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# Theoretical Studies of $[MYR_2]_n$ Isomers ($M = B, Al, Ga; Y = N, P, As; R = H, CH_3$): Structures and Energetics of Monomeric and Dimeric Compounds ($n = 1, 2$)[†]

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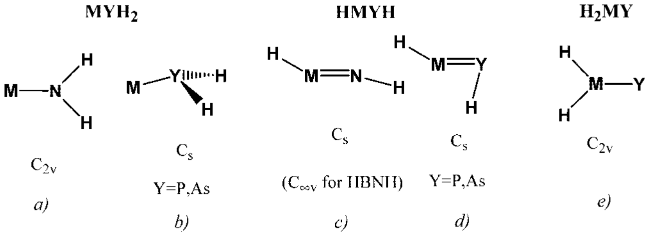
A series of group 13-15 compounds of the general formula $[MYR_2]_n$ ($M = B, Al, Ga; Y = N, P, As; n = 1, 2; R = H, CH_3$) have been theoretically studied at the B3LYP/TZVP level of theory. The stability of different isomer structures is discussed to reveal the competitiveness of group 13-13, group 13-15, and group 15-15 bonding. Preferential bonding patterns and trends in the stability with respect to M and Y are also discussed. For the dimeric compounds, $C_{2v}$ symmetric $[HMYH]_2$ rings are the lowest in energy, with the single exception of $Ga_2N_2H_4$, for which a somewhat unexpectedly $C_{2v}$ symmetric $[GaNH_2]_2$ ring is found to be the energy minimum, followed by the planar $H_2NGaGaNH_2$ chain. The higher stability of the $GaNH_2$ bonding pattern in oligomer compounds may be rationalized in terms of the increasing stability of the oxidation state I as compared to that for the boron and aluminum analogues. Methylation significantly reduces the energetic differences between monomeric $MYMe_2$ MeMYMe, and $Me_2MY$, isomers, especially for the AlP, AlAs, and GaAs systems, thus allowing a variety of structural types to be competitive in energy.

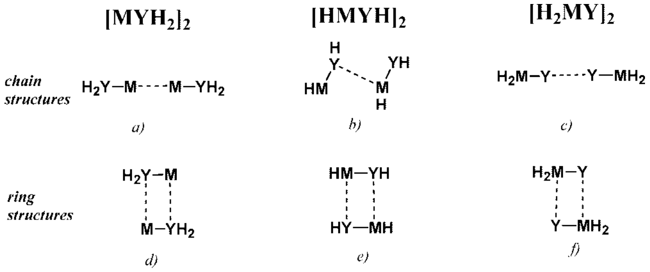
## Introduction

In the past decade, group 13-15 imido compounds $[RMNR']_n$ and their heavier analogues have attracted considerable attention as precursors to 13-15 binary and composite materials.[1−3] Recently, 13-15 hydride compounds have been examined as candidates for the hydrogen storage materials.[4] The majority of the experimentally known imido metallanes exist as oligomers that have coordination number four for all metal and pnictogen centers and form cage structures.[5] In particular, tetramers adopt cubane type structures. Rare examples of monomeric imido metallanes have been synthesized using very bulky protective groups.[6,7] In contrast to group 13 metals, the analogous boron-containing compounds prefer ring structures with coordination number 3 on the boron and nitrogen centers.[8,9] There is experimental evidence[10−12] for the existence of valence isomers of imido metallanes of $MYH_2$ composition. The photoactivated reaction of Al, Ga, and In atoms condensed with ammonia[10] and phosphine[11] in argon matrices results, among other products, in the identification of $MNH_2$ monomers, while no $MPH_2$ and HMYH species were observed. Matrix isolation IR spectra in solid argon showed that upon reaction of laser-ablated aluminum, gallium, and indium atoms with ammonia, major products formed are $HAlNH_2$ and $AlNH_2$; bent HAlNH molecules were identified only as a minor product.[12] In contrast, the formation of $CH_3BNCH_3$, $CH_3BNH$, and $HBNCH_3$ following the reaction of boron atoms with methylamines was identified by matrix isolation IR spectra.[13−15] Low valent element 13 species are believed to be important intermediates in CVD processes at high temperatures.[16] According to the GaN MOCVD simulation model of Cavallotti,[17] monomeric $GaNH_2$ contributes more than 50% to the overall GaN film growth rate from trimethylgallium and ammonia.

**SCHEME 1: Qualitative Structures of the Monomer Compounds Studied in the Present Work**



**SCHEME 2: Formation of Chain and Ring Structures of the Dimeric Compounds Considered in the Present Research**



Theoretical studies indicate that monomeric imido HM=NH isomers are 178 (Al), 189 (Ga), and 258 (In) kJ mol$^{-1}$ less stable than the corresponding amides $MNH_2$.[18] Imido MeGa=NMe (Ga in formal oxidation state III) lies 144 kJ mol$^{-1}$ higher in energy as compared to the $GaNMe_2$ isomer (Ga in formal oxidation state I).[19] The first stable monomeric $Ga^I$ amide was

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**TABLE 1: Selected Structural Parameters for Monomer Compounds of $MYH_2$ Composition[a]**

| | $MYH_2$, singlet | | HMYH, singlet | | | | $H_2MY$, triplet | |
|---|---|---|---|---|---|---|---|---|
| M, Y | $C_{2v}$ | $C_s$ | $C_{\infty v}$ | $C_s$ | ∠HMY | ∠MYH | $C_{2v}$ | method |
| BN | 1.376 | $\rightarrow C_{2v}$ | 1.235 | $\rightarrow C_{\infty v}$ | 180.0 | 180.0 | 1.449 | B3LYP/TZVP |
| BN | 1.380 | | | | | | | BP86/TZP[31] |
| BP | (1.912)[b] | 1.962 | (1.638)[c] | 1.697 | 177.2 | 52.7 | 1.848 | B3LYP/TZVP |
| BP | | | (1.651)[c] | 1.707 | 176.5 | 52.6 | | CCSD(T)/aug-cc-pVTZ[46] |
| BP | | 1.986 | | 1.718 | 176.0 | 52.9 | | CCSD(T)/DZP[48] |
| BAs | (2.015)[b] | 2.096 | (1.718)[c] | 1.800 | 179.5 | 46.6 | 2.015 | B3LYP/TZVP |
| AlN | 1.820 | $\rightarrow C_{2v}$ | (1.624)[c] | 1.637 | 166.8 | 159.7 | 1.801 | B3LYP/TZVP |
| AlN | | | (1.631)[c] | 1.658 | 161.4 | 147.2 | | CCSD(T)/aug-cc-pVTZ[46] |
| AlN | 1.803 | | | 1.633 | 165.2 | 154.5 | | CCSD/TZ2P[50] |
| AlN | 1.80 | | | 1.66 | 161.9 | 147.5 | | MP2/D95*[12] |
| AlP | (2.369)[b] | 2.446 | (2.017)[c] | 2.152 | 179.3 | 80.2 | 2.268 | B3LYP/TZVP |
| AlP | | 2.424 | | 2.149 | 177.0 | 76.4 | 2.346 | CCSD/TZ2P[61] |
| AlP | | | (2.032)[c] | 2.159 | 180.0 | 78.0 | | CCSD(T)/aug-cc-pVTZ[46] |
| AlAs | (2.456)[b] | 2.562 | (2.092)[c] | 2.242 | 174.6 | 73.4 | 2.452 | B3LYP/TZVP |
| GaN | 1.893 | $\rightarrow C_{2v}$ | (1.646)[c] | 1.705 | 161.2 | 123.6 | 1.940 | B3LYP/TZVP |
| GaP | (2.406)[b] | 2.483 | (2.014)[c] | 2.149 | 177.8 | 85.0 | 2.284 | B3LYP/TZVP |
| GaP | | 2.479 | | 2.145 | 177.7 | 85.1 | 2.222 | B3LYP/6−311++G(d,p)[66] |
| GaP | | 2.449 | | 2.148 | 180.0 | 82.3 | 2.253 | MP2/6−311++G(d,p)[66] |
| GaAs | (2.491)[b] | 2.596 | (2.092)[c] | 2.245 | 179.8 | 81.6 | 2.442 | B3LYP/TZVP |

[a] MY bond distances are in angstroms, and angles are in degrees. B3LYP/TZVP level of theory. [b] Transition state. [c] Stationary point of Hessian index 2.

**TABLE 2: Selected Structural Parameters for Monomer Compounds of $MYMe_2$ Composition[a]**

| | $MYMe_2$, singlet | | MeMYMe, singlet | | | | $Me_2MY$, triplet | |
|---|---|---|---|---|---|---|---|---|
| M, Y | $C_{2v}$ | $C_s$ | $C_{3v}$ | $C_s$ | ∠CMY | ∠MYC | $C_{2v}$ | method |
| BN | 1.376 | $\rightarrow C_{2v}$ | 1.241 | $\rightarrow C_{3v}$ | 180.0 | 180.0 | 1.470 | B3LYP/TZVP |
| BN | 1.39 | | 1.26 | | 180.0 | 180.0 | | MP2/D95*[13] |
| BN | | | | | | | 1.485 | MP2/6-311+G(d,p)[37,38] |
| BP | (1.888)[b] | 1.945 | (1.643)[c] | 1.735 | 173.4 | 99.9 | 1.941 | B3LYP/TZVP |
| BAs | (1.998)[b] | 2.073 | (1.727)[c] | 1.843 | 174.5 | 95.7 | 2.058 | B3LYP/TZVP |
| AlN | 1.829 | $\rightarrow C_{2v}$ | 1.630 | $\rightarrow C_{3v}$ | 180.0 | 180.0 | 1.811 | B3LYP/TZVP |
| AlN | | | | | | | 1.903 | MP2/6-311+G(d,p)[37,38] |
| AlP | (2.349)[b] | 2.431 | (2.020)[c] | 2.170 | 165.4 | 106.9 | 2.369 | B3LYP/TZVP |
| AlAs | (2.442)[b] | 2.543 | (2.098)[c] | 2.271 | 169.8 | 101.5 | 2.468 | B3LYP/TZVP |
| GaN | 1.904 | $\rightarrow C_{2v}$ | (1.654)[c] | 1.696 | 155.9 | 145.0 | 1.952 | B3LYP/TZVP |
| GaN | | | | | | | 1.974 | MP2/6-311+G(d,p)[37,38] |
| GaP | (2.387)[b] | 2.474 | (2.020)[c] | 2.166 | 168.5 | 104.2 | 2.365 | B3LYP/TZVP |
| GaAs | (2.477)[b] | 2.575 | (2.101)[c] | 2.265 | 171.9 | 100.0 | 2.462 | B3LYP/TZVP |

[a] MY bond distances are in angstroms, and angles are in degrees. B3LYP/TZVP level of theory. [b] Transition state. [c] Stationary point of Hessian index 2.

synthesized in 2006 by Power's group.[19] There is also experimental evidence for the existence of oligomeric $[MYR_2]_n$ species.

The synthesis and structural characterization of aluminum−nitrogen-bonded tetramer $Al_4(N(SiMe_3)2,6\text{-}^iPr_2C_6H_3)_4$ (**1**) was reported in 2003 by Roesky.[20] The structure consists of a tetrahedral (with almost perfect 60° angles) $Al_4$ core with four amino groups $N(SiMe_3)2,6\text{-}^iPr_2C_6H_3$ coordinated to aluminum as terminal ligands. From one perspective, this compound is an analogue of the well-known group 13 M(I) species[21] $Al_4L_4$, such as $(AlCp^*)_4$, where the substituent L is the NRR′ group. Alternatively, (**1**) may be considered as an isomer of the imido $[RAlNR']_4$ cubic tetramer cages $[(2,6\text{-}^iPr_2C_6H_3)AlN(SiMe_3)]_4$ or $[(SiMe_3)AlN(2,6\text{-}^iPr_2C_6H_3)]_4$, analogues of which are well-known experimentally.[5] Earlier, the compound $Al_4(Cp^*)_3(NRR')$, with only one Cp* ligand substituted for the amino group, was reported.[22] A similar attachment of the NRR′ ligands to the aluminum cluster core was demonstrated for the $Al_{77}(NR_2)_{20}{}^{2-}$ cluster by Schnöckel.[23] It is also noteworthy that the molecular peak of Roesky's compound (**1**) was observed in electron ionization mass spectra, while under similar conditions the analogous $Al_4Cp^*_4$ compound is monomeric.

The above experimental observations point to a higher stability for the metal−metal core in NRR′ substituted compounds. Complexes containing direct group 13-13 element donor−acceptor bonds have been prepared in the laboratory and structurally characterized.[24] It was theoretically predicted[25] with Frenking that the donor−acceptor bond dissociation energy of $Cl_3B\text{-}BCp^*$ (224 kJ mol$^{-1}$) is even greater than the dissociation energy of $Cl_3Al\text{-}NMe_3$ (199 ± 8 kJ mol$^{-1}$), which has been considered to be the most stable experimentally synthesized donor−acceptor complex of main group elements.[26] Therefore, it appears that donor−acceptor bonds formed by group 13-13 elements may be energetically comparable to those of group 13-15 elements. Knowledge of the preferential bonding patterns is of fundamental importance for the construction of the precursors for 13-15 CVD and for designing new materials for hydrogen storage.

