

π -Logic

Cover Based on Escher-type artwork provided by Dr. Joseph L. Teeters

π -Logic

M.H. van der Veen

Ph.D. Thesis

University of Groningen, The Netherlands

May 2006



The work described in this thesis was performed in the research group Chemistry of (Bio)Molecular Materials and Devices of the Stratingh Instituut, University of Groningen, The Netherlands.

MSC  ^{plus}

The work described in this thesis was financially supported by the

MSC^{plus}.

MSC^{plus} Ph.D. thesis series 2006-06

ISSN 1570-1530

ISBN 90-367-2518-6 (paperback version)

ISBN 90-367-2519-4 (electronic version)

Publisher Rijksuniversiteit Groningen, Groningen, The Netherlands

Printing Grafisch bedrijf Ponsen & Looijen BV, Amsterdam, The Netherlands

Copyright 2006, M. H. van der Veen

All rights reserved. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, recording, or otherwise, without permission from the author.

RIJKSUNIVERSITEIT GRONINGEN

π -Logic

Proefschrift

ter verkrijging van het doctoraat in de
Wiskunde en Natuurwetenschappen
aan de Rijksuniversiteit Groningen
op gezag van de
Rector Magnificus, dr. F. Zwarts,
in het openbaar te verdedigen op
maandag 22 mei 2006
om 14.45 uur

door

Maria Helena van der Veen

geboren op 13 januari 1978
te Hoogeveen

Promotor: Prof. dr. J. C. Hummelen

Copromotor: Dr. H. T. Jonkman

Beoordelingscommissie: Prof. dr. J. Knoester

Dr. S. Roth

Prof. dr. F. Wudl

Voor wie het leest

Yesterday is history

Today is a gift

Tomorrow is mystery

Mysteryland, 2005

Contents |

1 Molecular Electronics	5
1.1 On the Way to Molecular Electronics	6
1.2 The Conjugated Double Bond	7
1.3 Topological Aspects of Quasi-particles	9
1.4 Valence Bond Theory and Molecular Orbital Theory	11
1.5 Molecular Scale Electronics	12
1.6 Challenges	18
1.7 Thesis objectives	19
1.8 References	21
2 On the Classification of n-Terminal π-Conjugated Systems	27
2.1 Introduction	28
2.2 Systematic Analysis of n-Terminal Systems	30
2.3 Analysis of Fully Unsaturated n-Terminal Systems: Fundamentals, Definitions, and Conventions	33
2.4 Classification of n-Terminal π -Conjugated Systems	37
2.5 Generalized Analysis of n-Terminal Systems	44
2.6 Discussion	46
2.7 Conclusions	47
2.8 References and Notes	49
3 Topological Design of Omniconjugated Systems	53
3.1 Introduction	54
3.2 Wiring Molecular Wires	56
3.3 Design of Omniconjugated Models	58
3.3.1 Topological Design Program	58
3.3.2 Type B Omniconjugated Models	64
3.3.3 Quasi-omniconjugated Models	65
3.4 Topological Properties of Omniconjugated Models	67
3.5 Classification of n-Terminal π -Conjugated Systems: Extended	71
3.6 Real Chemical Examples of Omniconjugated Compounds	76
3.7 Conclusions	80
3.8 References and Notes	82

4 Electronic structure of Omniconjugated compounds	87
4.1 Introduction	88
4.2 Quantum-Chemical approach	89
4.3 Frontier Orbital Delocalization	91
4.4 Frontier Orbital Localization	94
4.5 Discussion and Conclusions	96
4.6 References	98
5 Group Theoretical Aspects: A Quest for Control and Understanding	101
5.1 Introduction	102
5.2 The Symmetry Properties of n-Terminal Systems	104
5.3 The Construction of a Group based on π -Topology	109
5.4 The Basis for Understanding π -Topological Properties	113
5.5 Mathematical Basis for the Design of π -Logic	119
5.6 Discussion	124
5.7 Conclusions	125
5.8 References and Notes	127
6 π-Logic: Topologies for Boolean Functions inside Single π-Conjugated Molecules	129
6.1 Introduction	130
6.2 Logic Gates from Two Switches Based on π -Conjugation	132
6.3 All Boolean Functions inside Compact π -Logic Gates	136
6.4 Increasing the Complexity: Bifunctional Logic Elements	141
6.5 On the Built-in Logic of n-Terminal π -Conjugated Systems	143
6.6 Discussion and Conclusions	148
6.7 References and Notes	151
Appendix A 5-Terminal Archetype Series	155
Appendix B G^{5A} Group Multiplication Table	156
Appendix C 6-Terminal Archetype Series	157
Appendix D Truth Tables of Boolean Functions	158

Contents

Summary	159
Samenvatting	161
Dankwoord	167

Chapter 1

Molecular Electronics

Abstract As the use of electronic systems become more vital to our society, demands for new technological developments are ever increasing. A brief overview of the history and developments within the field of molecular electronics is given in this introductory chapter. Here, molecular electronics refers to use of molecules to construct electronic devices on the nanoscale. Within this paradigm the flow of information is literally provided by the flow of (quasi-)particles. Most of the work in this field involves conjugated organic molecules in which charge transport is facilitated by π -orbitals. The first part of this chapter is devoted to the basic concepts and phenomena of π -conjugation relevant to the scope of this thesis. The emphasis in the second part is on single molecules that can mimic the behavior of conventional electronic components. This provides a basis for outlining the objective and motivation of the work presented in this thesis.

1.1 On the Way to Molecular Electronics

What will be the ultimate limit of the ever-decreasing size and increasing speed and complexity of electronic components? Will it be possible to create intellectual machines that have artificial neural networks, which mimic or are superior to humans in intellectual and cognitive capabilities? Are there any more fundamental physics left to discover or revolutionary technologies to develop? Decades from now, we will perhaps have answers to these questions. Right now, scientists are learning to further control and understand the properties of single molecules or assemblies of molecules with the objective to, for example, miniaturize the computer. Already in 1959, Richard Feynman discussed this issue during his famous and visionary lecture: "*There's Plenty of Room at the Bottom*".^[1] Feynman was one of the first scientists that recognized the challenges and possibilities of nanotechnology. In his lecture he called for making devices of extremely small dimensions:

“... The information cannot go any faster than the speed of light – so, ultimately, when our computers get faster and faster and more and more elaborate, we will have to make them smaller and smaller. But there is plenty of room to make them smaller. There is nothing that I can see in the physical laws that says the computer elements cannot be made enormously smaller than they are now. In fact, there may be certain advantages.”^[1]

One of the most famous axioms in computer industry is Moore's prediction from 1965. According to Intel co-founder Gordon Moore, the number of transistors per square centimeter of silicon doubles every 18 to 24 months.^[2] Moore's plot was originally used to determine the decrease in price per bit in memories. If plotted on a logarithmic scale, the decrease in size of micro-electronic components versus the year gives a straight line. In few decades to come, the dimensions of the components should approach the size of about one nanometer. Despite the fact that tremendous size-reduction (top-down approach) has been realized with (photo)lithographic techniques, there are signs that the conventional silicon transistor will soon reach its fundamental physical limitations of a few tens of nanometers.^[3] Currently there are no ways to overcome the problem of the leakage current approaching the order of magnitude of the signal current. An alternative approach is to use single molecules as basic components for electronic circuitry. Besides the advantage of their small size, molecules can have specific properties and behaviors that allow for tuning the functionality for specific applications. Molecules can be manipulated via synthesis or by means of self-assembly processes. The bottom-up approach, offered by the synthesis of molecules or nanostructures, has been proposed to be more promising than the downscaling of solid-state devices.^[4] When taking into account the relatively small mass of a large number of molecules

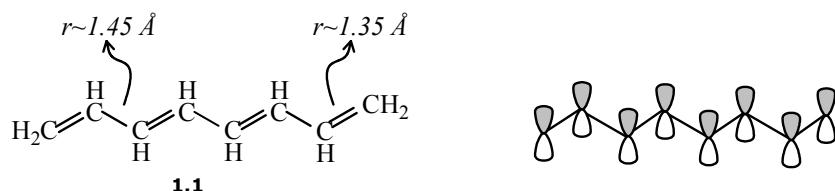


Figure 1.1 Schematic representation of the formation of π -bonds in the case of octatetraene (left), viewed from the most bonding pattern of p_z orbitals (right).

operating as, for example, switches, the bottom-up approach could result in much lower manufacturing costs. It is also envisaged that information processing at the molecular level can proceed at high speed while the required energy would be low.

1.2 The Conjugated Double Bond

One can trace the routes of interests in conjugated hydrocarbons to scientists that were trying to understand the phenomena of coloring in pigments and dyes, back in the nineteenth century.^[5] In those days, one of the most important contributions was made by August Kekulé. In 1865, he proposed that benzene is a six membered hydrocarbon ring consisting of double bonds separated by single ones.^[6] This double bond configuration is known as the Kekulé structure of benzene. The double bonds of benzene act collectively as manifested by their overlap and delocalization of π -electrons. As a result, conjugated double bonds give rise to interesting physical properties.

Linear conjugated pathways consist of strict alternating single and double bonds. Consider, for example, the octatetraene given in Figure 1.1. The bonding pattern between the two ends of this molecule is called a *conjugated pathway*. It is specified as *linear conjugated* and sometimes as *through conjugated*.^[7] The viewpoint for understanding the electronic properties of conjugated systems begins with the consideration of conjugated double bonds in terms of molecular orbitals. The mixing of π -orbitals in molecular orbitals comes with a significant gain in stability. The delocalization of π -electrons is usually found within the length of the conjugated path when the molecule is in a (nearly) planar conformation. This is also found for other multiple bonded units or atoms as long as the conjugation is maintained. For example, the lone-pair orbitals of nitrogen can be involved in the formation of the π -system when the nitrogen is incorporated in a hydrocarbon. Furthermore, the triple bonds of, for example, acetylene, which have a second out-of-plane π -orbital, can alternate with single bonds. Acetylenes are often used as conjugation spacers to prevent steric hindrance between adjacent hydrocarbon rings.

The electronic properties of conjugated systems depend on the kind of conjugation within the molecule. The delocalization of π -electrons becomes different

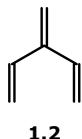


Figure 1.2 Cross-conjugated double bonds.

when cross-conjugated double bonds are involved. In a cross-conjugated pathway along adjacent sp^2 hybridized carbon atoms, the strict alternation of single and double bonds is interrupted by two consecutive single bonds at a point of cross-conjugation (see Figure 1.2).^[8] There is little interaction between π -orbitals left and right from the point of cross conjugation. Along such a cross-conjugated pathway there is a substantially lower degree of π -electron conjugation. This has been confirmed in several theoretical and experimental studies. For example, the electronic coupling parameter, which is a measure of the electronic interaction between two moieties in a molecule, can be severely reduced along cross-conjugated pathways compared with linear conjugated ones.^[9–12] As an other example, the maximum absorption wavelength of a molecule with a cross-conjugated π -system chromophore coincides often with that of the longest linear conjugated fragment of it.^[13–15] Hence, a lower degree of conjugation is ascribed to cross-conjugated systems compared to linear conjugated ones.

Standard empirical evidence of the importance of π -electron delocalization and how it differs between linear and cross-conjugated sites in a molecule can be found in any basic organic chemistry book. For example, the usual way to explain the behavior of mono-substituted benzenes in an electrophilic substitution reaction is based on the electronic effect that the substituent has on the other five carbon atoms in the ring.^[16] Certain substituents tend to activate the benzene ring and direct the second substitution to *ortho* and *para* positions, while other groups deactivate the *ortho* and *para* positions and, therefore, direct a second substitution toward *meta* positions. This can be fully explained on the basis of what is called the “resonance effect”. The resonance effect operates fully on the *ortho* and *para* positions, but little if at all on the *meta* position. This parallels the linear and cross-conjugation, existing between the substituents on the benzene ring in the *ortho* or *para* position on the one hand, and *meta* positions on the other. What is explained through the resonance effect in organic chemistry immediately surfaces from any modern and adequate calculation of static charges of the benzene ring carbon atoms in the starting material.^[17]

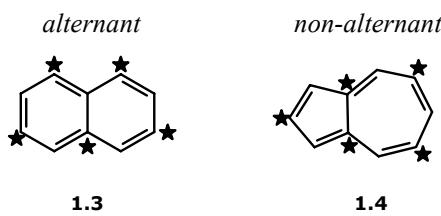


Figure 1.3 The starred and unstarred rule to divide polycyclic hydrocarbons in alternant (e.g., naphthalene 1.3) and non-alternant (e.g., azulene 1.4) classes.

Topological concepts that deal with the properties of conjugated hydrocarbons distinguish between linear and cross-conjugated bond sequences or deal with differences in connectivity such as alternant and non-alternant.^[18,19] According to the latter classification, the carbon atoms of (poly)cyclic hydrocarbons can be divided into two sets, called “starred” and “unstarred” (see Figure 1.3).^[20] The hydrocarbon is called alternant when neither set contains two adjacent atoms of the same kind. This criterion is not met with non-alternant hydrocarbons such as azulene **1.3**. Due to the odd-membered hydrocarbon ring the non-alternant azulene contains two adjacent atoms of the same set (here the “starred” carbons).

1.3 Topological Aspects of Quasi-particles

The foundations of molecular electronics were developed over the past fifty years.^[21] It began with the basic principles and ideas of the transmission of charges through organic materials, an aspect of prime importance in this field. Some older examples of studies on charge transport through molecules constitute crystals of anthracene^[22] and phthalocyanine.^[23] The breakthrough that boosted the interest in π -conjugated molecules came with the first description of the metallic complex of tetrathiafulvalene (TTF)^[24] and tetracyanoquinodimethane (TCNQ)^[25] in 1973. These findings led rapidly to the study of π -conjugated polymers. In 1974 it was found that polyacetylene (PA) can show metallic behavior upon exposure to dopants.^[26,27] This opened new perspectives in the field of conjugated polymers as active components in electronics. The electronic-structure aspects of π -conjugated systems play a key role in their charge transport capabilities. This makes the study of π -conjugated systems so fascinating.

The charge transport of electrons and/or holes in conjugated systems can be understood by considering their band structure. The basics are best presented with their simplest representative: *trans*-polyacetylene. From the viewpoint of solid state physics, the ideal situation is the metallic state (a one-dimensional system) in which the π -electrons are delocalized over the entire system.^[28] In physics, the existence of conjugated double bonds is explained by the electron-phonon coupling (Peierls distortion).^[29,30] An incompletely filled band of a one-dimensional system distorts so that a gap in the electronic density of states is obtained. This process is shown for *trans*-PA in Figure 1.4. Here, the π -electrons distribute unevenly (dimerization) over the bonds in such a way that there is an alternation of short and long C-C bonds (drawn as single and double bonds).

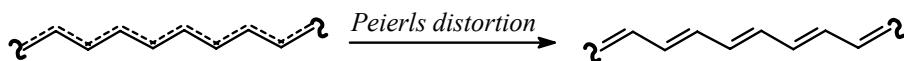


Figure 1.4 Schematic representation of the effect of electron-phonon coupling for a *trans*-PA with equal bond lengths (delocalized) yielding dimerized bonds (localized).^[35]

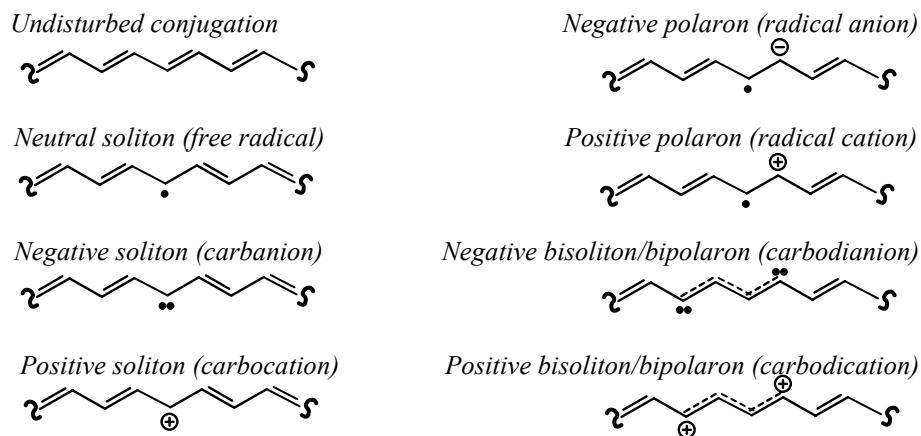


Figure 1.5 A physical-chemical representation of some quasi-particles in *trans*-PA.^[34]

The conductive behavior of conjugated systems results from introducing mobile charges via doping.^[31,32] This can be, for example, the injection of electrons in the empty conduction band above the gap (n-type doping). Positive charges (holes) are introduced in the valence band upon the removal of an electron (p-type doping). There are several kinds of “quasi-particles” that can be introduced in a *trans*-PA chain upon chemical doping, photogeneration, or charge injection (see Figure 1.5).^[33,34] The most important charged particles for conduction are charged polarons. (In chemist’s language, the radical cations or radical anions, which are the oxidized and reduced forms of π -bonds, respectively.) Generally speaking, the electronic motion of polarons along the conjugated chain (i.e., *intramolecular*) is considered as the efficient part of the charge transport mechanism in conjugated systems.^[35,36] The inefficient part that determines the macroscopic conductivity is the intermolecular charge transport.

A special kind of excitation is the soliton. It can only be generated in pairs: the soliton and anti-soliton. The presence of a soliton on a site (or a bond-alternation domain boundary) separates the conjugated chain into regions of different bond alternations patterns (see Figure 1.6a). A soliton can migrate along a chain by pairing with an adjacent electron and leaving its previous partner unbound. In this way, the lattice sites can be classified in even and odd sites with either a soliton or an anti-soliton. The propagation of a soliton along a conjugated chain induces an inverted double bond/single bond pattern.^[35,37]

Topological solitons are only stable and mobile in infinite systems with a degenerate ground state such as the highly symmetric *trans*-PA. Such quasi-particles can also be defined in systems with a non-degenerate ground state such as, for example, poly(paraphenylene vinylene) (PPV) and polythiophene. In both cases, the

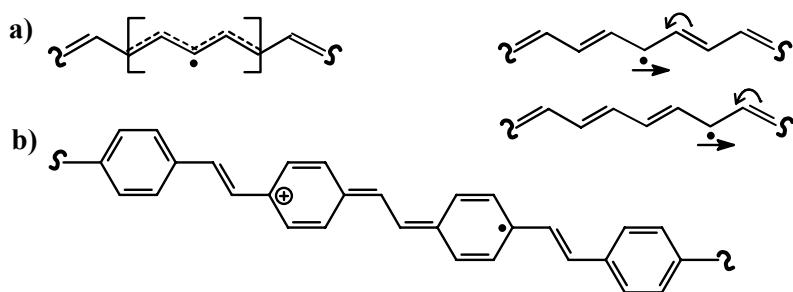


Figure 1.6 Schematic representation of a) a neutral soliton in PA showing the associated distorted chain structure (left) and the migration along the chain (right).^[31,34] b) A polaron in PPV illustrating the quinoidal structure of this defect.

motion of a soliton would involve driving a high-energy region (quinoidal part in PPV) through low-energy regions (aromatic). Therefore, the injection of a hole or an electron in a PPV chain results in the formation of a polaron, not of two (one charged, one neutral) solitons (see Figure 1.6b). The propagation of a polaron leaves the bond alternation pattern of a conjugated chain unchanged.

1.4 Valence Bond Theory and Molecular Orbital Theory

The first major step towards the understanding of the properties of conjugated materials came from the physicist Robert Mulliken. Together with Friedrich Hund (Hund's Rule), Mulliken introduced a method by which an appropriate solution of the Schrödinger equation can be obtained.^[38] The atomic orbitals overlap and combine to form molecular orbitals (MO), as Mulliken called them. The basis for a numerical solution of the Schrödinger equation is writing the molecular orbitals as a linear combination of atomic orbitals (LCAO). The self-consistent field (SCF) MO method is an iterative computational technique that gives numerical solutions for the wavefunctions and their energies. Nowadays, MO theory forms the basis of other theoretical approaches such as several semiempirical and *ab initio* theories.^[39]

Historically, the MO theory was developed after the introduction of the valence bond (VB) theory.^[40] The VB theory is an alternative approach to discuss the molecular structure.^[41] It considers the formation of bonds as arising from the overlap of atomic orbitals on two adjacent atoms and sharing the electrons in these orbitals.^[42] In contrast to VB theory, MO theory does not consider electrons belonging to specific bonds, but as being delocalized over a subset of atomic orbitals. The MO wavefunctions are equivalent to a linear combination of VB and ionic wavefunctions (see Equation 1.1).

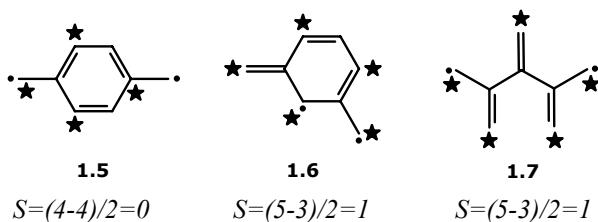


Figure 1.7 Illustration of the starred/unstarred rule with diradical systems used to predict their ground state spin (S). Ovchinnikov^[43] proposed that the number of starred (n^*) and unstarred (n) sites determines the spin according to: $S = (n^* - n)/2$.

$$\text{Equation 1.1} \quad \Phi_{MO} = \frac{1}{\sqrt{2}}(\Phi_{VB} + \Phi_{Ionic})$$

The VB description corresponds more closely with the conventional chemical picture. It is the natural language to discuss reaction mechanisms ("flow" of electrons) and to design molecules with certain properties. For example, the starred/unstarred rule developed by Ovchinnikov is often used as starting point for the design of high spin organic molecules.^[43] Ovchinnikov proposed that the magnetic properties of alternant hydrocarbons can be predicted from their most spin-alternant structure. For this, every other carbon is labeled with a star. This procedure is illustrated for three diradical systems in Figure 1.7. The total spin is given by the difference between number of starred (n^*) and unstarred (n) carbons divided by two: $S = (n^* - n)/2$. For many molecules, the predicted values for the ground-state spin are in accordance with experimental results.^[43-45]

The MO theory is superior in describing the electronic spectra of systems that encompass ionic structure and orbital symmetry restrictions.^[46,47] Furthermore, MO calculations are essential in providing insight into the charge distribution of π -conjugated systems. The charge transport capabilities of such systems are very much dependent on the π -electron distribution in the orbitals near the HOMO-LUMO gap (i.e., Highest Occupied Molecular Orbital and Lowest Unoccupied Molecular Orbital, respectively). The VB approach of analyzing π -conjugated systems is based on the enumeration of all (neutral) resonance structures. The "real" structure is a weighted average of all resonance structures, with the most stable resonance structures as the most important contributors. The MO and VB theory form an optimal combination to design organic materials and discuss their properties.^[48]

1.5 Molecular Scale Electronics

The drive to further miniaturize conventional inorganic electronics has led to enormous efforts to develop molecular-scale components. Usually, the concepts in the field of molecular electronics follow the paradigm of today's silicon-based

technology and involve molecular analogues of wires, transistors, switches, and logic gates.^[49-51] The basic challenge is to design functionality in single molecules or a very small collection of molecules. They could be used to decrease the size of electronic circuitry down to the nanometer scale and, with that, realize extremely high component density. It is envisaged that this would be the ultimate miniaturization of a future generation electronic circuits. The dimensions of such circuitry justify the use of the name "molecular electronics". This term originated with Carter who heavily promoted the idea of computation at the molecular level more than 25 years ago.^[52,53]

Usually, molecular electronic devices consist of organic molecules sandwiched between two macroscopic electrodes.^[54] This makes it an interesting combination of molecular and conventional electronics. The inherent difficulty is to address the individual molecules and to investigate their electronic properties *in situ* and non-destructively. Therefore, an important breakthrough in this field was scanning tunneling microscopy (STM), developed by IBM research in the early 1980s.^[55] The STM was soon followed by a number of related scanning microscopes such as, for example, atomic force microscope (AFM). These techniques are, together with the break-junction method,^[56] crucial for testing and constructing molecular electronic devices.^[57]

Molecular Rectifier

In 1974, Aviram and Ratner described the first concrete idea of an electronic component based on a molecule: a molecular rectifying diode.^[58] The chemical structure of the Aviram-Ratner diode is shown in Figure 1.8. It consists of an electron donating TTF derivative and a modified TCNQ acceptor connected via a saturated (*insulating*) σ bridge. According to their theoretical calculations, this insulating molecule becomes conductive after applying a certain threshold voltage that brings the π -levels in resonance. Hence, the molecule should show rectification in terms of a strongly asymmetric flow of current. After 25 years, it was proven experimentally by Metzger *et al.*^[59,60] that a related molecule indeed exhibits

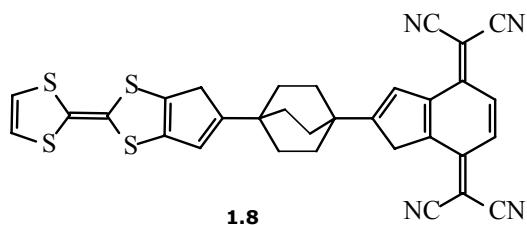


Figure 1.8 Proposal of Aviram and Ratner for a molecular rectifying diode.^[58] The TCNQ acceptor (right) is separated from the TTF donor (left) via the saturated bridge in the center (D- σ -A molecule).

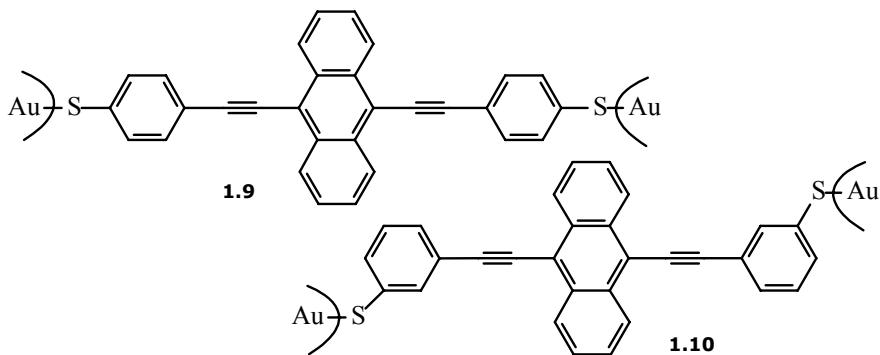


Figure 1.9 Examples of molecular wires based on phenyl-ethynylanthracene^[82] with the thiol anchor groups in *para* (left) and *meta* positions (right).

rectifying behavior and behaves very similar to p-n junction in a conventional semiconductor.^[61,62] The idea of using a saturated bridge is the basis for many other molecular-scale proposals^[63,64] such as transistors,^[65] resonant tunneling diodes,^[66,67] and gates.^[68]

Molecular Wires

One of the most obvious components of electronic circuitries is a wire. The wire is a passive element that interconnects other active elements and allows for communication between these elements.^[69] Suggested types of molecules that can act as wires include the polymers PA and PPV (see Figure 1.6). The basis of many wires is that they transmit charges through the MO's of their conjugated π -system. The group of James Tour is known for their research into molecular wires based on oligomers of phenylene-ethylene.^[70,71] Many wires have been tested and characterized as devices at the molecular level, both theoretically and experimentally.^[72-75]

The molecular wires are incorporated into circuits by attaching them to gold electrodes via strong thiol-Au bonds (see, for example, Figure 1.9). In many studies it is found that the conductive behavior of the wires not only depends on the intrinsic properties of the molecule but also on the interaction with such macroscopic contacts.^[76-81] The understanding of the observed transport properties of "simple" molecular wires is still a fundamental scientific challenge. Recently, Mayor and Weber have demonstrated that the electronic transport is influenced by the geometry at the molecule-metal interface.^[82] The conductivity was significantly reduced when the molecule was connected via the *meta* positions instead of the *para* positions (see Figure 1.9). This study strongly indicates that addressing a linear conjugated pathway through the molecule is crucial for an efficient electronic

communication between the electrodes. The importance of the topology of pathways has been reported in related electrochemical and theoretical studies.^[83-87]

Molecular Logic Gates

While the wire is essentially a passive element, a switch acts as an active circuit element that changes its state in response to an external signal. Molecular switches have been a subject of study in chemistry for a long time.^[88,89] The logic aspects of molecular switches have been recognized after de Silva and co-workers reported on a molecular switch that could operate as an AND gate. They showed that the fluorescence (the output signal) of a crown-ether derivative depends on whether the molecule binds hydrogen ions, sodium ions, or both (the input signals). This implies that the output signal depends on two input signals and that the system can mimic a logic operation.^[90,91] Logic gates are the subject of matter in proposition logic and are the key components in electronic devices. Therefore, they have become vital to our day-to-day communication. The elegant proof-of-principle experiment of de Silva *et al.* started the field of experimental molecular logic.^[92-94] Most of the proposed molecular logic gates are based on photophysical, photochemical, electrochemical, and chemical processes taking place in solution. In principle, all 16 fundamental logic operations (Boolean functions) can now be realized with molecules. Nowadays, even more complex logic functions can be implemented in molecular switches that responds to more than two input signals.^[95-98]

The vast majority of molecular logic gates is based on optical input and/or output signals and operates in a solution environment. If they are envisioned to operate as potential electronically controllable component then the gates should be a device for solid-state electronics. The ideal situation would be to construct molecular-scale logic circuits from switches that can control the transmission of charges and, with that, the current through the device.

A number of proposals can be found in literature that are based on the charge transport properties of molecules as switching mechanism.^[63,99,100] Figure 1.10 shows two recent examples. The first one is based on the Aviram and Ratner rectifying diode.^[68] This system could mimic the function of an AND gate as was indicated by current-voltage calculations of Joachim and co-workers. Generally speaking, the proposed molecular circuitries form supramolecular systems. This is because they consist of simple three-terminal units such as, for example, phenyl rings. According to Joachim *et al.*,^[101,102] "smaller" circuitries can only be constructed from multibranched molecules in which the current between two ends is controlled by two other branches of the molecule. The second proposal given in Figure 1.10b is based on the "Tour wires".^[67] In theory, it serves as an OR or NOR gate when applying different voltages (high or low) as input signal and measuring the impedance (high or low). The proposed electrical behavior of this gate would be

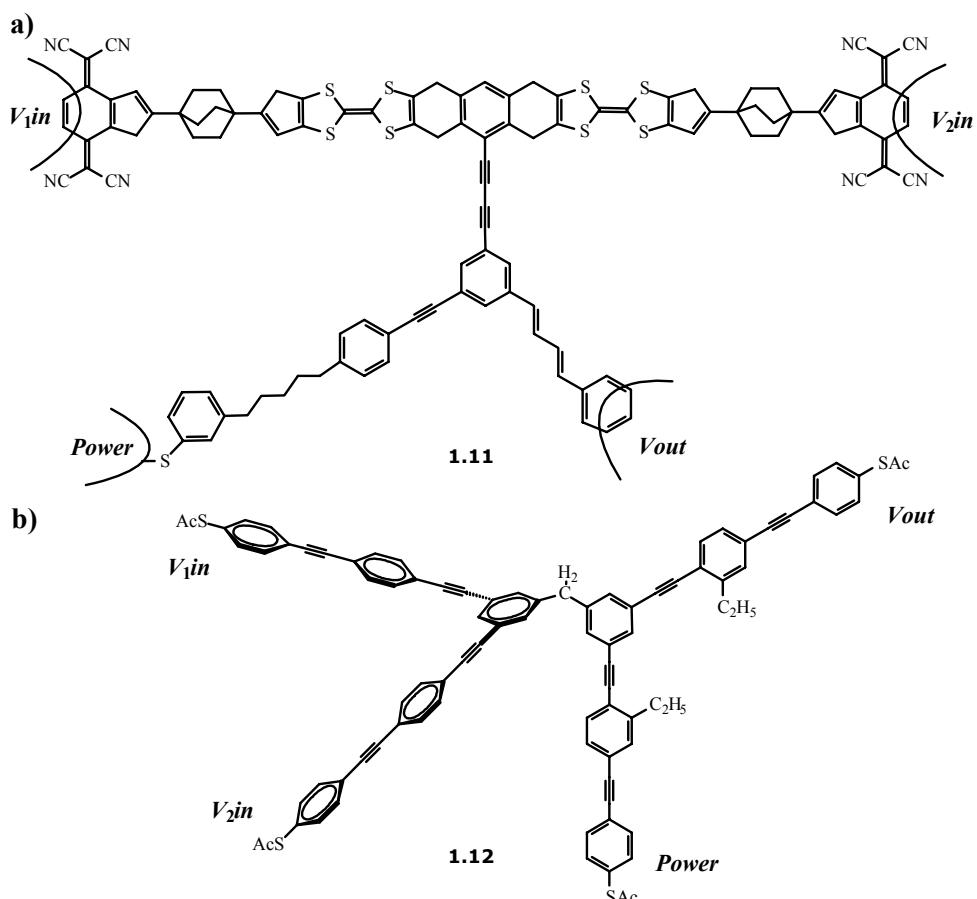


Figure 1.10 Proposals of implementation of logic gates in single molecules based on a rectifying behavior of the system: a) AND gate^[68] and b) OR gate from “Tour wires”.^[67]

related to a resonant-tunneling diode.^[103] The versatility of this approach is reviewed in the work of Ellenbogen and Love.^[63] They showed that large and somewhat unrealistic molecules would be required for the design of the standard logic gates from related wires and diodes.

Forrest Carter introduced a switching mechanism based on the change of bond alternation pattern by the passage of (charged) solitons.^[52] This soliton switching is a completely different approach to molecular logic. Figure 1.11 illustrates the incorporation of two PA chains into two different chromophores. Only the chromophore between the two sulfur atoms can be photo-activated in this double bond configuration (see situation emerging at the right). After the propagation of a soliton along, for example, the upper chain, the first chromophore is switched ‘on’ (it

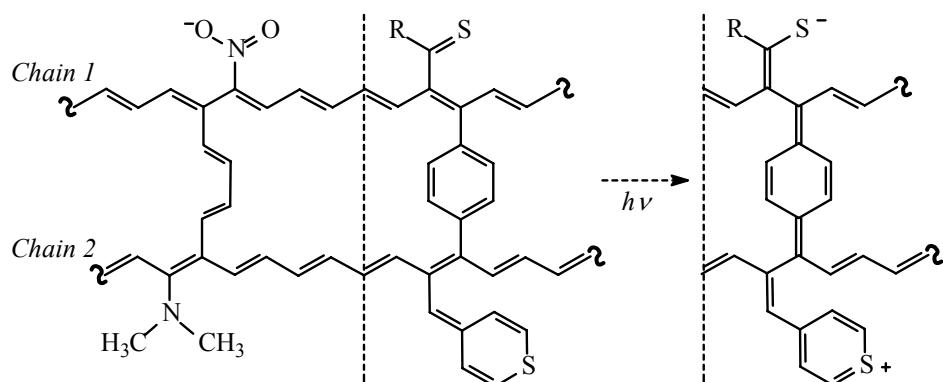


Figure 1.11 Soliton switching along two polyacetylene chains imbedded in two push-pull olefins. Only the second sulphur chromophore can absorb light.^[52]

can absorb light) leaving the second chromophore switched ‘off’. This is because the moving soliton leaves behind an inverted double bond/single bond pattern. In this way, the absorption spectra of the push-pull olefin serve as a detector for the passage of a soliton.

Carter extended the concept of soliton switching and proposed many related devices such as, for example, a junction (called “valve”) and memory elements. An example of a soliton junction is given in Figure 1.12.^[104] This junction has three states characterized by the position of the double bond on the central carbon atom. The soliton can only pass between two chain ends when the path consists of alternating double bonds and single bonds. The passage of a soliton from A to B (indicated by arrows in Figure 1.12) moves the double bond at the central carbon

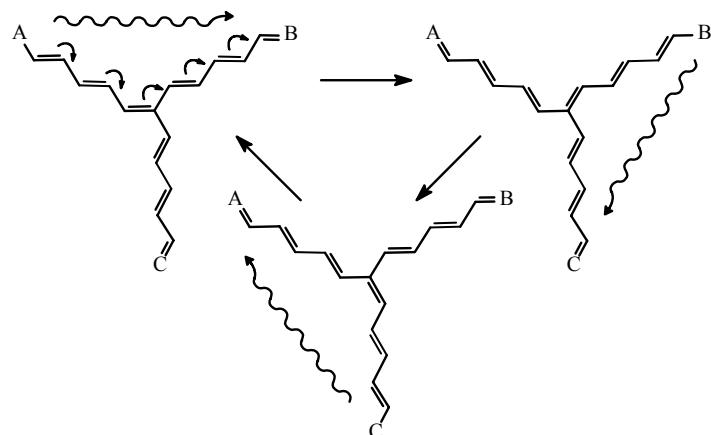


Figure 1.12 The three states of a soliton junction and examples of the effect of soliton propagation (indicated by the arrows) that changes the state of the junction.^[52]

and changes the alternation patterns along the other paths. After this passage, the pathway from A to C is blocked for solitons while the transmission is enhanced between B and C. The next soliton, an antisoliton, has to propagate to the same chain. In this manner, the molecule acts as an electrical switch: the passage of a soliton along either path (say A to B) controls the transport of charges along the other path (B to C).^[105]

Following Carter's work, Groves reported on how the soliton switches could be used to construct logic gates.^[106,107] These logic gates are simple structures of two soliton switches that are interconnected in series (AND gate) or in parallel (OR gate). The proposals of Carter are often regarded as unfeasible given that it would be problematic to put the soliton switching principle in practice. The value of soliton switching lies in the development of new concepts for computation at the molecular level. With respect to this, the real-time counting of charged solitons by means of a small tunnel junction is an important proof-of-principle experiment. Recently, quite promising results were reported by Bylander and co-workers.^[108]

1.6 Challenges

Molecules are already playing a key role in the development of new materials for electronic devices. They have the potential to become even more important in the near future.

Despite the aforementioned important contributions in the field of molecular electronics, there are still many challenges ahead. One is to fully understand the charge transport through molecules and interfaces. This enables the design of proper electrical contacts.^[109] It is still difficult to realize reproducibility in experiments carried out on the molecular scale. Therefore, it is still difficult to assess the characteristics of a "simple" molecular wire. The key to success of molecular electronics lies in achieving control at the molecular level. Furthermore, it must be demonstrated that molecules can perform as electronic devices.^[110] An important milestone towards miniaturizing the computer would be to mimic the behavior of logic gates with molecules.^[111] To reach this objective, new architectural designs that incorporate logic properties in molecular circuits are a must.^[112] If molecules are to function as electronic circuits, it is crucial to realize proper interconnections between the molecules so that they can communicate with each other. Such a covalent bonding must not change the functionality of the individual molecules. The quest for proper interconnections between molecules has been put forward by several research groups.^[93–96,102,113]

1.7 Thesis objectives

π -Conjugated molecules for single molecule electronics have been investigated for charge transport properties, either as static structures or as simple (optical) switches. However, an electronic circuit is made up of many complex (logic) elements, wired in a specific way to make it operate. Aside from further needed improvements, the development of new architectural concepts could become essential for success of molecular electronics in the long term. This is the motivation for the work presented in this thesis. The objective is to search for topologies of π -conjugated systems providing the built-in logic, as it could be used to construct passive and active elements for integrated molecular circuits. Whether passive or active, any such element must have at least two terminals to (inter)connect it. Hence, in this thesis only π -conjugated systems with at least two terminals are considered. The terminals are the potential attachment positions for other functional moieties (e.g., additional conjugated fragments and functional groups) or electrodes.

To develop a more basic understanding of the role of the degree of π -conjugation in the properties of organic n-terminal π -conjugated systems, in *Chapter 2* a new classification of organic systems by their degree of π -conjugation is presented. First, a systematic analysis of n-terminal systems is given in a purely abstract, topological way. It is based on a variation procedure of double bonds over n positions to find all possible double bond configurations of the n-terminal system. The analysis is then applied to n-terminal π -conjugated molecules and a relation to their degree of π -conjugation is established. The emphasis is on the terminals (the substituents) since these are considered as the keys for molecular electronic circuits. Furthermore, a new class of π -conjugated systems is introduced. These systems, providing linear conjugated pathways between all terminals, are defined as being "omniconjugated". The topological analysis discussed in this chapter is the foundation for the work described in the remainder of this thesis.

Omniconjugated systems are considered as promising candidates to interconnect (many) molecules in molecular electronic circuits. This brings us to the design of more and realistic omniconjugated structures in *Chapter 3*. First a "topological design program" is presented that allows for a stepwise design of any desired omniconjugated system from small basic key-models. The elegance of this approach is that it allows for the incorporation of an infinite number of substituents (terminals), in theory. Furthermore, the design method distinguishes different subclasses (levels) of omniconjugation, some having intriguing topological properties. At the end, the properties of some real examples of omniconjugated compounds are briefly discussed.

If omniconjugated molecules are to be used as intersection ("soldering points") between molecular wires in molecular electronic circuits or as material for electronic devices, the ideal situation would be that they have completely delocalized

π -systems. Only in this manner the molecules can provide for an efficient electronic communication between several elements. In *Chapter 4* of this thesis, the omniconjugated molecules are put to test in order to determine whether these systems indeed can function as envisioned or not. The focus is on their electronic structure. The delocalization of the frontier orbitals is studied qualitatively by employing quantum chemical calculations. From a molecular orbital point of view, some omniconjugated systems with four terminals show unexpected features. The (local) symmetry of the system can have a profound impact on the delocalization of the frontier orbitals. Some omniconjugated systems contain spatially separated channels for hole and electron transport. They could be of use for directional transport in advanced molecular electronic devices.

Having assessed the topological properties of different classes of π -conjugation it is time to understand the origin of their behavior. In *Chapter 5* the use of a group theoretical approach, to develop a more robust mathematical formulation of the topological properties of π -conjugated systems, is presented. The basis of the presented formulation is a classification of the symmetries of the propagation of a bond alternation (or quasi-particle) along a path between two terminals of the n-terminal system. This group theoretical approach offers insight into the relation between the π -topology of the n-terminal system and its switching properties when it comes to creating cross-conjugated pathways. It is found that it is possible to predict the outcome of successive switching events; hence, the π -logic is "built-in". A full mathematical description of the topological properties of n-terminal π -conjugated systems is still not achievable, yet very desirable.

The last chapter deals with the most challenging aspect of molecular electronics: the ability to use organic molecules in logic circuits to transform binary inputs to binary outputs. The obtained insights in the preceding chapters are combined in *Chapter 6* to design all 16 Boolean functions with one single molecule. The discussion starts with outlining the basic operating principle of a simple switch. Next, the implementation of all, but one, logic gates within a *single* molecule is presented. A major step towards ultra-compact complex logic gates are bifunctional elements based on single molecules. This is presented at the end of this chapter. These results show that the topologies of π -conjugated systems can fully provide for a complete collection of π -logic elements for the construction of integrated circuits based on molecules.

1.8 References

1. The transcript of the talk was first published in the February 1960 issue of *Caltech's Engineering and Science*, Volume XVII, 5, pp. 22. Nowadays, it is available on the web: <http://www.zyvex.com/nanotech/feynman.html>.
2. G. E. Moore, *Electronics* **1965**, 38, 114.
3. G. N. Parsons, in *Handbook of Nanoscience, Engineering and Technology*, Eds. W. A. Goddard, III, D. W. Brenner, S. E. Lyshevski, G. J. Lafrate, CRC Press, Boca Raton **2003**, Chpt. 3.
4. D. Bloor, in *Introduction to Molecular Electronics*, Eds. M. C. Petty, M. R. Bryce, D. Bloor, Edward Arnorld, London **1995**, pp. 1.
5. E. Clar, *Polycyclic Hydrocarbons Vol. I and II*, Academic Press and Springer, London and Berlin **1964**.
6. A. Kekulé, *Bull. Soc. Chim. Fr.* **1865**, 3, 98.
7. H. Wang, R. Helgeson, B. Ma, F. Wudl, *J. Org. Chem.* **2000**, 65, 5862.
8. N. F. Phelan, M. Orchin, *J. Chem. Educ.* **1968**, 45, 633.
9. D. Philp, V. Gramlich, P. Seiler, F. Diederich, *J. Chem. Soc., Perkin Trans. 2* **1995**, 875.
10. M. Bruschi, M. G. Giuffreda, H. P. Lüthi, *ChemPhysChem* **2005**, 6, 511.
11. C. Patoux, C. Coudret, J.-P. Launay, C. Joachim, A. Gourdon, *Inorg. Chem.* **1997**, 36, 5037.
12. J.-P. Launay, *Chem. Soc. Rev.* **2001**, 30, 386.
13. R. R. Tykwinski, Y. Zhao, *Synlett* **2002**, 12, 1939.
14. M. Bruschi, M. G. Giuffreda, H. P. Lüthi, *Chem. Eur. J.* **2002**, 8, 4216.
15. E. Burri, F. Diederich, M. B. Nielsen, *Helv. Chim. Acta* **2001**, 84, 2169.
16. M. B. Smith, J. March, *March's Advanced Organic Chemistry*, 5th ed., Wiley, New York **2001**, pp. 675.
17. M. Kondo, D. Nozaki, M. Tachibana, T. Yumura, K. Yoshizawa, *Chem. Phys.* **2005**, 312, 289.
18. J. Michl, E. W. Thulstrup, *Tetrahedron* **1976**, 32, 205.
19. G. Treboux, P. Lapstun, K. Silverbrook, *J. Phys. Chem. B* **1998**, 102, 8978.
20. D. M. Lemal, G. D. Goldman, *J. Chem. Educ.* **1988**, 65, 923.
21. N. S. Hush, *Ann. N.Y. Acad. Sci.* **2003**, 1006, 1.
22. H. Mette, H. Pick, *Z. Physik* **1953**, 134, 566.
23. D. D. Eley, *Nature* **1948**, 162, 819.
24. F. Wudl, D. Wobschall, E. J. Hufnagel, *J. Am. Chem. Soc.* **1972**, 94, 670.

25. J. Ferraris, D. O. Cowan, V. Walatka, J. H. Perlstein, *J. Am. Chem. Soc.* **1973**, 95, 948.
26. A. F. Garito, A. J. Heeger, *Acc. Chem. Res.* **1974**, 7, 232.
27. C. K. Chiang, C. R. Fincher, Jr., Y. W. Park, A. J. Heeger, H. Shirakawa, E. J. Louis, S. C. Gau, A. G. MacDiarmid, *Phys. Rev. Lett.* **1977**, 39, 1098.
28. S. Roth, D. Carroll, *One-Dimensional Metals*, 2nd ed., Wiley-VCH, Weinheim **2004**, pp. 53.
29. R. E. Peierls, *Quantum Theory of Solids*, Oxford University Press, London **1955**, pp. 108.
30. R. Hoffmann, C. Janiak, C. Kollmar, *Macromolecules* **1991**, 24, 3725.
31. A. J. Heeger, S. Kivelson, J. R. Schrieffer, W.-P. Su, *Rev. Mod. Phys.* **1988**, 60, 781.
32. M. Fahlman, W. R. Salaneck, in *Organic Electronic Materials*, Eds. R. Farchioni, G. Grossi, Springer-Verlag, Berlin Heidelberg **2001**, pp. 181.
33. C. W. Spangler, M. He, in *Handbook of Organic Conductive Molecules and Polymers, Vol. 2. Conductive Polymers: Synthesis and Electrical Properties*, Ed. H. S. Nalwa, Wiley, New York **1997**, pp. 389.
34. S. Roth, H. Bleier, *Adv. Phys.* **1987**, 36, 385.
35. S. Curran, A. Stark-Hauser, S. Roth, in *Handbook of Organic Conductive Molecules and Polymers, Vol. 2. Conductive Polymers: Synthesis and Electrical Properties*, Ed. H. S. Nalwa, Wiley, New York **1997**, pp. 1.
36. G. Horowitz, P. Delannoy, in *Handbook of Oligo- and Polythiophenes*, Ed. D. Fichou, Wiley-VCH, Weinheim **1999**, pp. 283.
37. M. Garavelli, B. R. Smith, M. J. Bearpark, F. Bernardi, M. Olivucci, M. A. Robb, *J. Am. Chem. Soc.* **2000**, 122, 5568.
38. R. S. Mulliken, *Phys. Rev.* **1932**, 41, 49.
39. P. W. Atkins, R. S Friedman, *Molecular Quantum Mechanics*, 3rd ed., Oxford University Press, Oxford **1997**, pp. 276.
40. W. Heitler, F. London, *Z. Phys.* **1927**, 44, 455.
41. G. N. Lewis, *J. Am. Chem. Soc.* **1916**, 38, 762.
42. C. A. Coulson, *Valence*, 2nd ed., Oxford University Press, London **1961**.
43. A. A. Ovchinnikov, *Theor. Chim. Acta* **1978**, 47, 297.
44. L. Ducasse, *Chem. Phys. Lett.* **2002**, 352, 454.
45. T. P. Radhakrishnan, *Chem. Phys. Lett.* **1991**, 181, 455.
46. P. W. Atkins, R. S Friedman, *Molecular Quantum Mechanics*, 3rd ed., Oxford University Press, Oxford **1997**, pp. 358.
47. S. Shaik, P. C. Hiberty, *Helv. Chim. Acta* **2003**, 86, 1063.
48. R. Hoffmann, S. Shaik, P. C. Hiberty, *Acc. Chem. Res.* **2003**, 36, 750.

