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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

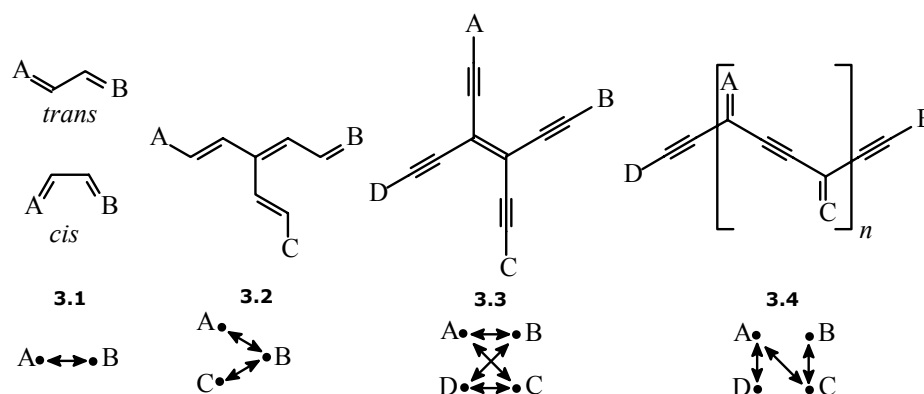


Figure 3.1 (Top) Schematic representation of conjugation in substituted (*A*, *B*, *C*, and *D*) compounds: 2-terminal linear (*cis/trans*) conjugated butane **3.1**; 3-terminal cross-conjugated 4-(1-propenyl)-heptatriene **3.2**; 4-terminal cross-conjugated tetraethynyl-ethene **3.3** and iso-poly(diacetylene) **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 ($A \times C$ in **3.2**) compared to linear conjugated one ($A \leftrightarrow B$ 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 $A \leftrightarrow B$ 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.

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,

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| <p>Omniconjugation is defined as the property of molecules, having direct linear π-conjugated pathways between <i>all</i> connected moieties.</p> |
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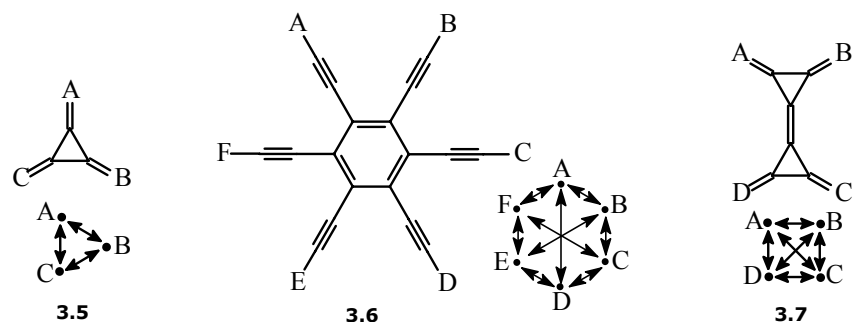


Figure 3.2 (Top) Schematic representation of 3- and 4-terminal substituted omniconjugated compounds [3]radialene **3.5** and cyclopropylidenecyclopropane **3.7**; six-terminals cross-conjugated hexa-ethynylbenzene **3.6**. (Bottom) Corresponding topological connectivity schemes of linear conjugated pathways.

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 $A \leftrightarrow B$ 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” ($A \leftrightarrow B$ in **3.6**), *cis* or *trans* ($A \leftrightarrow B$ 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: $A \leftrightarrow B$, $A \leftrightarrow C$, $A \leftrightarrow D$, $B \leftrightarrow C$, $B \leftrightarrow D$, and $C \leftrightarrow D$ 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 $A \times D$ and $B \times C$ (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.,

