European Journal of Chemistry 10 (4) (2019) 403-408

European Journal of Chemistry

View Journal Online
View Article Online

C-C and C-H bond cleavage reactions in acenaphthylene aromatic molecule, an ab-initio density functional theory study

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RESEARCH ARTICLE

10.5155/eurjchem.10.4.403-408.1889

Received: 07 May 2019
Received in revised form: 22 September 2019
Accepted: 27 September 2019
Published online: 31 December 2019
Printed: 31 December 2019

KEYWORDS
DFT
B3LYP
Ab initio
Reaction paths
Acenaphthylene
C-C and C-H bond cleavage

ABSTRACT

The ab-initio DFT method (B3LYP) is applied to the study of the C-C and C-H bond cleavage reactions in acenaphthylene molecule. It is found that the C-C bond cleavage proceeds via a singlet aromatic transition state, compelled through a disrotatoric ring opening reaction. A sigmatropic 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. The calculated activation and reaction energies for the C-C ring opening are 164-236 and 52-193 kcal/mol, respectively. The calculated cleavage reaction energies for the C-H bonds are 117-122 kcal/mol and the activation energies are 147-164 kcal/mol.

Cite this: *Eur. J. Chem.* **2019**, *10(4)*, 403-408 **Journal website**: www.eurjchem.com

1. Introduction

Due to their industrial importance, the study of the thermal degradations of polycyclic aromatic hydrocarbons (PAH) had been a subject for numerous experimental and theoretical investigations [1-13]. In previous papers, we reported quantum mechanically calculated structures and energies of the transition states (TS) and reaction products (RP) of the C-C and C-H bond cleavage reactions for a number of poly-aromatic hydrocarbon molecules [14-21]. We applied for these treatments the ab-initio Density Functional Theory (DFT) method [23-27]. On the basis of the obtained results, one could conclude the following facts concerning the C-C bond cleavage reactions; (i) Singlet (S) electronically configured transition states (TS) resulted for all the studied reactions. No triplet (T) TS's seemed probable. The ring opening reaction was of disrotatoric nature, (ii) All the calculated cyclic transition states obeyed the Hückel's (4n+2) rule for aromaticity. The law of aromatic transition state [28] seemed to be obeyed, (iii) For those C-C bond cleavage reactions, which ended in singlet reaction products, the ring cleavage was accompanied by sigmatropic shifts of a H· atom, which lead to the formation of =CH_2 or –CH= moieties on one side and of an acetylenyl-, allenyl- or butadienyl- group on another side of the product molecule. No such shifts were predicted for the triplet reaction products, and (iv) Molecular strain is an effective factor in determining the structure of both the transition states and reaction products.

As for the C-H bond cleavage reactions, they seemed to follow a common pattern, i.e. coplanar TS's and RP's with common reaction energy values of 116-123 kcal/mol. To achieve a wide generalization for these conclusions, it was necessary to extend the calculations to other members of the PAH family. In the present paper, we report such a study for the bond cleavage reactions of the acenaphthylene PAH molecule (Figure 1).

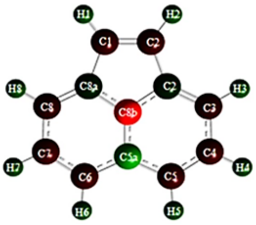


Figure 1. Acenaphthylene molecule.

European Journal of Chemistry
ISSN 2153-2249 (Print) / ISSN 2153-2257 (Online) –
http://dx.doi.org/10.5155/eurjchem.10.4.403-408.1889

