Electronic structure, geometry, and reactivity of arylsilenes: a quantum-chemical study

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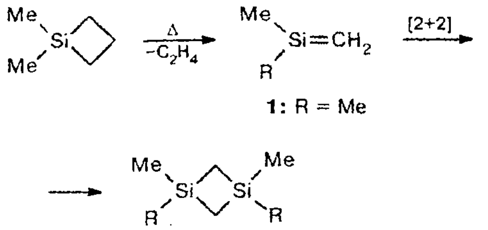
The geometry and electronic structure of 1,4-di(silaethen-1-yl)benzene (**2**), its *meta*- and *ortho*-isomers (**3** and **4**, respectively), and its carbon analog, 1,4-divinylbenzene (**5**), were studied by the semiempirical MNDO-PM3 method. Unlike **5**, two pairs of the frontier MOs in isomers **2**—**4** are mainly π-orbitals of Si=C bonds, while the structure of the lowest occupied π-MO indicates delocalization of π-electrons of the entire system. The main characteristic features of the double Si=C bonds (the high polarity and narrow HOMO—LUMO energy gap, which favors the [2+2]-cycloaddition reaction) remain in arylsilenes **2**—**4**. The interaction between π-electrons of benzene fragment and the double Si=C bonds results in violation of the benzene ring symmetry, which is most pronounced in structure **5**. Weakening of the C—H bonds in the *ortho*-positions of the aromatic nucleus in the compounds under study is observed.

Key words: arylsilene, 1,4-di(silaethen-1-yl)benzene, 1,4-divinylbenzene, dimethylsilene, quantum-chemical MNDO-PM3 method, frontier molecular orbital, π-electron delocalization, reactivity, stabilization energy, [2+2]-cycloaddition.

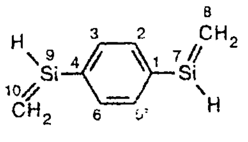
One of the most typical reactions of silenes generated by thermal [2+2]-cycloreversion of 1-silacyclobutanes is their cyclodimerization occurring with participation of the double Si=C bonds and resulting in the formation of 1,3-disilacyclobutanes:[1]



1: R = Me

However, in the case of arylsilenes (R = Ar) there is a competition between this reaction and rearrangements accompanied by 1,*n*-hydrogen shift from an aryl substituent toward the double Si=C bond and by the formation of heterocyclic silicon compounds condensed with aromatic nuclei.[2,3] The fact that the reaction follows such a route has been confirmed experimentally by the rearrangement of 1-methyl-1-phenylsilene into 3,4-benzo-1,1-dimethyl-1-silacyclobutene and by the structure of a polymer formed from 1,4-bis(1-methyl-1-silacyclobut-1-yl)benzene upon precipitation from the gas phase:[3]

To study the effect of electronic structure and geometry of arylsilenes on the reactivity of the double Si=C bond at the aromatic nucleus in the [2+2]-cycloaddition reactions, we carried out quantum-chemical calculations of 1,4-di(silaethen-1-yl)benzene (**2**) and its *meta*- and *ortho*-isomers (**3** and **4**, respectively).



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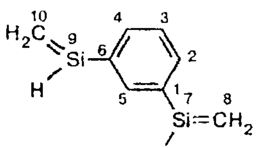

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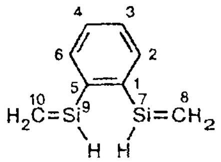

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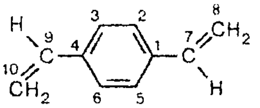
It was of interest to elucidate, first, to which extent is the conjugation between the double Si=C bond and the benzene fragment significant (as compared to the carbon analog **5**) and how can it affect the reactivity of arylsilenes in the [2+2]-cycloaddition reaction (as compared to the dimethylsilene **1**) and, second, how do the electronic structure and geometry of the benzene ring change due to the interaction with the double Si=C (C=C) bond.



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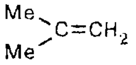

$Me_2C=CH_2$

6

Procedure for Calculations

The calculations were carried out by the semiempirical MNDO-PM3 method[4] with full optimization of geometric parameters. The energies of resonance stabilization (E_{st}) and Coulomb interaction (E_C) for [2+2]-cycloaddition reactions were evaluated in the framework of perturbation theory.[5]

Results and Discussion

Consideration of double Si=C bonds. As can be seen from the data listed in Table 1, the lengths of the ordinary Si—C bonds in molecule **1** are reproduced by the MNDO-PM3 method better than by the AM1 method,[8] according to which both the ordinary and multiple bonds in this molecule are appreciably shortened. The length of the multiple Si=C bond in this compound calculated by the MNDO-PM3 method is substantially underestimated as compared to the experimental value,[6] though it is somewhat longer than that obtained in the AM1 approximation. According to our calculations, the isomers **2**—**4** have planar skeletons.

