



## Endohedral complex of fullerene C<sub>60</sub> with tetrahedrane, C<sub>4</sub>H<sub>4</sub>@C<sub>60</sub>

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### ABSTRACT

B3LYP/6–31G(d) hybrid HF/DFT calculations were carried out to determine the structural and electronic properties of the endohedral complex of C<sub>60</sub> with tetrahedrane C<sub>4</sub>H<sub>4</sub>. It was demonstrated that C<sub>4</sub>H<sub>4</sub> was seated in the center of the C<sub>60</sub> cage and existed in a molecular form inside the fullerene. The formation of this complex was endothermic with inclusion energy of 141.05 kcal/mol. C<sub>4</sub>H<sub>4</sub> endohedral doping slightly perturbed the molecular orbitals of C<sub>60</sub>. The calculated HOMO–LUMO gaps, the electron affinity (EA) and the ionizational potential (IP) indicated that C<sub>4</sub>H<sub>4</sub>@C<sub>60</sub> seemed to be more kinetically reactive than C<sub>60</sub>. The IR active modes and harmonic vibrational frequencies of C<sub>4</sub>H<sub>4</sub>@C<sub>60</sub> were also discussed.

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### 1. Introduction

Since lanthanum atom was firstly placed into the fullerene C<sub>60</sub> cage [1], endohedral fullerenes, the spherical carbon molecules incorporating single atoms [2–5] and noble gases [6–8] or small molecules and clusters [9–11] inside the framework have attracted great interest in their physical and/or chemical properties such as pseudoatom behavior, magnetism, nonlinear optical behaviors, and superconductivity. However, the production rate of the endohedral fullerenes is quite low compared with the ordinary fullerenes. The preparation of endohedral fullerenes has so far relied on hard to control physical processes, such as co-vaporization of carbon and metal atoms [2] or high-pressure/high-temperature treatment with noble gases [7], which yield only limited quantities (e.g., only a few milligrams) of a pure product after laborious isolation procedures. Due to the extreme difficulties in producing macroscopic quantities and isolating pure samples, theoretical studies are helpful tools in investigating and predicting the structural and electronic properties of endohedral fullerenes. For example, theoretical calculations on lanthanum metallofullerene La@C<sub>82</sub> [12,13] suggested that the La atom donated its three valence electrons to C<sub>82</sub> to form an endohedral complex La<sup>3+</sup>C<sub>82</sub><sup>3-</sup>, which was confirmed by electron paramagnetic resonance (EPR) studies [14]. Gauge-independent atomic orbital (GIAO) and the nucleus-independent chemical shift (NICS) calculations for the

encapsulated hydrogen in H<sub>2</sub>@C<sub>60</sub> and its derivatives interpreted well the experimental data [11]. In N@C<sub>60</sub>, P@C<sub>60</sub> and C@C<sub>60</sub>, the N, P and C atoms retain their atomic character when trapped in the cage [4,15–17], while towards encaged small molecules, C<sub>60</sub> acted as a polarizable sphere that stabilized the polar molecules and destabilized the nonpolar ones [18,19].

Tetrahedrane C<sub>4</sub>H<sub>4</sub> (THD) is a theoretically interesting molecule, and the problem of its synthesis was recognized more than half a century ago but only its derivatives had been obtained [20,21]. As a result of the enormous angular strain [22], theoretical works predicted its stability in the absence of other reactants [23], while in the derivatives the lability of THD is circumvented by means of spatial shielding of the tetrahedrane framework by four bulky groups [21]. Since the fullerene cage may act as a partial Faraday cage that shields the atom on molecule trapped inside from the majority of the field applied [4,24], it can be viewed as a nearly ideal “container” or “trap” for any highly reactive complex. Here we study the endohedral complexes of fullerenes C<sub>60</sub> with THD. A question of major interest is whether the fullerene cage can stabilize the trapped tetrahedrane. On the other hand, as tetrahedrane can isomerize to cyclobutadiene [25], we also consider the inclusion of D<sub>2h</sub> cyclobutadiene in the fullerene cage. We hope that the present study will encourage further theoretical and experimental analysis of the system.

