

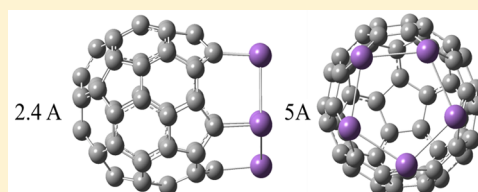
# Reactivity Indexes of Fullerene and Bismullene Mixed Clusters: How the Intruders Modify the Properties

Ana Martínez\*

Departamento de Materiales de Baja Dimensionalidad, Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Circuito Exterior s/n, Ciudad Universitaria, P.O. Box 70-360, Coyoacán, 04510, Ciudad de México, México

## Supporting Information

**ABSTRACT:** In this investigation, the feasibility of functionalizing fullerene and bismullene with Bi and C as intruders is theoretically explored. The systems analyzed are  $C_{60-x}Bi_x$  (with  $x = 0-10$ , fullerene-like) and  $Bi_{60-y}C_y$  (with  $y = 0-10$ , bismullene-like). Optimized geometries, reactivity indexes, and highest occupied molecular orbital to lowest unoccupied molecular orbital (HOMO–LUMO) gaps (for analyzing the potential application of these molecules as materials for solar cells) are reported. The most stable structures of bismullene-like systems have cage geometries. The most stable fullerene-like geometries resemble a cup with bismuth atoms at the edge of the bowl. The presence of intruders increases the electron acceptor power and decreases the electron donor power in most cases. HOMO–LUMO gaps indicate that bismullene-like clusters represent better candidates for building solar cells than fullerene-like clusters. This information could be useful for future experiments.



## INTRODUCTION

Buckminsterfullerene ( $C_{60}$ ) was discovered more than 30 years ago.<sup>1</sup> The properties of this interesting material motivated the production and the investigation of other larger or smaller fullerene-like cages, formed either with carbon atoms or with other atoms such as silicon<sup>2–4</sup> or bismuth.<sup>5</sup> It was reported<sup>5</sup> that  $Bi_N$  cages, in full analogy to  $C_{60}$ , show high binding energies, high symmetry, and large highest occupied molecular orbital to lowest unoccupied molecular orbital (HOMO–LUMO) energy gaps. Bismuth is a nontoxic semimetal<sup>6</sup> with potential applications as a nanostructured material.<sup>7–19</sup> Nanostructures of bismuth have been produced experimentally using diverse methods,<sup>8–13</sup> and their structure, stability, and electronic properties have also been analyzed theoretically.<sup>14–19</sup> It was demonstrated that bismuth nanotubes are identical analogues of carbon nanotubes.<sup>13</sup> Based on these results, it is possible to say that there is a reasonable hope that  $Bi_N$  clusters show potential for technological applications, such as electronic, optoelectronic nanodevices, and quantum computing.<sup>5</sup>

For the purpose of science and technology, it is interesting to examine the possibility of developing additional fullerenes with other elements that could modify these properties, increasing the possibility for further applications. In spite of all these investigations, there are no studies considering mixed fullerenes with bismuth and carbon. As reported previously,<sup>15,19</sup> the structure of fullerene-like bismuth nanostructures (named in this work bismullene for further reference) is interesting since bulk bismuth is a semimetal, but bismuth nanostructures are semiconductors. Therefore, Bi is a semimetal that can produce interesting properties when interacting with carbon fullerenes.

Most of the studies concerning mixed clusters analyzed metal mixed clusters. In this investigation, it was decided to study the

properties of mixed clusters containing nonmetal and semi-metal atoms. The Bi–C pair was chosen since the metallic bismuth could be obtained by reducing the oxide with carbon, and it could be that mixed clusters are formed during this process. In this investigation, the feasibility of functionalizing carbon and bismuth fullerenes is explored theoretically. The idea to functionalize both fullerene and bismullene (with bismuth and carbon, respectively) is investigated in order to determine the effect of the intruder (Bi or C) on potential reactivity. The general formula of the systems analyzed is  $X_nY_m$  (X and Y are C or Bi). Two systems were selected: fullerene and bismullene. For these two systems, up to 10 atoms were replaced one by one, by the intruder. The systems  $C_{60-x}Bi_x$  (with  $x = 0-10$ ) are named in this report as fullerene-like, whereas  $Bi_{60-y}C_y$  (with  $y = 0-10$ ) systems are given the name of bismullene-like. Bi and C are intruders for fullerene-like and bismullene-like systems, respectively. Reactivity indexes, HOMO eigenvalues, LUMO eigenvalues, and HOMO–LUMO gaps (for analyzing the potential application of these molecules as materials for solar cells) are also reported.