Although some of the possible monomeric, dimeric, or tetrameric structures for B−N,[9,13,27−45] B−P,[46−48] Al−N,[12,35,37,38,46,49−60] Al−P,[11,46,49,57,61,62] Al−As,[49,57] Ga−N,[37,38,49,54−58,63−65] Ga−P,[11,49,57,66,67] and Ga−As[49,57,68] systems have been studied before theoretically, there are no systematic theoretical studies on the concurrence between 13 and 15 and 13-13 bonded oligomers. To address this problem in a systematic way, a theoretical study of the series of compounds with formal composition $[MYR_2]_n$ (M = B, Al, Ga; Y = N, P, As; R = H, $CH_3$), which can be considered as built up from the $n$ $MYR_2$ monomer units, has

**TABLE 3: Relative Energies *E* (kJ mol$^{-1}$, 0 K, without ZPE Corrections) of the Different $MYH_2$ Isomers[a]**

| | $MYH_2$, singlet | | HMYH, singlet | | $H_2MY$, triplet | |
|---|---|---|---|---|---|---|
| M, Y | $C_{2v}$ | $C_s$ | $C_{\infty v}$ | $C_s$ | $C_{2v}$ | method |
| BN | 173.5 | $\rightarrow C_{2v}$ | 0.0 | $\rightarrow C_{\infty v}$ | 355.0 | B3LYP/TZVP |
| BP | (265.7)[b] | 219.3 | (117.3)[c] | 0.0 | 211.5 | B3LYP/TZVP |
| BP | | 218.4 | | 0.0 | 57.2 | MP4SDTQ/6-31G**//HF/6-31G*[47] |
| BP | | 200.4 | | 0.0 | | CCSD(T)/DZP[48] |
| | | | (118.9)[c] | 0.0 | | CBS [CCSD(T)/aug-ccpVTZ][46] |
| BAs | (290.7)[b] | 234.4 | (149.5)[c] | 0.0 | 40.9 | B3LYP/TZVP |
| AlN | 0.0 | $\rightarrow C_{2v}$ | (183.1)[c] | 183.0 | 462.2 | B3LYP/TZVP |
| AlN | 0.0 | | (185.5)[d] | 184.7 | | CCSD/TZ2P[50] |
| | 0.0 | | | 247.7 | | MP2/D95*[12] |
| | | | (0) | 0.0 | | CBS [CCSD(T)/aug-ccpVTZ][46] |
| AlP | (30.9)[b] | 0.0 | (162.7)[c] | 47.5 | 238.7 | B3LYP/TZVP |
| | | 0.0 | | 54.4 | 92.0 | CCSD/TZ2P[61] |
| | | | (114.0)[c] | 0.0 | | CBS [CCSD(T)/aug-ccpVTZ][46] |
| AlAs | (42.3)[b] | 0.0 | (165.8)[c] | 23.5 | 68.6 | B3LYP/TZVP |
| GaN | 0.0 | $\rightarrow C_{2v}$ | (231.5)[c] | 211.2 | 422.5 | B3LYP/TZVP |
| GaP | (33.9)[b] | 0.0 | (223.4)[c] | 74.0 | 300.0 | B3LYP/TZVP |
| GaP | | 0.0 | | 72.0 | 246.5 | B3LYP/6-311++G(d,p)[66] |
| GaP | | 0.0 | | 59.6 | 260.0 | MP2/6-311++G(d,p)[66] |
| GaAs | (44.7)[b] | 0.0 | (229.6)[c] | 52.6 | 127.2 | B3LYP/TZVP |

[a] B3LYP/TZVP level of theory. Structures are minima on their potential energy surfaces, unless noted otherwise. [b] Transition state. [c] Stationary point of Hessian index 2. [d] Saddle point.

**TABLE 4: Relative Energies *E* (kJ mol$^{-1}$, 0 K, without ZPE Corrections) of the Different $MYMe_2$ Isomers[a]**

| | $MYMe_2$, singlet | | MeMYMe, singlet | | $Me_2MY$, triplet | |
|---|---|---|---|---|---|---|
| M, Y | $C_{2v}$ | $C_s$ | $C_{3v}$ | $C_s$ | $C_{2v}$ | method |
| BN | 260.4 | $\rightarrow C_{2v}$ | 0.0 | $\rightarrow C_{3v}$ | 287.0 | B3LYP/TZVP |
| BN | 228.8 | $\rightarrow C_{2v}$ | 0.0 | $\rightarrow C_{3v}$ | | MP2/D95*[13] |
| BP | (272.4)[b] | 249.5 | (91.5)[c] | 0.0 | 27.2 | B3LYP/TZVP |
| BAs | (315.2)[b] | 276.4 | (137.5)[c] | 18.6 | 0.0 | B3LYP/TZVP |
| AlN | 0.0 | $\rightarrow C_{2v}$ | 92.6 | $\rightarrow C_{3v}$ | 301.5 | B3LYP/TZVP |
| AlP | (8.7)[b] | 0.0 | (101.1)[c] | 14.8 | 26.5 | B3LYP/TZVP |
| AlAs | (48.3)[b] | 24.4 | (129.9)[c] | 14.4 | 0.0 | B3LYP/TZVP |
| GaN | 0.0 | $\rightarrow C_{2v}$ | (155.0)[c] | 145.2 | 288.6 | B3LYP/TZVP |
| GaP | (11.3)[b] | 0.0 | (170.2)[c] | 46.1 | 105.3 | B3LYP/TZVP |
| GaAs | (24.6)[b] | 0.0 | (175.7)[c] | 22.0 | 54.2 | B3LYP/TZVP |

[a] B3LYP/TZVP level of theory. Structures are minima on PES, unless noted otherwise. [b] Transition state. [c] Stationary point of Hessian index 2.

been undertaken. In the present research, we address from a systematic theoretical perspective the relative stabilities of monomeric and group 13-13, 13-15, and 15-15 element bonded dimeric chain and ring compounds. A qualitative representation of the structures examined is given in Schemes 1 and 2.

## Computational Details

All structures were fully optimized and verified with subsequent vibrational analyses to be minima on their respective potential energy surfaces (PES). Density functional theory in the form of the hybrid B3LYP functional[69,70] was used together with the all-electron triple-ζ quality TZV basis set of Ahlrichs, augmented by d type polarization functions (TZVP).[71,72] For H, the standard 6-311G** basis set was employed. The Gaussian 94 suite of programs[73] was used throughout. Previously, this level of theory was successfully used with Frenking to study "true inorganic heterocycles" and their dimers.[49] As shown in our 2004 report on $[HAlYH]_n$ oligomers (Y = N, P; $n = 1-4$),[57] results from the B3LYP level of theory give quite satisfactory agreement with those obtained at the CCSD(T)/cc-pVTZ level.

## Results and Discussion

**Monomer Compounds.** For the monomeric compounds, three structural types may be considered, with the group 13 element having zero, one, or two nongroup 15 substituents: $MYH_2$, HMYH, and $H_2MY$. The structures of these compounds are summarized in Scheme 1.

Experimental observations of the monomer compounds of $MYR_2$ composition (M = B, Al, Ga; Y = N, P, As; R = H, halogen, organic radical) are scarce. Most of the isolated and structurally characterized compounds have bulky protecting groups (for known examples, see reviews in refs 5 and 8). Reactions of laser-ablated boron atoms with ammonia and methylamines have been studied,[13−15] and the formation of $CH_3BNCH_3$, $CH_3BNH$, and $HBNCH_3$ has been identified by matrix isolation IR spectra. The photoactivated reactions of Al, Ga, and In atoms condensed with ammonia[10] and phosphine[11] in argon matrices resulted, among other products, in the identification of $MNH_2$ monomers, while no $MPH_2$ and HMYH species were observed. Bent HAlNH molecules were identified as a minor product by matrix isolation IR spectra in solid argon; the observed major products are $HAlNH_2$ and $AlNH_2$.[12]

There is some prior theoretical work on the monomer compounds. Enthalpies of formation of the linear monomers HBNH and MeBNMe were predicted by Sana, Leroy, and Wilante[42] at the MP4(SDTQ)/6-311++G(3df,2p)//MP2(full)/6-31G(d,p) level of theory. For $^1\Sigma^+$ HBNH, their theoretical bond dissociation energy (BDE) is 778 kJ mol$^{-1}$, and for

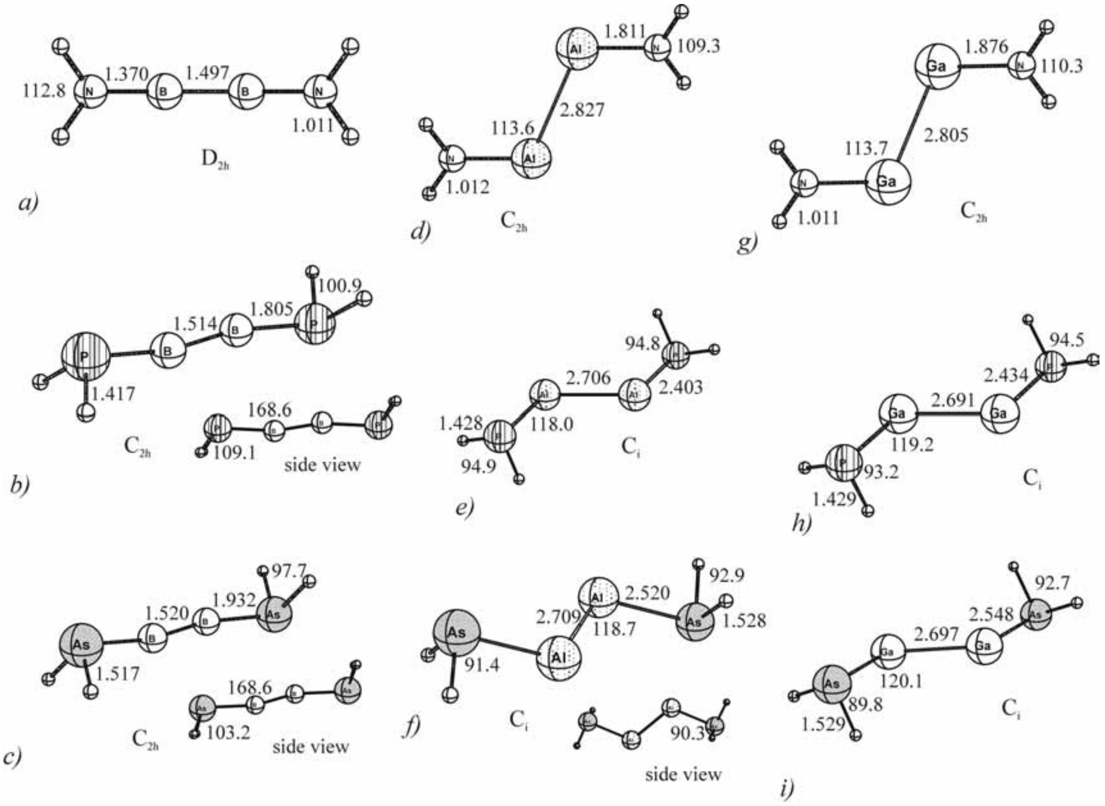


**Figure 1.** Optimized structures for chain isomers of the $H_2MYYMH_2$ dimeric compounds. (a) $H_2NBBNH_2$, (b) $H_2PBBPH_2$, (c) $H_2AsBBAsH_2$, (d) $H_2NAlAlNH_2$, (e) $H_2PAlAlPH_2$, (f) $H_2AsAlAlAsH_2$, (g) $H_2NGaGaNH_2$, (h) $H_2PGaGaPH_2$, and (i) $H_2AsGaGaAsH_2$. All distances are in angstroms, and angles are in degrees. B3LYP/TZVP level of theory.

**TABLE 5: Selected Bond Distances (in Angstroms) for the Chain $[R_2YMMYR_2]$ Isomers and Dissociation Energies into $MYR_2$ Monomers (kJ $mol^{-1}$)[a]**

| compound | point group | MY | MM | $E^{diss}$ |
|---|---|---|---|---|
| $H_2NBBNH_2$ | $D_{2h}$ | 1.370 | 1.497 | 295.6 |
| $Me_2NBBNMe_2$ | $D_{2h}$ | 1.369 | 1.495 | 292.8 |
| $H_2PBBPH_2$ | $C_{2h}$ | 1.805 | 1.514 | 447.3 |
| $Me_2PBBPMe_2$ | $C_{2h}$ | 1.781 | 1.509 | 485.3 |
| $H_2AsBBAsH_2$ | $C_{2h}$ | 1.932 | 1.520 | 424.1 |
| $Me_2AsBBAsMe_2$ | $C_{2h}$ | 1.910 | 1.517 | 448.9 |
| $H_2NAlAlNH_2$ | $C_{2h}$ | 1.811 | 2.872 | 29.5 |
| $Me_2NAlAlNMe_2$ | $C_{2h}$ | 1.820 | 2.850 | 24.5 |
| $H_2PAlAlPH_2$ | $C_i$ | 2.403 | 2.706 | 53.7 |
| $Me_2PAlAlPMe_2$ | $C_i$ | 2.366 | 2.647 | 68.8 |
| $H_2AsAlAlAsH_2$ | $C_i$ | 2.520 | 2.709 | 54.3 |
| $Me_2AsAlAlAsMe_2$ | $C_i$ | 2.504 | 2.666 | 62.1 |
| $H_2NGaGaNH_2$ | $C_{2h}$ | 1.876 | 2.805 | 20.4 |
| $Me_2NGaGaNMe_2$ | $C_{2h}$ | 1.888 | 2.841 | 16.1 |
| $H_2PGaGaPH_2$ | $C_i$ | 2.434 | 2.691 | 41.8 |
| $Me_2PGaGaPMe_2$ | $C_i$ | 2.406 | 2.623 | 57.3 |
| $H_2AsGaGaAsH_2$ | $C_i$ | 2.548 | 2.697 | 42.7 |
| $Me_2AsGaGaAsMe_2$ | $C_i$ | 2.534 | 2.644 | 55.2 |

[a] B3LYP/TZVP level of theory.

MeBNH, it is 929 kJ $mol^{-1}$. Singlet and triplet structures for $(CH_3)_2MN$ (M = B, Al, Ga) have been considered by Hayashi et al. at the MP2/6-311G+(d,p) level of theory.[37,38] Open shell singlet $(CH_3)_2MN$ states were predicted to lie 43 (M = B) and 75 kJ $mol^{-1}$ (M = Al, Ga) higher in energy than the triplet global minima. Gilbert's NBO analysis[35] showed that both MeBNMe and MeAlNMe have M−N triple bonds composed of one $\sigma$ bond and two $\pi$ bonds. In each case, the $\sigma$ bond is nearly an sp hybrid ($sp^{1.3}$ B, $sp^{0.7}$ N/$sp^{1.2}$ Al, and $sp^{0.9}$ N). The electronic structure of $BNH_2$ and $BN(CH_3)_2$ molecules and their complexes with transition metal carbonyls was discussed by Ehlers, Baerends, Bickelhaup, and Radius.[38]

The structures and energetics of $BPH_2$ isomers were considered in a 1989 study at the MP4SDTQ/6-31G**2//HF/6-31G* level of theory by Kerins, Fitzpatrick, and Nguyen.[47] They found the singlet state of HBPH to be the global minimum and $H_2BP$ to be the lowest lying isomer on the triplet potential energy surface. A reinvestigation of these isomers at CCSD(T)/DZP level of theory was performed in 1996 by Watts and Zant.[48] No hydrogen-bridging structures were found as minima. Recently, Grant and Dixon studied HBPH, HAlNH, and HAlPH at the CCSD(T)/aug-cc-pVTZ level.[46] Both linear and nonlinear structures were considered. For HAlNH, the bent and linear forms have essentially the same energies with the valence complete basis set (CBS) approach. This dovetails with the earlier results of Hamilton and Shaikh, who found HAlNH to be linear at all levels of theory with except MP2, which predicts a trans-bent HAlNH structure.[52]

Ab initio studies of the monomers $AlPH_2$, HAlPH, and $H_2AlP$ have been performed at the CCSD/TZP level of theory[61] and find $AlPH_2$ as the global minimum. Davy investigated bond orders in the different structures and concluded that nondative $\pi$ interaction does occur in HAlPH (bond orders of 1.07, 1.95, and 1.05 for $AlPH_2$, HAlPH, and $H_2AlP$, respectively). The aluminum atom maintains planarity in all isomers. Different isomers of the H−Al−N[50] and H−Ga−P[66] systems have been thoroughly studied at the CCSD/TZ2P level of theory. The $AlYH_2$ isomer was found to be lower in energy than the HAlYH structure. A theoretical study of the HMYH and $MYH_2$ isomers (M = Al, Ga, In; Y = N, P) was carried out at the B3LYP/6-311G(d) level of theory.[18] The latter isomers were found to be the global minima with either $C_{2v}$ symmetry (Y = N) or $C_s$ symmetry (Y = P, As).

