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Electronic states of C_{20} isomers

Wang Zhi-Gang(王志刚)[a)b)], Zhang Cun-Hua(张存华)[a)], Fan Xian-Hong(范鲜红)[a)], Pan Shou-Fu(潘守甫)[a)b)†], Yan Bing(闫 冰)[a)], and Jin Ming-Xing(金明星)[a)]

[a)] *Institute of Atomic and Molecular Physics, Jilin University, Changchun 130012, China*

[b)] *State Key Laboratory of Theoretical and Computational Chemistry, Institute of Theoretical Chemistry Jilin University, Changchun 130023, China*

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Using quantum chemistry *ab initio* method, geometry optimization of the singlet and triplet electronic states are performed for three isomers (ring, bowl and cage structures) of C_{20}. From the optimized geometries, MP2 calculation gives a result which does not agree with Hund's rule, i.e. the singlet state has a lower energy for all the three isomers. Further more, total charge densities and electrostatic potentials of three isomers are given by the UHF wavefunctions, the results indicate negative charges located in the central area of cage and bowl structures, and the bond character of ring structure is analysed.

Keywords: C_{20} isomers, *ab initio* calculations, electronic states
PACC: 6148, 3120A, 7125X

1. Introduction

At the end of the last century, C_{20} received a great deal of attention. Because C_{20} is the smallest fullerene cluster found so far,[1] and it has three main structures (ring, bowl and cage), many studies are concentrated on the three structures of C_{20} isomers.

In the previous theoretical calculations, people always consider the ground state of all isomers is the singlet electronic state, and accordingly, they calculated the stable structure of ground state,[2−10] and further studied the process of isomerization.[11−13] By studying previous papers about singlet states of C_{20}, we can find the single point energy calculated by MP2 (Møller–Plesset perturbation theory of second order)[14] and CCSD(T) (coupled cluster with single, double and quasi-perturbative triple substitutions)[15] have the same general feature (using HF/6-31G(d) optimized reference geometries), though with some differences in correction of the two methods. Using the HF (Hartree–Fock) method to optimize the three structures of C_{20} isomers, ring structure is the most stable, then the bowl and cage in succession. But the energy of bowl is the lowest by MP2 correction or CCSD(T) calculation, then the cage and ring. This calculation result of singlet states is prevalently accepted.[6] And the QMC (quantum Monte Carlo) studies also predict that the bowl is more stable than the ring and cage structures.[3,5]

However, few papers have mentioned the triplet state of C_{20} isomers, or gave the quantitative results.[16] So we think the past works are imperfect. First, bond character is the intrinsic factor of system structure regardless of the multiplicity and symmetry of each isomer, but people have not yet concentrated on this point. Second, we need to study the multiplicity, because the C_{20} is an unsaturated bonding system, and we need to know if the multiplicity of ground state has the uncertainty.

In order to better understand the C_{20} isomers, in this paper we report the computational results of singlet and triplet states of C_{20} isomers (with ring, bowl and cage structures).

2. Method

ROHF (restrained open shell Hartree–Fock) and UHF (unrestrained Hartree–Fock) were used to optimize the structures of singlet and triplet states of C_{20} isomers, respectively. 6-31G(d) basis set [17]was employed in all calculations; the d exponent used in the polarization functions was 0.8. Precision of the energy gradient was 10^{-5}hartree/bohr. From the optimized

†E-mail: pansf@jlu.edu.cn

geometry on UHF level, energy corrections were carried out by MP2 calculation. All calculations were made using Gamess program.[18]

In the end, we used Hyperchem7.0 program[19] to depict the bond character of C_{20} system. The Koopmans theorem[20] is not tenable for the open shell system by the ROHF method, it cannot give the correct molecular orbital character,[21] and so this section has been carried out on the HF level.

3. Results and discussion

Firstly we optimized the three isomers of C_{20} on the ROHF level. Table 1 gives the calculation results.

For the singlet state, because of using the same method as Ref.[5], the results have almost no difference in credible precision. From the optimized results of ROHF method (without MP2 energy correction), we can conclude that the energy of triplet state is lower than that of singlet state for the cage structure.

From this result, we consider it is the Hund's rule that apparently acts on this kind of unsaturated bonding molecule. Because the ROHF method itself insufficiently considered the electronic correlation, peroration is now too early. Especially for discussing the open shell problem, from the ROHF results, the Koopmans theorem does not come into existence, it cannot give the correct molecular orbit character. So on the basis of UHF, we optimized the structure over again and finished the MP2 energy correction, finally using UHF wavefunctions to depict the bond character of the C_{20} system.

Table 1. Calculated total energies (units of hartree) for C_{20} isomers, values in parentheses are relative energies (units of eV).

Method	Singlet state			Triplet state		
	ring	bowl	cage	ring	bowl	cage
ROHF*	–756.689	–756.651	–756.558	–756.545	–756.644	–756.568
	(0.0)	(1.03)	(3.56)	(3.92)	(1.22)	(3.29)
UHF*	–756.689	–756.651	–756.558	–756.562	–756.649	–756.609
	(0.0)	(1.03)	(3.56)	(3.46)	(1.09)	(2.18)
MP2*	–759.165	–759.265	–759.234	–759.106	–759.190	–759.197
	(0.0)	(–2.72)	(–1.88)	(1.61)	(–0.68)	(–0.87)
Ref.						
MP2						
Ref.[5]	(0.0)	(–2.73)	(–1.88)			
Ref.[2]	(0.0)	(–3.1)	(–3.9)			
CCSD(T)						
Ref.[4]	(0.0)	(–1.5)	(–0.8)			
Ref.[2]	(0.0)	(–2.8)	(–2.2)			
QMC						
Ref.[5]	(0.0)	(–1.1)	(1.1)			
Ref.[3]	(0.0)	(–1.1)	(1.0)			

*In this work, the results of singlet state have almost no difference from Ref.[5] with credible precision in both structure optimization and energy correction.

From Table 1, for the open shell triplet state, the difference is prominent based on UHF, and because the singlet state is the closed shell, its results are consistent with the results at ROHF level. Energy of the triplet state is found to be still lower than that of singlet state (below 1.38eV) for the cage structure. But the result by MP2 energy correction is different: the structure of singlet state is more stable, i.e. the electronic correlation of singlet state is stronger than that of triplet state for the cage structure, and the energy of the triplet state is 1.01eV higher than that of singlet state. The results of MP2 correction did not agree with Hund's rule. The energy of singlet state is also lower than that of triplet state for the other two isomers.

Results of MP2 correction show that the energy of singlet state of the bowl structure is the lowest, which is consistent with the well-known conclusion. For the triplet state, energy of the cage structure is the lowest and the next is bowl structure, but the difference is

not obvious.

Three-dimensional contour maps of total charge densities and two-dimensional contour maps of electrostatic potentials for C_{20} isomers are drawn by UHF wavefunctions in Fig.1. For cage and bowl structures, specific molecular bond character is very complex because the molecular orbital delocalization is high. We can get more comprehensive information if we concentrate on total charge densities map and electrostatic potentials map. The charge density figure indicates more negative charges in the central area of cage structure, and a little negative charges in the central pentagon for bowl structure. Because the ring structure is more distinct than the others, we present its bond character in Fig.2.

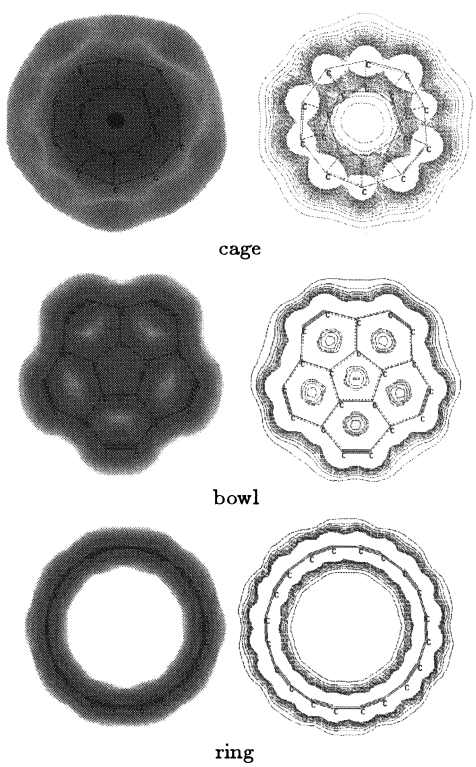


Fig.1. 3D contour maps of total charge densities and 2D contour maps of electrostatic potentials of C_{20} isomers.

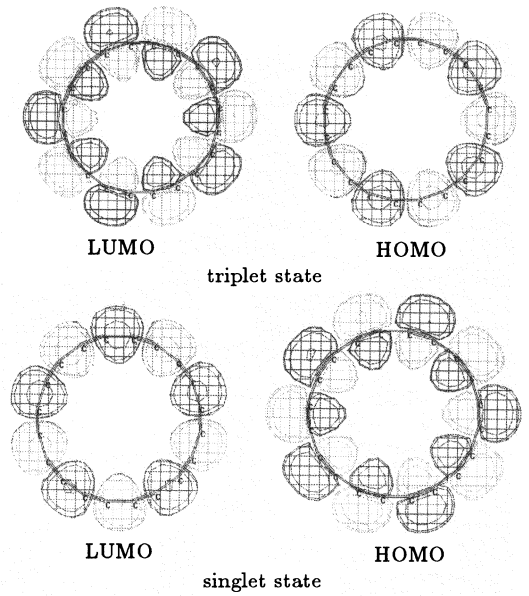


Fig.2. 3D contour maps of the highest occupied orbitals and the lowest unoccupied orbitals of singlet and triplet electronic states of ring structure for C_{20} isomer, respectively.

For singlet state of ring structure, the HOMO (highest occupied molecular orbital) is the 60th molecular orbital, and the LUMO (lowest unoccupied molecular orbital) is the 61st molecular orbital, their energies are –0.311 and 0.006 hartree, respectively. Correspondingly, the HOMO of triplet state is the 61st molecular orbital, its energy is –0.199 hartree, and the energy of LUMO is –0.016 hartree. The 60th molecular orbital becomes the NHOMO (next highest occupied molecular orbital), its orbital energy is –0.275 hartree, the energy difference is 0.076 hartree between HOMO and NHOMO. From Fig.2, for each molecular orbital, two adjacent p orbits form pi bonding, two pi bonds form antibonding to each other. For the HOMO of triplet state and LUMO of singlet state, all bonds are vertical to the plane of the ring. Because of the plane ring structure, each orbital map shows a very interesting case that pi electronic clouds extrude each other in the ring, especially for the case of singlet state HOMO and triplet state LUMO, in which the pi bond direction is located in the ring plane.

4. Conclusion

At UHF/6-31G(d) level, the result of MP2 shows that the energy of triplet state is higher than that of the corresponding singlet state: that is to say, Hund's rule doesn't have decisive influence on structure of C_{20} isomers. However, more precise calculation is needed to prove our conclusions.

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