

FSGO Calculations of Octahydrotriborate Anion and Tetraborane

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The FSGO quantum mechanical model is used to make *ab initio* calculations of the geometrical structures and energies of the ground state configurations of the octahydrotriborate anion, $B_3H_8^-$, and tetraborane, B_4H_{10} . Both molecules are assumed to belong to the C_{2v} symmetry point group during these computations. Comparisons with available experimental data show good agreement. B_4H_{10} calculations are also compared with results of SCF calculations.

Key words: Octahydrotriborate anion – Tetraborane – Floating spherical gaussian orbital (FSGO) model

1. Introduction

The Floating Spherical Gaussian Orbital (FSGO) Model of molecular structure, described in detail previously [1], makes *ab initio* predictions of the electronic and geometric structures of singlet ground states of molecules. The localized orbitals are constructed from single normalized spherical Gaussian functions:

$$G_j(\mathbf{r} - \mathbf{R}_j) = \left(\frac{2}{\pi q_j^2} \right)^{3/4} \exp[-(\mathbf{r} - \mathbf{R}_j)^2/q_j^2]$$

where \mathbf{R}_j is the position vector, and q_j is the radius of the j th orbital. The total electronic wave function is represented by a single Slater determinant. The total energy, including the nuclear repulsion, can be minimized by a direct search procedure with respect to all parameters, i.e., the orbital radii q_j , the orbital positions \mathbf{R}_j , and the nuclear positions. The parameters are usually varied cyclically, each to within a few tenths of a per cent. These calculations have parameter variations restricted to C_{2v} symmetry. Also the inner shell orbitals have been held centered on the B nuclei, a restriction that has been found to have no appreciable effect on the resulting molecular geometry.

This model has been successful especially with the compounds of the first-row atoms, and has also been extended to complex molecules by the molecular fragments technique of Christoffersen [2], and to crystals by Erickson and Linnett [3, 4].

The FSGO Model is advantageous because with absolute minimum basis sets (and thence less computer time), it enables one to make fairly reasonable *ab initio* predictions of bond lengths and bond angles.

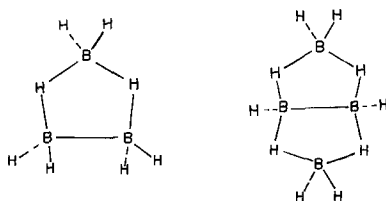


Fig. 1. Schematic diagrams of $B_3H_8^-$ (left) and B_4H_{10} (right)

In this paper we present the results for the full minimization of energy in the octahydrotriborate anion, $B_3H_8^-$, and tetraborane, B_4H_{10} . Schematic diagrams of these species are shown in Fig. 1.

2. Octahydrotriborate Anion, $B_3H_8^-$

This ion was unknown until 1956 when it was accidentally synthesized by Hough and co-workers [5, 6]. Its chemical and physical properties, and some alternative syntheses have been reported [5–8]. The B^{11} spectrum, a nonet, implies the equivalence of all three boron atoms, and that a rapid hydrogen exchange is taking place [7, 9]. Adams [10] shows how to deduce electron distributions and the numbers of bridge bonds from the total numbers of electrons and orbitals.

Many of the starting parameters for the energy minimization were taken from the X-ray study of $[(H_3N)_2BH_2^+][B_3H_8^-]$ [11]. Some were taken or deduced from an FSGO investigation of diborane by Frost [12]. C_{2v} symmetry and planar ring were assumed. Table 1 lists the geometrical results, together with available X-ray data. Other *ab initio* calculations on this ion have not been reported. Table 2 lists the nuclear and orbital coordinates, nuclear charges, and orbital radii. Table 3 contains one-electron energy levels and ionization potentials. Figure 2 is a diagram of the ion.

As can be seen from Table 1 and Fig. 2, the geometry is comparable to the X-ray data with a slight magnification of all the dimensions. This may be due to the fact that the ion is calculated in empty space rather than in a crystal.

Table 1. Geometrical results for $B_3H_8^-$

Bond lengths, Å		
Bond ^a	Calculated	Experiment ^b
B–B'	1.86	1.77
B'–B'	2.03	1.80
B–H _t	1.24	1.05–1.20 (estimate)
B–H _b	1.71	1.5
B'–H _b	1.37	1.2

^a B, apex boron; B', base boron; H_t, terminal H; H_b, bridge H.

^b X-ray diffraction, Ref. [11].