Table 1. Calculated energy values for the C-C and C-H bond cleavage reactions in acenaphylene 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)
C2a-C3	3.9	192.317 db	4.0	124.471	4.0	154.808
C3-C4	3.9	173.570 sb	4.0	52.230	4.0	117.697
C2a-C8b	3.2	163.963 sb	3.4	139.791	3.4	126.105
C2a-C2	3.8	143.619 sb	3.9	24.540	3.9	105.464
C8b-C5a	3.6	236.251 db	3.7	192.755	4.0	214.682
C5a-C5	3.8	164.241 sb	3.9	120.127	4.1	128.298
C5-C4	4.1	190.447 db	4.3	122.048	4.4	166.601
C1-C2	3.8	212.010 db	3.9	181.186	3.9	178.561
C3-H3	3.6	151.296	-	-	3.7	117.220
C2-H2	4.0	164.002	4.1	121.399	4.1	121.681
C4-H4	3.9	156.694	-	-	4.0	117.237
C5-H5	4.1	147.169	4.2	117.438	4.2	117.674

* db: Essential double bond, sb: Essential single bond.

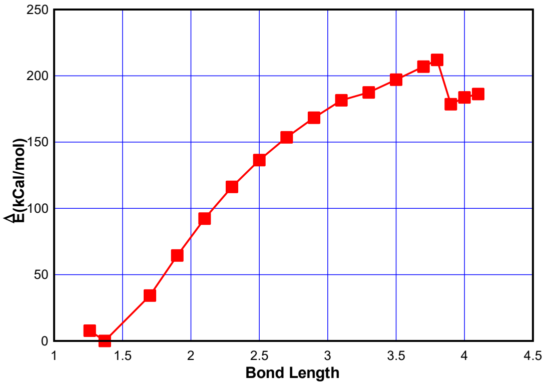


Figure 2. Potential energy curve for C1-C2 bond cleavage of acenaphthylene molecule showing the activation energy (E_a = 212.010 kcal/mol) and reaction energy for the product, in the triplet state (E_r = 178.561 kcal/mol).

2. Experimental

The Gaussian 03 program package was operated to obtain all calculations. B3LYP method with the standard 6-311G(d,p) basis set were used for the calculation [28,29]. Restricted energy minimization was applied, such that each value of the reaction coordinate (the bond length) was kept constant whereas total minimization was carried out for the other (3N-5) internal coordinates.

3. Results and discussion

Accurate evaluation of the reaction path is required for the quantitative description of the C-C and C-H bond cleavage [14,15]. For this purpose, we chose the evaluation of the total energy of the reacting molecule as function of the corresponding C-C or C-H bond length, where both singlet and triplet electron configurations are considered. The configuration with the lower energy value was adopted on plotting the reaction path, in which the reaction transition state and final products could be determined graphically, Figure 2.

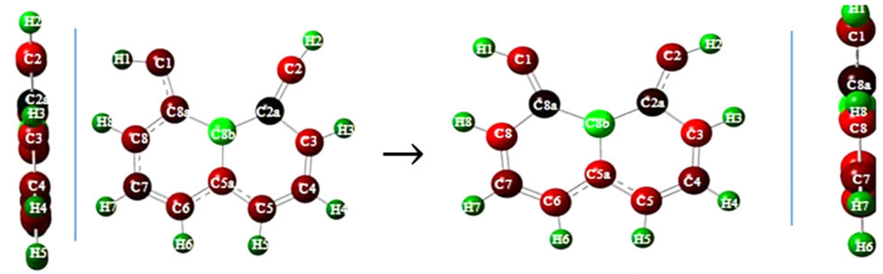
Figure 3 and 4 show the illustrated calculation results for the different C-C bonds in acenaphthylene. As for the C1-C2 bond the reaction proceeds via a singlet transition state towards the triplet reaction product (Figure 3). No H atom shift results for this reaction, a fact which seems common for all triplet product C-C cleavage reactions. Both the reaction transition state and the reaction product exhibit a coplanar conformation. As for the C3-C4 bond cleavage reaction, a coplanar singlet reaction product is formed in which a C5 to C3 H atom shift is obvious (Figure 3). The coplanar reaction product includes a $C3H_2$ group together with a C4(H)C5··· acetenyl group conjugated to the coplanar molecular rings. The C4-C5 bond cleavage proceeds through the singlet transition state towards a coplanar reaction product with a simultaneous H atom shift from C3 to C4 (Figure 4). The transition state conforms to a six carbon atoms ring with 6π electrons. The C2a-C3 bond cleavage proceeds towards a singlet reaction product with a H atom shift from C4 to C3 forming a $C3H_2$ and a C3-C4-C5-allenyl group. The reaction product depicts an out of plane conformation in which the six membered ring is twisted out of the molecular plane (C_6H_6 group out of the molecular plane), as shown in Figure 3 and 4.

