

Research Article

I_h Symmetrical (4,6)-Fullerenes and Their Local Ring Aromaticity: A First Principle Study

Jing Wang, Haigang Lu, Yingfang Fan, and Si-Dian Li

Key Laboratory of Chemical Biology and Molecular Engineering of the Education Ministry, Institute of Molecular Science, Shanxi University, Taiyuan, Shanxi 030006, China

Correspondence should be addressed to Haigang Lu; luhg@sxu.edu.cn

Received 6 April 2015; Accepted 30 May 2015

Academic Editor: Stefano Bellucci

Copyright © 2015 Jing Wang et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

As the natural extension of carbon fullerene, a series of I_h symmetrical (4,6)-fullerenes were constructed and investigated using first principle methods. These I_h (4,6)-fullerenes consist of many four- and six-membered rings and are classified into two types: (1) those with isolated four- and six-membered rings and (2) those with connected four- and/or six-membered rings. Though these (4,6)-fullerenes are less stable than I_h C_{60} and C_{240} (5,6)-fullerene, it is possible to synthesize them from their elemental unit, anti-kekulene, which was nearly synthesized experimentally. Though the (4,6)-fullerenes are mainly spherical and antiaromatic compounds, the local aromatic indexes indicate that all of the planar π -conjugated rings have local aromaticity in fullerenes, which provides reasonable delocalization, which is consistent with our chemical intuition. Because of the huge cavities and suitable pore sizes present in the (4,6)-fullerenes, they can be taken as potential nanocontainers for the storage of small molecules.

1. Introduction

Since the striking developments of carbon fullerenes, many fullerenes with novel topology have been proposed theoretically in the search for new materials [1–6]. The famous I_h C_{60} fullerene consists of 20 six-membered rings (6-MR) and 12 five-membered rings (5-MR) made up of sp^2 -hybridized carbon atoms. Recently, cubane-like D_{2d} B_{40} and C_3 B_{39} fullerenes have been discovered using both experimental and theoretical methods [7, 8]. In the experiments, benzene-like anti-kekulene, which consists of six 6-MRs connected by six four-membered rings (4-MR), has been nearly synthesized [9]. Just like the 6-MR and 5-MR, the 4-MR should also be regarded as an elemental unit that can be used for the construction of low-dimensional carbon materials. Therefore, it is natural to consider the carbon fullerenes that consist of some 6-MRs and 4-MRs, the so-called (4,6)-fullerenes.

The topological rules of (4,6)-fullerenes have now been systematically deduced by Ashrafi and Mehranian [10]. Two-dimensional carbon materials made up of 6-MRs and 4-MRs have been proposed theoretically [11, 12], from which the (4,6)-fullerenes can be formed by rolling up these materials. Fullerenes with 4-MRs can also be investigated for storage of

noble gas and hydrogen [13, 14]. However, there is no systematical investigation reported to date on the three-dimensional geometrical and electronic structures of (4,6)-fullerenes. Among the large number of the (4,6)-fullerenes, the I_h symmetrical derivatives are the most important and will be taken as the model compounds to be investigated in this work.

In the polycyclic π carbon system, the aromaticity is one of the most important properties to understand their geometrical and electronic structures. For two-dimensional carbon materials, the aromaticity of graphene is localized with two π -electrons delocalized over every 6-MR [15], while two-dimensional (4,6) graphenylene is composed of cyclohexatriene units with two quite distinct C-C bonds within a 6-MR [11]. The spherical aromaticity [16–18] and nucleus-independent chemical shift (NICS) [19, 20] value at the cage center are proposed for the fullerenes. The sphere currents of fullerene provide the global and local descriptive views of the aromaticity on the surface [21]. The C_{60} fullerene displays only weak spherical aromaticity because its absolute diamagnetic and paramagnetic currents almost cancel each other out. The ring aromaticity of the fullerenes has been investigated using several approaches [22]. To quantitatively describe the electron delocalization in the rings of

