

Article

Eu@C₇₂: Computed Comparable Populations of Two Non-IPR Isomers

Zdeněk Slanina ^{1,*}, Filip Uhlík ², Shigeru Nagase ³, Takeshi Akasaka ¹, Ludwik Adamowicz ⁴ and Xing Lu ¹

¹ State Key Laboratory of Materials Processing and Die & Mould Technology, School of Material Science and Engineering, Huazhong University of Science and Technology, Wuhan 430074, China; akasaka@tara.tsukuba.ac.jp (T.A.); lux@hust.edu.cn (X.L.)

² Department of Physical and Macromolecular Chemistry, Faculty of Science, Charles University, Albertov 6, 128 43 Praha 2, Czech Republic; uhlik@sals.natur.cuni.cz

³ Fukui Institute for Fundamental Chemistry, Kyoto University, Kyoto 606-8103, Japan; nagase@ims.ac.jp

⁴ Department of Chemistry and Biochemistry, University of Arizona, Tucson, AZ 85721-0041, USA; ludwik@email.arizona.edu

* Correspondence: zdeneks@email.arizona.edu

Received: 18 May 2017; Accepted: 21 June 2017; Published: 24 June 2017

Abstract: Relative concentrations of six isomeric Eu@C₇₂—one based on the IPR C₇₂ cage (i.e., obeying the isolated-pentagon rule, IPR), two cages with a pentagon–pentagon junction (symmetries C₂ and C_{2v}), a cage with one heptagon, a cage with two heptagons, and a cage with two pentagon–pentagon fusions—are DFT computed using the Gibbs energy in a broad temperature interval. It is shown that the two non-IPR isomers with one pentagon–pentagon junction prevail at any relevant temperature and exhibit comparable populations. The IPR-satisfying structure is disfavored by both energy and entropy.

Keywords: metallofullerenes; non-IPR fullerenes; relative populations of isomers

1. Introduction

C₇₂ has a special position among medium-size fullerenes [1–3] as it has not been isolated in the pristine form. A low solubility in conventional solvents or polymerization may be among the reasons for the difficulties [4]. As C₇₂ could only be recorded [5] in the gas phase, its structure is not known. Still, C₇₂ can act as a host cage for some metallofullerenes like Ca@C₇₂ [6], La₂@C₇₂ [7], or La@C₇₂ [8]. There is just one isolated-pentagon-rule (IPR) satisfying structure for C₇₂, namely [1–3,9–11] with D_{6d} symmetry and spiral-code number 11190. Nevertheless, it was pointed out [10] in conjunction with the Ca@C₇₂ computations that two non-IPR (i.e., IPR-violating) structures with one pentagon–pentagon junction and the C₂ and C_{2v} symmetries (code numbers [1–3,10,11] 10612 and 11188, respectively) produce Ca-endohedrals with lower energy than encapsulation in the IPR cage. It has been known for isomeric sets of fullerenes and metallofullerenes (e.g., Refs. [12–16]) that potential energy itself cannot generally decide stability order at high temperatures as the entropic part of the Gibbs energy becomes essential—this feature was also demonstrated for Ca@C₇₂ [11] or La@C₇₂ [8].

In this paper, density-functional theory (DFT) computations are carried out on another observed [17,18] C₇₂-based metallofullerene, namely isomers of Eu@C₇₂, in order to clarify their structures and stabilities and to enrich the knowledge on the whole C₇₂-based endohedral family [19–29], considering IPR, classical non-IPR, and heptagon-containing structures [30].

2. Calculations

The computations started with DFT geometry optimizations, namely using Becke's three parameter functional [31] combined with the non-local Lee–Yang–Parr correlation functional [32] (B3LYP). The basis set applied to C atoms is the standard 6-311G* basis [33] while Eu atom is treated in the SDD basis set [34] with the SDD effective core potential (the combined basis set is coded B3LYP/6-311G*~SDD). The geometry optimizations were performed with the analytically constructed energy gradients. In the optimized B3LYP/6-311G*~SDD geometries, the harmonic vibrational analysis was carried out with the analytical force-constant matrix. The inter-isomeric separation potential energies were further improved by the geometry optimizations at the B3LYP/6-311+G*~SDD level. The electronic excitation energies were evaluated with the time-dependent (TD) DFT response-theory method [35,36]. The computations have been performed with the Gaussian 09 program package [37].

