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Computational Design of Cation Doped Polyacenes

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

Abstract

The Barrier Heights of cation doped polyacenes are calculated computationally using DFT method and B3LYP functional. The barrier heights in kJ/mol using B3LYP functional and 6-31+G(d,p) basis set in Gaussian09 has furnished a source to design one-dimensional materials and to study rate of hopping of charges in one-dimensional materials. It is observed that rate of reaction increases when barrier heights decreases and H_{mn} coupling matrix element increases. The barrier heights of reactions decreases as size of cation increases $Li^+ > Na^+ > K^+$. For OligoaceneLi$^+$ complexes rate of reaction increases with temperature, the barrier height is 24.26kJ/mol in AnthraceneLi$^+$ complex. This is observed in NaphthaleneLi$^+$, AnthraceneLi$^+$, TetraceneLi$^+$, PentaceneLi$^+$,and HexaceneLi$^+$ complexes. Quantum-mechanical tunneling takes place in AnthraceneNa$^+$ complex which can be possible in all OligoaceneNa$^+$ complexes such as NaphthaleneNa$^+$, AnthraceneNa$^+$,TetraceneNa$^+$,PentaceneNa$^+$ and HexaceneNa$^+$ complexes. Quantum tunneling found out in OligoaceneNa$^+$ complexes ,which depends on smaller barrier height. Since barrier height is very low 2.52kJ/mol, tunneling also takes place in AnthraceneK$^+$ complexes. In OligoaceneLi$^+$ complexes ,the most typical tunneling region is about 1.25kJ/mol lower than barrier top. Since tunneling occurs from regions that are closer to barrier top instead of lowest vibrational ground state,tunneling is strongly vibrationally assisted.This explains apparent lack of curvature in CVT+SCT Arrhenius plot .Because rate is very high and rate of diffusion also very high in OligoaceneNa$^+$ complexes, these materials has applications in electrodes, biological systems , solid state graphene battery, and in electrochemical energy storage applications.

Keywords: barrier height ;quantum tunneling; dft ;functional; semiconductors ; canonical variational transition State Theory.

I. Introduction

This theoretical research work urges computational modelling and designing of cation doped polyacenes in field of semiconductors and to reveal molecular forces and interactions.The work aims not only in improving performance of organic materials for possible incorporation in devices, but also for satisfying need for insight into the relevant physical processes that govern the electrical conduction in these materials and complexes.The main objective of this work is to design cation doped oligoacenes or polyacenes as high mobility and high rate semiconductors in field of optoelectronic devices and to calculate parameters that enhance rate of reactions. Barrier Height is difference between energy of ground state structure and energy of transition state structure.

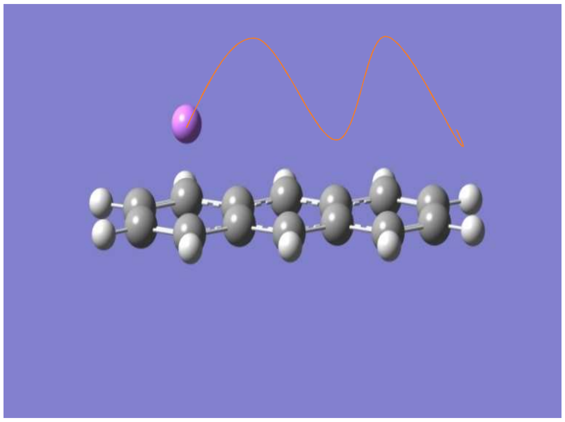
II. Materials and Methods

The Barrier Height calculations based on density functional theory(DFT) method were performed on a series of polyacenes with one-dimension. All $\Delta E^{\#}$ barrier height energies in kJ/mol were produced using B3LYP functional and 6-31+G(d,p) basis set in Gaussian09 computationally[11,12]. The 6-31+G(d,p) polarized basis set was used. All frequency calculations for Transition state structures were computed in this method. The role of dispersion interactions in stabilization of ground state structures were assessed by calculations at M05-2X functional and 6-31+G(d,p) basis set[13]. A cation Li^+, Na^+ and K^+ is placed at a distance of 2.5 Angstrom units above each ring and binding energy in each fused ring acene systems(Oligoacenes) and ground state structure energy in kcal/mol can be calculated. Then same cation Li^+, Na^+ and K^+ is allowed to move horizontally from one end of ring to other end and transition state energy (TS)in each of ring in kJ/mol can be calculated .Difference in energy between these two structures gives barrier height in these complexes.

