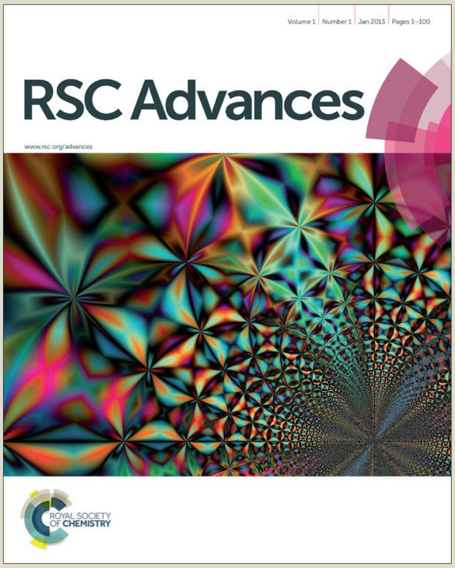
RSC Advances



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

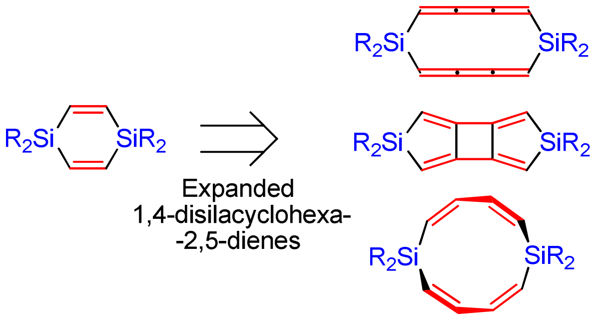
Expanding the (Cross-)Hyperconjugation of 1,4-Disilacyclohexa-2,5-dienes to Larger Monomers and Oligomers: A Computational Investigation†

Aleksandra V. Denisova,[1] Rikard Emanuelsson[2] and Henrik Ottosson*[1]

[1] Department of Chemistry – BMC, Uppsala University, Box 576, 751 23 Uppsala, Sweden.

[2] Nanotechnology and Functional Materials, Department of Engineering Sciences, Uppsala University, Box 534, 751 21 Uppsala, Sweden.

† Electronic supplementary information (ESI) available: molecular orbitals, orbital energies, bond lengths, excitation energies of cumulenes, cartesian coordinates and absolute energies. See DOI:



Abstract: We used density functional theory calculations to examine molecules that can be regarded as expanded 1,4-disilacyclohexa-2,5-dienes as well as oligomers based on these or 1,4-disilacyclohexa-2,5-diene with the aim to identify systems with extended (cross-)-hyperconjugation. Among the three “expanded 1,4-disilacyclohexa-2,5-dienes” considered cyclobutadisilole is the most interesting as it has a higher thermodynamic stability than the isomeric 1,6-disilacyclodeca-2,3,4,7,8,9-hexaene and significantly lower first electronic excitation energy than 1,6-disilacyclodeca-2,4,7,9-tetraene. Cyclobutadisilole with trimethylsilyl substituents at Si shows particularly low excitations with the first strong transition at 3.46 eV (358 nm), *i.e.*, ~1.1 eV lower than in 1,4-disilacyclohexa-2,5-diene. The monomers were connected into oligomers via their Si atoms using *bis*(dimethylsilanediyl) linkers, and some extended hyperconjugation was revealed. The first allowed UV/Vis excitation in the cyclobutadisilole-based tetramers is calculated at 2.57 eV (482 nm), although the lowering in excitation energies when going from monomer to tetramer is merely ~0.5 eV and hyperconjugation has modest impact on geometries. Yet, the tetra(cyclobutadisilole) has a significantly lower first allowed excitation when compared to a previously studied tetra(1,4-disilacyclohexadiene) with first excitation at 3.9 eV (318 nm).

Introduction

Mulliken introduced and investigated the hyperconjugation concept, showing on the presence of some conjugative interaction between a C=C double bond and a methyl group, even though the interaction was considered to be much smaller than that between a C=C double bond and a cyano or ethynyl group.[1] In his early work Mulliken also suggested a similarity between cyclopentadiene and pentafulvene because the two C-H bond orbitals of the methylene moiety in cyclopentadiene can jointly be treated as a molecular segment with group orbitals that resemble those of the exocyclic C=C double bond of pentafulvene. Both the CH_2 group and the exocyclic C=C double bond have π-symmetric orbitals which can enter into conjugation with those of the diene segment (Fig. 1).[2] Yet, Mulliken concluded that “the differences in conjugation power of these groups are more quantitative rather than qualitative”.1 These seminal studies are the foundation of the concept of hyperconjugation, described as the interaction between a local π-symmetric orbital at a saturated molecular segment and a local π-symmetric orbital at an unsaturated segment. Its introduction into organic chemistry was subsequently furthered by Baker and Dewar in the 1950s and 60s,[3,4] and in the 70s Hoffmann and co-workers explored the concept and introduced the term through-bond conjugation.[5,6] During the same decade, studies showed that incorporation of silicon or other organometallic substituents into the molecular framework improve hyperconjugation[7-10.] More recently, cyclic hyperconjugated systems were extensively investigated by Schleyer and co-workers,[11-14] and Alabugin *et al.* showed on the donor-acceptor nature of the interaction.[15-17]

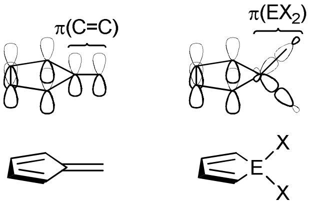


Fig. 1 The valence isolobal analogy between pentafulvene (left) and siloles and cyclopentadienes (right); E = Si or C, respectively.

We recently examined compounds with saturated organosilicon segments (SiR$_2$) inserted between two π-conjugated segments, and showed that these can have electronic and optical properties that resemble those of analogous cross-π-conjugated compounds. Thus, they could be labeled as cross-hyperconjugated.[18-23] Comparison of the electron transfer through cross-hyperconjugated and cross-π-conjugated compounds confirmed the similarities between these compound classes,[19] and cross-hyperconjugated oligomers could display a low conformational variation in the single-molecule conductance.[20] We in particular examined 1,4-disilacyclohexa-2,5-dienes (Fig. 2) and 1-silacyclopentadienes (siloles, Fig. 1),[21,22] the latter compound class being well-established in organic electronics,[24] as exemplified by the recent 2,5-dicarbazole substituted siloles by Tang and co-workers displaying high aggregationenhanced electroluminescence useful in organic light-emitting diodes (OLEDs).[25] Similar to pentafulvenes,[26] siloles and cyclopentadienes are "aromatic chameleons" which can adapt their electronic structures to the different π-electron counts for aromaticity in the electronic ground state (S_0) *versus* the first ππ* excited states (T_1 and S_1),[22] as given by Hückel's and Baird's rules, respectively.[27-31] Substituent effects on the excitation energies of siloles could be rationalized in terms of a combined consideration of ground and excited state (anti)aromaticity, as done earlier for pentafulvenes,[32,33] thus providing a comprehensive understanding based on electronic states which is alternative to the orbital-based σ*-π* model regularly applied to siloles.[24] It was also found that the two SiR_2 segments, as parts of a 1,4-disilacyclohexa-2,5-diene, allow for extensive variation in the cyclic cross-hyperconjugation. A strong cross-hyperconjugation was observed when R = $SiMe_3$, and a much weaker one when R = Cl or Me. In general, the hyperconjugation strength in 1,4-ditetrelcyclohexa-2,5-dienes can be tuned by varying the combinations of group 14 elements (tetrel elements E and E′) incorporated in the ring and/or used as substituents (Fig. 2).[23]

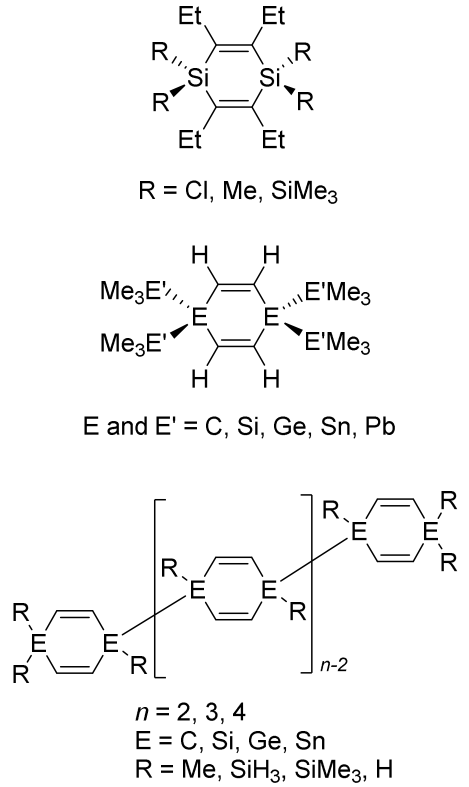
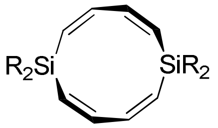
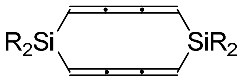


Fig. 2 Previously investigated 1,4-tetrelcyclohexa-2,5-diene containing structures.

