One-Handed Helical Orbitals in Conjugated Molecules

Yuriko Aoki† Yuuichi Orimoto† and Akira Imamura‡

†Department of Material Sciences, Faculty of Engineering Sciences, Kyushu University, 6-1 Kasuga-Park, Fukuoka 816-8580, Japan
‡Hiroshima Kokusai Gakuin University, Nakano 6-20-1, Aki-ward, Hiroshima 739-0321, Japan

Cumulenes with two degenerate helical molecular orbitals could be modified for use in spintronics, analysis, and enantioselective reactions.

In conjugated linear molecules (H₂C≡Cₙ⁻¹═CH₃) p-orbitals exhibit interesting shapes, depending on the number of carbon atoms in the main chain and the dihedral angle in the terminal CH₂ groups. Garner et al. systematically analyzed the relationship between the structure of such conjugated π-systems, [n]cumulenes, and helical frontier molecular orbitals (MOs) using Hückel theory and density functional theory calculations.1 The authors discussed similarities between helical orbitals of even [n]cumulenes (n = even number of double bonds and odd number of carbon atoms) and those of Möbius cyclopolyenes (Figure 1).

They proposed an intriguing classification of orbital nature by molecular symmetry using the Hückel method. In 1968 Buenker calculated the electronic structure of allene2 and demonstrated the rotational barriers of ethylene and allene using closed-shell self-consistent-field approach. Although many theoretical studies of chiral allenes have been reported, the existence of helical frontier MOs for even [n]cumulenes was not known until 2013.3–5 Helical MOs do not exist in odd [n]cumulenes (even number of carbon atoms), which form planar, stable structures.

Garner et al. tested their approach on several existing concepts.1 Their mathematical derivation used simple Hückel theory and density functional theory calculations with large basis sets for recognizing orbital shapes. Although this approach is classical and topological, the authors produced a simple and elegant description that included important principles of basic science.

The results could be extended to more quantitative discussions toward advanced molecular design. For example, the excited states of twisted structures in [n]cumulenes have been directly used in the analysis of reactions, absorption spectra, optical and magnetic properties, etc. The symmetry within coarctate Möbius systems (Figure 1) might be an essential tool for the elucidation of coarctate transition states.6

Helical MOs7–9 were demonstrated in real systems and recognized as a key factor in various phenomena. Anderson et al. proposed experimental and computational evaluations of the rotation barrier in a butadiyne-linked porphyrin dimer.7 They showed that the transition between excited states of the molecule arises predominantly from the delocalization via helical frontier MOs on the butadiyne linker. Low et al. demonstrated helical orbitals on a butadiyne linker between diruthenium complexes.8 They proposed that the helical orbitals on the linker determined the relative orientation of the end groups. Misra et al. showed that cumulenes linking two radicals exhibit magnetic properties: ferromagnetic when cumulenes contain an odd number of carbon atoms and antiferromagnetic when the number is even.9 The work was focused on establishing relations between magnetic properties, the number of carbon atoms, and bond alternation behavior of the linker. Helical orbitals were found on the disubstituted cumulene linker when the substituents were the same type of spin center.

We obtained helical orbitals for even [n]cumulenes and polyynes by starting the closed-shell self-consistent-field calculations with an initial guess having helical orbitals.5 When the program recognizes a specific symmetry in the molecular

Published: May 16, 2018
structure, the calculations start with the initial guess that initial orbitals are rectilinear, and the self-consistent-field calculations will converge to rectilinear orbitals again (Figure 2).

However, when the program recognizes it as a specific molecular symmetry, even if we use helically adapted initial orbitals, the final orbitals will also be helical. The mixing of left-handed and right-handed helical orbitals also provides nonhelical (rectilinear), doubly degenerate MOs in unitary transformation frameworks without any loss of density, which is correctly pointed out in all the papers cited herein.