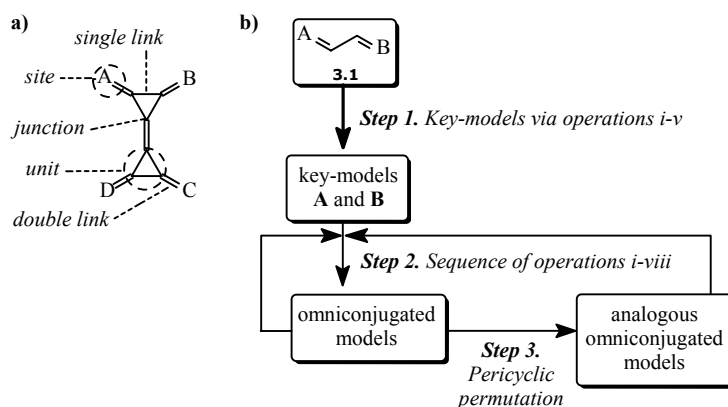


Figure 3.3 (a) The terminology used in the topological algorithm. (b) The flow diagram for the design of omniconjugated models.

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:

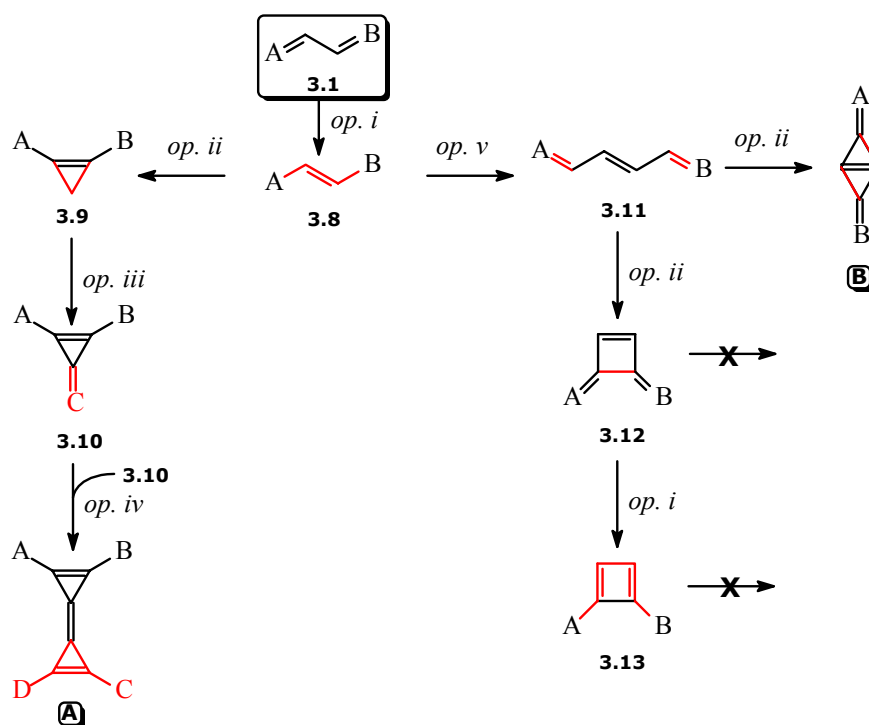
- Op. i)** Permutation of all links from single to double and *vice versa* along a conjugated pathway.
- Op. ii)** Units are created upon insertion of any desired link(s) between junctions.

- 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 $C \leftrightarrow A$ and $C \leftrightarrow B$. *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.

