ESKİŞEHİR TEKNİK ÜNİVERSİTESİ BİLİM VE TEKNOLOJİ DERGİSİ
B- TEORİK BİLİMLER

Eskişehir Technical University Journal of Science and Technology B- Theoretical Sciences

Estuscience – Theory, 2025, 13 [1] pp. 35-42, DOI:10.20290/estubtdb.1565576

RESEARCH ARTICLE

EFFECT OF OPTIMIZATION SEQUENCE ON THE STRUCTURAL AND ELECTRONIC PROPERTIES OF IMPURITY ADDED C_{20} FULLERENE: A DFT ASSESMENT

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Abstract

Due to its advantages over experimental works, density functional theory as a computational approach provides many insights before going over the expensive and timely costs of experimental studies. However, the time required to perform a computational study depends on the number of atoms or size of the investigated molecular system and the capacity of the computational sources. In the framework of this study, we have investigated different optimization procedures to see the effect on optimization energy, electronic parameters and some important structural parameters by using modified fullerene-C_{20}. The question that was tried to be answered here is, independent of the computational source, “do we really have to build a given molecular system from the very beginning of its components or can the final structure be directly optimized?”. The preliminary results suggested very small differences such as (1-2) cm^{-1} for OH vibrations, 0.003 Å for inter atomic distances at the interaction sites and 0.003-0.018 eV energy alterations for frontier molecular orbitals. The results suggest a way to room more space and time for further studies based on impurity added C_{20}-fullerenes.

Keywords

C_{20},
DFT,
Optimization sequence,
Electronic parameters

Time Scale of Article

Received :11 October 2024
Accepted : 18 December 2024
Online date : 28 February 2025

1. INTRODUCTION

In recent years to evaluate the possible sensor and drug delivery assessments of fullerene-based systems, increasing numbers of theoretical calculations based on the density functional theory (DFT) have been given to the literature [1-4]. DFT assessments of drug interactions with various structural systems seem particularly an ongoing work with increasing number of publications, because of its useful insights and advantages compared to experimental applications [5,6]. Due to their unique physical, chemical and electronic properties, fullerene nano cages have been increasingly popular within the scientific environments particularly for the investigation of sensor and drug delivery applications [7-10]. Therefore, a special attention seems required for the grounded scientific works.

In the essence of many computational studies, the aim is to find the global energy minima or the most stable structure of the examined molecular systems. At this point, there are several factors that might

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*Corresponding Author: ozguralver@eskisehir.edu.tr affect the obtained energy values. If the initial input structure is far from reality, the structure might not converge to a true minimum energy case. It is also expected that the results of vibrational frequency calculations must all yield positive frequency values [11, 12]. The selection of basis sets and functionals depending on their properties, requires different calculation times. Using larger basis sets, require larger computational sources and strong computer systems which might not be available for many scientists around the world due to scarcity of aimed conditions.

In this work, besides already known conditions to obtain true energy minima, we also investigated the effect of the optimization sequence on the energetic parameters using C_{20} fullerene as the main structure. Due to its strong polar nature, water molecule was chosen as the interacting molecule with C_{20} and modified C_{20} systems. The interaction energies were calculated for water interacted surface and endohedrally boron and lithium modified fullerene-C_{20} systems by taking into account different optimization protocols. The effect of the initial geometric structure and the optimization protocol on the resultant geometric structure with its various chemical, physical and electronic characteristics have been discussed in brief.

2. COMPUTATIONAL STUDIES

For all the calculations B3LYP/6-31G(d) level of theory was used. No geometric boundaries were applied, and no point group was considered during the optimization process. At the end of each optimization process, vibrational frequency calculations were also carried out to make sure that the resultant structure is free of any imaginary or negative frequencies. Many medical studies have been carried out in water media because of high natural abundance of water molecules in many organic and inorganic media. Henceforth, the effect of solvent was considered using the polarizable continuum model [13].