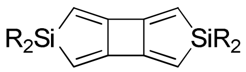
So can cross-hyperconjugation be enhanced in larger molecules and can it lead to extensive hyperconjugation in oligomers and polymers? The silole ring could be expanded with one C=C double bond to yield a seven-membered ring, a silepin. However, silepins adopt non-planar structures,[22] making them less suitable as monomers in conducting polymers. An expansion of the 1,4-disilacyclohexadiene would be to replace the two C=C double bonds with either two 1,3-butadienylene or two [3]cumulene units (Fig. 3) as these would couple to the SiR$_2$ segments similarly as the C=C bonds but with different energies of the local orbitals. Yet, the ten-membered ring of 1,6-disilacyclodeca-2,4,7,9-tetraene will be overly flexible conformationally, and the 1,6-disilacyclodeca-2,3,4,7,8,9-hexaene is likely not realistic. Instead, a compound in which the two central C=C double bonds of the two [3]cumulene units have dimerized to a cyclobutane ring, cyclobuta[1,2-c:3,4-c']disilole, or shortly, cyclobutadisilole, could be feasible. This compound can also be described as a [4]radiallene with the four exocyclic C atoms joined pairwise via two SiR_2 segments. Although the parent [4]radiallene polymerizes rapidly when exposed to air and is stable only in dilute solution at -78 °C under nitrogen atmosphere (Fig. 4),[34] phenyl substituents improve the stability of [4]radiallenes because 1,1,4,4-tetraphenyl-[4]radiallene dimerizes first at 60 °C and 1,1,4,4,6-pentaphenyl-[4]radiallene is thermally stable.[35] Thus, cyclobutadisiloles could be likely persistent provided they are properly substituted, and consequently, potentially they could be interesting new targets for synthesis.



1,6-disilacyclodeca-2,4,7,9-tetraene



1,6-disilacyclodeca-2,3,4,7,8,9-hexaene



cyclobuta[1,2-c:3,4-c']disilole
(cyclobutadisilole)

Fig. 3 Compounds considered herein as expanded 1,4-disilacyclohexa-2,5-dienes.

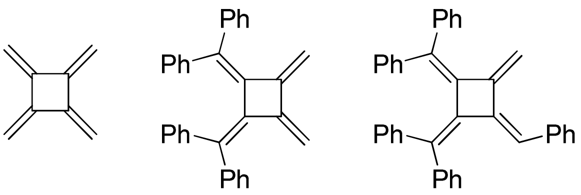


Fig. 4 Previously synthesized [4]radiallenes.

A question is how these monomers are best connected into oligomers so as to achieve some degree of hyperconjugation. Using quantum chemical computations we previously explored the linkage of 1,4-disilacyclohexadienes through single Si-Si (or Sn-Sn) bonds, and we evaluated these oligomers as potential molecular electrical cords (Fig. 2).[20] It was shown that the oligomers display neutral hyperconjugative interactions between adjacent σ(E-E) and π(C=C) bond orbitals, and when compared to linear oligosilanes this led to oligomers with HOMO energies and conductances which remain much less influenced by back-bone conformation. The lowest excitation energies (~3.9 eV) were found for the tetrameric oligo(1,4-disilacyclohexadiene)s with trimethylsilyl groups at the two Si atoms.[20] Now, we explored if 1,4-disilacyclohexa-2,5-diene and cyclobutadisilole can be linked into rigid hyperconjugated oligomers with even lower excitation energies. In order to achieve an orbital analogy between the saturated (hyperconjugated) linkers and a purely π-conjugated one we connect the 1,4-disilacyclohexadienes via two dimethylsilanediyl fragments and the *para*-xylylenes via a C=C double bond, leading to tetrasilacyclobutane and [3]cumulene units, respectively. Even though the units have different numbers of valence electrons, they should function similarly since the frontier orbital patterns resemble each other (Fig. 5).

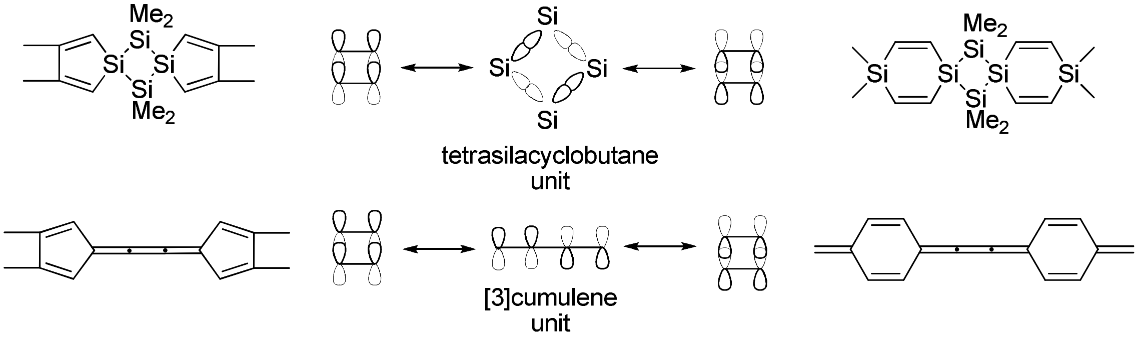
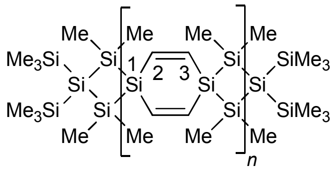


Fig. 5 The orbital analogy between 1,4-disilacyclohexa-2,5-diene and cyclobutadisilole oligomers linked with tetrasilacyclobutane (leading to hyperconjugation) and [3]cumulene units (leading to π-conjugation).

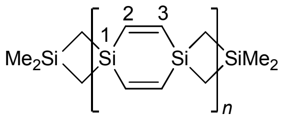
Results and Discussion

We begin with an analysis of computational results on the oligomers of the recently synthesized 1,4-disilacyclohexa-2,5-dienes, and subsequently discuss “expanded 1,4-disilacyclohexadiene” and their oligomers. Comparisons with analogous purely π-conjugated all-carbon oligomers are made throughout, and we also compare with oligomers in which the *bis*(dimethylsilanediyl) linkers have been replaced by *bis*(methylene) linkers, which should lead to weaker (cross-)hyperconjugation.

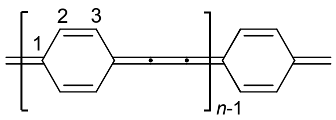
1,4-Disilacyclohexa-2,5-diene based oligomers: Herein we first discuss the analogy between the *bis*(dimethylsilanediyl)-linked 1,4-disilacyclohexadiene-based oligomers (**1a-d(Si)**, Fig. 6) and the corresponding purely π-bonded oligomers with *para*-xylylene units connected via C=C double bonds (**2a-d**, Fig. 6).



1a-d(Si)



1a-d(C)



2a-d

a: $n = 1$; **b**: $n = 2$; **c**: $n = 3$; **d**: $n = 4$

Fig. 6 *Bis*(dimethylsilanediyl)-linked 1,4-disilacyclohexa-2,5-dienes (**1a-d(Si)**), *bis*(methylene)-linked 1,4-disilacyclohexa-2,5-dienes (**1a-d(C)**), and olefin-linked *para*-xylylenes (**2a-d**).

