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Inclusion of X_3N (X = Ti, Zr, Hf) in Fullerene C80

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ABSTRACT

In this paper, we have studied stability, structural and electronic properties of Endohedral fullerene C_{80}-X_3N (X = Ti, Zr, Hf) by using HF/6-31 G as the basis set. In the first step, we have done geometrical optimization. After optimization, we have done different type of calculations. It is found that the X_3N molecule is more compact when the X_3N is seated in the center of the C80 cage due to transfer of electrons from X_3N to C80.

Keywords: Stability , Fullerenes, Hartree-Fock, band gap, energy

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INTRODUCTION

Nowadays, the interest in nanoscale materials has rapidly increased due to their positive use in various technical and scientific researches relating on the energy, environment, and biomedical fields. Carbon is one of the most amazing elements with a vast range of exotic properties. These properties have shed the light on carbon-based nanostructures, such as fullerenes [1], carbon nanotubes [2], and graphene [3]. Since its discovery in 1985 (Nobel Prize in 1996) [1], the subject of fullerene molecule C60, the closed-cage carbon molecules, has attracted immense interest and attention due to its fascinating chemical and physical properties [4–7]. Cislowski found that C60 cage could act as a polarizable sphere that stabilizes the polar molecules and destabilizes the non-polar (or weakly polar) ones. These results indicate that formation of the endohedral complexes, from nonpolar or slightly polar molecules such as H2, N2 and CO separated molecules is an endothermic process. The C60 can stabilize molecules such as HF and LiH, encased inside its skeleton [8]. Pupysheva et al. studied the possible structure and stability of nH2O@C60 where n represents the number of H2O molecules encapsulated in C60 [9]. Ren and Liu [10] investigated the endohedral complex of fullerene C60 with N4 using hybrid DFTB3LYP functional in conjunction with 6-31G (d) basis sets. Their results prove that formation of the endohedral complexes consisting of N4 and C60 is an endothermic process with destabilization energies of 37.92 kcal/mol [10]. Shameema et al. studied the encapsulation of molecule NH3 inside the C60 cage [11]. Ganji et al. studied the possibility of formation of endohedral complexes of NH3 and C60. The DFT calculations showed that maximum of 7 ammonia molecules inside the C60 cage have metastable structures [12].

As a part of our ongoing work [13-16], here in this paper, we have done a theoretical study on the electronic structure and stability of X3N@C80 (X = Ti, Zr, Hf). We hope that X3N@C80 species is sufficiently stable, and our results may provide a suitable path for further experimental analysis.

MATERIALS AND METHODS

Computational methods

The theoretical methods used in this study were based on ab-initio methods within the Hartree Fock approximation using HF/6-31 G as the basis set in Gaussian 09 and Gauss View software package [17, 18].

RESULTS AND DISCUSSION

Firstly we have modeled the structures which are given in figure 1 and 2 while optimized structures are shown in figures 3 and 4. The first step of calculation was the geometry optimization which was followed by the single-point MO and energy calculation. Stability of the models was evaluated by ΔEt, the difference of total energy (Et) between the resulting model and the starting one. The previous experimental researches showed that it was very difficult to obtain C80-Ih and C80-D5h in quantity because of their low stability, but the endohedral C80 with rare earth metal atoms or their nitride had the increased stability that made it possible to prepare those endohedral fullerenes quantitatively [19]. It can be seen from the optimized geometric structures of X3N@C80 in Figure 3 that X3N (X = Ti, Hf) has the plane form in both of C80-Ih and C80-D5h, but Zr3N has the pyramid form, which resembles the previous XRD measurement of Gd3N@C80-Ih [20]. In the optimized X3N@C80 models the bond lengths of Ti-N and Hf-N were shortened from those of free X3N, but that of Zr-N increased as seen in table 1. Similar results were obtained by in literature [21].

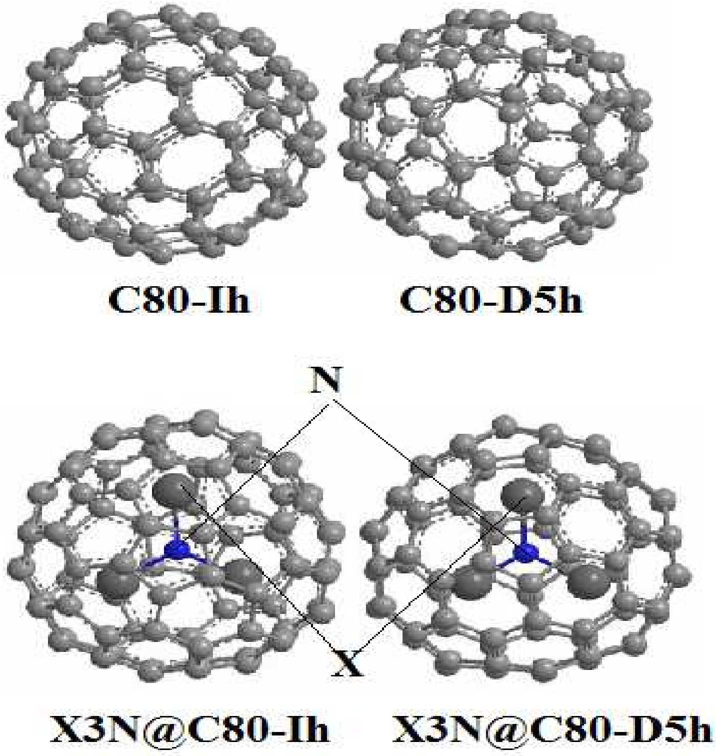


Fig-1 Models of X3N@C80

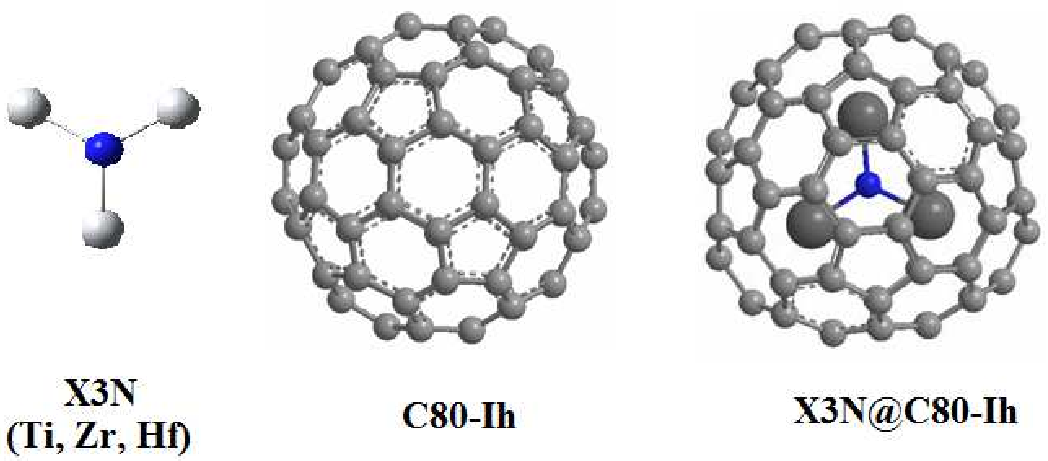

X3N
(Ti, Zr, Hf)
C80-Ih
X3N@C80-Ih

Fig-2 Models of mixed X3N@C80-Ih

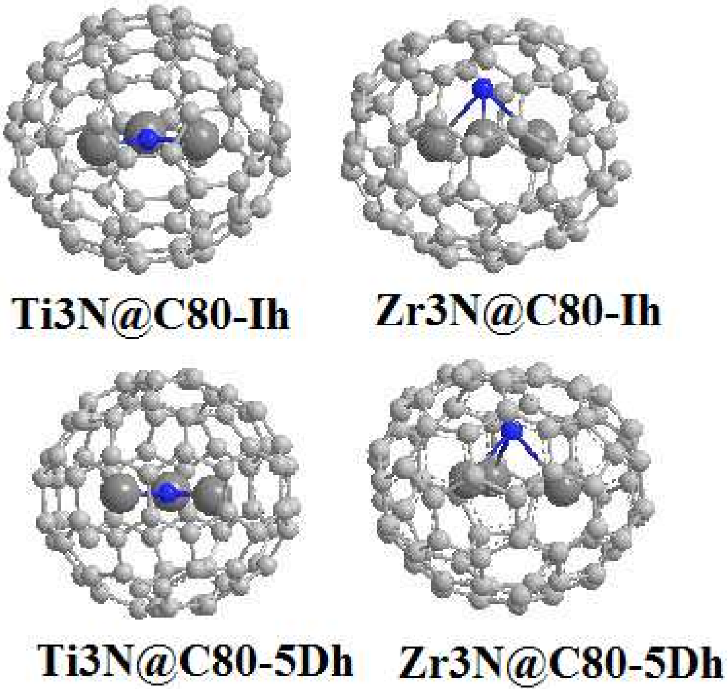
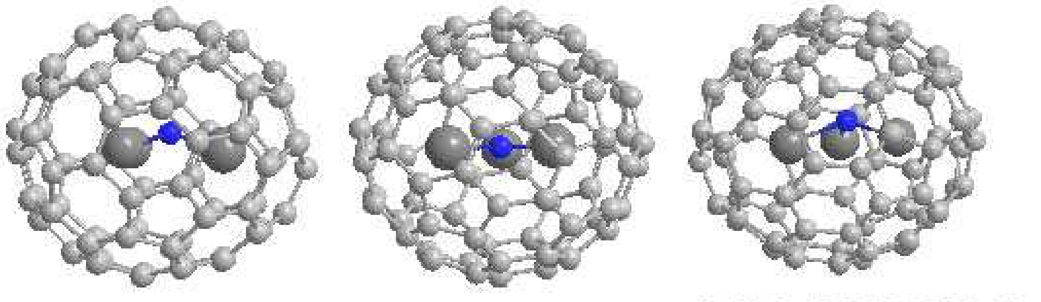

Ti3N@C80-Ih
Zr3N@C80-Ih
Ti3N@C80-5Dh
Zr3N@C80-5Dh

Fig -3 Optimized structures of some X3N@C80



HfZr2@C80-Ih Hf2ZrN@C80-Ih TiZr2N@C80-Ih

Fig -4 Optimized structures of mixed X3N@C80-Ih

From the electronic structures calculated from the optimized geometry, it was found out that the positive charge of X atoms was increased and the negative charge of N atom decreased in the cluster fullerene compared with those in free X3N, which shows more portions of electrons of X transferred to fullerene cage than those to N. In Table 2, C- means the carbon atom with the maximum negative charge among those of the fullerene cage. Changes of the electronic structure of the cluster fullerenes by encapsulation of X3N were different according to their geometric symmetry. In X3N@C80-Ih, its dipole moment (μ) and the maximum negative atomic charge (Q^{C-}) among 80 carbon atoms increased, but in X3N@C80- D5h, μ was decreased and Q^{C-} decreased or unchanged. Both of Zr3N@C80- Ih and Zr3N@C80- D5h had much larger dipole moment than others because in these cluster-fullerenes N atom was located over the Y-Y-Y plane, no forming the plane structure like others, but forming the pyramid structure. In case of the empty C80 without X3N, C80-D5h was a bit more stable than C80-Ih. Inserting X3N (X = Ti, Hf) into C80 made the fullerene more stable, especially in C80-Ih. But Zr3N made both of C80 isomers (Ih and D5h) unstable, more apparently in C80-D5h. as shown in Table 3. To simplify the problem, the entire fullerene cages discussed below was fixed as C80-Ih. Figure 5 shows the optimized geometric structures of the mixed X3N@C80, where most of the mixed X3N had the plane form, but the mixed X3N containing two Zr atoms, Zr2TiN@C80 and Zr2HfN@C80, had the pyramid form. In table 4, △Hf (heat of formation) and ΔEt of the mixed X3N@C80 shows that the more portions of electrons transferred from the mixed X3N to C80, the more stability it obtained. It was already known that charge transfer (△Q) from the encapsulated cluster to the fullerene cage is the main reason of the stabilization of the cluster-fullerene. From the above results, it was found out that more portions of Ti and Hf in the mixed X3N offers higher stability to their mixed X3N@C80, but more Zr makes it unstable.

Table 1 Bond lengths (A^0) in free X3N and X3N@C80

Fullerene	**C80-Ih**			**C80-D5h**		
X	**Ti**	**Zr**	**Hf**	**Ti**	**Zr**	**Hf**
X-N in free X3N	2.435	2.107	2.865	2.435	2.107	2.865
X-N in X3N@C80	1.897	2.327	1.764	1.807	2.334	1.763
X-C (the nearest)	2.358	2.649	2.586	2.335	2.606	2.505

Table 2 The electronic structures of C80 and RE3N@C80

Fullerene	**X**	**μ (D)**	**Atomic charge**		
			X	**N**	**C^-**
C80-Ih	-	0.012	-	-	-0.056
	Ti	0.121	2.009	-1.698	-0.223
	Zr	2.645	1.356	-1.198	-0.159
	Hf	0.027	1.715	-1.356	-0.113
C80- D5h	-	4.974	-	-	-0.213
	Ti	0.468	2.023	-1.694	-0.225
	Zr	1.926	1.113	-1.243	-0.176
	Hf	0.017	1.763	-1.397	-0.123

Table 3 Total energy (eV) of X3N@C80

X	C80-Ih			C80-D5h		
	Starting state	**Resulting state**	**ΔEt**	**Starting state**	**Resulting state**	**ΔEt**
Ti	-10005.9	-10010.8	-4.9	-10104.4	-10104.8	-0.4
Zr	-10079.5	-10071.6	7.9	-10072.0	-10059.3	11.7
Hf	-10008.9	-10109.2	-10.3	-10008.4	-10104.0	-5.6

Table 4 The electronic structure of mixed RE3N@ C80- Ih

X3N	∆Hf (kJ·mol-1)	ΔEt (eV)	ε (eV)		∆Q (e)
			HOMO	**LUMO**	**X3N⇒C80**
Ti2ZrN	4327	-1.03	-8.234	-3.234	-3.927
Ti2HfN	3367	-4.98	-8.387	-3.764	-3.103
Zr2TiN	5098	4.23	-8.119	-3.657	-3.675
Zr2HfN	4478	3.97	-8.327	-4.059	-3.054
Hf2TiN	2799	-6.64	-8.467	-4.023	-3.112
Hf2ZrN	3303	-2.19	-8.327	-3.289	-3.121
TiZrHfN	3315	-0.95	-8.299	-3.589	-3.124

CONCLUSION

Rare earth atoms in X3N@C80 are the strong electron donors to the fullerene cage. X3N (X=Ti, Zr) makes the fullerene more stable, but Zr3N seems to be unfavorable for it. These calculated properties of the endohedral fullerene may provide a reference for further experimental analysis.

Finally, the Hartree Fock method shows that one is able to produce accurate spectroscopic and physical data in a very reasonable computation time. Despite the anharmonicity effects, the Hartree Fock method is recommended in research laboratories where large-scale supercomputers are not available.

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