Hyperconjugation in Group 14 Organic Compounds

Design and Property Investigations

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Abstract
Denisova, A. 2017. Hyperconjugation in Group 14 Organic Compounds. Design and Property Investigations. *Digital Comprehensive Summaries of Uppsala Dissertations from the Faculty of Science and Technology* 1613. 61 pp. Uppsala: Acta Universitatis Upsaliensis. ISBN 978-91-513-0190-7.

Nowadays π-conjugated molecules are widely used as materials for devices in organic and molecular electronics. This is due to the ability of such molecules to conduct electricity. However, π-conjugation leads to molecular rigidness and associated lower solubility, which limits possible applications. Meanwhile, there are other types of conjugation that do not cause molecular rigidness but still provide conductivity. One of them is so called hyperconjugation. While π-conjugation involves only p atomic orbitals, hyperconjugation is characterized by interaction of π and σ orbitals. Hyperconjugation is normally weaker than π-conjugation, thus, in order to get strongly hyperconjugated molecules they should be enhanced in some way.

In this thesis, I describe methods for design of strongly hyperconjugated molecules. It is possible to increase the strength of hyperconjugation by various methods and some of them are discussed. We performed quantum chemical calculations in order to investigate optical and geometric properties of the hyperconjugated molecules and evaluate the relative strength of hyperconjugation. In some cases, results of calculations were compared with experimental results aiming to confirm the relevance of the calculations. First, we have investigated how the change of group 14 elements in the 1,4-ditetrelocyclohexa-2,5-dienes influence the hyperconjugation strength. Next, the substituent effect was considered in fulvenes and their hyperconjugated analogs. We showed this effect from the perspective of the substituents influence on the aromatic properties of molecules in the ground and first electronically excited states. Further, the gradual shift when going from monomer to oligomers were investigated. For this hyperconjugated oligomers were constructed from 1,4-disilacyclohexa-2,5-diene and cyclobutadisilole fragments. Additionally we showed the influence of electron withdrawing and electron donating groups on hyperconjugation in siloles and 1,4-disilacyclohexa-2,5-dienes. Finally, hyperconjugation was investigated in a set of silicon-containing omni-hyperconjugated compounds.

The results obtained from this research showed that hyperconjugation strength can be increased significantly up to levels comparable to purely π-conjugated molecules. We hope that these results will be useful in development of other hyperconjugated small molecules, oligomers, and polymers, which can be further used as material for electronic devices.

Keywords: 1, 4-disilacyclohexa-2, 5-diene, aromaticity, computational chemistry, conjugation, cross-hyperconjugation, hyperconjugation, group 14 elements, organosilicon chemistry, silole

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To my little family

List of Papers

This thesis is based on the following papers, which are referred to in the text by their Roman numerals.

I   Emanuelsson, R.;[†] Denisova, A. V.;[†] Ottosson, H. Optimization of the Cyclic Cross-Hyperconjugation in 1,4-Ditetrelcyclohexa-2,5-dienes. *Organometallics*, **2014***, 33,* 2997–3004.
[†]These authors contributed equally

II   Jorner, K.;[†] Emanuelsson, R.;[†] Dahlstrand, C.; Tong, H.; Denisova, A. V.; Ottosson, H. Impact of Ground- and Excited-State Aromaticity on Cyclopentadiene and Silole Excitation Energies and Excited-State Polarities. *Chem. Eur. J.*, **2014**, *20*, 9295–9303.
[†]These authors contributed equally

III   Denisova, A. V.; Emanuelsson, R.; Ottosson, H. Expanding the (Cross-)Hyperconjugation of 1,4-Disilacyclohexa-2,5-dienes to Larger Monomers and Oligomers: a Computational Investigation. *RSC Adv.,* **2016**, *6*, 36961–36970.

IV   Denisova, A. V., Tibbelin, J., Emanuelsson, R., Ottosson, H. A Computational Investigation of the Substituent Effects on Geometric, Electronic, and Optical Properties of Siloles and 1,4-Disilacyclohexa-2,5-dienes. *Molecules*, **2017**, *22*, 370.

V   Denisova, A.V., Yadav, S., Ottosson, H. Computational Design of Strongly σ/π-Conjugated Compounds with a Start at the Omni-Conjugated [3]Radialene. *Preliminary manuscript*.

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Contribution report

The author wishes to clarify her contribution to the included papers I – V:

I   Performed the majority of the calculations. Contributed to the manuscript writing.

II   Performed calculations on ring size effects.

III   Performed all the calculations and major part of data analysis. Wrote the manuscript with feedbacks from the middle and last authors.

IV   Performed all the calculations and major part of data analysis. Wrote the manuscript with feedbacks from the middle and last authors.

V   Performed part of the calculations and part of the data analysis. Co-wrote the manuscript together with the other two authors.

Contents

Abbreviations

AO	Atomic Orbital
b_{AB}	Bond order
CC	Coupled Cluster
CI	Configuration Interaction
CSF	Configuration State Function
DFT	Density Functional Theory
EDG	Electron Donating Group
eV	Electron volt
EWG	Electron Withdrawing Group
GGA	Generalized Gradient Approximation
HF	Hartree-Fock method
HOMA	The Harmonic Oscillator Model of Aromaticity
HOMO	Highest Occupied Molecular Orbital
HOMO-n	The orbital n levels below HOMO
HOMO-LUMO gap	Energy gap between HOMO and LUMO
ISE	Isomerization Stabilization Energy
IUPAC	International Union of Pure and Applied Chemistry
LCAO-MO	Linear Combination of Atomic Orbitals to Molecular Orbitals
LDA	Local Density Approximation
LSDA	Local Spin-Density Approximation
LUMO	Lowest Unoccupied Molecular Orbital
MBPT	Many-Body Perturbation Theory
MO	Molecular Orbital
MCSCF	Multiconfiguration Self-Consistent Field
nm	Nanometer
$NICS(1)_{zz}$	The tensor component of Nucleus-Independent Chemical Shift 1.0 Å above the ring plane
NRT	Natural Resonance Theory
OFET	Organic field-effect transistor
OLED	Organic light-emitting diode
OPVC	Organic photovoltaic cell
SA	Shannon Aromaticity
SCF	Self-Consistent Field method
S_0	Singlet ground state
S_1	First excited singlet state

T_1	First excited triplet state
TDDFT	Time-Dependent Density Functional Theory
UPS	Ultraviolet Photoelectron Spectroscopy
Å	Ångström
$\Delta E_{S\text{-}T}$	Energy gap between S_0 and T_1 states
$\Delta \mu_{S\text{-}T}$	Dipole moment difference between S_0 and T_1 states

1. Introduction

The ability of an organic molecule to conduct electricity is a property of a great interest today. Such molecules can be used in molecular electronics or as components in materials used in organic electronics. Electron delocalization is the phenomenon that causes conductivity in a molecule. Going further, conjugation provides electron delocalization. However, the most well-known type of conjugation, π-conjugation, usually leads to molecular rigidness. This is an undesired property as it causes lower solubility and, as a result, limits the potential applications. Meanwhile, other types of conjugation do not cause this disadvantage. Conjugation types other than π-conjugation are not equally well investigated nowadays. This thesis deals with hyperconjugated compounds, their electronic and optical properties, and possible ways to tune these properties.

1.1 Organic electronics

Organic semiconductors is a class of organic molecules of high importance nowadays.[1] Organic electronics uses these compounds as materials for various devices such as organic light-emitting diodes (OLEDs), photovoltaic cells (OPVCs), field-effect transistors (OFETs), sensors etc. The interest to the miniaturization of electronic devices is still growing and these materials are widely spread now.

   The first works on organic conducting materials appeared in the 1950s and early 1960s. At that point, research in this field was mostly performed on π-conjugated polymers such as polyacetylene,[2] polypyrrole,[3] and polyaniline.[4] Nevertheless, other types of compounds were investigated as well, for instance, charge-transfer complexes based on aromatic compounds.[4] In 2002 Alan J. Heeger, Alan G. MacDiarmid, and Hideki Shirakawa received the Nobel Prize in Chemistry for their work on conductive π-conjugated polymers.[5] The effects of hyperconjugation on properties of conductive polymers and materials are also significant.[6] For example, polymers and individual molecules based on siloles are widely used in this field (Figure 1).[7-10]

Application in OLEDs

X = Si, Ge
R = Ph, 2-ethylhexyl

Application in OFETs

Application in OPVCs

Z = S, CH=CH
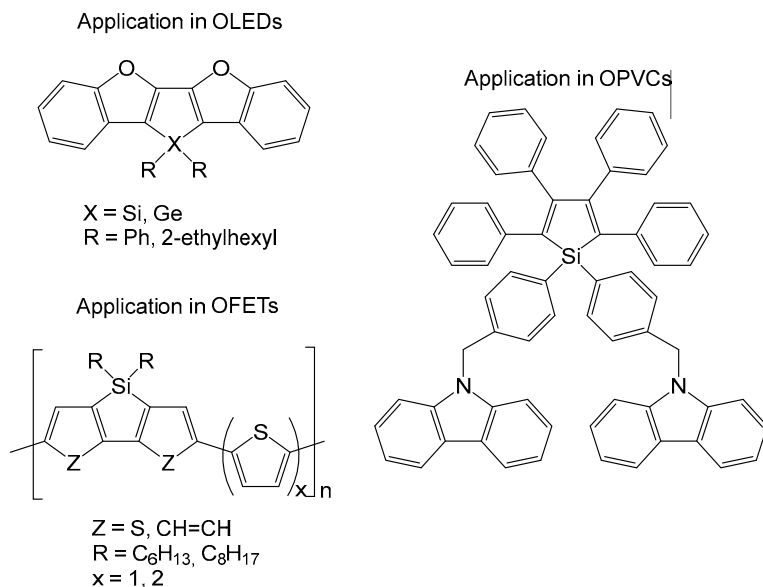R = C_6H_{13}, C_8H_{17}
x = 1, 2

Figure 1. Various siloles applied in organic electronics.

1.2 Molecular electronics

The first paper reporting on electron transport through a single molecule was published in 1974.[11] However, it was a theoretical investigation, while the first paper on measurements of single-molecule transport was published in 1997 by Tour *et al.*[12] To perform described experiment benzene-1,4-dithiol molecule was used, where benzene acted as the conducting π-conjugated unit while the sulfur atoms linked the molecule to the surface of the gold electrodes.

Now, besides commonly used π-conjugated molecules, there are molecules with other types of conjugation involved into electron transport measurements. Nuckolls *et al.* constructed σ-conjugated α,ω-bis(4-methylthio)-phenyloligosilanes that conduct electricity comparable to that of a conjugated chain of C=C π bonds (Figure 2a).[13] Later they showed how the strained silicon molecular wire conducts through two different pathways (Figure 2b).[14] Finally, in a recent paper they explored how π-σ-π interaction influences the conduction in molecular wires. In that work, they considered molecules containing heavier germanium atoms besides carbon and silicon (Figure 2c).[15]
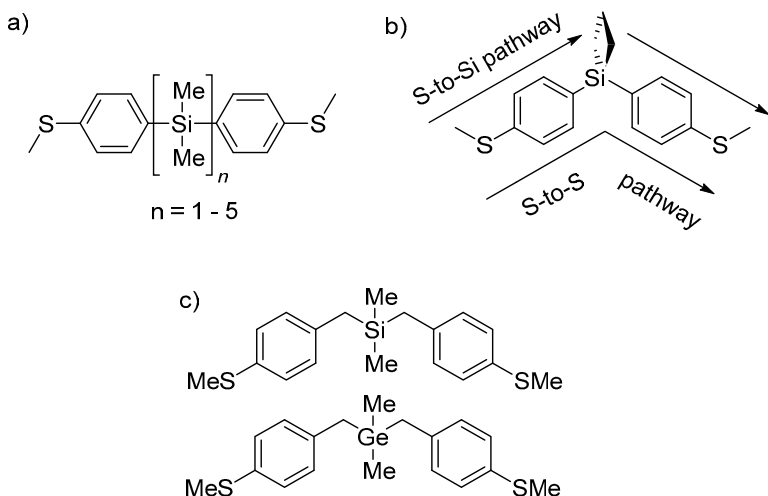
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Figure 2. Molecular wires containing silicon and germanium atoms.

1.3 Aim of this work

In this thesis, I review the results from my research, which was done in the projects devoted to the hyperconjugation phenomena. The aim of this research is to find possible ways to design molecules that demonstrate sufficiently strong hyperconjugation. For this purpose, we investigated both small molecules and oligomers with the goal in mind to further apply this knowledge in design of hyperconjugated polymers. We investigated possibilities to tune hyperconjugation strength with a few different approaches:

1. Involvement of group 14 elements starting from light C atoms going to heavy Pb atoms both incorporated into the rings of cyclic molecules and included as substituents on them;
2. Substitution with electron donating and electron withdrawing groups with the focus on aromatic properties in the ground and the first excited states;
3. Gradual elongation going from monomers to oligomers using a few different types of linkages;
4. Substitution of small cyclic molecules with electron donating and electron withdrawing groups at the various positions of the ring;
5. Omni-conjugated pathways in [3]radialene and π-conjugated compounds based on it, and further in their hyperconjugated analogs.

2. Types of conjugation

2.1 π-Conjugation

The term "conjugation" in organic chemistry is used to define a phenomena found in molecules with alternating single and multiple bonds. According to IUPAC *"conjugation is interaction of one p atomic orbital with another across an intervening σ bond"*.[16] Conjugation leads to a delocalization of π electrons across all the adjacent aligned p atomic orbitals.[17] As a result, conjugated molecules often appear to be stabilized and less reactive than non-conjugated ones. However, there are some exceptions, such as antiaromatic compounds that are conjugated and destabilized at the same time.[18] Finally, as discussed earlier, delocalization of electrons allows the molecule to conduct electricity.