Multiple doping and endohedral impurity addition of fullerene systems appear as promising enhancement methods for sensor and drug delivery purposes [14-16]. The main goal of this study is to suggest an optimization procedure yielding the most stable structures for multiple and endohedral impurity added fullerene systems. In Fig. 1, the optimization protocol was summarized. In this figure, the question is what happens if the system is optimized step-by-step or directly to reach the final structure. The related possible differences were discussed in the results and discussion section. According to Fig. 1, six different optimization protocols were suggested labelled as I, II, III, A, B and C. I, II and III are related to the surface modification of C_{20} with boron (B) atom. A, B and C are related to both endohedral with lithium (Li) and surface modification with B of C_{20} fullerene cage.

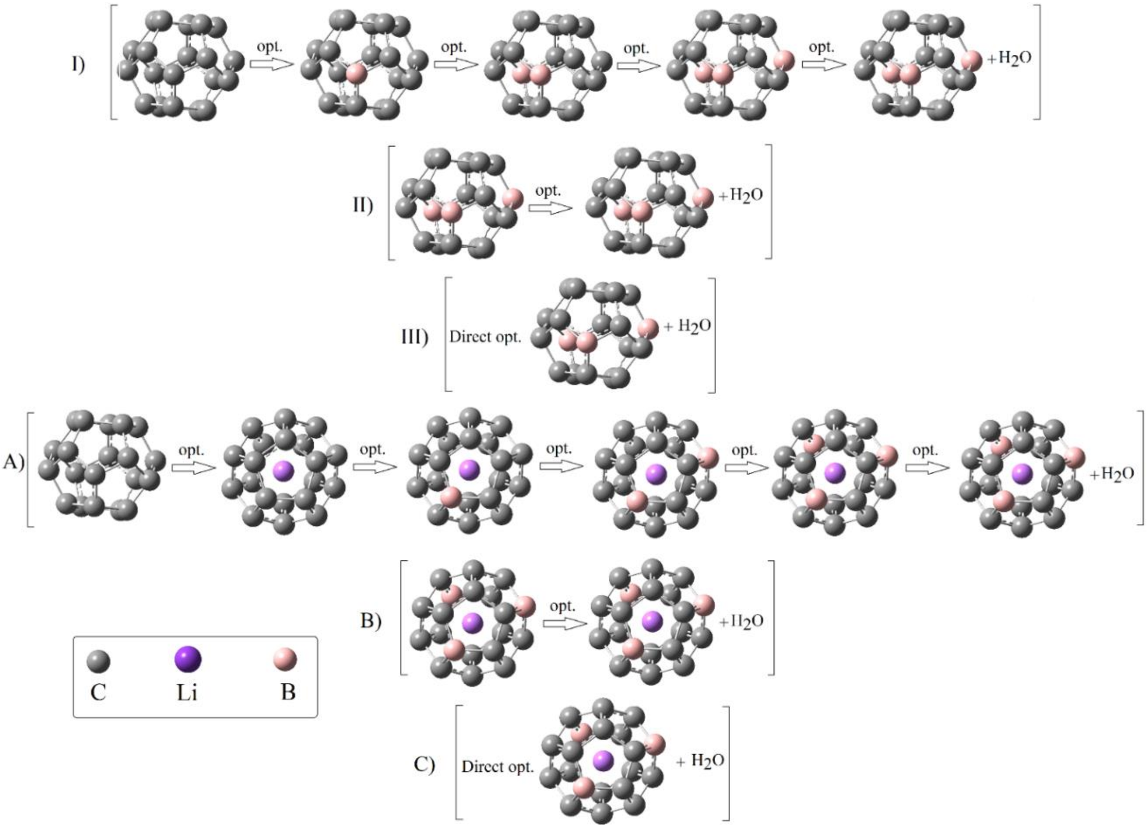

Figure 1. Optimization protocols with initial geometric structures and color codes.

