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Quantum Chemical Calculations of Proposed Multicage Boron Fullerenes[†]

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We have previously noted a geometrical correspondence existing between known carbon and suggested boron fullerene molecules. For example, known[1,2] C_{60} (which had been predicted theoretically[3−6] prior to its discovery) is the geometrical dual (or reciprocal) structure of the long-proposed[7] $B_{32}H_{32}$. Both molecules are aromatic, of icosahedral symmetry, possess equivalent numbers of interatomic bonds, and are of equal sphericity. That the geometrical correspondence of carbon and boron fullerenes is in fact quite general[8] follows from application of the Descartes−Euler formula

$$P + F = C + 2 \qquad (1)$$

where for a given polyhedral molecule, P is the number of points (vertexes), F is the number of faces, and C is the number of connections (interatomic contacts). It may be seen immediately as shown in ref 8 that interchanging the role played by P and F has the geometrical effect of generating from any given carbon fullerene C_P its dual analogue boron fullerene B_FH_F, and vice versa. In this way, for example, the single cage carbon fullerenes C_{28}, C_{60}, C_{70}, and C_{80} suggest their corresponding geometrical duals $B_{16}H_{16}$, $B_{32}H_{32}$, $B_{37}H_{37}$, and $B_{42}H_{42}$, respectively. It occurs moreover, that quantum molecular orbital studies[9] of the boron fullerenes show them to be energetically stable, physically reasonable ions or molecules that we expect are capable of being chemically synthesized.

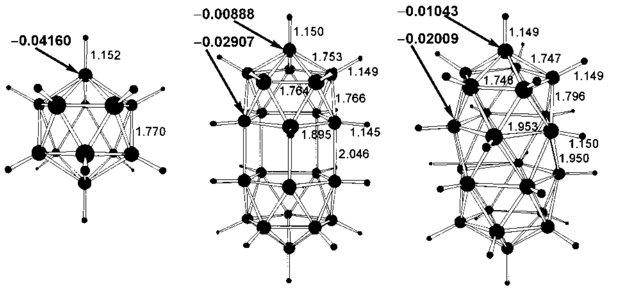

Figure 1. HF/STO-3G geometries of $B_{12}H_{12}^{2-}$ (I_h), $B_{22}H_{22}^{2-}$ (D_{5h}), and $B_{22}H_{22}^{2-}$ (D_{5d}). The lowest and the highest charges derived from Mulliken population analysis are also indicated.

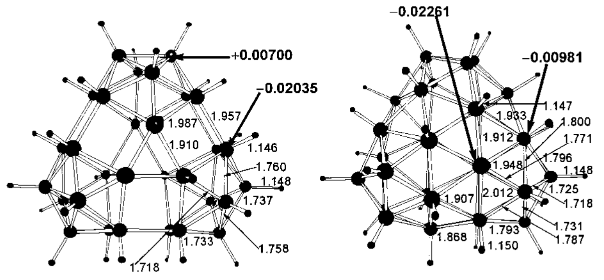

Figure 2. HF/STO-3G geometries of $B_{30}H_{30}^{2-}$ (D_{3h}) and $B_{30}H_{30}^{2-}$ (D_3). The lowest and the highest charges derived from Mulliken population analysis are also indicated.

In a modest extension to less spherical molecules, which do not have internal bonding contacts, we also applied the Descartes−Euler formula, eq 1, to suggest the probable geometries of multicage boron fullerenes.[10,11] In this paper such molecules are studied with molecular orbital calculations to establish their energetic stability, bond lengths, and ionic charge state.

In our previous study of highly spherical single cage boron fullerenes we employed a variety of quantum chemical methods which included HF/3-21G, PRDDO, LDF, and AM1 calculations. The different methods agreed fairly closely in their predictions of geometries, charge states and relative stabilities of the boron fullerenes. In this paper, we report only ab initio (HF/STO-3G) calculations. We leave for later work calculations which employ more sophisticated basis functions and higher level methods, but we anticipate results will remain similar to those reported here.

In Table 1 we highlight the geometrical correspondence between multicage carbon fullerenes and their geometrical dual multicage boron fullerene analogues consistent with the Descartes−Euler formula, eq 1. The carbon species, C_{20}, C_{35}, and C_{47}, are like polyhedra suggested[12] for Zr_8C_{12}, $Zr_{13}C_{22}$, and $Zr_{18}C_{29}$. Our C_{56} molecule of symmetry T_d, differs from the known analogue of C_{57} which has internal bonds and does not yield in an obvious manner a dual polyhedron satisfying the Descartes−Euler formula. This, of course, does not speak against the carbon 57-vertex structure as a reasonable one. The carbon species C_{40}, C_{56} (D_3), and C_{68} all arise as duals of their boron analogues obtained from boron "diamond" geometries, as in $B_{22}H_{22}^{2-}$ (D_{5d}), $B_{30}H_{30}^{2-}$ (D_3), $B_{36}H_{36}^{2-}$ (T), which in turn are obtained from the transition state "square" geometries as in $B_{22}H_{22}^{2-}$ (D_{5h}), $B_{30}H_{30}^{2-}$ (D_{3h}), $B_{36}H_{36}^{2-}$ (T_d). Such diamond−

[†] This paper is dedicated to Heinrich Nöth on the occasion of his 70th birthday.