It is worth mentioning that the term "conjugation" is not always used now to denote particularly π-conjugation. There are a few other types of conjugation and to distinguish them from π-conjugation the interaction type should always be accentuated. Other types of conjugation can include σ and δ orbitals in the interaction.[19,20] Orbitals of the same type or combination of various types can be involved into the conjugation in this case.

2.2 σ-Conjugation

There are few types of conjugation where the orbital interaction occurs between other types of orbitals than local π orbitals. One of these conjugation types is σ-conjugation involving local σ orbitals only. Linear tetrasilane chain is a good example to describe σ bond delocalization in saturated molecules. In this case, according to molecular orbital theory calculations include the interaction integrals between the two-center σ or σ* bond orbitals. The primary resonance integrals β_{prim} generate the primary electronic structure of the system. They describe the interaction between the local sp^3 hybrid orbitals at the neighboring atoms when these orbitals point to each other (Figure 3). Then the primary resonance integrals produce the corresponding local bonding (nodeless) and antibonding (with one node) σ orbitals, respectively.

However, instead of the primary resonance integrals other smaller integrals describe σ-delocalization, such as the geminal resonance integrals, β_{gem}, and vicinal resonance integrals, β_{vic}. The geminal resonance integrals define the

interaction between two sp^3 hybrid orbitals at the same atom, and the vicinal resonance integrals the interaction between two lobes at adjacent atoms that are not pointing towards each other. While primary resonance integrals are large and always negative, geminal and vicinal are smaller and their sign depends on the geometry of the molecule. The geminal integrals provide for σ-conjugation and if larger lobes have the same sign they are negative. Meanwhile, the sign and value of the vicinal integrals depend on the angle of rotation about the silicon-silicon bond. These integrals are negative in syn-periplanar alignment and positive in anti-periplanar; they go through zero while twisting between these two positions. Vicinal resonance integrals provide for σ-hyperconjugation. As it was mentioned before primary integrals are larger than geminal and for oligosilanes the difference is two to three times. Furthermore, geminal integrals appear to be larger than the vicinal integrals in syn-periplanar position. When going from C to Si and further down group 14 the importance of σ-hyperconjugation declines while that of σ-conjugation grows.[21,22]
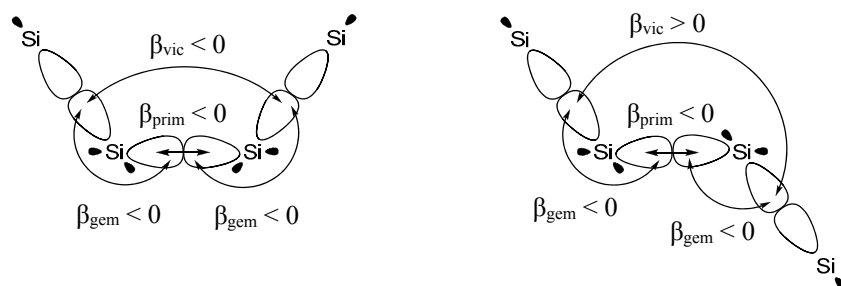

Figure 3. Resonance integrals in a linear tetrasilane chain.

2.3 Hyperconjugation

Hyperconjugation is another type of conjugation that involves the interaction of both σ and π orbitals. In 1937 Kistiakowsky *et al*. found that the heat of hydrogenation for cyclopentadiene is only 50.9 kcal/mol, which is 6.2 kcal/mol less than for 1,3-butadiene.[23] Mulliken in his pioneering work proposed that this stabilizing effect takes place due to a phenomenon, which he called hyperconjugation. [24,25] He showed that cyclopentadiene could be viewed as an analog to fulvene (Figure 4). In this case, the CH_2 group in cyclopentadiene is represented as a double bond comparable to the $C=CH_2$ moiety in fulvene. Similarly, Mulliken demonstrates the analogy between a methyl group and an ethynyl group by displaying the methyl group as $C≡H_3$.
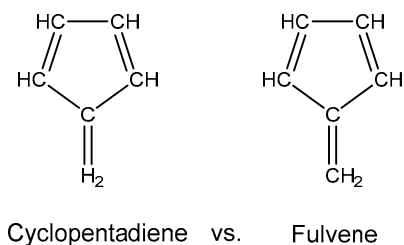
Cyclopentadiene   vs.   Fulvene

Figure 4. Cyclopentadiene and fulvene representation by Mulliken.

Mulliken also introduces various classifications of hyperconjugation depending on the type of bonds involved. First-order hyperconjugation includes one quasi-multiple bond and one true multiple bond. This is the case for cyclopentadiene where CH_2 and $CH=CH$ groups are involved in the hyperconjugation. Second-order hyperconjugation involves two quasi-multiple bonds.[24] The effects of first-order hyperconjugation are usually more pronounced than the second-order one.

Later Mulliken modified the classification of hyperconjugation. He mentioned that π-conjugation and hyperconjugation are qualitatively the same types of interaction. Considering this, he denoted π-conjugation, hyperconjugation, and σ-conjugation as first-order conjugation, second-order conjugation, and third-order conjugation, respectively (Table 1).[25] Undoubtedly, it is not always possible to distinguish between various types of conjugation. Lone pairs are often hybridized and show notable s-character. Such as in phenylamine, conjugation involves a p orbital and as the result, it is not possible to distinguish between hyperconjugation and π-conjugation in such cases.[26]

Table 1. Mulliken's classification of conjugation types.

$H_2C=CH–CH=CH_2$	Ordinary (first-order) conjugation
$H_3≡C–CH=CH_2$	Second-order conjugation (first-order hyperconjugation)
$H_3≡C–C≡H_3$	Third-order conjugation (second-order hyperconjugation)

Resonance theory describes hyperconjugation by the so called "double bond/no-bond resonance" structures and there are two different ways of classification. The first classification divides hyperconjugative interactions into two types: heterovalent and isovalent hyperconjugation (Figure 5). Heterovalent hyperconjugation is typical for neutral molecules. In the contributing resonance structure, one two-electron bond disappears compared with the regular Lewis formula. Isovalent hyperconjugation is typical for cations. In this case, the contributing structure has the same number of two-electron bonds as the

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main Lewis formula.[26] Mulliken denoted heterovalent hyperconjugation as ordinary or sacrificial hyperconjugation.[27]

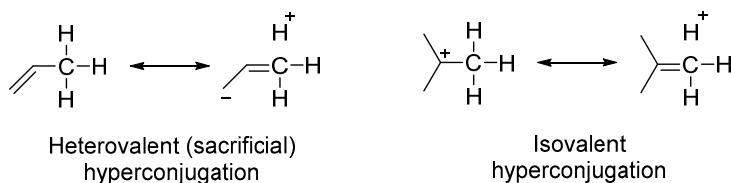Heterovalent (sacrificial) hyperconjugation

Isovalent hyperconjugation

Figure 5. Contributing resonance structures in heterovalent and isovalent hyperconjugation.

According to another type of classification, hyperconjugation is divided into neutral, positive, and negative hyperconjugation (Figure 6). Neutral hyperconjugation is observed if there are no dominating directions for the interaction. Interaction between filled π or p orbitals and antibonding σ^* orbitals leads to negative hyperconjugation. Donation of electron density from filled σ orbitals into π^* orbitals or p type unfilled orbitals results in positive hyperconjugation.[26]

Positive hyperconjugation

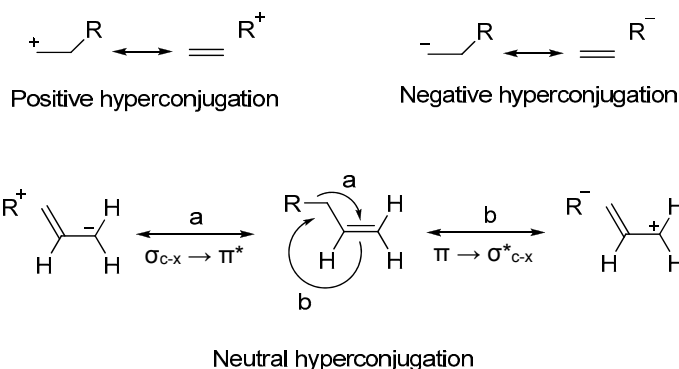Negative hyperconjugation

Neutral hyperconjugation

Figure 6. Contributing resonance structures in positive, negative, and neutral types of hyperconjugation.

2.4 Cross-hyperconjugation

Various types of conjugation were described in details in previous sections. However, not only the type of conjugation but also the type of connectivity in conjugated molecules influences their properties. There are three possible types of connectivity in π-conjugated molecules: linear or through-conjugation, cross-conjugation, and omni-conjugation (Figure 7). A succession of single and double bonds in a straight line is characteristic for linear conjugation.[28]

In the case when there are three parts of the molecule, two of which are conjugated to the third one but not to each other, such type of connection is typical for cross-conjugation.[29] Finally, if all groups in a non-linear molecule are conjugated in a linear fashion, this will result in omni-conjugated pathway.[30]
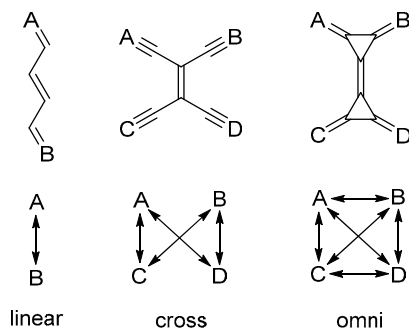

Figure 7. Various connection pathways in π-conjugated molecules.

As hyperconjugation is qualitatively the same type of orbital interaction as π-conjugation, the connectivity patterns are applicable also to hyperconjugated systems. The concept of cross-hyperconjugation was first proposed by Ottosson and co-workers in 2013. It is described as "the fusion of two neutral hyperconjugated paths to a cross-hyperconjugated molecule with geminal connectivity between the two paths".[31] There is valence isolobal analogy between structure of cross-hyperconjugated systems and regular cross-π-conjugation (Figure 8). The term "valence isolobal" is applied to the moieties with the similar energy and orbital shape. Additionally, they should contain the same number of electrons.[32]
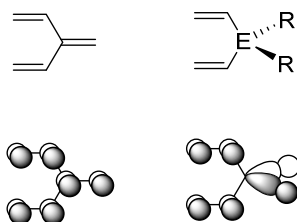

Figure 8. Valence isolobal analogy between a C=C double bond in a cross-π-conjugated molecule and an ER₂ group in a cross-hyperconjugated one.

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2.5 Quantification of hyperconjugation

2.5.1 UV/Vis absorption spectroscopy

The measurement of transitions from the electronic ground state to electronically excited states of molecules is performed with UV/Vis spectroscopy. In an experiment, the molecule absorbs photons of a certain energy matching the energy difference between the states whereby the corresponding transitions become possible. These transitions involve only valence electrons (Figure 9). From the results of UV/Vis spectroscopy measurements, *i.e.*, the absorption bands and their intensities, one can to a certain extent conclude how strongly the electrons are bonded in a molecule.[33] However, ultraviolet photoelectron spectroscopy (UPS) is more suitable for this purpose as it deals with photoionization process.[34]
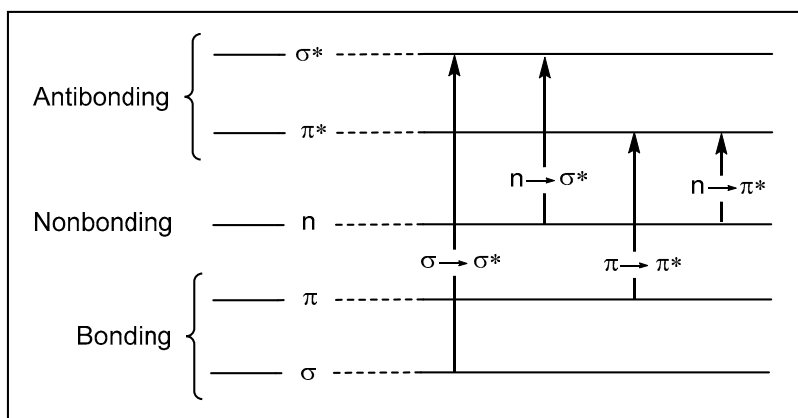

Figure 9. Transitions that are included into UV/Vis spectroscopy measurements.

Most electronic transitions can be included in the measurements, as UV/Vis spectroscopy operates between 160 nm and 2500 nm (from 0.5 to 7.7 eV). The particular operational range depends on the type of a lamp used in spectrophotometer. In some cases, transitions can be found at shorter wavelengths. For example, in alkanes the only possible transitions are of $\sigma \rightarrow \sigma^*$ type which are of very high energy and only absorb at wavelengths shorter than 160 nm: the absorption maxima of methane and ethane are found at 122 and 135 nm, respectively.[35,36] Chromophores in organic molecules are functional groups that are responsible for the absorption at certain wavelengths.[37]

UV/Vis absorption spectroscopy is one of the typical methods used for investigation of π-conjugation strength. The highest occupied molecular orbital (HOMO) is placed higher in energy in a π-conjugated molecule than that of a non-conjugated system, while the lowest unoccupied molecular orbital

(LUMO) is lower in energy. As a result, the HOMO-LUMO gaps decrease and conjugated systems have smaller excitation energies and therefore absorb at longer wavelengths. For example, 1,3-butadiene absorbs at 220 nm (5.6 eV), while ethylene has an absorption maximum at 185 nm (6.7 eV). Considering longer polyenes it is clear that a greater wavelength of the absorption is characteristic of a longer conjugated carbon chain (with higher degree of conjugation). Thus, the degree of conjugation can be evaluated with the help of UV/Vis absorption spectroscopy. This is applicable to all types of conjugation. However, the correlation between the conjugation strength and the values of absorption maxima is not always obvious. For instance, molecules with strong electron donor and acceptor substituents reveal such behavior.[38-40] Moreover, the lowest transition can be forbidden and thus it is not visible in the UV/Vis spectrum. This should be taken into account when analyzing results obtained with the UV/Vis spectroscopy.

