

## B14: An all-boron fullerene

Longjiu Cheng

Citation: *J. Chem. Phys.* **136**, 104301 (2012); doi: 10.1063/1.3692183

View online: <http://dx.doi.org/10.1063/1.3692183>

View Table of Contents: <http://jcp.aip.org/resource/1/JCPSA6/v136/i10>

Published by the [American Institute of Physics](#).

---

### Additional information on J. Chem. Phys.

Journal Homepage: <http://jcp.aip.org/>

Journal Information: [http://jcp.aip.org/about/about\\_the\\_journal](http://jcp.aip.org/about/about_the_journal)

Top downloads: [http://jcp.aip.org/features/most\\_downloaded](http://jcp.aip.org/features/most_downloaded)

Information for Authors: <http://jcp.aip.org/authors>

#### ADVERTISEMENT

**AIP**Advances

*Submit Now*

### Explore AIP's new open-access journal

- Article-level metrics now available
- Join the conversation! Rate & comment on articles

## B<sub>14</sub>: An all-boron fullerene

Longjiu Cheng (程龙玖)<sup>a)</sup>

School of Chemistry and Chemical Engineering, Anhui University, Hefei, Anhui 230039, China

(Received 20 December 2011; accepted 17 February 2012; published online 8 March 2012)

Experiments revealed that small boron cluster anions and cations are (quasi-)planar. For neutral boron cluster, (quasi-)planar motifs are also suggested to be global minimum by many theoretical studies, and a structural transformation from quasi-planar to double-ring tubular structures occurs at B<sub>20</sub>. However, a missing opportunity is found for neutral B<sub>14</sub>, which is a flat cage and more stable than the previous quasi-planar one by high level *ab initio* calculations. The B<sub>14</sub> cage has a large HOMO-LUMO gap (2.69 eV), and NICS values reveal that it is even more aromatic than the known most aromatic quasi-planar B<sub>12</sub> and double-ring B<sub>20</sub>, which indicates a close-shell electronic structure. Chemical bonding analysis given by AdNDP reveals that the B<sub>14</sub> cage is an all-boron fullerene with 18 delocalized  $\sigma$ -electrons following the  $2(n+1)^2$  rule of spherical aromaticity. The geometry and bonding features of the B<sub>14</sub> cage are unique denying conversional thinking. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.3692183>]

### I. INTRODUCTION

Boron is only the fifth element in the periodic table, however, it never ceases to surprise. From simple hydrides to bulk structures, boron offers a rich variety of bonding features that defy conventional thinking.<sup>1,2</sup> Bulk boron has a huge variety of crystal structures. In most of the boron compounds, a polyhedral or three-dimensional structure, especially B<sub>12</sub> icosahedra, is a recurring structural pattern.<sup>3,4</sup> Besides, some extended systems of lower dimensions have also been investigated by theory, such as 2D sheet<sup>5,6</sup> and 1D nanotube.<sup>7</sup>

Boron tends to form a strong and directional covalent bond with other elements because of its small covalent radius and  $sp^2$  hybridization of the valence electron. Because of its electron deficiency and large coordination number, the bonding features in boron clusters are very diverse. As a consequence, boron can form diverse nanostructure. At small cluster size, all of the theoretical and experimental studies suggested that (quasi-)planar isomers are most stable.<sup>8–17</sup> A structural transformation from (quasi-)planar to double-ring tubular structures occurs in the size range of B<sub>16</sub> to B<sub>24</sub>, depending on the charge state of the clusters.<sup>13,18–22</sup> For larger boron clusters, some tubular, cage, and core-shell structures are theoretically suggested.<sup>23–29</sup> Chemical bonding analyses reveal that (quasi-)planar B clusters show multiple ( $\sigma$ - and  $\pi$ -) aromaticity or antiaromaticity,<sup>30</sup> and among which B<sub>12</sub> are particularly unique, which displays triple-aromaticity<sup>31</sup> and has the largest HOMO-LUMO (H-L) gap. Moreover, (quasi-)planar B clusters are analogous to hydrocarbon molecules according to the Hückel's rule, such as B<sub>12</sub> and B<sub>16</sub><sup>2-</sup> are analogous of benzene and naphthalene, respectively.<sup>9,14</sup>

Too many surprises have been given by B clusters due to its novel bonding features and structures, and small B clusters have been extensively studied both theoretically and experimentally, which suggested that small B clusters adopt (quasi-)planar structures.

