

# Molecular and electronic structure of 1,2-disilacyclobutabenzenes. Ab initio molecular orbital and density functional study

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## Abstract

The geometric and electronic structure of 1,2-disilacyclobutabenzene and its polyannulated analogues is examined by the MP2(fc)/6-31G\* and B3LYP/6-31G\* methods. It is found that the bond distances alternate in the benzene fragment, the *ipso* bond being the longest. This finding is rationalised by the rehybridization at the carbon junction atoms. The average C–C distances are larger than in the free benzene, reflecting an interesting blow-up phenomenon. The latter is interpreted by the  $\pi$ -electron charge transfer interaction between the highest occupied MOs of the benzene ring and the  $\varphi^*(\text{SiH}_2)$  antibonding fragment orbitals of the SiH<sub>2</sub> groups. The destabilisation energy of these systems was examined by the homodesmotic reactions. It is shown that the total strain energy is additive to a good approximation, depending on the number of annulated four-membered rings.

**Keywords:** 1,2-disilacyclobutabenzene; Electronic structure; Geometric structure; Ab initio calculations; DFT calculations

## 1. Introduction

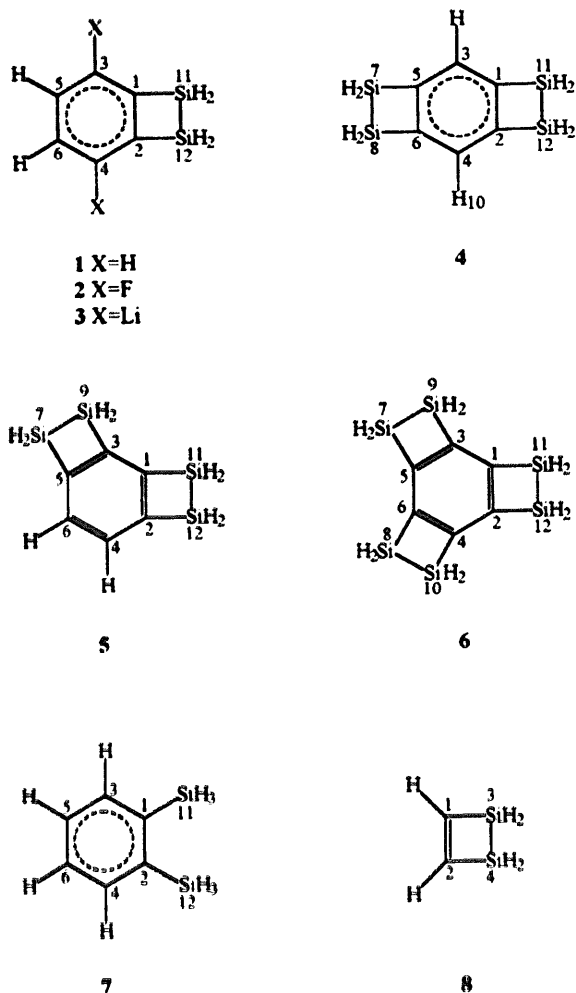
Small ring polysilenes have been the subject of long-standing research interest, which is not surprising in view of their high strain and remarkable reactivity [1,2]. The benzodisilacyclobutenes [3] constitute a particularly interesting family of this kind of compound. The parent system has not yet been synthesised, but its 1,1,2,2-tetramethyl and 1,1,2,2-tetraethyl derivatives were recently prepared by Shiina [4] and Ishikawa et al. [5] respectively. Their chemical appeal is provided by their unique behaviour in thermolytic [6] and photolytic [7] reactions. Not less fascinating are their reactions with transition metals in the presence of various trapping agents [8]. Furthermore, disilacyclobutabenzenes are also important from a practical point of view as precursors in polymer chemistry [3,4].

Despite considerable accumulation of experimental data, many interesting questions regarding these

molecules remain unanswered. For example, the geometry, relative stabilities, strain and electronic structure are features of key importance which deserve close scrutiny. Unfortunately, the reactive nature of these species makes it difficult to obtain such information experimentally. To fill this gap we deemed it worthwhile to consider some of these issues by employing modern computational methods of quantum chemistry. Apart from shedding more light on the energetic properties and (in)stability, we are particularly interested in ascertaining the effect of 1,2-disilacyclobutene annelation on the geometry of the aromatic ring in order to make a comparison with the available data for the closely related benzoecyclobutene(s) [9,10]. Therefore, in addition to the parent system **1**, calculations were also performed on the higher homologues **4–6** shown in Scheme 1.