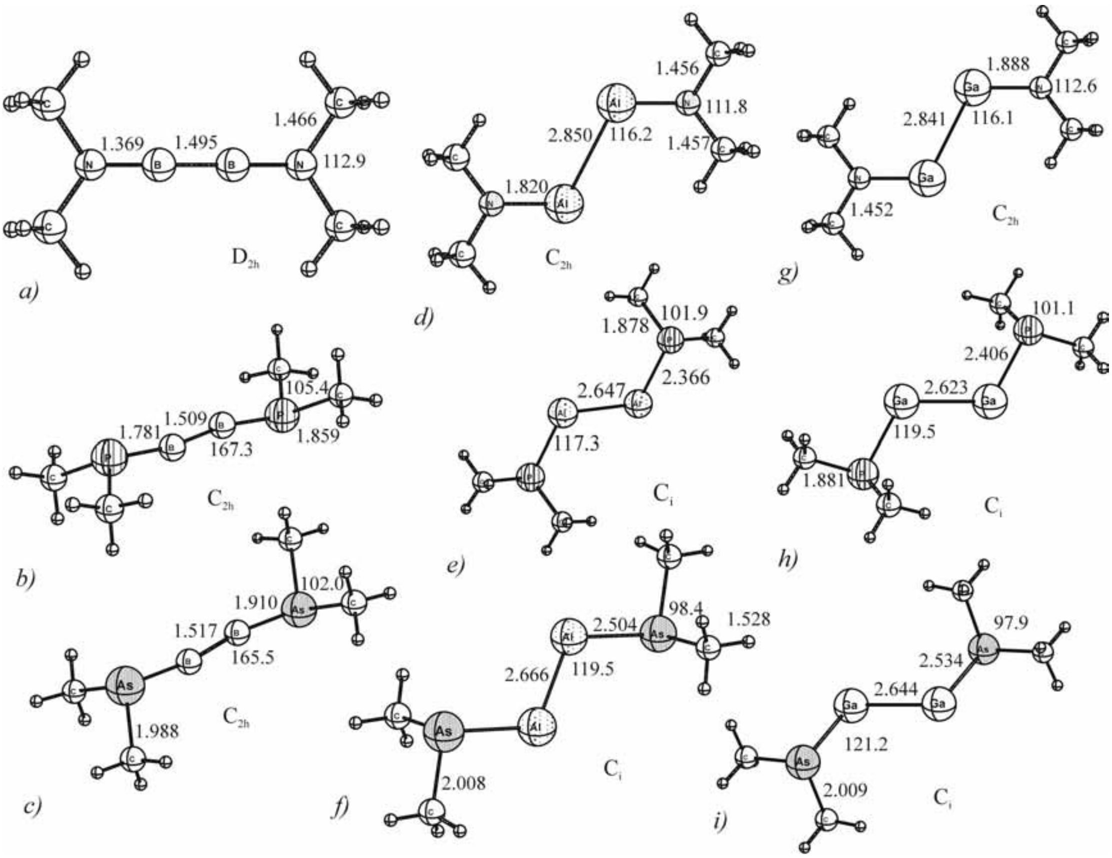


**Figure 2.** Optimized structures for chain isomers of the $Me_2MYYMMe_2$ dimeric compounds. (a) $Me_2NBBNMe_2$, (b) $Me_2PBBPMe_2$, (c) $Me_2AsBBAsMe_2$, (d) $Me_2NAlAlNMe_2$, (e) $Me_2PAlAlPMe_2$, (f) $Me_2AsAlAlAsMe_2$, (g) $Me_2NGaGaNMe_2$, (h) $Me_2PGaGaPMe_2$, and (i) $Me_2AsGaGaAsMe_2$. All distances in are angstroms, and angles are in degrees. B3LYP/TZVP level of theory.

Let us now turn to the results of the present research. Scheme 1 represents the general structures of the monomer compounds considered in the present work. Critical structural parameters of the $MYH_2$, HMYH, and $H_2MY$ isomers are summarized in Table 1, and those of their methyl substituted analogues are in Table 2. Relative energies of compounds are listed in Tables 3 and 4 for R = H and R = $CH_3$, respectively. In accord with previous theoretical findings,[18,46,47,61,66] the $M-YH_2$ isomers are global minima for M = Al, Ga, while for M = B the HBYH isomers are much preferable. All nitrogen-containing compounds of this type are planar. Linear HMYH coordination represents a true minimum only for HBNH, while all other HMYH isomers possess distorted geometries but remain planar ($C_s$ point group). Note the very small energy differences between the linear and the bent structures for HAlNH and HGaNH, 0.1 and 20 kJ $mol^{-1}$, respectively. Himmel, Downs, Green, and Greene note that the "potential well is extremely shallow with respect to the bending coordinates".[18] This may explain the differences between bond angles predicted for the HMYH structures at different levels of theory (Table 1).

Considering the trends in M−Y bonds, one observes substantial MY bond shortening on going from $M-YH_2$ to HMYH isomers for all pairs M, Y. This is in accord with previous findings of Himmel and co-workers[18] that the M−Y bond length decreases in the order: $M-YH_3 > H_3MYH_3 > MYH_2 > HMYH_2 \geq H_2MYH_2 > HMYH$.

Note that despite the significant M−Y bond shortening in all HMYH structures (10−14% with respect to $MYH_2$), only for the boron compounds are the HBYH isomers lower in energy. Note also that both "planarization" of the $M-YH_2$ isomer or "linearization" of the HMYH isomer lead to MY bond length shortening. Despite this fact, all P and As compounds are found to be either pyramidal ($M-YH_2$) or nonlinear (HMYH). The linear HMYH structures (stationary points of Hessian index 2 for Y = P, As) lie 115−177 kJ $mol^{-1}$ higher in energy with respect to the $C_s$ symmetric HMYH minima. This finding agrees well with the high pyramidalization energies of phosphine and arsine molecules reported by Jemmis (30, 149, and 192 kJ $mol^{-1}$ for $NH_3$, $PH_3$, and $AsH_3$, respectively).[74] In contrast, planarization of the $M-YH_2$ species is much less demanding (34−56 kJ $mol^{-1}$). Very similar values for $R-YH_2$ planarization have been obtained for $H_2M-YH_2$ compounds (39−63 kJ $mol^{-1}$).[57] Thus, substitution of a H atom in $YH_3$ both by an $MH_2$ group and by a "naked" M atom results in significant reductions of the planarization energies. It is argued that $\pi$ interactions can contribute to the significant stabilization of the planar structure. For a detailed discussion of $\pi$ and $\sigma$ bonding in different $H_2MYH_2$ conformers (M = B, Al; Y = N, P), see the recent study of Grant and Dixon.[75]

Methyl substitution slightly shortens the M−Y distances for $MYMe_2$ isomers (as compared to $MYH_2$); on the contrary, the M−Y bond distances for MeMYMe and $Me_2MY$ are slightly longer as compared to respective hydrogen analogues. For MeBNMe, the structure with staggered orientation of the methyl groups was found to be a minimum on the PES. The conformer with eclipsed orientation of the methyl groups is a transition state and lies only by 0.05 kJ $mol^{-1}$ higher in energy. For the triplet state of $Me_2BN$, the $C_{2v}$ symmetric conformer was found to be a stationary point of Hessian index 2, lying only 1.8 kJ $mol^{-1}$ higher in energy than $C_2$ symmetric minimum. These very small energy differences point out the essentially free rotation of the Me groups in such monomeric compounds.

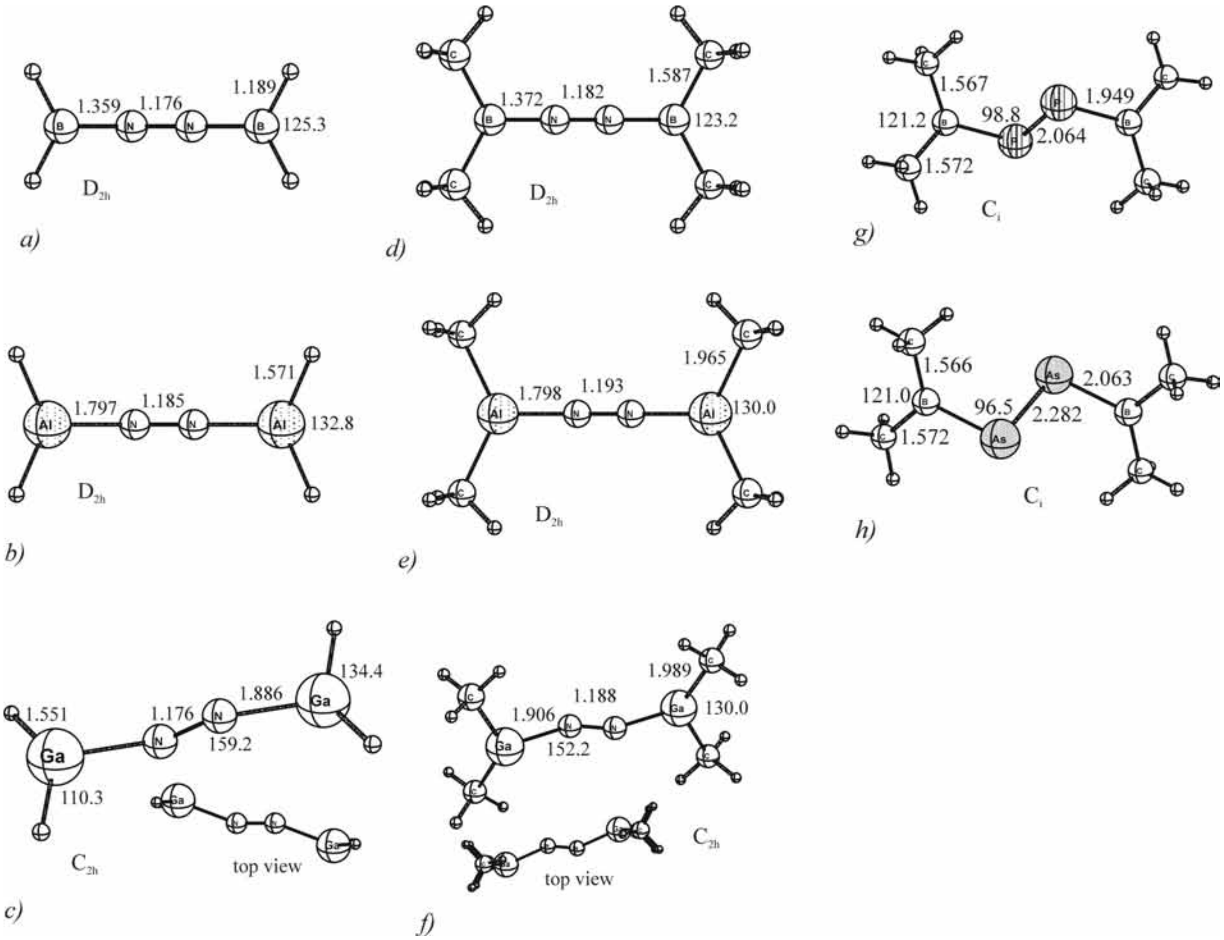


**Figure 3.** Optimized structures for chain isomers of the $H_2MYYMH_2$ dimeric compounds and their methyl derivatives $Me_2MYYMMe_2$. (a) $H_2BNNBH_2$, (b) $H_2AlNNAlH_2$, (c) $H_2GaNNGaH_2$, (d) $Me_2BNNBMe_2$, (e) $Me_2AlNNAlMe_2$, (f) $Me_2GaNNGaMe_2$, (g) $Me_2BPPBMe_2$, and (h) $Me_2BAsAsBMe_2$. All distances are in angstroms, and angles are in degrees. B3LYP/TZVP level of theory.

**TABLE 6: Bond Distances (in Angstroms) for the Chain $[R_2MNNMR_2]$ Isomers and Energies of Dissociation into Triplet $R_2MN$ Monomers[a] ($E^{diss}$, kJ mol$^{-1}$) and Nitrogen Elimination Energies[b] ($E^{elim}$, kJ mol$^{-1}$)[c]**

| compound | point group | MY | YY | $E^{diss}$ | $E^{elim}$ |
|---|---|---|---|---|---|
| $H_2BNNBH_2$ | $D_{2h}$ | 1.395 | 1.176 | 623.3 | 40.9 |
| $Me_2BNNBMe_2$ | $D_{2h}$ | 1.372 | 1.182 | 560.0 | 15.3 |
| $H_2AlNNAlH_2$ | $D_{2h}$ | 1.797 | 1.185 | 722.2 | −68.4 |
| $Me_2AlNNAlMe_2$ | $D_{2h}$ | 1.798 | 1.193 | 696.6 | −67.1 |
| $H_2GaNNGaH_2$ | $C_{2h}$ | 1.886 | 1.176 | 535.4 | −180.6 |
| $Me_2GaNNGaMe_2$ | $C_{2h}$ | 1.906 | 1.188 | 510.8 | −182.6 |
| $Me_2BPPBMe_2$ | $C_i$ | 1.949 | 2.064 | 310.3 | |
| $Me_2BAsAsBMe_2$ | $C_i$ | 2.063 | 2.282 | 268.0 | |

[a] Process $R_2MNNMR_2 = 2\ R_2MN$. [b] Process $R_2MNNMR_2 = R_2MMR_2 + N_2$. [c] B3LYP/TZVP level of theory.

