Ground and Excited State Aromaticity

Design Tools for $\pi$-Conjugated Functional Molecules and Materials

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Abstract

The main focus of this thesis is on the aromaticity of the ground state and electronically excited states of π-conjugated molecules and polymers, as well as how aromaticity is connected to their properties.

The electronic structures of polybenzenoid hydrocarbons (PBHs) were explored through density functional theory (DFT) calculations and the π-component of the electron localization function (ELF). The study revealed how the π-electronic structure is influenced by the fusion of double bonds or benzene rings to the PBHs. We also demonstrated that the π-electrons of benzene extend to accommodate as much aromaticity as possible when bond length distorted.

The aromatic chameleon property displayed by fulvenes, isobenzofulvenes, fulvalenes, bist(fulvene), and polyfulvenes were investigated using DFT calculations. The tria-, penta-, and heptafulvenes were shown to possess ionization energies and electron affinities which can be tuned extensively by substitution, some of which even outperform TTF and TCNQ, the prototypical electron donor and acceptor, respectively. The singlet-triplet energy gap of pentafulvenes can be tuned extensively by substitution to the point that the triplet state is lower than the singlet state and thus becomes the ground state. The ELFₐ of isobenzofulvene shows that the benzene ring in an electronically excited state can be more aromatic than the corresponding ring in the ground state. We have shown that the 6-ring of [5,6,7]quinarene is influenced by a Hückel aromatic resonance structure with 4n+2 π-electrons in the excited quintet state. The bist(fulvene) which are composed of a donor type heptafulvene and an acceptor type pentafulvene, retain the basic donor-acceptor properties of the two fragments and could function as compact donor-acceptor dyads. A few of the designed polyfulvenes were found to have band gaps below 1 eV at the PBC-B3LYP/6-31G(d) level.

Various 2,7-disubstituted fluorenones and dibenzofulvenes were synthesized and their excited state properties were investigated by absorption spectroscopy and time-dependent DFT calculations. It was found that the 1'A → 1'B transition of ππ* character can be tuned by substitution in the 2,7-positions. The 2,7-bis(N,N-dimethyl) derivatives of fluorenone and dibenzofulvene displayed low energy transitions at 2.18 and 1.61 eV, respectively, in toluene.

Keywords: fulvene, fulvalene, polyfulvene, aromaticity, triplet state, excited state, Clar structure, polybenzenoid hydrocarbons (PBH), conjugated polymers, computational chemistry, optical spectroscopy


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List of Papers

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


V Rosenberg, M.; Dahlstrand, C.; Ottosson, H.; Kilså, K. Manipulation of Excited State Energies in Fulvenic Molecules. *Preliminary manuscript (2012)*


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Works not included in this thesis:


Author Contribution

The author wishes to clarify his contributions to the included papers.

I  Performed a large part of the calculations and contributed partly to manuscript writing.

II  Performed a large part of the calculations and contributed extensively to project development, data analysis and manuscript writing.

III  Performed a majority of the calculations, and contributed extensively to data analysis and manuscript writing.

IV  Performed a majority of the calculations. Contributed extensively to project development, manuscript writing and data analysis.

V  Preformed all synthetic work and provided the initial computational results.

VI  Performed all oligomer calculations and a few initial PBC calculations. Contributed extensively to project development, manuscript writing, and data analysis.
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<tr>
<td>$\Delta E_{ST}$</td>
<td>Singlet-Triplet Energy Gap</td>
</tr>
<tr>
<td>$\Delta BV$</td>
<td>Bifurcation Value Difference</td>
</tr>
<tr>
<td>ANO</td>
<td>Atomic Natural Orbital</td>
</tr>
<tr>
<td>AO</td>
<td>Atomic Orbital</td>
</tr>
<tr>
<td>BLA</td>
<td>Bond Length Alternation</td>
</tr>
<tr>
<td>BV</td>
<td>Bifurcation Value</td>
</tr>
<tr>
<td>CASSCF</td>
<td>Complete Active Space Self-Consistent Field</td>
</tr>
<tr>
<td>CASPT2</td>
<td>CASSCF with Second-Order Perturbation Theory</td>
</tr>
<tr>
<td>CGTF</td>
<td>Contracted Gaussian Type Function</td>
</tr>
<tr>
<td>DCM</td>
<td>Dichloromethane</td>
</tr>
<tr>
<td>DFT</td>
<td>Density Functional Theory</td>
</tr>
<tr>
<td>DMSO</td>
<td>Dimethylsulfoxide</td>
</tr>
<tr>
<td>$E_g$</td>
<td>Band Gap Energy</td>
</tr>
<tr>
<td>$E_F$</td>
<td>Fermi Energy</td>
</tr>
<tr>
<td>EA</td>
<td>Electron Affinity</td>
</tr>
<tr>
<td>EDG</td>
<td>Electron Donating Group</td>
</tr>
<tr>
<td>ELF</td>
<td>Electron Localization Function</td>
</tr>
<tr>
<td>ELF$_\pi$</td>
<td>$\pi$-Component of Electron Localization Function</td>
</tr>
<tr>
<td>eV</td>
<td>Electron Volt</td>
</tr>
<tr>
<td>EWG</td>
<td>Electron Withdrawing Group</td>
</tr>
<tr>
<td>f</td>
<td>Fulvenoid-type Structure</td>
</tr>
<tr>
<td>FET</td>
<td>Field-Effect Transistor</td>
</tr>
<tr>
<td>GGA</td>
<td>Generalized Gradient Approximation</td>
</tr>
<tr>
<td>GIAO</td>
<td>Gauge Including Atomic Orbital</td>
</tr>
<tr>
<td>GTF</td>
<td>Gaussian Type Function</td>
</tr>
<tr>
<td>HF</td>
<td>Hartree-Fock</td>
</tr>
<tr>
<td>HOCO</td>
<td>Highest Occupied Crystal Orbital</td>
</tr>
<tr>
<td>HOMA</td>
<td>Harmonic Oscillator Measure of Aromaticity</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest Occupied Molecular Orbital</td>
</tr>
<tr>
<td>HOPG</td>
<td>Highly Oriented Pyrolytic Graphite</td>
</tr>
<tr>
<td>Acronym</td>
<td>Definition</td>
</tr>
<tr>
<td>-----------</td>
<td>-----------------------------------------------</td>
</tr>
<tr>
<td>IE</td>
<td>Ionization Energy</td>
</tr>
<tr>
<td>KS-DFT</td>
<td>Kohn-Sham Density Functional Theory</td>
</tr>
<tr>
<td>LCAO-MO</td>
<td>Linear Combination of Atomic Orbitals to Molecular Orbitals</td>
</tr>
<tr>
<td>LSDA</td>
<td>Local Spin Density Approximation</td>
</tr>
<tr>
<td>LUO</td>
<td>Lowest Unoccupied Crystal Orbital</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest Unoccupied Molecular Orbital</td>
</tr>
<tr>
<td>MBS</td>
<td>Minimal Basis Set</td>
</tr>
<tr>
<td>MO</td>
<td>Molecular Orbital</td>
</tr>
<tr>
<td>NICS</td>
<td>Nucleus Independent Chemical Shift</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear Magnetic Resonance</td>
</tr>
<tr>
<td>OTFT</td>
<td>Organic Thin Film Transistor</td>
</tr>
<tr>
<td>OFET</td>
<td>Organic Field Effect Transistor</td>
</tr>
<tr>
<td>OLED</td>
<td>Organic Light Emitting Diode</td>
</tr>
<tr>
<td>OPVC</td>
<td>Organic Photovoltaic Cell</td>
</tr>
<tr>
<td>OVGF</td>
<td>Outer Valence Greens’ Function</td>
</tr>
<tr>
<td>PBC</td>
<td>Periodic Boundary Conditions</td>
</tr>
<tr>
<td>PBH</td>
<td>Polybenzenoid Hydrocarbon</td>
</tr>
<tr>
<td>PCM</td>
<td>Polarized Continuum Model</td>
</tr>
<tr>
<td>PGTF</td>
<td>Primitive Gaussian Type Function</td>
</tr>
<tr>
<td>PMO</td>
<td>Perturbation Molecular Orbital Theory</td>
</tr>
<tr>
<td>q</td>
<td>Quinoid-type Structure</td>
</tr>
<tr>
<td>Qu1</td>
<td>Lowest Excited Quintet State</td>
</tr>
<tr>
<td>RCBV</td>
<td>Ring Closure Bifurcation Value</td>
</tr>
<tr>
<td>S0</td>
<td>Singlet Ground State</td>
</tr>
<tr>
<td>S1</td>
<td>Lowest Excited Singlet State</td>
</tr>
<tr>
<td>SCF</td>
<td>Self-Consistent Field</td>
</tr>
<tr>
<td>SOMO</td>
<td>Singly Occupied Molecular Orbital</td>
</tr>
<tr>
<td>STF</td>
<td>Slater Type Function</td>
</tr>
<tr>
<td>T1</td>
<td>Lowest Excited Triplet State</td>
</tr>
<tr>
<td>TCNQ</td>
<td>Tetracyanoquinodimethane</td>
</tr>
<tr>
<td>TD-DFT</td>
<td>Time-Dependent Density Functional Theory</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
</tr>
<tr>
<td>TTF</td>
<td>Tetrathiafulvalene</td>
</tr>
<tr>
<td>TV</td>
<td>Translational Vector</td>
</tr>
<tr>
<td>UV-Vis</td>
<td>Ultraviolet-Visible</td>
</tr>
<tr>
<td>VEH</td>
<td>Valence Effective Hamiltonian</td>
</tr>
<tr>
<td>VSEPR</td>
<td>Valence-Shell Electron-Pair Repulsion</td>
</tr>
</tbody>
</table>
1. Introduction

The concept of aromaticity in the ground state and electronically excited states of \( \pi \)-conjugated molecules and polymers is the main focus of this thesis. A molecule that is \( \pi \)-conjugated has several \( p \)-atomic orbitals on adjacent atoms that form a network of \( \pi \)-orbitals though which electrons and holes can travel. These networks of \( \pi \)-electrons give the molecules a range of different properties that makes them interesting for applications in electronic and optoelectronic devices. Here a distinction should be made between single molecule electronics and electronics based on molecular materials as the former exploits the charge transport properties of single molecules while the later makes use of the conductive properties of ensembles of molecules in crystals and films.

In 1965 Gordon Moore, a co-founder of Intel, made a prediction of the future development of the integrated circuits. This prediction is referred to as Moore’s law and states that the number of transistors on an integrated circuit will double every 18 months.\(^1\)\(^2\) Hitherto, this law has been fulfilled, but for it to keep on doing so in the future we will soon have to build components which are on the molecular scale.

1.1. Single Molecule Electronics

In 1974, Aviram and Ratner published a milestone paper in which they presented a molecule that according to calculations would display rectification (Figure 1), i.e., the electric current should flow more easily in one direction than in the other.\(^3\)

![Figure 1. The molecular rectifier proposed by Aviram and Ratner in 1974.](image)

Since this publication molecular electronics has matured into an established field. It is nowadays possible to measure the current-voltage (I-V) characteristic of single molecules in experimental setups.\(^4\) Some of the fundamental
components that can be envisioned are wires, switches, transistors, memories, and of course rectifiers. One of the major differences between molecular and macroscopic electronics is that on the molecular scale quantum effects become important, such as electron tunneling.  

1.2. Electronics based on Molecular Materials

Molecular materials often refer to small molecules or polymers in crystals or films which typically are semiconducting or metallic. Electronics components made of these materials have, for example, enabled the realization of very flat and flexible screens. Two examples of such components are organic field effect transistors (OFETs) and organic light emitting diodes (OLEDs). The OLEDs emit light in response to an electric current and are usually constructed with the organic layer between two metallic contacts (Figure 2).  

π-Conjugated compounds have also found applications in solar cells. In dye-sensitized solar cells these organic molecular dyes function as light harvesting antenna that absorbing the energy coming from the sun. Other forms of solar cells that transform the solar light into electric current are the organic photovoltaic cells (OPVCs) which are very promising due to their potential of providing inexpensive photovoltaic cells which are lightweight, flexible, and environment friendly.  

![Figure 2. Compounds found in the emissive layer of OLEDs.](image)

In the design of functional materials for applications within electronics and optoelectronics there is a need for a precise understanding of the electronic structure of the molecular species involved and how their properties can be influenced and redesigned (optimized). Throughout this thesis we will see that the concept of aromaticity in the ground and electronically excited states is very important for the properties of π-conjugated compounds which can be applied in single molecule electronics and molecular materials for electronics.
2. Aromaticity

After reading this chapter I hope the reader has gained an appreciation of aromaticity. First, a short historical background will be given, followed by an explanation of the aromaticity concept in the electronic ground state and how it can be expanded into electronically excited states.

One of the difficulties with the aromaticity concept is that it has no single definition. Also, the amount of literature that deals with aromaticity is vast. Much of the literature is collected in the book *Aromaticity and Antiaromaticity, Electronic and Structural Aspects* by Minkin et al. from 1994, and in two thematic issues of *Chemical Reviews* from 2001 and 2005 edited by Schleyer.

2.1. A Short Historical Background

For a more thorough introduction to the history of aromaticity the reader is referred to several good reviews. Only a brief introduction is given here with some highlights of what I believe is important.

The dawn of aromaticity was in 1825 when Faraday isolated “dicarburet of hydrogen”, i.e., benzene. He assumed that the molecular formula was \((C_2H)_3\), but this was due to the erroneous atomic weight of carbon which at that time was thought to be 6 instead of 12. In 1872, Kekulé described benzene as “a regular arrangement of the six carbon atoms”, thus implying a \(D_{6h}\) symmetric structure, however, benzene was drawn with alternating single and double bonds indicating a \(D_{3h}\) symmetric structure. To resolve this symmetry problem the centric formula was developed by Armstrong in 1890 and it strongly resembles the Clar structure that is still used today (Figure 3). Astonishingly, all these initial findings were made before the discovery of the electron. Experiments performed in 1897 lead to the discovery of the electron by Thomson which received the Nobel Prize for his finding in 1906. Already in his Nobel Lecture Thomson speaks of the two prevailing views on the electrons; one that they are “negatively electrified bodies” and the other that they are some kind of “ethereal vibrations or wave”. In 1922 Crocker noticed that “aromatic structure is observed only in those combinations of elements which furnish six extra or aromatic electrons above those needed to complete a single-bonded ring”. He was thereby first to recognize the six aromatic electrons and in this way correctly described benzene,
pyridine, thiophene, furan, and pyrrol. The circle, signifying the six aromatic electrons, was introduced by Armit and Robinson in 1925, but as they state that “the deletion of the central connecting bonds is more apparent than real”, it seems that they knew already from the beginning that their representation of polyaromatic hydrocarbons was flawed. In 1931, Hückel published the theory of cyclic $4n+2$ $\pi$-electron systems which forms the basis for Hückel’s rule for aromaticity. It was not until 1959 that Clar made the refinements to the resonance structures (Figure 3).