Relative concentrations (mole fractions) x_i of m isomers can be expressed [38] through their partition functions q_i and the enthalpies at the absolute zero temperature or ground-state energies $\Delta H_{0,i}^0$ (i.e., the relative potential energies corrected for the vibrational zero-point energies) by a compact formula:

$$x_i = \frac{q_i \exp[-\Delta H_{0,i}^0 / (RT)]}{\sum_{j=1}^m q_j \exp[-\Delta H_{0,j}^0 / (RT)]}, \quad (1)$$

where R is the gas constant and T the absolute temperature. Equation (1) is an exact formula that can be directly derived [38] from the standard Gibbs energies of the isomers, supposing the conditions of the inter-isomeric thermodynamic equilibrium. Rotational-vibrational partition functions were constructed from the calculated structural and vibrational data using the rigid rotator and harmonic oscillator (RRHO) approximation. No frequency scaling is applied as it is not significant [39] for the x_i values at high temperatures. The geometrical symmetries of the optimized cages were determined by Gaussian 09 built-in procedure [37], and confirmed also by a procedure [40], which considers precision of the computed coordinates. The electronic partition function was evaluated by a direct summation. Finally, the chirality contribution [41] was included accordingly (for an enantiomeric pair its partition function q_i is doubled).

However, the conventional RRHO treatment applied with Equation (1) is modified here by an approach for description of the encapsulate motions, namely in order to respect somehow [15,16] the findings that encapsulated atoms can exercise large amplitude motions, especially so at elevated temperatures (unless the motions are restricted by cage derivatizations). One can expect that if the encapsulate is relatively free, then, at sufficiently high temperatures, its behavior in different cages will bring about the same contribution to the partition functions. However, such uniform contributions would then cancel out in Equation (1). This simplification is called [15,16] free, fluctuating, or floating encapsulate model (FEM) and requires two steps. In addition to removal of the three lowest vibrational frequencies (belonging to the metal motions in the cage), the symmetries of the cages should be treated as the highest (topologically) possible. This step reflects the averaging effects of the large amplitude motions, showing themselves in the ^{13}C -NMR spectra just by the observed high cage symmetries [15,16]. For example, for the Eu@C₇₂ IPR isomer based on the D_{6d} cage (Table 1), the D_{6d} symmetry is indeed employed within the FEM scheme though its statical symmetry (i.e., after the geometry optimization) is only C_1 (Table 2). It has been established that the FEM treatment generally gives a better agreement [15,16] with the available observed data than the RRHO approach.

Table 1. Eu@C₇₂ relative potential energies $\Delta E_{pot,rel}$ [kcal/mol].

Species ^a	Point Group ^b	$\Delta E_{pot,rel}$	
		B3LYP/6-311G*~SDD	B3LYP/6-311+G*~SDD
(a) IPR	<i>D</i> _{6d}	36.41	36.04
(b) 5/5 fusion	<i>C</i> ₂	2.35	2.40
(c) 5/5 fusion	<i>C</i> _{2v}	0.0	0.0
(d) 7-ring	<i>C</i> _s	18.59	18.56
(e) two 7-rings	<i>C</i> _s	29.99	29.94
(f) two 5/5 fusions	<i>D</i> ₂	35.80	35.73

^a For (b), (c)—see Figure 1. ^b Symmetry of the empty cage.

Table 2. The shortest Eu-C contact d_{Eu-C} and metal charge q_{Eu} for the Eu@C₇₂ isomers.

Species ^a	Symmetry ^b	d_{Eu-C} [Å] ^c	q_{Eu} ^d
(a) IPR	<i>C</i> ₁	2.705	2.207
(b) 5/5 fusion	<i>C</i> ₂	2.712	2.277
(c) 5/5 fusion	<i>C</i> _{2v}	2.643	2.201
(d) 7-ring	<i>C</i> ₁	2.648	2.277
(e) two 7-rings	<i>C</i> _s	2.567	2.206
(f) two 5/5 fusions	<i>C</i> ₂	2.690	2.270

^a For (b), (c)—see Figure 1. ^b Symmetry of the fully optimized ^c endohedral. ^c Computed in the B3LYP/6-311G*~SDD optimized structures. ^d The B3LYP/3-21G~SDD Mulliken atomic charge ^c (given as multiply of the elementary charge).

