A Computational Investigation of the Substituent Effects on Geometric, Electronic, and Optical Properties of Siloles and 1,4-Disilacyclohexa-2,5-dienes

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Abstract: Thirty two differently substituted siloles 1a–1p and 1,4-disilacyclohexa-2,5-dienes 2a–2p were investigated by quantum chemical calculations using the PBE0 hybrid density functional theory (DFT) method. The substituents included σ-electron donating and withdrawing, as well as π-electron donating and withdrawing groups, and their effects when placed at the Si atom(s) or at the C atoms were examined. Focus was placed on geometries, frontier orbital energies and the energies of the first allowed electronic excitations. We analyzed the variation in energies between the orbitals which correspond to HOMO and LUMO for the two parent species, here represented as ΔεHL, motivated by the fact that the first allowed transitions involve excitation between these orbitals. Even though ΔεHL and the excitation energies are lower for siloles than for 1,4-disilacyclohexa-2,5-dienes the latter display significantly larger variations with substitution. The ΔεHL of the siloles vary within 4.57–5.35 eV (ΔΔεHL = 0.78 eV) while for the 1,4-disilacyclohexa-2,5-dienes the range is 5.49–7.15 eV (ΔΔεHL = 1.66 eV). The excitation energy of the first allowed transitions display a moderate variation for siloles (3.60–4.41 eV) whereas the variation for 1,4-disilacyclohexa-2,5-dienes is nearly doubled (4.69–6.21 eV). Cyclobutadisiloles combine the characteristics of siloles and 1,4-disilacyclohexa-2,5-diene by having even lower excitation energies than siloles yet also extensive variation in excitation energies to substitution of 1,4-disilacyclohexa-2,5-dienes (3.47–4.77 eV, variation of 1.30 eV).

Keywords: 1,4-disilacyclohexa-2,5-diene; cyclobutadisilole; silole; substituent effects; cross-hyperconjugation

1. Introduction

Small cyclic π-conjugated compounds with saturated silicon atoms in their rings are an interesting class of compounds, often investigated for their optoelectronic properties [1–12]. Here, siloles, i.e., silacyclopenta-2,4-dienes, have received the greatest attention and their properties can be tuned by variation of the electron donating (EDG) and electron withdrawing (EWG) strengths of the ring substituents [9]. Among their usage in organic electronics can particularly be noted the recent studies on variously substituted siloles for organic light-emitting diodes (OLEDs) [4–8].
Inspired by Mulliken’s seminal studies on hyperconjugation [13,14], we have explored saturated silicon fragments (SiX2) inserted between two π-conjugated segments, as found in siloles, and shown that the SiX2 fragment contributes with local π(SiR2) and π*(SiR2) orbitals in a similar way as a geminally connected C=C double bond provides local π(CC) and π*(CC) orbitals [15]. We call this interaction cross-hyperconjugation since it is analogous to regular cross-π-conjugation. Experimental comparisons of electron transfer rates as well as computations of the electron transport through cross-hyperconjugated and cross-π-conjugated segments confirm these similarities [16,17]. Applying the cross-hyperconjugation rational to siloles suggests that siloles can be considered as analogous to the cross-π-conjugated pentafulvenes (Figure 1). Indeed, similar as pentafulvenes, siloles behave as “aromatic chameleons” [18], giving them the ability to adapt their electronic structures to the different π-electron counting rules for aromaticity in the electronic ground state (S0) and the first ππ* excited states (T1 and S1), as given by Hückel’s and Baird’s rules, respectively [19–23]. Utilizing the fact that siloles are cross-hyperconjugated “aromatic chameleons” we could rationalize the substituent effects on the energies of the lowest singlet and triplet excited states [16].

![Figure 1](image-url)

**Figure 1.** Local π(SiR2) fragment orbitals interact in a similar way as exocyclic local π(C=C) orbitals, giving an electronic structure similarity between siloles and pentafulvenes.

During our studies of cross-hyperconjugation another small silacyle, the 1,4-disilacyclohexa-2,5-diene, attracted our interest as a potential complement to siloles in optoelectronic applications [24,25]. Using both experiments and computations we earlier studied its electronic properties, focusing on groups with different tetrel elements as substituents on the two saturated Si ring atoms [26,27]. Although the relative synthetic availability of siloles makes them attractive synthetic targets, the recent account by Stratakis and co-workers shows that 1,4-disilacyclohexa-2,5-dienes are also synthetically obtainable [28]. Thus, we now probed if the 1,4-disilacyclohexa-2,5-dienes respond to substitution similar as siloles, i.e., do electron withdrawing and electron donating groups at the Si or C atoms have the same effects?

