**Designing Stuffed Hetero Fullerene Clusters: C26B46N12 and C14B58N12Li12**

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Designing Stuffed Hetero Fullerene Clusters: $C_{26}B_{46}N_{12}$ and $C_{14}B_{58}N_{12}Li_{12}$

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Abstract

The stuffed fullerene-like nano clusters based on the approximately spherical $B_{84}$, ($B_{12}@B_{12}@B_{60}$), fragment of the β-rhombohedral boron are proposed using Wade’s Rules and the criterion of overlap matching. Thus the fifty additional electrons required to make the $B_{84}$ skeleton electron sufficient, are provided by replacing 26 boron atoms by carbon atoms and 12 boron atoms by nitrogen atoms giving rise to $C_{26}B_{46}N_{12}$. This particular combination has the added advantage that the fullerene surface made from the $C_2B_3N$ five membered rings has less strain arising from the pyramidalization of the sp$^2$ hybridised trigonal planar carbon or nitrogen; the natural angle needed to have optimum overlap is not far from the 31.7 degrees required for the icosahedral symmetry. The advantage from overlap-matching can be further increased by capping the two pentagonal faces of the cluster by a Li each, keeping the electron count same by replacing 12 carbon atoms by 12 boron atoms. DFT based computational results support these formulations.
1 Introduction

Molecules, which exhibit unusual bonding patterns and structures away from the precept bonding picture exhibited by carbon were always exciting to chemists. Computational chemists have led this exploration of new structures, which breaks the tenets of conventional molecular structure and bonding. Studies of planar tetra coordinate carbon and related rule breaking structures have become part of the chemistry “classics”. The chemistry of the neighboring element boron differs largely in structure and bonding from those of carbon. The discovery of C60 (Fig.1, a) has spurred many scientists to explore new atomic clusters even though its first prediction by Eiji Osawa went unnoticed. In contrast to the few and elegant rules of carbon chemistry of the neighboring element boron differs largely in structure and bonding from those of carbon. The discovery of C60 and borides present extreme complexity. Our attempt here is to combine the beauty of fullerene and the complexity of boron to predict stable fullerene-like molecules based largely on boron.

![Fig.1](image1.png)

A fullerene based on boron B60 is deficient by 60 electrons. Addition of 60 electrons to B60 is a possible way to stabilize it. A physical approach would be to add extra 20 boron atoms which could provide the 60 electrons. The resulting boron cluster (Fig.1, b) B90 where a boron atom is placed nearly in the center of each B4 ring is found to be less stable in terms of binding energy per atom than the spherical icosahedral fullerene like stuffed B84 fragment of β-rhombohedral boron. The stuffed fullerene-like boron nano clusters are based on the approximately spherical B84 (Fig.1, c) fragment of the β-rhombohedral boron. B84 fragment has a central close-B12 unit and its 12 vertices are connected to 12 pentagonal pyramids (nido-B5) via 2c-2e oxohedral B-B bonds (Fig.2, a). The 12 pentagons in the periphery are connected to the C40-like surface. The B84 fragment can thus be described as B12@B12@B60. However B84 is not electron sufficient. The required number of electrons can be estimated using Wade’s n+1 skeletal electron pair rule. The Central B12 requires -2 charge. Each pentagonal pyramidal B5 needs n+2 skeletal electron pairs, which makes for B84. Thus, the B84 requires 50 electrons more, which can be given by substituting appropriate number of boron atoms by carbon and nitrogen atoms.