49. J. M. Tour, D. K. James, in *Handbook of Nanoscience, Engineering and Technology*, Eds. W. A. Goddard, III, D. W. Brenner, S. E. Lyshevski, G. J. Lafrate, CRC Press, Boca Raton **2003**, Chpt. 4.
50. C. Joachim, J. K. Gimzewski, A. Aviram, *Nature* **2000**, 408, 541.
51. M. A. Ratner, J. Jortner, in *Molecular Electronics*, Eds. J. Jortner, M. A. Ratner, IUPAC, Oxford **1997**, pp. 5.
52. F. L. Carter, *Molecular Electronic Devices*, Marcel Dekker, New York **1982**, pp. 51.
53. F. L. Carter, *J. Vac. Sci. Technol. B* **1983**, 1, 959.
54. M. A. Reed, C. Zhou, C. J. Muller, T. P. Burgin, J. M. Tour, *Science* **1997**, 278, 252.
55. G. Binning, H. Rohrer, *Rev. Mod. Phys.* **1987**, 59, 615.
56. C. J. Muller, J. M. van Ruitenbeek, L. J. de Jongh, *Physica C* **1992**, 191, 485.
57. D. K. James, J. M. Tour, *Chem. Mater.* **2004**, 16, 4423.
58. A. Aviram, M. A. Ratner, *Chem. Phys. Lett.* **1974**, 29, 277.
59. R. M. Metzger, B. Chen, U. Höpfner, M. V. LakshmiKantham, D. Vuillaume, T. Kawai, X. Wu, H. Tachibana, T. V. Hughes, H. Sakurai, J. W. Baldwin, C. Hosch, M. P. Cava, L. Brehmer, G. J. Ashwell, *J. Am. Chem. Soc.* **1997**, 119, 10455.
60. T. Xu, I. R. Peterson, M. V. LakshmiKantham, R. M. Metzger, *Angew. Chem., Int. Ed.* **2001**, 40, 1749.
61. A. Nitzan, *Annu. Rev. Phys. Chem.* **2001**, 52, 681.
62. K. Stokbro, J. Taylor, M. Brandbyge, *J. Am. Chem. Soc.* **2003**, 125, 3674.
63. J. C. Ellenbogen, J. C. Love, *Proc. IEEE* **2000**, 88, 386.
64. R. M. Metzger, *Chem. Rev.* **2003**, 103, 3803.
65. A. Aviram, *J. Am. Chem. Soc.* **1988**, 110, 5687.
66. Y. Karzazi, J. Cornil, J. L. Brédas, *J. Am. Chem. Soc.* **2001**, 123, 10076.
67. J. M. Tour, M. Kozaki, J. M. Seminario, *J. Am. Chem. Soc.* **1998**, 120, 8486.
68. S. Ami, M. Hliwa, C. Joachim, *Chem. Phys. Lett.* **2003**, 367, 662.
69. N. Robertson, C. A. McGowan, *Chem. Soc. Rev.* **2003**, 32, 96.
70. S. Huang, J. M. Tour, *J. Am. Chem. Soc.* **1999**, 121, 4908.
71. D. W. Price, J. M. Tour, *Tetrahedron* **2003**, 59, 3131.
72. J. Reichert, R. Ochs, D. Beckmann, H. B. Weber, M. Mayor, H. von Löhneysen, *Phys. Rev. Lett.* **2002**, 88, 176804.
73. J. Heurich, J. C. Cuevas, W. Wenzel, G. Schön, *Phys. Rev. Lett.* **2002**, 88, 256803.
74. A. Nitzan, M. A. Ratner, *Science* **2003**, 300, 1384.
75. G. Pourtois, D. Beljonne, J. Cornil, M. A. Ratner, J. L. Brédas, *J. Am. Chem. Soc.* **2002**, 124, 4436.

76. S. N. Yaliraki, M. Kemp, M. A. Ratner, *J. Am. Chem. Soc.* **1999**, *121*, 3428.
77. H. Basch, M. A. Ratner, *J. Chem. Phys.* **2003**, *119*, 11926.
78. F. Dulić, S. J. van der Molen, T. Kudernac, H. T. Jonkman, J. J. D. de Jong, T. N. Bowden, J. van Esch, B. L. Feringa, B. J. van Wees, *Phys. Rev. Lett.* **2003**, *91*, 207402.
79. A. S. Blum, J. G. Kushmerick, D. P. Long, C. H. Patterson, J. C. Yang, J. C. Henderson, Y. Yao, J. M. Tour, R. Shashidhar, B. R. Ratna, *Nature Mater.* **2005**, *4*, 167.
80. A. Salomon, D. Cahen, S. Lindsay, J. Tomfohr, V. B. Engelkes, C. D. Frisbie, *Adv. Mater.* **2003**, *15*, 1881.
81. H. B. Weber, J. Reichert, F. Weigend, R. Ochs, D. Beckmann, M. Mayor, R. Alrichs, H. von Löhneysen, *Chem. Phys.* **2002**, *281*, 113.
82. M. Mayor, H. B. Weber, J. Reichert, M. Elbing, C. von Hänsch, D. Beckmann, M. Fischer, *Angew. Chem., Int. Ed.* **2003**, *42*, 5834.
83. S. N. Yaliraki, M. A. Ratner, *Ann. N.Y. Acad. Sci.* **2002**, *960*, 153.
84. M. Mayor, M. Büschel, K. M. Fromm, J.-M. Lehn, J. Daub, *Ann. N.Y. Acad. Sci.* **2002**, *960*, 16.
85. R. Stadler, M. Forshaw, C. Joachim, *Nanotechnology* **2003**, *14*, 138.
86. R. Kucharczyk, S. G. Davison, *Phys. Rev. B* **2004**, *69*, 195402.
87. A. Pogantsch, A. K. Mahler, G. Hayn, R. Saf, F. Stelzer, E. J. W. List, J. L. Brédas, E. Zojer, *Chem. Phys.* **2004**, *297*, 143.
88. V. Ramamurthy, K. S. Schanze, *Optical Sensors and Switches*, Marcel Dekker, New York **2001**.
89. J.-P. Sauvage, *Molecular Machines and Motors*, Springer-Verlag, Berlin Heidelberg **2001**.
90. C. I. Lewis, C. H. Langford, *Symbolic Logic*, 2nd ed., Dover Publications, New York **1959**.
91. M. Morris Mano, *Digital Design*, 3rd ed., Prentice-Hall, New Jersey **2002**, pp. 33, 111, 167.
92. A. P. de Silva, N. D. McClenaghan, *Chem. Eur. J.* **2004**, *10*, 574.
93. M. D. Ward, *J. Chem. Educ.* **2001**, *78*, 321.
94. A. P. de Silva, T. Gunnlaugsson, C. P. McCoy, *J. Chem. Educ.* **1997**, *74*, 53.
95. V. Balzani, A. Credi, M. Venturi, *ChemPhysChem* **2003**, *3*, 49.
96. Y. Shiraishi, Y. Tokitoh, T. Hirai, *Chem. Commun.* **2005**, 5316.
97. L. Gobbi, P. Seiler, F. Diederich, *Angew. Chem., Int. Ed.* **1999**, *38*, 674.
98. K. Szacilowski, *Chem. Eur. J.* **2004**, *10*, 2520.
99. Y. Wada, *Ann. N.Y. Acad. Sci.* **2002**, *960*, 39.
100. A. Bandyopadhyay, A. J. Pal, *Chem. Phys. Lett.* **2003**, *371*, 86.

101. S. Ami, C. Joachim, *Phys. Rev. B* **2002**, *65*, 155419.
102. C. Joachim, *Nanotechnology* **2002**, *13*, R1.
103. Y. Karzazi, J. Cornil, J. L. Brédas, *J. Am. Chem. Soc.* **2001**, *123*, 10076.
104. F. L. Carter, *Physica D* **1984**, *10*, 175.
105. G. M. E. Silva, P. H. Acioli, Y. Ono, *J. Phys. Soc. Jpn.* **1998**, *67*, 3881.
106. M. P. Groves, in *Molecular Electronic Devices II*, Ed. F. L. Carter, Marcel Dekker, New York **1987**, pp. 149.
107. M. P. Groves, C. F. Carvalho, R. H. Prager, *Mater. Sci. Eng.* **1995**, *C3*, 181.
108. J. Bylander, T. Duty, P. Delsing, *Nature* **2005**, *434*, 361.
109. R. A. Wassel, C. B. Gorman, *Angew. Chem., Int. Ed.* **2004**, *43*, 5120.
110. J. M. Seminario, *Nature Mater.* **2005**, *4*, 111.
111. R. F. Service, *Science* **2002**, *295*, 2398.
112. J. R. Barker, in *Introduction to Molecular Electronics*, Eds. M. C. Petty, M. R. Bryce, D. Bloor, Edward Arnorld, London, **1995**, pp. 345.
113. M. A. Reed, J. M. Tour, *Sci. Am.* **2000**, *282*, 86.

Chapter 2

On the Classification of n-Terminal π -Conjugated Systems

Abstract The basic requirement for constructing complex logic circuits from single molecules is that the molecules are provided with substituents that serve as terminals. When attached, the molecules can trigger other entities or transform information to our macroscopic world. We propose a classification by degree of π -conjugation for molecules that have n terminals ($n = 2 - \infty$). By explicitly taking into account the terminals this approach is distinctly different from other methods dealing with conjugation. The method consists of deducing the collection of structures that represents all possible double bond terminal patterns of the system. It is found that such a series determines the degree of conjugation. An unambiguous difference is found between linear and cross-conjugated n -terminal systems. In contrast to linear conjugated systems, the series of cross-conjugated systems contain at least one structure which is an open shell system. The types and number of non-Kekulé structures provide insight into the nature of the pathways between two terminals within all structures of the series. This aspect is closely related to the switching properties of n -terminal π -conjugated systems when it comes to creating cross-conjugated pathways. It suggests that the topology of π -conjugated systems provides built-in logic, as it could be used for complex molecular electronics.

2.1 Introduction

Conjugated double bonds have been studied for more than a century because they are interesting from a fundamental point of view and essential for dye industry. One of the most famous and early contributors in the field of π -conjugated systems is August Kekulé. In 1865, a few years after he deduced that a carbon atom forms four bonds, he proposed benzene as the first cyclic chemical substance.^[1] This so-called Kekulé structure of benzene is a six membered hydrocarbon ring consisting of double bonds separated by single bonds. The strict alternation of single and double bonds is called, in classical terms, linear conjugation. As the words implies, conjugated bonds, like the ones in benzene, act collectively as manifested by π -electron delocalization. The notion of conjugation is fundamental to the electronic behavior of organic materials. In the early seventies it was the work of Ferraris and co-workers^[2] on the electron transport properties of the first highly conducting complex between TTF and TCNQ that initiated so much research in this field. Nowadays, materials based on functional π -conjugated molecules or polymers have great potential for new electronic applications based on molecular materials or, more recently, on single molecules.^[3] When aiming at electronic devices built from single molecules, the molecules have to be provided with external connection points to allow for communication between many molecules or with the macroscopic world. From our point of view, the substituents of molecules are the keys for molecular electronic circuits. We propose a classification by degree of π -conjugation for molecules *with* substituents. The method only applies to substituents that are conjugated with the central molecular framework. By explicitly taking into account the substituents, this approach is distinctly different from all other methods dealing with conjugation or aromaticity.^[4–7]

For a long time, conjugation has been studied with the objective to understand the phenomena and to explain the behavior of molecules. Conjugated double bonds play their special role in organic chemistry (e.g., in leading to conjugate addition patterns). It is for that reason that organic chemists have tried to formulate simple theoretical models that describe the distribution and “flow” of electrons in conjugated systems. The rules proposed by pioneering chemists like Lewis, Langmuir, Robinson, and Ingold^[8–10] are now being used on a daily basis. Topological concepts based on the arrangement and nature of bonds between atoms, are useful tools for explaining the (π -electronic) properties of molecules. Some empirical concepts are supported by experimental facts and have become a theory without any rigorous proof. A nice example is the rule describing the relative stability of conjugated alkenes for which the stability decreases with increasing degree of branching (see Figure 2.1a). Another famous empirical rule is the *ortho–para* orientation for the electrophilic aromatic substitution of benzene derivatives. This can be quite easily predicted from

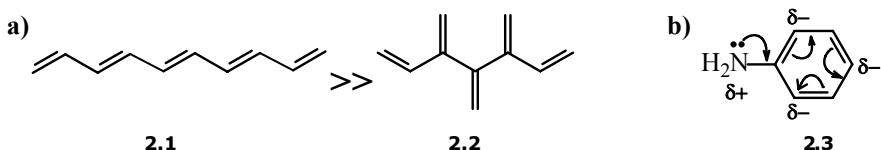


Figure 2.1 Examples of general rules for the behavior of π -electrons in organic systems: a) the relative stability decreases upon branching alkenes like 2.1, and b) ortho-para orientation effect in electrophilic aromatic substitution of aniline 2.3.

the “flow” of π -electrons using the organic electron theory proposed by Robinson and Ingold (see Figure 2.1b).^[11] For chemists, there is no doubt that the structural formula is a powerful tool for discussing the properties of compounds. The valence bond (VB) structures are used because of their simplicity and appeal to intuition.

When it comes to π -conjugated systems, topological concepts either distinguish between linear and cross-conjugated sequences or deal with differences in connectivity, such as, for example, alternant and non-alternant. Though trivial, a classification of molecular structures based on the topology of π -conjugated pathways between substituents, from here on called the π -topology, has not been recognized or investigated so far. The aim of the work presented here is to classify substituted conjugated systems by their degree of π -electron conjugation from a topology point of view. The substituents are called terminals and are the potential attachment positions for other functional moieties (e.g., additional conjugated fragments and functional groups) or electrodes.

First, a systematic analysis of n-terminal systems is given in a purely abstract, topological way. In this formulation the π -conjugated system is reduced to a representation called *archetype*. The advantage of employing archetypes is that it avoids a detailed discussion of every molecule and allows for the analysis of classes of conjugation. The term archetype will be used in two different ways. From the context it will become evident whether it denotes an abstract object, which only reveals the topology of the terminals (i.e., singly or doubly bonded), or if it denotes the corresponding molecular formula. Concepts like an archetype are akin to art and more often found in chemistry today.^[12] They stem from the Greek aesthetic (notions of beauty) where the central idea is to search for the essential core by representing the reality by a universal form or essence. This is exactly what the archetypal analysis is intended for, revealing the essential π -topological properties from simple representations. The archetypal analysis will be used as a tool to understand how the topology of conjugated systems determines the number of cross-conjugated pathways it may have. It is the foundation of the hypothesis that the topologies of conjugated systems can fully provide for a complete system of π -logic operations using single molecule electronics. The symmetry and switching

properties of n-terminal π -conjugated systems will be discussed in Chapter 5 and 6, respectively.

2.2 Systematic Analysis of n-Terminal Systems

The challenge of the systematic analysis of n-terminal systems is to describe the topological properties of conjugated systems *without* reference to their structural details. From now on, the conjugated system is considered in the form of an archetype. In this section the standard archetype series are defined on the basis of a statistical permutation of double bonds over n-terminals. In a later stage it is used to deduce the collection of structures representing the conjugated system and to determine its degree of conjugation.

The archetype is a visual object that consists of a circle and line(s), symbolizing the n-terminal system (see Figure 2.2). In reality, the terminals can be all kinds of groups or chemical elements, but hydrogens, for which the conjugation with other substituents is of interest. In this context, the single (double) covalent bond of the terminal with the central framework is called a single (double) link (see structure **2.7** and **2.8**, respectively). The number of terminals is indicated with the indices n (i.e., $n = 1$ for **2.7** and **2.8**). The basis of the n-terminal analysis concerns the nature and number of the terminals. All what is brought about by the analysis is, for a given number of n-terminals, a statistical permutation of double link terminals over n positions. It is our choice to use the number of double link terminals as the basis of the n-terminal analysis. A formulation based on the number of single link terminals would result in the same analysis. The statistics for the arrangement of double links in some order can be described by one of the mathematical models from the theorem of combinations.^[13] In the present context, the number of combinations without repetitions is the kind of probability theory of interest. An archetype with n terminals, which either have a single or double linked character, has a total of 2^n representations. This formalism is analogous to binary statistics over n positions when the single and double link terminals are considered from a digital point of view (e.g., zero and one).

An overview of the possible permutations for archetypes up to $n = 5$ terminals is presented in Table 2.1. The size and thereby the complexity of a series increases



Figure 2.2 The archetypal representation of a) 2-phenyl-1-ethenethiol **2.7** and the b) fulvene derivative **2.8**.

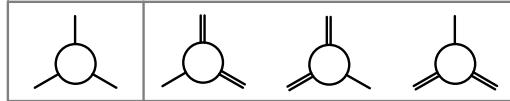
Table 2.1 Overview of the basic permutations of n -terminal systems ($n = 1\text{--}5$).

n	Number of archetypes per set (2^{n-1})	Even (E)		Odd (O)
1	$2^0 = 1$			
2	$2^1 = 2$			
3	$2^2 = 4$			
4	$2^3 = 8$			
5	$2^4 = 16$			

rapidly with the number of terminals. For the sake of brevity, only archetypes with $n = 2$, 3, or 4 terminals will play a central role in the remainder of this chapter. In Chapter 6, a higher order series (up to $n = 6$) will be discussed given that it is a versatile tool for the design of complex molecular logic gates. In terms of conjugation between two terminals, the archetype series of $n = 1$ terminal systems becomes irrelevant and is therefore left out of discussion here. As outlined in Table 2.1, a system with $n = 3$ terminals has four distinct permutations for the number of double link terminals: zero, one, two, or three double link terminals. The total number of forms is given by **n+1**.

The collection of n -terminal systems is subdivided in two sets with respect to the number of double link terminals: Even and Odd (see Table 2.1). Each Even and Odd subset of archetype series consists of 2^{n-1} archetypes (n is the number of terminals). An Odd set only contains archetypes with an odd number of double link terminals. The subdivision in Even and Odd sets is different from the total number of terminals, which in addition can be even or odd. The archetypes of the Even set of a 3-terminal

3-Terminal archetype series: $3E^{0(1)2(3)}$



$$2^{n-1} = 4 \text{ archetypes}$$

Figure 2.3 Archetype series of 3-terminal systems with an even number of double link terminals (Even set). Archetypes with the same number of double links are contained in individual boxes.

system are outlined in Figure 2.3. This series contains one member with zero double links and three members with two double link terminals (note the even number of double link terminals here). In order to keep the analysis systematic, the permutation of the terminals is always performed in the same order. Every terminal is assigned a double link in a clockwise manner upon increasing the number of double link terminals (see Figure 2.3).

As a consequence of the “binary” character of the links, the n-terminal systems can be symmetrically degenerate (see, for example, the archetypes with two double link terminals in Figure 2.3). The composition of an archetype series is given by indexes in superscript, which reveal the degeneracy of its members. For example, $3E^{0(1)2(3)}$ denotes the archetypes of an Even (E) set of 3-terminal systems. It has two basic forms: one with 0 and one with 2 double links. The form with two double link terminals is three-fold degenerate (i.e., 2(3)). The indexes are also displayed below every cartoon in Table 2.1.* The shorthand notation $3E^{0(1)2(3)}$ is called a descriptor. The composition of the archetype series with an increasing number of terminals follows the binomial distribution. The number of different combinations of n things (here the number of terminals), taken k at the time, without repetitions is given by Equation 2.1.^[13]

$$\text{Equation 2.1} \quad \binom{n}{k} = \frac{n!}{k!(n-k)!}$$

The formula of binomial coefficients is often referred to as the “binomium of Newton”, called after Isaac Newton in being the first to prove this sequence. Numerical values for coefficients n and k are given in Figure 2.4a. The distribution of numbers, given by the integer of the coefficients, is better known as the Pascal’s triangle named after Blaise Pascal (see Figure 2.4b). This triangle has a recognizable symmetry, in which the numbers of the n^{th} row are the same from left and right. In chemistry, Pascal’s triangle is used in nuclear magnetic resonance (NMR). Each row represents the pattern and intensity distribution of the splitting of signals resulting

* The sum of degenerate and non-degenerate members (in parenthesis) is given by 2^{n-1} . For 3-terminal systems it is: $(3) + (1) = 2^{n-1} = 2^2 = 4$.

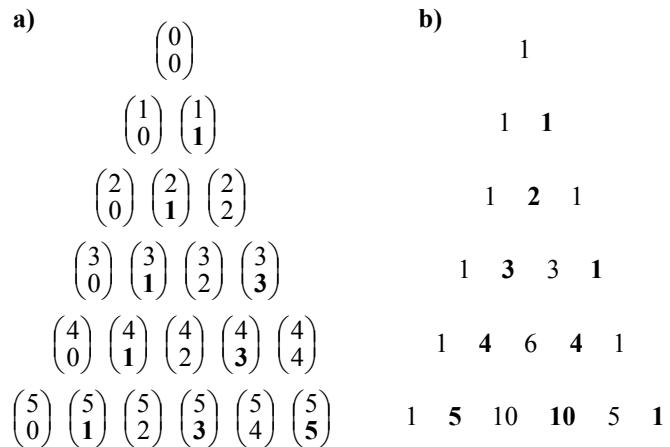


Figure 2.4 a) Binomial coefficients (n/k) for n -terminals and k double link terminals and b) Pascal's triangle. The values for an odd number of double links are marked bold.

from successive spin-spin couplings.^[14] A similar relation is found here. Each row of the Pascal's triangle reveals the composition of the archetype series of a system with n terminals (from left to right and Odd after Even). In Figure 2.4, the values for archetypes of the Odd set are displayed in bold and denote their number of double link terminals (Figure 2.4a) and their symmetrical degeneracy (Figure 2.4b). For example, upon combining the numbers from the fourth row of both diagrams (i.e., $n = 3$ terminals, as indicated by the upper coefficient in Figure 2.4a) one reads the following sequence of integers for "k double links (degeneracy)": $0(1)\mathbf{1(3)}2(3)\mathbf{3(1)}$. To guide the eye, the numbers for the Odd set are once again marked bold. The descriptor of the Odd set is $3O^{1(3)3(1)}$ and the one for the Even set is $3E^{0(1)2(3)}$.[†] In the next section it is shown that the archetype descriptors describe in an indirect manner the π -topology of all molecular structures of an archetype series. This is because the double link terminals impose a certain arrangement of double bonds within the structures.

2.3 Analysis of Fully Unsaturated n-Terminal Systems: Fundamentals, Definitions, and Conventions

The analysis of π -conjugated systems consists of deducing all possible double bond terminal patterns within the nuclear framework. This provides the basis for the classification of n-terminal π -conjugated systems by their degree of conjugation. This

[†] The binomial coefficients are a powerful tool for deducing the composition of higher order series. Upon expanding the Pascal triangle one can simply 'read' the degeneracy of, for example, the 7-terminal archetype series: $7E^{0(1)2(21)4(35)6(7)}$ and $7O^{1(7)3(35)5(21)7(1)}$.

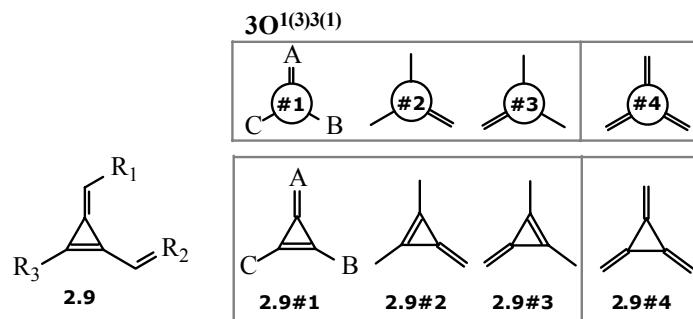


Figure 2.5 (Top) Standard 3-terminal archetype series (Odd set) required for the enumeration of the molecular archetypes (bottom) of the cyclopropene derivative **2.9**.

is the conjugation between the terminals as is facilitated by the molecular framework. An important requirement for the analysis is that the terminals should be conjugated with the central molecular framework. The formulation of archetype series for conjugated systems and their relevance to classify such systems is, as with the classification itself, new.

The collection of structures that represent a certain conjugated system is derived from the corresponding standard archetype series. In this context, the term archetype is used twofold. An archetype may refer to a structure as member of the archetypes series, which is called molecular archetype (see Figure 2.5, bottom), or refers to an abstract object from the standard archetype series (Figure 2.5, top). From the formulation of standard archetypes it follows that the analysis only holds for two-dimensional (2D) conjugated systems. It is a general procedure for the analysis of neutral fully unsaturated hydrocarbons regardless of the number of terminals or the size of carbon rings. With the exception of saturated carbons, the carbon atoms are depicted as their hydrogen suppressed junctions. Based on a valence bond description of the system, conjugation is defined here as the alternation of single and double bonds, which are represented by single and double lines (see also footnote [15] and [17]).

It is rather straightforward to deduce all available double bond patterns of an n-terminal π -conjugated system from the standard archetype series. The first example discussed here is an archetypal analysis of a 3-terminal conjugated system (see Figure 2.5). Prior to the analysis, the terminals of this cyclic hydrocarbon are reduced in size and length to either just one single or double bond (compare **2.9**, in which R denotes any desired moiety, with **2.9#1**). The terminals of acyclic systems need not to be reduced in length as can be seen in Figure 2.6. In the remainder of

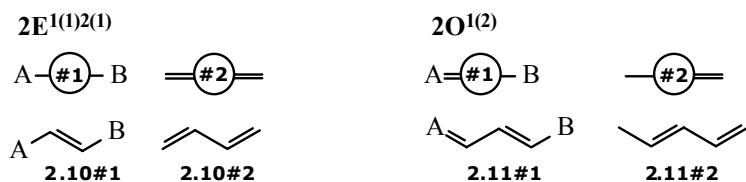


Figure 2.6 Standard 2-terminal archetype series (Even and Odd set; top) and the corresponding molecular archetypes of linear alkenes **2.10** and **2.11**.

this thesis, this compact representation of terminals is symbolized with a capital letter.[‡]

The terminals of the standard archetypes provide the basis for deriving the archetype series of an n-terminal π -conjugated system. The appropriate standard archetype series is determined from the original molecule by counting the total number of terminals and those terminals that are doubly bonded. The cyclopropene derivative **2.9** has three terminals in which only one of them (R_1) is doubly bonded. The kind of archetype series that needs to be considered for **2.9** is the Odd set of a 3-terminal archetype series. To make life easy, it is chosen to launch the archetypal analysis of molecules always from the same archetype, the so-called principal archetype #1. The principal archetype has the lowest number of double bond terminals. For archetype series of the Even set this is the archetype without double bonds, while the principal archetype of the Odd set always has just one double bond.

The archetype series of the benzene derivative **2.12** is chosen as example to demonstrate the essence of the analysis (see Figure 2.7). In sharp contrast to all aforementioned archetypes, it is not possible to find an arrangement of bonds in **2.12#2** so that each carbon has one single and double bond. This structure is an open shell π -system and is called the non-Kekulé member of the series.[§] Archetype **2.12#2** is the only one of its kind within the series. At this point the essence of the analysis of n-terminal π -conjugated systems has been brought up: archetype series *may or may not* contain one or more members that are non-Kekulé structures. The existence of non-Kekulé structures is related to the fact that some structures of the archetype series are not fully conjugated. For example, the pathway between terminal A and B in **2.12** is cross-conjugated (i.e., (AxB)). Archetype series with structures that only have linear conjugated pathways between the terminals do not contain non-Kekulé structures (see **2.9** in Figure 2.5). The emergence of non-Kekulé

[‡] Unless mentioned otherwise, the convention used for the terminals is alphabetically in a clockwise manner. The top left terminal is assigned the label "A". This labeling is often only given for archetype #1. The terminals of the other members are also specified as such.

[§] The structural formula with the lowest number of radicals is the preferred representation for archetypes of this kind.

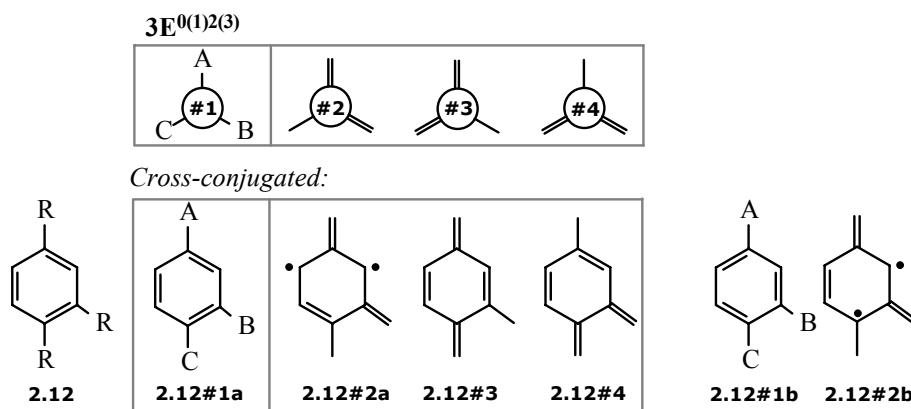


Figure 2.7 (Top) Standard 3-terminal archetype series (Even set). (Bottom) Corresponding molecular archetypes of **2.12**. Structures **2.12#1b** and **2.12#2b** are examples of resonance structures. The non-Kekulé structure of this series is **2.12#2**.

structures identifies a lower degree of π -conjugation given that it is commonly accepted that cross-conjugated pathways are less π -conjugated than linear ones.^[19] In the next section, it is shown that the *number* of non-Kekulé structures can be used as simple criterion to differentiate between the various classes of conjugation. Furthermore, in Chapter 5 the non-Kekulé structures are used to determine the number and identity of all potential cross-conjugated pathways.

Before going into the main stream of the analysis it is necessary to comment on some typical features of the molecular archetype series. First of all, in many cases one can think of more than one double bond pattern for the same archetype, which was for convenience neglected up until now. The *only* difference between such archetypes is the position of double bonds *within* the molecular framework, as is illustrated for **2.12#1a**, #1b and for **2.12#2a**, #2b in Figure 2.7. Hence, these are resonance structures. Resonance structures are embedded within the same archetype just as each of these structures would contribute to the same hybrid of real molecules. This is an important observation and supports the idea that the archetypal analysis is a meaningful topological concept for the classification of conjugated compounds.

The analysis of n-terminal systems is based on the number and topology of the terminals. The formulation uses a strict distinction between archetypes from an Even and an Odd set. This is because the analysis is for conjugated molecules, which are also confined to either set as is explained as follows. A neutral molecule with an odd number of double bond terminals cannot be converted to one with an even number unless one modifies the system. As illustrated for **2.9#1** in Figure 2.8a, an even number of double bond terminals can be created after modifying the nuclear

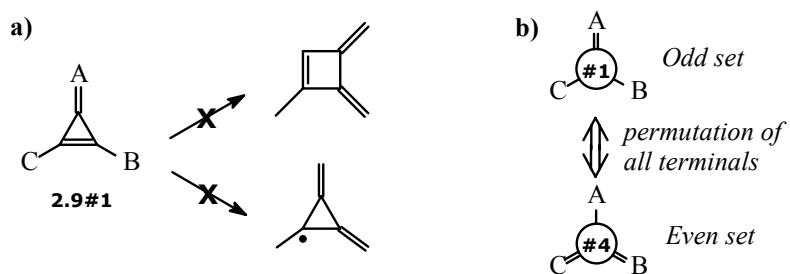


Figure 2.8 a) Two unacceptable ways to construct a molecular archetype from the Even set while the 2.9#1 has an odd number of double bond terminals. b) Standard archetypes of different sets are related by symmetry.

framework (here the creation of a four-membered ring system). Another way is to change the neutral system into an open shell system. In any case, the change is unacceptable since it represents a different molecule. It seems that, except for the number of terminals, there is no relation between Even and Odd set of molecular archetypes. However, there is a certain symmetry relation between both sets with respect to the topology of terminals. Each individual standard archetype is related to an archetype from the other set upon permutation of all terminals from single to double and vice versa (see Figure 2.8b).

2.4 Classification of n-Terminal π -Conjugated Systems

The systematic analysis of n-terminal π -conjugated systems provides for a straightforward method to elucidate all possible double bond patterns within a molecular framework. In the following, a further classification of π -conjugated systems into classes and some categories is defined. The motivation for such a classification is to gain a better understanding of the structure-property relation of π -conjugated systems.

The first examples to be considered are 3-terminal conjugated systems with an increasing number of cross-conjugated pathways. Typical examples for this purpose are easily obtained from the 3-terminal systems that already have been discussed. By combining structure 2.9 and 2.12 the number of cross-conjugated pathways is raised by one in the case of 2.13#1 ($A \times C$ and $B \times C$, see Figure 2.9). The two closed shell structures from the series of 2.13 contain two cross-conjugated pathways. Therefore, system 2.13 is classified as cross-conjugated subgroup (2x). By modifying the substitution pattern of the benzene derivative 2.12, as many as three cross-conjugated pathways can be created (see $A \times B$, $A \times C$, and $B \times C$ in 2.14#1). In these examples, the number of non-Kekulé structures is increased by one (two for 2.13 and up to three for 2.14) and the degree of conjugation is lowered. For these

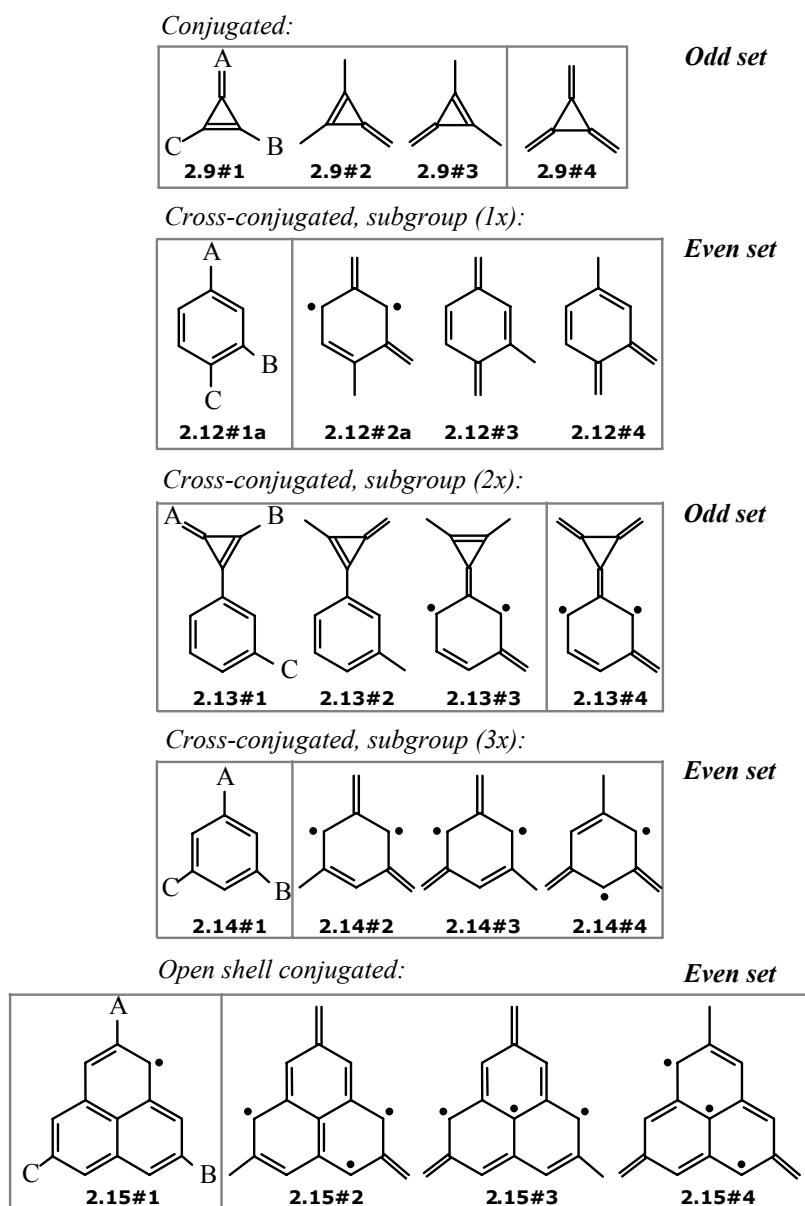


Figure 2.9 (From the top) Archetype series (from the Odd and Even set) of all $(2^{n-1}+1)$ categories of conjugation available for 3-terminal systems, ordered by degree of conjugation. The series of 2.15 represents the lowest degree of conjugation. The standard archetype series are given in Figure 2.5 and Figure 2.7.

archetype series, a simple relation is thereby found: the number of non-Kekulé structures is equivalent to the number of cross-conjugated pathways. This is *not* trivial as will be shown later in this chapter. Interestingly, the non-Kekulé structures pinpoint the cross-conjugated pathways within the remaining structures of the series. This is because the non-Kekulé structure is always found for the archetype member with an opposite bond topology of terminals compared to the “cross-conjugated” terminals of the closed shell structures of the series. For example, upon changing the cross-conjugated terminals A and C in **2.13#1** from single to double, one obtains the non-Kekulé structure **2.13#3**. The second non-Kekulé structure of this series (**2.13#4**) emerges after permutation of the terminals of pathway BxC in **2.13#1**. Hence, the types and number of non-Kekulé structures are closely related to the switching properties of conjugated systems! More details concerning this symmetry-related property and the identification of cross-conjugated pathways are given in Chapter 5.

The lowest degree of conjugation is found for another class of conjugation is defined as open shell conjugated. An example of an open shell π -system is the phenalene **2.15#1**. With the three terminals at the indicated positions, there is no way the bonds can be distributed so that each carbon has one single and one double bond. The series of **2.15** contains the maximum number of non-Kekulé structures that can be found: all! This class completes the proposed categories of π -conjugated systems as far as the number of non-Kekulé structure is concerned. The kind of alternation between the terminals in these open shell conjugated systems is irrelevant.

With the above, all five categories of π -conjugation within 3-terminal systems have been defined: three classes in which one class contains three subgroups. With an increasing number of non-Kekulé structures (from zero to four), these conjugated categories are: conjugated (between all terminals) **2.9**, singly cross-conjugated **2.12**, doubly cross-conjugated **2.13**, triple cross-conjugated **2.14**, and open shell conjugated **2.15**.

Let us now consider 4-terminal systems. The archetypal analysis is a convenient approach to elucidate all possible double bond configurations of conjugated systems with four terminals. The first class of π -conjugation that is considered with 4-terminal systems is one without non-Kekulé structures (i.e., the highest degree of conjugation). It was rather difficult to prove the existence of this class at first. In getting such a system, the simplest example for this what turns out to be a unique class of conjugation was found in structure **2.16#8** (see Figure 2.10). In fact, this system is derived from two fused units of the conjugated [3]radialene **2.9#4** (Figure 2.5). In being an extension of **2.9**, the archetype series of **2.16** does not contain non-Kekulé structures. This coincides with the existence of linear conjugated pathways between all terminals of the structures of this series. Structure **2.16** is a

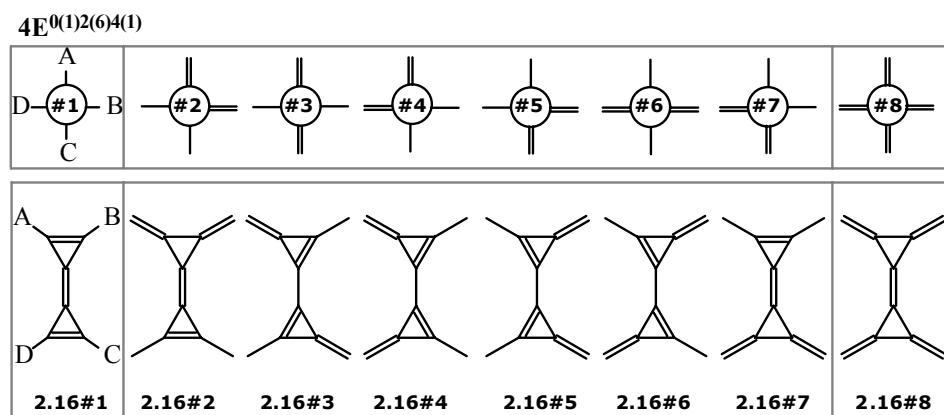


Figure 2.10 Standard 4-terminal archetype series (Even set) and corresponding molecular archetypes of an omniconjugated system (i.e., no non-Kekulé structures).

nice example of a more general phenomenon that has never been explicitly recognized or investigated from a topological point of view. Therefore, a new class of conjugation is introduced as “omniconjugation”. Omniconjugated systems have linear conjugated pathways between all terminals. They allow for the interconnection of several (functional) moieties in a fully conjugated manner. This is a crucial issue in constructing single molecule electronic devices. For this reason, omniconjugated systems are a potential interesting class of π -conjugated systems. Simply by trial and error, it is not easy to find more examples of structures from the omniconjugated class. Chapter 3 of this thesis is devoted to the systematic design of omniconjugated systems. At this point, four classes of conjugation in n-terminal systems have been characterized. The general properties of these classes are summarized in Table 2.2.

Table 2.2 Overview of the classes of π -conjugation in n-terminal systems. The number of non-Kekulé structures is used criterion for the classification.

Class	Number of non-Kekulé structures	Number of terminals	Bond alternation?
Omniconjugated	0	$n > 2$	Yes; linear, between all terminals.
Normal conjugated	0	$n = 2$	“ ”
Cross-conjugated ^{a)}	1 to $(2^{n-1} - 1)$	n	No; presence of two consecutive single bonds.
Open shell conjugated	2^{n-1}	n	Not applicable.

^{a)} This category contains subgroups (1x), (2x), etc., which refer to different levels of cross-conjugation.

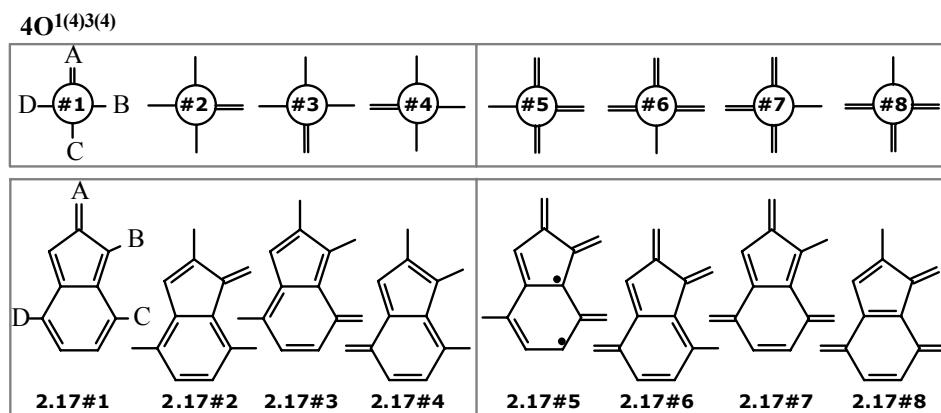


Figure 2.11 Standard 4-terminal archetype series (Odd set; top) and the corresponding molecular archetypes of the indene derivative **2.17#1** (principal archetype).

The archetype series of an example of a 4-terminal system from the Odd set is given in Figure 2.11. This series contains only one non-Kekulé structure (i.e., **2.17#5**), which relates to the fact that, for example, **2.17#1** has one cross-conjugated pathway (BxC).^{**} This system has a lower degree of conjugation than the omniconjugated system **2.16**.

An interesting aspect of molecular archetype series is the parity relation (even/odd) for the topology of terminals with the size of the hydrocarbon rings. Structures with an *odd* number of double bond terminals, like **2.17**, always have an *odd* number of even-membered carbon rings (i.e., even-rings, **2.17** has *one* even-ring consisting of six carbon atoms). The contrary is found for the 4-terminal archetype series of the Even set: an *even* number of double bond terminals imposes an *even* number of even-rings (see Figure 2.10). This feature is independent of the number of terminals as can be understood from the 3-terminal archetype series of structure **2.13** (see Figure 2.9). Here, archetype **2.13#1** has one double bond terminal and one even-ring; both numbers are odd. The fact that an *even* (*odd*) number of even-rings comes with an *even* (*odd*) number of double bond terminals is an intrinsic property of all archetype series. Obviously, this reasoning cannot be used for conjugated systems without rings (i.e., acyclic systems such as **2.11** in Figure 2.6). Even more surprising is the one-to-one correlation with the total number of carbon atoms. It is found that acyclic *n*-terminal systems with an odd number of double bond terminals have an odd number of carbons. In the continuing search for π -topological answers, the origin of the parity relation is found in the definition of

^{**} Some π -topological properties of **2.17** are discussed in Section 3.3.2 of this thesis.

Table 2.3 The categories of π -conjugation in n -terminal systems ($n = 2 - 4$). There are $(2^{n-1} + 1)$ categories (i.e., classes and subgroups), which differ in number of non-Kekulé structures (given in parentheses above the models). Some classes of π -conjugation are categorized in subgroups according to the number (x) of cross-conjugated pathways. The classes are: open shell conjugated (open shell), cross-conjugated (cross), subgroup (x), normal conjugated (linear), and omniconjugated (omni).

n=2: 3 categories *		
(0)	(1)	(2)
linear	cross (1x)	open shell
n=3: 5 categories		
(0)	(1)	(2)
omni	cross (1x)	cross (2x)
		(3)
		(4)
n=4: 9 categories		
(0)	(1)	(2)
omni	cross (1x)	cross (2x)
		(3)
		(4)
		(5)
		(6)
		(7)
		(8)
		open shell

* $2^{n-1}+1$

conjugation. The alternation of one single and one double bond (C=C–C) represents the same kind of topological condition since an *odd* number of carbons (three) requires an *odd* number of double bond terminals (one) to be conjugated.

An overview of all categories of conjugation per n-terminal ($n = 2 - 4$) system is presented in Table 2.3. Here, an example system is given for every category. The distinctive categories are abbreviated as follows: open shell conjugated (open shell), cross-conjugated (cross, for different subgroups 'x'), normal conjugated (linear), and omniconjugated (omni). The number of categories (i.e., classes and subgroups) per n-terminal system is $2^{n-1}+1$. Some of the archetype series of systems belonging to the 2-, and 4-terminal categories are not discussed. The main reason for the limited analysis is the large number of archetypes that have to be elucidated to fully cover all categories of higher order systems. For instance, 4-terminal systems have $2^{n-1}+1 = 9$ categories, each consisting of series with $2^{n-1} = 8$ archetypes. The complete analysis of all 4-terminal systems involves 72 archetypes.

A close look at the number of non-Kekulé structures within the categories given in Table 2.3, shows that, while all categories are systematically increasing in number of non-Kekulé structures, the one with 4-terminals is visibly different. To be more specific, there is a difference between the cross-conjugated subgroup (3x) in the 3-terminal category, which has four non-Kekulé structures, and the subgroup (3x) in the 4-terminal category, in which either three or four out of the eight archetypes are non-Kekulé structures. Apparently, the number of non-Kekulé structures is not always equivalent to the number of cross-conjugated pathways. This inconsistency is not a coincidence as the number of non-Kekulé structures continues to be raised by one compared to the number of cross-conjugated pathways (see subgroup (5x), (6x), and (7x)). This means that the rule proposed in the previous section is not applicable to higher order ($n > 3$) systems. This observation suggests that the conjecture in which the number of non-Kekulé structures is equivalent to the number of cross-conjugated pathways is merely a coincidence for systems with less than four terminals. These anomalies stimulate a full mathematical description of the π -topology of n-terminal conjugated systems. In an attempt, a group theoretical approach was developed that will be discussed in Chapter 5 of this thesis. This approach gives an explanation for the anomalies found for the number of non-Kekulé structures in systems with four or more terminals.

The question can be raised why one should consider the analysis of n-terminal systems as yet another empirical concept if it only would allow for classification by degree of conjugation. Therefore, a few words about the merits of the archetypal analysis are required. There is a wealth of hard evidence that linear conjugated systems have a higher degree of π -conjugation (delocalization) than cross-conjugated systems. As it should, the present analysis unambiguously distinguishes these generally accepted classes of conjugation. Further empirical evidence that the

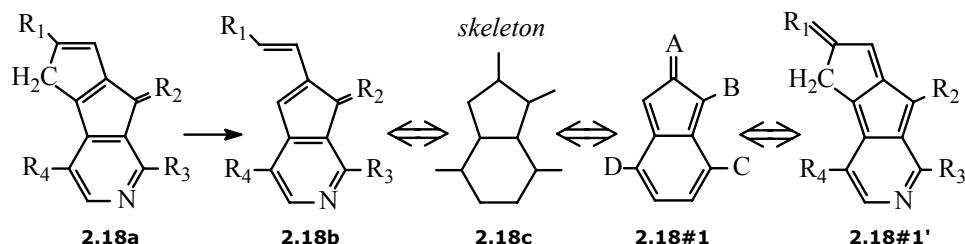
classification by degree of conjugation foresees quite well the properties of conjugated systems is found in the omniconjugated category. This is the class with the highest possible degree of conjugation. Real examples from the omniconjugated class can have interesting physical properties. For example, derivatives of [3]radialene **2.9#4** possess an extensively delocalized π -electron system stretching all the way across the molecule *into the terminals*.^[20-22] Due to the extended conjugation of [3]radialenes the absorption maxima of the parent molecule can be easily shifted far into the visible region upon introducing donor and acceptor groups at the terminal positions.^[23]

The high degree of conjugation that was ascribed to [3]radialenes coincides with a high π -electron delocalization. From our point of view, the extended delocalization of π -electrons is the foremost reason for the unique properties of [3]radialenes. Hence, the proposed classification can provide further insight into the properties of conjugated systems.

2.5 Generalized Analysis of n-Terminal Systems

The method of the classification by degree of conjugation has been outlined with simple, representative n-terminal systems. However, the archetypal analysis can be applied to any n-terminal acyclic, mono- or polycyclic hydrocarbon regardless whether it is alternant or non-alternant. It is beyond the scope of this thesis to fully cover this broad field of (fully) unsaturated hydrocarbons with archetypal analyses. Nonetheless, an interpretation for acyclic systems and systems containing saturated carbons or heteroatoms is presented in the following.

