

The molecular structure and electronic spectrum of the C@C₆₀ endohedral complex: An ab initio study

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We performed ab initio quantum-chemical studies at the HF and B3LYP levels of theory to determine the geometry and electronic spectra of the C@C₆₀ complex. The STO-3G and 6-31G(d) basis sets were employed. Two different types of stable conformations for the endohedral atom related to the centers of five- and six-member rings were found. The estimated potential barrier between those conformations is small; under certain conditions, the endohedral atom can transfer from one location in the molecular cage to another. The influence of the location of endohedral carbon atom on the electronic spectrum of C₆₀ is discussed. © 2001 by Elsevier Science Inc.

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INTRODUCTION

The unusual properties of fullerene molecules allows us to assume that they will be widely used in the future to create new materials with unique characteristics. Reports on the prospective applications of fullerene structures, i.e., soft ferromagnetics, three-dimensional organic conductors, lubricant materials, etc., have been published recently. Of special significance is the superconductivity discovered in fullerene films doped with alkaline metals. The temperature of transition into the superconducting state achieved at the present time (approximately 45 K) is exceeded only by ceramic superconductors, but fullerene films have higher critical-current values.^{1,2} The application of materials on the fullerene basis for nanotechnology and catalysis is also of interest.

It is well known that crystal lattice defects and impurities significantly influence the properties of traditional materials. In

the case of solid C₆₀ it is possible to expect that this influence will be even more distinct because, along with defects of a crystal lattice in fullerit, various defects of molecules creating this lattice are observed. The isomers of C₆₀, C₅₈ clusters, C₅₉M-type clusters, and other carbon clusters have been synthesized but in insignificant quantities, which prohibits detailed experimental characterization of these systems.^{3–5} Besides these structures, a strong influence on electronic structure is rendered by endohedral inclusions in C₆₀. Since the radius of the fullerene molecule is approximately 3.5 Å, many atoms and small molecules can be placed inside the C₆₀ sphere.

A number of studies devoted to the C₆₀ endohedral complexes with the atoms of metals, noble gas, etc. have been performed.^{6–8} In this article, we extend our previous studies on fullerene-type structures^{9–11} to the endohedral complex of the fullerene molecule and carbon atom. It is of interest because of the various types of bonding common for carbon systems. The conditions necessary for the formation of this complex, and its structure and the influence on physical and chemical properties remain scarcely investigated.

COMPUTATIONAL METHOD

Ab initio quantum-chemical calculations without symmetry restrictions have been performed to determine the structure and electronic spectra of the investigated complex. The GAUSS-IAN94¹² package was used for the SCF MO calculations at the Hartree-Fock and hybrid DFT levels of theory. The STO-3G and 6-31G(d) basis sets were employed.

The effect of electron correlation was estimated using the empirically parameterized Becke3LYP method.^{13,14} These functionals implemented in the GAUSSIAN94 program are slightly different than the original formula suggested by Becke. Becke3LYP uses a combination of the LYP¹⁵ and the VWN¹⁶ correlation functionals instead of PW91.

RESULTS AND DISCUSSION

Figure 1, Table 1, and Table 2 summarize the optimized geometry and energy parameters for the C@C₆₀ complex. Two

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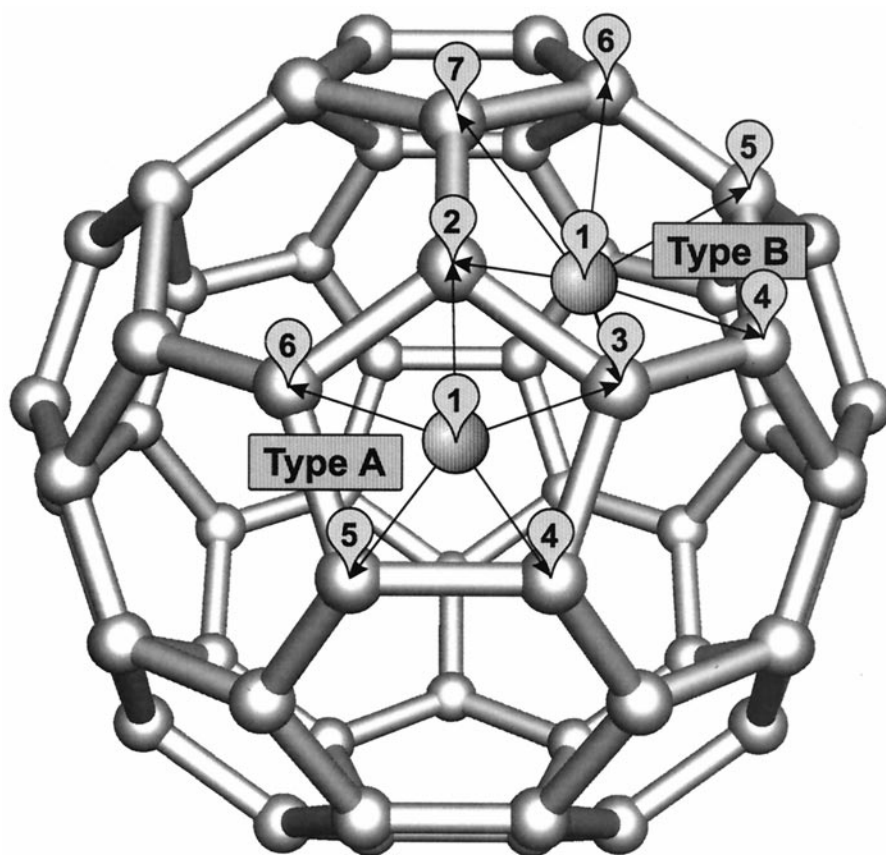


Figure 1. Two different types of location of the carbon atom inside of the fullerene molecule and atomic numeration scheme.

Table 1. Selected geometrical and energy parameters of the $C@C_{60}$. All distances are in angstroms; energies and HOMO-LUMO gaps are in atomic units

	Type A			Type B		
	HF/STO-3G	HF/6-31(d)	B3LYP/6-31G(d)	HF/STO-3G	HF/6-31G(d)	B3LYP/6-31G(d)
Bond length:						
C_1-C_2	1.807	1.704	1.759	1.796	1.693	1.691
C_1-C_3	1.805	1.719	1.758	1.795	1.693	1.691
C_1-C_4	1.731	1.688	1.742	1.634	1.624	1.776
C_1-C_5	1.731	1.688	1.742	—	—	—
C_1-C_6	1.805	1.719	1.758	—	—	—
C_1-C_7	—	—	—	1.634	1.625	1.776
HOMO-LUMO gap	0.21	0.25	0.04	0.27	0.20	0.06
Total energy	-2281.2679	-2309.3944	-2324.0102	-2281.3004	-2309.3939	-2324.0066

different sites (Type A and Type B) for the endohedral carbon atom were revealed. The first position is near the center of the five-member faces of the fullerene molecule while the second one is slightly shifted from the center of the six-member face in the direction of the neighboring five-member face. All employed methods are shown to give very similar geometries for the investigated system.

Formation of the endohedral complex leads to a significant change in cohesive energy (the difference of total energy between $C@C_{60}$ and C_{60} is approximately 39 a.u. at the HF/6-31G(d) level). However a more detailed consideration, in

particular an analysis of the bond orders and Mulliken overlap populations, point out that the formed bonds are much weaker than the bonds of a C_{60} cluster. The change in the total energy of the system is caused basically by the symmetry break and local distortion of the molecular structure.

It should be pointed out that, except for HF/STO-3G predictions, all other levels of theory give the same order of stability for the endohedral complex: the total energy of the Type A complex is slightly higher than that of the Type B complex.

Because of the small difference in total energy between the

Table 2. Mulliken overlap population of the C@C₆₀ selected bonds

	Type A			Type B		
	HF/STO-3G	HF/6-31(d)	B3LYP/6-31G(d)	HF/STO-3G	HF/6-31G(d)	B3LYP/6-31G(d)
Mulliken overlap population:						
C ₁ –C ₂	0.068	.017	–.042	0.029	–.017	–.057
C ₁ –C ₃	0.064	.053	.005	0.029	–.017	–.057
C ₁ –C ₄	0.095	.033	–.026	0.240	.213	.069
C ₁ –C ₅	0.095	.033	–.026	–	–	–
C ₁ –C ₆	0.064	.053	.005	–	–	–
C ₁ –C ₇	–	–	–	0.240	.213	.069

Type A and Type B complexes, the question is whether the transition of the atom from one stable position into another is possible under the influence of thermal fluctuation. The molecular dynamics calculations (with the MNDO force field model) show that the dynamic barrier of migration is only 0.12 eV for the transition from site A into site B and 0.16 eV for the transition between the sites of type A.

Such findings mean that even at room temperatures there is a system with two metastable levels, and under certain conditions, the endohedral atom can move from one location in the molecular cage to another. It is similar to the known effect of caging (easy migration) of the impurity atom in the lattice of heavier atoms; however, in the case of the system studied here, all atoms are of the one type.

Figure 2 displays the electronic level structure of C@C₆₀ near the HOMO–LUMO energy gap obtained from the HF/6-31G(d) level calculations. Unlike an ideal fullerene molecule in which all sites of the atoms are equivalent, one can

see the reduction of the degeneration of electronic levels. Thus, the higher the energy of formation for such defects, the larger the difference between electronic structure of such species and the parent fullerene. Besides the reduction of the degeneration of states, the reduction in the energy gap between the HOMO and LUMO levels is observed for all types of defects.

SUMMARY

We have found two different types of location of the carbon atom inside of the fullerene molecule. The endohedral atom of the C@C₆₀ complex can migrate from one stable position to another under the influence of thermal fluctuation (for example at the expense of a laser pulse). The electronic spectrum predicted for those two types of stable conformations has essential differences.

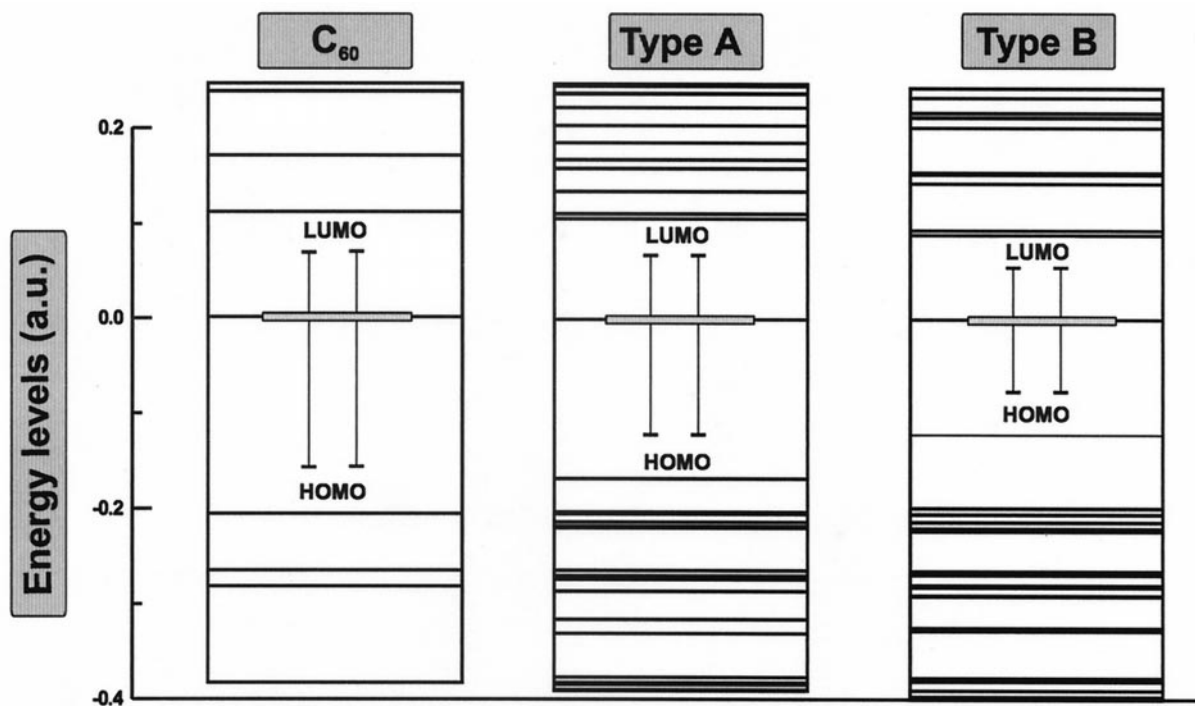


Figure 2. Electronic energy levels of the C₆₀ and C@C₆₀ near the HOMO–LUMO gap. HF/6-31G(d) level of theory.

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