenic structure. In the diagram β represents the dihedral angle $X_1{-}Si_1{-}Si_3{-}X_3$ illustrated in Scheme 1. (The trisilaallene skeleton is obtained by looking down the axis through the two terminal silicones, Si_1 and Si_3.)

In the D_{2d} and the fully planar C_{2v} structures $\beta = 90°$ and 180°, respectively. Although at $\alpha < 90°$ the molecule is of slightly C_s symmetry and at $\alpha > 90°$ it is of C_2, the small energy difference between the planar and nonplanar structures suggests a reasonable flexibility of the molecules. Therefore we may consider that in this Si−Si−Si bond angle region the molecule is close in electronic structure to silylene of **d**-type, but above $\alpha = 100°$ it is approaching trisilaallene (**c**). This assumption is also supported by studying the NBO charges on the central silicon (Figure 3). By bending the Si−Si−Si chain, the in-plane orbital becomes more and more localized on the central silicon as it forms the lone electron pair. Also, the out-of-plane 2e π-system pushes electrons to the center of the molecule; therefore, it is expected that with decreasing α the central silicon becomes more and more negative. An opposite effect is expected at very small α when the $Si_1{-}Si_3$ bond is forming to give structure **a**. This can be seen in Figure 3: around 90° a charge

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(10) Some other possible isomers such as $HSi{\equiv}Si{-}SiH_3$ and $H_2Si{=}SiH{-}SiH$ were not considered in this work.

(11) Kosa, M.; Karni, M.; Apeloig, Y. *J. Am. Chem. Soc.* **2004**, *126*, 10544.

(12) The transition state frequency analysis was performed and the existence of only one imaginary frequency was checked at the B3LYP/cc-pVTZ level. Also, IRC calculations were performed at the same level to confirm the reaction coordinates for the TS to stable products **1a** and **1d**. The total energy and geometry of the TS are listed in the Supporting Information.

Table 1. Selected Data of the Investigated Molecules[a]

	$d(\mathrm{Si_1{-}Si_2})$ [Å]	$d(\mathrm{Si_1{-}Si_3})$ [Å]	NBO charge ($\mathrm{Si_2}$)	Wiberg index ($\mathrm{Si_1{-}Si_2}$)	α^b [deg]	β^c [deg]	$-\Delta E^d$ [kcal/mol]	sym
1a	2.441	2.280	0.289	0.96	55.7		16.5	C_2
	2.447	*2.291*	*0.273*	*0.97*	*55.8*		*21.6*	(C_{2v})
	2.436	**2.284**	**−0.358**	**1.10**	**55.9**		**18.5**	
1b	2.307	2.117	0.352	1.03	54.6		19.1	C_{2v}
	2.309	*2.120*	*0.347*	*1.03*	*54.7*		*18.7*	
1c	2.121	4.242	−0.190	1.97	180.0	90.0	0.0	D_{2d}
	2.124	*4.248*	*−0.196*	*1.97*	*180.0*	*90.0*	*0.0*	
	2.126	**4.252**	**−0.237**	**1.98**	**180.0**	**90.0**	**0.0**	
1d	2.260	2.600	0.042	1.34	70.2		21.9	C_s
	2.268	*2.585*	*0.058*	*1.33*	*69.5*		*17.9*	
	2.255	**2.571**	**0.064**	**1.31**	**69.5**		**21.2**	
	2.262	***2.566***			***69.1***			
2	2.246	2.788	−0.165	1.41	76.7		17.4	C_s
	2.255	*2.724*	*−0.128*	*1.39*	*74.3*		*16.9*	
3	2.201	4.017	0.091	1.76	131.7	98.1	3.5	C_2
	2.212	*3.954*	*0.055*	*1.75*	*126.7*	*100.0*	*4.6*	
4	2.204	4.408	0.481	1.55	180.0	90.0	0.0	D_{2d}
	2.206	*4.412*	*0.422*	*1.59*	*180.0*	*90.0*	*0.0*	
5	2.232	3.062	−0.603	1.45	86.6	119.7	39.7	C_2
	2.239	*3.065*	*−0.602*	*1.46*	*86.4*	*113.2*	*39.1*	
6	2.245	3.170			89.8	100.5		C_2
	2.251	*3.166*	*−0.546*	*1.45*	*89.4*	*97.2*	*35.0*	
7	2.231	2.949	−0.500	1.47	82.7	133.9	52.3	C_2
	2.240	*2.932*	*−0.490*	*1.53*	*81.8*		*55.8*	
8	2.229	2.914	−0.490	1.47	81.7	180.0	50.8	C_{2v}
	2.231	*2.945*	*−0.538*	*1.46*	*82.6*	*180.0*	*48.0*	
9								C_s
	2.246	*2.877*	*−0.199*	*1.45*	*79.7*		*22.3*	
10								C_2
	2.234	*3.509*	*−0.340*	*1.65*	*103.5*	*127.7*		
11								C_2
	2.234	3.594	−0.273	1.63	107.1	113.0		
12								C_2
	2.230	*4.044*	*−0.445*	*1.68*	*130.2*	*110.0*		
13[e]	2.173				180.0	90.0	0.0	D_{2d}
14	2.234	2.932	−0.483	1.42	82.0	78.3		C_2
	2.243	*2.914*	*−0.471*	*1.41*	*81.0*	*68.4*		
15	2.238	2.921	−0.486	1.42	81.4	51.0		C_2
	2.247	2.843	−0.467	1.40	78.5	35.9		
16								C_2
	2.263	*3.183*	*−0.579*	*1.41*	*89.4*	*48.4*		
17	2.246	2.815	−0.245	1.40	77.6	180.0		C_{2v}
	2.254	*2.837*	*−0.261*	*1.40*	*78.0*	*180.0*		
18	2.262	2.713	0.017	1.29	73.7			C_s
	2.268	*2.674*	*0.013*	*1.29*	*72.3*			

