Heats of Hydrogenation of Compounds Featuring Main Group Elements and with the Potential for Multiply Bonding

Hans-Jörg Himmel* and Hansgeorg Schnöckel[a]

Abstract: Reaction enthalpies are calculated for the hydrogenation reactions of main group hydrides with the potential for multiple bonding, and thus the *unsaturated* character of these species is determined. In addition to the global minimum structures, which leave in some cases no hope for even a single E–E bond (E = Group 13, 14, or 15 element), calculations are also performed for geometries with maximum potential for multiple bonding. The trends down the groups and the periods are established. Interpretations have to take several factors into account. These factors sometimes work hand in hand but also against each other. We also include in our survey the species $[HGaGaH]^{2-}$ as a free anion and $Na_2[HGaGaH]$ as well as their hydrogenation products $[H_2GaGaH_2]^{2-}$ and $Na_2[H_2GaGaH_2]^{2-}$. The results show that the presence of the Na^+ ions has a significant impact on their chemistry, and thus suggests that they are involved to a large extent in the bonding. Our results indicate that the compounds should be described as cluster compounds.

Keywords: hydrogenation · isomers · main group elements · multiple bonds · subvalent compounds

Introduction

The question of multiply bonding involving heavier main group elements is hotly debated in literature.[1] First, arguments are provided by the structures of the molecules, and these might suggest at first glance that the heavier elements do not tend to multiple bonding. Thus compounds like R_2SiSiR_2 are, in contrast to the corresponding planar ethylene derivatives, often nonplanar, and this nonplanarity certainly reduces the overlap of the orbitals, which would be capable of forming the π bonds. However, it might still be argued that other effects are responsible for the nonplanarity, and that in a hypothetical planar geometry the multiple bond character would be quite high. That this argument cannot be just ignored is evident when H_2AlNH_2 is compared with H_2AlPH_2. The former was observed and characterized experimentally in matrix experiments;[2] the latter is still unknown. Both compounds are formally isoelectronic to ethylene, but H_2AlNH_2 is planar, while H_2AlPH_2 is calculated to be pyramidal at the phosphorus.[3] The same holds also for the pair $HAlNH_2$ and $HAlPH_2$, and in this case both molecules were already characterized experimentally in matrix experiments.[2, 4] However, the nonplanarity reflects the larger barriers to inversion of phosphines with respect to amines rather than the missing potential for π interactions. In fact the barriers to rotation of the planarized molecules suggest that the π interactions in the planarized molecules are comparable. Recently it has been argued that the σ bond in *trans*-bent disilenes is stronger than in their linear forms. This strengthening of the σ bond, which overcompensates for the weakening of the π bond, is responsible for the nonlinearity of the molecule.[5] There are also examples showing that multiple bonding can be present even if the geometry seems not to be optimal. Thus bent acetylenes in rings, for example, benzyne,[6] apparently still feature triple bonds, although the molecules are not linear. The bond length also proved to be a criterion to be treated with caution, most obviously in the presence of ionic contributions. Therefore, a search for other criteria commenced. In the past, barriers to rotation,[7] dissociation energies,[8] and force constants[9] have been employed as measures of the multiple bonding character. However, each of these methods has its limitations. Hence the breakage of the π interaction during the rotation leads to an increase in the strength of the σ bond,[1, 2] and therefore the barriers to rotation are believed to be lower limits for the π-bond energies. The dissociation energies on the other hand tend to overestimate the bond strength if the fragments are allowed to optimize their geometries, and there is also often the problem of two possible electronic states (e.g. CH_2 exhibits a triplet, but SiH_2 a singlet electronic state). Furthermore, the dissociation energies and the force constants share the difficulty of not being capable of distinguish-

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ing between covalent and electrostatic contributions. Other problems related with the interpretation of force constants in the case of large off-diagonal elements in the force constant matrix were reported.[10] However, the method of using inverted force constants, which has recently been praised as a major improvement, is still not widely accepted.[10]

The enthalpies for reactions with H_2 are expected to give insight into the *differences in chemical reactions.* It is clear that a number of factors are at work when bonds are broken, and new bonds formed and structures changed. Moreover, hydrogen is known to be a ligand with remarkable mutability,[11] resulting in very different structures. Thus Al_2H_2 does not have a global minimum structure of the form HAlAlH with two terminal hydrogens, but $Al(\mu\text{-}H)_2Al$ with two bridging hydrogen atoms, and $AlNH_2$ is not stable in its HAlNH isomeric form, like its lighter homologue HBNH, but prefers to form the Al^I amide $AlNH_2$. We therefore performed calculations not only for the global minimum structures, which in some cases leave very little possibility for bonding involving the elements of interest, but also for the structures bearing the best possibilities for π interactions. We also include in our survey the species $[HGaGaH]^{2-}$ as a free anion and $Na_2[HGaGaH]^{2-}$, and their hydrogenation products $[H_2GaGaH_2]^{2-}$ and $Na_2[H_2GaGaH_2]^{2-}$.

The motivation for the study of hydrogenation reactions also arises from the fact that these reactions were studied extensively in the past, especially for carbon compounds, and the compounds were, on the basis of these experiments, classified in terms of their *unsaturated* character. Thus acetylene was found to be more *unsaturated* than ethylene. However, it is evident that the unsaturated character cannot be linked directly with the degree of multiple bonding, and we will see more examples of the failure of such a classification. The past decades saw the characterization of several hydrides, and especially matrix experiments helped to investigate some very unstable ones. Therefore, as to the optimum structures of the molecules, the present work has not only to rely on theoretical predictions, but to a large extent on hard experimental facts.

Computational Details

Calculations relied on the Gaussian98 program package.[12] The B3LYP (HF/DFT) method in combination with a 6-311G* basis set was firstly used to pre-optimize the structures and to calculate the vibrational modes. In the second step the structures were optimized applying the MP2 method and a 6-311 + G(df,p) basis set. The calculated MP2 energies were corrected by their zero-point energies and thermally by their vibrational, rotational, and translational energies at 298.2 K (all corrections were taken from the B3LYP calculations) to first give reaction energies at 298 K. Then *RT* (2.5 kJ mol^{-1}) was subtracted where necessary to get to the standard enthalpies for the reactions in the gas phase. Both the reaction enthalpy values derived from B3LYP and MP2 are quoted for all reactions, but the results obtained with MP2/6-311 + G(df,p) should be more accurate than the B3LYP/6-311G* ones. However, the trends are the same for both B3LYP/6-311G* and MP2/6-311 + G(df,p), while the numbers do vary to some extent. Table 1 includes the reaction enthalpies as well as the E–E distance (E being the element, for which multiple bonding is considered) for all hydrides discussed in this work.