![Evolution of resonance structures of benzene and polybenzenoid hydrocarbons from Kekulé to Clar.](image)

2.2. Different Types of Aromaticity

The aromaticity discussed in this thesis only refers to the type found in compounds which are planar and have a cyclic array of $p_{\pi}$-atomic orbitals that form an unbroken $\pi$-circuit. However, it should be mentioned that the aromaticity concept has been applied to many different types of molecules, e.g., fullerenes, carbon nanotubes, heteroaromatic compounds, polyaromatic hydrocarbons, Möbius annulenes, ionic species, homoaromatic compounds, polycyclic hydrocarbons, cage compounds, metallacycles, and perhaps more are to come. Aromaticity can also be found in transition states and in electronically excited states.

Interestingly, the electron counting rules for aromaticity are different for annulenes depending on molecular topology and electronic state (Figure 4). Compounds with Hückel topology are aromatic in the electronic ground state if they contain $4n+2$ $\pi$-electrons and antiaromatic if they contain $4n$ $\pi$-electrons, like benzene and cyclobutadiene, respectively. In the lowest excited $\pi\pi^*$ triplet state the electron counting rules are reversed, so the annulenes with $4n$ $\pi$-electrons are aromatic while those with $4n+2$ are antiaromatic.\(^{23}\) Compounds with Möbius topology have a $180^\circ$ half-twist in the array of p-AOs leading to an odd number of nodes in the cycle.\(^{24}\) This is in contrast to annulenes of Hückel topology which have an even number of
nodes between the p-AOs. The compounds with Möbius topology have the opposite electron counting rules for aromaticity as compared to the compounds with Hückel topology, i.e., the $S_0$ and the $T_1$ states are aromatic with $4n$ and $4n+2$ $\pi$-electrons, respectively.\textsuperscript{25,26} Compounds displaying Möbius aromaticity have in fact been synthesized, showing that exotic forms of aromaticity are more than theoretical excursions.\textsuperscript{27-29}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure4.png}
\caption{\textit{\pi}-Electron counting rules for aromaticity in Hückel and Möbius annulenes in the singlet ground state ($S_0$) and lowest triplet state ($T_1$).}
\end{figure}

2.3. Spin State Multiplicity

In the previous section the different types of aromaticity were introduced and shown to apply to different electronic states. But what is an electronic state and what is the difference between a singlet, a doublet, and a triplet state? As the electrons are fermions they have a spin which is either up ($M_s = 1/2$; $\alpha$) or down ($M_s = -1/2$; $\beta$). If all electron spins are paired, which is typically the case for ground state molecules consisting of carbon and hydrogen, the total spin is zero ($S = 0$). The multiplicity ($M$) of a molecule can be calculated from its total spin by $M = 2S + 1$. A molecule with $S = 0$ has singlet multiplicity and is said to be in a singlet state (\textit{Figure 5}). If this molecule would lose or gain an electron and thus contain one single unpaired electron of either $\alpha$ or $\beta$ spin, it is said to be in a doublet state ($S = 1/2$). If a molecule in a doublet state is subjected to a magnetic field the $\alpha$ and $\beta$ spin states will be of slightly different energy.

\begin{figure}[h]
\centering
\includegraphics[width=0.7\textwidth]{figure5.png}
\caption{The electron configurations of a singlet (S) and a doublet (D) state.}
\end{figure}
A molecule with two unpaired electrons with the same spin ($S = 1$) will show three non-degenerate states when subjected to a magnetic field and is therefore called a triplet. A compound of quintet multiplicity ($S = 2$) can be constructed by combining two rings which each are of triplet multiplicity. The singlet ground state is usually designated as $S_0$, the lowest triplet excited state as $T_1$ and the lowest quintet state as $Qu_1$.

### 2.4. Aromaticity in the Singlet Ground State

In the mind of a synthetic organic chemist, aromaticity is synonymous with the aromaticity found in the singlet ground state of annulenes with $4n+2$ $\pi$-electrons. There are many properties associated with the term aromaticity and these properties are in several cases used as aromaticity criteria.

#### 2.4.1. Aromaticity Criteria

The properties associated with aromaticity have during the last ~150 years evolved into aromaticity criteria which should be considered when designating a compound as aromatic.\textsuperscript{7,8,12} The four most important criteria for aromaticity are discussed below.

**Energetic:** One of the most fundamental properties of aromatic compounds is their greater thermodynamic stability than analogous isoelectronic linear polyenes. This is due to large resonance energies as aromatic compounds are influenced by a cyclic $\pi$-electron delocalization which is not found in the linear compounds.

**Magnetic:** As aromatic rings are cyclically conjugated their $\pi$-electrons can move in response to a magnetic field and generate a ring current. This ring current will in turn result in a small magnetic field which can indirectly be measured by nuclear magnetic resonance (NMR) spectroscopy, or alternatively, investigated computationally through diamagnetic susceptibility exaltations and nucleus independent chemical shifts.

**Structural:** Aromatic rings show a tendency toward bond length equalization and planarization.

**Reactivity:** With regard to reactivity, aromatic compounds usually display a low reactivity toward additions and favor electrophilic aromatic substitutions. The large problem with this criterion is that it can be severely misleading as reactivity is primarily governed by the energy of the transition state and not of the ground state.
2.5. Aromaticity in the Lowest Triplet and Quintet Excited States

In 1972, Baird expanded the concept of aromaticity to the lowest $\pi\pi^*$ state of triplet multiplicity, and showed that triplet annulenes with $4n\pi$-electrons are aromatic. He used perturbation molecular orbital theory and Dewar resonance energy arguments in his proposal. These findings were corroborated by Gogonea et al. in 1998, and then by several other groups. Experimentally it has been shown that the annulenyl cations $C_5H_5^+$ and $C_5Cl_5^+$ have triplet ground states, thus supporting the theory that triplet state aromaticity is a stabilizing molecular property for annulenes with $4n\pi$-electrons. It should also be mentioned that the same electron counting rules have been shown to apply to the $S_1$ state in a similar manner as for $T_1$. In their lowest quintet state some molecules can be described as being constructed of two triplets that reside on two different ring fragments. These can also be influenced by triplet state aromaticity, e.g., fulvalenes and azulene.

2.6. Aromaticity Indices

There have been many attempts to quantify aromaticity with regard to the effect that aromaticity exerts on different structural, magnetic, and electronic properties. There is a range of different aromaticity indices which measure the influence of aromaticity on a certain compound. The indices that have been used in this thesis are introduced in the following four sections.

One item that should be clarified is that aromaticity indices do not explicitly measure aromaticity! They simply embody results that are caused by aromaticity.

2.6.1. Harmonic Oscillator Model of Aromaticity (HOMA)

This structure based aromaticity index uses the bond lengths of the investigated ring to evaluate its degree of aromaticity. The HOMA index was first formulated in 1972 by Krygowski and co-workers, but was later refined in 1993 to include several different types of bond types, i.e., CC, CN, CO, CP, CS, NN, and NO. The HOMA of a ring is easily calculated by the formula

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

where $R_{opt}$ is the optimal value for the prototypical aromatic compound and $R_{ij}$ is the bond length between adjacent atoms of the investigated cycle. The aromatic or antiaromatic compounds in this thesis only contain CC bonds in
the rings. This means that $R_{opt}$ will be 1.388 Å, which is the optimal bond length of benzene in its ground state. The parameter $n$ is the number of bonds in the ring and $\alpha$ is an empirical constant chosen so that HOMA = 0 when the bond lengths are equal to those found for the non-aromatic reference compound.

The largest advantage of HOMA is probably its ease of use. However, HOMA will not reflect the aromaticity of an annulene if distortions imposed by, e.g., steric congestion do not allow the ring to assume its optimal bond lengths. This is discussed in chapter 5.3.5 regarding the fulvenes, but should also apply to other annulenes. Another case where HOMA might not be the best choice of aromaticity index is for excited states as the HOMA parameters have been calculated for the ground states. Other bond lengths have been applied for the excited states but have not been used to any large extent.$^{52}$

2.6.2. Nucleus Independent Chemical Shifts (NICS)

In 1996, Schleyer and co-workers proposed the use of nucleus independent chemical shifts (NICS) as a magnetically based aromaticity index.$^{53}$ Since then it has grown enormously in popularity and the original paper has now over 2000 citations. The first NICS index was calculated by taking the negative of the absolute magnetic shielding tensor of a dummy atom placed at the geometric center of an annulene, the so-called NICS(0) index. One problem with this index was the large effect of the $\sigma$-orbitals on the NICS(0) value. To alleviate this problem the dummy atom was later moved to 1 Å above the molecular plane (NICS(1)), thus decreasing the influence of the $\sigma$-framework.$^{54}$

Negative NICS values indicate a diatropic ring current (aromaticity) while positive NICS values indicate a paratropic ring current (antiaromaticity). The isotropic chemical shift is the average of the $xx$, $yy$, and $zz$ tensor components. As the $xy$ plane is defined by convention to be the molecular plane, and as the magnetic field is applied along the $z$-direction, the $zz$ tensor (out-of-plane) component will contain the most relevant information with regard to aromaticity.$^{55}$ The NICS index which only regards the $zz$ component of the isotropic chemical shift tensor is designated with a $zz$ subscript, i.e., NICS(1)_{zz}.

A disadvantage of the NICS aromaticity index is that only one point in space is regarded. To alleviate this problem the NICS scan protocol was introduced by Stanger,$^{36}$ and it will be described next.

2.6.3. NICS scan

Stanger introduced an alternative NICS based method due to the problems of using the NICS(0) and NICS(1) single point approaches.$^{36}$ In the NICS-scan method the NICS values are “scanned” from the ring center to 5 Å above the ring with an increment of 0.1 Å. The isotropic chemical shift together with
its in-plane and out-of-plane components are plotted vs. distance from the ring. The plots for aromatic compounds should display relatively deep minima for both the out-of-plane component and the overall isotropic chemical shift, while antiaromatic compounds should have an out-of-plane component which is highly positive close to the ring center and then decrease smoothly to zero as the distance is increased.

The disadvantage of using magnetically based indices for aromaticity stems from the fact that the magnetic properties are caused by the dia- or paramagnetic ring currents in the investigated annulene, which are not directly connected to aromaticity. It has been shown that aromaticity indices which reflect the electron delocalization of annulenes are the most appropriate. One such method to explore the electronic structure is by investigation of the properties of the electron localization function as described below.

2.6.4. Electron Localization Function (ELF)

The electron localization function was presented in 1990 by Becke and Edgecombe and can be viewed as a mathematical description of the valence-shell electron-pair repulsion (VSEPR) theory. The ELF has been used to show the localization of electrons into core, bonding, and lone-pair basins (attractors), and it is defined as

\[
\text{ELF}(r) = [1 + (\chi(r))^2]^{-1} = \left[ 1 + \frac{T(r)}{T_h(r)} \right]^{-1}
\]

(2.2)

where \(\chi(r)\) is a dimensionless localization index referenced to the uniform electron gas. \(T(r)\) represents the local excess of kinetic energy due to the Pauli repulsion, and \(T_h(r)\) is the Tomas-Fermi kinetic energy which relates to the uniform electron gas. The ELF is designed to attain values between 1 and 0. In regions where electrons are alone or paired with opposite spins the ELF attains values close to 1 whereas in regions between electron pairs a smaller value for the ELF is afforded due to Pauli repulsion. The \(\pi\)-component of the electron localization function (ELF\(_\pi\)) has been used as an indicator of aromaticity. A discussion on how the ELF\(_\pi\) can be used as an aromaticity index and its implications are given in section 4.1.3.
3. Computational Quantum Chemistry

The 1927 paper by Heitler and London, in which they rationalized the covalent bonding of the dihydrogen molecule (H₂), marks the birth of quantum chemistry. Quantum chemistry offers a way to understand and explain a range of areas within chemistry, such as reactivity and spectroscopy. But quantum chemistry can also be used to calculate many different molecular properties which could be useful in the design of molecular materials.

To understand a chemical problem, imagine putting it in a “box”. Quantum chemistry offers a way to step outside this box (of reality) and to look at it from all sides. The box might symbolize what is possible to synthesize but to get an appreciation of this box it can be instructive to do calculations on compounds which are not stable or synthesizable. In this way quantum chemistry can put a chemical problem into an understandable context.

In this chapter the basic concepts and ideas behind computational quantum chemistry are discussed. The aim of the chapter is that it should serve as an introduction for newcomers to the field of computational quantum chemistry. For further introductory reading, the books by Jensen and Leach are recommended.

3.1. Elementary Quantum Mechanics

Due to the wave-particle duality of elementary particles, electrons can be described as both waves and particles. In quantum mechanics the electrons are described by wavefunctions \( \psi \).

One of the most fundamental papers in the early developments of quantum mechanics was published by Schrödinger in 1926 where he calculated the spectral lines for hydrogen. To describe electrons in a molecular system the fundamental equation is the Schrödinger equation. In its general form it can be written as

\[
\hat{H} \psi = E \psi
\]  

(3.1)

where \( \hat{H} \) is the Hamiltonian operator which acts on the wavefunction \( \psi \) to return the wavefunction \( \psi \) and an eigenvalue, \( E \). This eigenvalue, \( E \), can be interpreted as the energy that corresponds to the wavefunction \( \psi \). The
Schrödinger equation is an eigenvalue equation which is only fulfilled for certain discrete eigenvalues (energies) corresponding to associated eigenfunctions (AOs or MOs).

The Hamiltonian, $\hat{H}$, can in its simplest form be given as

$$\hat{H} = \hat{H}_V + \hat{H}_T$$  (3.2)

where $\hat{H}_V$ is the potential energy operator describing the different repulsive/attractive Coulomb forces involving the electrons and nuclei and $\hat{H}_T$ is the kinetic energy operator that describes the kinetic energy of the electrons and nuclei.

One problem with the Schrödinger equation is that it can only be solved exactly for one-electron systems, i.e., $H^-$ and $H_2^+$. In a strict sense it can only handle two-particle systems but thanks to the Born-Oppenheimer approximation the two protons in $H_2^+$ can be viewed as being fixed in space while the electronic part of the wavefunction is solved. This is due to the enormous mass difference between the electron and the nuclei, the nuclei can be assumed to be standing still as the electrons move about them. This means that the total wavefunction can be divided into its electronic and nuclear parts and that the total energy is equal to the sum of these.

### 3.2. Hartree-Fock (HF) and post-Hartree-Fock Methods

One of the early methods of solving the Schrödinger equation for a many-body problem was the Hartree-Fock (HF) method. It assumes that the electron moves through a mean-field of all the other electrons and nuclei, the so-called mean-field approximation. In the HF method the wavefunction is solved via the self-consistent field (SCF) method which is an iterative procedure starting from an initial guess. The procedure is finished when the retrieved wavefunction is the same as the one of the preceding iteration, within a set of convergence criteria. It is then said to be self-consistent.

