Inorg. Chem. **1991**, *30*, 3919–3927 **3919**

Table VIII. ^{195}Pt NMR Chemical Shifts (ppm) of H–T Amidate-Bridged Dimer and Monomer Complexes

compound	coord sphere	chem shift, ppm	ref
H–T $[Pt_2(NH_3)_4(DMGI)_2](NO_3)_2$ (**1**)	N_3O	−1770	this work
cis-$[Pt(NH_3)_2(DMGI)(H_2O)]^+$	N_3O	−2008	this work
H–T $[Pt_2(NH_3)_4(\alpha\text{-pyridone})_2](NO_3)_2$	N_3O	−1810	4
cis-$[Pt(NH_3)_2(\alpha\text{-pyridone})(H_2O)]^+$	N_3O	−2015	4
H–T $[Pt(NH_3)_2(\alpha\text{-pyrrolidone})_2]^{2+}$	N_3O	−1940	17
cis-$[Pt(NH_3)_2(DMGI)(DMSO)]^{2+}$ (**2**)	N_3S	−3133	this work
$[Pt(NH_3)_3(Me_2SO)]^{2+}$	N_3S	−3224	25
cis-$[Pt(^{15}NH_3)_2(H_2O)_2]^{2+}$	N_2O_2	−1593	25
cis-$[Pt(^{15}NH_3)_2(DMSO)(H_2O)]^{2+}$	N_2OS	−2813	25

$(DMSO)(H_2O)]^{2+}$ (−2813 ppm)[25] (Table VIII) indicates that substitution of a coordinated oxygen atom by a sulfur atom greatly displaces the chemical shift about −1300 ppm to higher field. The large high-field shift observed also in **2** strongly supports the sulfur coordination in **2**.

In D_2O, a similar solvolysis reaction occurs and a monomeric *cis*-$[Pt(NH_3)_2(C_7H_{10}NO_2)(H_2O)]^+$ is produced. However, unlike the case of DMSO, the coordinated DMGI rotates rapidly about the Pt–N bond, since only a single methyl ^{13}C peak is observed in Figure 3b. The difference of the rotational movement of the coordinated DMGI in DMSO and in D_2O seems to stem from the difference of the bulkiness of the coordinated DMSO and D_2O molecules. A DMSO molecule is considerably larger and therefore would hinder the free rotation of the adjacent DMGI molecule.

In other analogous amidate-bridged binuclear Pt complexes, ^{13}C and ^{195}Pt NMR measurements exhibit H–T and H–H isomerization in solution.[15–17] The present complex (**1**) does not undergo such isomerization; instead, it is solvolyzed to a monomer complex. The ease of the solvolysis reaction observed for **1** is probably due to the existence of the noncoordinating carbonyl group, which withdraws electrons from the amidate nitrogen atom and reduces electron density at the exocyclic oxygen atom coordinating to the Pt atom. Therefore, the coordinating oxygen atom becomes more easily displaced by other ligands, such as a solvent molecule. In α-pyridonate and α-pyrrolidonate ligands, whose analogous Pt(II) dimeric complexes exhibit only H–H to H–T isomerizaton, no such noncoordinating oxygen atom exists, and therefore the coordinating exocyclic oxygen atom would be more negatively charged and thus more favorable for coordination. This difference of the electron density and of the coordination ability of the carbonyl oxygen atoms in amidate ligands would be the cause of the different solution behaviors of amidate-bridged Pt(II) dimeric complexes. The cyclic voltammogram of **1** exhibits a quasi-reversible single redox wave at 0.665 V ($=(E_{pa} + E_{pc})/2$) vs SCE (E_{pa} = 0.69 V and E_{pc} = 0.64 V), which was confirmed by coulometry to correspond to a two-electron process, $[Pt^{III}{}_2(NH_3)_4(C_7H_{10}NO_2)_2L_2]^{n+} + 2e^- \rightleftarrows$ **1** (L is a solvent molecule or a counteranion). This potential is considerably higher than those of the previously reported analogous complexes with a α-pyridonate[6] or a α-pyrrolidonate[17] bridging ligand and is considered to reflect the fact that the electron-donating ability of the present ligand to a platinum atom is much decreased due to the electron-withdrawing nature of the noncoordinating oxygen atom.

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Supplementary Material Available: Details of the X-ray data collection (Table S1), anisotropic temperature factors (Table S2), the possible hydrogen bondings (Table S4), and the ^{195}Pt NMR spectrum (Figure S1) (6 pages); the observed and calculated structure factors (Table S3) (14 pages). Ordering information is given on any current masthead page.

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Structure and Bonding Trends in Two- and Three-Coordinate Boron Cations

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The electronic structure of two- and three-coordinate boron cations has been investigated with ab initio Hartree–Fock methods. The calculations successfully reproduce known boron cation molecular structures and can be used to predict reasonable geometries for cations that have not been characterized crystallographically. Substituent effects in both normal covalent and dative bonds were studied via calculated hydrogenation and dissociation reaction energies along with standard charge distribution analysis. The relative importance of σ and π effects in covalent bonding is dependent upon overall molecular coordination number and charge, with two-coordinate borinium cations relying most heavily on ligand π-donor ability, three-coordinate neutral boranes dominated by the ligand electronegativity (σ-donor capability), and three-coordinate borenium cations representing a compromise between these two. Dative bonding in the borenium cations is controlled by completely different effects; borinium cations are hard acids and thus bond strongly to hard bases and weakly to soft bases.

The structural chemistry of mononuclear boron is similar to that of traditional transition-metal coordination compounds. The bonding in the latter is typically characterized in terms of a two-electron dative donation from a formally neutral or anionic ligand to a central metal atom. A similar analysis is possible for boron compounds. For instance, the distribution of electrons in a neutral homoleptic three-coordinate boron compound can be represented as $B^{3+}(R^-)_3$, in which three anionic R groups donate two electrons each to the central cation to form three dative R–B σ bonds.[4] This complete charge separation does not accurately represent the bonding in either transition-metal or boron compounds, but it is suggestive of their reactivity and of possible variability in the coordination sphere. As with the transition-metal elements, we can envision a series of boron "coordination compounds" $BR_nL_m{}^{(3-n)+}$ that contain a variable number of neutral and anionic ligands (but with boron restricted to the +3 oxidation state). Such a coordination chemistry has been demonstrated for four-coordinate boron, for which all species ranging from $BL_4{}^{3+}$

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(4) Throughout this paper we will use R to denote a formally anionic two-electron donor, such as an alkyl, alkoxide, or amide, and L to denote a neutral two-electron donor, such as an amine, ether, or phosphine.

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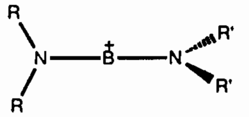
to BR_4^- are possible to prepare.[5] Lower coordinate boron complexes do not span such a broad range, but it is possible to generate stable two-coordinate borinium (BR_2^+) cations and three-coordinate borenium (BR_2L^+) cations along with the much more common neutral boranes (BR_3).[6]

The low-coordinate cations are of particular interest as possible intermediates in the reactions of substituted boranes. They are inherently reactive toward nucleophiles because of their coordinative unsaturation and electron-deficient character. In order to isolate members of these two series, it is necessary to employ bulky ligands that inhibit nucleophilic attack at the boron center. Steric bulk alone cannot compensate for inherent thermodynamic instability, however. It is further necessary to utilize ligands that can offset the large positive charge at the boron center by donating electron density through their σ or π manifolds. The amide (NR_2^-) ligand has been used most successfully to satisfy these steric and electronic requirements.

Nöth and co-workers[7,8] and Parry and co-workers[9] have synthesized two principle types of sterically encumbered borinium cations: $B(NR_2)_2^+$ (**1**) and $B(NR_2)R'^+$ (**2**) (R' = alkyl, aryl).