A one-handed helical frontier orbital extracted from twisted even [n]cumulenes (odd number of carbon atoms) would play an important role in enantioselective reactions and other functional phenomena. Garner et al. suggested that the concept of helical MOs could be extended to molecular design, which could be useful for enantioselective synthesis, for example, by attaching a donor and acceptor at the terminal groups of cumulene (Figure 2). We suggest using helical frontier MOs localized into the donor to create anisotropy along the molecular chain. As a way to separate the doubly degenerate helical MO levels into left-handed and right-handed, the substituent modification might be considered for the extraction of one of the two types of helices. In addition, we confirmed that the helical orbital coefficients decrease rapidly with chain length and localize into the central part when both the terminal groups are –CH2. Therefore, the conjugated “rings” are expected to produce fascinating helical orbitals designed for longer chains. For efficient and highly accurate large-ring calculations, our three-dimensional elongation method would be useful for the molecular design utilizing different substitutions and conformations.10,11

A one-handed helical frontier orbital extracted from twisted even [n]cumulenes (odd number of carbon atoms) would play an important role in enantioselective reactions and other functional phenomena.

Figure 2. Even [n]cumulenes have both frontier and degenerate (helical and rectilinear) molecular orbitals. If the degenerate helical MO levels are split by chemical modification (for example, by donor and acceptor attachments at the terminal groups), it is expected that one of the left-handed or right-handed helical orbitals will possess a special meaning as a frontier orbital and play an important role as a functional material using the nature of the anisotropic orbital.

Moreover, the calculations start with the initial guess that initial orbitals are rectilinear, and the self-consistent-field calculations will converge to rectilinear orbitals again (Figure 2). The mixing of left-handed and right-handed helical orbitals also provides nonhelical (rectilinear), doubly degenerate MOs in unitary transformation frameworks without any loss of density, which is correctly pointed out in all the papers cited herein.

A one-handed helical frontier orbital extracted from twisted even [n]cumulenes (odd number of carbon atoms) would play an important role in enantioselective reactions and other functional phenomena. Garner et al. suggested that the concept of helical MOs could be extended to molecular design, which could be useful for enantioselective synthesis, for example, by attaching a donor and acceptor at the terminal groups of cumulene (Figure 2). We suggest using helical frontier MOs localized into the donor to create anisotropy along the molecular chain. As a way to separate the doubly degenerate helical MO levels into left-handed and right-handed, the substituent modification might be considered for the extraction of one of the two types of helices. In addition, we confirmed that the helical orbital coefficients decrease rapidly with chain length and localize into the central part when both the terminal groups are –CH2. Therefore, the conjugated “rings” are expected to produce fascinating helical orbitals designed for longer chains. For efficient and highly accurate large-ring calculations, our three-dimensional elongation method would be useful for the molecular design utilizing different substitutions and conformations.10,11

A one-handed helical frontier orbital extracted from twisted even [n]cumulenes (odd number of carbon atoms) would play an important role in enantioselective reactions and other functional phenomena.

Figure 2. Even [n]cumulenes have both frontier and degenerate (helical and rectilinear) molecular orbitals. If the degenerate helical MO levels are split by chemical modification (for example, by donor and acceptor attachments at the terminal groups), it is expected that one of the left-handed or right-handed helical orbitals will possess a special meaning as a frontier orbital and play an important role as a functional material using the nature of the anisotropic orbital.

Moreover, the calculations start with the initial guess that initial orbitals are rectilinear, and the self-consistent-field calculations will converge to rectilinear orbitals again (Figure 2). The mixing of left-handed and right-handed helical orbitals also provides nonhelical (rectilinear), doubly degenerate MOs in unitary transformation frameworks without any loss of density, which is correctly pointed out in all the papers cited herein.

A one-handed helical frontier orbital extracted from twisted even [n]cumulenes (odd number of carbon atoms) would play an important role in enantioselective reactions and other functional phenomena. Garner et al. suggested that the concept of helical MOs could be extended to molecular design, which could be useful for enantioselective synthesis, for example, by attaching a donor and acceptor at the terminal groups of cumulene (Figure 2). We suggest using helical frontier MOs localized into the donor to create anisotropy along the molecular chain.