The Electrochemical Society
Advancing solid state & electrochemical science & technology

Ho@C$_{82}$ Metallofullerene: Calculated Isomeric Composition

View the article online for updates and enhancements.

Ho@C$_{82}$ Metallofullerene: Calculated Isomeric Composition

Zdeněk Slanina,[1,z] ● Filip Uhlík,[2] Lai Feng,[3] and Ludwik Adamowicz[1]

[1]*Department of Chemistry and Biochemistry, University of Arizona, Tucson, AZ 85721-0041, United States of America*
[2]*Department of Physical and Macromolecular Chemistry, Charles University in Prague, Faculty of Science, 128 43 Praha 2, Czech Republic*
[3]*Soochow Institute for Energy and Materials Innovation (SIEMIS), Jiangsu Key Laboratory of Advanced Carbon Materials and Wearable Energy Technologies, School of Energy, Soochow University, Suzhou 215006, People's Republic of China*

Relative populations of the three energy-lowest IPR (isolated-pentagon-rule) isomers of Ho@C$_{82}$ under the high-temperature synthetic conditions are computed using the Gibbs energy based on characteristics from the density functional theory calculations (B3LYP/3-21G ∼ SDD entropy term, B3LYP/6-31G* ∼ SDD energetics). Two major species are predicted, Ho@C$_{2v}$; 9-C$_{82}$ and Ho@C$_s$(c); 6-C$_{82}$, with rather comparable populations under supposed synthetic temperatures. Roles of the inter-isomeric thermodynamic equilibrium and solubility are discussed.

Various metallofullerenes have been studied as promising agents for single-molecule electronics as well as superconductive or magnetic properties. Such studies have also been dealing with holmium metallofullerenes,[1–7] especially with Ho@C$_{82}$. However, just one of its isomers has been considered, namely the endohedral with the isolated-pentagon-rule (IPR) obeying carbon cage conventionally labeled[8] as Ho@C$_{2v}$; 9-C$_{82}$. The C$_{82}$ cages are known to encapsulate also several other metals, frequently yielding at least two isomers.[9–16] In this study, the isomeric interplay is simulated for the set of three energy-lowest Ho@C$_{82}$ IPR isomers in order to supply still missing information on their relative populations (as it is useful for more comprehensive interpretation of experiments).

Although stabilities of nanocarbons are mostly studied with the potential energy only, there is a growing group of examples[17–23] that the entropic part of the Gibbs energy for metallofullerenes becomes important at high temperatures. In some systems, a structure that is not the lowest in potential energy can still be calculated as the most populated one at high synthetic temperatures. Moreover, other higher-energy structures can sometimes undergo relative stability interchanges with increasing temperature. Such relative-stability aspects cannot at all be obtained just from the potential energies. Thus, calculations are carried out in this paper for the relative populations of three potential-energy lowest Ho@C$_{82}$ IPR isomers at elevated temperatures, consistently using both enthalpy and entropy components of the Gibbs energy, in order to understand the isomeric interplay at synthetic conditions.

Calculations

The molecular-geometry optimization for the isomers started from the structures optimized in a combined basis set, 3–21G basis[24] for C atoms and SDD basis[25] with the SDD effective core potential on Ho (coded here 3–21G ∼ SDD), using density functional theory (DFT) approach, namely Becke's three parameter functional[26] with the non-local Lee-Yang-Parr correlation functional,[27] i.e., the unrestricted B3LYP/3–21G ∼ SDD treatment. Moreover, the structures were further re-optimized using the standard 6-31G* basis set[28] for C atoms, i.e., the B3LYP/6–31G* ∼ SDD level. The analytical energy gradient was used in the geometry optimizations. The wavefunction stability was systematically checked in order to avoid unstable solutions. In the search for low-energy species, all nine[8] IPR C$_{82}$ cages were considered. The optimizations at the B3LYP/3-

21G ∼ SDD and B3LYP/6-31G* ∼ SDD levels point out three species lowest in the potential energy (Table 1). All other isomers are more than 6 kcal/mol higher at the B3LYP/3-21G ∼ SDD level than the stabilomer Ho@C$_{2v}$; 9-C$_{82}$ (more than 9 kcal/mol in the B3LYP/6-31G* ∼ SDD energy) which in this case, in combination with their disfavouring entropy factors, renders their relative populations insignificant. The inter-isomeric energetics was also checked using the restricted open-shell second order Møller-Plesset perturbation treatment[29] considering all electrons (ROMP2=FU) with the 6-31G* ∼ SDD basis set (in the optimized B3LYP/6-31G* ∼ SDD geometries).

