Endohedral complex of fullerene C_{60} with tetrahedrane, $C_4H_4@C_{60}$

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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_{60} with tetrahedrane C_4H_4. It was demonstrated that C_4H_4 was seated in the center of the C_{60} 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_4H_4 endohedral doping slightly perturbed the molecular orbitals of C_{60}. The calculated HOMO–LUMO gaps, the electron affinity (EA) and the ionizational potential (IP) indicated that $C_4H_4@C_{60}$ seemed to be more kinetically reactive than C_{60}. The IR active modes and harmonic vibrational frequencies of $C_4H_4@C_{60}$ were also discussed.

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1. Introduction

Since lanthanum atom was firstly placed into the fullerene C_{60} 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 metallofuller-ene La@C_{82} [12,13] suggested that the La atom donated its three valence electrons to C_{82} to form an endohedral complex La^{3+}$C_{82}$$^{3-}$, 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$_2$@C_{60} and its derivatives interpreted well the experimental data [11]. In N@C_{60}, P@C_{60} and C@C_{60}, the N, P and C atoms retain their atomic character when trapped in the cage [4,15–17], while towards encaged small molecules, C_{60} acted as a polarizable sphere that stabilized the polar molecules and destabilized the nonpolar ones [18,19].

Tetrahedrane C_4H_4 (THD) is a theoretically interesting mole-cule, 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_{60} with THD. A question of major interest is whether the fullerene cage can stablize the trapped tetrahedrane. On the other hand, as tetrahedrane can isomerizes to cyclobutadiene [25], we also consider the inclusion of D_{2h} 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 ξ 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, $\alpha_1 = 144.7°$, $\alpha_2 = 60.0°$. The C–C–C angles deviate far from the normal 109° 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, $\alpha_{C–C–C} = 90°$, $\alpha_{C–C–H} = 134.6°$ or 135.4°. The C–C–C angles also deviate from 120° 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 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
α_1	144.7		144.4–145.3
α_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: $nX + mY = XnYm$. This means that $BE(XnYm) = E(XnYm) − nE(X) − mE(Y)$, and a more thermodynamic stable species should have a more negative BE. The inclusion energy (E_{inclu}) 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, $E_{inclu} = E(C_4H_4@C_{60}) − [E(C_4H_4) + E(C_{60})]$. 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 π-electron systems [38–44]. A large HOMO–LUMO gap can be associated with high-kinetic stability
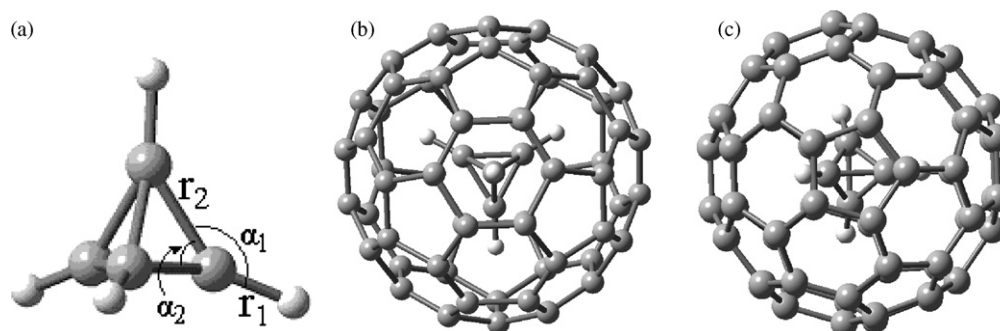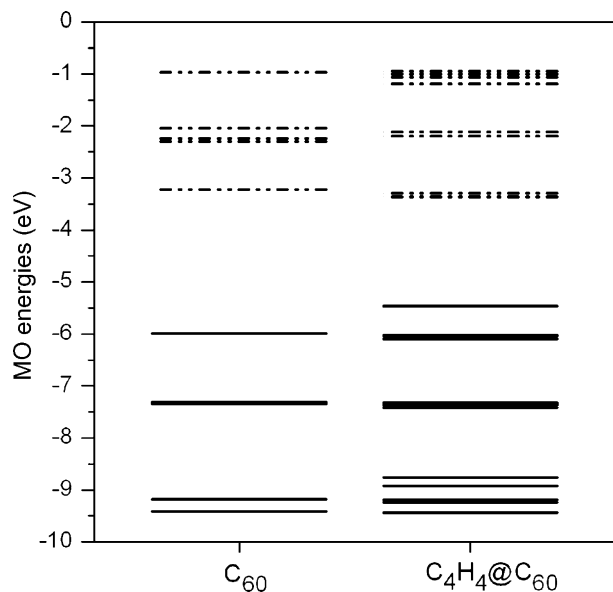

Fig. 1. B3LYP/6–31G(d) hybrid HF/DFT optimized geometries: (a) C_4H_4, (b) C_3 axis view of $C_4H_4@C_{60}$, and (c) σ_v plane view of $C_4H_4@C_{60}$.