A simple solution in dealing with saturated carbon atom is by taking away the root of the problem. The saturated carbons are removed from the nuclear framework prior to the n-terminal analysis (see **2.18a** and **2.18b** in Scheme 2.1). As can be seen from **2.18b** and the corresponding pristine skeleton **2.18c**, the implementation



Scheme 2.1 Construction of the principal archetype #1 of a saturated heteroatomic system after removal of the saturated carbon in **2.18a**. The skeleton **2.18c** is used as intermediate to construct archetype **2.18#1'**.

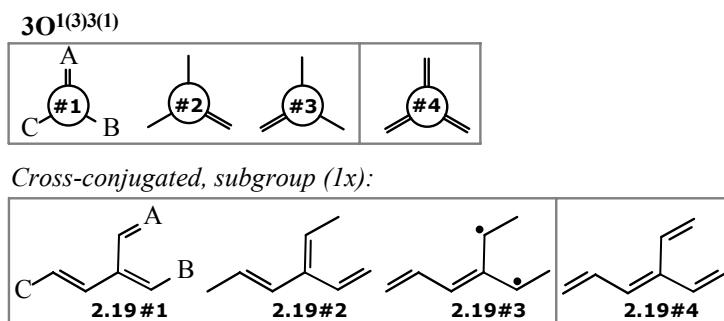


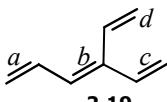
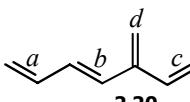
Figure 2.12 Standard 3-terminal archetype series (Odd set; top) and the corresponding molecular archetypes of the branched alkene **2.19**.

of certain heteroatoms (like nitrogen) is in this case rather straightforward.^[24] The skeleton **2.18c** serves as an intermediate for constructing the molecular archetypes of **2.18** (see **2.18#1** or **2.18#1'**). Hence, the skeleton forms the basis for elucidating the π -topological properties of the parent system. This implies that different *n*-terminal systems with exactly the same skeleton have the same degree of conjugation. The structures of the archetype series of **2.17** (see Figure 2.11) have the same skeleton as the one given for **2.18**. From the series of **2.17** it follows that **2.18a** is cross-conjugated (subgroup (1x)) with archetype #5 as the non-Kekulé structure of the series (see also **2.17#5**). The generalization of the archetypal analysis is only an extension for conjugated systems containing saturated carbons and is not intended for saturated terminals.

The construction of archetype series of an acyclic system is somewhat trivial. Unsaturated carbon chains are not reduced in length since the carbons at the far ends serve as the terminals of the system. This is illustrated for **2.19** in Figure 2.12. According to this analysis, structure **2.19** is cross-conjugated (subgroup (1x)).

Some empirical concepts that deal with aromaticity are closely related to our approach. For example, conjugated systems can be evaluated based on the sum of contributions from smaller structural elements such as conjugated circuits^[5] or paths of different lengths.^[25,26] The latter approach is shown for acyclic system **2.19** in Table 2.4. Here, the system is decomposed in smaller units containing conjugated paths that differ in number of double bonds involved (the length). Subsequently, the count of conjugated paths of different lengths is used as criterion to discern conjugated systems in terms of stabilization by resonance. The shortcoming of this method is that systems with the same counts of conjugated paths can have a different connectivity or subtle differences in connectivity may give rise to different counts.^[7] This latter situation is well illustrated with the count of conjugated paths for structure **2.19** and its isomer **2.20** (see Table 2.4). These isomers have a different count for the longest sequence (see last row). Although they have the same

Table 2.4 The count of conjugated paths of branched alkenes. For every conjugated path depicted in the left, the bonds involved are given in parentheses behind the count.

	 2.19	 2.20
Path	Counts (<i>C=C</i> bonds involved)	
≡	4 (a; b; c; d)	4 (a; b; c; d)
≡ ≡ ≡	3 (a-b; b-c; b-d)	3 (a-b; b-d; c-d)
≡ ≡ ≡ ≡	2 (a-b-c; a-b-d)	1 (a-b-d)

degree of conjugation according to an archetypal analysis, these isomers are treated differently in expressions based on connectivity. Our approach does not distinguish between these isomers simply because the number of non-Kekulé structures of their archetype series is the same.

2.6 Discussion

The archetypal analysis is a simple formulation based on the nature and number of terminals. The distinction between an Even and Odd set of archetypes is based on the number of double bond terminals. In the end, this turns out to be related to the connectivity of the nuclear framework. A system with an *odd* number of double bond terminals contains an *odd* number of even-rings or, in case of acyclic systems, has an *odd* number of carbon atoms. In search for π -topological answers, the origin of this curiosity is found in the topology of one single and double bond (C=C–C). Another kind of analysis could have been formulated on the basis of this conjugated fragment. For example, one could scan the π -topology of conjugated systems by determining to what extent they meet the following arguments for every carbon junction with adjacent sites (or terminals) A, B, and C: if B is doubly bonded, than A and C are single bonded: $B(=) \Rightarrow A(-) \wedge C(-)$; and if B is single bonded, than either A or C is doubly bonded: $B(-) \Rightarrow A(=) \vee C(=)$. Related arguments for the immediate bond environment can be employed in algorithms to construct conjugated systems computationally (see footnote [27]). Unfortunately, this did not result in any additional (mathematical) understanding or new insights regarding the π -topology of conjugated systems.

The key elements of the archetypal analysis are the non-Kekulé structures. Their existence is related to the fact that the *n*-terminal system is not fully conjugated in all possible double bond configurations. In general, fully unsaturated non-Kekulé systems are an important class of compounds for the design of high spin molecules. These are molecules with a permanent magnetic moment resulting from the interaction between unpaired electrons. There are many topological rules for the design of high spin systems.^[28-31] The formulation of molecular archetypes series is somewhat related to the “spin rule” proposed by Radhakrishnan.^[32] With this rule one can predict the ground state spin after writing down the fully conjugated non-Kekulé structures and by only taking into account the resonance structures with the least number of π -electrons between the radical sites. The ground state spin predicted by this rule depends on whether the number of π -electrons of the shortest path between radical sites is even or odd. As with the molecular archetype series, parity does matter. In many cases, the prediction of the ground state spin was found to be in agreement with the data obtained from experiments.^[33] This confirms that empirical concepts based on the structural formula can be useful tools to elucidate the structure–property relation of conjugated systems.

A comment about the molecular graph theory might be in place here to prevent any mystification with the presented archetypal description of *n*-terminal systems. Graphs are also abstract objects of no fixed geometrical form that may, for instance, symbolize molecules. However, the analysis of chemical graphs comes with matrices consisting of elements, such as connectivity indices, describing the detailed topology of the molecular framework.^[34,35] In the present context of archetypes, such an elaborated description of the connectivity is not necessary to determine the degree of conjugation in a qualitative manner.

Similarly, it is important to mention that the proposed classification of π -conjugated systems is not related to a certain degree of *aromaticity* of (poly)cyclic hydrocarbons. Here, the resonance energy is a measure of extra stability and allows for classification of (poly)cyclic hydrocarbons by fully aromatic, aromatic, and anti-aromatic.^[7,36-38] Our approach only deals with the degree of *conjugation* in an *n*-terminal system. One could search for an analogy between the degree of π -conjugation and aromaticity. No efforts have been made to relate the topological properties of archetype series (such as the number of non-Kekulé structures or the degeneracy of archetypes) with a certain degree of aromaticity.

2.7 Conclusions

The archetype series of *n*-terminal systems can be utilized to describe the π -topological properties of any conjugated system. The enumeration of archetypes is a general procedure based on a statistical permutation of double bonds over *n* terminals. It allows for a classification by degree of π -conjugation in categories

containing common π -topological features. In a way, the terminals manage all possible double bond configurations within the molecular framework. There was only one rudimentary limitation; the terminals of the system have to be π -conjugated with the central molecular framework. The majority of topological concepts that deal with the structure-property relation in conjugated systems are concerned with a detailed description of the molecular structure. In the archetypal analysis the search for conjugated pathways was prevented by the use of non-Kekulé structures. It was found that the type and number of non-Kekulé structures control the π -topological properties of the series of structures representing the n-terminal conjugated system.

Among the two commonly accepted classes of conjugation, the normal (linear) conjugated systems have a higher degree of conjugation than cross-conjugated ones. Difficulties with various levels of cross-conjugation were nicely resolved by the count of non-Kekulé structures. This further differentiates the cross-conjugated class in subgroups. The proposed method for classification of conjugated systems allowed for the introduction of a new class of π -conjugation called omniconjugation. In discussing the definition of omniconjugation, one may informally refer to the borderline case of normal conjugated where the number of non-Kekulé structures is also zero. However, the latter class can only be found for simple systems with two terminals. This allowed the label "omniconjugated" to be reserved for systems with more than two terminals. Omniconjugated systems appeal for a more complex π -topology to prevent the emergence of cross-conjugated pathways. So far, the archetypal analysis distinguishes four classes of conjugation (including subgroups for the cross-conjugated class) and is believed to cover all possible π -topologies. A full mathematical description of the π -topology of conjugated systems is still missing, yet very desirable.

The analysis of cross-conjugated systems showed that non-Kekulé structures disclose more π -topological information than initially expected. They provided insight into the nature of individual alternating pathways between the terminals of all structures of the archetype series. This was because all archetypes are, somehow, related by symmetry. This interesting feature plays an essential role in elucidating all potential cross-conjugated pathways of a conjugated system. Therefore, the analysis of the n-terminal systems is the foundation of the work presented in the rest of the thesis.

One of the most intriguing aspects of molecular archetype series was their apparent relation with the smallest conjugated fragment. The even-odd symmetry of one double-single bond sequence was reminiscent of the structural formula of all molecular archetypes. There was a strict relation between the (even/odd) number of double bond terminals and the (even/odd) number of even-rings or carbon atoms. This suggests that all curiosities of π -topology can be revealed from their origin: the conjugated double bond.

2.8 References and Notes

1. A. Kekulé, *Bull. Soc. Chim. Fr.* **1865**, 3, 98.
2. J. Ferraris, D. O. Cowan, V. Walatka, J. H. Perlstein, *J. Am. Chem. Soc.* **1973**, 95, 948.
3. A. F. Garito, A. J. Heeger, *Acc. Chem. Res.* **1974**, 7, 232.
4. E. Clar, *The Aromatic Sextet*, Wiley, New York **1972**.
5. M. Randić, *J. Am. Chem. Soc.* **1977**, 99, 444.
6. A. T. Balaban, *Pure Appl. Chem.* **1980**, 52, 1409.
7. M. Randić, *Chem. Rev.* **2003**, 103, 3449.
8. G. N. Lewis, *J. Am. Chem. Soc.* **1916**, 38, 762.
9. I. Langmuir, *Phys. Rev.* **1921**, 18, 104.
10. C. K. Ingold, *Chem. Rev.* **1934**, 15, 225.
11. R. Robinson, *J. Soc. Chem. Ind.* **1925**, 44, 456.
12. R. Hoffmann, *J. Aest. Art. Crit.* **1990**, 48, 191.
13. E. Kreyszig, *Advanced Engineering Mathematics*, 8th ed., Wiley, New York **1999**, pp. 1066.
14. M. Hesse, H. Meier, B. Zeeh, *Spectroscopic Methods in Organic Chemistry*, Thieme, New York **1997**, pp. 77.
15. In contrast to cumulated double bonds (i.e., double bonds that share one carbon),^[16] triple carbon-carbon bonds can be part of conjugated pathways. However, triple bonds are not commonly found in cyclic unsaturated hydrocarbons and are therefore left out of discussion here. The same holds for cumulated double bonds. The fully unsaturated hydrocarbon systems considered here consist of single and double bonds.
16. R. T. Morrison, R. N. Boyd, *Organic Chemistry*, 6th ed., Prentice-Hall, London **1992**, pp. 410.
17. Carbon atoms can, in classical terms, form four bonds although some interesting exceptions are known.^[18] Every carbon of the nuclear framework is considered as sp²-hybridized and bonded to three other atoms via two single bonds and one double bond. The reasoning for leaving out saturated carbons, as well as ions and radicals, becomes evident in the course of the analysis.
18. F. Scherbaum, A. Grohmann, B. Huber, C. Krüger, H. Schmidbaur, *Angew. Chem.* **1988**, 100, 1602.
19. N. F. Phelan, M. Orchin, *J. Chem. Educ.* **1968**, 45, 633.
20. K. Takahashi, S. Tarutani, *J. Chem. Soc., Chem. Comm.* **1994**, 519.

21. C. Lepetit, M. Brøndsted Nielsen, F. Diederich, R. Chauvin, *Chem. Eur. J.* **2003**, 9, 5056.
22. K. Takahashi, S. Tarutani, *Adv. Mater.* **1995**, 7, 639.
23. H. Hopf, G. Maas, *Angew. Chem., Int. Ed. Engl.* **1992**, 31, 931.
24. It is clear that many heteroatoms could give great complications due to the possible involvement of lone pairs of electrons (e.g., push-pull systems). Such systems cannot be treated in this way. They are way beyond the scope of the present n-terminal analysis.
25. T. G. Schmalz, T. Živković, D. J. Klein, *Stud. Phys. Theor. Chem.* **1988**, 54, 173.
26. J. Gálvez, R. García-Domenech, C. de Gregorio-Alapont, *J. Comput. Aided Mol. Des.* **2000**, 14, 679.
27. This was confirmed with an algorithm that was developed to construct omniconjugated systems computatively from pristine, but fixed, nuclear frameworks (unpublished work of H. T. Jonkman). In this iterative procedure, double bonds are assigned to carbons as long as the resulting pathway between any pair of terminals is or remains conjugated. The topology of the resulting conjugated systems was in agreement with the predicted position of double bonds.
28. L. Ducasse, *Chem. Phys. Lett.* **2002**, 352, 454.
29. D. A. Dougherty, *Acc. Chem. Res.* **1991**, 24, 88.
30. X. Li, J. Paldus, *Chem. Phys.* **1996**, 204, 447.
31. N. Tyutyulkov, F. Dietz, K. Müllen, M. Baumgarten, *Theor. Chim. Acta* **1993**, 86, 353.
32. T. P. Radhakrishnan, *Chem. Phys. Lett.* **1991**, 181, 455.
33. T. P. Radhakrishnan, *Chem. Phys. Lett.* **1993**, 207, 15.
34. I. V. Stankevich, M. I. Skvortsova, N. S. Zefirov, *J. Mol. Struct. (Theochem)* **1995**, 342, 173.
35. L. Pogliani, *Chem. Rev.* **2000**, 100, 3827.
36. E. Hückel, *Z. Phys.* **1931**, 70, 204.
37. E. Clar, *Polycyclic Hydrocarbons Vol. I and II*, Academic Press and Springer, London and Berlin **1964**.
38. D. Plavšić, S. Nikolić, N. Trinajstić, *J. Mol. Struct. (Theochem)* **1992**, 277, 213.

Chapter 3

Topological Design of Omniconjugated Systems

Abstract In this chapter, omniconjugation is introduced as a topological phenomenon in n -terminal π -conjugated systems. Omniconjugated molecules have in common that they provide direct and fully π -conjugated pathways between all terminals, attached to them. Surprisingly, up until now such topologies have never been explicitly recognized or investigated. A topological design scheme that originates from a valence bond description of the π -system is presented as a tool that enables for the axiomatic construction of a large number of realistic omniconjugated models. Molecular building blocks with three or more connection points to the external moieties are being proposed. These allow for the interconnection of many functional entities in a fully conjugated manner. This new class of π -conjugated systems can be divided in two subclasses (Type A and Type B) that differ in their π -topological properties. Due to the unique topological properties of both Type A and Type B systems, omniconjugation may play an important role in the design of complex electronic circuitry based on passive and active elements.

The work presented in this chapter is partially covered by the following paper: M. H. van der Veen, M. T. Rispens, H. T. Jonkman, J. C. Hummelen, *Adv. Funct. Mater.* **2004**, 14, 215–223.

3.1 Introduction

In the continuing race for faster computers and new electronic devices, enormous research effort is put into the miniaturization of classical semiconductor components. A fascinating alternative for the ongoing size reduction of silicon-based technology is the bottom-up approach based on molecules. The idea to implement molecules as elementary parts in electronic circuits stems from the early seventies.^[1,2] During the last decade, scientists have published on successful fabrication of single molecule devices that indeed can function as, for example, wires, diodes or transistors.^[3-5] However, a device or an electronic circuit is made up of many (complex) elements, wired in a specific way to make it operate. In these nanoscale circuitries, it is the topology of the conductive paths in the molecular structures (linear pathways, loops, nodes, the number of interconnections, branches, etc.) that will define their functionality.^[6-8] Of particular importance for the transmission of charges is a proper combination of the degree of π -electron delocalization and conjugation along the conductive pathway.

Up until now, the trivial aspect of interconnecting several elements has not been truly addressed on the molecular level. Therefore, rather complicated supramolecular architectures are being proposed for the design of molecular circuitries.^[3,9] It has been reported that the realization of new architectural concepts for organic molecules will be crucial for their implementation in fully integrated molecular circuits.^[10] One of the simplest elements missing is the single molecule version of a T-piece or an intersection of two molecular wires like **3.1** (see Figure 3.1). When using simple molecular architectures like **3.2** or **3.3**, which would represent these molecular junctions, it is not possible to create a situation in which efficient transport can happen in all, preferable more than two or three, directions. That is, between the three substituents or external moieties labeled as terminal A, B, and C in Figure 3.1. It is very likely that the transmission of charges is unequal in **3.3** and will have a higher probability for the linear conjugated pathway between A to B ($A\leftrightarrow B$) compared with cross-conjugated pathway A to D ($A\times D$). This situation will not improve by changing the arrangement of double bonds or after slightly modifying the system as shown in **3.4**. In fact, the overall conjugation in **3.4** is the same as in **3.3** since it contains the same number of cross-conjugated pathways (i.e., two namely, $A\times C$ and $B\times D$). This is schematically represented by a topological connectivity scheme below the models in Figure 3.1. Here, the double-headed arrows are used to indicate a conjugated pathway.

In Chapter 2 of this thesis, a classification of substituted conjugated systems was introduced that allows for establishing the degree of π -conjugation without having to find the conjugated pathways. This method consists of deducing all possible double bond patterns within a certain molecular framework. It was found that such a collection of molecular representations (called archetype series) reveals

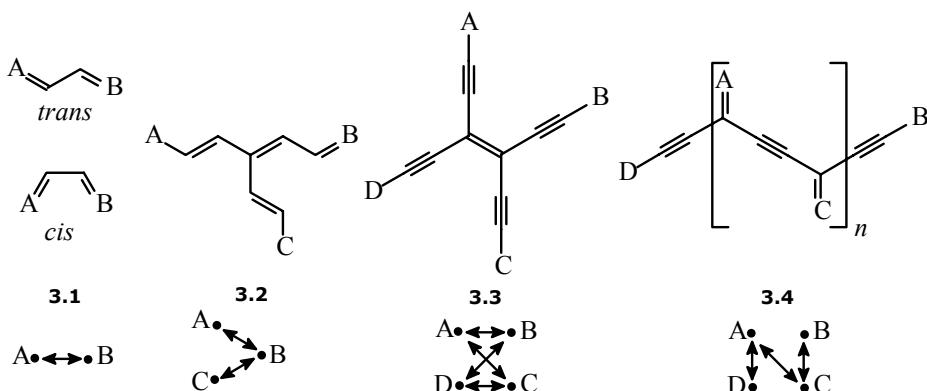


Figure 3.1 (Top) Schematic representation of conjugation in substituted (A, B, C, and D) compounds: 2-terminal linear (*cis/trans*) conjugated butane **3.1**; 3-terminal cross-conjugated 4-(1-propenyl)-heptatriene **3.2**; 4-terminal cross-conjugated tetraethynyl-ethene **3.3** and iso-poly(diacetylene) **3.4**. (Bottom) Corresponding topological connectivity schemes of linear conjugated pathways.

the degree of conjugation of the n-terminal system. An unambiguous difference was found between linear and cross-conjugated n-terminal systems. In contrast to linear conjugated systems, cross-conjugated systems contain at least one molecular representation in their series which is an open shell system (i.e., non-Kekulé structure). This is related to the fact that cross-conjugated systems are not fully conjugated. The number of non-Kekulé structures is used as simple criterion to differentiate between the various classes of conjugation. The cross-conjugated systems have a lower degree of π -conjugation compared to linear conjugated systems. The analysis further differentiates cross-conjugated systems into subclasses, which contain an increasing number of cross-conjugated pathways and an even lower degree of conjugation. Hence, the approach ascribes a lower degree of conjugation to model **3.4** and **3.3** (cross-conjugated, three and two times) compared to **3.2** (cross-conjugated, once) and **3.1** (normal/linear conjugated).

Concerning the physical properties, the most important difference between the linear and cross-conjugated classes of conjugation is that there is substantially less π -electron delocalization over a cross-conjugated path (AxC in **3.2**) compared to linear conjugated one (A↔B in **3.2**).^[11-13] As a result, charges can flow less efficiently between terminals A and C where the strict alternation of single and double bonds is interrupted by an extra single bond. Hence, the notion of conjugation is an important factor in molecular electronics. Another property, relevant for transmission of charges, is the electronic coupling parameter that provides a measure of the electronic interaction between two moieties. Even though there may be a considerable delocalization of π -electrons over the entire framework

of models like **3.3**, theoretical and experimental studies confirm that the electronic coupling between cross-conjugated moieties is severely reduced compared with those having linear conjugated pathways.^[14,15] As a consequence, a substantial decrease in electron transfer efficiency along cross-conjugated systems was found.^[6,16,17] In several studies with *iso*-poly(diacetylene)s (**3.4**), only a small contribution from the cross-conjugated segments to the overall electronic properties was found.^[18,19] The electronic properties of these compounds are dominated by their longest linearly conjugated segment (see A↔B in **3.4**),^[20] again as a result of the reduced π-electron mediated interaction between cross-conjugated terminals.^[21,22]

It appears advantageous to prevent cross-conjugation between specific terminals in molecules when trying to optimize their mutual π-electronic interaction and charge transport capabilities. The work described in this chapter addresses compounds that fulfill the conditions for efficient charge transport, in theory. The aim is to search for more conjugated systems that have fully conjugated pathways and to investigate their π-topological properties. Particularly, we will discuss those molecules with at least four terminals that could, in principle, mimic the simple function of an intersection ("soldering point") between molecular wires.

3.2 Wiring Molecular Wires

Whereas the majority of n-terminal conjugated compounds were found to be not fully conjugated in all possible double bond arrangements, the analysis of n-terminal conjugated systems (see Chapter 2) revealed a class of molecules that do have such a π-topology. n-Terminal molecules of this kind have the highest degree of π-conjugation and were called omniconjugated. A typical omniconjugated system with three terminals is the [3]radialene model **3.5** (Figure 3.2). As can be seen from its connectivity scheme, this model has linear conjugated pathways between all terminals. In contrast to all higher radialenes, which do possess cross-conjugated pathways, derivatives of **3.5** exhibit a complete delocalization of the π-electron density at the three terminals,^[23,24] as well as alternating shortening of bonds, induced by conjugation.^[25,26] From the present point of view, the existence of fully conjugated pathways between all sites is the foremost reason of the unique properties of [3]radialenes (see Section 2.4). This makes model **3.5** an interesting building block for the construction of molecular electronic circuits.

Omniconjugation is defined as the property of molecules, having direct linear π-conjugated pathways between *all* connected moieties.

An omniconjugated system is a conjugated molecule with direct linear π-conjugated pathways between *all* connected moieties. "Direct" meaning that an alternation of single and double bonds between any two terminals must exist,

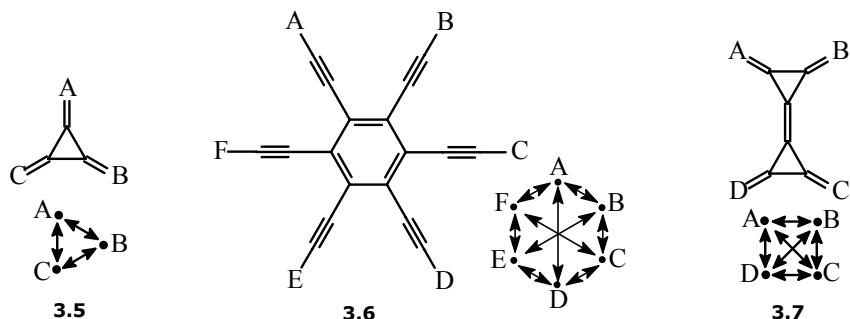


Figure 3.2 (Top) Schematic representation of 3- and 4-terminal substituted omniconjugated compounds [3]radialene **3.5** and cyclopropylidenecyclopropane **3.7**; six-terminals cross-conjugated hexa-ethynylbenzene **3.6**. (Bottom) Corresponding topological connectivity schemes of linear conjugated pathways.

without the need for using any bond twice in such an alternating pathway. Systems in which one or more of the pathways can only be found using one or more bonds twice are called “looped” systems, because they contain “looped” pathways. As will be explained later on, they are only “quasi-omniconjugated” (Scheme 3.4). In some cases, a distinction is made based on the geometrical properties of a conjugated pathway. For instance, the bonding pattern between substituents at the *ortho*-position of benzene (terminals A and B in model **3.6**) may be identified as “bent” conjugated^[27] and pathway A↔B in **3.1** as *cis* or *trans* conjugated^[28] analogous to the isomerism process of double bonds. The former interpretation is used in a study to gain a better understanding of the geometrical aspects of the charge-transfer pathways in phenylacetylene macrocycles.^[27] Here, such details are not relevant since the strict alternation of single and double bonds is only considered from a topological point of view. Therefore, the term linear conjugation is used regardless whether it is “bent” (A↔B in **3.6**), *cis* or *trans* (A↔B in **3.1**) conjugated.

Within the above definition of omniconjugation, the 2-terminal model **3.1** and the 3-terminal radialene **3.5** are rudimentary examples of omniconjugated systems. In a 4-terminal omniconjugated molecule as many as six conjugation pathways should be present: A↔B, A↔C, A↔D, B↔C, B↔D, and C↔D to meet the condition of being omniconjugated. According to Diederich *et al.*, these six pathways are found in derivatives of tetraethynylethene (TEE) having model **3.3** as central building block.^[14,29,30] However, these so-called “fully π -conjugated systems” have two pathways that are cross-conjugated, these are A↔D and B↔C (see the missing arrows in the connectivity scheme of **3.3**). Hence, TEE-derived compounds are not omniconjugated systems. There is also some controversy in literature about extended dimensions of π -conjugation. Some studies refer to systems comprising units like **3.3**^[31,32] and **3.6**^[33,34] as representative examples of fully two-dimensional

(2D) conjugated systems. One indeed can find linear conjugated paths in at least two directions between the three possible combinations of *para*-substituents in **3.6**. However, these pairs are cross-conjugated to one another. There are as many as six out of fifteen conjugated pathways absent. The overall system should not be referred to as fully conjugated in the desired two dimensions. The discrepancy concerning fully π -conjugated systems and the structural conditions that are required to truly realize conjugated pathways have been recognized by several authors.^[35,36,37]

With the [3]radialenes at hand, the first topological example of a 4-terminal omniconjugated system (with the necessary six conjugated pathways between the four terminals) can be introduced: model **3.7** (Figure 3.2). The fact that real molecules of **3.7** are hard to prepare, relatively unstable and thus difficult to isolate^[38] is irrelevant at this point. Model **3.7** serves as a building block in designing more omniconjugated systems (among which some very realistic ones) that can be stable enough to be synthesized and investigated. As such, they can mimic the simple function of a soldering point between molecular wires in electronic circuits.

3.3 Design of Omniconjugated Models

The omniconjugated systems are obtained starting with small and elementary topological structures, like **3.5** and **3.7**, using simple topological expansion rules. The topological design program only serves as a tool for the axiomatic construction of possibly all omniconjugated systems.

3.3.1 Topological Design Program

The topological design strategy presented in the following originates from a valence bond description of the molecular system. This approach utilizes a fundamental set of design rules, directly translated into topological operations that are formulated and elucidated in this section. It results in a more fundamental understanding of the π -topological properties of omniconjugated models. Here, the discussion is limited to two-dimensional, hydrocarbon-based systems. However, omniconjugation can also be found in three-dimensional molecular building blocks as well as in systems containing proper heteroatoms in their conjugated paths.

In order to adequately describe the topological design program, some terminology and definitions used in the remainder of this section will be explained first. The main reason that alternative names such as "molecule", "substituent", "carbon atom" etc. are used, is to differentiate between chemistry and an abstract topological method as it is discussed here. A topological model that finds its basis in a valence bond description of the system represents the electronic structure of π -conjugated molecules. From a bond order point of view, carbon atoms (*junctions*) have a valence of four and have a maximum of four bonds connected to them (i.e.,

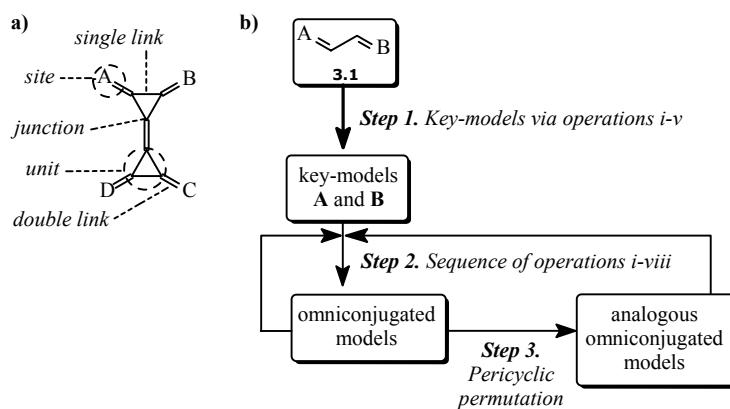


Figure 3.3 (a) The terminology used in the topological algorithm. (b) The flow diagram for the design of omniconjugated models.

connectivity index of four). There are three possible combinations of double and single links: either two double ones, two single ones and a double one, or four single ones. In this context, conjugation, as denoted in chemistry by the alternation of single and double bonds, is represented here by single and double lines, which are named *links* (see Figure 3.3). Hence, carbon atoms are depicted as their hydrogen-suppressed junctures in the topological models. The terminals of a central building block, which are the covalent connection points for other external moieties, are called *sites*. Hence, the sites A, B, C, D, etc. are the abstract equivalents of “terminals” in n-terminal conjugated systems.^[39] At last, the rings of the building blocks, as in (poly)cyclic conjugated systems, are called *units*. Due to the restrictions that are imposed on the molecular skeleton, the design method should be considered as a zero-order approach. In other words, in real chemical systems, conjugation may be affected by geometry factors like, for instance, ring torsion, strain, and steric hindrance. These effects are neglected in the topological search. However, in Chapter 4 the effect of these simplifications is addressed by means of molecular orbital calculations of the models.

The flow diagram for the design of omniconjugated models is presented in Figure 3.3b. This is a topological algorithm that consists of three steps, in which two of them comprise some of the eight fundamental design rules, directly translated into operations. The set of operations (op.) is formulated in the following way:

- Op. i)** Permutation of all links from single to double and *vice versa* along a conjugated pathway.
- Op. ii)** Units are created upon insertion of any desired link(s) between junctions.

Op. iii) A new site can be inserted when it is conjugated to **all** existing site(s).

Op. iv) Units can be merged via corresponding links.

Op. v) The connection of a site can be lengthened by extending a single link by a double or *vice versa*.

Op. vi) Units can be enlarged by replacing links: a) a single link by a single-double-single sequence, or b) a double link by a double-single-double sequence.

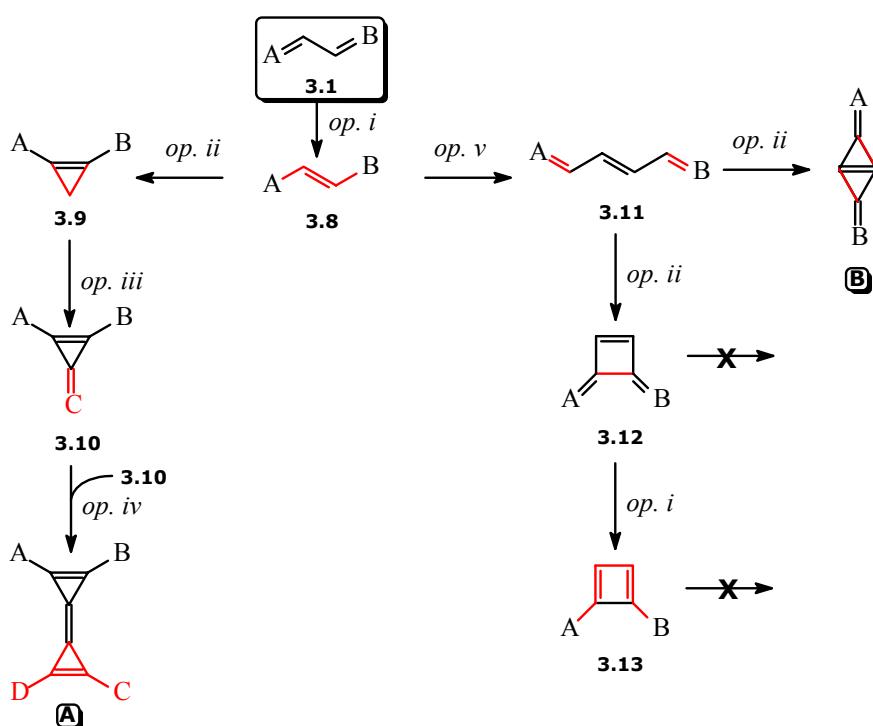
Op. vii) Within a conjugated pathway a site can be moved by an even number of links while not passing a neighbor site.

Op. viii) Links that are not involved in conjugated pathways can be altered freely.

The eight topological operations serve as a fundamental set of rules for the design and modification of omniconjugated models. It is unclear at this moment whether or not the proposed set of topological operations constitutes all fundamental manipulations for the design of omniconjugated models. This has to be explored mathematically. The eight operations all originate from one central argument: preservation of the existing conjugated pathways between sites. A warning not to introduce "looped" but only *direct* linear conjugated pathways comes with operation (iii) and (vii).

The designing strategy of omniconjugated models starts with model **3.1**. From this trivial template two so-called *key-models* are constructed. The key-models are the precursors to any desired omniconjugated model, created in the second and third step as illustrated in the flow diagram. Hence, all omniconjugated models are (or can be) derived from key-models **A** and/or **B**. As shown in Scheme 3.1, the key-models **A** and **B** emerge during first step of the algorithm by applying the first five operations. The net result of an operation when it is applied to the model is marked with red lines compared to the rest of the model.

Operation i. The construction starts by converting model **3.1** into its linear conjugated counterpart **3.8** via operation (i), in the scheme abbreviated to op.i, by changing all links from double to single and *vice versa*. The fact that the conjugated pathway $A \leftrightarrow B$ is preserved during operation (i) should be evident. *Operation ii.* The same is true for operation (ii) that is utilized en route to key-model **A**. Unit formation is achieved through the insertion of two single links, resulting in model **3.9**. Again, the alternation of links between existing sites remains unaffected upon the formation of this unit and conjugation is maintained. Operation (ii) is, in combination with operation (iii) and (iv), of crucial importance to extend any conjugated model with more sites, while keeping the existing conjugation between the sites of the system. A clear example is found in this systematic construction of key-model **A**.



Scheme 3.1 Construction of key-models **A** and **B** during step 1 of the algorithm.

Operation iii. Although initially the added single links in **3.9** were not involved in the conjugated pathways, they become part of the conjugated system after the insertion of site C via operation (iii). This operation is *only* allowed when the new site is conjugated to *all* the existing site(s). It comes as no surprise that a (double-single) alternating pathway in **3.10** is present from C↔A and C↔B. *Operation iv.* The second method to expand a model with more sites is via operation (iv): merging of two units via a corresponding link. Key-model **A** originates from the fusion of the two identical three-membered units **3.10** through the double link at the “former” position of site C. Since both sites A and B were conjugated to this double link, double-single alternation between all sites is automatically accomplished when merging both units via this link. As a result, the number of sites in the model is easily increased by one, while the bond topology of the individual units is not changed.

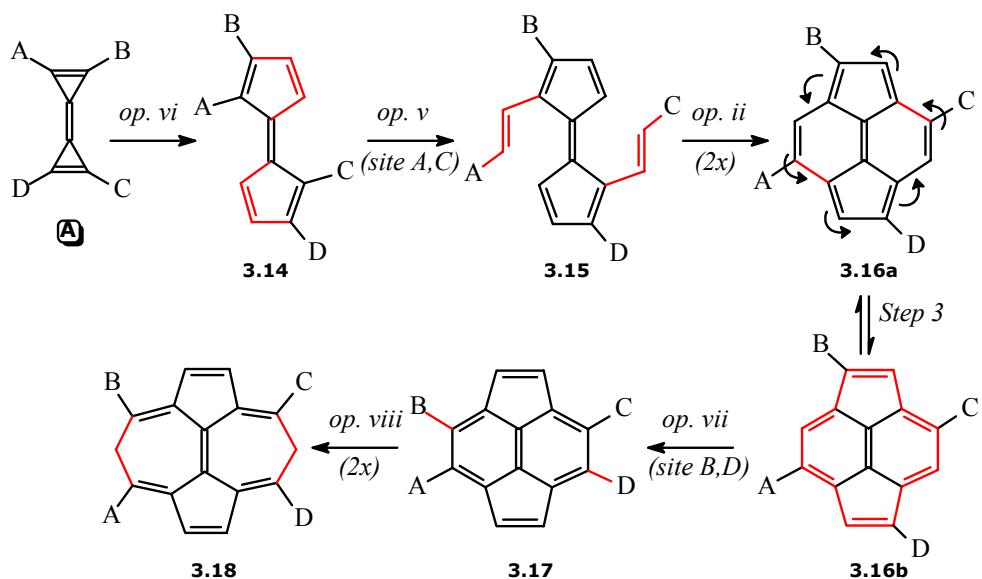
The second key-model, **B**, is derived from the same linear conjugated counterpart of model **3.1** as shown in Scheme 3.1. *Operation v.* First, the linear analogue **3.11** is created via operation (v) by extending both single links with a double link. The conjugated path is not changed, only extended. Subsequently, operation (ii) is applied to obtain key-model **B**. By the same operation, the four-

membered model **3.12** can be made. This latter building block could, in principle, become a precursor to systems based on even-membered units. However, no new key-models can be obtained from this building block because the insertion of a new site is not possible in model **3.12** or in its analogue **3.13**. According to operation (iii) this is simply not allowed. Hitherto, it was not possible to design systems having only even-membered units, which contain a third site in linear conjugation to two other, mutually conjugated sites (see also model **3.6**).

Owing to their topological properties there are two classes of omniconjugated systems. The *Type B* omniconjugated systems can *only* be derived from key-model **B**. All other omniconjugated models are derivable from key-model **A**. This means that, despite the fact that some models can be obtained from both key-models, they are considered as a Type A omniconjugated system. The key-models are useful tools for structural design. For example, key-model **B** can be used as precursor in a straightforward design of systems based on condensed units. On the other hand, key-model **A** is of use for the design of systems having two units connected via a central link. Both key-models can be used to design systems with exocyclic connections to all external moieties. This can be easily understood taken into account that the model **3.7** (Figure 3.2) is a simple derivative of key-model **A**. Model **3.7** can be obtained after applying operation (i) on pathway $A \leftrightarrow B$ and $C \leftrightarrow D$. There are more derivatives of **3.7** with two doubly linked sites (see for an extensive overview Figure 2.10). During the second step in the design program (Figure 3.3) either key-model **A** or **B** is utilized as precursor for the construction of more omniconjugated models. As will be shown below, the distinction in classes of omniconjugation is made not only because the construction starts at different levels (i.e., number of sites), but merely due to their dissimilar topological behavior when utilizing certain operations, as will be explained later on.

The second step of the design process is the creation of omniconjugated models by freely applying sequences of operations to one of the key-models. For this, the next three operations (vi), (vii), and (viii) are introduced. Despite the fact that these operations will be demonstrated using key-model **A**, they are also applicable to key-model **B**.

Operation vi serves as an important tool to modify the models by expanding a unit through replacing a link by an extended version of that link. As exemplified for key-model **A**, a single link can be replaced by a single-double-single link sequence (see model **3.14** in Scheme 3.2). The conjugation between all sites remains unaffected by this operation. In being applicable to every link, individual units can be systematically expanded. Therefore, operation (vi) is the ultimate method for the design of models that all originate from the same key-model. Clearly, a random sequence of operations during this stepwise design can have a large impact on the architecture of omniconjugated models. For example, the original framework of key-model **A** is easily changed into the large omniconjugated model **3.16a**,



Scheme 3.2 Design of Type A omniconjugated models from key-model **A** via a sequence of operations in step 2 and by a pericyclic permutation conform step 3 of the topological algorithm.

consisting of several fused units, by subsequently applying operation (vi), (v) and (ii) (see Scheme 3.2). Model **3.16a** has an overall cyclic arrangement of alternating links and can therefore be subjected to step 3 of the design program.

The third (optional) step in the topological algorithm (Figure 3.3) is the permutation of all links involved in the perimeter of the model (i.e., permutation of the pericyclic single and double links). Although this step 3 is somewhat related to operation (i), it only induces a shift of links without changing the overall number of single and double links (compare Scheme 3.1 versus Scheme 3.2). After permutation of the links, omniconjugation is maintained, independent of the position of the other links in these models. As the result of step 3, model **3.16b** is obtained as an analog of **3.16a** and can be further modified at will through operations in step 2 of the topological algorithm. *Operation vii & viii.* Although any desired operation can be applied in step 2, the remaining two operations will be used at this point, as shown in Scheme 3.2, to demonstrate their meaning: both sites B and D in **3.16b** are moved (operation (vii); yielding model **3.17**), and the six-membered units are expanded by insertion of single links (operation (viii); giving model **3.18**). The conjugation is again preserved during an operation as can be recognized in **3.16b** and **3.17**. Prior to operation (viii) all conjugation pathways have to be elucidated! Operation (viii) differs in not being essential but embedded, to a certain degree, in

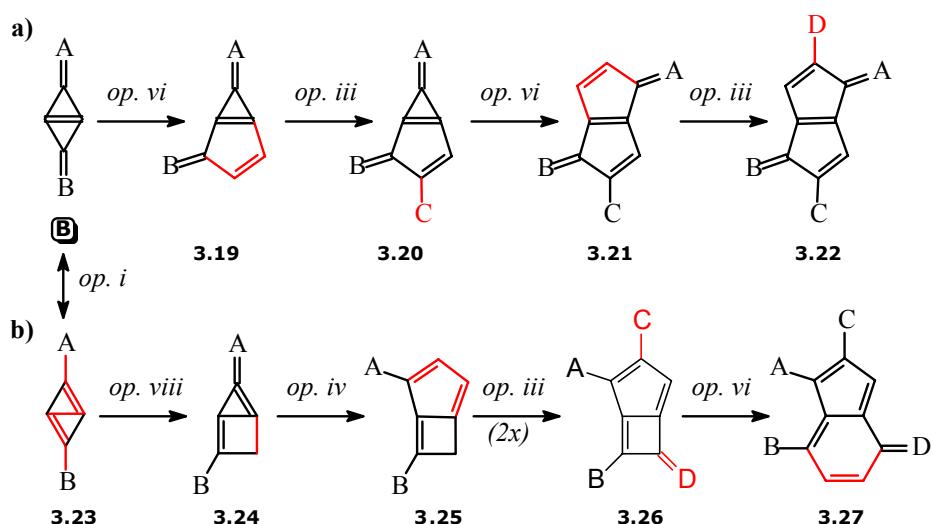
the other operations. As an extension, it serves as a tool for an interactive design of a target omniconjugated architecture reducing thereby a long-lasting design algorithm. The single link between site A and B in **3.17** is not involved in *any* conjugated pathway. The same is true for the link between site C and D. Consequently, these links can be modified freely by means of, for instance, separation, elimination, and conversion to or extension with any desired link(s). It is important to note that considering operation (viii) as applied on **3.17**, none of the above is true for **3.16b**. Topologically this model differs in having links between the aforementioned sites that *are* involved in conjugation pathways. As a result, it is not allowed to alter these links in **3.16b** by means of operation (viii). With the above, all operations of the design process have been illustrated with models obtained from key-model **A**. Hence, these models (**3.14 – 3.18**) are Type A omniconjugated.

3.3.2 Type B Omniconjugated Models

In principle, key-model **B** is only omniconjugated in a trivial manner since it only has two sites. Omniconjugated models are formed from key-model **B** upon the insertion of more sites via operation (iii) or (iv). As shown above, the models developed from key-model **A** can either consist of linked polycyclic models, such as **3.14**, or after further modifications can be changed into condensed polycyclic building blocks like model **3.16a**. In contrast, key-model **B** primarily allows for the construction of condensed polycyclic architectures and is therefore the precursor to be used for a straightforward design process of such models.

The models given in Scheme 3.3 are all Type B omniconjugated because they are only derivable from key-model **B**. The procedure to obtain **3.22** from key-model **B** is a representative example of the approach for the expansion of key-model **B** to a system with more sites. It is important to point out that this is only allowed when this new site is in conjugation with all the existing sites of the model as imposed by operation (iii). More importantly, after insertion of the fourth site in Type B models, such as **3.22**, it is not allowed to modify these systems with operation (i) any longer. This is because, as soon as Type B models have four sites, they are not conjugated in all available double bond arrangements, as will be explained later on. In sharp contrast to Type B models, there are no problems encountered when executing operation (i) on Type A models. Therefore, we distinguish Type B from Type A omniconjugated models. However, it is allowed to execute operation (i) on Type B models with less than four sites, as can be seen in the transition from Scheme 3.3a to Scheme 3.3b.

The design process outlined for **3.27** is typical for the design of omniconjugated models based on an even- and an odd-membered unit. In fact, model **3.26** is the smallest omniconjugated model with four sites and one even-membered unit. In short, Type B omniconjugated models with four or more sites are distinctly different



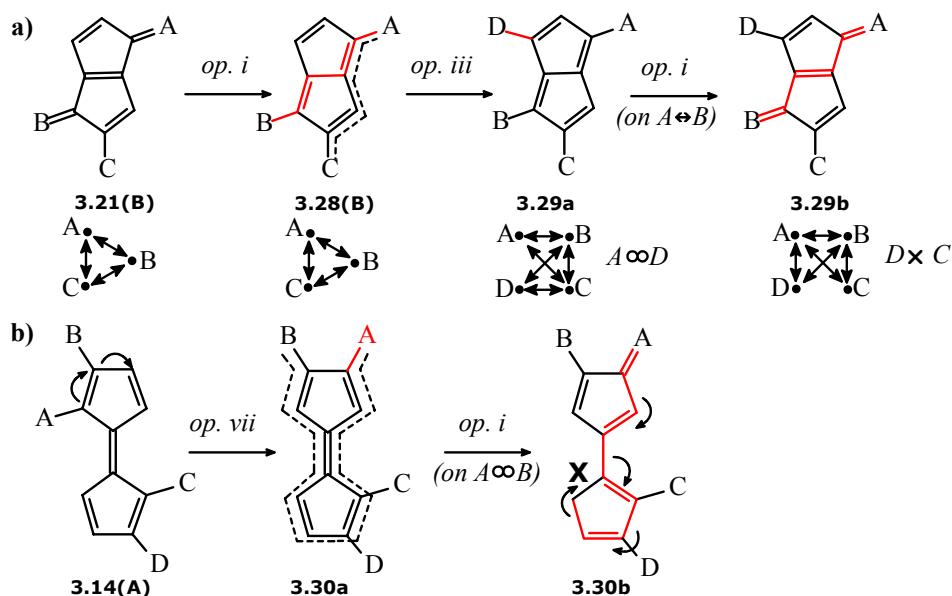
Scheme 3.3 Systematic construction of omniconjugated models from key-model **B** resulting in odd-membered units in a) or even- and odd-membered unit in b).

from all Type A omniconjugated models in that they do *not* remain omniconjugated upon operation (i) on certain pathways.

3.3.3 Quasi-omniconjugated Models

Type B models like **3.27** are omniconjugated because they have *direct* linear conjugated pathways between all sites and can *only* be designed from key-model **B**. However, these systems show a similar behavior towards operation (i) as "looped systems" when they have more than three sites. Some n-terminal systems have alternating pathways with loops in them (between one or more of the pairs of terminals). The dashed links in Scheme 3.4 are used to mark an example of a direct alternating pathway in **3.28** and a looped pathway in **3.30a**. Models like **3.30a** are *not* omniconjugated; they are defined as looped systems and they are "quasi-omniconjugated" at best.

The looped model **3.30a** has a topology imposing that at least one link has to be used *twice* in order to find the alternating pathway between site A and B; the looped pathway $A\infty B$. Loop pathways are often found between sites connected to the same unit, when that unit itself does not provide for the pathway between those sites. A second unit is necessary to realize that alternating pathway. Loop pathways *may* be introduced via two of the eight operations (see Scheme 3.4): either after the insertion of a new site (e.g., operation (iii) on **3.28** leading to $A\infty D$ in **3.29a**) or by changing the position of a site (e.g., operation (vii) on **3.14** leading to $A\infty B$ in **3.30a**). The preference for models without loops is supported by the



Scheme 3.4 Failures upon executing operation (i) on a) direct alternating pathway $A \leftrightarrow B$ in Type B system **3.29a** or in b) quasi-omniconjugated model **3.30a** on “looped” pathway $A \infty B$. The precursors **3.21**, **3.28**, and **3.14** are Type A or B omniconjugated (as indicated in parentheses).

observation that looped systems are, in two ways, inconsistent with operation (i). First, quasi-omniconjugation may be lost (!) when operation (i) is applied on a direct conjugated pathway as is shown for model **3.29a** in Scheme 3.4a. Although the looped pathway vanishes ($A \infty B$ in **3.29a** becomes $A \leftrightarrow D$ in **3.29b**), another existing alternating pathway is removed ($C \leftrightarrow D$ becomes $C \times D$) as shown in the topological connectivity schemes.

