

Thermochemistry and electronic structure properties of cyclacenes using homodesmotic reactions and DFT

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Belt shaped molecules consisting of fused conjugated hydrocarbons are potential nanostructures due to their radially oriented p orbitals and superior optoelectronic properties. $[m]$ Cyclacenes are molecules formed by fusing m membered conjugated rings. $[\delta]_n$ Cyclacenes are formed by fusing n benzene rings. $[\delta]_n$ Cyclacenes can be considered as the basic unit of zigzag carbon nanotubes (CNTs)^[1]. Chemical Synthesis of $[\delta]_n$ cyclacenes is very difficult due to their high strain which results from bending of benzene, reactivity and their predicted open-shell character. If we use molecules with in-built bending, like cyclooctatetraene, it is easier to synthesize belt shaped molecules. But the major concern is change in their electronic properties. In this work, we have studied the thermochemistry and the electronic structure properties of different cyclacenes fused by benzene, cyclobutadiene and cyclooctatetraene using homodesmotic reactions^[2] and density functional theory.

Homodesmotic reactions are theoretically proposed reaction schemes in which reactants and products should have equal number of hybridized carbon atoms with 0,1,2 and 3 hydrogens attached to them and equal number of bonds formed between different hybridized carbon atoms. The scheme is devised so as to provide nearly identical chemical environments for hypothetical reactants and products so as to minimize computational errors^[3].



Figure 1: Examples of Cyclacenes studied in this work

References

1. R. Gleiter, B. Esser and S. C. Kornmayer, *Acc. Chem. Res.* **42** (2009), 1108.
2. S. E. Wheeler, *WIREs Comput Mol Sci* **2** (2012), 204.
3. M. A. Ali and M. S. Krishnan, *J. Org. Chem.* **75** (2010), 5797; M. A. Ali and M. S. Krishnan, *Mol. Phys.* **107** (2009), 2149-2158.