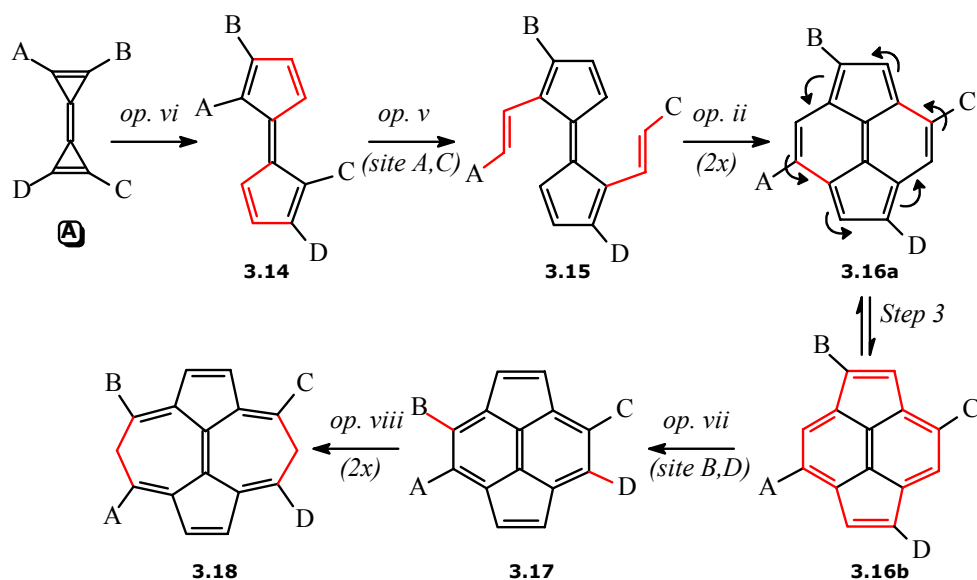
The second key-model, **B**, is derived from the same linear conjugated counterpart of model **3.1** as shown in Scheme 3.1. *Operation v.* First, the linear analogue **3.11** is created via operation (v) by extending both single links with a double link. The conjugated path is not changed, only extended.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

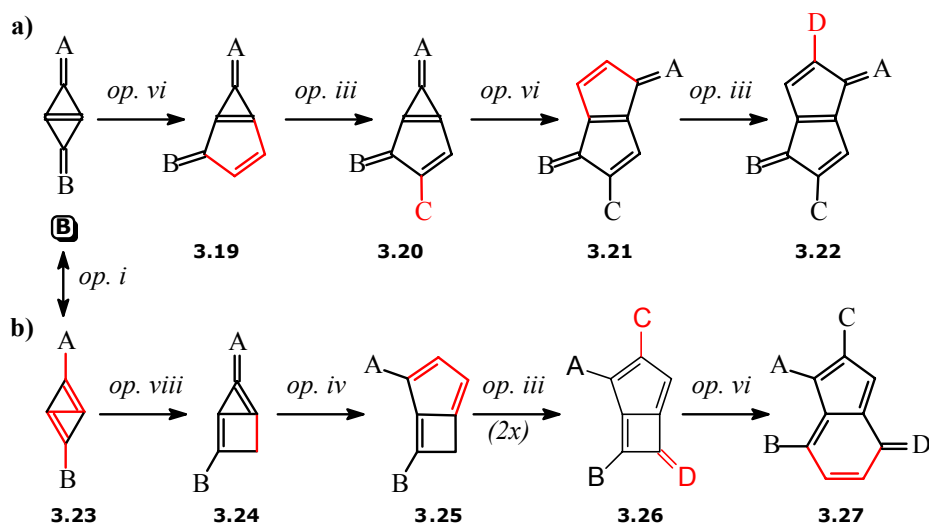
the other operations. As an extension, it serves as a tool for an interactive design of a target omniconjugated architecture reducing thereby a long-lasting design algorithm. The single link between site A and B in **3.17** is not involved in *any* conjugated pathway. The same is true for the link between 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



