

Reorganization Energies of Oligoacenes

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Abstract---The reorganization energies of Oligoacenes from benzene to nonacene were studied using DFT method at B3LYP functional and 6-31+G(d,p) basis set in Gaussian09. Reorganization energy (λ_{hole}) and ($\lambda_{\text{electron}}$) from cationic and anionic state are calculated to determine rate of charge transfer and Diffusion coefficient in pair of molecules. The diffusion coefficient is used to determine mobility properties and electronic properties of organic semiconductors. Electron and hole reorganization energies (λ_{hole}) and ($\lambda_{\text{electron}}$) decrease with increase in number of benzene rings in oligoacenes and rate of charge transfer increases. Thus oligoacenes act as high mobility and high efficiency organic semiconductors. The calculation of electron and hole Reorganization energies is an important method for determining mobility of organic molecular solids. Oligoacenes with low reorganization energy values can act as high mobility Organic semiconductors for Organic Field effect Transistors. These properties are used to determine mobility properties of Organic Semiconductors. Thus low reorganization energies has applications in designing of materials.

Keywords--- Reorganization energy, Transport property, mobility, Oligoacene

I. INTRODUCTION

Reorganization energy of oligoacenes is one of its most important Transport property, studied and calculated computationally. It is total sum of inner component reorganization energy and outer component reorganization energy, $\lambda = \lambda_i + \lambda_o$. ie, The total reorganization energy of material includes modification of molecular geometry (change in bond length) as well as surrounding medium due to polarization effect (solvent) with addition and removal of a charge carrier and is expressed as $\lambda = \lambda_i + \lambda_o$. Here λ_i is inner component reorganization energy and λ_o is outer component reorganization energy.[1,2,3]

<http://www.iaeme.com/ijaret.asp>

Reorganization energies studied on Oligoacenes from benzene to nonacene are calculated in electron volts. These reorganization energies decrease from benzene to nonacene as seen from values given computationally. These calculations are performed using B3LYP functional and 6-31+G(d,p) basis set in Gaussian09. These calculations were based on Marcus theory of equations. Reorganization energy depends upon structure of molecule in neutral state and cationic state.[4]

II. REORGANIZATION ENERGIES FOR OLIGOACENES

Acenes	λ_{hole} (eV)	$\lambda_{\text{electron}}$ (eV)
Benzene	0.313	0.249
Naphthalene	0.179	0.235
Anthracene	0.136	0.193
Phenanthrene	0.213	0.304

Tetracene	0.110	0.158
Pyrene	0.149	0.210
Pentacene	0.095	0.129
Hexacene	0.078	0.110
Heptacene	0.068	0.093
Octacene	0.057	0.071
Nonacene	0.049	0.060

These calculations are obtained using B3LYP functional and 6-31+G(d,p) basis set of DFT. In these reorganization energy of oligoacenes, it is observed that bond lengths, structure, plane of the molecule changes for product obtained. The bond length and bond angles changes, which depends upon relaxation energies. Reorganization energy λ_{hole} and $\lambda_{\text{electron}}$ is decreasing from benzene to nonacene and rate of charge transfer increases as from electron transfer equation. These molecules can be used as organic semiconductors in optoelectronic devices, due to low λ values. These reorganization energy is related with Diffusion coefficient and distance between pair of molecules. The theoretical values of the reorganization energies are in agreement with values obtained experimentally. It is observed that Reorganization energy is according to the Franck-Condon principle. The reorganization energy (λ_{hole}) and ($\lambda_{\text{electron}}$) of cation and anion of the molecule in ground state and in excited state are calculated, as from the Franck-Codon principle.[2,3] This property is an important parameter for determining mobility property of organic semiconductors (λ values).

The reorganization energy includes inner component factor and an outer component factor Reorganization energies are

calculated as

$$\lambda_{\text{hole(electron)}} = (E^*_{\text{cation(anion)}} - E) + (E^*_{+(-)} - E_{+(-)})$$

where E describes energy of optimization of neutral molecule, $E_{+(-)}$ explains energy of optimization of cationic or anionic molecule, $E^*_{\text{cation(anion)}}$ describes energy of neutral molecule in cationic or anionic geometry, $E^*_{+(-)}$ describes energy of cationic or anionic molecule in neutral geometry. This equation explains cationic and anionic energy in Hartrees and energy of neutral molecule. The reorganization energies were calculated at B3LYP functional and 6-31+G(d,p) basis set in Gaussian09. From rate of electron transfer equation, λ depends on nuclear wavefunctions and overlapping of wavefunctions occur which makes rate of electron transfer in these Oligoacenes. Using B3LYP functional and 6-31+G(d,p) basis set, λ has been shown to give values decreasing from benzene to nonacene.

Molecules for Reorganization Energy(eV) are determined.	$\lambda_{\text{hole}}(\text{eV})$	$\lambda_{\text{electron}}(\text{eV})$
PTCDA	0.144	0.251
PTCDA(N-CH ₃)	0.157	0.259

In the above examples Perylene - 3,4,9,10 tetracarboxylic - 3,4,9,10 dianhydride(PTCDA) and its N-methylated analogues, the hole reorganization energy is less than electron reorganization energy. These molecules can act as high mobility organic semiconductors, due to low λ values, where π - π stacking, planarity, molecular layers add to high mobility.

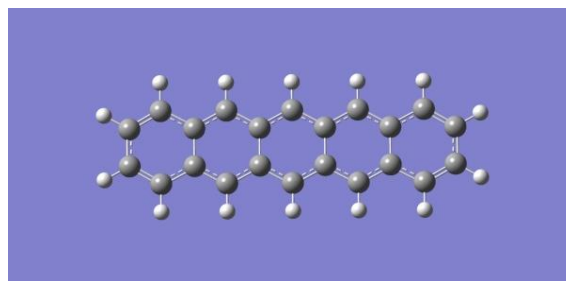
Oligoacenes with good reorganization energy values are used as good organic semiconductors. Pentacene to nonacene show a sharp decrease in reorganization energy values. When λ decreases, rate of charge transfer W increases, as seen in the Marcus Equation.

$$W = \frac{2H_{mn}^2}{h} \sqrt{\frac{\pi^3}{\lambda K_B T}} e^{-\lambda/4K_B T}$$

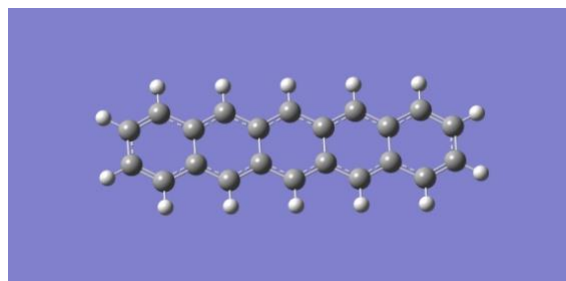
where H_{mn} , is coupling matrix element (electronic coupling) between pair (m,n) of molecules, λ is Reorganization energy and K_B is Boltzmann constant. When W increases, Diffusion coefficient (D) will increase and mobility will increase. Thus these oligoacenes from pentacene to nonacene act as High mobility good organic semiconductors in optoelectronic devices [5]. Other factors which depends on Reorganization energy are Intermolecular coupling and Transfer Integral [8,9]. Thus these reorganization energy are based on these factors also. Reorganization energy is energy required for reactants to convert to products as seen in Gibbs energy diagram with displacement coordinate. λ is reorganization

energy required to convert reactant molecules to product complex, where it is utilized or used for structural rearrangement of reactant molecules and its relative orientation. These molecular rearrangements include relative reorientation of reactant molecules and relative reorientation of solvent molecules. Electron transfer can occur only after thermal fluctuations bring geometry of reactant molecules to the point, where electron transfer takes place according to Franck Codon principle. [6,7]. Rate of electron transfer in these molecules depends upon λ , which is reorganization energy and H_{mn} which is coupling matrix element between pair of molecules. H_{mn} depends upon wavefunctions of two charge localised states φ_m and φ_n between molecular pairs, which makes strength of interactions in these molecules [10].

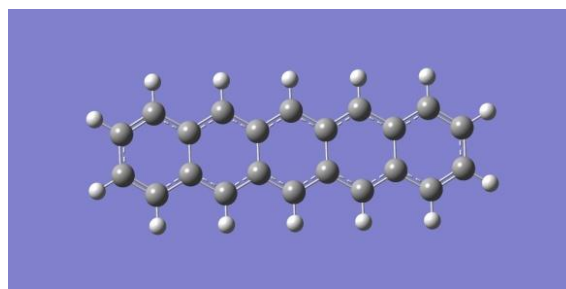
Figure showing reorganization energies of optimized structures of Pentacene in cationic and anionic geometry using B3LYP functional and 6-31+G(d,p) basis set.



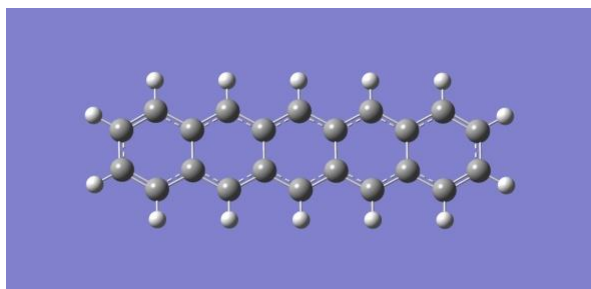
Energy of optimization of neutral molecule



Energy of cationic charged molecule in neutral structure



Energy of Optimized structure of cationic molecule



Energy of neutral molecule in cationic structure

III. SUMMARY

The development and analysis of charge carrier mobility and its electronic properties can be possible in any general computational technique like DFT. Calculation of electron and hole Reorganization energies is an important method for determining mobility and hence electronic properties of organic molecular solids. Oligoacenes with low reorganization energy values can act as high efficiency Organic Semiconductors for Organic Field effect Transistors and has applications in hole transporting materials and electron transporting materials. These low reorganization energy values has applications in Designing of molecules and biological materials.

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