Results and Discussion

The methods and basis sets were first tested by calculating the standard enthalpies for the reactions of C_2H_2 with H_2 to C_2H_4 and of C_2H_4 with H_2 to C_2H_6, and the results were compared with experimental data for these reactions. The standard enthalpies derived from experiments for these reactions are known to be 170 and 137 kJ mol^{-1}, respectively. As evidenced by comparison with the calculated values given in Table 1, the general level of agreement is encouraging.

Encouraged by the results of these tests, we began calculations on other Group 14 homologues with the general formulas E_2H_2, E_2H_4, and E_2H_6 (E being Si or Ge), and the results were also added to Table 1. In addition to the global minimum geometries, which now exhibit C_{2v} rather than $D_{\infty h}$ symmetry for HEEH (with two bridges)[13] and C_{2h} rather than D_{2h} symmetry for H_2EEH_2, we also performed calculations in which the symmetries were constrained to $D_{\infty h}$ and D_{2h}, respectively, because these geometries have optimal chances for π interactions. The weakening of the E–H σ bond down the group should assist the change in the structures (e.g. $D_{\infty h}$ versus C_{2v}) for higher homologues. As already mentioned, the global minimum geometries already suggest a reduced π stabilization, although it might be argued that they do not directly reflect the potential for multiply bonding in the presence of other effects. Moreover, the energy difference between disilene in its C_{2d} global minimum and its D_{2h} geometry is very small (less than 5 kJ mol^{-1}). The relevant geometries of all compounds are illustrated in Figure 1. Our calculations predict energy differences of not more than 2.0–2.4 and 6.7–19.2 kJ mol^{-1} between the C_{2h} minimum structures and the planar D_{2h} structures for E = Si and Ge, respectively.

Figure 2a shows the reaction enthalpies for the molecules in their global minimum structures. The reaction enthalpy is in the case of the reaction of disilene to give disilane about 60 kJ mol^{-1} higher than in the case of ethylene to ethane. This reflects the instability of disilene rather than the stability of disilane. This instability should be caused by the reduced double bond character in disilene compared with ethylene. Thus disilene is more *unsaturated* than ethylene, and linear disilene more *unsaturated* than acetylene, but this does not go with a higher degree of multiple bonding. But there is not always a trend towards higher reaction enthalpies for heavier homologues since the reaction of digermene to digermane is associated with an enthalpy of approximately −155 kJ mol^{-1} for digermene in its C_{2h} global minimum geometry and approximately −170 kJ mol^{-1} in the case of the more energetic linear D_{2h} geometry. This is about 50 or 40 kJ mol^{-1} less than for the corresponding reactions of the silicon compounds. The obvious reason behind this behavior is the reduced strength of the E–H bond.

In Figure 2b the reaction enthalpies are plotted for the reactions of HEEH in its linear geometry ($D_{\infty h}$) and of H_2EEH_2 in its planar geometry (D_{2h}), which are, as already mentioned, only for E = C global minimum structures. The general pattern is that for all E = C, Si, and Ge, the reaction from HEEH to H_2EEH_2 is associated with a higher value of the reaction enthalpy than is the reaction from H_2EEH_2 to

Table 1. Standard reaction enthalpies [kJ mol^{-1}, at 298.2 K] for reactions with H_2.