The second way in which looped systems clearly differ from omniconjugated systems is the following: the stepwise replacement of all links from single to double and vice versa, as it is read from operation (i), will fail at all times in a looped pathway. This is illustrated for **3.30a**, starting from site A, where a junction with a forbidden connectivity index of five in the looped conjugated pathway is created at a certain point during the process (see the situation in **3.30b**). The emergence of a penta-valent carbon atom has not been observed in Type B models upon executing operation (i) on any pathway. However, a special feature of 4-terminal Type B models is that they respond to operation (i) conform pathway $C \leftrightarrow D$ in the looped model **3.29a** upon operation (i) on pathway $A \leftrightarrow B$. Such disappearance of a conjugated pathway (i.e., it becomes cross-conjugated) has been the motivation to impose a restricted use of operation (i) during the design and modification of Type B

models. That is, only up to three sites. The application of operation (i) and its impact on (omni)conjugated systems will be discussed in more detail in Chapter 5 and 6.

3.4 Topological Properties of Omniconjugated Models

The topological design program allows for the design of very many omniconjugated models. Just to give a glimpse on the versatility of the topological algorithm, a few examples of different types of 4-terminal omniconjugated models are depicted in Figure 3.4. They are generated from either one of the key-models. The overall structure of the models can be designed at will via the key-models as can be seen from the typical examples of a linked (**3.31**) and a condensed (**3.32**) polycyclic model. Model **3.34** is shown as an example of a model with an equivalent number of links between the sites (i.e., seven) when considering the shortest alternating pathways. A consequence of the topological design scheme is that it only yields omniconjugated models with at least one odd-membered unit. A famous and simple rule for the design of high spin organic molecules has a related (kind of inverted) limitation in being only applicable to alternant systems.^[40,41] Alternant hydrocarbons are compounds with carbon rings containing only an even number of carbon atoms. All omniconjugated models, necessarily having at least one unit containing an odd number of carbon atoms, are non-alternant.^[42,43] It is not possible to construct omniconjugated models based on even-membered units only, as has been addressed in the previous section. Additional mathematical studies are required to understand this topological property of omniconjugated models.

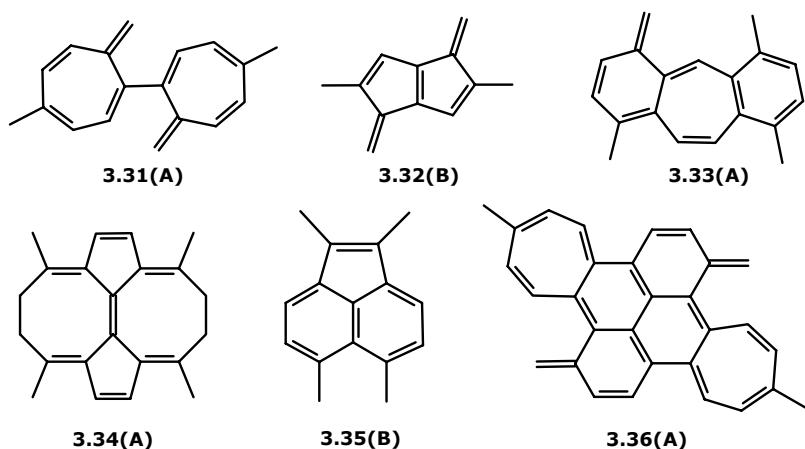


Figure 3.4 Examples of different architectures of omniconjugated models with four sites (without their labeling), obtained from key-model A or B (in parentheses): linked polycyclic model **3.31**; cata-condensed polycyclic models **3.32** and **3.33**; peri-condensed polycyclic models **3.34**, **3.35**, and **3.36**.

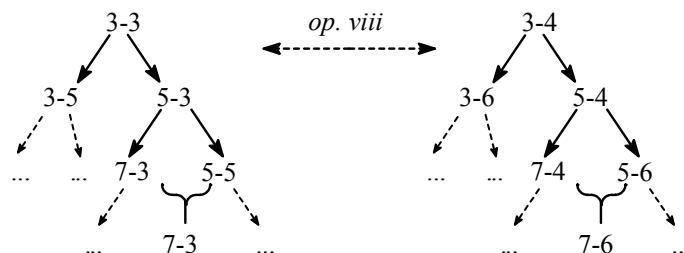
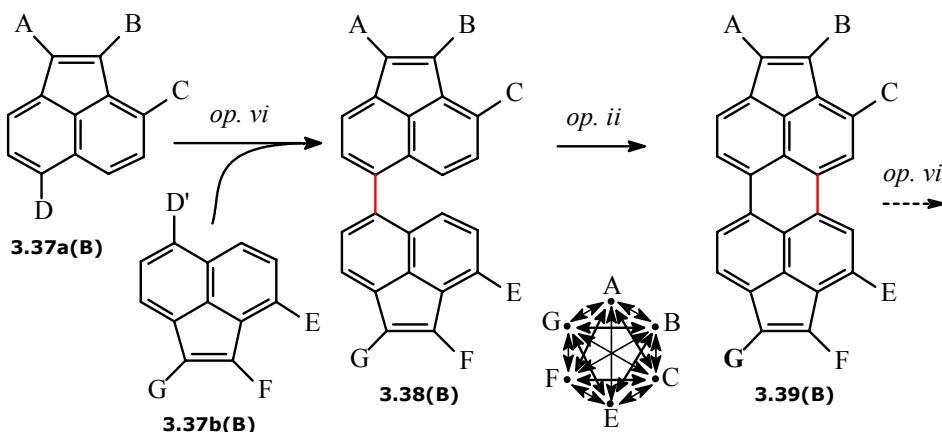


Figure 3.5 Flow diagrams illustrating the systematic growth of bicyclic models by means of operation (vi), for models containing only odd-membered units (left) or with an even- and odd-membered unit (right). They are interchangeable via operation (viii).

A powerful and systematic modification of the models is the replacement of links within a unit via operation (vi). In principle, this can yield an unlimited number of omniconjugated models as outlined with the flow-diagram given in Figure 3.5. Here, the numbers symbolize the size of each unit (i.e., number of carbons) in bicyclic models. After each successive replacement of a link (i.e., single link by a single-double-single sequence or *vice versa*), the size of a unit increases with two carbons. In this way, the two three-membered units (3-3) of key-model **B** can be easily enlarged to a 5-3 framework and, subsequently, to a 5-5 framework (see Figure 3.5 (left), and for an example Scheme 3.3a). This expansion is not limited to either two odd units or a combination of an even and an odd unit. When allowed, one can transform from one to the other upon executing operation (viii). This operation is the removal (insertion) of links that are not (yet) involved in any conjugated pathway. This approach has been used to construct the Type B model **3.24**.

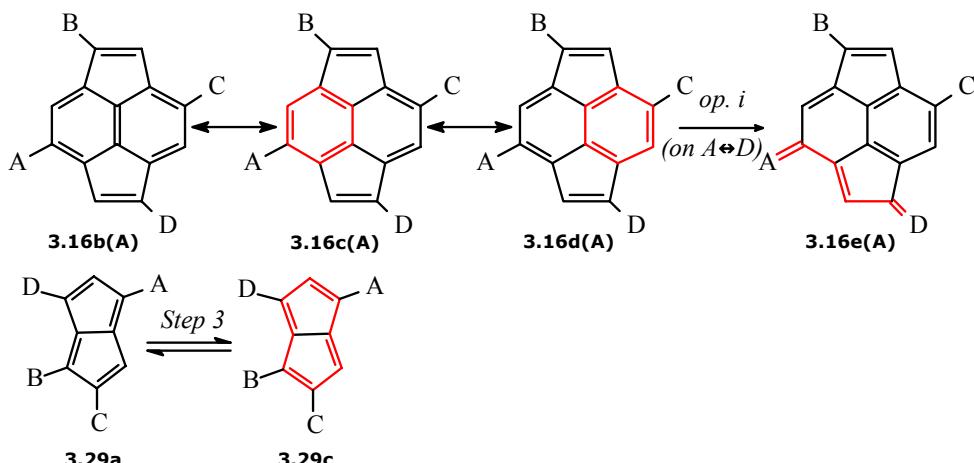
All omniconjugated models discussed up to this point have four sites while it is straightforward to go beyond this number. This can be realized with operation (iv) that allows for the interconnection of omniconjugated models. In this way, omniconjugated models with an unlimited number of sites can be obtained. Although a likewise flow-diagram as in Figure 3.5 is not given, this operation has a bigger impact on the models than operation (vi). The power of operation (iv) becomes evident when **3.37a** is simply “doubled” – with **3.37b**, which is identical, but drawn differently to guide the eye – to yield model **3.38** (see Scheme 3.5). Thus, by rational design, as many as fifteen conjugated pathways are obtained between the six sites A, B, C, E, F, and G in **3.38**. The resulting connectivity scheme is rather complex, in particular when comparing it with the incomplete scheme of a hexa-substituted benzene (see model **3.6** in Figure 3.2). It would be quite cumbersome to construct such a complex omniconjugating model by trial and error and without the use of the topological algorithm. Hence, the emergence of model **3.38** confirms the versatility of the design program in going beyond 4-terminal fully conjugated architectures. Note that operation (iv) can, in principle, be repeated to yield higher



Scheme 3.5 Systematic construction of a Type B omniconjugated oligomer (in parentheses), which has up to fifteen conjugated pathways (see connectivity scheme).

order omniconjugated models at will. In chemistry, this can be of use for the design of omniconjugated macromolecules such as **3.39**. This ladder-type oligomer is obtained from **3.38** by means of operation (ii). Upon repeating operation (iv) and (ii), one could end up with an omniconjugated ladder polymer. The “polymerization” over any two of the sites of an omniconjugated model can result in omniconjugated linear polymers.

An important aspect in considering the topological models as real chemical compounds is their resonance structures. These can be obtained by the rearrangement of all the links that are *involved in* the perimeter (step 3 of the design process) or located *inside* the perimeter of a building block. A nice example of the permutation of links according to step 3 is given for the Type A pyracylene derivatives **3.16a/b** (see Scheme 3.2). The rearrangement of links inside the perimeter is demonstrated for **3.16b** in Scheme 3.6. After any of these permutations the models remain omniconjugated. The fact that all such neutral resonance structures^[44] are fully conjugated certainly adds value to the concept of omniconjugation. With respect to resonance contributors, quasi-omniconjugated models such as **3.29a** show familiar characteristics while they are not considered as being truly omniconjugated: all resonance structures of omniconjugated models are omniconjugated. After permutation of the links involved in the perimeter, which *can* be executed in quasi-omniconjugated models in sharp contrast to operation (i) (see Scheme 3.4), the nature of the conjugated pathways remains unaffected (e.g., A \approx D in **3.29a/c** in Scheme 3.6). In general, resonance structures have the same sites (same in the sense of being singly or doubly linked), as can be seen from models **3.16a-d**.^[45,46] They only differ in the arrangement of double links *within* the nuclear



Scheme 3.6 (Top) Rearrangement of links inside the perimeter of the Type A omniconjugated (in parentheses) model **3.16** and (bottom) within the perimeter of the quasi-omniconjugated model **3.29** ($A \leftrightarrow D$).

framework. In Chapter 2 it was found that such models are embedded within the same member of the archetype series of an n-terminal system (i.e., archetype #1 for **3.16**, see Figure 2.10) just as each of them contributes to the same hybrid of real molecules. This clearly demonstrates that the archetypal analysis and the topological design program come to the same conclusion: resonance structures have the same π -topological properties.

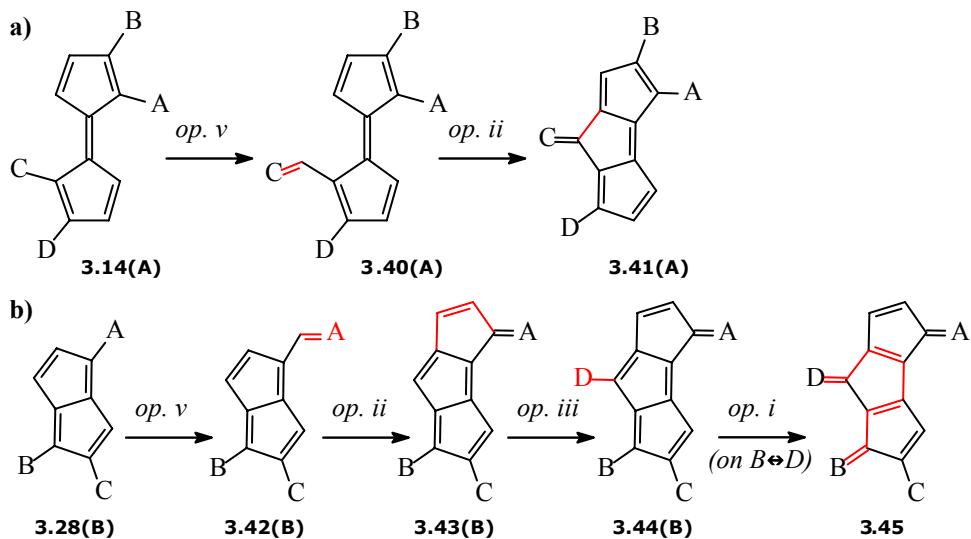
Operation (i) can be employed to quickly determine whether the omniconjugated model with four or more sites is a Type A or Type B system. While Type A models always remain omniconjugated (see for example **3.16d/e**), Type B models possess a cross-conjugated pathway after executing operation (i). For example, the Type B model **3.22** (Scheme 3.3) will dispose of the same conjugated pathway as the looped model **3.29a** in Scheme 3.4a: upon permutation of all links between $A \leftrightarrow B$ in **3.22**, the pathway $C \leftrightarrow D$ will end up being cross-conjugated ($C \times D$). This is the reason why it is not allowed to execute operation (i) on Type B models with four or more sites. When an odd number of links is involved, operation (i) is chemically analogous to a redox operation on a conjugated pathway. This implies that omniconjugation is topologically preserved upon such redox events. This is a unique property: in *all* but three-terminal Type B models or models derivable from key-unit **A**, a redox operation on one conjugated pathway *does* influence the (cross-) conjugation in other pathways. Interestingly, the topological properties of both Type A and Type B omniconjugated models results in sometime complex and highly intriguing switching-type relations between the various pathways. That subject will be discussed in more detail in Chapter 6.

The key-models not only serve as prototypes for the structural design but also pass on some typical topological properties. It is important to mention that, while obeying the empirical design rules, a Type B model can be converted to a Type A model during the design process. This may happen after, for example, several unit fusions by means of operation (ii). In those specific situations, the topological properties that come with a Type A omniconjugated model, such as the behavior upon executing operation (i), overrule that of a Type B system. It is found that in the end some Type A models that are constructed from key-model **B** could also have been created via key-model **A**. With respect to this, model **3.36** is a typical example (see Figure 3.4). Though occasionally elusive, it is important to verify the origin of an omniconjugated model by means of a backward design process, in chemistry known as a retrosynthesis.

3.5 Classification of n-Terminal π -Conjugated Systems: Extended

The discussion now shifts from the pure topological (abstract) n-site models to their counterparts in chemistry: n-terminal π -conjugated systems. In a way, the topological design program allows for a classification of n-terminal conjugated systems, based on the π -topological changes upon executing operation (i). However, the systematic analysis of n-terminal systems, as discussed in Chapter 2, provides for a classification *without* the need to find all the alternating pathways, or changes thereof. The Chapter 2 analysis distinguishes four classes of conjugation, based on the number of non-Kekulé structures n-terminal conjugated systems may have. This is realized by deducing the collection of structures that represents all possible states (single or double) of the terminals of the system, which was called an archetype series.

The highest degree of conjugation was ascribed to omniconjugated systems, which have no non-Kekulé structures in their series. However, in the previous section different kinds of omniconjugated models were found. This implies that the classification of conjugated systems by degree of conjugation should be extended with subclasses of omniconjugation. From a topological point of view, quasi-omniconjugated systems are distinctly different from Type A and Type B omniconjugated systems. Quasi-omniconjugated systems are not truly omniconjugated because they contain looped (indirect) alternating pathways between some terminals. The Type A and B systems also differ in π -topological properties but merely by means of operation (i). In sharp contrast to Type A systems, omniconjugation may be lost after executing operation (i) in Type B systems. This is a severe problem when it is not properly understood because omniconjugation was not originally defined that way. The advantage of the



Scheme 3.7 Design of Type A and B (in parentheses) omniconjugated systems having the same building block. Executing operation (i) on **3.44** confirms its Type B character.

archetypal analysis is that it ascribes only one specific kind of conjugation to n-terminal systems that will not change upon executing operation (i).

The π -topological differences between Type A and Type B systems are best presented with the archetype series of two analogues building blocks. The design of the Type A and B systems that are used for this purpose is outlined in Scheme 3.7 (i.e., **3.41** and **3.44**, respectively). The kind of archetype series that needs to be considered here is determined by the nature and number of the terminals. In both cases, there is only one (odd number) out of the four terminals which is doubly bonded. Hence, the 4-terminal archetypes of the Odd set have to be elucidated. The collection of the molecular archetypes of **3.41** and **3.44** is given in Figure 3.6. The labels of the terminals in, for example, archetype **3.41**#1 are changed compared to structure **3.41**; although, in principle, the two structures are the same. This is because the terminals of archetypes are for practical reasons labeled in a systematic way (see Chapter 2). This was ignored for convenience in Scheme 3.7.

At this point, it can be clearly seen that these Type A and B systems only differ in the position of one terminal. For example, **3.41**#2 can be easily transformed to **3.44**#1 by changing the position of terminal A in **3.41**#2. This modification does not involve one of the topological design rules. What is more interesting is that such a small modification changes the π -topological properties of the system. Like all other Type B systems, **3.44** does not remain omniconjugated upon executing operation (i). This is confirmed with **3.45** (Scheme 3.7b) in which pathway A↔C in **3.44** is converted into AxC.

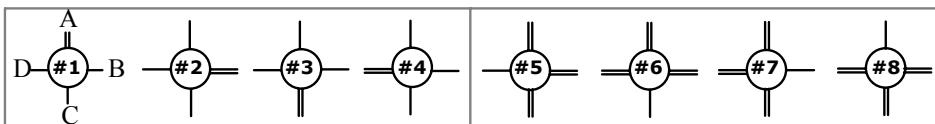
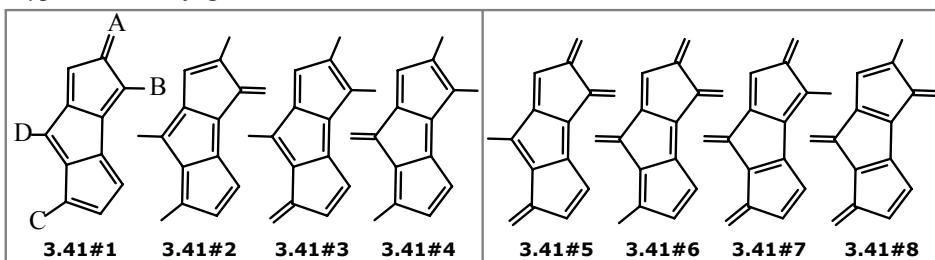
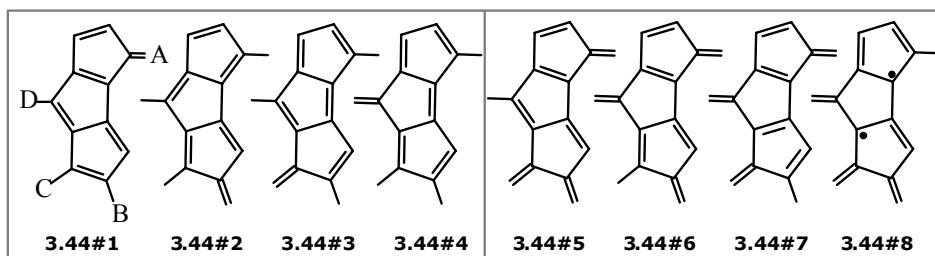
4O¹⁽⁴⁾³⁽⁴⁾

Type A omniconjugated:

Type B omniconjugated:


Figure 3.6 (Top) Standard 4-terminal archetype series (Odd set). (Bottom) The corresponding archetype series of the Type A and Type B omniconjugated systems **3.41** and **3.44**, respectively. Archetype **3.44#8** is a non-Kekulé structure.

Archetype series contain non-Kekulé structures when one or more of its structures have cross-conjugated pathways. This is indeed what is observed here. In contrast to **3.41**, the series of the Type B system **3.44** contains a non-Kekulé structure (see **3.44#8** in Figure 3.6). This explains why a cross-conjugated pathway is obtained upon executing operation (i): Type B systems do not remain omniconjugated in *all* possible double bond arrangements. An example was already given with **3.45**, which is one of the molecular archetypes of **3.44** (see **3.44#7**). On the other hand, Type A systems, like **3.41**, do not have non-Kekulé structures in their archetype series and, hence, remain omniconjugated. The emergence of non-Kekulé structures is the basis for the different π -topological properties of Type A and Type B omniconjugated systems. It also confirms that a seemingly small change in connectivity (e.g., the position of one terminal) can have a large impact on the characteristics of the archetype series and, with that, on the π -topological properties.

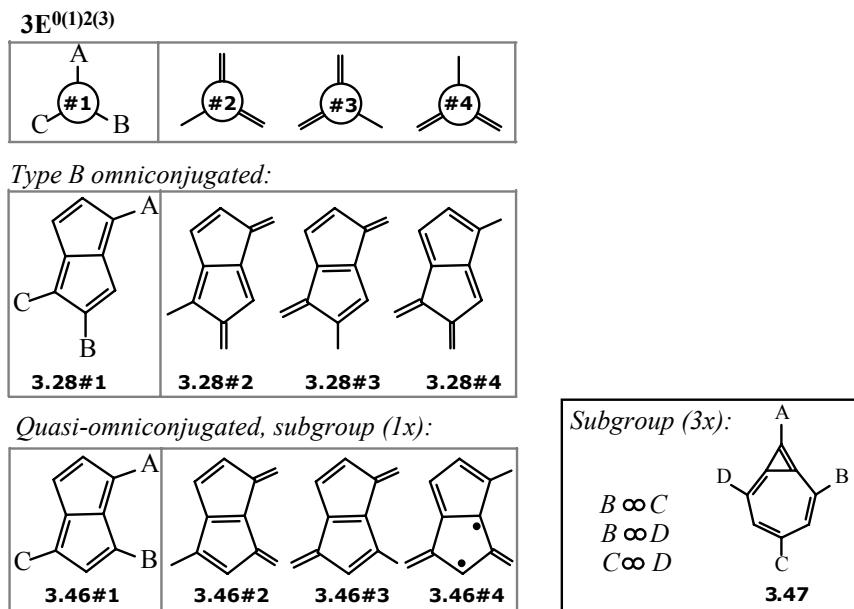


Figure 3.7 (Top) Standard 3-terminal archetype series (Even set). (Bottom) The corresponding archetype series of Type B omniconjugated system **3.28** and quasi-omniconjugated system **3.47**. (Index) Quasi-omniconjugated system with three looped pathways (i.e., subgroup (3x)).

At this point, it is interesting to address the exceptional behavior of 3-terminal ones among the Type B systems. When it comes to the design of Type B omniconjugated systems it is not allowed to utilize operation (i) once the system contains more than three terminals, because omniconjugation gets lost. But it is allowed to modify 3-terminal Type B systems via operation (i) because they *do* remain omniconjugated, as can be seen in Figure 3.7. The archetype series of **3.28** does not contain a non-Kekulé structure. The archetypal analysis of a quasi-omniconjugated system is necessary to complete the discussion of the three subclasses of omniconjugation. A representative example of this class is obtained from **3.28** by changing the position of one terminal in such a way that it violates one of the topological design rules. For this purpose, terminal B of **3.28#1** is moved by one position to create **3.46#1** and not by an even number of links (i.e., operation (vii), see Section 3.3). This immediately results in a quite different π -topology as can be understood from the looped pathway $B \leftrightarrow C$ and the non-Kekulé structure **3.46#4**. Due to this non-Kekulé structure, the looped system **3.46** is not omniconjugated. Loop systems have a lower degree of π -conjugation compared to Type B systems, and are thus quasi-omniconjugated.

Table 3.1 Overview of the classification of n -terminal conjugated systems based on the number of non-Kekulé structures and the kind of bond alternation between the terminals. Compared with Table 2.2, the classification includes the subclasses of omniconjugation.

Class	Number of non-Kekulé structures	Number of terminals	Bond alternation?	
Type A	0	$n > 2$	Yes; linear, between all terminals.	
Type B	0	$n = 3$	“ “	
Normal conjugated	0	$n = 2$	“ “	
Type B	≥ 1	$n > 3$	“ “	
Quasi-omniconjugated	1 to $(2^{n-1} - 1)$	n	Yes; indirect, bonds are used twice.	
Cross-conjugated ^{a)}	“ “	“	No; presence of two consecutive single	
Open shell conjugated	2^{n-1}	n	Not applicable.	

^{a)} This category contains subgroups (1x), (2x), etc.

The above presented archetype series are typical examples of the different subclasses of omniconjugation. At this point it is worthwhile to take another look at the classification of n -terminal π -conjugated systems (see Table 3.1). In Chapter 2 four classes of conjugation were proposed: omniconjugated, normal conjugated, cross-conjugated (with subgroups (\times)), and open shell conjugated (see also Table 2.2). There can be no doubt that the Type A omniconjugated systems have the highest degree of conjugation. These systems are fully conjugated in all possible states of the terminals, regardless of the number of terminals. What follows are the Type B omniconjugated systems. These systems can be omniconjugated as well but contain at least one non-Kekulé structure when they have more than three terminals. Therefore, 4-terminal Type B systems have a lower degree of π -conjugation. Next in line are the normal conjugated systems. As with the Type A and 3-terminal Type B systems, they do not possess non-Kekulé structures in their series. However, the reason for attributing a lower degree of conjugation to normal conjugated systems is that this kind of conjugation can only be found in simple 2-terminal systems. An even lower degree of conjugation is attributed to quasi- and cross-conjugated systems. Here, the intuitive preference goes to the looped systems since they do have, in sharp contrast to cross-conjugated systems, alternating bonds between all terminals, only not in a direct manner. As with the cross-conjugated class, the count of looped pathways in quasi-omniconjugated systems further differentiates the class into subgroups. A typical example is **3.47** (subgroup (3 \times)) which is related to **3.46** (subgroup (1 \times)) but has up to three looped pathways instead of one (see the inset of Figure 3.7).

One final remark is necessary for a clear definition of the classes in borderline situations. It is often found that the individual structures of archetype series have different kinds of conjugation between a pair of terminals. For example, archetype **3.44#1** is Type B omniconjugated, while **3.44#4** contains a looped pathway ($B\infty C$) and **3.44#5** a cross-conjugated pathway ($A\times D$). The *degree* of conjugation is, however, set by the archetype with the highest *kind* of conjugation. This means that the quasi- and cross-conjugation are simply overruled by the Type B omniconjugation found for **3.44**. This is because the π -topological properties of the molecules from this series are determined by the class Type B omniconjugated. Therefore, archetype **3.44#1** is used to represent all molecules from this series, despite the fact that it is the only one of his class in the series. Hence, **3.44** is only omniconjugated in a trivial manner. Similarly, the looped pathway $B\infty C$ in **3.46#1** overrules the cross-conjugated pathway $A\times C$ in **3.46#2**. When it comes to two different subgroups in the same archetype series, the one with the highest count of the same kind of pathway determines the degree of π -conjugation. This means that when an archetype series contains structures with one looped pathway as well as some with two cross-conjugated pathways, the n-terminal system is classified cross-conjugated, subgroup (2 \times).

3.6 Real Chemical Examples of Omniconjugated Compounds

The topological design program yields all different kinds of omniconjugated models, including some realistic ones from a *chemical* point of view. Some omniconjugated compounds have been prepared in the past and will be discussed here. Recently, Palmer and co-workers presented a stable acenaphthylene-derived macrocycle with intriguing properties.^[47] Compound **3.48** (Figure 3.8) was successfully synthesized by means of precursor **3.49** (a Type B omniconjugated acenaphthylene derivative) and showed a high thermal and photochemical stability, in spite of the fully unsaturated annulene backbone. The fact that omniconjugated compounds can reveal remarkable properties is supported by the observation that the slow evaporation of a saturated solution of **3.48** led to "dark purple crystals with a golden metallic luster". In their attempt to synthesize **3.48**, the tetra-substituted fluoranthene **3.50** was also prepared that, unfortunately, had a low solubility. Besides being a well-known class of compounds that can upon substitution adopt interesting colors^[48,49] and chemical behavior,^[50-53] fluoranthenes with the proper substitution patterns are interesting from the present point of view because of their available Type A omniconjugation.

A nice example of an omniconjugated compound that has been described by more authors as a fully π -conjugated system, is the double-stranded (ladder) oligomer **3.51** synthesized by Schlüter and co-workers.^[54,55] The backbone of this oligomer is based on a Type A omniconjugated pyracylene derivative (e.g., model

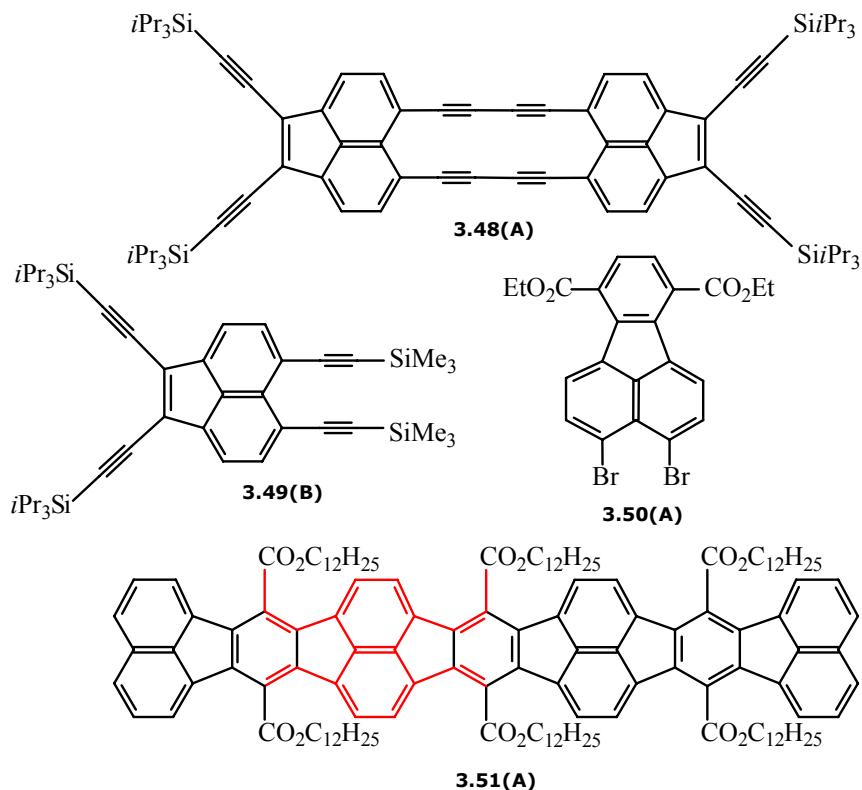


Figure 3.8 Existing Type A and B omniconjugated compounds (in parentheses) which have not been recognized as such: tetra-substituted triisopropyl-silylethyne macrocycle **3.48** and the related tetrayne **3.49**; diethyl 3,4-dibromo-7,10-fluoranthenedicarboxylate **3.50**; (dodecyloxy)carbonyl substituted ladder oligomer **3.51**.

3.16). This structurally perfect oligomer served as model compound for analogous polymers that have a visual appearance in solution very similar to [60]fullerene and showed in their doped state room-temperature conductivities up to 0.01 S cm^{-1} .^[56] Therefore, they are interesting materials for electroluminescent,^[57] photovoltaic, and molecular electronic applications.^[58,59] Upon substitution of this oligomer at the omniconjugated sites (i.e., the positions of the alkoxy carbonyl chains) with donor or acceptor groups, this compound could show interesting nonlinear optical properties stimulated by omniconjugated topology.

The topological design process is in principle limited to hydrocarbon based models. However, it is possible to substitute one or several carbon atoms of the models by heteroatom(s). This could enlarge the possibility of finding interesting molecular architectures. As shown in Figure 3.9 sulphur atoms can be inserted in

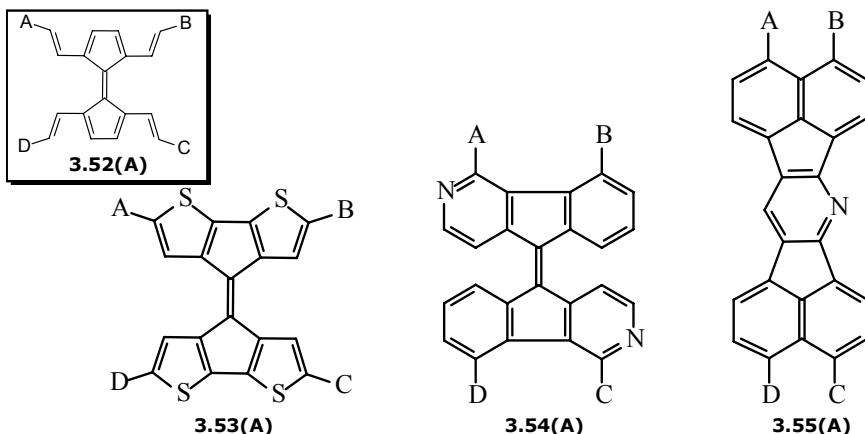
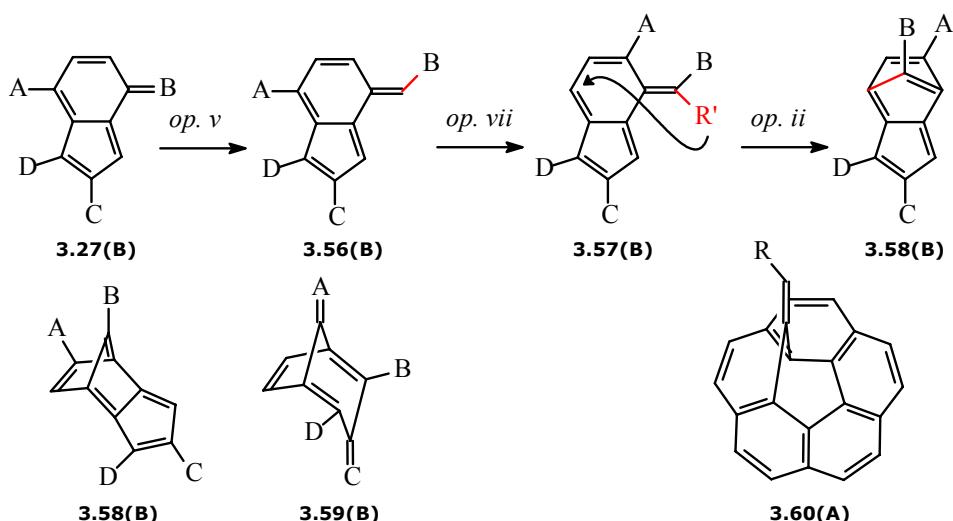


Figure 3.9 Heteroatomic Type A omniconjugated (in parentheses) templates 3.53 – 3.55 based on cyclopentadithio-phene, indenopyridine, and acenaphthopyridine, respectively. The sites A, B, C, and D are the substitution positions for other (functional) moieties.

3.52 through operation (viii). This results in a realistic template 3.53 for Type A omniconjugated compounds. Note that the sulfur atoms are not playing a direct role in the conjugated pathways, in this case. At present, such a fully conjugated dicyclopenta-dithiophene derivative^[60] has not yet been implemented nor recognized as a potential intersection for molecular wires. It could act as a true omni π -conjugating crosslink point in polythiophene-like macromolecules.

In addition to inserting heteroatom(s) in the hydrocarbon system, it is also allowed to replace a carbon by, for example, a nitrogen atom. This is only allowed when the bonding pattern of the parent omniconjugated model is not changed as shown for 3.54 (Figure 3.9).^[61] Another known and omniconjugated pyridine derivative is 3.55.^[62] Evidently, the structures obtained from the topological design method are easily converted to certain heteroatomic compounds.^[63]

On the contrary, it is harder to come across 3D systems since it is not that straightforward to change a 2D system while preserving the existing conjugation. Given that the topological design method is not directly applicable to 3D systems; such a (blind) search is poised to be rather cumbersome. However, when having a certain 3D configuration in mind, one can try to construct it from a 2D omniconjugated model. An example is given in Scheme 3.8 for 3.58, utilizing 3.27 as precursor (see also Scheme 3.3) and a temporary substituent R as the potential bridging position. It is very unlikely that the highly unsaturated tricyclodecane derivative^[64] 3.58 is stable enough to be synthesized, not to mention the low orbital overlap and π -electron delocalization due to its large deviation from planarity. Interestingly, the 3D omniconjugated compounds contain, as well as the 2D systems, at least one odd-membered ring (see also bicyclo-octane^[65] 3.59). This



Scheme 3.8 (Top) Design of 3D omniconjugated model **3.58** from a Type B omniconjugated model (in parentheses) by utilizing the topological design rules for 2D omniconjugated models. (Bottom) 3D representation of the tricyclo-[5.2.1.0^{2,6}]decane **3.58**, and bicyclo[3.2.1]octane **3.59**. The open[5,6]corannulene **3.60** contains a substituent in conjugation with the central nuclear framework.

implies that omniconjugation cannot be found in compounds derived from 3D systems such as, for example, adamantine. Adamantine only has even-membered rings. Fullerenes or other cycles with a fully conjugated periphery are not considered as being omniconjugated: although the molecular framework is fully conjugated, these systems do not possess terminals to make it an omniconjugated system. Interestingly, the circumference of [60]fullerene consists of pyracylene fragments^[53,66,67] and can, in principle, be used to construct Type A omniconjugated systems by putting terminals on it. This is illustrated for the fullerene fragment corannulene **3.60**. Here, the “omniconjugated” position is created in a manner analogous to **3.59**.

Another possible configuration for 3D systems is a dendrimer. Dendrimers are sometimes considered as fully π -conjugated architectures. In general, dendrimers are spherical architectures originating in one core with at least one branch at each repeat unit (tecton). The conjugation in dendrimers is interrupted when the system is built from generations segmented by *meta*-substituted benzene rings. Hence, such dendrimers are not fully conjugated. One could envision that dendrimers can be designed as fully conjugated using an omniconjugated linker in sharp contrast to systems reported thus far.^[16,68,69]

3.7 Conclusions

The concept of omniconjugation was introduced and a topological algorithm for the construction of omniconjugated systems was presented. In chemistry, molecules with such topology are entities that have *direct* and fully π -conjugated pathways between *all* properly connected external moieties. The proposed topological design process, derived from a valence bond description of the π -electron skeleton, resulted in a more fundamental understanding of the concept. It encompasses a set of empirical design rules to allow for the construction of two-dimensional, non-alternant omniconjugated models. These operations all originate from one central argument: preservation of the existing conjugated pathways and avoiding the emergence of cross-conjugation. The rules are particularly attractive since they seem to allow for the design of an infinite number of possible candidates.

The key-models are the prototypes for the structural design and pass on the topological properties of omniconjugated models. The *Type A omniconjugated models* have the topological property that they always remain omniconjugated upon a redox operation (i.e., executing operation (i)). On the other hand, *Type B omniconjugated models*, defined as only derivable from key-model **B**, have the intriguing property that omniconjugation was *not* always preserved. As a consequence, these models have topological properties that are closely related to ordinary cross-conjugated models. The archetypal analysis allows for a better differentiation between the subclasses of omniconjugation. The overlap between both methods was evident. First of all, Type A omniconjugated models remained omniconjugated upon executing operation (i); these were the systems without non-Kekulé structures in their archetype series. Secondly, it was possible to create cross-conjugated pathways in all other, lower level conjugated models upon executing operation (i); these systems have non-Kekulé structures in their archetype series. Furthermore, both methods attributed similar topological properties to resonance structures. The resonance contributors of Type A omniconjugated models were all omniconjugated and were found to originate from the same archetype member or the n-terminal system. The fact that the topological properties were the same for resonance structures was a crucial property, suggesting that omniconjugation is not simply a topological curiosity based on the valence bond theory.

The omniconjugated building blocks allow for the construction of molecular architectures (among which some very realistic ones) with more than two terminals that are *truly* π -conjugated. The Type B omniconjugated systems may be of considerable use for the development of active elements for electronic circuits, like molecular gates, since their conjugation can change (switch). The Type A omniconjugated systems are envisioned as potential passive elements. As interconnecting building blocks, they could be useful construction elements in the design of complex molecular electronic circuitry or serve as central units for highly

polarized donor–acceptor-type systems and dendrimers. Omniconjugated systems can also be used to construct even more complicated – for example 6-terminal – systems, which can be used to construct highly intriguing molecular logic elements, as will be shown in Chapter 6.

We want to stress at this point that the *topological* analyses, the one as outlined in this chapter, as well as the ones from other parts of this thesis, remain mathematically valid, independent of the applicability in terms of chemistry.

3.8 References and Notes

1. A. Aviram, M. A. Ratner, *Chem. Phys. Lett.* **1974**, 29, 277.
2. F. L. Carter, *Molecular Electronic Devices*, Marcel Dekker, New York **1982**, pp. 51.
3. C. Joachim, J. K. Gimzewski, A. Aviram, *Nature* **2000**, 408, 541.
4. J. M. Tour, M. Kozaki, J. M. Seminario, *J. Am. Chem. Soc.* **1998**, 120, 8486.
5. A. Nitzan, M. A. Ratner, *Science* **2003**, 300, 1384.
6. S. N. Yaliraki, M. A. Ratner, *Ann. N.Y. Acad. Sci.* **2002**, 960, 153.
7. Z. L. Mišković, R. A. English, S. G. Davison, F. O. Goodman, *J. Phys.: Condens. Matter* **1997**, 9, 10749.
8. J. Reichert, R. Ochs, D. Beckmann, H. B. Weber, M. Mayor, H. von Löhneysen, *Phys. Rev. Lett.* **2002**, 88, 176804.
9. S. Roth, H. Bleier, *Adv. Phys.* **1987**, 36, 385.
10. J. C. Ellenbogen, J. C. Love, *Proc. IEEE* **2000**, 88, 386 and references cited therein.
11. M. Trætteberg, H. Hopf, *Acta Chem. Scand.* **1994**, 48, 989.
12. J.-P. Gisselbrecht, N. N. P. Moonen, C. Boudon, M. B. Nielsen, F. Diederich, M. Gross, *Eur. J. Org. Chem.* **2004**, 2959.
13. M. Klokkenburg, M. Lutz, A. L. Spek, J. H. van der Maas, C. A. van Walree, *Chem. Eur. J.* **2003**, 9, 3544.
14. D. Philp, V. Gramlich, P. Seiler, F. Diederich, *J. Chem. Soc., Perkin Trans. 2* **1995**, 875.
15. M. Bruschi, M. G. Giuffreda, H. P. Lüthi, *ChemPhysChem* **2005**, 6, 511.
16. M. Mayor, M. Büschel, K. M. Fromm, J.-M. Lehn, J. Daub, *Ann. N.Y. Acad. Sci.* **2002**, 960, 16.
17. C. Patoux, C. Coudret, J.-P. Launay, C. Joachim, A. Gourdon, *Inorg. Chem.* **1997**, 36, 5037.
18. R. R. Tykwinski, Y. Zhao, *Synlett* **2002**, 12, 1939.
19. M. Bruschi, M. G. Giuffreda, H. P. Lüthi, *Chem. Eur. J.* **2002**, 8, 4216.
20. S. Eisler, R. R. Tykwinski, *Angew. Chem., Int. Ed.* **1999**, 38, 1940.
21. E. Burri, F. Diederich, M. B. Nielsen, *Helv. Chim. Acta* **2001**, 84, 2169.
22. Y. Zhao, K. Campbell, R. R. Tykwinski, *J. Org. Chem.* **2002**, 67, 336.
23. C. Lepetit, M. Brøndsted Nielsen, F. Diederich, R. Chauvin, *Chem. Eur. J.* **2003**, 9, 5056.
24. K. Takahashi, S. Tarutani, *Adv. Mater.* **1995**, 7, 639.
25. F. H. Allen, *Acta Crystallogr., Sect. B: Struct. Sci.* **1981**, 37, 890.

26. T. Lange, V. Gramlich, W. Amrein, F. Diederich, M. Gross, C. Boudon, J.-P. Gisselbrecht, *Angew. Chem., Int. Ed. Engl.* **1995**, 34, 805.
27. J. A. Marsden, J. J. Miller, L. D. Shirtcliff, M. M. Haley, *J. Am. Chem. Soc.* **2005**, 127, 2464.
28. M. G. Giuffreda, M. Bruschi, H. P. Lüthi, *Chem. Eur. J.* **2004**, 10, 5671.
29. F. Diederich, *Chem. Commun.* **2001**, 219.
30. Y. Zhao, R. McDonald, R. R. Tykwienski, *J. Org. Chem.* **2002**, 67, 2805.
31. F. Diederich, *Pure Appl. Chem.* **1999**, 71, 265.
32. S. Sengupta, *Synlett* **2004**, 2004, 1191.
33. M. Kondo, D. Nozaki, M. Tachibana, T. Yumura, K. Yoshizawa, *Chem. Phys.* **2005**, 312, 289.
34. T. Ozawa, M. Akita, *Chem. Lett.* **2004**, 33, 1180.
35. M. Mayor, C. Didschies, *Angew. Chem., Int. Ed.* **2003**, 42, 3176.
36. J. Krömer, I. Rios-Carreras, G. Fuhrmann, C. Musch, M. Wunderlin, T. Debaerdemaeker, E. Mena-Osteritz, P. Bärle, *Angew. Chem., Int. Ed.* **2000**, 39, 3481.
37. C. A. van Walree, V. E. M. Kaats-Richters, S. J. Veen, B. Wieczorek, J. H. van der Wiel, B. C. van der Wiel, *Eur. J. Org. Chem.* **2004**, 3046.
38. R. Neidlein, V. Poignée, W. Kramer, C. Glück, *Angew. Chem., Int. Ed. Engl.* **1986**, 25, 731.
39. The terminals are potential attachment positions for substituents that can be, for example, additional conjugated fragments, desired functional groups, or logic elements, or electrodes. Although the substituents are in principle undefined, their linking position (i.e., the position of the site) is an essential element of the omniconjugated system.
40. A. A. Ovchinnikov, *Theor. Chim. Acta* **1978**, 47, 297.
41. N. Tyutyulkov, F. Dietz, K. Müllen, M. Baumgarten, *Theor. Chim. Acta* **1993**, 86, 353.
42. D. M. Lemal, G. D. Goldman, *J. Chem. Educ.* **1988**, 65, 923.
43. J. Michl, E. W. Thulstrup, *Tetrahedron* **1976**, 32, 205.
44. M. B. Smith, J. March, *March's Advanced Organic Chemistry*, 5th ed., Wiley, New York **2001**, pp. 32.
45. R. W. A. Havenith, J. H. van Lenthe, L. W. Jenneskens, *J. Org. Chem.* **2005**, 70, 4484.
46. R. W. A. Havenith, L. W. Jenneskens, P. W. Fowler, E. Steiner, *Phys. Chem. Chem. Phys.* **2004**, 6, 2033.
47. G. J. Palmer, S. R. Parkin, J. E. Anthony, *Angew. Chem., Int. Ed.* **2001**, 40, 2509.

48. A. C. Sircar, S. K. Cuha, *J. Chem. Soc.* **1924**, 125, 335.
49. L. K. Steffen, B. F. Plummer, T. L. Braley, W. G. Reese, K. Zych, G. van Dyke, M. Gill, *J. Phys. Org. Chem.* **1997**, 10, 623.
50. P. W. Rabideau, A. H. Abdourazak, H. E. Folsom, Z. Marcinow, A. Sygula, R. Sygula, *J. Am. Chem. Soc.* **1994**, 116, 7891.
51. L. T. Scott, P.-C Cheng, M. M. Hashemi, M. S. Bratcher, D. T. Meyer, H. B. Warren, *J. Am. Chem. Soc.* **1997**, 119, 10963.
52. L. T. Scott, *Pure Appl. Chem.* **1996**, 68, 291.
53. H. A. Wegner, L. T. Scott, A. de Meijere, *J. Org. Chem.* **2003**, 68, 883.
54. A.-D. Schlüter, M. Löfller, V. Enkelmann, *Nature* **1994**, 368, 831.
55. B. Schlicke, J. Frahn, A.-D. Schlüter, *Synth. Met.* **1996**, 83, 173.
56. B. Waage, A.-D. Schlüter, G. Leising, *Synth. Met.* **1997**, 933.
57. B. Dicker, A. Hohenau, W. Graupner, S. Tasch, M. Graupner, A. Hermetter, B. Schlicke, N. Schulte, A.-D. Schlüter, U. Scherf, K. Müllen, G. Leising, *Synth. Met.* **1999**, 102, 873.
58. A.-D. Schlüter, *Adv. Mater.* **1991**, 3, 282.
59. T. Zambelli, H. Tang, J. Lagoute, S. Gauthier, A. Gourdon, C. Joachim, *Chem. Phys. Lett.* **2001**, 348, 1.
60. K. Loganathan, E. G. Cammisa, B. D. Myron, P. G. Pickup, *Chem. Mater.* **2003**, 15, 1918.
61. E. P. Kyba, S.-T. Liu, K. Chockalingam, B. R. Reddy, *J. Org. Chem.* **1988**, 53, 3513.
62. K. Panda, C. Venkatesh, H. Ila, H. Junjappa, *Eur. J. Org. Chem.* **2005**, 2005, 2045.
63. It is clear that many heteroatoms could give great complications due to the possible involvement of lone pairs of electrons. Such systems are way beyond the scope of the present analysis of omniconjugated systems.
64. K. Mackenzie, P. R. Young, *J. Chem. Soc. C* **1970**, 1242.
65. D. I. Rawon, B. K. Carpenter, H. M. R. Hoffmann, *J. Am. Chem. Soc.* **1979**, 101, 1786.
66. R. W. Alder, J. N. Harvey, *J. Am. Chem. Soc.* **2004**, 126, 2490.
67. C. Koper, M. Sarobe, L. W. Jenneskens, *Phys. Chem. Chem. Phys.* **2004**, 6, 319.
68. M. Nakano, M. Takahata, S. Yamada, K. Yamaguchi, R. Kishi, T. Nitta, *J. Chem. Phys.* **2004**, 120, 2359.
69. H. Chen, M. He, X. Cao, X. Zhou, J. Pei, *Rapid. Commun. Mass. Spectrom.* **2004**, 18, 367.