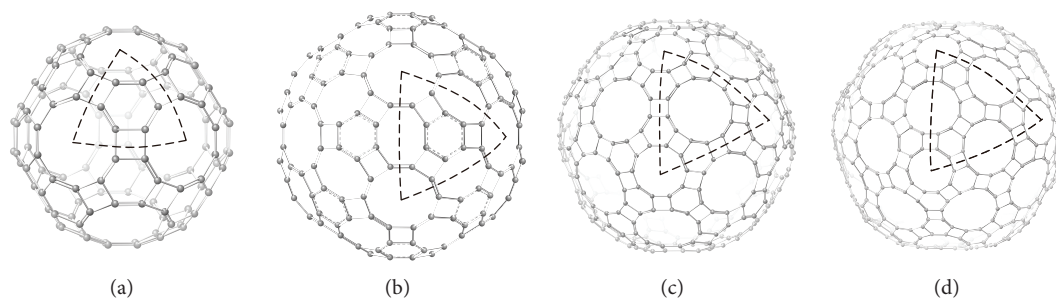


FIGURE 1: The geometrical structures of the $I_h C_{120}$ (a), C_{240} (b), C_{360} (c), and C_{480} (d) (4,6)-fullerenes with isolated four- and six-membered rings. The dashed triangles show the symmetrically unique fragments of the fullerenes with respect to the icosahedron.

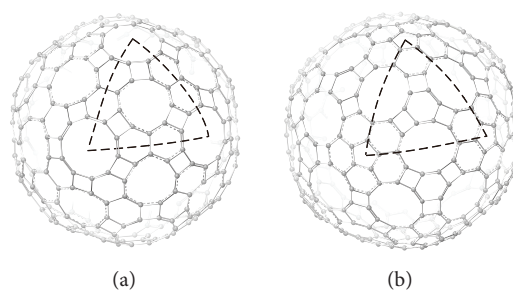


FIGURE 2: The geometrical structures of the $I_h C_{300}$ (a) and C_{360}' (b) (4,6)-fullerenes with connected four- and/or six-membered rings. The dashed triangles show the symmetrically unique fragments of the fullerenes with respect to the icosahedron.

the fullerenes, a local aromatic index will be proposed using natural bonding orbital (NBO) and natural chemical shielding (NCS) analyses [23, 24].

2. Computational Methods

A series of I_h (4,6)-fullerenes were constructed in three steps: (1) construction of the symmetrical unique fragments with respect to the icosahedron, (2) formation of the other symmetrically equivalent atoms, and (3) optimization of the original geometrical structures using density functional theory (DFT). The geometry optimizations were carried out using Becke's three-parameter functional (20% Hartree-Fock nonlocal exchange) [25] with the nonlocal Lee-Yang-Parr correlation functional [26] (B3LYP) in the standard 6-31G* basis set (B3LYP/6-31G*). The NICS values were calculated using the gauge-independent atomic orbital (GIAO) [27] method at the B3LYP/6-31G* level. The first principle calculations were carried out using the Gaussian 09 program [28]. The NBOs and natural chemical shifts (NCS) were analyzed using a combination of the Gaussian 09 package and NBO 6.0 software [29].

3. Results and Discussion

As shown in Figures 1 and 2, sp^2 -hybridized carbon atoms can form a series of I_h (4,6)-fullerenes that can be classified into two types: (1) those with isolated 4- and 6-MRs ($I_h C_{120}$, C_{240} , C_{360} , and C_{480} , Figure 1) and (2) those with connected 4- and 6-MRs ($I_h C_{300}$ and C_{360}' , Figure 2). The C_{120} (4,6)-fullerene, which displays minimum I_h symmetry, was formed

by substituting each atom at C_{20} with cyclohexatriene. The larger fullerenes were formed by the addition of some 4-MRs and/or 6-MRs to each of the equivalent fragments with respect to the icosahedron. In contrast to the buckyball (5,6)-fullerenes, there are many large rings on the surface of the (4,6)-fullerenes, such as 8-, 9-, 10-, and 12-membered rings.

To investigate the stability of the (4,6)-fullerenes studied, we evaluated their binding energies $E_b = E_f - E_{\text{atom}}$, where E_f and E_{atom} are the energies per atom in the fullerenes and in the free state, respectively (Table 1). The difference in the binding energy of the C_{60} and C_{120} fullerenes was only 0.02 eV/atom between the B3LYP/6-31G* and MP2/6-31G* levels [30]. Then, the B3LYP/6-31G* level was used to investigate the stability of a series of fullerenes. Obviously, the (4,6)-fullerenes were about 0.13–0.32 eV/atom less stable than C_{60} fullerene and about 0.38–0.57 eV/atom less stable than C_{240}' (5,6)-fullerene. In addition, the HOMO-LUMO gaps of all the (4,6)-fullerenes studied were less than those of C_{60} and C_{240}' (5,6)-fullerene. Both of these results indicate that the (4,6)-fullerenes are energetically less favorable when compared to the buckyball (5,6)-fullerenes. However, antikekulene was nearly synthesized experimentally [8] and can be taken as an elemental fragment of the (4,6)-fullerenes. Therefore, it is possible to synthesize these I_h (4,6)-fullerenes from the synthetic pathway used to prepare antikekulene.