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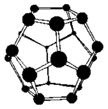
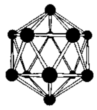
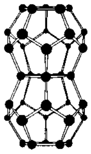
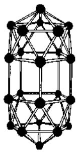
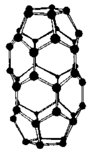
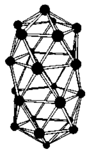
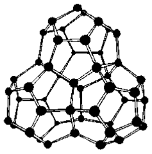
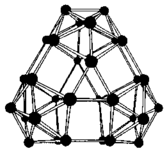
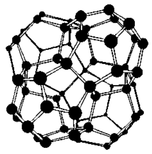
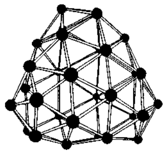
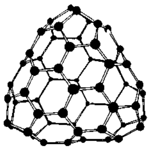
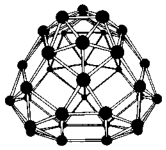
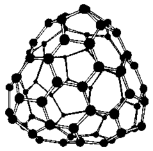
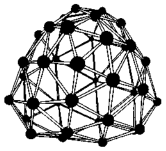
Table 1. Carbon Compounds and Their Boron Analogs; Hydrogen Atoms Are Not Shown in the Diagrams for Simplicity

Diagram	Formula	P	F	C+2	Sym	P	F	Formula	Diagram
	C_{20}	20	12	32	$\mathbf{I_h}$[a]	12	20	$B_{12}H_{12}^{-2}$	
	C_{35}	35	22	57	$\mathbf{D_{5h}}$	22	35	$B_{22}H_{22}^{-2}$	
	C_{40}	40	22	62	$\mathbf{D_{5d}}$	22	40	$B_{22}H_{22}^{-2}$	
	C_{47}	47	30	77	$\mathbf{D_{3h}}$	30	47	$B_{30}H_{30}^{-2}$	
	C_{56}	56	30	86	$\mathbf{D_3}$	30	56	$B_{30}H_{30}^{-2}$	
	C_{56}	56	36	92	$\mathbf{T_d}$	36	56	$B_{36}H_{36}^{-2}$	
	C_{68}	68	36	104	$\mathbf{T}$	36	68	$B_{36}H_{36}^{-2}$	

[a] As a result of Jahn−Teller distortion C_{20} (though not $C_{20}H_{20}$) has a C_1 symmetry.

square−diamond (DSD) rearrangement mechanisms had been predicted earlier[13] and have been verified numerically in the cases suggested above.

The geometries were optimized by minimization of the STO-3G Hartree−Fock energies of all boron species listed in Table 1. The geometries were constrained to have the assumed point group symmetries of the carbon fullerenes which were duals of the boron fullerenes studied. When the symmetry constraint for the "square" boron geometries was lifted, they spontaneously reverted to the "diamond" geometries of reduced overall molecular symmetry. The independent bond lengths associated with all multicage boron fullerenes of Table 1 are displayed in Figures 1−3. The BH bonds and triangular BB bonds are not very different from standard distances previously used for known closo boron hydrides.[7] Also shown are variations in boron atomic charges, derived from Mulliken population analysis. Although the qualitative trends in atomic charge analysis are probably good, we would expect a much improved basis to accentuate atomic charge differences among the boron atoms, and to give improved quantitative atomic charges.

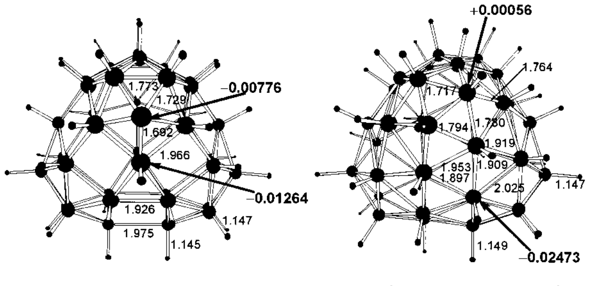


Figure 3. HF/STO-3G geometries of $B_{36}H_{36}^{2-}$ (T_d) and $B_{36}H_{36}^{2-}$ (T). The lowest and the highest charges derived from Mulliken population analysis are also indicated.

The preferred charge state for each of the boron multicage fullerenes was assumed to be 2− for all calculations reported here. This conforms with most earlier calculations for the single cage boron fullerenes[9] and with AM1 semiempirical calculations[14] of the multicage boron fullerenes. Knowledge of the preferred charge states may well be important to plans for synthesis of these compounds, which we would like to encourage.

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Table 2. Stability Factors for the Boron ($B_NH_N^{2-}$) Fullerenes: HF/STO-3G Results

N	sym	E/N[a]	$(E/N)_r$[b]	$\Delta\epsilon$[c]
1		−24.75299	0.99175	0.516
12	I_h	−24.95883	1.00000	0.725
22	D_{5h}	−24.94410	0.99941	0.406
22	D_{5d}	−24.95233	0.99974	0.467
30	D_{3h}	−24.93737	0.99914	0.344
30	D_3	−24.94857	0.99959	0.434
36	T_d	−24.93278	0.99896	0.204
36	T	−24.94648	0.99951	0.411

[a] Total energy (au)/N. [b] $(E/N)_N/(E/N)_{12}$. [c] The HOMO−LUMO energy gap (au).

In Table 2 we report energetic stability factors for the multicage boron fullerenes. For each molecule we list E/N (the total energy per BH unit) and $\Delta\epsilon$ (the HOMO−LUMO gap). We also report $(E/N)_r$, the relative total energy per BH unit compared against the case of $B_{12}H_{12}^{2-}$. Judging stability by examining E/N and $\Delta\epsilon$, as expected, one sees that $B_{12}H_{12}^{2-}$ is the most stable case. There is a trend toward slightly decreasing stability in the low-energy isomers of multicage compounds of increasing size, i.e., in the series $B_{22}H_{22}^{2-}$ (D_{5d}), $B_{30}H_{30}^{2-}$ (D_3), $B_{36}H_{36}^{2-}$ (T). All these molecules are stable relative to separated BH groups. The stability of the multicage boron fullerenes is comparable to that of the single cage highly spherical boron fullerenes reported earlier.[9]

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