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# Reaction pathways and transition states of the C-C and C-H bond cleavage in the aromatic pyrene molecule - A Density Functional study

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## ARTICLE INFORMATION

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## ABSTRACT

The activation and reaction energies of the C-C and C-H bonds cleavage in pyrene molecule are calculated applying the Density Functional Theory and 6-311G Gaussian basis. Different values for the energies result for the different bonds, depending on the location of the bond and the structure of the corresponding transition states. The C-C bond cleavage reactions include H atom migration, in many cases, leading to the formation of $CH_2$ groups and H-C≡C-acetylenic fragments. The activation energy values of the C-C reactions are greater than 190.00 kcal/mol for all bonds, those for the C-H bonds are greater than 160.00 kcal/mol. The reaction energy values for the C-C bonds range between 56.497 to 191.503 kcal/mol. As for the C-H cleavage reactions the activation energies range from 163.535 to 165.116 kcal/mol, the reaction energies are nearly constant, 117.500kcal/mol. The geometries of the transition states and reaction products are discussed too.

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## 1. Introduction

The industrial and environmental importance of polycyclic aromatic hydrocarbons (PAH's) is documented in the literature [1-4]. They are present with considerable amounts in the crude oil of different sources in the world [5]. Their degradation represents an important route towards additional consumable energy sources. However, they are known to be strong carcinogenic and may be formed through incomplete combustion reactions of organic compounds [6]. Many experimental and theoretical studies were reported [7-15] which investigate the possibilities of converting PAH's to smaller molecules that are suitable as fuels or starting material for the chemical industries, such as methane, acetylene, ethylene, or single-ring aromatic molecules. In former studies, it was found that for most PAH's the energies required for the C-H bond cleavage are lower than those for the C-C bonds [15]. These results showed that the thermal cracking for most PAH's should start with the cleavage of a C-H bond forming PAH radicals. It was realized that the estimation of the energies required for the thermal cracking of PAH's demands an accurate evaluation of the C-H cleavage activation and reaction energies. Such evaluation should proceed through the study of the corresponding reaction path enabling the assignment of the transition state and reaction products. It requires the application of an elaborate theoretical method such as the quantum mechanical Hartree-Fock [16] or the Density Functional Theory methods [17-20].

In former papers, we reported quantum mechanical descriptions of the reaction paths and transition states of C-H and C-C bond cleavage in benzene, toluene, naphthalene and anthracene molecules [21-23]. Applying the Hartree-Fock and Density Functional methods (of the B3LYP type [20]), it was possible to evaluate the energies of the transition states and the final products of the reactions. The calculated values agreed satisfactorily with the available experimental literature values [24-27]. The structures of the transition states (TS) as well as the final products could be elucidated. Neither fixed pattern of the reaction paths nor structures of the TS's resulted from the studies. In fact different C-C or C-H bonds showed different TS and reaction product structures and conformations. For this reason, a detailed study of the cleavage reaction for each bond in each molecule had to be done. In the present paper, we describe such a study for pyrene, a prominent 4 ring PAH molecule (Scheme 1).

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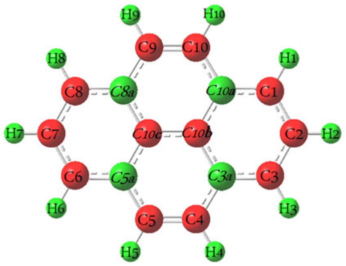


**Scheme 1**

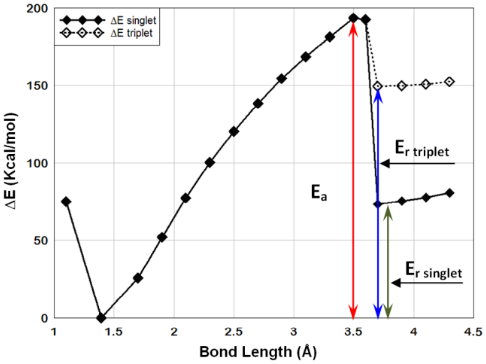


**Figure 1.** Potential energy curve for (C1-C2) bond breakage in pyrene molecule according to DFT calculation ($E_a$ = 192.425, $E_{r\ singlet}$ = 73.484, $E_{r\ triplet}$ = 149.379 kcal/mol).