3. Results and Discussion

The four C₇₂ cages originally selected [10] for Ca@C₇₂ are also treated here: the IPR *D*_{6d} cage (a), two non-IPR cages (b) and (c) with one pentagon–pentagon junction each with the symmetries *C*₂ and *C*_{2v}, respectively, and a *C*_s structure with one heptagon (d). Selection of the structures is based on a common procedure that searches for low-energy dianionic cages (both Ca and Eu donate about two electrons to cage). Once such low-energy dianionic cages are selected, the next step is search for the lowest electrostatic-potential minimum, still in the charged cages, which suggests a starting position for the metal atom in following geometry optimizations. Moreover, other two interesting structures are added (Table 1) for the sake of illustration: a *C*_s cage (e) with two heptagons pointed-out in Ref. [42], and a *D*₂ structure (code number 10611) with two pentagon–pentagon junctions (f) suggested in Ref. [25].

Table 1 reports the separation energetics computed for the B3LYP/6-311G*~SDD and B3LYP/6-311+G*~SDD optimized geometries. The energetics in both approaches are quite similar. The (c) structure based on the *C*_{2v}-symmetry cage with just one pentagon–pentagon fusion represents the potential-energy lowest isomer in both treatments, being closely followed by the (b) isomer employing the *C*₂ cage again with one 5/5 fusion. The remaining four cages are located at least more than 18 kcal/mol above the lowest one. The (d) isomer with one heptagon comes as the third potential-energy lowest species while other three endohedrals are at least 30 kcal/mol above the *C*_{2v} stabilomer. Actually, the only IPR-cage based isomer is the highest-located in energy. The considered computational level is about the highest presently applicable and both the energies and structures should be quite reliable [43]. The all reported optimized structures are confirmed to be local energy minima by the vibrational analysis. The geometry optimizations produce some symmetry reductions (Table 2), which is rather common with endohedrals [44,45]. However, the symmetry of the two energy-lowest species does not undergo a reduction (Figure 1).

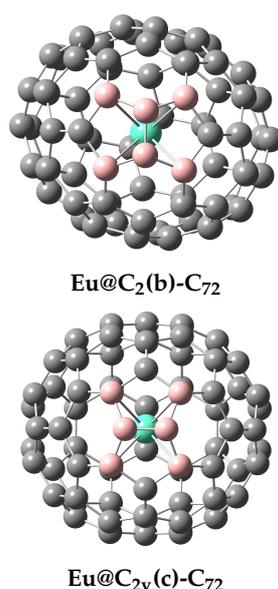


Figure 1. The B3LYP/6-311G*~SDD optimized structures of (b) and (c) Eu@C₇₂ (the carbons closest to Eu are in a lighter color and with the C-Eu links).

The computed shortest contacts between Eu and the cage carbons are rather uniform, spanning just a narrow interval between 2.643 and 2.712 Å (Table 2). The metal is never located in the cage center—it is placed relatively close to some portion of the cage. Formation of metallofullerenes is connected with a strong charge transfer from the metal to the cage [2,3]. The charge transfer is computed in Table 2 using the Mulliken atomic charges at the B3LYP/3-21G~SDD level (this combination is known to give a good agreement with the observed charges [46] for metallofullerenes). The charge transfer is again rather uniform for all the isomers and is slightly larger than two electrons. The reported values agree with what previously found [47] for Eu@C₇₄.

Figure 2 presents the temperature development of the relative concentrations for the six Eu@C₇₂ isomers evaluated within the FEM treatment in a wide temperature region. The enthalpy part of the Gibbs energy is based on the B3LYP/6-311+G*~SDD energetics while the entropy contributions come only from the B3LYP/6-311G*~SDD level (this is about the highest level that can presently be applied for the vibrational analysis of metallofullerenes). It should be noted that the relative populations are derived in Equation (1) from a ratio that allows for a cancellation of possible systematic errors between the numerator and denominator. Although the temperature region where fullerene or metallofullerene electric-arc synthesis takes place is not well known, the recent observations [48] supply some arguments to expect it around or above 1500 K. Thus, the computed results should also be discussed in the temperature region. The lowest energy structure (c) based on the C_{2v}-symmetry cage is the most populated species only until a temperature of 1910 K. After this crossing point, the (b) structure with the C₂ cage becomes the most-populated one, however with a near-equimolarity of both endohedrals with one 5/5 fusion. All other structures are rather negligible, only the (d) endohedral with one heptagon, which is the third potential-energy lowest species, could represent a minor isomer. On the other hand, the only IPR-cage based structure (a) is the least populated. Its suppression should not be ascribed to the potential-energy term only. In fact, two other structures high in potential energy, (e) and (f), exhibit populations in a high-temperature limit approaching some 5%. Clearly enough, the IPR-cage based structure is suppressed not only by its energy but also by its unfavorable entropy term. One reason is its high symmetry, which in the FEM treatment also means a high rotational symmetry number (this factor would not operate in the simple RRHO approach that does not respect the averaging effects of the encapsulate large-amplitude motions).