In siloles the influence is generally largest for substituents at the 2- and 5-positions since substituents at these positions can exhibit strong π-interaction with the silole core; strong π-donors destabilize HOMO while strong π-acceptors stabilize LUMO [9]. On the other hand, it is known that substituents at Si only have minor effects on optical properties (absorption and fluorescence characteristics) [9]. Due to synthetic limitations, substitution at 3- and 4-positions is not equally thoroughly examined as substitution at the other positions. However, DFT calculations of 2,3,4,5-tetraarylsiloles reveal that substituents at those positions give considerably smaller extensions of both HOMO and LUMO when compared to similar substitution at the 2- and 5-positions [2,29–34].

Using quantum chemically calculated properties, such as electronic transitions and geometric parameters, herein we analyze how the substituent patterns in the different compounds are linked to their cross-hyperconjugation. Are the substituent effects more pronounced in the siloles or in the 1,4-disilacyclohexa-2,5-dienes? And how could one go about to design compounds that combine the beneficial features of siloles with those of 1,4-disilacyclohexa-2,5-dienes?
2. Results and Discussion

The comparison of the variously substituted 1 and 2 (Figure 2) is based on both geometric and electronic structural data, and we discuss each of the properties (geometrical data, molecular orbital data, and electronic excitation energies) separately. Rather than comparing a silole having a particular substituent against the 1,4-disilacyclohexa-2,5-diene with the same substituents we analyze the spread in the values of the selected properties for the chosen set of substituents. We then primarily discuss the compounds at the end points in the spreads. For tabulations of the properties of each individual silole and 1,4-disilacyclohexa-2,5-diene, see the Supporting Information.

As indicators of hyperconjugation we examined SiC(ring) and C=C bond lengths as well as R-Si-R angles. The spread in these geometrical parameters are displayed in the bar diagrams of Figures 3–5. Improved conjugation generally leads to elongation of double bonds and shortening of single bonds, and hyperconjugation also has this effect [23]. In the analysis herein we separated between the siloles and 1,4-disilacyclohexa-2,5-diienes having substituents at Si (1b–1i and 2b–2i) and those having substituents at C (1j–1p and 2j–2p). The latter compounds can in addition to the electronic effects also display geometric distortions that are caused by steric congestion between substituents. For that reason we do not analyze the C=C bond lengths of these compounds, except in a few selected cases.

The average SiC(ring) bond lengths in 1a–1p and 2a–2p are 1.871 and 1.874 Å, respectively, and the shorter average bond length in the siloles than in the 1,4-disilacyclohexa-2,5-diienes is reflected in the bond length intervals (Figure 3). Both among the siloles and the 1,4-disilacyclohexa-2,5-diienes are species with SiC(ring) bond lengths in the range 1.850–1.859 Å. However, no silole has SiC bonds in the interval 1.890–1.899 Å whereas two 1,4-disilacyclohexa-2,5-diienes have (2m and 2n). The generally shorter SiC bonds in 1a–1p than in 2a–2p suggest stronger hyperconjugation between the single SiR2 segment and the diene segment in siloles than between the SiR2 segments and the two formally non-conjugated C=C bonds in the 1,4-disilacyclohexa-2,5-diienes.

When considering the effect of the substituents at Si (the R groups) it is clear that σ-electron withdrawing groups lead to the shortest SiC(ring) bonds both in siloles and in 1,4-disilacyclohexa-2,5-diienes. On the other hand, R = NH2 in siloles (compound 1i) and R = SiMe3 in 1,4-disilacyclohexa-2,5-diienes (compound 2h) lead to the longest ones. With regard to the effect of the R’ substituent on the SiC(ring) bond length we only considered the effect for 1,4-disilacyclohexa-2,5-diienes as the steric congestion in a few of the siloles is extensive. Among the substituents at the C=C bonds
of the 1,4-disilacyclohexa-2,5-diene the trifluoromethyl groups, leading to 2m, give SiC(ring) bonds which are elongated when compared to 2a. With R\' = NH\(_2\) (compound 2p) they are the shortest. From this one can deduce that among the 1,4-disilacyclohexa-2,5-dienes the shortest SiC(ring) bond should be found with R = F and R\' = NH\(_2\) while the longest would be found with R = SiMe\(_3\) and R\' = CF\(_3\). Indeed, this is supported by computations because the 1,4-disilacyclohexa-2,5-diene with R = F and R\' = NH\(_2\) has a SiC(ring) bond length of 1.840 Å whereas when R = SiMe\(_3\) and R\' = CF\(_3\) it is 1.915 Å.

![Figure 3](Molecules 2017, 22, 370)

**Figure 3.** Distributions of SiC(ring) bond lengths of (a) 1a–1p and (b) 2a–2p calculated at PBE0/6-31G(d) level. The compound numbers substituted at the Si atoms are displayed in black and those substituted at the C atoms in red.

