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Articles

Quantum Chemical Studies of Boron Fullerene Analogues

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In the polyhedral B_NH_N series, charge states are −2 for $N = 12$ (the known $B_{12}H_{12}^{-2}$ ion), zero for $N = 16$ (T_d symmetry), −2 for $N = 32$ (I_h symmetry, the dual polyhedron of the C_{60} fullerene), −2 for $N = 37$ (D_{5h} symmetry) and −2 for $N = 42$ (I_h symmetry), as calculated by ab initio (3-21G level), PRDDO (partial retention of diatomic differential overlap), AM1 (semiempirical), and LDF (local density functional) methods. These methods are in agreement, although the AM1 results did not converge for $N = 37$. The most stable species per BH unit is $B_{12}H_{12}^{2-}$, and the next most stable is predicted to be $B_{42}H_{42}^{2-}$.

We present quantum chemical calculations relating to geometry, charge state, and stability of boron fullerenes which should prove to be of interest for attempts at synthesis of these molecules. A structure had been proposed long ago[1] for the aromatic molecule $B_{32}H_{32}$ of icosahedral symmetry, a geometrical dual of the Buckminsterfullerene molecule C_{60}. It has been pointed out[2] that the geometrical correspondence of dualism holds generally between boron and carbon fullerenes. The mapping of boron and carbon Fullerenes into one another may be carried out by means of the Descartes−Euler formula

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

where in a given polyhedral molecule, P is the number of vertices, C is the number of contacts, and F is the number of faces.

The dual of a given carbon fullerene may be established by setting a correspondence between each carbon polyhedral face (vertex) and a boron polyhedral vertex (face). Boron and carbon duals thus established will have the same number of atom−atom contacts, the same symmetry and the same sphericity. The mapping between boron and carbon fullerenes based on the Descartes−Euler formula may also be extended to multicage compounds.[3]

Quantum chemical calculations of the boron fullerenes have been reported earlier.[4] A very recent local density functional study[5] examined two analogs of C_{60}, viz., isoelectronic $B_{60}H_{60}$ and the geometrical dual $B_{32}H_{32}$, finding the latter to be more stable. The same order of stability holds for these two C_{60} analogs whether neutral or of charge −2.[6]

Table 1. Independent Bond Distances (Å) for Boron Fullerenes B_NH_N

$N = 1$	PRDDO	B−H	1.182			
	AM1		1.220			
$N = 12$	PRDDO	B−B	1.710			
	AM1		1.758			
	PRDDO	B−H	1.145			
	AM1		1.18			
$N = 16$	PRDDO	B−B	1.604	1.728	1.831	
	AM1		1.637	1.734	1.846	
	PRDDO	B−H	1.138	1.141		
	AM1		1.189	1.191		
$N = 32$	PRDDO	B−B	1.751	1.917		
	AM1		1.748	1.901		
	PRDDO	B−H	1.140			
	AM1		1.199	1.200		
$N = 37$	PRDDO	B−B	1.688	1.698	1.741	1.792
			1.828	1.916	1.986	
	PRDDO	B−H	1.130	1.134	1.137	1.138
$N = 42$	PRDDO	B−B	1.731	1.938		
	AM1		1.703	1.89		
	PRDDO	B−H	1.134	1.139		
	AM1		1.199	1.201		

In this paper we employ ab initio, PRDDO, AM1, and LDF methods to study the boron fullerenes B_NH_N ($N = 1$, 12, 16, 32, 37, 42). The different methods largely agree in their predictions of geometries, charge states and relative stabilities of the boron fullerene, thus mutually reinforcing their individual predictions of these properties.

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(6) We note that PRDDO predicts $B_{60}H_{60}$ to be a Jahn−Teller molecule in the neutral charge state (Derecskei-Kovacs, A.; Dunlap, B.; Lipscomb, W. N.; Lowrey, A.; Marynick, D. S.; Massa, L., Unpublished results).

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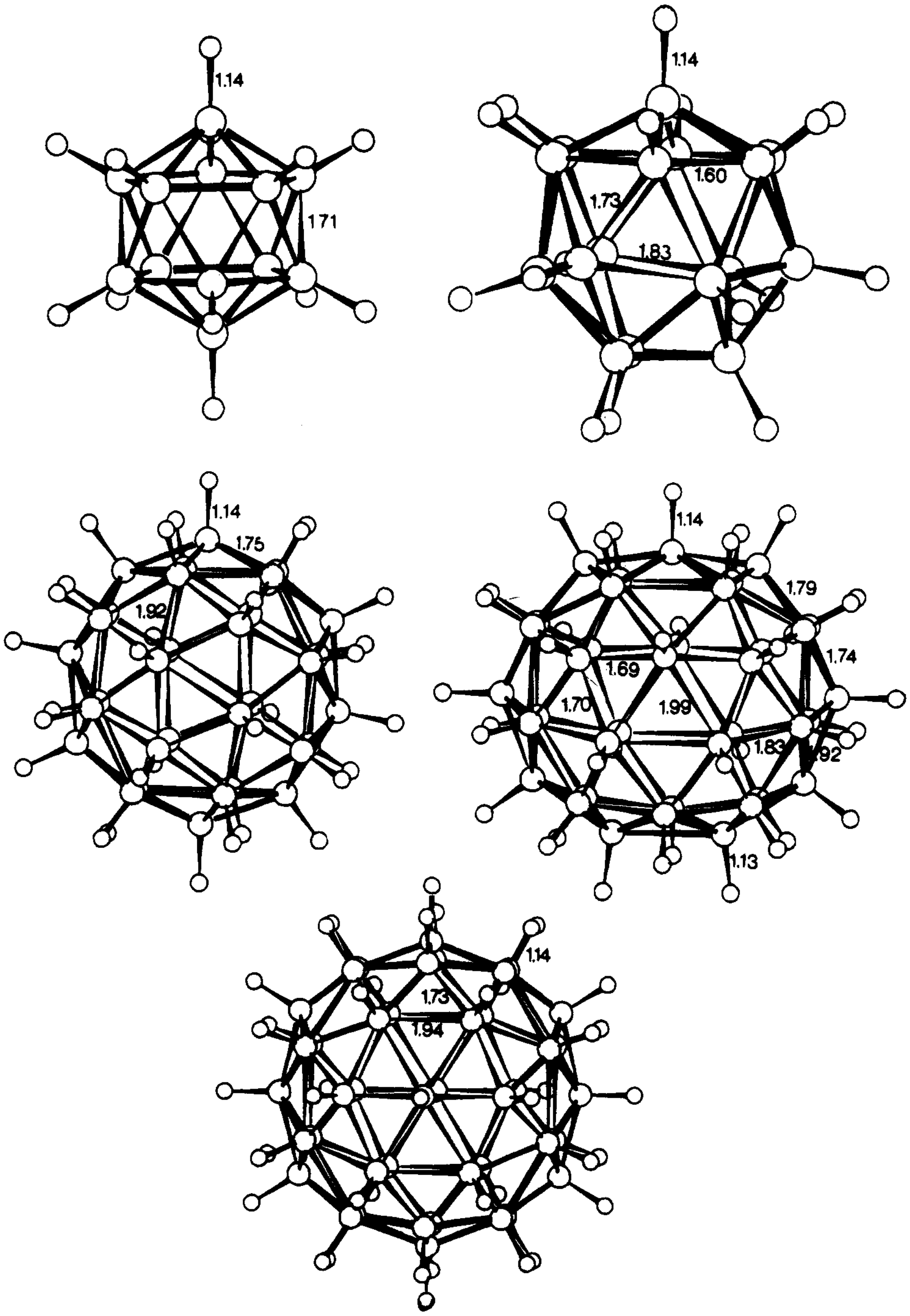

Figure 1. Geometry of the boron fullerenes. The bond lengths shown are in ångstroms and correspond to the PRDDO optimized geometries. The point groups are as follows: I_h for $B_{12}H_{12}$, $B_{32}H_{32}$, and $B_{42}H_{42}$, T_d for $B_{16}H_{16}$, and D_{5h} for $B_{37}H_{37}$.

The geometries were optimized using the approximate ab initio method of partial retention of diatomic differential overlap (PRDDO)[7] and the semiempirical AM1[8] method. Energies were then evaluated at the PRDDO optimal geometries by performing ab initio calculations with Gaussian 92[9] at the 3-21G basis set level, and local density functional (LDF) calculations using the Perdew–Zunger exchange and correlation functionals;[10] the Gaussian basis sets used were 11s/7p/1d contracted 5/3/1 for B and 6s/1p contracted 3/1 for H.

The geometries were constrained to have the generally assumed point group symmetries of the carbon fullerenes which are the geometrical duals of the boron fullerenes studied here.[2] The independent bond distances for each of the boron fullerene molecular structures are listed in Table 1. Pictures of the corresponding structures and their point group symmetries are

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Table 2. Charge States for the Boron Fullerenes[a]

B_NH_N molecule	$N = 12$	$N = 16$	$N = 32$	$N = 37$	$N = 42$
charge	−2	0	−2	−2	−2

[a] The same charge states are predicted by ab initio, PRDDO, LDF, and AM1 methods. (AM1 did not converge for the case $N = 37$.)

shown in Figure 1. In general, there is good agreement between the PRDDO and AM1 predictions of bond distances. The magnitudes listed in Table 1 are not very different from standard distances previously used for known closo boron hydrides.[1]

In Table 2, we indicate the preferred charge state for each of the molecules. The molecules shown have preferred charge state −2, except for $B_{16}H_{16}$ which is predicted to have a charge of zero. The four different computational methods all predict the same charge state in each case. Knowledge of the charge states is thought to be important for plans to synthesize these compounds. Thus, synthesis of the negatively charged boron fullerenes would presumably become stabilized in the presence of charge compensating positive ions.

In Table 3, the properties indicative of energetic stability are shown. For each molecule B_NH_N, we report, for each computational method, the quantities E/N, the total energy per BH unit and $\Delta\epsilon$, the HOMO−LUMO gap. We also report the magnitude of the relative total energy per B−H unit compared with that of $B_{12}H_{12}$, denoted $(E/N)_r$. The E/N quantities calculated by the AM1 method do not compare directly to values from the other methods because AM1 considers only valence electrons. The relative values $(E/N)_r$ give a direct comparison of trends predicted by all four methods.

We judge stability by examining E/N and $\Delta\epsilon$ for each of the molecules. All four methods agree that the molecules are stable relative to separated BH groups. $B_{12}H_{12}{}^{2-}$ known to be an extremely stable molecule, yields the largest stabilization per BH unit and the largest HOMO−LUMO gap. The most stable of the remaining −2 ions is $B_{42}H_{42}{}^{2-}$ according to both E/N and $\Delta\epsilon$ criteria in all four computational methods. Ab initio, PRDDO and LDF methods give a trend of increasing stability in the series $N = 32, 37, 42$, again judging by both the E/N and $\Delta\epsilon$ criteria. AM1 results are consistent with this trend, but the case of $N = 37$ is lacking because of AM1 convergence failure in that case.

Table 3. Stability Factors for the Boron Fullerences B_NH_N

N		ab initio 3-21G	PRDDO	LDF	AM1
1	E/N[a]	24.9759	25.0375	24.9727	2.9286
	$(E/N)_r$[b]	0.9941	0.9909	0.9910	0.9553
	$\Delta\epsilon$[c]	0.4087	0.4785	0.2690	0.4127
12	E/N	25.1247	25.2666	25.1995	3.0655
	$(E/N)_r$	1.0000	1.0000	1.0000	1.0000
	$\Delta\epsilon$	0.5889	0.7069	0.1969	0.3816
16	E/N	25.1126	25.2600	25.1839	3.0579
	$(E/N)^r$	0.9995	0.9997	0.9994	0.9975
	$\Delta\epsilon$	0.3688	0.3895	0.0858	0.2985
32	E/N	25.1000	25.2325	25.1866	3.0567
	$(E/N)_r$	0.9990	0.9989	0.9995	0.9971
	$\Delta\epsilon$	0.1324	0.1392	0.0251	0.1316
37	E/N	25.1091	25.2394	25.1871	no convergence
	$(E/N)_r$	0.9994	0.9989	0.9995	
	$\Delta\epsilon$	0.2549	0.2776	0.0573	
42	E/N	25.1114	25.2407	25.1896	3.0618
	$(E/N)_r$	0.9995	0.9990	0.9996	0.9988
	$\Delta\epsilon$	0.3813	0.4185	0.1403	0.2939

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

Thus, ab initio, PRDDO, LDF, and AM1 methods applied to the proposed boron fullerenes yield good qualitative agreement in predicting geometry, charge state, and stability. These quantities are thought to be useful for the possible synthesis of these molecules whose properties might prove to be interesting, as has occurred with carbon fullerenes.

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