## 2. Experimental

### 2.1. Method of calculation

The density functional theory method of the B3LYP type [18,19] and in the open shell form, was applied as it is programmed within the Gaussian 03 program system [28]. The 6-311G Gaussian basis was considered within the same study of the cleavage reactions for the C-C and C-H bonds. The calculations were done for the energy of the molecule at various lengths of the corresponding bond. For all points along the reaction path, open shell DFT calculations were done for both singlet (S) and triplet (T) electron configurations. The treatment showed that for all discussed reactions, the (S) configuration was the more stable up to the transition state. After that the electronic configuration of the product varied from one bond to the other. For the calculation of the energy value for each point along the reaction path, which is chosen to be equivalent to the C-H or the C-C internal coordinate, the corresponding bond length was kept constant, i.e. “frozen”, while the other (3N-5) internal coordinates were varied to obtain the minimum of the molecular energy. The obtained energy values were plotted then against the "frozen" bond length values to yield the required reaction path. It was possible then to assign graphically, and study the structure of, the transition state and the product of the reaction (Figure 1).

## 3. Results and discussion

### 3.1. Cleavage of the C1-C2 bond

Density Functional Theory (DFT) treatment was done for the C1-C2 bond cleavage of pyrene, following the same strategy of work as described above. The resulting potential energy curve showed similar shape to that reported formerly for other polyaromatic compounds [20-22] (Figure 1). A study of the curve leads to the following conclusions;

(a) A singlet (S) electronically configured transition state (TS) appears at C1⋯C2 distance of approximately 3.6 Å;

(b) The singlet (S) reaction product is more stable than the triplet (T) product;

(c) The activation energy $E_a$ = 192.428 kcal/mol and the (S) reaction energy is 73.484 kcal/mol.

On departing from the TS, the H3 atom migrates from C3 to C1 forming an exo-methylene group which seems to stabilize the (S) reaction product. The formed H2-C≡C-C3-C3a group remains in the plane of the molecule, Figure 2. No H atom migration results for the (T) reaction route. The same treatment shows that at the TS the atoms H1C1-C10a are tilted out of the plane of the aromatic residue, whereas the H3 atom is moved out of the plane but in the opposite direction.

The formation of an acetylenic (C2) atom due to this reaction is apparent on studying the variation of the atomic charges at C1 and C2 atoms along the reaction path, Figure 3. The charges of the two atoms at the initial geometry are C1(-0.10) and C2(-0.12). They deviate more from each other at longer distances to meet again at the TS, 3.6 Å. At the reaction product, their values are (C1, -0.32 and C2, -0.58). The bigger charge at C2 indicates the formation of a (more electro-negative) *sp* hybridized C atom.

### 3.2. Cleavage of the C3-C3a bond

The cleavage of this bond proceeds through a coplanar transition state at the C3-C3a bond distance of 4.1 Å, Figure 4. The final singlet configured reaction product shows a coplanar geometry. The reaction includes H2 migration from C2 to C3a forming a $CH_2$ group. The conjugated HC3≡C2-C1= group remains coplanar relative to the rest of the molecule. The formation of the acetylenic bond is concluded on the basis of the calculated C3 charge density, Figure 5, and the length of the C3-C2 bond (1.220 Å).

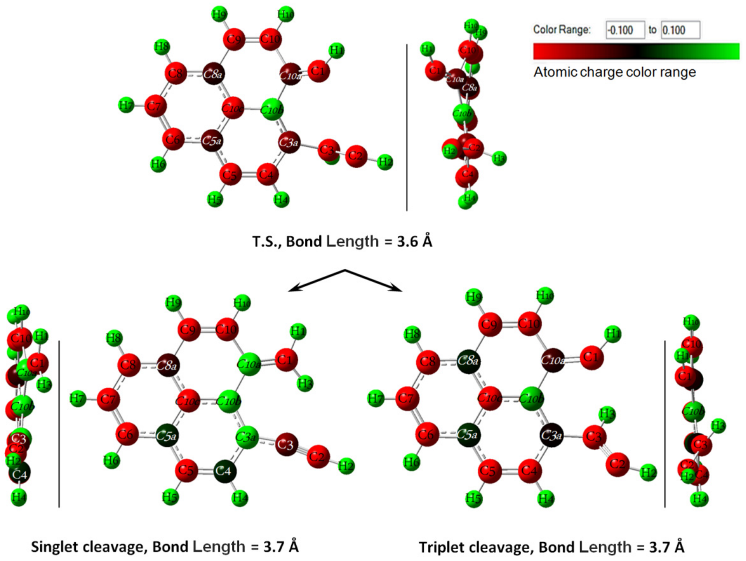


**Figure 2.** Molecular conformations of pyrene molecule due to C1-C2 bond cleavage reaction, showing the transition state (T.S.) and the singlet and triplet reaction products.