2.5.2 Bond lengths

It is common knowledge that multiple bonds are moderately elongated while single bonds are significantly shortened in π-conjugated molecules.[41,42] This consideration is valid for hyperconjugation too, as it is qualitatively the same type of interaction as π-conjugation. Nevertheless, hyperconjugation is much weaker than π-conjugation, and therefore the bond lengths are not changed considerably for multiple bonds but primarily for single bonds involved.[24] In this fashion, comparison between bond lengths in a hyperconjugated molecule and its purely π-conjugated analog can help to figure out the strength of hyperconjugation.

2.5.3 Bond orders

Resonance theory is widely used in organic chemistry. Besides other applications within organic chemistry, it can be useful for understanding hyperconjugation concept. Resonance theory represents the electronic structure of a molecule as a combination of contributing (or resonance, or mesomeric) structures. In this case the wavefunction is a mixture of different contributing structures. Delocalization is often described by resonance structures,[43] and amide resonance in formamide is a classical example illustrating the basic resonance theory (Figure 10). The properties of this molecule are intermediate between those of the localized structures I and II, and the structure has therefore fractional bond orders. The relative weightings w_I and w_{II} are 0.6 and 0.4, respectively.[44]
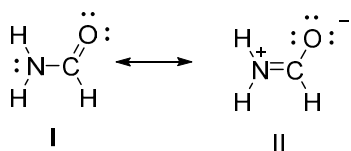
Figure 10. Resonance structures of formamide.

In general, the weighted average of idealized values P_α related to localized structural formulas α can describe a molecular property P. In such a case, weighting factors should be nonnegative and their sum should be equal to 1:

$$P = \sum_\alpha w_\alpha P_\alpha; \quad w_\alpha \geq 0; \quad \sum_\alpha w_\alpha = 1.$$

Then, each bond between atoms A and B has a fractional bond order according to the equation:

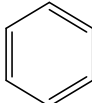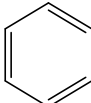$$b_{AB} = \sum_\alpha w_\alpha \, b_{AB}^{(\alpha)},$$

where $b_{AB}^{(\alpha)}$ is the number of bonds between atoms A and B in idealized Lewis-type structural formula for resonance structure α; w_α is the effective weight of this resonance structure.[45] In calculations with natural resonance theory (NRT) various resonance structures are calculated and their contribution to the structure is revealed. These calculations give the NRT bond orders and show if formal multiple and single bond orders in a hyperconjugated molecule are similar to those in its purely π-conjugated analog.

2.5 Aromaticity and antiaromaticity

So far cyclic conjugated compounds were not considered among the other connectivity pathways as in this case another important concept arises; the concept of aromaticity and antiaromaticity. In 1931, Erich Hückel developed the quantum mechanical basis for the principle, which was later called Hückel's rule.[46] According to this rule, a planar, cyclic, and fully conjugated molecule can be called aromatic in the case its number of π electrons equals $4n + 2$ where "n" is zero or any positive integer. In the same way, if a planar, cyclic, and fully conjugated molecule has $4n$ π electrons this molecule is anti-aromatic.[47] Aromatic compounds have increased thermodynamic stability compared to the nonaromatic ones. In contrast to aromaticity, antiaromaticity leads to destabilization of the molecule and gives it high reactivity. To avoid destabilization, some antiaromatic molecules can change shape that leads to bond length alternation and loss of planarity leading to nonaromaticity. The

classical examples of aromatic and antiaromatic molecules are benzene and cyclobuta-1,3-diene, respectively (Table 2).

Table 2. Hückel's and Baird's rules.

	Hückel's rule	Baird's rule
	ground state	first excited state
aromatic	$4n + 2$ π electrons	$4n$ π electrons
antiaromatic	$4n$ π electrons	$4n + 2$ π electrons

Hückel's rule is applicable to the electronic ground state of a molecule, while for the first electronic excited state there is another principle called Baird's rule.[48] Baird's rule is the exact opposite of Hückel's rule: in the lowest ππ* excited state (singlet or triplet) a molecule with $4n$ π-electrons is aromatic, while a molecule with $4n + 2$ π electrons is antiaromatic. Thus, in the lowest excited state benzene and cyclobuta-1,3-diene become antiaromatic and aromatic, respectively (Table 2).

3. Computational chemistry

3.1 Quantum chemistry

In classical mechanics, Newton's second law describes the behavior of the system. However, there is a border between classical mechanics and quantum mechanics and it lays approximately at the mass of the proton. Particles with such low masses show characteristics of both particles and waves. Hence, the laws of quantum mechanics should always be used to describe electrons as they are much lighter than protons. In quantum mechanics, the analogy to Newton's second law is the Schrödinger equation. The main difference between these two concepts is that the interpretation of the Schrödinger equation is probabilistic while classical mechanics is deterministic.[49] In the general form, the time-independent Schrödinger equation can be expressed as follows:

$$\hat{H}\Psi = E\Psi,$$

where the Hamiltonian operator $\hat{H}$ acts on a wavefunction Ψ giving back the same wavefunction Ψ multiplied by a constant E being the energy eigenvalue corresponding to the eigenfunction Ψ.

It is not possible to solve the Schrödinger equation exactly for systems that contain more than one electron. To solve this problem one can use the Born–Oppenheimer approximation that separates the motion of atomic nuclei and electrons.[50] This approximation assumes that the nuclei are infinitely heavier than the electrons. As a result, it is possible to ignore the couplings between the nuclear and electronic motions. The positions of the nuclei become parameters, and the part of the equation that describes the electrons can be solved separately.

3.2 Qualitative molecular orbital theory

An atomic orbital (AO) is a one-electron wavefunction and it is used to calculate the probability of finding an electron in a specific region around the nucleus of an atom.[51] Going further from atomic orbitals, the concept of molecular orbitals arises. According to molecular orbital (MO) theory, one can represent MOs as linear combinations of AOs. This method is called the linear combination of atomic orbitals to molecular orbitals (LCAO-MO) method.[52]

Formation of the H_2 molecule MOs is a simple and illustrative example of this method. For graphical representation of molecular orbitals and their formation from atomic orbitals, a molecular orbital diagram (MO diagram) is generally used (Figure 11).
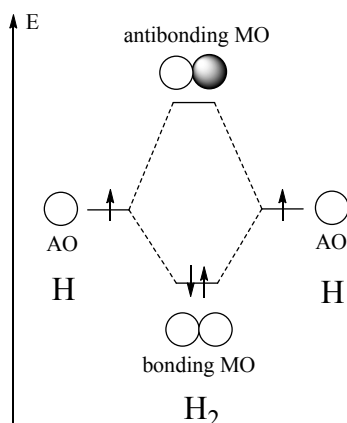

Figure 11. MO diagram of the H_2 molecule.

In an MO diagram the energy is shown on the vertical axis, and two AOs form bonding and antibonding MOs, respectively. Antibonding molecular orbitals are always higher in energy than the bonding ones and they are more destabilized than the latter are stabilized. Due to symmetry and energy requirements, some AOs will not mix with any of the other AOs. These MOs stay at the same energy level that they have as AOs, and they are called nonbonding MOs. When all the molecular orbitals are displayed on the diagram, one fills them with electrons starting from the orbital lowest in energy. In this way, qualitative MO theory can help to predict the electronic structure of a molecule.

3.3 Hartree-Fock and post-Hartree-Fock methods

The Hartree-Fock (HF) method offers a solution of the Schrödinger equation through the mean-field approximation. This approximation replaces real electron-electron interaction by an average interaction. An electron moves in the field generated by all other electrons, and the field does not respond to its movement. The orbitals are self-consistent with the field, and thus, this method is often denoted as the self-consistent field (SCF) method. Technically, the wavefunction of the system is derived from a Slater determinant. In a Slater determinant, the columns define atomic orbitals (AOs), while the rows provide electron coordinates.[53]

Generally, the HF method is able to provide ~99% of the total energy, while the rest of the energy can be added by including electron correlation energy. In a physical sense, this means that electrons are further apart than the HF method describes it. Nevertheless, some amount of electron correlation is already included to the HF method, this is the correlation between same-spin electrons that is called Fermi correlation.[49]

There are two types of methods that include either dynamic or static electron correlation. The static electron correlation adds flexibility in the wavefunction: instead of double occupation, orbitals are allowed to become (partly) singly occupied. The dynamic correlation deals with the motion of the electrons. Practically, correlation associated with electrons occupying the same orbital is the dynamic correlation, while the static correlation is associated with electrons occupying different spatial orbitals.

There are three main methods for calculating dynamic electron correlation: Configuration Interaction (CI), Many-Body Perturbation Theory (MBPT), and Coupled Cluster (CC).[49] The CI method adds a linear combination of configuration state functions (CSF) to the HF reference configuration. The CSF is a symmetry-adapted linear combination of Slater determinants, representing various electronic configurations of a molecule.[54] With regard to the MBPT method, it defines the Hamiltonian operator as a combination of reference and perturbation operators where the perturbation part of the operator introduces the electron correlation.[55] The CC method includes a Coupled Cluster operator, which allows the calculations to include all corrections of a given type to an infinite order. For this purpose, an exponential operator acts upon a single-determinant wavefunction, derived from HF calculation.[56] A good example of a method including static electron correlation, is multiconfigurational self-consistent field theory (MCSCF). This method, similarly to CI, includes linear combination of CSFs and, in addition, optimizes the MOs that are within the window of so-called active orbitals.

3.4 DFT and TDDFT methods

Density functional theory (DFT) assumes that the ground state electronic energy of a molecular system can be derived from the electron density. The proof by Hohenberg and Kohn is the basis for this assumption.[57] To connect the energy of a system and the electron density, DFT uses functionals (functions of another function):

$$E = F[\rho(\mathrm{r})].$$

According to the Kohn-Sham approach the energy of the system can be approximated as the sum of four terms:

$$E[\rho(r)] = E_{KE}[\rho(r)] + E_v[\rho(r)] + E_H[\rho(r)] + E_{XC}[\rho(r)],$$

where $E_{KE}[\rho(r)]$ is the electron kinetic energy, $E_v[\rho(r)]$ is the potential energy (nucleus-nucleus and nucleus-electron interactions), $E_H[\rho(r)]$ is the electron-electron Coulombic repulsion energy, and $E_{XC}[\rho(r)]$ is the exchange-correlation energy.[58] The main problem of the DFT method is that it does not define the functionals for exchange and correlation. To solve this issue it is possible to use the local density approximation (LDA) or the generalized gradient approximation (GGA). While using these approximations the exchange-correlation energy is usually separated into exchange and correlation parts. LDA treats the density as the uniform electron gas, so that the functional only depends on the density at each point in space. To include spin into LDA, one can use local spin-density approximation (LSDA). However, both LDA and LSDA suggest the exchange-correlation energy of the particle to be dependent only on the density at a particular point, which leads to errors. A non-uniform electron gas model can provide necessary improvement. For this, GGA methods use functionals that depend on the spin density gradients. Finally, hybrid methods can also provide significant improvement. To do so, they include into the exchange-correlation energy calculations various combinations of LDA, GGA, and HF parts.

DFT methods do not allow the calculation of excitation energy of the molecule, but Time-Dependent Density Functional Theory (TDDFT) can be used for this purpose. The basis of TDDFT is the Runge–Gross theorem.[59,60] According to this theorem, there is a connection between time-dependent densities and time-dependent potentials. With the help of TDDFT, one can obtain information on excitation energies, oscillator strengths and which orbitals are involved in particular electronic transitions.

3.5 Aromaticity indices

One of the most important characteristics of aromatic compounds is the ability to provide diatropic ring currents. Antiaromatic compounds on the contrary provide paratropic ring currents. This feature forms the basis for the magnetic aromaticity index denoted as the nucleus-independent chemical shift (NICS).[61] NICS is an absolute magnetic shielding, calculated at the center of the investigated ring. Negative values of NICS represent aromatic compounds, while positive values represent antiaromatic ones. Nevertheless, it was found that the functional groups as well as the C-H and C-C single bonds influence their magnetic environment significantly, and, as a result, NICS values cannot be considered as valid anymore. NICS(1) is an alternative to the initial NICS measure, as it is computed 1 Å above the ring plane where effects of a σ-framework are at minimum while the contribution from the π electrons is at maximum.[62] $NICS_{zz}$ corresponds to the out-of-plane shielding tensor component

measurements, but it includes both σ- and π-environment. Meanwhile, $NICS(1)_{zz}$ is calculated at a significant distance from the ring whereby the effect of only π orbitals is included. Stanger[63] and Jiménez-Halla *et al.*[64] independently introduced plots of $NICS_{zz}$ vs. distance, namely the NICS scans. Stanger pointed out that aromatic compounds display a deep minimum at approximately 1 Å above the ring plane. On the other hand, Jiménez-Halla *et al.* noticed that the NICS scans depend on many factors, such as the ring size, electronic structure and the nature of the atoms involved.