Not surprisingly, there is a drastic decrease in the TD-B3LYP computed excitation energies for the first strong transition with increasing oligomer length of the π-conjugated oligomers **2a-d**; from 4.28 to 1.14 eV (Table 1). Oligomers **1a-d(Si)**, on the other hand, show a much more modest decrease from 3.93 to 3.41 eV, indicating that the hyperconjugation does not expand significantly beyond the monomer. The oligomers **1a-d(C)** show a similar trend as **1a-d(Si)** but the first strongly allowed excitations are significantly higher in energy (5.17 eV in **1a(C)** and 4.46 eV in **1d(C)**). It becomes clear that incorporation of silicon into the linkage leads to lowerings of excitation energies, and it resembles the substituent effects found experimentally for 1,4-disilacyclohexadienes with four silyl or germyl groups at the two Si atoms as compared to four alkyl groups.[21,23]

Yet, a concern should be raised; the B3LYP method is widely used, but at the same time DFT and TD-DFT methods suffer from severe pitfalls that narrow their application areas.[36,37] It has been shown that (TD-)DFT overestimates conjugation, torsional barriers, and electronic couplings, and that it underestimates bond-length alternations and excited-state energies in low-band-gap polymers. [38-43] Meanwhile it is possible to solve these problems by including long-range corrections in the calculations,[43-47] and for this reason we tested the CAM-B3LYP method for the three tetramers **1d(Si)**, **1d(C)** and **2d** (Table 2). As CAM-B3LYP is a long-range corrected version of B3LYP, it could possibly provide more realistic results for the long oligomers studied here.[48] We found that TD-CAM-B3LYP gave higher excitation energies for hyperconjugated **1d(Si)** and **1d(C)** and slightly lower ones for the purely π-conjugated **2d** than those that were calculated with TD-B3LYP. Still, the general trends are the same, and the strongly allowed transitions for all three tetramers with both methods involve the HOMO-LUMO transitions. However, at this point it is important to note that a comparison of the TD-B3LYP and TD-CAM-B3LYP results against previous experimental data for the first allowed excitations of linear oligosilanes,[49] ranging from Si_2Me_6 to n-$Si_{10}Me_{22}$, shows that TD-B3LYP provides much better agreement than TD-CAM-B3LYP (see the Supporting Information). In short, the excitation energies calculated at the TD-CAM-B3LYP are significantly higher than the experimental values (often by ~0.5 eV), while TD-B3LYP gives energies which differ by at most 0.15 eV from the experimentally observed excitation energies. Moreover, with the lengthening of the oligosilane chain TD-B3LYP gives gradually better agreement with experiment. For this reason we discuss the TD-B3LYP results. It can also be noted that the TD-CAM-B3LYP energy for the strongly allowed transition in **2d** is slightly lower than that at TD-B3LYP level (Table 2).

Additionally, we have also tested the influence of diffuse functions on results obtained from TD-B3LYP and TD-CAM-B3LYP calculations (see Supporting Information). Additionally, we also probed the influence of dispersion correction in the B3LYP optimizations of **1a(Si)** and **1b(Si)**, and the geometry data of these calculations were compared with those of standard B3LYP calculations (see Supporting Information). The influence on the geometries were found to be small with a maximal difference being in a dihedral angle which differed by ~5 °.

Table 1 The lowest five vertical excitation energies of **1a-d(Si)**, **1a-d(C)** and **2a-d** calculated with TD-B3LYP.[a,b]

Electronic State	**1a(Si)**	**1b(Si)**	**1c(Si)**	**1d(Si)**	**1a(C)**	**1b(C)**	**1c(C)**	**1d(C)**	**2a**	**2b**	**2c**	**2d**
S_1	3.88	**3.60**	**3.48**	**3.41**	4.91	4.66	**4.55**	**4.46**	**4.28**	**2.56**	**1.74**	**1.14**
S_2	**3.93**	3.69	3.67	3.61	5.07	**4.73**	4.58	4.54	4.59	3.34	2.19	1.66
S_3	4.03	3.88	3.74	3.67	**5.17**	4.91	4.74	4.66	4.83	3.57	3.35	2.55
S_4	4.04	3.90	3.77	3.71	5.22	4.97	4.92	4.76	5.80	3.80	3.37	2.65

S_5	4.28	3.96	3.86	3.75	5.56	5.02	4.93	4.79	5.98	3.81	3.39	**3.09**

[a] Excitation energies (in eV) calculated at TD-B3LYP/6-311G(2d,p)//B3LYP/6-311G(2d,p) level.

[b] Transitions with calculated oscillator strengths above 0.2 are marked in bold and those within the range 0.05-0.20 are underlined.

Table 2 The lowest five vertical excitation energies of **1d(Si)**, **1d(C)** and **2d** calculated with TD-CAM-B3LYP.[a,b]

Electronic state	**1d(Si)**	**1d(C)**	**2d**
S_1	4.06	5.27	**1.04**
S_2	**4.11**	5.34	1.76
S_3	4.13	**5.35**	2.78
S_4	4.17	5.35	2.92
S_5	4.36	5.37	3.47

[a] Excitation energies (in eV) calculated at TD-CAM-B3LYP/6-311G(2d,p)//B3LYP/6-311G(2d,p) level.

[b] Transitions with calculated oscillator strengths above 0.2 are marked in bold and those within the range 0.05-0.20 are underlined.

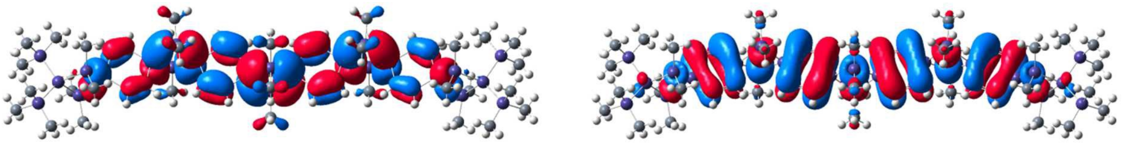
Similar trends as for the excitation energies were found in the orbital energies (Table 3). Upon oligomer elongation from **1a(Si)** to **1d(Si)** the LUMO energies (E_{LUMO}) decrease slightly from -1.02 to -1.24 eV while the HOMO energies (E_{HOMO}) are raised from -5.41 to -5.13 eV so that the HOMO-LUMO gap ($\Delta E_{\mathrm{HOMO\text{-}LUMO}}$) decreases by 0.50 eV. Oligomers **1a-d(C)** reveal the same orbital behavior as **1a-d(Si)** but the HOMO energies are lower and the HOMO-LUMO gaps are larger. On the other hand, the π-conjugated **2a-d** display a much larger change in the orbital energies upon the elongation since $\Delta E_{\mathrm{HOMO\text{-}LUMO}}$ decreases by 3.35 eV (Table 3), *i.e.*, nearly seven times that of **1a-d(Si)**, although this is likely an exaggeration due to the insufficiencies of DFT (*vide supra*). Yet, it should be noted that the HOMOs and LUMOs of

1a-d(Si), **1a-d(C)** and **2a-d** are analogous (see Fig. 7, and the Supporting Information), and that the symmetries and nodal characteristics of these orbitals remain the same when going from monomers to tetramers. It is particularly noteworthy that the orbital patterns of HOMO at the linking units of all the oligomer types agree with the qualitative view of Figure 5.

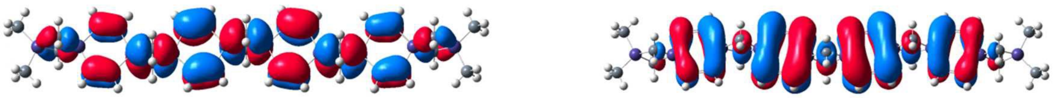
Table 3 Orbital energies and HOMO-LUMO energy gaps of **1a-d(Si)**, **1a-d(C)** and **2a-d**.

Orbital energies[a]	**1a(Si)**	**1b(Si)**	**1c(Si)**	**1d(Si)**	**1a(C)**	**1b(C)**	**1c(C)**	**1d(C)**	**2a**	**2b**	**2c**	**2d**
E_{LUMO}	-1.02	-1.15	-1.21	-1.24	-1.04	-1.36	-1.49	-1.56	-1.83	-2.96	-3.46	-3.74
E_{HOMO}	-5.41	-5.24	-5.17	-5.13	-6.74	-6.60	-6.56	-6.53	-5.63	-4.84	-4.43	-4.19
$\Delta E_{\mathrm{HOMO\text{-}LUMO}}$	4.39	4.09	3.96	3.89	5.69	5.25	5.07	4.98	3.80	1.88	0.97	0.45

[a] Orbital energies (in eV) calculated at B3LYP/6-311G(2d,p) level.