The presence of the benzene ring in isomers **2**—**4** causes insignificant changes in the lengths and orders of their Si=C bonds as compared to dimethylsilene **1**; however, it is responsible for the shortening of the ordinary Si—C bonds and affects the charges on the Si and C atoms participating in the multiple bonds (the positive charges on the Si atoms in **2** and **3** slightly increase, whereas the negative charges on the C atoms decrease in all isomers; in this case the polarities of the Si=C bonds in **2** and **3** increase only slightly, while those in **4** decrease to the same extent). According to the conclusions drawn from the results of quantum-chemical calculations of a number of substituted silenes,[9] there is a rather good correlation between the length of the double Si=C bond and its polarity. The latter is also a fundamental characteristic of the Si—C bond, which reflects the large difference in the electronegativities of Si and C atoms. It should be noted that, according to the calculations of silenes with successive OH-substitution at the Si and C atoms performed in the 3-21G basis set, π-conjugation between the substituent and the double Si=C bond has little effect on the length of this bond.[9]

A very small (by ~1%) increase in the σ-order and analogous decrease in the π-order of Si=C bonds is observed in systems **2**—**4** as compared to **1**. It is likely that the contribution of the resonance structure $C^{\bullet}H_2—SiH=Ar=SiH—C^{\bullet}H_2$ has no effect on the lengths of the Si=C bonds, which has also been noted previously.[9]

Table 1. Geometric, energy, and electronic parameters of compounds **2**—**6** calculated by the MNDO-PM3 method

Compound	l/Å		q^a/au			^bP		P^{π}		P^{σ}		$E^{HOMO} - E^{LUMO}$ [c]/eV
	Si=C	Si—C	Si	C=	C—(Si)	Si=C	Si—C	Si=C	Si—C	Si=C	Si—C	
2	1.614 1.604[d]	1.795 1.801[d]	0.475	−0.417	−0.218	1.907	0.980	0.963	0.064	0.944	0.916	7.42, 8.64
3	1.614 1.604[d]	1.793 1.801[d]	0.477	−0.419	−0.249	1.907	0.979	0.964	0.064	0.943	0.915	7.75, 8.08
4	1.615 1.604[d]	1.802 1.809[d]	0.427	−0.423	−0.181	1.899	0.977	0.965	0.063	0.934	0.914	7.66, 8.22
1	1.614 1.605[d] 1.692[e]	1.855 1.809[d] 1.869[e]	0.423	−0.448	−0.252	1.902	0.983	0.971	0.034	0.931	0.949	8.34
5[f]	1.332	1.461	−0.091	−0.157	−0.050	1.929	1.030	0.951	0.079	0.978	0.951	8.35, 11.45
6[f]	1.333	1.487	−0.114	−0.175	−0.073	1.938	0.999	0.966	0.035	0.972	0.964	10.92

[a] q are atomic charges.

[b] P are bond orders according to Wiberg.[7]

[c] The energy difference for the frontier π-MOs participating in [2+2]-cycloaddition reaction: for compounds **2**—**4**, MOs *25, 26* and *24, 27* are considered, for compound **5**, MOs *25, 26* and *23, 28* are considered.

[d] Bond lengths l calculated by the AM1 method are also given.

[e] Experimental data.[6]

[f] For carbon atoms.

Apparently, the shortening of the ordinary Si—C bonds is to an appreciable extent due to the contribution of such structures. This is confirmed by the fact that in isomers **2**—**4** the π-orders of the bonds in question (initially very small in **1**) are twice as high as that in compound **1**, whereas their σ-orders decrease (approximately to the same extent) simultaneously with the increase in σ-orders of the multiple Si=C bonds. It is noteworthy that in the series **2**—**4** the lengths of the ordinary Si—C bonds correlate with their polarities: the bonds in isomer **3** are the shortest, those in **2** are somewhat longer, and the bonds in **4** are the longest.