In the optimized B3LYP/3-21G ∼ SDD geometries, the harmonic vibrational analysis was carried out with the analytical force-constant matrix. The electronic excitation energies were evaluated by means of the time-dependent (TD) DFT response theory[30] at the B3LYP/6-31G* ∼ SDD level. The computations are carried out with the Gaussian 09 program package.[31]

Relative concentrations (mole fractions) x_i of m isomers can be expressed[32,33] through their partition functions q_i and the enthalpies at the absolute zero temperature or ground-state energies $\Delta H_{0,i}^o$ (i.e., the relative potential energies corrected for the vibrational zero-point energies) by a compact formula:

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

where R is the gas constant and T the absolute temperature. Equation 1 is an exact formula that can be directly derived[32] from the standard Gibbs energies of the isomers, supposing the conditions of the inter-isomeric thermodynamic equilibrium. Rotational-vibrational partition functions are evaluated[33] here using the conventional rigid rotator and harmonic oscillator (RRHO) approximation. No frequency scaling is applied as it is not significant[34] for the x_i values at high temperatures. The first ten electronic excitation energies are used for the construction of the electronic partition function q_{el}. Finally, the chirality contribution[35] was included accordingly (for an enantiomeric pair its partition function q_i is doubled). Although the temperature region where fullerene or metallofullerene electric-arc synthesis takes place is not yet known, the recent observations[36] supply some arguments to expect it around 1500 K. Thus, the computed results discussed here are also focused on the temperature region.

However, a modified[21,37] RRHO approach for description of the encapsulate motions is actually considered here, following findings[38]

zE-mail: zdeneks@email.arizona.edu

Table 1. Ho@C$_{82}$ relative potential energies $\Delta E_{pot,rel}$ for the three energy-lowest isomers calculated in the B3LYP/6-31G* ~ SDD optimized structures.

Species	$\Delta E_{pot,rel}$ / kcal.mol^{-1}		
	B3LYP/3-21G ~ SDD[a)]	B3LYP/6-31G* ~ SDD	ROMP2=FU/6-31G* ~ SDD
$C_2(c)$; 5	2.68	4.40	5.40
$C_s(c)$; 6[b)]	0.79	1.83	1.30
C_{2v}; 9[b)]	0.0	0.0	0.0

a) In the B3LYP/3-21G ~ SDD optimized structure. b) See Fig. 1.

that the encapsulated atoms can exercise large amplitude motions, especially so at elevated temperatures (unless the motions are restricted by cage derivatizations[39]). One can expect that if the encapsulate is relatively free then, at sufficiently high temperatures, its motions in different cages will produce about the same contribution to the partition functions. However, such uniform contributions would then cancel out in Eq. 1. This simplification is called[21,37] 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, which reflects averaging effects of the large amplitude motions. For example, for the Ho@C$_{82}$ IPR isomer based on the C_{2v}; 9 cage (Table 1), the C_{2v} symmetry is employed within the FEM scheme though its static[40] symmetry (i.e., after the geometry optimization) is only C_s (Fig. 1). Generally, the FEM treatment gives a better agreement[21,37] with the available observed data compared to the conventional RRHO approach and it is therefore also preferred here.

Results and Discussion

Table 1 presents the Ho@C$_{82}$ relative isomeric energetics computed at the three selected levels (just the differences in the potential energy without the zero-point vibrational energies). There are nine[8,41] IPR satisfying topologies for the empty C$_{82}$ cages. Two labeling systems for the C$_{82}$ IPR cages are employed[8,41] in the literature. One of them uses the symmetries of the cages (actually, the highest topologically possible symmetries): $C_{3v}(a)$, $C_{3v}(b)$, C_{2v}, $C_2(a)$, $C_2(b)$, $C_2(c)$, $C_s(a)$, $C_s(b)$, and $C_s(c)$. The other system labels them with enumeration serial numbers, their assignment is:

$C_{3v}(a)$; 7, $C_{3v}(b)$; 8, C_{2v}; 9, $C_2(a)$; 3, $C_2(b)$; 1, $C_2(c)$; 5, $C_s(a)$; 2, $C_s(b)$; 4, and $C_s(c)$; 6. The lowest-energy Ho@C$_{82}$ isomer is the C_{2v}; 9 species (Fig. 1), being rather closely followed by the $C_s(c)$; 6 and $C_2(c)$; 5 species (while all other isomers are at the B3LYP/6-31G* ~ SDD level more than 9 kcal/mol higher than Ho@C_{2v}; 9-C$_{82}$ - cf. an extended Table in SI available online at stacks.iop.org/JSS/11/053018/mmedia). Thus, only the three isomers from Table 1 are considered in the thermodynamic treatment.

Table 2 presents selected calculated characteristics for the three potential-energy-lowest Ho@C$_{82}$ isomers. The B3LYP/6-31G* ~ SDD calculated closest contacts between Ho and the cages are similar to those found previously with other C$_{82}$ based metallofullerenes.[14,16,41] The lowest vibrational frequencies in Table 2 are in agreement with the generally known relatively-free motions of encapsulates in metallofullerenes. The lowest electronic excited state has a rather similar excitation energy for the three isomers. The B3LYP/3-21G ~ SDD computed Mulliken atomic charges on Ho are close to 2. Let us mention that the Mulliken charges from the 3-21G ~ SDD basis, in contrast to, e.g., the 6-31G* ~ SDD level, give[23] for metallofullerenes a good agreement with the observed charges.[42] Moreover, there are more general arguments[43–46] why larger basis sets should be avoided for the Mulliken charges.

Figure 2 presents the main output of this study—temperature development of the relative equilibrium populations for the three potential-energy-lowest Ho@C$_{82}$ isomers in a wide temperature region. The relative populations are evaluated in the FEM treatment (for comparison, with and without the electronic partition functions q_{el}). At very low temperatures the structure lowest in the $\Delta H_{0,i}^o$ scale must be prevailing, i.e., the Ho@C_{2v}; 9-C$_{82}$ isomer. However, the second lowest species in the potential energy, Ho@$C_s(c)$; 6-C$_{82}$,
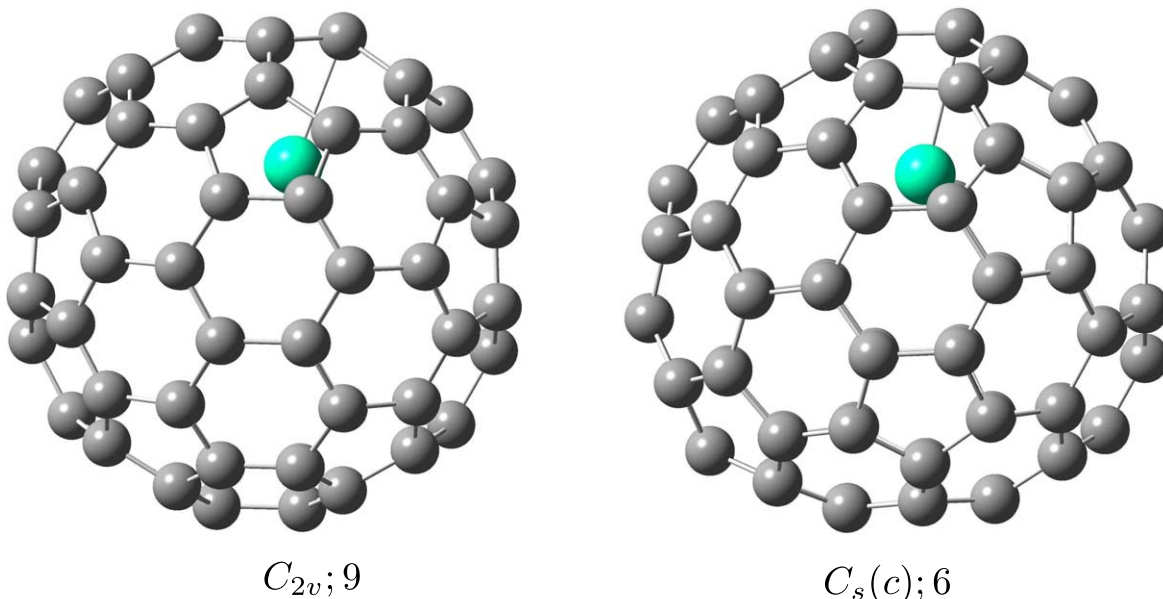

$C_{2v}; 9$ $C_s(c); 6$

Figure 1. The B3LYP/6-31G* ~ SDD optimized structures of the two most populated Ho@C$_{82}$ isomers (the shortest Ho-C contact is indicated by a link).
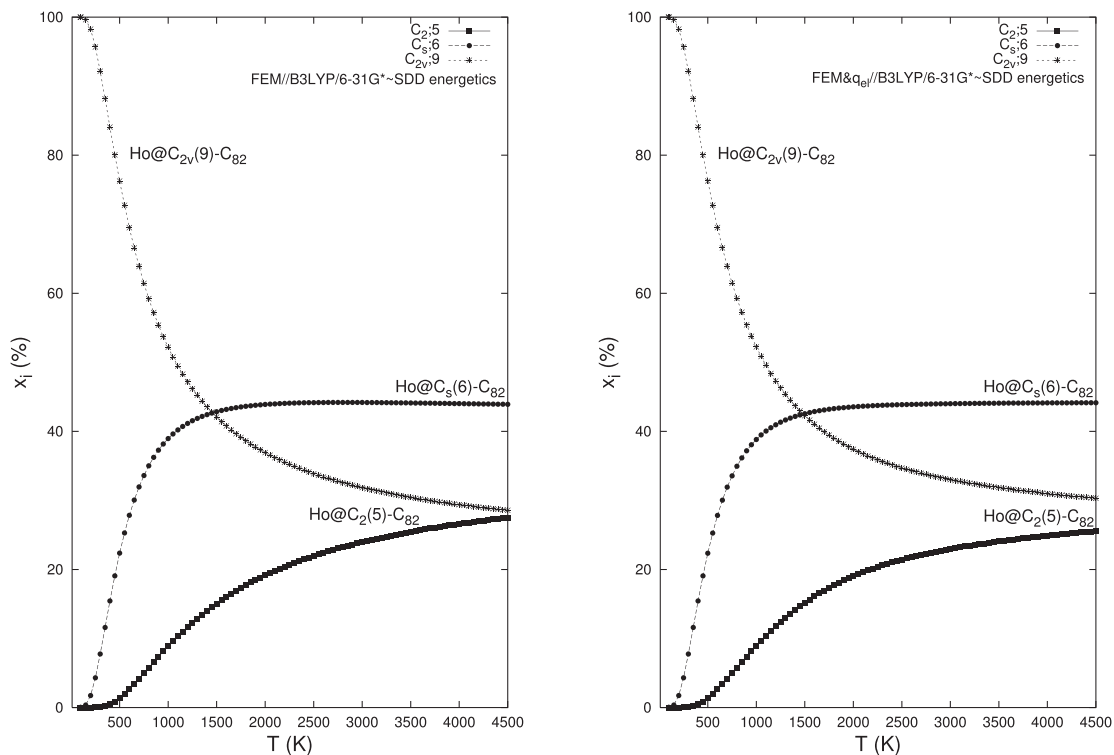
Figure 2. The relative populations of the Ho@C_{82} isomers based on the FEM treatment without (left) and with the electronic partition function q_{el} (right) with the B3LYP/3-21G $\sim$ SDD entropy and B3LYP/6-31G* $\sim$ SDD energetics.

Table 2. The selected characteristics of the three energy-lowest Ho@C_{82} isomers—the closest Ho-C contact[a] r_{Ho-C}, the Mulliken charge[b] on Ho q_{Ho}, the lowest vibrational frequency[b] ω_{low}, and the lowest electronic excited state[a] Ω_{low}.

