

THE WAYS OF STABILIZATION OF C_{74} BIRADICAL FULLERENE MOLECULE

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Introduction

The stabilization of the higher fullerenes is a problem for production of substances with new unusual properties. Generally, the instability of fullerenes can be caused by presence of not coupled electrons in a molecule (an open shell) and/or by strained geometrical structure of a molecule [1]. "Missing" fullerenes C_{74} and C_{72} are characteristic examples of these two types of instability, accordingly [2]. Nevertheless, there are various endohedral metallofullerenes: $Ca@C_{74}$, $Sc@C_{74}$, $Sc_2@C_{74}$, etc.

On the basis of a developed technique of the bonds distribution analysis and the subsequent quantum-chemical calculations it has been shown earlier [3] that the reason of fullerene C_{74} instability is biradical structure caused by presence of two phenalenyl-radical substructures [2]. Hence, being based on known molecule structure it is possible to assume ways of stabilization of fullerene C_{74} (and others fullerenes having similar biradical structure, for example, isomers 3 (C_{2v}) and 4 (D_3) of fullerene C_{80} [4], isomers 3 (C_s), 8 (C_2) and 9 (C_2) of fullerene C_{84}).

The stabilization in this case means the various ways of production of closed shell structure, for example, by electrons donation on fullerenes shell by endohedral atom; or bond formation between not coupled electrons of fullerene and other molecule, for example by means of additions reaction (synthesis of $C_{74}H_2$ or similar $C_{74}R_2$) or polymerization reactions. Really, some fullerene, including C_{74} , can easily polymerize and depolymerize in different conditions [5]. So, existence of stable 2D hexagonal network of polymeric form C_{74} was offered in [5].

Quantum-chemical calculations (B3LYP/6-311G**/B3LYP6-31G) of energetic and geometrical parameters of various isomers of $C_{74}H_2$ have been carried out for research of C_{74} stabilization in reactions of addition. All calculations were carried out using the GAUSSIAN 98 program [6]. To ensure the optimized geometries are indeed minima, vibrational analyses were carried out for all isomers.

Results and discussion

The hypothetical molecules of $C_{74}H_2$ have been constructed by covalent addition of two hydrogen atoms to pair of the central carbon atoms of both phenalenyl-radical substructures laying on C_3 symmetry axis. In the first case two hydrogen atoms are outside of carbon shell (Fig. 1, **a**), in the second case - inside (Fig. 1, **b**) and in the third case two hydrogen atoms have been located both inside and outside of fullerene shell (Fig. 1, **c**).

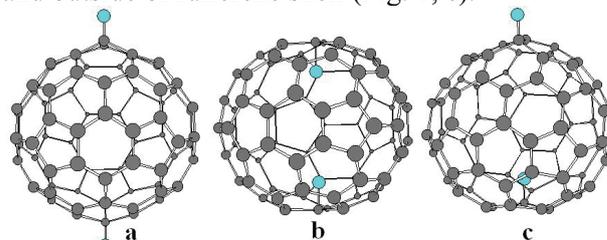


Fig.1. Molecular structures of hypothetical isomers of $C_{74}H_2$.

It is shown that according to structural and energy characteristics the most stable $C_{74}H_2$ has a C_{3h} symmetry structures with hydrogen atoms outside of carbon shell (Fig. 1, **a**): there is an alternation of double and single bonds on border of phenalenyl substructures.

The optimization of $C_{74}H_2$ with hydrogen atoms inside of carbon shell has revealed that structure have D_{3h} symmetry. The hydrogen atoms inside fullerene spheres essentially decrease the relative stability of fullerene. The carbon atoms, to which hydrogen is attached, are drawing in carbon sphere (Fig. 1, **b**). These results are agreed with [7-8] in which possibility of a chemical bond in various heterofullerene was considered. Energy of "internal" bond is less than energy of the same bonds formed outside of fullerene sphere. It means that at exo-addition the stronger bond is formed, which confirmed by the lengths of corresponding bonds.

In case of $C_{74}H_2$ in which hydrogen atoms are located inside and outside of a carbon shell (Fig. 1, **c**), it is possible mentally to "divide" a carbon shell on two hemispheres which will be identical to structures **a** and **b**, respectively. Really, on the one part of fullerene spheres the alternation

of bonds is observed (as well as in a case with fullerene with hydrogen atoms outside) and similar distortion of sphere is on another part (as in a case with fullerene with hydrogen atoms inside).

It is revealed by analysis of electronic density in fullerene hydrides that there is a redistribution of electronic density from hydrogen atoms and carbon atoms of phenalenyl-radical moiety to the central carbon of that moiety that diminishes symmetry of fullerene cage to C_{3h} . It is unlike to initial structure of molecule C_{74} where on the central atom of a phenalenyl-radical substructure deficiency of electronic density is observed. Also as well as in a case with bonds lengths, distribution of electronic density in two various hemispheres of $C_{74}H_2$ (structure **c**) is accordingly similarly to two other isomers of $C_{74}H_2$ (**a** and **b**).

Conclusions

It is shown that the most stable $C_{74}H_2$ has a C_{3h} symmetry structures with hydrogen atoms outside of carbon shell. It is revealed that in fullerene hydrides there is a redistribution of electronic density from hydrogen atoms and carbon atoms of phenalenyl-radical moiety to the central carbon of that moiety.

It is established that C-H exo-bonds are stronger than corresponding endohedral bonds. Basing on results of research the stability of hydride fullerene $C_{74}H_2$ assumes possibility of its synthesis.

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