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Evaluation of the bond energy terms for the various types of boron-nitrogen bonds*

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Summary. We have determined a series of bond energy terms in compounds containing dative, single, double and/or triple boron-nitrogen bonds. We describe various interesting applications based on these bond energy terms namely the determination of enthalpies of atomization and stabilization energies. More particularly, the conventional ring strain energies of three- and four-membered small ring containing boron and nitrogen atoms could be determined and the aromaticity of borazine, reexamined.

Key words: Boron-nitrogen bonds – Enthalpies of atomization – Stabilization energies – Aromaticity of borazine

1 Introduction

It is commonly assumed that the enthalpy of atomization of a compound is equal to its total chemical binding energy [1]. This quantity may be generally divided into three terms corresponding respectively to chemical bonds and to stabilizing and destabilizing contributions. These contributions can be considered to be insignificant for many compounds, on the basis of chemical intuition. Thus, for those species, the enthalpy of atomization is written as:

$$\Delta H_a^0 = \sum N_{AB} E_{AB} \tag{1}$$

where E_{AB} is a bond energy term supposed to be constant and transferable from one compound to another if the nearest neighbours of the bond are the same. Therefore, the energies of individual bonds can be derived from the enthalpies of atomization of a set of "reference compounds". In this work, we have determined a series of bond energy terms in molecules containing the various types of boron-nitrogen bonds.

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2 The bond energy terms in amine-borane derivatives

In amine-borane and its alkyl derivatives, the B–N bond is commonly considered as a prototype of a dative bond. It is characterized by a large N–B bond length (1.658 Å [2]) and a small bond strength (28.5 kcal mol^{-1} [3]). The enthalpy of atomization of amine-borane and a set of methyl derivatives were derived from the corresponding enthalpies of formation reported in Table 1. The bond energy terms were calculated by the least squares method using the MULFRA computer program [5] and the terms $E(\mathrm{C{-}N})$ and $E(\mathrm{C{-}H})_p^{\mathrm{N}}$ previously determined [6]. The results obtained are collected in Table 2.

It is seen that the bond energy of a dative N–B bond is rather small. The difference between the bond strength, $BDE(\mathrm{N \rightarrow B})$, and the bond energy term, $E(\mathrm{N \rightarrow B})$, comes from the fact that $E(\mathrm{B{-}H})_3^{\mathrm{BH_3}}$ and $E(\mathrm{N{-}H})_3^{\mathrm{NH_3}}$ are not equal to $E(\mathrm{B{-}H})_3^{\mathrm{N}}$ and $E(\mathrm{N{-}H})_3^{\mathrm{B}}$, respectively (see Table 2). One may effectively write, for $\mathrm{H_3N \rightarrow BH_3}$:

$$\begin{aligned} BDE(\mathrm{N \rightarrow B}) = {} & 3E(\mathrm{N{-}H})_3^{\mathrm{B}} + E(\mathrm{N \rightarrow B}) + 3E(\mathrm{B{-}H})_3^{\mathrm{N}} \\ & - 3E(\mathrm{N{-}H})_3^{\mathrm{NH_3}} - 3E(\mathrm{B{-}H})_3^{\mathrm{BH_3}} \end{aligned} \tag{2}$$

or, more explicitly

$$BDE(\mathrm{N \rightarrow B}) = E(\mathrm{N \rightarrow B}) + 10.9\ \mathrm{kcal\ mol^{-1}} \tag{3}$$

Table 1. Enthalpies of formation of some methyl derivatives of amine-borane (kcal mol^{-1})

Compounds	ΔH_f^0	Refs.
$\mathrm{BH_3{-}NH_3}$	−17.52	[3]
$\mathrm{CH_3BH_2{-}NH_3}$	−29.50	[3]
$\mathrm{(CH_3)_2BH{-}NH_3}$	−42.45	[3]
$\mathrm{(CH_3)_3B{-}NH_3}$	−55.17	[3]
$\mathrm{BH_3{-}NH_2CH_3}$	−14.84	[3]
$\mathrm{BH_3{-}NH(CH_3)_2}$	−14.32	[3]
$\mathrm{BH_3{-}N(CH_3)_3}$	−14.27	[3]
$\mathrm{(CH_3)_3B{-}N(CH_3)_3}$	−52.60	[4]

Table 2. Bond energy terms in alkyl amine-boranes (kcal mol^{-1})

Bond term[a]	Energy
$E(\mathrm{N{-}H})_3^{\mathrm{NH_3}}$	93.42
$E(\mathrm{N{-}H})_3^{\mathrm{B}}$	92.62
$E(\mathrm{N{-}H})_2^{\mathrm{B}}$	91.84
$E(\mathrm{N{-}H})_1^{\mathrm{B}}$	91.52
$E(\mathrm{B{-}H})_3^{\mathrm{BH_3}}$	89.62
$E(\mathrm{B{-}H})_3^{\mathrm{N}}$	94.00
$E(\mathrm{B{-}H})_2^{\mathrm{N}}$	93.75
$E(\mathrm{B{-}H})_1^{\mathrm{N}}$	93.77
$E(\mathrm{N \rightarrow B})$	17.58

[a] $E(\mathrm{N{-}H})_3^{\mathrm{NH_3}}$ is the energy of a N–H bond in ammonia: $E(\mathrm{N{-}H})_3^{\mathrm{NH_3}} = \frac{1}{3}\Delta H_a^0(\mathrm{NH_3})$ [7]; $E(\mathrm{N{-}H})_m^{\mathrm{B}}$ ($m = 3$, 2 or 1) is the energy of a N–H bond in the species $\mathrm{(CH_3)_{3-m}NH_mBH_n(CH_3)_{3-n}}$; $E(\mathrm{B{-}H})_3^{\mathrm{BH_3}}$ is the energy of a B–H bond in borane: $E(\mathrm{B{-}H})_3^{\mathrm{BH_3}} = \frac{1}{3}\Delta H_a^0(\mathrm{BH_3})$ [3]; $E(\mathrm{B{-}H})_n^{\mathrm{N}}$ ($n = 3$, 2 or 1) is the energy of a B–H bond in the species $\mathrm{(CH_3)_{3-m}NH_mBH_n(CH_3)_{3-n}}$; $E(\mathrm{N \rightarrow B})$ is the energy of a dative N–B bond

3 Bond energy terms related to the B–N double bond

It is generally assumed [22] that in the aminoborane system, boron and nitrogen are linked together by a normal covalent bond; but the unshared electron pair of

Table 3. Enthalpies of formation of BH_2NH_2 and some of its methyl derivatives (kcal mol^{-1})

Compounds	ΔH_f^0 [8]
BH_2NH_2	−23.02
CH_3BHNH_2	−38.64
$(CH_3)_2BNH_2$	−54.66
BH_2NHCH_3	−20.88
$BH_2N(CH_3)_2$	−18.08
$(CH_3)_2BN(CH_3)_2$	−46.69

Table 4. Bond energy terms related to the B−N double bond (kcal mol^{-1})

Bond term[a]	Energy
$E(N_d\text{-}H)_1^B$	95.21
$E(N_d\text{-}H)_2^B$	94.88
$E(B_d\text{-}H)_1^N$	91.40
$E(B_d\text{-}H)_2^N$	91.60
$E(B{=}N)$	106.70

[a] $E(N_d\text{-}H)_n^B$ ($n = 1$ or 2) is the energy of a N_d-H bond in a $NHCH_3$ or a NH_2 group where N_d represents a trigonal nitrogen atom bonded to a trigonal boron atom; $E(B_d\text{-}H)_m^N$ ($m = 1$ or 2) is the energy of a B_d-H bond in a $BHCH_3$ or a BH_2 group where B_d represents a trigonal boron atom bonded to a trigonal nitrogen atom; $E(B{=}N)$ is the energy of a "double" BN bond

the nitrogen can participate in this linkage thereby introducing a degree of double-bond character. This is actually confirmed by the short B−N bond in BH_2NH_2 (1.391 Å [9]). Thus this bond may be formally considered as a "double bond" (one covalent σ-bond plus one dative π-bond). The enthalpies of formation of BH_2NH_2 and some of its methyl derivatives are given in Table 3. They allowed us to determine the bond energy terms listed in Table 4.

4 Bond energy terms related to the B−N triple bond

A formal B−N triple bond (one covalent σ-bond plus one π-bond plus one dative π-bond) may be found in the species BHNH. The optimized geometry of BHNH calculated at the MP2/6-31G** level shows a B−N bond length of 1.25 Å. The enthalpies of formation of BHNH and its methyl derivatives are listed in Table 5 and the corresponding bond energy terms, in Table 6.

Table 5. Enthalpies of formation of BHNH and its methyl derivatives (kcal mol^{-1})

Compounds	ΔH_f^0 [3]
BHNH	7.05
CH_3BNH	−12.58
$BHNCH_3$	4.91
CH_3BNCH_3	−14.12

Table 6. Bond energy terms related to the B−N triple bond (kcal mol^{-1})

Bond term[a]	Energy
$E(N_t\text{-}H)^B$	89.81
$E(B_t\text{-}H)^N$	87.33
$E(B{\equiv}N)$	167.63

[a] $E(N_t\text{-}H)^B$ is the energy of a N_t-H bond where N_t represents a digonal nitrogen atom bonded to a digonal boron atom; $E(B_t\text{-}H)^N$ is the energy of a B_t-H bond where B_t represents a digonal boron atom bonded to a digonal nitrogen atom; $E(B{\equiv}N)$ is the energy of a "triple" BN bond

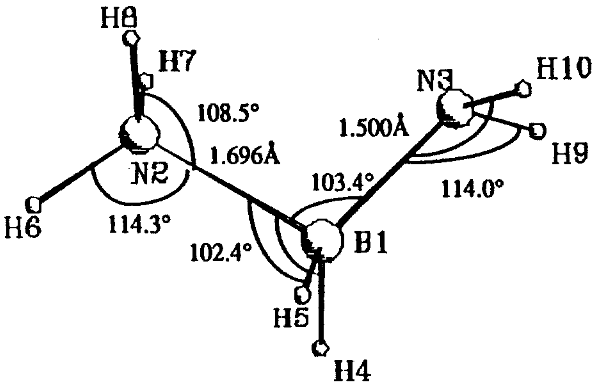


Fig. 1. Equilibrium structure of $NH_2-BH_2 \leftarrow NH_3$

5 Bond energy terms related to the B–N single bond

In the species $NH_2BH_2NH_3$, the boron vacancy can be fulfilled by the lone pair of the nitrogen atom of the NH_3 group. Thus the B–N bond in the BH_2-NH_2 fragment must lose its π-dative double bond character. The optimized geometry of the species $NH_2BH_2NH_3$ calculated at the RHF/6-31G* level is described in Fig. 1. It is seen that the boron atom has a tetrahedral environment. Moreover, the B–N bond in the BH_2-NH_2 fragment is significantly larger than the B–N double bond in the compound BH_2NH_2. Then it may be considered as a prototype for the B–N single covalent bond, the other B–N bond being clearly a dative one. Thus, the electronic structure of $NH_2BH_2NH_3$ can be described by the formula:

$$H_3N \rightarrow BH_2-NH_2$$

The bond energy terms related to the B–N single bond were derived from the enthalpies of atomization of the compounds listed in Table 7. The (RHF/6-31G*) energies of these species, the isodesmic reactions used to determine their enthalpies of formation and the latter quantities are also reported in Table 7.

The enthalpies of formation of the N-methyl and N-dimethyl derivatives are very sensitive to the choice of the isodesmic reaction. As we do not have any particular reason to prefer one to the other, we calculated the enthalpies of formation of those species as the arithmetic mean of the results derived from the two isodesmic reactions.

The bond energy terms related to the B–N single bond and the data used to calculate them are collected in Table 8. The characteristics of the various types of BN bonds are listed in Table 9. It is worth noticing that the value of E(B–N) is quite similar to the rough estimate of Haaland [10].

6 Miscellaneous applications

The bond energy terms collected in Tables 2, 4, 6 and 8 allow us to calculate the enthalpies of atomization of normal compounds and the stabilization energies of species where some particular effects do exist. For this purpose some additional

Table 7. Total energies (a.u.), isodesmic reactions and corresponding enthalpies of formation (kcal mol^{-1}) for some methyl derivatives of $NH_2-BH_2 \leftarrow NH_3$

Compounds	E	Isodesmic reaction	ΔH_f^{0a}
$NH_2BH_2NH_3$	−137.67181	$NH_2BH_2NH_3 + BH_3 \rightarrow BH_3NH_3 + BH_2NH_2$	−37.94
$NH_2BHCH_3NH_3$	−176.71673	$NH_2BHCH_3NH_3 + BH_3 \rightarrow NH_2BH_2NH_3 + BH_2CH_3$	−50.81
$NH_2B(CH_3)_2NH_3$	−215.76122	$(NH_2)B(CH_3)_2NH_3 + BH_3 \rightarrow NH_2BH_2NH_3 + BH(CH_3)_2$	−64.25
$CH_3NHBH_2NH_3$	−176.69620	$CH_3NHBH_2NH_3 + BH_3 \rightarrow BH_3NH_3 + BH_2NHCH_3$	−33.92
		$CH_3NHBH_2NH_3 + NH_3 \rightarrow NH_2BH_2NH_3 + NH_2CH_3$	−31.79
$(CH_3)_2NBH_2NH_3$	−215.72281	$(CH_3)_2NBH_2NH_3 + BH_3 \rightarrow BH_3NH_3 + BH_2N(CH_3)_2$	−32.79
		$(CH_3)_2NBH_2NH_3 + NH_3 \rightarrow NH_2BH_2NH_3 + NH(CH_3)_2$	−29.21

[a] Calculated without ZPE and thermal corrections

Table 8. Bond energy terms related to the B–N covalent single bond (kcal mol^{-1})[a]

Compound	ΔH_f^0	ΔH_a^0	$(B_s\text{-}H)_2^{N/N}$	$(B_s\text{-}H)_1^{N/N}$	$(N_s\text{-}H)_2^B$	$(N_s\text{-}H)_1^B$	B–N
$NH_2BH_2NH_3$	−37.94	763.10	2	0	2	0	1
$NH_2BHCH_3NH_3$	−50.81	1051.46	0	1	2	0	1
$NH_2B(CH_3)_2NH_3$	−64.25	1340.40	0	0	2	0	1
$CH_3NHBH_2NH_3$	−32.86	1033.51	2	0	0	1	1
$(CH_3)_2NBH_2NH_3$	−31.00	1307.15	2	0	0	0	1
Bond energies			93.50	93.22	95.11	93.50	90.43

[a] $(B_s-H)_n^{N/N}$ represents a B–H bond in a BH_n group ($n = 2$ or 1) where the boron atom is bonded to two nitrogen atoms by a single bond (subscript s) and a double bond respectively; $(N_s-H)_m^B$ represents a N–H bond in a NH_m group ($m = 2$ or 1) where the nitrogen atom is bonded to a boron atom by a single bond (subscript s); B–N represents a "single" B–N bond

Table 9. Comparison of various BN bonds

Bond	R (Å)	E (kcal mol^{-1})
N→B	1.66	17.58
N–B	1.50	90.43
N=B	1.39	106.70
N≡B	1.25	167.63

bond energy terms must be derived from the previous ones by using the notion of bond increment explicitly defined in other papers [11, 12]. For example, the energy of a N–H bond connected to two boron atoms by a single and a double bond respectively is calculated as follows:

$$E[(B{=})NH({-}B)] = E(N{-}H)_1^C + \Delta(N_d{-}H)_1^B + \Delta(N_S{-}H)_1^B \tag{4}$$

where

$$\Delta(\mathrm{N_d{-}H})_1^{\mathrm{B}} = E(\mathrm{N_d{-}H})_1^{\mathrm{B}} - E(\mathrm{N_d{-}H})_1^{\mathrm{C}} \tag{5}$$

$$4.68 = 95.21 - 90.53 \ (\mathrm{kcal\,mol^{-1}})$$

and

$$\Delta(\mathrm{N_s{-}H})_1^{\mathrm{B}} = E(\mathrm{N_s{-}H})_1^{\mathrm{B}} - E(\mathrm{N{-}H})_1^{\mathrm{C}} \tag{6}$$

$$2.97 = 93.50 - 90.53 \ (\mathrm{kcal\,mol^{-1}})$$

Thus

$$E[(\mathrm{B{=}})\mathrm{NH}(\mathrm{-B})] = 98.18\ \mathrm{kcal\,mol^{-1}} \tag{7}$$

A series of additional bond energy terms is given in Table 10.

Moreover, assuming that $\mathrm{NH_2{=}BH{-}NH{=}BH_2}$ is a reference compound, the term $E(\mathrm{B_d{-}N_d})$ can be directly deduced from the corresponding enthalpy of atomization [13]:

$$\begin{aligned}\Delta H_a^0 = {} & 2E(\mathrm{N_d{-}H})_2^{\mathrm{B}} + E[(\mathrm{N{=}})\mathrm{BH}(\mathrm{-N})] + E(\mathrm{B_d{-}N_d}) + E[(\mathrm{B{-}})\mathrm{NH}(\mathrm{=B})] \\ & + 2E(\mathrm{B_d{-}H})_2^{\mathrm{N}} + 2E(\mathrm{B{=}N})\end{aligned} \tag{8}$$

$$871.68[13] = 2(94.88) + 90.85 + E(\mathrm{B_d{-}N_d}) + 98.18 + 2(91.60) + 2(106.70) \tag{9}$$

Therefore

$$E(\mathrm{B_d{-}N_d}) = 96.29\ \mathrm{kcal\,mol^{-1}} \tag{10}$$

Table 10. Additional bond energy terms ($\mathrm{kcal\,mol^{-1}}$)

Bond term	Energy
$E(\mathrm{B_s{-}H})_2^{\mathrm{N}} = E(\mathrm{B{-}H})_2^{\mathrm{C}} + \Delta(\mathrm{B_s{-}H})_2^{\mathrm{N}}$ [a] $89.79 - 0.25$	89.49
$E(\mathrm{B_s{-}H})_1^{\mathrm{N}} = E(\mathrm{B{-}H})_1^{\mathrm{C}} + \Delta(\mathrm{B_s{-}H})_1^{\mathrm{N}}$ [b] $89.92 - 0.55$	89.37
$E[(\mathrm{B{=}})\mathrm{NH}(\mathrm{-B})] = E(\mathrm{N{-}H})_1^{\mathrm{C}} + \Delta(\mathrm{N_d{-}H})_1^{\mathrm{B}} + \Delta(\mathrm{N_s{-}H})_1^{\mathrm{B}}$ $90.53 + 4.68 + 2.97$	98.18
$E[(\mathrm{B{=}})\mathrm{NH}(\mathrm{-N})] = E(\mathrm{N{-}H})_1^{\mathrm{C}} + \Delta(\mathrm{N_d{-}H})_1^{\mathrm{B}} + \Delta(\mathrm{N{-}H})_1^{\mathrm{N}}$ $90.53 + 4.68 - 1.30$	93.91
$E[(\mathrm{B{-}})\mathrm{NH}(\mathrm{-N})] = E(\mathrm{N{-}H})_1^{\mathrm{C}} + \Delta(\mathrm{N_s{-}H})_1^{\mathrm{B}} + \Delta(\mathrm{N{-}H})_1^{\mathrm{N}}$ $90.53 + 2.97 - 1.30$	92.20
$E[(\mathrm{B{-}})\mathrm{NH_{(2)}}(\rightarrow\mathrm{B})] = E(\mathrm{N{-}H})_2^{\mathrm{C}} + \Delta(\mathrm{N_s{-}H})_2^{\mathrm{B}} + \Delta(\mathrm{N{-}H})_2^{\mathrm{B}}$ $91.54 + 3.57 + 0.30$	95.41
$E[(\mathrm{N{=}})\mathrm{BH}(\mathrm{-N})] = E(\mathrm{B{-}H})_1^{\mathrm{C}} + \Delta(\mathrm{B_d{-}H})_1^{\mathrm{N}} + \Delta(\mathrm{B_s{-}H})_1^{\mathrm{N}}$ $89.92 + 1.48 - 0.55$	90.85
$E[(\mathrm{N{=}})\mathrm{BH}(\mathrm{-B})] = E(\mathrm{B{-}H})_1^{\mathrm{C}} + \Delta(\mathrm{B_d{-}H})_1^{\mathrm{N}} + \Delta(\mathrm{B{-}H})_1^{\mathrm{B}}$ $89.92 + 1.48 + 1.28$	92.68
$E[(\mathrm{B{-}})\mathrm{BH}(\mathrm{-N})] = E(\mathrm{B{-}H})_1^{\mathrm{C}} + \Delta(\mathrm{B{-}H})_1^{\mathrm{B}} + \Delta(\mathrm{B_s{-}H})_1^{\mathrm{N}}$ $89.92 + 1.28 - 0.55$	90.65
$E[(\mathrm{N{-}})\mathrm{BH_{(2)}}(\leftarrow\mathrm{N})] = E(\mathrm{B{-}H})_2^{\mathrm{C}} + \Delta(\mathrm{B_s{-}H})_2^{\mathrm{N}} + \Delta(\mathrm{B{-}H})_2^{\mathrm{N}}$ $89.74 - 0.25 + 4.01$	93.50

[a] $\Delta(\mathrm{B_s{-}H})_2^{\mathrm{N}} = E(\mathrm{B_s{-}H})_2^{\mathrm{N/N}} - E(\mathrm{B{-}H})_2^{\mathrm{C}} - \Delta(\mathrm{B{-}H})_2^{\mathrm{N}}$

[b] $\Delta(\mathrm{B_s{-}H})_1^{\mathrm{N}} = E(\mathrm{B_s{-}H})_1^{\mathrm{N/N}} - E(\mathrm{B{-}H})_1^{\mathrm{C}} - \Delta(\mathrm{B{-}H})_1^{\mathrm{N}}$

Table 11. Theoretical and experimental enthalpies of atomization of some normal boron-containing species (kcal mol^{-1})

Compound	$\Delta H_a^0 = \sum N_{AB}E_{AB}$	ΔH_a^0(Exper.)
$BH_3N(C_2H_5)_3$	2246.32	2246.05 [1]
$(CH_3)_2BHN(CH_3)_3$	1977.43	1979.06 [14]
$(CH)_3BNH_2CH_3$	1715.22	1714.66 [15]
$(CH_3)_3BNH(CH_3)_2$	1990.19	1990.54 [15]
$(CH_3)_3BNH_2C_2H_5$	1997.05	1996.19 [15]
$(CH_3)_3BNH(C_2H_5)_2$	2553.85	2551.48 [15]

As a first application, we calculated the enthalpies of atomization of a set of normal compounds. The results obtained are listed in Table 11 with the corresponding experimental data. It is seen that the agreement between the two series of values is quite satisfactory. Therefore, the bond energy terms determined in this work can be confidently used to predict the enthalpies of atomization of normal boron containing molecules.

We have also calculated the stabilization energies of the boron derivatives listed in Table 12. The theoretical methods used to determine the optimized geometries and the total energies of these compounds are summarized in Table 13. The vibrational frequences needed to evaluate the zero point energies (Z.P.E.) and thermal corrections (T.C.) were computed at the HF/6-31G**//HF/6-31G** level. These quantities are known to be overestimated by approximately ten percent [16, 17]. Then, we used the next scaling procedure to correct the theoretical frequencies [18].

$$\nu(\text{exper.}) \approx \nu(\text{scaled}) = -45.99 + 0.92227\nu(\text{theor.})(\text{cm}^{-1}) \qquad (11)$$

The enthalpies of formation of species 5 and 6 have been obtained using the following hydrogenation reactions:

$$cNH(BH)_2 + H_2 \rightarrow NH(BH_2)_2$$
$$cBH(NH)_2 + H_2 \rightarrow BH(NH_2)_2$$

Table 12. Stabilized or destabilized boron-containing compounds considered in this work

Numbering	Compound
1	$BH(NH_2)_2$
2	$NH(BH_2)_2$
3	NH_2BNH
4	BH_2NBH
5	$cNH(BH)_2$
6	$cBH(NH)_2$
7	BH_2NBNH_2
8	$c(NHBH)_2$
9	$c(NBH_3)_2$
10	$c(NH_2BH_2)_2$
11	Borazine

Table 13. Properties calculated and theoretical methods

Compound	Optimized geometries	Total energies
1–6	MP2(full)/6-31G(d,p)	MP4 = SDTQ/6-31 + G(2df,p)
7–10	MP2(full)/6-31G(d,p)	MP2(full)/6-31G(d,p)
11	RHF/6-31G**	RHF/6-31G**

The enthalpies of formation of the other compounds were determined by means of chosen isodesmic reactions. All the data needed in the computations and the results obtained are collected in Table 14. The enthalpies of atomization of the species under consideration and the corresponding stabilization energies are reported in Table 15. Furthermore, some typical structural parameters are given in Table 16. These theoretical results call for the following comments.

– The BN bonds in diaminoborane are intermediate between single and double bonds. This compound is significantly stabilized by the delocalization of the lone pairs of the nitrogen atoms. A similar effect is observed in diborylamine.

– The large difference between the stabilization energies of the species 3 and 4 is not reflected by the BN bond lengths.

– The ring strain energy of azadiboridine is slightly larger than that of cyclopropane (-27.8 kcal mol^{-1}) when the C.R.S.E. of diazaboridine is slightly smaller than that of cyclopropene (-54.4 kcal mol^{-1}).

– The BN bond lengths and the stabilization energy of compound 7 suggest the existence of a significant interaction between the two terminal groups of opposite polarity.

– *s*-Diazadiborine has a non-planar structure. Its conventional ring strain energy is approximately equal to that of cyblobutane (-26.8 kcal mol^{-1}).

Table 14. Reference data and enthalpies of formation of various boron-containing compounds

Compounds	E (a.u.)	ZPE + T.C.[a]	Reaction	ΔH_f^0[a]
1	-137.15512[b]	43.403	$BH(NH_2)_2 + BH_3 \rightarrow 2BH_2NH_2$	-55.60
2	-107.24263[b]	38.956	$NH(BH_2)_2 + NH_3 \rightarrow 2BH_2NH_2$	-26.68
3	-135.91469[b]	29.221	$NH_2BNH + BH_3 \rightarrow BHNH + BH_2NH_2$	-14.73
4	-106.02227[b]	25.262	$BH_2NBH + NH_3 \rightarrow BHNH + BH_2NH_2$	2.09
5	-105.99410[b]	26.527	$cNH(BH)_2 + H_2 \rightarrow NH(BH_2)_2$	21.90
6	-135.82156[b]	28.268	$cBH(NH)_2 + H_2 \rightarrow BH(NH_2)_2$	43.63
7	-161.18552[c]	37.307	$BH_2NBNH_2 + BHNH \rightarrow NH_2BNH + BHNBH_2$	-26.12
8	-161.21240[c]	37.656	$c(NHBH)_2 + 3BH_3NH_3 + 2NH_3 \rightarrow 2BH_2NH_2 + 2NH_3BH_2NH_2$	-41.16
9	-162.38813[c]	51.722	$c(NBH_3)_2 \rightarrow c(NHBH)_2 + c(NH_2BH_2)_2$	-46.32
10	-163.58748[c]	65.596	$cNH_2(BH_2)_2 + 2NH_3 \rightarrow 2NH_3BH_2NH_2$	-66.31
11	-241.16686[d]	—	$c(NHBH)_3 + 2BH_3 + 2NH_3 \rightarrow 6BH_2NH_2$	-131.37

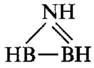
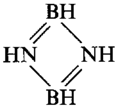
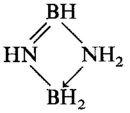
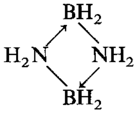
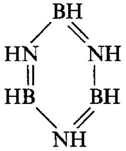
[a] kcal mol^{-1}

[b] MP4 = SDTQ/6-31 + G(2df,p)//MP2(full)/6-31G(d,p)

[c] MP2(full)/6-31G(d,p)//MP2(full)/6-31G(d,p)

[d] RHF/6-31G**//RHF/6-31G**

Table 15. Enthalpies of atomization and stabilization energies of various boron-containing compounds (kcal mol^{-1})

Compounds	Reference formula	ΔH_a^0	$\sum N_{AB}E_{AB}$	SE
1	$H_2N{=}BH{-}NH_2$	676.55	667.96	8.59
2	$H_2B{=}NH{-}BH_2$	669.15	657.49	11.66
3	$H_2N{-}B{\equiv}NH$	531.48	538.09	−6.62
4	$H_2B{-}N{\equiv}BH$	536.17	524.37	11.80
5		516.36	546.93	−30.57
6		473.12	524.63	−51.51
7	$H_2N{-}B{\equiv}N{-}BH_2$	729.46	717.69	11.77
8		744.50	772.32	−27.82
9		853.87	871.99	−18.12
10		978.06	971.66	6.40
11		1177.21 [19]	1158.48	18.73
		1186.38[a]		27.90
		1189.46 [20]		30.98

[a] This work

– Cyclo-1-aza-2-borine borazane is a planar four-membered cycle with a typical double bond and a σ-dative one connected by two opposite rather long single bonds. Its C.R.S.E. is not very large due to the important size of the cycle.

– Cyclodiborazane is a saturated four-membered ring characterized by BN bonds intermediate between σ-dative and covalent single bonds. Its C.R.S.E. seems to be overcompensated by generalized anomeric effects at boron and nitrogen atoms.

– The enthalpy of formation of borazine is still a controversial question. The experimental value (−122.2 kcal mol^{-1}) is actually different from the most

Table 16. Typical structural parameters in various boron-containing compounds (Å)

Compound	BN bond lengths
1	1.41
2	1.42
3	1.41 (B–N)
	1.25 (B≡N)
4	1.42 (B–N)
	1.25 (B≡N)
5	1.41
6	1.42
7	1.38 (NH_2–B)
	1.27 (B≡N)
	1.39 (N–BH_2)
8	1.45
9	1.66 (N → B)
	1.56 (B–N)
	1.42 (B=N)
10	1.61
11	1.44
NH_2=BH–NH=BH_2	1.40 (NH_2–B)
	1.46 (B–N)
	1.41 (N–BH_2)

recent theoretical values (−131.4 at the RHF/6-31G**//RHF/6-31G** level and −134.46 at the MP4 = STDQ/6-31G*//RHF/6-31G* level). Furthermore the value of the stabilization energy and its interpretation is tightly related to the choice of the bond energy terms used in the calculation. To make this remark clear, we shall estimate the stabilization energy of benzene with various choices of bond energy terms. The results obtained are reported in Table 17. The first choice leads to the so-called global stabilization energy including hyperconjugation and delocalization effects. It corresponds actually to the enthalpy change of the isodesmic reaction:

$$C_6H_6 + 3CH_3CH_3 \rightarrow 3CH_2{=}CH_2 + C_6H_{12}$$

In this case, ethane and ethylene are considered as reference species ($SE = 0$). The second choice leads to the usual stabilization energy containing only the

Table 17. The stabilization energy of benzene for different choices of bond energy terms (kcal mol^{-1})

$\sum N_{AB}E_{AB}$	ΔH_a^0	SE
1) $3E(C{-}C) + 3E(C{=}C) + 6E(C_d{-}H)_2$		
$3(85.44) + 3(137.23) + 6(100.3) = 1269.81$	1320.61	50.80
2) $3E(C{-}C) + 6\Delta(C_d{-}C) + 3E(C{=}C) + 6E(C_d{-}H)_1$		
$3(85.44) + 6(3.88) + 3(137.23) + 6(99.78) = 1289.97$	1320.61	30.64
3) $3E(C_d{-}C_d) + 3E(C{=}C) + 6E(C_d{-}H)_1$		
$3(96.28) + 3(137.23) + 6(99.78) = 1299.21$	1320.61	21.40

Table 18. The stabilization energy of borazine for different choices of bond energy terms and enthalpies of formation (kcal mol^{-1})

$\sum N_{AB}E_{AB}$		ΔH_a^0(Theor.)	*SE*(Theor.)	ΔH_a^0(Exper.)	*SE*(Exper.)
1) 3*E*(B–N)	3(90.43)				
3*E*(B=N)	3(106.70)				
3*E*[(B=)NH(–B)]	3(98.18)				
3*E*[(N=)BH(–N)]	3(90.85)				
	1158.48	1189.46	30.98	1177.21	18.73
2) 3*E*(B_d–N_d)	3(96.29)				
3*E*(B=N)	3(106.70)				
3*E*[(B=)NH(–B)]	3(98.18)				
3*E*[(N=)BH(–N)]	3(90.85)				
	1176.06	1189.46	13.40 [21]	1177.21	1.15

effect of the delocalization of the six π electrons. This *SE* value is equal to the enthalpy change of the isodesmotic reaction:

$$C_6H_6 + 3CH_2{=}CH_2 + 3CH_3CH_3 \rightarrow 6CH_3{-}CH{=}CH_2$$

Here, ethane, ethylene and propene are all reference compounds. Finally, the stabilization energy obtained with the third choice of bond energy terms is equal to the enthalpy change of the homodesmotic reaction:

$$C_6H_6 + 3CH_2{=}CH_2 \rightarrow 3CH_2{=}CHCH{=}CH_2$$

As butadiene is now also considered as a reference species, this last *SE* value corresponds to the cyclic delocalization of π electrons and represents the true aromatic stabilization of benzene.

In the case of borazine, two choices of bond energy terms lead to the results reported in Table 18. Both the experimental and theoretical enthalpies of formation of borazine were used in the calculations. The *SE* values obtained with the second choice of bond energy terms correspond to the enthalpy change of the homodesmotic process:

$$B_3N_3H_6 + 3BH_2{=}NH_2 \rightarrow 3BH_2{=}NHBH{=}NH_2$$

Here $BH_2{=}NH_2$ and $BH_2{=}NHBH{=}NH_2$ are considered as reference species ($SE = 0$ [21]). Retaining the theoretical value of ΔH_f^0 (borazine), it is seen that the aromaticity of this compound, as measured by the *SE* value (13.4 kcal mol^{-1}), is relatively important though significantly smaller than that of benzene. An experimental confirmation of this result should be most interesting.

7. Conclusions

The bond energy terms determined in this work allow us to evaluate the enthalpies of formation of normal compounds containing boron and nitrogen atoms. Furthermore, the stabilization energies of species where some particular effects do exist can be calculated. More particularly the aromaticity of borazine could be estimated in this way.

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Compound	E (a.u.)	ΔH_f^0 (kcal mol^{-1})	ZPE + T.C. (kcal mol^{-1})
$BH_2NHBHNH_2$	−162.41408	(−64.14)	51.41
BH_3NH_3	−82.93229	−17.52 [3]	45.48
NH_3	−56.38692	−10.97 [7]	23.94
BH_2NH_2	−81.77437	−23.02 [8]	32.04
$NH_3BH_2NH_2$	−138.17074	−37.94 [3]	56.69

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