Since the aromatic ring distortion can be modulated through a judicious choice of substituents [11], difluoro (**2**) and dilithio (**3**) derivatives of **1** are considered too. Finally, structural features of the *ortho*-disilabenzene **7** and the fragment molecule **8** will be discussed for the sake of comparison.

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Scheme 1.

It is well known that fusion of small, highly strained, carbocycle(s) distorts the aromatic fragment of the composite molecule, thus affecting its structure [9,10,12], aromatic stability [12b] and consequently its chemical reactivity [13–15]. It affects also the electronic structure of the annelated systems. The origin of the effect is customarily ascribed to the rehybridization at the annelated carbon centres and (hyper)conjugation involving the peripheral atomic groups [16].

The silanes considered here provide an interesting case in this regard, owing to the electropositive character of the silicon, the strong hyperconjugative ability of the  $\phi(\text{SiH}_3)$  groups MOs, and eventually  $\pi$  back-donation from the highest occupied benzene MOs to the low lying vacant  $\sigma^*_{\text{SiH}_3}$  orbitals [17,18]. The latter is expected to influence  $\pi$ -electron distribution within the aromatic ring to a considerable extent [19]. Hence, the present results should contribute to the better understanding of the role of  $\pi$ -electrons in determining the geometry of the annelated aromatic fragments.

## 2. Methodology

In performing calculations we made use of the ab initio molecular orbital [20] and density functional (DFT) [21,22] based methods, aiming to assess the applicability of the latter approach in elucidating the electronic structure of the examined molecules. Ab initio calculations were performed at the Hartree–Fock (HF) and MP2 levels of theory by employing the 6-31G\* basis set [23], which in turn is known to provide a satisfactory description of the angularly strained molecules [20]. DFT calculations were carried out by using the three-parameter Becke 3LYP [24] functional, which is a hybrid of exact (Hartree–Fock) exchange terms and gradient-corrected exchange and correlation terms, similar to that first suggested by Becke [25,26]. The usual 6-31G\* basis set was employed in the DFT calculations [23]. Following the standard nomenclature the latter calculation will be referred to as B3LYP/6-31G\*. In discussing geometrical parameters, use is made of simple qualitative bond indices such as hybridization parameters and Coulson's  $\pi$ -bond orders of the mobile  $\pi$ -electrons, since they prove particularly valuable in rationalising the bonding features of a large number of aromatic compounds annelated with the strained ring(s) [9,27]. For this purpose, s-characters were calculated by employing natural bond order (NBO) analysis [28] at the MP2/6-31G\* level. The  $\pi$ -bond orders are derived from the MP2/6-31G\* wave functions by symmetric Löwdin orthogonalization [29a]. Finally, effective atomic charges are listed, estimated by the Löwdin and NBO recipes. Although atomic charges do not have an absolute meaning, they represent a crude but useful description of the electron density distribution in molecules [29b] (results are given in Table 2).

The calculations were performed utilising Gaussian 92 [30], Gaussian 94/DFT [31] and GAMESS-US [32] program packages.

## 3. Results and discussion

The calculated structural parameters of molecules 1–8 are presented in Table 1. Their perusal shows that the salient feature of all systems considered here is substantial lengthening of the aromatic C–C bond linking annelated centres. A closer scrutiny of the presented data reveals that both MP2 and B3LYP methods give internally consistent and mutually compatible results. This is evidenced by the average absolute deviations between these two sets of bond distances of 0.001, 0.002 and 0.006 Å for C–C, C–Si and Si–Si bonds respectively. It is also noteworthy that molecular shapes (bond angles) are practically the same with both approaches. In contrast, we note in passing that the HF method systematically underestimates bond distances. Additionally, they lack any regular pattern of changes in

Table 1

Structural parameters in disilabenzocyclobutene and its bis- and tris-annelated analogues as calculated by the MP2(fc)/6-31G\* and B3LYP/6-31G\* methods (distances in angstroms and angles in degrees); atom numbering corresponds to Scheme 1