While structural changes upon methylation are minor in all series, the energetic effect of the methyl groups is much more pronounced. Methyl substitution dramatically (by 60−200 kJ mol$^{-1}$) lowers the relative energy of the triplet $Me_2MY$ state. This leads to the triplet structures $Me_2BAs$ and $Me_2AlAs$ as global minima, reflecting the greater stability of $As^{+I}$ species as compared to the lighter analogues of arsenic. Interestingly, $Me_2GaAs$ does not follow the same pattern, being 54 kJ mol$^{-1}$ higher in energy than the $GaAsMe_2$ minimum. This shows that the the $Ga^{I}As^{III}$ combination is preferred to $Ga^{III}As^{I}$, which correlates well with a large number of known $Ga^{I}$ compounds, reflecting the greater stability of Ga in oxidation state I.

The major effect of methyl substitution is the fact that the concurrence between different bonding patterns becomes much more pronounced. If for the hydrogen species *the lowest* energy difference between the most stable isomer and the next stable is 41 kJ mol$^{-1}$ for the BAs system (HBAsH being by 41 kJ mol$^{-1}$ lower than $H_2BAs$), for methyl analogues, the situation becomes really competitive. Thus, MeBPMe lies only 27 kJ mol$^{-1}$ below $Me_2BP$, while MeBAsMe is only 19 kJ mol$^{-1}$ higher in energy than $Me_2BAs$. For the Al−P and Al−As systems, the competing isomers are very close in energy. Note that the trends in the stability of P and As compounds are totally different. While $AlPMe_2$ lies only 15 and 27 kJ mol$^{-1}$ below MeAlPMe and $Me_2AlP$, respectively, $AlAsMe_2$ and MeAlAsMe are predicted to lie 24 and 14 kJ mol$^{-1}$ above $Me_2AlAs$. For the Ga−As system, $GaAsMe_2$ is predicted to lie 22 kJ mol$^{-1}$ below MeGaAsMe. Thus, methylation significantly reduces energy differences between isomers.

We conclude that while for boron compounds the RBYR structures are lowest in energy (with the exception of $Me_2BAs$), for aluminum compounds, the $AlYR_2$ structures are the lowest in energy (with the exception of $Me_2AlAs$), and for gallium compounds, the $GaYR_2$ structures lie the lowest in energy. Our conclusions are in accord with the experimentally observed formation of $MYH_2$ species[10−12] as major products of reactions of laser-ablated Al and Ga atoms with ammonia and phosphine and RBNR species in reactions of laser-ablated B atoms with ammonia and methylamines.[13−15] Our prediction of the greater

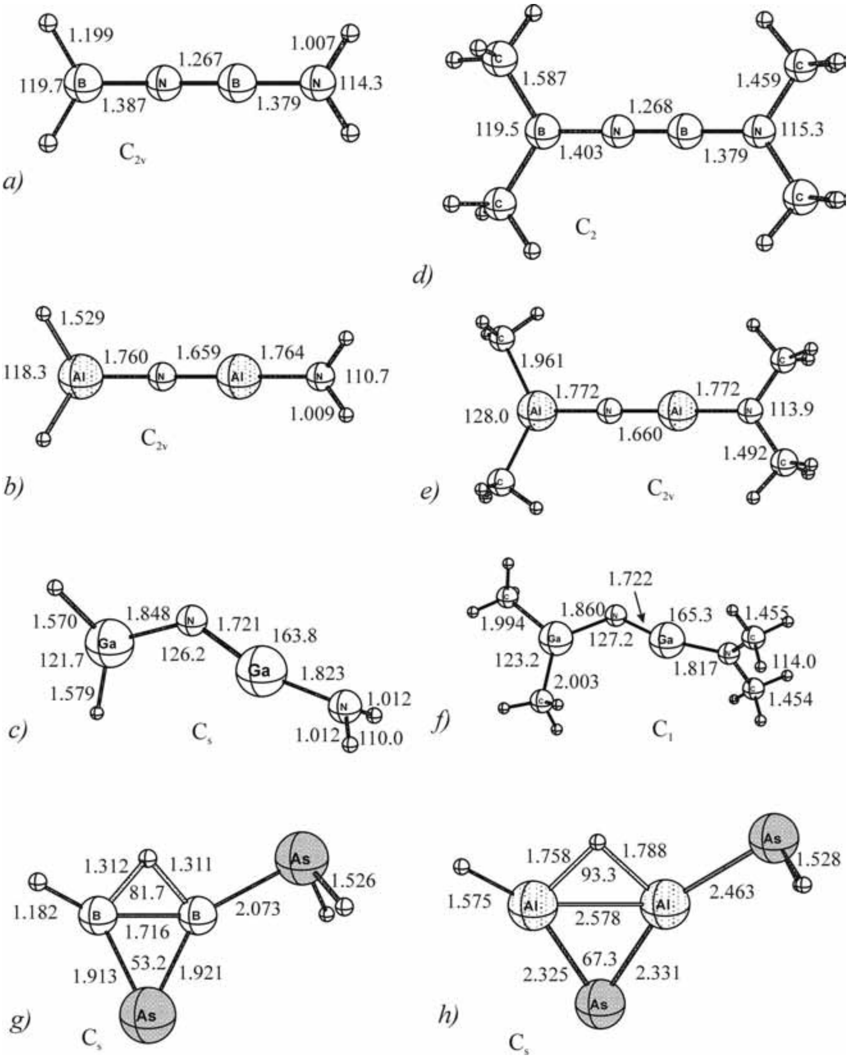


**Figure 4.** Optimized structures for chain isomers of the “mixed type” $H_2MYMYH_2$ dimeric compounds and their methyl derivatives $Me_2MYMYMe_2$. (a) $H_2BNBNH_2$, (b) $H_2AlNAlNH_2$, (c) $H_2GaNGaNH_2$, (d) $Me_2BNBNMe_2$, (e) $Me_2AlNAlNMe_2$, (f) $Me_2GaNGaNMe_2$, (g) optimized structure starting from $H_2BAsBAsH_2$, and (h) optimized structure starting from $H_2AlAsAlAsH_2$. All distances in are angstroms, and angles are in degrees. B3LYP/TZVP level of theory.

**TABLE 7: Bond Distances (in Angstroms) for the Chain $[R_2MN^1MN^2R_2]$ Isomers and Dissociation Energies into $R_2MN$ and $MNR_2$ Monomers (kJ mol$^{-1}$)**[a]

| compound | point group | $MN^1$ | $N^1M$ | $MN^2$ | $E^{diss}$ |
|---|---|---|---|---|---|
| $H_2BNBNH_2$ | $C_{2v}$ | 1.387 | 1.267 | 1.379 | 708.4 |
| $Me_2BNBNMe_2$ | $C_2$ | 1.403 | 1.268 | 1.379 | 680.1 |
| $H_2AlNAlNH_2$ | $C_{2v}$ | 1.760 | 1.659 | 1.764 | 450.4 |
| $Me_2AlNAlNMe_2$ | $C_{2v}$ | 1.772 | 1.660 | 1.772 | 310.1 |
| $H_2GaNGaNH_2$ | $C_1$ | 1.849 | 1.722 | 1.822 | 258.9 |
| $Me_2GaNGaNMe_2$ | $C_1$ | 1.860 | 1.722 | 1.817 | 243.2 |

[a] B3LYP/TZVP level of theory.

**TABLE 8: Bond Dissociation Energies for the Fragmentation of Nitrogen-Containing Chains into Respective Monomers (kJ mol$^{-1}$)**[a]

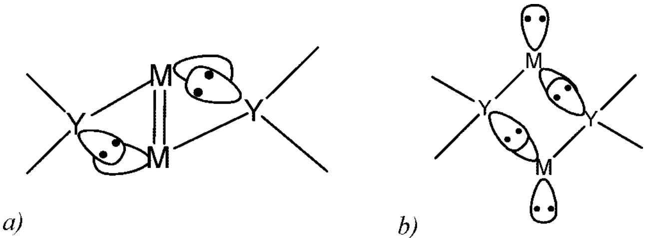
| M | 13-13<br>$H_2NM$-$MNH_2$ | 13-15<br>$H_2NM$-$NMH_2$ | 15-15<br>$H_2MN$-$NMH_2$ |
|---|---|---|---|
| B | 296 | 708 | 623 |
| Al | 30 | 450 | 722 |
| Ga | 20 | 259 | 535 |

[a] B3LYP/TZVP level of theory.

stability of the $Me_2BAs$ and $Me_2AlAs$ isomers awaits experimental confirmation.

**Dimer Compounds.** Early ab initio and semiempirical studies of $[HBNH]_2$ were reported by Baird[41] (SCF/STO-2G) and by Haddon ($D_{2h}$ symmetric minimum at SCF/STO-3G).[27] The dimers $[HBNH]_2$ and $[MeBNMe]_2$ were investigated by Paetzold[43] with the MNDO method. $[HBNH]_2$ was earlier studied by Dewar and McKee[47] with MNDO, where nonplanar structure with equal B−N distances and the pyramidal environment of the N atoms was noted. Bonacic-Koutecky and co-workers[39] studied the rhombic and $C_s$ symmetry structures of $[HBNH]_2$ at the RHF and CASSCF levels of theory with the 4-31G basis set. Triplet states were found to be 335−418 kJ mol$^{-1}$ higher in energy. Suresh and Koga[32] reported that planar $B_2N_2H_4$ is a stationary point of Hessian index 2 lying 5.4 kJ mol$^{-1}$ above the puckered minimum with pyramidalized nitrogen atoms, at the B3LYP/6-31G(d) level of theory (B−N distance, 1.45 Å). Liang and Allen[29] found that planar $[HBNH]_2$ is the true global minimum at the MP2 and RHF/3-21G levels. At the MP2 level, the B−N distances were found to be inequivalent. The aromaticity of $[HBNH]_{2,3,4}$ has been recently analyzed by Soncini et al.[34] and re-evaluated by Rehaman et al.[76] At the B3LYP/6-311G++(d,p) level of theory Rehaman found that the $B_2N_2H_4$ ring has rhombohedral geometry, with equal bond lengths and unequal diagonal distances, puckering 17.3° from planarity. The

**SCHEME 3: Formation of $[MYH_2]_2$ Cyclic Dimers**



a) rhomb isomer

b) ring isomer

equivalence of the B−N distances suggest that lone pairs are localized on the N atoms and not transferred to the nearby B atom. A degree of resonance similar to that exhibited by $C_4H_4$ is not found; therefore, $B_2N_2H_4$ was concluded to be aromatic, in opposition to the well-studied cyclobutadiene. The planar well-studied structure is a TS, which lies only 4 kJ mol$^{-1}$ higher in energy. The dissociation into two $BNH_2$ units was found to require 205 kJ mol$^{-1}$. Dimeric and tetrameric $[HAlNH]_{2,4}$ were studied theoretically by Hamilton and Shaikh.[52] The dimerization energy of HAlNH was computed to be 586 kJ mol$^{-1}$ and that of $[HAlNH]_2$ was 276 kJ mol$^{-1}$.

Jouany, Barthelat, and Daudey theoretically studied $H_2NBBNH_2$ at the SCF/4-31G(d) level.[30] They found a $D_{2h}$ symmetric $^1A_g$ ground state, with a triplet $^3B_2$ ($D_{2d}$ symmetry) electronic state lying 34.3 kJ mol$^{-1}$ higher. Thus, in contrast to HBBH, where $^3\Sigma^-$ is the electronic ground state, the existence of a singlet ground state of the molecule $H_2NBBNH_2$ with a B−B $\pi$ bond was predicted.

Gilbert theoretically considered the dimerization of RBNR′ iminoboranes and the 4 + 2 Diels−Alder reactions at the B3LYP/6-31+G* level of theory.[36] Dimerization of HBNH proceeds via an early, rather asymmetric, puckered TS, where two B and two N atoms are not coplanar. This mimics the symmetry-forbidden dimerization of ethyne, where, at the transition state, the alkynes are nearly at right angles to each other. The TS for the dimerization of MeBNMe is puckered and lies early on the reaction coordinate, but it is symmetric ($C_2$ point group), in contrast to HBNH. The energetic parameters are similar, and Gilbert concluded that methylation does not create significant steric congestion, that is, the energetics are not significantly affected. For $F_3CBNMe_3$, a significantly lower barrier and greater exothermicity are reported, due to the increased Lewis acidity at the boron atom. A far more asymmetric TS was found for $C_6F_5BN^tBu$ (incipient formation of only one B−N bond). Steric bulk raises the TS barrier there by about 42 kJ mol$^{-1}$, despite the increased basicity on N. For $^tF_9C_4BN^tBu$, the dimerization process should be viewed as stepwise, with the second B−N bond formation well after the first, resulting in a very large barrier and low exothermicity. Thus, electron-withdrawing fluorinated groups on boron lower the barrier and increase the reaction exothermicity. On the other hand, attachment of bulky substituents to the boron and nitrogen atoms raises the reaction barrier and lowers the exothermicity.

Lets us turn now our attention to the dimeric compounds studied in the present research. As we start with three types of monomeric structures, which differ in the placement of the hydrogen substituents $MYH_2$, HMYH, and $H_2MY$ (Scheme 1), we end up with dimers of the following kind: $[MYH_2]_2$, $[HMYH]_2$, and $[H_2MY]_2$. We considered formation of chain structures with one M−Y bond (Scheme 2a−c) and ring structures with two M−Y bonds (Scheme 2d−f). In addition, we will discuss chain compounds of mixed types, resulting from interactions between $MYH_2$ and $H_2MY$.

***Chain Isomers.*** *$H_2YMMYH_2$ Chain Isomers (Scheme 2a).* Optimized structures for the $H_2YMMYH_2$ chain isomers (singlet states) are presented in Figure 1. Only for $H_2NBBNH_2$ does the highly symmetric structure of $D_{2h}$ point group (Figure 1a) correspond to a minimum on the PES. For other 13-15 pairs, such a structure is either a transition state (AlN, GaN) or a high order stationary point (Table 5). Lowering the symmetry to $C_{2h}$ point group results in perfectly planar (Figure 1d,g) structures for (AlN, GaN), with distorted N−M−M−N bond arrangements (N−M−N angles of 113.6 and 113.7 for Al and Ga, respectively). Note that for the BP and BAs species, the $C_{2h}$ symmetric structures are also minima on PES, but in these cases, the hydrogen atoms lie above and below the plane due to pyramidalization of the P and As centers (Figure 1b,c). Note also that the YBY angles are 168.6° for both P and As, indicating relatively small deviations from the linear YBBY arrangement. For the remaining 13-15 compounds, $C_i$ symmetric structures were found to be true minima on their PES (Figure 2e,f,h,i). In this case, the YMMY atoms are still coplanar, but the YMY angles are 118−120°, indicating much higher distortions from the linear YMMY arrangement.