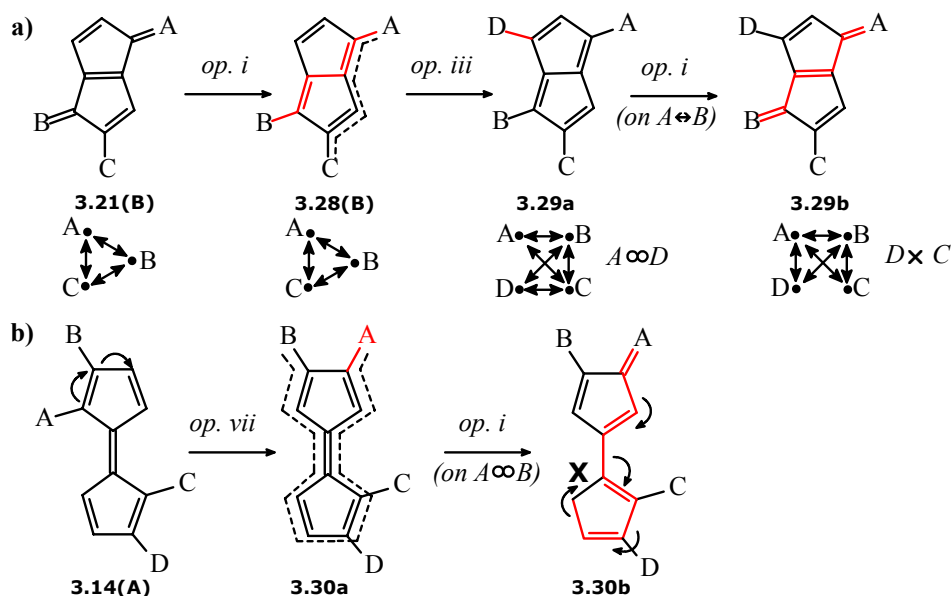
Scheme 3.3 Systematic construction of omniconjugated models from key-model **B** resulting in odd-membered units in a) or even- and odd-membered unit in b).

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 $A \infty B$. Looped 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. Looped 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 ($A \infty D$ 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.

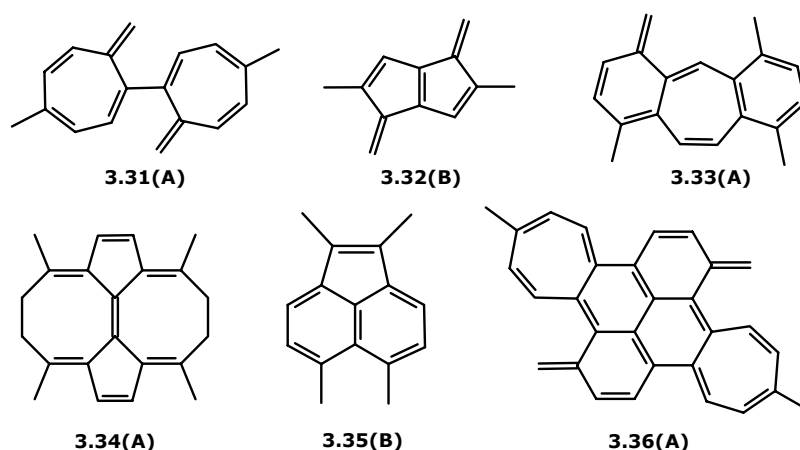


Figure 3.4 Examples of different architectures of omniconjugated models with four sites (without their labeling), obtained from key-model *A* or *B* (in parentheses): linked polycyclic model **3.31**; cata-condensed polycyclic models **3.32** and **3.33**; peri-condensed polycyclic models **3.34**, **3.35**,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

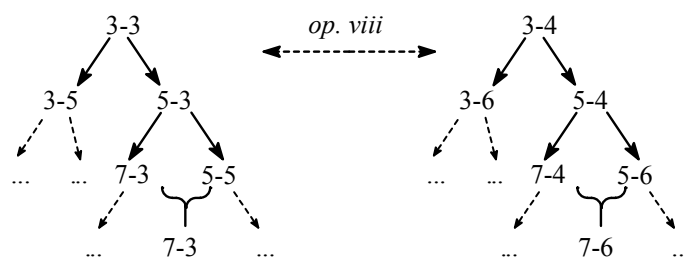
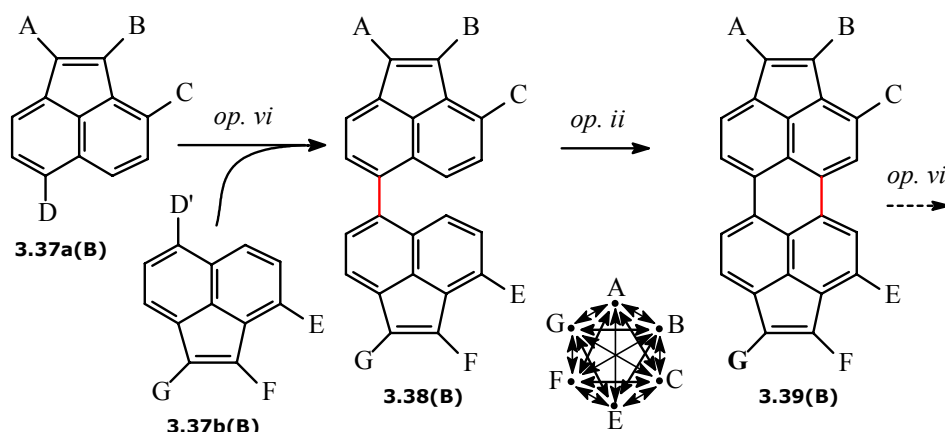


