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Reaction Pathway and Intermediates in Carbonaceous Nanoparticles ($C_{60}^{\cdot+}$, $C_{60}^{\cdot 2+}$) Amination Process: An Ab Initio Study.

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Research Article

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ABSTRACT

Recently, much attention has been drawn to the studies of fullerene functionalizations. Ab initio density functional calculations were used to study the microscopic amination mechanism of cation radicals of fullerene ($C_{60}^{\cdot+}$, $C_{60}^{\cdot 2+}$) and its reaction pathway. In this study, we examine the "direct" interaction of cation radicals of fullerene with ammonia. Structures of transition states, and intermediates, have been studied by using the same computational levels. Our results indicate that the optimal mono and diadditions reactions are exothermic. It is found that the interaction potential of $C_{60}^{\cdot+}$ and $C_{60}^{\cdot 2+}$ radicals with the ammonia is 127.3 and 84.27 kcal/mole respectively, with respect to the dissociation products.

INTRODUCTION

Fullerenes, the highly symmetric molecular carbon clusters, have superior physical, chemical, electronic and mechanical properties, thus making it one of the most explored nanomaterials, with vast potentials in applications, among many others.

In recent years, a great deal of achievement has been done in the field of nanometric carbon particles. The unexpected overwhelming development is of course parallel to the improvement of techniques for the synthesis [1,2]. Lately interest of researchers engaged in different fields of knowledge is seen to be focused on fullerene functionalizations (additional reaction on fullerene).

Study on amination of fullerene, greatly increased the knowledge of C_{60} chemistry. In addition, these chemical transformations also provide a very powerful tool for the fullerene functionalization. The amino-aromatic interaction was presaged by important observations of Levitt and Perutz.[3,4]. In a study of hemoglobin-drug interactions, they observed a "hydrogen bonding" type of interaction between aromatic π electrons and the N-H of an amide group. Empirical potential functions suggested that the amide-benzene hydrogen bond is worth approximately 3 kcal/mol, with the nitrogenbenzene distance between 2.9 and 3.6 Å [4].

Chemical functionalization of well-defined carbon nanostructures such as C_{60} is an important direction to obtain a new class of molecules with intriguing properties. One basic way to understand the interaction of carbon nanostructures with other molecules is by means of theoretical modeling. Furthermore, we can predict new properties or model the interactions with new molecules. Almost any functional group can be covalently linked to C_{60} by the cycloaddition reactions of suitable addends with C_{60} [5]. In the present calculations, we examine the "direct" interaction of cation radicals of fullerene with ammonia.

COMPUTATIONAL METHOD

In the present study, the geometry optimizations of all the structures leading to energy minima were achieved by using AM1 semi-empirical [6] method at the restricted Hartree–Fock (RHF) level [7-10]. The optimizations were obtained by the application of the steepest-descent method followed by conjugate gradient methods, Fletcher-

Rieves and Polak-Ribiere, consecutively (convergence limit of 4.18 × 1024 kJ/mol (0.0001 kcal/mol) and RMS gradient of 4.18 × 107 (kJ/m.mol) (0.001 kcal/(A° .mol)). All these computations carried out by using the Hyperchem (release 5.1) and Chemplus (2.0) package programs. Final optimization for each structures carried out by HF/6-31G* and B3LYP/6-31G* with Guassian 98 program packaging [11].

RESULT AND DISCUSSION

In this research, fullerene amination process, its mechanism and reaction pathway, has been studied by quantum mechanics calculations.

To explore the possibility of different reaction paths and to decide if the optimum reaction path is a one-step or a multistep process, we investigated the energetic of the system, constraining the reaction progress. The primary binding contribution is attributed to a dispersive interaction between the electron-rich aromatic system of the guest and the electron poor host. In other word, the first step in reaction pathway study of radical cation $C_{60}^{+\cdot}$, is formation of TS, that involved closing of ammonia to $C_{60}^{+\cdot}$. By this action, positive charge transfers to the nitrogen atom from the ring and makes a primary intermediate. At the next step, positive nitrogen (N^{+}), with elimination one hydrogen and adsorption of its electron convert to the natural state and makes amination product. Pathway of reaction and diagram of energy was shown in Fig. 1. All structures were named by bold number and theirs energy was given in parenthesis. Inspection of Table 1 shows bond orders and their length and their repetition in each structure (according to their numbers in Fig. 1).

Figure 1. Diagram energy of $C_{60}^{\cdot+}$ amination, obtained by ab initio calculations with B3LYP/6-31G*.

