

Molecules with Linear π -Conjugated Pathways between All Substituents: Omniconjugation**

By Marleen H. van der Veen, Minze T. Rispens, Harry T. Jonkman, and Jan C. Hummelen*

In this paper, omniconjugation is introduced as a topological phenomenon in π -conjugated systems. Omniconjugated molecules are defined by the fact that they provide direct and fully π -conjugated pathways between all substituents attached to them. Surprisingly, until now such topologies have never been explicitly recognized or investigated from this point of view. A topological design scheme is presented as a tool, which enables for the systematic construction of this novel class of π -electron molecular structures. Molecular building blocks with three or more connection points to the external moieties are proposed, which for the first time allows for the interconnection of many functional entities in a fully conjugated manner. In being truly conjugated, these pathways are expected to provide high transmission probabilities for holes and/or electrons. Omniconjugated structures may play an important role in the design of complex electronic circuitry based on organic molecules. On a larger scale, they may also give rise to special material properties. Although omniconjugation is based on a valence-bond description of the system, it is shown that our concept is in good agreement with results obtained from a molecular-orbital description of the electron probability distribution in the frontier orbitals.

1. Introduction

Over the past few decades, the miniaturization of electronic circuitry has had a profound impact on the technological developments of our society. Nowadays, state-of-the-art lithographic technology seems to be approaching its natural limits in constructing electronic circuitry from inorganic semiconductor materials, with characteristic single-component dimensions on a 20–100 nm scale. The work of MacDiarmid and co-workers^[1] in the late seventies on the electric transport properties of (doped) conjugated polymers has opened the way for a quantum leap in a further miniaturization of electronic circuitry. At present, it has been shown that one can functionalize single molecular entities in such a way that they can be used as linear or nonlinear components in electronic circuitry.^[2,3] This opens a completely new active area of research in the field of electronics by drastic reduction in component dimensions (down to the nanometer scale), combined with potentially very low power consumption.^[4,5] In times to come, one could even imagine electronic circuitry based on molecular materials that self-assemble on specific templates reminiscent to the synthesis of proteins in cells. However, there is a need for new architectural concepts for the design of organic molecules that carry specific

electronic circuit properties.^[6] Currently, single-molecule electronics is limited to single two- or three-terminal building blocks, which confines the theoretical applicability to simple elements, such as conductors, switches, diodes, and (field-effect) transistors. It is imperative for future molecular electronics to search for structures that allow for interconnection of these elements to form complex molecular electronic circuits. Lack of such interconnecting building blocks has led to proposals of complicated supramolecular architectures to accomplish multi-terminal circuitry.^[3,7,8] Although in real devices, terminals of multifunctional molecules may be connected to metallic electrodes, and the transport characteristics of the circuit will not only depend on the electronic structure of the molecular entity but also on the mechanism of charge injection,^[9–12] these parameters are left out of the discussion here.

In this paper we will describe a topological method for the systematic design of a new class of molecular structures, which could provide extensive interconnectivity in more complex molecular devices. 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.^[13–15] Our method originates from a valence-bond description of the molecular system and can be understood by defining the concept of omniconjugation as the property of π -conjugated systems having direct and fully conjugated pathways between *all* connected moieties. To clarify this concept, we will first introduce the terminology and definitions used in this paper.

Conjugation is defined here in the classical, chemical sense of systems having strictly *alternating* single and double bonds.^[16] If the succession of single and double bonds between substituents is in a straight line, as in, for example, model **1** in Figure 1, the conformation is often classified as linear or through-conjugated.^[17] The term ‘cross-conjugation’ refers to the presence of two double bonds that are in conjugation with

[*] Prof. J. C. Hummelen, M. H. van der Veen, Dr. M. T. Rispens, Dr. H. T. Jonkman
Molecular Electronics, Materials Science Centre^{plus}
University of Groningen
Nijenborgh 4, NL-9747 AG, Groningen (The Netherlands)
E-mail: j.c.hummelen@chem.rug.nl

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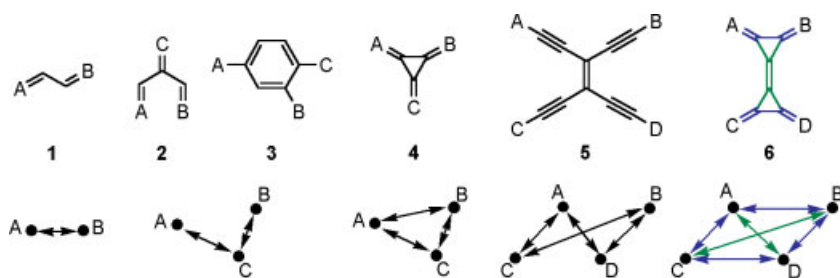


Figure 1. Top row: schematic representation of different categories of conjugation between substituents: linear conjugated **1**; cross-conjugated **2**; conjugation ($A \leftrightarrow C$ and $B \leftrightarrow C$) and cross-conjugation ($A \times B$) in substituted benzene **3**; [3]radialene **4**; cross-conjugated TEE **5**; and omniconjugated cyclopropylidenecyclopropane derivative **6**. Bottom: the corresponding topological connectivity schemes of conjugated pathways for, from left to right, two-terminal conjugation in **1**, three-terminal conjugation and cross-conjugation in **2** and **3**, three-terminal omniconjugation in **4**, four-terminal conjugation and cross-conjugation in **5**, and four-terminal omniconjugation in **6**.

a third one, but are not conjugated to each other, as seen in a simple model **2** (hence, there is conjugation between sites A and C, and between B and C, but not between A and B).^[18] At each point of cross-conjugation in a cross-conjugated pathway, there are *two consecutive single bonds*. Physically, the most important difference between these two classes of conjugation is that there is substantially less π -electron delocalization over a cross-conjugated path compared to a linear conjugated one.^[19] In a two-dimensional aromatic system based on a phenyl ring, like 1,2,4-substituted model **3** (or *any* other tri-substituted benzene), it is not possible to create conjugated pathways between *all* three sites: a conjugated pathway is present in **3** between sites A and C and for the pathway $B \leftrightarrow C$, whereas the pathway from A to B is cross-conjugated ($A \times B$). Even though there may still be a considerable delocalization of π -electrons over the entire framework, theoretical and experimental studies confirm that the electronic coupling between cross-conjugated sites is severely diminished compared to that with linear conjugated pathways between the sites.^[20–22] In several studies a substantial decrease of electron transfer efficiency in cross-conjugated systems was observed.^[13,23] In basic organic chemistry, a very similar effect is commonly recognized in the difference in chemical reactivity between *meta*- and *para*- or *ortho*- positions of substituted benzenes. In studies with *iso*-polydiacetylenes, only a small contribution of the cross-conjugated segments to the overall electronic properties was found.^[24] The electronic properties of these compounds were dominated by their longest linearly conjugated segment, again as a result of the reduced π -electron-mediated interactions between cross-conjugated sites.^[25,26] Based on such observations, it appears advantageous to prevent cross-conjugation between specific sites in molecules when trying to optimize their mutual π -electronic interaction and electronic transport capabilities.

Radialenes form a class of molecules with remarkable properties. These molecules possess an uninterrupted cyclic arrangement of exocyclic double bonds.^[27,28] Of special interest are compounds based on [3]radialenes (see model **4** in Fig. 1). In contrast to all higher radialenes, derivatives of [3]radialene exhibit complete delocalization of the π -electron density at the

three sites,^[29] as well as alternating shortening of bonds, induced by conjugation.^[30,31] When searching for conjugated pathways between sites A, B, and C in **4**, one finds that every one of them is indeed in linear conjugation with the other ones. From our point of view, this existence of fully conjugated pathways between all sites is the foremost reason of the unique properties of [3]radialenes.

We define omniconjugation as the property of molecules, having direct linear π -conjugated pathways between *all* connected moieties.^[32] Within this definition, the two-terminal model **1** and the three-terminal radialene **4** are rudimentary examples of omniconjugated systems. For example, the latter one contains three conjugated pathways (i.e., alternating single and double bonds) from

$A \leftrightarrow B$, $A \leftrightarrow C$, and $B \leftrightarrow C$, which are schematically indicated by arrows in a topological scheme (see Fig. 1, bottom). In a four-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 $C \leftrightarrow D$. According to Diederich and co-workers, these six pathways are found in derivatives of tetraethynylethene (TEE) having model **5** as central building block.^[20,25,33] However, within our definition of conjugation, these so-called ‘fully conjugated systems’ have two pathways that are cross-conjugated, namely $A \times B$ and $C \times D$ (see also the missing arrows in the topological connectivity scheme of model **5**). Hence, TEE-derived compounds are not omniconjugated systems. With the [3]radialenes at hand, we can introduce a first topological example of a four-terminal omniconjugated system (with the necessary six conjugated pathways between the four terminals): model **6** (Fig. 1). The fact that real molecules of the structure of model **6** are relatively unstable and hard to make is irrelevant at this point.^[34] We will show that, starting with small and elementary topological structures, like **6**, an infinite number of omniconjugated systems (among which some very realistic ones) can be obtained using simple topological expansion rules. A fundamental set of such design rules, directly translated into operations, is formulated and elucidated in Section 2.1. Although omniconjugation finds its basis in a valence-bond description of the molecular system, it will be shown in Section 2.2. that our concept is in good agreement with results obtained from a molecular-orbital description of the electron probability distribution in the relevant orbitals. However, we also found that the local symmetry limits the applicability of our design program for a few smaller molecular systems.

2. Results and Discussion

2.1. Topological Design Program for Omniconjugated Systems

In this section, we present a design process, using a set of topological operations, for the construction of omniconjugated organic molecular systems. Although the discussion in this pa-

per is limited to two-dimensional, hydrocarbon-based systems, omniconjugation can also be found in three-dimensional molecular frameworks and within systems containing heteroatoms. As will be shown below, the topological approach rationalizes the search for omniconjugated systems and results in a more fundamental understanding of the concept.

In the remainder of this section, a topological model, which has its basis in a valence-bond description of the system, mimics the electronic structure of π -conjugated organic molecules. In this description, we denote conjugation by the alternation of single and double bonds that are represented by single and double lines, which we will refer to as *links* (see Fig. 2a). From a bond-order point of view, carbon atoms have a valence of four and have a maximum of four lines connected to them (i.e.,

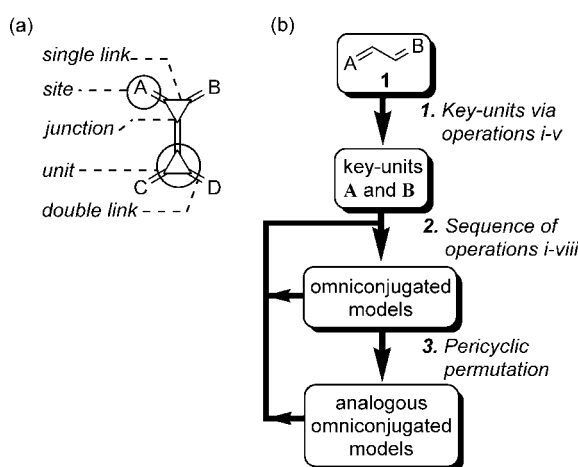


Figure 2. a) The terminology used in the topological algorithm. b) The flow diagram for the design of omniconjugated models.

connectivity index of four), with three possible combinations of single and double links: either four single ones, two single ones and a double one, or two double ones. The carbon atoms are depicted as their hydrogen-suppressed junctures in the topological models. The *sites* A, B, C, D, etc. mimic the terminals of a central building block and are to be the potential covalent connections for other moieties, such as additional conjugated fragments, desired functional groups, or logic elements. Finally, the rings of the building blocks are called *units*. Because of the restrictions that we impose on the molecular framework, the method should be considered as a zero-order approach. 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 Section 2.2. we will explore the effect of these simplifications by comparing our resulting topological models with the outcome of molecular-orbital calculations.

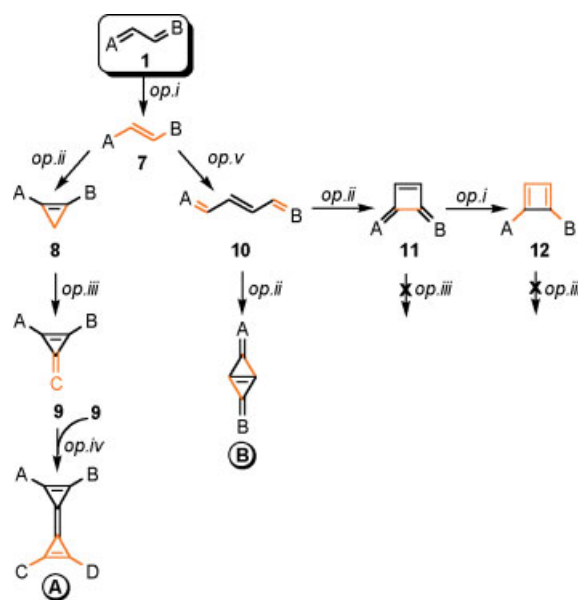
Figure 2b presents the flow diagram for the design of omniconjugated models. This topological algorithm consists of three steps, in which two of them comprise some of the eight operations (op.). The set of operations is formulated in the following way:

- op. i) Permutation of all links within 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.
- op. viii) Links that are not involved in conjugated pathways can be altered freely.

All eight topological operations originate from one central argument: preservation of the existing conjugated pathways between sites. They serve as a fundamental set of rules for the design and modification of omniconjugated models.^[35] A warning not to introduce ‘looped’ but only direct conjugated pathways comes with operation (iii) and (vii) (see footnote^[32]). The construction of omniconjugated models starts with one of the smallest possible conjugated structures: model **1** (see Fig. 2b). From this template the so-called *key-units* are developed. This is done in the first step of the algorithm by applying the first five operations. The resulting key-units **A** and **B** are the precursors to any desired omniconjugated molecule, created in the second and third step as presented in the flow diagram.

Scheme 1 illustrates the emergence of the key-units during the first step. The colored parts mark the result of an operation when it is applied to the model.

- Operation i) Model **1** is easily converted to its linear conjugated counterpart **7** via operation (i), in the scheme abbrevi-



Scheme 1. Construction of key-units **A** and **B** during step 1 of the topological algorithm.

viated to 'op.i', by changing all links from single to double, and vice versa. The fact that the conjugated pathway $A \leftrightarrow B$ is maintained during operation (i) is evident.

- Operation ii) The same is true for operation (ii), which is utilized en route to key-unit **A**. Ring formation is achieved through the insertion of two single links, resulting in model **8**. Again, the alternation of links between existing sites remains unaffected upon the formation of this cyclic unit (i.e., conjugation is preserved). Operation (ii) is, in combination with operations (iii) and (iv), of crucial importance to extend any conjugated model with more sites, while keeping the existing omniconjugation between sites in the system. A clear example is found in the systematic construction of key-unit **A**.
- Operation iii) Although initially the added single links in **8** 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 this new site is conjugated to *all* the existing site(s), which means that a (double–single) alternating pathway in **9** is present from $C \leftrightarrow A$ and $C \leftrightarrow B$.
- Operation iv) The second way to expand a model with more sites is via operation (iv): merging of two units via a corresponding link. Key-unit **A** originates from the fusion of the two identical three-membered units **9** through the double link at the 'former' 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-unit **B** is derived from the same linear conjugated counterpart of model **1** as shown in Scheme 1.

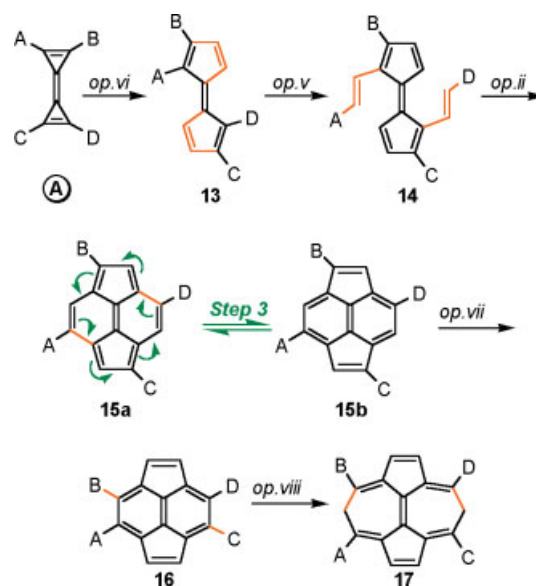
- Operation v) First, the linear analogue **10** is obtained via operation (v) by extending both single links with a double link. Subsequently, operation (ii) is applied to obtain key-unit **B**. By the same operation, the four-membered model **11** can be made. This latter building block could, in principle, become a precursor to systems based on even-membered rings. However, no new key-units can be obtained from this building block because the insertion of a new site (operation (iii)) is not possible in this four-membered model, or in its analogue **12**.

We have been unable to find or design systems having only even-membered units that contain a third site that is in linear conjugation to two other, mutually conjugated sites (see also model **3**). Although key-unit **B** is only omniconjugated in a trivial manner (it has only two sites), omniconjugated systems are formed upon the insertion of more sites via operation (iii) or (iv), as will be demonstrated later in this section. The key-units, utilized as precursors in the topological design program, are useful tools for the construction of different classes of omniconjugated models. They serve as prototypes for the structural design. For example, key-unit **A** is used as precursor in step 2 of the design process (Fig. 2b) when aiming at models with two units that are connected via a link. Moreover, three additional derivatives with a different bond topology can be created from

key-unit **A** by means of operation (i). A clear example is model **6** (see Fig. 1) where the links between site A and B, and between site C and D, are inverted compared to key-unit **A**. This model serves as a convenient prototype for omniconjugated systems with exocyclic connections to all external moieties. Key-unit **B** is the precursor for straightforward design of systems based on condensed rings.

The second step in the design program (Fig. 2b) is the creation of more omniconjugated models by randomly applying sequences of operations to the key-units. For this, we introduce three operations (i.e., (vi), (vii), and (viii)) that will allow for the construction of an unlimited number of omniconjugated models.

- Operation vi) This operation serves as an important tool to modify the models by expanding a unit through replacing a link by an elongated link. In being applicable to every link, individual units can be systematically expanded. Therefore, operation (vi) is the ultimate method for the design of molecules that all originate from the same key-unit. As exemplified for key-unit **A**, a single link can be replaced by a single–double–single link sequence (see model **13** in Scheme 2). The conjugation between all sites remains unaffected by this operation. Clearly, a random sequence of operations during this stepwise design can have a large impact



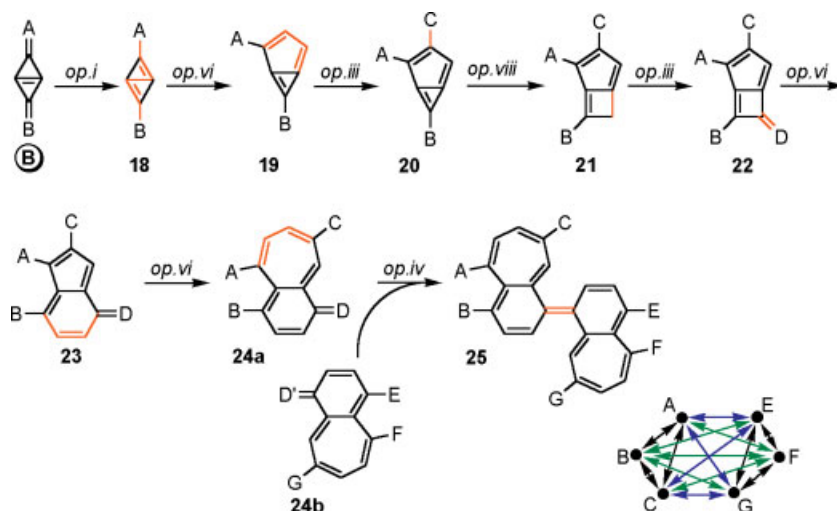
Scheme 2. Design of omniconjugated models from key-unit **A** via a sequence of operations in step 2 and by pericyclic permutation in step 3 of the topological algorithm.

on the architecture of omniconjugated systems. For example, the original framework of key-unit **A** is easily changed into the large omniconjugated model **15a**, consisting of several fused units, by subsequently applying operation (vi), (v), and (ii) (see Scheme 2). Model **15a** has an overall cyclic arrangement of alternating links and can therefore be subjected to step 3.

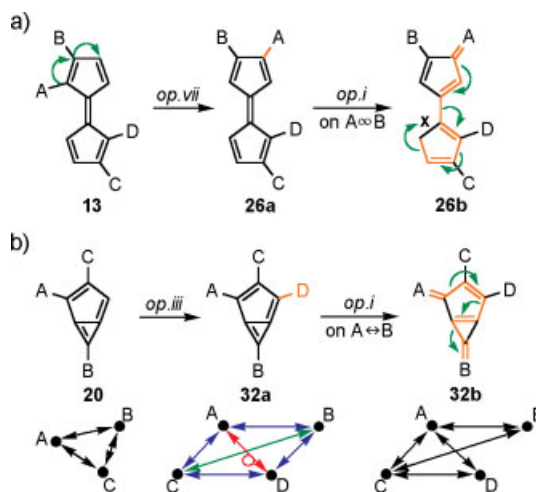
This third (optional) step in the topological algorithm (Fig. 2b) is the permutation of all links involved in the perimeter of the model (i.e., permutation of the pericyclic single and double links). Although this step 3 is related to operation (i), it only induces a shift of links without changing the overall number of single and double links (compare Scheme 2 versus Scheme 1). 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 **15b** is obtained as an analogous model of **15a** and can be further modified at will through operations in step 2 of the topological algorithm.

- Operations vii,viii) Although any desired operation can be applied in step 2, we have chosen to perform the remaining two operations at this point, as shown in Scheme 2, to demonstrate their meaning: both sites B and C in **15b** are moved (operation (vii)); yielding model **16**), and the six-membered units are expanded by insertion of single links (operation (viii)); yielding model **17**). Prior to this latter operation, all conjugation pathways have to be elucidated.^[36] The single link between site A and B in **16** 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 **16**, none of the above is true for **15b**. Topologically this model differs in having links between the above-mentioned sites that *are* involved in conjugation pathways. As a result, it is not allowed to alter these links in **15b** by means of operation (viii).

We will now discuss some features of key-unit **B**. As shown above, the models developed from key-unit **A** can either consist of linked polycyclic models, such as **13**, or after further modifications can be changed into condensed polycyclic building blocks like model **15a**. In contrast, key-unit **B** primarily allows for the construction of condensed polycyclic architectures and is therefore the precursor to be used for a straightforward design process of models of this class, as depicted in Scheme 3 for model **24a**. The procedure to obtain **24a** from key-unit **B** is a representative example of the approach for the expansion of key-unit **B** to a system with more sites. Such condensed polycyclic models having more than three sites that can *only* be obtained from key-unit **B**, show a similar behavior as the ‘looped’ systems with respect to operation (i) (to be discussed later in this section, see Scheme 4b). Therefore, modification of these specific omniconjugated systems like **24a** via operation (i) is not allowed. The power of operation (iv) becomes evident when **24a** is simply ‘doubled’—with **24b**, which is identical, but drawn differently to guide the eye—to yield model **25**. Thus, by rational design, as many as fifteen conjugated pathways are obtained between the six terminals A, B, C, E, F, and G in model



Scheme 3. Systematic construction of omniconjugated models from key-unit **B** up to a model with fifteen conjugated pathways.



Scheme 4. Failures upon executing operation (i) in quasi-omniconjugated models on: a) ‘looped’ alternating pathway $A \infty B$, or on b) direct alternating pathway $A \leftrightarrow B$.

25, resulting in a complex topological connectivity scheme, shown at the bottom of Scheme 3 (see Fig. 1 for comparison with a four-terminal model). It would be quite cumbersome to construct such a complex omniconjugating block by trial and error and without the use of the topological algorithm. Hence, the emergence of model **25** confirms the versatility of the design program in going beyond four-terminal fully conjugated architectures. Note that operation (iv) can, in principle, be repeated to yield higher order omniconjugated models at will. This can be of use, for instance, in the design of omniconjugated polymers. With the above, we have discussed all operations of the design process.

The π -conjugated systems can have alternating pathways with or without loops as is shown in, for example, models **26a** and **27**, respectively (Fig. 3). The so-called ‘looped’ system **26a**

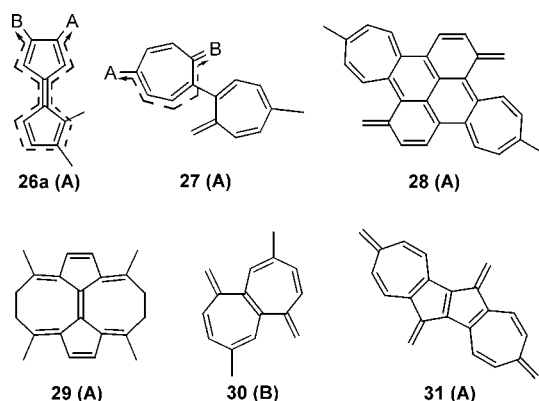


Figure 3. An example of a quasi-omniconjugated, 'looped', system (**26a**), and examples of different classes of four-terminal omniconjugated systems, obtained from either key-unit **A** or **B** (in parenthesis) without the labeling of all sites: linked polycyclic model **27**; peri-condensed polycyclic molecules **28** and **29**; cata-condensed polycyclic systems **30** and **31**.

has a topology that imposes the restriction 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 $A \infty B$.^[32] Looped pathways are often found between sites connected to the same unit, when that unit itself does not provide the pathway between those sites, but a second unit (i.e., a ring) is required to realize that alternating pathway. Looped pathways *may* be introduced via two of the eight operations (see Scheme 4): either by changing the position of a site (e.g., operation (vii) on **13** leading to $A \infty B$ in **26a**) or after the insertion of a new site (e.g., operation (iii) on **20** leading to $A \infty D$ in **32a**). Our, originally 'intuitive', preference for systems without loops is supported by the observation that looped systems are, in two ways, inconsistent with operation (i) (Scheme 4), meaning they are *not* omniconjugated systems; we therefore call these systems 'quasi-omniconjugated'. First, 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 **26a**, 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 emerging in **26b**). The second way in which looped systems clearly differ from omniconjugated systems is the following: quasi-omniconjugation may be lost when operation (i) is applied on a direct conjugated pathway as in, for example, Scheme 4b. Although the looped pathway vanishes ($A \infty D$ in **32a** becomes $A \leftrightarrow D$ in **32b**), another existing alternating pathway is removed ($B \leftrightarrow D$ becomes $B \times D$) as shown in their topological connectivity schemes.

Just as a glimpse of the versatility of the topological algorithm, a few examples of different classes of four-terminal omniconjugated systems (structures **27–31**), generated from key-units **A** and **B**, are depicted in Figure 3. A consequence of the topological design scheme, which makes use of key-units **A** and **B**, is that it only yields omniconjugated structures with at least one odd-membered ring. Model **29** is shown as an example of a structure with an equivalent number of links between

all sites (i.e., seven) when considering their shortest alternating pathways. All of these omniconjugated systems, with rings containing an odd number of carbon atoms, are called non-alternant.^[37] We have been unable to construct omniconjugated systems based on even-membered units only. Additional mathematical analysis is required to understand this topological property of omniconjugated models.

Finally, in considering topological models as real chemical systems, permutation of all bonds by means of either operation (i) (on a pathway consisting of an even number of links) or step 3 results in resonance structures (see for instance models **15a** and **15b** in Scheme 2). It is important to note that after any of these permutations the models always remain omniconjugated: *all* neutral resonance structures of omniconjugated molecules are omniconjugated. This property certainly adds value to the concept of omniconjugation. When an odd number of links is involved, operation (i) is chemically analogous to a redox operation on a conjugated pathway, therefore on the molecule as a whole. This implies that omniconjugation is topologically preserved upon such redox events. This is a unique property: in *all* but omniconjugated systems derivable from key-unit **A**, a redox operation on one conjugated pathway *does* influence the (cross-) conjugation in other pathways, leading to sometimes complex and highly intriguing switching-type relations between the various pathways.

2.2. Comparing the Valence-Bond Results with Molecular Orbital Theory

In this section, we will compare the results obtained by the valence-bond approach in the previous section with the results of molecular-orbital calculations. The molecular-orbital structure provides a suitable observable to obtain insight into the transport properties of the building blocks, which were, in principle, designed to facilitate the charge transport between the moieties connected to the omniconjugating block. Related studies have already shown that the character of orbitals can be used to understand the observed transport properties of single molecules or an assembly of molecules.^[38–40] It should be realized that the hole- and electron-transport properties of molecular systems are strongly dependent on the π -electron probability distribution near the HOMO–LUMO (HOMO = highest occupied molecular orbital; LUMO = lowest unoccupied molecular orbital) gap. The electron- and/or hole-transmission coefficients, which are a measure for charge transport, are strongly dependent on the degree of delocalization of the relevant orbitals between specific functionalized sites of the building blocks. Hence, we performed semi-empirical quantum-chemical calculations in order to elucidate the π -electron density distribution in the frontier orbitals. For simplicity, we functionalized the active sites of the omniconjugated models (**A**, **B**, **C**, **D**, etc.) with simple π -conjugated moieties instead of more realistic large and complex entities. The molecular orbital structure of the central building blocks was evaluated on a qualitative basis upon substitution with either methylene ($=CH_2$) or vinyl groups ($-CH=CH_2$), representing the doubly

or singly linked sites, respectively. Although we fully optimized the molecular geometry of the building blocks, we restrained the external moieties to a co-planar configuration with respect to the central π -electron framework. This approach is expected to yield results that are more representative when other realistic, larger, or complicated functional groups are used as substituents.^[41] All molecular orbital calculations and geometry optimizations were carried out for the single molecules in vacuum, using the semi-empirical AM1 (AM = Austin model) method, implemented in the HyperChem 6.0 program package of Hypercube Inc.^[42] In this paper we use the electron probability distribution $|\psi(x,y)|^2$ in the frontier orbitals for an evaluation of the importance of intramolecular conducting pathways between the moieties. In Section 2.1., we used a valence-bond approach in which we, in principle, cannot make a distinction between hole and electron transport. However, with the molecular-orbital description of the system, the occupied and a virtual-orbital manifold are elucidated, which will allow us to distinguish between hole and electron transport, respectively.

As mentioned before, the spatial extend of the electron probability distribution is analyzed qualitatively in order to determine whether there is sufficient delocalization of charge to allow for transport between all π -bonded moieties. Figure 4 shows the electron probability distribution for the HOMO and LUMO of the tetravinylene-substituted compound **15a**. The HOMO and LUMO of **15a** are strongly delocalized over the

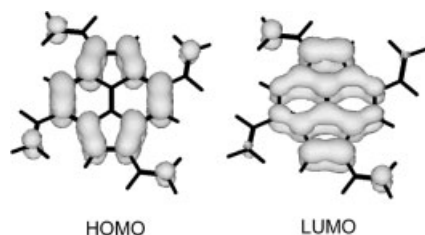


Figure 4. AM1-calculated representations of the electron probability distribution $|\psi(x,y)|^2$ in the frontier orbitals of planar tetravinylene-substituted compound **15a**.

entire molecular framework. The electronic structure of the HOMO is reminiscent to the valence-bond structure of the most stable resonance contributor to this molecule (see model **15a** in Scheme 2). The effect of local symmetry, which introduces a nodal plane in the HOMO, does not seem to invalidate this conjecture. Moreover, it is important to notice that the molecular-orbital structure of the LUMO resembles the situation described by the valence bond structure of the less stable resonance contributor model **15b**. Since in both orbitals 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 latter. Note that pyracenes—fragments in fullerenes—**15a** and **15b** are not two independently existing structures; they just serve as a basis for the description of the electronic structure of the real system, for which **15a** is the dominant contributor. Both reso-

nance contributors are omniconjugated and they only differ by permutation of all pericyclic bonds (step 3 of the topological algorithm). The molecular orbital theory does not distinguish resonance contributors. 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. With that limit, the molecular-orbital description converges towards the valence-bond representation of the π -electron probability distribution.

The HOMO and LUMO levels of compound **17** are schematically given in Figure 5. Although this molecule is generated from **15b** in the topological design process of omniconjugated systems, the basic transport properties have changed. For a valence-bond description of the ground state, only one resonance

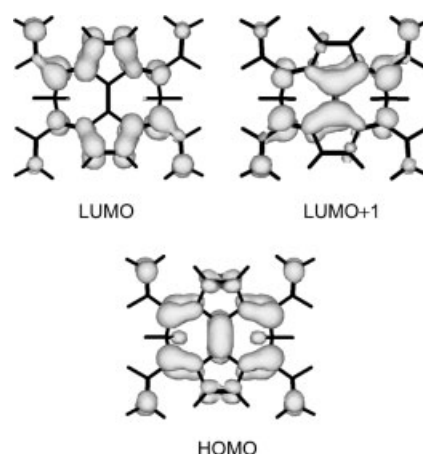


Figure 5. AM1-calculated representations of the electron density distribution $|\psi(x,y)|^2$ in the HOMO and LUMO (near degenerate) of tetravinylene-substituted compound **17**.

contributor now fully dominates and nicely mimics the overall charge distribution in the HOMO. This would make this system an efficient hole-transport medium. An analysis of the electron-transport properties, deduced from the relevant orbitals, requires the evaluation of the two nearly degenerate unoccupied levels corresponding to the LUMO. These unoccupied orbitals with equal symmetry will both have an important contribution to the electron-transport channels. In terms of efficiency, compound **17** would therefore be a better transport medium for electrons compared to compound **15a**, which had a less pronounced and more asymmetrical delocalization on the four terminals.

So far, we have analyzed the electron probability distributions in the frontier orbitals to obtain a qualitative prediction of the transport properties. However, transport channels in larger molecular systems arise in general from the contributions of many individual (energetically close) molecular orbitals. Each of them may contribute to the current transmitted through the molecule. This would imply that for our omniconjugated systems, in spite of the fact that the HOMO is completely delocalized, high currents are not guaranteed. A detailed investigation of this phenomenon, based on quantum-

mechanical density functional theory (DFT) calculations, has been reported for a one-dimensional molecular wire.^[43] Based on such observations, it is not sufficient to only consider the topology of the HOMO and/or LUMO in analyzing the transport properties for larger π -electron systems in a qualitative manner. In addition, the topology of all energetically close orbitals should be included as well.

Another intriguing feature, a possible topological asymmetry for the hole- and electron-conduction channels in this new class of compounds, is observed in model **31**. The spatial distribution of the π -electron density in the HOMO of **31** is limited to a path between two terminals, as seen in Figure 6a. This localization of the HOMO restricts the hole-conduction channel to the long axis of the molecule. In contrast, the LUMO is mainly lo-

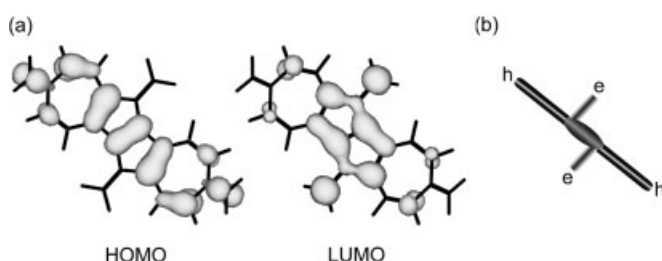


Figure 6. a) Plots of the π -electron probability distribution in the frontier orbitals of the tetramethylene-substituted derivative of model **31**. b) Cartoon of the preferred transport direction for holes (h) and electrons (e), as proposed for **31**.

calized to the short axis of the molecule through which electron transport is strongly favored. These results suggest that we have designed a molecular system with separate hole- and electron-conduction channels, as represented by the cartoon in Figure 6b. In fact, compound **31** is a theoretical example of a molecularly induced transport direction for holes and electrons, constructed with the topological design program for omniconjugated molecules. In agreement with our findings, separated electron- and hole-transport regimes are also found in other, typically non-alternant hydrocarbons.^[44] A theoretical explanation is found in the intrinsic property of non-alternant unsaturated hydrocarbons. Most of them do not have 'mirror-related' molecular orbitals; i.e., orbital pairing does not usually happen.^[45] We expect that the non-alternant character is instrumental for the asymmetry in the hole- and electron-conduction characteristics in some of these omniconjugated compounds. A difference between omniconjugated model **31** and classic non-alternant systems is that we propose with our four-terminal system *spatially* separated conduction channels for electrons *and* holes. As described before, the existence of different channels for hole- and electron-conduction cannot be predicted in a simple manner from the valence-bond description of the system and is not a consequence of the omniconjugated character of the molecular entity. The topological asymmetry of the channels originates from local symmetry effects on the spatial structure of the individual molecular orbitals, which are dictated by the symmetry of the nuclear framework. In these cases, the om-

niconjugated character of the molecule merely influences the efficiency of the conduction channels.

3. Concluding Remarks

In this paper, the concept of omniconjugation is introduced and a topological algorithm for the construction of omniconjugated molecules is presented. These molecules are entities that have direct and fully π -conjugated pathways between *all* properly connected external moieties. The proposed topological design process, which results in a more fundamental understanding of the concept, is particularly attractive since it allows for the design of an infinite number of possible candidates while keeping the existing omniconjugation in the system. The concept of omniconjugation is derived from a valence-bond description of the π -electron skeleton. However, the transmission coefficients for charge transport in π -conjugated molecules are dependent on the electron probability distribution in the frontier orbitals near the HOMO–LUMO gap, which is in general evaluated from a molecular-orbital description of the system. Our results, presented in this paper, show that these two different approaches converge to a large extent. There are often a number of possible resonance contributors in a valence-bond description. A linear combination of those resonance contributors, in which each structure usually has a different weight, represents the overall π -electron distribution in the ground state. Despite some local symmetry considerations, it is often found that the charge and bond-order distribution in the HOMO is reminiscent of the major resonance contributor in the valence-bond description. Furthermore, an impression of the electronic structure of the LUMO can often be obtained from the remaining resonance structures. These observations convinced us that the magnitude of the electron- or hole-transmission coefficients can simply be related to the presence of an uninterrupted alternating sequence of single and double bonds between the π -bonded external moieties. From this we conclude that the omniconjugation of molecular units might play a promising role in future molecular electronics. A valence-bond description cannot make a real distinction between hole- and electron-transport capabilities. Molecular-orbital computations are essential in providing insight into this difference. We have shown that some omniconjugated blocks have spatially separated channels for hole and electron transport. This latter property may be of use to construct more advanced molecular-electronics devices.

In conclusion, we explored omniconjugation via building blocks as a means to allow for the construction of molecular architectures with more than three terminals that are *truly* π -conjugated. 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. In this context, we deal with *intramolecular* transport. In molecular crystals, two types of transport can be distinguished: *intramolecular* (in quasi one-dimensional ex-

tended conjugated molecules: band-like) and *intermolecular* (scaling with a hopping or transfer integral). Transfer integrals are, in a first-order approach, a function of an intermolecular overlap integral and a molecular-interaction parameter. Since omniconjugation distributes charge in a more uniform way over the relevant orbitals, it may enhance the intermolecular overlap, opening efficient conduction channels for a hopping-like transport mechanism. Omniconjugated blocks may also serve as central units for highly polarized donor–acceptor-type molecules. One could even envision that branched conjugated systems, like dendritic structures, can also be designed as fully conjugated using an omniconjugated linker, in sharp contrast to systems reported thus far.

We are presently investigating the topological consequences of the propagation of quasi-particles in (omni-) conjugated systems.

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- [1] 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.
- [2] Aviram, M. A. Ratner, *Chem. Phys. Lett.* **1974**, 29, 277.
- [3] J. C. Ellenbogen, J. C. Love, *Proc. IEEE* **2000**, 88, 386.
- [4] C. Joachim, J. K. Gimzewski, A. Aviram, *Nature* **2000**, 408, 541.
- [5] J. M. Tour, M. Kozaki, J. M. Seminario, *J. Am. Chem. Soc.* **1998**, 120, 8486.
- [6] S. Ami, C. Joachim, *Phys. Rev. B* **2002**, 65, 155 419.
- [7] S. Ami, M. Hliwa, C. Joachim, *Nanotechnology* **2003**, 14, 283.
- [8] S. Ami, M. Hliwa, C. Joachim, *Chem. Phys. Lett.* **2003**, 367, 662.
- [9] A. Nitzan, M. A. Ratner, *Science* **2003**, 300, 1384.
- [10] V. Mujica, A. E. Roitberg, M. A. Ratner, *J. Chem. Phys.* **2000**, 112, 6834.
- [11] A. Nitzan, *Annu. Rev. Phys. Chem.* **2001**, 52, 681.
- [12] S. N. Yaliraki, M. Kemp, M. A. Ratner, *J. Am. Chem. Soc.* **1999**, 121, 3428.
- [13] S. N. Yaliraki, M. A. Ratner, *Ann. N. Y. Acad. Sci.* **2002**, 960, 153.
- [14] Z. L. Mišković, R. A. English, S. G. Davison, F. O. Goodman, *J. Phys.: Condens. Matter* **1997**, 9, 10 749.
- [15] J. Reichert, R. Ochs, D. Beckmann, H. B. Weber, M. Mayor, H. Von Löhneysen, *Phys. Rev. Lett.* **2002**, 88, 176 804.
- [16] R. Hoffmann, C. Janiak, C. Kollmar, *Macromolecules* **1991**, 24, 3725.
- [17] a) H. Wang, R. Helgeson, B. Ma, F. Wudl, *J. Org. Chem.* **2000**, 65, 5862. b) M. Bruschi, M. G. Griuffreda, H. P. Lüthi, *Chem. Eur. J.* **2002**, 8, 4216.
- [18] N. F. Phelan, M. Orchin, *J. Chem. Educ.* **1968**, 45, 633.
- [19] M. Trættemberg, H. Hopf, *Acta Chem. Scand.* **1994**, 48, 989.
- [20] D. Philp, V. Gramlich, P. Seiler, F. Diederich, *J. Chem. Soc. Perkin Trans. 2* **1995**, 875.
- [21] M. Klokkenburg, M. Lutz, A. L. Spek, J. H. Van der Maas, C. A. Van Walree, *Chem. Eur. J.* **2003**, 9, 3544.
- [22] a) J.-P. Launay, *Chem. Soc. Rev.* **2001**, 30, 386. b) C. Rovira, D. Ruiz-Molina, O. Elsner, J. Vidal-Gancedo, J. Bonvoisin, J.-P. Launay, J. Veciana, *Chem. Eur. J.* **2001**, 7, 240.
- [23] C. Patoux, C. Coudret, J.-P. Launay, C. Joachim, A. Gourdon, *Inorg. Chem.* **1997**, 36, 5037.
- [24] a) S. Eisler, R. R. Tykwinski, *Angew. Chem. Int. Ed.* **1999**, 38, 1940. b) R. R. Tykwinski, Y. Zhao, *Synlett* **2002**, 12, 1939.
- [25] F. Diederich, *Chem. Commun.* **2001**, 219.
- [26] Y. Zhao, R. McDonald, R. R. Tykwinski, *J. Org. Chem.* **2002**, 67, 2805.
- [27] H. Hopf, G. Maas, *Angew. Chem. Int. Ed. Engl.* **1992**, 31, 931.
- [28] M. Iyoda, S. Tanaka, H. Otani, M. Nose, M. Oda, *J. Am. Chem. Soc.* **1988**, 110, 8494.
- [29] a) K. Takahashi, S. Tarutani, *J. Chem. Soc. Chem. Commun.* **1994**, 519. b) K. Takahashi, S. Tarutani, *Adv. Mater.* **1995**, 7, 639.
- [30] F. H. Allen, *Acta Crystallogr., Sect. B: Struct. Sci.* **1981**, B37, 890.
- [31] T. Lange, V. Gramlich, W. Amrein, F. Diederich, M. Gross, C. Boudon, J.-P. Gisselbrecht, *Angew. Chem. Int. Ed. Engl.* **1995**, 34, 805.
- [32] ‘Direct’ means here that a linear conjugated pathway between any two terminals must exist, without the need to use any bond *twice* in such a pathway. We call systems in which one or more of all pathways can only be found using one or more bonds twice ‘looped’ systems, because they contain ‘looped’ pathways. As will be explained at the end of Section 2.1., they are only quasi-omniconjugated.
- [33] F. Diederich, *Pure Appl. Chem.* **1999**, 71, 265.
- [34] R. Neidlein, V. Poignée, W. Kramer, C. Glück, *Angew. Chem.* **1986**, 98, 735; *Angew. Chem. Int. Ed. Engl.* **1986**, 25, 731.
- [35] Whether or not the proposed set of topological operations constitutes all fundamental manipulations for the design of omniconjugated models has to be explored mathematically.
- [36] Operation (viii) differs in not being essential but embedded, to a certain degree, in aforementioned 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.
- [37] D. M. Lemal, G. D. Goldman, *J. Chem. Educ.* **1988**, 65, 923.
- [38] Y. Karzazi, J. Cornil, J. L. Brédas, *J. Am. Chem. Soc.* **2001**, 123, 10 076.
- [39] J. M. Seminario, A. G. Zacarias, J. M. Tour, *J. Am. Chem. Soc.* **2000**, 122, 3015.
- [40] M. Girlanda, M. Macucci, *J. Phys. Chem. A* **2003**, 107, 706.
- [41] This was confirmed by calculations without geometry restraints for the tetrakis(2-phenylethynyl) substituted derivative of compound **15a** and **15b**. The fully AM1-optimized conformations present no significant deviation from planarity. The resulting delocalization of the wave functions in the frontier orbitals is in agreement with the presented data for the tetravinylene derivative.
- [42] M. J. S. Dewar, E. G. Zoebisch, E. F. Healy, J. J. P. Stewart, *J. Am. Chem. Soc.* **1985**, 107, 3902.
- [43] J. Heurich, J. C. Cuevas, W. Wenzel, G. Schön, *Phys. Rev. Lett.* **2002**, 88, 256 803.
- [44] G. Treboux, P. Lapstun, K. Silverbrook, *J. Phys. Chem. B* **1998**, 102, 8978.
- [45] J. Michl, E. W. Thulstrup, *Tetrahedron* **1976**, 32, 2.

Molecules with Linear π -Conjugated Pathways between All Substituents: Omniconjugation

By Marleen H. van der Veen, Minze T. Rispens,
Harry T. Jonkman, and Jan C. Hummelen*

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In Figure 4, the energy level labeled 'HOMO' should be labeled 'LUMO' and vice versa. By this mistake, the paragraph below Figure 4 should be corrected as follows: **15a** should be replaced by **15b** and vice versa. As a result, the last sentence of the paragraph below Figure 5 should read holes instead electrons. This error does not affect any other results or conclusions in this paper. The authors apologize for this oversight.