Similar to graphenylene, the surface of the (4,6)-fullerenes has some pores available to transport small gas molecules. The ring diameters of the 10-MRs and 12-MRs are from 4.5 to 5.5 Å on the surface and their pore sizes are from 2.2 to 3.2 Å, which are suitable for small molecules to pass through.

TABLE 1: The geometrical, energetic, and electronic properties of the fullerenes^a.

	n	D_f	D_r	D_p	E_b	E_g	NICS	NICS ^{m+}
C_{60}	5, 6				6.98	2.73	-2.7	
C_{240}'	5, 6				7.24	2.23	-13.9	
C_{120}	4, 6, 10	10.5	4.5	2.2	6.67	1.89	9.3	-35.4 ⁶⁺
C_{240}	4, 6, 8, 10	15.1	4.5	2.2	6.69	1.57	13.8	-5.3 ¹⁰⁺
C_{360}	4, 6, 10, 12	19.0	5.5	3.2	6.69	1.21	2.7	-22.0 ⁸⁺
C_{480}	4, 6, 10, 12	22.6	5.5	3.2	6.70	1.66	2.0	-23.4 ¹⁰⁺
C_{300}	4, 6, 9, 10	16.4	4.5	2.2	6.75	0.51	6.8	-3.2 ¹⁰⁺
C_{360}'	4, 5, 6, 10	18.5	4.5	2.2	6.86	1.94	-4.2	-17.7 ⁸⁺

^aThe n -ring in the carbon fullerenes (n), the diameter of the fullerenes (D_f , Å), the diameter of the maximum n -rings (D_r , Å), the diameter of the maximum pores (D_p , Å), binding energy (E_b , eV/atom), HOMO-LUMO energy gap (E_g , eV), and spherical NICS values for the fullerenes (NICS, ppm) and their $m+$ charged ions (NICS^{m+}).

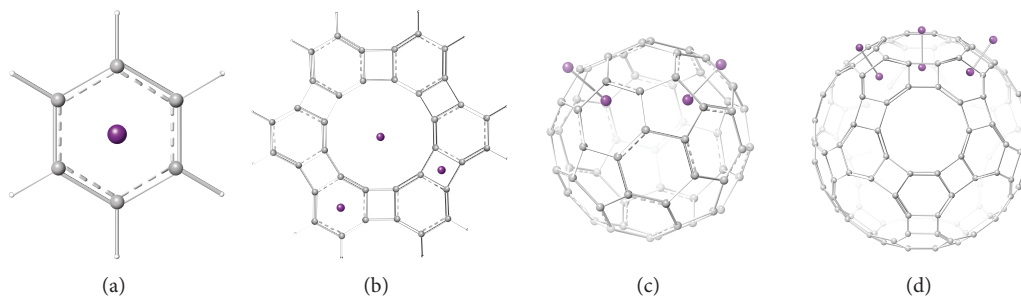


FIGURE 3: The geometrical structures of benzene (a), anti-kekulene (b), $I_h C_{60}$ fullerene (c), and $I_h C_{120}$ (4,6)-fullerene (d). The purple spheres indicate the sites of the ghost atoms in the NICS calculations.

In particular, the pore size of the 12-MR (about 3.2 Å) is, in principle, larger than the kinetic diameter of H_2 (2.89 Å), but smaller than those of CO (3.76 Å), N_2 (3.65 Å), CO_2 (3.30 Å), and CH_4 (3.80 Å). Therefore, the 12-MR provides a selective channel that allows H_2 molecules to access the cavity. In addition, the (4,6)-fullerenes have spherical cavities with diameters from 10.5 to 22.6 Å. Theoretically, these (4,6)-fullerenes have potential as nanocontainers to store small molecules using their huge spherical cavities and suitable pore sizes on their surface.

As the polycyclic π systems of sp^2 -hybridized carbon atoms, (4,6)-fullerenes have many conjugated π bonds. As shown in Figures 1 and 2, the 6-, 10-, and 12-MRs are π -conjugated rings, while most of the 4-MRs consist of only four single σ bonds and no π bond. To understand the electronic characteristics of the (4,6)-fullerenes, it is necessary to investigate their aromaticity.

