Theses Booklet of the Ph.D. Dissertation

titled as

Growth Mechanisms of Polycyclic Aromatic Hydrocarbons – A Case Study of Benzo(a)pyrene

presented by

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1. INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) consist of a set of several thousand ubiquitous pollutants in the environment and belong to the persistent organic pollutants (POPs) class [1]. Their structure is composed of multiple aromatic rings, with a pair of carbon atoms shared between them [2].

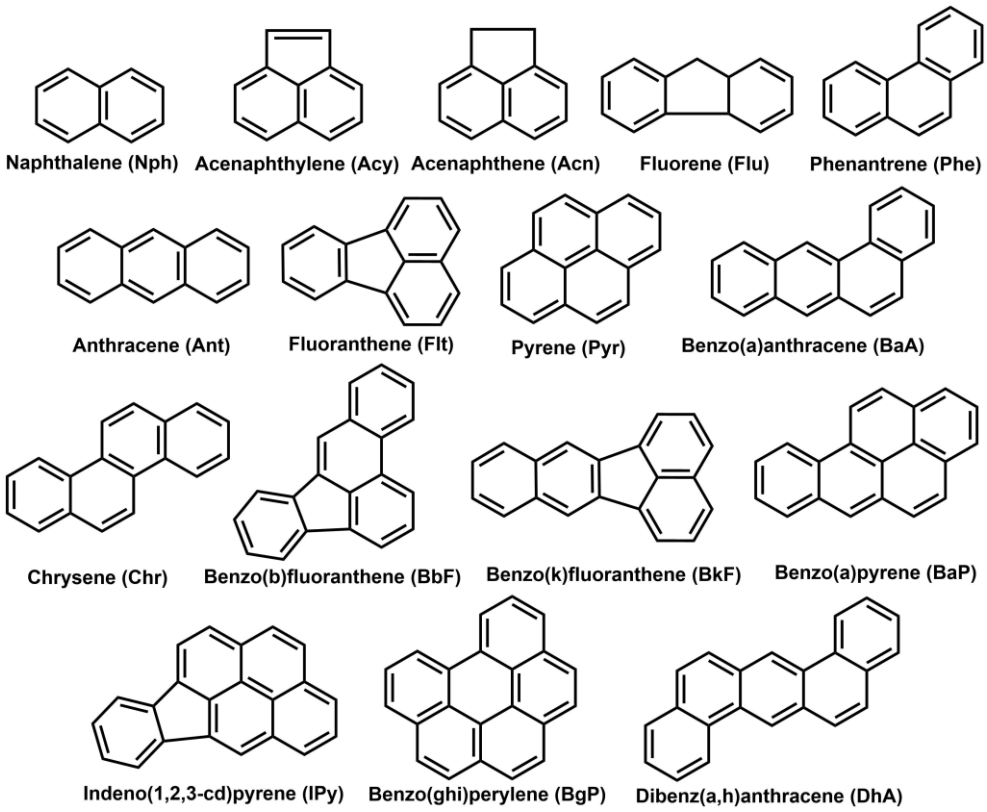

Figure1 *2D representation of of the 16 priority PAHs or "parent PAHs".*

PAHs are formed during the incomplete combustion of organic material, thus, they can be emitted during natural processes like forest fires and volcanic eruptions [3]. However, the most predominant emissions originate from anthropogenic activities, such as biomass burning, coke production, thermal industrial processes, vehicle use, waste burnings, *etc.* [4], [5]. An essential feature of PAHs is that they play an important role in the formation of combustion-generated particles. They are considered precursors for soot, initiating the soot formation by their inception and through their further reactions [8]. The mutagenic and teratogenic effects of PAHs had been thoroughly proven. They can react with DNA, inducing thereby mutations in the lung, liver, and skin [6], [7]. It is also proven that the carcinogenic potency of PAHs increases with the size of the molecules [11]. In the last few decades, strong efforts have been made to create an appropriate model for the growth of PAHs [12], [13]. Various models have been developed and validated with a large array of

possible reactions due to the diversity of species that are present in significant concentrations in hydrocarbon flames [14]. Consequently, since the research system is influenced by many factors, the goal to fill the blanks in the giant map of PAH formation mechanisms is still far from being accomplished.