From the analysis of the MOs of compounds **2**—**4** it follows that two highest occupied MOs (HOMOs) have nodes on the ordinary Si—C bonds. The p-AOs of the atoms participating in the Si=C bonds make the major contribution to the frontier MOs (FMOs), whereas the contribution of the π-electron system of the benzene fragment is rather small. It is likely that the reason for such a weak conjugation of π-electrons upon the formation of the molecular HOMO is that the π-HOMO energies of two mixing subsystems differ appreciably ($E\pi$ = −9.75 eV for benzene with a doubly degenerate HOMO and −8.41 eV for **1**), which hampers their interaction thus determining the pattern of the splitting of energy levels.

Thus, the energies of the two HOMOs of isomers **2**—**4** and that of the HOMO of **1** are close. In particular, for **2** these values are respectively −8.17 and −8.81 eV; the next π-MO (−9.54 eV) whose energy is close to that of the benzene HOMO, is an orbital of the π-system of the benzene fragment in structure **2**. The lowest occupied π-MO (−10.53 eV) is completely delocalized and belongs equally to π-electrons of both the benzene ring and the Si=C bonds (for vacant π-MOs, a picture analogous to that described for the occupied MOs is observed). As a result, the coefficients at the p-AOs of the Si and C atoms in the HOMO and in the lowest unoccupied MO (LUMO) are 20—30% smaller than those in the FMO of molecule **1**. As will be shown below, this can affect the reactivity of the multiple Si=C bonds of isomers **2**—**4** in [2+2]-cycloaddition reactions.

For each pair of orbitals, the widths of the HOMO—LUMO energy gaps for structures **2**—**4** differ slightly; for the reasons mentioned above, they are even somewhat smaller than that for **1** (see Table 1) and remain as narrow as those in related silene[9] for which the first vertical ionization potential is 8.85 eV, which is 2.5 eV lower than those of simple alkenes (in particular, of ethylene[10]).

Many authors believe[9,12] that the fundamental characteristics of the multiple Si=C bonds, the extremely high polarity and the narrow HOMO—LUMO energy gap, are responsible not only for their high reactivity in [2+2]-cycloaddition reactions, but also for the removal of the restrictions associated with the formal symmetry forbiddenness of such reactions according to the Woodward—Hoffmann rules.[11] As a result, the "head-to-tail" type cycloaddition of silenes occurs by the concerted ($2\pi_s$ + $2\pi_s$) mechanism.[9,12] Recently, this conclusion, drawn when analyzing the results of different quantum-chemical calculations of the cyclodimerization mechanism of a related silene (the 3-21G and 4-31G basis sets, partial geometry optimization; semiempirical methods),[9] has been confirmed at a high level of theory (SCF and CISD calculations using a double-ζ basis set augmented with d-polarization functions on C and Si atoms (DZ + d)).[12] It has also been shown that the "head-to-head" type dimerization reaction must occur by a two-stage mechanism involving the formation of a diradical intermediate.[12] The high exothermicity of the "head-to-tail" type cyclodimerization reaction (79.1 kcal mol^{-1})[12] indicates that the transition state should be more similar to the reagents rather than to the reaction products. At the same time, the authors of Ref. 13 who studied a "head-to-tail" type ($2\pi_s$+$2\pi_s$)-cycloaddition reaction of a related silene (the multi-configuration CAS-SCF/3-21G*, DZ+d[6] method), have come to the conclusion that it must occur by a stepwise diradical mechanism analogously to ethylene cyclodimerization reaction studied previously by the CAS-SCF/4-31G method,[14] for which the stepwise mechanism has been established experimentally.[15]

According to the reported data,[12] the activation energy of the concerted "head-to-tail" [2+2]-cycloaddition of silaethylene is 5.2 kcal mol^{-1}, *i.e.*, virtually coincides with that obtained for the stepwise diradical process (5.3 kcal mol^{-1}),[13] though that of ethylene cyclodimerization is 51.3 kcal mol^{-1}.[14] Without considering the problem of the mechanism of cycle formation, which is beyond the scope of this work, it should be emphasized that, apparently, it is these two characteristics of multiple Si=C bonds mentioned above that are responsible for such low activation energies of silene cyclodimerization. By comparing their values for a series of silenes one can estimate their reactivity in cyclodimerization reactions.

