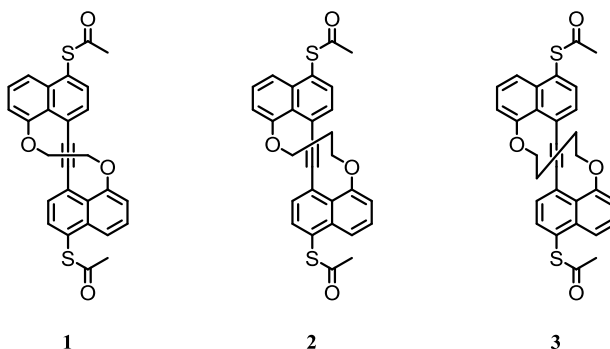


Ethyne π -Orbitals: Discrete or Degenerated?

Florian Degen, Marcel Mayor

Department of Chemistry, University of Basel, St. Johannis-Ring 19, 4056 Basel, Switzerland
f.degen@unibas.ch

Ethyne is a widely used structural motive in molecular electronics due to its conductance properties and its rigidity. [1] Despite its prevalence in applications, the definitions used to describe the ethyne π -orbitals are often ambiguous. Based on linear combination of atomic orbitals (LCAO) they are described as two discrete π -bonds, perpendicular to the other. [2] However, based on topological analysis of electron localization, the π -bonds are described to be degenerated to a ring or a torus. [3] To our knowledge, neither has been shown in an experimental setup.



To clarify this, we are synthesizing a series of bridged molecular rods **1**, **2** and **3**, which are based on 8,8'-(ethyne-1,2-diyl)bis(naphthalen-1-ol). A non-conjugated alkoxy chain of variable length connecting the 1,1'-position of the naphthalenes is introduced to tune the angle between the planes of the aromatic moiety. From previous works in our group, we learned that phenyl substituted ethynes with helical chirality possess considerable rotational flexibility. [4, 5] To slow down the racemisation, we employ naphthalenes instead of benzene.

We aim to compare the conductance measurement of these molecules in a single-molecule break junction (SMBJ) to investigate the influence of the angle on the conductance properties. For the purpose of electrode contacting, thioacetyl anchoring groups *para* to the ethynyl bridge are introduced.

- [1] Chen, J., Wang, W., Klemic, J., Reed, M. A., Axelrod, B. W., Kaschak, D. M., Rawlett, A. M., Price, D. W., Dirk, S. M., Tour, J. M., Grubisha, D. S., Bennett, D. W., *Ann. N.Y. Acad. Sci.*, **2002**, 960, 69 – 99.
- [2] Flemming, I., *Molecular Orbitals and Organic Chemical Reactions, Student Edition*, John Wiley & Sons Ltd, Chichester, **2009**.
- [3] Silvi, B., Savin, A., *Nature*, **1994**, 371, 683 – 686.
- [4] Rickhaus, M.; Bannwart, L. M.; Neuburger, M.; Gsellinger, H.; Zimmermann, K.; Haeussinger, D.; Mayor, M., *Angew. Chem. Int. Ed.*, **2014**, 53, 14587 – 14591.
- [5] Rickhaus, M., Unke, O. T., Mannancherry, R., Bannwart, L. M., Neuburger, M., Haeussinger, D., Mayor, M., *Chem. Eur. J.*, **2015**, 21, 18156 – 18167.