European Journal of Chemistry

Reaction paths and transition states of the C-C and C-H bond cleavage in the aromatic anthracene and phenanthrene molecules

Muthana Abduljabbar Shanshal *, Muntadhar Abdulbary Al-Yassiri and Qhatan Adnan Yusof

Department of Chemistry, College of Science, University of Baghdad, Jadirriya, Baghdad, 00964-01, Iraq

* Corresponding author at: Department of Chemistry, College of Science, University of Baghdad, Jadirriya, Baghdad, 00964-01, Iraq.
Tel.: +964.790.2824400. Fax: +964.790.2824400. E-mail address: mshanshal2003@yahoo.com (M.A. Shanshal).

ARTICLE INFORMATION

KEYWORDS

ABSTRACT

The reaction paths of the C-C and C-H bond cleavage in the anthracene and phenanthrene aromatic molecules are studied by applying the ab-initio DFT method. It is found that the C-C bond cleavage proceeds via a singlet aromatic transition state, compelled through a disrotatoric ring opening reaction. A suprafacial H atom shift follows the transition state, leading to the formation of a methylene -CH_2 and an acetylenic or allenic moiety. The calculated activation energies for anthracene range from 158.81-208.90 kcal/mol and the reaction energies from 96.106-156.976 kcal/mol. For phenanthrene, the energy values are 157.39-202.34 kcal/mol and 62.639-182.423 kcal/mol, respectively. For the C-H cleavage reactions, the calculated reaction energies for all C-H bonds in both molecules are almost similar, 116-117 kcal/mol. The activation energy values for anthracene and phenanthreneare 149.75-161.27 and 161.24-163.00 kcal/mol, respectively.

1. Introduction

Applying advanced quantum mechanical methods, it is possible to study the geometries and energies of the transition states (TS) and reaction products (RP) of the C-C and C-H bond cleavage reactions for various aromatic molecules [1-6]. For all the investigated molecules, different structures and energies resulted for the different C-C bonds, i.e. no fixed pictures for the reactions of these bonds were obtained. These results imposed the necessity of studying the reactions for the different bonds in a sufficient number of aromatic molecules aiming at achieving a possible general description of the C-C cleavage reaction. In contrast to that the C-H bond cleavage reactions seemed to follow a common pattern, i.e. coplanar transition state and reaction product for all such bonds in these molecules. However as far as the C-C bond cleavage reactions are concerned, the following properties of the reactions seemed to be common;

1. For all the studied reactions, the singlet electron configuration (S) for the reaction transition state (TS) seems to be common. No TS with a triplet (T) electron configuration seemed probable.
2. For all the studied reactions, the law of the aromatic transition states [7] seems to hold, i.e. all calculated transition states satisfied Hückel's (4n+2) rule for aromaticity.
3. For most of the studied reactions, the singlet reaction product was formed through sigmatropic shifts of a H·atom leading to the formation of =CH_2 or –CH= as well as an acetylenic or allenic bond. No such shift was predicted for the triplet product.
4. Molecular strain is a strong and effective factor in determining the conformation of the transition state and RP.

Due to the industrial and environmental importance of the polyaromatic hydrocarbons (PAH), many theoretical and experimental studies for their degradation reactions appeared formerly in the literature [8-18]. A common result seemed to be that the energies required for the C-H bond cleavage are lower than those required for the C=C cleavage in PAH molecules. Accordingly, the PAH degradation reactions should start, in most molecules, with the C-H cleavage rather than the C-C cleavage reactions, a fact that is usually documented in the organic chemical literature [19,20].

In the present paper, we describe such a study for the bond degradation reactions in the PAH molecules, anthracene and phenanthrene (Scheme 1).
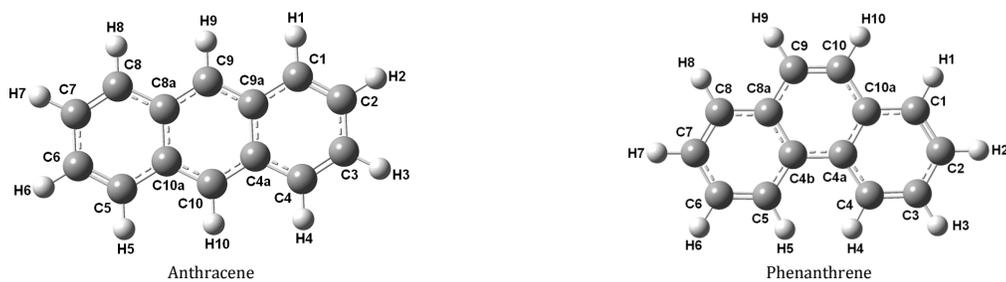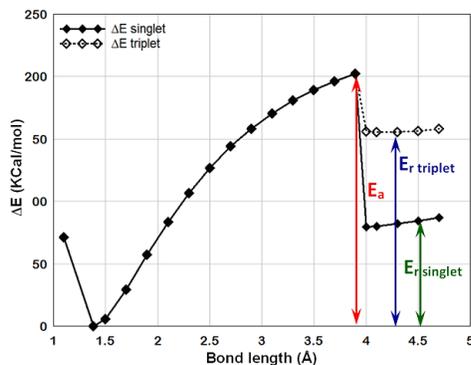
Scheme 1

Figure 1. Calculated reaction path for the C1-C2 bond cleavage in phenanthrene; E_a = 202.341 kcal/mol, $E_{r\,singlet}$ = 79.393 kcal/mol, $E_{r\,triplet}$ = 155.974 kcal/mol.