However, in this work we report another surprise of B, a novel lowest energy cage structure for neutral B<sub>14</sub>, whose structure and bonding features are different from any other known clusters or molecules.

### II. COMPUTATIONAL METHODS

The low-energy isomers of B<sub>14</sub> clusters are obtained by unbiased global search of the *ab initio* potential energy surface with genetic algorithm directly using the TPSSH (Ref. 32) functional that was proven to give reasonably accurate energetic properties of small boron clusters.<sup>27</sup> At the global optimization procedure, a small basis set (3-21G) and a loose convergence criterion are adopted for saving calculation time. After global optimization, the low-lying TPSSH/3-21G geometries are fully relaxed at the TPSSH/6-311+G\* level. For comparison, relative energies at B3LYP/6-311+G\* (Refs. 33–35) and CCSD(T)/aug-cc-pVTZ (Ref. 36) level of theories are also given using the TPSSH/6-311+G\* geometries. All first principle calculations in this work are carried out on the GAUSSIAN 09 package.<sup>37</sup>

### III. RESULTS AND DISCUSSION

Figure 1 plots the newly located global minimum (isomer **I**), which can be seen as a flat cage composed of two open cycles in  $D_{2d}$  symmetry. Other low-lying isomers are also given for comparison in Figure 2: isomers **II** and **IV** are quasi-planar in agreement with earlier studies;<sup>9,12</sup> isomer **III** is a new quasi-planar structure; isomers **V** and **IX** are convex; isomer **VIII** is a double-ring structure; isomers **VI** and **VII** are 3D. Isomer **I** is more stable than isomer **II** by 0.49 eV at TPSSH/6-311+G\* and the value is 0.25 eV at higher CCSD(T)/aug-cc-pVTZ level. However, relative energies of the (quasi-)planar, convex, and double-ring isomers are largely undervalued by the B3LYP functional, in which the three quasi-planar isomers are even lower in energy than Isomer **I** by  $\sim 0.6$  eV.

<sup>a)</sup>Electronic mail: clj@ustc.edu. Tel./Fax: +86-551-5107342.

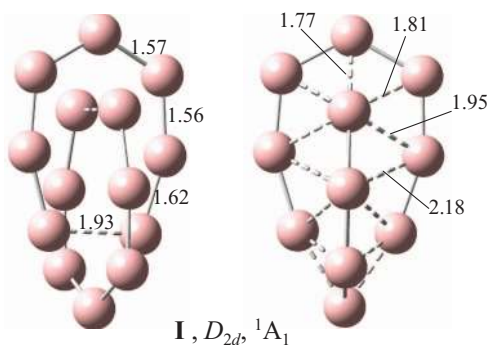


FIG. 1. Optimized geometry of the global minimum structure (I) of  $B_{14}$  at TPSSh/6-311+G\*. Two sides of views are given. Labeled are B–B bond lengths (solid stick) and distances (dashed stick) in angstrom, symmetry, and electronic state.

