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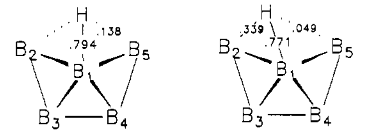
Theoretical Refinement of the B_5H_{11} Structure. Application of IGLO Chemical Shift Calculations†

Although the general structural features of B_5H_{11} have been established by a number of experimental[1,2] and theoretical investigations,[3,4] the accurate molecular geometry remains unsolved. The situation is well summarized by Beaudet in a recent review.[5] The main problem is "the ambiguity about the location of the apical hydrogen (H_b in **1**). The question of whether this hydrogen exists as a terminal endo hydrogen at the apex, as a tautomerizing bridge hydrogen between the apical hydrogen and the two approximate basal borons (**1b**), or finally as a four-centered bridge hydrogen (**1a**) (see Figure 1) has been of enough interest to warrant numerous theoretical and X-ray diffraction publications over the years, but the problem still eludes solution". Beaudet's critically evaluated structure, based on Lipscomb's early X-ray studies,[1] was provided conveniently in an cartesian coordinate format to encourage further investigation (see Table I). Beaudet concluded that "the resolution of this quandary can come only from a gas phase structure determination". Greatrex, Greenwood, Rankin, and Robertson's more recent gas-phase electron diffraction (GED) study[2] did indeed locate the unique hydrogen (although not "with high precision") and established an asymmetric structure (as in **1a**). However, the "rest of the molecule" was constrained to have C_s symmetry in the refinement. We show here that this assumption is not justified and that there are surprisingly large differences in the lengths of "equivalent" bonds.

Theoretical calculations are capable of providing a definitive answer to this problem. Indeed, both the structure tabulated by Beaudet[5] and the newer GED geometry[2] are unsatisfactory energetically, as they are calculated to be 130 and 20 kcal/mol, respectively, less stable than the minimum located in the present work (Table II). We also have employed another criterion to judge the quality of the different geometries: comparisons of experimental boron chemical shifts for B_5H_{11}[6] with those calculated ab initio by the IGLO (individual gauge for localized molecular orbitals) method[7] (Table II). This approach is particularly effective when the calculated chemical shifts are sensitive to geometrical changes.[8]



1a **1b**

Figure 1. Structural alternatives for B_5H_{11} (schematic, top views from the apical boron; other hydrogens omitted for clarity). The NLMO/NPA bond orders[11] at the HF/6-31G* level are included.

McKee's recent theoretical investigation[4] refined his earlier ab initio study with Lipscomb.[3] McKee showed the symmetrically bridged form **1a** to be a transition state at the HF/3-21G level, whereas the unsymmetrical form **1b** is slightly more stable. However, the 3-21G basis set is too small to give accurate structural parameters. There are significant deviations (e.g. nearly 0.1 Å in B_3–B_4) between the 3–21G and the electron diffraction data.[2] In addition, our IGLO chemical shift evaluations show the 3-21G (**1b**) structure (Table I) not to give good agreement with the experimental $\delta(^{11}B)$ $B_{2,5}$ values.[6a] Polarized basis sets are known to be necessary when multicenter bonding is involved.[8,9] Hence, we reoptimized both **1a** and **1b** at the 6-31G* level. This structural refinement at 6-31G*//6-31G* influences the geometry but does not change the relative energies of the C_1 vs the C_s form nor even lower the absolute energies over those at 6-31G*//3-21G[4] appreciably. However, the agreement between the IGLO and experimental chemical shifts (particularly for $B_{2,5}$ in the C_1 form) is improved significantly with the 6-31G* geometries (Table II). Because electron correlation is known to favor bridging and multicenter bonding arrangements,[8,9] **1a** and **1b** were further optimized at the correlated MP2/6-31G* level (Table I). These are our most refined B_5H_{11} structures. Indeed, **1b** gives IGLO results that agree best with experiment (Table II). In contrast, the rather large deviation encountered for the apical boron B_1 in

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† Dedicated to W. N. Lipscomb on the occasion of his 70th birthday.

