

Computed Stabilization for a Giant Fullerene Endohedral: $Y_2C_2@C_1(1660)-C_{108}$

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Abstract

The very recently prepared clusterfullerene $Y_2C_2@C_1(1660)-C_{108}$ is computed and the observed structural features are confirmed, including the quasi-linear arrangement of the encapsulate and its near-triple CC bond. Its stability is explained by sizeable encapsulation energy. The endohedral stability is evaluated at both DFT and MP2 levels.

1. Introduction

In nanocarbon research, calculations have from early days supported interpretation of observations and predictions of new species [1-4], this being true even for cages with about one hundred carbon atoms [5-7]. In the metallofullerene family with such sizeable cages [8-17], by far the largest species has very recently been characterized [18] by X-ray diffraction, viz. $Y_2C_2@C_1(1660)-C_{108}$. In this report, the giant species is calculated using the density functional theory (DFT), and even the MP2 technique, in order to supply further structure and stability data.

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2. Calculations

The $C_1(1660)-C_{108}$ fullerene is one of 1799 isolated-pentagon-rule (IPR) cages of C_{108} [19], this IPR cage being rather spheroidal. The $Y_2C_2@C_1(1660)-C_{108}$ structure was first optimized here using the Becke's three parameter functional with the non-local Lee-Yang-Parr correlation functional [20-22] (B3LYP) in a combined basis set: the standard 3-21G basis for C atoms and for Y using the SDD basis set with the SDD effective core potential [23] (B3LYP/3-21G~SDD). The geometry optimization started from the X-ray structure [18] and was, after the optimization, followed by the harmonic vibrational analysis. The basis set was then stepwise extended using the standard 6-31G* and 6-31+G* basis sets for carbons. Moreover, the geometry optimizations were also repeated using the more recently developed M06-2X functional [24] (i.e., M06-2X/3-21G~SDD, etc.). Some calculations were also performed with the second order Møller-Plesset (MP2) perturbation treatment [25] with all electrons as MP2(FU)/3-21G~SDD in the B3LYP/3-21G~SDD optimized geometry. All the computations were carried out with the Gaussian 09 program package [26].

3. Results and Discussion

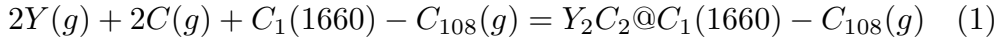
In agreement with experiment [18], the Y_2C_2 encapsulate in the optimized endohedrals also has a near linear structure (see Fig. 1). Table 1 shows that the computed encapsulate bond lengths are rather similar regardless the choice of the DFT functional and basis set. The encapsulate CC bond is slightly longer than the observed triple-bond of 1.203 Å in acetylene [27]. However, it is longer than the observed value

[18] obtained for a co-crystal, i.e., not in the isolated free endohedral treated in the calculations. Moreover, the computed structural parameters correspond to the equilibrium geometries with motionless nuclei. The computed Wiberg bond index for the encapsulate CC bond supports the picture as it comes as 2.59, 2.61, and 2.32 at the B3LYP/3-21G~SDD, M06-2X/3-21G~SDD, and MP2(FU)/3-21G~SDD level, respectively. On the other hand, the encapsulate CY bonds can be described as weaker single bonds as their average Wiberg bond index is computed as 0.531, 0.533, and 0.526 at the B3LYP/3-21G~SDD, M06-2X/3-21G~SDD, and MP2(FU)/3-21G~SDD level, respectively. The average Wiberg bond indexes for the closest contacts between the Y atoms and cage carbons are reduced further: 0.14, 0.13, and 0.13 at the B3LYP/3-21G~SDD, M06-2X/3-21G~SDD, and MP2(FU)/3-21G~SDD level, respectively. The bonding in $Y_2C_2@C_1(1660)-C_{108}$ can also be visualized by depicting electron density via a cross-section of the B3LYP/3-21G~SDD electron-density isosurface with a preselected constant value, namely of 0.07 a.u. (Fig. 1). The Laplacian $\nabla^2\rho$ of the electron density ρ offers another tool [28,29] for bond analysis of metallofullerenes [30,31]. The relatively-high negative $\nabla^2\rho$ values point out regions of strong covalent bond (Fig. 2).