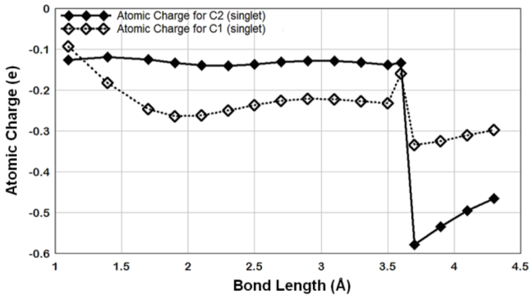


**Figure 3.** Variation in atomic charges for C1 and C2 atoms during (C1-C2) bond breakage in pyrene molecule (Singlet state).

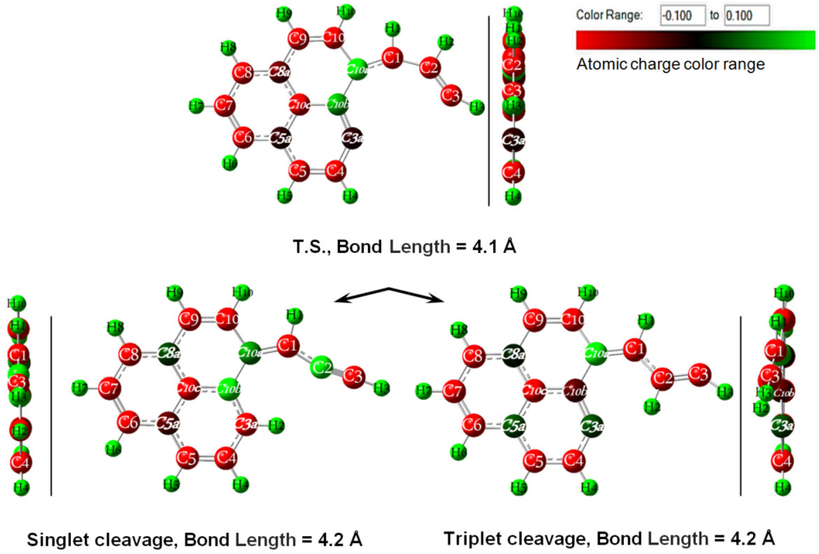


**Figure 4.** Geometry of the transition state, the singlet and the triplet final products of the C3-C3a bond cleavage reaction.

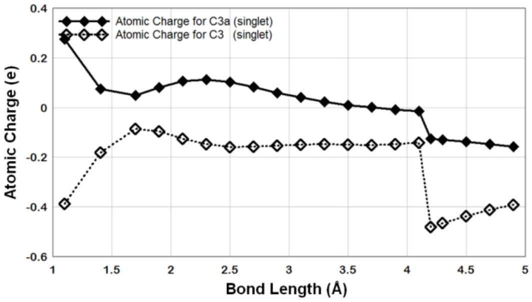
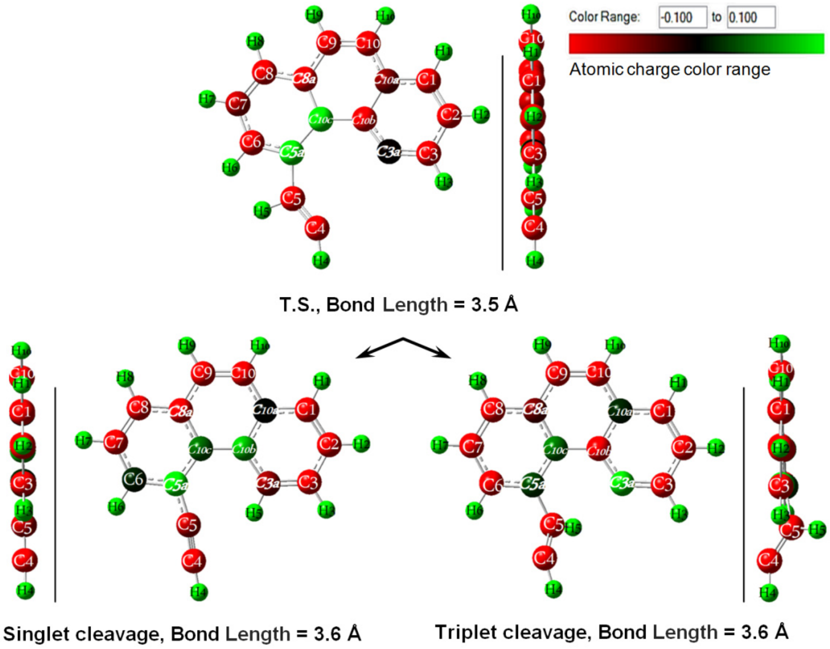


**Figure 5.** Variation in atomic charges for C3 and C3a atoms during (C3-C3a) bond breakage in pyrene molecule (Singlet state).