This doctoral dissertation aimed to systematically study the growth of PAHs. In order to determine potential reaction initiation points on the skeletons of polycyclic aromatic hydrocarbons, all unique C-H bond dissociation enthalpies (BDE) of the 16 priority PAHs were determined. By using the previously determined initiation points, several different reaction pathways have been proposed and studied which led to the formation of one of the most carcinogenic PAH, benzo(a)pyrene. All in all, four types of possible reaction mechanisms - hydrogen abstraction, acetylene addition (HACA), Diels-Alder (DA), hydrogen abstraction ethynyl radical addition (HAERA), and methyl addition cyclization (MAC) - were examined step by step starting from chrysene and benzo(a)anthracene and leading to benzo(a)pyrene (**Figure 2**). A wide range of computational chemistry methods was used and the calculations were carried out by using the Gaussian 09 program package [15].

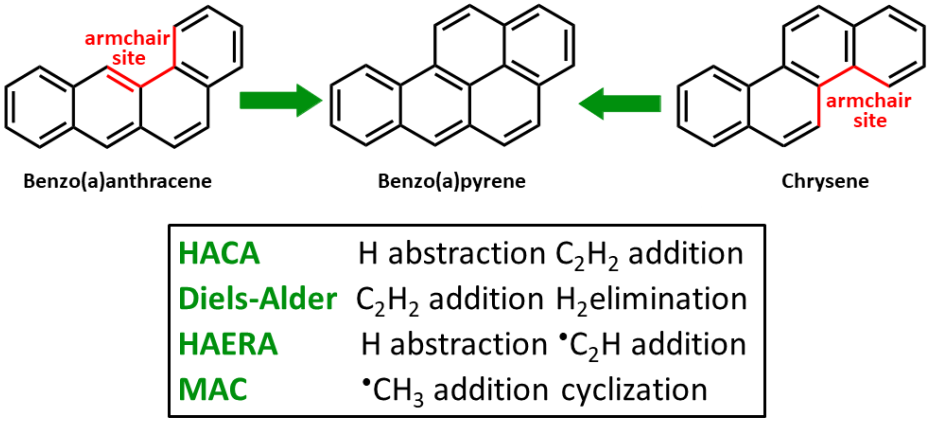

Figure 2 *The applied reaction mechanisms for benzo(a)pyrene formation from Chrysene and Benzo(a)anthracene.*

2. NEW SCIENTIFIC RESULTS

Based on my computational research carried out during my PhD studies on the reaction mechanism of polycyclic aromatic hydrocarbons the following main conclusions were drawn as new scientific results:

1st Thesis

Bond dissociation enthalpies (BDEs) of the 16 priority PAHs are calculated for each unique C-H bond by applying the ωB97X-D/6-311++G(d,p) level of theory and are categorized into seven groups: zig-zag, peak, armchair, penta-bay, anthracene type, aliphatic, and next-to-aliphatic type (**Figure 3**).

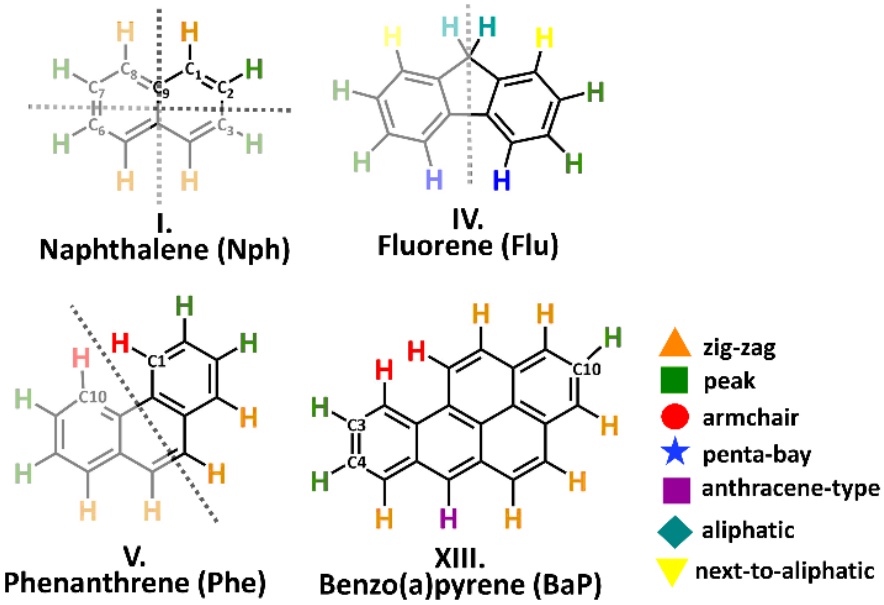

Figure 3 *Categorization of the H atoms of the studied PAHs.*

The BDE and bond length values for the C-H bonds within the 16 priority PAH are in the range between 342.0 – 485.6 kJ/mol and 1.081 – 1.095 Å, respectively. Based on the calculated bond dissociation enthalpy (BDEs) values the potential reaction initiation points are determined on each 16 priority PAHs. The reaction initiation points are in armchair and peak positions for seven and six molecules from the 16 priority PAHs, respectively (**Figure 4**).

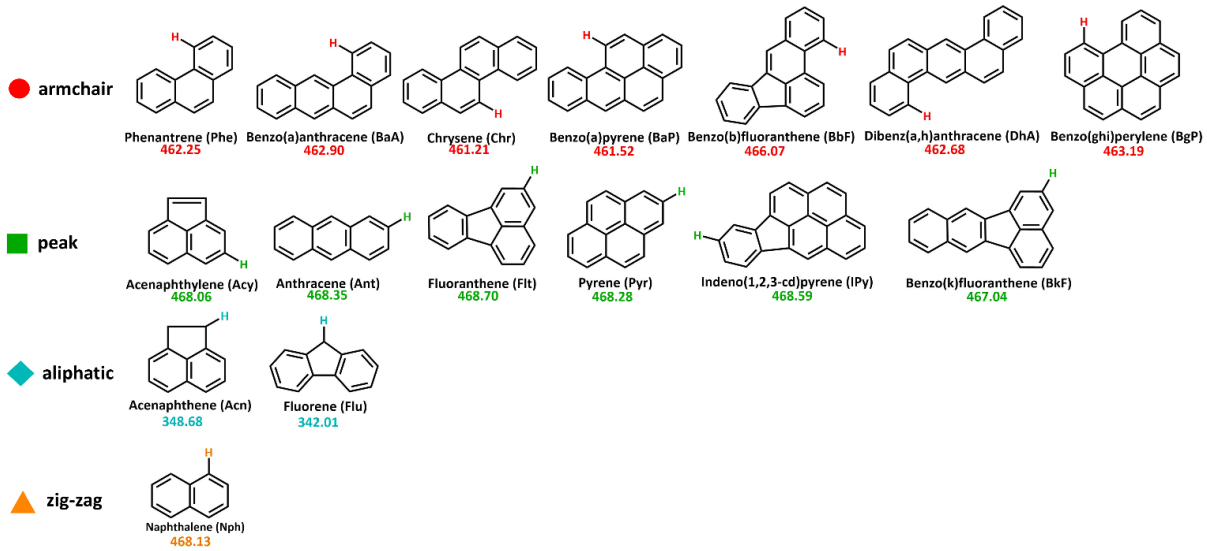

Figure 4 *Reaction initiation points of the 16 priority PAHs along with the corresponding bond dissociation enthalpy (BDE, in kJ/mol) values.*

2nd Thesis

Benzo(a)pyrene (BaP) formation starting from armchair positions of benzo(a)anthracene (BaA) and chrysene (Chr) are explored by computational methods and a new growth mechanism has been proposed. The mechanism is a hydrogen abstraction ethynyl radical addition process (HAERA) within which two hydrogen abstractions, one ethynyl addition and one hydrogen atom addition occurred. Four possible HAERA reaction pathways are identified and each of these have four transition states and four intermediate structures (**Figure 5**).

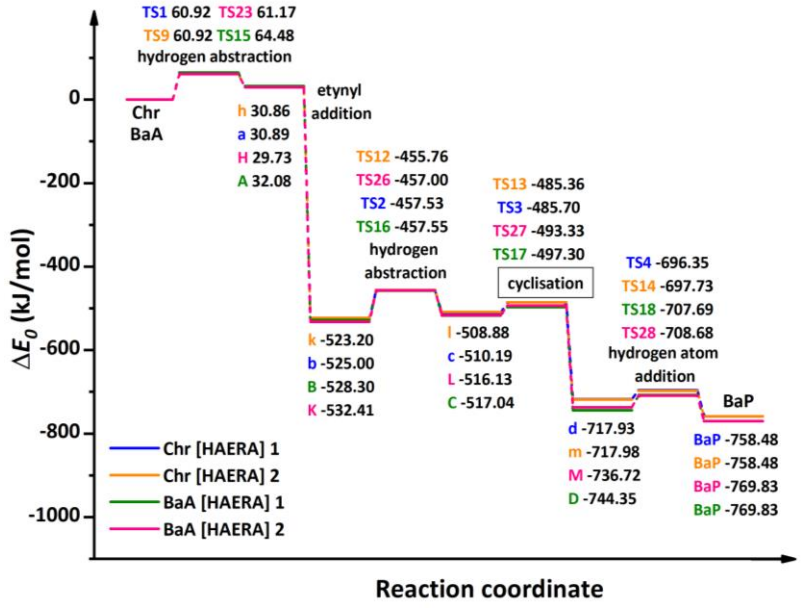

Figure 5 *The potential energy curves obtained for the four HAERA reaction routes.*

3rd Thesis

The hydrogen abstraction acetylene addition mechanism (HACA) has also been considered as a potential growth mechanism leading to benzo(a)pyrene (BaP) and four new reaction pathways explored starting from benzo(a)anthracene (BaA) and chrysene (Chr), each involving one hydrogen abstraction, one acetylene addition, one cyclization and one hydrogen atom addition. The reaction pathways have three transition states and three intermediate structures. In the reaction pathways the barrier heights for the first steps are 60.92 kJ/mol for Chr and 61.17 kJ/mol and 64.48 kJ/mol for the BaA routes, respectively (**Figure 6**).

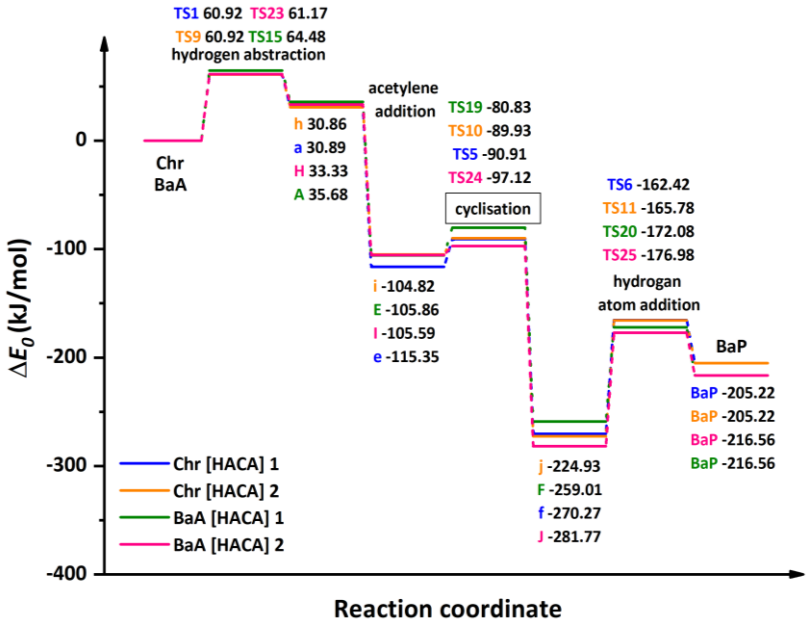

Figure 6 *The potential energy curves obtained for the four HACA reaction routes.*

4th Thesis

Two Diels-Alder (DA) reaction pathways are proposed and analysed by applying computational methods for the formation of the strongly carcinogenic benzo(a)pyrene (BaP) starting from benzo(a)anthracene (BaA) or chrysene (Chr) and involving one acetylene molecule addition along with one hydrogen molecule elimination. Both reaction routes had 2 transition state structures and one intermediate structure. The reaction pathways have 220.07 kJ/mol and 164.61 kJ/mol activation energy values having Chr and BaA as reactants, respectively (**Figure 7**).

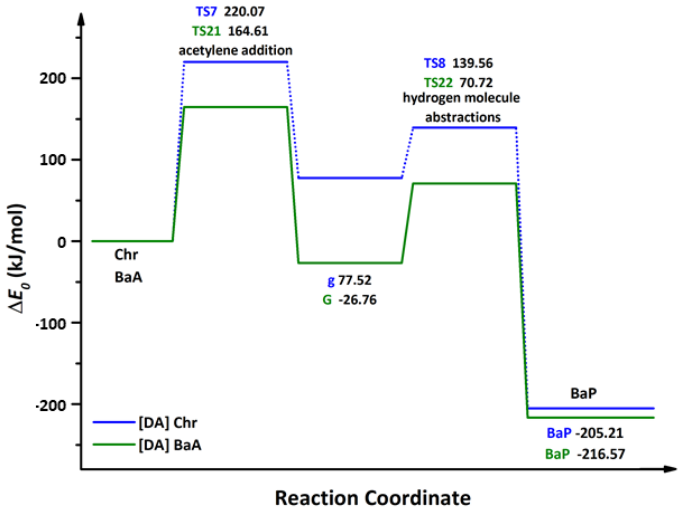

Figure 7 *The potential energy curves obtained for the two Diels-Alder reaction routes.*

5th Thesis

By applying computational methods, a new methyl addition/cyclization (MAC) mechanism leading to the toxic benzo(a)pyrene (BaP) starting from benzo(a)anthracene (BaA) or chrysene (Chr) is proposed. The mechanisms include four hydrogen abstractions, two methyl radical additions, three hydrogen atom eliminations, one ring closure, and one rearrangement step. In the studied pathways, methyl additions (intermediate c, C) are the most exoergic steps with –313.5 kJ/mol and –307.4 kJ/mol which occurred in the case of the chrysene and benzo(a)anthracene, respectively. The rate determining steps are 92.2 kJ/mol and 94.5 kJ/mol having Chr and BaA as reactants, respectively (**Figure 8**).

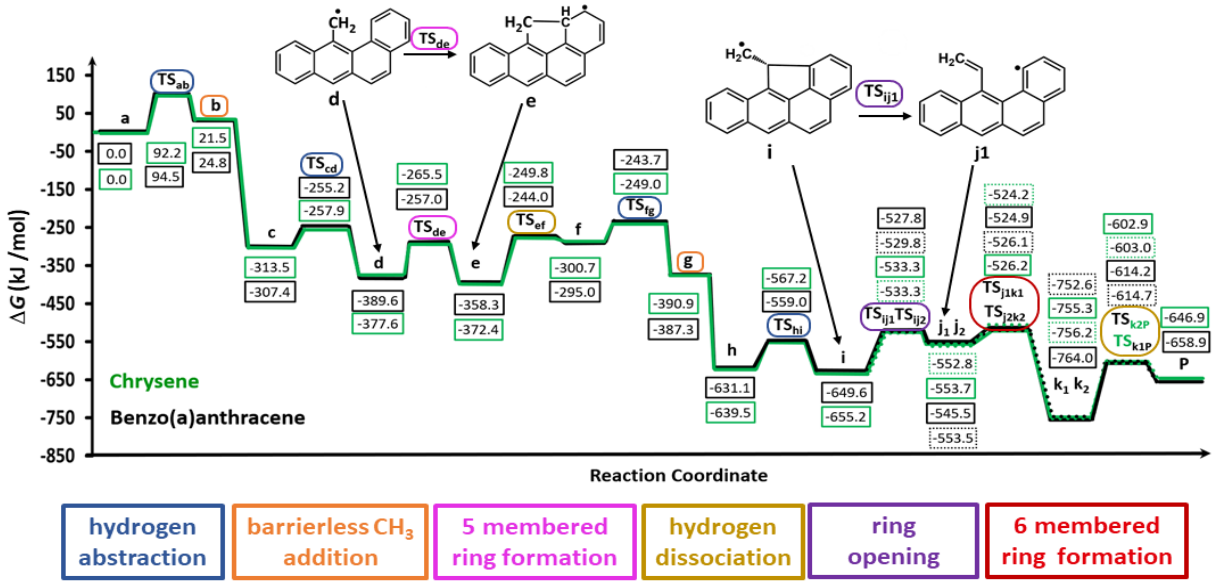

Figure 8 *The potential energy curves obtained for the two MAC reaction routes.*

3. SUMMARY

Polycyclic aromatic hydrocarbons (PAH) are harmful chemicals emitted to the environment by incomplete combustion. As the aromatic structure grows, the carcinogenic effect increases, and thus understanding their formation mechanisms is crucial. In this doctoral dissertation, reaction initiation points of the 16 priority PAHs are determined by computing the BDE and C-H bond lengths values. The results are in a range between 342.0 – 485.6 kJ/mol and 1.081 – 1.095 Å, in the case of the BDE and C-H bond lengths, respectively. The obtained results also showed that most of the initiation points are hydrogens in the armchair and peak positions.

