(C≡C≡C≡C)@C_{60}: A Bonding C_{60}-Endohedral Molecular Allotrope of Carbon

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ABSTRACT: The allotropes of carbon have been the focus of attention in recent years. In this work, we reported a molecular allotrope of carbon, (C≡C≡C≡C)@C_{60}. The smallest vibrational frequency is 226.0 cm\(^{-1}\), which confirms that (C≡C≡C≡C)@C_{60} is a minimum on the potential energy hypersurface. Its geometry, NMR diagram, IR spectrum, heat of formation, and bonding interactions have been predicted using the density functional theory (DFT) method at the B3LYP/6-311G(d) level of theory. Since there must be a large family of the fullerene−endohedral allotropes of carbon, the research studies on these allotropes of carbon will open an avenue for allotropes of carbon.

1. INTRODUCTION

Since the characterization of cyclocarbon molecule C\(_{18}\) by high-resolution atomic force microscopy\(^{1}\), the allotropes of carbon have become one of the exciting topics for chemists.\(^{2}\) Among the known allotropes of carbon, diamond and T-carbon\(^{3}\) consists exclusively of 4-coordinate carbon atoms. Fullerences\(^{4}\), carbon nanotubes\(^{5}\), and graphene\(^{6}\) are entirely made up of 3-coordinate carbon atoms. Cyclocarbons have only 2-coordinate carbon atoms. Graphdiyne\(^{7}\) is composed of 2- and 3-coordinate carbon atoms. Cyclocarbons have only 2-coordinate carbon atoms. Graphdiyne\(^{7}\) is composed of 2- and 3-coordinate carbon atoms. Is there any molecular allotrope of carbon with three or more kinds of coordinate carbon atoms? To answer this question, the design of a molecular allotrope of carbon with three kinds of coordinate carbon atoms is the goal of this work.

The molecular allotropes of carbon that have been characterized are the fullerenes\(^{8}\) and cyclocarbon C\(_{18}\)^{1}. Fullerences, C\(_{60}\), C\(_{70}\), C\(_{84}\), and a variety of related species, have cage-like shapes resembling geodesic domes. A great number of compounds of fullerenes, not only the groups attached to the outside of cages but also small atoms or molecules trapped inside cages, have been reported. The fullerenes encapsulated atoms or molecules inside the carbon cages are called endohedral fullerenes. Endohedral fullerene is expressed using the notation M\(_n\)@C\(_m\), where M is the encapsulated atoms or molecules, and the subscripts n and m represent the number of carbon atoms of a fullerene molecule and atoms or molecules inside the cage, respectively. Endohedral fullerene C\(_n\)@C\(_m\), where C\(_n\) is a group with n carbon atoms bonding to the atoms on the surface of the fullerene cage, will be a novel molecular allotrope of carbon. Since C\(_{60}\) is the prototypical fullerene, we designed a bonding C\(_{60}-\)endohedral molecular allotrope: (C≡C≡C≡C)@C\(_{60}\) with a group C≡C≡C≡C using carbon atoms of two ends to bond to four carbon atoms of two C−C bonds at the fusion of hexagon−hexagon in C\(_{60}\). (C≡C≡C≡C)@C\(_{60}\) is a novel molecular allotrope of carbon with 2-, 3-, and 4-coordinate carbon atoms. Because fullerences are a series of cage-like molecules, we think that the investigation of the bonding fullerene−endohedral allotropes will open an avenue for studies of molecular carbon allotropes. Here, the word “bonding” means that the group inside the cage forms the bonding interactions with atoms on the surface of the fullerene cage.

When the fragment of C≡C≡C≡C was trapped in the cage of C\(_{60}\), (C≡C≡C≡C)@C\(_{60}\) could be obtained. In the
preparation of fullerenes, this allotrope of carbon might be obtained. The key is characterization and separation. We think that the other potential fabrication pathways to prepare the allotrope of carbon are the gas-phase collisions and the formation of fullerene—endohedral complexes.8

2. RESULTS AND DISCUSSION

2.1. Geometries and Electronic Properties. Geometry and properties of (C≡C≡C≡C)@C60 have been computed using the density functional theory (DFT) method at the B3LYP/6-311G(d) level of theory. To verify whether the B3LYP/6-311G(d) level of theory is suitable for research of fullerene-like molecules or not, C60 was optimized first at the B3LYP/6-311G(d) level of theory. Bond lengths at the fusion of hexagon—hexagon and pentagon—hexagon are 0.1392 and 0.1451 nm, respectively, and correspond to the experimental values."Thus, the DFT method at the B3LYP/6-311G(d) level of theory is appropriate for studying fullerenes and their derivatives. The symmetry of (C≡C≡C≡C)@C60 converged at D2h after the optimization at the B3LYP/6-311G(d) level of theory. Based on the B3LYP/6-311G(d) geometry, the vibrational frequencies of (C≡C≡C≡C)@C60 have been calculated at the same level of theory. Its smallest vibrational frequency is 226.0 cm⁻¹, which confirms that it is a minimum on the potential energy hypersurface. Its structure with key parameters at the B3LYP/6-311G(d) level of theory is shown in Figure 1.

