COMPUTATIONS OF BORON AND BORON-NITROGEN CAGES

Z. Slanina*, M.-L. Sun and S.-L. Lee

Department of Chemistry, National Chung-Cheng University
Ming-Hsiung, Chia-Yi 62117, Taiwan

*On a leave of absence from the Academy of Sciences of the Czech Republic, Prague

(Accepted June 17, 1997)

Abstract -- The article surveys computations of several hetero-fullerenes: $B_{30}N_{24}$, $B_{30}P_{24}$, $Al_{30}N_{24}$, $Al_{30}P_{24}$, and various $B_mN_n$ ($m + n \neq 60$). For $m + n = 60$ cases, the following stability order is predicted: $B_{30}N_{24} > B_{30}P_{24} > Al_{30}N_{24} > Al_{30}P_{24}$. In addition to the pentagon-hexagon fullerene pattern, the square-hexagon route is considered as an alternative. The new pattern always requires six squares, while the number of hexagons increases linearly with the number of atoms. The route can produce species of similar or even higher stability compared to the conventional pentagon-hexagon approach. It has a unique significance for the BN clusters as it allows for a mutual compensation of the steric strain in four-membered rings by maximizing the number of B-N bonds (and suppressing B-B and N-N ones). On the other hand, the square/hexagon route does not produce a particular $C_{60}$ stabilomer (as there is no compensation for the four-membered ring strain).

Clusters purely based on boron are exemplified with $B_{32}$ ($I_1$), which could be considered as a topological analogy of $C_{60}$ owing to dual relationships. The species however is not a local energy minimum at the HF/STO-3G and HF/3-21G ab initio level. In the MNDO computations the cage relaxes into a $D_{2d}$ symmetry. Atomization heat is used in evaluation of its stability. © 1997 Acta Metallurgica Inc.

1. INTRODUCTION

Heterofullerenes have become a subject of research interest soon after the establishment of the fullerene research itself (1-3). Fullerenes containing boron and/or nitrogen atoms (4-13) represent one distinguished class, though other elements have been combined with the fullerenes, too (14-16). This interest may be linked to the fact that boron nitride has a stable crystalline phase similar to graphite. The doped clusters have even been suggested as molecular electronics agents and they have a potential for the nanotechnology field in general. However, these studies still represent the first approaches to the problem of potentially substantial significance, but it cannot yet be compared with the fullerenes themselves. Owing to an interplay between theory and experiment, the situation with the small BN clusters is a bit clearer (see, e.g., (17-20)). For large clusters a systematic check of all possible stoichiometries would in principle be needed, this being
beyond the present possibilities. Here, we primarily concentrate on selected special stoichiometries, like \( \text{B}_{30}\text{N}_{24} \) or \( \text{B}_{32} \), and related species.

2. BORON-NITROGEN CLUSTERS

The non-carbon species \( \text{B}_n\text{N}_m \) can be considered as a limiting case of the B/N doped fullerenes. The study of \( \text{B}_n\text{N}_m \) cages is apparently a more complex problem as even in the stoichiometry we have two free parameters. It is not obvious which \( n, m \) choices should yield particularly stable species. Computations have been reported \((7,9)\) for \( \text{B}_{30}\text{N}_{30} \) and \( \text{B}_{12}\text{N}_{12} \). In fact, three \( \text{B}_{30}\text{N}_{30} \) isomers have been considered \((7)\), but it is only a small fraction of all possibilities.

There is basically no experimental information on the \( \text{B}_n\text{N}_m \) cluster thermochemistry, though some information for small aggregates can be derived from \textit{ab initio} calculations \((17-20)\). Even before some larger thermochemical data set is available, one can hypothesize that B-N bonds bring larger stabilization compared to B-B or N-N bonds. Based on this scheme, isomers with a large number of the B-N bonds are considered in this study. The traditional fullerene pattern, pentagons and hexagons \((5/6)\), always needs some B-B and/or N-N bonds owing to the five-membered rings. In order to eliminate the B-B and N-N bonds completely, we have to deal with even-numbered rings only, which leads to a choice of squares and hexagons \((4/6)\), and an equal number of B and N atoms. In this part we shall examine the structural pattern, select some candidates for higher cluster stability, and to some extent also compare with the traditional \(5/6\) approach.

