Designing Stuffed Hetero Fullerene Clusters: C26B46N12 and C14B58N12Li12

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

Kaipanchery Vidya [a] **and Eluvathingal D. Jemmis*** [b]

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 10 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.

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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".[1-4] The chemistry of the neighboring element boron differs largely in structure and bonding from those of carbon. The discovery of C_{60} (Fig.1, **a**) has spurred many scientists to explore new atomic clusters even though its first prediction by Eiji Osawa went unnoticed.[5] In contrast to the few and elegant rules of carbon chemistry, the structure and bonding in elemental boron, boranes and borides present extreme complexity.[6] 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.
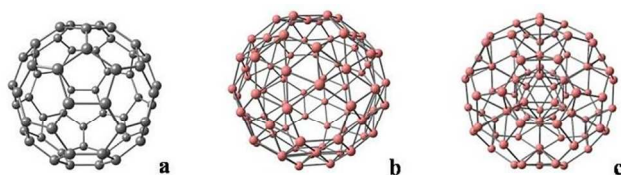

Fig.1

Fig.1: Structures of C_{60} (**a**), B_{80} (**b**) and B_{84} (**c**).

A fullerene based on boron B_{60} is deficient by 60 electrons. Addition of 60 electrons to B_{60} 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**) B_{80} where a boron atom is placed nearly in the center of each B_6 ring is found to be less stable in terms of binding energy per atom than the spherical icosahedral fullerene like stuffed B_{84} fragment of β-rhombohedral boron.[7-9] The stuffed fullerene-like boron nano clusters are based on the approximately spherical B_{84} (Fig.1, **c**) fragment of the β-rhombohedral boron.[10-15] B_{84} fragment has a central closo-B_{12} unit and its 12 vertices are connected to 12 pentagonal pyramids (nido-B_6) via 2c-2e exohedral B-B bonds (Fig.2, **a**). The 12 pentagons in the periphery are connected to form the C_{60}-like surface. The B_{84} fragment can thus be described as $B_{12}@B_{12}@B_{60}$. However B_{84} is not electron sufficient. The required number of electrons can be estimated using Wade's n+1 skeletal electron pair rule.[16] The central B_{12} requires -2 charge. Each pentagonal pyramidal B_6 needs n+2 skeletal electron pairs, which makes for B_6^{4-}. Thus, the B_{84} requires 50 electrons more, which can be given by substituting appropriate number of boron atoms by carbon and nitrogen atoms.
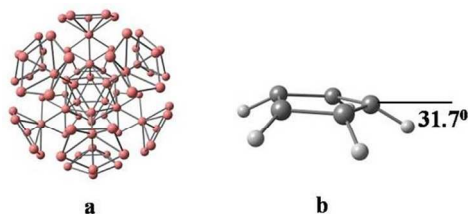

Fig.2

Fig.2: (**a**) $B_{12}@B_{12}@B_{60}$ and (**b**) the out-of-plane bend angle in the five membered ring of fullerenes.

What are the factors in addition to electron count that can be used to stabilize the boron fullerene skeleton? An obvious source of instability in C_{60} is the strain involved in pyramidalizing the trigonal planar sp^2 hybridized arrangement around each atom to what is needed in C_{60}. The distortion from planarity is 31.7^0 by symmetry (Fig.2b). How do we design a fullerene where the bent geometry is naturally favored? This is achieved to a large extend by a judicious design in B_{84} based stuffed fullerenes with the atoms inside the fullerene assisting in pyramidalization to enhance orbital overlaps as described below.

1.1 Controlling the pyramidalization by overlap matching

The out-of-plane distortion from planarity of the trigonal carbon in C_{60} is 31.7^0.[17-18] Let us construct the B_{84} fullerene from C_{60} by considering its anion, C_{60}^{-12}, which is synthesized as $C_{60}^{-12}(Li^+)_{12}$.[19-20] From the point of view of three-dimensional delocalization each C_5^- is isoelectronic with pentagonal pyramidal $B_6H_6^{4-}$. We can study the structural details of $B_6H_6^{4-}$ and the isoelectronic neutral analogues of $B_6H_6^{4-}$, namely $C_4B_2H_6$ and $C_2B_3NH_6$. 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 C_5^- pentagons in C_{60}^{-12} by pentagonal pyramids with apex atom pointing towards the centre of the fullerene. These 12 apex boron atoms are bonded to a central B_{12}^{2-} icosahedron to form B_{84} fullerene.
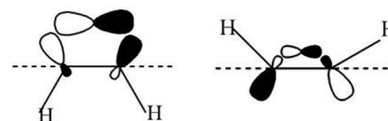

Fig.3

Fig.3: The ring-cap overlap and resulting out-of-plane bending of hydrogens for a diffuse cap orbital and a less diffuse cap orbital respectively.

The charge in B_{84}^{50-} can be reduced by replacement of boron atoms. A neutral carborane C_2B_{10} unit can replace the central icosahedral B_{12}^{2-} unit in B_{84} fullerene. There are several options for the pentagonal pyramidal B_6^{4-} units.[21,22] 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 $C_4B_2H_6$ and $C_2B_3NH_6$ so that the pentagonal pyramid 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 $C_4B_2H_6$ unit is only 18.8^o which is considerably less compared to 31.7^o in C_{60}.[23] The twelve pyramidal nido-B_6^{4-} units can be replaced by a neutral nido-C_2B_3N 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 $C_2B_3NH_6$ must have a five membered ring with the

ring hydrogens bent towards the apical atom, be it B, C or N. The structure of $C_{60}^{-12}(Li^+)_{12}$ suggests yet another possibility. If two borons of the B_6 unit is replaced by a carbon and nitrogen, and a Li is used to bridge the open face of the pentagonal pyramid, an isoelectronic bipyramidal structure, CB_4NLi, 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 $C_2B_3NH_6$ (I-VIII) are presented in Table 1. The relative energies of fullerene clusters of molecular formula $C_{26}B_{46}N_{12}$ derived from these pentagonal pyramids were also calculated. Similarly CB_4NLi (IX) and its B_{84} analog $C_{14}B_{58}N_{12}Li_{12}$ are also studied. The energies are given with ZPE correction.

3 Results and Discussions

The nido-$C_2B_3NH_6$ 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 pentagonal pyramids are used in constructing the stuffed fullerene in the following way. The five membered rings of the C_2B_3N pentagonal pyramid are connected through sigma bonds to form the fullerene surface. The twelve apex atoms are bonded to a central C_2B_{10} unit so that a neutral cluster with composition $C_{26}B_{46}N_{12}$ ($12C_2B_3N+C_2B_{10}$) results. Optimized structures of all eight isomers of $C_2B_3NH_6$ 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 **θ** is calculated for all the pentagonal pyramidal isomers given in Table 1. The isomer (**II**) with nitrogen as a cap has got the largest θ value (=23.9⁰), which is closest to 31.7⁰, 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 $C_{26}B_{46}N_{12}$ 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.

No.	Cap	ΔE₁ (in kcal/mol)	Average θ	ΔE₂ (in kcal/mol)
	NH cap			
I	η² (broken)	107.3	-	73.0
II	η⁵	100.8	23.9	47.6
	CH cap			
III	η⁵	98.2	21.9	65.3
IV	η⁵	59.9	22.1	12.6
	BH cap			
V	η⁵	42.8	13.3	52.7
VI	η⁵	0.0	12.7	0.00
VII	η⁵	60.9	14.1	80.0
VIII	η⁵	18.5	12.3	27.3
IX	(CB₄NLiH₆) η⁵	-	26.0	-

Table 1: The relative energies ΔE_1 of pentagonal pyramidal isomers of $C_2B_3NH_6$ in kcal/mol, their average X-H out-of-plane bend angle θ, relative pentagonal ring sigma bond energies ΔE_2 respectively computed at B3LYP/6-31g* level. Lower values of ΔE_1 and ΔE_2 indicate greater stability. The relative energy in kcal/mol and out-of-plane bend angle θ of CB_4NLiH_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 $C_{26}B_{46}N_{12}$ clusters are generated by taking twelve pentagonal pyramids of one particular isomer of C_2B_3N 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 $C_{48}B_{12}$ fullerene leads to numbers of the order of 10^{11}.[26] 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. With 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-5e** from **V**, **6a-6c** 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 B_{84} based CBN cluster results. The relative energies of the eight clusters calculated from the eight C_2B_3N 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
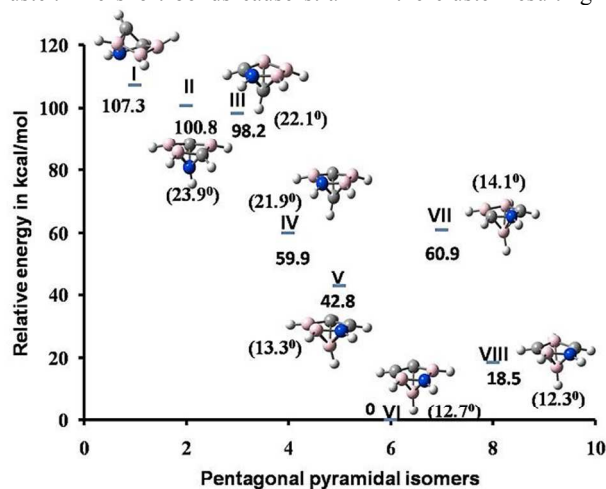

Fig.4

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 $C_2B_3NH_6$ 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=0.59kcal/mol, which indicates they are stable at room temperature.[29] Also the intensities of the lower frequencies are less in these above mentioned clusters. Cluster **1b** has a low frequency of 207.05cm^{-1}=0.59kcal/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 0.77kcal/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 C_{60} 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 1.5kcal/mol which is much greater than room temperature kT value indicating its stability.[30] 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.

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

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 $C_{26}B_{46}N_{12}$ clusters out of the thirty eight clusters from pentagonal pyramids **I** to **VIII** and $C_{14}B_{58}N_{12}Li_{12}$ (**9**) calculated at B3LYP/6-31g* level.

The HOMO-LUMO gaps of the selected eight closo minimum energy clusters are compared with that of C_{60} HOMO-LUMO gap of 2.3±0.1 eV.[31] 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 C_{60} 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
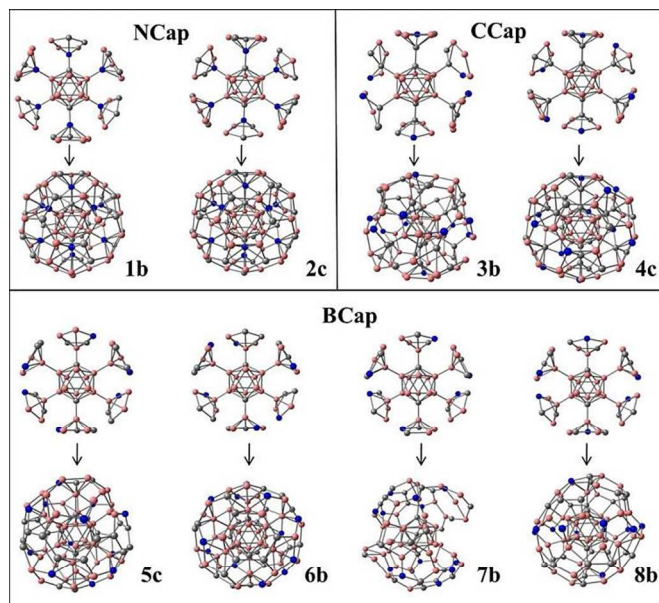
Fig.5

Fig.5: The closo minimum energy structures for $C_{26}B_{46}N_{12}$ clusters out of the thirty eight clusters calculated from the eight pentagonal pyramidal isomers **I-VIII** of $C_2B_3NH_6$ at B3LYP/6-31g* level.

synthesis of CBN fullerenes based on B_{84} structure. The qualitative idea of overlap matching to reduce the strain of the surface atoms appears to be valid.

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_4NLi (**IX**) is 26° (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 $C_2B_{10}@(C_2B_3N)_{12}$ 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 $C_2B_{10}@(CB_4NLi)_{12}$ i.e.; $C_{14}B_{58}N_{12}Li_{12}$ (**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.
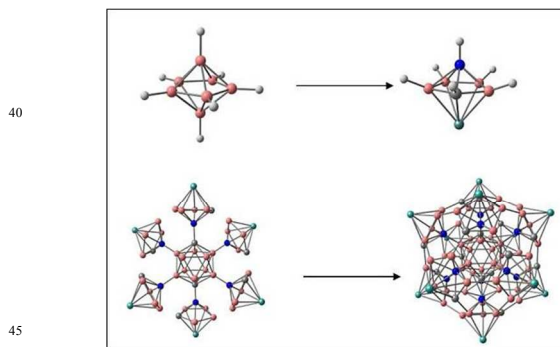

Fig 6

Fig.6: The minimum energy structure for $C_{14}B_{58}N_{12}Li_{12}$ cluster computed at B3LYP/6-31g* level.

3.1 Experimental possibilities

Various C–B–N fullerenes were synthesized by polymer pyrolysis, chemical reactions, arc-melting and electron-beam irradiation. Atomic structure and formation mechanism were investigated by High Resolution Electron Microscopy(HREM), Energy Dispersive Spectrometer(EDS) studies, and *Electron Energy Loss Spectroscopy*(EELS).[32] Laser vaporization of a graphite pellet containing boron nitride powder was found to produce fullerenes in which one or more atoms of the hollow carbon cage was replaced by a boron atom.[33] Numerous fullerenes were synthesized in various B-C-N materials by *in-situ* electron beam irradiation in a high-resolution transmission analytical electron microscope. Starting materials like chemical-vapor deposited graphitic carbon (B-C materials), fused mixtures of boric acid and urea (hexagonal BN, /iBN), boric acid, urea and saccharose (B-C-N materials) and sodium tetrahydroborate and ammonium (rhombohedral BN, rBN) 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_{84} based stuffed fullerenes. In the B_{84} based stuffed CBN clusters in addition to charge neutralization of $B_{84}{}^{50-}$ 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_2B_3N 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 $C_{14}B_{58}N_{12}Li_{12}$ is also a good candidate for realizing stuffed fullerenes.

Acknowledgements

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[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.*
E-mail: jemmis@iisertvm.ac.in.

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: