Calculated Enthalpies for Dimerisation of Binary, Unsaturated, Main-Group Element Hydrides as a Means to Analyse Their Potential for Multiple Bonding

Hans-Jörg Himmel[a]

Dedicated to Professor Hansgeorg Schnöckel

Keywords: Main-group element hydrides / Dimerization / Enthalpy / Multiple bonding / Calculations

Herein, the dimerisation of subvalent, binary, main-group element hydrides with the potential for multiple bonding is studied using both hybrid DFT (B3LYP) and ab initio [MP2 and CCSD(T)] methods. The [2+2] cycloaddition is an important and characteristic reaction of derivatives of ethylene. A comparison of dimerisation reactions for several compounds with the potential for multiple bonding should, therefore, shed light on the properties of these species. Our study includes the hydrides E_2H_2 (E = B, Al, Ga, N P or As), E_2H_4 (E = C, Si or Ge) and ENH_4 (E = B, Al or Ga) and their dimers. Several isomeric forms of the monomers and dimers have to be considered. The trends within a group and a period are established and the factors responsible for them are discussed. It turns out that, generally, the enthalpies for dimerisation increase for heavier homologues, reflecting that the most important factor is the reduced strength of the E–E bonds in the monomers prior to dimerisation and, to some degree, also the reduced ring strain in the cyclic dimers. The exceptions are the dimerisations of B_2H_2 and Al_2H_2, both of which lead to the tetrahedral E_4H_4 species (E = B or Al). Dimerisation of Al_2H_2 is associated with a smaller enthalpy than that for the dimerisation of B_2H_2. Comparisons and analyses are made complicated because of the changes in the structures of the isomeric global minima between homologues.

Introduction

There is an ongoing interest in the characterization of binary compounds of the heavier main-group elements with the potential for multiple bonding.[1−9] As early as 1976, for example, a first stable dialkylgermylene, $Dis_2GeGeDis_2$ [Dis = bis(trimethylsilyl)methyl] was synthesized and later characterized by X-ray diffraction to exhibit a nonplanar geometry with a Ge−Ge bond length of 2.347 Å and an angle sum of 348° at each of the Ge atoms.[10] At the same time, the first corresponding tin compound, $[Sn\{CH(SiMe_3)_2\}_2]_2$, was structurally characterized.[11] It took 26 more years, however, until the first compounds of Ge and Sn formally isoelectronic to an alkyne were discovered, both exhibiting bent *trans*-type structures with Ge−Ge and Sn−Sn bond lengths of 2.2850(5) and 2.6675(4) Å, respectively.[12,13] Only in the last two decades has more information about these species came to light, with the most-celebrated successes lying almost exclusively in the field of binary group-14 and group-15 element compounds and group-13/15 compounds with a direct bond between a group-13 and a group-15 element.[14]

B/N compounds with a direct bond between a boron and a nitrogen atom have been well known for a long time, and the isoelectronic and isolobal connections between alkenes and aminoboranes R_2NBR_2 ("inorganic ethylene"), cyclobutanes and dimeric aminoboranes $[(R_2NBR_2)_2]$, cyclobutenes and diazadiboretidines $[(RNBR)_2]$, and benzene and borazine $(RNBR)_3$ are well established.[15] Monomeric compounds, however, with tricoordinated Al or Ga atoms and the general formula $R_2AlNR'_2$ and $R_2GaNR'_2$ are stable under normal conditions only in the presence of bulky substituents at Al, Ga and/or N.[16−18] Otherwise, they are stable only as oligomers of the general formula $[R_2MNR'_2]_n$, with n being often 2 or 3. Recently, the monomers H_2AlNH_2, H_2GaNH_2 and H_2InNH_2 were generated and characterized in a matrix of solid Ar at 12 K.[19]

Despite considerable effort, binary group-13 element compounds with the potential for multiple bonding, RGaGaR (R being a sterically demanding organic group), have been synthesized and characterized only very recently. Species that are formally valence-isoelectronic with acetylene were discovered with the synthesis of compounds of the formula $Na_2[ArGaGaAr]$ (e.g., Ar = $Mes^*{}_2C_6H_3$ or 2,4,6-$iPr_3C_6H_2$).[20] An adequate description of the Ga−Ga bond in related compounds is at present hotly debated.[21−24] Very recently, a neutral compound ArGaGaAr (Ar = 2,6-$Dipp_2C_6H_3$, Dipp = 2,6-$iPr_2C_6H_3$) has been synthesized as

---

[a] Institut für Anorganische Chemie der Universität Karlsruhe, Engesserstr., Geb. 30.45, 76128 Karlsruhe, Germany

DOI: 10.1002/ejic.200200637

the first derivative of a compound that is formally valence-isoelectronic with ethylene.[25] Additionally, the hydride HGaGaH was generated in an Ar matrix at 12 K as one of the products of the reaction between Ga_2 and H_2, and it was characterized experimentally by its IR spectrum. The antisymmetric ν(Ga−H) stretching vibration of this species occurs at a wavenumber not far away from that of GaH (also isolated in a matrix of solid Ar).[26] This result indicates that the interaction between the Ga atoms in HGaGaH cannot be very strong. Finally, a molecule of the general formula ArInInAr (Ar again being 2,6-$Dipp_2C_6H_3$, Dipp = 2,6-$i Pr_2C_6H_3$) was characterized in the solid state.[27] The In−In interaction [bond length of 2.9786(5) Å] is weak, however, and therefore this compound cannot feature a strong In−In bond.

This work follows two others dealing with the differences in the chemistry of binary, main-group element compounds with the potential for multiple bonding. In the first of these two previous accounts, we have reported the trends of theoretically determined heats of hydrogenation for several binary, main-group element hydrides.[28] Heats of hydrogenation have been used extensively in the past to determine the degree of unsaturation of hydrocarbons and their derivatives. Our survey also included a comparison between the heats of hydrogenation of the model compounds Na_2[HGaGaH], $[HGaGaH]^{2-}$ and HGaGaH. The results indicate that the Na^+ ions in Na_2[HGaGaH] are deeply engaged in the bonding. Therefore, we and others[29] have suggested to describe this species and its derivatives as "Na_2Ga_2" cluster compounds. In the second report, we analyzed the energies for fragmentation.[30] To this end, dissociation was separated into two processes: the first one consists of fragmentation into fragments that still exhibit the same geometry as they had previously before fragmentation; in the second process, the fragments relax into their electronic ground state and their global energy-minimum structure. The separation in the two processes allows for a much more accurate determination of the bond energies, which can, at least principally, also be verified experimentally. Herein, we evaluate the standard enthalpies for dimerisation of several binary main-group element hydrides that are formally valence-isoelectronic to ethylene. Cycloaddition is a very well known and thoroughly investigated process for ethylene and its derivatives. Dimerisation reactions of some other corresponding binary main-group element compounds have been looked at earlier. To name just two of many examples, very recently the [2+2] cycloaddition reactions of a stiba(III)alkene and an arsa(III)imine were investigated experimentally,[31] and the [2+2] cycloaddition enthalpies for 1,3-disilacyclobutanes were determined by quantum chemical calculations.[32] In this paper, the calculated trends down the group and within a period will be discussed for the compounds under consideration. It should be noted that in this work we intend to accumulate information about the *chemistry* of subvalent, binary, main-group element hydrides. It is especially our aim to analyse theoretical aspects of the chemistry that can, at least in principle, be verified experimentally, although some species are too reactive to be investigated in experiments that rely on presently known techniques. A close inspection of the molecular orbitals or the electron density distribution is not the topic of this work.

Calculational Details

Calculations relied on the GAUSSIAN 98 programme package.[33] The B3LYP hybrid-DFT method, in combination with a 6-311+G(2df,p) basis set, was first used to pre-optimize the structures and to calculate their vibrational modes. In the second step, the structures were again fully optimized applying the MP2 method and a 6-311+G(2df,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 obtain the standard enthalpies for the reactions in the gas phase. Subsequently, the MP2 calculations were repeated, but this time using the TZVPP basis set and employing the TURBOMOLE programme package.[34] The reaction enthalpy values are quoted for all reactions and were derived from the calculations on the B3LYP and MP2 level of theory in combination with the 6-311+G(2df,p) and on the MP2 level of theory in combination with the TZVPP basis set. Tables 1−4 include the calculated dimensions of all the compounds addressed in this work and also first estimates of the enthalpies for dimerisation on the basis of the B3LYP and MP2 methods. Finally, the optimized geometries were used in "single-point" Coupled-Cluster Single Double Triple [CCSD(T)] calculations [again using the 6-311+G(2df,p) basis set and on the basis of the geometry optimized with B3LYP] to calculate the dimerisation energies once again, and (with the help of the zero-point energy and thermal corrections calculated with B3LYP) the dimerisation enthalpies. Table 5 contains all dimerisation energies and enthalpies calculated with the CCSD(T) method.