T.S., Bond Length = 3.5 Å

Singlet cleavage, Bond Length = 3.6 Å

Triplet cleavage, Bond Length = 3.6 Å

**Figure 6.** Geometry of the transition state, the singlet and the triplet final products of the C3a-C4 bond cleavage reaction in pyrene molecule.

No H atom migration results from the treatment for the (T) configured reaction. The calculated energies for the reaction are; $E_a(S)$ = 201.125 kcal/mol, $E_r(S)$ = 70.383 kcal/mol and $E_r(T)$ = 144.308 kcal/mol. Figure 5 shows the variation in the atomic charges of C3 and C3a atoms along the C3-C3a bond cleavage reaction path.

### *3.3. Cleavage of the C3a-C4 bond*

According to the DFT study carried out for this reaction, the bond cleavage proceeds *via* a (S) TS at a C-C distance 3.5 Å, Figure 6. The final reaction product possesses an (S) electron configuration too. It falls energetically lower than the triplet final state.

The calculated energy values for the reaction are; $E_a$ = 173.615 kcal/mol, $E_r(S)$ = 56.497 kcal/mol and $E_r(T)$ = 131.648 kcal/mol. Figure 6 shows that all three reaction species possess coplanar conformations. The stable final (S) product is formed via H atom migration from C5 to C3a. No such H migration results for the (T) final product. The H migration forms a 5a-acetinyl- derivative of phenanthrene.

Figure 7 shows the variation of the calculated atomic charges for atoms C3a and C4. A study of the graphs reveals that the charges of both atoms approach each other at the transition state and depart at the (S) final product. The value of the (negative) charge at C4 is higher than at C3a. At the (S) final product the C4-C5 bond length is 1.218 Å, indicating the acetylenic bond nature.

### *3.4. Cleavage of C3a-C10b bond*

The cleavage of this central bond is expected to proceed under considerable strain. In fact the potential energy curve for both electron configurations, (S) and (T) exhibit narrow and sharp minima followed by rapid elevation of the total molecular energy, Figure 8. The resulting (T) product is more stable than the (S) product. The calculated $E_a$ = 206.523 kcal/mol, $E_r$ (T) is 184.788 kcal/mol and $E_r(S)$ = 194.975 kcal/mol. Both TS and (T) final product are calculated to be coplanar, Figure 9.

For all 3 species, the TS and final products, the (4N+2) electron rule is satisfied. As for the atomic charges for both C3a and C10b atoms, they have equal values at the initial geometry of the molecule and differ along the reaction path to meet at a common value at R = 3.6 Å, Figure 10.

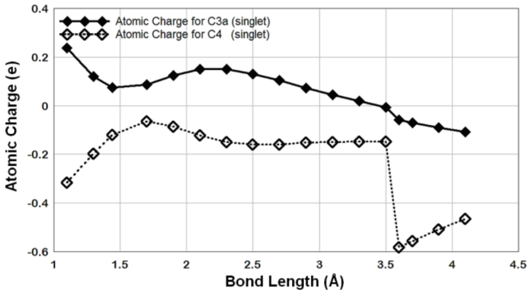


**Figure 7.** Variation in atomic charges for C3a and C4 atoms during (C3a-C4) bond breakage in pyrene molecule (singlet state).

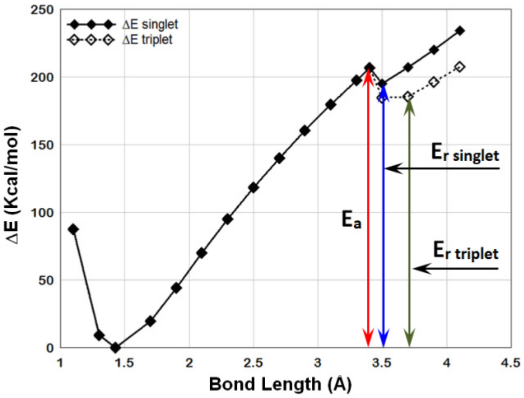


**Figure 8.** Potential energy curve for (C3a-C10b) bond breakage in pyrene molecule according to DFT calculation. ($E_a$ = 206.523, $E_{r\ singlet}$ = 194.975, $E_{r\ triplet}$ = 184.788 kcal/mol).