Single and double bond equalization is typical for aromatic compounds. Accordingly, one can consider indices based on bond lengths as the tool for aromaticity evaluation. One of such indices is the harmonic oscillator model of aromaticity (HOMA):[65]

$$\text{HOMA} = 1 - \frac{\alpha}{n}\sum(R_{opt} - R_i)^2,$$

where n is the number of bonds, R_{opt} is the bond length for the hypothetical aromatic compound, and R_i is an actual bond length of the investigated cycle. The coefficient α is a constant that gives HOMA = 0 for the hypothetical nonaromatic reference system. The main disadvantage of the HOMA method is that it is not valid for systems with a steric congestion (strain due to non-planarity of cycles, bulky substituents) as it influences bond lengths.

The isomerization stabilization energy (ISE) method overcomes the steric factor complications. The ISE is calculated as the energy difference between two isomers: a methyl derivative of an aromatic compound and a nonaromatic exocyclic methylene isomer. The ISE method is effective both for the strained annulenes and planar aromatic molecules.[66]

Finally, the Shannon entropy of the probability of the electronic charge distribution is derived from the electron density. The concept of Shannon aromaticity is based on the Shannon entropy.[67] When considering an aromatic system, the Shannon entropy $S_t(r)$ is given as the sum of the entropies of the bonds in the ring:

$$S_t(r) = \sum_{i=1}^{N} S_i(r_c).$$

The bonds are characterized by bond critical points (extrema in points) of the electron density $(\rho_i(r_c))$. Thereby, the Shannon entropy can be expressed in the following way:

$$S_i(r_c) = -\rho_i(r_c) \ln \rho_i(r_c).$$

In a hypothetical ideal aromatic system, the electron densities should be the same at all bond critical points. Then $\rho_i = 1/N$ and the total Shannon entropy can be shown as follows:

$$S_{max}(r_c) = ln(N).$$

The Shannon aromaticity index measures the extent of antiaromaticity in the system as the difference between the total Shannon entropy and the expected maximum entropy:

$$SA = S_{max} - S_t.$$

After all, the best strategy is to use aromaticity indices of various types when assessing the aromaticity or antiaromaticity of a molecule. This provides a sufficient basis for a discussion of the aromaticity or antiaromaticity strength in an investigated cyclic molecule.

4. Cross-hyperconjugation in cyclic organic group 14 element compounds (Paper I)

The Ottosson group previously investigated cross-hyperconjugation in 1,4-disilacyclohexa-2,5-dienes.[31,68] The goal of Paper I was to expand the range of group 14 elements involved in hyperconjugated molecules. We studied the tuning possibilities of hyperconjugation in molecules based on the 1,4-disilacyclohexa-2,5-diene structure, and tested computationally all possible combinations of E and E′ as the tetrel elements C, Si, Ge, Sn, and Pb (Figure 12). Experimental studies were performed on the compounds with E = Si and E′ = Si or Ge and always tetrasubstituted with ethyl groups at the C=C double bonds. We also examined the influence of σ electron withdrawing and σ electron donating substituents at the C=C double bonds by computational means.

E and E′ = C, Si, Ge, Sn, Pb
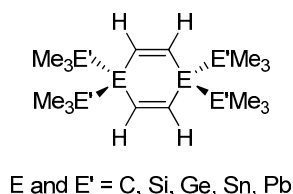
Figure 12. The 1,4-ditetrelocyclohexa-2,5-dienes investigated in this study.

4.1 Quantum chemical calculations

Bond/no-bond resonance structures are often used to describe hyperconjugation. Considering resonance structures of 1,4-ditetrelcyclohexa-2,5-dienes, one can mention that structure **III** contributes to some extent in cross-hyperconjugated compounds. As a result, endocyclic C=C double bonds are elongated while endocyclic C-E single bonds are shortened (Figure 13). This is more typical for strongly cross-hyperconjugated compounds than for those that are weakly or not cross-hyperconjugated at all.
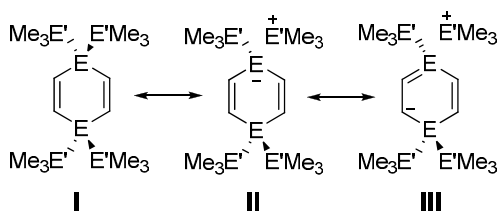
Figure 13. Resonance structures for 1,4-ditetrelcyclohexa-2,5-dienes.

Natural resonance theory is used to calculate the NRT bond orders. This type of calculations evaluate the contribution of every resonance structure to the conjugated system. *p*-Xylylene was a reference system as it is a purely π-conjugated analog of 1,4-ditetrelcyclohexa-2,5-diene. Calculated data for 1,4-ditetrelcyclohexa-2,5-dienes were compared to those of *p*-xylylene to estimate the degree of hyperconjugation.

In the rings with E = C, when going from E′ = C to E′ = Pb, bond orders of the C=C double bonds gradually decrease, whereas for the C-C single bonds they increase. However, when E is changed to heavier elements, this tendency weakens. As a result, the **CPbMe₃** ring behaves similarly to *p*-xylylene; the C=C double bonds show bond orders of 1.88 and 1.86 for **CPbMe₃** and *p*-xylylene, respectively, while the C-C single bonds reveal bond orders of 1.05 and 1.06 for **CPbMe₃** and *p*-xylylene, respectively.

Regarding bond length changes, both single and double bonds in the ring are influenced by change of elements E and E′ (Figure 14). The calculated changes in bond lengths confirm the trend revealed by NRT bond order calculations. For E = C, the C=C double bonds increase significantly when going from E′ = C to E′ = Pb. When element E is changed this tendency weakens, and reverses when E = Sn and Pb. The single bond lengths also show the most significant shortenings when going from E′ = C to E′ = Pb for E = C, while this trend becomes weaker when E was changed to heavier elements.
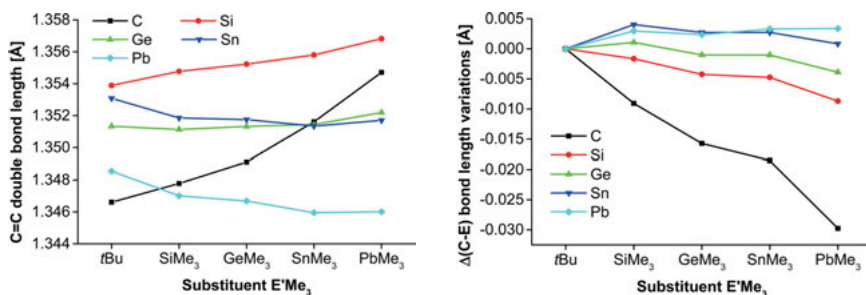

Figure 14. The C=C double bond lengths and the E-C bond length differences of the 1,4-ditetrelcyclohexa-2,5-dienes.

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The element variation in 1,4-ditetrelcyclohexa-2,5-dienes influences the orbital energies as well. We compared HOMOs of the investigated compounds, as they are of the same character for the whole range of compounds. The change of substituents E′Me$_3$ from E′ = C to E′ = Pb raises the HOMO energy, and the most effective change is found for E = C. This tendency is in line with the changes of bond orders and bond lengths that I discussed earlier. Qualitative MO theory can explain this by the fact that more electropositive groups raise the energy of π(ER$_2$) groups resulting in raise of HOMO energies as well (Figure 15). Additionally, local orbital overlap is also important, and for this reason, small C atom is preferable in the ring. As the result, in case when E = C and E′ = Pb the HOMO is expected to have the highest energy among the compounds investigated, and this is confirmed by the calculations.
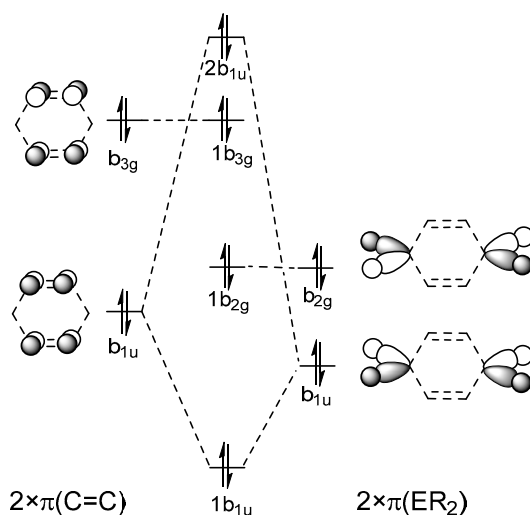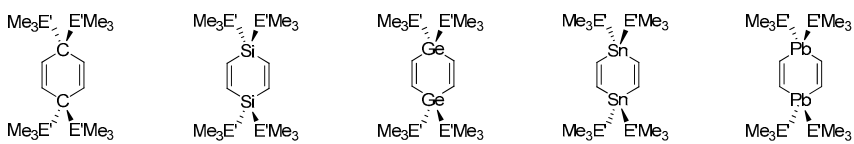

Figure 15. Interaction between 2 × π(C=C) and 2 × π(ER$_2$) local orbitals leading to formation of four MOs, including HOMO.

Further we have calculated excitation energies for the whole range of 1,4-disilacyclohexa-2,5-dienes. We found three sets of data for the calculated excitation energies, which show different behavior. In the case of E′ = C, the change from E = C to E = Pb causes a gradual lowering of the first excitation energies (Table 3, marked in red). Assuming E′ ≠ C and E = C, Si, Ge, the characters of electronic transitions are very similar: the first transition is forbidden and dominated mostly by the HOMO→LUMO excitation while the second transition is allowed and consists mainly of the HOMO→LUMO+1 excitation (Table 3, marked in green). Finally, if E = Sn or Pb and E′ ≠ C, the transitions become very complex and it is not possible to reveal any trends.

Table 3. Calculated first and second electronic excitations of the 1,4-ditetrelcyclo-hexa-2,5-dienes.

E'	C		Si		Ge		Sn		Pb	
	$E(S_1)$, f conf.	$E(S_2)$, f conf.	$E(S_1)$, f conf.	$E(S_2)$, f conf.	$E(S_1)$, f conf.	$E(S_2)$, f conf.	$E(S_1)$, f conf.	$E(S_2)$, f conf.	$E(S_1)$, f conf.	$E(S_2)$, f conf.
C	5.74, 0.002 H→L	5.97, 0.000 H→L+5	5.25, 0.223 H→L	5.27, 0.080 H→L H-2→L	5.11, 0.030 H→L	5.17, 0.300 H→L+1	4.72, 0.002 H-3→L	4.89, 0.305 H→1	4.60, 0.000 H-1→L	4.83, 0.021 H-2→L
Si	3.91, 0.000 H→L	4.44, 0.002 H→L+1	4.19, 0.000 H→L	4.74, 0.555 H→L+1	4.45, 0.000 H→L	4.84, 0.546 H→L+1	4.68, 0.000 H+1→L	4.81, 0.514 H→L	4.79, 0.000 H-3→L	4.84, 0.002 H-2→L
Ge	3.70, 0.000 H→L H→L+1	4.15, 0.004 H→L H→L+1	4.06, 0.000 H→L	4.55, 0.630 H→L+1	4.33, 0.000 H→L	4.66, 0.610 H→L+1	4.59, 0.000 H→L+1	4.66, 0.567 H→L	4.76, 0.001 H-2→L	4.76, 0.008 H→L+5 H→L+6
Sn	3.13, 0.000 H→L H→L+1	3.55, 0.016 H→L H→L+1	3.73, 0.000 H→L	4.31, 0.740 H→L+1	4.03, 0.000 H→L	4.44, 0.707 H→L+1	4.35, 0.002 H→L+1 H→L+2	4.48, 0.643 H→L	4.37, 0.364 H→L	4.53, 0.006 H→L+2 H→L+6
Pb	3.13, 0.009 H→L H→L+1	3.23, 0.073 H→L H→L+1	3.70, 0.000 H→L H→L+1	3.90, 0.803 H→L H→L+1	3.99, 0.003 H→L+1 H→L+2	4.03, 0.756 H→L	4.13, 0.677 H→L	4.29, 0.216 H→L+1 H→L+2	3.88, 0.494 H→L	4.23, 0.250 H→L+2

Additionally, **CSnMe₃** and **CPbMe₃** displayed the most redshifted allowed transitions at 3.55 eV (349 nm) and 3.23 eV (380 nm), respectively.

4.2 Comparison between experimental and calculated data

We synthesized **SiGeMe₃Et** by the same synthetic method as for the synthesis of **SiSiMe₃Et** that was reported previously.[68] Different conditions were tested for the synthesis of **SiSnMe₃Et** but we did not succeed in obtaining it. The **SiSiMe₃Et** and **SiGeMe₃Et** compounds were examined with X-ray crystal-lography. Both showed shortened C-Si single bonds: 1.882 and 1.876 Å for **SiSiMe₃Et** and **SiGeMe₃Et**, respectively. The calculated C-Si single bond lengths are 1.878 and 1.875 Å for **SiSiMe₃Et** and **SiGeMe₃Et**, respectively. This result is in a good agreement with experimental values and the general trend of the increase in cross-hyperconjugation upon change of E′ from Si to Ge.

We performed the investigation of optical properties of 1,4-ditetrelcyclohexa-2,5-dienes not only computationally but also experimentally. The UV/Vis absorption spectra were recorded for **SiSiMe₃Et** and **SiGeMe₃Et**, and the computational results are in accordance with the

experimentally obtained data. The excitation wavelengths for **SiSiMe₃Et** and **SiGeMe₃Et** of 273 nm (4.54 eV) and 277 nm (4.48 eV), respectively, are in line with the computational results. In this case, the influence of ethyl groups on endocyclic double bonds was excluded.