Species	r_{Ho-C} / Å	q_{Ho}	ω_{low} / cm^{-1}	Ω_{low} / cm^{-1}
$C_2(c)$; 5	2.555	2.146	28.6	2232
$C_s(c)$; 6[c]	2.454	2.155	11.4	2428
C_{2v}; 9[c]	2.481	2.153	30.7	2364

a) B3LYP/6-31G* $\sim$ SDD terms. b) B3LYP/3-21G $\sim$ SDD terms. c) See Fig. 1.

exhibits rather fast increase of its relative population so that the two isomers have comparable concentrations in the supposed synthetic temperature region. Interestingly, the effect of the electronic partition functions is not really important in this system. The equimolarity of the two most populated isomers is reached at a temperature of 1483 K and 1457 K for the FEM treatment with and without the electronic partition functions q_{el}, respectively. Let us note that the population results are sensitive to the inter-isomeric energetics. For example, if the separation energy of the Ho@$C_s(c)$; 6-C_{82} isomer is increased by 0.5 kcal/mol, the equimolarity temperature would be increased from 1457 K to 1852 K. On the other hand, the third energy-lowest isomer, Ho@$C_2(c)$; 5-C_{82}, is already rather unimportant in the relevant temperature region. Let as add for completeness that if the three-memebered isomeric set is expanded to include five energy-lowest isomers, at a representative synthetic temperature of 1500 K the $C_{3v}(a)$; 7 and $C_{3v}(b)$; 8 isomers represent mere 0.8 and 1.1 % of the five-membered equilibrium mixture, respectively. Hence, the FEM approach supports the fact that the Ho@C_{2v}; 9-C_{82} isomer has by now been considered in the experimental studies.[1–6] However, the calculations also predicted that the Ho@$C_s(c)$; 6-C_{82} isomer should also be produced in a comparable population if the supposed thermodynamic-equilibrium conditions can be achieved.

The presented results are somewhat similar to the previous calculations[11,21,47–49] for the C_{82} based metallofullerenes with a similar metal-to-cage charge transfer (while different relative-population pictures come in systems[12,50] with a higher charge transfer). This similarity stresses the fact that metallofullerenes are not formed via some new covalent bond but rather stabilized by just an ionic bond.[51–55] Let us add that observed populations can depend on the applied metal sources[56] that could be related to kinetic and catalytic aspects,[57,58] i.e., to different degrees to which the expected inter-isomeric thermodynamic equilibrium could be achieved in the synthesis. Another issue is solubility[59,60] of different isomers in the applied extraction solvents—it can hardly be exactly the same (as supposed when comparing the results from the computational treatment of the isomeric relative populations with observed data). Hence, the thermodynamic-equilibrium issue and/or solubility should be a primary explanation why by now only the Ho@C_{2v}; 9-C_{82} isomer has been treated in experiments.

Acknowledgments

ORCID

Zdeněk Slanina ⓘ https://orcid.org/0000-0003-0292-9350

References

1. A. Bartl, L. Dunsch, J. Fröhner, and U. Kirbach, *Chem. Phys. Lett.*, **229**, 115 (1994).
2. W. Wang, J. Ding, S. Yang, and X.-Y. Li, *Fullerenes, Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials*, ed. K. M. Kadish and R. S. Ruoff (Electrochemical Society, Pennington) 4, p. 417 (1997).
3. C. Knapp, N. Weiden, and K.-P. Dinse, *Appl. Phys. A*, **66**, 249 (1998).

