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The structural properties of boron and nitrogen adsorption on benzene molecule: a density functional study

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Abstract The structural properties of boron and nitrogen atoms added on benzene (Bz) molecule are studied using density functional theory within Gaussian 03 program package. The adsorption energy, HOMO–LUMO energy gap (Δ_{H-L}) and also the optimized bond lengths (C–C and C–H bond lengths) of the structures are evaluated. In this work, three adsorption sites for both boron and nitrogen were selected, hollow site (H), middle site (M) and top site (T), as their initial positions. It is found that for boron adsorption on Bz molecule, the relaxed middle site configuration has the most stable geometry, while in NBz, we obtained similar positions after optimization process. We have also illustrated that the relaxed NBz positions are in higher stability than the relaxed BBz positions. As a consequence, it is found that the stability of an isolated benzene molecule increases by adding boron or nitrogen on top of it.

Keywords Density functional theory · Electronic structure · Configuration · Adsorption energy · HOMO–LUMO energy gap · Optimized bond length

Introduction

Benzene, one of the organic molecules, because of its special properties has long been on the focus of both theoretical and experimental research. In chemical studies, benzene is used as a useful substance including as a solvent or also as a precursor of many synthetic materials, and so

on [1]. While some works studied mono-benzene or multi-benzene molecules solely [2, 3], yet others considered benzene rings with hetero-atoms or hetero-molecules [4, 5]. Among all hetero-atoms, we have selected boron and nitrogen as two atoms on both sides of carbon atom in periodic table with difference of one electron less and more than the number of valence electrons in carbon, respectively. Some experimental and theoretical studies were performed on benzene with boron and nitrogen atoms. Kostic et al. [6] have theoretically studied borabenzene anion (BBz$^-$) and its sandwich complexes [(BBz)$_2$Fe and (BBz)$_2$Co] to obtain their bonding, electronic structure and substitution reactions properties. A quantum mechanical ab initio calculations of benzene–BX$_3$(X=H, F, Cl) interaction at the level of Mp2/6-311++G**, was performed by Tarakeshwar et al. [7]. They also carried out some single-point calculations at a much higher level of correlation with larger basis set (MP4/6-311++G(2df,p) + diffuse(d,p)). Their binding energy calculations suggest that all of these complexes have weakly bound van der Waals and the weakest one is for benzene-BF$_3$. Another investigation on boron with benzene was carried out by Zhang et al. [8]. In their experimental work, the reactions of ground-state were studied using the crossed molecular beam technique. Venturo et al. [9] have done some theoretical calculations on neutral solute-(solvent)$_n$ clusters for the benzene-(N$_2$)$_n$ case, where n = 1–32. The size evolution of N$_2$ in benzene-(N$_2$) clusters was measured by mass-selective ionization-loss stimulated Raman spectroscopy in this experimental work. A theoretical study on the complexes of benzene with isoelectronic nitrogen was performed by Wang et al. [10] at the MP2 and DFT-SAPT calculations. They have calculated the C–H bond length and binding energies and have found that all energy components increase with the number of nitrogen atoms.

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Srivastava et al. [11] have investigated the influence of adding boron and nitrogen to benzene as impurities instead of the last carbon atom or the last hydrogen atom. They have analyzed their data based on single electron transition (SET) using density functional theory. Their calculations have indicated that at zero gate potential in SET environment, C_5H_6N has more stability in its positively charged state, whereas C_6H_6, C_5H_6B and C_6H_5N are more stable in their neutral state. Besides, C_6H_5B shows more stability in both neutral and positively charged states.

In this work, we have theoretically investigated the stable positions of benzene with boron (BBz) and with nitrogen (NBz) using density functional theory with the Gaussian 03 program package. In addition, the adsorption energies, HOMO–LUMO gaps and optimized bond lengths have been evaluated.

The paper is organized as follows; in the next section the method and numerical approach are presented. In "Results and Discussion", we have discussed our results. Finally, we end the paper with a brief conclusion.

Methods

All of our electronic structure calculations in this work were carried out using density functional theory (DFT) [12] within Gaussian 03 program package [13]. The selected structures of adsorbing boron and nitrogen on benzene were fully optimized at the B3LYP [14, 15] level using 6-31++G(d, p) basis set. In the present work for both boron and nitrogen three adsorption sites were selected, namely hollow site (H), middle site (M) and top site (T) as initial geometric configurations which can be seen in Fig. 1. The most stable structures and optimized bond lengths have been obtained via optimizing these positions. Moreover, the highest occupied and lowest unoccupied molecular orbital (HOMO and LUMO) energy gaps and the adsorption

energies (E_{ads}) $\{E_{ads} = E_{Bz} + E_{adatom} - E_{complex}\}$ have been calculated, where E_{Bz} and E_{adatom} are the energy of the isolated benzene and adatom, respectively, and $E_{complex}$ is the energy of the fully relaxed benzene with adatom.