4.3 Influence of substitution on the C=C double bonds

Further we have tested the influence of substitution at the C=C double bonds. For this purpose, σ electron withdrawing fluoro and donating stannyl substituents were attached onto the strongly cross-hyperconjugated **CSnMe₃** (Figure 16).
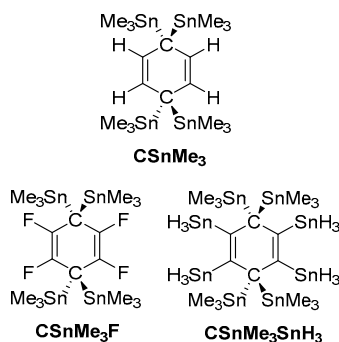
Figure 16. Compounds investigated in order to show the effect of substitution at the C=C double bonds.

We observed the shift from 3.12 to 3.82 eV in the excitation energy of the first transition for **CSnMe₃F** when compared to **CSnMe₃**. Additionally, the C=C double bonds shortened by 0.007 Å. The effect was different in **CSnMe₃Sn** as there was a shift of the excitation energy of the first forbidden transition to 2.83 eV and the excitation energy of the first allowed transition moved to 3.45 eV (0.1 eV lower than **CSnMe₃**). Moreover, the C=C double bonds in **CSnMe₃Sn** elongated by 0.015 Å according to the computations.

In summary, 1,4-ditetrelcyclohexa-2,5-dienes are strongly hyperconjugated compounds that potentially can become promising alternatives to siloles and stannoles. Staubitz *et al.* synthesized a stannole with UV absorption maxima at 441 nm, while a polymer obtained from it showed a maximum at 536 nm.[69] Proper substitution of 1,4-ditetrelcyclohexa-2,5-dienes may result in strongly redshifted absorption comparable to these results, and additionally, provide necessary stabilization, as they are usually synthetically challenging. Further, it is also possible to investigate the properties of oligomers and polymers based on 1,4-ditetrelcyclohexa-2,5-dienes, and one could use the findings of this study in design of similar cross-hyperconjugated compounds.

5. Ground and excited state aromaticity in cyclic cross-π-conjugated and cross-hyperconjugated compounds (Paper II)

In this chapter we consider the combination of cross-hyperconjugation and partial aromaticity in a set of cyclic compounds in both their electronic ground states and lowest $\pi\pi^*$ excited states. More specifically, we investigated the behavior of pentafulvenes, cyclopentadienes, and siloles in their ground and excited states.

5.1 Aromatic chameleon behavior in five-membered rings

Pentafulvenes are known to display the behavior of "aromatic chameleons", *i.e.*, they can adapt to the aromaticity rules in both the ground and first excited states by changing their electronic structure (Figure 17a).[70-73] This behavior is in line with both Hückel's and Baird's rules. The strong influence in the S_0 state is typical for the resonance structure with six π electrons in the ring (resonance structure **III**), while the one with four π electrons in the ring (resonance structure **I**) displays strong influence in S_1 and T_1. Electron withdrawing groups (EWG) attached to the structure of pentafulvene as X decrease the S_0-T_1 energy gap and this way, the aromatic character of the pentafulvenes in the T_1 state increases. As expected, the opposite situation occurs if X is an electron donating group (EDG).

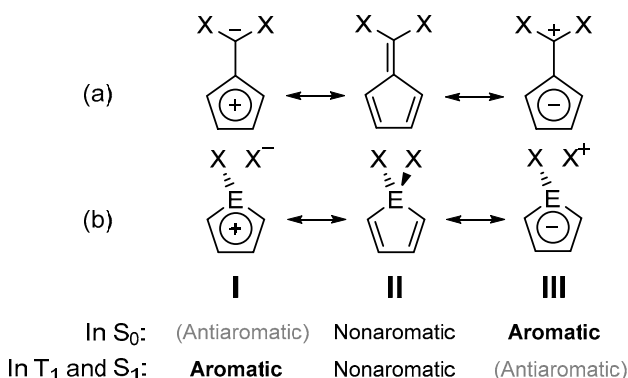|	I	II	III
In S_0:	(Antiaromatic)	Nonaromatic	**Aromatic**
In T_1 and S_1:	**Aromatic**	Nonaromatic	(Antiaromatic)

Figure 17. Resonance structures of a) pentafulvenes and b) cyclopentadienes and siloles.

Mulliken showed that cross-hyperconjugated cyclopentadienes are analogous to the cross-π-conjugated pentafulvenes.[24] In our group we have shown that EX_2 fragments (E = C, Si) inserted between two π-bonded fragments can provide cross-hyperconjugation analogous to cross-π-conjugation. Additionally, the incorporation of silicon enhances the cross-hyperconjugation.[31,68,74] In Paper II, these findings are used to explore the analogy between pentafulvenes, cyclopentadienes, and siloles (Figure 18).
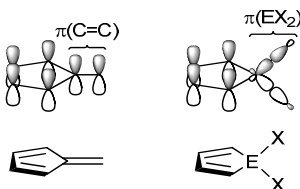
Figure 18. The valence isolobal analogy between pentafulvene (left) and siloles and cyclopentadienes (right); E = Si or C, respectively.

Thus, cyclopentadienes and siloles act as cross-hyperconjugated aromatic chameleons and their properties are analogous to pentafulvenes (Figure 17b). To examine this model, a series of calculations with hybrid DFT and electron correlated wavefunction methods were performed. We have chosen to test a set of pentafulvenes, cyclopentadienes and siloles substituted with groups X. These groups range from highly electron donating to highly electron withdrawing (Figure 19). Additionally, we have considered some of the electron donating groups for cyclopentadienes and siloles that could possibly enhance hyperconjugation. These groups contain group 14 elements, more specifically silicon and germanium.
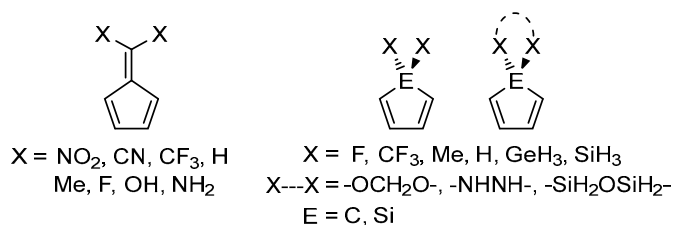
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Figure 19. The pentafulvenes, cyclopentadienes and siloles studied computationally herein with substituents X listed in the order from EWGs to EDGs.

First, the changes in dipole moments when going from the S_0 to the T_1 states were calculated. In this way, we confirmed a correlation between a low degree of aromaticity in S_0 and a higher degree of aromaticity in T_1/S_1 with low excitation energy. At the same time, a higher degree of aromaticity in S_0 is characteristic for high excitation energy. Additionally, it was found that the dipole moments and changes in the dipole moments in S_1 and T_1 ($\Delta\mu_{S-T}$) are smaller in cyclopentadienes and siloles than in pentafulvenes. We attribute this finding to a weaker strength of cross-hyperconjugation in comparison with cross-π-conjugation.

Further, we performed calculations with various aromaticity indices in order to evaluate the aromaticity strength. Four indices of different types were chosen: magnetic (NICS(1)$_{zz}$), geometric (HOMA), energetic (ISE), and electronic (SA). The results of the calculations showed that pentafulvenes, cyclopentadienes, and siloles with X = EDG to some extent are aromatic in the S_0 state and non-aromatic to slightly antiaromatic in the T_1 state. On the contrary, compounds with X = EWG are non-aromatic to slightly antiaromatic in S_0 and to some extent aromatic in T_1. Meanwhile, strong correlations were revealed between the excitation energies and all calculated aromaticity-index differences when going from S_0 to T_1.

We compared calculated results to previously published UV absorption data of cyclopentadienes and siloles to verify obtained data. The agreement with minor exceptions was excellent, which means that calculated data are relevant and methods of calculation and the model of aromatic chameleons can be used in further investigations.

5.2 Ring size effect

We investigated a range of tria- and heptafulvenes and their hyperconjugated analogs in order to test the ring size influence on the properties (Figure 20). In this case, the influence of EWGs and EDGs is reversed when compared to pentafulvenes, as there are two π electrons less and more in the cycles of tria- and heptafulvenes, respectively (Figure 21). Indeed, cyclopropenes and

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silirenes are analogs to triafulvenes, and cycloheptatrienes and silepins are analogs to heptafulvenes, respectively, and they act as aromatic chameleons. The whole range of compounds display $\Delta\mu_{S-T}$ that correspond to the movement of negative charge towards the ring when going from S_0 to T_1. As expected, the compounds with EDG reveal the lowest excitation energies.
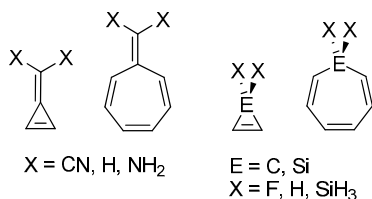

Figure 20. Tria- and heptafulvenes and their hyperconjugated analogs cyclopropenes, silirenes, cycloheptatrienes and silepins.
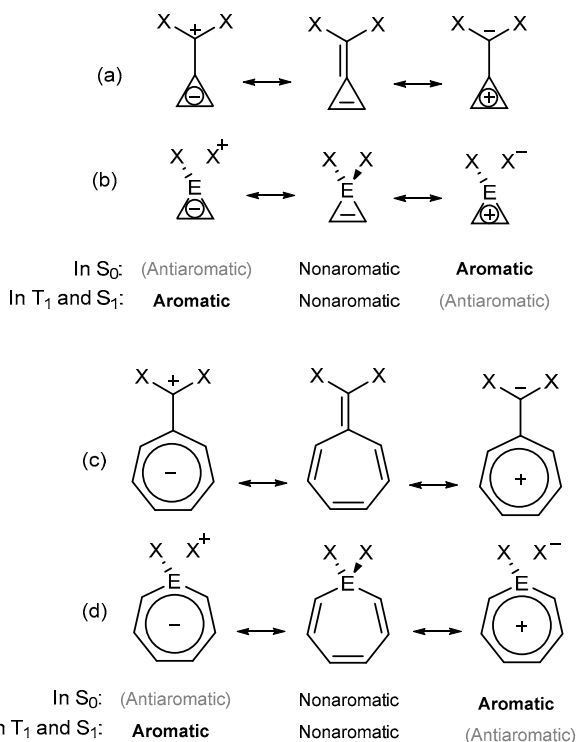
Figure 21. Resonance structures of a) triafulvenes, b) cyclopropenes and silirenes, c) heptafulvenes and d) cycloheptatrienes and silepins.

Upon moving from S_0 to T_1 the changes are more pronounced for the systems with three-membered rings than for the compounds with seven-membered rings. Also, the difference in dipole moments between cross-hyperconjugated

and cross-π-conjugated rings is more pronounced for three-membered rings than for seven-membered. Larger rings can pucker and in this way avoid antiaromaticity, and this is most likely the reason for the behavior observed. Thus, the application of the cross-hyperconjugated aromatic chameleons concept is not limited to five-membered rings, it can be used for design of other potentially interesting compounds for organic and molecular electronics. For example, to avoid puckering one could tentatively insert seven-membered rings into a rigid framework.

In summary, the concept of aromatic chameleons is applicable not only to π-conjugated pentafulvenes, but also to analogous cross-hyperconjugated compounds. Although the strength of hyperconjugation is not equally high as in π-conjugated compounds, it still influences significantly the aromaticity patterns of the molecule. Furthermore, the concept of aromatic chameleons is applicable to different ring sizes. It was clearly shown on the example of three-membered and seven-membered ring compounds.

6. Conjugation in oligomers composed of cyclic cross-hyperconjugated monomers (Paper III)

Previously I discussed studies on cross-hyperconjugation in 1,4-disilacyclohexa-2,5-dienes and 1-silacyclopentadienes (siloles). We used these findings to investigate larger molecules and oligomers in the third paper. It is possible to expand the 1,4-disilacyclohexa-2,5-dienes by replacing the two C=C double bonds with two C=C=C=C cumulenic units, leading to the 1,6-disilacyclodeca-2,3,4,7,8,9-hexaene molecule (Figure 22). This molecule is likely nonrealistic, yet, the two central [3]cumulene units can dimerize to a cyclobutane ring leading to a cyclobuta[1,2-c:3,4-c']disilole, or simply, a cyclobutadisilole.

1,4-disilacyclohexa-2,5-diene

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

cyclobuta[1,2-c:3,4-c']disilole
(cyclobutadisilole)
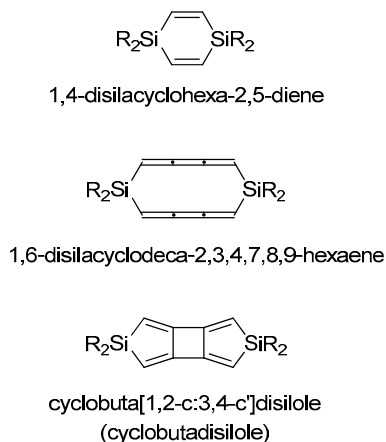
Figure 22. 1,4-Disilacyclohexa-2,5-diene and its possible expansions.

Oligomers can be constructed in many different ways. We have chosen for investigation oligomers based on 1,4-disilacyclohexa-2,5-diene and cyclobutadisilole units which are connected with two dimethylsilanediyl groups. This construction leads to creation of hyperconjugated oligomers (Figure 23). Tetrasilacyclobutane and 1,2,3-butatriene were considered as a linkage due to an analogy in their frontier orbitals (Figure 23).
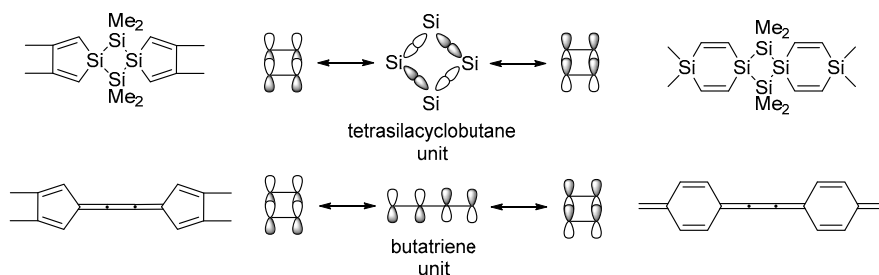
Figure 23. Linkage possibilities for 1,4-disilacyclohexa-2,5-dienes and cyclobu-tadisilole.

The two methylene linkages were also considered for comparison as a weaker type of hyperconjugation (**1a-d(C)**, **4a-d(C)** Figure 24), and the fully π-conjugated oligomers (**2a-d**, **5a-d**, Figure 24) as a strongly π-conjugated analogs, respectively. Two types of oligomers are presented in the paper; one based on 1,4-disilacyclohexa-2,5-dienes and another based on cyclobutadisiloles. We examined the excitation energies, the HOMO-LUMO gaps, and the bond lengths of the oligomers.
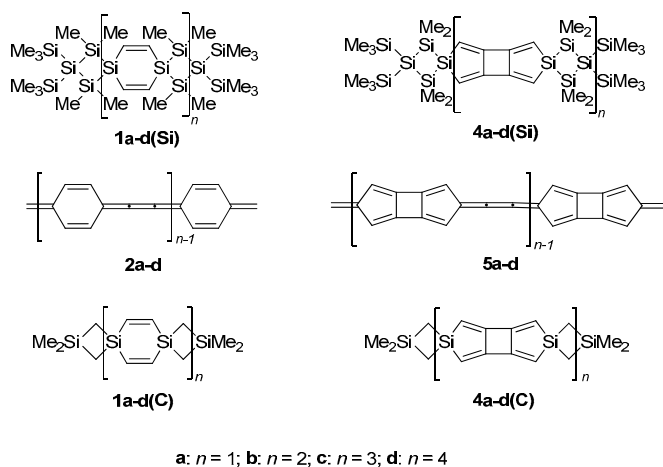
Figure 24. Oligomers investigated in the article.

In all 1,4-disilacyclohexa-2,5-diene-based oligomers the excitation energies decrease upon elongation. At the same time, **1a-d(Si)** display more extended hyperconjugation than **1a-d(C)** as the excitation energies for the first allowed transitions lower from 3.93 to 3.41 eV and from 5.17 to 4.46 eV for **1a-d(Si)** and **1a-d(C)**, respectively. Nevertheless, the conjugation strength in the π-conjugated **2a-d** increases more significantly with elongation than in the hyperconjugated oligomers: the excitation energies for the first allowed transitions range from 4.46 to 1.14 eV. Both HOMO and LUMO of **1a-d(Si)** are

40

influenced by elongation: HOMO raises in energy, while LUMO slightly decreases, giving total HOMO-LUMO gap decrease of 0.5 eV. Oligomers **1a-d(C)** show similar behavior, although the effect is less pronounced. Again purely π-conjugated **2a-d** show the same character of changes in orbital energies although the effect is significantly more evident. Thus, the hyperconjugation in oligomers is extended upon elongation, which is confirmed by the excitation energies and HOMO-LUMO gaps of the 1,4-disilacyclohexa-2,5-diene-based oligomers.

The double bonds of **1a-d(Si)** and **1a-d(C)** are slightly elongated in comparison with the reference cyclohexa-1,4-diene. However, their lengths do not change with elongation. As the hyperconjugation is not equally strong as π-conjugation, bond length changes in multiple bonds are not always significant or even detectable. In the present case, this is likely due to a small difference in hyperconjugation strengths. On the contrary, the π-conjugated **2a-d** shows significant elongations of the double bonds with elongation of the oligomers.

Expansion of 1,4-disilacyclohexa-2,5-diene can lead to various structures. We decided to investigate cyclobutadisilole as it is a tentatively realistic molecule and this expansion will likely lead to improved hyperconjugation. We tested a few substituents on the Si atoms and have found that the $SiMe_3$ group show the lowest excitation energies for the first allowed transition. The HOMO–n – LUMO gaps are also in accordance with the trend and the smallest gap is displayed by cyclobutadisilole with $SiMe_3$ substituents. This result demonstrates that cyclobutadisilole is a suitable unit for construction of hyperconjugated oligomers.

The cyclobutadisilole-based oligomers behave similarly to 1,4-disilacyclohexa-2,5-diene-based oligomers regarding their excitation energies. Particularly, the excitation energies decrease with elongation is approximately the same, the difference in excitation energies in the pairs **1a-d(Si)** and **1a-d(C)** as well as **4a-d(Si)** and **4a-d(C)** is similar too. However, not HOMO but the HOMO-n orbitals are involved in the symmetry allowed excitations of **4a-d(Si)**, **5a-d**, and **4a-d(C)**. In all these cases, HOMO-n orbitals have the same symmetries and nodal properties. Although cyclobutadisilole-based oligomers reveal the same tendencies as 1,4-disilacyclohexa-2,5-diene-based, lower excitation energies and smaller HOMO-n – LUMO gaps are characteristic for them. This suggests higher degree of hyperconjugation. Similarly to 1,4-disilacyclohexa-2,5-diene-based oligomers, the bond lengths are approximately the same in **4a-d(Si)**, **4a-d(C)**, and the reference tricyclo<5.3.0.0^{2,6}>-decatetraene. Only the π-conjugated **5a-d** reveal elongation of the double bonds and shortening of the single bonds with elongation of oligomers.

To study the influence of heavier 14 group elements on hyperconjugation strength in the oligomers, we have tested tin incorporation into the framework

(Figure 25). Considering 1,4-disilacyclohexa-2,5-diene-based oligomers, excitation energies were found to be 0.24–0.35 eV lower for **1a-d(Sn)** than for **1a-d(Si)**. The double bonds are also slightly longer in **1d(Sn)** than in **1a(Si)**. However, cyclobutadisilole-based tetramer **4d(Sn)** displayed very similar results to those obtained for **4d(Si)**. Additionally, for monomer **4a(Sn)** there was no difference in the results when compared to **4a(Si)**. Thus, incorporation of tin moderately enhances hyperconjugation in 1,4-disilacyclohexa-2,5-diene-based oligomers, but does not show any detectable influence on the cyclobutadisilole-based oligomers.

1a-d(Sn)

4a-d(Sn)

a: *n* = 1; **d**: *n* = 4
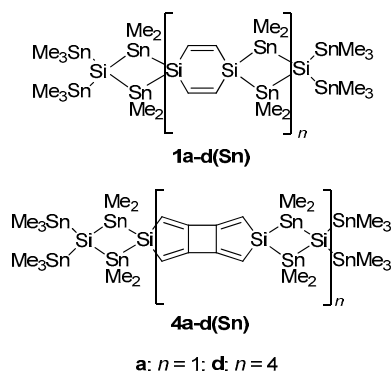
Figure 25. Tin-containing monomers and tetramers.

It was shown previously that DFT and TDDFT methods could fail to predict some properties of oligomers.[75,76] For this reason, we have tested TD-CAM-B3LYP method on oligomers based on 1,4-disilacyclohexa-2,5-diene. TD-CAM-B3LYP includes long-range correction that could possibly solve this problem. The general trends were found to be the same as for TD-B3LYP, although excitation energies were higher for hyperconjugated compounds and slightly lower for π-conjugated compounds. Additionally, we tested both TD-B3LYP and TD-CAM-B3LYP methods for linear oligosilanes and compared computational results with experimental data. It was found that TD-B3LYP, in general, shows much smaller deviation from experiment than TD-CAM-B3LYP. Moreover, going to longer oligosilanes TD-B3LYP gives gradually better agreement with experiment. This result shows that TD-B3LYP is a reasonable choice for the present study.

To conclude, in Paper III we discussed geometrical and optical properties of hyperconjugated oligomers based on 1,4-disilacyclohexa-2,5-diene and cyclobutadisilole. Although hyperconjugation strength does not change significantly with elongation of the oligomers, they show some degree of hyperconjugation and their properties are potentially interesting for molecular electronics.

7. Substituent effect on properties of small hyperconjugated cycles (Paper IV)

We have shown in the Paper I that variation of the 14 group elements involved in the hyperconjugated system significantly influence the hyperconjugation strength. In the present paper the investigation is done on the influence of various electron withdrawing (EWG) and electron donating groups (EDG) on the hyperconjugation in siloles and 1,4-disilacyclohexa-2,5-dienes. We compare the effect of substitution in siloles and 1,4-disilacyclohexa-2,5-dienes, determine in which system the hyperconjugation is stronger and how the substituent position influences it. A range of EWGs and EDGs as well as two different substitution patterns were chosen; (*i*) substitution at the C=C double bonds of the ring and (*ii*) at the Si atoms (Figure 26). Instead of comparing siloles and 1,4-disilacyclohexa-2,5-dienes with same substituents, we analyze the spread in the values of the particular properties.

1a-1p   **2a-2p**

a R = H, R' = H   **j** R = H, R' = F
b R = F, R' = H   **k** R = H, R' = Cl
c R = Cl, R' = H   **l** R = H, R' = CH_3
d R = CH_3, R' = H   **m** R = H, R' = CF_3
e R = CF_3, R' = H   **n** R = H, R' = SiF_3
f R = SiF_3, R' = H   **o** R = H, R' = SiH_3
g R = SiH_3, R' = H   **p** R = H, R' = NH_2
h R = $Si(CH_3)_3$, R' = H
i R = NH_2, R' = H
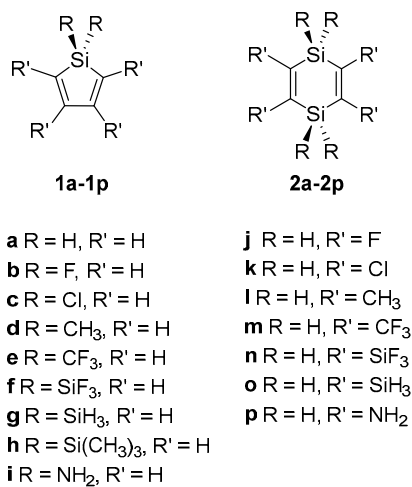
Figure 26. The compounds investigated in this paper.

As already mentioned, hyperconjugation influences bond lengths. For this reason we have considered SiC(ring) bond and C=C double bond lengths. Siloles depict generally shorter SiC(ring) bond lengths which indicates stronger hyperconjugation than in 1,4-disilacyclhexa-2,5-dienes. Considering the substituents on silicon atoms only, the shortest silicon-carbon bonds are characteristic for σ

electron withdrawing groups such as fluorine, chlorine and trifluoromethyl, both in siloles and 1,4-disilacyclohexa-2,5-dienes. The longest SiC(ring) bonds are observed for the amino group in siloles (**1i**) and the TMS group in 1,4-disila-cyclohexa-2,5-dienes (**2h**) (Figure 27). In the 1,4-disilacyclohexadienes substituted at the double bonds the shortest bonds are found for the amino group as substituent (**2p**), and the longest for the trifluoromethyl group (**2m**) (Figure 27b). Substitution at the double bonds in siloles was not considered due to steric congestion in a few of them. It should be noted that the spread in the SiC(ring) bond lengths is wider for 1,4-disilacyclohexa-2,5-dienes than for siloles.
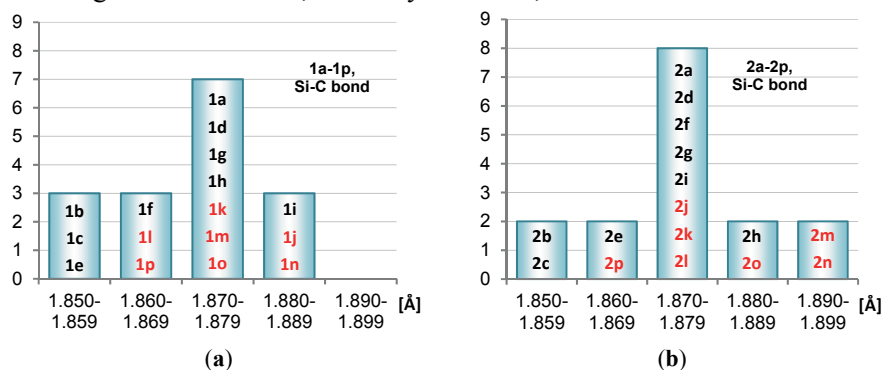
Figure 27. Distribution of SiC(ring) bond lengths. Compounds, substituted on Si atoms are shown in black, at the C atoms in red.

Regarding the C=C double bond lengths, we used a formula that takes into account the difference in the nature of the double bonds in siloles and 1,4-disilacyclohexa-2,5-dienes. In siloles two double bonds are connected into a diene fragment, while in 1,4-disilacyclohexa-2,5-dienes they are separated from each other by the Si atoms. According to the formula, one compares deviations in bond lengths from the parent nonsubstituted compound. For compounds with electron donating silyl groups at the silicon (**1f-h**), C=C double bonds are elongated more in siloles than in 1,4-disilacyclohexa-2,5-dienes. At the same time, σ electron withdrawing groups lead to more significant shortenings of the double bonds in siloles than in 1,4-disilacyclohexa-2,5-dienes or changes in bond lengths are the same (**1b-e**). In order to exclude the steric congestion factor, we examined compounds with substituents at Si atom only.

The HOMO and LUMO for each silole are of the same type, which is not the case for 1,4-disilacyclohexa-2,5-dienes. We consider energy gaps between the orbitals, which are of the same type as HOMO and LUMO of the unsubstituted **1a** and **2a**. Excitation energies are also considered for transitions, which include orbitals of this type and it turns out that they are always the first allowed transitions. In **2a** HOMO is the $2b_{1u}$ orbital and LUMO is the $2b_{2g}$ orbital, thus, further on we discussed transitions between orbitals of these two symmetries only (Figure 29).
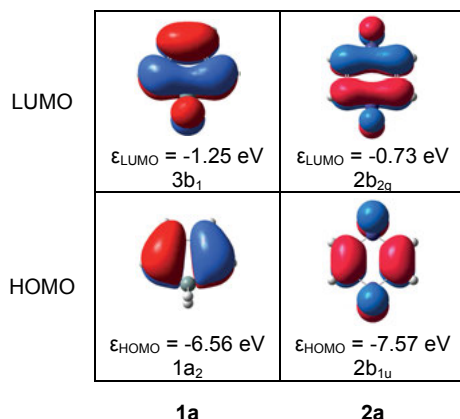
LUMO	ε_{LUMO} = -1.25 eV $3b_1$	ε_{LUMO} = -0.73 eV $2b_{2g}$
HOMO	ε_{HOMO} = -6.56 eV $1a_2$	ε_{HOMO} = -7.57 eV $2b_{1u}$
	1a	**2a**

*Figure 28. Plots of HOMO and LUMO of **1a** and **2a**, respectively.*

The smallest HOMO-LUMO gap energy ($\Delta\varepsilon_{HL}$) among siloles is shown by **1k** and **1p**, while the largest value by **1h**. The variation of $\Delta\varepsilon_{HL}$ for siloles is very small, and is only 0.78 eV, while the energy difference between orbitals $2b_{1u}$ and $2b_{2g}$ ($\Delta\varepsilon_{2b1u-2b2g}$) for 1,4-disilacyclohexa-2,5-dienes varies within 1.66 eV. The smallest and largest $\Delta\varepsilon_{2b1u-2b2g}$ are observed for **2h** and **2b**, respectively. This result can be explained by the fact that HOMO of siloles does not include the Si atom, and the variation in HOMO energies is smaller than the variation in the energies of $2b_{1u}$ orbitals of 1,4-disilacyclohexa-2,5-dienes. All other orbitals considered here include the Si atom, whereby the shape of HOMO of siloles can influence the $\Delta\varepsilon_{HL}$.
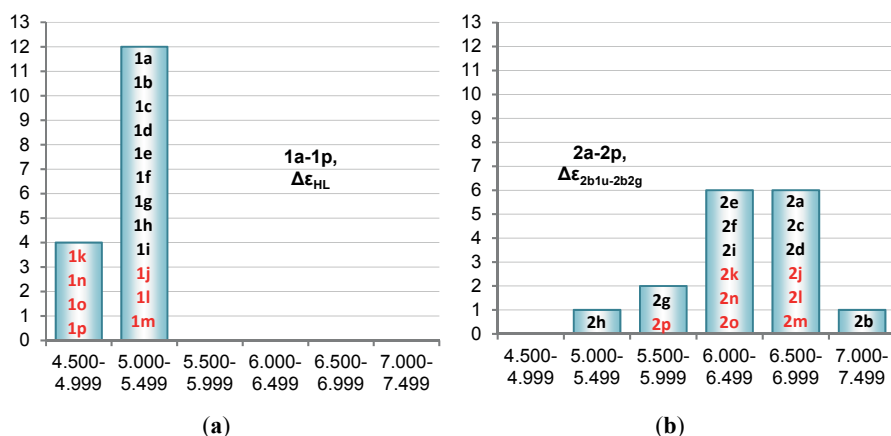
Figure 29. Distribution in (a) the HOMO-LUMO gaps for siloles and (b) the $2b_{1u}$-$2b_{2g}$ energy gaps for 1,4-disilacyclohexa-2,5-dienes.

The span of excitation energies for siloles is in line with the $\Delta\varepsilon_{HL}$ results as it is also rather small, and equals only to 0.88 eV. For the entire range of siloles the first allowed transitions are dominated by the HOMO to LUMO excitations, which is not the case for 1,4-disilacyclohexa-2,5-dienes. For **2a-p** the first excitations are mostly forbidden or nearly forbidden, while the first allowed excitations include transitions between previously discussed $2b_{1u}$ and $2b_{2g}$ orbitals. The distribution of excitation energies for 1,4-disilacyclohexa-2,5-dienes is significantly wider than that of siloles: the range is 2.13 eV, which again is in accordance with the distribution of $\Delta\varepsilon_{2b1u-2b2g}$ values.

As siloles dimerize, unless properly substituted, we have examined how the nature of substituents influences the reactivity in this case. The dimerization occurs through [4+2] cycloaddition reaction. We introduced substituents on Si atom only to exclude the steric congestion factor. In total, electron donating SiH_3 group leads to an increase in the activation barrier, while the electron withdrawing fluoro group decreases it; the activation barrier difference of siloles substituted with these two groups is 10.6 kcal/mol.

Finally, we have investigated cyclobutadisiloles as alternatives to siloles and 1,4-disilacyclohexa-2,5-dienes. The structure of cyclobutadisiloles is related both to siloles and 1,4-disilacyclohexa-2,5-dienes. As a result, cyclobutadisiloles showed low excitation energies and wide spread in their values upon variation of substituents. Thus, cyclobutadisiloles combine preferable properties of both siloles and 1,4-disilacyclohexa-2,5-dienes.

In this paper we have analyzed how substituents of different nature influence the electronic and geometrical properties of small hyperconjugated cycles, *i.e.*, siloles and 1,4-disilacyclohexa-2,5-dienes. Additionally, we have shown that cyclobutadisiloles combine good features of both siloles and 1,4-disilacyclohexa-2,5-dienes.

8. Omni-hyperconjugation in compounds based on [3]radialene (Paper V)

Cross-hyperconjugated compounds were mainly discussed in the previous chapters. This present chapter deals with another type of connectivity and conjugation, omni-hyperconjugation. Herein, the omni-conjugated [3]radialene was taken as template for design of hyperconjugated compounds. Analogous to cross-hyperconjugation, omni-hyperconjugation is a combination of omni-conjugation and hyperconjugation, *i.e.*, hyperconjugation with linearly conjugated pathways between all parts of a molecule. In this paper, we compared omni-hyperconjugated compounds with their purely π-conjugated analogs in order to test the scope and limitations of the omni-hyperconjugation concept. Comparisons are made based on (*i*) orbitals (their shapes and energies), (*ii*) geometries and bond indices, and (*iii*) UV/Vis excitations. We considered compounds which are potentially first-order omni-hyperconjugated, *i.e.*, compounds **5**, **8**, and **11** (Figure 30), and compounds which are potentially second-order omni-hyperconjugated, *i.e.*, compounds **6**, **8**, and **12** (Figure 30).
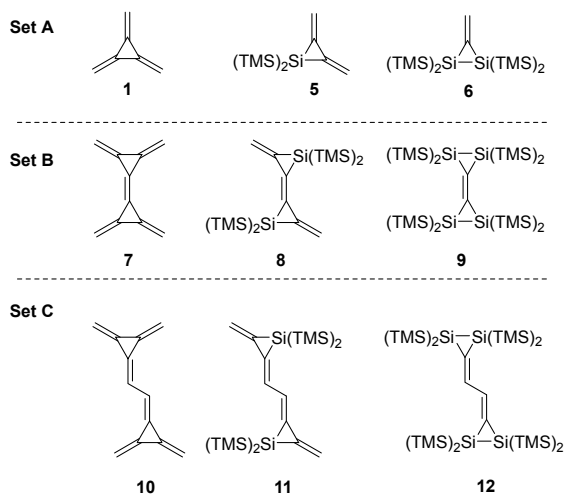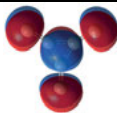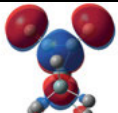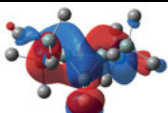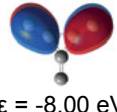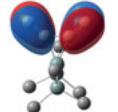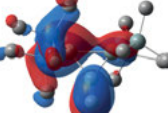
Figure 30. The omni-hyperconjugated compounds investigated in this study and their π-conjugated analogs.

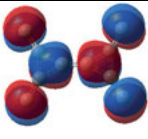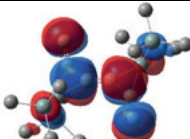*Table 4. Plots of frontier orbitals of 1 and analogous orbitals of 5 and 6.*
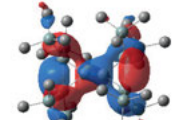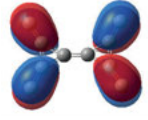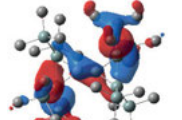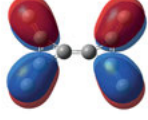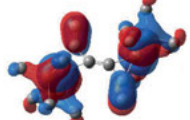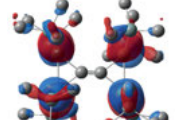
Orbital	Compound 1	Compound 5	Compound 6
π_4	ε = -1.09 eV (LUMO)	ε = -0.44 eV (LUMO)	ε = 0.32 eV (LUMO+1)
π_3	ε = -8.00 eV (HOMO)	ε = -7.69 eV (HOMO)	ε = -7.40 eV (HOMO-2)
π_2	ε = -8.00 eV (HOMO)	ε = -7.77 eV (HOMO-1)	ε = -7.45 eV (HOMO-3)
π_1	ε = -12.31 eV (HOMO-4)	ε = -10.77 eV (HOMO-8)	ε = -9.22 eV (HOMO-4)

Comparing the orbital plots and orbital energies of [3]radialene with those of its analogs **5** and **6**, one can see a clear resemblance for **1** and **5** (Table 4). Compound **1** has doubly degenerate HOMOs and **5** has HOMO and HOMO-1 of similar shapes. Although HOMO and HOMO-1 of **5** are not of the same energy, they are nearly degenerate. Additionally, the LUMO of **5** has the analogous shape of LUMO of **1**. In general, the highest π-symmetry orbitals of **1** and **5** are close in energy, although for **1** the energies are lower by 0.3-0.7 eV. This difference is more or less constant, likely due to lower electronegativity of an sp^2 carbon atom in comparison with an sp^3 silicon. At the same time, the fully π-bonding orbitals HOMO-4 of **1** and HOMO-8 of **5**, which are equivalent**,** show a larger difference, and it turns out that the orbital energy gaps are very similar between compounds **1** and **5**. Meanwhile, there is no such obvious similarity between the orbitals of **1** and **6**. The symmetry of **6** is lower than that of **1**, leading to orbitals of mixed σ-π type. However, it is still possible to observe some resemblance in orbital shapes of **1** and **6**. The LUMO+1 of **6** which is analogous to LUMO of **1** has a significantly higher energy than the latter. The HOMO-2 and HOMO-3 of **6** are only slightly higher in energy than analogous orbitals HOMO and HOMO-1 of **5**. Yet, the fully bonding orbital HOMO-4 of **6** again reveals significant difference in energy when compared

to the equivalent HOMO-8 of **5**. In general, one can see that the orbital energies in **6** show the same tendencies as those of **5**, but these tendencies are more pronounced for **6**.

The transitions which participate in the first two excitations of **1** are doubly degenerate HOMO→LUMO transitions and these excitations are strongly allowed according to TD-PBE0/6-31G(2d,p)//M06-2X/6-31G(d) calculations. In **5**, the first two strongly allowed excitations are third and fourth and they are dominated by the HOMO-1→LUMO and HOMO→LUMO transitions that are analogous to the HOMO→LUMO transition of **1**. The first strongly allowed excitation of **6** is much more complex as it consists of five different transitions and the one which is dominating includes orbitals not analogous to orbitals included in transitions of the strongly allowed excitations of **1** and **5**. The calculated excitation energies of the first allowed excitations are of 4.64, 4.59, and 4.49 eV for **1**, **5**, and **6**, respectively.

*Table 5. Plots of frontier orbitals of **7** and analogous orbitals of **8** and **9**.*

Orbital	Compound **7**	Compound **8**	Compound **9**
π_4	ε = -2.01 eV (LUMO)	ε = -0.93 eV (LUMO)	ε = -0.42 eV (LUMO)
π_3	ε = -7.33 eV (HOMO)	ε = -6.67 eV (HOMO)	ε = -6.48 eV (HOMO-1)
π_2	ε = -8.04 eV (HOMO-1)	ε = -7.50 eV (HOMO-2)	ε = -6.59 eV (HOMO-2)
π_1	ε = -8.09 eV (HOMO-2)	ε = -7.52 eV (HOMO-3)	ε = -7.33 eV (HOMO-4)

The combination of two [3]radialenes sharing a double bond gives compound **7**. Here we consider its analogs **8** and **9**, and clearly can see the similarities in the behavior of the orbitals with those of **7** (Table 5). Although for **8** and **9** some orbitals are of a mixed type, one can see the similarity with **7** in the orbital shapes. The LUMOs are of the analogous shape for all three compounds, while the HOMO-n orbitals of **8** and **9** are moved down in order when compared to **7**. The orbital energies of **7** are approximately 0.5-0.7 eV lower than the energies of the analogous orbitals of **8**, and 0.9-1.6 eV lower than those of **9**. Thus, the orbital energy gaps appear to be similar, resembling the situation in the previous set of compounds.

