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STRUCTURES AND ENERGIES FOR SMALL BORANE COMPOUNDS: ONE AND TWO BORON COMPOUNDS

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We report optimized structures and harmonic vibrational frequencies at the Hartree Fock level of theory with a double zeta plus polarization basis set for a number of B_1 and B_2 boranes. Atomization energies for these species are computed using full fourth order perturbation theory. Molecular heats of formation are then determined using the computed energies, vibrational frequencies and a system of additive bond correction factors. Due to the paucity of experimental thermochemical data on small boranes, these correction factors are determined from large basis set ab-initio calculations on prototypical molecules.

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I. INTRODUCTION

Establishing the structure and bonding of borane and carborane molecules has been a significant area of chemical research for many decades. While much has been learned, as Beaudet's recent review emphasizes,[1] there are still many borane and carborane systems for which the molecular structure is poorly resolved or unknown. It is therefore not surprising that there is little reliable empirical data describing the basic thermochemical properties of the boranes. We present here a discussion of structures, harmonic vibrational frequencies, and heats of formation for a series of small boranes. The predictions of molecular heats of formation presented here use a scheme which is similar to the bond-additivity correction (BAC) method pioneered by Melius and Binkley.[2] The technique is based on the observation that although the accurate first principles calculation of bond dissociation energies is prohibitive for most systems of interest, the error incurred using a correlated quantum chemical method with a modest basis set is fairly constant for a given bond type. This notion has been exploited by Melius and Binkley by combining quantum chemical calculations and bond-additive correction factors to calculate the heats of formation for hundreds of molecules, in many cases providing important data that is not experimentally accessible.

The success of the BAC technique is due in part to the availability of accurate experimental heats of formation for a number of the molecules in question. This data is compared with the calculated results to determine correction factors for each type of chemical bond.

The BAC technique, as described, cannot be applied to the boranes because there are not nearly enough known heats of formation to determine the bond correction factors. We seek to circumvent this problem by using the capabilities of modern quantum chemical methods to predict acceptably accurate atomization energies for certain small prototypical molecules. With this information and available atomic heats of formation, we can directly compute accurate values of heats of formation for these species. These calculations are at a high level and cannot be applied generally. However, by comparing these high level calculations to calculations performed on the same molecules at a more widely applicable level of theory, we determine bond correction factors.

We report here results for 13 molecules containing one or two boron atoms and between zero and six hydrogen atoms. Many of these compounds have been studied at both levels of theory alluded to above. Bond correction factors are determined for terminal BH bonds, three center BHB bonds, and BB bonds. Structures, harmonic vibrational frequencies, and heats of formation are presented for all of these species.

II. DESCRIPTION OF THE CALCULATIONS

Molecular structures and harmonic frequencies for all the compounds studied were obtained using the Hartree-Fock method with a double zeta plus (DZP) polarization basis set.[3,4] The Gaussian-82 computer codes were used for these studies.[5] Standard double-zeta basis sets were augmented by polarization functions with exponents optimized for correlation energy calculations[6] (0.421 for the boron and 0.725 for hydrogen). The SCF optimized geometries were used to determine atomization energies by computing

correlation energy using full fourth-order perturbation theory as implemented in Gaussian-82. Most of these calculations employed the double zeta plus polarization basis. Several calculations, however, employed an extended basis set built upon the 6-311G basis set.[7] The extended basis added diffuse functions in the valence shell, three sets of functions in each atom's first polarization space and a set of functions in each atom's second polarization space. Exponents for these functions were those recommended by Frisch, et al.[8] The atomization energy is computed as the difference between the sume of atomic electronic energies and the electronic energy of the molecule.

III. RESULTS FOR MONOBORANES

Pople and coworkers have reported accurate atomization energies for the three B_1 monoboranes using an extended basis set in full fourth-order perturbation theory calculations.[9] Our calculations differ from those reported in several ways. Rather than including the effects of the basis set extensions as seperate contributions to the electronic energy, we computed the fourth-order energy in a single calculation that included all the basis functions. Since we used the full basis set, we did not include estimates of energy contributions from higher-order perturbation theory terms. A thorough description of our methods is given in an earlier contribution.[10] Here we report fourth-order results using both the double-zeta plus polarization basis set, and the extended basis set.

