the LMCT band increases as $E_{1/2}$ for the complex increases. The values of $10^2 f$ for the trans-pyridine and trans-isonicotinamide species are 7.4 and 8.3, respectively. Increasing the strength of the π acid will have two effects: (a) it will tend to contract the πd orbitals and therefore decrease overlap with those of the ligand by withdrawing charge from the metal center and (b) it will decrease the energy gap between the πd and π orbitals. These factors will exert opposing effects on the oscillator strength. In our system, that of factor b is clearly dominant.

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Registry No. $[(Ru(NH_3)_5)_2HN(CN)_2](PF_6)_4$, 81572-55-6; $[($*trans*-$Ru(NH_3)_4py)_2N(CN)_2](ClO_4)_5$, 81572-57-8; $[($*trans*-$Ru(NH_3)_4isn)_2N(CN)_2](ClO_4)_5$, 81572-59-0; *trans*-$[Ru(NH_3)_4(SO_4)py]Cl$, 80584-24-3; *trans*-$[Ru(NH_3)_4(SO_4)isn]Cl$, 81572-23-8; $[Ru(NH_3)_5N(CN)_2](PF_6)_2$, 81572-25-0; *trans*-$[Ru(NH_3)_4(SO_2)Cl]Cl$, 23346-07-8; $[Ru(NH_3)_5H_2O](CF_3SO_3)_3$, 53195-18-9; $[(Ru(NH_3)_5)_2N(CN)_2]^{5+}$, 81572-26-1; $[($*trans*-$Ru(NH_3)_4py)_2N(CN)_2]^{3+}$, 81572-27-2; $[($*trans*-$Ru(NH_3)_4py)_2N(CN)_2]^{4+}$, 81642-83-3; $[($*trans*-$Ru(NH_3)_4isn)_2N(CN)_2]^{3+}$, 81572-52-3; $[($*trans*-$Ru(NH_3)_4isn)_2N(CN)_2]^{4+}$, 81642-84-4.

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Ab Initio Study[1] of the Transient Boron Hydrides B_3H_7, B_3H_9, B_4H_8, and B_4H_{12} and the Fluxional Anion $B_3H_8^-$

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The most stable structures of B_3H_7, B_3H_9, B_4H_8, B_4H_{12}, and $B_3H_8^-$ are predicted by geometry optimization at the 3-21G basis level with the GAUSSIAN 80 program. At each minimum for a given symmetry, the 6-31G level is extended by polarization on boron (6-31G*) and by correlation at the MP3/6-31G level. Additivity of these two corrections to the 6-31G energy gives the total energy. The most stable structures are C_s2102 for B_3H_7, D_{3h}3003 for B_3H_9, $C_1$3111 for B_4H_8, D_{4h}4004 for B_4H_{12}, and C_{2v}2102 for $B_3H_8^-$. For B_3H_7, C_{2v}1103ST is only 4 kcal/mol less stable; for B_4H_8, C_s2112 and C_{2v}4200 are less stable by 4 and 6 kcal/mol, respectively; and for $B_3H_8^-$, C_s1104 is less stable by only 1 kcal/mol.

Introduction

Optimization procedures for locating stationary points on the potential energy surfaces of molecules have advanced considerably in recent years. In addition, the improvements in quality of wavefunctions have included corrections for polarization (e.g., d orbitals on first-row atoms) and for correlation (configuration interaction).[3-5]

These corrections are particularly important in those boranes where alternative structures exist in which a terminal hydrogen can become a bridge hydrogen. Electron correlation can more readily be accommodated by the bridge hydrogen because the two electrons of this three-center bond can, with high probability, avoid one another more easily than they can in a two-center terminal bond. More generally, the varieties of bonding situations in the boranes provide further opportunity for effects of both polarization and correlation.

Because of these advances, we felt it would be worthwhile to restudy the structures of the transient hydrides B_3H_7, B_3H_9, B_4H_8, and B_4H_{12}, as well as the fluxional behavior in $B_3H_8^-$. In the earlier investigation,[6] the choice of most stable structure was thought to be sensitive to the completeness of polarization and correlation corrections for B_3H_7. We find here that this is indeed the case. In addition, we felt that the removal of some symmetry constraints in the early study might lead to the prediction of a more stable structure for B_4H_8. This, also, is demonstrated below.

Table I. Relative Energies (kcal/mol) at 6-31G, Increments to 6-31G* and MP3/6-31G, and Estimated MP3/6-31G* Relative Energies

species	fig	*styx*[a]	6-31G	increment 6-31G*	increment MP3/ 6-31G	est MP3/ 6-31G*
B_3H_7	1a	C_{2v}1103ST[b]	−5.4	3.9	5.9	4.4
	1b	C_{2v}1103EC	8.2	2.9	4.5	15.6
	1c	C_s1103EC	7.3	2.5	3.4	13.2
	1d	C_s2012	−5.3	3.5	9.2	7.4
	1e	C_s2102	0	0	0	0
B_4H_8	3a	C_{2v}4020	10.1	−1.2	−3.2	5.7
	3b	C_{2v}0204ST	−1.1	8.6	14.8	22.3
	3c	C_s1113	−12.8	9.6	16.2	13.0
	3d	C_s2112	−7.0	4.8	6.4	4.2
	3e	$C_1$3111	0	0	0	0
$B_3H_8^-$	4a	C_s1104	−1.2	0.5	1.5	0.8
	4b	C_{2v}2013	0	0	0	0
B_2H_6[c]		D_{2h}2002	−13.7	−6.6	−15.2	−35.5
B_3H_9[c]	5	D_{3h}3003	−0.4	−5.1	−25.9	−31.4
B_4H_{12}[c]	6	D_{4h}4004	6.1	0.9	−28.0	−21.0

[a] The symmetry is given first and then the numbers are *s* for bridge hydrogens, *t* for three-center BBB bonds, *y* for single bonds, and *x* for each additional terminal H on a BH unit. [b] ST and EC refer to staggered or eclipsed orientations of BH_2 relative to the remainder of the molecule. See ref 6. [c] Energies are relative to separated BH_3 units.

Methods

For each substance, the few or several structures were geometry optimized, with or without symmetry constraints as indicated below. The GAUSSIAN 80 program[7] was used in the 3-21G basis[8] in order to provide efficient calculation of ana-

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(1) For convenience, the abbreviations in this paper are collected here: 6-31G, 6 Gaussians to inner shell, 3 Gaussians plus one with different exponent for valence shell; DZ, double-ζ calculation equivalent to 6-31G; 6-31G* adds polarization (d orbitals) to nonhydrogen atoms; PRDDO, partial retention of diatomic differential overlap; ST, staggered; EC, eclipsed.

(2) To whom correspondence should be addressed.

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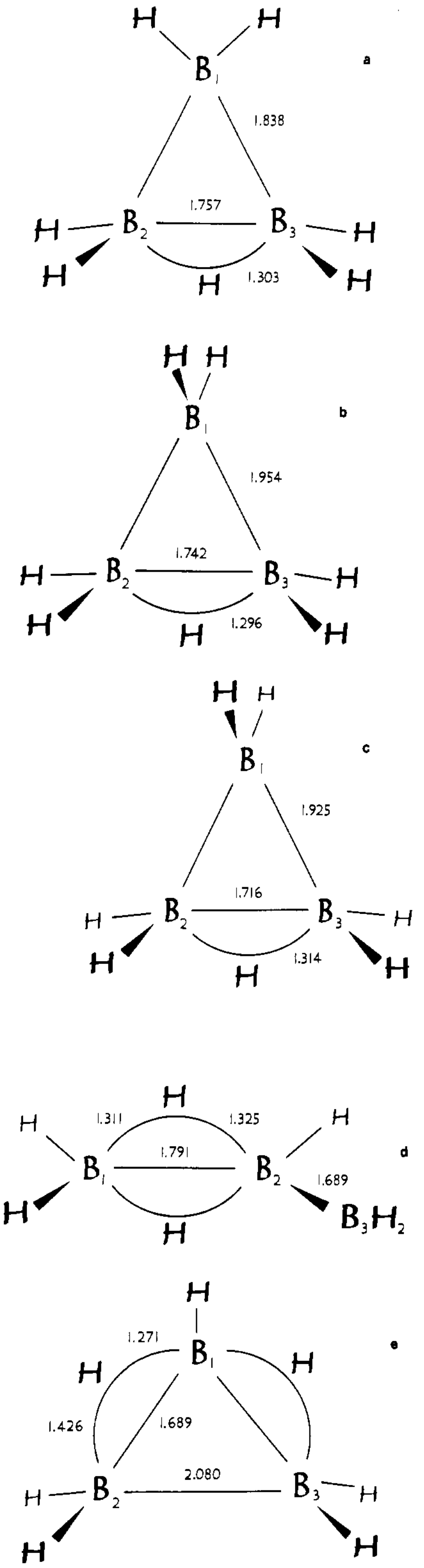

Figure 1. B_3H_7: (a) 1103ST, C_{2v}, (b) 1103EC, C_{2v}, (c) 1103EC, C_s, (d) 2011, C_s, and (e) 2102, C_s.

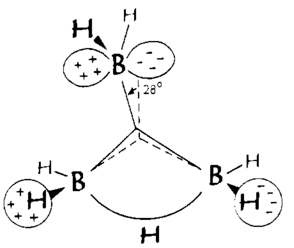

Figure 2. C_s structure of 1103EC "*styx*" notation. The BH_2 group is rotated out of the BH_bB plane to increase hyperconjugation with the terminal hydrogen on each boron.

Table II. Comparison (Å) of the X-ray Structure of B_3H_7L with the Theoretical 1103ST Structure of B_3H_7

	X-ray		theor	
bond[a]	L = NH_3[b]	L = CO[c]	3-21G	PRDDO[d]
B_1B_2 or B_1B_3	1.81[e]	1.83[e]	1.838	1.816
B_2B_3	1.74	1.73	1.757	1.727
B_2H_b or B_3H_b	1.31[e]	1.27[e]	1.303	1.321
B_3H	1.75[f]	1.90[f]	2.250	

[a] Figure 1a. [b] Reference 13. [c] Reference 14. [d] Reference 12. [e] Average of two bond lengths in adduct. [f] The adduct shows a "near bridging" interaction between a terminal hydrogen on the apex B_1 and a basal boron B_3.

lytical derivatives with respect to coordinate displacements. When the geometry of minimum energy is found, a 6-31G basis is extended to 6-31G* (polarization on nonhydrogen atoms) and to the MP3/6-31G level (Møller–Plesset correlation corrections[9] to third order[10] for all valence electrons). We have previously found that the addition of these polarization and correlation energy corrections is a good approximation to the effect of including both in a single calculation in somewhat smaller molecules.[11] Here, the inclusion of both would be prohibitively expensive.

Results and Discussion

Optimized geometries of B_3H_7, B_4H_8, $B_3H_8^-$, B_3H_9, and B_4H_{12} are shown in Figures 1–7. The Cartesian coordinates of these structures have been deposited as supplementary material. The relative energies of each species are given in Table I, where the MP3/6-31G* estimate has been obtained by adding the increments due to polarization (addition of d orbitals to B, 6-31G* minus 6-31G) and due to electron correlation (Møller–Plesset third-order corrections minus the 6-31G level). Except for energies of B_2H_6, B_3H_9, and B_4H_{12}, which are relative to $2BH_3$, $3BH_3$, and $4BH_3$, respectively, the energies are all relative to the energy of the most stable isomer. We now discuss each species in turn.

B_3H_7. The structures of the NH_3[12] and CO[13] adducts of B_3H_7 show only one bridge hydrogen. When the ligand is removed, the B_3H_7 unit has a vacant orbital which can be filled, with some strain, by conversion of a terminal hydrogen of the 1103ST structure (Figure 1a) to the 2102 structure (Figure 1e). Both polarization and correlation corrections are required to exhibit the relative stability of the 2102 structure (Table I). The marginal stability of 2102 over the 1103ST structure by only 4.4 kcal/mol suggests that B_3H_7 is probably fluxional. Thus there is a near balance between stabilization due to additional bonding and strain as the terminal BH is converted to a bridge hydrogen.

The next most stable structure for B_3H_7 is the 2012 B_2H_5–BH_2 isomer (Figure 1d), which is analogous to the metastable bis(diborane) structure of B_4H_{10}.[4] Further study is required to see if this isomer of B_3H_7 is of importance in its formation or reactions.

The theoretical 1103ST structure at the 3-21G level and the PRDDO level[14] is compared with the X-ray results for two

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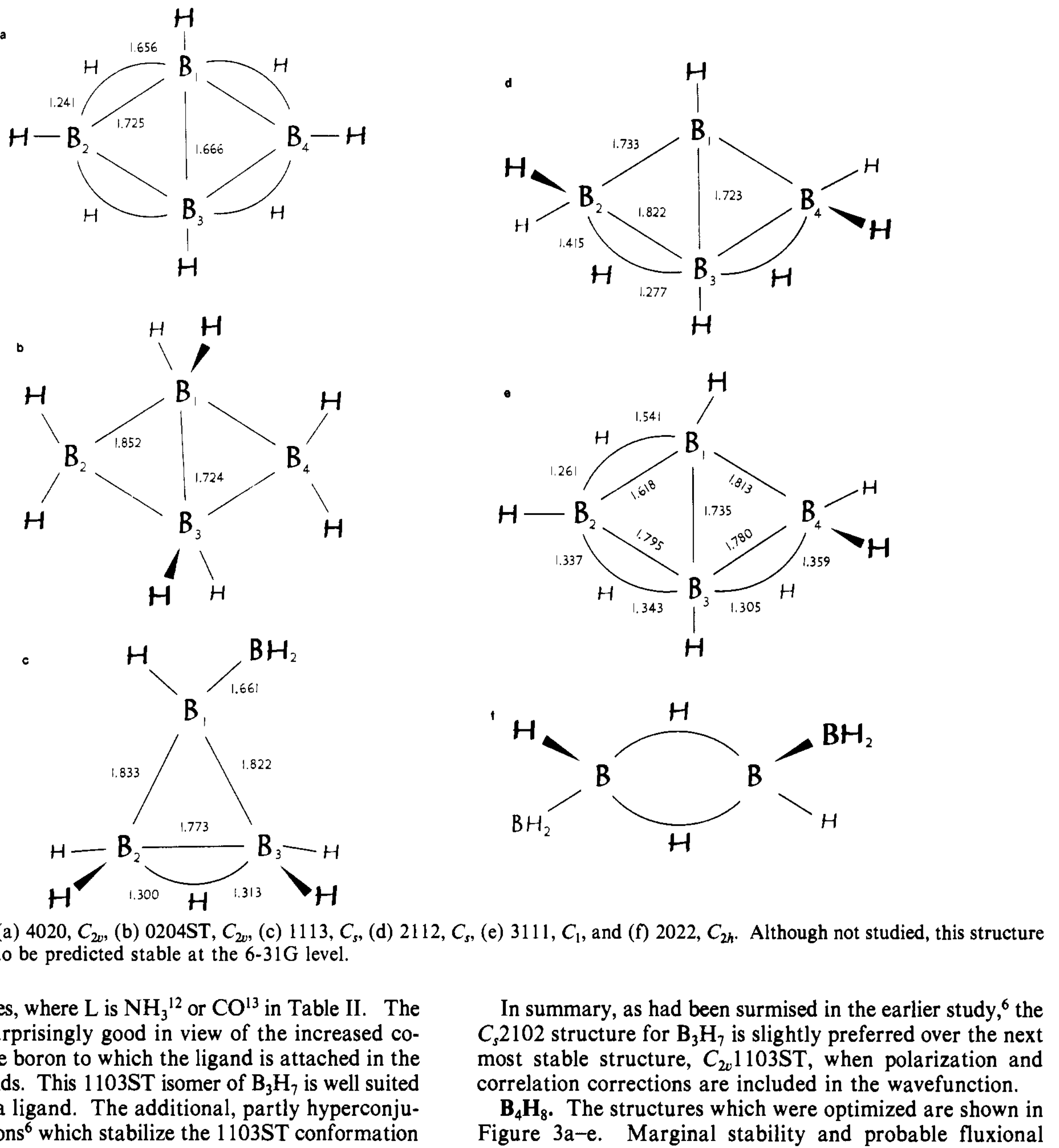

Figure 3. B_4H_8: (a) 4020, C_{2v}, (b) 0204ST, C_{2v}, (c) 1113, C_s, (d) 2112, C_s, (e) 3111, C_1, and (f) 2022, C_{2h}. Although not studied, this structure (v = 2) is likely to be predicted stable at the 6-31G level.

B_3H_7L derivatives, where L is NH_3[12] or CO[13] in Table II. The agreement is surprisingly good in view of the increased coordination of the boron to which the ligand is attached in the B_3H_7L compounds. This 1103ST isomer of B_3H_7 is well suited for addition of a ligand. The additional, partly hyperconjugative, interactions[6] which stabilize the 1103ST conformation of B_3H_7 relative to the 1103EC conformation (Figure 1b) are preserved when polarization and correlation corrections are made[15] (Table I). As the 1103EC isomer is formed from the 1103ST isomer, the apical–basal BB distance increases from 1.838 to 1.954 Å, while the basal–basal BB distance decreases slightly from 1.757 to 1.742 Å. If the symmetry restriction of C_{2v} is lowered to C_s for the 1103EC form, the structure optimizes upon rotation of the apical BH_2 group out of the plane by about 28° (Figure 2). This rotation increases hyperconjugation of the vacant orbital with terminal hydrogens on the other boron atoms, although little additional stability is gained (Table I: 1b and 1c). An attempt to optimize a linear BBB structure of 4002 topology yielded an energy less stable than the triangular 2102 form by 80 kcal/mol.

In summary, as had been surmised in the earlier study,[6] the C_s2102 structure for B_3H_7 is slightly preferred over the next most stable structure, C_{2v}1103ST, when polarization and correlation corrections are included in the wavefunction.

B_4H_8. The structures which were optimized are shown in Figure 3a–e. Marginal stability and probable fluxional character are indicated (Table I) for the three-bridged $C_1$3111 structure, as compared with the two-bridged C_s2112 isomer (4.2 kcal/mol less stable) and the four bridged C_{2v}4020 isomer (5.7 kcal/mol less stable). These conclusions are different from those that would be reached at the 6-31G level without polarization and correlation corrections (Table I). It is still not clear whether further improvements in the wavefunction will eventually favor the four-bridged structure.

Vacancy structures, especially the C_s1113 structure (Figure 3c) and probably the 2022 structure (Figure 3f), which we did not optimize, tend to be favored at the 6-31G level (Table I). However, polarization and correlation corrections favor the more highly bridged isomers.

The four isomers 0204ST (Figure 3b), 2112 (Figure 3d), $C_1$3111 (Figure 3e), and C_{2v}4020 (Figure 3a) involve increasing numbers of bridge hydrogens while the boron–boron connectivity remains constant. A clear consequence of increased bridging is that the molecule becomes more compact: around the perimeter the average B–B distances are 1.852, 1.777, 1.752, and 1.725 Å, respectively, in this series. (The cross annular B–B distance shows less effect: 1.724, 1.723, 1.735 and 1.666 Å, respectively.) In addition, the folding angle decreases in the series: 180, 145, 139, and 138°, respectively.

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(15) (a) This assessment has been confirmed elsewhere: (6-31G*) Dill, J.; Schleyer, P. v. R.; Pople, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 3402. These authors find the staggered form to be the more stable by 10.5 kcal/mol. (b) (FSGO) Bulstin, P. H.; Linnett, J. W. *J. Chem. Soc., Faraday Trans. 2* **1975**, *71*, 1058. The staggered form is found to be 1.9 kcal/mol more stable than the eclipsed form. (c) Armstrong, D. R. *Inorg. Chim. Acta* **1976**, *18*, 13. The ST form of 1103 B_3H_7 is found to be ~18 kcal/mol more stable than the EC for unoptimized EC.

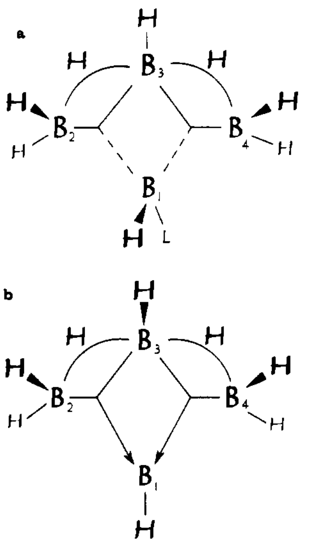

Figure 4. Localized orbital description from a PRDDO wavefunction. The following are the electron population contributions to the localized three-center bonds (presented in the same order as the bond description): (a) $B_1B_2B_3$, -0.81 e/-0.72 e/-0.40 e; (b) $B_1B_2B_3$, -0.91 e/-0.75 e/-0.33 e. Legend for boron bonding: solid arrow drawn from LMO centroid, contribution of 0.25-0.35 e; dashed line, 0.35-0.50 e; solid line, >0.5 e. The PRDDO calculations for (a) are for the CO adduct and are approximately that of the X-ray structure in Table IV. The 3-21G optimized structure is used for the analysis of (b).

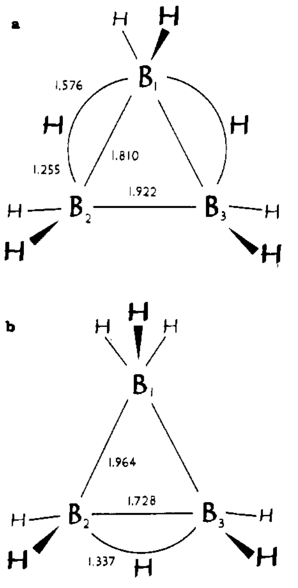

Figure 5. $B_3H_8^-$: (a) 2103, C_{2v}, and (b) 1104, C_s.

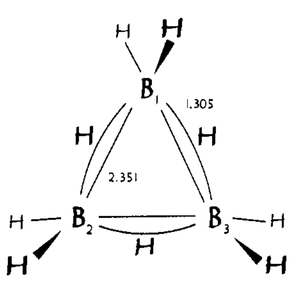

Figure 6. B_3H_9, 3003, D_{3h}.

The effect of basis set extension on this series of isomers shows that for two-, three-, and four-hydrogen bridges, the stabilizations per hydrogen bridge due to polarization are 1.9, 2.9, and 2.4 kcal/mol, respectively, while the stabilizations per hydrogen bridge due to correlation correction are 4.2, 4.9, and 4.5 kcal/mol, respectively. These values support an earlier estimate per hydrogen bridge of 1-3 kcal/mol of extra stabilization due to extension from single-ζ to double-ζ basis sets and of 2-4 kcal/mol further stabilization upon inclusion of configuration interaction.

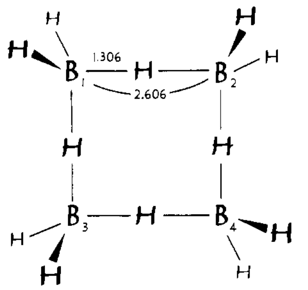

Figure 7. B_4H_{12}, 4004, D_{4h}.

Table III. Comparison (Å) of X-ray Structure of B_4H_8 Adduct with Theoretical Structures of Free B_4H_8 (2112)

bond[a]	X-ray[b] L = $PF_2N(CH_3)_2$	theor 3-21G	PRDDO
B_1B_3	1.67	1.723	1.760
B_2B_3 or B_4B_3	1.75[c]	1.822	1.860
B_1B_2 or B_1B_4	1.82[c]	1.733	1.676
B_2H_b or B_4H_b	1.27[c]	1.415	1.538
B_3H_b	1.12[c]	1.277	1.236

[a] Figure 3d. [b] Reference 16. [c] Average of two bond lengths in adduct.

An X-ray diffraction structure is known[16] for the $PF_2N(CH_3)_2$ adduct of B_4H_8, which has some similarity to the 2112 structure for B_4H_8 (Table III). Although the localized molecular orbitals at the PRDDO level are rather similar (Figure 4), a detailed comparison of bond distances and bond orders is not justifiable in view of the obvious geometrical differences between B_4H_8 and B_4H_8L structures.

$B_3H_8^-$. The ^{11}B NMR spectrum[17] of the $B_3H_8^-$ has been interpreted by Lipscomb[18] as a pseudorotation process which permutes all hydrogens and makes all borons equivalent. The barrier between equivalent structures is probably less than 8 kcal/mol inasmuch as the equivalence is preserved down to 137 K.[18] An X-ray diffraction study[19] is compatible with a structure having two hydrogen bridges and three BH_2 groups, idealized to C_{2v} symmetry in Figure 5a. The alternative or intermediate structure (Figure 5b) has one bridge hydrogen. The distinct phases of the intramolecular rearrangement include (1) conversion of a bridge hydrogen to a terminal hydrogen, (2) an optional rotation of the resulting BH_3 group, and (3) conversion of a terminal hydrogen of this BH_3 group to a bridge hydrogen. The strict pseudorotation pathway does not involve the BH_3 rotation, which, however, is required for complete equivalence of all H atoms on the NMR time scale.

Theoretical studies have supported this proposal for facile internal rearrangement within $B_3H_8^-$. A nonempirical molecular orbital (NEMO) method gave barriers of 4.4 and 2.5 kcal/mol for the terminal-bridge conversion and the rotation of BH_3, respectively.[20] In a more accurate study[21] geometries were optimized at the PRDDO level, which showed that the C_{2v} isomer was 2.5 kcal/mol less stable than the C_s isomer. However, a 4-31G basis on these PRDDO geometries reversed

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Table IV. Comparison (Å) of X-ray Structure of $B_3H_8^-$ with Theoretical Structures

			theor	
styx no.	bond	X-ray[a,b]	3-21G	PRDDO
2103[c]	B_1B_2	1.77	1.810	1.78
	B_2B_3	1.80	1.922	1.83
	B_1H_b	1.50	1.576	1.60
	B_2H_b	1.20	1.255	1.24
1104[d]	B_1B_2		1.964	1.90
	B_2B_3		1.728	1.87
	BH_b		1.337	1.36

[a] Reference 19. [b] Counterion $(NH_3)_2BH_2^+$. [c] Figure 5a. [d] Figure 5b.

this order, showing that the double-bridged structure was 0.8 kcal/mol more stable than the single-bridged structure.

The results of the present study indicate that the double-bridged C_s2013 isomer is more stable than the single-bridged C_s1104 isomer by 0.8 kcal/mol (Table I). A comparison of these structures, optimized at the 3-21G level, is given in Figure 5a,b, and the relation to the X-ray diffraction study is given in Table IV. The larger B_{basal}–B_{basal} distance of the 3-21G optimized geometry may be due to inadequency of the basis set; in addition, the X-ray diffraction distances may need correction for molecular torsional motion and further refinement. Of course, the B–H distances in the X-ray diffraction study are short due to the displacement of electrons in the chemical bond.

At least three effects make the energy difference small between these two isomers of $B_3H_8^-$. First the two hydrogen bridges of the 2013 structure are very asymmetric (1.576, 1.255 Å), while the BHB bridge of the 1104 structure is symmetric. Thus, the 2013 structure has a slight tendency to be like a 0105 structure. Second, the two-center bond of the 2013 structure has appreciable three-center character,[6] and therefore the correlation correction for this bond changes less than usual as the structure changes from 2013 to 1104. Third, in a multicenter bonding situation adjustments in electron density can compensate for relatively large movements of nuclei, e.g., in B_5H_{11}[5], as compared with the usual more highly localized bonds of most of organic chemistry.

Of course, it would be desirable in a future study to optimize geometries including polarization and correlation in the wave function. For example, in the isomerization of HNC to HCN,[22] the H–N and H–C distances are 1.471 and 1.155 Å without correlation, while they are 1.427 and 1.168 Å when corrections for configuration interaction are included.