The first strongly allowed excitations of **7** and **8** include HOMO→LUMO transition, and these orbitals are of the similar shapes in the two compounds. The second strongly allowed excitation is dominated by the transitions which again involve orbitals of similar shapes. These are transitions HOMO-1→LUMO for **7** and HOMO-2→LUMO for **8**. The energies of the first two strongly allowed excitations are 3.49 and 3.87 eV for **7** and 3.62 and 4.07 eV for **8**, respectively. Again, the excitations of **9** are more complex and include more transitions, first two allowed excitations are dominated by the same two transititons each, one of them is analogous to HOMO→LUMO transition of **7**. However, only the second among them is strongly allowed, while the first is weakly allowed. At the same time, the excitation energies are quite low: 3.53 and 3.60 eV for the first and second allowed excitations, respectively.

A dimer of [3]radialene connected with the C=C double bonds leads to compound **10**. As in previous discussions, we consider **11** and **12** as omnihyperconjugated analogs of **10**. The trends for orbital shapes and energies are the same as for previously discussed **7**, **8** and **9**; by incorporating more silicon atoms in the molecules one achieves higher energies of the orbitals with analogous shapes. The difference is more significant for unoccupied orbitals such as LUMO and LUMO+1, while HOMO and lower occupied orbitals are much less influenced by the change from sp^2 carbon atoms to sp^3 silicon atom.

Considering the excitations of **10**, **11** and **12**, for all of them one can see only one strongly allowed excitation among the first five calculated excitations. All of them are dominated by the HOMO→LUMO transitions (HOMO and LUMO have analogous shapes in all three cases). The only difference is that for **12** this excitation is third, while for **10** and **11** they are first. The excitation energies of strongly allowed excitations are gradually increased when going from **10** to **12**, *i.e.*, they are 3.08, 3.25 and 3.51 eV for **10**, **11** and **12**, respectively.

Finally, we investigated larger compounds of [3]radialene-segment and their analogs (Figure 31). Compounds **13** and **14** display strongly allowed excitations with excitation energies of 2.64 and 2.59 eV, respectively. Additionally, we replaced Si(TMS)$_2$ groups of **14** by CH$_2$ groups and this compound

shows significantly higher first allowed excitation energy at 3.25 eV than **13** and **14** do.
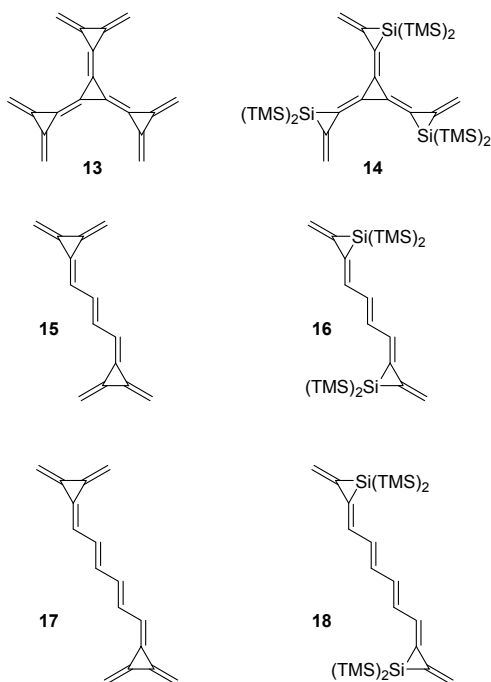

Figure 31. [3]Radialene oligomers and their analogs.

Gradually longer polyene units connecting the two [3]radialene and their omni-hyperconjugated analogs were also tested (Figure 31, **15** – **18**). The omni-hyperconjugated **16** and **18** have transitions that are 0.16 and 0.14 eV higher in energy than the corresponding excitations in the omni-π-conjugated **15** and **17**, respectively. The first allowed excitation in linear 1,3,5,7,9,11-do-decahexaene, corresponding to the purely π-conjugated segment of **18**, reveals the excitation energy to be 0.56 eV higher than that of **18**. Thus, findings for the smaller molecules based on [3]radialene can be also applied to larger compounds.

To conclude, we examined omni-hyperconjugated compounds starting from [3]radialene. We showed that the concept of first-order omni-hyperconjugation is very promising as the design tool for compounds with mixed σ/π-conjugation. According to the results, these compounds can reveal low excitation energies, comparable to those of purely π-conjugated compounds.

Concluding remarks

This thesis describes the hyperconjugation phenomenon and the ways to design the strongly hyperconjugated compounds. For this purpose, geometrical and optical properties of compounds were investigated by computational means. Additionally, calculated data was compared to experimental results in order to confirm feasibility of calculations performed.

The first part of the thesis describes the potential applications of the hyperconjugated compounds in organic and molecular electronics. Further, I discussed different types of conjugation, basic concepts related to hyperconjugation, and methods for its quantification. In the third chapter, computational chemistry concepts are disclosed: basic concepts of quantum chemistry, various methods of calculation. Next, I showed possible ways to tune cross-hyperconjugation when using heavier group 14 elements in various combinations. We used both computational and experimental methods for investigation; they provided us with bond lengths, bond orders and calculated UV/Vis absorption energies. Additionally, substituent effects on C=C double bonds are discussed. Further, cross-hyperconjugation concept is applied to partially aromatic systems, and we take into account aromaticity effects in the ground and excited states. We demonstrated that siloles behave as "aromatic chameleons" and the possibility to use them as cross-hyperconjugated alternatives to pentafulvenes. Moreover, we considered substituent and ring size effects. The sixth chapter describes the design of oligomers from hyperconjugated fragments for potential use as molecular wires. For this, we created oligomers from previously investigated siloles and 1,4-disilacyclohexa-2,5-dienes. In the seventh chapter, we have described substituent effects on electronic and geometrical properties of siloles and 1,4-disilacyclohexa-2,5-dienes. We considered substitution on C=C double bonds and Si atoms and proposed cyclobutadisiloles as improved alternative to siloles and 1,4-disilacyclohexa-2,5-dienes. Finally, we investigated omni-hyperconjugation in a range of compounds analogous to [3]radialene and to π-conjugated compounds based on [3]radialene. First-order omni-hyperconjugation provides means to design compounds with properties very similar to the π-conjugated analogs.

The results summarized can potentially be used for design of both small molecules and polymers useful as materials for molecular and organic electronics. More specifically, one can design and construct hyperconjugated oli-

gomers that can play role of molecular wire. Siloles are already used in materials for molecular and organic electronics, thus, it is possible to tune their properties with the help of knowledge gained in this thesis. In summary, the results presented in this thesis can be spread to other compounds and can further be applied in material science.

Svensk sammanfattning

All materia i universum - gaser, vätskor, fasta ämnen och plasma - består av atomer. Atomer kan bilda molekyler genom att attrahera varandra. Denna typ av attraktion kallas kemisk bindning. Atomerna själva består av kärnor och elektroner och det är elektronerna som deltar i bindningsbildning. Detta är karakteristiskt för den vanligaste typen, den kovalenta bindningen, som finns i organiska molekyler. Då delas elektroner mellan atomer och dessa leder till bildandet av bindningar. På grund av elektroners extremt låga massa så uppför de sig emellertid inte som klassiska partiklar, och därmed är den klassiska mekanikens lagar inte tillämpbara på elektroner. Icke desto mindre kan atomorbitalmodellen (AO-modellen) beskriva beteendet och egenskaperna av elektroner i viss utsträckning. En AO är en matematisk funktion som beskriver sannolikheten att finna en elektron vid någon punkt i rymden runt atomkärnan och den kan innehålla upp till två elektroner. Nästa steg är bildandet av molekylorbitaler (MOer) som beskriver beteendet hos elektroner i hela molekylen. MOer är utformade som linjärkombinationer av AOer, d.v.s. summan och skillnaden mellan dem, vilket resulterar i bindande och antibindande MOer (Figur 32). Två elektroner från AOer fyller den bindande MOen som är lägre i energi än den antibindande MOen.
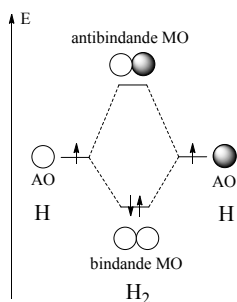
Figur 32. Bildandet av två MOer för H$_2$ molekylen utgående från AOer hos två väteatomer.

Enkel-, dubbel- eller trippelbindningar är möjliga mellan kolatomer i organiska molekyler. Enkelbindningar bildas genom överlapp av atomorbitaler, så att det inte finns några noder i molekylplanet, dvs ingen ändring av tecken i orbitalen (Figur 33a). Denna typ av bindning kallas σ bindning, och de MOer som bildas

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är σ orbitaler. Andra och tredje bindningarna i dubbel- och trippelbindningarna bildas av p orbitaler som har två lober av olika tecken (Figur 33b). Dessa orbitaler överlappar med varandra med två lober över och under molekylplanet och bildar därmed MOer av π typ som har en nod i molekylplanet.
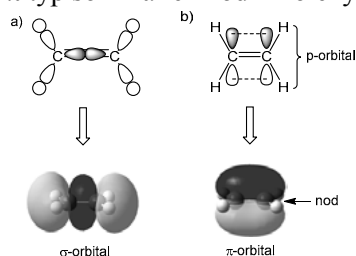
Figur 33. Två typer av bindningar i etenmolekylen: (a) σ bindning och (b) π bindning.

Om molekylens enkel- och multipelbindningar alternerar kan p orbitaler inte bara växelverka via dubbelbindningar utan även över enkelbindningar. Detta kallas konjugation och elektronerna i ett sådant system är delokaliserade över hela det konjugerade systemet (Figur 34a). Delokalisering av elektroner leder till förbättrad konduktivitet och gör att sådana molekyler kan användas för att leda elektrisk ström i applikationer. Substituenter bundna till dubbelbindningar kan inte rotera fritt kring dessa och detta innebär att konjugerade föreningar ofta är svårlösliga i organiska lösningsmedel, vilket begränsar dess användning i applikationer. Fast även andra orbitaltyper än p orbitaler kan delta i konjugerade system, t.ex. interaktionen mellan σ och π bindningar leder till hyperkonjugation (Figur 34b). För att skilja hyperkonjugation från klassisk konjugation kallar jag hädanefter den senare π-konjugationen. Hyperkonjugation är vanligtvis svagare än π-konjugation men kvalitativt är det samma typ av orbital-växelverkan. Samtidigt är hyperkonjugerade molekyler mer flexibla än konjugerade, vilket gör hyperkonjugation intressant för applikationer. För att få starkare hyperkonjugation kan man förändra molekylerna på olika sätt. Hur detta kan göras för att identifiera molekyler med stark hyperkonjugation är huvudtemat i denna avhandling.
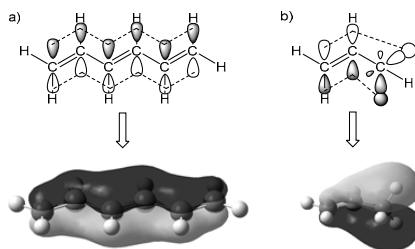
Figur 34. Bildandet av (a) π-konjugation från p orbitaler och (b) hyperkonjugation från π and σ orbitaler.

Det är inte möjligt att direkt mäta hur stark konjugationen är i en viss förening. Men varje typ av konjugation påverkar de geometriska och optiska egenskaperna hos molekylen. Med detta i åtanke kan vi jämföra egenskaperna hos hyperkonjugerade molekyler med analoga π-konjugerade molekyler. På detta sätt kan man dra en slutsats om relativ hyperkonjugeringsstyrka. I de arbeten som diskuteras i min avhandling använder vi mest beräkningsmetoder för beräkningar av geometriska och optiska egenskaper. I vissa fall jämfördes beräkningsresultat med experimentaldata för att bekräfta rimligheten av de beräknade resultaten. Genomgående undersöktes hyperkonjugation mellan en π bindning och elementen i det periodiska systemets grupp 14, från kol till tenn. Dessa atomer ur grupp 14 substituerades med elektrondragande eller elektrondonerande grupper och molekylära egenskaper i grundtillståndet och det första exciterade tillståndet beräknades. Vidare undersöktes dessa egenskaper inte bara i monomerenheter utan också i gradvis längre oligomerer. Slutligen studerades substitution av små cykliska molekyler med elektrondonerande och elektrondragande grupper på olika ställen i molekylen. Vi fann stark hyperkonjugation i vissa av molekylsystemen, ibland till och med jämförbar med dess π-konjugerade analoger. De metoder som demonstrerats i avhandlingen för att öka styrkan hos hyperkonjugerade system kan användas vid utformning av både små molekyler och polymerer som är lämpliga som material för molekylär och organisk elektronik. Dessa material kan eventuellt användas i organiska lysdioder (OLED), fotovoltaiska celler (OPVCs), fälteffekttransistorer (OFETs) etc. OLEDs används för att skapa digitala displayer i bl.a. TV-skärmar, datorskärmar och mobiltelefoner. OPVC är huvudkomponenten i organiska solpaneler vars huvuduppgift är att omvandla solenergin till elektricitet. OFETs används ofta i organisk elektronik, till exempel finns de i flexibla skärmar. Sammanfattningsvis behandlar min avhandling design av starkt hyperkonjugerade molekyler som potentiellt kan vara intressanta som material för elektroniska enheter.

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