Figure 1. (C≡C≡C≡C)@C60’s structure with bond lengths (Å).

Since (C≡C≡C≡C)@C60 reserves the cagelike structure of C60, the number of pentagons and hexagons on the surface of the cage are the same as C60. In contrast to C60, the environments of pentagons are different, and the same is true for hexagons. Three different environments of pentagons and four of hexagons are present in (C≡C≡C≡C)@C60. There are 11 different carbon environments and 17 different C—C bonds (see Figure 1). The shortest bond length of the C10—C11 bond, formed by two different endohedral carbon atoms C10 and C11, is 1.2461 Å and the longest bond length of the C1—C10 bond, formed by the 4-coordinate carbon C1 and endohedral C10, is 1.5579 Å.

The net atomic charges in (C≡C≡C≡C)@C60 were gained using the Weinhold’s NBO procedure.10 The largest negative net charges (q/e = -0.150) are on C11 and its equivalent atoms, and the largest positive net charges (q/e: 0.111) are on C10 and its equivalent atoms. Apart from the C10, C11, and their equivalent atoms, the other carbon atoms at the cage surface of (C≡C≡C≡C)@C60 molecule have very little net charges, arranging from ~0.045e to 0.040e.

Table 1. Some Properties of (C≡C≡C≡C)@C60 and C60 at the B3LYP/6-311G(d) Level of Theory

| properties          | C60       | (C≡C≡C≡C)@C60 |
|---------------------|-----------|---------------|
| E /a.u.             | -2286.589826 | -2438.572595  |
| E_HOMO /eV          | -6.39 (H_u) | -5.44 (H_u)   |
| E_LUMO /eV          | -3.66 (T_mB) | -3.98 (T_mB)  |
| ΔE_L−H /eV          | 2.73      | 1.46          |
| point group         | 4 1    | D2h           |
| electronic state    | 1A_g    | 1A_g          |
| ν_min (cm⁻¹)        | 265.6    | 226.0         |
| ZPE /kJ mol⁻¹       | 982.2    | 1022.4        |

“E is the total energy of the molecule computed at the B3LYP/6-311G(d) level of theory. The orbital symmetry of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) is given in parentheses. ΔE_L−H is the energy gap between HOMO and LUMO. ν_min is the smallest vibrational frequency of the molecule, its unit is cm⁻¹. ZPE is the zero-point vibrational energy determined at the same level, and the values were not scaled.

The potential of (C≡C≡C≡C)@C60 is lower than that of C60 but the electron affinity is larger than that of C60. Thus, (C≡C≡C≡C)@C60 would draw electrons more strongly than C60. As we know, C60 could form a charge-transfer complex with an electron donor.11 According to the equation of McConnell-Hoffmann-Metzger,12 with electron donor (C≡C≡C≡C)@C60 would form a charge-transfer complex with higher conductivity. This is one of the applications of (C≡C≡C≡C)@C60.

Figure 2 shows frontier orbitals, HOMO and LUMO, of (C≡C≡C≡C)@C60. Since the σ bond of C1—C10 and its equivalent bonds are weak (Table 2), it could be seen that the HOMO possesses predominantly character of these bonds (Figure 2). As for the LUMO, it possesses more character of atoms around C1 and its equivalent sites because of these atoms with positive charges. The HOMO—LUMO gap is related to the stability of the molecule. A large HOMO—LUMO gap has long been recognized as being related to the kinetic and structural stability, while a small gap is associated with instability and reactivity.13—15 According to the HOMO—LUMO gaps in Table 1, (C≡C≡C≡C)@C60 is less stable than C60.
According to the gauge-including-atomic-orbital (GIAO) method, the 13C NMR chemical shifts have been calculated using the Gaussian 09 program for future experimental identification by NMR. The 13C NMR chemical shift can be calculated according to the formula \( \delta = \sigma_{\text{iso}}^{\text{TMS}} - \sigma_{\text{iso}}^{\text{sample}} \), where \( \sigma_{\text{iso}}^{\text{TMS}} \) and \( \sigma_{\text{iso}}^{\text{sample}} \) are the \( \sigma_{\text{iso}} \) of (C=C=C=C=C@C60)@C60 and the reference tetramethysilane (TMS), respectively. Since the symmetry of (C=C=C=C=C@C60) is D2d, it has 11 13C NMR signals; the results are shown in Figure 4.

### Table 2. Electron Density \( \rho(r_c)/(e\cdot\text{bohr}^{-3}) \), Laplacian of Electron Density \( \nabla^2 \rho(r_c)/(e\cdot\text{bohr}^{-3}) \), Total Electronic Energy Density \( E_{\text{el}}(r_c)/(\text{hartree}\cdot\text{bohr}^{-3}) \), and the Ellipticity \( \epsilon \) of BCPs in (C=C=C=C=C@C60) and Cyclopropane at the B3LYP/6-311G(d,p) Level of Theory

| bond          | \( \rho(r_c) \)  | \( \nabla^2 \rho(r_c) \) | \( E_{\text{el}}(r_c) \) | \( \epsilon \) |
|---------------|------------------|--------------------------|---------------------------|-----------------|
| C1–C1'        | 0.2595           | -0.5668                  | -0.2302                   | 0.2756          |
| C1–C2         | 0.2624           | -0.6331                  | -0.2343                   | 0.1126          |
| C1–C10        | 0.2088           | -0.2306                  | -0.1543                   | 0.6643          |
| C2–C3         | 0.3010           | -0.7981                  | -0.3002                   | 0.2206          |
| C2–C7         | 0.2812           | -0.7038                  | -0.2616                   | 0.1659          |
| C3–C4         | 0.2893           | -0.7438                  | -0.2768                   | 0.1915          |
| C4–C5         | 0.2952           | -0.7790                  | -0.2888                   | 0.1987          |
| C4–C9         | 0.2753           | -0.6844                  | -0.2503                   | 0.1444          |
| C5–C5'        | 0.2771           | -0.6952                  | -0.2535                   | 0.1406          |
| C5–C6         | 0.2810           | -0.7069                  | -0.2609                   | 0.1669          |
| C6–C7         | 0.3036           | -0.8213                  | -0.3054                   | 0.2134          |
| C6–C8         | 0.2771           | -0.6952                  | -0.2535                   | 0.1406          |
| C7–C7'        | 0.2639           | -0.6212                  | -0.2295                   | 0.1558          |
| C8–C8'        | 0.3088           | -0.8454                  | -0.3164                   | 0.2246          |
| C9–C9'        | 0.3099           | -0.8548                  | -0.3180                   | 0.2188          |
| C10–C11       | 0.3719           | -1.0472                  | -0.4868                   | 0.1610          |
| C11–C11'      | 0.3449           | -1.0201                  | -0.4122                   | 0.1348          |
| C–C (6–6)     | 0.3082           | -0.8443                  | -0.3150                   | 0.2213          |
| C–C (6–5)     | 0.2786           | -0.7002                  | -0.2565                   | 0.1494          |
| C–C           | 0.2348           | -0.4129                  | -0.1900                   | 0.4862          |

*a*Labels of atoms of (C=C=C=C=C@C60) are shown in Figure 1. The C–C (6–6) and (6–5) bonds are at the fusions of hexagon–hexagon and hexagon–pentagon of C60, respectively. The C=C bond is in cyclopropane.
Figure 5. All CPs and bond paths of (C≡C≡C≡C)@C_{60}. Purple big balls are atoms. Orange, yellow, and green small spheres correspond to bond, ring, and cage CPs. Brown lines denote the bond paths.

respectively, \( n = 64, b = 97, r = 42, \) and \( c = 8 \), they satisfied the Poincaré–Hopf relationship \(^{20}\) 
\[
\sum_{1}^{2} n - b + r - c = 64 - 97 + 42 - 8 = 1.
\]

The properties of bond CPs can be used to characterize bonds to some degree. Because of the \( D_{h} \) symmetry, there are 17 different C–C bonds in (C≡C≡C≡C)@C_{60}. Table 2 lists the properties of all bond CPs of the 17 C–C bonds in (C≡C≡C≡C)@C_{60} and cyclopropane, respectively. According to the data in Table 2, it can be seen that all C–C bonds are typically covalent bonds with a large \( \pi \)-bonding.\(^{22,23}\) Apart from the C1–C1′ bond, the bonding interactions of all other C–C bonds in (C≡C≡C≡C)@C_{60} are similar to the corresponding C–C bonds in C_{60}. In addition, according to the data in Table 2, the strongest C–C bond is C10–C11 and the weakest C–C bond is C1–C10, which are in accordance with the calculated bond lengths in Figure 1. In the substructure of the triangle formed by C1–C1′–C10, the C–C bonds are similar to the C–C bond in cyclopropane, but the C1–C1′ bond is stronger and the C1–C10 (and its equivalent C1′–C10) bond is weaker than the C–C bond in cyclopropane.

3. CONCLUSIONS

In summary, a molecular allotrope of carbon, C_{60}-endohedral: (C≡C≡C≡C)@C_{60}, was studied using the DFT method. Its geometry, NMR diagram, IR spectrum, heat of formation, and bonding interactions were predicted at the B3LYP/6-311g(d) geometry, NMR diagram, IR spectrum, heat of formation, and future challenges.

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors are grateful for the financial support from the Natural Science Foundation of Shandong Province (Grant ZR2011BM022).

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