

# Computational Study of Electronic Properties in Oligoacenes

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**Abstract:** Calculations were performed for closed shell singlet states, open shell singlet states and open-shell triplet states using DFT and B3LYP functional in oligoacenes. 6-31+G(d,p) basis set was used to calculate energies for polyacenes in Hartrees at various levels of spin-state configuration. For systems beyond pentacene, open shell singlet state is more stabilized for hexacene, heptacene, octacene and nonacene and singlet triplet gap decreases as size of polyacene increases. This work is used to describe unrestricted DFT calculations, spin contamination and quantum mechanical applications..

**Keywords:** Electronic Properties in Oligoacenes

## I. INTRODUCTION

Organic semiconductors can be broadly classified into two categories: small molecules or oligomers (usually processed in vacuum) and polymers (usually processed by wet chemical techniques). Oligoacenes with fused rings in a linear or extended two-dimensional shape such as graphite are promising candidates for optoelectronic devices because of their notable co-planar  $\pi$  conjugated conformation and outstanding crystalline structure facilitating formation of highly ordered domain. Also oligoacenes which are composed of linearly fused benzene rings have high application potential since they possess large charge carrier mobilities and tunable electronic band gaps. These compounds are generally subject of great interest from both fundamental and applied perspectives, particularly for use in organic electronics [1-6].

In this work, the ground state energies for oligoacene systems at various levels of spin-configurations were calculated using B3LYP functional and 6-31+G(d, p) basis set, to study disjoint nature of orbitals in polyacenes [7,8]. Calculations were performed at a closed shell configuration under restricted spin-state where up ( $\alpha$ ) and down spin ( $\beta$ ) were forced to occupy same energy level and electron-pairing was done according to Aufbau principle. Based on such constraint, variational optimization was performed.

Higher spin- for triplet state were performed via unrestricted method [9,10,11] whereby two highest energy electrons were separately placed in highest energy orbitals so that these two orbitals remain half-filled with a configuration of up-up ( $\alpha\alpha$ ). Calculations for open-shell singlet states were performed by broken symmetry (BS) formalism whereby up-down configuration was mapped to disjoint singlet diradical character ( $\alpha\beta$ ) [12]. The table shows energies of polyacenes for restricted-singlet (RB3LYP), unrestricted open shell singlet (UB3LYP, BS) and unrestricted triplet (UB3LYP, M=3) calculations. All calculations have been performed at 6-31+G(d,p) Gaussian polarised basis set level.

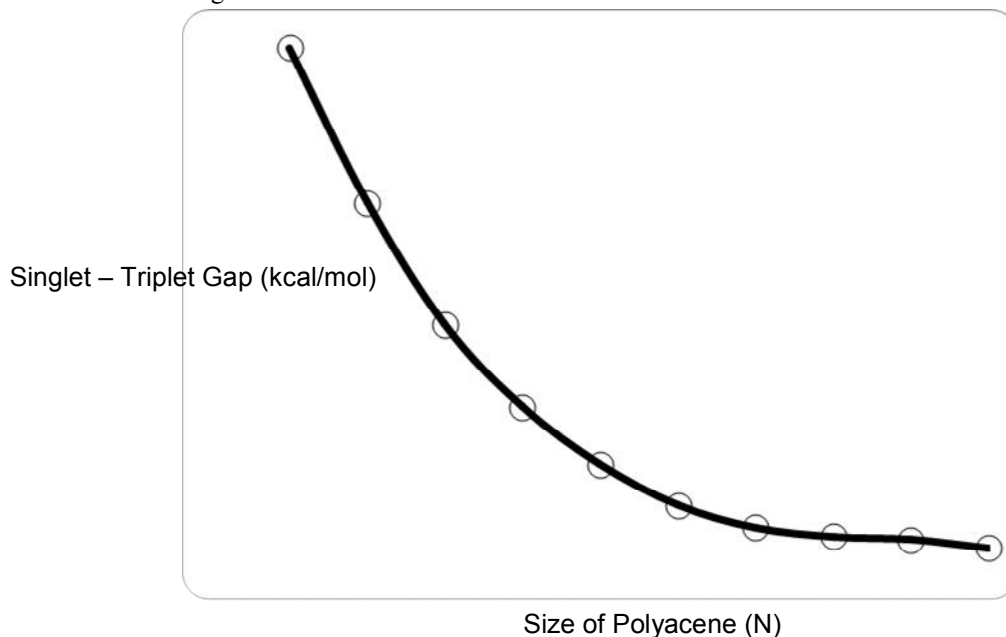
Acenes	0,1 RB3LYP	0,1 UB3LYP	0,3 UB3LYP
Benzene	-232.2683969	-232.2683982	-232.1272604
Naphthalene	-385.9195241	-385.9195241	-385.820521
Anthracene	-539.5643166	-539.5643166	-539.4981868
Phenanthrene	-539.5725331	-539.5725331	-539.4713998
Tetracene	-693.2067599	-693.2067614	-693.1627549
Pyrene	-615.8078875	-615.8078875	-615.7309617
Pentacene	-846.8478843	-846.8478843	-846.8194678
Hexacene	-1000.483519	-1000.488631	-1000.471252
Heptacene	-1154.128821	-1154.131290	-1154.119849