Results and discussion

It should be mentioned that the position of relaxed structure depends on its initial geometric configuration. Thus if we change the primary configuration, we could obtain another final position. We discuss the results as follows;

Boron on benzene

As it is clear in Figs. 1 and 2, all of the initial structures are deformed after optimization process. In hollow site position we have a curved benzene molecule with a boron atom on top of it, whereas in middle site case the boron atom with benzene molecule has formed a flat stable structure. In the third position an approximately plane benzene molecule with a boron atom on it can be seen. According to our calculations the structure with middle site initial configuration has the maximum value of adsorption energy, so it is the most stable structure. Another important quantity that was investigated in this work is HOMO–LUMO energy gap (Δ_{H-L}) as an indicator of chemical reactivity for a structure, in which a larger Δ_{H-L} means less reactivity. It must be noted that, the most sustainable structure in this process has minimum Δ_{H-L} and so maximum chemical reactivity. Our results are shown in Table 1.

Comparing the results of boron on benzene molecule with an isolated benzene (see Table 1) shows that the isolated benzene is less stable than complex forms with lower chemical reactivity. The optimized bond lengths are shown in Table 2. By comparing the results of these structures with an isolated benzene molecule after

Fig. 1 The initial positions of adsorbing X (X=B, N) on benzene molecule
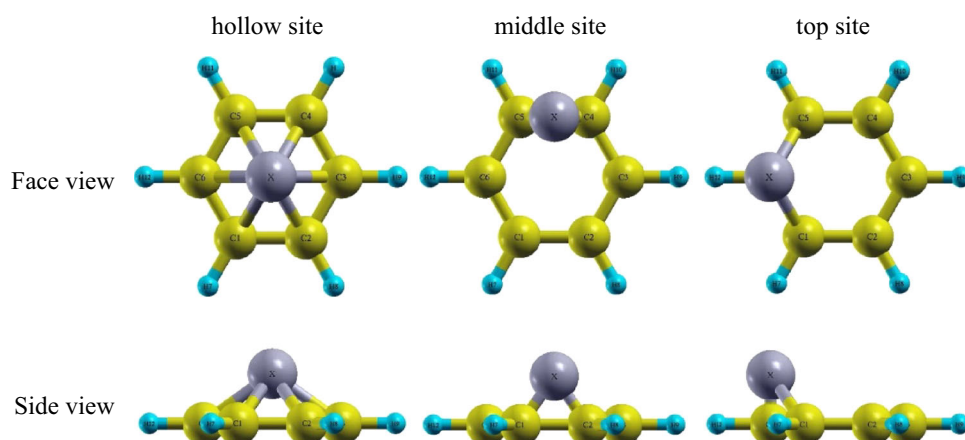
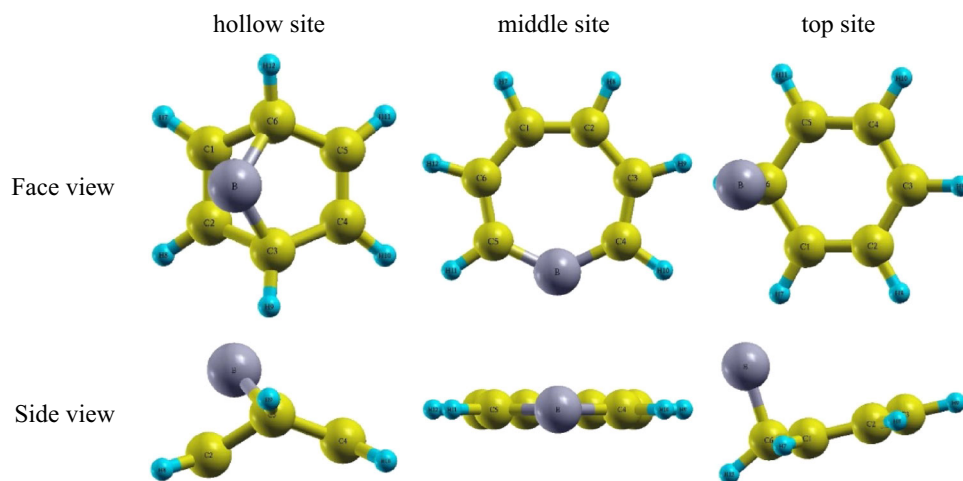**Fig. 2** The relaxed structures of adsorbing a boron atom on benzene molecule

Table 1 The total energies (E_t), the adsorption energies (E_{ads}) and the HOMO–LUMO gaps (Δ_{H-L}) for all of the relaxed structures

	E_t	E_{ads}	Δ_{H-L}
Bz	−6,320.3494	–	0.242
BBz(H)	−6,992.8105	1.440	0.172
BBz(M)	−6,993.8674	2.497	0.083
BBz(T)	−6,991.7476	0.377	0.103
NBz(H)	−7,806.8440	3.864	0.185
NBz(M)	−7,806.8440	3.864	0.185
NBz(T)	−7,806.8440	3.864	0.184