B_3H_9 and B_4H_{12}. Optimized geometries are shown in Figures 6 and 7 for these two molecules, of symmetries D_{3h} and D_{4h}, respectively. The increase of B–B distance from 2.351 to 2.606 Å at relatively constant bridge hydrogen distances (1.305, 1.306 Å) occurs as the bent BHB bond in B_3H_9 becomes very nearly linear in B_4H_{12}. The stabilization per BH_3 unit decreases from −17.8 kcal/mol in B_2H_6 to −10.4 kcal/mol in B_3H_7 to −5.3 kcal/mol in B_4H_{12} (Table V). The direct boron–born interaction decreases as the distance increases and the BHB bond becomes more nearly linear.

Table V. Stabilization per BH_3 for 6-31G and Estimated MP3/6-31G* Basis and Contribution of Polarization and Correlation to the Correction

B_nH_{3n}	stabilizn/ BH_3 at 6-31G level	polarizn cor/BH_3	correln cor/BH_3	tot cor/BH_3	estd stabilizn/ BH_3 at MP3/ 6-31G* level
B_2H_6 ($n = 2$)	−6.9	−3.3	−7.6	−10.9	−17.8
B_3H_9 ($n = 3$)	−0.1	−1.7	−8.6	−10.3	−10.4
B_4H_{12} ($n = 4$)	1.5	0.3	−7.0	−6.8	−5.3

Table VI. Total Energies (hartrees) for Boron Hydrides and Ions

molecule	6-31G	6-31G*	MP2/6-31G	MP3/6-31G
B_3H_7 (1a)	78.005 658	78.049 711	78.193 712	78.225 511
B_3H_7 (1b)	77.984 025	78.029 615	78.173 413	78.206 160
B_3H_7 (1c)	77.985 361	78.031 737	78.176 920	78.209 280
B_3H_7 (1d)	78.005 520	78.050 170	78.187 676	78.220 098
B_3H_7 (1e)	77.997 060	78.049 339	78.195 003	78.226 327
B_4H_8 (3a)	103.212 209	103.279 720	103.484 351	103.520 268
B_4H_8 (3b)	103.230 077	103.282 035	103.470 501	103.509 577
B_4H_8 (3c)	103.248 796	103.299 189	103.486 652	103.525 965
B_4H_8 (3d)	103.239 486	103.297 475	103.494 808	103.532 329
B_4H_8 (3e)	103.228 331	103.293 912	103.495 273	103.531 418
B_3H_8 (4a)	78.614 171	78.658 857	78.831 221	78.865 366
B_3H_8 (4b)	78.612 230	78.657 755	78.831 999	78.865 760
BH_3	26.376 783	26.390 007	26.431 681	26.444 283
B_2H_6	52.775 392	52.812 366	52.910 371	52.934 650
B_3H_9	79.130 921	79.178 771	79.338 431	79.374 714
B_4H_{12}	105.497 482	105.548 985	105.764 283	105.812 173

The correlation correction per BH_3 unit is about constant at 8 kcal/mol, compared to the 6-31G level, while the polarization correction decreases by about 1.5 kcal/mol per BH_3 as the size of the ring increases. As the B–B distance increases, the effect of polarization should decrease. On the other hand, the distance from boron to the bridge hydrogen stays approximately constant as the ring size increases, so the correlation correction per BH_3 should remain nearly constant.

Finally, we summarize total energies of these various structures in Table VI.

Conclusion. Our hope is that some degree of transferability can be established in these corrections for polarization and correlation and that their additivity will continue to be useful in estimating results of much larger calculations than we can now carry out. At least, we have shown that both types of corrections are needed to study systems in which multicenter bonding can give alternative and possibly fluxional structures of nearly the same stability.

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Registry No. B_3H_7, 12429-70-8; B_3H_9, 36350-66-0; B_4H_8, 12007-71-5; B_4H_{12}, 60349-62-4; $B_3H_8^-$, 12429-74-2.

Supplementary Material Available: Cartesian coordinates for the boron hydrides studied in this paper (8 pages). Ordering information is given on any current masthead page.

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[22] Brooks, B. R.; Laidig, W. D.; Saxe, P.; Goddard, J. D..; Yamaguchi, Y.; Schaefer, H. F., III *J. Chem. Phys.* **1980**, *72*, 4562.