III. Analysis

For studying cation doped Oligoacenes , CVT and CVT+SCT calculations were performed for acene-metal ion complexes using M052x/6-31 +G(d,p) method[1,2]. CVT is Canonical Variational Transition state Theory method and SCT is Small-Curvature Tunneling approximation method[14,15,16] where SCT includes tunneling.

CVT and CVT+SCT calculations were performed for naphthalene, anthracene, tetracene,pentacene, hexacene Li$^+$ and Na$^+$ complexes



Anthracene……Li$^+$

Fig.1 Structure of cation doped polyacene using B3LYP functional and 6-31+G(d,p) basis set.

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The above is structure of Anthracene….Li$^+$ complex using DFT method and B3LYP 6-31+ G(d,p) basis set. Barrier height of Anthracene….Li$^+$ from first ring to second ring is 24.26kJ/mol and second ring to third ring is 21.25kJ/mol. At 77K the rate of hopping of Li$^+$ is $5 * 10^{-4}$ s^{-1} and $8*10^{-3}s^{-1}$ for CVT and CVT+SCT calculations[17,18]. At 300K, the rate of hopping increases for Li$^+$ hopping to $8*10^{8}s^{-1}$ and $10* 10^{8}s^{-1}$ at CVT and CVT+SCT calculations . As temperature increases from 77K to 300K, the rate of hopping of Li$^+$ increases in both CVT and CVT+SCT calculations[10].

3.1 Li$^+$ hopping in Oligoacenes and Arrhenius plot

In OligoaceneLi$^+$ complexes, the barrier is very high, large amount of energy is needed to cross the barrier for example 24.68kJ/mol in NaphthaleneLi$^+$ and Li$^+$ moves along the barrier according to classical mechanics. Barrier decreases as the length of acene increases. In contrast to Li$^+$ complexes,barrier height is 7.4kJ/mol in Na$^+$ complexes.

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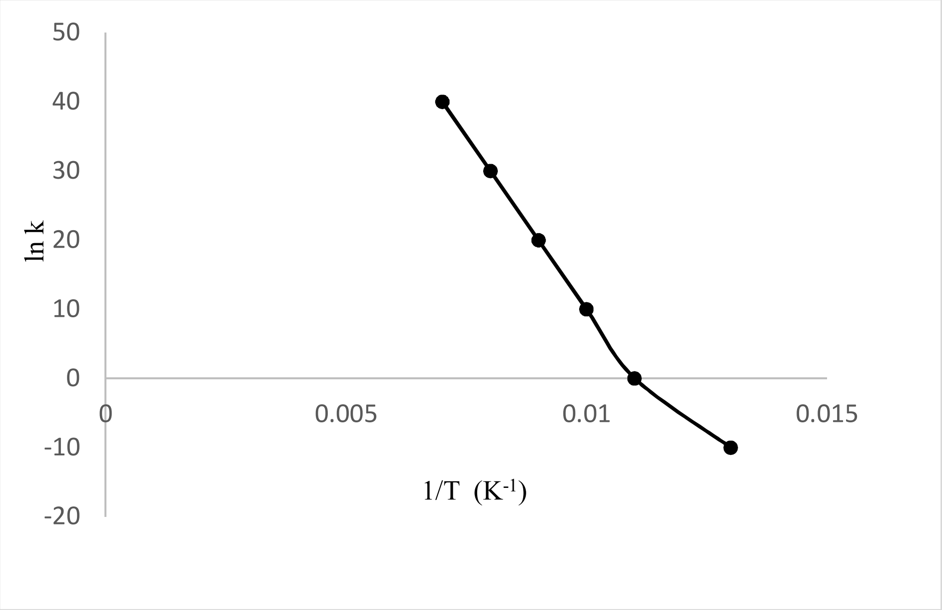

Fig.2 Arrhenius plot of CVT and CVT+SCT rate constant for Li^+ hopping in Oligoacenes

The above is a Arrhenius CVT and CVT+SCT plot for anthracene,tetracene, pentacene,hexacene, naphthalene Li^+ complexes. In above graph 1/T is plotted along x axis and ln k is plotted along y axis. . The rate of hopping can be calculated as

$$k = \frac{2H_{mn}^2}{h}\sqrt{\frac{\pi^3}{\lambda kbT}}\, e^{-\Delta E^{\#}/nRT} \qquad (1)$$

H_{mn} is coupling matrix element between pair of molecules, $\Delta E^{\#}$ is barrier height of oligoacenes, k_b is Boltzmann constant, T is temperature. The rate of hopping k increases if barrier height is low and H_{mn} increases[5].The same type of plot can be applied for AnthraceneLi$^+$, TetraceneLi$^+$,PentaceneLi$^+$, HexaceneLi$^+$ and NaphthaleneLi$^+$ complexes. CVT+SCT plot of OligoaceneLi$^+$ complexes is also the same.