The formal C=C double bonds of 1a and 2a are 1.348 and 1.346 Å, respectively. However, in siloles they are part of the diene segment whereas in 1,4-disilacyclohexa-2,5-dienes they are instead two isolated double bonds. For that reason we do not compare the C=C bonds directly but instead compare the deviations in bond lengths against those of the respective parent compounds. Thus, we consider \(\Delta r_{c=c} = |r_{c=c}(1a) - r_{c=c}(2a)| - |r_{c=c}(1x) - r_{c=c}(2x)|\) (Figure 4) where positive values show that a C=C double bond lengthening is more pronounced in 1,4-disilacyclohexa-2,5-dienes, while negative values correspond to situations with more elongated double bonds in siloles. The species investigated only include those with substituents at Si so as to exclude effects caused by steric congestion. Here it should be noted that siloles with small electron withdrawing substituents at the double bonds can show shortening of these bonds. E.g., the fluoro substituents in 1j lead to the shortest C=C double bonds among all siloles considered here (1.341 Å), and the chloro and trifluoromethyl substituents (1k and 1m) reveal double bonds of 1.349 Å, which are only slightly longer than those of 1a.

For compounds with electron donating silyl groups as substituents at the silicon (1f–1h), the elongations of the C=C bonds are more pronounced in the siloles than in the 1,4-disilacyclohexa-2,5-dienes. Conversely, \(\sigma\)-electron withdrawing groups as R lead to more significant shortenings of the double bonds in siloles than in the 1,4-disilacyclohexa-2,5-dienes or display
similar \( r_{C=C} \) values (1b–1e). Attachment of two amino groups at silicon results in significantly more pronounced double bond shortenings in the silole 1i than in the 1,4-disilacyclohexa-2,5-diene 2i.

For the various siloles the R-Si-R angles are found mainly in the range 105.2°–113.8°, but one silole (1h, \( R = \text{SiMe}_3 \)) is found in the interval 116.0°–117.9° (Figure 5a). The average value is 109.4°. Interestingly, the R-Si-R angles of the siloles cluster into two groups. To some extent the R-Si-R angles are also affected by steric bulk of the R groups (particularly applicable to 1h). Yet, for the siloles with \( R = \text{H} \) (1j–1p) there is still a spread in the angles of 5.8°, indicating that the variation to a substantial extent is of electronic origin.

For the full set of 1,4-disilacyclohexa-2,5-dienes, the R-Si-R angles are found in the smaller range 103.7°–110.9°, with an average value of 107.2°. The larger average R-Si-R angle of the siloles could be explained by a general tendency that a smaller bond angle at an atom with tetrahedral bond arrangement obtained through inscription of this atom in a ring is often compensated by a larger bond angle between the two bonds that are not inscribed into the cycle [35,36]. The C(ring)-Si-C(ring) angles of 1a–1p and 2a–2p are found in the range 90.6°–95.0°, i.e., they are significantly smaller than the ideal tetrahedral value, and this results in the large R-Si-R angles observed. Similar as for the siloles, the species 2i–2p have a spread in the H-Si-H angles (Figure 5b), also now revealing the electronic effect of the substituents at the C atoms on this angle.

For both siloles and 1,4-disilacyclohexa-2,5-dienes it is clear from the bar diagrams that the compounds with \( \sigma \)-withdrawing substituents at Si in general have small R-Si-R angles, although among 2a–2p the species with the smallest R-Si-R angles are those with \( \pi \)-donating substituents (2i and 2p).

**Figure 4.** Distribution of \( \Delta r_{C=C} = [r_{C=C}(1a) - r_{C=C}(2a)] - [r_{C=C}(1x) - r_{C=C}(2x)] \) values calculated at PBE0/6-31G(d) level, with \( x = b \) to \( i \).

**Figure 5.** Cont.
1,4-disilacyclohexa-2,5-dienes (Figure 7). To examine the effect of the substituents on the frontier orbital energies we regard the Kohn-Sham orbitals from the PBE0/6-31G(d) calculations.

### 2.2. Molecular Orbitals

The MOs of π-symmetry are constructed qualitatively by regarding the proper symmetry combinations of the π-orbitals of the unsaturated carbon segments, with the bonding and antibonding orbitals of π-character at the single SiR₂ fragment in siloles (Figure 6) or the two SiR₂ fragments in 1,4-disilacyclohexa-2,5-dienes (Figure 7). To examine the effect of the substituents on the frontier orbital energies we regard the Kohn-Sham orbitals from the PBE0/6-31G(d) calculations.