Octacene	-1307.769007	-1307.775104	-1307.766201
Nonacene	-1461.408978	-1461.419089	-1461.410933

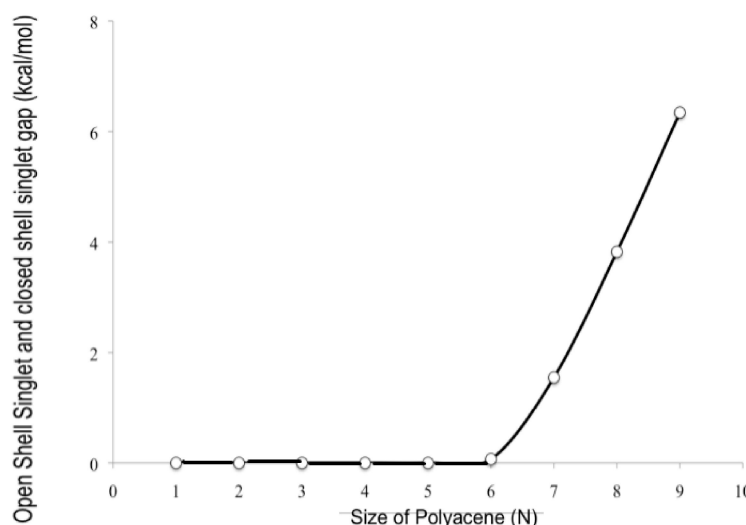
**Figure 1:** Energies for polyacenes in Hartrees at various levels of spin-state configuration B3LYP functional and 6-31+G(d,p) basis set

As size of system increases, triplet state comes closer in energy to singlet state though triplet state never becomes more stable than singlet state.



**Figure 2:** Variation in Singlet-Triplet gap for polyacene with increase in size of systems in conjugation

The singlet-Triplet gap for polyacenes decreases monotonically as number of rings in polyacene increase. For systems beyond hexacene, lowest energy configuration of singlet state corresponds to open shell singlet. Hence while up to pentacene, open shell singlet and closed shell singlet states are degenerate, system starts to stabilize open shell singlet beyond pentacene. For hexacene, heptacene, nonacene and decacene, open-shell singlet configurations are substantially stabilized in comparison to closed shell structures [13,14].



**Figure 3:** Variation in energy difference between closed shell singlet and open-shell singlet states for polyacene with increase in size of systems in conjugation

This graph shows energy difference between closed shell singlet RB3LYP calculations and open shell singlet (UB3LYP,BS) calculations. The energies for these two states are identical till hexacene. As number of fused rings increase, open-shell singlet gets progressively stabilized and for nonacene, structure is stabilized by as much as 6kcal/mol.

## II. CONCLUSION

This study is used to understand disjoint nature of orbitals in oligoacenes and singlet-triplet energies of oligoacenes. Calculations for closed shell configuration, open-shell singlet states and triplet states were performed using B3LYP functional and 6-31+G(d,p) basis set. These low singlet-triplet gap molecules has applications in Molecular orbital theories, unrestricted DFT calculations, spin-contamination and in electronic properties.

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