Chapter 4

Electronic structure of Omniconjugated compounds

Abstract In this chapter the electronic structure of omniconjugated systems with four terminals is evaluated to verify whether or not such compounds encompass a complete delocalization within their frontier orbitals. If so, they would allow for the interconnection of many functional entities in a fully conjugated manner. The presented results indicate that the topological phenomenon of omniconjugation indeed may give rise to a pronounced delocalization within the relevant molecular orbitals into all the terminals. The observed uniform π -electron distribution in the frontier orbitals suggests that the building blocks facilitate hole and electron transport. In some cases, a new and intriguing phenomenon was observed from the electronic structure that was not obvious from the topology of the bonds. As a result of the local symmetry of the skeleton, certain 4-terminal conjugated systems seem to show orthogonal directionality for hole and electron transport. Hence, in the plane of the molecule there could be preferential transmission pathways for transport of either charge. These preliminary results indicate that 4-terminal (omni)conjugating molecular building blocks could play a promising role in future molecular electronics.

The work presented in this chapter is partially covered by the following paper: M. H. van der Veen, M. T. Rispens, H. T. Jonkman, J. C. Hummelen, *Adv. Funct. Mater.* **2004**, 14, 215–223.

4.1 Introduction

The concept of omniconjugation finds its basis in a valence-bond description of the π -electron system. Omniconjugated systems are envisioned as useful construction elements in the design of complex molecular-electronic circuitry. From a topological point of view, omniconjugated systems can serve as, for example, interconnecting building blocks because they have conjugated pathways between all terminals. This may give rise to efficient pathways for the transmission of charge between all the external connected moieties. However, the transport properties of organic systems are controlled by their electronic structure. Therefore, a quantum chemical evaluation of orbitals of omniconjugated systems is a necessary second step in order to determine whether they can function as envisioned or not.

The concepts of molecular physics are essential to gain insight into the ability of organic molecules to transport charges. A tremendous volume of literature^[1,2] has been published that addresses the question which electron transfer mechanism dominates in the case of molecular systems.^[3,4] A precise understanding of the flow of electrons is important for the rational design of molecular junctions. The most obvious requirement is that the molecules have to be electron or hole conducting in order to transport charges through a circuit. Over these distances the electron travels through unoccupied orbitals. This process is usually referred to as the "through-bond" mechanism. The basic structural requirement for molecular wires is that they should have alternating single and double (or triple) bonds. In this way, molecular wires can efficiently transport the charges through their π -system.^[5,6] The π -system provides for a pathway from one end to the other end of the molecule that is more efficient than the intermolecular charge transport.

There are many different methods available to model the transport of charges across a molecular junction. The theoretical approaches are based on a combination of a description of the transport level (e.g., scattering theories based on the Landauer formula,^[7,8] and Green's functions)^[9–11] and the electronic structure of the system (e.g., semiempirical,^[12,13] *ab initio* Hartree-Fock,^[14,15] and density functional theory).^[16,17] Enormous efforts are being made to improve the models to be able to account for the experimental observations. Still though, the various approaches often give different conclusions. A common observation is that the electronic structure and morphology at the metal contact plays a crucial role in the transport properties.^[18–20] Furthermore, the frontier molecular orbitals (MO's), as well as other MO's, are necessary to study the electronic structure–property relation of conjugated molecules. The analysis of the electronic levels has been used to gain a better understanding of the behavior of molecular wires,^[21] bridges,^[22,23] and diodes.^[24–28] It has been demonstrated that the MO's form conduction channels for the transmission of charged species (charged quasi-particles) through the molecules.

Furthermore, it is found that the delocalization of the frontier orbitals depends on the topology of the available pathways (linear or cross-conjugated) between the two ends of the molecule.^[29–32] Even though there can be a considerable delocalization of the π -electron system, the electronic coupling between two moieties attached to the molecule can be severely reduced along cross-conjugated pathways compared to linear conjugated ones.^[33–36] Another key issue in understanding the transmission of charged species in conjugated materials are correlation effects such as Coulomb interaction or self localization.

The 4-terminal omniconjugated systems were designed in Chapter 3 to facilitate charge transport between four external connected moieties, at least from a topological point of view. The electron and/or hole transmission coefficients, which are a measure for charge transport, are strongly dependent on the degree of delocalization within the relevant orbitals between the terminals of the molecular building block. Hence, the π -electron probability distribution near the HOMO–LUMO gap can be used to explore the transport properties of omniconjugated systems.

4.2 Quantum-Chemical approach

The objective of the quantum chemical (QC) calculations is to probe the charge distribution of the frontier orbitals of omniconjugated systems in order to get estimates for the charge transfer coefficients. For simplicity, the terminals of the omniconjugated systems (A, B, C, D, etc.) are functionalized with π -conjugated moieties without explicitly accounting for the nature of these moieties. The double bond terminals and single bond terminals are represented by methylene ($=\text{CH}_2$) or vinyl groups ($-\text{CH}=\text{CH}_2$), respectively. It is expected that this will result in more representative evaluation of the omniconjugated systems than when other larger or complicated functional moieties are used instead. Such moieties could have a pronounced effect on the electronic structure of a molecule.

The molecular orbital structure of the central building blocks was evaluated on a qualitative basis. The calculations were carried out for the single molecules in the gas phase using QC methods implemented in the HyperChem package.^[37] The geometric structures of the model systems were optimized with the Molecular Mechanics (MM+) force field prior to the semiempirical calculations. The Polak-Ribiere (conjugate gradient) was used as optimization algorithm with a root mean square gradient of 0.1 kcal/Å mol. Subsequently, the structures were optimized with the semiempirical Restricted Hartree-Fock method in the Austin Model 1 approximation (AM1-RHF). This method has been parameterized to provide accurate geometries for organic molecules in their ground state.^[38]

The electronic structures were obtained for the fully optimized conformations by treatment of the neutral molecules at the AM1-RHF level. This gives a reliable description of the one-electron structure of organic conjugated molecules in the

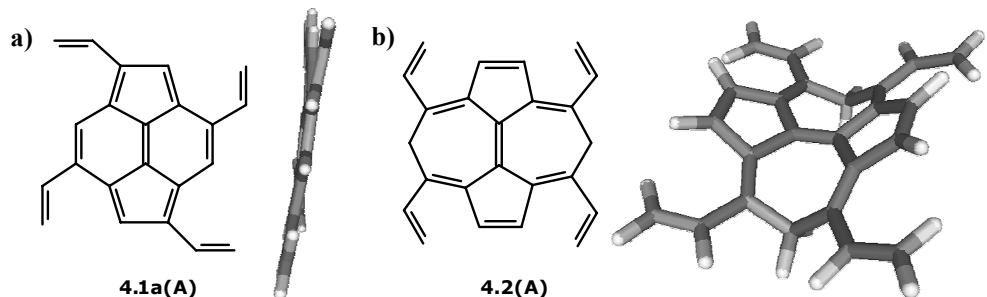


Figure 4.1 Chemical structures of the tetravinylene-substituted systems 4.1a (a) and 4.2 (b). Both are Type A omniconjugated (as indicated in parentheses). Their 3D representations of the AM1-optimized geometries are viewed from the right (4.1a) and bottom (4.2). The four external moieties are restricted to a planar conformation with respect to the central part of the nuclear framework.

ground state.^[39] The importance of intramolecular conducting pathways between the terminals is qualitatively evaluated via the plots of the frontier orbitals obtained from the molecular orbital coefficients. The degree of delocalization of the electronic levels is represented by the orbitals. However, the key-parameter to be determined is the electron density, given by the square of an electronic wavefunction, since it displays the probability distribution $\psi(x,y)^2$ of finding an electron at a certain position. In the figures of the electron density, the distribution is given for a 90 percent probability.

Even though the electronic properties are of primary interest, it is important to first consider the geometry of the model systems. This is because the delocalization within the orbitals can be seriously influenced upon torsional motion and/or steric hindrance within the conjugated system.^[40] The first conformational searches showed that the vinylene moieties were twisted relative to the plane of the molecules. The π -orbitals tend to localize when the vinylene moiety was in a nearly perpendicular conformation. This may reduce, or even break, the π -electron delocalization across the nuclear framework of the molecule.^[41,42]

To reduce the effect of large torsion angles, the bond angle of the vinylene moieties with respect to the adjacent ring was constrained parallel using either a *cis* or *trans* conformation. This approach resulted in realistic description of the actual geometry of the central part of the omniconjugated system. This was confirmed by geometry optimizations *without* restraints for a tetrakis(2-phenylethynyl) substituted derivative of pyracylene. The triple bonds of acetylene are often used as conjugation spacers to prevent steric hindrance between adjacent conjugated hydrocarbon rings. These spacers are rigid and planar and have a second out-of-plane π -orbital in conjugation with the single bond. The fully AM1-optimized conformation of the tetrakis(2-phenylethynyl) substituted derivative presented no significant deviation from planarity and was in agreement with the 3D representation of the

tetravinylene-substituted pyracylene derivative **4.1a** given in Figure 4.1a. The central core of **4.1a** adapts a slightly bended conformation (as fragments of fullerenes do). This is a consequence of the strain present within the central rings and the steric hindrance induced by the connected hydrogen atoms.^[43] As expected, structure **4.2** (a dehydrodicyclopenta heptalene) reveals a larger geometric distortion of the central core owing to the two hydrogens attached to the sp³-hybridized carbons of the two inter-ring bridges. Apparently, the imposed geometry constraints for the four external moieties have no major impact on the geometry of the central part of nuclear framework of the conjugated systems.

4.3 Frontier Orbital Delocalization

The spatial extent of the π -electron probability distribution is analyzed qualitatively in order to determine whether there is sufficient delocalization to allow for charge transport between all connected moieties. The presented valence bond approach in Chapter 3 of this thesis cannot be used to understand hole and electron transport. However, with the molecular orbital description of the systems, the occupied and a virtual orbital manifold are elucidated, which does allow for distinguishing between hole and electron transport, respectively.

Figure 4.2 presents the electron probability distribution for the HOMO and LUMO of the tetravinylene-substituted structure **4.1a**. The HOMO and LUMO of **4.1a** have a π -character and are strongly delocalized over the entire molecular framework. The electronic structure of the HOMO is reminiscent to the valence bond structure of the most stable resonance contributor of this molecule (see **4.1b-d** in Figure 4.3). Moreover, the molecular orbital structure of the LUMO resembles the situation described by the valence bond structure of the less stable resonance contributor structure **4.1a**. The effect of local symmetry of the skeleton, which introduces a nodal plane in the LUMO, does not seem to invalidate this conjecture. Note that pyracylenes **4.1a** and **4.1b** are not two independently existing structures; they just serve as a basis for the description of the electronic structure of the real system. Here, **4.1b** is energetically more favorable than **4.1a** and thus the dominant contributor. Both resonance contributors are omniconjugated and only differ by permutation of all pericyclic bonds as described by step 3 of the topological design method (Section 3.3.1). In the limit of large building blocks, a substantial number of orbitals (within kT) have to be considered in the evaluation of the transmission coefficients. Within that limit, the molecular orbital description converges towards the valence bond picture. In both frontier orbitals of **4.1a** a significant π -electron density is observed on the four terminals. This building block seems to facilitate both hole and electron transport, even though there is an asymmetry for the former.

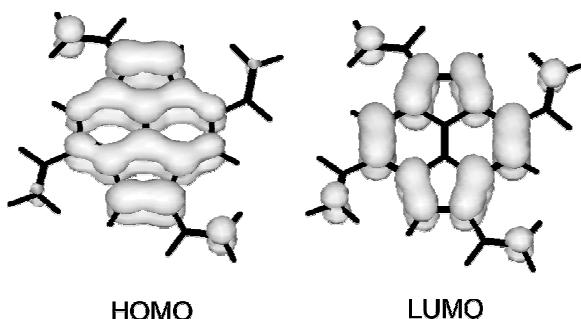


Figure 4.2 AM1-calculated representations of the electron probability distribution $\psi(x,y)^2$ in the frontier orbitals of tetravinylene-substituted pyracylene **4.1a**.

The nature of the HOMO and LUMO of structure **4.2** are given in Figure 4.4. This molecule is generated from the same building block as **4.1** during its topological design process (see Scheme 3.2). However, the delocalization within the frontier orbitals is different. For a valence bond description of the ground state, only one resonance contributor now fully dominates and nicely mimics the overall charge distribution in the HOMO. This would make this system an efficient hole transport medium. It confirms that a significant deviation from planarity (see Figure 4.1) does not hinder an efficient π -orbital overlap (in this case). In terms of efficiency, **4.2** would be a better transport medium for holes compared to **4.1**. The HOMO of the latter one displayed a less pronounced and more asymmetrical delocalization on the four terminals. However, this asymmetry of the HOMO of **4.1** is of less importance. This was observed in QC calculations after proper substitution of **4.1** with, for example, phenylethynyl moieties. These moieties did not lead to marked changes in the shapes of the orbitals. On the other hand, the π -electron densities were considerably higher at the vinylene positions of **4.1**, most likely due to inductive effects of the phenylethynyl spacers.

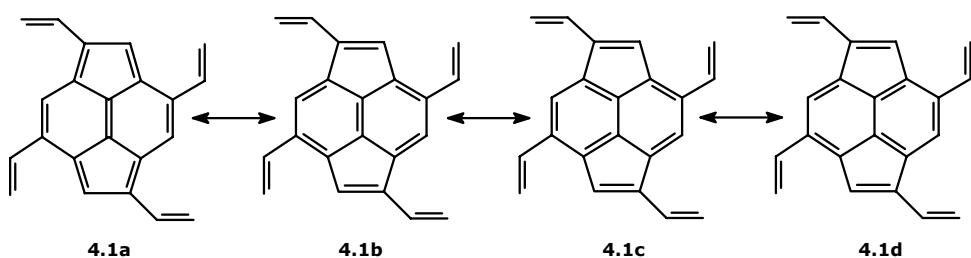


Figure 4.3 Valence bond structures of the resonance contributors of **4.1**.

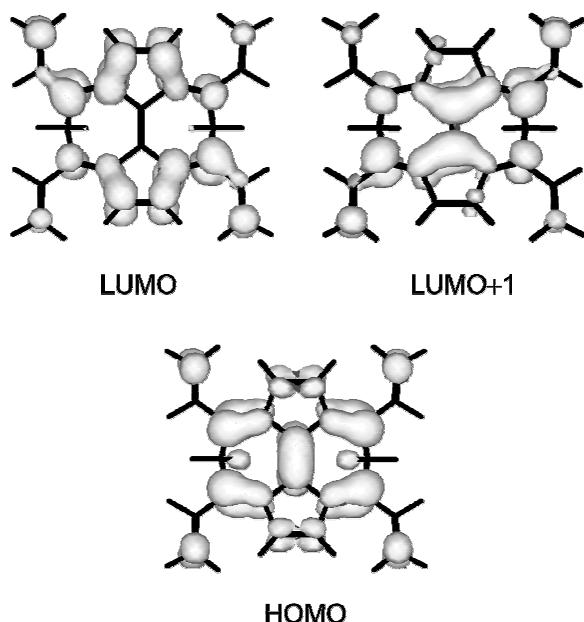


Figure 4.4 AM1-calculated representations of the electron probability distribution $\psi(x,y)^2$ in the HOMO and LUMO (near degenerate) of the tetravinylene-substituted system **4.2**.

A qualitative analysis of the electron transport properties of **4.2** requires the evaluation of two nearly degenerate unoccupied levels. The energy gap in the order of 0.01 eV is small enough to account for a strong interaction between these unoccupied orbitals. Therefore, they will both have an important contribution to the electron transport channels.

So far, the electron probability distribution in the frontier orbitals has been analyzed to obtain a qualitative prediction of the transport properties. However, transport channels in larger molecular systems arise from the contributions of many individual (energetically close) molecular orbitals. Each of them may contribute to the charge transport properties of the molecule. A detailed investigation of this phenomenon, based on quantum-mechanical DFT calculations, has been reported for a one-dimensional molecular wire.^[44] Based on such observations, it is not sufficient to only consider the delocalization within the HOMO and LUMO when analyzing larger π -electron systems in a qualitative manner. Although all energetically close, as well as, other (lower lying) orbitals should be included, the presented approach serves as a proper indication for the efficiency to transmit charges.

4.4 Frontier Orbital Localization

Another intriguing feature, a possible topological asymmetry for the hole and electron conduction channels in this new class of compounds, is observed with structure **4.3**. The spatial distribution of the π -electron density in the HOMO of **4.3** is limited to a path between two terminals, as can be seen in Figure 4.5a. The localization of the HOMO, as a consequence of local symmetry considerations, restricts the hole conduction channel to the long axis of the molecule. On the other hand, the LUMO is mainly localized to the short axis of the molecule through which electron transport is strongly favored. These results suggest this molecular system has separate hole and electron conduction channels. This anticipated feature is represented by the cartoon in Figure 4.5b. In agreement to the present findings, separated electron and hole transport regimes are also found in other, typical non-alternant hydrocarbons.^[45] A theoretical explanation is found in the intrinsic properties of non-alternant unsaturated hydrocarbons. Most of them do not have "mirror-related" molecular orbitals implying that orbital pairing usually does not happen.^[46,47] More generally, it is expected that the non-alternant character is instrumental for the asymmetry in the hole and electron conduction characteristics in most of these omniconjugated systems. A difference between omniconjugated system **4.3** and other classic non-alternant systems is that with the 4-terminal

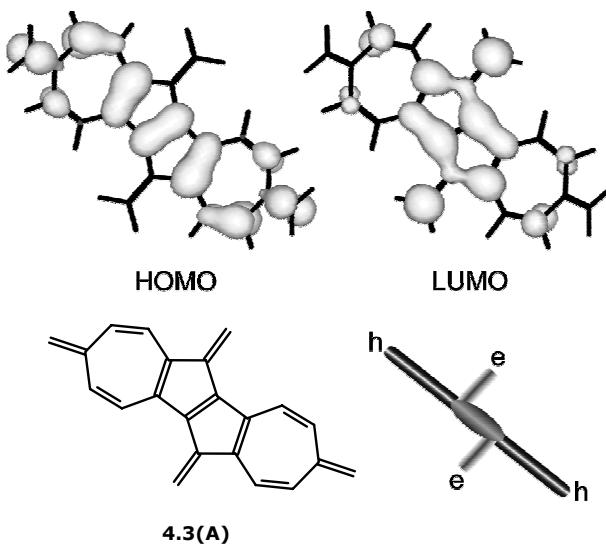


Figure 4.5 (Top) Plots of the π -electron probability distribution in the frontier orbitals of the tetramethylene-substituted structure **4.3**. (Bottom). Cartoon of the preferred transport direction for holes (*h*) and electrons (*e*) as proposed for **4.3** (left).

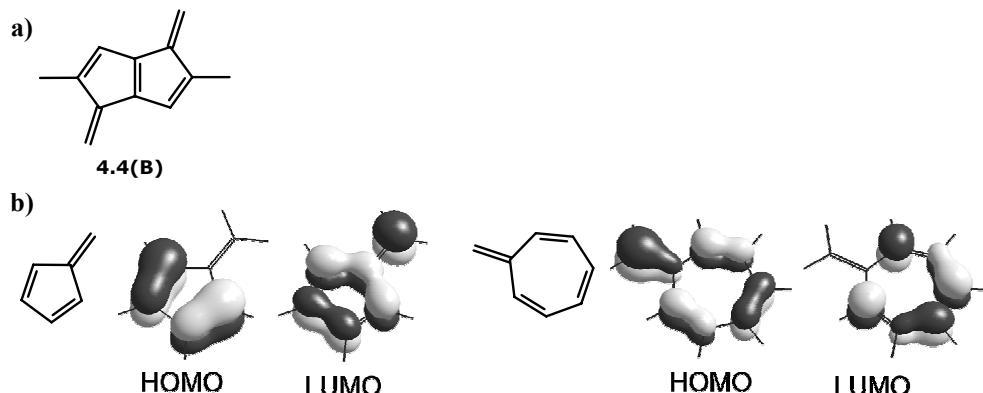


Figure 4.6 a) Type B omniconjugated system **4.4**. b) The amplitude distribution (AM1-calculated; $\psi(x,y)$) of the HOMO and LUMO of fulvene units (left) and heptafulvene (right) units of **4.3**.

omniconjugated example, a system having *spatially* separated conduction channels for electrons *and* holes is proposed. As with the conjugated pathways between the respective pairs of terminals, these two channels coincide at the central part of the nuclear framework. In theory, spatially separated electron and hole channels can be observed for other (cross-)conjugated systems with *four* terminals as well.

The existence of different channels for hole and electron transport cannot be predicted from the valence bond description of the system. It is not a consequence of the *omniconjugated* character of the molecular entity. Similarly, it is not related to the *class* of omniconjugation (i.e., Type A or B) as was confirmed with QC-calculations for the Type B system **4.4** (see for the structure Figure 4.6a) that showed a related response in directionality for charge transport. The topological asymmetry of the channels originates from local symmetry effects on the spatial structure of the individual molecular orbitals. In the neutral systems, the distribution of the doubly occupied orbitals is dictated by the (local) symmetry of the nuclear framework. This means that the orbitals can be localized to certain parts of the system. From a topological point of view, this would be the same as excluding some of the valence bond conjugated pathways. This is illustrated with the plot of the frontier orbitals of the fulvene and heptafulvene systems (see Figure 4.6b). These rings constitute part of the nuclear framework of **4.3**. The local symmetry of the nuclear framework plays an important decisive role in the QC analysis of omniconjugated systems. For systems like **4.3**, the omniconjugated character could perhaps only influence the efficiency of the charge transporting channels.

4.5 Discussion and Conclusions

The concept of omniconjugation was derived from a topological description of the π -electron skeleton. A valence bond description did not make a real distinction between hole and electron transport capabilities of a conjugated system. Molecular orbital computations were essential in providing insight into this difference. The transmission coefficients for charge transport within π -conjugated molecules are dependent on the electron probability distribution in the frontier orbitals near the HOMO–LUMO gap. The presented results obtained with a small selection of 4-terminal conjugated systems showed that the MO and VB approaches converge to a large extent. There were often a number of possible resonance contributors in a valence bond description. A linear combination of those resonance contributors, in which each structure has usually a different weight, represented the overall π -electron distribution in the ground state. Despite some local symmetry considerations, it was often found that the charge and bond order distribution in the HOMO was reminiscent of the major resonance contributor in the valence bond description. Furthermore, an impression of the electronic structure of the LUMO could often be obtained from the remaining resonance structures. This suggests that the magnitude of the electron or hole transmission coefficients can be related to the presence of an uninterrupted alternating sequence of single and double bonds between the external π -bonded moieties. In this context, intramolecular transport is the most important charge transport mechanism.

In molecular crystals two types of transport can be distinguished: *intramolecular* (in quasi 1D extended conjugated molecules: band-like) and *intermolecular* (scaling with a hopping or transfer integral). The transfer integrals are in a first-order approach a function of an intermolecular overlap integral and a molecular interaction parameter. Since omniconjugation may distribute charge in a more uniform way over the relevant orbitals, it could enhance the intermolecular overlap, opening efficient conduction channels for an, for example, additional hopping-like transport mechanism. The geometric structure of conjugated systems can be significantly affected upon formation of charged species such as a radical cation or radical anion. Other conformational distortions that may influence the orbital delocalization are moieties with a large torsion angle relative to the plane of the central part of the nuclear framework. These effects were minimized during the QC calculations by imposing geometric constraints for the moieties. It is expected that the size of the conjugated segments of the presented 4-terminal conjugated systems is more or less equivalent to localization length of charge carriers. Hence, it is expected that charged species like polarons will not lead to (additional) marked changes in the shapes of their orbitals.^[48]

In conclusion, a number of omniconjugated systems have been investigated using computational chemistry methods. These interconnecting building blocks may

have efficient (although not necessarily equally efficient) pathways for electron and/or hole transport between *all* external moieties. As such, they could be envisioned as potentially useful construction elements in the design of complex molecular electronic circuitry. Some omniconjugating building blocks have spatially separated channels for hole and electron transport. This latter property may be of use to construct more advanced molecular electronic devices.

4.6 References

1. A. Nitzan, *Annu. Rev. Phys. Chem.* **2001**, *52*, 681.
2. D. M. Adams, L. Brus, C. E. D. Chidsey, S. Creager, C. Creutz, C. R. Kagan, P. V. Kamat, M. Lieberman, S. Lindsay, R. A. Marcus, R. M. Metzger, M. E. Michel-Beyerle, J. R. Miller, M. D. Newton, D. R. Rolison, O. Sankey, K. S. Schanze, J. Yardley, X. Zhu, *J. Phys. Chem. B* **2003**, *107*, 6668.
3. G. Pourtois, D. Beljonne, J. Cornil, M. A. Ratner, J. L. Brédas, *J. Am. Chem. Soc.* **2002**, *124*, 4436.
4. M. U. Winters, K. Pettersson, J. Mårtensson, B. Albinsson, *Chem. Eur. J.* **2005**, *11*, 562.
5. N. Robertson, C. A. McGowan, *Chem. Soc. Rev.* **2003**, *32*, 96.
6. R. L. McCreery, *Chem. Mater.* **2004**, *16*, 4477.
7. V. Mujica, A. Nitzan, S. Datta, M. A. Ratner, C. P. Kubiak, *J. Phys. Chem. B* **2003**, *107*, 91.
8. E. G. Emberly, G. Kirczenow, *Phys. Rev. B* **2000**, *61*, 5740.
9. Z. G. Yu, D. L. Smith, A. Saxena, A. R. Bishop, *Phys. Rev. B* **1999**, *59*, 16001.
10. G. Treboux, *J. Phys. Chem. B* **2000**, *104*, 9823.
11. V. Mujica, M. Kemp, M. A. Ratner, *J. Chem. Phys.* **1994**, *101*, 6856.
12. V. Mujica, A. E. Roitberg, M. A. Ratner, *J. Chem. Phys.* **2000**, *112*, 6834.
13. S. Ami, C. Joachim, *Phys. Rev. B* **2002**, *65*, 155419.
14. V. Mujica, M. Kemp, A. E. Roitberg, M. A. Ratner, *J. Chem. Phys.* **1996**, *104*, 7296.
15. S. N. Yaliraki, M. A. Ratner, *Ann. N.Y. Acad. Sci.* **2002**, *960*, 153.
16. F. Evers, F. Weigend, M. Koentopp, *Phys. Rev. B* **2004**, *69*, 235411.
17. J. M. Seminario, C. de la Cruz, P. A. Derosa, L. Yan, *J. Phys. Chem. B* **2004**, *108*, 17879.
18. Y. Karzazi, X. Crispin, O. Kwon, J. L. Brédas, J. Cornil, *Chem. Phys. Lett.* **2004**, *387*, 502.
19. S. N. Yaliraki, M. Kemp, M. A. Ratner, *J. Am. Chem. Soc.* **1999**, *121*, 3428.
20. H. Basch, M. A. Ratner, *J. Chem. Phys.* **2003**, *119*, 11926.
21. J. Reichert, R. Ochs, D. Beckmann, H. B. Weber, M. Mayor, H. von Löhneysen, *Phys. Rev. Lett.* **2002**, *88*, 176804.
22. F. Remacle, R. D. Levine, *Chem. Phys. Lett.* **2004**, *383*, 537.
23. M. Girlanda, M. Macucci, *J. Phys. Chem. A* **2003**, *107*, 706.
24. K. Stokbro, J. Taylor, M. Brandbyge, *J. Am. Chem. Soc.* **2003**, *125*, 3674.
25. P. A. Derosa, S. Guda, J. M. Seminario, *J. Am. Chem. Soc.* **2003**, *125*, 14240.

26. Y. Karzazi, J. Cornil, J. L. Brédas, *J. Am. Chem. Soc.* **2001**, *123*, 10076.
27. J. M. Seminario, A. G. Zacarias, J. M. Tour, *J. Am. Chem. Soc.* **2000**, *122*, 3015.
28. J. Cornil, Y. Karzazi, J. L. Brédas, *J. Am. Chem. Soc.* **2002**, *124*, 3516.
29. A. Pogantsch, A. K. Mahler, G. Hayn, R. Saf, F. Stelzer, E. J. W. List, J. L. Brédas, E. Zojer, *Chem. Phys.* **2004**, *297*, 143.
30. M. Bruschi, M. G. Giuffreda, H. P. Lüthi, *Chem. Eur. J.* **2002**, *8*, 4216.
31. M. Klokkenburg, M. Lutz, A. L. Spek, J. H. van der Maas, C. A. van Walree, *Chem. Eur. J.* **2003**, *9*, 3544.
32. M. Kondo, D. Nozaki, M. Tachibana, T. Yumura, K. Yoshizawa, *Chem. Phys.* **2005**, *312*, 289.
33. D. Philp, V. Gramlich, P. Seiler, F. Diederich, *J. Chem. Soc., Perkin Trans. 2* **1995**, *875*.
34. M. Bruschi, M. G. Giuffreda, H. P. Lüthi, *ChemPhysChem* **2005**, *6*, 511.
35. C. Patoux, C. Coudret, J.-P. Launay, C. Joachim, A. Gourdon, *Inorg. Chem.* **1997**, *36*, 5037.
36. J.-P. Launay, *Chem. Soc. Rev.* **2001**, *30*, 386.
37. HyperChem™ Release 6.0 for Windows, Molecular Modeling System : © Hypercube, Inc. and Autodesk, Inc..
38. M. J. S. Dewar, E. G. Zoebisch, E. F. Healy, J. J. P. Stewart, *J. Am. Chem. Soc.* **1985**, *107*, 3902.
39. J. L. Brédas, D. Beljonne, J. Cornil, J. Ph. Calbert, Z. Shuai, R. Silbey, *Synth. Met.* **2002**, *125*, 107.
40. E. Zojer, P. Buchacher, F. Wudl, J. Cornil, J. Ph. Calbert, J. L. Brédas, G. Leising, *J. Chem. Phys.* **2000**, *113*, 10002.
41. P. Brocorens, E. Zojer, J. Cornil, Z. Shuai, G. Leising, K. Müllen, J. L. Brédas, *Synth. Met.* **1999**, *100*, 141.
42. J. Birgerson, N. Johansson, A. Pohl, M. Löglund, Y. Tsukahara, K. Kaeriyama, W. R. Salaneck, *Synth. Met.* **2001**, *122*, 67.
43. R. W. A. Havenith, L. W. Jenneskens, P. W. Fowler, E. Steiner, *Phys. Chem. Chem. Phys.* **2004**, *6*, 2033.
44. J. Heurich, J. C. Cuevas, W. Wenzel, G. Schön, *Phys. Rev. Lett.* **2002**, *88*, 256803.
45. G. Treboux, P. Lapstun, K. Silverbrook, *J. Phys. Chem. B* **1998**, *102*, 8978.
46. J. Michl, E. W. Thulstrup, *Tetrahedron* **1976**, *32*, 205.
47. D. M. Lemal, G. D. Goldman, *J. Chem. Educ.* **1988**, *65*, 923.
48. G. R. Hutchison, M. A. Ratner, T. J. Marks, *J. Am. Chem. Soc.* **2005**, *127*, 2339.

Chapter 5

Group Theoretical Aspects: A Quest for Control and Understanding

Abstract When aiming at electronic devices built from single molecules, the molecules have to be provided with external connection points to allow for a direct communication between many (functional) molecules or with the macroscopic world. From our point of view, the substituents (or terminals) of π -conjugated systems are the keys for molecular electronic circuits. In this chapter, a group theoretical approach to describe the topological properties of n -terminal π -conjugated systems is presented. The basis for this description is a classification of the symmetries of the propagation of a bond alternation along a path between two terminals of the n -terminal π -conjugated system. The symmetry properties of n -terminal π -conjugated systems are completely governed by their π -topology. It is found that the topological operation of changing the bonds along a pathway can have a crucial impact on the properties of the molecule. The available linear conjugated pathways within the π -conjugated system are collected in a group multiplication table. Such a collection of the potential transmission pathways for charges can be used to predict the topological changes upon their propagation through the system. Hence, the group theoretical approach may be of considerable use to study the charge transport properties of π -conjugated systems and/or for the design of functional molecules for molecular electronic circuits.

5.1 Introduction

Many years before Aviram and Rather proposed the idea of electrical rectification, by a single molecule,^[1] Richard Feynman discussed the possibility of processing information on a small scale. Already in 1959, he suggested to use atoms to, for example, miniaturize the computer.^[2] What was perhaps far from reality in those days comes now within reach. Perhaps the biggest advantage of carrying out information processing at the nanoscale is the anticipated increased computational power upon increasing the density of electronic components. This is one of the reasons that molecular electronics is a fascinating area of research and is receiving a great deal of scientific interest. The basic challenge in this field is to realize electronic devices based on materials such as molecules, polymers, or a combination thereof.^[3] In principle, the electronic properties of such materials are governed by conjugated bonds that are formed by π -electrons. One of the essential processes of conduction is the transport of charges, such as electrons and holes, along conjugated chains. What is even more interesting is that the molecular architecture can be used for switching processes and with that, provides for the implementation of logic elements in nanoscale circuitry.^[4,5] Some of the earlier proposals for switching at the molecular level are now being realized.^[6,7] These studies indicate that any progress in this field depends on gaining fundamental knowledge of the electronic properties of the molecular electronic circuits. Moreover, it is of prime importance to address and control the states of the elements, based on molecules. For that purpose, one can use substituted molecules with different degrees of π -conjugation. The substituents (or terminals) are the potential attachment positions for additional conjugated fragments or functional groups. The π -topology governs the (electronic) function of the single n-terminal molecule or, alternatively, the corresponding molecular material, as it can be used in electronic devices. We have proposed a systematic analysis of n-terminal π -conjugated systems that can be used to classify conjugated systems by their degree of π -conjugation. The challenge of the work presented in this chapter is to realize a better understanding of the π -topological properties of conjugated systems. This is accomplished by utilizing the basic principles of group theory. It will be shown that symmetry considerations alone describe the π -topological properties of n-terminal π -conjugated systems.

Group theory is a powerful method for the analysis of abstract and physical systems that contain symmetry.^[8] Much of the early work in group theory was performed by the young mathematician Evariste Galois (1811-1832). The beauty of the mathematical formulation of a group is that it can be applied in many scientific areas. For example, group theory is used in physics for studying elementary particles and in chemistry for determining the properties of molecules (e.g., crystal structures

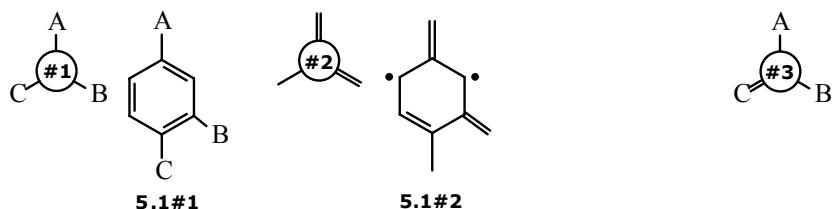


Figure 5.1 Some standard archetypes (cartoons) with an even number of double link terminals (i.e., from the Even set of archetypes; left) and one with an odd number of double link terminals (i.e., Odd set; right). Structure **5.1#1** and **5.1#2** are examples of corresponding molecular archetypes. The latter one is a non-Kekulé structure.

and spectroscopic transitions).^[9] The aspect that will be addressed with group theory here is the symmetry of n-terminal systems.

The systematic analysis of conjugated systems with n-terminals (see Chapter 2) is the foundation for the work presented here. This is because this analysis already revealed several kinds of symmetry-related aspects in the topology of π -conjugated systems. The analysis of n-terminal systems is a method to deduce all possible double bond terminal patterns within a molecular framework. Each pattern, as can be obtained from the statistical permutation of n-terminals, is represented by a standard archetype (see cartoons in Figure 5.1). The corresponding collection of structures is called a molecular archetype series. It was found that the archetype series reveals the degree of conjugation of the n-terminal system. In some cases, it is not possible to find an arrangement of bonds in the structure so that each carbon has one single and one double bond (see, for example, molecular archetype **5.1#2** in Figure 5.1). Such a double bond configuration is an open shell system (i.e., non-Kekulé structure). The number of non-Kekulé structures among the members of the archetype series is used as simple criterion to differentiate between the various classes of conjugation. The symmetry relations that were encountered during the archetypal analysis are summarized in Figure 5.1. First of all, it was found that each standard archetype of the Even (Odd) set has a related archetype in the Odd (Even) set upon permutation of all the terminals from single to double and vice versa (see, for example, standard archetype #2 and #3). Related to this is that the non-Kekulé structures specify, in an indirect manner, the cross-conjugated pathways within the other structures of the series. This was found to be related to the opposite ("mirror related") double bond pattern of terminals of the archetypes (compare terminal A and B in **5.1#1** and **5.1#2**). Another intriguing feature related to symmetry, was encountered in the balanced relation between the number of double bond terminals and the size of the molecular framework. Here, an even (odd) number of double bond terminals imposes an even (odd) number of even-membered rings (see **5.1#1**).

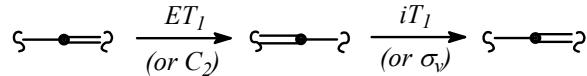
The abovementioned properties of archetype series suggest that it is possible to describe the topology of π -conjugated systems in group theoretical terms. This is highly desirable since it could be of use to reveal the origin of some π -topological features that could not be explained with the archetypal analysis. For example, the emergence of cross-conjugated pathways in some, but not all, structures is still not fully understood. These pathways can emerge after the permutation of all bonds from single to double and *vice versa*, along a conjugated pathway between two terminals. In Chapter 3 of this thesis, this permutation of bonds was called operation (i) of the topological design program.

In this chapter the following question is tackled: What is the symmetry relation between the members of archetype series and what can we learn from this with respect to the topological properties of n-terminal π -conjugated systems? To determine how many essentially different ways there are to convert one archetype into another archetype, one can use a case-by-case determination of the conjugated pathways between the terminals. However, the formulation of groups will provide for a more systematic and general method. First, the group theoretical approach for the analysis of the symmetry properties of n-terminal systems is outlined. It provides the basis for understanding the topological properties of n-terminal π -conjugated systems. Subsequently, the symmetry properties of the series of structures (the archetype series) that represent an n-terminal π -conjugated system will be considered. Here, the formulation of the groups is based on topological operations and not on symmetry operations. At the end of this chapter, the beauty and the power of the presented group theoretical approach becomes evident when it is shown that it accounts for the π -topological properties of the different classes of n-terminal π -conjugated systems. The advantage of this group theoretical approach is that it suffices, no matter the complexity of the π -topology of n-terminal π -conjugated systems.

5.2 The Symmetry Properties of n-Terminal Systems

As an extension of the archetypal analysis presented in Chapter 2, the characteristics of the standard archetype series are now viewed in the context of group theory using symmetry operations. This is a general (abstract) approach to express the symmetry properties of n-terminal systems.

In order to classify the symmetries of the propagation (or translation) of alternant and non-alternant bond sequences along a path between two terminals of n-terminal systems, group theory can be helpful. The symmetry operators for such a system are the sets $\{ET_m\}$ and $\{iT_m\}$. Here, E is the identity, i is the inversion, and T_m is the translation operator over m positions. Because there are only translations of bonds over two specific positions (terminals) in the standard archetypes, the



Scheme 5.1 Schematic illustration of the effect of the symmetry operations ET_1 and iT_1 on an alternant 2-terminal system (with periodic boundary conditions).

translations are limited to T_0 and T_1 (i.e., $m = 0$ denotes the same position and $m = 1$ stands for the adjacent position). The sets $\{ET_m\}$ and $\{iT_m\}$ reduce to four elements ET_0 , ET_1 , iT_0 , and iT_1 .^[10] These symmetry elements form the subgroup $\mathbf{G}^{2(xy)}$, where x and y are the positions of the terminals.

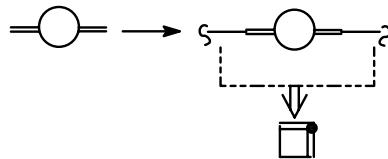
The effect of the elements (ET_1) and (iT_1) on a 2-terminal system is illustrated in Scheme 5.1. The inversion of a translation over one position (iT_1) counteracts the effect of the translation operator over one position (ET_1). The corresponding transformation matrices of the elements are obtained by letting the elements of the subgroup operate on the symmetry of the 2-terminal system. As can be seen from Table 5.1, this gives the two-dimensional reducible representation Γ . In principle, this group theoretical description accounts for the transport properties of 2-terminal systems with alternating and non-alternating bond sequences. An overview of all possible sequences is given in the right column of Table 5.1. These objects form a basis for the reducible representation. The subgroup $\mathbf{G}^{2(xy)}$ can be reduced to form a group with two irreducible representations Γ_1 and Γ_2 . The characters of these irreducible representations are worked out in Table 5.2. The irreducible representations Γ_1 and Γ_2 have different parities. They have either an even (Γ_1) or odd number (Γ_2) of single or double bonds. The subgroup $\mathbf{G}^{2(xy)}$ has a one-to-one correspondence with the point group \mathbf{C}_{2v} (see the Schoenflies symbol in the lower left corner of the table).

Table 5.1 The character table of the reducible representation Γ of the group $\mathbf{G}^{2(xy)}$. The 2-terminal systems depicted at the right form the basis of Γ .

$\mathbf{G}^{2(xy)}$	ET_0	ET_1	iT_0	iT_1	
Γ	2	0	2	0	$\text{S}=\text{S}$, $\text{S}=\text{S}$, $\text{S}-\text{S}$, $\text{S}-\text{S}$

Table 5.2 The $\mathbf{G}^{2(xy)}$ character table of irreducible representations Γ_1 and Γ_2 .

$\mathbf{G}^{2(xy)}$	ET_0	ET_1	iT_0	iT_1		
Γ_1	1	1	1	1	A_1	$\text{S}-\text{S}$, $\text{S}=\text{S}$
Γ_2	1	-1	1	-1	B_1	$\text{S}-\text{S}$, $\text{S}=\text{S}$
	E	C_2	σ_h	σ_v	\mathbf{C}_{2v}	



Scheme 5.2 The functional space is expanded by extending the terminals of a 2-terminal archetype with alternating bonds and upon introducing periodic boundary conditions. The abstract object depicted at the bottom forms the basis of one of the representations of the $\mathbf{G}^{4(xy)}$ group.

Now a problem arises. The symmetry operations of the subgroup $\mathbf{G}^{2(xy)}$ describe the bond reversal (from single to double and *vice versa*) originating from the passage of a soliton between the two terminals of an archetype with an alternating bond pattern (Γ_2 , B_1). However, the operations do not describe the change of the bonding pattern which should occur upon soliton passage through an archetype with two non-alternant terminals (Γ_1 , A_1). As a result, the basis sets of the irreducible representations ($=\bullet=$, $-\bullet-$, $-\bullet=$, $=\bullet-$) poses a rather severe restriction on the description of 2-terminal archetypes. It precludes the soliton propagation through archetypes that have a non-alternating bonding pattern for the terminals. In fact, this restriction finds its origin in the finite size of the system: it is the limited functional space which creates artificial restrictions. This problem can be dealt with by expanding the functional space by adding extra bonds to the terminals of the archetypes in such a way that the extended terminals show bond alternation ($=-\bullet=-$, $=-\bullet-=$, $=-\bullet-=$) and, in addition, by applying periodic boundary conditions for all 2-terminal archetypes. This is outlined in Scheme 5.2 for an example 2-terminal archetype with a non-alternating bonding pattern for the terminals.

The extended 2-terminal systems with periodic boundary conditions transform according to the elements of subgroup $\mathbf{G}^{4(xy)}$. This subgroup has a one-to-one correspondence with the point group \mathbf{C}_{4v} . The characters of the reducible representation Γ are given in Table 5.3. This subgroup can be reduced to a subgroup with three irreducible representations Γ_1 , Γ_2 and Γ_3 (see Table 5.4).

Table 5.3 The character table of the reducible representation Γ of the group $\mathbf{G}^{4(xy)}$.

$\mathbf{G}^{4(xy)}$	ET_0	ET_1, ET_3	ET_2	iT_0, iT_2	iT_1, iT_3	
Γ	4	0	0	2	0	All extended 2-terminal archetypes
	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$	\mathbf{C}_{4v}

Table 5.4 The $\mathbf{G}^{4(xy)}$ character table representing the extended 2-terminal archetypes (with periodic boundary conditions, see Scheme 5.2). The group represents the alternant and non-alternant bonding patterns for the terminals depicted in the right column.

$\mathbf{G}^{4(xy)}$	ET ₀	ET _{1,ET₃}	ET ₂	iT _{0,iT₂}	iT _{1,iT₃}		
Γ_1	1	1	1	1	1	A ₁	
Γ_2	1	-1	1	1	-1	B ₁	
Γ_3	2	0	-2	0	0	E	
	E	2C ₄	C ₂	2σ _v	2σ _d	C_{4v}	

We have now explored the group theoretical aspects of soliton transport between two terminals of archetypal representations of more complex (omni)conjugated organic molecules. In the following, the overall symmetry properties of the members of n-terminal archetype series will be considered.

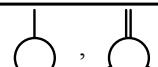
The full symmetry group of an n-terminal archetype series is a rotational group \mathbf{G}^n . The symmetry operators are formed by the sets $\{ER_n\}$ and $\{iR_n\}$, where R_n is the rotation operator over n terminals. Consider, for example, a 3-terminal system. The archetypes of this system are subject to the transformation properties of the rotational group \mathbf{G}^3 . By letting the elements of the group \mathbf{G}^3 operate on the symmetry of the system it is possible to find the transformation matrices of these elements. The different archetypes of the 3-terminal system form the basis for the three-dimensional reducible representation Γ (see Table 5.5).

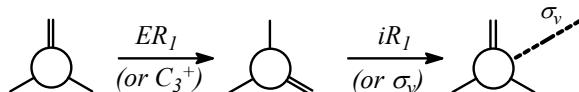
The reducible representation Γ can be reduced to a one-dimensional representation (Γ_1) and one two-dimensional representation (Γ_2). The characters of the two irreducible representations are worked out in Table 5.6. The same technique as that illustrated in the 2-terminal system is applied to establish the characters of the two irreducible representations. The characters of Γ_1 and Γ_2 match the characters of the representations A_1 and E , respectively. The group \mathbf{G}^3 has a one-to-one correspondence with the point group \mathbf{C}_{3v} . Scheme 5.3 illustrates the correspondence between symmetry elements of the rotational group \mathbf{G}^3 and the point group \mathbf{C}_{3v} . With the above, the transformation properties of the individual members of the

Table 5.5 The reducible representation Γ of the group \mathbf{G}^3 for 3-terminal archetype series. The elements of the corresponding C_{3v} point group are given as well.

\mathbf{G}^3	ER ₀	ER _{1,ER₂}	iR _{0,iR_{1,iR₂}}		
Γ	3	0	1	All 3-terminal archetypes	
	E	2C ₃	3σ _v	C_{3v}	

Table 5.6 The \mathbf{G}^3 character table for the irreducible representations and the members of the 3-terminal archetype series which form the basis of the representations.

\mathbf{G}^3	ER ₀	ER _{1,ER₂}	iR _{0,iR_{1,iR₂}}		
Γ_1	1	1	1	A ₁	
Γ_2	2	-1	0	E	
	E	2C ₃	3σ _v	C _{3v}	



Scheme 5.3 Illustration of the effect of the rotation operator over one position (ER_I) and the inversion (i.e., anti-clockwise instead of clockwise) of the rotation operator over one position (iR_I). The corresponding operations of the C_{3v} point group are given in parentheses.

archetype series of a 3-terminal system have been established. This procedure can be easily extended to a system with four terminals.

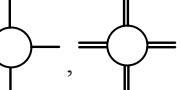
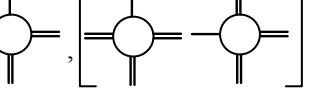
As a next case the transformation properties of the rotational group \mathbf{G}^4 is considered. The 4-terminal archetype series form the basis for the reducible representation Γ (see Table 5.7). In this case, the representation Γ can be reduced to two one-dimensional representations (Γ_1 and Γ_2) and one two-dimensional representation (Γ_3). The characters of the group \mathbf{G}^4 are collected in Table 5.8. All even and odd archetypes of the 4-terminal system transform according to the \mathbf{G}^4 group.

