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C-C and C-H bond cleavage reactions in the chrysene and perylene aromatic molecules: An ab-initio density functional theory study

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Dedicated to Prof. Rehab M. Kubba, University of Baghdad

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ABSTRACT

The ab-initio DFT (B3LYP) method is applied for the study of C-C and C-H bond cleavage reactions in chrysene and perylene aromatic molecules. 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 in some of these reactions, where the formation of a methylene -CH_2, acetylenyl-, allenyl- or butadienyl-moiety in the final product is possible. Activation energies are calculated for the ring opening and show the following values; for chrysene, 136.97-197.69 kcal/mol and for perylene, 160.87-187.33 kcal/mol. The reaction energies range from 95.57-162.42 kcal/mol for chrysene and 98.12-168.28 kcal/mol for perylene. The calculated cleavage reaction energies for all C-H bonds in both molecules are almost similar, 116-117 kcal/mol. Their activation energies however are different, for chrysene they range from 148.57-154.97 kcal/mol and for perylene 148.30-162.73 kcal/mol.

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1. Introduction

In former reports, we described the application of the ab-initio DFT, quantum mechanical method, for the estimation of the structures and energies of the transition states (TS) and reaction products (RP) of the C-C and C-H bond cleavage reactions for a series of polyaromatic hydrocarbon (PAH) molecules [1-7]. The following properties of the C-C bond cleavage reactions could be concluded;

1. For all the studied reactions, a singlet configured (S) transition state resulted; no triplet (T) electron configuration for the TS seemed probable.
2. The law of aromatic transition state [8] seemed to apply, i.e. all calculated transition states obeyed Hückel's (4n+2) rule for aromaticity.
3. For many of the studied C-C bond cleavage reactions, the transition state was followed by a sigmatropic shift of a $H^{\cdot}$ atom leading to the formation of =CH_2 or –CH= group accompanied with an acetylenyl-, allenyl- or butadienyl- group. No such shift was predicted for the (T) reaction products.
4. Molecular strain is a strong and effective factor in determining the structure of the transition state and reaction products.
5. The C-H bond cleavage reactions seemed to follow a common pattern, i.e. coplanar transition state and reaction products and a common reaction energy value of 116-117 kcal/mol.

In order to achieve a generalization of the former conclusions drawn for this type of reactions, it was found necessary to extend these calculations for a broader number of PAH molecules in order to achieve a conclusive and general picture of these reactions.

The problem of molecular degradation of PAH molecules had been a subject for many experimental and theoretical investigations, a fact which indicates the industrial and theoretical importance of the reactions [9-22]. In general, the assumption was done, that such reactions should be initiated with a C-H cleavage rather than a C-C cleavage reaction, a statement that is usually documented in the organic chemical texts. In the present paper, we report a study of the bond cleavage reactions for two PAH molecules, chrysene and perylene, and compare the energetic properties of their C-C and C-H bond cleavage (Figure 1).

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Chrysene **Perylene**

Figure 1. Molecular structure of chrysene and perylene.

2. Computation details

In the present study, we adopt a strategy based on the fact that the inspection of the C-C or C-H bond cleavage reaction requires the accurate description of the corresponding reaction path derived from a proper and accurate energy hypersurface of the reaction [8]. Accordingly, the total energy of the reacting molecule should be evaluated for the different lengths of the corresponding bond, considered as the reaction coordinate. For this purpose, an adequate Gaussian basis (6-311G) was chosen for the ab-initio DFT treatment. For the calculation of the reaction path, no other orbital representtations such as the NBO (compelled through an optional similarity transformation of the resulting molecular orbitals) is required. In the present work, the molecular total energies, important for the description of the reaction path, are calculated for both (S) and (T) electron configurations for all the points along the reaction path. As expected, the configuration with the lower energy of each bond length (point along the reaction path) is accepted for the description of the path.