2. Experimental

To study the C-C or C-H bond cleavage reaction, the corresponding reaction path had to be described accurately, such that the energy of the reacting molecule is calculated for the different values of the corresponding bond length (reaction coordinate). In the present work, the energy calculations were done for the singlet and triplet electron configurations for all the points along the reaction path. The configuration with the lower energy was accepted then for the description of the path. For each point along the reaction path, the corresponding value of the reaction coordinate (bond length) was kept constant and the remaining (3N-5) coordinates were varied to obtain the minimum of the molecular energy. As then the obtained energy values were plotted against the corresponding lengths of the reaction coordinate to yield the required reaction path. As commonly known, knowledge of the reaction path enables the evaluation of energies and geometric parameters of the reaction transition state and reaction products.

In the present work, the energy calculations were carried out applying the ab-initio Density Functional Theory method [21-23] of the B3LYP type [24,25] as programmed within the Gaussian03 program system of Pople *et al.* [26]. As for the basis functions the 6-311G set was applied. For the discussion of the corresponding geometries the Molek9000 program of P. Bischof, Heidelberg was used [27].

3. Results and discussion

3.1. The C-C bond cleavage reactions

3.1.1. Phenanthrene

Due to the C_{2v} symmetric structure of the phenanthrene molecule, the number of C-C bonds to be studied is reduced to nine.

3.1.1.1. C1-C2 bond cleavage

According to the calculated reaction path, Figure 1, the cleavage of this bond proceeds through an aromatic transition state leading to a singlet electron configured reaction product that is more stable than the corresponding triplet reaction product too.

The singlet configured transition state is associated with a high activation energy value of 202.341 kcal/mol. It exhibits a distorted conformation, in which the C1H1 and C3H3C2H2 fragments are tilted out of the plane of the remaining 2 ring fragment of the molecule.

The disrotatoric ring opening leads to an aromatic transition state. Figure 2 shows that the transition state undergoes a suprafacial H3 atom shift from C3 to C1 forming a C1H$_2$ group and an acetylene C2-C3 bond (d = 1.217 Å). No such H atom shift was predicted for the triplet reaction product.
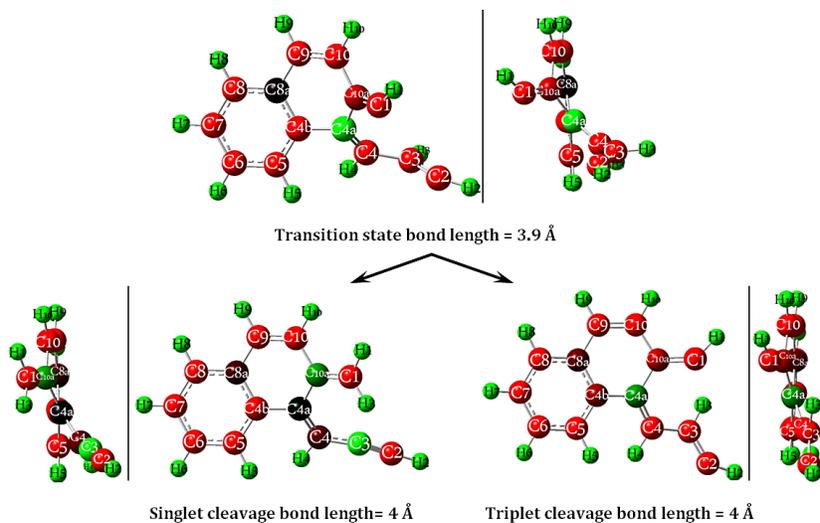
3.1.1.2. C1-C10a bond cleavage

The geometry of this reaction's transition state is depicted by the rotation of the C1H1C2H2 group out of the plane of the remaining aromatic moiety. Further rotation of the same group leads to the formation of the singlet reaction product. No such rotation is calculated for the triplet product, i.e. it shows a similar conformation to that of the transition state, Figures 3 and 4.

3.1.1.3. C2-C3 bond cleavage

According to the present treatment, this reaction proceeds via singlet transition state, Figure 5, with an activation energy of 182.369 kcal/mol. The preferred reaction product is of a singlet electron configuration, too.

The calculated reaction path indicates 2 aromatic transition state processes; a) a disrotatoric ring opening represented by the C2-C3 bond cleavage and b) a suprafacial H atom shift from C2 to C3 atom, forming an acetylenic C2≡C1 bond of a length 1.208 Å, Figure 6.
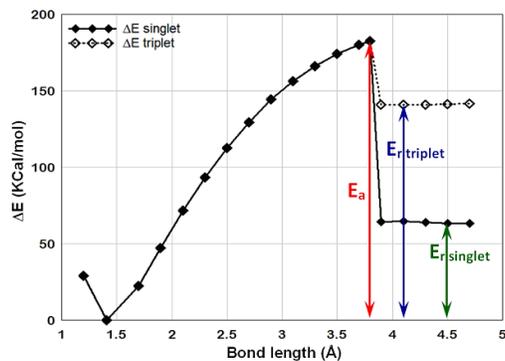
Figure 2. Calculated structures of the transition state, the single and triplet reaction products of the C1-C2 bond cleavage in phenanthrene.
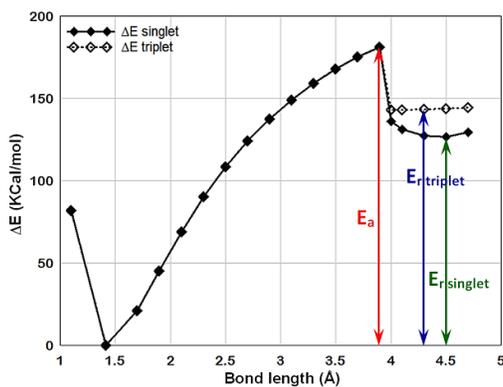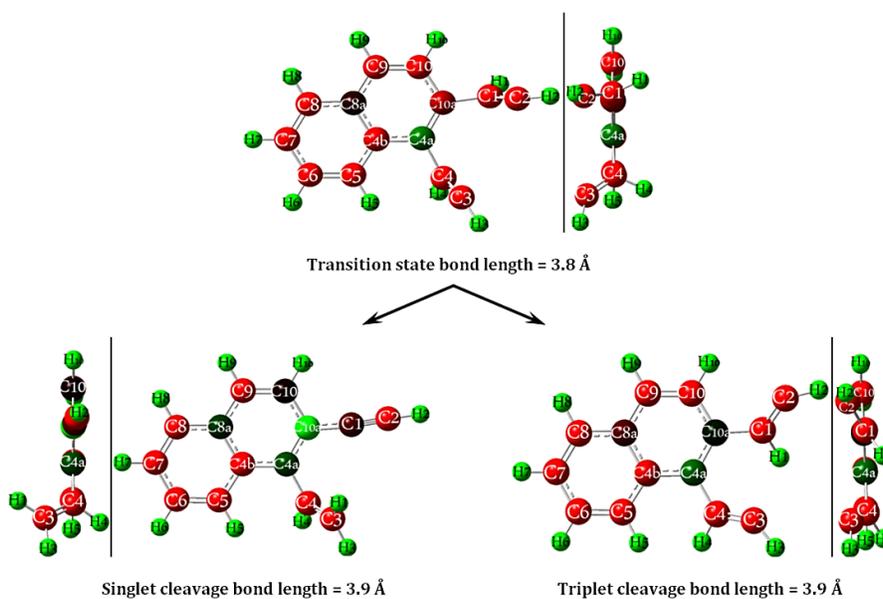

Figure 3. Calculated reaction path for the C1-C10a bond cleavage reaction in phenanthrene; E_a = 181.061 kcal/mol, $E_{r\ singlet}$ = 136.156 kcal/mol, $E_{r\ triplet}$ = 143.008 kcal/mol.
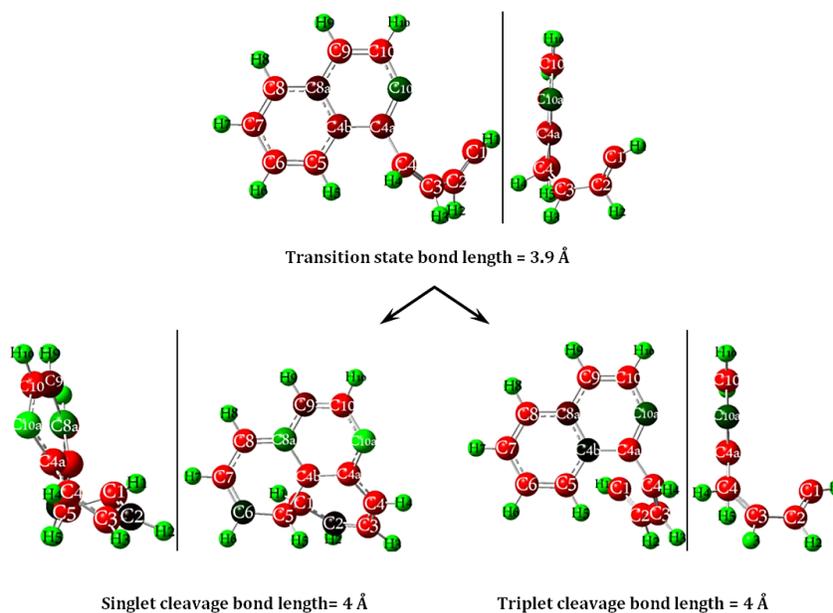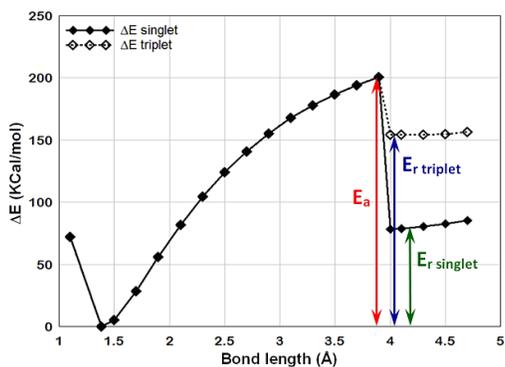

Figure 4. Calculated structures of the transition stage, the singlet and triplet reaction products of the C1-C10a bond cleavage in phenanthrene.

Figure 5. Calculated reaction path of the C2-C3 bond cleavage in phenanthrene, E_a = 182.369 kcal/mol, $E_{r\ singlet}$ = 64.239 kcal/mol and $E_{r\ triplet}$ = 140.994 kcal/mol.

Transition state bond length = 3.8 Å

Singlet cleavage bond length = 3.9 Å   **Triplet cleavage bond length = 3.9 Å**

Figure 6. Calculated structures of the transition state, the singlet and triplet reaction products of the C2-C3 bond cleavage reaction in phenanthrene.

Figure 7. Calculated reaction path for the C3-C4 bond cleavage in phenanthrene, E_a = 200.567 kcal/mol, $E_{r\ singlet}$ = 78.0412 kcal/mol, $E_{r\ triplet}$ = 154.490 kcal/mol.

3.1.1.4. C3-C4 bond cleavage

The cleavage of this bond proceeds through a singlet transition state formed by a disrotatoric ring opening of an activation energy of 200.567 kcal/mol, Figures 7 and 8. A following suprafacial H atom shift from C2 to C4 causes the formation of the singlet final product. A C2≡C3 bond is formed through this H shift too. The length of this bond is 1.217 Å.
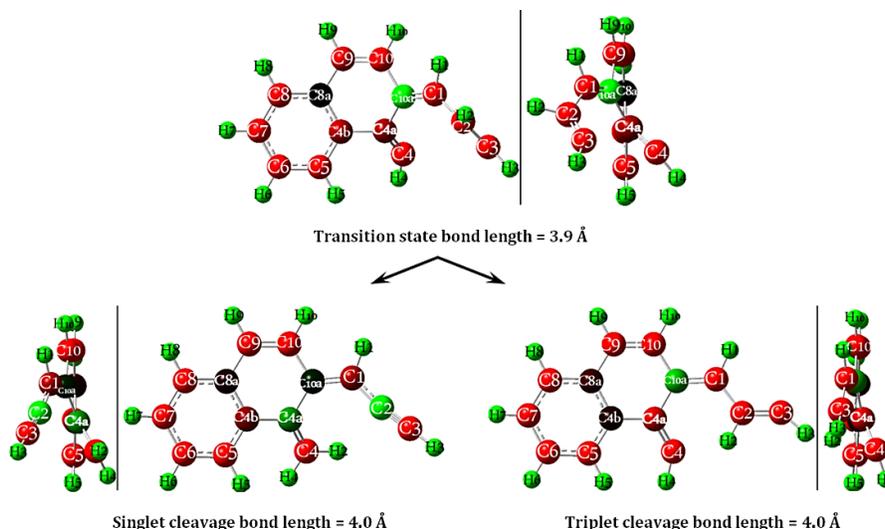
Figure 8. Calculated structures of the reaction transition state, singlet and triplet reaction products of the C3-C4 bond cleavage in phenanthrene.
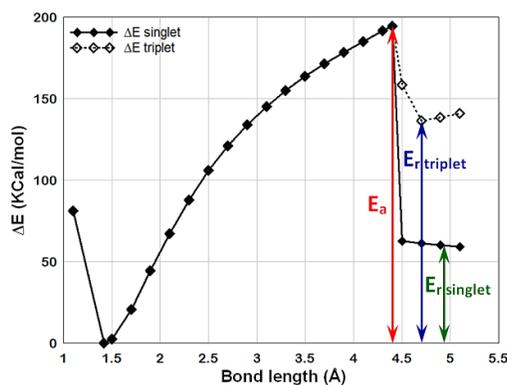

Figure 9. Calculated reaction path for the C4-C4a bond cleavage in phenanthrene, E_a = 194.503 kcal/mol, $E_{r\,singlet}$ = 62.639 kcal/mol, $E_{r\,triplet}$ = 158.460 kcal/mol.

3.1.1.5. C4-C4a bond cleavage

The study for this bond reveals that the ring opening proceeds through a planar and aromatic transition state, too, Figures 9 and 10, with an activation energy of E_a = 194.503 kcal/mol. Further progress of the reaction leads to a singlet product in which the H3 atom is shifted towards the C4a atom. The singlet product is by 95 kcal/mol more stable than the triplet. The singlet product exhibits a non-coplanar conformation in which the C2C3C4 fragment is twisted out of the plane of the rest of the molecule.

3.1.1.6. C4a-C4b bond cleavage

No stable singlet final product could be calculated for the cleavage of this bond. The reaction proceeds through a coplanar aromatic transition state too with an activation energy of 180.447 kcal/mol. The reaction proceeds then adopting the triplet electron configuration and reaction energy of 130.624 kcal/mol, Figure 11.

The geometry of the final product shows a twisting of a single aromatic ring out of the plane of the rest of the molecule with a rotation angle of 155 degrees. The twisting proceeds such that C4b atom is displaced away from the C4a atom, Figure 12.

3.1.1.7. C4a-C10a bond cleavage

The singlet transition state of this reaction falls at the bond distance 3.1Å. It represents a 10 π-e system, too. The singlet reaction product is found more stable than the triplet state by 13 kcal/mol, Figure 13.

At the reaction product the molecular geometry deviates from the planarity in that the C1C2C3C4 fragment is tilted out of the plane of the rest of the molecule. The geometry of the triplet reaction product is depicted by the deformation of the molecular fragment C10C10aC1C2C3 out of the plane of the molecule, Figure 14.

3.1.1.8. C8a-C9 bond cleavage

The reaction of this bond proceeds through a (S, TS), at 3.7 Å, Figure 15. It is composed of 2 aromatic rings, a phenyl and a styrene ring, that are almost perpendicular to each other, Figure 16. The related activation energy is 169.751 kcal/mol. The reaction ends with a singlet final product in which C5 approaches C9 placing the C6C7C8 fragment out of the molecular plane. The calculated singlet reaction energy is 97.296 kcal/mol. The calculated structure of the triplet reaction product is similar to that of the transition state i.e. no further rotation of the aromatic rings relative to each other takes place. Its calculated reaction energy is 132.336 kcal/mol.
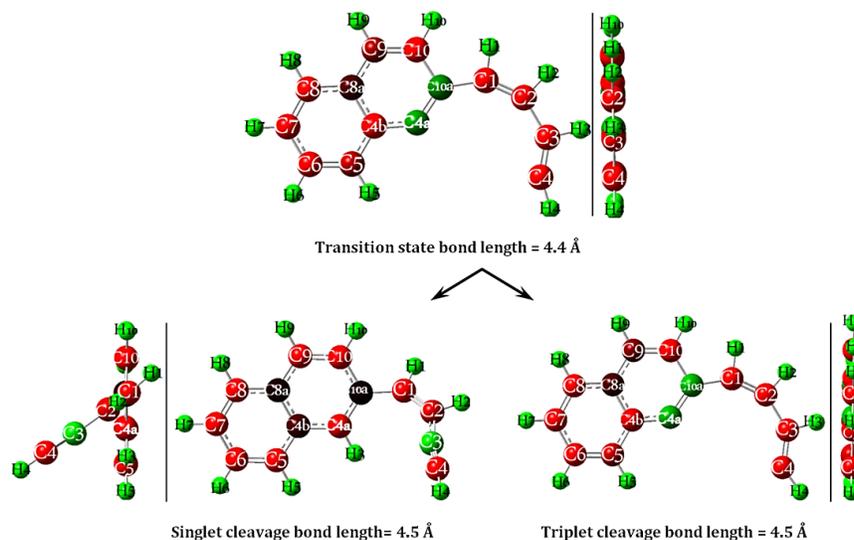
Figure 10. Calculated structures of the transition state, the singlet and the triplet end products of the C4-C4a bond cleavage in phenanthrene.
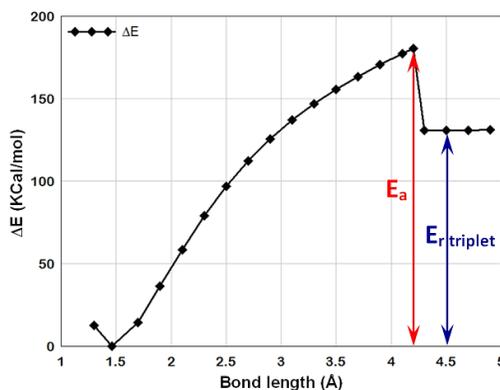

Figure 11. Calculated reaction path for the C4a-C4b bond cleavage in phenanthrene, E_a= 180.447 kcal/mol, $E_{r\,triplet}$ = 130.624 kcal/mol.
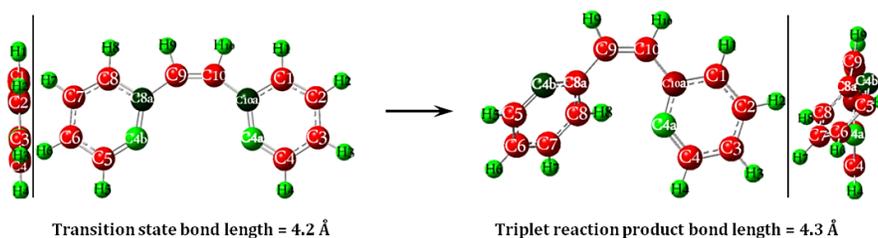

Figure 12. Calculated structures of the transition state and the triplet reaction product of the C4a-C4b bond cleavage in phenanthrene.

3.1.1.9. C9-C10 bond cleavage

The cleavage of this bond proceeds through a singlet transition state in which the formed phenyl rings are twisted relative to each other, Figure 17 and 18. The calculated activation energy is 191.594 kcal/mol. The reaction ends with a triplet final product of a similar conformation as that of the transition state. The calculated reaction energy is $E_{r\,trip}$ = 182.423 kcal/mol.
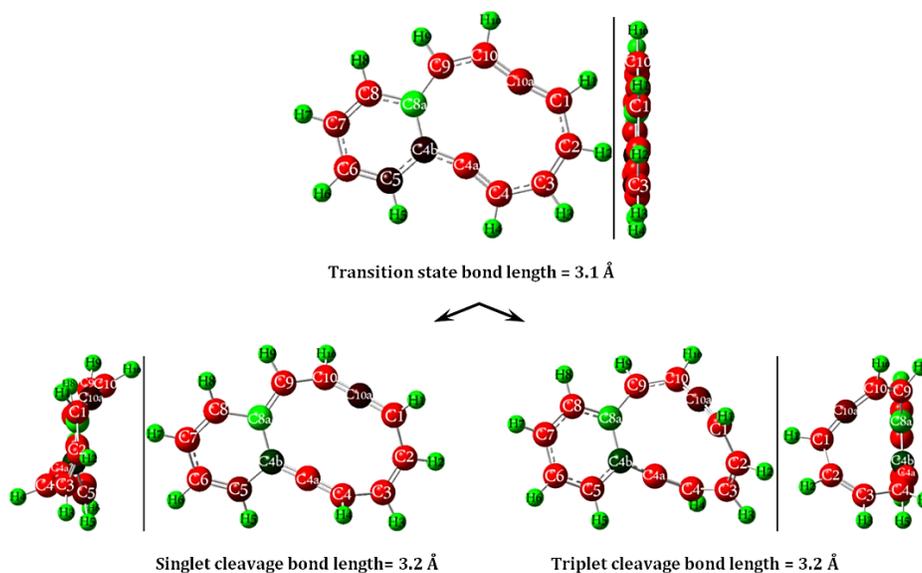
3.1.2. Anthracene

### 3.1.2.1. C1-C2 bond cleavage

The cleavage of this bond proceeds through a non-planar transition state in which the H1 and H2 atoms are tilted out of, and to the same side of the molecular plane. It represents a disrotatoric ring opening going through an aromatic transition state. The transition state falls at a C1-C2 bond distance of 3.5 Å. Further progress of the reaction leads to a singlet reaction product stabilized through a shift of a H atom from C3 to C2 forming an allenic C2-C3-C4 group in which both H2 and H3 are twisted out of the molecular plane.
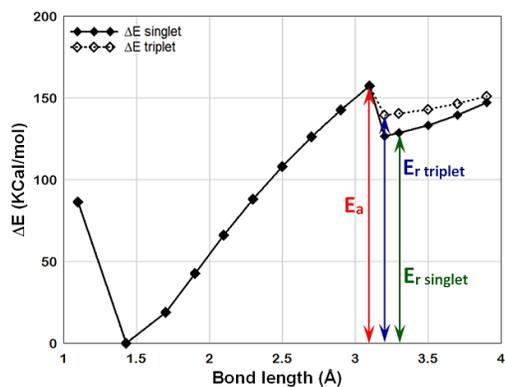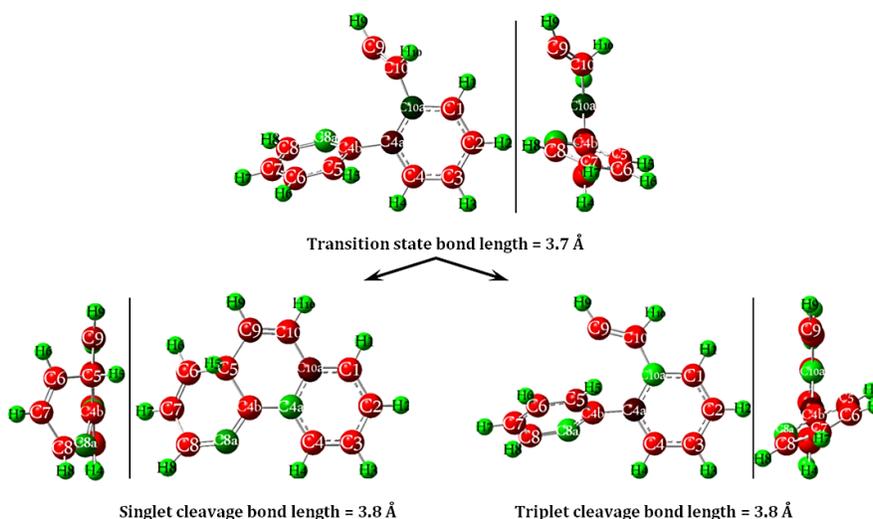
Figure 13. Calculated reaction path of the C4a-C10a bond cleavage in phenanthrene, E_a = 157.392 kcal/mol, $E_{r\ singlet}$ = 126.671 kcal/mol, $E_{r\ triplet}$ = 139.462 kcal/mol.

Transition state bond length = 3.1 Å

Singlet cleavage bond length= 3.2 Å   Triplet cleavage bond length = 3.2 Å

Figure 14. Calculated structures of the transition state, the singlet and the triplet reaction products of the C4a-C10a bond cleavage in phenanthrene.
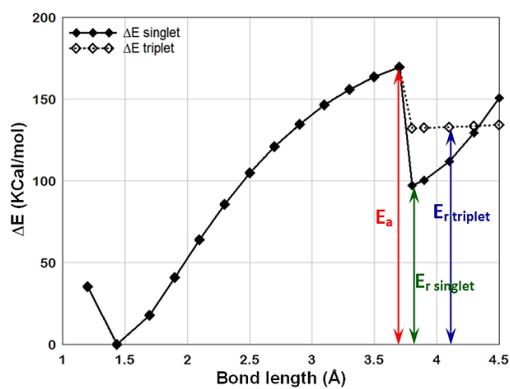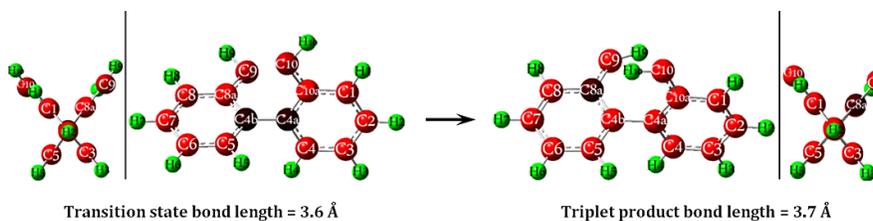

Figure 15. Reaction path of the C8a-C9 bond cleavage in phenanthrene, E_a = 169.751 kcal/mol, $E_{r\ singlet}$ = 97.2962 kcal/mol, $E_{r\ triplet}$ = 132.336 kcal/mol.

Figure 16. Calculated geometries of the transition state, the singlet and the triplet reaction products of the C8a-C9 bond cleavage reaction in phenanthrene.
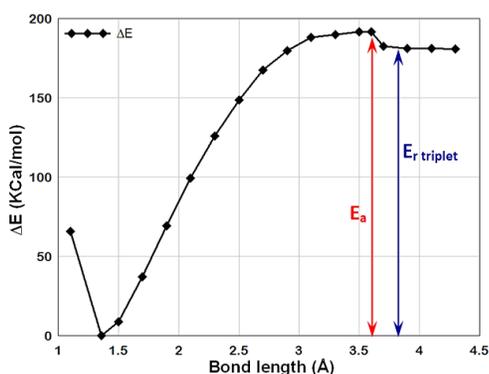
Figure 17. Calculated reaction path for the C9-C10 bond cleavage in phenanthrene, E_a = 191.594 kcal/mol, $E_{r\,triplet}$ = 182.423 kcal/mol.

Figure 18. Calculated geometries of the transition state and triplet reaction product of the C9-C10 bond cleavage in phenanthrene.

The triplet reaction path shows no such H shift and ends up with a reaction product that is more stable than the singlet reaction product. The calculated activation energy of the reaction is 192.507 kcal/mol, the singlet product reaction energy is 122.311 kcal/mol and triplet product reaction energy is 116.794 kcal/mol.

3.1.2.2. C2-C3 bond cleavage

Unlike the C1-C2 bond cleavage reaction, the C2-C3 reaction proceeds towards a singlet reaction product that is more stable than the triplet RP by 41.650 kcal/mol.

The structure of the transition state is depicted by the synchronized out of plane deformation of the C2H2 and C3H3 moieties in terms of a disrotatoric opening of the 6-ring and the formation of an aromatic transition state [7]. The obtained data shows that the reaction proceeds towards a completely coplanar and more stable singlet reaction product in which the neighbored H1 and H4 atoms are shifted simultaneously to form the two terminal CH2 groups. No such H shift was calculated for the less stable triplet product. The singlet reaction product conforms to a C_{2v} symmetry. In fact maintaining the symmetry throughout the reaction is confirmed by the similar electron density values calculated for C2 and C3 atoms along the reaction path.

3.1.2.3. C1-C9a bond cleavage

The reaction path for the C1-C9a bond cleavage reaction is calculated, it is seen that beyond the (S, TS) a (S) reaction product, more stable than the triplet product is formed. The calculated activation energy for the reaction is 158.812 kcal/mol, the calculated reaction energy is 97.717 kcal/mol for the singlet product.
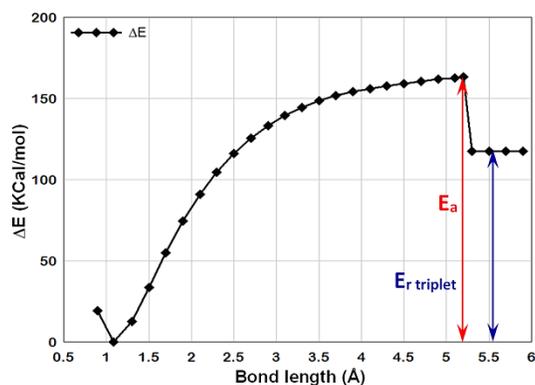
Figure 19. Calculated reaction path for the C1-H1 bond cleavage in phenanthrene, E_a = 163.197 kcal/mol, $E_{r\,triplet}$ = 117.324 kcal/mol.

Transition state bond length = 5.2 Å   **Triplet product bond length= 5.3 Å**
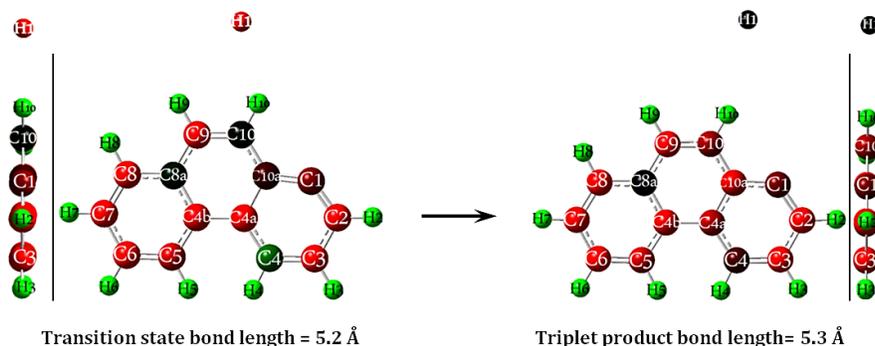
Figure 20. Calculated structures of the transition state and triplet reaction product of theC1-H1 bond cleavage in phenanthrene molecule.

Increasing the C1...C9a distance beyond 3.6 Å causes an increase in energy, probably due to the increase in the strain of the side chain.

3.1.2.4. C4a-C9a bond cleavage

According to the calculated reaction path for C4a-C9a bond, neither a transition state nor a stable reaction product should be formed. A continuous increase in the molecular energy is predicted beyond the distance 2.5 Å. Apparently the increase in this bond's length causes a deformation of the C4aC4C3C2C1C9a fragment out of the molecular plane and consequently an increase in the molecular strain energy.

3.1.2.5. C9-C9a bond cleavage

The cleavage reaction of this bond proceeds through a non-planar singlet transition state, in which two phenyl rings are connected to each other, in a skew form and through a methyne HC group. The calculated activation energy is 202.866 kcal/mol and the reaction energy for the singlet product is 156.976 kcal/mol and for the triplet state 226.887 kcal/mol. The structure of the singlet reaction product includes an allenic bond ending with a c, pentadienyl ring that is formed from the original phenyl ring through the release of its C4a atom for the favor of the allene bond formation. The calculated structure of the triplet reaction product includes a bicycle, hexadienyl ring.

3.2. Cleavage reactions of the C-H bonds

In general the DFT calculation for the cleavage reactions of the C-H bonds in both molecules yielded reaction paths of common properties i.e. of singlet transition states, triplet reaction products and of reaction energies with an average value 116-117 kcal/mol. The reactions proceed maintaining the coplanar nature of the molecular system.

3.2.1. Phenanthrene

Typical shape for the reaction path was obtained for all C-H bonds in phenanthrene; i.e the (S, TS) and the triplet reaction product, Figures 19 and 20. The calculated average cleavage energy for all bonds is ~117.0 kcal/mol. The activation energies for these reactions vary from one bond to the other (Table 1).

Table 1. Calculated activation energies (E_a) and reaction energies (E_a) of the C-H bond cleavage reactions for phenanthrene molecule.