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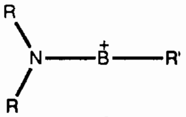
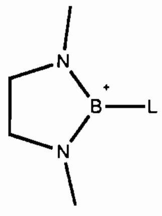


2

The linear, dicoordinate geometry about the central boron atom in these molecules is confirmed by ^{11}B and ^{13}C NMR spectroscopy. Crystal structures have been obtained for both (dimethylamino)(2,2,6,6-tetramethylpiperidino)borinium(1+)[7] (**3**) and bis(benzyl-*tert*-butylamino)borinium(1+)[8a] (**4**). In both structures the geometry about the ligand nitrogen atoms is planar rather than pyramidal, and the amide ligand planes are normal to one another, as diagramed in **1**. This conformation minimizes interligand steric repulsion and maximizes π overlap between the two vacant p orbitals on the central boron atom and the ligand π-donor orbitals. The staggered geometry is similar to that of the isoelectronic allene molecule and indicates significant double-bond character between boron and amide ligands. The B–N bond distance in **4** is 1.33 Å, which is intermediate between the 1.41-Å "single"-bond separation in chlorobis(benzyl-*tert*-butylamino)borane[8a] and the 1.21-Å triple-bond separation in (*tert*-butylimino)(2,2,6,6-tetramethylpiperidino)borane.[10]

A somewhat larger number of borenium cations have been isolated and characterized.[6,11] The majority contain two amide groups along with a neutral amine (NR_3) or, in one case, a triphenylphosphine ligand. While acyclic members of this class, such as $(Me_2N)_2B(py)^+$,[12] are possible to prepare, the cyclic analogues **5** and **6** are much easier to generate and study. Crystal structures of 1,3-dimethyl-2-phenanthridin-5-yl-1,3,2-diazaborolidinium(1+) (**5**, L = phenanthridine)[11b] and 2-(diphenylamino)-1,3-dimethyl-1,3,2-diazaborolidinium(1+) (**6**, R = phenyl)[11c] have been obtained. Both contain planar BN_3 units and two short (amide) and one long (amine) B–N separation. The B–NR_2 bond distances are in the range 1.38–1.41 Å. The planes of the amide groups are nearly coincident with the BN_3 plane and thus allow maximal B–N π overlap. Because both groups compete for bonding with one boron π orbital, the B–N bonds are longer than those in the related borinium cations but probably shorter and stronger than in neutral boranes. The boron-to-amine separations are much longer (1.53–1.55 Å), which reflects the difference in nitrogen hybridization and absence of significant π interactions. Dialkylborenium cations have also been prepared with aromatic amines as the third ligand. Again, the available data suggest a planar BX_3 core. The only crystallographically characterized species is a 9-borafluorenium cation, in which the electron-deficient boron atom is incorporated into an unsaturated organic ring.[11a] The π-donating ability of the aromatic amine has been suggested to play an important role in stabilizing all these cations.[6]



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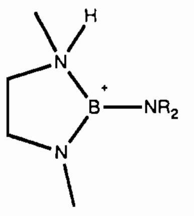

6

The known members of the two cationic series provide a rather limited basis for the comparison of boron-to-ligand bonding in unusual coordination environments. In almost all instances, it has been necessary to employ amide substituents in order to prepare isolable complexes. We want to analyze the boron-to-substituent bonding in a broader range of ligand sets, particularly for comparison to the corresponding neutral compounds. Electronic structure calculations provide an excellent means for obtaining and correlating bonding trends and substituent effects in boron cations. The calculations can be performed, and geometries and energies obtained, for molecules that are experimentally elusive but that are expected to have reasonable electronic stability. By comparison of the results to those for known compounds, the relative abilities of groups to stabilize an electron-deficient boron atom and the relative importance of π interactions in determining bond strength can be assessed.

Ab initio calculations are capable of making just such comparisons and predictions of structures and properties of small main-group compounds,[13] as has already been demonstrated for neutral boranes.[14] We present here the results of Hartree–Fock calculations on series of boranes, borinium cations, and borenium cations. We have investigated the influence of varying the σ- and π-donor ability of substituents on the molecular and electronic structure and stability of these compounds. Our goal is to obtain a better understanding of the factors that contribute to the stabilization of boron cations of mononuclear boron compounds in general.

Computational Details

Ab initio calculations have been performed on a series of homoleptic two-coordinate borinium cations BR_2^+ and related three-coordinate borenium cations BR_2L^+. Several mono- (RBH_2), di- (R_2BH), and trisubstituted (R_3B) neutral boranes have also been investigated to provide a basis for comparison of molecular and electronic structures. All calculations were performed by using either the Gaussian 86[15] or Gaussian 88[16] program suites on the Ohio Supercomputer Center Cray Y-MP/864 computer. For each molecule a geometry optimization and

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Table I. Total Energy and Proton Affinity for Small Molecules, Evaluated at the 6-31G*//6-31G* (STO-3G//STO-3G) Level

	total energy, au	proton affinity, kcal/mol
NH_3	−56.184 36 (−55.455 42)	217.4 (259.4)
$MeNH_2$	−95.209 83 (−94.032 86)	228.2 (268.4)
py	−246.695 82 (−243.638 61)	235.3 (277.1)
HCN	−92.875 20 (−91.675 21)	178.1 (202.5)
H_2O	−76.010 75 (−74.965 90)	174.8 (228.8)
H_2S	−398.667 32 (−394.311 63)	172.3 (223.0)
PH_3	−342.447 96 (−338.636 42)	196.8 (243.9)
CO	−112.737 88 (−111.225 45)	143.1 (175.6)
H_2	−1.126 83 (−1.117 51)	
CH_4	−40.195 17 (−39.726 86)	
HF	−100.002 91 (−98.572 85)	

analytical frequency calculation were performed at the restricted Hartree–Fock[17] (RHF) level with the STO-3G[18] basis set. The computed force constants and eigenvectors were then used to begin a second geometry optimization with the larger 6-31G*[19] basis set. This two-step procedure reduces significantly the amount of computation time relative to using the 6-31G* basis from the outset and facilitates the investigation of correspondingly larger systems.

For the two-coordinate borinium cations, complete gradient-based geometry optimizations were performed on the linear molecules (Table II). For the three-coordinate boranes (Table III) and borenium cations (Tables V–VII), geometry optimizations were performed with three restrictions. First, boron and the three adjoining atoms were constrained to be coplanar. Investigations with this condition relaxed did not reveal the existence of any nonplanar minima. Second, a plane of symmetry was imposed normal to the molecular plane, bisecting the two equivalent substituents, so that every molecule has at least C_s symmetry. Third, all trigonal ligands were constrained to have local C_{3v} symmetry. Relaxation of this constraint yields insignificantly perturbed molecular geometries and total energies (decrease in energy <0.2 kcal/mol). Standard Mulliken population analysis was used to partition the molecular charge density.[20]

In the cases in which comparisons can be made, there is excellent agreement between our calculated structures and experimentally determined ones. Computations at this level of theory are known to generate reasonable geometries for molecules that incorporate "normal" bonding modes.[21] However, we restrict ourselves to the comparison of geometries in like molecules, in the hopes that any systematic errors in the treatment cancel each other out. Similarly, when investigating various substitution and dissociation reactions, we do not suppose to calculate accurately the absolute energy of these processes but rather to reproduce the trends in a series of molecules.

