Uptake Effects of Two Electrons for Relative Stability and Atomic Structures of Carbon Cluster Isomers of C20: *ab initio* Methods

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This study examined the effect of the uptake of one and two electrons on the atomic structure of three isomers of C_{20} clusters, namely the ring, bowl (corannulene like), and cage (the smallest fullerene). Geometry optimizations were performed using the hybrid density functional (B3LYP) methods for neutral, singly and doubly charged C_{20}, C_{20}^{-}, and C_{20}^{2-}. These results show that the symmetry of the lowest energies for ring and bowl isomers were not changed, whereas the increasing order of energy for the cage (the smallest fullerene) isomers was changed from $D_{2h} < C_{2h} \leq C_2$ of C_{20} through $C_i < C_{2h} < C_2 < D_{2h}$ of C_{20}^{-} to $C_i < C_2 < D_{2h} < C_{2h}$ of C_{20}^{2-}. The reduced symmetry isomers of the cage have comparative energy and the ground state symmetry of the neutral and single and double charged C_{20} decreased with increasing number of electrons taken up in the point of energetics. Interestingly, the difference in energy between the ground state and the next higher energy state of C_{20}^{2-} was 3.5kcal/mol, which is the largest energy gap of the neutral, single anion and double anion of the cage isomers examined.

Key Words: C_{20} cluster isomers, Electron uptake effects, Atomic structures, Hybrid density functional (B3LYP) calculations

Introduction

A flat graphite sheet can be made from carbon atoms arranged in a hexagonal arrangement. Inserting pentagons into the sheet will cause it to pucker and curve. In principle, adding just twelve pentagon creates sufficient curvature to make the sheet wrap up and connect together to form a spherical shell (a fullerene) or even a closed tube. How the pentagons and hexagons are arranged is the deciding factor. The archetypical fullerene, C_{60}, is a sphere with all 12 pentagons distribution evenly over its surface; each one perfectly surrounded by a ring of hexagons. Fullerenes have been the topic of several studies[1-5] since the discovery of buckminsterfullerene, C_{60}, in 1985 because C_{60} and its derivatives exhibit interesting material properties, such as superconductivity[6] and a non-linear optical response.[7,8]

Considerable attention has also been focused on the smallest carbon cluster to form a closed fullerene structure, C_{20}. The attraction of C_{20} is due not only to its relevance to C_{60} but its possibility of being an intermediate in the formation of C_{60} and larger fullerenes. Studies of various C_{20} structures have established fairly well the existence of several spatial arrangements. Among the variety of carbon clusters, C_{20} is the smallest possible fullerene. However, there is experimental evidence showing that the dominant structure of C_{20} is a monocyclic ring and a bicyclic ring.[9,10] Recently Prinzbach et al[11] provided experimental evidence for the existence of three different isomers: cage, bowl, and ring (see Fig. 1). They characterized the mass-selective anion photoelectron spectra of C_{20} clusters generated from the two brominated, and from graphite in a standard laser evaporation cluster source. The observed electron affinities and vibrational structures of these three C_{20} isomers differ significantly from each other. Although experiments are consistent with the existence of these structures, it is unclear which of them is the most stable.

Theoretical studies are analogous to experimental studies. Theoretical methods provide a variety of relative energies.[12-21] Hartree-Fock Self Consistence Field (HF-SCF) calculations favor a ring structure.[12] Møller-Plesset second order perturbation theory (MP2) method with a small and large basis set favors a cage geometry[12] and bowl, respectively.[18] The Coupled-Cluster Single and Double excitations (CCSD) and Coupled-Cluster Single and Double excitations with the triples added perturbatively method (CCSD(T)) favor the bowl and bowl/cage.[16,21] Density Functional (LDA, BLYP (B3LYP), and BPW91(B3PW91)) calculations favor the cage, ring and bowl.[15,21] The valence-only (pseudopotential)
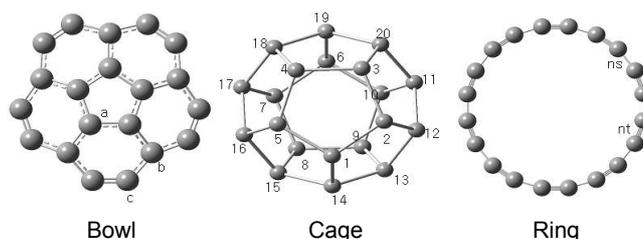
Figure 1. Three classes of structures of C_{20} cluster isomers (Bowl, cage, and ring). Here a, b, c, and the numbers in bowl and cage isomers represent the specific atomic site, but ns and nt in ring the nominal single and triple bonds.

