Molecular Orbital Theory of the Electronic Structure of Organic Compounds. XXIV. Geometries and Energies of Small Boron Compounds. Comparisons with Carbocations

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Abstract: Ab initio molecular orbital theory is used to predict geometries, stabilities, and charge distributions of 17 neutral one- and two-heavy-atom molecules containing boron and C, N, O, or F. At the STO-3G level, geometries and conformational preferences are found to correspond to those previously calculated for the isoelectronic carbocations. However, the boron atom is found to be a stronger σ donor and weaker π acceptor than C^+. At the 6-31G* level, boron is seen to be stabilized in the following ways: by attachment of π donors (NH_2, OH, F), which stabilize BH_2X relative to BH_3 by 53–58 kcal/mol; by hyperconjugation, which stabilizes H_2BCH_3 by 12 kcal/mol; by dimerization, $2BH_3 \rightarrow B_2H_6$, predicted to be exothermic by 20 kcal/mol (6-31G*) or 37 kcal/mol if the previously determined correction for correlation energy is applied; or by complexation with Lewis bases, leading to H_3BNH_3 (stable relative to $BH_3 + NH_3$ by 21 kcal at 6-31G*) and H_3BOH_2 (6 kcal), but not H_3BFH (−8 kcal). Triplet ground states are predicted for BH, BCH, and B_2H_2. H_2BNH_2 and H_2BOH are predicted to be planar with barriers to nonrigid rotation of 29 and 14 kcal/mol, respectively, while H_2BCH_3 has a negligible barrier, and H_2BBH_2 prefers a perpendicular D_{2d} conformation by 10 kcal/mol, relative to planar. Stabilities deduced from stabilization energies, calculated heats of hydrogenation, heats of formation, and bond energies follow the order $H_2BBH_2 < H_2BCH_3 < H_2BNH_2 < H_2BOH < H_2BF$; B–H bonding in the latter three compounds (X = NH_2, OH, F) is nearly double in character. For unsaturated species, the stability order is HBBH < $HBCH_2$ < HBNH < HBO, where HB=NH and HB=O have nearly triple bonds. Polarization functions are seen to be important in describing the bonding in B_2H_6 and the H_3BNH_3 and H_3BOH_2 adducts.

The study of boron is becoming an increasingly important area of chemical interest.[2,3] Although a number of theoretical studies have appeared, the majority have dealt with boron hydrides[3g] and boron-nitrogen compounds;[3h] there has been no systematic study of small organic molecules containing boron and other first-row elements. In this paper, we examine a number of such compounds, focusing on those aspects of electronic and geometric structure most closely related to our previous studies of first-row organic systems.[4-9] As many of the species considered here are unknown, emphasis will be made on predicting structures, stabilities, and relationships to known species, particularly the isoelectronic carbocations.

This study has several purposes. First, an examination of coordinate, multicenter, and covalent bonding in these structures will suggest similarities and differences between compounds of boron and those of heavier first-row atoms, thus supplementing our understanding of the interactions occurring in small organic molecules. Second, we wish to gain a deeper understanding of carbocations by comparing them with this series of electron-deficient, but uncharged, molecules. Third, these calculations are the necessary first step toward predicting properties of larger boron-containing molecules, and it is hoped that the theoretical study of such molecules may, in this relatively young field, lead experiment.

Quantum Mechanical Method

The calculations utilize standard self-consistent molecular orbital techniques described in detail elsewhere.[5,10] Two levels of approximation are used. First, a minimal basis of Gaussian-fitted Slater-type orbitals (STO-3G) is employed for full geometry optimization of each structure. This involves variation of all bond lengths and angles, subject to assumed symmetry constraints, until variations of 0.001 Å and 0.1° lead to no further lowering of the total energy. In most cases considered here, the structure obtained was of higher symmetry than that assumed initially; the final geometrical variations were carried out at this higher symmetry. Equilibrium geometries calculated in this manner have been shown[7-9,11] to reproduce experimental data consistently for a wide range of compounds.

The STO-3G geometry is then used as the basis for a single calculation at the second level of approximation, designated 6-31G*, for which d-type polarization functions are added to an extended, split-valence (6-31G) basis on the heavy atoms. 6-31G basis sets have been fully specified for carbon through fluorine,[12] and more recently, lithium through boron.[13] Full details of the polarization methods are given elsewhere.[14] Open-shell states were calculated by the unrestricted Hartree–Fock (UHF) procedure of Pople and Nesbet.[15]

It is appropriate to mention here the effect of adding d functions to the boron 6-31G basis, as previously reported for other first-row atoms.[14a] Calculations at 6-31G and 6-31G* were compared on four molecules; energy lowerings per heavy atom were found to be 8.1 kcal/mol for BH_3, 7.8 for $H_3C\text{-}BH_2$, 9.7 for $H_3B\text{-}NH_3$, and 11.7 for B_2H_6. On the average, these are smaller than values reported for other first-row atoms, where the lowerings tend to increase with increasing atomic number (values for CH_4, NH_3, H_2O, and HF are 9.2, 12.9, 15.6, and 12.2, respectively). It seems probable that polarization is more important for multicenter bonds, as also found for bridged carbocations.[14b]

Results

Seventeen molecules were considered in the electronic and conformational states listed in Table I. All conformational isomers were geometry-optimized at the STO-3G level so that tabulated relative energies for the larger species represent nonrigid barriers to rotation (and, in the case of H_2BOH, to linear inversion). Calculated equilibrium geometries are presented in Tables II and III. In Table II, each structure $H_nB\text{-}XH_m$ is described as the union of

Table I. Total Energies in Hartrees

Molecule	Conformation or state[a]	STO-3G	Relative energy[b]	6-31G*	Relative energy[b]
BH	$^1\Sigma^+$	−24.75299	0	−25.11819	0
	$^3\Pi$	−24.75145	0.97	−25.10667	7.23
BH_2	$^2A_1$, bent	−25.41035	0	−25.74888	0
	$^2\Pi_u$, linear	−25.38401	16.53	−25.73116	11.12
BH_3	$^1A_1$	−26.07070		−26.38877	
HB=BH	$^3\Sigma_g^-$	−49.75184	0	−50.41584	0
	$^1\Delta$	−49.71198[c]	25.01	−50.36213[c]	33.70
$H_2B—BH_2$	Perpendicular, D_{2d}	−51.01071	0	−51.63216	0
	Planar, D_{2h}	−50.99053	12.66	−51.61545	10.49
B_2H_6	Bridged	−52.16610		−52.81028	
BCH	$^3\Pi$	−62.12643	0	−62.95078	0
	$^1\Delta$	−62.01947[c]	67.12	−62.83338[c]	73.67
	$^1\Sigma^+$	−62.01540	69.67	−62.82993	75.83
$HB=CH_2$	C_{2v}	−63.41037		−64.21673	
$H_2B—CH_3$	HBCH perpendicular	−64.66769	0	−65.44052	0
	HBCH cis	−64.66761	0.05	−65.44041	0.07
HB=NH	Linear	−79.25842		−80.28924	
$H_2B—NH_2$	Planar	−80.46590	0	−81.48675	0
	Rotated 90°	−80.40917	35.60	−81.43996	29.36
$H_3B—NH_3$	Staggered	−81.59951	0	−82.60650	0
	Eclipsed	−81.59613	2.12	−82.60343	1.93
HB=O	Linear	−98.82690		−100.16565	
$H_2B—OH$	Planar	−99.98619	0	−101.31901	0
	Perpendicular	−99.95156	21.73	−101.29605	14.41
	BOH linear	−99.94103	28.34	−101.28836	19.23
$H_3B—OH_2$	Staggered	−101.10193	0	−102.40745	0
	Eclipsed	−101.09968	1.41	−102.40632	0.71
$H_2B—F$	C_{2v}	−123.60361		−125.32117	
$H_3B—FH$	Staggered	−124.69460	0	−126.37928[d]	0
	Eclipsed	−124.69353	0.68	−126.37920[d]	0.05

[a] States not specified are closed-shell singlets. Refer to Table II and Figure 1 for exact geometrical descriptions. [b] In kcal/mol. [c] Molecular orbitals allowed to become complex. [d] Not bound relative to BH_3 + HF.

the appropriate H_nB fragment (Figure 1, A-D) and XH_m fragment (E-I). The molecular geometry is then specified by the corresponding pair of labels A-D plus E-I and can be visualized by joining the two illustrated fragments without rotating them from the plane of the paper. Where the number of hydrogens borne by a fragment is less than that implied by Figure 1, the appropriate labels are specified (e.g., "H = n"). The geometry of B_2H_6 cannot be described by this scheme and is given separately in Table III.

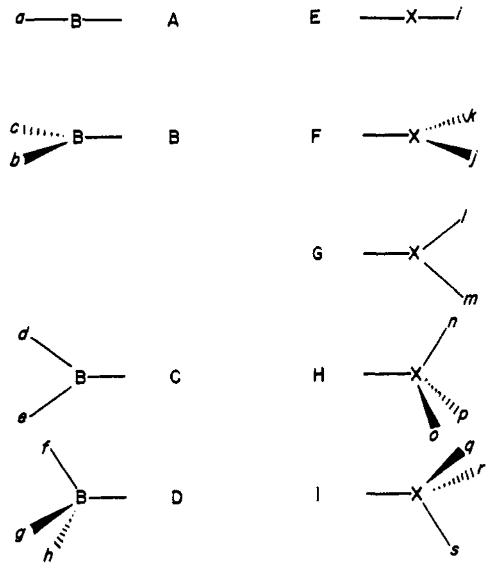


Figure 1. Geometrical fragments.

Discussion

A. B-H Compounds. Current nomenclature[16] specifies the number of hydrogens for boron hydrides and diboranes. Thus, BH is designated "borane(1)". Experimental data[17] for this species indicate a $^1\Sigma^+$ ground state with r_{BH} = 1.236 Å, the first excited state being $^3\Pi$ with r = 1.200. STO-3G bond lengths are shorter, being 1.213 and 1.155 Å, respectively. A small singlet-triplet separation is predicted (7.23 kcal/mol at 6-31G*); however, single-determinant theory is known to favor triplet states unduly. The singlet-triplet difference is given by Harrison and Allen[18] as 12.1 kcal/mol, using a double-ζ basis, and 19.3 by VB-CI calculation. Of the numerous other theoretical studies in the literature,[19-21] we mention only that of Cade and Huo,[20] who find the Hartree-Fock limit for the borane(1) ground state to be −25.13137 hartrees. References 20 and 21 give thorough tabulations of published results.

Borane(2) (BH_2) has been frequently discussed as a classic example of the application of Walsh's rules for predicting molecular geometries.[22] The ground state ($^2A_1$) is predicted to be bent due to the lowering of the $3a_1$ orbital as θ_{HBH} decreases from 180°; in the excited state, the $1b_1$ orbital (HOMO) is raised as θ decreases, leading to a linear conformation, $^2B_1 \rightarrow {}^2\Pi_u$. At the STO-3G level, we find for the ground state r = 1.161 Å, θ = 123.5°, comparable to experiment[23] (r = 1.18 Å, θ = 131°), a recent ab initio study[24] (r = 1.192 Å, θ = 128.8°), and a large configuration interaction (CI) calculation[24] (r = 1.211 Å, θ = 129.4). Corresponding values for the excited state are STO-3G (r = 1.143 Å), experiment (r = 1.17 Å)[23] and CI (r = 1.18)[24] all having θ = 180°.

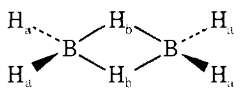
The structure of borane(3) (BH_3) has not been determined experimentally, but numerous theoretical studies have indicated a planar D_{3h} geometry.[22,25] Both C_{2v} and C_{3v} starting geometries collapsed to D_{3h} at STO-3G. The STO-3G bond length (1.16 Å) is short compared with other calculated values of 1.19,[22c] 1.22,[25a] and 1.192 Å.[25b] The Hartree-Fock limit for borane(3) has not been calculated,

Table II. Equilibrium Geometries

Molecule	Symmetry	Description[a]	Geometrical parameters[b]
$BH(^1\Sigma^+)$	$C_{\infty v}$		BH = 1.213
$(^3\Pi)$	$C_{\infty v}$		BH = 1.155
$BH_2(^2A_1)$	C_{2v}		BH = 1.161; HBH = 123.5
$(^2\Pi_u)$	$D_{\infty h}$		BH = 1.143
$BH_3(^1A_1)$	D_{3h}		BH = 1.160
$HB{=}BH(^3\Sigma_g^-)$	$D_{\infty h}$	A–E	BX = 1.430; BH = 1.148
$(^1\Delta)$	$D_{\infty h}$	A–E	BX = 1.436; BH = 1.146
$H_2B{-}BH_2$	D_{2d}	B–G	BX = 1.644; BH = 1.162; HBH = 117.2
	D_{2h}	B–F	BX = 1.713; BH = 1.162; HBH = 116.7
B_2H_6	D_{2h}	Table III	See Table III
$BCH(^3\Pi)$	$C_{\infty v}$		BX = 1.309; XH = 1.072
$(^1\Delta)$	$C_{\infty v}$		BX = 1.257; XH = 1.071
$(^1\Sigma^+)$	$C_{\infty v}$		BX = 1.221; XH = 1.069
$HB{=}CH_2$	C_{2v}	A–F	BX = 1.339; BH = 1.147; XH = 1.079; HXH = 114.3
$H_2B{-}CH_3$	C_s	B–H	BX = 1.570; BH = 1.162; XH_n = 1.089; XH = 1.084; HBH = 118.5; H_oXH_p = 109.0; BXH_n = 107.4; BXH_{op} = 132.4; XBH_{bc} = 178.1[c]
	C_s	C–H	BX = 1.571; BH = 1.162; BH_e = 1.163; XH_n = 1.083; XH_o = 1.087; XBH_d = 121.9; XBH_e = 119.6; H_oXH_p = 106.3; BXH_{op} = 124.3; BXH_n = 114.1
$HB{=}NH$	$C_{\infty v}$	A–E	BX = 1.196; BH = 1.141; XH = 1.009
$H_2B{-}NH_2$	C_{2v}	B–F	BX = 1.372; BH = 1.160; XH = 1.019; HBH = 121.1; HXH = 112.3
	C_s	C–H (H = o,p)	BX = 1.490; BH_d = 1.166; BH_e = 1.169; XH = 1.035; XBH_d = 120.1; XBH_e = 121.6; HXH = 102.3; BXH_{op} = 118.5
$H_3B{-}NH_3$	C_{3v}	D–I	BX = 1.657; BH = 1.162; XH = 1.032; XBH = 104.2; BXH = 111.7
	C_{3v}	D–H	BX = 1.678; BH = 1.161; XH = 1.032; XBH = 104.4; BXH = 111.9
$HB{=}O$	$C_{\infty v}$		BX = 1.176; BH = 1.142
$H_2B{-}OH$	C_s	C–H (H = n)	BX = 1.334; BH_d = 1.165; BH_e = 1.163; XH = 0.984; XBH_d = 121.8; XBH_e = 117.2; BXH = 112.3
	C_s	B–H (H = n)	BX = 1.370; BH = 1.170; XH = 0.980; BXH = 113.2; HBH = 118.6; XBH_{bc} = 183.5[d]
	C_{2v}	B–E	BX = 1.280; BH = 1.172; XH = 0.953; HBH = 118.6
$H_3B{-}OH_2$	C_s	D–I (H = q,r)	BX = 1.613; BH_f = 1.166; BH_g = 1.162; XH = 0.984; H_gBH_h = 115.6; HXH = 105.3; XBH_f = 103.8; XBH_{gh} = 115.0; BXH_{qr} = 127.5
$H_2B{-}F$	C_{2v}		BX = 1.293; BH = 1.167; HBH = 121.0
$H_3B{-}FH$	C_s	D–I (H = s)	BX = 1.605; BH_f = 1.161; BH_g = 1.163; XH = 0.952; H_gBH_h = 115.4; XBH_f = 101.3; XBH_{gh} = 112.5; BXH = 110.1
	C_s	D–H (H = n)	BX = 1.611; BH_f = 1.163; BH_g = 1.162; XH = 0.951; H_gBH_h = 116.3; XBH_f = 101.3; XBH_{gh} = 113.0; BXH = 110.9

[a] Refer to text and Figure 1. [b] Bond lengths in angstroms, angles in degrees. The notation "BAH_{gh}" specifies the angle between the plane H_gAH_h and the BA bond. [c] H_b, H_c trans to H_o, H_p. [d] H_b, H_c trans to H_n.

Table III. Geometry of Diborane, D_{2h}



Parameter	STO-3G	Bartell[a]	Kuchitsu[b]
B–B (Å)	1.805	1.775	1.774
$B{-}H_a$ (Å)	1.154	1.196	1.180
$B{-}H_b$ (Å)	1.327	1.339	1.329
$H_a{-}B{-}H_a$ angle	122.6°	120.2°	118.8°

[a] Electron-diffraction structure, ref 32a. [b] Refined structure, ref 32b.

but the 6-31G* energy appears to be the lowest single-determinant value available.[21]

B. B–B Compounds. Diborane(2) (HBBH) is predicted to have a linear triplet ground state ($^3\Sigma_g^-$) and is thus similar to the O_2 molecule. In O_2, two unpaired electrons occupy two degenerate π^* orbitals while, in B_2H_2, the two singly occupied orbitals are the degenerate π_u orbitals. At higher energy is the two π-electron $^1\Delta$ state, which was calculated with complex molecular orbitals.[26] There is no experimental evidence for BB multiple bonding.

Diborane(4) (H_2BBH_2), was optimized in both D_{2h} (planar) and D_{2d} (perpendicular) conformations; the latter is preferred by 10.5 kcal (6-31G*). This is qualitatively in accord with available data on the tetrachloro derivative, both theoretical[27] and experimental[28] investigations indicating a D_{2d} structure for B_2Cl_4, with r_{BB} = 1.702 Å. Not surprisingly, the bond length in B_2H_4 is predicted to be shorter (1.644 Å) and the rotation barrier higher than that found for B_2Cl_4 (1.85 kcal).

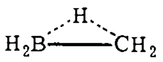
Diborane(6) (B_2H_6) is an important molecule synthetically[2,29,30] and theoretically[31-33] and has been the subject of numerous studies. The structure is well established and represents the first electron-deficient bridged structure for which the STO-3G geometry is experimentally verifiable. In Table III, the predicted structure is compared with the electron-diffraction structure of Bartell and Carroll[32a] and the refined structure of Kuchitsu[32b] which represents the nuclear configuration adjusted to absolute zero and for the effect of vibrational amplitude. The overall agreement is satisfactory.

In addition to the bridged B_2H_6 structure, we have investigated several alternative conformations, none of which were found to represent local minima on the potential-energy surface. Staggered and eclipsed homomorphs of ethane (H_3B-BH_3) were constructed with standard B-H lengths (1.16 Å), tetrahedral angles, and B-B = 1.70 Å; energies were −51.96044 and −51.95575 hartrees, respectively. Thus the staggered form lies 129 kcal above the bridged structure, in rough agreement with the value of 96 calculated by Allen and coworkers.[31a] At still higher energies were the planar D_{2h} structures obtained by 90° rigid rotation of the terminal hydrogens about the B-B axis (total energy = −51.75505), and a standard geometrical model of H_3B-H-BH_2 having one hydrogen on the B-B axis at 0.9 Å from each boron atom (energy = −51.91687, with no barrier to rotation). A discussion of the energies of B_2H_6 decomposition is reserved for a later section.

C. B–C Compounds. BCH is isoelectronic with the ethynyl cation,[7] and both structures are predicted to have triplet ground states. For BCH, this $^3\Pi$ state has three π electrons, while the excited singlet states have two ($^1\Delta$) and four ($^1\Sigma^+$); bond lengths vary accordingly, the shortest being that of the $^1\Sigma^+$ state. No other work has been reported on this species.

$HB{=}CH_2$ is isoelectronic and isostructural with the classical vinyl cation.[7,8] The BC bond is short (1.339 Å) and is indicated by population analysis to be of order two. Partial BC double bonding has been discussed, notably in vinylboranes,[34] but the isolated B=C moiety has not appeared in the literature. An STO-3G search was made for H-bridged structures, but no local minima were found.

Methylborane (H_2B-CH_3) has a sixfold rotational barrier which, as for other such barriers,[35,36] is small. Both conformations show strong structural similarities to the corresponding classical ethyl cations.[7,8] BCH_5 was not found to have a potential minimum corresponding to a bridged



$$H_2B\overset{H}{\text{———}}CH_2$$

structure. Methylborane has been isolated in dimeric form but prefers to disproportionate to B_2H_6 and its tetramethyl derivative.[2b,30] Structural data for trimethylborane[37] indicate a B-C length of 1.578 Å, in good agreement with our predicted methylborane value of 1.570 Å.

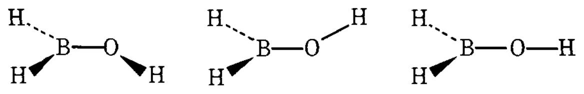
D. B–N Compounds. Iminoborane (HBNH) is predicted to be linear with a B-N bond slightly shorter than that found in a recent STO-3G study employing optimized exponents (1.196 vs. 1.23 Å).[38] Our results lead to similar conclusions concerning the bonding, as discussed below. Other recent ab initio studies have dealt with the processes of dimerization to a four-membered ring (predicted to be highly favorable, despite the unfavorability of the isoelectronic formation of cyclobutadiene)[39,40] and the trimerization to borazine.[40] Although unsubstituted iminoborane is not known, there is some experimental evidence for the existence of various Ar—B=N—Ar species.[41]

Aminoborane (H_2BNH_2) is isoelectronic with ethylene and has received much theoretical attention.[42] A reported partial geometry optimization[42d] gave a BN distance of 1.36 Å compared with the STO-3G value of 1.372. The favored conformation is predicted to be planar C_{2v}, with a barrier to rotation of 29.4 kcal (6-31G*). Previous determinations of this barrier have varied widely but have assumed rigid rotation; we find that, upon rotation from the planar form, the nitrogen assumes a pyramidal conformation so that rigid rotation is not a valid assumption here. At STO-3G, the barrier is 35.6 kcal assuming nonrigid rotation but increases to 43.1 if the amino group is held planar. This is in agreement with a very recent ab initio study[42f] employing full optimization of both conformations, resulting in BN distances of 1.378 (planar) and 1.469 Å (perpendicular), with a barrier to nonrigid rotation of 33.3 kcal. The barrier to rigid rotation was calculated as 42.7. Though planar H_2B-NH_2 is written formally with a single bond, we find the bond order to be close to two. In this light, we mention a recent ab initio study[39] examining the dimerization process, which is analogous to the dimerization of ethylene. The process is calculated to be favorable by 3 kcal/mol.

H_3B-NH_3 (amine-borane) has been studied extensively from several viewpoints. Of major interest is the relationship between amine-borane and ethane,[43] particularly with regard to the rotational barrier,[43-45] and the energetics of complex formation between BH_3 and NH_3;[46] other studies have addressed the questions of the degree of covalency in the BN bond[47] and the comparison of H_3BNH_3 with the $C_2H_6^{2+}$ dication.[48] We find that the barrier to nonrigid rotation is 1.93 kcal at 6-31G*, the staggered conformation being favored. Upon rotation to the eclipsed form, the BN bond increases in length from 1.657 to 1.678 Å, similar to the CC lengthening upon rotation of C_2H_6,[8] from 1.538 in the staggered conformation to 1.548 in the eclipsed. Previous theoretical studies have assumed rigid rotation. The best of these[43] employed a large basis with polarization functions on all atoms, giving a lower total energy than 6-31G* and a barrier of 3.06; however, for ethane the barrier was found to decrease from 3.65, assuming rigid rotation, to 3.07 with partial optimization, and a similar decrease might be expected for H_3B-NH_3. The BN distance in this compound was determined from X-ray data by two groups, who found 1.56[49a] and 1.6 Å.[49b] These are considerably shorter than the STO-3G value and other theoretical determinations of 1.66[46] and 1.73 Å.[48] The experimental dipole moment,[50] 4.9 D, compares acceptably with the 6-31G* value of 5.58 D for the staggered conformation. The topic of the binding energies of such Lewis acid-base complexes will be dealt with in a later section.

E. B–O Compounds. HBO is isoelectronic with HCO^+ and HCN; like these, it is predicted to be linear with four π electrons and short bond lengths. The species has been observed by ir spectroscopy.[51]

Hydroxyborane (H_2BOH) was considered in three conformations: a, b, and c. At both STO-3G and 6-31G*, the



a planar

b perpendicular

c BOH linear

planar form (a) is favored, and 90° rotation to b is predicted to be 4.82 kcal/mol (6-31G*) more favorable than linear inversion via c. This is in agreement with the qualitative conclusions of Mislow and coworkers[52] regarding rotation and inversion barriers in diarylalkoxyboranes. The 6-31G* rotation barrier (14.4 kcal/mol) is in rough agreement with that calculated in a recent ab initio study[53c] (16.4 kcal/mol) and is near those found experimentally[52] for B-OR rotation (12.6-13.7 kcal/mol). Structural data on $B(OH)_3$ indicate a BO length of 1.36 Å[53a] compared with the H_2BOH value predicted here of 1.334 Å. The microwave structure of F_2BOH has recently become available;[53b] it is planar with B-O = 1.34 Å and a B-O-H angle of 114.1°, compared with 112.3° predicted for hydroxyborane.

Evidence for the existence of the borane-water complex (H_3B-OH_2) has recently been deduced from kinetic studies

Table IV. Population Analyses[a]

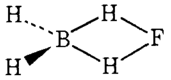
Molecule[b]	π overlap[c]	Charge (B)	Charge (X)	Gross charge transfer BH_n to XH_m
H_2B-BH_2	0.053	0.122	0.122	0.000
H_2B-CH_3	0.036 (0.082)	0.259 (0.239)	−0.303 (−0.206)	0.116 (−0.316)
H_2B-NH_2	0.238 (0.320)	0.269 (0.201)	−0.479 (−0.283)	0.099 (−0.386)
H_2B-OH	0.206 (0.262)	0.287 (0.284)	−0.338 (−0.117)	0.121 (−0.265)
H_2B-F	0.172 (0.191)	0.332 (0.390)	−0.175 (0.098)	0.175 (−0.098)
$HB=CH_2$	0.490 (0.518)	0.252 (0.283)	−0.339 (−0.060)	0.204 (−0.439)
$HB=NH$	0.802 (0.862)	0.290 (0.377)	−0.475 (−0.135)	0.261 (−0.298)
$HB=O$	0.706 (0.736)	0.298 (0.518)	−0.290 (0.110)	0.290 (−0.110)

[a] Consult text for definitions. Values in parentheses refer to isoelectronic carbocations, calculated in ref 8. [b] In lowest energy conformation. [c] Compare $HC\equiv CH$ (0.98) and $H_2C=CH_2$ (0.40).

in which $HOBH_3^-$ was identified by ^{11}B NMR.[54] Like the isoelectronic analog, CH_3NH_2,[8] we find a slight favoring of the staggered conformation over the eclipsed, both having long coordinate bonds (1.613, 1.624 Å). Though these bonds are not as long as those in H_3B-NH_3, the rotation barrier, 0.71 kcal, is somewhat smaller.

F. B-F Compounds. H_2BF is found to be planar, with a BF distance of 1.293 Å, close to that (1.295) observed for BF_3.[53a] Many R_2BF species are known, but the parent R = H compound tends to disproportionate to BF_3 and B_2H_6.[55]

6-31G* calculations on STO-3G minimized geometries of H_3B-FH indicate a very small barrier to rotation, 0.05 kcal/mol. However, the total energy is above the 6-31G* energy for the separated species, BH_3 + HF. As with H_3BNH_3 and H_3BOH_2, no potential minima were found corresponding to bridged forms, such as shown below.



Charge Distributions. In Table IV are presented selected quantities from the Mulliken population analyses[56] of the STO-3G wave functions. The species listed are those having closed-shell ground states and are considered in lowest energy geometries. The following quantities are given.

A. π overlap is the population of the overlap between the formally empty 2p orbital on boron [the p(B) orbital] and the coplanar 2p orbital on X. For multiply bonded structures, such overlap occurs in two planes (π_x and π_y) so the value given is the sum or total π overlap. An assessment of the π-bond order is possible by comparing the corresponding values for ethylene (0.40) and acetylene (0.98).

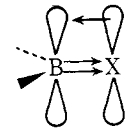
B. Charge is the total electronic deficiency or atomic charge on the boron (B) or the attached atom (X).

C. Gross charge transfer is the total number of electrons, both σ and π, polarized toward the substituent group from the BH_n group. This number is obtained by summing the total charges on the atoms of the BH_n group and subtracting from the sum of the atomic numbers. Thus, the value of +0.204 for $HB=CH_2$ indicates that the BH group is deficient by 0.204 electrons. Values in parentheses are the corresponding quantities for the appropriate carbocations. We first discuss the boron values.

In H_2B-BH_2, electron deficiency at boron is relieved by B-H hyperconjugation, which accounts for the substantial π overlap, the perpendicular structure, and the sizeable barrier to rotation (10.5 kcal/mol at 6-31G*). In the planar form (not given in Table IV), hyperconjugation is conformationally inhibited, p(B) orbitals empty, and there is no π overlap. Furthermore, as stated above, the rotation barrier in B_2Cl_4 is much smaller than in B_2H_4, presumably for two reasons: first, because B-Cl hyperconjugation is expected to be less effective than B-H;[36] and second, because p(B) orbitals are populated by π overlap with Cl atoms and need not rely on hyperconjugative stabilization.

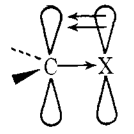
The π overlap values indicate that boron-carbon bond orders are accurately represented by classical valence structures. Values for $HBCH_2$ and H_2BCH_3 indicate double and single bonding, respectively. For other substituents, however, formal structures are somewhat misleading, as bond orders in H_2B-X species are substantially above one, and those in HB=X species are close to three. As has been observed in other contexts,[5] π donation decreases with increasing electronegativity, N > O > F.

In every case, the boron atom is positively charged, the more so the more electronegative the substituent. Furthermore, gross charge-transfer values are all positive, indicating a net polarization of electrons away from the borane group. Considered together, these figures lead to an interpretation of boron as a strong σ donor and weaker π acceptor, the overall effect being a transfer of electrons towards X:



As has been pointed out by Hoffmann,[42a] this implies that resonance forms are not accurately represented with a negative charge on boron.

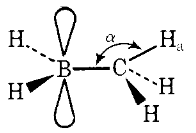
π-Overlap values for the cations are uniformly higher than those for boranes. Analogous observations apply concerning bond orders. The carbon atom is in every case more positive than the substituent heavy atom, but gross charge-transfer values in the cations are negative. Thus, the major difference between the cations and boranes appears to be one of degree. Electron-deficient carbon, like boron, is a σ donor and π acceptor but, unlike boron, the latter dominates:



Net polarization is in this case away from the substituent X.[36,57]

These arguments are supported by examination of the optimized geometries (those for two-heavy-atom cations are summarized in ref 8). It is most illustrative to consider distortions from idealized geometries in which dicoordinate B or C^+ is linear; tricoordinate, trigonal planar; and tetracoordinate, tetrahedral. The following general rule appears to hold for these electron-deficient centers: distortions from idealized geometries occur in such a way as to maximize overlap with, and hence population of, one or both formally empty p orbitals. An example is illustrative.

For methylborane, we consider the perpendicular conformation:



Population of the p(B) orbital is possible by hyperconjugation with the CH_a bond, as has been discussed for the STO-3G structure of the classical ethyl cation.[36,58] In order to maximize this overlap, there is a tendency for H_a to move toward a bridging position, i.e., for α to decrease from its idealized value of 109.5°. For H_2B-CH_3, the STO-3G optimized value of α is found to be 107.4°, whereas the ethyl cation value is reduced still further to 102.2°. This is in accord with the higher π-overlap population in the latter. Other distortions from idealized geometries occur, e.g., as a result of hybridization changes from ideal $sp^{2.0}$ and $sp^{3.0}$ values; the majority of these occurs in the same direction in both cation and borane but are uniformly greater in magnitude in the cation. The case of $HB{=}CH_2$ vs. the vinyl cation is similar; $\angle HCH$ is 114.3° in the former, and 118.6° in the latter.[8]

In all structures, B-X bonds and B-H bonds are, of course, longer than the carbon analogs because of the larger covalent radius of boron. However, it is observed that the differences are not uniform and, in general, the situation is as follows: When there is a greater increase in π overlap upon going from the borane to the cation, the difference between B-X and C^+-H bond lengths is larger. Similarly, the difference between B-H and C^+-H bond lengths reflect varying degrees of change in hybridization. Thus the relatively large difference in π overlap between H_2B-NH_2 and H_2C^+-NH_2 is accompanied by substantial shortening of the central bond as well as of the C-H bonds.

We note briefly the relation between BN compounds and their neutral isoelectronic analogs. As mentioned above, BN bonds are close to, but not fully, triple and double for HBNH and H_2BNH_2; however, unlike the bonds in acetylene and ethylene, BN bonds are polarized. The implication is that, whereas the hydrocarbons are uniformly electron rich and are thus relatively poor 1,3-dipolarophiles, BN compounds should react more readily with dipolar reagents. A number of BN-containing five-membered rings have been synthesized on this basis.[41]

Stabilities

A. Hydrogenation Energies. Table V lists energies of reaction of selected structures with 1 mol of hydrogen, giving the indicated products. Although STO-3G hydrogenation energies are generally found to be unsatisfactory,[6] it has been shown that 6-31G* energies reproduce experimental data consistently.[14a] The following discussion refers to the 6-31G* results.

As for hydrocarbons, the negative hydrogenation energies for unsaturated structures indicate a preference for boron to be singly bonded. Apparently the stabilization gained from π overlap in multiply bonded structures is too small to offset the effect of decreasing the coordination number at boron, with concomitant decrease in electron delocalization due to β hydrogens.

For saturated structures, hydrogenation reactions may be written with various products, as follows:

$$H_2 + H_2B{-}XH_n \begin{cases} \longrightarrow BH_3 + XH_{n+1} & \text{(a)} \\ \longrightarrow {}^1\!/_2\, B_2H_6 + XH_{n+1} & \text{(b)} \\ \longrightarrow H_3B{-}XH_{n+1} & \text{(c)} \end{cases}$$

Reaction energies corresponding to (a) are given in the table, despite the fact that they do not represent quantities of experimental significance. These are expected to be subject to smaller correlation errors than reactions (b) and to fewer difficulties in interpretation than (c). Except for the case X = C, the (a) energies are positive with $E_N < E_O < E_F$. It is apparent that stabilization results from substitution of BH_3 with a π donor. Although the hydrogenation reactions are not isodesmic, and the bond correlation energies of H-H plus X-B might be different from those of B-H plus X-H, the 6-31G* basis generally gives hydrogenation energies correctly to within ±4 kcal/mol.[14a]

Table V. Calculated Hydrogenation Energies in kcal/mol

Reactant[a]	Product	STO-3G	6-31G*
H_2BBH_2	$2BH_3$	−8.27	−11.68
H_2BCH_3	$BH_3 + CH_4$	−7.76	−10.38
H_2BNH_2	$BH_3 + NH_3$	35.95	25.73
H_2BOH	$BH_3 + H_2O$	42.10	29.57
H_2BF	$BH_3 + HF$	48.67	35.36
HBBH[b]	H_2BBH_2	−101.05	−90.01
$HBCH_2$	H_2BCH_3	−87.73	−60.88
HBNH	H_2BNH_2	−56.45	−44.39
HBO	H_2BOH	−26.22	−16.69

[a] STO-3G energies for H_2 and XH_n species are from ref 8, 6-31G* from ref 14a. [b] Excited ($^1\Delta$) state.

Table VI. Estimated Heats of Formation

Molecule	$\Delta H_f°$, kcal/mol
BH_3	23[a]
H_2BBH_2	58
$H_2B{-}CH_3$	15
$H_2B{-}NH_2$	−14
H_2BOH	−64
H_2BF	−77
HBBH[b]	148
$HB{=}CH_2$	76
$HB{=}NH$	31
$HB{=}O$	−48
B_2H_6	10[c]

[a] Deduced from experimental B_2H_6 dissociation energy.[29e] [b] Excited ($^1\Delta$) state. [c] Experimental, from JANAF tables.[59]

Table VII. Estimated Bond Energies

Bond	Molecule	Bond energy, kcal/mol
B—H	BH_3	89
B—B	H_2BBH_2	61
B—C	H_2BCH_3	74
B—N	H_2BNH_2	104
B—O	H_2BOH	124
B—F	H_2BF	155
B=B	HBBH ($^1\Delta$)	44
B=C	$HBCH_2$	97
B=N	HBNH	137
B=O	HBO	204

B. Heats of Formation. The experimental heat of formation of B_2H_6 [$\Delta H_f°$ (298) = +9.8 kcal/mol][59] combined with the best experimental dimerization energy of BH_3 (36 kcal/mol)[29e] gives 23 kcal/mol as the heat of formation of BH_3. This value, combined with the 6-31G* hydrogenation energies of Table V and known data for NH_3, H_2O, and HF, allows the estimation of the heats of formation of the compounds we have studied (Table VI).

C. Bond Energies. Combining the heats of formation from Table VI with experimental values for the atomic ground states,[60] we may deduce the bond energies for the various bonds involving boron, assuming constant BH, CH, NH, and OH bond energies from BH_3, CH_4, NH_3, and H_2O. These are given in Table VII. Two points are noteworthy. First, formal double bonds B=C and B=N are only slightly stronger than the single bonds B—C and B—N. B=B is actually weaker than B—B, but the former

Table VIII. Borane Stabilization Energies[a] in kcal/mol

Molecule	STO-3G	6-31G*
$H_2B—BH_2$	−0.51	−1.30
$H_2B—CH_3$	11.09 (30.91)	11.97 (27.83)
$H_2B—NH_2$	55.97 (93.73)	53.24
$H_2B—OH$	58.46 (66.02)	57.37
$H_2B—F$	56.92 (32.07)	58.36

[a] Defined by the reactions $CH_4 + X–AH_2 \rightarrow X–CH_3 + AH_3$ where A = boron or C^+; values for the latter, in parentheses, are available from ref 8 and 14a.

Table IX. Complexation Energies[a] in kcal/mol

$H_3B \leftarrow D$	STO-3G	6-31G*
$H_3B—NH_3$	−46.05	−21.33
$H_3B—OH_2$	−40.99	−5.53
$H_3B—FH$	−32.03	+7.72

[a] Defined by $BH_3 + {:}D \rightarrow H_3B–D$. Donor energies from ref 8 (STO-3G) and 14a (6-31G*).

Table X. Standard Bond Lengths for B—X Bonds

Bond[a]	Length, Å
Single Bonds	
B3—H	1.16
B2—H	1.14
B3—B3	1.64
B3—C4	1.57
B3—C3	1.54
B3—N3	1.37
B3—O2	1.33
B3—F	1.29
Double Bonds	
B2=B2	1.43
B2=C3	1.34
B2=N2	1.20
B2=O1	1.18

[a] B3 represents tricoordinate boron, B2 dicoordinate, etc.

corresponds to a singlet excited state. The second point to note is that the strengths of the single bonds increase along the series:

$$\text{B-B} \sim \text{B-C} < \text{B-N} < \text{B-O} < \text{B-F}$$

Electronegativity differences, and, to a smaller extent, π-donating abilities are responsible for this order. The corresponding bonds between methyl and CH_3, NH_2, OH, and F follow the order:[60]

$$\begin{array}{ccccccc} \text{C—C} & \sim & \text{C—N} & < & \text{C—O} & < & \text{C—F} \\ 88 & & 87 & & 91 & & 109 \quad \text{kcal/mol} \end{array}$$

D. Stabilization Energies. A direct method of evaluating substituent stabilization of BH_3 is by means of stabilization energies. Ideally, these should be deduced from isodesmic reactions, but we will, instead, define the "borane stabilization reaction" as the isoelectronic analog of the methyl cation stabilization reaction[36] as follows:

$$CH_4 + X—BH_2 \longrightarrow X—CH_3 + BH_3$$

$$(\text{isoelectronic with } CH_4 + X—CH_2^+ \longrightarrow X—CH_3 + CH_3^+)$$

The former is not isodesmic and is subject to correlation error to the extent that C-H and B-X bonds differ from B-H and C-X.

Borane stabilization energies are presented in Table VIII for X = BH_2, CH_3, NH_2, OH, and F with corresponding cation stabilization energies in parentheses. Positive values indicate that stabilization is afforded by all substituents except BH_2.

If correlation errors are small, as seems probable, then the π-donating substituents NH_2, OH, and F all stabilize BH_3 by roughly the same amount, 53-58 kcal/mol, while CH_3 stabilizes by hyperconjugation to a much lesser degree (12 kcal/mol) and BH_2 is slightly destabilizing. This suggests, first, that unlike carbocation species, boranes are relatively sensitive to σ effects. Stabilization remains constant because of the compensating σ-donating and π-accepting ability of boron. For cations, it is observed that stabilization falls off in the order $NH_2 > OH > F > CH_3$, largely because of the difference in π-donor effects. This seems plausible in view of the fact that charged carbon, as mentioned above, is more reluctant to lose σ electrons than is neutral boron. Also, compared with N, O, and F, the weaker stabilization due to hyperconjugation by methyl is expected; such π donation is not as effective as that involving a lone pair.[5,36]

E. Dissociation of B_2H_6. A great deal of work has dealt with the dissociation reaction $B_2H_6 \rightarrow 2BH_3$. Experimental determinations of the reaction energy have varied widely,[29,30] reported values ranging from 25 to 59 kcal/mol, although it appears that they are converging to a limit near 35-40 kcal/mol. A recent kinetic study gave 36 kcal/mol.[29e]

Theoretical determinations also give a range of energies, but these are consistently lower than the experimental.[33] Kutzelnigg et al.[33b] find the discrepancy to arise from correlation, which, in their independent electron-pair approximation study, accounts for two-thirds of the diborane binding energy. Recently Lipscomb et al.[31d] have calculated B_2H_6 with a large basis, obtaining the lowest single-determinant energy yet calculated (−52.8331 hartrees), although they have not reported the same level of calculation of BH_3. Thus our 6-31G* energy represents the best near Hartree-Fock determination of the BH_3 dimerization energy to date; we find this energy to be 20.5 kcal. Applying Kutzelnigg's correlation difference (16.8 kcal) we estimate the reaction energy to be 37 kcal, which seems to agree reasonably with experiment. As mentioned above, the inclusion of d orbitals is important to this problem; without polarization, the dimerization energy is lower by 7.2 kcal. A full configuration interaction study is indicated, with inclusion of d orbitals in the boron basis.

F. Complexation Energies. Table IX gives energies of complex formation, corresponding to the reactions where D = NH_3, OH_2, and FH:

$$BH_3 + D \longrightarrow H_3B–D$$

6-31G* results indicate that H_3B-NH_3 is a stable complex, H_3B-OH_2 less so, and H_3B-FH is not stable. We may assess the effect of including polarization functions on H_3B-NH_3 formation; at 6-31G, complexation energy is −32.6 kcal, compared with −21.3 at 6-31G*. Clearly, minimal and unpolarized basis sets are inadequate to describe reactions of this type.

Standard Geometrical Models

To the table of standard bond lengths reported for compounds of carbon to fluorine,[4b] we add those given in Table X for B-X bonds, determined on the basis of the geometries given in Table II and those of other unpublished studies. Standard bond angles are taken to be 180, 120°, and tetrahedral (109.47122°) for di-, tri-, and tetracoordinate boron centers.

Conclusions

On the basis of this examination of one- and two-heavy-atom boron compounds, we suggest the following.

(1) Boron is best stabilized by direct attachment to lone pair π donors, and to strong σ acceptors; stabilization is also

afforded by hyperconjugation, multicenter bonding, and complexation with certain σ-donor molecules.

(**2**) Boranes are reasonable analogs of carbocations with regard to molecular geometry but exhibit reduced π-bonding ability, greater sensitivity to substituent inductive effects, and less tendency to form structures analogous to hydrogen-bridged carbocations.

(**3**) Polarization functions appear to be important in describing coordinate and multicenter bonds.

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