Total minimization is done to evaluate the minimal total energy for each point along the reaction path, keeping the corresponding value of the reaction coordinate (bond length) constant and varying the remaining (3N-5) coordinates. The obtained energy values for all points are plotted then against the corresponding lengths of the reaction coordinate to describe the required reaction path, the knowledge of which enables the assignment of energies and geometric parameters of the reaction (TS) and (RP).

For the energy calculation, we apply the ab-initio Density Functional Theory method (DFT) [23-25] in the B3LYP form [26, 27] as programmed within the Gaussian03 program system of Pople *et al*. [28]. The 6-311G Gaussian basis set was chosen for the application. The Molek9000 program of P. Bischof, Heidelberg was used [29] for the discussion of the corresponding geometries.

3. Results and discussion

Following the above described strategy in discussing the bond cleavage problem, the following results are obtained for the two aromatic molecules chrysene and perylene.

3.1. Chrysene

3.1.1. C1-C2 bond cleavage

According to the DFT results, the singlet (TS) of this reaction is depicted by an aromatic 6-electron ring, in which the C1…C2 distance is 3.6 Å. It is formed through a disrotatoric ring opening mechanism [8] (Figure 2).

Beyond the TS a H3 migration from C3 atom to C2 follows, forming a CH_2 and an allenyl-, $H_2C2=C3=HC4-C4a-$ group. The reaction proceeds maintaining the coplanarity of the molecule towards the (S) reaction product. The reaction is of the following energy values, E_a = 197.69 kcal/mol, E_r (S) = 132.36 kcal/mol and E_r (T) = 157.78 kcal/mol. According to the calculated (endothermic) reaction energies, the singlet product is of a smaller energy content and should represent the actual reaction product.

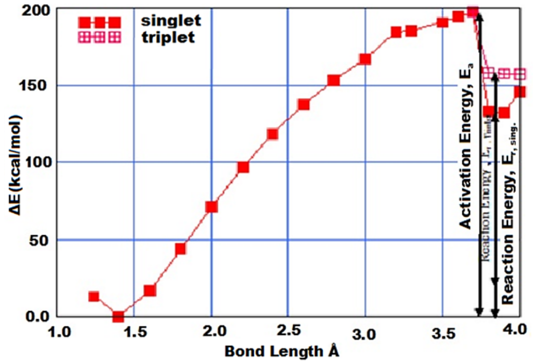

Figure 2. Calculated reaction path for the C1-C2 bond cleavage in chrysene molecule. The calculated activation energy is 197.69 kcal/mol; the calculated reaction energy for the (S) RP is 132.36 kcal/mol and for the (T) product is 157.78 kcal/mol.

3.1.2. C2-C3 bond cleavage

The cleavage of this bond proceeds via a (S) coplanar (TS) in the form of a disrotatoric ring opening. No H atom migration occurs after the ring opening, probably due to the impossible formation of an allenyl- or butadienyl- group. The calculated activation energy of the reaction is 179.60 kcal/mol. the reaction energy for the (S) RP is 88.61 kcal/mol and that for the (T) product is 124.16 kcal/mol. The energy values suggest that the singlet is favored over the triplet (RP) formation. Both the activation energy and energy of the reaction product are smaller in magnitude than the corresponding values for the C1-C2 bond. They suggest an essential single bond character for the C2-C3 bond.

3.1.3. C3-C4 bond cleavage

According to the present treatment, this reaction occurs via a coplanar (S) transition state at the C3…C4 distance of 3.3 Å. It proceeds then towards the (S) product maintaining the coplanarity of the molecule. No H atom migration, and thus no CH_2 group formation, is predicted. It appears that keeping the molecular planarity of the (S) product, and consequently increasing the π-conjugation energy stabilizes the reaction product. The calculated energy of C3-C4 (S) reaction product, 118.11 kcal/mol is smaller than that of C1-C2 (S) product, 132.36 kcal/mol. Figure 2, and higher than that of C2-C3 (S) product, 88.61 kcal/mol.

Table 1. Calculated energies and C_i…C_j bond lengths at the TS of the C-C and C-H bond cleavage reactions of chrysene molecule.

Bond	**Transition state**		**Singlet state**		**Triplet state**	
types	**Bond length (Å)**	**Energy (kcal/mol)**	**Bond length (Å)**	**Energy (kcal/mol)**	**Bond length (Å)**	**Energy (kcal/mol)**
C1-C2	3.6	197.69	3.7	132.36	3.7	157.78
C2-C3	3.5	179.60	3.6	88.61	3.6	124.16
C3-C4	3.3	179.66	3.4	118.11	3.4	166.59
C4-C4a	3.6	165.71	3.7	106.69	3.7	136.47
C4a-C4b	3.9	171.63	4.0	118.58	4.0	131.64
C1-C12a	3.6	170.79	3.7	108.80	3.7	146.61
C10b-C11	3.5	162.13	3.6	95.57	3.6	131.13
C4a-C12a	2.8	136.97	2.9	114.55	2.9	138.43
C12-C12a	3.5	165.81	3.6	102.75	3.6	132.59
C1-H1	3.5	148.57	-	-	3.6	117.69
C2-H2	3.7	154.28	-	-	3.8	117.25
C11-H11	4.0	154.96	-	-	4.1	115.17
C12-H12	3.8	152.59	3.9	116.77	3.9	117.23

Assigning an essential double bond character for C1-C2, the (S) reaction product of which appreciates an extra stabilization due to the H atom migration, the high energy of the C3-C4 (S) product suggests an essential double bond character to this bond too.

3.1.4. C4-C4a bond cleavage

The cleavage reaction of this bond proceeds through a coplanar aromatic TS of an activation energy 165.71 kcal/mol. A stable (S) reaction product is then formed via a H atom shift from C3 to C4. The so formed butadienyl- segment exerts an extra conjugation which stabilizes the reaction product. No such H atom shift nor a formation of a butadienyl- group is predicted for the (T) product. Relative to the energy of the stable chrysene molecule, considered to be 0.0 kcal/mol. The calculated energy of the (S) product is 106.69 kcal/mol that of the (T) reaction product is 136.47 kcal/mol. The energy difference of 30.2 kcal/mol demonstrates the stabilization of the (S) over the (T) reaction product.

3.1.5. C4a-C4b bond cleavage

A disrotatoric bond cleavage of this bond takes place, with no H atom shift following. The (S) product is of a deformed *cis*-stilbene shaped structure in which the phenyl- and naphthyl- rings are rotated out of the H-C=C H plane in a disrotatoric conformation. In the (T) reaction product only one ring (phenyl) is rotated out of the H-C=C H plane. The calculated activation energy of the reaction is 171.63 kcal/mol, the calculated reaction energies are E_r = 118.58 kcal/mol for thesinglet and 131.64 kcal/mol for the triplet reaction product.

3.1.6. C1-C12a bond cleavage

The cleavage of this bond takes place through a disrotatoric ring opening too, where the C1-C2-C3 segment is rotated out of the phenanthrenyl- rest of the molecule maintaining an expected (+) interaction between the C1 and C12a atomic orbitals. The calculated reaction TS is non-coplanar and aromatic. Further progress of the reaction includes a H3 atom shift from C3 to C2 forming a CH_2 group. The stable final (S) product is a coplanar diradical. For the virtual (T) reaction product no H atom shift is predicted and the molecule maintains a conformation similar to that of the TS. The calculated activation energy of the reaction is 170.79 kcal/mol. The calculated reaction energy is 108.80 kcal/mol. The C1-C12a bond might be assigned an essential single bond on the basis of the calculated energy values.

3.1.7. C10b-C11 bond cleavage

A disrotatoric ring opening leads to the (S) TS at the C10…C11 bond distance of 3.4 Å. Further progress of the reaction leads to the rotation of the phenyl ring around its bond to the naphthyl ring by approximately 180°. The final (S) RP shows the C11H11 bond facing the C5H5 bond. No H atom shift is predicted. The calculated energy values are 162.13 for the activation energy, 95.57 for the (S) and 131.13 kcal/mol for the (T) reaction energies.

3.1.8. C4a-C12a bond cleavage

A coplanar (S) TS is calculated for this bond. The progress of the reaction is depicted by a disrotatoric out of plane motion of the C3a and C12a atoms towards the final (S) reaction product. The calculated energy values are 136.97 for the activation energy and 114.55 as well as 138.43 kcal/mol for the (S) and (T) reaction products, respectively. No H atom shift was predicted for the reaction. The calculated energy values indicate an essential double bond character for this bond.

3.1.9. C12-C12a bond cleavage

The calculated structure of the (S) TS of this reaction corresponds to the out of plane displacement of the terminal C12 and C12a atoms in a disrotatoric position, forming a 6-π electron aromatic ring. The formation of the TS is followed by H11 shift to C12 forming a CH_2 group, no such shift is calculated for the (T) RP. The calculated energy values are 165.81 kcal/mol for the activation energy, 102.75 and 132.59 kcal/mol. For the reaction energies of the (S) and (T) products, respectively. These values suggest that the (S) reaction product is preferred and that the inspected bond is of an essential single bond character.

Table 1 shows the calculated activation and reaction energies as well as the C…C and C…H bond distances at the TS's of the C-C and C-H bond cleavage reactions for chrysene molecule. Inspection of the calculated energies suggests the classification of the studied bonds in essential double bonds, with E_r >114.0 kcal/mol. and essential single bonds with E_r < 114.0 kcal/mol. Comparing both classes with each other reflects the bond alternating nature of the molecule with C1-C2 and C3-C4 as essential double bonds.

3.2. Perylene

Due to the high symmetry of perylene molecule (D_{2h}) the discussion of the bond cleavage reactions is reduced to one bond among the many that might be generated through proper symmetry operations.

3.2.1. C1-C2 bond cleavage

According to the present treatment this reaction is described as a disrotatoric ring opening in which both C1 and C2 atoms move to the same side of the molecular plane towards the aromatic TS, (at the C1…C2 distance 3.3 Å).

Table 2. Calculated activation and reaction energies * for the C-C and C-H bond cleavage of perylene molecule.

Bond types	**Transition state**		**Singlet state**		**Triplet state**	
	Bond length (Å)	**Energy (kcal/mol)**	**Bond length (Å)**	**Energy (kcal/mol)**	**Bond length (Å)**	**Energy (kcal/mol)**
C1-C2	3.3	187.33	3.4	107.70	3.4	158.24
C2-C3	3.1	164.49	3.2	163.00	3.2	140.37
C3-C3a	3.5	178.30	3.6	113.53	3.6	151.05
C3a-C3b	4.1	162.25	-	118.33	4.2	117.97
C12a-C12b	3.5	176.57	3.6	168.28	3.6	176.17
C1-C12a	3.6	170.48	3.7	98.12	3.7	137.48
C1-H1	4.1	156.98	4.2	117.48	4.2	117.72
C2-H2	4.6	162.73	-	-	4.7	117.28
C3-H3	3.5	148.30	-	-	3.6	116.00

* Energies calculated relative to the energy of the equilibrium non-reacting state of the molecule accepted as 0.0 kcal/mol.

Further progress of the reaction leads to the H3 atom shift from C3 to C2, building a CH_2 moiety within the (S) product. No such shift is predicted for the (T) product. The calculated activation energy is 187.33 kcal/mol. the calculated reaction energies are 107.70 kcal/mol for the (S) reaction product and 158.24 kcal/mol for the triplet product. The energy values suggest an S final product for the reaction.