## COMPUTATIONAL DETAILS

Calculations related to optimization of geometries were undertaken using Gaussian 09 implementation.<sup>20</sup> Several initial geometries were tested. The schematic representation of the initial geometries that were used and the total energies of the optimized structures are included in the [Supporting Information](#). Initial geometries were fully optimized at the M06 level of

Received: July 25, 2016

Revised: October 18, 2016

Published: October 19, 2016

theory in the gas phase,<sup>21</sup> using LANL2DZ for metal atoms and DSDV basis sets for light atoms.<sup>22–24</sup> The M06 is a new hybrid meta exchange–correlation functional that is parametrized including both transition metals and nonmetals, as it is explained in detail in ref 21. Harmonic analyses were calculated to verify local minima (zero imaginary frequencies). It is useful to remember that the M06 functional is recommended for application in organometallic and inorganometallic chemistry and for noncovalent interactions.

In order to analyze the influence of Bi or C on the reactivity of the systems, two reactivity indexes were calculated,  $\omega^-$  and  $\omega^+$ . These two parameters were named electrodonating and electroaccepting power, which have been reported recently by Gázquez et al.<sup>25,26</sup> These authors conclude that the propensity to donate charge (electrodonating power) is defined as

$$\omega^- = \frac{(3I + A)^2}{16(I - A)} \quad (1)$$

Lower values of  $\omega^-$  imply a greater capacity for donating charge. The definition for the propensity to accept charge, or electroaccepting power, is as follows:

$$\omega^+ = \frac{(I + 3A)^2}{16(I + A)} \quad (2)$$

Higher values of  $\omega^+$  indicate a greater capacity for accepting charge.  $I$  is the vertical ionization energy, and  $A$  is the vertical electron affinity. These two values were obtained from single point calculations of the correspondent cationic and anionic molecules, using the optimized structure of the neutrals. It is possible to build a donor–acceptor map with these two parameters (DAM, Figure 1) that is a powerful tool for

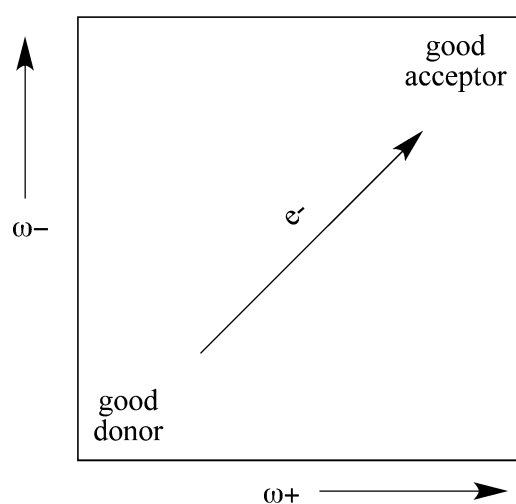


Figure 1. Donor–acceptor map.

visualizing the results.<sup>27</sup> Electrons are transferred from molecules located down to the left of the map (good electrons donors) to those molecules that are up to the right (good electron acceptors).

## RESULTS AND DISCUSSION

**Geometry Optimization.** In order to obtain stable structures, two options were used for the initial geometries: the first one with the intruders bonded together, and the second one with the intruders randomly placed and separated

from each other. These two options reveal the most stable structure to us, considering these two alternatives, given that the chemical properties are different in each case. When the intruders were bonded together in one section of the molecule, several options were tested. All the initial geometries that were used are included in the Supporting Information. Only the most stable one was selected for further discussion. Figures 2

