Synthesis of chiral [5]cumulenes

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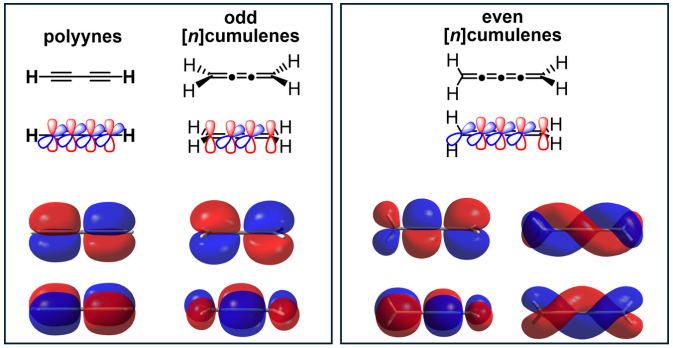
Introduction

Cumulenes:

[*n*]Cumulenes are molecules with numerous contiguous double bonds (*n* = number of contiguous double bonds).[1,2] [*n*]Cumulenes fall under two classes, odd or even [*n*]cumulenes. Odd [*n*]cumulenes (*n* = 3, 5, 7...) are found more stable than their even [*n*]cumulenes (*n* = 4, 6, 8...) counterparts, although the reason for the difference in stability is not yet clear. The two classes of [*n*]cumulenes have vastly different electronic structures, where the orbitals are degenerate (same energy) and non-degenerate (different energy) in even and odd [*n*]cumulenes, respectively.

Helical orbitals:

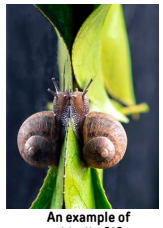
Recent literature suggests that when the molecular symmetry is lowered (e.g., we make the molecule chiral), the previously degenerate π-orbitals rearrange to make a pair of helical frontier molecular orbitals.[3,4] So far, there are few examples for examining helical FMOs (Frontier Molecular Orbital). Recent literature (Dr. Marc Garner) indicates a link between the "Helical" orbitals and their Chiroptical response.[5] This gives a beginning for the conformation of Helical FMOs using chiral cumulenes.



Motivation:

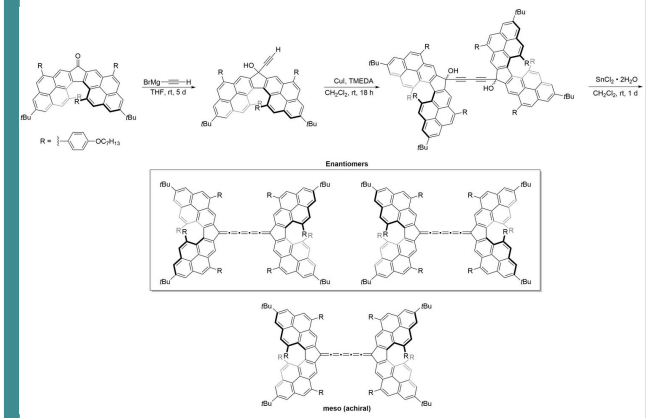
The goal is that synthesizing a [5]cumulene with chiral end groups will help support or refute helical orbitals. The source of chirality we choose is a helicene (a helically shaped polycyclic aromatic hydrocarbon).

In this presentation, I will discuss the synthesis of a helicene end-capped [5]cumulene, as well as the interaction with light through the use of UV-Vis and circular dichroism spectroscopies. The synthesis of chiral [5]cumulenes is an important first step toward the eventual synthesis of the chiral [4]cumulenes which are direct model compounds toward helical molecular orbitals.



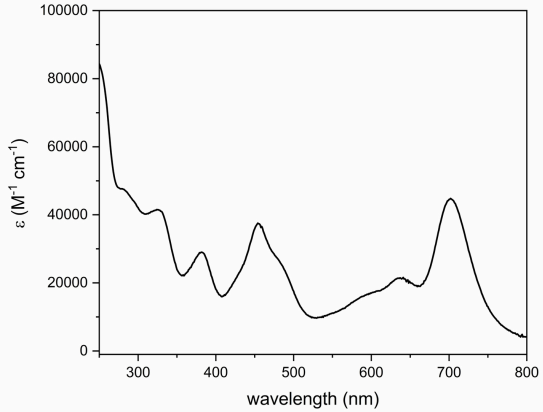
An example of chirality[6]

Synthesis



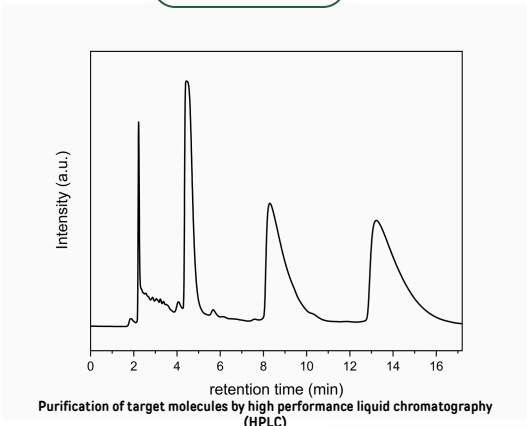
Synthesis of target molecules

UV-vis



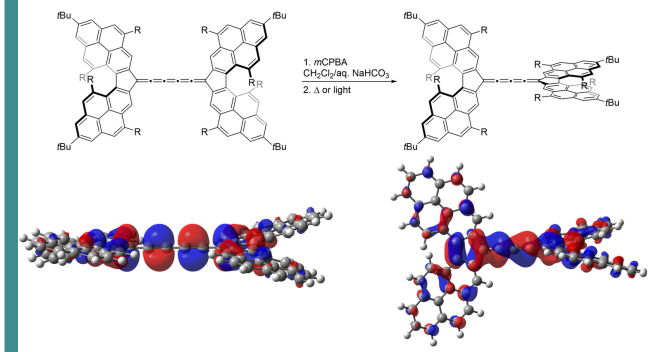
UV-vis spectrum of target molecule taken in DCM

Chiral HPLC



Purification of target molecules by high performance liquid chromatography (HPLC)

Future Directions



Computer predicted 'helical orbital' of an even cumulene (right)

Acknowledgments and References

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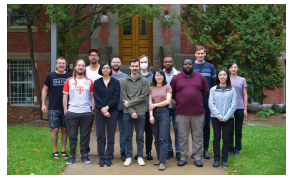
3. C. H. Hendon, D. Tiana, A. T. Murray, D. R. Carbery, A. Walsh, *Chem. Sci.* **2013**, *4*, 4278.
4. M. H. Garner, R. Hoffman, S. Rettrup, G. C. Solomon, *ACS Cent. Sci.* **2018**, *4*, 688.
5. M. H. Garner, C. Corminboeuf, *Org. Lett.* **2020**, *22*, 8028.
6. Source: © Audrey Zwahlen/EyeEm/Getty Images



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