The C2a-C8b inner bond cleavage proceeds in a disrotatoric manner, via a singlet transition state, towards a triplet reaction product (Figure 3). No H atom shift results from the calculation. The transition state is reached at a relatively short C...C distance, 3.3 Å, as compared with C...C distances of other bonds, 3.8 to 4.3 Å. Cleavage of the essential single bond C2a-C2 yields a coplanar singlet reaction product with a H atom shift from C1 to C2a. An in-plane C2-C1 acetylenic group is formed, too.

The cleavage of C8b-C5a bond conforms to a disrotatoric motion of both C atoms (Figure 4). The singlet transition state exhibits a slight deformation from planarity, whereas the singlet reaction product possess a tub type 12 carbon atom frame, with the C5a-C8b distance 3.7 Å. As for the C5a-C5 essential single bond, the cleavage reaction proceeds through a coplanar transition state towards an allenyl- substituted indane structure. A H atom shift, from C4 atom to C5 proceeds together with the ring opening (Figure 4).

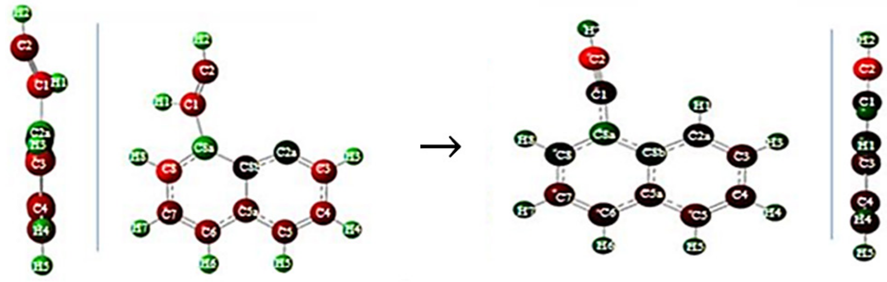
Figure 5 includes the calculated structures and energy values for the C-H bond cleavage reactions in acenaphthylene. It is easily seen that all the reactions proceed in a coplanar manner, and that the reaction energy values range from 117 to 122 kcal/mol, Table 1. Table 1 includes the ab-initio DFT calculated energy values for the C-C and C-H bond cleavage in acenaphthylene molecule.

E* (kcal/mol) 212.010 | **E_r (kcal/mol)** 178.561 | **H-shift** Not determined



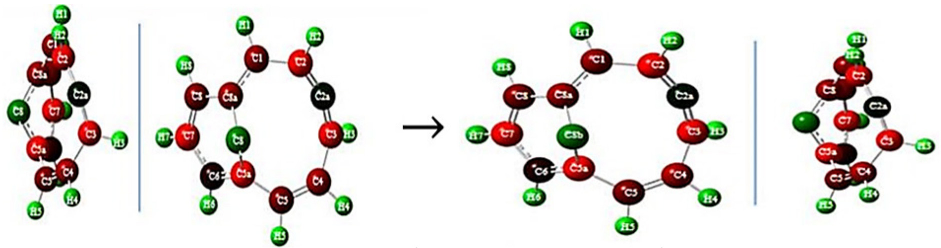
T.S. BL. = 3.8 Å R.P. (T), B.L. = 3.9 Å
C1-C2

E* (kcal/mol) **143.619** | **E_r (kcal/mol)** **24.540** | **H-shift** **C1→C2a**



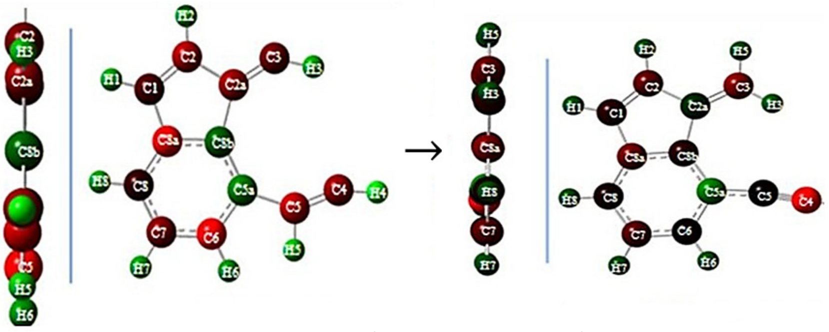
T.S. BL. = 3.8 Å Singlet R.P., B.L. = 3.9 Å
C2-C2a

E* (kcal/mol) **163.96** | **E_r (kcal/mol)** **126.105** | **H-shift** **Not determined**



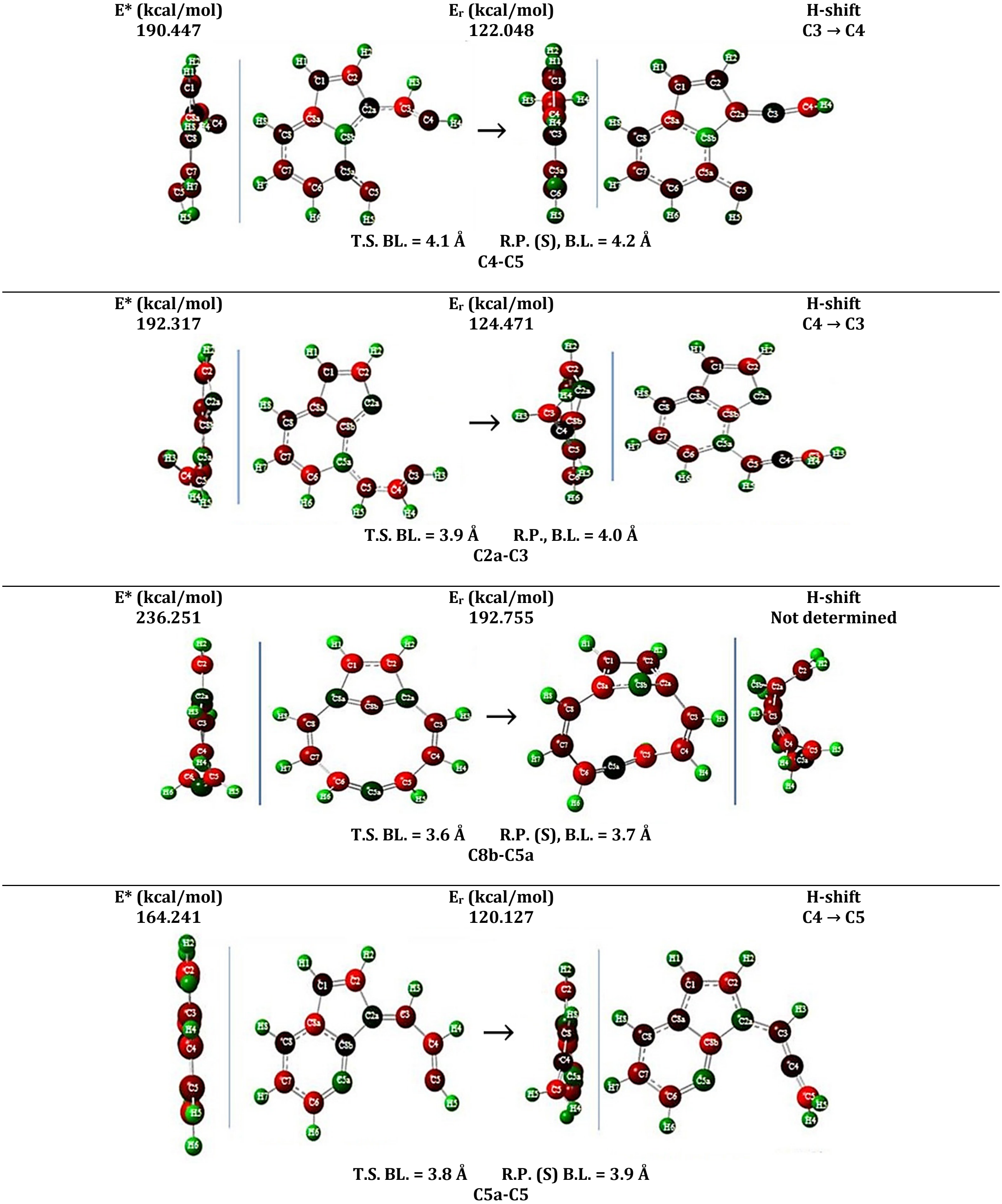
T.S. BL. = 3.2 Å R.P. (T), B.L. = 3.3 Å
C2a-C8b