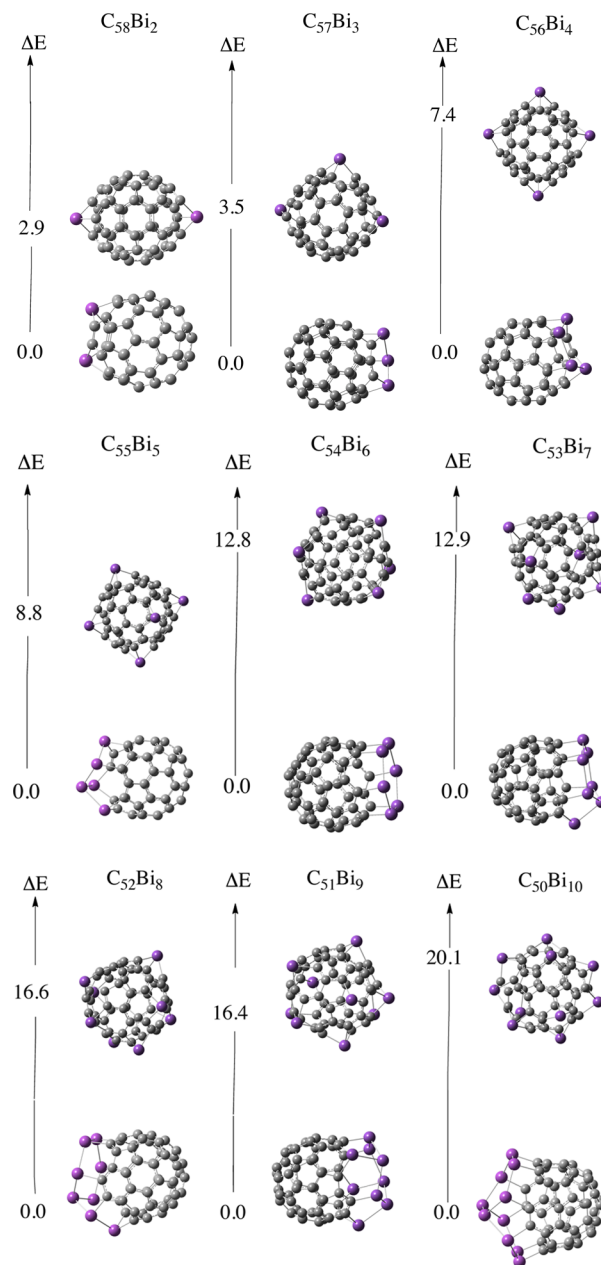
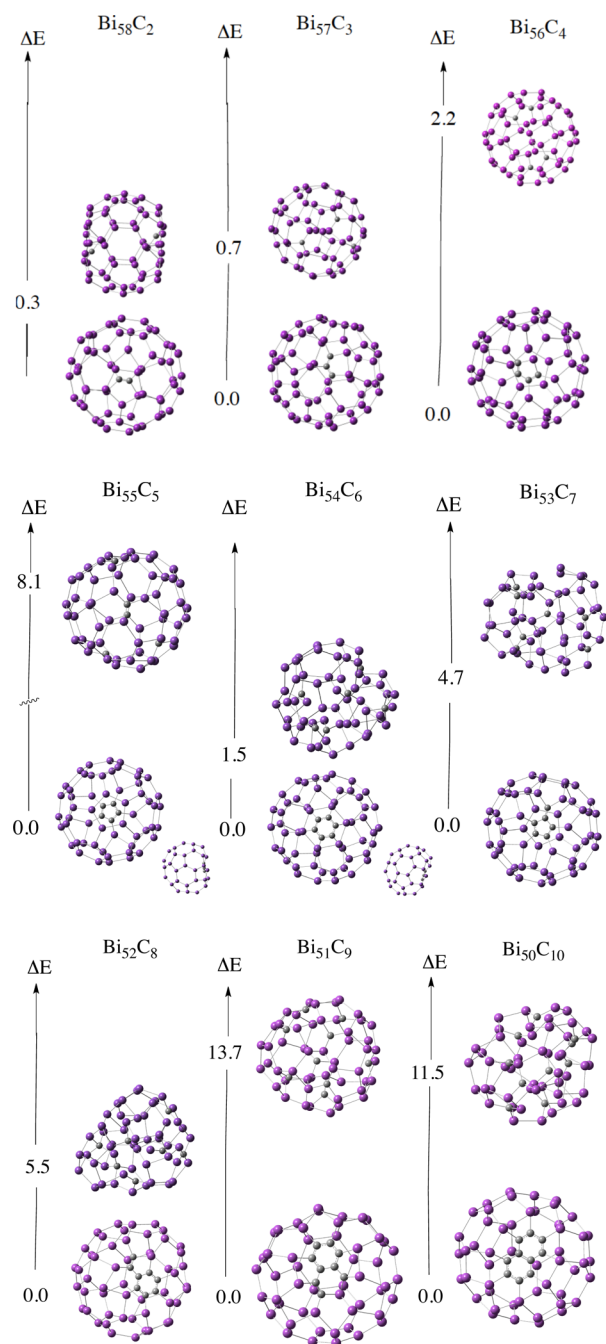