In addition, new reaction pathways leading to benzo(a)pyrene, a PAH with well-known carcinogenic effects, are also explored. Starting from armchair positions of both chrysene or benzo(a)anthracene, four types of reaction mechanisms are studied: hydrogen abstraction acetylene addition (HACA), hydrogen abstraction ethynyl radical addition (HAERA), Diels-Alder (DA) and methyl addition cyclization (MAC) processes. A total of 12 reaction pathways are explored, with 50 intermediate and 52 transition state structures. Results show that HAERA is the most, and DA is the least exergonic reaction mechanism for benzo(a)pyrene formation using validated computational chemistry methods. It can be stated, that through this doctoral dissertation a deeper understanding of PAH growth and benzo(a)pyrene formation is achieved (**Figure 9**).

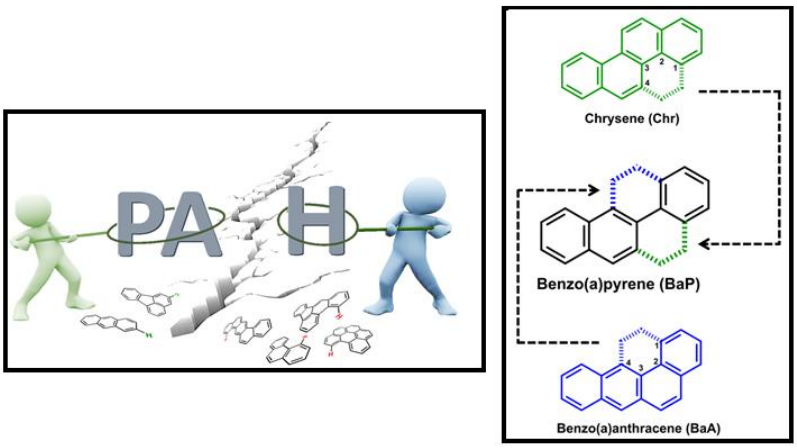

Figure 9 *The schematic representation of the successfully achieved aims of the doctoral dissertation.*

4. ÖSSZEFOGLALÁS

A szerves anyagok tökéletlen égése során policiklusos aromás szénhidrogének (PAH-ok) keletkeznek. Ahogy az aromás szerkezet növekszik, a vegyületek rákkeltő hatása fokozódik, ezért nagyon fontos a képződési mechanizmusaik feltárása és megértése. A doktori értekezésem első harmadában 16 ún. „parent" PAH kötésdiszociációs entalpiáit (BDE) vizsgálom és kategorizálom. Az eredmények azt mutatják, hogy a vizsgált molekulák BDE értékei és C-H kötéshosszai a 342,0 - 485,6 kJ/mol és 1,081 - 1,095 Å értékek közé esnek. Az eredmények alapján, a növekedési mechanizmusok lehetséges kezdőpontjait is meghatároztam. Az eredmények azt mutatják, hogy a reakciók az ún. karosszék („armchair") és csúcshelyzetekben („peak") elhelyezkedő hidrogének absztrakciójával kezdődnek.

A doktori disszertációmban az erősen rákkeltő benzo(a)pirén különböző reakció mechanizmusait is feltártam számításos kémiai módszerek alkalmazásával. Hidrogén absztrakció acetilén addíció (HACA), hidrogén absztrakció etinil gyök addíció (HAERA), Diels-Alder (DA) és metil addíciós ciklizáció (MAC) mechanizmusokat vizsgáltam, s ezek összesen 12 reakcióúton, 50 intermeridert és 52 átmeneti állapotot tartalmaznak. Az eredmények azt mutatják, hogy a HAERA a leginkább és a DA a legkevésbé exergonikus reakció útvonal. A számolásokhoz különböző elméleti szinteket alkalmaztam, de csak validált módszerekkel kapott eredmények kerültek tárgyalásra. Összességében elmondható, hogy a doktori értekezésem eredményei elősegítik a PAH-ok, s különösen a benzo(a)pirén, képződésének és növekedésének mélyebb megértését.