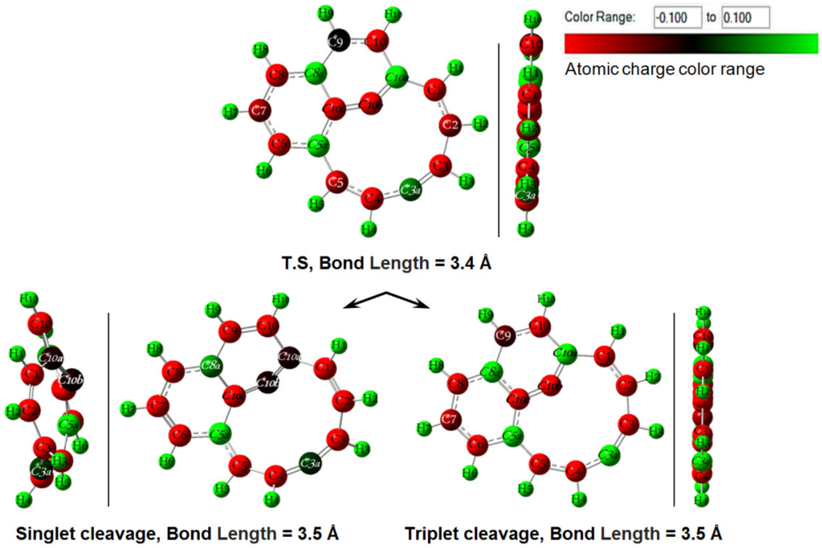


**Figure 9.** Geometry of the transition state, the singlet and the triplet final products of the C3a-C10b bond cleavage reaction in pyrene molecule.

### *3.5. Cleavage of C4-C5 bond*

This bond cleaves at a bond distance >3.1Å of the (S) transition state, Figure 11. The calculated activation energy of this reaction is 207.192 kcal/mol, the reaction energies for the two differently electron-configured products fall near each other, i.e. $E_r(S)$ = 193.152 kcal/mol and $E_r(T)$ = 191.503 kcal/mol.

Figure 12 shows the calculated geometries of the reaction transition state (S), the (S) and (T) reaction products. Figure 13 shows the symmetric behavior of the C4 and C5 atomic charges along the entire reaction path.

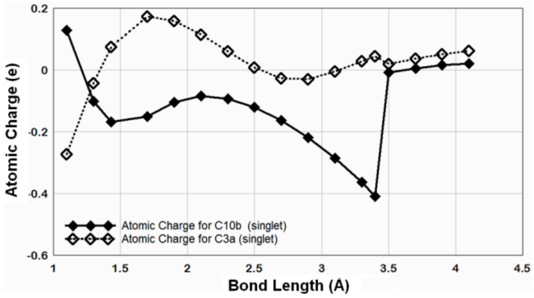


**Figure 10.** Variation in atomic charges for C3a and C10b atoms during (C3a-C10b) bond breakage reaction in pyrene molecule (Singlet state).

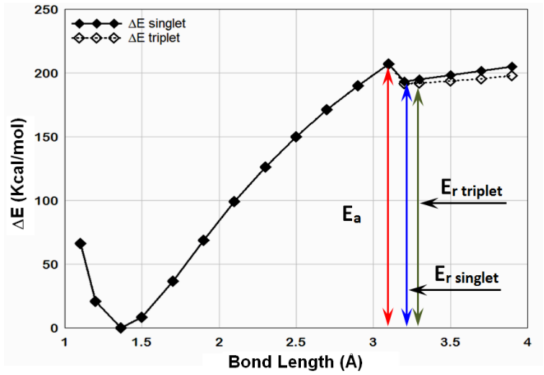


**Figure 11.** Potential energy curve for (C4-C5) bond breakage in pyrene molecule according to DFT calculation ($E_a$ = 207.192, $E_{r\ singlet}$ = 193.152, $E_{r\ triplet}$ = 191.503 kcal/mol).

