Structure and Energetics of $(C_{60})_2{}^{2+}$ Conformers

Bull. Korean Chem. Soc. **2010**, Vol. 31, No. 2   457

Structure and Energetics of $(C_{60})_2{}^{2+}$ Conformers: Quantum Chemical Studies

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The geometrical structures and energetics of positively doubly charged fullerene dimer $(C_{60})_2{}^{2+}$ conformers were studied using semiempirical PM3 and MNDO, Hartree-Fock (HF), and Hybrid B3LYP density functional methods. The shape of the HOMO-LUMO for the three conformers was also analyzed. The *gauche* conformer was the most stable of the three conformers. The *anti* conformer was more stable than the *syn* conformer.

Key Words: *Ab initio* quantum chemical methods, Fullerenes dimer dication, Conformer

Introduction

Fullerenes are a new allotrope of carbon with a closed polyhedral framework, which have attracted considerable interest for their unique properties. For example, Rb_3C_{60} exhibits superconducting properties with a transition temperature of 28 K.[1] Another amazing material, $C_{60}(TDAD)_{0.86}$, is an organic ferromagnet with a higher Curie temperature than any other known organic ferromagnet.[2] In addition, polyvinyl-carbazole doped with C_{60} is an outstanding thiapyrillium dye.[3] C_{70} can be used as a nucleus for diamond growth[4] and many applications have been reported.[5] The doping of fullerenes has a strong influence on the molecular and bulk properties of the new modification of carbon. The discovery of superconductivity in alkali metal doped C_{60} has attracted considerable interest in fullerene doped systems.[6]

The electronic and atomic structures of hole-doped and electron-doped fullerenes were theoretically studied.[7] In semiconductors, hole doping can be achieved by doping pure semiconductor materials with boron atoms. The idea of substituting atoms in the relatively large carbon cage of fullerenes with heteroatoms has intrigued scientists. After the initial proof with C_{60}, Smalley *et al*. reported substitutions of the carbon cage with heteroatoms.[8] Smalley *et al*. demonstrated the first experimental production of boron-doped fullerene (borafullerene) in the gas phase by laser vaporization.[9] This is outstanding because "doped bucky ball" is a completely new material and is expected to have higher chemical reactivity than buckminsterfullerene. Muhr *et al*. generated borafullerenes by arc evaporation of doped graphite rods.[10] In addition Zou *et al*. synthesized the borafullerene films by radio frequency plasma assisted vapor deposition.[11] Borafullerene has been the subject of various calculations.

Andrei *et al.* used the Car-Parrinello method to determine that the B atom is threefold coordinated and most of the distortion is localized on the B-C bonds.[12] Kurita *et al*. calculated the molecular structures, binding energies and electronic properties of heterofullerenes using a molecular orbital (MO) me-

thod with Harris functional and spin-restricted approximation.[13] In the point of the isoelectronic view, it is expected that the fullerene cation will have similar properties to those of borafullerene. Therefore, it will be interesting to understand the structure and electronic properties of hole doped fullerene dimer. We previously reported the relative stability of negatively charged fullerene dimer, $(C_{60})_2{}^{2-}$ conformers.[14] Here we will compare them with positively charged fullerene dimer conformers, $(C_{60})_2{}^{2+}$.

However, as far as we know, there are no published *ab initio* computational calculations on a fullerene dimer dication, although there was a paper of the full potential muffin-tin orbital calculations of the *anti* conformer of borafullerene dimer.[15] In addition, no attempt has been made to analyze the conformers of $(C_{60})_2{}^{2+}$. Therefore, it is appropriate to use quantum chemical methods that are already well established for organic molecules to analyze the conformers of $(C_{60})_2{}^{2+}$, which are the basic unit of new molecular arrays. [13]C nuclear magnetic resonance (NMR) experiments[16] on solid C_{60} showed that it is only below T = 260 K that the free C_{60} rotation is hindered by the a-sphericity of the intermolecular potential, due to the discrete atomic positions. With the advanced computational power, it is now possible to understand the free spinning around the intercage single C-C bond of fullerene dimers at the *ab initio* level. Also for molecular systems, there is still an interesting question concerning the molecule that can detach two or more electrons with both electronic stability (against electron attachment) and thermodynamic stability (against fragmentation) in the gas phase.

The aim of this study was to understand the geometrical structures, electronic structure, and energetics of the single bonded fullerene dimer dication conformers.

Calculations and Model

Different theoretical methods, semiempirical parameterized method (MNDO), *ab initio* Hartree-Fock and density functional methods (using 3-21G and 6-31G* basis sets), were used to optimize the structures of the fullerene dimer dication, $(C_{60})_2{}^{2+}$
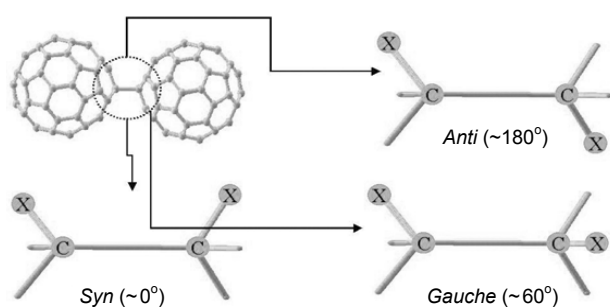
Figure 1. Molecular structures of the three conformers of a single bonded $(C_{60})_2^{2+}$.

conformers. Here, the density functional method of Becke's three parameter hybrid method and the Lee-Yang-Parr correlation functional (B3LYP) were employed.[17] All geometries at the local minima and transition states were fully optimized using the Gaussian 98 suite of programs.[18] Although there were some variations between the different methods, the results of the calculations are consistent. Among them, the B3LYP results should be considered to be most reliable.[19] Therefore, this discussion will be based mainly on the B3LYP/6-31G*//B3LYP/6-31G* results.

A semiempirical calculation was performed using a PM3 parameterized MNDO method for various XCCX dihedral angles to determine the energy barrier for the free rotation of a fullerene C-C single bond (in Figure 1). Figure 1 shows the geometric structures considered in this paper. There are three distinct stable conformers with respect to rotation around a single C-C bond: two enantiomeric *gauche* forms with a XCCX dihedral angle ω of approximately 60° (right-handed helix) and −60° (left-handed helix) and an *anti* form with ω = 180°. The others are the highest energy *syn* form with ω = 0° and the 2nd highest energy eclipsed form with ω = 120°, which are the two transition states between the *gauche* (+) and *gauche* (−) and between *anti* and *gauche* (±).

Results and Discussion

Table 1 shows the highest occupied molecular orbital (HOMO)-lowest unoccupied molecular orbital (LUMO) gap of the three conformers of $(C_{60})_2$ dication. It is very interesting that although the HOMO-LUMO gap of the *syn* conformer of $(C_{60})_2$ dication is larger than the others, the energy of the *syn* conformer of $(C_{60})_2$ dication is the highest among the three conformers, as shown in Table 1. The rotational potential surface has two minima (*gau, anti*) and one transition state (*syn*). It may be informative whether transition states and minima were all conformed numerically. Also supplementary figure for potential energy surface of Table 1 is in supporting information.

Table 2 shows the relative energies of the three conformers of $(C_{60})_2^{2+}$. The semiempirical and *ab initio* HF methods showed that the *anti* conformer with C_{2h} symmetry has the lowest energy, while the *gauche* conformer with C_2 symmetry of $(C_{60})_2^{2+}$ is the most stable in the DFT (B3LYP) method. The energy of the *gauche* conformer was calculated to be −0.2 kcal/mol using B3LYP method, 0.4 kcal/mol from the HF/6-31G* calculation,

Table 1. Bond length, HOMO-LUMO gap, total energy of $(C_{60})_2$ dication at the level of semiempirical PM3 calculations

Dihedral angle(°)	Energy (Hartree)	HOMO-LUMO Gap(eV)	C-C Distances (Å)
0(C_{2v})	3.41940	4.91	1.578
30(C_1)	3.41751	4.87	1.575
60(C_1)	3.41544	4.83	1.572
70(C_1)	3.41551	4.83	1.572
80(C_1)	3.41594	4.84	1.573
90(C_1)	3.41658	4.86	1.574
120(C_1)	3.41777	4.90	1.577
150(C_1)	3.41608	4.89	1.575
180(C_{2h})	3.41441	4.86	1.572
Gau(63.47)	3.41542	4.83	1.572

Dihedral angle ($\angle$ XCCX)

Table 2. Energies of the $(C_{60})_2^{2+}$ conformers relative to their *anti* conformers (kcal/mol)

Structure (symmetry)	*Syn*(C_{2v})	*gauche*(C_2)	*anti*(C_{2h})
Dihedral angle (deg)	0	~ 60	180
PM3	2.6	0.7	0.0
MNDO	3.1	0.6	0.0
HF/STO-3G	5.5	0.4	0.0
HF/3-21G	7.6	0.4	0.0
HF/6-31G*	7.7 (1.637)[a]	0.4 (1.605)[a] (57.7)[b]	0.0 (1.604)[a]
B3LYP/STO-3G	3.5	−0.2	0.0
B3LYP/3-21G	5.4	−0.4 (1.624)[a] (58.3)[b]	0.0
B3LYP/6-31G*	5.6 (1.669)[a]	−0.2 (1.637)[a] (55.4)[b]	0.0 (1.635)[a]

[a]The intercage C-C bond lengths (Å). [b]The optimized dihedral angles (deg).

and 0.7 kcal/mol from the MNDO calculation when the energy of the *anti* conformer is taken as a reference. This suggests that in the B3LYP results, the relative energy of the *gauche* conformer was 0.2 kcal/mol lower than that of the *anti* conformer. Since the B3LYP results are considered to be most reliable in this study, it suggests that the gauche form should be the most stable structure among the fullerene dimer dication conformers.

The difference between the relative energy of the $(C_{60})_2^{2+}$ conformers and that of $(C_{60})_2^{2-}$ is quite interesting because in the case of the fullerene dimer dianion, the *anti* conformer is more stable than the *gauche* conformer, as reported elsewhere.[14] The difference in the order of stability in the results of the fullerene dimer dication and fullerene dimer dianion was analyzed using the change in energy levels near the HOMO. Figure 2 shows the energy levels of the $(C_{60})_2^{2+}$ conformers (*anti* and *gauche*) and $(C_{60})_2^{2-}$ conformers (*anti* and *gauche*). In the case of the fullerene dimer dianion, the HOMO-3 (B_g) of the *anti*
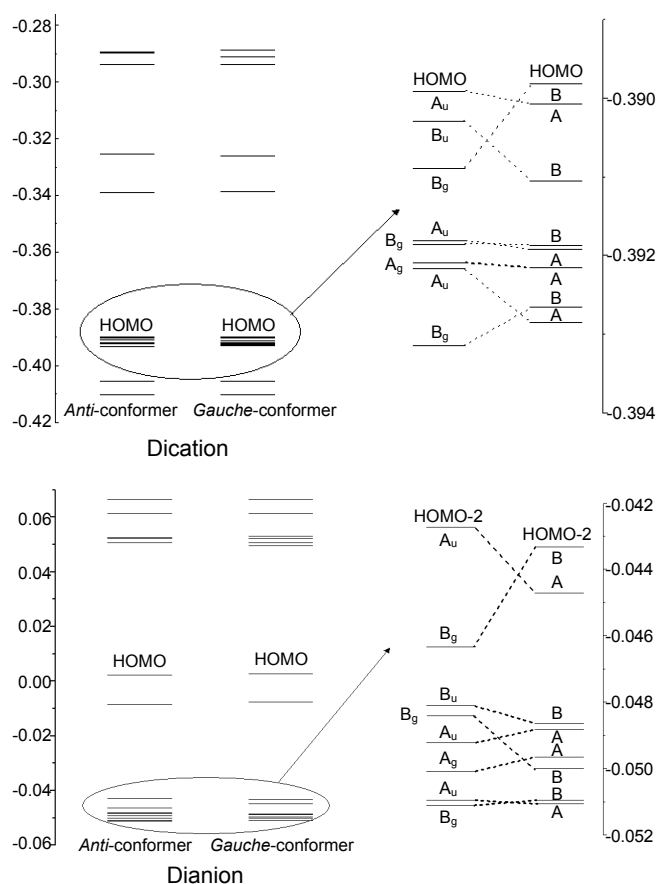
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Figure 2. The energy (Hartree) levels of the fullerene dimer dication and dianion (*anti*, *gauche* conformers).

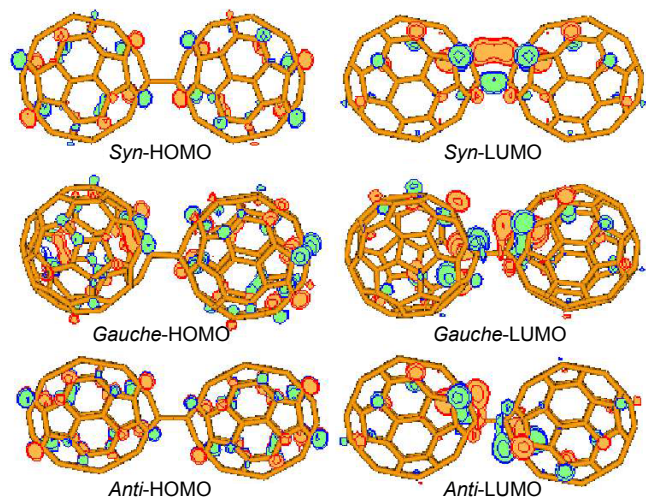**Figure 3.** The morphology of the HOMOs and LUMOs of the three conformers of intercage single bonded, $(C_{60})_2^{2+}$.

levels are related to the difference in the total number of electrons of the dication and dianion. This can explain why the *gauche* conformer is the most stable structure of the three conformers of fullerene dimer dication, but the *anti* conformer is the most stable of the $(C_{60})_2^{2-}$ conformers.

The HOMO and LUMO were analyzed to understand electronic structure of the $(C_{60})_2^{2+}$ conformers. Figure 3 shows the shape of B3LYP/6-31G* of the HOMO and LUMO for the three conformers of the single bonded $(C_{60})_2^{2+}$. Figure 3 shows how the LUMO of $(C_{60})_2^{2+}$ can contribute to bond formation between the cages of $(C_{60})_2$ and $(C_{60})_2^{2-}$. The electron densities of the *syn* conformer were doubly concentrated along the intercage bond, whereas the *anti* and the *gauche* conformers were spread to the atoms neighboring the intercage bond. The LUMO of the *syn* conformer has the shape of a C-C double bonded C_{60} dimer. Therefore, it is believed that the *syn* conformer is a closely related state to the C-C double bonded C_{60} dimer. Therefore, the *gauche* and *anti* conformers have analogous energetic properties.

For the $(C_{60})_2^{2+}$ conformers, the rotational potential surfaces have two minima (*anti* and *gauche*) and two transition states (*syn*, C_{2v} and eclipsed, C_2). The pattern of this rotational potential surface is the same as that of *n*-butane.[20] In addition, by calculating the rotation barrier energy of the single intercage bond, these molecules should be an equilibrium mixture between the *anti* and *gauche* conformers. In addition, these results can be understood in terms of the *gauche* effect on the change in energy, which is a tendency to adopt a structure with the maximum number of *gauche* interactions between the adjacent electron pairs and/or polar bonds.[21] *Gauche* conformations about the C-C bond are also favored in $NCCH_2CH_2CN$ and $H_3COCH_2CH_2OCH_3$.[22]

In conclusion, the rotational potential energy surfaces and electronic structures of $(C_{60})_2^{2+}$ were examined. The results suggest that this hole-doped fullerene dimer molecule should be an equilibrium mixture of *anti* and *gauche* conformers.

Supporting Information. Supplementary potential energy surface of Table 1 is available at the bkcs website (http://www.kcsnet.or.kr/bkcs).

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conformer was largely stabilized compared to the HOMO-3 (*B*) of the *gauche* conformer, whereas this stabilization effect was relatively small in the fullerene dimer dication. However, the HOMO-6 (A_u) of the *gauche* conformer was remarkably stable compared to the HOMO-6(*A*) of the *anti* conformer in the case of the fullerene dimer dication. The different shifts in the energy

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