Particularly, at the final stage of the optimization protocol, it is very important to provide similar initial input geometric structures which requires identical structural parameters before the optimization. In this way, it is truly possible to see the effect of ordered and direct optimization procedures. Otherwise, the deviations of optimized energy values which is expected to be small might result from different initial geometries as well. The initial geometric structures for the H_2O interacted system are given in Fig. 2.

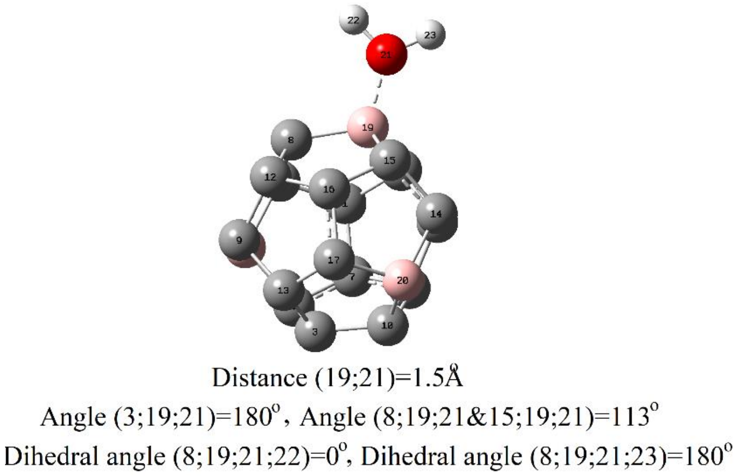

Figure 2. Initial geometry of H_2O interacted system.

E_g energies refer to the magnitudes of differences between the highest occupied molecular (HOMO) and the lowest unoccupied molecular orbitals (LUMO). Binding energies (E_b) were calculated as given below:

$$E_b = [E_{C_{17}B_3 \ldots H_2O} - (E_{H_2O} + E_{C_{17}B_3})]$$

$$E_b = [E_{Li@C_{17}B_3 \ldots H_2O} - (E_{H_2O} + E_{Li@C_{17}B_3})]$$

In the equations given above, all the structures refer to the energies of the optimized systems. Li@$C_{17}B_3$ indicates the endohedral lithium (Li) doped $C_{17}B_3$ fullerene. It is worth noting that Li atom was inserted at the centroid of the fullerene cage before the optimization process. Gaussian and GaussView programs were used for DFT calculations, molecular design of the structures and visualization [17,18].

3. RESULTS AND DISCUSSIONS

In this part of the study, comparisons were made for different optimization protocols. The obtained structural, electronic, and vibrational properties of the examined systems were compared against each other, and the results were analyzed in brief.

3.1. Analysis of Surface Modified C_{20}

In Table 1, the optimized energies (in a.u.) of the examined structures were given. Interestingly, in sequence-II which refers to the direct optimization of the $C_{17}B_3$ system, a slightly more stable structure was obtained from the energy consideration. However, this difference is around 0.0026 kcal/mol and it is quite small to make a visible and a healthy comparison. However, with the help of this fact it can be still suggested that rather than step-by-step insertion of boron atom on the surface of C_{20} (sequence-I), the direct replacement of three carbon atoms with three boron atoms (sequence-II) can be preferred for the optimization process which means saving a large amount of time for similar C_{20} based studies.

Table 1. Optimized energies (a.u.) for the examined structures for sequences I, II and III.

Sequence-I	**C_{20}**	**$C_{19}B$**	**$C_{18}B_2$**	**$C_{17}B_3$**	**$C_{17}B_3 \ldots H_2O$**
Optimized energy	-761.44532737	-748.24879814	-735.04276533	-721.79826583	-798.26233830
Sequence-II	**$C_{17}B_3$**	**$C_{17}B_3 \ldots H_2O$**			
Optimized energy	-721.79827001	-798.26235056			
Sequence-III	**$C_{17}B_3 \ldots H_2O$**				
Optimized energy	-798.26235065				

As for H_2O interacted fullerene system similar results were observed. The energetically most favorable structure was observed with sequence-III which refers to the directly optimized structure. The optimized energy difference between sequence III and sequence II was found as 0.000056 kcal/mol. Further, the optimized energy difference between sequence II and sequence I was calculated as 0.007693 kcal/mol. Henceforth, the surface modified C_{20} fullerenes with boron atoms can be directly optimized by building the structures. Step-by-step optimization seems not necessarily required. The antisymmetric & symmetric stretching (3717.26, 3718.21 and 3718.22 & 3636.46, 3637.95 and 3638.00 cm^{-1}) and bending (1691.26, 1689.45 and 1689.52 cm^{-1}) vibrations of H_2O molecule showed a very small difference around 1 cm^{-1} when compared to results of all optimization sequence. Therefore, it is hard to differentiate the obtained results regarding to their optimization procedure from the point of view of vibrational band assignment. Mulliken charge analyses particularly for O, B atom at the interaction site and the rest two B atoms on the surface of fullerene cage produced nearly the same results for all three optimization sequences with the respective values (in a.u.) -0.639, 0.338, 0.188 and 0.186 & 0.187. Therefore, it can be concluded that partial charge behavior is almost independent of the optimization protocol followed in this study. The B…O interatomic distance at the interaction site was calculated as 1.578 Å for all the optimization sequences. The average carbon-to-carbon bond length over the isolated

C_{20} was calculated between 1.400-1.540 Å. The average B—C bond distances of boron atom with three adjacent carbon atoms at the interaction site was calculated as 1.617 Å for the optimization sequences I and III. As for the optimization sequence II, the related bond length was calculated as 1.620 Å. It was seen that replacement of carbon atom with boron atom leads increasing bond length where the impurity atoms inserted. Furthermore, as can be seen from the findings, the effect of the optimization sequence is quite small for the mentioned interatomic distances or bond lengths.

The total CPU time (hour/minute/second) required for the optimization of structures given in sequences I, II and III are 9/5/7.1, 3/50/53.8 and 2/6/35.1, respectively. This result shows that there is around a 7-hour difference which can be saved between sequence I and sequence III. For more complicated interacting molecules rather than H_2O, this difference is supposed to be higher. E_b energies for optimization sequences I, II and III were calculated as -29.9799, -29.9849 and -29.9850 kcal/mol, respectively. The largest difference in here is 0.0051 kcal/mol. It is seen that there is a very small difference between the E_b energies for the ordered optimization sequences and the direct optimization of the examined structure. HOMO-LUMO, E_g energy for optimization sequence I was calculated as 2.855 eV. As for sequences II and III, it was calculated as 2.858 eV.

3.2. Analysis of Endohedral and Surface Modified C_{20}

The optimized energies of the examined systems are given in Table 2. The most stable energy configuration for the final structure which is the H_2O interacted system was obtained in sequence-C which is related to the directly optimized system. For the endohedral Li added system it seems not necessary to follow a partial optimization procedure as it happens for sequence-A. However, the final structure obtained in sequence-A appears slightly more stable than in sequence-B. Therefore, both endohedral and surface impurity inserted systems, in here they are Li and B atoms, it seems enough to build and optimize the interacted system rather than to follow a step-by-step optimization procedure.

Table 2. Optimized energies (a.u.) for the examined structures for sequences A, B and C.

