

Endohedral Metallofullerenes. Are the Isolated Pentagon Rule and Fullerene Structures Always Satisfied?

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Fullerenes, closed carbon cage molecules (C_n) with only pentagons and hexagons, have been widely investigated since the discovery of the special stability of C_{60} .¹ Although many fullerene structures are possible,² only the isomers satisfying the isolated pentagon rule (IPR)³ have been isolated and experimentally characterized.⁴ Since the first success in the extraction of $La@C_{82}$ in 1991,⁵ endohedral metallofullerenes have attracted special attention because of the potentially novel properties which cannot be expected from empty fullerenes. The interesting electronic properties and reactivities have been extensively investigated, as summarized in a recent review.⁶ The structural determination is currently of primary interest.

Recently, the structures of isolated, representative metallofullerenes such as $M@C_{82}$ ($M = Ca, Sc, Y,$ and La), $La_2@C_{80}$, and $Sc_2@C_{84}$ have been disclosed through close interplay between theoretical prediction⁷ and experiment,⁸ as summarized in recent reviews.^{9,10} In all these cases, IPR-satisfying fullerene cages are found, as in the case of empty fullerenes.¹¹ However,

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(11) However, note that the cage structures of metallofullerenes do not necessarily coincide with the most stable (or abundant) fullerene structures of C_n ,^{7–10} because electron transfer from metals to carbon cages changes drastically the relative stability of fullerene cages.^{7c–8} For example, there are seven fullerene isomers for C_{80} satisfying IPR. In $La_2@C_{80}$, however, two La atoms are encapsulated inside the most unstable isomer^{8d} since this encapsulation is most stable owing to three-electron transfer from each La to C_{80} (the isomer is most stable for C_{80}^{6-}).^{7b–d}

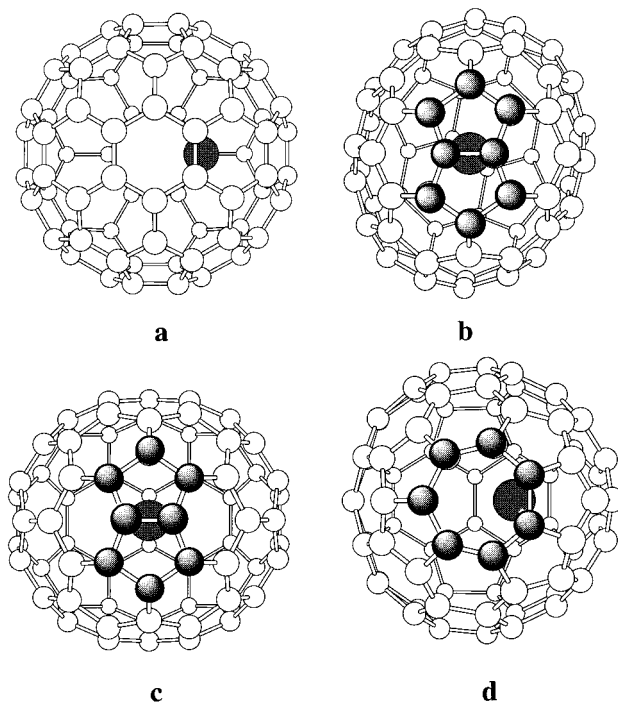


Figure 1. The optimized structures of $Ca@C_{72}$. Structure **a** (C_{72}) satisfies the isolated pentagon rule, **b** (C_2) and **c** (C_{2v}) contain a pair of adjacent pentagons, and **d** (C_s) has one heptagon surrounded by five adjacent pentagons.

it is an open question whether metal atoms stabilize unconventional cage structures during growth and annealing processes. We now report possible violation of IPR and the appearance of a heptagon-containing structure through theoretical calculations of $Ca@C_{72}$ and C_{72} .

Geometries were optimized at the Hartree–Fock (HF) level with use of the Gaussian 94 program,¹² with the effective core potential and contracted (5s5p)/[4s4p] basis set on Ca¹³ and split-valence 3-21G basis set on C.^{14a} Energies were improved by single-point nonlocal hybrid density functional calculations at the B3P and B3LYP levels¹⁵ with a larger 6-31G basis set on C.^{14b}

For the present purpose, a total of 431 240 closed cage structures composed of pentagons, hexagons, and one heptagon was generated for C_{72} with use of the GSW program developed recently.¹⁶ Among these, 11 190 structures correspond to conventional fullerenes,² and one of them with D_{6d} symmetry satisfies IPR. The endohedral structure (**a**) of $Ca@C_{72}$ optimized with this D_{6d} cage is shown in Figure 1, which has C_s symmetry.

