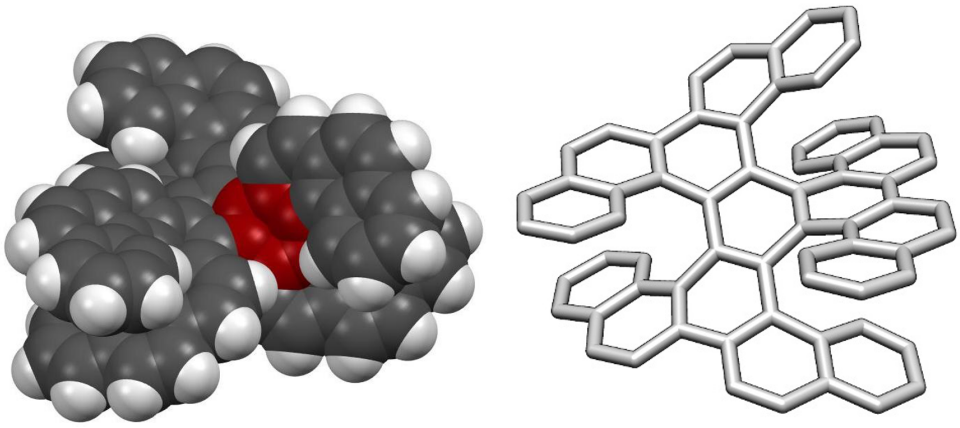
Severely twisted hexagon-based polycyclic aromatic hydrocarbons

A seminar by Dr. Yoann Coquerel
Université Grenoble Alpes | January 25, 2024

In a series of papers published in 1865 – 1866, Prof. Friedrich August Kekulé proposed a cyclic structure for benzene based on his theory of the tetratomicity of carbon. In 1872, he refined his proposal with now a *fully symmetric* structure for benzene with D_{6h} symmetry: he postulated that the structure of benzene is the average between two isomers of hexagonal 1,3,5-cyclohexatriene.[1] Note this was six decades before the introduction of the resonance structures theory and the concept of mesomery by Linus Pauling,[2] and the introduction of the Hückel (4n+2) rule of aromaticity for monocyclic conjugated systems.[3]

In this lecture, I will discuss the stereoselective syntheses and some properties of large inherently chiral polycyclic aromatic hydrocarbons recently prepared in our group. The two (beautiful!) multihelicenes shown below are illustrative.[4,5] Notably, these molecules are composed of hexagonal rings only, some of which exhibit a severe torsion and a marked non-alternant 1,3,5-cyclohexatriene character.



Left: Space-filling representation of a triple carbo[7]helicene that embed the most twisted 'benzene' ring ever observed. **Right:** Tube representation of a triply fused carbo[7]helicene that embed two negative curvatures.

---

[1] P. De Clercq, We Need to Talk about Kekulé: The 150th Anniversary of the Benzene Structure, *Eur. J. Org. Chem.* **2022**, e202200171, DOI: 10.1002/ejoc.202200171.

[2] L. Pauling, The nature of the chemical bond. II. The one-electron bond and the three-electron bond, *J. Am. Chem. Soc.* **1931**, *53*, 3225–3237, DOI: 10.1021/ja01360a004.

[3] E. Hückel, Quantentheoretische Beitrgge zum Benzolproblem. I. Die Elekfronenkonfigurafion des Benzols und verwandfer Verbindungen, *Z. Phys.* **1931**, *70*, 204–286, DOI: 10.1007/BF01339530.

[4] M. Roy, V. Berezhnaia, M. Villa, N. Vanthuyne, M. Giorgi, J. Naubron, S. Poyer, V. Monnier, L. Charles, Y. Carissan, D. Hagebaum-Reignier, J. Rodriguez, M. Gingras, Y. Coquerel, Stereoselective Syntheses, Structures, and Properties of Extremely Distorted Chiral Nanographenes Embedding Hextuple Helicenes, *Angew. Chem. Int. Ed.* **2020**, *59*, 3264–3271. DOI: 10.1002/anie.201913200.

[5] A. Artigas, F. Rigoulet, M. Giorgi, D. Hagebaum-Reignier, Y. Carissan, Y. Coquerel, Overcrowded Triply Fused Carbo[7]helicene, *J. Am. Chem. Soc.* **2023**, *145*, 15084–15087. DOI: 10.1021/jacs.3c05415.