![Fig.2](image2.png)

![Fig.3](image3.png)

The out-of-plane distortion from planarity of the trigonal carbon in C60 is 31.7°. Let us construct the B84 fullerene from C60 by considering its anion, C60-12, which is synthesized as C60 (Li)12. From the point of view of three-dimensional delocalization each C6 is isoelectronic with pentagonal pyramidal B12H4+. We can study the structural details of B12H4+ and the isoelectronic neutral analogues of B12H4+, namely C12B12H4 and C12B12NH4. The electronic structure of these pentagonal pyramidal molecules are better understood through a ring-cap interaction diagram where the π-MOs of the five membered rings are stabilized by the interaction with the orbitals of the capping group, as schematically shown in Fig. 3. This also provides a way to control the surface curvature. When the orbitals of the capping groups are small or the ring is large, the ring X-H bonds bend towards the cap to increase bonding. This is ideal for the design of fullerenes that requires a curved surface by symmetry. Thus we can replace all of the C6 pentagons in C60 by pentagonal pyramids with apex atom pointing towards the centre of the fullerene. These 12 apex boron atoms are bonded to a central B12icosahedron to form B84 fullerene.

The charge in B84 can be reduced by replacement of boron atoms. A neutral carborane C12B10 unit can replace the central icosahedral B12+ unit in B84 fullerene. There are several options for the pentagonal pyramidal B5+ units. Replacement of four boron atoms by four carbons or three boron atoms by two carbons and one nitrogen atom removes the charge. We study the out-of-plane bending in isomers of C12B12H4 and C12B12NH4 so that the pentagonal pyramidal with maximum out-of-plane bending can be selected for construction of the fullerene structure. The out-of-plane bend angle for the pentagonal pyramidal C12B12H4 unit is only18.8° which is considerably less compared to 31.7° in C60. The twelve pyramidal nido-B5+ units can be replaced by a neutral nido-C12B12N unit with the anticipation that with less diffuse orbitals of nitrogen as cap makes the ring hydrogens bent more towards N, which helps in pyramidalization. The pentagonal pyramidal C12B12NH4 has 12 permutations of the five membered ring. The five membered ring of fullerenes.
ring hydrogens bent towards the apical atom, be it B, C or N. The structure of \( C_{60}^{40}(Li)_{12} \) suggests yet another possibility. If two borons of the \( B_4 \) unit is replaced by a carbon and nitrogen, and a Li is used to bridge the open face of the pentagonal pyramid, an isoelectronic bipyrivalid structure, \( CB_NLi \), is obtained. This is anticipated to increase the bending of the X-H bond in the required direction.

### 2 Computational Methods

All the computations were carried out using G03 and G09 programs at B3LYP/6-31G* level.\(^{24,25} \) The Relative energies, out-of-plane X-H bend angle, bond energies of pentagonal rings of eight isomers of pentagonal pyramidal \( C_2B_3N_6H_6 \) (I-VIII) are presented in Table 1. The relative energies of fullerene clusters of molecules formula \( C_2B_3^{12}N_12 \) derived from these pentagonal pyramids were also calculated. Similarly \( CB_NLi \) (IX) and its \( B_4 \) analog \( C_1B_3^{12}N_12Li_{12} \) are also studied. The energies are given with ZPE correction.

### 3 Results and Discussions

The nido-\( C_2B_3N_6H_6 \) has eight isomers; two of these have nitrogen as a cap, two carbon as a cap and four boron as a cap. Twelve such \( C_2B_3N_6 \) pentagonal pyramids are used in constructing the stuffed fullerene in the following way. The five membered rings of the \( C_2B_3N_6 \) pentagonal pyramid are connected through sigma bonds to form the fullerene surface. The twelve apex atoms are bonded to a central \( C_2B_3^{12} \) unit so that a neutral cluster with composition \( C_2B_3^{12}N_12 \) results. \(^{26} \)

