Square/hexagon route towards the boron–nitrogen clusters

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Abstract

A new route towards B/N clusters is considered, based on squares and hexagons. The 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 pattern. Four particular stoichiometries emerge from the available AM1 computations: B_{12}N_{12}, B_{28}N_{28}, B_{36}N_{36}, and B_{36}N_{24}.

1. Introduction

Heterofullerenes have become a subject of research interest soon after the establishing fullerene research itself [1–3]. The 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]. The non-carbon species B_{n}N_{m} can be considered as a limiting case of the B/N doped fullerenes. The study of B_{n}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 B_{30}N_{30} and B_{12}N_{12}. In fact, three B_{30}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 B_{n}N_{m} cluster thermochemistry, though some information for small aggregates can be derived from ab initio calculations [17–20]. Even before some larger thermochemical data set is available, one can hypothesize that B–N bonds bring larger stabilization comparing 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 Letter, 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.

2. Six square rule

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 twelve pentagons (twelve pentagon rule). Let us allow now for the usage of squares (the word square means here a four-mem-
bered ring rather than a rectangle with equal sides) and hexagons only in construction of a polyhedron (altogether $n_4$ squares and $n_6$ hexagons, so that the number of rings or faces $F$ of the polyhedron reads $F = n_4 + n_6$), and let us consider altogether V three-coordinated atoms (i.e. vertices). Then, the total number of bonds or edges ($E$) in the cage is $\frac{3}{2}V$, where the factor of 2 prevents a double counting of each bond (and the number of atoms has to be even). The number of bonds can be counted not through atoms but through the rings, and then another expression, $\frac{1}{2}(4n_4 + 6n_6)$, is obtained and thus

$$4n_4 + 6n_6 = 3V.$$  \hspace{1cm} (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 $E$,

$$V + n_4 + n_6 = \frac{3}{2}V + 2.$$  \hspace{1cm} (2)

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

$$n_4 = 6,$$  \hspace{1cm} (3)

$$n_6 = \frac{1}{2}V - 4.$$  \hspace{1cm} (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).

It is obvious from Eq. (4) that the smallest possible number of atoms is 8 (then there are 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, a truncated octahedron [21], and thus with the real squares and regular hexagons. Similarly 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.

3. Computations

The computations were performed with the standard parametrizations of the AM1 semiempirical quantum-chemical method [22] available in the SPARTAN program package [23]. The main part of the computations was done with this program implementation at an Iris/Silicon Graphics XZ4000 workstation (though some computations were also carried out with the MOPAC 5.0 [24] and GAUSSIAN92 [25] program packages). The full geometry optimizations were carried out using the analytical energy gradient. Only singlet electronic states were considered.

4. Results and discussion

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 [26] for the carbon aggregates (Fig. 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 [27] as reported in Ref. [28]). Hence, we have to look for another computationally feasible term. Traditionally, a relatively large HOMO–LUMO gap has been accounted for chemical stability [29,30]. This approach indeed points out C$_{60}$ as the most abundant fullerene (Fig. 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 a good use, after adding entropy effects, so that even the observed stability relationships could be recovered – see Refs. [31,32] – but it is a computationally more demanding task.

Let us mention for the 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 construct-
Fig. 1. The MNDO heats of formation per atom (upper part) and HOMO–LUMO gaps (lower part) for the Cₙ clusters (derived from computations [26]).

Fig. 2. The AM1 optimized BₙNₙ structures with the 4/6 pattern and their symmetries.

Fig. 3 plots the computed atomization heats per particle and HOMO–LUMO gaps. Similar to the Cₙ 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 – B₁₂N₁₂, B₂₈N₂₈, and B₃₆N₃₆ (all with a tetrahedral symmetry – Table 1).

A comparison with the conventional 5/6 approach should be made. There are three MNDO isomers of B₃₀N₃₀ in the literature [7] but their description is not sufficient 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 T₈B₂₈N₂₄ cluster (Fig. 4). Its HOMO–LUMO gap is higher than any one found in the 4/6 route (Fig. 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 BₙNₙ species. Finally,
let us mention that cyclic and linear structures of B\textsubscript{30}N\textsubscript{30} are estimated to be located some 400 and 600 kcal/mol, respectively, above the lowest B\textsubscript{30}N\textsubscript{30} isomer ($S_6$) in Table 1 at the AM1 level (however, convergency behaviour is poor for the two non-cage cases).

One can ask what the consequences are for the C\textsubscript{n} 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 $C_{60}$, derived from $D_2$

Table 1

<table>
<thead>
<tr>
<th>Species</th>
<th>Symm. group</th>
<th>$\Delta H_f^{298.15}$ (kcal/mol)</th>
<th>$\Delta H_f^{298.15}/z$ (kcal/mol/atom)</th>
<th>HOMO–LUMO gap (eV)</th>
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</thead>
<tbody>
<tr>
<td>$B_4N_4$</td>
<td>$T_d$</td>
<td>219.2</td>
<td>-97.0</td>
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<tr>
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<td>$T_h$</td>
<td>-238.4</td>
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<td>$B_{20}N_{20}$</td>
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<tr>
<td>$B_{24}N_{24}$</td>
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<td>-140.8</td>
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<td>-141.1</td>
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<td>-145.4</td>
<td>5.18</td>
</tr>
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</table>

\*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, $z (z = n + m$ and $z = n$ for the $B/N$ and $C$ clusters, respectively). 

\*See Fig. 2. \* See Fig. 4.
B_{30}N_{30} (Fig. 2), is located more than 500 kcal/mol above the well-established I_6 structure. Apparently, in the pure carbon clusters there is no compensation for a destabilization owing to smaller four-membered rings. Although a further considerable computational effort is needed for a more comprehensive picture of the B_{n}N_{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.

Acknowledgement

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Note added in proof

Rubio et al. [33] reported calculations on boron nitride nanotubes based on bending a BN graphitic sheet. Boulanger et al. [34] observed the BN nanotubes and concentric shells (though it is yet not known whether they are closed by means of pentagons or squares). Stabilities of some analogies of B_{36}N_{24} have been considered, too [35].

References