It should be obvious that it is possible to extend this treatment to any n-terminal system. This group theoretical way of describing n-terminal archetype series forms the basis for the topological analysis of n-terminal π -conjugated systems, discussed

Table 5.7 The reducible representation Γ of the rotational group \mathbf{G}^4 representing a 4-terminal system. The elements of the corresponding C_{4v} point group are given as well.

\mathbf{G}^4	ER ₀	ER _{1,ER₃}	ER ₂	iR _{0,iR₂}	iR _{1,iR₃}	
Γ	4	0	0	2	0	All 4-terminal archetypes
	E	2C ₄	C ₂	2σ _v	2σ _d	C _{4v}

Table 5.8 The \mathbf{G}^4 character table of the irreducible representations and the members of the 4-terminal archetype series which form the basis of the representations.

\mathbf{G}^4	ER ₀	ER _{1,ER₃}	ER ₂	iR _{0,iR₂}	iR _{1,iR₃}		
Γ_1	1	1	1	1	1	A ₁	
Γ_2	1	-1	1	1	-1	B ₁	
Γ_3	2	0	-2	0	0	E	
	E	2C ₄	C ₂	2σ _v	2σ _d	C _{4v}	

in the remainder of this chapter. This description allows us to subject the propagation of quasi-particles between two terminals to the transformation properties of the group $\mathbf{G}^{4(xy)}$. The positions x and y denote the terminals A, B, C, etc. of such a system and can be classified accordingly. The rotational group \mathbf{G}^n could be used to study the correlation between the members of the archetype series, based on the symmetry characteristics of the n-terminal system.

5.3 The Construction of a Group based on π -Topology

Having assessed the correlation between standard archetypes using symmetry considerations, it is possible to translate this into a formulation based on the topological operations. First we shall discuss what kind of groups can be obtained based on the topology of the terminals of standard archetypes. It is natural to consider the topology of the terminals since this is what all archetypes (i.e., standard archetypes and the corresponding molecular archetypes) have in common. These groups will be used in a later stage to discuss the π -topological properties of n-terminal π -conjugated systems.

A first step towards the formulation of a group is defining a set of elements that are related according to some rules. Just as symmetry operations can transform an archetype into another archetype, the same is true for operation (i) of the topological design strategy. Operation (i) is defined as changing all bonds from single to double and *vice versa* along a pathway between two terminals (see Section 3.3). Operation (i) has the same impact on the topology of n-terminal systems as the translation operator T_m over two terminals (group $\mathbf{G}^{4(xy)}$). Each archetype is

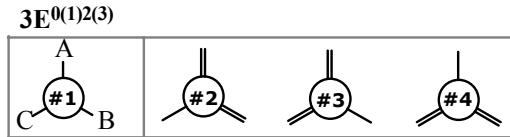


Figure 5.2 Standard archetype series for 3-terminal systems with an even number of double link terminals (Even set). Archetype #1 is the principal archetype of the series.

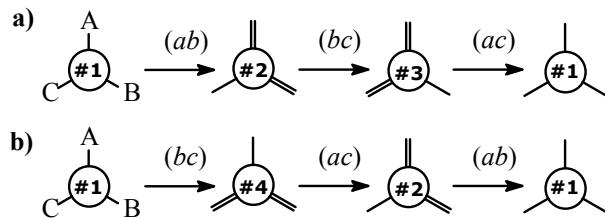
recognized by the topology of the terminals. A change by means of operation (i) immediately results in a different archetype. Operation (i) is a topological tool to transform archetypes. In other words, the archetypes of a series are related to one another through operation (i).

The elements of the group are all possible ways to perform operation (i) on the members of an archetype series. The set of operations can be deduced from the viewpoint of the first archetype of the series (see Figure 5.2).^{*} For example, archetype #1 is converted into archetype #2 by changing the bonds between terminal A and B. This is called operation (*ab*) of the group. The other operations of the group then become: operation (*ac*) between terminal A and C (towards #3) and operation (*bc*) between terminal B and C (towards #4). The very last operation of the group is the identity operation (*E*), which stands for "the act of doing nothing". The set of operations representing the 3-terminal archetype series that form the group are: $\mathbf{G}^{3A} = \{E, ab, ac, bc\}$. The superscript 'A' in \mathbf{G}^{3A} stands for the set of operations defined from the viewpoint of terminal A of the principal archetype #1.[†] The order of the group is said to be '4' since it contains four operations. There can only be a finite number of operations for each n-terminal archetype series, namely 2^{n-1} (*n* is the number of terminals). This means that the set of operations forms a discrete group.

The general idea is that each n-terminal system gives rise to its own group. The objective is using the correlation between archetypes to develop, in a later stage, a method for elucidating the conjugated pathways within the individual structures of the molecular archetype series. In general, the complete set of topological operations has to satisfy the following four conditions in order to form a group in a mathematical sense.^[11]

* The formulation of groups from the perspective of any other archetype would result in the same discussion.

[†] The main reason to use the index A is to keep the formulation of the operations of the groups clear. A set of operations derived from the perspective of terminal C could involve the same operations, however, described in a different way such as, for example, $\mathbf{G}^{3C} = \{E, ca, cb, ab\}$. This suggests a different group, albeit that the operations and objects (the n-terminal archetypes) are exactly the same.



Scheme 5.4 The sequence of operations (ab) , (ac) , and (bc) results in archetype #1 (Even set) regardless of the order in a) or b). Operation (i) of the group is associative.

1. Closure: $AB \in G$

The product of two operations is also an operation of the set.

2. Identity element: $AE = EA = A$ for all $A \in G$

The identity is an operation, which has no effect on the other operations of the set.

3. Associative law: $A(BC) = (AB)C$ for all $A, B, C \in G$

The outcome of successive operations is the same regardless of the order.

4. Inverse element: $A^{-1} \in G$ such that $A^{-1}A = E$ for all $A \in G$

Every operation must have an inverse, which, when combined with it, produces the identity E .

It is easily recognized that the group $\mathbf{G^{3A}} = \{E, ab, ac, bc\}$ satisfies the first condition. If one takes any pair of operations, for example (ab) and (ac) , this forms another element of the set, in this case (bc) . This is called their product. The other products of this set that are: $(ab)(bc) = (ac)$ and $(ac)(bc) = (ab)$. The products are the same as the individual operations and, with that, the closure condition is satisfied. The second condition is also satisfied with operation (E) since it has no effect on the objects (archetypes) of the group. The sequence of operations outlined in Scheme 5.4 demonstrates that operation (i) is associative (third condition). There is no difference between the outcomes of the permutation of bonds in the order of (ab) , (bc) followed by (ac) , and a randomly chosen other sequence, such as (bc) , then (ac) , followed by (ab) . In both cases, the net result is the principal archetype #1. Thus, the operations of the group are associative and $((ab)(bc))(ac) = ((bc)(ac))(ab)$ holds. The last property common to all groups is that each operation has to have an inverse operation. Here, the reciprocal stands for the hypothetical action of changing the topology of terminals the other way around. The inverse of operation (ab) is the changing the bonds from terminal B to A instead of from terminal A to B (e.g., operation (ba)). There is no difference between the outcome of operation (ab) and its inverse $(ab)^{-1}$. What follows from $(ab) = (ab)^{-1}$ is

Table 5.9 Group multiplication table of the group $\mathbf{G}^{3A} = \{E, ab, ac, bc\}$ representing a 3-terminal archetype series. The labels around the table denote the standard archetypes associated with a certain operation of the group.

		#1	#2	#3	#4
	\mathbf{G}^{3A}	E	ab	ac	bc
#1	E	E	ab	ac	bc
#2	ab	ab	E	bc	ac
#3	ac	ac	bc	E	ab
#4	bc	bc	ac	ab	E

that $(ab)(ab)^{-1} = E = (ab)(ab)$. Therefore, the elements of this group are called "self-inverse".

With the above, it was shown that the elements based on operation (i) meet the conditions to form a group in a mathematical sense. Therefore, it is possible to use group theory to study the topological properties of n-terminal systems in terms of operation (i). A special kind of group is a group for which the commutative law holds. This can be an additional property to the aforementioned four conditions to form a group. The operations of a group are commutative when $AB = BA$ for all $A, B \in G$.^[12] For the group described here it is found that a pair of operations performed in either way results in the same outcome. Hence, the operations commute. Groups of this kind are called abelian, named after the 19th century mathematician Niels Hendrik Abel.^[11]

For any group, one can set up a multiplication table that tabulates the complete set of products of the elements of the group. The group $\mathbf{G}^{3A} = \{E, ab, ac, bc\}$ has $4^2 = 16$ products (i.e., the square of the order), which are given in Table 5.9. The construction of the table for groups of this kind is rather straightforward because the outcome of two consecutive operations is the net result of a simple multiplication. For example, the third entry of the second row of Table 5.9 is obtained from $(ab) \otimes (ac) = (bc)$. Without proof, one can see that every row and column contains every operation exactly once, that no row or column is identical, and that the diagonals consist of the same element (either (E) or (bc)). The high symmetry of the table with respect to the diagonal is in line with the characteristics of abelian groups (i.e., $AB = BA$ for all products).

The labels of the archetypes are, for convenience, given above the first row and to the left from the first column of the multiplication table (see Table 5.9). The archetypes are *not* the elements of the group or are part of the table. It is only a way to associate the archetypes to the elements of the group. This labeling is used to ease the search for correlations between the archetypes. The entries of the table represent how to transform one archetype into another by means of operation (i).

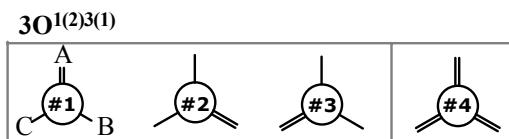


Figure 5.3 Standard archetype series for 3-terminal systems with an odd number of double link terminals (Odd set).

For example, operation (i) has to be applied to terminal B and C (i.e., operation (*bc*)) to convert archetype #2 into archetype #3. This transformation is also depicted in Scheme 5.4a for an archetype with an even number of double link terminals (Even set). However, the multiplication table reveals the correlation between the archetypes of the Odd set as well (Figure 5.3). Obviously, it does not matter whether the operations are performed on an Even or an Odd set of archetypes, the multiplication table is exactly same. This is certainly an advantage, because there is no need to construct a new multiplication table for every other archetype series.^[13]

At this point it is possible to analyze the properties of the topological groups in terms of *n*-terminal π -conjugated systems. However, the multiplication tables and the method to analyze the structures are quite general. Therefore, we will first define the group for a higher order *n*-terminal archetype series and, subsequently, discuss the implementation for *n*-terminal π -conjugated systems. Especially when it comes to the properties of conjugated systems with more than three terminals, or a more complex π -topology, the group theoretical analysis proves to be very useful.

5.4 The Basis for Understanding π -Topological Properties

The fact that a group multiplication table reveals the correlation between standard archetypes is the most important feature when it comes to molecular archetype series. The tables contain additional information and play a key role in elucidating the π -topological properties of π -conjugated systems. This is illustrated here for the molecular archetype series of 4-terminal omniconjugated systems. Omniconjugated systems have linear conjugated pathways between all terminals and have the highest degree of π -conjugation (see Section 2.4). Let us consider a Type A and a Type B omniconjugated system, models **5.2** and **5.3**, respectively (see Figure 5.4). Type A systems are derived from key-model **A**. On the other hand, Type B systems are defined as systems that are *only* derivable from key-model **B**. The motivation to discuss Type A and B systems comes from their π -topological properties. The origin of their distinct different behavior with respect to operation (i) was not fully elucidated in Chapter 3. Now it is possible to fully understand the π -topological properties, in the broad sense of all *n*-terminal π -conjugated systems.

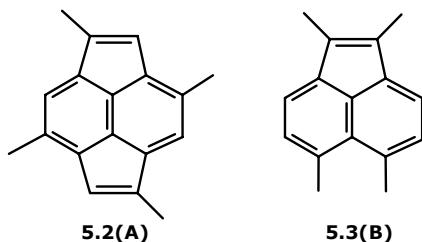


Figure 5.4 Examples of 4-terminal omniconjugated systems: tetrasubstituted derivatives of pyracylene **5.2** and acenaphthylene **5.3**. They are either obtained from key-model **A** or **B** (in parentheses) of the topological design program.

Before discussing the molecular archetype series, it is necessary to define the appropriate set of operations of the group representing the archetype series of the 4-terminal omniconjugated systems **5.2** and **5.3**. As with the 3-terminal archetype series, the operations can be deduced from the viewpoint of the principal archetype #1 of the Even set (see Figure 5.5a). This **G^{4A}** group contains eight elements because the order of this 4-terminal ($n = 4$) group is $2^{(n-1)} = 8$. At this point it becomes necessary to introduce a new operation to be able to account for the relation between archetype #1 and archetype #8. Archetype #8 is the only member of the series with two pairs of double link terminals. Therefore, it can only be obtained from #1 after two consecutive operations. There are several combinations of operation (i) for the permutation of *all* terminals. These combination include (ab) and (cd), (ac) and (bd), and finally, (ad) and (bc). The net result is called the joint operation '(abcd)', which is written of as 'J' instead of '(abcd)' for convenience. Roughly speaking, operation (J) complements the identity (E) in the sense that it stands for "doing all that is possible" instead of "doing nothing". With the

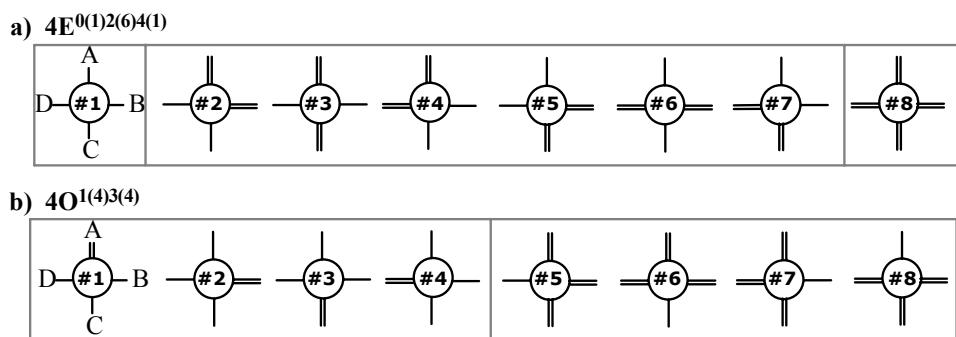


Figure 5.5 The standard archetype series of 4-terminal systems with a) an even number of double link terminals or in b) an odd number of double link terminals.

Table 5.10 The group multiplication table of the group $\mathbf{G}^{4A} = \{E, ab, ac, ad, bc, bd, cd\}$ representing a 4-terminal archetype series (Even and Odd set). The labels around the table denote the standard archetypes associated with a certain operation of the group.

	#1	#2	#3	#4	#5	#6	#7	#8
\mathbf{G}^{4A}	<i>E</i>	<i>ab</i>	<i>ac</i>	<i>ad</i>	<i>bc</i>	<i>bd</i>	<i>cd</i>	$J^{(l)}$
#1	<i>E</i>	E	ab	ac	ad	bc	bd	cd
#2	<i>ab</i>	ab	E	bc	bd	ac	ad	J
#3	<i>ac</i>	ac	bc	E	cd	ab	J	ad
#4	<i>ad</i>	ad	bd	cd	E	J	ab	ac
#5	<i>bc</i>	bc	ac	ab	J	E	cd	bd
#6	<i>bd</i>	bd	ad	J	ab	cd	E	bc
#7	<i>cd</i>	cd	J	ad	ac	bd	bc	E
#8	<i>J</i>	J	cd	bd	bc	ad	ac	ab

^(l) $J = abcd$

introduction of this new operation, the complete set of operations representing the 4-terminal archetype series becomes $\mathbf{G}^{4A} = \{E, ab, ac, ad, bc, bd, cd, J\}$. The corresponding group multiplication table is given in Table 5.10. For the products that come with operation (J) it is necessary to take into account the specification (abcd) of this operation. This means that the entry of the second row (i.e., '#2') in the last column (i.e., '#8') results from $(J) \otimes (ab) = (abcd) \otimes (ac) = (bd)$. The \mathbf{G}^{4A} multiplication table of the Odd set of 4-terminal archetype series is exactly the same. The objects of the Odd set are outlined in Figure 5.5b.

The standard archetypes only differ in the number of double link terminals and the position of these terminals. The archetype series of an n-terminal π -conjugated system can consist of many more degenerate archetypes. This is nicely illustrated with the collection of structures representing the tetra-substituted pyracylene derivative **5.2** (see Figure 5.6). It certainly is an archetype series consisting of a relatively large number of structures. This is because some have their own specific arrangement of double bonds *inside* the building block (see, for example, **5.2**#1a-d). Thus, molecular archetypes with identical terminals can be degenerate. Any organic chemist recognizes these simply as resonance structures. For the sake of brevity, the aspect of degenerate molecular archetypes was not considered until now.[‡] This particular archetype series is used here to emphasize the versatility of the group theoretical approach.

[‡] In Chapter 3 of this thesis, some of the archetypes of **5.2** were already found by means of operation (i) or Step 3 of the topological design program (see Scheme 3.6 and Scheme 3.2).

One of the most important features of the group multiplication table is that it tabulates how one can convert one double bond configuration into another one upon executing operation (i). A simple example is the transformation of structure **5.2#3** into **5.2#4**. The correlation of these two archetypes is given by the product of their *associated* operations as given in Table 5.10. Structure **5.2#3** can be converted into **5.2#4** upon executing operation (i) on the pathway between terminal C and D (i.e., operation (cd), see the table). This pathway can be found along the central bond of the two benzene rings of the pyracylene system (marked red in structures **5.2#3** and **5.2#4** in Figure 5.6). By means of the multiplication table, it is easy to find the correlation between any pair of archetypes *without* the need to “search” for the required conjugated pathways.

A word comes with the interpretation of operation (J). The joint operation (J) represents two consecutive executions of operation (i). It denotes an *indirect* correlation between two archetypes. There is always a third archetype involved that serves as an intermediate state for the two operations that come with (J). For example, archetype **5.2#4** can be used as intermediate to convert archetype **5.2#3** into **5.2#6** via operation (cd) and (ab) (see Table 5.10).[§]

The molecular archetype series of structure **5.2** form a group under “operation (i)” as operation. From its group multiplication table it follows that operation (i) is associative, commutative, and self-inverse. However, a word of warning comes with degenerate archetypes because they seem to contradict this conjecture. Although degenerate archetypes have the same correlations within the group, the execution of operation (i) between the same pair of terminals may give rise to different structures. This is due to the various double bond configurations that are available within the perimeter of the degenerate structures. Consider the archetypes **5.2#1a** and **5.2#1b** in Figure 5.6. These molecules are resonance structures because they have the same kind of terminals (same in the sense of being single or double link). They are only degenerate by conjugated pathway(s). The conjugated pathway between terminal A and B differs in length. It consists of two and four double bonds in, respectively, **5.2#1a** and **5.2#1b**.

A molecular archetype can also have more than one conjugated pathway between the same pair of terminals. An example is molecular archetype **5.2#1d**. The alternating pathway between terminal A and B is either found for bonds *along* or *within* the perimeter of **5.2#1d**. Both pathways can be used for transformations, and they lead to the *same* molecular archetype **5.2#7**, but to the other degenerate form of it (in this case, “along” results in **5.2#7a** and “within” gives **5.2#7b**). Hence, the group theoretical approach automatically accounts for topological properties of

[§] There are many other ways to realize the joint operation ‘abcd’ for this transformation such as, for example, (ad) and (bc) via archetype #7, or (bc) and (ad) via #2.

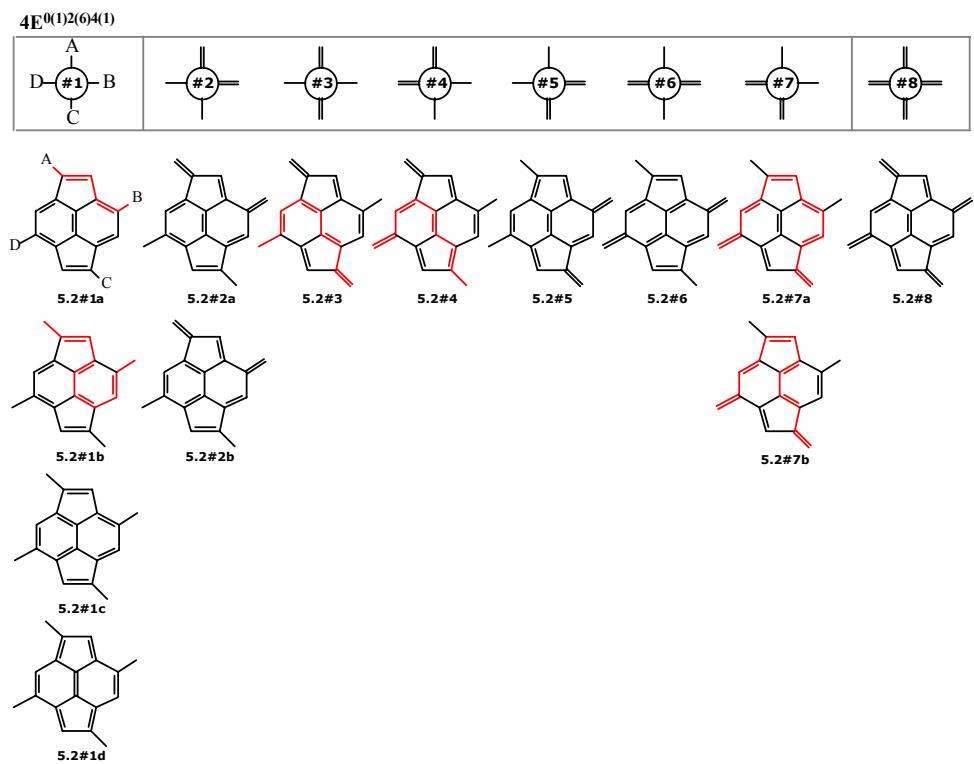


Figure 5.6 (Top) Standard 4-terminal archetype series (Even set). (Bottom) Corresponding molecular archetypes of structure **5.2**. The degenerate archetypes are displayed in the same column. The marked pathways are discussed in the text.

resonance structures. This is crucial as it means that the possibility for a real chemical structure to have various resonance forms does not influence the outcome of operations (i) when it comes to transformation between molecular archetypes. This is in full accord with the chemical meaning of resonance structures!

Let us now turn to Type B omniconjugated system **5.3**. The archetype series of this structure is given in Figure 5.7. Although the molecular architecture of **5.3** is somewhat similar to that of **5.2**, there are various differences in the topological properties of these series. The difference in number of degenerate structures in the respective series is trivial and irrelevant. The most important difference is that the archetype series of **5.3** contains an open shell system (i.e., non-Kekulé structure **5.3#8**). The emergence of non-Kekulé structures has a large impact on properties of the group. This is because the non-Kekulé structure cannot be used as an intermediate state in successive operations (i). For instance, it is not possible to

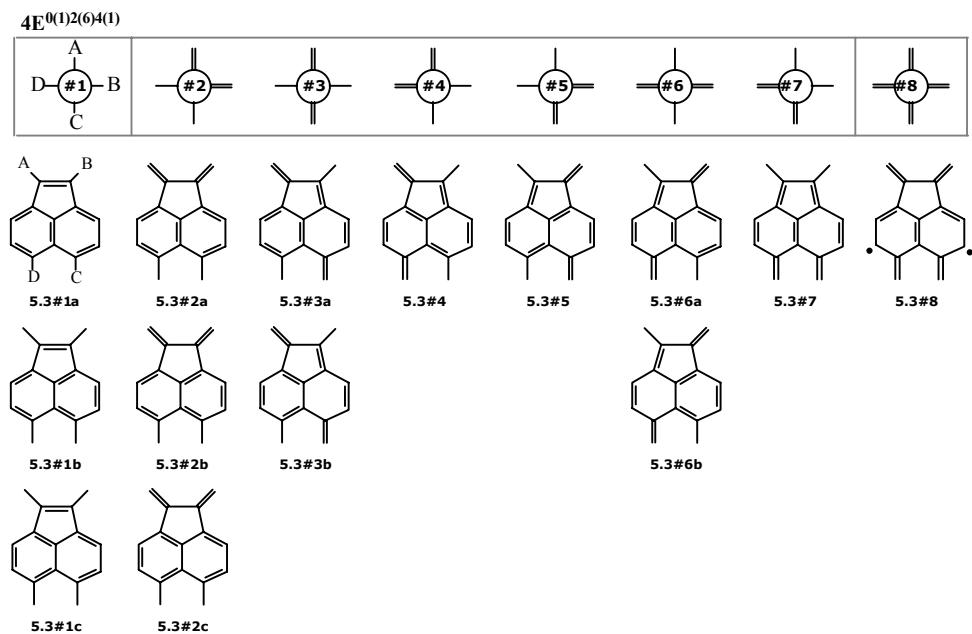


Figure 5.7 (Top) Standard 4-terminal archetype series (Even set). (Bottom) Corresponding molecular archetype series for structure **5.3** with the non-Kekulé structure **5.3#8**. The degenerate archetypes are displayed in the same column. The marked pathways are discussed in the text (see also Table 5.11).

convert archetype **5.3#4** into **5.3#5** by means of first operation (*bc*) on **5.3#4** and, subsequently, operation (*ad*) on **5.3#8** (see also Table 5.11 for this relation). In both cases the involved pathways are not linear conjugated (see Figure 5.7), making it impossible to perform operation (i). Hence, operation (*bc*) and (*ad*) of the group representing structure **5.3** cannot be performed on all archetypes. This is true for all products in the multiplication table that come with operation (*J*). The rows and columns of operation (*J*) are highlighted in the group multiplication table of structure **5.3**.

With the operations involving the non-Kekulé structure identified, it is straightforward to show that the remaining operations of this table do not meet the conditions to form a group. Starting with archetype **5.3#4**, it is not possible to perform operation (i) in the sequence (*bc*), (*ad*), and (*ac*). This would involve the non-Kekulé structure **5.3#8**. A different order of the same operations, for example (*ad*), (*bc*), followed by (*ac*), can transform **5.3#4** into another archetype of the series (i.e., **5.3#5**, see Table 5.11). Thus, the order of operations *does* matter: $((bc)(ad))(ac) \neq ((ad)(bc))(ac)$. Hence, the set of operations representing this Type B omniconjugated system does not meet the associative law (i.e.,

Table 5.11 The group multiplication table for the G^{4A} group representing the 4-terminal archetype series of the Type B omniconjugated system 5.3 (see Figure 5.7). The highlighted entries are associated with the non-Kekulé structure 5.3#8.

	#1	#2	#3	#4	#5	#6	#7	#8
G^{4A}	E	ab	ac	ad	bc	bd	cd	$J^{(l)}$
#1	E	E	ab	ac	ad	bc	bd	cd
#2	ab	ab	E	bc	bd	ac	ad	J
#3	ac	ac	bc	E	cd	ab	J	ad
#4	ad	ad	bd	cd	E	J	ab	bc
#5	bc	bc	ac	ab	J	E	cd	bd
#6	bd	bd	ad	J	ab	cd	E	bc
#7	cd	cd	J	ad	ac	bd	bc	ad
#8	J	J	cd	bd	bc	ad	ac	ab

^(l) $J = abcd$

$A(BC) = (AB)C$ for all $A, B, C \in G$. This constitutes the mathematical basis for the different π -topological properties found for Type A and Type B omniconjugated systems. The Type A omniconjugated systems have a set of operations that do form a group in the mathematical sense.** This is because they are conjugated in all double bond configurations and have no non-Kekulé structures in their archetype series. On the other hand, the set of operations that represents Type B omniconjugated systems ($n > 3$) does not form a group. The Type B systems are not fully conjugated in all double bond configurations. The latter is found for all n -terminal π -conjugated systems that have non-Kekulé structures in their archetype series. Hence, *only* Type A omniconjugated systems have a set of operations that form a group in the sense of group theory, and it is of the abelian type.

5.5 Mathematical Basis for the Design of π -Logic

The entries of the group multiplication table specify the pathways that can be used to convert an archetype by executing operation (i). A different way to interpret this is that every row or column contains the list of conjugated pathways within the corresponding structure of the archetype series. Here we arrive at the key point of the group theoretical approach because it can fully describe all π -topological

** The same holds for 3-terminal Type B omniconjugated and normal (2-terminal) conjugated systems (see also Table 3.1).

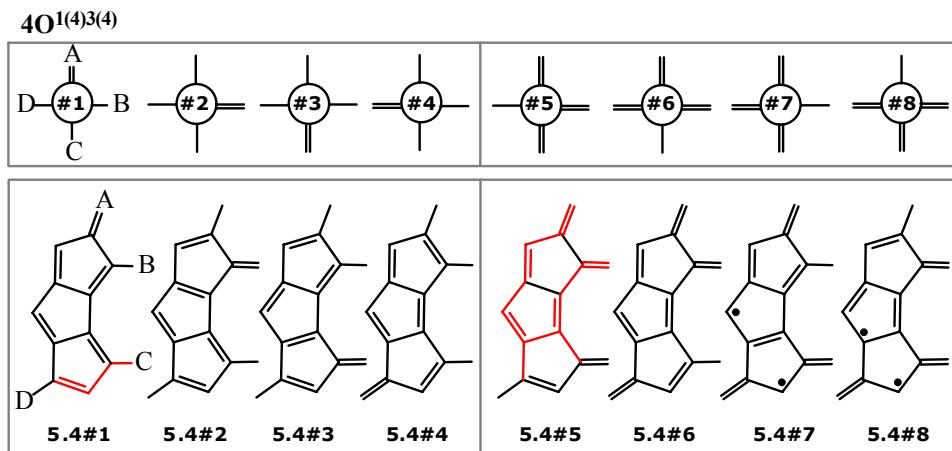


Figure 5.8 (Top) Standard 4-terminal archetype series for systems with an odd number of double bond terminals (Odd set). (Bottom) The corresponding molecular archetype series of a cross-conjugated system with two non-Kekulé structures. Archetype **5.4#1** has one cross-conjugated pathway ($C \times D$) while **5.4#5** has two: ($A \times D$) and ($B \times D$).

properties in a mathematical way: the group multiplication table reveals all (potential) cross-conjugated pathways within the π -conjugated system.

Consider, for example, the archetype series of the 4-terminal system **5.4** given in Figure 5.8. This archetype series contains two non-Kekulé structures. The rows and columns that are associated with non-Kekulé archetypes #7 and #8 are highlighted in Table 5.12. The strength of the group theoretical approach is that one can directly determine from the group multiplication table which pathways are cross-conjugated. The highlighted operation (cd) of the first row has a one-to-one correlation with the cross-conjugated pathway between terminal C and D ($C \times D$) in archetype **5.4#1**. To guide the eye, this pathway is marked by the red bonds in Figure 5.8, up to the cross-conjugated point, where the alternation of single and double bonds is interrupted by two consecutive single bonds. All the highlighted entries, but (J), represent a cross-conjugated pathway. This is a simple and very useful result of the group theoretical approach that is applicable to all classes of n-terminal π -conjugation. It makes the elucidation of the topology of all individual pathways within every structure of the series superfluous.

The structures given in Figure 5.8 are all classified as cross-conjugated (subgroup $(2\times)$) because this archetype series contains two non-Kekulé structures

Table 5.12 Group multiplication table for the G^{4A} group of the 4-terminal archetype series of the cross-conjugated system 5.4 (subgroup $(2\times)$, see Figure 5.8). The highlighted entries are associated with the two non-Kekulé structures of this series.

	#1	#2	#3	#4	#5	#6	#7	#8
G^{4A}	E	ab	ac	ad	bc	bd	cd	$J^{(I)}$
#1	E	E	ab	ac	ad	bc	bd	cd
#2	ab	ab	E	bc	bd	ac	ad	J
#3	ac	ac	bc	E	cd	ab	J	ad
#4	ad	ad	bd	cd	E	J	ab	bc
#5	bc	bc	ac	ab	J	E	cd	bd
#6	bd	bd	ad	J	ab	cd	E	bc
#7	cd	cd	J	ad	ac	bd	bc	E
#8	J	J	cd	bd	bc	ad	ac	ab

^(I) $J = abcd$

(see also Chapter 2 of this thesis).^{††} However, this does not mean that all structures of this series have two cross-conjugated pathways. This can be understood as follows: operation (J) is the only operation of the group that does not encounter a cross-conjugated situation. The joint operation (J) is the net result of the following complementary pairs of operations: (ab) and (cd), (ac) and (bd), or, (ad) and (bc). This implies that (J) only relates to a cross-conjugated situation when all the pathways between the terminals are cross-conjugated. (This would be the only way to not be able to execute operation (J).) This is clearly not the case, as can be seen upon examination of the structures outlined in Figure 5.8. Due to operation (J) in the highlighted columns of the table, the number of cross-conjugated pathways differs for the members of the same archetype series. For example, some archetypes, like **5.4#1**, have one cross-conjugated pathway while others, like **5.4#5**, have two (see Table 5.12 and Figure 5.8).

Hence, this property of (J) explains why the number of cross-conjugated pathways is not always identical to the number of non-Kekulé structures. All structures of 4-terminal archetype series with archetype #8 as non-Kekulé member (i.e., having (J) in the highlighted columns) have one cross-conjugated pathway less compared to the number of non-Kekulé structures. This aspect was not fully established during the classification of n-terminal π -conjugated systems (see section 2.4).

^{††} The terminals of this model only differ in one position compared with the Type A and Type B omniconjugated analogues displayed in Figure 3.6. This shows that minor topological differences can have a large impact on the π -topological properties.

There is another remarkable feature that comes with operation (J). In the case of archetype **5.3#1** of the acenaphthylene derivative **5.3** (see Figure 5.7) operation (J) is the only highlighted entry in the first row of the multiplication table (see Table 5.11 in the previous section). It follows that archetype **5.3#1** does not have a cross-conjugated pathway (i.e., it is omniconjugated). To be more precise, it is the *only* omniconjugated structure of this series. In other words, operation (J) “identifies” the omniconjugated structure within the archetype series.^{‡‡} This surely is a special situation and is only found for Type B omniconjugated systems. This is why *only* the structures from the series of an n-terminal system that is classified as Type B omniconjugated *may or may not* create cross-conjugated pathways upon executing operation (i).

The group multiplication table cannot be used to distinguish between cross-conjugated and looped^{§§} pathways. Consider for example archetype **5.4#1** and **5.4#2**. A close look at the structural formula of the archetypes tells us that the corresponding operation (i) pathway is cross-conjugated ($C \times D$) in **5.4#1** and looped ($C \circ D$) in **5.4#2**. Obviously, the actual meaning of the marked entries of the multiplication table is that these pathways are simply not linear conjugated. Hence, the group theoretical approach does not indicate any special significance to looped pathways. The same is true for the archetypal analysis, given that archetype series of looped systems (i.e., quasi-omniconjugated) have the same overall characteristics as the series of cross-conjugated systems (see also section 3.5). From the physical viewpoint, it is unclear whether or not looped and cross-conjugated pathways can be experimentally distinguished, for example, in charge transmission properties. Up until now, the only argument to distinguish them has been based on the π -topology: in looped pathways, bonds have to be used twice in order to draw the alternating pathway.

One final interesting application of the group theoretical approach can be usefully introduced at this point. The looped and cross-conjugated pathways can be considered as “closed” in the sense that they do not allow for executing operation (i). The opposite is true for linear conjugated pathways (i.e., they are “open”). In this way, we define a switching mechanism for molecular switches, based on the π -topology of the pathways. From that point of view, every structure of the archetype series represents a different state of the switch. Each state has its own specific set of open/conjugated and closed/cross-conjugated pathways. The group

^{‡‡} Type B omniconjugated systems with $n > 4$ can have more than one omniconjugated structures in their archetype series. As with the 4-terminal systems, the omniconjugated structures of the series are found for the archetypes that have joint operations only as highlighted entries in the group multiplication table (see Appendix A and Appendix B).

^{§§} Looped pathways contain at least one link that has to be used twice in order to find the alternating pathway between two terminals (see Section 3.3.3).

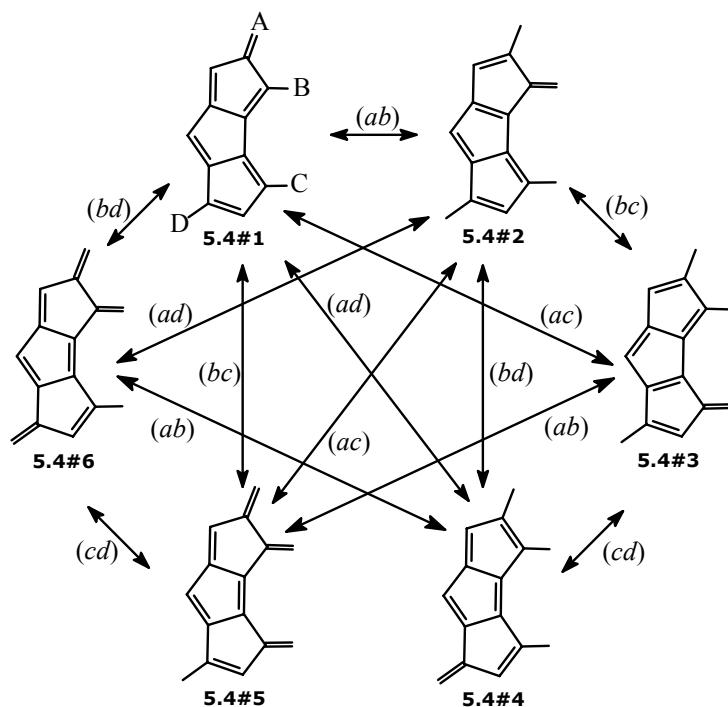


Figure 5.9 The six possible structures ("states") of the cross-conjugated system **5.4**. All structures are accessible via operation (i) as indicated by the arrows. This diagram outlines all linear conjugated pathways of the group multiplication table (Table 5.12).

multiplication table reveals which pathways become cross-conjugated upon executing operation (i) and addressing a different state. Therefore, it is possible to predict the outcome of successive switching events. Hence, it allows for the design of logic, embedded in an n-terminal π -conjugated system.

Figure 5.9 shows all the available structures ("states") of **5.4**. The arrows denote the required operation (i) to convert a certain structure. The collection of arrows represents all available linear conjugated pathways (i.e., the entries that are not highlighted in Table 5.12). There are only six out of eight possible states available for this system because the two non-Kekulé structures **5.4#7** and **5.4#8** (see Figure 5.8) cannot be addressed using operation (i). Only the 4-terminal systems without non-Kekulé structures in their archetype series, such as the Type A omniconjugated system **5.2**, have eight states. The design of molecular logic gates based on switching the conjugation of an n-terminal π -conjugated system is presented in Chapter 6.

5.6 Discussion

The *symmetry* properties of n-terminal systems are used as a basis for the formulation of a group theoretical approach to elucidate the *topological* properties of n-terminal π -conjugated systems. However, there are some clear differences between both methods. Firstly, the description of the topology of π -conjugated systems cannot be considered as a real group theoretical analysis. This is because operation (i) changes the topological properties of the conjugated systems. The resulting structure is therefore distinguishable from the original. Formally, this is not allowed in group theory. However, because group theory is systematic, its rules can be applied to elucidate the topological properties of n-terminal π -conjugated systems. Secondly, there is a clear difference in degeneracy of the groups of standard archetypes and the groups of molecular archetypes. For example, the Odd set of a 4-terminal standard archetypes series has two basic forms (i.e., with one or three double link terminals), which are both four-fold degenerate. On the other hand, the structures of conjugated systems *can* be “degenerate by path” when the system has several double bonds configurations for the same set of terminals (i.e., resonance structures). A typical example is archetype **5.3#1**, which is four-fold “degenerate by path” (see Figure 5.6).

It is important to mention that it was Forrest Carter who recognized the possibility of describing conjugated pathways from a group theoretical point of view. In general, the work of Carter comprises rather conceptual ideas for the development of a computer at the molecular scale.^[14] He proposed that a change in bonding pattern at every carbon corresponds to a group operation in the sense that the double bond is rotated by 120 degrees.^[15] The change of the double bond pattern in a cyclic configuration, such as the [3]radialene (see model **3.5**, Figure 3.2), is considered as a group operation with the corresponding point group D_2 . This is the group containing symmetry elements with three perpendicular two-fold axes. In our approach, the symmetry operations are performed between two terminals rather than on a carbon junction. This concept is however related to that of Carter when it comes to the *idea* of using symmetry operations. Up until now, this work of Carter did not initiate a detailed study of the symmetry aspects of n-terminal π -conjugated systems.

The group multiplication table can be considered as a collection of all potential transmission pathways for quasi-particles. These are the linear conjugated pathways. Within our paradigm, they are of prime importance when considering the charge transport properties of π -conjugated systems. The tables can be useful tools in algorithms that model the transport properties. With respect to this, it is good to mention that the group multiplication table can be reduced to a single array of elements such as the one given in Figure 5.10. Here, the column index [] of the array denotes the member of the series. It is rather straightforward to “calculate”

	[1]	[2]	[3]	[4]	[5]	[6]	[7]*	[8]*
E	ab	ac	ad	bc	bd	cd	J	

Figure 5.10 The array of elements representing a reduced version of the G^{4A} group multiplication table given in Table 5.12. The column index [] stands for the archetype number and the asterisks indicate the non-Kekulé structures of the series.

the cross-conjugated pathways of all the structures after specifying the elements that come with the non-Kekulé structures (here [7]* and [8]*). For example, the cross-conjugated pathways for archetype #4 are (see also Table 5.12): $[4] \otimes [7]^* = (ad) \otimes (cd) = (ac)$, and $[4] \otimes [8]^* = (ad) \otimes (J) = (ad) \otimes (abcd) = (bc)$. This procedure is exactly the same as the one used to construct the group multiplication tables.

5.7 Conclusions

The presented group theoretical framework is the key towards understanding the topological properties of n-terminal π -conjugated systems. The archetype series of n-terminal systems were considered as a group under operation (i). Not all n-terminal π -conjugated systems have archetype series that form a group: only those series without non-Kekulé structures do. The formulation of groups under operation (i) gave a *mathematical* basis for the existence of Type A omniconjugated systems. The method accounted for the π -topological properties of resonance structures of a molecular archetype as well. They did not influence the outcome of operations (i). This certainly adds value to the group theoretical approach since it coincides with chemical meaning of resonance structures.

The question remains why certain molecular skeletons, rather than a specific conjugated system, were prone to have non-Kekulé structures (like the ones of Type B systems) while others are not. Because of this, it was still not possible to determine beforehand which archetypes are non-Kekulé structures. This is highly desirable since it would circumvent the enumeration of all archetypes in order to find the non-Kekulé structures. The ideal situation would be to have algebraic topological descriptors, based on the molecular skeleton, which can specify the double bond configuration of the non-Kekulé structure. In combination with the presented group theoretical approach, such topological descriptors would provide for a complete mathematical description of the π -topological properties of n-terminal π -conjugated systems.

The elegant aspect of the presented group theoretical approach is that it provides for a straightforward method to elucidate all cross-conjugated pathways within a conjugated system. The group multiplication tables summarize all available linear conjugated pathways and reveal which pathways are or can become cross-conjugated. The pathways are of prime importance when it comes to the charge transport properties of π -conjugated systems. Therefore, the tables can be of use for

modeling the charge transport properties of n-terminal π -conjugated systems and to predict the topological changes upon the propagation of quasi-particles such as solitons.

A powerful mathematical tool to determine the symmetry and switching properties of n-terminal π -conjugated systems was presented. These properties were completely governed by the π -topology. In this approach, the group multiplication tables outlined the built-in logic of the topology of π -conjugated systems, as it can be used for the design of complex single molecule electronics.

5.8 References and Notes

1. A. Aviram, M. A. Ratner, *Chem. Phys. Lett.* **1974**, 29, 277.
2. The transcript of the talk was first published in the February 1960 issue of *Caltech's Engineering and Science*, Volume XVII, 5, pp. 22. Nowadays, it is available on the web: <http://www.zyvex.com/nanotech/feynman.html>.
3. R. Farchioni, G. Grossi, *Organic Electronic Materials*, Springer-Verlag, Berlin Heidelberg **2001**.
4. M. A. Ratner, J. Jortner, in *Molecular Electronics*, Eds. J. Jortner, M. A. Ratner, IUPAC, Oxford **1997**, pp. 5.
5. J. C. Ellenbogen, J. C. Love, *Proc. IEEE* **2000**, 88, 386.
6. R. M. Metzger, B. Chen, U. Höpfner, M. V. Lakshmikantham, D. Vuillaume, T. Kawai, X. Wu, H. Tachibana, T. V. Hughes, H. Sakurai, J. W. Baldwin, C. Hosch, M. P. Cava, L. Brehmer, G. J. Ashwell, *J. Am. Chem. Soc.* **1997**, 119, 10455.
7. R. M. Metzger, *Chem. Rev.* **2003**, 103, 3803.
8. F. A. Cotton, *Chemical Application of Group Theory*, Wiley, New York **1963**.
9. E. W. Thulstrup, J. Michl, *Elementary Polarization Spectroscopy*, VCH Publishers, New York **1989**.
10. S. Huizinga, J. Kommandeur, H. T. Jonkman, C. Haas, *Phys. Rev. B* **1982**, 25, 1717.
11. P. W. Atkins, R. S Friedman, *Molecular Quantum Mechanics*, 3rd ed., Oxford University Press, Oxford **1997**, Chpt. 5, pp. 122.
12. K. A. Ross, C. R. B. Wright, *Discrete Mathematics*, 5th ed., Pearson Education, New Jersey **2003**, Chpt. 12, pp. 464.
13. The group multiplication tables of higher order n-terminal systems ($n > 4$) have several joint operations depending on the number of terminals involved. See for an example system in Appendix B.
14. F. L. Carter, *Molecular Electronic Devices*, Marcel Dekker, New York **1982**, pp. 51.
15. F. L. Carter, *Physica D* **1984**, 10, 175.

Chapter 6

π -Logic: Topologies for Boolean Functions inside Single π -Conjugated Molecules

Abstract In this chapter, it is shown that, in principle, all 16 fundamental logic operations can be performed by single π -conjugated molecules having two input channels (A and B) and one read-out channel (T). The read-out channel is used to determine whether the combination of the status of the A channel and the status of the B channel yields a “true” or “false”. The read-out value is determined by the read-out path being switched between linear conjugated and cross-conjugated and, hence, set by its ability to transport charges. By choosing the appropriate topology of the π -conjugated system to which the terminals are connected, any logic operation can be obtained. Furthermore, in an extended version by adding a third input channel, single molecule logic elements can be defined that can perform different logic operations depending on the status of the third channel. By combining the various elements, this approach allows for the design of ultra-compact and highly complex logic circuits, including recursive networks, in theory.

6.1 Introduction

Until now, increasing the speed and complexity of electronic circuits has been achieved mainly by physical downscaling the universally applied basic element: the transistor. Combining two or three transistors, logic functionality is obtained. NAND and NOR logic operations are the basis on which all presently used computers function.^[1] An enormous effort is put in by both academic and industrial laboratories to make smaller transistors. At present, characteristic single component dimensions on a 20–100 nanometer scale are being realized. The standard kind of transistor is the field effect transistor (FET), having three electrodes (gate, source, and drain), a semiconducting part (between source and drain), and an insulating part (between the gate and the semiconductor). By combining p-type and n-type transistors, so-called CMOS (Complementary Metal-Oxide-Semiconductor) logic is obtained. Ambipolar FETs (i.e., FETs that can operate both in p- and in n-mode) based on silicon have been constructed, but they are costly. To miniaturize further, Carter invoked the quite conceptual idea for developing a computer based on molecular elements.^[2-4] The term “molecular electronic devices” originated with Carter.^[5] Recent developments in molecular electronics have yielded several examples of ambipolar FETs. This opens the way for constructing low-cost CMOS-type devices, in principle. Over the past few decades, an increasing number of reports have appeared in which suggestions were put forward for the construction of logic elements, based on π -conjugated organic molecules.^[6-8] Interestingly, most proposals concern the construction of molecular analogues of known basic elements in present microelectronics (e.g., wires,^[9] diodes,^[10,11] resistors,^[12,13] transistors,^[14-17] switches,^[18,19] etc.) Only recently, the logic aspects of molecular switches are used to mimic the behavior of the most well-known Boolean functions. Various single molecular systems that are capable of performing the AND,^[20] OR,^[21] IF THEN (Implication),^[22] NAND,^[23] and NOR^[24] operations have been proposed.^[25] In other words, the new proposals for molecular nano-electronics have been put forward mostly as molecular analogues within the paradigm of circuitry construction in common silicon-based technology.^[26,27]

For some molecules it has been shown that they can function as non-linear components in electronic circuits. In such experiments, a single functional molecule is placed between two electrodes. The so-called break-junction technique is used to make such nano-devices.^[28,29] Promising results are obtained with this technique and with monolayer experiments, which indicate molecules can function as diodes, for example, as originally proposed by Aviram and Ratner.^[10,30,31] Furthermore, it has been shown within our institute that one can construct a break-junction with a well-known type of photo-switching molecule inside, and that it is possible to switch at least from the open to the closed state by irradiation of the device.^[32] The reverse

switching was hindered by quenching of the intermediate excited state by the metal electrodes, but work is underway to circumvent that problem. Other workers have convincingly shown in a series of experiments that molecules with a cross-conjugated π -system transmit charges far less than linear conjugated analogues in a break-junction setup.^[32,33] The photo-switch experiment by van Wees *et al.* is considered as an example of switching from a cross-conjugated molecule to a linear conjugated one (i.e., with respect to the charge transport path through the molecule from one gold-bound terminal to the other). A difference in conductivity of a factor 10³ was reported between the “open” (i.e., in this case the *low* conduction, cross-conjugated) and the “closed” (i.e., the *high* conduction, linear conjugated) form. This is a strong indication that cross-conjugated pathways in π -conjugated systems are (far) less electrically conducting than linear conjugated ones in single molecule devices.