NICS has proved to be a simple and efficient aromaticity probe. Spherical fullerenes represent a special group of polycyclic π systems, whose aromaticity can be described as spherical aromaticity. Because the electron number does not follow the $2(N+1)^2$ rule for spherical aromaticity [16], the $I_h C_{60}$ and C_{240}' (5,6)-fullerenes display weak spherical aromaticity. However, most of the I_h (4,6)-fullerenes display weak spherical antiaromaticity, except the C_{360}' derivative (Table 1). However, after losing some electrons, most of the (4,6)-fullerenes (C_{120} , C_{240} , C_{360} , and C_{360}') show spherical aromaticity (Table 1). This indicates that the (4,6)-fullerenes

should become more stable when losing some electrons via chemical modification, such as halogenation [31].

Because the absolute diamagnetic and paramagnetic currents partly cancel each other out in the three-dimensional cages [21], their global NICS, which is calculated directly, only partially describes the aromaticity of the electron delocalization in the π -conjugated rings. For instance, the π -conjugated 6-MRs are nonaromatic (NICS (1) = -0.5) in the C_{60} fullerenes, which cannot describe their high local diamagnetic and paramagnetic currents.

To describe the local aromaticity of the rings, we propose a local NICS value based on the NBOs and natural chemical shielding (NCS) analyses. There were three steps used to calculate the local NICS value of a ring: (1) calculation of the global NICS on the ring, (2) decomposition of the global NICS into the individual NBO contributions, and (3) adding all the contributions from the core and bonding NBO on the ring. In addition, because of the different chemical environments in the exterior and interior of fullerene, the average NICS values at 1 Å above and below a ring were used to represent their local ring aromaticity (Figure 3).

The global and local NICS values of some typical π -conjugated systems are given in Table 2. Obviously, the local NICS values are always less than the global ones because the gross contribution of the other atoms is antiaromatic.

In benzene, the local NICS for the six carbon atoms was nearly equal to its global value. Because benzene is the model of aromaticity, its local NICS (-12.0) can be taken as

TABLE 2: The global and local NICS values of the individual n -rings in some typical π -conjugated systems^a.

	n	NICS(1)	NICS(1) ^L	NICS(-1)	NICS(-1) ^L	NICS ⁰	NICS ^{0L}
C ₆ H ₆	6	-11.2	-12.0				
	4	4.7	-4.3				
	12	3.8	-4.1				
Antikekulene	6	-1.8	-7.1				
	12	3.8	-4.1				
	6	-1.8	-7.1				
C ₆₀	5	6.4	1.0	3.1	-3.6	4.8	-1.3
	6	-0.5	-8.6	-5.2	-6.6	-2.9	-7.6
	4	5.1	-3.9	11.6	3.7	8.4	-0.1
C ₁₂₀	6	0.8	-9.4	6.8	-3.1	3.8	-6.3
	10	2.2	-4.6	7.2	-3.7	4.7	-4.2
	4	5.1	-3.9	11.6	3.7	8.4	-0.1

^aThe n -ring (n), the global NICS values at 1 Å above (NICS(1)) and below (NICS(-1)) the ring, the local NICS values at 1 Å above (NICS(1)^L) and below (NICS(-1)^L) the ring, and the average values for the global NICS (NICS⁰) and local NICS (NICS^{0L}).

a standard value of local ring aromaticity. In antikekulene, all of the 4-, 6-, and 12-MRs are π -conjugated, in which the 6-MR displays local aromaticity (NICS = -7.1) and the 4- and 12-MRs show weak aromaticity (NICS = -4.3 and -4.1, resp.).

In the C₆₀ fullerene, the 6-MR is a π -conjugated aromatic (NICS = -7.6), while the 5-MR is nonaromatic (NICS = -1.1) due to the absence of a π bond(s). In the I_h C₁₂₀ (4,6)-fullerene, the π -conjugated 6- and 10-MRs are aromatic (NICS = -6.3) and weakly aromatic (NICS = -4.2), respectively. Similarly, its 4-MR is nonaromatic because it only consists of single bonds and no π bond.

In general, the π -conjugated 6-MR is aromatic, the other π -conjugated rings are weakly aromatic, and the rings without π bonds are nonaromatic, which is consistent with our chemical intuition. In addition, the aromaticity of the 6-MRs in the fullerenes is obviously less than that of benzene, which provides a quantitative description of the difference between benzene and the π -conjugated rings in the fullerenes.