Optimized structures of all eight isomers of \( C_2B_3N_6H_6 \) are shown in Fig.4 and relative energies in Table 1. The isomer VI with boron as a cap has the lowest energy. The relative energies of the eight isomers are given in Table 1. The average ring hydrogen out-of-plane bending angle \( \theta \) is calculated for all the pentagonal pyramidal isomers given in Table 1. The isomer (II) with nitrogen as a cap has got the largest \( \theta \) value \((\approx 23.9^\circ)\), which is closest to \( 31.7^\circ \), calculated for the ideal icosahedral \( C_{60} \). Isomer I, which also has nitrogen cap, does not have a pentagonal pyramidal structure and it is therefore not easy to calculate an out of plane bending. However the ring-cap overlap matching criteria in pyramidal molecules suggests that the isomer II and also I will be better candidates to construct the \( C_2B_3^{12}N_12 \) cluster compared to other isomers even though I and II are not the lowest energy isomers. The relative energies for isomers with a given cap vary considerably, Table 1. Obviously, not only the ring-cap orbital compatibility but also the pentagonal ring bond energies also control the relative stabilities. The relative ring bond energy for each pentagonal ring for a given cap, calculated using sigma-bond energies of the bonds involved in the five membered ring, is given in Table 1. Among the isomers with N as cap II is more stable than I because the pentagonal ring sigma bond energies for II is more than I. In the isomers with C as cap, \( IV \) is more stable than \( III \) since the bond energy for pentagonal ring for \( IV \) is large. Among the isomers with B as cap \( VI \) is the most stable and has highest pentagonal ring bond energy. In \( VI \), there is a homonuclear C-C bond and four hetero nuclear B-N, B-C bonds. In addition B as a cap is more appropriate for a pentagonal ring, whose X-H bonds are tilted from planarity by the least amount in V-VIII. However this is not as helpful from the point of view of non-planarity required for fullerene surface.

<table>
<thead>
<tr>
<th>No.</th>
<th>Cap</th>
<th>( \Delta E_1 ) (in kcal/mol)</th>
<th>Average ( \theta )</th>
<th>( \Delta E_2 ) (in kcal/mol)</th>
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</thead>
<tbody>
<tr>
<td>I</td>
<td>( \eta^\circ ) (broken)</td>
<td>107.3</td>
<td>-</td>
<td>73.0</td>
</tr>
<tr>
<td>II</td>
<td>( \eta^\circ )</td>
<td>100.8</td>
<td>23.9</td>
<td>47.6</td>
</tr>
<tr>
<td></td>
<td>CH cap</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>III</td>
<td>( \eta^\circ )</td>
<td>98.2</td>
<td>21.9</td>
<td>65.3</td>
</tr>
<tr>
<td>IV</td>
<td>( \eta^\circ )</td>
<td>59.9</td>
<td>22.1</td>
<td>12.6</td>
</tr>
<tr>
<td></td>
<td>BH cap</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>( \eta^\circ )</td>
<td>42.8</td>
<td>13.3</td>
<td>52.7</td>
</tr>
<tr>
<td>VI</td>
<td>( \eta^\circ )</td>
<td>0.0</td>
<td>12.7</td>
<td>0.0</td>
</tr>
<tr>
<td>VII</td>
<td>( \eta^\circ )</td>
<td>60.9</td>
<td>14.1</td>
<td>80.0</td>
</tr>
<tr>
<td>VIII</td>
<td>( \eta^\circ )</td>
<td>18.5</td>
<td>12.3</td>
<td>27.3</td>
</tr>
<tr>
<td>IX</td>
<td>( (CB_NLiH_6) \eta^\circ )</td>
<td>-</td>
<td>26.0</td>
<td>-</td>
</tr>
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</table>

Table 1: The relative energies \( \Delta E_1 \) of pentagonal pyramidal isomers of \( C_2B_3N_6H_6 \) in kcal/mol, their average X-H out-of-plane bend angle \( \theta \), relative pentagonal ring sigma bond energies \( \Delta E_2 \) respectively computed at B3LYP/6-31G* level. Lower values of \( \Delta E_1 \) and \( \Delta E_2 \) indicate greater stability. The relative energy in kcal/mol and out-of-plane bend angle \( \theta \) of \( CB_NLiH_6 \) (IX) also given.

(The bond energies (in kcal/mol) (C-N=72.8, B-N=106.5, C-C=82.6, B=B=70.0, B-C=89.0, N-N=40.0 C-H=98.3, B-H=93.0, N-H=92.0.) are taken from Inorganic Chemistry: Principles of Structure and Reactivity (4th Edition) by James E. Huheey, Ellen A. Keiter, Richard L. Keiter, Prentice Hall; 4 edition, 1997.)