E* (kcal/mol) **173.570** | **E_r (kcal/mol)** **52.230** | **H-shift** **C5→c3**



T.S. BL. = 3.9 Å R.P., B.L. = 4.0 Å
C3-C4

Figure 3. Calculated illustration figures and energy values for the different C-C bond cleavage reactions of acenaphthylene molecule.



E* (kcal/mol) **190.447** **E$_r$ (kcal/mol)** **122.048** **H-shift** **C3 → C4**

T.S. BL. = 4.1 Å **R.P. (S), B.L. = 4.2 Å**
C4-C5

E* (kcal/mol) **192.317** **E$_r$ (kcal/mol)** **124.471** **H-shift** **C4 → C3**

T.S. BL. = 3.9 Å **R.P., B.L. = 4.0 Å**
C2a-C3

E* (kcal/mol) **236.251** **E$_r$ (kcal/mol)** **192.755** **H-shift** **Not determined**

T.S. BL. = 3.6 Å **R.P. (S), B.L. = 3.7 Å**
C8b-C5a

E* (kcal/mol) **164.241** **E$_r$ (kcal/mol)** **120.127** **H-shift** **C4 → C5**

T.S. BL. = 3.8 Å **R.P. (S) B.L. = 3.9 Å**
C5a-C5

Figure 4. Calculated illustration figures and energy values for the different C-C bond cleavage reactions of acenaphthylene molecule.

4. Conclusion

The obtained results in this manuscript indicate the following results; i. they confirm our former findings that all the C- C bond cleavage reactions proceed via disrotatoric ring opening passing through singlet transition states, ii. for reactions ending with singlet products a H shift occurs provided that the formation of conjugated acetenyl-, butadienyl- or allenylyl- side chain is possible, such as for the C3-C4, C4-C5, C2a-C3, C2a-C2, and C5a-C5 bonds. No such shift result for the triplet state product reactions, iii. The calculated reaction activation energies range from 192.32 to 236.25 kcal/mol for the C-C essential double bonds (db) and from 143.62 to 173.65 kcal/mol for the C-C essential single bonds