![Figure 5](image)

**Figure 5.** Distributions of the R-Si-R angles of (a) 1a–1p and (b) 2a–2p given in degrees and calculated at the PBE0/6-31G(d) level. The compound numbers substituted at the Si atoms are displayed in black and those substituted at the C atoms in red.

![Figure 6](image)

**Figure 6.** Qualitative molecular orbital (MO) diagram of silole with the lowest few occupied and unoccupied MOs of π-character constructed from suitable fragment orbitals. Red arrows indicate changes in fragment orbital energies in dependence of substituent R and blue arrows indicate changes of substituent R'. The orbitals are labeled in accordance with the irreducible representations of the C₂ᵥ point group.
The HOMO for each of the siloles 1a–1p is of the same type, and it belongs to the either the a or the a₂ irreducible representation, depending on whether the silole is C₂ or C₂ᵥ symmetric. In 1a HOMO is the 1a₂ orbital (Figure 8). The \( \epsilon_{\text{HOMO}} \) in the siloles is on average \(-6.78\) eV, whereas the span ranges from \(-8.75\) to \(-4.58\) eV with the two extreme values found for 1n and 1p (Figure 9), respectively. However, there are only two siloles which have \( \epsilon_{\text{HOMO}} \) below \(-8.0\) eV (1m and 1n), the others have \( \epsilon_{\text{HOMO}} \) at energies \(-7.33\) eV or above. Since HOMO lacks contributions from the Si atom, the variation in \( \epsilon_{\text{HOMO}} \) among 1a–1l, in which R at Si is varied, is merely \(1.19\) eV (from \(-7.33\) to \(-6.14\) eV), compared to \(4.17\) eV for the complete series 1a–1p. Thus, the variation in \( \epsilon_{\text{HOMO}} \) for the siloles is best achieved through substitution at the diene segment, in line with the conclusions by Marder and co-workers who pointed out that 2,5-disubstitution has more pronounced effects on the electronic and optical properties than 1,1-disubstitution [9].
The silole with the highest-energy HOMO (1p) has a small H-Si-H angle, yet, there is no obvious connection between the \( \varepsilon_{\text{HOMO}} \) and the geometrical parameters for the siloles. In contrast, the HOMO-1 orbital (2b\(_1\)) is clearly the orbital with contributions from both the diene and SiR\(_2\) segments, and which therefore impacts on the interaction.

Furthermore, the LUMO throughout 1a–1p belong either to the b or the b\(_1\) irreducible representation, depending on molecular symmetry (C\(_2\) or C\(_{2v}\)). In 1a LUMO is the 3b\(_1\) orbital (Figure 8). The average value of \( \varepsilon_{\text{LUMO}} \) among all siloles is \(-1.70\) eV, with the lowest LUMO found for 1n (\( \varepsilon_{\text{LUMO}} = -3.78\) eV) followed by 1m (\( \varepsilon_{\text{LUMO}} = -3.25\) eV), both having electron withdrawing substituents (trifluorosilyl and trifluoromethyl groups) at the diene segment (Figure 10). The highest \( \varepsilon_{\text{LUMO}} \) is found for 1p (\(-0.01\) eV) having tetraamino substitution at the diene segment. As LUMO has contributions from both the diene and SiR\(_2\) segments it varies in energy slightly more with substitution at Si (\( \Delta\varepsilon_{\text{LUMO}} = 1.32\) eV ranging from \(-2.11\) to \(-0.79\) eV) than reported above for the variation in energy of HOMO. However, to achieve a large variation in the \( \varepsilon_{\text{LUMO}} \) of siloles the positions at both the C and Si atoms need to be utilized.
An interesting feature is the HOMO-LUMO gap (\(\Delta\varepsilon_{HL}\)) and its variation among the differently substituted siloles. As seen in Figure 11 the variation in \(\Delta\varepsilon_{HL}\) is small because most siloles have \(\Delta\varepsilon_{HL}\) in the range from \(-5.35\) to \(-4.57\) eV (\(\Delta\Delta\varepsilon_{HL} = 0.78\) eV) with the smallest for 1k and 1p, and the largest for 1h. Despite this, the separate spans in the HOMOs and LUMOs of 1a–1p are 4.17 and 3.77 eV, i.e., the two orbitals are essentially affected to the same extents by the various substituents so that a small \(\Delta\Delta\varepsilon_{HL}\) results.