In order to make energy comparisons among the boron compounds under consideration, the energies of various other small molecules are required, evaluated at a consistent level of theory. We have independently performed 6-31G* geometry optimization calculations for all the relevant species, and the results are collected in Table I. They are in agreement with published data.[22]

Results and Discussion

Structures of Borinium Cations. The molecular and electronic structure of borinium cations provides a good starting point for our investigation of boron coordination chemistry. The electronic factors that contribute to the stabilization of borinium cations have been investigated previously. Nöth and co-workers performed ab initio Hartree–Fock calculations using the STO-3G basis set on amide-, phenyl-, methyl- and hydrido-substituted dicoordinate boron cations $B(R)(R')^+$.[7] The relative stabilizing ability of these ligands was calculated to be R = H < CH_3 < Ph < NH_2 < NMe_2, consistent with the relative σ- and π-donating abilities of these groups. Further, in accord with NMR and crystal structure data, they found that the stabilization is maximized when the ligands orient themselves in a staggered (D_{2d}) geometry; for example, the all-planar (D_{2h}) form of $B(NH_2)_2^+$ was calculated to be 18 kcal/mol higher in energy than the staggered (D_{2d}) form. The calculated B–N bond distance in $B(NMe_2)_2^+$ is 1.325 Å, in good agreement with the crystal structure of bis(benzyl-*tert*-butylamino)borinium(1+) (4, B–N = 1.33 Å).[8a]

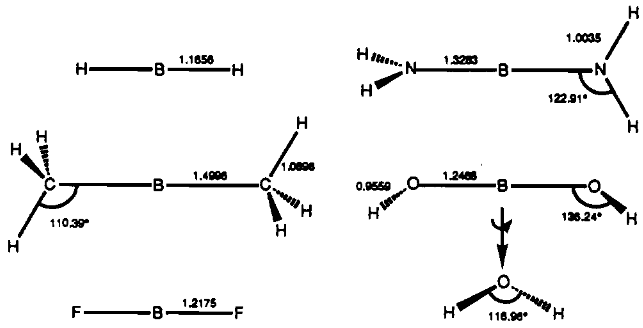

Figure 1. Important bond distances (Å) and bond angles (deg) for the two-coordinate borinium cations determined at the 6-31G*//6-31G* level.

We are interested in probing a wider range of substituents, in particular to compare them in the two-coordinate borinium and three-coordinate borenium cation environments. In order to evaluate more accurately the relative stabilizing abilities of various ligand sets, we have extended the earlier investigation to include restricted Hartree–Fock STO-3G and 6-31G* calculations on a series of five homoleptic two-coordinate boron cations BR_2^+, with R = H, CH_3, NH_2, OH, and F. This series spans a broad range of σ- and π-donating ability. Other workers have reported calculations on various members of this series, ranging from highly accurate geometry and potential energy surface investigations of BH_2^+[23] to qualitative semiempirical studies of the hydride-, methyl-, and amide-substituted cations.[24] The present report constitutes the first uniform theoretical treatment of these compounds.

The results of the borinium cation calculations are presented in Table II and Figure 1. For comparison, we also report the data for the corresponding disubstituted boranes R_2BH in Table III.[25] The STO-3G results for BH_2^+ and $B(NH_2)_2^+$ are identical with the ones reported earlier.[7] The equilibrium geometries determined with the two basis sets also agree rather well. In contrast, the Mulliken populations are very different, although population trends are similar.[13] In each case the equilibrium geometry has a linear R–B–R backbone with a boron-to-ligand bond distance shorter than that in the corresponding boranes (Tables II and III). Three factors combine to produce this decrease in bond length; first, the boron atom is more electron deficient and bonds more tightly to its ligands in the cations; second, interligand steric repulsion is diminished in the two-coordinate compounds; third, the availability of two vacant boron p orbitals facilitates greater boron–ligand π bonding than is possible with the one available p in the boranes. These influences are reflected both in the geometrical differences and in the Mulliken populations. For example, in every case the population of the boron pπ orbital, and by inference the degree of R–B π bonding, is greater in BR_2^+ than in R_2BH.

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Table II. Results of 6-31G*//6-31G* (STO-3G//STO-3G) Calculations on Linear Two-Coordinate Borinium Cations

	BH_2^+	$B(CH_3)_2^+$	$B(NH_2)_2^+$	$B(OH)_2^+$	BF_2^+
sym point group[a]	$D_{\infty h}$	D_{3d}	D_{2d}	C_{2v}	$D_{\infty h}$
tot. energy, au	−25.470 80 (−25.174 43)	−103.646 36 (−102.450 12)	−135.732 96 (−134.054 74)	−175.377 58 (−173.082 65)	−233.310 88 (−220.273 69)
B–R, Å	1.1656 (1.1864)	1.4996 (1.5126)	1.3283 (1.3258)	1.2468 (1.2548)	1.2175 (1.2415)
q_B[b]	0.5661 (0.7116)	0.7632 (0.7062)	0.7702 (0.7451)	0.8728 (0.8510)	1.0264 (1.0080)
p_π[c]	0.0 (0.0)	0.1289 (0.1488)	0.3355 (0.4402)	0.3143[d] (0.4762)	0.2629 (0.4281)

[a] Point group used in determining the structure of the lowest energy conformer. [b] Mulliken gross charge on the central boron atom. [c] Mulliken population of one of the two equivalent boron p orbitals normal to the R–B–R line. [d] Average of p_x and p_y populations.

Table III. Results of 6-31G*//6-31G* (STO-3G//STO-3G) Calculations on Neutral Planar Disubstituted Boranes R_2BH[a]

	BH_3	$BH(CH_3)_2$	$BH(NH_2)_2$	$BH(OH)_2$	BHF_2
tot. energy, au	−26.390 01 (−26.070 70)	−104.491 69 (−103.263 60)	−136.568 30 (−134.834 88)	−176.247 33 (−173.886 91)	−224.262 40 (−221.135 21)
B–R, Å	1.1883 (1.1600)	1.5829 (1.5769)	1.4123 (1.3989)	1.3561 (1.3554)	1.3057 (1.3024)
B–H, Å	1.1883 (1.1600)	1.1985 (1.1653)	1.1953 (1.1612)	1.1845 (1.1619)	1.1803 (1.1680)
R–B–R, deg	120.0 (120.0)	123.84 (123.16)	122.86 (121.82)	124.36 (124.62)	118.16 (118.24)
q_B[b]	0.1230 (0.1823)	0.4581 (0.3370)	0.5251 (0.4212)	0.5574 (0.4286)	0.7014 (0.4894)
p_π[c]	0.0 (0.0)	0.0647 (0.0740)	0.3291 (0.4241)	0.2727 (0.4232)	0.2178 (0.4046)

[a] All molecules optimized under C_{2v} symmetry, except for BH_3, which has D_{3h} symmetry. [b] Mulliken gross charge on the central boron atom. [c] Mulliken population of the boron p orbital normal to the molecular plane.

The BR_2^+ (R = CH_3, NH_2, OH) cations adopt staggered conformations consistent with the minimization of interligand steric repulsions and maximization of boron-to-ligand multiple bonding. Essentially no barrier to ligand rotation is present in $B(CH_3)_2^+$, because the methyl groups are well-separated by the central boron atom and π hyperconjugation between the methyl groups and boron is essentially invariant to methyl orientation. In contrast, the calculated barrier to ligand rotation in $B(NH_2)_2^+$ is 11.7 kcal/mol at the 6-31G* level. The more stable D_{2d} conformation, which is isoelectronic with allene, contains two independent, degenerate B–N π bonds (**7**). Rotation to the D_{2h} conformation replaces these two with a π-bonding molecular orbital delocalized over all three centers and a nonbonding orbital localized on the nitrogens (**8**)—a structure isoelectronic with the allyl anion. Thus, rotation to the D_{2h} geometry leads to a net loss of π bonding. The total boron pπ population decreases from 0.67 to 0.54 electrons and the B–N bond length increases 0.01 Å, both manifestations of this loss.

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The B–O–H linkages in $B(OH)_2^+$ are bent to 136.2° at the 6-31G* level, and the dihedral angle between the two B–O–H planes is 117°. The hydroxide ligands can donate up to eight electrons for π-bond formation, but the central boron atom has only two orbitals available for accepting π-electron density. To avoid excessive build-up of π density and unfavorable electron–electron repulsions at the central atom, each of the hydroxide ligands rehybridizes one of its occupied π orbitals away from boron by bending at oxygen. The two remaining pairs of unhybridized π orbitals form π bonds of the type diagramed in **7**. The optimal orbital situation occurs when the B–O–H planes are perpendicular, although the majority of π bonding is maintained in any rotamer. Steric repulsion between the two hydrogens forces these two planes apart to the calculated 117° angle. The barrier to rotation in the dihydroxide cation is 1.2 kcal/mol, with the eclipsed geometry highest in energy. This small barrier reflects the weak dependence of π bonding on orientation and the minimal steric interactions between the well-separated hydrogens.

Bonding Trends in Borinium Cations. The influence of substituent groups on the structure, bonding, and reactivity of neutral, anionic, and cationic organic species has received considerable attention.[26] We have explored the effects of various substituents on the stability of BR_2^+ cations by calculating their relative "R affinity". While it is difficult to construct an absolute affinity scale, particularly at the Hartree–Fock level of calculation, it is possible to devise a relative scale by comparing the exchange of R groups between boron and a given reference fragment, such as a methyl group (eq 1).[14,27] The enthalpy change for the

$$BH_2R + CH_4 \rightarrow BH_3 + RCH_3 \qquad (1)$$

reaction in eq 1 is related to the difference in strength of the $R–BH_2$ and $R–CH_3$ bonds. When analyzed as a function of R, the energy of the reaction is a gauge of the relative R affinity of the boron fragment. In this study we have found it more convenient to utilize the related hydrogenation reaction (eq 2).[27] This

$$BH_mR_n + nH_2 \rightarrow BH_{m+n} + nRH \qquad (2)$$

scheme compares R–B and R–H bond energies and facilitates a readier generalization to both boranes and borinium cations. We

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(26) (a) Schleyer, P. v. R. *Pure Appl. Chem.* **1987**, *59*, 1647–1660 and references therein. (b) Reference 13, pp 346–356 and references therein.

(27) (a) Pross, A.; Radom, L. *Tetrahedron* **1980**, *36*, 673–676. (b) Dill, J. D.; Schleyer, P. v. R.; Pople, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 3402–3409.

Table IV. Energy of Hydrogenation of Substituted Boranes and Borinium Cations BH_mR_n (Eq 2) Evaluated at the 6-31G*//6-31G* Level (kcal/mol)

	$m = 2$, $n = 1$[a]	$m = 1$, $n = 2$	$m = 0$, $n = 3$[b]	$m = 0$, $n = 2$
H	0.0	0.0	0.0	0.0
CH_3	−10.5	−22.0	−33.8	24.4
NH_2	26.1	39.7	47.2	92.3
OH	29.8	56.2	87.8	87.2
F	35.2	75.4	111.2	55.2

[a] Calculated from data in ref 14. [b] Calculated independently by us but consistent with data in ref 22.

prefer hydrogen as a standard because of the absence of π-bonding modes in X–H bonds, hydrogen's intermediate electronegativity, and its small size (for computational expediency). The conclusions drawn from the energies of eqs 1 and 2 should be equivalent.

The energy changes for eq 2 as a function of m, n, and R are presented in Table IV. The first, second, and third columns in the table contain the substituent stabilization energies of mono-, di-, and trisubstituted boranes, respectively, while the last column contains the stabilization energy of the BR_2^+ cations. For all the neutral boranes, the order of stabilization is $CH_3 < H < NH_2 < OH < F$. This ordering is similar to that observed by Schleyer et al. in their application of eq 1.[14] We consider first the monosubstituted boranes H_2BR. With use of the transition-metal chemistry analogy, the B–R bond in H_2B–R can be decomposed into the interaction of an anionic, two-electron donor R^- group with a cationic H_2B^+ fragment. The strength of this interaction depends on the electron-donating ability of the R^- group and the electron-accepting ability of the H_2B^+ fragment. Because H_2B^+ is more electron-rich than the H^+ reference employed in eq 2, it should have a greater preference for bonding to weak σ donors, such as F^-, but a lesser preference for bonding to strong donors, such as CH_3^-. The intermediate members of the substituent series fall in line according to their relative donor ability or, equivalently, group electronegativity. Because the relative strength of the H_2B–R interaction is a function of the match in donor and acceptor abilities, or electronegativities, of the R^- and H_2B^+ components, σ-bond effects play the largest role in determining the stability of these boranes.[25,27a]

The more highly substituted boranes HBR_2 and BR_3 also show a direct correlation between substituent donor ability and borane hydrogenation energy. In fact, a linear relation exists between the hydrogenation energy and the number of substituents in the H, CH_3, OH, and F derivatives: the B–R hydrogenation energies are nearly additive upon di- and trisubstitution. It strikes us as rather remarkable that inductive effects do not play a larger role in dictating the relative B–R bond strengths and that these bond strengths are virtually invariant to the number of R substituents. In contrast, the amide derivatives do not conform to an additive bond-energy relationship. Each additional amide substituent decreases the energy necessary to replace a B–N bond with a B–H bond, because of the complications of B–N π bonding. The central boron atom is nearly saturated with π-electron density with only one pendant amide group, and additional groups compete for and reduce the average π interaction. This π effect is of only secondary importance, however, since the comparatively low electronegativity of the amide group assures that it is more easily replaced than the weaker donor groups.

The order of substituent stabilization for the borinium cations is $H < CH_3 < F < OH < NH_2$. This ordering is consistent with the one that was reported earlier,[7] but it is decidedly different from the one described above for the saturated boranes. The calculations indicate that the different ordering is due to changes in σ- *and* π-bonding effects. In the BR_2^+ cations the central boron atom is less electron-rich than in the substituted boranes; strong σ-donor substituents are more readily accommodated in the former than in the latter. For instance, hydrogenation of $B(CH_3)_2^+$ is calculated to be 46 kcal/mol more endothermic than hydrogenation of $HB(CH_3)_2$. The methyl group is a strong σ-donor substituent and is better accommodated in the borinium cation than in the borane. In contrast, hydrogenation of BF_2^+ is calculated to be 20 kcal/mol more exothermic than hydrogenation of HBF_2, because fluoride is a poor σ-donor substituent. On the basis of σ effects alone, one would anticipate the amide and hydroxide complexes to fall between these two extremes, but the π-donating ability of these substituents must also be considered.

The two vacant p orbitals on the central boron atom, plus the net positive charge of the molecule, greatly increase the propensity for and importance of π-bond formation in the borinium cations relative to the boranes. In $B(CH_3)_2^+$, hyperconjugation increases the strength of the B–C bonds, although the exact extent is difficult to estimate. Mulliken population analysis indicates that the pπ population in $HB(CH_3)_2$ is only 0.065 electrons, as compared to 0.129 electrons in each of the two perpendicular pπ orbitals of $B(CH_3)_2^+$, for a net 4-fold increase in total π population in the latter. A commensurate increase in π-bond strength is expected. Hydrogenation of $B(NH_2)_2^+$ is calculated to be 53 kcal/mol more endothermic than hydrogenation of $HB(NH_2)_2$. This difference is greater than that calculated for the methyl ligand above and clearly cannot be the result of the amide ligand's σ-donating ability alone. Rather, π bonding adds substantially to the energy of the B–N bond in the two-coordinate cation compared to the three-coordinate molecule. Similarly, the hydrogenation energy of $B(OH)_2^+$ is 31 kcal/mol greater than that of $HB(OH)_2$. It is interesting to note that the Mulliken populations of the boron pπ orbitals correlate directly with the borinium hydrogenation energy and therefore presumably with the extent of π bonding. By this measure, BH_2^+ is the least stable and $B(NH_2)_2^+$ the most stable borinium cation. We expect alkoxide ligands, which are also potent π donors, to be good candidates for the formation of stable borinium cations, if ligands can be designed to provide sufficient kinetic stabilization.

Structures of Borenium Cations. Now that the relative importance of the bonding components in the borinium cations has been assessed, the corresponding borenium cations can be analyzed. It is convenient to consider a borenium cation R_2BL^+ to arise from the addition of a neutral base L to a borinium cation (eq 3).

$$BR_2^+ + L \rightarrow BR_2L^+ \tag{3}$$

Besides representing an important synthetic method for forming borenium cations, eq 3 emphasizes the electronic similarities between the two- and three-coordinate cations and promotes a comparison of substituent effects in both. As in transition-metal compounds, the B–R interactions are expected to be much more robust than the B–L ones (because the boron oxidation state is fixed), and the former will have a greater influence on the structure and stability of the three-coordinate cations than the latter. Thus, the BR_2^+ and L fragments are naturally separable. A neutral borane BR_2R' can also be decomposed into BR_2^+ and R'^- fragments, but because the B–R and B–R′ interactions are of comparable energetic magnitude, the separation of structural and energetic effects is not as clean. Nonetheless, the series of compounds BR_2^+, BR_2L^+, and BR_2H can be considered as unsubstituted, neutrally substituted, and anionically substituted borinium cations, and the structural and stability trends in each class can be compared. As will be shown below, the borenium cations are electronically and structurally intermediate between the borinium cations and the neutral boranes.

We first consider structural variations among the borenium cations as a function of the R group, holding L constant. Because amine ligands are ubiquitous in borenium cation chemistry, the ammonia adduct series $R_2B(NH_3)^+$ (R = H, CH_3, NH_2, OH, F) is a logical starting point. The computed results for the series are presented in Table V and Figure 2 and are representative of other adducts. Several unifying features are immediately apparent. The B–R bond lengths are intermediate between those in BR_2^+ (Table II) and R_2BH (Table III) but are closer to the latter. Addition of a third ligand into the BR_2^+ coordination sphere (be it H^- or NH_3) changes the hybridization of boron from sp to sp^2, leading to an increase in B–R bond lengths. Further, one less p orbital is available for π-bond formation in the three-coordinate species, and π bonding is commensurately weaker. In contrast,

Table V. Results of 6-31G*//6-31G* (STO-3G//STO-3G) Calculations on Ammonia-Substituted Borenium Cations $R_2B(NH_3)^+$[a]

	$H_2B(NH_3)^+$	$(CH_3)_2B(NH_3)^+$	$(H_2N)_2B(NH_3)^+$	$(HO)_2B(NH_3)^+$	$F_2B(NH_3)^+$
tot. energy, au	-81.801 00 (-80.842 31)	-159.921 49 (-158.054 43)	-192.005 46 (-189.638 23)	-231.681 58 (-228.687 68)	-279.657 04 (-275.909 40)
B-R, Å	1.1729 (1.1636)	1.5572 (1.5596)	1.3863 (1.3799)	1.3202 (1.3253)	1.2752 (1.2795)
B-N, Å	1.5607 (1.5619)	1.5991 (1.5929)	1.5859 (1.5868)	1.5641 (1.5834)	1.5519 (1.5935)
R-B-R, deg	128.76 (128.48)	131.88 (131.22)	129.71 (129.14)	135.76 (137.26)	127.72 (128.38)
q_B[b]	0.3435 (0.4263)	0.7004 (0.5491)	0.8259 (0.6400)	0.8099 (0.6682)	0.9693 (0.7629)
p_π[c]	0.0108 (0.0231)	0.1049 (0.1212)	0.4051 (0.5237)	0.3290 (0.5074)	0.2553 (0.4586)
B-N BDE,[d] kcal/mol	91.5 (133.3)	57.0 (93.4)	55.3 (80.4)	75.1 (93.9)	101.5 (113.1)

[a] All molecules optimized under C_s symmetry with NH_3 and CH_3 groups restricted to local C_{3v} symmetry. [b] Mulliken gross charge on the central boron atom. [c] Mulliken population of the boron p orbital normal to the molecular plane. [d] Homolytic bond dissociation energy, $R_2B-NH_3^+ \rightarrow R_2B^+ + NH_3$. See text.

Table VI. Results of 6-31G*//6-31G* (STO-3G//STO-3G) Calculations on H_2BL^+ Cations

L	coplanar H_2O	perpendicular H_2O	coplanar py	perpendicular py	NH_2Me	HCN	CO	PH_3[a]	H_2S
sym point group	C_{2v}	C_s	C_{2v}	C_{2v}	C_s	C_{2v}	C_{2v}	C_s	C_s
tot. energy, au	-101.600 58 (-100.347 48)	-101.578 18 (-100.320 45)	-272.350 07 (-269.062 68)	-272.330 02 (-269.044 82)	-120.839 85 (-119.429 76)	-118.459 21 (-117.005 34)	-138.263 31 (-136.508 10)	-368.024 72 (-363.989 25)	-424.225 22 (-419.649 82)
B-H, Å	1.1695 (1.1637)	1.169[b] (1.168)	1.1756 (1.1602)	1.1766 (1.1651)	1.1744 (1.1628)	1.1708 (1.1666)	1.1704 (1.1678)	1.1754 (1.1612)	1.1722 (1.1618)
B-L, Å	1.4577 (1.4278)	1.5385 (1.4993)	1.4893 (1.4917)	1.5337 (1.5364)	1.5414 (1.5516)	1.5189 (1.5336)	1.6806 (1.6679)	1.9880 (1.9470)	1.9192 (1.8897)
H-B-H, deg	132.90 (130.62)	133.30 (130.28)	125.86 (125.70)	126.24 (125.64)	127.71 (127.70)	130.69 (130.24)	134.40 (132.44)	127.28 (126.29)	130.88 (136.94)
q_B[c]	0.3651 (0.4386)	0.4393 (0.4662)	0.3075 (0.3862)	0.3503 (0.4142)	0.3313 (0.4115)	0.3453 (0.4602)	0.2853 (0.4082)	0.0406 (0.2161)	0.1213 (0.2542)
$p_\pi(B)$[d]	0.0568 (0.0983)	0.0109 (0.0230)	0.0760 (0.0946)	0.0105 (0.0171)	0.1199 (0.1331)	0.0276 (0.0375)	0.0031 (0.0060)	0.0066 (0.0101)	0.0309 (0.0436)
B-L BDE,[e] kcal/mol	74.7 (130.0)	60.6 (113.0)	115.1 (156.6)	102.5 (145.4)	99.9 (139.6)	71.0 (97.7)	34.3 (67.9)	66.5 (112.0)	54.7 (102.8)

[a] PH_3 ligand restricted to local C_{3v} symmetry. [b] Average of two inequivalent values under C_s symmetry. [c] Mulliken gross charge on the central boron atom. [d] Mulliken population of the boron p orbital normal to the molecular plane. [e] Homolytic bond dissociation energy, $H_2BL^+ \rightarrow H_2B^+ + L$. See text.

the overall positive charge of the three-coordinate cations contracts the boron atomic orbitals and reduces all bond lengths relative to the neutral boranes. These competing effects interact to produce the observed bond length trends.

The borenium cations are trigonal planar, in accord with simple bonding considerations, but the R-B-R bond angles are all at least 8° greater than ideal trigonal, even with the small hydride and fluoride R groups, and are up to 11° larger than the corresponding angles in R_2BH (Table III). Even though ammonia is a larger substituent than hydride, the latter impinges more strongly on the boron coordination sphere and causes a greater bending back of the R groups. The $B-NH_3$ bond distances (1.55-1.60 Å) are substantially longer, and the interactions correspondingly weaker, than the $B-NH_2$ bond (1.471 Å) in the essentially σ-only perpendicular H_2BNH_2.[28] The dative interaction between R_2B^+ and NH_3 is not as strong as the more covalent B-H interaction in R_2BH; the structural properties of the $R_2B(NH_3)^+$ cations reflect its close relationship to the parent BR_2^+ cation.

It is equally informative to consider structural variations as a function of L substituent. Table VI and Figure 3 contain the results of calculations on the series of molecules H_2BL^+ for L = pyridine, H_2O, HCN, CO, PH_3, $MeNH_2$, and H_2S. Combined with the results presented above for ammonia, this series spans a broad range of adduct sizes and donor abilities. The same information for a somewhat smaller series of $(H_2N)_2BL^+$ compounds is presented in Table VII. In both cases the calculated geometrical variations are fairly narrow. In the H_2BL^+ cations, the B-H bond distances range only from 1.170 to 1.177 Å, which is just between the 1.166-Å separation in BH_2^+ and the 1.188-Å

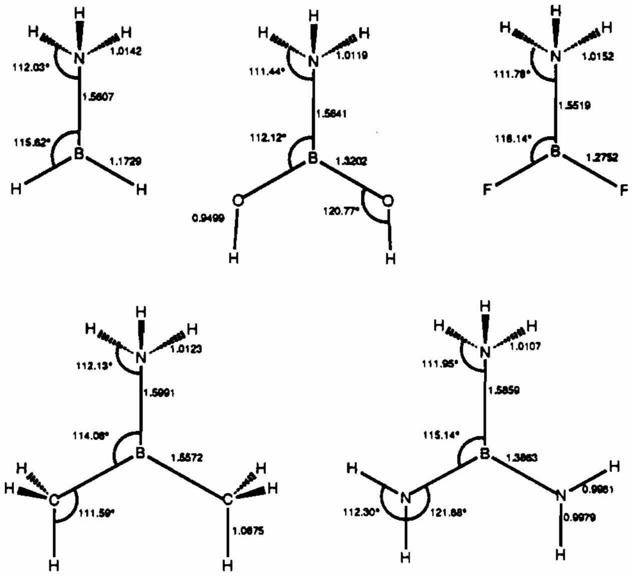

Figure 2. Important bond distances (Å) and bond angles (deg) for amine-substituted borenium cations determined at the 6-31G*//6-31G* level.

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(28) Ortiz, J. V. *Chem. Phys. Lett.* **1989**, *156*, 489-493.

Table VII. Results of 6-31G*//6-31G* (STO-3G//STO-3G) Calculations on $(H_2N)_2BL^+$ Cations

L	coplanar H_2O	perpendicular H_2O	coplanar py	NH_2Me	HCN	CO	PH_3[a]
sym point group	C_{2v}	C_s	C_{2v}	C_s	C_{2v}	C_{2v}	C_s
tot. energy, au	−211.797 91 (−209.134 47)	−211.795 18 (−209.128 62)	 (−377.832 60)	−231.040 74 (−228.222 26)	−228.663 76 (−225.804 32)	−248.480 59 (−245.317 86)	−478.226 70 (−472.781 89)
B−N, Å	1.3808 (1.3798)	1.376[b] (1.376)	 (1.3888)	1.3893 (1.3814)	1.3811 (1.3771)	1.3750 (1.3737)	1.3876 (1.3812)
B−L, Å	1.5215 (1.4837)	1.5620 (1.5152)	 (1.5570)	1.5718 (1.5802)	1.5695 (1.5823)	1.7111 (1.6936)	2.0104 (1.9653)
N−B−N, deg	132.78 (131.16)	134.51 (131.53)	 (122.58)	128.68 (128.46)	132.52 (132.24)	136.40 (133.90)	129.36 (127.54)
q_B[c]	0.8782 (0.6736)	0.8277 (0.6604)	 (0.6306)	0.8457 (0.6315)	0.8261 (0.6752)	0.8012 (0.6138)	0.5714 (0.4545)
$p_\pi(B)$[d]	0.4035 (0.5341)	0.4341 (0.5457)	 (0.5095)	0.3907 (0.5174)	0.4196 (0.5458)	0.4547 (0.5959)	0.4186 (0.5308)
B−L BDE,[e] kcal/mol	34.0 (71.4)	32.2 (67.7)	 (87.4)	61.5 (84.5)	34.9 (46.7)	6.1 (23.6)	28.7 (56.9)

[a] PH_3 ligand restricted to local C_{3v} symmetry. [b] Average of two inequivalent values under C_s symmetry. [c] Mulliken gross charge on the central boron atom. [d] Mulliken population of the boron p orbital normal to the molecular plane. [e] Homolytic bond dissociation energy, $H_2BL^+ \rightarrow H_2B^+ + L$. See text.

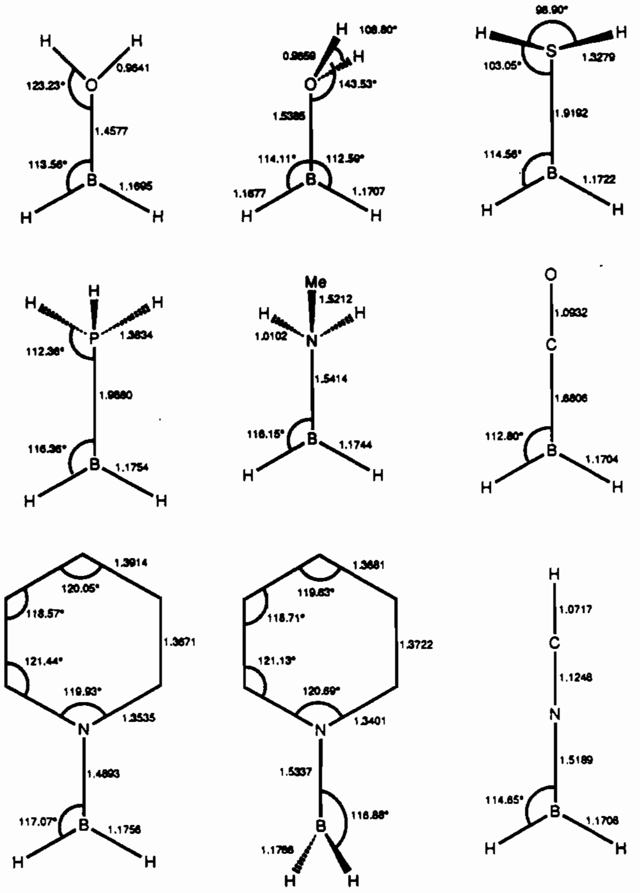

Figure 3. Important bond distances (Å) and bond angles (deg) for various substituted dihydroborenium cations determined at the 6-31G*//6-31G* level.

separation in BH_3. Similarly, the B−N separations in the $(H_2N)_2BL^+$ cations fall in the narrow region between those in $B(NH_2)_2^+$ and $B(NH_2)_3$ but closer to the latter. The B−R bond lengths in R_2BL^+ cations are relatively insensitive to changes in L because B−L bonding is weak compared to the B−R bonding.

Pyridine and water adducts have been studied in both a coplanar and a perpendicular conformation to examine the contribution of π bonding for these neutral ligands. We consider first the H_2BL^+ cations. Because the hydride ligands provide no π stabilization of the boron center, there is a preference for orientations that maximize the B−L π interaction. Both water and pyridine coordinate preferentially in a coplanar orientation with BH_2, which suggests that some π-bond interactions are present. The transition state for rotation about the B−N bond in the pyridine adduct is the perpendicular C_{2v} orientation. In the water adduct, the water ligand is pyramidalized rather than planar in the perpendicular transition state, as is the nitrogen in the isoelectronic perpendicular H_2BNH_2.[28] Pyramidalization alleviates the potential antibonding interaction between the occupied antisymmetric B−H σ bonds and the water lone pair (a two-orbital/four-electron hyperconjugative interaction). The hydrogen sulfide ligand prefers a pyramidal local geometry even in the coplanar orientation, indicating that π bonding between boron and sulfur is not as great as in the water adduct. π bonding between first- and second-row elements is known to be less effective than that between two first-row atoms.[29]

The loss of π bonding upon rotation of the L group is reflected both in a decrease in boron pπ population and an increase in boron charge in the perpendicular orientation, as well as in a substantial increase in B−L separation. Barriers to rotation, while not necessarily equivalent to π-bond energies, provide a good estimate of π interactions. The rotation barriers for water and pyridine in H_2BL^+ are calculated to be 14.1 and 12.6 kcal/mol, respectively, and indicate that both ligands act as π donors in these compounds, as was previously postulated for the latter.[6a] Further calculations on substituted borenium cations reveal that their ability to π donate is diminished in compounds that incorporate better donor R groups. For example, the barrier to water rotation in $(CH_3)_2B(OH_2)^+$ is 10.6 kcal/mol and in $(H_2N)_2B(OH_2)^+$ only 1.8 kcal/mol. Similar decreases are anticipated for pyridine adducts. As we will show below, the ubiquity of aromatic amine ligands in borenium cation chemistry is more a result of their σ basicity rather than their π basicity.

Bonding Trends in Borenium Cations. As with the borinium cations, it is possible to investigate trends in B−R bond strength by comparing the energies of hydrogenation. For this purpose we use the reaction in eq 4, which is similar to eq 2 used above

$$R_2B(NH_3)^+ + 2H_2 \rightarrow H_2B(NH_3)^+ + 2RH \qquad (4)$$

with the borinium cations. The energy change for eq 4 was computed at the 6-31G* level for five different R groups, and the energetic ordering obtained is CH_3 (−10.2 kcal/mol) < H (0.0) < NH_2 (56.1) < F (65.2) < OH (70.7). Comparing the two $n = 2$ columns in Table IV with these results, we see that this ordering is different from that in the borinium cations, where π effects were found to dominate, and from that in the disubstituted boranes, in which σ effects dominate. These trends are not unique

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(29) See for example: Magnusson, E. *J. Am. Chem. Soc.* **1986**, *108*, 11-16 and references therein.

to the ammonia adducts. Calculations using other neutral ligands, including water, hydrogen cyanide, and phosphine, yield the same results within a range of roughly 5 kcal/mol. Incorporation of a neutral donor ligand into BR_2^+ results in a fundamental change in the factors that determine B–R bond strengths. This reordering can be understood in terms of the same effects that govern the bonding in borinium cations and boranes.

The bonding in borenium cations is the result of a compromise between σ- and π-electronic effects. We compare first the differences in the σ-bonding effects in BR_2^+ and BR_2L^+ cations. In the former, the overall positive charge, combined with the presence of only two donor ligands, creates a local electron deficiency at the boron: strong σ- and π-donor ligands are necessary to stabilize the two-coordinate cation. When a neutral donor ligand is incorporated into the boron coordination sphere, the local electron density at boron increases via σ donation from L, and consequently the demand for σ- and π-electron density from the R groups is diminished. Thus, fluoride, which is a weak σ donor, is a much better ligand in BF_2L^+ than in BF_2^+: hydrogenation of both B–F bonds in $F_2B(NH_3)^+$ requires 10 kcal/mol more energy than hydrogenation of F_2B^+. On the other hand, the methyl ligand, which is a strong σ donor, is better accommodated in a two-coordinate cation than in a three-coordinate one. More than 30 kcal/mol more energy is required to hydrogenate both B–C bonds in $(CH_3)_2B^+$ than in $(CH_3)_2B(NH_3)^+$. A similar comparison can be made for disubstituted boranes R_2BH and borenium cations BR_2L^+. The hydrogen in the borane compounds is analogous to a strong donor, anionic L group. It donates more σ-electron density to boron than a neutral L group can, and hence, the boranes accommodate weak σ-donor R groups more readily than borenium cations can. Again with use of fluoride and methyl ligands as examples, 10 kcal/mol *more* energy is required to hydrogenate the B–F bonds in F_2BH than in $F_2B(NH_3)^+$, but 12 kcal/mol *less* energy is needed to hydrogenate the B–C bonds in $(CH_3)_2BH$ than in $(CH_3)_2B(NH_3)^+$.

π bonding in the borenium cations is also of intermediate importance between that in R_2BH and R_2B^+. For example, for the strong π-donor amide ligand, the energy to replace both amide groups with hydrogens falls in the order $(H_2N)_2BH$ (39.7 kcal/mol) < $(H_2N)_2B(NH_3)^+$ (56.1) < $B(NH_2)_2^+$ (92.3). The boron pπ orbital population increases in the same order, from 0.329 to 0.405 to 0.671 electrons. A nearly linear correlation exists between these two quantities. Note that the biggest incremental difference is between the borenium and borinium cations, so that π bonding is more similar in the two three-coordinate molecules than in the two cations. Similarly, the greater stability of B–C bonds in $(CH_3)_2B^+$ than in $(CH_3)_2B(NH_3)^+$, which was attributed above to the methyl group's strong σ-donor character, is also due in part to π stabilization brought about by hyperconjugation. Again, a linear correlation exists between the hydrogenation energy and boron pπ population. Hydroxide also fits into this category, but fluoride does not.

We can partition the R substituents into two sets, those whose hydrogenation energies increase in the series borinium to borenium to borane (eq 5) and those whose energies decrease in that order

$$BR_2^+ > BR_2L^+ > BR_2H \qquad R = F \tag{5}$$

$$BR_2^+ < BR_2L^+ < BR_2H \qquad R = CH_3, NH_2, OH \tag{6}$$

(eq 6). The former form strong polar-covalent σ bonds but are relatively poor π donors (fluoride). The latter are strong σ donors (methyl) and relatively good π (hydroxide and amide) donors. In borinium cations, the amide ligand is the most tightly bound ligand because of its strong π-donor ability. Hydroxide and fluoride are progressively poorer substituents; methyl is superior to hydride because it is a better σ donor (last column of Table IV). In the disubstituted boranes, fluoride is the most strongly bound ligand because it is the most electronegative and best accommodates an unequal sharing of electron density in the (relatively) electron-rich boron. Hydroxide and amide ligands are worse because of their greater electron-donating character. Likewise hydride is superior to methyl (first column of Table IV). Borenium cations represent a middle ground, both in terms of σ and π influences, and the most strongly bound R group is the one that represents the best compromise between the two. We calculate hydroxide to be the most difficult ligand to remove from the borenium cation coordination sphere, followed by fluoride and amide, and therefore expect that thermodynamically stable borenium cations with alkoxide substituents should be possible to prepare as long as sufficient kinetic stabilization can be obtained.

Neutral Ligand Affinities in Borenium Cations. So far we have concerned ourselves with structural variations and energy trends in B–R bonding in compounds of the form $R_2B(L)^+$ as a function of the presence and type of L substituent. This investigation has given us insight into the factors that determine the strength of B–R bonds, not only in the compounds that we have specifically considered but in boron compounds in general. Now we consider the electronic factors that govern the dative B–L interaction.

What ligands provide the greatest stabilization of borenium cations? To answer this question, we need to consider the relative strength of the B–L interactions for a series of L groups. As was posited above, it is natural to consider the B–L bond to arise from electron pair donation from L to a borinium cation, i.e. as a coordinate covalent bond. It is most useful, then, to investigate the heterolytic fission of the B–L bond (eq 7). Bond dissociation

$$R_2B{-}L^+ \rightarrow R_2B^+ + L \tag{7}$$

energies are notoriously difficult to examine, particularly at the Hartree–Fock level, but eq 7 represents the separation of a closed-shell singlet molecule into two other closed shell-singlet molecules and should therefore be handled reasonably well at this level of theory, and we expect the relative dissociation energies to be meaningful.

The calculated adduct bond dissociation energies for dihydrido- and diaminoborenium cations are presented in Tables VI and VII. Large quantitative discrepancies are present between the STO-3G and 6-31G* results, but both sets agree qualitatively. The former basis set is known to be inadequate to describe proton affinities[30] and four-coordinate boronium cation dissociation energies,[27b] but the latter performs reasonably well. The 6-31G* data span a wide energetic range, with CO forming the worst and pyridine the best adducts. It has been suggested on the basis of core electron binding energies that a correlation exists between the proton affinity of L and the strength of the B–L interaction in the boronium cations H_3BL^+.[31] We have investigated a similar relation for the borenium cations. Figure 4 is a plot of the calculated bond dissociation energy (eq 7) vs the calculated proton affinity of the ligand L for H_2BL^+ and $(H_2N)_2BL^+$ adducts. A linear correlation appears to exist between the two quantities: linear regression yields correlation coefficients of 0.946 (slope = 0.606, intercept = −78.6) and 0.977 (slope = 0.729, intercept = −68.3) for the $(H_2N)_2BL^+$ and H_2BL^+ data, respectively. Two points are plotted for both pyridine and water, corresponding to the coplanar and perpendicular orientations of these groups. The difference corresponds to the rotational barrier discussed above. The perpendicular data points, which do not contain the influence of π effects on bonding, correlate much better with the rest of the data and are used in generating the lines shown.

The approximately linear energy relationship that exists between the bond dissociation energy and proton affinity in the series of Lewis bases considered suggests an electronic kinship between the bonding forces in the two Lewis acids involved, the proton and the borinium cations. While there is surprisingly little agreement on the precise balance of factors that control Lewis acid reactivity in general,[32] it is clear that there is a large electrostatic or "charge-control" influence in the reactivity of protons in the gas phase.[33] The linear energy relationship allows us to draw a similar conclusion for the borinium cations. The electrostatic interaction between cation and base is more significant than the orbital

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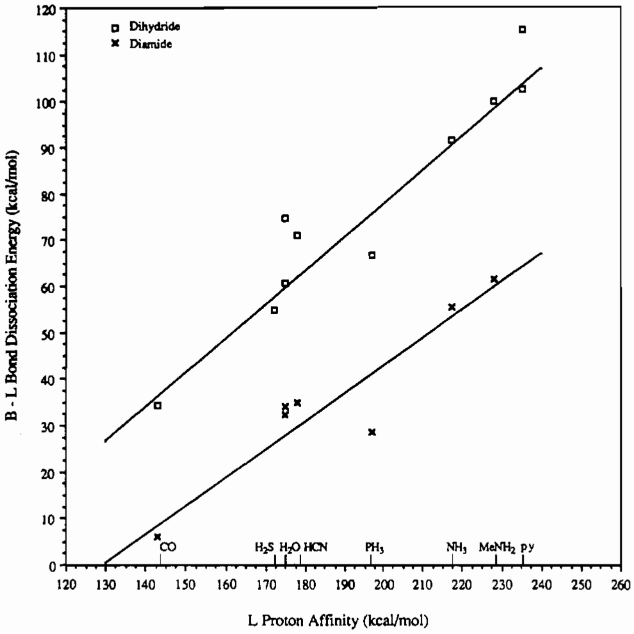

Figure 4. Plot of heterolytic bond dissociation energies for B–L bonds in H_2BL^+ and $(H_2N)_2BL^+$ vs proton affinity of L. All quantities were evaluated at the 6-31G*//6-31G* level.

interactions in dictating bond energetics, which is just the behavior expected for the bonding of a hard acid to a hard base.[34] This characterization is readily understood in terms of the "symbiosis" effect. The acidity of a BR_3 molecule can be tuned by the R groups, so that BF_3 and $B(OR)_3$ are considered hard acids while $B(CH_3)_3$ and BH_3 are borderline to soft acids. Removal of one of the three R groups not only imparts a charge on the new acid but also decreases the total electron donation to boron, so that the softening effect of the R groups is diminished: the BR_2^+ fragment becomes a harder acid. The slopes of the two sets of data in Figure 4 are similar, which indicates that the softening influence of the R groups is diminished. We might expect the dihydride data to have a smaller slope because of the greater softening influence of two hydrogens. Rather the dihydride data rises slightly faster because of the greater unsaturation at the boron center in BH_2^+ relative to $B(NH_2)^+$. Clearly, this behavior is in accord with that expected for hard acids.

Particularly curious is the trend in $R_2B-NH_3^+$ dissociation energies and bond lengths (Table V). Intuitively, we expect the most stable borinium cations (e.g. $B(NH_2)_2^+$) to bind a third ligand most weakly and the least stable borinium cations (e.g. BH_2^+) to bond a third ligand most tightly. The B–L bond dissociation energy should be inversely related to the B–R hydrogenation energies. The calculations indicate a very different ordering; the $R_2B-NH_3^+$ dissociation energies, as well as the B–N bond lengths, fall in the order R = $NH_2 < CH_3 < OH < H < F$. The same ordering is also found for other choices of L group. This ordering does not correlate with the energetic properties or Lewis acidity of the BR_2^+ cations; it does, however, correlate well with the effective steric bulk of the R group and thereby the steric congestion in the BR_2L^+ cations. That steric effects play a large role in determining the extent of adduct bonding in these small molecules is in accord with the hard acid/hard base characterization of the B–L interaction.

Conclusions

Hartree–Fock calculations with the 6-31G* basis are successful in modeling the structural variations in substituted boranes and boron cations. More important, they provide the flexibility and information necessary to analyze the bonding effects in these molecules. We have found it convenient to consider the compounds as coordination complexes of B^{3+} and have used this perspective to analyze covalent and dative substituent effects in several series of molecules, including R_2B^+, $R_2B(NH_3)^+$, and R_2BH. By analyzing trends in the hydrogenation energy of R–B bonds, along with structural modifications and charge redistributions associated with their variation, it is possible to determine the factors that dictate bond strengths and molecular stability. We find that both σ- and π-bonding effects are significant but that their relative contributions vary depending on the overall nature of the molecule: π bonding is most important in the two-coordinate cations, in which electron density at boron is the most scarce; σ-bonding factors dominate in the neutral boranes, in which the boron center is relatively electron rich; the three-coordinate cations occupy a middle ground in which both effects balance to generate the strongest bonds. In contrast, adduct bond formation between the borinium cations and neutral donor ligands is influenced more heavily by electrostatic and steric rather than orbital considerations, as demonstrated by the correlation between dissociation energy and ligand proton affinity.

While the results we have obtained are probably not quantitatively accurate, the calculations do point out the important electronic considerations that dictate energetic and structural variations in these and other boron compounds. For both steric and electronic reasons, deviations from our predictions are certainly expected with substituted R groups, such as dialkylamides or alkoxides instead of our hydrogen-containing models, and with different L groups, such as substituted amines, ethers, or phosphines. However, these variations are understandable within the framework of bonding characterization that we have delineated. Finally, while we have considered a rather restrictive class of boron compounds, namely symmetric BR_2^+ cations and their bonding to various two-electron donor groups, the conclusions reached are more general and may be applied to all mononuclear boron compounds.

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