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Accurate Binding Energies of Diborane, Borane Carbonyl, and Borazane Determined by Many-Body Perturbation Theory

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Abstract: Binding energies including valence-shell electron correlation are obtained from many-body perturbation theory (MBPT) for diborane, borane carbonyl, and borazane. Results are given for basis sets of double ζ quality and for basis sets with polarization functions added on all atoms. The binding energies ($-\Delta E$) are found to be (respectively) 35, 21, and 30 kcal/mol. Correlation effects account for 48, 62, and 32% of the binding. The size-consistent nature of the MBPT method enables the computation of enthalpies of reaction for four different reactions involving monoborane, diborane, carbon monoxide, and borane carbonyl. When the theoretical values are corrected for vibrational zero-point energies and the experimental data are adjusted for temperature effects, the results agree (within 5%) and thus confirm the set of experimental enthalpies corresponding to ΔH (300 °C) = -34 kcal/mol for the association reaction yielding diborane. The result for the binding energy of borazane constitutes a prediction in the absence of an experimental value.

I. Introduction

Binding energies of molecules having weak dative bonds have been difficult to ascertain, either experimentally or theoretically. Experimentally, there have been several problems, particularly for complexes of monoborane. First, BH_3 has a very short lifetime (owing to its reactivity) which does not permit direct determination of its energy. Of more significance, proper interpretation of experimental data (from electron impact of products of pyrolysis or kinetic studies) requires the knowledge of reaction mechanisms.[1] Complications arise from multiple rates resulting from surface and gas-phase reactions.[2,3] Additionally, mass spectrographic analysis of products (used in conjunction with appearance potentials) does not necessarily lead to infallible conclusions regarding energy disposal.

Historically, there has been either a lack of experimental evidence (in the case of borazane) or the presence of conflicting results (for diborane). Furthermore, the possibility of error propagation is present because of the common use of energetic relationships between molecules. For example, the dissociation (binding) energies of B_2H_6 and H_3BCO are related (as we shall see in the Discussion) by the equation[4]

$$D(B_2H_6) - 2D(H_3BCO) = 9.1 \text{ kcal/mol} \qquad (1)$$

Unfortunately, internal checks of consistency do not preclude the presence of errors and may succeed only in deferring their detection.

Theoretical difficulties arise primarily because correlation effects[5] account for a significant and sometimes dominant part of the binding energy. By coincidence, in some cases, the early self-consistent field (SCF) calculations obtained reasonable values owing to cancellation of the errors resulting from the use of inadequate basis sets and from the neglect of correlation. However, this was not consistently the case, and typically systematic improvement of basis sets destroyed the fortuitous SCF agreement. Thus, as improved methods are available,[6-11] theoretical (re)examinations of reactions of molecules of this type are in order. In this regard, there have been discourses concerning the proper treatment of the correlation problem.[6-18] The many-body perturbation theory (MBPT) methods[6,7] which we shall employ will also have distinct computational advantages, as discussed in sections II and IV.

II. Methodology

Sophisticated ab initio quantum mechanical methods based on many-body perturbation theory (MBPT) are now available for the calculation of correlated energies for closed-shell (or UHF open-shell) ground-state systems. The calculation of the total correlated energy

$$E_{\text{total}} = E_{\text{SCF}} + E_{\text{corr}} = E_0 + \Delta E \qquad (2)$$

(where $E_0 = \Sigma_i^{\text{occ}}\epsilon_i$ and $E_{\text{SCF}} = E_0 + E_1$) is based on the linked diagram expansion[18]

$$\Delta E = \sum_{n=0}^{\infty} \langle \Phi_0 | V[(E_0 - H_0)^{-1} V]^n | \Phi_0 \rangle_{\text{L}} \qquad (3)$$

where L indicates the limitation to linked diagrams. Φ_0 is the SCF reference function and $\{\epsilon_i\}$ are the (Hartree–Fock) orbital energies. V comes from the Moeller–Plesset separation of the Hamiltonian[19]

$$H = H_0 + V \qquad (4)$$

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Table I. Geometries of BH_3 and B_2H_6

BH_3	present	ref 27		ref 29
B-H[a]	1.19	1.19		1.160
∠HBH	120	120		120
B_2H_6	exptl[25]	exptl[26]	exptl[28]	ref 29
B-B	1.77	1.775	1.770	1.805
B-H_b	1.33	1.339	1.329	1.327
B-H_t	1.19	1.196	1.192	1.154
∠H_tBH_t	120	120.2	121.8	118.8

[a] Bond lengths are in angstroms and angles in degrees. Subscripts b and t denote bridging and terminal hydrogens in diborane.

where

$$H_0\Phi_0 = E_0\Phi_0$$

for the reference function Φ_0.

Although other methods, such as configuration interaction (CI), also exist, MBPT is particularly well suited for the calculation of binding energies because of its size-extensive[6,16] (sometimes called "size-consistent") nature. The term "size extensivity" denotes that the energy has the correct linear dependence on the number of particles in a homogeneous system, commonly exemplified by an ensemble of noninteracting helium atoms. Since linked energy diagrams are individually size extensive, any linked-diagram MBPT method (or approximation to ΔE above) has this property, independent of the choice of reference function (RHF, UHF, or MCSCF).

Size consistency, according to the definition of Pople et al.,[14] requires that a method result in the computed energy of a supermolecule A-B (with its substituent A and B infinitely separated) being equal to the sum of the energies of the substituents computed separately. Although these properties are closely related, in the general case neither size extensivity nor size consistency is sufficient to guarantee the other. It is interesting to note that RHF is *not* size consistent for N_2 (i.e., it does not separate properly) while UHF is; but either reference function, combined with linked-diagram MBPT, will produce size-extensive results and the size (in)consistency is preserved. Thus, both properties are ensured as long as the unperturbed wave function is size consistent and only linked-energy diagrams are included in the correlating method. For the He_N problem or the molecules studied here, which are closed-shell molecules whose substituents are also closed shell, RHF reference functions are size consistent and the MBPT-correlated results are both size extensive and size consistent.

Obviously, these two features are expected to be important in determining accurate binding energies or other features of potential surfaces. In particular, the energy of two BH_3 molecules as a supermolecule should be twice that of BH_3 alone, which is not usually the case for CI methods. Although complete CI is both size consistent and size extensive, its application for the binding energies of interest here is out of the question, especially in light of the basis set quality required for chemical accuracy. More practical CI models, such as all single and double excitation CI (SD-CI), are not size extensive or size consistent. These disadvantages (as well as the variational property) come about because the method in effect includes terms corresponding to *un*linked diagrams, which are eliminated in the linked-diagram expansion of MBPT by proper consideration of certain quadruple and higher even-ordered excitations.[6] In general, binding energies obtained from CI calculations seem to be more reliable when the zero of energy is taken to be the appropriate supermolecule energy rather than the sum of substituent energies. Although MBPT approximations are not necessarily variational, they are nevertheless very accurate. Furthermore, no supermolecule calculations are required, thus reducing computational expenditures.

More detailed discussions of size extensivity and the relationships among various correlated methods have been presented elsewhere.[6-8,11,12,16]

The level of theory used for these calculations will generally be D-MBPT(6).[7] This approximation includes the linked diagrams associated with double excitations[6] through the sixth order ($n = 6$ in eq 3). For diborane, the SDQ-MBPT(4) model[6] is used to assess the importance of single and quadruple excitations. In the language of CI, the SDQ model considers (in a basis of 68 basis functions) on the order of 10^7 symmetry-adapted configurations.

III. Binding Energies of Diborane, Borane Carbonyl, and Borazane

A. Diborane. For our diborane calculations we choose to start from Dunning's[20] [4s3p] contraction of Huzinaga's[21] (9s5p) primitive basis set for boron. Similarly, we use a (4s)/[2s] set (with a scale factor[20] of 1.2) for hydrogen. A set of six polarization functions (five d's and one s) on boron and a set of p's on each hydrogen are roughly optimized to minimize the frozen core D-MBPT(6)[22] total energy of BH_3. The exponents are found to be (respectively) 0.471 and 0.725. These values correspond to orbitals more diffuse than those which optimization at the SCF level yields. A corresponding basis is employed for B_2H_6, resulting in a total of 68 contracted Gaussian orbitals (CGOs). Thus, the optimization advantage for BH_3 (the bridge hydrogens in B_2H_6 might not be described quite as optimally[24] as the terminal ones) and any possible basis set enrichment effect for B_2H_6 tend to be offsetting. Both quantities are expected to be small for a basis set of the size employed here. Only the valence-shell electrons are explicitly correlated in the present calculations. This restriction is considered to be justified because the dimerization process is expected to be predominantly a valence-shell phenomenon.

The experimental geometry[25] of diborane is used in these calculations, and the monoborane geometry is chosen by borrowing the B-H_t (terminal) bond length from B_2H_6. These geometries and those[26] used by Ahlrichs[27] are among those shown in Table I. Also included is a more recent, but similar, experimental geometry.[28] The minor differences in the geometries used for these correlated treatments of diborane are considered to be insignificant. The theoretical equilibrium has been obtained at the SCF level by Dill et al.[29] (also given). We investigated the problem at the fourth-order correlated level as well, using an unpolarized basis set of 32 CGOs.[30] In general, the optimal bond lengths are shorter when optimized at the SCF level than the correlated level, and in either case the B-B distance is predicted to be within 0.06 Å of the experimental value.

Figure 1 shows the theoretical energy of dimerization as a function of the total energy (defined as the SCF total energy plus correlation, if calculated) of B_2H_6. Table II provides the same information in quantitative form. In the figure, the SCF contributions are indicated by the lower (black) areas. The results for our smaller (unpolarized [4s2p]/[2s]) basis (d) verify the importance of polarization functions in calculating either SCF[29] or correlated contributions to the dimerization energy of diborane.[35] A horizontal line indicates the most accurate (lowest total energy for B_2H_6) SCF value obtained to date.[32] The shaded portions correspond to the correlation contributions. Arrows indicate the present results obtained in the DZ (left, [43]/[2]) basis and DZP (right, [431]/[21]) basis. The widely varying experimental values (represented by "X"s and listed in Table III) are plotted chronologically and have been shifted to correspond to the potential minimum (at 0 K). This adjustment will be discussed in a subsequent section. The experimental band has been (arbitrarily) drawn to match

Table II. Calculations of the Binding Energy of Diborane[a]

	ref	method	$E_{B_2H_6}{}^{tot}$	$E_{BH_3}{}^{tot}$	$-\Delta E^{SCF}$	$-\Delta E^{corr}$	$-\Delta E^{tot}$
	present	D-MBPT(6)	-53.1312	-26.5373	18.5	17.0	35.6
(a)[b]	present	FC-D-MBPT(6)	-53.0957	-26.5198	18.5	16.7	35.2
	present	FC-DQ-MBPT(4)	-53.0878	-26.5164	18.5	16.0	34.5
	present	FC-SDQ-MBPT(4)	-53.0892	-26.5167	18.5	16.5	35.0
(b)	27	CEPA	-53.0908	-26.5162	20.7	15.9	36.6
	27	PNO-CI*	-53.0659	-26.5057	20.7	13.5	34.2
	27	PNO-CI	-53.0659	-26.5111	20.7	6.7	27.4
	27	IEPA	-53.1224	-26.5258	20.7	23.5	44.3
(c)	31	IEPA	-53.0204	-26.4901	8.5	16.8	25.2
(d)	present	D-MBPT(4)	-52.9490	-26.4522	13.4	14.7	28.1
(e)	32	SCF	-52.8331	-26.4014	19.0		
(f)	33	CI	-52.8298	-26.4016	7.3	9.4	16.7
(g)	34	SCF	-52.8236	-26.3960	19.9		
(h)	35	SCF	-52.8211	-26.3959	18 3		
(i)	29	SCF	-52.8103	-26.3888	20.5		
(j)	36	SCF	-52.7690	-26.3753	11.5		
(k)	24	SCF	-52.7551	-26.3622	19.3		
(l)	34	SCF	-52.7183	-26.3533	7.3		
(m)	36	SCF	-52.6913	-26.3309	18.5		

[a] Total energies are in hartrees, energy differences in kcal/mol. Energies are not adjusted for vibrational zero point. [b] Labels correspond to Fgure 1. [c] These calculations do not include polarization functions in the basis sets.

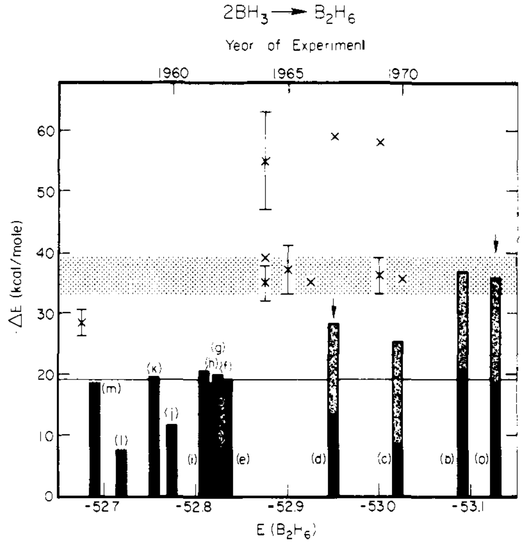

Figure 1. Theoretical and experimental determinations of the binding energy of diborane.

Table III. Experimental Enthalpies of Complexation (Δ*H*) of Diborane and Borane Carbonyl[a]

year	ref	$\Delta H(2BH_3 \rightarrow B_2H_6)$	$\Delta H(BH_3 + CO \rightarrow H_3BCO)$
1970	2	35.5	[22.3][b]
1969	37	(36 ± 3)[b]	22.8
1969	38	(58)	33.7
1967	39	59.0	[34]
1966	40	(35.0 ± 0.5)	[22.1 ± 0.3]
1965	41	37.1 ± 4	[23.1 ± 2]
1964	42	39	[24]
1964	43	55 ± 8	[32 ± 4]
1964	1	35 ± 3	[22 ± 1.5]
1956	44	28.4 ± 2	[18.8 ± 1]

[a] Units are kcal/mol. Enthalpies not adjusted for temperature effects. [b] Parentheses indicate original authors' prediction concluded indirectly from measurements of other reactions. Brackets indicate present authors' prediction from formula (1) based on $\Delta H(2BH_3 \rightarrow B_2H_6)$ values reported.

the predicted value of Fehlner and Mappes[37] based on their borane carbonyl measurements and eq 1.

It is apparent that correlation plays an important role in the dimerization of B_2H_6. For this reason and because the faults of the earliest correlated treatments[31] have already been discussed in the literature, we omit discussion of the SCF results and focus on calculations (a), (b), and (e) of Figure 1 (Table II). Of these, the SCF energies of BH_3 are essentially identical for (a) and (b). Our SCF contribution (a) comes within 0.5 kcal/mol of the best SCF value (e).[32] Based on our geometry studies in the smaller basis, only 20% of the difference between our SCF total energy and that of Ahlrichs (b)[27] can be explained by geometry relaxation, with the remainder due to basis set differences.

We see that the frozen core approximation in the present work affects the dimerization energy by only 0.4 kcal/mol at the D-MBPT(6) level. Although our basis set is not ideal for describing the core electrons, the insensitivity of the binding energy of diborane to the core-correlation effects partially justifies neglecting those terms in a study of the binding energies for the current series of molecules.

In order to further assess the utility of calculations at the FC-D-MBPT level, we have also obtained the exact fourth-order contributions from single and quadruple excitation diagrams within the frozen core approximation (FC-SDQ-MBPT(4)). The fourth-order quadruple excitation diagrams account for ~2% of the valence correlation energy of diborane, and 2% of the binding energy as well.[64] However, single excitations (in fourth order) have a countereffect. The combined contribution (quadruples decrease the magnitude of the complexation energy, while singles increase it) is a net decrease in magnitude of 0.4 kcal/mol. Triple excitations would be expected to have an effect similar to that of single excitations, but possibly larger, further offsetting the effect of quadruple excitation diagrams and suggesting the efficacy of D-MBPT studies for systems of this type.

B. Borane Carbonyl. The basis set for borane carbonyl is developed similarly to that for diborane, except that we choose to start from the [4s2p] contraction[20] for the heavy atoms. The polarization functions are added and optimized at the correlated level in the substituent molecules. The optimal polarization exponents for boron through oxygen plus hydrogen (in two environments) are shown in Table IV. Thus, the basis for borane carbonyl consists of 63 CGOs.

Table IV. Optimized Polarization Functions for Correlated Treatments

atom	molecule	basis	orbital	exponent
B	BH_3	(9s5p)/[4s2p]	d	0.386
C	CO	(9s5p)/[4s2p]	d	0.654
N	NH_3	(9s5p)/[4s2p]	d	0.902
O	CO	(9s5p)/[4s2p]	d	1.211
H	BH_3	(4s)/[2s]	p	0.686
H	NH_3	(4s)/[2s]	p	0.735

The geometric parameters for this study (and for borazane) are given in Table V. We use the experimental values[45] for the CO and BC bond lengths, assuming that the CO distance is unchanged in the complex as is commonly done.[51] We use the same pyramidal BH_3 geometry as for borazane (which will be explained in the next section). The resultant borane carbonyl geometry is similar to the experimental geometry[48] used in ref 35 (also shown in Table V) and to that of ref 51. Figure 2 (Table VI) displays our results, as well as those of previous efforts.[35,51-54]

The inadequacy of the SCF method alone is obvious; the SCF values diverge from the experimental data as the SCF limit is approached. Furthermore, our discussions will involve exothermic reactions of H_3BCO which are predicted to be endothermic at the SCF level. The figure shows that correlated (MBPT) calculations bring theory into reasonable agreement with experiment.

C. Borazane. The basis set for borazane is analogous to that of borane carbonyl, resulting in a basis of 62 CGOs. The optimal polarization exponents are included in Table IV. We initially intended to study a single geometry at the large basis level. We used the experimental ("crystalline") B-N bond length[47] (the complete structure has not yet been determined), the experimental N-H bond length of ammonia,[46] and a B-H bond length of 2.25 au ($\approx$1.19 Å), which is the calculated equilibrium value for BH_3 at the SCF level in a minimum STO basis[55] or at the correlated (CEPA) level[27] in a more extensive basis. The angles of the hydrogen atoms were chosen to be the average of the optima determined by Palke[55] for the staggered and eclipsed configurations; i.e., we used the Palke "experimental" geometry, except that the H angles were not tetrahedral. The resultant HNH angle was essentially identical with that in ammonia. The results are reported in Table VII.

We can see from a comparison of the various geometries given in Table V that the major difference from recent calculations is the B-N bond length. The discrepancy between the experimental value (1.56 Å) used in our calculation and the calculated optima obtained by Ahlrichs and Koch[49] prompted us to investigate the effects of geometric relaxation. We find a similar dependence (of the SCF energy) upon BN bond length to that of Ahlrichs and Koch;[49] the energy at 1.65 Å is 2 kcal/mol lower than at 1.56 Å (with the hydrogen parameters kept fixed). Also, the minimum SCF energy corresponds to a BN length of 1.67 Å, which is almost identical with that found by Ahlrichs and Koch (1.68 Å) using a larger basis set. We note that our binding energy at the SCF level is closer to their extended basis value. Based on their reported CEPA correlation energies we expect the optimal bond length (at the correlated level) to be somewhat shorter. Therefore, we calculate the binding energy at the FC-D-MBPT(6) level using our hydrogen positions and BN bond length of 1.65 Å. Our final result is

$$-\Delta E^{\text{tot}} = -\Delta E^{\text{SCF}} - \Delta E^{\text{corr}} = 20.5 + 9.7 = 30.2 \text{ kcal/mol}$$

Umeyama and Morokuma[51] have estimated the experimental value (uncorrected for temperature and zero-point vibrational energies) to be 30.9 kcal/mol.

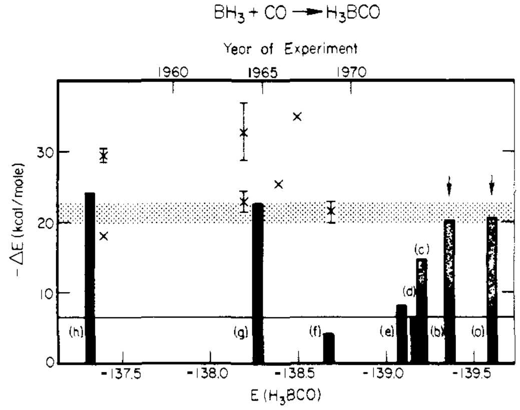

Figure 2. Theoretical and experimental determinations of the binding energy of borane carbonyl.

Table V. Geometries for Borane Carbonyl, Borazane, and Their Substituents[g]

	present	ref 35	ref 49
	BH_3 (D_{3h})		
BH	1.19	1.196	1.19
	BH_3 (C_{3v})		
BH	1.191	1.194^{a,48}	1.22^{c}
∠ZBH	106.7	(104.6)	104.2^{b,29}
∠HBH	(112.02)	113.52^{a,48}	
	H_3BCO		
CO	1.13^{a,45}	1.131^{a,48}	
BC	1.57	1.540^{a,48}	
	NH_3 (alone)		
NH	1.0173^{a,46}		1.01^{a,50}
∠HNH	107.25^{a,46}		107.2^{a,50}
	H_3BNH_3		
BN	1.56,^{a,57} 1.65^{49}		1.68,^{d} 1.65^{e}
NH	1.0173		1.007^{c,f}
∠BNH	111.6		111.7^{b,29}

[a] Experimental data. [b] Optimized at SCF level in STO-3G basis. [c] Optimized at SCF level in DZP basis. [d] Optimized at SCF level in larger DZP basis. [e] Optimized at correlated (CEPA) level in DZP basis. [f] The authors of ref 49 have pointed out that this parameter was originally misprinted. [g] Bond lengths in angstroms and angles in degrees.

The barriers to rotation calculated in the nonpolarized basis (for BN bond length of 1.56 Å) are 3.06 kcal/mol at the SCF level and 3.16 kcal/mol at the sixth-order frozen core MBPT level. The SCF value obtained by Veillard[57] in a basis of 68 Gaussians for a similar geometry (except having tetrahedrally located hydrogens) is also 3.06 kcal/mol. As is the case in ethane,[58] the correlation effect on the barrier is found to be very small.

IV. Discussion

There are several reactions involving borane, diborane, carbon monoxide, and borane carbonyl which are energetically related. We consider four:

$$\begin{array}{lll} \text{(A) } 2BH_3 \rightarrow B_2H_6 & \Delta H_A & \\ \text{(B) } BH_3 + CO \rightarrow H_3BCO & \Delta H_B & \\ \text{(C) } B_2H_6 + 2CO \rightarrow 2H_3BCO & \Delta H_C & (5) \\ \text{(D) } BH_3 + H_3BCO \rightarrow B_2H_6 + CO & \Delta H_D & \end{array}$$

A change in enthalpy (ΔH_R) accompanies each of these reactions; however, these quantities are not independent. We can

Table VI. Calculations of the Binding Energy of Borane Carbonyl[a]

	ref	method	$E_{H_3BCO}^{tot}$	$E_{BH_3}^{tot}$	E_{CO}^{tot}	$-\Delta E^{SCF}$	$-\Delta E^{corr}$	$-\Delta E^{tot}$
(a)[b]	present	FC-D-MBPT(6)	−139.6023	−26.5129	−113.0567	8.0	12.5	20.5
(b)	present[c]	FC-D-MBPT(6)	−139.3612	−26.4443	−112.8845	10.6	9.7	20.3
(c)	52	CI	−139.2055	(total of −139.1823)		11.0	3.6	14.6
(d)	35	SCF	−139.1723	−26.3959	−112.7662	6.4		
(e)	35	SCF	−139.0896	−26.3799	−112.6969	8.1		
(f)	35	SCF	−138.6832	−26.3509	−112.3260	4.0		
(g)	53	SCF	−138.2654	−26.2317	−111.9975	22.7		
(h)	54	SCF	−137.3143	−26.0634	−111.2073	24.2		

[a] Total energies in hartrees, energy differences in kcal/mol. Energies are not adjusted for vibrational zero point. [b] Labels correspond to Figure 2. [c] These calculations do not include polarization functions in the basis sets.

Table VII. Calculations of the Binding Energy of Borazane[a]

	ref	method	$E_{H_3BNH_3}^{tot}$	$E_{BH_3}^{tot}$	$E_{NH_3}^{tot}$	$-\Delta E^{SCF}$	$-\Delta E^{corr}$	$-\Delta E^{tot}$
(a)	present	FC-D-MBPT(6)	−82.9766	−26.5129	−56.4156	20.5	9.7	30.2
(b)	49	CEPA	−82.9367	−26.5041	−56.3839	25.0	5.6	30.6
(c)	present[b]	FC-D-MBPT(6)	−82.7902	−26.4443	−56.3036	20.6	6.0	26.6
(d)	49	SCF	−82.6475	−26.3974	−56.2163	21.3		
(e)	29	SCF	−82.6065	−26.3888	−56.1837	21.3		
(f)	56	SCF	−82.5754	−26.3652	−56.1632	29.5		
(g)	56	SCF	−82.5414	−26.3453	−56.1422	33.8		
(h)	53	SCF	−82.1323	−26.2317	−55.8472	33.5		
(i)	29	SCF	−81.5995	−26.0707	−55.4554	46.1		

[a] Total energies in hartrees, energy differences in kcal/mol. Energies are not adjusted for vibrational zero point. [b] These calculations do not include polarization functions in the basis sets.

Table VIII. Vibrational Zero-Point Energies

molecule	E_V[a]
BH_3	17.3[b,59]
B_2H_6	39.64[61]
CO	3.10[62]
H_3BCO	22.37[63]

[a] Units are kcal/mol and values were derived from the frequencies given in the referenced sources. [b] Theoretical value is 17.3; previous estimate[60] was 18.11.

write (A) and (B) as

$$\text{(A)}\quad 2H_f(BH_3) + \Delta H_A = H_f(B_2H_6)$$

$$\text{(B)}\quad H_f(BH_3) + H_f(CO) + \Delta H_B = H_f(H_3BCO)$$

where we have denoted the heats of formation (usually ΔH_f°) as simply H_f to avoid confusion with ΔH_R. Then, taking twice (B) and substituting for $2H_f(BH_3)$ using (A), we get

$$H_f(B_2H_6) + 2H_f(CO) - \Delta H_A + 2\Delta H_B = 2H_f(H_3BCO)$$

Since the energy relationship for (C) is

$$H_f(B_2H_6) + 2H_f(CO) + \Delta H_C = 2H_f(H_3BCO)$$

we see that

$$\Delta H_C = 2\Delta H_B - \Delta H_A \tag{6}$$

which can be arranged as

$$\Delta H_A = 2\Delta H_B - \Delta H_C \tag{6'}$$

or

$$\Delta H_B = \tfrac{1}{2}[\Delta H_A + \Delta H_C] \tag{6''}$$

Similarly

$$\Delta H_D = \Delta H_A - \Delta H_B = \Delta H_B - \Delta H_C \tag{7}$$

Experimentalists have apparently long accepted the value of Burg:[4]

$$\Delta H_C(\sim 326\ \text{K}) = -9.142\ \text{kcal/mol} \tag{1}$$

Using this value and measurements of ΔH_B they have arrived at values for ΔH_A, and vice versa. Table III gives the available experimental measurements, with corresponding predictions (ignoring temperature effects) in parentheses. The consistency dilemma is apparent. The results for each binding energy fall into two groups, high and low values. The low values for one are consistent with the low values for the other via eq 1, and likewise for the higher sets. Theory has tended toward the lower results, having only now obtained reliable values even that large.

If we consider the theoretical heat of formation

H_f = total energy (molecule) −
$\sum$ total energy (constituent in its standard state) constituents

and the partitioning of energy

total energy
= (electronic + vibrational + rotational) energy

we see that to a first approximation

$$\Delta H_R = \Delta E_R^{(el)}$$

since the constituent total energies in reactant and product H_f values cancel. It is important to recognize that the theoretical total (electronic) energies for the species involved in reactions 5A–D can be directly added and subtracted to yield ΔH values only because of the size-consistent nature of the MBPT method. Similar total energies obtained from a truncated CI approach, such as a CI limited to single and double excitations (SDCI), could not be added and subtracted in a completely analogous fashion without making rather significant errors. The alternative in SDCI is to do supermolecule calculations at very large separations. Obviously, this can become quite excessive. In particular, the direct determination of ΔH for reaction 5C would require a calculation involving three molecules at mutually infinite separation plus a second calculation for two separated borane carbonyl molecules. This calculation

Table IX. A Comparison of Theoretical and Experimental Enthalpies of Complexation for Reactions 5A–D[a]

reactions	ΔE_R^{calcd}	ΔV_R[b]	$\Delta H_R^{calcd}(0\ K)$[e]	$\Delta H_R^{exp}(0\ K)$	ΔT_R[c]	T	$\Delta H_R^{exp}(T)$
A	−35.2	5.0	−30.2	(−31.6 [±3])[d]	$4RT = -3.9$	488	(−35.5)[d]
B	−20.5	2.0	−18.5	−19.4 [±1.5]	$3.5RT = -3.4$	488	−22.8[37]
C	−5.8	−1.1	−6.9	−7.2	$3RT = -1.94$	326	−9.14[4]
D	−14.7	3.0	−11.7	(−12.2)[d]	$0.5RT = -0.3$	300	(−12.5)

[a] Units are kcal/mol and K. [b] Vibrational zero-point correction (see text). [c] Temperature correction (see text). [d] Parentheses indicate predictions obtained from eq 6′ and 7. [e] The experimental and calculated $\Delta H_R(0\ K)$ values agree to within 5% for each reaction.

is totally impractical. Alternatively, ΔH_C could be obtained (by SDCI) via eq 6, where ΔH_A and ΔH_B were determined using supermolecule calculations. The utility of size-consistent theoretical methods is evident in this case, in which the CI method would require almost twice the computational effort. For the molecules of interest here, the SCF total energies themselves are size consistent, but for these reactions (5A–D) the neglect of correlation is a serious limitation. The SCF ΔE values are all too small in magnitude by factors of 1.5–2.5, and even obtain the wrong sign for reaction 5C.

To compare the theoretical and experimental results quantitatively, several corrections are necessary since the calculated results do not take into account the zero-point vibrational energies of the molecules, and they correspond to 0 K temperature. Therefore, we make the following adjustments. We define the enthalpy of reaction at absolute zero

$$\Delta H_R^{calcd}(0\ K) \equiv \Delta E_R^{calcd} + \Delta V_R$$

where, for example, ΔV_A is the vibrational zero-point correction

$$\Delta V_A = E_V(B_2H_6) - 2E_V(BH_3)$$
$$= \tfrac{1}{2}h\left[\sum_{i=1}^{18} \nu_i(B_2H_6) - 2\sum_{j=1}^{6} \nu_j(BH_3)\right]$$

and 18 and 6 are the respective numbers of degrees of freedom. The zero-point energies are given in Table VIII. Then we adjust the experimental enthalpy to 0 K:

$$\Delta H_R^{exp}(0\ K) = \Delta H_R^{exp}(T) - \Delta T_R$$

Since the heat capacities of BH_3 and H_3BCO have not been determined, we use the empirical correction of $\tfrac{1}{2}RT$ ($R = 1.0$ cal/mol·K) per translational or rotational degree of freedom (i.e., 1.776 kcal/mol for each molecule except CO (1.480 kcal/mol) at 298 K) and one (Δn) RT for the PV work term due to molar decrease (except for (5D)). Similarly, the experimental points of Figures 1 and 2 correspond to

$$\Delta E_R^{exp} \equiv \Delta H_R^{exp}(T) - \Delta T_R(\sim 300\ K) - \Delta V_R$$

in order to compare roughly with ΔE_R^{calcd}.

Table IX shows these adjustments for each of the reactions 5, correcting theory for vibrational zero-point energies and experiment for temperature effects. The experimental values $\Delta H^{exp}(0\ K)$ for reactions A and D have been derived from those for B and C since these enthalpies have not been measured directly. The corresponding $\Delta H^{exp}(T)$ for reaction A is consistent with measurements of the rate constant for this reaction.[2] The resultant ΔH_D^{exp} at room temperature is consistent with values given by Garabedian and Benson.[1] Incorporating their notation

$$\Delta H_D \equiv E_4 - E_3$$

we obtain E_3 from

$$E_3 = -26.75 - \Delta H_B$$

where −26.75[1] is the ΔH for the composite[4] reaction (B and D). Using $\Delta H_B(300\ °C) = -21.5$ (derived from ref 37) and

Table X. Contributions to the Binding Energy at the FC–D-MBPT(6) Levels[a]

	B_2H_6	H_3BCO	H_3BNH_3
ΔE^{SCF}[b]	−18.505	−7.961	−20.504
ΔE_2	−18.992	−17.118	−11.472
ΔE_3	+1.641	+3.316	+1.235
ΔE_4(DE)	+0.496	+0.608	+0.320
ΔE_5(DE)	+0.148	+0.495	+0.135
ΔE_6(DE)	+0.044	+0.148	+0.047
ΔE^{corr}(DE)	−16.663	−12.551	−9.736
ΔE^{tot}	−35.17	−20.51	−30.24

[a] Energies in kcal/mol. [b] $\Delta E^{SCF} = \Delta E_0 + \Delta E_1$.

$$E_4 = -17.7^{1}$$

$$\Delta H_D^{exp} = -17.7 + 26.75 - 21.5 = -12.45\ \text{kcal/mol}$$

which agrees to within 2% of the value shown.

Thus we compare the resultant calculated and experimental values for the enthalpy of complexation at absolute zero (two center columns of Table IX). The largest discrepancy is 1.4 kcal/mol (for reaction 5A), with the theoretical results smaller in magnitude than the experimental ones by ~4% for all reactions (5A–D). Our full D-MBPT(6) result for (5A) (−35.6) reduces the difference to 1.0 kcal/mol. This suggests that core effects neglected in our calculations due to the frozen core correlation treatment or to inadequacies of the basis set would slightly improve the agreement.

The selection of a high value, $\Delta H_B^{exp} = -33.7$ (Table III), would have resulted (using $\Delta H_C = -9.1$ kcal/mol) in the $\Delta H_R^{exp}(0\ K)$ values: −55.9, −31.6, −7.3, −24.3. The average discrepancy of theory (relative to these experimental values) is 36%, the theoretical values being smaller by roughly a factor of 2 for all except ΔH_C. Thus we reject the higher experimental values.

Table X shows the contribution to the binding energies ($-\Delta E$) of diborane, borane carbonyl, and borazane from each order of (frozen core) D-MBPT. We can see that the double excitation contributions have converged satisfactorily, in that the potential errors due to the basis sets used and the exclusion of single and higher than double excitation (in an MBPT sense[6]) effects are of more significance. Geometry relaxation could also have a small effect. However, we expect the resultant errors to be no more than a few kilocalories per mole.

Since the accuracy of our calculations seems competitive with experimental errors, we confirm that the lower experimental values (Table III) are the more correct ones. We concur and find the enthalpies of complexation for diborane and borane carbonyl to be −32.6 and −20.6 kcal/mol at room temperature. We predict the binding energy of borazane to be approximately 30 kcal/mol at 0 K with no zero-point correction included.

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