As a consequence of the mean-field approximation in the HF method, the interactions between electrons are not well described. The motions of the electrons are correlated and they tend to avoid one another more than the HF method predicts. Proper treatment of this electron correlation leads to a lower energy than found by HF. The difference between HF energy and the exact energy is defined as the correlation energy. It is thus important to incorporate electron correlation to achieve accurate results. Some of the methods based on HF which explicitly include electron correlation are coupled cluster (CC) theory, Møller-Plesset perturbation theory, and the complete active space self-consistent field (CASSCF) method.
3.3. Basis Sets

To describe molecular orbitals in computational chemistry mathematical functions are used. These functions are called basis functions and are centered on the nuclei. There are basically two types of basis functions, the Slater type functions (STF) and the Gaussian type functions (GTF). Slater type functions resemble the atomic orbitals to a larger extent but are computationally demanding. This is the main reason why the Gaussian type functions are used. Another attractive feature of these primitive Gaussian type functions (PGTF) is that they can be linearly combined to resemble the Slater type functions. These new Gaussian type functions are called contracted Gaussian type functions (CGTF).

Three types of basis sets have been used throughout the works in this thesis. Amongst these, the Pople type basis sets of X-YZG type have been used to the largest extent. These basis sets are of so-called split valence type which means that the contraction scheme is different for the valence and the core orbitals. One such basis set is the 6-31G basis set which uses six PGTFs to describe each core orbital while the valence orbitals are constructed from two basis functions (CGTFs) signifying a double-zeta split valence set. The first of these two basis functions is a linear combination of three PGTFs and it describes the inner part of the valence orbitals while the other, which only contains one PGTF, describes the outer part.

To allow polarization of p-orbitals, p-type functions are mixed with functions of higher angular momentum, e.g., d-type functions. This allows the p-orbitals to “lean forward” when in a bonding π-MO or backward when in an anti-bonding π*-MO. To describe the polarization of s-orbitals they are mixed with p-type basis functions. The Pople type basis sets that contain polarization functions are signified with either one or two stars (* or **) which is synonymous with (p) and (d,p) indicating the type of polarization functions used in the basis set, i.e., 6-31G(d) or 6-31G*.

3.4. Density Functional Theory (DFT)

As an alternative to the HF based methods, the electron density \( \rho(r) \) can be used to calculate the energy and other molecular properties. The DFT methods incorporate electron correlation and their use leads to considerable savings with regard to computer time. They can also be applied to larger systems than the traditional wavefunction based methods.

In DFT, the total energy \( E[\rho(r)] \) can be written as

\[
E[\rho(r)] = E_T[\rho(r)] + E_V[\rho(r)] + E_J[\rho(r)] + E_{XC}[\rho(r)]
\]

(3.3)

where \( E_T \) is the electron kinetic energy, \( E_V \) is the potential energy which
includes both electron-nuclear attraction and nuclear-nuclear repulsion, $E_I$ is the Coulomb self-interaction term which evaluates the electron-electron repulsion. $E_{XC}$ is the exchange-correlation term which is found in many different varieties depending on DFT method. The $E_{XC}$ can be divided into an exchange part and a correlation part.

$$E_{XC}[\rho(r)] = E_X[\rho(r)] + E_C[\rho(r)]$$ (3.4)

As a first approximation of the exchange-correlation term the electron density is assumed to only change slowly and so the local density can be considered to be constant. This is the local spin density approximation (LSDA) and is nowadays rarely used except for cases were the approximation is valid, i.e., extended systems or metals. LSDA can be improved by taking into account the change in electron density, i.e., the gradient together with the original electron density input. This is the generalized gradient approximation (GGA) and gives more reliable results as compared to the LSDA approach and is more generally applicable. Some of the methods used in this thesis are of the GGA type, e.g., BLYP, OLYP, and PBE. A further DFT improvement is accomplished by combining LSDA, GGA, and exact exchange from HF into the hybrid-DFT methods. The most well-known and frequently applied hybrid-DFT method is B3LYP, which is a composite method that utilizes HF exact exchange together with Becke’s exchange functional and the LYP correlation functional by Lee, Yang, and Parr.67

Even though DFT gives superior results at a computational cost equivalent to HF, there are some hazards that one should be aware of. Several of the major deficiencies of DFT are listed below.

DFT deficiencies:

- Anions from compounds with low electron affinity as well as Rydberg states are poorly described due to the self-interaction error.
- Transition-state structures are poorly described, especially with methods that do not include exact HF exchange.
- Excited states of the same symmetry as the ground state are impossible to handle in KS-DFT (DFT in the Kohn-Sham formulation is a theory for the electronic ground state).
- Charge-transfer excitations calculated with time-dependent DFT (TD-DFT) are often found at too low transition energies due to the absence of long-range correlation.
- DFT methods generally give smaller HOMO-LUMO gaps than HF. This is especially true for LSDA methods.
• DFT exaggerates the degree of delocalization, thus, the degree of delocalization with regard to spin and charge creates problems and may lead to unrealistic energy surfaces.
• van der Waals interactions are poorly described, which can lead to an under- or overestimation of attractive forces.
• DFT cannot describe near-degenerate states.

Some of the listed deficiencies have already been solved by newer functionals. The M06 series (M06-L, M06, M06-2X, and M06-HF) of functionals are very promising in this regard but should be used with some caution when optimizing geometries. In certain aspects of computational chemistry these functionals outperform the standard B3LYP.

3.5. Calculating Molecular Properties

One important aspect of computational chemistry is the calculation of molecular properties. Often the property is calculated as a response of a perturbation to the wavefunction. The perturbation can be a change in external electric or magnetic field, nuclear magnetic moment, or in the geometry. The calculated properties discussed herein will be explained in their respective chapters.
4. Aromaticity of Polybenzenoid Hydrocarbons

This chapter is based on a computational investigation of the ground state aromaticity of polybenzenoid hydrocarbons (Paper I). The aromaticity of the polybenzenoid hydrocarbons PBHs has been evaluated in terms of the $\pi$-contribution to the electron localization function which is a way of investigating the degree of delocalization in the $\pi$-electron network. The change in $\pi$-electron delocalization as a consequence of topological changes, i.e., benzanulation or fusion of an ethylene moiety, will be discussed. The consequence of bond length distortions on the $\pi$-electronic structure will also be considered in the final part of this chapter.

4.1. Properties of Polybenzenoid Hydrocarbons

Polybenzenoid hydrocarbons (PBHs) are a subcategory of polyaromatic hydrocarbons that only contains hexagons. The PBHs can be described in two fundamentally different ways; either as clusters of fused benzene rings or as very small fragments of graphene. The PBHs are planar compounds where all carbon atoms are sp$^2$ hybridized, thus leaving a singly occupied p$_\pi$-atomic orbital perpendicular to the molecular plane at each C atom. Whether the electrons of the $\pi$-network are localized into rings or delocalized depends on the topology. One way of understanding the electronic structure of PBHs is by drawing Clar structures.

4.1.2. Clar Resonance Structures

To account for the difference in properties of a set of constitutional isomers of PBHs the Clar resonance structures were developed. Before discussing this form of representation we should start by defining the aromatic sextet. An aromatic sextet is when a hexagon contains six $\pi$-electrons in a cyclic array and this is drawn with an inscribed ring into this hexagon (Figure 6). The Clar structure is the resonance structure which has the maximal number of aromatic sextets inscribed. No aromatic sextets are allowed in adjacent rings. The rings that do not exhibit an aromatic sextet must have a Kekulé structure with uniquely defined single and double bonds. The triphenylene
structure containing three aromatic sextets is the best description of the molecular properties and also corresponds to the Clar resonance structure.

![Figure 6. Clar structure and the aromatic sextet for triphenylene.](image)

The arrows in some Clar structures indicate the movement of two electrons to form a new aromatic sextet (Figure 7). For linear acenes and other linear fragments of PBHs the aromatic sextet will become more diluted throughout the whole linear segment as hexagons are added. This means that the stabilizing effect of aromaticity will decrease as the acenes are elongated and thus the reactivity of pentacene is higher than that of the shorter anthracene. The number of aromatic sextets that can be inscribed into a PBH is related to the thermodynamic stability. A strong correlation is revealed \( R^2 = 0.947 \) when plotting the relative energies of different heptabenzenoid isomers vs. the number of inscribed aromatic sextets. This is a clear indication of the stabilizing effect that aromaticity has on the ground state.

The number of inscribed aromatic sextets also influences the colors of the compounds, going from dark-green, via blue-green, red, violet-red, yellow, and finally, to colorless when going from 1 to 6. This represents a blue-shift in the lowest absorption and it is a consequence of the aromatic stabilization of the ground state relative to the excited states as one goes along the series.
4.1.3. Properties of the Electron Localization Function

An alternative to using Clar resonance structures to describe the \( \pi \)-electron distribution is through the \( \pi \)-component of the electron localization function (ELF\( _\pi \)). The properties of the ELF\( _\pi \) for polybenzenoid hydrocarbons suggest a large degree of cyclic delocalization in the rings exhibiting a Clar aromatic sextet. The fully benzenoid PBHs are well described by a set of aromatic sextets which can also be seen from the ELF\( _\pi \) isosurface (Figure 8).

Figure 8. The Clar structure and corresponding ELF\( _\pi \) isosurface for a fully benzenoid PBH.

The ELF\( _\pi \) indicates where the \( \pi \)-electron pairs are localized due to Pauli repulsion between same-spin electrons and assumes values between 0 and 1.\(^{57}\) The ELF\( _\pi \) is high in regions where a \( \pi \)-electron pair is localized, \( i.e., \) at double bonds (Figure 9), and low in regions with large Pauli repulsion, \( i.e., \) in regions between \( \pi \)-electron pairs.
The ELF is plotted as an isosurface where the surface value corresponds to the function value and encloses a so-called basin (Figure 8). When the ELF value is lowered the basins become larger and finally merge with neighboring basins. The point at which one basin becomes two, or the opposite, is called the bifurcation point and the corresponding value of the ELF is the bifurcation value (BV). The bifurcation points can be interpreted as the degree of communication between basins, i.e., large BV(ELF) indicate a large degree of communication while a small BV(ELF) indicate a localization.72,73

The π component of the ELF (ELFπ) can be used to evaluate the aromaticity of planar compounds because the behavior of the π-electrons is reflected in the ELFπ. It can be expected that the more uniform distribution of electron density in the π-orbitals, the more aromatic the compound will be. This can be evaluated by examination of the difference between the highest and lowest BV(ELFπ) in the ring, i.e., ΔBV(ELFπ).74 An example is the ΔBV(ELFπ)s of the archetypical aromatic and anti-aromatic compounds benzene (ΔBV(ELFπ) = 0) and D4h symmetric cyclooctatetraene (ΔBV(ELFπ) = 0.658).72

Figure 9. The bifurcation values (BV(ELFπ)) of benzene when one basin splits into six basins. The two BV(ELFπ) for cyclooctatetraene (D4h) when one basin becomes four and when four becomes eight. The largest difference in bifurcation values (ΔBV(ELFπ)) is also given.

The ELFπ has been used to corroborate new methods in evaluating aromaticity, i.e., the aromatic cyclic energy.75 Villaume et al. set up two criteria for aromaticity to evaluate the degree of aromaticity of singlet and triplet state annulenes.30 The first criterion was that the ring closure bifurcation value, RCBV(ELFπ) that is the first bifurcation point for the ELFπ basin should be large (≥ 0.7). This criterion was later refined in Paper I so RCBV(ELFπ) ≥ 0.65. The second criterion was that the difference in BV(ELFπ) in a ring, ΔBV(ELFπ), should be small and preferable zero. The ELF has also been
used to study the aromaticity along the lowest triplet-state path in the double bond rotation of annulenyl-substituted olefins. 76

4.1.4. Describing PBHs through the $\pi$-Component of the Electron Localization Function

The connection between the $\pi$-electron delocalization in heptabenzenoids and Clar resonance structures has been introduced. In this section the same heptabenzenoids will be discussed but in terms of the $\pi$-electron delocalization as described by the ELF$_{\pi}$ and how the properties of these PBHs are dependent on how the hexagons are arranged relative each other. Before moving on to the analysis of the heptabenzenoids it should be mentioned that an attractor in the context of PBHs is a component that attracts electron density giving regions of high ELF$_{\pi}$ values, i.e., double bonds and benzene rings.

The terminal rings in heptacene 1, 2 and 4 are characteristic for acenes and acene-like fragments as they have two double-bond attractors (Figure 10). These attractors have slightly better $\pi$-communication between each other than with the rest of the $\pi$-system which is indicated by the slightly higher BV(ELF$_{\pi}$)s between the attractors. The peripheral bonds of 1 in the central segment have BV(ELF$_{\pi}$)s in the aromatic range while they in turn are only weakly coupled to each other as seen from the single bond type BV(ELF$_{\pi}$)s connecting the linear segments. The general observations for the remaining compounds 2 - 6 are given below

• BV(ELF$_{\pi}$)s at CC bonds between strong attractors, i.e., fully benzenoid rings and double-bonds, are typically low and of single-bond character, i.e., below a BV(ELF$_{\pi}$) of 0.65.
• Strongly localized double-bonds have typical BV(ELF$_{\pi}$)s above 0.96.
• BV(ELF$_{\pi}$)s for fully benzenoid rings, as in compound 6, are in between the values for the single- and double-bonds.
Figure 10. The BV(ELF<sub>π</sub>)s and ΔBV(ELF<sub>π</sub>)s (in bold) of heptabenzenoids calculated at the B3LYP/6-311G(d,p) level. The bonds are drawn as single (BV(ELF<sub>π</sub>) < 0.65), single plus dashed (0.65 ≤ BV(ELF<sub>π</sub>) < 0.96), and double bonds (0.96 ≤ BV(ELF<sub>π</sub>)).
4.2. Influence on $\pi$-Electronic Structure due to the Fusion of Ethylene or Benzene Ring Fragments onto PBHs

The $\pi$-electron distribution will change in PBHs when an ethylene or benzene ring fragment is fused onto the system. In the following sections the topological effect on the $\pi$-system will be discussed. Knowledge of how the electronic properties can be manipulated is of great importance for the design of novel materials with predictable properties.

4.2.1. Fusion of Ethylene onto a PBH

When adding ethylene fragments to biphenyl (7) to form phenanthrene (8) and pyrene (9) the rest of the $\pi$-electron network adapts to the new topography. The first observation that can be made is that the A-ring decreases in aromaticity along the series (Figure 11). The increase in $\Delta$BV(ELF$_{\pi}$) is particularly large in the addition of the first ethylene fragment. The inter-ring communication will also increase along the series as the A-rings will be pulled together with increasing number of ethylene fragments. This is seen in the BV(ELF$_{\pi}$)s for the bond connecting the two A-rings which goes from 0.320 in 7 to 0.543 in 8 and 0.710 in 9.