Table 2
Results of B3LYP/6–31G(d)//B3LYP/6–31G(d) calculations.

	Charges on C_4H_4	Total dipole moment (D)	$\Delta E_{HOMO-LUMO}$ (eV)	Total energies (a.u.)
C_4H_4	C1 −0.144, H_1 0.144 C_2 −0.144, H_2 0.144 C_3 −0.144, H_3 0.144 C_4 −0.144, H_4 0.144	0	−9.25	−154.636686560
C_60		0	−2.77	−2286.17306739
$C_4H_4@C_60$	C_1 −0.022, H_1 −0.043 C_2 0.018, H_2 −0.082 C_3 0.018, H_3 −0.082 C_4 0.018, H_4 −0.082	0.0461	−2.10	−2440.58498211

Fig. 2. Electronic energy levels of C_60 and $C_4H_4@C_60$ other oxides near the HOMO–LUMO gap obtained at B3LYP/6–31G(d) level of theory, solid and dashed lines refer to the occupied and unoccupied states, respectively.

fullerene cage more reactive. Relative to C_60, the HOMOs and LUMOs of the $C_4H_4@C_60$ are perturbed by the inclusion and the degenerate energy levels are split. Fig. 2 displays the electronic levels near the HOMO and LUMO energy gap obtained from the B3LYP/6–31G(d) level calculations. Compared with C_60, the HOMO of $C_4H_4@C_60$ is slightly lifted by 0.52 eV and LUMO is lowered by 0.15 eV. The reduction of the degeneration of electronic levels is obvious for $C_4H_4@C_60$. The HOMOs are two degenerate orbitals and LUMO is one orbital. The energy gap between the HOMO and LUMO levels is 2.10 eV, 0.67 eV less compared with 2.77 eV of C_60. From this point of view, $C_4H_4@C_60$ seems to be more kinetically reactive than C_60 [6,29].

The electron affinity (EA) and ionization potential (IP) of $C_4H_4@C_60$ are calculated at B3LYP/6–31G(d)/B3LYP/6–31G(d) to be 3.37 and 5.47 eV, respectively. Compared with the values of 3.22 and 5.99 eV for C_60 calculated at the same theory of level, it is more possible for $C_4H_4@C_60$ to accept or donate electrons from the enhanced EA and reduced IP. Then, $C_4H_4@C_60$ is more chemically reactive than C_60 and other oxides, as suggested by the above-mentioned HOMO–LUMO gap. In order to gain insight into the HOMO and LUMO properties of $C_4H_4@C_60$, we plot the probability density contours of the two levels. As shown in Fig. 3, electron distribution away from the C_4H_4 site is clearly seen. HOMO and LUMO are found to be localized on the carbon cage, suggesting the reactive sites of this compound.

Our calculation on HF/STO-3G theory of level indicated that there are 18 infrared active modes in $C_4H_4@C_60$. The harmonic vibrational frequencies and intensities of these modes are 599 (1), 639 (12), 640 (3), 643 (16), 646 (31), 648 (3), 666 (2), 912 (1), 975 (1), 1363 (23), 1566 (4), 1569 (3), 1574 (10), 1621 (1), 1658 (1), 1754 (2), 4432 (87) and 4466 (60); IR intensities (in km/mol) of
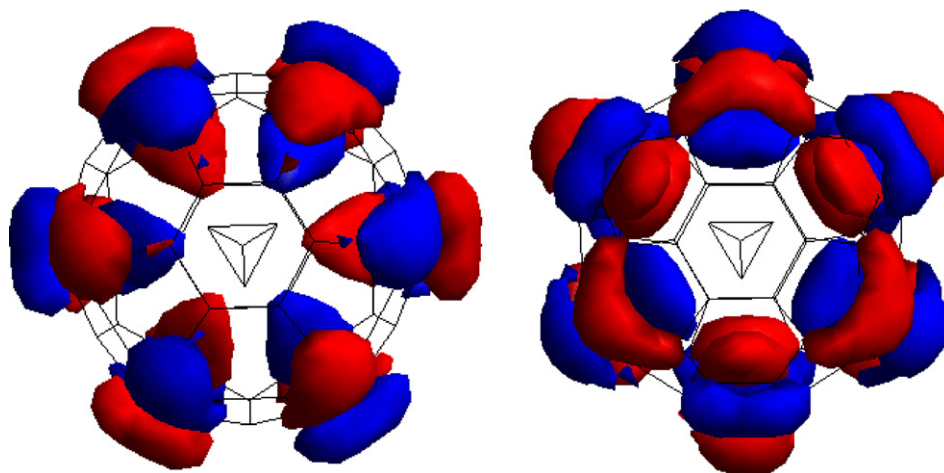
because it is energetically unfavorable to add electrons to a high-lying LUMO or to extract electrons from a low-lying HOMO and so to form the activated complexes of any potential reaction [38].