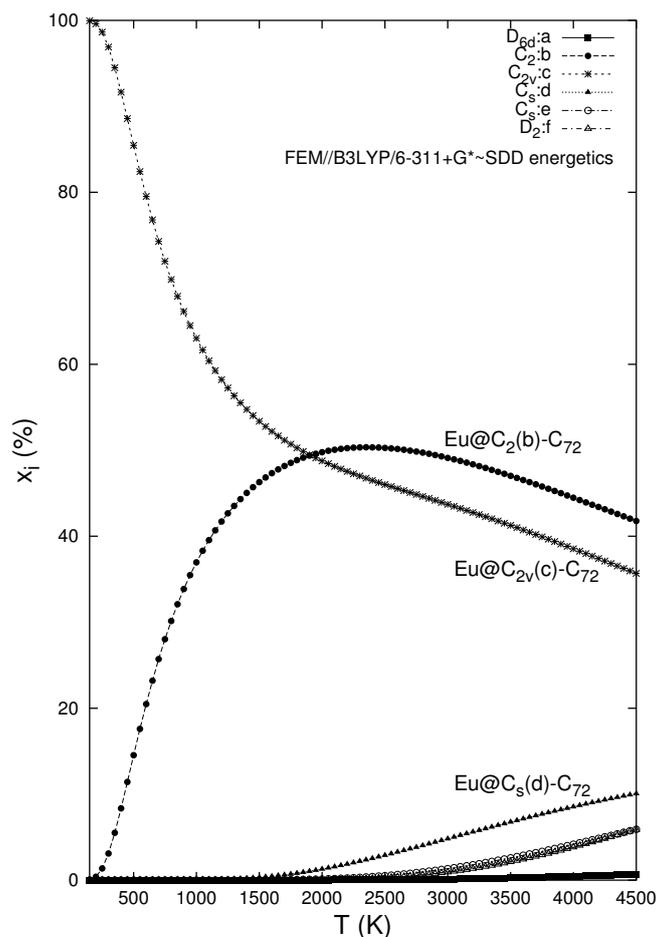


Figure 2. Relative concentrations of the Eu@C_{72} isomers (see Table 1) based on the B3LYP/6-311+G*~SDD energetics, the B3LYP/6-311G*~SDD entropy, and the FEM treatment.

Although rotational, vibrational, and electronic partition functions contribute to the overall picture, low vibrational frequencies are particularly important. Although we deal with the harmonic frequencies, Equation (1), owing to its already mentioned convenient form, allows for at least partial cancellation of anharmonicity corrections. This expectation is supported by model computations [49] for C_6 (and also by a good agreement with the observed concentration ratios available for several fullerene systems [15,16,50]). The enthalpy–entropy interplay can be visualized by the following data. If all the partition functions are neglected together with the zero-point vibrations, Equation (1) is reduced to the simple Boltzmann isomeric factors governed purely by the potential energy. At a selected temperature of 2000 K, Equation (1) gives the concentration ratios (a):(b):(c):(d):(e):(f) = 0.005:49.8:48.8:1.3:0.1:0.04 (Figure 2). If the entropy contributions are neglected and only the Boltzmann factors with the B3LYP/6-311+G*~SDD potential-energy terms are applied, the concentration ratios are changed considerably (a):(b):(c):(d):(e):(f) = 0.007:35.1:64.3:0.6:0.03:0.008. Interestingly, the simple Boltzmann factors can never cross in any isomeric system, and, thus, they are not convenient for the relative-population evaluations.

The computations predict co-existence of two major isomers for Eu@C_{72} , both having non-IPR cages with one pentagon–pentagon junction each. A third, minor isomer has a cage with one heptagon (i.e., a non-classical fullerene cage [13,51]), while the IPR-cage based Eu -endohedral is ruled out. The prediction agrees with Bucher et al.’s observations [14,15] of two Eu@C_{72} isomers (though yet without structural conclusions based on NMR or X-ray crystal analysis). The present computations, however, refer to the equilibrium gas-phase conditions and do not cover such aspects like polymerization, solubility or reactions with solvent. The computations also do not

deal with the relative stabilities compared to other Eu-metallofullerenes as the question involves pressure considerations [52–54]. However, another issue is a possibility of kinetic control of the formation process, including a catalytic enhancement [55,56]. The study nevertheless expands the family of isomeric metallofullerene systems [57–60] for which the Gibbs-energy treatment produces an encouraging agreement with available observations, and, thus, other C_{72} -based endohedrals [17,18,61,62] should in future be treated with the present or even higher approaches too.