Table 1 reports the structural parameters and scaled harmonic frequencies for BH, BH_2 and BH_3 and Table 2 summarizes the perturbation theory energy predictions for these compounds and both the hydrogen and boron atoms.

Table 1. Structural Parameters and Frequencies: BH, BH_2, and BH_3

	R_{BH} (A)		θ_{HBH} (Deg.)		Harmonic Frequencies (cm^{-1})	
Molecule	Theory	Exp.	Theory	Exp.	Theory	Exp.
BH	1.238	1.234	-----	-----	2474	2368
BH_2	1.190	1.178*	128.0	180.0*	2843	2650
					2681	1430
					1076	840(2)
BH_3	1.195	1.164*	120.0	120.0*	2776(2)	2976(2)
					2640	2348
					1263(2)	1765(2)
					1218	802

*Data estimates from Reference 11.

Table 2. Total and Atomization Energies: H, B, BH, BH_2, and BH_3

Molecule (Atom)	MP4 Energy (h)* DZP	MP4 Energy (h)* Extended	Atomization Energy (h) DZP	Atomization Energy (h) Extended
H	-0.4976	-0.4998	------	------
B	-24.5993	-24.6117	------	------
BH	-25.2243	-25.2448	0.1274	0.1336
BH_2	-25.8559	-25.8819	0.2614	0.2709
BH_3	-26.5259	-26.5578 -26.53676(FC)	0.4338	0.4467

*Energy units are hartrees. One hartree = 627.5 kcal/mole.

Of all the boron hydrides discussed in this paper, the BH molecule appears to have the most accurately known structure and heat of formation. The $X^1\Sigma^+$ state has been studied using spectroscopic techniques by Gaydon.[12] There is excellent agreement between the experimental and theoretical values for the equilibrium bond length, while the vibrational frequency prediction is too high. It should be noted that the bond length for the diatomic is substantially longer than the bond lengths for the other B_1 boranes. The electronic energy calculations display a large energy difference between the two basis sets, more than 20 millihartrees (20 millihartrees corresponds to ca. 12.5 kcal/mole). The predicted atomization energy differences, on the other hand, are relatively small, ca. 3.6 kcal/mole. Were it assumed that the extended basis set calculation yielded the correct atomization energy, then the calculated bond-additivity correction relevant to the DZP basis for this molecule is equal to that difference. Since empirically derived BACs have been found to depend parametrically on bond length, this value provides a long bond estimate of the correction factor. Our best prediction of the atomization energy is 83.7 kcal/mole, a number that agrees well with Pople's prediction of 85.3 kcal/mole and with the experimentally derived value, 82.2 kcal/mole.

In contrast to the BH molecule, there is no reliable empirical data for the BH_2 molecule. The estimates of the structure, vibrational frequencies and heat of formation presented in the JANNAF tables are incorrect. The predicted structural parameters presented in Table 2 are those for the lowest energy doublet state of this free radical species. The spin-eigenfunction of the UHF wavefunction is almost equal to two, so we expect that the effects of "spin-contamination" are small. The total energy difference between the DZP and extended basis set calculations is large, but as was the case with BH, the predicted atomization energies differ by a relatively small amount, .0095 h. This is equivalent to almost exactly 6 kcal/mole difference between the two atomization energy predictions.

The last of the monoborane compounds is BH_3. While one expects to find a significant literature detailing the molecular structure and properties of borane[3], there is surprisingly little data available for this molecule (the notation borane[3] denotes a single boron atom bonded to these hydrogen atoms). There are no reliable measurements of the structure of the molecule nor of the vibrational frequencies. The published heat of formation values are all derived indirectly based upon the value assumed for diborane, B_2H_6. The molecular structure parameters and vibrational frequency estimates reported here agree well with the values predicted in other theoretical studies of the molecule.[9,10] In this case, the electronic energy difference between our two basis sets is 19 millihartrees, while the predicted atomization energy difference is almost 13 millihartrees, or 8.1 kcal/mole. As the number of bonds increases, the difference between the atomization energy computed with the extended basis set differs more and more from that computed with the standard basis, while the total electronic energy difference for the molecules remains relatively stable. This dichotomy exemplifies two effects. The total energy difference between the two basis sets is principally an atomic effect. In the case of these three compounds, the contribution of the boron atom dominates. On the other hand, the increasing disparity in the atomization energy results with the increase in the number of B-H bonds clearly demonstrates the importance of the extended basis set in obtaining accurate predictions for this quantity. As the molecular structure becomes more complicated, the magnitude of the error that must be corrected grows larger. That the difference depends upon the number of bonds indicates that a bond-additivity correction scheme may provide a method for systematically estimating thermochemical parameters for the boranes.