Results and Discussion

In the course of this discussion, we show that any attempt to connect the different reactivities of the species addressed in this work with the E−E bond character within the reactant is complicated, mainly because of the changes of the structures of the global energy minima between homologues. It is, therefore, crucial for this work to start with a detailed analysis of the global energy-minimum structures for all homologues. Most of these structures have been discussed in earlier works, but they generally have concentrated on only one compound and did not discuss the *differences* in the structures.

In some cases (e.g., for E_2H_2, where E = Al or Ga), the global minimum structures feature no significant E−E interaction [E_2H_2 exhibits a D_{2h}-symmetric ring structure E(μ-H)$_2$E in its lowest-energy isomer].[35,36] In these cases, we have considered both the global minimum structure and the isomer that has the best chance for a significant E−E interaction (e.g. the bent *trans* isomer HEEH in the case of E_2H_2).

Structures of the Monomers and Dimers

Group 13 (E = B, Al and Ga)

All E_4H_4 species exhibit a global energy-minimum structure with a tetrahedral E_4 unit. A ring structure defines a local minimum on the potential energy surface only in the case of calculations using the B3LYP method. Ab initio (MP2) methods failed to find a minimum for a cyclic structure. This cyclic structure found using the B3LYP method has an energy 190.5, 138.4 and 98.1 $kJ{\cdot}mol^{-1}$ (for E = B, Al and Ga, respectively) higher than the one of the tetrahedral global energy-minimum structure. The standard enthalpy differences between both isomers amount to 179.7, 136.9 and 98.7 $kJ{\cdot}mol^{-1}$, respectively. For E = B and Al, the E−E distances are smaller for the tetrahedral isomer (1.6750 and 2.5902 Å vs. 1.6695 and 2.6387 Å for E = B and Al, respectively). In the case of Ga_4H_4, the ring structure has a slightly smaller Ga−Ga distance (2.5506 vs. 2.5615 Å). The E−H distances undergo only minuscule alterations (see Table 1). In the light of the calculations carried out using the MP2 method, however, it appears doubtful whether the ring-type structures really do define local minima on the potential energy surface.

For B_4H_4, T_d- and square-planar D_{4h}-symmetric structures have been reported previously.[37] The T_d-symmetric structure was found to be 349 $kJ{\cdot}mol^{-1}$ lower in energy than the D_{4h}-symmetric one. The B−B and B−H bond lengths for the T_d-symmetric form were calculated to be 1.7098 and 1.1875 Å, respectively. Thus, the B−B distance is very close to the one found experimentally in the known compound B_4Cl_4, which also exhibits a T_d-symmetric structure (1.71 Å).[38] The distances are in satisfying agreement with the results of our calculations (B−B and B−H bond lengths of 1.6695 and 1.1861 Å).

The derivatives $[Al(\eta^5\text{-}C_5Me_5)]_4$,[39] $[Al(Si\textit{t}Bu_3)]_4$ [40] and $[AlSi(SiMe_3)_3]_4$,[41] have been synthesized and investigated structurally. They all consist of tetrahedral Al_4 units, in which the Al−Al distances are 2.77, 2.60 and 2.61 Å, respectively. These values are in good agreement with the Al−Al distance of 2.5902/2.6076 Å calculated herein for Al_4H_4. Previous calculations have led to Al−Al and Al−H distances of 2.617 and 1.589 Å.[42] A cyclic Al_4 unit can be stabilized in the presence of donors like NEt_3, resulting in a molecule $[Al_4Br_4(NEt_3)_4]$ in which the Al−Al separation is 2.64 Å.[43] The structures, as calculated for the tetrahedral Ga_4H_4 isomers, are in agreement with earlier accounts (see Figure 1). For example, the Ga−Ga bond

Table 1. Geometrical parameters (bond lengths [Å], bond angles [°]), energies and enthalpies [$kJ{\cdot}mol^{-1}$] for isomerization and dimerisation of group-13 element hydrides studied in this work

E	Parameter	E_2H_2		$(E_2H_2)_2$	
		Linear/bent *trans*[a] B3LYP/MP2/MP2TM	Cyclic[b] B3LYP/MP2/MP2TM	Cyclic[c] B3LYP	Tetrahedral[d] B3LYP/MP2 /MP2TM
B	B−B	1.5051/1.5085/1.5099	–	1.6695	1.6750/1.6866/1.6885
	B−H	1.1714/1.1743/1.1715	–	1.1861	1.1813/1.1848/1.1818
	B−B−B		–	80.9	60.0/60.0/60.0
	H−B−B	180/180/180	–		
	Δ*E* [$(B_2H_2)_2$ cycl. T_d]			190.5	
	Δ*H* [$(B_2H_2)_2$ cycl. T_d]			179.7	
	Δ*H* for dim.			−244.3	−424.0/−481.5/−510.0
Al	Al−Al	2.6693/[e]/2.6399	2.9648/2.9274/2.9381	2.6387	2.5902/2.6076/2.6090
	Al−H	1.6213/[e]/1.6109	1.8267/1.8112/1.8148	1.5928	1.5932/1.5881/1.5903
	Al−Al−Al			87.6	60.0/60.0/60.0
	H−Al−Al	119.4/[e]/120.5	35.8/36.1/36.0		
	Δ*E* [Al_2H_2 D_{2h} − C_{2h}]		−59.7/[e]/−65.5		
	Δ*H* [Al_2H_2 D_{2h} − C_{2h}]				
	Δ*E* [$(Al_2H_2)_2$ cycl. T_d]			138.4	
	Δ*H* [$(Al_2H_2)_2$ cycl. T_d]			136.9	
	Δ*H* for dim. (D_{2h})			−74.1	−211.0/−185.5/−308.9
	Δ*H* for dim. (C_{2h})			−193.3	−330.2/[e]/−442.3
Ga	Ga−Ga	2.6090/2.5944/2.5121	3.0385/3.0148/2.9642	2.5506	2.5615/2.5961/2.5198
	Ga−H	1.6291/1.6226/1.5916	1.8758/1.8656/1.8377	1.5778	1.5809/1.5903/1.5560
	Ga−Ga−Ga			86.8	60.0/60.0/60.0
	H−Ga−Ga	120.7/121.7/122.7	35.9/36.1/36.3		
	Δ*E* [Ga_2H_2 D_{2h} − C_{2h}]		−56.9/−49.4/−48.8		
	Δ*H* [Ga_2H_2 D_{2h} − C_{2h}]		−58.9/−51.4/−50.8		
	Δ*E* [$(Ga_2H_2)_2$ cycl. T_d]			98.1	
	Δ*H* [$(Ga_2H_2)_2$ cycl. T_d]			98.7	
	Δ*H* for dim. (D_{2h})			−12.4	−111.1/−105.6/−277.7
	Δ*H* for dim. (C_{2h})			−130.3	−229.0/−208.6/−402.6

[a] Symmetry: $D_{\infty h}$ for B_2H_2, C_{2h} for Al_2H_2 and Ga_2H_2. [b] Symmetry: D_{2h}. [c] Symmetry used in the calculations: C_2. [d] Symmetry: T_d. [e] Calculation failed.

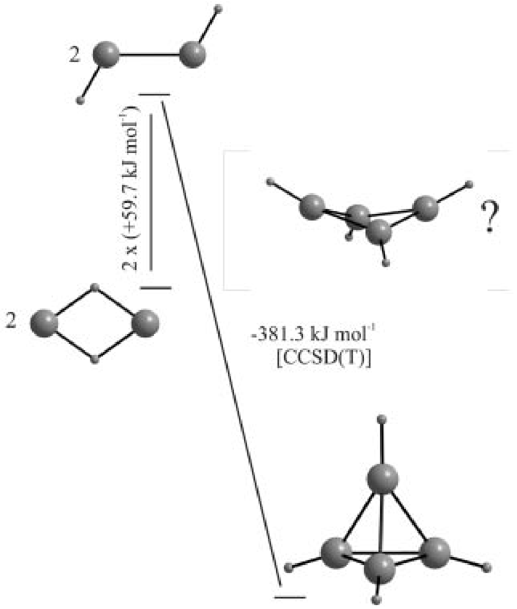

Figure 1. Geometries of cyclic Al(μ-H)$_2$Al, bent *trans*-HAlAlH and the dimerisation product Al_4H_4 with T_d symmetry and enthalpy for dimerisation (the cyclic structure that, according to B3LYP calculations, possibly defines a local energy minimum, is also visualized)

length in Ga_4H_4 was calculated previously to be 2.567 Å.[44] An example of a structurally characterized derivative is provided by the species [Ga{C(SiMe$_3$)$_3$}]$_4$,[45] for which Ga−Ga bond lengths of 2.680−2.702 Å were derived experimentally.

As to the monomers, B_2H_2 has a linear global energy-minimum structure with a triplet electronic ground state ($^3\Sigma_g^-$).[46] The B−B and B−H distances were calculated to be 1.516 and 1.177 Å, respectively. These values are in good agreement with the ones calculated herein (1.5051/1.5085 and 1.1714/1.1743 Å, respectively). Al_2H_2 and Ga_2H_2 both prefer a ring structure with two bridging H atoms, Al(μ-H)$_2$Al and Ga(μ-H)$_2$Ga.[35,36,47,48] According to the calculations presented herein, the bent *trans* structures, HAlAlH and HGaGaH (see Figure 1), have energies 59.7 and 57.0 kJ·mol^{-1} higher than the cyclic global energy-minimum form (the differences in standard enthalpy amount to 59.6 and 58.9 kJ·mol^{-1}, respectively). Previous calculations for bent *trans*-HAlAlH have yielded Al−Al and H−Al bond lengths of 2.782−2.602 Å (with more accurate methods tending to predict smaller values) and 1.608−1.602 Å, with the H−Al−Al bond angle being 119.3−120.0°.[49] These values compare with Al−Al and Al−H distances and H−Al−Al bond angles of 2.6693, 1.6213 Å and 119.4°, respectively, calculated herein. In the case of bent *trans*-HGaGaH, previous DFT calculations have resulted in Ga−Ga and Ga−H bond lengths of 2.5848 and 1.6261 Å and an H−Ga−Ga bond angle of 121.3°,[35] which are in good agreement with the values obtained herein (2.6090/2.5944 and 1.6291/1.6226 Å and 120.7/121.7°, respectively). As already mentioned, a derivative, ArGaGaAr (Ar = 2,6-Dipp$_2$C$_6$H$_3$, Dipp = 2,6-*iPr*$_2$C$_6$H$_3$), was very recently synthesized and characterized by X-ray diffraction.[25] The Ga−Ga bond length of 2.6268(7) and the C−Ga−Ga bond angle of 123.16(7)° were obtained for this compound in the solid phase.

Group 14 (E = C, Si and Ge)

Cyclic structures define the global energy minima for all E_4H_8 species. The E−E and E−H distances were calculated to be 1.5509/1.5448 and 1.0920/1.0910 Å, 2.3724/2.3602 and 1.4865/1.4837 Å, and 2.4688/2.4653 and 1.5422/1.5427 Å for E = C, Si and Ge, respectively (see Table 2). The E−E−E angles are 88.5/87.8, 88.1/86.2 and 88.3/88.1° for E = C, Si and Ge, respectively. The values are in good agreement with the ones reported earlier. Thus, for cyclobutane, the C−C and C−H bond lengths have been determined to be 1.543 and 1.094 Å and the C−C−C and H−C−H bond angles have been determined to be 87.9 and 108.8°.[64] In the case of Si_4H_8, previous calculations have predicted a D_{2d}-symmetric global energy-minimum struc-

Table 2. Geometrical parameters (bond lengths [Å], bond angles [°]), energies and enthalpies [kJ·mol^{-1}] for isomerization and dimerisation of group-14 element hydrides studied in this work

E	Parameter	E_2H_4 [a] B3LYP/MP2/MP2TM	$(E_2H_4)_2$ [b] B3LYP/MP2/MP2TM
C	C−C	1.3244/1.3313/1.3323	1.5509/1.5448/1.5452
	C−H	1.0840/1.0835/1.0804	1.0920/1.0910/1.0873
	C−C−C		88.5/87.8/87.8
	H−C−H	116.5/117.1/117.3	108.4/109.0/109.3
	Δ*H* (dim.)		−49.8/−40.0/−100.2
Si	Si−Si	2.1624/2.1552/2.1532	2.3724/2.3602/2.3595
	Si−H	1.4787/1.4736/1.4733	1.4865/1.4837/1.4800
	Si−Si−Si		88.1/86.2/86.2
	H−Si−H	112.5/114.3/114.2	108.7/109.9/109.6
	Δ*H* (dim.)		−319.7/−358.7/−365.9
Ge	Ge−Ge	2.2945/2.2756/2.2427	2.4688/2.4653/2.4270
	Ge−H	1.5440/1.5374/1.5197	1.5422/1.5427/1.5218
	Ge−Ge−Ge		88.3/88.1/87.8
	H−Ge−H	108.0 /111.0/111.3	108.7/109.1/109.2
	Δ*H* (dim.)		−274.4/−328.3/−353.8

[a] Symmetry used in the calculations: D_{2h} for C_2H_4, C_{2h} for Si_2H_4 and Ge_2H_4. [b] Symmetry: D_{4h} for C_4H_8, D_{2d} for Si_4H_8 and Ge_4H_8.

ture with a folded Si_4 ring, which is characterized by Si−Si and Si−H bond lengths of 2.368 and 1.470/1.472 Å and a H−Si−H bond angle of 109.4°.[50] The barrier leading to a D_{4h}-symmetric form with a planar Si_4 ring, however, apparently amounts to less than 10 kJ·mol^{-1},[51] which shows the high flexibility of the Si_4 ring. The derivatives with the general formula $[R_2Si]_4$, for which the structures in the solid crystalline phase were determined from experimental X-ray data, confirm this high flexibility. For example, folded Si_4 rings were found to be present, for R = *t*BuCH$_2$ or *i*Pr, in which the Si−Si bond lengths are 2.359−2.409 Å.[52] In the case where R = CH_3 or Me_3Si, however, the experimental data show that a planar Si_4 ring is formed (Si−Si bond length of 2.375 Å for R = CH_3).[53−55] It has been claimed that the Si−Si bond in Si_4H_8 is significantly weaker than the C−C bonds in corresponding alkanes, and the smaller contributions of the s valence orbitals to the formation of hybrid orbitals is one of the factors that have been proposed to be responsible for this trend.[56]

At 1.3244/1.3313 Å, the calculated C−C distance in H_2CCH_2 is close to the experimentally derived value of 1.339 Å. Previous calculations for H_2SiSiH_2 predict an Si−Si bond length of 2.116 or 2.217 Å (for calculations relying on the SCF or MCSCF method, respectively). Tetramesityldisilene is one derivative that had been already characterized experimentally by its X-ray diffraction pattern in 1983, yielding a value of 2.160 Å for the Si−Si bond length.[57] These experimental and calculated values are close to the one calculated herein (2.1624/2.1552 Å). For H_2GeGeH_2, previous calculations resulted in Ge−Ge and Ge−H bond lengths of 2.275−2.341 and 1.550 Å and an H−Ge−Ge bond angle of 109.0°.[58] As already mentioned, some stable dialkylgermylenes have been known for a long time to experimentalists[10] [including $(CH_3)_2GeGe(CH_3)_2$, which was investigated in Ar and N_2 matrices at 5 K by vibrational (IR and Raman) spectroscopy],[59] and in the ones that have been studied by X-ray diffraction, a typical Ge−Ge bond length of about 2.34 Å has been found, in satisfying agreement with the length predicted on the basis of quantum chemical calculations.[59,60] The values calculated herein (2.2945/2.2756 and 1.5440/1.5374 Å for the Ge−Ge and Ge−H bond lengths and 108.0/111.0° for the H−Ge−Ge bond angle) are in reasonable agreement with these numbers.

Group 15 (E = N, P and As)

In the gas phase, N_4H_4 prefers an open chain-like structure with two hydrogen atoms at both ends of the N_4 chain.[61,62] Crystals of this compound can be prepared, but they decompose at temperatures above −20 °C, with its isomer NH_4N_3 (exhibiting a high lattice energy) being among the detectable products.[63] According to our calculations, the N−N distances are 1.3770 Å for the separations of the terminal N atoms to their neighbouring ones and 1.2361 Å for the distance between the two inner N atoms of the chain. The cyclic structure defines a local minimum on the potential energy surface that exhibits an energy 242.4 kJ·mol^{-1} higher [222.3 kJ·mol^{-1} according to CCSD(T)] than the open chain-like isomer. Thus, the stand-

Table 3. Geometrical parameters (bond lengths [Å], bond angles [°]), energies and enthalpies [kJ·mol^{-1}] for isomerization and dimerisation of group-15 element hydrides studied in this work

E	Parameter	E_2H_2[a] B3LYP/MP2/MP2TM	$(E_2H_2)_2$ Cyclic[b] B3LYP/MP2/MP2TM	Chain[c]B3LYP/MP2/MP2TM
N	N−N	1.2354/1.2541/1.2544	1.4720/1.4711/1.4710	1.3770, 1.2361/1.3769,1.2538/1.3793, 1.2533
	N−H	1.0347/1.0320/1.0286	1.0208/1.0226/1.0186	1.0180, 1.0105/1.0189, 1.0116/1.0082, 1.0151
	N−N−N		89.8/89.6/89.6	113.1/111.8/111.6
	H−N−N	107.2/106.0/105.6	105.3/104.3/103.9	113.2, 109.5/112.3, 108.9/111.6, 108.4
	H−N−H			113.1/112.8/112.1
	Δ*E* $[(N_2H_2)_2$ cycl. chain]			−242.4/−229.0/−231.0
	Δ*H* $[(N_2H_2)_2$ cycl. chain]			−247.9/−234.5/−236.5
	Δ*H* (dim.)		+133.2/+149.0/+118.0	−114.7/−85.5/−118.5
P	P−P	2.0311/2.0372/2.0393	2.2618/2.2376/2.2407	2.2349, 2.0330/2.0413,2.2174, 2.0428/2.2192
	P−H	1.4259/1.4195/1.4193	1.4207/1.4164/1.4154	1.4184, 1.4193/1.4130,1.4142, 1.4130/1.4119
	P−P−P		90.0/89.6/89.6	101.6/99.3/99.4
	H−P−P	94.3/93.7/93.4	93.8/93.0/92.7	94.8, 99.9/94.9, 99.0/94.8, 98.7
	H−P−H			94.6/94.9/94.8
	Δ*E* $[(P_2H_2)_2$ cycl. chain]			47.2/69.2/59.5
	Δ*H* $[(P_2H_2)_2$ cycl. chain]			45.4/67.4/57.7
	Δ*H* (dim.)		−140.5/−161.8/−174.5	−95.1/−94.4/−116.8
As	As−As	2.2542/2.2601/2.2396	2.5017/2.4691/2.4415	2.4843, 2.2529/2.4530, 2.2652/2.4259, 2.2442
	As−H	1.5325/1.5248/1.5142	1.5291/1.5235/1.5118	1.5254, 1.5268 /1.5193, 1.5196/1.5080, 1.5083
	As−As−As		89.9/89.1/89.1	99.7/97.6/97.4
	H−As−As	92.6/92.2/91.8	91.6/91.0/90.5	97.0, 93.2/96.5, 93.5/96.2, 93.4
	H−As−H			92.7/93.3/93.2
	Δ*E* $[(As_2H_2)_2$ cycl. chain]			54.1/71.1/67.8
	Δ*H* $[(As_2H_2)_2$ cycl. chain]			52.8/69.8/66.5
	Δ*H* (dim.)		−142.5/−161.4/−187.0	−89.7/−91.6/−120.5

[a] Symmetry used in the calculations: C_{2h}. [b] Symmetry used in the calculations: D_{2d}. [c] Symmetry used in the calculations: C_i.

ard enthalpy for conversion of the open chain-like isomer into the cyclic one amounts to 247.9 kJ·mol^{-1} according to B3LYP and 227.8 kJ·mol^{-1} according to CCSD(T). The tendency of N_4H_4 to form chains that feature a double bond between the inner N atoms, instead of a cyclic structure in which only single bonds are present, demonstrates the strength of the π bond relative to the σ bond. The cyclic isomer, tetrazetidine, is unstable and dissociates into two *trans*-diazene (N_2H_2) molecules, with the standard enthalpy for this dissociation calculated previously to be −121.5 kJ·mol^{-1}.[63] This value is in good agreement with our results (dissociation energy: −116.7 kJ·mol^{-1}; standard enthalpy: −133.2 kJ·mol^{-1}). Tetrazetidine exhibits a D_{2d}-symmetric global energy-minimum structure that is characterized by N−N and N−H bond lengths of 1.4720/1.4711 and 1.0208/1.0226 Å (cf. 1.479 and 1.025 Å)[64] and N−N−N and H−N−N bond angles of 89.8/89.6 and 105.3/104.3° (cf. 89.8° and 104.1°).[64] At 135.8 kJ·mol^{-1}, the strain energy of the cyclic tetrazetidine N_4H_4 isomer was previously calculated to be slightly higher than the one derived for cyclobutane (110.2 kJ·mol^{-1}).

In contrast to its lighter homologue, P_4H_4 prefers a cyclic structure, which has, according to our calculations, an energy that is 47.2 kJ·mol^{-1} lower [56.9 kJ·mol^{-1} using the CCSD(T) method] than the chain-like isomer (standard enthalpy difference of 45.4 kJ·mol^{-1} according to B3LYP, see Table 3). The cyclic P_4H_4 isomer exhibits D_{2d} symmetry. The calculated geometric parameters (2.2618/2.2376 and 1.4207/1.4164 Å for the P−P and P−H bond lengths and 90.0/89.6 and 93.8/93.0° for the P−P−P and H−P−P bond angles) are in good agreement with the results of earlier calculations (2.238 and 1.417 Å for the P−P and P−H bond lengths and 89.8° and 95.3° for the P−P−P and H−P−P bond angles).[64] As_4H_4 also exhibits a cyclic global energy-minimum structure, with the energy and the standard enthalpy differences relative to the open chain-like isomer amounting to 54.1 and 53.8 kJ·mol^{-1}, respectively, using the B3LYP method [90.4 and 90.1 kJ·mol^{-1} using the CCSD(T) method, see Figure 2]. In the cyclic form, the As−As and As−H bond lengths amount to 2.5017/2.4691 and 1.5291/1.5235 Å, respectively.

The value calculated herein for the N−N distance in HNNH (1.2354/1.2541 Å) is close to the experimentally determined value of 1.252 Å. In the case of HPPH, a P−P bond length of 2.099 was previously calculated,[64] with values for the P−H distance and the H−P−P bond angle of 1.420 Å and 94.9°, respectively. These numbers compare with the P−P bond lengths of 2.0311/2.0372 Å, the P−H bond lengths of 1.4259/1.4195 Å, and the H−P−P bond angles of 94.3°/93.7° calculated herein. Experimentally, a number of derivatives bearing the formula RPPR (R being a bulky organic group) were studied by X-ray diffraction, yielding typical P−P bond lengths of about 2.01 Å,[65] in good agreement with the theoretically derived value. Finally, for HAsAsH, a *trans* C_{2h} structure was predicted previously to be characterized by an As−As bond length of 2.227 Å and an H−As−As bond angle of 94.4°.[66] These values tally nicely with the ones calculated herein (2.2542/2.2601 Å and 92.6°/92.2°, respectively). One example of several derivatives characterized experimentally is the compound (2,4,6-tBu$_3$C$_6$H$_2$)AsAsCH(SiMe$_3$)$_2$, which was structurally characterized already in 1983 and exhibits an As−As bond length of 2.224(2) Å and C−As−As bond angles of 93.6(3) and 99.9(3)°.[67]

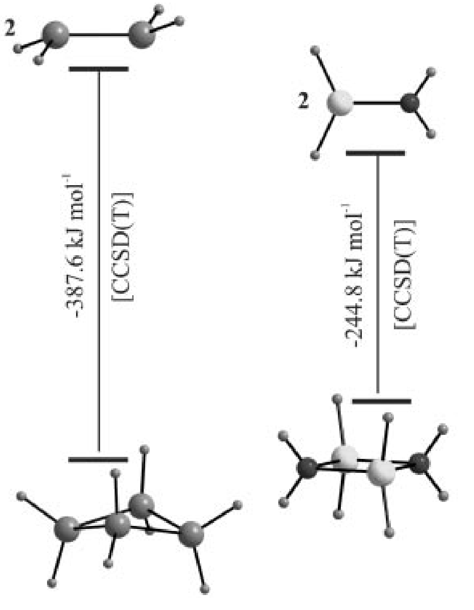

Figure 2. Comparison between the geometries of H_2GeGeH_2 and H_2GaNH_2 and their dimerisation products, the cyclic species Ge_4H_8 and $Ga_2N_2H_8$, and the standard enthalpies of their dimerisation

Group-13/Group-15 Compounds (H_2BNH_2, H_2AlNH_2 and H_2GaNH_2)

The dimers $(H_2ENH_2)_2$ are composed of planar E_2N_2 rings. Although there is a tendency, especially for E = Al or Ga, to form trimers instead of dimers, some derivatives of the dimers were synthesized and characterized either in the gas or crystal phase. Thus, for example, $(H_2GaNMe_2)_2$ has been characterized in the gas phase using electron diffraction,[68] and $[H_2GaN(H)NMe_2]_2$ has also been characterized experimentally.[69] In those studies, the Ga−N and Ga−H bond lengths and the Ga−N−Ga and H−Ga−H bond angles of $(H_2GaNMe_2)_2$ were determined to be 2.027 and 1.487 Å, and 90.6 and 109°. In the case of $[H_2GaN(H)NMe_2]_2$, values of 1.991−2.024 and 1.51 Å, and of 86.9/97.3 and 92.1/93.6° were obtained for the Ga−N and Ga−H bond lengths and the N−Ga−N and Ga−N−Ga bond angles, respectively. In both compounds, the Ga_2N_2 ring was shown to be planar. All experimental values are in excellent agreement with the results of our calculations for $(H_2GaNH_2)_2$ [D_{2h} symmetry, Ga−N and Ga−H bond lengths of 2.035 and 1.567 Å, respectively, and N−Ga−N and H−Ga−H bond angles of 86.0 and 125.5° (B3LYP values), see Figure 3] and previous calculations.[70] Very recently, the apparently air-stable derivative [tBu(H)GaNEt$_2$]$_2$ was synthesized and structurally characterized.[71] The Ga−N and Ga−H bond lengths of this compound were reported to be 2.025(3) and 1.57(4) Å; the N−Ga−N bond angle is 88.8°. The trimer $[H_2GaNH_2]_3$ is also known and has been proved to be a valuable single-source precursor to solid GaN.[72] Another example, from Al chemistry, is provided by the compound $[Me_2AlN(H)NMe_2]_2$, for which an Al−N bond length and a N−Al−N bond angle were determined to be 1.958−1.953 Å and 87.2°, respectively.[73] These values compare with values of 1.9686 Å and 87.4° calculated herein for $(H_2AlNH_2)_2$.

