Structures and Stabilities of Rings Composed of C_{20} Cages

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The ring structures with D_{ab}, D_{ac}, C_{nh} and C_{nh} symmetries composed of C_{20} cages have been investigated using the self-consistent field molecular orbital method. It is found that the formation of the C_{20}-rings is favorable to stability of the C_{20} systems. The influence of structure symmetries and distortion on the stabilities of the C_{20}-rings is explored. The strain change due to the structure distortion greatly affects the stabilities of the C_{20}-rings. Furthermore, the bonding and electronic properties of the C_{20}-ring are also discussed and compared with those of other fullerene-rings such as C_{60}-rings and C_{24}-rings.

Keywords: fullerene, structure, electronic property

1. Introduction

The C_{20} cage is considered to be the smallest fullerene. It only consists of twelve pentagons which lead to large curvature and contravention of the “isolated pentagon rule”. Possibly, its special structure makes it one of the unstable fullerenes. In fact, the products of C_{20} cage obtained from perhydrogenation and gas-phase debromination processes have a lifetime of only about 0.4 ms. Moreover, it is known that a larger π-orbital axis vector (POAV) angle can cause a larger strain on the sp^{2} carbon atom and high reactive activity. The POAV angle on the atoms of Ih C_{20} cage is equal to 110.90^\circ which is larger than those of C_{60} and C_{36} fullerene balls. Therefore, the C_{20} cages should have a stronger tendency to form the intermolecular bonds for releasing the cage strain. Theoretical studies on various structures consisting of C_{20} cages such as dimer, trimer and tetramer structures have been carried out, as well as one-dimensional (1D), two-dimensional (2D) and three-dimensional (3D) polymers. Moreover, connection through intermolecular bond should also result in ring structures, similar to the case in C_{60} and C_{36} cages. So far as we know, there is no report on the ring structures composed of C_{20} cages, but study of the C_{20}-ring structures would help us to understand more about the structures and electronic properties of the C_{20} cage and the possible ring structures. In this paper, we investigate the structures, stabilities and electronic properties of C_{20}-rings using the self-consistent field molecular orbital (SCF-MO) method and compare the results with those of C_{60} and C_{36} rings. Four symmetries D_{ab}, D_{ac}, C_{nh} and C_{nh} are considered for the C_{20}-rings here.

2. Construction of C_{20}-Rings and Computation Details

We have constructed a series of C_{20}-rings with D_{ab}, D_{ac}, C_{nh} and C_{nh} symmetries using the same method used for those C_{60} and C_{36} rings. Similarly, we can build a reference frame for a ring composed of n C_{20} cages with D_{ab} symmetry as shown in Fig. 1. The center of the Ih C_{20} cage O is set as the origin point, the Z-axis is vertical to the ring (XY) plane. If the C_{20} cages rotate 30^\circ around X-axis, a D_{a} ring will appear. If the cages rotate 30^\circ around Y-axis, a C_{nh} structure is obtained. If the cages rotate 30^\circ around Z-axis, a C_{nh} ring will be formed. Adjacent C_{20} cages in the ring will form intercage bonds through carbon atoms situated on their adjacent faces and the connected area will move on the surface of the C_{20} cages with the change of the ring size. Likewise the possible bonding area on the C_{20} cages defines a “bonding-belt”. The five bonding-belts for constructing the C_{20}-rings are shown in Fig. 2. The size of the C_{20}-rings is considered from three to eight (n = 3–8).

We denote the C_{20}-rings as followings: <Bonding-belt> - <linking pattern described by indices of bonding atoms in bonding-belts>. For example, the ring C_{6v}-B-\beta\gamma\delta\varepsilon\delta expresses a C_{6v} ring that consists of six C_{20} cages and the connection between adjacent C_{20} cages is through two C_{5} bond, one C_{gamma}-C_{gamma} bond, and two C_{delta}-C_{delta} bonds on C_{6v}-B bonding-belt. Since C_{nh} rings contain the intercage bonds of C_{gamma}-C_{gamma} and C_{alpha}-C_{alpha}, we use two Greek letters to describe these intercage bonds. For example, there are two C_{beta}-C_{gamma} bonds and one C_{alpha}-C_{alpha} bond in the ring C_{5y}-C_{gamma}-\gamma-\alpha_{0}.