Bond	E_a (kcal/mol)	dC...H (Å)	$E_{r\,triplet}$ (kcal/mol)
C1-H1	163.197	5.2	117.324
C2-H2	164.667	4.8	117.649
C3-H3	165.643	5.1	117.432
C4-H4	161.244	4.8	115.539
C9-H9	163.008	5.2	117.274

3.2.2. Anthracene

Discussion of the C-H bonds cleavage in anthracene appeared in a former paper [5]. The average calculated bond cleavage energy for all such bonds in anthracene was ~117.0 kcal/mol. A common property for these reactions was that the departing H atom selects a geometric path deviating slightly from the expected straight path, towards the other neighbored H atoms in the molecule. The calculated energy values for these reactions are given in Table 2.

Table 2. Calculated activation energies (E_a) and reaction energies (E_a) of the C-H bond cleavage reactions for anthracene molecule.

Transition state		Triplet reaction product	
C...H distance (Å)	E_a (kcal/mol)	C...H distance (Å)	E_r (kcal/mol)
C1-H1 3.6	149.752	C1-H1 3.7	117.320
C2-H2 4.4	161.270	C2-H2 4.5	116.725
C9-H9 4.1	156.703	C9-H9 4.2	117.341

4. Conclusion

The present computative study for the C-C bond cleavage reactions in anthracene and phenanthrene, confirms our former results obtained for other aromatic hydrocarbons, in which it was found that such reactions proceed through singlet aromatic transition states formed via a disrotatoric opening of the corresponding ring. The singlet final product is usually formed through a H atom "suprafacial" shift which forms a –CH_2 methylene group and a neighbored acetylenic or allenic moiety. The steric conformations of the transition states and products are adapted to both ring opening and "suprafacial" H atom shift. Different values for the activation and reaction energies are obtained for the different bonds of each molecule. The C-H bond cleavage proceeds in a similar manner to that of the former aromatic hydrocarbons represented by the coplanarity of the reacting molecule up to the reaction product and a slight deviation of the H atom towards the neighboured H atoms in its motion towards the final product. The reaction energies of the C-H bond cleavage for all such bonds are almost similar, i.e. 116-117 kcal/mol, their activation energies however are different.

References

[1]. Shanshal, M.; Hadi, H. Proceeding of the 6thJordanien International Conference of Chemistry, Irbid, Jordan, 2011.
[2]. Shanshal, M.; Hadi, H, *Jordan J. Chem.* **2012**, *7*, 329-337.
[3]. Shanshal, M.; Muala, M. M. *Jordan J. Chem.* **2011**, *6(2)*, 165-173.
[4]. Shanshal, M.; Muala, M. M. *Jordan J. Chem.* **2013**, *8*, 113-124.
[5]. Shanshal, M.; Muala, M. M.; Al-Yassiri, M. A. *Jordan J. Chem.* **2013**, *8*, 213-224.
[6]. Al-Yassiri, M.; Shanshal, M. *Eur. J. Chem.* **2015**, *6(3)*, 261-269.
[7]. Dewar, M. J. S. The Molecular Orbital Theory of Organic Chemistry, McGraw-Hill, N. York, 1969, pp. 169-190.
[8]. Ren, R. L.; Itoh, H.; Ouchi, K. *Fuel* **1989**, *68*, 58- 65.
[9]. Ninomiza, Y. D.; Suzuki, Z. Y. *Fuel* **2000**, *79*, 449-457.
[10]. Guerrin, M. R. Energy Sources of Polycyclic Aromatic Hydrocarbons, in Polycyclic Hydrocarbons and Cancer, Academic Press Inc. N. York, 1978.
[11]. Luch, A. The Carcinogenic Effects of Polycyclic Aromatic Hydrocarbons, Imperial College Press, Singapore, 2005.
[12]. Frenklach, M.; Wang, H. *Proc. Combust. Inst.* **1991**, *23*, 1559-1566.
[13]. Frenklach, M.; Moriatry, N. W.; Brown, N. *Proc. Combust Inst.* **1998**, *27*, 1655-1661.
[14]. Ling, Y.; Martin, J. M. L.; Lifschitz, C. *J. Phys. Chem. A* **1997**, *101*, 219-226.
[15]. Mebel, A. M.; Lin, S. H; Yang, X. M.; Lee, Y. T. *J. Phys. Chem. A* **1997**, *101*, 6781-6789.
[16]. Boehm, H.; Jander, H. *Phys. Chem. Chem. Phys.* **1999**, *1*, 3775-3781.
[17]. May, K.; Dopperich, S.; Furda, F.; Untereiner, B. V.; Ahlrichs, R. *Phys. Chem. Chem. Phys.* **2000**, *2*, 5084-5088.
[18]. Untereiner, B. V.; Sierka, M.; Ahlrichs, R. *Phys. Chem. Chem Phys.* **2004**, *6*, 4377-4384.
[19]. Harvey, R. G. Polycyclic Aromatic Hydrocarbons; Chemistry and Carcinogenity, Cambridge University Press, Cambridge, 1991.
[20]. Harvey, R. G. Polycyclic Aromatic Hydrocarbons, Wiley-VCH, New York, 1997.
[21]. Roothaan, C. C. J. *Rev. Mod. Phys.* **1951**, *23*, 69- 89.
[22]. Kohn, W.; Sham, L. J. *Phys. Rev. A* **1965**, *140*, 1133-1138.
[23]. Hohenberg, P.; Kohn, W. *Phys. Rev. B* **1964**, *136*, 864-871.
[24]. Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098-3001.
[25]. Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785-789.
[26]. 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.; Pople, J. A. Gaussian, Inc. Pittsburgh, PA, 2003.
[27]. MOLEK-9000 (ISKA-Bensheim) program package, developed by P. Bischof, UniversitatHeidelberg, and by ISKA, Bensheim.