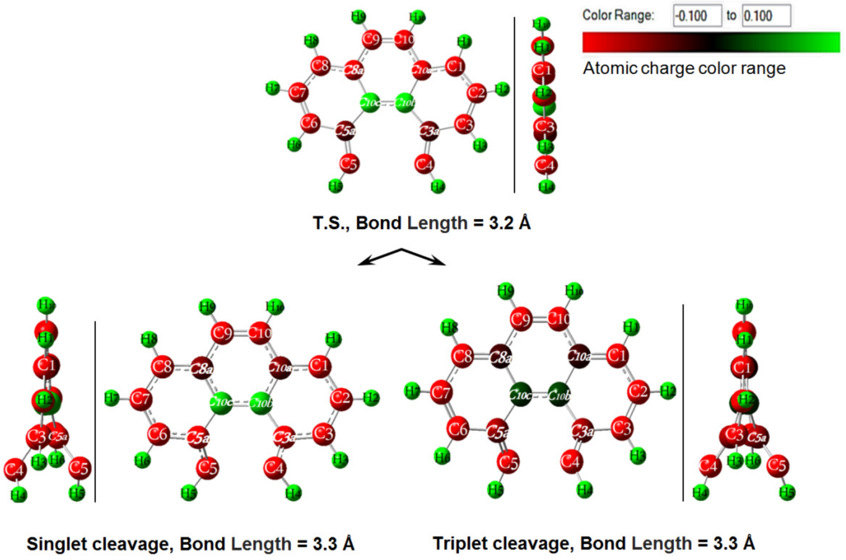


**Figure 12.** Geometry of the transition state, the singlet and the triplet final products of the C4-C5 bond cleavage reaction in pyrene molecule.

### *3.6. Cleavage of the C10b-C10c bond*

Cleavage of the C10b-C10c central bond in the molecule causes the motion of the two atoms to the opposite sides, relative to the molecular plane. According to the calculation results the motion leads to (S) transition state and proceeds to the (T) final product, Figure 14.

The transition state falls at the C10b-C10c distance 3.0 Å followed by the formation of the (T) final product. The calculated activation energy for the reaction is 200.458 kcal/mol and the reaction energy is 188.400 kcal/mol. The atomic charges of both atoms remain similar throughout the reaction.

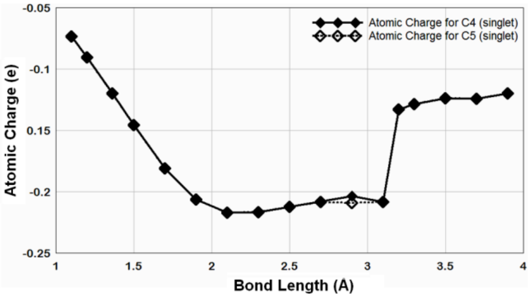
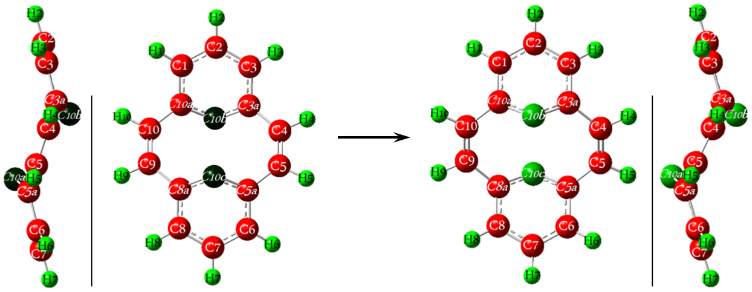


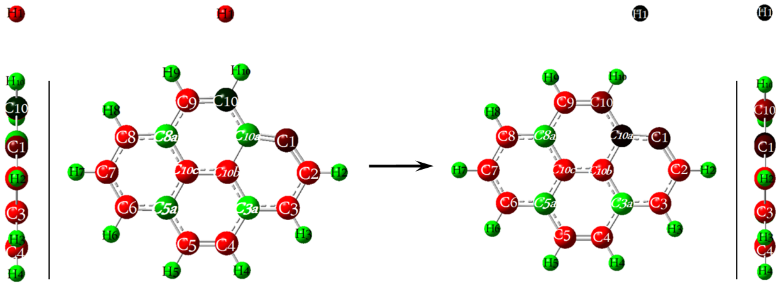
**Figure 13.** Variation in atomic charges for C4 and C5 atoms during (C4-C5) bond breakage reaction in pyrene molecule (Singlet state).



T.S., Bond Length = 3.0 Å

Triplet Cleavage, Bond Length = 3.1 Å

**Figure 14.** Geometry of the transition state, and the triplet final product of the C10b-C10c bond cleavage reaction in pyrene molecule.



T.S., Bond Length = 5.2 Å

Triplet Breakage, Bond Length = 5.3 Å

**Figure 15.** Geometry of the transition state, and the triplet final product for the C1-H1 bond cleavage reaction in pyrene molecule.