As already mentioned, the fullerenes themselves have mostly been constructed from pentagons and hexagons, although some other polygons have occasionally been considered, too. This pattern requires an even number of carbon atoms and always 12 pentagons \((\text{twelve pentagon rule})\). Let us allow now for the usage of squares \((\text{the word square means here a four-membered ring rather than a rectangle with equal sides})\) and hexagons only in construction of a polyhedron \((\text{altogether } n_4 \text{ squares and } n_6 \text{ hexagons, so that the number of rings or faces } F \text{ of the polyhedron reads } F = n_4 + n_6, \text{ and let us consider altogether } V \text{ three-coordinated atoms (i.e., vertices)}\). Then, the total number of bonds or edges \((E)\) in the cage is \(3V/2\), where the factor of 2 prevents a double counting of each bond \((\text{and the number of atoms is to be even})\). The number of bonds can be counted not through atoms but through the rings, then another expression, \((4n_4 + 6n_6)/2\), is obtained and thus:

\[
4n_4 + 6n_6 = 3V. \quad [1]
\]

For a further simplification let us apply now the powerful Euler formula \((V + F = E + 2)\), but implement in it what we already know for \( F \) and \( E \):

\[
V + n_4 + n_6 = \frac{3}{2}V + 2. \quad [2]
\]

Thus, we have two equations for three variables, and we can readily find that:

\[
n_4 = 6 \quad [3]
\]
\[ n_6 = \frac{V}{2} - 4. \]  

This result means that in each polyhedron built from four- and six-membered rings and three-coordinated atoms the number of the four-membered rings will always be six (clearly enough, we have only shown that this is a necessary condition).

Figure 1. The MNDO heats of formation per atom (the upper part) and HOMO-LUMO gaps for the \( C_n \) clusters (derived from computations (21)).
It is obvious from Eq. [4] that the smallest possible number of atoms is 8 (then only six squares and no hexagons, i.e., one of the five regular solids, a cube, if all atoms are equivalent). There is still another unique case in the series, namely for $V = 24$, when we deal (for equivalent atoms) with one of the thirteen semi-regular polyhedrons, truncated octahedron, and thus with the real squares and regular hexagons. Similar to the isolated pentagon rule, we can introduce a concept of the isolated squares. As we deal with six squares we cannot meet the requirement with less than 24 atoms. However, in the truncated octahedron indeed there is no junction of two squares so that it is the smallest 4/6 polyhedron with the isolated square property.

Although we would like to search for particularly stable species, we have to admit that there is no clear, computationally accessible measure of the cluster stability. In general terms, we can of course suggest measures of thermodynamic or kinetic stability but we cannot compute them for a real system. Then, we have to deal with some approximations. Heat of formation related to one particle may come as a reasonable parameter. However, if we plot the available MNDO data (21) for the carbon aggregates (Figure 1) we can readily check that the famous C$_{60}$ does not emerge from the picture as a particularly stable species (a similar picture has been observed at the ab initio HF/STO-3G level (22), as reported in Ref. 23). Hence, we have to look for another computationally feasible term. Traditionally, a relatively large HOMO-LUMO gap accounts for a chemical stability. This approach indeed points out C$_{60}$ as the most abundant fullerene (Figure 1). This represents a justification for a usage of the HOMO-LUMO gap for stability reasoning with the B$_n$N$_m$ clusters, too. (Interestingly enough, the heat of formation can still be made of good use, after adding entropy effects, but it is a computationally more demanding task.)

Let us mention for completeness that once we deal with mixed clusters, the heat of formation per particle cannot be a good parameter either, simply because of differences in the reference thermochemical states. We can get rid of the dependency by constructing a convenient class of derived reactions; for example, atomization reactions (which after all should correspond to high-temperature conditions). Therefore, for the B$_n$N$_m$ clusters we shall employ here the atomization heats per particle when discussing energetics. For the uniform clusters like C$_n$, the difference between the heat of formation per particle and atomization heat per particle is insignificant as it represents a mere constant shift in the series.

Figure 2 surveys the studied 4/6 clusters B$_n$N$_n$. It is a sample in which the dimension increases with a step of (BN)$_4$. However, three B$_3$N$_3$O$_3$ species are included, and a B$_4$I$_4$ body turned out to be more easily assembled than B$_4$N$_4$. Figure 3 plots the computed atomization heats per particle and HOMO-LUMO gaps. Similar to the C$_n$ case, the heat of atomization per particle does not allow for a clear stability conclusion. However, the HOMO-LUMO gap points out three local maxima and thus, higher stability candidates— B$_{12}$N$_{12}$, B$_{28}$N$_{28}$, and B$_{36}$N$_{36}$ (all with a tetrahedral symmetry - Table 1).

A comparison with the conventional 5/6 approach should be made. There are three MNDO isomers of B$_3$N$_3$O$_3$ in the literature (7), but their description is not sufficient enough in order to perform the related AM1 computations. If we recompute our 4/6 structures at the MNDO level, our lowest heat of formation falls about 100 kcal/mol below the lowest 5/6 structure (7). This supports a usefulness of the new 4/6 route. We could find another interesting stoichiometry with the 5/6 pattern and a significant stability, viz. the T$_{6}$B$_{36}$N$_{24}$ cluster (Figure 4). Its HOMO-LUMO gap is higher than any one found in the 4/6 route (Figure 3). However, as it has non-unit B/N ratio it is not obvious if such a direct comparison is possible. In any case, our computations point out the 4/6 route as an interesting alternative to the conventional 5/6 pattern in building the B$_n$N$_n$
TABLE 1
AM1 Energetics of BₙNₘ and Cₙ Clusters

<table>
<thead>
<tr>
<th>Species</th>
<th>Symm. group</th>
<th>Δ(H^{o,298.15}_f) (\frac{\text{kcal}}{\text{mol}})</th>
<th>Δ(H^{o,298.15}_{at}/z) (\frac{\text{kcal}}{\text{mol.atm}})</th>
<th>HOMO-LUMO gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B₄N₄</td>
<td>(T_d)</td>
<td>219.2</td>
<td>-97.0</td>
<td>7.42</td>
</tr>
<tr>
<td>B₈N₈</td>
<td>(S_4)</td>
<td>34.1</td>
<td>-122.2</td>
<td>8.08</td>
</tr>
<tr>
<td>B₁₂N₁₂  (b)</td>
<td>(T_h)</td>
<td>-238.4</td>
<td>-134.3</td>
<td>8.85</td>
</tr>
<tr>
<td>B₁₆N₁₆  (b)</td>
<td>(T_d)</td>
<td>-428.1</td>
<td>-137.7</td>
<td>8.55</td>
</tr>
<tr>
<td>B₂₀N₂₀  (b)</td>
<td>(C_2)</td>
<td>-569.6</td>
<td>-138.6</td>
<td>8.50</td>
</tr>
<tr>
<td>B₂₄N₂₄  (b)</td>
<td>(S_4)</td>
<td>-788.4</td>
<td>-140.8</td>
<td>8.66</td>
</tr>
<tr>
<td>B₂₈N₂₈  (b)</td>
<td>(T)</td>
<td>-1013.3</td>
<td>-142.4</td>
<td>8.78</td>
</tr>
<tr>
<td>B₃₀N₃₀  (b)</td>
<td>(C_1)</td>
<td>-853.8</td>
<td>-138.6</td>
<td>6.48</td>
</tr>
<tr>
<td>B₃₀N₃₀  (b)</td>
<td>(D_2)</td>
<td>-999.0</td>
<td>-141.0</td>
<td>8.38</td>
</tr>
<tr>
<td>B₃₀N₃₀  (b)</td>
<td>(S_6)</td>
<td>-1003.2</td>
<td>-141.1</td>
<td>8.58</td>
</tr>
<tr>
<td>B₃₂N₃₂  (b)</td>
<td>(C_1)</td>
<td>-1191.9</td>
<td>-143.0</td>
<td>8.70</td>
</tr>
<tr>
<td>B₃₆N₃₆  (b)</td>
<td>(T_d)</td>
<td>-1416.2</td>
<td>-144.0</td>
<td>8.91</td>
</tr>
<tr>
<td>B₄₁N₄₁  (b)</td>
<td>(C_s)</td>
<td>-1663.7</td>
<td>-144.6</td>
<td>8.73</td>
</tr>
<tr>
<td>B₃₆N₂₄  (c)</td>
<td>(T_h)</td>
<td>-964.1</td>
<td>-142.7</td>
<td>9.51</td>
</tr>
<tr>
<td>C₆₀</td>
<td>(I_h)</td>
<td>973.3</td>
<td>-154.7</td>
<td>6.70</td>
</tr>
<tr>
<td>C₆₀</td>
<td>(D_2)</td>
<td>1531.7</td>
<td>-145.4</td>
<td>5.18</td>
</tr>
</tbody>
</table>

\(^a\) The formation and atomization heat is denoted by the index \(f\) and \(at\), respectively, both types of terms refer to the room temperature. The atomization heat is divided by number of atoms in a cluster, \(z (z = n + m \text{ and } z = n \text{ for the B/N and C clusters, respectively).} \)

\(^b\) See Figure 2.

\(^c\) See Figure 4.

species. Finally, let us mention that cyclic and linear structures of B₃₀N₃₀ are estimated to be located some 400 and 600 kcal/mol, respectively, above the lowest B₃₀N₃₀ isomer (\(S_6\)) in Table 1 at the AM1 level (however, convergency behavior is poor for the two non-cage cases).

One can ask what are the consequences for the Cₙ clusters themselves. Table 1 shows that the 4/6 route should not be significant for the pure fullerenes. For example, the 4/6 \(D_2\) symmetry C₆₀, derived from the \(D_2\) B₃₀N₃₀ (Figure 2), is located more than 500 kcal/mol above the well established \(I_h\) structure. Apparently, in the pure carbon clusters there is no compensation for a destabilization, owing to smaller four-membered rings.
Figure 2. The AM1 optimized $B_nN_m$ structures with the 4/6 pattern and their symmetries.
Figure 3. The AM1 heats of atomization per atom (the upper part) and HOMO-LUMO gaps for the $B_nN_m$ clusters ($T_h$: $B_{36}N_{24}$).

Although a further considerable computational effort is needed for a more comprehensive picture of the $B_nN_m$ clusters, it is obvious that the development would follow along both 4/6 and 5/6 lines. Moreover, a complete thermodynamic or even kinetic stability evaluation will probably be necessary for a reliable selection of dominant species. The available fragments of computational information nevertheless supply a sufficient impetus for a parallel experimental search through the B/N cluster system.
Let us now switch again to the conventional pentagon/hexagon topology, namely let us concentrate on one special stoichiometry $B_{36}N_{24}$. One can point out some geometrical reasons for selecting the 36/24 stoichiometry. In a fullerene-like aggregate $X_{60}$ twelve isolated pentagons or five-membered rings are present. They are responsible for the five-fold axes of symmetry in the icosahedral $X_{60}$ cage. One possibility to generate some symmetric $X_n Y_m \ (n + m = 60)$ derivatives is to keep a constant composition (however, not necessarily the mutual arrangement of the $X$ and $Y$ atoms) throughout the pentagons (though, the five-fold axes themselves cannot be retained, if we do not consider the trivial case of $Y_5$). Then, we have six basic options: $X_5, X_4 Y, X_3 Y_2, X_2 Y_3, XY_4, Y_5$ (although there are only three really different ratios). Clearly enough, all the material necessary for a construction of a ball $X_{12} Y_{12}$ is contained in the twelve pentagons $X_i Y_j$. From this line of reasoning the following stoichiometries arise: $X_{60}, X_{48} Y_{12}, X_{36} Y_{24}, X_{24} Y_{36}, X_{12} Y_{48}, Y_{60}$. Let us mention for completeness, that the complementary line of reasoning (keeping composition constant throughout all the hexagons) readily yields ratios 50/10, 40/20, 30/30, 20/40, 10/50. This related set falls, however, outside the scope of our report.

For each of the above four non-uniform stoichiometries (48/12, 36/24, 24/36, 12/48) a considerable number of isomers can be expected. Let us start with the $X_{36} Y_{24}$ stoichiometry, originating from the $X_3 Y_2$ modification of each of the pentagons. We still have not mentioned the conditions for the twenty six-membered rings involved. In fact, they cannot be of the same type. The 24 $Y$ atoms mean an average of 2.4 $Y$ atoms per hexagon (each $Y$ atom is shared by two hexagons). Hence, at least two different hexagon types are to be allowed. An obvious choice (though not only one) is hexagons with two and three $Y$ atoms. This particular arrangement then leads to the requirement of twelve double-substituted and eight triple-substituted hexagons. The
set of pentagons and hexagons can indeed be arranged into a highly symmetric cage, namely $T_h$ symmetry species (see Figure 4).

The AM1 geometry optimization shows that there is a stationary point (in fact, a local energy minimum) of the symmetry on the B$_{36}$N$_{24}$ potential hypersurface (Table 2). At this stage we decided to check conditions for other possible analogues of the boron-nitrogen cluster. Hence, AM1 geometries of other three related species were optimized: B$_{36}$P$_{24}$, Al$_{36}$N$_{24}$, Al$_{36}$P$_{24}$. It has turned out that only the Al$_{36}$N$_{24}$ species obeys the high $T_h$ symmetry. In the other two cases the symmetry is lowered, supposedly owing to a Jahn-Teller distortion, though the pentagon/hexagon pattern is still kept. An effective diameter of the cages is of course increased comparing to that of B$_{36}$N$_{24}$ or C$_{60}$.

There is a key question—how to compare (thermodynamic) stability of the four species in question. The heat of formation itself cannot be used as it refers to quite varied thermodynamic reference states. Recently, the usage of the atomization heats was suggested (24) for the purpose. For example, while the heat of formation of B$_{36}$N$_{24}$ is related to the process:

\[ 36\text{B(s)} + 12\text{N}_2(g) = \text{B}_{36}\text{N}_{24}(g), \]  

[5]
TABLE 3
Formation and Atomization Heats\textsuperscript{a} (kcal/mol) of B\textsubscript{32} and C\textsubscript{60}

<table>
<thead>
<tr>
<th>Species</th>
<th>$\Delta H^o_{f,298.15}$</th>
<th>$\Delta H^o_{at,298.15}$</th>
<th>$\Delta H^o_{at,298.15,rel}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>B\textsubscript{32}, $D_2d$, MNDO</td>
<td>688.4</td>
<td>-3654</td>
<td>-114</td>
</tr>
<tr>
<td>B\textsubscript{32}, $D_2d$, AM1</td>
<td>895.2</td>
<td>-3447</td>
<td>-108</td>
</tr>
<tr>
<td>C\textsubscript{60}, $I_h$, MNDO</td>
<td>869.3</td>
<td>-9384</td>
<td>-156</td>
</tr>
<tr>
<td>C\textsubscript{60}, $I_h$, AM1</td>
<td>973.3</td>
<td>-9280</td>
<td>-155</td>
</tr>
</tbody>
</table>

\textsuperscript{a}The formation and atomization heat is denoted by the index $f$ and $at$, respectively, both types of terms refer to the room temperature; the relative atomization heat is in (kcal/(mol.atm)) units.

The atomization heat is defined by the reaction:

$$36\text{B}(g) + 24\text{N}(g) = B_{36}\text{N}_{24}(g).$$

[6]

The atomization heats bring a uniformity to the left sides of the underlying chemical reactions, and also it better reflects high-temperature conditions. As can be seen in Table 2, in the atomization-heat stability scale the order reads: $B_{36}\text{N}_{24} > B_{36}\text{P}_{24} > Al_{36}\text{N}_{24} > Al_{36}\text{P}_{24}$. However, with respect to the AM1 atomization (24) heat of C\textsubscript{60}, the buckminsterfullerene still remains the most stable species.

Interest in heterofullerenes has further been supported by the interesting results reported for hetero-nanotubes. Rubio \textit{et al.} (25) published calculations on boron nitride nanotubes based on bending a BN graphitic sheet. The BN nanotubes and concentric shells have also been observed (26-28). Related theoretical works have been reported (29-31), too. Zhu \textit{et al.} (29) published extensive computations on boron nitride cages and polymers.

3. PURE BORON CLUSTERS

Let us turn our attention now to the pure boron clusters; we can hardly use the previous experience in order to predict some particularly stable B\textsubscript{n} species. For example, the truncated icosahedron of B\textsubscript{60} exhibits Jahn-Teller distortion towards triangular faces. Then, B\textsubscript{32} comes as another particular choice owing to duality relationship (32), and we shall discuss its properties based on \textit{ab initio} and semiempirical calculations. The duality relationship transforms any
standard fullerene into a polyhedron with triangular faces only (this comes from the three-coordinated nature of the fullerene atoms).

Two polyhedra are duals when atoms of one correspond to the ring-centers of the other. If we take any fullerene and create a new polyhedron from the centers of all rings we obtain a triangular cage. In particular, C₆₀ is transformed into a 32-atom cage, the atoms in which are either five or six-coordinated. The symmetry is preserved in this transformation and thus, we deal with an icosahedral B₃₂ (Figure 5). There are only two degrees of freedom if we constrain the geometry to the I₄h symmetry; such structures can be optimized at ab initio level. We have found imaginary vibrational frequencies in both HF/STO-3G and HF/3-21G treatments (though it is not related to a Jahn-Teller distortion). Hence, we deal with higher saddle points, and the symmetry must be relaxed. This second step was followed at semiempirical level and a D_{2d} minimum-energy
structure was obtained (Figure 5). The conditions are somewhat different for the MNDO and AM1 descriptions as the $I_6$ symmetry produces (in contrast to the ab initio treatments) a degenerate partially filled frontier orbitals. Table 3 presents the computed energetics—the atomization heat per particle is not as good as for C$_{60}$ but better than for Si$_{60}$ (24).

ACKNOWLEDGMENTS

Acknowledgments are made to the National Science Council, Taiwan and the National Chung-Cheng University for financial support. The authors also thank the National Center for High-Performance Computing in Hsinchu for computer time on the Convex C3840 and SPP 1000.

REFERENCES