Reorganization Energies of Oligoacenes

Dr. Sharon Achamma Abraham
Assistant Professor, Department of Chemistry, Mar Thoma College, Tiruvalla, Kerala, India
Email: sharon.1384@gmail.com

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 ($\lambda_{\text{hole}}$) 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 ($\lambda_{\text{hole}}$) 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 bondlength) 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 $\lambda_i$ is inner component reorganization energy and $\lambda_o$ is outer component reorganization energy.[1,2,3]

Reorganization energies studied on Oligoacenes from benzene to nonacene are calculated in electron volts. These reorganization energies decreases 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 OLGIOACENES

<table>
<thead>
<tr>
<th>Acenes</th>
<th>$\lambda_{\text{hole}}$(eV)</th>
<th>$\lambda_{\text{electron}}$(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>0.313</td>
<td>0.249</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>0.179</td>
<td>0.235</td>
</tr>
<tr>
<td>Anthracene</td>
<td>0.136</td>
<td>0.193</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>0.213</td>
<td>0.304</td>
</tr>
</tbody>
</table>

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 bondlengths, structure, plane of the molecule changes for product obtained. The bond length and bond angles changes, which depends upon relaxation energies. Reorganization energy $\lambda_{\text{hole}}$ 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 $\lambda$ 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 ($\lambda_{\text{hole}}$) and ($\lambda_{\text{electron}}$) of cation and anion of the molecule in groundstate and in excited state are calculated, as from the Franck-Condon principle.[2,3] This property is an important parameter for determining mobility property of organic semiconductors($\lambda$ values). The reorganization energy includes inner component factor and an outer component factor. Reorganization energies are...
calculated as

\[ \lambda_{\text{hole(electron)}} = (E_{\text{cation(anion)}} - E) + (E_{\text{neutral}} - E_{\text{cation(anion)}}) \]

where \( E \) describes energy of optimization of neutral molecule, \( E_{\text{cation(anion)}} \) explains energy of optimization of cationic or anionic molecule, \( E_{\text{neutral}} \) describes energy of neutral molecule in cationic or anionic 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, \( \lambda \) 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, \( \lambda \) has been shown to give values decreasing from benzene to nonacene.

<table>
<thead>
<tr>
<th>Molecules for Reorganization Energy(eV) are determined.</th>
<th>( \lambda_{\text{hole}} ) (eV)</th>
<th>( \lambda_{\text{electron}} ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTCDA</td>
<td>0.144</td>
<td>0.251</td>
</tr>
<tr>
<td>PTCDA(N-CH\text{\textsubscript{3}})</td>
<td>0.157</td>
<td>0.259</td>
</tr>
</tbody>
</table>

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 \( \lambda \) values, where \( \pi-\pi \) 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 \( \lambda \) decreases, rate of charge transfer \( W \) increases, as seen in the Marcus Equation.

\[ W = \frac{2\hbar m n^2}{h} \left( \frac{\pi}{2K_{\text{B}}T} \right)^{\frac{1}{2}} e^{-\lambda/K_{\text{B}}T} \]

where \( H_{mn} \) is coupling matrix element(electronic coupling) between pair (m,n) of molecules, \( \lambda \) is Reorganization energy and \( K_{\text{B}} \) 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. \( \lambda \) 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 \( \lambda \), 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 \( \varphi m \) and \( \varphi n \) 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.
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.

REFERENCES