Figure 2. Optimized structures of fullerene-like systems. Energy difference ( $\Delta E$  in eV) between the most stable geometry and the structure with the intruders located at random positions.

and 3 report the most stable structures and the optimized geometry with the intruders located randomly. There are many other structures less stable than the ground state that can be seen in the Supporting Information.

As apparent in Figures 2 and 3 in most cases, the geometries with the intruders located close to each other are more stable than when the intruders are located randomly. The energy



**Figure 3.** Optimized structures of bismullene-like systems. Energy difference ( $\Delta E$  in eV) between the most stable geometry and the structure with the intruders located at random positions.

difference with respect to the most stable structure is at least 0.3 eV. These results reveal that Bi–Bi bonds in fullerene-like structures stabilize the systems and also that C–C bonds in bismullene-like structures make the systems more stable.

Figure 2 shows bismuth atoms functionalizing fullerene. The stable structures are like a cup with bismuth atoms at the edge of the bowl. In Figure 3, bismullene with carbon atoms present a deformed cage structure. When the intruder atoms are located randomly, in some cases, the cage structure disappeared (for example,  $C_{50}Bi_{10}$ ,  $Bi_{56}C_4$ ,  $Bi_{54}C_6$ ,  $Bi_{53}C_7$ , and  $Bi_{52}C_8$ ). Analyzing Figure 2, it is clear that for fullerene-like systems, the “cup like” structures are more stable than geometries with randomly located Bi atoms. The energy difference between these two

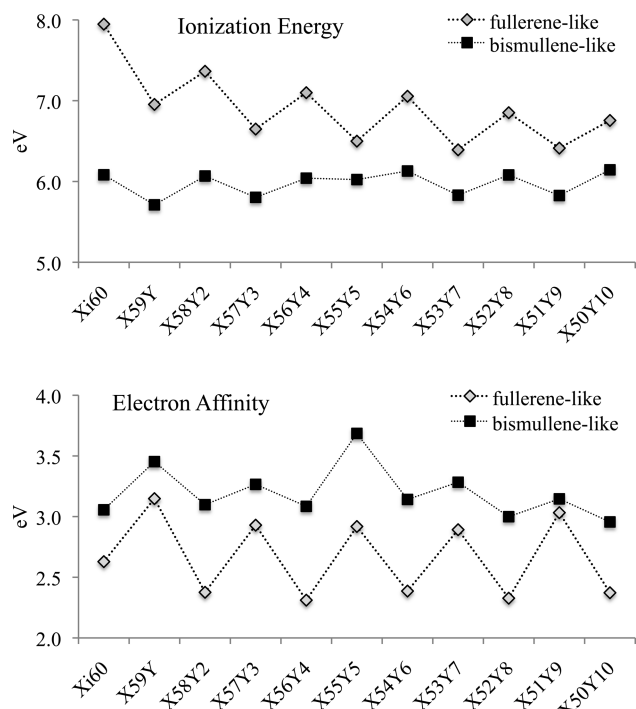
structures increases as the number of bismuth atoms in fullerene augments. This means that Bi–Bi bonds stabilize the cage structures.

Bismullene-like structures with a different number of carbon atoms substituting for Bi are shown in Figure 3. In all these systems, the most stable structures are with the carbon atoms bonded together. Given the atomic radius of the carbon atoms, which is smaller than the atomic radius of the bismuth atoms, the area of the bismullene-like structures where the carbons are located is sunk. It is like a dented bismullene. The energy difference between dented bismullene-like structures and the structures with randomly located C atoms ranges from 0.3 and 13.7 eV. Analyzing  $Bi_{56}C_4$  (Figure 3), it is apparent that the structure with the C atoms randomly bonded is deformed, with atoms inside the cage. The structure with the C atoms bonded together within a pentagon of the bismullene has a cavity, and it is 2.2 eV more stable. The structure with the C atoms replacing the Bi atoms of one hexagon was also optimized (not shown in the figure), but it is less stable than the two structures presented in Figure 3.

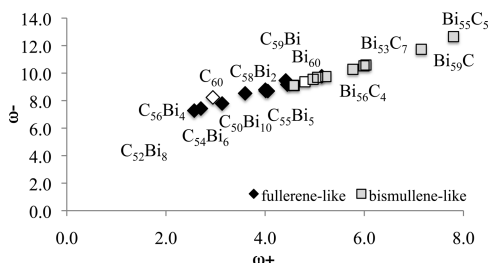
Notably, the less stable structures of bismullene-like clusters are three-dimensional formless structures. The most stable structures have cage geometries. It was reported previously<sup>15</sup> for  $Bi_{60}$  that many three-dimensional unstructured geometries with nine Bi atoms collapsed inside the cluster are more stable than the cage structure. Results from Figure 3 apparently indicate that the presence of C atoms substituting Bi atoms stabilizes the cage structures. This could be important for future applications.

**Reactivity Indexes.** The presence of intruder atoms modified the structures and also the reactivity, as shown previously with gold–bismuth mixed clusters.<sup>28</sup>  $I$  and  $A$  are two parameters that are important for electron transfer. Electron transfer is evidently the first step in many reactions and is also a mechanism for scavenging free radicals. Figure 4 reports  $I$  and  $A$  for all the most stable structures. Fullerene-like structures have higher  $I$  values than the bismullene-like systems. Therefore, the latter are better electron donors than the first ones. Bismullene-like structures have higher  $A$  values and consequently they are better electron acceptors than fullerene-like systems. Spin multiplicity is singlet when  $X_nY_m$  has even numbers of  $n$  and  $m$ , and doublet when  $n$  and  $m$  are odd numbers.  $I$  and  $A$  present a more or less even–odd oscillation, being most obvious for fullerene-like structures. When  $n$  and  $m$  are even numbers,  $I$  is larger than when  $n$  and  $m$  are odd numbers. For  $A$  the situation is the reverse, i.e.,  $A$  is greater when  $n$  and  $m$  are odd numbers. Based on these results, it is possible to conclude that intruders influence the electron donor–acceptor capacity. Bismullene-like structures are better for the transfer of electrons (either accepted or donated) than fullerene-like systems. Considering all the systems studied, the best electron donor is  $Bi_{59}C$  and the best electron acceptor is  $Bi_{55}C_5$ .

$I$  and  $A$  are parameters that indicate the full electron transfer. This is important for scavenging free radicals. In order to analyze reactivity, two other parameters ( $\omega^+$  and  $\omega^-$ , already explained in the computational details) are very useful as they indicate the partial charge transfer capability. The DAM for fullerene-like and bismullene-like systems is included in Figure 5.  $C_{60}$  and  $Bi_{60}$  are included for comparison. The presence of Bi atoms on fullerene-like structures augments the electron acceptor power ( $\omega^+$  is greater) and decreases the electron donor power ( $\omega^-$  is larger) in most of the cases. Similar results



**Figure 4.** Vertical ionization energy and vertical electron affinity for the most stable structures of each system under study.