The \( C_2B_3^{12}N_12 \) clusters are generated by taking twelve pentagonal pyramids of one particular isomer of \( C_2B_3N_6 \) and an icosahedral \( C_2B_10 \) in the centre. Each pentagonal pyramidal isomer can lead to a family of different stuffed boron cluster by rotating the five membered rings on the surface of large cluster, forming new orientations with respect to each other. This results in large number of isomers for the boron based stuffed fullerene. The enumeration of isomers of a classical \( C_2B_3^{12} \) fullerene leads to numbers of the order of \( 10^{11} \). Here we have selected thirty eight structures (Supplementary material), by chemical knowledge based on the following reasoning. The bond energy of different bonds formed between each pentagonal pyramid to be as high as possible. In addition, the bond lengths should not be much smaller than the B-B distances as the outer shell should not break by strain. Similarly smaller atoms, carbon and nitrogen are to be kept at apex of the pentagonal pyramids so that maximum advantage is available by the overlap match and consequent reduction of strain of the outer shell. These restrictions in mind, the substitution of B atoms by C and N atoms are done in a way where maximum B-N, B-C and B-B bonds are formed.\(^{27,28} \) Short bonds, e.g., C-C, C-N are avoided wherever possible to reduce strain of the outer ring and consequent breakage of other bonds in the cluster. Thirty-eight clusters (Supplementary material) are generated using this strategy. Here 1a-1e are generated from I, 2a-2f from II, 3a-3e from III, 4a-4g from IV, 5a-5g from V, 6a-6e from VI, 7a-7d from VII, and 8a-8c from VIII. (Supplementary material). Out of these 19 have an approximately spherical (closo) structure. These are examined and eight low energy structures from this
list, (Fig.5), are selected for discussion. Even though the isomer I is largely distorted from a pentagonal pyramidal structure, the pyramidal structure is brought back when it becomes part of the large fullerene cluster and a stable closo B₉₄ based CBN cluster results. The relative energies of the eight clusters calculated from the eight C₂B₇N₃ isomers are given in Table 2. The clusters 1b, 2c, 4c, 6b have an approximately spherical closo fullerene-like structure compared to clusters 3b, 5c, 7b and 8b where distortions in spherical symmetry occur due to breakage of some bond leading to open spaces in the cluster. This is seen in clusters where the nitrogens are on the surface of the cluster, which results in the formation of short C-N bonds on the surface of the cluster. The short bonds cause strain in the cluster resulting in breakage of the other bonds in the cluster. As a result the cluster loses its spherical shape and takes a less symmetric open structure.

Fig.4: Given are the global minimum structures of pentagonal pyramidal isomers of C₂B₇N₃ calculated at B3LYP/6-31g* level and their relative energies in kcal/mol and given in brackets are their out-of-plane bend angle θ.

However, clusters 4c and 6b with nitrogens on the surface still retain approximately spherical, closo structures. Obviously nitrogen on the surface is not the only reason for the breakage of bonds, but the clusters having pentagonal pyramids with C-N, C-C bonds in the pentagon ring show a tendency to break bonds and to distort. We anticipate that these inherent distortions in the pentagonal ring of the cluster can be reduced by replacing the B or C or N by Al or Si or P, so that the bond shortening in one part of the pentagonal pyramid in the cluster due to shorter C-N, C-C bonds leading to breakage of bonds can be compensated. Even though 4c and 6b may form closed stable fullerene clusters, they can have isomers having C-N, C-C bonds leading to the rupture of cluster. This can be avoided in clusters with N as cap since they also help more in pyramidalization of the triagonal arrangement of the surface atoms due to their large θ value (Table 1) compared to other pentagonal pyramidal isomers.

