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Omniconjugation

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Abstract. Omniconjugation is introduced as a new architectural concept for the design of complex molecular structures that allows for the interconnection of many functional entities in a fully conjugated manner. So far, such π -conjugated topologies have never been explicitly recognized or investigated from this point of view. A topological design method has been developed by which a large number of realistic omniconjugated structures can be constructed. This new class of π -conjugated systems can be divided in two sub-classes that differ in their 'switching' behavior upon passage of solitons. Furthermore, we found that the principle of omniconjugation may give rise to a pronounced and, sometimes, unique π -electron delocalization of the frontier orbitals. These preliminary results indicate that omniconjugation could be applicable in several ways (as passive or active elements) in future nanoelectronic devices.

INTRODUCTION

In the continuing race for faster computers and new electronic devices, enormous research effort is put into the miniaturization of classical semiconductor components and other crucial electronic devices. An intriguing 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 already from the early seventies [1,2]. During the last decade, scientists have reported on successful fabrication of single molecular 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. Up to now, the trivial aspect of interconnecting several elements has not been addressed on the molecular level. This of course will be crucial for the realization of fully integrated molecular circuits [6]. One of the simplest elements missing is the single-molecule version of a T-piece or an intersection of two wires. A first requirement for the transmission of charges through such a molecular junction is a complete π -electron delocalization between the three or four terminals. For organic systems it is the topology of the conductive path that determines its degree of delocalization. Charges can flow efficiently between two ends when the chain is linear conjugated, i.e., a strict alternation of single and double bonds. This condition is not met in cross-conjugated pathways where the strict alternation of single and double bonds is interrupted by an extra single bond (see model **1** and **2** in Fig. 1).

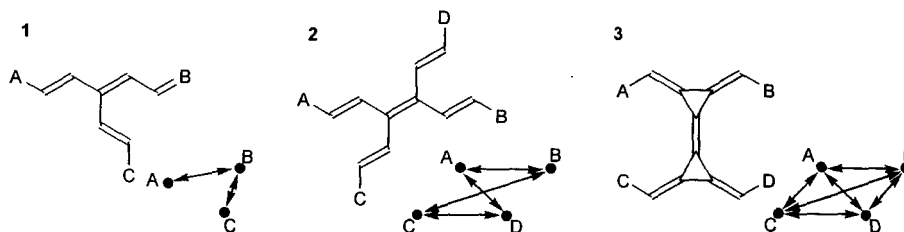


FIGURE 1. (Top) Schematic representation of three- and four-terminal cross-conjugation in **1** and **2**, and four-terminal omniconjugation in **3**. (Bottom) Corresponding topological connectivity schemes of conjugated pathways.

When using simple molecular architectures like **1** or **2**, which would mimic a T-piece or an intersection, respectively, it is not possible to create a situation in which transport can happen in all, preferable more than two or three, directions. Hence, we have sought for π -conjugated systems that do have direct linear conjugated pathways between *all* terminals. We call such systems, like model **3**, omniconjugated. In being truly conjugated, these systems could fulfill the simple function of an intersection between two molecular wires.

TOPOLOGICAL DESIGN OF OMNICONJUGATED MODELS

The fact that real molecules of the structure **3** are unstable makes it necessary to search for more realistic alternatives. A topological design scheme consisting of three steps has been developed for the systematic construction of molecules from small entities, the so-called, key-unit A or B (see Fig. 2) [7]. A large number of realistic models can be obtained by applying sequences of operations to one selected key-unit. The collection of eight operations all originate from one central argument: preservation of the existing conjugated pathways and avoiding the emergence of cross-conjugation.

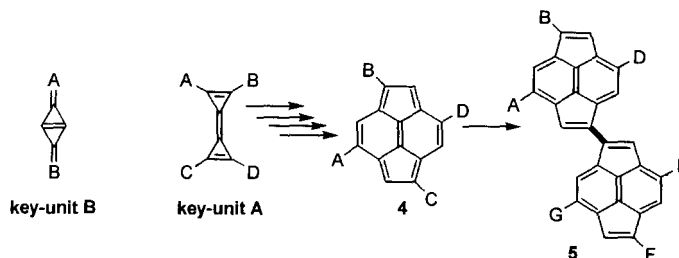


FIGURE 2. The key-units A and B, and the topological design of omniconjugated models from, for example, key-unit A. Model **5** is obtained after applying five operations (see Ref. [7]) and has fifteen conjugated pathways between the six terminals.

The design process allows for the number of interconnected molecules to be chosen anywhere between two and infinity, in principle. For example, model **5** is obtained by connecting two models of **4** through 'former' terminal C yielding a junction with six terminals (i.e., for six other moieties). The versatility of the design method is confirmed upon the emergence of complex though realistic models like **5**. In general, this class of molecules belongs to the group of nonalternant hydrocarbons since they all contain at least one odd-membered ring. As with any other organic system, one can draw the resonance contributors for an omniconjugated system. Interestingly, however, all resonance structures are also omniconjugated. This is a crucial property, because if this were not the case, omniconjugation would have been simply a topological curiosum based on the valence bond theory.

PROPERTIES OF OMNICONJUGATED SYSTEMS

As a result of some topological properties, we discriminate two classes of omniconjugated systems:

Type A omniconjugated systems, they stem from key-unit A, have the topological property that they remain omniconjugated upon a redox operation. A redox operation implies that all single bonds within a conjugated pathway become double and vice versa. The oxidation of an alternating pathway will induce a net change in the number of double bonds as shown in Fig. 3 for model **4**. Such a redox operation on any of the pathways (or combination thereof) is, regarding the topology of the path, analogous to the passage of a soliton [8]. In other words, a redox event does not influence the charge transport properties because the bond alternation pattern is not changing from linear to cross-conjugated.

Type B omniconjugated systems, defined as only obtainable from key-unit B (see Fig. 2), have the intriguing property that omniconjugation is *not* preserved upon a redox event. That is: in Type B systems a redox event between two terminals (say A and B in model **8** in Fig. 4) results in changing the topology between the two complementary terminals (C and D). Thus in *any* case the complementary path *always* changes from linear to cross-conjugated (hence, switched from 'on' to 'off'): $C \times D$ in

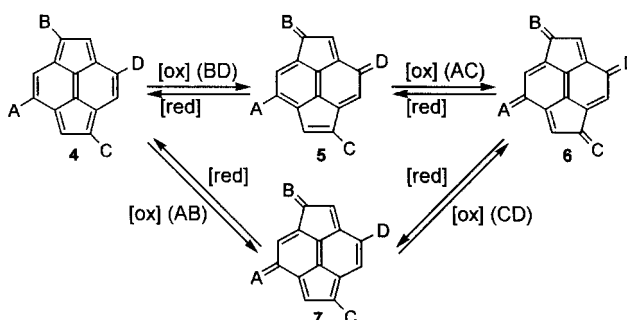


FIGURE 3. Topological property of Type A systems: omniconjugation is preserved upon redox operations as illustrated for repetitive oxidations.

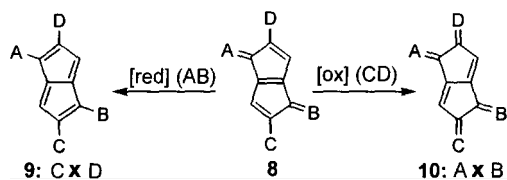


FIGURE 4. Topological property of Type B systems: in any case the complementary pathway to the redox event is not linear conjugated anymore: it is switched from ‘on’ to ‘off’.

model **9**) while all other pathways (e.g., five in the case of **9**) remain linear conjugated. Note that, although Type B systems have a topology that is omniconjugated, they are closely related to ordinary conjugated systems in terms of their topological switching behavior upon redox events.

To determine whether or not these systems indeed can function as envisioned or not, we investigated the systems using quantum chemical calculations. One of the parameters to study is the charge delocalization between the four substituents, which should be strong due to the presence of fully conjugated pathways. For the qualitative evaluation we used simple π -conjugated moieties that represent the single and double bonded substituents at the terminals A, B, C and D (either, vinyl or methylene groups, respectively). Preliminary results indicate that the topological phenomenon of omniconjugation indeed may give rise to a pronounced delocalization of the (frontier) molecular orbitals into all terminals. As seen from Fig. 5, the π -electron density distribution suggests that this building block facilitates hole and electron transport between *all* moieties.

In some cases, a new and intriguing phenomenon was observed from the electronic structure that was not obvious from its topological framework. As a result of the local orbital symmetry, certain omniconjugated systems seem to show orthogonal preferential directionality for hole and electron transport. Hence, in the plane of the molecule, there could be different (preferential) transmission pathways for transport of either charge as illustrated in Fig. 6.

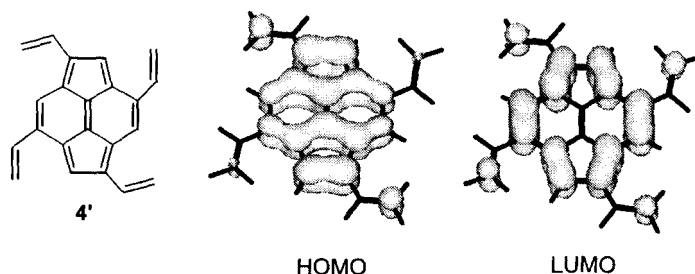


FIGURE 5. Spatial distribution of the π -electron density $|\psi(x,y)|^2$ in the frontier orbitals calculated by AM1 for the tetravinylene substituted model **4'**.

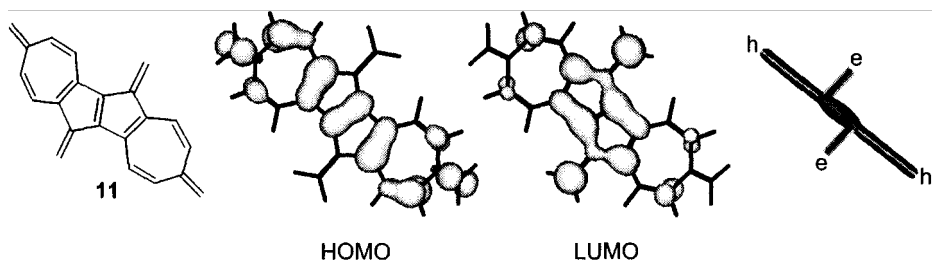


FIGURE 6. Shape of the HOMO and LUMO (AM1 calculated; $|\psi(x,y)|^2$) of the tetramethylene substituted molecule **11**. At the right a schematic representation is given of the preferred intramolecular transport direction of holes (h) and electrons (e).

From the above presented results we envision that the concept of omniconjugation could become important in the design of molecular electronic circuits. Omniconjugated entities are systems having conjugated pathways between all possible terminals. In going beyond three-terminal systems, this architectural concept is of interest to incorporate many logic functions inside a single molecule. Omniconjugation within a Type A system may become the single-molecule version of what is a quite trivial aspect of electronics, namely the wiring of various basic elements. The Type B systems have a π -conjugation topology that is closely related to that of the (passive) Type A systems, but are, on the other hand, of use as active switching elements. These systems have the intriguing property that the complementary pathway to the redox event changes from linear to cross-conjugated.

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