For the \(\pi\)-symmetric MOs of the 1,4-disilacyclohexa-2,5-dienes the fragment represented by the two C=C double bonds contribute with a set of fragment orbitals which are analogous to the four \(\pi\)-MOs of \(D_{2h}\) symmetric cyclobutadiene. And the local \(\pi(SiR_2)\) and \(\pi^*(SiR_2)\) orbitals combine into two \(b_{1u}\) and into two \(b_{2g}\) symmetric \(2 \times \text{SiR}_2\) fragment orbitals, respectively. In addition, from the shapes of the calculated orbitals it can be concluded that the two Si atoms contribute with 3d AOs in an \(a_u\) symmetric combination (Figure 7) contained in the 1a\_u orbital which for several of the 1,4-disilacyclohexa-2,5-dienes is the LUMO.
As there is a variation among 2a–2p as to which orbital is HOMO and LUMO, we consider herein the two orbitals which correspond to HOMO and LUMO of 2a (Figures 9 and 10, and the Supporting Information). The HOMO of 2a is the 2b_{1u} orbital and its LUMO is the 2b_{2g} orbital. For each of the 1,4-disilacyclohexa-2,5-diene considered here the first strongly allowed excitations involve transitions between these two orbitals, although they are not always HOMO and LUMO. For 2j, 2k, 2n, 2o and 2p the 2b_{1u} orbital is HOMO-1, for 2b and 2c it is HOMO-2, for 2i it is HOMO-4, while for the other eight 1,4-disilacyclohexa-2,5-dienes it is the HOMO. With regard to the 2b_{2g} orbital it is LUMO for 2a–2e, 2i–2m and 2p and LUMO+1 for 2f–2h and 2n–2o. Yet, it is not possible to see any distinct pattern relating the characteristics of the substituents with the ordering of the orbitals of the 1,4-disilacyclohexa-2,5-dienes.

On average the $\epsilon_{2b_{1u}}$ of 2a–2p is $-7.64$ eV, i.e., at a lower energy than that of siloles ($\epsilon_{\text{HOMO}} = -6.78$ eV). The lowest $\epsilon_{2b_{1u}}$ is found for 2b ($-9.16$ eV), whereas 2p is highest in energy ($-5.45$ eV). Thus, the span in the $\epsilon_{2b_{1u}}$ among the various 2a–2p is 3.71 eV, slightly lower than the corresponding span of the siloles (4.17 eV). If one regards the orbital energy variation through variation of the substituents at Si as in 2a–2i, the $\epsilon_{2b_{1u}}$ can be tuned within a larger interval (3.55 eV) than the $\epsilon_{\text{HOMO}}$ of the siloles (1.19 eV), a result that stems from the lack of contribution from the SiR$_2$ segment.

Figure 10. Distribution of (a) the $\epsilon_{\text{LUMO}}$ for 1a–1p and (b) the $\epsilon_{2b_{2g}}$ for 2a–2p ($\epsilon_{\text{LUMO}}$ for 2a). Compound numbers of compounds substituted at the Si atoms in black and those substituted at the C atoms in red.
1,4-disilacyclohexa-2,5-dienes do not respond similarly to the substitution leading to a factor 2.1 larger ε than for the siloles (2b (R = F) and 2h (R = SiMe3), respectively.

![Figure 11](image)

**Figure 11.** Distribution in (a) the HOMO-LUMO energy gaps (ΔεHL) for 1a–1p and (b) the 2b1u−2b2g energy gaps for 2a–2p (the ΔεHL for 2a). Compound numbers of compounds substituted at the Si atoms in black and those substituted at the C atoms in red.

The variation in orbital symmetries is large also for the LUMOs of 2a–2p, and for that reason we analyze the 2b2g orbitals of 2b–2p that are analogous to LUMO of 2a. First, the variation in the ε2b2g with the substituents R at Si in 2a–2i (2.12 eV) is larger than found for εLUMO in the corresponding siloles (1.32 eV). When regarding all 1,4-disilacyclohexa-2,5-dienes the average value of ε2b2g is −1.28 eV, which is higher than for the siloles (−1.70 eV). The ε2b2g ranges from −2.86 to 0.21 eV, so that the energy variation in this orbital among 2a–2i (3.07 eV) is smaller than εLUMO among 1a–1p (3.77 eV). Naturally, the electron withdrawing trifluorosilyl group gives ε2b2g that is the lowest in energy (2n) and the electron donating amino group gives the highest (2p). Yet, the HOMO and LUMO of 1,4-disilacyclohexa-2,5-dienes do not respond similarly to the substitution leading to a factor 2.1 larger span in the ΔεHL for the 1,4-disilacyclohexa-2,5-dienes than for the siloles.