Na^+ hopping in Oligoacenes and Arrhenius plot

In OligoaceneNa$^+$ complexes, the barrier is very less when compared to Li^+ complexes.Therefore Na^+ tunnel or leak through the barrier and its probabllity is very

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high.Hence Na^+ doped materials can be designed and has industrial applications.

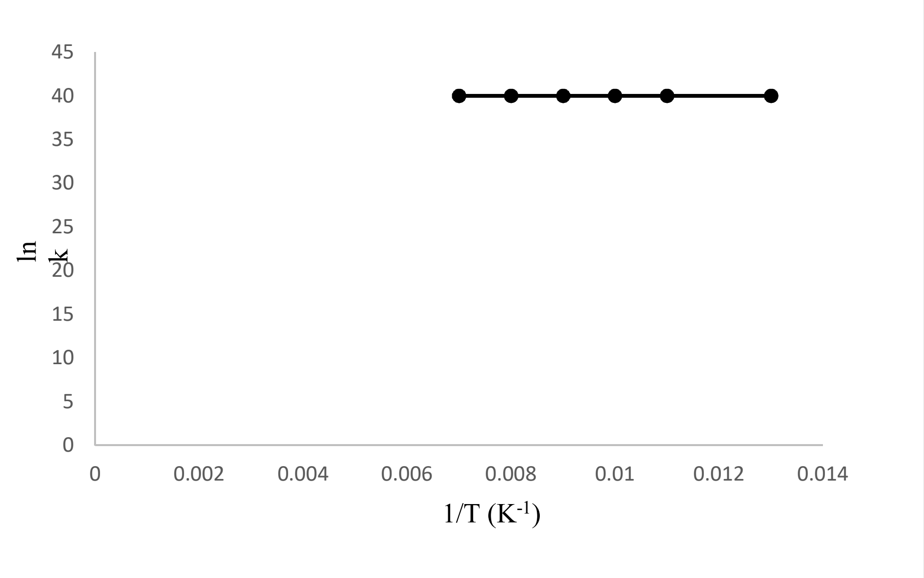


Fig.3 Arrhenius plot of CVT+SCT rate constant for Na^+ hopping in Oligoacenes

The above plot is CVT+SCT graph for OligoaceneNa$^+$ complexes.In CVT graph,ln k decreases with temperature 1/T and is similar as in OligoaceneLi$^+$ complexes. Na^+ complexes shows faster rate than Li^+ complexes. High rate is observed in Na^+ complexes due to Quantum tunneling and is independent of 1/T values[4]. In Na^+ complexes,on plotting 1/T along x axis and ln k along y axis , high rate and is constant , observed because of smaller barrier height(7.82kJ/mol in AnthraceneNa$^+$) in the above graph. The above plot can be used for anthraceneNa$^+$, tetraceneNa$^+$, pentaceneNa$^+$, naphthaleneNa$^+$,hexaceneNa$^+$ complexes. . The rate of hopping of Na^+ complexes is very high and discussedtunneling is very high. Na^+ diffuses completely via tunneling or Quantum tunneling[9].

IV. Result and Discussion

The rate of cation hopping shows a marked variation in Li^+,Na^+ and K^+. Li^+ hopping is discussed according to Arrhenius equation. Tunneling decreases and less in Li^+

hopping.Tunneling increases and its probability is very high in Na^+ complexes. In K^+ Oligoacene complexes, tunneling occurs.

Table1. Barrier Heights $\Delta E^{\#}$ in kJ/mol of Li^+,Na^+ and K^+ to various rings in polyaromatic hydrocarbons.

