Enthalpies of Formation and Bond Energies in Lithium, Beryllium, and Boron Derivatives. 2. Dative, Single, and Triple Bonds

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For a set of small XYH_n singlet-state molecules (where X stands for Li, Be, or B and Y is one of the second-row atoms), we have calculated the enthalpies of formation at the MP4(sdtq)/6-311++G(3df,2p) level by using MP2(full)/6-31G(d,p) fully optimized structures. At this level of theory, the heats of formation are expected to be in the range of the so-called "chemical accuracy" (±1 kcal/mol). Some alkyl derivatives of the previous XYH_n compounds have been studied at the RHF/6-31G(d) level (with fully optimized geometries). The theoretical enthalpies of formation reproduce the available experimental results quite satisfactorily. In addition to compounds with usual dative single bonds, we also describe molecules with covalent (nondative) single B-N and B-O bonds. We use all the available (experimental and theoretical) data to calculate new bond energies for lithium, beryllium, and boron derivatives.

Introduction

Although many features of electron-deficient compounds have been established by a number of experimental and theoretical investigations, accurate thermochemical properties remain undetermined, at least for the simplest derivatives. Except for LiOH, BeHF, and BH_2OH, very few enthalpies are known for lithium-, beryllium-, and boron-based materials (XYH_n). Most often, those species cannot be handled easily. For example, $BH_3{\cdot}NH_3$ is stable but not easily vaporized[2] and it rapidly decomposes when the temperature increases. BH_2NH_2 is unstable;[3] its lifetime was reported to be several minutes, and it prefers to exist as cyclic oligomers or polymers.[4] BHNH may have a fairly long lifetime under arc discharge[5] but is difficult to observe under other conditions. Therefore, direct determination of the energy content for such species is not easy. Nevertheless, a few alkyl and fluoro derivatives of the previously mentioned XYH_n molecules have been investigated with success.

From a theoretical point of view, difficulties arise because correlation effects account for a significant part of the energy content and can become a dominant part of reaction heats.[6] Therefore, it is not surprising to observe large discrepancies in the calculated dissociation energies depending on the theoretical method in use. This has specially been pointed out for diborane(6)[6,7] and for molecules with weak dative bonds. For example, the dissociation energy of ammonia-borane is predicted to be 46 kcal/mol at the HF/6-31G level, 21 kcal/mol at the HF/6-31G* level,[8] and 35 kcal/mol when the correlation energy is taken into account.[9]

The aim of this work is to calculate accurate (±1 kcal/mol) heats of formation for the smallest lithium-, beryllium- and boron-containing compounds not investigated in a previous study.[14] We also want to check the consistency of our theoretical values with available thermochemical data for the corresponding alkyl and fluoro derivatives. A target accuracy of ±2 kcal/mol should be considered a satisfactory goal.

Theoretical Enthalpies of Formation of XYH_n Compounds

We consider first a series of singlet XYH_n molecules containing at least one lithium, beryllium, or boron atom. Results concerning BeBH ($^3\Sigma^-$), $BeCH_2$ ($^3B_1$), HBBH ($^3\Sigma_g^-$), B_2 ($^3\Sigma_g^-$), HBC ($^3\Sigma^-$), and BCH ($^3\Pi$) may be found elsewhere.[8,10-12] In our previous papers,[13,14] we described in detail, and carefully checked, a method to obtain accurate standard heats of formation (ΔH_f) for small molecules. Let us summarize here the main features of this method. (i) The energies are calculated at the fourth order of Møller-Plesset perturbation theory (MP4 with single, double, triple, and quadruple replacements) using the 6-311++G(3df,2p) basis set.[15] (ii) The MP4 energies are single-point calculations on MP2 fully optimized structures at the 6-31G(d,p) level. (iii) The classical formalism of statistical thermodynamics is used to obtain the thermal correction (TC = ZPE + ΔH(0-298.15 K)), assuming motion separation, ideal gas, rigid rotator, and harmonic potential approximations. (iv) The TC calculation is based on scaled theoretical harmonic frequencies at the HF/6-31G(d,p) level using optimized structures; as theoretical frequencies are known to be overestimated by approximately 10%, the following scaling procedure[11] (in cm^{-1}) is used:

$$\nu(\text{exptl}) \approx -45.99 + 0.92227[\nu(\text{theor})]$$

This method can be referred to as MP4(sdtq)/6-311++G(3df,2p)//MP2(full)/6-31G(d,p) energies + TC at scaled HF/6-31G(d,p)//HF/6-31G(d,p) level. Both MP2 struc-

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Table I. Standard Heats of Formation at 298.15 K (kcal/mol) for Reference Species and a Series of XYH_n Compounds[a]

compd	state	E(MP4)	reacn[b]	ΔH_f(theor)	ΔH_f(exptl)	BDE[c]
H_2	$^1\Sigma_g^+$	−1.170 23	exptl value[19]		0	
LiH	$^1\Sigma^+$	−8.020 07	exptl value[19]		33.61 ± 0.01	
BeH	$^2\Sigma^+$	−15.192 54	theor value[13]	81.62		
BeH_2	$^1\Sigma_g^+$	−15.844 10	theor value[14]	39.31		
BH	$^1\Sigma$	−25.224 17	$BH + H \rightarrow B + H_2$	104.11	105.8 ± 2[19]	
BH_2	$^2A_1$	−25.858 84	theor value[13]	75.96	(48 ± 15[19])	
BH_3	$^1A'_1$	−26.532 78	theor value[14]	21.94	(22–26[7])	
CH_2	$^3B_1$	−39.073 45	$CH_2 \rightarrow C + H_2$	94.62	92.4 ± 1[19]	
CH_3	$^2A_1$	−39.755 96	exptl value[17]		35.1	
CH_4	$^1T_2$	−40.432 46	exptl value[19]		−17.90 ± 0.08	
NH	$^3\Sigma^-$	−55.058 00	$NH + H \rightarrow N + H_2$	87.15	(90 ± 4[19])	
NH_2	$^2B_1$	−55.790 93	exptl value[19]		45.5	
NH_3	$^1A_1$	−56.471 38	exptl value[19]		−10.97 ± 0.1	
OH	$^2\Pi$	−75.636 21	exptl value[19]		9.32 ± 0.3	
H_2O	$^1A_1$	−76.333 01	exptl value[19]		−57.8 ± 0.01	
$HLi{\cdot}NH_3$	$^1A_1$	−64.523 73	$LiH{\cdot}NH_3 \rightarrow LiH + NH_3$	3.02		19.62
$HLi{\cdot}OH_2$	-	−84.380 27	$LiH{\cdot}OH_2 \rightarrow LiH + H_2O$	−39.91		15.72
$H_2Be{\cdot}NH_3$	$^1A'$	−72.354 10	$H_2Be{\cdot}NH_3 \rightarrow BeH_2 + NH_3$	5.15		23.20
$HBeNH_2$[14]	$^1A_1$	−71.182 58	$HBeNH_2 + H_2 \rightarrow BeH_2 + NH_3$	1.79		125.33
BeNH	$^1\Sigma^+$	−69.860 42	$BeNH + H_2 \rightarrow HBeNH_2$	94.55		70.04
$H_2Be{\cdot}OH_2$	$^1A_1$	−92.207 75	$H_2Be{\cdot}OH_2 \rightarrow BeH_2 + H_2O$	−36.00		17.52
$H_2B{\cdot}BH_2$[14]	^1E	−51.889 81	$BH_2BH_2 + H_2 \rightarrow 2BH_3$	45.35		106.58
HBH_2BH[14]		−51.892 76	$HBH_2BH + H_2 \rightarrow 2BH_3$	43.90		108.03
$H_2BH_2BH_2$		−53.134 17	$H_2BH_2BH_2 \rightarrow 2BH_3$	5.10	6.5–17.3[19]	38.79
$H_2B{\cdot}CH_3$[14]	$^1A'$	−65.789 12	$BH_2CH_3 + H_2 \rightarrow BH_3 + CH_4$	5.00		106.07
$HB{\cdot}CH_2$	$^1A_1$	−64.538 15	$BHCH_2 + H_2 \rightarrow BH_2CH_3$	50.57		147.63
$H_3B{\cdot}NH_3$	$^1A_1$	−83.054 64	$BH_3{\cdot}NH_3 \rightarrow BH_3 + NH_3$	−17.52		28.49
$H_2B{\cdot}NH_2$[14]	$^1A_1$	−81.885 00	$BH_2NH_2 + H_2 \rightarrow BH_3 + NH_3$	−23.01		144.48
$HB{\cdot}NH$	$^1\Sigma^+$	−80.657 96	$BHNH + H_2 \rightarrow BH_2NH_2$	7.05		185.90
$H_3B{\cdot}OH_2$	-	−102.889 24	$BH_3{\cdot}OH_2 \rightarrow BH_3 + H_2O$	−47.42		11.56
$H_2B{\cdot}OH$[14]	$^1A'$	−101.746 36	$BH_2OH + H_2 \rightarrow BH_3 + H_2O$	−68.73	−69.4[35]	154.01
$HB{\cdot}O$	$^1\Sigma^+$	−100.558 99	$BHO + H_2 \rightarrow BH_2OH$	−62.90 −60[22]	−20 ± 20[21] −198.3 ± 3[19]	228.25

[a] The energies (au) are obtained at the MP4(sdtq)/6-311++G(3df,2p)//MP2(full)/6-31G** level. The thermal corrections are introduced as mentioned in the text. [b] For the atoms, we employ (in kcal/mol) $\Delta H_f(H) = 52.103$, $\Delta H_f(Li) = 38.074$, $\Delta H_f(Be) = 77.438$, $\Delta H_f(N) = 112.973$, $\Delta H_f(C) = 171.288$, and $\Delta H_f(O) = 59.553$ from ref 19 and $\Delta H_f(B) = 134.49$ from ref 18. [c] BDE according to $H_nX{-}YH_m \rightarrow XH_n + YH_m$, as denoted by the hyphen in column 1; for $H_nXH_2XH_n$ compounds, the BDE corresponds to $H_nXH_2XH_n \rightarrow 2XH_{n+1}$.

tures and thermal corrections have been previously reported for atoms and hydrides,[13] for B_2H_n[16] and BXH_n[12] compounds, and for various lithium and beryllium derivatives.[11] The enthalpies of formation obtained by this procedure are reported in Table I. A typical example is given below.

The enthalpy of formation of $LiH{\cdot}NH_3$ is calculated using the reaction (see Table I)

$$LiH{\cdot}NH_3 \rightarrow LiH + NH_3$$

then

$$\Delta H_f(LiH{\cdot}NH_3) = \Delta H_f(LiH) + \Delta H_f(NH_3) - \Delta H_r(298.15)$$

where

$$\Delta H_r = E_{MP4}(LiH) + E_{MP4}(NH_3) - E_{MP4}(LiH{\cdot}NH_3) + TC(LiH) + TC(NH_3) - TC(LiH{\cdot}NH_3)$$

Very few comparisons with experimental values are available. As pointed out previously,[14] our theoretical approach reproduces the experimental ΔH_f of LiOH (−57.3 kcal/mol versus −56 from kcal/mol from 19) and BH_2OH (−68.7 kcal/mol theoretically versus −69.4 kcal/mol from Pedley[35]). For HBO, our value (−63 kcal/mol) is very different from the experimental results (−20[21] or −198 kcal/mol[19]). Nevertheless, it is close to the theoretical value recommended by Page (−60 kcal/mol[22]). For ammonia–borane ($NH_3{\cdot}BH_3$), the BDE (bond dissociation energy or $\Delta H_{dissociation}$ at 298.15 K) reported in Table I (28.5 kcal/mol) compares well with the theoretical value of Ahlrichs[23] (27.6 kcal/mol at DZP + CEPA level) and Binkley[9] (28.7 kcal/mol at TZP + MP4 level) but not at all with less accurate ab initio calculations: 35.2 kcal/mol[24] (MP2/6-31G*), 34.7 kcal/mol[9] (MP4/6-311G**), 41.7 kcal/mol[25] (HF/3-21G), and 44.7 kcal/mol[26] (HF/4-31G). The bond strengths of $LiH{\cdot}NH_3$ and $LiH{\cdot}OH_2$ (BDE in Table I) are also in agreement with the values calculated by Schleyer (respectively 21.8 and 15.7 kcal/mol[27,28]). For

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diborane(6) (B_2H_6), the electronic energy reported in Table I is one of the best values available at the present time.[29] The obtained BDE compares well with the previous value of Page.[29] Nevertheless, our diborane(6) heat of formation (5.1 kcal/mol) remains smaller than the JANAF recommended value (9.8 ± 4 kcal/mol,[19] selected from values in the range 6.5–17.3 kcal/mol) but is larger than the theoretical value of Page (2.7 kcal/mol[29]). It must also be remembered that $\Delta H_f(B_2H_6)$ depends on $\Delta H_f(B)$[18] as well as on $\Delta H_f(BH_3)$. Furthermore, the comparison between theoretical and experimental data favors the highest ΔH_f value for B and the lowest ΔH_f for borane(3) and diborane(6). We feel that the accuracy of the enthalpies of formation reported in Table I is in the range of ±1 kcal/mol as in the case of more classical species.[13] In the following sections, we give indirect evidence of the quality of the results reported in Table I.

Enthalpies of Formation of Alkyl Derivatives

Let us now consider a few methyl and fluoro derivatives. Some of them are experimentally known. The molecules under consideration are now too large to be studied by the previous MP4 procedure. Therefore, we use the less expansive isodesmic approach,[30] neglecting the thermal corrections. Isodesmic reaction energies are usually small and depend very little on the temperature (usually TC does not contribute more than ±1 kcal/mol to the isodesmic heat of reaction). The electronic energies have been calculated at the HF/6-31G(d) level with fully optimized structures. The results obtained are collected in Table II. The enthalpies of formation are given at room temperature, as the theoretical energy changes of the isodesmic reactions are practically equal to the corresponding enthalpy changes at 298.15 K. Being calculated from ΔH_f (298.15 K), the BDE's are also given at 298.15 K. Table III makes it possible to compare the theoretical gas-phase results and the corresponding experimental values. A satisfactory agreement between the two series of data can be observed. The results of Table II show some interesting regularities in the bond strengths. It can be observed that the $H_3B{\cdot}NH_nMe_{3-n}$ (n = 1–3) complexation energies are very close to each other. The mean value is 31.22 kcal/mol for n in the range 1–3. This value is 2.73 kcal/mol larger than the corresponding value for the unsubstituted compound ($BDE(H_3B{\cdot}NH_3) = 28.49$ kcal/mol). For the *B*-methyl derivatives, the BDE depends on the number of methyl groups. Each CH_3 lowers the binding energy by approximately 4.5 kcal/mol (the B–N bond length increases concurrently by increments of 0.02 Å). Those observations can be summarized as

$$BDE(H_3B{\cdot}NH_{3-n}Me_n) = BDE(H_3B{\cdot}NH_3) + 2.73(1 - \partial_n) \tag{1a}$$

$$\partial_n = 0 \text{ except } \partial_0 = 1$$

$$\begin{aligned} BDE(H_{3-n}(Me)_nB{\cdot}NH_3) &= 28.28 - 4.53n \\ &\approx BDE(H_3B{\cdot}NH_3) - 4.53n \end{aligned} \tag{1b}$$

$$r = 0.999$$

Relations (1) enable us to deduce the complexation energy of the trimethylamine–trimethylborane from the ammonia–borane dissociation energy:

$$BDE((CH_3)_3B{\cdot}N(CH_3)_3) = 28.28 - (4.53 \times 3) + 2.73 = 17.43 \text{ kcal/mol}$$

This result corresponds to the value obtained from the experimental heat of formation (−52.6 kcal/mol[36]) i.e. 17.80 kcal/mol. Haaland's review[54] has already reported this trend of methyl substitution. This author mentions that the dissociation enthalpy is reduced by replacement of three H atoms on the acceptor center with three methyl groups and that, on the donor side, only the first substitution is significant. Numerical values reported by Haaland are also based on McCoy's work,[37] but using different data for diborane, this author obtains different BDE's.

Similarly, the following relations are deduced for BO derivatives:

$$BDE(H_3B{\cdot}OH_{2-n}Me_n) = BDE(H_3B{\cdot}OH_2) + 1.96(1 - \partial_n) \tag{2a}$$

$$\partial_n = 0 \text{ except } \partial_0 = 1$$

$$\begin{aligned} BDE(H_{3-n}(Me)_nB{\cdot}OH_2) &= 11.41 - 2.90n \\ &\approx BDE(H_3B{\cdot}OH_2) - 2.90n \end{aligned} \tag{2b}$$

$$r = 0.992$$

The application of relations (2) for $(CH_3)_3B{\cdot}O(CH_3)_2$ yields

$$BDE((CH_3)_3B{\cdot}O(CH_3)_2) = 11.41 - (2.90 \times 3) + 1.96 = 4.67 \text{ kcal/mol}$$

versus 4.23 kcal/mol from Table II.

Studies on corresponding beryllium and lithium compounds are scarce, and, to our knowledge, no experimental thermochemical data have been reported. Thus, we can only hope that the values given in Table II are not worse for Be and Li compounds than those for boron species. Relations such as (1) or (2) also exist in the Li and Be series:

$$BDE(H_2Be{\cdot}NH_{3-n}Me_n) = 23.47\ (\pm 0.99) \approx BDE(H_2Be{\cdot}NH_3)\ \forall\ n = 1, 3 \tag{3a}$$

$$\begin{aligned} BDE(H_{2-n}(Me)_nBe{\cdot}NH_3) &= 23.09 - 3.30n \\ &\approx BDE(H_2Be{\cdot}NH_3) - 3.30n \end{aligned} \tag{3b}$$

$$r = 0.998$$

$$\begin{aligned} BDE(HLi{\cdot}NH_{3-n}Me_n) &= 19.91 - 0.90n \\ &\approx BDE(HLi{\cdot}NH_3) - 0.90n \end{aligned} \tag{4}$$

$$r = 0.980$$

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Table II. ΔH_f's and BDE's at 298.15 K (kcal/mol) for the Methylated Derivatives[a]

compd	E(6-31G*)	isodesmic reacns	ΔE_r[d]	ΔH_f[d]	BDE[d]
$CH_3Li\cdot NH_3$	−103.238 24	$CH_3Li\cdot NH_3 + LiH \rightarrow LiH\cdot NH_3 + CH_3Li$	−1.74	−3.62	17.89
$HLi\cdot NH_2CH_3$	−103.231 25	$HLi\cdot NH_2CH_3 + NH_3 \rightarrow HLi\cdot NH_3 + CH_3NH_2$	−0.35	8.84	19.28
$HLi\cdot NH(CH_3)_2$	−142.258 64	$HLi\cdot NH(CH_3)_2 + NH_3 \rightarrow HLi\cdot NH_3 + NH(CH_3)_2$	−1.37	10.93	18.25
$HLi\cdot N(CH_3)_3$	−181.287 15	$HLi\cdot N(CH_3)_3 + NH_3 \rightarrow LiH\cdot NH_3 + N(CH_3)_3$	−2.58	10.91	17.04
$CH_3Li\cdot N(CH_3)_3$	−220.318 90	$CH_3Li\cdot N(CH_3)_3 + LiHNH_3 \rightarrow HLi\cdot N(CH_3)_3 + CH_3Li\cdot NH_3$	−0.10	4.37	15.21
$CH_3Li\cdot OH_2$	−123.059 72	$CH_3Li\cdot OH_2 + LiH \rightarrow LiH\cdot OH_2 + CH_3Li$	−1.59	−46.70	14.13
$HLi\cdot OHCH_3$	−123.052 87	$HLi\cdot OHCH_3 + OH_2 \rightarrow HLi\cdot OH_2 + CH_3OH$	0.39	−30.68	16.11
$HLi\cdot O(CH_3)_2$	−162.077 77	$HLi\cdot O(CH_3)_2 + OH_2 \rightarrow LiH\cdot OH_2 + CH_3OCH_3$	−2.38	−23.72	13.34
$CH_3Li\cdot O(CH_3)_2$	−201.109 67	$CH_3Li\cdot O(CH_3)_2 + LiH\cdot OH_2 \rightarrow LiH\cdot O(CH_3)_2 + CH_3Li\cdot OH_2$	−0.15	−30.36	11.60
$CH_3BeH\cdot NH_3$	−111.030 77	$CH_3BeH\cdot NH_3 + BeH_2 \rightarrow BeH_2\cdot NH_3 + HBeCH_3$	−3.33	−9.55	19.87
$(CH_3)_2Be\cdot NH_3$	−150.074 98	$(CH_3)_2Be\cdot NH_3 + BeH_2 \rightarrow H_2Be\cdot NH_3 + CH_3BeCH_3$	−6.59	−23.89	16.61
$H_2Be\cdot NH_2CH_3$	−111.013 25	$BeH_2\cdot NH_2CH_3 + NH_3 \rightarrow BeH_2\cdot NH_3 + CH_3NH_2$	1.11	9.50	24.31
$H_2Be\cdot NH(CH_3)_2$	−150.042 07	$BeH_2\cdot NH(CH_3)_2 + NH_3 \rightarrow BeH_2\cdot NH_3 + CH_3NHCH_3$	0.99	10.70	24.19
$H_2Be\cdot N(CH_3)_3$	−189.069 30	$H_2Be\cdot N(CH_3)_3 + NH_3 \rightarrow H_2Be\cdot NH_3 + N(CH_3)_3$	−1.03	11.49	22.17
$(CH_3)_2Be\cdot N(CH_3)_3$	−267.155 63	$(CH_3)_2Be\cdot N(CH_3)_3 + H_2Be\cdot NH_3 \rightarrow H_2Be\cdot N(CH_3)_3 + (CH_3)_2Be\cdot NH_3$	−1.66	−15.89	13.93
$CH_3BeH\cdot OH_2$	−130.850 08	$CH_3BeH\cdot OH_2 + BeH_2 \rightarrow BeH_2\cdot OH_2 + HBeCH_3$	−3.06	−50.97	14.46
$(CH_3)_2Be\cdot OH_2$	−169.894 72	$(CH_3)_2Be\cdot OH_2 + BeH_2 \rightarrow CH_3BeCH_3 + H_2Be\cdot OH_2$	−6.04	−65.58	11.48
$H_2Be\cdot OHCH_3$	−130.832 80	$BeH_2\cdot OHCH_3 + OH_2 \rightarrow BeH_2\cdot OH_2 + CH_3OH$	2.04	−28.43	19.56
$H_2Be\cdot O(CH_3)_2$	−169.857 39	$H_2Be\cdot O(CH_3)_2 + OH_2 \rightarrow BeH_2\cdot OH_2 + CH_3OCH_3$	−0.92	−21.27	16.59
$(CH_3)_2Be\cdot O(CH_3)_2$	−247.943 98	$(CH_3)_2Be\cdot O(CH_3)_2 + BeH_2 + OH_2 \rightarrow CH_3BeCH_3 + CH_3OCH_3 + H_2Be\cdot OH_2$	−9.00	−48.81	8.51
$BeNCH_3$	−108.578 30	$BeNCH_3 + CH_3NH_2 \rightarrow BeNH + CH_3NHCH_3$	2.22	93.40	-
$H_2BH_2BHCH_3$	−91.856 22	$H_2BH_2BHCH_3 + BH_2CH_3 \rightarrow H_2BH_2BH_2 + BH(CH_3)_2$	−4.44	−7.90	34.84
$CH_3HBH_2BHCH_3$	−130.905 18	$CH_3HBH_2BHCH_3 + 2BH_2CH_3 \rightarrow H_2BH_2BH_2 + 2BH(CH_3)_2$	−5.65	−24.14	34.13
$H_2BH_2B(CH_3)_2$	−130.902 77	$H_2BH_2B(CH_3)_2 + 2BH_2CH_3 \rightarrow H_2BH_2BH_2 + 2BH(CH_3)_2$	−7.16	−22.63	32.12
$(CH_3)_2BH_2BHCH_3$	−169.949 94	$(CH_3)_2BH_2BHCH_3 + 3BH_2CH_3 \rightarrow H_2BH_2BH_2 + 3BH(CH_3)_2$	−9.25	−37.98	30.52
$(CH_3)_2BH_2B(CH_3)_2$	−208.993 27	$(CH_3)_2BH_2B(CH_3)_2 + 4BH_2CH_3 \rightarrow H_2BH_2BH_2 + 4BH(CH_3)_2$	−14.24	−50.60	25.70
CH_3BH_2BH	−90.651 79	$CH_3BH_2BH + BH_2CH_3 \rightarrow HBH_2BH + BH(CH_3)_2$	−0.87	27.33	120.93
$CH_3BH_2BCH_3$	−129.699 68	$CH_3BH_2BCH_3 + 2BH_2CH_3 \rightarrow HBH_2BH + 2BH(CH_3)_2$	−2.75	11.76	132.82
$CH_3B\cdot CH_2$	−103.274 06	$CH_3BCH_2 + BH_2CH_3 \rightarrow BHCH_2 + BH(CH_3)_2$	2.86	30.27	-
$HB\cdot CHCH_3$	−103.252 30	$BHCHCH_3 + BH_2CH_3 \rightarrow BHCH_2 + BH_2CH_2CH_3$	−1.03	46.38	-
$HB\cdot C(CH_3)_2$	−142.282 76	$BHC(CH_3)_2 + BH_2CH_3 \rightarrow BHCH_2 + BH_2CH(CH_3)_2$	0.33	44.24	-
$CH_3B\cdot CHCH_3$	−142.306 90	$CH_3BCHCH_3 + BHCH_2 \rightarrow CH_3BCH_2 + BHCHCH_3$	−0.53	26.62	-
$CH_3B\cdot C(CH_3)_2$	−181.336 58	$CH_3BC(CH_3)_2 + BHCH_2 \rightarrow CH_3BCH_2 + BHC(CH_3)_2$	−1.02	24.96	-
$CH_3BH_2\cdot NH_3$	−121.655 32	$CH_3BH_2\cdot NH_3 + BH_3 \rightarrow BH_3\cdot NH_3 + BH_2CH_3$	−4.96	−29.50	23.53
$(CH_3)_2BH\cdot NH_3$	−160.699 04	$(CH_3)_2BH\cdot NH_3 + BH_3 \rightarrow BH_3\cdot NH_3 + BH(CH_3)_2$	−9.46	−42.45	19.03
$(CH_3)_3B\cdot NH_3$	−199.742 40	$(CH_3)_3B\cdot NH_3 + BH_3 \rightarrow BH_3\cdot NH_3 + B(CH_3)_3$	−13.59	−55.17	14.90
$H_3B\cdot NH_2CH_3$	−121.641 73	$BH_3\cdot NH_2CH_3 + NH_3 \rightarrow BH_3\cdot NH_3 + CH_3NH_2$	2.79	−14.84	31.28
$H_3B\cdot NH(CH_3)_2$	−160.671 63	$BH_3\cdot NH(CH_3)_2 + NH_3 \rightarrow BH_3\cdot NH_3 + CH_3NHCH_3$	3.34	−14.32	31.83
$H_3B\cdot N(CH_3)_3$	−199.700 05	$BH_3\cdot N(CH_3)_3 + NH_3 \rightarrow N(CH_3)_3 + BH_3\cdot NH_3$	2.07	−14.27	30.56
$CH_3BH_2\cdot OH_2$	−141.460 99	$CH_3BH_2\cdot OH_2 + BH_3 \rightarrow BH_3\cdot OH_2 + BH_2CH_3$	−3.56	−60.80	8.00
$(CH_3)_2BH\cdot OH_2$	−180.509 04	$(CH_3)_2BH\cdot OH_2 + BH_3 \rightarrow BH_3\cdot OH_2 + BH(CH_3)_2$	−5.35	−76.46	6.21
$(CH_3)_3B\cdot OH_2$	−219.556 97	$(CH_3)_3B\cdot OH_2 \rightarrow OH_2 + B(CH_3)_3$	2.49	−89.59	2.49
$H_3B\cdot OHCH_3$	−141.443 19	$BH_3\cdot OHCH_3 + OH_2 \rightarrow BH_3\cdot OH_2 + CH_3OH$	2.04	−39.84	13.60
$H_3B\cdot O(CH_3)_2$	−180.472 24	$BH_3\cdot O(CH_3)_2 + H_2O \rightarrow BH_3\cdot OH_2 + CH_3OCH_3$	1.87	−35.48	13.43
$(CH_3)_3B\cdot O(CH_3)_2$	−297.609 82	$(CH_3)_3B\cdot O(CH_3)_2 + BH_3 + H_2O \rightarrow BH_3\cdot OH_2 + B(CH_3)_3 + CH_3OCH_3$	−7.33	−77.52	4.23
$CH_3B\cdot NH$	−119.346 24	$CH_3BNH + CH_2CH_3 \rightarrow HBNH + BH(CH_3)_2$	2.18	−12.58	222.32
$HB\cdot NCH_3$	−119.326 01	$BHNCH_3 + CH_3NH_2 \rightarrow BHNH + CH_3NHCH_3$	3.21	4.91	-
$CH_3B\cdot NCH_3$	−158.379 43	$CH_3BNCH_3 + BH_2CH_3 + CH_3NH_2 \rightarrow BHNH + BH(CH_3)_2 + CH_3NHCH_3$	4.80	−14.12	-
$CH_3B\cdot O$	−139.224 83	$CH_3BO + BH_2CH_3 \rightarrow BHO + BH(CH_3)_2$	4.89	−85.23	219.24
$F_3B\cdot NH_3$	−379.412 53	$BF_3\cdot NH_3 + BH_3 \rightarrow BH_3\cdot NH_3 + BF_3$	−2.98	−307.89	25.51
$F_3B\cdot OH_2$	−399.220 55	$BF_3\cdot OH_2 + BH_3 \rightarrow BH_3\cdot OH_2 + BF_3$	−0.11	−340.66	11.45
$H_3B\cdot NF_3$	−178.931 41	$BH_3NF_3 + NH_3 \rightarrow BH_3NH_3 + NF_3$	−22.65	−15.46	5.84
$NH_2BH_2\cdot NH_3$[b]	−137.671 81	$NH_2BH_2\cdot NH_3 + BH_3 \rightarrow BH_2NH_2 + BH_3\cdot OH_2$	−24.53	−37.94[55]	3.96
$NH_2BH_2\cdot OH_2$[c]	−157.502 43	$NH_2BH_2\cdot OH + BH_3 \rightarrow BH_3\cdot NH_3 + BH_2NH_2$	−7.48	−84.89	4.08
$NH_2B(CH_3)_2\cdot NH_3$[b]	−215.761 22	$NH_2B(CH_3)_2\cdot NH_3 + BH_3 \rightarrow NH_2BH_2\cdot NH_3 + BH(CH_3)_2$	−8.09	−64.25	−1.38
$HOBH_2\cdot NH_3$[b]	−157.515 69	$HOBH_2\cdot NH_3 + BH_3 \rightarrow BH_3\cdot NH_3 + BH_2OH$	−17.26	−91.60	11.23
$HOBH_2\cdot OH_2$[c]	−177.337 90	$HOBH_2\cdot OH_2 + BH_3 \rightarrow BH_3\cdot OH_2 + BH_2OH$	−5.49	−133.27	6.07
$HOBH_2\cdot OH_2$[b]	−177.322 97	$HOBH_2\cdot OH_2 + BH_3 \rightarrow BH_3\cdot OH_2 + BH_2OH$	−4.86	123.90	−3.30
$HOB(CH_3)_2\cdot NH_3$[b]	−235.607 43	$HOB(CH_3)_2\cdot NH_3 + BH_3 \rightarrow HOBH_2\cdot NH_3 + BH(CH_3)_2$	−6.63	−119.36	4.69
$(CH_3)_2B(OCH_3)\cdot NH_3$[b]	−274.631 68	$(CH_3)_2BOCH_3\cdot NH_3 + BH_3 \rightarrow (CH_3)_2BOCH_3 + BH_3\cdot NH_3$	−22.70	−111.94	5.79
$BH_2F\cdot NH_3$[b]	−181.533 69	$BH_2F\cdot NH_3 + BH_3 \rightarrow BH_3\cdot NH_3 + BH_2F$	−6.43	−109.62	22.06
$BH_2F\cdot OH_2$[b]	−201.343 20	$BH_2FOH_2 + BH_3 \rightarrow BH_3OH_2 + BH_2F$	−2.62	−143.32	8.94
$(CH_3)_2BF\cdot NH_3$[b]	−259.629 00	$(CH_3)_2BF\cdot NH_3 + BH_3 \rightarrow BH_2F + (CH_3)_2BH\cdot NH_3$	−1.35	−139.62	15.48
$(CH_3)_2BF\cdot OH_2$[b]	−279.447 18	$(CH_3)_2BF\cdot OH_2 + BH_3 \rightarrow BH_2F\cdot OH_2 + BH(CH_3)_2$	1.05	−178.77	7.79

[a] Total energies (au) and ΔE_r values (kcal/mol) are at the HF/6-31G(d)//HF/6-31G(d) level. [b] Tetrahedral boron atom. [c] Planar boron atom (molecular complex). [d] ΔE_r, ΔH_f, and BDE are calculated using data reported in Tables I–III of ref 14 and from unpublished values given in ref 31. BDE refers to the bond quoted in column 1 by a hyphen (see also footnote *b* of Table I).

Thus, the $(CH_3)_2Be\cdot N(CH_3)_3$ and $CH_3Li\cdot N(CH_3)_3$ BDE's could be estimated respectively as

$$\mathrm{BDE}(H_2Be\cdot NH_3) - (3 \times 3.30) = 13.30 \text{ kcal/mol}$$

(versus 13.92 kcal/mol from Table II) and

$$\mathrm{BDE}(CH_3Li\cdot NH_3) - (3 \times 0.90) = 15.9 \text{ kcal/mol}$$

(versus 15.21 kcal/mol from Table II).

We can extend the use of relations (1a) and (2a) for BF_3 derivatives. Substituting BF_3X for BH_3X, one writes

$$\mathrm{BDE}(F_3B\cdot NMe_3) = \mathrm{BDE}(F_3\cdot NH_3) + 2.73 = 28.24 \text{ kcal/mol}$$

versus 27.33[36] or 26.6[37] for the experimental values and

$$\mathrm{BDE}(F_3B\cdot OMe_2) = \mathrm{BDE}(F_3B\cdot OH_2) + 1.96 = 13.41\ \mathrm{kcal/mol}$$

versus 12.79[36] or 13.90[39] for the experimental values. The complexation energy for $F_3B{\cdot}OH_2$ reported here (11.45 kcal/mol) is lower than that proposed by Archibald (16.73 kcal/mol[40]) or by Pradeep (34.4 kcal/mol[41]). Actually, our result seems to be more reliable compared with the experimental complexation energy of $F_3B{\cdot}O(CH_3)_2$ (12.8,[36-38] 13.9 kcal/mol[39]). Moreover, methyl substitution usually lowers the B←X bond strength (see $BF_3{\cdot}NH_3$ and $BF_3{\cdot}N(CH_3)_3$). The binding energy of $F_3B{\cdot}NH_3$ is also slightly lower (25.5 kcal/mol) than that of $H_3B{\cdot}NH_3$ (28.5 kcal/mol); therefore, we do not expect a stronger bond strength in $F_3B{\cdot}OH_2$ than in $H_3B{\cdot}OH_2$.

For $BF_3{\cdot}NH_3$, our ΔH_f value combined with the experimental value in the solid state ($\Delta H_f(BF_3{\cdot}NH_3,\mathrm{cr}) = -323.6$ kcal/mol[36]) gives a sublimation enthalpy of 15.7 kcal/mol, which seems reasonable ($\Delta H_{\mathrm{subl}}(BH_3{\cdot}N(CH_3)_3) = 14$ kcal/mol,[37] $\Delta H_{\mathrm{vap}}(BF_3{\cdot}O(CH_3)_2) = 13.1$ kcal/mol[39]).

$BH_3{\cdot}NF_3$ has never been isolated, and the explosive character of the B_2H_6–NF_3 mixture could preclude its existence.[42] The strong electron-withdrawing tendency of fluorine atoms reduces the donor ability of the nitrogen. Therefore, the lone-pair basicity and the dative N→B bond strength become weaker. The BDE decreases to 5.84 kcal/mol. If, in ammonia–borane and *B*-trifluoro ammonia–borane, the boron center has a tetrahedral environment, it becomes trigonal in *N*-trifluoro ammonia–borane as in borane(3). This confirms the weak dative character of the nitrogen in this compound.

Bond Energies in Alkyl Derivatives

A series of bond energies involving Li, Be, and B have been calculated using a simple thermochemical model.[43] The heat of atomization decomposes to a sum of bond energies (E_b) augmented with a term which measures the deviation with respect to the additive scheme, namely the so-called "stabilization energy" (SE):

$$\Delta H_a = \sum_b E_b + \mathrm{SE} \qquad (5)$$

Details on how to build the bond energy table can be found elsewhere.[14,43,44] We consider the bond terms $E_b(XY)$ for each multiplicity of the bond, where X and Y stand for heavy atoms, and $E_b(XH)_n{}^Y$ for X–H single bonds. The subscript "n" is an integer depending on the number of adjacent X–H bonds; for C–H bonds, it may be replaced by the characters p, s, or t when n = 3, 2, or 1, respectively. $E_b(XH_{n/\max}{}^Y$ gives the number of X–H bonds (n) and the maximum possibilities (max) according to the X center hybridization. It is used to avoid confusion when different situations can be considered. The superscript Y corresponds to the occurrence of one X–Y bond adjacent to the X–H bond; when Y stands for C, the superscript is omitted. We also write

$$E_b(XH)_n{}^Y = E_b(XH)_n + \Delta(XH)_n{}^Y \qquad (6a)$$

$$E_b(XH)_n{}^{Y,Z} = E_b(XH)_n + \Delta(XH)_n{}^Y + \Delta(XH)_n{}^Z \qquad (6b)$$

Table IV collects the bond energies. They are obtained by a least-squares fit procedure[45] on data given in Table II. These values are used in Table V to estimate some atomization enthalpies and to compare them with available experimental values. The theoretical ΔH_f or BDE (depending on the experimentally reported property) seems to be overestimated by no more than 0.6 kcal/mol.

Table III. Direct Comparison of Theory versus Experiment (Values in kcal/mol)

compd	property[a]	theor	exptl	ref
$H_3B{\cdot}NH_2CH_3$	ΔH_f	−14.84	−13 ± 1	32
$H_3B{\cdot}NH(CH_3)_2$	ΔH_f	−14.32	−14 ± 1	32
$H_3B{\cdot}N(CH_3)_3$	ΔH_f	−14.28	−20.3	32, 33
	BDE	30.56	31.5	37
	BDE		32.3	34
$(CH_3)_3B{\cdot}NH_3$	ΔH_f	−55.17	−54.1	36–38
	BDE	14.90	13.75	35
$(CH_3)_2BH_2B(CH_3)_2$	BDE[b]	25.70	25	37

[a] BDE values are relative to B–N or B–O bonds. [b] Dissociation in 2 $BH(CH_3)_2$.

Table IV. New Bond Energies (kcal/mol)

bond	E_b	Δ	bond	E_b	Δ
dative LiN bond environment			dative LiO bond environment		
$E_b(LiH)^N$	58.35	1.79	$E_b(LiH)^O$	58.23	1.66
$E_b(NH)_p{}^{Li}$	94.29	0.88	$E_b(OH)_{2/2}{}^{Li}$	111.90	1.12
$E_b(NH)_s{}^{Li}$	92.70	1.15	$E_b(OH)_{1/2}{}^{Li}$	110.76	2.73
$E_b(NH)_t{}^{Li}$	91.66	1.12			
$E_b(Li \leftarrow N)$	15.23		$E_b(Li \leftarrow O)$	11.86	
dative BeN bond environment			dative BeO bond environment		
$E_b(BeH)_{2/2}{}^N$	74.87	3.71	$E_b(BeH)_{2/2}{}^O$	74.69	3.53
$E_b(BeH)_{1/2}{}^N$	75.05	3.67	$E_b(BeH)_{1/2}{}^O$	74.87	3.49
$E_b(NH)_p{}^{Be}$	94.04	0.62	$E_b(OH)_{2/2}{}^{Be}$	111.64	0.86
$E_b(NH)_s{}^{Be}$	92.85	1.30	$E_b(OH)_{1/2}{}^{Be}$	111.44	3.40
$E_b(NH)_t{}^{Be}$	92.85	2.32			
$E_b(Be \leftarrow N)$	14.34		$E_b(Be \leftarrow O)$	9.24	
dative BN bond environment			dative BO bond environment		
$E_b(BH)_p{}^N$	94.00	4.38	$E_b(BH)_p{}^O$	92.22	2.60
$E_b(BH)_s{}^N$	93.75	4.01	$E_b(BH)_s{}^O$	91.36	1.63
$E_b(BH)_t{}^N$	93.77	3.85	$E_b(BH)_t{}^O$	91.72	1.80
$E_b(NH)_p{}^B$	92.62	0.80	$E_b(OH)_{2/2}{}^B$	111.38	−0.40
$E_b(NH)_s{}^B$	91.84	0.30	$E_b(OH)_{1/2}{}^B$	108.77	0.74
$E_b(NH)_t{}^B$	91.52	0.99			
$E_b(B \leftarrow N)$	17.58		$E_b(B \leftarrow O)$	5.21	
triple BeN bond environment			triple BO bond environment		
$E_b(Be{\equiv}N)$	57.46		$E_b(B_t{-}H)^O$	84.33	−5.59
			$E_b(B{\equiv}O)$	224.72	
triple BN bond environment			double BC bond environment		
$E_b(B_t{-}H)^N$	87.33	−2.59	$E_b(C_d{-}H)_2{}^B$	101.84	1.54
$E_b(N_t{-}H)^B$	89.81	−0.73	$E_b(C_d{-}H)_1{}^B$	102.85	3.07
$E_b(B{\equiv}N)$	167.63		$E_b(B_d{-}H)$	86.88	−3.04
			$E_b(B{=}C)$	121.21	
BHB bond in $\rangle BH_2B\langle$			BHB bond in $-BH_2B-$		
$E_b(B_bH)_1{}^{>BH_2B<}$	93.14	3.48	$E_b(B_bH)^{-BH_2B-}$	90.60	0.67
$E_b(B_bH)_2{}^{>BH_2B<}$	92.52	2.10			
$E_b(>BH_2B<)$	205.85		$E_b(-BH_2B-)$	252.47	

The standard deviation of the error does not exceed 1.2 kcal/mol. If we consider the difficulties in obtaining accurate experimental heats of formation, we can be convinced of the overall quality of the theoretical values, including those of Table I (values in Table I being used in Table II). In the case of X–H bonds, where X stands for an atom involved in a dative bond, one observes an increase ($\Delta(XH) > 0$) of the bond energy compared with the normal X–H term. The variations can reach 4.3 kcal/mol. We summarize this conclusion as

$$\langle \Delta(XH)_n{}^Y \rangle = 3.0 \pm 1.0\ \mathrm{kcal/mol}$$
$$X = Li, Be, B;\ Y = N, O$$

$$\langle \Delta(XH)_n{}^Y \rangle = 1.0 \pm 0.9\ \mathrm{kcal/mol}$$
$$X = N, O;\ Y = Li, Be, B$$

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Table V. Prediction of Atomization Energy Based on the Bond Energies (kcal/mol)

compd	$\Sigma E_b \approx \Delta H_a$-(theor)	ΔH_a-(exptl)	origin of exptl value		ref[a]
$H_3B{\cdot}N(C_2H_5)_3$	2246.32	2245.95	ΔH_f	−32.5 ± 0.5	32
		2246.05	ΔH_f	−33.	33
$(CH_3)_2BH{\cdot}N(CH_3)_3$	1977.43	1979.06	BDE	23.4	37
$(CH_3)_3B{\cdot}NH_2CH_3$	1715.22	1714.66	BDE	17.64	35
$(CH_3)_3B{\cdot}NH(CH_3)_2$	1990.19	1990.54	BDE	19.26	35
$(CH_3)_3B{\cdot}NH_2(C_2H_5)$	1997.05	1996.19	BDE	18.	35
$(CH_3)_3B{\cdot}NH(C_2H_5)_2$	2553.85	2551.48	BDE	16.31	35
$(CH_3)_3B{\cdot}N(CH_3)_3$	2265.45	2265.64	ΔH_f	−52.6	36
		2265.67	BDE	17.62	37
$F_3B{\cdot}N(CH_3)_3$	1591.73	1591.58	ΔH_f	−304.4	36
		1590.85	BDE	26.6	37
$F_3B{\cdot}O(CH_3)_2$	1235.63	1234.36	ΔH_f	−328.2	36–38
		1235.46	BDE	13.9	39
$F_3B{\cdot}O(C_2H_5)_2$	1802.86	1801.31	BDE	12.5	39
$(CH_3)_2BH_2B(CH_3)_2$	1734.17	1733.47	BDE[b]	25	37

[a] BDE values are relative to B–N or B–O dative bonds; for the calculation of ΔH_a from BDE, the ΔH_f values are taken from ref 20, except $\Delta H_f(B(CH_3)_3)$,[33] $\Delta H_f(BF_3)$,[36] and $\Delta H_f(CH_3BHCH_3)$.[14] [b] Dissociation in 2 $BH(CH_3)_2$.

Finally, Table IV contains two types of BH_2B ($B\overset{H}{\underset{H}{}}B$) bonds. They are denoted $> BH_2B <$ and $-BH_2B-$. The first can be found in normal diborane(6) and the latter in bridged diborane(4), namely $H_2BH_2BH_2$ and HBH_2BH, or their derivatives. We prefer to consider those bonds as diprotonated $>B{=}B<^{2-}$ double bonds and $-B{\equiv}B-^{2-}$ triple bonds, respectively. A single B–B bond only exists in H_2BBH_2 (which is 1.5 kcal/mol higher in energy than its isomer HBH_2BH at the MP4(sdtq)/6-311++G-(3df,2p)//MP2(full)/6-31G(d,p) level;[14] other theoretical works also report smaller differences[12,46,47]). Including the single B–B bond energy calculated in ref 14, we write the sequence (kcal/mol)

$$E_b(>B{-}B<) = 68.29 < E_b(>BH_2B<) = 205.85 < E_b(-BH_2B-) = 252.47$$

The triple bond ($-BH_2B-$), which contains six electrons between the two borons, has an energy lower than the sum of single and double bonds, as in the case of C–C bonds. Half of the value obtained for the double bond is close to the values reported for BHB bond strength in some other works (105–108 kcal/mol[48–50]). For single B–B bond energy Sanderson also uses 68 kcal/mol.[51] This value comes from the $B_2(^3\Sigma_g^-)$ dissociation energy. Other values have been proposed for this bond energy (kcal/mol):

$$\mathrm{BDE}(B_2(^3\Sigma_g^-)) = 70.7 \pm 8,^{19}\ 62.5,^{52}\ 64.7,^{12}\ 64.8^{53}$$

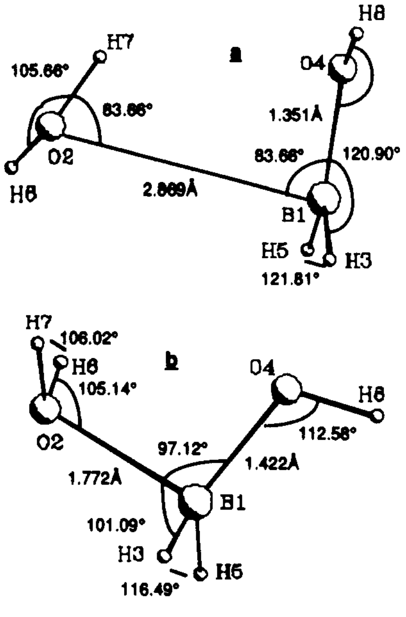

Figure 1. Two $HOBH_2{\leftarrow}OH_2$ structures: (a) water–hydroxyborane, (b) *B*-hydroxy water–borane.

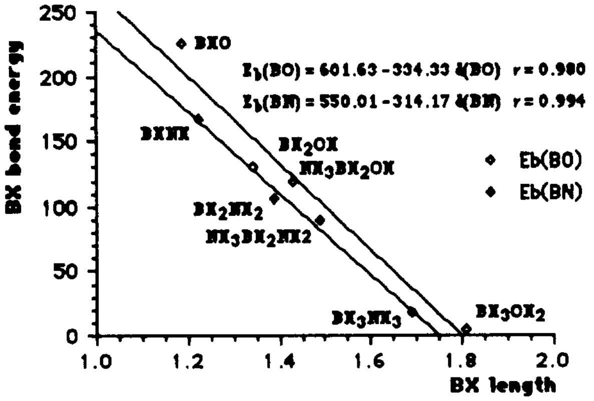

Figure 2. Relation between bond energies and bond lengths: the case of B–O and B–N.

Table VI. B–N and B–O Bond Energies (kcal/mol)

bond	B–O	B–N	bond	B–O	B–N
dative	5.21	17.58	double[14]	129.92	106.70
single	119.05	90.89	triple	224.72	167.63

Single B–O and B–N Bonds

Let us now consider $HOBH_2{\cdot}OH_2$. As shown in Figure 1, we find two nuclear structures (both are really minima, their Hessian matrix being positively defined). The first, the more stable one, is a molecular complex between BH_2OH (which remains planar) and water. In the second, the boron has a tetrahedral environment. This is a hydroxy derivative of water–borane. The sp^3 character of the boron atom reduces its electron-withdrawing tendency. The B vacancy has already been fulfilled by one of the water lone pairs in $HOBH_2{\leftarrow}OH_2$ (or by the ammonia lone pair in $HOBH_2{\leftarrow}NH_3$). This means that there is a single covalent B–O bond which could have an strength intermediate between those of dative (as in $BH_3{\leftarrow}OH_2$) and double (as in $BH_2{=}OH$) B–O bonds.

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In $HOBH_2 \leftarrow X$, the increase of the $B \leftarrow X$ dative bond strength enhances the single-bond character of the B–O bond. This is why we prefer using ammonia derivatives (rather than water compounds) to calculate the single-bond energies. With $\Delta H_f((CH_3)_2BOCH_3 \cdot NH_3)$ from Table II and bond energies from ref 14, one writes (assuming SE-$((CH_3)_2BOCH_3 \cdot NH_3) = 0$):

$$\Delta H_a((CH_3)_2BOCH_3 \cdot NH_3) = 6E_b(CH)_p{}^B + 2E_b(B\text{-}C) + 3E_b(CH_p{}^O + E_b(C\text{-}O) + 3E_b(NH)_p{}^B + E_b(B \leftarrow N) + E_b(B\text{-}O) = (6 \times 101.66) + (2 \times 77.17) + (3 \times 95.87) + 91.66 + (3 \times 92.62) + 17.58 + E_b(B\text{-}O)$$

One obtains $E_b(B\text{-}O) = 119.05$ kcal/mol. This value is 10.87 kcal/mol lower than the value previously reported for the B=O double bond (see Table VI). Let us mention that the use of $(CH_3)_2BOH \cdot NH_3$ instead of $(CH_3)_2BOCH_3 \cdot NH_3$ for evaluating the B–O bond strength does not change the result significantly (in this case, $E_b(B\text{-}O) = 118.68$ kcal/mol). These bond energies correlate with the bond lengths (see Figure 2).

We also find a single covalent B–N bond. This bond appears in $NH_2BH_2 \leftarrow NH_3$[55] or in $NH_2B(CH_3)_2 \leftarrow NH_3$. From the following relation, we deduce the value of E_b-(B–N):

$$\Delta H_a((CH_3)_2BNH_2 \cdot NH_3) = 6E_b(CH)_p{}^B + 2E_b(B\text{-}C) + 2E_b(NH)_2{}^B + 3E_b(NH)_p{}^B + E_b(B \leftarrow N) + E_b(B\text{-}N) = (6 \times 101.66) + (2 \times 77.17) + (2 \times 94.88) + (3 \times 92.62) + 17.58 + E_b(B\text{-}N)$$

It is found that $E_b(B\text{-}N) = 90.89$ kcal/mol. This value is 15.81 kcal/mol lower than the value obtained for the corresponding double bond ($E_b(B{=}N) = 106.70$ kcal/mol). It also corresponds to a rough estimate of Haaland[54] (91–92 kcal/mol or 88 ± 2 kcal/mol). Finally, for the B–F bond, only one bond term is found. We determined a B–F bond strength of 157.52[14] and 157.82 kcal/mol for $(CH_3)_2BF$ and $(CH_3)_2BF \cdot NH_3$, respectively. In the latter molecule, however, the B–F length is significantly greater (1.39 Å) than in the former compound (1.33 Å). Nevertheless, dimethylfluoroborane has an sp^2 arrangement around the boron atom. The boron is sp^3 in ammonia–dimethylfluoroborane. For $(CH_3)_2BF \cdot OH_2$, one obtains 160.90 kcal/mol for the B–F bond. It is 3 kcal/mol greater than for the previous B–F bonds. This stronger character of B–F must be related to the less dative tendency of the water lone pair, compared with that of ammonia.

Conclusion

In this theoretical study, we consider several electron-deficient compounds not studied in a recent paper.[14] Accurate heats of formation have been obtained for the simplest boron, beryllium, and lithium adducts. Methyl and fluoro derivatives of the previous molecules have also been investigated, in order to have a larger number of comparisons with experimental values at our disposal. Finally, our bond energy table has been completed with new terms coming from the molecules considered in this work. They can be useful in calculating the stabilization energy according to eq 5 for larger compounds. Despite the limited number of tests of our theoretical results, we are convinced that the ΔH_f values reported are reliable. The quality of our theoretical predictions has been established whenever accurate experimental values have been available, especially for $B \leftarrow N$ and $B \leftarrow O$ derivatives. Moreover, all the reported values seem consistent with each other through isodesmic reactions as well as through the thermochemical model in use. In the case of Be and Li compounds, there is no reason to think our heats of formation are more suspicious than those determined for boron species. Finally, some support for single B–O and B–N bonds has been obtained from calculations on various substituted ammonia– and water–borane species. They are respectively 11 and 16 kcal/mol weaker than the corresponding π-dative double bonds.

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[55] $\Delta H_f(NH_2BH_2NH_3)$ has been recalculated at the MP4(sdtq)/6-31+G(2df,p)//MP$_2$(full)/6-31G(d,p) + TC (HF/6-31G*//HF/6-31G*) level to check the accuracy of the value reported in Table II. From $NH_3BH_2NH_2 + H_2 \rightarrow NH_3NH_3 + NH_3$ one obtains $\Delta H_f(NH_3BH_2NH_2) = -37.36$ kcal/mol, and $NH_3BH_2NH_2 + BH_3 \rightarrow NH_3NH_3 + NH_2BH_2$ yields $\Delta H_f(NH_3BH_2NH_2) = -38.41$ kcal/mol, versus −37.94 kcal/mol from Table II at the 6-31G* level.