Overall these data compare reasonably well with Pople's results, in spite of significant differences in our application of the perturbation theory methods. The predicted data are certainly better than the data available from experimental sources. This is encouraging, since there is virtually no experimental data for any of the diborane species.

IV. RESULTS FOR DIBORANES

Here we describe results for nine diboranes and the lowest closed shell singlet state of the B_2 molecule. Except for the diborane[6] molecule, we report electronic energy results only for the double zeta plus polarization basis set. Schematic structures for the molecules are presented in the figures. Detailed structural parameters are summarized in the tables. Only boron-hydrogen bonds were encountered in the monoborane calculations. The diboranes provide data on both boron-boron sigma and pi bonds, as well as examples of the characteristic BHB three-center bond. Data on these bonding types are essential to the concept of bond-related correction factors.

Table 3 contains data on the B_2 molecule. We are interested in the closed shell state of this molecule. The bond length is predicted to be long, almost two Angstroms, but the second derivative calculation identifies the extremum as a stable point. We have computed the atomization energy for this structure using the extended basis set, and the molecule is predicted to be bound. There is the possibility that our molecular structure prediction is, in this case, not as accurate as those obtained in the case of the B_1 molecules, because of the exceptionally weak nature of this bond. It seems

likely that a multiconfiguration wavefunction based calculation is needed to accurately determine the structure and atomization energy of the molecule.

Table 3. Results for B_2, B_2H_2, and B_2H_2: Molecular Structures, Frequencies and Electronic Energy

	Structural Parameters	Harmonic Frequencies (cm^{-1})	SDTQ-MP4 Energy Atomization Energy (hartrees)
B_2:	r_{BB} 1.910 A	395	-49.2456 0.0469
B_2H:	r_{BB} 1.714 A	2851	-49.9111
	r_{BH} 1.1799	917	0.2149
	Θ_{BBH} 180.0°	504	
B_2H_2:	r_{BB} 1.5291A	2946	-50.5843
	r_{BH} 1.1730 A	2903	0.3906
	Θ_{BBH} 180.0°	678(2) 685(2)	

We predict the B_2H molecule to be a linear free radical. We are unaware of any experimental observation of this species. The predicted BB bond distance is much less than that for the B_2 molecule, and the predicted atomization energy is much greater.

The addition of a hydrogen to form the B_2H_2 molecule leads to a molecule that appears to be the borane analog of the ethylene molecule, a double-bonded borane. The BB bond distance is much shorter than that of either the B_2H radical or the B_2H_4 molecule, and a population analysis indicates that a double bond connects the boron atoms. It seems likely that the bonding that characterizes this molecule is a rarity. In addition, it should be noted that we have found no closed-shell, nonclassical isomer of this molecule. This distinguishes the molecule from the other B_2 compounds described here. Schematic structures of these molecules are shown in Figure 1.

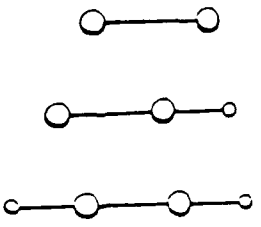

Figure 1. Molecular Structures for B_2, B_2H, and B_2H_2

Table 4 summarizes the data for the B_2H_3 and B_2H_4 molecules. Both classical and nonclassical (bridged) structures have been found for each of these molecules, and these structures are shown in Figure 2. Note that in each case, the boron-boron seperation is shorter for the bridged structure. This consequence of the three-centered bonding in these isomers emphasizes the special problem faced in developing a bond-additivity correction scheme for such compounds. That is, even though the boron-boron distance is shorter in the bridged compound, there is not a boron-boron bond. Electrostatic potential maps for such molecules show that the electron density is located along the three-center bonds. The BAC should be interpreted in terms of the two three-center BHB bonds. For both these isomer pairs, our results suggest that the atomization energy for the classical isomer is greater than that for the bridged compound.