Educt	Sym.[a]	d(E–E) [Å]	Product	Sym.	d(E–E) [Å]	ΔH°_{R} [kJ mol^{-1}]	
						B3LYP	MP2
HCCH	$D_{\infty h}$ (GM)	1.2135	H_2CCH_2	D_{2h}	1.3345	– 182.7	– 166.8
H_2CCH_2	D_{2h} (GM)	1.3345	H_3CCH_3	D_{3d}	1.5243	– 140.8	– 141.1
H_3CCH_3	D_{3d}	1.5243	2 CH_4	T_d	–	– 68.9	– 55.4
Si(μ-H)$_2$Si	C_{2v} (GM)	2.2022	H_2SiSiH_2	C_{2h}	2.1547	– 130.8	– 118.9
Si(μ-H)$_2$Si	C_{2v} (GM)	2.2022	H_2SiSiH_2	D_{2h}	2.1327	– 128.8	– 116.5
HSiSiH	$D_{\infty h}$	1.9837	H_2SiSiH_2	C_{2h}	2.1547	– 285.4	– 276.8
HSiSiH	$D_{\infty h}$	1.9837	H_2SiSiH_2	D_{2h}	2.1327	– 283.4	– 274.4
H_2SiSiH_2	C_{2h} (GM)	2.1547	H_3SiSiH_3	D_{3d}	2.3354	– 203.1	– 209.9
H_2SiSiH_2	D_{2h}	2.1327	H_3SiSiH_3	D_{3d}	2.3354	– 205.1	– 212.3
H_3SiSiH_3	D_{3d}	2.3354	2 SiH_4	T_d	–	– 20.2	– 10.6
Ge(μ-H)$_2$Ge	C_{2v} (GM)	2.3799	H_2GeGeH_2	C_{2h}	2.2811	– 48.3	– 47.6
Ge(μ-H)$_2$Ge	C_{2v} (GM)	2.3799	H_2GeGeH_2	D_{2h}	2.2344	– 29.1	– 40.9
HGeGeH	$D_{\infty h}$	2.0849	H_2GeGeH_2	C_{2h}	2.2811	– 266.7	– 234.8
HGeGeH	$D_{\infty h}$	2.0849	H_2GeGeH_2	D_{2h}	2.2344	– 247.5	– 228.1
H_2GeGeH_2	C_{2h} (GM)	2.2811	H_3GeGeH_3	D_{3d}	2.4437	– 149.2	– 163.4
H_2GeGeH_2	D_{2h}	2.2344	H_3GeGeH_3	D_{3d}	2.4437	– 168.4	– 170.1
H_3GeGeH_3	D_{3d}	2.4437	2 GeH_4	T_d	–	+ 6.5	+ 14.0
HBBH(trip)	$D_{\infty h}$ (GM)	1.5116	H_2BBH_2	D_{2h}	1.7491	– 175.2	– 184.4
HBBH(trip)	$D_{\infty h}$ (GM)	1.5116	H_2BBH_2	D_{2d}	1.6543	– 237.5	– 236.9
H_2BBH_2	D_{2h}	1.7491	2 BH_3	D_{3h}	–	– 64.4	– 56.6
H_2BBH_2	D_{2d} (GM)	1.6543	2 BH_3	D_{3h}	–	– 2.0	– 4.1
Al(μ-H)$_2$Al	D_{2h} (GM)	2.9169	$Al^+(AlH_4)^-$	C_{3v}	2.4822	– 139.2	– 153.9
Al(μ-H)$_2$Al	D_{2h} (GM)	2.9169	H_2AlAlH_2	D_{2h}	2.6079	– 96.6	– 108.0
HAlAlH (trip)	$D_{\infty h}$	2.2953	H_2AlAlH_2	D_{2h}	2.6079	– 200.6	– 205.5
HAlAlH (trip)	$D_{\infty h}$	2.2953	$Al^+(AlH_4)^-$	C_{3v}	2.4822	– 243.1	– 251.4
H_2AlAlH_2	D_{2h}	2.6079	2 AlH_3	D_{3h}	–	– 25.8	– 18.9
$Al^+(AlH_4)^-$	C_{3v} (GM)	2.4822	2 AlH_3	D_{3h}	–	+ 16.8	+ 27.1
Ga(μ-H)$_2$Ga	D_{2h} (GM)	3.0235	H_2GaGaH_2	D_{2h}	2.5541	– 25.7	– 58.6
Ga(μ-H)$_2$Ga	D_{2h} (GM)	3.0235	$Ga^+(GaH_4)^-$	C_{3v}	2.5625	– 67.5	– 90.9
HGaGaH (trip)	$D_{\infty h}$	2.2560	H_2GaGaH_2	D_{2h}	2.5541	– 159.8	– 157.1
HGaGaH (trip)	$D_{\infty h}$	2.2560	$Ga^+(GaH_4)^-$	C_{3v}	2.5625	– 201.7	– 189.4
$Ga^+(GaH_4)^-$	C_{3v} (GM)	2.5625	2 GaH_3	D_{3h}	–	+ 50.4	+ 41.4
H_2GaGaH_2	D_{2h}	2.5541	2 GaH_3	D_{3h}	–	+ 8.5	+ 9.1
HBNH	$C_{\infty v}$ (GM)	1.2427	H_2BNH_2	C_{2v}	1.3924	– 133.3	– 124.3
H_2BNH_2	C_{2v} (GM)	1.3924	$H_3B \cdot NH_3$	C_{3v}	1.6489	+ 26.6	+ 28.8
$H_3B \cdot NH_3$	C_{3v}	1.6489	$BH_3 + NH_3$	–	–	+ 125.4	+ 124.0
HAlNH	$C_{\infty v}$	1.6288	H_2AlNH_2	C_{2v}	1.7760	– 259.4	– 249.5
$AlNH_2$	C_{2v} (GM)	1.8047	H_2AlNH_2	C_{2v}	1.7760	– 97.1	– 100.7
H_2AlNH_2	C_{2v} (GM)	1.7760	$H_3Al \cdot NH_3$	C_{3v}	2.0653	– 27.9	– 13.1
$H_3Al \cdot NH_3$	C_{3v}	2.0653	$AlH_3 + NH_3$	–	–	+ 121.4	+ 118.1
HGaNH	$C_{\infty v}$	1.6832	H_2GaNH_2	C_{2v}	1.8797	– 244.9	– 228.7
$GaNH_2$	C_{2v} (GM)	1.9396	H_2GaNH_2	C_{2v}	1.8797	– 35.1	– 47.0
H_2GaNH_2	C_{2v} (GM)	1.8797	$H_3Ga \cdot NH_3$	C_{3v}	2.1578	– 45.7	[b]
$H_3Ga \cdot NH_3$	C_{3v}	2.1578	$GaH_3 + NH_3$	–	–	+ 94.9	[b]
N_2	$D_{\infty h}$ (GM)	1.1161	HNNH	C_{2h}	1.2542	+ 198.2	+ 224.3
HNNH	C_{2h} (GM)	1.2542	H_2NNH_2	C_2	1.4216	– 90.2	– 103.7
H_2NNH_2	C_2 (GM)	1.4216	2 NH_3	C_{3v}	–	– 161.3	– 180.7
P_2	$D_{\infty h}$ (GM)	1.9189	HPPH	C_{2h}	2.0307	– 25.7	– 0.4
HPPH	C_{2h}	2.0307	H_2PPH_2	C_2	2.1987	– 97.9	– 93.4
H_2PPH_2	C_2 (GM)	2.1987	2 PH_3	C_{3v}	–	– 24.5	– 12.7
As_2	$D_{\infty h}$ (GM)	2.1504	HAsAsH	C_{2h}	2.2658	+ 58.2	+ 94.2
HAsAsH	C_{2h}	2.2658	H_2AsAsH_2	C_2	2.4490	– 67.3	– 58.3
H_2AsAsH_2	C_2	2.4490	2 AsH_3	C_{3v}	–	+ 8.6	+ 21.8

[a] GM = global minimum. [b] For $H_3Ga \cdot NH_3$, the Gaussian population analysis failed with MP2.

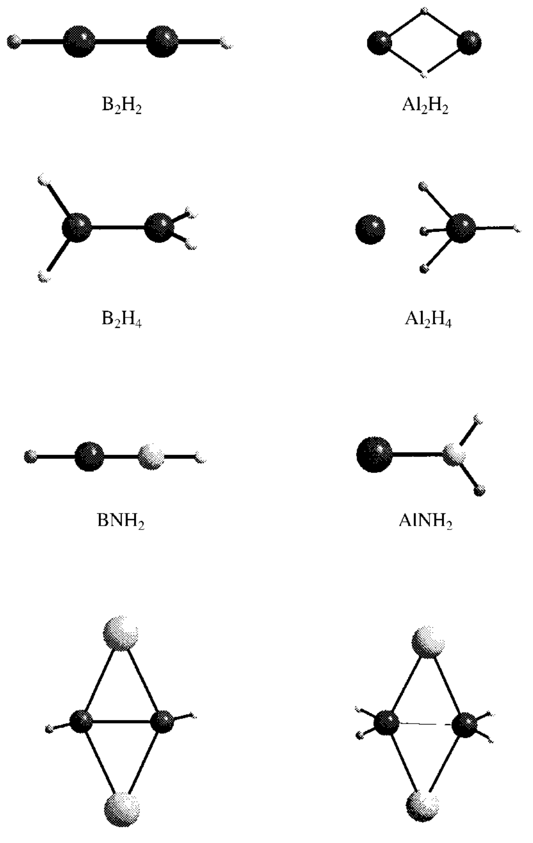


Figure 1. Geometries of some of the hydrides in this work showing the variations of structures between homologues.

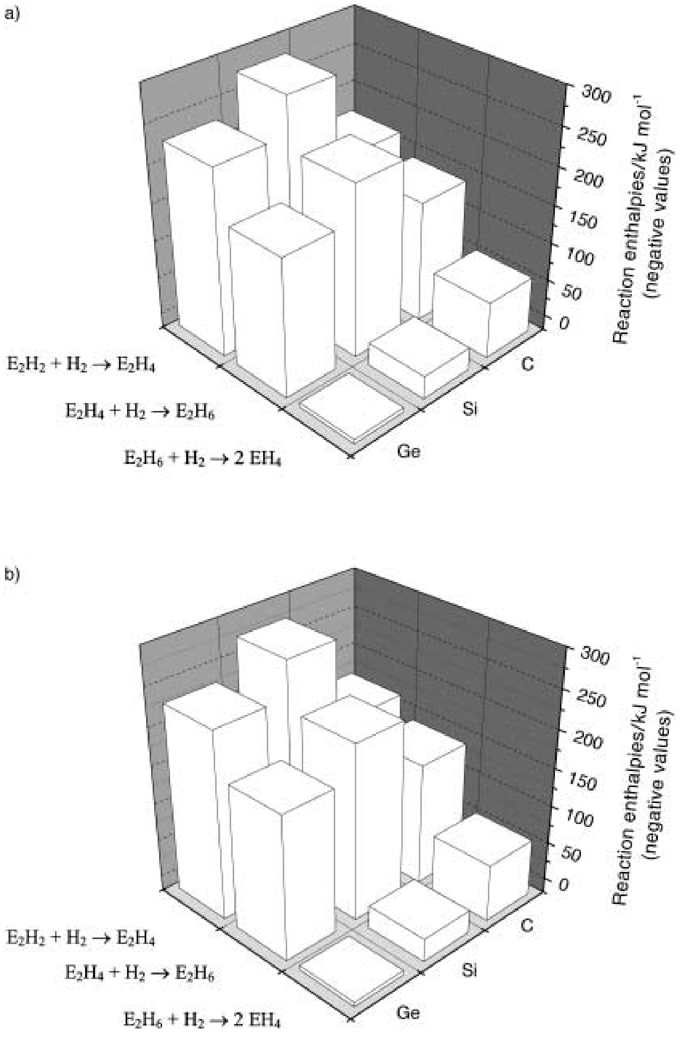


Figure 2. Standard enthalpies for hydrogenation reactions involving compounds of Group 14 elements: a) compounds in their global minimum geometries; b) compounds in structures with optimum chances for multiple bonding.

H_3EEH_3. In the case of E = C, this is due to the lower energy of the second π bond with respect to the first one. As already mentioned, the second π interaction is further weakened by the nonlinearity, which increases the σ-bond energy.[5] The same trend can be seen for the heavier homologues. The enthalpy increase from hydrogenation of H_3EEH_3 to give two EH_4 molecules decreases down the group. The strong σ bond in ethane in the case of E = C and the increase in H_2 bond strength with respect to the E–H bond strength for heavier E are the factors at work here.

We now turn our attention to the compounds of the Group 13 elements, for which interpretations become more difficult, especially due to the structural variety of the species. The reactions of HEEH and H_2EEH_2 with H_2 were calculated, and again linear (in the case of HEEH) and planar (in the case of H_2EEH_2) structures were taken into account, which are now rarely global minimum structures (the only exception being HBBH, which, however, exhibits a triplet ground state) but might offer the best possibilities for π interactions. The dimers E_2 all exhibit triplet ground states with bond properties, which are not at all comparable with the ones in acetylene.[14] The reactions of Ga_2 and In_2 with H_2 in an Ar matrix were already investigated experimentally, and E(*μ*-H)$_2$E, *trans*-bent HEEH (E = Ga or In), and EEH_2 (E = Ga) were identified and characterized.[15] However, because of the unusual bonding properties of the dimers, we have excluded them from our discussion herein. B_2H_2 and Al_2H_2 isomers were also studied in rare gas matrices.[16] The results show, as already mentioned, that HBBH is a linear molecule with a triplet electronic ground state. In the case of the other HEEH molecules (E = Al, Ga, or In), the *trans*-bent structure is more stable, and the preferred electronic state switches to singlet. However, when constrained to linear geometry, the molecules still prefer triplet electronic states.[17] One factor could be the increasing E–E distance in E_2H_2 compounds down the group which certainly reduces the chances for π–π interaction in the higher homologues. On the other hand, a reduction of this distance results in a weakening of the σ bond (see also ref. [5] for similar arguments). But neither the linear nor the *trans*-bent structures, but the doubly bridged planar E(*μ*-H)$_2$E structures (D_{2h} symmetry) are the global minima for E = Al or Ga.[15, 18] According to our calculations, the linear structures exhibiting triplet electronic states lie energetically about 100 kJ mol^{-1} above the doubly bridged global minimum structures for E = Al and Ga, respectively.

In the case of H_2EEH_2, calculations predict for E = B that two structures have almost the same energy: the first one exhibits D_{2d} symmetry and two perpendicular BH_2 groups; the other features two H atoms in a bridging position, which results in C_{2v} symmetry. According to one estimate, the energy difference between both structures amounts to less than 5 kJ mol^{-1}.[19] We obtained an energy difference of approximately 55 kJ mol^{-1} between the planar D_{2h} arrangement and the D_{2d} global minimum structure (including ZPE and thermal corrections) in our calculations. For E = Al or Ga, several structures lie energetically very close together, but the saltlike structures $E^+[EH_4]^-$ with the E^+ cation located near the face of a tetrahedral EH_4^- anion, resulting in C_{3v} symmetry, appear to be the lowest energy structures in the most accurate calculations.[20, 21] It is still a challenge to experimentally verify these structures. According to our calculations, these saltlike structures are about 45 and 35 kJ mol^{-1} more stable than the planar D_{2h} structures for E = Al and Ga, respectively. It is noteworthy that although the chances for multiple bonding should be higher for the molecules in their D_{2h} geometries, the E–E bond length is somewhat shorter in their $E^+[EH_4]^-$ global minimum geometries. This is another example of many that the bond length has to be taken with caution as a criterion for the bond order.

Figure 3a shows the reaction enthalpies for the compounds in their global minimum structures, while Figure 3b displays the ones with HEEH in its linear geometry ($D_{\infty h}$) and H_2EEH_2 in its planar D_{2h} symmetry. The trend for the molecules in their optimum geometries is that the enthalpies decrease in the order B > Al > Ga. However, when considering the molecules in structures with optimum possibilities for multiple bonding, we observed that the enthalpies show again a maximum for Al in the case of the reactions of HEEH, and thus it mirrors to some extent the trend found for the Group 14 hydrides.

Turning now to the reactions of III/V compounds with dihydrogen, we observe that the products have the formulae HENH and H_2ENH_2 (E being B, Al, or Ga). Again, the global minimum structures of the boron compounds differ from the ones adopted by the heavier homologues. Thus HBNH has a linear global minimum structure,[22] while HAlNH and HGaNH prefer *trans*-bent structures, if only terminal E–H bonds are allowed.[23] However, our calculations agree with previous ones in predicting global minimum structures ENH_2 with C_{2v} symmetry for E = Al and Ga, respectively. Both $AlNH_2$ and $GaNH_2$ have also been identified in matrix experiments.[2, 24] According to our calculations, the energy difference between the ENH_2 (C_{2v}) structure and the linear structure amounts to approximately 155 or 190 kJ mol^{-1} for E = Al and Ga, respectively. On the other hand, all H_2ENH_2 compounds exhibit "ethylene-like" global minimum structures with C_{2v} symmetry.[2] The adducts $H_3E \cdot NH_3$ feature a E ··· N interaction that is not comparable with the single bond in ethane, as ammonia acts as a donor.

The trends are shown in Figure 4a and b for both the global minimum structures and the ones believed to be optimal for π interactions. Beginning with the global minimum structures, it can be seen that the enthalpies for hydrogenation of ENH_2 compounds decrease in the order B > Al > Ga and reflect to some extent the trend towards monovalent compounds for heavier Group 13 compounds ($AlNH_2$ and $GaNH_2$ both are monovalent). The planar $H_2E \cdot NH_2$ compounds follow exactly the opposite trend when reacting with H_2. Thus the enthalpies for hydrogenation are found to *increase* now in the order B < Al. It is tempting to attribute this behavior to the decrease in strength of the π interaction, and the behavior should result in a decreasing stability in the order B > Al > Ga for the H_2ENH_2 compounds. However, it is also clear that the ionic versus covalent bond contributions exhibit changes and might partially overshadow the trend. We also have included the enthalpies for the dissociation of $H_3E \cdot NH_3$, although these are not hydrogenation reactions. Here it is found that the enthalpies increase in the order B > Al.

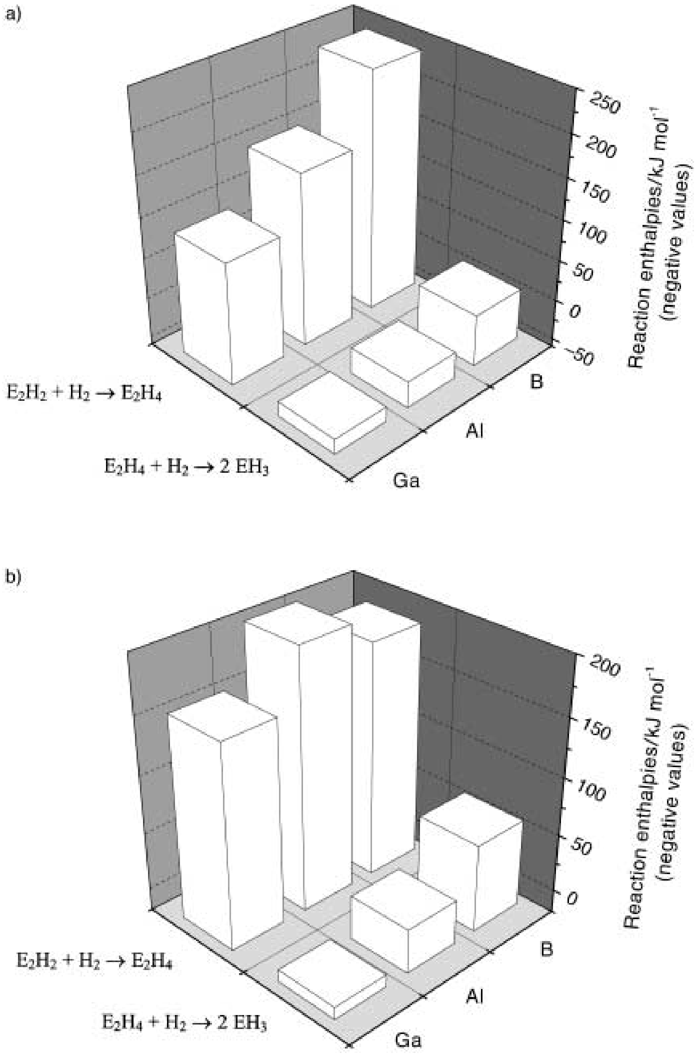


Figure 3. Standard enthalpies for hydrogenation reactions involving compounds of Group 13 elements: a) compounds in their global minimum geometries; b) compounds in structures with optimum chances for multiple bonding.

Turning to Figure 4b and linear structures for HENH, it is found that the hydrogenation of HENH compounds passes through a maximum for E = Al, and this mirrors thus again the results obtained for Group 13 and 14 HEEH compounds.

$[HEEH]^{2-}$ and $[H_2EEH_2]^{2-}$ (M = B, Al, Ga, and In) are formally isoelectronic with HCCH and H_2CCH_2, respectively, and the multiply bonding character is especially hotly debated

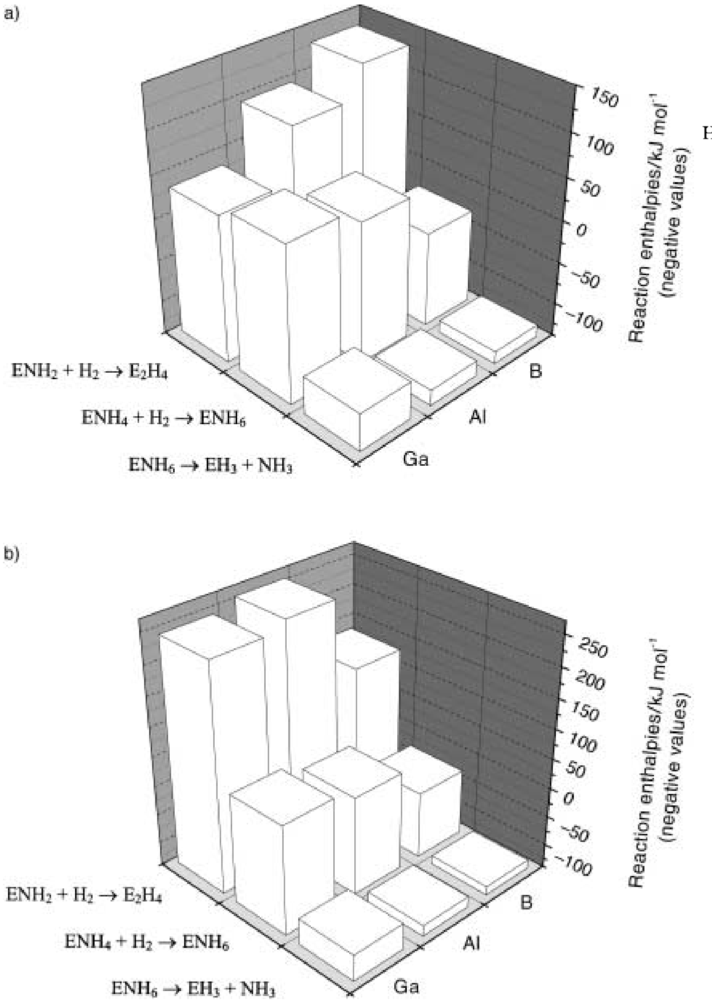
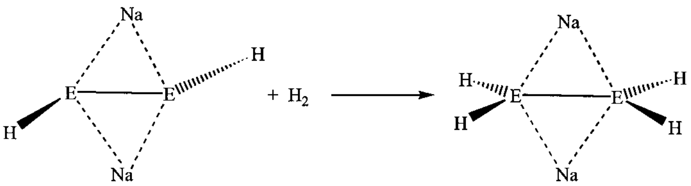


Figure 4. Standard enthalpies for hydrogenation reactions involving compounds featuring a Group 13 and a Group 15 element: a) compounds in their global minimum geometries; b) compounds in structures with optimum chances for multiple bonding.

for compounds such as $[HGaGaH]^{2-}$,[25–27] since the derivative $Na_2[ArGaGaAr]$ (Ar = bis-2,6-triisopropylphenyl-C_6H_3) featuring a short Ga–Ga distance of only 2.319 Å[28] was synthesized and structurally characterized. Therefore we also performed calculations on these species (see Scheme 1). Table 2 summarizes the results obtained for the free ions and the compounds, which are neutralized by Na^+ ions. It has been argued that the alkali atoms contribute to the electronic structure, and that there is Ga_2Na_2 cluster present rather than a simple Ga–Ga bond.[26] Calculations performed for the corresponding Li species $Li_2[HEEH]$ also suggest a significant influence of the Li^+ ions on the bonding.[27]



Scheme 1. Hydrogenation of $Na_2[HEEH]$ (E = B, Al, or Ga).

Our results show that the Na^+ ions decrease the reaction enthalpies in all cases. The E–E distances help to decide whether this is because of the influence they bear on the bonding properties or because of the reduced repulsion of the two negative charges in the hydrogenated compounds without Na^+ ions (longer E–E distance). As an upper limit for the coulombic contributions, we have assumed that each of the E centers carries a full negative charge. Then the increase of the E–E distance brings about a reduction in the coulombic repulsion of 2.1 $kJ\,mol^{-1}$ for hydrogenation of $[HGaGaH]^{2-}$ in its C_{2h} symmetry (but as much as 48.9 $kJ\,mol^{-1}$ for the molecule in its $D_{\infty h}$ geometry). Therefore it is clear that the reduction of the coulombic repulsion is not the dominating factor at work here. Our results thus show that the Na^+ ions have a significant impact on the chemistry of the molecules, and they suggest that they are indeed involved to a great extent in the bonding. The compounds are better described as cluster compounds, and the synthesis and characterization of other cluster compounds involving Group 13 and Na atoms, for example, $Na_2Ga_4R_4$ (R being Si*t*Bu_3) and $K_2Ga_4R_2$ (R = C_6H_3-2,6-$Trip_2$, Trip = 2,4,6-*i*Pr_3) lend support to this interpretation.[29, 30]

Finally, the enthalpies for reactions with H_2 were calculated for the representatives E_2, HEEH, and H_2EEH_2 (E = Group 15 element). The global minimum structures of these compounds show little variations compared with the ones of Group 13 or 14 elements. Hence all HEEH compounds exhibit C_{2h} and all H_2EEH_2 C_2 symmetry (*gauche* conformations), although the barriers to other conformers are often extremely small.[31] The results are illustrated in Figure 5. The π-bonding increment in N_2 is larger than the σ increment, and this leads to a positive value for the hydrogenation enthalpy. Again, hydrogenation of the HEEH compounds is associated with a maximum increase of the absolute enthalpy value not for the first period element (E = N), but for the second (E = P), and the absolute enthalpy value decreases if P is replaced by As, although the change from E = N to P is not as large as,

Table 2. Standard reaction enthalpies for the reactions of $[HEEH]^{2-}$ and $Na_2^{2+}[HMMH]^{2-}$ with H_2.

Educt	Sym.	d(E–E) [Å]	Product	Sym.	d(E–E) [Å]	ΔH°_R [kJ mol−1] B3LYP	ΔH°_R [kJ mol−1] MP2
$Na_2^{2+}[HBBH]^{2-}$	D_{2h}	1.4845	$Na_2^{2+}[H_2BBH_2]^{2-}$	D_{2h}	1.6267	−190.3	−168.4
$[HAlAlH]^{2-}$	C_{2h}	2.4386	$[H_2AlAlH_2]^{2-}$	D_{2h}	2.4822	−168.9	−155.3
$[HAlAlH]^{2-}$	$D_{\infty h}$	2.2926	$[H_2AlAlH_2]^{2-}$	D_{2h}	2.4822	−234.6	−213.7
$Na_2^{2+}[HAlAlH]^{2-}$	C_{2h}	2.4607	$Na_2^{2+}[H_2AlAlH_2]^{2-}$	D_{2h}	2.5102	−122.3	−108.6
$[HGaGaH]^{2-}$	C_{2h}	2.4338	$[H_2GaGaH_2]^{2-}$	D_{2h}	2.4428	−111.1	−116.1
$[HGaGaH]^{2-}$	$D_{\infty h}$	2.2494	$[H_2GaGaH_2]^{2-}$	D_{2h}	2.4428	−197.3	−152.0
$Na_2^{2+}[HGaGaH]^{2-}$	C_{2h}	2.4239	$Na_2^{2+}[H_2GaGaH_2]^{2-}$	D_{2h}	2.4491	−69.4	−66.8

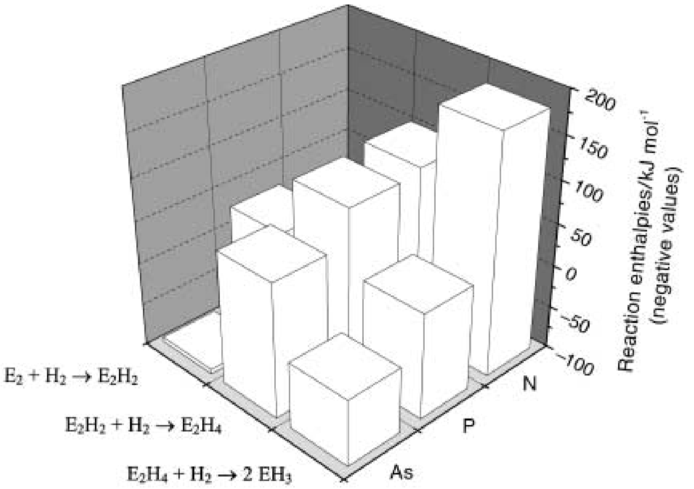


Figure 5. Standard enthalpies for hydrogenation reactions of compounds of Group 15 elements.

for example, for E = C to Si. In the same vein, the negative hydrogenation enthalpies of the E_2 dimers pass through a maximum for E = P. Like the Group 13 and 14 compounds, the enthalpies for the hydrogenation reactions leading to the breakage of the σ E–E bond (hydrogenation of H_2EEH_2) decrease down the group. In the same order the strength of the E–H bond decreases, which is expected to be one of the dominating factors in this case.

We have also plotted the reaction enthalpies in the way shown in Figure 6. Therein the hydrogen elimination reactions are considered, and for each elimination step the enthalpy is given either for the formation of dihydrogen or of two hydrogen atoms (numbers in parentheses). This representation aids the visualization of the unsaturated character of each compound. The change in molecular structures from C → Si or B → Al is also clearly visible. For the Group 15 element compounds, the changes are more subtle. Low-valent compounds featuring the heavier elements Ge, Ga, or As more willingly eliminate dihydrogen than their lighter homologues. For example, the elimination reactions of Ge_2H_4 to give Ge_2H_2 and of Ga_2H_4 to give Ga_2H_2 are less endothermic than are the elimination reactions of C_2H_4 to give C_2H_2 or of B_2H_4 to give B_2H_2. Of course, this does not absolutely mean that the heavier element compounds exhibit a pronounced multiple bonding character, but shows the tendency of the heavier elements to keep some of their electrons in atomlike orbitals, which do not interact significantly. Thus Ge and Ga have less electrons to share with other elements or fragments. In C_2H_2 the C–C bond can be described correctly as a [6 electrons – 2 center] bond. However, the Ge–Ge bond in Ge_2H_2 is not adequately described in this way.

Conclusion

The standard enthalpies for reactions of compounds with (on the basis of their general formula) the potential for multiple bonding with dihydrogen were determined, and the trends between compounds of elements within a group and a period were established. We have studied not only the molecules in their global minimum geometries, which in some cases leave not much hope for any π or even σ E–E interaction, but also in the geometries, which should provide the best possibilities for π interactions. The general trends that have been worked out herein include:

1) The negative enthalpy values of all HEEH and HENH compounds in their linear geometries have a maximum (E = an element of the *second period*) following the pattern: C < Si > Ge, B < Al > Ga, and N < P > As, regardless of whether the products H_2EEH_2 are in their global minimum structures or in the optimum geometry for π interactions.
2) For reactions leading to the breakage of the σ bond, the negative enthalpy values decrease always in the order C > Si > Ge (hydrogenation of H_3EEH_3), B > Al (hydrogenation of E_2H_4), and N > P > As (hydrogenation of H_2EEH_2).
3) The hydrogenation of HEEH compounds is associated with a higher negative enthalpy value than the hydrogenation of H_2EEH_2 (E is a Group 14 element), and the formally isoelectronic HENH and H_2ENH_2 (E = Group 13 element) compounds follow the same trend. The same can also be said for E_2H_2 compounds (E = Group 13 element) in their global minimum geometries, although bonding in these compounds is very much different.
4) In the case of hydrogenation of $[HEEH]^{2-}$ and $Na_2[HEEH]$ (E = Group 13 element) it is found that the reaction enthalpy is significantly less negative for $Na_2[HEEH]$ than it is for $[HEEH]^{2-}$. This shows that the alkali ion influences the chemistry of the species, and it suggests that they are involved in the bonding. Our results thus indicate that the compound should be described as a cluster compound, as has been done in the case of other compounds involving Group 13 elements and Na.[29]

The reasons for the trends and other observations were discussed, and some of the factors at work were named and discussed. In summary, this work should shed some light upon the reactions of these interesting compounds.

An important point in our discussion is that the hydrogenation reactions are *less exothermic* for low-valent compounds of the heavier elements, like Ge or Ga, than they are for their lighter homologues. In other words, compounds like Ge_2H_4 and Ga_2H_4 eliminate hydrogen more readily than do C_2H_4 or B_2H_4. We have already mentioned at several stages of the discussion that this does not mean that the heavier element compounds are efficient at multiple bonding. Instead we observed the tendency of the heavier elements to keep some of their electrons in atomlike orbitals. In general, we propose the expressions [$(6-x)$ electrons – 2 center)] bond instead of the sometimes misleading term triple bond and [$(4-x)$ electrons – 2 center)] bond instead of double bond.[32] With these expressions, all compounds can be classified without difficulty. The quantification of the variable x is then the remaining task, but it is clear that x should increase for heavier homologues. So, for example, x is 0 for C_2H_2 but close to 4 for Ge_2H_2. In reality, Ge_2H_2 prefers the doubly bridged isomer, but the fact that four electrons are almost not involved in the bonding remains.

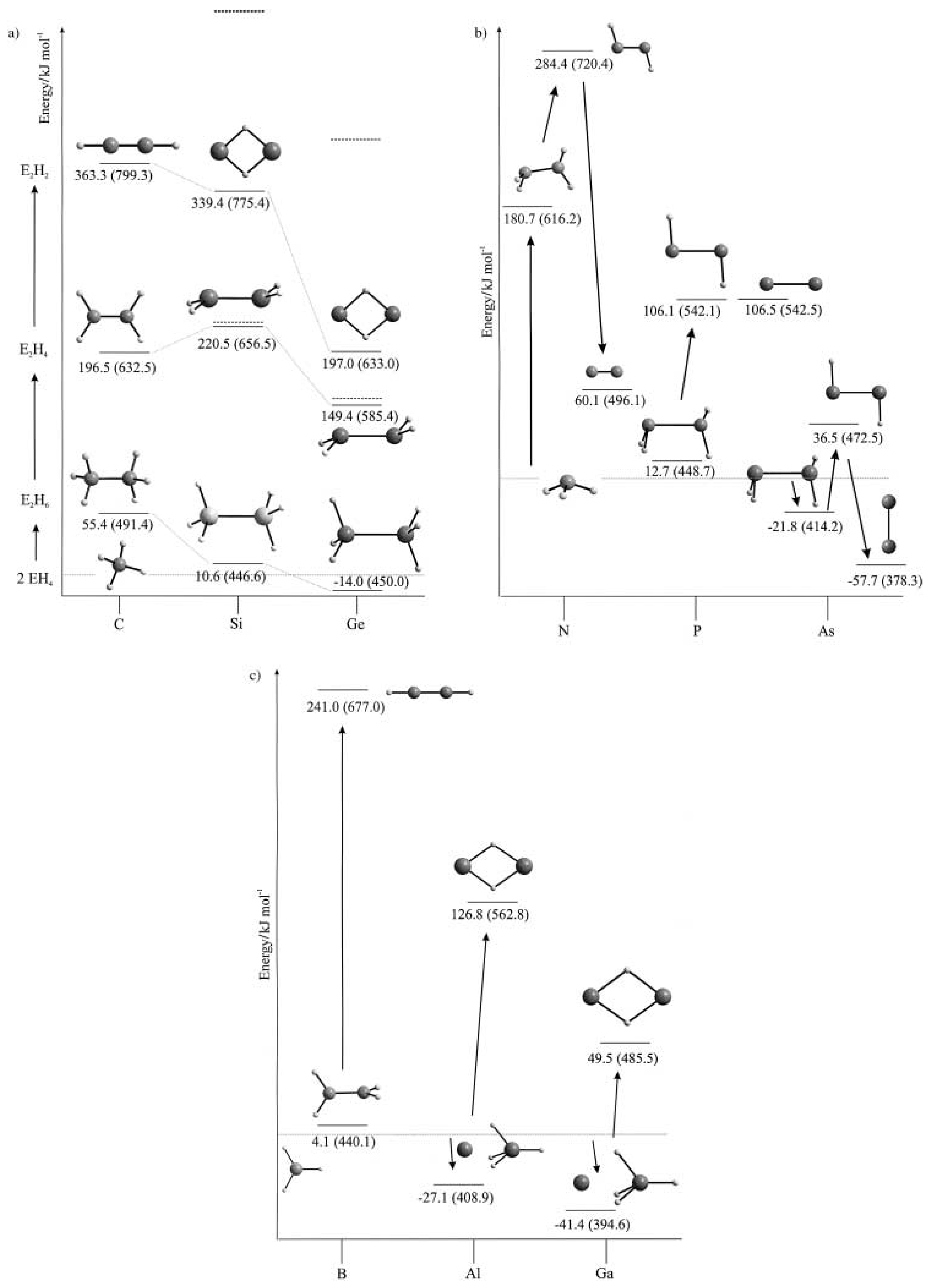


Figure 6. a) Scheme showing the enthalpies for hydrogen elimination reactions for compounds featuring Group 14 elements starting with two EH_4 molecules (the energy of which is indicated by the dashed line). Note that Si_2H_2 and Ge_2H_2 exhibit nonplanar (C_{2v}) structures (E−E interactions are not shown); b) scheme showing the enthalpies for hydrogen elimination reactions for compounds featuring Group 15 elements starting with two EH_3 molecules (the energy of which is indicated by the dashed line); c) scheme showing the enthalpies for hydrogen elimination reactions for compounds featuring Group 13 elements starting with two EH_3 molecules (the energy of which is indicated by the dashed line). The quoted energy values refer to reactions with H_2 and with H atoms (values in parenthesis).

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