4. Conclusions

In summary, a series of I_h symmetrical (4,6)-fullerenes were constructed and investigated using first principle methods. These I_h (4,6)-fullerenes consist of many 4- and 6-MRs that can be classified into two types: (1) those with isolated 4- and 6-MRs and (2) those with connected 4- and 6-MRs. Though the (4,6)-fullerenes are about 0.13–0.32 eV/atom less stable than the I_h C₆₀ and about 0.38–0.57 eV/atom less than the C₂₄₀ (5,6)-fullerene, it is possible to synthesize them from their elemental fragment, antikekulene, which has been nearly synthesized experimentally. Though the (4,6)-fullerenes are mainly spherical and antiaromatic compounds, their local NICS values indicate that the planar π -conjugated rings are aromatic, which provides some reasonable electronic delocalization, which is consistent with our chemical intuition. The C₃₆₀ and C₄₈₀ (4,6)-fullerenes have pore sizes of 3.2 Å so that only hydrogen gas molecules can easily access their cavities. Consequently, the C₃₆₀ and C₄₈₀ (4,6)-fullerenes can be regarded as potential nanocontainers for hydrogen storage.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

This work was supported by the NSFC (Grant no. 21473106) and High Performance Computing Center of Shanxi University.

References

- [1] H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, and R. E. Smalley, "C₆₀: buckminsterfullerene," *Nature*, vol. 318, pp. 162–163, 1985.
- [2] U. H. F. Bunz, Y. Rubin, and Y. Tobe, "Polyethynylated cyclic π -systems: scaffoldings for novel two and three-dimensional carbon networks," *Chemical Society Reviews*, vol. 28, pp. 107–119, 1999.
- [3] H. Prinzbach, A. Weller, P. Landenberger et al., "Gas-phase production and photoelectron spectroscopy of the smallest fullerene, C₂₀," *Nature*, vol. 407, no. 6800, pp. 60–63, 2000.
- [4] D. Sundholm, "C₇₂: gaudiene, a hollow and aromatic all-carbon molecule," *Physical Chemistry Chemical Physics*, vol. 15, no. 23, pp. 9025–9028, 2013.
- [5] J. An, L.-H. Gan, X. Fan, and F. Pan, "Fullerene C₄₆: an unexpected non-classical cage," *Chemical Physics Letters*, vol. 511, pp. 351–355, 2011.
- [6] M. V. Diudea, A. E. Vizitiu, T. Beu, A. Bende, C. L. Nagy, and D. Janežič, "Circulene covered fullerenes," *Journal of Molecular Structure: THEOCHEM*, vol. 904, no. 1–3, pp. 28–34, 2009.
- [7] H. J. Zhai, Y. F. Zhao, W. L. Li et al., "Observation of an all-boron fullerene," *Nature Chemistry*, vol. 6, pp. 727–731, 2014.
- [8] Q. Chen, W.-L. Li, Y.-F. Zhao et al., "Experimental and theoretical evidence of an axially chiral borospherene," *ACS Nano*, vol. 9, no. 1, pp. 754–760, 2015.
- [9] A. Fonari, J. Röder, H. Shen, T. Timofeeva, and K. Vollhardt, "Toward antikekulene: angular 1,2-Di-, 2,3-Di-, and 1,2,15,16-tetrachloro[6]phenylene," *Synlett*, vol. 25, no. 17, pp. 2429–2433, 2014.