Sequence-A	**Li@C_{20}**	**Li@$C_{19}B$**	**Li@$C_{18}B_2$**	**Li@$C_{17}B_3$**	**Li@$C_{17}B_3$...H_2O**
Optimized energy	-768.93631771	-755.74376962	-742.54642271	-729.33894887	-805.79668140
Sequence-B	**Li@$C_{17}B_3$**	**Li@$C_{17}B_3$...H_2O**			
Optimized energy	-729.33889044	-805.79667125			
Sequence-C	**Li@$C_{17}B_3$...H_2O**				
Optimized energy	-805.79686511				

The antisymmetric & symmetric stretching and bending vibrations of the H_2O molecule showed only a difference around 1-2 cm^{-1} when compared to the results of all optimization sequences. Therefore, no matter if one flows as step-by-step optimization protocol or directly optimize the given system undertaken in this study. The total CPU time (hour/minute/second) required for the optimization of structures given in sequences A, B and C are 10/26/42.8, 2/44/18.8 and 1/33/35.4, correspondingly. This result also indicates that there is around 9-hour difference between sequence A and sequence C. E_b energies for optimization sequences A, B and C were found as -26.0016, -26.0319 and -26.1535 kcal/mol, respectively. It is seen that the difference between the E_b energies for the ordered optimization sequences and for the direct optimization of the examined structure is negligible. HOMO-LUMO, E_g energy for optimization sequences A, B and C were calculated as 2.503, 2.502 and 2.520 eV. Mulliken charge analyses for O, endohedrally inserted Li, B at the interaction site and the rest two B atoms on the surface of fullerene yielded -0.646, -0.946, 0.437 & 0.439 & 0.441, 0.327 and 0.328 & 0.327. As can be seen from the obtained results, optimization protocol or the sequence has nearly no effect on the partial charge distribution for selected atoms. It was further observed that partial charges of surface dopant atoms for Li@$C_{17}B_3$ system became more positive when compared to surface modified $C_{17}B_3$ system which indicates that upon insertion of Li atom some number of electrons move away from the dopant atoms. The B…O interatomic distances at the interaction site were calculated as 1.585, 1.586 and 1.583 Å, for optimization sequences A, B and C. The average B—C bond distance of boron atom with three neighbor carbon atoms at the interaction site was calculated as 1.628 Å for all the optimization sequences. In addition to that the average carbon to carbon bond length over the isolated and endohedrally Li inserted C_{20} was calculated between 1.410-1.530 Å. It was also seen that endohedrally inserted Li atom has negligible effect on carbon-to-carbon bond lengths.

3.3. Analysis of Recovery Times

Another important parameter to investigate the reversibility of the interaction process is known as the recovery time (τ) which can be calculated using the following relation [19]:

$$\boldsymbol{\tau = \upsilon_0^{-1} \exp\left(\frac{-E_b}{K_B T}\right)}$$

In this equation υ_0, K_B and T are known as attempt frequency, Boltzmann constant and temperature in the corresponding order. In the scope of this work, υ_0 was chosen as 10^{12} Hz. For the examined structures undertaken in this work, the values of τ were calculated around $9.4\text{x}10^9$s for sequence I and $9.5\text{x}10^9$s for sequences II and III. Further, the related τ values for sequence A, B, and C were calculated around $1.1\text{x}10^7$, $1.2\text{x}10^7$ and $1.5\text{x}10^7$s, respectively. It was observed that the only differences were occurred in the decimal parts and around 0.1 and 0.4 s, for both systems.

4. CONCLUSIONS

For all the examined systems, endohedral or surface impurity addition over the C_{20} fullerene, direct replacement of the required number of carbon atoms on the surface of C_{20} and direct addition and optimization of endohedral impurity atom inserted system resulted in a slightly more stable structure. Recovery time measurements yielded negligible differences between the examined systems. Therefore, to save time and to reach the minimum energy case, instead of step-by-step optimization direct optimization can be preferred for C_{20} based impurity added systems.

ACKNOWLEDGEMENTS

Authors acknowledge Fencluster system of Ege University for the calculations.

CONFLICT OF INTEREST

The authors stated that there are no conflicts of interest regarding the publication of this article.

CRediT AUTHOR STATEMENT

Özge Bağlayan: Investigation, Methodology, Writing – Review & Editing. **Cemal Parlak:** Supervision, Software, Visualization, Resources. **Özgür Alver:** Conceptualization, Validation, Writing – original draft.

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