Figure 3.5 Flow diagrams illustrating the systematic growth of bicyclic models by means of operation (vi), for models containing only odd-membered units (left) or with an even- and odd-membered unit (right). They are interchangeable via operation (viii).

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**.

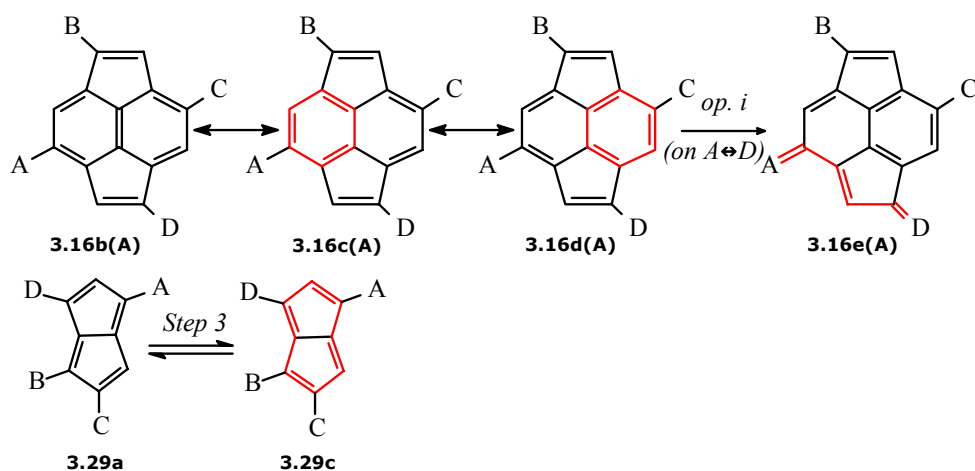
All omniconjugated models discussed up to this point have four sites while it is straightforward to go beyond this number. This can be realized with operation (iv) that allows for the interconnection of omniconjugated models. In this way, omniconjugated models with an unlimited number of sites can be 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., $A\infty D$ 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** ($A \infty D$).

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.