![Figure 11](image_url)

*Figure 11.* In the top part of the figure the Clar resonance structure is given and the BV(ELF$_{\pi}$) for the inter-ring bond. The lower part gives $\Delta$BV(ELF$_{\pi}$)s (in bold) for the individual rings calculated at B3LYP/6-311G(d,p) level. The bonds in the lower part are drawn as single ($\text{BV(ELF}_\pi) < 0.65$), single plus dashed ($0.65 \leq \text{BV(ELF}_\pi) < 0.96$), and double bonds ($0.96 \leq \text{BV(ELF}_\pi)$).

4.2.2. Fusion of a Benzene ring onto a PBH

The $\pi$-electron structure of PBHs can be altered by the fusion of benzene. Two different ways of achieving this are discussed below. In the first approach a double bond fragment is replaced by a benzene ring (Figure 12). The benzene ring, which also is an attractor, is of greater strength as compared to the double bond fragment. This replacement of the double bond fragment enhances the aromaticity of already aromatic rings and decreases the aromaticity of the ring to which the new benzene ring is fused.
Figure 12. The effect of replacing a double-bond with a benzene ring on the $\Delta BV(\text{ELF}_\pi)$s (in bold) calculated at B3LYP/6-311G(d,p) level. The bonds are drawn as single ($BV(\text{ELF}_\pi) < 0.65$), single plus dashed ($0.65 \leq BV(\text{ELF}_\pi) < 0.96$), and double bonds ($0.96 \leq BV(\text{ELF}_\pi)$).

The second way to alter the $\pi$-electron structure of a PBH is perhaps more interesting as it will have a greater influence. The fusion of benzene to a ring which is described by a Clar sextet will disrupt the aromaticity of the Clar sextet ring. This is especially true if the fusion is not done in a linear fashion to produce something that is reminiscent of an acene. When going from 8 to 12 the aromaticity of the terminal rings of phenanthrene are disrupted while the aromaticity of the central ring increases (Figure 13). This indicates that the central ring can be disconnected electronically from the rest of the $\pi$-electron network by the fusion of benzene.

Figure 13. Demonstration of the disruption of the aromaticity in the terminal rings of phenanthrene. $\Delta BV(\text{ELF}_\pi)$s (in bold) calculated at B3LYP/6-311G(d,p) level. The bonds are drawn as single ($BV(\text{ELF}_\pi) < 0.65$), single plus dashed ($0.65 \leq BV(\text{ELF}_\pi) < 0.96$), and double bonds ($0.96 \leq BV(\text{ELF}_\pi)$).
The fusion of ethylene or benzene can, in this way, lead to an altering of the overall \( \pi \)-electronic structure. However, if the goal is to tune the energies of HOMO and LUMO then a MO-diagram is needed to elucidate the specific interactions between these orbitals and the butadiene fragment. An example of such a MO-diagram is given in Chapter 7.3.2 of this thesis (Figure 45).

4.3. Influence on the \( \pi \)-Electronic Structure of Benzene due to Distortions of the \( \sigma \)-Framework

With a greater knowledge about how the \( \pi \)-electronic structure of PBHs can be manipulated we shall now take a step back and look at the compound which started it all, benzene. The questions discussed in this section are more fundamental in character and will hopefully shed some new light on an old problem.

Benzene has suffered through many theoretical investigations into why the preferred symmetry is \( D_{6h} \) and the most famous of these are likely those by Shaik, Hiberty and co-workers.\(^{77-79}\) From these investigations it has become generally accepted that the high symmetry of benzene is due to the \( \sigma \)-framework which serves as the driving force for bond length equalization. It is even considered that the \( \pi \)-electrons prefer the lower \( D_{3h} \) symmetry. However, recent investigations have shown that there also exist an anti-distortive cyclic delocalization energy associated with the \( \pi \)-electrons.\(^{80,81}\)

We have investigated the connection between BV(ELF\( \pi \))s and the corresponding bond lengths which show that there is a sigmoidal relationship going from a BV(ELF\( \pi \))s of 1 for short bonds to BV(ELF\( \pi \))s of 0 for long bonds (Figure 14). This relationship is followed by the PBHs as well as the antiaromatic compounds cyclobutadiene (in \( D_{2h} \)) and cyclooctatetraene (\( D_{4h} \)). Interestingly, the degree of \( \pi \)-electron delocalization for bond length distorted benzene is much larger than expected from Figure 14. It is as if benzene tries its best to retain as large a degree of aromaticity as possible, by \( \pi \)-electron delocalization, despite the distortions of the \( \sigma \)-framework.
Figure 14. BV(ELF\textsubscript{π}) of CC bonds for PBHs, distorted benzene (D\textsubscript{3h}), cyclobutadiene, and cyclooctatetraene as a function of bond length.

I hope that the reader now has obtained an appreciation of how the properties of polybenzenoid hydrocarbons can be altered as a consequence of the fusion of ethylene or benzene fragments. As a note, it should be mentioned that the direct fusion of a benzene ring or ethylene fragment onto a molecule is not synthetically viable. The knowledge from this chapter should instead go into the initial design of the compounds. In the following chapter a group of compounds that can adapt its electronic structure to become influenced by aromaticity in several different electronic states will be discussed. The compounds have been termed aromatic chameleons and the unifying characteristics of these compounds is that they contain a ring with an odd number of carbons, \textit{i.e.}, three, five, or seven, as well as an exocyclic bond which either can push in or pull out electrons.
5. Aromatic Chameleons

In the same way as a chameleon can adapt to its environment by changing color the compounds in this chapter can adapt their electron density distribution as to accommodate an influence of aromaticity in several electronic states (Papers II, III, and IV). Compounds with this ability have been termed aromatic chameleons. In this chapter it is shown how aromaticity can influence a vast array of different electronic, structural, magnetic, and energetic properties of fulvenes and fulvenoids in the electronic ground and excited states. We will first see how the electronic ground states of tria-, penta-, and heptafulvenes are influenced by substitution and how this is connected to orbital symmetry and aromaticity. Later in the chapter it will be shown how substituents on pentafulvenes influence the aromaticity of different electronic states and the energies of these states. In the final part of the chapter the aromaticity of other types of aromatic chameleons will be investigated.

5.1. Electron Affinity and Ionization Energy

The electron affinity (EA) and ionization energy (IE) of a compound can be viewed as its ability to attach or remove an electron. According to Koopmans’ theorem the EA and IE can be approximated by the negative of the HOMO and LUMO energy levels, respectively (Figure 15). A refinement of this theorem is to use the outer valence Green’s function (OVGF) method in the calculation of EAs and IEs of molecular systems. One of the major advantages with OVGF is that there is no need for the explicit treatment of both the initial state and the final radical state. This function incorporates electron correlation and orbital relaxation into the calculation giving energies which in general are in good agreement with experimental values. The EAs and IEs are intrinsic properties of LUMO and HOMO. If the energies of these orbitals can be tuned in a predictable way this would open the opportunity to influence the ability of electron attachment (EA) and electron detachment (IE) of a compound.

In the field of molecular and organic electronics there is a massive interest for compounds with high EAs and/or low IEs. If a compound has both a high EA and a low IE it could potentially be an electrochemically amphoteric compound, thus being both a potential electron donor and acceptor. Two of the most studied compounds in electronics based on single molecules or
molecular materials are the prototypical electron donor (low IE) tetrathiafulvalene (TTF) and tetracyanoquinodimethane (TCNQ) which is an electron acceptor (high EA).

![Diagram](image)

*Figure 15. The electron affinity and ionization energy according to Koopmans’ theorem.*

5.1.1. Tetrathiafulvalene and tetracyanoquinodimethane

Possibly the most well-known and used electron acceptor (high EA) and electron donor (low IE) is tetracyanoquinodimethane (TCNQ) and tetrathiafulvalene (TTF), respectively (*Figure 16*). The reason for the low IE of TTF and the high EA of TCNQ is because in their final radical states they are more influenced by aromaticity than in their initial states. Both of these compounds and derivatives thereof have found use in the field of organic electronics. The single crystal of TTF and TCNQ in a 1:1 complex is highly conducting. It has even been shown that there is conductance at the interface between a pure crystal of TTF and a pure crystal of TCNQ as a consequence of partial charge transfer.

![Diagram](image)

*Figure 16. Tetrathiafulvalene (TTF) and tetracyanoquinodimethane (TCNQ) and their calculated ionization energies and electron affinities at the OVGF/6-311G(d)//B3LYP/6-311G(d) level.*
It is well known that the OVGF results are dependent on the size of the basis set. To validate our results in Paper II a comparison of different basis sets was made.

5.1.2. Basis Set Dependence of the Outer Valence Greens’ Function Calculations

The calculated IEs and EAs of TTF and TCNQ show a basis set dependence. To evaluate the basis set dependence the IEs and EAs where calculated for TTF and TCNQ as well as a small set of tria- (Tf), penta- (Pf), and heptafulvenes (Hf) (Table 1).

As the outer valence Greens’ function (OVGF) calculations are computationally demanding there is a need to use a relatively small basis sets. The problem with using a small basis set is that it might give erroneous values for the EAs and IEs. Another and potentially larger problem is that a small basis set might lead to an imbalance in the description of the EAs and IEs. To describe electron attachment there is a greater need for diffuse functions as compared to the description of electron detachment. It has been suggested that a basis set of at least triple-zeta quality should be used for OVGF calculations. To investigate the basis set dependence of the EAs and IEs, calculations were performed with the 6-311G(d) Pople type basis set, as well as the cc-pVTZ and aug-cc-pVDZ Dunning type basis sets (Table 1).

Table 1. Comparison between different basis sets in the calculations of EAs and IEs at the OVGF/6-311G(d)//B3LYP/6-311(d) level. Values are in eV. The exocyclic (X) and ring (Y) substituents were varied for the fulvenes.

<table>
<thead>
<tr>
<th>Compound</th>
<th>X</th>
<th>Y</th>
<th>6-311G(d)</th>
<th>cc-pVTZ</th>
<th>aug-cc-pVDZ</th>
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</thead>
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<td></td>
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<td>EA</td>
<td>IE</td>
<td>EA</td>
</tr>
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<td>-</td>
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<td>-</td>
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<td>-</td>
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<td>9.11</td>
<td>2.88c</td>
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<td>0.78</td>
</tr>
<tr>
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<td></td>
<td></td>
<td>0.51</td>
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<td>0.78</td>
</tr>
<tr>
<td>PF1</td>
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<td>Cl</td>
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<td>0.47</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
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<td>0.47</td>
</tr>
<tr>
<td>HF1</td>
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<td>8.00</td>
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<tr>
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<td>8.00</td>
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<tr>
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<td></td>
<td></td>
<td>3.63</td>
<td>10.31</td>
<td>3.85</td>
</tr>
</tbody>
</table>

| a Calculated EAs with negative values are not given. |
| b Experimental values are 6.70 – 6.72 eV. |
| c Experimental values are 2.8 ± 0.1 and 2.84 ± 0.05 eV. |

The correlations between EAs calculated with the 6-311G(d) basis set and the larger Dunning type basis sets is excellent (Figure 17, \( R^2 = 0.999 \)). When looking at the IEs the correlation is almost equally excellent (\( R^2 > 0.991 \)).
This shows that the results calculated in paper II with the 6-311G(d) basis set are reliable and qualitatively sound.

\[ y = 0.281 + 0.985x \quad R^2 = 0.999 \]
\[ y = 0.383 + 0.948x \quad R^2 = 0.999 \]

Figure 17. Plots of EAs and IEs calculated with OVGF comparing the 6-311G(d) basis set and the two Dunning type basis sets, cc-pVTZ and aug-cc-pVDZ.

In principle the EAs and IEs calculated with the cc-pVTZ and aug-cc-pVDZ Dunning basis sets can be approximated by performing the calculation with a smaller basis set and then apply the correct equation. It could potentially be rewarding to investigate whether this relationship between the results from different basis sets can be applied for a more diverse set of molecules. That could potentially lead to large savings in computer time as the OVGF calculations are rather demanding.

5.1.3. Orbital Symmetry Considerations

The parent tria-, penta-, and heptafulvenes belong to the \( C_{2v} \) point group. The HOMO and LUMO will either belong to the \( b_1 \) or the \( a_2 \) irreducible representations. The orbitals of \( b_1 \) symmetry have a lobe at the exocyclic carbon while those of \( a_2 \) symmetry have a nodal plane going through the exocyclic double bond (Figure 18). The effect of an exocyclic substituent X will be larger on the \( b_1 \) symmetry orbitals as these have orbital density at this position.
Figure 18. The HOMO and LUMO of tria-, penta-, and heptafulvene as well as the dipole moments of these molecules calculated at B3LYP/6-311G(d) level.

In paper II the EAs and IEs were calculated for the fulvenes in Figure 19 at the OVGF/6-311G(d)//B3LYP/6-311G(d) level. Several of the compounds have previously been synthesized but the bulk of the calculations were performed on compounds yet to be realized.

Figure 19. The IE and EA of these fulvenes were calculated at the OVGF/6-311G(d)//B3LYP/6-311G(d) level.

The degrees of aromaticity of the initial and final states will influence the IEs and EAs. Those species which still can be drawn with an aromatic resonance structure in the final oxidized or reduced state will be stabilized (Figure 20). It is the tria- and heptafulvenes which retain an aromatic resonance structure upon electron removal and this will in turn give relatively low values of IE. The opposite is the case for the pentafulvenes because it is when they attain another electron that they retain the aromatic resonance structure and thus yield higher values of EA.
Figure 20. The range in IEs and EAs for differently substituted tria-, penta-, and heptafulvenes at the OVGF/6-311G(d)//B3LYP/6-311G(d) level. The values for the best donors (low IE) and best acceptor (high EA) have been underlined.

By comparing the ranges in IE and EA for the differently substituted fulvenes with the prototypical electron acceptor and electron donors TTF and TCNQ, it is seen that some of the fulvenes will outperform TTF or TCNQ. The degree of aromaticity and thus the “stabilities” were evaluated with the structural HOMA index (Figure 21). As some of the investigated compounds are influenced by antiaromaticity they might prove to be difficult synthetic targets. Interestingly, the best donors and the best acceptors have more aromatic HOMA values than the 2,3,4,5-tetrachloro-6,6-dicyanopentafulvene (Pf4) which is synthesizable and quite stable at ambient conditions. This shows that these fulvene donors and acceptors could serve as viable synthetic targets.

Figure 21. The IE or EAs as well as HOMA values for the best electron donors and acceptor compared with 2,3,4,5-tetrachloro-6,6-dicyanopentafulvene (Pf4).