In clear difference to the ΔεHL of siloles, the 1,4-disilacyclohexa-2,5-dienes have a large variation in the Δε2b1u−2b2g (ΔεHL for 2a) ranging from 5.49 to 7.15 eV. The two species with the largest and smallest
$\Delta \varepsilon_{2b_{1u}-2b_{2g}}$ are 2b and 2h, respectively. Although the spread in $\Delta \varepsilon_{2b_{1u}-2b_{2g}}$ of 2a–2p is distributed among the different energy intervals most 1,4-disilacyclohexa-2,5-dienes have $\Delta \varepsilon_{2b_{1u}-2b_{2g}}$ within the range 6.00–7.00 eV (Figure 11b). Still, the frontier orbital energies of 1,4-disilacyclohexa-2,5-dienes reveal a much stronger response to the choice of substituents than what is the case for the siloles.

2.3. Singlet State Excitation Energies

The goal is to identify means that can be used to qualitatively predict the excitation energies for the first allowed transitions of siloles and 1,4-disilacyclohexa-2,5-dienes. For all siloles 1a–1p the lowest vertically excited singlet state is of B or B$_2$ symmetry, depending on whether a particular silole is C$_2$ or C$_{2v}$ symmetric, and these transitions are dominated by the HOMO to LUMO excitation. Furthermore, the first transitions are allowed throughout the siloles.

Most of the siloles also have a strong low-energy transition to a state of A or A$_1$ symmetry. However, the excitation energies to the lowest singlet excited state of 1a–1p are relatively similar (within 0.88 eV, Figure 12a), which is linked to the fact that $\Delta \varepsilon_{H_L}$ of 1a–1p display only a small variation with the substituents. As noted earlier, the substituents R at Si have only a small influence on the first excitation, and this is confirmed through our TD-DFT calculations because for 1a–1i the first excitation energy varies within the interval 4.06–4.41 eV, i.e., a range of merely 0.35 eV. For 2a–2p the first vertically excited singlet states are dark, or nearly dark, and distributed over a range of 2.13 eV, from 3.46 to 5.59 eV. The first allowed excitation for all 1,4-disilacyclohexa-2,5-dienes includes the transition from the 2b$_{1u}$ to the 2b$_{2g}$ orbitals which for 2a are the HOMO and LUMO, respectively. Hence, we will consider here only the first allowed transitions (Figure 12). The first allowed excitations of 2a–2p are distributed over a range of 1.52 eV, from 4.69 eV in 2h to 6.21 eV in 2b. The wide distribution in the lowest allowed excitation energies goes well with the wide distribution in the $\Delta \varepsilon_{2b_{1u}-2b_{2g}}$ observed above. Importantly, for the 1,4-disilacyclohexa-2,5-diene the substituents R at Si (2a–2i) also have a much larger impact on the lowest allowed excitation energy than for the siloles as the variation spans the same values as the variation of the entire set 2a–2p, i.e., from 4.69 to 6.21 eV. As the corresponding siloles (1a–1i) only display a range of 0.35 eV, that of the 1,4-disilacyclohexa-2,5-dienes is a factor 4.3 larger.

Considering that electron withdrawing and electron donating groups can have opposing effects on HOMO and LUMO the usage of both as substituents at either the single Si atom in siloles or the two Si atoms in 1,4-disilacyclohexa-2,5-dienes could have intriguing results. For the silole having an SiF(SiMe$_3$) moiety we calculate the lowest strongly allowed excitation at 4.01 eV, however, this is not a markedly shifted transition when compared to what is regular for siloles as seen in Figure 12a. In contrast, for the two 1,4-disilacyclohexa-2,5-diene isomers having two SiF(SiMe$_3$) moieties we calculate a first strongly allowed transition at energies 4.44 (E-isomer) and 4.65 eV (Z-isomer), respectively, i.e., even lower than calculated for 2h (4.69 eV). The low-lying transition of the E-isomer is particularly interesting and points to an additional means for influencing the excitation energies through choice of substituents. Clearly, as the R = SiMe$_3$ substituents lead to a species (2h) with a high-lying occupied 2b$_{1u}$ orbital while the R = F substituents lead to a species (2b) with a low-lying empty 2b$_{2g}$ orbital, it is obvious that the 1,4-disilacyclohexa-2,5-diene having both fluoro and trimethylsilyl substituents at Si will have a small $\Delta \varepsilon_{2b_{1u}-2b_{2g}}$ gap (5.49 eV for E-isomer and 5.67 eV for Z-isomer) and a low-lying excitation for the transition involving these orbitals. Interestingly, a similar effect is not achieved with a 1,4-disilacyclohexa-2,5-diene having one SiF$_2$ and one Si(SiMe$_3$)$_2$ moiety as this species has its first strongly allowed excitation at an energy of 4.81 eV.
substituents. As noted earlier, the substituents R at Si have only a small influence on the first excitation, and this is confirmed through our TD-DFT calculations because for $1a$–$1i$ the first excitation energy varies within the interval 4.06–4.41 eV, i.e., a range of merely 0.35 eV. For $2a$–$2p$ the first vertically excited singlet states are dark, or nearly dark, and distributed over a range of 2.13 eV, from 3.46 to 5.59 eV. The first allowed excitation for all 1,4-disilacyclohexa-2,5-dienes includes the transition from the $2b_{1u}$ to the $2b_{2g}$ orbitals which for $2a$ are the HOMO and LUMO, respectively. Hence, we will consider here only the first allowed transitions (Figure 12). The first allowed excitations of $2a$–$2p$ are distributed over a range of 1.52 eV, from 4.69 eV in $2h$ to 6.21 eV in $2b$. The wide distribution in the lowest allowed excitation energies goes well with the wide distribution in the $\Delta\varepsilon_{2b_{1u}-2b_{2g}}$ observed above. Importantly, for the 1,4-disilacyclohexa-2,5-diene the substituents R at Si ($2a$–$2i$) also have a much larger impact on the lowest allowed excitation energy than for the siloles as the variation spans the same values as the variation of the entire set $2a$–$2p$, i.e., from 4.69 to 6.21 eV. As the corresponding siloles ($1a$–$1i$) only display a range of 0.35 eV, that of the 1,4-disilacyclohexa-2,5-dienes is a factor 4.3 larger.