4. H. J. Huang, S. H. Yang, and X. X. Zhang, *J. Phys. Chem. B*, **103**, 5928 (1999).
5. H. Huang, S. Yang, and X. Zhang, *J. Phys. Chem. B*, **104**, 1473 (2000).
6. I. E. Kareev, V. M. Nekrasov, A. E. Dutlov, and V. M. Martynenko, *Russ. J. Phys. Chem.*, **91**, 536 (2017).
7. L. Feng, Y. Hao, A. Liu, and Z. Slanina, *Acc. Chem. Res.*, **52**, 1802 (2019).
8. Z. Slanina, F. Uhlík, S.-L. Lee, T. Akasaka, and S. Nagase, *Handbook of Carbon Nano Materials, vol 4. Materials and Fundamental Applications*, ed. F. D'Souza and K. M. Kadish (World Scientific Publishing Co., Singapore) p. 381 (2012).
9. S. Suzuki, S. Kawata, H. Shiromaru, K. Yamauchi, K. Kikuchi, T. Kato, and Y. Achiba, *J. Phys. Chem.*, **96**, 7159 (1992).
10. E. Nishibori, M. Takata, M. Sakata, M. Inakuma, and H. Shinohara, *Chem. Phys. Lett.*, **298**, 79 (1998).
11. Z. Slanina, K. Kobayashi, and S. Nagase, *J. Chem. Phys.*, **120**, 3397 (2004).
12. Z. Slanina, K. Kobayashi, and S. Nagase, *Chem. Phys. Lett.*, **388**, 74 (2004).
13. M. Suzuki, Z. Slanina, N. Mizorogi, X. Lu, S. Nagase, M. M. Olmstead, A. L. Balch, and T. Akasaka, *J. Am. Chem. Soc.*, **134**, 18772 (2012).
14. Z. Slanina, F. Uhlík, S.-L. Lee, M. Suzuki, X. Lu, N. Mizorogi, S. Nagase, and T. Akasaka, *Fulleren. Nanotub. Carb. Nanostruct*, **22**, 147 (2014).
15. Z. Hu, Y. Hao, Z. Slanina, Z. Gu, Z. Shi, F. Uhlík, Y. Zhao, and L. Feng, *Inorg. Chem.*, **54**, 2103 (2015).
16. Z. Slanina, F. Uhlík, L. Feng, and L. Adamowicz, *Fulleren. Nanotub. Carb. Nanostruct*, **26**, 233 (2018).
17. Z. Slanina, S.-L. Lee, and L. Adamowicz, *Int. J. Quantum. Chem.*, **63**, 529 (1997).
18. Z. Slanina and F. Uhlík, *J. Phys. Chem.*, **95**, 5432 (1991).
19. Z. Slanina, X. Zhao, S.-L. Lee, and E. Ōsawa, *Chem. Phys.*, **219**, 193 (1997).
20. Z. Slanina, S.-L. Lee, L. Adamowicz, F. Uhlík, and S. Nagase, *Int. J. Quantum Chem.*, **104**, 272 (2005).
21. Z. Slanina, S.-L. Lee, F. Uhlík, L. Adamowicz, and S. Nagase, *Theor. Chem. Acc.*, **117**, 315 (2007).
22. Y. Wang, R. Morales-Martínez, X. Zhang, W. Yang, Y. Wang, A. Rodríguez-Fortea, J. M. Poblet, L. Feng, S. Wang, and N. Chen, *J. Am. Chem. Soc.*, **139**, 5110 (2017).
23. Z. Slanina, F. Uhlík, S. Nagase, T. Akasaka, L. Adamowicz, and X. Lu, *Molecules*, **22**, 1053 (2017).
24. J. S. Binkley, J. A. Pople, and W. J. Hehre, *J. Am. Chem. Soc.*, **102**, 939 (1980).
25. X. Y. Cao and M. Dolg, *J. Mol. Struct. (Theochem)*, **581**, 139 (2002).
26. A. D. Becke, *J. Chem. Phys.*, **98**, 5648 (1993).
27. C. Lee, W. Yang, and R. G. Parr, *Phys. Rev. B*, **37**, 785 (1988).
28. W. J. Hehre, R. Ditchfield, and J. A. Pople, *J. Chem. Phys.*, **56**, 2257 (1972).
29. C. Møller and M. S. Plesset, *Phys. Rev.*, **46**, 618 (1934).
30. M. E. Casida, C. Jamorski, K. C. Casida, and D. R. Salahub, *J. Chem. Phys.*, **108**, 4439 (1998).
31. M. J. Frisch et al., *Gaussian Inc 09, Rev. C.01* (Gaussian Inc., Wallingford, CT) (2009).
32. Z. Slanina, *Int. Rev. Phys. Chem.*, **6**, 251 (1987).
33. Z. Slanina, *Comput. Chem.*, **13**, 305 (1989).
34. Z. Slanina, F. Uhlík, and M. C. Zerner, *Rev. Roum. Chim.*, **36**, 965 (1991).
35. Z. Slanina and L. Adamowicz, *Thermochim. Acta.*, **205**, 299 (1992).
36. R. J. Cross and M. Saunders, *J. Am. Chem. Soc.*, **127**, 3044 (2005).
37. Z. Slanina, L. Adamowicz, K. Kobayashi, and S. Nagase, *Mol. Simul.*, **31**, 71 (2005).
38. T. Akasaka, S. Nagase, K. Kobayashi, M. Walchli, K. Yamamoto, H. Funasaka, M. Kako, T. Hoshino, and T. Erata, *Angew. Chem. Int. Ed.*, **36**, 1643 (1997).
39. K. Kobayashi, S. Nagase, Y. Maeda, T. Wakahara, and T. Akasaka, *Chem. Phys. Lett.*, **374**, 562 (2003).
40. Z. Slanina, "Contemporary Theory of Chemical Isomerism."(Academia, Prague & D. Reidel Publ. Comp., Dordrecht) p. 21 (1986).
41. Z. Slanina, F. Uhlík, L. Bao, T. Akasaka, X. Lu, and L. Adamowicz, *Chem. Phys. Lett.*, **726**, 29 (2019).
42. M. Takata, E. Nishibori, M. Sakata, and H. Shinohara, *New Diam. Front. Carb. Technol.*, **12**, 271 (2002).
43. W. J. Hehre and A. Guide, *A Guide to Molecular Mechanics and Quantum Chemical Calculations* (Wavefunction, Irvine) p. 435 (2003).
44. F. Jensen, *Introduction to Computational Chemistry* (Wiley, Chichester) p. 319 (2017).
45. J. M. Campanera, C. Bo, and J. M. Poblet, *Angew. Chem. Int. Ed.*, **44**, 7230 (2005).
46. Z. Slanina, F. Uhlík, C. Pan, T. Akasaka, X. Lu, and L. Adamowicz, *Chem. Phys. Lett.*, **710**, 147 (2018).
47. Z. Slanina, F. Uhlík, S.-L. Lee, and S. Nagase, *J. Comput. Meth. Sci. Engn.*, **10**, 569 (2010).
48. Z. Slanina, F. Uhlík, W. Shen, T. Akasaka, X. Lu, and L. Adamowicz, *Fulleren. Nanotub. Carb. Nanostruct.*, **27**, 710 (2019).
49. Z. Slanina, F. Uhlík, T. Akasaka, X. Lu, and L. Adamowicz, *ECS J. Solid State Sci. Technol.*, **10**, 071013 (2021).
50. Q. Y. Meng, R. Morales-Martínez, J. X. Zhuang, Y. R. Yao, Y. F. Wang, L. Feng, J. M. Poblet, A. Rodríguez-Fortea, and N. Chen, *Inorg. Chem.*, **60**, 11496 (2021).
51. W. Andreoni and A. Curioni, *Phys. Rev. Lett.*, **77**, 834 (1996).
52. A. A. Popov and L. Dunsch, *Chem. Eur. J.*, **15**, 9707 (2009).
53. Z. Slanina, F. Uhlík, S.-L. Lee, L. Adamowicz, T. Akasaka, and S. Nagase, *Int. J. Quant. Chem.*, **111**, 2712 (2011).
54. A. Rodríguez-Fortea, A. L. Balch, and J. M. Poblet, *Chem. Soc. Rev.*, **40**, 3551 (2011).
55. A. A. Popov, S. Yang, and L. Dunsch, *Chem. Rev.*, **113**, 5989 (2013).
56. H. Yang, M. Yu, H. Jin, Z. Liu, M. Yao, B. Liu, M. M. Olmstead, and A. L. Balch, *J. Am. Chem. Soc.*, **134**, 5331 (2012).
57. Z. Slanina, X. Zhao, F. Uhlık, M. Ozawa, and E. Ōsawa, *J. Organomet. Chem.*, **599**, 57 (2000).
58. Y. Hao, Q. Tang, X. Li, M. Zhang, Y. Wan, L. Feng, N. Chen, Z. Slanina, L. Adamowicz, and F. Uhlík, *Inorg. Chem.*, **55**, 11354 (2016).
59. Y. Lian, Z. Shi, X. Zhou, and Z. Gu, *Chem. Mater.*, **16**, 1704 (2004).
60. Y. Maeda et al., *Carbon*, **98**, 67 (2016).