There are interesting structural trends for the group 13-13 bond distances. While for boron compounds the B−B distances increase in the order $NH_2 > PH_2 \approx AsH_2$, the trend is the opposite for the Al and Ga compounds: $NH_2 < PH_2 \approx AsH_2$. The weaker interactions between two $AlNH_2$ molecules as compared to those for $AlPH_2$ can be explained by stronger $\pi$ interactions in monomeric $AlNH_2$. Very long Al−Al and Ga−Ga distances in $H_2YMMYH_2$ suggest that these dimers are only weakly bound. In fact, the dissociation energies of chain $H_2YMMYH_2$ into $MYH_2$ monomers are only 20−54 kJ mol$^{-1}$ for the Al−Al and Ga−Ga bonded species, as compared to 300−450 kJ mol$^{-1}$ for B−B bonded compounds (Table 5). This trend is a general one for 13-13 species, and B−B compounds are much more strongly bound than the heavier group 13 analogues.[25] Structures of methyl derivatives are given in Figure 2. With the exception of $Me_2NAlAlNMe_2$ and $Me_2NGaGaNMe_2$, the 13-13 distances only slightly shorten upon methylation. Dissociation energies are also only slightly affected (Table 5).

*HYMH···HYMH Chain Isomers (Scheme 2,b).* Our attempts to optimize such chain isomers were unsuccessful, with the guessed structures collapsing to the $[HMYH]_2$ ring structures for all 13-15 pairs.

*$H_2MYYMH_2$ Chain Isomers (Scheme 2,c).* $D_{2h}$ point group optimizations revealed that only for the BN and AlN systems are such high symmetry structures minima on their PES (Figure 3a,b). Upon decreasing the symmetry to $C_{2h}$, a minimum structure with the chain MYYM bond arrangement is obtained for $H_2GaNNGaH_2$ (Figure 3c). Optimization of the P and As chain structures in the framework of $C_{2h}$ symmetry results in rhombic ring structures (Figure 11, vide infra). Similar results have been obtained for the methylated analogues, with the exception of boron compounds, which resulted in $C_i$ symmetric $Me_2BPPBMe_2$ and $Me_2BAsAsBMe_2$ chain isomers (Figure 3g,h). For the nitrogen-containing species, geometries of the respective Me derivatives are given in Figure 3d−f and are similar to those predicted for the hydrogen analogues. Methylation slightly increases both N−N (by 0.006−0.012 Å) and M−N (by 0.001−0.020 Å) bond distances. Nitrogen−nitrogen bond distances are very short in all compounds (1.176−1.193 Å), being intermediate between the nitrogen−nitrogen distance in $N_2$ (1.093 Å) and in HNNH (1.237 Å). As a consequence, the dissociation energies of $H_2MNNMH_2$ into two $H_2MN$ monomers in their triplet state are quite large: 623, 722, and

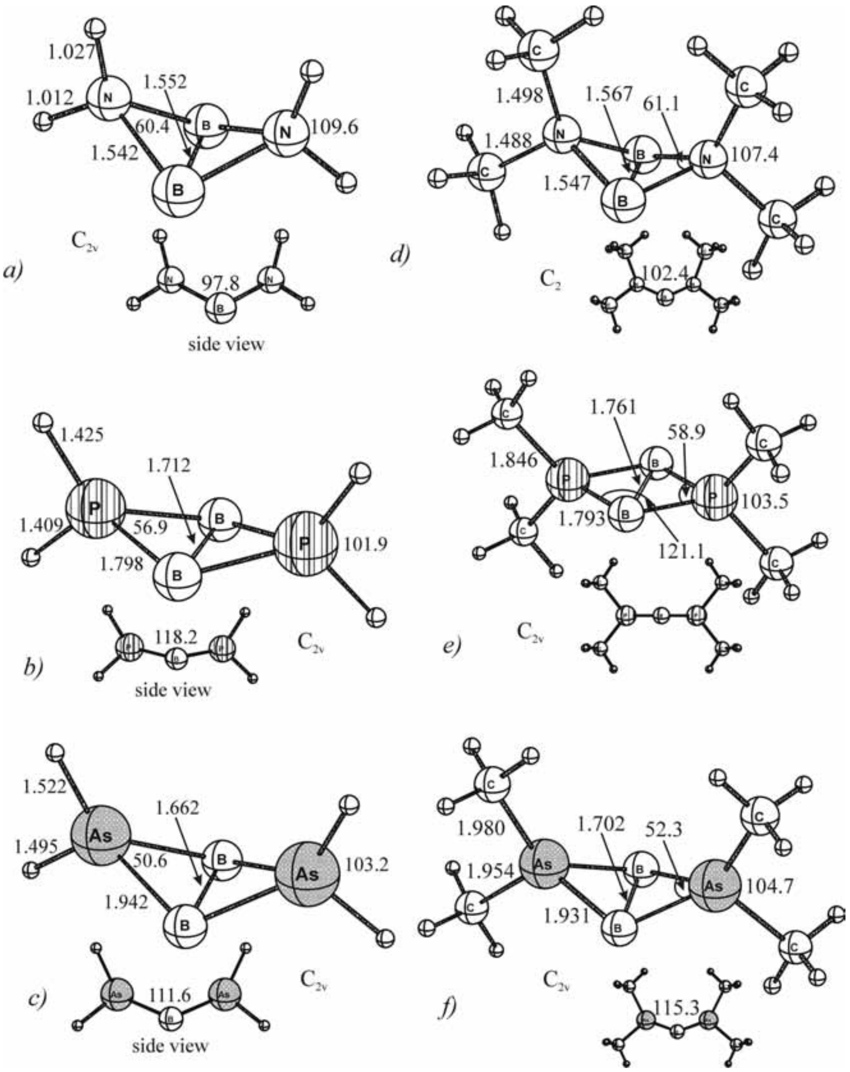


**Figure 5.** Optimized structures for rhombic isomers of the $[BYH_2]_2$ dimeric compounds and their methylated derivatives $[BYMe_2]_2$. (a) rhomb-$[BNH_2]_2$, (b) rhomb-$[BPH_2]_2$, (c) rhomb-$[BAsH_2]_2$, (d) rhomb-$[BNMe_2]_2$, (e) rhomb-$[BPMe_2]_2$, and (f) rhomb-$[BAsMe_2]_2$. All distances in are angstroms, and angles are in degrees. B3LYP/TZVP level of theory.

535 kJ mol$^{-1}$ for B, Al, and Ga, respectively. For $Me_2MNNMMe_2$ the dissociation energies into triplet $Me_2MN$ are slightly lower: 560, 697, and 511 kJ mol$^{-1}$ for B, Al, and Ga, respectively. These results demonstrate the high stability of the nitrogen−nitrogen bond in the molecules considered. Despite this strong N−N bond, these chain isomers are predicted to be much higher in energy than other structures (Table 13, vide infra). Major structural parameters for the $R_2MNNMR_2$ chain dimers are summarized in Table 6.

Because the N−N bond in chain $R_2MNNMR_2$ isomers is quite strong, it is interesting to consider the stability with respect to dissociation into $N_2$ and $R_2MMR_2$. Optimized structures of the $D_{2d}$ symmetric $R_2MMR_2$ compounds are given in Table 3S (Supporting Information). Computed values of the energetics of nitrogen elimination $R_2MNNMR_2 = R_2MMR_2 + N_2$ are given in the last column in Table 6. Nitrogen elimination from boron compounds is endothermic, while both aluminum and gallium analogues eliminate nitrogen exothermically.

*$H_2MYMYH_2$ Chain Isomers.* Our attempts to identify chain structures composed of monomers of mixed types, that is, $H_2MY$ and $MYH_2$, have been successful only for nitrogen-containing compounds. Optimized structures of the $C_{2v}$ symmetric $H_2BNBNH_2$ and $H_2AlNAlNH_2$ are given in Figure 4a,b. Both compounds feature linear arrangements of the heavy atoms. For the gallium analogue, such a linear structure is a second order stationary point, while the asymmetric structure with nonlinear GaNGaN arrangement (Figure 4c) is a minimum on the PES. Methylated compounds feature similar structures (Figure 4d−f). For phosphorus and arsenic compounds, optimization procedures yielded hydrogen-bridged structures, examples of which are shown in Figure 4g,h for the B−As and Al−As systems. Because our primary goal was to address the MY bond preferences upon oligomerization of $MYH_2$ monomers, we will not discuss hydrogen-bridged structures in the present work. Major structural parameters for the $R_2MYMYR_2$ chain dimers are given in Table 7.

Summarizing our results for the chain isomers, we note that nitrogen- and boron-containing compounds form strongly bound chain structures, which make them kinetically stable with respect to dissociation. Comparison of 13-13, 13-15, and 15-15 bond energies is possible only for nitrogen compounds, and obtained results are summarized in Table 8. The order of bond dissociation energies is N−N > MN ≫ MM. Chains with Al−Al and Ga−Ga bonds have very low dissociation energies.

***Cyclic Isomers.*** *$[MYH_2]_2$ Dimers (Scheme 2,d).* The $[MYH_2]_2$ cyclic dimers may be constructed in two different ways, resulting in ring and rhombic isomers. The bonding pattern in these dimers is schematically presented in Scheme 3. Ring isomers

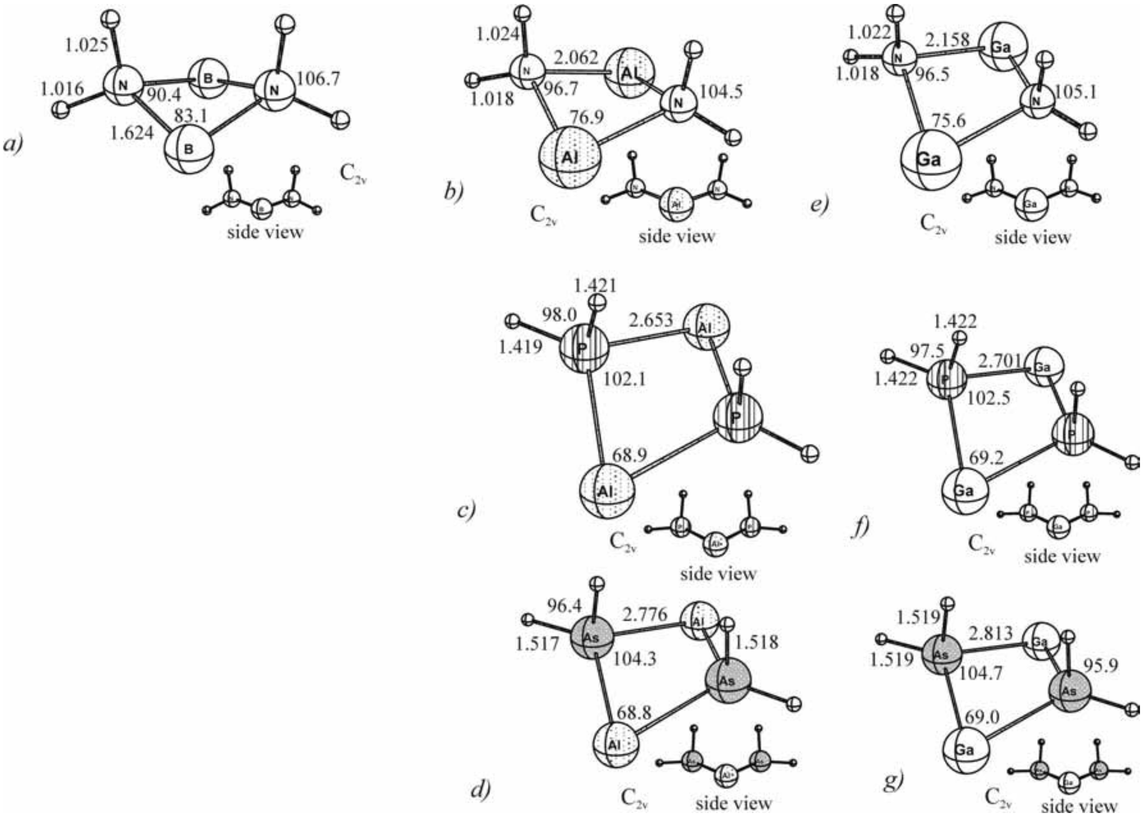


**Figure 6.** Optimized structures for ring isomers of the $[MYH_2]_2$ dimeric compounds. (a) ring-$[BNH_2]_2$, (b) ring-$[AlNH_2]_2$, (c) ring-$[AlPH_2]_2$, (d) ring-$[AlAsH_2]_2$, (e) ring-$[GaNH_2]_2$, (f) ring-$[GaPH_2]_2$, and (g) ring-$[GaAsH_2]_2$. All distances are in angstroms, and angles are in degrees. B3LYP/TZVP level of theory.

**TABLE 9: Selected Structural Parameters for the $[MYR_2]_2$ Rhombic Isomers (in Angstroms and Degrees) and Dissociation Energies into $MYR_2$ Monomers (kJ $mol^{-1}$)[a]**

| compound | point group | MM | MY | M−Y−M | Y−M−Y | torsion | $E^{diss}$ |
|---|---|---|---|---|---|---|---|
| rhomb-$[BNH_2]_2$ | $C_{2v}$ | 1.552 | 1.542 | 60.4 | 97.8 | 48.1 | −68.7 |
| rhomb-$[BNMe_2]_2$ | $C_2$ | 1.567 | 1.547 | 61.1 | 102.4 | 43.0 | −83.6 |
| rhomb-$[BPH_2]_2$ | $C_{2v}$ | 1.712 | 1.798 | 56.9 | 118.2 | 25.4 | 305.9 |
| rhomb-$[BPMe_2]_2$ | $C_{2v}$ | 1.761 | 1.793 | 58.9 | 121.1 | 0.1 | 419.2 |
| rhomb-$[BAsH_2]_2$ | $C_{2v}$ | 1.662 | 1.942 | 50.6 | 111.6 | 45.9 | 203.6 |
| rhomb-$[BAsMe_2]_2$ | $C_{2v}$ | 1.702 | 1.931 | 52.3 | 115.3 | 39.1 | 292.0 |

[a] B3LYP/TZVP level of theory.

(Scheme 3a) feature lone pair electrons on the group 13 center (oxidation state I) and involve four MY bonds formed by both covalent DA interactions. The rhombic isomer (Scheme 3b) features a formally double MM bond and four MY single bonds.