5. PUBLICATIONS RELATED TO THE SUBJECT OF THE DISSERTATION

Q1 **Edina Reizer**, Imre G. Csizmadia, Árpád B. Palotás, Béla Viskolcz, and Béla Fiser, "Formation mechanism of benzo(a)pyrene: One of the most carcinogenic polycyclic aromatic hydrocarbons (PAH)," *Molecules*, vol. 24, no. 6, 2019, doi: 10.3390/molecules24061040.
Number of Independent Citations: 10

Q2 **Edina Reizer**, Imre. G. Csizmadia, Károly Nehéz, Béla Viskolcz, and Béla Fiser, "Theoretical investigation of benzo(a)pyrene formation", *Chemical Physics Letters.*, p. 138564, Mar. 2021, doi: 10.1016/j.cplett.2021.138564.
Number of Independent citations: 1

D1 **Edina Reizer**, Béla Fiser, Béla Viskolcz, Formation and growth mechanisms of polycyclic aromatic hydrocarbons: A mini-review", *Chemosphere,* 2021, doi: 10.1016/j.chemosphere.2021.132793

Edina Reizer, Béla Fiser, "Reaction initiation points of polycyclic aromatic hydrocarbons", *submitted*, 2021.

Further Publications

Q1 Vanyorek, László, Ádám Prekob, Emőke Sikora, **Edina Reizer**, Gábor Muránszky, Ferenc Kristály, Béla Viskolcz, and Béla Fiser. "Application of carbon nanotube coated aluminosilicate beads as "support on support" catalyst for hydrogenation of nitrobenzene." *Journal of Industrial and Engineering Chemistry* 79 (2019): 307-313. doi: 10.1016/j.jiec.2019.07.006

Presentations and posters

1. Doktoranduszok Fóruma
   Miskolc, Hungary, 2017.11.16.
   Study of atmospheric pollution with aromatic polycyclic hydrocarbons using various bioindicators.
2. 3. MÉB Égéstudományi Konferencia
   Budapest, Hungary, 2017.11.17
   The use of moss, lichen and pine needle for the investigation of PAH molecules in 02the air in six European countries.
3. Műszaki Tudomány az Észak-Kelet Magyarországi Régióban
   Szolnok, Hungary, 2018. 05. 31
   Lignit égetése során keletkező policiklikus aromás szénhidrogének (PAH) áttekintése és vizsgálata.
4. 8th Visegrad Symposium on Structural System Biology
   Lučenec, Slovakia, 2018.06.20.
   Computational Study on the formation of benzo(a)pyrene.

5. 5th Anniversary Celebration of Confucius Institute
   Miskolc, Hungary, 2018.10.11.
   Computational Study on the formation of benzo(a)pyrene.
6. 1st Science Unlimited Conferenc - Eötvös Symposium
   Miskolc, Hungary, 2019.05.23.
   A DFT Application for Benzo(a)pyrene Formation.
7. KeMoMo -QSAR Symposium
   Szeged, Hungary, 2019.06.06.
   Mechanistic Studies of Benzo(a)pyrene Formation.
8. 9th Visegrad Symposium on Structural Systems Biology
   Szilvásvárad, Hungary, 2019. 06.18
   Growth Mechanism of Benzo(a)pyrene -A Theoretical Study.
9. Kémiai Előadói Napok
   Szeged, Hungary, 2019. 10. 28.
   A mechanistic investigation of benzo(a)pyrene formation with acetylene additions.
10. Környezetmérnöki Konferencia és Szakmai Nap
    Debrecen, Hungary, 2019. 11. 8.
    A Benzo(a)pirén képződésének vizsgálata metil addíció ciklizáció mechanizmus alkalmazásával.

6. KÖSZÖNETNYÍLVÁNÍTÁS/ ACKNOWLEDGEMENT

Ez a dolgozat nem jöhetett volna létre, ha nincs egy olyan remek témavezetőm mint *Dr. Fiser Béla*, ezért elsősorban neki szánom köszönetemet. Amellett, hogy azonnal elvállalta a témavezetésemet, nyitottsággal, jókedvvel és főleg kreatívitással vezetett be a számítógépes kémia elbüvölő világába. Köszönöm, hogy mind a szakmai, mind a személyes kérdések megválaszolásában mentorom volt. Hálás vagyok a törődésért, és a figyelemért amelyeket nyújtott az évek során, valamint azért, hogy velem együtt örült a sikereimnek. Türelmes magyarázatait és bátorító szavait biztosan továbbviszem a szakmai pályámon.

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