

Super-valence phenomenon of carbon atoms in C₂₀ molecule

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Abstract

Fourteen structures of C₂₀ are studied at DFT/B3LYP/6-31G* theoretical level. Except ring, bowl, cage and isomer 1 which have been studied before, other isomers have not been reported so far. Calculated results show that the ring has the lowest energy at this level and isomers 1, 2, 3 and 4 have lower energies than that of cage. Analyses of optimized bond lengths, electronic structure indicate that some carbon atoms express super-valence property. In addition, NICS value is consistent with molecular orbital character in denoting aromaticity of C₂₀ molecule. Delocalization character averts influence of curvature strain, which can well explain the stability of the cage.

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1. Introduction

Since the discovery of C₆₀ molecule, detailed study on pure carbon clusters and (BN)_n clusters has attracted much interest in the past two decades [1–9]. As the smallest fullerene among carbon clusters, C₂₀ has been found in experiment with three structures [10] (ring, bowl and cage) by Prinzbach et al. who have provided spectroscopic evidence for their existence. However, there are still a lot of fundamental questions yet to be adequately addressed [11,12]. Why is the ring the most stable structure at this level? Are there other stable structures that have not been found? In addition, cage is composed solely of pentagons, resulting in extreme curvature and reactivity which have led to doubts about its stability, but it has been synthesized in experiment with good stability. Definite explanation about this its stability has not been made yet [13–17]. Solving all these problems is very important for further studying of C₂₀ cluster.

2. Computation method

Ring, bowl, cage and isomers 1–11, 14 isomers of C₂₀, are calculated using density functional theory (DFT). The

optimized geometry, electronic structure and the lowest vibrational frequency are studied at B3LYP/6-31G* level. Nucleus independent chemical shift (NICS) value, based on magnetic shielding, is calculated employing NMR=GIAO method. Recently, NICS value has been used to evaluate aromaticity of some molecule [18–22]. Generally, a negative NICS value denotes aromaticity and a positive value shows antiaromaticity. And NICS value fluctuating around zero indicates nonaromaticity.

All calculations are performed on SGI Origin 3800 server using GAUSSIAN03 package of programs and molecular orbital figures are generated using Gaussview programs.

3. Results and discussion

3.1. Geometry optimizations

Fourteen optimized structures of C₂₀ are shown in Fig. 1 in which only ring, bowl, cage and isomer 1 [23] have been reported before. Isomers 2–11 are originally proposed in this paper. There is no symmetry constrains in optimizations of these structures. And the following two points are considered (1) averting appearance of strain rings (delta, quadrangle and pentagon) as soon as possible; (2) making strain rings isolate to the full. It can be seen from Fig. 1 that isomer 1 is composed of three arcs with eight carbon atoms. Isomers 2 and 3 are planar and both have two big rings and two deltas. Isomer 4 has two crooked 10-membered rings that are linked together by four

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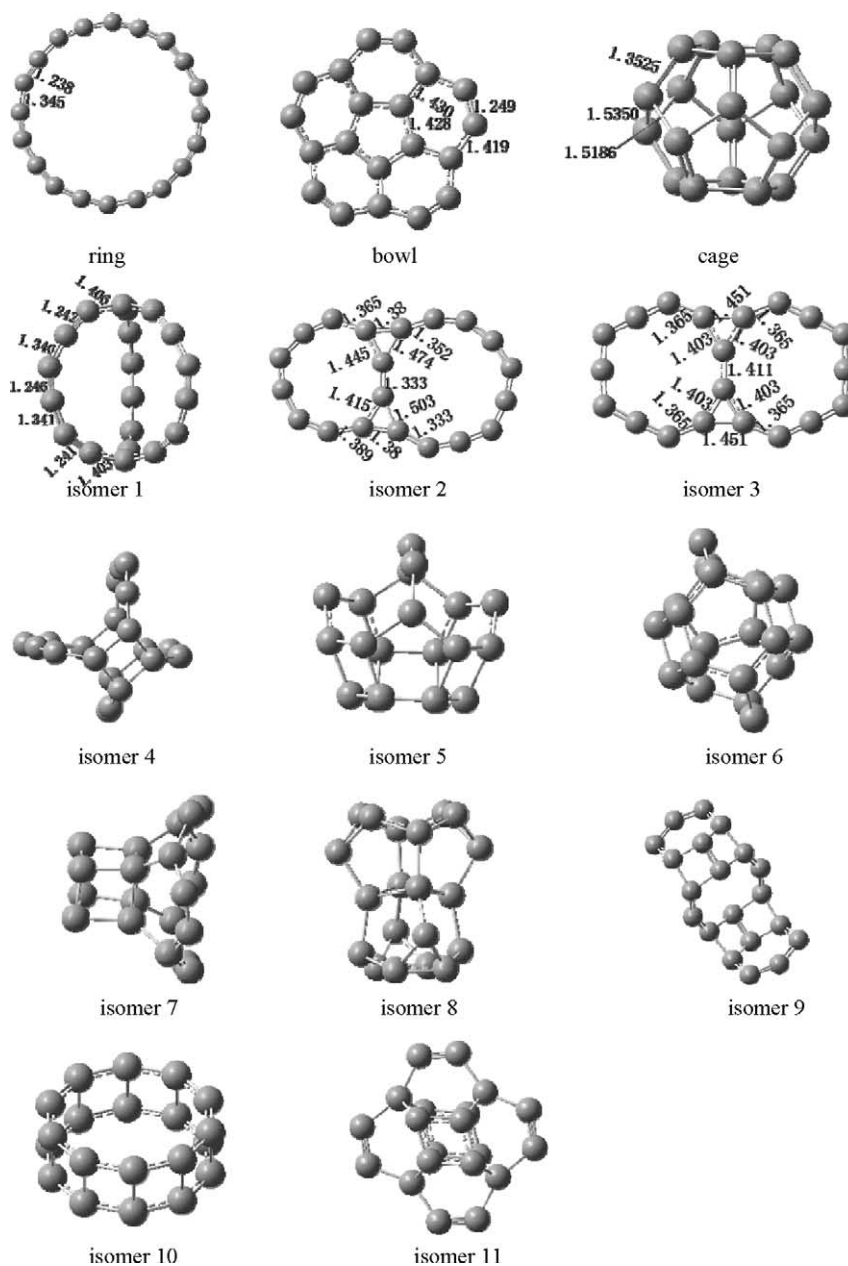


Fig. 1. Optimized geometries and bond lengths for C_{20} at the B3LYP/6-31G* method.

chemical bonds. Except isomer 10, which is a standard tubular structure, isomers 5–11 have complex conformations. These isomers have adjacent strain rings and higher energies than those of the forenamed structures. Their conformations are not introduced in detail here.

The corresponding relative energies, symmetries, the lowest vibrational frequencies and the area of bond lengths are listed in Table 1. Relative energies are generated by the difference between ring and other isomers (for example, $\Delta E_{\text{cage}} = E_{\text{cage}} - E_{\text{ring}}$). Obviously, isomer 1 does not contain strain ring and it has lower energy than that of cage (the energy difference is 2.6124 eV). Although strain rings exist in isomers 2, 3 and 4, they are not adjacent to each other. Isomers 2, 3 and 4 obey ‘isolated strain ring’ (ISR [24,25]) rule and their energies are lower than that of the cage too (the difference is 1.1511, 0.7048

and 0.6340 eV, respectively). For isomers 5–11, they violate ISR rule leading to having higher energies than that of the cage, although they do not have imaginary frequency in theory calculation. In addition, free energies and vibrational entropies are all used to investigate the stability of structures (Table 2). It is clear that the ring has the lower free energy and larger vibrational entropy than those of other isomers, which contributes to its stability.

It is noticeable that ring has two types of bond lengths, 1.238 and 1.345 Å, which are just about the lengths of triple and double bonding lengths of carbon atom, respectively (comparing with bond lengths of acetylene and ethylene). Simultaneous existence of these two types of bond length at the same carbon atom makes the appearance of $\equiv C=$ type valence bond structure as well as super-valence phenomena

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