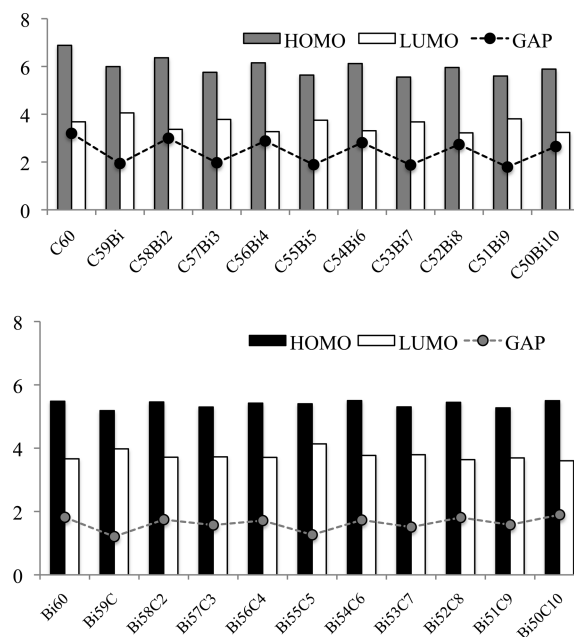


**Figure 5.** DAM of the systems under study.

are found for bismullene-like structures with C atoms. A process of partial charge transfer process can occur between  $C_{56}Bi_4$  and  $Bi_{55}C_5$  (the best donor and the best acceptor). Finally, systems are surprisingly aligned on the DAM, suggesting further studies. In summary, the presence of intruders modifies the electron donor–acceptor capabilities, increasing the electron acceptor power and decreasing the electron donor power.

HOMO–LUMO gaps (for analyzing the potential application of these molecules as materials for solar cells) are reported in Figure 6. Absolute values of HOMO and LUMO eigenvalues are also included. The HOMO–LUMO eigenvalue difference obtained from Kohn–Sham calculations provides a rather good representation of the first excitation energy.<sup>29–33</sup> To see if the trends observed are preserved with other functionals, the calculations were repeated with two different functionals: PBE and M06L. The results are included in the Supporting Information. As can be seen, the conclusions from all the calculations are the same, and the trends are preserved.

The HOMO values of fullerene-like structures are larger than the HOMO of the bismullene-like molecules, whereas the LUMO values resemble each other more. The fullerene-like molecules present an even–odd oscillation on the HOMO–



**Figure 6.** Absolute values of the eigenvalues of the HOMO and the LUMO of the systems under study. HOMO–LUMO gap (GAP) is also included. Values reported in eV.

LUMO values that is also reflected in the gap, whereas this does not occur with bismullene-like clusters.

For solar energy devices, a reduction in excitation energy is required. The HOMO–LUMO gap is a decisive factor indicating potential materials for the construction of solar cells. The HOMO–LUMO gap of the electron donor has to be around 2 eV, as the maximum in the solar energy radiation spectrum corresponds approximately to this value. Bulk bismuth is a semimetal but bismuth nanostructures are semiconductors with a small gap. Figure 6 shows that the HOMO–LUMO gap ranges between 1.79 and 3.20 eV for fullerene-like systems, whereas it ranges between 1.21 and 1.90 eV for bismullene-like clusters. Comparing  $C_{60}$  with  $Bi_{60}$ , it is evident that the latter has a smaller HOMO–LUMO gap than the first. The presence of an odd-number of intruders (Bi or C, respectively) diminishes the gap in both systems, which also have open-shell configurations (doublets). Apparently, the presence of Bi atoms may be important to build solar cells with this type of material. Even though there are a lot of other factors required to have a working solar cell, the HOMO–LUMO gap is a good indication of light absorption. These results suggest that bismullene-like clusters are better candidates for building solar cells than fullerene-like clusters.

## CONCLUSIONS

The presence of intruders (Bi and C) modifies the structure and also the chemical properties of mixed clusters. Bismullene-like structures are better for the transfer of electrons (either accepted or donated) than fullerene-like systems. Of all the systems studied, the best partial electron donor is  $C_{56}Bi_4$  and the best electron acceptor is  $Bi_{55}C_5$ .

$C_{60}$  has a larger HOMO–LUMO gap than  $Bi_{60}$ . The HOMO–LUMO gap ranges between 1.79 and 3.20 eV for fullerene-like systems, whereas it ranges between 1.21 and 1.90 eV for bismullene-like clusters. The presence of an odd-number of intruders (Bi or C, respectively) diminishes the gap in both systems, which also have open-shell configurations (doublets).

It is evident that bismullene-like clusters represent the best candidates for building solar cells compared to fullerene-like clusters.

The properties of mixed clusters formed from nonmetal and semimetal atoms are interesting. This paper offers more knowledge about the chemical properties of these mixed clusters.