Analysis of dimerization processes of a number of substituted silenes in the framework of FMO theory has shown that in most cases the role of the polarity in controlling the reactivity of silenes and the products of their dimerization is more important than that of FMO energies.[16] In this work, we performed analogous estimates of the reactivity of the multiple Si=C bonds in the "head-to-tail" type [2+2]-cycloaddition reactions of **1**—**4** (according to the experimental data for **2**,[2,3] it is this type of cyclodimerization that actually occurs). It can be seen that, as could be expected, the energy of the Coulomb interaction (E_C/kcal mol^{-1}) in the series **1**—**4** varies slightly, and the resonance stabilization energies (E_{st}/kcal mol^{-1}) for molecules **2**—**4** are 2 to 3 times lower than that for **1**.

	2 + 2	**3 + 3**	**4 + 4**	**1 + 1**
E_{st}	−1.0	−0.8	−0.8	−2.5
E_C	−1.2	−1.2	−1.4	−1.5

These estimates were obtained for the concerted transition state;[12] the resonance integral β was accepted to be equal to 1 eV; the distance between the Si=C bonds (5 Å) corresponded to a negligible perturbation,[17] and only the Coulomb interaction between skeletal atoms was taken into account. In the case of slightly differing polarity of the double bonds in the series **1**—**4** this could reflect some increase in the activation energies (E_{act}) upon dimerization of isomers **2**—**4** as compared to cycloaddition **1**.

Comparison of the results of calculations for the *ortho*-, *meta*-, and *para*-isomers shows that the characterisrics of the double Si=C bonds in this series change insignificantly, though some increase in the π-electron mixing of the Si=C bonds and the benzene fragment in isomers **3** and **4** can result in a slight decrease in their reactivity as compared to that of **2** in the [2+2]-cycloaddition reactions.

According to our calculations, all three isomers are equally stable (the enthalpies of their formation are approximately equal).

Comparison with the carbon analog. From consideration of compound **5**, which is a carbon analog of molecule **2**, it follows that the degree of conjugation between the double C=C bonds and the benzene fragment in this compound is higher. First of all this follows from the analysis of MOs, indicating a strong π-electron mixing of the above subsystems in **5**, which manifests itself in the structure of the HOMO and LUMO. It should be noted that the calculated energies of the π-MOs of isolated molecules (benzene and **6**) are very close ($E\pi$ = −9.80 eV for the HOMO in **6**) and differ by only 0.05 eV. This must apparently result in a large splitting of corresponding π-MOs and an appreciable delocalization of π-electrons upon the formation of system **5**. As a result, the HOMO *25* (−8.79 eV) in **5** (as well as the LUMO) is completely delocalized and is to a somewhat greater extent an orbital of the π-electron system of the benzene ring.

The next energy level (−9.81 eV) is a π-electron level of the benzene fragment, while the energy of the π-MO *23* composed mainly of the p-AOs of C atoms of the double C=C bonds is −10.47 eV. For this reason, its contribution to the [2+2]-cycloaddition reaction should be extremely small. As should be expected, the coefficients at the p-AOs of the C atoms of the double C=C bonds in the FMOs of compound **5** become more than halved as compared to those of the FMOs of **6**.

Unlike the double Si=C bonds in arylsilenes and **1**, the double C=C bonds in **5** and **6** are characterized by low polarity and a wide π→π* transition energy gap (see Table 1). For instance, the HOMO—LUMO gap in **6** is 2.6 eV wider than in **1**, while that in **5** is ~1 eV wider than in **2**, (the contribution of π-electrons of the double C=C bonds to these MOs is not large). The orbital energies of MOs *23* and *28* differ by 4 eV.

The values obtained are in agreement with the results of other quantum-chemical calculations, according to which the energy of the π→π* transition for ethylene is ~2.5 eV higher than for the related silene.[9] This is characteristic of simple alkenes: according to electronic spectroscopy data, the energies of electronic π→π* transition (HOMO→LUMO) for simple alkenes are much higher than for analogous silenes, which is the explanation for a strong π-interaction in alkenes and a weak π-interaction in silenes,[10] respectively.

Despite the appreciable π-conjugation between the benzene fragment and double C=C bonds, the lengths of the latter in **5** and **6** are virtually the same (analogously to arylsilenes considered), though tendencies for their π-orders to decrease and (to a lesser extent) for their σ-orders to increase are evident (see Table 1). As can be seen from the data in Table 1, a shortening of the ordinary C—C bonds in **5** is accompanied by a substantial (more than twofold) increase in their π-order and a slight (less pronounced than for **2**—**4**) decrease in the σ-order; on the whole, an increase in the order of these bonds (due to the increase in the π-order) as compared to compound **6** is observed in **5**. From comparison of the characteristics of compounds **2** and **5** it can be seen that the difference in the polarities of Si—C and C—C bonds, responsible for the appreciable difference in the energies of the two-center Coulomb repulsion (1.84 eV for the Si—C bond *vs.* 5.15 eV for C—C bond), has no effect on the shortening of the Si—C and C—C bonds, respectively.

No unambiguous inference about the possibility for a hypothetical [2+2]-cycloaddition reaction of the carbon analog of **5** to occur can be drawn on the basis of the analysis of the results of our calculations. It is obvious that this reaction is even less feasible than the reaction of ethylene dimerization because of the low population of the HOMO by π-electrons of the double C=C bond

Table 2. Bond lengths, bond orders, and charges on the atoms in the benzene molecule and in the benzene fragments of compounds **2**—**5** calculated by the MNDO-PM3 method

Bond, atom	C_6H_6	**2**	**3**	**4**	**5**
	Bond length, l/Å				
C(1)—C(2)	1.391	1.392	1.393	1.393	1.399
C(2)—C(3)	1.391	1.391	1.390	1.391	1.387
C(1)—C(5)	1.391	1.392	1.392	1.393	1.399
C(2)—H	1.095	1.097	1.097	1.096	1.098
	Bond order, P^{σ}				
C(1)—C(2)	0.967	0.962	0.962	0.959	0.960
C(2)—C(3)	0.967	0.960	0.963	0.963	0.968
C(1)—C(5)	0.967	0.962	0.959	0.958	0.960
C(2)—H	0.966	0.961	0.962	0.960	0.956
	Bond order, P^{π}				
C(1)—C(2)	0.458	0.430	0.430	0.442	0.420
C(2)—C(3)	0.458	0.469	0.460	0.457	0.477
C(1)—C(5)	0.458	0.430	0.439	0.412	0.420
	Atomic charge, q/au				
C(1)	−0.102	−0.218	−0.249	−0.181	−0.050
C(2)	−0.102	−0.076	−0.043	−0.077	−0.098
C(3)	−0.102	−0.076	−0.141	−0.108	−0.089

and of the wide energy gap between the MO *23* and MO *28*. In the case of a two-stage dimerization mechanism, the rotation of radical fragments of the diradical intermediate[14] can also produce additional steric hindrances.

Consideration of the benzene ring. As can be seen from the data listed in Table 2, the replacement of H atoms by Si=C (C=C) double bonds violates the symmetry of the geometry and electronic structure of the benzene ring. The lengthening of the C(1)—C(2) and C(1)—C(5) bonds (and those similar to these bonds) and the shortening of the C(2)—C(3) bond (and those similar to this bond) of the benzene fragment are observed in the series of isomers **2—4** and in **5**. These changes respectively correlate with the decrease (by 6—10%) and increase (by 2.5—4%) of π-orders of the above bonds as compared to C_6H_6. In this case the deviations of σ-orders are rather small (not more than 0.8%). Distortions of the geometry of the benzene fragment in compounds **2** and **5** are stereotypic, despite the fact that the replacement of H atoms by Si=C (C=C) bonds induces appreciable changes opposite in sign in the charges on its atoms due to the difference in the electronegativities of the Si and C atoms (see Table 2).

Thus, the analysis shows that it is the π-interaction between the benzene fragment and the double bonds that results in the violation of the symmetry of the aromatic ring in isomers **2—4** and in **5** and that corresponding changes in the aryl nucleus are dependent on the position (α, β, or γ) of the second substituent. In the series of compounds **2—4** these changes are most pronounced for the *ortho*-isomer (**4**) because of the higher π-conjugation. On the whole, they are manifest to the greatest extent in molecule **5** because of the strong delocalization of π-electrons (see above).

As can be seen from the data in Table 2, the *ortho*-C—H bonds of the benzene ring in **2—4** (to a greater extent in **5**) become lengthened and their σ-orders decrease (the σ-densities on the *ortho*-C atoms decrease insignificantly). Weakening of these bonds also manifests itself in a decrease in corresponding total energies of two-center interactions due to the decrease in the two-center resonance and exchange energies (by ~2 kcal mol^{-1} in compounds **2—4** and by 3 kcal mol^{-1} in **5**). One can assume that such a weakening of the *ortho*-C—H bond in the aromatic nucleus favors the proton migration towards the Si atom followed by intramolecular cyclization observed in the experiment[2,3] in parallel with cyclodimerization (this requires a separate consideration).

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