These structures are found to be minima on their PES. The stability of these fullerene like clusters are further checked by the theoretical IR spectrum of the eight closo minimum energy clusters (Supplementary information). The kT value of lowest frequency mode with non-zero intensity in kcal/mol for these eight clusters is given in Table 2. The clusters 1b, 2c, 4c and 6b have frequencies with energies greater than the room temperature kT value=0.59 kcal/mol, which indicates they are stable at room temperature. Also the intensities of the lower frequencies are less in these above mentioned clusters. Cluster 1b has a low frequency of 207.05 cm⁻¹~0.59 kcal/mol with zero intensity. So we can neglect this low frequency. The next low frequency with non-zero intensity is much above the room temperature kT value which is around 0.77 kcal/mol. This points out that these clusters may remain as closo fullerene like clusters because none of the bonds are broken at room temperature. The C₆₀ fullerene has four strong IR absorptions at 528, 577, 1183, and 1429 cm⁻¹. Among these the lowest frequency when converted to kT have a value of 1.5 kcal/mol which is much greater than room temperature kT value indicating its stability. This may pave the way for the future experimental work on these molecules. Whereas, 3b, 5c, 7b and 8b clusters have frequencies whose energies are below the room temperature kT indicating there are bonds that may break leading to less stable open structures.

Table 2: HOMO-LUMO Gap (in eV), kT values (in kcal/mol) and Relative energies (in kcal/mol) of the lower energy closo structures (1b-8b) of C₂B₇N₃ clusters out of the thirty eight clusters from pentagonal pyramids I to VIII and C₁₄B₉N₃Li₁₂ (9) calculated at B3LYP/6-31g* level.

<table>
<thead>
<tr>
<th>Cluster Isomer</th>
<th>HOMO-LUMO Gap (in eV)</th>
<th>kT value of lowest frequency mode with non-zero intensity (kcal/mol)</th>
<th>Relative energy in kcal/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>1b(I)</td>
<td>2.87</td>
<td>0.77</td>
<td>1099.10</td>
</tr>
<tr>
<td>2c(II)</td>
<td>3.58</td>
<td>0.79</td>
<td>960.31</td>
</tr>
<tr>
<td>3b(III)</td>
<td>2.00</td>
<td>0.38</td>
<td>647.75</td>
</tr>
<tr>
<td>4c(IV)</td>
<td>4.27</td>
<td>0.76</td>
<td>515.67</td>
</tr>
<tr>
<td>5c(V)</td>
<td>1.36</td>
<td>0.27</td>
<td>838.92</td>
</tr>
<tr>
<td>6b(VI)</td>
<td>4.04</td>
<td>0.62</td>
<td>493.35</td>
</tr>
<tr>
<td>7b(VII)</td>
<td>1.82</td>
<td>0.34</td>
<td>415.10</td>
</tr>
<tr>
<td>8b(VIII)</td>
<td>1.20</td>
<td>0.57</td>
<td>0.00</td>
</tr>
<tr>
<td>9</td>
<td>2.24</td>
<td>0.45</td>
<td>-</td>
</tr>
</tbody>
</table>

The HOMO-LUMO gaps of the selected eight closo minimum energy clusters are compared with that of C₆₀ HOMO-LUMO gap of 2.3±0.1 eV. The HOMO-LUMO gaps for the eight clusters 1-8 are given in Table 2. Clusters 1b, 2c, 4c, 6b have larger HOMO-LUMO energy gaps than C₆₀ indicating their stability. Out of these the two structures with N as cap give the largest HOMO-LUMO gap. Both of them also have bond frequencies above room temperature kT value indicating that they can be selected as candidate out of these clusters for the...
Further reduction in strain of the surface atoms can be achieved in the following way. The out-of-plane X-H bend angle for CB$_2$NLi ($\mathbf{IX}$) is $26^\circ$ (Table 1). A Li atom on the top of the five membered ring pushes the ring substituents away from Li, while a nitrogen atom on the opposite side would prefer the ring substituents move towards it. The net result is that the strain is reduced further. Incorporation of the five membered ring in the cluster surface must reduce strain further. The structure C$_{2}\text{B}_{10}$(C$_{2}$B$_{3}$N)$_{12}$ can be visualized as having 12 negative charges if one carbon of the pentagonal pyramid is replaced by a boron atom and a Li is placed on the open five membered ring. This leads to C$_{2}\text{B}_{10}$(C$_{2}$B$_{3}$N)$_{12}$ i.e.; C$_{14}$B$_{3}$N$_{12}$Li$_{12}$ (9) (Fig.6), the HOMO-LUMO gap and the $kT$ value of lowest frequency mode with non-zero intensity are given in Table 2. The two lowest vibrational modes are having $kT$ values less than 0.59 kcal/mol with very low intensities 0.09 and 1.4 respectively, but the other higher intensity frequency modes much above $kT$ value. Li at the apex provides an additional advantage. A Li atom on the top of the five membered ring pushes the ring substituents away from Li, while a nitrogen atom on the opposite side would prefer the ring substituents move towards it. The net result is that the strain is reduced further. Cartesian coordinates and energies of all the structures generated are given in the supplementary material.

