Theoretical Investigations on the Geometrical Structures, Energies, and Electronic Properties of the Heterofullerenes Made of the Smallest Fullerene

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In this paper, the heterofullerenes made of the smallest fullerene, C20 were investigated by quantum chemistry calculations based on density functional theory. The geometrical structures, energies, electronic properties, and the aromaticities of the C19X (X = B, N, O, Al, Si, P, S, Ga, Ge, As, and Se) cages were studied systematically and compared with those of the pristine C20 cage. It is found that the doped cages with different heteroatoms exhibit various structural, electronic, and aromatic properties. Several doping behaviors of the C19X cages are different from those of the C59X cages. These results imply the possibility to modulate the physical properties of heterofullerenes by tuning the sizes of the carbon cages as well as the substitution elements.

Keywords: fullerenes, doping, C20, aromaticity, DFT

1. Introduction

Fullerenes have aroused considerable attention due to the novel structures and properties (1). Because carbon cages smaller than C60 violate the isolated pentagon rule (IPR) (2), small fullerenes with lower stabilities have been synthesized successfully only recent years. Zettl’s group claimed the fullerene C36 was prepared (3). In 2004, Xie et al. (4) successfully synthesized the first C50 derivative, C50Cl10. In 2000, C20 was also produced by Prinzbach and co-workers (5). It is known that C20 is the smallest fullerene with classical structure, and it only contains 12 pentagons and no hexagon is present in the structure, which is different from all other fullerenes (6).

During the last two decades, a great number of studies have been carried out to investigate the structures and physical properties of the carbon cages as well as their derivatives (3–10). Among various nanostructures derived from fullerenes, the heterofullerenes, in which one or more carbon atoms of the cage are substituted by heteroatoms, have especially caught the eyes of the researchers. The heterofullerenes exhibit unique structural, electronic, and nonlinear optical properties due to the existence of the heteroatom, which are considerably different from those of the pure carbon cages (11–17). Therefore, heterofullerenes should be interesting new nanoscaled materials to be expected in the future. However, most of the studies mainly focus on the geometries and ordinary electronic structures of the doped carbon cages made of C60. Up until now a systematic study on the relationship of structure and property for C20-based heterofullerenes by a single approach has not been reported according to our best knowledge. Furthermore, the doped carbon cages are good candidates of materials for hydrogen storage, optical device, and molecular sensor (17–19), and they have become the state-of-the-art research in recent years. Additionally, the heterofullerenes are of prominent importance since they are the building blocks of various polymerized fullerenes structures (13, 15, 16). Thus, in order to achieve a further understanding of structure–property relationship of carbon cages and the derivatives, it is desirable to study heterofullerenes made of C20 cage.

In this paper, we carried out systematic calculations on the heterofullerenes obtained by doping C20 cage with B, N, O, Al, Si, P, S, Ga, Ge, As, and Se atoms using self-consistent
field molecular orbital (SCF–MO) method based on density functional theory (DFT).

2. Models and Computational Methods

The perfect C_{20} cage has I_h symmetry and all 20 carbon atoms are equivalent (6). In the present studies, the initial structures of the heterofullerenes C_{19}X are obtained by only one carbon atom of the C_{20} cage substituted by other atoms. The atom of several main group elements, including III (B, Al, and Ga), IV (Si and Ge), V (N, P, and As), and VI (O, S, and Se) subgroups, are considered as the heteroatom to replace the carbon atom of the C_{20} cage. Thus totally 11 heterofullerenes made of C_{20} cage are investigated in this paper.

The DFT hybrid functional B3LYP method (20) is adopted to calculate C_{19}X cages, because it has become an efficient tool for theoretical studies on fullerene nanostructures (8, 9, 12–14). Both the geometrical optimizations and the electronic property calculations through out this paper are performed using SCF-MO method at 6-31G* level with Gaussian 09 program (21). The unrestricted open shell calculation is adopted for the heterofullerenes with odd electrons. To verify whether these doped cages are local minima on the potential energy surface or not, the vibrational frequency analysis is performed with the same theory of level. The calculated vibrational frequencies for all the cages show no imaginary vibrational frequency, indicating that these doped structures all correspond to the true minima on the potential energy surface.

3. Results and Discussion

3.1 Geometrical Structures

The optimized structures of the C_{19}X (X = B, N, O, Al, Si, P, S, Ga, Ge, As, and Se) and C_{20} cages are shown in Figure 1, and the bond lengths are listed in Table S1 in the supplementary material. The C_{20} cage with the point group of C_{2h} is obtained after the geometrical optimizations. This is due to the Jahn-Teller effect (22), and would lower its energy. To evaluate the sphericity of the cages, the sphericity parameter (SP) is calculated through the equation (23, 24):

$$SP = \left[ \left( \frac{1}{A} - 1 \right)^2 + \left( \frac{1}{A} - 1 \right)^2 + \left( \frac{1}{B} - 1 \right)^2 \right]^{1/2}$$

where A, B, and C are the rotational constants (in GHz) of the corresponding cages. The structure with larger SP value is distorted more away from perfect sphere. SP of C_{20} cage with I_h symmetry will be zero because it has a perfect sphere shape and the three rotational constants A, B, and C are equivalent. Here the calculated SP of the C_{20} with C_{2h} symmetry is 0.122 as shown in Table 1, and thus the obtained C_{20} cage is not a perfect ball. As for the doped cages, the values of SP are in the range of 0.026–1.203, indicating that deformations of the cage are also occurred when the heteroatom is introduced into the pristine cage. It can be seen that SP are less than 0.19 for C_{19}X with X = B, N, and O, while in the range of 0.32–0.54 for X = Al, Si, P, and S. However, the values of SP are even as large as about 1.0 for X = Ga, Ge, As, and Se. These results clearly release the fact that the

![Fig. 1. Geometrical structures of C_{19}X (X = B, N, O, Al, Si, P, S, Ga, Ge, As, and Se) and C_{20} cages.](image)
doped cage with larger heteroatom gives larger SP values and more obvious distortions. This phenomenon can also be found for those of the doped C_{60} cages (25). Thus, we may conclude that the size of the doping atom may play crucial role for the distortions away from perfect sphere for the doped fullerenes from view point of SP results.

The SP mentioned above is calculated based on the rotational property, and we also would like to discuss the distortions of the C_{19}X cages directly from their geometries. Thus the asphericity parameter, ASP, is also adopted to evaluate the geometrical distortion for the doped cages. ASP is introduced by Fowler and can be calculated by (26):

\[ ASP = \sum (R_i - R_0)^2 / R_0^2 \]

where \( R_i \) is the radial distance of atom \( i \) from the cage central of mass, and \( R_0 \) is the average radius. Here the structures with smaller ASP values are more close to a perfect sphere shape. The obtained ASPs are listed in Table 1. It can be seen that the calculated ASP are all nonzero for the heterofullerenes, with the values in the range of 0.005–0.129. This result also conforms the fact that the larger the heteroatom is, the more obvious distortions of the cage away from the perfect sphere.

Then we pay attention to the bond lengths of the heterofullerenes. The six nonequivalent C–C bonds in C_{2h} C_{20} are 1.400, 1.422, 1.443, 1.445, 1.486, and 1.536 Å, respectively, based on our DFT calculations, which agree well with previous results (27). When the carbon cage is doped by the heteroatom, the C–X bonds are presented. From Table S1, it can be seen that the C–X bond lengths are in the range of 1.477–1.987 Å. The C–X bonds are in the range of 1.477–1.686 Å for C_{19}X with \( X = B, N, \) and \( O, \) and vary not very large compared with those in the pristine cage. However, the bond lengths increase obviously for \( X = Al, Si, P, S, Ga, Ge, As, \) and Se, ranking from 1.839 to 1.987 Å. Thus, the C–X bond lengths increase more significantly for the larger heteroatoms.

These results also agree with our SP and ASP analyses as well as the previous studies of the C_{60} doped cages (25). Now we focus on the C–C bonds in the doped fullerenes. As shown in Table S1, the C–C bonds exhibit slight changes, with the lengths in the range of 1.381–1.534 Å. Moreover, it is also can be seen that the C–C bond lengths change more significantly near the region of the heteroatom, but almost inert in the region away from the heteroatom.

The \( \pi \)-electrons are of great significance for the nonplanar conjugated molecules (28). On the basis of the fact, the poibital axis vector (POAV) analysis (29) was usually performed to study these aromatic systems with distortions as shown in Figure 2. According to the POAV theory, the pyramidization angle \( \theta_p \) is defined as:

\[ \theta_p = (\theta_{\pi\pi} - 90) = (180 - \theta - 90) = \pi - \theta \]

Here, we use the solution method we developed to perform the POAV analysis (30). The angle \( \theta \) can be obtained by

\[ \theta = \arccos \left( \frac{j(x_a - x_o) + m(y_a - y_o) + n(z_a - z_o)}{\sqrt{(x_a - x_o)^2 + (y_a - y_o)^2 + (z_a - z_o)^2}} \right) \]
where

\[
\begin{align*}
    l &= \frac{a_2 b_3 - a_3 b_2}{\sqrt{(a_2 b_3 - a_3 b_2)^2 + (a_1 b_1 - a_3 b_3)^2 + (a_1 b_2 - a_2 b_1)^2}}, \\
m &= \frac{a_1 b_1 - a_2 b_2}{\sqrt{(a_2 b_3 - a_3 b_2)^2 + (a_1 b_1 - a_3 b_3)^2 + (a_1 b_2 - a_2 b_1)^2}}, \\
n &= \frac{a_1 b_3 - a_3 b_1}{\sqrt{(a_2 b_3 - a_3 b_2)^2 + (a_1 b_1 - a_3 b_3)^2 + (a_1 b_2 - a_2 b_1)^2}}.
\end{align*}
\]

The values of \(a_1, a_2, a_3, b_1, b_2, \) and \(b_3\) can be obtained by:

\[
\begin{align*}
    a_1 &= \sqrt{(x_b - x_o)^2 + (y_b - y_o)^2 + (z_b - z_o)^2(x_a - x_o)} \\
    &\quad - \sqrt{(x_a - x_o)^2 + (y_a - y_o)^2 + (z_a - z_o)^2(x_b - x_o)}, \\
    a_2 &= \sqrt{(x_b - x_o)^2 + (y_b - y_o)^2 + (z_b - z_o)^2(y_a - y_o)} \\
    &\quad - \sqrt{(x_a - x_o)^2 + (y_a - y_o)^2 + (z_a - z_o)^2(y_b - y_o)}, \\
    a_3 &= \sqrt{(x_b - x_o)^2 + (y_b - y_o)^2 + (z_b - z_o)^2(z_a - z_o)} \\
    &\quad - \sqrt{(x_a - x_o)^2 + (y_a - y_o)^2 + (z_a - z_o)^2(z_b - x_o)}, \\
b_1 &= \sqrt{(x_c - x_o)^2 + (y_c - y_o)^2 + (z_c - z_o)^2(x_a - x_o)} \\
    &\quad - \sqrt{(x_a - x_o)^2 + (y_a - y_o)^2 + (z_a - z_o)^2(x_c - x_o)}, \\
b_2 &= \sqrt{(x_c - x_o)^2 + (y_c - y_o)^2 + (z_c - z_o)^2(y_a - y_o)} \\
    &\quad - \sqrt{(x_a - x_o)^2 + (y_a - y_o)^2 + (z_a - z_o)^2(y_c - x_o)}, \\
b_3 &= \sqrt{(x_c - x_o)^2 + (y_c - y_o)^2 + (z_c - z_o)^2(z_a - z_o)} \\
    &\quad - \sqrt{(x_a - x_o)^2 + (y_a - y_o)^2 + (z_a - z_o)^2(z_c - x_o)}.
\end{align*}
\]

where \(O(\text{x}_o, \text{y}_o, \text{z}_o)\), \(A(\text{x}_a, \text{y}_a, \text{z}_a)\), \(B(\text{x}_b, \text{y}_b, \text{z}_b)\), and \(C(\text{x}_c, \text{y}_c, \text{z}_c)\), respectively, are the coordinates of the conjugated atom (\(O\)) and its three attached atoms (\(A\), \(B\), and \(C\)). Using the relation of equations above, we can get the pyramidalization angle \(\theta_p\) of the heteroatoms of the doped cages. The detailed descriptions can be seen from our previous studies (30). From Table 1, we can see that \(\theta_p\) are in the range of 22.81–41.19°. Thus, \(\theta_p\) of the heteroatoms in the doped cages are all increased, except for C\(_{19}\)B, which is decreased about 0.1°. For a comparison, the POAV of doped C\(_{60}\) cages are also calculated with the same method. The results show that POAV of carbon atoms in C\(_{60}\) is 11.64° and those for the heteroatoms in C\(_{59}\)X (X = B, N, Al, Si, P, Ga, Ge, and As) cages are in the range of 13.16–35.32°. Thus all the heteroatoms exhibit larger POAV angle than carbon atom in the doped cages made of C\(_{60}\), including the boron doped C\(_{60}\) cage. This is different from those of the boron doped C\(_{20}\) cages. Thus, the size of the cage may also be one of the important facts to the POAV of the doped cage. Nevertheless, it is still can be see that larger heteroatoms usually exhibit larger pyramidalization angles for the heterofullerenes made of both C\(_{20}\) and C\(_{60}\).

### 3.2 Energies and Relative Stabilities

In Table 1, we summarized the obtained electronic energies as well as the energies with the zero-point correction. Furthermore, the cohesive energies (\(E_{\text{coh}}\)) per atom are calculated in order to study the thermodynamic stabilities of the doped cages. Here the system with larger \(E_{\text{coh}}\) is more stable. We can see that \(E_{\text{coh}}\) of C\(_{20}\) is calculated to be 6.148 eV/atom. From Table 1 and Figure 3(a), it is found that \(E_{\text{coh}}\) of the heterofullerene cages is in the range of 5.886–6.165 eV/atom. The \(E_{\text{coh}}\) of the doped cages are all slightly smaller than that of the pristine cage, except for C\(_{19}\)N, for which \(E_{\text{coh}}\) is increased by 0.017 eV/atom. Thus the thermodynamic stability of the doped cages here is increased for nitrogen atom while are decreased for other heteroatoms compared with that of the C\(_{20}\) cage. To get a further understanding of the doping behavior of fullerenes with different sizes, \(E_{\text{coh}}\) of the doped C\(_{60}\) cages are also calculated with the same method. The obtained \(E_{\text{coh}}\) of the doped cages are all smaller than that of C\(_{60}\), indicating the lower thermodynamic stabilities of the doped C\(_{60}\) than that of pristine C\(_{60}\). This is different from the nitrogen doped C\(_{20}\). Thus, the doping behaviors of the C\(_{20}\) are not always the same as those of the C\(_{60}\) cage due to its high strain and novel structure.

**Fig. 3.** The obtained \(E_{\text{coh}}\) and \(\Delta E\) of the doped and pristine C\(_{20}\) cages. (a) \(E_{\text{coh}}\) and (b) \(\Delta E\).
If we regard the formation of the C$_{19}$X cage as the following reaction:

$$C_{20} + X = C_{19}X + C$$  \hspace{1cm} (7)

Then the energy difference of the above process, $\Delta E$, can be calculated by:

$$\Delta E = E(C_{19}X) + E(C) - E(C_{20}) - E(X)$$  \hspace{1cm} (8)

where $E(C_{19}X)$ and $E(C_{20})$, respectively, are the energies of C$_{19}$X and C$_{20}$ cage with the minimum structures, while $E(C)$ and $E(X)$ are energies of a carbon atom and heteroatom, respectively. It is noted that all the species in the equation here are considered as in the gas phase. The results are listed in Table 1 and Figure 3(b).

We can see that $\Delta E$ of the doped cages are all positive except for C$_{19}$N with $\Delta E$ of $-0.352$ eV. This indicates that it is an exothermic process for C$_{19}$N, but the formations of other doped cages are endoergic. Thus it is energetically favorable to form the C$_{19}$N cage from viewpoint of total energy change. We also calculated $\Delta E$ of C$_{59}$N, and the value is 0.393 eV. This indicates that the formation of C$_{59}$N is endoergic. This may come from two reasons. One is that C$_{60}$ is IPR fullerene, while C$_{20}$ only contains pentagons, thus C$_{20}$ exhibits more distortions than C$_{60}$. The other is that the C–N bond length is more close to that of the C–C bond compared with those of other C–X bonds according to the bond lengths listed in Table S1. As a matter of fact, the C$_{19}$N has been observed in the experiments (31).

The obtained $\Delta E$s are in the range of $-0.352$ to 5.242 eV for the heterofullerenes studied in this paper. From Figure 3(b), we can see that the curves of $\Delta E$ are just reversed compared with those of $E_{coh}$. Thus, we may conclude that the formation of the doped cage with smaller heteroatom is energetically more favorable according to the results of both the total energy change and the cohesive energy.

### 3.3 Electronic Properties

It is well-known that the frontier orbitals are very crucial in chemical reaction for the reactant molecule, thus, the frontier orbital analysis of the doped cages is necessary. In Table 2, we listed the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels of the heterofullerenes made of C$_{20}$ cage. It can be seen that HOMO levels of the doped cages are all increased compared with that of C$_{20}$, except for C$_{19}$O and C$_{19}$Ge. Thus the abilities to lose electrons are enhanced for most doped cages according to the Koopmans’ theorem. As for LUMO levels, they are decrease by 0.46–1.27 eV when doping with O, Si, Ga, and Ge atoms, but nearly unchanged for doping with other atoms compared with that of the pristine cage.

Figure 25 in supplementary material shows the distributions of HOMO and LUMO for the cages studied in this paper. From the distributions of the HOMO and LUMO, we can predict the nucleophilic and electrophilic sites of the molecules, respectively. It can be seen that all the heteroatoms contributed very little to the HOMO of the doped cages, indicating that the heteroatom is not the nucleophilic site of the doped cages. However, there are obvious localizations original from the heteroatoms for LUMO of the C$_{19}$Al, C$_{19}$Si, C$_{19}$Ga, and C$_{19}$Ge. Thus the heteroatoms would play important roles in the electrophilic reaction for these four doped cages.

We all know that besides the thermodynamic stability, the kinetic stability also has crucial influence on the relative abundances of different fullerene structures. Aihara has pointed out that higher kinetic stability is usually related with a larger HOMO-LUMO energy gap ($E_g$) (32), because exciting electrons from a low HOMO to a high LUMO is energetically unfavorable, which would be necessary to activate a reaction. The calculated $E_g$ of the doped cages are listed in Table 2. It can be found that all the doped cages present smaller $E_g$ than that of C$_{20}$ cage. Thus kinetic stability of the cage is decreased by substitution from viewpoint of HOMO-LUMO gap. We are also aware that $E_g$ of C$_{19}$Al C$_{19}$Si, C$_{19}$Ga, and C$_{19}$Ge cages are all within 1.0 eV, and much smaller than other cages. Thus observations of the four doped cages may be more difficult than other doped cages studied here.

### 3.4 Aromaticity and Nuclear Independent Chemical Shift

Aromaticity is a concept in chemistry with great significance. The aromaticity can be evaluated by using the nuclear independent chemical shift (NICS), which has proven to be a simple and efficient aromaticity probe (33–35). In this paper the NICS of the cages is defined as the negative of the isotropic magnetic shielding constant of a ghost atom located at the central of the cage. Negative NICS value means the aromaticity of the cage. In this study, the NICS values listed in Table 2 is computed with the gauge-including atomic orbital (GIAO) method at B3LYP/6-31G* theory level. NICS of C$_{20}$ we obtained is $-19.5$, which indicates the obvious aromaticity of C$_{20}$ and also agrees with previous DFT calculations.

| Cage | HOMO | LUMO | $E_g$ | NICS |
|------|------|------|------|------|
| C$_{19}$B | $-4.801$ | $-3.157$ | $1.644$ | $-28.049$ |
| C$_{19}$Al | $-4.406$ | $-3.413$ | $0.993$ | $-15.316$ |
| C$_{19}$Ga | $-4.517$ | $-3.570$ | $0.948$ | $-17.151$ |
| C$_{20}$ | $-5.055$ | $-3.110$ | $1.946$ | $-19.429$ |
| C$_{19}$Si | $-5.022$ | $-4.243$ | $0.779$ | $-35.336$ |
| C$_{19}$Ge | $-5.084$ | $-4.406$ | $0.678$ | $-18.031$ |
| C$_{19}$N | $-4.861$ | $-3.280$ | $1.581$ | $-16.784$ |
| C$_{19}$P | $-4.951$ | $-3.223$ | $1.728$ | $-30.933$ |
| C$_{19}$As | $-4.626$ | $-3.124$ | $1.502$ | $-15.717$ |
| C$_{19}$O | $-5.301$ | $-3.785$ | $1.516$ | $-16.508$ |
| C$_{19}$S | $-4.759$ | $-3.080$ | $1.679$ | $8.632$ |
| C$_{19}$Se | $-4.654$ | $-3.010$ | $1.644$ | $4.239$ |

Notes: HOMO, LUMO, and $E_g$ in eV.
4. Conclusion

Systemic studies based on DFT calculations have been performed to investigate the heterofullerenes made of the smallest fullerene, C_{20} in this paper. The main group elements, including III (B, Al, and Ga), IV (Si and Ge), V (N, P, and As), and VI (O, S, and Se) subgroups, are considered as the heteroatoms to form the C_{19}X cages. The geometrical structures, relative stabilities, electronic properties, and the aromaticities of the doped cages were discussed and compared with the pristine cage to achieve a further understanding of structure–property relationship of the doped cages. It is found that the hybrid cages undergo some distortions due to the substitution of the heteroatoms. The thermodynamic stabilities of the heterofullerenes are all decreased, except for C_{19}N. C_{10}X cage with smaller heteroatom is more stable. The abilities to lose electrons are enhanced for most doped cages according to the Koopmans’ theorem based on the results of HOMO energy levels. The heteroatoms would play important roles in the electrophilic reaction for C_{19}Al, C_{19}Si, C_{19}Ga, and C_{19}Ge since there are obvious localizations original from the heteroatoms for their LUMO. It is also found that all the doped cages present smaller $E_g$ than that of C_{20} cage. The calculated NICS indicates that all the doped cages in this paper give negative NICS, except for C_{19}S and C_{19}Se, and the two doped cages are anti-aromatic heterofullerenes.

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