Why is the cage the most stable? First, we focus on the nature of the bonding in the structure.  $B_{14}$  adopts a  $D_{2d}$  ground state geometry with two seven-membered ( $B_7$ ) open cycles (Figure 1), and the two  $B_7$  cycles are vertical to each other. The B–B bond lengths in the  $B_7$  open cycles (1.56, 1.57, and 1.62 Å) are remarkably shorter than the B–B distance at the open end (1.93 Å) and the B–B distances between two cycles (1.77, 1.81, 1.95, and 2.18 Å). Note that the B–B single bond distance in  $B_3H_3$  ( $D_{3h}$ ) is 1.73 Å and experimentally characterized B=B double bond lengths vary between 1.57 and 1.59 Å.<sup>31</sup> There must be strong delocalization of electrons between and within the open cycles. Chemical bonding analysis by the natural bond analysis<sup>38</sup> confirms that there are only 12 localized two-center two-electron (2c-2e) bonds within the  $B_7$  open cycles with occupation numbers  $ON = 1.82$ – $1.89$  lel.

Note that  $B_{14}$  has 42 valence electrons ( $14 \times 3$ ), with each boron atom contributing three valence electrons. The

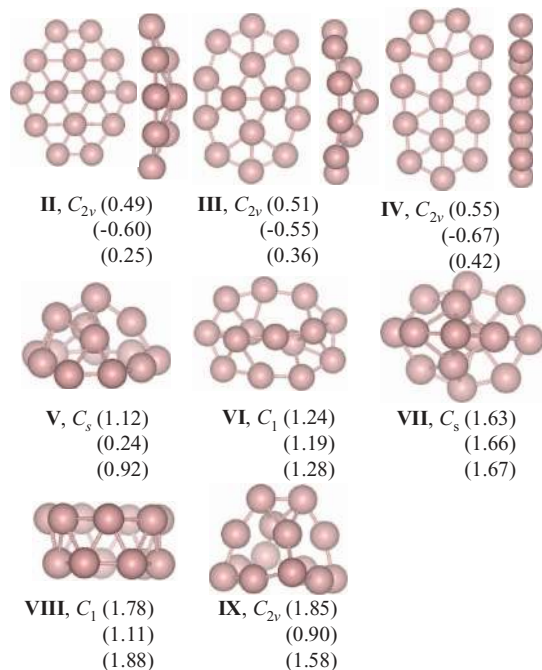


FIG. 2. Optimized geometry of the low-energy isomers (II–IX as labeled) of  $B_{14}$  at TPSSh/6-311+G\*. Symmetry of each isomer is labeled, and enclosed are relative energies in eV to the first isomer: first row at TPSSh/6-311+G\*; second B3LYP/6-311+G\*; last CCSD(T)/aug-cc-pVTZ.

manner in which these electrons are arranged can be rationalized as follows. First, 24 electrons are localized along the twelve B–B single bonds of the  $B_7$  cycles. The remaining 18 electrons are delocalized between two cycles. Figure 3(a) plots the 21 canonical molecular orbitals (MO = 15–35) of the valence electrons. From the picture of the canonical MOs, some delocalized orbitals can be easily identified (such as

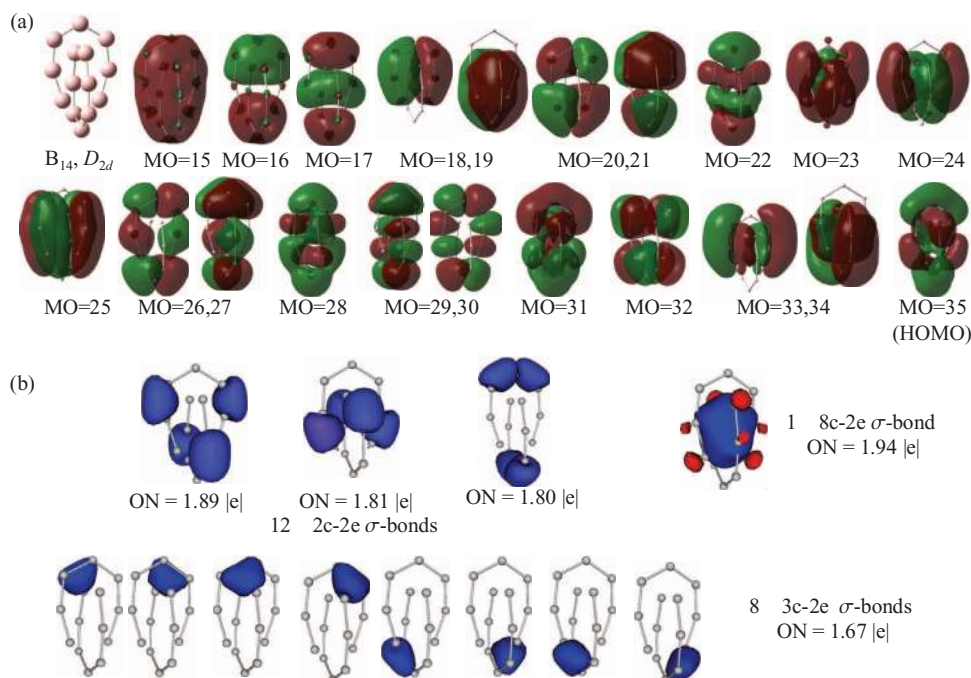


FIG. 3. (a) Structure and canonical MOs of the  $B_{14}$  ( $D_{2d}$ ) cluster; (b) results of the AdNDP localization (molecular visualization was performed using MOLEKEL 5.4).

MO = 23, 25, 31–35). However, it is hard to distinguish the localized and delocalized orbitals from the canonical MOs at some cases because of the unique molecular building.

Since chemical bonding in the all-boron fullerene is anticipated to involve delocalized bonding we selected the adaptive natural density partitioning (AdNDP) method as a tool for chemical bonding analysis. This method was recently developed by Zubarev and Boldyrev<sup>39</sup> and used to analyze chemical bonding in quasi-planar boron clusters.<sup>39,14,15</sup> AdNDP recovers both Lewis bonding elements (1c-2e and 2c-2e objects) and delocalized bonding elements ( $nc-2e$ ), which achieves seamless description of systems featuring both localized and delocalized bonding without invoking the concept of resonance. As shown in Figure 3(b), the AdNDP analysis reveals twelve localized 2c-2e  $\sigma$ -bonds, eight delocalized 3c-2e  $\sigma$ -bonds, and one delocalized 8c-2e  $\sigma$ -bond in the B<sub>14</sub> cage. The bonding framework of the all-boron fullerene is very novel, in which no  $\pi$ -bond is revealed different from any other previous boron clusters.

Aromaticity is an important property determining the stability of molecules. The total number of 18 delocalized electrons in the cluster satisfies the  $2(n+1)^2$  criterion<sup>41</sup> of spherical aromaticity (where  $n=2$ ). Therefore, the B<sub>14</sub> cage is a magic number all-boron fullerene with 18 delocalized  $\sigma$  electrons, and should be highly aromatic. Nucleus-independent chemical shifts (NICS) value<sup>40</sup> is a popular measurement for aromaticity, where negative value means aromaticity, and positive value shows antiaromaticity. As shown in Table I, NICS values reveal that the B<sub>14</sub> cage is highly aromatic (−44.23 ppm), and is even more aromatic than the magic number quasi-planar B<sub>12</sub> (−28.36 ppm) and double-ring B<sub>20</sub> (−39.54 ppm) according to NICS values at the center. Moreover, the H-L gap of the B<sub>14</sub> cage (2.69 eV) is also very large only next to B<sub>12</sub> (3.01 eV) and larger than that of B<sub>20</sub> (2.04 eV). The large H-L gap and high aromaticity indicate that the B<sub>14</sub> cage has a close-shell electronic structure and is of high molecularity. To further confirm the close-shell electronic structure of the B<sub>14</sub> cage, we optimized the dication and dianion of the B<sub>14</sub> cage where the 18-electron structure is broken. NICS values reveal that the dication is antiaromatic (+4.48 ppm) and the dianion shows much lower aromaticity (−8.56 ppm). Moreover, the H-L gaps of the double charged cluster are also much lower (all in Table I).

The vibrational frequencies of the B<sub>14</sub> cage are verified to be all positive, so it is an indeed local minimum. The calculated IR spectra of the cage and quasi-planar B<sub>14</sub> are shown in Figure 4. The frequencies of the cage are mainly around 354, 474, 625, 918, 1173, and 1280 cm<sup>−1</sup>, where the highest peak

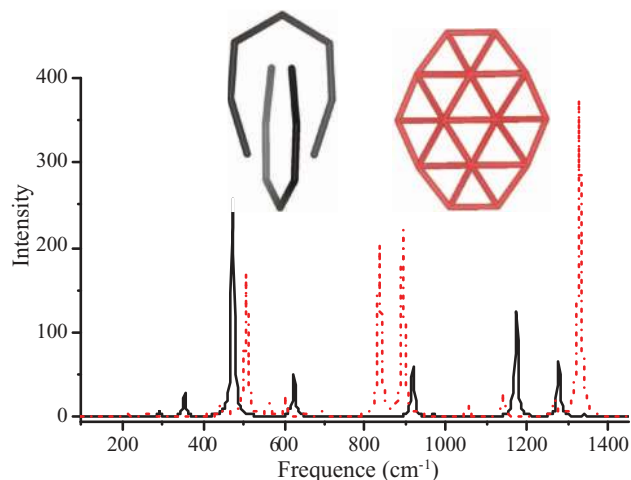


FIG. 4. Computed infrared spectra of the cage (solid line) and quasi-planar (dotted line) structures of B<sub>14</sub>. The frequencies are GAUSSIAN broadened by 4.0 cm<sup>−1</sup>.

(474 cm<sup>−1</sup>) is due to the vibration between two cycles. The frequencies of the quasi-planar one are much different mainly around 507, 836, 894, and 1331 cm<sup>−1</sup>. Therefore, measurement of IR spectrum is a feasible way to distinguish the cage and quasi-planar structures experimentally.

The B<sub>14</sub> cage is a missing opportunity, but why is the opportunity missed by experiments and so extensive theoretical studies? The reason may be as follows: (1) experiments can only deal with charged B clusters, and the anionic and cationic cage of B<sub>14</sub> are higher in energy than the quasi-planar one by 0.09 eV and 0.04 eV, respectively, at TPSSH/6-311+G\*. (2) Quasi-planar is the dominant packing at such a size range, and the magic number B<sub>14</sub> cage is dominant only when the quasi-planar one shows conflicting aromaticity ( $\sigma$ -aromaticity and  $\pi$ -antiaromaticity),<sup>30</sup> and so the B<sub>14</sub> cage lies in the deepest but very narrow funnel in the energy landscape. (3) The theoretical determination of low-energy boron cluster structures still faces various problems because of the multiple-reference character of electronic structures.

#### IV. CONCLUSIONS

In summary, a missing opportunity of boron clusters, B<sub>14</sub> cage of two coupled open cycles, is proposed in this work, which is more stable than the previous quasi-planar one. The AdNDP analysis reveals 18 delocalized  $\sigma$ -electrons in the B<sub>14</sub> cage which follows the  $2(n+1)^2$  rule of spherical aromaticity, and NICS values reveal that the B<sub>14</sub> cage is even more aromatic than the previous known most aromatic quasi-planar B<sub>12</sub> and double-ring B<sub>20</sub>. Such a geometry and bonding features of the all-boron fullerene continue the surprises given by boron.

#### ACKNOWLEDGMENTS

This work is supported by the National Natural Science Foundation of China (20903001), by the outstanding youth foundation of Anhui University, and by the 211 Project of Anhui University. We acknowledge Professor Boldyrev for permission of the AdNDP program.

TABLE I. The NICS values (at the center) and HUMO–LUMO gaps (H-L) of neutral and charged B<sub>14</sub> and the global minimum B<sub>12</sub> and B<sub>20</sub>.

