

Predicted Structures of Precursors $B_4N_6H_8$, $B_4N_8H_8$, and $B_4N_8H_6$, and the $B_{24}N_{36}$ Analogue of C_{60}

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Heteroatomic fullerenes are cage-like molecules made up of 12 pentagons and an even number of hexagons. Such species have been synthesized and are currently being studied experimentally and theoretically. Employing laser vaporization techniques, Smalley and co-workers¹ show that $C_{59}B$ and $C_{58}B_2$ are formed by doping C_{60} with boron. Calculation of the delocalization energy for $C_{12}B_{24}N_{24}$ suggests that it and similar structures of the type $C_{60-2n}B_nN_n$ are also stable.² Calculations³ also indicate that the nitrogen-containing compounds $C_{58}N_2$, $C_{58}BN$, and $B_{30}N_{30}$ have lower total energies than C_{60} , whereas $C_{58}B_2$ has a higher energy. Spectroscopic studies have tentatively identified $C_{70}N_2$, $C_{59}N_6$, $C_{59}N_4$, and $C_{59}N_2$ in the vaporization of graphite.⁴

Stable carbonless molecules with unequal numbers of boron and nitrogen are also possible, as demonstrated by the formation of $B_nN_m^+$ cluster ions for various combinations of n and m which arise from the plasma produced by laser ablation of hexagonal BN in an N_2 atmosphere.⁵ The existence of $B_{36}N_{24}$ is hypothesized in connection with another laser ablation study leading to the discovery of B_n clusters.⁶ This molecule contains B–B and B–N bonds, and has a structure which may be consistent with the observed clusters with $m < n$. On the other hand, molecules with $m > n$ may also be stable, particularly when B–B bonds are absent and strong N–N bonds can exist along with B–N linkages.

One such fullerene, $B_{24}N_{36}$, is depicted in Figure 1. We call it “bonnyball” to emphasize the presence of boron and the important N–N bonds. For bonnyball, Figure 1 shows that there are 12 B_2N_3 pentagons, 12 B_2N_4 hexagons, and eight B_3N_3 hexagons. The paired rings (B_2N_3 , B_2N_4) and (B_3N_3 , B_3N_3) share 12 and six N–N bonds, respectively. It is seen that there are no B–B bonds in bonnyball.

The structure in Figure 1 has the equilibrium geometry calculated with the MNDO method.^{7,8} The optimized bond lengths shown in Figure 1 apply to all of the remaining bonds and correspond to an energy minimum as confirmed by force constant calculations. The MNDO total energies and heats of formation are listed in Table 1 for three different fullerenes.

- (1) Guo, T.; Jin, C.; Smalley, R. E. *J. Phys. Chem.* **1991**, *95*, 4948.
- (2) Bowser, J. R.; Jelski, D. A.; George, T. F. *Inorg. Chem.* **1992**, *31*, 156.
- (3) Xia, X.; Jelski, D. A.; Bowser, J. R.; George, T. F. *J. Am. Chem. Soc.* **1992**, *114*, 6493.
- (4) Pradeep, T.; Vijaykrishnan, V.; Santra, A. K.; Rao, C. N. R. *J. Phys. Chem.* **1991**, *95*, 10564.
- (5) Becker, S.; Dietze, H. J. *Int. J. Mass Spectrom. Ion Processes* **1986**, *73*, 157.
- (6) La Placa, S. J.; Roland, P. A.; Wynne, J. J. *Chem. Phys. Lett.* **1992**, *190*, 163.
- (7) Dewar, M. J. S.; Thiel, W. J. *J. Am. Chem. Soc.* **1977**, *99*, 4907.
- (8) Stewart, J. J. P. MOPAC-MNDO Program. *QCPE* **1986**, *18*, 455.