The structure of the nonclassical isomers of B_2H_3 and B_2H_4 are noteworthy. All the hydrogen atoms lie on one side of an imaginary plane that contains the boron-boron bond. It is interesting to conjecture possible transition states for the interconversion of the two B_2H_4 isomers. These studies, however, will certainly require the application of multiconfiguration surface walking methods.

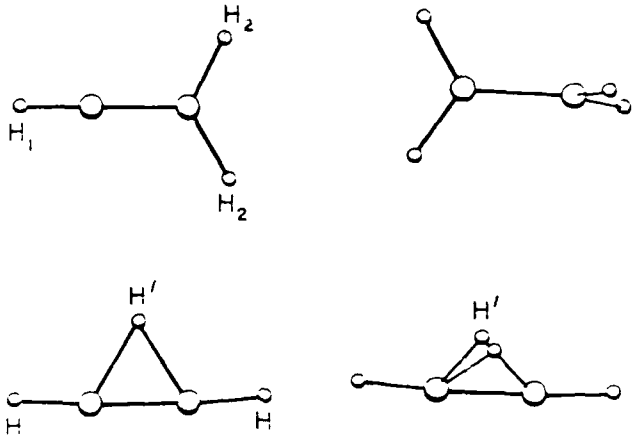

Figure 2. Molecular Structures for the Classical and Nonclassical Isomers of B_2H_3 and B_2H_4

Data for two isomers of B_2H_5 and the B_2H_6 molecule are presented in Table 5, and the molecular structures are shown in Figure 3. The two isomers reported here are clearly stable structures.* For the singly-bridged isomer, the triangle formed by the two borons and the bridge hydrogen bisects the angles formed by the BH_2 groups. The doubly-bridged has an asymetric ring

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*It is possible to suggest other bonding possibilities for the B_2H_5 molecule. These include a molecule with three bridged hydrogens, or a classically bonded system. We have recently determined the tri-bridged isomer structure.

Table 4. Results for B_2H_3 and B_2H_4: Molecular Structures, Frequencies and Electronic Energies

Structural Parameters			Harmonic Frequencies (cm^{-1})	SDTQ-MP4 Energy Atomization Energy (hartrees)
B_2H_3				
Classical:	r_{BB}	1.601 A	2871, 2748	-51.2379
	r_{BH_2}	1.195 A	2665, 1245	0.5465
	r_{BH_1}	1.177 A	1016, 943	
	θ_{H_2BB}	120.3°	903, 450	
	θ_{BBH_1}	179.9°	434	
Bridged:	r_{BB}	1.487 A	2937, 2883	-51.2370
	r_{BH}	1.173 A	1998, 1375	0.5456
	r_{BH}'	1.393 A	1216, 841	
	θ_{BBH}	176.1°	690, 634	
	θ_{HBH}	118.3°	381	
B_2H_4				
Classical:	r_{BB}	1.686 A	2729, 2725	-51.8787
	r_{BH}	1.198 A	2669, 2643	0.6897
	θ_{BBH}	121.6°	1296, 1234	
	θ_{HBH}	118.6°	1070, 1070	
			869, 503	
			487, 486	
Bridged:	r_{BB}	1.467 A	2941, 2887	-51.8739
	r_{BH}	1.172 A	2144, 2643	0.6849
	r_{BH}'	1.365 A	1415, 1383	
	θ_{BBH}	176.1°	1257, 1220	
	θ_{HBH}	120.1°	853, 503	
	$\theta_{H,BH}$	83.4°	566, 535	

Table 5. Results for B_2H_5 and B_2H_6: Molecular Structures, Frequencies and Electronic Energies

Structural Parameters			Harmonic Frequencies (cm^{-1})	SDTQ-MP4 Energy Atomization Energy (hartrees)
B_2H_5:				
1-Bridge:	r_{BB}	1.793	2848, 2843	-52.4526
	r_{BH}	1.187	2718, 2700	0.766
	$r_{BH'}$	1.343	1925, 1339	
	Θ_{BBH}	116.1	1237, 1195	
	$\Theta_{BH'B}$	83.7	1097, 999	
	$\Theta_{HBH'}$	126.7	933, 853	
			726, 497	
			478	
2-Bridge:	$r_{BB'}$	1.772	2815, 2788	-52.4451
	$r_{BH'}$	1.347, 1.346	2707, 2265	0.758
	$r_{BH'}$	1.310	2073, 1758	
	$r_{B'H'}$	1.310	1677, 1245	
	r_{BH_t}	1.186	1073, 983	
	r_{BH_c}	1.188	966, 907	
	$r_{B'H}$	1.184	851, 832	
	Θ_{HBH}	122.4	408	
	$\Theta_{BB'H}$	127.3		
	$\Theta_{B'BH_t}$	120.1		
	$\Theta_{B'BH}$	117.3		
	$\Theta_{B'H'B}^{c}$	83.7		
B_2H_6:	r_{BB}	1.794	2823, 2809	DZP Basis
	r_{BH}	1.187	2722, 2702	-53.1161
	$r_{BH'}$	1.329	2238, 2010	0.932
	Θ_{HBH}	122.5	1875, 1770	Extended Basis
	$\Theta_{BH'B}$	84.9	1259, 1241	-53.1424
			1148, 1063	0.9624
			1061, 973	
			886, 875	
			821, 398	

that is nearly planar, with terminal hydrogens located in a perpendicular plane. The perturbation theory results predict that the singly-bridged isomer has a higher atomization energy.

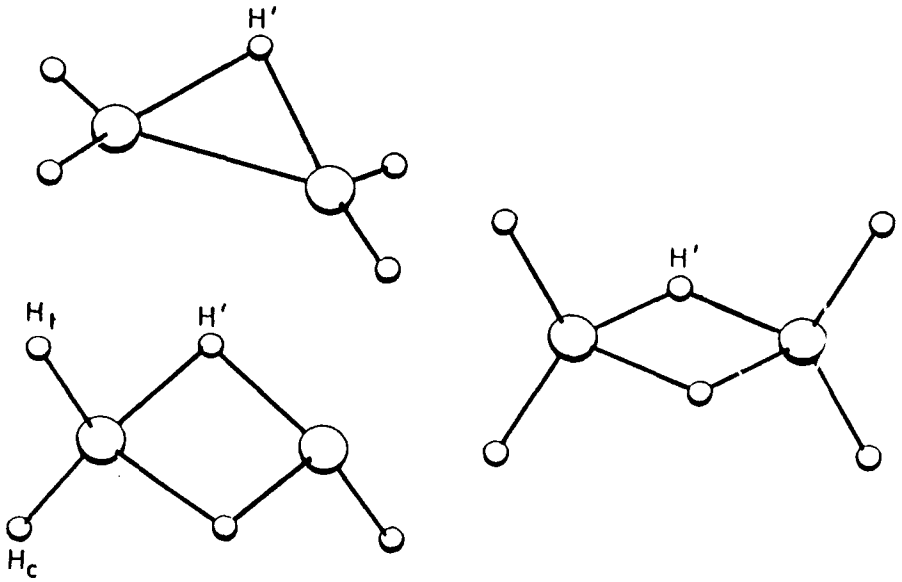

Figure 3. Molecular Structures for Two Bridged Structures of B_2H_5 and B_2H_6

We have discussed our diborane[10] results in a previous paper. Here we note that the calculations contain no surprises. We have not attempted to locate other possible stable isomers of this compound. Since B_2H_6 is a crucial molecule in our effort to devise a bond-additivity scheme based upon the results of ab initio calculations, we must briefly review the results of our extended basis set calculations for this molecule. These results are required, since this molecule is the only bridged borane that we have studied with an extended basis set. The computations took full advantage of the molecules C_{2v} symmetry. We provide the extended basis set results in Table 3 along with the DZP data.

V. SUMMARY OF B_2H_6 RESULTS

There have been a number of calculations dedicated to predicting the dimerization energy of borane and we have reviewed many of those results in Reference 10. Our calculations employed the largest basis set, and included all the terms that contribute to the electronic energy through fourth-order perturbation theory. We cannot claim that the perturbation theory series has converged; we rely on the hope of judicious cancellation of the higher order terms when we evaluate the atomization energy. Additionally, in the case of diborane, we have not correlated the core orbitals in order that we could perform the fourth-order calculation using the full basis set. Thus, in order to predict the dimerization energy of borane, we have also computed the fourth-order perturbation theory energy of BH_3 using the frozen core approximation. The value we obtain is -43.23 kcal/mole. This value is

substantially lower than the value reported by Ortiz and Lipscomb[13] in a third-order perturbation theory calculation (-39.86 kcal/mole) and our value of -40.81 kcal/mole obtained using their basis set. Since we know the atomization energy of BH_3, we can compute the atomization energy of diborane directly using this value of the dimerization energy. We obtain 603.9 kcal/mole (0.9623 h). This is substantially lower than the DZP result, 584.8 kcal/mole (0.932 h). We would, in the spirit of the BAC approach, claim that the energy difference is represented by correction factors from four B-H bonds and two B-H-B three-center bonds. We do not consider a BB bond correction factor, since there is no BB bond in diborane.

We have, to this point, discussed our results in terms of the electronic energy differences alone. To estimate the more familiar heat of formation, we must include zero-point energy differences and temperature effects. Our calculations predict a zero point energy difference contribution to the dimerization energy of 6.1 kcal/mole, and the temperature effects equal -22.6 kcal/mole, for T=298 K. Therefore, we predict that the dimerization energy of BH_3 is -39.6 kcal/mole.

Similarly, we can correct the atomization energy prediction for these effects, and obtain the heat of formation for diborane,[6] 1.6 kcal/mole. The heat of formation for borane[3] equals, 20.6 kcal/mole. These estimates used scaled values of the predicted harmonic frequencies rather than experimental values. The results described in our previous paper used the experimental frequencies for diborane. While those values are to be preferred to the scaled theoretical data, similar data is not available for many of the other compounds described in this note. Consistency requires the choice of the theoretically predicted data.

VI. BOND-ADDITIVITY CORRECTIONS AND HEAT OF FORMATION ESTIMATES

The data described here is insufficient to accurately derive bond-additivity correction factors to provide the basis for the development of a model thermochemistry for the boranes. We have neither enough data on the boranes in general, nor enough accurate data upon which to develop reliable BACs. We will, however, provide estimates of the heats of formation for the radicals described in this study relying on the data described for borane[3], diborane[6], and the results of an extended basis set calculation for the classical isomer of diborane[4], where we used the basis set additivity technique of Pople, et al.[9] Using the BH_3 data, we determine that the BAC for a boron-hydrogen bond is 2.7 kcal/mole, and the diborane studies predict the BAC for a B-H-B three-center bond to be 4.7 kcal/mole, and that of the B-B single bond to be 7.0 kcal/mole. We do not have enough data to estimate bond-length dependence od the BACs, nor do we have enough data to treat asymmetric three-center bonds differently than we treat the symmetric bond of diborane.[6] The estimated heats of formation for all the species are collected in Table 6. These values depend directly upon the assumed value of the heat of formation assigned to the boron atom. Since that parameter has a large error bar, the assigned heats of formation have a nontrivial uncertainty.

Clearly, more work is needed if one is to develop a reliable method for predicting the heats of formation of the boranes. We must extend our ability to compute accurate values of the atomization energy to molecules containing three or four boron atoms. Note that we have chosen to describe the

correction factors in terms of the bonding types that characterize the boranes, rather than in terms of internuclear seperations between pairs of atoms. This selection is motivated by the desire to develop group-additivity schemes for this class of compounds. With the emergence of efficient, accurate quantum chemical methods and the availability of modern supercomputers, one expects that a sufficient database could be generated for development of an "empirical" approach to thermochemistry based upon ab initio data.

Table 6. Heat of Formation at 298 K (kcal/mole)

Molecule	H_f^{298}
BH	103.5
BH_2	73.6
BH_3	20.6
B_2H	176.3
B_2H_2	117.4
$B_2H_3(c)$	75.8
$B_2H_3(nc)$	73.3
$B_2H_4(c)$	38.4
$B_2H_4(nc)$	37.2
$B_2H_5(1b)$	54.1
$B_2H_5(2b)$	56.3
B_2H_6	1.6

VII. SUMMARY

We have reported data on the structure, harmonic vibrational frequencies and heat of formation for thirteen mono and diboranes. This provides the minimal data needed to estimate the heats of formation for these compounds using a consistent ab initio approach. By using extended basis fourth-order perturbation theory methods to predict atomization energies, we develop the basis for a bond-additivity correction scheme that may be used to systematically correct calculations done with more standard basis sets. Since the smaller calculations may be applied to many more compounds than the extended calculations, enough ab initio data may be obtained to develop a method for estimating thermochemical properties based entirely upon ab initio data.

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REFERENCES

1. R. Beaudet, The Molecular Structure of Boranes and Carboranes in Molecular Structure and Energetics - Advances in Boron and the Boranes, J.F. Liebman, A. Greenberg, and R.E. Williams, eds., VCH Publisher, NY, 1988.

2. P. Ho, M.E. Coltrin, J.S. Binkley, and C.F. Melius, "Structures and Energetics for Silane Reactions," J. Phys. Chem., Vol. 89, p. 4647, 1985.

3. T.H. Dunning, Jr., "Gaussian Basis Functions for Use in Molecular Calculations. I. Contraction of (9s,5p) Atomic Basis Sets for the First-Row Atoms," J. Chem. Phys., Vol. 53, p. 2823, 1970.

4. S. Huzinaga, "Gaussian Type Basis Functions for Polyatomic Systems," J. Chem. Phys., Vol. 42, p. 1293, 1965.

5. J.S. Binkley, M.J. Frisch, D.J. DeFrees, K. Raghavachari, R.A. Whiteside, H.B. Schlegel, E.M. Fluder, R. Seeger, and J.A. Pople, Gaussian-82, Release-H, Department of Chemistry, Carnegie-Mellon University, Pittsburgh, PA.

6. L.T. Redmon, G.D. Purvis, III, and R.J. Bartlett, "Accurate Bonding Energies of Diborane, Borane, and Borazane Determined by Many-Body Perturbation Theory," J. Am. Chem. Soc., Vol. 101, p. 2856, 1979.

7. R. Krishnan, J.S. Binkley, R. Seeger, and J.A. Pople, "Self-Consistent Molecular Orbital Methods. XX. A Basis Set for Correlated Wave Functions," J. Chem. Phys., Vol. 72, p. 650, 1980.

8. M.J. Frisch, J.A. Pople, and J.S. Binkley, "Self-Consistent Molecular Orbital Methods. 25. Supplementary Functions for Gaussian Basis Sets," J. Chem. Phys., Vol. 80, p. 3265, 1984.

9. J.A. Pople, M.J. Frisch, B.T. Luke, and J.S. Binkley, "A Moller Plesset Study of the Energies of AH_n Molecules (A = Li to F)," Int. J. Quantum Chem., Vol. 17S, p. 307, 1983.

10. M.J. Page, G.F. Adams, J.S. Binkley, and C.F. Melius, "Dimerization Energy of Borane," J. Phys. Chem., Vol. 91, p. 2675, 1987.

11. D.H. Stull and H. Prophet, Project Directors, JANAF Thermochemical Tables, 2nd Ed., NSRDS-NBS 37, Catalog No. C13.48:13, 1971.

12. A.G. Gaydon, Dissociation Energies and Spectra of Diatomic Molecules, Chapman and Hall, London, 1963.

13. J.V. Ortiz and W.N. Lipscomb, "Correlation and Polarization Effects in the Thermochemical Properties of Small Boron Compounds," Chem. Phys. Letters, Vol. 1103, p. 59, 1983.

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