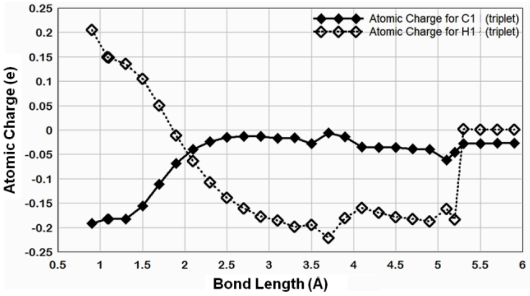


**Figure 16.** Variation in atomic charges for C1 and H1 atoms during (C1-H1) bond breakage in pyrene molecule (Triplet state).

## *4. Cleavage of the C-H bonds*

Due to its symmetry, $D_{2h}$, three different types of C-H bonds exist for pyrene molecule. These are C1-H1, C2-H2 and C4-H4 bonds. For all three bonds, the DFT calculation shows a (S) transition state followed by a (T) final product. As for the C1-H1 bond the H1 atom departs from C1 atom to the direction of H9 and H10 atoms to reach the planar TS at C1-H1 distance 5.2 Å. Further motion of H1 leads to the planar (T) final product (Figure 15). Figure 16 shows the variation of the C1 and H1 atomic charges due to the cleavage reaction.

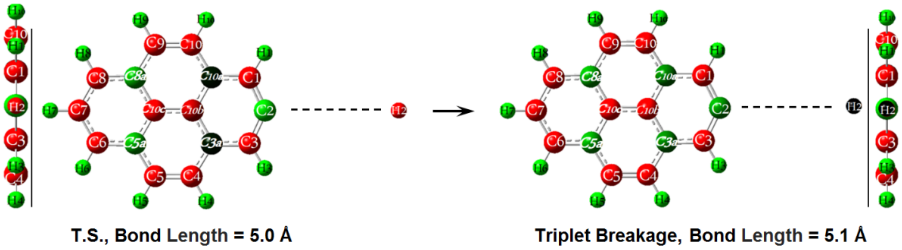


**Figure 17.** Geometry of the transition state, and the triplet final product for the C2-H2 bond cleavage reaction of pyrene molecule.

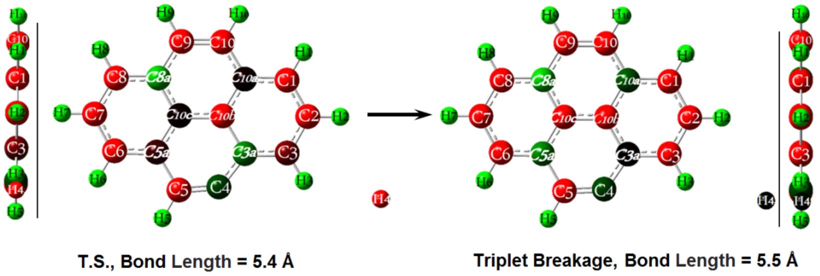


**Figure 18.** Geometry of the transition state, and the triplet final product for the C4-H4 bond cleavage reaction in pyrene molecule.

The reaction starts with a H1 charge of +0.2 to end at the charge +0.0, confirming the neutrality of the departing H atom. The calculated activation energy of the reaction $E_a$ = 163.535 kcal/mol the calculated reaction energy $E_r$ = 117.690 kcal/mol.

As for C2-H2 bond, the cleavage reaction proceeds through the coplanar TS towards the (T) final product maintaining the $C_{2v}$ symmetry, Figure 17. In a similar behavior to the reaction of C1-H1 bond the H2 atom starts the reaction with a positive (+0.2) charge to end with a charge value (0.0).

For this reaction the calculated activation energy $E_a$ = 165.116 kcal/mol and the calculated reaction energy $E_r$ = 117.350 kcal/mol. The cleavage of C4-H4 bond was studied too, Figure 18. This reaction proceeds with a (S) electron configuration up to the transition state. It follows then the (T) path towards the final product. Its calculated $E_a$ = 163.785 kcal/mol, its reaction energy is 117.293 kcal/mol. Similar to the charge variation of the former reactions, the H4 atom starts the reaction with a positive charge (+0.22) to end it with a neutral charge (0.0) at the final product.