It should be mentioned that out of the compounds calculated in paper II none have as high EA (4.35 eV) as that of the recently synthesized 6,6-
dicyanopentafulvene (Pf5) in Figure 22. This compound also shows an intense CT band with a \( \lambda_{\text{max}} \) at 782 nm (1.59 eV), and certainly deserves further attention in the future to understand the reason underlying the high EA and the low energy transition.

Figure 22. The 6,6-dicyanopentafulvene synthesized by Diederich and co-workers.

5.2. Donor-Acceptor Dyads

What will happen if one of the best donors is connected to one of the best acceptors and form a donor-acceptor dyad (Figure 23)? The incorporation of a fulvene unit into a larger \( \pi \)-system can yield molecules with interesting and peculiar properties that potentially can be used in functional materials. In this section we will see what happens with the IEs and EAs when two (un)substituted fulvenes are fused into a bis(fulvene). For classes B and C it is the heptafulvene segment which behaves as the electron donor while in the class A the donor is made up of the pentafulvene segment as it would have two amino groups at the exocyclic position (Figure 23).

Figure 23. The bis(fulvene)s included in the donor-acceptor dyads.

Interestingly, even though the HOMO and LUMO of the dyad belong to the same irreducible representation both orbitals are very much characterized by the original fragment orbitals, \( i.e., \) those originating from the fulvenes. The
EAs and IEs which are intrinsic properties of LUMO and HOMO do not change to any large degree when the donor-acceptor dyad is formed from its fragment orbitals (Figure 24).

Figure 24. Combination of donor and acceptor into a donor-acceptor dyad.

It is also clear from Table 2 that the EAs and IEs are largely characterized by the original fragment orbitals as the EAs and IEs of the fragment orbitals are given in parenthesis. The dipole moments signify a large degree of charge transfer in the ground state which is a prerequisite for a molecule to function as an organic metal. These compounds could potentially show electrochemically amphoteric properties, i.e., they could function as both an electron acceptor and an electron donor.

It should now be clear that fulvenes and related compounds have very interesting electronic properties in the ground state, and if properly substituted, they could potentially be used for materials applications. In the following section the excited states of substituted pentafulvenes will be discussed.
Table 2. Calculated electron affinities, ionization energies, and dipole moments of the donor-acceptor dyads at the OVGF/6-311G(d)//B3LYP/6-311G(d) level. The EAs and IEs of the fulvenes constituting the segments are given in parenthesis. Values are given in eV and Debye. The compound names as well as Z and W are defined in Figure 23.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Z</th>
<th>W</th>
<th>EA</th>
<th>IE</th>
<th>Dipole</th>
</tr>
</thead>
<tbody>
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<td>IA</td>
<td>CN</td>
<td>NH</td>
<td>0.48 (0.53)</td>
<td>7.00 (7.07)</td>
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</tr>
<tr>
<td>IB</td>
<td>H</td>
<td>H</td>
<td>0.08 (n/a)</td>
<td>7.06 (7.12)</td>
<td>2.3</td>
</tr>
<tr>
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<td>NH₂</td>
<td>CN</td>
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<td>6.04 (6.35)</td>
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</tr>
<tr>
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<td>H</td>
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<td>6.86 (7.12)</td>
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<td>CN</td>
<td>1.22 (1.21)</td>
<td>6.15 (6.35)</td>
<td>14.3</td>
</tr>
</tbody>
</table>

5.3. Excited States of Pentafulvenes

It has now been shown that aromaticity plays a major role in the properties of fulvenes in the electronic ground state (Paper II). In this section the effect of substitution of pentafulvenes on the lowest triplet state (T₁) (anti)aromaticity and how this relates to the relative energy of the T₁ state will be discussed (Paper III).

As a consequence of the opposing electron counting rules for aromaticity in the singlet ground state (S₀; Hückel’s 4n+2 rule) and the lowest ππ* excited triplet state (T₁; Baird’s 4n rule) the dipole moments of fulvenes will have opposite directions (Figure 25). In the singlet ground state the pentafulvene ring will be influenced by a zwitterionic (Hückel aromatic) resonance structure with six π-electrons in the ring. In the T₁ state the pentafulvene ring will also be influenced by a zwitterionic (Baird aromatic) resonance structure but with four π-electrons in the ring.

![Figure 25](image)

*Figure 25. Properties associated with the different resonance structures of a 6,6-disubstituted pentafulvene.*
This means that if it is possible to change the relative influence of the two resonance structures by substitution the properties associated with these resonance structures should also change (Figure 25). If the exocyclic substituent X is an EDG then the resonance structure with six π-electrons will be enhanced and increase the influence of aromaticity in the singlet ground state. If the exocyclic substituent X is an EWG the effect will be opposite and the ground state will be destabilized while the T₁ will be stabilized. When considering ring substituents, the influence will be opposite, i.e., an electron withdrawing group stabilizes the resonance structure with six π-electrons and thus stabilizes the S₀ state relative the T₁ state.

5.3.1. Rotation about the Exocyclic Bond of Substituted Pentafulvene

In an attempt to validate our DFT results as well as to understand the excited states of substituted pentafulvenes, the two lowest excited triplet states were calculated in planar and perpendicularly twisted conformations constrained to C₂ᵥ symmetry (Figure 26). The T₁ state (1³B) is mainly characterized by a HOMO to LUMO excitation and is more stable at a planar (1³B₂) conformation than the perpendicularly twisted (1³B₁) conformation. The T₂ state (1³A) is mainly characterized by a HOMO-1 to LUMO transition and is more stable close to the perpendicularly twisted (1³A₂) conformation than the planar (1³A₁) conformation at the DFT level of theory.

![Figure 26](image_url)

Figure 26. The general shape of the energy surfaces along the rotation of the exocyclic bond of substituted fulvenes.

When the calculations are performed with CASPT2 optimized geometries, both the planar and perpendicular conformations are almost isoenergetic for X = CN (Table 3). The relative energies calculated at the OLYP level of theory are otherwise in good agreement with the CASPT2 optimized structures ($R^2 = 0.983$).
Table 3. Relative energies of the lowest triplet excited states of substituted fulvenes calculated at planar and perpendicularly twisted exocyclic bond. All compounds are in \( C_2 \) symmetry. The number of active orbitals is the same as the number of active electrons. CASSCF and CASPT2 calculations were performed with the ANO-S basis set.

<table>
<thead>
<tr>
<th>X</th>
<th>( \omega )</th>
<th>Electronic state</th>
<th>(U)OLYP// cc-pVTZ(^a)</th>
<th>Active space</th>
<th>CASPT2//CASSCF</th>
<th>Active space</th>
<th>CASPT2(^a)</th>
</tr>
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</tr>
<tr>
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<td>2.2.4.4</td>
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<td>51.3</td>
<td>2.3.4.3</td>
<td>42.7</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Performed by Prof. Raül Crespo at Universitat de València.
\(^b\) Performed with the 6-311+G(d) basis set.

5.3.2. The Gauge Including Atomic Orbitals Method for Nuclear Magnetic Shieldings

To calculate magnetic properties the gauge including atomic orbitals (GIAO) method can be used.\(^97\) The NMR shielding is a tensor property which can be divided into its \( x \), \( y \), and \( z \) tensor components. In this thesis the GIAO method is used to calculate the nucleus independent chemical shifts (NICS) which are used to evaluate aromaticity in the next section. The NICS values are taken as the negative of the calculated shielding. The GIAO method can also be used in the prediction of NMR chemical shifts and help in the assignment of peaks in experimental spectra.\(^98\)

5.3.3. The Connection Between Aromaticity and the Singlet-Triplet Energy Gap

The singlet-triplet energy gap (\( \Delta E_{ST} \)) of 49 differently substituted pentafulvenes were calculated at the (U)OLYP/6-311+G(d) level. The relative energies were compared to the aromaticity differences between the \( S_0 \) and \( T_1 \) states as quantified by the difference in NICS(1) values (\( \Delta \text{NICS}(1)_{ST} \)) and HOMA values (\( \Delta \text{HOMA}_{ST} \)) between the two states (Figure 27). There is an excellent correlation (\( R^2 = 0.963 \), Figure 27) between \( \Delta E_{ST} \) and the aromaticity changes, as described by NICS(1), when going from \( S_0 \) to \( T_1 \) for the differently substituted fulvenes. If the aromaticity is described by the HOMA
aromaticity index the correlation with $\Delta E_{ST}$ ($R^2 = 0.568$, Figure 27) is not as good.

Figure 27. Relationships between $\Delta E_{ST}$ and aromaticity differences as described by NICS(1) and HOMA. A) $\Delta E_{ST}$ vs. $\Delta$NICS(1)$_{ST}$ ($R^2 = 0.963$) B) $\Delta E_{ST}$ vs. $\Delta$HOMA$_{ST}$ ($R^2 = 0.568$).

The excellent correlation found between $\Delta$NICS(1)$_{ST}$ and $\Delta E_{ST}$ indicates that the magnitude of effect that a certain substituent has in $S_0$ should be proportional but opposite in the $T_1$. This means that $\Delta E_{ST}$ can be predicted by knowing only ground state aromaticity. The plot of $\Delta E_{ST}$ against NICS(1)$_{S0}$ shows a relatively good correlation ($R^2 = 0.878$, Figure 28) supporting that $\Delta E_{ST}$ can be predicted from the aromaticity of the ground state.

Figure 28. Relationship between $\Delta E_{ST}$ and NICS(1)$_{S0}$ ($R^2 = 0.878$).

In conclusion, the relative energy of the $T_1$ state can be manipulated by substitution. The energy ordering of $S_0$ and $T_1$ can even be reversed by making the $S_0$ state strongly antiaromatic, and the $T_1$ state aromatic. So by having strong electron acceptors like CN or CF$_3$ at the exocyclic position and strong
electron donors such as NH₂ or OH on the ring one can change the order of the S₀ and T₁ states. This would mean that the ground state is a triplet, a feature which could be interesting for the design of a molecular magnet.⁹⁹

5.3.4. NICS-scan on a Potential Ground State Triplet

According to OLYP calculations 6,6-dicyano-2,5-dihydroxyfulvene has a triplet ground state while at the CASPT2 level the singlet state is more stable by 4.5 kcal/mol. The aromaticities of the parent pentafulvene and 6,6-dicyano-2,5-dihydroxyfulvene were evaluated by the NICS-scan protocol. The NICS-scan offers an alternative method for evaluating aromaticity as it does not depend on the positioning of a single ghost atom.³⁶,¹⁰⁰ From the isotropic chemical shift as well as its out-of-plane component it can be seen that the pentafulvene is less influenced by aromaticity in the T₁ state than in the S₀ state (Figure 29A and C). The opposite is true for 6,6-dicyano-2,5-dihydroxyfulvene as the out-of-plane component in the T₁ state has a minimum while it behaves as an antiaromatic compound in the S₀ state (Figure 29B and D).
Interestingly, there is a strong resemblance between pentafulvene in the S0 state (Figure 29A) and 6,6-dicyano-2,5-dihydroxyfulvene in the T1 state (Figure 29D). This resemblance suggests that the T1 state of 6,6-dicyano-2,5-dihydroxyfulvene should be termed non-aromatic in the same way as the S0 state of the parent pentafulvene is non-aromatic.

5.3.5. Dependence of HOMA, NICS, and $\Delta E_{ST}$ on the C-C Bond Lengths

Partial geometry optimizations were performed in order to deduce how the calculated properties of pentafulvenes vary as a consequence of bond length alteration. The r1 bond was constrained to values between 1.34 and 1.50 Å at 0.02 Å intervals while all other geometric parameters were allowed to relax.
fully during the optimization (Figure 30). The same procedure was performed for the two $r_2$ bonds when varied in the range 1.32 - 1.46 Å.

\[ \text{Figure 30. Partial optimizations with either } r_1 \text{ or } r_2 \text{ frozen.} \]

The OLYP/6-311+G(d) optimized values for $r_1$ and $r_2$ are 1.473 and 1.360 Å for the parent pentafulvene. When shortening the $r_1$ bond or elongating the $r_2$ bonds in relation to their optimal values the $S_0$ state is destabilized while $T_1$ is stabilized, thus leading to a lower $\Delta E_{ST}$ (Figure 31A and B). Interestingly, the relationship between the bond lengths and the relative energies of the two states is not linear. Instead, it is the energy difference between the two states that is linear in relation to the bond lengths.

When investigating the relationship between bond lengths and HOMA values it becomes apparent that HOMA to a large degree only describes the bond length deviation from the optimal bond length of benzene (1.388 Å) (Figure 31C and D). Still, the difference in HOMA values between the two states is linearly dependent on the bond length. The HOMA index should thus be used with care on bond length distorted molecules and possibly be complemented with another aromaticity index in order to get a better view of the aromaticity of an annulene.
Figure 31. The dependence of the relative energy and energy difference of S₀ and T₁ as well as HOMA on bond lengths.

A comparison between the HOMA and NICS aromaticity indices is particularly interesting with regard to how they vary with bond lengths and ΔE_{ST}. The aromaticity indices should ideally display the same behavior if the two indices measure the same property, in this case aromaticity (Figure 32). The HOMA values show a decrease in aromaticity for both S₀ and T₁ as ΔE_{ST} increases toward higher values. This is in contrast to the aromaticity as measured by NICS(1) which shows that the T₁ state aromaticity decreases while the S₀ state aromaticity increase as ΔE_{ST} goes to higher values.

A similarity between the two indices is that they both reveal that the aromaticity differences between the S₀ and T₁ states decrease as the energy differences between the states become smaller. This could potentially lead to a T₁ state which is more aromatic than the S₀ when the energy difference between the states decreases. Such a situation is found in the case of the HOMA index (Figure 32A) where the bond lengths of the T₁ state pentafulvene to a larger degree resemble those of benzene than the bond lengths of...
the $S_0$ pentafulvene. It should finally be mentioned that a change in the $r_2$ parameter has a larger influence on the graphs than $r_1$ as there are two $r_2$ bonds while there is one $r_1$ bond (Figure 31).

![Graph A](image1)

![Graph B](image2)

![Graph C](image3)

![Graph D](image4)

*Figure 32. $\Delta E_{ST}$ plotted versus HOMA and NICS(1) for fulvenes with frozen $r_1$ or $r_2$ bond lengths. The $r_1$ bond length is varied from 1.34 to 1.50 Å and the $r_2$ bond lengths are varied from 1.46 to 1.32 Å. The increment is 0.02 Å.*

The implication of this investigation is that the introduction of large substituents might alter the geometry of the fulvene, and thus HOMA, more than it actually changes the aromaticity. This could be an explanation as to why the correlation between HOMA(1) and $\Delta E_{ST}$ is worse than that found between NICS(1) and $\Delta E_{ST}$. 


5.4. \( \pi \)-Electronic Structure of Other Fulvenoid Compounds

Now we know that the relative (anti)aromaticity of the electronic ground state and excited states influence the energies of the respective states. In the following section the changes in electronic structure as a consequence of structural alterations in a set of fulvenes and fulvalenes will be investigated. Here we will mix compounds with five-, six- and seven-membered rings and see how the compounds distribute their \( \pi \)-electrons between the different rings when going from the electronic ground state to either the triplet or the quintet excited states.

5.4.1. Fulvenes and Fulvalenes Investigated by the \( \pi \)-Component of the Electron Localization Function

For an explanation of the ELF\( _{\pi} \) the reader is referred to Chapter 4.1.3. Pentafulvene (13) is a non-aromatic compound when in the S\(_0\) state; on the other hand this cannot be said for the triplet state where the molecule displays a significantly larger degree of cyclic delocalization (Figure 33). The same is seen for isobenzofulvene (14) where the \( \Delta BV(\text{ELF}_{\pi}) \)s are much lower in the two rings when in the excited state. It thus seems that the benzannulation of pentafulvene destabilizes the ground state but stabilizes the triplet excited state which is also indicated by the low energy of the triplet state (0.51 eV).

When it comes to the heptafulvene in the S\(_0\) state (15) it can also be described as non-aromatic with relatively isolated double bonds. Interestingly, the T\(_1\) state has a more delocalized \( \pi \)-electron network, however, it contains one break in the network. The influence that benzannulation has on heptafulvene, upon isobenzoheptafulvene (16) formation is opposite to that of pentafulvene. The relative energy of the triplet excited isobenzoheptafulvene is higher than that of the parent heptafulvene in T\(_1\). This is probably due to the aromaticity of the benzene ring which is decreased significantly when the isobenzoheptafulvene goes from the S\(_0\) state to the T\(_1\) state.
Figure 33. BV(ELF$_\pi$) and ΔBV(ELF$_\pi$) (bold) calculated at the OLYP/6-311G(d,p) level. The bonds are drawn as single (BV(ELF$_\pi$) < 0.65), single plus dashed (0.65 ≤ BV(ELF$_\pi$) < 0.96), and double bonds (0.96 ≤ BV(ELF$_\pi$)). The relative energy (in eV) is given in parenthesis. The superscript indicates the electronic state.

The pentaheptafulvalene (17) and [5.6.7]quinarene (18) were investigated in their planar and perpendicularly twisted conformations in both the S$_0$ and Qu$_1$ states. The $\pi$-electron delocalization across the interring bond decreases as planar pentaheptafulvalene ($^1$17) goes to the Qu$_1$ state, thus indicating an influence of the resonance structure containing cyclopentadienyl cation (cp$^+$) and tropylium anion (hp$^-$) rings (Figure 34). When going from the planar $^5$17 to the perpendicularly twisted pentaheptafulvalene ($^5$T17) the influence of the zwitterionic resonance structure increases. Similar incremental increases of aromaticity are seen if one proceeds from $^1$17 via the perpendicularly twisted pentaheptafulvalene $^1$T17 to $^5$T17.
Figure 34. $\text{BV(ELF}_\pi\text{)}$ and $\Delta\text{BV(ELF}_\pi\text{)}$ calculated at the (U)OYLP/6-311G(d,p) level. The bonds are drawn as single ($\text{BV(ELF}_\pi\text{)} < 0.65$), single plus dashed ($0.65 \leq \text{BV(ELF}_\pi\text{)} < 0.96$), and double bonds ($0.96 \leq \text{BV(ELF}_\pi\text{)}$). The dashed single bonds are not included in the $\text{ELF}_\pi$. The energy (in eV) relative to the planar singlet state is given in parenthesis. The superscript indicates the electronic state.

When going from the $S_0$ to the $Q_{u1}$ state of [5.6.7]quinarene (18) the delocalization across the interring bonds decrease for the bond close to the 5-ring but increase for the bond interlinking the 7- and 6-ring (Figure 35). There is no general increase in cyclic delocalization as indicated by the relatively constant $\Delta\text{BV(ELF}_\pi\text{)}$. If the $S_0$ state of [5.6.7]quinarene (18) is twisted to its perpendicularly twisted conformation (1T18) a large increase in cyclic delocalization is seen. The level of aromaticity in the twisted conformation is reflected in the low relative energy of 1T18 (0.93 eV). When going from the perpendicularly twisted singlet to the quintet state (5T18) a decrease in cyclic delocalization is seen for the 5- and 7-ring but the 6-ring shows the same degree of cyclic delocalization as the twisted singlet. This indicates that the $Q_{u1}$ state of [5.6.7]quinarene is influence by Hückel type aromaticity with $4n+2$ $\pi$-electrons in the 6-ring.
The most fascinating finding is that the Qu₁ of [5.6.7]quinarene (\(^5\text{18}\) and \(^5\text{T18}\)) is influenced by both Baird \(4n\pi\)-electron aromaticity as well as Hückel \((4n+2)\pi\)-aromaticity (Figure 36). This can be understood by considering that the [5.6.7]quinarenes excitation is mostly localized to the 5- and 7-ring. This suggests that the 6-ring can be viewed as being in the singlet ground state as it is unaware of the molecule being in an excited state if the excitation is localized to the outer 5- and 7-rings.

Figure 36. Aromatic resonance structures influencing [5.6.7]quinarene.

In this chapter the focus has been on how the \(\pi\)-electronic structure can adopt to different electronic states so as to attain as much aromaticity as possible, i.e., the compounds are aromatic chameleons.
6. Excited State Properties of Substituted Fluorenones and Dibenzofulvenes

In the previous chapter we learned that fulvenes and fulvene like compounds possess an array of interesting properties in both the ground and the excited states (Paper V). A difficulty with these fulvenoids is that they are generally difficult to synthesize and are quite often unstable. In this chapter we will build on the knowledge from the previous chapter and apply it on compounds which are more accessible. The fluorenones and dibenzofulvenes fulfill the criteria of being stable, relatively easy to synthesize, and have the basic features of a fulvene (Figure 37). Before describing the properties of these compounds I will discuss their syntheses.

![Figure 37. The 2,7-disubstituted fluorenones and dibenzofulvenes investigated in this section.](image)

6.1. Synthetic Aspects

The synthesis of these compounds is rather pedagogical as most synthetic steps involve a color change and a distinctly different behavior on silica. One of the largest difficulties with the synthesis was solubility, which was only solved at a later stage of the project when \(N,N\)-dihexylamino groups were introduced, however, we started out with simple \(N\)-methylation. With certain methods of \(N\)-methylation of amines there is a risk of over-alkylation, i.e., the forming a quaternary ammonium salt, but this is not the case with the method used to synthesize \(\text{Fl-\text{NMe}_2}\) (Scheme 1).\(^{101-103}\) It has been proposed that the mechanism proceeds via an intermediate imine and an iminium cation which are subsequently reduced by sodium borohydride to form the
product. A further advantage of this procedure is that if the amino groups are not fully dimethylated it is easy to run the reaction a second time with the crude product. The oxidation of fluorene $\text{Fl-NMe}_2$ to form the fluorenone derivative $\text{FlO-NMe}_2$ was performed in a DCM/DMSO mixture with cesium carbonate under aerobic conditions. The subsequent Knoevenagel condensations were performed under solvent free conditions. The fluorenones, $\text{FlO-NO}_2$ or $\text{FlO-NMe}_2$, malononitrile, and ammonium acetate were ground to a fine powder and heated at 75-80 °C in a round-bottom flask to attain the dibenzofulvenes product $\text{FlCN-NO}_2$ or $\text{FlCN-NMe}_2$.

To achieve compounds with higher solubility the methyl groups had to be exchanged to longer alkyl groups. A different approach was taken in the synthesis of the $N,N$-dihexyl derivatives (Scheme 2). Starting from the commercially available 2,7-dinitrofluorenone ($\text{FlO-NO}_2$) the corresponding diamine, $\text{FlO-NH}_2$, could be afforded through reduction with tin(II)chloride in refluxing ethyl acetate. In the $N$-alkylation of $\text{FlO-NH}_2$ there had to be a trade off with regard to which alkylidiodide to chose as the shorter iodoalkanes tend to overalkylate amines, while the longer ones gave poor yield. Using 1-iodohexane in the presence of K$_2$CO$_3$ seemed to be a reasonable choice giving a total yield of 11 % for the dialkylation of the two amino groups. The final dibenzofulvene was afforded through Knoevenagel condensation of $\text{FlO-NO}_2$ with malononitrile. This reaction was performed in a water and ethyl acetate mixture and was stirred vigorously at 70 °C for 24 h giving a yield of 67 %.
Scheme 2. (i) SnCl₂, EtOAc, reflux, 24 h, 33%. (ii) C₆H₁₃I, K₂CO₃, EtOH, reflux, 96 h, 11%. (iii) malononitrile, NH₄OAc, H₂O:EtOAc (1:1), 70 °C, 24h, 67%.

After accomplishing the synthesis of all the compounds their properties were evaluated by UV-Vis spectroscopy and time-dependent density functional theory calculations, and is discussed in the following section.

6.2. Excited State Properties of Substituted Fluorenones and Dibenzofulvenes

The excited state properties of the newly synthesized fluorenones and dibenzofulvenes were studied by UV-Vis spectroscopy and as a tool to interpret the results time-dependent density functional theory (TD-DFT) computations were used.

6.2.2. Time-Dependent Density Functional Theory

To fully understand the results of UV-Vis spectroscopy the use of TD-DFT calculations to model the excited states has become a useful tool. These allow for the calculation of vertical excitation energies and oscillator strengths for the different transitions. TD-DFT calculations also give the ground state orbital contributions to the different transitions and thus contains information regarding the character of the transition, whether being \( n \rightarrow \pi^* \) or \( \pi \rightarrow \pi^* \). In the current implementation of TD-DFT it is also possible to perform geometry optimizations of the excited states in the presence of solvents, thus permitting the calculation of emission spectra. The M06-2X functional was used and is an overall good choice when performing calculations of excited states for both singlet and triplet states. To attain good agreement with experimental results which were performed in different solvents a solvent model was used when performing geometry optimizations and the TD-DFT calculations. One such solvent model is the polarizable continuum model.
6.2.3. Polarizable Continuum Model (PCM)

The default case in quantum chemical calculations is to perform the calculation in the gas phase. This means that the molecule is isolated in space and does not interact with its environment. In order to account for solvent interactions a solvent model can be used. The one used in Paper V is the integral equation formalism polarizable continuum model (IEF-PCM). \(^{112}\) In this model the investigated molecule is placed inside a cavity of a continuous dielectric medium which is mainly characterized by a dielectric constant, \(\varepsilon\). The molecule and the medium are mutually allowed to be polarized by the other. The use of a solvent model is especially important if the goal of the investigation is to compare the calculated results with experiments performed in different solvents. The PCM model comes to its own right when comparing the TD-DFT results with the experimental spectra given in Paper V. For the remainder of this chapter only the gas phase results will be discussed and how the transitions can be tuned by substitution.

6.2.4. Exchange of O for C(CN)$_2$

In this and the following section the results from the TD-DFT calculations and the UV-Vis spectra will be discussed. To make proper comparisons between the transitions for the different compounds the character of the transition should be the same and the involved orbitals should be comparable.

To compare fluorenone (FIO) and the dibenzofulvene (FICN) we first have to find transitions which are equivalent (Table 4). The lowest energy transition of FIO is an \(n \rightarrow \pi^*\) transition which involves the carbonyl oxygen, and does not have a good counterpart on FICN. The transition of FIO to \(S_2\) on the other hand, is a \(\pi \rightarrow \pi^*\) transition of \(B_2\) symmetry which corresponds to the \(S_1\) transition of FICN. This \(B_2\) symmetric transition of FICN is a HOMO to LUMO transition and is 0.6 eV lower in energy than the corresponding \(B_2\) symmetric transition of FIO. The \(S_2\) transition of FICN is of \(\pi \rightarrow \pi^*\) character which corresponds to a HOMO-1 to LUMO transition.

Table 4. Calculated lowest two vertical excitation energies (eV) and the corresponding oscillator strength (\(f\)) calculated at the TD-M06-2X/6-311+G(2d,p)//B3LYP/6-311G(d,p) level.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Transition</th>
<th>Character</th>
<th>(\Delta E) [eV]</th>
<th>(f) (x 10$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FIO ((C_{2v}))</td>
<td>(S_0(1^1A_1) \rightarrow S_1(1^1A_2))</td>
<td>(n (b_2) \rightarrow \pi^* (b_1))</td>
<td>3.24</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>(S_0(1^1A_1) \rightarrow S_2(1^1B_2))</td>
<td>(\pi (a_2) \rightarrow \pi^* (b_1))</td>
<td>3.56</td>
<td>4.0</td>
</tr>
<tr>
<td>FICN ((C_{2v}))</td>
<td>(S_0(1^1A_1) \rightarrow S_1(1^1B_2))</td>
<td>(\pi (a_2) \rightarrow \pi^* (b_1))</td>
<td>2.96</td>
<td>0.4</td>
</tr>
<tr>
<td></td>
<td>(S_0(1^1A_1) \rightarrow S_2(1^1A_1))</td>
<td>(\pi^* (a_2) \rightarrow \pi^* (b_1))</td>
<td>3.89</td>
<td>444.1</td>
</tr>
</tbody>
</table>
Figure 38. The orbitals involved in the two lowest transitions of FIO and FICN calculated at the TD-M06-2X/6-311+G(2d,p)//B3LYP/6-311G(d,p) level.

We have now seen that the $B_2$ transitions of FIO and FICN are comparable as they are mainly characterized by orbitals with similar nodal patterns (Figure 38). In the following section we will see how transitions change when the compounds are disubstituted in the 2- and 7- positions.

6.2.5. Substitution at the 2- and 7- positions

Before discussing the substituents effect on the transitions we should start by discussing how the frontier orbitals are influenced by substitution. The symmetries of LUMO ($b/b_1$), HOMO ($a/a_2$), and HOMO-1 ($b/b_2$) of FIO and its derivatives enable a comparison between the orbitals on the different compounds. The nitro groups have the largest orbital density in the LUMO while for the dimethylamino groups it is the HOMO which has the highest orbital density at the substituents (Figures 7 in Paper V).

The situation is slightly different for FICN and its derivatives as there is a deviation with regard to the shape of one orbital. The LUMO, HOMO, HOMO-1 all belong to the $b/b_1$, $a/a_2$, and $b/b_1$ symmetries. The HOMO-1 of FICN-Me$_2$ has a markedly different shape when compared to HOMO-1 of FICN and FICN-NO$_2$ (Figures 8 in Paper V).

Through the 2,7-disubstitution the transitions of FIO and FICN can be further tuned (Table 5). The lowest energy transition for FIO is of $n \rightarrow \pi^*$ character and the second lowest is a $\pi \rightarrow \pi^*$ transition. This energy order is
still the same in \textit{FIO-NO}_2 but for \textit{FIO-NMe}_2 the order changes and the lowest energy transition is of $\pi \rightarrow \pi^*$ character.

