Full Geometry Optimizations of Bond-Stretch Isomers of C$_{20}^{2+}$ Fullerene Dication by the Hybrid Density Functional B3LYP Methods

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We studied the relative stability and atomic structure of five C$_{20}^{2+}$ isomers obtained by two-electron ionization of a C$_{20}$ cage (the smallest fullerene). All the isomers are bond-stretch isomers, i.e., they differ in bond length. In particular, in one of the isomers with I$_h$ symmetry, all the bond lengths are equal. Full geometry optimizations of the dipositive ion C$_{20}^{2+}$ were performed using the hybrid density functional (B3LYP/6-31G(d)) methods. All isomers were found to be true minima by frequency analysis at the level of B3LYP/6-31G(d) under the reinforced tight convergence criterion and a pruned (99,590) grid. The zero-point correction energy for the cage bond-stretch isomers was in the increasing order D$_{2h}$ < C$_{2h}$ < C$_2$ < T$_h$ < I$_h$ of C$_{20}^{2+}$. The energy difference among the isomers of cage dipositive ions was less than that among neutral cage isomers. Our results suggest that these isomers show bond-stretch isomerism and that they have an identical spin state and an identical potential energy curve. Although the predominant electronic configurations of the isomers are similar, the frontier orbital characteristics are different, implying that we could anticipate an entirely different set of characteristic chemical reactions for each type of HOMO and LUMO.

Key Words: Dipositive fullerene C$_{20}^{2+}$ ion, Bond-stretch isomers, Hybrid density functional (B3LYP) calculations, HOMO and LUMO

Introduction

Isomerism is a fundamental concept in chemistry. Molecules that differ in the length of one or more bonds have been termed bond-stretch isomers. The term bond-stretch isomerism was introduced for isomers with the same spin state.[1,2] Although the definition of the concept is simple, experimental examples are difficult to find.[3] Early reports of distortion isomers of molybdenum oxo complexes[2] are now thought to refer to mixtures of distinct chemical compounds, and claims for other bond-stretch pairs are regarded as nonproven.[3] Partkin and Hoffmann reported that the phenomenon of bond-stretch isomerism is found in isomers with the same spin state and the same potential energy curve[4] and that it is not related to the concept of spin-crossover complexes, which are known to show spin-state isomerism and related phenomena such as deformed isomerism.[5] The bond-stretched invertomer for the ring opening of hexafluorocyclopropane was reported on the basis of (6/6)CASPT2/6-311+G (2d1f,2p)//(6/6)CASSCF/6-31G* calculations.[6] Bond-stretch isomerism ("π-tautomers" would be a better term) of the fullerene C$_{28}$ with D$_2$ symmetry was reported by using molecular graphs and semiempirical AM1, PM1, and MNDO methods.[7] In the present paper we report that a new and as yet imperfectly explored with fullerene C$_{20}^{2+}$ may yield examples of a specific form of bond-stretch isomerism. The reason for C$_{20}^{2+}$ offering such examples is that all the isomers of this fullerene are bond-stretch isomers, i.e., they differ in bond length. In particular, in one of the isomers with I$_h$ symmetry, all the bond lengths are equal.

Since the discovery of the C$_{60}$ carbon cluster in 1985, fullerenes have been the topic of several studies.[8] Experimental studies on various C$_{20}$ structures have established the existence of several spatial arrangements. Although C$_{20}$ is the smallest possible fullerene, experimental evidences indicate that the dominant structures of C$_{20}$ are monocyclic and bicyclic rings.[9,10] Recently, Prinzbach *et al.*[11,12] provided experimental evidence for the existence of three different isomers: cage, bowl, and ring isomers (see Figure 1). Vibration spectra of these three isomers differ significantly from each other. In addition, the high intensity of the C$_{20}^+$ and C$_{20}^{2+}$ ions and the very low abundance of smaller fragments in the cation mass spectrum of C$_{20}$HBr$_{13}$ show the remarkable kinetic stability of the C$_{20}$ cluster and its cations. Although the experiments are unequivocally consistent with the existence of the various structures, the change in the atomic structure of the fullerene isomers after two-electron ionization and the symmetry of the most stable structure are yet to be determined.
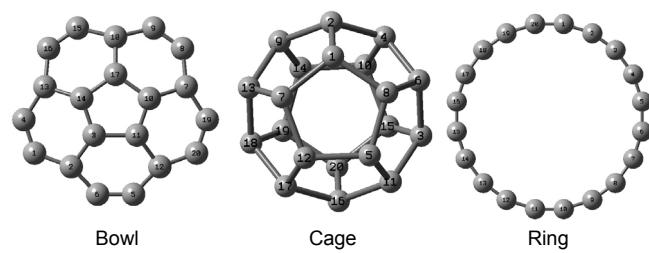

Figure 1. Three classes of structures of C$_{20}$ cluster isomers (bowl, cage, and ring).

Theoretical studies of neutral C_{20} isomers have provided a variety of relative energies.[13-18] Hartree-Fock self-consistent field (HF-SCF) calculations favor the ring structure;[13] the Møller-Plesset second-order perturbation theory (MP2) method favors the cage[13] and bowl geometries for small and large basis sets, respectively;[14] studies involving coupled-cluster single and double excitations (CCSD) and coupled-cluster single and double excitations with perturbative triple excitations (CCSD(T)) indicate the bowl and bowl/cage geometries;[15,16] density functional calculations – LDA, BLYP (B3LYP), and BPW91 (B3PW91) – favor the cage, ring, and bowl geometries, respectively;[17,18] and valence-only (pseudopotential) quantum Monte Carlo (QMC) calculations favor the bowl geometry.[14] Also supplementary Table S1 for each isomer with the lowest energy and calculation methods for three class of isomer structures in Figure 1 is in Supporting Information.

The Jahn-Teller distortion in certain low-symmetry isomers of neutral molecules,[16,18-20] monoanions,[16,18,21] and dianions[22] of C_{20} have been investigated. A complete path from I_h to C_1 symmetry through intermediate structures with T_h, D_{2h}, D_2, C_{2h}, C_i, C_2, and C_s symmetries was studied. On the basis of both geometry optimization by the B3LYP/6-31+G(d) method and single-point energy calculations by using the MP2 and CCSD(T), they concluded that the structure with D_{2h} symmetry was the most stable. There are a few papers on the C_{20}^{2+} dication; these papers pertain to the determination of D_3 and I_h symmetries by semi-empirical PM3 calculations[23] and first-principle calculations, respectively.[24,25] To the best of our knowledge, there are no first-principle calculations that can be used to fully optimize atomic structures of C_{20}^{2+} dication isomers without applying a constraint.

Recently, the planarity of benzene was analyzed with various theoretical methods, and the B3LYP/6-31G(d) level calculation was found to be very good for simulating the experimentally determined structure of benzene.[26] For molecular systems, it is of interest to find the smallest molecule that can bind two or more excess charges with high electronic stability (against electron detachment) and high thermodynamic stability (against fragmentation) in the gas phase.[27]

The capability of ab initio total energy calculations to directly identify the lowest energy isomer for the C_{20} cluster has been a topic of discussion for many years.[13-18] Over the past few years, the relative stability of the different symmetries of fullerene has been debated. However, to the best of our knowledge, no calculations have been performed for the full optimization of C_{20}^{2+} isomers at the level of B3LYP/6-31G(d), even though many calculations have been reported for neutral as well as single and double negatively charged C_{20} isomers. In this study, we obtained the relative energies and atomic structures for I_h, T_h, D_{2h}, C_{2h}, and C_2 symmetries that are bond-stretch isomers. Thus, we could anticipate an entirely different set of characteristic chemical reactions for each type of HOMO and LUMO.