Acknowledgments: The reported research has been supported by the National Thousand Talents Program of China, the NSFC (numbers 21171061 and 51472095), and the Program for Changjiang Scholars and Innovative Research Team in University (IRT1014); and by the Czech Science Foundation/GACR (P208/10/1724). Access to the MetaCentrum (LM2010005) and CERIT-SC (CZ.1.05/3.2.00/08.0144) computing facilities is also acknowledged.

Author Contributions: All the authors contributed accordingly in various stages of the research study to conceiving, designing, managing computational resources, analyzing and discussing the results.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Fowler, P.W.; Manolopoulos, D.E. Magic Numbers and Stable structures for fullerenes, fullerides, and fullerenium ions. *Nature* **1992**, *355*, 428–430.
2. Tan, Y.-Z.; Xie, S.-Y.; Huang, R.-B.; Zheng, L.-S. The stabilization of fused-pentagon fullerene molecules. *Nat. Chem.* **2009**, *1*, 450–460.
3. Popov, A.A.; Yang, S.; Dunsch, L. Endohedral fullerenes. *Chem. Rev.* **2013**, *113*, 5989–6113.
4. Diener, M.D.; Alford, J.M. Isolation and properties of small-bandgap fullerenes. *Nature* **1998**, *393*, 668–671.
5. Boltalina, O.V.; Ioffe, I.N.; Sidorov, L.N.; Seifert, G.; Vietze, K. Ionization energy of fullerenes. *J. Am. Chem. Soc.* **2000**, *122*, 9745–9749.
6. Wan, T.S.M.; Zhang, H.W.; Nakane, T.; Xu, Z.D.; Inakuma, M.; Shinohara, H.; Kobayashi, K.; Nagase, S. Production, isolation, and electronic properties of missing fullerenes: $Ca@C_{72}$ and $Ca@C_{74}$. *J. Am. Chem. Soc.* **1998**, *120*, 6806–6807.
7. Kato, H.; Taninaka, A.; Sugai, T.; Shinohara, H. Structure of a missing-caged metallofullerene: $La_2@C_{72}$. *J. Am. Chem. Soc.* **2003**, *125*, 7782–7783.
8. Wakahara, T.; Nikawa, H.; Kikuchi, T.; Nakahodo, T.; Rahman, G.M.A.; Tsuchiya, T.; Maeda, Y.; Akasaka, T.; Yoza, K.; Horn, E.; et al. $La@C_{72}$ having a non-IPR carbon cage. *J. Am. Chem. Soc.* **2006**, *128*, 14228–14229.
9. Slanina, Z.; Ishimura, K.; Kobayashi, K.; Nagase, S. C_{72} isomers: The IPR-satisfying cage is disfavored by both energy and entropy. *Chem. Phys. Lett.* **2004**, *384*, 114–118.
10. Kobayashi, K.; Nagase, S.; Yoshida, M.; Ōsawa, E. Endohedral metallofullerenes. Are the isolated pentagon rule and fullerene structures always satisfied? *J. Am. Chem. Soc.* **1997**, *119*, 12693–12694.
11. Slanina, Z.; Kobayashi, K.; Nagase, S. $Ca@C_{72}$ IPR and non-IPR structures: Computed temperature development of their relative concentrations. *Chem. Phys.* **2003**, *372*, 810–814.
12. Slanina, Z.; Lee, S.-L.; Kobayashi, K.; Nagase, S. Si_{60} clusters: AM1 computed I_h/C_{2v} relative populations. *J. Mol. Struct.* **1994**, *312*, 175–178.
13. Slanina, Z.; Zhao, X.; Deota, P.; Ōsawa, E. Relative stabilities of C_{92} IPR fullerenes. *J. Mol. Model.* **2000**, *6*, 312–317.
14. Slanina, Z.; Uhlík, F.; Zhao, X.; Ōsawa, E. Enthalpy-entropy interplay for C_{36} cages: B3LYP/6-31G* calculations. *J. Chem. Phys.* **2000**, *113*, 4933–4937.
15. Slanina, Z.; Lee, S.-L.; Uhlík, F.; Adamowicz, L.; Nagase, S. Computing relative stabilities of metallofullerenes by Gibbs energy treatments. *Theor. Chem. Acc.* **2007**, *117*, 315–322.
16. Slanina, Z.; Uhlík, F.; Lee, S.-L.; Adamowicz, L.; Akasaka, T.; Nagase, S. Calculations of metallofullerene yields. *J. Comput. Theor. Nanosci.* **2011**, *8*, 2233–2239.
17. Bucher, K.; Epple, L.; Mende, J.; Mehring, M.; Jansen, M. Synthesis, isolation and characterization of new endohedral fullerenes $M@C_{72}$ ($M = Eu, Sr, Yb$). *Phys. Stat. Solid* **2006**, *243*, 3025–3027.
18. Bucher, K.; Mende, J.; Mehring, M.; Jansen, M. Isolation and spectroscopic characterization of $Eu@C_{72}$. Fulleren. *Nanotub. Carbon Nanostruct.* **2007**, *15*, 29–42.

19. Slanina, Z.; Zhao, X.; Uhlík, F.; Ōsawa, E. Non-IPR fullerenes: C₃₆ and C₇₂. In *Electronic Properties of Novel Materials—Science and Technology of Molecular Nanostructures*; Kuzmany, H., Fink, J., Mehring, M., Roth, S., Eds.; AIP: Melville, NY, USA, 1999; pp. 179–182.
20. Slanina, Z.; Zhao, X.; Deota, P.; Ōsawa, E. Calculations of higher fullerenes and quasi-fullerenes. In *Fullerenes: Chemistry, Physics, and Technology*; Kadish, K.M., Ruoff, R.S., Eds.; John Wiley: New York, NY, USA, 2000; pp. 283–330.
21. Slanina, Z.; Zhao, X.; Grabuleda, X.; Ozawa, M.; Uhlík, F.; Ivanov, P. M.; Kobayashi, K.; Nagase, S. Mg@C₇₂: MNDO/d evaluation of the isomeric composition. *J. Mol. Graph. Model.* **2001**, *19*, 252–255.
22. Slanina, Z.; Uhlík, F.; Adamowicz, L.; Kobayashi, K.; Nagase, S. Electronic excited states and stabilities of fullerenes isomers of C₇₈ and Mg@C₇₂. *Int. J. Quantum Chem.* **2004**, *100*, 610–616.
23. Slanina, Z.; Kobayashi, K.; Nagase, S. Ca@C₇₄ isomers: Relative concentrations at higher temperatures. *Chem. Phys.* **2004**, *301*, 153–157.
24. Slanina, Z.; Adamowicz, L.; Kobayashi, K.; Nagase, S. Gibbs energy-based treatment of metallofullerenes: Ca@C₇₂, Ca@C₇₄, Ca@C₈₂, and La@C₈₂. *Mol. Simul.* **2005**, *31*, 71–77.
25. Slanina, Z.; Chen, Z.; Schleyer, P.V.R.; Uhlík, F.; Lu, X.; Nagase, S. La₂@C₇₂ and Sc₂@C₇₂: Computational characterizations. *J. Phys. Chem. A* **2006**, *110*, 2231–2234.
26. Lu, X.; Nikawa, H.; Nakahodo, T.; Tsuchiya, T.; Ishitsuka, M.O.; Maeda, Y.; Akasaka, T.; Toki, M.; Sawa, H.; Slanina, Z.; et al. A chemical understanding of a non-IPR metallofullerene: Stabilization of encaged metals on fused-pentagon bonds in La₂@C₇₂. *J. Am. Chem. Soc.* **2008**, *130*, 9129–9136.
27. Lu, X.; Nikawa, H.; Tsuchiya, T.; Maeda, Y.; Ishitsuka, M.O.; Akasaka, T.; Toki, M.; Sawa, H.; Slanina, Z.; Mizorogi, N.; et al. Bis-carbene adducts of non-IPR La₂@C₇₂: Localization of high reactivity around fused pentagons and electrochemical properties. *Angew. Chem. Int. Ed.* **2008**, *47*, 8642–8645.
28. Feng, Y.; Wang, T.; Wu, J.; Feng, L.; Xiang, J.; Ma, Y.; Zhang, Z.; Jiang, L.; Shua, C.; Wang, C. Structural and electronic studies of metal carbide clusterfullerene Sc₂C₂@Cs-C₇₂. *Nanoscale* **2013**, *5*, 6704–6707.
29. Yamada, M.; Muto, Y.; Kurihara, H.; Slanina, Z.; Suzuki, M.; Maeda, Y.; Rubin, Y.; Olmstead, M.M.; Balch, A.L.; Nagase, S.; et al. Regioselective cage opening of La₂@D₂(10611)-C₇₂ with 5,6-Diphenyl-3-(2-pyridyl)-1,2,4-triazine. *Angew. Chem. Int. Ed.* **2015**, *54*, 2232–2235.
30. Gan, L.-H.; Wu, R.; Tian, J.-L.; Fowler, P.W. An atlas of endohedral Sc₂S cluster fullerenes. *Phys. Chem. Chem. Phys.* **2017**, *19*, 419–425.
31. Becke, A.D. Density-functional thermochemistry. III. The role of exact exchange. *J. Chem. Phys.* **1993**, *98*, 5648–5652.
32. Lee, C.; Yang, W.; Parr, R.G. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev. B* **1988**, *37*, 785–789.
33. Krishnan, R.; Binkley, J.S.; Seeger, R.; Pople, J.A. Self-consistent molecular orbital methods. XX. A basis set for correlated wave functions. *J. Chem. Phys.* **1980**, *72*, 650–654.
34. Cao, X.Y.; Dolg, M. Segmented contraction scheme for small-core lanthanide pseudopotential basis sets. *J. Mol. Struct.* **2002**, *581*, 139–147.
35. Casida, M.E.; Jamorski, C.; Casida, K.C.; Salahub, D.R. Molecular excitation energies to high-lying bound states from time-dependent density-functional response theory: Characterization and correction of the time-dependent local density approximation ionization threshold. *J. Chem. Phys.* **1998**, *108*, 4439–4449.
36. Slanina, Z.; Uhlík, F.; Adamowicz, L.; Akasaka, T.; Nagase, S.; Lu, X. Stability issues in computational screening of carbon nanostructures: Illustrations on La endohedrals. *Mol. Simul.* **2017**, in press.
37. Frisch, M.J.; Trucks, G.W.; Schlegel, H.B.; Scuseria, G.E.; Robb, M.A.; Cheeseman, J.R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G.A.; et al. *Gaussian 09, Rev. C.01*; Gaussian Inc.: Wallingford, CT, USA, 2013.
38. Slanina, Z. Equilibrium isomeric mixtures: Potential energy hypersurfaces as originators of the description of the overall thermodynamics and kinetics. *Int. Rev. Phys. Chem.* **1987**, *6*, 251–267.
39. Slanina, Z.; Uhlík, F.; Zerner, M.C. C₅H₃⁺ isomeric structures: Relative stabilities at high temperatures. *Rev. Roum. Chim.* **1991**, *36*, 965–974.
40. Sun, M.-L.; Slanina, Z.; Lee, S.-L.; Uhlík, F.; Adamowicz, L. AM1 computations on seven isolated-pentagon-rule isomers of C₈₀. *Chem. Phys. Lett.* **1995**, *246*, 66–72.
41. Slanina, Z.; Adamowicz, L. On relative stabilities of dodecahedron-shaped and bowl-shaped structures of C₂₀. *Thermochim. Acta.* **1992**, *205*, 299–306.