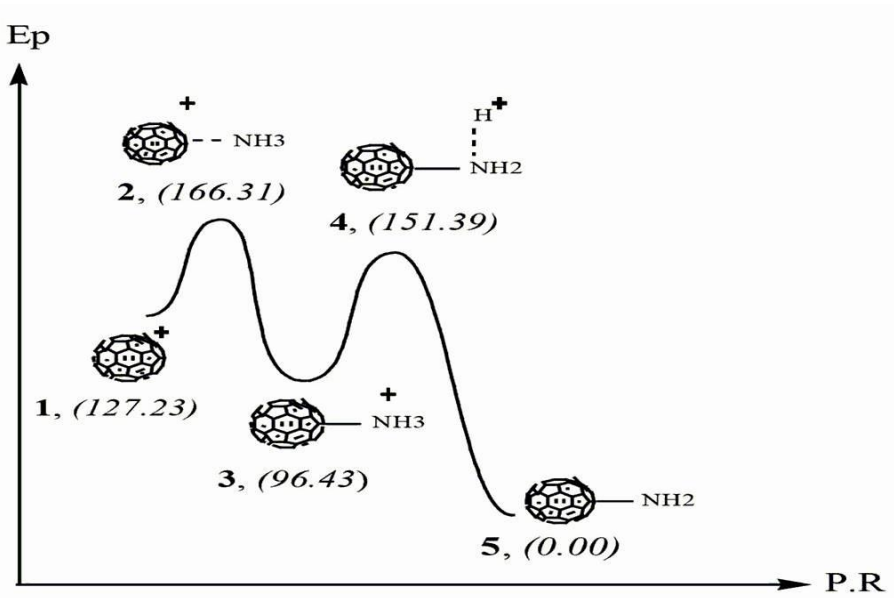

Table 1. Repetition of Bond Orders (BO) and their length in each structure

Structure No. BO (length A°)	1	2	3	4	5
1(1.47)	57	57	59	59	57
1.5(1.40)	23	24	23	23	10
2(1.37)	10	9	8	8	23

At these structures, resonance and aromaticity, are localized in six members ring and this system is isolated than other rings. Formation of cation in fullerene, will lead to generate a new link of resonance bonding in total of the ring. Distribution of resonance at the ring and going out of ground state will cause instability. Therefore, with increasing of resonance bonds (bond order = 1.5) at the structure, instability increases at the ring, because of indisposition of aromaticity of local system and distribution of it as a belt resonance around the ring. For example the repetition of resonance bonds in “2” and “5” are 24 and 10 respectively, hence they have the maximum and minimum instability, among all structures in Fig. 1.

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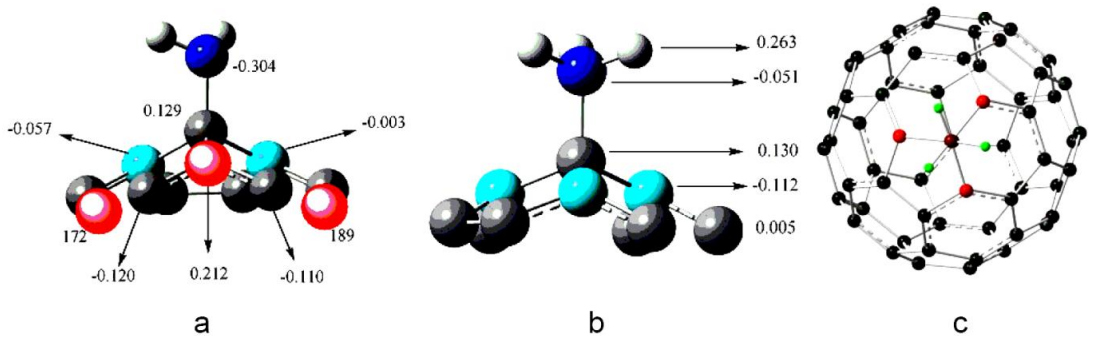
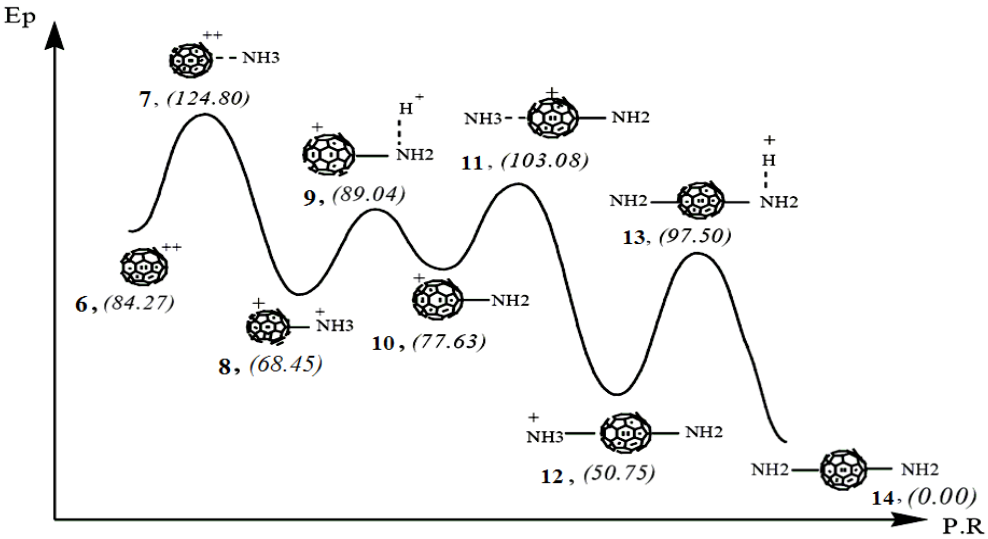
Figure 2: Different views of "3" and "5" structures. The average of atomic charge at three top layers in "5" (a) and "3" (b). the top view of "3" (c).



Different views of these structures are shown in Fig. 2. At Figures 2a and 2b, the average of atomic charge was shown at three top layers in "5" and "3" structures respectively. Figures 2c shows the top view of "3".

Amination process for C_{60}^{2+} is similar to C_{60}^{+}, but has an extra step. Reaction pathway and diagram of energy for C_{60}^{2+} was shown in Fig. 3. According to the calculations for C_{60}^{2+} amination, monoamino fullerene (structure 12) and diamino fullerene (structure 14), because of their high alkalinity power, have strong proton adsorption affinities. Therefore process of missing proton from these structures is endotermic.

Figure 3: Diagram energy of C_{60}^{2+} amination, obtained by ab initio calculations with B3LYP/6-31G*.



At Fig. 4, a different view of these structures was shown. All of these structures are symmetric. Fig. 4a, belongs to structure "8", that array of atomic charges are absolutely symmetric in it. At 4b, a face view of structure "14" was seen and 4c is a top view of same structure.

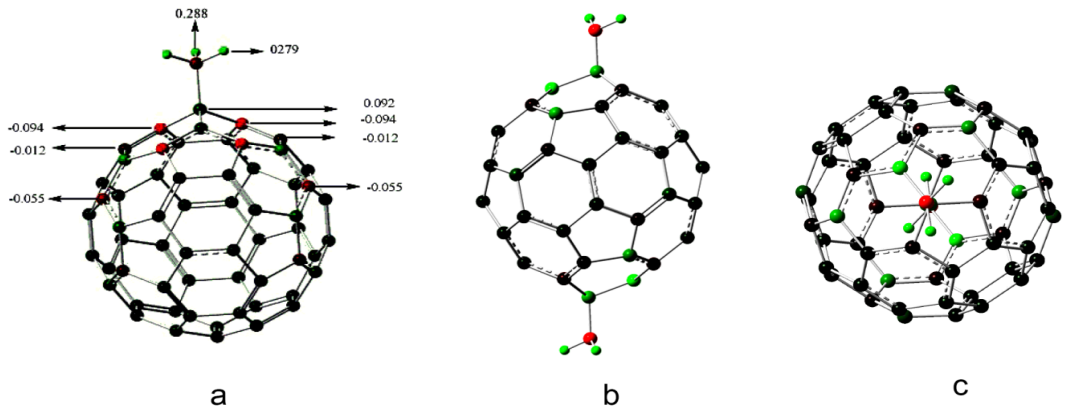


Figure 4: Array of absolutely symmetric atomic charges in "8" (a). Face view of symmetric structure of "14" (b) and top view of "14" (c).

CONCLUSION

In conclusion, we have performed *ab initio* density functional theory (DFT) treatments to investigate the microscopic mechanism of cation radicals of fullerene ($C_{60}^{\cdot+}$, $C_{60}^{\cdot 2+}$) amination process. The obtained results showed that the optimal mono and diadditions reactions are exothermic and interaction between $C_{60}^{\cdot+}$ and NH_3 molecule generated more stable complex via $C_{60}^{\cdot 2+}$. It was found that increasing of resonance bonds at the intermediates, has an important role and makes them more instable structures, because of indisposition of aromaticity.

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