## 5. Conclusion

Whereas all the C-H bond cleavage reactions for pyrene proceed in a similar pattern for all such bonds, maintaining the planarity of the molecule, the C-C cleavage reactions show different conformational changes along the reaction path depending on the location of the bond. Molecular strain at the transition state may cause the change of electron configuration from (S) to (T) state, such as for C10-C10b bond, accompanied with severe deviation of the conformation from planarity. Sigmatropic H atom shift reactions [29] towards the formation of $CH_2$ groups are predicted for many C-C cleavage reactions. The obtained results provide new and significant knowledge to the bond cleavage reactions of polyaromatic hydrocarbons.

## References

[1]. Harvey, R. G. Polycyclic Aromatic Hydrocarbons; Chemistry and Carcinogenity, Cambridge University Press, Cambridge, 1991.
[2]. Harvey, R. G. Polycyclic Aromatic Hydrocarbons, Wiley-VCH, New York, 1997.
[3]. Ren, R. L.; Itoh, H.; Ouchi, K. *Fuel* **1989**, *68*, 58-65.
[4]. Ninomiza, Y. D.; Suzuki, Z. Y. *Fuel* **2000**, *79*, 449-457.
[5]. Guerrin, M. R. Energy Sources of Polycyclic Aromatic Hydrocarbons, in Polycyclic Hydrocarbons and Cancer, Academic Press Inc. N. York, 1978.
[6]. Luch, A. The Carcinogenic Effects of Polycyclic Aromatic Hydrocarbons, Imperial College Press, Singapore, 2005.
[7]. Frenklach, M.; Wang, H. *Proc. Combust. Inst.* **1991**, *23*, 1559-1566.
[8]. Frenklach, M.; Moriatry, N. W.; Brown, N. *Proc. Combust Inst.* **1998**, *27*, 1655-1661.
[9]. Ling, Y.; Martin, J. M. L.; Lifschitz, C. *J. Phys. Chem. A* **1997**, *101*, 219-226.
[10]. Mebel, A. M.; Lin, S. H.; Yang, X. M.; Lee, Y. T. *J. Phys. Chem. A* **1997**, *101*, 6781-6789.
[11]. Boehm, H.; Jander, H. Phys. *Chem. Chem. Phys.* **1999**, *1*, 3775-3781.
[12]. May, K.; Dopperich, S.; Furda F.; Untereiner, B. V. Ahlrichs, R. *Phys. Chem. Chem. Phys.* **2000**, *2*, 5084-5088.
[13]. Untereiner, B. V.; Sierka, M.; Ahlrichs, R. *Phys. Chem. Chem Phys.* **2004**, *6*, 4377-4384.
[14]. Shanshal, M.; Abdullah, H. H. Proceeding of the 6thJordanien International Conference of Chemistry, Irbid, Jordan, 2011.
[15]. Shanshal, M.; Hadi, H. *Jordan J. Chem.* **2012**, *7*, 329-337.
[16]. Roothaan, C. C. J. *Rev. Mod. Phys.* **1951**, *23(2)*, 69-89.
[17]. Kohn, W.; Sham, L. J. *Phys. Rev.* **1965**, *140*, A1133-A1138.
[18]. Hohenberg, P.; Kohn, W. *Phys. Rev.* **1964**, *136*, B864-B871.
[19]. Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098-3001.
[20]. Lee, C.; Yang, W. Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785-789.
[21]. Shanshal, M.; Muala, M. M. *Jordan J. Chem.* **2011**, *6(2)*, 165-173.
[22]. Shanshal, M.; Muala, M. M. *Jordan J. Chem.* **2013**, *8(2)*, 113-124.
[23]. Shanshal, M.; Muala, M. M.; Al-Yassiri, M. A. *Jordan J. Chem.* **2013**, *8*, 213-224.
[24]. Davico, G. E.; Bierbaum, V. M.; DePuy, C. H.; Ellison, G. B.; Squires, R. R. *J. Amer. Chem. Soc.* **1995**, *117*, 2590-2599.
[25]. Laarhoven, L. J. J.; Mulder, P. *J. Phys. Chem. B* **1997**, *101*, 73-77.
[26]. Barckholtz, C.; Barckholtz, T.; Hadad, C. M. *J. Amer. Chem. Soc.* **1999**, *121*, 492-500.
[27]. Luo, Y. R. Comprehensive Handbook of Chemical Bond Energies, CRC Press, BocaRaton, FL, 2007.
[28]. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr. , J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; P. Hratchian, H.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J. , Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.;

Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A.; Gaussian, Inc. Pittsburgh, PA, 2003.

[29]. Dewar, M. J. S. The Molecular Orbital Theory of Organic Chemistry, McGraw-Hill, N. York, 1969, pp. 169-190.