Calculations

In this study, the hybrid density functional theory (DFT), Becke's three-parameter hybrid method, and the Lee-Yang-Parr exchange-correlation functional theory (B3LYP)[28-30] were used to optimize the geometries of C_{20} dication isomers. The electron basis set 6-31G(d) was used throughout this study.[31] We fully optimized all the geometries of the C_{20}^{2+} isomers using the Gaussian 2003 B.04 package suite.[32] To obtain geometries with a higher accuracy, we used the convergence criterion with tight optimization and ultrafine grid of a pruned (99,590) grid (using keywords Opt = Tight, Grid = ultrafine). We analyzed the relative energies of the isomers by performing vibrational frequency computations at the same level.

Results and Discussion

In Table 1, we report the relative energies of neutral and double positively charged (C_{20} and C_{20}^{2+}) carbon cluster isomers of C_{20} cage geometries; the energies are obtained by considering the fully optimized geometry at the level of the hybrid B3LYP methods. All were found to be true minima by frequency analysis at the level of B3LYP/6-31G(d) under the reinforced tight convertgence criterion.

Although the cage is formed exclusively of pentagons, its

Table 1. Total energies (a.u.) and relative energies (in parentheses, in units of kJ/mol) of C_{20}^{2+} cage isomers. The energies were obtained through the B3LYP/6-31G(d) calculations[a]

Charge	0	2+	2+	2+	
Symmetry	Energy	Energy	Tightened Energy	ZPE corrected Energy	ZPE
D_{2h}	−761.44444 (0)	−760.78082 (0)	−760.7806816 (0)	−760.662902 (0)	0.11778
C_{2h}	−761.44425 (0.499)	−760.78070 (0.315)	−760.7807155 (−0.089)	−760.662888 (0.037)	0.117827
C_2	−761.44425 (0.499)	−760.78054 (0.735)	−760.7807165 (−0.092)	−760.662877 (0.066)	0.117839
T_h	−761.43829 (16.147)	−760.78082 (0.000)	−760.7806808 (0.002)	−760.662865 (0.097)	0.117816
I_h		−760.78024 (1.523)	−760.7806871 (−0.014)	−760.662858 (0.116)	0.117829

[a]The relative energy is the energy of each cage isomer with different symmetry minus the energy of isomer with D_{2h} symmetry. Here ZPE denotes the zero-point correction energy.

symmetry has so far not been determined with certainty. Thus, in this study, we considered five cage geometries (D_{2h}, T_h, C_{2h}, C_2, and I_h) obtained by full optimization, reinforced optimization, and reinforced optimization with zero-point correction. Among the five cage isomers whose geometries were fully optimized, the relative energies of the D_{2h} and T_h cage structures with higher symmetry were lower than those of the C_{2h} and C_2 isomers with lower symmetry and that of the I_h isomer with the highest icosahedral symmetry. The results showed that the energy of cage isomers is in the increasing order (T_h, D_{2h}) < C_{2h} < C_2 < I_h, unlike the order in the case of neutral C_{20} cage isomers (D_{2h} < (C_{2h}, C_2) < T_h). When the cutoffs on the forces and step size are reduced and a pruned (99,590) grid (using keyword Opt = Tight, Grid = ultrafine) used to obtain more accurate geometries, the energy of the cage isomers of C_{20}^{2+} is in the increasing order C_2 < C_{2h} < I_h < D_{2h} < T_h. With the zero-point correction in the case of reinforced optimization, the energy of the cage isomers of C_{20}^{2+} increases in the order D_{2h} < C_{2h} < C_2 < T_h < I_h. The energy difference among the isomers of C_{20}^{2+} was less than that in the case of neutral cage isomers.

Thus, it is interesting to see that in the cage dication, the isomer with D_{2h} symmetry was more stable than the isomers with other symmetries, implying that the I_h symmetry is reduced to the D_{2h} symmetry. However, a simple Huckel model calculation for C_{20} isomers suggests that the cage dication isomer

should have I_h symmetry.[23,24] It has also been reported that in double negatively charged cage structures, the most stable geometry corresponds to C_i symmetry, and this is followed by C_2, not D_{2h}.[22] Therefore, the strength of the Jahn-Teller distortion would depend on the HOMO of the C_{20} isomers, which would be closely related to the order of the relative energies of their atomic structures. Figure 2 shows the cage structures with T_h, D_{2h}, C_{2h}, C_2, and I_h symmetries in the case of reinforced optimization.

Figure 3 shows the HOMOs and LUMOs of the bond-stretch isomers. Also supplementary Table S2 for the HOMO and LUMO energies of isomers in Figure 3 is in Supporting Information. Our results suggest that these isomers have the same spin state and the same potential energy curve.[4] Although the predominant electronic configurations of the isomers are similar, the HOMOs and LUMOs differ among these five bond-stretch isomers, implying that we could anticipate an entirely different set of characteristic chemical reactions for each type of HOMO and LUMO. The LUMOs of the isomers with C_2 and D_{2h} symmetry are isomorphic to the LUMO of the isomer with T_h symmetry, but each LUMO of the isomers with C_{2h} and I_h symmetry is not mapping to the LUMO of the isomer with T_h symmetry.

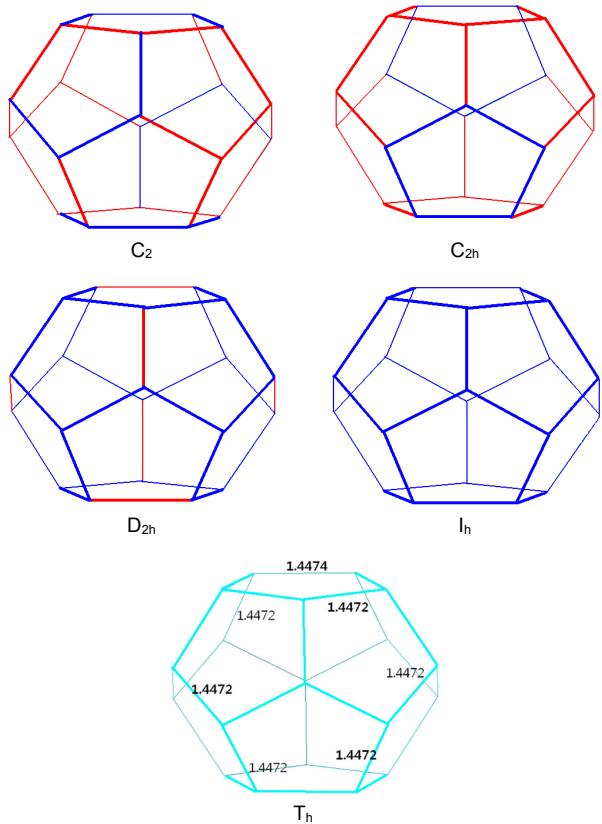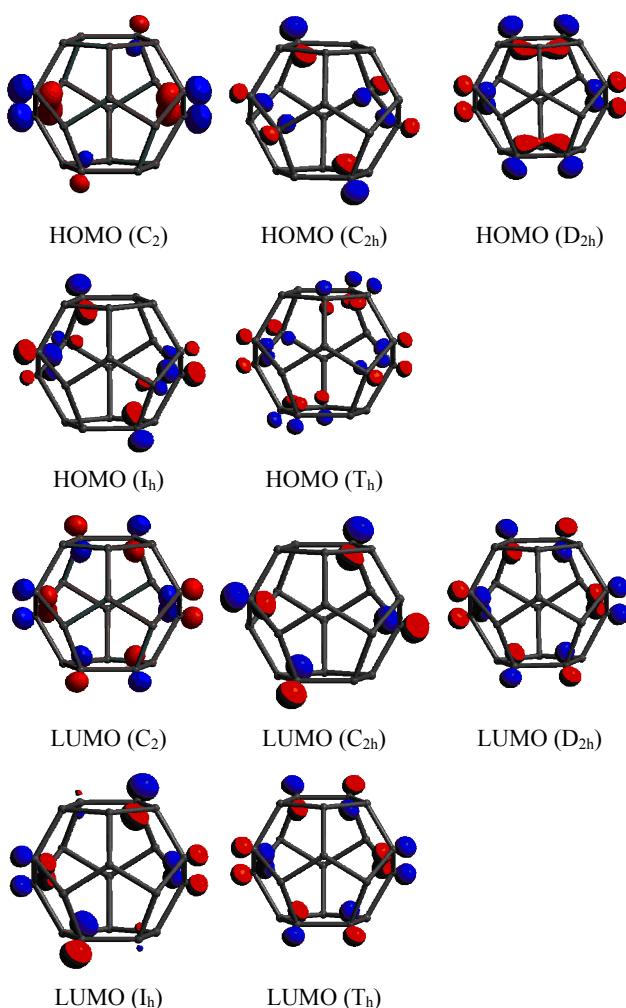Therefore, from the viewpoint of LUMO mapping, there could

