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Fully Inorganic (Carbon-Free) Fullerenes? The Boron–Nitrogen Case

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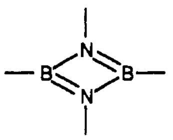
Closed cages containing only boron and nitrogen atoms can be constructed from four-membered B_2N_2 rings and six-membered B_3N_3 rings. The ring-spiral algorithm applied to such cages and Hückel molecular orbital calculations suggest that a series of stable "accordion-shaped" cages, with the general formula $B_{12+3n}N_{12+3n}$ can exist. In addition, on the basis of different principles, a $B_{22}N_{22}$ cage seems also possible.

The discovery by Kroto et al.[1] of the 60-vertex cluster of carbon atoms and its laboratory scale synthesis[2-4] began the fullerene "buckyball" boom in chemistry. The "epidemic"-like development of this field[5] resulted in several reviews,[6-10] and a special issue (No. 3) of Vol. 25 of the *Accounts of Chemical Research* has been devoted to this subject. It is perhaps time to ask whether carbon is the unique element selected by Nature to display the beauty of structure and interesting properties of the buckyball. Apparently the answer is negative, since boron is the element second to carbon in its ability to bond to itself and large clusters of three-dimensionally connected boron atoms are well documented in various boron allotropes or metal borides.[11] Large truncated icosahedral units have been also found in some aluminum alloys.[12] Silicon, the next neighbor of carbon, is another possible candidate for neofullerenes. There is already some evidence in the appearance of magic numbers in Si_n^+ clusters.[13,14] It is extremely unlikely that nitrogen alone would form even small clusters with stabilities comparable with those of boron or aluminum. However, the boron–nitrogen bond is isoelectronic with a carbon–carbon bond and this, together with the tendency of boron to form closed structures, suggests the possible existence of 1:1 heteroatom relatives of fullerenes. The idea of fully inorganic fullerenes becomes more attractive in view of the recent report that a number of closed (spherical) cage species with the composition $M_{12}C_8^+$ (M = Ti, Zr, Hf) detected by mass spectrometry also seem to be extremely stable.[15]

Substitution of carbon atoms in diamond by pairs of alternating boron and nitrogen atoms gives the cubic form of polymeric boron nitride. Hexagonal boron nitride is also known and has some resemblance to graphite since it also consists of fused planar six-membered B_3N_3 rings. It differs from graphite, however, since there are strong interlayer boron–nitrogen interactions.[16] An analogous substitution on C_{60} would give $B_{30}N_{30}$, and the resulting exact fullerene analogue would require the presence of 12 five-membered and 20 six-membered rings. In this case, however, even the most favorable arrangement of atoms, i.e. the maximum number of alternating BN bonds, would leave 11 BB and 11 NN bonds in addition to the 68 "normal" BN bonds. A simple Hückel MO treatment ($\alpha_N = 1.5$, $\alpha_B = -1$, $\beta = 0.9$) of such a system shows that the NN and BB π-bond orders are about four times smaller than the BN π-bond orders. The HOMO–LUMO gap is quite low, about 0.22β units, compared with the values found in a systematic theoretical study on C_{34} to C_{70} fullerenes.[17] Therefore, such a hypothetical molecule would be destabilized by the low homonuclear π-bond orders and in addition kinetic factors would also contribute to destabilization. This will reduce the stability of any $B_{30}N_{30}$ molecule based only on six- and five-membered rings. This subject was addressed in some detail in a paper published while this work was in progress,[18a] and to avoid the presence of BB and NN bonds, Jelski et al.[18b] allowed one carbon atom to remain in each of the 12 pentagonal faces of the original fullerene. Thus, in the $C_{12}B_{24}N_{24}$ molecule the spherical aspect of the fullerene is preserved and the π-bond system extends over the BN, BC, and NC bonds in all the six electron rings. There is a further way of bypassing the weak homonuclear bonding in a closed B_xN_x system involving replacement of five-membered rings by four-membered B_2N_2 rings, ensuring perfect alternation of heteroatoms. The entire structure can therefore be built up from two basic rings:



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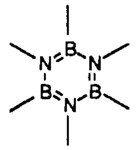

b

Both of these are well documented as individual cyclic boron–nitrogen ring compounds.[19] Moreover, formally unsaturated diazadiboretidines (cyclodiborazenes) are more stable than the

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(1) Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. *Nature (London)* **1985**, *318*, 162.

(2) Howard, J. B.; McKinnon, J. T.; Makarovsky, Y.; Lafleur, A. L.; Johnson, M. E. *Nature (London)* **1991**, *352*, 139.

(3) Kratschmer, W.; Lamb, L. D.; Fostiropoulos, K.; Huffman, D. R. *Nature (London)* **1990**, *347*, 354.

(4) Taylor, R.; Hare, J. P.; Abdul-Sada, A. K.; Kroto, H. W. *J. Chem. Soc., Chem. Commun.* **1990**, 1423.

(5) Braun, T. *Angew. Chem.* **1992**, *104*, 602.

(6) Kroto, H. W.; Allaf, A. W.; Balm, S. P. *Chem. Rev.* **1991**, *91*, 1213.

(7) Kroto, H. W. *Angew. Chem.* **1992**, *104*, 113.

(8) Stoddart, F. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 70.

(9) Dietrich, F.; Whetten, R. L. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 678.

(10) Miller, J. S. *Adv. Mater.* **1991**, *3*, 262.

(11) Wells, A. F. *Structural Inorganic Chemistry*, 5th ed.; Clarendon Press: Oxford, U.K., 1986.

(12) Phillips, J. C. *J. Chem. Phys.* **1988**, *88*, 2090.

(13) Zybill, C. *Angew. Chem.* **1992**, *104*, 180.

(14) Lange, Th.; Martin, T. P. *Angew. Chem.* **1992**, *104*, 179.

(15) (a) Guo, B. C.; Kerns, K. P.; Castelman, A. W., Jr. *Science* **1992**, *255*, 1411. (b) Guo, B. C.; Wei, S.; Purnell, J.; Buzza, S.; Castelman, A. W., Jr. *Science* **1992**, *256*, 515.

(16) Wentorf, R. H. *J. Chem. Phys.* **1957**, *26*, 956.

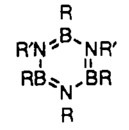
(17) Manolopoulos, D. E.; May, J. C.; Down, S. E. *Chem. Phys. Lett.* **1991**, *181*, 105.

(18) (a) Xia, X.; Jelski, D. A.; Bowser, J. R.; George, T. F. *J. Am. Chem. Soc.* **1992**, *114*, 6493. (b) Bowser, J. R.; Jelski, D. A.; George, T. F. *Inorg. Chem.* **1992**, *31*, 154.

0020-1669/93/1332-3755$04.00/0

isoelectronic cyclobutadiene. Further, although it is a crude estimate, it is worth mentioning that dimeric $(HNBH)_2$ dimer is more stable by ca. 74 kcal/mol than two monomers,[20] while cyclobutadiene C_4H_4 is less stable (by 0–30 kcal/mol) than two acetylene units.[21] π-Bond orders in the four-membered fragment are also reasonably high (0.38 in endocyclic BN bonds and 0.43 in exocyclic BN bonds).[22]

These arguments show that boron and nitrogen atoms can be accommodated much more easily than carbon atoms in unsaturated four-membered rings. Recently Paetzold et al.[23] have obtained evidence for ring expansion/contraction in the diazadiboretidine/borazine system by showing that $(R'NBR)_2$ adds R'NBR to give either a six-membered borazine (c) ring or a Dewar borazine alternative (d). Such behavior could be support for isomerization in any boron–nitrogen cluster based on four- and six-membered rings, via migration of the four-membered rings by a mechanism involving the formation of intermediate Dewar borazine rings.



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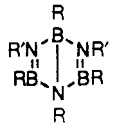


d

Semiquantitative Arguments. The ring-spiral algorithm[17] successfully applied in generating all isomers of fullerenes has been modified to search for isomers of $(AB)_n$ clusters containing six- and four-membered rings. It can be shown that for any cubic planar graph having f_i faces of i vertices, the following relation is obeyed:[24]

$$12 = 3f_3 + 2f_4 + f_5 - f_7 - 2f_8 - 3f_9 ...$$

If there are only f_4 and f_6 faces, it follows that $f_4 = 6$; i.e., any cluster containing only four- and six-membered rings will have exactly six four-membered rings. On the other hand, for a cluster with v vertices there are $(v/2 + 2)$ faces, and the number of six-membered faces is $(v/2 - 4)$. By analogy with genuine fullerenes, which obey the rule of isolated pentagons (IPR),[25] here we generate only structures with isolated four-membered rings. In this way, excess strain due to connections between two four-membered rings will be somewhat reduced. On the other hand, it should be noted that Dewar borazine is equivalent to two adjacent B_2N_2 rings and there would probably be a continuous transformation between the two forms on the surface of the cage of a BN buckyball. Such cages are not, however, considered here.

According to Hückel theory, the resonance energy per electron (REPE) can be taken as a gross estimate of the *thermodynamic stability* of fullerenes.[17] Similar REPE values for B_xN_x clusters can be calculated (see Table I) but they show only a slight increase across the series, and none of the structures considered seems to have outstanding relative thermodynamic stability.

Table I. REPE (Resonance Energy per Electron) Values for B_xN_x Clusters (β Units)

x	REPE	x	REPE
12	0.3785	19	0.3862
13[a]		20	0.3869
14[a]		21	0.3876
15	0.3827	22	0.3881
16	0.3836	23	0.3886
17	0.3846	24	0.3891
18	0.3856	25	0.3895

[a] No structures with isolated four-membered rings found in these cases.

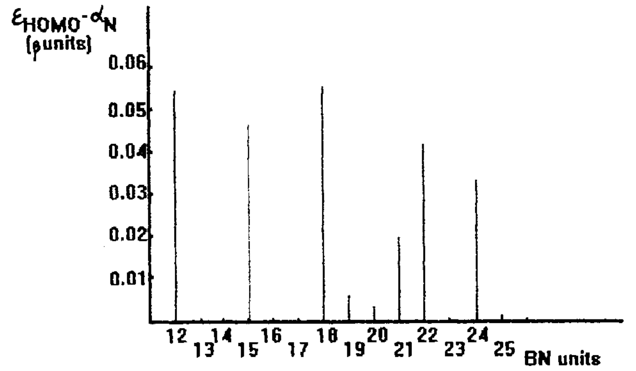
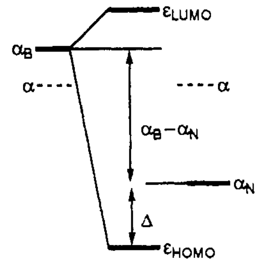


Figure 1. Calculated $\Delta = \epsilon_{HOMO} - \epsilon_N$ energy differences for various B_xN_x cages.

Therefore, on the basis of the arguments in ref 17, we concentrate on the *kinetic stabilities* of such hypothetical clusters and relate this to the HOMO–LUMO gap. However, the minimum possible HOMO–LUMO gap for any 4/6 B_xN_x cluster with alternating boron and nitrogen atoms is α_N–α_B (see diagram e for a diatomic analogy), and from this point of view any B_xN_x cluster should be kinetically stable. For this reason, instead of the HOMO–LUMO differences, we have used the difference Δ between ϵ_{HOMO}–α_N, which might be a better electronic stability indicator. From the whole set of possible isomers of a given composition we select only those for which a maximum Δ value is calculated, assuming that these will be kinetically the most stable. Figure 1 shows the variation in Δ values for species with the formulas $B_{12}N_{12}$ to $B_{25}N_{25}$. The most notable boron nitrogen (4/6) clusters are the neutral $B_{12}N_{12}$ and $B_{18}N_{18}$, which have a global maximum for Δ (0.0544β) and also substantial resonance energies per atom (0.378β and 0.386β, respectively). The structure of $B_{12}N_{12}$ (shown in Figure 2) consists of two basket- or bowl-shaped tetracyclic B_6N_6 units with C_{3v} symmetry joined by six boron–nitrogen bonds (the dashed lines in Figure 2) giving a truncated octahedron. The symmetry is, however, reduced to S_6 due to the alternation of the heteroatoms. The basic tetracyclic B_6N_6 unit consists of a six-membered B_3N_3 ring fused with three non-coplanar four-membered B_2N_2 rings:



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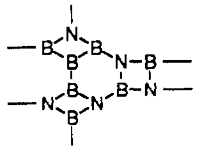

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(19) (a) Haiduc, I. *The Chemistry of Inorganic Ring Systems*; Wiley-Interscience: London, 1970; Vol. 1, p 240. (b) Maringgele, W. In *The Chemistry of Inorganic Homo- and Heterocycles*; Haiduc, I., Sowerby, D. B., Eds.; Academic Press: New York, 1987; Vol. 1, Chapter 2, p 17.

(20) Armstrong, D. R.; Perkins, P. G. *J. Chem. Soc. A* **1970**, 2748.

(21) Buenker, R. J.; Peyerimhoff, S. D. *J. Am. Chem. Soc.* **1969**, *93*, 4342.

(22) Baird, N. C. *Can. J. Chem.* **1967**, *45*, 2059.

(23) Paetzold, P.; Kiesgen, J.; Krahe, K.; Maies, H. U.; Bose, R. *Z. Naturforsch.* **1991**, *46B*, 853.

(24) Wilson, R. J. *Introduction to Graph Theory*; Oliver & Boyd: Edinburgh, U.K., 1972; Chapter 5.

(25) Haufler, R. E.; Chai, Y.; Chibante, L. P. F.; Concicao, J.; Jin, L.; Wang, L.-S.; Maryama, S.; Smaley, R. E. *Mater. Res. Soc. Proc.* **1991**, *216*, 627.

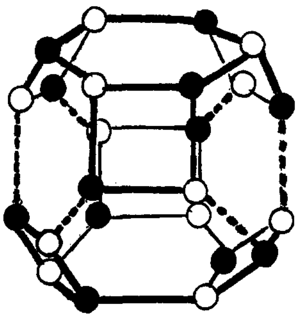


Figure 2. Construction of a $B_{12}N_{12}$ cage from two B_6N_6 tetracyclic bowls.

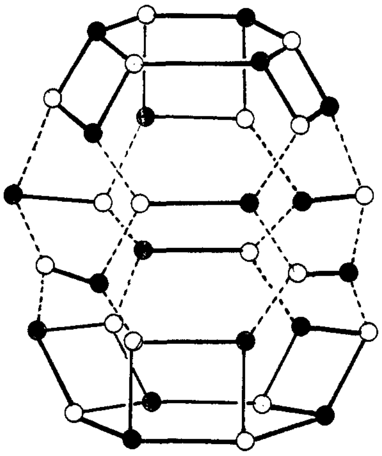


Figure 3. Construction of a $B_{18}N_{18}$ cage from two B_6N_6 bowls as capping units and six intercalated BN units (n = 2).

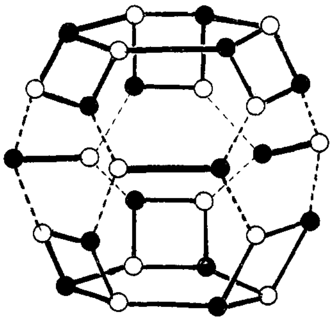


Figure 4. Construction of a $B_{15}N_{15}$ cage from two B_6N_6 capping units and three intercalated BN units (n = 1).

From the whole set of possible $B_{18}N_{18}$ isomers, the most stable found by the spiral algorithm is shown in Figure 3. This structure can be derived from that of $B_{12}N_{12}$ by inserting 6 BN units between the two tetracyclic B_6N_6 bowls. The two B_6N_6 bowls can be now regarded as two capping units (like the north and south ice caps of our planet) with the additional BN units inserted in the equatorial zone. The overall symmetry is again S_6.

Insertion of only three BN units between the two B_6N_6 capping units, as shown in Figure 4, gives the composition $B_{15}N_{15}$, but the relative orientation of two B_6N_6 bowls is different (120° rotation) from that in $B_{12}N_{12}$ and $B_{18}N_{18}$.

A whole series of "accordion-like" structures can, in fact, be formed by inserting multiples of 3 BN units between the B_6N_6 capping groups and will have the general formula $B_{12+3n}N_{12+3n}$, where n is the number of intercalated triplets of BN fragments. Thus, for n = 0, 1, 2, and 3 the compositions $B_{12}N_{12}$, $B_{15}N_{15}$, $B_{18}N_{18}$, and $B_{21}N_{21}$, respectively, will result. All these compositions correspond to relatively high Δ values, as shown in Figure 1, and are the most stable BN cage species expected.

If n is odd, accordion-like cylinders with C_{3h} symmetry are formed (see for example $B_{15}N_{15}$ in Figure 4), while clusters with even n values have S_6 symmetry as shown above for $B_{18}N_{18}$. A matter of concern in such structures is the deviation from planarity of the three bonds at both boron and nitrogen. In C_{60} buckminsterfullerene and related carbon cages, such deviations do not prevent the formation of closed systems. In the boron–nitrogen

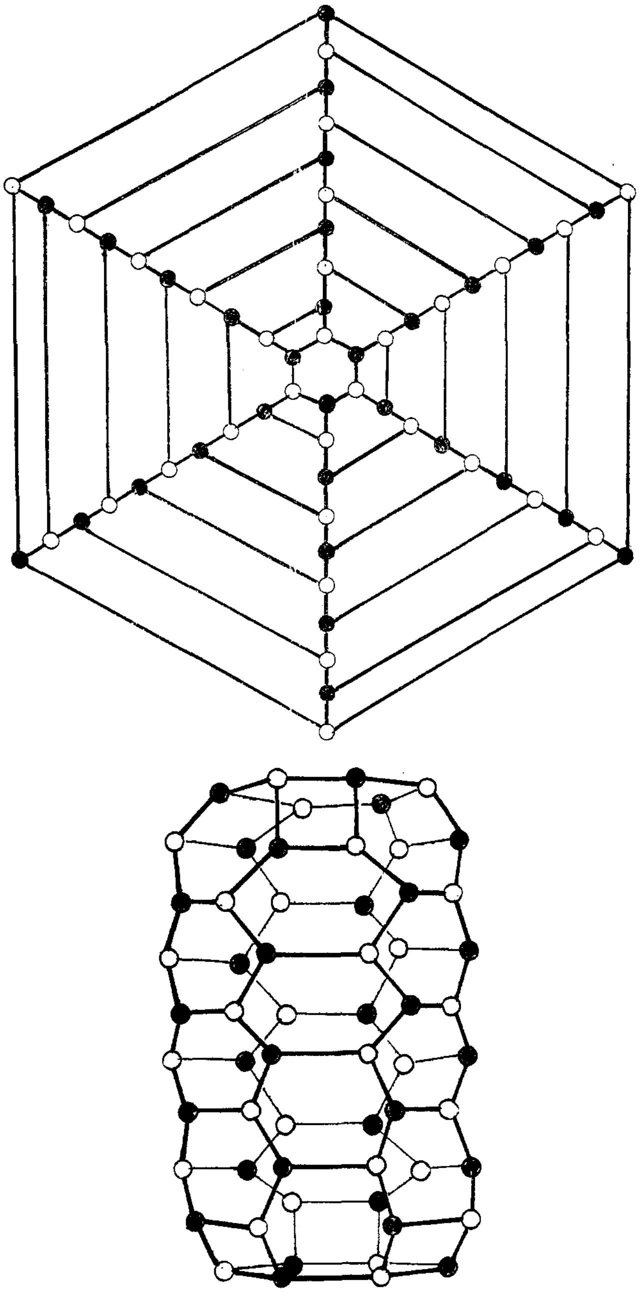


Figure 5. (a) Top: Planar graph representing the $B_{30}N_{30}$ cage. (b) Bottom: Three-dimensional structure of the $B_{30}N_{30}$ cage, consisting of two B_6N_6 capping units and 18 BN units (n = 6).

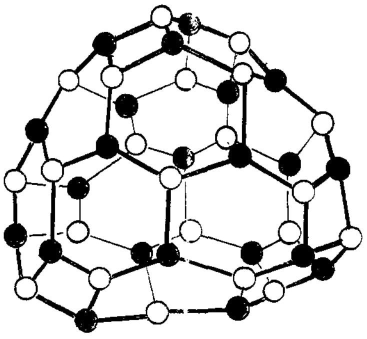


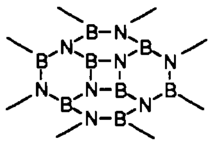
Figure 6. Structure of a $B_{22}N_{22}$ cage built up of 6 B_2N_2 and 18 B_3N_3 rings.

analogues, deviations from planarity are, in general, not much greater than in the carbon systems. It seems that the largest deviations occur in the bowl-shaped capping B_6N_6 units, while the intercalated triplets of BN units, leading to the "side wall" of the resulting cylinder ("accordion"), display even lower deviations from planarity. Therefore, whatever the fate of π-electrons in the carbon fullerenes, the same can be expected for the π-electron system in the boron–nitrogen structures, and a simple Hückel treatment will still give a rough estimate of the relative positions of the (quasi)-π-levels.

Fowler and Manolopoulos have found that stable fullerene cations have two carbons more and stable anions two carbon less than the corresponding neutral cluster.[26] If this applies equally to the boron–nitrogen system, then $B_{17}N_{17}^{2-}$ with the same electron count as the neutral $B_{18}N_{18}$ should also be relatively stable, but it should be noted that, for the expected dication, $B_{19}N_{19}^{2+}$, the $\epsilon_{HOMO}-\epsilon_N$ gap is not satisfactory.

Since $B_{30}N_{30}$ has a reasonable Δ value (ca. 0.04β), such a cluster could also exist. It is however probable that it would contain four- and six-membered rings and not be similar to C_{60}. The ring-spiral algorithm gives the following sequence of six- and four-membered rings: 64646466666666666666666666464646. This sequence can be conveniently represented by the planar graph shown in Figure 5a. Note that similar graphs can be generated easily for all the systems discussed above, by deleting successively the peripheral B_3N_3 units and closing the resulting four-membered rings. The three-dimensional structure shown in Figure 5b reveals a striking resemblance to $B_{18}N_{18}$. Both have the capping B_6N_6 fragments joined by zigzag-arranged BN units. The $B_{30}N_{30}$ composition corresponds to a value of $n = 6$ in the $B_{12+3n}N_{12+3n}$ series mentioned above. The intermediate members, with $n = 4$ and $n = 5$, would have the compositions $B_{24}N_{24}$ and $B_{27}N_{27}$, and the former has a favorable value. We have not searched for all the $B_{27}N_{27}$ isomers (because of the long operating time required by our computing facilities), but probably this structure also has an acceptable value.

Another cluster having a substantial Δ value but differing in shape from this series is $B_{22}N_{22}$. This is the smallest cage built from six pentacyclic B_8N_8 fragments sharing 12 BN edges (Figure 6). The B_8N_8 unit is based on a four-membered B_2N_2 ring fused to four surrounding six-membered B_3N_3 units, to form a nonplanar bowl:



A possible practical way of obtaining B_xN_x clusters would perhaps be the evaporation of boron nitride under nitrogen pressure, to avoid decomposition to elemental boron and nitrogen as found in the case of laser ablation of boron nitride in vacuo.[27]

We realize that in some cases the proposed compositions may exhibit several skeletal isomers and even enantiomers. This subject is under consideration and will be discussed separately.

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(26) Fowler, P. W.; Manolopoulos, D. E. *Nature* **1992**, *355*, 428.

(27) La Placas, J.; Roland, P. A.; Wynne, J. J. *Chem. Phys. Lett.* **1992**, *190*, 163.