However, we have succeeded in finding much more stable structures **b** (C_2) and **c** (C_{2v}). As Figure 1 shows, these

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structures contain a pair of adjacent pentagons. Nevertheless, **b** is 38.2 (B3P) and 37.4 (B3LYP) kcal/mol more stable than **a**, while **c** is 36.6 (B3P) and 36.2 (B3LYP) kcal/mol more stable than **a**. These are the first examples invalidating the IPR established in fullerene chemistry.¹⁷ The HOMO levels of -7.0 and -6.4 eV for **b** and **c** are 1.4 and 0.8 eV lower than that of -5.6 eV for **a** at the HF level, respectively, suggesting that **b** and **c** are less reactive (especially toward oxygen) than **a**.¹⁸ Upon geometry optimization without Ca, the carbon cage of **b** is 10.6 (B3P) and 10.2 (B3LYP) kcal/mol less stable than the C_{72} (D_{6d}) cage. On the other hand, it was found that the carbon cage of **c** is 8.7 (B3P) and 8.4 (B3LYP) kcal/mol more stable than C_{72} (D_{6d}) even after optimization without Ca. This finding, a stable non-IPR structure for C_{72} , is also noteworthy since the structure and stability of C_{72} have long been controversial among IPR-satisfying fullerenes.^{2,19} It is interesting to note that the carbon cage of **c** is formally obtainable by adding C_2 onto a hexagonal ring in the belt of the C_{70} (D_{5h}) fullerene.

Another important finding is structure **d** (C_s) shown in Figure 1. The carbon cage contains one heptagonal ring (surrounded by five adjacent pentagons), thereby not obeying the traditional definition of fullerenes. However, **d** was calculated to be 19.0 (B3P) and 18.4 (B3LYP) kcal/mol more stable than **a**. To our knowledge, this is the first example of a heptagon-containing structure that is more stable than the conventional fullerene structure. A stable structure with one heptagonal ring has been recently calculated for C_{62} .²⁰ However, it should be noted that C_{62} has no isolated-pentagon structure. The heptagon-containing cage of **d** becomes much less stable by 26.2 (B3P and B3LYP) kcal/mol than C_{72} (D_{6d}), upon optimization without Ca.

The carbon cages of **b**, **c**, and **d** were found from the 431 240 structures of C_{72} in the following way. First, all structures reachable within three steps of generalized Stone–Wales rearrangements starting from C_{72} (D_{6d}) were collected by using an option in the GSW program.¹⁶ The 283 structures thus

collected were optimized with use of the MM3 method.²¹ The most stable 50 structures within the energy range of ca. 50 kcal/mol were then reoptimized with use of the AM1 method.²² Among these, the most stable for C_{72}^{2-} was the carbon cage of **b**.²³ Next, the neighboring index of each hexagon (defined as the number of other hexagons to which it is adjacent)²⁴ was employed as a strain energy criterion. As a result, a total of 10 structures with small hexagon indices was searched. By optimizing these, the most stable C_{72}^{2-} cage was selected for **c**.²³ Finally, the number of pentagon–heptagon fusions was counted since the stability of heptagon-containing structures increases with an increase in the number,²⁰ and the energies of C_{72}^{2-} were compared. The carbon cage of **d** was thus found.

Very recently, $Ca@C_{72}$ has been isolated and purified.²⁵ At least three isomers could be separated, for which a ^{13}C NMR study is in progress.²⁶ We predict that **b** and **c** should be found among the possible structures of $Ca@C_{72}$.²⁷ In addition, we could suggest that $La_2@C_{72}$ also takes on similar cage structures.²⁸ It is expected that the present findings, a stable heptagon-containing structure as well as the violation of the isolated pentagon rule, will extend and enrich the research area of endohedral metallofullerenes.

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(27) The binding energy of **a** (relative to $Ca + C_{72}$) was calculated to be repulsive, unlike those of **b–d**. This suggests that Ca is not wrapped in C_{72} (D_{6d}) during annealing rearrangements. A search for other stable structures near in energy to **b–d** is in progress.

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(17) A similar trend was also found even for $La@C_{60}$. The I_h structure of C_{60} is 41.4 (B3P) and 41.2 (B3LYP) kcal/mol more stable than the C_{2v} isomer with two pairs of adjacent pentagons. Upon endohedral La-doping (followed by three-electron transfer from La to C_{60}), the energy difference decreases significantly to 15.1 (B3P) and 14.9 (B3LYP) kcal/mol, since the C_{2v} isomer has the higher electron affinity due to the defects.

(18) The HOMO level for **b** is lower than that of -6.8 eV for $Ca@C_{74}$, but it is higher than that of -7.3 eV for the most stable C_{2v} isomer of $Ca@C_{82}$.^{7c} In addition, **b** and **c** have a local strain at the pentagon–pentagon fusion. These explain that $Ca@C_{72}$ is more reactive and somewhat less abundantly produced than $Ca@C_{82}$. For the product distribution of $Ca@C_n$, see: Xu, Z.; Nakane, T.; Shinohara, H. *J. Am. Chem. Soc.* **1996**, *118*, 11309.

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