For \textit{FICN} the two lowest transitions are of $\pi \rightarrow \pi^*$ character with the lowest transition being of $B_2$ symmetry. Introduction of nitro groups in the 2- and 7-positions increases the energy of the $B_2$ symmetric transition but also introduces an $n \rightarrow \pi^*$ as the second lowest transition. When the substituents instead are changed to dimethylamino groups the $B/B_2$ symmetric transition is significantly lowered in energy. The second lowest transition of \textit{FICN-Me}_2 is not comparable to the others as it originates from an orbital with a very different nodal pattern as compared to \textit{FICN} and \textit{FICN-NO}_2.

Table 5. \textit{The calculated lowest two vertical excitation energies (eV) and the corresponding oscillator strengths (f) calculated at the TD-M06-2X/6-311+G(2d,p)//B3LYP/6-311G(d,p) level.}

<table>
<thead>
<tr>
<th>Compound</th>
<th>Transition</th>
<th>Character</th>
<th>$\Delta E$ [eV]</th>
<th>$f$ (x $10^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>\textit{FIO-NO}<em>2 ($C</em>{2v}$)</td>
<td>$S_0(^1A_1) \rightarrow S_1(^1A_2)$</td>
<td>$n \rightarrow \pi^*$</td>
<td>3.18</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>$S_0(^1A_1) \rightarrow S_2(^1B_2)$</td>
<td>$\pi \rightarrow \pi^*$</td>
<td>3.70</td>
<td>91.3</td>
</tr>
<tr>
<td>\textit{FIO-NMe}_2 ($C_2$)</td>
<td>$S_0(^1A) \rightarrow S_1(^1B)$</td>
<td>$\pi \rightarrow \pi^*$</td>
<td>2.63</td>
<td>19.3</td>
</tr>
<tr>
<td></td>
<td>$S_0(^1A) \rightarrow S_2(^1A)$</td>
<td>$n \rightarrow \pi^*$</td>
<td>3.29</td>
<td>0</td>
</tr>
<tr>
<td>\textit{FICN-NO}<em>2 ($C</em>{2v}$)</td>
<td>$S_0(^1A_1) \rightarrow S_1(^1B_2)$</td>
<td>$\pi \rightarrow \pi^*$</td>
<td>3.25</td>
<td>20.0</td>
</tr>
<tr>
<td></td>
<td>$S_0(^1A_1) \rightarrow S_2(^1A_2)$</td>
<td>$n \rightarrow \pi^*$</td>
<td>3.89</td>
<td>0</td>
</tr>
<tr>
<td>\textit{FICN-NMe}_2 ($C_2$)</td>
<td>$S_0(^1A) \rightarrow S_1(^1B)$</td>
<td>$\pi \rightarrow \pi^*$</td>
<td>1.85</td>
<td>8.9</td>
</tr>
<tr>
<td></td>
<td>$S_0(^1A) \rightarrow S_2(^1A)$</td>
<td>$\pi \rightarrow \pi^*$</td>
<td>3.35</td>
<td>5.8</td>
</tr>
</tbody>
</table>

Interestingly, the $\pi \rightarrow \pi^*$ transition of $B/B_2$ symmetry is most influenced by the substitution in the 2- and 7-positions (Figure 39). This opens the possibility to selectively tune only one of the low energy transitions. If this selective tuning of different energy levels also can be transferred to the low lying states of triplet multiplicity it opens the possibility for applications in the field of dye-sensitized solar cells. This is because of the phenomenon called singlet fission where one photon can give two charge separated states and thus potentially two electrons.\textsuperscript{113,114} For a candidate compound to function as a singlet fissions dye a requirement on the order of the $S_n$ and $T_n$ state energies is that $2E(T_1) < E(S_1)$ and $2E(T_1) < E(T_2)$. The tailoring of compounds that fulfill these criteria could exploit excited state aromaticity and the findings shown within this thesis.

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The experimental absorption spectra for \textbf{FIO-NMe}_2 and \textbf{FICN-NMe}_2 are extraordinary as the minimum energy absorption is exceptionally red-shifted. The $\lambda_{\text{max}}$ for \textbf{FICN-Me}_2 is at $\sim$1.6 eV, but if the methyl groups are exchanged to hexyl groups the $S_0$ to $S_1$ transition is further red-shifted to 1.5 eV which is a very low energy transition for such a small molecule. Finding materials which absorb light at low energies is important as this allows a larger part of the solar spectrum to be harvested in photovoltaic cells.\textsuperscript{115}

\textbf{Figure 39.} Calculated transition energy (in eV) as a function of substituent at the 2- and 7-positions for different type of transitions.

\textbf{Figure 40.} Absorption spectra of \textbf{FIO-NMe}_2 (top), and \textbf{FICN-NMe}_2 (bottom) in toluene (black), dichloromethane (red), and acetonitrile (green). Spectroscopy performed by Dr. Martin Rosenberg at Copenhagen University.
We have now seen that fulvenoid species can display very interesting properties and could potentially be applicable in functional materials. Hitherto we have only discussed molecules as discrete entities, but what would happen to the fulvenes if they were put into a polymer, and how would the polymeric properties be influenced by the fulvenes? This is what will be discussed in the following chapter.
The field of conducting polymers shows a lot of promise as there is potential for a large array of applications (from solar cells to organic light emitting diodes (OLEDs)). In this chapter, the design of fulvene based polymers will be discussed and how these offer new insights which can be generally applicable to the design of conjugated polymers (Paper VI). There is a large number of review articles which discuss the design and properties of conjugated polymers.\textsuperscript{116-123} Also, the Nobel prize in chemistry year 2000 was awarded to Heeger, MacDiarmid, and Shirakawa for their work on conjugated polymers.\textsuperscript{124}

7.1. Conducting Polymers

A good introduction into the field of conducting polymers is given by polyacetylene (\textit{Figure 41}), which can be viewed as constructed from 1,3-butadiene fragments \((n = 1, \textit{Figure 42})\).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{polyacetylene.png}
\caption{The conjugated polymer polyacetylene drawn with Lewis structure (top) and with the p\textsubscript{\pi}-AOs responsible for the conjugation (bottom).}
\end{figure}

\text{1,3-Butadiene has four p\textsubscript{\pi}-orbitals of which two are doubly occupied and two are unoccupied. If the butadiene is extended with another butadiene fragment the orbitals on the first fragment will interact with the orbitals on the second fragment in a bonding and antibonding fashion, thus creating an energy splitting \((n = 2, \textit{Figure 42})\). If the elongation is continued the energy spacing between the orbital levels will become smaller resulting in bands of energies. The occupied bands of a polymer are called the valence band and the unoccupied bands are called the conduction band. The energy difference between the top of the valence band and the bottom of the conduction band is called}
the band gap and is an important parameter to categorize a polymer as a metal, semiconductor, or an insulator (Figure 42). In polymers the molecular orbitals can be called crystal orbitals, i.e., HOCO and LUCO correspond to HOMO and LUMO.

![Figure 42. Band structures that result from the energy splitting of discrete orbitals (n = 1). The infinite band can either have metallic, semiconducting or insulating properties depending on the band gap energy ($E_g$), which is the difference between the top of the valance band and bottom of the conduction band ($E_F$ = Fermi energy).](image)

Polyacetylene can be drawn in two different forms where the single and double bonds have changed places. If these were two resonance forms, all bonds would be of equal length, and the band gap of the polymer would be zero. However, this is not the case as the bond lengths alternate and to go from one form to the other an energy barrier has to be traversed.

### 7.2. Oligomer Extrapolations

One way of modeling in order to understand polymers, is to start from a smaller oligomer and than investigate how the properties of this oligomer changes as it is elongated. Depending on what kind of polymer is investigated different lengths have to be considered before saturation of a certain property has been reached. To get a crude approximation of for instance the
band gap a linear fit can be used when plotting the HOMO-LUMO energy gap of the oligomers against their reciprocal chain length (*Figure 43*). A linear fit will in general give a too low band gap for the extrapolated polymer band gap. This is because the HOMO-LUMO gaps reach saturation at a certain oligomer length at which point the values will bend toward higher values than would be predicted by a linear fit. To account for this, a second order polynomial fit can be used and only applied on values for oligomers of longer lengths (>6 subunits). One of the large issues that have to be considered when using oligomers to model polymers is the termination of the oligomers.

*Figure 43.* The HOMO-LUMO energy gap is extrapolated to the polymeric limit for oligomers with fulvenoid-enforcing (f) or quinoid-enforcing (q) end groups.

In paper VI we investigated end groups that either enforce a fulvenoid (f) or a quinoid (q) type structure (*Figure 44*). In *Figure 43* two different ways of terminating the oligomers have been used to estimate the properties of the same three polyfulvenes and the results are tremendously different as is apparent. In a qualitative sense the extrapolated band gaps of the parent polyfulvene where \( X = H \) (0.51 eV (f) and 1.49 eV (q)) are in reasonable agreement with those at the valence effective Hamiltonian (VEH) level (0.87 eV (f) and 1.80 eV (q)) considering that the extrapolated structures are allowed to be non-planar while in the VEH they are not.
Figure 44. The two mesomeric forms of polyfulvene PFv-C₂H₂-X (X = H, CN, NH₂). Benzannulated polymers will be written as PFv-C₂H₂-X-Bz. Oligomers are named according to number of subunits followed by Fv-C₂H₂-X.

As a way to determine whether a structure is fulvenoid or quinoid the bond length difference between bonds C₁C₂ and C₂C₃ (BLA₁₂-₂₃ = C₂C₃ - C₁C₂) was calculated. If a BLA₁₂-₂₃ value is positive the structure is termed fulvenoid and if it is negative the structure is termed quinoid. The BLA₁₂-₂₃ values will form the beginning of the polymer discussions but first we have to introduce a way to model the polymers without the influence of end groups. This is done by performing calculations using periodic boundary conditions.

7.3. Periodic Boundary Conditions (PBC)

The modeling of an infinitely long polymer with only a limited number of atoms is enabled by the use of periodic boundary conditions (PBC). One can imagine that a small portion of the polymer is cut out and put in a box. This box can then mathematically be replicated in one, two, or three dimensions to achieve an infinite number of boxes. The number of particles in the box is always constant so if a particle leaves the box on one side it will come back on the opposite side. The box can be defined by translational vectors (TV) which link equivalent particles in adjacent boxes.

7.3.1. Fulvenoid or Quinoid Polyfulvenes

In Chapter 7.2 it was shown that the choice of end groups will strongly influence the results. We also introduced a way to model the polymers without the need of end groups by using periodic boundary conditions. What happens when we compare the results of the oligomer extrapolations and the PBC calculations? In Table 6 it is seen that the oligomeric BLA₁₂-₂₃ values converge toward the BLA₁₂-₂₃ values of the polymers when the number of subunits increase. When X = CN or H the quinoid-type structure is preferred and when X = NH₂ it is the fulvenoid-type structure which is preferred in the polymer. If the correct end group is chosen the oligomeric BLA value will almost be converged to the polymeric value already at the trimer. Interestingly, the CN group has a stronger influence on the structure of the oli-
ogomers than the choice of end groups. This gives oligomers which all are of quinoid structure because that is what the CN group has dictated as it has strongly stabilized the LUMO to the point that it is converted to the HOMO.

Table 6. BLA_12-23 values for oligomers of varying length (2-6 subunits) at the B3LYP/6-31G(d) level and for the polymer calculated at the PBC-B3LYP/6-31G(d) level. (f) signifies fulvenoid end groups and (q) quinoid end groups.

<table>
<thead>
<tr>
<th>Species</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>PBC-B3LYP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fv-C_2H_2-CN (f)</td>
<td>-0.087</td>
<td>-0.103</td>
<td>-0.103</td>
<td>-0.101</td>
<td>-0.101</td>
<td>-0.102</td>
</tr>
<tr>
<td>Fv-C_2H_2-H (f)</td>
<td>0.063</td>
<td>0.046</td>
<td>0.040</td>
<td>0.033</td>
<td>0.028</td>
<td>-0.085</td>
</tr>
<tr>
<td>Fv-C_2H_2-NH_2 (f)</td>
<td>0.031</td>
<td>0.026</td>
<td>0.026</td>
<td>0.025</td>
<td>0.025</td>
<td>0.024</td>
</tr>
<tr>
<td>Fv-C_2H_2-CN (q)</td>
<td>-0.112</td>
<td>-0.102</td>
<td>-0.102</td>
<td>-0.102</td>
<td>-0.102</td>
<td>-0.102</td>
</tr>
<tr>
<td>Fv-C_2H_2-H (q)</td>
<td>-0.101</td>
<td>-0.088</td>
<td>-0.087</td>
<td>-0.086</td>
<td>-0.086</td>
<td>-0.085</td>
</tr>
<tr>
<td>Fv-C_2H_2-NH_2 (q)</td>
<td>-0.110</td>
<td>-0.094</td>
<td>-0.088</td>
<td>-0.084</td>
<td>-0.081</td>
<td>0.024</td>
</tr>
</tbody>
</table>

We have already seen that the choice of end group will strongly influence the extrapolated band gap. If we compare the extrapolated band gaps with those calculated with PBC we see that when the correct end group is chosen the extrapolation works very nicely and yields a slightly underestimated band gap which is according to expectation (Table 7). Interestingly, when X = CN the oligomeric extrapolations using either fulvenoid- and quinoid-type end groups yield a similar band gap and it corresponds to the PBC band gap which is of a quinoid-type structure. If we now compare the results found for the BLA_12-23 values and the band gaps we find that when the BLA_12-23 values converge quickly to the value of the polymer, then the extrapolated technique will give a good approximation of the band gap.

Table 7. HOMO-LUMO energy gap (in eV) for oligomers of varying length (2-6 subunits) at the B3LYP/6-31G(d) level and for the band gap of polymers calculated at the PBC-B3LYP/6-31G(d) level. (f) signifies fulvenoid-enforcing end groups and (q) quinoid-enforcing end groups.