In contrast to the calculated encapsulate bond lengths, the Mulliken charges on atoms depend more on the selected method. In particular, the charge transfer to the cage is 5.55, 5.28, and 4.79 electrons at the B3LYP/3-21G~SDD, M06-2X/3-21G~SDD, and MP2(FU)/3-21G~SDD level, respectively. However, if an older LanL2DZ basis set [32,33] is applied instead, the charge transfer to the cage drops to 4.07 electrons at the

B3LYP/3-21G~LanL2DZ level. The approximative orbital-energy analysis [34] performed at the B3LYP/3-21G~SDD level also rather supports the four-electron transfer. In order to clarify the charge transfer further, some observed information would still be needed like that available for simple metallofullerenes [35,36].

The energy change connected with the (formal thermodynamic) encapsulation process:



is an important characteristics though it can only be computed at present. Calculated reaction thermodynamic changes are mostly treated as the reaction potential-energy change ΔE_{pot} . However, a more adequate approach deals with the enthalpy change at absolute zero temperature ΔH_0^o , i.e., the potential energy change corrected for the vibrational zero-point energies ZPE:

$$\Delta H_0^o = \Delta E_{pot} + \Delta ZPE. \quad (2)$$

The encapsulation enthalpy ΔH_0^o is refined here by inclusion of the basis set superposition error [37] (BSSE/CP5) and so-called steric correction [38] that reflects the cage distortion upon encapsulation [39]. Table 2 presents the ΔH_0^o term for reaction (2) at the selected computational levels. The ΔH_0^o enthalpy (together with the related entropy term) is a key value for stability/population reasoning on nanocarbons. Interestingly, the values in Table 2 are not particularly method-dependent. A part of the relatively large encapsulation enthalpy is formation of the near-triple bond (the observed CC bond energy in C_2H_2 is 228.8 ± 0.7 kcal/mol [40]). The agreement between the DFT approaches and the more ad-

vanced MP2 treatment is encouraging. However, it is one of the very first attempts [41,42] to apply the latter treatment with nanocarbons (in fact, the present system is the largest by now) and thus, to improve their present computational description.

The encapsulation (1) creates 12 new vibrational modes, six of them with considerably low frequencies - at the B3LYP/3-21G~SDD level between 32 and 104 cm^{-1} (for comparison, the lowest frequency of $C_1(1660)$ - C_{108} is 172 cm^{-1}). Such low frequencies represent motions of the whole encapsulate inside the cage, including relatively free rotations. The motions are particularly important for the endohedral thermodynamics [43,44]. Moreover, for further characterization, the time-dependent DFT response treatment [45] at the B3LYP/6-31G*~SDD level produces for $Y_2C_2@C_1(1660)$ - C_{108} interesting low electronic excited states, possibly also significant for the encapsulation thermodynamic [46,47]. The first excited triplet and singlet state is located 0.282 and 0.443 eV, respectively, above the singlet ground state. The computed data should be useful for future evaluations of stabilities and populations of endohedrals with polyatomic encapsulates.

Acknowledgements

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Table 1. The computed structural characteristics (in Å or deg) of the encapsulate in $Y_2C_2@C_1(1660)-C_{108}$

Method	C-C	C-Y ^a	Y...Y	C...Y ^{a,b}	∠ CCY ^a
B3LYP/3-21G~SDD	1.253	2.291	5.792	2.491	172.1
B3LYP/6-31G*~SDD	1.250	2.308	5.812	2.450	171.2
B3LYP/6-31+G*~SDD	1.249	2.314	5.796	2.456	169.2
M06-2X/3-21G~SDD	1.253	2.304	5.735	2.482	165.8
M06-2X/6-31G*~SDD	1.249	2.326	5.738	2.438	163.7
M06-2X/6-31+G*~SDD	1.248	2.330	5.756	2.447	164.5
Observed [18]	1.08	2.38	5.85	2.108	173.1

^a The arithmetic mean.

^b The shortest Y contact with the cage carbons.

Table 2. The computed^a encapsulation enthalpy ΔH_0° for $Y_2C_2@C_1(1660)-C_{108}(g)$

Method	ΔH_0° (kcal/mol)
B3LYP/3-21G~SDD	-468.6
B3LYP/6-31G*~SDD	-469.3
B3LYP/6-31+G*~SDD	-466.7
MP2(FU)/3-21G~SDD ^b	-461.7

^a See process (1); in the respective optimized geometry.

^b In the B3LYP/3-21G~SDD optimized geometry.

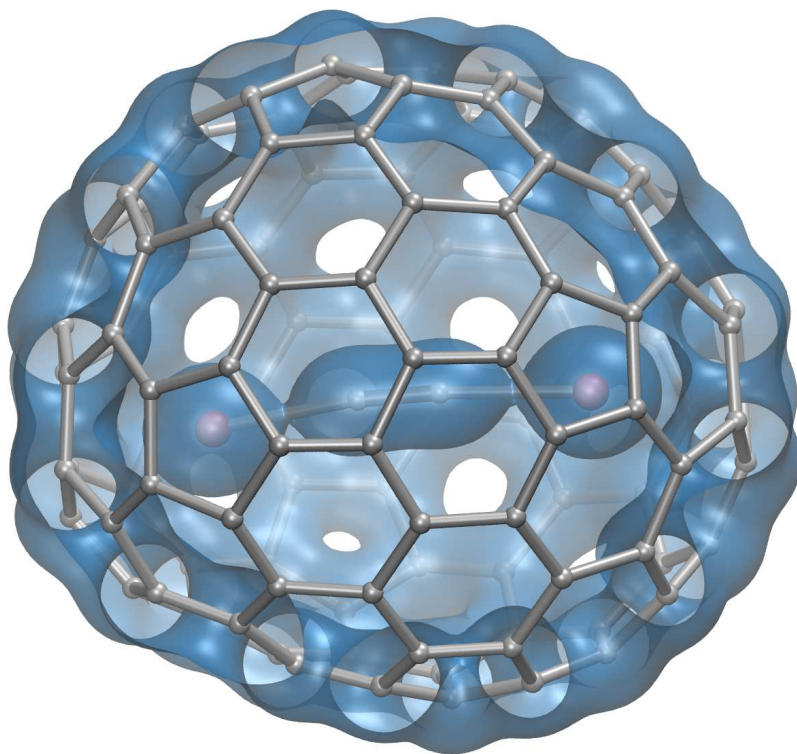


Fig. 1. A cross-section of the B3LYP/3-21G~SDD electron density isosurface of 0.07 a.u. for $Y_2C_2@C_1(1660)-C_{108}$.

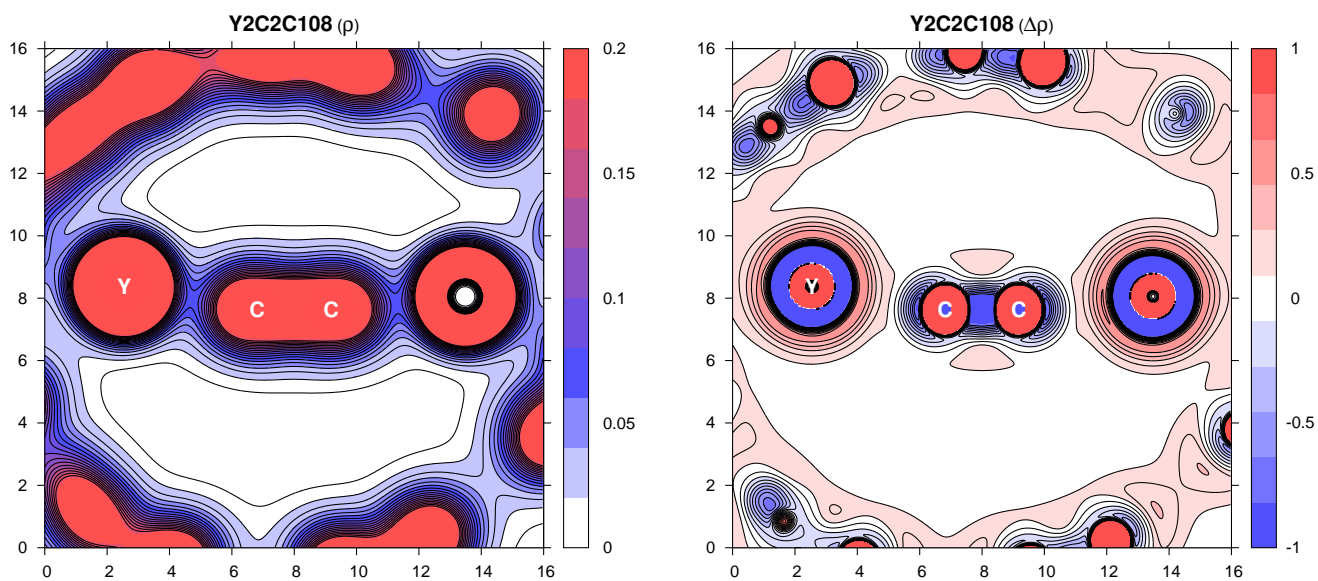


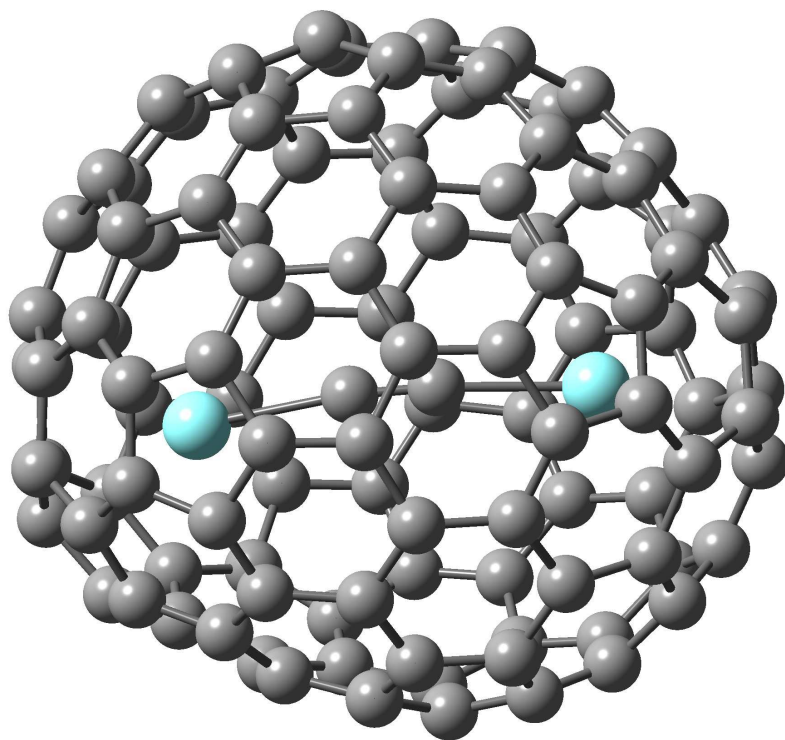
Fig. 2. YCC plane cross-section of the B3LYP/3-21G~SDD electron density ρ (left) and its Laplacian $\nabla^2\rho$ (right) for $\text{Y}_2\text{C}_2@C_1(1660)\text{-C}_{108}$, indicating region of strong covalent bond by relatively high positive ρ (red) or relatively high negative $\nabla^2\rho$ (blue); all values in a.u.

Keywords: Clusterfullerenes; Polyatomic encapsulates; $Y_2C_2@C_1(1660)-C_{108}$; Encapsulation energetics; Computational evaluations.

Highlights:

- A four-atom chain encapsulated into a giant fullerene
- The very recently prepared clusterfullerene $Y_2C_2@C_1(1660)-C_{108}$ is computed
- The observed structural features are confirmed: a near-linear Y_2C_2 encapsulate with a near-triple CC bond
- The endohedral stability comes from a relatively large energy gain upon encapsulation
- The encapsulation energy can presently be calculated but not measured

Graphical Abstract (pictogram):



The B3LYP/3-21G~SDD optimized structure of $Y_2C_2@C_1(1660)-C_{108}$.