*Rhombic Structures $M_2(YR_2)_2$.* Rhombic structures $M_2(YR_2)_2$ are predicted to be minima only for the boron-containing compounds. Their optimized structures are presented in Figure 5 for both hydrogen (a−c) and methyl (d−f) substituents. Attempts to optimize rhombic isomers for Al and Ga resulted in the ring structures presented in Figure 6. The B−B distance in the rhombic compounds changes nonmonotonically in the series N−P−As: from 1.552 in $B_2(NH_2)_2$ to 1.712 in $B_2(PH_2)_2$ and 1.662 in $B_2(AsH_2)_2$. Thus, the shortest B−B distance is observed for the $NH_2$ compound, while the longest is formed for the $PH_2$ compound. Introduction of methyl substituents slightly increases the B−B distance, but the qualitative trend remains the same. Methylation reduces the torsion MYMY angle, and $B_2(PMe_2)_2$ has an almost planar PBBP ring (torsion angle, 0.1°). Boron−nitrogen rhombic structures $B_2(NR_2)_2$ are predicted to exothermically dissociate into monomers (Table 9); therefore, such compounds are only kinetically stable. In contrast, P- and As-containing compounds have substantial dissociation energies (200−420 kJ $mol^{-1}$).

Another way of looking at the rhombic compounds involves an interaction of the triplet $B_2$ molecule with two $YR_2$ radicals. As compared to the B−B distance in free $B_2$ (1.613 Å), the formation of $B_2(NH_2)_2$ significantly decreases the B−B distance but increases it for $B_2(PH_2)_2$ and $B_2(AsH_2)_2$.

*$[MYH_2]_2$ Ring Structures.* The structure of $D_{2h}$ symmetry is not a minimum on the PES for $[MYH_2]_2$ ring dimers for all 13-15 pairs. The minima on the PES are $C_{2v}$ symmetric structures (Figure 6), with $M_2Y_2$ rings puckered by 25−46°. It is interesting that for the boron−nitrogen compound, the ring isomer (Figure 6a) has been predicted to be a minimum on its PES. In contrast, optimization attempts for the B−P and B−As ring structures lead to rhombic isomers (Figure 5) for both H and Me substituents. Substitution of hydrogens by methyl groups also result in minima, generally of $C_{2v}$ symmetry (Figure 7).

Structural parameters for the $[MYH_2]_2$ ring structures are summarized in Table 10. An interesting feature of the boron−nitrogen-containing rings is that both ring and rhombic isomers are identified as minima on the PES. The rhombic

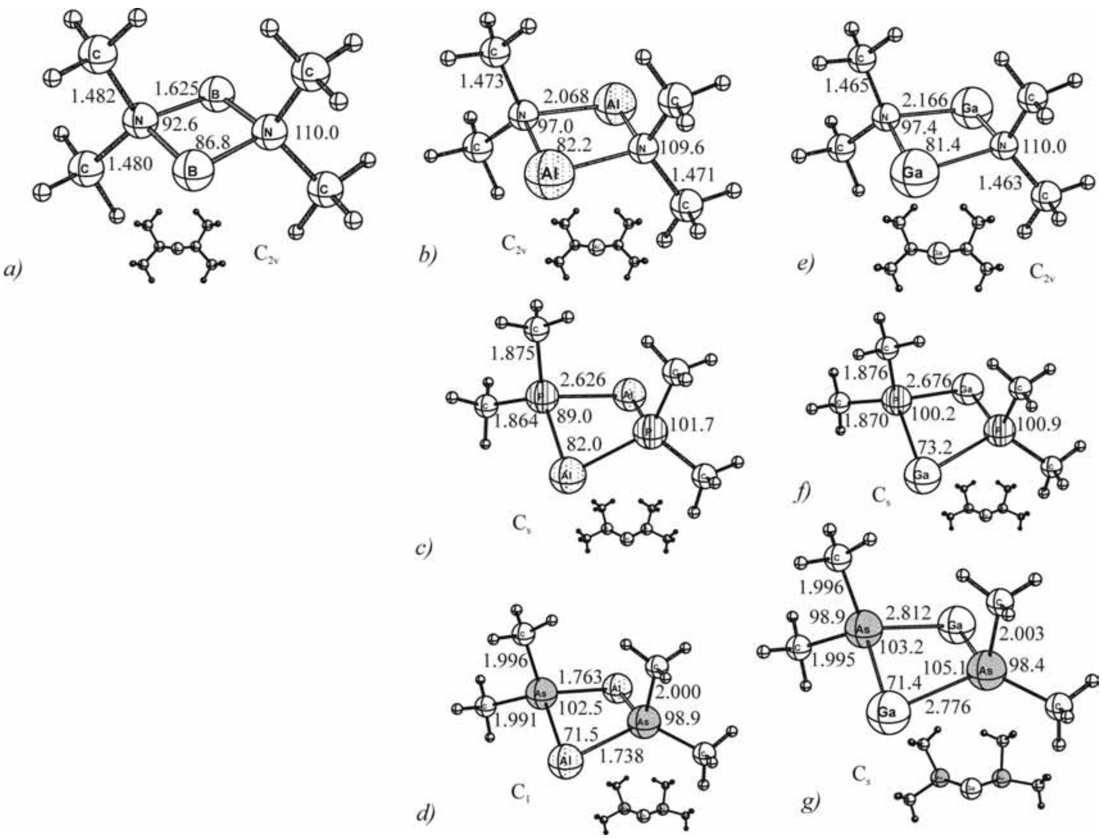


**Figure 7.** Optimized structures for ring isomers of the $[MYMe_2]_2$ dimeric compounds. (a) ring-$[BNMe_2]_2$, (b) ring-$[AlNMe_2]_2$, (c) ring-$[AlPMe_2]_2$, (d) ring-$[AlAsMe_2]_2$, (e) ring-$[GaNMe_2]_2$, (f) ring-$[GaPNMe_2]_2$, and (g) ring-$[GaAsMe_2]_2$. All distances are in angstroms, and angles are in degrees. B3LYP/TZVP level of theory.

**TABLE 10: Structural Parameters for the $[MYR_2]_2$ Ring Isomers (in Angstroms and Degrees) and Dissociation Energies into $MYR_2$ Monomers (kJ mol$^{-1}$)[a]**

| compound | point group | MY | MM | YY | M−Y−M | Y−M−Y | torsion | $E^{\text{diss}}$ |
|---|---|---|---|---|---|---|---|---|
| ring-$[BNH_2]_2$ | $C_{2v}$ | 1.624 | 2.306 | 2.154 | 90.4 | 83.1 | 26.8 | −104.9 |
| ring-$[BNMe_2]_2$ | $C_{2v}$ | 1.625 | 2.350 | 2.234 | 92.6 | 86.8 | 8.4 | −110.9 |
| ring-$[AlNH_2]_2$ | $C_{2v}$ | 2.062 | 3.081 | 2.563 | 96.7 | 76.9 | 26.8 | 80.1 |
| ring-$[AlNMe_2]_2$ | $C_{2v}$ | 2.068 | 3.098 | 2.719 | 97.0 | 82.2 | 9.4 | 54.8 |
| ring-$[AlPH_2]_2$ | $C_{2v}$ | 2.653 | 4.126 | 3.002 | 102.1 | 68.9 | 32.0 | 81.0 |
| ring-$[AlPMe_2]_2$ | $C_s$ | 2.626,2.467 | 3.570 | 3.235 | 89.0 | 76.0, 82.0 | 35.1 | 126.0 |
| ring-$[AlAsH_2]_2$ | $C_{2v}$ | 2.776 | 4.383 | 3.136 | 104.3 | 68.8 | 28.3 | 65.0 |
| ring-$[AlAsMe_2]_2$ | $C_1$ | 2.738, 2.736 | 4.311 | 3.215 | 102.5, 103.8 | 71.5 | 24.9 | 98.0 |
| ring-$[GaNH_2]_2$ | $C_{2v}$ | 2.158 | 3.221 | 2.644 | 96.5 | 75.6 | 29.6 | 78.8 |
| ring-$[GaNMe_2]_2$ | $C_{2v}$ | 2.166 | 3.253 | 2.823 | 97.4 | 81.4 | 12.0 | 53.8 |
| ring-$[GaPH_2]_2$ | $C_{2v}$ | 2.701 | 4.212 | 3.068 | 102.5 | 69.2 | 30.7 | 76.7 |
| ring-$[GaPMe_2]_2$ | $C_s$ | 2.676 | 4.107 | 3.192 | 100.2 | 73.2 | 27.3 | 111.8 |
| ring-$[GaAsH_2]_2$ | $C_{2v}$ | 2.813 | 4.454 | 3.188 | 104.7 | 69.0 | 26.9 | 63.6 |
| ring-$[GaAsMe_2]_2$ | $C_s$ | 2.776, 2.812 | 4.408 | 3.260 | 103.2, 105.1 | 71.4 | 23.0 | 95.2 |

[a] B3LYP/TZVP level of theory.

$B_2(NH_2)_2$ isomer is only 36 kJ mol$^{-1}$ more stable than the $[BNH_2]_2$ ring. Interestingly, both structures are only kinetically stable (exothermic dissociation into monomers). Boron-containing ring and rhombic structures are significantly higher in energy as compared to the $H_2YBBYH_2$ chains, while for the Al and Ga compounds, the ring structures are much lower in energy than the Al−Al and Ga−Ga bonded chains (Table 13). This is in large part due to substantially reduced Al−Al and Ga−Ga bonding in the chain compounds (16−69 kJ mol$^{-1}$) as compared to that for the B−B (293−485 kJ mol$^{-1}$) structures. Thus, formation of multiple ($\sigma + \pi$) bonds in chain structures is favored for B but unfavored for Al and Ga.

*$[HMYH]_2$ Ring Dimers.* Structures of the $[HMYH]_2$ isomers (M = Al, Ga, In; Y = N, P, As) have been previously studied at the B3LYP/LANL2DZ(d,p) level of theory.[57] It was found that nitrogen-containing rings are planar with $D_{2h}$ symmetry, while the phosphorus and arsenic centers adopt pyramidal geometries, with the $C_{2v}$ symmetry structures being the lowest in energy. Alternative $C_{2h}$ isomers with planar $M_2Y_2$ core were found to be higher in energy. Our results obtained with the all-electron TZVP basis set are in agreement with the earlier findings. Optimized structures for the ring compounds are presented in Figures 8, 9, and 10 for the boron, aluminum, and gallium compounds, respectively. For the H compounds, both $C_{2v}$ and $C_{2h}$ symmetric isomers were found. In all cases, $C_{2h}$ symmetric isomers with planar $M_2Y_2$ core are less stable than puckered structures of $C_{2v}$ symmetry, but the energy

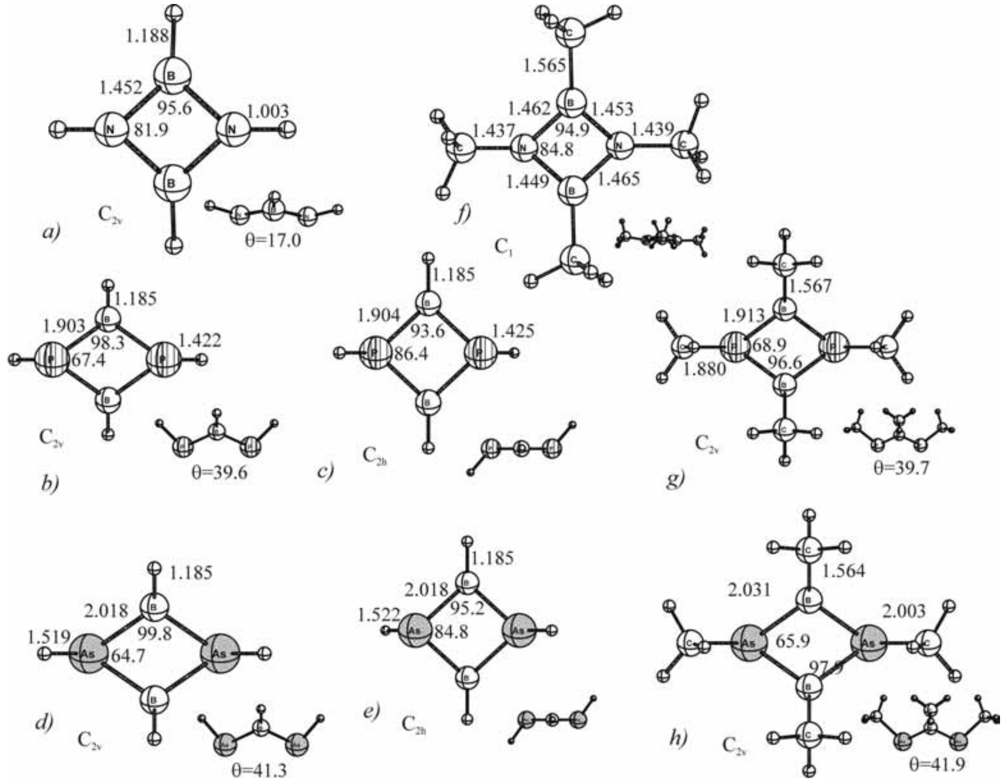


**Figure 8.** Optimized structures for ring isomers of the $[HBYH]_2$ dimeric compounds. (a) $[HBNH]_2$, (b) $[HBPH]_2$, (c) $[HBPH]_2$, (d) $[HBAsH]_2$, (e) $[HBAsH]_2$, (f) $[MeBNMe]_2$, (g) $[MeBPMe]_2$, and (h) $[MeBAsMe]_2$. All distances are in angstroms, and angles are in degrees. B3LYP/TZVP level of theory.

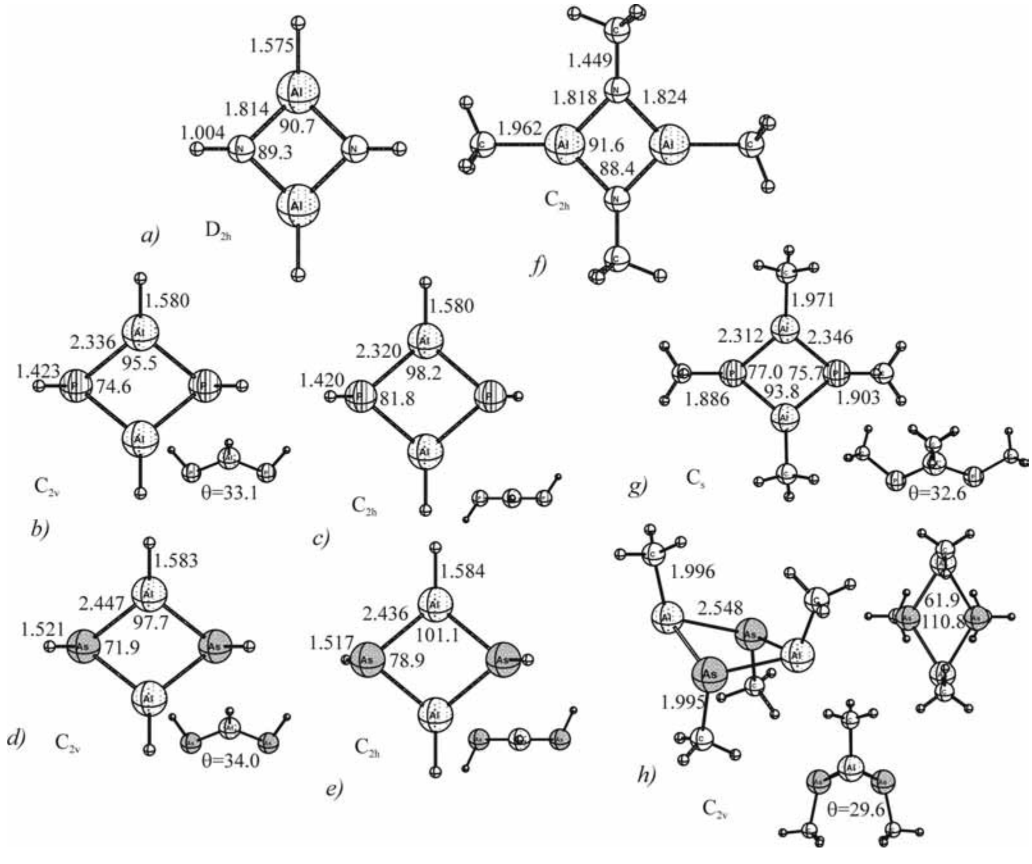


**Figure 9.** Optimized structures for ring isomers of the $[HAlYH]_2$ dimeric compounds. (a) $[HAlNH]_2$, (b) $[HAlPH]_2$, (c) $[HAlPH]_2$, (d) $[HAlAsH]_2$, (e) $[HAlAsH]_2$, (f) $[MeAlNMe]_2$, (g) $[MeAlPMe]_2$, and (h) $[MeAlAsMe]_2$. All distances are in angstroms, and angles are in degrees. B3LYP/TZVP level of theory.

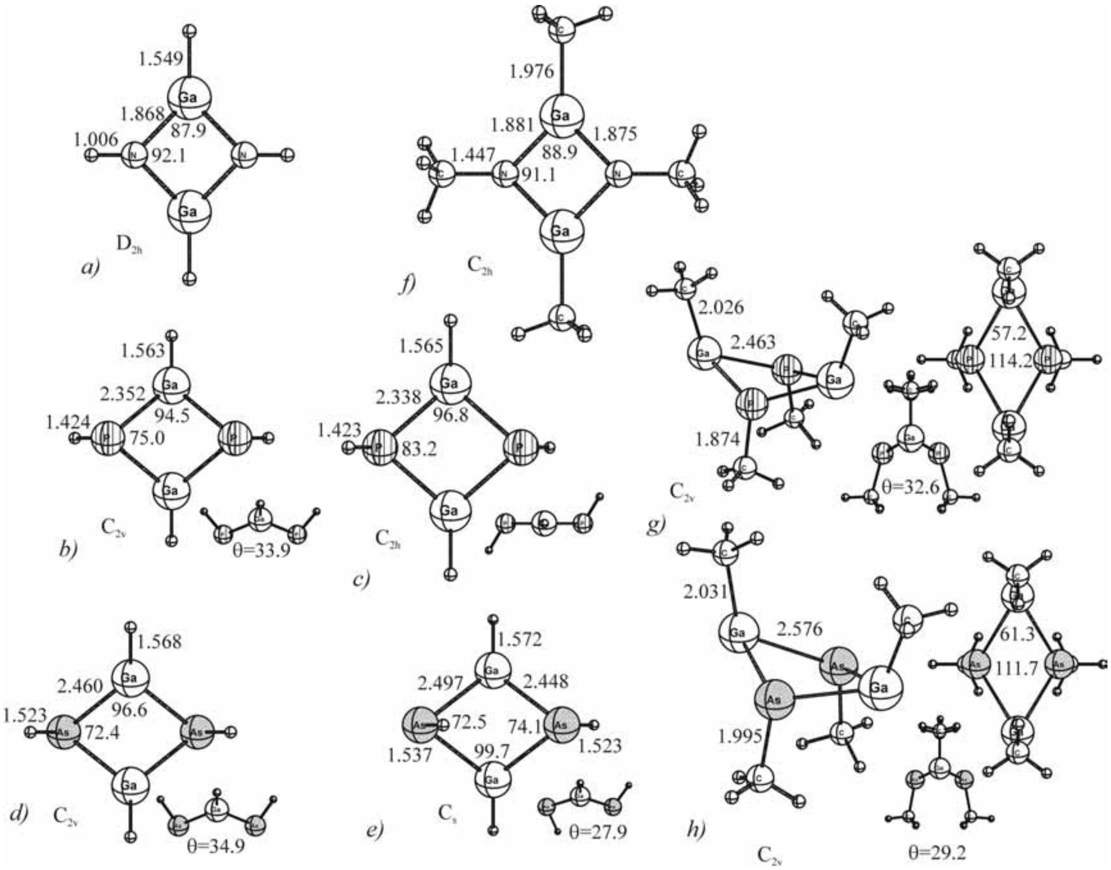


**Figure 10.** Optimized structures for ring isomers of the $[HGaYH]_2$ dimeric compounds. (a) $[HGaNH]_2$, (b) $[HGaPH]_2$, (c) $[HGaPH]_2$, (d) $[HGaAsH]_2$, (e) $[HGaAsH]_2$, (f) $[MeGaNMe]_2$, (g) $[MeGaPMe]_2$, and (h) $[MeGaAsMe]_2$. All distances are in angstroms, and angles are in degrees. B3LYP/TZVP level of theory.

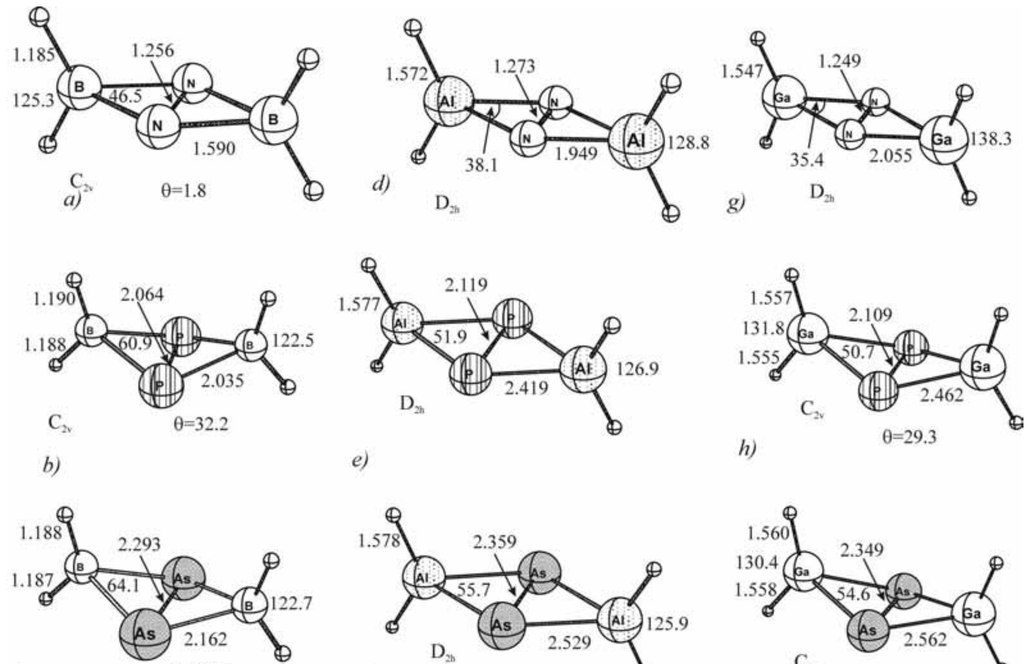


**Figure 11.** Optimized structures for rhombic isomers of the $[H_2MY]_2$ dimeric compounds. (a) rhomb-$[H_2BN]_2$, (b) rhomb-$[H_2BP]_2$, (c) rhomb-$[H_2AsB]_2$, (d) rhomb-$[H_2AlN]_2$, (e) rhomb-$[H_2AlP]_2$, (f) rhomb-$[H_2AlAs]_2$, (g) rhomb-$[H_2GaN]_2$, (h) rhomb-$[H_2GaP]_2$, and (i) rhomb-$[H_2GaAs]_2$. All distances in are angstroms, and angles are in degrees. B3LYP/TZVP level of theory.

difference is relatively small (10−35 kJ $mol^{-1}$). For the Me-substituted species, only the puckered isomers have been optimized. Major structural parameters and dissociation energies are presented in Table 11. In agreement with previous studies,[32,29,76] we predict the puckered $[RBNR]_2$ structures to be minima on their PES.

**TABLE 11: Structural Parameters for the $[RMYR]_2$ Ring Isomers (in Angstroms and Degrees) and Dissociation Energies into RMYR Monomers (kJ $mol^{-1}$)[a]**

| compound | point group | MY | MM | YY | M−Y−M | Y−M−Y | tors. | $E^{diss}$ |
|---|---|---|---|---|---|---|---|---|
| $[HBNH]_2$ | $C_{2v}$ | 1.452 | 1.902 | 2.151 | 81.9 | 95.6 | 17.0 | 225.0 |
| $[MeBNMe]_2$ | $C_1$ | 1.451; 1.463 | 1.962 | 2.148 | 84.8 | 94.9 | 7.2 | 185.7 |
| $[HBPH]_2$ | $C_{2v}$ | 1.903 | 2.110 | 2.878 | 64.7 | 98.3 | 39.6 | 254.3 |
| $[MeBPMe]_2$ | $C_{2v}$ | 1.913 | 2.165 | 2.856 | 68.9 | 96.9 | 39.7 | 268.7 |
| $[HBPH]_2$ | $C_{2h}$ | 1.904 | 2.607 | 2.777 | 86.4 | 93.6 | 0 | 219.5 |
| $[HBAsH]_2$ | $C_{2v}$ | 2.017 | 2.159 | 3.086 | 64.7 | 99.8 | 41.3 | 209.0 |
| $[MeBAsMe]_2$ | $C_{2v}$ | 2.031 | 2.210 | 3.064 | 65.9 | 97.9 | 41.9 | 238.9 |
| $[HBAsH]_2$ | $C_{2h}$ | 2.017 | 2.720 | 2.980 | 84.8 | 95.2 | 0 | 174.5 |
| $[HAlNH]_2$ | $D_{2h}$ | 1.814 | 2.549 | 2.581 | 89.3 | 90.7 | 0 | 565.5 |
| $[MeAlNMe]_2$ | $C_{2h}$ | 1.818; 1.824 | 2.539 | 2.611 | 88.4 | 91.6 | 0 | 512.4 |
| $[HAlPH]_2$ | $C_{2v}$ | 2.336 | 2.830 | 3.457 | 74.6 | 95.5 | 33.1 | 333.3 |
| $[MeAlPMe]_2$ | $C_s$ | 2.312; 2.346 | 2.879 | 3.401 | 75.7; 77.0 | 93.8 | 32.6 | 356.1 |
| $[HAlPH]_2$ | $C_{2h}$ | 2.320 | 3.037 | 3.508 | 81.8 | 98.2 | 0 | 323.5 |
| $[HAlAsH]_2$ | $C_{2v}$ | 2.447 | 2.873 | 3.684 | 71.9 | 97.7 | 34.0 | 301.4 |
| $[MeAlAsMe]_2$ | $C_{2v}$ | 2.548 | 4.194 | 2.622 | 110.8 | 61.9 | 29.6 | 139.3 |
| $[HAlAsH]_2$ | $C_{2h}$ | 2.436 | 3.094 | 3.763 | 78.9 | 101.1 | 0 | 286.0 |
| $[HGaNH]_2$ | $D_{2h}$ | 1.868 | 2.690 | 2.594 | 92.1 | 87.9 | 0 | 412.0 |
| $[MeGaNMe]_2$ | $C_{2h}$ | 1.881; 1.875 | 2.682 | 2.630 | 91.1 | 88.9 | 0 | 387.1 |
| $[HGaPH]_2$ | $C_{2v}$ | 2.352 | 2.862 | 3.454 | 75.0 | 94.5 | 33.9 | 253.8 |
| $[MeGaPMe]_2$ | $C_{2v}$ | 2.463 | 4.135 | 2.359 | 114.2 | 57.2 | 32.6 | 120.9 |
| $[HGaPH]_2$ | $C_{2h}$ | 2.338 | 3.105 | 3.496 | 83.2 | 97.8 | 0 | 241.7 |
| $[HGaAsH]_2$ | $C_{2v}$ | 2.460 | 2.906 | 3.673 | 72.4 | 96.6 | 34.8 | 234.6 |
| $[MeGaAsMe]_2$ | $C_{2v}$ | 2.576 | 4.263 | 2.627 | 117.7 | 61.3 | 29.2 | 103.2 |
| $[HGaAsH]_2$ | $C_s$ | 2.448; 2.479 | 2.951 | 3.781 | 72.5; 74.1 | 99.7 | 27.9 | 224.6 |

[a] B3LYP/TZVP level of theory.

**TABLE 12: Structural Parameters for the rhomb-$[R_2MY]_2$ Isomers (in Angstroms and Degrees) and Dissociation Energies into Triplet $R_2MY$ Monomers (kJ $mol^{-1}$)[a]**

| compound | point group | MY | YY | MM | M−Y−M | Y−M−Y | tors. | $E^{diss}$ |
|---|---|---|---|---|---|---|---|---|
| $[H_2BN]_2$ | $C_{2v}$ | 1.590 | 1.256 | 2.921 | 133.4 | 46.5 | 1.8 | 473.5 |
| $[H_2BP]_2$ | $C_{2v}$ | 2.035 | 2.064 | 3.342 | 110.4 | 60.9 | 32.2 | 592.7 |
| $[H_2BAs]_2$ | $C_{2v}$ | 2.162 | 2.293 | 3.541 | 110.0 | 64.1 | 26.7 | 278.8 |
| $[H_2AlN]_2$ | $D_{2h}$ | 1.949 | 1.273 | 3.683 | 141.9 | 38.1 | 0 | 776.5 |
| $[Me_2AlN]_2$ | $D_{2h}$ | 1.954 | 1.278 | 3.692 | 141.8 | 38.2 | 0 | 758.6 |
| $[H_2AlP]_2$ | $D_{2h}$ | 2.419 | 2.119 | 4.349 | 128.1 | 51.9 | 0 | 608.4 |
| $[Me_2AlP]_2$ | $D_{2h}$ | 2.436 | 2.119 | 4.387 | 128.4 | 51.6 | 0 | 365.0 |
| $[H_2AlAs]_2$ | $D_{2h}$ | 2.529 | 2.359 | 4.463 | 124.3 | 55.7 | 0 | 324.0 |
| $[Me_2AlAs]_2$ | $C_{2h}$ | 2.543 | 2.356 | 4.508 | 124.8 | 55.2 | 0 | 315.0 |
| $[H_2GaN]_2$ | $D_{2h}$ | 2.055 | 1.248 | 3.915 | 144.6 | 35.4 | 0 | 546.4 |
| $[Me_2GaN]_2$ | $D_{2h}$ | 2.063 | 1.257 | 3.931 | 144.5 | 35.5 | 0 | 528.9 |
| $[H_2GaP]_2$ | $C_{2v}$ | 2.462 | 2.109 | 4.324 | 123.0 | 50.7 | 29.3 | 570.8 |
| $[Me_2GaP]_2$ | $C_{2v}$ | 2.488 | 2.113 | 4.427 | 126.1 | 50.4 | 22.5 | 319.2 |
| $[H_2GaAs]_2$ | $C_{2v}$ | 2.562 | 2.349 | 4.440 | 120.1 | 54.6 | 26.5 | 285.3 |
| $[Me_2GaAs]_2$ | $C_1$ | 2.580;2.586 | 2.352 | 4.544 | 123.2 | 54.2 | 19.1 | 274.8 |

[a] B3LYP/TZVP level of theory.

**TABLE 13: Relative Energies $E$ (kJ $mol^{-1}$, 0 K, without ZPE Corrections) of the Different $[M_2Y_2H_4]$ Isomers with Respect to the Analogous $[HMYH]_2$ Structures[a]**

| | $[MYH_2]_2$ | | $[H_2YMMYH_2]$ | | | $[HMYH]_2$ | | | $[H_2MY]_2$ | |
|---|---|---|---|---|---|---|---|---|---|---|
| M, Y | $D_{2h}$ | $C_{2v}$ | $D_{2h}$ | $C_{2h}$ | $C_i$ | $D_{2h}$ | $C_{2v}$ | $C_{2h}$ | $D_{2h}$ | $C_{2v}$ |
| BN | (693.8)[b] | 676.9 | 276.4 | | | (3.8)[b] | 0.0 | | (461.5)[b] | 461.5 |
| BP | (388.2)[b] | 387.0 | (278.6)[c] | 245.6 | | (128.6)[c] | 0.0 | 34.9 | (98.8)[b] | 84.5 |
| BAs | (495.7)[b] | 474.2 | (325.2)[c] | 253.7 | | (160.8)[c] | 0.0 | 34.6 | (18.3)[b] | 12.1 |
| AlN | (124.6)[b] | 119.5 | (350.0)[b] | 170.0 | | 0.0 | | | 347.4 | |
| AlP | (177.0)[c] | 157.2 | (392.0)[d] | (298.8)[b] | 184.5 | (73.4)[c] | 0.0 | 9.8 | 107.3 | |
| AlAs | (205.1)[c] | 189.5 | (448.4)[d] | (312.1)[b] | 200.2 | (107.4)[c] | 0.0 | 15.4 | 67.6 | |
| GaN | (−81.8)[b] | −89.2 | (201.0)[b] | −30.8 | | 0.0 | | | 288.3 | |
| GaP | (47.2)[c] | 29.1 | (330.3)[d] | (212.0)[b] | 64.1 | (92.8)[c] | 0.0 | 12.1 | (138.2)[b] | 135.1 |
| GaAs | (80.6)[c] | 65.8 | (400.0)[d] | (194.4)[b] | 86.8 | (130.1)[c] | 0.0 | 10.0[e] | (101.1)[b] | 98.6 |

[a] B3LYP/TZVP level of theory. Structures are minima on the PES, unless noted otherwise. [b] Transition state. [c] Stationary point of Hessian index 2. [d] Stationary point of Hessian index 3. [e] $C_s$ point group.

Methylation results in significant structural changes for the P, As containing rings. In contrast to $[HMYH]_2$, where three-coordinated Al and Ga atoms keep their planar environment, in $[MeMYMe]_2$, the aluminum and gallium centers adopt pyramidal geometries (Figures 9h and 10g,h). This is accompanied by significant shortening of P−P and As−As distances in the ring, making these structures nearly rhombic.

All $[RMYR]_2$ compounds have substantial dissociation energies into RMYR monomers, ranging from 103 kJ $mol^{-1}$ for $[MeGaAsMe]_2$ to 566 kJ $mol^{-1}$ for [HAlNH[2. Methylation

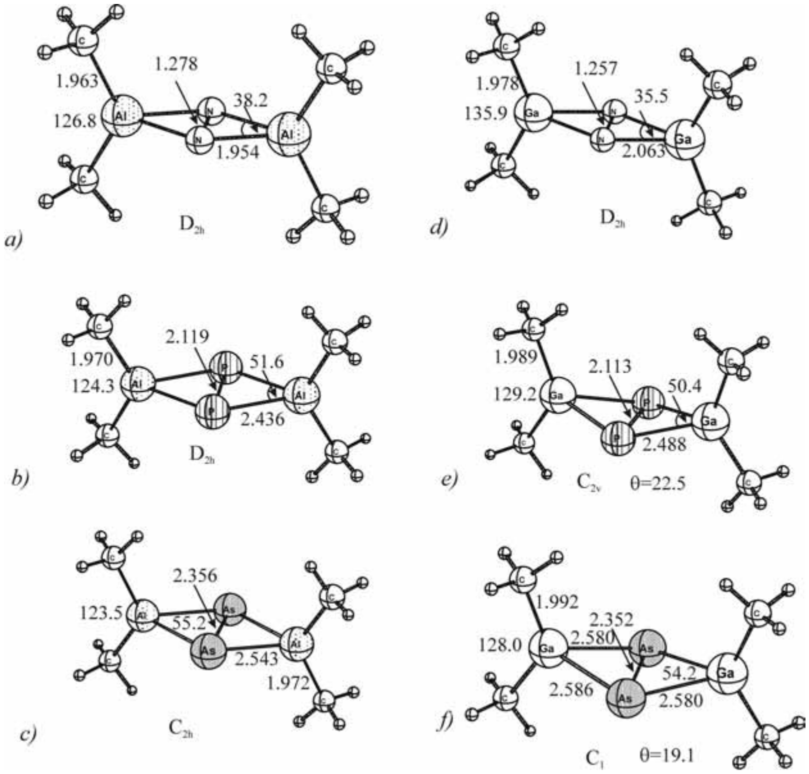


**Figure 12.** Optimized structures for rhombic isomers of the $[Me_2MY]_2$ dimeric compounds. (a) rhomb-$[Me_2AlN]_2$, (b) rhomb-$[Me_2AlP]_2$, (c) rhomb-$[Me_2AlAs]_2$, (d) rhomb-$[Me_2GaN]_2$, (e) rhomb-$[Me_2GaP]_2$, and (f) rhomb-$[Me_2GaAs]_2$. All distances are in angstroms, and angles are in degrees. B3LYP/TZVP level of theory.

**TABLE 14: Relative Eenergies *E* (kJ mol$^{-1}$, 0 K, without ZPE Corrections) of the Different $[M_2Y_2Me_4]$ Isomers with Respect to $[MeMYMe]_2$ Structures[a]**

| M, Y | $[MeMYMe]_2$ | rhomb-$[MYMe_2]_2$ | ring-$[MYMe_2]_2$ | $[Me_2YMMYMe_2]$ | $[Me_2MYMYMe_2]$ | $[Me_2MYYMMe_2]$ | rhomb-$[Me_2MY]_2$ |
|---|---|---|---|---|---|---|---|
| BN | 0 | 790.2 | 817.4 | 413.7 | 53.0 | 199.7 | |
| BP | 0 | 348.5 | | 282.5 | | 12.9 | |
| BAs | 0 | 462.5 | | 305.6 | | −66.2 | |
| AlN | 0 | | 272.5 | 302.7 | 318.6 | 233.6 | 171.6 |
| AlP | 0 | | 200.4 | 257.6 | | | 14.4 |
| AlAs | 0 | | 61.3 | 97.2 | | | −204.5 |
| GaN | 0 | | 42.9 | 80.6 | 142.1 | 163.0 | 144.9 |
| GaP | 0 | | −83.0 | −28.6 | | | −80.0 |
| GaAs | 0 | | −36.1 | 3.9 | | | −107.3 |

[a] B3LYP/TZVP level of theory. Structures are minima on the PES.

dramatically lowers the dissociation enethalpies (by as much as 160 kJ mol$^{-1}$ for $[RAlPR]_2$).

The dissociation energies of $[HMYH]_2$ decrease in the order: AlN > GaN > AlP > AlAs > GaP ≈ BP > GaAs ≥ BN > BAs. Aluminum−nitrogen rings are found to be the most strongly bound. Note that BN rings have very moderate dissociation energies, due to both the destabilization of the dimer and the high stability of the linear monomers RBNR.

*$[H_2MY]_2$ Rhombic Dimers.* Optimization of the ring dimers resulted in the rhomboidal structures presented in Figure 11, and the dissociation energies to $H_2MY$ monomers in the triplet state are reported in Table 12. The AlN, AlP, AlAs, and GaN species are perfectly planar ($D_{2h}$ point group), while for others $C_{2v}$ symmetric puckered structures were found as minima on PES. The N−N distances (1.249−1.256 Å) are larger than in the chain isomers (1.176−1.193 Å, Figure 3). Dissociation into triplet $H_2MY$ is endothermic by 285−776 kJ mol$^{-1}$. Again, the AlN structure is the most strongly bound.

Optimization attempt of the ring structures of the methylated analogues of boron compounds $[Me_2BY]_2$ does not lead to the rhombic structures. Optimization of $[Me_2BN]_2$ converges to the $D_{2h}$ symmetric chain isomer $Me_2BNNBMe_2$ (shown in Figure 3d), while in case of P and As $C_i$ symmetric chains are obtained (Figure 3g,h). Optimization of aluminum and gallium analogues leads to the rhombic minima, which feature planar $M_2Y_2$ ring, with exception of puckered $[Me_2GaP]_2$ and $[Me_2GaAs]_2$.

*Relative Stability of the Dimers.* Relative energies of the dimeric compounds considered here are summarized in Table 13, and those for the methylated derivatives are in Table 14. For the hydrogen-containing species in Table 13, we report not only true minima but also high order stationary points located in the present research. The $C_{2v}$ symmetry $[HMYH]_2$ rings lie lowest in energy, with the single exception of $Ga_2N_2H_4$, for which the somewhat unexpectedly $C_{2v}$ symmetric $[GaNH_2]_2$ ring is found to be an energy minimum, followed by the planar $H_2NGaGaNH_2$ chain (Table 13). The higher stability of the $GaNH_2$ bonding pattern in oligomer compounds in the case of gallium may be rationalized in terms of the increasing stability of oxidation step I as compared to that for boron and aluminum. The formation of such Ga−Ga bonded species may be a starting point toward formation of Ga metal in MOCVD processes. Although neither dimer is strongly bound (dissociation energies are 79 kJ $mol^{-1}$ for the ring and only 20 kJ $mol^{-1}$ for the chain dimer), they are the lowest lying isomers on the PES.

For methylated analogues, the Ga−N system does not show exceptional behavior. The $[MeGaNMe]_2$ dimer is the lowest in energy. However, for Ga−P and Ga−As systems, the ring-$[GaYMe_2]_2$ is by 83 and 36 kJ $mol^{-1}$ lower in energy, as compared to the respective $[MeGaYMe]_2$ structures. With the exception of $Me_2PGaGaPMe_2$, all chain isomers are higher in energy as compared to their imido dimers $[MeMYMe]_2$. Note the very small energetic differences between $[MeGaAsMe]_2$, ring-$[GaAsMe_2]_2$, and chain $Me_2AsGaGaAsMe_2$ structures; they all lie in a range of 36 kJ $mol^{-1}$. Thus, a variety of GaAs structures with different bonding patterns are expected to be viable. It is interesting to note that for As-containing compounds the chain $Me_2BAsAsBMe_2$ and rhombic $[Me_2MAs]_2$ structures (M = Al, Ga) become the lowest in energy.

## Conclusions

A series of group 13-15 compounds of the general formula $[MYR_2]_n$ (M = B, Al, Ga; Y = N, P, As; $n$ = 1, 2; R = H, $CH_3$) have been theoretically studied at the B3LYP/TZVP level of theory. For the dimeric compounds, the $C_{2v}$ symmetric $[HMYH]_2$ rings are the lowest in energy, with the single exception of $Ga_2N_2H_4$, for which a somewhat unexpected $C_{2v}$ symmetric $[GaNH_2]_2$ ring is found to be a minimum, followed by the planar $H_2NGaGaNH_2$ chain. The higher stability of the $GaNH_2$ bonding pattern in these oligomer compounds may be rationalized in terms of the increasing stability of oxidation state I as compared to that for the boron and aluminum analogues. Thus, the possibility of formation of $Ga^I$ species under GaN CVD conditions should be taken into account. Methylation significantly reduces the energetic differences between the monomeric $MYMe_2$, MeMYMe, and $Me_2MY$ isomers, especially for the AlP, AlAs, and GaAs systems, allowing a variety of structural types to be competitive energetically. This trend also holds for the weakly bound dimeric compounds in the GaAs system. For the methyl-substituted compounds, the $C_{2v}$ symmetric $[MeMYMe]_2$ rings are the lowest in energy, with the exception of $Al_2As_2Me_4$, $Ga_2P_2Me_4$, and $Ga_2As_2Me_4$, for which $[Me_2MY]_2$ rhombic structure is found as an energetic minimum. It is the gallium compounds in both cases that behave differently from the rest. In this regard, it would be interesting to see if such trends will continue for larger $[MYR_2]_n$ species. Theoretical studies of tetramers are expected to shed more light on the competition between 13 and 13, 13-15, and 15-15 bonded structures.

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**Supporting Information Available:** Table 1S with total energies, zero-point vibrational energies, sum of electronic and thermal enthalpies, and standard entropies, Table 2S with computed harmonic vibrational frequencies and IR intensities, and Table 3S with optimized structural parameters for the $R_2MMR_2$ compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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