42. Nagase, S.; Kobayashi, K.; Akasaka, T. Unconventional cage structures of endohedral metallofullerenes. *J. Mol. Struct.* **1999**, *461/462*, 97–104.
43. Cioslowski, J. *Electronic Structure Calculations on Fullerenes and Their Derivatives*; Oxford University Press: Oxford, UK, 1995.
44. Slanina, Z.; Uhlík, F.; Lee, S.-L.; Suzuki, M.; Lu, X.; Mizorogi, N.; Nagase, S.; Akasaka, T. Calculated temperature development of the relative stabilities of Yb@C₈₂ isomers. *Fuller. Nanotub. Carbon Nanostruct.* **2014**, *22*, 147–154.
45. Slanina, Z.; Uhlík, F.; Feng, L.; Adamowicz, L. Sc₂O@C₇₈: Calculations of the yield ratio for two observed isomers. *Fuller. Nanotub. Carbon Nanostruct.* **2017**, *25*, 124–127.
46. Okubo, S.; Kato, T.; Inakuma, M.; Shinohara, H. Separation and characterization of ESR-active lanthanum endohedral fullerenes. *New Diam. Front. Carbon Technol.* **2001**, *11*, 285–294.
47. Uhlík, F.; Slanina, Z.; Lee, S.-L.; Adamowicz, L.; Nagase, S. Stability calculations for Eu@C₇₄ isomers. *Int. J. Quantum Chem.* **2013**, *113*, 729–733.
48. Cross, R.J.; Saunders, M. Transmutation of fullerenes. *J. Am. Chem. Soc.* **2005**, *127*, 3044–3047.
49. Slanina, Z.; Uhlík, F.; Lee, S.-L.; Adamowicz, L.; Nagase, S. Computations of endohedral fullerenes: The Gibbs energy treatment. *J. Comput. Methods Sci. Eng.* **2006**, *6*, 243–250.
50. Slanina, Z.; François, J.-P.; Kolb, M.; Bakowies, D.; Thiel, W. Calculated relative stabilities of C₈₄. *Fuller. Sci. Technol.* **1993**, *1*, 221–230.
51. Gan, L.H.; Lei, D.; Fowler, P.W. Structural interconnections and the role of heptagonal rings in endohedral trimetallic nitride template fullerenes. *J. Comput. Chem.* **2016**, *37*, 1907–1913.
52. Slanina, Z.; Zhao, X.; Kurita, N.; Gotoh, H.; Uhlík, F.; Rudziński, J.M.; Lee, K.H.; Adamowicz, L. Computing the relative gas-phase populations of C₆₀ and C₇₀: Beyond the traditional $\Delta H_{f,298}^{\circ}$ scale. *J. Mol. Graph. Model.* **2001**, *19*, 216–221.
53. Slanina, Z.; Uhlík, F.; Lee, S.-L.; Adamowicz, L.; Nagase, S. MPWB1K calculations of stepwise encapsulations: Li_x@C₆₀. *Chem. Phys. Lett.* **2008**, *463*, 121–123.
54. Slanina, Z.; Uhlík, F.; Lee, S.-L.; Wang, B.-C.; Adamowicz, L.; Suzuki, M.; Haranaka, M.; Feng, L.; Lu, X.; Nagase, S.; et al. Towards relative populations of non-isomeric metallofullerenes: La@C₇₆(T_d) vs. La₂@C₇₆(C_s,17490). *Fuller. Nanotub. Carbon Nanostruct.* **2014**, *22*, 299–306.
55. Eggen, B.R.; Heggie, M.I.; Jungnickel, G.; Latham, C.D.; Jones, R.; Briddon, P.R. Autocatalysis during fullerene growth. *Science* **1996**, *272*, 87–96.
56. Slanina, Z.; Zhao, X.; Uhlík, F.; Ozawa, M.; Ōsawa, E. Computational modelling of the metal and other elemental catalysis in the Stone-Wales fullerene rearrangements. *J. Organomet. Chem.* **2000**, *599*, 57–61.
57. Mercado, B.Q.; Stuart, M.A.; Mackey, M.A.; Pickens, J.E.; Confait, B.S.; Stevenson, S.; Easterling, M.L.; Valencia, R.; Rodríguez-Forteza, A.; Poblet, J.M.; et al. Sc-2(μ₂-O) trapped in a fullerene cage: The isolation and structural characterization of Sc-2(μ₂-O)@C-s(6)-C-82 and the relevance of the thermal and entropic effects in fullerene isomer selection. *J. Am. Chem. Soc.* **2010**, *132*, 12098–12105.
58. Slanina, Z.; Uhlík, F.; Lee, S.-L.; Akasaka, T.; Nagase, S. Carbon nanostructures: Calculations of their energetics, thermodynamics and stability. In *Carbon Nanotubes and Related Structures*; Guldi, D.M., Martín, N., Eds.; Wiley-VCH Verlag: Weinheim, Germany, 2010; pp. 491–523.
59. Rodríguez-Forteza, A.; Balch, A. L.; Poblet, J. M. Endohedral metallofullerenes: A unique host-guest association. *Chem. Soc. Rev.* **2011**, *40*, 3551–3563.
60. Slanina, Z.; Uhlík, F.; Feng, L.; Adamowicz, L. Evaluation of the relative stabilities of two non-IPR isomers of Sm@C₇₆. *Fuller. Nanotub. Carbon Nanostruct.* **2016**, *24*, 339–344.
61. Chi, M.; Zhang, Z.; Han, P.; Fang, X.; Jia, W.; Dong, H.; Xu, B. Geometric and electronic structures of new endohedral fullerenes: Eu@C₇₂. *J. Mol. Model.* **2008**, *14*, 465–470.
62. Yang, T.; Zhao, X. Missing metallofullerene Yb@C₇₂: A density functional theory survey. *Chem. Phys.* **2013**, *423*, 173–177.

Sample Availability: The optimized isomeric structures are available from the corresponding author.



© 2017 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).