[a] Using B3LYP/cc-pVTZ (normal), B3LYP/6−31g* (italics), CCSD/6-311++g** (bold), and CAS(2,2)/cc-pVTZ (bold italics) levels of theory. [b] Si−Si−Si bond angle [c] For the definition of β see the text and Scheme 1. [d] Energy relative to the analogous linear silaallene [e] See ref 10.

minimum (maximum negative charge) on the central silicon can be observed in accord with the previous considerations.

The first cyclotrisilene (stabilized by bulky *tert*-butyldimethylsilyl substituents) was synthesized in 1999.[13] Compound **1b** is higher in energy by 2.8 kcal/mol than **1d** and lower by 3.6 kcal/mol than **1a**. The energy of **1c** is even higher by 21.9 and 16.5 kcal/mol than those of **1d** and **1a**, respectively. On the basis of this rough comparison of the energies the feasibility of the stabilization of both structures **1a** and **1d** seems to be a reasonable idea.

The simplest route to stabilization is the use of huge groups on the terminal silicon atoms to increase the steric hindrance (Chart 1, $-R = -CH_3$ (**2**), $-SiH_3$ (**3**)). In that way, however, the Si−Si−Si bond angle (α) at the minimum becomes obviously larger: by changing H to CH_3 (**2**) α increases to 76.7°, and by changing H to SiH_3 (**3**), it increases to 132° (Table 1), indicating the stabilization of the allenic (**c**) structure. (It is well known that the SiH_3 groups work as electron donor to the terminal silicon and stabilize the π-system.) This is supported by the increasing Si−Si bond order and the value of the β dihedral angle. Considering these criteria, the molecule with huge substituted cyclic groups, the one synthesized by Kira (**12**), is obviously a silaallene, despite the strongly bent (α = 136.5°) $Si_1-Si_2-Si_3$ chain (Chart 2).

Another way to stabilize **a-** and **d**-type silylenes is to enhance the thermodynamic stability varying the substituents on the terminal silicon atoms. As Apeloig suggested, using electropositive, π-electron acceptor groups on the silicon atoms (like $-BH_2$ groups (**4**)), linear trisilaallene is expected as a minimum of the PES.[11] To enlarge the kinetic stability, Apeloig proposed using cyclic diboryl substituents (**13**).

For the stabilization of the highly bent **a-** or **d**-type silylenes, we studied first the effect of electronegative, π-donor substituents on the terminal silicon atoms (Chart 1: $R = -NH_2$ (**5**), −OH (**7**), −F (**8**)). In these cases, as it is expected, the global minima are of **d**-type planar (R = −F (**8**), with C_{2v} symmetry) or near planar ($-NH_2$ (**5**), −OH (**7**) with C_2 symmetry) silylenes with a delocalized π-electron system over the three silicon atoms and with highly increased stability relative to the respective silaallenes (ΔE in Table 1). Significant conjugation between the nonbonding electron pairs of the substituents and the delocalized π-system increases the stability. If, however,

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[13] Iwamoto, T.; Kabuto, C.; Kira, M. *J. Am. Chem. Soc.* **1999**, *121*, 886.

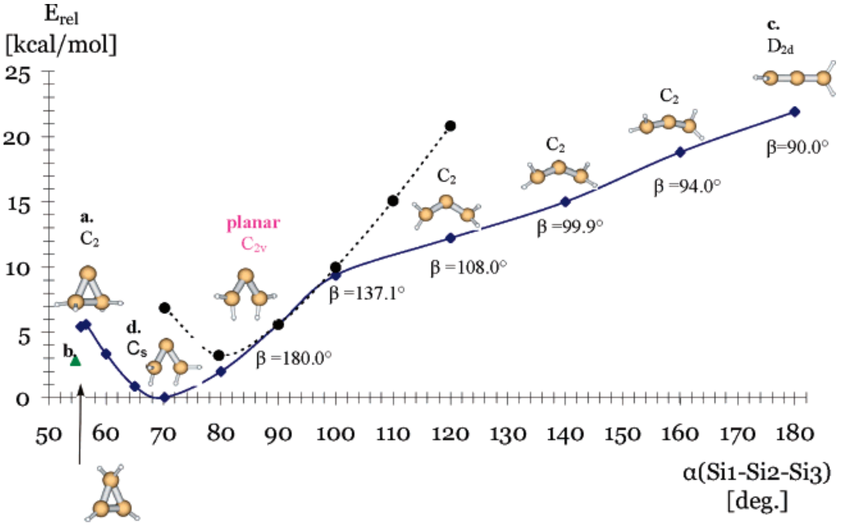


Figure 2. Relative energy of $H_2Si{=}Si{=}SiH_2$ as a function of Si−Si−Si bond angle. The transition from **1a** to **1c** is continuous. The dotted line indicates the relative energy of the structures forced into a planar C_{2v} arrangement. The **1b** cyclotrisylene is also displayed in the diagram.

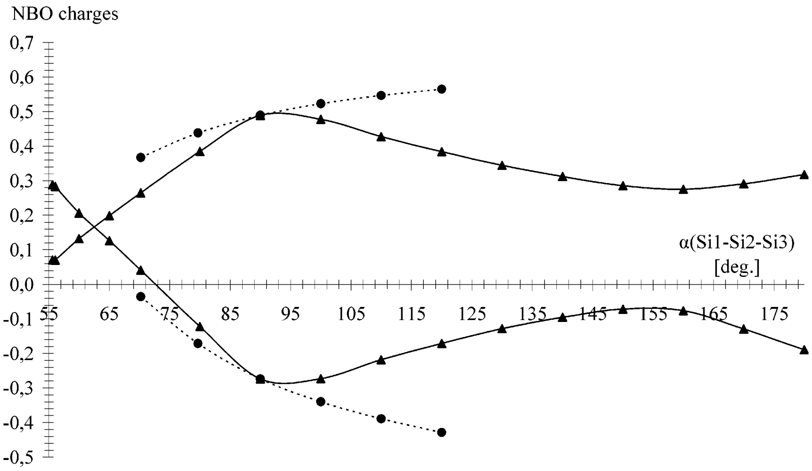
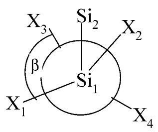


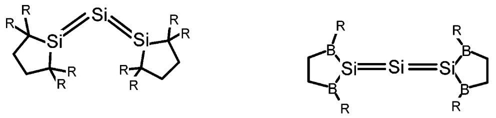
Figure 3. NBO charges on the central Si_2 (lower diagram) and on the Si_1 atoms (upper diagram) as a function of Si−Si−Si bond angle. The dotted line indicates the NBO charges of the structure forced into a planar C_{2v} arrangement.

Scheme 1



hydrogen atoms on nitrogen are changed to methyl groups (R = −N(CH$_3$)$_2$ (**6**)), the steric hindrance increases α and the C−N−C planes rotate toward the allenic structure. To harmonize the rotation of the substituent, we studied **14**, a derivative of the well-known stable diazasilol-2-ylidene, as it is potentially a promising precursor for synthesis (Chart 3). In this case the structural data clearly support the **d**-type structure (Table 1). The results do not change significantly with methyl or *tert*-butyl substitution of the five-membered rings (**15**, **16**).

