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Effect of Different Substituents on Geometrical Structure of [60] Fullerene Derivatives

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Effect of different substituents on geometrical structure of [60] fullerene derivatives was investigated by Dmol3. The results indicated that LUMO of three [60] fullerene derivatives mainly focued on [60] fullerene and degree of concentration of LUMO decreased with increasing of substituent number. However, the HOMO of [60] fullerene derivatives did not only focus on [60] fullerene and the HOMO moved other group. The value of energy gaps ΔE was the largest when [60] fullerene without substituents and the ΔE was the smallest when the substituents number of pyrrolidine of [60] fullerene derivatives was the most, the value was 0.053347 eV. The variety of bond length and angle of [60] fullerene derivatives were affected by substituents.

Key Words: [60] fullerene, Geometrical structure, Substituents.

INTRODUCTION

[60] fullerene has attracted more and more interest since [60] fullerene was found and [60] fullerene was widely used in materials sciences[1], chemical sciences[2], bio-sciences[3], *etc.* due to its unique geometrical structure. In order to further wide the appication of [60] fullerene, more and more [60] fullerene derivatives were synthesized by chemical modification. However, there existed a little literature about the geometrical structure of [60] fullerene derivatives. The geometrical structure is very important to know the properties of [60] fullerene derivatives and wide the application of [60] fullerene derivatives. Belosludov *et al.*[4] reported that the complex of hydroquinone and C_{60} has been studied by *ab initio* and lattice dynamics calculations. These results showed that the equilibrium geometry of C_{60} in the cage was similar to the geometry of the isolated C_{60} and no charge transfer occured. The geometrical structures of $N@C_{60}{}^{*}FeCp$ were investigated. there existed two isomers with the energy difference of 0.13 eV, one is that the encased nitrogen atom is located at the center of the fullerene cage. The Fe atom is η^5-coordinated to both Cp and R*. The another is that the atom is coordinated to R* with η^4-hapticity and the nitrogen atom is bonded to a carbon atom of the R* ring in the other isomer[5].

In this paper, in order to confirm the geometrical structure of [60] fullerene derivatives and effect of substituents on geometrical structure of [60] fullerene derivatives, we investigate the geometrical structure of three [60] fullerene derivatives with different substituents.

THEORETICAL CALCULATION METHOD

Three [60] fullerene derivatives with different substituents were labled as A, B, C (Fig. 1). The theoretical calculation was performed using Dmol3 and the calculation quality was fine and use symmetry.
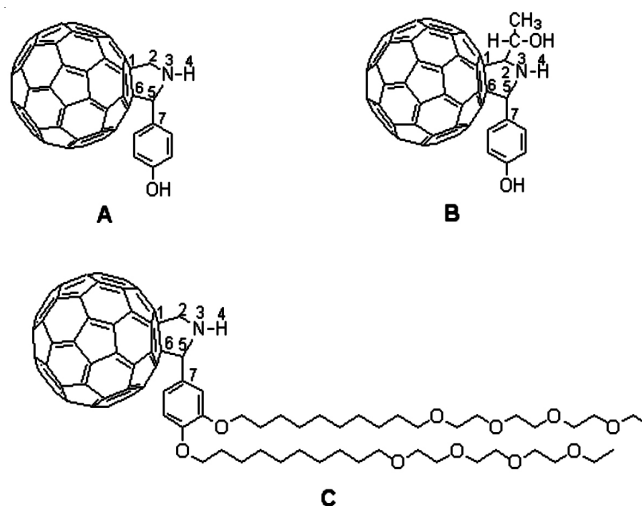

Fig. 1. Three [60] fullerene derivatives with different substituents

RESULTS AND DISCUSSION

Optimization structure of [60] fullerene derivatives:
The optimization structure of [60] fullerene derivatives were showed in Fig. 2 and the relative energies and the energy gaps between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) were calculated (Figs. 3 and 4). As shown in Fig. 3, LUMO of three [60] fullerene derivatives with different substituents mainly focus on [60] fullerene and degree of concentration of LUMO decreases with increasing of substituent number. However, the HOMO of substituents [60] fullerene derivatives do not only focus on [60] fullerene and the HOMO moves other group such as the benzene and pyrrolidine. HOMO in benzene and pyrrolidine increases with increasing of substituent number.
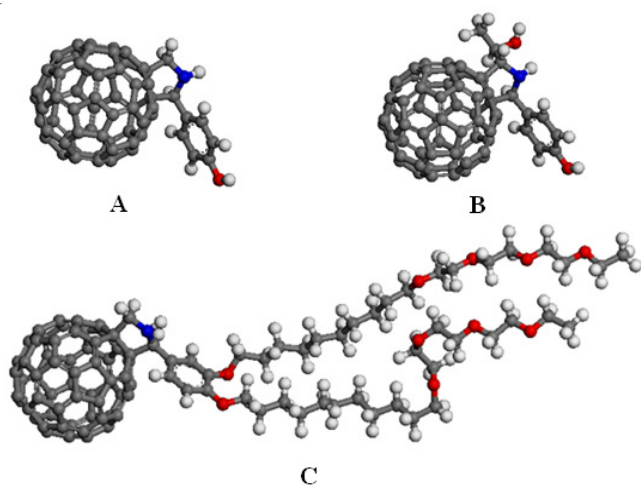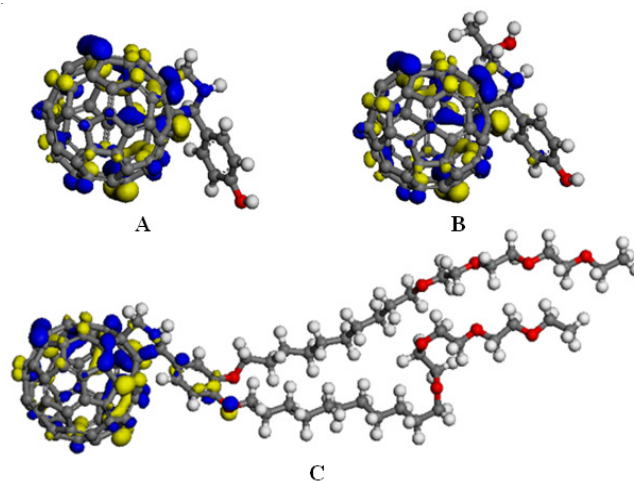

Fig. 3. HOMO of three [60] fullerene derivatives with different substituents

Fig. 2. Optimized geometrical structure of three [60] fullerene derivatives with different substituents

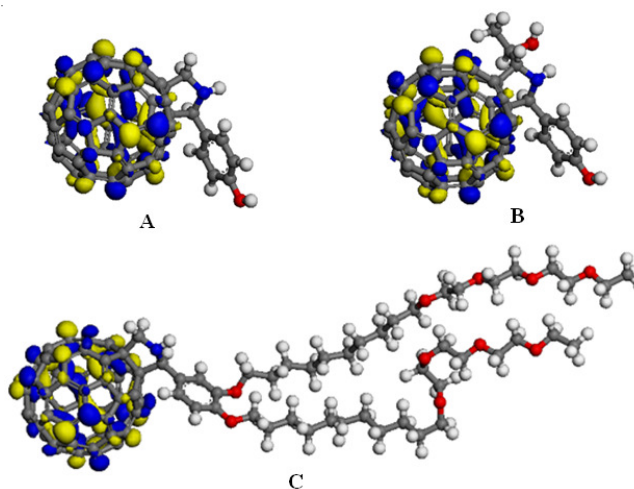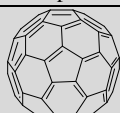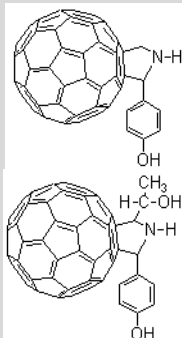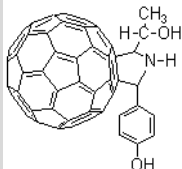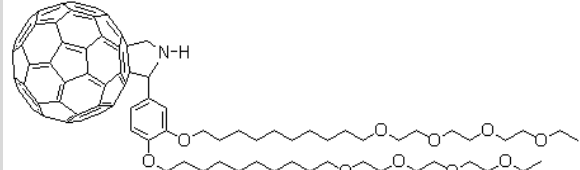Fig. 4. LUMO of three [60] fullerene derivatives with different substituents

TABLE-1
FRONTIER ORBITAL ENERGY OF [60] FULLERENE AND THREE [60] FULLERENE
DERIVATIVES WITH DIFFERENT SUBSTITUENTS

Compound	HOMO (eV)	LUMO (eV)	ΔE (eV)
	-0.212043	-0.150671	0.061372
	-0.195875	-0.142078	0.053797
	-0.196173	-0.142826	0.053347
	-0.192779	-0.139204	0.053575

The energy gaps (ΔE) between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) were also calculated by Dmol3 (Table-1). The value of ΔE is the largest when [60] fullerene without substituents and the ΔE is the smallest when the substituents number of pyrrolidine of [60] fullerene derivatives is the most, the value is 0.053347 eV. The possible reason is that the electron density of pyrrolidine with more substituents is the highest and the electron easily move [60] fullerene.

Bond length and angle of [60] fullerene derivatives with different substituents: Effect of different substituents on geometrical structure of [60] fullerene derivatives also reflects the variety of bond length and bond angle. Tables 2 and 3 show the bond length and angle of [60] fullerene derivatives with different substituents. As seen in Table-2, the variety of bond length is distinct under the pyrrolidine with two substituents of [60] fullerene derivatives, the reason is that substituents may compress bond. It is this reason that makes bond angle of A, B and C evidently change. Especially, bond angle of ∠C2N3H4 is the most obvious.

TABLE-2
BOND LENGTH OF [60] FULLERENE DERIVATIVES
WITH DIFFERENT SUBSTITUENTS

Bond length (nm)	A	B	C
C1-C2	1.546	1.558	1.544
C2-N3	1.435	1.440	1.432
N3-H4	1.028	1.034	1.028
N3-C5	1.437	1.440	1.442
C5-C6	1.564	1.559	1.565
C5-C7	1.484	1.486	1.485

TABLE-3
BOND ANGLE OF [60] FULLERENE DERIVATIVES
WITH DIFFERENT SUBSTITUENTS

Bond angle (º)	A	B	C
∠C1C2N3	102.864	102.877	102.468
∠C2N3H4	113.660	108.838	114.192
∠N3C5C6	101.429	101.541	101.132
∠N3C5C7	115.034	114.443	112.873
∠C6C5C7	113.070	112.749	117.719

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