HOMO of **1d(Si)** LUMO of **1d(Si)**



HOMO of **1d(C)** LUMO of **1d(C)**

HOMO of **2d** LUMO of **2d**

Fig. 7 HOMOs and LUMOs of **1d(Si)**, **1d(C)** and **2d** calculated at B3LYP/6-311G(2d,p) level.

π-Conjugation and hyperconjugation effects should also be visible in elongations of formal double bonds and shortenings of formal single bonds. In Fig. 8 the C2=C3 double bond lengths of oligomers **1a-d(Si)**, **1a-d(C)** and **2a-d** are displayed. When compared to the C=C bond length in cyclohexa-1,4-diene, used as a reference, the endocyclic C2=C3 double bond is elongated in all three oligomer types (Fig. 8). Yet, the bond length changes when going to longer oligomers reveal similar trends as found for the orbital energies, i.e., the C2=C3 bond lengths increase dramatically in oligomers **2a-d** while in **1a-d(Si)** and **1a-d(C)** they have constant lengths. Thus, although **1a-d(Si)** and **1a-d(C)** reveal slightly elongated C2=C3 bonds in comparison with cyclohexa-1,4-diene (the difference is 0.014 - 0.017 Å) neither of these oligomer types demonstrate geometric evidence that hyperconjugation extends beyond the monomer unit.

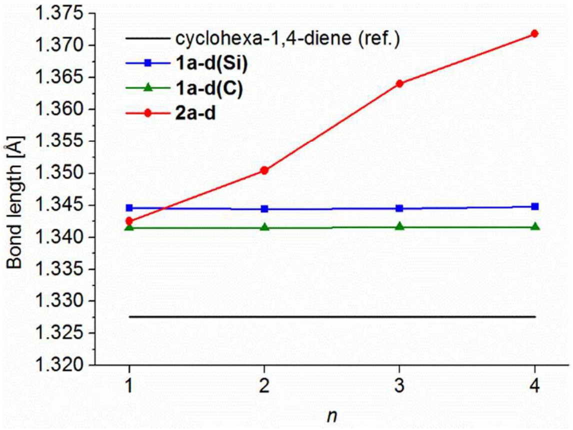


Fig. 8 The formal C2=C3 double bond lengths of **1a-d(Si)**, **1a-d(C)** and **2a-d**, with the reference length being the bond length of the corresponding double bonds in cyclohexa-1,4-diene. Results from B3LYP/6-311G(2d,p) calculations. The bonds measured are for the monomers at or closest to the center of the oligomers.

The differences in these bond lengths between the oligomers can be rationalized by use of resonance structures (Fig. 9) as the longest π-conjugated oligomers **2** to a significant extent should be described by **2-IV** with a central benzene ring and a C5≡C6 triple bond, a type of resonance structure that should have minute contributions in oligomers **1(Si)** and **1(C)**. Moreover, the influence of this resonance structure to the repeat units in the centers of the oligomers **2** should increase with oligomer length as the C2=C3 bond extends towards 1.39-1.40 Å (Fig. 8), the C-C bond length of benzene.

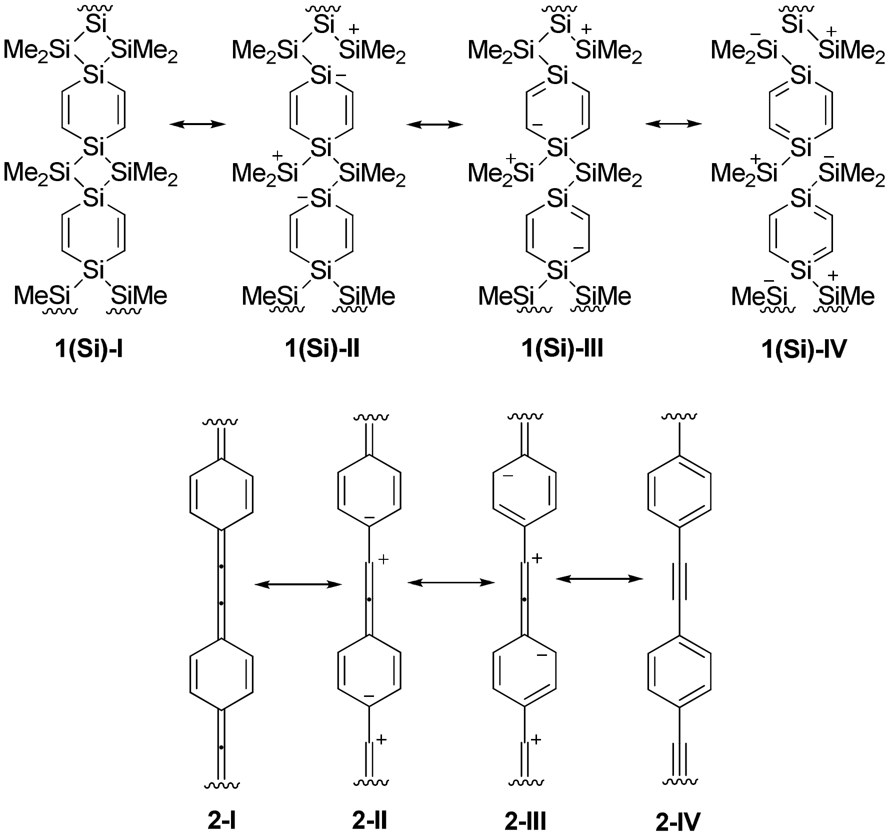
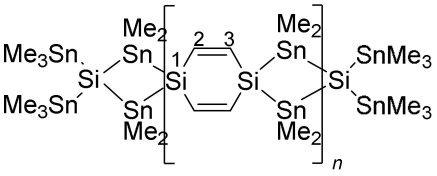


Fig. 9 Resonance structures of the oligomers **1(Si)** and **2**.

To investigate the influence of heavier group 14 elements on the hyperconjugation strength, the tetramer **1d(Sn)** with two dimethylstannanediyl instead of the two dimethylsilanediyl linkers was examined (Fig. 10). Calculations were performed at the TD-

B3LYP/LANL2DZdp//B3LYP/LANL2DZdp level, and the excitation energy for the first strong transition of this compound is 3.06 eV, which is 0.35 eV lower than that of **1d(Si)** at the same level. This corresponds to an excitation wavelength of 405 nm. Also, the endocyclic C2=C3 bond demonstrates a slight elongation by 0.02 Å when compared to **1d(Si)**, leading to a bond length of ~1.37 Å. However, the monomer **1a(Sn)** has the same C2=C3 bond length as **1d(Sn)**, again revealing no bond elongation when going from the monomer to the tetramer. The calculated excitation energy of the first strong transition of the monomer **1a(Sn)** is 3.68 eV, which is 0.24 eV lower than that of **1a(Si)**. Thus, while the geometries of the tin-containing **1(Sn)** oligomers do not reveal any extensive hyperconjugation, the lowering of excitation energies is more pronounced than that observed when going from **1a(Si)** to **1d(Si)**. These characteristics give evidence of a moderate enhancement of the hyperconjugation with tin incorporation into the oligomers.

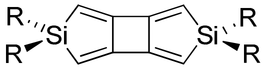


1a-d(Sn)

a: *n* = 1; **b**: *n* = 2; **c**: *n* = 3; **d**: *n* = 4

Fig. 10 The tin-containing oligomers **1a-d(Sn)**.

Expanded monomer units: To enhance the cross-hyperconjugation, the 1,4-disilacyclohexa-2,5-diene can be expanded by replacement of the two C=C double bonds with diene segments such as 1,3-butadienylene or [3]cumulenic units, leading to 1,6-disilacyclodeca-2,4,7,9-tetraene and 1,6-disilacyclodeca-2,3,4,7,8,9-hexaene, respectively (Fig. 3). Ten-membered rings result in both cases. However, the first of these will be conformationally very flexible, and the second is likely not synthetically realistic. Yet, cyclobutadisilole could function as more reasonable “expanded 1,4-disilacyclohexa-2,5-diene” monomer than the isomeric 1,6-disilacyclodecahexaene, particularly as the two compounds have rather similar first excitation energies (*vide infra*). According to B3LYP/6-311G(2d,p) calculations the energy difference between the parent cyclobutadisilole and 1,6-disilacyclodeca-2,3,4,7,8,9-hexaene is 18.0 kcal/mol, in favor of the first. To reveal how substituents at the two Si atoms influence the electronic structure when compared to 1,4-disilacyclohexadienes, we examined substituted 1,6-disilacyclodecahexaene, 1,6-disilacyclodeca-2,4,7,9-tetraene and cyclobutadisilole, using the substituents R shown for the latter compound in Fig. 11.



3a: R = H
3b: R = F
3c: R = CF_3
3d: R = Me
3e: R = $SiMe_3$

Fig. 11 The substituent pattern used in our calculations of cyclobutadisiloles.

First, the energies of the first transitions of the variously substituted 1,6-disilacyclodeca-2,4,7,9-tetraenes were shown to be significantly higher than for 1,6-disilacyclodecahexaenes and cyclobutadisiloles as they were found in the range 4.08 - 4.93 eV (see Supporting Information). The high excitation energies are presumably an effect of the extensively non-planar structure (the two C=C-C=C dihederal angles in the parent 1,6-disilacyclodecatetraene are 50.0°). For this reason the 1,6-disilacyclodeca-2,4,7,9-tetraenes were excluded from the further consideration herein (for the calculated excitation energies, see the Supporting Information).

The similarity between 1,6-disilacyclodecahexaenes and cyclobutadisiloles is found by comparison of the orbital properties; HOMO-*n* – LUMO gaps and orbital symmetries (see the

Supporting Information). While the substituted 1,6-disilacyclodecahexanes have slight lower first calculated excitation energies than the cyclobutadisiloles (2.57 - 2.97 eV *vs.* 2.84 - 3.26 eV), the latter are synthetically more realistic and thermodynamically more stable (*vide supra*). Therefore, the further discussion is focused on cyclobutadisiloles **3a-e**. For these the first excitations are forbidden (Table 4), and the oscillator strengths of the next higher excitations depend significantly on the substituents at Si. The first excitation is of lowest energy in the tetrafluoro substituted **3b** and highest in the *tetrakis*(trimethylsilyl) substituted **3e**. Yet, the situation is opposite for the first allowed transitions.

Cyclobutadisilole **3e**, with trimethylsilyl substituents at Si, has a strongly allowed excitation at even lower energy and longer wavelength (3.46 eV, 358 nm) than the slightly allowed excitations of the other cyclobutadisiloles, and it approaches the visible region. This falls in line with our earlier finding that R = $SiMe_3$ provides a strong red-shifted absorption in 1,4-disilacyclohexadienes when compared to those with R = Me or Cl.[21] Here it should particularly be noted that the parent [4]radiallene has higher calculated excitation energies than **3e**; 3.78 *vs.* 3.26 for the first (forbidden) transitions and 4.83 *vs.* 3.46 eV for the first strongly allowed transitions, respectively. Thus, the two $Si(SiMe_3)_2$ moieties, which pair-wise join the four exocyclic methylene positions of [4]radiallene, have a clear cross-hyperconjugative effect.

Table 4 The five lowest calculated vertical excitations of **3a-e**[a, b]

Electronic excitations	Substituents				
	H	F	CF_3	Me	$SiMe_3$
	3a	**3b**	**3c**	**3d**	**3e**

S$_1$	3.13	2.84	2.95	3.10	3.26
	(396)	(437)	(421)	(399)	(380)
S$_2$	4.07	3.92	3.88,	3.87	**3.46**
	(305)	(316)	(320)	(320.0)	**(359)**
S$_3$	4.14	4.31	3.97	4.12	3.64
	(300)	(287)	(312)	(301)	(341)
S$_4$	**4.52**	4.38	**4.30**	**4.42**	4.14
	(274)	(283.0)	**(288)**	**(280)**	(300)
S$_5$	4.94	**4.69**	4.86	4.71	4.23
	(251)	**(265)**	(255)	(263)	(293)

[a] Excitation energies (in eV) and wavelengths (in nm) calculated on TD-B3LYP/6-311G(2d,p)//B3LYP/6-311G(2d,p) level.

[b] Transitions with oscillator strengths above 0.2 are marked in bold and those with $0.05 < f \leq 0.20$ are underlined.

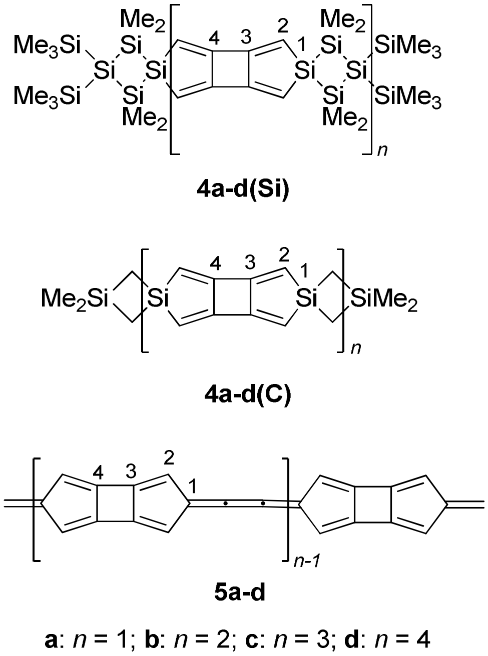
The HOMO-LUMO gaps demonstrate the same trend as found for the first (forbidden) excitations as they increase by 0.39 eV when going from R = F to R = SiMe$_3$ (Table 5). However, the strongly allowed transitions involve two configurations, with one of them (the HOMO-*n* → LUMO configuration) being the far most dominant one. The orbitals related to this configuration have the same symmetries and nodal properties throughout **3a** to **3e** (see the Supporting Information), so that the first allowed transitions in the cyclobutadisiloles are analogous. Also, the HOMO-*n* – LUMO energy gaps of **3a-e** show a clear trend with a decrease by 1.36 eV when going from fluoro to trimethylsilyl substituents, attributable to a significant raise in the energy of HOMO-*n* by nearly 3 eV when going from **3b** to **3e**.

Table 5 Calculated orbital energies, HOMO - LUMO and HOMO-*n* - LUMO gaps of **3a-d**.[a]

Orbital energies	Substituents				
	H	F	CF_3	Me	$SiMe_3$
	3a	**3b**	**3c**	**3d**	**3e**
E_{LUMO}	-2.77	-3.66	-3.94	-2.39	-2.13
E_{HOMO}	-6.29	-6.93	-7.31	-5.88	-5.79
$E_{HOMO\text{-}n}$	-7.78 $n = 2$	-8.90 $n = 2$	-8.75 $n = 2$	-7.34 $n = 3$	-6.01 $n = 1$
$\Delta E_{HOMO\text{ - }LUMO}$	3.52	3.27	3.37	3.49	3.66
$\Delta E_{HOMO\text{-}n\text{ – }LUMO}$	5.02	5.24	4.81	4.95	3.88

[a] Orbital energies (in eV) calculated at B3LYP/6-311G(2d,p) level

Noteworthy, both the excitation energies for the strongly allowed transitions and the $\Delta E_{HOMO\text{-}n\text{ – }LUMO}$ for cyclobutadisilole **3e** are similar to the corresponding values of the tetramer **1d(Si)** among the *bis*(dimethylsilanediyl)-linked 1,4-disilacyclohexa-2,5-diene oligomers. Thus, cyclobutadisiloles could display interesting properties, and therefore, two cyclobutadisilole oligomer types and their purely π-conjugated analogue were investigated (Fig. 12).



4a-d(Si)

4a-d(C)

5a-d

a: n = 1; **b**: n = 2; **c**: n = 3; **d**: n = 4

Fig. 12 Oligo(cyclobutadisilole)s and oligo(tricyclo<5.3.0.0^{2,6}>decatetraene)s.

Cyclobutadisilole-based oligomers: Oligomers **1a-d(Si)** and **4a-d(Si)** display similar results with regard to the decrease in excitation energies because the energies of the allowed transitions when going from monomer to tetramer decrease by 0.49 eV (**4a-d(Si)**) and 0.47 eV (**1a-d(Si)**), respectively (see Table 6 and 1, respectively). However, for **5a-d**, *i.e.*, the purely π-conjugated analogues of **4a-d(Si)**, the decrease in the first allowed excitation energies is 2.46 eV upon elongation (Table 6), although this could be an exaggerated energy lowering. Yet, the number of forbidden transitions below the first allowed excitations in **5a-d** grows with elongation. With regard to **4a-d(C)** the decrease in energy of the first allowed excitations (0.47 eV) is similar to that when going from **4a(Si)** to **4d(Si)**, but the excitation energies are higher by ~1 eV. Furthermore, and similar to **5a-d**, one can note a shift of the allowed excitations in **4a-d(C)** to higher excitation levels. In summary, long oligomers of **4(Si)**, **5** and **4(C)** should display strongly allowed transitions at ~2.5 eV (~480 nm), well below 1 eV (~980 nm), and ~3.5 eV (~350 nm), respectively.

Table 6 The lowest five vertical excitations of **4a-d(Si)**, **4a-d(C)** and **5a-d**.[a, b]

State	**4a(Si)**	**4b(Si)**	**4c(Si)**	**4d(Si)**	**4a(C)**	**4b(C)**	**4c(C)**	**4d(C)**	**5a**	**5b**	**5c**	**5d**
S_1	2.98	**2.74**	**2.63**	**2.57**	2.98	2.81	2.75	2.73	2.44	1.59	1.30	1.15
S_2	3.05	2.93	2.90	2.80	3.26	2.82	2.77	2.74	3.55	1.59	1.32	1.15
S_3	**3.06**	2.94	2.91	2.88	3.96	3.08	2.77	2.75	**3.63**	**2.27**	1.32	1.16
S_4	3.45	2.95	2.91	2.90	4.01	3.19	3.02	2.76	4.44	2.82	**1.65**	1.16
S_5	3.58	3.10	2.92	2.91	**4.04**	3.21	3.06	2.99	4.50	2.82	1.90	**1.27**
S_n	-	-	-	-	**-**	**3.74** $n = 7$	**3.63** $n = 14$	**3.57** $n = 22$	-	-	-	**-**

[a] Excitation energies (in eV) calculated at TD-B3LYP/6-311G(2d,p)//B3LYP/6-311G(2d,p) level.

[b] Transitions with oscillator strengths above 0.2 are marked in bold and those above 0.05 are underlined.

The decrease in $\Delta E_{\text{HOMO-LUMO}}$ when going from monomer to tetramer for the three oligomer classes are 0.45 eV (**4a-d(Si)**), 2.18 eV (**5a-d**), and 0.31 eV (**4a-d(C)**), respectively. Despite that the π-conjugated oligomers **5a-d** display smaller $\Delta E_{\text{HOMO-LUMO}}$ and much more extreme decrease in this energy gap when going from short to longer oligomers, the values for **4a-d(Si)** still demonstrate some extension in the hyperconjugation upon oligomer elongation. Moreover, the decrease in $\Delta E_{\text{HOMO-LUMO}}$ when going from monomer to tetramer of the 1,4-disilacyclohexadiene oligomers **1a-d(Si)** (0.50 eV) is very similar to that of **4a-d(Si)**, although the HOMO-LUMO gaps are lower by ~1 eV for **4a-d(Si)**.

Table 7 Orbital energies, HOMO-LUMO and HOMO-*n* – LUMO gaps of **4a-d(Si)**, **4a-d(C)** and **5a-d** [a]

	4a(Si)	4b(Si)	4c(Si)	4d(Si)	4a(C)	4b(C)	4c(C)	4d(C)	5a	5b	5c	5d
E_{LUMO}	-2.25	-2.43	-2.51	-2.56	-2.51	-2.74	-2.85	-2.91	-2.80	-3.80	-4.21	-4.45
E_{HOMO}	-5.70	-5.60	-5.57	-5.55	-5.90	-5.95	-5.98	-5.98	-5.79	-5.68	-5.42	-5.26
$E_{\mathrm{HOMO}\text{-}n}$	-5.70 $n = 0$	-5.60 $n = 0$	-5.57 $n = 0$	-5.55 $n = 0$	-7.01 $n = 2$	-6.96 $n = 4$	-6.95 $n = 5$	-6.95 $n = 7$	-6.24 $n = 1$	-5.68 $n = 0$	-5.42 $n = 0$	-5.26 $n = 0$
$\Delta E_{\mathrm{HOMO\ -\ LUMO}}$	3.45	3.17	3.05	3.00	3.39	3.21	3.13	3.08	2.99	1.87	1.22	0.81
$\Delta E_{\mathrm{HOMO}\text{-}n\ –\ \mathrm{LUMO}}$	3.45	3.17	3.05	3.00	4.50	4.22	4.10	4.05	3.45	1.87	1.22	0.81

[a]Orbital energies (in eV) calculated at B3LYP/6-311G(2d,p) level.

Yet, the most important results are the energy gaps between the orbitals involved in the first allowed excitations (Table 7). These orbitals have analogous symmetries and nodal properties in each of **4a-d(Si)**, **4a-d(C)** and **5a-d** (see the Supporting Information). For **4a-d(Si)** and **5a-d** the HOMO-*n* orbital is HOMO except for **5a** for which it is HOMO-1. On the other hand, for **4a-d(C)** the HOMO-*n* orbital shifts down among the occupied orbitals upon oligomer elongation. The decrease in $\Delta E_{\mathrm{HOMO}\text{-}n\ –\ \mathrm{LUMO}}$ with elongation of **4a-d(Si)** and **4a-d(C)** is the same and only moderate (0.45 eV), while for **5a-d** it is significantly higher (2.64 eV). Still, the $\Delta E_{\mathrm{HOMO}\text{-}n\ –\ \mathrm{LUMO}}$ values of **4a-d(Si)** are smaller than those of **4a-d(C)** by ~1 eV.

The geometries could tentatively reflect the presence of conjugation to a larger extent for **4(Si)** and **4(C)** than the case for **1(Si)** and **1(C)**. However, in Fig. 13A one sees stark differences in the endocyclic C3-C4 single bond lengths between the π-conjugated **5a-d** and the hyperconjugated **4a-d(Si)** and **4a-d(C)**. The C3-C4 bond lengths of **5a-d** shorten from 1.483 to 1.455 Å, while in **4a-d(Si)** and **4a-d(C)** these bonds remain at a constant value (1.495 Å) throughout the series. Clearly, the central tricyclic unit in **5d** adopts some 10π-electron aromaticity (Fig. 14), which is not possible in **4d(Si)** or **4d(C)**.

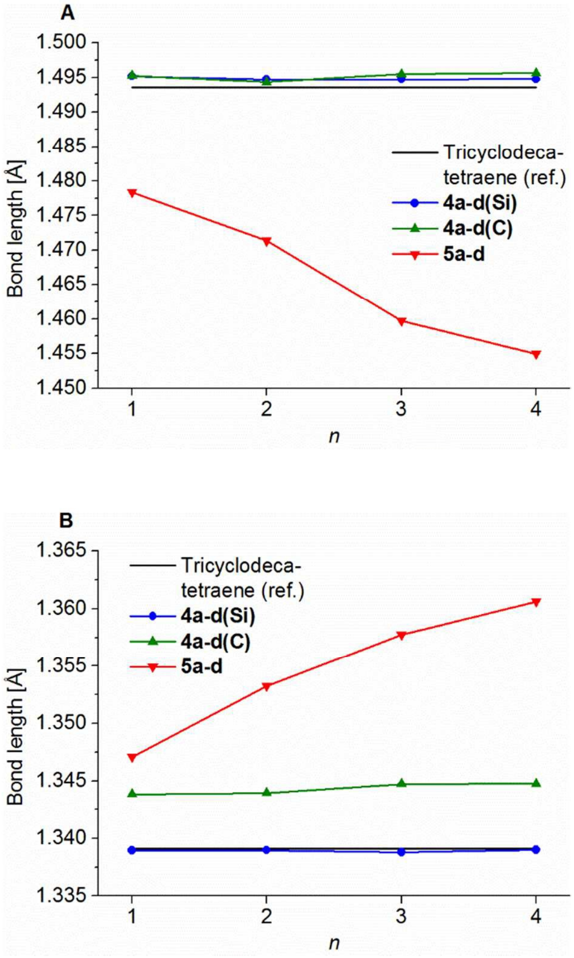


Fig. 13 The C3-C4 bond lengths (A) and C2-C3 bond lengths (B) of **4a-d(Si)**, **4a-d(C)** and **5a-d**. The reference lines are the bond length of the corresponding C-C bond in tricyclo<5.3.0.0^{2,6}>decatetraene. Results from B3LYP/6-311G(2d,p) calculations. The bonds are measured in the repeat unit nearest to the middle of the oligomers.

Moreover, the C2-C3 bonds in **4a-d(Si)** and **4a-d(C)**, which are formal double bonds, demonstrate no elongation and are all 1.34 Å (Fig. 13B). The elongation of the corresponding bonds in **5a-d** are, however, much more significant, again revealing the impact of resonance structure **5-III** (Fig. 14) with a 10π-electron aromatic moiety. According to our B3LYP/6-311G(2d,p) calculations, tricyclodecapentaene displays geometrical characteristics of an aromatic structure because the C1-C2 and C2-C3 bonds are 1.422 and 1.383 Å, respectively, and the molecule is planar. The corresponding resonance structure (**4-III**) should have minuscule contribution in **4(Si)** and **4(C)**.

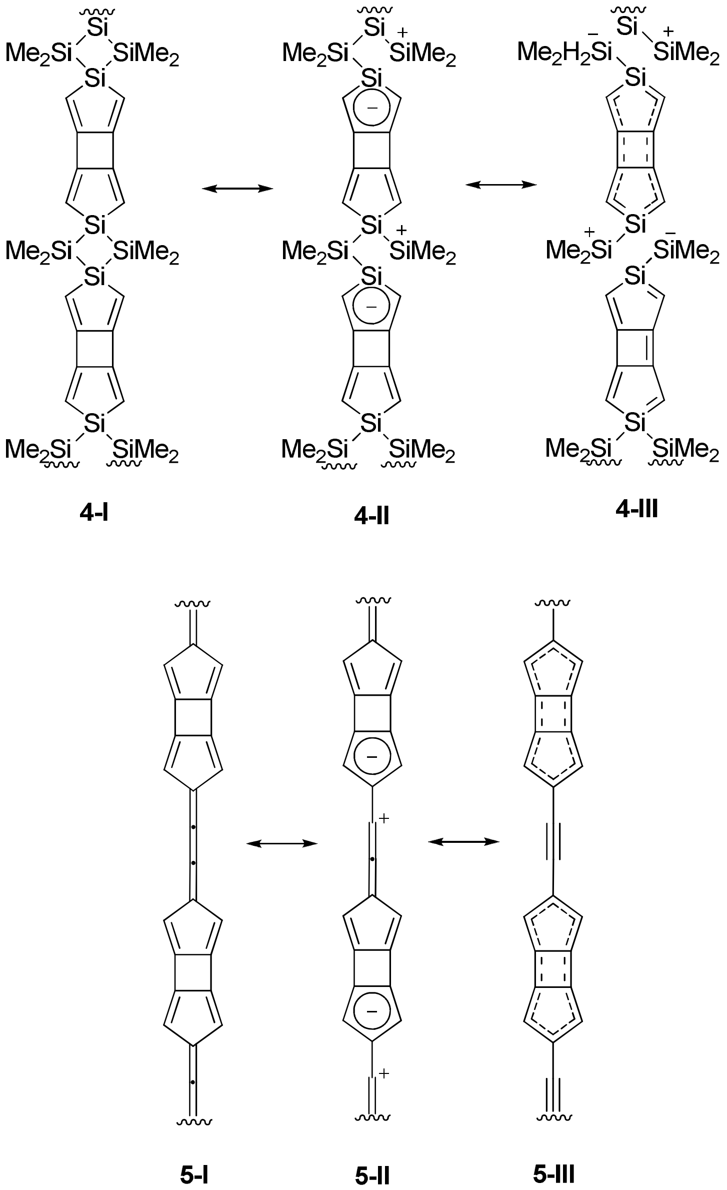
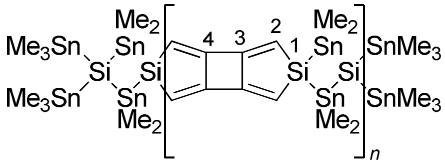


Fig. 14 Resonance structures of oligomeric **4** and **5**.

Finally, the tin-containing tetramer **4d(Sn)**, analogous to **4d(Si)**, was studied with the purpose of revealing possible hyperconjugation strengthening (Fig. 15). Calculations were performed at the TD-B3LYP/LANL2DZdp//B3LYP/LANL2DZdp level. The excitation energy for the first strong transition of this compound is 2.53 eV, which is essentially identical to that of tetramer **4d(Si)** at the same level of computation (2.57 eV). The endocyclic C2=C3 double bonds in **4d(Sn)** are slightly elongated by ~0.02 Å in comparison with **4d(Si)** while the C3-C4 single bonds are approximately of the same length. However, monomer **4a(Sn)** shows the same bond lengths as the tetramer, and its first strong transition has an excitation energy of 3.06 eV which is very similar to that of **4a(Si)**. Thus, in contrast to the oligomers of 1,4-disilacyclohexa-2,5-dienes, incorporation of tin in place of silicon in the linking unit of the cyclobutadisilole-based oligomers seems not to be an effective means for enhancement of the hyperconjugation.



4a-d(Sn)

a: *n* = 1; **b**: *n* = 2; **c**: *n* = 3; **d**: *n* = 4

Fig. 15 The tin-containing oligomers **4a-d(Sn)**.

Conclusions and outlook

Cyclobutadisilole, which can be viewed both as an “expanded 1,4-disilacyclo-2,5-hexadiene” and as a silicon-bridged [4]radiallene, has been investigated by computational means. The monomeric unit with two Me_3Si substituents at each Si has a calculated first allowed excitation at 3.46 eV (358 nm), and this cyclobutadisilole should represent an interesting synthetic target with potential optoelectronic applications. We also explored oligomers based on 1,4-disilacyclohexa-2,5-diene or cyclobutadisilole as these monomer units, when connected via the Si atoms through *bis*(dimethylsilanediyl) linkers, can lead to rigid hyperconjugated oligomers with excitation energies at ~2.5 eV (~500 nm). However, analogs which are purely π-conjugated display much larger lowerings in the corresponding excitation energies. Still the oligomers of cyclobutadisilole should represent fascinating targets for synthesis and subsequent experimental studies as they can be described as [4]radiallenes coupled through saturated molecular segments. Also, as the cross-hyperconjugated silole molecule is able to act as an "aromatic chameleon" similar to the cross-π-conjugated fulvene,[22] and since fulvene-based polymers can display very low band gaps,[50] we postulate that polymers based on the cyclobutadisilole could have particularly appealing properties.

Computational details

All computations were performed with the Gaussian 09 program package, revision D.01. The structures discussed were optimized at the B3LYP/6-311G(2d,p) hybrid density functional theory level,[51-53] and frequency calculations were performed at the same level to verify that stationary points correspond to minima. Structures **1a(Sn)**, **1d(Sn)**, **4a(Sn)** and **4d(Sn)** were optimized at the B3LYP/LANL2DZdp level[54]. Time-dependent density functional theory (TD-DFT) calculations[55] were performed as implemented in Gaussian 09, using TD-B3LYP/6-311G(2d,p) on the optimized B3LYP geometries. The five lowest excitations were calculated, in some cases for finding the first strongly visible excitation (oscillator strength > 0.2) up to twenty two lowest excitations were calculated. In order to test a long-range corrected method, the **1d(Si)**, **2d** and **1d(C)** were also investigated at the TD-CAM-B3LYP/6-311G(2d,p) level.[48] At the same time, permethylated linear silanes Si_4Me_{10}, Si_7Me_{16}, $Si_{10}Me_{22}$ were investigated at the TD-B3LYP/6-311G(2d,p), TD-LC-ωPBE/6-311G(2d,p)[56-58] and TD-CAM-B3LYP/6-311G(2d,p) levels in order to compare calculated results with experimental data. These structures were always optimized at the B3LYP/6-311G(2d,p) level.

Acknowledgements

We first thank Prof. Christoph Marschner for stimulating discussions on tetrasilacyclobutane and hyperconjugation. We are further grateful to the Swedish Research Council (Vetenskapsrådet) for financial support. The Swedish National Infrastructure for Computing (SNIC) is acknowledged for generous allotment of computer time at the National Supercomputer Center (NSC).

References

---

1 R. S. Mulliken, C. A. Rieke and W. G. Brown, *J. Am. Chem. Soc.*, 1941, **63**, 41.

2 R. S. Mulliken, *J. Chem. Phys.*, 1939, **7**, 339.

3 J. W. Baker, *Hyperconjugation*, Oxford University Press, London, 1952.

4 M. J. S. Dewar, *Hyperconjugation*, Ronald Press Co., New York, 1962.

5 R. Hoffmann, E. Heilbronner and R. Gleiter, *J. Am. Chem. Soc.*, 1970, **92**, 706.

6 R. Hoffmann, *Acc. Chem. Res.*, 1971, **4**, 1.

7 T. G. Traylor, W. Hanstein, H. J. Berwin, N. A. Clinton and R. S. Brown, *J. Am. Chem. Soc.*, 1971, **93**, 5715.

8 H. Sakurai, S. Tasaka and M. Kira, *J. Am. Chem. Soc.*, 1972, **94**, 9285.

9 C. G. Pitt and H. Bock, *J. Chem. Soc., Chem. Commun.*, 1972, 28.

10 R. Hoffmann, L. Radom, J. A. Pople, P. v. R. Schleyer, W. J. Hehre and L. Salem, *J. Am. Chem. Soc.*, 1972, **94**, 6221.

11 S. Sieber, P. v. R. Schleyer and J. Gauss, *J. Am. Chem. Soc.*, 1993, **115**, 6987.

12 L. Nyulászi and P. v. R. Schleyer, *J. Am. Chem. Soc.*, 1999, **121**, 6872.

---

13 P. v. R. Schleyer, L. Nyulászi and T. Kárpáti, *Eur. J. Org. Chem.*, 2003, 1923.

14 I. Fernández, J. I. Wu and P. v. R. Schleyer, *Org. Lett.*, 2013, **15**, 2990.

15 I. V. Alabugin, K. M. Gilmore and P. W. Peterson, *WIREs Comput. Mol. Sci.*, 2011, **1**, 109.

16 I. V. Alabugin and T. A. Zeidan, *J. Am. Chem. Soc.*, 2002, **124**, 3175.

17 I. V. Alabugin and M. Manoharan, *J. Org. Chem.*, 2004, **69**, 9011.

18 R. Emanuelsson, A. Wallner, E. A. M. Ng, J. R. Smith, D. Nauroozi, S. Ott and H. Ottosson, *Angew. Chem., Int. Ed.*, 2013, **52**, 983.

19 E. Göransson, R. Emanuelsson, K. Jorner, T. F. Markle, L. Hammarström and H. Ottosson, *Chem. Sci.*, 2013, **4**, 3522.

20 R. Emanuelsson, H. Löfås, J. Zhu, R. Ahuja, A. Grigoriev and H. Ottosson, *J. Phys. Chem. C*, 2014, **118**, 5637.

21 J. Tibbelin, A. Wallner, R. Emanuelsson, F. Heijkenskjöld, M. Rosenberg, K. Yamazaki, D. Nauroozi, L. Karlsson, R. Feifel, R. Pettersson, J. Baumgartner, S. Ott and H. Ottosson, *Chem. Sci.*, 2014, **5**, 360.

22 K. Jorner, R. Emanuelsson, C. Dahlstrand, H. Tong, A. V. Denisova and H. Ottosson, *Chem. Eur. J.*, 2014, **20**, 9295.

23 R. Emanuelsson, A. V. Denisova, J. Baumgartner and H. Ottosson, *Organometallics,* 2014, **33**, 2997.

24 (a) S. Yamaguchi and K. Tamao, *J. Chem. Soc., Dalton Trans*., 1998, 3693; (b) H. Y. Fu and Y. R. Cheng, *Curr. Org. Chem.*, 2012, **16**, 1423; (c) L. Sambri and A. Baschieri, *Mini-Rev. Org. Chem.*, 2013, **10**, 254; (d) X. W. Zhan, S. Barlow and S. R. Marder, *Chem. Commun.*, 2009, 1948.

25 L. Chen, H. Nie, B. Chen, G. Lin, W. Luo, R. Hu, F. Huang, A. Qin, Z. Zhao and B. Z. Tang, *J. Photon. Energy*, 2015, **5**, 053598.

---

26 H. Möllerstedt, M. C. Piqueras, R. Crespo and H. Ottosson, *J. Am. Chem. Soc.*, 2004, **126**, 13938.

27 N. C. Baird, *J. Am. Chem. Soc.*, 1972, **94**, 4941.

28 H. Ottosson, *Nat. Chem.*, 2012, **4**, 969.

29 M. Rosenberg, C. Dahlstrand, K. Kilså and H. Ottosson, *Chem. Rev.*, 2014, **114**, 5379.

30 R. Papadakis and H. Ottosson, *Chem Soc. Rev.*, 2015, **44**, 6472.

31 Y. M. Sung, M.-C. Toon, J. M. Lim, H. Rath, K. Naoda, A. Osuka, D. Kim, *Nat. Chem.*, 2015, **7**, 418.

32 H. Ottosson, K. Kilså, K. Chajara, M. C. Piqueras, R. Crespo, H. Kato and D. Muthas, *Chem. Eur. J.*, 2007, **13**, 6998.

33 M. Rosenberg, H. Ottosson and K. Kilså, *Phys. Chem. Chem. Phys.*, 2011, **13**, 12912.

34 G. W. Griffin and L. I. Peterson, *J. Am. Chem. Soc.*, 1963, **85**, 2268.

35 K. Tanaka and F. Toda, *Tetrahedron Lett.*, 1980, **21**, 2713.

36 A. Dreuw and M. Head-Gordon, *J. Am. Chem. Soc.*, 2004, **126**, 4007.

37 A. J. Cohen, P. Mori-Sánchez and W. Yang, *Chem. Rev.*, 2012, **112**, 289.

38 J. Gierschner, J.Cornil and H.-J. Egelhaaf, *Adv. Mater.*, 2007, **19**, 173.

39 M. Wykes, B. Milián-Medina and J. Gierschner, *Front. Chem.*, 2013, **1**, 35.

40 S. Yang, P. Olishevski and M. Kertesz, *Synth. Met.*, 2004, **141**, 171.

41 U. Salzner, P. G. Pickup, R. A. Poirier and J. B. Lagowski, *J. Phys. Chem. A.*, 1998, **102**, 2572.

42 H. Sun and J. Autschbach, *J. Chem. Theory Comput.*, 2014, **10**, 1035.

43 T. Körzdörfer and J.-L. Brédas, *Acc. Chem. Res.*, 2014, **47**, 3284.

44 D. Jacquemin, E. A. Perpète, G. E. Scuseria, I. Ciofini and C. Adamo, *J. Chem. Theory Comput.*, 2008, **4**, 123.

45 Z.-L. Cai, K. Sendt and J. R. Reimers, *J. Chem. Phys.*, 2002, **117**, 5543.

---

46 U. Salzner and A. Aydin, *J. Chem. Theory Comput.*, 2011, **7**, 2568.

47 T. Tsuneda and K. Hirao, *WIREs Comput. Mol. Sci.*, 2014, **4**, 375.

48 T. Yanai, D. P. Tew and N. C. Handy, *Chem. Phys. Lett.*, 2004, **393**, 51.

49 M. K. Raymond and J. Michl, *Int. J. Quant. Chem.*, 1999, **72**, 361.

50 C. Dahlstrand, B. O. Jahn, A. Grigoriev, S. Villaume, R. Ahuja and H. Ottosson, *J. Phys. Chem. C*, 2015, **119**, 25726.

51 A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648.

52 K. Kim and K. D. Jordan, *J. Phys. Chem.*, 1994, **98**, 10089.

53 P. J. Stephens, F. J. Devlin, C. F. Chabalowski and M. J. Frisch, *J. Phys. Chem.*, 1994, **98**, 11623.

54 W. R. Wadt, P. J. Hay, *J. Chem. Phys.*, 1985, **82**, 284.

55 E. Runge and E. K. U. Gross, *Phys. Rev. Lett.*, 1984, **52**, 997.

56 O. A. Vydrov and G. E. Scuseria, *J. Chem. Phys.*, 2006, **125**, 234109.

57 O. A. Vydrov, J. Heyd, A. Krukau and G. E. Scuseria, *J. Chem. Phys.*, 2006, **125**, 074106.

58 O. A. Vydrov, G. E. Scuseria and J. P. Perdew, *J. Chem. Phys.*, 2007, **126**, 154109.