- [10] A. R. Ashrafi and Z. Mehranian, "Topological study of (3,6)- and (4,6)-fullerenes," in *Topological Modelling of Nanostructures and Extended Systems*, vol. 7 of *Carbon Materials: Chemistry and Physics*, pp. 487–510, Springer, Berlin, Germany, 2013.
- [11] Q. Song, B. Wang, K. Deng et al., "Graphenylene, a unique two-dimensional carbon network with nondelocalized cyclohexatriene units," *Journal of Materials Chemistry C*, vol. 1, no. 1, pp. 38–41, 2013.
- [12] H. Lu and S.-D. Li, "Two-dimensional carbon allotropes from graphene to graphyne," *Journal of Materials Chemistry C*, vol. 1, no. 23, pp. 3677–3680, 2013.
- [13] W.-W. Wang, J.-S. Dang, and X. Zhao, "Impact of tetragonal rings on the stability of small fullerenes encapsulated with noble gas: a density functional theory survey," *Chemical Physics Letters*, vol. 536, pp. 77–81, 2012.
- [14] X.-L. Sheng, H.-J. Cui, F. Ye, Q.-B. Yan, Q.-R. Zheng, and G. Su, "Octagraphene as a versatile carbon atomic sheet for novel nanotubes, unconventional fullerenes, and hydrogen storage," *Journal of Applied Physics*, vol. 112, Article ID 074315, 2012.
- [15] I. A. Popov, K. V. Bozhenko, and A. I. Boldyrev, "Is graphene aromatic?" *Nano Research*, vol. 5, no. 2, pp. 117–123, 2012.
- [16] A. Hirsch, Z. Chen, and H. Jiao, "Spherical aromaticity in I_h symmetrical fullerenes: the $2(N+1)^2$ rule," *Angewandte Chemie International Edition*, vol. 39, no. 21, pp. 3915–3917, 2000.
- [17] M. Bühl and A. Hirsch, "Spherical aromaticity of fullerenes," *Chemical Reviews*, vol. 101, no. 5, pp. 1153–1183, 2001.
- [18] Z. Chen and R. B. King, "Spherical aromaticity: recent work on fullerenes, polyhedral boranes, and related structures," *Chemical Reviews*, vol. 105, no. 10, pp. 3613–3642, 2005.
- [19] P. V. R. Schleyer, C. Maerker, A. Dransfeld, H. Jiao, and N. J. R. van Eikema Hommes, "Nucleus-independent chemical shifts: a simple and efficient aromaticity probe," *Journal of the American Chemical Society*, vol. 118, no. 26, pp. 6317–6318, 1996.
- [20] Z. Chen, C. S. Wannere, C. Corminboeuf, R. Puchta, and P. von Ragué Schleyer, "Nucleus-independent chemical shifts (NICS) as an aromaticity criterion," *Chemical Reviews*, vol. 105, no. 10, pp. 3842–3888, 2005.
- [21] M. P. Johansson, J. Jusélius, and D. Sundholm, "Sphere currents of buckminsterfullerene," *Angewandte Chemie International Edition*, vol. 44, no. 12, pp. 1843–1846, 2005.
- [22] J. Poater, X. Fradera, M. Duran, and M. Solà, "An insight into the local aromaticities of polycyclic aromatic hydrocarbons and fullerenes," *Chemistry—A European Journal*, vol. 9, no. 5, pp. 1113–1122, 2003.
- [23] E. D. Glendening, C. R. Landis, and F. Weinhold, "NBO 6.0: natural bond orbital analysis program," *Journal of Computational Chemistry*, vol. 34, no. 16, pp. 1429–1437, 2013.
- [24] J. A. Bohmann, F. Weinhold, and T. C. Farrar, "Natural chemical shielding analysis of nuclear magnetic resonance shielding tensors from gauge-including atomic orbital calculations," *The Journal of Chemical Physics*, vol. 107, no. 4, pp. 1173–1184, 1997.
- [25] A. D. Becke, "Density-functional thermochemistry. III. The role of exact exchange," *The Journal of Chemical Physics*, vol. 98, no. 7, pp. 5648–5652, 1993.
- [26] C. Lee, W. Yang, and R. G. Parr, "Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density," *Physical Review B*, vol. 37, no. 2, pp. 785–789, 1988.
- [27] K. Wolinski, J. F. Hinton, and P. Pulay, "Efficient implementation of the gauge-independent atomic orbital method for NMR chemical shift calculations," *Journal of the American Chemical Society*, vol. 112, no. 23, pp. 8251–8260, 1990.
- [28] M. J. Frisch, G. W. Trucks, H. B. Schlegel et al., *Gaussian 09, Revision D.01*, Gaussian Inc., Wallingford, UK, 2009.
- [29] E. D. Glendening, J. K. Badenhoop, A. E. Reed et al., *NBO 6.0*, Theoretical Chemistry Institute, University of Wisconsin, Madison, Wis, USA, 2013.
- [30] C. Møller and M. S. Plesset, "Note on an approximation treatment for many-electron systems," *Physical Review*, vol. 46, no. 7, pp. 618–622, 1934.
- [31] S.-Y. Xie, F. Gao, X. Lu et al., "Capturing the labile fullerene[50] as $C_{50}Cl_{10}$," *Science*, vol. 304, no. 5671, p. 699, 2004.



Hindawi

Submit your manuscripts at
<http://www.hindawi.com>