Species	Motif	Point group	H-L (eV)	NICS(0) (ppm)
B <sub>14</sub>	Cage	<i>D</i> <sub>2d</sub>	2.69	−44.23
B <sub>14</sub> <sup>2+</sup>	Cage	<i>D</i> <sub>2d</sub>	0.90	+4.48
B <sub>14</sub> <sup>2−</sup>	Cage	<i>D</i> <sub>2d</sub>	1.85	−8.56
B <sub>12</sub>	quasi-planar	<i>C</i> <sub>3v</sub>	3.01	−28.36
B <sub>20</sub>	Double ring	<i>D</i> <sub>2d</sub>	2.04	−39.54

- <sup>1</sup>E. D. Jemmis, M. M. Balakrishnarajan, and P. D. Pancharatna, *Chem. Rev.* **102**, 93 (2002).
- <sup>2</sup>J. Bauer and J. F. Halet, *Boron, Borides, and Related Compounds: Proceedings of the 13th International Symposium on Boron, Borides, and Related Compounds (ISBB'99)*, Dinard, France, 5–10 September 1999 (Academic Press, Orlando, 2000).
- <sup>3</sup>C. L. Perkins, M. Trenary, and T. Tanaka, *Phys. Rev. Lett.* **77**, 4772 (1996).
- <sup>4</sup>E. D. Jemmis and E. D. L. V. K. Prasad, *J. Solid State Chem.* **179**, 2768 (2006).
- <sup>5</sup>H. Tang and S. Ismail-Beigi, *Phys. Rev. Lett.* **99**, 115501 (2007).
- <sup>6</sup>T. R. Galeev, Q. Chen, J. C. Guo, H. Bai, C. Q. Miao, H. G. Lu, A. P. Sergeeva, S. D. Li, and A. I. Boldyrev, *Phys. Chem. Chem. Phys.* **13**, 11575 (2011).
- <sup>7</sup>A. K. Singh, A. Sadrzadeh, and B. I. Yakobson, *Nano Lett.* **8**, 1314 (2008).
- <sup>8</sup>I. Boustani, *Phys. Rev. B* **55**, 16426 (1997).
- <sup>9</sup>H. J. Zhai, B. Kiran, J. Li, and L. S. Wang, *Nat. Mater.* **2**, 827 (2003).
- <sup>10</sup>M. A. L. Marques and S. Botti, *J. Chem. Phys.* **123**, 014310 (2005).
- <sup>11</sup>D. E. Bean and P. W. Fowler, *J. Phys. Chem. C* **113**, 15569 (2009).
- <sup>12</sup>A. N. Alexandrova, A. I. Boldyrev, H. J. Zhai, and L. S. Wang, *Coord. Chem. Rev.* **250**, 2811 (2006).
- <sup>13</sup>E. Oger, N. R. M. Crawford, R. Kelting, P. Weis, M. M. Kappes, and R. Ahlrichs, *Angew. Chem., Int. Ed.* **46**, 8503 (2007).
- <sup>14</sup>A. P. Sergeeva, D. Y. Zubarev, H. J. Zhai, A. I. Boldyrev, and L. S. Wang, *J. Am. Chem. Soc.* **130**, 7244 (2008).
- <sup>15</sup>W. Huang, A. P. Sergeeva, H. J. Zhai, B. B. Averkiev, L. S. Wang, and A. I. Boldyrev, *Nat. Chem.* **2**, 202 (2010).
- <sup>16</sup>A. P. Sergeeva, B. B. Averkiev, H. J. Zhai, A. I. Boldyrev, and L. S. Wang, *J. Chem. Phys.* **134**, 224304 (2011).
- <sup>17</sup>N. Akman, M. Tas, C. Özdoğan, and I. Boustani, *Phys. Rev. B* **84**, 075463 (2011).
- <sup>18</sup>I. Boustani, A. Rubio, and J. A. Alonso, *Chem. Phys. Lett.* **311**, 21 (1999).
- <sup>19</sup>S. Chacko, D. G. Kanhere, and I. Boustani, *Phys. Rev. B* **68**, 035414 (2003).
- <sup>20</sup>B. Kiran, S. Bulusu, H. J. Zhai, S. Yoo, X. C. Zeng, and L. S. Wang, *Proc. Natl. Acad. Sci. USA* **102**, 963 (2005).
- <sup>21</sup>W. An, S. Bulusu, Y. Gao, and X. C. Zeng, *J. Chem. Phys.* **124**, 154310 (2006).
- <sup>22</sup>M. P. Johansson, *J. Phys. Chem. C* **113**, 524 (2009).
- <sup>23</sup>F. Y. Tian and Y. X. Wang, *J. Chem. Phys.* **129**, 024903 (2008).
- <sup>24</sup>N. G. Szwacki, A. Sadrzadeh, and B. I. Yakobson, *Phys. Rev. Lett.* **98**, 166804 (2007).
- <sup>25</sup>L. Wang, J. J. Zhao, F. Y. Li, and Z. F. Chen, *Chem. Phys. Lett.* **501**, 16 (2010).
- <sup>26</sup>C. Özdoğan, S. Mukhopadhyay, W. Hayami, Z. B. Güvence, and I. Boustani, *J. Phys. Chem. C* **114**, 4362 (2010).
- <sup>27</sup>J. J. Zhao, L. Wang, F. Y. Li, and Z. F. Chen, *J. Phys. Chem. A* **114**, 9969 (2010).
- <sup>28</sup>B. Shang, L. F. Yuan, X. C. Zeng, J. L. Yang, *J. Phys. Chem. A* **114**, 2245 (2010).
- <sup>29</sup>H. Li, N. Shao, B. Shang, L. F. Yuan, J. L. Yang, and X. C. Zeng, *Chem. Commun.* **46**, 3878 (2010).
- <sup>30</sup>D. Y. Zubarev and A. I. Boldyrev, *J. Comput. Chem.* **28**, 251 (2007).
- <sup>31</sup>B. Kiran, G. Kumar, M. T. Nguyen, A. K. Kandalam, and P. Jena, *Inorg. Chem.* **48**, 9965 (2009).
- <sup>32</sup>T. Tao, J. P. Perdew, V. N. Staroverov, and G. E. Scuseria, *Phys. Rev. Lett.* **91**, 146401 (2003).
- <sup>33</sup>A. D. Becke, *J. Chem. Phys.* **98**, 5648 (1993).
- <sup>34</sup>C. Lee, W. Yang, and R. G. Parr, *Phys. Rev. B* **37**, 785 (1988).
- <sup>35</sup>B. Miehlich, A. Savin, H. Stoll, and H. Preuss, *Chem. Phys. Lett.* **157**, 200 (1989).
- <sup>36</sup>A. D. Becke, *Phys. Rev. A* **38**, 3098 (1988).
- <sup>37</sup>M. J. Frisch, G. W. Trucks, H. B. Schlegel *et al.*, GAUSSIAN 09, Revision B.01, Gaussian, Inc., Wallingford, CT, 2009.
- <sup>38</sup>A. E. Reed, L. A. Curtiss, and F. Weinhold, *Chem. Rev.* **88**, 899 (1988).
- <sup>39</sup>D. Yu. Zubarev and A. I. Boldyrev, *Phys. Chem. Chem. Phys.* **10**, 5207 (2008).
- <sup>40</sup>P. von R. Schleyer, C. Maerker, A. Dransfeld, H. Jiao, and N. J. R. van Eikema Hommes, *J. Am. Chem. Soc.* **118**, 6317 (1996).
- <sup>41</sup>A. Hirsch, Z. Chen, and H. Jiao, *Angew. Chem., Int. Ed.* **39**, 3915 (2000).