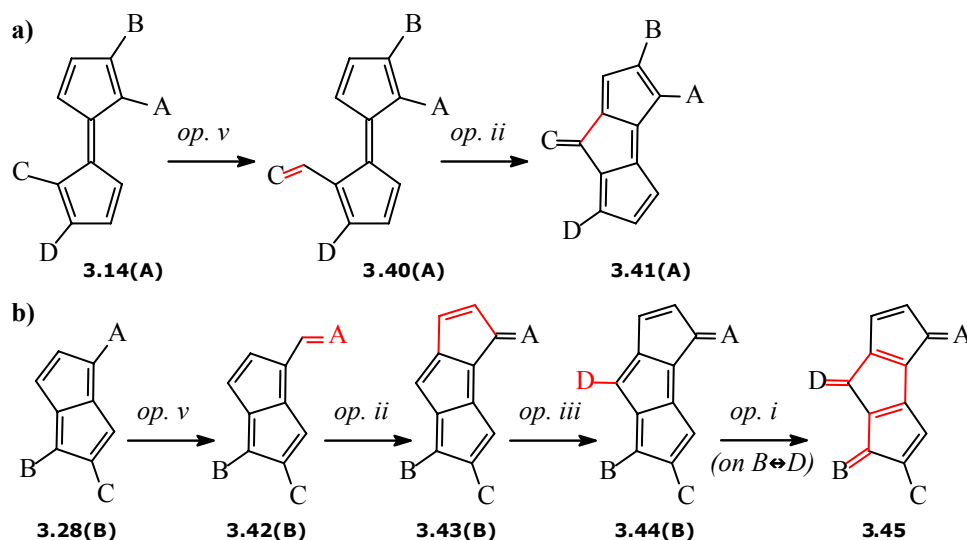
Operation (i) can be employed to quickly determine whether the omniconjugated model with four or more sites is a Type A or Type B system. While Type A models always remain omniconjugated (see for example **3.16d/e**), Type B models possess a cross-conjugated pathway after executing operation (i). For 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 $A \leftrightarrow C$ in **3.44** is converted into $A \times C$.

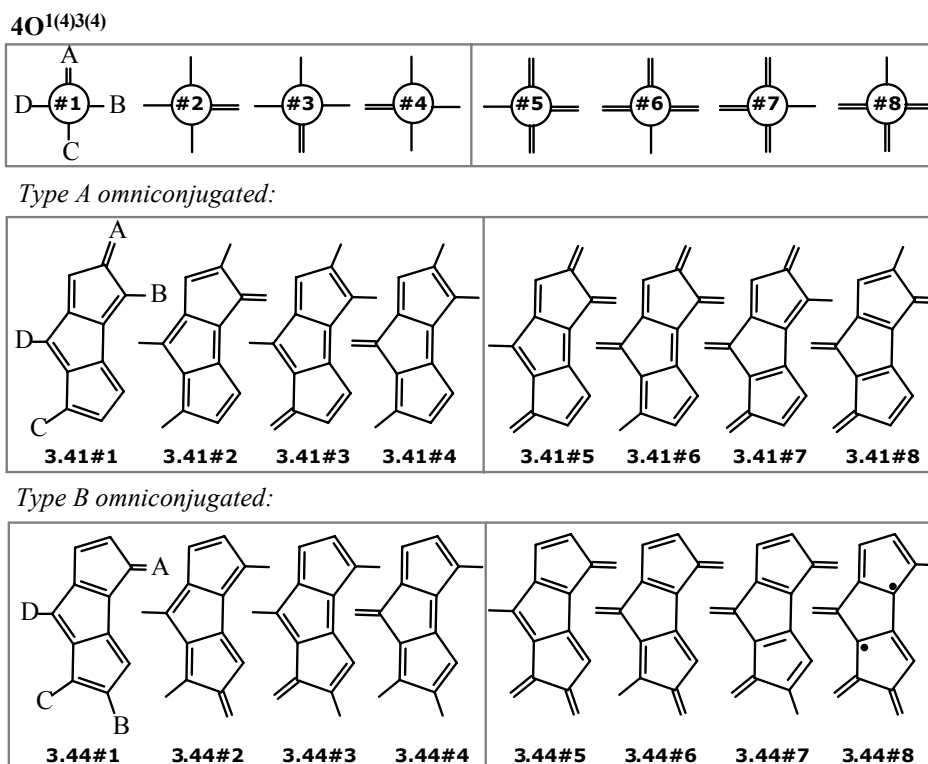


Figure 3.6 (Top) Standard 4-terminal archetype series (Odd set). (Bottom) The corresponding archetype series of the Type A and Type B omniconjugated systems **3.41** and **3.44**, respectively. Archetype **3.44#8** is a non-Kekulé structure.

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.