The structures and electronic properties of C_{20}-rings are calculated using the ab initio Hartree-Fock (HF) method at 3-21G level with fully geometric optimization and the GAMESS package. From the viewpoint of the time

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Fig. 1 Reference frame for C_{20}-rings of D_{ab} symmetry.
3. Results and Discussion

3.1 Stability and geometric configuration

The $C_{20}$-rings are constructed by forming intercage bonds on the bonding-belts shown in Fig. 2 between adjacent $C_{20}$ cages. The full optimization gives twenty-nine stable ring structures. Among these optimized ring structures, there are six $D_{ab}$ rings, eleven $D_n$ rings, six $C_{nv}$ rings, and six $C_{nh}$ rings, respectively. The binding energy per $C_{20}$ cage related to a single $C_{20}$ with $I_h$ symmetry is defined as

$$E_b = E(C_{20})_b / n - E_{C_{20}}$$

Here $E(C_{20})_b$ is the energy of the $C_{20}$-rings, and $E_{C_{20}}$ is the energy of the single $C_{20}$ cage calculated with the same method. The formation of the $C_{20}$-rings is favorable to the stability of the systems when $E_b$ is less than zero. The calculated results are listed in Table 1. From Table 1, we can see that the intercage bond lengths between adjacent $C_{20}$ cages are in the range of 1.450–1.644 Å. Accordingly, the rings can be considered as covalent $C_{20}$ oligomers, similar to $C_{60}$-rings and $C_{36}$-rings. The binding energies of all the rings except for the $C_{60}$-$C_{60}$ and $C_{70}$-$C_{70}$ are less than zero, namely most of the systems become more stable after the formation of the ring structures. This indicates that the $C_{20}$ cages, indeed, have a tendency to form intercage bonds from a view of thermodynamics. Since the $C_{20}$ cage is smaller, the number of rings with the highest symmetry $D_{ab}$ is much less than those of $C_{60}$-rings and $C_{36}$-rings. Figure 3 shows the most stable $C_{20}$-ring structures for different symmetries. It can be seen that the size of the most stable rings is different for different symmetries. The most stable rings with lower symmetries ($C_{nv}$ and $C_{nh}$) are three-member rings, but the corresponding $D_{ab}$ and $D_n$ rings are seven-member and five-member structures respectively. It seems that the most stable $C_{20}$-rings with higher symmetries are favorable to the structures with larger size.

From the binding energies of the rings, we can find that the rings with $C_{nh}$ symmetry have the lowest stability whose binding energy averages 2.831 eV higher than the others, and the energy differences of rings among the other three symmetries ($D_{ab}$, $D_n$ and $C_{nv}$) are small. In fact, for $C_{nh}$ rings, the intercage bonds are not parallel to the ring plane before optimization but become parallel after the formation of stable rings, which is different from those in the $D_{ab}$, $D_n$ and $C_{nv}$ rings and thus leads to larger distortion of the $C_{20}$ cage and higher energy structures. Thus the symmetry of the ring structures has something to do with the stability of $C_{20}$-rings, since different symmetries cause different degrees of structure distortion.

The change of the strain energy is an important factor for the stabilities of $C_{20}$-rings. To estimate the distortion strain, a parameter $\sigma$ has been suggested and successfully applied to the fullerene rings. Likewise, as shown in Fig. 1, we build a ball which touches every vertex on the $C_{20}$ cage. The tangent plane of the ball, $\alpha_n$, is perpendicular to line $OO'$ where $O$ and $O'$ is the center of the two adjacent balls, respectively. $P_n$ is the tangent point and $T$ is the position of a possible bonding atom on the bonding-belt. $TQ$ is the vertical distance from the possible bonding atom to $\alpha_n$. Then the parameter $\sigma$ can be expressed by

$$\sigma = \sqrt{\frac{\sum (TQ - \bar{T}Q)^2}{m}}$$

where $m$ is the number of $TQ$. More detailed description of eq. (2) is in Ref. 5). Larger $\sigma$ reflects greater strain, higher energy and lower stability, and vice versa. Hence, the smaller value of $\sigma$ is favorable to the construction of the $C_{20}$-ring. We also like to point out that the calculation of parameter $\sigma$ is only dependant on the structure of a single undistorted $C_{20}$ cage, the linking pattern and the ring size, and need not to have the optimized ring structures. Figure 4 shows the relation of the binding energies of $C_{20}$ rings and the standard deviation parameter $\sigma$. With the same linking pattern, the binding energies of most $C_{20}$-rings increase with the increasing of the $\sigma$ values, even some are nearly linear functions of their $\sigma$ values. This demonstrates that the parameter $\sigma$ can also be used to estimate the relative stability of the $C_{20}$-rings with the same linking pattern. Thus the change of strain always has an important impact on the stability of the ring structures consisting of fullerene cages.
The optimized bond lengths of the single \( I_h \) \( C_{20} \) cage are all equal to 1.447 Å. After formation of the rings, the intracage bonds related to the bonding atoms (C-C\_bonding) are elongated, which leads to the distortion of the cage. It seems that

![Fig. 3 Structures of the most stable \( C_{20} \)-rings for each symmetry (\( D_{2h}, D, C_{3v}, C_{3h} \)).](image)

![Fig. 4 \( E_b \sim \sigma \) distribution. The numbers are the size of rings.](image)
the more unstable rings have longer C-C\textsubscript{bonding} lengths. For example, the C-C\textsubscript{bonding} lengths of the most unstable C\textsubscript{6h}-β-\textgamma-\alpha\alpha' ring are 1.613–1.637 Å, and at least there is one C-C\textsubscript{bonding} bond longer than 1.583 Å for relatively more unstable rings. These indicate that the C-C\textsubscript{bonding} bonds for more unstable C\textsubscript{20}-rings are easier to be broken than those in more stable ones. In other words, the C\textsubscript{20} cages seem to be disrupted more easily for rings with higher energy.

Previous studies\textsuperscript{8,14} show that the open C\textsubscript{20} cage polymers with broken intracage bonds are most stable among the C\textsubscript{20} linear oligomers, 1D polymers and 3D solid-state structures. And Miyamoto \textit{et al.}\textsuperscript{9} also showed that the simple-cubic-like condensed phase with opened C\textsubscript{20} cages is stable. However the situation is different in the C\textsubscript{20}-rings. The rings with closed intracage bonds are relatively more stable, but the two energetically unfavorable rings have broken intracage bonds. The intracage γ-\nu bonds (see Fig. 2, C\textsubscript{20} bonding-belt) in the most unstable C\textsubscript{6h}-β-\textgamma-\nu-α\alpha' are broken and elongated to 2.791 Å after formation of the rings. This is a distinct difference between the ring structures and the 1D or 3D polymers composed of C\textsubscript{20} cages. In addition, energetically favorable 3D solid-state structure\textsuperscript{35} forms intercage bonds similar to the C\textsubscript{6h}-C\textsubscript{3v} intercage bonds on D\textsubscript{nh} bonding-belt in Fig. 2, but only C\textsubscript{6n}-C\textsubscript{3v} intercage bonds can be obtained by our optimization for the D\textsubscript{nh} C\textsubscript{20}-rings, except for the smallest D\textsubscript{3h} ring. The bonding characters are quite different between the C\textsubscript{20}-rings and the 1D, 3D C\textsubscript{20} polymers.

3.2 Electronic properties

The calculated energy levels and irreducible representation of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), as well as the energy gaps (E\textsubscript{g}) between them, are listed in Table 2 for the C\textsubscript{20}-rings studied. It can be seen that the HOMOs of most C\textsubscript{20}-rings are lower than that of the single C\textsubscript{20} cage from 0.180 eV to 1.336 eV with only four exceptions, leading to a decreasing of the ability to lose electrons in these systems.

But the changes of LUMO levels are not as consistent, though more than half are higher than that of the single C\textsubscript{20} cage. Moreover, the energy gaps for most of the rings obviously become larger compared with that of the single C\textsubscript{20} cage, which is similar to the case in D\textsubscript{nh} C\textsubscript{36}-rings\textsuperscript{60} but contrary to the C\textsubscript{60}-rings\textsuperscript{59} and the D\textsubscript{3d} C\textsubscript{36}-rings.\textsuperscript{7} A larger energy gap may be favorable to the kinetic stability for the systems. Besides, the two most unstable C\textsubscript{6h}-β-\textgamma-β-α\nu\alpha' and C\textgammah-α\nu\alpha'\nu\nu rings have the smallest energy gaps, hence the two rings are not favorable to both thermodynamic and kinetic stabilities. We notice that the energy gap has some relation to the thermodynamic stability for all the C\textsubscript{20}-rings. The energy of the C\textsubscript{20}-rings decreases with the increase of energy gap for the same linking patterns. Thus it seems that higher thermodynamic stability is accompanied with higher kinetic stability for the C\textsubscript{20}-rings. In addition, it can also be found that the doubly degenerate frontier orbitals exist in the rings with not only odd numbers of C\textsubscript{20} cages but also even numbers. This is similar to the situation of the D\textsubscript{nh} C\textsubscript{36}-rings, but different from that of the C\textsubscript{60}-rings and D\textsubscript{3d} C\textsubscript{36}-rings among which only odd number rings have doubly degenerate frontier orbitals. Moreover, the energy gaps of energetically unfavorable C\textsubscript{60}-rings and the C\textsubscript{36}-rings are not the smallest ones. Therefore, different fullerene-rings have different characteristics for their electronic properties.

4. Conclusion

Four series of C\textsubscript{20}-rings with D\textsubscript{nh}, D\textsubscript{3h}, C\textsubscript{nv} and C\textsubscript{nh} symmetries are investigated by using the HF SCF-MO method. The calculations show that the formation of the C\textsubscript{20} rings is energetically favorable for most of the systems. It is found that the change of the strain energy plays an important role in the stability of the C\textsubscript{20}-rings. The relative energy change due to the C\textsubscript{20} cages for the C\textsubscript{20}-rings can be estimated by the strain-associated parameter σ which has been successfully used for the C\textsubscript{60}-rings and the C\textsubscript{36}-rings. The most stable ring sizes are different for different
symmetric structures. The electronic properties show that most of the energy gaps of C_{20} rings are larger than that of the single H_{C_{20}} cage, and the change tendency of kinetic stability is in accordance with that of thermodynamic stability for the C_{20} rings with the same linking patterns. Moreover, the degeneracy of the frontier orbital is different from those of C_{60} rings and D_{2d} C_{36} rings.

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