Numerous fullerenes were synthesized in various B-CN materials by in-situ electron beam irradiation in a high-resolution transmission analytical electron microscope. Starting materials like chemical-vapor deposited graphic carbon (B-C materials), fused mixtures of boric acid and urea (hexagonal BN, hBN), boric acid, urea and saccharose (B-C-N materials) and sodium tetrahydroborate and ammonium (rhombohedral BN, /iBN) were used for irradiation experiments. The transformation to fullerene-like morphology from originally flat or curled and jumbled graphene-like sheets or polygonal particles takes place through a solid-state phase transition by rearrangement of atoms, which is drastically enhanced by thermal and irradiation-induced diffusion. In all of the above reported CBN clusters, the doping of B and N atoms take place on a C$_{60}$ fullerene which has an inherent strain due to curving. In addition, as the number of nitrogen atoms increases in these CBN clusters based on C$_{60}$ fullerene, the possibilities for C-N, N-N bonds which cause breakage or distortion in the C$_{60}$ increase.$^{34-38}$ This can be reduced in B$_{6}$ based stuffed fullerenes. In the B$_{6}$ based stuffed CBN clusters in addition to charge neutralization of B$_{6}$ by replacing B atoms by C and N atoms, there is an inherent bend angle (curvature) for the pentagonal pyramids that makes the curving easier during the formation of the fullerene. Variations on these strategies may be tried for generating the (CBN based) stuffed fullerenes.

### Conclusions

The strain involved in bending away from the trigonal planar structure of spherical C$_{60}$ fullerene can be reduced in stuffed boron fullerene clusters by selecting pentagonal pyramids that have high curvature (bend angle). The most appropriate pyramidal structure for this purpose is calculated to be C$_{2}$B$_{3}$N where N is in the apex position. The curvature effect is only one contributor to stability; the individual bond energies, type of bonds formed also add up to decide the relative energies.
stability and structure of the cluster. The strain involved in the rings due to shorter C-C, C-N, C-B bonds can be decreased by appropriate substitutions so that approximate spherically symmetric clusters can be made. A fullerene analog with \( \text{C}_4\text{B}_{30}\text{N}_{12}\text{Li}_{12} \) is also a good candidate for realizing stuffed fullerenes.

**Acknowledgements**

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**References**


35. D. Golberg, Y. B., O. Stepkan1, L. Bourgeois, K. Ghorbani, M and Songhori, M, *Supplementary Information (ESI) : Cartesian coordinates of optimized geometries and energies of structures are given. The individual X-H out-of-plane bend angles of all the eight pentagonal pyramids are given. See DOI: a School of Chemistry, Indian Institute of Science Education and Research Thiruvananthapuram, CET Campus, Thiruvananthapuram, 695 016, India.

b Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560012, India.

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Supplementary Information (ESI) : Cartesian coordinates of optimized geometries and energies of structures are given. The individual X-H out-of-plane bend angles of all the eight pentagonal pyramids are given. See DOI: