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The Question of Fluxional Behavior in $B_3H_8^-$ and B_5H_{11}

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The structures of $B_3H_8^-$ and B_5H_{11} have been examined by molecular orbital techniques to study whether they exhibit fluxional behavior. The PRDDO (partial retention of diatomic differential overlap) method was employed in this study, and the negative ion $B_3H_8^-$ was also examined by ab initio extended-basis 4-31G calculations. The pseudorotation process, which involves conversion of the equilibrium geometry double-bridge structure to a single-bridge structure, followed by rotation of the BH_3 group, was found to afford a low-energy pathway. The calculated 4-31G barrier to hydrogen exchange is about 1 kcal/mol (in the gas phase) and is consistent with fluxional behavior for $B_3H_8^-$. The bonding in $B_3H_8^-$ is examined in terms of localized molecular orbitals, vacant-orbital topology theory, and donor/acceptor interactions of the molecular subunits. Geometry optimization of B_5H_{11} was performed in C_s symmetry starting from a set of crystal coordinates. A recently reported asymmetric crystal structure of C_1 symmetry was also examined. After substantial optimization, this C_1 structure was less stable than the C_s structure, but only by about 1 kcal/mol. An identical energy increase was obtained for the C_s structure by displacing the unique terminal hydrogen on the apical boron by 10° . Thus, B_5H_{11} appears to have C_s symmetry and not to be fluxional. A low-lying vibration involving substantial displacement of the unique hydrogen on the apex is indicated, however.

Fluxional behavior in the boron hydrides has been observed in a number of instances.¹ Two systems that have been postulated to be fluxional (i.e., to be comprised of two or more structures which interconvert rapidly on the NMR time scale) are $B_3H_8^-$ and B_5H_{11} . Observation of the former in solution by NMR shows that all protons and borons remain equivalent on the NMR time scale even down to 137 K.² Thus, a rapid intramolecular tautomerization occurs, the activation energy for which has been estimated to be no greater than 8 kcal/mol.² In the solid state, only one structural study of the ion, an x-ray diffraction study of $((NH_3)_2BH_2^+)(B_3H_8^-)$,³ has been reported for other than transition-metal complexes. This study indicates that the anion has C_{2v} symmetry, as shown in Figure 1a, and has two hydrogen bridges and three BH_2 groups. Solid-state NMR results have also been obtained for KB_3H_8 and for $(CH_3)_4NB_3H_8$. At room temperature, the proton and ^{11}B spectra indicate equivalent borons and protons on the NMR time scale.⁴

The pseudorotation process proposed by Lipscomb for $B_3H_8^-$ (Figure 2) involves transformations between a one-bridge and a two-bridge structure.⁵ The two distinct phases of this mechanism are (1) an exchange of bridge and terminal hydrogens, which corresponds to the interconversion of the double- and single-bridge structures, and (2) a subsequent rotation of the BH_3 group in the single-bridge structure. Since the single-bridge structure can reclose to either of the two equivalent two-bridge structures, all borons and all hydrogens can exchange. A theoretical study employing the NEMO method in conjunction with unoptimized geometries yielded barriers of 4.4 and 2.5 kcal/mol, respectively, for the successive bridge-terminal exchange and BH_3 -rotation steps.⁶

An unambiguous experimental determination of the molecular structure of B_5H_{11} has proven to be difficult to obtain.⁷

The initial crystal structure of Lavine and Lipscomb (LL) suggests that the molecule has C_s symmetry.⁷ NMR studies have also been reported⁸ but do not establish whether B_5H_{11} has C_s symmetry or has two equivalent interconverting forms of C_1 (no) symmetry. This perplexing question has not been resolved, despite the new crystal structure determination by Huffman and Schaeffer,⁹ who reported a C_1 structure. If the ground state of the molecule in fact lacks symmetry, then, as noted, it must have a fluxional structure.

Theoretical studies of systems such as these may have predictive value, even though such studies strictly apply only to processes occurring in the gas phase, where solvation effects are absent. The NEMO studies on $B_3H_8^-$ are subject to this limitation and are further suspect because of the sizable approximations to ab initio theory employed in the method. Ab initio SCF and localized-orbital studies have been reported for B_5H_{11} .¹⁰ However, these studies employed geometries based on the C_s crystal structure of Lavine and Lipscomb and thus do not answer the question of the symmetry of the molecule.

In this study, we have examined various structures for $B_3H_8^-$ using both PRDDO¹¹ and 4-31G¹² calculations. PRDDO is an efficient approximate method which employs minimum basis sets of Slater atomic orbitals and which accurately reproduces the results of ab initio calculations using minimum-basis sets. The ab initio 4-31G calculations are much more expensive but employ more flexible basis sets which circumvent some of the special difficulties which arise in minimum-basis-set calculations on negative ions; the larger basis sets allow for the necessary expansion of the charge distribution in regions of excess electron density. For B_5H_{11} , several structures have been examined at the PRDDO level, and a characterization of the bonding in terms of the localized

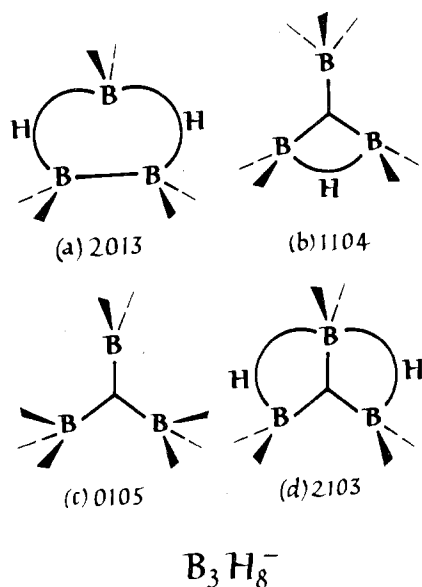


Figure 1. Possible topological structures for $B_3H_8^-$: (a) 2013 topologically allowed double bridge; (b) 1104 topologically allowed single bridge; (c) 0105 vacant-orbital zero bridge; (d) 2103 topologically forbidden double bridge.

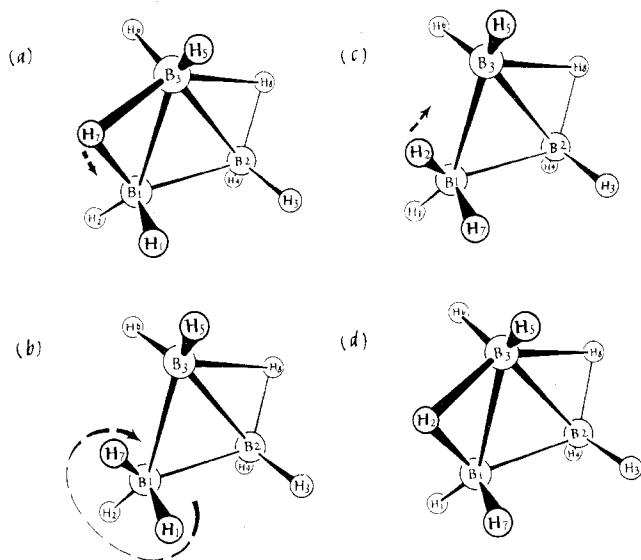


Figure 2. Proposed tautomerism mechanism: (a) interconversion of double bridge to single bridge; (b) single bridge with rotation; (c) single to double bridge conversion; (d) double bridge structure with interconverted hydrogens.

Table I. Exponents

$B_3H_8^-$		B_5H_{11}	
B 1s	4.690	B 1s	4.680
2s	1.477	2s	1.443
2p	1.466	2p	1.477
H_t 1s	1.066	H_t 1s	1.147
H_b 1s	1.138	H_b 1s	1.209

molecular orbitals¹³ (LMO's) is presented. We find, in brief, that $B_3H_8^-$ is a fluxional molecule but that B_5H_{11} evidently is not. Instead, the latter appears to have a C_s equilibrium geometry, though one which is rather easily deformed.

$B_3H_8^-$

Potential Surface. Geometries for the single- and double-bridge structures were optimized at the PRDDO level using ab initio optimized exponents¹⁴ taken from $B_2H_7^-$ (Table I). All bond angles and internuclear distances were refined se-

Table II. Coordinates of Unique Centers for $B_3H_8^-$

Structure	Atom	\hat{x}^a	\hat{y}	\hat{z}
(A) Double bridge	$1H_t$	2.431 30	0.991 97	1.861 87
	$5H_t$	0.0	-4.067 91	1.882 76
	$7H_b$	2.895 86	-2.038 28	0.0
	1B	1.732 58	0.0	0.0
	3B	0.0	-2.887 24	0.0
(B) Single bridge	$1H_t$	2.770 66	0.306 58	1.852 95
	$5H_t$	0.0	-3.961 55	-2.114 90
	$6H_t$	1.832 46	-3.961 55	1.057 61
	$8H_b$	0.0	2.013 69	0.0
	1B	1.582 66	0.0	0.0
	3B	0.0	-3.214 01	0.0
(C) BH_3 pivot	1H	2.739 98	1.379 42	1.978 48
	2H	2.864 68	1.446 29	-1.749 47
	3H	-2.891 74	1.393 61	-1.727 13
	4H	-2.671 56	1.444 77	-2.013 21
	5H	2.033 53	-2.929 25	-0.417 12
	6H	-0.736 59	-2.778 96	2.005 55
	7H	-1.347 61	-2.981 92	-1.562 59
	$8H_b$	0.005 31	3.064 03	0.042 64
	1B	1.628 12	1.052 99	0.069 52
	2B	-1.620 39	1.059 29	-0.079 32
3B	-0.003 56	-2.093 03	-0.001 06	
(D) Zero bridge	$1H_t$	2.443 74	1.001 03	1.854 60
	$5H_t$	0.0	-4.051 98	1.865 04
	7H	2.931 65	-1.876 78	0.0
	1B	1.738 65	0.0	0.0
	3B	0.0	-2.843 49	0.0

^a Coordinates are given in au; 1 au = 0.529 16 Å.

Table III. Energies for $B_3H_8^-$

Structure	PRDDO ^a	STO-4-31G
(A) Single bridge	-78.6513	-78.5236
(B) Double bridge	-78.6473	-78.5249
(C) Zero bridge	-78.6472	-78.5184
$\Delta(B-A)$, kcal/mol	2.5	-0.8

^a Total molecular energies in au; 1 au = 627.5 kcal/mol.

Table IV. Comparison of Structural Parameters for $B_3H_8^-$

	Double bridge ^b	Exptl ^a	PRDDO
$B_{\text{basal}}-B_{\text{basal}}$	1.80	1.83	
$B_{\text{basal}}-B_{\text{apex}}$	1.77	1.78	
$B_{\text{basal}}-H_{\text{bridge}}$	1.50 ^c	1.60	
$B_{\text{apex}}-H_{\text{bridge}}$	1.20 ^c	1.24	

^a Reference 3. ^b Bond distances in Å. ^c These distances reflect the systematic shortening of ~0.1 Å in x-ray determined B-H distances (cf. ref 16). Atom B_3 is apical, while B_1 and B_2 are basal (Figure 2a).

quentially, subject to imposed C_s and C_{2v} symmetry constraints, until consecutive optimization cycles yielded structures which differed by less than 1.0° in bond angles and 0.01 au in bonded distances. The optimized coordinates are given in Table II.

The single-bridge structure (C_s) was found to show essentially free rotation of the apical BH_3 group. The PRDDO barrier to rotation was 0.6 kcal/mol, as compared to the NEMO value of 2.5 kcal/mol.⁶ The present result was obtained by orthogonally optimizing the candidate transition state found midway along the approximately least-motion linear synchronous transit (LST)¹⁵ pathway computed between structures differing only in the orientation of the BH_3 group (Figure 2b). A quadratic synchronous transit (QST) pathway was then constructed to verify that the optimized transition state was indeed the structure of maximum energy on the pathway.

The optimized double-bridge structure (C_{2v}) was found to be approximately 2.5 kcal/mol less stable than the single-bridge structure on the PRDDO energy surface (Table III). The optimized geometry for this structure was in close

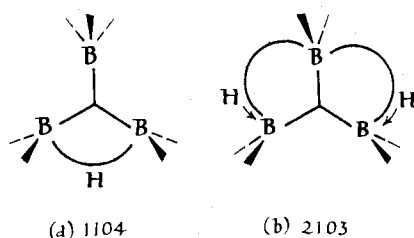


Figure 3. Localized molecular orbital structures for $B_3H_8^-$: (a) single bridge; (b) double bridge.

agreement with the crystallographic data presented by Peters and Nordman,³ especially when allowance is made for the systematic shortening of ~ 0.1 Å in x-ray-determined B–H distances¹⁶ (Table IV). Considerable bridge bond asymmetry is evident in both the calculated and experimental structures, the $B_{\text{apex}}-H_b$ and $B_{\text{basal}}-H_b$ distances being 1.24 and 1.60 Å (calculated) and 1.2 and 1.5 Å (experimental), respectively.

The experimentally observed asymmetry of the bridge bonds led Stevenson⁶ to suggest that a zero-bridge structure of 0105 topology (Figure 1c) might be more stable than the double-bridge structure. To test this supposition, the geometry of the 0105 structure was optimized at the PRDDO level under the constraint that all B–H distances remain those of terminal B–H bonds. The resultant structure was comparable in energy to the double-bridge structure on the PRDDO energy surface (Table III).

Because several structures were found to have nearly equal energies at the PRDDO level and because minimum basis sets are especially restrictive for negative ions, as noted above, we recomputed the energies for the PRDDO-optimized structures at the 4-31G level. This more flexible basis finds the double-bridge structure to be 0.8 kcal/mol more stable than the single-bridge structure, reversing the order of stability found at the PRDDO level, and places the 0105 zero-bridge structure 4 kcal/mol higher in energy than the double-bridge structure. An examination of the (PRDDO) LMO's of the 0105 structure showed that the new "terminal" hydrogens retain significant bridge-hydrogen character. Thus, the 0105 structure is merely an unoptimized form of the double-bridge structure; it was not studied further. Finally, the barrier to rotation of the BH_3 group in the single-bridge structure becomes 0.4 kcal/mol at the 4-31G level, in good agreement with the PRDDO value of 0.6 kcal/mol.

In order to determine whether an additional energy barrier to the exchange of boron and hydrogen atoms might exist beyond that implied by the energy differences reported in the previous paragraph, a linear synchronous transit (LST) pathway was employed to interconnect the single- and double-bridge structures. No additional barrier was found along this pathway at the 4-31G level; the energy varied monotonically. The analogous PRDDO calculations were in agreement on this point, though we note that the process is more difficult to model at the minimum-basis-set level, because the exponent for one hydrogen changes from a terminal- to a bridge-hydrogen value along the path. Thus, the energy differences cited above appear to account for the whole of the barrier, which amounts to only about 1 kcal/mol if the 4-31G calculations are reliable. (We again point out that the present calculations strictly apply only to the gas phase.) We note that the PRDDO barrier is also quite low, ~ 2.5 kcal/mol, though the two calculations disagree as to whether the single- or double-bridge structure is the equilibrium geometry. For the reasons stated above, the 4-31G result is more likely to be reliable.

Bonding in $B_3H_8^-$. Given the similarity in energy of the single- and double-bridge structures, comparison of their electronic structures seems especially appropriate. The fol-

Table V. Valence LMO's for $B_3H_8^-$

A-B-C	Population ^a			% s ^b			d ^c
	A	B	C	A	B	C	
Double Bridge							
B_1-H_1	0.77	1.25		28			10.2
B_3-B_5	0.80	1.23		31			10.6
B_1-H-B_3	0.64	1.12	0.27	17		14	12.9
$B_1-B_2-B_3$	0.74	0.74	0.57	28	28	43	17.9
Single Bridge							
B_1-H_1	0.80	1.23		30			9.9
B_1-H_3	0.80	1.23		29			10.4
B_3-H_2	0.75	1.24		25			11.3
B_3-H_7	0.76	1.28		26			11.3
B_1-H-B_2	0.47	1.10	0.47	16		16	12.5
$B_1-B_2-B_3$	0.72	0.72	0.63	36	36	27	17.3

^a Mulliken population in units of electrons, e. ^b Percent 2s character on boron in the LMO. ^c Percent delocalization: $d = 100[1/2(\phi^I - \phi^T)^2 d\tau]^{1/2}$ where ϕ^L is an LMO and ϕ^T is obtained from ϕ^L by truncating nonlocal contributions and renormalizing.

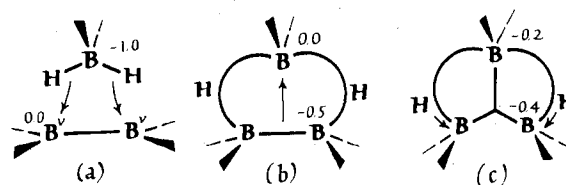


Figure 4. Formation of $B_3H_8^-$ in terms of donor/acceptor relations: (a) BH_4^- plus B_2H_4 ; (b) single bond forming three-center bond to delocalize charge; (c) asymmetrization of bridge hydrogen bonds. Resultant PRDDO group charges are shown (cf. ref 20).

lowing discussion is based on localized molecular orbitals (LMO's) obtained by the Boys criterion^{13b,17} using PRDDO wave functions (Table V).

The LMO's for the single-bridge structure display the expected 1104 topology (Figure 3). The double-bridge structure also has a central B–B–B bond and thus has a topologically forbidden 2103 structure in which five "bonds" are found to one boron, in *apparent*¹⁸ violation of the octet rule. A two-center B–B bond would be found for the predicted structure of 2013 topology.⁵

The genesis of the 2103 topology, together with certain aspects of its electronic and geometric structures, can perhaps best be understood by considering the double-bridge structure to arise from the interaction of BH_4^- and B_2H_4 subunits. The nature of this interaction is shown sequentially in Figure 4 for purposes of illustration. First, donation of charge from each of two terminal hydrogens of the BH_4^- subunit into the two vacant orbitals of the B_2H_4 subunit (Figure 4a) produces two bridge bonds, reduces the number of vacant orbitals from two to zero, and yields the idealized 2013 structure. This unilateral interaction would, however, place a relatively large (-0.5 e) accumulation of charge on the basal borons. As a result, some charge (-0.33 e from each basal boron, assuming idealized two- and three-center bonds) is channeled back to the BH_4^- subunit via formation of the three-center B–B–B bond of the 2103 structure (Figure 4b). Finally, some charge flows in the opposite direction through a readjustment of the B–H–B bridges which places their LMO centroids closer to the basal borons (Figure 4c); the LMO populations become 0.27 and 0.64 e, respectively, on the apical and basal borons, as compared to idealized values of 0.5 e for symmetric bridge bonds. These reciprocal donor/acceptor interactions knit the subunits firmly together, produce a nearly symmetric B–B–B bond but highly asymmetric B–H–B bridges, and result in a nearly uniform distribution of the excess negative charge over the boron framework.

Table VI. Unique Coordinates^a and PRDDO Energies for Symmetric Structures for B₅H₁₁^b

	Exptl (LL) ^c			PRDDO		
	x	y	z	x	y	z
1H _t	0.0	1.997 50	3.994 70	0.0	1.657 58	3.903 81
2H _b	0.0	4.190 50	0.770 60	0.0	4.440 81	1.544 73
3H _t	2.789 80	-1.645 80	1.048 10	2.657 92	-1.738 39	1.049 32
5H _t	4.707 46	3.288 40	1.334 50	4.826 83	3.250 34	1.141 56
7H _t	2.480 90	4.683 00	-1.052 50	2.626 33	4.545 41	-1.571 85
1H _b	0.0	-0.301 20	-1.877 30	0.0	-0.931 20	-1.637 30
2H _b	2.721 20	1.359 70	-1.861 00	3.146 20	0.684 70	-1.696 00
1B	0.0	2.167 40	1.752 40	0.0	2.167 40	1.752 40
2B	1.672 40	0.0	0.0	1.752 95	-0.052 83	0.0
4B	2.911 40	3.006 30	0.0	2.963 79	3.040 66	0.0

E(PRDDO) = -129.5303 au *E*(PRDDO) = -129.6087 au

^a Coordinates are reported in atomic units. ^b *yz* is the symmetry plane for all structures. ^c These coordinates are from ref 10.

Since there are now five "bonds" to the apical boron but only four available valence atomic orbitals (to the extent that a minimum-basis-set description suffices), certain of these bonds (particularly the three three-center-bonds) are fractional¹⁸ to this center. The observed asymmetry in the three-center bonds is consistent with this fractionality, but it is important to note that fractionality and polarity are distinct concepts; neither implies the simultaneous occurrence of the other.¹⁸

Alternatively, the double-bridge structure can be viewed as being intermediate in structure between the idealized 2013 topologically allowed (TA)¹⁹ and the 0105 vacant-orbital structures in boron hydrides has recently been discussed.²⁰ In this instance, some charge flows from each of two terminal hydrogens attached to the basal borons into the vacant 2p orbital of the 0105 structure, raising the Mulliken atomic orbital population (PRDDO) of this orbital from 0.0 to 0.39 e. In compensation, the B-B-B bond concentrates to some degree on the basal borons (Table V), though not to the extent required to generate the idealized 2013 structure.

In either interpretational framework, the result is a maximization of the total atomic valency. Indeed, the total atomic valency is higher for the double-bridge structure (18.998 as computed from the PRDDO wave function using the Armstrong, Perkins, and Stewart criterion^{20,21}) than for the single-bridge structure (18.930). Normally, the more highly bridged structure would have the higher valency and would be clearly the more stable structure. Here, however, the difference in valency is considerably smaller than might be expected²⁰ in view of the net conversion of one terminal to one bridge bond. Consequently, the strain associated with B-H-B bridges (which reduces their energetic contributions relative to their valency contributions²⁰) leads PRDDO to favor the single-bridge structure. In the more flexible 4-31G basis, this strain is less severely felt, and, as observed in other similar cases,²⁰ the order of stability is reversed.

Finally, we note that inclusion of the effects of electron correlation, neglected in the present single-determinant calculations, and perhaps additional increases in the size of the basis set, can be expected²⁰ to further stabilize the double-bridge structure relative to the single-bridge structure. Thus, it seems quite certain that the double-bridge structure represents the equilibrium geometry and that the single-bridge structure is a saddle-point (transition-state) structure. It also seems likely that the 4-31G estimates of ≤ 1 kcal/mol for the barriers to boron and hydrogen exchange are somewhat too small, though we again point out that possible differential effects of solvation are not included in our physical model.

B₅H₁₁

The calculations on B₅H₁₁ reported here were all carried out in the PRDDO approximation. The exponents employed

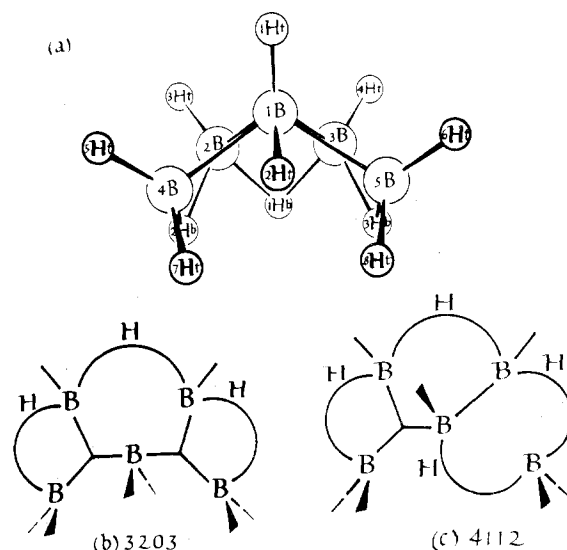


Figure 5. Structures for B₅H₁₁: (a) geometry; (b) LMO's for C₃ structure; (c) topology of C₁ structure.

Table VII. Overlap Populations^a

Bonds	Exptl (LL)		PRDDO	
	Dist	Overlap	Dist	Overlap
1B-2B	1.722	0.477	1.760	0.436
1B-4B	1.852	0.328	1.879	0.349
2B-3B	1.769	0.342	1.855	0.266
2B-4B	1.720	0.413	1.757	0.420
1B-1H _t	1.190	0.832	1.170	0.824
1B-2H _t	1.190	0.612	1.208	0.651
2B-3H _t	1.189	0.833	1.154	0.842
4B-5H _t	1.193	0.816	1.161	0.825
4B-7H _t	1.213	0.802	1.165	0.835
2B-1H _b	1.340	0.385	1.351	0.394
2B-2H _b	1.340	0.424	1.225	0.579
4B-2H _b	1.318	0.331	1.539	0.178
4B-2H _t	1.712	0.095	1.917	0.059

^a All distances are in Å.

are listed in Table I. Localized molecular orbitals were obtained using the Boys criterion. A geometry optimization was first carried out in C_s symmetry. Boron positions were initially set at their positions as determined, presumably fairly accurately, by x-ray diffraction⁷ (Figure 5a). Hydrogen positions were then refined until consecutive optimization cycles yielded geometries which differed by less than $\sim 1^\circ$ in bond angles and 0.01 au in bonded distances. This refinement lowered the energy by ~ 48 kcal/mol. A single optimization cycle was then carried out on the boron positions but lowered the total energy by only 2 kcal/mol. The final coordinates are given in Table VI. Further optimization is unlikely to

Table VIII. Localized Molecular Orbitals for Symmetric Structures for $B_3H_{11}^a$

A-B-C	Populations						<i>d</i>	
	LL			PRDDO			LL	PRDDO
	A	B	C	A	B	C		
1B-1H _t	0.94	1.08		0.94	1.07		9.2	10.1
1B-2H _t	0.76	0.96		0.81	0.99		20.5	16.9
2B-3H _t	0.97	1.05		0.95	1.07		9.2	10.1
4B-5H _t	0.93	1.09		0.93	1.09		8.9	9.0
4B-7H _t	0.89	1.10		0.92	1.11		12.8	10.9
2B-1H _b -3B	0.53	0.96	0.53	0.53	0.96	0.53	14.7	13.3
2B-2H _b -4B	0.61	0.95	0.45	0.74	0.98	0.29	14.3	12.9
2B-1B-4B	0.76	0.73	0.44	0.74	0.71	0.53	20.6	17.9

^a See Table V for notation.Table IX. Charge Distributions^a of Symmetric Structures for B_3H_{11}

Atom	LL	PRDDO	Atom	LL	PRDDO
1H _t	-0.065	-0.055	1H _b	0.045	0.050
2H _t	0.073	0.042	2H _b	0.063	0.045
3H _t	-0.033	-0.044	1B	-0.108	-0.125
5H _t	-0.071	-0.079	2B	0.045	-0.002
7H _t	-0.074	-0.079	4B	0.099	0.196

^a Mulliken atomic charges in electrons, e.

cause further significant decreases in energy or changes in geometry.

The asymmetry in the bridge-hydrogen positions for 2H_b and 3H_b is striking. Thus, the original x-ray coordinates (LL) placed 2H_b insignificantly closer (~0.02 Å) to 4B than to 2B.⁷ However, an ab initio calculation¹⁰ employing the LL coordinates found overlap populations of 0.424 e for 2B-2H_b and 0.330 e for 4B-2H_b and thus predicted that the latter distance should in fact be substantially longer than the former, as we now find. For the optimized coordinates, the overlap populations are 0.579 and 0.178 e (Table VII). A further indication of this hydrogen asymmetry is found in the 2B-2H_b-4B localized-bond populations (Table VIII) in that there is a higher population on the boron which has a single terminal hydrogen (2B). Thus, the 2H_b and 3H_b bridge hydrogens in B_3H_{11} appear to lie significantly closer to the BH groups (1.23 Å) than to the BH₂ groups (1.56 Å). The more recent crystal structure reported by Huffman and Schaeffer⁹ also shows this asymmetry.

Optimization of the coordinates also slightly altered the involvement in the bonding of the unique 2H_t. This hydrogen

was designated, by choice of orbital exponent, as a normal terminal hydrogen in localization studies using both the LL and the PRDDO optimized coordinates (Table VIII). However, 2H_t exhibited different degrees of bridge bond character in the LL and optimized structures. In the former, the bonding to 2H_t shows much multicentered character. Thus, an abnormally small overlap population (0.64 e vs. a normal 0.80 e) is observed between 2H_t and its parent boron 1B (Table VII), and rather large positive overlap populations (0.094 e) were found between 2H_t and the two neighboring borons 4B and 5B. In the optimized structure, the "nonbonded" overlap populations to 4B and 5B decreased to 0.059 e, signifying a somewhat weakened interaction. The population analysis for the localized molecular orbitals is also consistent with this decreased interaction (Table VIII). Thus, the LMO for 1B-2H_t has a population of 0.96 e on 2H_t for the LL coordinates but of 0.99 e in the optimized structure. In addition, the 1B contribution increases from 0.76 to 0.81 e after geometry optimization. The optimized structure, therefore, has a somewhat stronger 1B-2H_t interaction. The charge on 2H_t was also affected by optimization. In general, terminal hydrogens are slightly negative (≤-0.1 e), while bridge hydrogens are slightly positive. For the LL coordinates, 2H_t possessed a charge of +0.072 e. For the optimized coordinates, this charge decreased to +0.042 e (Table IX), again indicating more terminal character. Thus, while 2H_t clearly participates to some degree in multicenter bonding, this bonding is centered on four atoms (1B-2H_t-4B-5B), rather than on three (1B-2H_t-5B), at least in the C_s structure. Four-center interactions which involve two strong and two weak contributions are not uncommon in boron hydrides.²²

Table X. Coordinates^a and PRDDO Energies for Asymmetric Structures for $B_3H_{11}^b$

	HS			HS'			HS''		
	x	y	z	x	y	z	x	y	z
1H _t	0.010 99	1.901 46	3.827 85	0.038 66	1.670 75	3.928 82	0.009 69	1.664 28	3.912 56
2H _t	-0.249 01	3.884 98	1.056 62	-0.259 06	4.311 47	1.497 95	-0.068 93	4.391 61	1.540 66
3H _t	2.628 35	-1.703 66	0.871 58	2.682 58	-1.777 04	0.946 05	2.656 53	-1.735 51	1.028 32
4H _t	-2.576 99	-1.672 50	0.931 93	-2.660 77	-1.807 91	1.029 90	-2.646 51	-1.739 66	1.044 82
5H _t	4.690 67	3.100 33	1.101 09	4.855 47	3.221 75	1.074 24	4.825 89	3.238 69	1.120 47
6H _t	-4.496 78	3.298 46	1.110 82	-4.729 27	3.387 19	1.091 00	-4.788 14	3.290 07	1.133 99
7H _t	2.478 77	4.526 65	-1.394 68	2.529 23	4.583 68	-1.489 14	2.580 02	4.560 16	-1.539 54
8H _t	-2.525 84	4.358 59	-1.630 31	-2.547 12	4.493 27	-1.720 35	-2.596 61	4.527 28	-1.613 81
1H _b	-0.050 05	-0.799 05	-1.503 21	-0.038 08	-0.809 42	-1.493 90	0.001 12	-0.941 77	-1.615 27
2H _b	3.013 09	1.033 88	-1.447 33	3.113 45	0.804 90	-1.656 01	3.139 19	0.711 63	-1.691 23
3H _b	-3.013 40	0.953 98	-1.389 20	-3.120 63	0.731 06	-1.591 68	-3.145 64	0.697 08	-1.677 60
1B	0.019 52	2.035 30	1.803 97	0.023 39	2.059 83	1.783 20	0.004 37	2.139 47	1.762 89
2B	1.693 25	-0.074 28	-0.000 40	1.701 19	-0.069 74	0.006 31	1.734 66	-0.045 61	0.000 70
3B	-1.690 35	-0.121 42	0.065 41	-1.682 60	-0.114 22	0.062 56	-1.730 97	-0.049 28	0.012 64
4B	2.914 35	3.001 72	0.004 55	2.962 36	3.010 15	-0.019 72	2.951 86	3.029 26	-0.004 04
5B	-2.846 57	3.069 29	0.000 86	-2.868 81	3.098 52	-0.039 63	-2.926 52	3.056 55	-0.005 95
	<i>E</i> (PRDDO) = -129.5325 au -81290.3 kcal/mol			<i>E</i> (PRDDO) = -129.6000 au -81332.7 kcal/mol			<i>E</i> (PRDDO) = -129.6079 au -81337.6 kcal/mol		

^a Coordinates are reported in atomic units. ^b Each structure has been rotated and translated into maximum coincidence with the PRDDO structure so that the yz plane is still the "symmetry" plane.

Table XI. Localized Molecular Orbitals for Asymmetric Structures for B_5H_{11} ^a

A-B-C	Populations						<i>d</i>	
	HS			HS''				
	A	B	C	A	B	C	HS	HS''
1B-1H _t	0.95	1.07		0.94	1.08		9.24	10.13
1B-2H _t				0.79	0.99			17.03
2B-3H _t	0.97	1.05		0.96	1.06		9.80	10.12
3B-4H _t	0.96	1.06		0.96	1.06		9.52	10.13
4B-5H _t	0.93	1.09		0.93	1.09		9.19	9.06
4B-7H _t	0.92	1.10		0.92	1.10		11.25	11.92
5B-6H _t	0.94	1.09		0.93	1.09		9.03	9.10
5B-8H _t	0.93	1.09		0.92	1.10		11.86	11.03
2B-1H _b -3B	0.53	1.00	0.51	0.54	0.96	0.53	13.21	13.29
2B-2H _b -4B	0.64	1.01	0.37	0.73	0.98	0.31	12.76	12.83
3B-3H _b -5B	0.67	0.99	0.37	0.74	0.97	0.30	12.87	12.88
1B-2H _t -5B	0.73	1.01	0.24				16.00	
1B-2B-4B	0.76	0.69	0.54	0.72	0.73	0.54	18.88	17.92
3B-1B-5B	0.82	0.77	0.30	0.75	0.72	0.50	20.56	18.20

^a See Table V for notation.

An asymmetric crystal structure for B_5H_{11} , recently obtained by Huffman and Schaeffer⁹ (coordinates are given in Table X), indicates a 4112 topology with C_1 symmetry (Figure 5). A PRDDO localization of the Huffman-Schaeffer (HS) structure (Table XI) did indeed reveal some three-center bonding of $2H_t$ to the neighboring $5B$, which has a population of 0.24 e in the localized $1B-2H_t-5B$ orbital. We felt that the asymmetry might be caused by crystal forces, however, and therefore have examined the HS structure in order to determine whether it or a C_s structure has the lower energy.

Examination of the HS structure revealed that $2H_t$ is displaced in the HS structure by $\sim 10^\circ$ toward $5B$ from the C_s plane of the symmetric configuration. Accordingly, successive perturbations of the symmetric structure were made in which $2H_t$ was displaced toward $5B$ in increments of 1° . These successive displacements monotonically increased the energy of the symmetric structure by ~ 1 kcal/mol when the displacement reached the full 10° . The relatively small amount of energy required for the movement of $2H_t$ suggests that a considerable degree of vibrational freedom is available to this unique hydrogen.

An investigation was then made to determine whether the transition from the HS structure to a symmetric structure entailed an activation barrier. A correction for the systematic x-ray shortening of B-H distances¹⁶ and a partial optimization of the HS structure produced a somewhat more symmetric conformation, the HS' structure (Table X), and lowered the energy by 42 kcal/mol. A procedure based on the synchronous-transit method of Halgren and Lipscomb¹⁵ was then employed to symmetrize the molecule in parts, while retaining the structure-defining asymmetry in the $2H_t$ angular position. For this purpose, the molecule was divided into fragments which consisted of adjacent sets of atoms (e.g., $2B-1H_b-3B$, $2B-2H_b-4B$). The following procedure was then employed for each fragment. We first constructed a linear synchronous transit (LST) pathway¹⁵ between the HS' and the C_s structures (designated by path coordinates p of 0.0 and 1.0, respectively) after the two structures had been brought into maximum coincidence.¹⁵ From the calculated structure lying midway along the LST pathway ($p = 0.5$), we extracted the coordinates of the fragment under study. The coordinates of that fragment were substituted for the corresponding coordinates in the HS' ($p = 0.0$) structure, and the PRDDO energy was calculated. A second PRDDO calculation was then performed in which the HS' coordinates of that fragment were replaced by those of the C_s ($p = 1.0$) structure. Total energies were thus obtained for two new structures containing fragments which were half ($p^\dagger = 0.5$) and fully ($p^\dagger = 1.0$) symmetrized. (The symbol

\dagger is used to indicate that only a fragment of the structure corresponds to the stated path coordinate.) Together with the $p = p^\dagger = 0.0$ (no symmetrization) initial structure, the p^\dagger 's for these structures were plotted against their corresponding energies, and a smooth parabolic curve was obtained through the three points to locate the minimum-energy structure, whose coordinates were then employed for the current fragment to define the $p = 0$ point in the symmetrization of the next fragment. Successive refinements resulted in the nearly symmetric form of the HS' structure denoted as HS'' in Table X. The energy of the HS'' structure was considerably lower (~ 47 kcal/mol) than that of the original asymmetric HS structure but was still ~ 1 kcal/mol higher than that of the optimized C_s structure. This HS'' structure is essentially the structure obtained by displacing the hydrogen $2H_t$ of the optimized structure by 10° from the C_s plane. An LST¹⁵ between the HS'' and optimized C_s structures exhibited no activation barrier. A localization of the HS'' configuration gave localized bond populations which matched those of the optimized C_s coordinates to within ~ 0.02 e; these populations demonstrated the conversion of the $1B-2H_t-5B$ bond of the original HS structure upon geometry optimization to a $1B-2H_t$ two-center bond possessing weak four-center interactions.

We therefore suggest that the differences between the HS and the C_s structures, apart from systematic differences involving x-ray shortened B-H bond lengths, principally result from crystal-packing forces. Although further optimizations and/or reinvestigation with a larger basis set might alter this conclusion, the similarities in structure, bonding, and energies of the HS'' and optimized C_s structures, the ease of transition between them, the ease of angular deformation of the $2H_t$ bond, and the evidence for four-center $1B-2H_t-4B-5B$ interactions support the hypothesis of a C_s structure for B_5H_{11} .

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Registry No. $B_3H_8^-$, 12429-74-2; B_5H_{11} , 18433-84-6.

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Cleavage of the Ring Trimer $[(CF_3)_2PBH_2]_3$ by Trimethylamine or by Trimethylphosphine: Neutral and Ionic Complex Products and Their Borane(3) Complexes; Evidence for F-P Through-Space NMR Coupling

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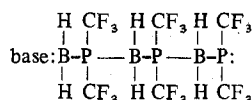
The ring trimer $[(CF_3)_2PBH_2]_3$ is easily cleaved by excess trimethylamine to give nearly equal yields of the sublimable monomer complex $(CH_3)_3N \cdot BH_2P(CF_3)_2$ (mp 81 °C) and the ionic oil $[(CH_3)_3N]_2BH_2^+(CF_3)_2PBH_2P(CF_3)_2^-$. The similar but faster trimethylphosphine reaction yields a more volatile monomer complex (mp 48 °C) and an analogous ionic oil. With deficient base, the PBPBP⁻ anion $(CF_3)_2PBH_2P(CF_3)_2BH_2P(CF_3)_2^-$ persists as a major product; less persistent, especially in the amine reaction, is the dimer complex (DC) $base \cdot BH_2P(CF_3)_2 \cdot BH_2P(CF_3)_2$. Yet longer chains are obscure but seem to be favored in the phosphine reaction. In all of these ring-cleavage products, any three-bonded P atom easily forms a BH_3 complex of the nonpolar, nonhydridic type, which HCl attacks at a central BH_2 group rather than at an end BH_3 group. Such complexes are stable at 100 °C but lose BH_3 by action of trimethylamine. The ¹⁹F NMR spectrum of the PBPBP⁻ anion (or either DC) strongly indicates through-space coupling of F in a central $P(CF_3)_2$ group to a three-bonded end-P atom; the same principle seems applicable to the second-order spectrum of the PBP⁻ anion. Such coupling is lost when a BH_3 complex is formed.

The action of trimethylamine upon the ring trimer $[(CF_3)_2PBH_2]_3$ was explored in our laboratories during 1960 by Dr. Arnold Wittwer, who found that excess amine at 100 °C led to an air-stable product, vacuum sublimable at 80 °C (mp 82 °C) and analyzable by HCl methanolysis to demonstrate the formula $(CH_3)_3N \cdot BH_2P(CF_3)_2$. Its molecular weight (by vapor pressure lowering of trimethylamine) seemed to be in the neighborhood of 300, reasonably suggesting a monomer. However, the recoverable yield of this monomer complex was only 49%, and the parallel product was a nonvolatile oil, apparently containing 0.92 amine per monomer unit $(CF_3)_2PBH_2$. At that time there seemed to be no feasible way to obtain satisfactory knowledge of the structural character of this oil, especially since it resisted attempts at analysis by the HCl-methanol method.

Recent resumption of this study with the aid of NMR spectra quickly led to confirmation of the monomer complex $(CH_3)_3N \cdot BH_2P(CF_3)_2$, and the analogous $(CH_3)_3P \cdot BH_2P(CF_3)_2$ also was made and confirmed. However, the by-product oils seemed to be mixtures having NMR spectra not easily understood, even with the aid of proton decoupling.

With the hope of obtaining a less complicated mixture of such by-products, the attack by trimethylamine was tried at 21 °C and found to be quite extensive after 2 days; and the analogous trimethylphosphine reaction seemed about equally rapid at 0 °C. The resulting oils, after brief heating in vacuo to sublime out the monomer complexes, were pure enough for dependable structural interpretations of their NMR spectra.

The main principle is fairly obvious: when the base opens the $(PB)_3$ ring by donor-acceptor bonding to boron, the initial product must be the open-chain trimer complex



Then further base action to cleave B-P bonds would lead to the observable variety of fragments. The exception would be failure to cleave off an end $P(CF_3)_2$ unit, for if the $P(CF_3)_2^-$ anion were formed, it would be expected to decompose to F^- and $(CF_3)PCF_2)_2$,¹ which is not observed. Hence the tris-(boranium) cation $base \cdot BH_2P(CF_3)_2BH_2P(CF_3)_2BH_2 \cdot base^+$ also would not be present. Then the remaining possibilities would be designated:

monomer complex (MC), $base \cdot BH_2P(CF_3)_2$
boranium cation (BC⁺), $(base)_2BH_2^+$
bis(phosphinide) anion (PBP⁻), $(CF_3)_2PBH_2P(CF_3)_2^-$
dimer complex (DC), $base \cdot BH_2P(CF_3)_2 \cdot BH_2P(CF_3)_2$
bis(boranium) cation (BPB⁺), $base \cdot BH_2P(CF_3)_2BH_2 \cdot base^+$
tris(phosphinide) anion (PBPBP⁻),
 $(CF_3)_2PBH_2P(CF_3)_2BH_2P(CF_3)_2^-$
the trimer complex

In fact, the moderate-temperature experiments with excess base, allowed to go to completion, always gave yields of the monomer complex approaching 50% and an oil consisting almost exclusively of BC⁺ and PBP⁻. The failure of this ionic "salt" $(base)_2BH_2^+(CF_3)_2PBH_2P(CF_3)_2^-$ to crystallize would be due to poor ion-packing and low lattice energy. Also, its persistence confirms that a chain-terminal B-P bond is not cleaved.

Also fairly persistent was the PBPBP⁻ anion, the virtual elimination of which required much extra time, especially when the base was trimethylphosphine. Indeed, in one experiment, using a deficient proportion of this base, the PBPBP⁻ anion was the major fluorine-containing product. In any experiment not completing all possible cleavages, it was the most prevalent intermediate product, and it probably was the chief reason for the deficient consumption of trimethylamine in the Wittwer experiments. If it can be isolated in reasonably pure condition,