3.2.2. C2-C3 bond cleavage

This reaction starts with a ring opening in which both CH groups move in the molecular plane reaching an aromatic TS at the C2…C3 distance 3.1 Å. Further progress of the reaction includes a disrotatoric motion of the two CH groups at the same side of the molecular plane. No H shift is predicted for the reaction. The calculated activation energy of the reaction is 164.49 kcal/mol the calculated reaction energies are 163.0 and 140.37 kcal/mol for the (S) and (T) products, respectively. The calculated energy values predict a (T) final product for the reaction.

3.2.3. C3-C3a bond cleavage

A coplanar TS, at the C3…C3a distance 3.5 Å is calculated for the cleavage reaction of this bond. H2 atom shift to C3 follows the initial step and causes the formation of a CH_2 group and a C1C2C3 allenyl rest. The non-coplanar S reaction product is preferred with a reaction energy of 113.53 kcal/mol. The less stable T product possess a reaction energy of 151.05 kcal/mol.

3.2.4. C3a-C3b bond cleavage

The ab-initio DFT treatment for this reaction results in a similar conformation for the TS as well as the S and T reaction products, signified by the rotation of the two formed naphthyl rings, around the C9a-C9b single bond, relative to each other. The calculated activation energy for the reaction is 162.25 kcal/mol. The calculated reaction energies for both S and T reaction products are almost equal, 118.33 kcal/mol for the S and 117.97 kcal/mol for the T product. Accordingly the reaction may lead to each of the two reaction products.

3.2.5. C12a -C12b bond cleavage

A non-planar aromatic TS (10 π-electrons) is calculated for this reaction in which both C12a and C12b atoms move to the same side of the molecular plane. The distance between the 2 atoms at the TS is 3.5 Å. The calculated activation energy for the reaction is 176.57 kcal/mol, the calculated reaction energy is 168.28 kcal/mol for the S and 176.17 kcal/mol for the triplet state. The reaction should yield an S configured final product.

3.2.6. C1-C12a bond cleavage

A disrotatoric ring opening is calculated for this reaction. It leads to an aromatic (10 π-electrons) TS state in which the C1C2C3 group is bent out of the molecular plane and the C1…C12a distance is 3.5 Å. H2 atom shift to C1 follows the TS forming a CH2 group and a C1C2C3C3a butadienyl moiety. Whereas the TS shows a significant non-planarity, the more stable S reaction product is completely planar. The calculated activation energy is 170.48 kcal/mol and the reaction energy for the S product is 98.12 kcal/mol and for the T product is 137.45 kcal/mol. Based on the calculated reaction energies the S product is the more stable among the two.

Table 2 shows the calculated energies and C…C bond distances of the C-C and C-H bond cleavage reactions for perylene molecule.

The ab-initio DFT study for the C-H bond cleavage reaction of both molecules, similar to those of the formerly calculated molecules [1-7], shows common features, for both chrysene and perylene which might be concluded in the following statements; (i) All these reactions pass through planar S, TS's, (ii) They show common reaction energy, for the S and T products, of ~116-117 kcal/mol (iii) They show different values for the activation energy, Tables 1 and 2.

4. Conclusion

The present results confirm our former findings concerning the mechanism of the C-C and C-H bond cleavage in PAH molecules, which included a disrotatoric ring opening of the corresponding ring, an S configured transition state, a H atom shift towards the formation of a CH_2 and allenyl- or butadienyl moiety, if possible. However the calculated energy values for the different bonds in the different PAH`s are not the same. These differ from each other due to the topology of the reacting molecules and the location of the corresponding bond in them. For the organic as well as industrial chemists, the knowledge of average energy increments for such reactions is very important, by in day by day work. To achieve such trustful energy values further calculations for other PAH's are required. As known, the bigger the basis of knowledge the more accurate is the results. We have adopted this task as our future aim.

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