![Figure 12](image-url)

**Figure 12.** The distributions in the vertical excitation energies for the first allowed transitions to singlet excited states of (a) $1a$–$1p$ and of (b) $2a$–$2p$ calculated at TD-PBE0/6-31+G(2d,p)// PBE0/6-31G(d) level. Compound numbers of compounds substituted at the Si atoms in black and those substituted at the C atoms in red.

### 2.4. On Dimerization Reactions

An aspect that influences the utility of the substituted siloles and 1,4-disilacyclohexa-2,5-dienes is their various tendencies to undergo dimerization and further oligomerization reactions. It is well-established that siloles dimerize through $[4 + 2]$ cycloaddition reactions when not properly substituted [37]. However, we now find that the activation barrier for this dimerization to a significant extent is influenced by the substituent at Si. Furthermore, this influence seems to be of electronic rather than of steric origin because the activation barrier for silole $1g$, having two sterically unencumbered, yet, $\sigma$-electron donating SiH$_3$ substituents, is 7.6 kcal/mol higher than that of $1a$ (Table 1).

Conversely, for silole $1b$ with electron withdrawing fluoro substituents at Si the activation energy is 3.0 kcal/mol lower than for $1a$. Indeed, the activation barrier for $1g$ is sufficiently high to significantly hampered dimerization.
In addition to the electronic effect exercised by the SiH₃ group, larger silyl groups will introduce steric congestion at the transition state, further raising the activation barrier. Thus, with moderate steric bulk imposed by silyl groups at the Si it should be possible to vary the substituents at the C atoms more widely than what is the case in siloles presently found in the field of organic electronics.

With regard to the 1,4-disilacyclohexa-2,5-dienes, these have not been found to oligomerize to any detectable extent \[21,23,25\], a feature explained by the fact that their dimerization would involve a symmetry-forbidden \([2 + 2]\) cycloaddition in contrast to the siloles which dimerize following a \([4 + 2]\) cycloaddition path.

### 2.5. Cyclobutadisiloles

The variation of the substituents at the Si atom in siloles only leads to a modest change in the first excitation of 0.35 eV. The 1,4-disilacyclohexa-2,5-dienes, on the other hand, display a large response to this substitution but have much higher excitation energies for the first allowed transitions. Now, can the good features of siloles and 1,4-disilacyclohexa-2,5-dienes be combined, i.e., can one identify a compound class with large variation in the energies of their lowest strongly allowed excitations at the same time as they are at fairly low energies? Indeed, cyclobutadisiloles, or more fully cyclobut[a,2-c:3,4-c′]disiloles, investigated by us earlier are those species \[24\]. They can be deduced formally through replacement of the two C=C double bonds with two C=C=C=C cumulene segments, providing diene-type fragment orbitals, followed by a collapse of their central C=C double bonds into a cyclobutane ring (Figure 13). The cyclobutadisiloles can also be regarded as silole dimers. Indeed, the HOMO of the parent cyclobutadisilole can be viewed as the out-of-phase combination of the HOMO of 1a, and the LUMO can be seen as the in-phase combination of the corresponding orbital of 1a (Figure 14). Yet, the first strongly allowed transition involves an excitation from HOMO-2 to LUMO, and these orbitals are analogous to what is found for 1,4-disilacyclohexa-2,5-dienes.

### Table 1. Activation (\(\Delta G^\dagger\)) and reaction (\(\Delta G\)) free energies (kcal/mol) for the dimerization of three selected siloles following a \([4 + 2]\) cycloaddition path \(^1\).