In Chapter 3 of this thesis reported on the construction of topologies of all-carbon π -conjugated systems by which it is possible to interconnect any number of terminals mutually in such a way that linear conjugation pathways exist between all of them.^[34] These systems are defined as “omniconjugated”. There are two types of omniconjugated topologies: the Type A, that is of the type that remains omniconjugated upon all relevant permutations of bonds that mimic single quasi-particle transport between any two terminals, and Type B, which does *not* remain omniconjugated but shows intriguing switching behavior.^[35] The Type A omniconjugated systems can be considered as “soldering” points for molecular wires. Hence, constructs were proposed for the most elementary part of electronic circuitry: the interconnection between functional elements.

Here, a universal method will be described for the construction of topologies of π -conjugated systems that allow for logic operations as performed in proposition logic (“switching logic”). The processing of binary data in computer components proceeds via sequences of logic operations. Although it is possible to construct logic elements based on other connection principles, the discussion is limited to functional elements that have one, two, or more input channels and one read-out channel. Each channel is made up by two terminals of the π -conjugated system. Hence, a simple switching element with only one input channel has four terminals. An element that performs a logic operation on two inputs A and B consists of a six-terminal device (i.e., four input terminals and two read-out terminals). The transport pathway between the two read-out terminals T is either linear conjugated (high conductivity; ‘on’) or cross-conjugated (low conductivity; ‘off’), depending on the states of the input channels. In a simple switch (having one input channel), the two levels ‘on’ and ‘off’ simply represent the open and closed forms of the switch. In a system with two input channels (the input channels being analogous to the propositions in proposition logic),^[36] the ‘on’- and ‘off’-level represent the ‘true’ and ‘false’ function value of a logic operation on input signals A and B. There are 16 fundamental logic

operations that can be implemented in situations based on two arguments that are either ‘true’ or ‘false’.^[37] In the following, it is shown that it is possible to construct π -conjugated systems (topologies) for each of the 16 fundamental logic operations. Obviously, these are only examples of what can be constructed. In principle, an infinite number of variations on the theme can be drawn. Furthermore, the approach allows for extension of the module with extra input channels. Some examples of topologies with three input channels will be presented, which allow for switching the module between performing two types of logic operations.

6.2 Logic Gates from Two Switches Based on π -Conjugation

In this section, the basic idea for switching the transmission of charges is introduced that will be used in the remaining of this chapter. Subsequently, some illustrative examples of simple switches, based on this principle, will be presented. The discussion is limited to two-dimensional, hydrocarbon-based systems for simplicity. The principle can be extended to systems containing heteroatoms and/or consisting of spatially more complex architectures.

The switching principle used throughout this chapter is based on going between a linear conjugated and a cross-conjugated path through a π -conjugated system. This is most clearly visible in the valence bond representation of the hydrocarbon skeleton. A linear conjugated path is one made up of alternating single and double carbon-carbon bonds. In a cross-conjugated path, there is (at least) one point at which the alternation between single and double carbon-carbon bonds is disrupted by a sequence of two single bonds (domain boundary).^[38] In such a switch, the π -conjugated system is changing between one in which there is at least one linear conjugated path between two (measuring) terminals and one in which there is none. This is to yield two states for the system: the ‘on’-level, in which there is linear conjugation, and the ‘off’-level, in which there is no linear conjugation (hence, cross-conjugation) between the measuring terminals (i.e., along the measuring channel). To perform the switching, we use an input channel that interacts with the measuring channel in the π -conjugated system. The input channel is to remain linear conjugated independent of the state of the whole switch. This is essential for reversible switching, as will be explained later on. Turning the switch is realized by reversing the alternation of single and double bonds in the switching path in such a way that all single bonds become double bonds and *vice versa*.^[39] A simple example of the principle is shown in Figure 6.1. In the open form ('on'-level), there is conjugation between the two measuring terminals T_1 and T_2 . This linear conjugated pathway is represented by red links in **6.1a**. When the links of the switching path A_1-A_2 are changed according to the description above, the quinoid structure **6.1b** is formed, in which the T_1-T_2 path is cross-conjugated. This state is considered as the

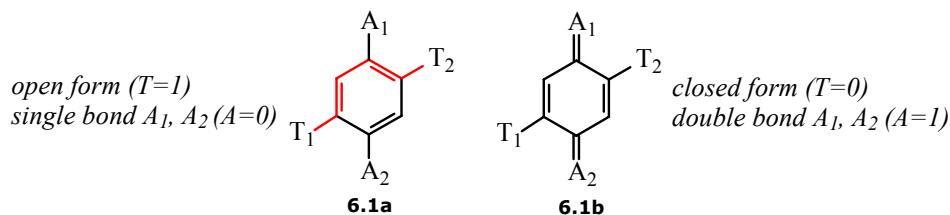


Figure 6.1 The read-out pathway T_1-T_2 is switched between open, linear conjugated (red bonds in **6.1a**) and closed, cross-conjugated (**6.1b**) upon changing the bonds of the switching path A_1-A_2 from single to double and vice versa.

'off'-level of the switch since it is expected to show a lower conductivity compared to the open, linear conjugated pathway. This implies that the electronic communication through the measuring channel is controlled by the topology of the input channel. The behavior of the switch in terms of high/low conductivity can be described with the universal use of false/'0' as low, and true/'1' as high. The high/low notation is very concrete, and usually refers to voltage of electronic devices. This so-called "positive convention" is used here to specify the input terminals of the π -conjugated system. The quinoid structure **6.1b** is higher in molecular energy than **6.1a**. Therefore, it is natural to use the value '1' for the double bond input terminals of **6.1b** and '0' as value for the complementary single bond input terminals of **6.1a**. (Although, strictly spoken, the choice of which of the two structures represent the '1' is arbitrary.) This switching principle is our key concept that allows for implementation of logic gates in π -conjugated systems.

As a consequence of the switching event, the either low ('0') or high ('1') conductivity of the read-out channel T depends on the binary values of the input terminals A ('0'/single and '1'/double). Based on this principle, the switch proposed in Figure 6.1 can be converted from the logical *constant* '0' or '1' into a logic *function* of any argument. For this purpose, the conjugated system should contain at least four input terminals that are utilized for the two input signals (arguments) of the logic function. Because there are two arguments, there are four argument combinations as can be understood from the four states of **6.2** given in Figure 6.2. In this example, a quinone-like switch is connected in series with an identical one. The two input channels A and B behave independently and both can have the value '0' or '1'. More important, they both can switch the conjugation of the read-out pathway between the measuring terminals T . This yields a well-defined logical system, and a Boolean function, solely determined by the input signals. According to the aforementioned switching principle, the read-out value is '1' only when all input terminals of **6.2** are single linked ('0'). Only in this situation the pathway between terminal T_1 and T_2 is linear conjugated (see **6.2a**). The other possible combinations of input arguments A and B give rise to an output value of '0'. The table on the

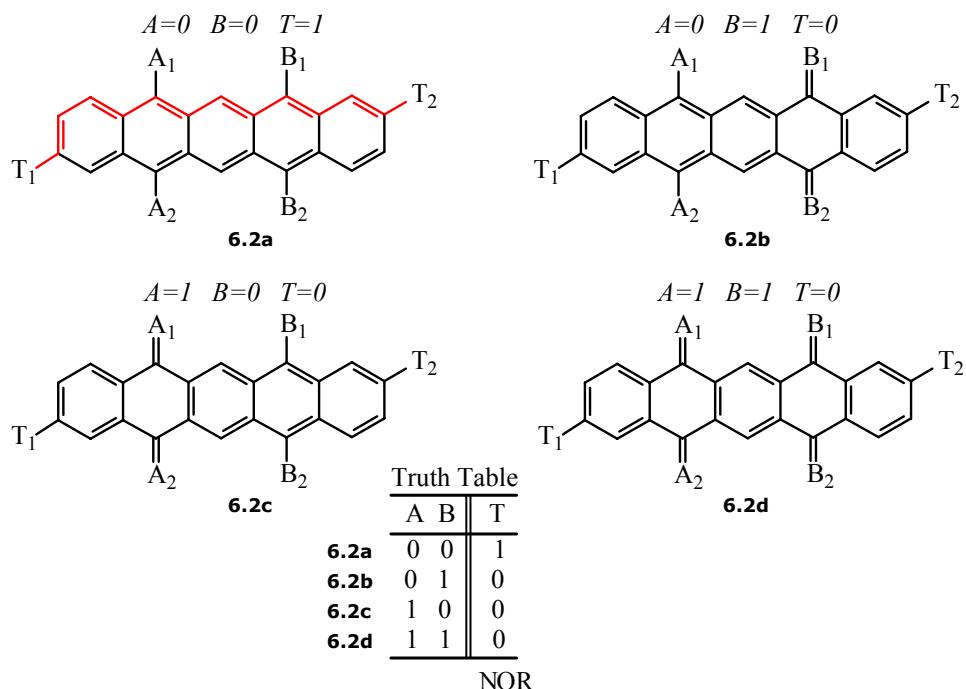


Figure 6.2 (Top) The four logical states of a 6-terminal molecular switch based on two quinone derivatives (*A* and *B*) which is capable of performing the NOR operation. (Bottom) Corresponding truth table of the Boolean function.

bottom shows the listing of binary output values *T* for every possible combination of input signal *A* and *B*. In the truth tables the '0' indicates that the read-out channel *T* is off (false) and a '1' that it is on (true). The input arguments *A* and *B* are '0' when the terminals are single bonded and '1' in the case of double bond terminals. The truth table describes precisely the effect of a Boolean function. The last column gives the definition of the logic operation and reveals the "truth" or "falsity" of the function for each binary combination of arguments *A* and *B*.

The as obtained Boolean function is a NOR operation since it only returns '1' when "NOT (A or B)" is true. In other words, the logic gate returns true/'1' only when both arguments of the function are false/'0'. With this simple switch at hand it is rather straightforward to design the Boolean function that duals the NOR gate. This is the NAND operation, which stands for "NOT (A and B)" in terms of proposition logic. A different architecture is necessary to achieve the NAND operation inside one single molecule. It can be designed when the two switches operate in parallel instead of in series (see **6.3** in Figure 6.3). To make the system look

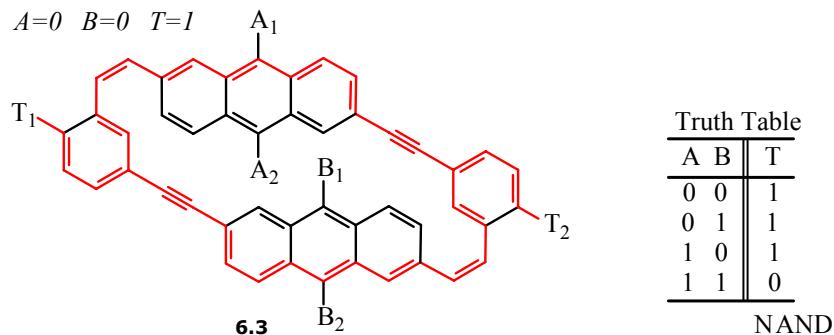


Figure 6.3 (Left) Parallel configuration of two quinone-like switches capable of performing a NAND operation. (Right) Corresponding truth table.

somewhat realistic, some extra acetylene and vinylene spacers are used for the example NAND gate **6.3**.

The logical complements of the NAND and NOR are the AND and OR gate, respectively. Examples of these logic types can easily be constructed using a molecular switch complementary-like to **6.1**. An example of such a switch is structure **6.4** in Figure 6.4a. Structure **6.4** is only linear conjugated between the read-out terminals when both input terminals are doubly bonded. Combination of two switches of this type results in the logic of an AND gate (see the truth table depicted in the Figure 6.4b). Consistent with the example mentioned above, connecting the two switches of type **6.4** in parallel results in the operator that duals the AND gate, that is the OR gate. Further elaboration of this procedure can lead to the implementation of more logic gates. For example, a combination of the intrinsic logic of **6.1** and **6.4**, either connected in series or in parallel, results in additional logic operations in truth tables that respond to the same input conditions. It seems like this is a convenient way to implement all Boolean functions inside one

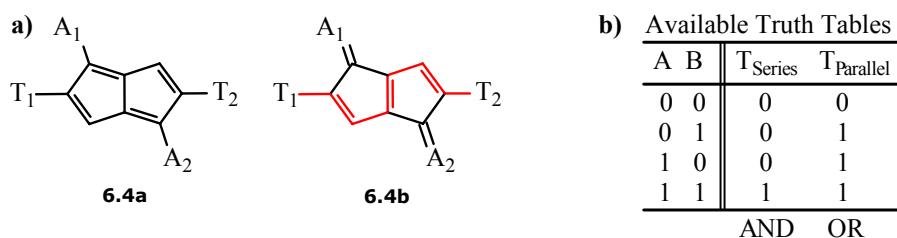


Figure 6.4 a) Molecular switch which is open (6.4b) when the input terminals A are doubly bonded. b) Truth tables showing the implementation of the AND and OR gate depending on the interconnection of two switches of the type **6.4**.

conjugated system. Unfortunately, not all 16 standard logic operations can be obtained in this way.^[40] It was not possible to design modules based on a combination of the proposed, or somewhat related, simple switches that resemble the logic of an XOR or an XNOR operator. In general, the exclusive-OR logic, abbreviated XOR, is employed as a means to compare the state of two input signals. The XOR is similar to OR but excludes the combination of both input arguments A and B being equal to 1. Thus, the outcome of the XOR operator stems from a simultaneous verification of both input signals. This implies that the input terminals of the molecular gate should manipulate the conjugation of the read-out channel in a cooperative manner. Therefore, the implementation of an XOR and XNOR in conjugated systems is not possible, as long as the switching pathways A and B, like the ones proposed above, act independently.

The NAND and NOR gate are the most important gates on which all modern computing is based. These are universal gates since they allow for the construction of all Boolean functions when using multiple copies.^[1] This means that it is possible to obtain the XOR and XNOR gates by interconnecting several NAND gates, like **6.3**, in a logic circuit. This would result in larger logic modules, though. In order to avoid this, the objective is performing all 16 fundamental logic operations inside one π -conjugated molecule instead of constructing circuit diagrams based on many molecular switches. As will be demonstrated in the next section, an alternative strategy to implement the XOR and XNOR gates is the use of conjugated systems with a more complex π -topology. In this way, all operators can be realized without the need to interconnect individual switches in series or in parallel.

6.3 All Boolean Functions inside Compact π -Logic Gates

Above, the logic gates were constructed by combining two individual, independent switching elements. That is, for each input channel, there was always a strictly separated direct linear conjugated pathway: there were no atoms *necessarily* shared by the two pathways although it was possible to draw shared pathways in some of the states. Now it is shown that it is possible to construct more compact molecular structures, in which the pathways of the input channels are sometimes interwoven, but still always independently linear conjugated. Ultimately, with the number of input terminals being 4 for the two inputs, the possible number of logic operations that can be achieved with *one* single molecule is 16, in theory (i.e., all possible Boolean functions). With the inclusion of the read-out pathway, the system has to be provided with six terminals, as was shown in the previous section. As far as the two input channels are concerned, these have to be linear conjugated in all logic states to allow for reversible switching in all of these states. Meanwhile, as the result, the read-out pathway is to be switched between linear and cross-conjugated. The

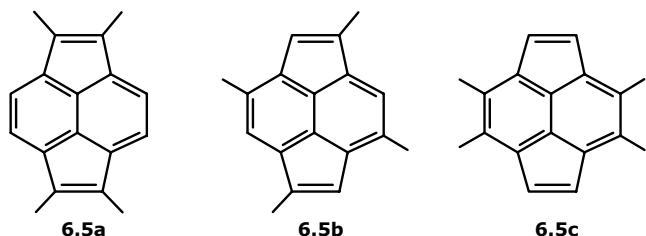


Figure 6.5 Three possible substitution patterns of a 4-terminal pyracylene system with conjugation between all terminals (omniconjugated).

inherent difficulty in achieving complex logic operations with single conjugated molecules is to find a π -topology with intrinsic conjugated pathways between the four input terminals as well as a read-out channel that can be modulated by those pathways. In this section, examples will be presented of conjugated systems that exhibit such complex logic behavior due to their remarkable π -topology.

In Chapter 3 of this thesis, the concept of omniconjugation was introduced. It was speculated that this class of π -conjugation is valuable for the design of complex logic circuits. Here it will be shown that omniconjugation allows for the implementation of any desired Boolean function inside single molecules. Although it only is to serve as an example, the emphasis throughout the remaining of this chapter is placed on one specific molecular building block, the pyracylene system. This will be the standard system because it contains several omniconjugated substitution patterns. Suppose the pyracylene has four terminals and they are positioned according to one of the substitution patterns outlined in Figure 6.5. In any case, the system is omniconjugated because the pathways between all terminals are linear conjugated in a direct manner. The intriguing aspect is that any pathway between two terminals remains conjugated when changing the links between the complementary pair of terminals.^[41] This implies that the pyracylene system satisfies quite well the requirement that the two input channels should be conjugated in all states to ensure for independent and fully reversible switching events. The second reason why this system is of particular interest is that it allows for a number of choices where to put the read-out terminals.^[42]

The construction of logic functions from the pyracylene system consists of selecting the proper combination of input terminals that provide for the generation of the desired read-out values. There is a systematical way of determining what kind of logic operations are available within a given 6-terminal system, but that will be discussed later in this chapter. An example of a logic operation embedded in the pyracylene system is offered by its derivative **6.6**, depicted in Figure 6.6a. The input terminals of this structure are configured using the substitution pattern of structure **6.5c**. This ensures that the input channels A and B are conjugated in all states. The read-out terminals are attached to the same five-membered ring and are therefore

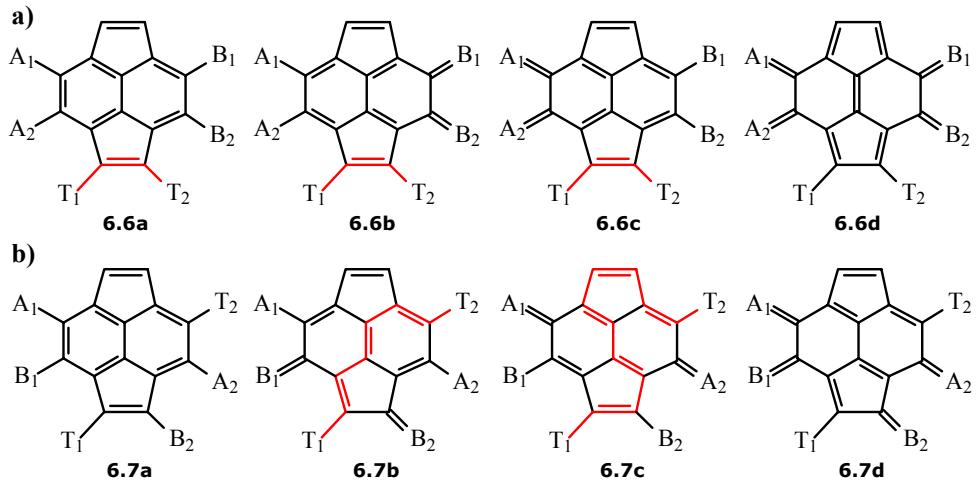


Figure 6.6 The four states of an a) NAND gate and b) XOR (exclusive-OR) gate inside the same 6-terminal pyracylene system, but with two different configurations of input and read-out channels.

conjugated with each other in almost every state. Only when both input terminals are doubly bonded (**6.6d**) the read-out pathway T_1-T_2 becomes cross-conjugated. Obviously, the as obtained 6-terminal system is not omniconjugated in contrast to the original 4-terminal derivative **6.5c** (see Figure 6.5). As a consequence, this module mimics the function of a NAND gate (see for the corresponding truth table Figure 6.3). Structure **6.6** is a compact alternative for the parallel architecture of the NAND gate proposed in Figure 6.3. Hence, a more complex π -topology can be used to simplify the molecular architecture of the logic gate.

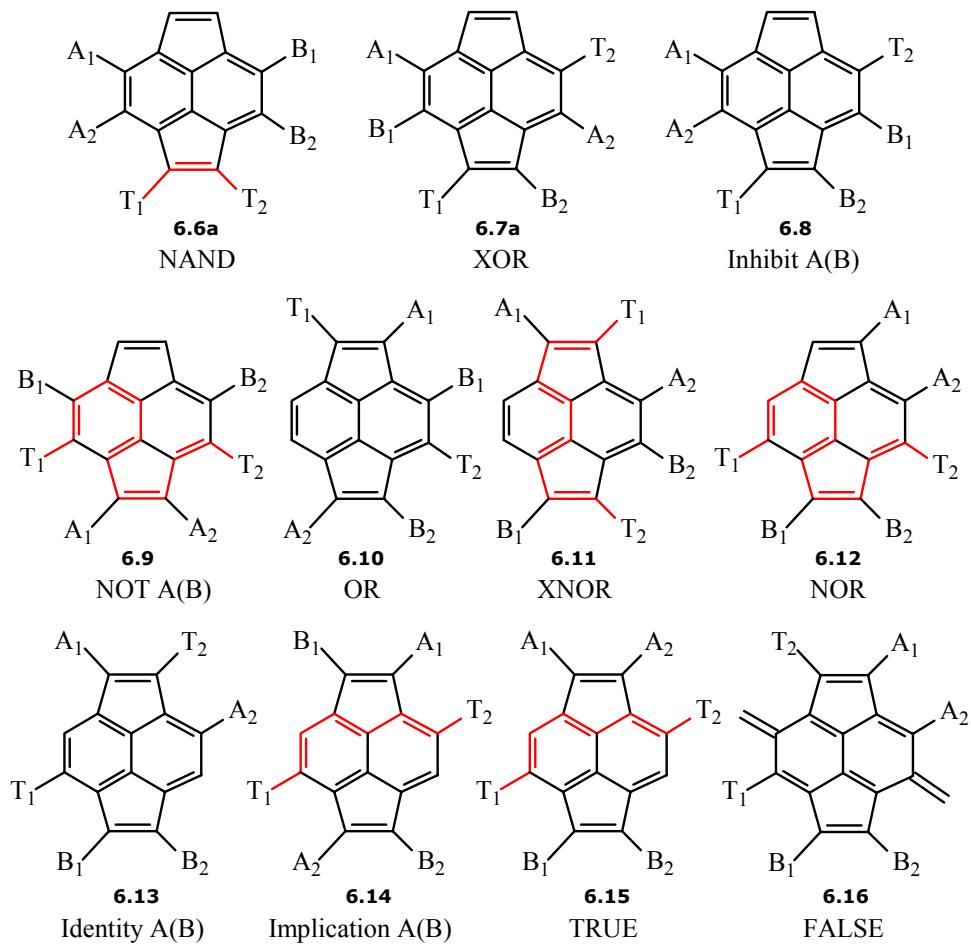
The second Boolean function that will be considered here is the XOR (or XNOR) gate. This is the most challenging one in the design of logic functions inside single molecules. As mentioned before, the XOR operator needs to compare both input signals. This is achievable with the pyracylene derivative because the channels can be configured in such a way that some of the links of the measuring channel are shared by both input channels. Interestingly, the same substitution pattern for the implementation of the XOR gate as in the NAND gate **6.6a** can be employed. The first and the last state of the XOR operator (i.e., for input arguments A and B being both '0' or '1') should have a read-out value of '0' implying that the read-out channel must be cross-conjugated. The easiest way to select the proper read-out terminals is to first determine which pathways are cross-conjugated in these two states. The pathways between A_1-T_2 and B_1-T_1 are cross-conjugated in **6.6a** as well as in **6.6d** and can be utilized as measuring channel. Because these pathways are analogous in terms of symmetry, both combinations will result in the same logic function. An

overview of the four states of an XOR gate based on B_1-T_1 as measuring channel is given in Figure 6.6b.

A special feature of this particular substitution pattern of pyracylene is that its intrinsic logic capabilities enable for the implementation of four additional logic operators. Another type of logic gate is obtained when using the same read-out terminals as in **6.7a** but with a different combination of input terminals. This is the “Inhibit A” operation implemented in **6.8**, which is depicted in the overview of a selection of the available Boolean functions based on the pyracylene system (see Figure 6.7). The “Inhibit B” operator can be obtained by exchanging the input terminals A and B of **6.8**. This option is indicated in parentheses. The same is true for the “NOT A” operator **6.9**. In fact, operators of this kind repeat the same logic because they are functions of less than two arguments. Reference to the second argument is superfluous in Boolean functions of this kind. This means that despite the fact that input channel A of, for example, **6.8** can change the route of the conjugated path between the read-out terminals, it does not control the kind of conjugation of the measuring channel. In **6.8**, only terminal B has the power to disable this read-out pathway and, with that, the whole system. In general, this reasoning holds for the NOT A(B), Inhibit A(B), Identity A(B), and Implication A(B) gates (see Figure 6.7).

At this point, there are six standard Boolean functions left to be considered with the pyracylene system. The ideal situation would be to design all operators using the same substitution pattern. This is not possible as can be seen from the overview given in Figure 6.7. However, small changes in the substitution pattern do allow for the realization of most of the two-argument Boolean functions. (This was not an option with the simple switches discussed in the preceding section.) For example, the logic of an XNOR gate is provided by module **6.11**. Just as with the XOR **6.6**, which is the complement function, the input terminals of **6.11** are positioned to act cooperatively on the read-out channel. In **6.11**, the input channels can only keep the read-out pathway “open” when they have the same input value (i.e., A equals B).

Due to the high degree of conjugation of pyracylene, it is not straightforward to implement the logical constant FALSE (i.e., the path between the two measuring terminals being *always* cross-conjugated). However, a simple trick to ensure the read-out pathway is always closed regardless of the input signal is introducing two extra terminals. An example is given with **6.16**, in which the double bond terminals do *not* participate in the switching process. The terminals control the π -topology of the system so as to keep the read-out pathway cross-conjugated in all states. Their positions have been selected to ensure that the input terminals can still, in principle, provide for the input values of the Boolean operator. Thus, the input channels A and B in **6.16** are linear conjugated in all states although they are of no use in terms of controlling the output of the logic gate.



Truth Tables

A	B	T values														
		6.16	6.8^a	6.13^a	6.8	6.13^a	6.7	6.10	6.12	6.11	6.9^a	6.14^a	6.9	6.14	6.6	6.15
0	0	0	0	0	0	0	0	0	1	1	1	1	1	1	1	1
0	1	0	0	0	1	1	1	1	0	0	0	0	1	1	1	1
1	0	0	1	1	0	0	1	1	0	0	1	1	0	0	1	1
1	1	0	0	1	0	1	0	1	0	1	0	1	0	1	0	1

^aFunction of argument B when exchanging terminals A and B in the presented configuration.

Figure 6.7 (Top) Select overview of 15 different logic gates that can be constructed in 6-terminal pyracylene systems. (Bottom) Corresponding truth tables.

The π -topological properties of a single pyracylene system allow for an ultra-compact way of constructing all possible 16 Boolean functions, except for one! Intriguingly, it was not possible to design the AND gate using this carbon skeleton. Although the architecture based on the simple quinone-like switch presented in Figure 6.2 is a nice and compact alternative, yet another approach to achieve this gate will be presented in the next section.

6.4 Increasing the Complexity: Bifunctional Logic Elements

The next logical step in the development of molecular electronic circuits based on the proposed pyracylene derivatives is the creation of complex logic systems. In general, electronic circuits are built from a number of logic operators arranged in different geometric patterns.^[1] For example, when a logic gate accepts input signals from the outputs of other gates, the output of the gate can be determined entirely by those adjacent gates. Logic networks of this kind are used in complex electronic circuits. Related networks can also be easily obtained (on paper!) by interconnecting the pyracylene derivatives through their *read-out terminals* (i.e., in series or in parallel). Instead of using this combinational approach, which is often trivial, it will be demonstrated here that it is possible to integrate multiple functions inside one molecule.

A means of reconfiguring a molecular logic gate of the present study is by employing a third input signal: the control channel. The effect of changing the state of the control channel (between terminals C), leading to different logic functions is shown in Figure 6.8. When the terminals of the control channel C are single linked ('0' state) or when they are removed, the available logic function follows directly from the input channels A and B (see Figure 6.8, left). According to logic values of the output terminals, module **6.17** operates as a "NOT B" gate when C = 0.

The pathway between the control terminals C is conjugated in all the four states of **6.17**. This can be seen clearly in, for example, **6.17c**. Hence, the control channel C can be used at any time (i.e., in any state of the gate) to switch the *logic* of the module. This is demonstrated with **6.18**, where the control line goes to the value '1'. As a consequence, the effect of the input signals A and B on the read-out pathway changes, and the embedded logic of the module is reconfigured. For C = 1, the read-out channel is only conjugated when all input terminals are doubly bonded. Hence, the system has become an AND gate. The module will again operate as a "NOT B" gate when C returns to '0'. In this manner, there are two logic functions embedded in the same π -system. The control input C acts as an enable signal for either one of them. Further elaboration of this approach can in theory lead to 16^2 possibilities of logic bifunctionality. Moreover, such a bifunctional element can be extended and coupled to other active elements to yield very complex logic networks.

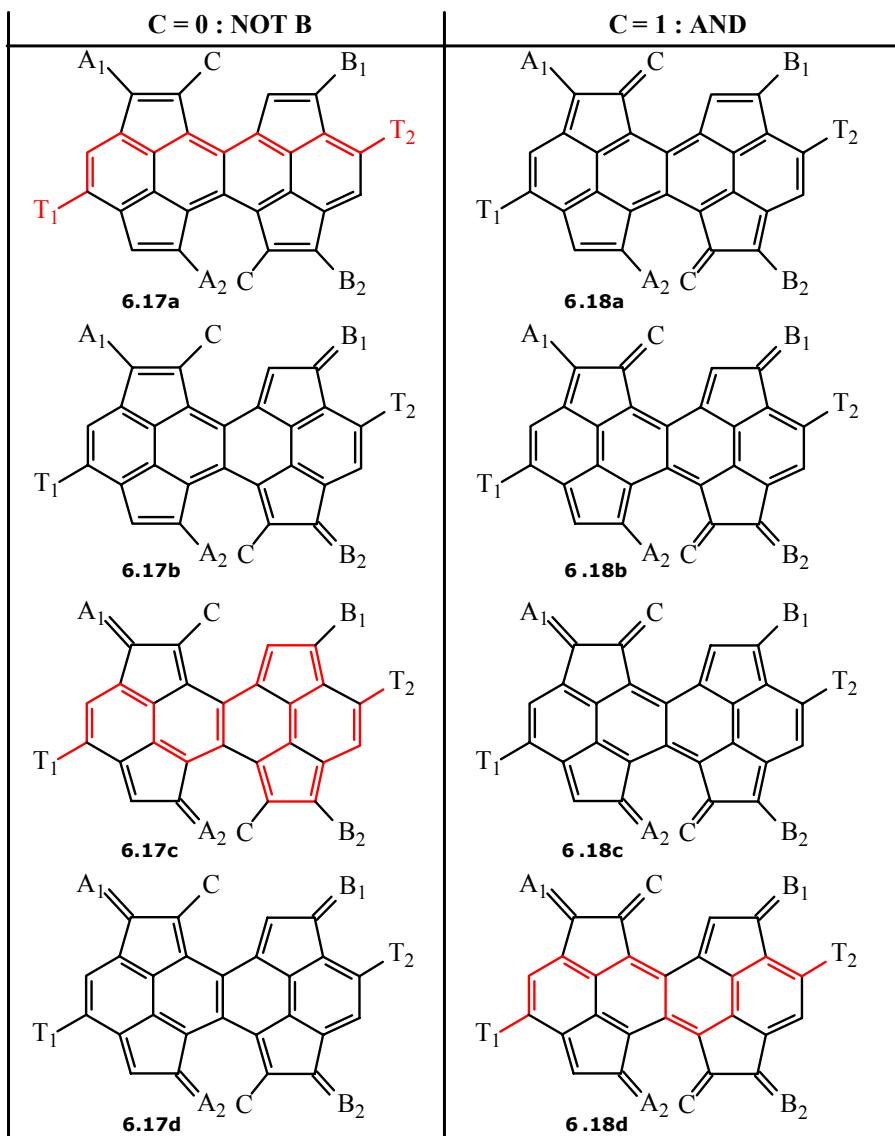


Figure 6.8 Bifunctional logic elements based on two fused pyracylene systems. The control channel ‘C’ determines the present logic (left or right) of the molecular gate.

The bifunctional elements have yet another useful property for molecular circuitry: the output depends not only on the *present* state of inputs A and B, but also on *past* inputs via control line C. This means that the bifunctional pyracylene-

based modules facilitate the design of storage elements, in principle. This is quite encouraging, since storage (or memory) elements are, together with logic gates, *the* essential components of electronic circuits.^[1]

Switching the logic functionality of the pyracylene-based gate by a third channel is somewhat related to the introduction of two extra, fixed terminals (see the FALSE gate **6.16** given in Figure 6.7). In this way, it was possible to implement the logic constant FALSE. However, the disadvantage of adding extra, static terminals to one pyracylene system is two-fold. Firstly, it often does not result in a true, reversible switch given that the extra terminals can also disable the input channels. On the other hand, the terminals cannot always control the read-out channel when they do leave the input channels intact. Basically, there are not enough positions available for extra terminals, which can be used to reconfigure a gate at will. Therefore, the most sophisticated approach is to change the logic function of a conjugated module is by utilizing bifunctional systems, such as, the above mentioned example, based on two fused pyracylene systems.

6.5 On the Built-in Logic of n-Terminal π -Conjugated Systems

So far the discussion was concentrated on what kind of logic gates are available within a 6-terminal pyracylene system. The logic depends on the *position* of the terminals and the *combination* of the terminals employed as input and read-out channels. Now it is shown that any π -conjugated system can be explored in a systematic manner by means of the analysis of n-terminal π -conjugated systems. The basic principles of the analysis of systems containing n-terminals (see Chapter 2) and its extension that allows for the elucidation of pathways (see Chapter 5) are the foundation of the work presented here. Especially when there are so many terminals involved, the analysis is a powerful tool to elucidate all (potential) closed, cross-conjugated pathways in the set of logic states available for a conjugated system.

The analysis of n-terminal π -conjugated systems consists of deducing all possible double bond patterns within its molecular framework. The pyracylene system will serve as an example again. The collection of structures representing the 6-terminal pyracylene derivative **6.19** is given in Figure 6.9. Generally speaking, such a series originates from a statistical permutation (without repetitions) of double bonds over n terminal positions.^[43] This implies that 6-terminal system with *either* an even or an odd number of double bond terminals contains $2^{n-1} = 32$ permutations. Every even and odd series contains 32 distinct double bond configurations within the framework. Here, the *even* series (i.e., the $6E^{0(1)2(15)4(15)6(1)}$ system) is considered. To guide the eye, structures with zero, two, four, or six double bond terminals are contained in individual boxes in Figure 6.9. An overview of the double bond terminals (expressed

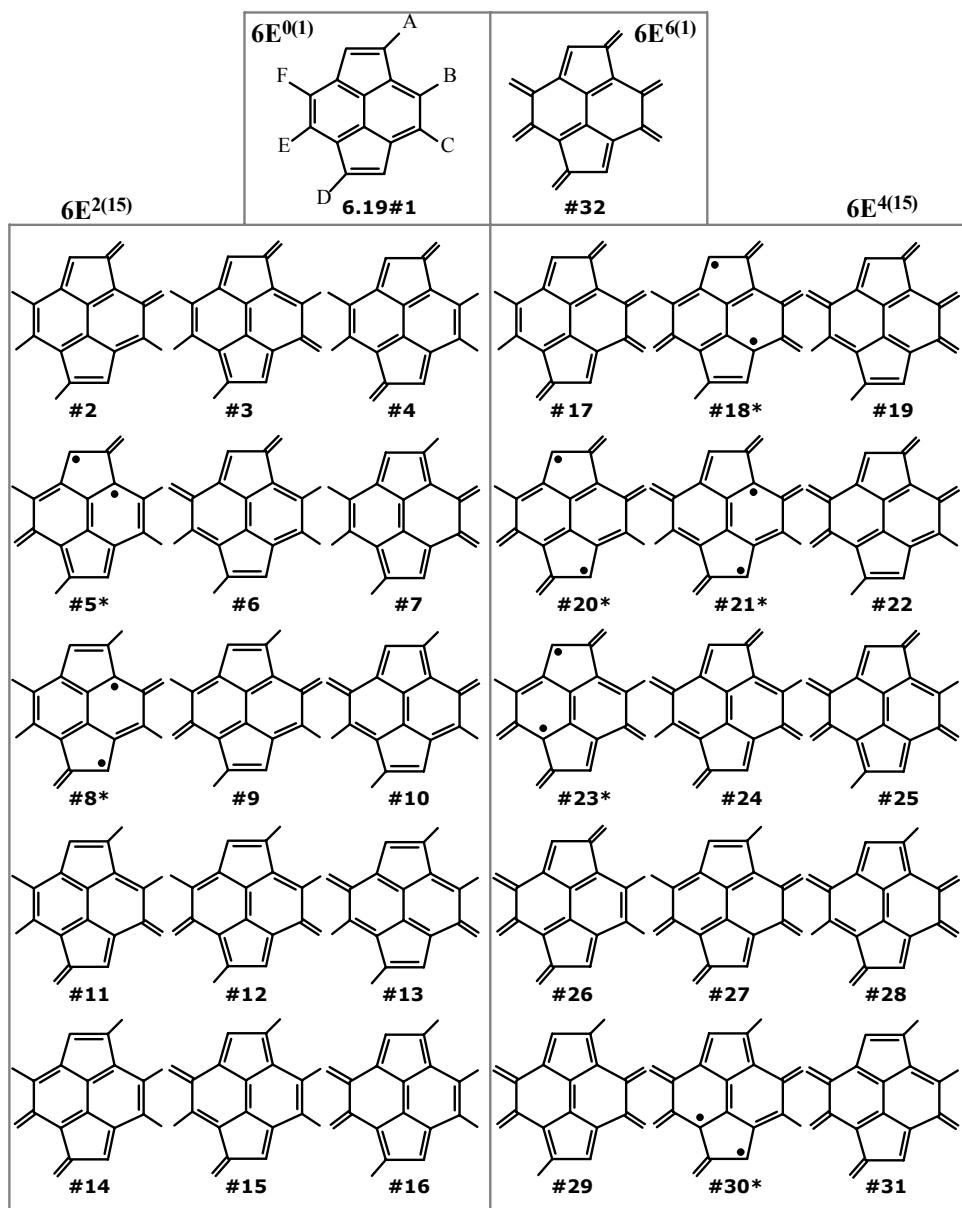


Figure 6.9 The collection of all structures, differing in arrangement of double bond terminals. The characteristics of the collection represent the π -topological properties of **6.19**. The non-Kekulé structures of this series are marked with an asterisk.

Table 6.1 Overview of the double bond terminals in structures from the collection that represents the π -topological properties of the 6-terminal pyracylene derivative **6.19**. The non-Kekulé structures are marked with an asterisk (see also Figure 6.9).

Structure	#1	#2	#3	#4	#5*	#6	#7	#8*	#9	#10	#11	#12	#13	#14	#15	#16
Double bond terminals	-	ab	ac	ad	ae	af	bc	bd	be	bf	cd	ce	cf	de	df	ef
Structure	#17	#18*	#19	#20*	#21*	#22	#23*	#24								
Double bond terminals	abcd	abce	abcf	abde	abdf	abef	acde	acdf								
Structure	#25	#26	#27	#28	#29	#30*	#31	#32								
Double bond terminals	acef	adef	bcde	bcd	bcef	bdef	cdef	abcdef								

in terms of their labels a, b, c, etc.) of every structure from this series is given in Table 6.1.^[44] In some cases, it is not possible to find a closed shell configuration. Structures of this kind (non-Kekulé structures) are marked with an asterisk (see, for example, structure **6.19#5**). The essence of the n-terminal analysis is that the types and number of non-Kekulé structure are related to the number and types of cross-conjugated pathways inside the structure under investigation. Hence, the non-Kekulé structures can be used to determine the switching properties of the conjugated system and are, therefore, of use for the design logic gates.

The cross-conjugated pathways can be determined from a simple calculation in the following way. The cross-conjugated pathways of a system are obtained from the product of its double bond terminals with those of each non-Kekulé structure of the series. For system **6.19**, all double bond terminals are given in tabulated form in Table 6.1. Let us consider **6.19#7** as an example. Structure **6.19#7**, having two double bond terminals, is accordingly to be multiplied with non-Kekulé structures #5, #8, #18, #20, #21, #23, and #30. The product of structure **6.19#7** with the non-

Table 6.2 Overview of the cross-conjugated pathways in structures of the series given in Figure 6.9 that have only terminals A and D single linked. Pathway (ad) is the read-out channel T for the potential logic gate. Structure #13 has no cross-conjugated pathways.

Structure	Cross-conjugated pathways					
#1			ae	bd		
#7			ae		cd	
#9	ab	ac	ad		de	df
#10			ad		de	df
#12	ab	ac	ad			
#13						
#16				af	bd	
#29				af		cd

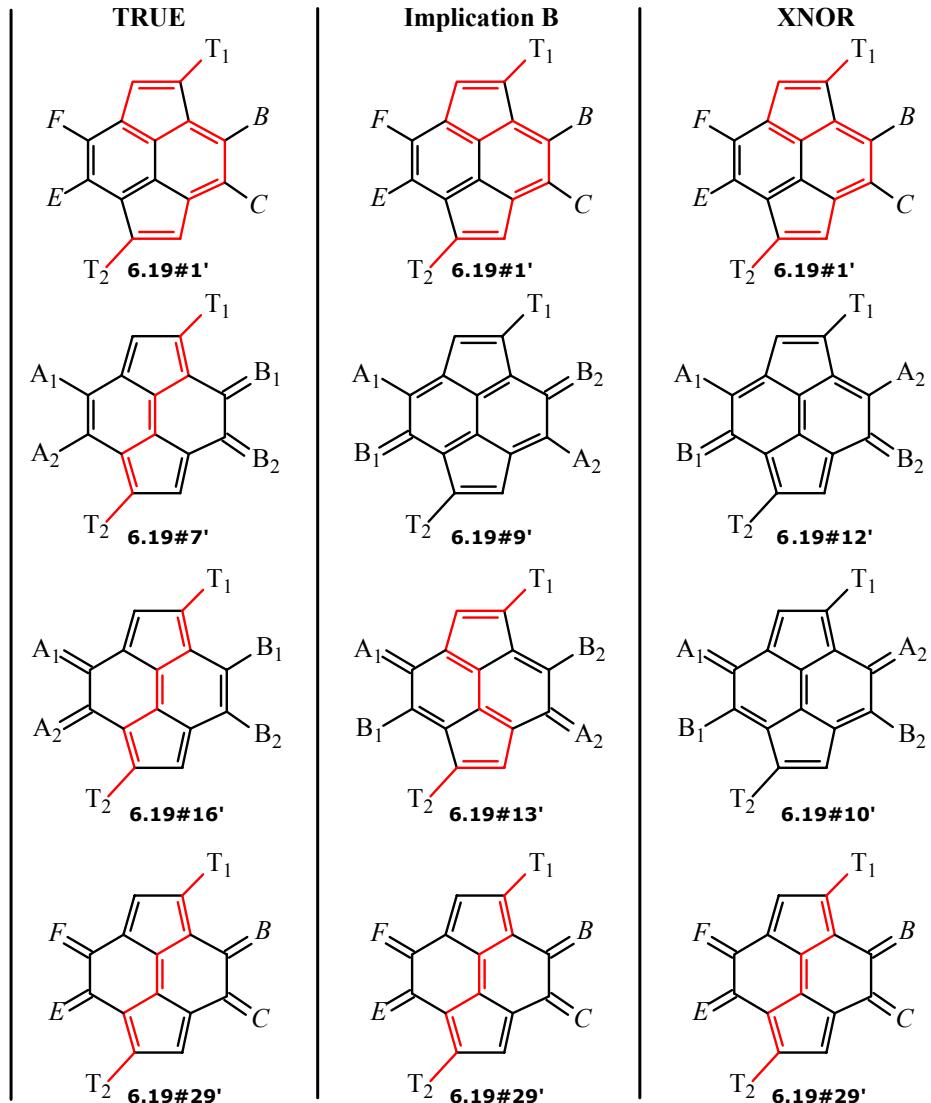


Figure 6.10 Implementation of three logic gates in the 6-terminal pyracylene system **6.19'**. The gates have the same read-out channel T_1-T_2 (i.e., pathway (ad) of **6.19**). The combination of input terminals determines the kind of embedded logic.

Kekulé structure #8 is $\#7 \otimes \#8^* = (bc) \otimes (bd) = (cd)$. Similarly, the product of #7 with #18 is $\#7 \otimes \#18^* = (bc) \otimes (abce) = (ae)$. The product of #7 with #5 is $\#7 \otimes \#5^* = (bc) \otimes (ae) = (abce)$. The latter product does not represent one cross-conjugated pathway simply because it consists of four terminals (a pathway exists between two terminals only). The same situation emerges in multiplications with non-Kekulé structures #20, #21, #23, and #30. Hence, **6.19#7** contains the two cross-conjugated pathways (cd) and (ae).

The topology of double bonds provides for the built-in logic of a π -conjugated system. This is because it is *a priori* clear which pathways can become cross-conjugated during successive switching events. In the following, it will be shown that it is rather straightforward to determine what types of logic gates are available within a certain n-terminal system. The easiest way to do this is to first assign the read-out terminals. Consider, for example, pathway (ad) between terminal A and D of **6.19**. As a read-out channel of a gate these terminals are single linked from the present point of view (see T_1 and T_2 of **6.19'** in Figure 6.10). Hence, all other structures that have terminal A and/or D doubly bonded are excluded from the set of structures that can be used to implement logic operations based on this read-out channel. The remaining eight structures are listed in Table 6.2. This table gives an overview of their cross-conjugated pathways as calculated by means of the approach given above.^[45]

Structures **6.19#1** and **6.19#29** have, with the exclusion of read-out terminals A and D, four singly and four doubly bonded terminals, respectively. Hence, these structures represent the input arguments of A and B being both '0' or '1'. This means that two out of the four required states of a logic gate are already found without even specifying the input terminals. In both states, the read-out channel (ad) is not cross-conjugated (see Table 6.2) and the module represents an output value of $T = 1$. The other six structures provide for the second and third logic states. For these states the input terminals should be complementary (i.e., either A or B doubly bonded) to yield the complete set of four possible states of the gate. This is found for the following combinations of structures: #7 and #16, #9 and #13, and #10 and #12. Figure 6.10 shows that the behavior of the read-out pathway T_1-T_2 is different for each of these options. As a consequence, up to three different logic functions can be implemented in this module: TRUE, Implication B (or, at choice, Implication A), and XNOR. Evidently, the logic function of the module depends on the choice of the input terminals when the read-out channel is fixed. Alternatively, this strategy can be extended to any other available read-out channel and will yield many more logic gates. The n-terminal analysis unveils the wealth of built-in logic in the 6-terminal pyracylene system in a systematic way. Much more important, a complete n-terminal analysis unveils *all* built-in logic in *any* n-terminal π -conjugated system.

6.6 Discussion and Conclusions

Up until now, π -conjugated systems for single molecule electronics have been investigated for their transport properties, either as static structure or as optical switches. The proposed methodology allows for the design and construction of n-terminal π -conjugated systems that can perform any one of the 16 Boolean functions for two input arguments. The approach was based on switching the measuring channel between a high and low conductivity state. The logic gates were operated by two input signals that control the kind of conjugation of the read-out channel. The present treatment is limited to systems in which an input signal stems from two terminals that have the *same* bond topology: either singly or doubly bonded. In principle, the digital values of the input signals could also have been defined from channels with a dissimilar topology of terminals. This would have resulted in a related but different set of logic gates. The same possible extension applies to the read-out channels' symmetry of bond order, yielding even more cross-combination of possible sets of logic gates.

More fundamentally, it was chosen to use a two-terminal configuration for input and read signals to perform π -logic. This constitutes just one option. It is highly intriguing to investigate other possible ways to enter input and to obtain output from topological systems like the presented valence bond representations of n-terminal π -conjugated systems.

One challenging aspect of molecular logic devices is "wiring" the individual elements and the transmission of data between elements.^[46-48] In terms of linear versus cross-conjugation, solutions for both issues are at hand when using (omni)conjugated systems. First of all, many functional elements can be interconnected via the terminals of omniconjugated systems. Even more importantly, the elements can be wired in a fully conjugated manner. This is essential when the detection of output values and the transfer of information between elements proceed via conjugated pathways. Secondly, the basic principles of the presented approach rely on the *charge transport* properties of conjugated pathways to transfer data as well as on the *topologies* of pathways. The topologies of pathways were used as input signals and enabled for wiring many logic elements. The advantage of using the measure of charge transport is that the output signal of the logic gate is addressable in a nondestructive way. At least, it is expected that measuring the conductance will not decompose the molecule or change the logic state it represents.