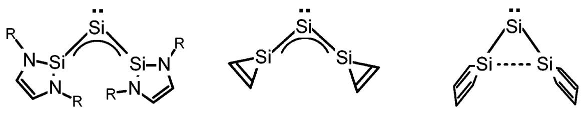
Chart 2



9 R = H
10 R = CH$_3$
11 R = SiH$_3$
12 R = SiMe$_3$

13

Chart 3



14 R = H
15 R = CH$_3$
16 R = C(CH$_3$)$_3$

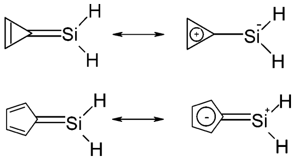
17

18

The effect of the unusual zwitterionic resonance structure of the tri- and pentafulvenes (Scheme 2) has also been studied (**17** and **18**) to utilize the electron donor or acceptor character of the trifulvene and pentafulvene groups, respectively. It was expected that in **17** the charge shifts toward the central silicon atom and stabilizes the silylene lone pair.

The data in Table 1 support our expectations. **17** is a fully planar C_{2v} molecule with α = 77.6°. The geometry, the Wiberg indices, and the NBO charges suggest a clear **d**-type silylene.

Scheme 2



In the case of **18** a charge shift in the opposite direction is expected, which may stabilize both the silylene **a**- and trisilaallene **c**-type structures. It is well known, however, that the silicon is strongly pyramidal in silole,[14] and as a consequence, the ring structure **a** is preferred. Indeed, in the optimum geometry of **18** the five-membered rings are almost perpendicular to the Si−Si−Si moiety with C_s symmetry. Despite the large substituents, the Si−Si−Si bond angle is smaller, the Si_1-Si_2 bond is longer, and the Si_2 atom is more positive than in **17**. The slightly positive central silicon atom and the reduced Wiberg bond index also suggest the approach toward the **a**-like structure. Nevertheless, the Si_1-Si_2 bond shows a partial double-bond character and the ring critical point is still missing.

Conclusions

Four possible structural isomers at the Si_3H_4 potential surface, a trisilene, a trisilaallene, and two silylenes, have been studied by quantum chemical methods. The aim of our work was to find appropriate structural conditions for the stabilization and possible synthesis of the hitherto unknown classes of silylenes **a** and **d**. With the investigation of the Si−Si−Si bond angle we could conclude that in the $80° < \alpha < 100°$ region the molecules are close to the **d**-type silylene structure. In this region the Si═Si bond order is about 1.5, and the molecule is planar or almost planar and can be characterized with an in-plane lone electron pair and a fully delocalized π-system. A cyclic silylene with single Si−Si bonds and C_2 symmetry could be found well below the $\alpha = 80°$ region. Bulky substituents or π-electron acceptors stabilize only the silaallene structure. On the other hand, using π-electron donors both type of silylenes may exist. Systematic calculations of some ring-type substituents lead to molecules **16**, **17**, and **18**, which seem to be promising targets of new stable silylenes.

Calculations

Quantum chemical calculations were carried out using the Gaussian03 suite of programs.[15] In our previous works we studied the effect of basis sets and electron correlation on several double-bonded silicon species[16] using different basis sets and several correlation methods. It was found that the geometry is not sensitive to the basis, and good results are expected with standard density functional theory methods. CASSCF (2,2)/cc-pVTZ optimization calculations for structure **1d** were carried out to assess the importance of nondynamic electron correlation and hence the adequacy of the single reference correlation methods used in the present study. It was found that no reference configuration other than the HF had significant weight (the $n_{Si}-\pi$ double excitation had a 0.03 CI coefficient) in the CASSCF wave function. Therefore, in the present work in all the reported calculations we used the same method with the hybrid B3LYP functional[17] and the correlation consistent, polarized cc-pVTZ or (for large molecules) the 6-31g* basis sets. To check the reliability of the results, in some cases the CCSD/6-311++g** level of theory was also used. Since no essential energy or geometry differences were found between the DFT and the CCSD calculations, in the following we consider only the DFT results.

The optimized geometry was confirmed as minima on the potential surface by second-derivative calculations. All the calculated energy data were corrected with the zero-point energy (ZPE). For electron density investigation, natural population analysis (NPA) charges[18] were obtained with the NBO program in Gaussian. For the topological analysis of electron density the AIM2000[19] program was applied using the output of B3LYP/cc-pVTZ calculations.

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Supporting Information Available: Cartesian coordinates, total energies of all the calculated molecules, and Laplacian distributions of **1** at different α. This material is available free of charge via the Internet at http://pubs.acs.org.

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