The energies are in (eV)

optimization process, it may be concluded that the C–H bond lengths are approximately similar, whereas some of the C–C bond lengths are different from the value in an isolated benzene which is approximately 1.398 Å. Based on our calculations, the difference between the maximum C–C bond length in complex structures and the C–C bond length in the isolated benzene is 0.104 Å.
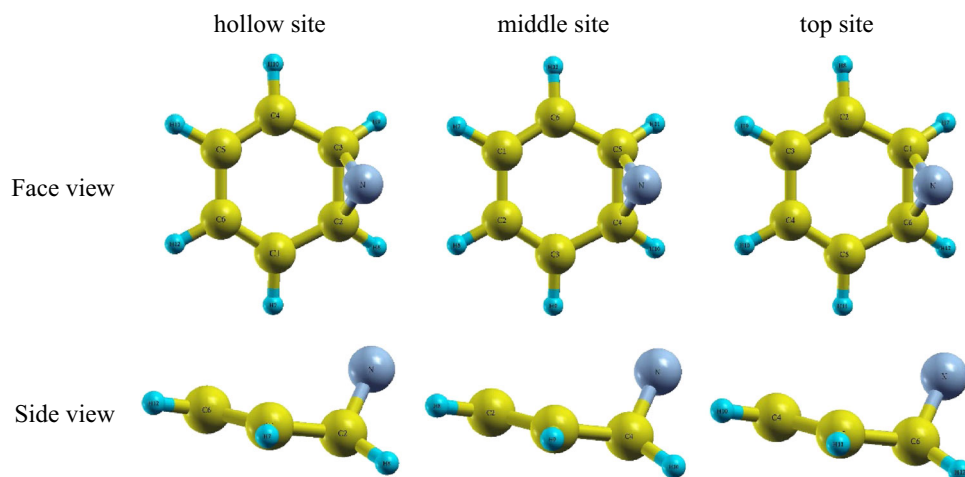
Nitrogen on benzene

As it is shown in Fig. 3 the optimized positions are almost similar to each other, so there is no significant difference between their E_{ads} and Δ_{H-L} values. The results are shown in Table 1. Similar to previous stage the isolated relaxed benzene molecule, because of its absolute value of energy, is more unstable and has less chemical reactivity (see Table 1). As it is evident in Table 2, the optimized bond lengths are similar in these three relaxed complex structures and only slight difference is observable. Our finding shows that the C–H bond lengths in complex forms are approximately similar to those in the isolated benzene after optimization process. Whereas the C–C bond lengths are changed and their maximum value is 1.539 Å.

Finally, as a comparative study on adsorption energies between BBz and NBz, we have found that the NBz is more stable than BBz in per position, whereas the chemical reactivity of BBz is higher than NBz. Therefore, as a consequence, our calculation indicates that we can obtain

Table 2 The optimized bond lengths of the relaxed structures

	Bz	BBz(H)	BBz(M)	BBz(T)	NBz(H)	NBz(M)	NBz(T)
C_1–C_2	1.398	1.384	1.379	1.377	1.472	1.451	1.473
C_2–C_3	1.398	1.501	1.426	1.416	1.539	1.355	1.355
C_3–C_4	1.398	1.501	1.380	1.417	1.472	1.473	1.452
C_4–C_5	1.398	1.343	–	1.376	1.355	1.539	1.355
C_5–C_6	1.398	1.502	1.380	1.492	1.451	1.473	1.472
C_6–C_1	1.398	1.500	1.426	1.493	1.355	1.355	1.539
C_1–H_7	1.086	1.085	1.089	1.085	1.086	1.086	1.090
C_2–H_8	1.086	1.085	1.089	1.087	1.090	1.086	1.086
C_3–H_9	1.086	1.086	1.092	1.084	1.090	1.086	1.086
C_4–H_{10}	1.086	1.086	1.091	1.087	1.086	1.090	1.086
C_5–H_{11}	1.086	1.086	1.091	1.085	1.086	1.090	1.086
C_6–H_{12}	1.086	1.086	1.092	1.097	1.086	1.086	1.090

The bond lengths are in Å

Fig. 3 The relaxed structures of adsorbing a nitrogen atom on benzene molecule

more stable structures by adsorbing nitrogen atom on a benzene molecule.

Conclusions

We studied the structural properties of adsorbing boron and nitrogen atoms on benzene molecule in three site positions using density functional theory method at the level of B3LYP/6-31++G(d, p). Via optimization process, the stable geometrical structures and optimized bond lengths have been obtained. We have investigated the most stable structures and their chemical reactivity by calculating the adsorption energies and HOMO–LUMO energy gaps, respectively. According to our results, the relaxed middle site position in the case of adsorbing boron atom is the most stable structure, whereas we obtained three similar configurations by relaxing the case of adsorbing nitrogen atom. Comparing these two groups of structures, we found that the NBz structures with higher adsorption energies are more stable, however, they are in less chemically reactive. Finally, we have realized that by adding boron and nitrogen, we are able to obtain the structures with more stability and chemical reactivity compared to isolated benzene.

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