<table>
<thead>
<tr>
<th>Species</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>Band gap Extrapolated</th>
<th>Band gap PBC-B3LYP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fv-C_2H_2-CN (f)</td>
<td>1.87</td>
<td>1.75</td>
<td>1.69</td>
<td>1.66</td>
<td>1.65</td>
<td>1.53</td>
<td>1.74</td>
</tr>
<tr>
<td>Fv-C_2H_2-H (f)</td>
<td>2.05</td>
<td>1.61</td>
<td>1.33</td>
<td>1.14</td>
<td>0.99</td>
<td>0.51</td>
<td>1.71</td>
</tr>
<tr>
<td>Fv-C_2H_2-NH_2 (f)</td>
<td>2.90</td>
<td>2.54</td>
<td>2.36</td>
<td>2.30</td>
<td>2.22</td>
<td>1.87</td>
<td>1.98</td>
</tr>
<tr>
<td>Fv-C_2H_2-CN (q)</td>
<td>2.19</td>
<td>1.96</td>
<td>1.87</td>
<td>1.82</td>
<td>1.80</td>
<td>1.59</td>
<td>1.74</td>
</tr>
<tr>
<td>Fv-C_2H_2-H (q)</td>
<td>2.80</td>
<td>2.36</td>
<td>2.14</td>
<td>2.02</td>
<td>1.94</td>
<td>1.50</td>
<td>1.71</td>
</tr>
<tr>
<td>Fv-C_2H_2-NH_2 (q)</td>
<td>2.57</td>
<td>1.95</td>
<td>1.59</td>
<td>1.38</td>
<td>1.23</td>
<td>0.58</td>
<td>1.98</td>
</tr>
</tbody>
</table>

7.3.2. Effect of Benzannulation

Now that we have come to an understanding of how the polyfulvenes are influenced by the exocyclic substituent, X, we shall look at how the BLA_12-23 values and the band gap change upon benzannulation. When the exocyclic substituent is CN or H the polymer becomes less quinoid upon benzannulation but when it is NH_2 there is almost no change in BLA_12-23 (Table 8). In-
Interestingly, the band gap increases for the polymers having $X = \text{CN}$ and $H$ but decrease when the $X = \text{NH}_2$. The reason for the low band gap of the $\text{NH}_2$ substituted polyfulvene can be rationalized by investigating the MOs in a MO-mixing diagram (Figure 45).

Table 8. $\text{BLA}_{12-23}$ values and polymer band gap for the benzannulated polyfulvenes at the PBC-B3LYP/6-31G(d) level.

<table>
<thead>
<tr>
<th>Species</th>
<th>$\text{BLA}_{12-23}$</th>
<th>Band gap PBC-B3LYP</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{PFv-C}_2\text{H}_2\text{-CN-Bz}$</td>
<td>-0.049</td>
<td>1.88</td>
</tr>
<tr>
<td>$\text{PFv-C}_2\text{H}_2\text{-H-Bz}$</td>
<td>-0.042</td>
<td>2.24</td>
</tr>
<tr>
<td>$\text{PFv-C}_2\text{H}_2\text{-NH}_2\text{-Bz}$</td>
<td>0.023</td>
<td>0.95</td>
</tr>
</tbody>
</table>

The HOCO and LUCO of $\text{PFv-C}_2\text{H}_2\text{-NH}_2$ will interact in a in-phase fashion and an out-of-phase fashion with the HOMO and LUMO of the butadiene fragment to form the corresponding crystal orbitals of benzannulated $\text{PFv-C}_2\text{H}_2\text{-NH}_2\text{-Bz}$. The fragment orbitals of equivalent symmetry will interact. This means that the HOCO of the polymer will interact with the HOMO of the butadiene fragment to create two new orbitals where one is stabilized and the other is destabilized. The interaction between LUCO of $\text{PFv-C}_2\text{H}_2\text{-NH}_2$ and LUMO of butadiene will be in a similar fashion, but will give as stabilization of the newly formed $\text{PFv-C}_2\text{H}_2\text{-NH}_2\text{-Bz}$ LUCO. This leads to a band gap of 0.95 eV for $\text{PFv-C}_2\text{H}_2\text{-NH}_2\text{-Bz}$ as HOCO will be destabilized through antibonding interaction and LUCO stabilized through bonding interactions.

![Figure 45.](image-url)

Figure 45. The MO diagram describing the benzannulation of $\text{PFv-C}_2\text{H}_2\text{-NH}_2$. The $\text{C}_2\text{H}_2$- linker is excluded for clarity. The energies of HOCOs and LUCOs are given in parenthesis.
7.3.3. Benzannulation and Aromaticity

The polyfulvenes which prefer the quinoid-type structure have negative HOMA values indicating antiaromaticity, while the fulvenoid-type structures have positive HOMA values indicating some influence of aromaticity. When the polyfulvenes are benzannulated the 5-rings become more influenced by antiaromaticity according to the HOMA index. For the benzannulated polymers with a large band gap the 5-ring is very antiaromatic, while the 6-ring is quite aromatic. This is in contrast to the low band gap polymer, PFv-C$_2$H$_2$-NH$_2$-Bz, were the 5-ring is comparatively aromatic and the 6-ring is relatively non-aromatic as compared to the other 6-rings.

![Figure 46. Bond lengths and HOMA values calculated at the PBC-B3LYP6-31G(d) level.](image)

It appears that there is no general effect of benzannulation, but the influence it will exert is governed by the bonding and anti-bonding orbital interactions between the butadiene fragment and the polyfulvene backbone.

In this chapter we have seen that band gaps below 1 eV can be achieved by substitution and benzannulation. The choice of end groups has also been shown to be of great importance if oligomer extrapolations are to give results which are in accordance with PBC calculations.
8. Concluding Remarks

In this thesis it is shown that with a basic knowledge of the aromaticity concept and how it influences the π-electron distribution, one can design molecules in a predictable way with targeted properties.

By adding ethylene or benzene fragments to a π-conjugated molecule the distribution of electrons can easily be altered. It is also shown that there still are mysteries regarding the origin of the $D_{6h}$ symmetric structure of benzene that need to be unraveled, even though this has been investigated for several decades.

It has been shown that the fulvenes and fulvene-like compounds can adapt their electronic structures to attain aromaticity in several different states displaying the aromatic chameleon property. The IEs and EAs of tria-, penta-, and heptafulvenes can easily be tuned by substitution which can be rationalized by orbital symmetry arguments and the aromaticity of the initial and final radical state. Substitution of pentafulvenes will also influence the singlet-triplet energy gap in a predictable fashion. This energy gap can even be tuned to the point where the energy ordering of the singlet and triplet states change giving a triplet ground state.

We have found that Hückel aromaticity with $4n+2$ π-electrons can have an influence in the excited states. This is applicable if the excitation can be localized to other parts of the molecule so that the ring displaying Hückel aromaticity is not aware of the fact that it is in an excited state.

By a spectroscopic and computational investigation of fluorenones and dibenzofulvenes we have shown that the $^1A \rightarrow ^1B$ transition can be tuned extensively by disubstitution in the 2- and 7-positions. Some of the investigated molecules have a low energy transition around 1.5 eV, which is rather extraordinary for a molecule of that small size.

Utilizing the tunability of the pentafulvene units we investigated how the polyfulvene band gaps could be varied. Band gaps below 1 eV were found by rational design of the polyfulvenes.

My hope is that you as a reader have enjoyed this thesis and that it has inspired you to design some new molecules to investigate in the future.
9.1. Aromaticitet

Aromaticitet är ett grundläggandebegrepp inom keminet och har använts för att förstå egenskaper hos många olika molekyler och tillstånd. I det elektroniska grundtillståndet är ringar med 
\[ 4n+2 \] \( \pi \)-elektroner aromatiska (Hückels regel) medan i det lägsta elektroniskt exciterade tillståndet med triplett multiplicitet (\( T_1 \)) så är ringar med 
\[ 4n \] \( \pi \)-elektroner aromatiska (Bairds regel). Att en molekyl är en triplett innebär att den har två oparade elektroner med samma spin (Figur 1).

\[ \begin{align*}
T_1 & \quad \text{Bensen} \quad 4n+2 \pi \text{-elektroner} \\
S_0 & \quad \text{cyclobutadien} \quad 4n \pi \text{-elektroner}
\end{align*} \]

Figur 1. Bensen har 
\[ 4n+2 \] \( \pi \)-elektroner och är aromatisk i grundtillståndet (\( S_0 \)) medan cyclobutadien har 
\[ 4n \] \( \pi \)-elektroner och är aromatisk i det lägsta exciterade triplett-tillståndet (\( T_1 \)).

Aromatiska molekyler uppvisar större stabilitet än motsvarande linjära föreningar. Dessutom brukar bindningslängder hos aromatiska föreningar sträva mot att vara lika långa. Slutligen så växelverkar aromatiska föreningar med externa magnetfält så att \( \pi \)-elektronerna börjar cirkulera i ringen (en ringström) och därmed generera ett eget magnetfält (jmf. spole i magnetfält). Med datorbaserad beräkningskemi kan man kvantifiera aromaticitet på ett indirekt sätt genom att utvärdera de ovannämnda egenskaperna.

En grupp av föreningar där aromaticitetsbegreppet är viktigt är polybenzenoida kolväten som diskuteras i nästa avsnitt.
9.2. Polybensenoida kolväten

Polybensenoida kolväten (PBH) tillhör en kategori av polyaromatiska kolväten med den enkla restriktionen att PBH endast har ringar med sex kolatomer (Figur 2). Med hjälp av π-bidraget till elektronlokaliseringsfunktionen (ELF_π) har graden av π-delokalisering och aromaticitet undersöks hos en rad polybensenoida kolväten. De beräknade ELF_π resultaten jämfördes med den kvalitativa beskrivningen av lokal aromaticitet hos de olika ringarna med sex kolatomer som kallas Clar strukturer.


![Clar struktur](image1)  ![ELF_π](image2)


9.3. Aromatiska kameleonter


Baserat på Hückels 4n + 2 regel för det elektroniska grundtillståndet (S_0) och Bairds 4n π-elektron regel för aromaticitet i det första elektroniskt excitierade triplett-tillståndet (T_1) kan aromaticiteten i de olika tillstånden enkelt regleras med substitution (Figur 3). Den elektroniska effekt en substituent
har i $S_0$ är den motsatta i $T_1$ vilket leder till att $S_0 - T_1$ energigapet kan varieras.

![Figure 3. Resonansstrukturken med 4π-elektroter i ringen är aromatisk i $T_1$ medan resonansstrukturken med 6π-elektroter är aromatisk i $S_0$.](image)

Kvantkemiska beräkningar visar att energiskilnaden mellan $S_0$ och $T_1$ är kopplad till aromaticitetskillnaden mellan de två tillstånden. För att kvantifiera aromaticiteten hos de två tillstånden används två så kallade aromaticitetsindex. Dessa index kan indirekt mäta hur aromatiskt ett system är och därmed kvantifiera denna egenskap. Det första indexet (NICS) är baserat på en aromatisk molekyls unika förmåga att växelverka med ett magnetfält. Det andra indexet (HOMA) är baserat på att aromatiska molekylers strävar att ha lika långa bindningslängder. Eftersom elektronräknereglerna för aromaticitet skiljer sig i $S_0$ och $T_1$ så kommer också en viss substituents effekt på aromaticiteten att vara motsatt i de två tillstånden. Det finns ett starkt samband mellan aromaticitetskillnaden och energigapet mellan grundtillståndet och det exciterade triplettillståndet. Dessutom visar det sig att genom att bara känna till grundtillståndets aromaticitet så kan vi förutspå energigapet till $T_1$.

Genom att använda de elektroniska effekterna av substituenter på specifika positioner är det möjligt att designa fulvener där ordningen på tillstånden har förändrats så att det exciterade tillståndet blir grundtillståndet och vice versa. Detta skulle ge ett triplett grundtillstånd vilket skulle kunna vara användbart för konstruktionen av exempelvis en molekylär magnet.

Sammanfattningsvis kan vi genom att förändra molekylära tillståndens aromaticitet också förändra molekylernas optiska och elektroniska egenskaper vilket kan leda till fördelar när man skall designa nya ljuvsönderande material för t.ex. solcellsapplikationer.

Med hjälp av π-komponenten av elektronlokaliseringsfuntionen (ELF$_\pi$) kunde föreningarnas π-delokalisering kvantifieras. Genom att studera besättningssgraden hos atomorbitalerna kunde vi följa hur elektrontätheten förändras då föreningarna går från $S_0$ till ett exciterat tillstånd.

Det visar sig att [5.6.7]quinaren (Figu 4) i det exciterade tillståndet är influerad av grundtillståndssromaticitet i den centrala 6-ringen. Denna influens blir starkare då ringarna vrids 90° grader i förhållande till varandra. I och med att dipolmomentet hos samtliga av de undersökta föreningarna är motsatta i grund- och exciterat tillstånd så skulle de kunna uppvisa ickelinjärt optiska egenskaper som är viktiga inom laserteknik.
Figur 4. Grundtillståndarsromaticitet kan göra sig gällande i exciterade tillstånd.

Eftersom många fulvener är svåra att framställa undersöktes föreningar som har liknande struktur men som är betydligt mer stabila. De optiska egenskaperna kan enkelt förändras med hjälp av den kunskap vi fått från de beräkningskemiska studierna av fulvenerna. FICN-NMe₂ har ett absorptionsmaximum vid ~1.6 eV men när metylgruppen byts mot en längre hexylgrupp ser vi en förändring på ~0.1 eV till 1.5 eV. Detta är väldigt låga excitationsenergier för så små föreningar, och jag tror det skulle vara mycket givande att undersöka deras halvledaregenskaper på olika ytor.

Figur 5. Några av de föreningar som har undersöktss experimentellt.

De aromatiska kameleonterna är alla intressanta ur en fotokemisk synvinkel eftersom deras optiska egenskaper enkelt kan förändras med substitution. Dessutom borde pentafulvenerna kunna finna tillämpningar som elektronacceptorer eftersom de på samma sätt som TTF kan vara aromatiska när de har tagit emot en elektron. I och med pentafulvenens justerbara elektriska och optiska egenskaper så är de också intressanta om man använder dem som monomerer i polymerer.

9.4. Ledande polymerer

Storleken hos bandgapet för ett material ger en indikation på om materialet är bra på att leda ström. Material brukar i detta hänseende kategoriseras som ledare, halvledare eller isolatorer. Polyfulvener med ett bandgap under 1.0 eV har designats av oss med hjälp av kvantkemiska datorberäkningar. Effekten av bensannulering och substitution av polyfulvenerna har undersömts på

De flest av de undersökta polyfulvenerna har bandgap under 2 eV, vilket klassificerar dem som halvledare. För att de skall leda ström vid rumstemperatur så krävs dock ett bandgap på mindre än 0.5 eV.

För att få en större förståelse för elektronstrukturen hos polyfulvenerna så beräknades också tillståndstätheten vilket kan liknas med antal kanaler som antingen elektroner eller hål kan färdas igenom.

Att designa polymerer med små bandgap handlar i stor utsträckning om att destabilisera en befintlig struktur på olika sätt. Vi visar att man kan utnyttja den lokala symmetriskillnaden mellan HOMO och LUMO för att destabilisera HOMO, alternativt stabilisera LUMO genom den exocykliska substituenten.

Figur 6. En polyfulven med bandgap under 1 eV.

9.5. Slutsats

Många av studierna i min avhandling är grundvetenskapliga. Det finns dock fulvenere med relativt hög stabilitet som skulle kunna utnyttjas i materialforskning. Genom rationell design kan nya intressanta föreningar designas som kan få tillämpningar inom många ämnesområden eftersom infogandet av ett fulvenfragment i en större förening öppnar för möjligheten att finjustera de optiska och elektroniska egenskaperna.
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