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpca.6b07435.

HOMO, LUMO, and HOMO–LUMO gap values obtained with PBE and M06L functionals, and all the initial geometries that were optimized including the total energies (PDF)

## ■ AUTHOR INFORMATION

### ■ Corresponding Author

\*E-mail: [martina@unam.mx](mailto:martina@unam.mx). Phone Number (52) 55 5622-4596.

### ■ Notes

The author declares no competing financial interest.

## ■ ACKNOWLEDGMENTS

This study was funded by DGAPA-PAPIIT, Consejo Nacional de Ciencia y Tecnología (CONACYT), and resources provided by the Instituto de Investigaciones en Materiales (IIM). This work was carried out using a NES supercomputer, provided by Dirección General de Cómputo y Tecnologías de Información y Comunicación (DGTIC), Universidad Nacional Autónoma de México (UNAM). I would like to thank the DGTIC of UNAM for their excellent and free supercomputing services and Caroline Karlake (Masters, Social Anthropology, Cambridge University, England) for reviewing the grammar and style of the text in English. The author would like to acknowledge Oralia L Jiménez, María Teresa Vázquez, and Caín González for their technical support.

## ■ REFERENCES

- (1) Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. C60: Buckminsterfullerene. *Nature (London, U. K.)* **1985**, *318*, 162–163.
- (2) Li, B.; Cao, P.; Que, D. Distorted icosahedral cage structures of Si<sub>60</sub> clusters. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2000**, *61*, 1685–1687.
- (3) Wang, L.; Li, D.; Yang, D. Fully exohydrogenated Si<sub>60</sub> fullerene cage. *Mol. Simul.* **2006**, *32*, 663–666.
- (4) Sheka, E. F.; Nikitina, E. A.; Zayets, V. A.; Ginzburg, I. Y. High-spin silicon fullerene Si<sub>60</sub> and its oligomers. *Int. J. Quantum Chem.* **2002**, *88*, 441–448.
- (5) Zdetsis, A. Theoretical predictions of a new family of stable bismuth and other group 15 fullerenes. *J. Phys. Chem. C* **2010**, *114*, 10775–10781.
- (6) Norman, N. C. *Chemistry of Arsenic, Antimony and Bismuth*, 1st ed.; Springer: Heidelberg, 1997; p 496.
- (7) Su, C.; Liu, H. T.; Li, J. M. Bismuth nanotubes: potential semiconducting nanomaterials. *Nanotechnology* **2002**, *13*, 746–749.
- (8) Zhou, G.; Li, L.; Li, G. H. Enhancement of thermoelectric figure of merit in bismuth nanotubes. *Appl. Phys. Lett.* **2010**, *97*, 023112/1–023112/3.
- (9) Ma, D.; Zhao, J.; Li, Y.; Su, X.; Hou, S.; Zhao, Y.; Hao, X. L.; Li, L. Organic molecule directed synthesis of bismuth nanostructures with

varied shapes in aqueous solution and their optical characterization. *Colloids Surf, A* **2010**, *368*, 105–111.

(10) Derrouiche, S.; Zoican Loebick, C.; Wang, C.; Pfefferle, L. Energy-induced morphology changes in bismuth nanotubes. *J. Phys. Chem. C* **2010**, *114*, 4336–4339.

(11) Yang, D.; Meng, G.; Xu, Q.; Han, F.; Kong, M.; Zhang, L. Electronic transport behavior of bismuth nanotubes with a pre-designed wall thickness. *J. Phys. Chem. C* **2008**, *112*, 8614–8616.

(12) Derrouiche, S.; Loebick, C. Z.; Pfefferle, L. Optimization of routes for the synthesis of bismuth nanotubes: implications for nanostructure form and selectivity. *J. Phys. Chem. C* **2010**, *114*, 3431–3440.

(13) Boldt, R.; Kaiser, M.; Kohler, D.; Krumeich, F.; Ruck, M. High-yield synthesis and structure of double-walled bismuth nanotubes. *Nano Lett.* **2010**, *10*, 208–210.

(14) Rasche, B.; Seifert, G.; Enyashin, A. Stability and electronic properties of bismuth nanotubes. *J. Phys. Chem. C* **2010**, *114*, 22092–22097.