Table 1. Total energies (a.u.) and the relative energies in parentheses (kcal/mol) of C_{20} isomers using the B3LYP/6-31G* calculations.[a]

Charge Structure		B3LYP/6-31G(d)			HF/6-31G(d)
		0	-1	-2	0
Ring (D_{10h})		-761.49272 (0.0)	-761.58349 (0.0)	-761.54290 (0.0)	-756.68903 (0.0)
Bowl	C_{5V}	-761.49159 (0.7)	-761.55552 (17.6)	-761.46414 (49.4)	-756.65092 (23.9)
	C_2	-761.49160 (0.7)	-761.55554 (17.5)	-761.46414 (49.4)	-756.65092 (23.9)
Cage	T_h	-761.43829 (34.2)			-756.54384 (91.1)
	D_{2h}	**-761.44444 (30.3)**	-761.50405 (49.8)	-761.39020 (95.8)	**-756.55258 (85.6)**
	C_{2h}	-761.44425 (30.4)	**-761.50531 (49.1)**	-761.39019 (95.8)	-756.55198 (86.0)
	C_2	-761.44425 (30.4)	-761.50426 (49.7)	**-761.39260 (94.3)**	-756.54384 (91.1)
	C_i		**-761.50658 (48.3)**	**-761.39842 (90.7)**	

[a]The relative energy is equal to the energy of each isomer minus the energy of the corresponding ring isomer.

Quantum Monte Carlo (QMC) calculations favor the bowl.[18]

Recently the planarity of benzene was analyzed using a variety of theoretical methods, which suggests that the B3LYP/6-31G(d) level calculation can simulate the experimental structure of benzene.[22]

For molecular systems, there is still some controversy regarding the smallest molecule that can bind two or more excess electrons with both electronic stability (against electron detachment) and thermodynamic stability (against fragmentation) in the gas phase.[23] However, as far as we know, there are little calculations for double charged C_{20}^{2-} at the level of B3LYP/6-31G(d), even though many calculations of neutral and single charged C_{20} and C_{20}^- have been reported. As shown in Table 1, this paper reports the energetics of neutral, single and double charged (C_{20}, C_{20}^-, and C_{20}^{2-}) carbon cluster isomers of C_{20} (cage, bowl, and ring geometries) using *ab initio* HF and hybrid B3LYP methods. In addition, the negatively double charged effect of the relative stability and structures of the neutral C_{20} ring, bowl, and cage isomers were analyzed.

Calculations

In this paper, ab initio HF-SCF and density functional theory (DFT) with Beck's three parameter hybrid method and Lee-Yang-Parr exchange-correlation functional theory (B3LYP)[24-26] were used to optimize the geometries of the C_{20} isomers. An all electron basis set, 6-31G(d), was used.[27] All geometries were fully optimized using the Gaussian 2003 B.04 package suite.[28] The neutral, single and double charged (C_{20}, C_{20}^-, and C_{20}^{2-}) isomers were calculated.

Results and Discussion

There is considerable debate regarding whether ab initio total energy calculations can identify the lowest energy isomer for the C_{20} cluster directly.[12-21] The stability of the different geometrical forms has been the center of a dispute that has lasted for many years. There is general consensus that there are three main candidates for the ground state structure: the cage, ring, and bowl isomers. Fig. 1 shows the three structures of C_{20} isomers.

The bowl has C_{5V} symmetry with a central pentagon surrounded by five hexagons. In the bowl structure, there three topologically distinct carbon atoms, two with a sp^3 coordination (**a** and **b** in bowl type of Fig. 1) and one with the sp^2 type. The cage is formed exclusively of pentagons but its symmetry has not yet been determined with certainty. Therefore, this study considered six cage geometries (D_{2h}, T_h, C_{2h}, C_2, C_i and I_h). The ring has the highest symmetry, D_{10h}. However, it shows two different alternative inter-atomic bond distances due to the Jahn-Tellor distortion.

Table 1 shows the energies of the C_{20} isomers (neutral and negatively charged compounds) using the hybrid DFT and HF approaches with a fully optimized geometry. Table 1 shows the HF results to illustrate the correlation effect of B3LYP functional. Each HF and B3LYP calculation using the 6-31G(d) basis set prefers a ring structure compared to the cage with D_{2h} symmetry, as illustrated by energy difference of 30.3 kcal/mol and 85.6 kcal/mol, respectively. Among the five cage isomers, the cage structure with D_{2h} symmetry is
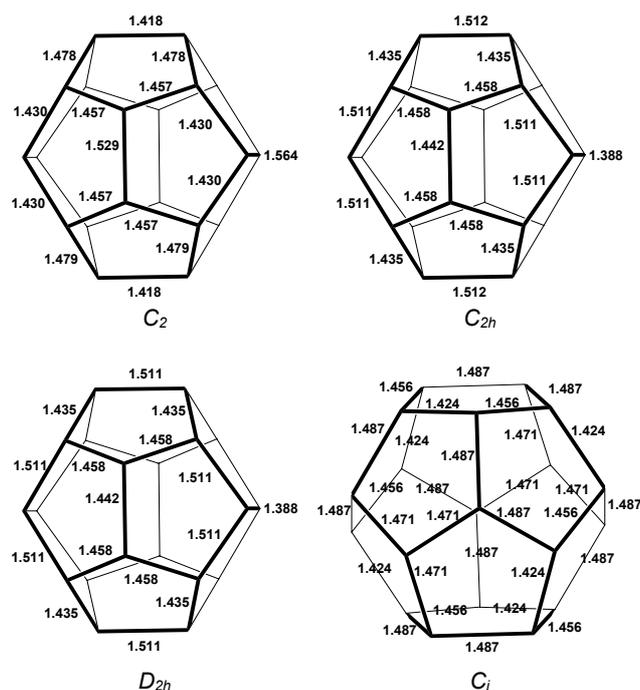
Figure 2. B3LYP-optmized geometries of cage isomers of C_{20}^{2-} cluster.

most stable. The HF and DFT results for neutral compounds agree with those reported elsewhere.[12-21] In neutral compounds, the HF and B3LYP geometries were almost the same

Table 2a. Bond lengths of bowl and ring structures of C$_{20}$, C$_{20}^-$, and C$_{20}^{2-}$ clusters with the geometry optimization by using the hybrid B3LYP and HF methods. Bond lengths of ns, nt, a-a, a-b, c-c, and b-c are shown in Fig. 1.

	Ring Structure (D$_{10H}$)			
charge	B3LYP			HF
	0	-2	-1	0
ns	1.348	1.323	1.334	1.381
nt	1.236	1.267	1.251	1.196
	Bowl Structure (C$_{5V}$)			
a-a	1.428	1.428	1.428	1.429
a-b	1.430	1.415	1.422	1.397
c-c	1.249	1.290	1.268	1.218
b-c	1.419	1.436	1.427	1.425

as those reported previously using a similar basis set.[15,16] However, the relative energies of the cage with respect to the ground state of ring isomer were lower than those reported previously. The ring was also the most stable in the ionized compounds of C$_{20}$ isomers. Interestingly, the single-charged anion of a cage with the C$_i$ isomer is more stable than the isomer with C$_{2h}$ symmetry, which is more stable than that with D$_{2h}$ symmetry. On the other hand, in the negatively double charged cage structures, the most stable geometry was C$_i$ symmetry followed by C$_2$, not D$_{2h}$. Figure 2 shows the optimized cage structures with D$_{2h}$, C$_{2h}$, C$_2$, and C$_i$ symmetry.

All the neutral and anion compounds of the C$_{20}$ isomers preferred the ring form. Table 2 shows the bond lengths calculated for the C$_{20}$ isomers (neutral and negatively charged states). The optimized geometries with different methods were slightly different. For example, in the lengths of the nominal single (ns) and triple (ts) bonds of the C$_{20}$ ring, the B3LYP result was approximately 3% different from the HF results. Table 2 shows the ring structure of the neutral C$_{20}$ isomer. The ns bond lengths decrease and the nt bond lengths increase with

Table 2b. Bond lengths of cage structures of C$_{20}$, C$_{20}^-$, and C$_{20}^{2-}$ cluster isomers with the geometry optimization by using the B3LYP calculations.

Symmetry	T$_h$	D$_{2h}$			C$_{2h}$			C$_2$		
Charge	0	0	-2	-1	0	-2	-1	0	-2	-1
C1-C2	1.453	1.445	1.458	1.450	1.451	1.435	1.456	1.422	1.457	1.455
C2-C3	1.453	1.422	1.435	1.429	1.405	1.435	1.411	1.422	1.457	1.455
C3-C4	1.453	1.537	1.511	1.529	1.517	1.511	1.499	1.486	1.479	1.443
C4-C5	1.446	1.422	1.435	1.429	1.405	1.388	1.420	1.399	1.418	1.478
C1-C5	1.453	1.445	1.458	1.450	1.447	1.511	1.453	1.486	1.479	1.443
C6-C7	1.453	1.444	1.442	1.443	1.443	1.458	1.436	1.445	1.430	1.481
C7-C8	1.453	1.486	1.511	1.496	1.517	1.511	1.499	1.486	1.479	1.443
C8-C9	1.453	1.422	1.435	1.429	1.447	1.511	1.453	1.486	1.479	1.443
C9-C10	1.453	1.422	1.435	1.429	1.450	1.458	1.465	1.445	1.430	1.481
C10-C6	1.446	1.486	1.511	1.496	1.515	1.511	1.527	1.538	1.529	1.443
C11-C12	1.453	1.445	1.458	1.450	1.443	1.458	1.436	1.445	1.430	1.481
C12-C13	1.453	1.486	1.511	1.496	1.451	1.435	1.456	1.422	1.457	1.455
C13-C14	1.453	1.400	1.388	1.394	1.405	1.435	1.411	1.422	1.457	1.455
C14-C15	1.453	1.486	1.511	1.496	1.450	1.458	1.465	1.445	1.430	1.481
C15-C16	1.446	1.445	1.458	1.450	1.444	1.442	1.478	1.444	1.564	1.415
C16-C17	1.453	1.445	1.458	1.450	1.443	1.458	1.436	1.445	1.430	1.481
C17-C18	1.453	1.486	1.511	1.496	1.451	1.435	1.456	1.422	1.457	1.455
C18-C19	1.453	1.400	1.388	1.394	1.405	1.435	1.411	1.422	1.457	1.455
C19-C20	1.453	1.486	1.511	1.496	1.450	1.458	1.447	1.445	1.430	1.481
C20-C11	1.446	1.445	1.458	1.450	1.444	1.442	1.448	1.444	1.564	1.415
C1-C14	1.453	1.537	1.511	1.529	1.517	1.511	1.448	1.486	1.479	1.443
C2-C12	1.446	1.422	1.435	1.429	1.405	1.388	1.448	1.399	1.418	1.478
C3-C20	1.453	1.445	1.458	1.450	1.447	1.511	1.447	1.486	1.479	1.443
C4-C18	1.453	1.445	1.458	1.450	1.451	1.435	1.447	1.422	1.457	1.455
C5-C16	1.453	1.422	1.435	1.429	1.405	1.435	1.447	1.422	1.457	1.455
C6-C19	1.453	1.422	1.435	1.429	1.450	1.458	1.447	1.445	1.430	1.481
C7-C17	1.453	1.422	1.435	1.429	1.447	1.511	1.447	1.486	1.479	1.443
C8-C15	1.453	1.486	1.511	1.496	1.517	1.511	1.448	1.486	1.479	1.443
C9-C13	1.453	1.444	1.442	1.443	1.443	1.458	1.448	1.445	1.430	1.481
C10-C11	1.446	1.486	1.511	1.496	1.515	1.511	1.447	1.538	1.529	1.443

increasing electron uptake. This suggests that the difference in ns and nt bond lengths decreases with increasing number of negative charges of the ring isomer. Therefore, the ns bond lengths of the neutral isomer are general longer than those of the negatively charged rings. In addition, in the bowl structures, single and double charged anions show C_{5V} symmetry. In the bowl structure, the a-a bond distances are maintained regardless of the change in charge, but the other structures slight changes. In the negatively charged compounds, the ab bond lengths are shortened while the bc, and cc bond lengths are elongated.

In summary, optimized geometries were obtained using both *ab inito* HF and DFT methods for three types of isomers of C_{20}, namely the ring, bowl (corannulene like), and cage (the smallest fullerene). The effect of the uptake of one and two electrons on the atomic structures of the three type of isomers of C_{20} clusters was also analyzed with geometry optimizations without constraint using the hybrid density functional (B3LYP) methods for C_{20}, C_{20}^-, and C_{20}^{2-}. The results show that the ring type structure is the most stable geometry in the point of energetics and the symmetry of the lowest energies for the ring and bowl isomers are not changed. On the other hand, the order of energy for the cage (the smallest fullerene) isomers is changed from $D_{2h} < C_{2h} \leq C_2$ for C_{20} through $C_i < C_{2h} < C_2 < D_{2h}$ for C_{20}^- to $C_i < C_2 < D_{2h} < C_{2h}$ for C_{20}^{2-}.

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