Parameters	1	2	3	4	5	6	7
<b>Bond <math>r</math> (Å)</b>							
C(1)–C(2)	1.424 (1.424)	1.422 (1.420)	1.438 (1.437)	1.430 (1.428)	1.425 (1.423)	1.426 (1.423)	1.420 (1.421)
C(1)–C(3)	1.403 (1.401)	1.390 (1.391)	1.420 (1.418)	1.402 (1.403)	1.406 (1.406)	1.410 (1.410)	1.406 (1.405)
C(2)–C(4)	1.403 (1.401)	1.390 (1.391)	1.420 (1.418)	1.402 (1.403)	1.407 (1.405)	1.410 (1.410)	1.406 (1.405)
C(3)–C(5)	1.396 (1.396)	1.392 (1.392)	1.413 (1.413)	1.402 (1.403)	1.425 (1.423)	1.426 (1.423)	1.397 (1.397)
C(4)–C(6)	1.396 (1.396)	1.392 (1.392)	1.413 (1.413)	1.402 (1.403)	1.396 (1.395)	1.426 (1.423)	1.397 (1.397)
C(5)–C(6)	1.402 (1.401)	1.400 (1.399)	1.408 (1.405)	1.430 (1.428)	1.407 (1.405)	1.410 (1.410)	1.394 (1.392)
C(6)–H	1.088 (1.087)	1.086 (1.085)	1.095 (1.094)	—	1.090 (1.088)	—	1.088 (1.087)
C(3)–X <sup>a</sup>	1.089 (1.088)	1.359 (1.352)	2.005 (1.973)	1.091 (1.089)	1.898 (1.901)	—	1.089 (1.087)
C(2)–Si(12)	1.895 (1.897)	1.893 (1.894)	1.889 (1.892)	1.899 (1.900)	1.898 (1.899)	1.901 (1.902)	1.886 (1.887)
Si(11)–Si(12)	2.345 (2.351)	2.354 (2.361)	2.336 (2.343)	2.345 (2.351)	2.346 (2.351)	2.347 (2.351)	—
Si(11)–H	1.490 (1.491)	1.487 (1.489)	1.500 (1.502)	1.489 (1.491)	1.490 (1.491)	1.489 (1.491)	1.486 (1.488)
<b>Angle <math>\alpha</math> (°)</b>							
C(2)–C(1)–C(3)	120.0 (119.9)	118.9 (119.0)	122.9 (122.8)	120.6 (120.5)	119.4 (119.4)	120.0 (120.0)	118.8 (118.8)
C(1)–C(3)–C(5)	119.4 (119.5)	121.8 (121.6)	113.2 (113.4)	118.8 (119.1)	120.5 (120.5)	120.0 (120.0)	121.5 (121.6)
C(3)–C(5)–C(6)	120.7 (120.6)	119.4 (119.5)	123.9 (123.7)	120.6 (120.5)	120.1 (120.1)	120.0 (120.0)	119.7 (119.7)
C(1)–C(3)–H	120.8 (120.8)	119.5 (119.5)	117.4 (117.1)	120.6 (120.5)	119.6 (119.6)	—	120.3 (120.4)
C(5)–C(6)–H	119.4 (119.5)	120.9 (120.9)	116.8 (117.0)	—	103.9 (104.2)	—	119.7 (119.6)
C(2)–C(1)–Si(11)	104.1 (104.2)	104.3 (104.4)	103.7 (103.9)	103.9 (104.0)	104.2 (104.1)	104.0 (104.1)	123.5 (123.6)

<sup>a</sup> For definition of X see Scheme 1.

systems 1–4. Apparently, an explicit account of the electron correlation is a prerequisite for a good description of these systems, where electrons have a better opportunity of avoiding each other due to delocalization. Consequently, we shall discuss in what follows the structural features of systems 1–6 by using results offered by the MP2(fc)/6-31G\* and B3LYP/6-31G\* methods.

We commence this discussion by considering the calculated geometry of **1** in more detail. For this purpose it is important to mention that the reference C–C bond distance in benzene is 1.397 Å as computed by both MP2 and B3LYP procedures. One observes a slight elongation of the bonds emanating from the substitution sites and a comparable lengthening effect in the bond opposite to the annelated C(5)–C(6) bond, whilst C(3)–C(5) and C(4)–C(6) bond distances remain practically unchanged. Finally, C<sub>Ar</sub>–Si and Si–Si bond distances are found to be slightly longer as a rule than in the parent 1,2-disilacyclobutene **8**, the dilithiated derivative **3** being a notable exception. It is interesting to note that calculations predict an almost identical decrease in  $\pi$ -bond orders (Table 2) for the annelated and *exo* bonds (0.62) relative to its value in free benzene (0.67). However, a glance at the calculated s-characters (Table 2) indicates that the difference in their s-contents makes these two types of bond different. More specifically, the hybrid orbitals belonging to the annelated bond have slightly lower s-character than the sp<sup>2</sup>–sp<sup>2</sup> bond, whereas the opposite is the case for the *exo* C(1)–C(3)/C(2)–C(4) bonds. Consequently, the annelated bond distance is expected to be longer. This is indeed the case, the difference being 0.023 Å. Since molecule **1** is paradigmatic for the whole series, it is instructive to

examine its  $\pi$ -bond orders more carefully. A bond order of 0.67 in the C(3)–C(5) bond is the largest one. It reveals the so-called anti-Mills–Nixon type of bond fixation [33] which increases the  $\pi$ -bond order in the *ipso* (annelated) bond and in bonds vicinal to the *ipso* one. The fact that the *ipso* bond order is slightly lower (0.63) indicates hyperconjugative interaction with the SiH<sub>2</sub> groups, also evidenced by the  $\pi$ -bond order in the C–Si bonds of 0.19.

It is interesting to mention that the difference (0.02 Å) in distances between *ipso* and *ortho* bonds is significantly larger than in the related carbocycle (0.005 Å), in spite of the larger strain imposed by the carbocyclic ring. The trend of distortion, however, is qualitatively the same: the *exo* (*ortho*) bonds in both molecules are found to be shorter than the annelated (*ipso*) bond. The same holds for their 5,8-difluoro (**2**) and 5,8-dilithio (**3**) derivatives, which are chosen to demonstrate the effect of rehybridization dictated by the additional substituents in the aromatic ring. According to the Walsh–Bent rule [34], replacement of H-atoms at the carbon sites C(3) and C(5) by fluorine is expected to diminish the s-content in the C–F bond. Concomitantly, the increase in the s-character of the neighbouring carbon–carbon bonds and their subsequent shortening is expected. This conjecture is corroborated by the computational models applied. The opposite is true in **3**, where lengthening of the aromatic bonds emanating from the C(3) and C(5) atoms is observed, because of the electropositive character of lithium. Obviously, distortion of the aromatic nucleus can be tuned by deliberate choice of substituents, which should make possible a detailed study of the interplay between  $\sigma$ - and  $\pi$ -electrons in determining the aromaticity.

The effect of di- and tri-annulation is noteworthy. Fusion of the additional disilacyclobutene ring in [a,d] fashion leading to **4** causes a slight elongation of the annelated bond relative to **1**. In contrast, fusion of the additional small ring(s) in [a,c] mode leading to **5** and **6** leaves the fused bonds unchanged but introduces a slightly increased elongation of the *exo* bonds. Inspection of  $\pi$ -bond orders offers a useful insight again. A tiny difference between the *exo* and *ipso* bonds in **4**, the latter being smaller, can easily be rationalised by hyperconjugation. This can be illustrated very simply by

the valence bond (VB) resonance structures involving no Si–H bonds. Similarly, it is easy to show with the hyperconjugation concept that C(4)–C(6) should have the highest  $\pi$ -bond order in **5**. By the same token bond orders of *ipso* bonds should be somewhat lower. Of most interest in this regard is tris-annelated system **6**, where the annelated and *exo* bonds assume the values of 1.426 (1.423) Å and 1.410 (1.410) Å at the MP2 and DFT levels of theory respectively. The DFT results are given within parentheses. In other words, tris-annulation yields lengthening of the *exo* (*ortho*) bonds relative to

Table 2

s-Characters,  $\pi$ -bond orders and atomic charges in **1**–**7** as calculated by the MP2(fc)/6-31G\* method. Atomic charges are extracted by using Löwdin and NBO approaches; atom numbering corresponds to Scheme 1

Compound	Bond	s-Character	$\pi$ -Bond order (Löwdin)	Atom	Atomic charge	
					(Löwdin)	(NBO)
<b>1</b>	C(1)–C(2)	32.9–32.9	0.63	C(1)	–0.17	–0.50
	C(1)–C(3)	36.2–35.4	0.62	C(3)	–0.15	–0.21
	C(3)–C(5)	34.9–35.4	0.67	C(5)	–0.16	–0.22
	C(5)–C(6)	35.00–35.00	0.64	Si(11)	0.18	0.86
	C(1)–Si(11)	30.8–23.6	0.19	H(C5)	0.17	0.23
	Si(11)–Si(12)	24.1–24.1	0.09	H(C3)	0.16	0.23
	C(5)–H	29.5		H(Si)	–0.02	–0.21
	C(3)–H	29.6				
<b>2</b>	C(1)–C(2)	33.2–33.2	0.61	C(1)	–0.14	–0.49
	C(1)–C(3)	35.8–39.8	0.62	C(3)	0.24	0.52
	C(3)–C(5)	38.3–34.8	0.64	C(5)	–0.19	–0.29
	C(5)–C(6)	35.4–35.4	0.65	Si(11)	0.15	0.80
	C(3)–F	21.7–35.1	0.23	H(C5)	0.18	0.24
	C(1)–Si(11)	30.9–23.2	0.18	F	–0.24	–0.41
	Si(11)–Si(12)	24.1–24.1	—	H(Si)	–0.01	–0.18
	C(5)–H	29.7				
<b>3</b>	C(1)–C(2)	34.0–34.0	0.61	C(1)	–0.16	–0.55
	C(1)–C(3)	37.6–36.8	0.59	C(3)	–0.10	–0.62
	C(3)–C(5)	36.6–36.7	0.63	C(5)	–0.15	–0.26
	C(5)–C(6)	35.9–35.9	0.66	Si(11)	0.16	0.83
	C(3)–Li	—	0.24	H(C5)	0.13	0.19
	C(1)–Si(11)	28.3–25.6	0.22	Li	0.20	0.87
	Si(11)–Si(12)	24.3–24.3		H(Si11)	–0.04	–0.23
	C(5)–H	27.4				
<b>4</b>	C(1)–C(2)	32.8–32.8	0.61	C(1)	–0.16	–0.48
	C(1)–C(3)	36.5–35.2	0.64	C(3)	–0.13	–0.18
	C(1)–Si(11)	30.6–23.5	0.19	Si(11)	0.18	0.86
	Si(11)–Si(12)	24.1–24.1		H(C3)	0.16	0.23
	C(3)–H	29.6		H(Si11)	–0.02	–0.20
<b>5</b>	C(1)–C(2)	32.6–33.1	0.64	C(1)	–0.15	–0.47
	C(1)–C(3)	36.6–36.6	0.60	C(2)	–0.16	–0.48
	C(2)–C(4)	36.1–35.3	0.61	C(6)	–0.14	–0.19
	C(4)–C(6)	35.2–35.2	0.69	Si(11)	0.17	0.86
	C(1)–Si(11)	30.8–23.5	0.19	Si(12)	0.18	0.86
	C(2)–Si(12)	30.7–23.5	0.19	H(C6)	0.17	0.23
	Si(11)–Si(12)	24.2–24.0		H(Si11)	–0.02	–0.20
	C(6)–H	29.5				
<b>6</b>	C(1)–C(2)	32.9–32.9	0.65	C(1)	–0.15	–0.46
	C(1)–C(3)	36.5–36.5	0.58	C(3)	–0.15	–0.46
	C(1)–Si(11)	30.6–23.4	0.19	Si(11)	0.18	0.86
	Si(11)–Si(12)	24.1–24.1	0.07	H(13)	–0.02	–0.20

the mono-annulated compound **1**, whereas the fused (*ipso*) bond distance is left practically unchanged. The latter is in harmony with the same s-character and very similar  $\pi$ -bond orders (0.63 vs. 0.65 for **1** and **6**, respectively) for that bond. The former finding is compatible with the very similar average s-content in the *ortho* bonds and significant drop in their  $\pi$ -bond orders in **6**. Once again we find higher  $\pi$ -bond orders in the *ipso* bonds, which is characteristic of the anti-Mills–Nixon systems [9a,b,33]. The question arises as to why the  $\pi$ -electron density tends to concentrate on the annulated bonds. A plausible answer is given by the low electronegativity of the Si atom. Consequently, they carry effective positive charges (Table 2), implying that the  $\pi$  double bond is stabilised by the two nearest neighbour positive centres. Finally, we would like to stress that *ortho* bonds are shorter than *ipso* ones, strongly indicating that  $\sigma$ -orbitals are responsible for alternation of C–C bonds in **6**, as exemplified for example in the distribution of the corresponding s-characters.

A comparison of **6** with the carbocyclic analogue 1,2,3,4,5,6-hexahydrotricyclobuta[a,c,e]benzene is interesting. The *ipso* and *ortho* bond distances in the latter compound are 1.406 and 1.389 Å respectively, as given by the MP2(fc)/6-31G\* calculations [10c]. Hence, both molecules exhibit the same alternation pattern of the C–C bonds within the benzene ring. There are, however, some remarkable differences. Tricyclobutabenzene involves one bond (*ortho*), which is shorter than the free benzene bond, whereas the other (*ipso*) is longer than the gauge benzene C–C bond [10c]. In tridisilacyclobutabenzene both types of bond are stretched so that the aromatic ring is somewhat blown up. Secondly,  $\pi$ -electrons in tricyclobutabenzene are more concentrated along *ortho* bonds, thus acting synergistically with  $\sigma$ -electrons, which is the case in the so called "Mills–Nixon" systems [9,13]. The blow-up (BU) effect can be quantified by comparing the average C–C bonds in the fused benzene ring with the free benzene C–C value, i.e.  $BU = d(C-C)_{av} - d(C-C)_{ben}$ . The MP2 results yield BU values of 0.007, 0.014 and 0.021 Å for **1**, **5** and **6** respectively. Apparently, the BU effect is additive, depending on the number of four-membered rings, the increment being 0.007 Å. Its origin will be discussed later.

Finally, it should be noted that replacement of the SiH<sub>2</sub>–SiH<sub>2</sub> bridge by the two *ortho* SiH<sub>3</sub> groups (leading to **7**) results, somewhat surprisingly, in similar elongation of the C(1)–C(2), C(1)–C(3) and C(2)–C(4) bonds as in **1**. Although the pattern is the same the reasons are different. Whereas the difference in *ipso* and *ortho* bond distances in **1** is caused by angular strain and rehybridization at the constant  $\pi$ -bond orders, just the opposite is true for **7** (Table 2). One observes a significant decrease in the  $\pi$ -density at fixed

hybridization, particularly in the *ipso* bonds, as evidenced by the  $\pi$ -bond order of 0.61. This is a consequence of the interaction between the antisymmetric HOMO orbital of the benzene ring with the low-lying unoccupied fragment orbitals of the SiH<sub>3</sub> groups, which will be discussed in the next section. Qualitative arguments show that this interaction is stronger in **7** than in **1**, thus explaining the difference in their  $\pi$ -bond orders.

#### 4. Electronic structure

In view of the exceptional reactivity of 3,4-benzo-1,2-disilacyclobut-3-enes, their electronic structure and in particular the energies of their highest occupied MOs are of special interest. Therefore, we compare in Table 3 the MP2(fc)/6-31G\* frontier orbital energies in **1**–**4** with the corresponding MO energies of benzene [35] and benzocyclobutene [36]. Additionally, the corresponding MO energies of *ortho*-disilylated benzenes are given for comparison. In benzene the two highest occupied  $\pi$ -orbitals (Ph<sub>A</sub>, Ph<sub>S</sub>) of the 1e<sub>g</sub> symmetry are degenerate. In benzocyclobutene, their degeneracy is lifted due to the inductive and hyperconjugative interaction with the bonding and antibonding linear combinations of the  $\varphi$ (CH<sub>2</sub>) fragment MOs within the ethano bridge [37]. As a result, both of the benzene HOMOs increase in energy, with the Ph<sub>S</sub> being influenced to a greater extent. The calculated Ph<sub>S</sub>/Ph<sub>A</sub> splitting energy of 0.4 eV is in reasonable agreement with the measured ionization energy (IE) gap of 0.5 eV [36]. Replacement of the ethano bridge with the SiH<sub>2</sub>–SiH<sub>2</sub> chain leading to **1** is expected to enhance hyperconjugative interaction between occupied MOs, owing to the higher energy of the  $\varphi$ (SiH<sub>2</sub>) fragment orbital relative to the  $\varphi$ (CH<sub>2</sub>). However, hyperconjugation of the highest occupied  $\pi$ -MOs with the corresponding linear combinations of the vacant  $\varphi^*$ (SiH<sub>2</sub>) fragment orbitals becomes possible in addition. In accordance with the PMO theory [38], this type of stabilising interaction will tend to cancel the Ph<sub>S</sub>/Ph<sub>A</sub> energy gap. In harmony with this observation, calculations predict near degeneracy, but also a minute

Table 3  
Energies of the frontier molecular orbitals in benzene and in compounds **1**, **2** and **5**–**7** as calculated using the MP2(fc)/6-31G\* basis set

Compound	– $\epsilon$ (eV)			
	HOMO-1	HOMO	LUMO	LUMO+1
benzene		–8.95	4.00	
benzocyclobutene*	–8.88	–8.48	3.79	4.25
<b>1</b>	–9.09	–9.06	3.02	3.27
<b>2</b>	–9.81	–9.22	2.59	2.87
<b>5</b>	–9.14	–9.12	2.48	2.61
<b>6</b>	–9.17	–9.17	2.10	2.10
<b>7</b>	–9.18	–9.14	2.76	3.56

\* Bicyclo-[4.2.0]-octa-1,3,5-trien.

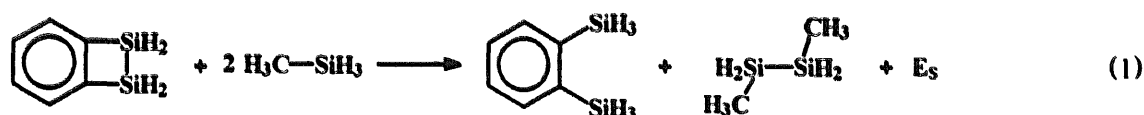
stabilisation of the two highest occupied MOs relative to benzene. Another point of interest is that multiple annelation has only a minor effect on the energies of HOMO and HOMO-1. In contrast, substantial splitting and considerable changes in energy upon increased degree of annelation are observed in the manifold of vacant orbitals. We mention in passing that exactly the opposite holds for the related benzocyclobutenes [37]. The  $\pi$  back-bonding effect in **1**, **5** and **6** from benzene towards the  $\varphi^*(\text{SiH}_2)$  antibonding orbitals is substantiated by the total  $\pi$ -bond orders in these systems. They are 3.9, 3.8 and 3.7 in **1**, **5** and **6** respectively, which is lower than the sum of the  $\pi$ -bond orders in free benzene (4.0). Obviously, the deficit arises due to the  $\pi$ -electron density transfer towards the  $\text{SiH}_2$  groups, and each four-membered ring absorbs  $0.1|e|$  of the  $\pi$ -electron mixed density. Depletion of the  $\pi$ -electron density in the benzene ring is compatible with the observed increase in the size of the aromatic perimeter and its additivity, as evidenced by the blow-up effect discussed earlier.

Finally, it should be noted that the two highest occupied MOs in the *ortho*-disilylbenzene are found at slightly lower energies than in **1**, which is again at variance with the trend observed both experimentally and theoretically in the related hydrocarbon [36,37]. This is of some interest in view of the recent proposition put forward by Houk and coworkers [37] that the difference in HOMO and HOMO-1 energies between benzocarboyclic systems and the corresponding methylated benzenes might be considered as a test of the aromatic ring distortion caused by a small ring fusion. In the case of silanes, such a test is obviously not applicable, presumably due to the more complex orbital interaction pattern.

A word on atomic charges deduced from MP2(fc)/6-31G\* wavefunctions is also in place here. A survey of the results presented in Table 2 reveals that the NBO procedure grossly exaggerates intramolecular charge transfer. The variation of Löwdin charges is much less pronounced, thus being more realistic. It is interesting to note that atomic charges are to a high degree transferable between the closely related molecules examined in this work. Moreover, Löwdin charges are compatible with chemical intuition, being in accordance with the electronegativity concept. For instance, hydrogens are positively charged if linked to carbon atoms. In contrast, H-atoms bonded to silicon carry a small but conceptually significant negative charge. Similarly, carbon atoms in unsubstituted silacyclobutabenzene possess a surplus of negative electron density, originating either from the directly bonded hydrogen or silicon atoms.

## 5. Energetic properties

Fusion of small angularly strained rings, like 1,2-disilacyclobutene, is expected to lead to considerable destabilisation of the resulting composite molecule. A useful way to estimate this effect is provided by hypothetical homodesmotic reactions in which the number of structural groups of specific types of covalent bonds, classified according to the hybridization states of atoms, is kept constant [39,40]. Thus, effects due to vibrational zero point energies, basis set deficiency, electron correlation, etc. are expected to largely cancel out. In order to estimate the destabilisation energy  $E_s$  caused by fusion of the small ring in **1**, we shall make use of the following homodesmotic reaction:



The conformation of dimethylsilene used in the calculations is shown in Eq. (1). The *ab initio* total energies of the fragment molecules are given in Table 4. Using the computed energies calculated at the MP2/6-31G\* (DFT/6-31G\*) level, destabilisation energies of 17.6 (16.5) kcal mol<sup>-1</sup> are obtained.

It is noteworthy that the calculated value for the parent 1,2-disilacyclobutene from the homodesmotic reaction shown in Eq. (2) is 16.3 (16.7) kcal mol<sup>-1</sup> at the MP2/6-31G\* (DFT/6-31G\*) level, thus being very close to the value calculated for **1**.

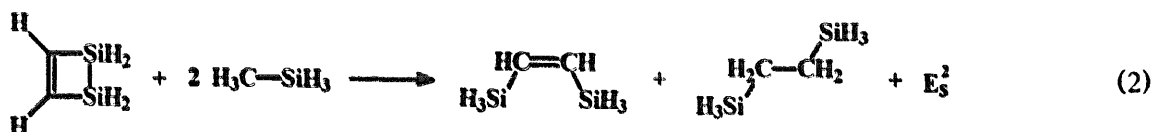
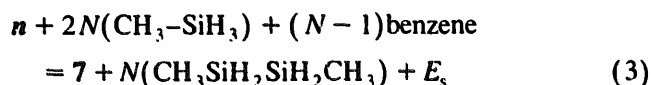


Table 4

Comparison of the total energies of **1** and **4–8** calculated by using the MP2(fc)/6-31G\* and DFT B3LYP/6-31G\* approaches. Total energies for fragment molecules used in calculating  $E_s$  are also included

Molecule	$E_{\text{tot}}$ (MP2) (a.u.)	$E_{\text{tot}}$ (DFT) (a.u.)
<b>1</b>	-810.59299	-812.42026
<b>4</b>	-1389.72857	-1392.59121
<b>5</b>	-1389.72933	-1392.59133
<b>6</b>	-1968.86706	-1972.76184
benzene	-231.45773	-232.24866
<b>7</b>	-811.77159	-813.63361
<b>8</b>	-657.41882	-658.76205
CH <sub>3</sub> SiH <sub>3</sub>	-330.48523	-331.21088
CH <sub>3</sub> SiH <sub>2</sub> SiH <sub>2</sub> CH <sub>3</sub>	-659.81997	-661.23464
SiH <sub>3</sub> CH=CHSiH <sub>3</sub>	-658.59528	-659.97580

Analogously, the homodesmotic reactions pertinent for **5** and **6** read



where  $n$  stands for compounds **5** and **6** and  $N$  is the number of annelated four-membered rings. The corresponding destabilisation energies  $E_s$  at the MP2 (DFT) level are 34.6 (33.3) and 50.7 (50.4) kcal mol<sup>-1</sup> respectively. It follows that the destabilisation energies in **1**, **5** and **6** are practically two and three times larger than that found in disilabenzocyclobutene **1** respectively, indicating that the strain is additive to a high degree depending on the number of four-membered rings. Finally, relative stability of the isomers **4** and **5** should be commented on briefly. A very small but conceptually significant energetic preference of the *ortho*-isomer **5** is in agreement with the higher  $\pi$ -density along the fused bonds, which is favourably influenced by the positively charged Si atoms.

It is important to mention that MP2 and DFT destabilisation energies are very similar, implying that the latter approach could be safely applied in much larger systems in view of its higher simplicity and feasibility.

## 6. Conclusion

The most striking feature of the disilacyclobuta-annelated benzenes is anisotropy of the C–C bond distances induced in the benzene ring. A representative example is provided by **6**, where *ipso* and *ortho* bonds alternate in a symmetric fashion. It appears that *ortho* (*exo*) bonds are shorter than *ipso* (fused) bonds. The simplest rationalisation is offered by the rehybridization picture, since the  $s$ -character drifts from *ipso* to *ortho* bonds. Somewhat paradoxically, the  $\pi$ -electron density is shifted towards the *ipso* bonds, indicating the antagonistic behaviour of the  $\sigma$ - and  $\pi$ -electrons. Such a

pattern is characteristic of the anti-Mills–Nixon systems. The simple fact that the *ortho* bonds are shorter shows that the  $\sigma$ -rehybridization effect prevails. In contrast, both *ortho* and *ipso* bonds are longer than the C–C bond in benzene. This finding is termed the blow-up effect and is interpreted by the  $\pi$ -electron charge transfer from the highest HOMOs of the benzene fragment to the  $\varphi^*$ (SiH<sub>2</sub>) antibonding fragment orbitals of the SiH<sub>2</sub> groups. This effect is missing in the pure hydrocarbon counterpart compounds. It should be stressed that both MP2(fc)/6-31G\* and B3LYP/6-31G\* methods have practically equal performance as far as structural parameters are concerned. Since the latter approach is more economical by far, it is strongly recommended for application in larger systems. Finally, the strain energies of the examined molecules are estimated by the corresponding homodesmotic reactions. It is found that the destabilisation energies are roughly additive, depending on the number of annelated four-membered rings. Deviations from the strict additivity are rationalised by the aromaticity defect and disconcerted action of the  $\sigma$ - and  $\pi$ -electrons within the aromatic fragment.

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