<table>
<thead>
<tr>
<th>R =</th>
<th>H (1a)</th>
<th>F (1b)</th>
<th>SiH₃ (1g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\Delta G^\dagger)</td>
<td>21.5</td>
<td>18.6</td>
<td>29.2</td>
</tr>
<tr>
<td>(\Delta G)</td>
<td>−23.8</td>
<td>−30.4</td>
<td>−15.2</td>
</tr>
</tbody>
</table>

\(^1\) Calculated at PBE0/6-31G(d) level.

Both the HOMO-2 and LUMO orbitals have large contributions from Si meaning that substituents at these atoms can have large effects on the excitation energies. Indeed, with \(R = H\) (3a) the transition is at 4.56 eV while with \(R = F\) (3b) it increases to 4.77 eV and with \(R = \text{SiMe}_3\) (3h) it decreases to 3.47 eV, i.e., a variation by 1.30 eV. An excitation energy of 3.47 eV corresponds to an absorption wavelength of 357 nm, i.e., nearly in the visible wavelength region. The variation in the first strong transition among the corresponding siloles (1a, 1b and 1h) and 1,4-disilacyclohexa-2,5-dienes (2a, 2b and 2h) are 0.29 and 1.52 eV, respectively. Thus, with the cyclobutadisiloles we have designed a compound (3h) with a...
first strongly allowed excitation which is lower by 0.94 and 1.22 eV than the analogous transitions in 1h and 2h, respectively. The further tailoring of the excitation energies can certainly be achieved through substituents at the C atoms, likely enabling design of cyclobutadisiloles with excitation energies well within the visible wavelength region.

![Figure 14. Frontier orbitals of unsubstituted cyclobutadisilole (R = H).](image)

### 3. Computational Methods

All calculations were carried out with the Gaussian 09 program package [38]. The geometry optimizations were performed using the PBE0 hybrid density functional theory (DFT) level [39,40], with the 6-31G(d) valence double-zeta basis set of Pople and Harirahan [41]. The stationary points were subjected to frequency calculations to examine their characters as minima or saddle points. To evaluate vertical excitations to electronically excited states, time-dependent DFT (TDDFT) calculations were carried out on the DFT optimized geometries. These TDDFT calculations were performed with the PBE0 functional using the 6-31+G(2d,p) valence double-zeta basis set [42–44].

### 4. Conclusions

Through DFT and TD-DFT computations of the geometrical, electronic, and optical properties we have revealed similarities and dissimilarities in the effects of substituents at siloles and 1,4-disilacyclohexa-2,5-dienes. The main differences are found in the impact substituents have on the electronic structure and the energies of the lowest electronically excited states. For siloles the lowest electronic transition is a HOMO-LUMO transition and it is strongly allowed. For 1,4-disilacyclohexa-2,5-dienes the first strongly allowed transition corresponds to the 2b$_{1u}$ to 2b$_{2g}$ transition which for some of the species is the HOMO to LUMO excitation. The HOMO-LUMO gap of the siloles can be varied in the range 4.5 to 5.4 eV, while for 1,4-disilacyclohexa-2,5-diene the 2b$_{1u}$ to 2b$_{2g}$ energy gap can be varied from 5.4 to 7.2 eV. As a consequence, the lowest strongly allowed electronic excitation varies with substituents to a much larger degree in 1,4-disilacyclohexa-2,5-dienes than in siloles. Thus, 1,4-disilacyclohexa-2,5-diene, or species derived based on them, could represent interesting new building blocks for molecular wires and materials for optoelectronics applications. In particular cyclobutadisiloles combine the good features of siloles and 1,4-disilacyclohexa-2,5-dienes as they display low-lying electronic transitions for which excitation energies can be varied extensively through substitution. Indeed, it should be possible to design cyclobutadisiloles with strongly allowed transitions in the visible wavelength region.

**Supplementary Materials:** The following are available online. Figures S1 and S2 with frontier molecular orbitals of siloles and 1,4-disilacyclohexa-2,5-dienes, respectively, Tables S1–S4 with orbital energies and orbital energy gaps, Tables S5 and S6 with excitation energies of siloles, Tables S7 and S8 with excitation energies of 1,4-disilacyclohexa-2,5-dienes, Tables S9 and S10 with data on bond length and angles of siloles, Tables S11 and S12 with data on bond lengths and angles of 1,4-disilacyclohexa-2,5-dienes, and listings of Cartesian coordinates of all investigated compounds.

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Conflicts of Interest: The authors declare no conflict of interest. The founding sponsors had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, and in the decision to publish the results.

References


**Sample Availability:** The paper reports on a purely computational study. Detailed data from the computations are available upon request from the authors.

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