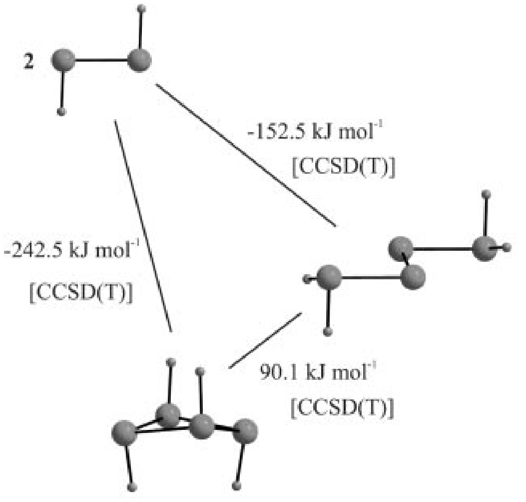

Figure 3. Geometries of HAsAsH and its dimerisation product As_4H_4 in its cyclic energy minimum and its chain-like forms, and enthalpies for dimerisation

Much effort has been put into the synthesis of monomeric compounds with the general formula $R^1R^2EE'R^3R^4$ (R^1−R^4 being bulky organic groups and E and E′ being group-13 and group-15 elements). The parent compounds $H_2EE'H_2$, however, are unstable and, therefore, special techniques, such as matrix isolation, are necessary to obtain access to them. The structure of H_2BNH_2 has been studied by microwave spectroscopy[74] and by matrix IR spectroscopy.[75] Recently, the heavier homologues H_2AlNH_2, H_2GaNH_2 and H_2InNH_2 were generated and characterized by matrix-isolation experiments.[19,76] All four of these monomers have been the subjects of several detailed theoretical works.[28,77−82] Experiments and calculations agree that they all are planar, C_{2v}-symmetric molecules. According to previous calculations using CCSD/TZ2P, H_2AlNH_2 is characterized by Al−N, Al−H and N−H bond lengths of 1.772, 1.576 and 1.004 Å, respectively, and H−Al−H and H−N−H bond angles of 124.1 and 110.0°, respectively.[83] Using DFT methods, the following parameters were calculated in a previous study of H_2GaNH_2: Ga−N 1.8211 Å, Ga−H 1.5621 Å, N−H 1.0086 Å, H−Ga−H 126.7° and H−N−H 111.7°.[19] All these values are in good agreement with the values calculated herein (see Table 4).

Standard Enthalpies for Dimerisation

The structures of the most relevant isomers of the monomers and dimers having now been established, we now turn our attention to a discussion of the dimerisation enthalpies. Tables 1−4 include the dimerisation enthalpies calculated using the B3LYP and MP2 methods, each in combination with the 6-311+G(2df,p) basis set, as well as the enthalpies derived from calculations with MP2, but this time with the TZVPP basis set. Finally, Table 5 lists the calculated values for the dimerisation enthalpies using the CCSD(T) method. The general trend is that the enthalpies as calculated with MP2/TZVPP are higher than the ones derived from MP2/6-311+G(2df,p) and B3LYP/6-311+G(2df,p) calculations. The differences are relatively small between the values calculated with CCSD(T)/6-311+G(2df,p) and MP2/TZVPP (see Table 5). This observation shows that expensive methods and/or large basis sets are necessary for calculating accurate enthalpies. The results give us confidence that the levels of calculations used herein are sufficient to establish, at least, the trends for the dimerisation enthalpies.

Figure 4 is presented to better visualize the observed trends of the enthalpies. We have calculated the enthalpies in several cases for two different isomeric forms of the monomers and dimers, and this process is necessary in some cases for a better comparison (if the global energy-minimum structures change for homologues). Nevertheless, Figure 4 shows only the trends for the global energy-minimum forms. The dimerisation of C_2H_4 to give cyclobutane can be used as a test system to judge the quality of the calculation methods, since reliable experimental enthalpy values exist for this reaction. With a standard enthalpy of -75.3 kJ·mol^{-1}, the value calculated with CCSD(T) comes very close to the experimental one of ca. -72 kJ·mol^{-1}.[84] With B3LYP and MP2 in combination with the 6-311+G(2df,p) method, this enthalpy comes out slightly lower than the experimental one.

The dimerisation enthalpies are all negative quantities (exothermic), with the only exception being the dimerisation of HNNH to give cyclic N_4H_4. The value of $+133.2$ kJ·mol^{-1} calculated with B3LYP is in good agreement with the results of earlier calculations, which gave a value of 121.5 kJ·mol^{-1}.[64] At 127.6 kJ·mol^{-1}, the enthalpy as calculated using the CCSD(T) method is also in pleasing agreement with this previous report. As already mentioned, N_4H_4 prefers an open chain-like structure where the inner N atoms can establish significant π bonding. The dimerisation to give this chain like structure is exothermic [dimerisation enthalpy of -115 kJ·mol^{-1} using the B3LYP and -99.2 kJ·mol^{-1} using the CCSD(T) method]. Therefore the positive value calculated for the enthalpy of dimerisation to the N_4H_4 ring reflects the instability of the N_4H_4 ring. This instability is partially caused by the strain energy, which was estimated to be even slightly higher than the one of cyclobutane, C_4H_8 (135.8 vs. 110.4 kJ·mol^{-1}).[64] The lone-pair repulsion is certainly one important factor to destabilize the cyclic form. Another factor is, in all certainty, the particularly strong N=N π bond, which can exist in the monomer and the dimer in its chain-like form, but not in the cyclic dimer. It has been pointed out that the π-bond increment (e.g., in N_2) is even higher than the σ-bond increment.[85]

Table 4. Geometrical parameters (bond lengths [Å], bond angles [°]), energies and enthalpies [kJ·mol^{-1}] for isomerization and dimerisation for group-13/group-15 element hydrides with the general formulas H_2ENH_2 and $(H_2ENH_2)_2$ (E = B, Al or Ga)

E	Parameter	H_2ENH_2[a] B3LYP/MP2 /MP2TM	$(H_2ENH_2)_2$[b] B3LYP/MP2 /MP2TM
B/N	B−N	1.3884/1.3923/1.3923	1.6080/1.6048/1.6066
	B−H	1.1920/1.1926/1.1903	1.2009/1.2022/1.1995
	N−H	1.0080/1.0077/1.0039	1.0123/1.0132/1.0092
	H−N−H	113.3/113.8/113.8	107.9/108.2/108.1
	H−B−H	122.0/122.4 /122.4	115.2/115.7/115.7
	N−B−N		92.0/92.1/92.1
	Δ*H* (dim.)		−32.2/−5.4/−77.3
Al/N	Al−N	1.7744/1.7759/1.7795	1.9686/1.9674/1.9705
	Al−H	1.5772/1.5756/1.5769	1.5861/1.5849/1.5862
	N−H	1.0096/1.0104/1.0063	1.0163/1.0177/1.0134
	H−N−H	110.0/110.0 /109.9	106.1/106.2/106.1
	H−Al−H	124.3/124.1/124.1	122.9/123.1/123.5
	N−Al−N		87.4/87.3/87.3
	Δ*H* (dim.)		−202.9/−211.3/−240.4
Ga/N	Ga−N	1.8235/1.8854/1.8119	2.0350/2.1359/2.0146
	Ga−H	1.5585/1.5718/1.5439	1.5670/1.5803/1.5537
	N−H	1.0085/1.0165/1.0051	1.0149/1.0354/1.0127
	H−N−H	111.7/110.9/111.4	106.8/107.0/106.5
	H−Ga−H	127.0/129.2/126.4	125.5/131.2/125.5
	N−Ga−N		86.0/85.4/86.5
	Δ*H* (dim.)		−163.0/−152.6/−213.3

[a] Symmetry used in the calculations: D_{2h}. [b] Symmetry used in the calculations: D_{2h}.

Table 5. Energies $\Delta_R E$ and standard enthalpies $\Delta_R H^0$ [kJ·mol^{-1}] of dimerisation as calculated using the CCSD(T) method; for better comparison, the standard enthalpies derived from MP2/TZVPP calculations are also included

	$\Delta_R E$ [CCSD(T)]	$\Delta_R H^0$ [CCSD(T)]	$\Delta_R H^0$ [MP2/TZVPP]
$2\ B_2H_2$ (linear) → $(B_2H_2)_2$ (T_d)	−493.7	−481.5	−510.0
$2\ Al_2H_2$ (cyclic) → $(Al_2H_2)_2$ (T_d)	−284.5	−271.9	−308.9
$2\ Ga_2H_2$ (cyclic) → $(Ga_2H_2)_2$ (T_d)	[a]	[a]	−277.7
$2\ C_2H_4 \rightarrow (C_2H_4)_2$	−90.3	−75.3	−100.2
$2\ Si_2H_4 \rightarrow (Si_2H_4)_2$	−364.0	−353.8	−365.9
$2\ Ge_2H_4 \rightarrow (Ge_2H_4)_2$	−398.6	−387.6	−353.8
$2\ N_2H_2 \rightarrow (N_2H_2)_2$ (chain)	−110.2	−99.2	−118.5
$2\ P_2H_2 \rightarrow (P_2H_2)_2$ (cyclic)	−167.2	−158.3	−174.5
$2\ As_2H_2 \rightarrow (As_2H_2)_2$ (cyclic)	−250.0	−242.5	−187.0
$2\ BNH_4 \rightarrow (BNH_4)_2$	−80.1	−67.2	−77.3
$2\ AlNH_4 \rightarrow (AlNH_4)_2$	−247.4	−236.5	−240.4
$2\ GaNH_4 \rightarrow (GaNH_4)_2$	−255.7	−244.8	−213.3

[a] The CCSD(T)/6-311+G(2df,p) calculation for Ga_4H_4 failed.