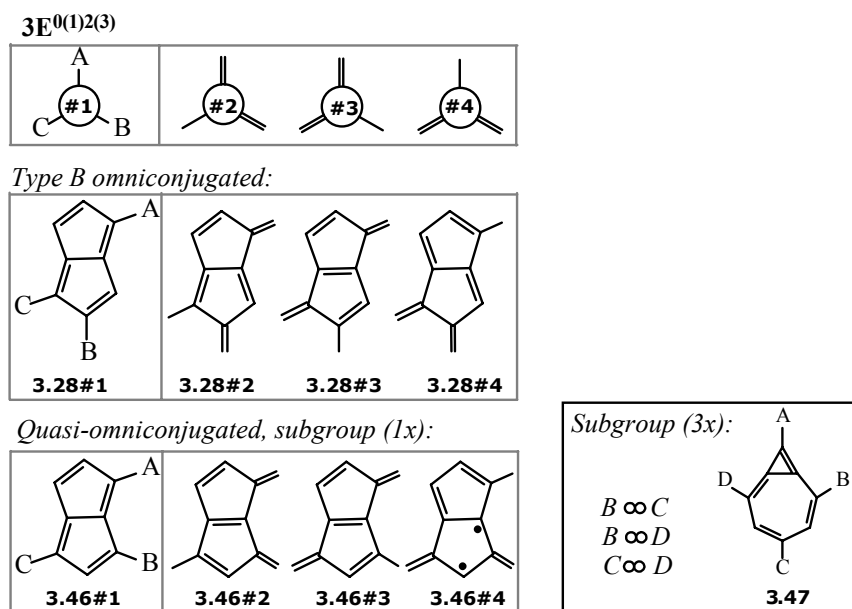


Figure 3.7 (Top) Standard 3-terminal archetype series (Even set). (Bottom) The corresponding archetype series of Type B omniconjugated system **3.28** and quasi-omniconjugated system **3.47**. (Index) Quasi-omniconjugated system with three looped pathways (i.e., subgroup (3x)).

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 $B \infty C$ and the non-Kekulé structure **3.46#4**. Due to this non-Kekulé structure, the looped system **3.46** is not omniconjugated. Looped 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