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Table I. Theoretical and Experimental Geometric Parameters for B_5H_{11} (Å)

	C_s			C_1					experiment	
param[a]	3-21G[b]	6-31G*	MP2/6-31G*	3-21G[b]	6-31G*		MP2/6-31G*		X-ray[c]	GED[d]
B_1B_2				1.893	1.896		1.855			
	>1.934	1.917	1.859			>1.917		>1.869	1.870	1.891
B_1B_5				1.952	1.939		1.883			
B_1B_3				1.795	1.761		1.737			
	>1.774	1.770	1.728			>1.760		>1.731	1.720	1.741
B_1B_4				1.772	1.758		1.724			
B_2B_3				1.835	1.856		1.810			
	G1.779	1.777	1.770			>1.803		>1.774	1.760	1.812
B_4B_5				1.762	1.750		1.737			
B_3B_4	1.870	1.860	1.785	1.852	1.830		1.778		1.770	1.760
B_1H_b	1.215	1.211	1.230	1.229	1.235		1.245		1.090	1.327[e]
B_2H_b	1.872	1.828	1.704	1.549	1.459		1.437		1.670	1.594
B_5H_b	1.872	1.828	1.704	1.993	2.134		2.043		1.670	1.898
B_2H_{23}				1.477	1.443		1.398			
	>1.446	1.435	1.395			>1.432		>1.389	1.300	1.394
B_5H_{45}				1.472	1.410		1.380			
B_3H_{23}				1.236	1.243		1.262			
	>1.244	1.250	1.268			>1.255		>1.272	1.220	1.274
B_4H_{45}				1.254	1.266		1.281			
B_3H_{34}				1.323	1.318		1.317			
	>1.330	1.335	1.335			>1.335		>1.336	1.180	1.335
B_4H_{34}				1.336	1.351		1.354			

[a] For numbering, see Figure 1a. [b] Reference 4; our values are identical. [c] Composite values recommended in ref 1. [d] Reference 2. [e] Fixed.

Table II. IGLO Results[a] for B_5H_{11}

	$\delta(^{11}B)$[b]			
geometry	B_1	$B_{2,5}$	$B_{3,4}$	rel energy[a,c]
exptl (X-ray),[d] C_s	-79.7	5.7	-5.0	134
exptl (GED),[e] C_1	-58.1	11.1[f]	-3.1[f]	22
1a, C_s 3-21G	-55.2	23.7	-2.1	0.3
1a, C_s 6-31G*	-57.8 [-56.1]	20.4 [22.0]	-1.7 [-0.9]	0.5
1a, MP2/6-31G*	-63.6 [-61.3]	11.6 [15.2]	-2.0 [0.3]	3.5
1b, C_1 3-21G	-51.6	18.8[f]	-3.7[f]	0.0
1b, C_1 6-31G*	-51.6 [-49.8]	12.8[f] [13.8]	-3.4[f] [-2.7]	0.0
1b, MP2/6-31G*	-55.8 [-53.9]	7.1[f] [8.0]	-2.6[f] [-1.6]	2.1
exptl chem shifts[g]	-55.3	7.4[f]	0.5[f]	

[a] Basis DZ; cf. ref 7. The IGLO values in square brackets were obtained by using a larger basis set, designated II′. [b] ppm relative to $BF_3{\cdot}OEt_2$; B_2H_6 was used as the primary reference with subsequent conversion to the $BF_3{\cdot}OEt_2$ scale by using the experimental value $\delta(B_2H_6) = 16.6$. For a detailed discussion, see ref 10. [c] The DZ basis set used for these comparisons is similar to 3-21G. More refined relative enegies for **1a** and **1b** are given in Table III. [d] Reference 5. [e] Reference 2. [f] Average values. [g] Reference 6a.

Table III. Total and Relative Energies of B_5H_{11}

	tot. energies, au		rel energies, kcal/mol	
level of theory	**1a**	**1b**	**1a**	**1b**
3-21G//3-21G[a]	-128.949 38	-128.949 60	0.1	0.0
6-31G*//6-31G*	-129.709 46	-129.710 82	0.9	0.0
MP2(FC)/6-31G*// MP2(FU)/6-31G*	-130.186 52	-130.188 04	1.0	0.0
MP2/6-31G*//3-21G[a]	-130.181 22	-130.183 78	1.6	0.0
MP2/6-31G*//6-31G*	-130.183 15	-130.185 67	1.6	0.0
MP3/6-31G*//6-31G*	-130.234 05	-130.236 63	1.6	0.0
MP4SDTQ/6-31G*// 6-31G*	-130.262 31	-130.264 81	1.6	0.0
ZPE/3-21G[a,b]	80.89 (1)	81.38 (0)		
ZPE/6-31G*[b]	81.42 (1)	82.35 (0)		
final estimate[c]			0.8	0.0

[a] Reference 4. [b] Zero-Point energies in kcal/mol. In parentheses: number of imaginary frequencies (1 and 0 denote transition states and minima, respectively). [c] MP4sdtq/6-31G*//6-31G* values corrected by the 6-31G* ZPE's, scaled by 0.89 recommended in ref 9.

Beaudet's tabulated structure (25 ppm) is noteworthy. The δ values for $B_{2,5}$ of the theoretical symmetrical structures **1a** also differ significantly from experiment (13–16 ppm). However, the GED structure[2] gives reasonably good IGLO $\delta(^{11}B)$ results (Table II), even though its imperfections are apparent on other grounds.

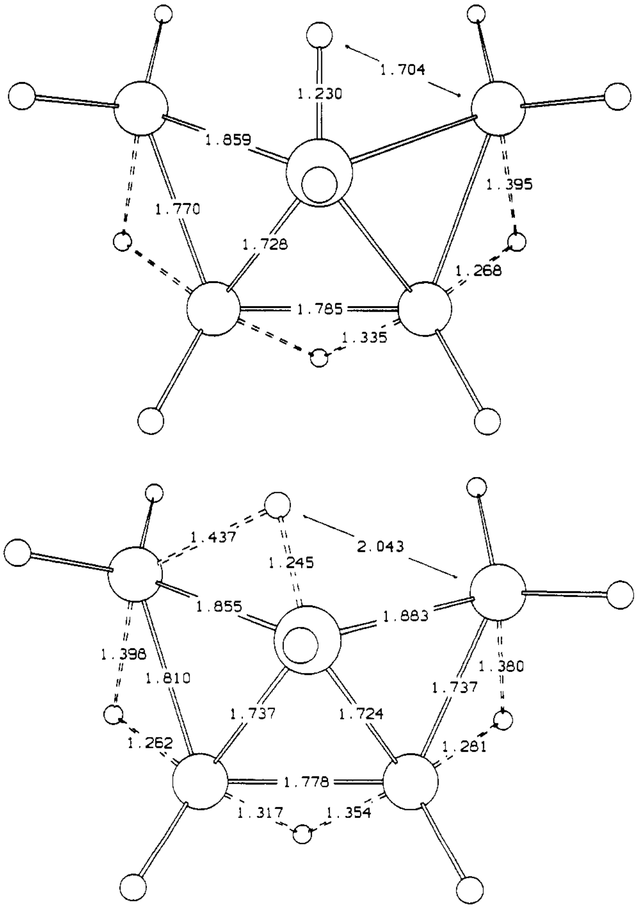

Figure 2. B_5H_{11}, C_s (top) and C_1 (bottom) forms, MP2/6-31G* optimized (top views from the apical boron).

The calculated energy differences between **1a** and **1b** are very small at 3-21G but were already found by McKee and Lipscomb[3,4] to be somewhat more pronounced at higher levels of theory, especially when electron correlation is included (cf. Table III). Although our calculations have been carried out at higher levels, our conclusions are similar. With correction for zero-point energies (ZPE), we find unsymmetrical **1b** to be ca. 1 kcal/mol more stable than symmetrical **1a** (which is a transition state also at the 6-31G* level). Since the effect of electron correlation is rather independent of the level employed (MP2, MP3, or MP4), this value—which agrees with McKee's results[4]—should be reliable. Since this barrier is very low, the C_1 forms interconvert rapidly and the NMR spectra reveal only C_s symmetry.[6] Despite the minor energetic changes during this interconversion, a substantial internal reorganization is involved. Not only the H_b distances but also those involving B_2 and B_5 differ appreciably in the transition state (**1a**) C_s from those in C_1 energy minimum (**1b**) (cf. Figure 2).

It seems conclusive: B_5H_{11} prefers an unsymmetrical structure of C_1 symmetry. The apical hydrogen H_b is involved in a "normal" three-center B–H–B bond (see Figure 2) rather than bridging three borons. A factor contributing to this structural preference is indicated by natural population analysis[11] (see Figure 1): In **1a**, the bond order between H_b and the basal borons B_2 and B_5 is significant but rather small (0.14). The stronger interaction of H_b with B_2 in **1b** (bond order 0.34) more than compensates for the reduced overlap to B_5.

IGLO calculations have been applied with great success to help solve carbocation structural problems.[8] This first application to boron compounds underscores the promise of this new approach for similar purposes.

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Thermal Control of Photoreactivity: Room-Temperature Photosubstitution vs 150 K Electron Transfer in $[(dmb)_2Ru(3\text{-}Br\text{-}py)_2](PF_6)_2$

An interesting feature of the photochemistry of ruthenium(II) diimine complexes is the observation of photosubstitution from ^{3}LF states[1–5] and photoredox reactivity from ^{3}MLCT states.[1,6–10]

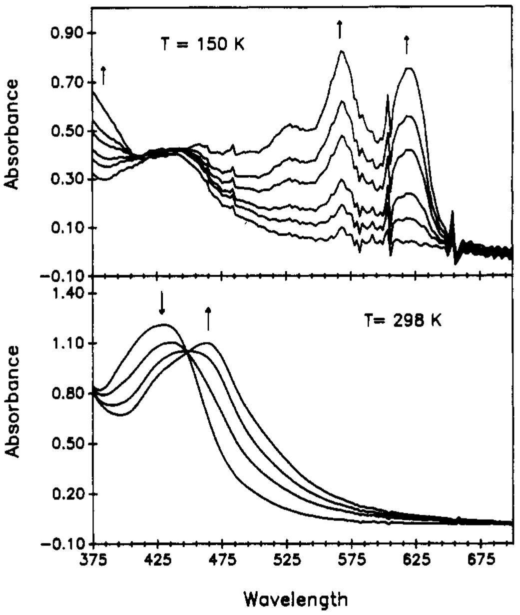
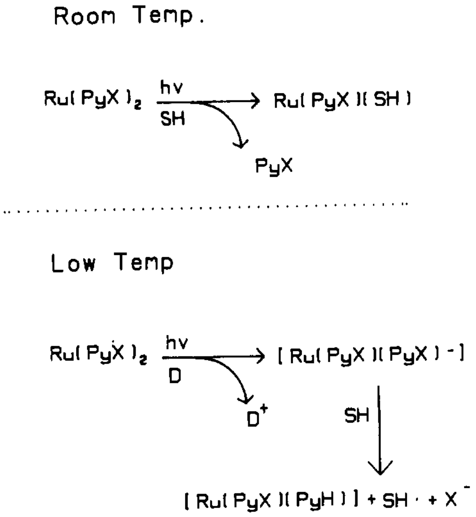


Figure 1. Photolysis of mixtures of $[(dmb)_2Ru(3\text{-}Br\text{-}py)_2](PF_6)_2$ and TMPD (0.05 M) in 4:1 ethanol–methanol at 150 K and 298 K using $\lambda > 450$ nm light from a Xe 150-W arc lamp (PTI). Spectra were taken at 30-s intervals.

Scheme I



For $[Ru(bpy)_3](PF_6)_2$ in room-temperature acetonitrile solutions, both photoredox reactions and, to a much smaller degree, pho-

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