Table 2 shows that $C_4H_4@C_60$ has a smaller HOMO–LUMO gap than C_60, which indicates that the inclusion of C_4H_4 can make the

Fig. 3. Isodensity surface (0.02 e/a.u.^{3}) associated with $C_4H_4@C_60$ Hartree–Fock: (a) HOMO and (b) LUMO.
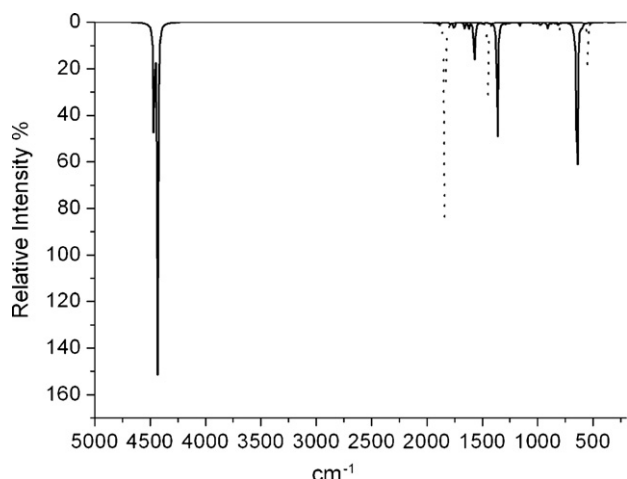
Fig. 4. . Calculated IR spectra of $C_4H_4@C_{60}$ and C_{60}, the latter is indicated by dashed lines.

active modes are in parenthesis. The strongest band with intensity of 87 km/mol is associated with highest frequency mode at 4432 cm^{-1}. This normal mode is identified to correspond mainly with C–H stretches for the guest molecule C_4H_4 in the σ_v plane. A complete list of all vibrational modes (a total of 198) is available upon request from the corresponding author. The calculated spectrum of $C_4H_4@C_{60}$ is shown in Fig. 4; for comparison, the spectrum of C_{60} calculated at the same theory level was also given. The most intensive vibration of spectrum of the endohedral complex is about two times more intensive than that of C_{60}. The IR spectrum of single T_d C_4H_4 was also computed at the same theory level. The strongest band with intensity of 62 km/mol is associated with the frequency 772 cm^{-1}. This mode is identified to correspond with bending vibrations of C–H bonds in the σ_v plane.

4. Summary

We have studied the structural and electronic properties of $C_4H_4@C_{60}$ via Hartree–Fock self-consistent field (SCF) and density functional B3LYP levels of theory with the STO-3G and 6–31G(d) basis sets. 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. However, the encapsulated C_4H_4 only exists in a molecular form inside the fullerene and does not adsorb to the internal surface of the carbon structure. With the fullerene cage acting as an electron donor, the highly strained tetrahedrane C_4H_4 might be stabilized in the fullerene cage as negative charge accumulates on the skeleton. The inclusion energy and binding energy were evaluated to assess the relative stabilities. The calculated HOMO–LUMO gaps as well as the EA and the IP are also presented as an indicator of the kinetic stability. There are 18 infrared active modes in $C_4H_4@C_{60}$ and the most intensive vibration of $C_4H_4@C_{60}$ is nearly two times more intense than that of C_{60}. The molecular properties calculated for this compound may serve as valuable predictions for future experimental research.

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