B₁₄²⁺: A magic number double-ring cluster

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B₂₀ is a “magic number” cluster with double-ring structure. Surprisingly, we also find that B₁₄²⁺ is a “magic number” cluster with double-ring structure, which has the largest HOMO-LUMO gap (3.31 eV) and the highest aromaticity in double-ring clusters. This double-ring B₁₄²⁺ cluster is energetically lower than the quasi-planar one by even ∼1.2 eV using high level ab initio calculations. B₁₄²⁺ also has 40 valence electrons as in Al₁₅⁻ cluster. The reason leading to the unusual properties of B₁₄²⁺ may be the electronic shell closing as in Al₁₅⁻ cluster based on the jellium model, besides the double aromaticity in all double-ring clusters. © 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.4738957]

I. INTRODUCTION

Atomic boron is the first light element of group IIIA with one p valence electron. The short covalent radius, electron deficiency, large coordination number, and sp² hybridization of valence electrons allow boron to form strong directed chemical bonds with other atoms. As a result, boron can form diverse nanostructures, including quasi-planar, ring, nanotube, and cage structures.¹⁻¹⁵ At small cluster size, it is found that the planar or quasi-planar isomers are more stable than the three-dimensional (3D) ones.¹,² The 2D to 3D (planar-to-tubular) structural transition occurs at B₂₀.³ The neutral B₂₀ was suggested to be a very stable double-ring structure with high symmetry and aromaticity.⁴ The experimentally known B₂₀ was found to possess very strong ring currents and there is a strong correlation between ring current strength and aromaticity.¹⁶ Similarly, the double-ring B₁₆, B₂₀, and B₂₄ are electronically closed-shell clusters.¹⁶ For larger boron clusters, some tubular, cage, and core-shell structures are competitive.⁵,¹⁴,¹⁷⁻²¹ This structural trend has been attributed to variations of aromatic characters. On one hand, the π systems of (quasi-)planar boron clusters are suggested to be delocalized and aromatic for some small clusters but to become localized with increasing cluster size.² On the other hand, the high aromaticity of a delocalized π system covering the inner and outer surfaces of the molecule may be beneficial to the stability of the double-ring B₂₀.²² Very recently, we reported a novel lowest-energy cage structure for neutral B₁₆, which undergoes a transition between 2D and 3D structures.²³

In this article, we report an investigation of the “magic number” double-ring structure of B₁₄²⁺. This double-ring B₁₄²⁺ has a very large HOMO-LUMO (H-L) gap and high aromaticity, which is different from the other double-ring structures in many aspects.

II. COMPUTATIONAL METHODS

The TPSSh functional²⁴ is selected in density functional theory (DFT), which was proven to give reasonably accu-
CCSD(T)/aug-cc-pVTZ are also labeled. TPSSh/6-311G* tent with the energies without thermal corrections. At CCSD(T)/aug-cc-pVTZ level. And free energies are consistent with the energies without thermal corrections.

The double-ring B\(14^{2+}\) is much lower than the quasi-planar one energetically, which is surprising at such a cluster size and so we suppose that it may be a “magic number” in electronic structure. For neutral clusters, a structural transition from 2D to 3D occurs at B\(12^{+}\), and the double ring B\(20\) is lower than the quasi-planar one by about 0.6 eV in energy at TPSSh/6-311+G* level in agreement with the value (1.20 eV) at CCSD(T)/aug-cc-pVTZ level. And free energies are consistent with the energies without thermal corrections.

The double-ring B\(14^{2+}\) has the largest HOMO-LUMO gap with 3.31 eV in the double-ring clusters and even larger than the “magic number” quasi-planar B\(12\) (3.01 eV) and cage B\(14\) (2.69 eV). Additionally, according to the NICS values, the double-ring B\(14^{2+}\) is most aromatic (−44.14 ppm) in the double-ring clusters, and is very close to the B\(14\) cage (−44.23 ppm) which is an all-boron fullerene with 18 delocalized electrons in the highest spherical aromaticity. As a result, the double-ring B\(14^{2+}\) is suggested to be more stable in electronic structure and more aromatic than the known most aromatic double-ring B\(20\), which indicates a “magic number” in double-ring clusters.

Why is this double-ring structure unusually stable? First, we focus on the bonding nature in this structure. B\(14^{2+}\) has a \(D_{4h}/Ci\) ground state double-ring geometry. The B–B bond lengths within the B\(7\) rings are 1.62 Å, and those connecting the two rings are 1.72 Å. Note that the B–B single bond distance is about 1.73 Å and B–B double-bond lengths experimentally characterized vary between 1.57 and 1.59 Å. According to the distribution of bond lengths above, we suggest that there must be strong delocalization of electrons within and between the rings.

In order to gain insight into the nature of the bonding in the double-ring B\(14^{2+}\), we carried out canonical molecular orbital (MO) analysis. Note that B\(14^{2+}\) has 40 valence electrons. Figures 3(a) and 3(b) depict the 20 MOs (MO = 15–34) of various aromaticity and positive NICS values mean anti-aromaticity.

As shown in Table I, the double-ring B\(14^{2+}\) has the largest HOMO-LUMO gap with 3.31 eV in the double-ring clusters and even larger than the “magic number” quasi-planar B\(12\) (3.01 eV) and cage B\(14\) (2.69 eV). Additionally, according to the NICS values, the double-ring B\(14^{2+}\) is most aromatic (−44.14 ppm) in the double-ring clusters, and is very close to the B\(14\) cage (−44.23 ppm) which is an all-boron fullerene with 18 delocalized electrons in the highest spherical aromaticity. As a result, the double-ring B\(14^{2+}\) is suggested to be more stable in electronic structure and more aromatic than the known most aromatic double-ring B\(20\), which indicates a “magic number” in double-ring clusters.

**FIG. 1.** Optimized geometry of the low-energy isomers (I-VII as labeled) of B\(14^{2+}\) at TPSSh/6-311+G*. Symmetry and electronic state of each isomer are labeled, and enclosed are energies/free energies in eV relative to the first isomer at TPSSh/6-311+G*. For the first two isomers, relative energies at CCSD(T)/aug-cc-pVTZ are also labeled.

**FIG. 2.** Energies of the lowest-energy double ring clusters relative to the lowest-energy quasi-planar ones (\(\Delta E_{D-R,QP}\)) at neutral (filled square) B\(12\), B\(16\), and B\(20\), dication (square) B\(14^{2+}\) and B\(18^{2+}\), and dianion (filled triangle) B\(18^{2−}\).

<table>
<thead>
<tr>
<th>Isomer</th>
<th>Motif</th>
<th>Point group</th>
<th>H-L (eV)</th>
<th>NICS(0) (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Quasi-planar</td>
<td>C(_{3v})</td>
<td>3.01</td>
<td>−28.36</td>
</tr>
<tr>
<td>II</td>
<td>Cage</td>
<td>D(_{2h})</td>
<td>2.69</td>
<td>−44.23</td>
</tr>
<tr>
<td>III</td>
<td>Double ring</td>
<td>D(_{2d})</td>
<td>2.38</td>
<td>−31.77</td>
</tr>
<tr>
<td>IV</td>
<td>Double ring</td>
<td>D(_{2d})</td>
<td>3.31</td>
<td>−44.14</td>
</tr>
<tr>
<td>V</td>
<td>Double ring</td>
<td>C(_{4v})</td>
<td>1.86</td>
<td>−30.87</td>
</tr>
<tr>
<td>VI</td>
<td>Double ring</td>
<td>C(_{2v})</td>
<td>1.18</td>
<td>−37.29</td>
</tr>
<tr>
<td>VII</td>
<td>Double ring</td>
<td>C(_{2v})</td>
<td>1.50</td>
<td>−27.85</td>
</tr>
<tr>
<td>B(_{20})</td>
<td>Double ring</td>
<td>D(_{2d})</td>
<td>2.05</td>
<td>−39.54</td>
</tr>
</tbody>
</table>

**TABLE I.** The HOMO-LUMO gaps (H-L) and NICS values (at the center) of the global minimum B\(12\) and B\(14\) and the lowest-energy double-ring B\(12\), B\(14^{2+}\), B\(16\), B\(18^{2+}\), B\(18^{2−}\), and B\(20\).
lene electrons. From the MOs diagrams, we can identify the delocalized orbitals easily (MO = 25, 30–34 in Fig. 3b), including three radial and three tangential orbitals in tensor surface harmonic theory of cluster bonding that are similar to the double-ring B12 cluster. For example, the double-ring B12 (D_{6d}) has 6 tangential and 6 radial electrons achieving a 4n+2 count in each of the tangential and radial subsystems, which is double-aromatic; the double-ring B14 (C_{1}) has 6 tangential and 8 radial electrons, which is tangential-aromatic and radial-antiaromatic; the double-ring B16 (D_{6h}) has 6 tangential and 10 radial electrons, which is double-aromatic; B18 has 8 tangential and 10 radial electrons, which is tangential-aromatic and radial-aromatic; B20 has 10 tangential and 10 radial electrons, which is double-aromatic. Similarly, the double-ring B14^{2+} with 6 radial and 6 tangential electrons is double-aromatic consisted of both radial and tangential Hückel’s aromaticity, which is consistent with the above-mentioned double-aromatic double rings. The remaining 14 pairs of valence electrons are localized on 14 B−B σ-bonds. However, there is some dispute about the B−B σ-bonds (2c−2e or 3c−2e) of the double-ring structure. Usually, two patterns of covalent bonds are disputed: one pattern of two-center bonds in each ring and another one of three-center trilaterally formed bonds between two rings. For the purpose of settling this dispute, we apply a new tool named adaptive natural density partitioning (AdNDP) to obtain patterns of chemical bonding. The method was recently developed by Zubarev and Boldyrev. AdNDP is based on the concept of the electron pair as the main element of chemical bonding models, which recovers both Lewis bonding elements (1c−2e and 2c−2e objects) and delocalized bonding elements (nc−2e).

According to the results of AdNDP analysis, two patterns of B−B bonding frameworks are displayed in Fig. 3c: fourteen 2c−2e B−B σ-bonds with occupation numbers ON = 1.73 |e| and fourteen 3c−2e B−B σ-bonds with ON = 1.97 |e|. In the former pattern, the 2c−2e σ-bonds are equivalent and each boron atom contributes about 0.87 |e| equally. The latter pattern (3c−2e) is based on 2c−2e σ-bonds, but the 3c−2e σ-bonds are extremely inequivalent, and the third boron atom at the vertex of a triangle contributes only 0.24 |e| (1.97–1.73). So the B−B bonding of the double-ring B14^{2+} is between Lewis bonding and delocalized σ-bonding. If the remaining 14 pairs of valence electrons are suggested to be involved in fourteen 3c−2e B−B σ-bonds, the 40 valence electrons of B14^{2+} should be delocalized as in Al_{13}− cluster. The double-ring B14^{2+} can also be taken as a 3D structure, which may be in electronic shell closing as in Al_{13}− cluster based on the jellium model. Jellium model is often used as a simple model of delocalized electrons in metal clusters, in which all valence electrons are delocalized in the cluster volume and fill discrete energy levels.

To verify the effect of jellium model, we compare the aromaticity of double-ring B14^{2+} with spherical aromatic C_{20}^{2+} and current aromatic B20. Spherical aromaticity arises from the π-electron system and follows the 2(n+1)^2 rule, i.e., C_{20}^{2+} (n = 2) and C_{60}^{10+} (n = 4) are spherical aromatic, and it decays fast. The π-electron system of an icosahedral fullerene can be considered approximately as a spherical electron gas, which surrounds the surfaces of a sphere in a double skin. Current aromaticity is induced by diamagnetic ring currents and follows the Hückel rule, i.e., benzene and annulenes with 4n+2 π electrons are current aromatic, and it decays more slowly than spherical aromatic. Note that the cage C_{20}^{2+} is an icosahedral fullerene satisfying the 2(n+1)^2 rule for spherical aromaticity (n = 2), in which spherical aromaticity decays rapidly. The aromaticity of the double-ring B20 is induced by diamagnetic ring currents, in which the aromaticity decays more slowly than spherical aromaticity. In terms of aromaticity, we suspect that the decaying speed of the double-ring B14^{2+} may be between the one of the cage C_{20}^{2+} and the one of the double-ring B20. In order to confirm this supposition, Fig. 4 plots the NICSzz-scan curves for the double-ring B14^{2+}, B20, and the cage C_{20}^{2+} within the range of 0.0–8.0 Å above the geometric centers of the systems. The NICS-sscan is similar to the aromatic ring current shieldings approach, which can provide a clear picture of the type of the ring current in aromatic and antiaromatic systems and can be used to characterize whether an inorganic system is aromatic, non-aromatic, and antiaromatic.

![Image](417x159 to 450x183)

FIG. 3. (a) and (b) Structure and canonical MOs of the B_{14}^{2+} (C_{1}) cluster; (c) Results of the AdNDP localization (molecular visualization was performed using MOLEKEL 5.4).

![Image](437x130 to 463x150)

FIG. 4. The NICSzz-scan curves for B_{20} (dotted line), B_{14}^{2+} (dashed line), and C_{20}^{2+} (solid line), within the range of 0.0–8.0 Å above the geometric centers of the systems.)
HF from H2 and F2 is. The structure of B14F2 is similar to the one of the dication double-ring B20. That is, the aromaticity of the double-ring B142+ is between spherical and current aromaticity, which is in agreement with our prediction. Thus, the effect of jellium model may exist in the double-ring B142+ cluster.

For the dication B142+ molecule, reaction energies cannot be achieved. To further prove the effect of jellium model, the enthalpies of formation of B14F2 and B18F2 from neutral double-ring B14 (B18) cluster and F2 are compared and the results are shown in Fig. 5. The B14F2 is stable and the enthalpy is −10.38 eV (for comparison, the enthalpy of formation of HF from H2 and F2 is −5.47 eV), which still keeps the double-ring structure with a large HOMO-LUMO gap (2.79 eV) and high aromaticity (NICS(0) ≈ −37.76 ppm). The electronic structure of B14F2 is similar to the one of the dication double-ring B142+. However, the enthalpy of formation of the B18F2 (−8.62 eV) is smaller than the one of B14F2 by about 1.76 eV. B18F2 also keeps the double-ring structure, but the HOMO-LUMO gap of B18F2 (1.47 eV) is also smaller than the one of B14F2. The above analysis suggests that neutral B14 cluster is unstable and tends to lose two electrons. In B13F2 cluster, two extra electrons of neutral B14 are mostly localized on two B–F bonds, which further prove that the 40 delocalized valence electrons of B142+ fill electronic shells as in Al13− cluster based on the jellium model and the effect of jellium model also may make the enthalpy of formation of B13F2 cluster lower.

Briefly, the reasons leading to the unusual properties of the double-ring B142+ may be the effect of jellium model besides the radial and tangential Hückel’s aromaticity. The unusual aromaticity and the lower enthalpy of formation of B14F2 also provides an indirect proof for that B142+ may be the electronic shell closing as in Al13− cluster based on the jellium model. The reasons for the unusual properties of the double-ring B142+ may be radial and tangential Hückel’s aromaticity and the effect of jellium model.

IV. CONCLUSIONS

In conclusion, we report an unusual double-ring structure of B142+ cluster. The double-ring B142+ has a very large HOMO-LUMO gap and is more aromatic than the known most aromatic double-ring B20, which suggests that it is a “magic number” in the double-ring clusters. The canonical MOs analysis reveals that it is doubly aromatic and the AdNDP analysis indicates that B–B bonding of the double-ring B142+ is between Lewis bonding and delocalized σ-bonding. The 40 delocalized valence electrons of B142+ fill electronic shells as in Al13− cluster based on the jellium model. The effect of jellium model is found first in a non-metallic cluster, although the evidence is indirect and the effect is small. The lower enthalpy of formation of B14F2 also provides an indirect proof for that B142+ may be the electronic shell closing as in Al13− cluster based on the jellium model. The reasons for the unusual properties of the double-ring B142+ may be radial and tangential Hückel’s aromaticity and the effect of jellium model.

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