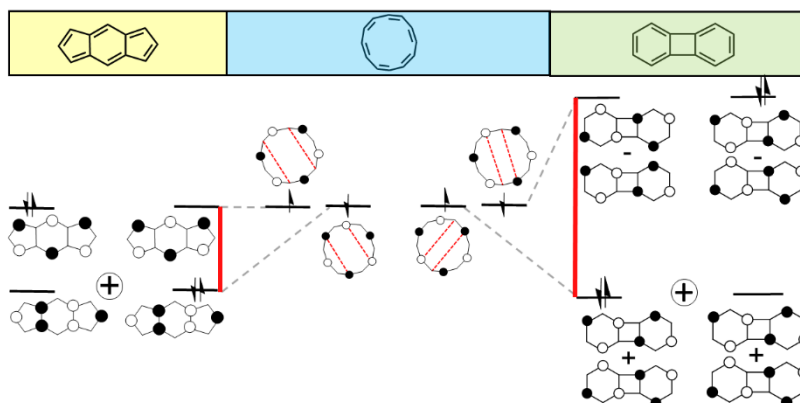


Diradicaloids from [4n] antiaromatic circuits

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Diradicaloid molecules[1] represent cornerstone systems to explore the nature of the chemical bond and the validity of its theories. Recently, they have also gained relevance as multipurpose substrates for organic electronic applications.[2] There are several approaches to design these molecules: (i) diradicaloids made of non-alternant antiaromatic [4n]annulene hydrocarbons, (ii) those developed from quinoidal cores (and (iii) those made of a combination of (i) and (ii).



Despite this strong interest, detailed explanations of the origin of the mosaic of diradicaloid properties are not provided in many cases. Here, the basic conceptual insights that give rise to the emergence of the diradical character in the important area of polycyclic hydrocarbon compounds based on [4n]annulene peripheries with internally “functionalized” covalent structures are presented. For this, we will attempt to connect the orbital structure of these systems with two key energy factors, correlation energy (E_{corr}) and hybridization energy (E_{hybr}) and these with the diradical character, y_0 .

The article begins with pentalene and, subsequently, extends the discussion to s-indacene. These two cases are not consecutive in the arguments but are chosen as the first representative cases of (i) and (iii), respectively. The first [4n] annulenes are all reviewed with special emphasis in $n=3$ given its rich family of antiaromatic molecules, either bicyclic and tricyclic, systems such as heptalene, biphenylene and phenalene and some of their pi-extended derivatives. Finally, from the odd electron benzenoid phenalenyl radical, we explore the antiaromatic fingerprints of olympicene, triangulene and rhombene.

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[2] T. Y. Gopalakrishna, W. Zeng, X. Lu, J. Wu, *Chem. Commun.* **2018**, *54*, 2186–2199.

[3] G. E. Rudebusch, J. L. Zafra, K. Jorner, K. Fukuda, J. L. Marshall, C. J. Gómez-García, L. N. Zakharov, M. Nakano, H. Ottosson, J. Casado, M. M. Haley, *Nat. Chem.* **2016**, *8*, 753-759.