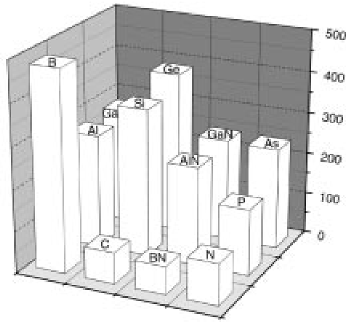

Figure 4. Standard enthalpies for dimerisation, ΔH_D^0, for the hydrides addressed in this work, as calculated using the CCSD(T) method (see Table 5); note that all species are considered in their global energy-minimum forms

It is clearly visible from Figure 4 that, while the compounds composed of group-14, -15 or -13/15 elements follow the same trend (increase of the dimerisation enthalpy down the group), the compounds composed of group-13 elements follow a different behaviour. The hydrides of the first long-period elements, H_2CCH_2, H_2BNH_2 and HNNH, have absolute dimerisation enthalpy values that are smaller than 100 kJ·mol^{-1}. The eye-catching exception is HBBH, which has the highest dimerisation enthalpy of all compounds addressed herein at −481.5 kJ·mol^{-1} [CCSDT(D) calculation]. Compound HBBH also is the only compound with a triplet electronic ground state. In total, the bond order in HBBH is two, as it is in H_2CCH_2 and HNNH. The two binding valence π orbitals, however, are each filled with *one* electron. In previous reports, we have probed the response of HBBH to hydrogenation (to give H_2BBH_2)[28] and fragmentation (to give two HB fragments).[30] Hydrogenation is accompanied by a gain in enthalpy of ca. −180 kJ·mol^{-1}. This value is only slightly higher than the one derived for hydrogenation of H_2CCH_2 (ca. −140 kJ·mol^{-1}). The fragmentation of HBBH to give two BH units in their singlet electronic state consumes ca. 450 kJ·mol^{-1}, a value close to the one computed for H_2SiSiH_2 (440 kJ·mol^{-1}). Thus, the bond in HBBH is not very weak and cannot be the only reason for the extremely high dimerisation enthalpy. The stability of the B_4H_4 tetrahedron certainly must be considered in this context.

Moving from the first to the second long period, the dimerisation enthalpies increase generally. The only exception can again be found in the compounds of group-13 elements. First we turn our attention, however, to compounds of group-15 elements. The dimerisation enthalpies calculated herein for P_2H_2 of −141 kJ·mol^{-1}, using the B3LYP method, and of −158.3 kJ·mol^{-1}, using the CCSD(T) method, compare nicely with a value of 149.5 kJ·mol^{-1} reported previously.[64] The smallest change is found for the compounds of group-15 elements. Note that the enthalpies as plotted in Figure 4 are for dimerisation to give the open chain-like structure for N_4H_4, but the ring-type ones for P_4H_4 and As_4H_4. As already mentioned, the global energy-minimum structure of the dimer changes from the chain-like geometry of N_4H_4 to the cyclic one of P_4H_4. As pointed out earlier, the strain energies drop dramatically from 134.8 kJ·mol^{-1} in N_4H_4 to no more than 24.1 kJ·mol^{-1} in P_4H_4.[64] This feature means that at least two factors have to be considered to explain the changes that are only moderate within the binary group-15 hydrides. The first, and maybe most important, factor certainly is that the capability to form significant π-bonding is still quite high for the phosphane and arsane compounds. This phenomenon implies that the stability of the monomers HEEH (E = group-15 element) does not decrease as much down the group as for the compounds composed of of group-14, -13 or -13/15 elements. The other factor is the stability of the dimer. As already mentioned, the lone-pair repulsion and the strain energy should decrease down the group, the latter because of the larger affordability of bond-angle deformations. It has been suggested that the strain energy in P_4H_4 is close to zero.[86] When considering dimerisation to give the *cyclic* isomers E_4H_4 in the case of E = N, P, and As (see Table 3), the enthalpies are only very small (at −118.5, −116.8, and −120.5 kJ·mol^{-1} for E = N, P, and As, respectively) according to the MP2/TZVPP method.

In the case of group-14 element compounds, the increase in the dimerisation enthalpy is larger than that for group-15 element compounds. Dimerisation of Si_2H_4 is accompanied by an enthalpy gain of 353.8 kJ·mol^{-1} according to the CCSD(T) estimate (and 365.9 kJ·mol^{-1} according to MP2/TZVPP). This means that the dimerisation enthalpy is 4.7 times higher than for the C analogue, while P_2H_2 dimerises with an enthalpy only 1.6 times higher than that of N_2H_2. One of the most important factors at work here is certainly the instability of the H_2SiSiH_2 reactant. In contrast to HPPH, which features a "classical" and comparably strong π bond, H_2SiSiH_2 features a different, weaker sort of π-interaction ("donor−acceptor" interactions). Another factor is again the strain energy in the cyclic dimer, which in both cases drops for the heavier homologues and increases the stability of the cyclic dimers. The experimental values for the strain energies of $(CH_2)_4$ and $(SiH_2)_4$ amount to ca. 118 and 96 kJ·mol^{-1}, respectively.[87][88] These values are in good agreement with the results of theoretical studies, which gave values of 119 and ca. 70 kJ·mol^{-1} using ab initio methods.[89,90] Apparently, the smaller ring strain in the silicon-containing rings is partially explained by efficient π−σ* interactions.[91] The decrease of the ring strain is certainly also of some importance for the smaller increase observed in the absolute values of the dimerisation enthalpy in moving from the second to the third long period (hydrides of Ge and As).

In the case of mixed group-13/15 element compounds, the trend, as well as the absolute values, of the dimerisation enthalpies are very similar to the ones calculated for binary group-15 element hydrides. Certainly it should be noted here that the bond properties change significantly from H_2BNH_2 to H_2AlNH_2 and again to H_2GaNH_2. In this series, the ionic contributions increase. In H_2GaNH_2 the charge separation is already substantial. These ionic contributions might be responsible for the differences between the group-13/15 element compounds and the binary group-14 element compounds. The dimerisation of H_2BNH_2 is only very weakly exothermic [dimerisation enthalpy of −67.2 kJ·mol^{-1} using the CCSD(T) method and −77.3 kJ·mol^{-1} using MP2/TZVPP]. Thus, H_2BNH_2 has the smallest dimerisation enthalpy of all compounds under investigation herein, even slightly smaller than the one calculated for C_2H_4 [−75.3 kJ·mol^{-1} according to CCSD(T)]. Nevertheless, H_2BNH_2 is much more reactive than H_2CCH_2 and is stabilized only in the form of adducts (e.g., $B_2H_4{\cdot}BH_3$) or by replacement of the H atoms by halogen and/or organic groups (e.g., Cl_2BNMe_2). Otherwise, this class of compounds oligomerises [e.g., to its trimer $(B_2H_4)_3$] or polymerises rapidly.

Finally, we now proceed to the discussion of the binary group-13 element hydrides. As indicated already, the situation here is much more complicated than that for the other groups. We have already mentioned and analysed the exceptionally high dimerisation enthalpy of HBBH. Moving to Al_2H_2 brings about a great change in the geometry of the global energy-minimum isomer. The large Al−Al separation in the global energy-minimum isomer, planar and cyclic Al(μ-H)$_2$Al (D_{2h} symmetry), does not permit any significant interaction between the two atoms. The bent *trans*-HAlAlH isomer with two terminal Al−H bonds has an energy that is about 60 kJ·mol^{-1} higher than the one of the cyclic Al(μ-H)$_2$Al form. The dimerisation of Al(μ-H)$_2$Al to give tetrahedral Al_4H_4 is associated with an enthalpy change of −271.9 kJ·mol^{-1} according to the CCSD(T) method (−308.9 kJ·mol^{-1} according to MP2/TZVPP). This change is only 56% of the standard enthalpy for the dimerisation of HBBH. This value is even significantly smaller than the one calculated for dimerisation of Si_2H_4 (-353.8 kJ·mol^{-1}), but larger than the one calculated for dimerisation of H_2AlNH_2 and P_2H_2 (-236.5 and -158.3 kJ·mol^{-1}). The standard enthalpy for dimerisation of Ga_2H_2 (for which the cyclic form has been shown again to be the lowest-energy isomer) is higher by a factor of 1.57 than the one calculated for dimerisation of Al_2H_2. In summary, the behaviour of the binary group-13 element hydrides differs significantly from the one found for the hydrides of group-14 and -15 elements and for mixed group-13/15 element compounds. If only the isomers with an intact E−E bond are considered for the E_2H_2 species, the dimerisation enthalpies are found to decrease down the group (-510.0, -442.3, and -402.6 kJ·mol^{-1} for E = B, Al and Ga, respectively, see Table 1).

Conclusions

This works attempts to shed light on the differences in reactivity between binary main-group element hydrides with the potential for multiple bonding. Although the chemical reactivity gives only indirect insight into the bond properties, it has the advantage that it can be verified, at least principally, by experiments. In two previous accounts we have studied the response of the compounds towards fragmentation and hydrogenation reactions. In this work, the standard enthalpies for dimerisation were calculated. The [2+2] cycloaddition is a characteristic and important reaction of derivatives of ethylene and, therefore, the comparison of the dimerisation enthalpies should shed light on the differences in the chemistry between compounds that formally are capable of forming a "double" bond. First, the structures of the monomers and dimers were analysed applying hybrid DFT (B3LYP) and ab initio (MP2) methods. In a second step, the MP2 and the CCSD(T) methods were used to determine the dimerisation enthalpies. The trends of the dimerisation enthalpies were established, and important factors responsible for these trends discussed. The results show that a general pattern is the increase of the dimerisation enthalpy for heavier homologues, with the largest changes occurring between the first and the second long period. Although structural differences in the energy-minimum structures of the monomers and dimers have to be considered (e.g., N_4H_4 exhibits a chain-like energy-minimum structure while P_4H_4 prefers a cyclic structure), the trend generally reflects the increasing weakness of the E−E bond in the monomers for the heavier homologues as the most-dominating effect. Other effects, such as the reduced ring strain in the cyclic dimers, play a significant, but most likely not the dominating, role. The eye-catching exception from this general pattern is found in group 13. Compound HBBH exhibits an unusually high dimerisation enthalpy; in fact, it is the highest value of all dimerisation processes studied herein. Possible reasons for this high enthalpy have been discussed.

The values derived herein for the dimerisation enthalpies give useful and reliable information about the differences in the chemistry of main-group element hydrides with the potential for multiple bonding. The results show that these differences are substantial and some trends are visible.

Acknowledgments

The author gratefully acknowledges the financial support by the Deutsche Forschungsgemeinschaft and the award of a Habilitanden-Stipendium.

---

[1] M. Driess, H. Grützmacher, *Angew. Chem.* **1996**, *108*, 900; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 828.
[2] P. P. Power, *J. Chem. Soc., Dalton Trans.* **1998**, 2939.
[3] A. J. Downs, H.-J. Himmel, L. Manceron, *Polyhedron* **2002**, *21*, 473.
[4] T. Tsumuraya, S. A. Batcheller, S. Masamune, *Angew. Chem.* **1991**, *103*, 916.
[5] A. H. Cowley, *Acc. Chem. Res.* **1984**, *17*, 386.
[6] K. W. Klinkhammer, *Angew. Chem.* **1997**, *109*, 2414.
[7] A. H. Cowley, N. C. Nicholas, *Prog. Inorg. Chem.* **1986**, *34*, 1.
[8] F. G. A. Stone, R. West, (Eds.), *Advances in Organometallic Chemistry: Multiple Bonded Main Group Metals and Metalloids,* Academic, San Diego, CA, **1996**
[9] P. Jutzi, *Angew. Chem.* **2000**, *112*, 3953; *Angew. Chem. Int. Ed.* **2000**, *39*, 3797.
[10] D. E. Goldberg, D. H. Harris, M. F. Lappert, K. M. Thomas, *J. Chem. Soc., Chem. Commun.* **1976**, 261. P. J. Davidson, D. H. Harris, M. F. Lappert, *J. Chem. Soc., Dalton Trans.* **1976**, 2268. P. B. Hitchcock, M. F. Lappert, S. J. Miles, A. J. Thorne, *J. Chem. Soc., Chem. Commun.* **1984**, 480.
[11] D. E. Goldberg, D. H. Harris, M. F. Lappert, K. M. Thomas, *J. Chem. Soc., Chem. Commun.* **1976**, 261. D. E. Goldberg, P. B. Hitchcock, M. F. Lappert, K. M. Thomas, A. J. Thorne, T. Fjelberg, A. Haaland, B. E. R. Schilling, *J. Chem. Soc., Dalton Trans.* **1986**, 2387.
[12] M. Stender, A. D. Phillips, R. J. Wright, P. P. Power, *Angew. Chem. Int. Ed.* **2002**, *41*, 1785.
[13] A. D. Phillips, R. J. Wright, M. M. Olmstead, P. P. Power, *J. Am. Chem. Soc.* **2002**, *124*, 5930.
[14] R. T. Paine, H. Nöth, *Chem. Rev.* **1995**, *95*, 343.
[15] P. Paetzold, *Adv. Inorg. Chem.* **1987**, *31*, 123.
[16] A. J. Downs (Ed.), *Chemistry of Aluminium, Gallium, Indium and Thallium*, Blackie, Glasgow, U.K., **1993**.
[17] K. Knabel, I. Krossing, H. Nöth, H. Schwenk-Kirchner, M. Schmidt-Amelunxen, T. Seifert, *Eur. J. Inorg. Chem.* **1998**, 1095.
[18] P. P. Power, *Chem. Rev.* **1999**, *99*, 3463.
[19] [19a] H.-J. Himmel, A. J. Downs, T. M. Greene, *Chem. Commun.* **2000**, 871. [19b] H.-J. Himmel, A. J. Downs, T. M. Greene, *J. Am. Chem. Soc.* **2000**, *122*, 9793.
[20] J. Su, X. W. Li, R. C. Crittendon, G. H. Robinson, *J. Am. Chem. Soc.* **1997**, *119*, 5471.
[21] Y. Xie, H. F. Schaefer, III, G. H. Robinson, *Chem. Phys. Lett.* **2000**, *317*, 174.
[22] F. A. Cotton, A. H. Cowley, X. Feng, *J. Am. Chem. Soc.* **1998**, *120*, 1795. M. M. Olmstead, R. S. Simons, P. P. Power, *J. Am. Chem. Soc.* **1997**, *119*, 11705. T. L. Allen, W. H. Fink, P. P. Power, *J. Chem. Soc., Dalton Trans.* **2000**, 407.
[23] J. Grunenberg, N. Goldberg, *J. Am. Chem. Soc.* **2000**, *122*, 6045.
[24] A. J. Bridgeman, L. R. Ireland, *Polyhedron* **2001**, *20*, 2841.
[25] N. J. Hardman, R. J. Wright, A. D. Phillips, P. P. Power, *Angew. Chem.* **2002**, *114*, 2966.
[26] P. Pullumbi, C. Mijoule, L. Manceron, Y. Bouteiller, *Chem. Phys.* **1994**, *185*, 13.
[27] R. J. Wright, A. D. Phillips, N. J. Hardman, P. P. Power, *J. Am. Chem. Soc.* **2002**, *124*, 8538.
[28] H.-J. Himmel, H. Schnöckel, *Chem. Eur. J.* **2002**, *8*, 2397.
[29] N. Takagi, M. W. Schmidt, S. Nagase, *Organometallics* **2001**, *20*, 1646.
[30] H.-J. Himmel, H. Schnöckel, *Chem. Eur. J.*, **2003**, *9*, 748.

[31] P. C. Andrews, C. L. Raston, B. W. Skelton, V.-A. Tolhurst, A. H. White, *Chem. Commun.* **1998**, 575.

[32] L. E. Gusel′nikov, V. G. Avakyan, S. L. Guselnikov, *J. Am. Chem. Soc.* **2002**, *124*, 662.

[33] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Lui, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle and J. A. Pople, *Gaussian 98*, Revision A.3, Gaussian Inc., Pittsburgh PA, **1998**.

[34] R. Ahlrichs, M. Bär, M. Häser, H. Horn, C. Kölmel, *Chem. Phys. Lett.* **1989**, *162*, 165. K. Eichkorn, O. Treutler, H. Öhm, M. Häser, R. Ahlrichs, *Chem. Phys. Lett.* **1995**, *240*, 283. K. Eichkorn, O. Treutler, H. Öhm, M. Häser, R. Ahlrichs, *Chem. Phys. Lett.* **1995**, *242*, 652. K. Eichkorn, F. Weigend, O. Treutler, R. Ahlrichs, *Theor. Chem. Acc.* **1997**, *97*, 119. F. Weigend, M. Häser, *Theor. Chem. Acc.* **1997**, *97*, 331. F. Weigend, M. Häser, H. Patzelt, R. Ahlrichs, *Chem. Phys. Lett.* **1998**, *294*, 143.

[35] H.-J. Himmel, L. Manceron, A. J. Downs, P. Pullumbi, *Angew. Chem.* **2002**, *41*, 796; *Angew. Chem. Int. Ed.* **2002**, *114*, 829.

[36] H.-J. Himmel, L. Manceron, A. J. Downs, P. Pullumbi, *J. Am. Chem. Soc.* **2002**, *124*, 4448.

[37] R. Ahlrichs, P. Scharf, C. Ehrhardt, *J. Chem. Phys.* **1985**, *82*, 890. D. J. Swanton, R. Ahlrichs, *Theoret. Chim. Acta* **1989**, *75*, 163.

[38] M. Atoji, W. N. Lipscomb, *Acta Crystallogr.* **1953**, *6*, 547.

[39] C. Dohmeier, C. Robl, M. Tacke, H. Schnöckel, *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 564.

[40] A. Purath, C. Dohmeier, A. Ecker, H. Schnöckel, *Organometallics* **1998**, *17*, 1894.

[41] A. Purath, C. Dohmeier, A. Ecker, H. Schnöckel, *J. Organomet. Chem.* **1999**, *579*, 373.

[42] R. Ahlrichs, M. Ehrig, H. Horn, *Chem. Phys. Lett.* **1991**, *183*, 227.

[43] M. Mocker, C. Robl, H. Schnöckel, *Angew. Chem.* **1994**, *106*, 1860; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1754.

[44] A. Schnepf, R. Köppe, H. Schnöckel, *Angew. Chem. Int. Ed.* **2001**, *40*, 1241.

[45] W. Uhl, W. Hiller, M. Layh, W. Schwarz, *Angew. Chem.* **1992**, *104*, 1378.

[46] L. B. Knight, Jr., K. Kerr, P. K. Miller, C. A. Arrington, *J. Phys. Chem.* **1995**, *99*, 16842. T. Tague Jr., L. Andrews, *J. Am. Chem. Soc.* **1994**, *116*, 4970.

[47] G. V. Chertihin, L. Andrews, *J. Phys. Chem.* **1993**, *97*, 10295. J. C. Stephens, E. E. Bolton, H. F. Schaefer, III., L. Andrews, *J. Chem. Phys.* **1997**, *107*, 119.

[48] G. Treboux, J.-C. Barthelat, *J. Am. Chem. Soc.* **1993**, *116*, 11922.

[49] Z. Palágyi, R. S. Grev, H. F. Schaefer, III, *J. Am. Chem. Soc.* **1993**, *115*, 1936.

[50] See, for example: R. S. Grev, H. F. Schaefer, III, *J. Am. Chem. Soc.* **1987**, *109*, 6569.

[51] A. F. Sax, *Chem. Phys. Lett.* **1986**, *127*, 163.

[52] H. Matsumoto, M. Minemura, K. Takatsuma, Y. Nagai, M. Goto, *Chem. Lett.* **1985**, 1005.

[53] C. Kratky, H.-G. Schster, E. Hengge, *J. Organomet. Chem.* **1983**, *247*, 253.

[54] Y.-S. Chen, P. P. Gaspar, *Organometallics* **1982**, *1*, 1410.

[55] J. Rubio, F. Illas, *THEOCHEM* **1984**, *19*, 131.

[56] W. W. Schöller, T. Dabisch, *Inorg. Chem.* **1987**, *26*, 1081.

[57] M. W. Schmidt, P. N. Truong, M. S. Gordon, *J. Am. Chem. Soc.* **1987**, *109*, 5217.

[58] M. J. Fink, M. J. Michalczyk, K. J. Haller, R. West, J. Michl, *J. Chem. Soc., Chem. Commun.* **1983**, 1010.

[59] G. Trinquier, J.-P. Malrieu, P. Rivière, *J. Am. Chem. Soc.* **1982**, *104*, 4529. T. L. Windus, M. S. Gordon, *J. Am. Chem. Soc.* **1992**, *114*, 9559.

[60] P. Bleckmann, R. Minkwitz, W. P. Neumann, M. Schriewer, M. Thibud, B. Watta, *Tetrahedron Lett.* **1984**, *25*, 2467.

[61] A. Márquez, G. G. Gonzàlez, J. F. Sanz, *Chem. Phys.* **1989**, *138*, 99. G. Trinquier, *J. Am. Chem. Soc.* **1990**, *112*, 2130.

[62] N. Wiberg, H. Bayer, H. Bachhuber, *Angew. Chem.* **1975**, *87*, 202. J. Kroner, N. Wiberg, H. Bayer, *Angew. Chem.* **1975**, *87*, 203.

[63] M. Veith, G. Schlemmer, *Z. Anorg. Allg. Chem.* **1982**, *494*, 7.

[64] M. N. Glukhovtsev, R. D. Bach, S. Laiter, *Int. J. Quantum Chem.* **1997**, *62*, 373.

[65] W. W. Schoeller, C. Begemann, U. Tubbesing, J. Strutwolf, *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 2957.

[66] A. H. Cowley, *Polyhedron* **1984**, *3*, 389.

[67] S. Nagase, S. Suzuki, T. Kurakake, *J. Chem. Soc., Chem. Commun.* **1990**, 1724.

[68] A. H. Cowley, J. G. Lasch, N. C. Norman, M. Pakulski, *J. Am. Chem. Soc.* **1983**, *103*, 5506.

[69] P. L. Baxter, A. J. Downs, D. W. H. Rankin, H. E. Robertson, *J. Chem. Soc., Dalton Trans.* **1985**, 807.

[70] B. Luo, W. L. Gladfelter, *Chem. Commun.* **2000**, 825.

[71] A. Y. Timoshkin, H. F. Bettinger, H. F. Schaefer, III, *J. Phys. Chem. A* **2001**, *105*, 3249.

[72] L. Grocholl, S. A. Cullison, J. Wang, D. C. Swenson, E. G. Gillan, *Inorg. Chem.* **2002**, *41*, 2920.

[73] See, for example: [73a] J. W. Hwang, S. A. Hanson, D. Britton, J. F. Evans, K. F. Jensen, W. L. Gladfelter, *Chem. Mat.* **1990**, *2*, 342. [73b] J. F. Janik, R. L. Wells, *Inorg. Chem.* **1997**, *36*, 4135. [73c] J. A. Jegier, S. McKernan, A. P. Purdy, W. L. Gladfelter, *Chem. Mat.* **2000**, *12*, 1003.

[74] Y. Kim, J. H. Kim, J. E. Park, H. Song, J. T. Park, *J. Organomet. Chem.* **1997**, *545−546*, 99.

[75] M. Sugie, H. Takeo, C. Matsumura, *J. Mol. Spectrosc.* **1987**, *123*, 286.

[76] J. D. Carpenter, B. S. Ault, *J. Phys. Chem.* **1991**, *95*, 3502.

[77] H.-J. Himmel, A. J. Downs, T. M. Greene, *J. Chem. Soc., Dalton Trans.* **2001**, *5*, 535.

[78] M. D. Allendorf, C. F. Melius, *J. Phys. Chem. A* **1997**, *101*, 2670.

[79] T. M. Gilbert, *Organometallics* **1998**, *17*, 5513.

[80] T. P. Hamilton, A. W. Shaikh, *Inorg. Chem.* **1997**, *36*, 754.

[81] R. D. Davy, K. L. Jaffrey, *J. Phys. Chem.* **1994**, *98*, 8930.

[82] R. D. Davy, H. F. Schaefer, III, *Inorg. Chem.* **1998**, *37*, 2291.

[83] A. Y. Timoshkin, H. F. Bettinger, H. F. Schaefer III, *J. Phys. Chem. A* **2001**, *105*, 3249.

[84] R. D. Davy, K. L. Jaffrey, *J. Phys. Chem.* **1994**, *98*, 8930.

[85] S. G. Lias, J. E. Bartmess, J. F. Liebman, J. L. Holmes, R. D. Levin, W. G. Mallard, *J. Phys. Chem. ref. Data (Suppl. 1)* **1988**, *17*.

[86] W. Kutzelnigg, *Angew. Chem.* **1984**, *96*, 262; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 272.

[87] H. Schiffer, R. Ahlrichs, M. Häser, *Theor. Chim. Acta* **1989**, *75*, 1.

[88] P. George, M. Trachtman, A. M. Brett, C. W. Bock, *J. Chem. Soc., Perkin Trans. 2* **1977**, 1036. P. George, M. Trachtman, C. W. Bock, A. M. Brett, *Perkin Trans. 2* **1976**, 1222. P. George, M. Trachtman, C. W. Bock, A. M. Brett, *Tetrahedron* **1976**, *32*, 317.

[89] H. Watanabe, H. Shimoyama, T. Muraoka, T. Okawa, M. Kato, Y. Nagai, *Chem. Lett.* **1986**, 1057.

[90] See, for example: M. Zhao, B. M. Gimarc, *Inorg. Chem.* **1996**, *35*, 5378.

[91] R. S. Grev, H. F. Schaefer, III, *J. Am. Chem. Soc.* **1987**, *109*, 6569.

[92] Y. Naruse, J. Ma, S. Inagaki, *Tetrahedron Lett.* **2001**, *42*, 6553.

Received November 18, 2002