Another severe problem encountered in the design of gates based on molecules is "cross-communication" between the different logic states.^[25,49] This is because, in many examples, the input and output signals both stem from the electronic structure of the system (i.e., interacting with light, ions, electric fields, etc.),^[50] which are present within a relatively large molecular distance. It is very likely that cross-talk can be prevented when not using output signals based on macroscopic signals. In

our approach, the read-out signal relies on the transport of charges and the input signals depend on the π -topology of the input terminals. Still though, the two external input channels of the logic operators have to be triggered independently to ensure that all logic states are addressable. One way to realize this is by changing the topology of the pairs of input terminals by different mechanisms such as, for example, by means of reduction/oxidation reactions along one input channel and using protection/deprotection (or acid/base) chemistry for the second one. However, the ultimate switching mechanism would be based on passage of single quasi-particles through the logic gate. For example, a single soliton (either charged or neutral) can be used as input signal given that it can invert the double bond/single bond pattern along an input channel. On the other hand, polarons leave the alternation pattern unchanged and can be used to determine the read-out of the gate. To date, preselecting and detecting a soliton path in a molecule remains an unresolved issue.

It is of prime importance that the change of bonding along the switching pathways is reversible. Furthermore, it is desirable to have a switching process without a high activation energy barrier for the transition between specific logic states. The ideal logic gate would be based on molecules that are of similar electronic stability in all four logic states. This might be endeavored by substituting the molecules with donating and accepting groups at suitable positions. From a chemical point of view, donors and acceptors can also enhance the stability of the quinoid-like forms. This would be highly desirable since stability issues could hinder the realization of logic gates based on conjugated systems.

One of the advantages of the switching principle proposed here was that different kinds of logic gates can be implemented in an extremely compact manner. This is an immediate consequence of the quite remarkable π -topological properties of 6-terminal pyracylene systems. Derivatives of this molecule were not only capable of demonstrating all 16 Boolean logic functions, but were also of use in the design of complex logic networks. Usually, chemical logic systems are based on supramolecular systems and are therefore complicated from a chemical point of view.^[6,51,52] On the other hand, much simpler switches do not provide for a straightforward implementation of multiple logic functions inside one molecule. From our point of view, the proposed molecular gates are the most densely integrated logic structures one can imagine for a wide variety of logic operations at the molecular level. These architectures might constitute the ultimate limit of the miniaturization of electronic circuits with molecules.

Conceptually, it is believed by many scientists that the basic principles of neurotransmission processes are related to the elaboration of binary data in Boolean algebra.^[53,54] The transfer of information from the environment to the human brain proceeds via chemical signals. Eventually, the input signals are converted into small

electrical signals transmitted within the neurons. Although not all neurons in the brain are alike, they all process signals in a way related to the basic principles of logic operations. With the realization of logic elements based on ultra-compact π -conjugated systems it might become possible to address many complex sequences of logic operations at once, as is being carried out by the human brain.

The presented method to construct Boolean functions from conjugated systems was based purely on topological considerations. It was shown by theory that it is possible to use the *topology* of a system to implement logic operations. Moreover, recursive networks are at hand since a single n-terminal π -conjugated system could control many other loops or chains of logic gates. At this stage, it is certainly unclear if practical application in electronic circuits can emerge for the presented molecular logic operators. However, the topological concept outlined in this chapter is appealing for other applications. Independent of the applicability in terms of conjugated molecules, the basic concepts are mathematically valid for other topological systems as well. The presented “topologic” treatment of binary systems allows for constructing extremely complex networks.

6.7 References and Notes

1. M. Morris Mano, *Digital Design*, 3rd ed., Prentice-Hall, New Jersey **2002**, pp. 33, 111, 167.
2. F. L. Carter, *Molecular Electronic Devices*, Marcel Dekker, New York **1982**, pp. 51.
3. F. L. Carter, *Molecular Electronic Devices II*, Marcel Dekker, New York **1987**, pp. 149.
4. F. L. Carter, *J. Vac. Sci. Technol. B* **1983**, 1, 959.
5. N. S. Hush, *Ann. N.Y. Acad. Sci.* **2003**, 1006, 1.
6. J. C. Ellenbogen, J. C. Love, *Proc. IEEE* **2000**, 88, 386.
7. M. D. Ward, *J. Chem. Educ.* **2001**, 78, 321.
8. A. P. de Silva, N. D. McClenaghan, *Chem. Eur. J.* **2004**, 10, 574.
9. J. Reichert, R. Ochs, D. Beckmann, H. B. Weber, M. Mayor, H. von Löhneysen, *Phys. Rev. Lett.* **2002**, 88, 176804.
10. A. Aviram, M. A. Ratner, *Chem. Phys. Lett.* **1974**, 29, 277.
11. D. B. Strukov, K. K. Likharev, *Nanotechnology* **2005**, 16, 137.
12. Y. Karzazi, J. Cornil, J. L. Brédas, *J. Am. Chem. Soc.* **2001**, 123, 10076.
13. J. M. Tour, M. Kozaki, J. M. Seminario, *J. Am. Chem. Soc.* **1998**, 120, 8486.
14. A. Aviram, *J. Am. Chem. Soc.* **1988**, 110, 5687.
15. H. W. Ch. Postma, T. Teepen, Z. Yao, M. Grifoni, C. Dekker, *Science* **2001**, 293, 76.
16. C. Joachim, J. K. Gimzewski, *Chem. Phys. Lett.* **1997**, 265, 353.
17. T. D. Anthopoulos, C. Tanase, S. Setayesh, E. J. Meijer, J. C. Hummelen, P. W. M. Blom, D. M. de Leeuw, *Adv. Funct. Mater.* **2004**, 16, 2174.
18. G. M. Tsivgoulis, J.-M. Lehn, *Chem. Eur. J.* **1996**, 2, 1399.
19. J. J. D. de Jong, L. N. Lucas, R. M. Kellogg, J. H. van Esch, B. L. Feringa, *Science* **2004**, 304, 278.
20. A. P. de Silva, H. Q. N. Gunaratne, C. P. McCoy, *Nature* **1993**, 364, 42.
21. F. M. Raymo, S. Giordani, *J. Org. Chem.* **2003**, 68, 4158.
22. K. Rurack, A. Koval'chuck, J. L. Bricks, J. L. Slominskii, *J. Am. Chem. Soc.* **2001**, 123, 6205.
23. D. Parker, J. A. G. Williams, *Chem. Commun.* **1998**, 245.
24. A. P. de Silva, I. M. Dixon, H. Q. N. Gunaratne, T. Gunnlaugsson, P. R. S. Maxwell, T. E. Rice, *J. Am. Chem. Soc.* **1999**, 121, 1393.
25. These systems all operate using optical processes for read-out. At molecular distances ‘cross-talk’ between different input and output signals is very likely and

hard to overcome with respect to the wavelength of light. Just like other macroscopic signals, light is not an ideal means to address *individual* molecules that are embedded in ultra-compact circuits at the nanoscale. If molecular logic circuits are to mimic the behavior of conventional electronic components, the logic gates should influence the flow of current in a device for solid-state electronics.

26. J. M. Seminario, *Nature Mater.* **2005**, *4*, 111.
27. R. F. Service, *Science* **2002**, *295*, 2398.
28. C. J. Muller, J. M. van Ruitenbeek, L. J. de Jongh, *Physica C* **1992**, *191*, 485.
29. M. A. Reed, C. Zhou, C. J. Muller, T. P. Burgin, J. M. Tour, *Science* **1997**, *278*, 252.
30. R. M. Metzger, B. Chen, U. Höpfner, M. V. Lakshmikantham, D. Vuillaume, T. Kawai, X. Wu, H. Tachibana, T. V. Hughes, H. Sakurai, J. W. Baldwin, C. Hosch, M. P. Cava, L. Brehmer, G. J. Ashwell, *J. Am. Chem. Soc.* **1997**, *119*, 10455.
31. K. Stokbro, J. Taylor, M. Brandbyge, *J. Am. Chem. Soc.* **2003**, *125*, 3674.
32. F. Dulić, S. J. van der Molen, T. Kudernac, H. T. Jonkman, J. J. D. de Jong, T. N. Bowden, J. van Esch, B. L. Feringa, B. J. van Wees, *Phys. Rev. Lett.* **2003**, *91*, 207402.
33. M. Mayor, H. B. Weber, J. Reichert, M. Elbing, C. von Hänisch, D. Beckmann, M. Fischer, *Angew. Chem., Int. Ed.* **2003**, *42*, 5834.
34. M. H. van der Veen, M. T. Rispens, H. T. Jonkman, J. C. Hummelen, *Adv. Funct. Mater.* **2004**, *14*, 215.
35. M. H. van der Veen, H. T. Jonkman, J. C. Hummelen, *AIP Conf. Proc.* **2004**, *723*, 321.
36. C. I. Lewis, C. H. Langford, *Symbolic Logic*, 2nd ed., Dover Publications, New York **1959**.
37. See Appendix D for an overview of the 16 Boolean functions.
38. N. F. Phelan, M. Orchin, *J. Chem. Educ.* **1968**, *45*, 633.
39. This is operation (i) of the topological design program discussed in Chapter 3 of this thesis.
40. The combination of **6.1** and **6.4** (input channel A and B, respectively) results in the operator 'Inhibit A' (**6.1** and **6.4** in series) and 'Implication A' (**6.1** and **6.4** in parallel). When either **6.1** or **6.4** is connected in series with, for example, a 1,2,3,4-four-terminal benzene moiety, which provides for the input channel B in the 2,3 position and a read-out path along the 1,4-position, the 'NOT A' and 'Identity A' gates are obtained, respectively. The operators 'Inhibit B', 'Implication B', 'NOT B', and 'Identity B' are also available when connecting the aforementioned switches in the reverse order. The remaining two logical

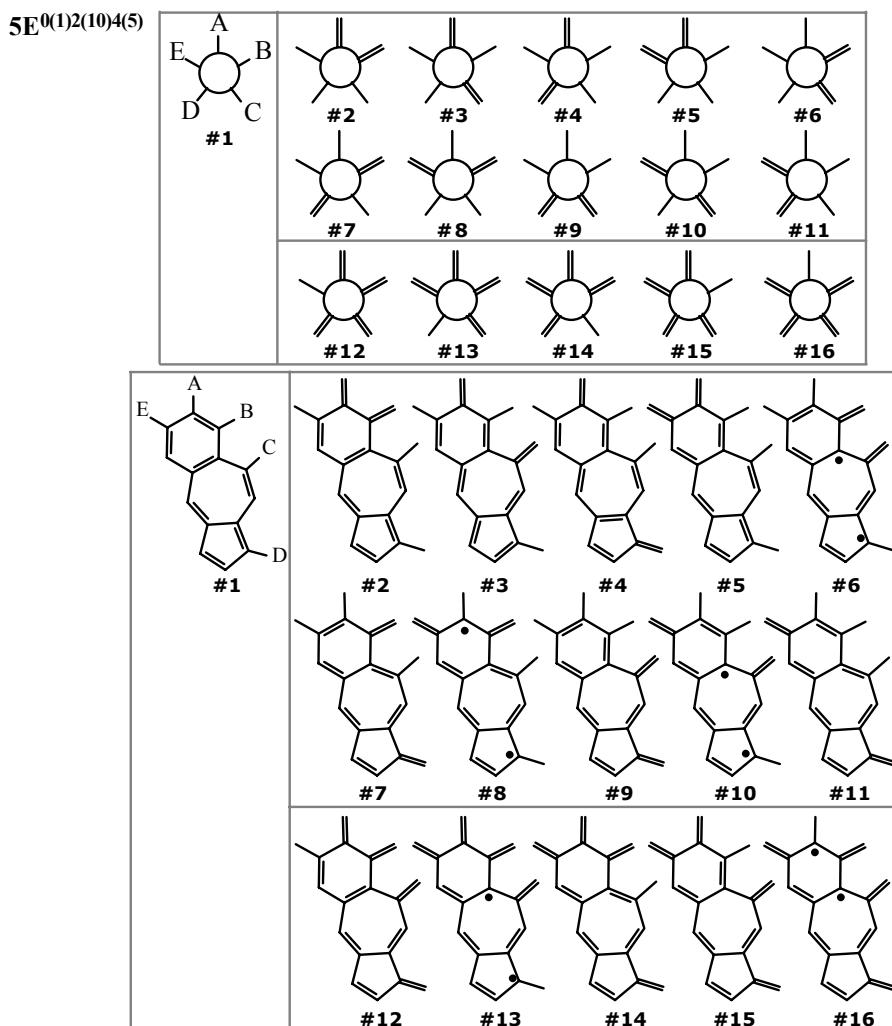
constants 'TRUE' and 'FALSE' can be constructed with two phenyl units of the same kind connected in series: 1,2,3,4-four-terminal benzene (TRUE; configured as given above) and 1,2,3,5-four-terminal benzene (FALSE for read-out paths along the 1,3-position).

41. These models are dubbed as Type A omniconjugated given that they are constructed from key-unit **A** of the topological design program for omniconjugated systems. More details of the topological properties of the pyracylene building block can be found in Chapter 3 of this thesis (see, Scheme 3.2).
42. The same can be done with distinctly different omniconjugated systems, however. Any omniconjugated system can be easily modified or extended by means of the topological design rules proposed in Chapter 3 of this thesis.
43. The standard archetype series of 6-terminal systems are given in Appendix C.
44. This table is an alternative way of outlining a group multiplication table as was discussed in Chapter 5.
45. The first structure of the series (i.e., **6.19#1**) has no doubly linked terminals. As a consequence, its cross-conjugated pathways follow directly from the non-Kekulé structures (i.e., (ae) from #5 and (bd) from #8). Model #13 is an omniconjugated molecule because it has no cross-conjugated pathways.
46. M. A. Reed, J. M. Tour, *Sci. Am.* **2000**, 282, 86.
47. M. Forshaw, R. Stadler, D. Crawley, K. Nikolić, *Nanotechnology* **2004**, 15, S220.
48. S. Ami, M. Hliwa, C. Joachim, *Chem. Phys. Lett.* **2003**, 367, 662.
49. A. P. de Silva, T. Gunnlaugsson, C. P. McCoy, *J. Chem. Educ.* **1997**, 74, 53.
50. V. Balzani, A. Credi, M. Venturi, *ChemPhysChem* **2003**, 3, 49.
51. V. Balzani, A. Credi, F. M. Raymo, J. F. Stoddart, *Angew. Chem., Int. Ed.* **2000**, 39, 3348.
52. S. Ami, M. Hliwa, C. Joachim, *Nanotechnology* **2003**, 14, 283.
53. B. Müller, J. Reinhardt, *Neural Networks: An Introduction*, Springer-Verlag, Berlin Heidelberg **1990**.
54. W. A. Goddard, III, D. W. Brenner, S. E. Lyshevski, G. J. Lafrate, *Handbook of Nanoscience, Engineering, and Technology*, CRC Press, Boca Raton **2002**, Chpt. 5.

Appendix A |

5-Terminal Archetype Series |

This appendix outlines the archetype series of a 5-terminal Type B omniconjugated system and the standard archetype series (top). Structure #4 is omniconjugated.



Appendix B

G^{5A} Group Multiplication Table

The table gives the correlation between the molecular archetypes (given around the table) of the 5-terminal archetype series outlined in Appendix A. The highlighted entries are related to the non-Kekulé structures and indicate cross-conjugated pathways. Only archetype #4 is omniconjugated.

	#1	#2	#3	#4	#5	#6	#7	#8	#9	#10	#11	#12	#13	#14	#15	#16	
G ^{5A}	E	ab	ac	ad	ae	bc	bd	be	cd	ce	de	abcd	abce	abde	acde	bcde	
#1	E	E	ab	ac	ad	ae	bc	bd	be	cd	ce	de	abcd	abce	abde	acde	bcde
#2	ab	ab	E	bc	bd	be	ac	ad	ae	abcd	abce	abde	cd	ce	de	bcde	acde
#3	ac	ac	bc	E	cd	ce	ab	abcd	abce	ad	ae	acde	bd	be	bcde	de	abde
#4	ad	ad	bd	cd	E	de	abcd	ab	abde	ac	acde	ae	bc	bcde	be	ce	abce
#5	ae	ae	be	ce	de	E	abce	abde	ab	acde	ac	ad	bede	bc	bd	cd	abed
#6	bc	bc	ac	ab	abcd	abce	E	cd	ce	bd	be	bede	ad	ae	acde	abde	de
#7	bd	bd	ad	abcd	ab	abde	cd	E	de	bc	bcde	be	ac	acde	ae	abce	ce
#8	be	be	ae	abce	abde	ab	ce	de	E	bcde	bc	bd	acde	ac	ad	abcd	cd
#9	cd	cd	abcd	ad	ac	acde	bd	bc	bcde	E	de	ce	ab	abde	abce	ae	be
#10	ce	ce	abce	ae	acde	ac	be	bcde	bc	de	E	cd	abde	ab	abcd	ad	bd
#11	de	de	abde	acde	ae	ad	bcde	be	bd	ce	cd	E	abce	abcd	ab	ac	bc
#12	abcd	abcd	cd	bd	bc	bcde	ad	ac	acde	ab	abde	abce	E	de	ce	be	ae
#13	abce	abce	ce	be	bcde	bc	ae	acde	ac	abde	ab	abcd	de	E	cd	bd	ad
#14	abde	abde	de	bcde	be	bd	acde	ae	ad	abce	abcd	ab	ce	cd	E	bc	ac
#15	acde	acde	bcde	de	ce	cd	abde	abce	abcd	ae	ad	ac	be	bd	bc	E	ab
#16	bcde	bcde	acde	abde	abce	abcd	de	ce	cd	be	bd	bc	ae	ad	ac	ab	E

Appendix C |

6-Terminal Archetype Series |

The standard archetype series of 6-terminal systems (Even set) displayed below is used to enumerate the molecular archetypes of the 6-terminal conjugated system discussed in Section 6.5.

6E ⁰⁽¹⁾²⁽¹⁵⁾⁴⁽¹⁵⁾⁶⁽¹⁾							
A F B E C D #1	#2	#3	#4	#5	#6	#7	#8
	#10	#11	#12	#13	#14	#15	#16
	#17	#18	#19	#20	#21	#22	#23
#32	#25	#26	#27	#28	#29	#30	#31

Appendix D

Truth Tables for Boolean Functions

In the following, truth tables of all 16 Boolean functions of two arguments (binary systems) are given. Above the values, the names of the operators are listed as used in this thesis. Each Boolean function can be expressed in terms of propositions A and B. The symbolic notation of the propositions is given below the name of the Boolean function. The propositions of TRUE and FALSE are tautology and contradiction, respectively.

Truth Tables

A	B	FALSE	AND	Inhibit B	Identity A	Inhibit A	Identity B	XOR	OR
			$A \wedge B$	$A \wedge \neg B$	$=A$	$\neg A \wedge B$	$=B$	$A \neq B$	$A \vee B$
0	0	0	0	0	0	0	0	0	0
0	1	0	0	0	0	1	1	1	1
1	0	0	0	1	1	0	0	1	1
1	1	0	1	0	1	0	1	0	1

Truth Tables

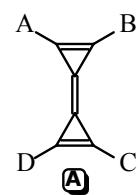
A	B	NOR	XNOR	NOT B	Implication B	NOT A	Implication A	NAND	TRUE
		$\neg(A \vee B)$	$A \equiv B$	$\neg B$	$B \supset A$	$\neg A$	$A \supset B$	$\neg(A \wedge B)$	
0	0	1	1	1	1	1	1	1	1
0	1	0	0	0	0	1	1	1	1
1	0	0	0	1	1	0	0	1	1
1	1	0	1	0	1	0	1	0	1

Summary

The use of electronic devices is indispensable in our daily life. The development of molecular electronics has an ambitious but realistic goal, the use of single molecules or an assembly thereof to achieve a huge density of devices on a very small scale. But how to wire more than two molecular wires? Are there realistic solutions and what would be the required kind of π -conjugation within the interconnecting molecules? And most of all: is it possible to use conjugated molecules to construct active and passive elements for complex integrated circuits? These fundamental questions which are essential for progresses in the field of molecular electronics are addressed in this thesis. It uses concepts and methods based on the topology of bonds within n -terminal π -conjugated systems. The terminals serve as attachment positions for other functional moieties.

A completely different way of describing conjugated molecules is by considering their topology of single and double bonds from a binary point of view. In this way, a statistical permutation procedure can be used in the search for a proper topology of bonds within the conjugated molecules, which should be able to interconnect many entities in a fully conjugated manner. All possible permutations of double link terminals over n terminals were represented by a collection of abstract objects called archetype series. An archetype with an even number of n double link terminals was member of a series consisting of 2^{n-1} archetypes. The archetypes only differ in arrangement and number of double linked terminals. It was now possible to use the archetypes as a tool to deduce the collection of structures representing all possible double bond patterns of an n -terminal π -conjugated system. An archetype series contained at least one non-Kekulé structure when it was obtained from a π -conjugated system that had a cross-conjugated pathway between two terminals. The number of non-Kekulé structures among the members of the archetype series was used as simple criterion to differentiate between the various classes of conjugation. This classification was in terms of the number of direct linear conjugated terminal pairs. By explicitly taking into account the conjugation between the terminals, this approach is distinctly different from all other methods dealing with conjugation.

n -Terminal π -conjugated systems without non-Kekulé structures in their archetype series contained molecules in their series that have conjugated pathways between all terminals. Molecules of this kind were defined as omniconjugated. For the first time, molecular architectures were proposed that can fulfill the simple function of wiring two or more molecular wires in a fully conjugated manner. A topological design scheme was presented as a tool for the axiomatic construction of a large number, possibly all, omniconjugated molecules. It was found that there are two types of omniconjugated systems. The Type A omniconjugated systems, constructed from key-model **A**, have the unique property that they remain omniconjugated upon the topological operation (i). This operation resembles the passage of a single quasi-particle through such





system. In having a persistent fully conjugated character, the Type A systems can be used as "soldering" points for many functional entities. In Type B omniconjugated systems, defined as obtainable from key-model **B** only, the permutation of single and double bonds along one pathway did create a cross-conjugated pathway between another pair of terminals. Type B systems have intriguing switching-type behavior and can be used to design active circuit elements.

From the quantum chemical evaluation of the electronic structure it was found that omniconjugated systems have the promise to facilitate the transport of charges between all terminals. The frontier orbitals of a 4-terminal omniconjugated system can be delocalized into the four terminals. In some cases, a new and intriguing phenomenon was observed: certain conjugated systems seem to show orthogonal directionality for positive and negative charges. This feature can be of use for many other applications of 4-terminal conjugated molecules.

A more robust theoretical understanding of the topological properties of n-terminal π -conjugated systems was obtained by considering their symmetry properties. The group multiplication table gave an overview of all possible cross-conjugated pathways as identified by the non-Kekulé structures of the system. This supports the explanation of the relation between the π -topology of an n-terminal system and its switching properties in terms of creating cross-conjugated pathways. It was possible to predict the topological changes upon the propagation of single quasi-particles (operation i) through n-terminal π -conjugated systems. This is essential for the design of logic gates based on this principle.

The ultimate step toward molecular electronic circuits is the implementation of logic functions within single molecules. It was shown that the π -topology of 6-terminal pyracylene derivatives could be used to implement many logic operations. This generic target type for this kind of logic gates is operated by two input signals A and B, which both control the kind of conjugation of the read-out channel T. This read-out path can be switched between linear conjugated ('1') and cross-conjugated ('0'), which changes its ability to transport charges. In an extended version, bifunctional elements can be defined that can perform different logic operations (e.g., "NOT B" and "AND") depending on the status of a control channel 'C'. These gates might constitute the most densely integrated logic structures one can imagine for a wide variety of logic operations at the molecular level. The discussion was limited to systems in which an input signal stems from two terminals that have the same topology, which constitutes just one option. It stimulates the study of other ways to enter the input and to obtain output from conjugated systems.

Independent of the applicability in terms of conjugated molecules, the binary treatment of single and double bonds are mathematically valid for other topological systems as well. It is highly intriguing to investigate other possible applications of the proposed "topologic" concepts for binary systems.

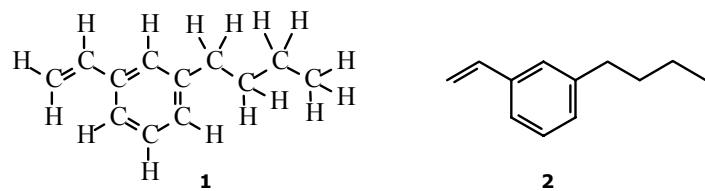
Samenvatting

π-Logica, ook een 'spel' voor niet chemici

Vandaag de dag is het de normaalste zaak om even een tekstberichtje te versturen per mobiele telefoon of iets op te zoeken op het internet. Computers zijn eigenlijk onmisbaar geworden in ons dagelijks leven. De enorme invloed van de markt dwingt de industrie tot miniaturisatie zodat snellere computers en geheugens met hogere opslagdichtheden gerealiseerd worden. De ontwikkeling van technologische systemen die de dimensie van een nanoschaalafmeting hebben wordt nanotechnologie genoemd. Hierbij is één nanometer (nm) een miljoenste millimeter (10^{-9} m) wat in de orde van grootte van enkele moleculen ligt. Eén van de mogelijkheden om het aantal schakelingen op een chip te vergroten kan het gebruik van moleculen als bouwstenen worden. Dit kan verstrekkende gevolgen hebben binnen de nanotechnologie. Gedacht kan worden aan nieuwe eigenschappen van materialen en nieuwe toepassingen, denk bijvoorbeeld aan LCD en TFT schermen, die wellicht op een andere manier niet te realiseren zijn.

Het onderzoek in de moleculaire elektronica richt zich voornamelijk op het gebruik van moleculen als bouwstenen van elektronische circuits. De moleculaire elektronica staat nog in de kinderschoenen: het is grotendeels in het stadium van fundamenteel wetenschappelijk onderzoek. Dit proefschrift hoopt een bijdrage te leveren aan de ontwikkeling van geïntegreerde schakelingen (integrated circuits, IC's) gebaseerd op enkele moleculen.

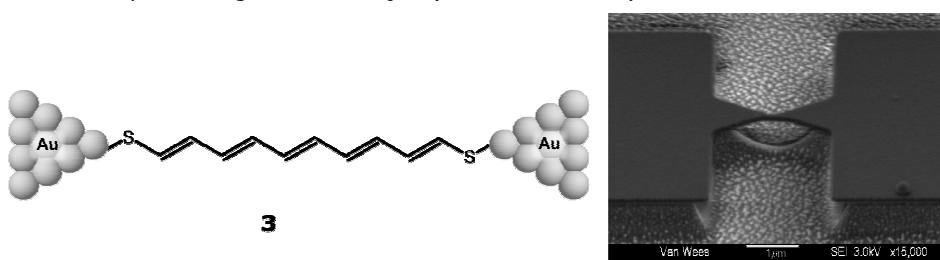
Moleculen hebben het voordeel dat je ze eenvoudig kunt veranderen en zo een andere functionaliteit kunt inbouwen. Eigenlijk zijn het de kleinste deeltjes die nog de eigenschappen van een materiaal kunnen bezitten. Een molecuul bestaat uit meerdere atomen. Ieder atoom wordt aangeduid met een letter, zoals 'C' voor koolstof en een 'H' voor waterstof. Chemici gebruiken schematische tekeningen om moleculen weer te geven. Hierin wordt een binding tussen atomen weergegeven met verbindingsstreeppjes. In Figuur 1 is een enkele binding tussen twee atomen afgebeeld met een '-' en een dubbele binding met een '='. Een dubbele binding bevat 'extra' elektronen welke een belangrijke rol spelen binnen de moleculaire elektronica. In Figuur 1 is molecuul **1** opnieuw getekend maar dan in een versimpelde weergave. Het is gebruikelijk om de koolstof (C) en waterstof (H) aanduiding zoveel mogelijk 'weg te laten'.



Figuur 1 Structuur 2 is de vereenvoudigde weergave van 1-butyl-3-vinylbenzeen 1.

Het 'solderen' van moleculaire stroomdraadjes

De huidige stand van zaken in de moleculaire elektronica is dat wetenschappers min of meer in staat zijn om moleculen te maken die de werking van elektronisch apparatuur ('device') of een onderdeel daarvan kunnen nabootsen. Een voorbeeld van een simpel molecuul dat als een elektrisch draadje kan werken is afgebeeld in Figuur 2. Dit molecuul heeft zwavel (S) groepen aan beide uiteinden die zich bij voorkeur met goud verbinden. Molecuul **3** kan zo tussen twee elektronische contacten geplaatst worden (wat niet eenvoudig is!). Op deze manier is het mogelijk om het transport van geladen deeltjes (zoals elektronen) te bestuderen.

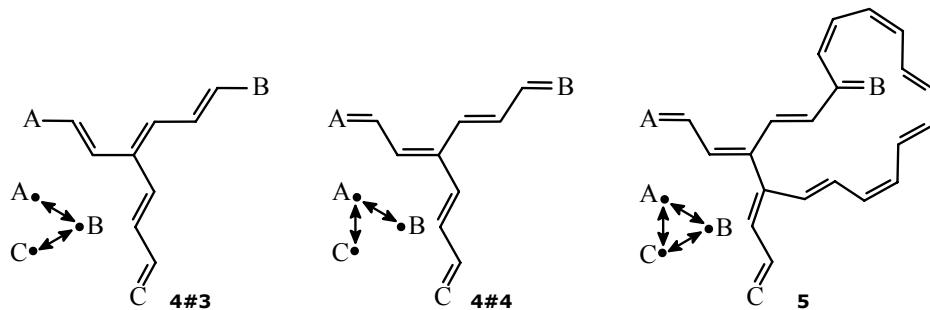


Figuur 2 Een cartoon van een molecuul tussen twee goud (Au) elektrodes. Rechts een foto* van zulke elektrodes (donkere gedeeltes) waarbij de witte balk 10^{-6} m aangeeft.

Niet alle moleculen kunnen gebruikt worden om de werking van een stroomdraadje na te bootsen. Dit kan eigenlijk alleen maar goed als een molecuul dubbele en enkele bindingen bevat die elkaar afwisselen (zie het '---' patroon van molecuul **3**). Door deze opeenvolging zijn de 'extra' elektronen van de dubbele bindingen niet strikt gebonden aan een bepaald atoom. Vandaar dat dergelijke moleculen een elektrische geleiding kunnen laten zien. De opeenvolging van enkele en dubbele bindingen wordt *conjugatie* genoemd. Chemici noemen een dubbele binding ook wel π -binding. Voor het transport van geladen deeltjes door een molecuul is π -conjugatie dus heel belangrijk. Molecuul **2** bevat niet het juiste bindingspatroon tussen de twee uiteinden en zal daarom een minder goed functioneren als 'stroomdraadje' in vergelijking met molecuul **3**.

Een ander essentieel onderdeel van een elektronisch circuit is een kruispunt van meerdere draadjes. Een voorbeeld van drie 'gesoldeerde' moleculaire draadjes A, B en C is afgebeeld in Figuur 3. Aan de hand van het patroon van de bindingen tussen de uiteinden A, B en C kunnen we beoordelen of molecuul **4#3** als een kruispunt van moleculaire draadjes kan fungeren. Dan valt op dat de afwisseling van bindingen tussen uiteinde A en C in **4#3** onderbroken is door een extra enkele binding. Dit

* Met dank aan Eek Huisman uit de vakgroep van Prof. dr. B. van Wees.



Figuur 3 Het ‘solderen’ van moleculaire draadjes tot een goed kruispunt in molecuul **5**.

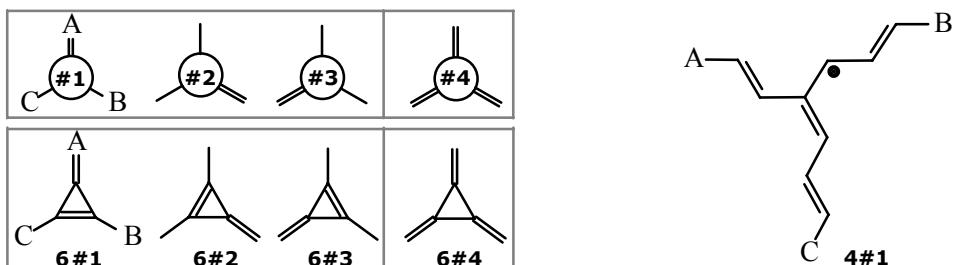
noemen we crossconjugatie in plaats van conjugatie. Het is bekend dat er langs dergelijke paden v  l minder transport van ladingen plaatsvindt.

Grofweg gezegd is het pad tussen **A** en **C** in **4#3** in een niet-geleidende toestand en tussen **A** en **B** in een geleidende toestand. Dat betekent dus dat er met molecuul **4#3** niet een echt kruispunt van moleculaire draadjes is gerealiseerd! Door de bindingen tussen **A** en **B** om te keren van enkel naar dubbel en vice versa wordt dit probleem niet verholpen. Een voorbeeld hiervan is molecuul **4#4**, dat eigenlijk slechts een andere vorm is van **4#3**. Alleen door een extra draadje ('fly-over') tussen **B** en **C** te plaatsen kan een goed kruispunt getekend worden. In molecuul **5** zijn alle paden wel π -geconjugueerd: tussen **A** en **B**, **A** en **C**, en tussen **B** en **C**. Het probleem is echter dat molecuul **5** waarschijnlijk niet gemakkelijk gemaakt kan worden. Mede door de gebruikte 'fly-over' zal het niet stabiel zijn.

De situatie wordt alleen maar erger wanneer er geprobeerd wordt om vier moleculaire draadjes met elkaar te verbinden. Er zijn nog meer 'fly-overs' nodig om het probleem van hierboven te omzeilen. Daar ligt meteen ook de uitdaging van het onderzoek gepresenteerd in dit proefschrift.

Dit proefschrift

Vreemd genoeg zijn er bij ons weten nog geen andere wetenschappers geweest die geprobeerd hebben om een antwoord te vinden op de vraag: "Hoe kun je meerdere moleculaire draadjes op de juiste manier aan elkaar 'solderen'?" Dit is echter essentieel voor de ontwikkeling van moleculaire elektronica. Naast draadjes bevat een elektronisch circuit ook actieve elementen zoals diodes en transistors. In het onderzoek beschreven in dit proefschrift is er op een slimme manier gebruik gemaakt van enkele en dubbele bindingen om (logische) schakelaars te ontwerpen. Eigenlijk is het een topologisch spelletje met π -geconjugeerde bindingen. Dit wordt hier '  -logica' genoemd.



Figuur 4 Een methode om alle mogelijke bindingspatronen te vinden van een molecuul (linksonder) is door deze af te leiden van oervormen (linksboven). Structuren die noodgedwongen twee opeenvolgende enkele bindingen bevatten (zoals **4#1**) zijn op die plaats gemarkeerd met een stip (radicaal) en worden open-shell structuren genoemd.

Zoals hierboven is uitgelegd, kan de conjugatie langs een pad tussen twee uiteinden veranderen als je alle bindingen van een ander pad omkeert (zie **4#3** en **4#4**). Dit kan grote consequenties hebben voor het transport van geladen deeltjes door het molecuul. Daarom is er in Hoofdstuk 2 allereerst gezocht naar een systematische methode om alle verschillende bindingspatronen van een molecuul te analyseren. Deze methode dient als basis voor al het overige werk dat beschreven is in dit proefschrift. Een object met n uiteinden heeft oervormen die onderling alleen verschillen in het aantal en de positie van dubbel gebonden uiteinden (zie Figuur 4 linksboven). In principe is dit een statistische analyse die ook gebruikt kan worden voor toepassingen buiten de chemie. De abstracte oervormen vertellen dus nog niets over de structuur van een molecuul maar zijn een hulpmiddel om alle mogelijke bindingspatronen van een molecuul te verzamelen (zie de vormen van molecuul **6** in Figuur 4). De oervormen geven precies aan welke uiteinden dubbel gebonden kunnen zijn (zie bijvoorbeeld object **#2** en structuur **6#2**). Vervolgens worden de overige dubbele bindingen in het molecuul geplaatst waarbij wordt gezorgd dat elk atoom twee enkele en één dubbele binding bevat.

Echter, er is niet altijd een bindingspatroon te vinden waarvoor alle atomen precies twee enkele en één dubbele binding bevatten. Een voorbeeld is gegeven voor één van de vormen van **4** (zie Figuur 4 rechts; er zijn nog twee andere vormen gegeven in Figuur 4). Nadat alle uiteinden van **4#1** een enkele binding gekregen hebben en na het plaatsen van de overige dubbele bindingen blijft er één atoom over met twee enkele bindingen. Dit atoom van **4#1** is gemarkeerd met een stip (radicaal). Molecuul **4#1** heeft een open-shell structuur (d.w.z. niet alle elektronen zijn gepaard).

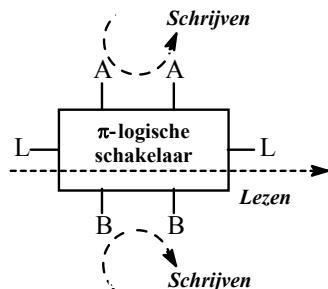
Er is een simpel verband gevonden tussen hoe goed een molecuul geconjugeerd is en hoeveel open-shell structuren zijn oervormen serie bevat: des te minder goed π -geconjugeerd (meer crossgeconjugeerde paden), des te meer open-shell

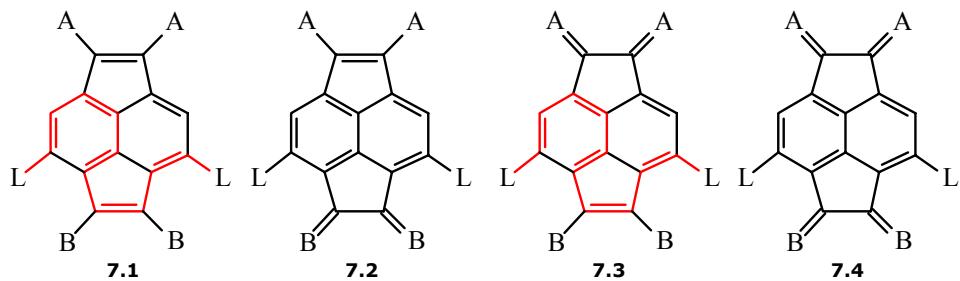
structuren. Daarnaast kwam er een ander belangrijk aspect aan het licht. Moleculen zonder open-shell structuren, zoals **6**, hebben geconjugeerde wegen tussen alle uiteinden. Dit betekent dat alle paden tussen de uiteinden zich in een 'geleidende' toestand bevinden en dat alle vormen kunnen dienen als kruispunt voor moleculaire draadjes! Om aan te geven dat moleculen als **6** een speciale soort van π -conjugatie bezit noemen we ze omnigeconjugeerd.

Naarmate een molecuul meer uiteinden heeft wordt het steeds moeilijker om realistische moleculen te bedenken die omnigeconjugeerd zijn. Daarom is er in *Hoofdstuk 3* een schema ontwikkeld om, in principe, een oneindig aantal omnigeconjugeerde moleculen te ontwerpen. Bovendien is er zo een beter beeld ontstaan van de topologische eigenschappen van deze moleculen. Daarna is er in *Hoofdstuk 4* gekeken of ze ook daadwerkelijk geladen deeltjes zouden kunnen transporteren. De vraag of omnigeconjugeerde moleculen als kruispunt zouden kunnen fungeren werd in de meeste gevallen positief beantwoord. Echter, theoretisch gezien bezitten sommige van hen gescheiden kanalen voor positief en negatief geladen deeltjes. Deze waarneming kan een interessante toepassing vinden in elektronische circuits gebaseerd op moleculen.

In het laatste deel van het proefschrift ligt de nadruk op actieve elementen zoals logische schakelaars. Er is bijna nog geen onderzoek gedaan naar hoe moleculen gebruikt kunnen worden om de *geleiding* van een systeem te schakelen. Vanuit ons oogpunt kan er met geconjugeerde moleculen op dezelfde manier geschakeld worden als de macroscopische schakelaars die een ieder kent.

De ontworpen π -geconjugeerde moleculen bezitten paden die in twee verschillende 'standen' kunnen voorkomen. Een pad tussen twee uiteinden kan geconjugeerd zijn ('geleidend/aan) of crossgeconjugeerd ('niet geleidend/uit). In Figuur 4 hebben we gezien dat een pad kan schakelen tussen geconjugeerd en crossgeconjugeerd (aan en uit) door de bindingen van een ander pad om te keren (zie **4#3** en **4#4**). De aan- en uit-stand van een pad kan gedefinieerd worden als een '0' en '1', ofwel als een binair systeem. Door nu een extra pad toe te voegen dat als tweede invoerwaarde dient, kunnen er *logische* elementen ontworpen worden. Een systeem met zes uiteinden (twee uiteinden om te lezen en vier uiteinden om te schrijven over twee paden, zie schema) kent vele manieren van schakelen. In *Hoofdstuk 5* wordt er een door ons ontwikkelde methode beschreven die de relatie beschrijft tussen de symmetrie en de schakel-eigenschappen van π -geconjugeerde moleculen. Door de symmetrie van het systeem te beschouwen is het relatief eenvoudig geworden om π -logische elementen te





Figuur 5 Elk molecuul van **7** geeft een toestand van een 'NOT B' logisch element weer. Het pad tussen A en B zijn de twee schrijfkanalen en L is het leeskanaal. De waarde van 'L' is '1' behalve als het pad niet geconjugeerd is: geen aaneenschakeling van -en = bindingen geeft een uitleeswaarde van '0' ('uit' in **7.2** en **7.4**).

ontwerpen. Dit laatste aspect vormt de grootste uitdaging van het onderzoek en wordt behandeld *Hoofdstuk 6*.

In Figuur 5 zijn de vier toestanden van molecuul **7** gegeven welke een NOT B logisch element nabootsen. Dit betekent dat alleen wanneer de uiteinden 'B' dubbel gebonden zijn, het pad tussen de lees uiteinden 'L' niet meer geconjugeerd is (zie **7.2** en **7.4**). Het centrale gedeelte van molecuul **7** bezit bijzondere topologische eigenschappen en biedt daarom nog veel meer mogelijkheden. Door de posities van de zes uiteinden te variëren is het mogelijk om alle standaard logische elementen van twee argumenten te ontwerpen (de 16 Boolean functies). Daarnaast kunnen er bifunctionele elementen ontworpen worden. Ook dit zijn nog steeds enkele moleculen, echter die, afhankelijk van een derde invoerwaarde, kunnen schakelen tussen twee logische functies. Deze resultaten zijn zeer bemoedigend voor het ontwerpen van zeer compacte en complexe circuits bestaande uit π -logische schakelmoleculen.

Samenvattend geeft dit proefschrift topologische 'regels' voor het ontwerpen van elektronische circuits gebaseerd op π -geconjugeerde moleculen. Verder laat het zien dat de topologie van π -geconjugeerde moleculen met n -uiteinden de benodigde interne logica bezit zoals die gebruikt kan worden voor het ontwerpen van logische elementen en geïntegreerde circuits gebaseerd op moleculen.

De ontwikkelde π -logica, het topologische 'spelletje' met dubbele en enkele bindingen, kan ook interessant zijn voor toepassing buiten de moleculaire elektronica. In feite is alles gebaseerd op twee mogelijke toestanden (een enkel of dubbel binding) en geldt dus voor binaire systemen in het algemeen.

Dankwoord

Dit zijn de laaste 1029 woorden van het proefschrift dat mijn werk van de afgelopen vier jaar beschrijft. Voor mij ze zijn nog belangrijker dan de overige 46171 woorden omdat ik ervan overtuigd ben dat zonder de hulp, begeleiding, steun en bijdrage van velen, dit proefschrift niet tot stand zou zijn gekomen. Ik kan slechts hopen dat de simpele woorden die ik hier gebruik een goede afspiegeling van de werkelijkheid zullen zijn. Aan allen die mij op een persoonlijk en wetenschappelijk vlak hebben verrijkt betuig ik mijn oprechte dank.

Allereerst wil ik mijn promotor Kees Hummelen bedanken voor zijn vertrouwen om mij als promovenda aan te stellen. (Toch een behoorlijk groot risico zo'n eerste.) We hadden allebei niet echt een goed idee waar ik aan zou beginnen waardoor voor mij de uitdaging alleen maar groter was. Jou enthousiasme tijdens onze ontelbare brainstorm sessies over het jou zo gelievende onderwerp waren voor mij zeer motiverend en inspirerend. Veel dank voor de begeleiding en de goede (!) zorgen. Dit geldt ook voor mijn copromotor Harry Jonkman. Harry, jij was, net als vele anderen, in het begin zeer sceptisch over dit onderzoek. Gelukkig hebben Kees en ik je kunnen overtuigen van de potentie ervan. Volgens mij hebben de resultaten beschreven in Hoofdstuk 4 definitief het tij doen keren. Door jouw begeleiding ben ik in staat geweest om de physische kant van het onderwerp te belichten. Onze vele discussies waren vaak ware veldslagen, zeer vermoeiend of verwarrend. Ik zal ze daarom, in de positieve zin van het woord, niet gauw vergeten. Echter, dit alles werd mede mogelijk gemaakt door Bert de Boer. Bert, jij hebt zo'n vijf jaar geleden een goed woordje voor mij gedaan bij Kees. Hartelijk dank voor deze goede start.

Special thanks are due to the members of the manuscript committee Jasper Knoester, Siegmar Roth and Fred Wudl for their effort reviewing the manuscript and for their valuable suggestions. I would like to thank Fred Wudl for a stimulating discussion during the preparation of the 'Omniconjugation' paper.

I wish to gratefully acknowledge Dr. Joseph L. Teeters from Laurel (Maryland) for allowing me to use his Escher-type artwork of ' π ' as inspiration for the cover of my thesis. With respect to this, I greatly appreciate the efforts of Dr. E. Maor.

Een speciaal woord van dank gaat uit naar Alex Sieval en Minze Rispens. Vooral voor de eerste jaren van mijn promotie ben ik jullie veel dank verschuldigd voor de vele suggesties en heftige discussies op onze kamer; ons whiteboard heeft veel geleden. Alex, ik ben blij jou als kritische en gezellige collega te hebben gehad. Gelukkig ben je na al die verschillende werkgevers nog steeds niet van werkplek veranderd (zal het er ooit nog van komen?). Minze, door jou heb ik dit onderzoek mogen doen. Bedankt voor het bedenken van het eerste omniconjugeerde molecuul zodat het project kon starten. Al 'mocht' het van de baas niet zo lang duren, ook de tijd op ons lab was erg gezellig. Ook de andere twee groepsleden van het eerste uur wil ik hier graag noemen: Joop Knol (koffie in de 'clean room') en Anthony England ("You've drawn an orbital of the Michelin Man!").

Mijn dank gaat uit naar Hennie van Dijk (en de dubbele gereduceerde versie ervan). Jij bent gestart met de realisatie van onze π -logische moleculen. Daar gaat het uiteindelijk om. Ik hoop dat je, net als mij, veel plezier hebt beleefd aan onze samenwerking. I would like to take this opportunity to thank the third member of the ‘ π -Logic team’ my colleague Daniel Myles who graciously give his time to polish the manuscript. Your helpful suggestions for improvements and corrections are gratefully acknowledged. I’m sure you will continue the synthetic and experimental part of this work together with Eek Huisman and, perhaps later on, Sense Jan van der Molen.

Mijn complimenten gaan uit naar alle ‘Bucky boys and girls’. De groep oogt klein maar de inzet, toewijding en saamhorigheid is groot. Dat mijn promotietijd een leuke tijd was, is daarom ook toe te schrijven aan volgende de mensen: Alfred, de ‘beerbrothers’ Frank en Floris, Linda (secretariaat), Patrick, Reinder (techniek) en de studenten Erik, Hans, Iwona, Jan Alma, Maaike, Renske en Ben (success with H. T.). Vooral de werkweken, vele uitstapjes en aktiviteiten ‘s avonds zal ik niet gauw vergeten. Lacra, it was a pleasure for me to share rooms with you during the many trips we’ve had. Verder wil ik Tineke Snijders bedanken. Helaas is het onderzoek dat jij gedaan hebt niet in dit proefschrift terecht gekomen, maar dat wil niet zeggen dat ik je niet met veel plezier heb begeleid. Naast de overige ex-leden van de Hummelen-groep wil ik de (ex-)bewoners van de Teuben/Hessen labzalen bedanken voor de soms rare maar plezierige sfeer tijdens de koffiepauzes, E-wing borrels en (‘stampende’) eet-bijeenkomsten.

Er nog een aantal (ex-)Zernike gangers die me de afgelopen jaren zeer dierbaar zijn geworden. Peter en Hilda, bedankt voor jullie vriendschap, steun, vele volleybalritjes, uitjes en gezelligheid! Renate, bedankt voor alle hulp en gezelligheid zowel binnen en vooral (!) buiten werktijd. Nu kunnen we samen spoken... Daarnaast wil ik alle ‘Upsewupsers’ bedanken voor de vele jaren van gekheid in Het Hok en daarbuiten. Ook Michiel, Marjon (vdV), Richard (kontie) en Maaike wil ik hier noemen. Ik hoop dat anderen die ik niet met name noem (waaronder de prominente leden van Zus & Zo en de RD350 motorclub) zich ook aansproken zullen voelen.

Arjen en Eelco wil ik graag bedanken voor de grappen en grullen tijdens de nachtelijke uren van het schrijven. Al wil ik niet al te veel denken, toch denk ik dat jullie ervoor hebben gezorgd dat de avondmens in mij geen kluizenaar is geworden. Kirsten, heel erg bedankt voor je professionele hulp voor het omslagontwerp.

Graag wil ik mijn naaste familie, mijn ouders in het bijzonder, hartelijk bedanken, voor alles.

Arjen (M), ik ben blij dat je keer op keer de strijd bent aangegaan met jou grootste concurrent van de afgelopen tijd: mijn laptop. Jij bent mijn grote steun en toeverlaat. Ook al leek het de afgelopen jaren niet altijd zo, jij staat tot nu toe (en hopelijk nog veel langer) steeds op de eerste plek.