(15) Li, S. F.; Gao, L.; Gong, X. G.; Guo, Z. X. No cage, no tube: relative stabilities of nanostructures. *J. Phys. Chem. C* **2008**, *112*, 13200–13203.

(16) Qi, J.; Shi, D.; Jiang, X. The structures and electronic properties of double-wall bismuth nanotubes from first-principle calculations. *Chem. Phys. Lett.* **2008**, *460*, 266–271.

(17) Gao, L.; Li, P.; Lu, H.; Li, S. F.; Guo, Z. X. Size- and charge-dependent geometric and electronic structures of Bi<sub>n</sub> (Bi<sub>n</sub><sup>−</sup>) clusters (n = 2–13) by first-principles simulations. *J. Chem. Phys.* **2008**, *128*, 194304/1–194304/9.

(18) Karttunen, A. J.; Linnolahti, M.; Pakkanen, T. A. Structural and electronic trends among group 15 polyhedral fullerenes. *Theor. Chem. Acc.* **2011**, *129*, 413–422.

(19) Kharisova, O. V.; Osorio, M.; Sánchez-Vázquez, M.; Kharisov, B. I. Computational chemistry calculations of stability for bismuth nanotubes, fullerene-like structures and hydrogen-containing nanostructures. *J. Mol. Model.* **2012**, *18*, 3981–3992.

(20) 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*, revision A.08; Gaussian, Inc.: Wallingford, CT, 2009.

(21) Zhao, Y.; Truhlar, D. G. The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, non-covalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals. *Theor. Chem. Acc.* **2008**, *120*, 215–241.

(22) Hay, P. J.; Wadt, W. R. Ab initio effective core potentials for molecular calculations-potentials for the transition-metal atoms Sc to Hg. *J. Chem. Phys.* **1985**, *82*, 270–283.

(23) Hay, P. J.; Wadt, W. R. Ab initio effective core potentials for molecular calculations- potentials for K to Au including the outermost core orbitals. *J. Chem. Phys.* **1985**, *82*, 299–310.

(24) Wadt, W. R.; Hay, P. J. Ab initio effective core potentials for molecular calculations- potentials for main group elements Na to Bi. *J. Chem. Phys.* **1985**, *82*, 284–298.

(25) Gázquez, J. L. Perspectives on the density functional theory of chemical reactivity. *J. Mex. Chem. Soc.* **2008**, *52*, 3–10.

(26) Gázquez, J. L.; Cedillo, A.; Vela, A. Electrodonating and electroaccepting powers. *J. Phys. Chem. A* **2007**, *111*, 1966–1970.

(27) Martínez, A.; Rodríguez-Gironés, M. A.; Barbosa, A.; Costas, M. Donator Acceptor Map for Carotenoids, Melatonin and Vitamins. *J. Phys. Chem. A* **2008**, *112*, 9037–9042.

(28) Martínez, A. Gold-Bismuth clusters. *J. Phys. Chem. A* **2014**, *118*, 5894–5902.

(29) Filippi, C.; Umrigar, C. J.; Gonze, X. Excitation energies from density functional perturbation theory. *J. Chem. Phys.* **1997**, *107*, 9994–10002.

(30) Savin, A.; Umrigar, C. J.; Gonze, X. Relationship of Kohn-Sham eigenvalues to excitation energies. *Chem. Phys. Lett.* **1998**, *288* (2–4), 391–395.

(31) Ayers, P. W.; Morrison, R. C.; Parr, R. G. Fermi-Amaldi model for exchange-correlation: atomic excitation energies from orbital energy differences. *Mol. Phys.* **2005**, *103*, 2061–2072.

(32) van Meer, R.; Gritsenko, O. V.; Baerends, E. J. Physical Meaning of Virtual Kohn–Sham Orbitals and Orbital Energies: An Ideal Basis for the Description of Molecular Excitations. *J. Chem. Theory Comput.* **2014**, *10*, 4432–4441.

(33) Yang, Z. H.; Peng, H. W.; Sun, J. W.; Perdew, J. P. More realistic band gaps from meta-generalized gradient approximations: Only in a generalized Kohn–Sham scheme. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2016**, *93*, 205205.