Table 2. Coordinates and parameters for unique nuclei and orbitals of $B_3H_8^-$ (a.u.)

Nuclei ^a	Coordinates ^b			
	x	y	z	
B	0.0	0.0	2.944	
B'	0.0	1.922	0.0	
H _b	0.0	3.156	2.276	
H _t	2.045	0.0	4.098	
H' _t	2.005	2.438	-1.108	
Orbitals ^a	Radii			
BIS	0.400	0.0	0.0	2.944
BIS'	0.400	0.0	1.922	0.0
BB	2.159	0.0	0.0	0.980
BH _t	1.855	1.503	0.0	3.792
BH' _t	1.880	1.473	2.301	-0.814
BHB _b	2.011	0.0	2.678	1.826

^a H_b is a bridge hydrogen: H_t terminal, BIS innershell orbital on B; BB bonding orbital between B nuclei; BH_t, BH bond terminal H; BHB_b three center bonding orbital.

^b z is the C₂ axis. x axis is perpendicular to the molecular plane. The coordinates of other nuclei and orbitals are obtained by reflections across the xz and yz planes.

Table 3. One-electron energy levels and total energy for $B_3H_8^-$

Level	Symmetry	Negative energy (a.u.)	Ionization potential (eV)
12	A ₁	0.0799	2.17
11	A ₂	0.1423	3.87
10	A ₁	0.1519	4.13
9	B ₁	0.1738	4.73
8	B ₂	0.1778	4.84
7	B ₁	0.2284	6.21
6	A ₁	0.3498	9.52
5	B ₂	0.3796	10.33
4	A ₁	0.5357	14.58
3	B ₂	5.8196	158.36
2	A ₁	5.8230	158.46
1	A ₁	5.8645	159.58
Total energy		- 66.2905 a.u.	

3. Tetraborane, B₄H₁₀

The NMR spectrum demonstrates that all boron atoms are not equivalent on the NMR time scale [13]. The two boron atoms that fuse the two rings are nonequivalent to the two apex borons. In the present calculations, most of the starting parameters were taken from the previously completed calculation on $B_3H_8^-$. Initially, both of the fused rings were assumed to remain planar, but to intersect at an angle. C_{2v} symmetry was assumed throughout the computations.

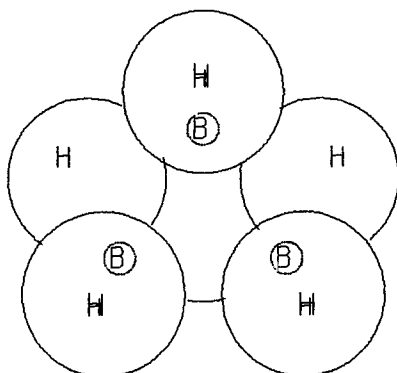


Fig. 2. Geometric and electronic structure of $B_3H_8^-$. Orientation is analogous to that in Fig. 1 (projection on the yz plane). Circles are drawn for each doubly-occupied FSGO with radius equal to its orbital parameter ρ . Atom symbols indicate calculated positions for energy minimum. Size of symbols relate to distance above or below plane of diagram

Table 4. Geometrical results for B_4H_{10}

Bond Lengths, Å		Experimental	
Bond ^a	This calculation	Elec. diff. ^b	X-ray diff. ^c
B-B'	1.93	1.85	1.845
B'-B'	2.31	1.76	1.750
B-B	2.45	2.88	2.786
B-H _t	1.24	1.19	1.11
B-H' _t	1.30	1.19	1.11
B'-H' _t	1.27	1.19	1.11
B-H _b	1.78	1.33	1.37
B'H _b	1.34	1.43	1.21
Dihedral angle between BB'B' planes			
	104.4°	124.5°	118.1°

^a B, apex boron; B', base boron; H_t, terminal H; H_b, bridge H.

^b Ref. [14].

^c Ref. [15].

Table 4 lists the geometrical results together with available electron diffraction [14] and X-ray [15] data. Comparison is also made with an SCF calculation [16]. The total energy and dipole moment are also indicated. Table 5 lists the nuclear and orbital coordinates and orbital radii. Table 6 presents the one-electron energy levels and ionization potentials along with the SCF [16] and experimental [17] values. Figure 3 is a diagram of the molecule.

As can be seen from these tables and diagrams, the geometry is comparable with experimental geometries. In the final results, the two fused rings are no longer planar. Also, the regular boron-hydrogen bond distances are seen to be slightly different for each of three types of such bonds distinguishable through

Table 5. Coordinates and parameters for unique nuclei and orbitals of B_4H_{10} (a.u.)

Nuclei ^a		Coordinates ^b			
		x	y	z	
1	H _t	1.572	0.0	-2.324	
3	H _r	0.0	3.696	3.692	
5	H _t	0.0	2.723	-0.633	
1	H _b	3.261	2.058	1.029	
1	B	2.186	0.0	0.0	
3	B	0.0	2.313	1.792	
Orbitals ^a		Radii			
1	BH _t	1.986	1.752	0.0	-1.569
3	BH _r	1.867	0.0	3.224	3.080
5	BH _t	2.009	0.0	2.439	0.151
1	BHB _b	1.989	2.778	1.536	0.834
1	BIS	0.400	2.186	0.0	0.0
3	BIS	0.400	0.0	2.313	1.792
1	BB	2.493	0.0	0.0	0.997

^a Notation of nuclei as in Ref. [16]. Orbital notation as in Table 2.

^b z is the C_2 axis. y axis lengthwise of molecule. Other coordinates obtained by reflections across xz and yz planes.

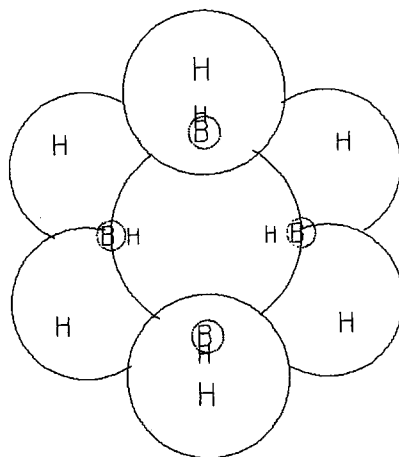


Fig. 3. Geometric and electronic structure of B_4H_{10} . See Fig. 2 for explanation (projection on the xy plane)

symmetry considerations. Finally, the slight delocalization of the boron–boron single bond (similar to the one seen in $B_3H_8^-$), pointed out by Libscomb [18], is also seen by the fact that the center of this orbital is not at the midpoint of the line joining these two borons (i.e., at the origin), but instead, at a nonzero z-coordinate position. The total energy is seen to be 84.4% of the SCF total energy, similar to the usual FSGO/SCF total energy ratios.

Table 6. One-electron energy levels and total energy for B_4H_{10}

Level	This calculation		SCF calculation ^a	
	Symmetry	$-\varepsilon$ (a.u.)	Symmetry	$-\varepsilon$ (a.u.)
15	B_2	0.2481	A_1	0.4312
14	A_1	0.2981	B_2	0.4544
13	B_1	0.3398	B_1	0.4898
12	A_1	0.3757	A_1	0.5033
11	A_2	0.4363	B_2	0.5141
10	A_1	0.4408	A_1	0.5534
9	B_2	0.4774	A_2	0.5579
8	A_1	0.5616	A_1	0.6291
7	B_1	0.6159	B_1	0.7441
6	B_2	0.6654	B_2	0.7727
5	A_1	0.8337	A_1	0.9455
4	A_1	6.0672	B_1	7.5976
3	B_1	6.0676	A_1	7.5979
2	B_2	6.1193	A_1	7.6174
1	A_1	6.1234	B_2	7.6174
Total energy		-87.9591 a.u.		-104.2559 a.u.
Dipole moment		1.44 D		1.00 D
		(Experimental ^b 0.56 ± 0.10 D)		
Experimental ionization potential		10.39 eV ^c		

^a Ref. [16]. - ^b Ref. [19]. - ^c Ref. [17].

4. Conclusions

The geometries of $B_3H_8^-$ and B_4H_{10} as obtained by this FSGO model are reasonable in terms of available experimental information and previous theoretical ideas. The use of a localized pair of electrons in forming each three-center BHB bridge is in agreement with that previously obtained in B_2H_6 [12] by the FSGO model.

The $B_3H_8^-$ structure compares with the ion in the solid state. The proposed pseudorotation [9] for the ion in solution can probably not be treated by the simple FSGO model.

These calculations illustrate once again how molecular geometries can be obtained economically with a greatly simplified *ab initio* model. Most SCF calculations on the other hand usually obtain wavefunctions and energies only for the experimental geometry.

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