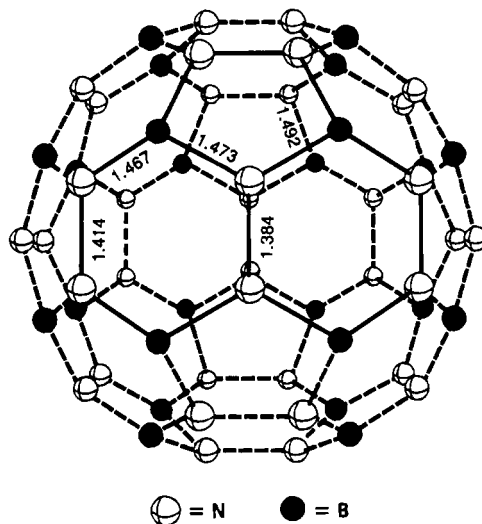


Figure 1. Predicted structure of $B_{24}N_{36}$, bonnyball. Bond lengths are given in Å.

Table 1. Comparison of Calculated Total Energies and Heats of Formation for Fullerenes^a

molecule ^a	energy (ev)	ΔH_f° (kcal/mol)
C_{60}	-7637	+869.3
$B_{30}N_{30}(B)$	-8351	-489.0
$B_{24}N_{36}$	-9162	-195.3

^a MNDO values for C_{60} and $B_{30}N_{30}(B)$ are from ref 3. Isomer B for $B_{30}N_{30}$ has nine N–N bonds.

The calculated diameter of bonnyball is 7.02 Å, as compared to 7.1 Å for C_{60} .

The structure of bonnyball was initially predicted on the basis of calculations of a variety of smaller stable molecules containing hexagons and pentagons of B and N. The MNDO calculated equilibrium structures for some of these species are shown in Figure 2. As with bonnyball, no symmetry constraints were imposed during energy minimization. In the case of planar hexagonal borazine $B_3N_3H_6$, the B–N bond length is seen to be in good agreement with the experimental value of 1.44 Å.⁹ The hexagonal rings in $B_2N_4H_6$ and $B_4N_6H_8$, which contain N–N bonds, are predicted to be approximately planar and coplanar, respectively, the distortions resulting from the presence of hydrogen atoms and lone pairs on the N atoms. The B–H bonds lie in the approximate planes of the rings, while the N–H bonds lie above and below these planes, corresponding to sp^3 hybridization.

As indicated by the solid lines in Figure 1, the rings of the molecule $B_4N_8H_6$ (Figure 2) conform approximately to the surface of $B_{24}N_{36}$. In $B_4N_8H_6$, the arrangement of the hydrogen atoms is similar to that in $B_4N_6H_8$, with the exception that two of the B–H bonds are replaced by B–N linkages to form the pentagon. As seen in Figure 2, the B–N and N–N bond lengths of the hexagons in $B_4N_8H_6$ are similar to those in $B_4N_6H_8$. In the presence of the new N–N and B–N bonds which form the pentagon, the near planarity of each of the hexagons is retained, although they are now rotated about the central N–N bond of $B_4N_6H_8$.

The structures of $B_4N_6H_8$ and $B_4N_8H_6$ suggest that nitrogen gas may play a role in the synthesis of bonnyball. The introduction of N_2 into the vicinity of $B_4N_6H_8$ may lead to the expulsion of the hydrogen atoms and to the stabilization of the

(9) Wells, A. F. *Structural Inorganic Chemistry*; Oxford University Press: London, 1962; p 851.

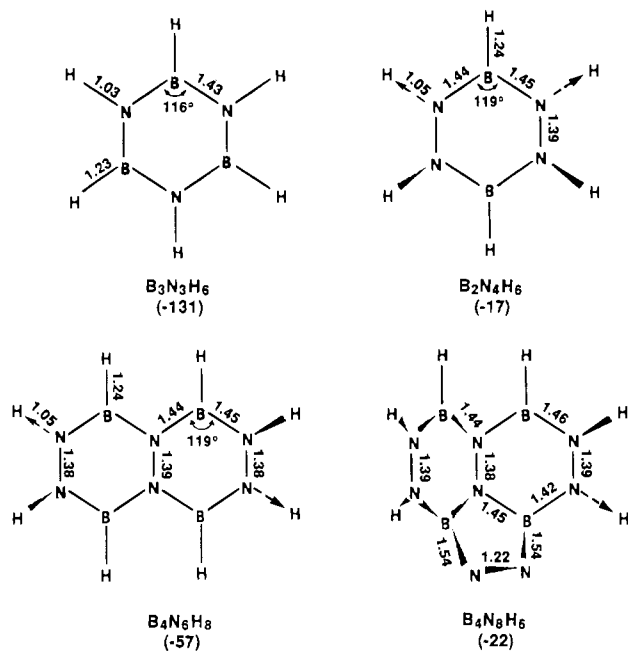
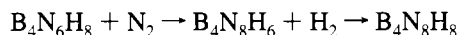


Figure 2. Calculated structures showing planar and near-coplanar rings in $B_3N_3H_6$, $B_2N_4H_6$, and $B_4N_6H_8$ and rotated planar hexagonal rings in $B_4N_8H_6$. Bond lengths are given in Å. Dashed lines denote bonds below molecular planes. Calculated heats of formation in kcal/mol are given in parentheses.

pentagon, suggesting the reaction sequence



Calculation shows that $B_4N_8H_8$ has nearly coplanar rings with H atoms bonded to both N atoms in the pentagon, giving an N–N distance of 1.41 Å which is 0.19 Å larger than the bond length in $B_4N_8H_6$. The B–N distance in the pentagon is shortened to 1.48 Å. All other bonds are similar to those of $B_4N_8H_6$ in Figure 2. From $\Delta H_f^\circ = -51$ kcal/mol for $B_4N_8H_8$ and the values of ΔH_f° in Figure 2, $\Delta H = +6$ kcal/mol for the above reaction sequence. Thus, the overall process is approximately thermoneutral.

The actual intermediates involved in the synthesis of bonnyball may, of course, be altogether different from the calculated ones of Figure 2. The role which N_2 gas may actually play depends, in part, on the planned evaluation of activation energies for a bimolecular reaction involving N_2 and $B_4N_6H_8$. It should be noted that Pradeep et al.⁴ have demonstrated that nitrogen gas reacts strongly with C_{60} to form a variety of CN-containing fullerenes.

It should be mentioned that the MNDO method tends to overestimate strain energies.¹⁰ For example, Table 1 lists $\Delta H_f = 869.3$ kcal/mol (1.21 kcal/g) for C_{60} which is larger than the experimental value of 545 kcal/mol (0.76 kcal/g). Thus, any comparisons of thermodynamic stabilities on the basis of heats of formation may be drawn into question. However, if ΔH_f is assumed to be overestimated by roughly the same amount per atom in all of the fullerenes, thermodynamic stabilities relative to expected products may be compared. As examples, phase transitions of C_{60} to diamond or graphite, $B_{24}N_{36}$ to diamond-like or "graphite" BN (experimental $\Delta H_f = -60$ kcal/mol) and 6 mol of N_2 gas, and $B_{30}N_{30}$ to BN will have, from Table 1, approximate values of -1.2 , -2.1 , and -1.7 kcal/g, respectively. These transitions are of particular interest, since solid C_{60} is known to undergo rapid phase changes to diamond and graphite at very high pressures on the order of 150 kbar.^{11,12}

The present study was carried out as part of a research effort designed to generate new, highly-energetic heteroatomic species. It should also be mentioned in this regard that novel, metastable polymers of the nitrogen oxides and other large molecules containing N–O bonds have been predicted.^{13,14} It would also be of great interest to determine possible stabilities of fullerenes containing N–O linkages.

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- (10) Bakowies, D.; Thiel, W. *J. Am. Chem. Soc.* **1991**, *113*, 3704.
- (11) Hirai, H.; Kondo, K.; Ohwada, T. *Carbon* **1993**, *31*, 1095.
- (12) Russell, T. Private communication.
- (13) Jones, W. H. *J. Phys. Chem.* **1991**, *95*, 2588.
- (14) Jones, W. H. *J. Phys. Chem.* **1992**, *96*, 594.