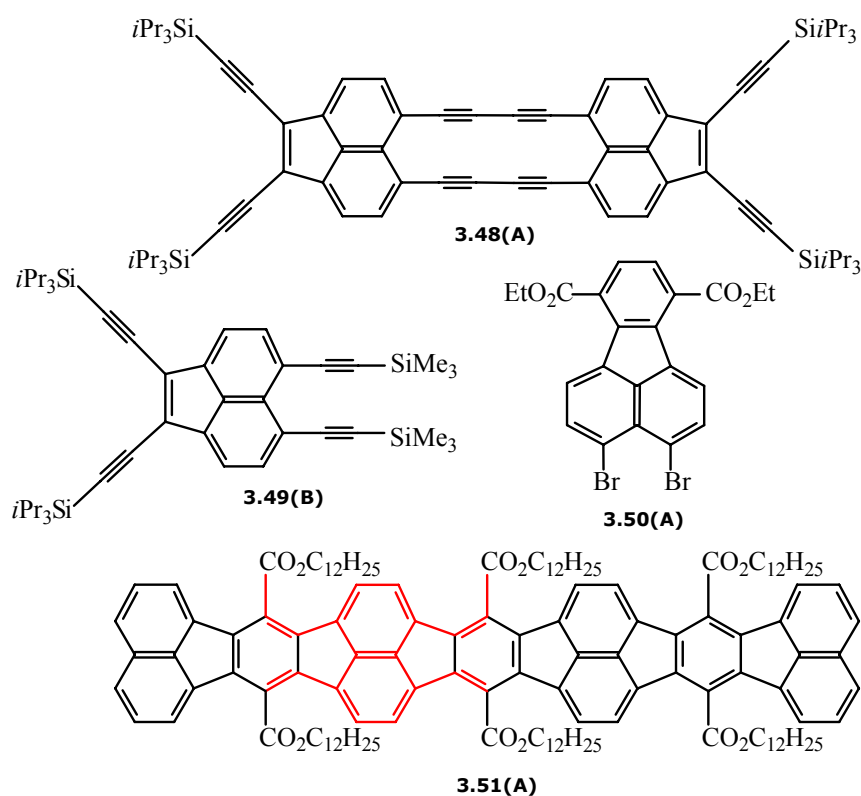


Figure 3.8 Existing Type A and B omniconjugated compounds (in parentheses) which have not been recognized as such: tetra-substituted triisopropyl-silylethynyl macrocycle **3.48** and the related tetrayne **3.49**; diethyl 3,4-dibromo-7,10-fluoranthenedicarboxylate **3.50**; (dodecyloxy)carbonyl substituted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

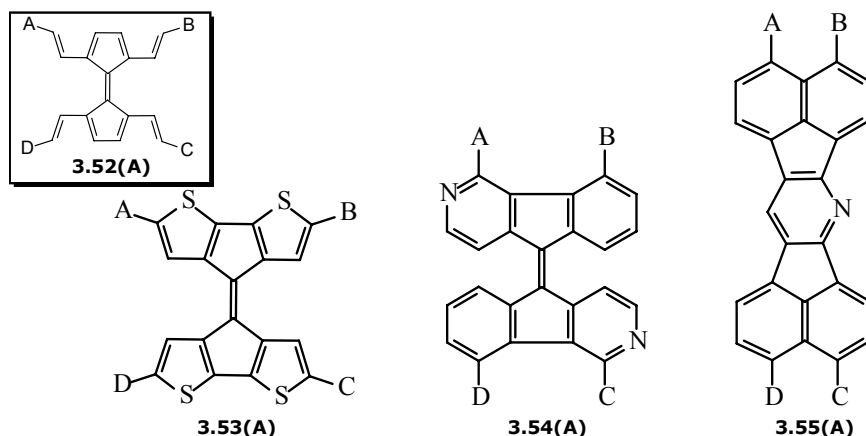
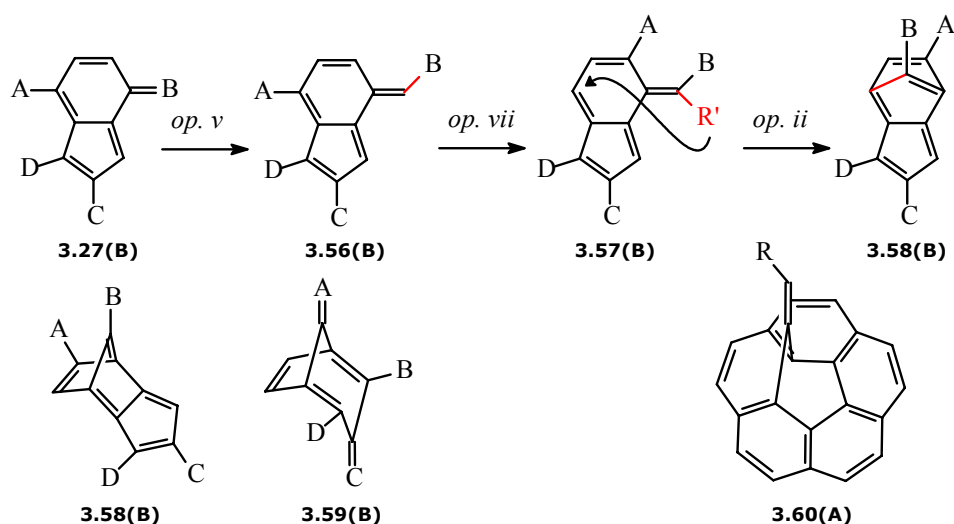


Figure 3.9 Heteroatomic Type A omniconjugated (in parentheses) templates **3.53** – **3.55** based on cyclopentadiene-phenylene, indenopyridine, and acenaphthopyridine, respectively. The sites A, B, C, and D are the substitution positions for other (functional) moieties.

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 omniconjugating 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, adamantane. Adamantane 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

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