Figure 2. Fully optimized geometries of cage isomers of the C_{20}^{2+} cluster at the level of B3LYP//6-31G(d). The lengths of the red- and blue-colored bonds are 1.448 and 1.447 Å, respectively, implying that in the isomer with I_h symmetry, the length of all the bonds is 1.447 Å. In the isomer with T_h symmetry, the length of all the bonds that are not accompanied by numerical values is 1.4474 Å.

Figure 3. HOMOs and LUMOs of the bond-stretch isomers of C_{20}^{2+} with C_2, C_{2h}, D_{2h}, T_h, and I_h symmetries.

be three different reactions. Each LUMO of the isomers with C_2, D_{2h}, and T_h symmetries suggests that there would be both suprafacial and antarafacial interactions for 1,2-addition and one of the two interactions for 1,3-addition.[16,33] There are strong bonding interactions which may arise from only four C2 units of each LUMO as active sites for olefin addition, implying that the number of olefin in the adduct should not be greater than 4. The LUMO of the isomer with I_h symmetry suggests that there would be suprafacial interactions for 1,2-addition if there is one site addition, and vice versa. Or there would be two 1,2,4-additions. Further, the LUMO of the isomer with C_{2h} symmetry suggests that 1,3-addition would be possible by using a suprafacial or antarafacial process.

All the HOMOs of the five isomers are also different, and therefore, there could be five different chemical addition reactions characteristic of each HOMO, implying that this is in line with the first suggestion of Stohrer and Hoffmann.[1] On the basis of the HOMO of the isomers with different symmetries, it is inferred that there would be 1,3-addition for I_h, η^3-addition for T_h, 1,2- and 1,3-addition for D_{2h}, 1,3-addition for C_{2h}, and 1,2-addition for C_2.

Conclusion

We obtained fully optimized geometries without any constraint at the B3LYP//6-31G(d) level by the hybrid density functional method for isomers of the C_{20}^{2+} cage (the smallest fullerene). The effect of two-electron release on the atomic structures of isomers showed that from the viewpoint of energetics, the relative energy of the C_{20}^{2+} cage (the smallest fullerene) isomers increased in the order $D_{2h} < C_{2h} < C_2 < T_h < I_h$. Therefore, it is interesting to see that the symmetry species of the isomer with the lowest energy was the medium symmetry D_{2h}, not the highest symmetry I_h and the most reduced symmetry C_2. All the isomers were found to be true minima by frequency analysis at the level of B3LYP/6-31G(d) under the reinforced tight convergence criterion. As for as we are aware, the D_{2h}, C_{2h}, C_2, and T_h symmetry structures of the isomers of the C_{20}^{2+} cage are reported for the first time in this paper as bond-stretch isomers with the same spin state and the same potential energy curve.

Although the predominant electronic configurations of the isomers did not differ, the HOMO and LUMO maps differed among the five bond-stretch isomers. Thus, we can anticipate an entirely different set of characteristic chemical reactions for each type of HOMO and LUMO. Our results suggest that these isomers would be verified only by the chemical reaction because the energy differences have nothing to do with thermochemistry.

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