PAH[a]	**Transition State1 or TS1[b] (kJ/mol)**			**Transition State2 or TS2**			**Transition State3 or TS3**			**Transition State4 or TS4**			**Transition State5 or TS5**		
Oligoacenes	Li^+	Na^+	K^+	Li^+	Na^+	K^+	Li^+	Na^+	K^+	Li^+	Na^+	K^+	Li^+	Na^+	K^+
Naphthalene	24.68	7.40	2.25												
Anthracene	24.26	7.82	2.52	21.25	5.69	3.13									
Tetracene	23.84	7.65	2.30	21.42	6.44	2.97	20.6	6.56	2.42						
Pentacene	23.22	7.19	2.63	22.5	6.23	2.34	20.92	6.35	2.92	20.2	6.27	2.71			
Hexacene	22.46	7.53	2.30	22.17	6.40	2.30	20.75	6.31	2.76	21.25	6.81	3.09	22.17	6.4	3.51

[a] Poly Aromatic Hydrocarbons(Oligoacenes).

[b] TS1 is the barrier height of hopping of metal ion from first ring to second ring Ref fig 1.

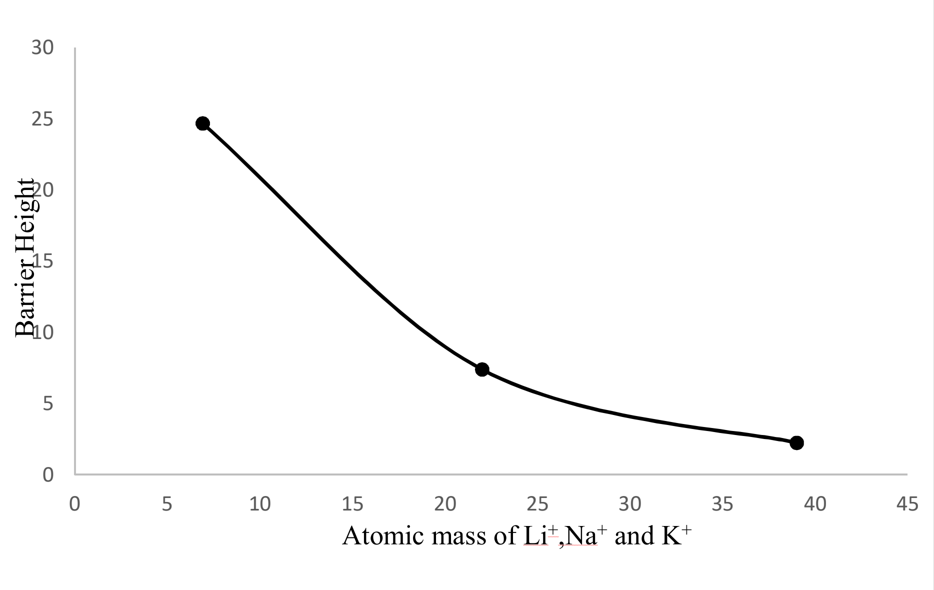
In the above table, the barrier height corresponds to NaphthaleneLi^+ is 24.68kJ/mol, NaphthaleneNa^+ is 7.40kJ/mol and Naphthalene K^+ is 2.25kJ/mol. The barrier height for NaphthaleneLi^+ differs from AnthraceneLi^+ by 0.42 kJ/mol.In the same ring in anthracene it varies by 3.01kJ/mol. However barrier height decreases as the size of cation increases[19,20].

4.1 Probability of Tunneling

The probability of tunneling across a barrier is given by

$$P = e^{\frac{-w\pi^2\sqrt{2mE}}{h}} \qquad (2)$$

where w is the barrier width, E is barrier height , m is the mass of the particle[3]. The probability of tunneling depends on barrier width and barrier height.



On plotting barrier height against atomic masses,it is found that barrier height decreases as atomic mass increases.Smaller atomic mass metal ions has high barrier height to cross the barrier and higher atomic masses has low barrier height.

V. Conclusions

Quantum-mechanical tunneling is particularly important in electron-transfer reactions and in reactions involving transfer of a proton. In OligoaceneLi$^+$ complexes , rate k increases with temperature, explained using Arrhenius equation.In OligoaceneNa$^+$ complexes, high rate and Quantum tunneling is observed due to smaller Barrier Height as seen in the above table. High diffusion constant is observed for Na$^+$ complexes[6,7]. In OligoaceneK$^+$ complexes, there is less tunneling than Na$^+$. Therefore Na$^+$ intercalated graphene π surface can be designed , can be used as one dimensional materials and it has applications in solid-state graphene batteries[8], electrochemical energy storage applications,one-dimensional materials, radioactive decay and in Scanning Tunneling microscopy.

Declaration of Interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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