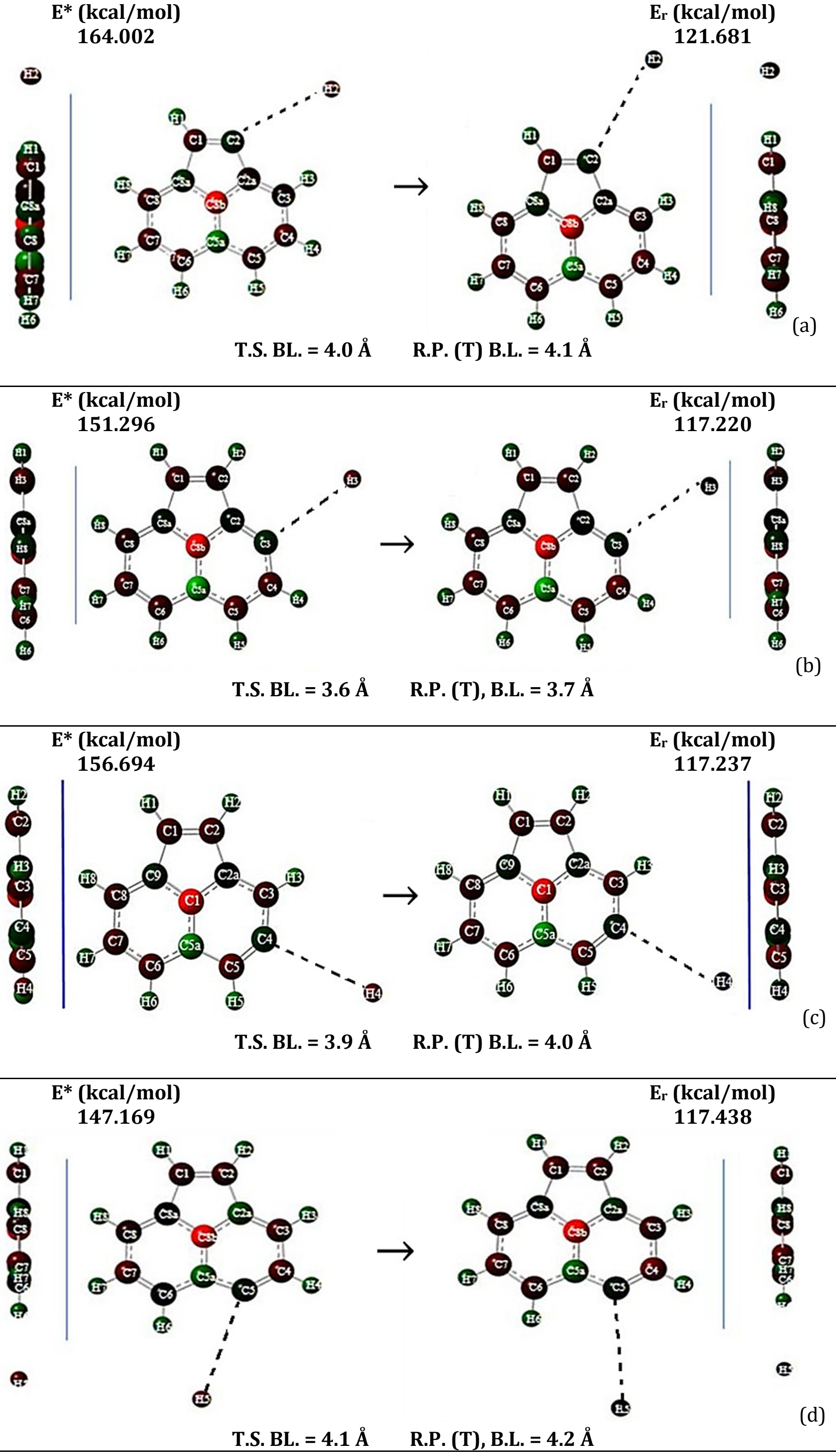


Figure 5. Calculated figures for the different C-H bond cleavage reactions of acenaphthylene molecule, (a) C2-H2, (b) C3-H3, (c) C4-H4, (d) C5-H5.

(sb), and iv. All C-H bond cleavage reactions proceed in a coplanar manner, the corresponding activation energies range from 147.17 to 164.00 kcal/mol and the reaction energies from 117.44 to 121.40 kcal/mol.

Acknowledgements

This article includes a part of the PhD thesis of Qhatan Adnan Yusuf with Muthana Abduljabbar Shanshal supervision, College of Science, University of Baghdad, Baghdad, Iraq.

Disclosure statement

Conflict of interests: The authors declare that they have no conflict of interest.
Author contributions: All authors contributed equally to this work.
Ethical approval: All ethical guidelines have been adhered.
Sample availability: Samples of the compounds are available from the author.

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