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THE FULLERENE NEIGHBOURS

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ABSTRACT

Semiempirical quantum-chemical calculations are reported for the fullerene structures C_{60}, Si_{60}, Ge_{60}, N_{60}; B_{32}N_{24}, B_{38}F_{24}, Al_{34}N_{24}, Al_{34}F_{24}; and various B_{n}N_{m}. A new route towards B/N clusters is considered, being based on squares and hexagons. The pattern always requires six squares. The route can produce species of similar or even higher stability comparing to the conventional pentagon/hexagon pattern. Four particular stoichiometries emerge from the available AMI computations: B_{12}N_{12}, B_{28}N_{28}, B_{36}N_{36}, and B_{38}N_{24}.

INTRODUCTION

During formation of the C_{60} research [1-3], silicon aggregates have become [4-16] a natural subject of study, and there are mass-spectrometric evidences [10,17] of large charged silicon and even germanium clusters. Nitrogen aggregate N_{20} [18,19] has also attracted attention. The doped fullerenes containing boron, nitrogen, and other atoms [20-34] represent another interesting class. The non-carbon species B_{n}N_{m} can be considered as a limiting case of the B/N doped fullerenes. In fact, three B_{38}N_{38} isomers have been computed [24,25], but it is of course only a small fraction of all possibilities.

COMPUTATIONS

The computations were performed with the standard parametrizations of the AM1 semiempirical quantum-chemical method [35] available in the SPARTAN program package [36]. 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 [37] and GAUSSIAN 92 [38] program packages). The Ge_{60} cage was computed at the MNDO level. The full geometry optimizations were carried out using the analytical energy gradient, and vibrational analysis was performed numerically for selected cases. Only singlet electronic states were considered.

RESULTS AND DISCUSSION

Table I deals with the C_{60}, Si_{60}, Ge_{60}, and N_{60} cages (Ge_{60} has a distorted structure, possibly owing to a (pseudo) Jahn-Teller effect, but it is not very different from the exact I_{h} symmetry - Figure 1). As different thermochemical reference states are involved, heats of formation cannot be directly applied and we use related heats of atomization instead.

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

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Table I. Formation and atomization heats* (kcal/mol) of C$_{60}$, Si$_{60}$, Ge$_{60}$, and N$_{60}$

<table>
<thead>
<tr>
<th>Species</th>
<th>$\Delta H_f^{\ddagger}$</th>
<th>$\Delta H_{at}^{o,298.15}$</th>
<th>$\Delta H_{ref,298.15}^{o}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_{60}$, AM1</td>
<td>973.3</td>
<td>-9280</td>
<td>0</td>
</tr>
<tr>
<td>Si$_{60}$, AM1</td>
<td>1296</td>
<td>-5207</td>
<td>4073</td>
</tr>
<tr>
<td>Ge$_{60}$, MNDO</td>
<td>2543</td>
<td>-2827</td>
<td>6453</td>
</tr>
<tr>
<td>N$_{60}$, AM1</td>
<td>3243</td>
<td>-3537</td>
<td>5743</td>
</tr>
</tbody>
</table>

* The formation and atomization heat is denoted by the index $f$ and $at$, respectively, both types of terms refer to the room temperature.

Figure 1. The MNDO optimized (near $I_h$) structure of Ge$_{60}$.
The difference between Si₆₀ and C₆₀ in ΔH²₄₁.₂₉₈.₁₅ is by one order of magnitude larger than in ΔH²₃₆.₉₅₈.₁₅. The related separation between Ge₆₀ and Si₆₀ in the new terms is about two times larger. It suggests that, thermodynamically, creation of C₆₀ is favored over Si₆₀ or even Ge₆₀. However, it does not take into account kinetic barriers. N₆₀ is close to Ge₆₀ in the scale. If we compare stabilities of the caged with respect to 30 diatomic molecules results are still more pronounced. Ge₆₀ is located some 5514 kcal/mol below 30 C₂ (AM1) but N₆₀ is 2008 kcal/mol above 30 N₂; clearly enough, the high stability of N₂ manifests here. Let us note that the AM1 HOMO-LUMO gap [39,40] is quite similar for C₆₀ (6.7 eV) and N₆₀ (7.7 eV); it seems that this stability measure would not be applicable here. Finally, Iₖ, Bₙ₀ is a Jahn-Teller case (as, e.g., Iₖ, C₆₀).

There is basically no experimental information on the BₙNₙ cluster thermochemistry, though some information for small aggregates can be derived from ab initio calculations [41-43]. Still, we can expect that B-N bonds bring larger stabilization comparing to B-B or N-N bonds. Based on this scheme, isomers with a larger number of the B-N bonds are considered. Figure 2 presents a Tₖ symmetry structure of B₃₆N₂₄. If we check stabilities of other three related species (B₃₄P₂₄, A₁₃N₂₄, A₁₅P₂₄) it turns out that B₃₆N₂₄ is preferred by the atomization heat and the HOMO-LUMO gap as well (Table II).

Even if we limit our considerations to B-N modifications only, we should try some other ratios, for example: B₃₄N₂₄, B₃₃N₁₂, B₃₂N₈. The first one just requires a systematic B-N exchange in the B₃₆N₂₄ body. The AM1 optimization yields an optimum structure of the Tₖ symmetry but less stable in both the atomization heat and HOMO-LUMO gap. S₄ and D₅ symmetries can be computed for the other two cases. The AM1 stationary points however turn out to be even less stable comparing to the ruled out B₃₄N₂₄.

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. It can be derived that the number of the four-membered rings is always six.

Table III surveys the studied 4/6 clusters BₙNₙ. It is a sample in which the dimension mostly increases with a step of (BN)₄. Similar to the Cₙ series 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, B₂₄N₂₄, and B₃₆N₃₆ (all with a tetrahedral symmetry, see Figure 3). It seems that we need a certain degree of similarity in order to judge a relative stability of compounds with different stoichiometries from the HOMO-LUMO gaps [39,40], and the similarity concept is not fully understood yet. A comparison with the conventional 5/6 approach should be made. There are three MNDO isomers of B₃₂N₃₂ in Ref. 24. If we recompute our 4/6 structures at the MNDO level, our lowest structure falls about 100 kcal/mol below the best 5/6 structure [24]. This could have consequences even for the supposed B-N nanotubes [44].

Table III shows that the 4/6 route should not be significant for the pure fullerenes. For example the 4/6 D₅ symmetry C₆₀, derived from the D₁₂ B₃₂N₃₂, is located more than 500 kcal/mol above the well established Iₖ structure. Apparently, in the pure carbon clusters there is no compensation for a destabilization owing to smaller four-membered rings. Although several stability candidates emerge from our computations, it is also clear that we need a more comprehensive stability measure. One option is to switch to equilibrium constants and to compute composition at plausible temperatures and pressures. This could be computationally feasible (before the matter can be settled by molecular dynamics within sophisticated potential hypersurfaces).
Figure 2. The AM1 $T_d$ structure of B$_{36}$N$_{24}$ (view along a two-fold rotational axis; •: B atoms).

Figure 3. The AM1 $T_d$ structure of B$_{36}$N$_{24}$ (view along a three-fold rotational axis.)
Table II. Basic AM1 structure and energy parameters of $X_{38}Y_{24}$ species

<table>
<thead>
<tr>
<th>Species</th>
<th>$D^*$ (Å)</th>
<th>$\Delta H_e^{\infty} f_{298.15}$ (kcal/mol)</th>
<th>$\Delta H_e^{\infty} f_{298.15}^{\text{at}}$ (kcal/mol)</th>
<th>HOMO-LUMO gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_{60}$</td>
<td>7.11</td>
<td>973.3</td>
<td>-9280.1</td>
<td>6.70</td>
</tr>
<tr>
<td>B$<em>{38}$N$</em>{24}$</td>
<td>7.48</td>
<td>-964.1</td>
<td>-8561.3</td>
<td>9.51</td>
</tr>
<tr>
<td>B$<em>{38}$P$</em>{24}$</td>
<td>9.64</td>
<td>-555.0</td>
<td>-7253.9</td>
<td>6.63</td>
</tr>
<tr>
<td>Al$<em>{38}$N$</em>{24}$</td>
<td>9.30</td>
<td>-1166.8</td>
<td>-6740.5</td>
<td>6.48</td>
</tr>
<tr>
<td>Al$<em>{38}$P$</em>{24}$</td>
<td>11.8</td>
<td>170.8</td>
<td>-4504.6</td>
<td>5.79</td>
</tr>
</tbody>
</table>

* The longest inter-atomic distance found in the cage; it can be viewed as its diameter.

$^b$ The formation and atomization heat is denoted by the index $f$ and $at$, respectively, both types of terms refer to the room temperature.

Table III. The AM1 energetics of $B_nN_m$ and $C_n$ clusters

<table>
<thead>
<tr>
<th>Species</th>
<th>Symm. group</th>
<th>$\Delta H_e^{\infty} f_{298.15}$ * (kcal/mol)</th>
<th>$\Delta H_e^{\infty} f_{298.15}/z^*$ (kcal/mol atom)</th>
<th>HOMO-LUMO gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B$_4$N$_4$</td>
<td>$T_d$</td>
<td>219.2</td>
<td>-97.0</td>
<td>7.42</td>
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<tr>
<td>B$_8$N$_8$</td>
<td>$S_4$</td>
<td>34.1</td>
<td>-122.2</td>
<td>8.08</td>
</tr>
<tr>
<td>B$<em>{12}$N$</em>{12}$</td>
<td>$T_h$</td>
<td>-238.4</td>
<td>-134.3</td>
<td>8.85</td>
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<tr>
<td>B$<em>{16}$N$</em>{16}$</td>
<td>$T_d$</td>
<td>-428.1</td>
<td>-137.7</td>
<td>8.55</td>
</tr>
<tr>
<td>B$<em>{20}$N$</em>{20}$</td>
<td>$C_4$</td>
<td>-509.6</td>
<td>-138.0</td>
<td>8.50</td>
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<tr>
<td>B$<em>{24}$N$</em>{24}$</td>
<td>$S_4$</td>
<td>-788.4</td>
<td>-140.8</td>
<td>8.66</td>
</tr>
<tr>
<td>B$<em>{28}$N$</em>{28}$</td>
<td>$T$</td>
<td>-1013.3</td>
<td>-142.4</td>
<td>8.78</td>
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<tr>
<td>B$<em>{30}$N$</em>{30}$</td>
<td>$C_1$</td>
<td>-853.8</td>
<td>-138.6</td>
<td>6.48</td>
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<tr>
<td>B$<em>{30}$N$</em>{30}$</td>
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<td>-999.0</td>
<td>-141.0</td>
<td>8.38</td>
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<tr>
<td>B$<em>{32}$N$</em>{32}$</td>
<td>$S_6$</td>
<td>-1002.2</td>
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<td>8.68</td>
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<tr>
<td>B$<em>{32}$N$</em>{32}$</td>
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<td>-143.0</td>
<td>8.70</td>
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<td>B$<em>{36}$N$</em>{36}$</td>
<td>$T_d$</td>
<td>-1416.2</td>
<td>-144.0</td>
<td>8.91</td>
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<tr>
<td>B$<em>{41}$N$</em>{41}$</td>
<td>$C_2$</td>
<td>-1063.7</td>
<td>-144.6</td>
<td>8.73</td>
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<tr>
<td>B$<em>{38}$N$</em>{24}$</td>
<td>$T_h$</td>
<td>-964.1</td>
<td>-142.7</td>
<td>9.51</td>
</tr>
<tr>
<td>C$_{60}$</td>
<td>$I_5$</td>
<td>973.3</td>
<td>-154.7</td>
<td>6.70</td>
</tr>
<tr>
<td>C$_{60}$</td>
<td>$D_2$</td>
<td>1531.7</td>
<td>-145.4</td>
<td>5.18</td>
</tr>
</tbody>
</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).
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REFERENCES