### 2. Computational details

Geometry optimizations were performed at the B3LYP/6–31G(d) hybrid HF/DFT level of theory. To ensure that true stationary points had been found, harmonic vibrational frequencies were also

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calculated by analytic evaluation of the second derivative of the energy with respect to nuclear displacement. The B3LYP functional was chosen because the inclusion of electron correlation was important for accurate geometry prediction. Our experiences of theoretical calculations on  $C_{60}$  related derivatives also indicate that DFT is a very successful method for studying fullerene compounds [17,26–29]. All calculations were carried out with the GAUSSIAN 03 program package [30] executed on a SGI Onyx3900 workstation and the results were calculated to machine precision.

### 3. Results and discussions

The B3LYP/6–31G(d) optimized geometries were shown in Fig. 1. Some geometry parameters were listed in Table 1. The bond lengths of  $C_{60}$  are 1.395 and 1.454 Å for the 6/6 and 6/5 bonds respectively. This calculation result agrees satisfactorily with the measured values [31] as well as the results of the previous highest level calculations, MP2 with triple  $\xi$  plus polarization basis set [32].

The optimized bond lengths and bond angles of tetrahedrane with  $T_d$  symmetry are  $r_1 = 1.073$  Å,  $r_2 = 1.480$  Å,  $\alpha_1 = 144.7^\circ$ ,  $\alpha_2 = 60.0^\circ$ . The C–C–C angles deviate far from the normal  $109^\circ 28'$  formed by  $sp^3$  hybridized carbon atoms, which means that the tetrahedrane is subject to large stress [33,34]. Geometry parameters of the optimized  $D_{2h}$  cyclobutadiene are  $r_{C-H} = 1.084$  Å,  $r_{C-C} = 1.334$  Å,  $r_{C-C} = 1.578$  Å,  $\alpha_{C-C-C} = 90^\circ$ ,  $\alpha_{C-C-H} = 134.6^\circ$  or  $135.4^\circ$ . The C–C–C angles also deviate from  $120^\circ$  formed by  $sp^2$  hybridized carbon atoms. To investigate if the fullerene cage can stabilize  $T_d$   $C_4H_4$ , we performed ab initio Hartree–Fock and density functional calculations on  $C_4H_4@C_{60}$ . The energy minimum was found by full geometry optimization without symmetry limitation at HF/STO-3G level of theory (the lowest frequency was  $84.54\text{ cm}^{-1}$ ) and the final B3LYP/6–31G(d) yielded the geometry of the complex as listed in Fig. 1. The  $T_d$   $C_4H_4$  is seated in the center of the  $C_{60}$  cage and the highly symmetrical  $I_h$  of the cage is reduced to  $C_{3v}$  for  $C_4H_4@C_{60}$ . Both the fullerene cage and the encaged tetrahedrane experienced considerable structural changes. The cage of  $C_{60}$  is elongated by about 0.8 Å. Confinement of  $T_d$   $C_4H_4$  in a cage of spherical symmetry leads to anisotropic deformation of atomic charge and spin distribution. According with the previous studies [18,19], the C–C and C–H bonds of the encaged nonpolar molecule tetrahedrane  $C_4H_4$  are shortened and the C–H bond along the 3-fold symmetry axis  $C_3$  is the mostly shortened. The C–C–H bond angles also are a bit distorted. These changes of the bond lengths, the bond angles and the twist angles of other neighboring carbon atoms thus lead to symmetry-reducing distortion of the cage. The distances between the H as well as the C atoms in  $C_4H_4$  and the nearest C atoms in  $C_{60}$  ( $d_{C-H}$ ,  $d_{C-C}$ ) are 1.814 and 2.794 Å, respectively, implying that the encapsulated  $T_d$   $C_4H_4$  only exists in a molecular form inside the fullerene and does not adsorb to the internal surface of the carbon structure. On the other hand, the

**Table 1**

B3LYP/6–31G(d) optimized geometry parameters (bond length in Å and bond angles in degrees).

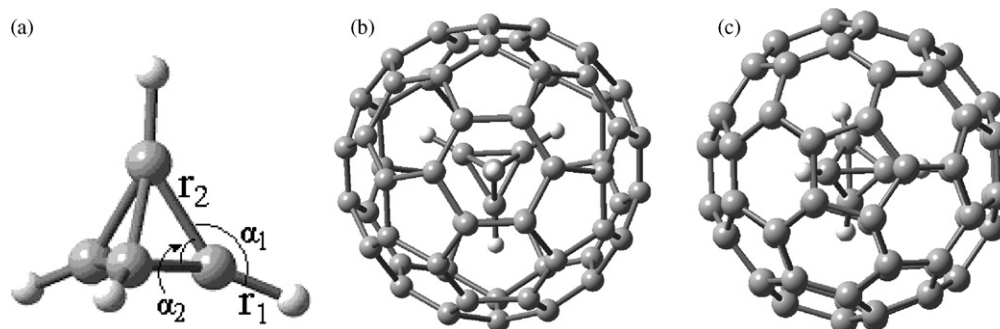
	$C_4H_4$	$C_{60}$	$C_4H_4@C_{60}$
$r_1$	1.073		1.022–1.024
$r_2$	1.480		1.432
$\alpha_1$	144.7		144.4–145.3
$\alpha_2$	60.0		60.0
$r_{6/5\ C-C}$		1.454	1.451–1.477
$r_{6/6\ C-C}$		1.395	1.398–1.422
$d$		7.101	7.117–7.182
$d_{C-H}$			1.814
$d_{C-C}$			2.794

study of  $C_{60}$  including  $D_{2h}$  cyclobutadiene gave no result. The larger geometrical dimensions of cyclobutadiene (the longest distance between two H atoms is 4.230 Å) prevent its formation in the  $C_{60}$  cage.

Mulliken population analysis showed that substantial electronic charge transfer had occurred from fullerene  $C_{60}$  cage to the  $C_4H_4$  sites in  $C_4H_4@C_{60}$ . As listed in Table 2, the central guest tetrahedrane  $C_4H_4$  gained appreciable charge ( $-0.257$ ) from the cage. This is different from other endohedral fullerenes in which the guests either gain positive charges from the cage or remain intact. It seems that with the fullerene cage acting as an electron-donating substituent [35], the highly strained tetrahedrane  $C_4H_4$  might be stabilized in the fullerene cage as negative charge accumulated on the skeleton.

To assess the relative stabilities, binding energies (BE) were calculated according to the gas phase reaction:  $nX + mY = X_nY_m$ . This means that  $BE(X_nY_m) = E(X_nY_m) - nE(X) - mE(Y)$ , and a more thermodynamic stable species should have a more negative BE. The inclusion energy ( $E_{includ}$ ) of endohedral complex was also evaluated by comparing the energy of  $C_4H_4@C_{60}$  to the sum of the energies of the isolated components  $T_d$   $C_4H_4$  and  $C_{60}$ , that is,  $E_{includ} = E(C_4H_4@C_{60}) - [E(C_4H_4) + E(C_{60})]$ . Our results indicated that the formation of  $C_4H_4@C_{60}$  from the free molecules  $T_d$   $C_4H_4$  and  $C_{60}$  is energetically unfavorable at B3LYP/6–31G(d)//B3LYP/6–31G(d) level with inclusion energy of 141.05 kcal/mol. However, the binding energy of  $C_4H_4@C_{60}$  is  $-10304.93$  kcal/mol, which is more negative than  $-9660.6$  kcal/mol of the ground state of  $N@C_{60}$ , suggesting that  $C_4H_4@C_{60}$  may exist as stable species but rigorous conditions are needed to synthesize this compound and experimental attempts in this direction should be rewarding.

It was well known that the highest occupied molecular orbital HOMO and the lowest unoccupied molecular orbital LUMO play a predominant role in chemical reactions [36,37]. HOMO–LUMO energy separation has been used as a conventional measure of kinetic stability for various  $\pi$ -electron systems [38–44]. A large HOMO–LUMO gap can be associated with high-kinetic stability



**Fig. 1.** B3LYP/6–31G(d) hybrid HF/DFT optimized geometries: (a)  $C_4H_4$ , (b)  $C_3$  axis view of  $C_4H_4@C_{60}$ , and (c)  $\sigma_v$  plane view of  $C_4H_4@C_{60}$ .

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